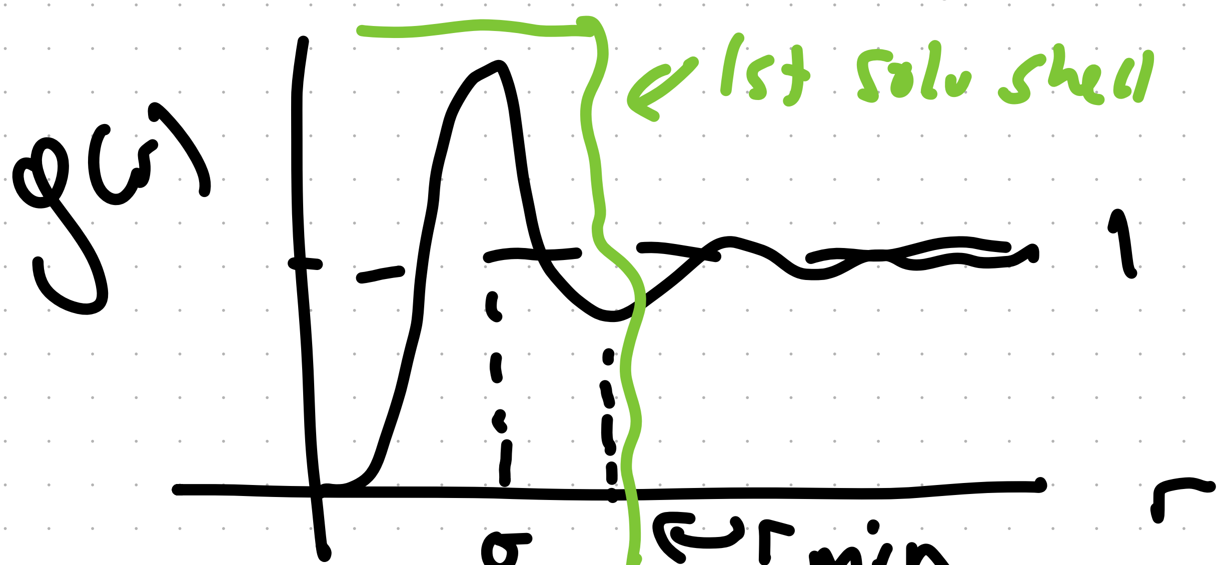
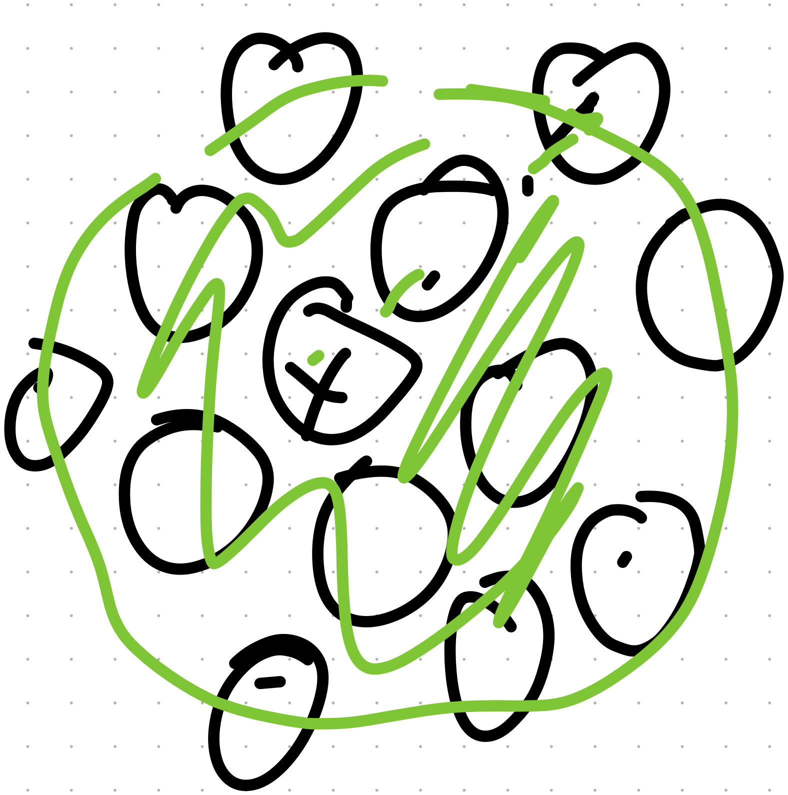
Lecture 10 – Energy & Pressure from Radial Distribution Functions

