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GRADIENT DYNAMICS MODELING OF LIQUID DROPS ON ELASTIC SUBSTRATES

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GRADIENT DYNAMICS MODELING OF
LIQUID DROPS ON ELASTIC SUBSTRATES

KURZFASSUNG

Seit jeher stellen Fluide in ihrer Vielfalt und ihrem komplexen Verhalten für viele Menschen eine große Faszination dar. Von riesigen Eruptionen der Sonne und den endlosen Zirkulationen von gewaltigen Luftmassen in der Atmosphäre bis hin zu den komplexen Strukturen der Milchwirbel im morgentlichen Kaffee und den Tropfen die sich am Deckel eines Kochtopfs sammeln, Fluide sind ein allgegenwärtiger Bestandteil unseres täglichen Lebens und haben großen Einfluss auf uns und unsere Umwelt. Es ist daher nicht verwunderlich, dass sich die Fluidodynamik als ein sehr großes und aktives Forschungsfeld entwickelt hat. Während großskalige Phänomene in der Regel maßgeblich von Gravitation und Trägheit beeinflusst werden und häufig auch chaotisches Verhalten, d.h. Turbulenz, aufweisen, spielen auf kleineren Skalen vor Allem Viskosität (also Reibung) und Grenzflächeneffekte zunehmend eine tragende Rolle. Letztere resultieren aus den intermolekularen Wechselwirkungen zwischen dem Fluid und seinen benachbarten Phasen. Insbesondere bei Flüssigkeiten in direktem Kontakt mit wie auch immer gearteten Oberflächen können diese Wechselwirkungen zu sehr vielfältigem Verhalten führen. Daraus erwuchs ein neues Forschungsfeld, dass sich gezielt mit der Benetzung von Oberflächen auseinandersetzt. Während man auf experimenteller Seite mit der Wechselwirkung zahlreicher (teils unbekannter) Mechanismen wie z.B. Kondensation und Evaporation, Unreinheiten und Temperaturschwankungen zu kämpfen hat, bieten die meisten modernen Modelle nur stark vereinfachte Beschreibungen, die viele dieser Effekte vernachlässigen. Das liegt zum Einen daran, dass ein umfassendes Modell unter Berücksichtigung aller bekannten Mechanismen sehr unhandlich wäre als auch daran, dass manche davon noch garnicht ausreichend verstanden sind, wie zum Beispiel die Dynamik der drei-Phasen-Kontaktlinie, wo die Grenzfläche zwischen Flüssigkeit und Gas auf die Oberfläche eines zugrundeliegenden Substrats trifft. Allerdings ist eine Beschreibung der Kontaktliniendynamik unumgänglich, wenn man die Dynamik von Tropfen untersuchen möchte, und so wurden diverse Alternativlösungen wie Rutsch-, Diffuse-Grenzflächen- oder Adsorptionsfilm-Modelle entwickelt, um mit dem Problem umzugehen. Mittlerweile gibt es viele Modelle, die in der Lage sind die fundamentalsten Benetzungsphänome-

ne zuverlässig zu beschreiben. Im Großteil der bisher veröffentlichten Studien werden die Substrate jedoch als starr angenommen, obwohl insbesondere im medizinischen und biologischen Kontext viel häufiger weiche, deformierbare Oberflächen wie Gewebe oder einzelne Zellen behandelt werden. Insbesondere bei der Benetzung viskoelastischer Substrate treten zahlreiche Phänomene auf, die auf starren Oberflächen gar keine Entsprechung haben. Die detaillierte Modellierung der elastisch-kapillaren Wechselwirkungen stellt eine große Herausforderung dar, sodass sich bisher meist auf einzelne Kontaktlinien bzw. Tropfen beschränkt wurde. In einem solchen Szenario wird die Kontaktlinie eines Tropfens maßgeblich durch die Verformungen des Substrats beeinflusst und kann nicht mehr durch einen einzigen Winkel umfassend charakterisiert werden. Diese Verformungen beeinträchtigen auch den Verschmelzungsprozess von Tropfen miteinander oder verhindern ihn sogar, was als umgekehrter Cheerios-Effekt bekannt ist. Darüber hinaus stellt die Viskosität des Substrats eine zusätzliche Dissipationsquelle dar, die die Benetzungsdynamik entscheidend beeinflusst. So kann beispielsweise die Bewegung der Kontaktlinie maßgeblich verlangsamt werden, was als viskoelastisches Bremsen bezeichnet wird, oder es kann zum Auftreten von komplexen Stick-Slip-Bewegungen kommen. Schließlich weisen elastische Materialien häufig eine Oberflächenenergie auf, die vom Dehnungszustand abhängt, ein Merkmal, das als Shuttleworth-Effekt bekannt ist. In dieser Arbeit wird die etablierte mesoskopische Dünnschichtgleichung mit der reduzierten Beschreibung eines Kelvin-Voigt-Materials gekoppelt, um die Dynamik des viskoelastischen Substrats zu beschreiben. Das Modell weist eine gradientendynamische Struktur auf, die die thermodynamische Integrität bezüglich eines zugrundeliegenden Energiefunktionalis gewährleistet. Dieses spiegelt Beiträge von Kapillarität, Benetzbarkeit und Elastizität wieder und kann einfach systematisch erweitert werden. Nach einer detaillierten Herleitung und Diskussion der zu Grunde liegenden Gleichungen werden numerische Methoden eingesetzt, um die wichtigsten statischen und dynamischen Merkmale der Benetzung weicher Substrate qualitativ zu reproduzieren. Zunächst wird die Statik eines einzelnen Tropfens in Abhängigkeit von der Weichheit des Substrats untersucht, wobei der doppelte Übergang der Gleichgewichtskontaktwinkel gefunden wird, der beim Übergang von ideal starren zu sehr weichen (d.h. quasi-flüssigen) Substraten auftritt. Dynamische Kontaktlinien werden am Beispiel von sich autonom ausbreitenden, teilweise und vollständig benetzenden Tropfen untersucht, wobei die Wirkung des viskoelastischen Bremsens nachgewiesen wird. Dabei werden auch die bekannten Abhängigkeiten des dynamischen Kontaktwinkels von der Kontaktliniengeschwindigkeit reproduziert. Die Einfachheit des Modells erlaubt es darüber hinaus, sowohl

Zwei-Tropfen-Systeme als auch große Tropfen-Ensembles zu behandeln, deren zeitliche Entwicklung zeigt, dass der dominante Vergrößerungsmodus in nicht-trivialer Weise von der Substratweichheit beeinflusst wird. Anschließend wird das Modell erweitert, um den Shuttleworth-Effekt einzubeziehen und seinen Einfluss auf das Benetzungsverhalten von Tropfen zu untersuchen. Um das Modell zu validieren, werden die Ergebnisse mit denen eines makroskopischen Neo-Hooke'schen Elastizitätsmodells verglichen, das große Verformungen auch im Innern des Substrats konsistent berücksichtigt. Es wird eine sehr gute qualitative Übereinstimmung festgestellt. Schließlich wird die Dünnschichtgleichung erweitert, um eine umgebende Dampfphase zu berücksichtigen und einen Phasenübergang der Flüssigkeit zu ermöglichen. Die Beschreibung geht von einem unendlichen Reservoir von übersättigtem Dampf aus. Unter Anwendung verschiedener numerischer Methoden wird die Energiebarriere der Keimbildung in Abhängigkeit von der Weichheit des Substrats untersucht. Die Ergebnisse werden mit analytischen makroskopischen Aussagen zum starren und quasi-flüssigen Grenzfall verglichen und zeigen, dass die Keimbildungsrate bzw. die Keimbildungswahrscheinlichkeit bei hoher Übersättigung von der makroskopischen Theorie deutlich unterschätzt wird. Allerdings kann auch das mesoskopische Modell die experimentell beobachteten Phänomene nicht zufriedenstellend erklären.

ABSTRACT

The diversity and the complex behavior of fluids has always been a source of fascination for many people. From giant solar flares in the sun and the endless circulation of tremendous air masses in the atmosphere to the complex structures of milk swirls forming in a morning cup of coffee and the droplets that collect on the lid of a saucepan, fluids are an ubiquitous part of our daily lives and have a major impact on us and our environment. It is therefore not surprising that fluid dynamics has emerged as great and very active field of research. While large-scale phenomena are usually significantly influenced by gravity and inertia and often exhibit chaotic behavior, i.e., turbulence, on smaller scales viscosity, i.e., friction, and interfacial effects become increasingly important. The latter result from the intermolecular interactions between the fluid and its neighboring phases. These interactions can lead to very diverse behavior, especially for fluids in direct contact with surfaces of any kind. This gave rise to a new field of research that deals specifically with the wetting of surfaces. While on the experimental side one has to struggle with the interaction of numerous (partly unknown) mechanisms such as condensation and evaporation, impurities and temperature fluctuations, most modern models offer only strongly simplified descriptions, neglecting many of these effects. This is partly because a comprehensive model taking into account all known mechanisms would be very unwieldy and partly because some of the latter are not yet understood in the first place, as, e.g., the dynamics of the three-phase contact line, where the liquid-gas interface meets the substrate surface. A description of the latter is inevitable, however, if drop dynamic are to be investigated, and so workaround methods were like slip, diffuse interface or precursor models were invented to deal with this problem. Many models exist today that are capable of reliably describing the most fundamental wetting phenomena. In the majority of studies published to date, however, the substrates are assumed to be rigid, although soft, deformable surfaces such as tissue or individual cells occur much more frequently, e.g., in medical and biological systems. Particularly the wetting of soft viscoelastic substrates exhibits many features that have no counterpart on rigid surfaces. Modeling the detailed elastocapillary interactions is challenging, and has so mostly been limited to single contact

lines or single drops. The contact line of a drop is not comprehensively characterized by a single angle anymore, but is affected by the substrate's bulk and surface deformations. These deformations further affect the coarsening of drops or even prevent it which is known as the inverted Cheerios effect. Further, the viscosity of the substrate represents an additional source of energy dissipation which crucially influences the wetting dynamics and may, e.g., slow down the movement of the contact line which is referred to as viscoelastic braking or cause complex stick-slip motion. Finally, elastic materials often exhibit a surface energy that depends on the state of stretching, a feature known as the Shuttleworth effect. In this work, the well-known mesoscopic thin-film equation is coupled to the reduced description of a Kelvin-Voigt material to account for the dynamics of the viscoelastic substrate. The model exhibits a gradient dynamics structure that ensures thermodynamic integrity based on an underlying free energy functional that reflects capillarity, wettability and compressional elasticity. After a detailed derivation and discussion of the governing equations, numerical methods are employed to qualitatively capture the main static and dynamic features of soft wetting. First the statics of a single drop is investigated in dependence of the substrate softness, recovering the double transition in the equilibrium contact angles that occurs when going from ideally rigid towards very soft (i.e., quasi-liquid) substrates. Dynamic contact lines are investigated on the example of autonomously spreading partially and completely wetting drops, verifying the effect of viscoelastic braking. In the course of that, also the known dependencies of the dynamic contact angle on the contact line velocity are well reproduced. The simplicity of the model further allows to treat two-drop systems as well as even large drop ensembles, the time evolutions of which demonstrate that the dominant coarsening mode is significantly influenced by the substrate softness in a nontrivial way. Afterwards, the model is extended to incorporate the Shuttleworth effect and to explore its influence on the wetting of drops. In order to validate the modeling, the results are compared to those produced via a macroscopic Neo-Hookean elasticity model which consistently accounts for large deformations also in the bulk. Qualitatively the two models are found to agree very well. Finally, the thin-film equation is extended to account for an ambient vapor phase and allow for a phase transition of the liquid. The description assumes an infinite reservoir of supersaturated vapor. Using different numerical approaches the model is used to investigate the nucleation energy barrier in dependence of softness. The results are compared to analytic macroscopic predictions in the rigid and quasi-liquid limit and indicate, that at high supersaturation the nucleation rate is significantly underestimated by macroscopic theory. Yet even the mesoscopic model cannot sufficiently

explain the experimentally observed phenomena.

CONTENTS

1	INTRODUCTION	1
1.1	AIM OF THIS THESIS	4
1.2	STRUCTURE OF THIS THESIS	5
1.3	DECLARATION ON DIVISION OF LABOR	6
2	CONTINUUM MECHANICS	7
2.1	FUNDAMENTALS	7
2.2	FLUID DYNAMICS IN THIN LIQUID FILMS	15
2.2.1	THE NAVIER-STOKES EQUATIONS	15
2.2.2	ADAPTATION TO LAYER GEOMETRY	16
2.2.3	LONG-WAVE APPROXIMATION	20
2.2.4	THE THIN-FILM EQUATION	22
2.3	LINEAR ELASTICITY	24
2.3.1	THE NAVIER-CAUCHY EQUATION	25
2.3.2	THE FUNDAMENTAL SOLUTION	28
2.3.3	LONG-WAVE APPROXIMATION	34
2.4	LINEAR VISCOELASTICITY	36
2.4.1	THE DYNAMIC MODULI	36
2.4.2	CIRCUIT CONSTITUTIVE MODELS	40
2.4.3	SURFACE DYNAMICS OF A FINITE ELASTIC LAYER	43
2.5	GRADIENT DYNAMICS	45
3	GRADIENT DYNAMICS MODELING OF THE TWO-LAYER SYSTEM	49
3.1	FREE ENERGY AND ITS VARIATIONS	51
3.1.1	ELASTIC ENERGY	51
3.1.2	GRAVITY	55
3.1.3	INTERFACIAL FREE ENERGY	57
3.2	CAPILLARITY AND STATIC DROPS	59
3.2.1	THE ELASTIC REGIME	61
3.2.2	THE RIGID LIMIT	65

3.2.3	THE QUASI-LIQUID LIMIT	66
3.3	THE MESOSCOPIC PICTURE	69
3.4	THE EVOLUTION EQUATIONS	73
3.4.1	DIMENSIONLESS FORMULATION	75
3.4.2	LONG-WAVE FORMULATION	76
3.5	CONSERVATION AND THICKNESS OF THE ELASTIC LAYER	79
3.6	ANALYTICS ON LONG-WAVE SUBSTRATE DEFORMATION	81
3.6.1	THE FUNDAMENTAL SOLUTION	82
3.6.2	MACROSCOPIC DROP	85
3.6.3	MOVING CONTACT LINE	88
3.6.4	HIGHER-ORDER EXPANSION OF THE ELASTIC ENERGY	90
4	THE DOUBLE TRANSITION OF STATIC DROPS	97
4.1	THE ELASTO-CAPILLARY LENGTH	98
4.2	CONTINUATION OF THE SUBSTRATE SOFTNESS	99
4.3	VIOLATION OF NEUMANN'S LAWS	106
4.4	ASSESSMENT	109
5	VISCOELASTIC BRAKING	111
5.1	PARTIAL WETTING	112
5.2	COMPLETE WETTING	116
5.3	ASSESSMENT	118
6	DROPLET COARSENING	119
6.1	TWO-DROP COARSENING	121
6.2	COARSENING OF DROP ARRAYS	129
6.3	ASSESSMENT	133
7	THE SHUTTLEWORTH EFFECT	135
7.1	THE MACROSCOPIC PERSPECTIVE	137
7.1.1	KINEMATICS OF SURFACE STRETCH	137
7.1.2	ENERGY, TENSION AND CHEMICAL POTENTIAL OF A SOFT SURFACE .	140
7.1.3	CONSTITUTIVE RELATION FOR THE SOLID INTERFACE	141
7.1.4	WETTING AND THE SYMMETRY OF STRETCH DEPENDENCE	143
7.1.5	THE NEO-HOOKEAN MODEL	144
7.2	TRANSLATION INTO THE MESOSCOPIC PICTURE	147
7.2.1	STRETCH DEPENDENT WETTING POTENTIAL	147
7.2.2	FULL-CURVATURE GRADIENT DYNAMICS MODEL	149

7.2.3	CONSISTENCY OF NEUMANN'S LAWS	150
7.2.4	THE LONG-WAVE LIMIT	152
7.3	COMPARISON OF THE TWO MODELS	154
7.3.1	CONTACT ANGLES	156
7.3.2	SUBSTRATE DEFORMATIONS	159
7.4	ASSESSMENT	163
8	SOFT CONDENSATION	167
8.1	CLASSICAL NUCLEATION THEORY	172
8.1.1	GIBBS FREE ENERGY AND LANDAU POTENTIAL BARRIER	177
8.1.2	BINARY MIXTURE OF WATER VAPOR AND N_2	178
8.2	MACROSCOPIC NUCLEI	179
8.3	MESOSCOPIC MODEL	182
8.3.1	STEADY FILM STATES	185
8.3.2	CRITICAL NUCLEI	186
8.4	ASSESSMENT	193
9	CONCLUSION	197
A	ADDITIONAL CONSIDERATIONS	205
A.1	NEWTON'S LAW OF FORCE AND ACCELERATION	205
A.2	METRIC FACTOR	205
A.3	STRESS EQUILIBRIUM AT THE FREE FLUID SURFACE	206
A.4	SUBTLITIES ON INCOMPRESSIBILITY	208
A.5	FUNDAMENTAL SOLUTION FOR THE SURFACE STATICS OF A FINITE LINEAR ELASTIC LAYER	210
A.5.1	3D PROBLEM	212
A.5.2	2D PROBLEM	218
A.6	FOURIER TRANSFORMATION OF THE TIME DEPENDENT CONSTITUTIVE LAW .	221
A.7	EULER-LAGRANGE EQUATION	221
A.8	ABSOLUTE HEIGHT FORMULATION	222
A.9	EULERIAN HORIZONTAL DISPLACEMENT RELATIVE TO PRE-STRETCH	224
B	METHODS	227
B.1	MESOSCOPIC CONTACT REGION MEASURES	227
B.2	FINITE ELEMENT METHOD	229
B.2.1	WEAK FORMULATION	230
B.2.2	GALERKIN METHOD	231

B.2.3	DISCRETIZATION AND SHAPE FUNCTIONS	232
B.2.4	APPLICATION TO THE THIN-FILM EQUATION	235
B.3	NEWTON-RAPHSON METHOD	237
B.4	PARAMETER CONTINUATION	238
B.5	LINEAR STABILITY ANALYSIS	242
B.5.1	LINEAR STABILITY OF THIN LIQUID FILMS	244
BIBLIOGRAPHY		274
AKNOWLEDGMENT		275
CURRICULUM VITAE		279

1. INTRODUCTION

In the context of fluid dynamics, the term *wetting* refers to the interaction of liquids with some kind of surface they are in contact with. More precisely, to the ability of a liquid to spread over or adhere to that surface. Such properties are governed mainly by the microscopic forces acting between the microscopic constituents of the different phases, which result from differences in the respective chemical structures. These interactions become particularly significant on small scales, where they are able to compete with inertia and gravity and lead to exciting behavior, such as drop formation. Understanding the static and dynamic wetting behavior of simple and complex liquids on surfaces of any type is highly relevant for many aspects of daily life like cosmetics, cleaning and painting. Consider only the perspiration of skin on a hot summer day, the spontaneous production of lachrymal fluid spreading on the eye and forming tears or the restricted visibility due to drops on the windshield when driving through a storm [examples in Fig. 1.1]. Obviously wetting phenomena have vast implication also in various scientific and engineering fields like, for example, (inkjet) printing, self-cleaning surfaces, microfluidics, lubrication and coating. It is further of crucial importance in pharmaceuticals, medicine and biology, such as the way plants manage the water transport through their leaves or how different liquids interact with biological tissues. Related phenomena are studied for more than two hundred years [dBQ04, SVRo7, Bor17].

Many works published in the past decades consider the wetting of smooth homogeneous and especially rigid solid surfaces [dG85, Bon+09]. The above examples have shown, however, that such assumptions are not appropriate in many cases. Particularly in medical and biological systems the surfaces are usually soft and deformable or liquid even rather than rigid. Therefore the research of wetting on *adaptive substrates* has received increasing attention recently [But+18]. This classification includes, among others, viscous liquids, plastic, elastic and viscoelastic materials like rubbers and gels which change their topography due to interfacial forces exerted by a drop [Pot+05, SD12, Kaj+13, Bom+13, AS20], polymeric materials that are able to rearrange their microscopic structure in order to change their wetting properties [Gru+15], as well as porous media like brushes, zeolites and fab-

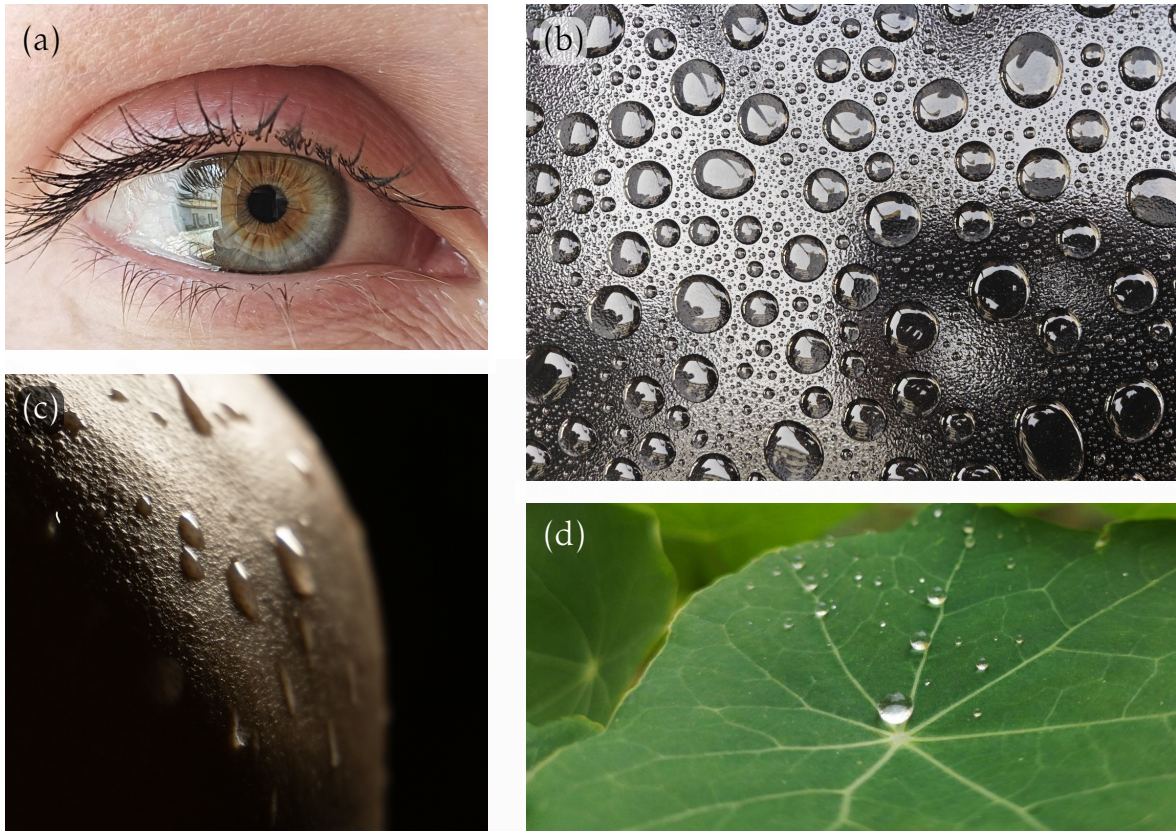


FIGURE 1.1.: Typical examples of wetting where it is encountered in every day life. Panel (a) shows the spontaneous tearing of an eye in response of contamination. The lacrimal fluid spreads autonomously over the soft eye surface. In (b) a systematic drop pattern is shown, which has formed on a rough rigid substrate via dewetting from a homogeneous liquid layer after a heavy rain. Panel (c) shows the formation of sweat drops on a bold head. In (d) the formation of almost perfectly spherical millimetric drops on a hydrophobic *Tropaeolum majus* (also nasturtium or Indian cress) leave is shown. Photograph (c) was made by Grégoire Delwaulle and is used here with his consent.

rics which are able to absorb the liquid and swell in the process [Sta+03, Gam14, Cen+20], but also rigid surfaces that are in any way altered by the wetting process, e.g., by getting charged which is known as *electro wetting* [YMA94, YJ95, Hel16, Ste+19].

A particularly interesting situation arises in the wetting of soft solid substrates which are able to deform under the forces exerted by the wetting liquid, yielding the subgenre of *soft wetting* [CGS96, CS01, Sty+17, AS20]. In particular the viscoelastic properties of such materials gives rise to a variety of interesting phenomena that have no counterpart in the rigid case. The most striking feature of soft wetting is the formation of a *wetting ridge*: a pointy deformation that is drawn out of the substrate by the vertically pulling force the liquid-gas interface exercises at the three-phase contact line [EK96, Jer+11, BSD14, Par+14]. This ridge is responsible for the occurrence of intricate static and dynamic behavior [AS20]. Recent work has shown that

substrates made from cross-linked polymer networks offer versatile routes to manipulate the contact angles of droplets [SD12, Sty+13b, Lub+14, BSD14, DL15], as well as their spreading dynamics [CGS96, LAL96, Kar+15, Gor+20], directed motion [Sty+13a, Bue+18, Zha+18], e.g., due to *durotaxis* which describes the movement due to softness gradients, and condensation [Beyo6, Sok+10, Gua+14, AlK17, KPN22, Bey22, Bou+25]. It is known that the ability of a substrate to deform under external pressure crucially influences the nucleation density [Sok+10]. The capillarity of soft solids introduces an other major complication as compared to liquid interfaces. Namely, the dependence of the surface free energy on local strain. This is known as *surface elasticity* or the *Shuttleworth effect* [Shu50, Mar+12a, WAS13, Lia+18, AS16, Sty+17]

Yet it turned out, that investigating the matter is not quite as trivial a thing as one might have expected. Describing the dynamics of the three-phase contact line, where the liquid-gas interface meets the substrate, has long posed a significant difficulty that many models continue to struggle with. From an experimental point of view, effects like the roughness, impurities and polarity of the materials as well as surface chemical groups or temperature gradients but also the technical limitations of the equipment, e.g., the temporal and spatial resolution of cameras, complicate the issue [Jd84, dBQ04]. At present even a quantitative understanding of the behavior of a single drop of nonvolatile simple liquid is not yet complete.

From the modeling perspective, various approaches to soft wetting have been proposed. Most analytical results have been obtained using linear elasticity theory [LAL96, Jer+11, SD12, Lim12, Lub+14, BSD14, Kar+15]. In these approaches the surface tension forces are treated as tractions that are imposed as boundary conditions at the free surface. This approach has now been extended to large deformations, including the possibility of the Shuttleworth effect [Wu+18, Pan+20]. Other studies employ an approach where the tractions are not imposed by hand, but computed via a Derjaguin (or disjoining) pressure [SV09], i.e., a hybrid approach coupling elasticity to a static thin-film equation [Whio3]. Only recently, dynamic calculations coupling full hydrodynamic and nonlinear elasticity models have become available [AM21, AA21, RB19, van+17, Bue+17, Bue+18]. Furthermore, molecular dynamics simulations are employed in some studies, exploring the elasto-capillary interactions at the nano-scale [WAS13, Lia+18]. Many of the more detailed modeling approaches do not lend themselves easily to large-scale simulations of the coupled dynamics of elastic and liquid layer considering, e.g., the coarsening behavior of large droplet ensembles on soft substrates. The collective behavior of such ensembles is of large interest in practical contexts like, for instance,

condensation or inkjet printing. Similar coarsening processes (Ostwald ripening) occur for emulsion droplets [Tay98], quantum dots [VGY01] or crystalline nanoparticles [Rin+14]. For simple nonvolatile liquids on horizontal homogeneous substrates coarsening is experimentally well studied [And+02, LGo3, Bla+12, Bar+18] and theoretically well understood through simulations and asymptotic considerations [GW09, Gla+09, Kit14] based on *thin-film models* [Wit20]. Such models usually rely on certain approximations and sacrifice universal applicability for accessibility and improved computational performance, which allows to carry out large-scale simulations. In particular, Refs. [MGK05, Gie+17, CK20] present a model for the dynamics of a liquid drop on an incompressible viscoelastic layer while Ref. [GV20] models the durotaxis of a liquid drop on a compliant Kirchhoff plate. However, the plate is modeled with a static long-wave description, i.e., the elastic layer dynamics is instantaneous and slaved to the dissipative liquid dynamics. In consequence, dissipation in the elastic layer is not considered. The long-wave model for a drop on a polymer brush in Ref. [TH20] contains an elastic contribution resulting from entropic influences while Ref. [Sib+21] describes a growing layer of ice under a droplet employing a periodic potential to capture micro-scale layering that resembles *periodic elasticity effects*.

After all there is a virtually inexhaustible range of phenomena to be discovered and understood. As such, the research presented in this thesis can be expected to be anything but dry.

1.1. AIM OF THIS THESIS

The aim of this thesis is to derive the simplest possible model for the dynamics of a simple liquid on a viscoelastic substrate that captures the most important features of soft wetting. Following a gradient-dynamics approach, the thin-film equation for a simple liquid [ODB97, Thio7, CM09] is coupled to the dynamics of a Kelvin-Voigt material [Tho65, Voi92] using a strongly simplified Winkler-foundation elasticity. The resulting model will be validated by reproducing known soft wetting behavior and utilized further to gain also new insights. Finally, the model will be expanded in different stages to investigate more intricate phenomena.

1.2. STRUCTURE OF THIS THESIS

First the general continuum mechanics description of both, fluids as well as solids, is discussed in Ch. 2. After introducing the fundamental concepts required for the mathematical description in Sec. 2.1, the governing equations of a viscous fluid are discussed in Sec. 2.2 and adapted to fit the geometry of an laterally extended layer that has a free surface at the top and is bounded by a solid substrate underneath. The substrate it self is addressed in the subsequent Sec. 2.3, applying the theory of linear elasticity. The equations are respectively approximated in the long-wave limit to derive evolution equations for the interface profiles. In order to derive an evolution equation for the substrate profile, viscoelasticity is introduced in Sec. 2.4. The obtained evolution equations are then shown to satisfy a gradient dynamic structure, which is based on the minimization of a free energy functional as discussed in Sec. 2.5. This structure enables a very versatile, almost modular construction of the model and allows to easily tailor it to the requirements of a specific problem.

In Ch. 3 the underlying energy function that is required to capture the main features of soft wetting is constructed in Sec. 3.1 and used to gain first insights into the statics of macroscopic drops in Sec. 3.2. Afterwards a mesoscopic perspective is adopted by introducing a wetting potential, resulting in a precursor model. Finally, the gradient dynamics evolution equations are derived and expanded in the long-wave limit.

In a first study the influence of the substrate softness on the statics of a liquid drop is investigated numerically in Ch. 4. The double transition in the equilibrium contact angles, that occurs when increasing substrate softness from ideally rigid towards very soft, i.e., quasi-liquid, is recovered and the contact angles are shown to obey Young's and Neumann's laws in the respective limits.

The precursor approach enables an easy treatment of moving contact lines, which is utilized to consider the spreading of single drops of partially and completely wetting liquids in Ch. 5. It is shown, that known dependencies of the dynamic contact angle on the contact line velocity are well reproduced and the effect of viscoelastic braking is captured by the model.

Beyond that, the computational efficiency of the model, owing to the reduced description in terms of the interface profiles, allows also for the treatment of larger

systems. This is exploited in Ch. 6 to analyze the coarsening for two-drop system as well as for large drop ensembles and it is shown that the dominant coarsening mode changes with substrate softness in a nontrivial way.

In Ch. 7 the versatility of the gradient dynamics approach is made use of to incorporate surface elasticity and explore the impact of the Shuttleworth effect on static drops. To validate the model, the results are compared to full nonlinear elasticity simulations.

Finally, the liquid is enabled to exchange mass with the surrounding gas phase in order to investigate the impact of softness on condensation and evaporation in Ch. 8, attempting to explain the experimentally found phenomena.

The thesis closes with a conclusion in Ch. 9, summarizing the results of all presented studies. At last, the performance of the model is evaluated, including its advantages and limitations, before suggestions for improvements and the further procedure are made.

1.3. DECLARATION ON DIVISION OF LABOR

In the following sections results will be presented that have to a large extend already been published. At the beginning of the chapters concerned a remark will be made regarding the details of publication as well as on the division of labor between the authors. I declare that all the results as well as the final version of the text have been produced by me, unless stated otherwise in the respective remark.

2. CONTINUUM MECHANICS

In this chapter the main concepts of continuum mechanics that are required for the description of both, liquids and solids, are introduced and used to derive the respective governing equations.

2.1. FUNDAMENTALS

The variety of materials that are encountered in every day life seems innumerable and classifying them is not an easy task. Depending on how they are differentiated, distinct categories arise, the number of which increases the more properties are taken into account. In particular, the research field of *rheology* investigates materials with regard to their mechanical properties, that is, their response to external forces. More precisely, the materials are characterized by the counteracting internal forces that emerge under deformation. These forces depend on the molecular structure, i.e., the interaction between the materials constituents, and include for example chemical bonds, electrostatic forces and van der Waals forces. A first rough classification distinguishes between solids (including also elastic materials) and fluids (including liquids as well as gases). A solid is a material whose constituents are strongly tied together and prevented from moving far away from each other. This usually goes hand in hand with some kind of ordered structure on the molecular level like crystalline lattices (e.g. in metals) or polymer networks (e.g. in rubbers). Within such a structure each constituent has an assigned position relative to its neighbors to which it is strongly bound. Any displacement away from that position is resisted by forces proportional to the distance. The molecular structure of Newtonian fluids, in contrast, is highly disordered and the constituents are indifferent regarding their neighbors. As compared to a solid the particles of a fluid are rather loosely bound and able to slip past one another with relative ease. This allows fluids to yield to shear stresses which are virtually not resisted. Such movement known as *flow* is only damped by viscous friction.

This classification of solids and fluids is strongly simplified, however, and corresponds to the idealized limiting cases of a wide spectrum of rheologies. Amor-

phous materials, like glasses, for example resemble solids regarding their mechanical properties, i.e., they do not flow, resist shape change (shear stresses in particular) and maintain structural integrity, even though their molecular structure is highly disordered like that of a Newtonian liquid. In fact the majority of real materials are *viscoelastic* and exhibit both, viscous as well as elastic behavior¹, e.g., due to ordered substructures like macromolecules as in blood or polymers. However, understanding the simplified limiting cases first, will prove useful for the description of the cases in between. To mathematically approach this problem, the deformation itself has to be described first, which is the aim of this section. In the course of this the classical derivation, as found, e.g., in Refs. [LKP86, LL87, Beso6, Sado9], is sketched with a focus on the Eulerian point of view.

Macroscopic bodies that consist of spatially extended bulk materials, be it fluids or solids or something in between, contain countless particles which makes a microscopic description in terms of particle trajectories virtually impossible.² Often the exact microscopic behavior is not even of great interest, however, and it is rather the macroscopic consequences that are relevant. On such scales, however, the body appears continuous rather than composed of discrete particles, which led to the idea of describing it in terms of infinitesimal volume elements dV instead. These elements are considered very large as compared to the particles, such that each element contains a large number of them, but is still very small as compared to the size of the body, such that the latter can still be considered continuous on the macroscopic scale. Properties like position $\vec{r}_n(t)$ or velocity $\vec{v}_n = d\vec{r}_n/dt$ that were originally assigned to a particle n , are then expressed as continuous fields. Extensive quantities that are carried by a volume element, like the total number or mass of the particles included, become densities. Describing the deformation of macroscopic bodies under influence of external forces in terms of these continuous quantities is the purpose of continuum mechanics and the basic equations have already been established by Cauchy and Poisson in the 1820's [LKP86]. Commonly, there are two descriptions to be distinguished [Beso6].

THE LAGRANGIAN PICTURE: In this description an initial state is defined by the positions $\vec{R}$ of its volume elements at arbitrary time $t = t_0$ (usually $t_0 = 0$). These elements are then traced over time and all fields are affiliated to

¹Often one influence clearly dominates the other, however, such that the approximation as Newtonian fluid of purely elastic solid is justified, e.g., for pure liquids like water or metals at low temperatures.

²Even though this approach is precisely what molecular simulations are about, the particle numbers N considered there are usually of order $\mathcal{O}(N) < 10^3$, effectively rendering the systems sub-macroscopic.

them. A deformation is then described in terms of their new positions $\vec{r}(t)$ and velocities $\vec{v}(t)$ at any other time t , which are always related to the coordinates of the initial state

$$\vec{r}(\vec{R}, t), \quad \vec{v} = \frac{d}{dt} \vec{r}, \quad (2.1)$$

i.e., $\vec{R} = \vec{r}(\vec{R}, t_0)$. In other words, all fields always refer to the properties of exactly the same volume elements that have been located at $\vec{R}$ at time $t = t_0$. Therefore, $\vec{r}$ is often referred to as the *material coordinates*. The positions $\vec{r}$ can in principle be found by integrating the velocity $\vec{v}$ over time, the latter of which can be determined by Newton's second law as long as all acting forces are known. Those, however, may depend on the positions $\vec{r}$ and therefore on $\vec{R}$ according to Eq. (2.1), intrinsically coupling the equations and making them hard to solve. In a way the Lagrangian description resembles classical particle mechanics, where positions and velocities of particles are considered, and may therefore seem more naturally, particularly when the initial state can be assigned a special meaning, e.g., if it defines the lowest energy configuration of the body.

THE EULERIAN PICTURE: In contrast to the Lagrangian picture, the *spatial coordinates* $\vec{r}$ used in the Eulerian description are absolute and not tied to specific volume elements. In other words, the coordinates $\vec{r}$ are not the trajectories of the volume elements but define fixed positions in space that do not change in time. The field quantities then assign values to these spatial coordinates at every time, independent of the volume element that is currently located there, e.g., the velocity is $\vec{v}(\vec{r}, t)$. This implies, of course, that there is always a volume element present at the given coordinates, making this description valid only under careful consideration of potential boundary conditions. The trajectories of the volume elements as used in the Lagrangian picture can still be recovered in the Eulerian picture, however, by integrating the velocity (2.1) over time. Another subtlety arises when considering the temporal behavior of a quantity ϕ that is actually carried by the volume elements. In the Lagrangian picture the change in time of such a quantity is simply given by the partial derivative

$$\frac{d}{dt} \phi(\vec{R}, t) = \left. \frac{\partial \phi}{\partial t} \right|_{\vec{R}}, \quad (2.2)$$

the so called *material derivative*. In other words, the change of that quantity

depends only on the condition within the associated volume element, independent of its trajectory. At fixed spatial position $\vec{r}$, however, the change of ϕ is additionally affected by the amount that is carried towards or away from that position by the movement of the volume elements

$$\frac{d}{dt}\phi(\vec{r}(t), t) = \frac{\partial\phi}{\partial t} + \sum_i \frac{\partial\phi}{\partial r_i} \frac{\partial r_i}{\partial t} = \partial_t\phi + (\vec{v} \cdot \nabla)\phi \quad (2.3)$$

where Lagrangian trajectory $\vec{r}(t)$ of the volume element has been employed again. Hence, at fixed Eulerian coordinates $\vec{r}$ it is important to know which volume element is present there at a given time to evaluate the value of ϕ . Likewise, the temporal change $d\phi/dt$ of that quantity at that position requires knowledge not only about the increase and decrease of ϕ it self, i.e., $\partial_t\phi$, but also about the movement of the volume elements $\vec{v}$, i.e., to know which element will be present there in the future, as well as about the variation $\nabla\phi$ to anticipate which values may be transported there by the volume elements in the surrounding. This contribution to the local change in ϕ by transport is described by the last term in Eq. (2.3) and commonly referred to as *convection derivative*. Note, that here and in the following the notation $\partial_t = \frac{\partial}{\partial t}$ is used.

Any deformation of a continuous body can be described by the change in position of its constituents. In the Lagrangian picture the difference between deformed state $\vec{r}(\vec{R}, t)$ and initial state $\vec{R}$ gives the *displacement*

$$\vec{U}(\vec{R}, t) = \vec{r}(\vec{R}, t) - \vec{R}. \quad (2.4)$$

It includes all information about changes in form, position and orientation of the body. The *mapping* χ from initial to deformed state can thus be written as

$$\vec{r}(\vec{R}) = \chi(\vec{R}) \equiv \vec{R} + \vec{U}(\vec{R}) \quad (2.5)$$

and the velocity is obviously given by

$$\vec{v}(\vec{R}, t) = \frac{d}{dt}\vec{r}(\vec{R}, t) = \frac{d}{dt}\vec{U}(\vec{R}, t). \quad (2.6)$$

Let us now consider the Eulerian coordinates $\vec{r}$. Even though these coordinates are fixed, a displacement field $\vec{u}(\vec{r}, t)$ can still be formulated and the initial state can be

recovered by inverting the mapping

$$\vec{R}(\vec{r}) = \chi^{-1}(\vec{r}) = \vec{r} - \vec{U}(\vec{R}(\vec{r})) \equiv \vec{r} - \vec{u}(\vec{r}), \quad (2.7)$$

i.e., $\vec{R}(\vec{r})$ are the coordinates from which the Eulerian coordinates $\vec{r}$ would be reached when applying a displacement $\vec{U}(\vec{R})$. Note, that the Eulerian displacement field $\vec{u}(\vec{r}) = \vec{U}(\vec{R}(\vec{r})) = \vec{U}(\vec{r} - \vec{U}(\vec{R}(\vec{r})))$ is a recursive expression that leads to $\vec{U}(\vec{R}) = \vec{U}(\vec{r})$ only in case of infinitesimal displacements. The change in distance between two infinitesimally separated points can for small deformations be expressed in the form of a linear coordinate transformation

$$d\vec{R} = \underline{F} d\vec{r}, \quad (2.8)$$

with the Eulerian *deformation gradient tensor*³

$$\underline{F}(\vec{r}) = \nabla \chi^{-1}(\vec{r}) = \nabla[\vec{r} - \vec{u}(\vec{r})] = \underline{1} - \nabla \otimes \vec{u} = \underline{1} - \underline{\beta}, \quad (2.9)$$

which is basically the *Jacobian* matrix. Here the symbol $\otimes$ indicates the dyadic product and is occasionally omitted in the following, i.e., a ∇ -operator acting on an object to the r.h.s. with no symbol in between means that the gradient is taken. Hence, $\underline{\beta} = \nabla \vec{u} = \nabla \otimes \vec{u}$ is the gradient of the displacement field, which is also commonly referred to as *displacement gradient* or *deformation tensor*. It gives the *relative displacement* of the considered points

$$d\vec{u} = d\vec{r} - d\vec{R} = (\underline{1} - \underline{F})d\vec{r} = \underline{\beta} d\vec{r}. \quad (2.10)$$

The determinant of $\underline{F}$ sets the infinitesimal volume elements of initial and deformed state into relation $d^3\vec{R} = \det \underline{F} d^3\vec{r}$ and is to linear order given by

$$\det \underline{F} \approx 1 - \nabla \cdot \vec{u} = 1 - \text{tr}(\nabla \vec{u}), \quad (2.11)$$

where $\nabla \cdot \vec{u}$ is the divergence of the displacement field, with the $\cdot$ symbol denoting the *inner product*, also referred to as *scalar* or *dot product*. The divergence of the displacement field $\nabla \cdot \vec{u}$ determines the local change in volume and has to vanish for incompressible media therefore. Since it corresponds to the trace of $\underline{\beta}$, the diagonal elements of the latter describe the compression and dilatation of a volume element in the respective directions. Despite its name, the deformation tensor accounts also

³Here and in the following the designation *tensor* refers to a matrix of rank(2) if the rank is not explicitly given.

for rigid body rotations, which technically do not count as deformations since no change in shape takes place. To distinguish between rotations and actual deformations, consider the squared distance of two infinitesimally separated points in the deformed and initial state respectively

$$(dl)^2 = \sum_{i=0}^3 dr_i dr_i, \quad (dL)^2 = \sum_{i=0}^3 dR_i dR_i. \quad (2.12)$$

With Eq. (2.9) the *strain tensor* $\underline{\varepsilon}$ is found

$$\begin{aligned} (dL)^2 &= \sum_{i,j,k=0}^3 J_{ij} J_{ik} dr_j dr_k \\ &= \sum_{i,j,k=0}^3 (\delta_{ij} - \beta_{ij}) (\delta_{ik} - \beta_{ki}) dr_j dr_k \\ &= (dl)^2 - \sum_{i,j,k=0}^3 (\beta_{jk} + \beta_{kj} - \beta_{ij} \beta_{ki}) dr_j dr_k \\ &= (dl)^2 - \sum_{i,j,k=0}^3 \left(\frac{\partial u_k}{\partial r_j} + \frac{\partial u_j}{\partial r_k} - \frac{\partial u_i}{\partial r_j} \frac{\partial u_i}{\partial r_k} \right) dr_j dr_k \\ &= (dl)^2 - \sum_{j,k=0}^3 2\varepsilon_{jk} dr_j dr_k \end{aligned} \quad (2.13)$$

Note, that these calculations can analogously be done in the Lagrangian picture yielding quantities that refer to the initial state $\vec{R}$. For small displacements, however, the resulting quantities can be used alike and the strain tensor is to linear order given by

$$\underline{\varepsilon} = \frac{1}{2} (\nabla \vec{u} + (\nabla \vec{u})^\top) \quad (2.14)$$

It accounts for all changes in length during a deformation and corresponds to the symmetric part of the deformation tensor, carrying its trace

$$\text{tr } \underline{\varepsilon} = \text{tr } \underline{\beta} = \nabla \cdot \vec{u}. \quad (2.15)$$

The traceless antisymmetric part

$$\underline{\varphi} = \frac{1}{2} (\nabla \vec{u} - (\nabla \vec{u})^\top) \quad (2.16)$$

in contrast accounts for rigid body rotations and the complete deformation tensor can be disassembled like [Sad09]

$$\underline{\beta} = \underline{\varphi} + \underline{\varepsilon}. \quad (2.17)$$

The strain tensor may be further decomposed like

$$\underline{\varepsilon} = \underline{\hat{\varepsilon}} + \underline{\tilde{\varepsilon}}, \quad (2.18)$$

to separately account for a normal contribution, given by the *spherical strain* (naturally including the trace)

$$\underline{\hat{\varepsilon}} = \frac{1}{3} \underline{\mathbb{1}} \operatorname{tr} \underline{\varepsilon} = \frac{1}{3} \underline{\mathbb{1}} (\nabla \cdot \vec{u}), \quad (2.19)$$

and a shear contribution, given by the (traceless) *deviatoric strain*

$$\underline{\tilde{\varepsilon}} = \underline{\varepsilon} - \frac{1}{3} \underline{\mathbb{1}} \operatorname{tr} \underline{\varepsilon} = \frac{1}{2} \left(\nabla \vec{u} + (\nabla \vec{u})^\top - \frac{2}{3} \underline{\mathbb{1}} (\nabla \cdot \vec{u}) \right), \quad (2.20)$$

Naturally, the spherical strain vanishes if the material is incompressible. In any case, no matter if the material is incompressible or not, the mass is globally conserved as demanded by the *continuity equation* [LL87]

$$\partial_t \rho + \nabla \cdot (\rho \vec{v}) = \partial_t \rho + (\vec{v} \cdot \nabla) \rho + \rho (\nabla \cdot \vec{v}) = \frac{d\rho}{dt} + \rho (\nabla \cdot \vec{v}) = 0, \quad (2.21)$$

with mass density $\rho(\vec{r}, t)$ and mass flux $\vec{j} = \rho \vec{v}$. It states that the change of mass in a given volume element is exclusively determined by its transport into or out of it. The temporal evolution of a volume element is then given by Newton's law of momentum conservation (see A.1)

$$\rho \frac{d\vec{v}}{dt} = \vec{f}_{\text{in}} + \vec{f}_{\text{ex}}. \quad (2.22)$$

The vector fields $\vec{f}_{\text{ex}}(\vec{r}, t)$ and $\vec{f}_{\text{in}}(\vec{r}, t)$ are the external and internal forces per unit volume, respectively. Such a force can without loss of generality be written as the divergence of a tensor [LKP86]

$$\vec{f}_{\text{in}} = \nabla \cdot \underline{\sigma}. \quad (2.23)$$

Integration over the whole volume yields the total force

$$\vec{F} = \int_{\mathbb{R}^3} \vec{f} d^3\vec{r} = \int_{\mathbb{R}^3} \nabla \cdot \underline{\sigma} d^3\vec{r} = \int_{\partial\mathbb{R}^3} \underline{\sigma} \cdot \vec{n} d^2\vec{r}_s. \quad (2.24)$$

where *Gauss's divergence theorem* has been used to express it as an integral of normal stresses along the surface $\vec{r}_s$ with normal vector $\vec{n}$. The entries σ_{ij} of the so called *stress tensor* give the forces per unit area acting on a volume element (cf. Fig. 2.1). Thereby, the first index i refers to the normal vector $\vec{e}_i$ defining the orientation of the surface while the second index j refers to the unit vector $\vec{e}_j$ defining the direction of the stress. Hence, equal indices indicate normal stresses perpendicular to the surface, i.e., compression and dilatation, while different indices indicate shear stress parallel to the surface. The components of the strain tensor $\underline{\varepsilon}$ could be visualized in the exact same way. Obviously, the stress tensor contains all information about the internal forces and thus determines the material's behavior. Arising only under deformation, these forces, and therefore the stress tensor, have to be related to the strain somehow. Linking these two quantities by formulating *constitutive laws* completes the mechanical description.

In the following chapters the two limiting cases, namely incompressible viscous Newtonian fluids and linear elastic solids, are considered in the context of wetting and described by means of the stress-strain relation.

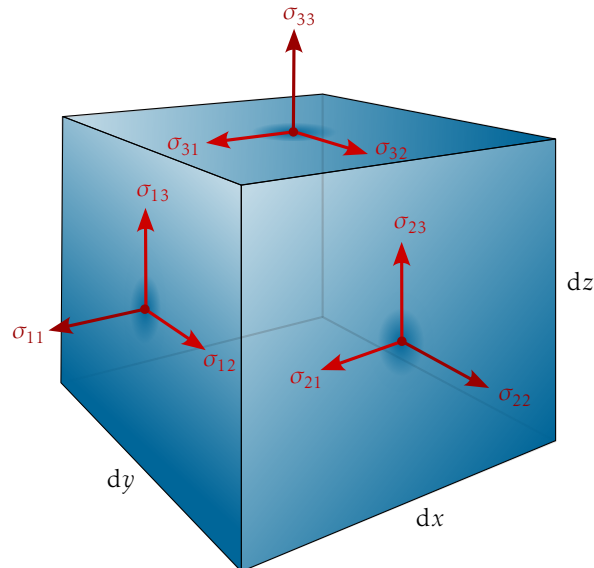


FIGURE 2.1.: Components of the stress tensor acting on the surfaces of a cartesian volume element. Normal stresses (darker red, equal indices) are aligned with the surface normal while shear stresses (lighter red, different indices) are perpendicular to them.

2.2. FLUID DYNAMICS IN THIN LIQUID FILMS

In the previous chapter the mechanical behavior of fluids has roughly been outlined. The latter shall now be reviewed in more detail with the ulterior motive of modeling thin liquid films on elastic substrates. In the following only viscous isotropic incompressible Newtonian fluids are considered.

2.2.1. THE NAVIER-STOKES EQUATIONS

In the frame of continuum mechanics the point of departure towards the description of such fluids is the conservation of momentum (2.22). The vector $\vec{f}_{\text{ex}}$ includes all external forces that drive the system like gravity or imposed pressure gradients and are assumed to be known. Now, the internal forces have to be formulated in terms of the stress tensor according to Eq. (2.23). As mentioned earlier, fluids own the ability to release externally applied tensions by flowing. Hence, in an *ideal* fluid no shear stresses arise and only normal forces are resisted. If that is true, the stress tensor has to be diagonal. Moreover, assuming the material to be isotropic, the stress tensor has to be rotation invariant and therefore proportional to identity [Bato0]

$$\underline{\sigma} = -p\mathbb{I}, \quad (2.25)$$

where $p(\vec{r}, t)$ is the scalar pressure field.⁴ Using this stress tensor in the momentum conservation equation yields the *Euler equation*. In case of viscous fluids, however, the irreversible momentum transfer from particles of high velocity to particles of lower velocity due to friction has to be taken into account [LL87]. As friction depends on the relative velocity between neighboring regions it has to be proportional to the temporal derivative of the strain tensor also referred to as the *strain rate tensor* [LL87, Sado9]

$$\underline{\dot{\varepsilon}} = \partial_t \underline{\varepsilon} = \frac{1}{2} (\nabla \vec{v} + (\nabla \vec{v})^\top). \quad (2.26)$$

Note, that this tensor has non-vanishing diagonal elements. indicating that friction plays a role also in the compressions of liquids [Bes06]. The strength at which shear and normal movements are resisted by friction may differ, however, which is why the spherical and deviatoric strain rates [see Eq. (2.18)] are scaled by two different

⁴At this point, one might have naively assumed at first that the trace of the stress tensor must vanish as it is directly proportional to the trace of the strain tensor. This is, however, not the case and the pressure field is even required to ensure incompressibility. More details on the subtleties of incompressibility are provided in App. A.4.

material constants, namely the *dynamic (first) viscosity* η and the *volumetric (second) viscosity* ζ [LL87, Beso6]

$$\underline{\sigma} = -p\underline{\mathbb{1}} + 3\zeta\partial_t\underline{\hat{\varepsilon}} + 2\eta\partial_t\underline{\hat{\varepsilon}}. \quad (2.27)$$

In general, both material constants, η and ζ , may be inhomogeneous scalar fields that depend, e.g., on the local temperature T . In the following, however, they are assumed constant and so is the temperature. Note, that sometimes the *kinematic viscosity* $\nu = \eta/\rho$ is used instead. With Eq. (2.27) the momentum conservation [Eq. (2.22)] becomes the *Navier-Stokes equation* (NSE) [Battoo, LL87, Popoo]

$$\rho \left[\frac{\partial \vec{v}}{\partial t} + (\vec{v} \cdot \nabla) \vec{v} \right] = -\nabla p + \eta \Delta \vec{v} + \left(\zeta + \frac{1}{3} \eta \right) \nabla (\nabla \cdot \vec{v}) + \vec{f}_{\text{ex}}, \quad (2.28)$$

where Eq. (2.3) has been used. The conservation and transport of mass has already been formulated in the continuity equation (2.21).⁵ For many real fluids it is further reasonable to assume incompressibility, i.e., constant mass density $\rho(\vec{r}, t) = \rho_0 = \text{const.}$, in which case the conservation laws reduce to

$$\rho_0 \left[\frac{\partial \vec{v}}{\partial t} + (\vec{v} \cdot \nabla) \vec{v} \right] = -\nabla p + \eta \Delta \vec{v} + \vec{f}_{\text{ex}}, \quad (2.29a)$$

$$\nabla \cdot \vec{v} = 0. \quad (2.29b)$$

Note, that the continuity equation for incompressible fluids (2.29b) agrees with the condition for volume conservation, that is the vanishing trace of the deformation tensor [Eq. (2.11)]. Nevertheless, the trace of the stress tensor can take finite values still, which is why the pressure gradient has to be taken into account. The equations (2.29) provide a comprehensive description of isotropic viscous incompressible fluids and can be used to approach the problem of wetting by fitting them to the layer symmetry as shown in Fig. 2.2.

2.2.2. ADAPTATION TO LAYER GEOMETRY

Consider a liquid layer of local thickness $h(x, y, t)$ with a free surface at $z = h + \xi$ on a deformable solid substrate as shown in Fig. 2.2. The substrate topography, given by the function $\xi(x, y)$, is assumed to be steady for now. To adapt the incompressible

⁵Sometimes also the collection of the three conservation equations, i.e., of energy, momentum and mass, are referred to as *the Navier-Stokes equations* (plural) in the diverse literature, while here only the momentum equation [Eq. (2.28)] is labeled as such. Since here the temperature is assumed homogeneous and constant, however, the corresponding equations are not considered.

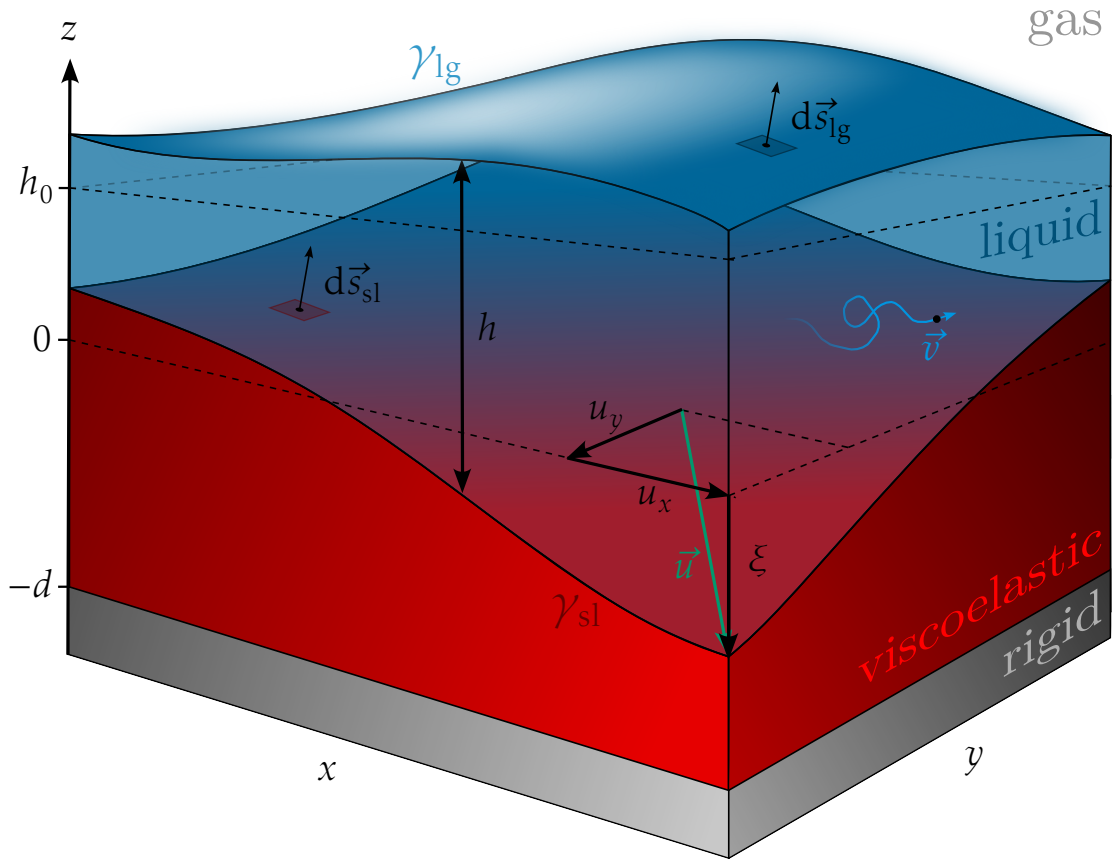


FIGURE 2.2.: Schematic of a two layer geometry system with a liquid layer (blue) of mean thickness h_0 on top of a viscoelastic layer (red). The $z = 0$ level is defined with respect to the undeformed homogeneous reference state of the latter. While the viscoelastic layer is fixed to a smooth rigid substrate at depth $z = -d$ underneath, it carries the liquid layer of local thickness $h(x, y)$ on top. The shape of the deformed interface between those two is given by the function $\xi(x, y)$ which corresponds to the vertical component u_z of the displacement vector $\vec{u}$ (green) at $z = 0$. The profile of the free liquid-vapour interface is consequently given by $h + \xi$ and its dynamics follows the flow of the liquid as described by the velocity field $\vec{v}$ at the surface. Both, the solid-liquid and the liquid-vapour interface are characterized by the excess free energies γ_{sl} and γ_{lg} per unit area ds , respectively. The directed surface elements $d\vec{s}$ at the two interfaces are determined by the profiles ξ and $h + \xi$ (see Fig. A.1).

NSE (2.29) to such a geometry, the corresponding boundary conditions have to be formulated. In the course of this it will prove convenient to distinguish horizontal and vertical directions. The velocity and gradient vectors are therefore decomposed

$$\vec{v}_{\parallel} = \begin{pmatrix} v_x \\ v_y \end{pmatrix}, \quad v_z \quad \text{and} \quad \nabla_{\parallel} = \begin{pmatrix} \partial_x \\ \partial_y \end{pmatrix}, \quad \partial_z. \quad (2.30)$$

NO-PENETRATION CONDITION

First of all, the liquid should neither be able to penetrate the substrate nor to detach from it, which is ensured by the *no-penetration condition* [LL87]. It demands that all

velocity components perpendicular to the solid-liquid (sl) interface vanish

$$(\vec{v} \cdot \vec{n}_{\text{sl}}) \Big|_{z=\xi} = 0, \quad (2.31)$$

with the normal vector

$$\vec{n}_{\text{sl}} = \frac{1}{\sqrt{1 + (\nabla_{\parallel} \xi)^2}} \begin{pmatrix} -\nabla_{\parallel} \xi \\ 1 \end{pmatrix}. \quad (2.32)$$

The denominator of the normalization factor in front of the normal vector is from here on referred to as the *metric factor* $m(\psi) = \sqrt{1 + (\nabla_{\parallel} \psi)^2}$. It relates an infinitesimal element ds of a surface $\psi(x, y)$ to its projection into the (x, y) -plane $ds = m(\psi) dx dy$ (see App. A.2).

NAVIER SLIP CONDITION

Further, the friction at the solid-liquid interface brakes down the tangential flow. This is commonly modeled by introducing the *Navier slip condition* [Batoo, LL87, ODB97]

$$\underline{P}(\vec{n}_{\text{sl}}) \cdot \vec{v} \Big|_{z=\xi} = \ell_s (\vec{n}_{\text{sl}} \cdot \nabla) [\underline{P}(\vec{n}_{\text{sl}}) \cdot \vec{v}] \Big|_{z=\xi}. \quad (2.33)$$

Here, the *projection operator* $\underline{P}(\vec{n}) = \underline{1} - \vec{n} \otimes \vec{n}$ projects a vector to the plane defined by $\vec{n}$ while the *directional derivative* $\vec{n} \cdot \nabla$ gives the change of a quantity in direction of $\vec{n}$.⁶ The *finite slip length* ℓ_s is a vertical length scale and can be imagined as the distance to an other hypothetical substrate lying underneath the real one. The tangential velocity $\vec{v}_{\parallel}$ is assumed to vanish at this imaginary second substrate and to increase linearly along the distance ℓ_s . Note, that there are also other slip models like, e.g., the one derived by RUCKENSTEIN and DUNN [RD77].

KINEMATIC BOUNDARY CONDITION

The no-penetration and Navier slip conditions define the restricted movement of the liquid at the solid-liquid interface. The liquid-gas interface at $z = h + \xi$ on the other hand is free and can be described by the *kinematic boundary condition*. It states that no flux across that boundary occurs, i.e., the free surface follows the velocity

⁶Here again $\vec{n} \otimes \vec{n} = \underline{N}$ is a dyadic product and yields a matrix $N_{ij} = n_i n_j$ while $\vec{n} \cdot \nabla = \sum_i n_i \partial_i$ is an inner product.

field $\vec{v}$ [LL87]

$$\partial_t(h + \xi) = \partial_t h = \left[v_z - \vec{v}_{\parallel} \cdot \nabla_{\parallel}(h + \xi) \right]_{z=h+\xi}. \quad (2.34)$$

Using the no-penetration condition (2.31), the vertical velocity component may be replaced by integrating the continuity equation (2.29b) in z -direction

$$v_z \big|_{z=h+\xi} = \vec{v}_{\parallel} \big|_{z=\xi} \cdot \nabla_{\parallel} \xi - \int_{\xi}^{h+\xi} \nabla_{\parallel} \cdot \vec{v}_{\parallel} \, dz. \quad (2.35)$$

The kinematic boundary condition (2.34) can then be rewritten using *Leibniz integral rule*

$$\begin{aligned} \partial_t h &= - \int_{\xi}^{h+\xi} \nabla_{\parallel} \cdot \vec{v}_{\parallel} \, dz - \vec{v}_{\parallel} \big|_{z=h+\xi} \cdot \nabla_{\parallel}(h + \xi) + \vec{v}_{\parallel} \big|_{z=\xi} \cdot \nabla_{\parallel} \xi \\ &= - \nabla_{\parallel} \cdot \left[\int_{\xi}^{h+\xi} \vec{v}_{\parallel} \, dz \right]. \end{aligned} \quad (2.36)$$

FORCE EQUILIBRIUM AT THE SURFACE

The velocity at the free surface is governed by the tensions that are present there and the surface boundary yields to them in order to achieve an equilibrium. There, the balance of external and internal forces is

$$(\underline{\sigma}_l - \underline{\sigma}_g) \big|_{z=h+\xi} \cdot \vec{n}_{lg} = \vec{\alpha}_{lg} = -p_{\alpha} \vec{n}_{lg} + \vec{\tau}, \quad (2.37)$$

where the normal vector $\vec{n}_{lg}$ now refers to the liquid-gas interface [see $d\vec{s}_{lg} = s_{lg} \vec{n}_{lg}$ in Fig. 2.2]. The internal forces are given by the stresses tensors $\underline{\sigma}_l$ in the liquid and $\underline{\sigma}_g$ gas phase according to Eq. (2.24) while the external stresses acting on the surface are summarized in the vector field $\vec{\alpha}_{lg}(\vec{r})$. The latter can be decomposed into the normal pressure $\vec{n}_{lg} \cdot \vec{\alpha}_{lg} = -p_{\alpha}$ and a tangential stresses $\vec{\tau} = \underline{P}(\vec{n}_{lg}) \cdot \vec{\alpha}_{lg}$. As compared to the stresses acting within the liquid, those exerted by the gas phase are assumed to be very small and are therefore neglected, i.e., $\underline{\sigma}_g \approx 0$. Projecting Eq. (2.37) onto the normal and tangential direction respectively results in two conditions

$$\vec{n}_{lg} \cdot \underline{\sigma}_l \big|_{z=h+\xi} \cdot \vec{n}_{lg} = -p_{\alpha}, \quad (2.38a)$$

$$\underline{P}(\vec{n}_{lg}) \left(\underline{\sigma}_l \big|_{z=h+\xi} \cdot \vec{n}_{lg} \right) = \vec{\tau}. \quad (2.38b)$$

Note, that Eq. (2.38b) is vectorial since the orientation of $\vec{\tau}$ is not uniquely determined by the profile $h+\xi$ of the liquid-gas interface but depends on $\vec{a}_{\text{lg}}$ as well. It is therefore generally advantageous to decompose $\vec{\tau}$ into two orthonormal tangential vectors that are unique with regard to $h+\xi$, i.e., $\vec{\tau} = \tau_1 \vec{t}_1 + \tau_2 \vec{t}_2$ with, e.g.,

$$\vec{t}_1 = \frac{\vec{n}_{\text{lg}} \times \vec{e}_y}{\sqrt{1 - (\vec{n}_{\text{lg}} \cdot \vec{e}_y)^2}} \quad \text{and} \quad \vec{t}_2 = \frac{\vec{n}_{\text{lg}} \times \vec{e}_x}{\sqrt{1 - (\vec{n}_{\text{lg}} \cdot \vec{e}_x)^2}}. \quad (2.39)$$

Here $\vec{e}_i$ is the Cartesian base vector in i -direction and $\tau_i = \vec{\alpha} \cdot \vec{t}_i$ such that $|\vec{\tau}| = \sqrt{\tau_1^2 + \tau_2^2}$. The horizontal force equilibrium [Eq. (2.38b)] is then given by

$$\vec{t}_i \cdot \underline{\sigma}|_{z=h+\xi} \cdot \vec{n}_{\text{lg}} = \tau_i \quad \text{with} \quad i = 1, 2. \quad (2.40)$$

Expressions (2.38a) and (2.40) are respectively expanded in terms of the velocity field $\vec{v}$ and the profiles h and ξ in App. A.3.

Together with all the above introduced boundary conditions the Navier-Stokes equations are complete and the problem is well defined. The only thing left is to solve it. Since it is a non-linear and non-local partial differential equation, doing so may turn out to be a pretty grueling affair. Therefore, the equations will first be simplified further.

2.2.3. LONG-WAVE APPROXIMATION

In the context of wetting the liquid layers are usually very thin as compared to the lateral extension of the system. This anisotropy can be exploited to simplify the Navier-Stokes equations as well as the boundary conditions. Therefore, it has proven practical to first rewrite the equations in dimensionless form, which reduces the overall number of parameters and allows for direct comparison of different systems in terms of the remaining dimensionless parameters. The basic idea is to express all quantities in units of arbitrary *scales* (denoted by capital letters) that carry the respective dimension

$$x = L\tilde{x}, \quad y = L\tilde{y}, \quad z = H\tilde{z}, \quad t = T\tilde{t}. \quad (2.41)$$

The distinction of horizontal and vertical lengths is now taken into account by different choice of L and H . Usually the values of these scales are chosen such that the dimensionless variables, denoted by a tilde, are of $\mathcal{O}(1)$. Thus, the ratio $\epsilon = H/L$ quantifies the anisotropy between vertical and horizontal extension of the system

and can be used to rate the impact of different terms. The velocity and pressure fields are non-dimensionalized analogously [ODB97]

$$v_x = \frac{L}{T} \tilde{v}_x, \quad v_y = \frac{L}{T} \tilde{v}_y, \quad v_z = \frac{H}{T} \tilde{v}_z, \quad p = \frac{\eta}{\epsilon^2 T} \tilde{p}. \quad (2.42)$$

Note, that in case of very thin liquid layers, i.e., $\epsilon \rightarrow 0$, the impact of external pressures increases as compared to other forces, which is why p is non-dimensionalized using ϵ^2 [ODB97, Batoo]. Introducing the dimensionless variables into the NSE and dropping the tildes gives

$$\epsilon \text{Re} \left[\partial_t \vec{v}_{\parallel} + (\vec{v}_{\parallel} \cdot \nabla_{\parallel} + v_z \partial_z) \vec{v}_{\parallel} \right] = -\nabla_{\parallel} p + (\epsilon^2 \Delta_{\parallel} + \partial_z^2) \vec{v}_{\parallel} \quad (2.43a)$$

$$\epsilon^3 \text{Re} \left[\partial_t v_z + (\vec{v}_{\parallel} \cdot \nabla_{\parallel} + v_z \partial_z) v_z \right] = -\partial_z p + \epsilon^2 (\epsilon^2 \Delta_{\parallel} + \partial_z^2) v_z \quad (2.43b)$$

with only one dimensionless physical parameter remaining; the *Reynolds number* $\text{Re} = \frac{LH\rho}{\eta T}$. It can be understood as the ratio of two characteristic momentum densities. On one hand, the convective momentum density $\rho L/T$ which includes the characteristic horizontal velocity scale $U = L/T$ and is related to the amount of kinetic energy in the system. On the other hand, the momentum diffusion density η/H which includes the dynamic viscosity and accounts for dissipation due to friction. Large Reynolds numbers usually indicate that turbulent flows are to be expected while low Reynolds numbers suggest the motion to be rather laminar [Popoo]. The stress equilibrium conditions at the free surface (2.38) can be non-dimensionalized just alike [see App. A.3]. Assuming the liquid layer to be very shallow, the ratio of characteristic length scales becomes accordingly small $\epsilon \ll 1$ and can be used to expand the equations. In the context of fluid mechanics such simplifications are known as *lubrication-* or *long-wave-approximations* [ODB97]. Up to leading order in ϵ the dimensionless NSE (2.43) and stress balances at the surface (A.6) and (A.9) are⁷

$$\nabla_{\parallel} p = \partial_z^2 \vec{v}_{\parallel}, \quad (2.44a)$$

$$\partial_z p = 0, \quad (2.44b)$$

$$p = p_{\alpha}, \quad (2.44c)$$

$$\partial_z \vec{v}_{\parallel} \Big|_{z=h+\xi} = \tau_1 \vec{e}_x + \tau_2 \vec{e}_y = \vec{\tau}. \quad (2.44d)$$

⁷Remember, that the tildes have been dropped here, i.e., p_{α} and τ_i refer to the dimensionless quantities, that is $\tilde{p}_{\alpha} = \epsilon^2 T p_{\alpha} / \eta$ and $\tilde{\tau}_i = \epsilon T \tau_i / \eta$.

Note, that in the long-wave limit $\vec{n}_{lg} \approx \vec{e}_z$, $\vec{t}_1 \approx \vec{e}_x$ and $\vec{t}_2 \approx \vec{e}_y$. Since Eq. (2.44b) demands constant internal pressure in z -direction, it is not surprising that it equals the normal stress at the surface as stated by Eq. (2.44c). Further on, the no penetration condition (2.31) and Navier slip condition (2.33) reduce to

$$v_z \big|_{z=\xi} = 0, \quad \vec{v}_{\parallel} \big|_{z=\xi} = \ell_s \partial_z \vec{v}_{\parallel} \big|_{z=\xi}. \quad (2.45)$$

Note, that the ratio ϵ can be used also to consider the opposite case, i.e., liquid layers that are very thick as compared to the lateral extension of the system, which is known as *deep-water approximation*. Note, that since the time derivative on the left hand side of Eq. (2.43) has been neglected, no inertia is considered in Eqs. (2.44) any more. In other words, the system is overdamped even though the Reynolds number has not explicitly been chosen particularly small. After all these approximations, the equations are sufficiently simplified to allow for the derivation of an evolution equation for the liquid-gas interface profile $\zeta = h + \xi$.

2.2.4. THE THIN-FILM EQUATION

The starting point for the derivation of an evolution equation for the free surface profile $\zeta = h + \xi$ of the liquid is the kinematic boundary condition (2.36). It determines the dynamics of the surface by integrating $\vec{v}_{\parallel}$ in z -direction.⁸ To do so, the z -dependence of the velocity field has to be known first. Since Eq. (2.44b) demands constant p in z -direction, Eq. (2.44a) can simply be integrated, yielding

$$\vec{v}_{\parallel} = \frac{1}{2} z^2 \nabla_{\parallel} p + \vec{c}_1 z + \vec{c}_2. \quad (2.46)$$

The first and second integration constants are determined by Eq. (2.44d) and the Navier slip condition (2.45), respectively

$$\vec{c}_1 = \vec{\tau} - (h + \xi) \nabla_{\parallel} p, \quad (2.47a)$$

$$\vec{c}_2 = (\ell_s - \xi) \vec{\tau} + \left[\frac{1}{2} \xi^2 + \xi h - \ell_s h \right] \nabla_{\parallel} p. \quad (2.47b)$$

⁸Since the substrate profile ξ is assumed static for now, the following considerations actually concern only the liquid layer thickness h .

Now, that the velocity field is known as a function of z , it can be placed into the integral (2.36) to obtain the *thin-film equation* [OR92, Mit93, Thio7]

$$\begin{aligned}\partial_t h &= -\nabla_{\parallel} \cdot \int_{\xi}^{h+\xi} \left[\left(\frac{1}{2}(z^2 + \xi^2) - z(h + \xi) + \xi h - \ell_s h \right) \nabla_{\parallel} p + \vec{\tau}(z + \ell_s - \xi) \right] dz \\ &= \nabla_{\parallel} \cdot \left[h^2 \left(\frac{h}{3} + \ell_s \right) \nabla_{\parallel} p + h \left(\frac{h}{2} + \ell_s \right) \vec{\tau} \right],\end{aligned}\quad (2.48)$$

or in dimensional form

$$\partial_t h = \nabla_{\parallel} \cdot \left[\frac{h^2}{\eta} \left(\frac{h}{3} + \ell_s \right) \nabla_{\parallel} p + \frac{h}{\eta} \left(\frac{h}{2} + \ell_s \right) \vec{\tau} \right]. \quad (2.49)$$

As far as the liquid is concerned no tangential forces are considered for now, i.e., $\vec{\tau} = 0$. According to Eq. (2.44c) the pressure p corresponds to the external normal stress p_{α} at the surface. The latter may include multiple contributions and its exact composition is discussed in Ch. 3. Note, that the thin-film equation corresponds to a volume conservation law [Thio, TAP16, Wil+15]

$$\partial_t h = -\nabla_{\parallel} \cdot \vec{j} \quad (2.50)$$

similar to the continuity equation [Eq. (2.21)], with h being a density, namely a volume per area. The flux, however, is now given by the product of a mobility $Q(h) = \frac{h^2}{\eta} \left(\frac{h}{3} + \ell_s \right)$ and the pressure gradient

$$\vec{j} = -Q(h) \nabla_{\parallel} p, \quad (2.51)$$

resulting in a *Cahn-Hilliard* type form [Cah65, Mit93]. Note, that in some special cases this form can be achieved even if $\vec{\tau} \neq 0$. The corresponding term has then to be expressed in a way that it takes the form $Q(h) \nabla f(h)$, such that the mobility can be excluded. See Refs. [OR92, TK04, TAP16] for examples and further details. Obviously, a steady state $\partial_t h = 0$ has to satisfy $\nabla_{\parallel} p = 0$, i.e., uniform pressure. The complete velocity field can still be recovered from h , ξ and p using Eq. (2.46) and

the continuity equation to obtain the vertical component

$$v_z = - \int_{\xi}^z \nabla_{\parallel} \cdot \vec{v}_{\parallel} dz \quad (2.52a)$$

$$= - \sum_{n=x,y} \left[\frac{1}{6}(z^3 - \xi^3) - \frac{1}{2}z^2(h + \xi) + \frac{1}{2}\xi^2(z - h) + h\xi z \right] \partial_n^2 p \quad (2.52b)$$

$$+ \left[\left(z\xi - \frac{1}{2}z^2 - \frac{1}{2}\xi^2 \right) \partial_n(h + \xi) + h(z - \xi) \partial_n \xi \right] \partial_n p ,$$

where $\ell_s = 0$ and $\vec{\tau} = 0$ has been assumed to obtain Eq. (2.52b).

2.3. LINEAR ELASTICITY

Since the governing equations for the liquid layer have been found, the elastic substrate is to be considered next. As mentioned in Sec. 2.1, elastic materials usually exhibit some kind of fixed structure on the molecular level, like crystalline lattices (e.g. in metals) or polymer networks (e.g. in rubbers), in which the particles are strongly bound. In the absence of external forces the particles adopt the energetically most favorable arrangement referred to as *reference state*. Any deformation away from that state is resisted by the binding forces⁹ and results in an increase in potential energy. Under exertion of a constant load, the material deforms until inner stresses equilibrate the external ones and a steady state is achieved. Once the exposure ends, the material yields to the inner forces and returns to its original state. This ability to reverse deformations is referred to as *elasticity*. According to that picture, the stress has to be directly related to the strain $\sigma(\varepsilon)$ in contrast to the stresses acting in viscous fluids which depend on the strain rate (2.27) instead. Depending on the material a variety of different *stress-strain relations* is conceivable. In the small strain limit, however, most materials exhibit an approximately linear behavior $\sigma \sim \varepsilon$ that tends to become non-linear as the strain increases. Eventually, the stress reaches a critical level at which the bonds between the particles break up completely and the body fractures which is sometimes referred to as *material failure* [Sadog]. If this point is reached already at smaller strains close to the linear regime the material is called *brittle*. However, a damaging or rearrangement of the internal structure may appear even before the fracturing point is reached. It so happens, that a so called *yielding point* is reached beyond which the deformation occurs partially *plastic*, meaning that it can not be completely reversed and the reference state

⁹These can be intermolecular forces but also purely entropic in origin, e.g., in polymer networks.

is changed. Materials that exhibit such behavior before they fracture are called *ductile*. A deformation is called plastic, if it is permanent, even upon removing the load [Sad09]. If the bonds are infinitely strong such that no deformations occur at all the material is referred to as *rigid*.

In the following, the mathematical description of elastic material mechanics shall be discussed, particularly focusing on the layer geometry of a soft substrate of finite thickness. Thereby, only linear stress-strain relations are considered, i.e., small strains far from yielding or fracturing points. Even though the Lagrangian picture may offer a potentially more intuitive approach for the description of elastic deformations due to the existence of a reference state, the Eulerian description is used in the following to remain consistent with the description of the liquid in Sec. 2.2.

2.3.1. THE NAVIER-CAUCHY EQUATION

Starting again from Newton's law of momentum conservation (2.22) the stress tensor is to be formulated in order to describe the internal resisting forces. Aside of linearly depending on strain, the stress is further assumed to do so only locally in space and time [LKP86, Beso6]. In other words, neither do strains at other locations influence the stress at the current one nor does the material have a memory, i.e., its history does not influence the current situation. The most general linear stress-strain relation is then given by *Hooke's law* [Sad09]

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl} . \quad (2.53)$$

The $3^4 = 81$ components of the rank(4) tensor $\underline{C}$ are called *material constants* and give the proportionalities between all stress and strain tensor components. Fortunately, the number of material constants reduces to only two different quantities in case of isotropic media.¹⁰ Now, only normal and shear strain are distinguished and the stress tensor is given by a superposition of spherical and deviatoric strain [Eqs. (2.19) and (2.20)]

$$\underline{\sigma} = 3K\underline{\hat{\varepsilon}} + 2\mu\underline{\tilde{\varepsilon}} . \quad (2.54)$$

The corresponding material constants are the *compression modulus* K and the *shear modulus* μ . In most of the literature, however, the stress is rather expressed in terms

¹⁰Note, that for the exact same reason there are only two viscosities in Eq. (2.27). The constitutive relation of a simple liquid in Sec 2.2 is thus perfectly analogue to the one of a linear elastic material as introduced here. One relates to the strain rate, while the other relates to the strain itself. It will be shown in Sec. 2.4 that both are required for the description of viscoelastic materials.

of the general strain [Sadog]

$$\underline{\sigma} = \lambda \mathbb{1} \text{tr} \underline{\varepsilon} + 2\mu \underline{\varepsilon}, \quad (2.55)$$

with $\lambda = K - 2\mu/3$ being the *first Lamé constant*. The trace of the stress tensor

$$\text{tr} \underline{\sigma} = (3\lambda + 2\mu) \text{tr} \underline{\varepsilon} = 3K \text{tr} \underline{\varepsilon} \quad (2.56)$$

can be used to invert Eq. (2.55) and express the strain as a function of stress

$$\underline{\varepsilon} = \frac{1}{2\mu} \left(\underline{\sigma} - \frac{\lambda}{3\lambda + 2\mu} \mathbb{1} \text{tr} \underline{\sigma} \right). \quad (2.57)$$

For scenarios where stresses are applied in only one direction $\vec{e}_a$, i.e., $\vec{e}_a \cdot \underline{\sigma} \cdot \vec{e}_a = \sigma_a$ and $(\underline{\sigma} \cdot \vec{e}_a) \times \vec{e}_a = 0$, it is useful to define the proportionality between these stresses and the strain they cause in the same direction

$$\vec{e}_a \cdot \underline{\sigma} \cdot \vec{e}_a = \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu} \vec{e}_a \cdot \underline{\varepsilon} \cdot \vec{e}_a = E \vec{e}_a \cdot \underline{\varepsilon} \cdot \vec{e}_a, \quad (2.58)$$

where the *Youngs modulus* E is identified using Eq. (2.57). The proportionality between all the other components can be expressed in terms of E as well [Sadog]

$$\underline{\varepsilon} = \frac{1 + \nu}{E} \underline{\sigma} - \frac{\nu}{E} \mathbb{1} \text{tr} \underline{\sigma}, \quad (2.59a)$$

$$\underline{\sigma} = \frac{E}{1 + \nu} \left(\underline{\varepsilon} + \frac{\nu}{1 - 2\nu} \mathbb{1} \text{tr} \underline{\varepsilon} \right), \quad (2.59b)$$

with the dimensionless *Poisson ratio* $\nu = \lambda/(2(\lambda + \mu))$. Obviously, there are various options on how to represent the constitutive law and even though only two different material constants are required, these can be chosen very differently. The connections between the most commonly used ones are given in Tab. 2.1. Proceeding with Eq. (2.55) for the time being, Newtons law of momentum conservation (2.22) yields the *Navier-Cauchy equation*

$$\rho \partial_t^2 \vec{u} = \mu \Delta \vec{u} + (\lambda + \mu) \nabla (\nabla \cdot \vec{u}) + \vec{f}_{\text{ex}}, \quad (2.60)$$

where the velocity field has been expressed in terms of the displacement field $\vec{v} = \partial_t \vec{u}$ and the non-linear convection term in the material derivative (2.3) has been neglected due to the assumption of small displacements. Note, that according to

TABLE 2.1.: Commonly used material constants of linear elasticity and their connections. The respective constants are referred to as *Youngs modulus* E , *Poisson ratio* ν , *bulk- or compression modulus* K , *shear modulus* μ and *first Lamé constant* λ , with $R = \sqrt{E^2 + 9\lambda^2 + 2E\lambda}$. The rheology of an isotropic purely linear elastic material is fully described by any pair of these constants. For the description of anisotropic materials up to $3^4 = 81$ different material constants are required, however. [Sado9]

REPRESENTATION	E	ν	K	μ	λ
E, ν			$\frac{E}{3(1-2\nu)}$	$\frac{E}{2(1+\nu)}$	$\frac{E\nu}{(1+\nu)(1-2\nu)}$
E, K		$\frac{3K-E}{6K}$		$\frac{3KE}{9K-E}$	$\frac{3K(3K-E)}{9K-E}$
E, μ		$\frac{E-2\mu}{2\mu}$	$\frac{\mu E}{3(3\mu-E)}$		$\frac{\mu(E-2\mu)}{3\mu-E}$
E, λ		$\frac{2\lambda}{E+\lambda+R}$	$\frac{E+3\lambda+R}{6}$	$\frac{E-3\lambda+R}{4}$	
ν, K	$3K(1-2\nu)$			$\frac{3K(1-2\nu)}{2(1+\nu)}$	$\frac{3K\nu}{1+\nu}$
ν, μ	$2\mu(1+\nu)$		$\frac{3\mu(1+\nu)}{3(1-2\nu)}$		$\frac{2\mu\nu}{1-2\nu}$
ν, λ	$\frac{\lambda(1+\nu)(1-2\nu)}{\nu}$		$\frac{\lambda(1+\nu)}{3\nu}$	$\frac{\lambda(1-2\nu)}{2\nu}$	
K, μ	$\frac{9K\mu}{3K+\mu}$	$\frac{3K-2\mu}{6K+2\mu}$			$\frac{3K-2\mu}{3}$
K, λ	$\frac{9K(K-\lambda)}{3K-\lambda}$	$\frac{\lambda}{3K-\lambda}$		$\frac{3}{2}(K-\lambda)$	
μ, λ	$\frac{\mu(3\lambda+2\mu)}{\lambda+\mu}$	$\frac{\lambda}{2(\lambda+\mu)}$	$\frac{3\lambda+2\mu}{3}$		

Eq. (2.59) the trace of the strain tensor is given by

$$\text{tr } \underline{\varepsilon} = \frac{1-2\nu}{E} \text{tr } \underline{\sigma}, \quad (2.61)$$

and vanishes for $\nu = \frac{1}{2}$ implying incompressibility. Even then, finite normal stresses $\text{tr } \underline{\sigma} \neq 0$ are possible (see App. A.4) and the stress tensor can be written as

$$\underline{\sigma} = \frac{1}{3} \mathbb{1} \text{tr } \underline{\sigma} + 2\mu \underline{\varepsilon}, \quad (2.62)$$

where $E = 2\mu(1+\nu) = 3\mu$ is used. Introducing the internal pressure field $p(\vec{r}, t) = -\frac{1}{3} \text{tr } \underline{\sigma}$ as was done in Sec. 2.2, the incompressible Navier-Cauchy equation writes

$$\rho \partial_t^2 \vec{u} = -\nabla p + \mu \Delta \vec{u} + \vec{f}_{\text{ex}}. \quad (2.63)$$

At this point, it may seem reasonable at first to proceed analogously to the derivation of the thin-film equation, i.e., to formulate boundary conditions and apply the long-

wave approximation to obtain an evolution equation for the substrate profile, which is equal to the vertical component of the displacement field at the interface

$$\xi(\vec{r}, t) = \vec{u}(\vec{r}, t) \cdot \vec{e}_z \Big|_{z=0} . \quad (2.64)$$

Doing so, however, quickly results in a steady state equation for $\vec{u}$, since the inertia term on the l.h.s. is neglected during the long-wave approximation and there are no other time derivatives present in the stress. The time derivatives in turn are required to derive an evolution equation for ξ according to the kinematic boundary condition [Eq. (2.34)]. In other words, without friction or inertia the response of the substrate is instantaneous. We shall therefore continue with static considerations and take care of the dynamics later.

2.3.2. THE FUNDAMENTAL SOLUTION

Even though we are restricted to a static description of elasticity for now, the static solution will turn out to be of good use, even for the dynamics. With the Navier-Cauchy equation (2.60) readily at hand only the boundary conditions are left to be defined in order to take into account the layer geometry of the substrate. As shown in Fig. 2.2 the substrate is restricted towards the bottom by a rigid ground level at depth $z = -d$ where the *no slip condition* is applied

$$\vec{u} \Big|_{z=-d} = 0 . \quad (2.65)$$

The plane $z = 0$ defines the solid-liquid interface of the undeformed reference state. However, this interface, described by the profile $\xi(\vec{r}, t)$ [Eq. (2.64)], is exposed to the stresses exerted by the overlying liquid layer $\underline{\sigma}_l$. The statics of the substrate is therefore governed by the equilibrium of stresses that are acting there, similar to Eq. (2.37)

$$(\underline{\sigma}_s - \underline{\sigma}_l) \Big|_{z=0} \cdot \vec{n}_{sl} = \vec{\alpha}'_{sl} , \quad (2.66)$$

with $\vec{n}_{sl} = \vec{e}_z$ and the inhomogeneity $\vec{\alpha}'_{sl}$ representing any additional stress acting at the surface.¹¹ Here the stress $\underline{\sigma}_l$ exerted by the liquid is assumed to be known while the one of the elastic substrate $\underline{\sigma}_s$ is given by Eq. (2.55). The latter can at the surface

¹¹Note, that the definition of the surface at $z = 0$, instead of $z = \xi$, is valid only because linear elasticity is assumed, since the Lagrangian displacement field $\vec{U}$ is then, to leading order, equal to the Eulerian displacement field $\vec{u}$.

be written in the form of a differential operator acting on the displacement field

$$\underline{\sigma}_s \Big|_{z=0} \cdot \vec{n}_{sl} = \mathcal{D}(\vec{u}) . \quad (2.67)$$

Due to linearity, the action of this differential operator can be expressed by a matrix

$$\mathcal{D}(\vec{u}) = \underline{D}(\nabla) \cdot \vec{u} \quad \text{with} \quad \underline{D}(\nabla) = \begin{pmatrix} \mu \partial_z & 0 & \mu \partial_x \\ 0 & \mu \partial_z & \mu \partial_y \\ \lambda \partial_x & \lambda \partial_y & (\lambda + 2\mu) \partial_z \end{pmatrix} . \quad (2.68)$$

The ∇ in the parenthesis is meant as a reminder that the matrix $\underline{D}$ contains spatial derivatives that act on the object to the right hand side. Condition (2.66) then yields a set of three coupled inhomogeneous linear partial differential equations

$$[\underline{D}(\nabla) \cdot \vec{u}]_{z=0} = \vec{\alpha}_{sl} = \underline{\sigma}_1 \Big|_{z=0} \cdot \vec{n}_{sl} + \vec{\alpha}'_{sl} . \quad (2.69)$$

Here $\vec{\alpha}'_{sl}$ represents all stress acting at the surface, including those exerted by the liquid, i.e., given by $\underline{\sigma}_1$, and any other contributions, summarized as $\vec{\alpha}'_{sl}$. Thanks to the linearity, the superposition principle applies and the problem can be treated via *Green's formalism*. Thereby, Eq. (2.69) is first solved using a localized inhomogeneity

$$[\underline{D}(\nabla) \cdot \vec{g}^i(\vec{r})]_{z=0} = \delta(x, y) \vec{e}_i , \quad (2.70)$$

for any set of vectors $\{\vec{e}_1, \vec{e}_2, \vec{e}_3\}$ forming an orthonormal basis of $\mathbb{R}^3$. The solution $\vec{g}^i(\vec{r})$ of that equation can then be viewed as the i -th column of a matrix $\underline{G}(\vec{r})$ which is called the *Green's function*

$$\vec{g}^i(\vec{r}) = \underline{G}(\vec{r}) \cdot \vec{e}_i \quad \Leftrightarrow \quad \vec{g}_j^i = G_{ji} . \quad (2.71)$$

The latter is desired because it is the *fundamental solution* of the system, meaning that for arbitrary inhomogeneity a solution can be constructed according to the su-

perposition principle

$$\begin{aligned}
\left[\underline{D}(\nabla) \cdot \vec{u}(\vec{r}) \right]_{z=0} &= \vec{\alpha}_{sl}(\vec{r}) = \delta(\vec{r}) * \vec{\alpha}_{sl}(\vec{r}) \\
&= \int_{\partial\Omega} \delta(\vec{r} - \vec{r}') \sum_i \alpha_i(\vec{r}') \vec{e}_i d^2\vec{r}' \\
&\stackrel{(2.70)}{=} \underline{D}(\nabla) \cdot \left[\int_{\partial\Omega} \sum_i \vec{g}^i(\vec{r} - \vec{r}') \alpha_i(\vec{r}') d^2\vec{r}' \right] \\
&\stackrel{(2.71)}{=} \underline{D}(\nabla) \cdot \left[\int_{\partial\Omega} \sum_i \left(\underline{G}(\vec{r} - \vec{r}') \cdot \vec{e}_i \right) \left(\vec{\alpha}(\vec{r}') \cdot \vec{e}_i \right) d^2\vec{r}' \right] \\
&= \underline{D}(\nabla) \cdot \left[\int_{\partial\Omega} \underline{G}(\vec{r} - \vec{r}') \cdot \vec{\alpha}(\vec{r}') d^2\vec{r}' \right] \\
\Rightarrow \vec{u}(\vec{r})|_{z=0} &= \int_{\partial\Omega} \underline{G}(\vec{r} - \vec{r}') \cdot \vec{\alpha}(\vec{r}') d^2\vec{r}' = \underline{G}(\vec{r}) * \vec{\alpha}_{sl}(\vec{r}), \quad (2.72)
\end{aligned}$$

where $\partial\Omega$ refers to the surface of the elastic layer at $z = 0$. The linear differential operator $\underline{D}(\nabla)$ can be pulled in front of the integral as it affects only $\vec{r}$ not $\vec{r}'$. Remember, that this solution emerges from the boundary condition at the interface. Consequently, it is evaluated at $z = 0$ effectively reducing the spatial dimension of the problem to the (x, y) -plane. Since $\underline{D}(\nabla)$ includes derivatives w.r.t. z , however, the problem has to be solved for the whole z -dependence of $\vec{u}$ within the bulk before a solution for the displacement at the surface can be obtained. Since only at the surface external forces are acting, the static Navier-Cauchy equation is

$$\nabla \cdot \underline{\sigma}_s = 0. \quad (2.73)$$

As simple as it looks, this equation is yet quite laborious to solve. It is therefore advantageous to take the symmetry of the problem into account to reduce the equations as much as possible. Assuming the substrate to be infinitely extended in x and y direction and the displacement to vanish as $|\vec{r}| \rightarrow \infty$ allows to employ *Fourier-* or *Hankel transformations* depending on the symmetry of the boundary condition. If a Cartesian description is considered, for example, the corresponding spatial coordinates and the associated partial derivatives are then replaced by Fourier modes, i.e., $\partial_n \rightarrow -ik_n$, and the problem reduces to a set of coupled ordinary differential equations depending only on the vertical coordinate z . Note also, that the convolution

(2.72) becomes a simple product in Fourier space

$$\vec{u}(\vec{k}) = \underline{G}(\vec{k}) \cdot \vec{\alpha}_{sl}(\vec{k}). \quad (2.74)$$

In other cases specific *stress functions* can be found that significantly simplify the equations. For a variety of different symmetries the Green's functions have already been calculated, e.g., in Refs. [Han51, Joh85, Ess+21], and even used in the context of wetting [DL15]. In Sec. A.5 the derivation of some components of the Green's function is shown in detail for the present system.

