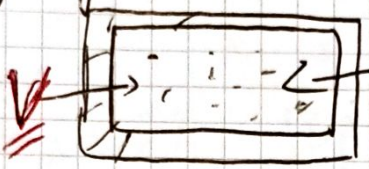
# Chap 3 : Microcanonical Ensemble

## 3.1 Introduction :

We consider in this chapter an isolated system.
For example a gaz of N molecules in a finite box without any exchange




⇒ Assumes Equilibrium
⇒ no flux $(\vec{E}, \vec{B})$

The only conserved quantity is thus $E$, $V$, $N$

Remember the Sinai numerical experiment showing ergodicity.
namely $\lim_{T\to\infty} \overline{O}_T = \langle O \rangle$

In the num. experiment, we found a uniform probability density in phase space. provided we wait long enough.

Therefore, this exp. suggests $\rho(\vec{\Gamma}) = \text{const}$ for $\vec{\Gamma} \in V_{Sinai}$
How about momentum ? In the sinai problem, momentum is conserved in modulus $||\vec{p}|| = p_0$ (not its direction)
A similar analysis would show that all possible $\vec{p}$ such that $||\vec{p}|| = p_0$ would be reached.
Therefore in phase space $\rho(\vec{r},\vec{p}) \to \frac{1}{V_{Sinai}} \delta(||\vec{p}|| - p_0)$ for $\vec{r} \in V_{Sinai}$

which implies $\rho(\vec{\Gamma}) = \text{const}$ for $\vec{\Gamma} = (\vec{r},\vec{p})$ allowed.

## 3.2 Boltzmann postulate

### 3.2.1) ~~Classical formulation~~ Formulation

We consider an isolated system of energy $E$ (up to $\delta E$) with $N$ particles
therefore $H(\vec{\Gamma}) = E$ (surface of dim $6N-1$ in a space of dim $6N$)

Idea → Extend the num. experiment of Sinai to any system

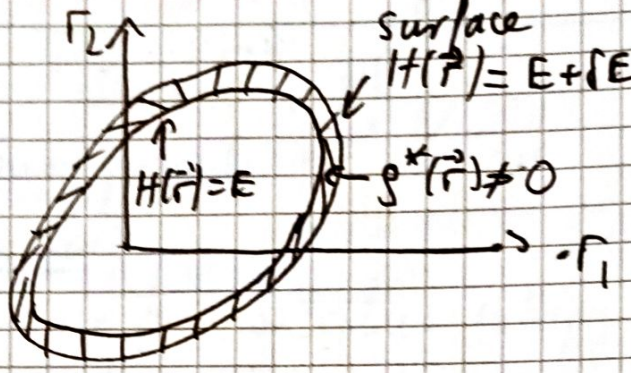
**Postulate:** All the accessible states of an isolated system of energy $E$ ($E \in [E, E+\delta E]$) in a macroscopic equilibrium have the same probability

$$\begin{cases} \rho^*(\vec{\Gamma}) = \text{constant} & \text{if } H(\vec{\Gamma}) \in [E, E+\delta E] \\ = 0 & \text{otherwise} \end{cases}$$

## 3.2.2 Classical formulation

What is the constant?

⇒ fixed by the normalization




Define $\nu(E, \delta E)$ the volume such that $E \leq H(\vec{\Gamma}) \leq E+\delta E$

$$\Rightarrow \begin{cases} \rho^*(\vec{\Gamma}) = \dfrac{1}{\nu(E, \delta E)} & \text{if } E \leq H(\vec{\Gamma}) \leq E+\delta E \\ \rho^* = 0 & \text{otherwise} \end{cases}$$

Therefore $\int \rho^*(\vec{\Gamma}) = 1$

One may also introduce $\nu(E) = \int d^{dN}\Gamma \; \theta_H(E - H(\vec{\Gamma}))$ $\theta_H$ Heaviside

the volume such that $H(\vec{\Gamma}) \leq E$

In that case $\nu(E, \delta E) = \dfrac{d\nu(E)}{dE} \delta E$

RQ: If $\delta E \to 0$ $\quad \rho^*(\vec{\Gamma}) = \dfrac{\delta(E - H(\vec{\Gamma}))}{\int d\vec{\Gamma}' \, \delta(E - H(\vec{\Gamma}'))}$

