# RDF & Virial Expansion

Last time showed we can obtain $g(r)$ by measuring $S(k)$ by scattering & fourier transform

Or predict $S(k)$ by knowing $g(r)$

Also showed reversible work theorem

$$g(r) = e^{-\beta w(r)}, \quad w(r) \text{ is}$$

potential of mean force

or L, if short range $u \to 0$ before L

$$\langle u_{pair} \rangle = 2\pi N \rho \int_0^\infty dr\, r^2 u(r) g(r)$$

What about pressure?

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

$$Z(N,V,T) = \int_V dr^N e^{-\beta u(r)}$$

, so where is volume dependence

Imagine changing volume as moving everything closer together or farther apart

Say $\vec{s}_i = \frac{1}{V^{1/3}} \vec{r}_i$

$$\Rightarrow Z(N,V,T) = V^N \int ds_N\, e^{-\beta u(V^{1/3}\vec{s}_1, V^{1/3}\vec{s}_2 \dots, V^{1/3}\vec{s}_N)}$$

$$\frac{dZ}{dV} = N V^{N-1} \int ds_N \cdots + V^N \int ds_N \cdot -\beta \frac{dU}{dV}(V^{1/3}\ldots)\, e^{-\beta U(\,)}$$

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

chain rule $$\frac{dU}{dV} = \sum_{i=1}^{N} \frac{\partial U}{\partial (V^{1/3} s_i)} \frac{\partial V^{1/3} s_i}{\partial V} = \sum_{i=1}^{N} \left(\tfrac{1}{3} V^{-2/3} s_i\right) \frac{\partial U}{\partial r_i}$$

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

$$\frac{dZ}{dV} = \frac{N}{V} Z + \int dr^N \cdot \frac{\beta}{3V} \sum_{i=1}^{N} r_i \cdot F_i \; e^{-\beta U(r)}$$

$$P = k_B T \frac{\partial \log Z}{\partial V} = k_B T \cdot \frac{1}{Z} \frac{dZ}{dV} = \frac{N k_B T}{V} + \underbrace{\frac{1}{3V} \left\langle \sum_{i=1}^{N} r_i \cdot F_i \right\rangle}_{\text{virial}}$$

$$\langle \Sigma p_i^2 / 2m \rangle = \tfrac{3}{2} N k_B T \Rightarrow$$

$$P = \frac{1}{3V} \left\langle \sum_{i=1}^{N} \frac{p_i^2}{m} + r_i \cdot F_i \right\rangle$$ ~ pressure estimator in MD

How does this connect to structure?

Lastly, consider $U_{pair} = \frac{1}{2} \sum_i \sum_j u(r_{ij})$

$$F_i = \sum_{j=1}^{N} -\frac{\partial u(r_{ij})}{\partial r_i} = \sum_{j=1}^{N} f_{ij} \quad , \text{ note } f_{ij} = -f_{ji}$$

$$\frac{1}{3V} \left\langle \sum_{i=1}^{N} r_i F_i \right\rangle = \frac{1}{3V} \cdot \frac{1}{Z} \int dr^N \sum_{i=1}^{N} \sum_{j=1}^{N} r_i f_{ij} \quad e^{-\beta U_{pair}}$$

$$= \tfrac{1}{3V} \cdot \frac{1}{Z} \int dr^N \sum_{i>j} r_{ij} f_{ij} \, e^{-\beta U_{pair}}$$

each integral identical by swapping particles

$$= \frac{N(N-1)}{2} \cdot \frac{1}{3V} \cdot \frac{1}{Z} \int dr_1 dr_2 \, r_{12} f_{12} \int dr^{N-2} e^{-\beta U(r)}$$

$$= -\frac{\rho^2}{2} \cdot \frac{1}{3V} \cdot \int dr_1 dr_2 \; r_{12} \frac{du}{dr_{12}} \; g(r_1, r_2)$$