The results presented in the remainder of this work are to a large extent considered in a two dimensional framework, i.e., translational invariance in y -direction. In that case the Green's function is given by [Han51, Ess+21]

$$\begin{aligned} G_{xz} &= \frac{i}{2\pi} \frac{(4k^2d^2 + 16\nu^2 - 20\nu + 6)e^{2kd} - (3 - 4\nu)(1 - 2\nu)(e^{4kd} + 1)}{2\mu k \left[(4k^2d^2 + 16\nu^2 - 24\nu + 10)e^{2kd} + (3 - 4\nu)(e^{4kd} + 1) \right]} \\ &= \frac{i}{2\pi} \frac{1}{2\mu k} \frac{2k^2d^2 + (3 - 4\nu)(1 - 2\nu)[1 - \cosh(2kd)]}{(3 - 4\nu)\cosh(2kd) + (3 - 4\nu)(1 - 2\nu) + 2(1 - \nu) + 2k^2d^2}, \end{aligned} \quad (2.75a)$$

$$\begin{aligned} G_{zz} &= \frac{1}{2\pi} \frac{(\nu - 1)[4kde^{2kd} - (3 - 4\nu)(e^{4kd} - 1)]}{\mu k \left[(4k^2d^2 + 16\nu^2 - 24\nu + 10)e^{2kd} + (3 - 4\nu)(e^{4kd} + 1) \right]} \\ &= \frac{1}{2\pi} \frac{1 - \nu}{\mu k} \frac{(3 - 4\nu)\sinh(2kd) - 2kd}{(3 - 4\nu)\cosh(2kd) + (3 - 4\nu)(1 - 2\nu) + 2(1 - \nu) + 2k^2d^2} \end{aligned} \quad (2.75b)$$

$$\begin{aligned} G_{xx} &= -\frac{1}{2\pi} \frac{(\nu - 1)[4dke^{2kd} + (3 - 4\nu)(e^{4kd} - 1)]}{\mu k \left[(4k^2d^2 + 16\nu^2 - 24\nu + 10)e^{2kd} + (3 - 4\nu)(e^{4kd} + 1) \right]} \\ &= \frac{1}{2\pi} \frac{1 - \nu}{\mu k} \frac{(3 - 4\nu)\sinh(2kd) + 2dk}{(3 - 4\nu)\cosh(2kd) + (3 - 4\nu)(1 - 2\nu) + 2(1 - \nu) + 2k^2d^2}. \end{aligned} \quad (2.75c)$$

Note, that due to the symmetry $G_{xz} = -G_{zx}$ and only G_{xz} will be explicitly mentioned in the following. The diagonal entries are further found to be real valued while the off-diagonal entries are purely imaginary, indicating that the associated deformations in position space are symmetric and antisymmetric respectively. In the following it will prove practical to define $\underline{K}(k) = \mu \underline{G}(k)$. The three independent components of the Green's function are shown exemplarily in Fig. 2.3 for an arbitrary set of parameters in Fourier space [panel (a)] and real space [panel (b)]. As one might expect the vertical displacement G_{zz} resulting from an upward pulling point

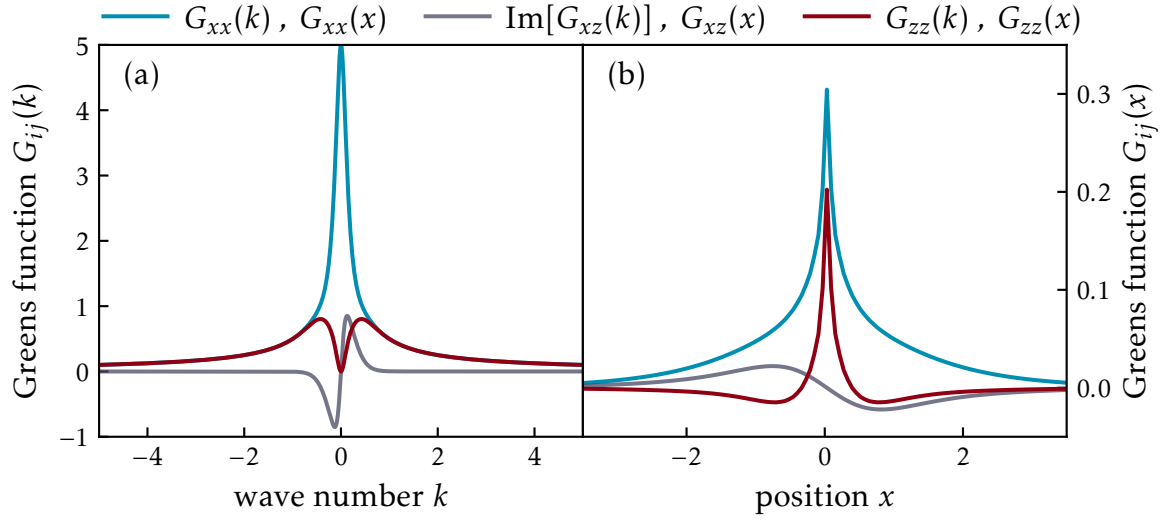


FIGURE 2.3.: Components of the two dimensional Green's function G for an incompressible material $\nu = \frac{1}{2}$. The components G_{ij} give the surface displacement in $\vec{u} \cdot \vec{e}_i$ resulting from a point force pulling in $\vec{e}_j$ direction at $x = z = 0$. Panel (a) shows the components in Fourier space against the wave number k . Panel (b) shows the respective representation in position space. The red colored area underneath G_{zz} represents the bulk of the elastic layer. Note, that in general vertical displacements are caused even by horizontally directed point forces and vice versa, since $G_{xz} \neq 0$. The remaining parameters are $\mu = 1$, $d = 5$ and $\nu = \frac{1}{2}$.

force shows a sharp peak. Due to incompressibility, i.e., $\nu = \frac{1}{2}$, a small depression also referred to as *undershooting* arises aside it. Further, it becomes clear that even horizontal forces cause vertical displacements and vice versa since $G_{xz} \neq 0$. At $k = 0$ the components become

$$\lim_{k \rightarrow 0} G_{xz}(k) = 0, \quad \lim_{k \rightarrow 0} G_{zz}(k) = \frac{1}{2\pi} \frac{d(2\nu - 1)(\nu - 1)}{2\mu(\nu - 1)^2}, \quad \lim_{k \rightarrow 0} G_{xx}(k) = \frac{d}{2\pi\mu}, \quad (2.76)$$

i.e., the global displacements $\int_{-\infty}^{\infty} G_{xx} dx$ and $\int_{-\infty}^{\infty} G_{zz} dx$ increase with increasing elastic layer thickness d and decreasing shear modulus μ , while $\int_{-\infty}^{\infty} G_{xy} dx = 0$ always. Note, that also $\int_{-\infty}^{\infty} G_{zz} dx = 0$ for $\nu = \frac{1}{2}$, reflecting the conservation of volume. In Fig. 2.4 the component G_{zz} is shown in real space for different Poisson ratios ν and layer thicknesses d . It is found that the undershooting reduces as the substrate becomes more compressible $\nu \rightarrow 0$ and that the lateral extension of the structure increases with the thickness of the elastic layer. In the majority of this work it is not the Green's function but rather its inverse that will be used

$$\underline{G}^{-1} = \frac{1}{\det \underline{G}} \begin{pmatrix} G_{zz} & -G_{xz} \\ -G_{zx} & G_{xx} \end{pmatrix}, \quad (2.77)$$

with

$$\det \underline{G} = G_{xx}G_{zz} + G_{xz}^2 = \frac{1}{(2\pi)^2} \frac{1}{\mu^2 k^2} \frac{(1-\nu)^2 [(3-4\nu)^2 \sinh^2(2kd) - 4k^2 d^2] - \frac{1}{4} [2k^2 d^2 - (3-4\nu)(1-2\nu)(1-\cosh(2kd))]^2}{[(3-4\nu)\cosh(2kd) + (3-4\nu)(1-2\nu) + 2(1-\nu) + 2k^2 d^2]^2}, \quad (2.78)$$

as it allows for calculating the surface stress from the displacement by inverting Eq. (2.74)

$$\vec{\alpha}_{sl}(\vec{k}) = \underline{G}^{-1}(\vec{k}) \cdot \vec{u}(\vec{k}), \quad (2.79)$$

or in real space

$$\vec{\alpha}_{sl}(\vec{r}) = \int_{\partial\Omega} \underline{G}^{-1}(\vec{r} - \vec{r}') \cdot \vec{u}(\vec{r}') d^2\vec{r}' = \underline{G}^{-1}(\vec{r}) * \vec{u}(\vec{r}). \quad (2.80)$$

With $\underline{G}$ and $\underline{G}^{-1}$ we are now able to calculate the surface displacement resulting from arbitrary surface forces $\vec{\alpha}$ and vice versa, at least in two spatial dimensions that is.

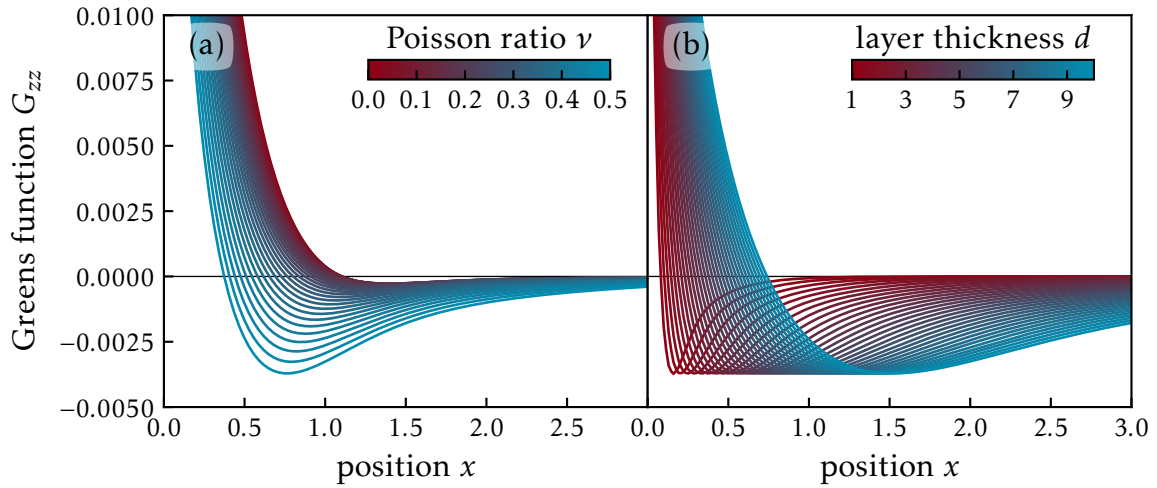


FIGURE 2.4.: Dependency of the vertical surface displacement G_{zz} on the elastic layer thickness d and the Poisson ratio ν at fixed shear modulus $\mu = 1$. Panel (a) shows the dependency of G_{zz} on the Poisson ratio ν at constant shear modulus $\mu = 1$ and layer thickness $d = 5$. With increasing Poisson ratio the material becomes increasingly incompressible and an undershooting arises next to the wetting ridge due to volume conservation. Panel (b) shows the dependency of G_{zz} on the layer thickness d at constant Poisson ratio $\nu = \frac{1}{2}$, i.e., for an incompressible material. The lateral extension of the whole ridge structure increases with d while the depth of the undershooting remains the same.

2.3.3. LONG-WAVE APPROXIMATION

To use the Green's function and its inverse in the same framework as the thin-film equation both must be accordingly approximated in the long-wave limit. Using the same non-dimensionalized variables as defined in (2.41) it is found that $kd = \epsilon \tilde{k} \tilde{d}$ with $\epsilon \ll 1$ in that limit. The expanded Green's function is

$$G_{xx} \approx \frac{d}{\mu} - \frac{d^3(3+4\nu)}{6\mu(1-\nu)}k^2 + \mathcal{O}(\epsilon^4), \quad (2.81a)$$

$$G_{zz} \approx \frac{d(1-2\nu)}{2\mu(1-\nu)} + \frac{d^3\nu(1-4\nu)}{6\mu(1-\nu)^2}k^2 + \mathcal{O}(\epsilon^4), \quad (2.81b)$$

$$G_{xz} \approx -\frac{id^2(1-4\nu)}{4\mu}k + \frac{id^4(3-14\nu-8\nu^2)}{24\mu(1-\nu)}k^3 + \mathcal{O}(\epsilon^4), \quad (2.81c)$$

and its inverse

$$(G^{-1})_{xx} \approx \frac{\mu}{d} + \frac{\mu d(15-38\nu+67\nu^2-120\nu^3+48\nu^4)}{24(1-\nu)(1-2\nu)}k^2 + \mathcal{O}(\epsilon^4), \quad (2.82a)$$

$$(G^{-1})_{zz} \approx \frac{\mu}{d} \frac{2(1-\nu)}{(1-2\nu)} + \frac{\mu d(3-22\nu+67\nu^2-120\nu^3+48\nu^4)}{12(1-2\nu)^2}k^2 + \mathcal{O}(\epsilon^4), \quad (2.82b)$$

$$(G^{-1})_{xz} \approx \frac{i\mu(1-5\nu+4\nu^2)}{2(1-2\nu)}k + \frac{i\mu d^2(3-10\nu+75\nu^2-324\nu^3+528\nu^4-192\nu^5)}{48(1-2\nu)^2}k^3 + \mathcal{O}(\epsilon^4). \quad (2.82c)$$

The long-wave approximation is further accompanied by the advantage that the convolution in real space is removed as the powers of the wave number translate into spatial derivatives $\mathcal{FT}^{-1}[k^n f(k)] = (-i)^n \partial_x^n f(x)$. Hence,

$$\int \underline{G}(x-x') \vec{\alpha}(x') dx' \approx \sum_{n=0} \underline{G}^n \frac{\partial^n \vec{\alpha}}{\partial x^n}, \quad (2.83)$$

with the matrices $\underline{G}^n$ respectively including the expansion coefficients of the n -th order terms. Considering only the zeroth order terms, i.e., $\mathcal{O}(k^0)$, results in a description of the elastic layer as a continuous spring with the stiffness per unit area $\frac{\mu}{d}$ and $\frac{\mu}{d} \frac{2(1-\nu)}{(1-2\nu)}$ in x and z direction, respectively. Since all off diagonal entries vanish in this limit, the horizontal and vertical displacements are entirely decoupled and with the vanishing dependency on the wave number k the non-locality is lifted as well. This strongly simplified description is known as the *Winkler-foundation* model [Joh85, Dil+18] and is frequently used, e.g., in soft lubrication problems [SMo4, SM15]. Note that, almost all terms in Eqs. (2.82) exhibit a singularity at

$\nu = \frac{1}{2}$, indicating that an incompressible elastic layer cannot deform under long-wave traction [CV20].¹² The reason for this is, that incompressible materials are usually deformed by shearing which is not incorporated in the Winkler model, since the displacements are local and decoupled, i.e., vertical displacements cannot cause horizontal ones and vice versa. This feature is quite unfavorable since most of the elastomeric materials used in experiments are incompressible or at least very close to it [Dog+18]. Yet the Winkler-foundation model performs reasonably well when it comes to the description of thin coatings, even if those are incompressible [Sai+16, Ral+17, Sai+20]. Nevertheless, many efforts have been made to extend the Winkler model to incorporate incompressibility [CV20]. For example, the second order term in the vertical component (2.81b) survives

$$G_{zz}\left(k, \nu = \frac{1}{2}\right) = -\frac{d^3}{3\mu}k^2, \quad (2.84)$$

which in real space yields

$$\xi(x) = u_z|_{z=0} = \frac{d^3}{3\mu} \frac{\partial^2 \alpha_z}{\partial x^2}. \quad (2.85)$$

This expression looks quite similar to the term $\frac{h^3}{3\eta} \partial_x^2 p$ found in the thin-film equation (2.49) and was previously used to describe the deformation of incompressible elastic layers of finite thickness [GM70, Dil89]. Note, that in the limit of an infinite half plane $d \rightarrow \infty$, i.e., $kd \sim \epsilon^{-1}$ which is in some sense the opposite of the long-wave approximation, the vertical displacement at the surface is found to be $\sim \log(x)$ and thus to diverge as the position $x = 0$ of the point force is approached. This is known as the *Flamant problem* [Fla92]. After all, the surface displacement caused by an external, assumingly known, surface stress $\vec{\alpha}$ is determined by Eq. (2.72), i.e., by simply calculating a single convolution integral. However, the situation becomes significantly more complicated if $\vec{\alpha}$ depends on the surface displacement itself in a non-linear manner, which is indeed the case for the soft wetting systems to be considered in the following, as is discussed in Ch. 3.2. Now, that the statics of the finite elastic layer is in place, it is time to address its dynamics, i.e., to introduce viscoelasticity.

¹²This is also reflected by the terms in Eqs. (2.81) becoming zero.

2.4. LINEAR VISCOELASTICITY

In the previous chapters we have seen, that the stress of a viscous Newtonian fluid is proportional to the strain rate $\sigma \sim \dot{\varepsilon}$ while for a perfectly linear elastic material $\sigma \sim \varepsilon$ is obeyed. As was mentioned above, these constitutive laws are idealizations that correspond to the limiting cases of a wide range of behaviors exhibited by real materials. While these limits may serve as reasonable approximations in many situations, providing a considerably simplified description, there are abundant real materials featuring both viscous and elastic behavior, with neither being negligible. Those materials are therefore comprehensibly referred to as *viscoelastic*. In this section the basic concepts that are required for the mechanical description of viscoelastic materials are introduced, following Refs. [LAL96, dG96, Jer+11, SD12, Lub+14]. In line with the description of linear elasticity in the preceding chapter, the discussion will be restricted to linear viscoelasticity, i.e., small deformations at all times.

2.4.1. THE DYNAMIC MODULI

One of the most striking properties of viscoelastic materials, besides their ability to dissipate kinetic energy via friction, is that their stress strain relation is not localized in time but depends on the entire history the material has undergone. Such a behavior is referred to as *memory effect* and can be described by the *Volterra expansion*

$$y(t) = \sum_{n=1}^N \int \dots \int \psi_n(\tau_1, \dots, \tau_n) \prod_{j=1}^n x(t - \tau_j) d\tau_j. \quad (2.86)$$

Hence, the output function $y(t)$, i.e., the stress, is given by a series of nested convolution integrals including the input function $x(t)$, i.e., the strain rate, and the n -th order *Volterra kernels* $\psi_n(\tau_1, \dots, \tau_n)$. Once again restricting ourselves to linear behavior, i.e., $N = 1$ in Eq. (2.86), a time-dependent equivalent to Hooke's law is found [DE78, WC86]

$$\sigma_{ij}(t) = \int_{-\infty}^t \sum_{k,l=0}^3 \psi_{ijkl}(t-t') \partial_{t'} \varepsilon_{kl}(t') dt', \quad (2.87)$$

with the strain rate being the input function and the Volterra kernels $\psi_{ijkl}(t)$ replacing the material constants [cf. Eq. (2.53)]. Just like the latter, the number of

convolution kernels can be reduced to only two independent functions by assuming isotropy of the material. In this case the stress-strain relation can be written in analogy to Eqs. (2.54) or (2.55)

$$\underline{\sigma}(t) = \int_{-\infty}^t \psi_{\lambda}(t-t') \mathbb{1} \operatorname{tr}[\partial_{t'} \underline{\varepsilon}(t')] + 2\psi_{\mu}(t-t') \partial_{t'} \underline{\varepsilon}(t') dt' \quad (2.88a)$$

$$= \int_{-\infty}^t 3\psi_K(t-t') \partial_{t'} \hat{\underline{\varepsilon}}(t') + 2\psi_{\mu}(t-t') \partial_{t'} \tilde{\underline{\varepsilon}}(t') dt', \quad (2.88b)$$

with $\psi_{\lambda}(t)$ or $\psi_K(t)$ and $\psi_{\mu}(t)$ regarding volumetric and shear strain, respectively. In the context of viscoelasticity these linear response functions $\psi_i(t)$ are also often referred to as *relaxation functions*. They determine the stresses that are caused in response to sudden constant strain. Let us first consider the incompressible case $\operatorname{tr}[\partial_t \underline{\varepsilon}(t)] = 0$. Application of sudden constant strain $\underline{\varepsilon}(t) = \underline{\varepsilon}_0 \Theta(t)$ then yields

$$\underline{\sigma}(t) = 2\underline{\varepsilon}_0 \int_{-\infty}^t \psi_{\mu}(t-t') \partial_{t'} \Theta(t') dt' = 2\underline{\varepsilon}_0 \int_{-\infty}^t \psi_{\mu}(t-t') \delta(t') dt' = 2\underline{\varepsilon}_0 \psi_{\mu}(t), \quad (2.89)$$

where $\Theta(t)$ is the Heaviside function. Indeed $\psi(t) \sim \sigma(t)/\varepsilon_0$ plays the role of an effective material constant at given time t . For $t \rightarrow \infty$ it converges to the elastic modulus of the static problem. Consequently, a material is declared a *viscoelastic solid* if $\lim_{t \rightarrow \infty} \psi(t) \neq 0$, i.e., if a finite stress persists at constant strain, or a *viscoelastic fluid* if $\lim_{t \rightarrow \infty} \psi(t) = 0$, i.e., if the stress is completely released in the long term. Causality further demands $\psi(t < 0) = 0$, i.e., the relaxation function can never affect the past. For that reason it is also sometimes referred to as *causal* or *retarded* Green's function. Note, that its counterpart, i.e., the linear response function that relates the current strain to the history of stress, is usually referred to as *creep function* $\psi^{-1}(t)$. Assuming the material to occupy an undeformed reference state in the far past $\lim_{t \rightarrow -\infty} \varepsilon(t) = 0$ a temporal Fourier transformation can be applied to Eqs. (2.88) which leads to

$$\underline{\sigma}(\omega) = \chi_{\lambda}(\omega) \mathbb{1} \operatorname{tr} \underline{\varepsilon}(\omega) + 2\chi_{\mu}(\omega) \underline{\varepsilon}(\omega) \quad (2.90a)$$

$$= 3\chi_K(\omega) \hat{\underline{\varepsilon}}(\omega) + 2\chi_{\mu}(\omega) \tilde{\underline{\varepsilon}}(\omega), \quad (2.90b)$$

where

$$\frac{\chi(\omega)}{i\omega} = \int_0^{\infty} \psi(t) e^{-i\omega t} dt = \mathcal{L}[\psi(t)](s), \quad (2.91)$$

is the *Laplace transform* of the relaxation function with $s = -i\omega$ (see App. A.6 for details). In the following the $\chi_i(\omega)$ are referred to as the spectral representations of the material constants or as *dynamic moduli*. Eqs. (2.90) can be transformed back to the temporal domain to obtain an alternative form of the stress-strain relation

$$\underline{\sigma}(t) = \int_{-\infty}^t \chi_\lambda(t-t') \underline{\mathbb{1}} \operatorname{tr} \underline{\varepsilon}(t') + 2\chi_\mu(t-t') \underline{\varepsilon}(t') dt' \quad (2.92a)$$

$$= \int_{-\infty}^t 3\chi_K(t-t') \underline{\hat{\varepsilon}}(t') + 2\chi_\mu(t-t') \underline{\varepsilon}(t') dt', \quad (2.92b)$$

where the kernels $\chi_i(t)$ now determine the stress response to singular strain $\underline{\varepsilon}(t) = \underline{\varepsilon}_0 \delta(t)$. Note, that the limiting cases can still be recovered from Eqs. (2.88). Assuming for example $\psi_K(t) = \zeta \delta(t)$ and $\psi_\mu(t) = \eta \delta(t)$ results in the stress-strain relation of a viscous Newtonian fluid (2.27). The dynamic moduli are purely imaginary then $\chi_K(\omega) = i\omega\zeta$ and $\chi_\mu(\omega) = i\omega\eta$. If, however, $\psi_K(t) = K$ and $\psi_\mu(t) = \mu$ the stress-strain relation of a linear elastic solid (2.54) is recovered. In this case the dynamic moduli are purely real valued and equal to the respective relaxation functions $\chi_K(\omega) = \psi_K(t) = K$ and $\chi_\mu(\omega) = \psi_\mu(t) = \mu$. It seems, that the imaginary parts of the dynamic moduli are related to viscous dissipation while the real parts account for elasticity. Due to causality the dynamic moduli have to be analytic in the upper-half plane and their real and imaginary parts are related via the *Kramers-Kronig relation*

$$\chi'(\omega) = \operatorname{Re} \chi(\omega) = \mathcal{P} \int_{-\infty}^{\infty} \frac{\operatorname{Im} \chi(\omega')}{\omega' - \omega} \frac{d\omega'}{\pi}, \quad (2.93a)$$

$$\chi''(\omega) = \operatorname{Im} \chi(\omega) = -\mathcal{P} \int_{-\infty}^{\infty} \frac{\operatorname{Re} \chi(\omega')}{\omega' - \omega} \frac{d\omega'}{\pi}, \quad (2.93b)$$

with $\mathcal{P}$ denoting the *Cauchy principal value* and

$$\chi(\omega) = \chi'(\omega) + i\chi''(\omega) = \omega \int_0^\infty \psi(t) \sin(\omega t) dt + i\omega \int_0^\infty \psi(t) \cos(\omega t) dt. \quad (2.94)$$

Since the dynamic moduli are real valued functions in the time domain, i.e., $\operatorname{Im} \chi(t) = 0$, the real and imaginary parts of their Fourier transforms are even and odd functions, respectively,

$$\chi'_i(\omega) = \chi'_i(-\omega) \quad \text{and} \quad \chi''_i(\omega) = -\chi''_i(-\omega), \quad (2.95)$$

and consequently $\chi_i(-\omega) = \chi_i^*(\omega)$. These symmetry properties are also inherent in their temporal representations. In particular, the inverse Fourier transforms of

the real parts $\chi'(t) = \mathcal{FT}^{-1}[\chi'_i(\omega)]$ are symmetric, that is invariant with respect to time reversal $t \rightarrow -t$. The inverse Fourier transforms of the imaginary parts $\chi''(t) = \mathcal{FT}^{-1}[\chi''(\omega)]$, however, are not. Consequently, a deformation is considered irreversible only if $\chi''_i(\omega) \neq 0$, which is why the latter must indeed be related to energy dissipation, i.e., viscosity. In contrast, the reactive parts $\chi'_i(\omega)$ are the same no matter the direction in time and thus account for the reversible elastic parts of the deformation. That is why $\chi'_i(\omega)$ and $\chi''_i(\omega)$ are called the *storage-* and *loss moduli*, respectively. This behavior can be seen also by considering the work per time and unit area

$$\dot{w}(t) = \sigma(t)\dot{\varepsilon}(t) = \dot{\varepsilon}(t) \int \chi(t-t')\varepsilon(t') dt' = \iint i\omega\varepsilon(\omega)\chi(\omega')\varepsilon(\omega')e^{i(\omega+\omega')t} \frac{d\omega d\omega'}{2\pi}, \quad (2.96)$$

which after integration over time yields

$$\begin{aligned} w(t) &= \int \dot{w}(t') dt' = \iint_{-\infty}^{\infty} i\omega\varepsilon(\omega)\chi(\omega')\varepsilon(\omega') \left[\frac{1}{2\pi} \int e^{i(\omega+\omega')t'} dt' \right] d\omega d\omega' \\ &= \iint_{-\infty}^{\infty} i\omega\varepsilon(\omega)\chi(\omega')\varepsilon(\omega')\delta(\omega+\omega') d\omega d\omega' \\ &= - \int_{-\infty}^{\infty} i\omega\chi(\omega) |\varepsilon(\omega)|^2 d\omega = \int_{-\infty}^{\infty} \omega\chi''(\omega) |\varepsilon(\omega)|^2 d\omega. \end{aligned} \quad (2.97)$$

After integration over a symmetric interval in the final step, the contribution of $\chi'_i(\omega)$ vanishes due to its symmetry. Hence, the loss modulus alone accounts for dissipation and can be associated with an effective viscosity $\eta(\omega)$. With $\chi'_i(\omega) = 0$ we find, e.g., for Eq. (2.90a)

$$\begin{aligned} \underline{\sigma}(\omega) &= \chi_\lambda(\omega) \underline{\mathbb{1}} \operatorname{tr} \underline{\varepsilon}(\omega) + 2\chi_\mu(\omega) \underline{\varepsilon}(\omega) \\ &= \frac{\chi''_\lambda(\omega)}{\omega} i\omega \underline{\mathbb{1}} \operatorname{tr} \underline{\varepsilon}(\omega) + 2 \frac{\chi''_\mu(\omega)}{\omega} i\omega \underline{\varepsilon}(\omega) \\ &= \eta_\lambda(\omega) \underline{\mathbb{1}} \operatorname{tr} \underline{\dot{\varepsilon}}(\omega) + 2\eta_\mu(\omega) \underline{\dot{\varepsilon}}(\omega). \end{aligned} \quad (2.98)$$

An other way to characterize a viscoelastic material is by considering the phase shift between stress and strain, which, however, is related to χ' and χ'' at the end of the day

$$\frac{\sigma(\omega)}{\varepsilon(\omega)} = \chi(\omega) = |\chi(\omega)| e^{i\phi} \quad \text{with} \quad \phi = \arctan\left(\frac{\chi''}{\chi'}\right). \quad (2.99)$$

Hence, a phase shift of $\phi = 0$ is achieved only if $\chi'' = 0$ and corresponds to perfect elastic behavior as it results in $\sigma \sim \varepsilon$, while $\chi' = 0$ causes a phase shift of $\phi = \pi/2$ and indicates that a Newtonian fluid is at hand since it results in $\sigma \sim \dot{\varepsilon}$. This behavior can further be exploited to measure the dynamic moduli. In a so called *rheometer* periodic strain is exerted to a material sample and the resistance, which corresponds to the stress response, is measured. The ratio of stress and strain as well as the phase lag between them then yields the dynamic modulus for a given ω . Following this procedure the spectral dynamic modulus can be scanned over a range of frequencies. The resulting curve may then be fitted using, e.g., the *Chasset-Thirion model* [Dou64, LAL96]

$$\chi(\omega) = \chi_0 [1 + (i\omega\tau)^n], \quad (2.100)$$

as was done in Refs. [LAL96, Kar+15, JCK23]. If no such equipment is available or the process seems too elaborate for your taste, a *circuit constitutive model* can be constructed instead.

2.4.2. CIRCUIT CONSTITUTIVE MODELS

The idea here is to model the viscoelastic rheology as some kind of circuit consisting of purely elastic springs and purely viscous dampers, obeying the stress-strain relations of linear elastics and Newtonian fluids respectively. In analogy to electric circuits the constitutive law, i.e., the stress-strain relation, can be derived from the *Kirchhoff laws* with the strain rate replacing the voltage $\dot{\varepsilon} \leftrightarrow U$ and the stress playing the role of the electric current $\sigma \leftrightarrow I$. The viscosity of a damper then corresponds to the inverse of an ohmic resistance $\eta \leftrightarrow R^{-1}$ and the elastic modulus of a spring can be interpreted as the inverse of an electric inductance $E \leftrightarrow L^{-1}$ as for an electromagnetic coil [cf. Tab 2.2]. The number constitutive models that can be constructed in this way is just as large as the number of circuits conceivable. For the purposes of this work, however, the two simplest arrangements shall suffice, namely in series and parallel.

TABLE 2.2.: Overview of the analogies between mechanical and electrodynamic quantities, used in the derivation of constitutive models. Different viscoelastic rheologies are obtained by construction of (electric) circuits and subsequent replacement of the respective quantities in the Kirchhoff laws.

MECHANICAL DESCRIPTION	ELECTRODYNAMIC ANALOGUE
Strain Rate $\dot{\varepsilon} = \frac{\partial \varepsilon}{\partial t}$	Voltage U
Stress σ	Current I
Viscosity η	Inverse Resistance $\frac{1}{R}$ (Conductance)
Elastic Modulus E	Inverse Inductance $\frac{1}{L}$
Viscous Damper $\sigma = \eta \dot{\varepsilon}$	Ohmic Resistor $I = \frac{U}{R}$
Elastic Spring $\frac{\partial \varepsilon}{\partial t} = \frac{1}{E} \frac{\partial \sigma}{\partial t}$	Electromagnetic Coil $U = L \frac{\partial I}{\partial t}$

MAXWELL MODEL

The serial connection of viscous damper and elastic spring is known as the

Maxwell model [Max67]. The corresponding constitutive law is the equivalent of Kirchhoff's voltage law and writes

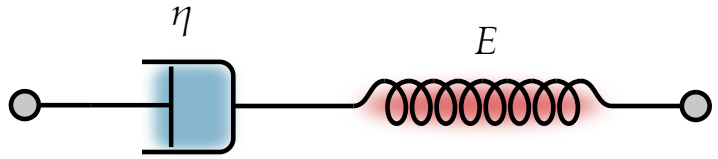
$$\eta \frac{\partial \varepsilon}{\partial t} = \sigma + \frac{\eta}{E} \frac{\partial \sigma}{\partial t}. \quad (2.101)$$

As was done in Eq. (2.89) the relaxation function $\psi(t)$ is found as response to sudden constant strain. Solving Eq. (2.101) for $\varepsilon(t) = \varepsilon_0 \Theta(t)$, leads to

$$\varepsilon_0 \psi(t) = \sigma(t) = \varepsilon_0 \Theta(t) E e^{-\frac{E}{\eta} t}, \quad (2.102)$$

where $\Theta(t)$ is the Heaviside function again. Since $\lim_{t \rightarrow \infty} \psi(t) = 0$ the Maxwell model describes a viscoelastic liquid. With Eq. (2.99) the spectral representation of the dynamic modulus is

$$\chi(\omega) = \frac{\frac{E}{\eta} + i\omega}{\frac{E^2}{\eta^2} + \omega^2}. \quad (2.103)$$



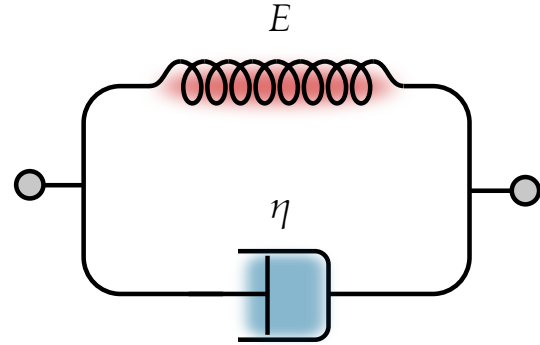
In the same way the creep function can be found by assuming sudden constant stress $\sigma(t) = \sigma_0 \Theta(t)$ and integrating Eq. (2.101) in time

$$\sigma_0 \psi^{-1}(t) = \varepsilon(t) = \frac{\sigma_0}{E} + \frac{\sigma_0}{\eta} t, \quad (2.104)$$

i.e., under constant stress the strain increases monotonically.

KELVIN-VOIGT MODEL

The parallel arrangement of viscous damper and elastic spring is known as *Kelvin-Voigt model* [Tho65, Voig92]. The corresponding constitutive law is the equivalent of *Kirchhoff's current law*



$$\sigma = E\varepsilon + \eta \frac{\partial \varepsilon}{\partial t}. \quad (2.105)$$

Inserting $\varepsilon(t) = \varepsilon_0 \Theta(t)$ directly yields the relaxation function

$$\varepsilon_0 \psi(t) = \sigma(t) = \varepsilon_0 E \Theta(t) + \varepsilon_0 \eta \delta(t), \quad (2.106)$$

with $\delta(t)$ being the Dirac delta function. Since $\lim_{t \rightarrow \infty} \psi(t) = E$ the Kelvin-Voigt model describes a viscoelastic solid. In spectral representation the dynamic modulus is given by

$$\chi(\omega) = E - i\omega\eta. \quad (2.107)$$

The creep function is obtained again by assuming sudden constant stress $\sigma(t) = \sigma_0 \Theta(t)$ and solving the differential equation, yielding

$$\sigma_0 \psi^{-1}(t) = \varepsilon(t) = \frac{\sigma_0}{E} \left(1 - e^{-\frac{E}{\eta} t} \right), \quad (2.108)$$

i.e., the material approaches a steady state which differs from the reference state $\varepsilon = 0$ and is governed by the balance of external and internal elastic forces σ_0/E .

The relaxation and creep functions of the Maxwell and Kelvin-Voigt model are shown in Fig. 2.5. Note, that the decay of stress in the Maxwell model and the decay of strain in the Kelvin-Voigt model are both characterized by the same time scale $T = \frac{\eta}{E}$.

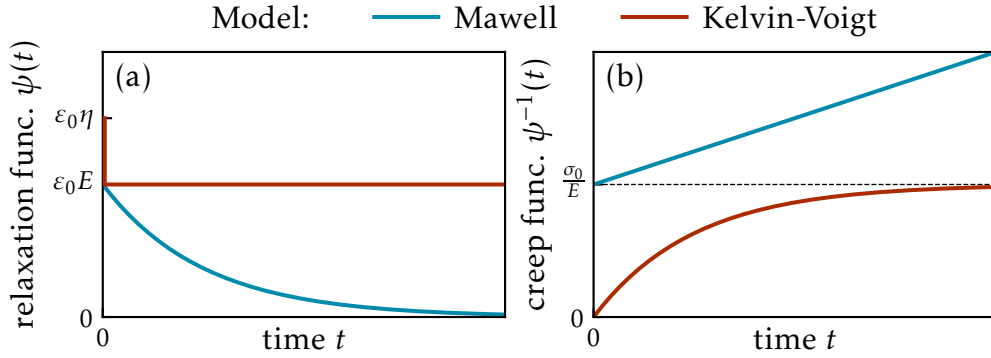


FIGURE 2.5.: Shown are (a) the relaxation functions $\varepsilon_0 \psi(t)$ and (b) the creep functions $\sigma_0 \psi^{-1}(t)$ of the Maxwell (red) and Kelvin-Voigt (blue) model, respectively. The relaxation function corresponds to the stress response to sudden constant strain $\psi(t) = \sigma(t)/\varepsilon_0$. If the relaxation function converges to a constant value like for the Kelvin-Voigt model it then corresponds to a material constant. The material is considered a viscoelastic solid in that case and a viscoelastic fluid otherwise. The creep function corresponds to the strain response to sudden constant stress $\psi^{-1}(t) = \varepsilon(t)/\sigma_0$.

2.4.3. SURFACE DYNAMICS OF A FINITE ELASTIC LAYER

In Sec. 2.3.1 the problem of instantaneous response has been faced during the attempt to derive an evolution equation for the surface displacement of a finite linear elastic layer. This issue is resolved by using the Kelvin-Voigt constitutive law (2.105) within the Navier-Cauchy equation (2.60) since the strain rate includes temporal derivatives. However, solving the resulting equation in the long-wave limit requires knowledge about the z -dependence of the displacement field $\vec{u}$. This approach is followed, e.g., in Refs. [MGK05, Gie+17, CK20], which derive a dynamic long-wave model for an incompressible viscoelastic material. The complexity of this model does not allow to easily discern a gradient dynamics structure with an underlying energy, however, and the derivation relies on the assumption of a parabolic displacement profile $\vec{u}(z) \sim z^2$. Such assumptions come at the cost of excluding solutions that do not meet them. In the following we follow an other approach utilizing the fundamental solution of the static problem.

The concepts introduced in Sec. 2.4.2 can without loss of generality be transferred to higher dimensional problems. Utilizing the Kelvin-Voigt model from here on, the dynamic modulus is given by Eq. (2.107). In more than one spatial dimension, however, there is not only one but up to 81 dynamic moduli [cf. Sec. 2.3.1]. Particularly in case of isotropic materials there are only two, each related to its own set of E and

η , e.g.,

$$\chi_K(\omega) = \chi'_K(\omega) + i\chi''_K(\omega) = E_K - i\omega\eta_K, \quad (2.109a)$$

$$\chi_\mu(\omega) = \chi'_\mu(\omega) + i\chi''_\mu(\omega) = E_\mu - i\omega\eta_\mu, \quad (2.109b)$$

according to Eqs. (2.90). Since the latter take just the same shapes as the constitutive laws of a linear elastic solid (2.54) and (2.55), the fundamental solution $\underline{G}$ of the static problem also solves the dynamics when replacing the material constants by their time dependent equivalents, e.g., $\lambda, \mu, K \rightarrow \chi_\lambda(\omega), \chi_\mu(\omega), \chi_K(\omega)$, and the stress and strain tensors by their temporal Fourier transforms. After spatial Fourier transformation the dynamics of the surface displacement is [cf. Sec. 2.3.2]

$$\vec{u}(\vec{k}, \omega) = \underline{G}(\vec{k}, \omega) \vec{\alpha}(\vec{k}, \omega). \quad (2.110)$$

Now, the Green's function $\underline{G}$ is formulated in terms of the shear modulus μ and the Poisson ration ν [cf. Eq. (2.75)]. Assuming the compressibility properties of the material to be time independent $\chi_\nu(\omega) = \nu_0$ only the shear modulus μ is to be replaced by its dynamic version [Eq. (2.109b)]¹³

$$\vec{u}(k, \omega) = \frac{\underline{K}(k)\vec{\alpha}(k, \omega)}{\chi_\mu(\omega)} \rightarrow -i\omega\vec{u}(k, \omega) = \frac{1}{\eta_\mu}\underline{K}(k)\left[\vec{\alpha}(k, \omega) - E_\mu\underline{K}^{-1}(k)\vec{u}(k, \omega)\right].$$

After reverse transformation back to the time domain it is

$$\begin{aligned} \partial_t \vec{u}(k, t) &= \frac{1}{\eta_\mu}\underline{K}(k)\left[\vec{\alpha}(k, t) - E_\mu\underline{K}^{-1}(k)\vec{u}(k, t)\right] \\ &= \frac{1}{\eta_\mu}\underline{K}(k)\vec{\alpha}(k, t) - \frac{\vec{u}(k, t)}{T_{KV}}. \end{aligned} \quad (2.111)$$

and back in position space

$$\partial_t \vec{u}(x, t) = \frac{1}{\eta_\mu} \int_{\Omega} \underline{K}(x - x') \left[\vec{\alpha}(x', t) - E_\mu \int_{\Omega} \underline{K}^{-1}(x' - \tilde{x}) \vec{u}(\tilde{x}, t) d\tilde{x} \right] dx' \quad (2.112a)$$

$$= \frac{1}{\eta_\mu} \int_{\Omega} \underline{K}(x - x') \vec{\alpha}(x', t) dx' - \frac{\vec{u}}{T_{KV}} \quad (2.112b)$$

$$= \frac{1}{\eta_\mu} \sum_n \underline{K}_n \partial_x^n \vec{\alpha}(x, t) - \frac{\vec{u}}{T_{KV}}, \quad (2.112c)$$

where the series expansion (2.83) has been used to replace the convolution. Hence,

¹³Recall, that $\underline{K} = \mu\underline{G}$ [cf. Sec. 2.3.3].

if $\vec{\alpha}(x, t)$ is known, so is the dynamics of $\vec{u}$. Using the long-wave approximations of $\underline{K}(k)$ and $\underline{K}^{-1}(k)$ [Eqs. (2.81) and (2.82)] the dynamics of $\vec{u}$ are in zeroth order given by

$$\partial_t u_x(x, t) = \frac{d}{\eta_\mu} \left[\alpha_x(x, t) - \frac{E_\mu}{d} u_x(x, t) \right], \quad (2.113a)$$

$$\partial_t u_z(x, t) = \frac{d}{\eta_\mu} \frac{(1-2\nu)}{2(1-\nu)} \left[\alpha_z(x, t) - \frac{E_\mu}{d} \frac{2(1-\nu)}{(1-2\nu)} u_z(x, t) \right]. \quad (2.113b)$$

Note, that Eq. (2.111) could in principle also be solved directly in k -space. However, it must be borne in mind that the surface stress $\vec{\alpha}(x)$ may be non-linear, which leads to convolutions in k -space in turn. Beyond that, the dynamics of h , given by the thin-film equation (2.49), depends on $\xi = u_z$, such that it is not possible to obtain a solution for h first and subsequently calculate $\vec{u}$ from it.¹⁴

2.5. GRADIENT DYNAMICS

In Sec. 2.2.4 it was shown that the thin-film equation can be written in the form of a Cahn-Hilliard equation with the flux being constructed from a mobility function Q and the gradient of the scalar pressure field p . It turns out, that this kind of dynamics applies also to numerous other conserved systems and it can be extended further to capture non-conserved behavior as well, by adding an *Allan-Cahn* type term. The evolution of a set $\vec{\psi}(t, \vec{r})$ of m independent fields in arbitrary spatial dimension $\vec{r} \in \mathbb{R}^n$ is then given by the general form [Doi11, TAP16, Thi18]

$$\partial_t \psi_\mu = \sum_{\nu=1}^m \sum_{j=1}^n \frac{\partial}{\partial r_j} \left(Q_{\mu\nu} \frac{\partial \phi_\nu}{\partial r_j} \right) - \sum_{\nu=1}^m M_{\mu\nu} \phi_\nu. \quad (2.114)$$

If multiple fields are considered, the mobilities are expressed as $m \times m$ matrices $\underline{Q}(\vec{\psi})$ and $\underline{M}(\vec{\psi})$ for the conserved and non-conserved contributions respectively. The mobilities usually take very specific forms that strongly depend on the boundary conditions and have to be derived from a more detailed low-level description, e.g., from the Navier-Stokes equation as was in Sec. 2.2. Their off-diagonal components determine the direct coupling of the different fields.¹⁵ Once the mobilities are known,

¹⁴This means also that both h as well as $\vec{u}$ have to be calculated in each step of the utilized numerical scheme, e.g., the Newton-Raphson method [cf. App. B.3].

¹⁵Note, that the equations may also be intrinsically coupled by the scalar functions $\phi_\nu(\vec{\psi})$ as these may depend on all components of $\vec{\psi}$ in general.

these scalar fields govern the behavior of the system. Analogously to the *Lagrange formalism* the ϕ_ν can be derived as variational derivatives of a governing potential $\mathcal{L}$ with respect to the components of $\vec{\psi}$ which play the role of generalized coordinates

$$\vec{\phi} = \frac{\delta \mathcal{L}}{\delta \vec{\psi}} \quad \text{with} \quad \phi_\nu = \frac{\delta \mathcal{L}}{\delta \psi_\nu}. \quad (2.115)$$

If the potential takes an integral form $\mathcal{L}[\vec{\psi}] = \int L[\vec{\psi}, \nabla] d^n \vec{r}$ the variation is given by the *Euler-Lagrange equation* [see App. A.7]¹⁶

$$\frac{\delta \mathcal{L}}{\delta \psi_\nu} = \frac{\partial L}{\partial \psi_\nu} - \nabla \cdot \left(\frac{\partial L}{\partial (\nabla \psi_\nu)} \right). \quad (2.116)$$

The integrand L then corresponds to the classical *Lagrangian*. If the integral is limited, i.e., $\mathcal{L}[\vec{\psi}] = \int_a^b L[\vec{\psi}, \nabla] d^n \vec{r}$ the variation is given by

$$\delta \mathcal{L} = \sum_{\nu=1}^m \int_a^b \left[\frac{\partial L}{\partial \psi_\nu} - \nabla \cdot \left(\frac{\partial L}{\partial (\nabla \psi_\nu)} \right) \right] \delta \psi_\nu d^n \vec{r} + \left[\sum_{\nu=1}^m \frac{\partial L}{\partial (\nabla \psi_\nu)} \delta \psi_\nu \right]_a^b. \quad (2.117)$$

In the context of thermodynamics $\mathcal{L}$ is usually identified as a thermodynamic potential that is to be extremized in the dynamics. These extrema demand $\frac{\delta \mathcal{L}}{\delta \vec{\psi}} = 0$ and characterize steady states. Systems that exhibit such behavior are usually close to equilibrium or strongly damped. If $\mathcal{L}$ is steadily decreasing in time, it is called a *Lyapunov functional* [Wil+15]. According to *Onsagers reciprocity relations* the mobility matrices then have to be symmetric and positive definite [Ons31]. It can indeed

¹⁶If the integrand L includes higher order derivatives they have to be reduced by partial integration or the Euler-Lagrange equation has to be extended accordingly, i.e., the *Euler-Poisson equation* has to be used in general.

be shown that $\mathcal{L}$ decreases steadily in time

$$\begin{aligned}
 \frac{d\mathcal{L}}{dt} &= \int_{\Omega} \sum_{\mu=1}^m \frac{\delta\mathcal{L}}{\delta\psi_{\mu}} \frac{\partial\psi_{\mu}}{\partial t} d^n\vec{r} \\
 &= \int_{\Omega} \sum_{\mu,\nu=1}^m \phi_{\mu} \left[\sum_{j=1}^n \frac{\partial}{\partial r_j} \left(Q_{\mu\nu} \frac{\partial\phi_{\nu}}{\partial r_j} \right) - M_{\mu\nu} \phi_{\nu} \right] d^n\vec{r} \\
 &= - \int_{\Omega} \sum_{\mu,\nu=1}^m \left[\sum_{j=1}^n \frac{\partial\phi_{\mu}}{\partial r_j} Q_{\mu\nu} \frac{\partial\phi_{\nu}}{\partial r_j} + \phi_{\mu} M_{\mu\nu} \phi_{\nu} \right] d^n\vec{r} \\
 &\quad - \int_{\partial\Omega} \sum_{\mu,\nu=1}^m \sum_{j=1}^n \left[\phi_{\mu} Q_{\mu\nu} \frac{\partial\phi_{\nu}}{\partial r_j} n_j \right] ds \leq 0,
 \end{aligned} \tag{2.118}$$

where $\vec{n}$ is the surface normal vector and the integral over $\partial\Omega$ vanishes if conserving boundary conditions are considered.¹⁷ From Eq. (2.114) it is seen already that a steady state must satisfy $\frac{\delta\mathcal{L}}{\delta\psi_{\nu}} = \text{const.}$ if the dynamics is conserved, that is $M = 0$, or even $\frac{\delta\mathcal{L}}{\delta\psi_{\nu}} = 0$ if not. In case of a steady state the *first integral* or *integral of motion*

$$\mathcal{H} = \sum_{\nu} \nabla\psi_{\nu} \cdot \frac{\partial L}{\partial(\nabla\psi_{\nu})} - L, \tag{2.119}$$

which in the above analogy corresponds to the *Hamiltonian*, must be constant across the domain as well.

Finally, the dynamics follows the gradient of $\mathcal{L}$ in function space until a minimum is reached, which is why the temporal evolution of such systems is referred to as *gradient dynamics* [Doi11, TAP16, Thi18]. The great advantage of this approach is its great versatility; Once the mobilities are known, further physical effects can easily be incorporated by simply adding the corresponding energy contributions to $\mathcal{L}$, instead of performing the whole derivation again. Note, that the gradient dynamics structure as introduced above is local in time. In order to incorporate

¹⁷Usually *Neumann* or *periodic boundary conditions* are considered. The Neumann boundary condition or *no-flux* condition demands $\nabla\psi_{\mu}|_{\partial\Omega} = 0$, i.e., no flux across the boundaries while the periodic boundary condition simply demands equality of $\vec{\psi}$ and its derivatives at the opposing ends of the domain.

memory effects an evolution equation of the shape [Zwa61]

$$\begin{aligned} \partial_t \psi_\mu = & \sum_{j=1}^n \frac{\partial}{\partial r_j} \left(\int_{-\infty}^t \sum_{\nu=1}^m Q_{\mu\nu}(t-t') \frac{\partial}{\partial t'} \left(\frac{\partial}{\partial r_j} \frac{\delta \mathcal{L}}{\delta \psi_\nu} \right) dt' \right) \\ & + \int_{-\infty}^t \sum_{\nu=1}^m M_{\mu\nu}(t-t') \frac{\partial}{\partial t'} \left(\frac{\delta \mathcal{L}}{\delta \psi_\nu} \right) dt' \end{aligned} \quad (2.120)$$

would be required.¹⁸

¹⁸Note the similarity with the time-dependent stress-strain relation Eq. (2.87).

3. GRADIENT DYNAMICS MODELING OF THE TWO-LAYER SYSTEM

In the previous chapter, the mathematical foundation, upon which the description of the dynamics of Newtonian fluids and linear viscoelastic materials is based, was laid and discussed under consideration of the layer geometry. It is now the point where both, liquid and solid dynamics, have to be brought together in order to approach the subject of soft wetting. While the surface of the liquid is considered free, i.e., there are no stresses transmitted by the overlaying gas phase $\underline{\sigma}_g = 0$, the stresses in its bulk are transmitted to the viscoelastic substrate underneath and add to the force balance at the solid-liquid interface. To properly such a two layer system, the dynamics for h and $\vec{u}$ would have to be derived again from the governing equations, i.e., the Navier-Stokes equations for the liquid and the Navier-Cauchy equations for the viscoelastic solid, thereby employing a time dependent constitutive law for the latter and coupling both equations by a boundary condition that reflects the stress equilibrium at the solid-liquid interface. In addition to that there are also additional stresses acting on the interfaces that so far have only ever been represented by unknown vector fields $\vec{\alpha}_{lg}(\vec{r})$ and $\vec{\alpha}'_{sl}(\vec{r})$, respectively for the liquid-gas and the solid-liquid interfaces [cf. Eqs. (2.37) and (2.66)] and which crucially determine the systems behavior.

As we have seen in the previous, such a derivation requires extensive calculations and is prone to errors, which is why we aspire a gradient dynamics approach instead. Particularly, in the case of vanishing shear stress at the liquid-gas interface, i.e., $\vec{\tau} = 0$, the thin-film equation (2.49), describing the dynamics of the local liquid layer thickness $h(x, y, t)$, can be cast into the form of a conserved gradient dynamics, depending only on the normal surface stress p_α

$$\partial_t h = \nabla \cdot [Q(h) \nabla p_\alpha] , \quad (3.1)$$

with the mobility $Q(h) = \frac{h^2}{\eta} \left(\frac{h}{3} + \ell_s \right)$.

But what about the surface displacement $\vec{u}(x, y, t)$ of the substrate? Being a vis-

coelastic material a first instinct might suggest to employ a dynamics of the form Eq. (2.120). Equations like that have already been used for similar problems, e.g., by DEVULT and MCLENNAN [DM65]. An evolution equation of that form requires knowledge about the time-dependent mobilities though, which in turn depend on the viscoelasticity model. Let us for now restrict our selves to the two dimensional scenario, i.e., translational invariance of the fields in y -direction.¹ The dynamics for the surface displacement of a finite thickness Kelvin-Voigt material is then already known to be given by Eq. (2.111) in spatial Fourier space. This equation takes the shape of a non-conserved Allen-Chan type dynamics

$$\partial_t \vec{u}(k, t) = -\underline{M}(k) \vec{\phi}_u(k, t), \quad (3.2)$$

with the time-independent mobility $\underline{M}(k) = \underline{K}(k)/\eta_\mu$ and surface stress balance²

$$\vec{\phi}_u(k, t) = E_\mu \underline{K}^{-1}(k) \vec{u}(k, t) - \vec{\alpha}_{sl}(k, t). \quad (3.3)$$

However, in position space the dynamics is given by Eqs. (2.112), i.e., it is of the form

$$\partial_t \vec{u}(x, t) = -\frac{1}{\eta_\mu} \int_{\Omega} \underline{K}(x - x') \vec{\phi}_u(x, t) dx', \quad (3.4)$$

and includes either convolution integrals or, if expanded using Eq. (2.83), spatial derivatives of arbitrary order³, both of which complicate matters. Yet in the long-wave limit it is reasonable to only consider the zeroth order of the expansion, leaving us with Eqs. (2.113), which in turn correspond to a non-conserved Allen-Chan type dynamics again

$$\partial_t \vec{u}(x, t) = -\underline{M} \vec{\phi}_u(x, t), \quad (3.5)$$

¹Even though the gradient of the profiles is identical to their partial derivative ∂_x then, the symbol ∇ will nevertheless be used in the following, if the equations are valid also in higher spatial dimensions.

²This surface stress balance $\vec{\phi}_u$ now includes all stresses at the solid-liquid interface, i.e., the external stress, the stress caused by the liquid as well as the elastic forces. Recall further, that $\underline{K} = \mu \underline{G}$ [cf. Secs. 2.3.2 and 2.3.3].

³Note, that these higher order derivative terms result also in Cahn-Hilliard type contributions, i.e., a conserved part. Thus, whether or not the dynamics is non-conserved depends on the Poisson ratio ν after all.

with constant mobility

$$\underline{M} = \begin{pmatrix} \frac{d}{\eta_\mu} & 0 \\ 0 & \frac{d}{\eta_\mu} \frac{1-2\nu}{2(1-\nu)} \end{pmatrix} \quad (3.6)$$

and

$$\vec{\phi}_u(x, t) = \begin{pmatrix} \alpha_x(x, t) - \frac{E_\mu}{d} u_x(x, t) \\ \alpha_z(x, t) - \frac{E_\mu}{d} \frac{2(1-\nu)}{(1-2\nu)} u_z(x, t) \end{pmatrix}. \quad (3.7)$$

Finally, the evolution equations of both, the Newtonian liquid [Eq. (3.1)] as well as the Kelvin-Voigt solid [Eq. (3.5)], can be written in gradient dynamics form, though only in the long-wave limit, assuming that both, the normal surface stress p_α at the liquid-gas interface as well as the surface stress balance $\vec{\phi}_u(\vec{r})$ at the solid-liquid interface can be derived as variations of a governing thermodynamic potential

$$p_\alpha = \frac{\delta \mathcal{L}}{\delta h}, \quad \vec{\phi}_u = \frac{\delta \mathcal{L}}{\delta \vec{u}}. \quad (3.8)$$

This thermodynamic potential remains yet to be formulated, which is the objective of the next section.

3.1. FREE ENERGY AND ITS VARIATIONS

When the temperature T , the liquid volume V and the particle number N are kept constant, the governing thermodynamic potential is identified as the *Helmholtz free energy* $\mathcal{F}$, the contributions of which are discussed in the following.

3.1.1. ELASTIC ENERGY

The first contribution considered is the one associated with the elastic deformation of the substrate. Following the argumentation of LIFSHITZ, KOSEVICH & PITAEVSKII [LKP86], the amount of energy required to achieve a small deformation $\delta \vec{u}$ of an elastic object is given by the work that has to be exerted against the restoring force per unit volume $\vec{f}$ summed up over the whole domain Ω

$$\delta \mathcal{W} = \int_{\Omega} \vec{f} \cdot \delta \vec{u} \, d^3 \vec{r} = \int_{\Omega} (\nabla \cdot \underline{\sigma}) \cdot \delta \vec{u} \, d^3 \vec{r}, \quad (3.9)$$

where the resisting forces were again expressed in terms of the stress tensor. Switching to index notation leads to

$$\begin{aligned}\delta\mathcal{W} &= \int_{\Omega} \sum_{i,j=1}^3 (\partial_j \sigma_{ij}) \delta u_i \, d^3\vec{r} = \int_{\Omega} \sum_{i,j=1}^3 \partial_j (\sigma_{ij} \delta u_i) \, d^3\vec{r} - \int_{\Omega} \sum_{i,j=1}^3 \sigma_{ij} \partial_j \delta u_i \, d^3\vec{r} \\ &= \int_{\partial\Omega} \sum_{i,j=1}^3 \sigma_{ij} \delta u_i n_j \, d^2\vec{r} - \int_{\Omega} \sum_{i,j=1}^3 \sigma_{ij} \partial_j \delta u_i \, d^3\vec{r}.\end{aligned}$$

where $\vec{n}$ is the surface normal vector and the divergence theorem has been used in the final step. We now assume an infinitely extended substrate in the (x, y) -plane with vanishing displacement $\vec{u}$ at the bottom $z = -d$ and at $|\vec{r}_{\parallel}| \rightarrow \infty$. In this case the surface integral vanishes despite the infinite surface $\partial\Omega$ of integration [LKP86]. The remaining bulk integral becomes

$$\begin{aligned}\delta\mathcal{W} &= - \int_{\Omega} \sigma_{ij} \sum_{i,j=1}^3 \partial_j \delta u_i \, d^3\vec{r} \\ &\stackrel{\langle 1 \rangle}{=} - \int_{\Omega} \frac{1}{2} \sum_{i,j=1}^3 (\sigma_{ij} \partial_j \delta u_i + \sigma_{ji} \partial_j \delta u_i) \, d^3\vec{r} \\ &\stackrel{\langle 2 \rangle}{=} - \int_{\Omega} \frac{1}{2} \sum_{i,j=1}^3 \sigma_{ij} \delta (\partial_j u_i + \partial_i u_j) \, d^3\vec{r} \\ &\stackrel{\langle 3 \rangle}{=} - \int_{\Omega} \sum_{i,j=1}^3 \sigma_{ij} \delta \varepsilon_{ij} \, d^3\vec{r}.\end{aligned}\tag{3.10}$$

In step $\langle 1 \rangle$ the summand is split up in two equal parts. Subsequently the symmetry of stress $\sigma_{ij} = \sigma_{ji}$ is exploited to swap the indices i and j in the second term in step $\langle 2 \rangle$. The stress is then excluded and the partial derivative shifted behind the δ . Finally, the strain tensor ε_{ij} [Eq. (2.14)] is identified in step $\langle 3 \rangle$. Hence the work per unit volume is given by

$$\delta w = - \sum_{i,j=1}^3 \sigma_{ij} \delta \varepsilon_{ij}\tag{3.11}$$

Together with the change in heat $\delta Q = T dS$ the characteristic state functions of the internal energy $\mathcal{U}$ as well as the Helmholtz free energy $\mathcal{F}$ and the *Gibbs free energy*

$\mathcal{G}$ can be formulated

$$d\mathcal{U} = \delta Q - d\mathcal{W} = TdS + \int_{\Omega} \sum_{i,j=1}^3 \sigma_{ij} d\varepsilon_{ij} d^3\vec{r}, \quad (3.12a)$$

$$d\mathcal{F} = d\mathcal{U} - d(ST) = -SdT + \int_{\Omega} \sum_{i,j=1}^3 \sigma_{ij} d\varepsilon_{ij} d^3\vec{r}, \quad (3.12b)$$

$$d\mathcal{G} = d\mathcal{U} - d(ST) - \int_{\Omega} \sum_{i,j=1}^3 d(\sigma_{ij}\varepsilon_{ij}) d^3\vec{r} = -SdT - \int_{\Omega} \sum_{i,j=1}^3 \varepsilon_{ij} d\sigma_{ij} d^3\vec{r}. \quad (3.12c)$$

From here on, the temperature T is assumed constant in time and space. As independent variables the stress and strain components then have to obey

$$\sigma_{ij} = \left. \frac{\partial f}{\partial \varepsilon_{ij}} \right|_T, \quad \varepsilon_{ij} = - \left. \frac{\partial g}{\partial \sigma_{ij}} \right|_T, \quad (3.13)$$

where f and g denote the Helmholtz- and Gibbs free energy per unit volume, respectively [LKP86]. As stress and strain are linearly related via the constitutive law, e.g., Eq. (2.55), the free energy per unit area is found to be [Sadog]

$$f = \frac{1}{2} \sum_{i,j=1}^3 \sigma_{ij} \varepsilon_{ij} = \sum_{i,j=1}^3 \frac{\lambda}{2} \varepsilon_{ii} \varepsilon_{jj} + \mu \varepsilon_{ij} \varepsilon_{ij}. \quad (3.14)$$

Expressing the strain using the displacement field, the total free energy can be calculated [LKP86]

$$\begin{aligned} \mathcal{F} &= \int_{\Omega} f d^3\vec{r} = \frac{1}{2} \int_{\Omega} \sum_{i,j=1}^3 \sigma_{ij} \varepsilon_{ij} d^3\vec{r} \\ &\stackrel{\langle 1 \rangle}{=} \frac{1}{2} \int_{\Omega} \sum_{i,j=1}^3 \sigma_{ij} \partial_j u_i d^3\vec{r} \\ &\stackrel{\langle 2 \rangle}{=} \frac{1}{2} \int_{\Omega} \sum_{i,j=1}^3 [\partial_j (\sigma_{ij} u_i) - (\partial_j \sigma_{ij}) u_i] d^3\vec{r} \\ &\stackrel{\langle 3 \rangle}{=} \frac{1}{2} \int_{\partial\Omega} \sum_{i,j=1}^3 \sigma_{ij} n_j u_i d^2\vec{r} - \frac{1}{2} \int_{\Omega} \sum_{i,j=1}^3 (\partial_j \sigma_{ij}) u_i d^3\vec{r}. \end{aligned} \quad (3.15)$$

Here the symmetry of stress is used again in step $\langle 1 \rangle$ to express the strain tensor in terms of the displacement field $\vec{u}$, i.e., the reverse of the transformation made in

Eq. (3.10). In step ⟨2⟩ the inverse Leibniz product rule is used on the summand. Subsequently, the volume integral over the first term in the sum is turned into a surface integral in step ⟨3⟩ using the divergence theorem. Under the assumption of vanishing body forces⁴, i.e., $\partial_j \sigma_{ij} = 0$, only the surface integral remains

$$\mathcal{F} = \frac{1}{2} \int_{\partial\Omega} (\underline{\sigma} \cdot \vec{n}) \cdot \vec{u} \, d^2\vec{r}. \quad (3.16)$$

Note, that $\partial\Omega$ refers to the surface at $z = 0$, i.e., the solid-liquid interface, as only there stresses are acting due to the no-slip condition at the bottom side [Eq. (2.65)]. To calculate the variation of the free energy w.r.t. $\vec{u}$ the surface stress in Eq. (3.16) has to be expressed accordingly. This can be done by means of the inverse Green's function [Eq. (2.80)]⁵ such that the Helmholtz free energy of a finite elastic layer deformed under surface stresses is given by [LAL96]

$$\mathcal{F}_{\text{el}}[\vec{u}] = \frac{1}{2} \int_{\partial\Omega} \left[\int_{\partial\Omega} \underline{G}^{-1}(\vec{r} - \vec{r}') \cdot \vec{u}(\vec{r}') \, d^2\vec{r}' \right] \cdot \vec{u}(\vec{r}) \, d^2\vec{r}, \quad (3.17)$$

or when using the convolution theorem

$$\begin{aligned} \mathcal{F}_{\text{el}}[\vec{u}] &= \frac{1}{2} \int_{\partial\Omega} \left[\int_{\partial\Omega} \underline{G}^{-1}(\vec{k}) \cdot \vec{u}(\vec{k}) \, e^{i\vec{k} \cdot \vec{r}} \frac{d^2\vec{k}}{2\pi} \right] \cdot \vec{u}(\vec{r}) \, d^2\vec{r} \\ &= \frac{1}{2} \int_{\partial\Omega} [\underline{G}^{-1}(\vec{k}) \cdot \vec{u}(\vec{k})] \cdot \left[\int_{\partial\Omega} \vec{u}(\vec{r}) \, e^{i\vec{k} \cdot \vec{r}} \frac{d^2\vec{r}}{2\pi} \right] d^2\vec{k} \\ &= \frac{1}{2} \int_{\partial\Omega} [\underline{G}^{-1}(\vec{k}) \cdot \vec{u}(\vec{k})] \cdot \vec{u}(-\vec{k}) \, d^2\vec{k} \end{aligned} \quad (3.18)$$

⁴This is a reasonable assumption in the long-wave limit, because gravity becomes increasingly negligible as the layer thickness decreases. Since no other body forces are explicitly introduced in the following, all deformations are exclusively caused by the influence of surface stress.

⁵Note, that the constant μ in Eq. (2.79) is to be replaced by the corresponding storage shear modulus χ'_μ , which in case of a Kelvin-Voigt material is given by the constant E_μ from Eq. (2.109b).

The variation of the linear elastic Helmholtz free energy [Eq. (3.17)] can be written in weak formulation as

$$\begin{aligned}
\int_{\partial\Omega} \frac{\delta\mathcal{F}}{\delta u_i} \phi(\vec{r}) \, d^2\vec{r} &= \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} \left[\mathcal{F}[\vec{u} + \epsilon \phi \vec{e}_i] - \mathcal{F}[\vec{u}] \right] \\
&= \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} \left\{ \frac{1}{2} \int_{\partial\Omega} \sum_{j=1}^3 \left(u_j(\vec{r}) + \epsilon \phi(\vec{r}) \delta_{ij} \right) \left[\int_{\partial\Omega} \sum_{k=1}^3 G_{jk}^{-1}(\vec{r} - \vec{r}') (u_k(\vec{r}') + \epsilon \phi(\vec{r}') \delta_{ik}) \, d^2\vec{r}' \right] d^2\vec{r} \right. \\
&\quad \left. - \frac{1}{2} \int_{\partial\Omega} \sum_{j=1}^3 u_j(\vec{r}) \left[\int_{\partial\Omega} \sum_{k=1}^3 G_{jk}^{-1}(\vec{r} - \vec{r}') u_k(\vec{r}') \, d^2\vec{r}' \right] d^2\vec{r} \right\} \\
&= \frac{1}{2} \iint_{\partial\Omega} \sum_{j,k=1}^3 \left[u_j(\vec{r}) G_{jk}^{-1}(\vec{r} - \vec{r}') \phi(\vec{r}') \delta_{ik} + \phi(\vec{r}) \delta_{ij} G_{jk}^{-1}(\vec{r} - \vec{r}') u_k(\vec{r}') \right] d^2\vec{r}' d^2\vec{r} \\
&= \frac{1}{2} \iint_{\partial\Omega} \left[\sum_{j=1}^3 u_j(\vec{r}) G_{ji}^{-1}(\vec{r} - \vec{r}') \phi(\vec{r}') + \sum_{k=1}^3 \phi(\vec{r}) G_{ik}^{-1}(\vec{r} - \vec{r}') u_k(\vec{r}') \right] d^2\vec{r}' d^2\vec{r} \\
&= \int_{\partial\Omega} \left[\int_{\partial\Omega} \sum_{j=1}^3 G_{ij}^{-1}(\vec{r} - \vec{r}') u_j(\vec{r}') \, d^2\vec{r}' \right] \phi(\vec{r}) \, d^2\vec{r}
\end{aligned}$$

where $\phi(\vec{r})$ is an arbitrary test function that satisfies $\phi(\vec{r})|_{\partial\Omega} = 0$. In the last step the symmetry of the Green's function is used, i.e., $G_{ij}^{-1} = -G_{ji}^{-1}$ and $G_{ij}^{-1}(-\vec{r}) = -G_{ij}^{-1}(\vec{r})$ for $i \neq j$. It is found, that the variation of the Helmholtz free energy at the surface corresponds to the surface stress [cf. Eq. (2.80)]

$$\frac{\delta\mathcal{F}}{\delta u_i} = \int_{\Omega} \sum_{j=1}^3 G_{ij}^{-1}(\vec{r} - \vec{r}') u_j(\vec{r}') \, d^2\vec{r}' = \sum_{j=1}^3 \sigma_{ij} n_j. \quad (3.19)$$

3.1.2. GRAVITY

The example of sliding rain drops on a window alone renders gravity the probably most obvious candidate when it comes to forces that drive liquids on solid surfaces. Being a ubiquitous fundamental interaction it surely has to be taken into account, however, its impact depends crucially on the system size or rather the amount of mass present. The gravitational force per unit volume of an material, say the liquid, is given by

$$\vec{f} = -\rho_\ell g \vec{e}_z,$$

with mass density ρ_ℓ and gravitational acceleration $g \approx 9.81 \text{ ms}^{-2}$ at earth's surface [CGPM01]. It acts in the negative z -direction and since the liquid is considered incompressible, i.e., $\rho_\ell = \text{const.}$, the gravitational force per unit volume is constant everywhere within the liquid bulk as well. Integration over the liquid layer thickness h yields the hydrostatic pressure at the solid-liquid interface⁶

$$p_g = \int_{\xi}^{h+\xi} \rho g \, dz = \rho g h .$$

Since gravity is a conservative force it can also be described by a scalar potential

$$\mathcal{F}_g[h, \xi] = \iiint_{\xi}^{h+\xi} \rho g z \, dz dx dy = \iint \frac{1}{2} \rho g (h^2 + 2h\xi) \, dx dy .$$

The variations of the energy w.r.t. h and ξ yield the liquid and substrate pressures

$$\frac{\delta \mathcal{F}_g}{\delta h} = \rho g (h + \xi) , \quad \frac{\delta \mathcal{F}_g}{\delta \xi} = \rho g h . \quad (3.20)$$

The variation w.r.t. ξ again yields the hydrostatic pressure [Eq. (3.20)] acting at the solid-liquid interface while the variation w.r.t. h gives the pressure acting on the liquid-gas interface and depends on the absolute height $h + \xi$ of that interface relative to $z = 0$ instead of $z = \xi$. The situation changes quite a bit if the system is inclined by an angle ϑ , e.g., about the y -axis. Let x and z be the coordinates parallel and perpendicular to the inclined substrate and $h(x, y)$ and $\xi(x, y)$ represent the liquid layer thickness and substrate profile in z -direction. The coordinates w.r.t. the equipotential plane of gravitation are then given by

$$x' = x \cos(\vartheta) - z \sin(\vartheta) , \quad z' = x \sin(\vartheta) + z \cos(\vartheta) ,$$

and the energy writes

$$\begin{aligned} \mathcal{F}_g[h, \xi] &= \int \rho g z' \, dV = \iiint_{\xi}^{h+\xi} \rho g [x \sin(\vartheta) + z \cos(\vartheta)] \, dz dx dy \\ &= \iint \rho g \left[x h \sin(\vartheta) + \frac{1}{2} (h^2 + 2h\xi) \right] \, dx dy , \end{aligned} \quad (3.21)$$

⁶As was found in Sec. 2.2.3 the pressure in the liquid is constant in z -direction. Hence, the hydrostatic pressure at the solid-liquid interface is actually present everywhere in the liquid bulk.

with its variations being

$$\frac{\delta \mathcal{F}_g}{\delta h} = \rho g x \sin(\vartheta) + \rho g (h + \xi) \cos(\vartheta), \quad \frac{\delta \mathcal{F}_g}{\delta \xi} = \rho g h \cos(\vartheta). \quad (3.22)$$

Since the gravitational contribution depends mainly on the mass per unit area ρh it becomes accordingly small if very thin films are considered, as is always the case in the following.

3.1.3. INTERFACIAL FREE ENERGY

Since gravitational effects are very weak in the long-wave limit there must be other forces acting in the system that are responsible for the formation of droplets which are so prominent in that regime. And indeed there are further forces arising at the interface between two phases, caused by their different molecular structure. As mentioned before, the particles of a simple one-component fluid are indistinguishable in the sense that they are not organized in certain substructures, i.e., switching the position of two such particles would not at all affect the state of the system or its energy. Hence, a fluid particle sitting within a bulk of its own kind is indifferent to its neighbors and interacts equally with all of them. The strength of that attractive *cohesion force* depends only on the particle distance and the distribution of the latter is assumed isotropic. In such a scenario a particle within the bulk occupies a state of minimal potential energy. However, a particle positioned at the interface to an other species, say a gas phase, perceives two distinct types of neighboring particles and experiences potentially different interactions therefore. If the attraction of its own kind dominates against the *adhesion force* exerted by the other, this asymmetry results in a net force pointing into the bulk of its own as shown in Fig. 3.1. Actually, the formation of such an interface between two phases is possible only if the particles are attracted stronger by their own kind than by the other, since otherwise the two phases would mix. There are of course also repulsive forces acting between the molecules, that resist normal stresses and prevent the material from collapsing. The sum of attractive and repulsive intermolecular forces is usually described by a *Lennard-Jones* potential. Since in a liquid the repulsive forces become stronger very quickly as the distance between the particles decreases, even strong attractive forces may be balanced without a significant change in density, i.e., the liquid is then considered incompressible. Further, the repulsive forces usually act on much shorter ranges as compared to the attractive ones and are thus much less sensitive to anisotropies such as represented by an interface [Mar+11]. In order to increase

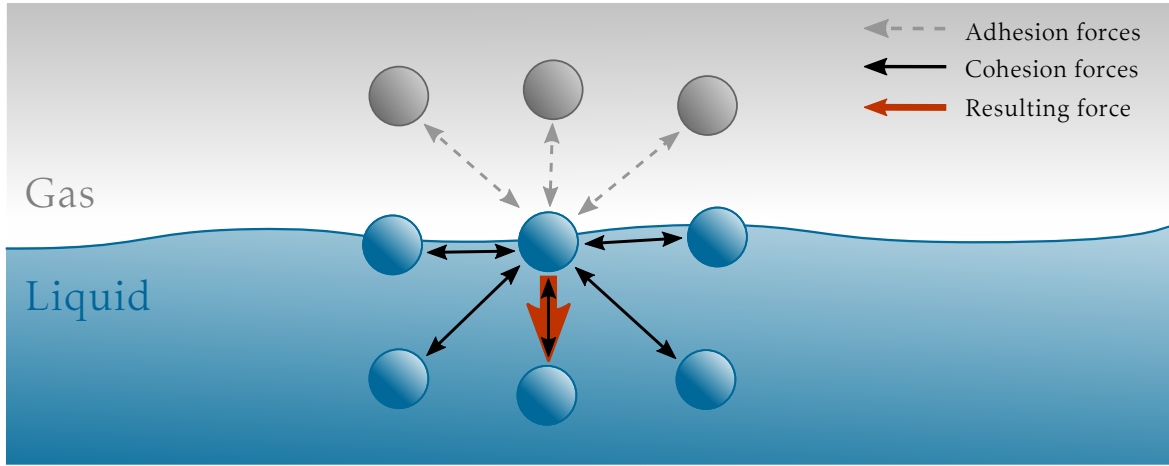


FIGURE 3.1.: Intermolecular forces at a liquid-gas interface. The black arrows denote cohesive interactions between particles of the same kind, while the gray dashed arrows denote adhesive interactions between particles of different kind. If the former are dominant against the latter the resulting net force acting on a particle at the interface points into the bulk of its own kind. This is the origin of interface energies or interface tensions.

such an interface, further particles would have to be brought to the surface from the bulk against that inward pointing force.⁷ The work required to create an infinitesimal interface area ds is called *interfacial free energy* or simply *interface energy* γ and corresponds to the difference in potential energy of a particle at the interface and one located in the energetically more favorable bulk [dG85, dBQ04]. The total free energy is therefore given by the integral of the interfacial free energy along the interface

$$\mathcal{F}_{\text{int}}[\psi] = \int_{\partial\Omega} \gamma \, ds = \int_{\partial\Omega} \gamma m(\psi) \, dxdy, \quad (3.23)$$

with the metric factor $m(\psi) = \sqrt{1 + (\nabla_{\parallel}\psi)^2}$ relating the surface element ds to the unit area $dxdy$ if the interface profile can be described by a function $\psi(\vec{r}_{\parallel})$ [cf. App. A.2]. The *Laplace pressure* resulting from the variation is given by

$$\frac{\delta\mathcal{F}}{\delta\psi} = -\gamma \nabla_{\parallel} \cdot \left(\frac{\nabla_{\parallel}\psi}{m(\psi)} \right) = -\gamma \frac{\Delta_{\parallel}\psi}{m^3(\psi)} = \gamma (\nabla \cdot \vec{n}) \quad (3.24)$$

⁷This assumes of course, that particles are even able to move from the bulk to the interface in the first place. In case of an elastic solid, however, the movement of its constituents is usually strongly restricted or even confined within a substructure. The consequences of such a behavior are further discussed in Ch. 7.

and is directly proportional to the local curvature $\kappa = -(\nabla \cdot \vec{n})$ of the interface ψ via the interface energy γ .⁸ The latter need not be constant across the interface, as has been assumed so far. Gradients in temperature or concentration of surface active agents (surfactants) may cause inhomogeneities in the interfacial free energy which in turn lead to additional tangential forces along the interface referred to as *Marangoni stresses* [dBQ04]. In case of the thin-film equation, such forces enter via the interfacial stress balance in the form of a surface derivative $[\underline{P}(\vec{n})\nabla]\gamma_{lg}$ which contributes to the r.h.s. of Eq. (2.44d). It therefore doesn't contribute to the pressure but rather causes a flux directly [Pot+05]. Note further, that Eq. (3.24) considers the *full curvature* [Thi18]

$$\kappa(\psi) = \nabla \cdot \left(\frac{\nabla \psi}{\sqrt{1 + (\nabla \psi)^2}} \right), \quad (3.25)$$

in the sense that $\kappa(\psi) = \text{const.}$ defines a spherical cap. In the long-wave limit, however, all gradients are considered small [cf. Sec. 2.2.3] and the curvature may be approximated as

$$\kappa(\psi) \approx \Delta \psi, \quad (3.26)$$

such that $\kappa(\psi) = \text{const.}$ defines a paraboloid instead.

3.2. CAPILLARITY AND STATIC DROPS

It is due to the interfacial free energy penalty that materials strive to minimize their interface area when ever they come to meet a relatively unappealing neighborhood. As is well known, the geometric body of least surface area for a given volume is a sphere. The latter in turn is characterized by overall constant curvature along the surface and exhibits constant Laplace pressure in consequence. Hence, considering a finite amount of liquid surrounded by a gas phase with an interface energy γ_{lg} , a sphere is exactly the shape we would expect it to assume, provided that no other forces interfere. This shape is commonly referred to as a *drop(let)*. Yet, the formulation of the problem in terms of a unique mapping $h(x, y)$ prohibits such a shape. However, liquids deposited on a substrate rarely take the shape of perfect spheres but rather spherical caps of different size and curvature or flat films even. This is due to the energies of the solid-liquid interface γ_{sl} and the solid-gas interface γ_{sg} ,

⁸Here and in the following a negative curvature refers to a concave function, while functions with positive curvature are convex.

which haven't been taken into account yet. The liquid's behavior resulting from the interplay of these three interface energies is referred to as *capillarity* and the field of research that deals with such systems is commonly called *wetting*.⁹ Since only very small droplets are considered in the following, gravity is neglected. Depending on the three interface energies γ_{lg} , γ_{sl} and γ_{sg} different scenarios are conceivable in which the liquid forming a sphere is not the energetically most favourable state and the penalty of larger liquid-gas interface areas are endured in order to reduce the overall free energy of the whole system including the substrate. If for example the solid-gas interface energy is higher than the sum of the liquid-gas and solid-liquid interface energies $\gamma_{sg} > \gamma_{lg} + \gamma_{sl}$ it is energetically favourable to cover the whole substrate with liquid in order to minimize the solid-gas interface area and the corresponding energy penalty, even if the liquid-gas and solid-liquid interfaces increase by the same amount. This scenario is referred to as *complete wetting* as the liquid spreads over the substrate as far as possible. If, on the other hand, the solid-liquid interface energy is larger than the sum of the liquid-gas and solid-gas interface energies $\gamma_{sl} > \gamma_{lg} + \gamma_{sg}$, the solid-liquid interface area is to be minimized which can be realized by the liquid forming a perfect sphere that touches the substrate at only one point. This scenario is referred to as *non-wetting* since the liquid retreats from the substrate. All cases in between these two limits are called *partial wetting* (cf. Fig. 3.2).

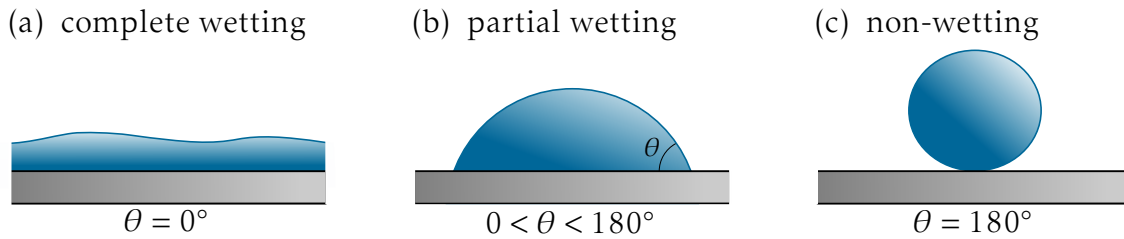


FIGURE 3.2.: Visualization of the three wetting scenarios in a cross section view considering a rigid level substrate. (a) complete wetting: the interface energies satisfy $\gamma_{sg} > \gamma_{lg} + \gamma_{sl}$ and the liquid spreads over the substrate as far as possible forming a thin film. In that case no contact line is present, i.e., $\theta = 0^\circ$. (b) partial wetting: the liquid forms a spherical cap in order to minimize the energies associated with the three interfaces. In this regime an additional distinction is made between high wetting $\theta < 90^\circ$ and low wetting $\theta > 90^\circ$ scenarios. (c) non-wetting: the interface energies satisfy $\gamma_{sl} > \gamma_{lg} + \gamma_{sg}$ and the liquid retreats from the substrate as far as possible forming a sphere. In that case the liquid is in contact to the substrate only at a single points, i.e., $\theta = 180^\circ$.

⁹Note, that the very fact that drop like structures, even if not perfectly spherical, can be observed by the naked eye at all indicates that capillarity and gravity forces are competing on the macroscopic scale already. Hence, the interface energy of a liquid forming such a drop can be estimated to be of order $10^{-2} \frac{\text{J}}{\text{m}^2} < \mathcal{O}(\gamma) < 10^0 \frac{\text{J}}{\text{m}^2}$.

From these considerations the *spreading parameter*

$$S = \gamma_{sg} - (\gamma_{sl} + \gamma_{lg}) \quad (3.27)$$

may be constructed to classify a system as non-wetting $S < -2\gamma_{lg}$, complete wetting $S > 0$ or partial wetting $-2\gamma_{lg} < S < 0$. Let us have a closer look at the latter case and see what characterizes drops in that regime.

3.2.1. THE ELASTIC REGIME

Consider a soft substrate with isotropic properties in the x - y -plane, such that a drop sitting on top and centered at $x = y = 0$ can be assumed axis-symmetric w.r.t. the z -axis. The liquid layer thickness and the substrate profile are once again described in terms of the scalar functions $h(r)$ and $\xi(r)$, respectively [cf. Fig. 2.2].¹⁰ These two profiles meet at base radius $r = R$ which defines the *three phase contact line*. The

¹⁰Remember that ξ corresponds to the vertical component of the surface displacement, i.e., $\xi = \vec{u} \cdot \vec{e}_z|_{z=0}$.

