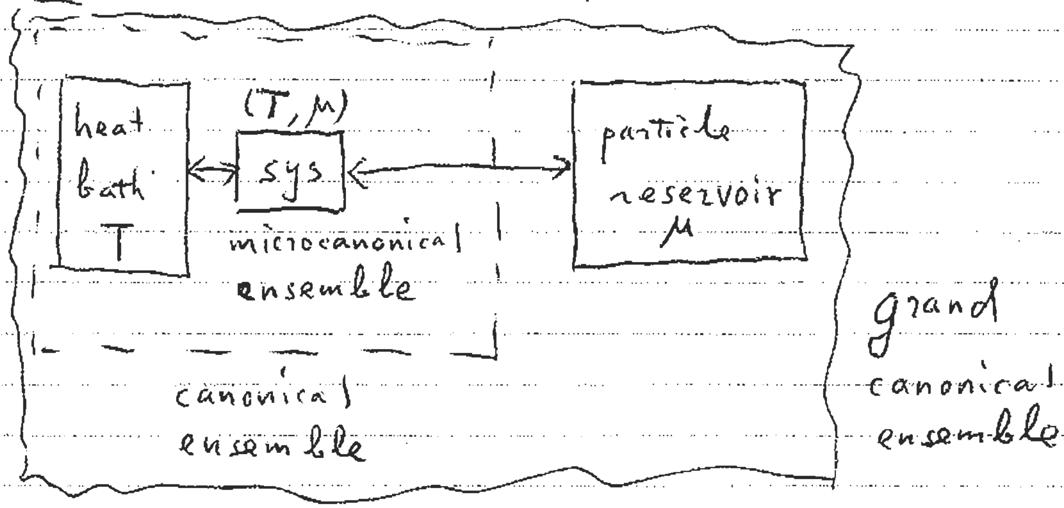
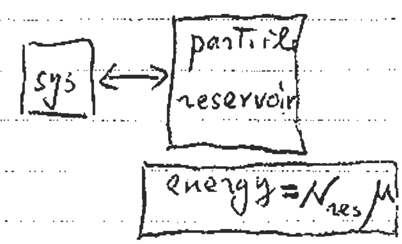
IV. Grand canonical ensemble



① Grand partion function = partition function of combind system



Energy of combind system

$$\underbrace{E_{n,N}}_{\text{system}} + \underbrace{N_{res}\mu}_{\text{particle reservoir}}$$

$$= E_{n,N} - N\mu + \underbrace{N_{tot}\,\mu}_{\text{constant \& droped.}}$$

partition function of the combined system
or grand partition function of the system $= \sum_{n,N} e^{-\beta(E_{n,N} - N\mu)}$

$= Q_G$

$$Q_G(\mu, V, T) = \sum e^{\beta\mu N} \underbrace{Q_N(V,T)}_{\text{partion funtion of } N \text{ particles}}$$

$$= \sum z^N Q_N(V,T) \qquad \boxed{z = e^{\beta\mu}} \text{ fugacity}$$

(3) Thermodynamical quantities:

$$\star\ \frac{\partial}{\partial V} \ln Q_G = \frac{\sum_{n,N} -\beta \frac{\partial E_{n,N}}{\partial V} e^{-\beta(E_{n,N}-N\mu)}}{\sum_{n,N} e^{-\beta(E_{n,N}-\mu N)}}$$

$$= -\beta \underbrace{\left\langle \frac{\partial E_{n,N}}{\partial V} \right\rangle}_{\text{Pressure}} = +\beta P$$

$$\Rightarrow \boxed{P = -\left.\frac{\partial \Omega(V,T,\mu)}{\partial V}\right|_{\mu,T}}$$

Note $\Omega = V\,\omega(T,\mu)$ — ω is intensive. It does not depend on extensive quantity V

$\Rightarrow \omega(T,\mu) = -P(T,\mu)$

or, $\boxed{\Omega = -PV}$

$$\star\ \left.\frac{\partial \Omega}{\partial T}\right|_{V,\mu} = \left.\frac{\partial\left[A(V,T,\overset{\uparrow N(\mu,V,T)}{N}) - \mu N\right]}{\partial T}\right|_{V,\mu}$$

$$= \left.\frac{\partial A(V,T,N)}{\partial T}\right|_{V,N} + \left.\frac{\partial A(V,T,N)}{\partial N}\right|_{V,T} \left.\frac{\partial N}{\partial T}\right|_{V,\mu} - \mu \left.\frac{\partial N}{\partial T}\right|_{V,\mu}$$

$$= \left.\frac{\partial A}{\partial T}\right|_{V,N} = -S$$

Dependent of T through $N(\mu,V,T)$. The two terms cancel.

