# Lecture 9

## 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

Today, how $g(r)$ connects to avg energy/pressure in non-ideal systems

Predict corrections for test potential

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Lets look at how the RDF is connected to the avg energy

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

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

$$= \underbrace{\frac{3}{2} N k_B T}_{\langle \text{kinetic } E \rangle} - \underbrace{\frac{\partial \log Z}{\partial \beta}}_{\langle U \rangle}$$

So to get potential energy, only need configurational partition function

Now let's consider potentials $\mathcal{U}_{pair}(\vec{r}) = \sum_i \sum_{j>i} u(r_{ij})$
(pairwise)

then $\langle \mathcal{U}_{pair} \rangle = \frac{1}{Z} \sum_i \sum_{j>i} \underbrace{\int dr^N u(r_i - r_j)\, e^{-\beta \mathcal{U}_{pair}(r)}}$

but by relabeling can just write
$\int dr^N u(r_1 - r_2)\, e^{-\beta \mathcal{U}(r)}$

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

$$= \frac{1}{2} \int dr_1 dr_2 u(r_{12}) \frac{N \cdot N-1}{Z} \int dr^{N-2} e^{-\beta \mathcal{U}_{pair}(r)}$$

$$= \rho^2/2 \int d\vec{r}_1 d\vec{r}_2 u(\vec{r}_{12})\, g^{(2)}(\vec{r}_1, \vec{r}_2)$$

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

$\underset{\text{if isotropic}}{=} \frac{N^2}{2V} \cdot 4\pi \int dr\, r^2 u(r) g(r) = \boxed{2\pi N \rho \int_0^{\infty} dr\, r^2 u(r) g(r)}$

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

note – kind of what you expect,

$N$ particles dist away is $4\pi\rho \int dr\, g(r)\, r^2$
so this is energy at that dist $\times$ # pairs at that dist $\cdot N/2$

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

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

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

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

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

virial

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

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

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

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

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

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

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

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

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

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

HW? prob 4.5

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

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

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

$\frac{d[g(r)-1]}{dr} = \frac{dg(r)}{dr}$

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

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

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