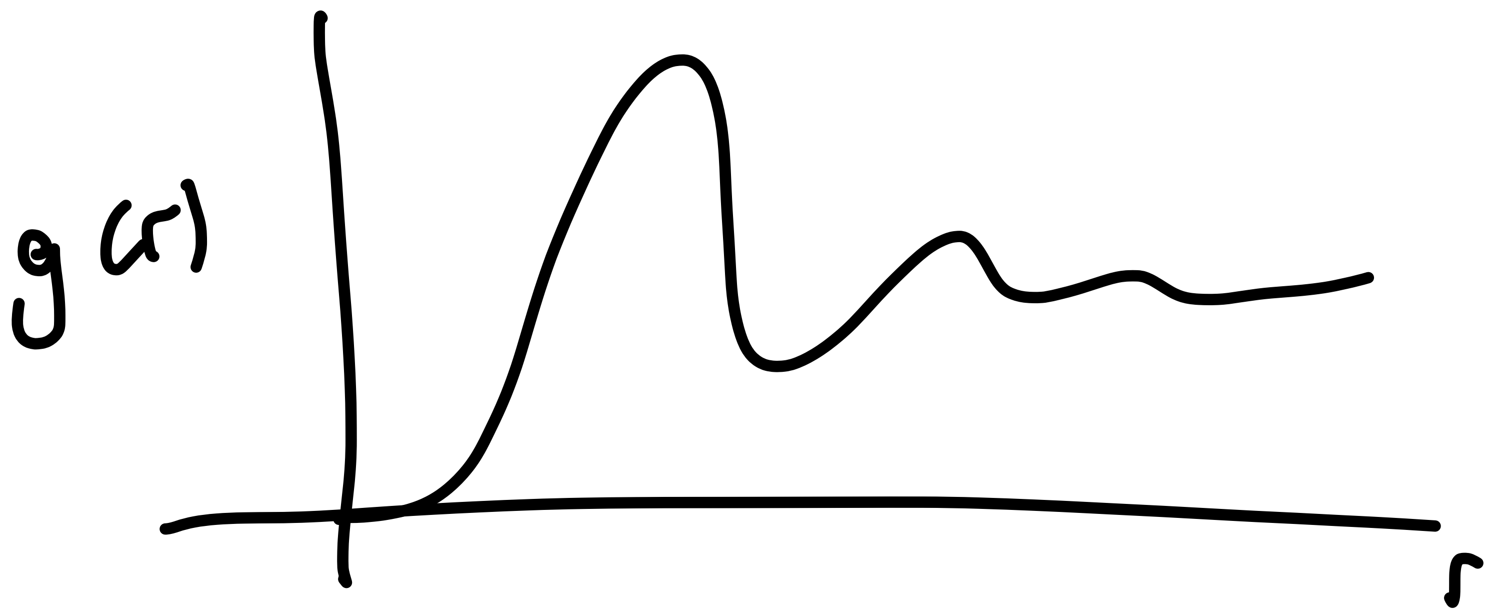
Lecture 13 - Energy & pressure from RDF

Last time, learned can measure



"2-body correlations" in liquid

Lets see how connected to pot. energy & pressure today

$$P.E. = \frac{-\partial \ln Z_{config}}{\partial \beta}$$

$$Z_{config} = \int dX e^{-\beta U(X)}$$

In general, make approx

$$U(\vec{x}) = \sum_{i>j} U_{pair}(r_{ij})$$

$$r_{ij} = |\vec{r}_j - \vec{r}_i|$$ [eg coulomb, approx to QM]

So $$\langle PE \rangle = \frac{1}{Z} \int dr_1 \ldots r_N \sum_{i>j} U(r_{ij}) e^{-\beta \sum_{i>j} U(r_{ij})}$$

$U_{12} + U_{13} + \ldots$, all same on average, can say

$$= \frac{N(N-1)}{2} \int dr_1 dr_2 U(r_{12}) \underbrace{\int dr^{N-2} e^{-\beta U(X)}}_{\frac{\rho^2}{N(N-1)} g^{(2)}(r_1, r_2)} / Z$$

[like before

$$= \frac{\rho^2}{2} \int d\vec{r}_1 \, d\vec{r}_2 \, u(r_{12}) \, g^{(2)}(r_1, r_2)$$

