Course 3. Ensemble representation

(1) Ensemble representation

- isolated system : microcanonical ensemble
- system ⊕ heat reservoir : canonical ensemble
- system ⊕ heat / particle reservoir : grandcanonical ensemble

(2) Applications

- classical identical particles : Gibbs paradox
- Equipartition theorem
- paramagnetism
- Maxwell velocity distribution

(3) Brief discussion on equilibrium between phases ~~or phase~~

(4) Others.

phase transition (?)

Motivation of Course 3.

In Course 2, the starting point is $\Omega^{(0)}(E)$.

If we know it, we can obtain all thermodynamic quantities.

$\boxed{\text{BUT}}$, in general, it is hard to obtain it.

So, in the present course, we will learn more tractable ways in terms of partition functions.

(1) Ensemble representation

◎ Isolated system : microcanonical ensemble

$\left\{ \begin{array}{l} \text{Constant energy} \in [E, E+\delta E]. \\ \text{Equilibrium.} \end{array} \right.$

$\Rightarrow$ P_r : probability of finding the system in state r,

$$P_r = \begin{cases} \text{Constant}, & \text{if } E < E_r < E + \delta E \\ 0 & \text{otherwise} \end{cases}$$

$\longleftrightarrow$ Postulate of equal a priori probability

$$\sum_r P_r = 1$$

⊙ System ⊕ heat reservoir with temperature T : Canonical ensemble

A ⊕ its heat reservoir A'

goal: probability P_r of finding the system A in any one particular state r with energy E_r? Note that $A \oplus A'$ is in equilibrium.

Assume : weak interaction between A and A' as usual

($A \oplus A'$ ~ isolated.

$$\Rightarrow \quad E_r + E' = E^{(0)}$$

$A \in$ a particular given state r

$A' \in$ state with energy $\in [\, E^{(0)} - E_r ,\ E^{(0)} - E_r + \delta E \,]$

$$\Rightarrow \quad P_r = C' \Omega' (E^{(0)} - E_r) \qquad (\because \text{equilibrium})$$

c' ~ independent of r.

$\sum P_r = 1$

Since A' acts as a heat reservoir of A.

$$E_r \ll E^{(0)} \qquad (~~remember~~ \text{ remember } \bar{E} \ll \bar{E}')$$

$$\ln \Omega' (E^{(0)} - E_r) = \ln \Omega' (E^{(0)}) - \underbrace{\left[\frac{\partial \ln \Omega'}{\partial E'} \right]_0}_{= \beta' = \beta} E_r \cancel{+ O(E_r^2)} \qquad (\because E_r \ll E^{(0)})$$

$(\because$ equilibrium$)$

$$\Rightarrow \quad \boxed{\begin{aligned} & P_r = C e^{-\beta E_r} \\ & C^{-1} = \sum_r e^{-\beta E_r} \equiv Z . \quad \text{partition function} \end{aligned}}$$

Canonical distribution

$e^{-\beta E_r}$ ~ Boltzmann factor

rapidly decreasing with E_r ↔ so is $\Omega' (E^{(0)} - E_r)$.

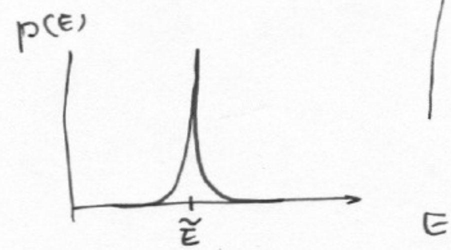
Canonical ~~distribution~~ ensemble :

$$\boxed{\text{An ensemble of systems all of which is in contact with a heat reservoir with temperature } T.}$$

ex: compare with the previous result of $P(E)$ in Course 2 :

