quantum fluctuations make g subextensive so that $S(0) \ll N$ &

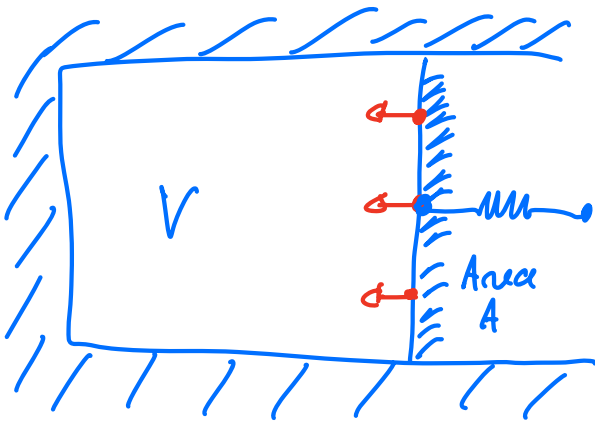$$S(T) \simeq \int_0^T \frac{C_V}{T}$$

Second law of thermodynamics

Take two systems with initial energy E_1 & E_2. Let them evolve in contact with each other and they will relax to E_1^* & E_2^* such that

$$S_{final} = S_1(E_1^*) + S_2(E_2^*) \geqslant S_{initial} = S_1(E_1) + S_2(E_2)$$

$\Rightarrow$ the entropy of the isolated system $S = S_1 \cup S_2$ has increased

$\Rightarrow$ this is the second law of thermodynamics. Note that it relies on $N \to \infty$.

3.1.4.3) Pressure & the 1st law of thermodynamics

We let the system equilibrate in a volume V, and we then exert a force per unit area f_a, that leads to a compression of the system during which the right wall moves by a distance dx. The force exerts a work that is $dW = f_a \cdot A \cdot dx = f_a \, dV$ so that the energy evolves as $E \to E + f_a \, dV$ and its variation reads $dE = f_a \, dV$

The entropy then evolves as

$$S_m(N,V,E) \to S_m(N,V+dV, E+dE) = S_m(N,V,E) + dV \frac{\partial S_m}{\partial V} \underbrace{ dE \frac{\partial S_m}{\partial E} }_{\equiv dS}$$

$$\underbrace{\phantom{dV \frac{\partial S_m}{\partial V} dE}}_{\equiv dS} \quad \frac{\partial S_m}{\partial E} = 1/T$$

$$\Rightarrow dS_m = \frac{\partial S_m}{\partial V} dV + f_\alpha \, dV \frac{1}{T} \qquad (*)$$

If the system does not evolve $dS_m = 0$ and $\frac{\partial S_m}{\partial V} = -\frac{f_\alpha}{T}$

In the steady state, the system exert a force per unit area that balances f_α, which is the pressure

$$\boxed{P_m = T \frac{\partial S}{\partial V}}$$

$(*)$ can then be rewritte $dS = \frac{P_m}{T} dV + \frac{dE}{T}$

so that $\boxed{dE = T_m d S_m - P_m dV} \Rightarrow 1^{st}$ law of thermodynamics.

<u>Take home message:</u>

• Finite system $\Rightarrow$ compute $\Omega(E)$ or $\tilde{\Omega}(E)$ to characterize the probability of microstate

• Compute $S(E)$ in the large N limit to compute thermodynamic observable (heat capacity, pressure)

• Define macrostates $q_M = \{q_m\}$, their probability

are given by $P(q_M) = \frac{\Omega(q_M)}{\Omega(E)}$ where $\Omega(q_M)$ is the number of

microstates in q_M

Then, the large system limit endows $P(q_M)$ with a simpler expression.

Let us now show how this microstate/macrostate formalism can
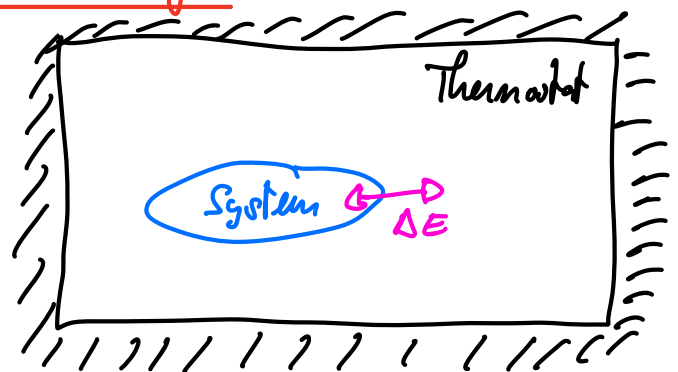
be used to **change ensemble**.