## 3.2.3 Quantum formulation

In the quantum limit, we know how to count states (due to discreteness)

$\Omega(E) = g(E)\delta E$ = nb of microstates between $[E, E+\delta E]$

$$\Rightarrow P_l^* = \begin{cases} \dfrac{1}{\Omega(E)} & \text{if } E \leq E_l \leq E+\delta E \\ 0 & \text{otherwise} \end{cases}$$

remember $g(E) = \dfrac{d\phi(E)}{dE}$ where $\phi(E) =$ integrated d.o.s

### 3.2.4 | Correspondence

Correspondance between the classical & quantum formulation

For N identical particles (undistinguishable)

$$\Omega(E) = g(E)\,dE = \frac{\mathcal{V}(E;\delta E)}{h^{3N}\,N!} = \frac{\mathcal{V}'(E)\,\delta E}{h^{3N}\,N!}$$

in 3D

This comes from $\phi(E) = \dfrac{\text{volume in } \Gamma\text{-space of microstates} \leq E = \mathcal{V}(E)}{h^{3N} \cdot N!}$

Examples

## 3.3 | Entropy and maximum entropy principle

### 3.3.1 | Entropy in thermodynamics

In thermodynamics, there is a state function called entropy from which we can derive all thermodynamic properties

2nd principle : $\Delta S = S_f - S_i \geq \int_{i \to f} \dfrac{\delta Q}{T}$ $\quad T$ = Temp.

Clausius : We cannot transfer heat from cold body to hot body

The measure of $\Delta S$ characterizes the degree of irreversibility

For a reversible (infinitesimal) transform :

1st principle : $\delta Q^{rev} = T\,dS$

($T$ : intensive, $dS$ : extensive)

$T$ and $S$ are conjugate variables

Similarly : $\delta W^{rev} = -p\,dV$ ; $p$, $\Delta V$ conjugate variables

($p$ : intensive, $dV$ : extensive)

$p$ controls the volume

$T$ ——— entropy (i.e. the degree of irreversibility)

$\sim$ quantifies the degree of microscopic disorder

## s.2] Gibbs entropy

So far, we have defined some principles and learnt how to calculate the density of states (d.o.s)
However, how to connect what phys to thermodynamics ?
Entropy ??? → Microscopic definition ?

Consider a discret set of microstates $\{i\}$ with proba $p_i$
Around 1875, Gibbs defined (also von Neumann)

$$S_G = -k \sum_i p_i \ln p_i \; ; \; k = \text{constant}$$

Properties :

* $S_G \geq 0$
* Consider two systems $\mathcal{S}$, $\mathcal{S}'$
  $\{p_i\}$, $\{p'_i\}$ independent.
  Microstates are $\{i, p_i\} \otimes \{j, p'_j\}$ with $i \in [\![1, N]\!]$, $j \in [\![1, N']\!]$
  Proba $\tilde{p}_\ell = \{p_i p'_j\}$ with $\ell \in [\![1, NN']\!]$

$$S_{tot} = -k \sum_\ell \tilde{p}_\ell \ln \tilde{p}_\ell = -k \sum_{ij} p_i p'_j \ln p_i p'_j$$

$$= -k \sum_{i,j} p_i p'_j \ln p_i - k \sum_{ij} p_i p'_j \ln p'_j$$

$$= -k \sum_i p_i \ln p_i - k \sum_j p'_j \ln p'_j$$

$$= S_{G,\mathcal{S}} + S_{G,\mathcal{S}'}$$

⇒ If $\mathcal{S} = \mathcal{S}_1 \otimes \mathcal{S}_2$ then $S_{\mathcal{S}} = S_{\mathcal{S}_1} + S_{\mathcal{S}_2}$ ||

$S_G$ is extensive ||

What this statistical quantity is actually measuring?

- Consider a system with equiprobable microstates $\ell \in \{1, \dots, \Omega\}$

with $p_1 = p_2 = \dots = p_\Omega = \frac{1}{\Omega}$

$$S_G = -k \sum_{i=1}^{\Omega} \frac{1}{\Omega} \ln\left(\frac{1}{\Omega}\right) = k \ln \Omega \rightarrow \text{maximum of } S \; \|$$

Therefore $S$ increases with $\ln\Omega = \ln(\text{N° microstates})$

- If $p_i = 1$ and $p_{i\neq 1} = 0$ $\quad S_G = 0$

↳ state is known exactly.

