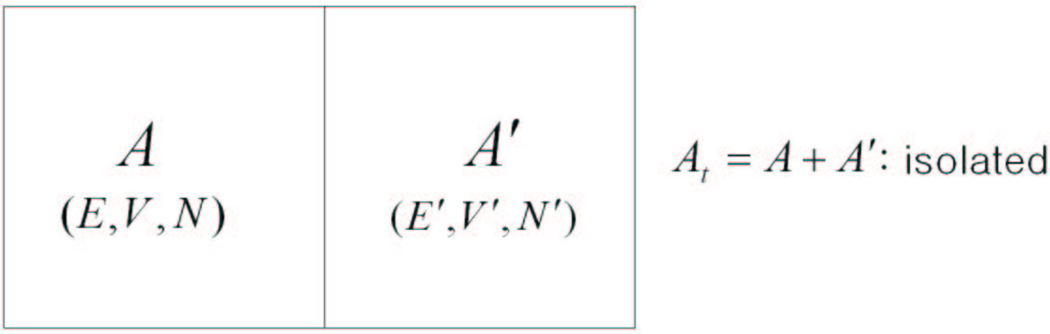
Chapter 4

Grandcanonical Ensemble

4.1 Chemical Diffusive Equilibrium and Chemical Potential



$$E + E' = E_t : \text{ fixed.} \tag{4.1}$$

$$V + V' = V_t : \text{ fixed.} \tag{4.2}$$

$$N + N' = N_t : \text{ fixed.} \tag{4.3}$$

$$S_t(E, V, N) = S(E, V, N) + S'(E', V', N') \tag{4.4}$$

Equilibrium Conditions: S_t: Max

$$\frac{\partial S_t}{\partial E} = 0 \quad \longrightarrow \quad \frac{\partial S}{\partial E} = \frac{\partial S'}{\partial E'} \tag{4.5}$$

$$\longrightarrow \quad T = T' : \text{ Thermal Equilibrium} \tag{4.6}$$

$$\frac{\partial S_t}{\partial V} = 0 \quad \longrightarrow \quad \frac{\partial S}{\partial V} = \frac{\partial S'}{\partial V'} \tag{4.7}$$

$$\longrightarrow \quad P = P' : \text{ Mechanical Equilibrium} \tag{4.8}$$

$$\frac{\partial S_t}{\partial N} = 0 \quad \longrightarrow \quad \frac{\partial S}{\partial N} = \frac{\partial S'}{\partial N'} \tag{4.9}$$

- **Def. Chemical Potential**

$$\mu \equiv -T \cdot \frac{\partial S}{\partial N} \tag{4.10}$$

Note: $\frac{\partial S}{\partial N}$ 값이 큰계가 (μ 값이 작은계) 입자를 획득해야, 다른계가 잃은 것보다 더 많은 엔트로피를 얻게된다.: 입자흐름 (μ 값이 큰 계$\longrightarrow \mu$ 값이 작은 계)

$$\mu = \mu' : \text{Chemical Diffusive Equilibrium} \tag{4.11}$$

$$S = S(E, V, N) \tag{4.12}$$

$$\longrightarrow dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN \tag{4.13}$$

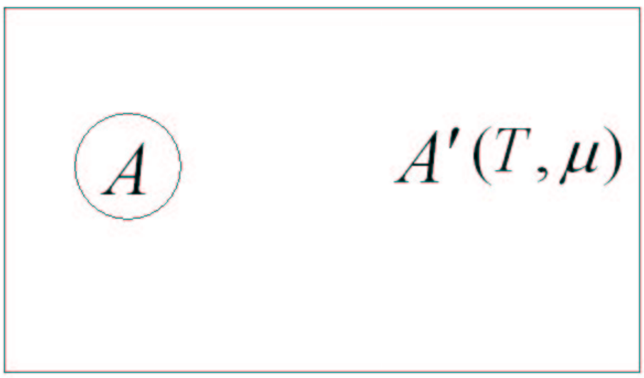
$$\longrightarrow dE = TdS - PdV + \mu dN : \text{ Thermodynamic 1st Law} \tag{4.14}$$