3.2) Canonical ensemble

3.2.1) Changing ensemble: the Boltzmann weight

System S + thermostat = isolated
but able to exchange energy

$E_{tot} = E_S + E_{th}$ fixed

but E_S & E_{th} can fluctuate.

① We consider large system so that $E_S, E_{th} \gg$ interaction energy
between S & thermostat.

② We consider large thermostat so that $E_{th} \gg E_S$.

③ System + thermostat are isolated $\Rightarrow$ microcanonical ensemble.

$\Rightarrow$ Configuration $q = (q_S, q_{th})$ such that $P_{tot}(q) = \frac{1}{\Omega_{tot}(E_{tot})} \delta_{E_{th}, E_S - E_{tot}}$

<u>Macrostate:</u> Since we do not care about the thermostat, we can define a macrostate of the system using q_s

$$\Rightarrow \hat{q}_s = \{ q = \{q_s, q_{th}\} \text{ such that } E_s(q_s) + E_{th}(q_{th}) = E_{tot} \}$$

This macrostate contains $\Omega_{th}(q_{th}) \gg 1$ states $\Rightarrow$ macro indeed.

$$P_{tot}(\hat{q}_s) = \sum_{q \in \hat{q}_s} P_{tot}(q) = \frac{1}{\Omega_{tot}(E_{tot})} \sum_{q_{th} | E(q_{th}) = E_{tot} - E(q_s)} 1 = \frac{\Omega_{th}(E_{tot} - E(q_s))}{\Omega_{tot}(E_{tot})}$$

$$= \frac{e^{k_B^{-1} S_m^{th}(E_{tot} - E(q_s))}}{\Omega_{tot}(E_{tot})}$$

Since $E(q_s) \ll E_{tot}$, $S_m^{th}(E_{tot} - E(q_s)) \simeq S_m^{th}(E_{tot}) - E(q_s) \underbrace{\frac{\partial S_m^{th}(E_{tot})}{\partial E}}_{\color{orange}{1/T_m^{th}}}$

$$\Rightarrow P_{tot}(\hat{q}_s) = \frac{e^{k_B^{-1} S_m^{th}(E_{tot})} \; e^{-\frac{E(q_s)}{k_B T_m^{th}}}}{\Omega_{tot}(E_{tot})}$$

$P_{tot}(\hat{q}_s)$ is the probability that the full system is in the macrostate $\hat{q}_s \Longleftrightarrow$ the probability that the system is in q_s, $P_s(q_s) \equiv P(q_s)$ for simplicity. All in all

$$\boxed{P(q_s) = \frac{\Omega_{th}(E_{tot})}{\Omega_{tot}(E_{tot})} e^{-\frac{E(q_s)}{k_B T_m^{th}}} \equiv \frac{1}{Z} e^{-\beta E(q_s)}} \quad (1)$$

where $\beta = \frac{1}{k_B T_m^{th}}$ is the inverse temperature (in J^{-1}) of the thermostat

and $\boxed{Z = \frac{\Omega_{tot}(\hat{E}_{tot})}{\Omega_{th}(E_{tot})}}$ (2') is a normalization factor such that

$\sum_{q_s} P(q_s) = 1 \implies \boxed{Z = \sum_{q_s} e^{-\beta E(q_s)}}$ (2)

Comment:

* (1) is called the "canonical distribution" or "the Boltzmann weight."

* Z is called the partition function. The definitions (2)' and (2) are equivalent but the second one is typically easier to use to compute Z and it only depends on the thermostat through β.

Control parameters: While systems in the microcanonical ensemble are characterized by N, E, V, the system is here controlled by N, T, V, where T is the temperature of the thermostat

Helmoltz free energy: $F(N,V,T) = -k_B T \ln[Z(N,V,T)]$ is called the Helmoltz free energy.