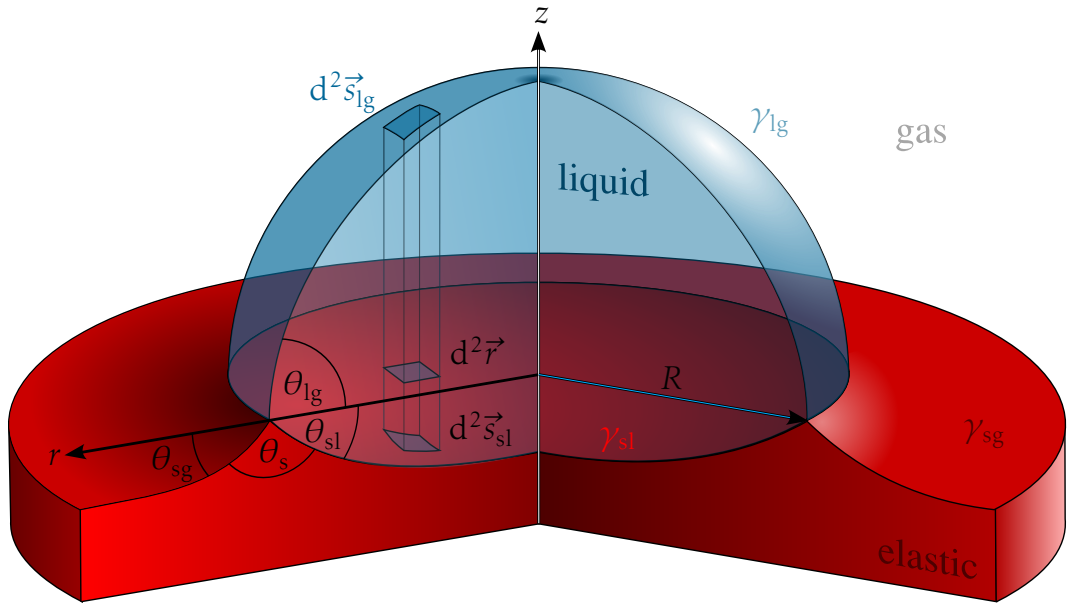


FIGURE 3.3.: Sketch of a radially symmetric partially wetting liquid drop on an elastic substrate. The liquid-gas interface hits the substrate surface along the circular three phase contact line at base radius $r = R$. The wetting ridge forming there is characterized by the contact angles θ_{lg} , θ_{sl} and θ_{sg} which are governed by the interface energies γ_{lg} , γ_{sl} and γ_{sg} in turn. The opening angle of the wetting ridge is $\theta_s = \pi - \theta_{sl} - \theta_{sg}$. The ratio of the surface elements ds_{lg} and ds_{sl} with their projection onto the x - y -plane is given by the metric factor.

latter can further be characterized by three *contact angles*

$$\partial_r(h + \xi)\big|_{r \uparrow R} = -\tan \theta_{lg} \ , \quad \partial_r \xi\big|_{r \uparrow R} = \tan \theta_{sl} \ , \quad \partial_r \xi\big|_{r \downarrow R} = -\tan \theta_{sg} \ , \quad (3.28)$$

as shown in Fig. 3.3. Here $r \uparrow R \Leftrightarrow r = \lim_{\epsilon \rightarrow 0} R - \epsilon$ and $r \downarrow R \Leftrightarrow r = \lim_{\epsilon \rightarrow 0} R + \epsilon$ indicate, that the position of the contact line $r = R$ is approached from lower values $r < R$ or larger values $r > R$, respectively.¹¹ Using Eqs. (3.23) and (3.17) total Helmholtz free energy of such a system is then given by

$$\begin{aligned} \mathcal{F}[h, \vec{u}] = & \int_0^R \left[\gamma_{lg} \sqrt{1 + (\partial_r h + \partial_r \xi)^2} + \gamma_{sl} \sqrt{1 + (\partial_r \xi)^2} - Ph \right] 2\pi r \, dr + \lambda h(R) \quad (3.29) \\ & + \int_R^\infty \gamma_{sg} \sqrt{1 + (\partial_r \xi)^2} 2\pi r \, dr + \int_0^\infty \frac{1}{2} \left[\int_0^\infty \underline{G}^{-1}(\vec{r} - \vec{r}') \cdot \vec{u}(\vec{r}') \, d^2 \vec{r}' \right] \cdot \vec{u}(\vec{r}) \, d^2 \vec{r}, \end{aligned}$$

where P and λ are *Lagrange multipliers* for volume conservation and fixation of the contact line at $r = R$, i.e.,

$$P \int_0^R (h - h_0) 2\pi r \, d^2 r = 0 \ , \quad (3.30a)$$

$$\lambda h(R) = 0 \ , \quad (3.30b)$$

with h_0 being some arbitrary preset liquid layer thickness that is to be conserved [NVC01]. According to Eq. (2.117) the variation w.r.t. h and ξ is then found to be

$$\begin{aligned} \delta \mathcal{F} = & \int_0^R \left[-\gamma_{lg} \left(\frac{1}{r} + \partial_r \right) \left(\frac{\partial_r(h + \xi)}{m(h + \xi)} \right) - P \right] \delta h \, 2\pi r \, dr + \left[\gamma_{lg} \left(\frac{\partial_r(h + \xi)}{m(h + \xi)} \right) \delta h \right]_0^R + \lambda \delta h(R) \\ & - \int_0^R \left[\left(\frac{1}{r} + \partial_r \right) \left(\frac{\gamma_{lg} \partial_r(h + \xi)}{m(h + \xi)} + \frac{\gamma_{sl} \partial_r \xi}{m(\xi)} \right) \right] \delta \xi \, 2\pi r \, dr + \left[\left(\frac{\gamma_{lg} \partial_r(h + \xi)}{m(h + \xi)} + \frac{\gamma_{sl} \partial_r \xi}{m(\xi)} \right) \delta \xi \right]_0^R \\ & - \int_R^\infty \left[\left(\frac{1}{r} + \partial_r \right) \left(\frac{\gamma_{sg} \partial_r \xi}{m(\xi)} \right) \right] \delta \xi \, 2\pi r \, dr + \left[\left(\frac{\gamma_{sg} \partial_r \xi}{m(\xi)} \right) \delta \xi \right]_R^\infty \\ & + \int_0^\infty \left[\int_0^\infty \sum_{j=1}^3 G_{zj}^{-1}(\vec{r} - \vec{r}') u_j(\vec{r}') \, d^2 \vec{r}' \right] \delta \xi \, d^2 \vec{r}, \end{aligned}$$

¹¹This distinction is necessary as ξ defines both, the solid-liquid as well as the solid-gas interface, depending on the position. Terms including liquid quantities, i.e., h , however, always approach the contact line as $r \uparrow R$ since h is not defined for $r > R$.

where the curvatures of the liquid-gas interface and substrate surface are given by

$$\kappa_{\text{lg}} = \kappa(h + \xi) = \left(\frac{1}{r} + \partial_r \right) \left(\frac{\partial_r(h + \xi)}{\sqrt{1 + (\partial_r h + \partial_r \xi)^2}} \right) = -\nabla \cdot \vec{n}_{\text{lg}}, \quad (3.31)$$

$$\kappa_s = \kappa(\xi) = \left(\frac{1}{r} + \partial_r \right) \left(\frac{\partial_r \xi}{\sqrt{1 + (\partial_r \xi)^2}} \right) = -\nabla \cdot \vec{n}_s. \quad (3.32)$$

For a drop at equilibrium the variations w.r.t. δh and $\delta \xi$ have to vanish independently, respectively in the integrals and the surface terms. The variations w.r.t. $\delta h(r)$ and $\delta h(R)$ yield

$$P = -\gamma_{\text{lg}} \left(\frac{1}{r} + \partial_r \right) \left(\frac{\partial_r(h + \xi)}{\sqrt{1 + (\partial_r(h + \xi))^2}} \right) = \gamma_{\text{lg}} (\nabla \cdot \vec{n}_{\text{lg}}) \quad \text{for } r \in [0, R], \quad (3.33a)$$

$$\lambda = -\gamma_{\text{lg}} \frac{\partial_r(h + \xi)}{\sqrt{1 + (\partial_r(h + \xi))^2}} = \gamma_{\text{lg}} \sin \theta_{\text{lg}} \quad \text{for } r = R, \quad (3.33b)$$

where $\partial_r(h + \xi)|_{r=0} = 0$ and the definitions (3.28) are used. It appears, that the liquid-gas interface is always given by a spherical cap of constant curvature $\kappa_{\text{lg}} = -P/\gamma_{\text{lg}}$, entirely independent of elasticity. Hence, the parameter P controls the Laplace pressure inside the liquid and therefore the curvature of the liquid-gas interface, while λ gives the vertical projection of the interface energy γ_{lg} . The variations w.r.t. $\delta \xi(r)$ and $\delta \xi(R)$ give

$$-\gamma_{\text{lg}} \kappa(h + \xi) + \int_0^\infty G_{zj}^{-1}(\vec{r} - \vec{r}') u_j(\vec{r}') d^2 \vec{r}' = \gamma_{\text{sl}} \kappa(\xi) \quad \text{for } r \in [0, R], \quad (3.34a)$$

$$\int_0^\infty G_{zj}^{-1}(\vec{r} - \vec{r}') u_j(\vec{r}') d^2 \vec{r}' = \gamma_{\text{sg}} \kappa(\xi) \quad \text{for } r \geq R, \quad (3.34b)$$

$$\frac{\gamma_{\text{lg}} \partial_r(h + \xi)}{m(h + \xi)} + \frac{\gamma_{\text{sl}} \partial_r \xi}{m(\xi)} \Big|_{r \uparrow R} - \frac{\gamma_{\text{sg}} \partial_r \xi}{m(\xi)} \Big|_{r \downarrow R} = 0 \quad \text{for } r = R, \quad (3.34c)$$

with $\partial_r(h + \xi)|_{r=0} = \partial_r \xi|_{r=0} = \partial_r \xi|_{r=\infty} = 0$. Further the Hamiltonian may be calculated according to Eq. (2.119)

$$\mathcal{H} = -\frac{\gamma_{\text{lg}}}{m(h + \xi)} - \frac{\gamma_{\text{sl}}}{m(\xi)} + Ph - \frac{1}{2} \left[\int_0^\infty \underline{G}^{-1}(\vec{r} - \vec{r}') \cdot \vec{u}(\vec{r}') d^2 \vec{r}' \right] \cdot \vec{u}(\vec{r}) \quad \text{for } r \in [0, R],$$

$$\mathcal{H} = -\frac{\gamma_{\text{sg}}}{m(\xi)} - \frac{1}{2} \left[\int_0^\infty \underline{G}^{-1}(\vec{r} - \vec{r}') \cdot \vec{u}(\vec{r}') d^2 \vec{r}' \right] \cdot \vec{u}(\vec{r}) \quad \text{for } r \geq R.$$

Since the Hamiltonian of a steady state has to be constant across the domain, an evaluation at $r = R$ yields

$$\frac{\gamma_{lg}}{m(h + \xi)} + \frac{\gamma_{sl}}{m(\xi)} \Big|_{r \uparrow R} = \frac{\gamma_{sg}}{m(\xi)} \Big|_{r \downarrow R}. \quad (3.36)$$

With Eqs. (3.28) the Equations (3.34c) and (3.36) can be expressed in terms of the three contact angles, yielding the vertical and horizontal *Neumann's laws*

$$\text{vertical:} \quad \gamma_{sl} \sin \theta_{sl} + \gamma_{sg} \sin \theta_{sg} = \gamma_{lg} \sin \theta_{lg}, \quad (3.37a)$$

$$\text{horizontal:} \quad \gamma_{lg} \cos \theta_{lg} + \gamma_{sl} \cos \theta_{sl} = \gamma_{sg} \cos \theta_{sg}. \quad (3.37b)$$

They reflect the vertical and horizontal force balance at the contact line, interpreting the interface energies γ_{sl} , γ_{lg} and γ_{sg} as *interface tensions* acting tangential to their respective interface of definition.¹² Hence, the Lagrange parameter λ gives the vertical component of the liquid-gas interface tension $\gamma_{lg} \sin \theta_{lg}$ pulling on the substrate. This strongly localized force results in a pointy deformation, as discussed in Sec. 2.3.2, which is referred to as *wetting ridge* in this context [cf. Fig. 3.3]. Since the Laplace pressure of the liquid drop causes a normal stress in negative z -direction, the substrate is expected to be depressed below the drop. Apparently, the relationship between the angles at the contact line (3.28) is not at all affected by elasticity and indeed the suspicion of a violation of Neumann's law due to elastic effects [SD12, Mar+12a, Lim12, Mas+19] turned out to be wrong [Pan+20]. However, interface energies and interface tensions, even though used alike in the previous, are not generally the same for elastic materials and not necessarily constant either. While they equal in dimension their value may differ depending on the state of stretching which is known as *Shuttleworth effect* [And+16] and will be addressed in Sec. 7. Newtonian fluids are rather an exception to this phenomenon, which is why interface energy and interface tension are usually treated interchangeably in fluid dynamics. In that sense Neumann's laws are really formulated in terms of surface tensions rather than energies and will be affected by elastic effects therefore. Even in the absence of the Shuttleworth effect, elasticity does still have an impact on the general shape of the contact region it self, if not on the angles forming there, as will be discussed in Sec. 4. Since we are using a Monge representation $h = h(x, y)$ and $\xi = \xi(x, y)$, the above description is restricted to drops of contact

¹²Note, that Neumann's laws give two equations for three unknown angles. In consequence, only the relation of the angles to each other is defined, not, however, their absolute value, i.e., the orientation of the interfaces. Hence, the picture can be rotated freely about the three phase contact line without violating Eqs. (3.37).

angles $0 < \theta_{ij} < \frac{\pi}{2}$. Even with this restriction the contact angles may still become larger than would be permitted for the long-wave approximation to be valid, i.e., $\mathcal{O}(\nabla(h + \xi)) = \mathcal{O}(\nabla\xi) \gg \mathcal{O}(\epsilon)$ where ϵ is the smallness parameter [cf. Ch. 2.2.3]. The largest contact angles are assumed in the limiting cases of very rigid or very soft substrates, which will be briefly discussed now.

3.2.2. THE RIGID LIMIT

In case of a very rigid material, all external forces are resisted and the substrate wont deform at all, i.e., $\vec{u} = 0$ and thus $d\vec{u}/dt = 0$. The solid-liquid interface area takes a circular shape of base radius R then and the three phase contact line is defined by only a single contact angle $\theta = \theta_{lg}$ as shown in Fig. 3.4. The free energy for such a system is given by

$$\mathcal{F}[h] = \int_0^R \left[\gamma_{sl} + \gamma_{lg} \sqrt{1 + (\partial_r h)^2} - Ph \right] 2\pi r dr + \int_R^\infty \gamma_{sg} 2\pi r dr + \lambda h(R), \quad (3.38)$$

and its variation are

$$\delta\mathcal{F} = \int_0^R \left[-\gamma_{lg} \left(\frac{1}{r} + \partial_r \right) \left(\frac{\partial_r h}{\sqrt{1 + (\partial_r h)^2}} \right) - P \right] \delta h 2\pi r dr + \left[\gamma_{lg} \frac{\partial_r h}{\sqrt{1 + (\partial_r h)^2}} \delta h \right]_0^R + \lambda \delta h(R).$$

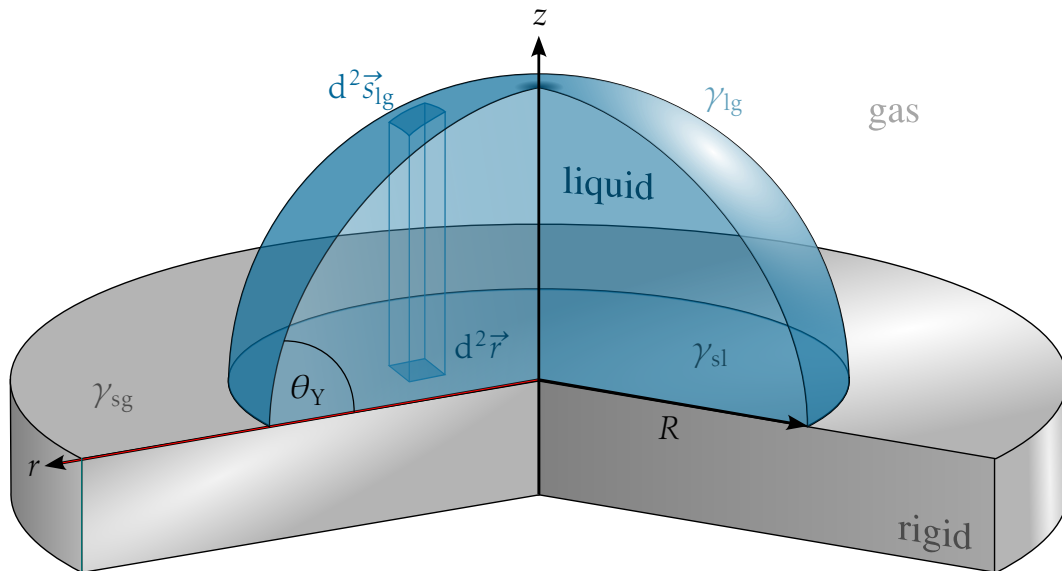


FIGURE 3.4.: Sketch of a radially symmetric partially wetting liquid drop on a rigid substrate. The liquid-gas interface takes the shape of a spherical cap and hits the substrate level along the circular three phase contact line at base radius $r = R$. This contact line is characterized by Young's contact angle θ_Y which is governed by the interface energies γ_{sg} , γ_{sl} and γ_{lg} .

The variation w.r.t. h gives the definitions of the Lagrange multipliers as already found in Eq. (3.33). Meanwhile the Hamiltonian becomes

$$\begin{aligned}\mathcal{H} &= -\gamma_{sl} - \frac{\gamma_{lg}}{\sqrt{1 + (\partial_r h)^2}} + Ph & \text{for } r \in [0, R], \\ \mathcal{H} &= -\gamma_{sg} & \text{for } r \geq R.\end{aligned}$$

Continuity of the Hamiltonian at $r = R$ then yields the well-known *Young's law* [You05]

$$\gamma_{sl} + \gamma_{lg} \cos \theta_Y = \gamma_{sg}, \quad (3.39)$$

which gives the horizontal force balance at the contact line. Young's law directly follows from the horizontal Neumann's law (3.37b) with $\theta_{sl} = \theta_{sg} = 0$. The vertical Neumann's law (3.37a), however, gives $\gamma_{lg} \sin \theta_{lg} = 0$ in that limit, which is why the Lagrange multiplier λ is required to enforce a balance. As compared to the spreading parameter S [Eq. (3.27)] Young's law provides a more quantitative classification of the wetting behavior in terms of the macroscopic equilibrium contact angle, which in the following is referred to as *Young's angle* θ_Y therefore. Young's law may be linked to the spreading coefficient, however, by means of the *Young-Dupré-Equation* [dBQ04]

$$\gamma_{lg} [\cos \theta_Y - 1] = S. \quad (3.40)$$

In terms of the Young's angle complete wetting would be characterized by $\theta_Y \rightarrow 0$ while the non-wetting case is approached as $\theta_Y \rightarrow \pi$. Everything in between corresponds to the partial wetting regime, within which a further distinction is made between *low wettability* $\theta_Y < \frac{\pi}{2}$ and a *high wettability* $\theta_Y > \frac{\pi}{2}$ [cf. Fig. 3.2]. Demanding $0 < \theta_Y < \frac{\pi}{2}$, i.e., uniqueness of h , leads to conditions for the interface energies

$$1 > \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}} > 0 \quad \Rightarrow \quad \gamma_{lg} > \gamma_{sg} - \gamma_{sl}, \quad \gamma_{sg} > \gamma_{sl} \quad (3.41)$$

3.2.3. THE QUASI-LIQUID LIMIT

In the very soft limit the influence of elastic forces becomes virtually negligible such that the resistance against deformation of the substrate is exclusively governed only by the interface tensions. Regarding its statics, the substrate effectively behaves like a liquid then, which is why this scenario is referred to as *quasi-liquid limit*.

From Eq. (3.34a) it is seen, that the Laplace pressures caused by the liquid-gas and substrate-liquid interfaces balance, resulting in a fixed ratio of the respective curvatures, which in turn is determined by the inverse ratio of the corresponding interface energies

$$\frac{\kappa(h + \xi)}{\kappa(\xi)} = \frac{\nabla \cdot \vec{n}_{lg}}{\nabla \cdot \vec{n}_{sl}} = -\frac{\gamma_{sl}}{\gamma_{lg}} = -\sigma. \quad (3.42)$$

Eq. (3.34b) further demands vanishing curvature and slope of the substrate outside the drop. Hence, in the quasi-liquid limit the drop is shaped like a *liquid lens* characterized by constant curvatures of both interfaces and $\theta_{sg} = 0$, as shown in Fig. 3.5. Neumann's laws (3.37) then reduce to

$$\text{vertical:} \quad \gamma_{sl} \sin \theta_{sl} = \gamma_{lg} \sin \theta_{lg}, \quad (3.43a)$$

$$\text{horizontal:} \quad \gamma_{lg} \cos \theta_{lg} + \gamma_{sl} \cos \theta_{sl} = \gamma_{sg}. \quad (3.43b)$$

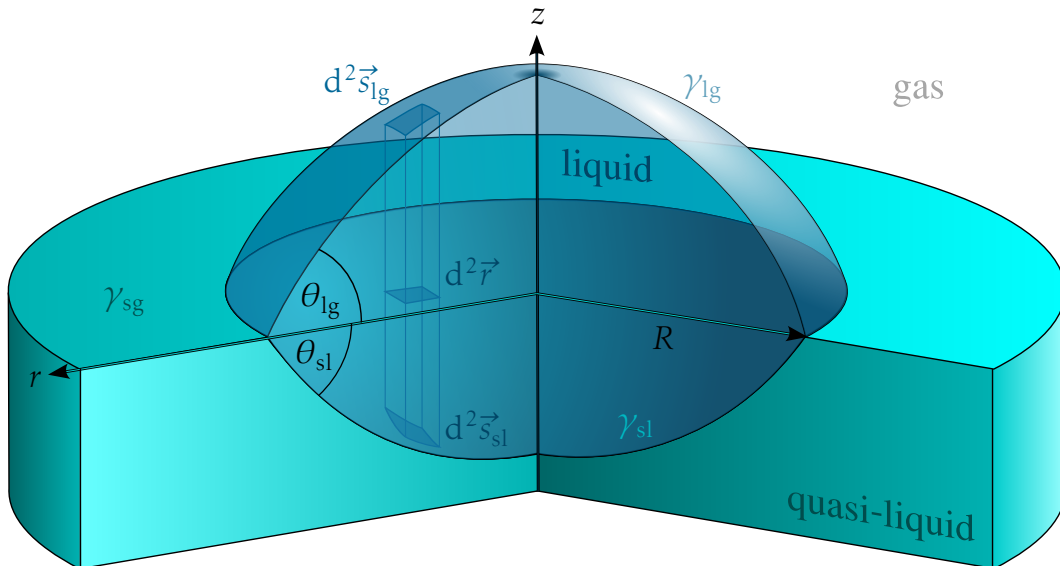


FIGURE 3.5.: Sketch of a radial symmetric partially wetting liquid drop on a quasi-liquid substrate, forming a liquid lens. The spherical cap shaped liquid-gas and substrate-liquid interfaces meet along the circular three phase contact line at base radius $r = R$. Outside the drop the substrate is level and the contact line is characterized by only two contact angles θ_{lg} and θ_{sl} .

Eq. (3.43a) shows, that the two remaining contact angles are related via the ratio of interface energies

$$\frac{\sin \theta_{lg}}{\sin \theta_{sl}} = \frac{\gamma_{sl}}{\gamma_{lg}} = \sigma, \quad (3.44)$$

in accordance with Eq. (3.42). They can further be written explicitly as functions of the interface energies

$$\cos \theta_{sl} = \frac{\gamma_{sg}^2 + \gamma_{sl}^2 - \gamma_{lg}^2}{2\gamma_{sg}\gamma_{sl}} = \frac{(\cos \theta_Y + \sigma)^2 + \sigma^2 - 1}{2\sigma(\cos \theta_Y + \sigma)}, \quad (3.45a)$$

$$\cos \theta_{lg} = \frac{\gamma_{sg}^2 + \gamma_{lg}^2 - \gamma_{sl}^2}{2\gamma_{sg}\gamma_{lg}} = \frac{(\cos \theta_Y + \sigma)^2 + 1 - \sigma^2}{2(\cos \theta_Y + \sigma)}, \quad (3.45b)$$

where Young's law (3.39) has been used to replace γ_{sg} by θ_Y . In case of the first uniqueness condition (3.41) holding it can be seen that θ_{lg} is always smaller than θ_Y

$$\begin{aligned} & \gamma_{lg} > \gamma_{sg} - \gamma_{sl} \quad |()|^2, +\gamma_{sg}^2 - \gamma_{sl}^2, : (2\gamma_{sg}\gamma_{lg}) \\ \Rightarrow \quad \cos \theta_{lg} = \frac{\gamma_{sg}^2 + \gamma_{lg}^2 - \gamma_{sl}^2}{2\gamma_{sg}\gamma_{lg}} & > \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}} = \cos \theta_Y. \end{aligned} \quad (3.46)$$

Since Neumann's laws are unaffected by elastic forces, $\theta_Y > \theta_{lv}$ indicates that an inward rotation of the contact region as a whole takes place when increasing the softness, i.e., the drop sinks into the substrate. Now also $0 < \theta_{sl} < \frac{\pi}{2}$ and $0 < \theta_{lg} < \frac{\pi}{2}$ is demanded to ensure uniqueness of h and ξ , leading to the conditions

$$1 > \cos \theta_{sl} > 0 \quad \Rightarrow \quad \gamma_{sg}^2 + \gamma_{sl}^2 > \gamma_{lg}^2 > (\gamma_{sg} - \gamma_{sl})^2, \quad (3.47a)$$

$$1 > \cos \theta_{lg} > 0 \quad \Rightarrow \quad \gamma_{sg}^2 + \gamma_{lg}^2 > \gamma_{sl}^2 > (\gamma_{sg} - \gamma_{lg})^2. \quad (3.47b)$$

For $\gamma_{sl} > \gamma_{lg}$ it is $\theta_{lg} > \theta_{sl}$ [Eq. (3.44)] and Eq. (3.47a) is automatically satisfied if Eq. (3.47b) is, while for $\gamma_{sl} < \gamma_{lg}$ it is the other way around. With that in mind Eqs. (3.45) allow to formulate an upper bound for θ_Y

$$\theta_Y < \arccos(\sqrt{|1 - \sigma^2|} - \sigma), \quad (3.48)$$

or from Eq. (3.45a) a lower bound for σ

$$\sigma > \frac{1}{2} \left[\sqrt{1 + \sin^2 \theta_Y} - \cos \theta_Y \right]. \quad (3.49)$$

In the limiting case of $\theta_Y \rightarrow \frac{\pi}{2}$ for example $\sigma > \frac{1}{\sqrt{2}}$ is required to ensure $\theta_{sl} < \frac{\pi}{2}$.

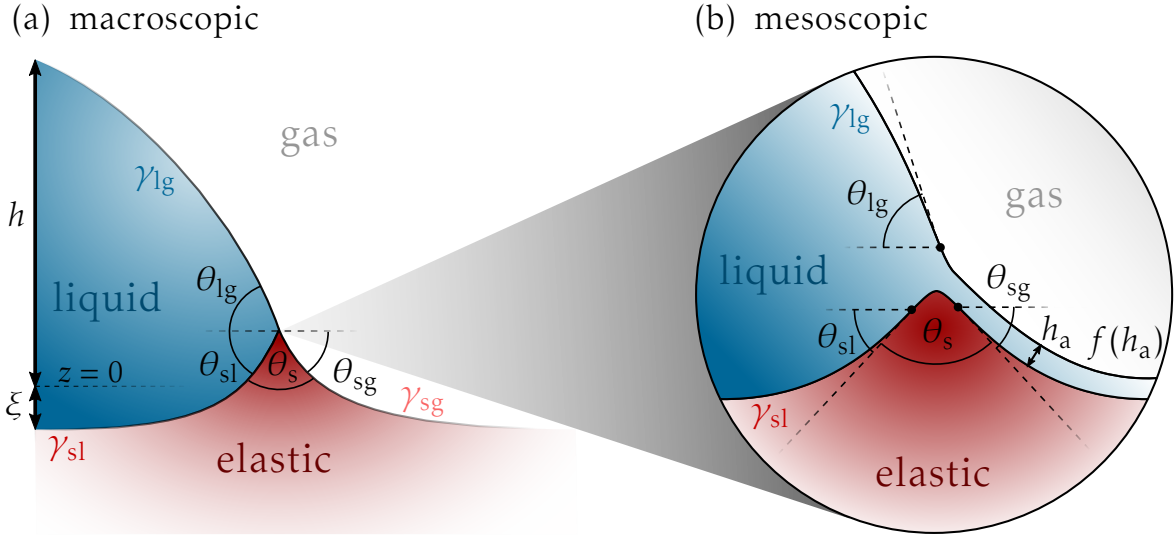


FIGURE 3.6.: Neumann region of a drop on a soft substrate. (a) in the macroscopic limit the force balance at the contact line is given by the interface tensions γ_{sl} , γ_{lg} and γ_{sg} pulling in the directions given by the contact angles θ_{sl} , θ_{lg} and θ_{sg} , respectively, resulting in the formation of a wetting ridge. (b) in the mesoscopic limit the substrate outside the drop is covered by an adsorption layer of height h_a and the corresponding interface energy is corrected by means of a wetting potential $\gamma_{sg} = \gamma_{sl} + \gamma_{lg} + f(h_a)$. consequently the wetting ridge is not singular at the tip any more but exhibits a smooth cap of size h_a . The contact angles are usually defined w.r.t the deflection points.

3.3. THE MESOSCOPIC PICTURE

The discussion on the three phase contact line in the previous chapter may have raised a crucial question: how can we model moving drops when the mobility $Q(h)$ as written in the thin-film equation (2.49), vanishes for $h = 0$, effectively preventing the contact line from changing its position even for finite slip length $\ell_s > 0$? This very prominent *moving contact line problem* has been extensively discussed in the past and since then various techniques have been developed to approach it [dG85, HS71]. In case of finite slip length an additional evolution equation can be derived for the contact line position, e.g., as in Ref. [SKP10]. However, even though slip on the solid-liquid interface has been observed both experimentally [Net+05, Tab10] as well as in molecular dynamics (MD) simulations [KBW89] there is yet no concrete theory on how to quantify it [SK11]. In most cases, as also in the following, the

friction at the interface is considered so high as that fluid elements are not able to slip along it at all. In other words $\ell_s = 0$ and $Q(h) = \frac{h^3}{3\eta}$, which is known as *no slip condition* [LL87]. It should be kept in mind, however, that changes to the mobility due to the choice of the slip model may crucially affect the systems behavior and enable or disable the occurrence of certain phenomena in the first place [Bäu+14, Pes+19]. An other possible solution to the moving contact line problem, the one that shall be employed in the following, is to not let the liquid-gas interface touch the substrate at all but to let it transit into an ultra thin film instead. That so called *adsorption layer* or *precursor* of thickness h_a is assumed to cover all macroscopically *dry* areas of the substrate, effectively replacing the solid-gas interface.¹³ In order to recover the correct solid-gas interface energy in the affected areas the *wetting potential* $f(h)$ is introduced, which has to satisfy the *consistency condition* [dG85]

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} + f(h_a). \quad (3.50)$$

Further, the wetting potential has to vanish as the liquid layer thickness increases $h \gg h_a$ such that the correct interface energy of a liquid covered substrate $\gamma_{lg} + \gamma_{sl}$ is recovered, i.e., $\lim_{h \rightarrow \infty} f(h) = 0$. To further ensure stability of the adsorption layer, f has to exhibit a minimum at $h = h_a$ and must diverge for values below in order to prevent the liquid-gas interface from approaching the solid-liquid interface even further, i.e., $\lim_{h \rightarrow 0} f(h) = \infty$ [dG85, Thi+18]. Physically, the wetting potential is assumed to result from long-range *Van der Waals* interactions and short-range repulsive interactions [Piso1, PPo4] and is commonly modeled like [Bon+09, Thi10]

$$f(h) = \frac{B}{5h^5} - \frac{A}{2h^2} = \frac{A}{2h^2} \left[\frac{2}{5} \left(\frac{h_a}{h} \right)^3 - 1 \right]. \quad (3.51)$$

The two contributions are respectively scaled by the *Hamaker constants* A and B , the ratio of which determines the position of the minimum, i.e., the adsorption layer height $h_a = \sqrt[3]{B/A}$ [Pot+05]. Resulting from molecular interactions the adsorption layer is of microscopic scale in nature barely perceptible from a macroscopic point of view. This somewhat intermediate perspective, in which microscopic interactions are taken into account while yet maintaining the continuous description, is referred

¹³Technically, the adsorption layer thickness h_a is defined perpendicular to the profiles and is thus not actually a vertical length [cf. Fig. 3.6(b)]. Instead, the vertical thickness of the adsorption layer is $\tilde{h}_a = h_a m(h + \xi)$ in general. This would result in a liquid layer thickness $h > h_a$ wherever large gradients are present, e.g., at the flank of a wetting ridge, and in a slightly increased mobility of the contact line in turn. At least in the long-wave limit the impact of this effect is negligible, however, which is why we dispense with this authoritative complication.

to as *mesoscopic*. On one hand, the adsorption layer model serves primarily as a remedy for the "moving contact line"-problem. On the other hand, experiments and molecular-dynamics simulations indeed verify the existence of such an adsorption layer [HFC89, Pop+12, II16]. Eq. (3.51) is of *Lennard-Jones*-like shape and meets all the requirements from above. Note, however, that there are also several other forms used in the diverse literature some of which exhibit multiple local minima resulting in additional (meta)stable film solutions of different height [Thio7, PEo8]. Also, the coupling of an effective interface potential with elastic deformations was previously considered in Refs. [Whio3, Das+11, NSD20]. Fixing the adsorption layer thickness h_a , the remaining Hamaker constant is determined by the consistency condition (3.50), e.g.,

$$A = -\frac{10}{3}h_a^2[\gamma_{sg} - (\gamma_{sl} + \gamma_{lg})] = \frac{10}{3}h_a^2\gamma_{lg}[1 - \cos\theta_Y] = -\frac{10}{3}h_a^2S, \quad (3.52)$$

where Eqs. (3.39) and (3.27) have been used. The partial derivative of the wetting potential yields the so called *Derjaguin pressure* or *disjoining pressure* [Der92, dG85, SVo9]

$$\Pi(h) = -\partial_h f(h) = \frac{A}{h^3} \left[\left(\frac{h_a}{h} \right)^3 - 1 \right], \quad (3.53)$$

which has a minimum $\Pi_{\min} = -\frac{A}{4h_a^3}$ at $h = \sqrt[3]{2}h_a$. Both, wetting potential and disjoining pressure are qualitatively displayed in Fig. 3.7. Just as smoothly as these two functions converge to zero with increasing liquid layer thickness h , the transition between drop and adsorption layer takes place as well. Consequently, the singular support of the contact line is lifted and rather replaced by a *contact region* as visualized in Fig. 3.6. The spatial extension of that transition is still of order $\mathcal{O}(h_a)$ and therefore noticeably only in the mesoscopic limit. This modification makes the determination of the macroscopic contact line position and the contact angles more intricate as discussed in the methods section B.1. From here on the contact angles are by default defined via the slopes of the profiles $h+\xi$ and ξ at the inflection points closest to the contact region, similar to Eqs. (3.28).

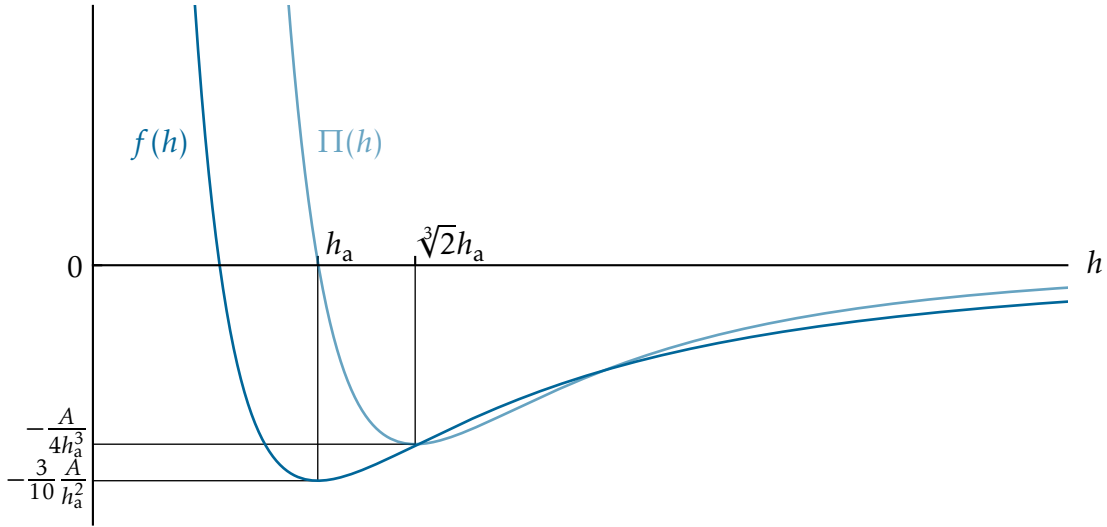


FIGURE 3.7.: Qualitative display of the wetting potential $f(h)$ and the disjoining pressure $\Pi(h) = -\partial_h f(h)$ as functions of the liquid layer height h . Both take a shape similar to a Lennard-Jones potential, i.e., diverge for $h \rightarrow 0$, vanish for $h \rightarrow \infty$ and exhibit a minimum in between. The disjoining pressure vanishes at $h = h_a$ where the wetting potential reaches a minimum. Consequently, the corresponding adsorption layer of height h_a is stable and replaces the solid-gas interface in the macroscopic view.

Using the consistency condition (3.50) Young's and Neumann's laws (NM) can be translated to the mesoscopic picture

$$\text{Young:} \quad \gamma_{lg} [\cos \theta_Y - 1] = f(h_a), \quad (3.54a)$$

$$\text{NM vertical:} \quad \gamma_{sl} \sin \theta_{sl} + [\gamma_{lg} + \gamma_{sl} + f(h_a)] \sin \theta_{sg} = \gamma_{lg} \sin \theta_{lg}, \quad (3.54b)$$

$$\text{NM horizontal:} \quad \gamma_{lg} \cos \theta_{lg} + \gamma_{sl} \cos \theta_{sl} = [\gamma_{lg} + \gamma_{sl} + f(h_a)] \cos \theta_{sg}. \quad (3.54c)$$

The free energy of the system is in the mesoscopic picture given a single integral over the whole domain

$$\begin{aligned} \mathcal{F}[h, \vec{u}] = & \int_{\Omega} \gamma_{lg} m(h + \xi) + [\gamma_{sl} + f(h)] m(\xi) + Ph \\ & + \frac{1}{2} \left[\int_{\Omega} \underline{G}^{-1}(\vec{r} - \vec{r}') \cdot \vec{u}(\vec{r}') d^2 \vec{r}' \right] \cdot \vec{u}(\vec{r}) d^2 \vec{r}. \end{aligned} \quad (3.55)$$

It is crucial to recognize, that the total liquid volume now depends on the domain size, since even macroscopically dry regions contribute with the adsorption layer now. In that sense, the Lagrange multiplier P does not actually conserve the total volume but the volume per area, i.e., a mean height h_0 . The variations of Eq. (3.55)

are now continuous functions of the fields h and $\vec{u}$

$$\frac{\delta \mathcal{F}}{\delta h} = -\gamma_{\text{lg}} \nabla \left(\frac{\nabla(h + \xi)}{\sqrt{1 + (\nabla h + \nabla \xi)^2}} \right) - \Pi(h) \sqrt{1 + (\nabla \xi)^2} + P, \quad (3.56a)$$

$$\begin{aligned} \frac{\delta \mathcal{F}}{\delta \xi} = & -\gamma_{\text{lg}} \nabla \left(\frac{\nabla(h + \xi)}{\sqrt{1 + (\nabla h + \nabla \xi)^2}} \right) - \nabla \left(\frac{[\gamma_{\text{sl}} + f(h)] \nabla \xi}{\sqrt{1 + (\nabla \xi)^2}} \right) \\ & + \int_{\Omega} G_{zj}^{-1}(\vec{r} - \vec{r}') \cdot u_j(\vec{r}') \, d^2 \vec{r}', \end{aligned} \quad (3.56b)$$

$$\frac{\delta \mathcal{F}}{\delta u_i} = \int_{\Omega} G_{ij}^{-1}(\vec{r} - \vec{r}') \cdot u_j(\vec{r}') \, d^2 \vec{r}, \quad \text{for } i = x, y. \quad (3.56c)$$

The advantage of the mesoscopic description is the solved issue of a pinned discontinuous three phase contact line. Now, that the whole domain is covered with a liquid layer of at least adsorption layer height h_a and dry and wetted regions are automatically distinguished by means of the wetting potential f we are able to write evolution equations for h and $\vec{u}$ using the gradient dynamics approach.

3.4. THE EVOLUTION EQUATIONS

Let us write down the entire model again to get a better overview. The complete mesoscopic gradient dynamics evolution equations for h and $\vec{u}$ are given by [Eqs. (3.1) and (3.5)]

$$\partial_t h = \nabla \cdot \left[Q(h) \nabla \frac{\delta \mathcal{F}}{\delta h} \right], \quad (3.57)$$

$$\partial_t \vec{u} = -\underline{M} \frac{\delta \mathcal{F}}{\delta \vec{u}}, \quad (3.58)$$

with the mobilities [cf. Eqs. (2.49) and (3.6)]

$$Q(h) = \frac{h^3}{3\eta}, \quad \underline{M} = \begin{pmatrix} \frac{d}{\eta^{-\mu}} & 0 \\ 0 & \frac{d}{\eta_\mu} \frac{(1-2\nu)}{2(1-\nu)} \end{pmatrix} \quad (3.59)$$

and the variations [Eqs. (3.56)]

$$\frac{\delta \mathcal{F}}{\delta h} = -\gamma_{\text{lg}} \nabla \left(\frac{\nabla(h + \xi)}{\sqrt{1 + (\nabla h + \nabla \xi)^2}} \right) - \Pi(h) \sqrt{1 + (\nabla \xi)^2} + P, \quad (3.60a)$$

$$\begin{aligned} \frac{\delta \mathcal{F}}{\delta \xi} = & -\gamma_{\text{lg}} \nabla \left(\frac{\nabla(h + \xi)}{\sqrt{1 + (\nabla h + \nabla \xi)^2}} \right) - \nabla \left(\frac{[\gamma_{\text{sl}} + f(h)] \nabla \xi}{\sqrt{1 + (\nabla \xi)^2}} \right) \\ & + \int_{\Omega} G_{zj}^{-1} (\vec{r} - \vec{r}') \cdot u_j(\vec{r}') d^2 \vec{r}', \end{aligned} \quad (3.60b)$$

$$\frac{\delta \mathcal{F}}{\delta u_i} = \int_{\Omega} G_{ij}^{-1} (\vec{r} - \vec{r}') \cdot u_j(\vec{r}') d^2 \vec{r}, \quad \text{for } i = x, y. \quad (3.60c)$$

In the current formulation, however, both dynamics combine long-wave evolution equations with the exact metrics of the interfaces, i.e., a full curvature formulation, which is not strictly consistent. It was found though, that such *hybrid* models still show correct behavior even in case of larger contact angles [HTA15]. See Sec. 3 of Ref. [Thi18] for a detailed discussion of the merits of this approach. Expanding the convolution within the elastic energy [Eq. (3.17)] and its variation [Eq. (3.19)] to zeroth order yields the Winkler-foundation model again [cf. Sec. 2.3.3]

$$\int_{\Omega} \underline{G}^{-1}(x - x') \vec{u} dx' \approx \begin{pmatrix} \frac{E_{\mu}}{d} u_x \\ \frac{E_{\mu}}{d} \frac{2(1-\nu)}{1-2\nu} \xi \end{pmatrix}. \quad (3.61)$$

Even though this approximation is strictly valid only in the long-wave limit, it will be used likewise in the full curvature formulation from here on. It should be noted, that this simplification comes at the expense of losing detail in the description of the elastic deformation of course. However, it remains to be shown, that this reduced model still captures the essential features of soft wetting. Finally, the variations are

$$\frac{\delta \mathcal{F}}{\delta h} = -\gamma_{\text{lg}} \nabla \left(\frac{\nabla(h + \xi)}{\sqrt{1 + (\nabla h + \nabla \xi)^2}} \right) - \Pi(h) \sqrt{1 + (\nabla \xi)^2} + P \quad (3.62a)$$

$$\frac{\delta \mathcal{F}}{\delta \xi} = -\gamma_{\text{lg}} \nabla \left(\frac{\nabla(h + \xi)}{\sqrt{1 + (\nabla h + \nabla \xi)^2}} \right) - \nabla \left(\frac{[\gamma_{\text{sl}} + f(h)] \nabla \xi}{\sqrt{1 + (\nabla \xi)^2}} \right) + \frac{E_{\mu}}{d} \frac{2(1-\nu)}{(1-2\nu)} \xi, \quad (3.62b)$$

$$\frac{\delta \mathcal{F}}{\delta u_x} = \frac{E_{\mu}}{d} u_x. \quad (3.62c)$$

A very similar model has already been used in Ref. [LL20]. Note, that the dynamics of u_x is completely decoupled from the others fields now, such that the profiles h

and ξ can be calculated without considering the horizontal displacement at all. For the sake of completeness, it is still considered in remainder of this section.

According to Eq. (2.118) the free energy can be shown to steadily decrease in time

$$\begin{aligned} \frac{d\mathcal{F}}{dt} &= \int_{\Omega} \frac{\delta\mathcal{F}}{\delta h} \frac{\partial h}{\partial t} + \frac{\delta\mathcal{F}}{\delta \vec{u}} \frac{\partial \vec{u}}{\partial t} dx \\ &= - \int_{\Omega} \left[Q(h) \left| \partial_x \frac{\delta\mathcal{F}}{\delta h} \right|^2 + \frac{\delta\mathcal{F}}{\delta \vec{u}} \underline{M} \frac{\delta\mathcal{F}}{\delta \vec{u}} \right] dx. \end{aligned} \quad (3.63)$$

which corresponds to the negative of the total dissipation $\mathcal{D} = -\frac{d\mathcal{F}}{dt}$. A useful feature of Eq. (3.63) is that it allows to individually measure the contributions coming from the liquid and elastic layer, respectively and to resolve them spatially using the dissipation density $\Gamma(x, t)$, i.e., $\mathcal{D} = \mathcal{D}_h + \mathcal{D}_u = \int_{\Omega} \Gamma_h dx + \int_{\Omega} \Gamma_u dx = \int_{\Omega} \Gamma dx$.

3.4.1. DIMENSIONLESS FORMULATION

Technically the above dynamics are consistent only in the long-wave limit. To consider the latter we proceed as discussed in Sec. 2.2.3 by introducing dimensionless variables

$$x = L\tilde{x}, \quad h = H\tilde{h}, \quad \xi = H\tilde{\xi}, \quad u_x = U\tilde{u}_x, \quad t = T\tilde{t}. \quad (3.64)$$

Since the characteristic scales can be arbitrarily chosen we use $H = h_a$ and $T = \frac{3\eta h_a}{\gamma_{lg}\epsilon^4}$ with $\epsilon = H/L$ and $\epsilon_u = U/L$. After introducing these variables, the dynamics (3.1) and (3.5) becomes¹⁴

$$\partial_t h = \nabla \left(h^3 \nabla \frac{\delta\mathcal{F}}{\delta h} \right), \quad (3.65a)$$

$$\partial_t \xi = -\frac{1}{\tau} \frac{\delta\mathcal{F}}{\delta \xi}, \quad (3.65b)$$

$$\partial_t u_x = -\frac{1}{\tau_u} \frac{\delta\mathcal{F}}{\delta u_x}, \quad (3.65c)$$

¹⁴In App. A.8 a discussion is found on how the equations can be transformed to account for the absolute height of the liquid-gas interface $\zeta = h + \xi$ instead of the local liquid layer thickness h .

with the variations

$$\frac{\delta \mathcal{F}}{\delta h} = -\nabla \left(\frac{\nabla(h + \xi)}{\sqrt{1 + \epsilon^2(\nabla h + \nabla \xi)^2}} \right) - C_\theta \Pi(h) \sqrt{1 + \epsilon^2(\nabla \xi)^2} + p, \quad (3.66a)$$

$$\frac{\delta \mathcal{F}}{\delta \xi} = -\nabla \left(\frac{\nabla(h + \xi)}{\sqrt{1 + \epsilon^2(\nabla h + \nabla \xi)^2}} \right) - \nabla \left(\frac{[\sigma + \epsilon^2 C_\theta f(h)] \nabla \xi}{\sqrt{1 + \epsilon^2(\nabla \xi)^2}} \right) + \frac{\xi}{s}, \quad (3.66b)$$

$$\frac{\delta \mathcal{F}}{\delta u_x} = \frac{u_x}{s_u}. \quad (3.66c)$$

Note, that the tildes have been dropped in Eqs. (3.65) and (3.66) and that in the following all quantities are dimensionless. The dimensionless wetting potential and disjoining pressure become

$$f(h) = \frac{1}{5h^5} - \frac{1}{2h^2}, \quad \Pi(h) = \frac{1}{h^6} - \frac{1}{h^3} \quad (3.67)$$

and the dimensionless parameters are

$$\begin{aligned} C_\theta &= \frac{AL^2}{\gamma_{lg} h_a^4} = \frac{10}{3\epsilon^2} (1 - \cos \theta_Y), \quad \sigma = \frac{\gamma_{sl}}{\gamma_{lg}}, \quad p = \frac{Ph_a}{\gamma_{lg} \epsilon^2}, \\ s &= \frac{\gamma_{lg}}{E_\mu} \frac{d}{h_a^2} \frac{(1 - 2\nu)}{2(1 - \nu)} \epsilon^2, \quad s_u = \frac{\gamma_{lg}}{E_\mu} \frac{d}{h_a^2} \frac{\epsilon^3}{\epsilon_u}, \\ \tau &= \frac{\eta_\mu}{\eta} \frac{h_a}{d} \frac{2(1 - \nu)}{3(1 - 2\nu)} \epsilon^2 = \frac{T_{KV}}{T} \frac{1}{s}, \quad \tau_u = \frac{\eta_\mu}{\eta} \frac{h_a}{3d} \epsilon \epsilon_u = \frac{T_{KV}}{T} \frac{1}{s_u}, \end{aligned} \quad (3.68)$$

where $T_{KV} = \eta_\mu / E_\mu$ is the characteristic time scale of the Kelvin-Voigt model. Now there are two characteristic scales left to be defined, namely L and U both of which are horizontal length scales. Even though their choices are arbitrary in principle they are meant to rescale all dimensionless variables to the same order of magnitude. In the full curvature formulation the dimensional variables are assumed to be of the same order of magnitude such that all characteristic length are chosen equally $L = U = H = h_a$, i.e., $\epsilon = \epsilon_u = 1$.

3.4.2. LONG-WAVE FORMULATION

In the long-wave limit the characteristic horizontal length scale of the system is considered much larger than the vertical one, such that $h_a/L = \epsilon \ll 1$ [ODB97, CM09, Thi10]. This assumption primarily concerns the gradients ∇h and $\nabla \xi$ which are considered small [cf. Sec. 2.2.3]. It is important to keep in mind, however, that the

same holds for the associated angles θ w.r.t. the horizontal, e.g.

$$\nabla(h + \xi) = \epsilon \tilde{\nabla}(\tilde{h} + \tilde{\xi}) = \tan(\theta_{\text{lg}}) = \tan(\epsilon \tilde{\theta}_{\text{lg}}) \approx \epsilon \tilde{\theta}_{\text{lg}} + \mathcal{O}(\epsilon^3). \quad (3.69)$$

Hence, gradients and their associated angles are equivalent in the long-wave limit $\tilde{\nabla}(\tilde{h} + \tilde{\xi}) = \tilde{\theta}_{\text{lg}}$. In consequence quantities such as $\arctan(\tilde{\nabla}\tilde{h} + \tilde{\nabla}\tilde{\xi})$ or $\tan \tilde{\theta}_{\text{lg}}$ have no meaning in the long-wave limit. Special care has to be taken with the solid angle θ_s , frequently used in the literature to describe the opening angle of the wetting ridge [cf. Fig. 3.6]. As it approaches $\theta_s \rightarrow \pi$ in the limit of a rigid substrate it is not a valid measure in the long-wave limit. Instead the angle $\theta_{\text{sl}} + \theta_{\text{sg}} = \pi - \theta_s$ is used, which is considered small in physical scales and therefore of $\mathcal{O}(1)$ in long-wave scaling. As was done for the characteristic time scale T before, it is convenient to choose L such that another dimensionless parameter is eliminated, i.e., normalized to one. Here we use

$$L^2 = \frac{\gamma_{\text{lg}} h_a^4}{A}, \quad (3.70)$$

such that $C_\theta = 1$. With the definition of the Hamaker constant A [Eq. (3.52)] and Eq. (3.69) in mind, we find

$$\frac{h_a^2}{L^2} = \epsilon^2 = \frac{10}{3} [1 - \cos(\theta_Y)] \approx \frac{5}{3} \epsilon^2 \tilde{\theta}_Y^2, \quad (3.71)$$

i.e., the choice of L fixes the rescaled long-wave Young's angle to $\tilde{\theta}_Y = \sqrt{3/5}$ always. Further, the consistency condition (3.50) is written in dimensionless form using (3.70)

$$\frac{\gamma_{\text{sg}}}{\gamma_{\text{lg}}} = 1 + \sigma + \epsilon^2 \tilde{f}(\tilde{h}_a), \quad (3.72)$$

i.e., $\gamma_{\text{sg}} \approx \gamma_{\text{lg}} + \gamma_{\text{sl}}$ in the long-wave limit. In the same manner Young's and Neumann's laws can be approximated as well. Dropping the tildes in the following, the mesoscopic dimensionless long-wave Young's and Neumann's laws become

$$\text{Young:} \quad \theta_Y = \sqrt{-2f(h_a)}, \quad (3.73a)$$

$$\text{NM vertical:} \quad \sigma \theta_{\text{sl}} + [1 + \sigma] \theta_{\text{sg}} = \theta_{\text{lg}}, \quad (3.73b)$$

$$\text{NM horizontal:} \quad \sigma \theta_{\text{sl}}^2 + \theta_{\text{lg}}^2 = [1 + \sigma] \theta_{\text{sg}}^2 - 2f(h_a), \quad (3.73c)$$

with $-2f(h_a) = 3/5$.¹⁵ In the quasi-liquid limit, i.e., $\theta_{sg} = 0$, Eqs. (3.73b) and (3.73c) reduce to

$$\text{vertical:} \quad \theta_{lg} = \sigma \theta_{sl}, \quad (3.74a)$$

$$\text{horizontal:} \quad \theta_{sl} = \sqrt{\frac{-2f(h_a)}{\sigma(1+\sigma)}} = \frac{\theta_Y}{\sqrt{\sigma(1+\sigma)}}. \quad (3.74b)$$

These relations give a well-defined macroscopic meaning to the dimensionless parameter σ and the wetting energy of the adsorption layer $f(h_a)$. Expanding the variations (3.66) up to leading order in ϵ yields

$$\frac{\delta \mathcal{F}}{\delta h} = -\Delta(h + \xi) - \Pi(h) + p \quad (3.75a)$$

$$\frac{\delta \mathcal{F}}{\delta \xi} = -\Delta(h + \xi) - \sigma \Delta \xi + \frac{\xi}{s}, \quad (3.75b)$$

$$\frac{\delta \mathcal{F}}{\delta u_x} = \frac{u_x}{s_u}, \quad (3.75c)$$

and the dimensionless parameters become

$$\begin{aligned} \sigma &= \frac{\gamma_{sl}}{\gamma_{lg}}, \quad p = \frac{3}{5} \frac{Ph_a}{\gamma_{lg}\theta_Y^2} \\ s &= \frac{5}{3} \frac{\gamma_{lg}}{\mu} \frac{d}{h_a^2} \frac{(1-2\nu)}{2(1-\nu)} \theta_Y^2, \quad s_u = \frac{5}{3} \frac{\gamma_{lg}}{\mu} \frac{d}{h_a^2} \frac{\epsilon}{\epsilon_u} \theta_Y^2, \\ \tau &= \frac{5}{9} \frac{\eta_s}{\eta} \frac{h_a}{d} \frac{2(1-\nu)}{(1-2\nu)} \theta_Y^2 = \frac{T_{KV}}{T} \frac{1}{s}, \quad \tau_u = \frac{5}{9} \frac{\eta_s}{\eta} \frac{h_a}{d} \frac{\epsilon_u}{\epsilon} \theta_Y^2 = \frac{T_{KV}}{T} \frac{1}{s_u}. \end{aligned} \quad (3.76)$$

In case of a large steady drop, i.e., $h \gg h_a$ such that $\Pi(h) \approx 0$, the shape of the liquid-gas interface profile is governed by

$$\frac{\delta \mathcal{F}}{\delta h} = -\Delta(h + \xi) + p = 0, \quad (3.77)$$

i.e., it assumes a parabolic shape. Finally, the characteristic scale U of the horizontal displacement u_x has to be determined. On the one hand, u_x is a horizontal length and could be rescaled accordingly using $U = L$. On the other hand, the horizontal displacement is assumed to be of the same order of magnitude as the vertical one, or, if it is caused exclusively by vertical forces, smaller even rather than larger [cf.

¹⁵Remember, that by dropping the tildes $\tilde{h}_a = h_a/H = 1 \rightarrow h_a$.

Fig. 2.3(b)]. Assuming $s = s_u$ and $\tau = \tau_u$ we find

$$\frac{U}{h_a} = \frac{2(1-\nu)}{(1-2\nu)}, \quad (3.78)$$

which has two limiting cases:

1. if the material is incompressible $\nu \rightarrow \frac{1}{2}$ the fraction on the r.h.s. diverges to infinity, i.e., $U/h_a \sim \epsilon^{-1}$, indicating $U = L$.
2. if it is perfectly compressible $\nu \rightarrow 0$ and we find $U = 2h_a$.

Since the horizontal displacement is not of interest for now, the decision is preliminarily postponed.

3.5. CONSERVATION AND THICKNESS OF THE ELASTIC LAYER

According to Eq. (3.62b) the effective softness of the substrate w.r.t. vertical displacements is

$$S = \frac{d(1-2\nu)}{2E_\mu(1-\nu)}. \quad (3.79)$$

Besides the storage shear modulus $E_\mu \neq 0$, also the Poisson ratio ν as well as the elastic layer thickness d crucially affect the shape of the wetting ridge as shown Fig. 2.4.¹⁶

A particularly remarkable feature is the depression that develops adjacent to the ridge and becomes more extinct with increasing ν , i.e., the it is a direct consequence of incompressibility. To put it bluntly, the mass required to form the ridge is taken from close surroundings where depressions form in consequence. As is seen from Eq. (3.79), however, the effective softness becomes zero in the incompressible limit $\nu = \frac{1}{2}$. In other words, the substrate effectively behaves as if it were rigid in that case. Thus, the elastic medium has to be considered compressible to some extent in order to allow for vertical deformations to occur under long-wave traction. This peculiarity is a direct consequence of the long-wave approximation that is applied to the Green's function of the linear elastic finite layer problem in Sec. 2.3.3. Considering Eq. (2.111) it can be seen, that the mobility matrix of the gradient dynamics

¹⁶Of course Fig. 2.4 shows only the deformation arising under action of a localized surface stress. This scenario is, however, closely related to the formation of a wetting ridge due to the vertically pulling liquid-gas interface tension at the three phase contact line.

form is actually determined by the matrix $\underline{K}(k) = E_\mu \underline{G}$. In zeroth order long-wave approximation this matrix becomes diagonal and constant, i.e., independent of k , resulting in the non-conserved dynamics (3.65b) for ξ . Performing the expansion up to second order, however, quadratic terms appear in the diagonal entries, which in real space translate to second order spatial derivatives in the mobility and in an additional conserved part of the dynamics therefore. Since there are no such conserved terms present at all in the zeroth order dynamics, one may demand not only $\nu < \frac{1}{2}$ but rather $\nu = 0$ such that no depressions occur at all. Even in such a case, however, perfect compressibility of the substrate does not necessarily mean that a conserved volume is not yet energetically favorable. When integrating Eq. (3.65b) over the domain, considering periodic or Neumann boundary conditions and the variations given by (3.66b), an ordinary differential equation is found for the global vertical displacement $\Xi = \int \xi dx = 0$

$$\frac{\partial \Xi}{\partial t} = -\frac{\Xi}{\tau s}.$$

From this equation it becomes clear, that in the absence of body forces all steady states, characterized by $\partial_t \xi = 0$, correspond to the stable fix point $\Xi = 0$, i.e., they exhibit no global vertical displacement and thus the same (conserved) volume. This phenomenon follows from the simple parabolic elastic energy of the Winkler foundation model and is also seen in the linear stability analysis discussed in App. B.5.1. There it is found that the real part of the eigenvalue, i.e., the growth rate, associated with a joint shift of h and ξ is strictly negative at $k = 0$ as long as $s > 0$ [cf. Fig. B.5]. Hence, even though the substrate is compressible during the dynamics, it is still energetically favorable to restore the original volume even so much that every homogeneous contribution to the deformation of the substrate would decay in time until a steady state is reached which exhibits $\Xi = 0$, i.e., the exact same volume as the undeformed state. Note, that the inclusion of a body force like gravity shifts this fixed global displacement away from zero.

The other problematic quantity is the elastic layer thickness d . From Fig. 2.4 (b) it is seen that the width of both, the ridge as well as the depressions, increases with increasing layer thickness. In experimental studies it was found that, in the incompressible limit, the thickness of the substrate has a crucial impact not only on the shape of the wetting ridge but also on the dynamics of wetting, e.g., the coarsening behavior [Kar+16]. Since in the following the substrate is considered compressible, however, no such effects are incorporated by the gradient dynamics model and the

layer thickness d has no effect other than to upscale the effective softness. Another issue arises from the linearity of the elasticity model, namely that the finite thickness of the elastic layer is not in fact maintained. In other words, the surface of the elastic layer could, in principle, be depressed below the interface with a hypothetical underlying rigid base at $z = -d$ [cf. Fig. 2.2] if the forces are strong enough, i.e., the local substrate thickness $\xi + d$ may become negative. In order to incorporate $z = -d$ as a lower bound for the vertical displacement, a pseudo-nonlinear elasticity model may be introduced by constructing the softness S as a function of ξ in such a way that it approaches $\lim_{\xi \rightarrow -d} S(\xi) = 0$ but becomes Eq. (3.79) for $\xi > -d$. Simple choices are

$$S(\xi) = S_0 \tanh\left(\frac{\xi + d}{b}\right), \quad (3.80)$$

or

$$S(\xi) = \frac{(\xi + d)S_0}{\xi + d + b}, \quad (3.81)$$

where S_0 is the constant effective softness (3.79) and b defines how smooth the transition from S_0 to 0 takes place as $\xi = -d$ is approached. This way its also easily possible to impose a topography on the rigid base by defining the layer thickness as a function of space $d(x)$. It should be kept in mind, however, that the elastic layer thickness enters in the constant value S_0 as well via Eq. (3.79). This approach is well suited, for example, for the investigation of *durotaxis*, which refers to the movement of drops induced by stiffness gradients in the elastic substrate.

3.6. ANALYTICS ON LONG-WAVE SUBSTRATE DEFORMATION

In the long-wave frame the dynamics of the substrate (3.65b) reduces to a linear partial differential equation of second order with the Laplace pressure of the liquid-vapor interface representing an inhomogeneity $\alpha(x, t)$. In dimensional form it writes

$$(M_{zz})^{-1} \partial_t \xi = \gamma \Delta \xi - \frac{\xi}{S} + \alpha(x, t), \quad (3.82)$$

with $(M_{zz})^{-1} = \frac{\eta_\mu}{d} \frac{2(1-\nu)}{(1-2\nu)}$ [Eq. (3.6)], the effective softness S [Eq. (3.79)] and γ being the interface energy of the substrate with the phase above. Due to linearity the dynamics can be solved analytically to obtain an expression for $\xi(x, t)$ if the inho-

mogeneity is known. In Fourier space the solution is given by

$$\xi(\omega, k) = \frac{S\alpha(\omega, k)}{1 + \gamma S k^2 + i\omega S M_{zz}^{-1}}, \quad (3.83)$$

and may be transformed back to real space again, which, depending on the exact form of α , may not allow for a closed expression for $\xi(x, t)$.

3.6.1. THE FUNDAMENTAL SOLUTION

As mentioned before the solution of an inhomogeneous linear differential equation can always be expressed in terms of a convolution with its fundamental solution. Let us consider the static case first, i.e. $\partial_t h = \partial_t \xi = 0$. From the discussion in Sec. 2.5 we know that a steady state of the gradient dynamics for h and ξ is characterized by vanishing variations $\delta\mathcal{F}/\delta h = 0$ and $\delta\mathcal{F}/\delta \xi = 0$, respectively. The fundamental solution is then found by solving the equation for the special case of $\alpha(x) = \delta(x)$. However, two subtleties emerge in that course which have to be considered. First, the inhomogeneity has to carry the dimension $[\alpha] = \text{J m}^{-3}$ which is handled more conveniently by introducing an amplitude $\alpha(x) = \alpha_0 \delta(x)$ with $\alpha_0 = 1 \text{ J m}^{-2}$ and $[\delta] = \text{m}^{-1}$. Note, that α_0 then takes the same dimension as γ . In other words, the inhomogeneity can be thought of as a vertically pulling interface tension and the fundamental solution as the shape of a wetting ridge that forms in consequence. Second, the order of magnitude of the inhomogeneity and the other terms should be the same. If α_0 is supposed to be of the same order as γ , the delta function has to be of the same order as the curvature $\Delta\xi \sim \epsilon/L$. Since technically $\delta(x) \sim L^{-1}$ we add a smallness parameter and write $\alpha(x) = \epsilon \alpha_0 \delta(x)$. In Fourier space the solution then becomes

$$\xi(k) = \frac{\epsilon \alpha_0^*}{\sqrt{2\pi}} \frac{S}{1 + \gamma S k^2}, \quad (3.84)$$

where now α_0^* carries the dimension of the inhomogeneity, i.e., $[\alpha_0^*] = \text{J m}^{-3}$. Since $\xi(k)$ has two complex conjugate singularities at $k_{1/2} = \pm i(\gamma S)^{-1/2}$, the solution is transformed back to real space using the *residue theorem*. The latter states, that the path integral over a function along a closed curve in the complex plane is given by the sum of residuals contributed by the enclosed singularities

$$\xi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \xi(k) e^{ikx} dk = i\sqrt{2\pi} \sum_{a \in \text{IH}^*} I(a) \text{Res}_a [\xi(k) e^{ikx}], \quad (3.85)$$

where the residuum of a singularity a with degeneracy n is given by

$$\text{Res}_a \left[\xi(k) e^{ikx} \right] = \frac{1}{(n-1)!} \lim_{k \rightarrow a} \frac{\partial^{n-1}}{\partial k^{n-1}} \left[(k-a)^n \xi(k) e^{ikx} \right]. \quad (3.86)$$

The sum is performed over all singularities in either the upper or lower complex half space $\mathbb{H}^\pm := \{z \in \mathbb{C} : \text{Im } z \gtrless 0\}$ governing ξ for either $x > 0$ or $x < 0$, respectively. Thereby, $I(a)$ is the winding number of a singularity a which is negative for clockwise and positive for counter clockwise encirclements. In this case it is simply given by $I(a) = \text{sgn}(\text{Im } a)$. Finally, the fundamental solution is found to be

$$\xi_g(x) = \frac{\epsilon \alpha_0^*}{2 \gamma} \sqrt{\gamma S} e^{-\frac{|x|}{\sqrt{\gamma S}}}, \quad (3.87)$$

or in dimensionless form

$$\xi_g(x) = \frac{1}{2} \frac{\alpha_0}{\gamma} \sqrt{\sigma s} e^{-\frac{|x|}{\sqrt{\sigma s}}}. \quad (3.88)$$

If the upward pulling force is the liquid-gas interface tension $\alpha_0 = \gamma_{lg}$ and the interface tension of the substrate is indeed the same for all x , we find

$$\xi(x) = \frac{1}{2} \sqrt{\frac{s}{\sigma}} e^{-\frac{|x|}{\sqrt{\sigma s}}}. \quad (3.89)$$

We see, that the vertical and horizontal extension of the wetting ridge is in the long-wave limit characterized by the dimensionless lengths

$$\text{vertical:} \quad \frac{H_{\text{rig}}}{h_a} = \sqrt{\frac{s}{\sigma}} = \epsilon \sqrt{\frac{\gamma_{lg} \gamma_{lg}}{\gamma_{sl} E_\mu} \frac{d}{h_a^2} \frac{(1-2\nu)}{2(1-\nu)}}, \quad (3.90a)$$

$$\text{horizontal:} \quad \frac{L_{\text{rig}}}{L} = \sqrt{\sigma s} = \epsilon \sqrt{\frac{\gamma_{sl}}{E_\mu} \frac{d}{h_a^2} \frac{(1-2\nu)}{2(1-\nu)}}. \quad (3.90b)$$

We now consider the dynamic case. Remaining in the dimensionless formulation we assume a sudden constant point force, i.e., $\alpha(x, t) = \delta(x) \Theta(t)$, the Fourier transform of which is

$$\alpha(\omega, k) = \frac{1}{2} \left(\delta(\omega) - \frac{1}{i\pi\omega} \right). \quad (3.91)$$

Inserting this expression into Eq. (3.83) and transforming back to real space yields the solution, though there is a different way. Instead of performing a Fourier trans-

formation of the dynamics in time and space, we only do the latter, yielding an inhomogeneous ordinary differential equation

$$\tau \partial_t \xi(k, t) = -\sigma k^2 \xi(k, t) - \frac{\xi(k, t)}{s} + \frac{\Theta(t)}{\sqrt{2\pi}},$$

which can be solve directly for the time dependence. The solution is found to be

$$\xi(k, t) = A(k) \left[1 - e^{-\lambda(k)t} \right], \quad (3.92)$$

$$\text{with} \quad A(k) = \frac{1}{\sqrt{2\pi}} \frac{s}{\sigma s k^2 + 1} \quad \text{and} \quad \lambda(k) = \frac{1}{\tau \sqrt{2\pi}} \frac{1}{A(k)}.$$

We see that $A(k) = \lim_{t \rightarrow \infty} \xi(k, t) = \xi_\infty(k)$ is the static solution (3.84). Expressing $A(k)$ in terms of $\lambda(k)$ leads to

$$\xi(k, t) = \frac{1}{\tau \sqrt{2\pi}} \frac{1}{\lambda} \left[1 - e^{-\lambda t} \right] = \frac{1}{\tau \sqrt{2\pi}} \int_0^t e^{-\lambda t'} dt' = \frac{1}{\tau \sqrt{2\pi}} \int_0^t e^{-\frac{1}{\sqrt{2\pi}} \frac{1}{\xi_\infty(k)} \frac{t'}{\tau}} dt',$$

and the inverse Fourier transformation yields

$$\xi(x, t) = \frac{1}{2} \int_0^t \frac{\exp\left(-\frac{x^2 \tau}{4\sigma t'} - \frac{t'}{s\tau}\right)}{\sqrt{\pi \sigma \tau t'}} dt'. \quad (3.93)$$

Considering only the evolution of the ridge tip, i.e., at $x = 0$, the expression reduces to

$$\xi(0, t) = \frac{1}{2} \int_0^t \frac{e^{-\frac{t'}{s\tau}}}{\sqrt{\pi \sigma \tau t'}} dt'$$

and the substitution $t' = s\tau u^2$ finally reveals

$$\xi(0, t) = \frac{1}{2} \sqrt{\frac{s}{\sigma}} \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{\frac{t}{s\tau}}} e^{-u^2} du = \xi_{\max} \operatorname{erf}\left(\sqrt{\frac{t}{s\tau}}\right), \quad (3.94)$$

with the *Gauss error function* $\operatorname{erf}(t)$ and $\xi_{\max} = \xi_\infty(0)$ being the maximum of the static solution (3.89). The relaxation dynamics of the viscoelastic substrate may thus be characterized by the half-value time which is given by

$$t_{1/2} = s\tau \left[\operatorname{erf}^{-1}\left(\frac{1}{2}\right) \right]^2 \approx \frac{s\tau \ln(2)}{3.0472265808348573}. \quad (3.95)$$

3.6.2. MACROSCOPIC DROP

The calculation of the previous part assumed a localized vertical point force and a homogeneous interface tension of the substrate along the domain. In case of a drop deposited on an elastic substrate some further adjustments have to be made, however. First of all, the liquid-gas interface is anything but orthogonal to the horizontal plane since the long wave frame is considered, i.e., $\theta_{lg} \ll \frac{\pi}{2}$. Consequently, the interface energy of the substrate differs inside and outside the drop $\gamma_{sl} \neq \gamma_{sg}$. In addition to that, the liquid-gas interface of a drop exhibits a non-vanishing curvature κ_{lg} which exerts a Laplace pressure on the substrate. Since no analytic solution is known to the mesoscopic liquid equations (due to the highly non-linear disjoining pressure) we proceed with the macroscopic description, where the liquid-gas interface of a drop is known to be of parabolic shape

$$\zeta(x) = h(x) + \xi(x) = \frac{\kappa_{lg}}{2}(x^2 - R^2) + \xi(R), \quad (3.96)$$

with fixed curvature $\kappa_{lg} = \Delta(h + \xi) = \text{const.} < 0$ and centered at $x = 0$, with the contact line located at $x = \pm R$. Then the inhomogeneity can be written like

$$\alpha(x) = \gamma_{lg} [\theta_{lg} \delta(R - |x|) + \kappa_{lg} \Theta(R - |x|)], \quad (3.97)$$

and the interface tension of the solid is

$$\gamma = \begin{cases} \gamma_{sl} & \text{for } |x| < R \\ \gamma_{sg} \approx \gamma_{lg} + \gamma_{sl} & \text{for } |x| > R \end{cases}. \quad (3.98)$$

Note, that here γ_{sg} results from Young's law [Eq. (3.39)] $\cos \theta_Y \approx 1$ in the long-wave limit. To solve Eq. (3.82) under these conditions, the domain is split up into three sections and since the fundamental solution is already known to be of exponential shape we can make the ansatz

$$\xi_1(x) = A \exp\left(\frac{x}{\sqrt{\gamma_{sg} S}}\right) \quad \text{for } x < -R, \quad (3.99a)$$

$$\xi_2(x) = B \exp\left(\frac{x}{\sqrt{\gamma_{sl} S}}\right) + C \exp\left(\frac{-x}{\sqrt{\gamma_{sl} S}}\right) \quad \text{for } -R < x < R, \quad (3.99b)$$

$$\xi_3(x) = D \exp\left(\frac{-x}{\sqrt{\gamma_{sg} S}}\right) \quad \text{for } x > R. \quad (3.99c)$$

Reflection symmetry further demands $\xi_3(x) = \xi_1(-x)$ and $\xi_2(x) = \xi_2(-x)$, i.e., $A = D$ and $B = C$. Adding the inhomogeneity caused by the Laplace pressure in the region $|x| < R$ to ξ_2 yields

$$\xi_2(x) = B \cosh\left(\frac{x}{\sqrt{\gamma_{sl}S}}\right) + \gamma_{lg}\kappa_{lg}S. \quad (3.100)$$

The three functions are connected at the section boundaries, i.e., $\xi_1(-R) = \xi_2(-R)$, revealing the first coefficient

$$A = \left[B \cosh\left(\frac{R}{\sqrt{\gamma_{sl}S}}\right) + \gamma_{lg}\kappa_{lg}S \right] \exp\left(\frac{R}{\sqrt{\gamma_{sg}S}}\right) \quad (3.101)$$

and therefore

$$\xi_{sg}(x) = \left[B \cosh\left(\frac{R}{\sqrt{\gamma_{sl}S}}\right) + \gamma_{lg}\kappa_{lg}S \right] \exp\left(\frac{R-|x|}{\sqrt{\gamma_{sg}S}}\right) \quad \text{for } |x| > R, \quad (3.102a)$$

$$\xi_{sl}(x) = B \cosh\left(\frac{x}{\sqrt{\gamma_{sl}S}}\right) + \gamma_{lg}\kappa_{lg}S \quad \text{for } |x| < R. \quad (3.102b)$$

Integrating equation Eq. (3.82) over a small interval $-\epsilon < x + R < \epsilon$ leads to

$$\lim_{\epsilon \rightarrow 0} \left(\left[-\gamma \nabla \xi(x) \right]_{-R-\epsilon}^{-R+\epsilon} + \int_{-R-\epsilon}^{-R+\epsilon} \frac{\xi(x)}{S} dx \right) = \lim_{\epsilon \rightarrow 0} \int_{-R-\epsilon}^{-R+\epsilon} \gamma_{lg} \left[\theta_{lg} \delta(R-|x|) + \kappa_{lg} \Theta(R-|x|) \right] dx$$

$$\Leftrightarrow -\gamma_{sl} \nabla \xi_{sl}(-R) + \gamma_{sg} \nabla \xi_{sg}(-R) = \gamma_{lg} \theta_{lg}$$

$$\Rightarrow B = \frac{\gamma_{lg} \theta_{lg} - \sqrt{\gamma_{sg}S} \gamma_{lg} \kappa_{lg}}{\sqrt{\frac{\gamma_{sg}}{S}} \cosh\left(\frac{R}{\sqrt{\gamma_{sl}S}}\right) + \sqrt{\frac{\gamma_{sl}}{S}} \sinh\left(\frac{R}{\sqrt{\gamma_{sl}S}}\right)}. \quad (3.103)$$

Note, that this condition corresponds to the vertical Neumann law (3.73b), i.e., the vertical force balance at the contact line. Writing the result in dimensionless form yields

$$\xi_{sg}(x) = \xi_{sl}(R) \exp\left(\frac{R-|x|}{\sqrt{s(1+\sigma)}}\right) \quad (3.104a)$$

$$\xi_{sl}(x) = B \cosh\left(\frac{x}{\sqrt{s\sigma}}\right) + \kappa_{lg}s \quad (3.104b)$$

where κ_{lg} is the dimensionless curvature of the liquid-gas interface and

$$B = \frac{-\kappa_{lg}R - \sqrt{s(1+\sigma)}\kappa_{lg}}{\sqrt{\frac{1+\sigma}{s}} \cosh\left(\frac{R}{\sqrt{\sigma s}}\right) + \sqrt{\frac{\sigma}{s}} \sinh\left(\frac{R}{\sqrt{\sigma s}}\right)}, \quad (3.105)$$

where the dimensionless liquid-gas contact angle was replaced by $\theta_{lg} = -\kappa_{lg}R$. Besides the material properties, i.e., s and σ , there are still two other pieces of information missing, namely the curvature of the liquid-gas interface κ_{lg} and the drop base radius R , both of which are unknown functions of s . Now there are two different scenarios:

1. The pressure inside the liquid is fixed and equal to the Laplace pressure such that the liquid-gas interface curvature is $\kappa_{lg} = -p/\gamma_{lg}$ always and independent of s therefore. In consequence, the volume of the liquid is not conserved any more as the softness s is changed.
2. The pressure adapts such that the volume of the liquid, i.e., the integral over $h = \zeta - \xi_{ls}$ [cf. Eqs. (3.96) and (3.104b)]

$$\begin{aligned} V &= \int_{-R}^R h \, dx = 2 \int_0^R \frac{\kappa_{lg}}{2} (x^2 - R^2) - B \left(\cosh\left(\frac{x}{\sqrt{\sigma s}}\right) - \cosh\left(\frac{R}{\sqrt{\sigma s}}\right) \right) dx \\ &= -\frac{\kappa_{lg}}{3} R^3 - \sqrt{\sigma s} B \sinh\left(\frac{R}{\sqrt{\sigma s}}\right) + RB \cosh\left(\frac{R}{\sqrt{\sigma s}}\right), \end{aligned}$$

is conserved and the curvature can be replaced by

$$-\frac{1}{\kappa_{lg}} = \frac{R^3}{3V} + \frac{\left[R^2 + R\sqrt{s(1+\sigma)}\right] \left[\cosh\left(\frac{R}{\sqrt{\sigma s}}\right) - \frac{\sqrt{\sigma s}}{R} \sinh\left(\frac{R}{\sqrt{\sigma s}}\right) \right]}{V \left(\sqrt{\frac{1+\sigma}{s}} \cosh\left(\frac{R}{\sqrt{\sigma s}}\right) + \sqrt{\frac{\sigma}{s}} \sinh\left(\frac{R}{\sqrt{\sigma s}}\right) \right)}. \quad (3.106)$$

In both scenarios the base radius R , or the liquid vapor contact angle θ_{lg} if used instead, and either the volume or the curvature depend on the softness s in an unknown manner. Using the horizontal Neumann law [Eq. (3.73c)] at $x = R$

$$\sigma \nabla \xi_{sl}^2 \Big|_{x=R} + (\kappa_{lg}R)^2 = (1+\sigma) \nabla \xi_{sg}^2 \Big|_{x=R} + \frac{3}{5},$$

together with Eq. (3.106) the volume can be written as a function of σ , s and R

$$V = \sqrt{\frac{2}{15}} \frac{\left(R^3 \sqrt{\frac{1+\sigma}{s}} + 3R^2 + 3R\sqrt{s(1+\sigma)}\right) \cosh\left(\frac{R}{\sqrt{\sigma s}}\right) + \left(R^3 \sqrt{\frac{\sigma}{s}} - 3R\sqrt{\sigma s} - 3s\sqrt{\sigma(1+\sigma)}\right) \sinh\left(\frac{R}{\sqrt{\sigma s}}\right)}{\sqrt{\left(1+2R\sqrt{\frac{1+\sigma}{s}} + \frac{R^2}{s}(1+2\sigma)\right) \cosh\left(\frac{2R}{\sqrt{\sigma s}}\right) + \left(2R\sqrt{\frac{\sigma}{s}} + 2R^2\sqrt{\frac{\sigma(1+\sigma)}{s}}\right) \sinh\left(\frac{2R}{\sqrt{\sigma s}}\right) - \frac{R^2}{s} - 1 - 2R\sqrt{\frac{1+\sigma}{s}}}}. \quad (3.107)$$

Since the liquid volume V is usually kept constant, e.g., in simulations, it would be more convenient to express the base radius as a function $R(s, \sigma, V)$. Unfortunately, Eq. (3.107) is transcendental regarding R and can thus not be transformed a desired.

3.6.3. MOVING CONTACT LINE

The same procedure can be followed to obtain a solution for the deformation of a substrate moving with velocity $V > 0$ relative to the external force in negative x -direction. The governing equation then is

$$-\gamma \Delta \xi - \vartheta \nabla \xi + \frac{\xi}{S} = \alpha(x), \quad (3.108)$$

with $\vartheta = \frac{V\eta_s}{d} \frac{2(1-\nu)}{(1-2\nu)}$. Assuming a steady meniscus of constant curvature in the range $0 < x < R$, i.e., a liquid wedge, the inhomogeneity is again

$$\alpha(x) = \gamma_{lg} [\theta_{lg} \delta(x-R) + \kappa_{lg} \Theta(R-x)]. \quad (3.109)$$

The solution using exponential functions is then found to be

$$\xi_{sl}(x) = A e^{-\frac{\vartheta(x-R)}{2\gamma_{sl}}} \exp\left(\sqrt{\frac{\vartheta^2}{4\gamma_{sl}^2} + \frac{1}{\gamma_{sl}S}}(x-R)\right) + \gamma_{lg} \kappa_{lg} S \quad \text{for } x \leq R, \quad (3.110a)$$

$$\xi_{sg}(x) = B e^{-\frac{\vartheta(x-R)}{2\gamma_{sg}}} \exp\left(-\sqrt{\frac{\vartheta^2}{4\gamma_{sg}^2} + \frac{1}{\gamma_{sg}S}}(x-R)\right) \quad \text{for } x \geq R, \quad (3.110b)$$

where $\lim_{x \rightarrow \infty} \xi(x) = 0$ and $\lim_{x \rightarrow -\infty} \xi(x) < \infty$ have been used with $\sqrt{\frac{\vartheta^2}{4\gamma^2} + \frac{1}{\gamma S}} > \frac{\vartheta}{2\gamma}$. Continuity demands $B = A + \gamma_{lg} \kappa_{lg} S$ and the jump in slope condition due to the delta function in α yields

$$\begin{aligned} \lim_{\epsilon \rightarrow 0} \left[-\gamma \nabla \xi(x) \right]_{R-\epsilon}^{R+\epsilon} &= \gamma_{sl} \nabla \xi_{sl} \big|_{x=R} - \gamma_{sg} \nabla \xi_{sg} \big|_{x=R} = \gamma_{lg} \theta_{lg} \\ \Rightarrow B &= \frac{\gamma_{lg} \theta_{lg} + \gamma_{lg} \kappa_{lg} S \left(-\frac{\vartheta}{2} + \sqrt{\frac{\vartheta^2}{4} + \frac{\gamma_{sl}}{S}} \right)}{\sqrt{\frac{\vartheta^2}{4} + \frac{\gamma_{sl}}{S}} + \sqrt{\frac{\vartheta^2}{4} + \frac{\gamma_{sg}}{S}}}. \end{aligned} \quad (3.111)$$

In dimensionless form we find

$$\xi_{sl}(x) = (B - \kappa_{lg}s)e^{-\frac{v\tau}{2\sigma}(x-R)} \exp\left(\sqrt{\frac{v^2\tau^2}{4} + \frac{\sigma}{s}} \frac{(x-R)}{\sigma}\right) + \kappa_{lg}s \quad \text{for } x \leq R, \quad (3.112a)$$

$$\xi_{sg}(x) = Be^{-\frac{v\tau}{2(1+\sigma)}(x-R)} \exp\left(-\sqrt{\frac{v^2\tau^2}{4} + \frac{(1+\sigma)}{s}} \frac{(x-R)}{(1+\sigma)}\right) \quad \text{for } x \geq R, \quad (3.112b)$$

with $v = 3\eta V/(\gamma_{lg}\epsilon^3)$ and

$$B = \frac{\theta_{lg} + s\kappa_{lg}\left(\sqrt{\frac{v^2\tau^2}{4} + \frac{\sigma}{s}} - \frac{v\tau}{2}\right)}{\sqrt{\frac{v^2\tau^2}{4} + \frac{\sigma}{s}} + \sqrt{\frac{v^2\tau^2}{4} + \frac{(1+\sigma)}{s}}}. \quad (3.113)$$

Lets further assume the liquid-gas interface $\zeta = h + \xi$ to satisfy the boundary conditions $\zeta|_{x=0} = \zeta_0$ and $\partial_x \zeta|_{x=0} = \zeta'_0$. It has to connect to the substrate at $x = R$ leading to

$$\zeta(x) = \zeta_0 + \zeta'_0 x + (B - \zeta_0 - \zeta'_0 R) \frac{x^2}{R^2}, \quad (3.114)$$

with curvature $\kappa_{lg} = 2(B - \zeta_0 - \zeta'_0 R)/R^2$ and liquid-gas contact angle $\theta_{lg} = \zeta'_0 - 2(B - \zeta_0)/R$. Then the prefactor can be expressed like

$$B = \frac{4\zeta_0 R + 2\zeta'_0 R^2 + 2(\zeta_0 + \zeta'_0 R)(sv\tau - \sqrt{4\sigma s + v^2\tau^2 s^2})}{4R + 2sv\tau - 2\sqrt{4\sigma s + v^2\tau^2 s^2} + \frac{R^2}{s}(\sqrt{4\sigma s + v^2\tau^2 s^2} + \sqrt{4s(1+\sigma) + v^2\tau^2 s^2})}. \quad (3.115)$$

In Fig. 3.8 some exemplary profiles are shown for $0 < v < 3$ (a), i.e., an advancing contact line, and $-0.5 < v < 0$ (b), i.e., an advancing contact line. Note, that assumption of constant curvature κ_{lg} is not exactly reasonable in a dynamic situation and also the position R of the contact line generally depends on the velocity v in an unknown manner. In principle, the missing dependence $R(v)$ is determined by the horizontal Neumann condition, however, the resulting equation is a polynomial of fourth order in R that can not be resolved.

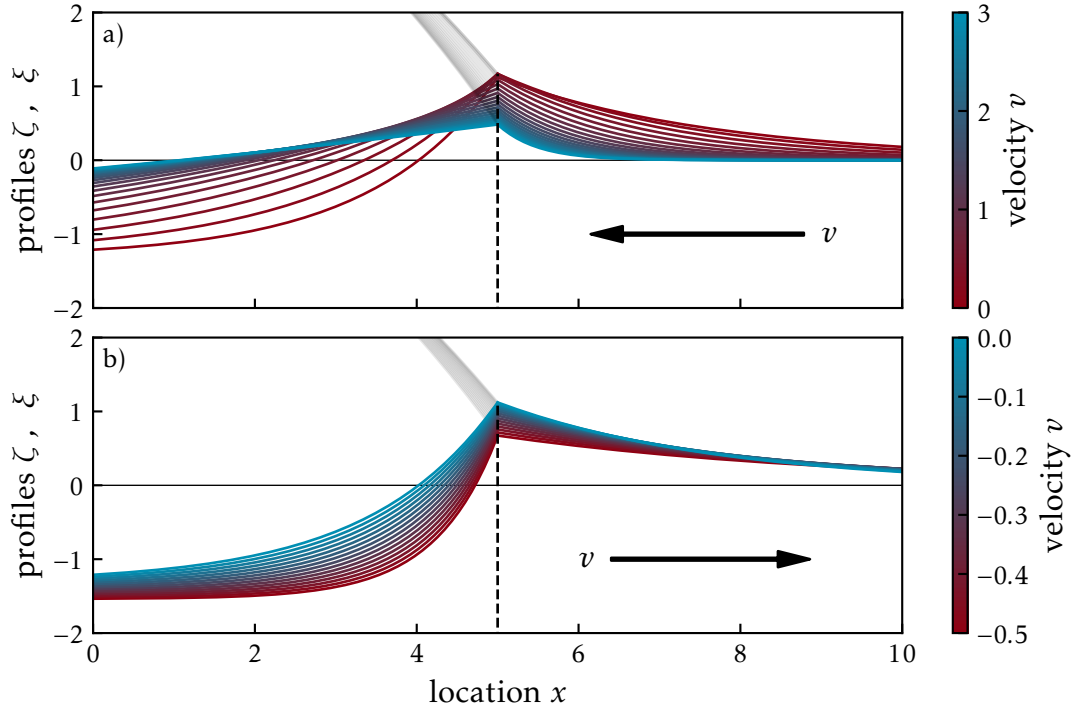


FIGURE 3.8.: Analytic solution for the profile ξ of a substrate moving under a constantly curved liquid-gas interface with velocity a) $0 < v < 3$ and b) $-0.5 < v < 0$. The remaining dimensionless parameters are fixed to $s = 5$, $\sigma = 0.5$, $\tau = 1$, $R = 5$, $\zeta_0 = 5$, $\zeta'_0 = -\frac{1}{4}$. Note, that realistically the curvature of the liquid-gas interface is not constant in a dynamic scenario and the contact line position R should depend on v such that the horizontal Neumann condition is satisfied.

3.6.4. HIGHER-ORDER EXPANSION OF THE ELASTIC ENERGY

As discussed in Sec. 2.3.3 the Green's function of the linear elastic problem may in the long-wave limit be expanded in a Taylor series. So far only zeroth order terms have been considered in which case the Green's function is a diagonal matrix such that the dynamics of vertical and horizontal displacement decouple. Considering higher orders, however, the matrix is not sparsely occupied anymore and the coupling has to be taken into account, which complicates the problem considerably. Let's for the moment consider only the G_{zz}^{-1} component. Continuing the expansion up to $\mathcal{O}(k^4)$ gives an expression of the form

$$G_{zz}^{-1}(k) \approx \frac{1}{s} + \alpha k^2 + \beta k^4, \quad (3.116)$$

which in real space becomes

$$G_{zz}^{-1} \approx \frac{1}{s} - \alpha \partial_x^2 + \beta \partial_x^4, \quad (3.117)$$

where the parameters s , α and β are considered dimensionless for convenience. Hence, the stored elastic energy is given by

$$\begin{aligned}\mathcal{F}_{\text{el}} &= \frac{1}{2} \int \frac{1}{s} \xi^2 - \alpha \xi \partial_x^2 \xi + \beta \xi \partial_x^4 \xi \, dx \\ &\stackrel{P.I.}{=} \frac{1}{2} \int \frac{1}{s} \xi^2 + \alpha (\partial_x \xi)^2 + \beta (\partial_x^2 \xi)^2 \, dx ,\end{aligned}$$

and the variation of the total free energy w.r.t. ξ is

$$\frac{\delta \mathcal{F}}{\delta \xi} = \beta \partial_x^4 \xi - \partial_x^2 (h + \xi) - (\sigma + \alpha) \partial_x^2 \xi + \frac{\xi}{s} .$$

Note, that α plays the role of a bending stiffness that contributes to the effective surface tension of the solid. Therefore, the effective surface tension $\tilde{\sigma} = \sigma + \alpha$ is introduced. As before this linear equation can be solved, replacing the Laplace pressure of the liquid by a vertically pulling point force, i.e.,

$$\beta \partial_x^4 \xi - \tilde{\sigma} \partial_x^2 \xi + \frac{\xi}{s} = \delta(x) . \quad (3.118)$$

A Fourier transformation leads to

$$\begin{aligned}\beta k^4 \xi + \tilde{\sigma} k^2 \xi + \frac{\xi}{s} &= \frac{1}{\sqrt{2\pi}} \\ \rightarrow \quad \xi(k) &= \frac{1}{\sqrt{2\pi}} \frac{1}{\beta k^4 + \tilde{\sigma} k^2 + \frac{1}{s}} = \frac{1}{\sqrt{2\pi}} \frac{1}{\beta} \frac{1}{k^4 + a k^2 + b}\end{aligned}$$

with $a = \frac{\tilde{\sigma}}{\beta}$ and $b = \frac{1}{\beta s}$. To obtain the solution in real space the inverse Fourier transformation has to be performed

$$\xi(x) = \frac{1}{2\pi} \frac{1}{\beta} \int_{-\infty}^{\infty} \frac{e^{ikx}}{k^4 + a k^2 + b} \, dk .$$

To do so the residue theorem is used again

$$\int_{-\infty}^{\infty} \frac{e^{ikx}}{k^4 + a k^2 + b} \, dk = 2\pi i \sum_{n \in \mathbb{H}^*} I(n) \text{Res}_n \left[\xi(k) e^{ikx} \right] . \quad (3.119)$$

Being the scaling factor of the highest order derivative $\beta > 0$ is demanded in order to ensure stability in the $k \rightarrow \infty$ limit¹⁷. Assuming $4b > a^2$, i.e. $4\beta > s\tilde{\sigma}^2$, the four

¹⁷cf. App. B.5 and remember the negative sign in front of the variation in the dynamics of ξ Eq. (3.65)

poles of the integrand are

$$k_0 = \pm i \sqrt{\frac{a}{2} \pm i \sqrt{b - \frac{a^2}{4}}} . \quad (3.120)$$

Note, that $a < 0 \Leftrightarrow \tilde{\sigma} < 0$ is not physical and for $4b < a^2$ the poles are purely imaginary such that no oscillatory behavior could occur in the solution. The complex number in the square root can be rewritten using

$$\sqrt{z} = \sqrt{|z|} e^{i\frac{\varphi}{2}} = \sqrt{|z|} \left[\frac{1}{\sqrt{\left(\frac{\text{Im}(z)}{|z|+\text{Re}(z)}\right)^2 + 1}} + \frac{\frac{i\text{Im}(z)}{|z|+\text{Re}(z)}}{\sqrt{\left(\frac{\text{Im}(z)}{|z|+\text{Re}(z)}\right)^2 + 1}} \right] , \quad (3.121)$$

where

$$\varphi = 2 \arctan\left(\frac{\text{Im}(z)}{|z| + \text{Re}(z)}\right) ,$$

was used. Thus the poles are found to be

$$\begin{aligned} k_0 &= \pm \sqrt[4]{b} \left[\pm \sqrt{\frac{b - \frac{a^2}{4}}{a\sqrt{b} + 2b}} + i \frac{\sqrt{b} + \frac{a}{2}}{\sqrt{a\sqrt{b} + 2b}} \right] \\ &= \pm \left(\pm \sqrt{\frac{4\beta - s\tilde{\sigma}^2}{4\beta[2\sqrt{\beta s} + s\tilde{\sigma}]}} + i \sqrt{\frac{1}{2\sqrt{\beta s}} + \frac{\tilde{\sigma}}{4\beta}} \right) \end{aligned} \quad (3.122)$$

Considering only the upper complex half space, the poles of negative imaginary part are neglected such that only two remain

$$k_{1/2} = \pm \sqrt{\frac{4\beta - s\tilde{\sigma}^2}{4\beta[2\sqrt{\beta s} + s\tilde{\sigma}]}} + i \sqrt{\frac{1}{2\sqrt{\beta s}} + \frac{\tilde{\sigma}}{4\beta}} . \quad (3.123)$$

The residuals are now given by

$$\text{Res}_n [\xi(k) e^{ikx}] = \frac{e^{ik_n x}}{4k_n^3 + 2ak_n} \quad (3.124)$$

and so the solution is found to be

$$\xi_r(x) = \sum_n \frac{ie^{ik_n|x|}}{4\beta k_n^3 + 2\tilde{\sigma}k_n} = i \left[\frac{e^{ik_1|x|}}{4\beta k_1^3 + 2\tilde{\sigma}k_1} + \frac{e^{ik_2|x|}}{4\beta k_2^3 + 2\tilde{\sigma}k_2} \right]. \quad (3.125)$$

In Fig. 3.9 this solution is compared to the one of the simple problem [Eq. (3.89)]. The found profile Eq. (3.125) takes the shape of a modulated cosine function which violates Neumann's laws due to $\partial_x \xi(x)|_{x=0} = 0$. It further exhibits depressions on both sides of the ridge, a feature that was missing in the simplified description. To find the deformation caused by a parabolic drop of radius R and contact angle θ_{lg} sitting on the substrate a solution can be constructed using

$$\xi_d(x) = \theta_{lg} [\xi_r(x+R) + \xi_r(x-R)] - \frac{\theta_{lg}}{R} [\Theta(x+R) - \Theta(x-R)] * \xi_r(x),$$

with $*$ denoting a convolution again. This convolution can further be written as

$$\begin{aligned} \xi^*(x) &= [\Theta(x+R) - \Theta(x-R)] * \xi_r(x) = \int_{-\infty}^{x+R} \xi_r(x') dx' - \int_{-\infty}^{x-R} \xi_r(x') dx' \\ &= \int_{x-R}^{x+R} \xi_r(x') dx' = \int_{-R}^R \xi_r(x' + x) dx'. \end{aligned}$$

Exploiting the symmetry $\xi^*(-x) = \xi^*(x)$ and $\xi_r(-x) = \xi_r(x)$ we find

$$\begin{aligned} \xi_-^*(x) &= 2 \int_0^{R-|x|} \xi_r(x') dx' + \int_{R-|x|}^{R+|x|} \xi_r(x') dx' \\ &= 2 [\Xi(R-|x|) - \Xi(0)] + \Xi(R-|x|) - \Xi(R+|x|) \end{aligned}$$

for $|x| < R$ and

$$\xi_+^*(x) = \int_{|x|-R}^{|x|+R} \xi_r(x') dx' = \Xi(|x|-R) - \Xi(|x|+R)$$

for $|x| > R$ with

$$\Xi(x) = \int \xi_r^+(x) dx = \frac{e^{ik_1 x}}{4\beta k_1^4 + 2\tilde{\sigma}k_1^2} + \frac{e^{ik_2 x}}{4\beta k_2^4 + 2\tilde{\sigma}k_2^2}, \quad (3.126)$$

where ξ_r^+ is ξ_r as defined for positive x , i.e., with $|x| = x$. Finally the solution for the substrate deformation underneath a droplet is given by

$$\begin{aligned} \xi_d(x) = & \theta_{lg} [\xi_r(x+R) + \xi_r(x-R)] + \frac{\theta_{lg}}{R} [\Xi(|x|+R) - \Xi(|x|-R)] \\ & + \frac{\theta_{lg}}{R} \Theta(R-|x|) [\Xi(R-|x|) + \Xi(|x|-R) - 2\Xi(0)] , \end{aligned} \quad (3.127)$$

and plotted together with the simple solution Eq. (3.104) in Fig. 3.10. It stands out, that the ridge of the simple solution is rotated, i.e., the flank of the wetting ridge is significantly steeper inside the drop then out side it, while the higher order solution is symmetric close to $x = \pm R$. An effect that might be caused by the missing influence of the horizontal displacement in the latter case.