$$[-\mu dN : \text{chemical work}] \tag{4.15}$$

$$E = E(S, V, N),\ H = H(S, P, N),\ F = F(T, V, N), \tag{4.16}$$

$$G = G(T, P, N) : \text{ Thermodynamic Potentials} \tag{4.17}$$

4.2 Grand Canonical Ensemble



$A_t = A$ (system) $+ A'$ (ptl-energy reservoir) : isolated

$N + N' = N_t =$ fixed, $E + E' = E_t =$ fixed

$$\frac{N}{N_t} \ll 1, \quad \frac{E}{E_t} \ll 1$$

- **Equilibrium Conditions**

$$P(E,N) \;=\; C\,\Omega_t(E,N) = C\,\Omega(E,N)\cdot\Omega'(E_t - E, N_t - N) \quad (4.18)$$

What is the most probable state?

$$P(E,N):\ \max \iff \Omega_t:\ \max \quad (4.19)$$

$$S_t \;=\; k_B \ln\Omega_t:\ \ \max \quad (4.20)$$

$$\;=\; S(E,N) + S'(E_t - E, N_t - N) \quad (4.21)$$

$$\frac{\partial S_t}{\partial E} \;=\; \frac{\partial S}{\partial E} - \frac{\partial S'}{\partial E'} = 0 \longrightarrow \frac{\partial S}{\partial E} = \frac{\partial S'}{\partial E'} \quad (4.22)$$

$$\frac{\partial S_t}{\partial N} \;=\; \frac{\partial S}{\partial N} - \frac{\partial S'}{\partial N'} = 0 \longrightarrow \frac{\partial S}{\partial N} = \frac{\partial S'}{\partial N'} \quad (4.23)$$

$$\frac{\partial S'}{\partial E'} \;=\; \frac{1}{T'},\quad \frac{\partial S'}{\partial N'} = -\frac{\mu'}{T'} \quad (4.24)$$

$$\therefore\ \text{평행조건}: T = T',\quad \mu = \mu' \quad (4.25)$$

A': reservoir $\longrightarrow$ $\frac{E}{E_t} \ll 1,\quad \frac{N}{N_t} \ll 1$

$$\therefore T' = \text{const.},\quad \mu' = \text{const.} \quad (4.26)$$

$\therefore$ 우리가 관심을 두는 계 A의 온도와 화학 포텐샬이 T'와 μ'이 되면 평행 상태에 도달함.

- **Probability Distribution in Equilibrium**

가정: 계 A의 입자가 N개이고 r상태에 있다고 하자.

$$\Omega_t(N, E_r(N)) = 1\cdot\Omega'(N_t - N, E_t - E_r(N)) \quad (4.27)$$

$$
\begin{aligned}
P_r(N) &= C \cdot \Omega'(E_t - E_r(N), N_t - N) && (4.28)\\
\therefore \ln P_r(N) &= \ln C + \ln \Omega'(E_t - E_r, N_t - N) && (4.29)\\
&\approx \text{const.} + \left.\frac{\partial \ln \Omega'}{\partial E'}\right|_{(E_t,N_t)} \cdot (-E_r) + \left.\frac{\partial \ln \Omega'}{\partial N'}\right|_{(E_t,N_t)} \cdot (-N) && (4.30)
\end{aligned}
$$

$$
\begin{aligned}
\therefore \quad \beta &\equiv \left.\frac{\partial \ln \Omega'}{\partial E'}\right|_{(E_t,N_t)} = \frac{1}{k_B}\frac{\partial S'}{\partial E'} = \frac{1}{k_B T} && (4.31)\\
\alpha &\equiv \left.\frac{\partial \ln \Omega'}{\partial N'}\right|_{(E_t,N_t)} = \frac{1}{k_B}\frac{\partial S'}{\partial N'} = -\frac{\mu}{k_B T} = -\beta\mu && (4.32)
\end{aligned}
$$