Continuous classical system: For a system described by N pairs of continuous positions & momenta $\vec{q_i}$ & $\vec{p_i}$, we can generalize this formalism as

classical	QM-compatible
$P(\{\vec{q_i}, \vec{p_i}\}) = \frac{1}{Z} e^{-\beta H(\{\vec{q_i}, \vec{p_i}\})}$	$P(\{\vec{q_i}, \vec{p_i}\}) = \frac{1}{\tilde{Z}} e^{-\beta H(\{\vec{q_i}, \vec{p_i}\})}$
$Z = \int \prod_i d^3\vec{q_i} d^3\vec{p_i} \, e^{-\beta H(\{\vec{q_j}, \vec{p_j}\})}$	$\tilde{Z} = \int \prod_i \frac{d^3\vec{q_i} d^3\vec{p_i}}{h^3} \, e^{-\beta H(\{\vec{q_i}, \vec{p_i}\})}$
$\langle o \rangle \equiv \frac{1}{Z} \int \prod_i d^3\vec{q_i} d^3\vec{p_i} \, O(\{\vec{q_j}, \vec{p_j}\}) e^{-\beta H(\vec{q_i}, \vec{p_i})}$	$\langle o \rangle \equiv \frac{1}{\tilde{Z}} \int \prod_i \frac{d^3\vec{q_i} d^3\vec{p_i}}{h^3} \, O \, e^{-\beta H}$

While this choice does not matter at the classical level, we typically adopt the QM-compatible formalism for the continuous case.

$\Rightarrow$ We stick to this notation, that we silently denote by Z from hereon.

Indistinguishability If the N degrees of freedom describe indistinguishable particles, we have over-counted the number of configurations in Z $\Rightarrow$

$$\boxed{Z = \frac{1}{h^{3N} N!} \int \prod_{i=1}^{N} d\vec{q_i} d\vec{p_i} \, e^{-\beta H(\{\vec{q_i}, \vec{p_i}\})}}$$

$\Rightarrow$ our phase-space measure is now $\frac{1}{h^{3N} N!} \int \prod_{i=1}^{N} d\vec{q_i} d\vec{p_i}$.

Again, our probability _measure_ $d\rho = \frac{1}{h^{3N} N!} \int \prod_{i=1}^{N} d\vec{q_i} d\vec{p_i} \frac{1}{Z} e^{-\beta H}$ is unaffected. While h^{3N} plays no role in classical stat mech, the $N!$ factor is crucial for systems with several species (see exercise 4, Part 5) or to compute the chemical potential.

The equipartition theorem

Consider a Hamiltonian $H(x_1, —, x_{2N})$, where $x_1, —, x_N = q_1, — , q_{3N}$

$$p_1, —, p_N = p_1, —, p_{3N}$$

We request that H diverges as $x_i \to \pm \infty$ so that $Z < \infty$. (Automatically true in a box).

$$\langle x_i \frac{\partial H}{\partial x_\ell} \rangle_c = \frac{1}{Z N!} \int \prod_m \frac{dq_m^{\to} dp_m^{\to}}{h^3} \underbrace{\frac{\partial H}{\partial x_\ell} e^{-\beta H}} \cdot x_i$$

$$\text{IBP} \Bigg\{ \qquad = \frac{1}{Z N!} \int \prod_m \frac{dq_m^{\to} dp_m^{\to}}{h^3} -k_BT \left(\frac{\partial}{\partial x_\ell} e^{-\beta H} \right) \cdot x_i$$

$$= \frac{k_BT}{Z N!} \int \prod_m \frac{dq_m^{\to} dp_m^{\to}}{h^3} e^{-\beta H} \underbrace{\frac{\partial x_i}{\partial x_\ell}}_{\delta_{i,\ell}}$$

$$\langle x_i \frac{\partial H}{\partial x_\ell} \rangle = k_BT \, \delta_{i,\ell}$$

E.g. $x_i = p_i ; x_\ell = p_\ell \Rightarrow \langle \frac{p_i p_\ell}{2m} \rangle = \frac{k_BT}{2} \delta_{i\ell}$

One recovers that each "quadratic degree of freedom" contributes $\frac{k_BT}{2}$ to the average energy.

Outline: Below we first compute Z & F for the ideal gas & the 2-level system, before studying the statistics of the system in the canonical ensemble to compare them with those in the microcano-mical ensemble.