2) Applications : (classical case
or, single quantum particle

① Classical ; identical particles : Gibbs paradox

N identical particles (mass m) in a box (volume V)

The total energy is assumed to be

$$E = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U(\{r_i\})$$

($U \to 0$ (Interaction between particles is negligible.)

Classical treatment :

$$Z_{\text{Wrong}} = \frac{1}{h_0^{3N}} \int d^3\vec{r}_1 \cdots d^3\vec{r}_N \, d^3\vec{p}_1 \cdots d^3\vec{p}_N \quad \exp\left(-\beta E(\{\vec{r}_i\}, \{\vec{p}_i\})\right)$$

(see note page 3-7)

$$Z_{\text{correct}} = \frac{1}{N!} Z_{\text{Wrong}} = Z$$

$\frac{1}{N!}$ ~ Gibbs factor ~ necessary for indistinguishable particles

classical treatment : every particle ~ distinguishable
(at least infinitesimal difference ?)
→ Gibbs paradox
(Maxwell - Boltzmann statistics (→ course 4.)

quantum treatment : identical particle ~ indistinguishable.
(no infinitesimal difference due to quantized discreteness.)

$$Z_{wrong} = \left(V \int_{-\infty}^{\infty} e^{-\frac{\beta \vec{p}^2}{2m}} \frac{d\vec{p}}{h_0^3} \right)^N$$

$$= \left[\frac{V}{h_0^3} \left(\sqrt{\frac{\pi 2m}{\beta}} \right)^3 \right]^N \qquad \left(\because \int_{-\infty}^{\infty} e^{-ap^2} dp = \sqrt{\frac{\pi}{a}} \right)$$

$$Z = \frac{1}{N!} Z_{wrong}$$

$$\ln Z = N \left[\ln V - \frac{3}{2} \ln \beta + \frac{3}{2} \ln \left(\frac{2\pi m}{h_0^2} \right) - \ln N + 1 \right]$$

$$= N \left[\ln \frac{V}{N} - \frac{3}{2} \ln \beta + \sigma_0' \right], \quad \sigma_0' = \frac{3}{2} \ln \frac{2\pi m}{h_0^2} + 1$$

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = \frac{3}{2} NkT$$

$$\bar{p} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} = \frac{1}{\beta} \frac{N}{V} \rightarrow \bar{p} V = NkT$$

$$C_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_V = \frac{3}{2} Nk$$

$$S = k(\ln Z + \beta \bar{E}) = kN \left(\ln \frac{V}{N} - \frac{3}{2} \ln \beta + \sigma_0' + \frac{3}{2} \right)$$

Note: ① Classical limit

Recognize $S \rightarrow -\infty$ as $T \rightarrow 0$, which contradicts the 3rd law of thermodynamics. The above partition function is valid only in classical limit: $\Delta q \Delta p \gg h$

$\Delta q \sim \bar{R}$, mean separation between particles $\bar{R} \sim \left(\frac{V}{N} \right)^{1/3}$

$\Delta p \sim \bar{p}$, mean momentum. $\bar{p} \sim \sqrt{2m \bar{E}/N} \sim \sqrt{3mkT}$

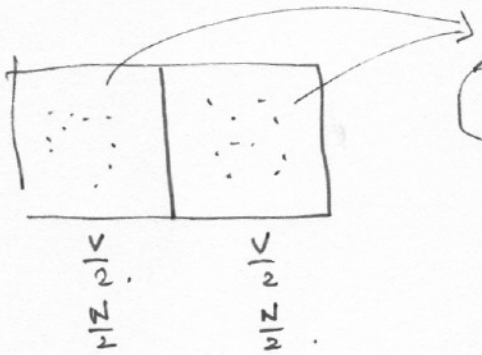
$\sim h/\lambda$, λ ~ wave length.