$$
\therefore P_r(N) = C \cdot e^{-\beta E_r - \alpha N} = C \cdot e^{-\beta(E_r - \mu N)} \quad [e^{-\beta(E_r-\mu N)}: \text{ Gibbs factor}] \quad (4.33)
$$

$$
\longrightarrow \sum_{N=0}^{\infty} \sum_r P_r(N) = C \cdot \sum_{N=0}^{\infty} e^{-\alpha N} \sum_r e^{-\beta E_r(N)} \quad (4.34)
$$

$$
= \; C \cdot \sum_{N=0}^{\infty} e^{-\alpha N} \cdot Z(N) = 1 \quad (4.35)
$$

- **Def. Grand Partition Function**

$$
Q_G = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(N); \quad Z(N) = \sum_r e^{-\beta E_r(N)} \quad (4.36)
$$

$$
\rightarrow C = 1/Q_G, \quad P_r(N) = e^{-\beta(E_r - \mu N)}/Q_G \quad (4.37)
$$

- **Grand Potential**

$$
Q_G = \sum_{N=0}^{\infty} e^{\beta\,\mu\,N} \cdot Z(N); \quad Z(N) = \sum_r e^{-\beta E_r(N)} \quad (4.38)
$$

$z \equiv e^{\beta\,\mu}$: absolute activity or fugacity of the system

$$
Q_G = \sum_{N=0}^{\infty} z^N \cdot Z(T, V, N) \quad (4.39)
$$

$$
\begin{aligned}
\Omega(\text{grand potential}) &= \Omega(T, V, \mu) && (4.40)\\
&\equiv F(T, V, \overline{N}) - \mu \overline{N} && (4.41)
\end{aligned}
$$

$$d\Omega = dF - d(\mu\overline{N}) = -SdT - PdV - \overline{N}d\mu \tag{4.42}$$

$$S = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu}, \quad P = -\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu}, \quad \overline{N} = -\left(\frac{\partial\Omega}{\partial \mu}\right)_{T,V} \tag{4.43}$$

$$S = -k_B \sum_{(N,r)} P_r(N) \cdot \ln P_r(N) \tag{4.44}$$

$$\downarrow P_r(N) = \frac{e^{-\beta(E_r(N))-\mu N)}}{Q_G} \tag{4.45}$$

$$S = -k_B \sum_{(N,r)} \frac{e^{-\beta[E_r(N)-\mu N]}}{Q_G} \cdot [-\beta E_r(N) + \beta\mu N - \ln Q_G] \tag{4.46}$$

$$= \beta k_B \overline{E} - \beta\mu k_B \overline{N} + k_B \ln Q_G \tag{4.47}$$

$$S = \beta k_B \overline{E} - \beta\mu k_B \overline{N} + k_B \ln Q_G \tag{4.48}$$

$$\downarrow$$

$$F = \overline{E} - TS = \mu\overline{N} - k_B T \ln Q_G \tag{4.49}$$

$$\downarrow$$

$$\Omega = F - \mu\overline{N} = -k_B T \ln Q_G \tag{4.50}$$

⋆ 열역학적 극한에서는, 에너지와 입자수 요동 무시 가능

$$\longrightarrow Q_G \simeq e^{\beta\mu\overline{N}} \cdot Z(\overline{N}) \quad \longrightarrow \quad -k_B T \ln Q_G \tag{4.51}$$

$$= -k_B T \ln Z(\overline{N}) - \mu\overline{N} \tag{4.52}$$

$$= F - \mu\overline{N} \tag{4.53}$$

$$= \Omega(T, V, \mu) \tag{4.54}$$

- **Summary**

  1) Calculate Q_G

  2) $\Omega(T, V, \mu) = -k_B T \ln Q_G(T, V, \mu)$ (4.55)

$$F(T,V,\overline{N}) = \Omega + \overline{N}\mu; \tag{4.56}$$

$$\downarrow$$

$$\overline{N} = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V} \tag{4.57}$$

$$\downarrow$$

$$\overline{N} = \overline{N}(T,V,\mu) \tag{4.58}$$

$$\downarrow$$

$$\mu = \mu(T,V,\overline{N}) \tag{4.59}$$

3) Other thermodynamic quantities

$$S = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu}, \quad -\left(\frac{\partial F}{\partial T}\right)_{V,\overline{N}} \tag{4.60}$$

$$P = -\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu}, \quad -\left(\frac{\partial F}{\partial V}\right)_{T,\overline{N}} \tag{4.61}$$