Course 2: $P(E) \sim C\,\Omega(E)\,\Omega'(E^{(0)}-E)$

$\Omega(E)$: increasing, $\Omega'(E^{(0)}-E)$: decreasing



Course 3: $P(E) = \sum_r{}' P_r$ ($\sum_r{}'$: contributed from state r with energy ~~$(E, E+\delta E)$~~ $[E, E+\delta E]$)

$= C\,\Omega(E)\,e^{-\beta E}$

$\Omega(E)$: increasing, $e^{-\beta E}$: decreasing

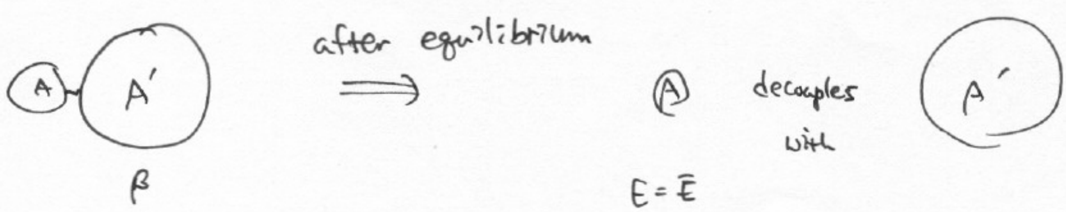
⊙ System with specified mean energy $\bar{E}$: canonical distribution

$\equiv$ system ⊕ heat reservoir with temperature T

$$\left(\bar{E} = \frac{\sum_r E_r e^{-\beta E_r}}{\sum e^{-\beta E_r}} \right)$$

A system A with ~~any~~ mean energy $\bar{E}$ ⊕ other systems acting as heat reservoirs (β)

proper choice of $\beta \to \bar{E}$.



◎ alternative derivation of canonical distribution :

$\boxed{\text{a system A with constant mean energy } \bar{E}}$

Its ensemble : a very large # a of such systems,

a_r of which $\in$ state r.

$$\begin{cases} \sum_r a_r = a \\ \frac{1}{a}\sum a_r E_r = \bar{E} \end{cases}$$

$\Gamma(a_1, a_2 \cdots)$: the # of distinct possible ways of

selecting a total of a distinct systems s.t.

$a_1 \in r=1$

$a_2 \in r=2$

$\vdots$

$$\Gamma(a_1, a_2 \cdots) = \frac{a!}{a_1! a_2! \cdots}$$

multinormial ~~[illegible]~~ factor

$\boxed{Q.}$ When has Γ a maximum ?

(Note $\sum_r a_r = a$, $\frac{1}{a}\sum a_r E_r = \bar{E}$ ~ constraints)

$\delta \ln \Gamma = 0$. $\Rightarrow$ $\ln \Gamma \simeq a \ln a - \sum a_r \ln a_r$ (Stirling formulas

$\delta a = 0$ $\qquad \delta \ln \Gamma = -\sum_r \delta a_r (1 + \ln a_r)$

$\delta \bar{E} = 0$

$\searrow \sum_r \delta a_r = 0$

$\Downarrow$

$\sum_r E_r \delta a_r = 0$.

the method of Lagrange multipliers

$\longrightarrow$

$$\sum_r (\ln a_r + \alpha + \beta E_r) \delta a_r = 0$$

all a_r's are independently varying.

$\Rightarrow$ $\ln \tilde{a}_r + \alpha + \beta E_r = 0$

$$\Rightarrow \quad \tilde{a}_r = e^{-\alpha} e^{-\beta E_r}$$

$$\left(\begin{array}{l} \sum_r a_r = a \\ \frac{1}{a} \sum a_r E_r = \bar{E} \end{array} \right) \Rightarrow$$ one can determine α and β.