$\Rightarrow$ $S_G$ is a measure of the lack of information on the system.

| | |
|---|---|
| System known | $S_G = 0$ |
| System more unknown | $S_G = k \ln \Omega$ |

RQ For 2-states variables (bits), we set $k = 1/\ln 2$

and define $S_S = -\sum p_i \log_2 p_i$ Shannon entropy 1948

used to develop information theory

quantum: pure state → $S_S = 0$

mix → $S_S > 0$

$S_S$ has the same properties as $S_G$ (lack of info)

Other properties

$S_G$ is concave $\{p_\ell^{(0)}\}$ & $\{p_\ell^{(2)}\}$

$$p_\ell^{(1)} = (1-\lambda)\, p_\ell^{(0)} + \lambda\, p_\ell^{(2)}$$

$$S_G(\{p_\ell^{(1)}\}) \geq (1-\lambda)\, S_G(\{p_\ell^{(0)}\}) + \lambda\, S_G(\{p_\ell^{(2)}\})$$

### 3.3.3 Statistical entropy

We have defined a function $S_G$ (or $S_S$) for a stat. system

The constant seems arbitrary for the moment.

Take $k = k_B = 1.3806\,4852\ 10^{-23}\ \mathrm{J\,K^{-1}}$ Boltzmann constant.

$k_B = \frac{R}{N_A}$ ← perfect gas

- Consider a microstate where the system lays.

$$S_{\text{G}} = 0$$

- Equiprobable states $S_{\text{G}} = k_B \ln \Omega$ with $p_i = \frac{1}{\Omega}$
  $\Leftrightarrow$ uniform distribut° — maximal entropy

⇒ According to the fundamental postulate, a system isolated of energy $E$ will tend toward the uniform distribut° with $p_i = \frac{1}{\Omega(E)}$

uniform distribut°

$$\boxed{S = k_B \ln \Omega(E)}$$ Boltzmann grave

This formula is fundamental: It relates the entropy to the probability distribut° of microstates (i.e a statistical measure)

⇒ This is the bridge / connect° between our stat approach and the macro. thermodynamical word

For a non uniform distribut°, what should we do?

Natural general definition $S = -k_B \int_{\text{GV}} d\Gamma \; \rho(\vec{\Gamma}) \ln \rho(\vec{\Gamma})$

Take 2 independent system $\rho(\vec{\Gamma}_A, \vec{\Gamma}_B) = \rho(\Gamma_A)\, \rho(\Gamma_B)$

then $S = S_A + S_B$

For a discrete (Quantum) system

$$S = -k_B \sum_i p_i \ln p_i$$

## 3.3.4) Reformulation of the fundamental postulate (optional)

We have written a general definition of $S = -k_B \int d\Gamma\, \rho(\vec{\Gamma}) \ln \rho(\Gamma)$

For a uniform distribution $\rho(\vec{\Gamma}) \to \frac{1}{\Omega(E)}$ and $S \to k_B \ln \Omega(E)$

which is the stat. distribution → maximizes $S$

of an isolated (eq.) system of energy $E$ according to 1st principle.

Let us work in phase space (the same also holds in Q, M)

$$S = -k_B \int d\vec{\Gamma}\, \rho(\vec{\Gamma}) \ln \rho(\vec{\Gamma}) \quad \text{with} \quad \int d\vec{\Gamma}\, \rho(\vec{\Gamma}) = 1$$

**Question**: What is the proba distribution that maximizes $S$ (with constraint)?

$S = S[\rho]$ + constraint.

**Method**: Extremize $S[\rho] + \lambda \int d\Gamma^{(N)} [\rho(\Gamma) - 1]$ ← surface $H(\Gamma) = E$ up to $\delta E$ ← μ-canonical

↑ Lagrange multiplier $\lambda = \text{const}$

$$\delta \left\{ -k_B \int d^{6N}\Gamma\, \rho(\vec{\Gamma}) \ln \rho(\vec{\Gamma}) + \lambda \int d^{6N}\Gamma\, (\rho(\vec{\Gamma}) - 1) \right\} = 0$$

