§ Part 1. Systems

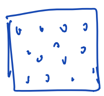
- isolated (U, N)
- thermal contact with reservoir (τ, N)
- thermal & diffusive contact with reservoir (τ, μ)

§ Part 2 Examples

- ideal gas
  - Classical
  - Fermi gas
  - Bose gas
- photon gas / black-body radiation (Boson) CH4
- phonon in a solid (Boson) CH4
- spin system
- two - state ε, 0 three - state
- harmonic oscillator. {discussion § Problem 2}

§1. Systems.

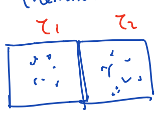
① isolated. (closed system, const. U, const. N, max σ)



g: accessible states #, most probable configuration

$P(s) = \frac{1}{g}$ $\qquad$ $\sigma(N,U) = \ln g(N,U)$

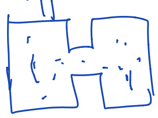
thermal



$g(s) = \sum_{U_1} g_1(U_1)\, g_2(U-U_1)$ $\qquad$ $\sum_{s_1} g_1(s_1)\, g_2(s-s_1)$

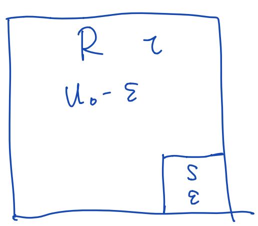
equilibrium. $\tau_1 = \tau_2$ $\qquad$ $\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U}\right)_N$

diffusive



@ equilibrium $\tau_1 = \tau_2$, $\mu_1 = \mu_2$

a thermal contact with a reservoir (const. τ, const N)



Boltzmann factor $\qquad \frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{e^{-\varepsilon_1/\tau}}{e^{-\varepsilon_2/\tau}}$

Partition sum. $\qquad Z \equiv \sum_s e^{-\varepsilon_s/\tau}$

$$P(\varepsilon_s) = \frac{e^{-\varepsilon_s/\tau}}{Z}$$

Free energy $\qquad F \equiv U - \tau\cdot\sigma = -\tau \ln Z$

for τ-N-V system

F is maximized @ equilibrium

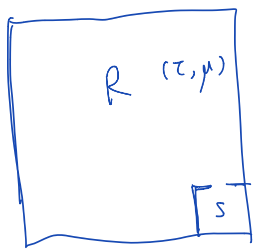
average energy $\qquad U = \tau^2 \frac{\partial \ln Z}{\partial \tau}$

heat capacity $\qquad C_V = \left(\frac{\partial U}{\partial \tau}\right)_V = \tau\left(\frac{\partial \sigma}{\partial \tau}\right)_V$

pressure $\qquad p = -\left(\frac{\partial F}{\partial V}\right)_\tau = -\left(\frac{\partial U}{\partial V}\right)_\sigma = \tau\left(\frac{\partial \sigma}{\partial V}\right)_U$

entropy $\qquad \sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V$

• Diffusive & thermal contact with a reservoir



Gibbs distribution

$$\frac{P(N_1, \varepsilon_1)}{P(N_2, \varepsilon_2)} = \frac{e^{(N_1\mu - \varepsilon_1)/\tau}}{e^{(N_2\mu - \varepsilon_2)/\tau}}$$

Gibbs sum

$$\mathcal{Z} = \sum_{ASN} e^{(N\mu - \varepsilon(N))/\tau}$$

$$P(N, \varepsilon) = \frac{e^{(N\mu - \varepsilon)/\tau}}{\mathcal{Z}}$$

$$\langle N \rangle = \frac{1}{\mathcal{Z}} \sum_{ASN} N \cdot e^{(N\mu - \varepsilon)/\tau} = \tau \frac{\partial \ln \mathcal{Z}}{\partial \mu}$$

"absolute activity" $\lambda = e^{\mu/\tau}$

$$\langle N \rangle = \lambda \frac{\partial}{\partial \lambda} \ln \mathcal{Z}$$

★ $$U = \left(\tau\mu \frac{\partial}{\partial \mu} - \tau^2 \frac{\partial}{\partial \tau} \right) \ln \mathcal{Z}$$

$$= \frac{1}{\mathcal{Z}} \sum_{ASN} \varepsilon \, e^{(N\mu - \varepsilon)/\tau}$$

Examples.

