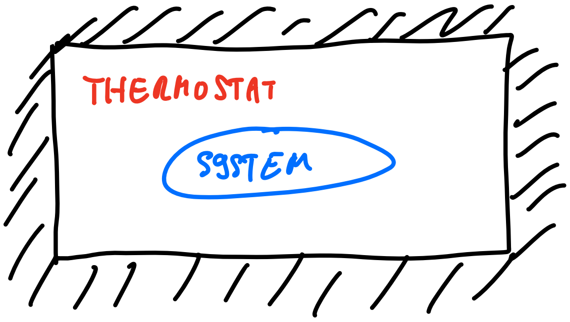

$$\boxed{P(\mathcal{C}) = \frac{1}{Z} e^{-\beta E(\mathcal{C})}}$$

with $\beta = \frac{1}{k_B T_{th}}$ and $Z = \sum_{\mathcal{C}} e^{-\beta E(\mathcal{C})}$

Helmoltz free energy $F(N,V,T) = -k_B T \ln Z(N,V,T)$

Continuous system For a system comprising N particles with positions $\vec{q}_i$ & momenta $\vec{p}_i$, the canonical probability density reads as: $P(\{\vec{q}_i,\vec{p}_i\}) = \frac{1}{Z} e^{-\beta H(\{\vec{q}_i,\vec{p}_i\})}$ where, to make the phase space measure dimension free, we use

$$d\Gamma = \prod_i \frac{d\vec{q}_i\, d\vec{p}_i}{h^3} \quad \& \quad Z = \int \prod_{i=1}^{N} \frac{d\vec{q}_i\, d\vec{p}_i}{h^3}\, e^{-\beta H(\{\vec{q}_i,\vec{p}_i\})}$$

so that $\langle \mathcal{O}(\{\vec{q}_i,\vec{p}_i\})\rangle = \int \prod_{i=1}^{N} \frac{d\vec{q}_i\, d\vec{p}_i}{h^3}\, \mathcal{O}(\{\vec{q}_i,\vec{p}_i\})\, \frac{e^{-\beta H(\{\vec{q}_i,\vec{p}_i\})}}{Z}$

Comment: the result of $\langle \mathcal{O}\rangle$ is the same if we consider instead $d\Gamma = \prod_i d\vec{q}_i\, d\vec{p}_i$, $Z = \int \prod_i d\vec{q}_i\, d\vec{p}_i\, e^{-\beta H}$ & $\langle \mathcal{O}\rangle = \int \prod_i d\vec{q}_i\, d\vec{p}_i\, \mathcal{O}\, \frac{e^{-\beta H}}{Z}$

The normalization by h^3 is however convenient since:

(i) it makes Z dimension free

(ii) it yields back the high T expansion of quantum stat mech

Indistinguishability If the particles are indistinguishable we correct the phase space measure into $d\Gamma = \frac{1}{N!} \prod_i \frac{d\vec{q}_i d\vec{p}_i}{h^3}$

such that $Z = \frac{1}{N!\, h^{3N}} \int \prod_{i=1}^{N} d\vec{q}_i d\vec{p}_i \; e^{-\beta \mathcal{H}}$

Again, the probability measure $d\rho = \frac{1}{h^{3N} N!} \int \prod_{i=1}^{N} d\vec{q}_i d\vec{p}_i \; \frac{e^{-\beta H}}{Z}$ is unaffected since it involves Z through $h^{3N} N!\, Z$.

Comment The factor $\frac{h^3}{N!}$ play a role in classical stat mech only when the number of $\left|\begin{array}{l}\text{degrees of freedom}\\ \text{number of particles}\end{array}\right.$ can change (see, e.g., exercise 4, part 5), or to compute the chemical potential.

The equipartition theorem

Consider a Hamiltonian $H(x_1, \dots, x_N)$, where $x_1, \dots, x_N = q_1, \dots, q_N$ & $x_{N+1}, \dots, x_{2N} = p_1, \dots, p_N$. We request that H diverges at least polynomially as $x_i \to \pm\infty$ so that $Z < \infty$.