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

$$= \frac{\rho^2 V}{2} \cdot 4\pi \int_0^L dr \, r^2 \, u(r) \, g(r)$$

$$= \boxed{2\pi N \rho \int_0^L dr \, r^2 u(r) \, g(r)}$$

how to compute avg radial prop

if $u(r)$ short range

$u(r) \to 0$ well before L so can

make $L \to \infty$

particles is dist away $= 4\pi \rho \int dr \, g(r) \, r^2$

this is energy at that dist * $N/2$ ← double counting

"Virial Expansion": What about pressure

$$P = -\frac{\partial A}{\partial V} = k_B T \frac{\partial \ln Z}{\partial V}$$

$$Z = \int_V d\vec{r}^N e^{-\beta U(\vec{r})}$$, where is volume dep

Imagine rescaling $s_i = \frac{1}{V_i^{1/3}} r_i$

$$Z(N,V,T) = V^N \int d\vec{s}^N e^{-\beta U(V^{1/3} s_1, \dots V^{1/3} s_N)}$$

$$\frac{\partial \ln Z}{\partial V} = \frac{1}{Z} \cdot \left[N V^{N-1} + V^N \int ds^N -\beta \frac{\partial U}{\partial V} e^{-\beta U(\,)} \right]$$

$$= \frac{1}{Z} \left[\frac{N}{V} Z + V^N \int ds^N \frac{\beta}{3V} \sum F_i r_i \, e^{-\beta U} \right]$$

$$\frac{\partial U}{\partial V} = \sum_{i=1}^{N} \frac{\partial U}{\partial r_i} \frac{\partial r_i}{\partial V} = \sum_{i=1}^{N} -F_i \cdot \frac{1}{3} V^{-\frac{2}{3}} s_i = \frac{-1}{3V} \sum F_i r_i$$

So $P = \frac{N k_B T}{V} + \frac{1}{3V} \int dr^N \sum r_i \cdot F_i \, e^{-\beta U(r^N)}$

$= \underbrace{\frac{N k_B T}{V}}_{\text{ideal gas}} + \underbrace{\frac{1}{3V} \left\langle \sum_{i=1}^{N} r_i \cdot F_i \right\rangle}_{\text{virial}}$

ideal gas + interactions

$\left[\left\langle \sum p_i^2 / 2m_i \right\rangle = \frac{3}{2} N k_B T \right.$

$\left. \Rightarrow P_{\text{estimator in MD}} = \frac{1}{3V} \left\langle \sum \frac{p_i^2}{m} + r_i \cdot F_i \right\rangle \right]$

How does this connect to struct?

For $U_{pair} = \sum_{i>j} u(r_{ij})$ $\quad // \; -\frac{\partial u}{\partial r_{ji}}$

$F_i = -\frac{\partial U_{pair}}{\partial r_i} = \sum_{j=1}^{N} -\frac{\partial u(r_{ij})}{\partial r_i} = \sum_{j=1}^{N} F_{ij}$

note $f_{ij} = -f_{ji}$

$$\frac{1}{3V}\left\langle \sum_{i=1}^{N} r_i \cdot F_i \right\rangle$$

$$= \frac{1}{3V} \cdot \frac{1}{Z} \int dr^N \sum_{i=1}^{N} \sum_{j=1}^{N} \vec{r}_i \vec{f}_{ij} \, e^{-\beta U_{pair}}$$

$$r_i f_{ij} + r_j f_{ji} = r_{ji} f_{ij}$$

so

$$= \frac{1}{3V} \cdot \frac{1}{2} \int dr^N \sum_{i>j}^{N} \vec{r}_{ji} \vec{f}_{ij} \, e^{-\beta U_{pair}}$$

each integral ident by swapping again

$$= \frac{N(N-1)}{6V} \cdot \int dr_1 dr_2 \, \vec{r}_{21} \vec{f}_{12} \, g_2(r_1, r_2) \cdot \frac{\rho^2}{N(N-1)}$$

$$= -\frac{\rho^2}{6V} \int dr_1 dr_2 \, r_{21} \frac{dU(r_{21})}{dr_{21}} g(r_1, r_2)$$

$$= -\rho^2/6 \int d\vec{r} \, \vec{r} \frac{du}{dr} g(\vec{r}) = -\frac{2}{3}\pi \rho^2 \int dr \, r^3 \frac{du}{dr} g(r)$$

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

note $g(r)$ depends on ρ & T

Imagine $g(r)$ as a power series

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

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

Virial expansion

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

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

Can show for low ρ [book prob 4.5]

$$g(r) \approx e^{-\beta u(r)}$$

$$u(r) \approx -k_B T \ln g(r)$$

← cf rev work thm

Then
$$B_2 \approx \frac{2\pi}{3} \int_0^\infty dr \, \underbrace{r^3}_{u} \cdot \underbrace{\frac{d[g(r)-1]}{dr}}_{dv}$$

$$\frac{dg(r)}{dr} = -\beta \frac{du(r)}{dr} g(r)$$

$$= \frac{2\pi}{3} \Big[r^3 (g(r)-1) \Big]_0^\infty - \frac{2\pi}{3} \int dr \, (g(r)-1) \cdot 3r^2$$

$$= -2\pi \int_0^\infty dr \, r^2 (g(r)-1)$$

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

So we can compute how a pair interaction perturbs the pressure of an ideal gas will show that this leads to the Van der Waal's eqn of state

$$\beta P = \frac{\rho}{1-\rho b} - a\rho^2\beta$$

using statistical mechanical perturbation theory later