↑ with respect to $\rho \to \rho + \delta\rho$

$$\int d\vec{\Gamma} \left\{ -k_B\, \delta\rho(\vec{\Gamma}) \ln \rho(\vec{\Gamma}) - k_B\, \delta\rho(\vec{\Gamma}) + \lambda \delta\rho(\vec{\Gamma}) \right\} = 0 \quad \forall \delta\rho(\vec{\Gamma})$$

$$-k_B\, \delta\rho \ln \rho(\vec{\Gamma}) - k_B\, \delta\rho + \lambda \delta\rho = 0 \Rightarrow \delta\rho \left[ k_B \ln \rho + k_B - \lambda \right] = 0$$

$$\Leftrightarrow \rho(\vec{\Gamma}) = \exp\left( \frac{\lambda}{k_B} - 1 \right) = \text{const independent of } \vec{\Gamma} \text{ uniform}$$

Pb what is $\lambda$?

remember $\int d\Gamma\, \rho(\vec{\Gamma}) = 1$

$$e^{\frac{\lambda}{k_B} - 1} \int d\Gamma = 1 \Leftrightarrow e^{\frac{\lambda}{k_B} - 1} = \frac{1}{\nu(E, \delta E)}$$

we thus recover $\rho(\vec{\Gamma}) = \dfrac{1}{\nu(E, \delta E)}$ → it is a maximum

Equiv

→ **Principle**: For an isolated system of energy $E$ at equilibrium, the proba density converges toward a quantity called entropy that maximizes its entropy

What is the entropy? $S = -k_B \int d^{6N}\Gamma \, \rho(\Gamma) \ln \rho(\Gamma)$

$\Rightarrow S \to S^* = -k_B \ln \tilde{\rho}(E) \underbrace{\int d^{6N}\Gamma \, \rho(\Gamma)}_{=1} = k_B \ln(\underbrace{\nu(E,\delta E)}_{\nu'(E)\delta E})$

In the quantum formulation

$$S \to S = k_B \ln \underbrace{\Omega(E)}_{\text{nb of microstates} \in [E, \delta E]}$$

Therefore, we recover another formulation of the fundamental postulate.
we should maximize the entropy

Advantages: We treate isolated system with only E conserved.
We can extend this approach to other types of constraints.
say for example angular momentum $\vec{L}_{tot}$.

<u>$S = S(E, V, N)$ plays the role of the generating function</u>

3.3 <u>Properties of entropy</u>: We have seen that if $\mathcal{Y} = \mathcal{Y}_1 \otimes \mathcal{Y}_2 \to$ independent.
then $S = S_1 + S_2$ <u>extensivity of entropy</u>

<u>Question</u>: when can we say that $\mathcal{Y} = \mathcal{Y}_1 \otimes \mathcal{Y}_2 - - \otimes \mathcal{Y}_N$?
For a system of N subsystems, (N particles), this is the case
when the interaction between its constituents are short-ranged

then $S(\mathcal{Y}_1 \otimes \mathcal{Y}_2 - - \otimes \mathcal{Y}_N) \simeq \sum_{i=1}^{N} S(\mathcal{Y}_i)$.

For N identical particles $S_N \simeq N S_{ind}$

and $\boxed{S(E, N, V) = N \, s\left(\frac{E}{N}, \frac{V}{N}\right)}$ ← entropy per particle

$\Omega \propto e^{S} \propto e^{N s(\cdots)}$

The nb of microstate <u>increases exponentially with N</u> !!

## 3.3.6 Examples

Ex 1 : Gas of free particles ($N$ identical)

$$\Omega(E) = \rho(E)\,\delta E = \phi'(E)\,\delta E$$

where $\phi(E)$ = total nb of microstates of energy $\leq E$

We found $\phi_{id}(E) = \dfrac{V^N}{N!\,h^{3N}} (2mE)^{3N/2} \dfrac{\pi^{3N/2}}{\Gamma\left(1+\frac{3N}{2}\right)}$

$$\phi'(E) = \frac{3N}{2E}\,\phi(E)$$

$$S = k_B \ln\left(\frac{3N}{2E}\,\phi(E)\,\delta E\right) = \underbrace{k_B \ln(\phi(E))}_{\text{of order } O(N)} + \underbrace{k_B \ln\left(\frac{3N}{2E}\,\delta E\right)}_{\sim \ln N}$$

if $N$ is of order $10^{23} \simeq N_A$

$$S \simeq k_B \ln \phi(E)$$

Basically, in the $N \to \infty$ limit, we can indifferently take inside the ln( the total volume accessible ($\in [E, E+\delta E]$) or ($\in [0, E]$)