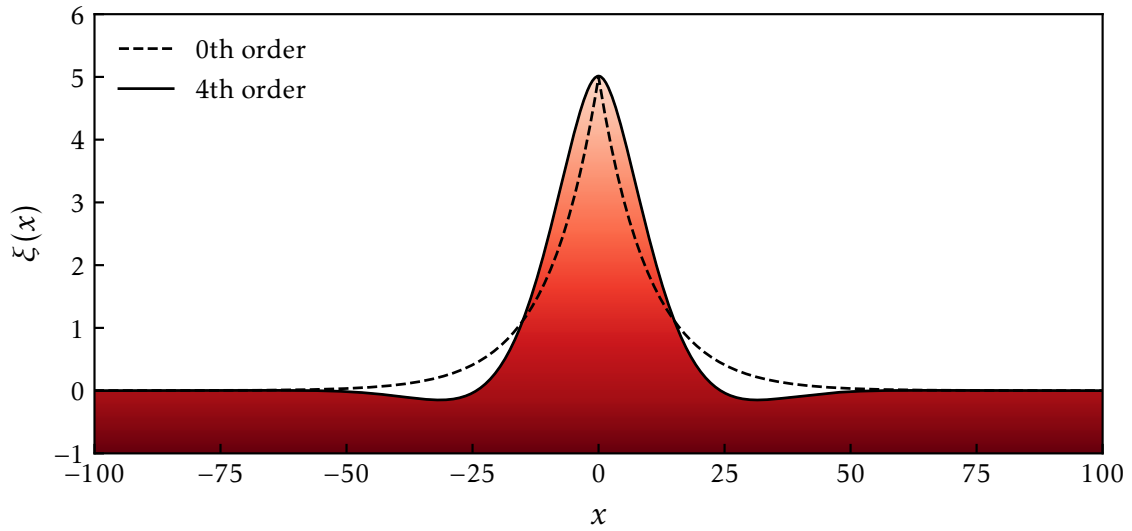


FIGURE 3.9.: Comparison of the profiles of an linear elastic substrate deforming under a vertically pulling point force. The black dashed line corresponds to Eq. (3.89), i.e., the deformation obtained by using only 0th order of the Green's function. The solid line corresponds to Eq. (3.125), obtained by expanding the Green's function up to 4th order and shows depressions next to the wetting ridge. Parameters were set to $s = 10^2$, $\sigma = 1$, $\alpha = -0.9$ and $\beta = 20$.

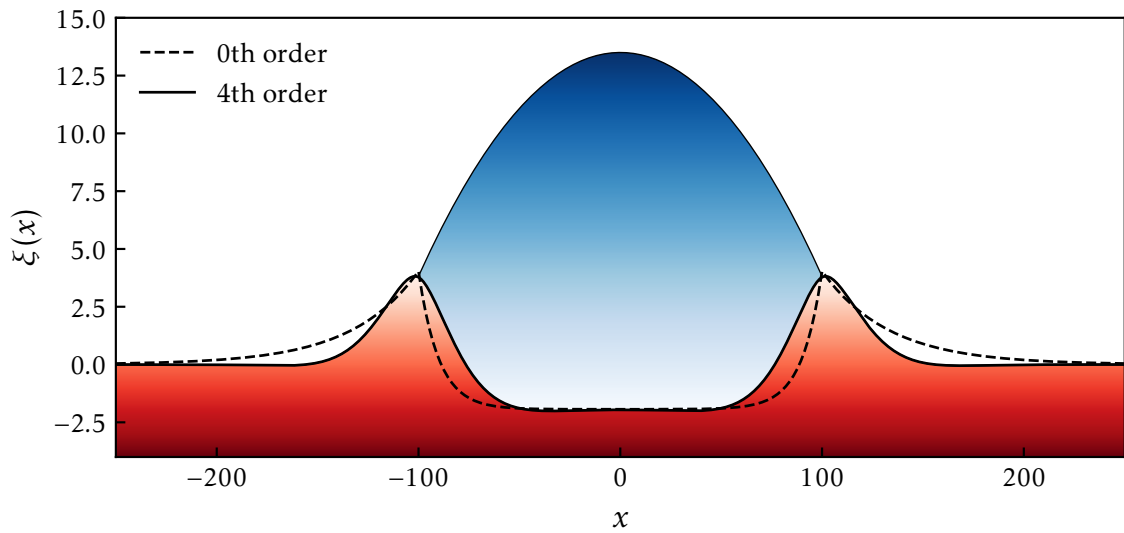


FIGURE 3.10.: Comparison of the profiles of an linear elastic substrate deforming under the pressure exerted by a parabolic drop. The black dashed line corresponds to Eq. (3.104), i.e., the deformation obtained by using only 0th order of the Green's function. The solid line corresponds to Eq. (3.127), obtained by expanding the Green's function up to 4th order. Like in Fig. 3.9 the higher order solution exhibits depressions next to the wetting ridges. The tip of the latter is smoothed out over a wide range and no rotation towards the drop center is visible. Hence, Neumann's laws are strongly violated. Parameters were set to $s = 10^4$, $\sigma = \tilde{\sigma} = 0.1$ and $\beta = 25$.

4. THE DOUBLE TRANSITION OF STATIC DROPS

The results presented in this chapter have to a large extent already been published in:

[HST21a] HENKEL, C., SNOEIJER, J. H., and THIELE, U. “Gradient-dynamics model for liquid drops on elastic substrates”. In: *Soft Matter* 17 (2021), pp. 10359–10375. DOI: [10.1039/D1SM01032H](https://doi.org/10.1039/D1SM01032H)

Many of the following figures were reproduced and adapted from the data presented in this reference.

The fine-structure of the wetting ridge arises from an intricate balance of elastic and capillary forces, with recent literature identifying a central role for the surface tension of the solid [Jer+11, SD12, Mar+12a, Lim12]. A central question is how the liquid angle, at equilibrium, is different from Young’s law for rigid substrates. It turns out that upon increasing the substrate softness, a double-transition is observed in the various angles between interfaces in the contact line region [Mar+12b, Lub+14]. Namely, when increasing softness from low values, i.e., starting in the rigid limit, first a strong increase in the size of the wetting ridge is observed while the droplet shape remains approximately constant and the substrate surface remains about flat off the contact line. Then, when the softness decreases several orders of magnitude, a strong increase of the substrate depression under the droplet occurs at constant opening angle of the wetting ridge. The latter is governed by a balance of surface tensions [SD12, Mar+12a, Lim12], analogously to the Neumann’s law known for floating lenses. In Fig. 4.1 this transition is sketched in three stages. Note, that in comparison to liquids the surface tension of solids brings in an additional complexity owing to its possible strain-dependence, i.e., the Shuttleworth effect [AS16, Xu+17, XSD18, Sch+18, Pan+20], which is discussed in Ch. 7. In Sec. 3.2 the statics properties of macroscopic drops have already been discussed, thereby introducing

the rigid limit, i.e., $s \rightarrow 0$, and the quasi-liquid limit, i.e., $s \rightarrow \infty$. In this Chapter the dimensionless mesoscopic long-wave gradient dynamics model as introduced in Sec. 3.4.2 is employed to study a static drop situation and to explore the double transition of steady drops in its dependence on drop size. In the course of that the validity of Neumann's laws is checked in the different softness regimes.

4.1. THE ELASTO-CAPILLARY LENGTH

In the literature of soft wetting, it is common to characterize the substrate softness in terms of the *elasto-capillary length* ℓ_{ec} , describing the typical size of the deformation induced by the balance of a surface tensions and elastic forces

$$\ell_{ec} = \frac{\gamma}{E_\mu}, \quad (4.1)$$

with E_μ being storage shear modulus. In case of rather rigid substrates, i.e., large E , the elasto-capillary length and therefore the wetting ridge become small. If $\ell_{ec} \ll R$ the liquid-vapor contact angle θ_{lv} matches fairly well with the Young's angle θ_Y . If in contrast E becomes rather small such that the wetting ridge grows to a size comparable to the drop itself $\ell_{ec} \sim R$, however, elastic effects become increasingly negligible and the quasi-liquid limit is approached. The drops begins to sink into the substrate eventually assuming the shape of a liquid lens. In Sec. 3.6 the height and width of the wetting ridge were in the long-wave limit found to be characterized by the dimensionless scales (3.90a) and (3.90b), respectively. Hence, depending on

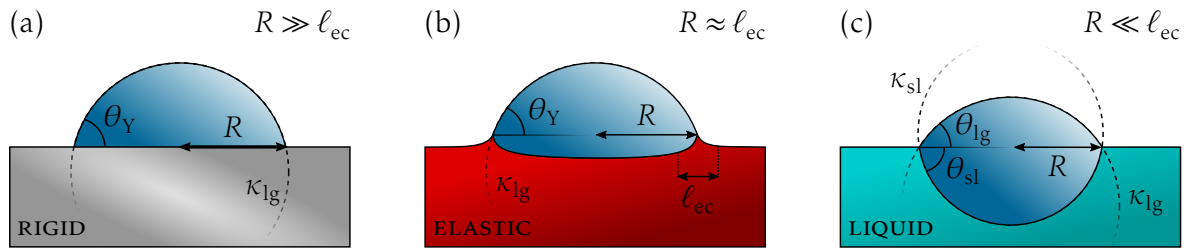


FIGURE 4.1.: Characteristic drop shapes of partially wetting liquid substrate of different softness. (a) The substrate is rigid and very resistant against deformations $R \gg \ell_{ec}$. The drop adopts the shape of a spherical cap with curvature κ_{lv} and contact angle θ_Y selected by Young's law. (b) The substrate is elastic and soft enough to allow for the formation of wetting ridges at the contact lines $R \approx \ell_{ec}$ but stiff enough to prevent the drop from sinking. The local angles of the wetting ridge tip are given by Neumann's law and as the softness increases the region rotates inwards such that the liquid-vapor contact angle and curvature increasingly deviate from those in the rigid case. (c) The substrate is so soft that it is considered quasi-liquid and elasticity is negligible $R \ll \ell_{ec}$. The drop resembles a liquid lens described by the intersection of two spherical caps with curvatures κ_{lg} and κ_{sl} . The angles at the three-phase contact are still related by Neumann's laws but the slope of the solid-liquid interface vanishes.

whether γ_{lg} or γ_{sl} is used in Eq. (4.1) the elasto-capillary length ℓ_{ec} is either a vertical or a horizontal scale and its dimensionless counterpart either (3.90a) or (3.90b) correspondingly. No matter which, the dimensionless elasto-capillary length always scales with the softness like

$$\tilde{\ell}_{ec} \sim \sqrt{s}. \quad (4.2)$$

4.2. CONTINUATION OF THE SUBSTRATE SOFTNESS

The dependence of the static drop state on the substrate softness s can be investigated using pseudo-arclength continuation, as is frequently employed for thin-film descriptions of layers and drops of simple or complex liquids on solid or liquid substrates [Pot+05, Thi10, Eng+16, Tri+20]. A detailed discussion on this method can be found in App. B.4. Here the packages `auto-07p` [DKK91] and `pde2path` [UWR14] have been utilized to solve the static equations, i.e., Eqs. (3.65) with $\partial_t h = \partial_t \xi = \partial_t u_x = 0$, in the long-wave limit, i.e., using the variations (3.75) and the cor-

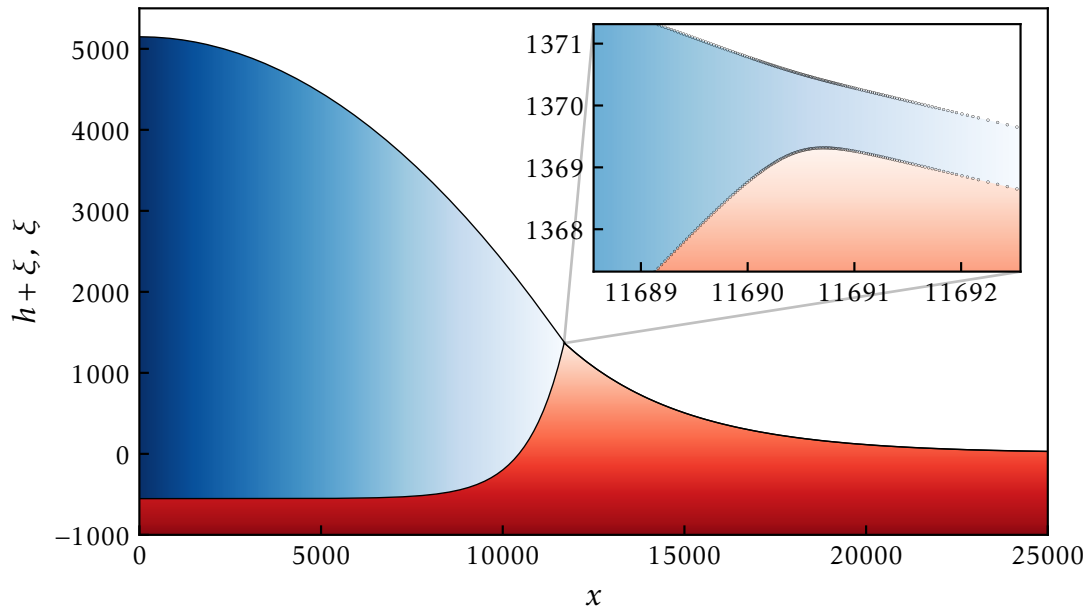


FIGURE 4.2.: Typical drop and substrate profile, $h + \xi$ and ξ , as obtained by solving Eqs. (4.3) numerically, in this case using `auto-07p`. The inset strongly magnifies the tip of the wetting ridge illustrating that it is indeed rounded although in the main panel it appears to be quite pointed. The black dots in the inset show an example of the nonuniform adaptive numerical grid. Note also the precursor of dimensionless height $h_a = 1$, covering the supposedly dry substrate outside the drop.

responding parameters (3.76). After integrating Eq. (3.65a) two times the static equations effectively are

$$\frac{\delta \mathcal{F}}{\delta h} = -\Delta(h + \xi) - \Pi(h) + p = 0, \quad (4.3a)$$

$$\frac{\delta \mathcal{F}}{\delta \xi} = -\Delta(h + \xi) - \sigma \Delta \xi + \frac{\xi}{s} = 0. \quad (4.3b)$$

The horizontal displacement is no further considered here as it is always $\vec{u}_{\parallel} = 0$ in the long-wave limit [cf. Sec.(3.4)]. Remember, that the constant p on the right hand side of Eq. (4.3a) is a *Lagrange multiplier* ensuring conservation of volume

$$p \int_{\Omega} (h - h_0) d^2 \vec{r} = 0, \quad (4.4)$$

where h_0 is the mean thickness of the liquid layer. Since the whole domain is covered by at least the adsorption layer, the effective liquid or drop volume is defined as

$$V = \int_{\Omega} (h_0 - h_a) d^2 \vec{r}. \quad (4.5)$$

In the following a one-dimensional domain Ω of size D extended in x -direction is considered with periodic or homogeneous Neumann boundary conditions.¹ The above equations remain valid with $\nabla \rightarrow \partial_x$, $\Delta \rightarrow \partial_{xx}$, $d^2 \vec{r} \rightarrow dx$, and $\vec{r} \rightarrow x$.

In the numerics the domain Ω is discretized into a nonuniform adaptive grid to ensure sufficient resolution and reduce computational cost. Fig. 4.2 illustrates that even quite sharp structures like the tip of a wetting ridge are properly resolved. Starting from the analytically known solution of a parabolic drop on a rigid substrate the steady solution is followed in parameter space, using the softness s as control parameter and fixing the drop volume via the Lagrange multiplier p . Typical profiles of $h + \xi$ and ξ are for different softnesses given in Fig. 4.3, visualizing how the equilibrium morphology changes as the substrate changes from very rigid to quasi-liquid. Of particular interest are the angles sketched in Fig. 3.6, namely, θ_{lg} , the angle the liquid-gas interface takes with the horizontal and $\theta_{sl} + \theta_{sg}$, the combined angles on both sides of the wetting ridge with the horizontal. Note, that the left axis of Figs. 4.4 and 4.6 gives $-(\theta_{sl} + \theta_{sg})$, as this is the long-wave equivalent to $\pi - \theta_s$, with θ_s being the opening angle of the wetting ridge, such that the

¹The Neumann boundary conditions enforce certain gradients on the domain boundaries, i.e., $\nabla(h + \xi)|_{\partial\Omega} = \vec{c}_1$ and $\nabla\xi|_{\partial\Omega} = \vec{c}_2$, and are not to be confused with the Neumann's laws for contact angles at the three phase contact line. For homogeneous Neumann boundary conditions it is $\vec{c}_1 = \vec{c}_2 = 0$.

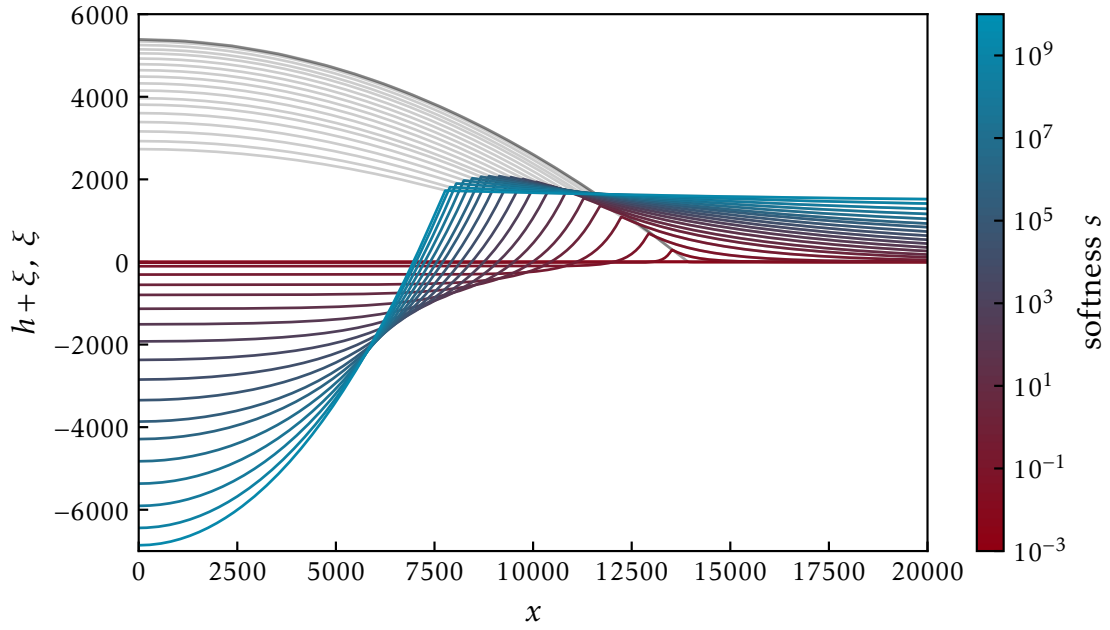


FIGURE 4.3.: Typical numerical drop and substrate profiles, i.e., $h + \xi$ (gray) and ξ (color-scaled), for different softness ranging from the rigid limit $s = 10^{-3}$ to the quasi-liquid limit $s = 10^{10}$. It can be seen that as the softness increases first the wetting ridge rises until it reaches a maximum and the drop begins to sink into the substrate. Note, that the drop base radius R reduces steadily as the softness increases, due to the fixed volume. Unfortunately, the way in which R depends on the softness s at fixed V is not analytically known.

plots visually resemble Fig. 3 of Ref. [Lub+14]. Both, θ_{lg} and $\theta_{sl} + \theta_{sg}$, are expected to smoothly transit from fulfilling Young's for a rigid substrate ($s \rightarrow 0$) to fulfilling Neumann's law in the limiting case of a quasi-liquid substrate ($s \rightarrow \infty$). The change of both angles with softness is given in Fig. 4.4 (a) with the scales for θ_{lg} and $\theta_{sl} + \theta_{sg}$ on the right and left hand side axis, respectively. Just as found from the full elastic theory for drops with contact angles $\theta_Y \sim \pi/2$ in Ref. [Lub+14], two distinguished separate transitions occur. Starting in the rigid limit and increasing the softness, first, the formation of wetting ridges is observed. As the overall shape of the drop itself barely changes, in this first transition θ_{lg} remains approximately constant while $\theta_{sl} + \theta_{sg}$ increases strongly [cf. Fig. 4.4 (a) at about $s = 1 \dots 10^2$]. In the same course, the wetting ridge grows as shown in Fig. 4.4 (b). Increasing the softness further, the substrate below the drop is compressed owing to the Laplace pressure imposed by the drop. In consequence, the drop gradually sinks into the elastic substrate accompanied by an inwards rotation of the three-phase contact region. This rotation marks the second transition at about $s = 10^5 \dots 10^7$ in Fig. 4.4 (a) and is reflected by the contact angles; θ_{lg} strongly decreases while $\theta_{sl} + \theta_{sg}$ remains approximately constant. In Fig. 4.4 (b) the second transition is also marked by a maximum in the wetting ridge height, which is calculated as the difference of the

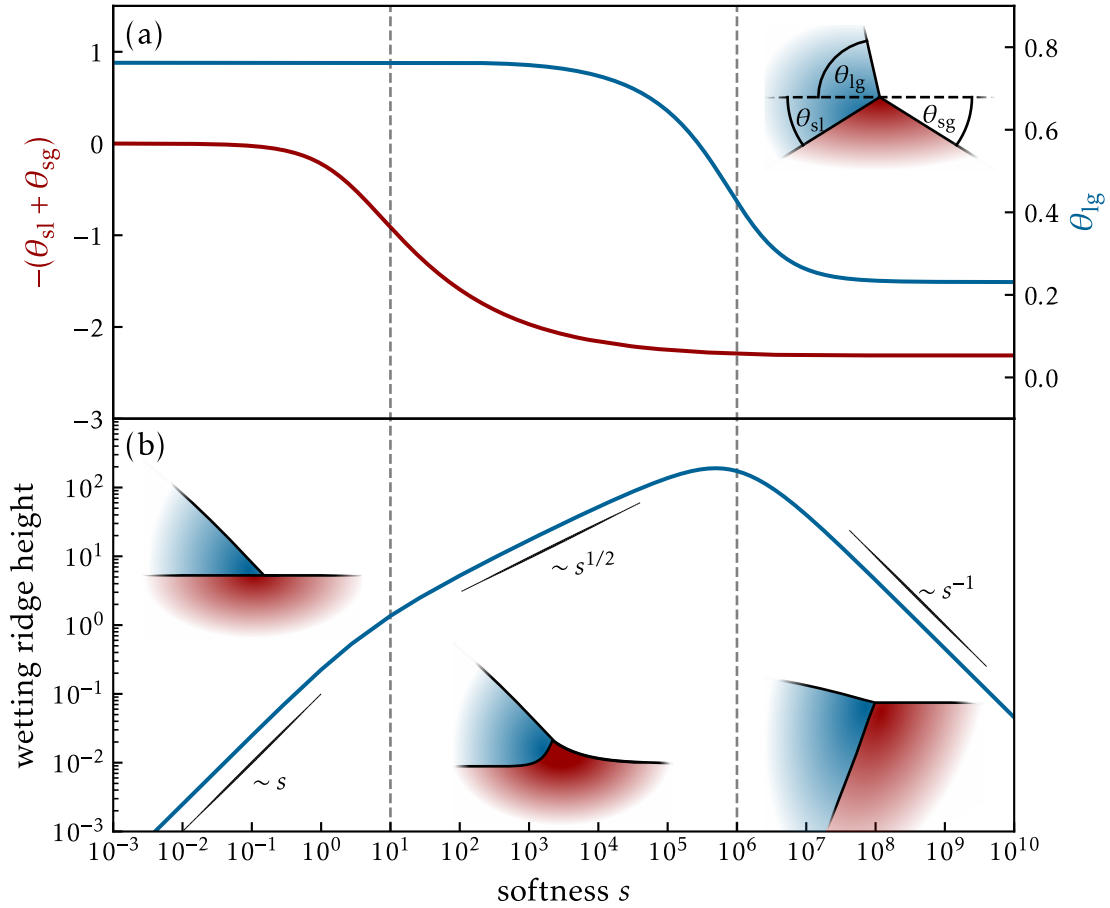


FIGURE 4.4.: Measurement of the wetting ridge at varying softness from $10^{-3} < s < 10^{10}$. (a) Dependence of the angles θ_{lg} (right hand side axis, blue line) and $-(\theta_{sl} + \theta_{sg})$ (left hand side axis, red line) at the wetting ridge (as defined in the inset) on the substrate softness s for a drop of volume $V = 10^6$ at $\sigma = 0.1$. The two vertical dashed lines indicate the softnesses where the transition from the rigid to the soft regime at $s \approx 10^1$ and the transition from the soft to the liquid regime at $s \approx 10^6$ occur, respectively. (b) Wetting ridge height against substrate softness s with same fixed volume and σ as in (a). Three different regimes of scaling laws are distinguished at the same softnesses as in (a). The three insets in (b) indicate how the profiles in the respective softness regions differ qualitatively at the contact line. A corresponding continuation video can be seen in HeSH2021-SupplMat-Video01-figo4.mp4 of the electronic supplementary material of Ref. [HST21a]

maximum of ξ and its value at $x \rightarrow \infty$.

The growth of the wetting ridge and the subsequent rotation of the contact region as the softness of the substrate increases is even better seen in Fig. 4.5. Here, softness is logarithmically encoded by the radius ranging from $s = 10^{-3}$ (in the center) to $s = 10^{10}$ (at the outer edge) as indicated by the concentric rings. The blue and red areas respectively indicate the angular ranges occupied by the liquid and the solid substrate at given softness. Thus, the angles at which the interfaces appear, measured at the center w.r.t. the horizontal dashed line, correspond to the contact angles in Fig. 3.6 and are obtained from the same numerical data as used in Fig. 4.3. Draw-

ing the radius through each of the three points at which the interfaces are located for fixed softness therefore results in a (macroscopic) sketch of the contact region, with the radii representing the interfaces. While θ_{lg} and θ_{sl} decrease steadily with increasing softness, θ_{sg} vanishes in the rigid as well as in the quasi-liquid limit but reaches a maximum $\theta_{sg}^{\max}$ at $s \approx 10^4$. The softness region around this point marks the intermediate elastic regime and a completed development of the wetting ridge. The corresponding radii (dotted lines) reveal, that also θ_{sl}^{int} is close to its maximum already while θ_{lg} barely deviates from Young's angle. This behavior shows nicely how first the wetting ridge grows before the whole contact region is rotated (here counter clock wise).

The two steps of the double transition can be related to the ratio of the elasto-capillary length ℓ_{ec} to the relevant microscopic and macroscopic length scales of the system [Lub+14]. Elasticity becomes important when ℓ_{ec} becomes comparable to the microscopic length scale, here $\ell_{ec} \sim h_a$. In terms of nondimensional quantities this implies that the first transition occurs when $\tilde{\ell}_{ec} = \sqrt{\sigma s} \approx 1$, i.e., for $s \approx 1/\sigma$. For $\sigma = 0.1$ we have $s \approx 10$ in agreement with Fig. 4.4. Upon entering the intermediate elastic regime, the ridge height scales with the substrate softness like $\sim s^{1/2}$ and is thus directly proportional to $\tilde{\ell}_{ec}$ as expected. Likewise, the second transition emerges when the droplet sinks in, which happens when $\tilde{\ell}_{ec}$ becomes comparable to the droplet size, e.g., the radius R or the drop height $h_{\max}$. For the simulation with $V \approx 10^6$ the drop height is $h_{\max} \approx 500$ (in the rigid limit) such that the second transition would be expected at $s \approx h_{\max}^2/\sigma = 2.5 \cdot 10^6$, which fits quite well with Fig. 4.4. Alternatively, a characteristic length can be estimated from the drop volume, i.e., the transition can be estimated to occur when $\tilde{\ell}_{ec} \approx \sqrt{V}^2$, i.e., $s \approx V/\sigma$. For $\sigma = 0.1$ and drop volume $V = 10^6$ the transition would be expected for $s \approx 10^7$ which is somewhat overestimated but still reasonably close.

It seems, that from the macroscopic perspective the deformation of the substrate under a drop depends not primarily on the substrate softness, but only on the ratio of the elasto-capillary length and the characteristic drop size, that is, if the softness s is changed the size of the drop can (at other wise fixed parameters) be adjusted in such a way that the substrate profile looks exactly the same as before only up scaled. Indeed, it can be seen that the analytic expression for the substrate profile under a drop (3.104) can be written in dependence on the ratio $\lambda = \frac{R}{\sqrt{s}}$ after rescaling ξ and

²Note, that for a one-dimensional system V is strictly speaking an area according to its definition Eq. (4.5).

x with R

$$\xi_{sl}(x) = \frac{\theta_{lg}}{\lambda^2} \left[B \cosh\left(\frac{\lambda x}{\sqrt{\sigma}}\right) - 1 \right] \quad (4.6a)$$

$$\xi_{sg}(x) = \xi_{sl}(1) \exp\left(\frac{\lambda(1-|x|)}{\sqrt{1+\sigma}}\right) \quad (4.6b)$$

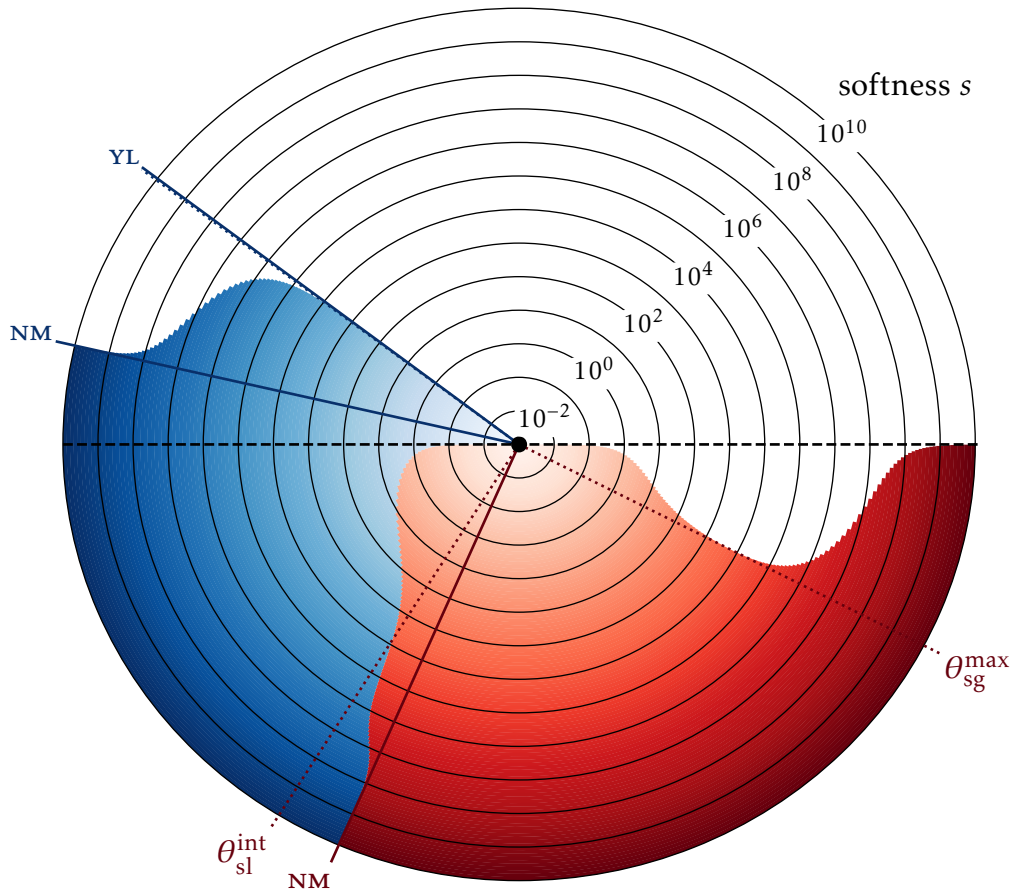


FIGURE 4.5.: Visualization of the contact line rotation with varying softness. The softness is logarithmically encoded by the radius ranging from $s = 10^{-3}$ (in the center) to $s = 10^{10}$ (at the outer edge) as indicated by the concentric rings. The blue and red areas respectively indicate the angular ranges occupied by the liquid and the solid substrate at given softness. Thus, the angles at which the interfaces between the areas appear, measured at the center w.r.t. the horizontal dashed line, correspond to the contact angles in Fig. 3.6 and are obtained from the same numerical data as used in Fig. 4.3. Drawing the radius through each of the three points at which the interfaces are located for given softness therefore results in a sketch of the associated macroscopic contact region. The solid lines marked with YL and NM give the sketches in the rigid and quasi-liquid limits, respectively. The dotted lines indicate the same sketch for a maximum solid-gas contact angle $\theta_{sg}^{\max}$, i.e. a fully grown wetting ridge. It can be seen, that the liquid-gas contact angle has barely deviated from Young's angle at that stage. This behavior shows nicely how first the wetting ridge grows before the whole contact region is rotated.

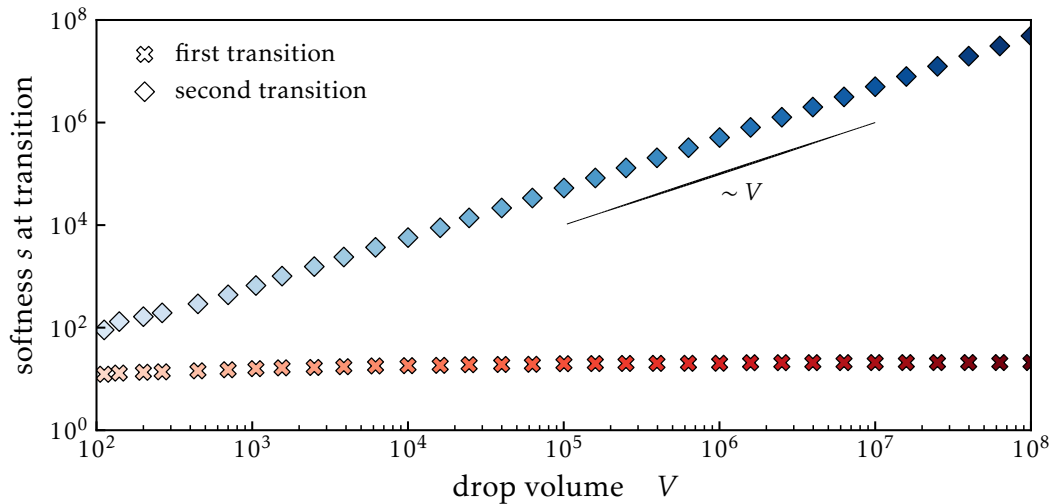
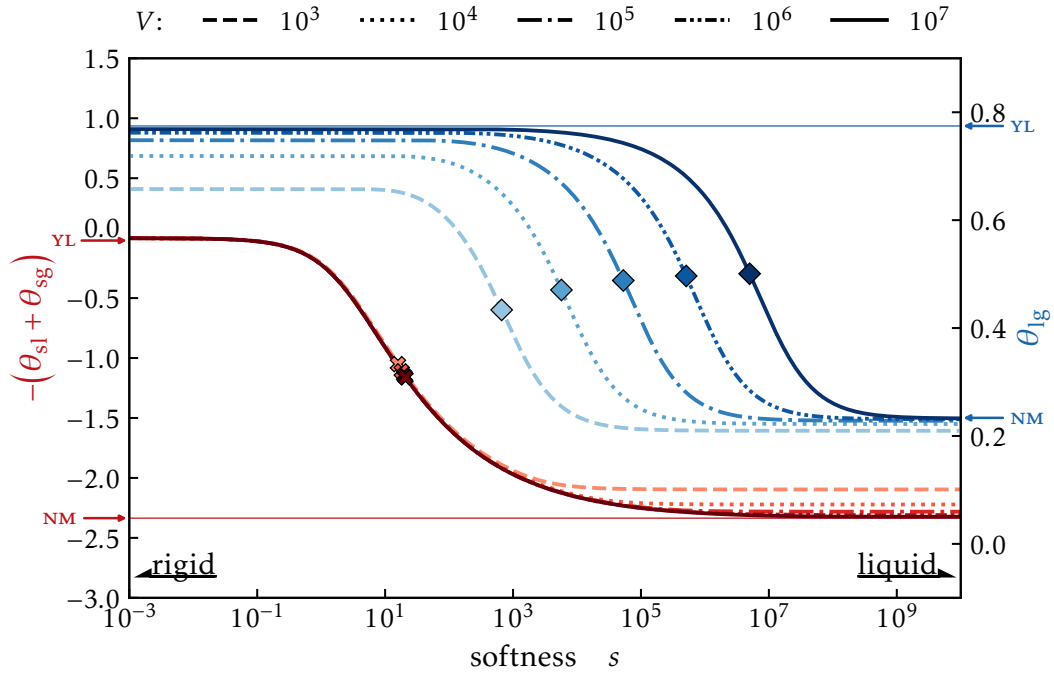


FIGURE 4.7.: The softness values where the two distinguished transitions occur are shown in dependence of the drop volume. The transition values are determined as the values where the respective angle is $\theta = (\theta_{\max} - \theta_{\min})/2$ (cf. Fig. 4.6). A linear dependence on the drop volume is clearly visible for the second transition.

with

$$B = \frac{\lambda + \sqrt{1 + \sigma}}{\sqrt{1 + \sigma} \cosh\left(\frac{\lambda}{\sqrt{\sigma}}\right) + \sqrt{\sigma} \sinh\left(\frac{\lambda}{\sqrt{\sigma}}\right)}. \quad (4.7)$$

In the mesoscopic model this picture is somewhat disturbed by the presence of the adsorption layer, constituting an other independent length scale.

The systematic occurrence of the transitions in dependence of the drop volume is further examined in Fig. 4.6 where the angles θ_{lg} and $\theta_{sl} + \theta_{sg}$ are shown as functions of s for six different volumes. The location of the first transition ($\otimes$ symbols) at $s \approx 10$ is clearly independent of drop volume. The location of the second transition ($\diamond$ symbols), however, shifts towards higher softnesses as the droplet volume increases. The term *transition location* refers to the value of s where $\theta = (\theta_{\max} - \theta_{\min})/2$ is reached. To quantify the tendencies of the transitions, the corresponding softnesses are plotted against the drop volume in Fig. 4.7. Indeed, the second transition position is found to increase linearly with drop volume, i.e., $s \sim V$, in agreement with the full elastic theory [Lub+14].

Finally, let's return to Fig. 4.6 and inspect the asymptotic values of the contact angles in the rigid and quasi-liquid limits again. It appears, that for large volumes the limiting angles are independent of drop size and these values perfectly agree with the predictions via Young's (YL) and Neumann's (NM) laws as indicated by the blue and red arrows in Fig. 4.6 for θ_{lg} and $\theta_{sl} + \theta_{sg}$ respectively. For smaller drops, however, an increasing deviation from these macroscopic predictions is observed which reflects the mesoscopic character of the model, i.e., the modeling of wettability using a wetting potential and the resulting diffuse contact region. However, macroscopic results of elastic wetting are correctly captured when drops are much larger than the thickness of the adsorption layer.

4.3. VIOLATION OF NEUMANN'S LAWS

Above it was stated, that Neumann's laws are not affected by elasticity aside of the Shuttleworth effect. It was found, however, that the softness of the substrate causes the contact region to rotate as a whole. Since Neumann's laws only relate the angles to each other and not to a specific horizon of definition, the latter can be arbitrarily chosen. Consequently, a rotation of the reference frame is not meant to affect its validity. Once the contact angles are known, i.e., measured, the validity of Neumann's

laws can be checked by calculating the errors

$$e_v = |\sigma\theta_{sl} + [1 + \sigma]\theta_{sg} - \theta_{lg}|, \quad (4.8a)$$

$$e_h = |\sigma\theta_{sl}^2 + \theta_{lg}^2 - [1 + \sigma]\theta_{sg}^2 + 2f(h_a)|. \quad (4.8b)$$

In Fig. 4.8 the errors e_v and e_h are plotted as dots (●) against the substrate softness. While the horizontal Neumann's law fits reasonably well in the rigid and liquid limit, a clear violation is visible in the intermediate elasticity regime. The situation is even worse for the vertical law, showing immense errors as the softness decreases. Beyond that, even for very rigid substrates there is always a wetting ridge present, albeit a tiny one, such that the angles θ_{sl} and θ_{sg} are always well defined and not zero. In the mesoscopic picture, however, both these arguments do not hold anymore, since the contact region is smoothened out over a range $\sim h_a$. In Fig. 4.9 the numerically obtained profiles are displayed as colored areas for $s = 10^7$, $\sigma = 0.1$ and $V = 10^7$ and compared to the analytic solution (3.104) visualized by black dashed lines. While both profiles seem to match quite well on a large scale $\gg h_a$ the inset clearly shows the deviation of the smoothened mesoscopic contact region from the sharp edge of the macroscopic wetting ridge tip. Consequently, the angles have to

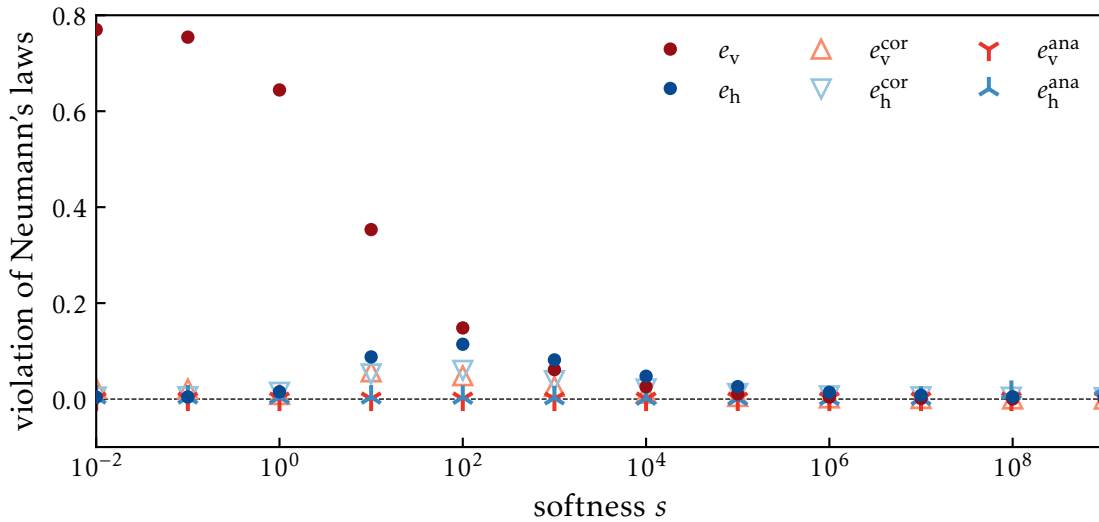


FIGURE 4.8.: Violation of Neumann's laws as derived in the mesoscopic long-wave limit (3.73) for different substrate softnesses. The dots (●) display the errors of the vertical (red) and horizontal (blue) laws, using the mesoscopic angles measured at the deflection points of the numerically obtained profiles, with $V = 10^7$ and $\sigma = 0.1$. The horizontal law agrees very well with the measured angles aside of the intermediate elasticity regime, while the vertical law shows increasing violation as the rigid limit is approached. Both can be corrected by considering elastic forces as indicated by the triangles (Δ , ∇). The angles can also be calculated more precisely from the analytic solutions if e.g. θ_{lg} and R are known, as shown by the (Υ , λ)-symbols.

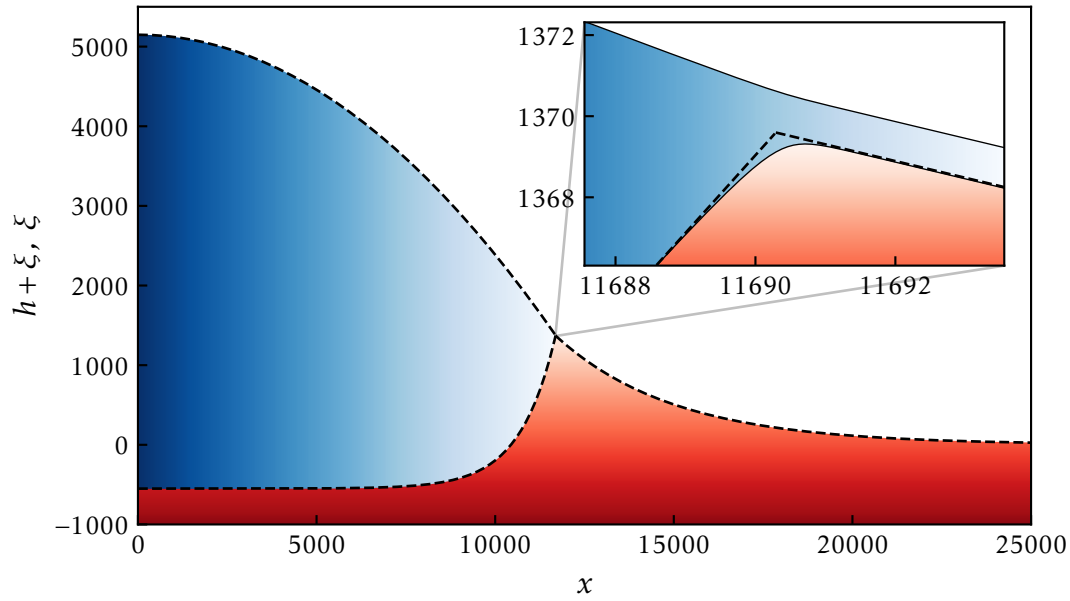


FIGURE 4.9.: Comparison of the numerically obtained solution of the mesoscopic model (colored areas) with the corresponding analytic solution in the long-wave limit (black dashed) for $V = 10^7$, $\sigma = 0.1$ and $s = 10^7$. On the large scale $\gg h_a$ both agree quite well, though, the inset shows how the mesoscopic model differs from the macroscopic one by the smoothed contact region, which complicates the definition of the contact line position and the associated angles.

be measured from the profiles, in this case from the slope of the profiles at the deflection points, and are therefore underestimated in general. This error increases the smaller the wetting ridge becomes as compared to the contact region, i.e., with the ratio h_a/ℓ_{ec} . Further, the adsorption layer sets a lower bound below which the wetting ridge is macroscopically *absent*. As the wetting ridge height falls below the adsorption layer height $\ell_{ec} < h_a$, the solid contact angles become very small and the horizontal Neumann's law becomes Young's law, which is fulfilled in the rigid limit. For the vertical Neumann law there is no such equivalent as mentioned in Sec. 3.2.2, resulting in a huge unbalance as the rigid limit is approached, which is why the Lagrange multiplier λ is needed. The latter is technically not a part of the mesoscopic model anymore, but might be identified as the elastic forces, which in the rigid limit are arbitrarily strong. The argument why elasticity does not contribute to Neumann's laws was, because the contact line is reduced to a single point in the macroscopic picture such that the integrals over the elastic surface stress vanish. In the mesoscopic picture, where the contact region as a spatial extension they might give considerable contributions to the force balance though, i.e., by integrating from one deflection point to the other. Note, that there should also be an elastic contribution in the horizontal Neumann law, emerging from the Hamilto-

nian [Eq. (3.35)]. Introducing the corresponding corrections to the error functions defined above leads to

$$e_v^{\text{cor}} = \left| \sigma \theta_{\text{sl}} + [1 + \sigma] \theta_{\text{sg}} - \theta_{\text{lg}} + \int_{x_1}^{x_2} \frac{\xi}{s} dx \right|, \quad (4.9a)$$

$$e_h^{\text{cor}} = \left| \sigma \theta_{\text{sl}}^2 + \theta_{\text{lg}}^2 - [1 + \sigma] \theta_{\text{sg}}^2 + 2f(h_a) + 2 \left[\frac{1}{2s} \xi^2 \right]_{x_1}^{x_2} \right|, \quad (4.9b)$$

with x_1 and x_2 being the x coordinates of the two deflection points of ξ . Such a correction by integrating the surface stress over the contact region was already used, e.g., by SHANAHAN [Sha87] and WHITE [Whio3]. Considering these corrections significantly decreases the error as indicated by the triangles (Δ , ∇) in Fig. 4.8. Alternatively, the contact angles can be calculated from the analytic solution (3.104) if any two of the quantities R , θ_{lg} and κ_{lg} are known. As displayed by the (Υ , $\blacktriangleright$)-symbols in Fig. 4.8 this (semi)analytically obtained pseudo-macroscopic values nicely satisfy Neumann's laws, except for a small deviation of the horizontal balance close to the liquid limit. It should also be mentioned, that enforcing homogeneous Neumann boundary conditions, i.e., $\nabla \xi = 0$ at the boundary, may impose additional pressure to the substrate as the natural shape of the wetting ridge outside a drop is exponential in the long-wave limit. However, this effect was found to be negligible in most cases and it has an impact only in the intermediate elasticity regime and when the system boundary is very close to the contact region.

4.4. ASSESSMENT

The mesoscopic long-wave model, as introduced in Sec. 3.4.2 has been employed to investigate the double transition that occurs in the equilibrium contact angles when increasing the softness from an ideally rigid substrate towards a very soft, i.e., quasi-liquid substrate [Mar+12b, Lub+14]. Both, the dependency on softness and the scaling of the two transitions with drop volume given by that model, closely resemble the behavior observed in Ref. [Lub+14] where a full elasticity model and drops of large contact angle $\theta_Y = \pi/2$ on thick incompressible elastic layers are considered. In particular, the scaling of the typical softnesses where the two transitions occur with drop volume and the scalings of the wetting ridge height with softness in the different regimes agree very well. Beyond that, Neumann's laws for the equilibrium contact angles were found to be fulfilled close to the quasi-liquid limit despite uncertainties in the calculation of the contact angles. Even in the rigid limit a vertical equilibrium could be established if elastic forces are taken into consideration,

or the contact angles are calculated via the analytic macroscopic solutions for $h + \xi$ and ξ .

The data that support the findings of this study are openly available [[HST21b](#)].

5. VISCOELASTIC BRAKING

The results presented in this chapter have to a large extent already been published in:

[HST21a] HENKEL, C., SNOEIJER, J. H., and THIELE, U. “Gradient-dynamics model for liquid drops on elastic substrates”. In: *Soft Matter* 17 (2021), pp. 10359–10375. DOI: [10.1039/D1SM01032H](https://doi.org/10.1039/D1SM01032H)

Many of the following figures were reproduced and adapted from the data presented in this reference.

Besides the statics of sitting drops, the wetting ridge further noticeably influences the dynamics of moving contact lines. A rather prominent consequence is the so called *viscoelastic braking*, describing the decreasing speed of a moving contact line with increasing softness of the substrate, due to increased dissipation within the latter. This effect was already investigated by CARRÉ and SHANAHAN [CGS96, CS01] and LONG, AJDARI & LEIBLER [LAL96], followed up in recent years in Refs. [CK20, Kar+15, Gor+20]. New phenomena were discovered, such as intricate dependencies of sliding velocity on substrate thickness [Zha+18] and stretching [Smi+21], as well as effects of free polymer chains that can be present in the substrate [Hou+17]. Besides slowing down the contact line, the wetting ridge can also cause complex periodic *stick-slip* motion [Kaj+13, Kar+15, Gor+18]. In this section the impact of viscoelastic braking on the spreading of a droplet is investigated.

Any motion of the contact line results in the displacement of the wetting ridge and thus induces a time-dependent deformation of the substrate. Owing to the viscoelasticity of the latter, this provides an additional source of dissipation that slows down the dynamics. It is now to be verified whether this viscoelastic braking is correctly accounted for by the mesoscopic long-wave model as introduced in Sec. 3.4.2. In that, the cases of partially wetting liquid and completely wetting liquid are regarded separately. A completely wetting liquid can be realized by switching the sign in front of the long-range contribution to the wetting energy [Eq. (3.67)], resulting

in a strictly repulsive disjoining pressure. The spreading is analyzed using direct time simulation of Eqs. (3.65) with (3.75). Note, that the reflection symmetry in x -direction w.r.t. the drop center is used in the following such that only one half of the drop is solved for using homogeneous Neumann boundary conditions. Crucial for interpretation of the results is the understanding and distinction of the parameters τ and s . While the softness s played a major role in the characterization of the substrate deformation below a steady drop in Chap. 4, it is rather viewed as a static quantity and as such assumed to be relevant only for the long term behavior. The parameter τ in contrast represents either a ratio of viscosities or a ratio of characteristic time scales divided by the softness s according to Eqs. (3.76). Hence, changing the softness s at fixed τ effectively also changes the characteristic Kelvin-Voigt time scale T_{KV} but leaves the ratio of viscosities unaffected. Being a Kelvin-Voigt material an excitation of the solid at slower time scales evokes a nearly elastic response, while at faster timescales the solid behaves highly dissipative. In other words, the larger τ is the higher is the viscosity (assuming fixed s) and thus the dissipation and the slower is the response of the solid substrate in turn.

5.1. PARTIAL WETTING

As initial condition the drop was approximated by a parabolic cap on a flat substrate with an initial contact angle that is three times greater than the equilibrium value resulting from Young's law, i.e., $\theta_{ini} = 3\theta_Y = 3\sqrt{3/5}$. The initial drop height is $h_{max} = 1000$, i.e., three orders of magnitude larger than the adsorption layer height $h_a = 1$. Typical time evolutions at intermediate softness $s = 10^2$ and $s = 10^4$ are shown in Fig. 5.1. Given that the initial contact angle is larger than its equilibrium value, the disjoining pressure will drive a flow of liquid towards the contact line, consequently inducing a motion of the latter towards equilibrium, as visible in Fig. 5.1 (a) and (c). The corresponding evolution of the wetting ridge is better visualized in Fig. 5.1 (b) and (d). At the very beginning, shortly after *releasing* the steepened drop, a ridge is growing out of the initially flat substrate and subsequently moves along with the contact line. This behavior closely resembles that observed in experiments [Gor+20]. The corresponding dissipations in the liquid and in the substrate are reported, respectively, in Fig. 5.2 (a) and (b) for $s = 10^2$. In both layers the largest dissipation is located near the contact line. It turns out that the magnitude of the dissipation peak at the contact line is larger inside the solid than in the liquid, for this particular set of parameters, showing that the substrate dissipation dominates over liquid dissipation. This is the viscoelastic braking effect

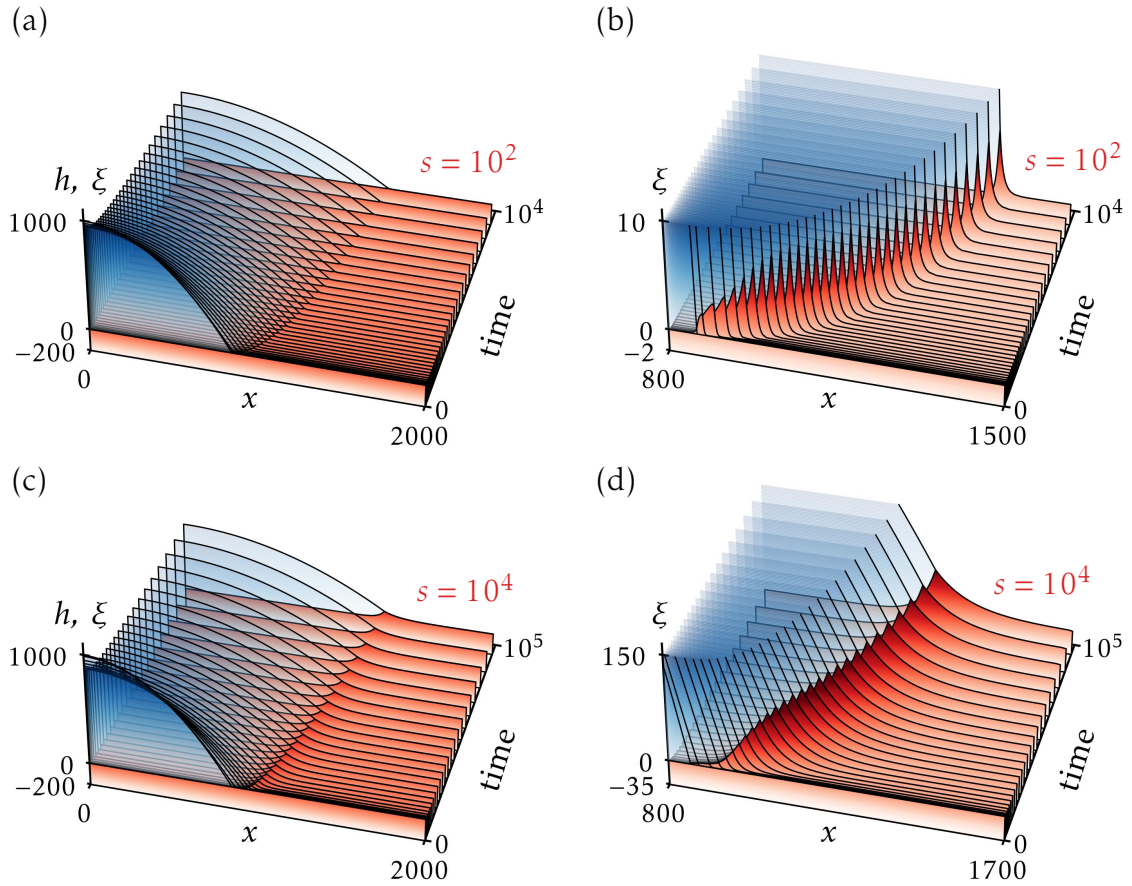


FIGURE 5.1: Shown are the profiles of a drop of partially wetting liquid spreading on elastic substrates of different softness obtained from the direct numerics. Panels (a) and (c) provide overviews of the whole time evolution with softnesses $s = 10^2$ and $s = 10^4$, respectively, while panels (b) and (d) show zooms into the corresponding contact regions. The remaining parameters are $D = 2000$, $V \approx 10^6$, $\tau = 1$ and $\sigma = 0.1$. Note, that the precursor layer has been hidden in favor of clarity. A corresponding time evolution can be seen in HeSH2021-SupplMat-Video02-figo7.mp4 of the electronic supplementary material of Ref. [HST21a].

we were looking for and that will be quantified in detail below. A common way to characterize dynamic wetting is via the dependence of the (dynamic) liquid-gas contact angle θ_{lg} on the contact line velocity v . To extract this information from the simulations the estimated macroscopic contact line position x_c , and the resulting velocity $v = dx_c/dt$, are traced during the spreading process. As discussed in App. B.1 there are many different ways of defining x_c in the mesoscopic picture.¹ Here, we determine x_c as the intersection point of the tangent to the liquid-gas interface at

¹In Ref. [CK20] the intersection of the tangent to the deflection point of the liquid profile with $z = 0$ was used to predict certain rather subtle differences in the $x_c(t)$ -dependence of the spreading of partially and completely wetting liquids on softness. This method is quite unreliable, however, as it entirely ignores the local geometry (see discussion in App. B.1). Here, the same method was used to only consider the dependence of dynamic contact angle on contact line speed dx_c/dt where it provides robust results.

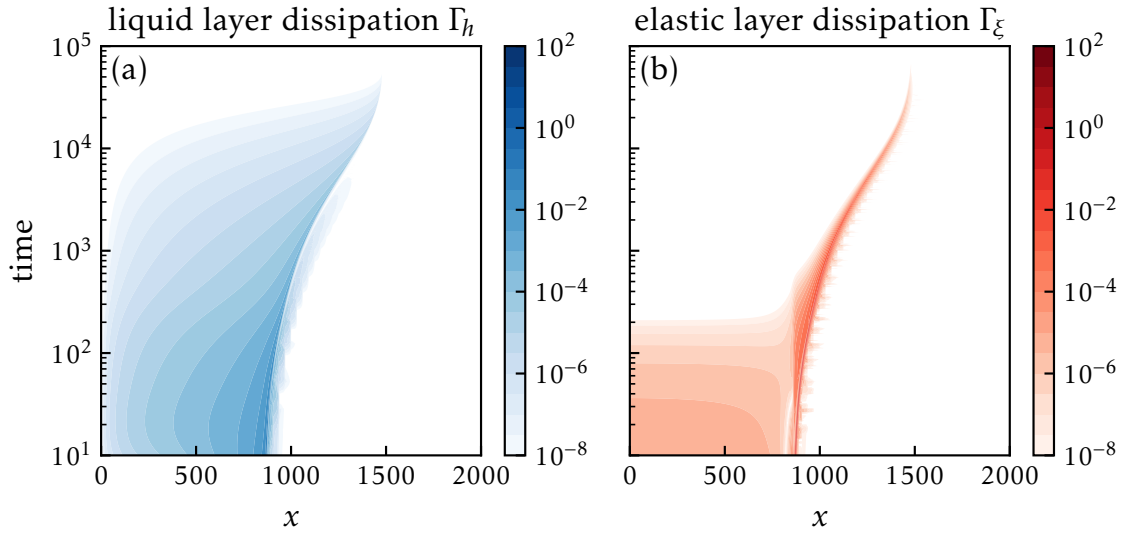


FIGURE 5.2.: Temporal evolution of the spatially resolved dissipation in the liquid (a) and the substrate (b) of a spreading drop of partially wetting liquid at intermediate softness $s = 10^2$. The dissipation in both, liquid as well as solid, is particularly strong near the contact region. The remaining parameters are as in Fig. 5.1.

the position of its steepest slope with the reference flat liquid-elastic interface at $z = 0$. Other, more precise methods have also been tried, yet the resulting differences in terms of the contact line speed dx_c/dt were found to be negligible and the influence on the qualitative behavior even more so. Figure 5.3 presents the resulting dynamic liquid contact angles, for different softness (varying s) and different degrees of substrate viscoelasticity (varying τ). More precisely, the difference in the liquid-gas contact angle with respect to its equilibrium value, $\Delta\theta_{lg} = \theta_{lg}(t) - \theta_Y$, is reported as a function of the contact line velocity $v = dx_c/dt$. In all cases there is an extended regime of proportionality $\Delta\theta_{lg} \sim v$ where the change in contact angle is linearly related to the contact line velocity. Such a linear dependence is indeed expected here. The liquid dynamics is governed by Stokes flow, for which the dynamic contact angle in partial wetting is linear with velocity [Dus79, Thi+01, Bon+09]. Similarly, a Kelvin-Voigt solid (as is used here), will give a linear dependence of the dynamic contact angle [Kar+15]. We remark that in experiments, the exponent is much lower than unity, with typical values around 0.5. This is because the dynamic contact angle inherits the scaling of the loss modulus. For the Kelvin-Voigt model this is linear in frequency but crosslinked polymer networks typically exhibit smaller exponents [AS20]. Yet the relative roles of liquid and solid dissipation are still to be disentangled. Fig. 5.3 (a) corresponds to a very small value of τ , so that the solid very quickly adapts to any changes in the stress exerted by the liquid. Apparently, the spreading dynamics is completely independent of the softness s in this

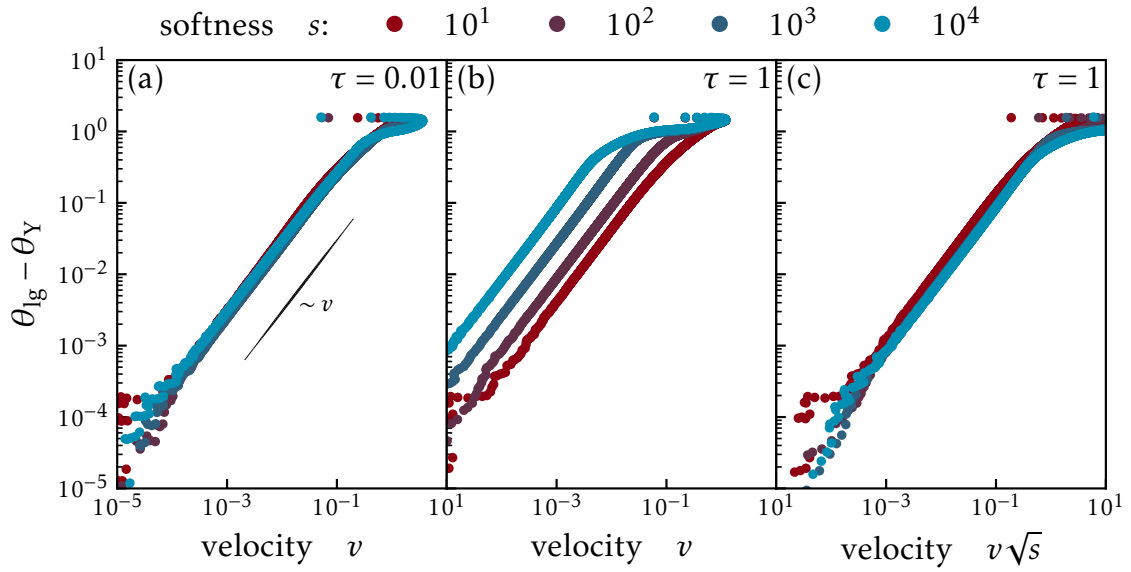


FIGURE 5.3.: Dynamic contact angle, characterized as $\Delta\theta_{lg} = \theta_{lg}(t) - \theta_Y$, over contact line velocity $v = dx_c/dt$. (a) Result for fast relaxation of the substrate ($\tau = 0.01$), for which the spreading dynamics is hardly affected when varying the softness s . The spreading dynamics is governed by dissipation in the liquid. (b) Result for slow relaxation of the substrate ($\tau = 1$), for which the spreading dynamics is strongly affected when varying the softness s . (c) Same data as in (b), but using the rescaled velocity $v\sqrt{s}$ (see text for motivation). The collapse of data shows that the dynamic angle is entirely governed by the solid dissipation, which is the hallmark of viscoelastic braking. The indicated power laws are discussed in the main text.

case, implying that the substrate has no influence on the spreading, in spite of the presence of a wetting ridge. Indeed, at very small τ the solid's response is nearly instantaneous, which corresponds to a perfectly elastic limit where there is no dissipation inside the substrate. By contrast, for larger values of τ the softness plays an important role, as seen in Fig. 5.3 (b). Softer substrates (larger s) give a larger departure from the equilibrium angle. This indeed is a signature of the viscoelastic braking effect: for a given value of $\theta_{lg} - \theta_Y$, the contact line velocity is lower on softer substrates. To verify whether the substrate dissipation indeed dominates over liquid dissipation, the same data is attempted to be collapsed using a characteristic velocity of the substrate. Following Refs. [Kar+15, AS20], this velocity is given by the ratio ℓ_{ec}/T_{KV} , which in the present scaling implies a dependence on softness as $\sim 1/\sqrt{s}$. Figure 5.3 (c) therefore shows the dynamic contact angle plotted against the rescaled dimensionless substrate velocity $v\sqrt{s}$: the data now collapses, confirming that the spreading dynamics is indeed completely governed by the substrate's viscoelasticity.

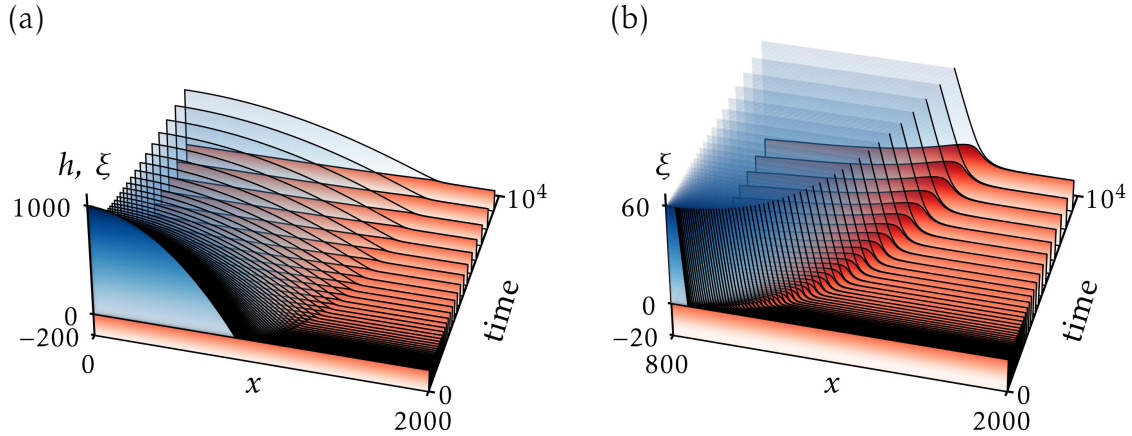


FIGURE 5.4.: Shown are the profiles of a drop of completely wetting liquid spreading on an elastic substrate of softness $s = 10^2$, obtained from the direct numerics. Panel (a) provide an overview of the whole time evolution, while panels (b) show a zoom into the contact regions. Note, that the wetting ridge is way less pronounced and rather smeared out as compared to the partial wetting case. The remaining parameters are as in Fig. 5.1 and also the precursor layer has been hidden again. A corresponding time evolution can be seen in HeSH2021-SupplMat-Video03-fig09.mp4 of the electronic supplementary material of Ref. [HST21a].

5.2. COMPLETE WETTING

The case of a completely wetting fluid can be analogously treated, by using a positive instead of the negative sign in the wetting energy (3.67). A corresponding typical time evolution is displayed in Fig. 5.4, using the exact the same initial conditions before. At early times, the dynamics is very similar to that of the partially wetting case. The liquid starts to spread and a ridge is pulled out of the initially flat solid, it remains quite small though. Owing to the complete wetting, however, the drop does not approach a steady shape of finite equilibrium angle, but continues spreading instead. During this process the wetting ridge gradually decays, cf. Fig. 5.4 (b), in contrast to the growth observed under partial wetting conditions. A trend that is attributed to the continuous decrease of the contact angles during spreading, which diminishes the upward pulling force of surface tension. In consequence, the dissipation in the substrate decays more rapidly than the dissipation in the fluid, as seen in Fig. 5.5 (a) and (b).

Fig. 5.6 shows the dynamic contact angle θ_{lg} against the spreading velocity v for various softness s and $\tau = 1$. While the strong viscoelastic braking under partially wetting conditions results in a clear shift of the curves, the complete wetting case, by contrast, shows no such significant dependence and only a slight shift indicates that viscoelastic braking is present at all. This reflects the observations in Fig. 5.5, where only a comparatively small and soon decaying wetting ridge is found. The observed

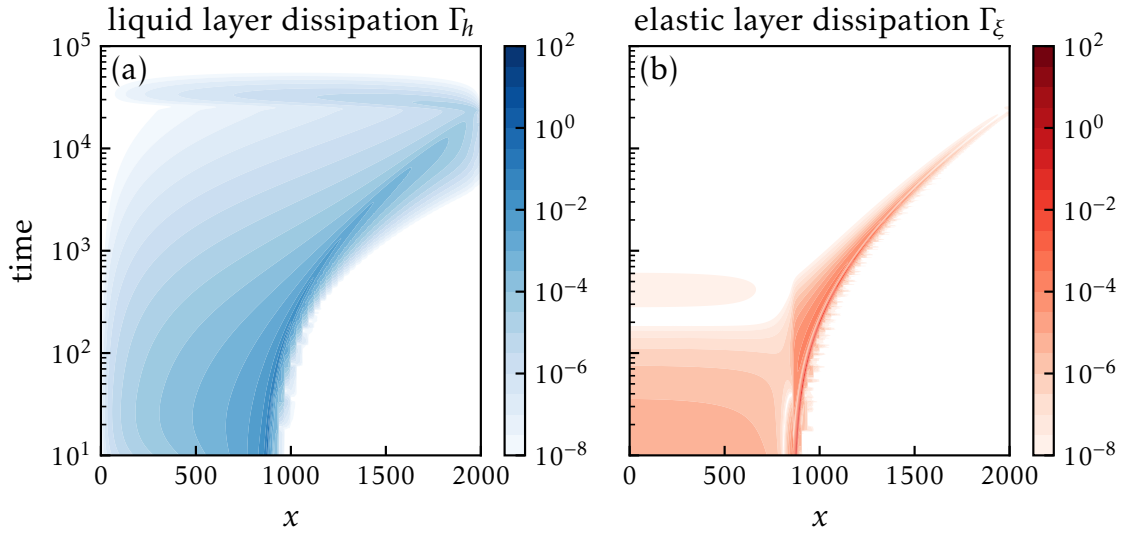


FIGURE 5.5.: Temporal evolution of the spatially resolved dissipation in the liquid (a) and the substrate (b) of a spreading drop of completely wetting liquid at intermediate softness $s = 10^2$. The dissipation in both, liquid as well as solid, is particularly strong near the contact region but more smeared out as compared to the partial wetting case. The remaining parameters are as in Fig. 5.1.

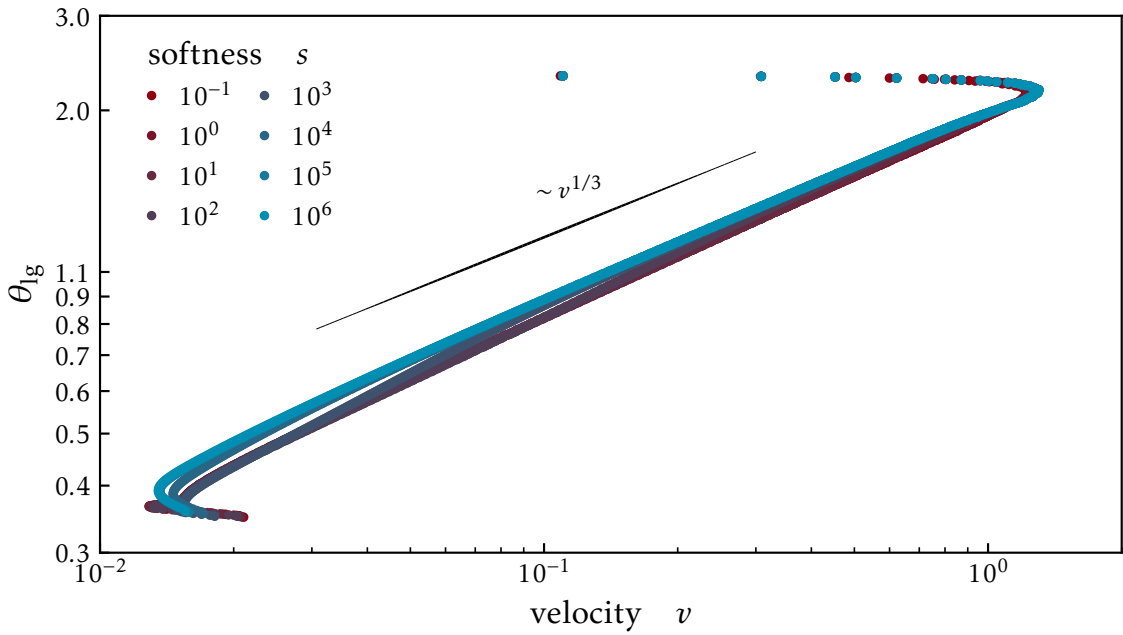


FIGURE 5.6.: For the completely wetting case the spreading dynamics is characterized by the dependency of the dynamic contact angle θ_{lg} on the contact line velocity $v = dx_c/dt$. Results are given for different softness s as given in the legend. Apparently, the softness of the substrate barely affects the spreading process, what so ever, and the dependency of the contact angle obeys the Tanner-Cox-Voinov relation for viscous spreading. The remaining parameters are as in Fig. 5.4.

relation for the dynamic angle is consistent with the scaling $\theta_{lg} \sim v^{1/3}$, which is the classical *Tanner-Cox-Voinov relation* [Tan79, Bon+09] for viscous spreading under complete wetting conditions. It can thus be concluded that the softness of the substrate has minor, if any, impact on the spreading of drops in the limit of complete wetting.

5.3. ASSESSMENT

As in the previous chapter the mesoscopic long-wave gradient dynamics model, as introduced in Sec. 3.4.2, has been employed here to investigate the spreading of a single drop of partially or completely wetting liquid on elastic substrates. Dependencies of the dynamic contact angle on contact line velocity have been studied for different softness. In the partial wetting case different scales could be introduced that allow to collapse sub-sets of curves, depending on the time scale ratio between elastic and liquid dynamics. This rescaling roots directly in the considerations in Refs. [Kar+15, AS20] and indicates, that the dissipation in the substrate is dominant and increases with softness, i.e. that viscoelastic braking is present [CGS96, CS01]. Beyond that, the simplicity of the model allows to also investigate the case of completely wetting liquids and it was found that viscoelastic braking is present in there as well, in contradiction to Ref. [CK20]. However, this effect is rather small and such is the shift between the curves for dynamic contact angles (Fig. 5.6) due to the less distinctive wetting ridge. In the end, viscoelastic braking was found to be negligible in the completely wetting case and consequently the classical Tanner-Cox-Voinov relation has been correctly recovered by the model.

The data that support the findings of this study are openly available [HST21b].

6. DROPLET COARSENING

The results presented in this chapter have to a large extent already been published:

[HST21a] HENKEL, C., SNOEIJER, J. H., and THIELE, U. “Gradient-dynamics model for liquid drops on elastic substrates”. In: *Soft Matter* 17 (2021), pp. 10359–10375. DOI: [10.1039/D1SM01032H](https://doi.org/10.1039/D1SM01032H)

Many of the following figures were reproduced and adapted from the data presented in this reference.

Up to this point, we have only ever considered single droplets, evolving undisturbed on a substrate of their own. Yet, in every day life we frequently observe droplets appearing in ensembles, dense patterns even. Think, for example, of a window facing outwards into the rain, or the lid of a pot on which water vapor condenses during cooking. In both these scenarios an other prominent phenomenon can be observed, namely the merging of smaller drops into larger ones, resulting in a *coarsening* of the pattern. When an ensemble of drops coarsens the average drop size and distance increase in time while their number decreases. This may occur at overall fixed liquid volume [LGo3] or involve condensation (and evaporation) [FKB91]. In any case, the underlying elementary process is the merging of two (and sometimes more) drops into one. For such, there exist two basic mechanisms, in the following referred to as *coarsening modes*:

MASS TRANSFER MODE: The transport of material occurs from one droplet to the other(s) without any lateral movement of the droplets themselves. The mass flux is always directed from smaller drops towards larger ones (guaranteeing coarsening) due to the difference in Laplace pressure between them until the smaller drops vanished. This transport can take place via different channels. It may occur via the vapor phase (for volatile liquids) or through an ultra thin adsorption layer (for nonvolatile, partially wetting liquids). In the literature this coarsening mode is also referred to as volume mode, (drop) col-

lapse mode, diffusion-controlled ripening, or Ostwald ripening [PP04, GW05, Gla+09, Dai10].

TRANSLATION MODE: The entire drops remain constant in size, that is volume, and migrate toward each other until their contact lines touch and they coalesce. Once the drops are in contact with each other the merging process is extremely fast and barely followed by the naked eye. This mode is also referred to as collision, coalescence, or migration mode in the literature [PP04, GW05, Gla+09, Dai10].

Sketches of mass transfer and translation modes can be found in Ref. [Gla+09] or Fig. 6.1 and their relation to the translation symmetry mode for single fronts or contact lines in a homogeneous system is discussed in section 3.4 of Ref. [Thio7]. Coarsening via Ostwald ripening is often considered dominant against translational coarsening. However, for the dewetting process of a liquid film on a rigid substrate, Refs. [GW05, Gla+09] find that, in contrast, there exist extended parameter regions

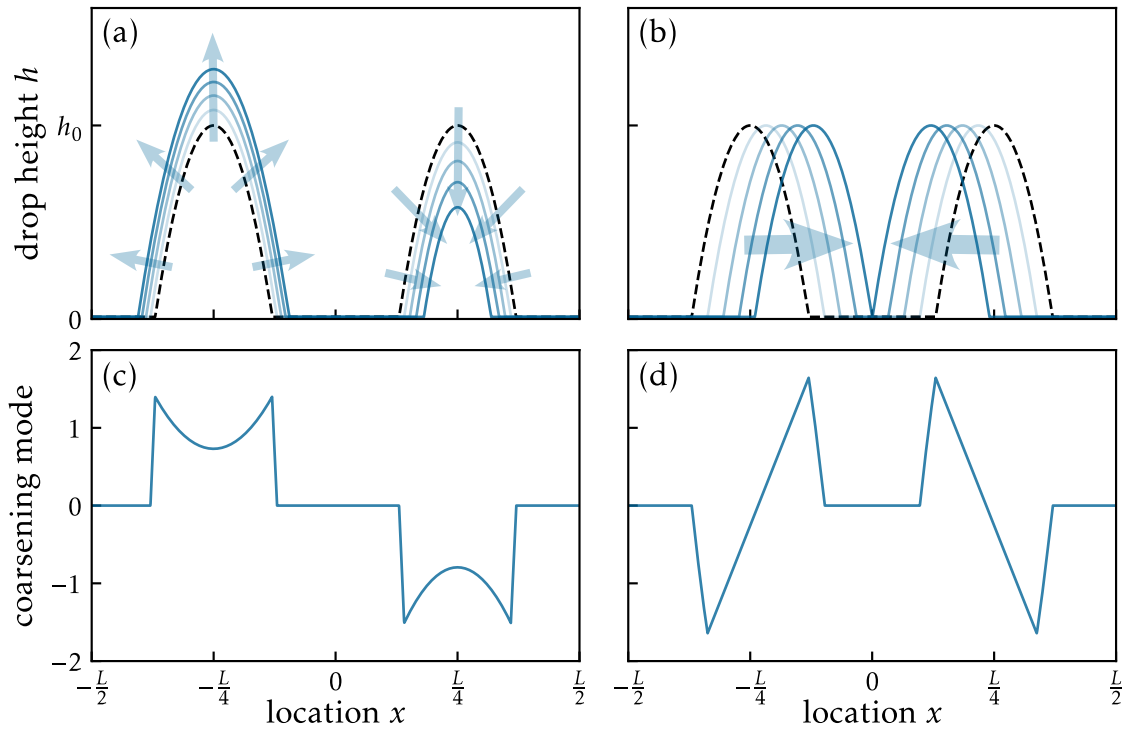


FIGURE 6.1.: Schematic visualization of two droplet coarsening via Ostwald ripening (left) and translation (right) on a rigid substrate. Panels (a) and (b) respectively show the time evolution of the liquid layer profiles (indicated by the arrows and with darker shades of blue referring to later times) starting from a state of two equally sized separated drops (black dashed lines). Panels (c) and (d) show the associated normalized modes, i.e., the eigenvector equivalents, reflecting the local change of the (initial) profile in time.

where coarsening by migration dominates. Further both coarsening modes may be stabilized by substrate heterogeneities which gives rise to intricate bifurcation behavior [Thi+03]. In most cases, both modes contribute to the coarsening process in a mixed manner [PP04, GW05] and can thus barely be distinguished in the resulting scaling laws that describe the continuously growing mean size and mean distance in coarsening drop ensembles. For the most common cubic mobility function (resulting from no-slip boundary conditions at the solid substrate as discussed in Sec. 2.2.4 and [ODB97, MWW05]) the scaling laws for the two modes only differ by a logarithmic factor [Gla+09]. Ref. [GW05] shows, that the translation mode for drops on a one-dimensional solid substrate becomes more prevalent with increasing mean drop size and decreasing mean drop distance until it finally dominates beyond a certain threshold (cf. Fig. 15 of Ref. [GW05] and also Refs. [GW03, Gla08]). Below the threshold, only the mass transfer mode is found active. The coarsening behavior of liquid drops is further noticeably influenced by the rheological properties of the substrate, i.e., the presence of a wetting ridge. Depending on the substrate layer thickness and softness the wetting ridge may develop local depressions on both sides which counteract coarsening by droplet translation and can even result in an effective repelling force between them, also referred to as the *inverted Cheerios effect* [Kar+16].

In this chapter the simple gradient dynamics model as introduced Sec. 3.4.2 is employed to study drop coarsening on soft substrates. A very similar model has been used before in Ref. [LL20] to investigate the coarsening of two drops on elastic substrates under the influence of condensation. In particular, the influence of substrate softness on the coarsening process, that is the activity of the coarsening modes, is investigated on the example of both, two drops and large drop ensembles. Note, that in this all the simulations were performed on an average standard working station, where handling even large drop ensembles is enabled by the efficient adaptive time stepping and mesh refinement routines provided by `oomph-lib`.

6.1. TWO-DROP COARSENING

Before moving to large ensembles of let us first investigate the dynamics of an individual coarsening step. Consider two steady parabolic drops of identical volume V that are placed at a distance L_0 (between the contact lines) on an initially flat but soft substrate. Their contact angle is set to equilibrium value in the corresponding rigid limit, i.e., to Young's angle $\theta_{lg} = \theta_Y$. Due to equal volume of the two drops this initial condition is considered steady yet unstable with regard to Ostwald ripen-

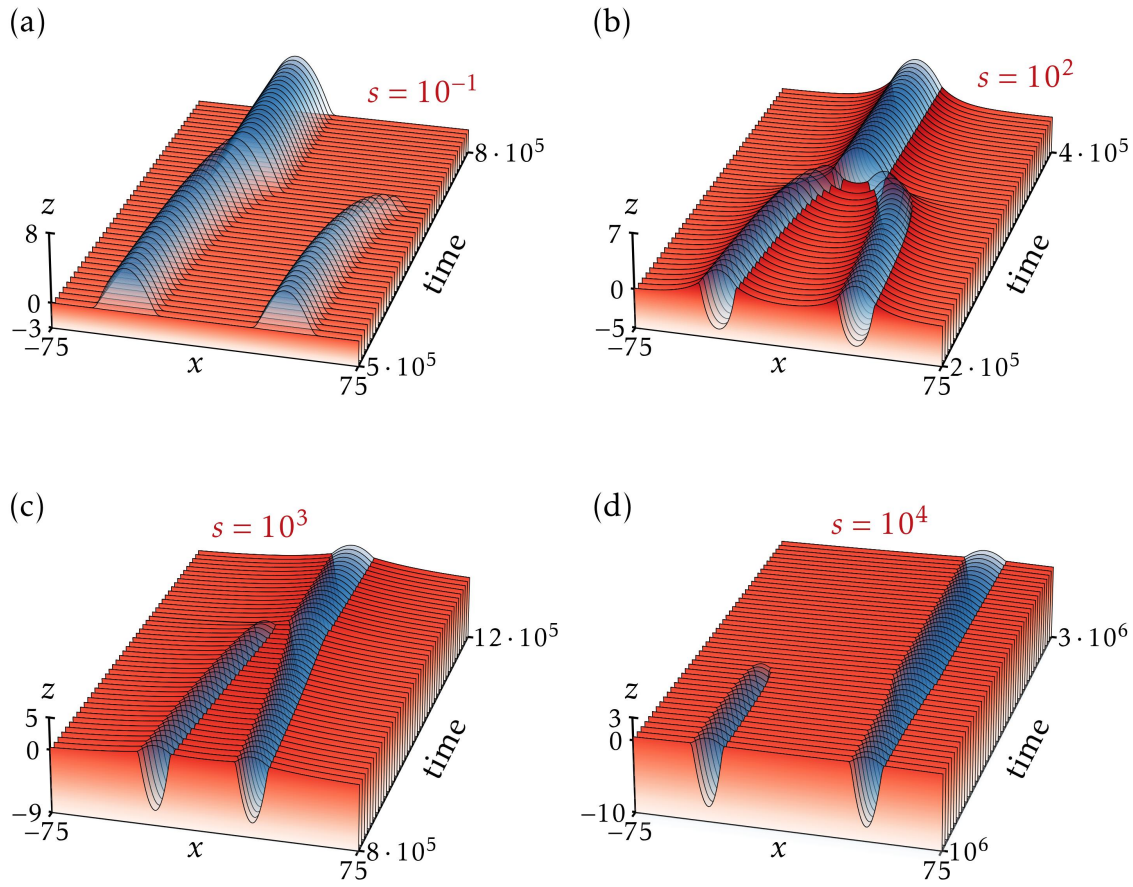


FIGURE 6.2.: Shown are waterfall representations of the coarsening dynamics of two drops of partially wetting liquid into a single drop. The softness increases from (a) $s = 10^{-1}$ in the rigid limit, via (b) $s = 10^2$ and (c) $s = 10^3$ (intermediate elasticity) to (d) $s = 10^4$ (quasi-liquid limit). With increasing softness the dominant coarsening mode changes. The volume of each drop is initialized as $V = 100$, the distance of their inner contact lines as $L_0 = 50$ and the domain size is $D = 400$. The remaining parameters are as in Fig. 5.1. The corresponding time evolutions can be seen in (a) HeSH2021-SupplMat-Video04-fig11.mp4, (b) HeSH2021-SupplMat-Video05-fig11.mp4, (c) HeSH2021-SupplMat-Video06-fig11.mp4 and (d) HeSH2021-SupplMat-Video07-fig11.mp4 of the supplementary material of Ref. [HST21a].

ing. This state is then initially perturbed using small amplitude (below precursor height) white noise to slightly break the reflection symmetry about the center $x = 0$. Typical time evolutions for selected softnesses s at fixed $V = 100$ and $L_0 = 50$ are represented in Fig. 6.2 in the form of waterfall plots. In all cases, the substrate-liquid interface initially relaxes till about $t = \mathcal{O}(10^2)$, i.e., the drops sink into the soft substrate. Note, that in Fig. 6.2 this initial relaxation is not shown and that the precursor has been hidden in favor of improved clarity. The amount of sinking, i.e., the size of the depression in the substrate, and the size and height of the developing wetting ridge all depend on softness (cf. Chap. 4). Then, multiple order of magnitude later, the coarsening process sets in on a much larger time scale. Depending on the softness, it is mostly found within the period of $t = 10^5 \dots 10^7$. From Fig. 6.2

it seems that the coarsening process qualitatively changes with softness in a non-monotonic manner. In panels (a) and (d), respectively corresponding to the rigid and quasi liquid limits, the droplets exchange volume with minor or without lateral translation, at least not towards each other, i.e., via Ostwald ripening. Panels (b) and (c), which correspond to the intermediate elastic regime, clearly exhibit a lateral movement of the drops towards one another by contrast, i.e., here the translation mode is active. In Fig. 6.3 snapshots of the liquid-gas and substrate-liquid profiles are shown shortly before completion of the coarsening process for different substrate softness, increasing from panel (a) to (b), using the same data as presented in Fig. 6.2. With Eqs. (2.46) and (2.52) the velocity field within the liquid is reconstructed and displayed as stream lines with the color indicating the absolute veloc-

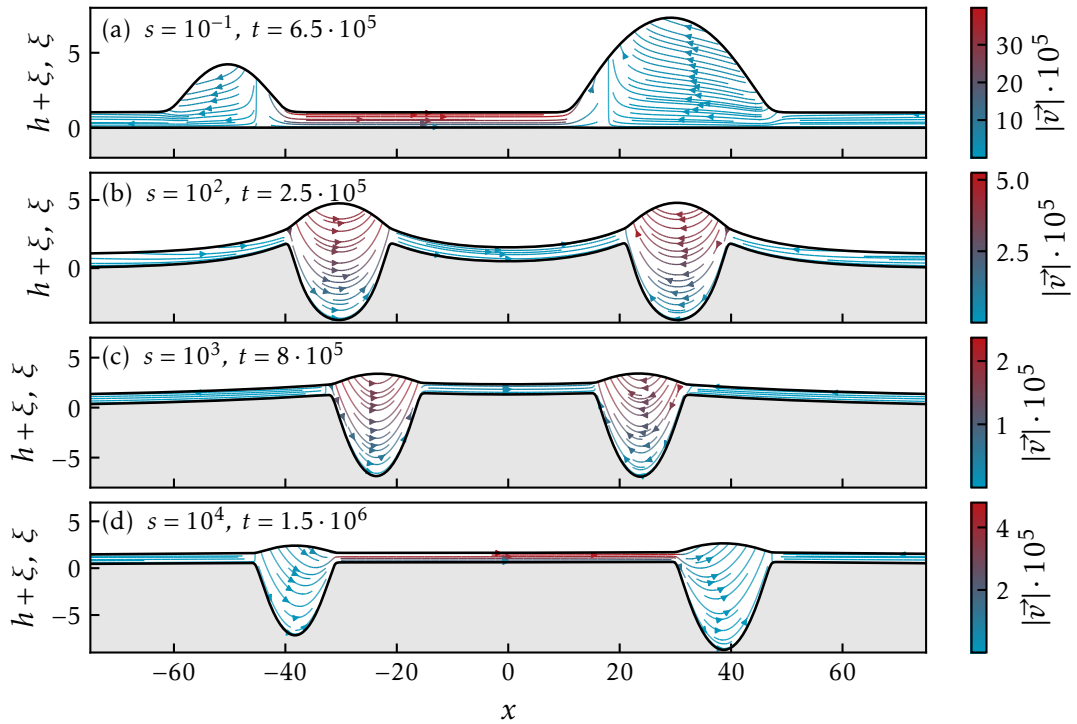


FIGURE 6.3.: Profiles $h + \xi$ and ξ of the liquid-gas and substrate-liquid interfaces shortly before coarsening for different substrate softness, increasing from panel (a) to (d). Within the liquid the velocity field was recovered using Eqs. (2.46) and (2.52) and plotted as streamlines, with the color indicating the total velocity $|\vec{v}|$. In the rigid and quasi-liquid limit, respectively displayed in the panels (a) and (b), the substrate profile between the drops is flat and high fluxes through the adsorption layer are visible, indicating coarsening via volume Ostwald ripening. At intermediate elasticity [panels (b) and (c)] the flow is highest within the drops and causes a drift of the latter towards each other, i.e., driving translational coarsening. This points towards a transmission of forces via the curved substrate profile ξ , i.e., the inverted Cheerios effect. This plot is created from the same data as Fig. 6.2.

ity $|\vec{v}|$, i.e., red refers to high velocities and blue to low velocities. In the rigid and quasi-liquid limit, respectively displayed in panels (a) and (d), the substrate profile ξ is flat between the drops and high fluxes (red) through the adsorption layer are clearly visible. These fluxes transport mass from the smaller drop to the larger one and reflect the coarsening via Ostwald ripening. Note, that the flux in Fig. 6.3(a) is asymmetric with respect to the drop center, resulting in a joint drift of both drops, as already observed in Fig. 6.2(a). At intermediate elasticity [panels (b) and (c)] in contrast, the substrate profile is curved and the highest velocities are found within the drops, while flow through the adsorption layer is relatively weak. Within the drops the flow points from one contact line to the other, causing a drift of the drops towards each other, i.e., the translation mode is active. This indicates that the translation regime is mediated by elastic deformation, as a form of the Cheerios effect [Kar+16]. Due to negligible mass flux through the adsorption layer the two drops remain approximately constant in size. This nonmonotonic coarsening behavior is reminiscent of the nonmonotonic change of the wetting ridge height with softness, observed for static drops in Fig. 4.4 (b).

