

Harmonic Oscillators  $\rightarrow f = 6N, \gamma = 2$

$$\langle \hat{q} \rangle = \frac{6N k_B T}{2} = 3N k_B T$$

$$\langle \hat{p}_r \hat{q}_r \rangle = k_B T$$

$$\langle \hat{q}_r \hat{p}_r \rangle = -k_B T$$

$$\sum_r \langle \hat{q}_r \hat{p}_r \rangle = -3N k_B T \quad \sum_r \langle \hat{p}_r \hat{q}_r \rangle = 3N k_B T$$



Vinod.

### Grand Canonical Ensemble

We now want to discuss the probability distribution of a system which not only exchanges energy but also number of particles. The equilibrium of the system is characterized by a definite temperature  $T$  and a definite particle number  $N$ . This is made possible by the system being in equilibrium with the surrounding with which it exchanges energy and particles.

Let the system  $S$  and the environment be characterized by  $E_{\text{tot}}$ ,  $N_{\text{tot}}$  and  $V_{\text{tot}}$ . At any instant the system has energy  $E$ , particle number  $N$  and volume  $V$  (fixed) such that  $E, N, V \ll E_{\text{tot}}, N_{\text{tot}}$  and  $V_{\text{tot}}$ .

Once again we have  $E + E_e = E_{\text{tot}}$   
 $N + N_e = N_{\text{tot}}$ .

The probability that the system has energy  $E$  & particle number  $N$  is proportional to the number microstates for which this occurs. This is in turn is proportional to the microstates for which the environment has energy  $E_{\text{tot}} - E$  and particle number  $N_{\text{tot}} - N$ . Thus,

$$S(E, N) \propto \Gamma_e(E_{\text{tot}} - E, N_{\text{tot}} - N)$$

$$\propto \Gamma_e(E_e - E, N_e - N)$$

Assuming  $E_{\text{tot}} \approx E_e$  or  $N_{\text{tot}} \approx N_e$

$$S(E, N) \propto \Gamma_e(E_e, N_e) + E \frac{\partial \Gamma_e}{\partial E} + N \frac{\partial \Gamma_e}{\partial N}$$

$$= \Gamma_e(E_e, N_e) - E \frac{\partial \Gamma_e}{\partial E_e} - N \frac{\partial \Gamma_e}{\partial N_e}$$

$$= \Gamma_e(E_e, N_e) \left[ 1 - E \frac{\partial \ln \Gamma_e}{\partial E_e} \Big|_{N,V} - N \frac{\partial \ln \Gamma_e}{\partial N_e} \Big|_{E,V} \right]$$

$$= \Gamma_e(E_e, N_e) \left[ 1 - \frac{E}{K_B} \frac{\partial S_e}{\partial E_e} \Big|_{N,V} - \frac{N}{K_B} \frac{\partial S_e}{\partial N_e} \Big|_{E,V} \right]$$

$$S(E, N) = \Gamma_e(E_e, N_e) \left[ 1 - \frac{E}{K_B T} + \frac{NM}{K_B T} \right]$$

Where we have used  $\frac{\partial S_e}{\partial E_e} = \frac{1}{T}$

$$\text{as } \left(\frac{\partial S_e}{\partial N_e}\right)_{E,N} = -\frac{\mu}{T}$$

$$\Rightarrow \ln f(E, N) = \ln \Gamma_e(E_e, N_e) + \ln \left[ 1 - \frac{(E - \mu_N)}{k_B T} \right]$$

$$\approx \ln \Gamma_e(E_e, N_e) - \frac{(E - \mu_N)}{k_B T} - \frac{(E - \mu_N)/k_B T}{1 - \frac{(E - \mu_N)}{k_B T}}$$

$$\text{leading to } f(E, N) = A e^{-\frac{(E - \mu_N)}{k_B T}}$$

Calculating  $A$  using the normalization condition

$$f(E, N) = \frac{1}{Q} e^{-\frac{(E - \mu_N)}{k_B T}}$$

$$\text{with } Q = \sum_{\text{states}} e^{-\frac{(E - \mu_N)}{k_B T}}$$

Once again, the contact with thermodynamics depends on the fact that the distribution is sharply peaked around some average value of  $E$  &  $N$ . To show that we write

$$\langle N \rangle = \frac{1}{Q} \sum_{\text{states}} N e^{-\frac{(E - \mu_N)}{k_B T}}$$

$$\frac{\partial \langle N \rangle}{\partial \mu} = \frac{B}{Q} \sum_{\text{states}} N^2 e^{-\frac{(E - \mu_N)}{k_B T}} - \frac{\beta}{Q^2} \left( \sum_{\text{states}} N e^{-\frac{(E - \mu_N)}{k_B T}} \right)^2$$

$$= \beta \left[ \langle N^2 \rangle - \langle N \rangle^2 \right] = \beta \langle \Delta N^2 \rangle$$

$$\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{V,T} = \left(\frac{\partial \langle N \rangle}{\partial P}\right)_{V,T} \left(\frac{\partial P}{\partial \mu}\right)_{V,T}$$

$$= \left(\frac{\partial \langle N \rangle}{\partial P}\right)_{V,T} \left(\frac{\partial \mu}{\partial P}\right)_{V,T}$$