Reminder:

$$g(\underline{r}) = \frac{N-1}{4\pi\rho r^2}\langle \delta(\underline{r}-\underline{r}')\rangle$$



$$4\pi\rho\int_0^\infty r'^2 g(r')dr' = (N-1)\int_0^\infty dr'\,\delta(r-r') = N-1$$



$$4\pi\rho\int_0^a r'^2 g(r')\,dr'$$

number of particles in distance 0–a

$$N_1 = 4\pi\rho\int_0^{r_{min}} dr'\, r'^2 g(r')$$

"coordination number"

$$\mathcal{E} = -\frac{\partial \log Q}{\partial \beta} \qquad Q = \frac{Z}{N!\,\lambda^{3N}} \qquad \lambda = \sqrt{\frac{2\pi m}{\beta h^2}}$$

$$= -\frac{\partial}{\partial \beta}\left[\log Z - \frac{3}{2} N \log \beta + \text{const}\right]$$

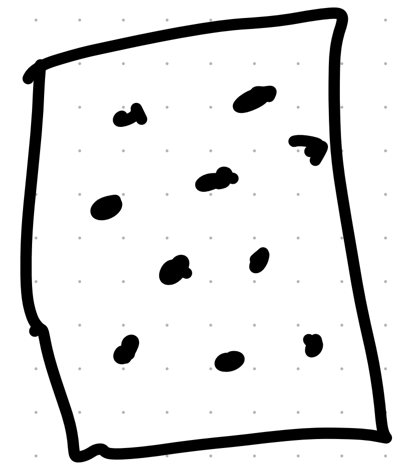
$$= -\frac{\partial \log Z}{\partial \beta} + \underbrace{\frac{3}{2} N \cdot \frac{1}{\beta}}_{\frac{3}{2} N k_B T}$$

potential energy

$\frac{3}{2} N k_B T \Leftarrow$ K.E.

$$\langle U \rangle = -\frac{\partial \log Z}{\partial \beta}$$

$$Z = \int_0^\infty d r^{3N} \, e^{-\beta U(\vec{r})}$$



consider potentials

$$U(\vec{r}) = \sum_i \sum_{j>i} u(r_{ij}) = \frac{1}{2} \sum_{i,j} u(r_{ij})$$

$$r_{ij} = |\vec{r}_i - \vec{r}_j|$$

$$\langle U_{pair} \rangle = \frac{1}{Z} \int dr^{3N}\, U_{pair}(\vec{r})\, e^{-\beta U(\vec{r})}$$

$$U_{pair} = \sum_{i>j} u(r_{ij})$$

$$= \frac{N(N-1)}{2} \cdot \frac{1}{Z} \int dr^{3N}\, u(r_{12})\, e^{-\beta U(\vec{r})}$$

$$= \frac{N(N-1)}{2} \cdot \frac{1}{Z} \int d\vec{r}_1 d\vec{r}_2\, u(r_{12}) \int dr^{N-2}\, e^{-\beta U(\vec{r})}$$

$$\approx \frac{\rho^2}{2} \int d\vec{r}_1 \int d\vec{r}_2\, u(r_{12})\, g^{(2)}(\vec{r}_1, \vec{r}_2)$$

$$= \frac{\rho^2 V}{2} \int d\vec{r}_{12}\, u(r_{12})\, g(\vec{r})$$

$$\approx \frac{N^2}{2V} \cdot 4\pi \int dr\, r^2 u(r)\, g(r)$$

$$\langle u_{pair} \rangle = 2\pi N \rho \int_0^\infty dr\, r^2 \underbrace{u(r)}_{\text{energy at dist} \times \text{Num pairs} \cdot \frac{N}{2}}\, g(r)$$

