The Cahn-Hilliard Equation

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The Cahn-Hilliard equation describes the process of spinodal decomposition of a binary mixture.

We consider a binary mixture of the two components A and B, which are described by their local per-volume densities $c_A(\mathbf{x},t)$ and $c_B(\mathbf{x},t)$, respectively. For a binary mixture, we can assume that $c_A(\mathbf{x},t) + c_B(\mathbf{x},t) = 1$, and therefore only use one concentration $c(\mathbf{x},t)$ for the description:

$$c_A(\mathbf{x},t) := c(\mathbf{x},t) \quad \text{and} \quad c_B(\mathbf{x},t) = 1 - c(\mathbf{x},t) \tag{1}$$

The corresponding flux can be determined to be

$$\mathbf{J} = -M\nabla\left(\mu_B - \mu_A\right), \tag{2}$$

where M is a mobility coefficient and μ_i is the chemical potential of component i.

According to classical thermodynamics, the difference of the two chemical potentials $\mu_B - \mu_A$ can be expressed in terms of a variation of a corresponding free energy potential $\mathcal{F}[c]$:

$$\mu_B - \mu_A = \frac{\delta \mathcal{F}[c]}{\delta c}, \tag{3}$$

$$\Rightarrow \mathbf{J} = -M\nabla \frac{\delta \mathcal{F}[c]}{\delta c}. \tag{4}$$

The assumption of mass conservation directly leads to the Cahn-Hilliard equation:

$$\frac{\partial}{\partial t} c(\mathbf{x},t) = -\nabla \cdot \mathbf{J} \tag{5}$$

$$= \nabla \cdot M\nabla \frac{\delta \mathcal{F}[c]}{\delta c}. \tag{6}$$

A typical choice for the free energy is

$$\mathcal{F}[c] = \int_\Omega \frac{\kappa}{2}\left|\nabla c\right|^2 + f(c)\,\mathrm{d}\mathbf{x}, \tag{7}$$

with a double well potential for the local energy $f(c)$

$$f(c) = \frac{a}{2}c^2 + \frac{b}{4}c^4 \tag{8}$$

$$\Rightarrow \frac{\partial}{\partial t} c(\mathbf{x},t) = \nabla \cdot M\nabla\left(-\kappa\Delta c(\mathbf{x},t) + ac(\mathbf{x},t) + bc(\mathbf{x},t)^3\right). \tag{9}$$

The coefficient a is related to the temperature T of the binary mixture and decides, whether a phase separation will occur. A typical phase diagram for such a system is shown in Fig. 1

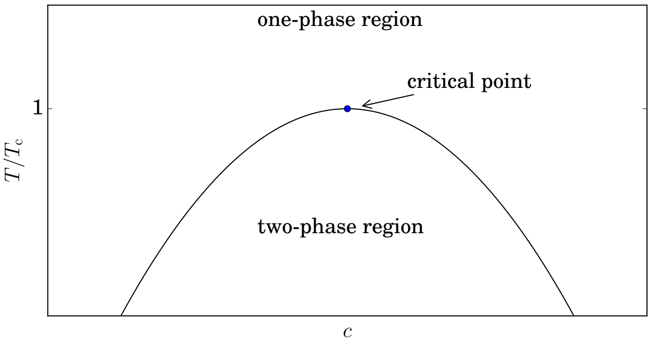

Figure 1: typical phase diagram of a binary mixture.

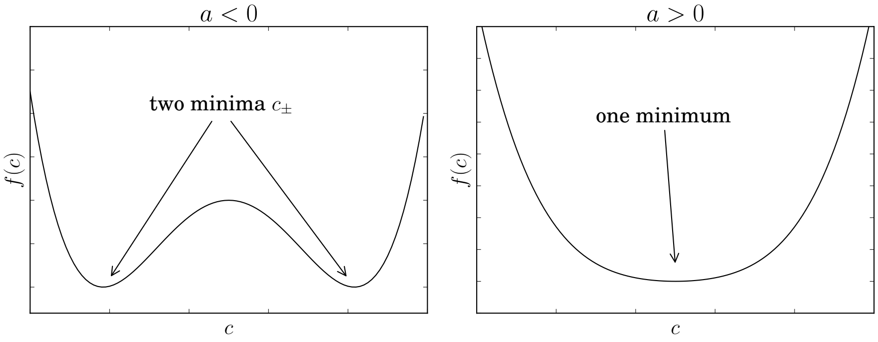

Figure 2: Local free energy $f(x)$ of a binary mixture below the critical temperature ($T < T_{\text{crit}}$, $a < 0$, left) and above the critical temperature ($T > T_{\text{crit}}$, $a > 0$). For $T < T_{\text{crit}}$, the free energy has two local minima $c_\pm$, which merge into only one minimum for $T \geq T_{\text{crit}}$.