Consider the free energy  $\bar{F} = E - TS - \mu N$

We know that  $G = \mu N$

$$\Rightarrow \bar{F} = E - TS - G = E - TS - (E - TS + PV)$$

$$\bar{F} = -PV$$

$$\begin{aligned} d\bar{F} &= dE - Tds - sdt - \mu dN - N d\mu \\ &= -sdt - pdv - N d\mu. \end{aligned}$$

$$\left(\frac{\partial \bar{F}}{\partial \mu}\right)_{V,T} = -N$$

$$\Rightarrow \frac{\partial (-PV)}{\partial \mu} = -N \quad \text{But } \mu \text{ can be a function of } P \text{ only.}$$

$$\left(\frac{\partial P}{\partial \mu}\right)_{V,T} = +\frac{N}{V}$$

$$\Rightarrow \left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{V,T} = +\frac{N}{V} \left(\frac{\partial \langle N \rangle}{\partial P}\right)_{V,T}$$

Now,  $P$  can be a function of only  $N/V = n$  and  $T$ .

Hence

$$\left(\frac{\partial P}{\partial V}\right)_{N,T} = \left(\frac{\partial P}{\partial n}\right)_{V,T} \left(\frac{\partial n}{\partial V}\right) = -\frac{N}{V^2} \left(\frac{\partial P}{\partial N}\right)_{V,T} \left(\frac{\partial N}{\partial n}\right)$$

$$\left(\frac{\partial N}{\partial P}\right)_{V,T} = -\frac{N}{V} \left(\frac{\partial V}{\partial P}\right)_{N,T} = -\frac{N}{V} \left(\frac{\partial P}{\partial N}\right)_{V,T}$$

$$\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{V,T} = n \left(\frac{\partial \langle N \rangle}{\partial P}\right)_{V,T} \quad \frac{\partial \langle N \rangle}{\partial n} = \frac{\partial n}{\partial P}$$

$$\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{V,T} = -n \frac{N}{V} \left(\frac{\partial V}{\partial P}\right)_{N,T}$$

$$\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{V,T} = -n^2 N \left(\frac{\partial (V/N)}{\partial P}\right)_{N,T} = -n^2 N \chi_T$$

$$\alpha_T = - \left(\frac{\partial (V/N)}{\partial P}\right)_{N,T}$$

$$\langle \Delta N^2 \rangle = n^2 N k_B T \chi_T$$

$$\text{Once again } \sqrt{\frac{\langle \Delta N^2 \rangle}{\langle N \rangle}} = O\left(\frac{\sqrt{N}}{N}\right) = O\left(\frac{1}{\sqrt{N}}\right)$$

What about energy fluctuations?

$$\frac{\partial \langle E \rangle}{\partial P} = \frac{\partial}{\partial \beta} \frac{1}{Q} \sum E e^{-\beta(E-\mu_N)}$$

$$= -\frac{1}{Q} \sum E (E-\mu_N) e^{-\beta(E-\mu_N)} - \frac{1}{Q^2} \frac{\partial Q}{\partial \beta} \sum E e^{-\beta(E-\mu_N)}$$

$$Q = \sum e^{-\beta(E-\mu_N)}$$

$$\frac{\partial Q}{\partial \beta} = -\sum (E-\mu_N) e^{-\beta(E-\mu_N)}$$

$$\frac{\partial \langle E \rangle}{\partial \beta} = -\frac{1}{Q} \sum E (E-\mu_N) e^{-\beta(E-\mu_N)} + \frac{1}{Q^2} \sum (E-\mu_N) e^{-\beta(E-\mu_N)} \frac{\sum E e^{-\beta(E-\mu_N)}}{\sum e^{-\beta(E-\mu_N)}}$$

$$\begin{aligned} \frac{\partial \langle E \rangle}{\partial \beta} &= -\frac{1}{Q} \sum (E^2 - \mu EN) e^{-\beta(E-\mu N)} + \frac{1}{Q^2} \left[ \left( \sum E e^{-\beta(E-\mu N)} \right)^2 \right. \\ &\quad \left. - \sum N \mu e^{-\beta(E-\mu N)} \sum E e^{-\beta(E-\mu N)} \right] \\ &= - \left[ \frac{1}{Q} \sum E^2 e^{-\beta(E-\mu N)} - \frac{1}{Q^2} \left( \sum E e^{-\beta(E-\mu N)} \right)^2 \right] \\ &\quad + \frac{1}{Q} \sum \mu EN e^{-\beta(E-\mu N)} - \frac{1}{Q} \sum \mu N e^{-\beta(E-\mu N)} \frac{1}{Q} \sum E e^{-\beta(E-\mu N)} \\ &= -\langle (\Delta E)^2 \rangle + \mu [\langle EN \rangle - \langle N \rangle \langle E \rangle]. \end{aligned}$$