$$\boxed{\left.\frac{\partial \Omega}{\partial T}\right|_{V,\mu} = -S}$$

$$\star\ \frac{\partial \Omega}{\partial \mu} = \frac{\partial\left(A(V,T,N(V,T,\mu)) - \mu N(V,T,\mu)\right)}{\partial \mu}$$

$$= \underbrace{\frac{\partial(A-\mu N)}{\partial N}}_{=0} \frac{\partial N}{\partial \mu} - N = -N \Rightarrow \boxed{N = -\frac{\partial \Omega}{\partial \mu}}$$

② Average number and number fluctuations.

$$Q_G = \sum_{n,N} \underbrace{e^{-\beta(E_{n,N} - N\mu)}}$$

$\hookrightarrow \propto$ prob. for the system to have N particles and in n^{th} state.

$$= \sum_N \underbrace{e^{\beta\mu N} Q_N}$$

$\hookrightarrow \propto$ prob. for the system to have N particles

$$\langle N \rangle = \frac{\sum_N N e^{\beta\mu N} Q_N}{\sum_N e^{\beta\mu N} Q_N}$$

system want to maximize $e^{\beta\mu N} Q_N = e^{-\beta\Omega}$ or minimize Ω

$$\boxed{\langle N \rangle = -\frac{\partial}{\partial\mu} \Omega(\mu, V, T)}$$

$$\boxed{\text{Thermopotential } \Omega \equiv -k_B T \ln Q_G}$$

Let $\bar{N}$ maximize $e^{\beta\mu N} Q_N = e^{\beta\mu N} e^{-\beta A_N}$

$$Q_G \approx e^{\beta\mu\bar{N}} Q_{\bar{N}} = e^{-\beta(A_{\bar{N}} - \mu\bar{N})} = e^{-\beta\Omega}$$

$$\Rightarrow \boxed{\Omega = A - \mu N} \quad \& \quad \boxed{\bar{N} = \langle N \rangle}$$

Fluctuation of N: $e^{\beta\mu N} e^{-\beta A_N} \simeq e^{-\frac{1}{2}\beta \left.\frac{\partial^2 A_N}{\partial N^2}\right|_{N=\bar{N}} (N-\bar{N})^2}$

Second way: $-\frac{\partial^2}{\partial\mu^2}\Omega = +\frac{\beta \sum N^2 e^{\beta\mu N} Q_N}{\sum e^{\beta\mu N} Q_N} - \frac{\beta(\sum N e^{\beta\mu N} Q_N)^2}{(\sum e^{\beta\mu N} Q_N)^2}$

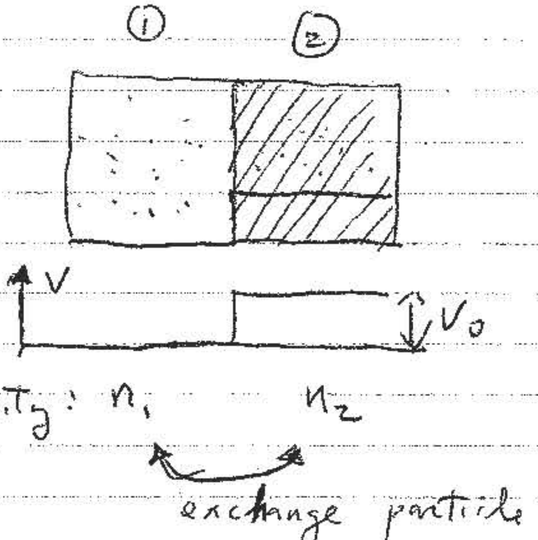
$$= \beta \langle N^2 \rangle - (\langle N \rangle)^2$$

$$\boxed{\langle (N-\bar{N})^2 \rangle = -k_B T \frac{\partial^2}{\partial\mu^2} \Omega(\mu, V, T)}$$

4 Applications

Ⓐ Two classical gases

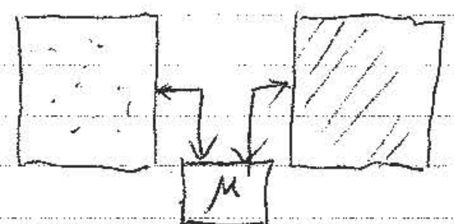
how n_1 & n_2 are related.