Does not change because, we are dominated by the edges

Using Stirling $N! \simeq N^N e^{-N} \sqrt{2\pi N} \Leftrightarrow \ln N! \simeq N(\ln N - 1) + \frac{1}{2}\ln(2\pi N)$

$$\phi(E) \simeq \frac{e^{5N/2}}{\pi \sqrt{6}\, N} \left(\frac{V}{N}\right)^N \left(\frac{mE}{3\pi\hbar^2 N}\right)^{3N/2}$$

$$\boxed{S(E) \simeq N k_B \left(\frac{5}{2} + \ln\left[\frac{V}{N}\left(\frac{mE}{3\pi\hbar^2 N}\right)^{3/2}\right]\right)}$$

formula of Sackur & Tetrode

RQ: we neglect a term in $-k_B \ln(\pi\sqrt{6}N)$ → subleading.

RQ: $S(E) = N k_B \left\{\ln\left(\frac{V}{N}\cdot\left(\frac{E}{N\varepsilon_0}\right)^{\alpha}\right) + \text{const}\right\}$ we could have guessed this by extensivity

## Ex2 : Paramagnetic crystal

We consider N atoms forming a crystal. (No kinetic energy)

The atom i has a magnetic moment $\vec{m}_i = \gamma \vec{S}_i$

here $S^i = \pm \frac{\hbar}{2}$ → 2 levels / atom.

Microstate = $|\uparrow\rangle_1 \otimes |\downarrow\rangle_2 \otimes \dots \otimes |\uparrow\rangle_N = |\uparrow\downarrow\dots\uparrow\rangle$

In a magnetic field $H_{mag} = -BM_z =$ where $\vec{B} = B\vec{e}_z$

$= -B\gamma S^z = \mp \gamma B \frac{\hbar}{2} = \mp \mu_B \varepsilon_B$ → $\varepsilon_\uparrow = -\varepsilon_B$, $\varepsilon_\downarrow = +\varepsilon_B$

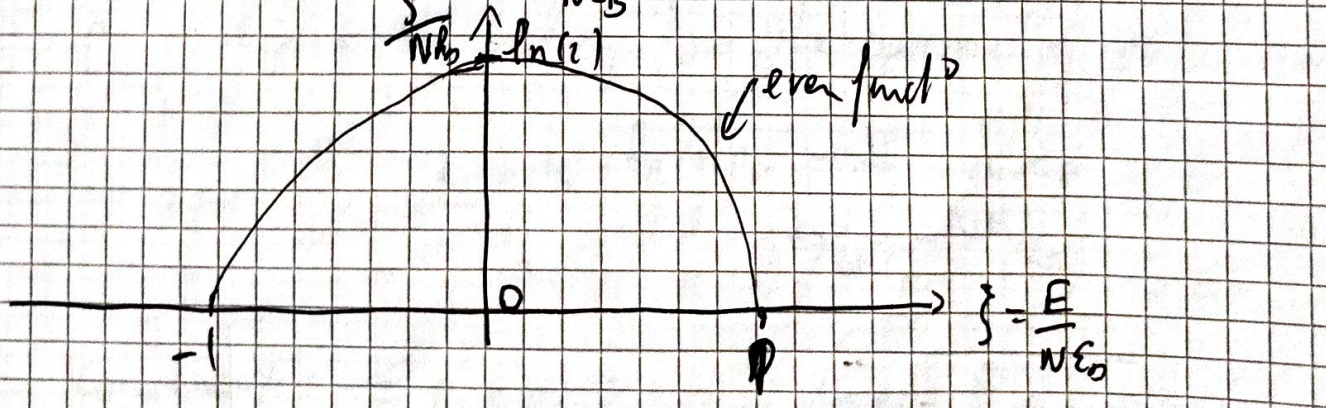
⇒ we are dealing with a system of N 2-states systems.