1. ideal gas

$$\begin{cases} \text{classical gas.} & f(\varepsilon,\tau) = \lambda e^{-\varepsilon/\tau} \\ \text{Fermi gas:} & f(\varepsilon,\tau) = \dfrac{1}{\lambda^{-1} e^{\varepsilon/\tau} + 1} \\ \text{Bose gas:} & f(\varepsilon,\tau) = \dfrac{1}{\lambda^{-1} e^{\varepsilon/\tau} - 1} \end{cases}$$

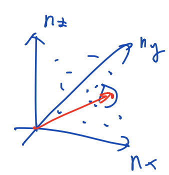
$$\varepsilon_n = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2) \qquad n_x, n_y, n_z = 0, 1, 2 \ldots$$

① Classical gas (CH3, CH6)

partition function for one particle

$$Z_1 = \sum_{n_x}\sum_{n_y}\sum_{n_z} e^{-\varepsilon_n/\tau}$$

$$= \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z \, e^{-\varepsilon_n/\tau}$$



$$n^2 = n_x^2 + n_y^2 + n_z^2 \qquad (n, \theta, \phi)$$

$$= \frac{1}{8}\int_0^\infty dn \; 4\pi n^2 \, e^{-\varepsilon_n/\tau}$$

$$= \frac{\pi}{2}\int_0^\infty dn \, n^2 e^{-\frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 \frac{1}{\tau} n^2}$$

$$= \frac{V}{(2\pi\hbar^2/m\tau)^{3/2}} = n_Q \cdot V, \qquad n_Q = \underbrace{\left(\frac{m\tau}{2\pi\hbar^2}\right)^{\frac{3}{2}}}_{\text{3D only}}$$

$$\boxed{Z = \frac{Z_1^N}{N!} = \frac{(n_Q \cdot V)^N}{N!}}$$

$$F = -\tau \ln Z = \tau \cdot N\left(\ln \frac{n}{n_Q} - 1\right)$$

$$pV = N\tau, \quad U = \frac{3}{2}N\tau, \quad \sigma = N\left(\ln\frac{n_Q}{n} + \frac{5}{2}\right), \quad C_V = \frac{3N}{2}$$

$$\mu = \tau \ln \frac{n}{n_Q} \quad , \quad \lambda = e^{\mu/\tau} = \frac{n}{n_Q}$$

- internal degree of freedom.

$$F = \tau N \left(\ln \frac{n}{n_Q^*} - 1 \right) \qquad n_Q^* = n_Q Z_{int} , \quad Z_{int} = \sum_{int} e^{-\varepsilon_{int}/\tau}$$

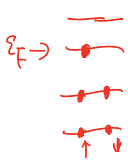
$$\Downarrow$$

$$P, \ U, \ \sigma, \ C_V$$

Alternative method

$$\boxed{\text{CH 6} \qquad f(\varepsilon, \tau) = \lambda e^{-\varepsilon/\tau} , \quad N \rightarrow \mu \rightarrow F}$$

② Fermi gas (CH 7) $\boxed{f(\varepsilon, \tau) = \frac{1}{\lambda^{-1} e^{\varepsilon/\tau} + 1}}$



$$\varepsilon_F = \frac{\hbar^2}{2m} \left(3\pi^2 n \right)^{3/2} = \tau_F = \mu_0$$

$$U = \int_0^\infty \varepsilon f(\varepsilon, \tau) D(\varepsilon) d\varepsilon$$

$D(\varepsilon)$ can be different in different case (1D, 2D, 3D, . .

$$N = \int_0^\infty f(\varepsilon, \tau) D(\varepsilon) d\varepsilon$$

$$C_V = \left(\frac{dU}{d\tau} \right)_V = \int_0^\infty (\varepsilon - \varepsilon_F) \frac{df}{d\tau} D(\varepsilon) d\varepsilon = \frac{1}{2} \pi^2 N \frac{\tau}{\tau_F}$$

only for 3D ideal gas

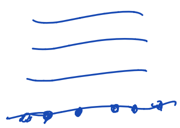
$$\sigma = \int \frac{C_V}{\tau} d\tau = \frac{1}{2} \pi^2 N \frac{\tau}{\tau_F}$$

$$C_V = \tau \left(\frac{\partial \sigma}{\partial \tau} \right)$$

$$\begin{cases} \tau = 0 \quad \text{ground state} \rightarrow \mu_0 = \varepsilon_F \rightarrow F = \int \mu \, dN \rightarrow P, \cdots \\ \tau > 0 , \quad \text{complicated.} \quad F = U - \tau \cdot \sigma \rightarrow P \cdots \end{cases}$$

③. Bose gas. $f(\varepsilon, \tau) = \dfrac{1}{\lambda^{-1} e^{\varepsilon/\tau} - 1}$

$\tau \to 0$ Einstein condensation



$$f(0, \tau) \approx -\frac{\tau}{\mu} \approx N$$

$$\Rightarrow \mu = -\frac{\tau}{N}, \quad \lambda \approx 1 - \frac{1}{N} \approx 1$$

$\tau > 0$

$$N_0 = \frac{1}{\lambda^{-1} - 1}$$

$$N_e = \int_0^\infty f(\varepsilon, \tau) D(\varepsilon) d\varepsilon \approx \underbrace{2.612\, n_Q \cdot V}_{\text{for 3D ideal Bose gas}}$$