$\Rightarrow \lambda \ll \bar{R}$. (high energy limit)

or $\left(\frac{V}{N} \right)^{1/3} \gg \frac{h}{\sqrt{3mkT}}$.

see numerical estimation in p. 247 – 248

② Gibbs paradox . : see the following example.



The system is in equilibrium before and after removing the partition

S_{wrong} • (with partition)

$= 2 \cdot \left(\frac{N}{2}\right) \left(\ln \frac{V}{2} - \frac{3}{2} \ln \beta + \boxed{\quad} \right) k$

S_{wrong} (without partition)

$= N \left(\ln V - \frac{3}{2} \ln \beta + \boxed{\quad} \right) k$

S_{wrong} (without) − S_{wrong} (with)

$= Nk \ln 2.$

$\neq 0$

But, the process of removing the partition is reversible.

$\Rightarrow$ ΔS should be zero.

To resolve it, one should use $S_{correct}$, which results from the "indistinguishability" of the identical particles.

$S_{correct}$ (without) − $S_{correct}$ (with) $= 0$.

⊙ Equipartition Theorem.

- classical system ⊕ heat reservoir (kT) ⊕ equilibrium

- $E = E(q_1, \cdots, q_f, p_1 \cdots, p_f)$

$$E = \epsilon_i(p_i) + E'(q_1 \cdots, p_f) \quad \text{— ①}$$

(E': independent of p_i)

$$\epsilon_i(p_i) = b p_i^2 \quad \text{— ②}$$

$$\Rightarrow \overline{\epsilon_i} = \frac{1}{2} kT$$

Proof

$$\overline{\epsilon_i} = \frac{\int_{-\infty}^{\infty} e^{-\beta E(q_1 \cdots, p_f)} \epsilon_i \, dq_1 \cdots dp_f}{\int_{-\infty}^{\infty} e^{-\beta E(q_1 \cdots, p_f)} dq_1 \cdots dp_f} \quad \because ①$$

$$= \frac{\int e^{-\beta \epsilon_i} \epsilon_i \, dp_i}{\int e^{-\beta \epsilon_i} dp_i}$$

$$= -\frac{\partial}{\partial \beta} \ln \left(\int_{-\infty}^{\infty} e^{-\beta \epsilon_i} dp_i \right)$$

$$= -\frac{\partial}{\partial \beta} \ln \left(\beta^{-\frac{1}{2}} \boxed{\quad} \right) = \frac{1}{2} \frac{1}{\beta} = \frac{1}{2} kT$$

Note: . If a coordinate q_i is satisfied with ① and ②, we have the same result of $\overline{\epsilon_i} = \frac{1}{2} kT$.

. The theorem is valid only in the classical limit.

quantum statistics ⊕ $T \to \infty$ ⇒ one can obtain ($kT \gg \Delta E$) the classical result of $\overline{\epsilon_i} = \frac{1}{2} kT$.

(We will see it again in Course 4.)

Example :

· a molecule @ kT

→ $E = \frac{1}{2m}(P_x^2 + P_y^2 + P_z^2)$

$\bar{E} = \frac{3}{2}kT.$

· N molecule # (the entire energy is kinetic)

$\bar{E} = \frac{3}{2}NkT.$, $C_V = \left.\frac{\partial \bar{E}}{\partial T}\right|_V = \frac{3}{2}Nk.$

· Brownian motion.

random collisions of a particle with the molecules in a liquid.

$\bar{v}_x = 0$ (kT)

$\overline{\frac{1}{2}mv_x^2} = \frac{1}{2}kT \quad \rightarrow \quad \overline{v_x^2} = \frac{kT}{m}$

· Harmonic oscillator.

$E = \frac{p^2}{2m} + \frac{1}{2}k_0x^2$

$\Rightarrow \quad \overline{\frac{p^2}{2m}} = \frac{1}{2}kT. \qquad \overline{\frac{1}{2}k_0x^2} = \frac{1}{2}kT.$

$\bar{E} = kT.$

※ Comparison with quantum ~~theory~~ results.