$$= -\frac{\rho^2}{6V} \int dr \, dR \; r \frac{du}{dr} \; g(r, R)$$

$$= -\rho^2/6 \int d\vec{r} \; \vec{r} \; \frac{du}{dr} \; g(r)$$

isotropic

$$= -\rho^2/6 \cdot 4\pi \int dr \; r^3 \frac{du}{dr} \; g(r)$$

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

$g(r)$ depends on $\rho$ & $T$

Imagine $g(r)$ can be written as

$$g(r, \rho) = \sum_{j=0}^{\infty} \rho^j g_j(r)$$

$g_j$ somehow related to $d^jg/d\rho^j$

Then $$P/k_BT = \rho + \sum_{j=0}^{\infty} B_{j+2} \, \rho^{j+2}$$

$$B_{j+2}(T) = -\frac{2\pi}{3k_BT} \int_0^\infty r^3 \; u'(r) \; g_j(r, T)$$

at small $\rho$, $\beta P \approx \rho + \rho^2 B_2$

$$B_2 \approx -\frac{2\pi}{3k_BT} \int_0^\infty dr \; r^3 \; u'(r) \, g(r)$$

HW? 4.5 prob

one can show for low $\rho$, $g(r) \approx e^{-\beta u(r)}$

$u(r) = -k_BT \log g(r)$

$$B_2 \approx + \frac{2\pi}{3} \int_0^\infty dr \; r^3 \cdot \frac{d[g(r)-1]}{dr}$$

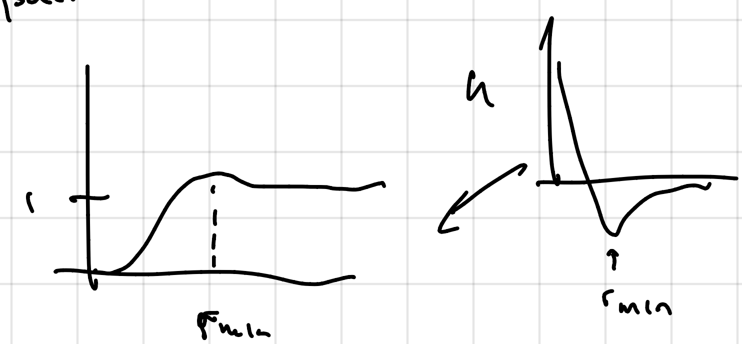
$u \qquad dv$

$$\left\{ \begin{array}{l} \frac{dg(r)}{dr} = -\beta \frac{du(r)}{dr} g(r) \\ \frac{dg(r)-1}{dr} = \frac{dg(r)}{dr} \end{array} \right.$$

$$= \frac{2\pi}{3} \left[ r^3 [g(r)-1] \Big|_0^\infty - \int_0^\infty 3r^2 (g(r)-1)\, dr \right.$$

$$= -2\pi \int_0^\infty r^2 (g(r)-1)\, dr = -2\pi \int_0^\infty r^2 (e^{-\beta u(r)} - 1)\, dr \quad ☆$$

Low $\rho$, $g(r) = e^{-\beta u(r)}$




What is this correction to pressure?

We can try to solve by perturbation theory

This means usually, $u(r) = u_0(r) + u_1(r)$

where we can solve the problem for $u_0(r)$

For this potential, what happens to $Z$?

$$Z = \int dr \, e^{-\beta u(r)} = \int dr \, e^{-\beta [u_0(r) + u_1(r)]}$$

$$= \frac{\int dr \, e^{-\beta u_0(r)}}{\int dr \, e^{-\beta u_0(r)}} \cdot \int dr \, e^{-\beta u_0(r)} e^{-\beta u_1(r)}$$

$Z_0 \longrightarrow \int dr \, e^{-\beta u_0(r)}$

$$= Z_0 \cdot \int dr\, e^{-\beta u_1(r)} \underbrace{\left[ \frac{e^{-\beta u_0(r)}}{Z_0} \right]}_{P_0(r)}$$

$$= Z_0 \langle e^{-\beta u_1} \rangle_0$$

$$\langle a \rangle_0 = \int dr \; a(r) \frac{e^{-\beta u_0(r)}}{Z_0}$$

Suppose $u_1$ is small compared to $u_0$

then $\langle e^{-\beta u_1} \rangle_0 = 1 - \beta \langle u_1 \rangle_0 + \beta^2/2 \langle u_1^2 \rangle_0 + \dots$

$$= \sum_{l=0}^{\infty} \frac{(-\beta)^l}{l!} \langle u_1^l \rangle_0$$

$$A = -k_B T \log Q = \underbrace{-k_B T \log \left[ \frac{Z^0}{N! \lambda^{3N}} \right]}_{A_0} \underbrace{- k_B T \log \langle e^{-\beta u_1} \rangle_0}_{A_1}$$

$$\log(1-x) = -(x + x^2/2 + x^3/3 + \dots)$$

so $A_1 \approx \beta \langle u_1 \rangle_0 + \left[ -\frac{\beta^2}{2} \langle u_1^2 \rangle_0 + \frac{\beta^2}{2} \langle u_1 \rangle_0^2 \right] + \dots$

$$\approx \langle u_1 \rangle_0 - \beta/2 \left[ \mathrm{Var}_0(u_1) \right] + \dots$$

cumulant expansion [pg 171]

So what is $\langle u_1 \rangle_0$?