Statistical Mechanics

reference: • Bühler: A brief introduction into class., stat., and quantum mechanics (we follow this mainly)
• Chandler: Introduction to modern statistical mechanics (aimed at physicists)
• Thompson: Mathematical statistical mechanics (aimed at mathematicians)
(latter two start off with introduction to macroscopic thermodynamics)

microstate of a system = its exact position $X(t) = (q_1(t), q_2(t), \ldots, p_1(t), p_2(t), \ldots, p_N(t))$ in phase space $\Gamma \subset \mathbb{R}^{2N}$ at current time t.
Often we cannot observe it, e.g. since N too large
(# gas molecules in $1m^3$ at room temp. & pressure $\sim 10^{25}$)

macrostate = observed state, characterized by few macroscopic quantities (e.g. pressure, temp., ...)
Measuring the macroscopic quantities corresponds to averaging microscopic quantities over the time interval of the measurement.

Ex: N gas molecules inside cube of sidelength ℓ.
pressure = average transferred normal momentum of molecules colliding with the wall per unit area & unit time interval,

$$p = \frac{1}{\Delta t\, \Delta A} \sum_{\substack{\text{collisions } i \\ \text{in } \Delta t \text{ on } \Delta A}} 2 \underbrace{p_i}_{m_i v_i} \cdot \underbrace{n}_{\text{unit normal on } \Delta A}$$

time average of any phase space fcn $f: \Gamma \to \mathbb{R}$: $\bar{f} := \lim_{T\to\infty} \frac{1}{T} \int_0^T f(X(t))\, dt$ (if it exists)
Limit $T \to \infty$ reflects that time interval of observation is $\gg$ time scale at which microstate changes.
f may in principle be a distribution (e.g. for the pressure, f is a sum of δ-peaks in phase space, wherever a molecule hits the wall).

Statistical mechanics tries to predict macroscopic quantities for microscopic systems without computing trajectories $X(t)$ and then averaging (infeasible for large systems & yields little insight). Trick:
probability measure induced by time average (if it exists) is given by

$$\mu(A) = \bar{1}_A = \lim_{T\to\infty} \frac{1}{T} \int_0^T \underbrace{1_A}_{\text{char. fcn of } A \subset \Gamma}(X(t))\, dt = \text{prob}(X(t) \in A)$$

$$\text{then } \bar{f} = \langle f \rangle := \int_\Gamma f\, \mu(d\Gamma).$$

Statistical mechanics identifies and approximates μ for different systems and then derives macroscopic quantities and relations just from the statistical information μ.

Ex: For the gas in the cube, assume identical molecules & that μ describes a uniform independent distribution of molecule positions $q_i^j \in [0, \ell]$, $i = 1, \ldots, N$, $j = 1,2,3$, and an independent & identical distribution of the momenta $p_i^j = m v_i^j$ according to a probability density ρ with $\rho(-v) = \rho(v)$
$\Rightarrow$ in δt time, the wall with normal e_j is hit by $\frac{v \delta t}{\ell} \rho(v) N$ molecules with j^{th} velocity comp. $= v$.

$$\Rightarrow p = \frac{1}{\ell^2 \delta t} \int_0^\infty \frac{v \delta t}{\ell} \rho(v) N\, (2mv)\, dv = \frac{2N}{\ell^3} \int_0^\infty m v^2 \rho(v)\, dv = \frac{2N}{V} \langle \tfrac{1}{2} m (v^j)^2 \rangle$$

$$= \frac{2}{3V} \langle N \tfrac{1}{2} m |v|^2 \rangle = \frac{2}{3\underbrace{V}_{\text{volume}}} \langle \underbrace{T}_{\text{kinetic energy}} \rangle$$

$\Rightarrow$ Boyle's law $pV = \frac{2}{3} \langle T \rangle$ (which is correct)

Rk: a) statistical mechanics make some assumptions which have not been amenable to mathematical proofs except for very simple systems (keyword: ergodicity).
$\Rightarrow$ always check results against experiments & simulations

b) other applications of stat. mech.: • What is likely macrostate of a system if we don't know initial microstate (assuming all initial states to be equally likely)? $\Rightarrow$ average over trajectories with different initial conditions
• What are statistics of long-term behavior of a system (even if we can observe the microstate, e.g. for solar system)? (E.g. average planet-distance)

c) Poincaré's recurrence thm told us that a mechanical system repeatedly returns to all regions
$\Rightarrow$ suggests well-definedness of limit $T \to \infty$

However, recurrence time may be millions of years $\gg$ measurement time.
Still we don't need to measure ~~f~~ over such a long time; only over a time over which the autocorrelation decays of $f(X(t))$. For highly symmetric f this is quite short (e.g. $f = \sum_{i=1}^{N} p_i^2$ is invariant under permutation $i \leftrightarrow j$).