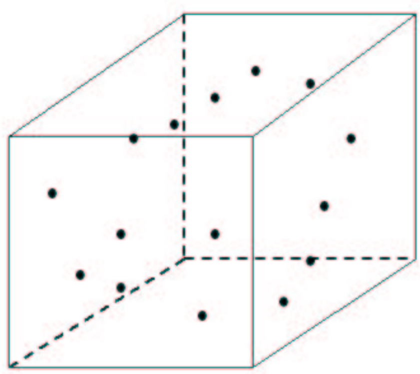
$$\overline{N} = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V} \tag{4.62}$$

$$\mu = \left(\frac{\partial F}{\partial\overline{N}}\right)_{T,V} \tag{4.63}$$

$$U = F - TS, \quad C_V = \left(\frac{\partial V}{\partial T}\right)_{V,\overline{N}} \tag{4.64}$$

4.3 Ideal Gas

e.g. Classical ideal gas



$$
\begin{aligned}
\mathcal{H} &= \sum_{i=1}^{3N} \frac{p_i^2}{2m} && (4.65)\\
Q_G &= \sum_{N=0}^{\infty} z^N \cdot Z_N, \quad z = e^{\beta\mu} && (4.66)\\
Z_N &= \frac{1}{N!} \cdot \int \frac{\prod_{i=1}^{3N} dq_i \cdot dp_i}{h_0^{3N}} \cdot e^{-\beta \sum_{i=1}^{3N} \frac{p_i^2}{2m}} && (4.67)\\
&= \frac{1}{N!} \cdot q^N, \quad q = \int \frac{\prod_{i=1}^{3} dq_i \cdot dp_i}{h_0^{3N}} \cdot e^{-\beta \sum_{i=1}^{3} \frac{p_i^2}{2m}} && (4.68)\\
&= V/\lambda_T^3, \quad \lambda_T = \sqrt{\frac{h_0^2}{2\pi m k_B T}} && (4.69)
\end{aligned}
$$

$$
\therefore Q_G = \sum_{N=0}^{\infty} z^N \cdot q^N / N! = e^{zq} \quad \text{for } zq < 1 \qquad (4.70)
$$

$$
\begin{aligned}
\Omega(T, V, \mu) = -k_B T \cdot \ln Q_G &= -k_B T \cdot zq && (4.71)\\
&= -k_B T \cdot e^{\beta\mu} \cdot V/\lambda_T^3 && (4.72)
\end{aligned}
$$

$$
\begin{aligned}
\overline{N} = -\frac{\partial \Omega}{\partial \mu} = e^{\beta\mu} \cdot V/\lambda_T^3 \longrightarrow \mu &= k_B T \cdot \ln(\lambda_T^3 \cdot \overline{n}), \quad \overline{n} = \overline{N}/V && (4.73)\\
&= k_B T \cdot \ln(\lambda_T^3/(V/\overline{N})) && (4.74)\\
&\text{Classical case: } \frac{V}{\overline{N}} \gg \lambda_T^3 \longrightarrow \mu < 0 && (4.75)
\end{aligned}
$$

$$
\begin{aligned}
P &= -\frac{\partial \Omega}{\partial V} = k_B T \cdot e^{\beta\mu}/\lambda_T^3 = k_B T \cdot \frac{\overline{N}}{V} \longrightarrow PV = \overline{N} k_B T && (4.76)\\
U &= -\frac{\partial \ln Q_G(T, V, z)}{\partial \beta} = \frac{3}{2} k_B T \cdot zq = \frac{3}{2} \overline{N} k_B T && (4.77)\\
u &= U/\overline{N} = \frac{3}{2} k_B T \longrightarrow C_V = \frac{\partial u}{\partial T} = \frac{3}{2} k_B && (4.78)
\end{aligned}
$$