Then
$$\boxed{\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = k_B T \, \delta_{ij}}$$

Proof:
$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{1}{Z N! \, h^{3N}} \int \prod_i d\vec{x}_i \; x_i \overbrace{\frac{\partial H}{\partial x_j} e^{-\beta H}}^{-kT \partial_{x_j} e^{-\beta H}}$$

$$\overset{\text{IBP}}{=} \frac{kT}{Z N! \, h^{3N}} \underbrace{\int \prod_i d\vec{x}_i \; e^{-\beta H}}_{Z N! \, h^{3N}} \overbrace{\frac{\partial x_i}{\partial x_j}}^{\delta_{ij}}$$

Ex: $x_i = p_i$; $x_j = p_j$ $\Rightarrow \left\langle p_i \frac{p_j}{m} \right\rangle = k_B T \delta_{ij} \Rightarrow \left\langle \frac{1}{2} m v_i^2 \right\rangle = \frac{k_B T}{2}$

Each "quadratic" degrees of freedom contributes $\frac{k_B T}{2}$ to the average energy.

Outline: We now consider the ideal gas & two-level systems for which we compute F & Z. Then, we compare statistics in micro-canonical & canonical ensembles.

3.2.2) Ideal gas & two-level systems

Ideal gas: N indistinguishable particles with $H = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}$

Partition function:

$$h^{3N} N!\, Z = \int \prod_i d\vec{q}_i\, d\vec{p}_i\; e^{-\beta \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}} = V^N \Big(\underbrace{\int dp\, e^{-\frac{p^2}{2m k_B T}}}_{\sqrt{2\pi m k_B T}} \Big)^{3N}$$

$$\Rightarrow \boxed{Z = \frac{1}{N!}\left(\frac{V}{\Lambda^3}\right)^N} \quad \text{where} \quad \boxed{\Lambda = \sqrt{\frac{h^2}{2\pi m k_B T}}}$$

Λ is called the thermal de Broglie wavelength. As we will show in quantum statistical mechanics, it is the length below which quantum effects matter.

Helmoltz free energy:

$$\boxed{F = -k_B T \ln Z = -N k_B T \ln\left(\frac{eV}{N\Lambda^3}\right)}$$

Two level system N particles on a lattice with $\varepsilon_i = 0, \varepsilon$.

Partition function

$$Z = \sum_{\{\varepsilon_1,\dots,\varepsilon_N\}} e^{-\beta \sum_i \varepsilon_i} = \sum_{\{\varepsilon_1,\dots,\varepsilon_N\}} \prod_i e^{-\beta \varepsilon_i}$$

$$= \sum_{\varepsilon_1} e^{-\beta\varepsilon_1} \cdot \sum_{\varepsilon_2} e^{-\beta\varepsilon_2} \cdot \;\dots\; \cdot \sum_{\varepsilon_N} e^{-\beta\varepsilon_N}$$

$$\boxed{Z = (1+e^{-\beta\varepsilon})^N}$$

Helmoltz free energy $\boxed{F = -N k_B T \ln(1+e^{-\beta\varepsilon})}$

Comment: The computations of F & Z are much easier than that of $\Omega(E)$ & $S(E)$ in the microcanonical ensemble.

3.2.3) Fluctuations of energy and ensemble equivalence

Contrary to the microcanonical ensemble, $E(q)$ is now a fluctuating quantity that can be used to define a macrostate. Let us characterize the statistics of E.

Finite system:

Moment generating function

$$\langle E\rangle = \frac{1}{Z}\sum_q E\, e^{-\beta E} = -\frac{1}{Z}\partial_\beta \overbrace{\sum_q e^{-\beta E}}^{Z} = -\partial_\beta \ln Z$$

Similarly $\left(-\partial_\beta\right)^n Z = \sum_q E(q)^n e^{-\beta E} = Z\langle E^n\rangle$

$$\Rightarrow \boxed{\langle E^n\rangle = \frac{(-1)^n}{Z}\frac{\partial^n}{\partial\beta^n} Z}$$

Z is (almost) the moment-generating function of E.

Why: $$Q(\lambda) = \langle e^{\lambda E} \rangle = \frac{1}{Z} \sum_{\psi} e^{\lambda E} e^{-\beta E} = \frac{Z(\beta-\lambda)}{Z(\beta)}$$

$$\langle E^n \rangle = \left(\frac{\partial}{\partial \lambda}\right)^n Q(\lambda)\Big|_{\lambda=0} = \frac{(-1)^n}{Z(\beta)} Z^{(n)}(\beta-\lambda)\Big|_{\lambda=0}$$