$$\rightarrow \begin{cases} N = n_\uparrow + n_\downarrow \\ E = (-n_\uparrow + n_\downarrow)\varepsilon_B \end{cases} \Leftrightarrow \begin{cases} n_\uparrow = \frac{1}{2}\left(N - \frac{E}{\varepsilon_B}\right) \\ n_\downarrow = \frac{1}{2}\left(N + \frac{E}{\varepsilon_B}\right) \end{cases}$$

$$\Omega = \frac{N!}{n_\uparrow!\, n_\downarrow!} \rightarrow S = k_B \ln \Omega$$

we find $S^*(E, B, N) \simeq N k_B \left[ \ln 2 - \frac{(1-\zeta)\ln(1-\zeta) + (1+\zeta)\ln(1+\zeta)}{2} \right]$

where $\zeta = \frac{E}{N\varepsilon_B} \in [-1, 1]$




We can also write $S_{spin} = \frac{S}{N} = -k_B(p_\uparrow \ln p_\uparrow + p_\downarrow \ln p_\downarrow)$ ← Gibbs entropy

with $p_\uparrow = \frac{n_\uparrow}{N}$ ; $p_\downarrow = \frac{n_\downarrow}{N}$

## Ex 3 Maxwell Boltzmann distribution

Consider $N$ particles, independent, in some external potential $V_{ext}(\vec{r})$
→ Assume they are isolated. $E = N\varepsilon$

What is the probability distribution?

Consider a single particle. Microstate: $\{\vec{r}, \vec{p}\}$

Energy: $\varepsilon = \frac{1}{2} m \vec{v}^2 + V_{ext}(\vec{r}) = \frac{\vec{p}^2}{2m} + V_{ext}(\vec{r})$

Suppose we partition the phase space in tiny volumes / boxes labelled by $\nu$


$$\varepsilon_\nu = \frac{1}{2} m \vec{v}_\nu^2 + V_{ext}(\vec{r}_\nu)$$

$E/N$

We are interested in $p_\nu$ such that $\sum_\nu p_\nu = 1$, $\sum_\nu \varepsilon_\nu p_\nu = \varepsilon$

Consider $\mathcal{F} = -k_B \sum_\nu p_\nu \ln p_\nu - \lambda_0 \left(\sum_\nu (p_\nu) - 1\right) - \lambda_1 \left(\sum_\nu \varepsilon_\nu p_\nu - \varepsilon\right)$

$p_\nu$ is found by looking for the extrema of $\mathcal{F}$

$$\frac{\partial \mathcal{F}}{\partial p_\nu} = 0 \Rightarrow -k_B - k_B \ln p_\nu - \lambda_0 - \lambda_1 \varepsilon_\nu = 0$$

$$p_\nu = e^{-1 - \lambda_0/k_B} e^{-\lambda_1 \varepsilon_\nu / k_B}$$

Constraint $\sum_\nu p_\nu = 1$ & $\sum_\nu \varepsilon_\nu p_\nu = \varepsilon$

$$p_\nu = \frac{e^{-\frac{\lambda_1}{k_B}\left(\frac{1}{2} m v_\nu^2 + V_{ext}(\vec{r}_\nu)\right)}}{\sum_\nu e^{-\frac{\lambda_1}{k_B}\varepsilon_\nu}}$$

This is the Maxwell-Boltzmann distribution for the velocities

We will see next that $\lambda_1 = T^{-1}$ the inverse of temp.

# 3.4 Relations with thermodynamics

## 3.4.1 Generalities

Thermodynamics deals with macroscopic bodies (gas, liquids, magnets, ...) subject to temperature and/or external forces

- This is a self-contained theory which relates observable quantities within each other
- No assumption is made on microscopics
- It was mainly developed empirically based on experiments (gas expansions and applications to heat engines)
  → It was realized that it can be applied to all sorts of systems such as magnets

In thermodynamics, a gas of $N$ particles of energy $E$ in a volume $V$ is characterized by $\{E, V, N\}$ (extensive variables)

$E = U$ in thermo

Entropy $S_{th}(E, V, N)$ = generating function

$$dS_{th} = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

($\frac{1}{T}$: temp., $\frac{P}{T}$: pressure, $\frac{\mu}{T}$: chemical potential)

$$\frac{1}{T} = \left(\frac{\partial S_{th}}{\partial E}\right)_{V,N} \quad ; \quad \frac{P}{T} = \left(\frac{\partial S_{th}}{\partial V}\right)_{E,N} \quad ; \quad \mu = -T\left(\frac{\partial S_{th}}{\partial N}\right)_{E,V}$$