→ We can conclude :

Canonical distribution corresponds to the one which makes the # Γ of possible configurations a maximum.

$$\tilde{P}_r \equiv \frac{\tilde{a}_r}{a} = \frac{1}{Z} e^{-\beta E_r}$$

$$\ln \Gamma = a \ln a - \sum_r a_r \ln a_r$$

$$= a \ln a - \sum_r a \tilde{P}_r \ln a \tilde{P}_r$$

$\swarrow$ $\sum P_r = 1$

$$= -a \sum_r P_r \ln P_r$$

$$\ln \tilde{\Gamma} = -a \sum_r \tilde{P}_r \left(-\ln Z - \beta E_r \right)$$

$$= +a \left(\ln Z + \beta \bar{E} \right)$$

$\swarrow$ ($S = k (\ln Z + \beta \bar{E})$ will be discussed later)

$$= \frac{a}{k} S$$

→ maximum $\overbrace{\text{value}}^{}$ possible of Γ → entropy of final equilibrium state.

※. $\boxed{S = -k \sum_r P_r \ln P_r}$ ~ it could be another good definition of entropy

Partition fn.

① Connection to thermodynamic quantities

$$\boxed{Z = \sum_r e^{-\beta E_r}}$$ - an unrestricted sum over all states.

$$\bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$$

$$\overline{(\Delta E)^2} = \overline{E^2} - \bar{E}^2 = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \bar{E}^2$$

$$= -\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial^2 \ln Z}{\partial \beta^2}$$

※ $\frac{\partial \bar{E}}{\partial \beta} \leq 0$ ($\because$ $\overline{(\Delta E)^2} \geq 0$ always)

a quasi-static change : $x \to x + dx$

$$đW = \frac{1}{Z}\sum e^{-\beta E_r}\left(-\frac{\partial E_r}{\partial x}dx\right)$$

$$= \frac{1}{Z}\left(\frac{1}{\beta}\frac{\partial}{\partial x}\right)\sum e^{-\beta E_r}dx = \frac{1}{Z\beta}\frac{\partial Z}{\partial x}dx = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x}dx$$

$$= \bar{X}\,dx. \qquad \bar{X} \equiv -\overline{\frac{\partial E_r}{\partial x}}$$

$$\rightarrow \bar{X} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x}$$

(e.g.) $x = V$: $\bar{p} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}$

Classical case :

$$Z = \int \frac{dq_1 \cdots dq_f\, dp_1 \cdots dp_f}{h_0^f} e^{-\beta E(q_1, \cdots, p_f)}$$

(※ see Gibbs paradox)

- external parameter x

$E_r = E_r(x)$

$\Rightarrow Z = Z(\beta, x)$

$$d\ln Z = \frac{\partial \ln Z}{\partial x} dx + \frac{\partial \ln Z}{\partial \beta} d\beta$$ quasi-static process

$$= \beta \, đW - \bar{E} \, d\beta$$

$$\Rightarrow d(\ln Z + \beta \bar{E}) = \beta(đW + d\bar{E}) = \beta \, đQ$$

$\because \; dS = \frac{đQ}{T}$ for quasistatic case

$$\boxed{S \equiv k(\ln Z + \beta \bar{E})}$$

This definition is identical to $S \equiv k \ln \Omega(\bar{E})$

$$\because \quad Z = \sum_r e^{-\beta E_r} = \sum_E \Omega(E) e^{-\beta E}$$

$$\simeq \Omega(\bar{E}) e^{-\beta \bar{E}} \frac{\Delta^* E}{\delta E}$$ ($\because$ $\Omega(E) e^{-\beta E}$ has a very sharp maximum)

$$\Rightarrow \ln Z = \ln \Omega - \beta \bar{E} + \cancel{\ln \frac{\Delta^* E}{\delta E}}$$