$$\begin{aligned} \frac{\partial \langle E \rangle}{\partial \mu} &= \frac{\partial}{\partial \mu} \frac{1}{Q} \sum E e^{-\beta(E-\mu N)} \\ &= \frac{\beta}{Q} \sum EN e^{-\beta(E-\mu N)} - \frac{1}{Q^2} \frac{\partial Q}{\partial \mu} \sum E e^{-\beta(E-\mu N)}. \end{aligned}$$

$$\begin{aligned} \frac{\partial Q}{\partial \mu} &= \sum \beta N e^{-\beta(E-\mu N)} \\ \frac{\partial \langle E \rangle}{\partial \mu} &= \frac{\beta}{Q} \sum EN e^{-\beta(E-\mu N)} - \frac{\beta}{Q} \sum N e^{-\beta(E-\mu N)} \frac{1}{Q} \sum E e^{-\beta(E-\mu N)} \\ &= \beta [\langle EN \rangle - \langle E \rangle \langle N \rangle] \end{aligned}$$

$$\Rightarrow \langle \Delta E^2 \rangle = -\frac{\partial \langle E \rangle}{\partial \beta} + \frac{\mu}{\beta} \frac{\partial \langle E \rangle}{\partial \mu}$$

$$= k_B T^2 \frac{\partial \langle E \rangle}{\partial T} + \mu k_B T \frac{\partial \langle E \rangle}{\partial \mu}$$

Hence  $\langle \Delta E^2 \rangle$  is  $\mathcal{O}(N)$  as therefore

$$\sqrt{\frac{\langle \Delta E^2 \rangle}{\langle E \rangle}} = \mathcal{O}\left(\frac{N^{1/2}}{N}\right) = \mathcal{O}\left(\frac{1}{\sqrt{N}}\right)$$

To relate the statistical mechanical quantity with thermodynamics we write

$$S = -k_B \langle \ln f(E, N) \rangle = -k_B \left\langle \ln \frac{1}{Q} e^{-\beta(E-\mu_N)} \right\rangle$$

$$= \frac{1}{T} \langle E - \mu_N \rangle + k_B \ln Q.$$

$$TS = E - \mu_N + k_B T \ln Q.$$

$$\Rightarrow -k_B T \ln Q = E - TS - \mu_N = \bar{F} = -PV$$

$$\Rightarrow PV = k_B T \ln Q$$

Alternatively, we can write the grand canonical partition function as

$$Q = \int e^{-\beta(E-\mu_N)} \Gamma(E, N) dE dN$$

$$= \int e^{-\beta(E-TS-\mu_N)/k_B T} dE dN.$$

Once again, in the limit of  $N \rightarrow \infty$ , the argument of the exponential is sharply peaked and is dominated by the minimum of  $E - TS - \mu_N$ . The extremization conditions are

$$1 - T \left( \frac{\partial S}{\partial E} \right)_N = 0 \quad \text{and} \quad \left( \frac{\partial S}{\partial N} \right)_E = -\frac{\mu}{T}$$

The solutions of the above equations are given by  $E = \bar{E}$  &  $N = \bar{N}$   
Therefore,

$$E - TS - \mu N = \bar{E} - \mu \bar{N} - TS(\bar{E}, \bar{N}) - T \left[ \frac{1}{2} \left( \frac{\partial^2 S}{\partial E^2} \right) \Delta E^2 + \frac{\partial^2 S}{\partial E \partial N} (\Delta E \Delta N) \right. \\ \left. + \left( \frac{\partial S}{\partial N^2} \right) (\Delta N)^2 \right]$$

$$\lambda_1 = \left( \frac{\partial S}{\partial E^2} \right) = - \frac{\partial}{\partial E} \left( \frac{1}{T} \right) = - \frac{1}{T^2} \left( \frac{\partial E}{\partial T} \right)^{-1} = - \frac{1}{T^2} \frac{1}{C}$$

$$\lambda_2 = \frac{\partial}{\partial N} \left( \frac{\partial S}{\partial E} \right) = - \frac{1}{T^2} \left( \frac{\partial T}{\partial N} \right)$$

$$\lambda_3 = \frac{\partial}{\partial N} \left( \frac{\partial S}{\partial N} \right) = \frac{\partial}{\partial N} \left( \frac{N}{T} \right) = - \frac{1}{T} \frac{\partial N}{\partial N} + \frac{\mu}{T^2} \frac{\partial T}{\partial N}$$

$$E - TS - \mu N = PV + \left[ \frac{1}{FC} (\Delta E)^2 + \frac{1}{T} \Delta N \right]$$

$$Q = e^{PV/k_B T} \int d(\Delta E) d(\Delta N) e^{-\frac{1}{2k_B T} (\lambda_1 (\Delta E)^2 + \lambda_2 \Delta E \Delta N + \lambda_3 (\Delta N)^2)}$$

$$\lambda_1 = -T \frac{\partial S}{\partial E^2} \quad \lambda_2 = -T \frac{\partial S}{\partial E \partial N} \quad \lambda_3 = -T \frac{\partial S}{\partial N^2}$$