$$\Omega_1 = A_1(V_1, T, N_1) - \mu N_1$$

$$= N_1 k_B T\,(\ln n_1 \lambda_1^3 - 1) - \mu N_1$$

$$\lambda_1 = \sqrt{2\pi \hbar^2 / m k T}$$



particle reservoir

Prob. $P(N_1) \propto e^{-\frac{\Omega}{k_B T}}$

N_1 minimize Ω

$$\Rightarrow \quad \left.\frac{\partial A_1}{\partial N_1}\right|_{V,T} = \mu = k_B T\left[\ln(n_1 \lambda_1^3) - 1\right] + k_B T$$

$$\boxed{\mu = k_B T \ln(n_1 \lambda_1^3)}$$ ← chemical potential of ideal gas

$$\boxed{n_1 = \frac{1}{\lambda_1^3}\, e^{+\frac{\mu}{k_B T_1}}} \qquad \Omega = N k_B T\left(\frac{\mu}{k_B T} - 1\right) - \mu N$$

$$= -N k_B T = -V \frac{1}{\lambda^3} e^{+\frac{\mu}{k_B T}}$$

$$\boxed{\Omega = -V \frac{1}{\lambda^3} e^{\mu / k_B T}}$$

$$\Omega_2 = A_2(V_2, T, N_2) - \mu N_2$$

$$= N_2 k_B T \left\{\ln(n_2 \lambda_2^3) - 1\right\} - \mu N_2$$

$$+ N_2 V_0$$ ← $A = E - ST$ E is shifted by $N_2 V_0$

$$\mu = \frac{\partial A_2}{\partial N_2} = k_B T_2 \ln(n_2 \lambda_2^3) + V_0$$

$$\boxed{n_2 = \frac{1}{\lambda_2^3}\, e^{+\frac{\mu - V_0}{k_B T_2}}}$$

n_1 & n_2 is related such that

$$\boxed{\frac{\partial A_1}{\partial N_1} = \mu = \frac{\partial A_2}{\partial N_1}}$$

chemical potentials are equal in the equilibrium state

$\lambda_1 = \lambda_2 \Rightarrow$

$$\boxed{\frac{n_2}{n_1} = e^{-V_0/k_BT}}$$

for O_2

$g m_{O_2} / k_B \cdot 300K$
$= 1.3 \times 10^{-4}/m$
$= 0.13/km$

$$\frac{n_{O_2}(10km)}{n_{O_2}(0)} = e^{-1.3} = 0.27$$

$n_{O_2}(0)/n_{N_2}(0) \simeq 1/4$

$n_{O_2}(10km)/n_{N_2}(10km) = ?$

(b) Adsorption on surface

T, P

energy cost ϵ_0

system 1 : classical gas

system 2 : $\boxed{\cdot}$ or $\square$

system 1 & system 2 has the same μ.

chemical potential of classical gas

$$\mu = k_BT \ln(n \lambda^3) \qquad P = k_BT\, n$$

$$\boxed{P_n \propto e^{-\frac{E_n - \mu N}{k_BT}}} \quad = k_BT \ln\left(\frac{P}{k_BT} \lambda^3\right) \qquad \lambda = \sqrt{2\pi\hbar^2/mkT}$$

$$P(\boxed{\cdot}) \propto e^{-\frac{\epsilon_0 - \mu \cdot 1}{k_BT}} = e^{-\frac{\epsilon_0 - \mu}{k_BT}}$$

$$P(\square) \propto e^{\frac{-0 - \mu \cdot 0}{k_BT}} = 1$$

average # of particles per site

$$\rho = \frac{e^{-\frac{\epsilon_0 - \mu}{k_BT}}}{1 + e^{-\frac{\epsilon_0 - \mu}{k_BT}}} = \frac{1}{1 + e^{\frac{\epsilon_0 - \mu}{k_BT}}} = \frac{1}{1 + \frac{k_BT}{\lambda^3 P} e^{\epsilon_0/k_BT}}$$

$$\rho = \frac{1}{1+e^{\frac{\epsilon_0}{k_BT} - \ln \frac{P}{k_BT}\lambda^3}} = \boxed{\frac{1}{1+\frac{k_BT}{\lambda^3 P}e^{\epsilon_0/k_BT}}}$$

$\rho \to 1$ as $P \to \infty$

$\rho \to 0$ as $P \to 0$ ✓

when $\rho \ll 1$ $\quad \rho \simeq \frac{P\lambda^3}{k_BT} e^{-\epsilon_0/k_BT}$

$$= n\lambda^3 e^{-\epsilon_0/k_BT}$$

(c) Chemical reactions

$$2H \rightleftharpoons H_2 + \epsilon_0$$

or $2H - H_2 = \epsilon_0$

or $\boxed{\sum_i \nu_i X_i = \epsilon_0}$ $\quad \nu_1 = 2 \quad \nu_2 = -1$, $\quad X_1 = H \quad X_2 = H_2$

At T, P what is n_H / n_{H_2} ?