To quantify the relative importance of volume and translation mode, we introduce an asymmetry measure for the considered two-drop configuration, namely,

$$x_c(t) = \frac{1}{2V} \int_D x[h(x,t) - h_a] dx, \quad (6.1)$$

which corresponds to the horizontal coordinate of the center of mass associated with the drop volume above the adsorption layer $h > h_a = 1$. A coarsening process exclusively involving the translation mode that symmetrically moves the drops towards each other would keep $x_c = 0$ as the center of mass remains at $x = 0$. By contrast, an exclusive transfer of liquid from one to the other drop via the volume transfer mode would result in a maximal increase to $x_c = x_c^{\max} \approx 40$ as all the volume is finally centered about the initial position of the remaining drop. If both coarsening modes contribute the resulting value of x_c lies between the two extremes. For the time evolutions shown in Fig. 6.2, the corresponding measures $x_c(t)$ are given in Fig. 6.4 (b) allowing us to quantitatively discuss the changes of the coarsening mechanism with increasing softness: For almost rigid substrates ($s = 10^{-1}$, Fig. 6.2 (a)) the mass transfer mode dominates, as one drop shrinks and vanishes while the other one grows. The center of mass $x_c(t)$ monotonically increases from zero and reaches a final value of $x_c^\infty = \lim_{t \rightarrow \infty} x_c(t) \approx 22 < x_c^{\max}$. It is interesting to note that in parallel to the volume transfer both drops slightly migrate into the same direction, pointing from the growing to the shrinking drop, resulting in a decrease of x_c . This effect is well

known for drops on rigid substrates, see e.g. Refs. [PPo4, GWo5], and is related to liquid motion in the adsorption layer. Increasing the softness to $s = 10$, mass transfer still remains dominant. The amount of migration into the same direction decreases though, resulting in an increase of x_c^∞ to about 30. The increase can be well appreciated in Fig. 6.4 (c) where the final asymmetry measure x_c^∞ is shown as a function of softness s . Reaching the regime of intermediate elasticity at about $s = 10^2$ (Fig. 6.2 (b)) the behavior abruptly changes and coarsening becomes entirely domi-

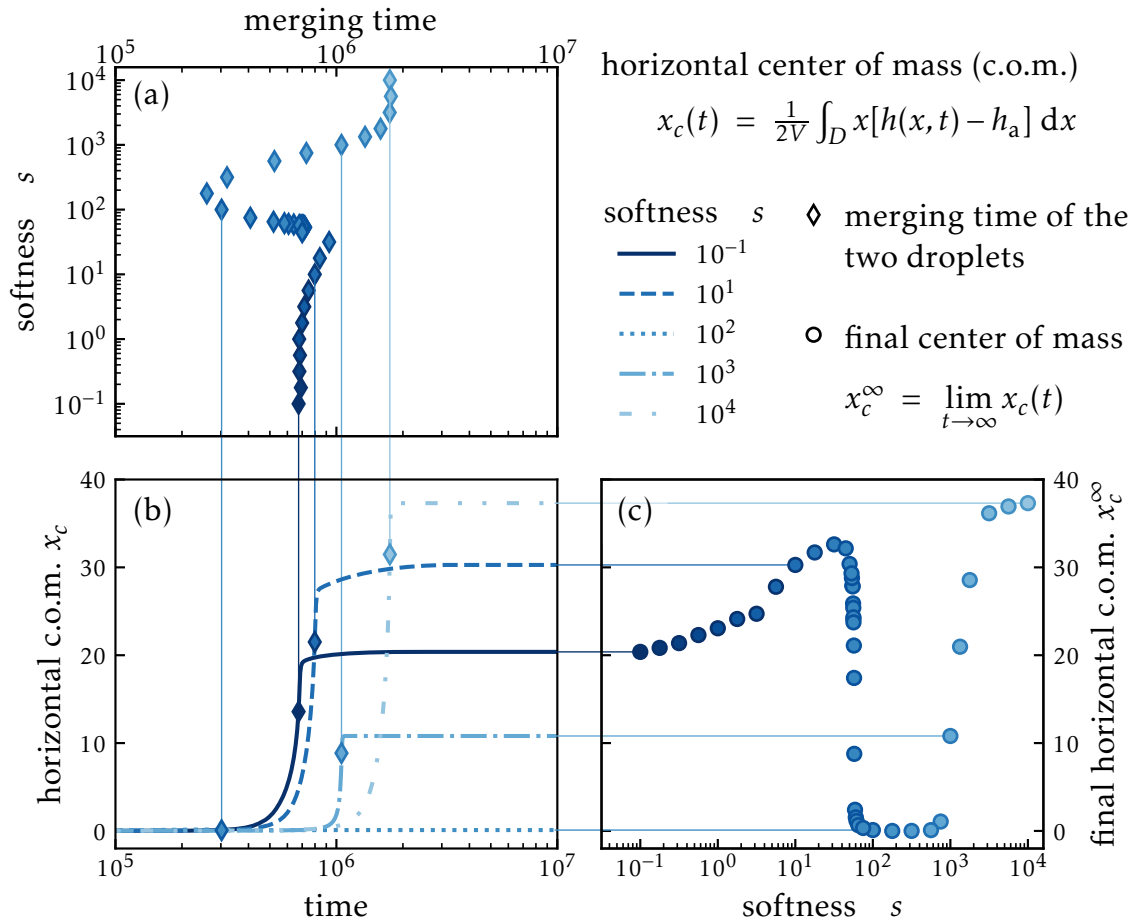


FIGURE 6.4.: (b) Shown is the temporal change in the horizontal center of mass coordinate $x_c(t)$ (Eq. (6.1)) for two-drop coarsening processes at softness values given in the legend (including the values of Fig. 6.2). The maximal possible value for the given drop volume and distance corresponds to the absolute value of the initial drop position $x_c^{\max} = |x_c^{\text{init}}| \approx 40$. The merging times at which no two drops can be distinguished any more are marked by diamonds. Panel (b) gives the intricate dependence of the final value x_c^∞ on softness s . It shows that the mass transfer mode is dominant apart from a finite range of intermediate softness ($s \approx 10^2 \dots 10^3$) where the translation mode dominates. Panel (a) gives the merging times against softness and indicates that coarsening by mass transfer is slowed down with increasing softness, while activity of the translation mode accelerates the process. The thin lines connecting the different panels are intended to aid the eye and show how the data transfers from one plot to the other.

nated by the translation mode characterized by $x_c^\infty \approx 0$, as seen from the dotted line in Fig. 6.4 (b). When further increasing s by about one magnitude, the volume mode starts to become important again. During the early stages of the process translation still prevails, as the final phase is approached, however, mass transfer becomes increasingly relevant as is visualized for $s = 10^3$ in Fig. 6.2 (c) where $x_c^\infty \approx 10$ is found. Then, in approaching the liquid limit at even larger s , the translation mode loses all its impact and the mass transfer mode again dominates the coarsening process. In contrast to the rigid limit, however, no drop migration occurs at the end ($s = 10^4$, Fig. 6.2 (d)) and x_c^∞ approaches $x_c^{\max}$. The described intricate change from mass transfer to translation mode and back can best be appreciated in Fig. 6.4 (c). To further quantify the time scales at which coarsening takes place the merging times of the two drops are marked by diamonds in Fig. 6.4 (b). These values are determined as the first measured times where no two local maxima in h can be distinguished any more. In Fig. 6.4 (a) the merging times are shown as a function of softness. It appears that coarsening is accelerated by the activity of the translation mode as indicated by the decreased merging times in a regime of softness that coincides with the one found in Fig. 6.4 (c) in which the translation mode was found to be dominant. After all Fig. 6.4 (a) and (c) show that, aside this translation dominated region, the regimes dominated by mass transfer show a quasi monotonic behavior, that is, both, the merging time as well as the shift in center of mass increases with softness. In other words, coarsening via mass transfer is slowed down with increasing softness and the tendency of the drops to travel laterally decreases in the same course. It should be mentioned, however, that even though coarsening via mass transfer takes place on considerably larger time scales, as compared to translation driven coarsening, it yet accelerates quite quickly towards the end as the difference in volume, and therefore in the Laplace pressure, increase as shown in Fig. 6.5.

To gain a deeper understanding of the transition between modes, we perform a linear stability analysis for the alternative constellation of a periodic drop array. Namely, two identical drops of volume V are placed in a domain of finite size $D = 200$ at respective positions of the maxima $x = \pm D/4$. Due to equal drop volume and distance in both directions (across the periodic boundaries) this state is considered steady yet unstable with regard to both, mass transfer as well as translation mode. This periodic two-drop state and its linear stability are continued in softness using `pde2path`. Starting in the rigid limit at $s = 10^{-3}$, the softness is increased up to $s = 10^6$, i.e., the liquid limit. From the linear stability analysis two destabilizing real eigenvalues are found. One corresponding to mass transfer mode, with the change in h during mass transfer being antisymmetric w.r.t. the center

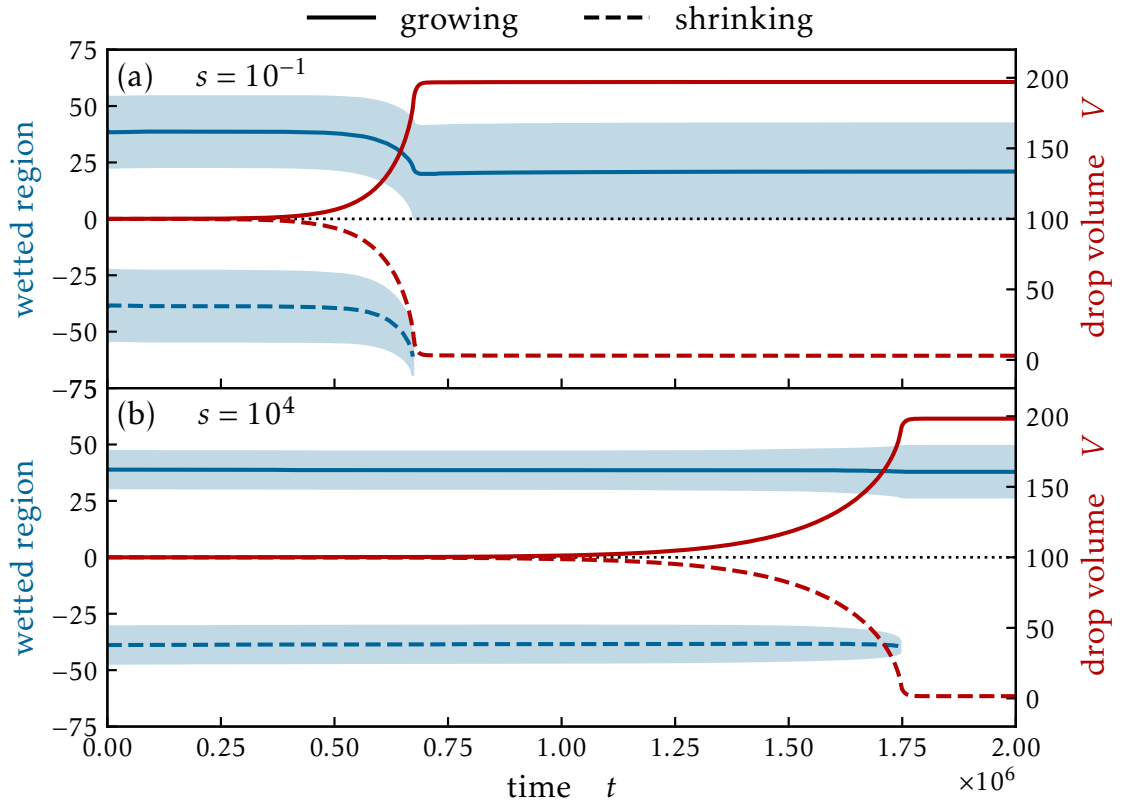


FIGURE 6.5.: Time evolution of two drops coarsening via mass transfer in (a) the rigid limit $s = 10^{-1}$ and (b) the liquid limit $s = 10^4$. The remaining parameters are as in Fig. 6.2. The wetted x -regions (l.h.s. axis) covered by the two drops are shaded in light blue with the dark blue lines representing their respective maxima. In the rigid limit coarsening occurs much earlier as compared to the liquid limit and a joint translation of the drops in the same direction is visible just before the smaller drop vanishes. As the difference in drop volumes (red lines, r.h.s. axis) increases the difference in Laplace pressure increases as well and the coarsening process accelerates. In this, the dashed lines always refer to the shrinking and the solid lines to the growing drops.

line $x = 0$ between drops, and the other one corresponding to the translation mode, associated with a symmetric change in h as the drops approach each other. The associated normalized modes, i.e., the eigenvector equivalents, reflecting the local change of the profile in time are schematically displayed in Fig. 6.1. The strength of coarsening modes is respectively determined by the absolute of the corresponding eigenvalues, which are shown as a function of softness in Fig. 6.6 for three selected V . The blue curves indicate the mass transfer mode, while red curves correspond to the translation mode. The volume mode is strongest in the rigid limit and decreases nearly monotonically with increasing softness (up to the small dip after the strong step-like decrease at intermediate softness $s = 10^1 \dots 10^2$). It further slightly decreases overall with increasing drop volume, an effect more pronounced in the rigid

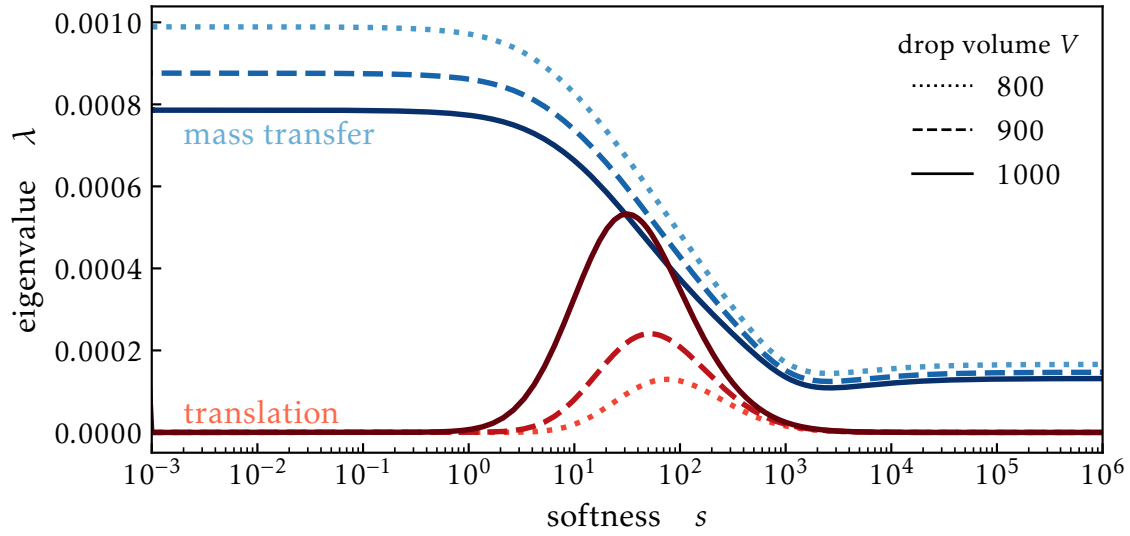


FIGURE 6.6.: Eigenvalues λ of the mass transfer mode (blue) and the translation mode (red) for a periodic system of equidistant steady drops of equal volume. Shown are results for three different drop volumes V as given in the legend. The domain size is fixed to $D = 200$, i.e., a larger drop volume corresponds to a smaller drop distance. The mass transfer mode weakens with increasing softness and drop size while the translation mode shows an increasingly pronounced maximum at intermediate elasticity that even exceeds the translation mode for the largest drop, indicating that the translation mode becomes dominant. The remaining parameters are as in Fig. 5.1.

limit. By contrast, the translation mode is nearly absent apart from a finite range at intermediate softness where it develops a peak that becomes more pronounced with increasing volume. In consequence, the translation mode eventually prevails against the mass transfer mode for sufficiently large drops at intermediate s in accordance with our time simulations Fig. 6.4 (c). The dominance of the translation mode in the range of intermediate softness approximately coincides with the intermediate regime found in the double transition of static drops discussed in Chap. 4. Compare in particular, Fig. 4.7 at $V \lesssim 1000$ with Fig. 6.4 (c) and Fig. 6.6. It is in this regime that a prominent wetting ridge occurs (cf. Fig. 4.4 (b)), through which the droplets interact via substrate deformations. Hence, it can indeed be concluded that the dominant translation mode is a direct consequence of the Cheerios effect. To confirm this result, further similar stability calculations were performed for other domain sizes D , though not shown here, where it was found that the critical drop volume V_c , at which the translation mode first becomes dominant at some critical softness s_c , increases with D . The corresponding s_c always nearly coincides with the lower bound of the softness range associated with the second transition (from elastic to liquid) discussed in Chap. 4. This agrees with the observed proportionalities $\sqrt{V_c} \sim \sqrt{s_c} \sim \tilde{\ell}_{ec} \sim \Delta_c$ where Δ_c is the critical distance of the contact lines of the two

drops.

6.2. COARSENING OF DROP ARRAYS

As teased earlier, the coarsening of large drop ensembles will be investigated now. Starting with a flat film of height $h_0 = 3$ on a rather large domain with $D = 5000$, early spinodal dewetting is initiated by imposing low amplitude noise to the liquid profile [TVNo1, Wit20]. The latter forms a large ensemble of about 100 – 200 droplets in consequence, which in turn begin to undergo coarsening. Fig. 6.7 gives a finite section (in both, space and time) of the space-time representation for an exemplary ensemble of initially ≈ 200 droplets coarsening on a substrate of intermediate softness $s = 10^2$. Note, how the shape of the growing drops changes as their size increases, from a liquid lens like structure to an upright drop with well pronounced wetting ridge as is representative for the intermediate elastic regime. This again makes clear how the second transition discussed in Chap. 4 can be undergone by changing the drop size at fixed softness instead of the other way around. In other words, the shape of the drop is characterized by the ratio of the elasto-capillary length with an other length scale describing its size, e.g., the radius R , height $h_{\max}$

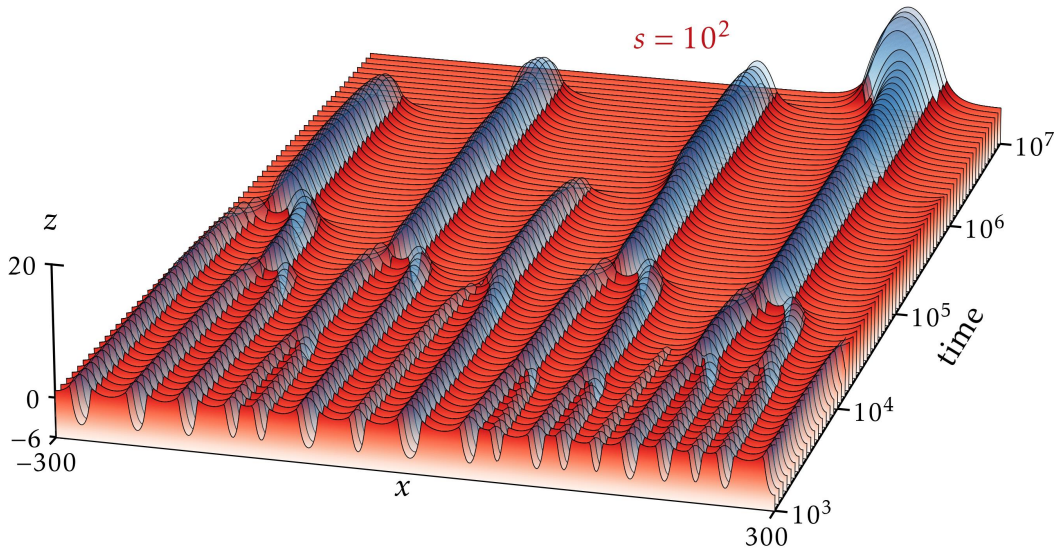


FIGURE 6.7.: The space-time plot illustrates the coarsening of a droplet ensemble initially consisting of $N \approx 200$ drops of partially wetting liquid on a substrate of intermediate softness $s = 10^2$ (parameters as in Fig. 6.2 (b)). The domain size is $D = 5000$, i.e., only a finite excerpt is shown. The remaining parameters are as in Fig. 5.1. A corresponding time evolution can be seen in HeSH2021-SupplMat-Video08-fig14.mp4 of the supplementary material of Ref. [HST21a].

or $\sqrt{V}$. The subsequent Fig. 6.8 shows space-time plots of all drop maxima positions along with their respective width for the same case of intermediate softness and, additionally, for the rigid and the liquid limit at $s = 10^{-1}$ and $s = 10^4$, respectively. The corresponding dependencies of drop number on time are presented in Fig. 6.9. Inspecting Fig. 6.8 (b) (also cf. the magnification in Fig. 6.7) shows that at intermediate softness nearly all coarsening events at early times occur by drop translation, i.e., two lines meet and join into one. As time moves on, the presence of the translation mode increasingly diminishing until coarsening via mass transfer prevails. The first events of coarsening via mass transfer appear at $t \approx 10^4$, i.e., single lines simply terminate, until translation driven coarsening ceases completely for $t \gtrsim 10^6$. This agrees with the transition from dominant translation to volume

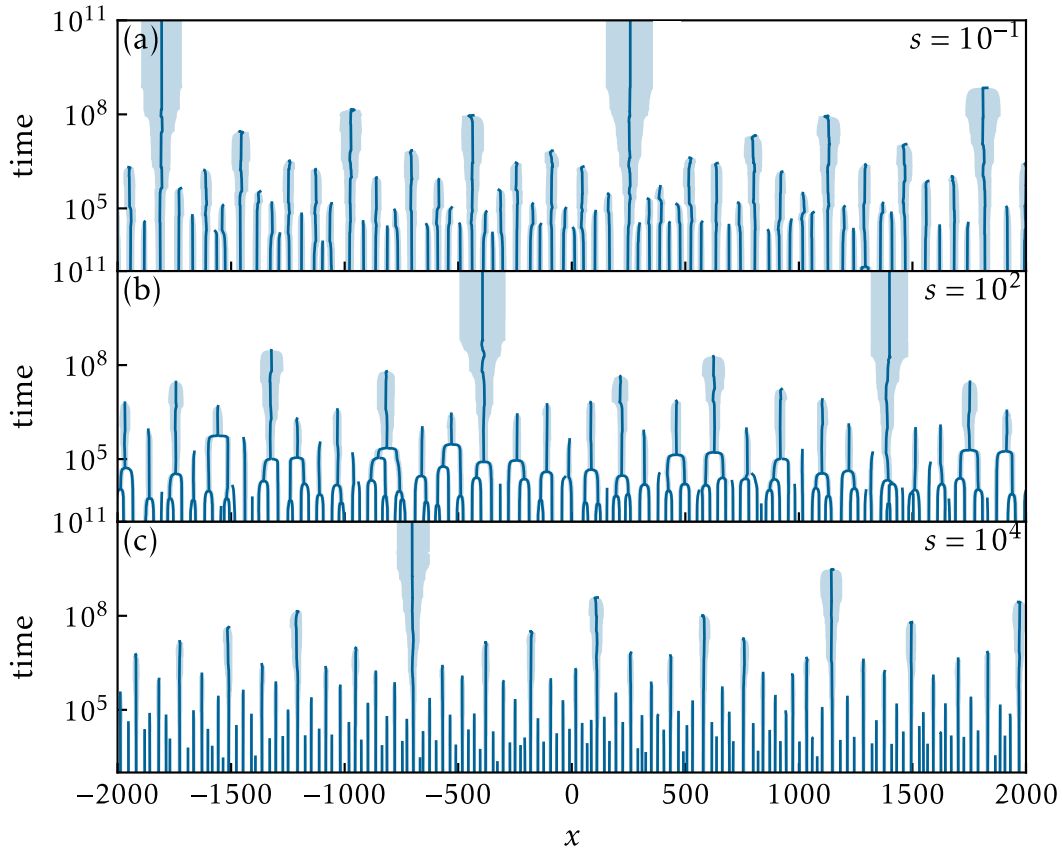


FIGURE 6.8.: Space-time plots of the positions of all drop maxima (blue lines) along with their respective width ($h > h_a$, light blue areas) on a logarithmic time scale. (a) in the rigid limit $s = 10^{-1}$ fewer initial drops are found and coarsening is driven mainly via mass transfer, slight migrations are visible. (b) at intermediate softness $s = 10^2$ (cf. Fig. 6.7) more initial drops show up and while translational coarsening dominates at early stages, the mass transfer mode prevails at larger drop size and distance. (c) in the soft limit $s = 10^4$ the initial drop number further increased and mass transfer dominates again, while no drop migration is visible anymore. The domain size is $D = 5000$, i.e., only a finite excerpt is shown. The remaining parameters are as in Fig. 5.1.

transfer mode with increasing drop distance discussed in section 6.1 and described for rigid substrates in Ref. [GW05]. Even though the mean drop volume increases in time, which should favor the translation mode, the accompanying increase in the mean drop distance is yet stronger. In the rigid and liquid limit coarsening by mass transfer clearly dominates, as is seen in Figs. 6.8 (a) and (c), respectively, and which perfectly agrees with the findings in section 6.1. A closer look at Figs. 6.8 (a) even reveals the previously mentioned joint migration of neighboring drops. Considering the evolution of drop numbers, even earlier times are regarded in Fig. 6.9 to point out the plateau around $t = 10^3$, indicating a time span between the completion of the initial spinodal dewetting and the onset of coarsening. Note, that during the dewetting phase, which is not entirely shown in Fig. 6.9, the routine counting the number of local maxima in the film profile effectively reflects a mean wave number. Further, the dispersion relation, obtained from the linear stability analysis of a homogeneous liquid film (cf. App. B.5), determines the wave number of the fastest growing mode and in Fig. B.5 (a) it is found that this wave number increases with softness, resulting in an increased number of drops after the spinodal dewetting in consequence. For parameters as used in the simulations the initial drop numbers can be predicted using $N \approx kL/(2\pi)$ and are found to be $N(s = 10^{-1}) \approx 104$, $N(s = 10^2) \approx 204$ and $N(s = 10^4) \approx 229$, which agree quite well with the num-

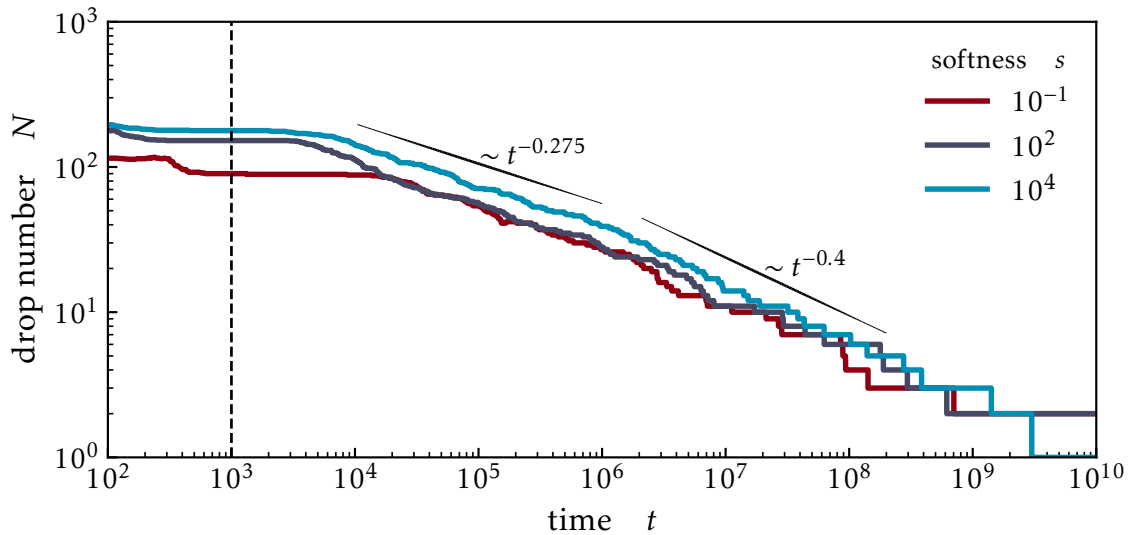


FIGURE 6.9.: Dependence of the drop number on time on a doubly logarithmic scale corresponding to the simulations shown in Fig. 6.8. The initial stage of drop formation (dewetting) is finished at about $t = 10^3$ as indicated by the vertical line. Coarsening sets in shortly after when the respective plateaus end. Empirically, one may distinguish two coarsening regimes with slightly different scaling laws as indicated by the short solid straight lines. Note, that the change of the scaling law at about $t = 10^6$ coincides with the change in the dominant coarsening mode from translation to mass transfer observed in Fig. 6.8 (b).

bers shown in Fig 6.9. For the present parameters the plateaus in Fig. 6.9 range from $t \approx 10^2$ to $t \approx 10^4$, and represent an approximate equilibrium, which is unstable with respect to combinations of the two-drop coarsening modes (discussed in section 6.1) and various multi-drop modes. The latter are, however, much weaker than the two-drop modes and thus not regarded in further detail. Once coarsening starts at the end of the plateau, the drop number continuously decreases. Due to the discrete nature of the measure (number of drops) and the extremely fast time scales at the end of the coarsening process (cf. Fig 6.5), individual steps show up in the curves and become increasingly pronounced at later times when only few drops remain. Qualitatively, the substrate softness does not seem to have an effect on long-time coarsening as the three curves are very similar. Empirically, a power

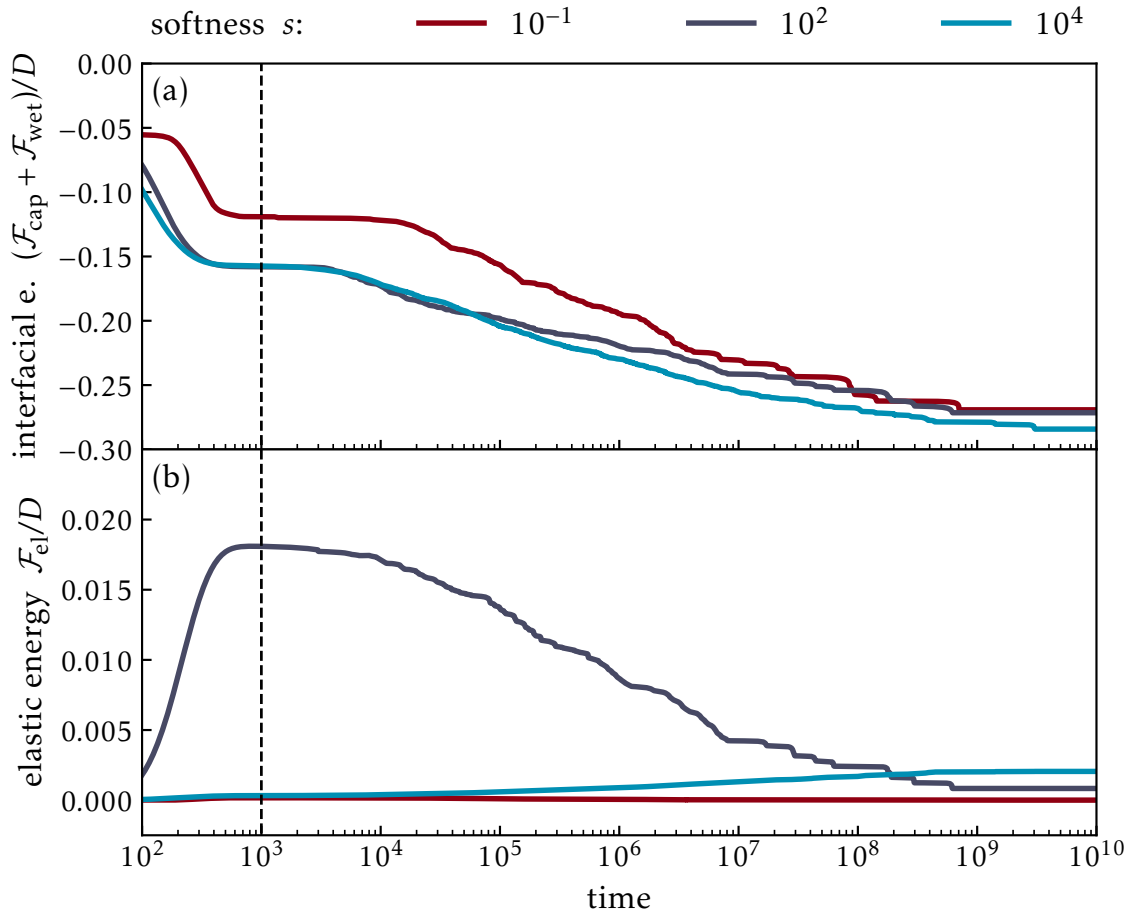


FIGURE 6.10.: Dependence of the interfacial (a) and stored elastic (b) mean energy densities on time corresponding to the simulations shown in Fig. 6.8. The strong decrease in interface energy for $10^2 \leq t \leq 10^3$ is associated with the initial spinodal dewetting. After the subsequent plateau marked by the vertical dashed line coarsening sets in. Note that the contribution of elastic energy is much smaller than the one of the interfacial energy and almost negligible outside the range of intermediate elasticity, i.e., here $s = 10^2$.

law fit $N(t) \sim t^{-\alpha}$ gives approximately identical scaling exponents for all values of s studied in Fig. 6.9. Based on the present low statistics one might even be tempted to distinguish two power laws. One in the range from $t \approx 10^4$ to $t \approx 10^6$ with $\alpha \approx 0.275$ and one in the range from $t \approx 10^6$ to $t \approx 10^8$ with $\alpha \approx 0.4$.

Let's finally have a look at how elasticity and interface effects contribute to the total energy and how the latter depends on time. Fig. 6.10 (a) gives the mean interface energy density $(\mathcal{F}_{\text{cap}} + \mathcal{F}_{\text{wet}})/D$ encompassing wetting

$$\mathcal{F}_{\text{wet}} = \int_D f(h) \, dx \quad (6.2)$$

with $f(h)$ as in Eq. (3.67), and capillary contributions

$$\mathcal{F}_{\text{wet}} = \int_D \frac{1}{2} (\partial_x h + \partial_x \xi)^2 + \frac{\sigma}{2} (\partial_x \xi)^2 \, dx. \quad (6.3)$$

The sum of both monotonically decreases with increasing time and substrate softness. Fig. 6.10 (b) gives the mean elastic energy density

$$\mathcal{F}_{\text{el}} = \int_D \frac{\xi^2}{2s} \, dx. \quad (6.4)$$

In the rigid and liquid limit the elastic contribution is rather small and almost negligible as compared to the capillary effects. Only at intermediate softness a considerable amount of work is initially stored in the substrate and then gradually released during the coarsening process, that is after the plateau. Though even at intermediate softness, where elasticity is most prominent, the elastic energy is much smaller than the interface energy. This indicates that coarsening is dominated by interface effects and might offer an explanation why the coarsening exponent observed in Fig. 6.9 is not sensitive to the substrate softness.

6.3. ASSESSMENT

Again, the mesoscopic long-wave gradient dynamics model, as introduced in Sec. 3.4.2, has been utilized to regard the coarsening dynamics of a pair of drops as well as large drop ensembles. In the case of two drops it was found that the dominant coarsening mode nonmonotonically changes when increasing the substrate softness. In both, the rigid and soft limit, the coarsening via mass transfer (volume transfer mode, collapse mode, diffusion-controlled ripening, or Ostwald ripening)

dominates while at intermediate softness a translation driven coarsening (collision, coalescence, migration mode) prevails for sufficiently large drops and short drop distances. As such, the model recovers the *inverted Cheerios effect*, describing an interaction of liquid drops mediated by elastic deformation of the solid substrate underneath [Kar+16] (in contrast to the Cheerios effect describing interaction of solid particles on a liquid substrate). In the rigid limit the volume transfer mode is accompanied by migration of both drops into the direction of the smaller one in accordance with literature [PP04, GW05]. Although, the nonmonotonic change in mode dominance has mainly been investigated by time simulations, it has furthermore been confirmed through a linear stability analysis for a closely related unstable steady two-drop constellation. With this results in mind, approaching the case of large coarsening drop ensembles revealed that the change in dominance of the coarsening mechanisms can be found there as well. The activity of the translation mode, however, was found to quickly fade with increasing separation of the drops, quicker, at least, than the volume mode does. Hence, the translation dominated regime ends at a critical threshold as the drop number decreases and the mean distance between the drops becomes too large. As the initial drop contribution emerges from a dewetting film the number of drops at the beginning of the coarsening process is not controlled directly. It was found, however, that the wave number of the fastest growing excitation mode increases with softness, resulting in an increased number of initial drops. To investigate the mechanisms of coarsening even further it would be reasonable to extend the analysis of the model to three dimensions, i.e., with a two-dimensional extension of the substrate. Beyond that, also higher order expansions of the Green's function may be considered to couple horizontal and vertical displacement as well as to incorporate incompressibility. The latter might result in more complex shapes of the wetting ridge that may result in drop-drop repulsion via the inverted Cheerios effect [Kar+16] and even cause coarsening to be arrested.

7. THE SHUTTLEWORTH EFFECT

The results presented in this chapter have to a large extent already been published:

[Hen+22] HENKEL, C., ESSINK, M. H., HOANG, T., VAN ZWIETEN, G. J., VAN BRUMMELEN, E. H., THIELE, U., and SNOEIJER, J. H. “Soft wetting with (a)symmetric Shuttleworth effect”. In: *Proc. R. Soc. A* 478.2264 (2022), p. 0132. DOI: [10.1098/rspa.2022.0132](https://doi.org/10.1098/rspa.2022.0132)

Many of the following figures were reproduced and adapted from the data presented in this reference.

In the previous chapters, surface energies and surface tensions of both, the liquid as well as the substrate, were regarded as constant along the interfaces and, therefore, as interchangeable concepts. While this may be a reasonable assumption for a liquid (at least in the absence of concentration or temperature gradients), for a soft substrate it is certainly not. Actually, the surface energy of an elastic material is expected to depend on the local strain in general, an effect known as *surface elasticity* or the *Shuttleworth effect* [Shu50, Mar+12a, WAS13, Lia+18, AS16, Sty+17]. It is thus to be distinguished between the (scalar) interface energy and the (tensorial) interface tension, neither of which can be treated as a universal material constant [Sty+17, AS20]. The influence of strain-dependent surface tension has recently been explored in experiments by measuring contact angles on stretched substrates [Xu+17, Sch+18, XSD18, Hey+21]. Surprisingly, these experiments have led to contradictory results though, e.g., in some cases the liquid-gas contact angle changed with increasing stretch while in other cases it did not. On the theoretical side, the Shuttleworth effect is only beginning to be explored for soft amorphous materials [SRA18, Pan+20], where most of the studies were restricted to isolated contact lines.

In this chapter the static wetting of droplets on elastic substrates is explored in the presence of the Shuttleworth effect. In the course of this, two different modeling approaches are simultaneously employed, each of which has its own specific merits.

THE MACROSCOPIC NEO-HOOKEAN MODEL: This model follows the macroscopic approach of Ref. [Pan+20], which consistently accounts for large elastic deformation via a Neo-Hookean elasticity in the presence of the Shuttleworth effect. Here, the description is extended to capture droplets of finite volume instead of only single contact lines [see examples in the top-row of Fig. 7.1]. While this model in principle offers the most complete description of the substrate bulk elasticity, resolving the interior stress while consistently accounting for large deformations, it is not able to capture the wetting dynamics. In the studies presented below, this model has been implemented and the corresponding results been produced by M. H. ESSINK  and T. HOANG .

THE MESOSCOPIC GRADIENT DYNAMICS MODEL: This model corresponds to the one introduced in Sec. 3.4. It is employed in full-curvature formulation and extended to incorporate the Shuttleworth effect [exemplary results in Fig. 7.1, bottom-row]. As discussed in the previously, this model sacrifices accuracy in the description of the elastic (bulk) deformation by employing a Winkler foundation model, in favor of simplicity and reduced computational cost. This reduced model enables the description of soft wetting dynamics and offers great potential towards the description of large drop ensembles.

In the following, a detailed description of the Shuttleworth effect will be given from the macroscopic perspective in Sec. 7.1 including both, the Lagrangian formulation (common in solid mechanics) and the Eulerian formulation (common in fluid mechanics). At the end of Sec. 7.1 also a short overview of the Neo-Hookean model will be given and the subtleties of contact lines in the presence of the Shuttleworth effect will be addressed as well. Afterwards, Sec. 7.2 addresses the translation of the macroscopic Shuttleworth effect into the mesoscopic picture and the implementation into the gradient dynamics model, including the presentation of consistency conditions [Thi+18, HST21a] that ensure the correct relation between macro- and mesoscale descriptions of wettability. Finally, a detailed comparison of the equilibrium states obtained with both models is performed in Sec. 7.3. In this, particular attention is granted the impact of asymmetry in the Shuttleworth effect between the dry and wet parts of the substrates. Previous studies on very small deformations in the rigid limit predict that horizontal displacements are caused by such asymmetries [WAS13, AS16], which is to be confirmed and generalized to the case of arbitrary softness in the following.

7.1. THE MACROSCOPIC PERSPECTIVE

The modeling of the Shuttleworth effect will first be discussed in the macroscopic framework of the Neo-Hookean model before translating it to the mesoscopic description in which the gradient dynamics model is formulated in Sec. 7.2.

7.1.1. KINEMATICS OF SURFACE STRETCH

As previously introduced, the Shuttleworth effect assumes a dependence of the solid interface energy γ_s (no matter the phase it is in contact with) on surface stretch λ , which is related to the strain $\varepsilon = \lambda - 1$. In order to model such behavior the latter has to be formulated first in both, the Lagrangian as well as in the Eulerian picture [cf. Ch. 2].

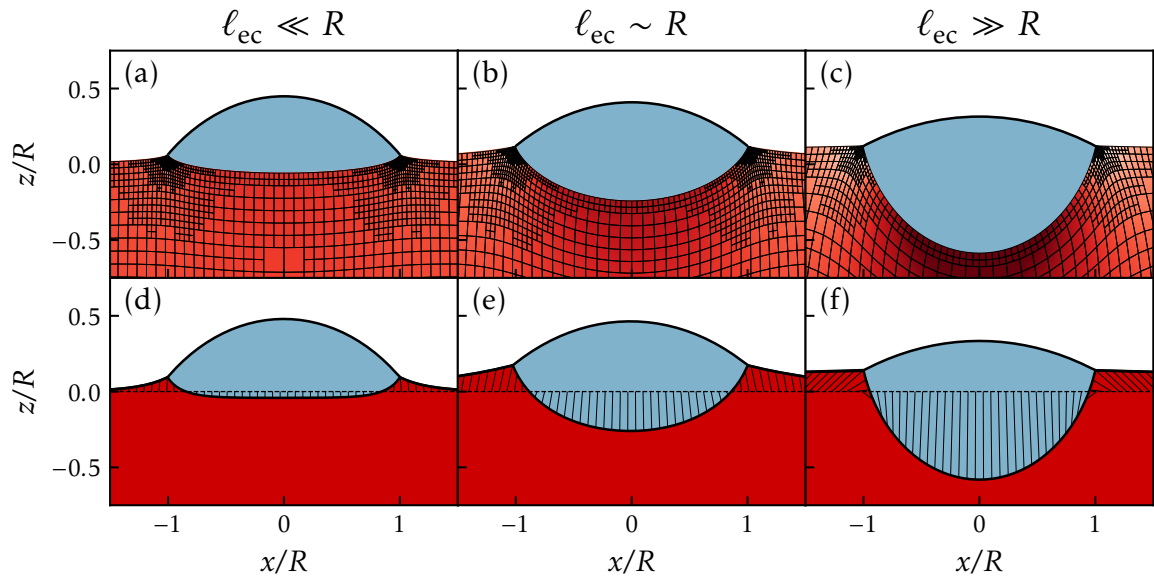


FIGURE 7.1.: Numerically calculated steady drops on elastic substrates of different softness, which increases from left to right. The profiles are obtained using two different modeling approaches: a macroscopic model based on a Neo-Hookean bulk elasticity (top row) and a mesoscopic gradient dynamics model using a Winkler foundation description (bottom row). In the top row (a-c) the elastic deformation of the substrate is visualized by the curved grid lines, which are horizontally/vertically straight in the reference state. In the bottom row (d-f) the thin vertical lines indicate the interface displacement vectors induced by the presence of the drop. Both models capture the transition from rigid to quasi-liquid wetting: The droplet sinks into the substrate and its liquid angle (with respect to the horizontal) decreases. This process is governed by the elasto-capillary length ℓ_{ec} normalized by the drop radius R . Model parameters are Young's angle $\theta_Y = 48.19^\circ$, Shuttleworth coefficients $\gamma_1^{sg} = \gamma_1^{sl} = \gamma_0^{sl}$, and liquid contact angles $\theta_{lg} \approx 42^\circ$ (left column), $\theta_{lg} \approx 32^\circ$ (center column), $\theta_{lg} \approx 22^\circ$ (right column).

LAGRANGIAN DESCRIPTION

As discussed in Ch. 2 elastic deformations are commonly described in terms of a (Cartesian) mapping $\vec{r} = \chi(\vec{R})$, where the *material coordinates* $\vec{R} = (X, Z)^\top$ in the reference configuration of the body, here the substrate, prior to any deformation, are shifted to the current coordinates $\vec{r} = (x, z)^\top$ in the new configuration after deformations have taken place [MH94, Hol01]. Thereby the deformation χ is assumed differentiable and invertible. Note, that the restriction to two spatial dimensions, i.e., one-dimensional profiles, assuming plain strain elasticity, facilitates a physical discussion in terms of scalar quantities, avoiding the tensor algebra associated with two-dimensional manifolds. As before, the mapping can be written in terms of the displacement vector $\vec{U} = (U_x, U_z)^\top$, i.e., $\vec{r} = \vec{R} + \vec{U}(\vec{R})$ as shown in Fig. 7.2.

Considering the free surface of the substrate to be flat and located at $Z = 0$ in the reference configuration, the relation of a surface element in the reference configuration $dS = dX$ and the current deformed configuration ds then follows as

$$(ds)^2 = (dx)^2 + (dz)^2 = \left[\left(\frac{\partial x}{\partial X} \right)^2 + \left(\frac{\partial z}{\partial X} \right)^2 \right] (dX)^2, \quad \text{at } Z = 0. \quad (7.1)$$

The *surface stretch* λ is defined as the ratio of these two lengths

$$\lambda^2 = \left(\frac{ds}{dS} \right)^2 = \left(\frac{\partial x}{\partial X} \right)^2 + \left(\frac{\partial z}{\partial X} \right)^2 = \left(1 + \frac{\partial U_x}{\partial X} \right)^2 + \left(\frac{\partial U_z}{\partial X} \right)^2 \quad \text{at } Z = 0. \quad (7.2)$$

This is the Lagrangian definition of surface stretch, expressed in terms of the horizontal material coordinate X .

EULERIAN DESCRIPTION

The gradient dynamics model utilized in all the previous sections describes the shape of the interfaces in terms of scalar functions, i.e., $z = \xi(x)$ [cf. Fig. 7.2]. Such a description is intrinsically *Eulerian* in nature, since it uses the current coordinate x as a variable to which z -values are assigned, and no allusion is made to any underlying material coordinate X . The length of the surface element then equals the metric factor $ds = m(\xi) = \sqrt{1 + (\partial_x \xi)^2} dx$. In order to compute the surface stretch λ , however, the length ds has to be related to the original length $dS = dX$ in the undeformed reference state. This relation can be found by defining the inverse mapping,

$\vec{R} = \chi^{-1}(\vec{r})$, or in terms of a displacement vector

$$\vec{R} = \vec{r} - \vec{U}(X(x, \xi(x)), 0) = \vec{r} - \vec{U}(x - U_x(\vec{R}), 0) \equiv \vec{r} - \vec{u}(x). \quad (7.3)$$

Here, the *surface displacement vector* $\vec{u}(x)$ has been introduced as a function of the Eulerian coordinate x . Since it always maps back to $Z = 0$, where the free surface in the reference state is located, the vertical displacement is identified to be $\vec{e}_z \cdot \vec{u} = \xi(x)$ and the horizontal component is simply referred to as $\vec{e}_x \cdot \vec{u}(x) = u(x)$ in the following. This basically recovers the exact same framework in which the gradient dynamics model was formulated. With these definitions in place, the original length of a surface element is found by considering a change in the horizontal coordinate $dX = (1 - \partial_x u)dx$, which, combined with the metric factor yields the Eulerian definition of surface stretch

$$\lambda = \frac{ds}{dX} = \frac{\sqrt{1 + (\partial_x \xi)^2}}{1 - \partial_x u}. \quad (7.4)$$

From this expression it is clear that one can change the material configuration of the substrate without changing its shape. Namely, even when the surface profile $\xi(x)$ is kept constant, the surface stretch can still be varied by changing $\partial_x u$.

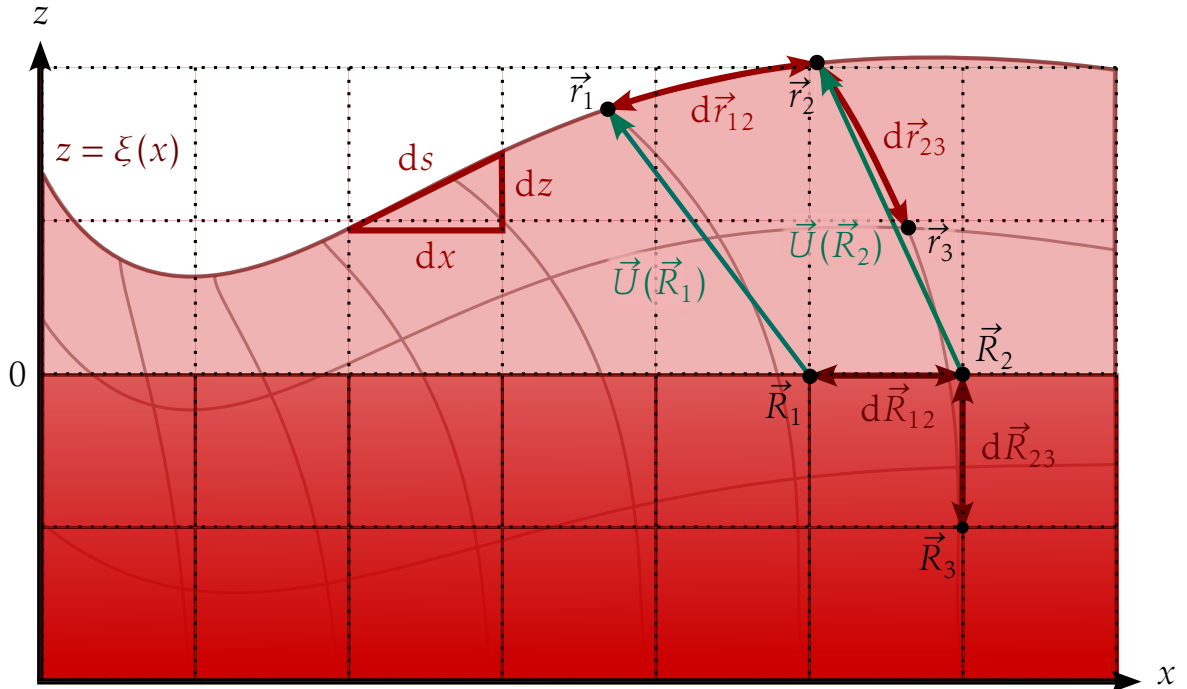


FIGURE 7.2.: Substrate deformation defined by the mapping of the material coordinates $\vec{R} = (X, Z)^T$ to the current coordinates $\vec{r} = (x, z)^T$, which can be expressed in terms of the displacement vector $\vec{U}(\vec{R}) = \vec{r} - \vec{R}$. The free surfaces of the reference configuration (dark red) and current configuration (light red) are defined by $Z = 0$ and $z = \xi(x)$, respectively. The surface stretch is defined as the ratio of surface elements $\lambda = ds/dX$.

7.1.2. ENERGY, TENSION AND CHEMICAL POTENTIAL OF A SOFT SURFACE

Now, that the definition of surface stretch is clear, its influence on the interface energy or interface tension can be investigated. Consider the interface of a soft solid with any other phase and stretch dependent interface energy $\gamma(\lambda)$. Stretching the interface increases its area from s_0 in the reference configuration to $s = \lambda s_0$ in the current configuration, i.e., $\frac{\partial s}{\partial \lambda} = \frac{s}{\lambda}$. The change in free energy with the interface area that is occupied by a fixed number of particles is then found to be

$$d\mathcal{F} = d(\gamma s) = \gamma ds + s d\gamma = \left(\gamma + s \frac{d\gamma}{ds} \right) ds = \left(\gamma + \lambda \frac{\partial \gamma}{\partial \lambda} \right) ds = \Upsilon ds. \quad (7.5)$$

Considering a fixed interface area s_0 , however, a stretching of the interface causes the density of particles at the surface to decrease, resulting in a reduction of the particle number from N_0 in the reference configuration to $N = N_0/\lambda$ in the stretched state, i.e., $\frac{\partial N}{\partial \lambda} = -\frac{N_0}{\lambda^2}$. The change in free energy is then given by

$$d\mathcal{F} = d(\gamma s_0) = s_0 d\gamma = s_0 \frac{\partial \gamma}{\partial \lambda} \frac{\partial \lambda}{\partial N} dN = -\frac{s_0}{N_0} \lambda^2 \frac{\partial \gamma}{\partial \lambda} dN = -\frac{s_0}{N_0} \mu dN. \quad (7.6)$$

Here the surface tension

$$\Upsilon(\lambda) \equiv \gamma(\lambda) + \lambda \frac{\partial \gamma}{\partial \lambda} \quad (7.7)$$

and the *surface chemical potential*

$$\mu(\lambda) \equiv \lambda^2 \frac{\partial \gamma}{\partial \lambda} \quad (7.8)$$

have been identified [SRA18, AS20, Pan+20]. These two quantities reflect the Shuttleworth effect and are related via $\lambda \partial_s \Upsilon = \partial_s \mu$ with $s_0 \partial_s = \partial_\lambda$. It becomes clear now why surface energy γ and surface tension Υ must be distinguished in case of soft materials. The stretch-dependence of Υ resembles the dependence of the surface tension of a liquid covered by surfactant molecules on the concentration of the latter [TAP16, Thi+18]. In consequence, a gradient in local stretch λ will give rise to tangential forces [Pan+20], in analogy to the solutal Marangoni effect [NVC01]. Note, that the surface chemical potential as defined by Eq. (7.8) takes the dimension of a surface energy $[\mu] = \text{J m}^{-2}$ and is thus rather a surface chemical potential density, which is related to the classical surface chemical potential $\tilde{\mu}$ via the surface

particle density $\rho_0 = N_0/s_0$ of the undeformed reference state

$$\tilde{\mu} = \frac{d\mathcal{F}}{dN} = -\frac{\mu}{\rho_0},$$

The surface chemical potential is related to the conservation of particles at the surface of the elastic substrate and governs their composition along it.¹ Returning to the Eulerian frame, i.e., the description of the elastic substrate surface in terms of the scalar function ξ , the free energy is given by

$$\mathcal{F}[\xi, u] = \int \gamma(\lambda) ds = \int \gamma(\lambda) \sqrt{1 + (\partial_x \xi)^2} dx.$$

Variation of this energy with respect to the substrate degrees of freedom, i.e., ξ and u , gives

$$\frac{\delta \mathcal{F}}{\delta \xi} = -\partial_x \left[\left(\gamma(\lambda) + \lambda \frac{\partial \gamma}{\partial \lambda} \right) \frac{\partial \xi}{\sqrt{1 + (\partial \xi)^2}} \right] = -\partial_x \left[\Upsilon(\lambda) \frac{\partial \xi}{\sqrt{1 + (\partial \xi)^2}} \right], \quad (7.9a)$$

$$\frac{\delta \mathcal{F}}{\delta u} = -\partial_x \left(\lambda^2 \frac{\partial \gamma}{\partial \lambda} \right) = -\frac{\partial \mu}{\partial x}, \quad (7.9b)$$

where both stretch-dependent quantities, i.e., $\Upsilon(\lambda)$ and $\mu(\lambda)$, are recovered once more. Note, that the relevant quantity that scales the Laplace pressure [Eq. (7.9a)] is identified to be the surface tension, not the surface energy, which only happened to be equivalent in the previous chapters. Another important feature is that Υ is no longer uniform in space and affected by the outer x -derivative therefore. Note, however, that the μ defined in Eq. (7.8) will not remain constant when the substrate's bulk elasticity is incorporated. It can thus be concluded that variations in the shape of the solid interface are governed by the surface tension Υ , while the composition of particles along it involves the surface-chemical potential μ . This is perfectly in line with previous results derived in Lagrangian formalism [Pan+20].

7.1.3. CONSTITUTIVE RELATION FOR THE SOLID INTERFACE

We have seen in the previous section, how the stretch dependence of the interface energy affects the free energy and the resulting variations. The exact functional connection in which this occurs, however, is yet to be specified. In the following the

¹The surface chemical potential density can be expressed in terms of the surface particle density by replacing the surface stretch $\lambda = \rho_0/\rho$. This directly yields $\mu = -\rho_0 \partial_\rho \gamma$, i.e., $\tilde{\mu} = \partial_\rho \gamma$.

empirical constitutive relation [Pan+20]

$$\gamma(\lambda) = \gamma_0 \varphi(\lambda) = \gamma_0 [1 - c_0 \log \lambda + c_1 (\lambda - 1)] , \quad (7.10)$$

is employed, where γ_0 is the interface energy of the undeformed reference configuration and $\varphi(\lambda)$ describes how the interface energy scales with stretch. Assuming small strain, $\varphi(\lambda)$ can be expanded about the minimum $\lambda_{\min} = c_0/c_1$, yielding a linear relation, which has already been used in previous studies [XSD18, Gor+20]. A convenient property of the proposed nonlinear form is that it diverges for $\lambda \rightarrow 0$, avoiding a singular mapping.² Thermodynamic admissibility requires γ to remain positive and convex, which puts constraints on the coefficients c_0 and c_1 . The corresponding surface tension (7.7) reads

$$\Upsilon(\lambda) = \gamma_0 \varphi(\lambda) + \gamma_0 \lambda \frac{\partial \varphi}{\partial \lambda} = \gamma_0 (1 - c_0 [1 + \log(\lambda)] - c_1) , \quad (7.11)$$

and the chemical potential follows as

$$\mu(\lambda) = \gamma_0 \lambda^2 \frac{\partial \varphi}{\partial \lambda} = \gamma_0 \lambda (c_1 \lambda - c_0) . \quad (7.12)$$

To reduce the number of free parameters $c_0 = c_1 = c$ is assumed in the following, such that the minimal surface energy is attained for the unstretched state $\lambda = 1$, i.e.,

$$\gamma(\lambda) = \gamma_0 + \gamma_1 g(\lambda) \quad \text{with} \quad g(\lambda) = \lambda - 1 - \log(\lambda) , \quad (7.13)$$

where the parameter $\gamma_1 = c \gamma_0$ governs the strength of the Shuttleworth effect. In the linear description of surface elasticity used in [XSD18], the coefficient γ_1 is referred to as the *modulus of surface elasticity*. The surface tension is then given by

$$\Upsilon(\lambda) = \gamma_0 + \gamma_1 g(\lambda) + \gamma_1 \lambda \frac{\partial g}{\partial \lambda} = \gamma_0 + \gamma_1 [2(\lambda - 1) - \log \lambda] , \quad (7.14)$$

and the chemical potential becomes

$$\mu(\lambda) = \gamma_1 \lambda^2 \frac{\partial g}{\partial \lambda} = \gamma_1 \lambda (\lambda - 1) . \quad (7.15)$$

²Here *singular mapping* refers to the scenario where $\lambda = 0$, which indicates a compression of the reference length $dX \neq 0$ to $ds = 0$, effectively mapping all material points included in dX to the same point. Note, that $\lambda < 0$ would cause a reversal of the material point sequence, i.e., a crossing of material points, which is not physical.

Note, that the above expressions for γ , Υ and μ are all nonlinear expressions in λ and can be consistently applied at large deformations. The specific choice for $\varphi(\lambda)$ or $g(\lambda)$, however, is empirical and its practical use for the description of real polymeric systems remains yet to be verified.

7.1.4. WETTING AND THE SYMMETRY OF STRETCH DEPENDENCE

As should be well internalized by now, the elastic substrate usually is not completely covered by the liquid in the context of partial wetting, in the macroscopic picture that is. It thus exhibits not only one but two distinct interfaces, namely the solid-liquid and the solid-gas interface, both of which have to be treated separately regarding the Shuttleworth effect, i.e.,

$$\gamma_{sl}(\lambda) = \gamma_0^{sl} + \gamma_1^{sl} g(\lambda), \quad (7.16a)$$

$$\gamma_{sg}(\lambda) = \gamma_0^{sg} + \gamma_1^{sg} g(\lambda). \quad (7.16b)$$

While γ_0^{sl} and γ_0^{sg} give the interface energies of the unstretched state and may differ as usual, now also the two moduli γ_1^{sl} and γ_1^{sg} have to be considered. Reviewing Eq. (3.39) we remember, that the Young's contact angle is governed by the difference in the solid interface energies

$$\theta_Y(\lambda) = \cos^{-1} \left(\frac{\gamma_{sg}(\lambda) - \gamma_{sl}(\lambda)}{\gamma_{lg}} \right) \quad (7.17)$$

and, therefore, depends on γ_1^{sl} and γ_1^{sg} . In consequence, a distinction can be made between two cases:

SYMMETRIC SHUTTLEWORTH EFFECT: The two moduli are equal $\gamma_1^{sl} = \gamma_1^{sg}$, implying that the increase in interface energy with stretch is the same on both sides of the contact line, i.e., in wetted and dry areas. Thus, a uniform stretching of the substrate would not cause a change in the contact angle [Eq. (7.17)], since the difference in interface energies remains the same. Such a situation was indeed observed in experiments of drops on elastomers where the liquid angle θ_{lg} , which was assumed to be approximately Young's angle [cf. Sec. 4], was found to be entirely unaffected by the stretching of the substrate [Sch+18], even though a Shuttleworth effect was identified in some other cases [Xu+17, SRA18].

ASYMMETRIC SHUTTLEWORTH EFFECT: The stretch dependence of the distinct interface energies differs, i.e., $\frac{\partial \gamma_{sl}}{\partial \lambda} \neq \frac{\partial \gamma_{sg}}{\partial \lambda}$. In the present modeling that relates to a difference in the respective moduli $\gamma_1^{sl} \neq \gamma_1^{sg}$. According to Young's law [Eq. (7.17)], a change in the contact angle would be expected to occur under uniform stretching of the substrate and was indeed observed on stiff glassy polymer substrates [Sch+18].

On soft substrates, the situation is much more intricate since there are two distinct, independent types of virtual displacements possible at the contact line [AS20]: (i) Eulerian displacement, exploring the variation of the horizontal and vertical contact line position in the lab-frame, (ii) Lagrangian displacement, exploring the variation of the substrate's material point that is located at the contact line. At equilibrium, where there is no contact line pinning to a specific material point, the energy should be minimal with respect to both kinds of virtual displacements. Variation (i) has been shown to lead to Neumann's law at the contact line [SRA18, Pan+20]. Variation (ii) is needed to prevent pinning to a material point, and gives a second local condition

$$\mu_{sl} = \mu_{sg} , \quad (7.18)$$

demanding continuity of the surface-chemical potential [Eq. (7.8)] across the contact line. It was shown, that in the limit of very large drops, that is large as compared to typical elastic deformations $\ell_{ec} \ll R$, Eq. (7.18) indeed leads to liquid contact angles that satisfy Young's law [Pan+20]. However, the equality of chemical potentials at the contact line is a strongly localized condition and as such independent of the drop size. Furthermore, the functional dependence of μ_{sg} and μ_{sl} on the surface stretching is the same according to Eq. (7.15), implying that the continuity of chemical potentials at the contact line [Eq. (7.18)] requires continuity of the stretch λ in case of a symmetric Shuttleworth effect, i.e., $\gamma_1^{sg} = \gamma_1^{sl}$. However, the possibility of an asymmetric Shuttleworth effect renders the condition (7.18) non-trivial and demands a jump in λ since $\gamma_1^{sg} \neq \gamma_1^{sl}$ [cf. Eq. (7.18)]. To date, Eq. (7.18) was only ever explored for infinitely large drops. In the following, also the case of large substrate deformations, comparable to the drop size, will be approached.

7.1.5. THE NEO-HOOKEAN MODEL

The Neo-Hookean model for macroscopic soft wetting was presented in detail by Ref. [Pan+20] for deformations induced by a single contact line. Here, the formalism is extended to droplets of finite volume. A hyperelastic solid is characterized by an

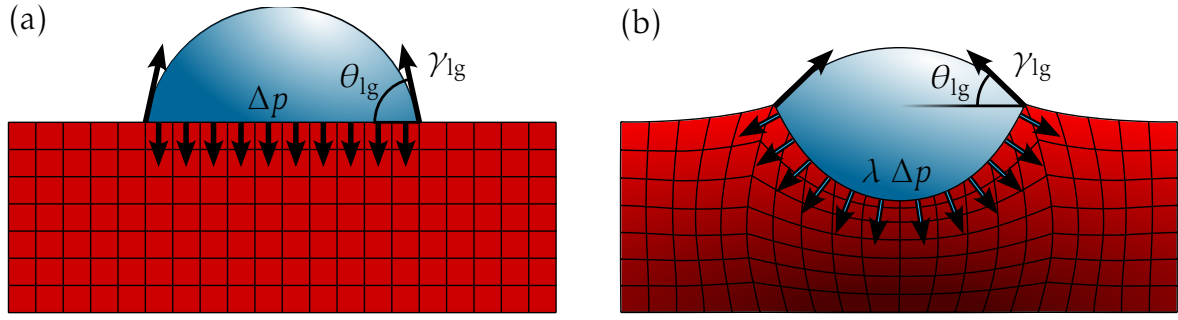


FIGURE 7.3.: The traction exerted by the droplet onto the substrate, consisting of two localized contact line forces and the Laplace pressure Δp inside the drop. The liquid contact angle θ_{lg} , measured with respect to the horizontal in both the (a) reference and (b) deformed configurations, is not known a priori, but determined consistently from (7.18).

energy density $W(\underline{E})$, where $F_{ij} = \frac{\partial r_i}{\partial R_j}$ is the gradient deformation tensor.³ In two dimensions, the combined elastic and capillary energy reads

$$\mathcal{F}[\chi] = \iint W(\underline{E}) \, dX dZ + \int \lambda \gamma(\lambda) \, dX, \quad (7.19)$$

where γ may stand for γ_{sl} or γ_{sg} , depending on whether the surface is macroscopically wet or dry locally. This energy is a functional of the mapping $\vec{r} = \chi(\vec{R})$. Since the hyperelastic description is Lagrangian, the surface energy has to be expressed as an integral over X at $Z = 0$. To account for the correct surface metric, the connection $ds = \lambda dX$ is used, where λ is the stretch at the surface [cf. Eq. (7.2)]. In the calculations below we use an incompressible Neo-Hookean energy density, which in two dimensions reads

$$W(\underline{E}) = \frac{1}{2} G' (\text{tr}(\underline{E} \cdot \underline{E}^T) - 2) - P (\det(\underline{E}) - 1). \quad (7.20)$$

Here, G' is the storage shear modulus [cf. Sec. 2.4.1], while the constraint of incompressibility is enforced via the Lagrange multiplier P .

The wetting is accounted for via the traction that is exerted by the drop onto the substrate. This traction is sketched in Fig. 7.3. It consists of two localized forces $\gamma_{lg} \vec{t}$ pulling along the liquid-gas interface at the two contact lines, located at $X = \pm R_0$ and $Z = 0$, i.e., R_0 is the initialized drop base radius before any deformations take place. Here, $\vec{t}$ is the tangential unit vector to the liquid-gas interface, i.e., the force pulls at an angle θ_{lg} . It is worth noting, that the localized forces would lead to an unstable minimization problem in the absence of solid surface tension, which provides sufficient regularization to render the minimization problem robust. In

³Note, that this is the inverse to the Eulerian gradient deformation tensor [Eq. (2.9)].

between the contact lines the Laplace pressure Δp , caused by the drop, is exerted on the substrate. It is related to the liquid angle θ_{lg} as $\Delta p = \gamma_{lg} \sin \theta_{lg} / R$, with R being the (Eulerian) base radius of the droplet. Formally, this traction is captured by a work functional

$$\mathcal{R}[\chi] = \gamma_{lg} \vec{t}(R) \cdot \vec{r}(R, 0) + \gamma_{lg} \vec{t}(-R) \cdot \vec{r}(-R, 0) - \int_{-R}^R \lambda \Delta p \vec{n}_{sl} \cdot \vec{r}(X, 0) dX, \quad (7.21)$$

where $\vec{n}_{sl}$ is the normal to the solid-liquid interface in the current configuration. The problem is then defined by minimization of $\mathcal{F} - \mathcal{R}$, with respect to the mapping $(X, Z) \mapsto \vec{r} = \chi(X, Z)$. Importantly, Neumann's laws are satisfied within this framework, since the minimization is explicitly done with respect to the Eulerian contact line position. However, the work functional [Eq. (7.21)] still contains an unknown liquid angle θ_{lg} . It can be found by imposing the no-pinning condition (7.18), which reflects the variation of the Lagrangian contact line position [see the discussion in Sec. 7.1.4]. The problem is therefore closed by introducing the liquid angle as an additional variable, with the no-pinning condition (7.18) as the corresponding residual.

In summary, the elasto-capillary problem thus consist of minimizing the functional

$$\begin{aligned} \mathcal{F}[\chi] - \mathcal{R}[\chi] = & \iint W(\underline{E}) dXdY + \int \lambda \gamma(\lambda) dX \\ & - \gamma_{lg} \vec{t}(R) \cdot \vec{r}(R, 0) - \gamma_{lg} \vec{t}(-R) \cdot \vec{r}(-R, 0) + \int_{-R}^R \lambda \Delta p \vec{n} \cdot \vec{r}(X, 0) dX, \end{aligned} \quad (7.22)$$

subject to the no-pinning condition $\mu_{sg} = \mu_{sl}$ at the contact line, to consistently determine the equilibrium liquid angle θ_{lg} . The minimization of the energy functional $\mathcal{F} - \mathcal{R}$ is based on the method presented in Ref. [Pan+20] and adapted to the specific problem at hand. For simplicity, the *goal-adaptive* finite-element method used in Ref. [Pan+20] is replaced by a *residual-based* method, in which elements are selected for refinement based on their residuals, obtained by projecting the current solution on a refined mesh. This method is implemented using the open-source numerical framework `Nutils` [Zwi+20].

For the simulations, the dimension of the substrate is set to $8R \times 8R$ in the undeformed configuration. The left and right boundaries of the substrate are only fixed in horizontal direction, allowing for movement in the vertical direction, which is required to ensure incompressibility. The bottom boundary is fixed in both directions. The results were verified to be virtually independent of domain-size. For example,

doubling the thickness from $8R$ to $16R$, the angle changes by $5 \cdot 10^{-5}$ degrees and the wetting ridge height by 10^{-6} . The substrate is initially divided into a mesh of 48×48 elements and undergoes a total of 13 refinement iterations subsequently. At maximum refinement the element size is reduced by a factor 2^{-13} , and a minimum element size of approximately $2R \cdot 10^{-5}$ is reached. Since these elements are significantly smaller than the elasto-capillary length, the wetting ridges are assumed to be accurately resolved.

7.2. TRANSLATION INTO THE MESOSCOPIC PICTURE

So far, the discussion of the Shuttleworth effect has been restricted to the macroscopic perspective. In this section, the versatility of the gradient dynamics approach is utilized to incorporate the Shuttleworth effect in the mesoscopic description.

7.2.1. STRETCH DEPENDENT WETTING POTENTIAL

The macroscopic features of the contact line, as discussed above, should emerge naturally in a mesoscopic description, which explicitly accounts for the finite range of molecular interactions as discussed in Sec. 3.3. According to Eq. (3.55), the free energy contributions of the interfaces, given in terms of the scalar Eulerian fields $h(x, t)$, $\xi(x, t)$, are

$$\mathcal{F}[h, \xi] = \int \gamma_{lg} m(h + \xi) + [\gamma_{sl} + f(h)] m(\xi) dx. \quad (7.23)$$

Now, that the solid-gas interface energy depends on stretch, and in a potentially different way than the solid-liquid interface energy does, the transition between these two interfaces becomes increasingly intricate and the mesoscopic wetting potential [Eq. (3.51)] has to be adapted to account for that. In particular, a stretch dependence has to be introduced in order to satisfy the consistency condition [Eq. (3.50)]

$$\gamma_{sg}(\lambda) = \gamma_{lg} + \gamma_{sl}(\lambda) + f(h_a, \lambda). \quad (7.24)$$

In consequence, the total mesoscopic free energy, accounting for capillarity, can be written as

$$\mathcal{F}[h, \xi, u_x] = \int \gamma_{lg} m(h + \xi) + \gamma_s(\lambda, h) m(\xi) dx, \quad (7.25)$$

with an effective solid interface energy

$$\gamma_s(\lambda, h) = \gamma_{sl}(\lambda) + f(h, \lambda), \quad (7.26)$$

that accounts for the solid-liquid as well as for the solid-gas interface energy via the wetting potential which smoothly interpolates between the two cases.⁴

Now, while the solid-liquid interface energy can be modeled directly as suggested by Eq. (7.10)

$$\gamma_{sl}(\lambda) = \gamma_0^{sl} \left[1 - c_0^{sl} \log(\lambda) + c_1^{sl} (\lambda - 1) \right] \quad (7.27)$$

the stretch dependence of the wetting potential has to be fashioned in such a way, that the same form is recovered for the equivalent of the macroscopic solid-gas interface tension as well, i.e., with Eq. (7.24) and (7.10)

$$\gamma_{sg}(\lambda) = \gamma_{lg} + \gamma_{sl}(\lambda) + f(h_a, \lambda) \stackrel{!}{=} \gamma_0^{sg} \left[1 - c_0^{sg} \log(\lambda) + c_1^{sg} (\lambda - 1) \right]. \quad (7.28)$$

Assuming the wetting potential to factorize $f(h, \lambda) = f_0(h)k(\lambda)$, with $f_0(h)$ given by Eq. (3.51), the stretch dependent part is found from Eq. (7.28) to be

$$k(\lambda) = \left[\gamma_0^{sg} - \gamma_0^{sl} - \gamma_{lg} - (\gamma_0^{sg} c_0^{sg} - \gamma_0^{sl} c_0^{sl}) \log(\lambda) + (\gamma_0^{sg} c_1^{sg} - \gamma_0^{sl} c_1^{sl}) (\lambda - 1) \right] f_0^{-1}(h_a).$$

Using $f_0(h_a) = \gamma_0^{sg} - \gamma_0^{sl} - \gamma_{lg} = \gamma_{lg}(\cos \theta_Y^0 - 1)$, the complete stretch dependent wetting potential then writes

$$f(h, \lambda) = f_0(h)k(\lambda) = -\frac{5h_a^2}{3h^2} \left[\frac{2}{5} \left(\frac{h_a}{h} \right)^3 - 1 \right] \left[\gamma_{lg}(\cos \theta_Y^0 - 1) - \tilde{c}_0 \log(\lambda) + \tilde{c}_1 (\lambda - 1) \right],$$

with $\tilde{c}_0 = \gamma_0^{sg} c_0^{sg} - \gamma_0^{sl} c_0^{sl}$, $\tilde{c}_1 = \gamma_0^{sg} c_1^{sg} - \gamma_0^{sl} c_1^{sl}$ and θ_Y^0 the Young's angle of the unstretched state, i.e., at $\lambda = 1$. In case of $c_0^i = c_1^i = c^i$, as will be assumed from here on, the stretch dependent wetting potential reduces to

$$\begin{aligned} f(h, \lambda) &= -\frac{5h_a^2}{3h^2} \left[\frac{2}{5} \left(\frac{h_a}{h} \right)^3 - 1 \right] \left[\gamma_{lg}(\cos \theta_Y^0 - 1) + (\gamma_1^{sg} - \gamma_1^{sl}) g(\lambda) \right] \\ &= f_0(h) \left[1 + (\gamma_1^{sg} - \gamma_1^{sl}) \frac{g(\lambda)}{f_0(h_a)} \right], \end{aligned} \quad (7.29)$$

⁴Note, that in principle the liquid-gas interface energy has to be added in order to recover the solid-gas interface energy according to the consistency condition. Since the liquid-gas interface is present everywhere in the domain, however, it is more convenient to consider it separately.

with $\gamma_1^{\text{sg}} = \gamma_0^{\text{sg}} c_0^{\text{sg}} = \gamma_0^{\text{sg}} c_1^{\text{sg}}$ and $\gamma_1^{\text{sl}} = \gamma_0^{\text{sl}} c_0^{\text{sl}} = \gamma_0^{\text{sl}} c_1^{\text{sl}}$. Note, that in the absence of stretch, i.e., for $\lambda = 1$, it follows that $g(\lambda = 1) = 0$ and $k(\lambda = 1) = 1$ such that $f(h, \lambda = 1) = f_0(h)$ is recovered. In addition to that, $f(h, \lambda) = f_0(h)$ is found also in case of the symmetric Shuttleworth effect when $\gamma_1^{\text{sl}} = \gamma_1^{\text{sg}}$, indicating that Young's angle is not affected by homogeneous stretching in that case. The associated mesoscopic solid surface tension is found to be

$$\Upsilon(h, \xi, u_x) = \gamma_s(\lambda) + \lambda \frac{\partial \gamma_s}{\partial \lambda} = \gamma_{\text{sl}}(\lambda) + f_0(h)k(\lambda) + \lambda \frac{\partial}{\partial \lambda} [\gamma_{\text{sl}}(\lambda) + f_0(h)k(\lambda)] \quad (7.30)$$

and the associated mesoscopic surface-chemical potential similarly follows as

$$\mu(h, \xi, u_x) = \lambda^2 \frac{\partial \gamma_s}{\partial \lambda} = \lambda^2 \frac{\partial}{\partial \lambda} [\gamma_{\text{sl}}(\lambda) + f_0(h)k(\lambda)] . \quad (7.31)$$

7.2.2. FULL-CURVATURE GRADIENT DYNAMICS MODEL

Finally, a gradient dynamics model in full curvature formulation, similar to the one introduced in Sec. 3.4, is employed. To do so, the elastic energy

$$\mathcal{F}_{\text{el}}[\xi, u] = \int \frac{E_\mu}{d} \frac{(1-\nu)}{(1-2\nu)} \xi^2 + \frac{E_\mu}{2d} (u - u'_\infty x)^2 dx \quad (7.32)$$

with respect to both, the vertical displacement ξ and the lateral displacement u is added.⁵ To enable the imposition of pre-stretch to the substrate, as is common in experiments and in the Neo-Hookean model, a constant gradient u'_∞ is added to the horizontal displacement. This gradient causes a pre-stretch $\lambda_\infty = 1/(1 - u'_\infty)$ to an initially flat substrate, i.e., with $\xi = 0$ prior to placing a droplet on top. The total free energy then reads

$$\mathcal{F}[h, \xi, u] = \int \gamma_{\text{lg}} m(h + \xi) + \gamma_s(h, \lambda) m(\xi) + \frac{E_\mu}{d} \frac{(1-\nu)}{(1-2\nu)} \xi^2 + \frac{E_\mu}{2d} (u - u'_\infty x)^2 dx , \quad (7.33)$$

⁵Note, that this form of the elastic energy corresponds to the Winkler foundation model, which is technically valid only in the long-wave limit. To spare the effort of solving the convolution integral included in the full elastic energy, however, the long-wave version is used in this full-curvature model nonetheless.

and its variations are

$$\frac{\delta \mathcal{F}}{\delta h} = -\gamma_{lg} \frac{\partial}{\partial x} \left(\frac{\partial_x(h+\xi)}{m(h+\xi)} \right) + \frac{\partial f}{\partial h} m(\xi), \quad (7.34a)$$

$$\frac{\delta \mathcal{F}}{\delta \xi} = -\gamma_{lg} \frac{\partial}{\partial x} \left(\frac{\partial_x(h+\xi)}{m(h+\xi)} \right) - \frac{\partial}{\partial x} \left(\gamma \frac{\partial_x \xi}{m(\xi)} \right) + \frac{E_\mu}{d} \frac{2(1-\nu)}{(1-2\nu)} \xi, \quad (7.34b)$$

$$\frac{\delta \mathcal{F}}{\delta u} = -\frac{\partial \mu}{\partial x} + \frac{E_\mu}{d} (u - u'_\infty x). \quad (7.34c)$$

While the variations (7.34a) and (7.34b) look quite familiar, the variation with respect to u [Eq. (7.34c)] now describes how the substrate's surface composition is controlled, leading to a shift of the surface chemical potential μ due to elasticity. Non-dimensionalization according to Sec. 3.4.1 yields

$$\frac{\delta \mathcal{F}}{\delta h} = -\frac{\partial}{\partial x} \left(\frac{\partial_x(h+\xi)}{m(h+\xi)} \right) + C_\theta \frac{\partial f}{\partial h} m(\xi), \quad (7.35a)$$

$$\frac{\delta \mathcal{F}}{\delta \xi} = -\frac{\partial}{\partial x} \left(\frac{\partial_x(h+\xi)}{m(h+\xi)} \right) - \frac{\partial}{\partial x} \left(\gamma \frac{\partial_x \xi}{m(\xi)} \right) + \frac{\xi}{s}, \quad (7.35b)$$

$$\frac{\delta \mathcal{F}}{\delta u} = -\frac{\partial \mu}{\partial x} + \frac{1}{s_u} (u - u'_\infty x), \quad (7.35c)$$

with the dimensionless surface energy

$$\gamma_s(h, \lambda) = \sigma + \sigma_1 g(\lambda) + \epsilon^2 C_\theta f_0(h) \left[1 + \frac{\sigma_2}{\epsilon^2 C_\theta} \frac{g(\lambda)}{f_0(h_a)} \right], \quad (7.36)$$

where $\sigma_1 = \gamma_1^{sl}/\gamma_{lg}$, $\sigma_2 = (\gamma_1^{sg} - \gamma_1^{sl})/\gamma_{lg}$ and the remaining dimensionless parameters are as given Eqs. (3.68). The definitions of the surface tension (7.30) and the surface chemical potential (7.31) remain valid with Eq. (7.36). The dynamics are finally given by Eqs. (3.65). For the sake of simplicity, the softness and viscosity w.r.t. the vertical and horizontal direction are chosen equally, i.e., $s_u = s$ and $\tau_u = \tau$ is assumed in the following. Note, that the gradient dynamics model is fully compressible in contrast to the incompressible Neo-Hookean substrate which is strictly volume conserving, locally and globally, also in the presence of body forces.

7.2.3. CONSISTENCY OF NEUMANN'S LAWS

Before proceeding with the numerical studies of the Shuttleworth effect, let us quickly check whether Neumann's laws [Eq. (3.37)] are correctly recovered by the formulated model. As was done in Sec. 3.2, the vertical and horizontal force equilibria

can respectively be derived from the pressure [Eq. (7.34b)] and the Hamiltonian [Eq. (2.119)], the latter of which is given by

$$\begin{aligned}\mathcal{H} &= \gamma_{lg} \frac{(\partial_x h + \partial_x \xi)^2}{m(h + \xi)} + \Upsilon \frac{(\partial_x \xi)^2}{m(\xi)} + \mu \partial_x u + \gamma_{lg} m(h + \xi) - \gamma_s m(\xi) - \frac{E_\mu}{d} \frac{(1 - \nu)}{(1 - 2\nu)} \xi^2 - \frac{E_\mu}{2d} u^2 \\ &= -\frac{\gamma_{lg}}{m(h + \xi)} - \frac{\Upsilon}{m(\xi)} + \mu - \frac{E_\mu}{d} \frac{(1 - \nu)}{(1 - 2\nu)} \xi^2 - \frac{E_\mu}{2d} u^2,\end{aligned}\quad (7.37)$$

where no pre-stretch $u'_\infty = 0$ is considered and $\mu \partial_x u - \gamma_s m(\xi) = \mu - \Upsilon m(\xi)$ is used. Since an equilibrium state has to exhibit vanishing pressure across the domain, integration of Eq. (7.34b) over the contact region yields

$$\int_{x_{sl}}^{x_{sg}} \frac{\delta \mathcal{F}}{\delta \xi} dx = \int_{x_{sl}}^{x_{sg}} \frac{E_\mu}{d} \frac{2(1 - \nu)}{(1 - 2\nu)} \xi dx - \left[\gamma_{lg} \frac{\partial_x(h + \xi)}{m(h + \xi)} + \Upsilon \frac{\partial_x \xi}{m(\xi)} \right]_{x_{sl}}^{x_{sg}} = 0, \quad (7.38)$$

where x_{sl} and x_{sg} respectively represent positions at the solid-liquid and solid-gas interfaces close to the contact region where tangents to the profiles are assumed to represent the Neumann angles.⁶ At x_{sl} the liquid layer is assumed to be very thick $h \rightarrow \infty$ already, while absorption layer height $h = h_a$ is considered at x_{sg} . Expressing the gradients in terms of the associated contact angles [cf. Eq. (3.28)], Eqs. (7.38) becomes

$$\gamma_{lg} \sin \theta_{lg} - \Upsilon(\infty, \lambda) \sin \theta_{sl} - [\gamma_{lg} + \Upsilon(h_a, \lambda)] \sin \theta_{sg} = \int_{x_{sl}}^{x_{sg}} \frac{E_\mu}{d} \frac{2(1 - \nu)}{(1 - 2\nu)} \xi dx. \quad (7.39)$$

In the same way, integration of Eq. (7.34c), without pre-stretch $u'_\infty = 0$, leads to

$$\mu(h_a, \lambda) - \mu(\infty, \lambda) = \int_{x_{sl}}^{x_{sg}} \frac{E_\mu}{d} u dx, \quad (7.40)$$

which is the mesoscopic equivalent of the continuity condition for the surface chemical potentials [Eq. (7.18)]. Further, the Hamiltonian is supposed to be constant across the domain. Evaluation of the Hamiltonian at x_{sl} and x_{sg} , i.e., $\mathcal{H}|_{x_{sl}} = \mathcal{H}|_{x_{sg}}$,

⁶Usually, the slopes at the deflection points of $h + \xi$ and ξ are used to determine the contact angles.

leads to

$$\begin{aligned} \mathcal{H}|_{x_{sl}} - \mathcal{H}|_{x_{sg}} &= [\gamma_{lg} + \Upsilon(h_a, \lambda)] \cos \theta_{sg} - \gamma_{lg} \cos \theta_{lg} - \Upsilon(\infty, \lambda) \cos \theta_{sl} \\ &+ \frac{E_\mu}{d} \frac{(1-\nu)}{(1-2\nu)} [\xi^2(x_{sg}) - \xi^2(x_{sl})] + \frac{E_\mu}{2d} [u^2(x_{sg}) - u^2(x_{sl})] \\ &+ [\mu(\infty, \lambda) - \mu(h_a, \lambda)] = 0. \end{aligned} \quad (7.41)$$

Let the two positions x_{sl} and x_{sg} be so close to each other, such that the integrals over the elastic contributions in Eqs. (7.38) and (7.40) can be neglected in good conscience. Then, the mesoscopic continuity condition of surface chemical potentials [Eq. (7.40)] becomes the macroscopic one [Eq. (7.18)], with $\mu(\infty, \lambda) \rightarrow \mu_{sl}$ and $\mu(h_a, \lambda) \rightarrow \mu_{sg}$. Demanding further continuity of the fields $\xi(x_{sl}) = \xi(x_{sg})$ and $u(x_{sl}) = u(x_{sg})$, the vertical and horizontal Neumann laws [Eqs. (3.37)] are recovered

$$\Upsilon(\infty, \lambda) \sin \theta_{sl} + [\gamma_{lg} + \Upsilon(h_a, \lambda)] \sin \theta_{sg} = \gamma_{lg} \sin \theta_{lg}, \quad (7.42a)$$

$$\gamma_{lg} \cos \theta_{lg} + \Upsilon(\infty, \lambda) \cos \theta_{sl} = [\gamma_{lg} + \Upsilon(h_a, \lambda)] \cos \theta_{sg}, \quad (7.42b)$$

with $\Upsilon(\infty, \lambda) \rightarrow \gamma_{sl}$ and $\gamma_{lg} + \Upsilon(h_a, \lambda) \rightarrow \gamma_{sg}$.⁷ It appears, that indeed it is the surface tensions, not the surface energies, that govern the equilibrium Neumann contact angles.

7.2.4. THE LONG-WAVE LIMIT

The mesoscopic gradient dynamics model introduced in Sec. 7.2.2 combines the exact metrics of the interfaces with long-wave dynamics in analogy to Refs. [GR88, Snoo6, BTH18]. It was stated in Sec. 3.4 that such hybrid models still provide reasonable results, and nonetheless the question arises as to why the variations are not also expanded in the long-wave limit, like it was done in all previous chapters. In Sec. 3.4.2 the issue of choosing a proper characteristic length scale U of the horizontal displacement in the long-wave limit has briefly been touched. In a first numerical simulation of the full curvature model, the ratio of maximum absolute horizontal and vertical displacements $|u|_{\max}/|\xi|_{\max}$ caused by the contact line of a steady

⁷Note, that all these assumptions, i.e., $x_{sl} = x_{sg}$, $h(x_{sl}) \rightarrow \infty$, $h(x_{sg}) = h_a$, $\Upsilon(\infty, \lambda) \rightarrow \gamma_{sl}$, $\gamma_{lg} + \Upsilon(h_a, \lambda) \rightarrow \gamma_{sg}$, $\mu(\infty, \lambda) \rightarrow \mu_{sl}$, $\mu(h_a, \lambda) \rightarrow \mu_{sg}$ and the expression of the gradients in terms of contact angles, render the scenario virtually macroscopic. It has been found in Sec. 4.3, however, that in the mesoscopic description the inclusion of the elastic forces improves the compliance of Neumann's laws, in particular the vertical one, as the rigid limit is approached.

drop was studied in dependence of Young's angle θ_Y^0 . In Fig. 7.4 the dependency is shown for symmetric Shuttleworth effect without pre-stretch (red lines) as well as for asymmetric Shuttleworth effect $\gamma_1^{sg} < \gamma_1^{sl}$ with pre-stretch $\lambda_\infty = 1.2$ (blue lines),⁸ each in the intermediate elastic regime $\sqrt{S/V} \approx 0.3$ (darker colors) and the quasi liquid regime $\sqrt{S/V} \approx 3$ (lighter colors).⁹ On one hand, it is found, that for a symmetric Shuttleworth effect in the absence of pre-stretch the ratio decreases as small angles are approached, in contradiction to the naive assumption that the horizontal displacement would become larger than the vertical one as the point force exerted by the contact line is inclined towards the horizontal plane. From Eq. (7.42b) it is seen, that the horizontal equilibrium at the contact line is not affected by the horizontal displacement and neither does the liquid-gas interface tension enter the horizontal surface stress balance [Eq. (7.34c)]. Indeed, the simulations show that both the horizontal as well as the vertical displacement decrease with decreasing contact angle. On the other hand, the ratio increases in the same course if an asymmetric Shuttleworth effect is considered in the presence of pre-stretch. In both cases, the respective tendency becomes less distinct as the quasi-liquid regime is approached. Using the ratio of the actual Young angle with the one rescaled in the long-wave limit [cf. Sec. 3.4.2] allows to estimate the smallness parameter $\epsilon = \theta_Y^0/\sqrt{3/5}$ [black dashed line in Fig. 7.4] and to put the ratio of maximum absolute displacements into proportion. The direct comparison, seems to indicate that different rescaling options of the horizontal displacement may be justified in the long-wave limit depending on the considered symmetry of the Shuttleworth effect. In case of a symmetric Shuttleworth effect without pre-stretch, the displacement ratio appears to be even smaller than the smallness parameter such that one might be tempted to even demand $U/H = \epsilon$ and therefore $U/L = \epsilon^2$. If an asymmetric Shuttleworth effect with pre-stretch is considered, however, the ratio becomes rather large and it seems reasonable to assume $U/H = \epsilon^{-1}$, i.e., $U = L$. At the end of the day, none of these choices provides an universally valid long-wave model that captures the entire spectrum of Shuttleworth scenarios including the two limits presented above. Therefore, and because the Neo-Hookean model performs way better for larger contact angles, we stick with the full-curvature formulation in this chapter.