Ensembles

ensemble = system with its specific distribution μ (which of course depends on the system dynamics)
some ensembles where μ takes a particular form get particular names. We will learn about

- microcanonical ensemble: μ = uniform distribution on phase space, "restricted" to accessible part
  classic example: N identical gas molecules in an isolated box
  macroscopic state fully described by molecule number N, volume V, energy E
- canonical ensemble: $d\mu(X) = \frac{1}{Z(\beta)} \exp(\beta H(X))\, dX$ for Hamiltonian H
  classic example: gas in box that exchanges energy with a large environment
  macroscopic state described by N, V, temperature $\Theta = \frac{1}{\beta}$
- grand-canonical ensemble: $d\mu(X) = \frac{1}{Z(\beta, M)} \exp(\beta(N(X) - H(X)))$ for number of particles N
  classic example: gas in box, where energy and molecules can be exchanged with large environment
  macroscopic state described by V, Θ, chemical potential M

Microcanonical ensemble

Here one assumes that dynamics produce μ = uniform distribution of Γ, "restricted" to accessible part.

(A) Finite discrete phase space: (a) If these dynamics reach all of Γ, $\mu(A) = \text{prob}(X(t) \in A) = \frac{|A|}{|\Gamma|}$; $\text{prob}(X(t)) = \frac{1}{\Omega}$ with $\Omega = |\Gamma|$

(b) If these dynamics conserve a quantity, e.g. energy E,
$$\mu(\{X\}) = \begin{cases} 1/\Omega(E) & \text{if } H(X) = E \\ 0 & \text{else} \end{cases}, \quad \text{where } \Omega(E) = |\{X \in \Gamma \mid H(X) = E\}|$$

Ex: Magnetic switches in 1D

d_1	d_2	d_3	$\cdots$	d_N	d_{N+1}

$\leftarrow$ little magnets with orientation $\uparrow (d_i = 1)$ or $\downarrow (d_i = -1)$

$$H(X) = H(d_1, \dots, d_{N+1}) = \sum_{i=1}^{N} \frac{|d_{i+1} - d_i|}{2}$$

change coordinates: $s_i = \begin{cases} 0 & \text{if } d_{i+1} = d_i \\ 1 & \text{else} \end{cases}$, $i = 1, \dots, N$

$$\Rightarrow H(X) = H(s_1, \dots, s_N) = \sum_{i=1}^{N} s_i$$

e.g. for $N = 3$

E	0	1	2	3
$\Omega(E)$	1	3	3	1

$\Rightarrow$ all accessible states have same probability

(B) Continuous phase space (finite): (a) If these dynamics reach all of Γ, $\mu(A) = \frac{|A|}{|\Gamma|} = \frac{|A|}{\Omega}$ for $\Omega = |\Gamma|$

(b) If these dynamics conserve a quantity, e.g. energy E, then μ is the "restriction" μ_E of the uniform probability measure onto
$$D(E) = \{X \in \Gamma \mid H(X) = E\}.$$

More precisely, consider the uniform prob. meas. $\tilde{\mu}(A) = \frac{|A|}{|\Gamma|}$ on Γ.
For the Hamiltonian $H: \Gamma \to \mathbb{R}$ define the pushforward measure $\nu = H_{\#}\tilde{\mu} = \tilde{\mu} \circ H^{-1}$ on $\mathbb{R}$. By the disintegration thm, for a.e. $E \in \mathbb{R}$, $\exists$ probability measure μ_E on Γ s.t.

- $E \mapsto \mu_E$ is Borel measurable
- $\mu_E(\Gamma \setminus H^{-1}(E)) = 0$
- $\int_\Gamma f\, d\tilde{\mu} = \int_{\mathbb{R}} \int_{H^{-1}(E)} f(X)\, d\mu_E(X)\, d\nu(E)$