The change of N_i due to the reaction

$$\boxed{\frac{\delta N_1}{\nu_1} = \frac{\delta N_2}{\nu_2} = \frac{\delta N_i}{\nu_i}}$$

Total Free energy $\sum_i A_i(V, T, N_i) = A_{tot}$

Chemical reaction minimize A_{tot} and reach equilibrium.

At equilibrium:

$$\delta A_{TOT} = \sum_i \delta N_i \frac{\partial A_i}{\partial N_i} = 0$$

$$\Rightarrow \boxed{\sum_i \nu_i \mu_i = 0}$$ equilibrium condition for one chemical reaction.

one condition for each reaction.

$$2H \rightleftharpoons H_2 + \epsilon_0$$

internal energy ϵ_H ϵ_{H_2} $2\epsilon_H - \epsilon_{H_2} = \epsilon_0$

$$A_H = N_H k_B T\left(\ln n_H \lambda_H^3 - 1\right) + N_H \epsilon_H$$

$$\mu_H = \frac{\partial A_H}{\partial N} = k_B T \ln\left(n_H \lambda_H^3\right) + \epsilon_H$$

$$\mu_{H_2} = k_B T \ln\left(n_{H_2} \lambda_{H_2}^3\right) + \epsilon_{H_2}$$

$$\sum_i \nu_i \mu_i = 0 \Rightarrow 2\mu_H - \mu_{H_2} = 0$$

$$2 k_B T \ln\left(n_H \lambda_H^3\right) - k_B T \ln\left(n_{H_2} \lambda_{H_2}^3\right) = -\left(2\epsilon_H - \epsilon_{H_2}\right)$$

$$\frac{\left(n_H \lambda_H^3\right)^2}{n_{H_2} \lambda_{H_2}^3} = e^{-\frac{2\epsilon_H - \epsilon_{H_2}}{k_B T}}$$

$$\boxed{\frac{n_H^2}{n_{H_2}} = \frac{1}{\left(2\pi\hbar^2/mkT\right)^{3/2}} \cdot \frac{1}{2^{3/2}} \cdot e^{-\frac{\epsilon_0}{k_B T}}}$$

in general $$\boxed{\prod_i \left(\lambda_i^3 n_i\right)^{\nu_i} = e^{-\epsilon_0/k_B T}}$$ for: $\boxed{\sum \nu_i \chi_i = \epsilon_0}$

$$2H = H_2 + 436\ kJ/mol$$

at 1 atm & 300 K $\quad n_H = ?$

$n_{H_2} = ?$ $\quad PV = k_B N T$

$$\Rightarrow \boxed{n_{H_2} = \frac{P}{k_B T} = 2.4\times10^{19}/cm^3}$$

$\boxed{\begin{array}{l} \text{cgs unit} \\ 1\ atm = 10.1\ N/cm^2 \\ \quad = 10^6\ dyne/cm^2 \\ k_B = 1.38\times10^{-16}\ erg/K \\ T = 300\ K \\ m_p = 1.68\times10^{-24}\ g \end{array}}$

$$\epsilon_0 = \frac{436\ kJ}{mol} = 7.24\times10^{-12}\ erg = 4.5\ eV$$

$$\epsilon_0/k_B \cdot 300 = 175$$

$$\frac{n_H^2}{n_{H_2}} = 3.5\times10^{23}/cm^3\ e^{-175} = 3.5\times10^{-53}/cm^3$$

$$n_H = \sqrt{2.4\times10^{19}\times3.5\times10^{-53}} = 2.9\times10^{-17}/cm^3$$

d) No spin order in 1D Ising model ($E = -J\sum_i s_i s_{i+1}$

$$\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow\downarrow\downarrow\uparrow\uparrow\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow\downarrow\downarrow$$

domain wall $\quad$ A $\quad$ B $\quad$ A

$\epsilon_A = 2J \quad \epsilon_B = 2J$

$$A + B = \epsilon_A + \epsilon_B = \epsilon_0 = 4J$$

not λ_A^3 since 1D

$$\Rightarrow (\lambda_A n_A)(\lambda_B n_B) = e^{-\epsilon_0/k_B T}$$

$\lambda_A = ?\quad \lambda_B = ?$

meaning of $\lambda^3 n = \frac{\lambda^3}{v} = \frac{1}{\#\text{ of state per particle}}$

so $\lambda_A n_A \simeq n_A \quad (\text{or } \lambda_A = \lambda_B \simeq 1)$

$$\Rightarrow n_A = n_B \approx e^{-2J/k_B T}$$

per link

$$\uparrow\uparrow\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\uparrow\uparrow\uparrow\uparrow\uparrow$$

$\longleftarrow e^{2J/k_B T} \longrightarrow$