$$\lambda_1 > 0, \quad \lambda_3 > 0 \quad \text{and} \quad \lambda_1 \lambda_3 > \lambda_2^2$$

$$\ln Q = \frac{PV}{k_B T} + C(\ln N)$$

$$\Rightarrow k_B T \ln Q = PV + C(\ln N)$$

and in the thermodynamic limit  $\because PV \sim \propto(N)$  we get-

$$k_B T \ln Q = PV$$

$$\Omega(T, V, \mu) = -k_B T \ln Q$$

$$\Omega = E - TS - \mu N$$

$$\Omega = -PV$$

$$d\Omega = -SdT - pdV - Nd\mu$$

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

$$k_B T \frac{\partial \ln Q}{\partial V} = P$$

$$-\left(\frac{\partial \Omega}{\partial T}\right)_{V, \mu} = S$$

$$\frac{\partial (k_B T \ln Q)}{\partial T} = S$$

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

$$k_B T \left(\frac{\partial \ln Q}{\partial \mu}\right)_{V, T} = N$$

$$E = \Omega + TS + \mu N$$

$$= -k_B T \ln Q + T \left[ k_B \ln Q + k_B T \left(\frac{\partial \ln Q}{\partial T}\right)_{V, \mu} \right]$$

$$+ \mu k_B T \left(\frac{\partial \ln Q}{\partial \mu}\right)_{V, T}$$

$$= k_B T \left(\frac{\partial \ln Q}{\partial T}\right)_{V, \mu} + \frac{\mu}{\beta} \left(\frac{\partial \ln Q}{\partial \mu}\right)_{V, T}$$

$$= -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{V, \mu} + \frac{\mu}{\beta} \left(\frac{\partial \ln Q}{\partial \mu}\right)_{V, T}$$

Relation with Canonical partition function.

$$Q = \sum_{\text{States}} e^{-\beta(E - \mu N)}$$

$$= \sum_{N_j} e^{\beta \mu N_j} \underbrace{\sum_{N_j; E} e^{-\beta E}}$$

Canonical partition function.

$$\text{So we rewrite } Q = \sum_N e^{\beta \mu N} Z_N.$$

Eg Ideal gas.

$$Z_N = \frac{V^N}{N! \lambda_T^N}$$

where  $\lambda_T$  is the thermal volume  
and is related to the de-Broglie wavelength.

$$\lambda_T = \frac{1}{C_D} (k_B T)^{-1/2} = \left( \frac{2\pi \hbar^2}{m k_B T} \right)^{3/2} = \lambda_D$$

$$\text{with } \lambda_D = \left( \frac{2\pi \hbar^2}{m k_B T} \right)^{1/2}$$

The grand canonical partition function takes the form

$$Q = \sum_{N=0}^{\infty} e^{\beta \mu N} \frac{1}{N!} \left( \frac{V}{\lambda_T} \right)^N$$

$$= 1 + e^{\frac{\beta \mu}{\lambda_T}} + \frac{1}{2} e^{2\frac{\beta \mu}{\lambda_T}} \left( \frac{V}{\lambda_T} \right)^2 + \dots$$

$$= \exp \left[ e^{\frac{\beta \mu}{\lambda_T}} \frac{V}{\lambda_T} \right]$$

$$\therefore PV = k_B T \ln Q$$

$$= k_B T e^{\frac{\beta \mu}{k_B T} V}$$

$$\Rightarrow P = \frac{e^{\frac{\beta \mu}{k_B T} V}}{Z(T)}$$

In the case where the micro systems are distinguishable  
then

$$Q = \sum e^{\frac{\beta \mu_n}{k_B T} V} Z(T)^N$$

$$= \sum \left[ e^{\frac{\beta \mu}{k_B T} V} Z(T) \right]^N = \frac{1}{1 - e^{\frac{\beta \mu}{k_B T} V}}$$

with the additional constraint that  $|e^{\frac{\beta \mu}{k_B T} V}| < 1$

$$Q = \exp \left[ e^{\frac{\beta \mu}{k_B T} V} \right]$$

$$\ln Q = e^{\frac{\beta \mu}{k_B T} V}$$

$$\langle N \rangle = \frac{1}{\beta} \left( \frac{\partial \ln Q}{\partial \mu} \right)_{k_B T} = \frac{V e^{\frac{\beta \mu}{k_B T}}}{k_B T}$$

$$S = \frac{\partial k_B T \ln Q}{\partial T} = k_B V e^{\frac{\beta \mu}{k_B T}} + k_B T \left( \frac{\partial \ln Q}{\partial T} \right)_{\mu, V}$$

$$S = k_B e^{\frac{V}{\lambda_T}} + \frac{1}{T} \left( \frac{\partial \ln Q}{\partial \beta} \right)_{V, \mu}$$