$E_n = (\frac{1}{2} + n)\hbar\omega. \quad , \omega = \sqrt{\frac{k_0}{m}}$

$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} \qquad Z = \sum_{n=0}^{\infty} e^{-(n+\frac{1}{2})\hbar\omega} = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$

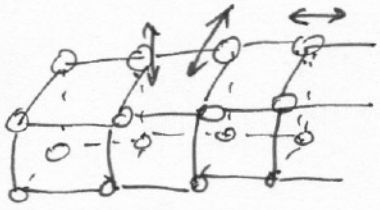
$= \hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right)$

if $\beta\hbar\omega \ll 1 \Rightarrow \quad \bar{E} \simeq \hbar\omega\left(\frac{1}{2} + \frac{1}{\beta\hbar\omega}\right) \simeq kT$

· Specific heats of solids

a simple solid with Avogadro's # N_a of atoms per mole.

⊕ lattice vibration (→ quantum version : phonon)



$$\Rightarrow E = \sum_{i=1}^{3N_a} \left(\frac{p_i^2}{2m} + \frac{1}{2} k_i q_i^2 \right) \qquad , k_i > 0$$

(i : normal mode index)

$$\bar{E} = 3N_a \left(\frac{1}{2} kT \times 2 \right) = 3N_a kT .$$

※ quantum version : (assume : all atoms vibrate with the same frequency ω)

$$\bar{E} = 3N_a \hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right)$$

~ Einstein phonon. → good approximation for overall behavior as a function of T. But it fails at very low T.

$$C_v = \left(\frac{\partial \bar{E}}{\partial T} \right)_V = -\frac{1}{kT^2} \left(\frac{\partial \bar{E}}{\partial \beta} \right)_V$$

$$= \frac{3N_a \hbar\omega}{kT^2} \frac{e^{\beta\hbar\omega}\, \hbar\omega}{(e^{\beta\hbar\omega} - 1)^2}$$

※ Read Ref P. 255 - 256.

$\beta\hbar\omega = \Theta_E / T$. Θ_E ~ Einstein temperature.

$T \gg \Theta_E$: $C_v \to 3N_a k$

$T \ll \Theta_E$: $C_v \to 3N_a k \left(\frac{\Theta_E}{T} \right)^2 e^{-\Theta_E/T}$

※ The quantum limit will be reconsidered in Course 4.

⊙ Paramagnetism

N noninteracting ~~spin~~ atoms in a substance at temperature T.

$\vec{H} \parallel \hat{z}$.

~~with magn~~ with magnetic moment $\vec{\mu}$

Cohat is $\bar{\mu}_z(\vec{H}, T)$?

$\epsilon = -\vec{\mu} \cdot \vec{H}$

$\vec{\mu} = g \mu_0 \vec{J}$

g ~ g factor of the atom ($O(1)$)

μ_0 ~ Bohr magneton $\mu_0 = e\hbar/(2mc)$

$\vec{J}$: total angular momentum.

$\Rightarrow \epsilon = -g\mu_0 H J_z$.

$J_z = m \qquad \epsilon \in \{ -J, -J+1, -J+2, \cdots, J-1, J \}$

$2J+1$.

$\epsilon_m = -g\mu_0 H m$

$\mu_z = g\mu_0 m$.

$$\bar{\mu}_z = \frac{\sum_{m=-J}^{J} e^{\beta g \mu_0 H} (g\mu_0 m)}{\sum_{m=-J}^{J} e^{\beta g \mu_0 H m}} = \frac{1}{\beta}\frac{\partial Z}{\partial H}\cdot\frac{1}{Z} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial H}.$$

$$Z = \sum_{m=-J}^{J} e^{\beta \mu_0 H m} = \frac{e^{-\eta J} - e^{\eta(J+1)}}{1 - e^{\eta}}, \quad \eta \equiv \beta g \mu_0 H$$

