Chap 6 | Equivalence between the ensembles

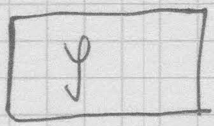
①

I) Comparisons

We introduce two ensembles and define similar quantities: T, P, S
However, the ensembles are distincts so are their proba distrib.

Comparing them? Relat° to thermodynamics?

μ canonical

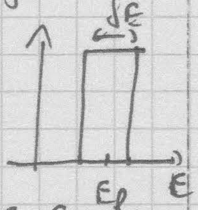


E fixed to δE

E fixed

$$\Omega(E)=\sum_{\ell}\delta(E-E_\ell)=\rho(E)\,\delta E$$

$$P_\ell^*(E)=\frac{\delta(E-E_\ell)}{\Omega(E)}$$



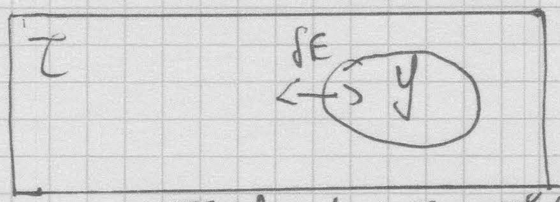
where $\delta(E-E_\ell)=\begin{cases}1 & E_\ell-\frac{\delta E}{2}<E<E_\ell+\delta E/2\\ 0 & \text{otherwise}\end{cases}$

$$S^*(E)=k_B\ln\Omega(E)$$

generating funct°

↓ thermo quantities

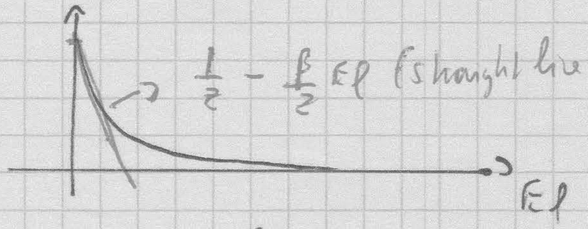
canonical



T fixed → $T=T^*(\tau)$

$$Z(T)=\sum_\ell e^{-\beta E_\ell}$$

$$P_\ell^c(E_\ell)=\frac{e^{-\beta E_\ell}}{Z}$$ regular



$$F(T)=-k_BT\ln Z$$

generating funct° of cumulants

thermo quantities

Example of the paramagnetic crystal (see tutorial)

μ canonical : $E=-\mu B\sum_{i=1}^{N}\varepsilon_i$

$\hookrightarrow \Omega=\frac{N!}{N_+!\,N_-!}$ with $N_\pm=\frac{1}{2}\left(N\mp\frac{E}{\varepsilon_B}\right)$ $(\varepsilon_B=\mu B)$

$$S^*(E)=k_B\ln\Omega\simeq Nk_B\left(\ln 2-\left(\frac{1-\xi}{2}\right)\ln(1-\xi)-\left(\frac{1+\xi}{2}\right)\ln(1+\xi)\right)$$

where $\xi=\frac{E}{\varepsilon_B}$

We find $T^{*-1} = \frac{\partial S}{\partial E} = \frac{k_B}{2\varepsilon_B} \ln \frac{1-\zeta}{1+\zeta} \Rightarrow \tilde{\beta}^* = \frac{\varepsilon_B}{k_B T^*} = \frac{1}{2} \ln \frac{1-\zeta}{1+\zeta}$

Canonical Treatment

$$Z = \left[2\cosh(\beta\varepsilon_B)\right]^N \rightarrow \overline{E}^c = -N\mu B \tanh(\beta\mu B)$$