⁸The reason why the asymmetric Shuttleworth effect is examined under the influence of pre-stretch while the symmetric one is not, is that further numerical simulations have shown that the horizontal displacement becomes particularly large if the Shuttleworth effect is asymmetric and small if not. These cases are intended to represent the limiting cases of spectrum of orders of magnitude that the horizontal displacement can assume. The knowledge about this behavior is of course anticipated at this point.

⁹Here, the volume $V = \int (h - h_a) dx$ is basically an area, since a two-dimensional view has been assumed, i.e., $\sqrt{V}$ is a characteristic length quantifying the drop size.

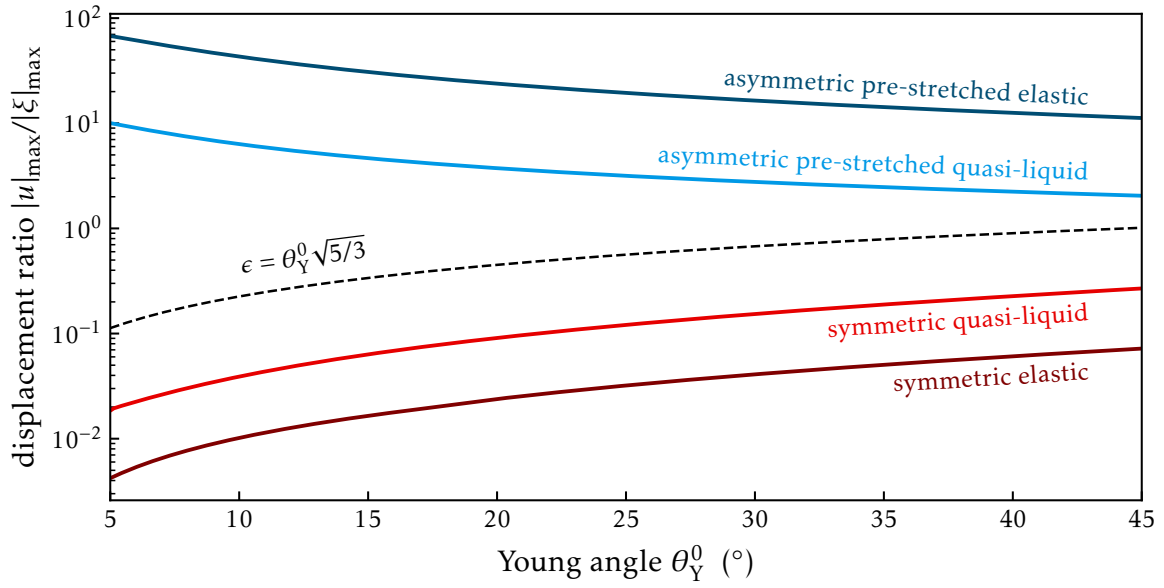


FIGURE 7.4.: Ratio of the maximum absolute displacements in horizontal and vertical direction $|u|_{\max}/|\xi|_{\max}$ (solid lines) caused by the contact line of a steady drop against Young's angle θ_Y (in degree) on a logarithmic scale. Simulations were performed for symmetric Shuttleworth effect without pre-stretch (red lines) as well as for asymmetric Shuttleworth effect $\gamma_1^{\text{sg}} < \gamma_1^{\text{sl}}$ with pre-stretch $\lambda_\infty = 1.2$ (blue lines), each in the intermediate elastic regime $\sqrt{S/V} \approx 0.3$ (darker colors) and the quasi-liquid regime $\sqrt{S/V} \approx 3$ (lighter colors). In case of a symmetric Shuttleworth effect in the absence of pre-stretch, the ratio decreases with decreasing θ_Y^0 , indicating that the horizontal displacement is much smaller than the vertical one in the long-wave limit. In contrast, the ratio increases with decreasing θ_Y^0 if the Shuttleworth effect is asymmetric and pre-stretch has been applied, such that the maximum horizontal displacement exceeds the vertical one. Comparison with the smallness parameter $\epsilon = \theta_Y^0/\sqrt{3/5}$, motivates different rescaling options for the horizontal displacement in the long-wave limit.

7.3. COMPARISON OF THE TWO MODELS

Typical results of the mesoscopic gradient dynamics and the Neo-Hookean model are shown in Fig. 7.1. On relatively stiff substrates, the droplet induces small wetting ridges at the contact line. Upon increasing the substrate softness, the drops gradually sink into the substrate, until attaining a liquid lens geometry. This rigid-to-soft transition was extensively discussed in Secs. 3.2 and 4 and will be quantitatively reviewed with regard to the Shuttleworth effect in the following, focusing on the liquid-gas contact angle θ_{lg} [cf. Fig. 3.6] and the deformations of the substrate.

The two models presented above contain various different parameters and so great care must be taken when comparing the results. The macroscopic surface energies can be chosen identical in both models and require a choice for the energy constants γ_{lg} , γ_0^{sl} , γ_0^{sg} , and the Shuttleworth coefficients γ_1^{sl} , γ_1^{sg} , as defined in Eqs. (7.16a) and (7.16b). Instead of the solid-gas interface energy γ_0^{sg} , the mesoscopic model contains the Hamaker constant in front of the wetting potential and

the adsorption layer thickness h_a as an additional parameter. The latter is chosen sufficiently small as compared to the drop size such that it is negligible as compared to the macroscopic elastic deformations. The Hamaker constant, however, is related to Young's angle or the solid-gas interface energy via Eq. (3.52). For all results shown in the following, the ratio of the solid-liquid to liquid-gas interface energy was set to $\sigma = \gamma_{sl}/\gamma_{lg} = \frac{1}{3}$, if not stated otherwise. While the capillarity and wetting energies of the two models can be set to fully agree in the macroscopic limit, this is not the case for the elastic energy. The elasticity of the Neo-Hookean model considers incompressibility, while the Winkler foundation model, utilized in the gradient dynamics formulation, is perfectly compressible. Technically, the connection of the (dimensional) effective softness S , as used in the gradient dynamics model, and the storage shear modulus G' , used in the Neo-Hookean model, is given by Eq. (3.79), i.e., with $G' \equiv E_\mu$. This connection would lead to a relation of the Neo-Hookean (NH) and gradient dynamics (GD) elastocapillary lengths like

$$\ell_{ec}^{NH} = \frac{\gamma_{lg}}{G'} \sim \gamma_{lg} S \frac{2(1-\nu)}{d(1-2\nu)} = \ell_{ec}^{GD}. \quad (7.43)$$

As $\ell_{ec}^{GD} = 0$ for $\nu = \frac{1}{2}$, however, this value is prohibited in the gradient dynamics description, i.e., such a systematic connection between the models cannot be established. This issue may be addressed in two different ways:

1. The relation (7.43) is used nevertheless and the Poisson ratio is set to an other value close to $\nu = \frac{1}{2}$ such that non zero values are maintained for the softness. However, such a procedure is rather arbitrary, since there is no rule on how such a value $\nu \neq \frac{1}{2}$ is to be assigned and even tiny differences in that value may cause huge changes in the effective softness.
2. The length scales in Eqs. (3.90) obtained from the analytic solution in the long-wave limit are used to quantify the extension of the wetting ridge

$$\ell_{ec}^{GD} \sim \sqrt{\gamma_{lg} S} \rightarrow S \sim \frac{1}{G'^2}. \quad (7.44)$$

On the one hand, this expression allows to relate the effective softness S to the storage shear modulus G' without having to consider the Poisson ratio at all. On the other hand, its reliability outside the long wave limit is questionable.

The scaling of the effective softness with the storage shear modulus is quite different in both methods. In method 1 it is $S \sim G'^{-1}$ [Eq. (3.79)] while method 2 assumes $S \sim G'^{-2}$. In the following, the softness of the substrate is quantified by the ratio

ℓ_{ec}/R of the elasto-capillary length to the base radius R of the drop in the deformed configuration. This enables a one-to-one comparison of the equilibrium shapes of drop and substrate obtained by the two models, without any adjustable parameters. The gradient dynamics model further involves dynamical parameters, namely the viscosities of the liquid layer η and the elastic substrate η_s , the ratio of which is reflected by the dimensionless parameter τ . As mainly static situations are considered in the following, the choice of τ is not relevant for now.

7.3.1. CONTACT ANGLES

In Fig. 7.5 the transition of the liquid contact angle θ_{lg} from the rigid to the quasi-liquid limit is reported as a function of the softness ℓ_{ec}/R and in the presence of the Shuttleworth effect. Thereby, method 2 is used for the estimation of the gradient dynamics elasto-capillary length, i.e., $S \sim G'^{-2}$ according to Eq. (7.44). The transition is shown for a pre-stretched ($\lambda_\infty = 1.2$, dashed lines) and an unstretched substrate ($\lambda_\infty = 1$, solid lines), respectively, for all three symmetry cases of the Shuttleworth effect reflected by the three panels in Fig. 7.5. In this, the black lines correspond to the results generated by the macroscopic Neo-Hookean model, while the blue lines represent the mesoscopic gradient dynamics results. In all calculations, the surface energies of the unstretched reference configuration ($\gamma^{lg}, \gamma_0^{sg}, \gamma_0^{sl}$) are fixed to constant values, such that the corresponding Young's angle is $\theta_Y^0 = 21.06^\circ$. All curves exhibit a transition from Young's law to Neumann's law, i.e., θ_{lg} decreases as the softness ℓ_{ec}/R of the substrate increases and the drop sinks in. The details of this transition depend on both, the choice of the Shuttleworth coefficients γ_1^{sg} and γ_1^{sl} , as well as also on the pre-stretch of the substrate $\lambda_\infty = 1$ vs. $\lambda_\infty = 1.2$.

SYMMETRIC SHUTTLEWORTH EFFECT

Figure 7.5(b) corresponds to a situation with a symmetric Shuttleworth effect, for which $\gamma_1^{sg} = \gamma_1^{sl}$. In the limit of rigid substrates ($\ell_{ec}/R \ll 1$), it is found that the liquid angle is independent of pre-stretch λ_∞ . This is expected since the difference in surface energies $\gamma_{sg}(\lambda) - \gamma_{sl}(\lambda)$ which governs Young's angle [Eq. (7.17)] is not affected by the imposed λ_∞ [cf. Sec. 7.1.4]. In other words, stretching a very rigid substrate does not render it more hydrophilic or hydrophobic if the Shuttleworth effect is symmetric. However, the effect of stretching becomes apparent as higher softnesses are approached. In the quasi-liquid limit ($\ell_{ec}/R \gg 1$) the liquid-gas contact angle is found to be $\theta_{lg} = 10.3^\circ$ without pre-stretch and $\theta_{lg} = 11.1^\circ$ for $\lambda_\infty = 1.2$. This difference in contact angles can be attributed to the changes in surface tensions

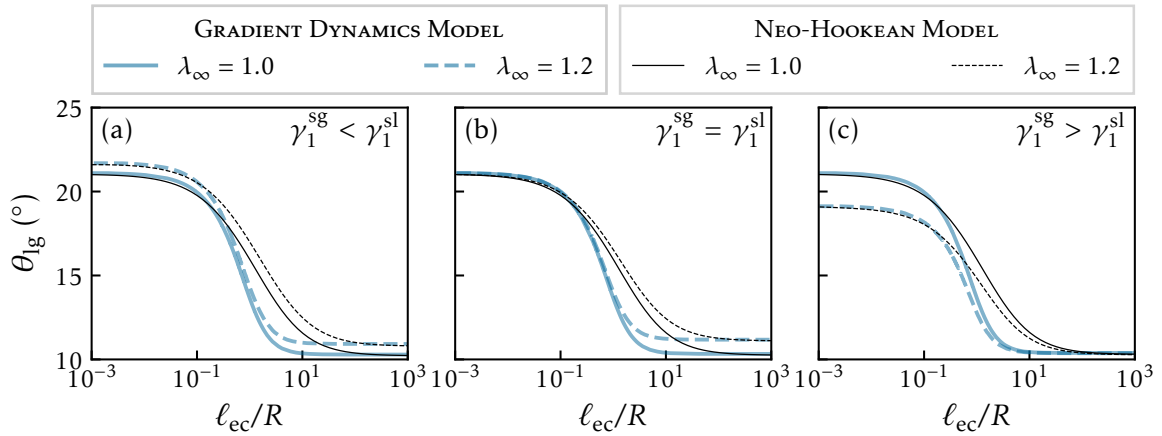


FIGURE 7.5.: Liquid contact angle θ_{lg} versus substrate softness ℓ_{ec}/R , for symmetric and asymmetric Shuttleworth effect i.e., (a) $\gamma_1^{sg} < \gamma_1^{sl}$, (b) $\gamma_1^{sg} = \gamma_1^{sl}$, (c) $\gamma_1^{sg} > \gamma_1^{sl}$. Black and blue lines correspond to the macroscopic Neo-Hookean and mesoscopic gradient dynamics model, respectively. Results without ($\lambda_\infty = 1$, solid lines) and with ($\lambda_\infty = 1.2$, dashed) pre-stretch are shown. The dimensionless elastocapillary length is for the gradient dynamics model estimated via $\ell_{ec} = \sqrt{\gamma_{lg} S}$. Even though the contact angles in the rigid and liquid limits and the onset of the transitions are aligned, the latter found to be more narrow by the gradient dynamics model. Parameters are set to $\theta_Y^0 = 21.06^\circ$ and $\gamma_1^{sl} = \gamma_0^{sl}$ while γ_1^{sg} is chosen such that $\gamma_1^{sg}/\gamma_1^{sl} = (1/3, 1, 3)$ for panels (a,b,c), respectively.

due to stretching, which affect Neumann's balance [cf. Eqs. (7.42a) and (7.42b)], even though Young's angle remains unaffected.

As for the comparison of the macroscopic Neo-Hookean model (black lines) and the mesoscopic gradient dynamics model (blue lines) it is found that both predict the same angles θ_{lg} in the rigid and quasi-liquid limits. This reflects that the limiting values for the liquid angle are exclusively determined by capillarity, i.e., Young's and Neumann's laws, respectively, and that capillarity is rigorously implemented in both models. However, it is clearly seen that the rigid-to-soft transition is predicted to be much more abrupt by the gradient dynamics model as compared to the Neo-Hookean simulations. The contact angle in the gradient dynamics model sharply changes within about one order of magnitude around $\ell_{ec}/R \sim 1$, while the Neo-Hookean model takes two to three orders of magnitude in softness to undergo the transition. In consequence, the Neo-Hookean liquid angles are larger than those in the gradient dynamics model during the transition. This *slower* transition of the Neo-Hookean solid may be attributed to the long-range nature of elastic interactions [Joh85]: The displacement induced by a localized traction exerted onto a two-dimensional elastic medium decays only logarithmically with distance, until the size of the system is encountered. This long-ranged nature of elasticity is lost when approximating the substrate by Winkler's foundation, for which the causality of traction and displacement is perfectly local.

It can thus be concluded that the mesoscopic gradient dynamics model with a reduced description of elasticity faithfully reproduces the equilibrium angles in the rigid and soft limits, including the effect of pre-stretch. When expressing the stiffness through ℓ_{ec}/R , the model captures the trends qualitatively, but significant quantitative differences appear in the transition range. Similar observations regarding the two models apply to all panels in Fig. 7.5, i.e., for the asymmetric Shuttleworth effect as well which we discuss in detail next.

ASYMMETRIC SHUTTLEWORTH EFFECT

Let's have a look at the asymmetric Shuttleworth effect, for which $\gamma_1^{sg} \neq \gamma_1^{sl}$. On the one hand, Fig. 7.5(a) corresponds to a situation with $\gamma_1^{sg} < \gamma_1^{sl}$, such that the increase of the solid-liquid interface energy with stretch exceeds the one of the solid-vapor interface energy. In this case, the substrate seems to become more *hydrophobic* when getting stretched. Indeed, larger contact angles θ_{lg} are found for $\lambda_\infty = 1.2$ as compared to the unstretched case $\lambda_\infty = 1$. It can be verified that in the rigid limit, the increase of θ_{lg} exactly matches the prediction by Young's law [Eq. (7.17)] based on the stretch dependent interface energies at λ_∞ . This change in θ_{lg} with stretch occurs regardless of the substrate softness. The opposite case where $\gamma_1^{sg} > \gamma_1^{sl}$ is shown in Fig. 7.5(c). Other than before, the substrate now appears to become more *hydrophilic* when being stretched. In the rigid limit ($\ell_{ec}/R \ll 1$) the contact angle θ_{lg} is indeed observed to be smaller for $\lambda_\infty = 1.2$ as compared to $\lambda_\infty = 1$. This again is in accordance with Young's law based on the imposed λ_∞ . Interestingly, the difference in contact angle is no longer apparent in the quasi-liquid limit ($\ell_{ec}/R \gg 1$) though. However, the prediction of the contact angle in this limit is not straightforward, since Neumann's balance depends on the local values of the surface tensions at the contact line. These local surface tensions depend not only on λ_∞ but also on the local stretch, which, as will be discussed below, changes across the substrate in a non-trivial manner.

Finally, and be it only out of curiosity, the transitions shown in Fig. 7.5 may be replotted using the definition (7.43) to quantify the elasto-capillary length instead of Eq. (7.44). As was discussed above, this approach requires to assign values to the elastic layer thickness d and the Poisson ratio ν . While the layer thickness can be set to $d = 8R$ in accordance with the Neo-Hookean model, the Poisson ratio can not be set to $\nu = \frac{1}{2}$ and $\nu = 0.49$ is used instead. The result is shown in Fig. 7.6. Surprisingly, this rescaling significantly improves the agreement between the models such that, besides the contact angles in the limiting cases, also the width of the transi-

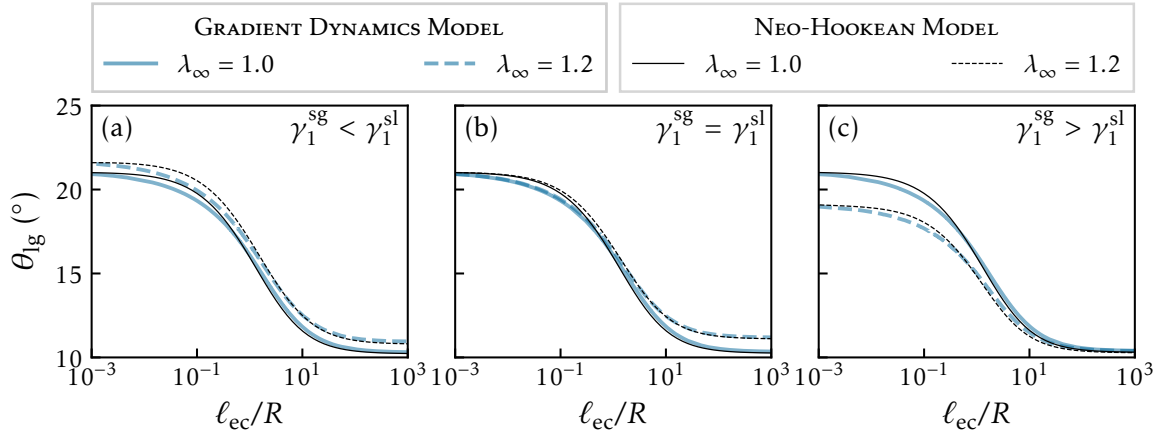


FIGURE 7.6.: Same data representation as in Fig. 7.5 except for the definition of the elasto-capillary length in the gradient dynamics model. Instead of $\ell_{ec} = \sqrt{\gamma_{lg} S}$ the relation (7.43) is used, with the dimensionless elastic layer thickness d and Poisson ratio ν . To get close to the neo-Hookean model the elastic layer thickness was chosen to be $d = 8R$ with $R = 1000$. Since the neo-Hookean model assumes incompressibility the Poisson ratio would have to be $\nu = \frac{1}{2}$. As that is not possible in the Winkler foundation description, $\nu = 0.49$ is chosen instead.

tions fit quite well now. Again, it has to be kept in mind that the choice of $\nu = 0.49$ is absolutely arbitrary and even tiny changes $\mathcal{O}(10^{-3})$ cause huge deviations, i.e., a shift of the transitions in direction of the softness. Nevertheless, the striking agreement seen in Fig. 7.6 seems to indicate that the softness should indeed scale with $S \sim G^{-1}$ rather than $S \sim G^{-2}$, at least in the full curvature formulation, which comes along with the disadvantage that the proportionality constant between S and G^{-1} must be fitted in order to match the transition positions.

7.3.2. SUBSTRATE DEFORMATIONS

After reviewing the transition of the liquid-gas contact angle as the softness of the substrate changes, the actual deformations of that substrate as obtained by the two different models is investigated with regard to the impact of the (a)symmetric Shuttleworth effect. To compare the profiles, the results in Fig. 7.5 are used as *calibration curves*, mapping the effective softness where identical liquid contact angles are found from one model to the other.¹⁰ If not stated otherwise, the contact angle is $\theta_{lg} \approx 16^\circ$, which lies about halfway the transition from rigid to quasi-liquid in Fig. 7.5, will serve as the default reference value to select the softness for comparisons in the following. In Figure 7.7 magnifications of the profiles, obtained by the

¹⁰While in the Neo-Hookean model the desired value of θ_{lg} can be directly initialized, the dependence of θ_{sl} on the effective softness S , used in the gradient dynamics model, is not known a priori, which is why continuation data are required.

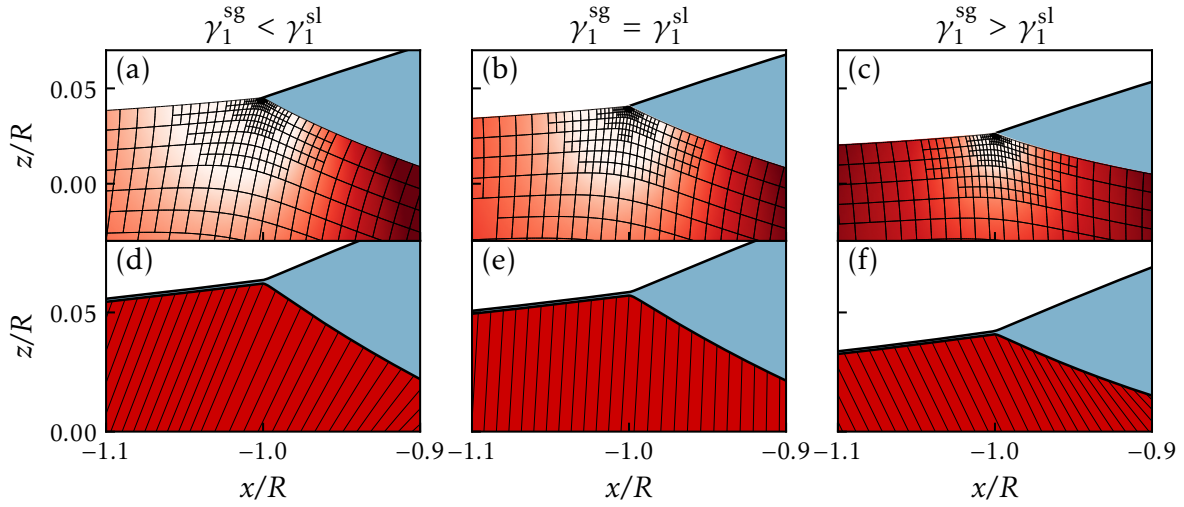


FIGURE 7.7.: Typical height profiles and substrate deformations in the vicinity of a contact line as obtained with the (a-c) macroscopic and (d-f) mesoscopic model in the cases of symmetric and asymmetric Shuttleworth effect as indicated above the panels. The central result is that horizontal displacements induced by the droplet are governed by the (a)symmetry of the Shuttleworth effect. In the top row (a-c), the deformation is visible from the grids that in the reference state consists of straight horizontal and vertical. In the bottom row (d-f), the lines indicate the interface displacement induced by the presence of the drop. The substrate is pre-stretched with $\lambda_\infty = 1.2$. Further parameters are $\theta_Y^0 = 21.06^\circ$, $\theta_{lg} \approx 16^\circ$, $\gamma_1^{sl} = \gamma_0^{sl}$, and $\gamma_1^{sg} = \frac{1}{3} \gamma_1^{sl}$ (left), $\gamma_1^{sg} = \gamma_1^{sl}$ (center), $\gamma_1^{sg} = 3 \gamma_1^{sl}$ (right). Note that for each panel ℓ_{ec}/R is selected by θ_{lg} , cf. Fig. 7.5.

Neo-Hookean (upper row) and the gradient dynamics (lower row) model, are shown in the vicinity of the contact line for all three symmetry cases of the Shuttleworth effect, given by the three columns. When comparing the latter, a clear difference is immediately noticed in the horizontal displacements.

Detailed quantitative comparisons are presented in Fig. 7.8, where black and red lines respectively represent the data obtained by the macroscopic and mesoscopic model, using a pre-stretch of $\lambda = 1.2$. The top row of Fig. 7.8 shows the vertical substrate displacements $\xi(x)$, normalized by the drop size R , for symmetric and asymmetric Shuttleworth effect. The profiles all look very similar, with a very good agreement between the neo-Hookean (black) and mesoscopic (red) models. The latter is found to produce slightly higher wetting ridges as compared to the Neo-Hookean model. Outside of the drop, the Neo-Hookean wetting ridges systematically decay over a wider range than the ones obtained by the gradient dynamics model, which are more narrow. This signals the previously mentioned long-ranged elastic interactions, which are not faithfully captured by the Winkler foundation model.

The middle row of Fig. 7.8, i.e., panels (d)-(f), shows the horizontal substrate displacements $u_{rel}(x) = u(x) - (\lambda_\infty - 1)X = u(x) - \varepsilon_\infty X$ induced by the droplet rel-

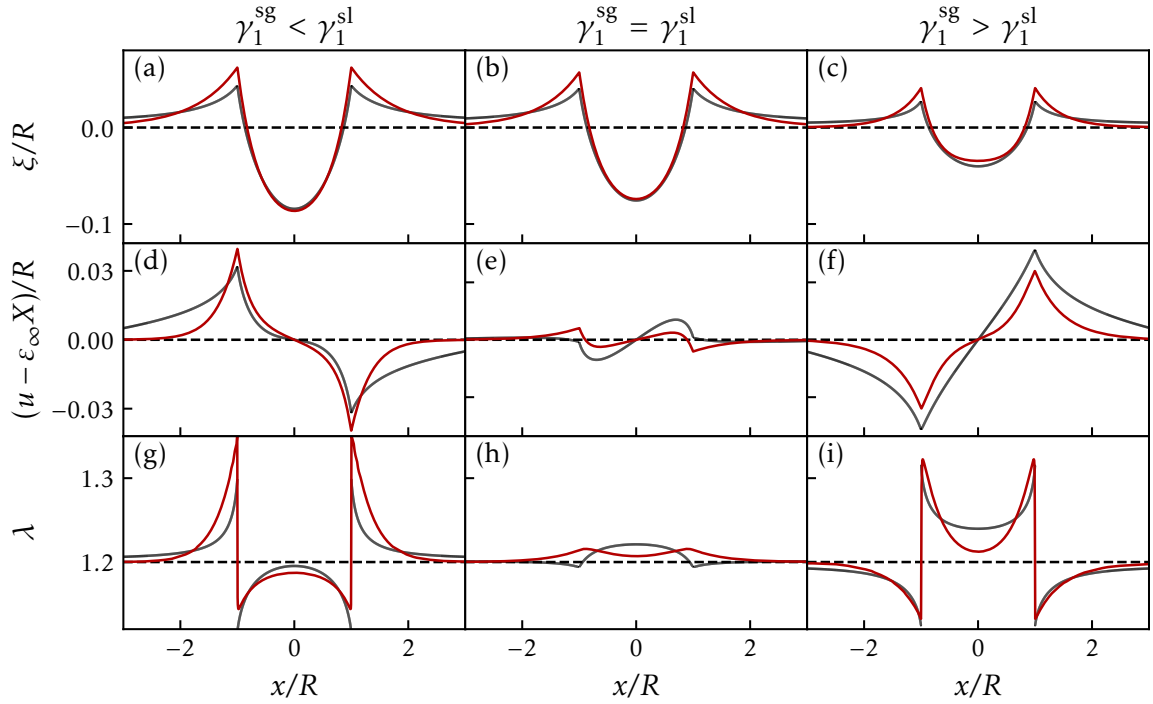


FIGURE 7.8.: Substrate deformations for symmetric and asymmetric Shuttleworth effect. In the top row the vertical displacements $\xi(x)$, normalized by drop size R , are shown. The middle row gives the horizontal displacements relative to the pre-stretch, i.e., $u(x) - (\lambda_\infty - 1)X$ with $\varepsilon_\infty = \lambda_\infty - 1$, normalized by drop size R . In the bottom row, the surface stretch λ is spatially resolved. Black lines correspond to the macroscopic Neo-Hookean model, red lines to the mesoscopic model. Parameters are chosen as in Fig. 7.7.

ative to pre-stretch [see App. A.9], where significant differences appear between the (a)symmetric cases. Comparing panel (d) where $\gamma_1^{sg} < \gamma_1^{sl}$ to panel (f) where $\gamma_1^{sg} > \gamma_1^{sl}$, a change of the horizontal displacement direction, from pointing inwards to pointing outwards, is observed. This can be interpreted along the lines of Refs. [WAS13, AS16], who show that in the rigid limit a resultant horizontal force $\gamma_1^{sl} - \gamma_1^{sg}$ is exerted onto the substrate, pointing towards the drop center. Indeed, it can be observed here that the horizontal displacement changes its orientation when the difference in Shuttleworth coefficients changes sign. Consistently, only very small horizontal displacements are present in case of a symmetric Shuttleworth effect in panel (e). Note, that, despite the localized nature of the Winkler foundation model, the deformations in both vertical and horizontal direction are laterally extended beyond the contact line. This is due to the Laplace pressure, resulting from the surface tension of the substrate, which penalizes severe curvatures such that the flanks of the wetting ridge are smoothened out. This effect further translates to the horizontal displacement, as it is coupled to the vertical displacements via stretch λ .

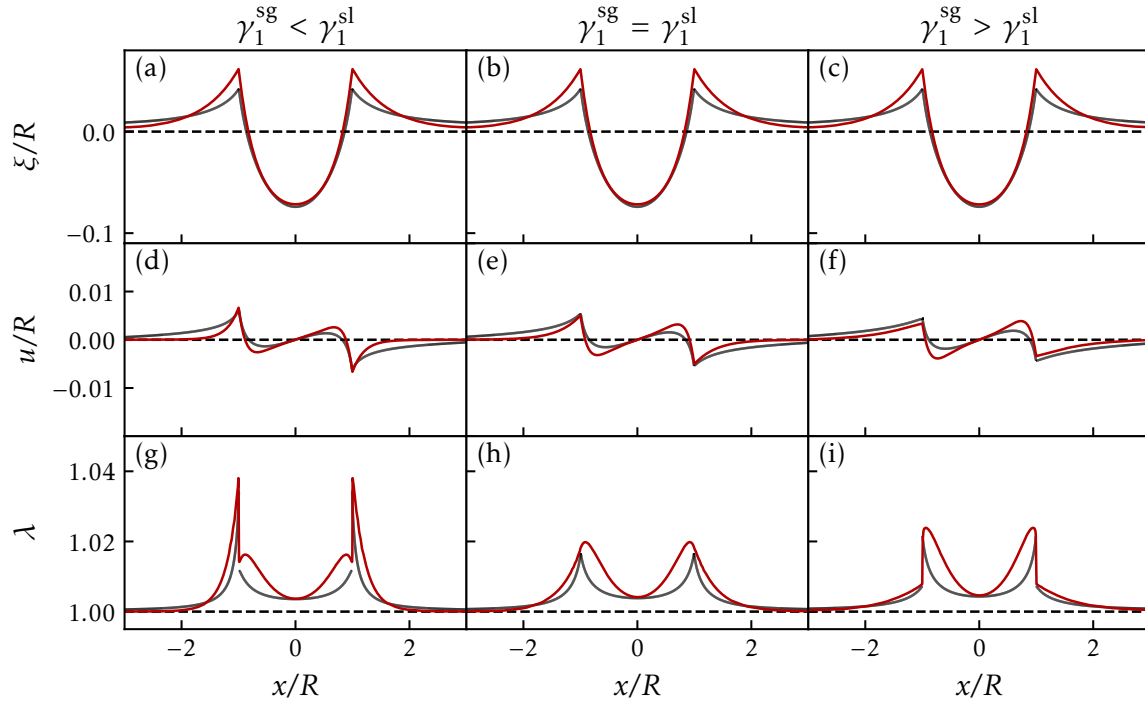


FIGURE 7.9.: Same as in Fig. 7.8, but without pre-stretch, i.e., for $\lambda = 1$. In this case, the Shuttleworth effect is quite weak and leads to much smaller horizontal displacements u and smaller changes in surface stretch λ in comparison to the pre-stretched case with $\lambda = 1.2$ in Fig. 7.8.

Finally, the bottom row of Fig. 7.8 shows the spatially resolved stretch $\lambda(x)$ along the substrate surface, which is subject to the conditions of continuous chemical potential $\mu_{\text{sg}} = \mu_{\text{sl}}$ across the contact line. In case of symmetric Shuttleworth effect, this continuity of μ implies a continuity of stretch λ in turn. In view of panel (h), λ is indeed found to be a continuous across the contact line position with only minor variations about the imposed value of $\lambda_{\infty} = 1.2$. Note, that the orientation of the mesoscopic stretch resembles the one in panel (i), while the orientation of the macroscopic stretch resembles the one in panel (g). This is due the way by which the parameters are translated between the two models.

In case of an asymmetric Shuttleworth effect, overall stronger variations in λ are observed, as shown by the panels (g) and (i). Thereby, the larger stretches are observed for the interface with the smaller γ_1 , i.e., outside the drop for $\gamma_1^{\text{sg}} < \gamma_1^{\text{sl}}$ in panel (g) and inside it for $\gamma_1^{\text{sg}} > \gamma_1^{\text{sl}}$ in panel (i). What is striking here, is that the stretch always exceeds the imposed pre-stretch λ_{∞} on one side of the contact line, while on the other side it falls below. This results in a non-monotonic behavior along the substrate and in a sudden jump of λ at the contact line which is necessary to ensure continuity of the surface chemical potential μ there. While this jump is truly discontinuous in the macroscopic description, in the mesoscopic picture it is

smoothened out on the scale of molecular interactions, that is h_a , and represented by steep gradients instead.

For completeness sake, the results of a similar study without pre-stretch, i.e., for $\lambda = 1$, are shown in Fig. 7.9. Comparison with Fig. 7.8 reveals that the Shuttleworth effect is much weaker in the absence of pre-stretch. This is due to the specific choice that has been made for the function $g(\lambda)$, which determines the stretch-dependence of the surface energy and in the present case exhibits a minimum at $\lambda = 1$. Owing to the weak Shuttleworth effect, the horizontal displacements in Fig. 7.9 are much smaller than those in Fig. 7.8. Similarly, the surface stretch $\lambda(x)$ exhibits only small variations along the interface. Beyond that, no qualitative changes are observed between the cases of different asymmetry anymore.

7.4. ASSESSMENT

The static wetting behavior of drops on elastic substrates in the presence of the Shuttleworth effect has been investigated, using two rather different models: a macroscopic one providing a detailed description of large-deformation elasticity, and a mesoscopic one offering the versatility of a gradient dynamics approach and being able to capture the dynamics and treat large drop ensembles. These two models were the first ones published (in [Hen+22]) to model the change of the liquid contact angle with stiffness in the presence of the Shuttleworth effect. Further, it turned out that (a)symmetry in the Shuttleworth effect is essential for the effective wettability. A central finding is that the influence of the Shuttleworth effect on the vertical displacements is rather minor, while its impact on the horizontal displacement crucially depends on whether the strain-dependence of the surface energy is symmetric or asymmetric between the wet and dry parts of the substrate. The shape of the wetting ridge is found to be slightly broadened and reduced in height, due to the local increase in surface tension and the resulting Laplace pressure. An effect that is barely recognizable in the absence of larger pre-stretch however. The most prominent aspect that is governed by the Shuttleworth effect pertains to the horizontal displacements below the contact line. When the Shuttleworth effect is strongly asymmetric, i.e., $\frac{\partial \gamma_{sg}}{\partial \lambda} \neq \frac{\partial \gamma_{sl}}{\partial \lambda}$, significant horizontal displacements appear, pointing in the direction highest surface tension, i.e., where the Shuttleworth effect is strongest. By contrast, the horizontal displacements remain much smaller than the typical vertical ones, if a symmetric Shuttleworth effect, i.e., $\frac{\partial \gamma_{sg}}{\partial \lambda} = \frac{\partial \gamma_{sl}}{\partial \lambda}$, is present. A similar conclusion was already drawn in the limiting case of stiff substrates [WAS13, AS16], for which a tangential force $\frac{\partial \gamma_{sl}}{\partial \lambda} - \frac{\partial \gamma_{sg}}{\partial \lambda}$ was found to be exerted

onto the elastic layer. The results presented here generalize this observation for substrates of arbitrary softness, including the possibility of large elastic deformations. It should be mentioned, that very large tangential displacements were recently observed for wetting of drops on hydrogels [Kim+21]. In that case, however, also a strong contact angle hysteresis was found. The pinning of the contact line leads to additional forces that can enhance or reduce the horizontal displacements. Importantly, the findings in this chapter show that strong horizontal displacements can persist at equilibrium, in the absence of pinning, when the Shuttleworth effect is strongly asymmetric.

Both symmetric and asymmetric Shuttleworth effects have been reported in experiments that explore the dependence of the liquid contact angle on pre-stretch applied to the substrate [Xu+17, Sch+18, SRA18]. According to Young's law, which involves only the difference of solid surface energies, a change in the liquid contact angle directly reflects an asymmetry of the Shuttleworth effect. While Young's law only holds in the limit of rigid substrates, the results presented here confirm that the magnitude and sign of the change in θ_{lg} with changing pre-stretch correlates with the asymmetry of the Shuttleworth effect, up to substrates of softness $\ell_{ec} \lesssim R$, as are typically considered in experiments. This makes the pre-stretch induced variation of the liquid contact angle a powerful tool to assess the symmetry of the Shuttleworth effect. Both, symmetric and asymmetric case, have indeed been reported in experiments on polymeric substrates. A pre-stretch independent θ_{lg} was observed for various types of elastomers [Sch+18]. Also for the case of PDMS a strong Shuttleworth effect was inferred by a number of different techniques [Xu+17, SRA18, Bai+21]. From the perspective of physical chemistry, this suggests that the surface-elasticity, that is responsible for the stretch dependence, is independent of whether or not the substrate is wetted. The case of an asymmetric Shuttleworth effect was further observed for glassy polymers [Sch+18]. Indeed, the physico-chemical properties that determine the surface energy for glassy polymers are quite different in nature as compared to those of an elastomer [Sch+18].

In summary, the results of this chapter emphasize that horizontal displacements and stretches offer an important quantitative probe for the Shuttleworth effect, which to date has not been explored as such. A discontinuity in the spatially resolved surface stretch is direct evidence for an asymmetric Shuttleworth effect. However, even in the absence of such a jump, i.e., for symmetric Shuttleworth effect, the stretch at the contact line offers information on the strength of the Shuttleworth effect [Pan+20]. Ideally, the results presented here would be confirmed by experiments that are complemented with simultaneous measurements of the contact angles (of

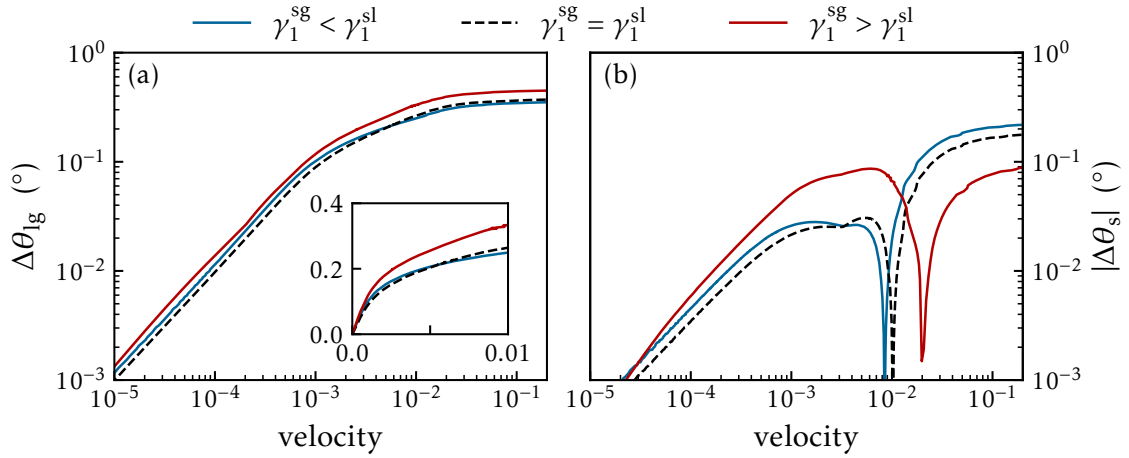


FIGURE 7.10.: The spreading of a droplet as determined by the mesoscopic gradient dynamics model in the case of asymmetric Shuttleworth effect with $\gamma_1^{\text{sg}} > \gamma_1^{\text{sl}}$. Here, time is rescaled by the characteristic scale $T = 3\eta h_a / \gamma_{lg}$, while all lengths are given in units of the final drop radius R . Panel (a) reports the dynamic liquid-gas contact angle relative to the equilibrium contact angle $\Delta\theta_{lg} = \theta_{lg}^{\text{dyn}} - \theta_{lg}^{\text{eq}}$ over the corresponding spreading velocity. In panel (b) the analogous curves for the absolute difference of the dynamic wetting ridge opening angle to its equilibrium value $|\Delta\theta_s| = |\theta_s^{\text{dyn}} - \theta_s^{\text{eq}}|$ are shown (cf. Fig. 3.6). The spreading velocity is scaled in terms of the characteristic velocity $\gamma_{lg}/(3\eta)$. The substrate softness is characterized by the elasto-capillary length normalized by the drop size $\ell_{ec}/\sqrt{V} \approx 8 \cdot 10^{-2}$ and the ratio of timescales was chosen to $\tau = 10$ (see Eqs. (3.68)). The remaining parameters including the Shuttleworth coefficients correspond to those of Fig. 7.8.

both the drop and of the solid ridge), as now a clear interpretation framework is found to relate all these quantities.

From the modeling perspective, it was found the gradient dynamics model is able to capture even nontrivial equilibrium features of soft wetting, including the Shuttleworth effect, despite of its reduced description of elasticity. This is a very promising validation as the mesoscopic gradient dynamics model naturally admits dynamical phenomena, such as viscoelastic braking and the Cheerios-effect as discussed in Ch. 5 and 6. To illustrate this perspective, now including the Shuttleworth effect, Fig. 7.10 shows the typical dynamics of a droplet, initialized with a liquid angle $\theta_{lg} = 30^\circ$ on an initially flat substrate, spreading towards its equilibrium state characterized by $\theta_Y = 10^\circ$, in analogy to the studies shown in Ch. 5 but in the presence of the asymmetric Shuttleworth effect. To investigate the influence of the latter on the spreading dynamics the difference of the liquid-gas contact angle to its equilibrium value $\Delta\theta_{lg} = \theta_{lg}^{\text{dyn}}(t) - \theta_{lg}^{\text{eq}}$ was calculated and displayed against the corresponding velocity of the contact line on a doubly logarithmic scale in Fig. 7.10 (a).¹¹ The

¹¹Here, the contact line position is estimated as the position of the wetting ridge tip, i.e., the maximum of ξ , instead of fitting the drop with a circle segment. To reduce oscillations caused by finite

substrate softness and viscosity ratio were chosen such that the dissipation in the substrate is significantly higher than the one within the liquid [cf. Ch. 5]. For all three symmetry cases the curves exhibit the same characteristic linear dependency $\Delta\theta_{lg} \sim v$ in the low velocity regime $v < 10^{-3}$, though shifted by up to a factor 1.5 to each other indicating a difference in dissipation [Gor+20]. In the regime of small velocity, the symmetric case $\gamma_1^{sg} = \gamma_1^{sl}$ is the most mobile, as less dissipation is caused due to the absence of horizontal displacements. Note, however, that there is more to the dynamics as observed in the inset of Fig. 7.10 (a), showing the same data on a linear scale. Specifically, it highlights that the large velocity regime, reached immediately after drop deposition, is nontrivial, with the red line standing out ($\gamma_1^{sg} > \gamma_1^{sl}$). This initial stage involves a rapid formation of the wetting ridge and is different in nature from the regime of viscoelastic braking at low velocities, which is characterized by a power-law. These two regimes are also observed for the dynamic opening angle of the wetting ridge θ_s [cf. Fig. 3.6] as shown in Fig. 7.10 (b). The solid angle initially is $\theta_s = \pi$ at $t = 0$, i.e., at large speeds, and rapidly decreases during this initial relaxation phase. For all cases, θ_s passes through a minimum and subsequently increases again to the equilibrium value θ_s^{eq} at slow velocity. Therefore the absolute value of $\Delta\theta_s = \theta_s^{dyn} - \theta_s^{eq}$ is shown in Fig. 7.10 (b), as this difference may transiently take on negative values. As for the liquid contact angle, the asymmetric case $\gamma_1^{sg} > \gamma_1^{sl}$ clearly differs from the others at first and all cases seem to satisfy a power law for low velocities again. Future systematic investigations using the presented model can demonstrate how the Shuttleworth effect changes dynamical wetting on elastic substrates.

spatial discretization, the profiles are additionally interpolated using cubic splines. The wetting ridge opening angle is obtained from the maximum and minimum slope of ξ , respectively, as $\theta_s = \pi - \tan^{-1}(\max[\partial_x \xi]) - \tan^{-1}(-\min[\partial_x \xi])$.

8. SOFT CONDENSATION

The content of this chapter are supposed to be published soon with indication of the co-authors AMBRE BOUILLANT , JACCO H. SNOEIJER  and UWE THIELE . In particular, all experiments and associated measurements presented in the following were performed by AMBRE BOUILLANT, unless cited otherwise.

The romantics among the readers have most certainly at least once breathed against a cold window pane to write the name of a dear person in the steamed up stain. If you are more of the investigative type, however, you probably forgot about that person in an instant, wondering instead why the glass has become opaque in the first place. A close look reveals, that this results from a rather dense random arrangement of numerous tiny drops that scatter the light. Such *breath figures* form on cool surfaces due to condensation of liquid from the adjacent vapor and are extensively investigated [Bey06, Gua+14, AlK17, KPN22, Bey22]. Depending on the surface properties, the liquid condenses into droplets or into a uniform film. Such a spontaneous local gathering of particles that initiate the formation of an other thermodynamic phase or structured state distinct to its surrounding is referred to as *nucleation*. While condensation, i.e., the clustering of vapor molecules into liquid drops, is a prominent and relatively simple example, nucleation plays a role in a great variety of processes ranging from various types of crystallization [Coq14], electron condensation in solids [Cha70] to tectonics including earthquakes [Run89] and volcanic eruptions [Bla79], meteorological phenomena including cloud formation, snow and rainfall [PKW98, Maroo], the initiation of diseases like decompression sickness [YH86] and even the formation of black holes [Kap84]. In general, nucleation is important for phase transitions of first order, which is a subject of great interdisciplinary interest and practical importance. Since Gibbs achieved the first insights into the matter [Gib78] various theories have developed. The widely used classical nucleation theory (CNT) [VW26, BD35, Fre39, KRK16] determines the energy cost of cluster formation based on purely macroscopic quantities such as interface and bulk energies and even though it is an approximate theory it dominated

the field for quite some years [KRR16]. The CNT is extended, e.g. by the dynamic nucleation theory (DNT) and the extended modified liquid drop (EMLD) model that incorporate the translational motions and small fluctuations in the particle number, respectively [SKG99, RRo4, KRR16, BSA25]. In contrast, to these phenomenological approaches, kinetic theory calculates the energy of cluster formation by directly considering the molecular interactions on the microscale thereby avoiding the use of macroscopic quantities. Considering the particles to be hard shapes molecular dynamics (MD) and Monte Carlo simulations are commonly utilized tools [Sek+08, Shi+14, FS23]. In contrast, density functional theory (DFT) describes the system in terms of a microscale ensemble-averaged density and is used, e.g., to consider colloidal crystals [NTO95]. The direct observation of nuclei of only a few molecules in size still remains an experimental challenge [RRo4, KRR16].

Here, the influence of soft substrate on nucleation and growth of sessile drops of partially wetting liquid from vapor is investigated, i.e., condensation onto soft substrates. It is known that the ability of a substrate to deform under external pressure crucially influences the nucleation density [Sok+10]. This observation is confirmed by Ref. [Che+19] using MD simulations. There, it was found further that also condensation rate and heat transfer efficiency increase with the softness of the substrate, which also affects the condensation mode, i.e., whether drops or films are formed. Sharma et al. [Sha+22] observed that even though the overall condensation of drops increases with the softness of the substrate the growth of individual drops may be reduced by cloaking effects, e.g. by uncrosslinked *polydimethylsiloxane* (PDMS) chains leaking from the substrate. Further more, the simple gradient dynamics model presented in Sec. 3.4.2 has been used to show that the coarsening of drops of nonvolatile liquid can be suppressed as the substrate softness changes in Ch. 6.

Just recently, experiments on dew formation were presented in Ref. [Bou+25] that were performed on substrates of different softness. There, homogeneous millimetric layers of silicone elastomers are deposited on a cooling stage in a chamber with controlled humidity (water vapor and N₂ mixture) as illustrated in Fig. 8.1(a). Condensation is achieved by cooling down the gel to about $T = 5\text{C}^\circ$ while simultaneously fixing the relative humidity r_{H}^0 and pressure p until a phase transition is induced. The threshold of phase transition as shown in Fig. 8.1(b) is referred to as *saturation* and can be predicted, e.g., by the empirical *Arden-Buck equation* [Buc81]

$$p_{\text{sat}}(T) = a \exp \left[\left(b - \frac{T}{c} \right) \left(\frac{T}{d + T} \right) \right], \quad (8.1)$$

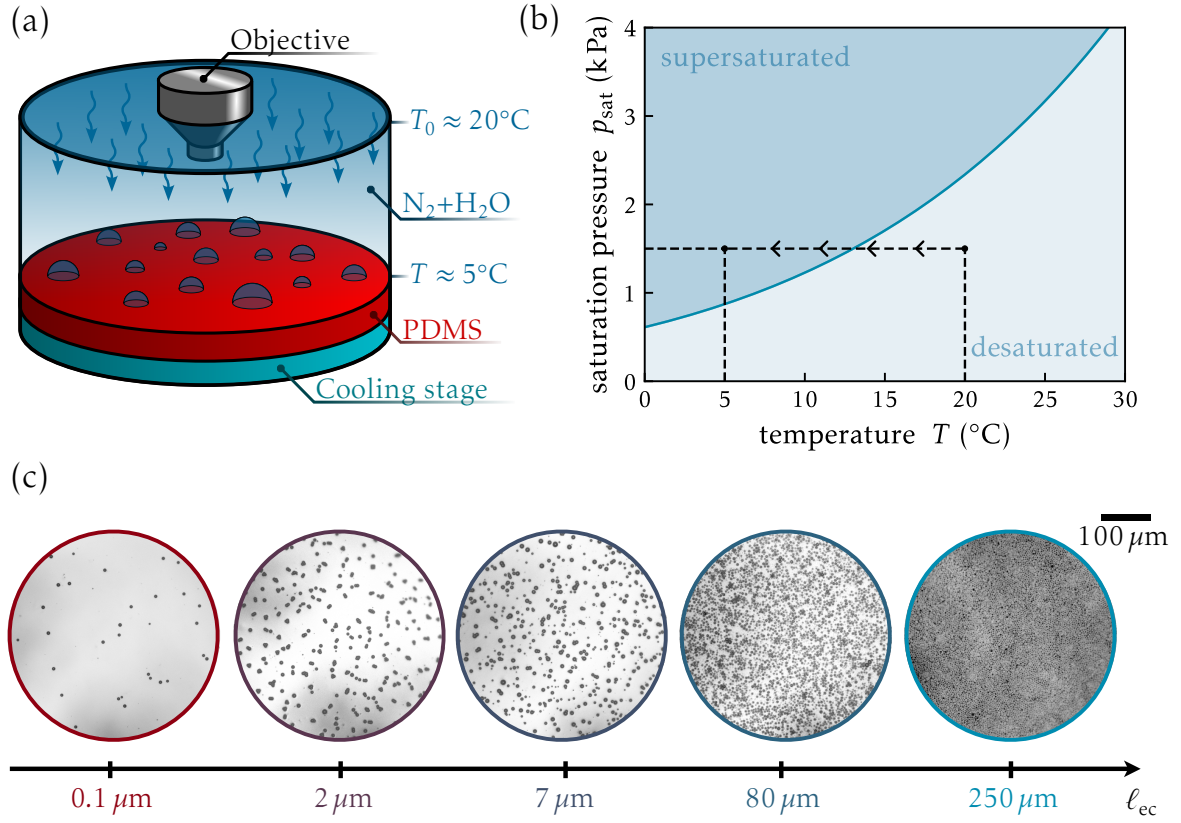


FIGURE 8.1.: (a) Scheme of the experimental setup. In a controlled-humidity chamber the PDMS substrate (red) at the bottom is cooled from below down to $T = 5^\circ C$ using a Peltier cooling stage (green). Due to the cooling, the relative humidity rises to $r_H > 1$, i.e., supersaturation, in the proximity of the substrate, inducing condensation. The saturation pressure p_{sat} at given temperature is described by the empirical Arden-Buck equation [Eq. (8.1)] in panel (b). In panel (c) top views of exemplary breath figures, taken as soon as drops were visible, are shown for different substrate softness quantified by the elastocapillary length ℓ_{ec} . The apparent nucleation density increases with softness. The breath figures in panel (c) were produced by AMBRE BOUILLANT and are presented here with her permission. The sketch of the experimental setup in panel (a) was adapted from Fig. 1 in Ref. [Bou+25].

which accounts for water vapor non-idealities over a wide range of temperatures and is widely used in meteorology and engineering for its accuracy and practicality. Thereby Eq. (8.1) considers the temperature T in $^\circ C$ and the pressure p in kPa, while $a \approx 0.61121$ kPa, $b \approx 18.678$, $c \approx 234.5^\circ C$ and $d \approx 257.14^\circ C$ are empirical constants that are valid for $T > 0^\circ C$. Eq. (8.1) can be used to calculate the relative humidity $r_H = \frac{p}{p_{sat}}$ at the substrate, i.e. at $T = 5^\circ C$, from the initialized humidity r_H^0

$$r_H = \frac{p_{sat}(20^\circ C)}{p_{sat}(5^\circ C)} r_H^0 \approx 2.68 r_H^0. \quad (8.2)$$

The impact of substrate softness, i.e., elasticity, on dew formation is investigated by tuning the gel stiffness through the polymer crosslinking density. Breath figures

are recorded from above using a high resolution magnifying objective. Fig. 8.1(c) provides examples of the resulting breath figures, each taken as soon as drops were visible, for increasing substrate softness (from left to right) quantified by the elasto-capillary length [cf. Sec. 4.1]. It is found, that the initial number of drops increases with decreasing storage shear modulus E_μ of the substrate, that is with increasing elasto-capillary length between the two asymptotic values obtained for rigid nanometric PDMS brushes grafted on a silicon wafer [Lhe+16] and quasi-liquid uncrosslinked PDMS. Remarkably, once condensation has started, there are no further nuclei forming in the dry regions between the already growing drops, which is due to desaturation of the vapor phase in the proximity of the substrate, as discussed in Ref. [Bou+25, BSA25]. In Fig. 8.2 the nucleation density ψ is displayed as a function of ℓ_{ec} for two different values of humidity, $r_H^0 = 0.5$ (Δ) and $r_H^0 = 0.9$ (Υ).¹ Remarkably, the nucleation density increases with softness, while changes in r_H^0 do not seem to considerably affect the ψ . This transition in the nucleation density ψ when going from rigid to quasi-liquid substrates is reminiscent to the transition in the contact angles between Young's and Neumann's laws [cf. Ch. 4], which was

¹These values correspond to the relative humidity imposed far from the substrate. Due to cooling, the relative humidity respectively increases to $r_H = 1.22$ and $r_H = 2.42$ in the proximity of the substrate.

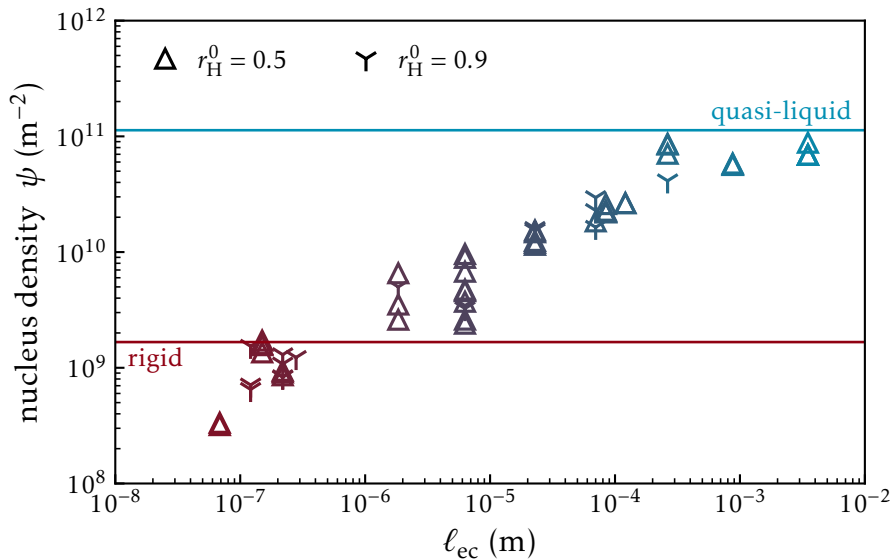


FIGURE 8.2.: The nucleus density ψ against substrate softness quantified in terms of the elasto-capillary length ℓ_{ec} . The experiment was performed for two different imposed relative humidities $r_H^0 = 0.5$ (Δ) and $r_H^0 = 0.9$ (Υ). The horizontal lines indicate the results obtained in the limiting cases of a rigid substrate (red), realized by a nanometric PDMS brush grafted on a silicon wafer, see [Lhe+16], and a quasi-liquid substrate (blue), using a thick layer of uncrosslinked oligomers of the same material. The red to blue color gradient indicates the transition between these two limits. This figure was reproduced from the data presented in Fig. 2 of Ref. [Bou+25].

theoretically predicted in [Lim12, Mar+12b, SD12, Lub+14] and is experimentally confirmed in Fig. 8.3. The cross-over between the rigid regime (Young) and liquid regime (Neumann) can be inferred from Fig. 8.3 to occur at $\ell_{ec} \approx R$. In Fig. 8.1(b) the transition is found at $\ell_{ec} \approx 10 \mu\text{m}$ and thus elasticity is expected to play a role when $\ell_{ec} \approx R \approx 10 \mu\text{m}$. This observation is enigmatic for the typical size of a nucleus is known to be $R^* \ll 10 \mu\text{m}$ and so it is not clear if the substrate softness directly affects the nucleation itself or rather the subsequent evolution.

In the following the gradient dynamics model as introduced in Sec. 3.4 will be further extended to capture condensation and evaporation by applying the one-sided approach presented in Ref. [Piso4, Aja05, Thi10] for evaporating sessile drops. Here, the full curvature formulation [Thi18] is employed using polar coordinates in order to more exactly describes the behavior radially symmetric drops, effectively rendering the system three dimensional. The resulting model is employed to investigate the increase of nucleation density with increasing softness.

First, the macroscopic CNT is discussed in Sec. 8.1 to determine the governing thermodynamic potential of a system such as described in the experiments. The result is then used in Sec. 8.2 to estimate the nucleation energy barrier in the limiting cases of perfectly rigid and quasi-liquid substrates, considering unstable steady macroscopic drop shapes to represent the *nuclei* [cf. Sec. 3.2]. In Sec. 8.3 the mesoscopic model is used to investigate the critical nucleus in the regime of intermediate softness. The meso- and macroscopic results are then compared in the liquid and rigid limits. Finally, the influence of substrate softness on the nucleation energy barrier is investigated and discussed in the context of the experimentally observed phenomena in Sec. 8.4.

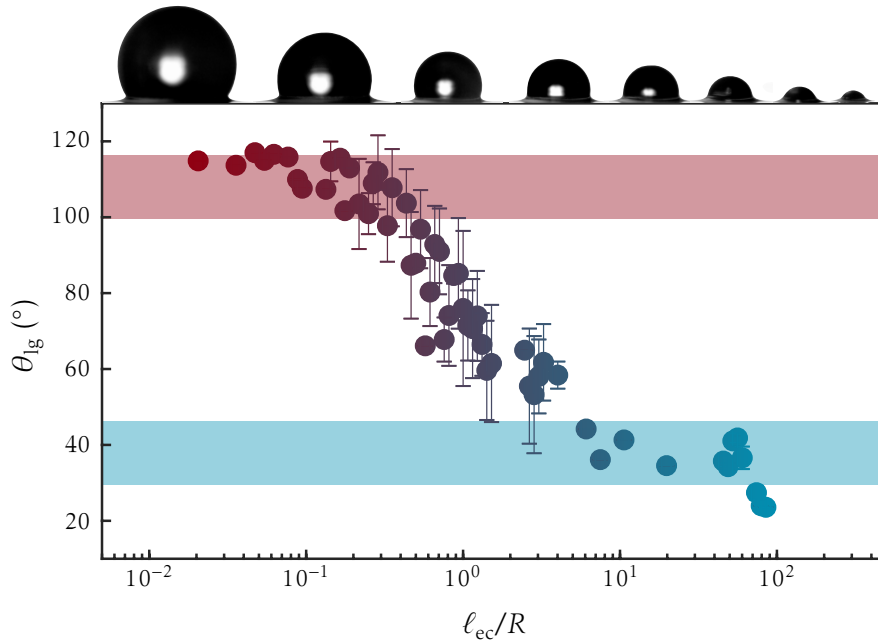


FIGURE 8.3.: Liquid-gas contact angle θ_{lg} as a function of the gel softness ℓ_{ec}/R . The angles are measured from side-view images of droplets with radii ranging from $R \approx 10 \mu\text{m}$ to $R \approx 1 \text{mm}$. The shear storage modulus of the gel substrate ranges from $E_\mu = 10^2 \text{Pa}$ to $E_\mu = 10^6 \text{Pa}$. The lightly shaded bands indicate the experimentally determined contact angles in the rigid limit (red) and in the quasi-liquid limit (blue) for the same materials as in Fig. 8.2. Again, the red to blue color gradient indicates the transition between these two limits. These data have not been published and are presented here with courtesy of AMBRE BOUILLANT.

8.1. CLASSICAL NUCLEATION THEORY

The transition of a particle from an initial phase to another may occur spontaneously only if that process is associated with a decrease in free energy. This condition must be met also in the context of nucleation in order for a new phase to spontaneously emerge and grow. The formation of the latter, however, is always accompanied by the creation of an interface (with the surrounding initial phase), which represents an energy penalty in turn. Assuming the new cluster to adapt a shape that minimizes the surface to volume ratio (provided the material is able to do that) the energy penalty is minimized as well. Since this ratio usually decreases further with increasing volume, the decrease in free energy per particle entering the new phase eventually predominates the penalty associated with the interface created in the same course. The minimal structure at which that happens corresponds to an energetic maximum and is referred to as a *nucleus*. It is these nuclei that initiate the formation of a new phase, once the associated energy barrier is overcome. In other words, the nucleus corresponds to a steady yet unstable threshold state, meaning that every smaller structure decays and every larger structure starts growing. The exact form of the governing energy and thus the characteristics of the

nucleus crucially depend on the considered scenario. Two general cases are distinguished:

HOMOGENEOUS NUCLEATION: A homogeneous initial phase, consisting of only one particle type, is considered. Due to thermal fluctuations these particles occasionally form small clusters of a new phase, that eventually start growing spontaneously if they exceed a critical size or particle number. In other words, these clusters of the same particle type may serve as nuclei. The energy penalty is exclusively governed by the interface energy between the initial and new phase and a lower bound may be estimated by assuming the nucleus to take a spherical shape.

HETEROGENEOUS NUCLEATION: The initial state is assumed heterogeneous in a sense that particles of different type may be present in some form ranging from microscopic impurities up to macroscopic structures (e.g. a solid substrate). If the interaction of the nucleating particle type with an other (expressed in terms of interface energies) is stronger than the interaction with its own, nucleation is energetically favored wherever that other type is present. An example are the considered breath figures, where water vapor condenses to the liquid state at the surface of a cooled substrate. The energy penalty is then given by the interplay of interface energies between all the various phases.

Note, that nucleation does not necessarily require the new phase to be denser than its surroundings. In the following, however, only the nucleation of a condensed liquid phase from its own vapor in contact with a third condensed phase forming a substrate is considered. While the description of interface energies has been extensively discussed in the previous chapters, only the bulk energy contribution remains to be addressed. The change in free energy per particle transiting from one phase to an other is given by the difference in *chemical potentials* μ between those two phases [Abr74, Kasoo, Pau11, Seo07, KRK16]. The latter is not necessarily constant, however, and might change during the process. In describing the condensation of a liquid, constant temperature T , particle number N and external pressure p are frequently assumed in the diverse literature. In such a case, the governing potential that determines thermodynamic equilibrium is the *Gibbs free energy* $\Delta\mathcal{G}$. In order to construct it, homogeneous nucleation scenario is considered. The chemical potentials μ_ℓ , μ_v of the liquid and vapor phase can be quantified either by employing a theory for a real gas, e.g., by considering a Van der Waals gas, and performing a standard Maxwell construction or by assuming the vapor to behave like an ideal gas

at fixed imposed chemical potential and particle density in the liquid. Following the latter route, the vapor obeys the corresponding equation of state $pV = Nk_B T$ and its chemical potential is

$$\mu_v = k_B T \ln \left(\Lambda^3 \frac{N}{V} \right), \quad (8.3)$$

with the Boltzmann constant k_B and the thermal wavelength Λ , i.e. the de Broglie wavelength at thermal energy. Note, that the chemical potential can be written as a function of temperature and pressure $\mu(T, p)$ via the equation of state. Accordingly, chemical potential and pressure are not independent variables in an isotherm. At equilibrium, the change in chemical potential associated with a change in pressure is then always determined by the *Gibbs-Duhem relation*

$$Nd\mu = Vdp. \quad (8.4)$$

Using the ideal gas law for the vapor, integration yields

$$\mu_v(p_v) - \mu_v(p'_v) = k_B T \ln \left(\frac{p_v}{p'_v} \right), \quad (8.5)$$

with p'_v being an arbitrary reference pressure. Assuming constant particle density in the liquid $\rho_\ell = N_\ell/V_\ell$, Eq. (8.4) leads to

$$\mu_\ell(p_\ell) - \mu_\ell(p'_\ell) = \frac{V_\ell}{N_\ell} (p_\ell - p'_\ell). \quad (8.6)$$

Then, the liquid pressure and chemical potential are directly related via the constant particle density. The difference in chemical potentials between liquid and vapor phase is

$$\Delta\mu = \mu_\ell(p_\ell) - \mu_v(p_v) = \frac{V_\ell}{N_\ell} (p_\ell - p'_\ell) - k_B T \ln \left(\frac{p_v}{p'_v} \right) + \mu_\ell(p'_\ell) - \mu_v(p'_v). \quad (8.7)$$

Demanding phase coexistence at a specific saturation pressure p_v^{sat} , i.e., $\mu_\ell(p_v^{\text{sat}}) = \mu_v(p_v^{\text{sat}})$, the reference pressures have to be set to $p'_\ell = p_v = p_v^{\text{sat}}$, leading to

$$\Delta\mu = \frac{V_\ell}{N_\ell} (p_\ell - p_v^{\text{sat}}) - k_B T \ln(r_H), \quad (8.8)$$

with the relative humidity $r_H = p_v/p_v^{\text{sat}}$. Fixing the chemical potential, and hence also the pressure, of the liquid to those of the vapor at saturation, i.e. $\mu_\ell = \mu_v(p_v^{\text{sat}})$

and $p_\ell = p_v^{\text{sat}}$, only the logarithmic term remains. If the gas phase is considered an ideal mixture of K species (e.g. water vapor in N_2) its total pressure p is the sum of all partial pressures p_i according to Dalton's law $p = \sum_i^K p_i$. The Gibbs-Duhem relation then writes

$$V \sum_i dp_i = \sum_i N_i d\mu_i. \quad (8.9)$$

Allowing only one component, e.g. $i = v$, to condense into a liquid phase, coexistence requires $\mu_\ell(p_{\text{sat}}) = \mu_v(p_v^{\text{sat}})$ where now $p_{\text{sat}} = p_v^{\text{sat}} + \sum_{i \neq v}^K p_i$ is the total pressure of the mixture at saturation of component v . In consequence, the reference pressures in Eq. (8.7) have to be chosen differently, namely $p'_\ell = p_{\text{sat}}$ and $p'_v = p_v^{\text{sat}}$, yielding

$$\Delta\mu = \mu_\ell(p_\ell) - \mu_v(p_v) = \frac{V_\ell}{N_\ell} (p_\ell - p_{\text{sat}}) - k_B T \ln \left(\frac{p_v}{p_v^{\text{sat}}} \right). \quad (8.10)$$

According to classical thermodynamics the Gibbs free energy is given by $\mathcal{G} = \mathcal{F} + pV$ with Helmholtz free energy $\mathcal{F} = \sum_i^K \mu_i N_i - p_i V_i$, the externally imposed total gas pressure p and the total volume V . The Gibbs free energies $\mathcal{G}$ of the coexisting liquid and gas phase (including vapor) state and the pure gas state $\mathcal{G}'$ are respectively given by

$$\mathcal{G}(T, N, p) = \mathcal{F}(T, N, V) + pV = \mu_\ell N_\ell - p_\ell V_\ell + \sum_i^K (\mu_i N_i - p_i V_i) + pV, \quad (8.11a)$$

$$\mathcal{G}'(T, N, p) = \mathcal{F}'(T, N, V') + pV' = \sum_i^K (\mu'_i N'_i - p'_i V'_i) + pV'. \quad (8.11b)$$

The energy difference then becomes

$$\begin{aligned}
 \Delta\mathcal{G} = \mathcal{G} - \mathcal{G}' &= \left[\mu_\ell N_\ell - p_\ell V_\ell + \sum_i^K (\mu_i N_i - p_i V_i) + pV \right] - \left[\sum_i^K (\mu'_i N'_i - p'_i V'_i) + pV' \right] \\
 &\stackrel{\langle 1 \rangle}{=} \mu_\ell N_\ell - (p_\ell - p)V_\ell + \sum_i^K (\mu_i N_i - \mu'_i N'_i) \\
 &\stackrel{\langle 2 \rangle}{=} \mu_\ell N_\ell - (p_\ell - p)V_\ell + \mu_v N_v - \mu'_v N'_v + \sum_{i \neq v}^K (\mu_i - \mu'_i) N_i \\
 &\stackrel{\langle 3 \rangle}{=} (\mu_\ell - \mu_v) N_\ell - (p_\ell - p)V_\ell + \sum_i^K (\mu_i - \mu'_i) N_i \\
 &\stackrel{\langle 4 \rangle}{=} -(p_{\text{sat}} - p)V_\ell - \rho_\ell k_B T \ln \left(\frac{p_v}{p_v^{\text{sat}}} \right) \approx -\rho_\ell k_B T \ln \left(\frac{p_v}{p_v^{\text{sat}}} \right) \quad (8.12)
 \end{aligned}$$

For clarification the separate steps are explained: At $\langle 1 \rangle$ the volume of the coexistence state is divided into a liquid and a gas part $V = V_\ell + V_g$. Further, all components of the gas mixture share the same volume $V_i = V_g = V - V_\ell$ and $V'_i = V'$, such that the respective partial pressure terms cancel with Eq. (8.9). At $\langle 2 \rangle$ the particle conservation in the gas phase $N_i = N'_i$ is used for all components of the mixture $i \neq v$. At $\langle 3 \rangle$ the global particle conservation of species v is used, i.e. $N'_v = N_\ell + N_v$. At $\langle 4 \rangle$ Eq. (8.9) is used again to eliminate the sum since $dp = 0$. Note, that not only the total pressure p but also the partial pressures $p'_i = p_i$ are held constant in the considered system. Hence, since chemical potential and pressure are not independent in an isotherm $\mu'_i = \mu_i$. The difference in chemical potentials is expressed using Eq. (8.10) and finally the pressure difference commonly neglected [Kasoo, Pau11]. Finally, the energy gap is exclusively governed by the difference in chemical potentials. For $r_H > 1$, i.e. $p_v > p_v^{\text{sat}}$, the difference in the Gibbs free energy is always negative such that a transition of particles from vapor to condensed state is always favourable. As mentioned above, this condition, referred to as *supersaturation*, is a prerequisite for spontaneous nucleation to occur and the new phase to grow. Finally, the change in Gibbs free energy associated with the creation of a liquid cluster of arbitrary shape from its own vapor in contact with a substrate is found by adding the interface energy penalties

$$\Delta\mathcal{G} = \gamma_{lv}A_{lv} + \gamma_{sl}A_{sl} + \gamma_{sv}(A_{sv} - A'_{sv}) - \rho_\ell V_\ell \Delta\mu, \quad (8.13)$$

with γ_{ij} and A_{ij} respectively being the energy and area of the liquid-vapor (lv), substrate-liquid (sl) and substrate-vapor (sv) interfaces and A'_{sv} referring to the substrate-vapor interface area of the pure gas state. The difference in chemical potentials per particle is

$$\Delta\mu = \mu_v - \mu_\ell = k_B T \ln(r_H). \quad (8.14)$$

8.1.1. GIBBS FREE ENERGY AND LANDAU POTENTIAL BARRIER

Let's consider a small region in the immediate vicinity of the substrate such that the temperature in the gas phase is approximately constant and equal to the temperature of the substrate.

In view of the experiments presented in the introduction, however, the assumption of conserved particle number seems rather unjustified since the system has access to an infinite particle reservoir. In fact, it would be more convenient to consider fixed volume V and chemical potential μ instead of N and p . In other words, the system represents a realization of a grand canonical ensemble and is driven by minimization of the corresponding *grand potential* Ω also called *Landau potential*. The difference in grand potential associated with the creation of a new phase in such a system, however, can also be expressed in terms of the Gibbs free energy again [Abr74, Yan85, LTG86, RR04], as will be discussed in the following. The difference in Landau potential (grand canonical potential) between the state of coexisting liquid and gas phase (including vapor) Ω and the pure gas state Ω' is given by

$$\Delta\Omega = \Omega - \Omega'$$

$$\begin{aligned} &\stackrel{\langle 1 \rangle}{=} \left[\mathcal{F} - \mu_v N_\ell - \sum_i^K \mu_i N_i \right] - \left[\mathcal{F}' - \sum_i^K \mu'_i N'_i \right] \\ &\stackrel{\langle 2 \rangle}{=} \left[\mu_\ell N_\ell - p_\ell V_\ell + \sum_i^K (\mu_i N_i - p_i V_i) - \mu_v N_\ell - \sum_i^K \mu_i N_i \right] - \left[\sum_i^K (\mu'_i N'_i - p'_i V'_i) - \sum_i^K \mu'_i N'_i \right] \\ &\stackrel{\langle 3 \rangle}{=} (\mu_\ell - \mu_v) N_\ell - (p_\ell - p) V_\ell + \sum_i^K (p'_i - p_i) V_i \\ &\stackrel{\langle 4 \rangle}{=} -(p_{\text{sat}} - p) V_\ell - \rho_\ell k_B T \ln\left(\frac{p_v}{p_{\text{sat}}}\right) V_\ell \approx -\rho_\ell k_B T \ln\left(\frac{p_v}{p_{\text{sat}}}\right) V_\ell. \end{aligned}$$

To clarify, the separate steps are explained: At $\langle 1 \rangle$ the Landau potentials of the final and initial state are expressed in terms of the Helmholtz free energy as $\Omega = \mathcal{F} - \mu N$. Thereby, the last term refers to the Gibbs free energy of a pure gas state with same

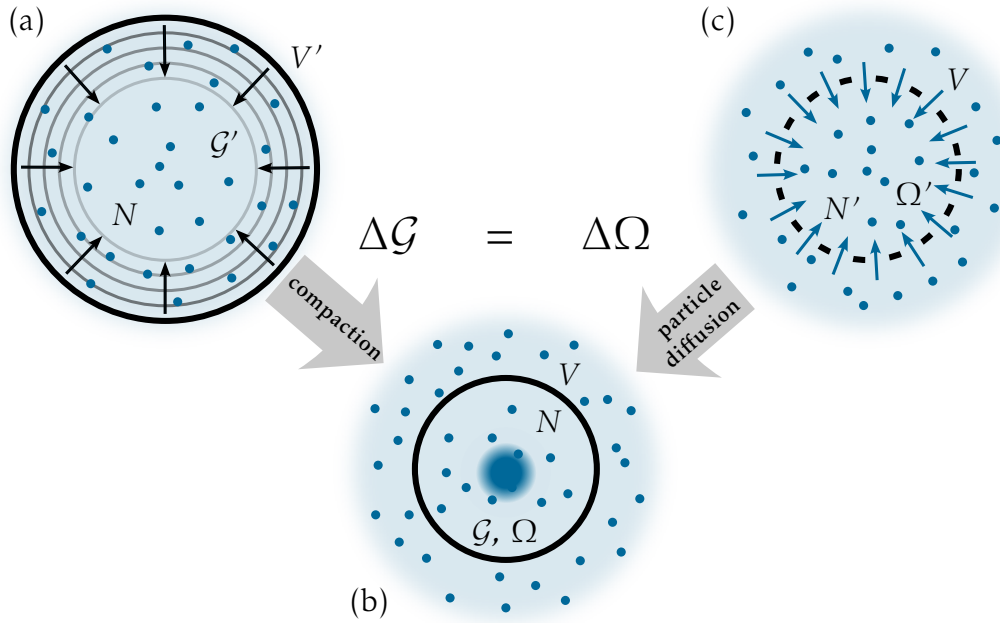


FIGURE 8.4.: Visualization of a nucleation process from two different perspectives. (a) consider a fixed particle number N of vapor particles in an initial volume V' . As the condensation of vapor into the liquid state takes place the pressure p is held constant and the volume occupied by the particles reduces to V . The energy difference is given by the change in Gibbs free energy $\Delta G = G - G'$. (c) consider a fixed volume V including an initial number of vapor particles N' . As the condensation of vapor into the liquid state takes place the chemical potential μ is held constant and particles diffuse into the area until N is reached. The energy difference is given by the change in grand potential $\Delta \Omega = \Omega - \Omega'$. If the final state (c), i.e., N and V , is the same in both scenarios, the change in Gibbs energy equals the change in grand potential $\Delta G = \Delta \Omega$ under certain assumptions as discussed in the main text.

total particle numbers and at the same fixed chemical potentials μ_i . At $\langle 2 \rangle$ the Helmholtz free energies are expressed like $\mathcal{F} = \sum_i^K \mu_i N_i - p_i V_i$. At $\langle 3 \rangle$ the fixed volume $V = V'$ and the shared gas volume $V'_i = V'$ and $V_i = V - V_\ell$ is used. At $\langle 4 \rangle$ Eq. (8.9) is used to eliminate the sum since $dp = 0$. The difference in chemical potentials is expressed using Eq. (8.8) and the pressure difference is neglected, as is common practice [Kasoo, Pau11]. This result is the same as Eq. (8.12), hence $\Delta \Omega = \Delta G$ in this case.

8.1.2. BINARY MIXTURE OF WATER VAPOR AND N_2

On the example of a binary mixture, e.g. water vapor in N_2 as used in the experiments, the change in Gibbs free energy can directly be calculated using the chemical potential of an ideal gas (8.3). The Gibbs free energy of a binary mixture coexisting

with a liquid state is

$$\begin{aligned}\mathcal{G} &= \mathcal{F} + pV = \left[\mu_\ell N_\ell - p_\ell V_\ell + \mu_v N_v - p_v V_v + \mu_{N_2} N_{N_2} - p_{N_2} V_{N_2} \right] + pV \\ &= (\mu_\ell - \mu_v) N_\ell - (p_\ell - p_v - p_{N_2}) V_\ell + \underbrace{\mu_v N_{H_2O} + \mu_{N_2} N_{N_2}}_{\mathcal{G}'}\end{aligned}\quad (8.15)$$

with $p = p_v + p_{N_2}$ being the constant imposed pressure and $V = V_\ell + V_g$ being the total volume with $V_g = V_v = V_{N_2}$. Further, conserved total particle number $N = N_{H_2O} + N_{N_2}$ as well as conserved particle numbers of the two species N_{N_2} and $N_{H_2O} = N_\ell + N_v$ are assumed. Enforcing equilibrium at $p_v = p_v^{\text{sat}}$ leads to

$$\begin{aligned}\frac{d\mathcal{G}}{dN_\ell} &= \mu_\ell - \mu_v(p_v^{\text{sat}}) - (p_\ell - p_v^{\text{sat}} - p_{N_2})/\rho_\ell \stackrel{!}{=} 0 \\ \rightarrow \mu_\ell &= \mu_v(p_v^{\text{sat}}) + \underbrace{(p_\ell - (p_v^{\text{sat}} + p_{N_2}))}_{p_{\text{sat}}}/\rho_\ell,\end{aligned}$$

with the liquid particle density $\rho_\ell = N_\ell/V_\ell$. Into Eq. (8.15) and using Eq. (8.3) yields

$$\begin{aligned}\mathcal{G} &= -\rho_\ell k_B T \ln\left(\frac{p_v}{p_v^{\text{sat}}}\right) V_\ell - \underbrace{(p_{\text{sat}} - p) V_\ell}_{\approx 0} + \underbrace{\mu_v N_{H_2O} + \mu_{N_2} N_{N_2}}_{\mathcal{G}'} \\ \rightarrow \Delta\mathcal{G} &= \mathcal{G} - \mathcal{G}' = -\rho_\ell k_B T \ln\left(\frac{\rho_v}{\rho_{\text{sat}}}\right) V_\ell\end{aligned}$$

Similarly, using the Landau potential

$$\begin{aligned}\Omega &= \mathcal{F} - \mu N = \left[\mu_\ell N_\ell - p_\ell V_\ell + \mu_v N_v - p_v V_v + \mu_{N_2} N_{N_2} - p_{N_2} V_{N_2} \right] - \left[\mu_{N_2} N_{N_2} + \mu_v (N_v + N_\ell) \right] \\ &= (\mu_\ell - \mu_v) \rho_\ell V_\ell - (p_\ell - p_v - p_{N_2}) V_\ell - \underbrace{(p_v + p_{N_2}) V}_{\Omega'}.\end{aligned}\quad (8.16)$$

Obviously $\Delta\Omega = \Delta\mathcal{G}$.

8.2. MACROSCOPIC NUCLEI

Now, that the governing thermodynamic potential is formulated it can be used to determine the work required to create a nucleus, characterized by the compensation of bulk energy gain and interface energy penalty, i.e., the maximum of the Gibbs free energy. Since the nucleation of droplets on a substrate is a stochastic process driven

by random fluctuations [KRK16] the nucleation probability is estimated using a Boltzmann factor

$$P \sim \exp\left(\frac{-\Delta\mathcal{G}^*}{k_B T}\right). \quad (8.17)$$

The ratio in the exponent relates the energy barrier $\Delta\mathcal{G}^*$ to the thermal energy $k_B T$. In the following, the energy barrier (8.13) is calculated for an axis-symmetric drop (w.r.t. the z -axis) of base radius R , sitting on a substrate that is extended in the (x, y) -plane. The statics of such drops has already been extensively discussed in Sec. 3.2. In the limits of a perfectly rigid ($\ell_{ec} = 0$) and quasi-liquid ($\ell_{ec} = \infty$) substrates, elasticity can be neglected and equilibrium drops are known to adapt spherical-cap shapes [cf. Secs. 3.2.2 and 3.2.3].

RIGID LIMIT

In the rigid limit the substrate is considered perfectly flat and the liquid-vapor interface of the nucleus is known to take the shape of a spherical cap with curvature κ_{lv} as shown in Fig. 3.4 and Fig. 4.1(a). While the contact angle is given by the interface energies according to Young's law [Eq. (3.39)] the curvature depends on the volume which in terms of κ_{lv} and θ_Y is

$$V = \frac{8\pi}{3\kappa_{lv}^3} (2 + \cos\theta_Y)(1 - \cos\theta_Y)^2, \quad (8.18)$$

while the interface areas are

$$A_{lv} = \frac{8\pi}{\kappa_{lv}^2} (1 - \cos\theta_Y), \quad A_{sl} = \frac{4\pi}{\kappa_{lv}^2} \sin^2\theta_Y. \quad (8.19)$$

Since the substrate is perfectly flat, the total area is equal to the area of the dry reference state $A'_{sv} = A_{sv} + A_{sl}$. With Eqs. (3.39), (8.18) and (8.19) the energy (8.13) becomes

$$\Delta\mathcal{G} = \gamma_{lv} \frac{4\pi}{\kappa_{lv}^2} (2 - 3\cos\theta_Y + \cos^3\theta_Y) - \rho_\ell \Delta\mu \frac{8\pi}{3\kappa_{lv}^3} (2 + \cos\theta_Y)(1 - \cos\theta_Y)^2, \quad (8.20)$$

where now $\Delta\mu = \mu_v - \mu_\ell = k_B T \ln(r_H)$. With $(2 + \cos \theta_Y)(1 - \cos \theta_Y)^2 = 2 - 3 \cos \theta_Y + \cos^3 \theta_Y$ we then find

$$\Delta\mathcal{G} = \pi(2 + \cos \theta_Y)(1 - \cos \theta_Y)^2 \left(\frac{4\gamma_{lv}}{\kappa_{lv}^2} - \frac{8\rho_\ell \Delta\mu}{3\kappa_{lv}^3} \right) \quad (8.21a)$$

$$= \pi g(\theta_Y) \left(\gamma_{lv} R^2 \sin \theta_Y - \frac{1}{3} R^3 \rho_\ell \Delta\mu \right), \quad (8.21b)$$

where the base radius $R = 2 \sin \theta_Y / \kappa_{lv}$ has been introduced and the function

$$g(\theta) = (2 + \cos \theta)(1 - \cos \theta)^2 / \sin^3 \theta, \quad (8.22)$$

is a geometric prefactor that monotonically increases with θ . Therefore, the energy barrier increases with hydrophobicity of the substrate, i.e. with the contact angle θ_Y . The critical nucleus has to satisfy $\partial_R \Delta\mathcal{G} = 0$ and its base radius is found to be

$$R^* = \frac{2\gamma_{lv} \sin \theta_Y}{\rho_\ell \Delta\mu}. \quad (8.23)$$

In consequence, a nucleated drop of base radius $R < R^*$ will shrink (evaporate) leaving behind the dry state, whereas a nucleus of base radius $R > R^*$ will grow (condense) without bound (at fixed $\Delta\mu$). The corresponding energy barrier is

$$\begin{aligned} \Delta\mathcal{G}^* = \Delta\mathcal{G}(R^*) &= \frac{4\pi\gamma_{lv}^3}{3\rho_\ell^2 \Delta\mu^2} g(\theta_Y) \sin^3 \theta_Y \\ &= \frac{\pi}{3} \gamma_{lv} R^{*2} g(\theta_Y) \sin \theta_Y. \end{aligned} \quad (8.24)$$

For example, fixing the chamber humidity to $r_H^0 = 0.9$ and cooling the gel from 20°C to 5°C , the relative humidity in immediate vicinity of the substrate is $r_H \approx 2.41$ [Eq. (8.1)]. With $\gamma_{lv} = 70 \cdot 10^{-3} \text{ J m}^{-2}$ and $\theta_Y = 70^\circ$ the critical nucleus has a size of $R^* \approx 1.166 \text{ nm}$ with an associated energy barrier $\Delta\mathcal{G}^*/k_B T \approx 30$. Note, that the θ_Y -dependent factor in Eq. (8.24) increases monotonically from $g(\theta_Y) \sin(\theta_Y)^3 = 0$ in the complete wetting case ($\theta_Y = 0^\circ$) to $g(\theta_Y) \sin(\theta_Y)^3 = 4$ in the non-wetting case ($\theta_Y = 180^\circ$). In other words, higher wettability may drastically reduce the nucleation barrier.

LIQUID LIMIT

In the quasi-liquid case, i.e., for $\ell_{ec} \rightarrow \infty$, the substrate is deformed under the influence of the Laplace pressure caused by the curved liquid-vapor interface until it is

balanced by the Laplace pressure of the substrate-liquid interface. This results in the shape of a liquid lens, characterized by constant curvatures of both interfaces as shown in Fig. 3.5 and Fig. 4.1(c). While the drop sinks into the substrate the liquid-vapor and substrate-liquid interfaces form angles θ_{lv} and θ_{sl} w.r.t. the horizontal, respectively. The angles are again governed by the interface energies according to the components of Neumann's laws (3.37). Note, that the substrate beyond the drop is considered to remain perfectly horizontal. Similar to Eq. (8.18) the lens volume can be expressed in terms of the curvatures and Neumann angles

$$V = \frac{8\pi}{3\kappa_{lv}^3}(2 + \cos \theta_{lv})(1 - \cos \theta_{lv})^2 + \frac{8\pi}{3\kappa_{sl}^3}(2 + \cos \theta_{sl})(1 - \cos \theta_{sl})^2. \quad (8.25)$$

With Eqs. (3.42) and (3.44) the difference in the Gibbs free energy (8.13) becomes

$$\Delta\mathcal{G} = \pi[g(\theta_{lv}) + g(\theta_{sl})]\left(\gamma_{lv}R^2 \sin \theta_{lv} - \frac{1}{3}R^3\rho_\ell\Delta\mu\right), \quad (8.26)$$

where $g(\theta_{lv}) + g(\theta_{sl}) = 3V/(\pi R^3)$. The critical radius and energy are then

$$R^* = \frac{2\gamma_{lv} \sin \theta_{lv}}{\rho_\ell \Delta\mu} \quad \text{and} \quad (8.27)$$

$$\Delta\mathcal{G}^* = \frac{4\pi\gamma_{lv}^3}{3(\rho_\ell \Delta\mu)^2} \sin^3 \theta_{lv} [g(\theta_{lv}) + g(\theta_{sl})] = \frac{\pi\gamma_{lv}R^{*2}}{3} \sin \theta_{lv} [g(\theta_{lv}) + g(\theta_{sl})], \quad (8.28)$$

respectively. Note, the definition of the critical radius R^* is the same in the rigid and quasi-liquid limit [cf. Eq. (8.23)] and that the energy for the rigid substrate [Eq. (8.21)] is recovered from Eq. (8.26) in the limit $\theta_{lv} = \theta_Y$ and $g(\theta_{sl}) = 0$. Further, the ratio $\Delta\mathcal{G}_{\text{rigid}}^*/\Delta\mathcal{G}_{\text{liquid}}^* \geq 1$ and depends only on the interface energies but not on supersaturation. For example, if the interface energies are $\gamma_{lv} = 70 \cdot 10^{-3} \text{ N/m}$, $\gamma_{sl} = 48 \cdot 10^{-3} \text{ N/m}$ and $\gamma_{sv} = 72 \cdot 10^{-3} \text{ N/m}$ the nucleation barrier differs by a factor $\Delta\mathcal{G}_{\text{rigid}}^*/\Delta\mathcal{G}_{\text{liquid}}^* = 2.28$ between the rigid and quasi-liquid case.