$\beta = \frac{1}{kT}$

$$\frac{\partial T}{\partial \beta} = -\frac{1}{kT}$$

$$S = k_B e^{\frac{V}{\lambda_T}} - \frac{\mu}{T} \frac{V}{\lambda_T} e^{\frac{\beta \mu}{V}} - \frac{1}{T} e^{\frac{\beta \mu}{V}} \frac{\partial}{\partial \beta} \left( \frac{1}{\lambda_T} \right)$$

$$E = - \left( \frac{\partial \ln Q}{\partial \beta} \right)_{V, \mu} + \frac{\mu}{\beta} \left( \frac{\partial \ln Q}{\partial \mu} \right)_{V, T}$$

$$= \mu \frac{V}{\lambda_T} e^{\frac{\beta \mu}{V}} + e^{\frac{\beta \mu}{V}} \frac{\partial}{\partial \beta} \left( \frac{1}{\lambda_T} \right) + \frac{\mu}{\beta} \rho e^{\frac{\beta \mu}{V}} \frac{V}{\lambda_T}$$

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

$$\frac{\partial}{\partial \beta} \left( \frac{1}{\lambda_T} \right) = -\frac{1}{\lambda_T^2} \frac{3}{2} \left( \frac{2\pi h^2}{m} \right)^{1/2} \beta^{1/2}$$

$$\theta = \frac{3}{2} \langle N \rangle k_B T$$

Paramagnetism

$$\mathcal{H} = - \sum_{i=1}^N \vec{\mu}_i \cdot \vec{H}$$

Where  $\vec{\mu}_i$  is the magnetic moment of the  $i^{th}$  spin.

Classical treatment

$$\mathcal{H} = - \sum_{i=1}^N \mu_i H \cos \theta_i$$

Where  $\theta_i$  is the angle between  $\vec{\mu}_i$  and the external field  $\vec{H}$ .

To obtain the one particle partition function we must integrate over the dynamical variable pertaining to a single particle. The relevant variable is the orientation angle. In 3D case, the orientation is specified by  $\theta$  &  $\phi$ . Therefore,

$$Z = \int_0^{2\pi} d\phi \int_{-1}^1 d(\cos \theta) e^{-\beta \mu H \cos \theta}$$

$$= \frac{4\pi}{\beta \mu H} \operatorname{Sinh} \beta \mu H$$

The partition function for the whole system is then

$$Z = Z^N = \left( \frac{4\pi}{\beta \mu H} \operatorname{Sinh} \beta \mu H \right)^N$$

and the free energy  $F = -k_B T \ln Z = -N k_B T \ln \left( \frac{4\pi}{\beta \mu H} \operatorname{Sinh} \beta \mu H \right)$

The magnetization is given by

$$M = - \left( \frac{\partial F}{\partial H} \right)_{N,T} = N k_B T \frac{\partial}{\partial H} \left( \ln \operatorname{Sinh} \beta \mu H - \ln \beta \mu H \right)$$

$$M = +N \frac{\beta \mu}{\beta} \frac{\partial}{\partial x} (\ln \coth x - \ln x)$$

$$= N \mu \left( \coth x - \frac{1}{x} \right) = N \mu L(\beta \mu H).$$

When  $L(x) = \coth x - \frac{1}{x}$  is called the Langevin function.

For  $x \gg 1$ , i.e.  $\beta \mu H \gg 1$  or  $k_B T \ll \mu H$  the function  $L(x)$  approaches unity.

On the other hand for small  $x$ ,  $\beta \mu H \ll 1$   $k_B T \gg \mu H$

$$\coth x = \frac{1}{x} + \frac{x}{3} + O(x^3)$$

$$\Rightarrow L(x) \approx \frac{x}{3}, \quad x \ll 1$$

$$\therefore M = N \mu \frac{\beta \mu H}{3} = \frac{\beta N \mu^2 H}{3}$$

$$\text{and the susceptibility is } \frac{\partial M}{\partial H} = \frac{N \mu^2}{3 k_B T}$$

This is Curie's law of paramagnetism.

### Quantum Mechanical Treatment

For the quantum mechanical case, we need to make several changes. First, if the spin of the particle is  $J$  then the magnetic moment is given by

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

where  $\mu_0$  itself is the product of two factors.

$$\mu_0 = g \left( \frac{e\hbar}{2mc} \right) \rightarrow \text{magneton}$$

Without loss of generality, we will take the magnetic field in the direction of  $\hat{x}$ -axis. The  $z$ -component of  $\vec{\mu}$  cannot be arbitrary, since  $J_z$  has discrete eigenvalues. If  $m_j$  denote the eigenvalues, then  $m_j$  can take integral values between  $-J$  to  $+J$ . Therefore, the one particle partition function take the form

$$\begin{aligned} Z &= \sum_{m_j=-J}^{+J} e^{\beta \mu_0 m_j H} \\ &= e^{\beta \mu_0 J H} \frac{(1 - e^{-\beta \mu_0 (2J+1)H})}{(1 - e^{-\beta \mu_0 H})} \\ &= \frac{\sinh((J+\frac{1}{2})\beta \mu_0 H)}{\sinh(\frac{\beta \mu_0 H}{2})} \end{aligned}$$