($\because$ $O(\ln f)$) $\quad \Delta^* E \sim \frac{1}{\sqrt{f}}$

$$\Rightarrow S = k(\ln Z + \beta \bar{E})$$

$$F = \bar{E} - TS = -kT \ln Z$$ F ~ Helmholtz free energy

$T \to 0$, $\quad Z \to \Omega_0 e^{-\beta E_0} \quad \Rightarrow S \to k(\ln Z + \beta \bar{E}) = k \ln \Omega_0$

energy shift $\quad E_r^* \to E_r + \epsilon_0$

$$\rightarrow Z^* = \sum_r e^{-\beta(E_r + \epsilon_0)} = e^{-\beta \epsilon_0} Z$$

$$\bar{E}^* = -\frac{\partial \ln Z^*}{\partial \beta} = \bar{E} + \epsilon_0$$

$$S^* = k(\ln Z^* + \beta \bar{E}^*) = k(\ln Z + \beta \bar{E})$$

- $A^{(0)} = A + A'$ (weakly interacting)

$E_{rs}^{(0)} = E_r + E_s'$

$$Z^{(0)} = \sum_{r,s} e^{-\beta E_{rs}^{(0)}} = Z Z'$$

$$\ln Z^{(0)} = \ln Z + \ln Z'$$

$$\Rightarrow \quad \bar{E}^{(0)} = \bar{E} + \bar{E}'$$

$$\left(\quad S^{(0)} = S + S' \right.$$

※ In course 2 : knowledge of $\Omega(E) \longrightarrow$ quantities

3 $\quad Z \quad \nearrow$

Notice that Z can be obtained more easily than ~~to~~ $\Omega(E)$, since Z contains unrestricted sums ~~but~~ while $\Omega(E)$ is obtained by counting only the states with energy $\in [E, E+\delta E)$

※ Summary of three definitions of entropy

- fluctuation

$\overline{\Delta E^2} = \langle E^2 \rangle - \langle E \rangle^2$

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln Z \qquad \frac{\partial \bar{E}}{\partial \beta} = -\frac{\partial^2}{\partial \beta^2} \ln Z = -\left(\langle E^2 \rangle - \langle E \rangle^2 \right)$$

$$\Rightarrow \overline{\Delta E^2} = -\frac{\partial \bar{E}}{\partial \beta} = kT^2 \left.\frac{\partial \bar{E}}{\partial T}\right|_{V,N} = kT^2 C_V$$

← if we fix V and N

$$\frac{\sqrt{\overline{\Delta E^2}}}{\bar{E}} = \frac{1}{\bar{E}} \sqrt{kT^2 C_V}$$

$$C_V \propto N . \quad \bar{E} \propto N \quad \Rightarrow \quad \frac{\sqrt{\overline{\Delta E^2}}}{\bar{E}} \propto \frac{1}{\sqrt{N}}$$

(system ⊕ reservoir)

⊙ Canonical ensemble can be used ~~as~~ an approximation of microcanonical ensemble (isolated system).

Let's consider $\bar{y} = \dfrac{\sum_r' y_r}{\Omega(E)}$ (microcanonical)

$\sum_r'$ ~ contributed from state r with $E_r \in [E, E+\delta E]$

~ rather difficult to obtain the restricted sum.

⇒ Consider weaker condition : mean energy $\bar{E} = E$

→ $\bar{y} = \dfrac{\sum_r y_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$

(β can be chosen to have $\bar{E} = \dfrac{1}{Z} \sum E_r e^{-\beta E_r}$.

$\boxed{\text{BUT.}}$ One cannot estimate dispersion $\overline{(y-\bar{y})^2}$.

The dispersion should be larger in the canonical ensemble case.

Canonical ensemble ≡ microcanonical ensemble

in the thermodynamic limit $N \to \infty$
(# of particle)

⊙ mathmatically :

① microcanonical $\Omega(E)$ ⟶ canonical Z

We know $P(E) \left(= \Omega(E)\, e^{-\beta E}\right)$ has a sharp maximum.
at $E = \tilde{E}$

So choose a rapidly decaying function $e^{-\beta E}$.