Cumulant generating function:

$$\Psi(\lambda) = \ln Q(\lambda) = \ln Z(\beta-\lambda) - \ln Z(\beta)$$

$$\langle E^n \rangle_c = \frac{\partial^n}{\partial \lambda^n} \ln Z(\beta-\lambda)\Big|_{\lambda=0} = (-1)^n \frac{\partial^n}{\partial \beta^n} \ln Z(\beta-\lambda)\Big|_{\lambda=0} = (-1)^n \frac{\partial^n}{\partial \beta^n} \ln Z(\beta)$$

$$\Rightarrow \quad \boxed{\langle E^n \rangle_c = (-1)^n \frac{\partial^n}{\partial \beta^n} \ln Z(\beta) = (-1)^{n+1} \frac{\partial^n}{\partial \beta^n} (\beta F)}$$

F is (almost) the cumulant generating function of the energy.

As you will see, equilibrium statistical mechanics has (almost) a beautiful mathematical structure, with lots of annoying factors & signs inherited from thermodynamics.

Large systems

We can directly use the result for $P(E_r)$ derived in the microcanonical ensemble to characterize $P(E)$:

$$P(E) \propto \mathrm{Exp}\left[-\frac{(E-E^*)^2}{2k_BT^2 \frac{C_V C_V^{th}}{C_V + C_V^{th}}}\right]$$

Since $N_{th} \gg N$, $C_V^{th} \gg C_V$ and

$$P(E) \propto e^{-\frac{(E-E^*)^2}{2k_BT^2 C_V}} \qquad \text{with } E^* \text{ such that } \left.\frac{\partial S}{\partial E}\right|_{E^*} = \frac{1}{T}$$

Q: Do we really need to go back to microcanonical ensemble?

Canonical ensemble $P(q) = \frac{1}{Z} e^{-\beta E} \Rightarrow P(E) = \frac{\Omega(E)}{Z} e^{-\beta E} = \frac{e^{-\beta[E-TS]}}{Z}$

$$Z = \sum_q e^{-\beta E} = \sum_E \Omega(E)\, e^{-\beta E} \sim \int dE\, \Omega(E)\, e^{-\beta E} = \int dE\, e^{-\beta[E-TS]}$$

$N \to \infty$, saddle point $\Rightarrow$ $\boxed{Z \sim e^{-\beta[E^* - TS(E^*)]}}$

where $E^* = \underset{E}{\operatorname{argmax}} \,(E - TS(E))$ & $1 - T\left.\frac{\partial S}{\partial E}\right|_{E^*} = 0 \Leftrightarrow \boxed{\left.\frac{\partial S}{\partial E}\right|_{E^*} = \frac{1}{T}}$

so that $\quad P(E) \propto e^{-\beta[E - E^* - TS(E) - TS(E^*)]}$

We can (again) expand E around its maximum E^* to get

$$\boxed{P(E) = \frac{e^{-\frac{(E-E^*)^2}{2k_BT^2C_V}}}{\sqrt{2\pi C_V k_B T^2}}}$$

Ensemble equivalence

* Since $P(E)$ is Gaussian, $E^* = \langle E \rangle$

* Since $\displaystyle\lim_{\sigma\to 0} \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-x_0)^2}{2\sigma^2}} = \delta(x-x_0)$

As $N\to\infty$, $P(E)$ converges in distribution to $\delta(E-E^*)$, which is the microcanonical distribution at an energy E^* such that

$$\frac{1}{T} = \left.\frac{\partial S_m}{\partial E}\right|_{E^*}.$$

Micro: set E, and T is such that $\frac{\partial S_m}{\partial E} = \frac{1}{T}$

Cano: set T, and $E^* = \langle E \rangle$ is such that $\left.\frac{\partial S_m}{\partial E}\right|_{E^*} = \frac{1}{T}$

* For any observable $O(E)$ that increase at most polynomially in E,

$$\langle O(E) \rangle_{\text{MICRO}} = \int dE\, \delta(E-E_0)\, O(E) = O(E_0)$$

$$\langle O(E) \rangle_{\text{MACRO}} = \int dE\, \omega(E)\, O(E) \frac{e^{-\beta E}}{Z} \underset{N\to\infty}{\sim} \int dE\, \delta(E-E^*)\, O(E) = O(E^*)$$

For macroscopic systems, the measurements in canonical & microcanonical ensemble of $O(E)$ are undistinguishable, provided $\frac{1}{T} = \frac{\partial S_m}{\partial E}$. One says that, under such conditions, one has ensemble equivalence.