The corresponding partition function for  $N$ -spins is

$$Z = Z^N$$

as the free energy

$$x = \beta \mu_0 H$$

$$\begin{aligned} F &= -Nk_B T \left[ \ln \sinh \left( \left(J+\frac{1}{2}\right)x \right) - \ln \sinh x/2 \right] \\ &= -Nk_B T \left[ \ln \sinh \left(1+\frac{1}{2J}\right)x - \ln \sinh x/2 \right] \end{aligned}$$

$$M = -\left( \frac{\partial F}{\partial H} \right)_{N,T} = Nk_B T \left[ \left(1 + \frac{1}{2J}\right) \coth \left(1 + \frac{1}{2J}\right)x - \frac{1}{2J} \coth \frac{x}{2J} \right] \beta \mu_0$$

$$M = N \mu_0 B_J (\beta \mu_0 H).$$

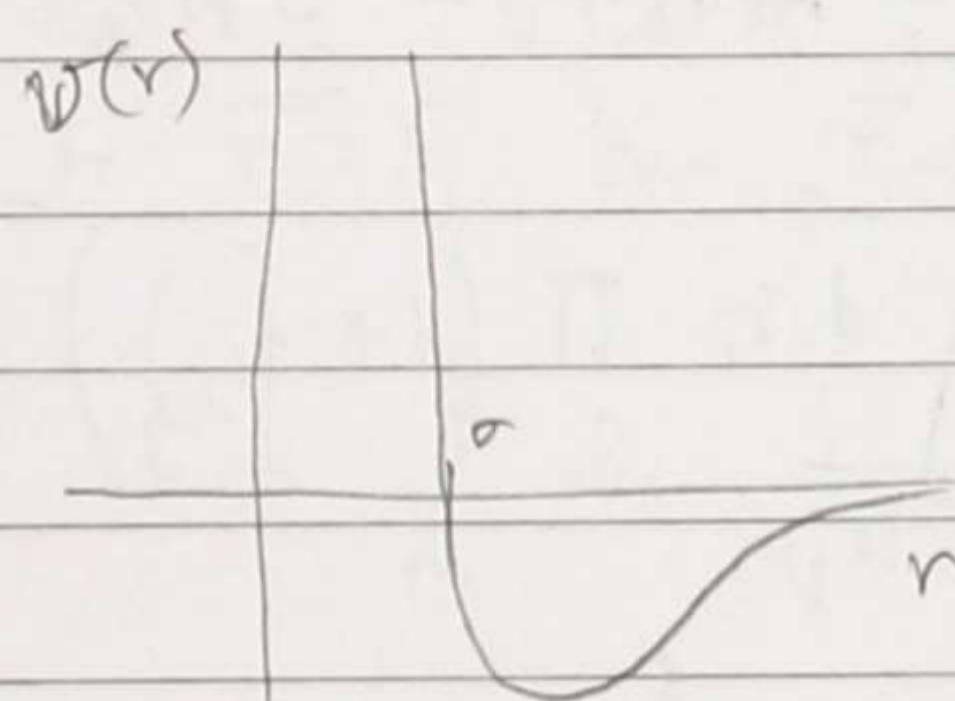
$$B_J(x) = \left[ \left( 1 + \frac{1}{2J} \right) \coth \left( 1 + \frac{1}{2J} \right) x - \frac{1}{2J} \coth \left( \frac{x}{2J} \right) \right]$$

For  $J \rightarrow \infty$

$$B_J(x) = L(x)$$

### Interacting Classical System

We now consider  $N$  molecules enclosed in a volume  $V$  interacting via a pairwise potential  $v(r_{ij})$  where  $r_{ij} = |\vec{r}_i - \vec{r}_j|$ . The potential corresponds to an attractive force at large distances and a very strong repulsion at short distances.



Before we proceed, we define an auxiliary function  $f_{ij}(r)$

$$f_{ij}(r_{ij}) = e^{-\beta v(r_{ij})} - 1$$

The potential has a zero at  $r=\sigma$ , which is roughly the molecular diameter. The energy of the system is given by

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{\substack{i,j \\ i < j}} v(r_{ij})$$

The canonical partition function is then given by

$$\begin{aligned} Z = \frac{1}{N!} \int \prod_i \frac{d^3 r_i d^3 p_i}{h^{3N}} e^{-\sum_i \beta \frac{p_i^2}{2m}} e^{-\beta \sum_{i < j} v(r_{ij})}. \\ = \frac{1}{N!} \left( \frac{V}{kT} \right)^N \left( \frac{V^N}{N!} \right) \int \prod_i d^3 r_i e^{-\beta \sum_{i < j} v(r_{ij})}. \end{aligned}$$

$$\mathcal{Z} = \frac{1}{N!} \left( \frac{V}{\Lambda_T} \right)^N \frac{1}{V^N} \int d^3 r_i \prod_{\text{pairs}} [1 + f(r_{ij})]$$