By analogy with thermo, we may define similar quantities

$$\frac{1}{T^*} = \frac{\partial S^*(E,V,N)}{\partial E} \quad ; \quad \frac{P^*}{T^*} = \left(\frac{\partial S}{\partial V}\right) \quad ; \quad \mu^* = -T^*\left(\frac{\partial S}{\partial N}\right)$$

and $$dS^* = \frac{1}{T^*} dE + \frac{P^*}{T^*} dV - \mu^* dN$$

$T^*, P^*, \mu^*$ = intensive variables

Similarly $C_V^* = \frac{\partial E}{\partial T^*} = \frac{1}{\left(\frac{\partial T}{\partial E}\right)^{-1}}$ heat capacity

$$\Rightarrow C_V^* = -\frac{1}{T^{*2}} \left(\frac{\partial^2 S^*}{\partial E^2}\right)^{-1} = -\frac{\left(\frac{\partial S^*}{\partial E}\right)^2}{\left(\frac{\partial^2 S^*}{\partial E^2}\right)}$$

### 3.4.2) Application to the gas of particles

From the Sackur-Tetrode formula, we directly get $\frac{\partial S^*}{\partial E} = \frac{3 N k_B}{2E}$

$$\frac{P^*}{T^*} = \frac{\partial S^*}{\partial V} = \frac{N k_B}{V} \; ; \; \frac{\partial S^*}{\partial N} = k_B \ln\left(\frac{V}{N}\left(\frac{mE}{3\pi\hbar^2 N}\right)^{\frac{3}{2}}\right)$$

$$\frac{1}{T^*} = \frac{3 N k_B}{2E} \Rightarrow E = \frac{3}{2} N k_B T^*$$

$$\frac{P^*}{T^*} = \frac{N k_B}{V} \Rightarrow \boxed{P^* V = N k_B T^*} \Rightarrow \text{eq. of state of a perfect gas}$$

This proves that our analogy is consistent because we recover the eq. of state of a perfect gas from our microscopic def. of the entropy!

This means (at least suggests) that $S^* = k_B \ln \Omega(E)$ corresponds also to the thermodynamic entropy (for the gas at least)

Similarly $C_V^* = \frac{3}{2} N k_B$

RQ => Note that our consideration on the perfect gas draw a bridge between microscopic considerations (through $S^*$) and macroscopic quantities => This is a conceptual breakthrough

## 4.3 Validity of the semi classical approach

Come back to the Sackur-Tetrode formula:

$$S^*(E) = N k_B \left[ \frac{5}{2} + \ln \left[ \frac{V}{N} \left( \frac{m E}{3\pi\hbar^2 N} \right)^{\frac{3}{2}} \right] \right]$$

intensive: entropy per particle

$$s^*(E) = \frac{S(E)}{N} = k_B \left[ \frac{5}{2} + \ln \left( v \left( \frac{2\pi m k_B T^*}{h^2} \right)^{\frac{3}{2}} \right) \right]$$

where we used $T = \frac{3}{2} N k_B T^*$ and $v = \frac{V}{N}$

$s(E)$ is as expected a funct° of intensive variables

$$s^*(E) = k_B \left[ \frac{5}{2} + \ln \left( \frac{v}{\lambda_T^3} \right) \right] \quad \text{where} \quad \lambda_T = \sqrt{\frac{h^2}{2\pi m k_B T^*}}$$

$\lambda_T$ = De Broglie wave-length

or $s(E) = k_B \left( \frac{5}{2} + \ln (n \lambda_T^3) \right)$ where $n = \frac{1}{v}$ particle density

RQ: $\lambda_T \propto \hbar$ → quantum wave-length

This is the quantum spatial extent of the particle

high $T$ → $\lambda_T \to 0$ ← $\lambda_T \to \infty$ At low $T$

$\lambda_T \nearrow$ when $T \searrow$

Limit of the ideal gas approximation:

$$s(E) \geq 0 \Rightarrow n \lambda_T^3 \ll 1$$

$$\Rightarrow \lambda_T^3 \ll d^3$$

where $d = \sqrt[3]{v}$ typical distance between particles

$$\Rightarrow \boxed{\lambda_T \ll d}$$

For our semi-classical treatment to be valid, we therefore need that the distance between particles to be larger than the De Broglie wave length.