$\left.\dfrac{\partial P(E)}{\partial E}\right|_{\tilde{E}} = 0 \quad \Rightarrow \quad \beta = \dfrac{\partial \ln \Omega}{\partial E}$

$Z \equiv \sum_E \Omega(E)\, e^{-\beta E}$

→ connection ~~between~~ from $\Omega(E)$ to Z.

$$Z = \sum_E \Omega(E)\, e^{-\beta E}$$

$$\simeq \Omega(\tilde{E})\, e^{-\beta \tilde{E}} \, \frac{\Delta^* E}{\delta E}$$

$$\Rightarrow \underline{\ln Z + \beta E = \ln \Omega(E)}$$

$$\frac{\partial \ln Z}{\partial \beta}\frac{\partial \beta}{\partial E} + \left(\beta + \frac{\partial \beta}{\partial E} E\right) = \frac{\partial \ln \Omega}{\partial E} = \beta$$

$$\Rightarrow \quad E = -\frac{\partial \ln Z}{\partial \beta} = \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

② $Z \to \Omega(E)$

$$\Omega(E) = \sum_r \delta(E_r - E)\, \delta E$$

use $\delta(E - E_r) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\beta'\, e^{(E-E_r)\underline{\beta}}$, $\quad \underline{\beta} = \beta + i\beta'$

$$\Rightarrow \Omega(E) = \frac{\delta E}{2\pi} \sum_r \int_{-\infty}^{\infty} d\beta'\, e^{(E-E_r)\underline{\beta}}$$

$$= \frac{\delta E}{2\pi} \int_{-\infty}^{\infty} d\beta'\, e^{\underline{\beta} E}\, Z(\underline{\beta})$$

$$Z(\underline{\beta}) = \sum_r e^{-\underline{\beta} E_r} = \sum_r e^{-(\beta + i\beta')E_r}$$

$$\beta' \neq 0 \Rightarrow Z(\underline{\beta}) \to 0$$

($\because$ random change of sign of $e^{-i\beta' E_r}$)

~~in them~~ (For more detail, see Reif p. 224 -225)

$$\Rightarrow \Omega(E) = \boxed{\;}\, e^{\beta E}\, Z(\beta)$$

$$\ln \Omega(E) = \beta E + \ln Z(\beta) \cancel{+ \ln \boxed{\;}}$$

Or, one can use Laplace transformation.

$$Z(\beta) = \int_0^{\infty} dE\, \Omega(E)\, e^{-\beta E}$$ → calculate inverse Laplace transformation.

⊙ Grand canonical ensemble

$A \oplus A'$ (heat , particle reservoir)

$E + E' = E^{(0)}$ = constant $\quad (E \ll E^{(0)})$

$N + N' = N^{(0)}$ = " $\quad (N \ll N^{(0)})$

$\Rightarrow \quad P_r(E_r, N_r) \propto \Omega'(E^{(0)} - E_r, N^{(0)} - N_r)$

$$\Rightarrow \ln \Omega'(E^{(0)} - E_r, N^{(0)} - N_r) = \ln \Omega'(E^{(0)}, N^{(0)}) - \underbrace{\left.\frac{\partial \ln \Omega}{\partial E'}\right|_0}_{\equiv \beta} E_r - \underbrace{\left.\frac{\partial \ln \Omega}{\partial N'}\right|_0}_{\equiv \alpha} N_r$$

$\Rightarrow \boxed{P_r \propto e^{-\beta E_r - \alpha N_r}}$ ~ grand canonical ensemble

$$\bar{E} = \frac{\sum_r e^{-\beta E_r - \alpha N_r} E_r}{\sum_r e^{-\beta E_r - \alpha N_r}}$$

$$\bar{N} = \frac{\sum_r e^{-\beta E_r - \alpha N_r} N_r}{\sum_r e^{-\beta E_r - \alpha N_r}}$$

$\mu \equiv -kT\alpha$ ~ chemical potential

※ system with $\bar{E}$ and $\bar{N}$ $\equiv$ grand canonical ensemble.