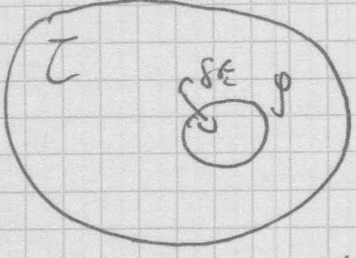
$$\overline{\zeta} = \frac{\overline{E}}{N\varepsilon_B} = -\tanh(\tilde{\beta}) \quad \text{with } \tilde{\beta} = \frac{\varepsilon_B}{k_B T} \Leftrightarrow \tilde{\beta} = \frac{1}{2} \ln \frac{1-\overline{\zeta}}{1+\overline{\zeta}}$$

$$\frac{S^c}{Nk_B} = S^* \text{ provided } \zeta = \overline{\zeta}$$

Both ensembles give the same thermodynamics if

$$\begin{cases} T^* = T \\ E = \overline{E}^c \end{cases}$$

II) General case



$$E_{tot} = \overset{E}{\overset{\parallel}{E_s}} + E_\tau \quad \text{conserved.}$$

$$\rho(E) = \frac{\Omega_S(E)\,\Omega_\tau(E_{tot}-E)}{\sum_E \Omega_S(E)\,\Omega_\tau(E_{tot}-E)}$$

Thus $\rho(E) \propto e^{-\beta E}\,\Omega_S(E)$ where $\beta = \frac{1}{k_B T_\tau^*} = \underbrace{\frac{\partial S_\tau}{\partial E}}_{\text{usual } T} \times \frac{1}{k_B}$

Thus $\rho(E) \propto e^{-\beta E + S^*(E)/k_B}$

where $S^*(E) = k_B \ln \Omega_S(E)$

$$\Rightarrow \rho(E) \propto e^{-\beta \mathcal{F}(E,T)} \quad \text{where } \boxed{\mathcal{F}(E,T) = E - T\,S^*(E)}$$

where $\mathcal{F}(E,T)$ is some "free energy"

⚠ $\mathcal{F}$ is not a microcanonical free energy : $\mathcal{F}^*(E) = E - T^* S^*(E)$

Through $\mathcal{F}(E,T)$, we see the competition between 2 terms:

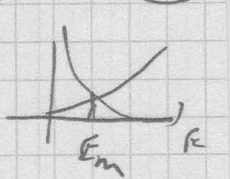
Maximum $\rho(E)$ $\Rightarrow$ Decrease E or increase $S^*(E)$ (entropy)

Max $\beta \frac{\partial}{\partial E}\mathcal{F}(E,T) = 0 \Rightarrow \frac{\partial}{\partial E}\left(\beta E - \frac{S^*(E)}{k_B}\right) = 0$

$E_m \equiv$ most likely value $\Rightarrow T^*(E_m) = T$

~~where E_m is the pt where the increase of E is compensated by S^*~~

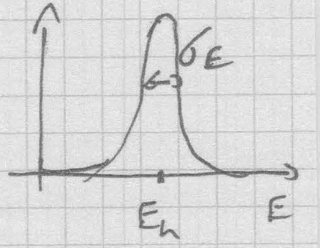
The value E_m or E^* correspond to a balance between the two distributions, the decrease of $e^{-\beta E}$ and the increase of $e^{S^*(E)}$



Actually, we can now expand $\rho(E)$ around E_m

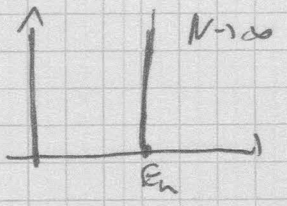
$$\rho(E) \propto e^{-(E-E_m)^2/2\sigma_E^2}$$

where $E_m \propto N$ and $\sigma_E \propto \sqrt{N}$



In the thermodynamical limit

$$\underset{\text{canonical}}{\rho(E,T)} \longrightarrow \rho^*(E, E_m) = \delta(E-E_m)$$



A mathematical way to view it is to calculate the partitio functio in the canonical formalism following the same approx.