The free energy is given by

$$\begin{aligned} F &= -k_B T \ln \mathcal{Z} = -k_B T \left[ N \ln V - \ln N! + N \ln \Lambda_T \right. \\ &\quad \left. + \ln \left( \frac{1}{V^N} \int d^3 r_i \prod_{\text{pairs}} (1 + f_{ij}) \right) \right] \\ &= -k_B T \left[ N \ln V - N \ln N + N - N \ln \Lambda_T \right. \\ &\quad \left. + \ln \left( \frac{1}{V^N} \int d^3 r_i \prod_{\text{pairs}} (1 + f_{ij}) \right) \right] \\ &= \left[ -N k_B T \ln V + N k_B T \ln N - N k_B T - \frac{3}{2} N k_B T \ln \lambda_D \right. \\ &\quad \left. - k_B T \ln \left( \frac{1}{V^N} \int d^3 r_i \prod_{\text{pairs}} (1 + f_{ij}) \right) \right] \end{aligned}$$

The pressure is given by

$$P = - \left( \frac{\partial F}{\partial V} \right)_T$$

$$P = \frac{N k_B T}{V} + k_B T \frac{\partial}{\partial V} \ln \frac{1}{V^N} \int d^3 r_i \prod_{\text{pairs}} (1 + f_{ij})$$

$$P = \frac{N k_B T}{V} \left[ 1 + \frac{V}{N} \frac{\partial}{\partial V} \ln \frac{1}{V^N} \int d^3 r_i \prod_{\text{pairs}} (1 + f_{ij}) \right]$$

$$P = \frac{N k_B T}{V} \left[ 1 + V \frac{\partial F}{\partial V} \right]$$

$$\text{with } \bar{F} = \frac{1}{N} \ln \frac{1}{V^N} \int d^3r_i \prod_{\text{pairs}} (1 + f_{ij})$$

Now, we assume that the particles are weakly interacting, which means that the magnitudes of  $f_{ij}$  is small. Consequently, we can retain the  $O(f)$  terms in the products

$$\prod_{\text{pairs}} (1 + f_{ij}) = 1 + \sum_{i < j} f_{ij} + O(f^2)$$

$$\bar{F} = \frac{1}{N} \ln \frac{1}{V^N} \left[ V^N + \frac{N(N-1)}{2} V^{N-2} \int d^3r_i d^3r_j f(r_{ij}) \right]$$

Now,  $r_{ij} = |\vec{r}_i - \vec{r}_j|$  and a transformation of variable from  $\vec{r}_i$  &  $\vec{r}_j$  to  $\vec{r}_i - \vec{r}_j$  and  $\vec{r}_i + \vec{r}_j$  yields

$$\bar{F} = \frac{1}{N} \ln \frac{1}{V^N} \left[ V^N + \frac{N^2}{2} V^{N-1} \int d^3r f(r) \right]$$

$$\bar{F} = \frac{1}{N} \ln \left[ 1 + \frac{N^2}{2V} \int d^3r f(r) \right]$$

$$\frac{\partial \bar{F}}{\partial V} = + \frac{1}{N} \frac{-\frac{N^2}{2V^2} \int d^3r f(r)}{1 + \frac{N^2}{2V} \int d^3r f(r)} \approx - \frac{N}{2V^2} \int d^3r f(r).$$

$$\Rightarrow \frac{P_V}{Nk_B T} = 1 - \frac{N}{2V} \int d^3r f(r) \Rightarrow \frac{P}{k_B T} = n - \frac{n^2}{2} \int d^3r f(r)$$

To see how this compares with a real system, we take

the phenomenological equation of state

$$\left( P + \frac{N^2 a}{V^2} \right) (V - Nb) = Nk_B T$$

Where  $a$  and  $b$  are constants for a given gas.

How do you get this form?

The Canonical partition function is given by

$$\mathcal{Z} = \frac{Z^N}{N!} \quad \text{Where} \quad Z = \left( \frac{V}{\lambda_T} \right)$$

In order to derive the form of the Van-der Waals equation you assume that a single particle is moving in an average potential field offered by the others. The interaction between the spheres can then be written as

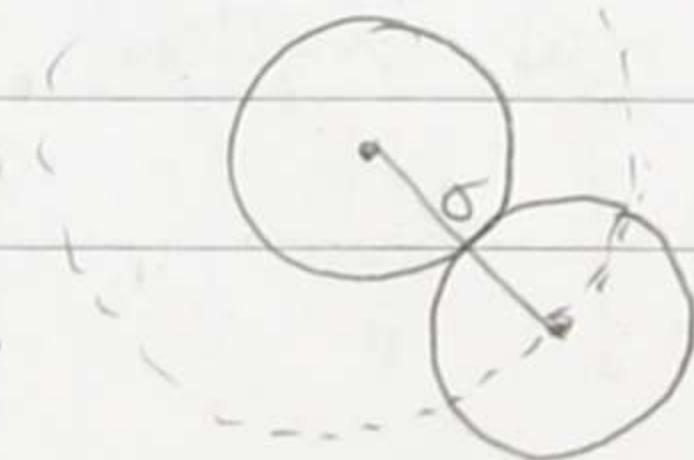
$$U(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon \left(\frac{\sigma}{r}\right)^6 & r \geq \sigma \end{cases}$$

Where  $\sigma$  is the distance where the hard spheres touch each other.