$$= \frac{\sinh\left(J+\frac{1}{2}\right)\eta}{\sinh\frac{1}{2}\eta}$$

$$\Rightarrow \bar{\mu}_z = \frac{1}{\beta}\frac{\partial \ln Z_a}{\partial H} = g\mu_0 \frac{\partial \ln Z}{\partial \eta}$$

$$= g\mu_0 J B_J(\eta)$$

$$B_J(\eta) \equiv \frac{1}{J}\left[\left(J+\tfrac{1}{2}\right)\coth\left(J+\tfrac{1}{2}\right)\eta - \tfrac{1}{2}\coth\tfrac{1}{2}\eta\right]$$

$\eta \gg 1$: $\coth\left(J+\frac{1}{2}\right)\eta \to 1$. $\quad \coth x = \dfrac{e^x + e^{-x}}{e^x - e^{-x}}$

$$\Rightarrow B_J(\eta) \to \frac{1}{J}\left(J+\tfrac{1}{2}-\tfrac{1}{2}\right) = 1.$$

$\eta \ll 1$: $\coth\left(J+\frac{1}{2}\right)\eta \to \dfrac{1}{\left(J+\frac{1}{2}\right)\eta} + \frac{1}{3}\left(J+\frac{1}{2}\right)\eta$

(use $\coth x \simeq \frac{1}{x} + \frac{1}{3}x$ as $x \to 0$)

$$\Rightarrow B_J(\eta) = \frac{J+1}{3}\eta$$

$\Rightarrow \bar{M}_z \equiv N_0 \bar{\mu}_z$ (N_0: # of atoms per unit volume)

(magnetization)

$\bar{M}_z = \chi H$ for $g\mu_0 H/kT \ll 1$

$\chi = N_0 \dfrac{g^2\mu_0^2 J(J+1)}{3kT}$

$N_0 g\mu_0 J$ for $g\mu_0 H/kT \gg 1$.

$\chi \propto \frac{1}{T}$ at high temperature ~ Curie's law.

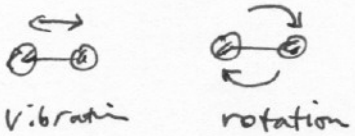
⊙ Maxwell velocity distribution

A molecule of mass m in a dilute gas

(1 energy)

$$\epsilon = \frac{p^2}{2m} + \epsilon^{(int)}$$

$\epsilon^{(int)}$: some internal energy



no interaction. → center of mass motion

Assume: (center of mass motion ~ classical
internal degrees of freedom ~ quantum.

the other molecules ~ heat reservoir of the specified molecule.

⇒

$P_s(\vec{r}, \vec{p})\, d^3\vec{r}\, d^3\vec{p}$ ~ probability of finding the molecule

with center of mass variables $\in$ ($(\vec{r}, \vec{r}+d\vec{r})$ / $(\vec{p}, \vec{p}+d\vec{p})$)

(the internal coordinate ~ quantum number s

$$P_s(\vec{r}, \vec{p}) \propto e^{-\beta p^2/2m}\, e^{-\beta \epsilon_s^{(int)}} \propto e^{-\beta p^2/2m}$$

↓ $\vec{p} \to \vec{v} = \vec{p}/m$. , single particle → N particles

$f(\vec{r}, \vec{v})\, d^3\vec{r}\, d^3\vec{v}$: the mean number of molecules

with C.M. motion $\in$ ($(\vec{r}, \vec{r}+d\vec{r})$ / $(\vec{v}, \vec{v}+d\vec{v})$)

⇒ $f(\vec{r}, \vec{v}) = C e^{-\beta m v^2/2}$

$$\int d^3\vec{r}\, d^3v\, f(\vec{r}, \vec{v}) = N = CV \left(\int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m v_x^2} dv_x \right)^3$$

$$= CV \left(\frac{2\pi}{\beta m} \right)^{3/2}$$

$\Rightarrow C = n \left(\frac{\beta m}{2\pi}\right)^{3/2} \cdot \quad n \equiv \frac{N}{V}$.