$$Z = \sum_\ell e^{-\beta E_\ell} = \int dE\, \rho(E)\, e^{-\beta E} = \int dE\, \frac{\Omega(E)}{\delta E}\, e^{-\beta E}$$

$$= \frac{1}{\delta E}\int dE\; e^{\frac{S^*(E)}{k_B} - \beta E} = \frac{1}{\delta E}\int dE\, e^{-\beta F(E,T)}$$

$$= \frac{1}{\delta E}\, e^{\frac{1}{k_B}S^*(E_m) - \beta E_m} \times \sqrt{2\pi k_B\, \sigma_E^2}$$

where $\sigma_E^{-2} = \left|\frac{\partial^2 S^*(E)}{\partial E^2}\right|\Big|_{E=E_m}$

$$F = -k_B T \ln Z = E_m - T S^*(E_m) - \underbrace{k_B T \ln\left(\sqrt{2\pi k_B}\,\frac{\sigma_E}{\delta E}\right)}_{\ln(N)}$$

In the thermo limit, we restore extensivity of F

$$F \simeq E_m - T S^*(E_m)$$

where E_m defined by $T^*(E_m) = T$

Canonical entropy $S^c = \frac{\bar{E}^c - F}{T} = -\frac{\partial F}{\partial T} = \frac{\bar{E}^c}{T} - k_B \ln Z$

$$= \underbrace{\frac{\bar{E}^c - E_m}{T}}_{\simeq 0} + S^*(E_m) + O(\ln N)$$

$$\Rightarrow \boxed{S^c = S^*(E_m) \quad \text{where} \quad T^*(E_m) = T}$$

In the thermodynamic limit, all macroscopic variables/observables become extensive (we can neglect the $\ln(N)$ terms in entropy) or term in $\sqrt{N}$ in the free energy.

In that limit $S^c = S^*$

$\bar{E}^c = E_m$

and all quantities which derive from S^* are equal

$p^* = p^c$, $\mu^* = \mu^c$; etc...

$\Rightarrow$ In the thermodynamical limit, where fluctuat° are negligible compared to their average, both ensembles coincide!

III) About indiscernability & Maxwell Boltzmann approximat°

III.1) Reminder ~~We~~ focus on identical particles. So far we have treated it classically by the adjunct° of the $1/N!$ in our counting factor. However, the quantum formalism has strong implications:

- For a set of N bosons, state vectors ~~of~~ must be invariant under permutations
  → integer spins → symmetrizat° of the many-body wave funct°
- For a set of N fermion, state vectors must be antisymmetric under permutat°
  → ½ integer spins

Therefore, identical particles have a much reduced Hilbert space compared to non-identical ones:

$$\mathcal{H}_{N\,\text{bosons}} = [\mathcal{H}_1 \otimes \mathcal{H}_2 - - - \otimes \mathcal{H}_N]_{\text{sym}}$$

$$\mathcal{H}_{N\,\text{fermion}} = [\;\underline{\qquad\qquad}\;]_{\text{antisym}}$$

Take two particles $\in \mathcal{H}_1 \otimes \mathcal{H}_2 \longrightarrow |\lambda_1\rangle_{p1} \otimes |\lambda_2\rangle_{p2}$

If they are identical bosons $|\lambda_1, \lambda_2\rangle_{\text{boson}} = \frac{1}{\sqrt{2}}\left[|\lambda_1\rangle_{p_1} \otimes |\lambda_2\rangle_{p_2} + |\lambda_2\rangle_{p_1} \otimes |\lambda_1\rangle_{p_2}\right]$

obtained by symmetrization

If they are identical fermions

$$|\lambda_1, \lambda_2\rangle_{\text{fermion}} = \frac{1}{\sqrt{2}}\left[\underline{\qquad} \ominus \underline{\quad}\right]$$

Consequences: • The antisymmetrizat° ~~principle~~ of the wave function implies the Pauli principle: A single state cannot be occupied by more than one fermion!

⇒ The symmetrizat° or (antisym.) of the states implies correlat° between particles → collective behaviour

⇒ This will dramatically change the way we count states. What matters is the occupat° of each individual states!

2 Consequences of indiscernability on counting of states

The physical space is the symmetric (resp. antisym.) under exchange.
Therefore we should forget thinking in terms of single state.