(β . α are determined by $\bar{E}$ and $\bar{N}$)

※ fluctuations of E and N are very small :

for purposes of calculating mean values, ⇒

description with isolated systems $\equiv$ description with $A \oplus$ heat reservoir

$\equiv$ description with system $\oplus$ (heat , particle) reservoir.

◎ Alternative derivation of Grand canonical ensemble

$a_{r,N}$: # of $\underbrace{\text{systems at } r\text{th state}}_{\text{with } N \text{ particles}}$

$$\left\{ \begin{aligned} a &= \sum_{r,N} a_{r,N} \\ \bar{E} &= \frac{1}{a} \sum_{r,N} a_{r,N} E_r \\ \bar{N} &= \frac{1}{a} \sum_{r,N} a_{r,N} N \end{aligned} \right\} \quad \text{restrictions}$$

$$\Gamma \equiv \frac{a!}{\prod_{r,N} a_{r,N}!}$$

find $\{a_{r,N}\}$ which makes Γ maximum under the three restrictions

⇒ use Lagrange multipliers

$$\sum_{r,N} \left(\ln a_{r,N} + \lambda + \beta E_r - \alpha N \right) \delta a_{r,N} = 0 .$$

$$\Rightarrow \quad P_{r,N} = \frac{a_{r,N}}{a} = \frac{e^{-\beta E_r + \alpha N}}{\sum_{r,N} e^{-\beta E_r + \alpha N}}$$

$$\mathcal{Z} = \sum_{r,N} e^{-\beta E_r + \alpha N}$$: Grand canonical partition fn.

∘ classical :

$$\mathcal{Z} = \sum_{N=0}^{\infty} \frac{1}{h_0^{3N}} \int d^{3N}q \, d^{3N}p \;\; \exp(-\beta E(\{q, p\}) + \alpha N)$$

(see Gibbs paradox.)

∘ entropy

$$S = -\sum_{r,N} P_{r,N} \ln P_{r,N}$$

$$= k \ln \mathcal{Z} + k\beta \bar{E} - k\alpha \bar{N}$$

$$TS = kT \ln \mathcal{Z} + \bar{E} + \mu \bar{N}$$

$$\Rightarrow \bar{E} - TS - \mu\bar{N} = -kT \ln \mathcal{Z}$$

microcanonical

$\Omega \leftrightarrow S = k \ln \Omega$

canonical

$Z \leftrightarrow F = -kT \ln Z$

grandcanonical

$\mathcal{Z} \leftrightarrow \bar{E} - TS - \mu\bar{N} = -kT \ln \mathcal{Z}$

∘ $$\underset{(T,V,\mu)}{\mathcal{Z}} = \sum_{N=0}^{\infty} e^{N\mu\beta} Z(T,V,N)$$

grand canonical ↔ canonical

$$\left(\text{cf.} \quad Z(\beta,N,V) = \sum_{E} e^{-\beta E} \Omega(E,N,V) \right)$$

canonical ↔ microcanonical

~~※ Gibbs paradox ; Gibbs factor~~

∘ fluctuation (skip)

$$\langle N^2 \rangle - \langle N \rangle^2 = kT \left. \frac{\partial \langle N \rangle}{\partial \mu} \right|_{T,V} , \quad \langle N \rangle = \left. \frac{\partial (kT \ln \mathcal{Z})}{\partial \mu} \right|_{T,V}$$

$$= \langle N \rangle^2 \frac{kT}{V} \kappa \qquad \kappa \equiv -\frac{1}{V} \left. \frac{\partial V}{\partial p} \right|_{T,N} \text{, compressibility.}$$

$$\Rightarrow \sqrt{\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle^2}} = \sqrt{\frac{kT}{V} \kappa}$$

$\kappa \rightarrow$ intensive parameter $\Rightarrow \sqrt{\dfrac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle^2}} \propto \sqrt{\dfrac{1}{V}}$