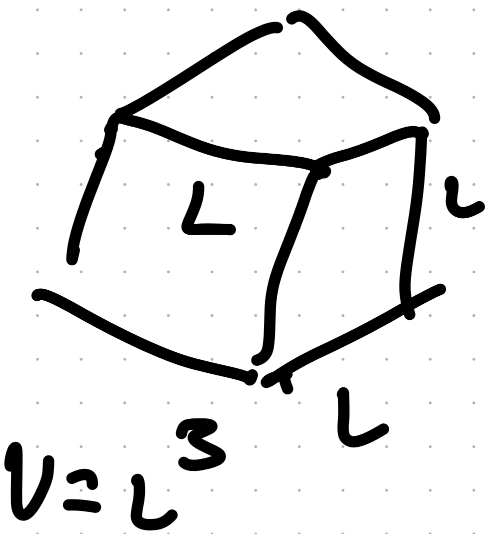
$$\# = 4\pi\rho \int dr\, g(r)\, r^2$$

Pressure of system → virial expansion

$$P = k_B T \frac{\partial}{\partial V} \ln Q(N,V,T) = k_B T \frac{\partial}{\partial V} \ln Z(N,V,T)$$

$$Q = (\quad) Z$$

$$Z = \int_0^L dr^{3N} e^{-\beta U(\vec{r})}$$



$$Z = \int_0^L dr_1 \, dr_2 \cdots dr_{3N} \, e^{-\beta U(\vec{r})}$$

$$s_i = \frac{1}{L} r_i = r_i \cdot V^{-1/3}$$

$$r_i = V^{1/3} s_i$$

$$Z = \underbrace{V^N}_{A} \underbrace{\int_0^1 ds_1 \, ds_2 \ldots ds_{3N} \, e^{-\beta U(V^{1/3} s_1, V^{1/3} s_2 \ldots)}}_{B}$$

$$\frac{dZ}{dV} = N V^{N-1} (B) + V^N \frac{\partial B}{dV}$$

$$= \frac{N}{V} Z$$

$$\frac{dZ}{dV} = \frac{N}{V} Z + V^N \frac{d}{dV} \int d\vec{s}\, e^{-\beta U(\sim\sim)}$$

$$\frac{d}{dV} e^{-\beta U(\,)} = e^{-\beta U(\,)} \cdot \frac{d}{dV} U(\,) \cdot (-\beta)$$

$$\frac{dU}{dV} = \sum_{i=1}^{3N} \frac{\partial U}{\partial r_i} \frac{\partial r_i}{\partial V} = \sum_{i=1}^{3N} \frac{\partial U}{\partial r_i} \frac{\partial (s_i V^{1/3})}{\partial V}$$

$$U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$

$$= \sum_{i=1}^{3N} -f_i \cdot \frac{1}{3} V^{-2/3} s_i \cdot \frac{V^{1/3}}{V^{1/3}}$$

$$\frac{dU}{dV} = \sum_{i=1}^{3N} (-\hat{F}_i) \cdot \frac{1}{3V} \cdot r_i$$

$$= -\frac{1}{3V} \sum_{i=1}^{3N} F_i \, r_i$$

$$= -\frac{1}{3V} \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_i$$

$$\frac{dZ}{dV} = \frac{N}{V} Z + \underbrace{V^N \int ds^{3N}}\ \underline{(-\beta)} \left(\quad \right) e^{-\beta U(r)}$$

$$\frac{dZ}{dV} = \frac{N}{V} Z + \int d\vec{r}^N \frac{\beta}{3V} \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_i \, e^{-\beta U(\vec{r})}$$

$$P = k_B T \frac{d \log Z}{dV} = k_B T \cdot \frac{1}{Z} \cdot \frac{dZ}{dV}$$

$$P = \frac{N k_B T}{V} + \frac{1}{3V} \left\langle \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_i \right\rangle$$

virial

$$P = \frac{N k_B T}{V} + \frac{1}{3V}\left\langle \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_i \right\rangle$$

virial

$$\left\langle \frac{p_i^2}{2m} \right\rangle = \frac{3}{2} N k_B T$$

$$\frac{1}{3V} \cdot \langle p_i^2 / m_i \rangle = \frac{N k_B T}{V}$$

in sim

$$P = \frac{1}{3V}\left\langle \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{m_i} + \vec{r}_i \cdot \vec{F}_i \right\rangle$$