Einstein temperature

@ $\tau_E = \tau$, $N_e = N$ $\Rightarrow$ $\tau_E = \underbrace{\dfrac{2\pi\hbar^2}{m}\left(\dfrac{N}{2.612\, V}\right)^{2/3}}_{\text{only for 3D ideal Bose gas}}$

$$\frac{N_e}{N} = \left(\frac{\tau}{\tau_E}\right)^{3/2}$$

$$\frac{N_0}{N} = 1 - \left(\frac{\tau}{\tau_E}\right)^{3/2}$$

2. Black-body radiation / photon gas

$$\varepsilon = s\hbar w$$

- single frequency.

$$Z = \sum_s e^{-s\hbar w/\tau} = \frac{1}{1-e^{-\hbar w/\tau}}$$

$$\langle s \rangle = \boxed{\frac{1}{e^{\hbar w/\tau}-1}}$$

Bose - Einstein distribution

photon is Boson with $\underline{\underline{\mu=0}}$

$\underline{\lambda = 1}$

$$\langle \varepsilon \rangle = \frac{\hbar w}{e^{\hbar w/\tau}-1}$$

- all frequency

$$w_n = \frac{n\pi c}{L}, \quad n = \sqrt{n_x^2+n_y^2+n_z^2}$$

$$U = \sum_n \langle \varepsilon_n \rangle = \sum_{n_x}\sum_{n_y}\sum_{n_z} \frac{\hbar w_n}{e^{\hbar w_n/\tau}-1}$$

$$= \int \varepsilon f(\varepsilon,\tau) D(\varepsilon)\, d\varepsilon$$

$$= \int \varepsilon \frac{1}{e^{\varepsilon/\tau}-1} D(\varepsilon)\, d\varepsilon$$

polarization

$$= \int \hbar w_n \frac{1}{e^{\hbar w_n/\tau}-1}\, 2\times\frac{1}{8}\times 4\pi n^2\, dn$$

$$= \frac{\pi^2}{15\hbar^3 c^3} \tau^4 \cdot V$$

$$\Downarrow$$

F, σ, p, C_V

3, phonon in a solid. Debye theory

$$\langle s(\omega) \rangle = \frac{1}{e^{\hbar\omega/\tau} - 1} \Rightarrow \text{phonon is Boson}$$

$$\sum_n (\cdots) = 3 \times \frac{1}{8} \int 4\pi n^2 \, dn \, (\cdots)$$

$$U = \int_0^{\varepsilon_D} \varepsilon f(\varepsilon, \tau) D(\varepsilon) d\varepsilon$$

$$= \int_0^{n_D} 3 \times \frac{1}{8} 4\pi n^2 \frac{\hbar\omega_n}{e^{\hbar\omega_n/\tau} - 1} dn$$

condition for n_D

$$\boxed{3N = \frac{3}{8} \int_0^{n_D} 4\pi n^2 \, dn} \Rightarrow n_D = \left(\frac{6N}{\pi}\right)^{\frac{1}{3}}$$

$$U(\tau) = \frac{3\pi^4 N \tau^4}{5(k_B \theta)^3} \qquad \theta = \frac{\hbar v}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{\frac{1}{3}}$$

4 spin system.

$\uparrow \downarrow \uparrow \downarrow$ $\quad N_\uparrow$, $N_\downarrow$ $\quad$ spin excess $s = \frac{N_\uparrow - N_\downarrow}{2}$

non interacting spins $\quad U = -2\, m \cdot B \cdot s$

interacting spins $\quad$ Ising model. totally different

$$g(N, s) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow!\, N_\downarrow!} = \frac{N!}{(N+\frac{1}{2}s)!\,(N-\frac{1}{2}s)!}$$

$$\approx g(N,0)\, e^{-\frac{2s^2}{N}} \quad , \quad g(N,0) \approx \sqrt{\frac{2}{\pi N}}\, 2^N$$

$$\sigma = \ln g = \sigma_0 - \frac{2s^2}{N} = \log g(N,0) - \frac{2s^2}{N}$$

$$\sigma(s) \to \sigma(U) \qquad \boxed{U = -2mB \cdot s}$$

method 1:

$$\boxed{\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U}\right)_N} \Rightarrow \tau(U) \Rightarrow U(\tau)$$

$$F = U - \sigma \cdot \tau$$

Method 2:

$$Z = \sum_s g(s)\, e^{-\varepsilon_s/\tau} = \sum_s \frac{N!}{(N-\frac{s}{2})!\,(N+\frac{s}{2})!}\, e^{2mBs/\tau}$$

$$F = -\tau \ln Z$$

Method 3:

$$Z_1 = e^{\frac{mB}{\tau}} + e^{\frac{-mB}{\tau}} \ , \qquad Z = Z_1^N \Rightarrow F = -\tau \ln Z$$

$$= 2\cosh\left(\frac{mB}{\tau}\right) \qquad\qquad = 2^N \cosh^N\left(\frac{mB}{\tau}\right)$$