If not

it means, particles wave functions start to overlap

$\Rightarrow$ Quantum effects need to be taken into account more rigorously. In particular, we need to incorporate the postulates about symmetrization {for bosons} and antisymmetrization {for fermions}

New effects pop in
- Bosons at very low $T$ condensate: Bose-condensation
- fermions obey Pauli principles

* Another to view it (see Nuorind)

Write $\frac{V}{N} = (\Delta x)^3 \sim$ volume per particle $= v$

$\frac{h}{\lambda_T} \sim \Delta p \sim$ momentum associated to the particle wave

$$S^* = 3Nk_B \ln\left(a \frac{\Delta x \Delta p}{h}\right) \quad \text{with } a \in e^{\frac{5}{3}} \sim 10$$

a number

$S^* \geq 0 \Rightarrow \underline{a \Delta x \Delta p \gg h}$ ||

we recover some uncertainty principle.

When $\Delta x \Delta p \sim h \Rightarrow$ Quantum effects must be treated with care

As $S = k_B \ln \Omega$

$\Rightarrow \Omega = \left( \frac{a \Delta x \Delta p}{h} \right)^{3N} >> 1$ $\quad \Omega = \#$ accessible states (taking into account indiscernability)

- For bosons (symmetrized)

The semi-classical limit is violated in a dilute gas of bosons for $T \leq (\quad \mu K)$ $\rightarrow$ Then they condensate

see Bose Einstein condensation

In dense matter, $T \leq (\quad (K))$. This leads to exotic but important phenomena such as superfluidity or superconductivity (high T superconductivity)

- For fermions (electrons)

A typical metal has a huge Fermi energy $O(eV)$

Therefore for a piece of metal (a coin), the semi-classical condition demands $T \geq O(10^4 K)$

$\Rightarrow$ At room T, your coin, demands a full quantum treatment. Electrons (in a metal) at room T are almost never in the dilute regime.

## Boson undistinguishability

In quantum mechanics, two identical particles are undistinguishable

Let's consider 2 particles and define the state vector associated to those particles

- If these 2 particles are **bosons**, the 2-particle state vector shall be invariant under permutation
- If these 2 particles are **fermions**, the 2-particle state vector shall be antisymmetric under permutation

Particles with an integer spin are bosons ($s = 0, 1, 2, \dots$)
Half-integer ——— fermions ($s = \frac{1}{2}, \frac{3}{2}, \dots$)

We can extend that to N-particles state vectors

Symmetrization or antisymmetrization put a lot of constraints on the Hilbert space.

Consider N bosons, where $\mathcal{H}_i$ denotes the Hilbert space for the $i^{th}$ part.

$$\mathcal{H}_{N\,\text{bosons}} = \left[\mathcal{H}_1 \otimes \mathcal{H}_2 \otimes \dots \otimes \mathcal{H}_N\right]_{\text{symm.}}$$

$$\mathcal{H}_{N\,\text{fermions}} = \left[\mathcal{H}_1 \otimes \mathcal{H}_2 \otimes \dots \otimes \mathcal{H}_N\right]_{\text{antisymm}}$$

where sym/antisym means we shall construct a symetrized/antisymetrized version of the state.

Ex: Consider 2 particles

$$|\psi_1\rangle_{\text{part}_1} \otimes |\psi_2\rangle_{\text{part}_2} \xrightarrow{\text{sym}} \frac{1}{\sqrt{2}}\left[|\psi_1\rangle \otimes |\psi_2\rangle + |\psi_2\rangle \otimes |\psi_1\rangle\right] = |\psi_1 \psi_2\rangle_{\text{boson}}$$

$$|\psi_1\rangle_{\text{part}_1} \otimes |\psi_2\rangle_{\text{part}_2} \xrightarrow{\text{antisym}} \frac{1}{\sqrt{2}}\left[|\psi_1\rangle \otimes |\psi_2\rangle - |\psi_2\rangle \otimes |\psi_1\rangle\right] = |\psi_1 \psi_2\rangle_{\text{fermions}}$$

A few consequences

- Bosons can occupy the same state in an unlimited number. Eventually, they can macroscopically occupy the same state
  → Bose condensation
- Fermions: the antisymmetrization induces Pauli principle: A single state can be occupied at most by one fermion

- Symmetrization between identical particles induce some correlations between particles (even without interactions!!)
  → bunching vs antibunching

⇒ In stat mech, what matters is what single states are occupied or not ⇒ somehow simpler. Do not label or follow the particles. Only the accessible states being empty or occupied matter