0.1 Linear Stability Analysis

To analyze the the linear stability of the Cahn-Hilliard equation, we use as an ansatz a homogeneous solution c_0 with a perturbation with small amplitude ϵ, growth rate β and spatial wavenumber k:

$$c(\mathbf{x}, t) = c_0 + \epsilon e^{\beta t} e^{ikx} \tag{10}$$

Inserting this ansatz in the Cahn-Hilliard equation and omitting all terms of $\mathcal{O}(\epsilon^2)$ and higher, one obtains:

$$\begin{aligned} \beta(k) =& M(-k^2)(\kappa k^4 + a + 3bc_0^2) && (11) \\ =& \underbrace{-M\kappa k^4}_{<0} \; \underbrace{-M(a + 3bc_0^2)k^2}_{\lesseqgtr 0\text{, depending on } a,b,c_0} && (12) \end{aligned}$$

Therefore the stability depends on the particular choice of a, b and c_0. The fastest growing mode can be determined by finding the local maximum k_{max} of the dispersion relation $\beta(k)$:

$$\begin{aligned} \left.\frac{\partial \beta}{\partial k}\right|_{k=k_{\mathrm{max}}} &= 0 && (13) \\ \Leftrightarrow k_{\mathrm{max}} &= \sqrt{\frac{a + 3bc_0}{2\kappa}} && (14) \\ & && (15) \end{aligned}$$

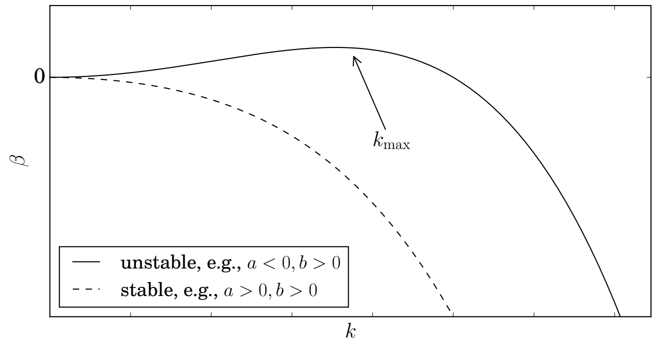

Figure 3: Growth rate β of a perturbation with wavenumber k determined by linear stability analysis.

0.2 Long-term behavior

Just as with the Allen-Cahn equation, the dynamics of the Cahn-Hilliard equation can only decrease the free energy $\mathcal{F}[c]$ over time:

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{F}[c] = \int\limits_{\Omega} \frac{\delta \mathcal{F}}{\delta c}\frac{\partial c}{\partial t}\mathrm{d}\mathbf{x} \tag{16}$$

$$\overset{\text{C-H eq.}}{=} \int\limits_{\Omega} \frac{\delta \mathcal{F}}{\delta c}\nabla \cdot M \nabla \frac{\delta \mathcal{F}[c]}{\delta c}\mathrm{d}\mathbf{x} \tag{17}$$

$$\overset{\text{int. by parts}}{=} -\int\limits_{\Omega} \nabla \frac{\delta \mathcal{F}}{\delta c} \cdot M \nabla \frac{\delta \mathcal{F}[c]}{\delta c}\mathrm{d}\mathbf{x} \tag{18}$$

$$= -\int\limits_{\Omega} \underbrace{M}_{>0} \underbrace{\left(\nabla \frac{\delta \mathcal{F}[c]}{\delta c}\right)^2}_{\geq 0} \mathrm{d}\mathbf{x} \leq 0. \tag{19}$$

The minimization of $\mathcal{F}$ can be achieved in two ways:
a) minimize $f(c)$,
b) minimize $\frac{\kappa}{2}\left|\nabla c\right|^2$.
a) After a short time, almost everywhere $c = c_+$ or $c = c_-$, as $f(c)$ is minimal there.
b) $\left|\nabla c\right|^2$ is an energetic penalty for gradients of c, therefore the dynamics tend to reduce boundaries between regions with $c = c_+$ or $c = c_-$. This leads to coarsening dynamics, where regions with equal concentration c merge to larger regions with less boundaries.

One can show that the typical length scale l of the observable pattern evolves as

$$l \sim t^{1/3}, \tag{20}$$

i.e., the coarsening process is very slow.