8.3. MESOSCOPIC MODEL

In contrast to the rigid and quasi-liquid limit, in the intermediate elastic regime the profiles of the liquid-vapor and substrate-liquid interfaces, i.e., $h(r) + \xi(r)$ and $\xi(r)$, are not analytically known. So far only steady macroscopic drop-like structures have been considered. Now a mesoscopic model is formulated, which is applicable

in the intermediate elastic regime as well as in the rigid and quasi-liquid limit, but which also captures the dynamics. The Gibbs free energy barrier is then constructed by expressing the interface areas and volumes in Eq. (8.13) in terms of h and ξ and the interface energy γ_{sv} by the wetting potential $f(h)$ [Eq. (3.51)], analogously to the procedure in Secs. 3.2 and 8.3. After adding the energy associated with the elastic deformation of the substrate

$$\mathcal{E}_{\text{el}} = \frac{1}{2S} \int_{\Omega} \xi^2 2\pi r \, dr, \quad (8.29)$$

where S is the effective softness [Eq. (3.79)], the energy difference between the wetted substrate state and the reference state of a dry undeformed substrate is given by

$$\Delta\mathcal{G} = \mathcal{G}_{\text{wet}} - \mathcal{G}_{\text{dry}}, \quad (8.30)$$

with

$$\mathcal{G}_{\text{wet}}[h, \xi] = \int_0^L \left[\gamma_{lv} m(h + \xi) + [\gamma_{sl} + f(h)] m(\xi) - \rho_{\ell} \Delta\mu h + \frac{\xi^2}{2S} \right] 2\pi r \, dr, \quad (8.31a)$$

$$\mathcal{G}_{\text{dry}}[h_-] = \pi L^2 [\gamma_{lv} + \gamma_{sl} + f(h_-) - \rho_{\ell} \Delta\mu h_-], \quad (8.31b)$$

where $m(\psi) = \sqrt{1 + (\partial_r \psi(r))^2}$ is the metric factor and the domain has been restricted to circular area of radius $L \gg R$. Note, that the Lagrange multiplier for volume conservation P as introduced in Sec. 3.2 is now identified as $P = \rho_{\ell} \Delta\mu$. Remember, that this Lagrange multiplier, i.e., the supersaturation, determines the curvature $\kappa_{lv} = -\rho_{\ell} \Delta\mu / \gamma_{lv}$ and therefore also the volume of a steady drop. Further the precise thickness $h_-(\Delta\mu)$ of the liquid film defining the dry substrate state also depends on the supersaturation and equals h_a only in case of $\Delta\mu = 0$ as will be discussed in Sec. 8.3.1. Finally, the variations become

$$\frac{\delta\Delta\mathcal{G}}{\delta h} = -\gamma_{lv} \kappa(h + \xi) - \Pi(h) \sqrt{1 + (\partial_r \xi)^2} - \rho \Delta\mu, \quad (8.32a)$$

$$\frac{\delta\Delta\mathcal{G}}{\delta \xi} = -\gamma_{lv} \kappa(h + \xi) - \left(\frac{1}{r} + \partial_r \right) \left(\frac{[\gamma_{sl} + f(h)] \partial_r (h + \xi)}{\sqrt{1 + (\partial_r h + \partial_r \xi)^2}} \right) + \frac{1}{S} \xi. \quad (8.32b)$$

The dynamics are still given by the TFE (2.49) and Eq. (3.5), however, the liquid dynamics is extended by a non-conserving term to incorporate mass exchange between liquid and vapor phase [LGP02, Thi10, Thi18] driven by the variation $\delta\Delta\mathcal{G}/\delta h$ and

scaled by the transfer rate M

$$\partial_t h = \nabla \cdot \left[Q(h) \nabla \frac{\delta \Delta \mathcal{G}}{\delta h} \right] - M \frac{\delta \Delta \mathcal{G}}{\delta h}, \quad (8.33)$$

$$\partial_t \xi = -\frac{1}{\zeta} \frac{\delta \Delta \mathcal{G}}{\delta \xi}, \quad (8.34)$$

with $Q(h) = h^3/(3\eta)$ and $1/\zeta$ being the zz -component of Eq. (3.6). After non-dimensionalization according to Sec. 3.4.1 and dropping the tildes, the equations write

$$\begin{aligned} \partial_t h = & -\left(\frac{1}{r} + \partial_r\right) \left(h^3 \partial_r \left[\kappa(h + \xi) + C_\theta \Pi(h) \sqrt{1 + (\partial_r \xi)^2} \right] \right) \\ & + m \left[\kappa(h + \xi) + C_\theta \Pi(h) \sqrt{1 + (\partial_r \xi)^2} + p \right] \end{aligned} \quad (8.35a)$$

$$\partial_t \xi = \frac{1}{\tau} \left[\kappa(h + \xi) + \left(\frac{1}{r} + \partial_r\right) \left(\frac{[\sigma + C_\theta f(h)] \partial_r \xi}{\sqrt{1 + (\partial_r \xi)^2}} \right) - \frac{\xi}{s} \right] \quad (8.35b)$$

with dimensionless parameters as in (3.68) except for

$$m = \frac{3\eta}{h_a} M, \quad p = h_a \frac{\rho \Delta \mu}{\gamma_{lv}} = \rho h_a^3 \log(r_H) = h_a \kappa_{lv}^*. \quad (8.36)$$

Here, $\kappa_{lv}^* = 2 \sin \theta_{lv}/R^*$ is the predicted curvature of the liquid-vapor interface of the macroscopic critical nucleus [Eq. (8.27)]. From here on, p refers to the (dimensionless) supersaturation, defined above. The thickness of the adsorption layer is chosen as $h_a = \sqrt{k_B T / \gamma_{lv}}$, such that all energies are given in terms of $\gamma_{lv} h_a^2 = k_B T$,² i.e., interpreting γ_{lv} as a binding force, h_a is the amplitude of the thermal oscillation of the liquid particles at the liquid-vapor interface, rendering the latter microscopically diffuse.

The shape of a steady drop sitting on an elastic substrate is once again characterized by the ratio of elastocapillary length to drop size, e.g., ℓ_{ec}/R or $\ell_{ec}/\sqrt[3]{V}$. It should be kept in mind, thereby, that at constant supersaturation p the volume V^* and thus also the radius R^* of the critical nucleus are unknown functions of the softness s their selves. In consequence, it is not clear how the ratios ℓ_{ec}/R^* and $\ell_{ec}/\sqrt[3]{V}$ depend on s .

²Hence, for $\mathcal{O}(\gamma) \sim 10^{-2}$ N/m and $\mathcal{O}(T) \sim 10^2$ K it follows $\mathcal{O}(h_a) \sim 10^{-9}$ m.

8.3.1. STEADY FILM STATES

Before turning to the critical nuclei, the case of a steady liquid layer of uniform thickness $h(r) = h_0$ on an undisturbed flat substrate $\xi(r) = 0$ is considered. In such a scenario, the Laplace pressure vanishes and the dimensionless total pressures [Eqs. (8.32)] reduce to

$$\frac{\delta \Delta \mathcal{G}}{\delta h} = -C_\theta \Pi(h_0) - p, \quad \frac{\delta \Delta \mathcal{G}}{\delta \xi} = 0. \quad (8.37)$$

In Fig. 8.5 (b) the total pressure $\frac{\delta \Delta \mathcal{G}}{\delta h}$ [Eq. (8.37)] is shown as a function of uniform liquid layer thickness for $p = 0.1$. Panel (a) displays the associated energy $f(h) - ph$. The respective thin lines give the case $p = 0$. According to Eq. (8.37) a steady film state may exist only if the supersaturation is balanced by the Derjaguin pressure, leading to

$$-\Pi(h_0) = \frac{p}{C_\theta}, \quad \text{i.e.,} \quad h_\pm = \left[\frac{C_\theta}{2p} \left(1 \pm \sqrt{1 - 4 \frac{p}{C_\theta}} \right) \right]^{\frac{1}{3}}. \quad (8.38)$$

Hence, up to two different steady film states may exist depending on the value of p , controlled by the relative humidity r_H . The adsorption layer height h_- represents the dry substrate state and corresponds to a minimum in the energy $f(h) - ph$, i.e., it is linearly stable [cf. Fig. 8.5 (b)]. Note, that, as h_- changes with p , the value of $f(h_-)$ changes as well resulting in an increased substrate-vapor interface energy in turn, according to the consistency condition [Eq. (3.50)]. From Eq. (8.38) it is found, that in the limit $p \rightarrow 0$ the liquid layer thickness either diverges to $h_+ \rightarrow \infty$ or becomes $h_- = 1$, i.e., $h_- = h_a$ in dimensional terms. From there, the two flat film states asymptotically follow $h_- \approx 1 + p/3C_\theta$ and $h_+ \approx (C_\theta/p)^{1/3}$. In increasing the supersaturation to $p > 0$ the pressure is correspondingly shifted while the energy is tilted by the linear term $-ph$. This results in a second zero crossing of the pressure, i.e., an additional maximum of the energy, associated with h_+ . The latter is hence unstable and represents a threshold similar to a nucleus but for uniform film states, that is, every uniform film of thickness $h > h_+$ grows by condensation while for $h < h_+$ it shrinks by evaporation until the dry state h_- is reached. As p increases even further, h_- and h_+ approach each other until they finally meet and vanish in a saddle-node bifurcation at $p_c = -\Pi_{\min} = C_\theta/4$ where $h_\pm = \sqrt[3]{2}$ [Eq. (8.38)] as shown in Fig. 8.5 (c). For $p > -\Pi_{\min}$ the Derjaguin pressure cannot compete with the supersaturation any more and nothing prevents the vapor from condensing into the liquid film.

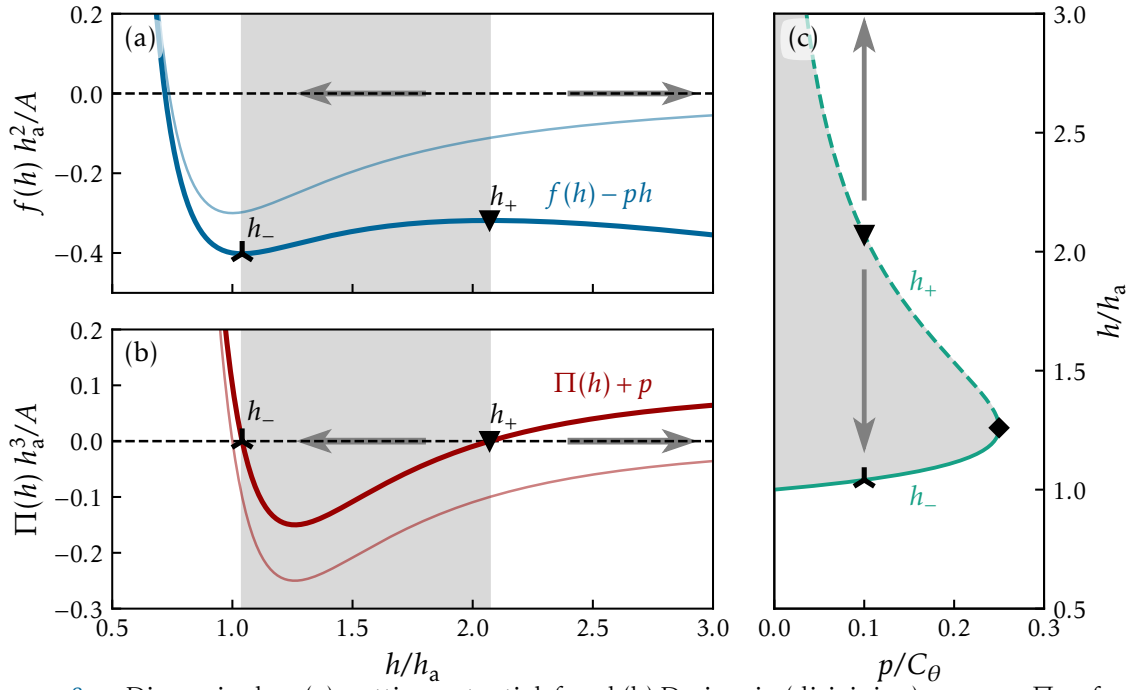


FIGURE 8.5.: Dimensionless (a) wetting potential f and (b) Derjaguin (disjoining) pressure Π as functions of the film thickness h with $C_\theta = 1$. Since $\Pi = -\partial_h f$ the zeros of Π correspond to the extrema of f and reflect steady film states. The functions at saturation (thin lines), i.e. $p = 0$, allow for only one stable steady film state h_- (♣). For $p > 0$ (thick lines show $p = 0.1$) a second unstable film state h_+ (♠) emerges. (c) With increasing p the two states approach each other and annihilate in a saddle-node bifurcation (◆). The sign of $\Pi + p$ determines whether the film grows due to condensation or shrinks by evaporation (gray shaded), as indicated by the arrows for $p = 0.1$.

8.3.2. CRITICAL NUCLEI

The mesoscopic model is now utilized to explore the critical nuclei in the regime of intermediate elasticity by numerically solving the Eqs. (8.35). To this end, the open source C++ library OOMPH-LIB is used to perform parameter continuation and time simulations. As discussed before, the critical nucleus is associated with a maximum in the Gibbs free energy $\Delta\mathcal{G}$. Thus, in the mesoscopic model it is found by solving $\frac{\delta\Delta\mathcal{G}}{\delta h} = \frac{\delta\Delta\mathcal{G}}{\delta\xi} = 0$. To do so numerically, a proper initial condition is required, which has to closely resemble the final solution. While in the rigid and quasi-liquid limit the macroscopic spherical cap profiles might be sufficiently suited, this is usually not the case in the intermediate elastic regime $0 < s < \infty$. Therefore, we make use of a little trick; In an isothermal-isobaric ensemble, as is considered here, only the critical nucleus, i.e., the drop of critical volume V^* , is steady (but unstable) and associated with a maximum in the Gibbs free energy difference $\Delta\mathcal{G}$. Prohibiting the exchange of particles between the liquid and vapor phase, by setting $m = 0$ in Eqs. (8.35), virtually renders the system canonical. The dynamics is then governed

by minimization of the Helmholtz free energy $\mathcal{F} = \mathcal{G} + \int p h 2\pi r dr$ and a steady state is characterized by $\frac{\delta \mathcal{F}}{\delta h} = c_0 = \text{const.}$ and $\frac{\delta \mathcal{F}}{\delta \xi} = 0$. One of such is the steady drop state which is now associated with a minimum in $\mathcal{F}$ and therefore stable. Such a stable steady drop state of volume V_0 can be identified with the mesoscopic critical nucleus state of volume $V^* = V_0$ if also $\frac{\delta \Delta \mathcal{G}}{\delta h} = 0$, i.e., if $\frac{\delta \mathcal{F}}{\delta h} = c_0 = p$. Hence, this method can be used to obtain a critical nucleus of preset volume $V^* = V_0$, however, the corresponding supersaturation is not known a priori but found to be $\frac{\delta \mathcal{F}}{\delta h} = p$. From here, a continuation routine may be used to obtain the critical nucleus at a specific value of p .

For all results the parameters are fixed to the values

$$\begin{aligned} \gamma_{lv} &= 70 \cdot 10^{-3} \text{ N/m}, \quad \gamma_{sl} = 48 \cdot 10^{-3} \text{ N/m}, \quad \gamma_{sv} = 72 \cdot 10^{-3} \text{ N/m} \\ \rho &= 3.34 \cdot 10^{28} \text{ m}^{-3}, \quad k_B T = 3.8 \cdot 10^{-21} \text{ kg m}^2 \text{ s}^{-2}, \quad r_H = 1.055 \end{aligned} \quad (8.39)$$

if not stated otherwise. The adsorption layer thickness is $h_a = \sqrt{k_B T / \gamma_{lv}} = 2.33 \cdot 10^{-10} \text{ m}$. The values of the corresponding dimensionless parameters are $p \approx 0.0226$, $C_\theta \approx 2.2$ and $\sigma \approx 0.6857$. Note, that in this setting a steady drop on a rigid substrate exhibits $\theta_Y = 70^\circ$ and $R^*/h_a \approx 83$.

CONSISTENCY IN THE RIGID AND QUASI-LIQUID LIMIT

To validate the numerical results, first, the mesoscopic pendant of the macroscopic energy $\Delta \mathcal{G}(R)$ [Eq. (8.26)] is calculated for comparison. In the mesoscopic picture, the base radius R of a steady drop, i.e., a critical nucleus, is not known a priori. However, the macroscopic calculations in the rigid and quasi-liquid cases provide reasonable estimates also for the elastic regime, since R is assumed to transit monotonically between these two limits. Since there is no sharp three phase contact line in the mesoscopic description, the base radius is instead defined by R of maximum curvature of the liquid-vapor interface, i.e., $\kappa(h + \xi)|_{r=R} = \max[\kappa(h + \xi)]$, which is equivalent to $\Pi(h)|_{r=R} = \min[\Pi(h)]$. It is thus encoded in the profiles h and ξ such that $\Delta \mathcal{G}[h, \xi]$ can be seen as $\Delta \mathcal{G}(R)$. Note, that the adsorption layer height h_- specifies a lower bound for the liquid layer thickness h , which in turn imposes a restriction to the minimum critical nucleus size $R_{\min}^* \sim h_-$, in contrast to the macroscopic picture where no such limit exists. This restriction in turn sets a critical supersaturation p_c , since $R^* \sim p^{-1}$, beyond which no steady nucleus states are possible anymore. The energy $\Delta \mathcal{G}(R)$ can be calculated in two different ways:

QUASI STATIC DYNAMICS: In the first method, we consider the dynamics of a drop state as given by Eqs. (8.35) using a very small m such that all hydrodynamic relaxation processes due to capillarity and wettability (the conserved part of the dynamics) take place much faster than the exchange of mass between the phases. Starting from the critical nucleus state, the liquid height profile h is disturbed using white noise with a small positive or negative mean to nudge condensation or evaporation, respectively. While the drop then slowly shrinks or grows, the base radius and energy are traced. Due to the very slow mass transfer the drop is considered quasi-static during the process, which allows for $\Delta\mathcal{G}(R)$ to be faithfully recovered.

CONTINUATION OF STEADY STATES: In the second method, continuation is used to trace the critical nucleus state over a range of p . As was stated before, the supersaturation determines the size of the critical nucleus. In consequence, a continuation in p effectively corresponds to a continuation in the nucleus size, i.e., in the base radius $R^* \sim p^{-1}$. The in the mesoscopic model the critical nucleus radius $R^*(p)$ is not an explicit variable, however, but encoded in the profiles $h^*(r;p)$ and $\xi^*(r;p)$ (see above), i.e., the steady state profiles that represent the critical nucleus for given p . According to Eq. (8.31), however, the energy depends on p not only via the profiles but also explicitly $\Delta\mathcal{G}[h(r;p), \xi(r;p); p]$. Inserting the p values from the continuation along with the corresponding profiles $h^*(r;p)$ and $\xi^*(r;p)$ gives the nucleation energy barrier as a function of supersaturation or base radius $\Delta\mathcal{G}[h^*(r;p), \xi^*(r;p); p] \rightarrow \Delta\mathcal{G}^*(p) = \Delta\mathcal{G}^*(R^*)$. However, inserting an arbitrary but fixed supersaturation $\tilde{p}$ (while still using the profiles from the continuation) instead gives the energy as a function of base radius as desired $\Delta\mathcal{G}[h^*(r;p), \xi^*(r;p); \tilde{p}] \rightarrow \Delta\mathcal{G}(R)$, i.e., with Eqs. (8.30) and (8.31)

$$\begin{aligned} \Delta\mathcal{G}[h^*, \xi^*; \tilde{p}] = & \int \left(\sqrt{1 + (\partial_r h^* + \partial_r \xi^*)^2} + [\sigma + C_\theta f(h^*)] \sqrt{1 + (\partial_r \xi^*)^2} \right. \\ & \left. + \frac{\xi^{*2}}{2s} - \tilde{p} h^* \right) 2\pi r dr - \pi L^2 [1 + \sigma + C_\theta f(h_-) - \tilde{p} h_-] . \end{aligned} \quad (8.40)$$

Note, that the thickness of the adsorption layer h_- [Eq. (8.38)] depends on p as well, which has to be considered in the reference energy of the *dry* state. Since the two energies $\Delta\mathcal{G}(R)$ and $\Delta\mathcal{G}^*(R^*)$ differ only in the value inserted for p , they

can be mapped to one another

$$\Delta\mathcal{G}[h^*(r;p), \xi^*(r;p); \tilde{p}] = \Delta\mathcal{G}^*[h^*(r;p), \xi^*(r;p); p] + V\Delta p, \quad (8.41)$$

with $V = \int (h^* - h_-) 2\pi r dr$ and $\Delta p = p - \tilde{p}$. Finally, only the profiles h and ξ associated with different R and the corresponding adsorption layer thicknesses h_- are required to calculate the energy for arbitrary p .

Fig. 8.6 shows $\Delta\mathcal{G}$ as a function of drop radius in the liquid limit (blue), the rigid limit (red) and for an intermediate elastic case (purple). Both described methods are compared with the macroscopic result. While the mesoscopic values obtained by continuation (Υ) agree very well with the ones obtained by the quasi-static approach (solid lines), both are slightly smaller than the macroscopic analytical predictions (black dashed). This results from the differences between the macroscopic and mesoscopic nucleus profiles, particularly, in the contact line region.³ More importantly, the positions of the energy maxima, i.e., the critical radii R^* ($\blacktriangledown$), are correctly recovered. The overall agreement between macroscopic and mesoscopic model is quite satisfactory, allowing us to use the latter for exploration of the criti-

³This difference is constant and does not depend on drop size. It therefore becomes less important as the drop size and the associated energies increase.

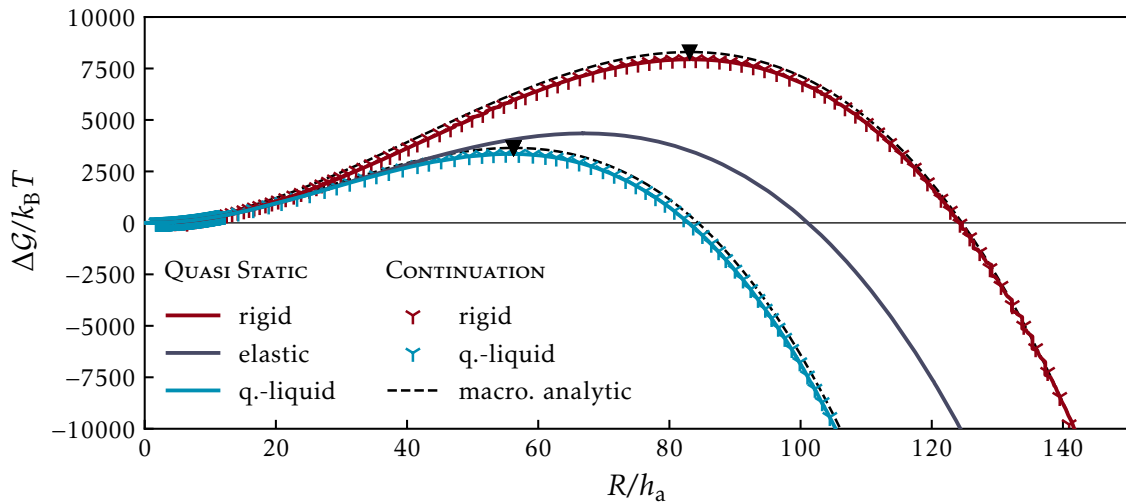


FIGURE 8.6.: Comparison of the macroscopic and mesoscopic energy barriers $\Delta\mathcal{G}$ as functions of the base radius R . The macroscopic energies are obtained analytically and plotted as black dashed lines for the quasi-liquid (blue) and rigid limit (red), respectively. The mesoscopic energies are calculated using quasi-static time simulations (1st method, solid lines) and continuation of steady states (2nd method, Υ). The ($\blacktriangledown$)-symbols indicate the critical radii and the energy maxima. The mesoscopic model is also used to capture the regime of intermediate elasticity, here the quasi-static method is used for $s = 10^3$ (dark purple curve).

cal nucleus characteristics in the elastic regime. The purple line in Fig. 8.6 already shows the energy as obtained by the first method for an exemplary intermediate softness $s = 10^3$ and lies in between the rigid and quasi-liquid limits as expected.

INFLUENCE OF SUPERSATURATION AND ELASTICITY

Key to the investigation of the nucleation probability are the critical nuclei, i.e., the steady states corresponding to the maxima in Fig. 8.6. The corresponding results obtained from the continuation in supersaturation p , explained in the previous section, is used to analyze the critical nuclei in dependence of p . In Fig. 8.7(a) the volume is shown as function of p on a log-log scale. The two flat film states h_- and h_+ , discussed in Sec. 8.3.1, are given as solid and dashed black lines, respectively. Their volumes are given by $V_{\pm} = \pi h_{\pm} L^2$. In addition, the volumes of the critical nuclei are shown for the rigid (red) and liquid (blue) limit. Thereby, the macro-

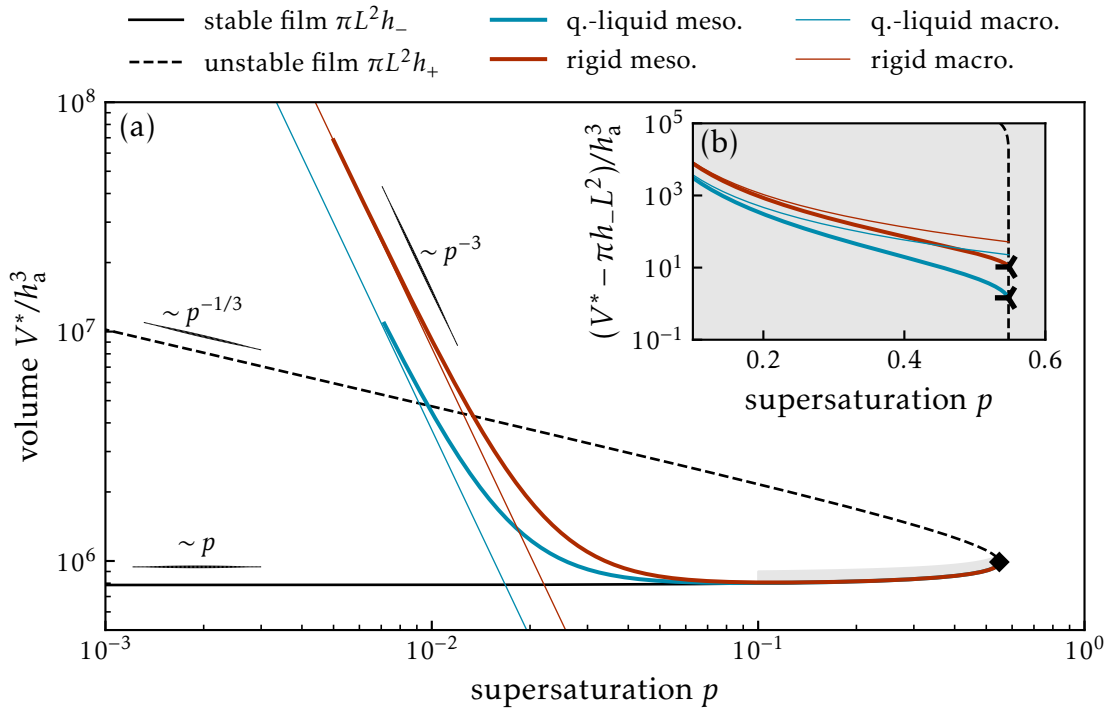


FIGURE 8.7.: Volume of the mesoscopic uniform film states (black) and of the critical nuclei in the rigid (red) and quasi-liquid (blue) limit as a function of the supersaturation p . (a) The total volume of the steady states, which in the mesoscopic picture includes the adsorption layer and therefore depends on system size. For small p the mesoscopic (thick lines) and macroscopic (thin lines) results agree and recover the scaling law $V \sim p^{-3}$. For larger p , the mesoscopic nuclei deviate from the macroscopic ones. All branches of mesoscopic states end at or near the saddle-node bifurcation point ($\blacklozenge$). (b) The inset gives the effective condensed volume, namely the volume above h_- , as a function of p in the range shaded gray in (a). The numerical domain was restricted to a circular region of radius $L = 500h_a$.

scopically obtained results (thin lines) [Eq. (8.18) and (8.25)] are compared to the mesoscopically obtained ones (thick lines). The volumes are obtained by integration of the numerically determined thickness profiles, $V = \int_0^L 2\pi h r dr$. The volumes of all states, except for h_- , increase with decreasing supersaturation p . In the low p limit, i.e., at large volume, the macroscopic and mesoscopic critical nucleus states well agree and show the predicted scaling $V \sim p^{-3}$. As the nucleus size decreases, i.e., with increasing p , the mesoscopic results deviate from the macroscopic prediction [see Sec. 8.3.2], approached $V_{\text{dry}} = \pi h_- L^2$, and eventually end in the pitch-fork bifurcation close to the saddle-node bifurcation of the uniform states ($\blacklozenge$). Note further, that the volumes of the mesoscopic states all depend on the system size L , since the adsorption layer contributes. Therefore, also the *effective condensed volume* $V^* - \pi h_- L^2$ for the mesoscopic states, i.e., the volume above the adsorption layer, is provided in the inset Fig. 8.7(b). This measure is independent of system size.

The insert Fig. 8.7(b) focuses on the range that corresponds to the gray shaded area in Fig. 8.7(a) and shows a better agreement of mesoscopic and macroscopic results that is maintained up to higher supersaturation. Only as $p_c = C_\theta/4$ is approached a clear deviation is visible. Linear stability analysis for an infinite domain size shows that the bifurcation point at which the branch mesoscopic critical nuclei

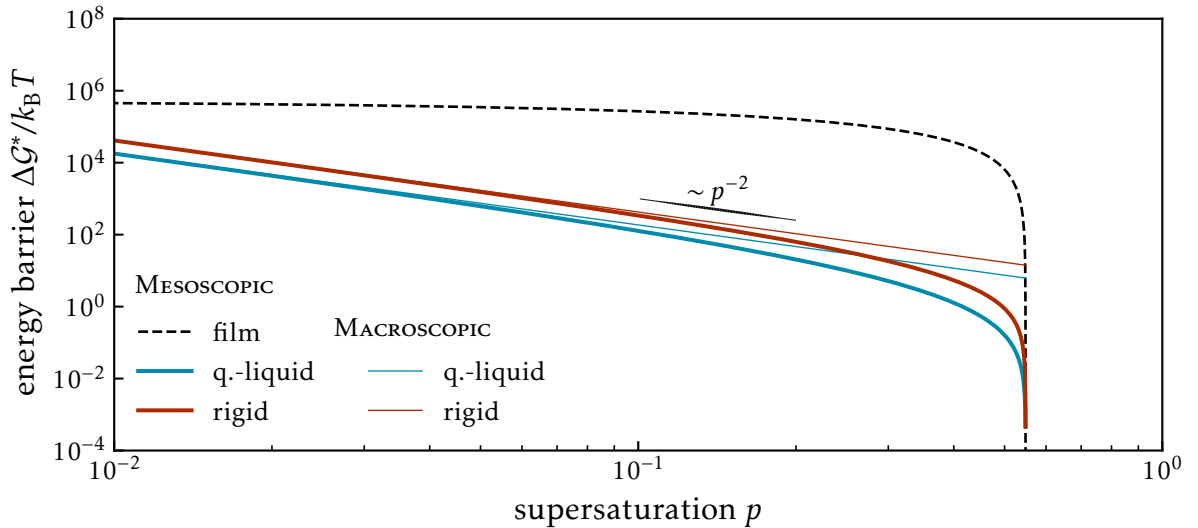


FIGURE 8.8.: Nucleation energy barrier ΔG^* (dimensionless) against supersaturation p . The numerical simulations of the mesoscopic model (thick lines) agree very well with the analytic macroscopic predictions (thin lines) given by Eq. (8.27), both in the liquid (blue) and rigid (red) limit, for low supersaturations. The energy barrier associated with the unstable steady film state (black dashed) is given by $\Delta G^*/\gamma_{lv} h_p^2 = \pi L^2 [C_\theta(f(h_2) - f(h_1)) - p(h_2 - h_1)]$ and hence dependent on the system size L unlike the nucleus states. As $p = C_\theta/4$ is approached the macroscopic model overestimates the energies barrier by multiple orders of magnitude.

emerges coincides with the saddle-node bifurcation. Due to finite domain effects, however, the actual position is shifted along the h_+ branch. Most remarkably, this bifurcation is found at different positions ($\prec$) in the rigid and quasi-liquid limit. Again, the disagreement of macroscopic and mesoscopic model for $p \rightarrow C_\theta/4$ is assumably caused by the different nucleus shapes due to the diffuse contact region present in the latter, which gains impact as the nucleus size decreases. More precisely, the agreement of the models increases with the scale separation $R \gg h_a$ and decreases as $R \rightarrow h_a$ is approached.

In the same way, the nucleation barrier can be calculated from the mesoscopic profiles using Eq. (8.31) and compared to the macroscopic prediction Eq. (8.28). In Fig. 8.8 the energy barrier is shown as a function of supersaturation (using the same line styles as in Fig. 8.7). Again, both models agree well in the small p limit, recovering the predicted power law $\Delta\mathcal{G}^* \sim p^{-2}$. The barrier increases with decreasing supersaturation and increasing nucleus size, i.e., in agreement with the discussion in Sec. 8.3.2. This, in turn, indicates that nucleation is favored at higher supersaturation. Beyond that, the mesoscopic model estimates the energy barrier for $p \rightarrow p_c$ to be up to several orders of magnitude smaller than the macroscopic value. This indicates that the CNT, i.e. the macroscopic model, strongly underestimates the nucleation probability close to the critical point. In Fig. 8.9 a mesoscopic critical nucleus on a soft substrate is shown for $p \approx p_c$. At $p_c = C_\theta/4$ the mesoscopic nucleation barrier even vanishes, such that the vapor condenses uncontrollably into the liquid phase for $p > p_c$. The dimensionless critical supersaturation $p_c = C_\theta/4$ translates to

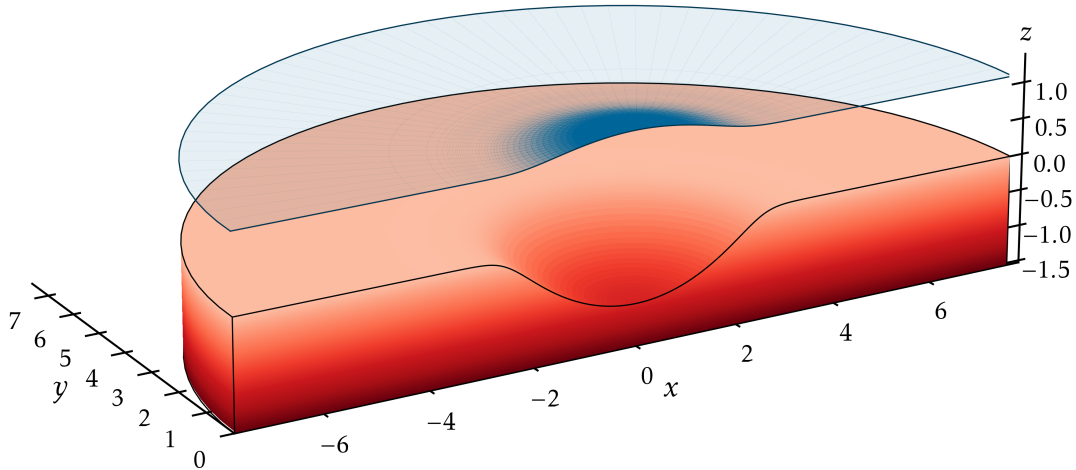


FIGURE 8.9.: Numerically obtained shape of a mesoscopic critical nucleus on an elastic substrate for $p \approx p_c = C_\theta/4$. The profiles $h + \xi$ and ξ exhibit only slight modulations of $\mathcal{O}(h_a)$ and barely resemble spherical caps.

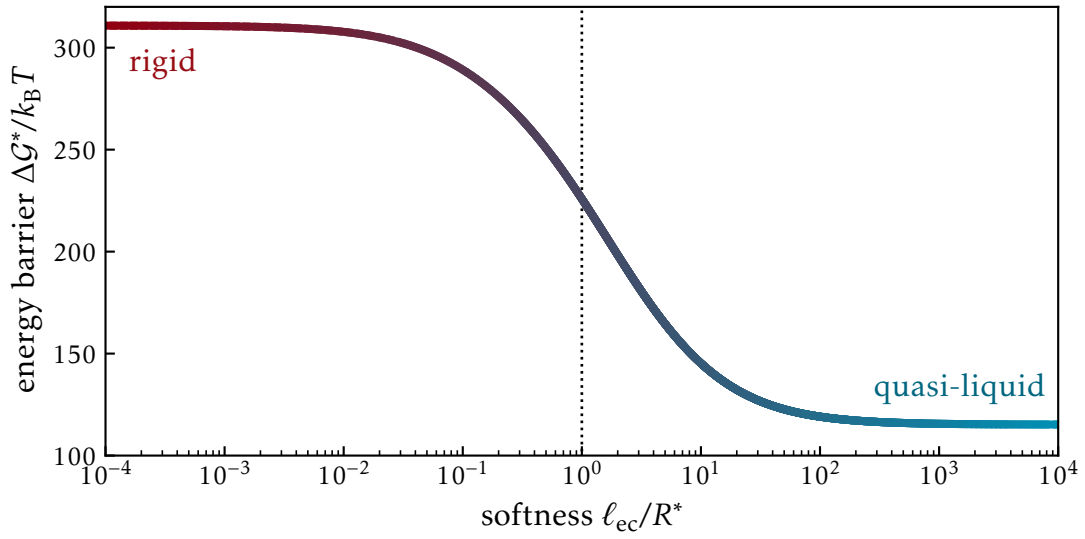


FIGURE 8.10.: Threshold energy as a function of substrate softness at fixed supersaturation $p = 0.1$. The energy barrier decreases with increasing softness, resulting in a strongly increased nucleation probability. Note, that the transition takes place at about $\ell_{ec} \sim R^*$.

the critical relative humidity

$$r_H^c = \exp\left(\frac{5}{6} \frac{\gamma_{sl} + \gamma_{lv} - \gamma_{sv}}{\rho \gamma_{lv} h_a^3}\right) = \exp\left(\frac{5}{6} \sqrt{\frac{\gamma_{lv}}{k_B T}} \frac{\gamma_{lv} + \gamma_{sl} - \gamma_{sv}}{\rho k_B T}\right), \quad (8.42)$$

which for the values given in Eq. (8.39) is $r_H^c \approx 3.6553$.

Finally, the mesoscopic model is used to investigate the influence of elasticity on the nucleation probability. Once again, continuation is employed, however, this time we explore the substrate softness ℓ_{ec}/R^* at fixed supersaturation p . The resulting energy barrier is displayed in Fig. 8.10. With the transition from the rigid to the quasi-liquid limit, i.e., with increasing softness, the energy barrier decreases by a factor greater than 2. This decrease in the energy barrier is amplified through the Boltzmann exponent [Eq. (8.17)] and may therefor strongly affect the nucleation probability and, consequently, the observed drop density. Note that this transition occurs approximately when $R^* \approx \ell_{ec}$.

8.4. ASSESSMENT

Recent experiments have shown, that the nucleation density of dew is strongly affected by the softness of the elastic substrate, controlled by the cross-linking ratio a material. The nucleation probability can be predicted as a Boltzmann factor and

is therefore governed by the energy barrier $\Delta\mathcal{G}^*$ related to the critical nuclei. This barrier in Gibbs free energy has been calculated in the macroscopic picture in both, the rigid and the quasi-liquid limit. For the given interface energies the nucleation energy barrier in the quasi-liquid limit is about half the one in the rigid limit. To further explore the regime of intermediate elasticity, a mesoscopic gradient dynamics model has been employed to determine the energy as a function of drop base radius R , supersaturation p and softness ℓ_{ec}/R^* . The macro- and mesoscopic models were found to agree in the limit of rigid and liquid substrates, as long as the critical nucleus is of sufficiently large volume, i.e., when a relatively small supersaturation is considered. Both models predict a decrease in the energy barrier with increasing supersaturation. At large supersaturation, the macroscopic model considerably overestimates the energy barrier by several orders of magnitude as compared to the mesoscopic theory, resulting in an underestimation of the nucleation probability. This deviation is caused by the difference in nucleus shape; while mesoscopic nuclei exhibit diffuse contact line regions that increasingly dominate their shape as $R^* \rightarrow h_-$, the shape of nuclei in the macroscopic model is (in the rigid and quasi-liquid limit) invariant under changes in size, which is most likely not justified as microscopic scales are approached. Next, the change of the energy barrier with increasing substrate softness at fixed supersaturation was investigated using the mesoscopic model. Again the energy barrier was found to decrease by more than a factor 2 when going from the rigid to the quasi-liquid limit. This transition in the energy barrier has been shown to coincide with the transition of contact angles from Young (rigid) to Neumann (quasi-liquid) at $\ell_{ec} \sim R^*$.

After all, the experiments presented in Ref. [Bou+25] have shown, that the change in the dew drop density occurs in a range of $10^{-7}\text{m} < \ell_{ec} < 10^{-3}\text{m}$. Since the critical nuclei are considered much smaller than that, it is still unclear why nucleation depends on the substrate softness at all.

Finally, the decrease in the energy barrier with increasing softness gives a qualitative argument in favor of an increased nucleation density as observed in Ref. [Bou+25]. Yet, the absolute values of the barrier $\mathcal{O}\left(\frac{\Delta\mathcal{G}^*}{k_B T}\right) = 10^2$ are about two orders of magnitude too high to explain drop densities as observed in the experiment, according to Ref. [Bou+25]. However, at higher supersaturation the energy barrier predicted by the mesoscopic model rapidly decreases. According to Fig. 8.8, the mesoscopic energy barrier becomes reaches $\mathcal{O}\left(\frac{\Delta\mathcal{G}^*}{k_B T}\right) = 1$ somewhere at supersaturation $0.4 < p < 0.5$, which relates to a range of relative humidities $2.58 < r_H < 3.27$. Further, the mesoscopic model has shown, that the critical nucleus volume decreases with the substrate softness, allowing for the formation of a larger number of nu-

clei if the vapor access is limited, e.g., by slow transport in the gas phase. As in Ref. [Bou+25] the vapor phase was found to form a desaturated boundary layer in the vicinity of the substrate, this effect may well play a role.

Aside of that, the classical nucleation theory is a strongly approximated description that considers macroscopic concepts like interface energies. The validity of the latter is at least questionable in the context of microscopic nuclei of only a few particles in size, which renders the entire CNT obsolete. The use of a more advanced model, e.g., the dynamic nucleation theory or extended modified liquid drop model, might deliver more satisfying results. Also, the experimental capabilities of capturing the nucleation process are strongly confined in regard of spatial as well as temporal resolution, both of which are of importance. In consequence, it cannot be ruled out that other physical processes are interfering. Particularly, the coarsening of drops was found to be suppressed certain regimes of substrate softness, both experimentally [Sok+10] and theoretically in Ch. 6, resulting in an increased drop density in turn. A further suspected cause that might enhance this effect is the cloaking of drops by liquids leaking from the substrate. In addition, the halted nucleation of new drops in the dry regions of the initial breath figure is caused by the formation of a saturated diffusive boundary layer close to the substrate [Bou+25, BSA25], which requires to spatially resolve the vapor density.

9. CONCLUSION

In addition to the assessments that are provided at the ends of Chapters 4 to 8, here a general overview is given, after which possible courses of further proceedings are briefly discussed.

The aim of this thesis was to derive a model for the dynamics of a simple liquid on a viscoelastic substrate that captures the most important features of soft wetting. To this end, the general continuum mechanics of both, fluids as well as deformable solids, have been discussed first in Ch. 2. It has been found in Sec. 2.2.4, that the dynamics of the liquid layer height profile can in the long-wave limit be described by the thin-film equation (TFE) [ODB97, Thio7, CM09], while an evolution equation for the substrate profile can be derived from Kelvin-Voigt viscoelasticity [Tho65, Voig92]. In the long-wave limit both equations are of gradient-dynamics structure [cf. Sec. 2.5], governed by an underlying free energy functional [Thi10]. In the subsequent Chapter 3, this free energy functional has been constructed to fit the requirements of soft wetting and its variations have been used to gain first insights into the statics of macroscopic drops in different softness regimes. Afterwards, the gradient dynamics evolution equations have been formulated from a mesoscopic perspective, yielding the desired coupled dynamics for soft wetting.

The model has been used first to numerically investigate the influence of the substrate softness on the liquid behavior in Ch. 4. The double transition of equilibrium contact angles, which occurs when varying the substrate softness from rigid to quasi-liquid [Mar+12b, Lub+14], has been recovered and found to closely resemble the behavior observed in Ref. [Lub+14]. In particular, the scaling of the typical softnesses where the two transitions occur with drop volume and the scalings of the wetting ridge height with softness in the different regimes agree very well. Beyond that, the model is consistent with Neumann's law for the equilibrium contact angles close to the quasi-liquid limit and also in the rigid limit an equilibrium of forces could be established in the contact region.

Afterwards, the spreading of single drops of partially and completely wetting liquid on a viscoelastic substrate has been addressed in Ch. 5 to demonstrate the effect of viscoelastic braking. The dependence of the dynamic liquid-gas contact angle

on the contact line velocity has been studied for different softness. In the partial wetting case certain sub-sets of curves can be collapsed by rescaling the velocity in terms of the viscoelastic time-scale, similar to Refs. [Kar+15, AS20]. This rescaling indicates, that the dissipation in the substrate is dominant and increases with softness, i.e., that viscoelastic braking is in fact present [CGS96, CS01]. In case of completely wetting liquids viscoelastic braking is present as well, in contradiction to Ref. [CK20]. However, its effect is negligible there due to the less pronounced wetting ridge, such that the classical Tanner-Cox-Voinov relation applies.

Subsequently, the coarsening of two-drop system as well as large drop ensembles has been investigated in Ch. 6. Time simulations have shown that the dominant coarsening mode of a two-drop system changes with varying substrate softness in a non-trivial way. In both, the rigid and soft limit, the Ostwald ripening dominates while at intermediate softness a translation driven coarsening prevails, for sufficiently large drops and short drop distances that is. This interaction of liquid drops mediated by elastic deformation of the solid substrate underneath is known as *inverted Cheerios effect* [Kar+16]. In the rigid limit the volume transfer mode is accompanied by a joint migration of the two coarsening drops in accordance with literature [PP04, GW05]. Furthermore, the linear stability analysis of an unstable steady two-drop constellation confirms the change in the dominant coarsening mode depending on the substrate softness. The same behavior is as well found in the coarsening of large drop ensembles. The activity of the translation mode quickly fades with increasing separation of the drops, i.e., the translation dominated regime ends at a critical threshold.

In Ch. 7 the model has been extended to capture surface elasticity in the full-curvature formulation and treated numerically to explore the impact of the Shuttleworth effect, which describes the dependence of the interface tension of an elastic surface on local strain, on the statics of liquid drops. The results have been compared to those produced by a macroscopic Neo-Hookean model which allows for a detailed description of large-deformation elasticity. Since the Shuttleworth effect is rather subtle, horizontal pre-stretch has been imposed in most cases to increase its impact. It has turned out that (a)symmetry in the Shuttleworth effect, i.e., the difference in strain dependence between solid-liquid and solid-gas interface, is essential for the effective wettability. In particular, significant horizontal displacements appeared when the Shuttleworth effect is strongly asymmetric in contrast, to the symmetric case, where the horizontal displacements remain much smaller than the typical vertical ones. The results presented in Ch. 7 generalize the observations made for stretched rigid substrates in Ref. [WAS13, AS16] to substrates of

arbitrary softness, including the possibility of large elastic deformations. An important finding is, that strong horizontal displacements can persist even at equilibrium and in the absence of pinning, when the Shuttleworth effect is strongly asymmetric. The results presented in Ch. 7 confirm the experimentally observed dependence of the equilibrium liquid-gas contact angle on the state of asymmetry in the Shuttleworth effect [Xu+17, Sch+18, SRA18] for $\ell_{ec} \lesssim R$. This makes the pre-stretch induced variation of the liquid contact angle a powerful tool to assess the symmetry of the Shuttleworth effect. Hence, horizontal displacements and stretches offer an important quantitative probe for the Shuttleworth effect, which to date has not been explored. A discontinuity in the spatially resolved surface stretch is direct evidence for an asymmetric Shuttleworth effect and even in the symmetric case the stretch at the contact line offers information on the strength of the Shuttleworth effect. The gradient dynamics model has proven to be able to capture even nontrivial equilibrium features of static drops in the presence of the Shuttleworth effect. Despite of its reduced description of elasticity, the mesoscopic gradient dynamics model has shown decent qualitative agreement with the Neo-Hookean model, which is a very promising validation as it also offers a dynamic description. As an example, time simulations on a spreading drop of partially wetting liquid have been performed, just as in Ch. 5 but now on a pre-stretched substrate with Shuttleworth effect [cf. Fig. 7.10]. Thereby the behavior of the asymmetric case $\gamma_1^{sg} > \gamma_1^{sl}$ has been found to differ from the other cases in the high velocity limit, where the wetting ridge formation takes place. In the low velocity regime, however, the dynamic contact angles have in all cases been found to satisfy power laws again, when plotted against the contact line velocity.

Finally, in Ch. 8 the liquid equations have been extended to allow for mass exchange with the surrounding gas phase in order to investigate the impact of softness on condensation and evaporation. Recent experiments have shown, that the softness of an elastic substrate significantly influences the nucleation density of liquid drops. According to classical nucleation theory, the nucleation probability can be predicted as a Boltzmann factor and is therefore governed by the barrier in Gibbs free energy associated with the critical nuclei. This barrier has been calculated in the macroscopic picture in the rigid and liquid limit. It was shown, that for the given interface energies the nucleation energy in the quasi-liquid limit is considerably smaller than in the rigid limit. The regime of intermediate elasticity has then been explored numerically employing the mesoscopic gradient dynamics model to determine the energy barrier as a function of drop base radius, supersaturation and softness ℓ_{ec}/R^* . The macro- and mesoscopic descriptions agree well in the limits of

rigid and liquid substrates, as long as a large nucleus volume, i.e. small supersaturation, is considered. Both models predict a decrease in the energy barrier with increasing supersaturation and thus an increase in the nucleation density. At large supersaturation, the macroscopic model considerably overestimates the energy barrier by several orders of magnitude as compared to the mesoscopic theory, resulting in an underestimated nucleation probability. The decrease of the energy barrier with increasing substrate softness at fixed supersaturation has been investigated using the mesoscopic model and has been found to coincide with the transition of contact angles from Young (rigid) to Neumann (quasi-liquid) at $\ell_{ec} \sim \sqrt[3]{V^*}$. Beyond that, the critical nucleus volume has been found to decrease with the substrate softness, allowing for the formation of a larger number of nuclei if the vapor access was limited, e.g., by slow transport in the gas phase. Finally, the absolute values of the energy barrier are far too high to explain an increase of the dew drop density as observed in the experiments in Ref. [Bou+25]. However, the general trend qualitatively agrees and at higher supersaturation the mesoscopic energy barrier decreases rapidly.

The presented gradient dynamics model does not come without its weaknesses. Most obvious is the restriction to partially wetting scenarios, more precisely to contact angles $< 90^\circ$, due to the Monge representation of the interfaces. While the full-curvature formulation of the governing energy enables the treatment of drop statics over the entire range of angles within this limitation, the gradient dynamics evolution equations are strictly permissible only in the long-wave limit, where much smaller contact angles are considered. On the one hand, combining a full-curvature formulation of the energy with the long-wave gradient dynamics evolution equations mathematically violates the asymptotic consistency [Thi18]. On the other hand, improvements to the governing energy generally improve the overall results and even outside the long-wave limit such combined models perform reasonable well [HTA15]. Aside of that, the long-wave approximated elastic energy and surface stress, i.e., the Winkler foundation model, has been used all along, even if full-curvature variations have been considered [cf. Chapters 7 and 8]. Due to this and other approximations, the model occasionally struggles in achieving quantitative compliance with other studies. However, the reasons for that can be manifold and are not necessarily due to the inadequacy of the model. If, for example, unknown mechanisms are involved, they are inherently included in experiments, whereas they are not taken into account in modeling, although this would be possible in principle.

In Ch. 8, for example, the decrease in nucleation energy barrier with increasing softness as predicted by the mesoscopic gradient dynamics model was qualitatively aligned with the findings in Ref. [Bou+25]. Only the exact value of the barrier was about two orders of magnitude too high to satisfactorily explain the experimentally observed increase in dew drop formation. However, as discussed in Ref. [Bou+25], the dynamics of the vapor phase plays a crucial role for the dew formation and is not included in the model. Also, the experiments were performed for contact angles $> 90^\circ$ which cannot be described by the presented model. However, the resolution of the experimental setup is limited as well and the processes taking place below this resolution can only be speculated upon.

It must also be acknowledged that the gradient dynamics model, in all its versatility, does not allow for the rheology to be easily changed. Instead the derivation as performed in Sec. 2.4.3 would have to be repeated using a different dynamic modulus to incorporate, e.g., the Maxwell model. Ultimately, the most restrictive disadvantage of the model in its current form, is its incapability to describe incompressible substrates [AS20, CV20], since this is precisely where the Winkler foundation model breaks down. In Ch. 7 the perfectly compressible localized Winkler foundation model has been compared side-by-side to the entirely different rheology of an incompressible Neo-Hookean material. Hence, the Poisson ratio could not be directly translated and a different method was required to compare the softness of the materials. In Sec. 7.3 two methods were presented to do so, both of which had their own merits. It turned out in Sec. 7.3.1, that the choice of the method has a crucial impact on the comparison.

Despite this criticism, the presented model proves to be quite capable of qualitatively describing the main static and dynamic features of soft wetting. The transparency and simplicity of the model rests in its gradient dynamics structure and the underlying free energy that reflects capillarity, wettability and compressional elasticity. It is due to this approach, that the model is very versatile and can easily be adapted to account for further physical effects. In particular, the model lends itself easily to the treatment of moving contact lines on elastic substrates, e.g., in the sliding of drops on an incline or in a Landau-Levich geometry [Sno+07, Gal+14]. The mesoscopic gradient dynamics is thus ideally suited to investigate the appearance of stick-slip motion, experimentally observed in Refs. [Kaj+13, Kaj+14, Gor+18], and should be used to approach that issue in the future. Stick-slip motion was previously investigated using similar models for drops on polymer bushes, covering a rigid substrate [GHT23, Har+24]. Introducing an explicit spatial dependency of

the softness will further allow to study durotaxis [Sty+13a, GV20]. The model can also be employed as an element of more complex models to study the interaction of complex fluids with soft substrates. For instance, it may be combined with thin-film models of active media [LEL20, Tri+20] or biofilms [Tri+17] to investigate the motion of active drops on soft substrates [LZA14] and the growth of biofilms and cell aggregates in that context [DDB12, Con+20, PJT25]. Even intricate phenomena like the Shuttleworth effect and the influence of its symmetry on the equilibrium contact angles are incorporated with ease. In the description of the latter, the great correspondence with the Neo-Hookean model, which provides a full nonlinear treatment of large amplitude incompressible elastic bulk deformation, despite the strongly simplified description used in the gradient dynamics model, is particularly remarkable. This agreement is all the more astonishing, if one remembers that the gradient dynamics model considers a full compressible linear Winkler foundation elasticity, i.e., a continuous spring, in the long-wave limit, although the full curvature formulation for large contact angles has been employed in Ch. 7. Even in the comparison of the liquid-gas contact angle as a function of softness in Sec. 7.3.1 excellent qualitative compliance could be achieved by careful adjustment of the parameters. Note, that even though all vertical dependencies are eliminated during the derivation of a long-wave model, both, the velocity vector field in the liquid as well as the static displacement in the bulk of the elastic layer can be reconstructed from the profiles using the continuity equation and the solution of the finite linear elastic layer problem, respectively. Last but not least, the reduction of the description, from vectorial velocity and displacement fields in three dimensions to scalar two dimensional functions, giving a Monge representation of the interfaces, is accompanied by a considerable reduction in computational costs and enables the treatment of very large systems in 3 spatial dimensions with multiple drops evolving in time.

In general it is always advisable to frequently validate a model and its results by comparing benchmark cases with other more detailed models, e.g., the Neo-Hookean model. Results would ideally be confirmed by experiments that are complemented with simultaneous measurements of characteristic quantities like the contact angles. Such measurements would allow to determine the effective parameters for the present model in terms of experimental ones while disagreements in the qualitative behavior hint towards missing mechanisms in the model. That being said, the gradient dynamics approach is perfectly suited to adapt to such requirements. For example, adding the vapor dynamics to the mesoscopic model, as done e.g. in [Har+23, Har+24], may improve the quantitative agreement with the experiments

in Ref. [Bou+25] and could be a worthwhile project for the future. Further including stochastic effects or using a more advanced nucleation theory, like dynamic nucleation theory or the extended modified liquid drop model, may add important mechanisms. Also the experiments on dew nucleation could be repeated for smaller contact angles and higher supersaturation, close to the regime where the mesoscopic nucleation energy barrier was found to rapidly decrease, to allow for a more direct comparison and to improve the quantitative agreement.

The results presented in the previous should in the future be generalized by performing simulations in three dimensions. Most important would be the improved of the elasticity model by introducing the full elastic surface stress (3.19), at the expense of having to solve the convolution integral. Doing so would also enable the treatment of incompressible materials, which is particularly beneficial since primarily incompressible materials, such as polymers, are the subject of experiments. In Sec. 2.3.2 it was found, that incompressibility changes the shape of the wetting ridge and causes depressions beside it [cf. Fig. 2.4]. The wetting ridge as well as these depressions become more narrow as the elastic layer thickness decreases [cf. Fig. 2.4(b)]. This crucially affects the drop-drop interaction and may cause an arrest of coarsening or even a repulsion of drops via the inverted Cheerios effect [Kar+16]. Also the sliding of drops has been found to be significantly affected [Zha+18]. For all these reasons, I consider this project to be most promising and highly recommend pursuing it in the future.

A. ADDITIONAL CONSIDERATIONS

A.1. NEWTON'S LAW OF FORCE AND ACCELERATION

The global change in momentum is given by Newtons second law

$$\frac{d\vec{P}}{dt} = \sum_i \vec{F}_i, \quad (\text{A.1})$$

with total momentum $\vec{P}$ and forces $\vec{F}_i$. In integral form it writes

$$\frac{d}{dt} \int \rho \vec{v} d^3r = \sum_i \int \vec{f}_i d^3r = \int \sum_i \vec{f}_i d^3r. \quad (\text{A.2})$$

Using Reynolds transport theorem for material points and the continuity equation (2.21) the left hand side of the momentum conservation law yields [Bes06]

$$\begin{aligned} \frac{d}{dt} \int \rho \vec{v} d^3r &= \int \frac{d}{dt}(\rho \vec{v}) d^3r + \int \rho \vec{v}(\vec{v} \cdot \vec{n}) d^2r \\ &= \int \frac{d}{dt}(\rho \vec{v}) + \rho \vec{v}(\nabla \cdot \vec{v}) d^3r \\ &= \int \underbrace{\vec{v} \left(\frac{d\rho}{dt} + \rho(\nabla \cdot \vec{v}) \right)}_{=0} + \rho \frac{d\vec{v}}{dt} d^3r. \end{aligned} \quad (\text{A.3})$$

A.2. METRIC FACTOR

The metric factor relates an infinitesimal element of a surface $\psi(x, y)$ to its projection into the (x, y) -plane $ds = m(\psi) dx dy$. It can be obtained geometrically by constructing an infinitesimal directed surface element $d\vec{s} = \vec{n} ds$ of $\psi(x, y)$ as a parallelogram spanned by two tangent vectors $\vec{t}_x$ and $\vec{t}_y$ as shown in Fig. A.1. The representation

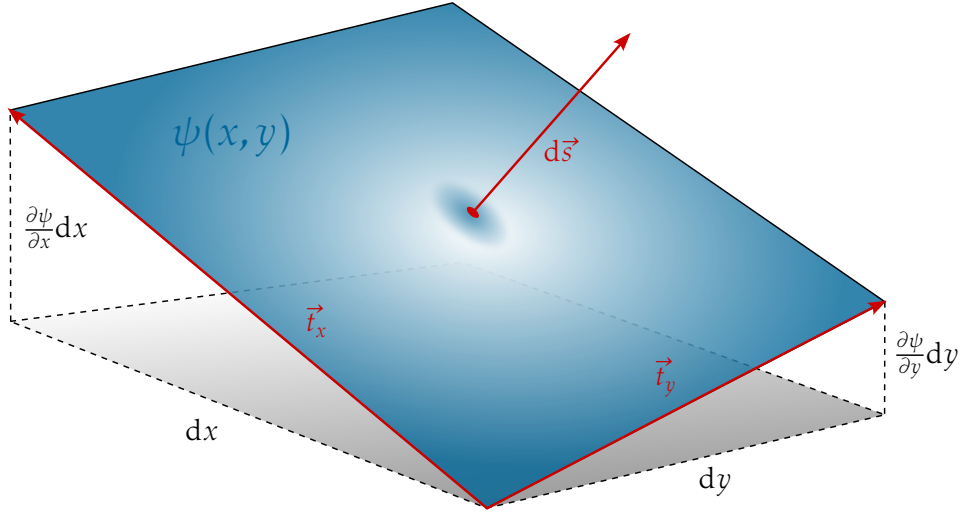


FIGURE A.1.: Geometrical visualization of an infinitesimal directed element $d\vec{s} = \vec{n}ds$ of a surface $\psi(x, y)$. It can be constructed from the cross product of two linear independent tangent vectors $d\vec{s} = \vec{t}_1 \times \vec{t}_2$. Writing the latter in the Cartesian basis of $\psi(x, y)$ allows to define the metric factor $m(\psi) = \sqrt{1 + (\partial_x \psi + \partial_y \psi)^2}$ which relates the surface element ds to its projection on the Cartesian x - y -plane.

in Cartesian coordinates is

$$d\vec{s} = \vec{t}_x \times \vec{t}_y = dx \begin{pmatrix} 1 \\ 0 \\ \frac{\partial \psi}{\partial x} \end{pmatrix} \times dy \begin{pmatrix} 0 \\ 1 \\ \frac{\partial \psi}{\partial y} \end{pmatrix} = dx dy \begin{pmatrix} -\frac{\partial \psi}{\partial x} \\ -\frac{\partial \psi}{\partial y} \\ 1 \end{pmatrix} = dx dy \begin{pmatrix} -\nabla_{\parallel} \psi \\ 1 \end{pmatrix}, \quad (\text{A.4})$$

and its absolute value gives the metric factor

$$|d\vec{s}| = ds = \sqrt{1 + (\nabla_{\parallel} \psi)^2} dx dy = m(\psi) dx dy. \quad (\text{A.5})$$

A.3. STRESS EQUILIBRIUM AT THE FREE FLUID SURFACE

The force balance at the free surface of the liquid is given by Eq. (2.38). Using the liquid stress tensor (2.27) and the normal vector of the free surface

$$\vec{n}_{\text{lg}} = \frac{1}{\sqrt{1 + (\nabla_{\parallel} h + \nabla_{\parallel} \xi)^2}} \begin{pmatrix} -\nabla_{\parallel} (h + \xi) \\ 1 \end{pmatrix}$$

the surface stress writes

$$\begin{aligned} m(h + \xi)(\underline{\sigma}_1 \cdot \vec{n}_{1g})_x &= p \partial_x(h + \xi) + \eta \left[\partial_x v_z + \partial_z v_x - 2 \partial_x(h + \xi) \partial_x v_x - \partial_y(h + \xi)(\partial_x v_y + \partial_y v_x) \right], \\ m(h + \xi)(\underline{\sigma}_1 \cdot \vec{n}_{1g})_y &= p \partial_y(h + \xi) + \eta \left[\partial_y v_z + \partial_z v_y - 2 \partial_y(h + \xi) \partial_y v_y - \partial_x(h + \xi)(\partial_x v_y + \partial_y v_x) \right], \\ m(h + \xi)(\underline{\sigma}_1 \cdot \vec{n}_{1g})_z &= -p + \eta \left[2 \partial_z v_z - \partial_x(h + \xi)(\partial_z v_x + \partial_x v_z) - \partial_y(h + \xi)(\partial_y v_z + \partial_z v_y) \right]. \end{aligned}$$

Projection on the normal vector yields the vertical force balance. Introducing the dimensionless variables according to Sec. 2.2.3 and dropping the tildes leads to

$$\begin{aligned} \vec{n}_{1g} \cdot \underline{\sigma}_1 \cdot \vec{n}_{1g} &= -\frac{\eta}{T \epsilon^2} p + \frac{2\eta}{T m(h + \xi)^2} \left\{ \partial_z v_z - \partial_x \xi \partial_z v_x - \partial_y \xi \partial_z v_y \right. \\ &\quad \left. + \epsilon^2 \left[(\partial_x \xi)^2 \partial_x v_x + (\partial_y \xi)^2 \partial_y v_y + \partial_x \xi \partial_y \xi (\partial_x v_y + \partial_y v_x) \right] \right\} = -\frac{\eta}{\epsilon^2 T} p_\alpha. \end{aligned} \quad (\text{A.6})$$

The tangential force balance is obtained from projection onto the tangential plane using the projection operator $\underline{P}(\vec{n}) = \underline{1} - \vec{n} \otimes \vec{n}$. If the external tangential forces are caused by the surface gradient of a scalar quantity γ , the force balance is.

$$\underline{P}(\vec{n}_{1g})(\underline{\sigma}_1 \cdot \vec{n}_{1g}) = \vec{t} = \left[\underline{P}(\vec{n}_{1g}) \nabla \right] \gamma. \quad (\text{A.7})$$

According to Eq. (2.39) the tangent vectors are

$$\vec{t}_1 = \frac{1}{\sqrt{1 + (\partial_x h + \partial_x \xi)^2}} \begin{pmatrix} 1 \\ 0 \\ \partial_x(h + \xi) \end{pmatrix}, \quad \vec{t}_2 = \frac{1}{\sqrt{1 + (\partial_y h + \partial_y \xi)^2}} \begin{pmatrix} 0 \\ 1 \\ \partial_y(h + \xi) \end{pmatrix}. \quad (\text{A.8})$$

After nondimensionalization and dropping the tildes the projections (2.40) then read

$$\begin{aligned} \vec{t}_1 \cdot \underline{\sigma}_1 \cdot \vec{n}_{lg} = & \frac{1}{\sqrt{1 + \epsilon^2(\nabla_{\parallel} h + \nabla_{\parallel} \xi)^2}} \frac{1}{\sqrt{1 + \epsilon^2(\partial_x h + \partial_x \xi)^2}} \frac{\eta}{\epsilon T} \left\{ \partial_z v_x \right. \\ & + \epsilon^2 \left[\partial_x v_z - 2\partial_x(h + \xi)\partial_x v_x - \partial_y(h + \xi)(\partial_x v_y + \partial_y v_x) \right. \\ & + 2\partial_z v_z \partial_x(h + \xi) - \partial_z v_x(\partial_x h + \partial_x \xi)^2 - \partial_z v_y \partial_x(h + \xi) \partial_y(h + \xi) \left. \right] \\ & \left. - \epsilon^4 \left[\partial_x v_z(\partial_x h + \partial_x \xi)^2 + \partial_y v_z \partial_x(h + \xi) \partial_y(h + \xi) \right] \right\} = \tau_1 \end{aligned} \quad (\text{A.9a})$$

$$\begin{aligned} \vec{t}_2 \cdot \underline{\sigma}_1 \cdot \vec{n}_{lg} = & \frac{1}{\sqrt{1 + \epsilon^2(\nabla_{\parallel} h + \nabla_{\parallel} \xi)^2}} \frac{1}{\sqrt{1 + \epsilon^2(\partial_y h + \partial_y \xi)^2}} \frac{\eta}{\epsilon T} \left\{ \partial_z v_y \right. \\ & + \epsilon^2 \left[\partial_y v_z - 2\partial_y(h + \xi)\partial_y v_y - \partial_x(h + \xi)(\partial_x v_y + \partial_y v_x) \right. \\ & + 2\partial_z v_z \partial_y(h + \xi) - \partial_z v_x \partial_x(h + \xi) \partial_y(h + \xi) - \partial_z v_y(\partial_y h + \partial_y \xi)^2 \left. \right] \\ & \left. - \epsilon^4 \left[\partial_x v_z \partial_y(h + \xi) \partial_x(h + \xi) + \partial_y v_z(\partial_y h + \partial_y \xi)^2 \right] \right\} = \tau_2 \end{aligned} \quad (\text{A.9b})$$

A.4. SUBTLETIES ON INCOMPRESSIBILITY

In Ch. 2 it is stated that the trace of the stress tensor is directly proportional to the trace of the strain tensor, e.g., in Eqs. (2.56) and (2.61). Further, the trace of the strain tensor was shown to vanish in case of incompressibility $\text{tr} \underline{\epsilon} = \nabla \cdot \vec{u} = 0$ [Eqs. (2.11), (2.15)]. The trace of the stress tensor, however, does not but gives the internal pressure p instead. This may seem contradictory at first, though the pressure field is actually even required to enforce incompressibility. A steady state requires equilibrium between internal and external forces, i.e., $\nabla \underline{\sigma} = -\vec{f}_{\text{ex}}$. According to the *Helmholtz decomposition* any forces can be expressed in terms of a scalar potential ϕ and a vector potential $\vec{A}$

$$\vec{f}_{\text{ex}} = -\nabla \phi + \nabla \times \vec{A}. \quad (\text{A.10})$$

Considering only the conservative compressive forces resulting from the scalar potential gives

$$\nabla \underline{\sigma} = -\vec{f}_{\text{ex}} = \nabla \phi = \nabla(\phi \underline{1}) \quad \rightarrow \quad \text{tr}(\underline{\sigma}) = 3\phi.$$

Hence, the trace of the stress tensor must not vanish. Since the strain tensor is traceless in the incompressible case, the pressure field is added to make the corre-

sponding contribution. For a solid body at equilibrium, i.e., $\partial_t \vec{u} = 0$, and a resting fluid, i.e., $\vec{v} = 0$, this directly leads to

$$p = -\frac{1}{3} \text{tr} \underline{\sigma} = -\phi. \quad (\text{A.11})$$

This implies $K \rightarrow \infty$ and $\nu \rightarrow \frac{1}{2}$ in the incompressible limit, in order for Eqs. (2.56) and (2.61) to hold. In case of a steady flow, i.e., $\vec{v} \neq 0$ and $\partial_t \vec{v} = 0$, the situation changes as the convective acceleration enters the equation [cf. Eq. (2.29)]

$$\rho_0(\vec{v} \cdot \nabla) \vec{v} + \nabla p - \eta \Delta \vec{v} = \vec{f}_{\text{ex}}. \quad (\text{A.12})$$

The stress equilibrium is then given by

$$\rho_0 v_i v_j + \delta_{ij} p - \eta \partial_j v_i = -\delta_{ij} \phi,$$

with $\eta \partial_j v_i = \frac{\eta}{2} \partial_t \tilde{\epsilon}_{ij}$. The spherical component of this equilibrium, i.e., the trace, is

$$\rho_0 |\vec{v}|^2 + 3p = -3\phi.$$

Hence, the kinetic energy contributes to the internal normal stress as well. In such a scenario, the pressure field is required even in the absence of external forces to prevent the liquid from expanding. Taking the divergence of Eq. (A.12) leads to

$$\begin{aligned} \rho_0 \partial_i [v_j \partial_j v_i] + \partial_i \partial_i p - \eta \partial_i \partial_j \partial_j v_i &= \rho_0 \left[\partial_i v_j \partial_j v_i + v_j \partial_j \underbrace{\partial_i v_i}_{=0} \right] + \partial_i \partial_i p - \eta \partial_j \partial_j \underbrace{\partial_i v_i}_{=0} \\ &= \rho_0 \partial_i v_j \partial_j v_i + \partial_i^2 p = -\partial_i^2 \phi. \end{aligned}$$

The pressure is thus determined by the Poisson equation

$$\Delta p = -\Delta \phi - \rho_0 \partial_i v_j \partial_j v_i, \quad (\text{A.13})$$

which is solved by

$$p(\vec{r}, t) = \frac{1}{4\pi} \int_{\Omega} \frac{\rho_0 \partial_i v_j \partial_j v_i + \Delta \phi}{|\vec{r} - \vec{r}'|} d^3 \vec{r}'. \quad (\text{A.14})$$

Note, that the pressure field corresponds to a Lagrange multiplier enforcing incompressibility, which can be seen by constructing the Lyapunov functional of the

Stokes equation

$$\mathcal{L}[\vec{v}, p] = \int_{\Omega} p(\nabla \cdot \vec{v}) - \frac{\eta}{2} \nabla \vec{v} : \nabla \vec{v} + \vec{f} \cdot \vec{v} \, d^3\vec{r}$$

with $:$ denoting the *Frobenius inner product*. The variations then are

$$\begin{aligned} \frac{\delta \mathcal{L}}{\delta \vec{v}} &= -\nabla p + \mu \Delta \vec{v} + \vec{f}, \\ \frac{\delta \mathcal{L}}{\delta p} &= \nabla \cdot \vec{v} = 0. \end{aligned}$$

A.5. FUNDAMENTAL SOLUTION FOR THE SURFACE STATICS OF A FINITE LINEAR ELASTIC LAYER

Consider a finite elastic layer of thickness d and with free surface at $z = 0$. The Green's function is to be found for singular stress acting on the surface in the direction $\vec{e}_i$ with strength f and vanishing displacement at the bottom

$$\underline{\sigma} \cdot \vec{e}_z = f_0 \delta(\vec{r}) \vec{e}_i, \quad (\text{A.15a})$$

$$\vec{u} \big|_{z=-d} = 0. \quad (\text{A.15b})$$

To obtain the solution at the surface, the bulk problem has to be solved first.

THE JORDAN NORMAL FORM

A problem of the shape

$$\partial_z \vec{\psi}(z) = \underline{A} \cdot \vec{\psi}(z) \quad (\text{A.16})$$

can be solved by using the ansatz $\vec{\psi} = \exp(\underline{A}z) \cdot \vec{c}$ with $\vec{c}$ including unknown constants that are determined by the boundary conditions. In case $\underline{A}$ is diagonalizable the solution can be found by solving the eigenvalue problem and is then given by

$$\vec{\psi}(z) = \sum_{i=1}^n C_i \vec{v}_i \exp(q_i z), \quad (\text{A.17})$$

with n different eigenvalues q_i of $\underline{A}$, their associated eigenvectors $\vec{v}_i$ and the unknown constants C_i , which are again determined by the boundary conditions. If the matrix exhibits degenerated eigenvalues, i.e. the multiplicity of at least one eigen-

value is $m(q) > 1$, however, a diagonal representation is not always possible. The problem can still be solved using the *Jordan normal form* representation

$$\underline{A} = \underline{P} \underline{J} \underline{P}^{-1}, \quad (\text{A.18})$$

with the transformation matrix $\underline{P}$ being constructed from the eigenvectors and the associated generalized eigenvectors as columns and $\underline{J}$ being the *Jordan matrix*. The latter is block diagonal and takes the form

$$\underline{J} = \text{diag}(\underline{J}_1, \dots, \underline{J}_n), \quad \underline{J}_i = q_i \underline{1} + \underline{N}_i, \quad (\text{A.19})$$

with the *Jordan blocks* $\underline{J}_i$ being squared $m(q_i) \times m(q_i)$ matrices with

$$(N_k)_{ij} = \delta_{i+1}^j \quad \text{and} \quad (N_k)_{ij}^\alpha = \delta_{i+\alpha+1}^j, \quad \alpha \in \mathbb{N}. \quad (\text{A.20})$$

Using the series expansion of the exponential function $\exp(x) = \sum_n x^n/n!$ the solution can be written like

$$\begin{aligned} \vec{\psi} &= \exp(\underline{A}z) \cdot \vec{c} = \exp(\underline{P} \underline{J} \underline{P}^{-1} z) \cdot \vec{c} = \sum_{k=0}^{\infty} \frac{z^k}{k!} (\underline{P} \underline{J} \underline{P}^{-1})^k \cdot \vec{c} \\ &= \underline{P} \left[\sum_{k=0}^{\infty} \frac{z^k}{k!} \underline{J}^k \right] \underline{P}^{-1} \cdot \vec{c} \\ &= \underline{P} \exp(\underline{J}z) \underline{P}^{-1} \cdot \vec{c} \end{aligned} \quad (\text{A.21})$$

with

$$\begin{aligned} \exp(\underline{J}z) &= \text{diag}(\exp(\underline{J}_1 z), \dots, \exp(\underline{J}_n z)) \\ &= \text{diag}(\exp(q_1 z) \exp(\underline{N}_1 z), \dots, \exp(q_n z) \exp(\underline{N}_n z)). \end{aligned} \quad (\text{A.22})$$

and

$$[\exp(\underline{N}_l z)]_{ij} = \sum_{k=1}^{m(q_l)} \frac{z^{k-1}}{(k-1)!} \delta_{i+k}^j \quad (\text{A.23})$$

since $\underline{N}_i^k = 0$ for $k \geq m(q_i)$.

A.5.1. 3D PROBLEM

AXIS SYMMETRY AND HANKEL TRANSFORMATION

Assuming the system to exhibit azimuthal symmetry about the z -axis, cylindrical coordinates can be introduced to reduce the complexity of the problem. The components of the displacement field are assumed to be independent of the azimuthal angle ϕ yielding

$$\vec{u}(\vec{r}) = u_r(r, z)\vec{e}_r(\phi) + u_z(r, z)\vec{e}_z. \quad (\text{A.24})$$

The strain tensor components are then given by

$$\varepsilon_{rr} = \partial_r u_r, \quad \varepsilon_{\phi\phi} = \frac{u_r}{r} + \frac{1}{r} \partial_\phi u_\phi, \quad \varepsilon_{zz} = \partial_z u_z, \quad (\text{A.25a})$$

$$\varepsilon_{r\phi} = \varepsilon_{\phi r} = \frac{1}{2} \left[\partial_r u_\phi - \frac{u_\phi}{r} + \frac{1}{r} \partial_\phi u_r \right], \quad (\text{A.25b})$$

$$\varepsilon_{rz} = \varepsilon_{zr} = \frac{1}{2} \left[\partial_z u_r + \partial_r u_z \right], \quad (\text{A.25c})$$

$$\varepsilon_{\phi z} = \varepsilon_{z\phi} = \frac{1}{2} \left[\frac{1}{r} \partial_\phi u_z + \partial_z u_\phi \right], \quad (\text{A.25d})$$

while the stress tensor is still given by

$$\sigma_{ij} = \lambda \varepsilon_{nn} \delta_{ij} + 2\mu \varepsilon_{ij}. \quad (\text{A.26})$$

The differential operators become

$$\nabla = \vec{e}_r \partial_r + \frac{1}{r} \vec{e}_\phi \partial_\phi + \vec{e}_z \partial_z, \quad (\text{A.27a})$$

$$\nabla \cdot = \left(\partial_r + \frac{1}{r} \right) \vec{e}_r + \frac{1}{r} \partial_\phi \vec{e}_\phi + \partial_z \vec{e}_z, \quad (\text{A.27b})$$

$$\Delta = \partial_r^2 + \frac{1}{r} \partial_r + \frac{1}{r^2} \partial_\phi^2 + \partial_z^2. \quad (\text{A.27c})$$

Note that the differential operators also act on the unit vectors, in particular

$$\partial_\phi \vec{e}_r = \vec{e}_\phi, \quad \partial_\phi \vec{e}_\phi = -\vec{e}_r, \quad (\text{A.28})$$

resulting in

$$\nabla \cdot \vec{u} = \left(\vec{e}_r \partial_r + \frac{1}{r} \vec{e}_\varphi \partial_\varphi + \vec{e}_z \partial_z \right) \cdot \vec{u}(r, z) = \partial_r u_r + \frac{u_r}{r} + \partial_z u_z, \quad (\text{A.29a})$$

$$\begin{aligned} \nabla(\nabla \cdot \vec{u}) &= \left(\vec{e}_r \partial_r + \frac{1}{r} \vec{e}_\varphi \partial_\varphi + \vec{e}_z \partial_z \right) \left(\partial_r u_r + \frac{u_r}{r} + \partial_z u_z \right) \\ &= \vec{e}_r \left[\partial_r^2 u_r + \frac{1}{r} \partial_r u_r - \frac{u_r}{r^2} + \partial_r \partial_z u_z \right] + \vec{e}_z \left[\partial_z \partial_r u_r + \frac{1}{r} \partial_z u_z + \partial_z^2 u_z \right], \end{aligned} \quad (\text{A.29b})$$

$$\begin{aligned} \Delta \vec{u} &= \left(\frac{1}{r} \partial_r (r \partial_r) + \frac{1}{r^2} \partial_\varphi^2 + \partial_z^2 \right) \vec{u}(r, z) \\ &= \vec{e}_z \left[\frac{1}{r} \partial_r (r \partial_r u_z) + \partial_z^2 u_z \right] + \vec{e}_r \left[\frac{1}{r} (r \partial_r u_r) + \partial_z^2 u_r \right] + \frac{u_r}{r^2} \partial_\varphi^2 \vec{e}_r \\ &= \vec{e}_z \left[\frac{1}{r} \partial_r (r \partial_r u_z) + \partial_z^2 u_z \right] + \vec{e}_r \left[\frac{1}{r} (r \partial_r u_r) + \partial_z^2 u_r - \frac{u_r}{r^2} \right]. \end{aligned} \quad (\text{A.29c})$$

For the statics of the bulk in the absence of body forces, i.e. $\vec{f}_{\text{ex}} = 0$, the Navier-Cauchy equation (2.60) writes

$$(\nabla \cdot \underline{\sigma}) \cdot \vec{e}_r = (\lambda + 2\mu) \left[\frac{1}{r} \partial_r (r \partial_r u_r) - \frac{u_r}{r} + \partial_z \partial_r u_z \right] + \mu \partial_z [\partial_z u_r - \partial_r u_z] = 0 \quad (\text{A.30a})$$

$$(\nabla \cdot \underline{\sigma}) \cdot \vec{e}_z = (\lambda + 2\mu) \left[\partial_z^2 u_z + \partial_z \left(\partial_r u_r + \frac{u_r}{r} \right) \right] + \mu \left[\frac{1}{r} \partial_r (r \partial_r u_z) - \partial_z \left(\partial_r u_r + \frac{u_r}{r} \right) \right] = 0 \quad (\text{A.30b})$$

These two coupled partial differential equations can be translated into a system of coupled ordinary differential equations by eliminating the radial derivatives. This can be done by employing *Hankel transformations*

$$\hat{\psi}(k, z) = \mathcal{H}_\nu[\psi(r, z)] = \int_0^\infty \psi(r, z) J_\nu(kr) r \, dr, \quad (\text{A.31a})$$

$$\psi(r, z) = \mathcal{H}_\nu^{-1}[\hat{\psi}(k, z)] = \int_0^\infty \hat{\psi}(k, z) J_\nu(kr) k \, dk, \quad (\text{A.31b})$$

with the *Bessel functions* of first kind and order ν

$$J_\nu(kr) = \frac{1}{2\pi} \int_{-\pi}^{\pi} e^{i(kr \sin(\varphi) - \nu\varphi)} \, d\varphi = \frac{1}{2\pi} \int_0^{2\pi} e^{-i\nu\frac{\pi}{2}} e^{-i(kr \cos(\varphi) + \nu\varphi)} \, d\varphi \quad (\text{A.32})$$

This transformation can be performed under the assumption of infinite horizontal expansion of the layer and vanishing displacement in the infinite $\lim_{r \rightarrow \infty} \vec{u}(\vec{r}) = 0$. The radial and vertical component of the displacement may then be expressed in terms

of their first and zeroth order Hankel transform respectively

$$u_r(r, z) = \mathcal{H}_1^{-1}[\hat{u}_r(k, z)] , \quad u_z(r, z) = \mathcal{H}_0^{-1}[\hat{u}_z(k, z)] . \quad (\text{A.33})$$

Introducing these into the cylindrical Navier-Cauchy equations (A.3o) leads to

$$0 = \int_0^\infty (\lambda + 2\mu) \left[\hat{u}_r(k, z) \frac{1}{r} \partial_r (r \partial_r J_1(kr)) - \hat{u}_r(k, z) \frac{1}{r} J_1(kr) + \partial_z \hat{u}_z(k, z) \partial_r J_0(kr) \right] k \, dk \\ + \int_0^\infty \mu \left[\partial_z^2 \hat{u}_r(k, z) J_1(kr) - \partial_z \hat{u}_z(k, z) \partial_r J_0 \right] k \, dk , \quad (\text{A.34a})$$

$$0 = \int_0^\infty (\lambda + 2\mu) \left[\partial_z^2 \hat{u}_z J_0(kr) + \partial_z \hat{u}_r(k, z) \left(\partial_r J_1(kr) + \frac{1}{r} J_1(kr) \right) \right] k \, dk \\ + \int_0^\infty \mu \left[\hat{u}_z(k, z) \frac{1}{r} \partial_r (r \partial_r J_0(kr)) - \partial_z \hat{u}_r(k, z) \left(\partial_r J_1(kr) + \frac{1}{r} J_1(kr) \right) \right] k \, dk . \quad (\text{A.34b})$$

These equations can be simplified further by using the connections between the Bessel functions of zeroth and first order

$$\partial_r J_0(kr) = -k J_1(kr) , \quad \partial_r J_1(kr) + \frac{J_1(kr)}{r} = k J_0(kr) , \\ \frac{1}{r} \partial_r (r \partial_r J_0(kr)) = -k^2 J_0(kr) , \quad \frac{1}{r} \partial_r (r \partial_r J_1(kr)) - \frac{J_1(kr)}{r^2} = -k^2 J_1(kr) ,$$

and by performing the radial derivatives yielding

$$\int_0^\infty \left[(\lambda + 2\mu)(-k^2 \hat{u}_r - k \partial_z \hat{u}_z) + \mu(\partial_z^2 \hat{u}_r + k \partial_z \hat{u}_z) \right] J_1(kr) k \, dk = 0 , \quad (\text{A.36a})$$

$$\int_0^\infty \left[(\lambda + 2\mu)(\partial_z^2 \hat{u}_z + k \partial_z \hat{u}_r) + \mu(-k^2 \hat{u}_z - k \partial_z \hat{u}_r) \right] J_0(kr) k \, dk = 0 . \quad (\text{A.36b})$$

The integrals vanish if the terms in the parentheses do, resulting in two coupled ordinary differential equations of second order

$$\partial_z^2 \hat{u}_r - k \left(\frac{\lambda + 2\mu}{\mu} - 1 \right) \partial_z \hat{u}_z - k^2 \left(\frac{\lambda + 2\mu}{\mu} \right) \hat{u}_r = 0 , \quad (\text{A.37a})$$

$$\left(\frac{\lambda + 2\mu}{\mu} \right) \partial_z^2 \hat{u}_z + k \left(\frac{\lambda + 2\mu}{\mu} - 1 \right) \partial_z \hat{u}_r - k^2 \hat{u}_z = 0 , \quad (\text{A.37b})$$

depending only on z and its partial derivatives. Replacing λ and μ by the Poisson ratio $\nu = \frac{\lambda}{2(\lambda+\mu)}$ leaves us with only one parameter

$$\partial_z^2 \hat{u}_r - \frac{k}{1-2\nu} \partial_z \hat{u}_z - k^2 \frac{2(1-\nu)}{1-2\nu} \hat{u}_r = 0, \quad (\text{A.38a})$$

$$\partial_z^2 \hat{u}_z + \frac{k}{2(1-\nu)} \partial_z \hat{u}_r - k^2 \frac{1-2\nu}{2(1-\nu)} \hat{u}_z = 0. \quad (\text{A.38b})$$

These equations can be further decomposed into a system of four coupled ordinary differential equations of order one by introducing two auxiliary fields

$$\partial_z \hat{u}_r = \hat{w}_r, \quad (\text{A.39a})$$

$$\partial_z \hat{u}_z = \hat{w}_z, \quad (\text{A.39b})$$

$$\partial_z \hat{w}_r = \frac{k}{1-2\nu} \hat{w}_z + k^2 \frac{2(1-\nu)}{1-2\nu} \hat{u}_r, \quad (\text{A.39c})$$

$$\partial_z \hat{w}_z = -\frac{k}{2(1-\nu)} \hat{w}_r + k^2 \frac{1-2\nu}{2(1-\nu)} \hat{u}_z, \quad (\text{A.39d})$$

and written more compact in the form of Eq. (A.16) with

$$\vec{\psi} = \begin{pmatrix} \hat{u}_r \\ \hat{u}_z \\ \hat{w}_r \\ \hat{w}_z \end{pmatrix}, \quad \underline{A} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ k^2 \frac{2(1-\nu)}{1-2\nu} & 0 & 0 & \frac{k}{1-2\nu} \\ 0 & k^2 \frac{1-2\nu}{2(1-\nu)} & -\frac{k}{2(1-\nu)} & 0 \end{pmatrix}. \quad (\text{A.40})$$

The eigenvalues of $\underline{A}$ are given by

$$\det(\underline{A} - \underline{1}q) = q^4 - 2k^2 q^2 + k^4 = 0. \quad (\text{A.41})$$

Hence, only $n = 2$ different Eigenvalues $q_1 = k$ and $q_2 = -k$ exist and both are degenerated with multiplicity $m(q_i) = 2$. Since $\underline{A}$ is not diagonalizable the solution of the system is given by the Jordan normal form (A.21) with

$$\underline{P} = \begin{pmatrix} \frac{k}{4(1-2\nu)} & \frac{1}{2} & -\frac{k}{4(1-2\nu)} & \frac{1}{2} \\ -\frac{k}{4(1-2\nu)} & \frac{1}{4(1-2\nu)} & -\frac{k}{4(1-2\nu)} & -\frac{1}{4(1-2\nu)} \\ \frac{k^2}{4(1-2\nu)} & \frac{k(3-4\nu)}{4(1-2\nu)} & \frac{k^2}{4(1-2\nu)} & -\frac{k(3-4\nu)}{4(1-2\nu)} \\ -\frac{k^2}{4(1-2\nu)} & 0 & \frac{k^2}{4(1-2\nu)} & 0 \end{pmatrix}, \quad \exp(\underline{J}z) = \begin{pmatrix} e^{q_1 z} \begin{pmatrix} 1 & z \\ 0 & 1 \end{pmatrix} & 0 \\ 0 & e^{q_2 z} \begin{pmatrix} 1 & z \\ 0 & 1 \end{pmatrix} \end{pmatrix}. \quad (\text{A.42})$$

VERTICAL POINT FORCE

Considering a vertically acting localized inhomogeneity the azimuthal symmetry with respect to the z -axis is fulfilled and the solution for the displacement field is given by the Jordan normal form (A.21) with (A.42). Now only the constant vector $\vec{c}$ is left to be determined from the boundary conditions (A.15). Those for the free surface $z = 0$ are in cylindrical coordinates given by

$$\sigma_{rz} = 0, \quad \sigma_{\varphi z} = 0, \quad \sigma_{zz} = f_0 \delta(\vec{r}) = f_0 \frac{\delta(r)}{\pi r}, \quad (\text{A.43})$$

with the azimuthal surface stress $\sigma_{\varphi z}$ vanishing naturally due to the symmetry of the displacement field. Using the cylindrical strain components (A.25) in Eq. (A.26) and employing Hankel transformation the other two conditions become

$$\sigma_{rz} = \mu \int_0^\infty [\partial_z \hat{u}_r - k \hat{u}_z] J_1(kr) k \, dk = 0, \quad (\text{A.44a})$$

$$\begin{aligned} \sigma_{zz} &= \int_0^\infty \left[(\lambda + 2\mu) \partial_z \hat{u}_z J_0(kr) + \lambda \hat{u}_r \partial_r J_1(kr) + \lambda \hat{u}_r \frac{1}{r} J_1(kr) \right] k \, dk \\ &= \int_0^\infty \left[(\lambda + 2\mu) \partial_z \hat{u}_z + \lambda k \hat{u}_r \right] J_0(kr) k \, dk = \frac{f_0}{2\pi} \int_0^\infty J_0(kr) k \, dk, \end{aligned} \quad (\text{A.44b})$$

where $\int_0^\infty \delta(r) J_0(kr) dr = \frac{1}{2} J_0(0) = \frac{1}{2}$ was used. Comparison of the integrands yields two differential equations

$$\partial_z \hat{u}_r - k \hat{u}_z = 0, \quad (\text{A.45a})$$

$$(\lambda + 2\mu) \partial_z \hat{u}_z + \lambda k \hat{u}_r = \frac{f_0}{2\pi}. \quad (\text{A.45b})$$

With $\lambda = 2\mu\nu/(1 - 2\nu)$ the solution is found to be

$$\begin{aligned} \tilde{u}_r(k, z) &= -\frac{f_0}{2\pi} \left\{ \frac{(4\nu - 3)(kz - 2\nu + 1)e^{2k(2d+z)} + (8\nu^2 - (4kd + 10)\nu + 3 + 2k^2 d(d+z) + k(2d-z))e^{2k(d+z)}}{2\mu k \left[(4k^2 d^2 + 16\nu^2 - 24\nu + 10)e^{2kd} + (3 - 4\nu)(e^{4kd} + 1) \right] e^{kz}} \right. \\ &\quad \left. + \frac{(8\nu^2 + (4kd - 10)\nu + 3 + 2k^2 d(d+z) - k(2d-z))e^{2kd} - (4\nu - 3)(kz + 2\nu - 1)}{2\mu k \left[(4k^2 d^2 + 16\nu^2 - 24\nu + 10)e^{2kd} + (3 - 4\nu)(e^{4kd} + 1) \right] e^{kz}} \right\}, \end{aligned} \quad (\text{A.46a})$$

$$\begin{aligned} \tilde{u}_z(k, z) &= \frac{f_0}{2\pi} \left\{ \frac{(4\nu - 3)(kz + 2\nu - 2)e^{2k(2d+z)} + (8\nu^2 + (4kd - 14)\nu + 6 + 2k^2 d(d+z) - k(4d+z))e^{2k(d+z)}}{2\mu k \left[(4k^2 d^2 + 16\nu^2 - 24\nu + 10)e^{2kd} + (3 - 4\nu)(e^{4kd} + 1) \right] e^{kz}} \right. \\ &\quad \left. + \frac{-(8\nu^2 - (4kd + 14)\nu + 6 + 2k^2 d(d+z) + k(4d+z))e^{2kd} + (4\nu - 3)(kz - 2\nu + 2)}{2\mu k \left[(4k^2 d^2 + 16\nu^2 - 24\nu + 10)e^{2kd} + (3 - 4\nu)(e^{4kd} + 1) \right] e^{kz}} \right\}. \end{aligned} \quad (\text{A.46b})$$

The displacement at the surface $z = 0$ then is

$$\tilde{u}_r(k) = -\frac{f_0}{2\pi} \frac{(4k^2d^2 + 16\nu^2 - 20\nu + 6)e^{2kd} - (3 - 4\nu)(1 - 2\nu)(1 + e^{4kd})}{2\mu k [(4k^2d^2 + 16\nu^2 - 24\nu + 10)e^{2kd} + (3 - 4\nu)(1 + e^{4kd})]} \quad (\text{A.47a})$$

$$= -\frac{f_0}{2\pi} \frac{1}{2\mu k} \frac{2k^2d^2 + (1 - 2\nu)(3 - 4\nu)[1 - \cosh(2kd)]}{2k^2d^2 + 2(1 - \nu) + (3 - 4\nu)[(1 - 2\nu) + \cosh(2kd)]}, \quad (\text{A.47b})$$

$$\tilde{u}_z(k) = \frac{f_0}{2\pi} \frac{(\nu - 1)[4kde^{2kd} + (3 - 4\nu)(1 - e^{4kd})]}{\mu k [(4k^2d^2 + 16\nu^2 - 24\nu + 10)e^{2kd} + (3 - 4\nu)(1 + e^{4kd})]} \quad (\text{A.47c})$$

$$= \frac{f_0}{2\pi} \frac{1}{\mu k} \frac{(\nu - 1)[2kd - (3 - 4\nu)\sinh(2kd)]}{2k^2d^2 + 2(1 - \nu) + (3 - 4\nu)[(1 - 2\nu) + \cosh(2kd)]}, \quad (\text{A.47d})$$

in agreement with Ref. [Gac+06, LC11]. Using the integral representation of Bessel functions

$$\begin{aligned} J_\nu(kr) &= \frac{1}{2\pi} \int_0^{2\pi} e^{i(kr \sin(\varphi) - \nu\varphi)} d\varphi \\ &= \frac{1}{2\pi} \int_0^{2\pi} e^{i\nu\frac{\pi}{2}} e^{-i(kr \cos(\varphi) + \nu\varphi)} d\varphi \\ &= \frac{1}{2\pi} \int_0^{2\pi} [\cos(\nu\varphi) - i \sin(\nu\varphi)] e^{i\nu\frac{\pi}{2}} e^{-ikr \cos(\varphi)} d\varphi, \end{aligned} \quad (\text{A.48})$$

the first and second order Hankel transformation yield

$$\begin{aligned} \mathcal{H}_0^{-1}[\hat{\psi}] &= \frac{1}{2\pi} \int_0^\infty \int_0^{2\pi} \hat{\psi} e^{-ikr \cos(\varphi)} k d\varphi dk \\ &= \frac{1}{2\pi} \int_{-\infty}^\infty \int_{-\infty}^\infty \hat{\psi} e^{-i\vec{k} \cdot \vec{r}} d^2\vec{k} = \mathcal{FT}^{-1}[\hat{\psi}] \end{aligned} \quad (\text{A.49a})$$

$$\begin{aligned} \mathcal{H}_1^{-1}[\hat{\psi}] &= \frac{1}{2\pi} \int_0^\infty \int_0^{2\pi} \hat{\psi} [i \cos(\varphi) + \sin(\varphi)] e^{-ikr \cos(\varphi)} k d\varphi dk \\ &= \frac{1}{2\pi} \int_{-\infty}^\infty \int_{-\infty}^\infty \left(\frac{ik_x + k_y}{k} \right) \hat{\psi} e^{-i\vec{k} \cdot \vec{r}} d^2\vec{k} = \mathcal{FT}^{-1} \left[\left(\frac{ik_x + k_y}{k} \right) \hat{\psi} \right], \end{aligned} \quad (\text{A.49b})$$

with $\vec{r}$ and $\vec{k}$ being vectors in the x - y -plane. Hence the Fourier transforms of the solutions are

$$\tilde{u}_r(k) = \hat{u}_r(k) \left(\frac{ik_x + k_y}{k} \right), \quad (\text{A.50})$$

$$\tilde{u}_z(k) = \hat{u}_z(k). \quad (\text{A.51})$$

The radial component can be written in Cartesian coordinates like

$$\tilde{u}_x(\vec{k}) = \tilde{u}_r(\vec{k}) \cos(\varphi) = \hat{u}_r(k) \left(\frac{ik_x + k_y}{k} \right) \frac{k_x}{k}, \quad (\text{A.52a})$$

$$\tilde{u}_y(\vec{k}) = \tilde{u}_r(\vec{k}) \sin(\varphi) = \hat{u}_r(k) \left(\frac{ik_x + k_y}{k} \right) \frac{k_y}{k}. \quad (\text{A.52b})$$

For $f_0 = 1$ the solution vector corresponds to the third column of the Green's function according to Eq. (2.71)

$$\vec{u}(\vec{k}) = \vec{g}_z(\vec{k}) = \underline{\tilde{G}}(\vec{k}) \cdot \vec{e}_z. \quad (\text{A.53})$$

With this result all displacements caused by any normal forces acting on the free surface of a linear elastic layer of thickness d can be calculated. Finding the solution for a horizontally acting point force as boundary condition is a little more tedious, unfortunately, as azimuthal symmetry is broken in that case.