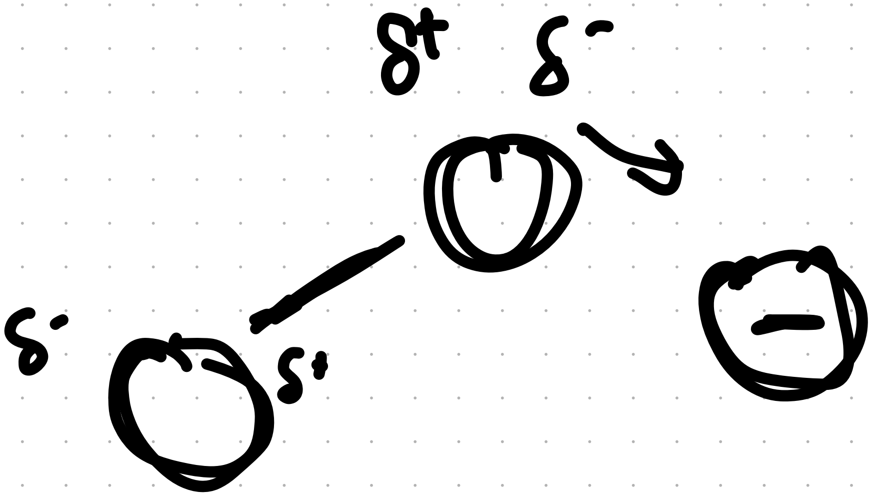
Assume $U(r) = \frac{1}{2} \sum_{i,j} u(r_{ij})$

$$F_i = \sum_{j=1}^{N} - \frac{dU(r_{ij})}{\partial r_i} = \sum_{j=1}^{N} f_{ij}$$

$$\vec{F} = -\nabla U \qquad f_{ij} = -f_{ji}$$

$$U_{total} = U(r_i) + \sum_{ij} U_{pair}(r_i, r_j) + \underbrace{\sum_{i,j,k} U_3(r_i, r_j, r_k) + \dots}$$

$$= U(r_i) + \sum_{i,j} \tilde{U}_{pair}(r_i, r_j)$$



$$\frac{1}{3V}\left\langle \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_i \right\rangle \qquad F_i = \sum_{j=1}^{N} f_{ij}$$

$$\frac{1}{3V}\left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \vec{r}_i \cdot \vec{f}_{ij} \right\rangle \qquad f_{ij} = -f_{ji}$$

$$r_2 f_{23} + r_3 f_{32} = r_2 f_{23} - r_3 f_{23}$$
$$= (r_2 - r_3) f_{23}$$

$$\frac{1}{3V}\left\langle \sum_{i>j} \vec{r}_{ij} \cdot \vec{f}_{ij} \right\rangle$$

$$\frac{1}{3V}\Big\langle \underbrace{\sum_{i>j}}_{\frac{N\cdot(N-1)}{2}} \vec{r}_{ij}\cdot\vec{f}_{ij} \Big\rangle = \frac{N(N-1)}{6V}\cdot\int d\vec{r}\; \vec{r}_{12}\,\vec{f}_{12}\,e^{-\beta u(r)}$$

$$\int d\vec{r}\;\vec{r}_{12}\,\vec{f}_{12}\,e^{-\beta u(r)} = \int dr_1 dr_2\;\vec{r}_{12}\,\vec{f}_{12}\int dr^{N-2}\cdots$$

$$= -\frac{\rho^2}{2}\cdot\frac{1}{3V}\int d\vec{r}_1 d\vec{r}_2\;\vec{r}_{12}\left(\frac{du}{dr_{12}}\right)\,g^{(2)}(\vec{r}_1,\vec{r}_2)$$

$$\cdots = -\rho^2/6 \cdot 4\pi \int_0^\infty dr\, r^3 \left(\frac{du}{dr}\right) g(r)$$

$$P/k_BT = \rho - \frac{2\pi\rho^2}{3k_BT} \int_0^\infty dr\, r^3 \left(\frac{du}{dr}\right) g(r)$$

imagine

$$g(r,\rho) = \sum_{i=0}^{\infty} \rho^i\, g_i(r)$$

$$g_i \sim \frac{\partial^i g}{\partial \rho^i}$$