What matters in such Hilbert space is the occupation of each individual states

→ Let us label them as $|\lambda_1, \ldots, \lambda_N\rangle \equiv \{|\lambda_1\rangle \otimes \ldots \otimes |\lambda_N\rangle\}$
where $|\lambda_1, \ldots, \lambda_N\rangle \in \mathcal{H}_1 \otimes \ldots \otimes \mathcal{H}_N$

Consider a non-interacting ph of bosons or fermion whose Hamiltonian is separable $H = \sum_{i=1}^{N} H_i \Rightarrow E_{\lambda_1, \ldots, \lambda_N} = \varepsilon_{\lambda_1} + \ldots + \varepsilon_{\lambda_N}$

Partition function ?

$$Z_{bos} = \sum_{\lambda_1, \ldots, \lambda_N} \frac{n_{\lambda_1}!\, n_{\lambda_2}! \ldots n_{\lambda_N}!}{N!} e^{-\beta E_{\lambda_1, \ldots, \lambda_N}}$$

$$Z_{fer} = \frac{1}{N!} \sum_{\lambda_1 \neq \ldots \neq \lambda_N} e^{-\beta E_{\lambda_1, \ldots, \lambda_N}}$$

where $n_{\lambda_i} \in \mathbb{N}$ is the number of particles occupying the single state $|\lambda_i\rangle$

→ we see that this is a priori not obvious to calculate Z

3 Maxwell-Boltzmann approximation

If we assume that the terms dominating these sums are such that the constraints do not matter → This will the case in the dilute limit where the probability of occupat° of a single state is weak

Then we expect $Z_{bos} \simeq Z_{fer} \simeq \frac{1}{N!} \sum_{\lambda_1, \ldots, \lambda_N} e^{-\beta(\varepsilon_{\lambda_1} + \ldots + \varepsilon_{\lambda_N})}$

$$\simeq \frac{1}{N!} \left(\sum_{\lambda} e^{-\beta \varepsilon_\lambda} \right)^N = \frac{1}{N!} z^N$$

This is the Maxwell-Boltzmann approximat°

Actually, such approx is similar to the semi-classical approx we used to calculate the density of states.

$$Z = \int dE\, \rho(E)\, e^{-\beta E} \rightarrow \text{Laplace transform of the d.o.s.}$$

The fact that particles are identical only enter through the $\frac{1}{N!}$

The nature of particles do not matter here. Validity?

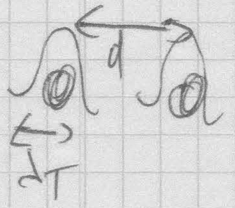
We have seen that $z = \frac{V}{(\lambda_T^3)}$ where $\lambda_T = \sqrt{\frac{2\pi\hbar^2}{m k_B T}}$

$$Z_{MB} \simeq \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N \simeq \frac{e^N}{\sqrt{2\pi N}}\left(\frac{V}{N\lambda_T^3}\right)^N$$

Semi-classical approx implies $\Omega >> 1$ which also implies $Z >> 1$

$$\left(\frac{V}{N\lambda_T^3}\right)^N >> 1 \Rightarrow \underbrace{\left(\underbrace{\frac{V}{N}}_{v}\right)^{1/3}}_{\text{average distance between particles}} >> \underbrace{\lambda_T}_{\text{De Broglie wave length}} \propto T^{-1/2}$$

This indeed corresponds to the dilute regime.



when $d \sim \lambda_T \Rightarrow$ quantum effects set in!
and therefore correlat°

Numbers: Consider Helium at room T and P, we obtain $\lambda_T \sim 0.5$ Å

No problem. M.B works.

we need to go to very low T to feel Quantum effects
and high pressure $\rightarrow$ large density.

Helium becomes superfluid

see fountain effect

Quantum effects set in when $\lambda_T \sim n^{-1/3}$ where $n = \frac{N}{V}$ density.

$$\Leftrightarrow \underline{T_* \sim \frac{\hbar^2}{m k_B}\, n^{2/3}}$$

$T > T^* \Rightarrow$ M.B

$T < T^* \Rightarrow$ Q. Correlat° set in