$\Rightarrow f(\vec{v})\, d^3\vec{r}\, d^3\vec{v} = n \left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\frac{1}{2}\beta m v^2}\, d^3\vec{r}\, d^3\vec{v}$

~ Maxwell distribution for a molecule of a dilute gas in thermal equilibrium.

※ $g(v_x)dv_x$: mean number of molecules per unit volume with $v_x \in [v_x,\ v_x+dv_x]$

$$g(v_x)dv_x = \left[\int dv_y \int dv_z\, f(\vec{v})\right] dv_x$$

$$= n \cdot \left(\frac{\beta m}{2\pi}\right)^{1/2} e^{-\beta m v_x^2/2}\, dv_x$$

~ Gaussian.

$$\bar{v}_x = \frac{1}{n}\int_{-\infty}^{\infty} v_x\, g(v_x)\, dv_x = 0.$$

$$\bar{v}_x^2 = \frac{1}{n}\int_{-\infty}^{\infty} g(v_x)\, v_x^2\, dx = \frac{kT}{m}$$

$$\left(\Leftrightarrow \frac{1}{2} m \bar{v}_x^2 = \frac{1}{2} kT. \quad \text{equipartition th.}\right)$$

$$\sqrt{\overline{\Delta v_x^2}} = \sqrt{kT/m}.$$

※ $F(v)\,dv$: mean # of molecules per unit volume with $|\vec{v}| \in [v,\ v+dv]$

$$F(v)\,dv = \left(\int dv_\theta dv_\varphi\right) f(\vec{v})\, dv$$

$$= 4\pi \cdot v^2 f(\vec{v})\, dv.$$

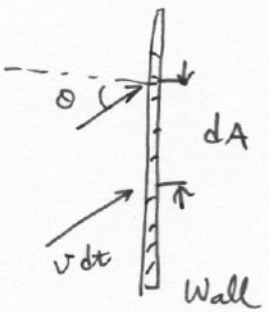
$$= 4\pi n \left(\frac{m\beta}{2m}\right)^{3/2} v^2 e^{-\beta m v^2/2}\, dv$$

$\left.\frac{dF}{dv}\right|_{v=\tilde{v}} = 0$

$$\bar{v} = \frac{1}{n}\int_0^\infty F(v)\, v\, dv = \sqrt{\frac{8kT}{\pi m}}, \quad \overline{v^2} = \frac{3kT}{m}, \quad \tilde{v} = \sqrt{\frac{2kT}{m}}$$

※ $\Phi(\vec{v})\, d^3\vec{v}$: the number of molecules, with $\vec{v} \in [\vec{v}, \vec{v}+d\vec{v}]$, which strike a unit area of the wall per unit time.

$$\Phi(\vec{v})\, d^3\vec{v} = d^3\vec{v}\, f(\vec{v}) \cdot v\cos\theta$$



Φ_0 : total # of molecules which strike a unit area of the wall per unit time

$$\Phi_0 = \int_{v_x>0} d^3\vec{v}\, f(\vec{v})\, v\cos\theta$$

$$= \int_{v_x>0} v^2 dv \sin\theta\, d\theta\, d\varphi \quad v\cos\theta\, f(v)$$

$$= \int_0^\infty f(v) v^3 dv \int_0^{\pi/2} \sin\theta\cos\theta\, d\theta \int_0^{2\pi} d\varphi$$

$$= \pi \int_0^\infty f(v) v^3 dv$$

$$\bar{v} = \frac{4\pi}{n} \int_0^\infty f(v) v^3 dv$$

$$\Rightarrow \Phi_0 = \frac{1}{4} n \bar{v} \quad , \; n = \frac{\bar{P}}{kT} \quad , \; \bar{v} = \sqrt{\frac{8kT}{\pi m}}$$

$$= \frac{\bar{P}}{\sqrt{2\pi m kT}}$$