A.5.2. 2D PROBLEM

Assuming homogeneity of $\vec{u}$ in y direction the problems dimension reduces to the x - z -plane. The fundamental solution can be found analogously to the three dimensional case using Fourier- instead of Hankel transformations. The boundary condition at the surface then writes

$$\underline{\sigma} \cdot \vec{e}_z = f_0 \delta(x) \vec{e}_i. \quad (\text{A.54})$$

The solution for the bulk displacement are then found to be

$$u_x^z(k, z) = \frac{if_0}{2\pi} \left\{ \frac{-(3-4\nu)(kz-2\nu+1)e^{k(4d+3z)} + [8\nu^2-(4dk+10)\nu+3+2k^2d(d+z)+k(2d-z)]e^{k(2d+3z)}}{2\mu k[(4k^2d^2+16\nu^2-24\nu+10)e^{2kd} + (3-4\nu)(e^{4kd}+1)]e^{2kz}} \right. \\ \left. + \frac{(3-4\nu)(kz+2\nu-1)e^{kz} + [8\nu^2+(4dk-10)\nu+3+2d(d+z)k^2+k(z-2d)]e^{k(2d+z)}}{2\mu k[(4k^2d^2+16\nu^2-24\nu+10)e^{2kd} + (3-4\nu)(e^{4kd}+1)]e^{2kz}} \right\}, \quad (\text{A.55a})$$

$$u_z^z(k, z) = -\frac{f_0}{2\pi} \left\{ \frac{(3-4\nu)(kz+2\nu-2)e^{2k(2d+z)} - [8\nu^2+(4dk-14)\nu+6+2d(d+z)k^2-k(z+4d)]e^{2k(d+z)}}{2\mu k[(4k^2d^2+16\nu^2-24\nu+10)e^{2kd} + (3-4\nu)(e^{4kd}+1)]e^{kz}} \right. \\ \left. + \frac{(3-4\nu)(kz-2\nu+2) + [8\nu^2-(4dk+14)\nu+6+2d(d+z)k^2+k(z+4d)]e^{2kd}}{2\mu k[(4k^2d^2+16\nu^2-24\nu+10)e^{2kd} + (3-4\nu)(e^{4kd}+1)]e^{kz}} \right\}, \quad (\text{A.55b})$$

$$u_x^x(k_x, z) = \frac{f_0}{2\pi} \left\{ \frac{(3-4\nu)(kz-2\nu+2)e^{k(4d+3z)} + [8\nu^2-(4dk+14)\nu+6+2d(d+z)k^2+k(z+4d)]e^{k(2d+3z)}}{2\mu k[(4k^2d^2+16\nu^2-24\nu+10)e^{2kd} + (3-4\nu)(e^{4kd}+1)]e^{2kz}} \right. \\ \left. + \frac{(3-4\nu)(kz+2\nu-2)e^{kz} - [8\nu^2+(4dk-14)\nu+6+2d(d+z)k^2-k(z+4d)]e^{k(2d+z)}}{2\mu k[(4k^2d^2+16\nu^2-24\nu+10)e^{2kd} + (3-4\nu)(e^{4kd}+1)]e^{2kz}} \right\}, \quad (\text{A.55c})$$

$$u_z^x(k_x, z) = -\frac{if_0}{2\pi} \left\{ \frac{(3-4\nu)(kz+2\nu-1)e^{k(4d+3z)} + [8\nu^2+(4dk-10)\nu+3+2d(d+z)k^2+k(z-2d)]e^{k(2d+3z)}}{2\mu k[(4k^2d^2+16\nu^2-24\nu+10)e^{2kd} + (3-4\nu)(e^{4kd}+1)]e^{2kz}} \right. \\ \left. + \frac{-(3-4\nu)(kz-2\nu+1)e^{kz} + [8\nu^2-(4dk+10)\nu+3+2d(d+z)k^2-k(z-2d)]e^{k(2d+z)}}{2\mu k[(4k^2d^2+16\nu^2-24\nu+10)e^{2kd} + (3-4\nu)(e^{4kd}+1)]e^{2kz}} \right\}. \quad (\text{A.55d})$$

with $k = k_x$. Remember that the subscript index refers to the component of the solution vector while the superscript index refers to the direction of the point force used in the boundary condition. For $f_0 = 1$ and evaluated at the surface $z = 0$ the

solutions correspond to the components of the Green's function

$$\begin{aligned}
 u_x^z(k,0) = G_{xz} &= \frac{i}{2\pi} \frac{(4k^2d^2 + 16v^2 - 20v + 6)e^{2kd} - (1-2v)(3-4v)(e^{4kd} + 1)}{2k\mu \left[(4k^2d^2 + 16v^2 - 24v + 10)e^{2kd} + (3-4v)(e^{4kd} + 1) \right]} \\
 &= \frac{i}{2\pi} \frac{1}{2k\mu} \frac{2k^2d^2 + (3-4v)(1-2v)[1 - \cosh(2kd)]}{(3-4v)\cosh(2kd) + (3-4v)(1-2v) + 2(1-v) + 2k^2d^2}, \quad (\text{A.56a})
 \end{aligned}$$

$$\begin{aligned}
 u_z^z(k,0) = G_{zz} &= \frac{1}{2\pi} \frac{(\nu-1) \left[4kde^{2kd} - (3-4v)(e^{4kd} - 1) \right]}{\mu k \left[(4k^2d^2 + 16v^2 - 24v + 10)e^{2kd} + (3-4v)(e^{4kd} + 1) \right]} \\
 &= \frac{1}{2\pi} \frac{1-\nu}{\mu k} \frac{(3-4v)\sinh(2kd) - 2kd}{(3-4v)\cosh(2kd) + (3-4v)(1-2v) + 2(1-\nu) + 2k^2d^2} \quad (\text{A.56b})
 \end{aligned}$$

$$\begin{aligned}
 u_x^x(k,0) = G_{xx} &= -\frac{1}{2\pi} \frac{(\nu-1) \left[4dke^{2kd} + (3-4v)(e^{4kd} - 1) \right]}{\mu k \left[(4k^2d^2 + 16v^2 - 24v + 10)e^{2kd} + (3-4v)(e^{4kd} + 1) \right]} \\
 &= \frac{1}{2\pi} \frac{1-\nu}{\mu k} \frac{(3-4v)\sinh(2kd) + 2dk}{(3-4v)\cosh(2kd) + (3-4v)(1-2v) + 2(1-\nu) + 2k^2d^2}, \quad (\text{A.56c})
 \end{aligned}$$

$$\begin{aligned}
 u_z^x(k,0) = G_{zx} &= -\frac{i}{2\pi} \frac{(4k^2d^2 + 16v^2 - 20v + 6)e^{2kd} - (3-4v)(1-2v)(e^{4kd} + 1)}{2\mu k \left[(16v^2 - 24v + 4k^2d^2 + 10)e^{2kd} + (3-4v)(e^{4kd} + 1) \right]} \\
 &= -\frac{i}{2\pi} \frac{1}{2\mu k} \frac{2k^2d^2 + (3-4v)(1-2v)[1 - \cosh(2kd)]}{(3-4v)\cosh(2kd) + (3-4v)(1-2v) + 2(1-\nu) + 2k^2d^2}, \quad (\text{A.56d})
 \end{aligned}$$

in agreement with Refs. [[Han51](#), [Ess+21](#)].

A.6. FOURIER TRANSFORMATION OF THE TIME DEPENDENT CONSTITUTIVE LAW

The time dependent constitutive law for linear viscoelastic materials writes [DE78]

$$\begin{aligned}\sigma_{ij}(\vec{r}, t) &= \int_{-\infty}^t \frac{E(t-t')}{1+\nu} \partial_{t'} \left[\varepsilon_{ij}(\vec{r}, t') + \frac{\nu}{1-2\nu} \varepsilon_{kk}(\vec{r}, t') \delta_{ij} \right] dt' \\ &= \int_{-\infty}^{\infty} E(t-t') \Theta(t-t') \partial_{t'} A_{ij}(t') dt',\end{aligned}\quad (\text{A.57})$$

where the upper integral limit has been extended towards infinity by introducing a Heaviside function and with

$$A_{ij}(t) = \frac{1}{1+\nu} \left[\varepsilon_{ij}(\vec{r}, t) + \frac{\nu}{1-2\nu} \varepsilon_{kk}(\vec{r}, t) \delta_{ij} \right]. \quad (\text{A.58})$$

Temporal Fourier transformation then gives

$$\begin{aligned}\tilde{\sigma}_{ij}(\vec{r}, \omega) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} E(t-t') \Theta(t-t') \partial_{t'} A_{ij}(t') e^{-i\omega t} dt' dt \\ &\stackrel{\tau=t-t'}{=} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} E(\tau) \Theta(\tau) \partial_{t'} A_{ij}(t') e^{-i\omega(\tau+t')} dt' d\tau \\ &\stackrel{\text{p.l.}}{=} \underbrace{i\omega \int_0^{\infty} E(\tau) e^{-i\omega\tau} d\tau}_{E(\omega)} \underbrace{\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A_{ij}(t') e^{-i\omega t'} dt'}_{\tilde{A}_{ij}(\omega)},\end{aligned}\quad (\text{A.59})$$

with $\tilde{A}_{ij}(\omega)$ being the temporal Fourier transform of Eq. (A.58) and

$$\frac{E(\omega)}{i\omega} = \int_0^{\infty} E(t) e^{-i\omega t} dt = \mathcal{L}[E(t)](s), \quad (\text{A.60})$$

being the Laplace transform of the relaxation function $E(t)$ with $s = i\omega$.

A.7. EULER-LAGRANGE EQUATION

Considering a functional given by the integral form

$$\mathcal{S}[\psi] = \int_{\Omega} s(\psi, \nabla \psi) d^n \vec{r},$$

its variation can be calculated using the weak formulation

$$\begin{aligned}
\int_{\Omega} \frac{\delta \mathcal{S}}{\delta \psi} \phi(\vec{r}) \, d^n \vec{r} &= \lim_{\epsilon \rightarrow \infty} \frac{1}{\epsilon} \left[\mathcal{S}(\psi + \epsilon \phi, \nabla(\psi + \epsilon \phi)) - \mathcal{S}(\psi, \nabla \psi) \right] \\
&= \lim_{\epsilon \rightarrow \infty} \frac{1}{\epsilon} \int_{\Omega} s(\psi + \epsilon \phi, \nabla(\psi + \epsilon \phi)) - s(\psi, \nabla \psi) \, d^n \vec{r} \\
&\stackrel{\text{Taylor}}{=} \int_{\Omega} \frac{\partial s(\psi, \nabla \psi)}{\partial \psi} \phi + \frac{\partial s(\psi, \nabla \psi)}{\partial(\nabla \psi)} \cdot \nabla \phi \, d^n \vec{r} \\
&\stackrel{\text{p.i.}}{=} \int_{\Omega} \left(\frac{\partial s(\psi, \nabla \psi)}{\partial \psi} - \nabla \cdot \frac{\partial s(\psi, \nabla \psi)}{\partial(\nabla \psi)} \right) \phi \, d^n \vec{r}
\end{aligned}$$

and is given by the Euler-Lagrange equation. The surface term arising during the partial integration (p.i.) of the second term vanishes due to $\phi(\vec{r})|_{\partial\Omega} = 0$.

A.8. ABSOLUTE HEIGHT FORMULATION

Consider the general form of a gradient dynamics [Eq. (2.114)]

$$\partial_t \vec{\psi} = \nabla \cdot \left[\underline{Q} \nabla \frac{\delta \mathcal{F}}{\delta \vec{\psi}} \right] - \underline{M} \frac{\delta \mathcal{F}}{\delta \vec{\psi}}, \quad (\text{A.61})$$

with mobility matrices $\underline{Q}$ and $\underline{M}$ and the vector of fields $\vec{\psi}$.

The gradient dynamics model for liquids wetting a soft substrate is introduced in Sec. 3.4 and describes the system in terms of the local liquid layer thickness $h(\vec{r})$ and the substrate profile $\xi(\vec{r})$. The evolution equations are given by Eqs. (3.65) with the variations according to Eqs. (3.66). Neglecting the horizontal displacement for the moment, the general gradient dynamics structure is given by Eq. (2.114) with

$$\vec{\psi} = \begin{pmatrix} h \\ \xi \end{pmatrix}, \quad \frac{\delta \mathcal{F}}{\delta \vec{\psi}} = \begin{pmatrix} \frac{\delta \mathcal{F}}{\delta h} \\ \frac{\delta \mathcal{F}}{\delta \xi} \end{pmatrix}, \quad \underline{Q} = \begin{pmatrix} h^3 & 0 \\ 0 & 0 \end{pmatrix}, \quad \underline{M} = \begin{pmatrix} 0 & 0 \\ 0 & \frac{1}{\tau} \end{pmatrix}. \quad (\text{A.62})$$

Now, the profile of the actual liquid-gas interface is given by $\zeta = h + \xi$ and it may be desirable to express the model in terms of ζ instead of h . The transformation between these variables is given by

$$\vec{\psi}' = \underline{T} \vec{\psi}, \quad \vec{\psi} = \underline{T}^{-1} \vec{\psi}' \quad (\text{A.63})$$

with

$$\vec{\psi}' = \begin{pmatrix} \zeta \\ \xi \end{pmatrix}, \quad \underline{T} = \frac{\partial \vec{\psi}'}{\partial \vec{\psi}} = \begin{pmatrix} 1 & 1 \\ 0 & 1 \end{pmatrix} \quad \text{and} \quad \underline{T}^{-1} = \begin{pmatrix} 1 & -1 \\ 0 & 1 \end{pmatrix}. \quad (\text{A.64})$$

The variation vectors transform like derivatives, i.e.,

$$\frac{\delta \mathcal{F}[\vec{\psi}]}{\delta \psi_i} = \frac{\delta \mathcal{F}[\vec{\psi}']}{\delta \psi'_j} \frac{\partial \psi'_j}{\partial \psi_i} \rightarrow \frac{\delta \mathcal{F}}{\delta \vec{\psi}} = \underline{T}^\top \frac{\delta \mathcal{F}}{\delta \vec{\psi}'} \quad (\text{A.65})$$

The dynamics in terms of ζ and ξ are thus obtained as

$$\partial_t \vec{\psi}' = \underline{T} \partial_t \vec{\psi} = \nabla \cdot \left[\underline{T} \underline{Q} \nabla \frac{\delta \mathcal{F}}{\delta \vec{\psi}} \right] - \underline{T} \underline{M} \frac{\delta \mathcal{F}}{\delta \vec{\psi}} = \nabla \cdot \left[\underline{T} \underline{Q} \underline{T}^\top \nabla \frac{\delta \mathcal{F}}{\delta \vec{\psi}'} \right] - \underline{T} \underline{M} \underline{T}^\top \frac{\delta \mathcal{F}}{\delta \vec{\psi}'}.$$

It seems the mobility matrices transform like

$$\underline{Q}' = \underline{T} \underline{Q} \underline{T}^\top \quad \text{and} \quad \underline{M}' = \underline{T} \underline{M} \underline{T}^\top, \quad (\text{A.66})$$

i.e., in this case

$$\underline{Q}' = \underline{Q} = \begin{pmatrix} (\zeta - \xi)^3 & 0 \\ 0 & 0 \end{pmatrix} \quad \text{and} \quad \underline{M}' = \frac{1}{\tau} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}. \quad (\text{A.67})$$

With a free energy of the form

$$\mathcal{F}[h, \xi] = \int \sqrt{1 + (\nabla h + \nabla \xi)^2} + [\sigma + f(h)] \sqrt{1 + (\nabla \xi)^2} + \frac{1}{2S} \xi^2 \, d^2 \vec{r} \quad (\text{A.68})$$

$$\Leftrightarrow \mathcal{F}[\zeta, \xi] = \int \sqrt{1 + (\nabla \zeta)^2} + [\sigma + f(\zeta - \xi)] \sqrt{1 + (\nabla \xi)^2} + \frac{1}{2S} \xi^2 \, d^2 \vec{r}, \quad (\text{A.69})$$

the variations in the absolute height description would be given by

$$\frac{\delta \mathcal{F}}{\delta \zeta} = -\nabla \cdot \left(\frac{\nabla \zeta}{\sqrt{1 + (\nabla \zeta)^2}} \right) - \Pi(\zeta - \xi) \sqrt{1 + (\nabla \xi)^2}, \quad (\text{A.70a})$$

$$\frac{\delta \mathcal{F}}{\delta \xi} = -\nabla \cdot \left(\frac{[\sigma + f(\zeta - \xi)] \nabla \xi}{\sqrt{1 + (\nabla \xi)^2}} \right) + \Pi(\zeta - \xi) \sqrt{1 + (\nabla \xi)^2} + \frac{1}{S} \xi, \quad (\text{A.70b})$$

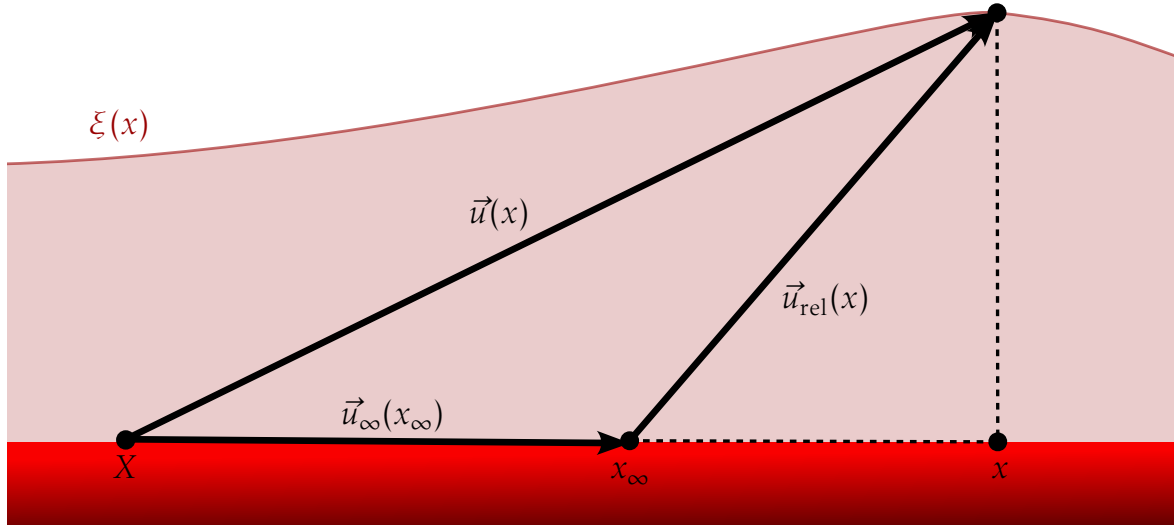


FIGURE A.2.: Visualization of the displacement vector $\vec{u}_{\text{rel}}(x)$ relative to the pre-stretched state, given by the displacement $\vec{u}_{\infty}(x_{\infty})$. To reconstruct it from $\vec{u}(x)$ the pre-stretched position x_{∞} has to be found assuming $\vec{e}_x \cdot \vec{u}_{\infty} = u'_{\infty} x_{\infty}$ with constant imposed u'_{∞} . Note, that X corresponds to the Lagrangian coordinate of the undeformed state.

and finally the dynamics write

$$\begin{aligned} \partial_t \zeta &= \nabla \cdot \left[(\zeta - \xi)^3 \nabla \frac{\delta \mathcal{F}}{\delta \zeta} \right] - \frac{1}{\tau} \left[\frac{1}{S} \xi - \nabla \cdot \left(\frac{\nabla \zeta}{\sqrt{1 + (\nabla \zeta)^2}} \right) - \nabla \cdot \left(\frac{[\sigma + f(\zeta - \xi)] \nabla \xi}{\sqrt{1 + (\nabla \xi)^2}} \right) \right], \\ \partial_t \xi &= -\frac{1}{\tau} \left[\frac{1}{S} \xi - \nabla \cdot \left(\frac{\nabla \zeta}{\sqrt{1 + (\nabla \zeta)^2}} \right) - \nabla \cdot \left(\frac{[\sigma + f(\zeta - \xi)] \nabla \xi}{\sqrt{1 + (\nabla \xi)^2}} \right) \right]. \end{aligned}$$

As required, $\partial_t \zeta = \partial h + \partial_{\xi}$ can be recovered from this form.

A.9. EULERIAN HORIZONTAL DISPLACEMENT RELATIVE TO PRE-STRETCH

In the investigation of the Shuttleworth effect often the displacement $\vec{u}_{\text{rel}}(x)$ relative to the state of applied pre-stretch, as given by $\vec{u}_{\infty}(x_{\infty})$, is desired. The position x_{∞} after application of the pre-stretch $\lambda_{\infty} = (1 - u'_{\infty})^{-1}$, where $u'_{\infty} = \partial_x(\vec{e}_x \cdot \vec{u}_{\infty}) = \partial_x u_{\infty}^x$, is found to be

$$\begin{aligned} x_{\infty} &= X + u_{\infty}^x(x_{\infty}) = X + u'_{\infty} x_{\infty} \\ \rightarrow \quad x_{\infty} &= \frac{X}{1 - u'_{\infty}} = \lambda_{\infty} X = \lambda_{\infty} [x - u^x(x)]. \end{aligned}$$

Hence the relative displacement is $u_{\text{rel}}^z(x) = u^z(x)$ and

$$\begin{aligned}
 u_{\text{rel}}^x(x) &= x - x_{\infty} = u^x(x) - u_{\infty}^x(x_{\infty}) \\
 &= u^x(x) - u_{\infty}' \lambda_{\infty} X \\
 &= u^x(x) - [\lambda_{\infty} - 1]X \\
 &= u^x(x) - [\lambda_{\infty} - 1][x - u^x(x)] \\
 &= \lambda_{\infty} u^x(x) - (\lambda_{\infty} - 1)x .
 \end{aligned}$$

Remember, that stretch and strain are related $\lambda - 1 = \varepsilon$.

B. METHODS

B.1. MESOSCOPIC CONTACT REGION MEASURES

As discussed in Sec. 3.3 and shown in Fig. 3.6 the three phase contact line, e.g., of a drop, becomes a continuous region in the mesoscopic picture. In consequence, the definition of an effective location for the macroscopic three phase contact line, e.g., to calculate the base radius of a drop, is rather diffuse too. There are multiple methods conceivable on how to quantify this position in the mesoscopic picture:

1. **Deflection point:** The certainly most frequently used method is to simply use the deflection point of the liquid-gas interface, i.e., the maximum of $|\nabla(h + \xi)|$. Since the curvature of the profile changes sign at the contact region the deflection point marks its inner boundary, i.e., the base radius of a drop is slightly underestimated with an error $\mathcal{O}(h_a)$. This method works well also in dynamic situation and independent of the softness regime.
2. **Analytic fit:** If a steady drop on a perfectly rigid or quasi-liquid substrate is considered, the shapes of the liquid-gas and solid-liquid interfaces, $h + \xi$ and ξ , are known to be spherical caps (in the full curvature formulation) or parabolas (in the long wave limit). The two interfaces can then be fitted by the respective functions and the intersection of both fits defines the contact line position. This method fails in situations where rapid dynamic are considered since the analytic shapes are valid for steady drops only. Further, this method requires knowledge of some characteristic quantities, like the curvature of the interfaces or base radius of. Note, that in the regime of intermediate elasticity an analytic expression for the substrate deformation is known only in the long-wave formulation.
3. **Wetting ridge tip:** A very solid way to determine the contact line position is by measuring the position of the wetting ridge tip, i.e. the local maximum of ξ . There are, however, situations conceivable where the position of the contact line does not coincide with a maximum in ξ , e.g., in the slip phase of a stick-

slip motion, or where the determination of a maximum of ξ becomes difficult, e.g., in the perfectly rigid or liquid limit.

4. **Tangent crossing:** Here a tangent is created to deflection points of $h + \xi$ and ξ inside the drop closest to the contact region. The intersection of these tangents defines the macroscopic contact line position. This method is quite reliable but slightly overestimates the base radius of a drop. This error increases with the curvature of the drop. It should be mentioned, that often only the liquid-gas interface tangent and its intersection with $z = 0$ is used. This procedure causes an even higher overestimation error $\sim \xi_{\max} / \tan(\theta_{\text{lg}})$, however, and should not be used off the rigid limit therefore.
5. **Pseudo Tangent:** Here a tangent is created to the deflection point of h (instead of $h + \xi$) and its intersection with $z = 0$ defines the contact line. This method usually provides values similar to method 4 but is computationally cheaper since only one tangent has to be calculated. Note, however, that in case of further deflection points in h close to the contact line, e.g., due to large deformations in the substrate close to the contact line as is the case in stick slip motion, a care has to be taken in the selection of the right one.
6. **Maximum curvature / minimum disjoining pressure:** The liquid-gas interface usually exhibits a very large positive curvature at the contact region where the transition from drop to adsorption layer takes place. The point of maximum curvature is thus well suited to define the position contact line. At equilibrium that exact same position corresponds to the minimum of the disjoining pressure $\Pi(h)$. The latter is known to exhibit a minimum at $\sqrt[3]{2}h_a$ and to quickly approach zero for values above. Since, this value is crossed only at a contact region, the minimum of $\Pi(h)$ gives almost the same results.

Except for case 2, where they can be calculated directly from the slope of the fit functions at their intersection point, the contact angles are usually defined by the slope at the three deflection points of $h + \xi$ (lg) and ξ , inside the wetted region (sl) and outside (sg) it. Further, it should be mentioned that if numerical data are considered the accuracy of the methods 1, 3 and 6 is limited by the spatial discretization. Hence, the measured position of the contact line changes stepwise which is an issue when it comes to numerical differentiation. This inconvenience can be avoided by fitting the profiles locally, meaning in immediate proximity of the selected point, and determining a new position from the fit. This is of course computationally more elaborate. In Fig. B.1 contact line positions determined by the different methods

are shown on the example of a spreading drop on a soft substrate in the long-wave limit.

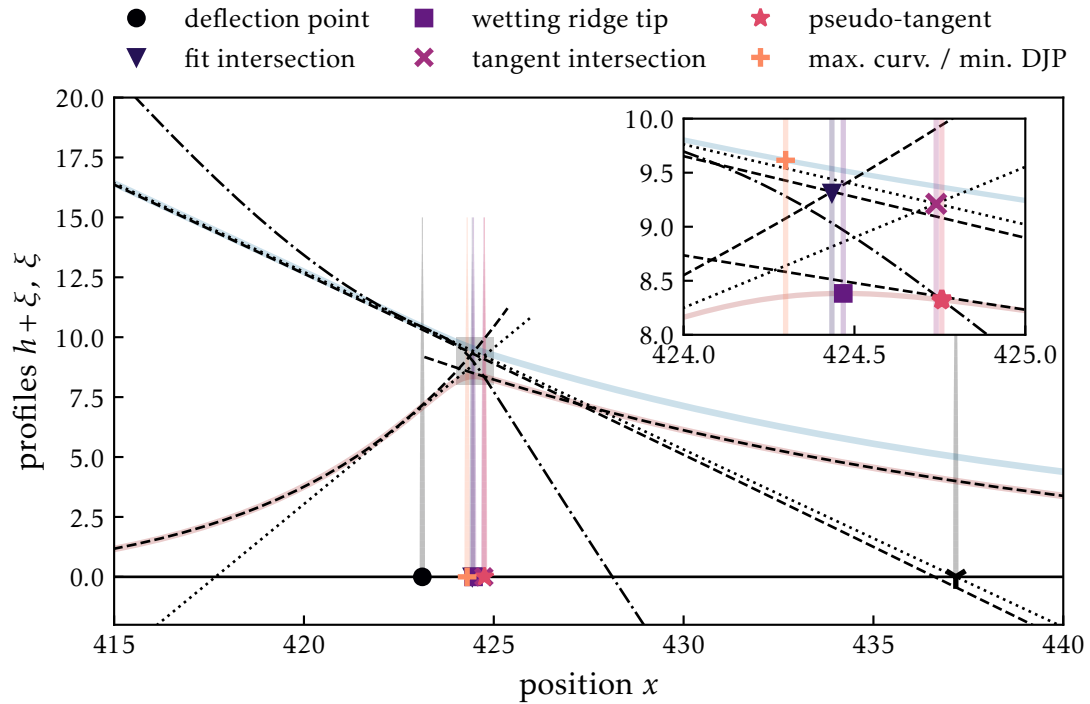


FIGURE B.1.: Visualization of different methods for the determination of the macroscopic contact line position in the mesoscopic picture on the example of a spreading drop on a soft substrate in the long-wave limit. The blue and red shaded regions represent the liquid and substrate, respectively. The delimiting solid lines are the solid-liquid and liquid-gas interface profiles, ξ and $h + \xi$. The symbols mark the x -values of the contact line positions determined by the different methods. The fit functions to the liquid-vapor and solid-liquid interfaces are shown as black dashed lines. The tangents to the inner deflection points are displayed as dotted lines and the pseudo-tangent as dashed-dotted line. The insert shows a zoom into the contact region and gives the x - z -positions obtained by the different methods. Obviously, the deflection point (●) and the tangent intersection with $z = 0$ (▼) are poorly suited to determine the contact line position, while all other methods provide very similar results.

B.2. FINITE ELEMENT METHOD

The finite element method (FEM) is a numerical discretization scheme that allows for easy treatment of low order spatial derivatives and is very useful e.g. for solving partial differential equations. This section is supposed to give a brief overview over the principal principles of FEM as used e.g. in the object-oriented open-source C++ library `oomph-lib` [HHo6b, HHo6a] or the MATLAB based continuation software `pde2path` [UWR14], both of which have been extensively used to produce the results

presented in this thesis. However, the FEM is a rather complex matter involving a variety of technical subtleties that are beyond the scope of this work and are therefore better read up in the more extensive literature e.g. Refs. [Bec+82, Hac86, EGo4, ZM13] on which the following section is based.

B.2.1. WEAK FORMULATION

Consider a problem of the form

$$\vec{D}(\vec{r}, \vec{u}(\vec{r})) = 0, \quad \vec{u}|_{\partial\Omega} = \vec{g}, \quad (\text{B.1})$$

with $\vec{u}(\vec{r}) : \Omega \rightarrow \mathbb{R}^n$ being an unknown function, that is desired to be found, defined on a connected and bounded subset $\Omega \subset \mathbb{R}^m$. The operator $\vec{D}$ is assumed to be of the same dimension as $\vec{u}$ and may contain partial differential operators $\frac{\partial^q}{\partial r_j^q}$ of any orders $q \in \mathbb{N}$. Hence, $n \in \mathbb{N} \setminus \emptyset$ defines both, the number of equations $\mathcal{D}_i$ and fields u_i and thereby it does not matter whether $n > m$ or vice versa. The principle of weak formulation claims that Eq. (B.1) is equally solved by extinguishing the *weighted residual*

$$\vec{\mathcal{R}}(\vec{u}) = \int_{\Omega} \vec{D}(\vec{r}, \vec{u}(\vec{r})) \phi(\vec{r}) \, d^m \vec{r} = 0, \quad (\text{B.2})$$

with $\phi(\vec{r})$ being any *test function* that satisfies the homogeneous boundary condition $\phi|_{\partial\Omega} = 0$. For this integral to exist the functions $\vec{u}$ and ϕ have to meet certain requirements, namely they have to be square integrable and $\vec{u}$ has to be at least $q_{\max}$ -times weakly differentiable. Since ϕ is not affected by any derivatives there is no requirement for its differentiability. The differentiability requirement (d.r.) of $\vec{u}$, however, is quite restrictive and can indeed be loosened a bit by using partial integration. Lets for example consider the homogeneous Laplace equation in two dimensions and with u being a scalar function $\mathcal{D}(x, y, u(x, y)) = \Delta u$, then the weighted residual can be written like

$$\mathcal{R}(u) = \int_{\Omega} (\Delta u) \phi \, dx dy = \underbrace{\int_{\partial\Omega} (\nabla u \cdot \vec{n}) \phi \, ds}_{=0} - \int_{\Omega} \nabla u \cdot \nabla \phi \, dx dy,$$

with the surface term vanishing due to the homogeneous boundary conditions $\phi|_{\partial\Omega} = 0$. That way a derivative acting on $\vec{u}$ can be easily diverted to act on ϕ instead, effectively reducing the d.r. of u by one but increasing the d.r. of the test function

to $k(\phi) \geq 1$. In principle, even further partial integrations can be carried out to distribute derivatives between $\vec{u}$ and ϕ , effectively relaxing the d.r. to $k(\vec{u}) + k(\phi) \geq q_{\max}$. It should be kept in mind, however, that the surface terms do not necessarily vanish in that case since no prerequisites were set for the derivatives of $\vec{u}$ and ϕ at the boundaries. An other way to reduce the d.r. of both, $\vec{u}$ and ϕ is by introducing auxiliary fields. Consider for example the simple problem

$$\mathcal{R}(u) = \int_{\Omega} \left(\partial_x^4 u(x) \right) \phi(x) dx = 0,$$

i.e. $m = n = 1$ and $q_{\max} = 4$. Introducing an auxiliary field $v(x) = \partial_x^2 u$, and thus the additional equation $\mathcal{D}_2 = \partial_x^2 u - v = 0$, we get

$$\begin{aligned} \mathcal{R}_1(u, v) &= - \int_{\Omega} (\partial_x v) (\partial_x \phi) dx = 0, \\ \mathcal{R}_2(u, v) &= \int_{\Omega} v \phi dx - \int_{\Omega} (\partial_x u) (\partial_x \phi) dx = 0, \end{aligned}$$

where partial integration has been carried out already. Now, the d.r. of u , v and ϕ is reduced to $k \geq 1$ in exchange for an increased number of equations that have to be solved. In many cases of FEM applications, and so in this thesis, this trade is readily made.

B.2.2. GALERKIN METHOD

The distinction of requirements placed on $\vec{u}$ and ϕ regarding e.g. their differentiability is quite inconvenient. It therefore seems reasonable to expand both of them in the same complete basis $\{\psi_i(\vec{r})\}$

$$\vec{u}(\vec{r}) = \sum_{i=0}^{\infty} \vec{U}_i \psi_i(\vec{r}) \quad \text{and} \quad \phi(\vec{r}) = \sum_{i=0}^{\infty} \Phi_i \psi_i(\vec{r}), \quad (\text{B.3})$$

effectively discretizing the problem in terms of the discrete coefficients $\vec{U}_i$ and Φ_i . Now, the requirements on differentiability and normalizability are placed on the basis functions. Formally speaking, they have to be elements of a *Sobolev space* $\mathcal{S}_0^{k,p}$, i.e. k -times weakly differentiable while maintaining the L^p -norms, where $p \geq 2$ and k depends on the formulation of the problem. The subscript in $\mathcal{S}_0$ implies that homogeneous boundary conditions are satisfied by its member functions and while this is absolutely desirable as far as ϕ is concerned, we might want to impose different boundary conditions for the field $\vec{u}$. As mentioned above Neumann boundaries of

the shape $\frac{\partial u_i}{\partial r_j} \big|_{\partial\Omega} = c$ can be imposed by evaluating the surface integrals, emerging during the partial integration, accordingly. To also realize Diriclet boundaries of the form $\vec{u} \big|_{\partial\Omega} = g$, or to enable the solution to assume values $\vec{u} \big|_{\partial\Omega} \neq 0$ in the first place, a partial function $\vec{u}_p$ can be added which takes the desired value at the boundary but vanishes everywhere else in the domain

$$\vec{u}(\vec{r}) = \vec{u}_p + \sum_{i=0}^{\infty} \vec{U}_i \psi_i(\vec{r}). \quad (\text{B.4})$$

Inserting the expansions into the weighted residual yields

$$\vec{\mathcal{R}}(\vec{u}) = \sum_{j=0}^{\infty} \Phi_j \underbrace{\int_{\Omega} \vec{\mathcal{D}} \left(\vec{r}, \vec{u}_p + \sum_{i=0}^{\infty} \vec{U}_i \psi_i(\vec{r}) \right) \psi_j(\vec{r}) \, d^m \vec{r}}_{\vec{\mathcal{R}}_j(\vec{u})} = 0. \quad (\text{B.5})$$

Since the solution must hold for any test function ϕ the value of the coefficients Φ_i are irrelevant and only $\vec{\mathcal{R}}_j(\vec{u}) = 0$ must be satisfied for all j . Further, the differential operators in $\vec{\mathcal{D}}$ acting on $\vec{u}(\vec{r})$, or after partial integration on $\phi(\vec{r})$, ultimately only affect the base functions $\psi_i(\vec{r})$. If the latter are wisely chosen, their derivatives are well known and at best also simple, such that the integral in $\vec{\mathcal{R}}_j(\vec{u})$ can be analytically calculated. The problem then reduces to a system of algebraic equations for the coefficients $\vec{U}_i$.

B.2.3. DISCRETIZATION AND SHAPE FUNCTIONS

The system of algebraic equations for the coefficients $\vec{U}_i$ is supposed to be solved numerically, which constitutes a significant restriction, namely the computation power of the used machine. This includes not only the limited amounts of data that can be processed but also the time period required to do so. Since solving infinitely many equations may take a moment and every minute of life time spend waiting for results is perceived as unbearable agony, one is usually content with a finite number of equations, trading quality of the solution for quality of life. In practice this is realized by canceling the series expansion (B.3) after a finite number M of terms, thus giving only an approximate representations of $\vec{u}$ and ϕ . Under all the assumptions made, there is still a whole range of function spaces that could serve as a basis $\{\psi_i(\vec{r})\}$, depending on the problem some are better suited then others, however. A very prominent example is the *Fourier expansion* where periodic functions like complex exponentials $\psi_i(\vec{r}) = \exp(i\vec{k}_i \cdot \vec{r})$ are used as basis functions and the coefficients

indicate how prominent a frequency $\vec{k}_i$ is represented in the solution. The extent M of the expansion thereby defines the number of frequencies that are used for the approximation. While the Fourier expansion is a formidable choice when it comes to the treatment of periodic problems, it suffers from Gibbs artifacts and aliasing effects when ever problems with strong scale separations are considered, i.e., strongly localized structures in an otherwise (in)homogeneous region or extreme gradients in general. In such cases it is convenient to directly discretize the domain Ω instead of the corresponding Fourier space. In FEM this is realized by dividing the domain Ω into multiple little segments, the name giving *elements* e , building a partition $P(\Omega)$, i.e., $\bigcup_{e \in P} e = \Omega$. Because of all the element edges that run through the domain like filaments, the partition is also commonly referred to as *mesh*. Even though the element shapes are arbitrary in principle, each must yet be definable by the same (finite) number of points $\vec{n} \in \Omega$, the so called *nodes*, usually describing the boundaries and/or corners. It is therefore recommended to keep it simple, e.g., by using triangles or rectangles or the like (in 2D). It is these nodes where the coefficients $\vec{U}_i = \vec{u}(\vec{n}_i)$ will be evaluated, i.e., $\vec{u}$ is sampled. Note, that the partition $P(\Omega)$ is not strictly disjunct in a sense that neighboring elements share a common border and the nodes that are part of it. More precisely, two elements $a, b \in P$ with $a \neq b$ are neighbors if their union $a \cup b$ forms a connected space and for such a pair $a \cap b = \partial a \cap \partial b \neq \emptyset$. One major advantage of this approach is that the resolution of the mesh can be flexibly adjusted locally where ever required, which is known as *adaptive mesh refinement*. Whether that is necessary is decided based on a local error which in `oomph-lib` is determined using a Z_2 error estimation [ZZ92a, ZZ92b]. If the local error exceeds a preset target error the resolution of the mesh is locally increased by splitting an element into multiple new ones, i.e., by adding further nodes. The key feature of FEM is the element-wise treatment of the problem, i.e., the element-wise evaluation of the integral in Eq. (B.5). For that to be accomplished piece-wise defined base functions of finite support are employed, such that the interpolation condition $\psi_i(\vec{n}_j) = \delta_{ij}$ is satisfied. In other words, every base function takes non-zero values only in the vicinity of the node it is assigned to and vanishes at every other. And still there are many conceivable options for such a basis to pick from, but the most common means of choice are polynomials. Thereby the order of the polynomial determines the quality of the interpolation, the differentiability and the number of nodes required per element. The decision on which order to choose should be made with regard to the requirements of the problem, e.g., the highest order derivative in $\vec{D}$. Note, that the finite support of the base functions usually exceeds the range of one element and that different base functions, even though

piece-wise defined, overlap with each other for their superposition to reconstruct the solution $\vec{u}$. Depending on the author the phrasing *element* in FEM may also refer to these finite support base functions ψ_i or their areas of definition or both. In Fig. B.2 a linear piece-wise base function, also referred to as *hat function*, ψ_i is shown in a two dimensional domain discretized with triangular elements, defined by three nodes each. In consequence, the summation in Eq. (B.5) is performed only over all those base functions, or their derivatives, that are supported by the respective element. Hence, the larger the spatial support of the base functions (in number of elements) the more base functions are supported by an element and the more terms have to be considered in the sum. The integration results can in principle be organized in a tensor K_{ij} acting on the coefficients $\vec{U}_i$ and which becomes sparser with increasing confinement of the base function support. Once evaluated this matrix has to be calculated anew only if the mesh has changed. As this happens quite often when adaptive mesh refinement routines are utilized, it is sometimes more efficient to keep looping over the elements instead. In practice the integration is performed only once on a normalized reference element. Since the actual elements are by no means always congruent with such a reference element or even of equal size for that matter, a transformation is required to map them. To evaluate the integral over the original element the normalized value is simply scaled by the Jacobian determinant of the transformation. In some problems it may occur that the boundaries of a variable and/or the conditions for $\vec{u}$ at this boundaries are not entirely known. This is usually the case if initial value problems of the form

$$\partial_t \vec{u} = \mathcal{D}(\vec{r}, t, \vec{u}(\vec{r}, t)) \quad (\text{B.6})$$

are considered. Instead of adding such a variable, lets call it t , as an other dimension to the grid and evaluating the derivative $\partial_t \vec{u}(t)$ from the base functions $\psi_i(t)$ the dependency remains in the coefficients $\vec{U}_i(t)$. Assuming the coefficients to be known at a certain value t_n a numerical integration scheme can be employed to numerically estimate the derivative $\partial_t \vec{U}_i(t_{n+1})$ at an other value $t_{n+1} = t_n + \Delta t_{n+1}$. The variable t is thus discretized by the finite step size Δt_n . In `oomph-lib` the implicit second order *Backward Differentiation Formula* (BDF2) [Foro1, CAC14] is used

$$\partial_t \vec{U}_i(t_{n+1}) = \frac{(1 + 2a_n)\vec{U}_i(t_{n+1}) - (1 + a_n)^2\vec{U}_i(t_n) + a_n^2\vec{U}_i(t_{n-1})}{(1 + a_n)\Delta t_{n+1}}, \quad (\text{B.7})$$

with $a_n = \Delta t_{n+1}/\Delta t_n$ and a potentially non uniform time discretization $\Delta t_{n+1} \neq \Delta t_n$. In fact Δt_n is adapted after every step such that a predetermined target error is

not exceeded analogously to the mesh refinement routine. This error is commonly calculated by comparing the estimated value with the one obtained by an other reference method, e.g., in `oomph-lib` the trapezoidal rule. Note, that the resolutions in such a variable t and the resolution of the mesh, i.e., the density of nodes $\vec{n}$, can not be arbitrarily chosen but are intrinsically coupled by the *Courant-Friedrichs-Lewy condition* [CFL67] $V\Delta t \leq \Delta\vec{n}$. It states, that the change V in $\vec{r}$ of a quantity during the change Δt must not exceed the minimum distance $\Delta\vec{n}$ of nodes in the mesh for numerical stability to be maintained. Obviously, the BDF2 requires knowledge about the previous solutions at times t_{n-1} and t_{n-2} to calculate the derivative at present time $\partial_t \vec{U}_i(t_n)$. Therefore, the numerics have to be given an initial guess for $\vec{u}$ to start from. Once the derivatives in t are calculated the system of algebraic equations can be solved for the coefficients $\vec{U}_i$ using the a *Newton-Raphson method* [Deu05], effectively searching for the zeros of the residual. In Fig. B.3 an exemplary reconstruction of a hypothetical function $u(x, y, t)$ as a superposition of piece-wise linear base functions on a two dimensional domain with triangular elements is shown.

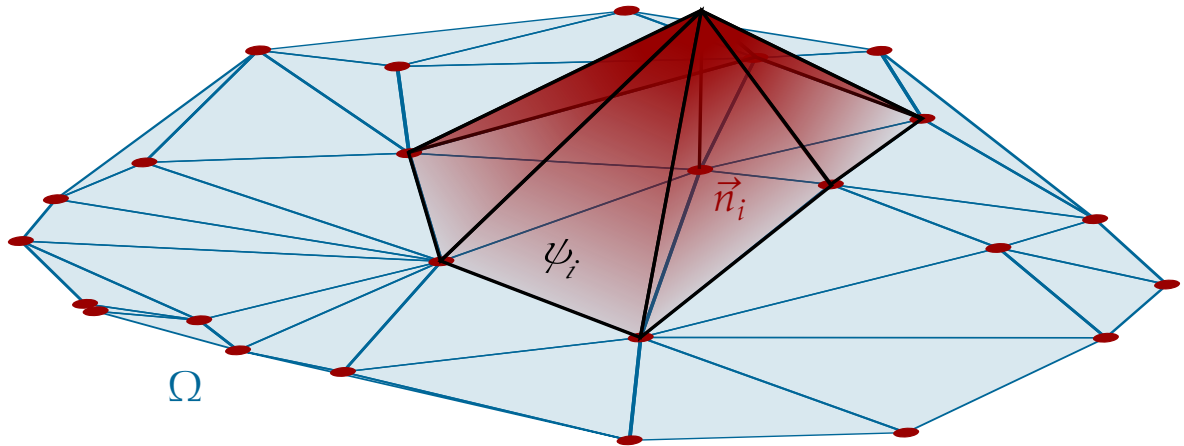


FIGURE B.2.: Visualization of the global piece-wise linear base function $\psi_i(\vec{r})$ (red shaded) corresponding to the node $\vec{r}_i$ (red dot) in domain Ω (blue shaded) with triangular discretization. Depending on the author the phrase *elements* may refer to either these piece-wise shape functions and their associated domains, or to the segments (here triangles) the domain is split up to, or both.

B.2.4. APPLICATION TO THE THIN-FILM EQUATION

In many cases Ω represents a spatial domain such that the nodes are coordinates in space and $\dim(\Omega) \leq 3$. The models considered in this work usually describe the vertical extension of a structure, e.g., a liquid drop, on a two dimensional domain. Furthermore, these structures are often assumed to be homogeneous in one direction reducing the spatial dimension of Ω to one. For the matter of this work we

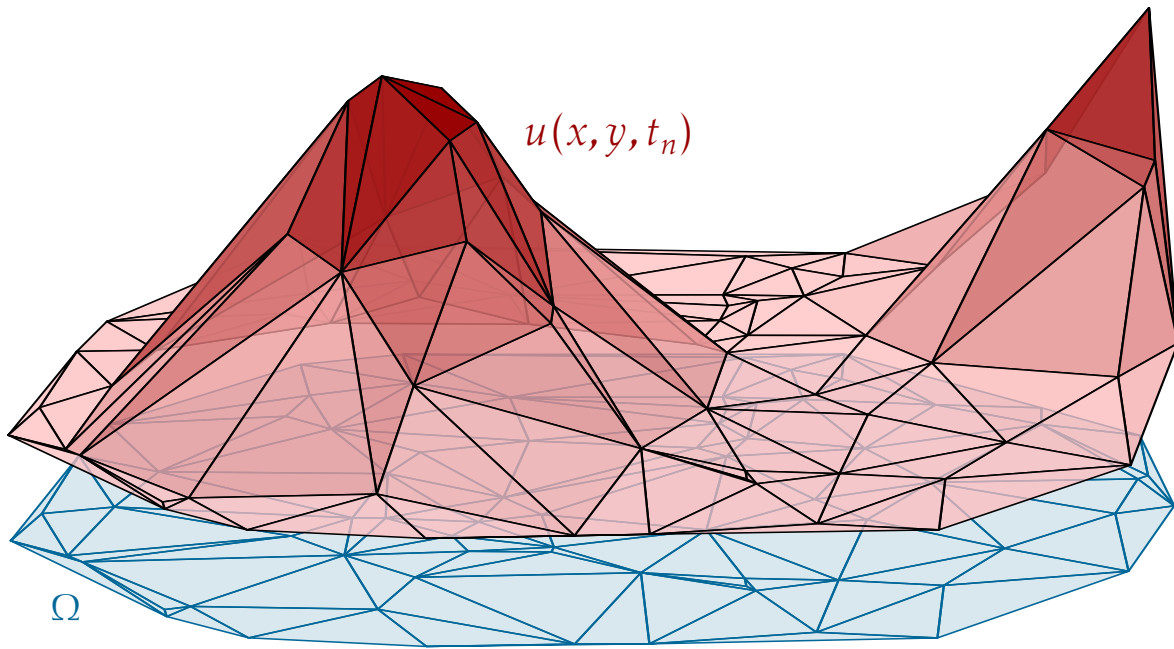


FIGURE B.3.: Exemplary reconstruction of a solution u at time t_n as a superposition of piece-wise linear base functions (red surface) on a two dimensional domain Ω of triangular elements (blue surface). Even though u is assumed to be a smooth function the structures look quite edgy, indicating that a mesh refinement is required.

settle with the already mentioned hat functions as finitely supported base functions. These are of differentiability $k = 1$ and consequently the equations have to be prepared in a way that only first order derivatives appear, by using partial integration and auxiliary fields. On the example of the thin-film equation this can be done by introducing the pressure p as an auxiliary field

$$\partial_t h = \nabla \cdot \left[\frac{h^3}{3\eta} \nabla p \right] \quad \text{and} \quad p = -\gamma_{lv} \Delta h - \Pi(h).$$

As this equation describes the dynamics of h starting from some arbitrary profile, we got an initial value problem in the time variable t . After using partial integration the weak formulation reads

$$\begin{aligned} \int_{\partial\Omega} \frac{h^3}{3\eta} (\nabla p \cdot \vec{n}) \phi \, ds - \int_{\Omega} \left[\frac{h^3}{3\eta} \nabla p \cdot \nabla \phi - \partial_t h \phi \right] d^2 \vec{r} &= 0, \\ \int_{\partial\Omega} \gamma_{lv} (\nabla h \cdot \vec{n}) \phi \, ds - \int_{\Omega} [\gamma_{lv} \nabla h \cdot \nabla \phi + (\Pi + p) \phi] d^2 \vec{r} &= 0, \end{aligned}$$

with only first order partial derivatives. Expanding in the basis $\{\psi_i\}$ the residuals write

$$\begin{aligned}\mathcal{R}_j^1 &= \frac{h^3}{3\eta} \sum_i p_i \underbrace{\int_{\partial\Omega} (\nabla\psi_i \cdot \vec{n}) \psi_j \, ds}_{K_{ij}^1} - \frac{h^3}{3\eta} \sum_i p_i \underbrace{\int_{\Omega} (\nabla\psi_i \cdot \nabla\psi_j) \, d^2\vec{r}}_{K_{ij}^2} + \sum_i \partial_t h_i(t) \underbrace{\int_{\Omega} \psi_i \psi_j \, d^2\vec{r}}_{K_{ij}^3} = 0, \\ \mathcal{R}_j^2 &= \gamma_{lv} \sum_i h_i \underbrace{\int_{\partial\Omega} (\nabla\psi_i \cdot \vec{n}) \psi_j \, ds}_{K_{ij}^1} - \gamma_{lv} \sum_i h_i \underbrace{\int_{\Omega} (\nabla\psi_i \cdot \nabla\psi_j) \, d^2\vec{r}}_{K_{ij}^2} - \sum_i (\Pi(h_i) + p_i) \underbrace{\int_{\Omega} \psi_i \psi_j \, d^2\vec{r}}_{K_{ij}^3} = 0.\end{aligned}$$

The integrals can now be calculated in an element-wise fashion, i.e. for each j , and eventually sorted in tensors K^i . The resulting system of algebraic equations can then be solved for the coefficients $\vec{U}_i = (h_i, p_i)^\top$ using the iterative Newton-Raphson method.

B.3. NEWTON-RAPHSON METHOD

The *Newton-Raphson method* is one of the most common (if not the one) algorithms for the determination of roots $\vec{u}_r$ of a given function $\vec{\mathcal{R}}(\vec{u})$ and was first invented by Isaac Newton (1669) and Joseph Raphson (1690) [Kelo3, SMO3, Pano6]. It is based upon the linear extrapolation of the tangent to $\vec{\mathcal{R}}$ at an initial guess $\vec{u}_0$. Using a Taylor expansion the problem can be linearized

$$\vec{\mathcal{R}}(\hat{\vec{u}}_r) \approx \vec{\mathcal{R}}(\vec{u}_0) + \underline{\mathcal{J}}(\vec{u}_0)(\hat{\vec{u}}_r - \vec{u}_0) = 0, \quad (\text{B.8})$$

and inverted to solve for the approximate root

$$\hat{\vec{u}}_r = \vec{u}_0 - \underline{\mathcal{J}}^{-1}(\vec{u}_0)\vec{\mathcal{R}}(\vec{u}_0). \quad (\text{B.9})$$

where $\mathcal{J}_{ij}(\vec{u}_0) = \frac{\partial \mathcal{R}_i}{\partial u_j} \Big|_{\vec{u}_0}$ is the Jacobian matrix evaluated at $\vec{u}_0$. Even though the solution $\hat{\vec{u}}_r$ is only the root of the tangent to $\vec{\mathcal{R}}$ at $\vec{u}_0$, it is still assumed to be much closer to the real root $\vec{u}_r$ than the initial guess $\vec{u}_0$ itself. Using $\hat{\vec{u}}_r$ as new initial guess and repeating the process should therefore yield an even better approximation. After multiple iterations the approximated root $\hat{\vec{u}}_r$ eventually satisfies $\max[\vec{\mathcal{R}}(\hat{\vec{u}}_r)] < \epsilon$, with ϵ being a predefined target error that has to be undercut. Even though the Jacobian can be analytically calculated and doing so would improve accuracy and spare computation time, it is often evaluated numerically, e.g., by a *lower-upper* (LU) *decomposition* as used in `oomph-lib` [Pano6, Wen17].

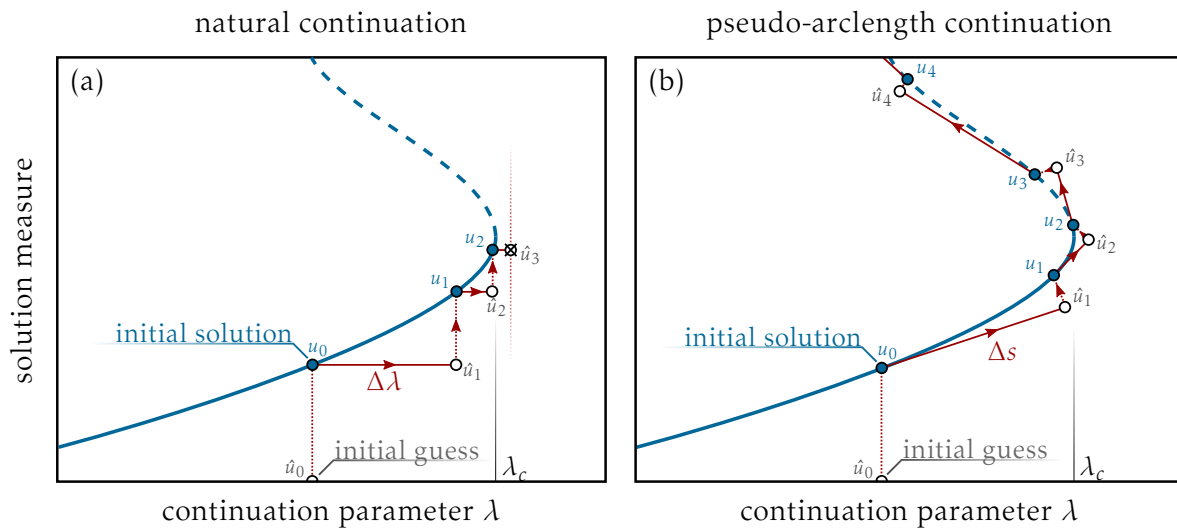


FIGURE B.4.: Schematic visualization of continuation routines. Starting from an initial guess $\hat{u}_0$ the initial solution u_0 is found using a Newton-Raphson method. The natural continuation (a) performs discrete steps $\Delta\lambda$ in the continuation parameter and calculates the next solution u_{n+1} using the previous one as initial guess $\hat{u}_{n+1} = u_n$. If a solution branch folds at a critical value λ_c the natural continuation routine fails to follow it. The pseudo-arclength continuation (b) predicts a guess for the next solution in tangential direction Δs (red solid line) and corrects it then (red dotted line). Since the corrector searches for a solution orthogonal to the tangent, also very steep or even folding branches can be followed.

B.4. PARAMETER CONTINUATION

In Sec. B.2 the procedure for solving partial differential equations using finite element methods has been discussed. It was mentioned, that a BDF2 scheme is employed for the treatment of initial value problems, e.g., the temporal integration of the dynamical equations for a field $\vec{u}(\vec{r}, t)$. In case of passive and dissipative thermodynamic systems, however, the dynamics usually terminate in a stable steady state associated with the minimum of a governing potential. Often it is just these steady states that are desired to be known, while the temporal evolution leading there might be of minor interest only. Furthermore, many systems depend on a set $\vec{\lambda}$ of independent parameters the values of which may dramatically influence the systems behavior. A previously stable state, for example, might suddenly become unstable or cease to exist upon even small changes $\Delta\vec{\lambda}$. Such sudden changes in a systems qualitative behavior in consequence of crossing a critical value $\vec{\lambda}_c$ are known as *bifurcations*. It is easily imagined, how the knowledge about those bifurcations is of crucial importance in many areas, e.g., when ever the stability of a state is to be guaranteed even under fluctuations in $\vec{\lambda}$. The naive numerical approach to such a problem would be to solve the dynamics for several values of $\vec{\lambda}$ in a given interval of interest and to evaluate the long-term behavior, effectively sampling the

solution branch in parameter space. Of course this approach is quite laborious and time intensive and fortunately there is a smarter way. Imagine a decent initial guess could be made directly for the stable steady state that might be reached at the end of a time simulation. In that case it was way more convenient to directly solve the static equations

$$\partial_t \vec{u} = \mathcal{D}(\vec{r}, \vec{\lambda}, \vec{u}(\vec{r}, t)) = 0, \quad (\text{B.10})$$

instead. Such an initial guess may not be available for arbitrary parameters though. Assuming the solution branch to be smooth, however, a single initial guess, for $\vec{\lambda}_0$ lets say, is all it takes. As discussed above the time stepping scheme is based on the estimation of the next solution, i.e., at a future time, from the current one using a BDF2 method. If the guess is close enough to the real solution the latter can be found using the Newton-Raphson routine. This way the dynamics is followed in time t in small steps. The same principle can be applied to changes in $\vec{\lambda}$ instead of t . Provided the changes $\Delta \vec{\lambda}$ are sufficiently small, a solution $\vec{u}_n$ at $\vec{\lambda}_n$ is assumed to serve as suitable initial condition for the static problem at $\vec{\lambda}_{n+1} = \vec{\lambda}_n + \Delta \vec{\lambda}_{n+1}$ to find $\vec{u}_{n+1}$. This way a solution branch can be followed through parameter space using a two step routine: 1) predicting the next solution, i.e., changing $\vec{\lambda}$ while keeping the solution $\vec{u}$ fixed, 2) correct the solution using the Newton-Raphson method. This procedure is known as *natural parameter continuation* and not only is it way more efficient, it also allows for the reconstruction of unstable steady solution branches once such a solution is found. While an initial solution of a stable steady state branch is easily obtained by solving the dynamics, an unstable state to start of is rather intricate to find. If the problem is linear an analytic solution can be sought, which is rarely possible in case in non-linear systems though. If the dynamics can not be solved for any reason or the solution it leads to is not the one desired the *homotopy method* can be used. In this method the equation is first linearized by multiplying the non-linear terms with a fake parameter ϵ which is initially set to zero. The linear equation can then be solved analytically and a continuation can be performed in ϵ until $\epsilon = 1$ is reached. Aside of that, unstable solutions may eventually be found via bifurcations from a stable one if only the right path in parameter space is followed. A very common example is the so called *fold* or *saddle node bifurcation*, where an initially stable solution branch becomes unstable at a critical value $\vec{\lambda}_c$ and turns around. Or to put it another way, a stable and an unstable steady solution branch meet at $\vec{\lambda}_c$ and annihilate. In Fig. B.4 an exemplary solution branch is shown for such a scenario in terms of a characteristic scalar solution measure as

a function of a single *continuation parameter* λ . A commonly used solution measure to characterize spatially extended fields is the L^2 -norm

$$L^2(\vec{u}) = \sqrt{\langle \vec{u} | \vec{u} \rangle} = \sqrt{\frac{1}{V} \int_{\Omega} \vec{u}(\vec{r}) \cdot \vec{u}(\vec{r}) \, d^m \vec{r}}, \quad (\text{B.11})$$

with $V = \int_{\Omega} d^m \vec{r}$ being the volume of Ω , though various other integral measures are conceivable. The example of the saddle node bifurcation furthermore demonstrates the limits of the natural parameter continuation routine, namely the inability to follow such a branch along the fold since very close to it the next continuation step would shoot beyond the critical point $\lambda > \lambda_c$ where no steady solution exists anymore (see Fig. B.4(a)). For that very reason the *pseudo-arclength continuation* method has been developed, the principle of which is roughly described in the following, following the Refs. [Kel79, TVNo1, KOG07, Eng+19]. As the name suggests, this method intends to follow the solution branch not in an orthogonal manner, i.e., by changing $\vec{\lambda}$ at fixed $\vec{u}$ and then correct $\vec{u}$ at fixed $\vec{\lambda}$, but along its arclength $s \in \mathbb{R}$. Instead of seeking for a solution $\vec{u}(\vec{\lambda})$ both the solution as well as the continuation parameters are parameterized by the arclength and the branch is defined by $s \rightarrow \vec{v}(s) := (\vec{u}(s), \vec{\lambda}(s))$, where now $\vec{\lambda}$ is treated as an additional vector of unknown variables. In practice, the arc is approximated by performing small discrete steps $\Delta s_n = s_n - s_{n-1}$ along the tangent $\vec{\tau}_n = \left. \frac{d\vec{v}}{ds} \right|_{s_n}$ to the solution branch. In order to approximate the arclength the normalization

$$\mathcal{N}(\vec{u}_{n+1}, \lambda_{n+1}, s_{n+1}) = \chi \left\langle \frac{\partial \vec{u}_n}{\partial s}, \Delta \vec{u}_{n+1} \right\rangle + (1 - \chi) \left\langle \frac{\partial \vec{\lambda}_n}{\partial s}, \Delta \vec{\lambda}_{n+1} \right\rangle - \Delta s_{n+1} = 0, \quad (\text{B.12})$$

is introduced, with $\langle \cdot, \cdot \rangle$ denoting the inner product and the factor $0 \leq \chi \leq 1$ weighting how the distances $\Delta \vec{u}_{n+1} = \vec{u}_{n+1} - \vec{u}_n$ and $\Delta \vec{\lambda}_{n+1} = \vec{\lambda}_{n+1} - \vec{\lambda}_n$ respectively contribute to the (pseudo-)arclength $\Delta s_{n+1} = s_{n+1} - s_n$. A common choice is $\chi = \dim(\vec{\lambda}) / \dim(\vec{u})$, i.e., weighting $\vec{u}$ and $\vec{\lambda}$ equally. Here $\vec{u}_n = \vec{u}(s_n)$ and $\vec{\lambda}_n = \vec{\lambda}(s_n)$. The problem is then given by

$$\vec{\mathcal{P}}(\vec{v}, \lambda, s) = \begin{pmatrix} \vec{\mathcal{D}}(\vec{u}, \lambda) \\ \mathcal{N}(\vec{u}, \lambda, s) \end{pmatrix}, \quad \vec{v}(s) = \begin{pmatrix} \vec{u}(s) \\ \lambda(s) \end{pmatrix}. \quad (\text{B.13})$$

with the Jacobian $\mathcal{J}_{ij} = \frac{\partial \mathcal{P}_i}{\partial v_j}$ taking the form

$$\underline{\mathcal{J}}(s) = \begin{pmatrix} \underline{\mathcal{D}}_u(s) & \partial_\lambda \vec{\mathcal{D}}(s) \\ \vec{\mathcal{N}}_u^\top(s) & \partial_\lambda \mathcal{N}(s) \end{pmatrix} \quad \text{with} \quad (\underline{\mathcal{D}}_u)_{ij} = \frac{\partial \mathcal{D}_i}{\partial u_j} \quad \text{and} \quad (\vec{\mathcal{N}}_u)_i = \frac{\partial \mathcal{N}}{\partial u_i}. \quad (\text{B.14})$$

It can be used to find the tangent vector by solving

$$\frac{d\vec{\mathcal{P}}}{ds} = \sum_i \frac{\partial \vec{\mathcal{P}}}{\partial v_i} \frac{\partial v_i}{\partial s} + \frac{\partial \vec{\mathcal{P}}}{\partial s} = 0 \quad \rightarrow \quad \vec{\tau} = -\underline{\mathcal{J}}^{-1} \frac{\partial \vec{\mathcal{P}}}{\partial s}, \quad (\text{B.15})$$

or when expanded

$$\underline{\mathcal{D}}_u \frac{\partial \vec{u}}{\partial s} + \frac{\partial \vec{\mathcal{D}}}{\partial \lambda} \frac{\partial \lambda}{\partial s} = 0 \quad (\text{B.16})$$

$$\vec{\mathcal{N}}_u \cdot \frac{\partial \vec{u}}{\partial s} + \frac{\partial \mathcal{N}}{\partial \lambda} \frac{\partial \lambda}{\partial s} = -\frac{\partial \mathcal{N}}{\partial s}. \quad (\text{B.17})$$

The tangent is normalized in the *weighted inner product*

$$\langle \vec{v}_1, \vec{v}_2 \rangle_\chi = \chi \langle \vec{u}_1, \vec{u}_2 \rangle + (1 - \chi) \langle \vec{\lambda}_1, \vec{\lambda}_2 \rangle. \quad (\text{B.18})$$

A prediction for the next solution can then be found by moving a distance Δs along the tangent

$$\hat{\vec{v}}_{n+1} = \begin{pmatrix} \hat{\vec{u}}_{n+1} \\ \hat{\vec{\lambda}}_{n+1} \end{pmatrix} = \begin{pmatrix} \vec{u}_n \\ \vec{\lambda}_n \end{pmatrix} + \begin{pmatrix} \frac{\partial \vec{u}_n}{\partial s} \Delta s_{n+1} \\ \frac{\partial \vec{\lambda}_n}{\partial s} \Delta s_{n+1} \end{pmatrix} = \vec{v}_n + \Delta s_{n+1} \vec{\tau}_n, \quad (\text{B.19})$$

and the solution branch then be approached by solving

$$\vec{v}_{n+1} = \hat{\vec{v}}_{n+1} - \underline{\mathcal{J}}^{-1}(\hat{\vec{v}}_{n+1}) \mathcal{P}(\hat{\vec{v}}_{n+1}) \quad (\text{B.20})$$

using a Newton-Raphson method. The advantage of the pseudo-arclength method is that solutions are searched for only in the complement of the tangent space associated with $\vec{\tau}$. More precisely within the hyperplane defined by $\mathcal{N} = 0$ which is perpendicular to $\vec{\tau}$ in the weighted inner product. That way even folds can be followed as shown in Fig. B.4(b). Note, that the real part of the eigenvalues of the Jacobian determine the linear stability of a solution and can be tracked to check if the stability changes, i.e., to detect bifurcations. Just as was done with the continuation parameter λ further equations may be added to the system, e.g., to ensure

specific secondary condition like conservation laws or the like. Though, every additional equation also requires an additional degree of freedom that can be solved for, a so called *Lagrange multiplier*. That way also bifurcation points can be followed through parameter space which requires multiple parameters to be set free, i.e., a multiple parameter continuation, which is quite useful to draw the borders at which stabilities change. For a deeper insight into the functionality of continuation techniques consult Refs. [Kel79, KOG07, Dij+14, Eng+19, Jer+11, SD12, Mar+12a, Lim12, Thi21] or the manuals of the two continuation softwares `pde2path` [UWR14] and `auto-07p` [DKK91], both of which have been used to produce the results of this work.

B.5. LINEAR STABILITY ANALYSIS

In the investigation of many systems continuation techniques such as described in App. B.4 represent a powerful tool to provide extensive information about the steady states that exist in a given section of parameter space. For a proper interpretation of the resulting bifurcation diagrams usually also the stability of the respective solution branches is required. Consider an equation of the form

$$\partial_t \vec{\psi} = \vec{D}(\vec{r}, \vec{c}, \vec{\psi}(\vec{r}, t)), \quad (\text{B.21})$$

with $\vec{D}$ being some kind of differential operator including spatial derivatives of arbitrary order and $\vec{c}$ being a set of parameters. Assume that a steady solution $\vec{\psi}_0$ of this equation is known for a fixed set of parameters $\vec{c}_0$ such that $\partial_t \vec{\psi}_0 = \vec{D}(\vec{c}_0, \vec{\psi}_0) = 0$. Such a solution can then be investigated regarding its stability by imposing an infinitesimal perturbation $\vec{\psi}_p(\vec{r}, t)$ to the known solution and solve the dynamics to observe whether it grows in time, then the steady state is unstable, or decays back to the initial solution, in which it is considered stable. Solving the dynamics is not a matter of ease of course, since the governing equations, that is the differential operator $\vec{D}$, may be highly nonlinear. As indicated by the naming, the idea of linear stability analysis is to linearize the dynamics such that they can, in principle, be solved analytically if an analytic expression of $\vec{\psi}_0$ is known. To do so, the perturbed solution $\vec{\psi} = \vec{\psi}_0 + \epsilon \vec{\psi}_p(\vec{r}, t)$ is introduced into the equations (B.21) and the latter are then expanded in a Taylor series about $\epsilon \approx 0$

$$\partial_t \vec{\psi} = \partial_t (\vec{\psi}_0 + \epsilon \vec{\psi}_p) = \vec{D}(\vec{r}, \vec{c}_0, \vec{\psi}_0 + \epsilon \vec{\psi}_p(\vec{r}, t)) \approx \vec{D}(\vec{r}, \vec{c}_0, \vec{\psi}_0) + \epsilon \underline{\mathcal{J}}(\vec{r}, \vec{c}_0, \vec{\psi}_0) \cdot \vec{\psi}_p + \mathcal{O}(\epsilon^2),$$

which, since $\vec{\psi}_0$ is a steady state and satisfies $\partial_t \vec{\psi}_0 = \vec{\mathcal{D}}(\vec{\psi}_0) = 0$, yields

$$\partial_t \vec{\psi}_p = \underline{\mathcal{J}}(\vec{r}, \vec{c}_0, \vec{\psi}_0) \cdot \vec{\psi}_p, \quad (\text{B.22})$$

where $\underline{\mathcal{J}}$ is the Jacobian matrix of the system

$$\mathcal{J}_{ij}(\vec{r}, \vec{c}, \vec{\psi}) = \frac{\partial \mathcal{D}_i}{\partial \psi_j}. \quad (\text{B.23})$$

Assuming the eigenvectors $\vec{v}_i(\vec{r})$ associated with the eigenvalues λ_i of $\underline{\mathcal{J}}$ to form an orthonormal basis, the perturbation may be expanded like

$$\vec{\psi}_p(\vec{r}, t) = \sum_i c_i \vec{v}_i(\vec{r}) e^{\lambda_i t}, \quad (\text{B.24})$$

to transforms Eq. (B.22) into an eigenvalue problem

$$\begin{aligned} \partial_t \vec{\psi}_p(\vec{r}, t) &= \sum_i \lambda_i \vec{v}_i(\vec{r}) e^{\lambda_i t} = \sum_i \underline{\mathcal{J}}(\vec{r}, \vec{c}_0, \vec{\psi}_0) \cdot \vec{v}_i(\vec{r}) e^{\lambda_i t} \\ \rightarrow \quad & \left[\underline{\mathcal{J}}(\vec{r}, \vec{c}_0, \vec{\psi}_0) - \lambda_i \mathbb{I} \right] \cdot \vec{v}_i(\vec{r}) = 0. \end{aligned} \quad (\text{B.25})$$

According to Eq. (B.24) the eigenvalues λ_i determine whether a perturbation of the shape $\vec{v}_i(\vec{r})$ would grow in time ($\text{Re}[\lambda_i] > 0$) when imposed to $\vec{\psi}_0$ or decay until it vanishes ($\text{Re}[\lambda_i] < 0$) and the original $\vec{\psi}_0$ is occupied once more. In addition a non vanishing imaginary part $\text{Im}[\lambda_i] \neq 0$ indicates, that a time periodic behavior will be induced by the perturbation. Indicating the *principal directions* of growth and decay of a perturbation, the eigenvectors associated to eigenvalues with positive and negative real part are also referred to as *destabilizing (excitation) modes* and *stabilizing modes*, respectively. If the projection of $\vec{\psi}_p$ on at least one destabilizing mode does not vanish, it is destabilizing as well. In general a steady state $\vec{\psi}_0$ is considered linearly stable only if all eigenvalues are $\lambda \leq 0$ and linearly unstable else. Being derived from the differential operator $\mathcal{D}$ (cf. Eq. (B.23)) the Jacobian also inherits the spatial derivatives, acting on $\vec{\psi}_p$ and complicating the matter. The Jacobian and its eigenvalues are therefore often evaluated numerically and some continuation softwares, like e.g. `pde2path`, directly calculate the stability of the states along the way. Striving for an analytical solution, this problem is circumvented by considering the equation in Fourier space as will be demonstrated in the next section.

B.5.1. LINEAR STABILITY OF THIN LIQUID FILMS

In what follows the principle of linear stability analysis is applied to the simple example of a liquid film on an elastic substrate to demonstrate how an analytical approach may look like. Consider the dimensionless gradient dynamics Eq. (3.65) along with the long-wave variations and the parameters given in Eqs. (3.75) and (3.76), respectively. A known steady solution of these equations is a homogeneous liquid layer of thickness $h(x) = h_0$ covering an undisturbed level substrate $\xi(x) = 0$, i.e., $\vec{\psi}_0 = (h_0, 0)^\top$. Next the equations are linearized by assuming an arbitrary perturbation of small amplitude $\epsilon \vec{\psi}_p = \epsilon(h_p, \xi_p)^\top$. Since the dynamics of the elastic substrate are linear already and the horizontal displacement u_x decouples from the other fields and is therefore not considered in the first place, only the liquid equation (3.75a) has to be treated. Here we find two nonlinear terms, namely the mobility $Q(h)$ and the disjoining pressure $\Pi(h)$ both of which are linearized by Taylor expansion, i.e., $Q(h) \approx Q(h_0) + \epsilon \partial_{h_0} Q(h_0) h_p$ and $\Pi(h) \approx \Pi(h_0) + \epsilon \partial_{h_0} \Pi(h_0) h_p$, revealing

$$\begin{aligned}
 \partial_t h &= \partial_x \left(Q(h) \partial_x [-\partial_x^2 (h + \xi) - \Pi(h)] \right) \\
 \partial_t (h + \epsilon h_p) &= \partial_x \left(Q(h + \epsilon h_p) \partial_x [-\partial_x^2 (h_0 + \epsilon h_p + \epsilon \xi_p) - \Pi(h_0 + \epsilon h_p)] \right) \\
 \partial_t (h + \epsilon h_p) &\approx \partial_x \left(Q(h_0) \partial_x [-\partial_x^2 h_0 - \Pi(h_0)] \right) \\
 &\quad + \epsilon \partial_x \left(\partial_{h_0} Q(h_0) h_p \partial_x [-\partial_x^2 h_0 - \Pi(h_0)] \right) \\
 &\quad + \epsilon \partial_x \left(Q(h_0) \partial_x [-\partial_x^2 (h_p + \xi_p) - \partial_{h_0} \Pi(h_0) h_p] \right) + \mathcal{O}(\epsilon^2) \\
 \partial_t h_p &\approx \partial_x \left(Q(h_0) \partial_x [-\partial_x^2 (h_p + \xi_p) - \partial_{h_0} \Pi(h_0) h_p] \right)
 \end{aligned}
 \begin{array}{l}
 \left. \begin{array}{l} \\ \\ \\ \end{array} \right\} \begin{array}{l} \text{perturb} \\ \text{linearize} \\ \text{simplify} \end{array}
 \end{array}$$

Note, that all derivatives can be shifted past h_0 as it is constant. The linearized evolution of the perturbation is thus given by

$$\partial_t h_p = Q(h_0) [-\partial_x^4 (h_p + \xi_p) - \partial_{h_0} \Pi(h_0) \partial_x^2 h_p], \quad (\text{B.26})$$

$$\partial_t \xi_p = \frac{1}{\tau} \left(\partial_x^2 (h_p + \xi_p) + \sigma \partial_x^2 \xi_p - \frac{\xi_p}{s} \right), \quad (\text{B.27})$$

and can be written in the form

$$\partial_t \begin{pmatrix} h_p \\ \xi_p \end{pmatrix} = \begin{pmatrix} -Q(h_0) [\partial_x^2 + \partial_{h_0} \Pi(h_0)] \partial_x^2 & -Q(h_0) \partial_x^4 \\ \frac{1}{\tau} \partial_x^2 & \frac{1}{\tau} \left[(1 + \sigma) \partial_x^2 - \frac{1}{s} \right] \end{pmatrix} \cdot \begin{pmatrix} h_p \\ \xi_p \end{pmatrix}, \quad (\text{B.28})$$

which takes the shape of Eq. (B.22). As mentioned in the previous section the issue of spatial derivatives in the Jacobian is to be avoided by transforming to Fourier space, effectively replacing $\partial_x \rightarrow -ik$. This is done by expanding the perturbation in harmonics, i.e.,

$$\vec{\psi}_p(\vec{r}, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \vec{\psi}_p(k) e^{-ikx + \lambda(k)t} dx, \quad (\text{B.29})$$

leaving us with the eigenvalue problem

$$\begin{pmatrix} Q(h_0)[-k^2 + \partial_{h_0}\Pi(h_0)]k^2 - \lambda & -Q(h_0)k^4 \\ -\frac{1}{\tau}k^2 & -\frac{1}{\tau}\left[(1+\sigma)k^2 + \frac{1}{s}\right] - \lambda \end{pmatrix} \cdot \begin{pmatrix} h_p(k) \\ \xi_p(k) \end{pmatrix} = 0. \quad (\text{B.30})$$

The eigenvalues are then found to be

$$\begin{aligned} \lambda_{1/2} &= \frac{1}{2} \text{tr}(\underline{\mathcal{J}}) \pm \sqrt{\frac{1}{4} \text{tr}(\underline{\mathcal{J}})^2 - \det(\underline{\mathcal{J}})} \\ \text{with } \text{tr}(\underline{\mathcal{J}}) &= Q_0[-k^2 + \Pi'_0]k^2 - \frac{1}{\tau} \left[(1+\sigma)k^2 + \frac{1}{s} \right] \\ \text{and } \det(\underline{\mathcal{J}}) &= -\frac{Q_0}{\tau}k^6 - k^2 \frac{Q_0}{\tau} \left[-k^2 + \Pi'_0 \right] \left[(1+\sigma)k^2 + \frac{1}{s} \right] \end{aligned}$$

or written out

$$\lambda_{1/2}(k) = \frac{1}{2} \left(Q_0[-k^2 + \Pi'_0]k^2 - \frac{1}{\tau} \left[(1+\sigma)k^2 + \frac{1}{s} \right] \right) \pm \sqrt{\frac{1}{4} \left(Q_0[-k^2 + \Pi'_0]k^2 - \frac{1}{\tau} \left[(1+\sigma)k^2 + \frac{1}{s} \right] \right)^2 + \frac{Q_0}{\tau} k^6} \quad (\text{B.31})$$

where the abbreviations $Q_0 = Q(h_0)$ and $\Pi'_0 = \partial_h \Pi(h)|_{h=h_0}$ are used. Inserting the eigenvalues into the eigenvalue problem Eq. (B.30) reveals the eigenvectors. It is found that λ_1 (plus sign in front of the square root) represents a contradictory behavior of h and ξ in a sense that a local increase of h_p comes along with a decrease in ξ_p . In other words, the respective entries of the corresponding eigenvector carry opposite signs. On the other hand, λ_2 represents a behavior in which the tendencies of h_p and ξ_p are aligned. Unfortunately, the expressions of the eigenvalues Eq. (B.31) are quite unwieldy and so are the corresponding eigenvectors, which are not written down here for that reason. Yet some information that can be drawn from this result. First of all, it is found, that a homogeneous perturbation, i.e., $k = 0$, leads to

$$\lambda_1(k=0) = 0, \quad \lambda_2(k=0) = -\frac{1}{s\tau}, \quad (\text{B.32})$$

with the corresponding eigenvectors

$$\vec{v}_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \vec{v}_2 = \begin{pmatrix} 0 \\ -1 \end{pmatrix}. \quad (\text{B.33})$$

This means, that a homogeneous perturbation of liquid layer thickness h at fixed ξ (with $\vec{\psi}_p = (h_p, \xi_p)^\top = \vec{v}_1 = (1, 0)^\top = (1, 0)^\top$) remains steady in time due to $\lambda_1 = 0$, while a homogeneous perturbation of the substrate at fixed liquid layer thickness ($\vec{\psi}_p = (h_p, \xi_p)^\top = \vec{v}_2 = (0, -1)^\top$) will decay with a characteristic time scale $T \sim -\frac{1}{\lambda_2} = \sigma\tau$ just as was found in Sec. 3.6.1. We further note, that λ_2 is always negative and the associated modes always stabilizing in consequence. In contrast, λ_1 gives rise to a short wave instability in a range $0 < k < k_{\max}$ with

$$k_{\max} = \sqrt{\frac{s(1+\sigma)\Pi'_0 - 1 + \sqrt{4\sigma s\Pi'_0 + (1-s(1+\sigma)\Pi'_0)}}{2\sigma s}}. \quad (\text{B.34})$$

Since $k_{\max}$ vanishes for $h_0 = h_c = \sqrt[3]{2}$, this is exactly the thickness where the liquid film is expected to become unstable against perturbations (of infinite wave length) in a pitchfork bifurcation. In Fig. B.5 the eigenvalues are shown as functions of the wave number (also referred to as *dispersion relation*) for different parameters along with the associated eigenvectors.

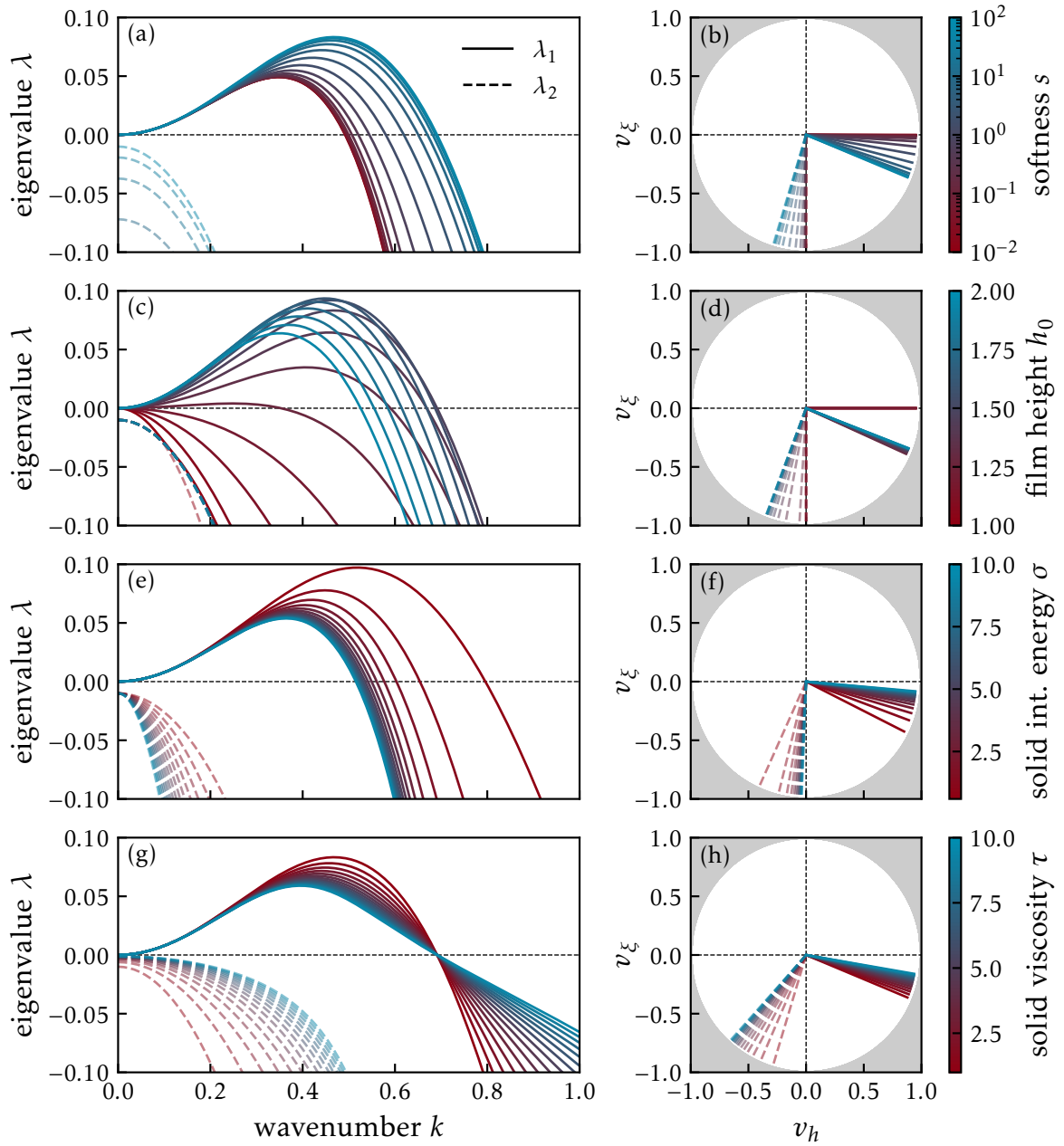


FIGURE B.5.: The eigenvalues and eigenvectors obtained from a linear stability analysis of a homogeneous liquid layer on an undisturbed soft substrate. Panels (a), (c), (e) and (g) show the dispersion relations, i.e., the eigenvalues λ_1 (solid) and λ_2 (dashed) as functions of the wave number k under variation of a parameter as given by the color bar of the respective line. Panels (b), (d), (f) and (h) show the corresponding eigenvectors $\vec{v} = (v_h, v_\xi)^T$ at the wave number corresponding to $\lambda = \lambda_{\max}$. While λ_2 is always negative, λ usually is positive in a finite wave number range $0 < k < k_{\max}$ and exhibits a maximum at $k > 0$. An exception is shown in panel (c) where the dispersion relations for the four lowest h_0 values have their maximum at $k = 0$ and are always stabilizing. Consequently, the two corresponding eigenvectors are aligned with the positive x - and negative y -axis respectively. If not varied the parameters are set to the default values $s = 10^2$, $h_0 = 1.5$, $\sigma = 1$ and $\tau = 1$.

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After finishing school, I originally wanted to study musics and I never had much to do with physics. As for today, I cannot really remember the reason why I started with physics in the end, but what I know is this: it certainly wasn't because it would be easy. Studying physics, and likewise pursuing a PhD, was for me primarily characterized by an intense learning process. I was constantly confronted with unfamiliar topics and questions, and acquiring knowledge in the respective fields proved challenging for me. In addition to delving into new scientific subjects, also the learning of new methods posed a major task, that was, above all, time-consuming. I believe anyone, who has pursued a PhD in physics, is all too familiar with the situation where a piece of code wont run without any apparent reason, despite knowing full well that, in principle, it should work. Sometimes weeks can pass by while one desperately searches for answers, seemingly without making any progress towards a solution.¹ Dealing with these challenges on a daily basis is demanding and, at times, frustrating and even disheartening. The sum of these aspects could have quickly nipped any initial enthusiasm in the bud if I had had to face them entirely alone.² This is why I consider myself very fortunate to have had some wonderful people around me who accompanied, supported, encouraged and inspired me throughout this process. These people I would like to thank here!

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¹ Learning, that ruling out sources of error is also a form of progress, is one of those subtle lessons that this time has taught me.

² The persisting isolation during the COVID-19 pandemic certainly didn't help with that.

³ Alias *Ant-man*, *Akro-Thony*.

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⁴Alias *The old Legend*, *Ehrenbrudi*.

⁵Alias *Backstab Ken*

⁶Alias *Sebbo*, *Sebsis*, *Sebbelin*.

⁷Alias *Tabea*, *Taboulé*, *Tabulator*, *Tabumeter*

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