Because the particles are still independent the total partition function is

$$\mathcal{Z} = Z^N / N!$$

but the intermolecular potential necessitates two changes. The first is that, not the whole volume is available to the particle.



The volume  $\frac{4\pi\sigma^3}{3}$  is not available to the two particles.

Hence, due to finite size of the particles, the accessible volume is given by  $(V - Nb)$  when  $b = \frac{2\pi\sigma^3}{3}$

Additionally, since a single particle moves in the average potential field  $u(r)$  we write the single particle partition function as

$$Z = \frac{(V - nb)}{k_T} e^{-\beta CP/2}$$

Where  $\phi$  is the average interaction energy shared by the two particles.

$$\phi = \int_0^\infty u(r) 4\pi r^2 \frac{N}{V} dr$$

$$= -\frac{\epsilon N}{V} \int_0^\infty \left(\frac{r}{\sigma}\right)^6 4\pi r^2 dr = -\frac{\epsilon N 4\pi}{V} \int_0^\infty \left(\frac{r}{\sigma}\right)^6 \frac{r^2}{\sigma^2} d\left(\frac{r}{\sigma}\right)$$

$$= -\frac{\epsilon N 4\pi \sigma^3}{V} \int_1^\infty \frac{dx}{x^4} = -4\pi \frac{\epsilon N}{V} \frac{1}{3}$$

$$= -\epsilon \frac{4\pi \sigma^3}{3} \frac{N}{V} = -2a' N/V$$

$$\text{with } a' = \epsilon \left(\frac{2\pi\sigma^3}{3}\right) = \epsilon b'$$

$$+ \beta a' N/V$$

$$\Rightarrow Z = \frac{(V - nb')}{k_T} e$$

$\Rightarrow Z = \frac{Z^N}{N!}$  and the free energy is

$$F = -k_B T \ln Z$$

$$\ln Z = N \ln(V-Nb) + \frac{N^2 a'}{2V k_B T} - \ln \lambda_f^3 - \ln N!$$

$$F = -k_B T \left[ N \ln(V-Nb) + \frac{N^2 a'}{2V k_B T} - \ln \lambda_f^3 - \ln N! \right]$$

$$-\left(\frac{\partial F}{\partial V}\right) = P = -\left[\frac{N k_B T}{(V-Nb)} - \frac{N^2 a' k_B T}{2V^2 k_B T}\right]$$

$$P = \frac{N k_B T}{(V-Nb)} - \frac{N^2 a'}{2V^2}$$

$$\Rightarrow \left(P + \frac{N^2 a'}{2V^2}\right)(V-Nb) = N k_B T$$

$$\left(P + \frac{n^2 a}{V^2}\right)(V-nb) = n k_B T$$

Coming back to the question in hand - does this equation look like the similar expansion we did?

$$P = \frac{n k_B T}{V-nb} \frac{n^2 a}{V^2} = \frac{n k_B T}{V} \left(1 + \frac{nb}{V}\right) - \frac{n^2 a}{V^2} + O\left(\frac{1}{V^3}\right)$$

$$= \frac{n k_B T}{V} + \frac{n^2 k_B T b}{V^2} - \frac{n^2 a}{V^2} + O\left(\frac{1}{V^3}\right)$$

$$= \frac{n k_B T}{V} + \frac{n^2 (k_B T b - a)}{V^2} + O\left(\frac{1}{V^3}\right)$$

$$\left( P + \frac{N a^2}{V} \right) (V - N b) = N k_B T$$

$$P = \frac{N k_B T}{V - N b} - \frac{N a^2}{V}$$

$$= \frac{N k_B T}{V} \left( 1 + \frac{N b}{V} \right) - \frac{N a^2}{V^2} + O\left(\left(\frac{N b}{V}\right)^3\right)$$

$$P = \frac{N k_B T}{V} + \frac{N^2 (k_B T b - a^2)}{V^2} + \dots$$

$$\frac{PV}{N k_B T} = 1 + \frac{N^2 (k_B T b - a^2)}{V^2} + \dots$$

$$\frac{PV}{N k_B T} = 1 + A_1 n + A_2 n^2 + \dots$$

Such an expansion is called the virial expansion and the coefficients are called virial coefficients.

### The Cluster Expansion

Consider the same problem that we started off with,  $N$ -particles which interact via the potential  $V(r_{ij})$ . We will calculate the thermodynamic properties of the system in the grand canonical ensemble. The partition function is given by

$$Q = \sum_{N=0}^{\infty} e^{\beta \mu N} Z(N, T, V) = \sum_{N=0}^{\infty} \frac{1}{N!} \left( \frac{e^{-\beta \mu}}{\lambda_T} \right)^N S_N$$