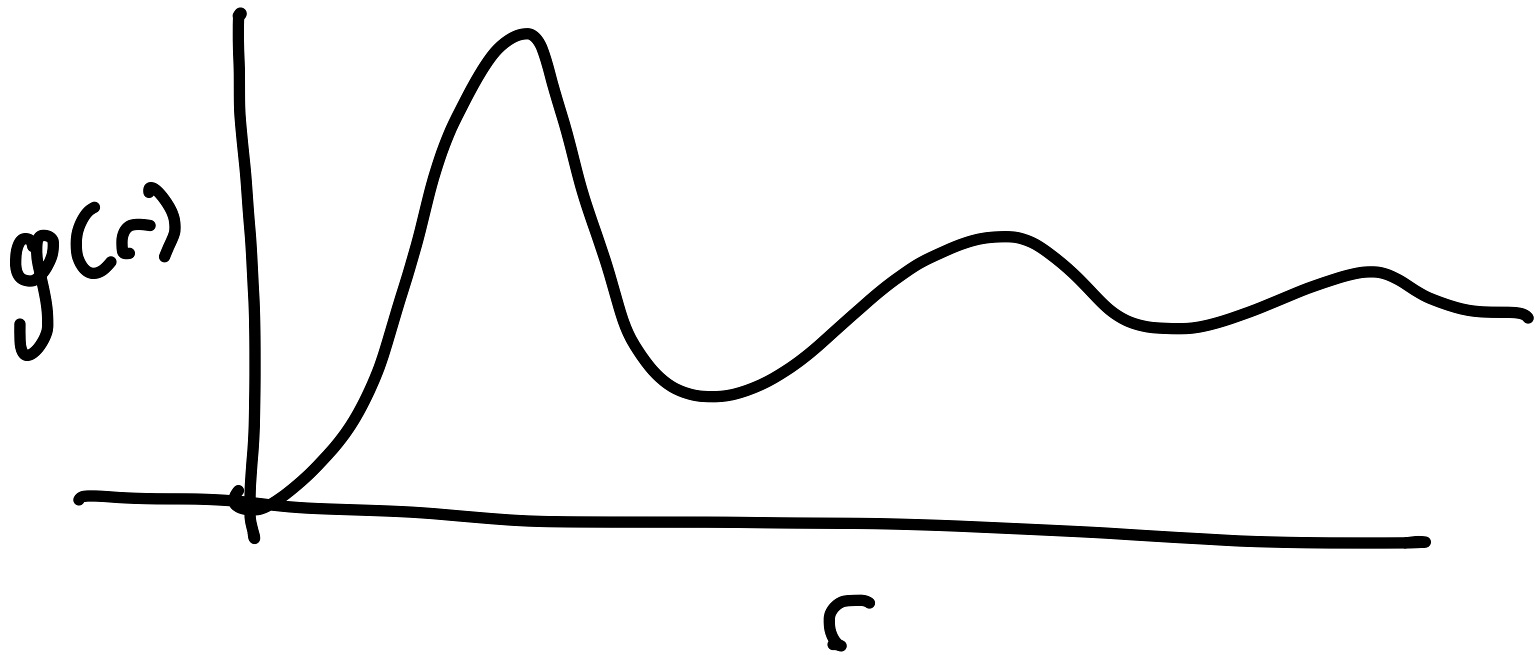
Lecture 13

[Midterm, Fri-Fri]
No class next week



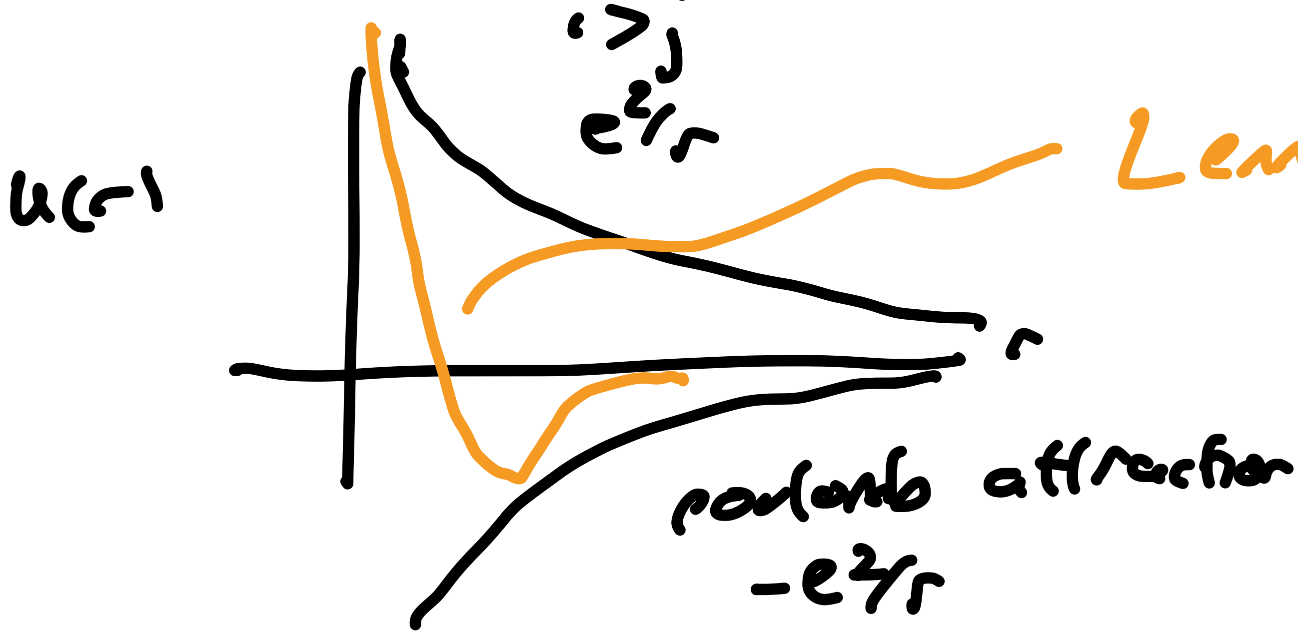
"2-body correlation function"

$$PE = -\frac{\partial \ln Z_{config}}{\partial \beta}$$

$$Z_{config} = \int dx\, e^{-\beta U(x)}$$

Approx: pair energies

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



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

$$\langle PE \rangle = \frac{1}{Z} \int dr_1 \cdots dr_N \sum_{i>j} u(r_{ij}) \, e^{-\beta \sum_{i>j} u(r_{ij})}$$

$$u_{12} + u_{13} + \cdots u_{1N} + u_{23} + \cdots$$

$$= \frac{N(N-1)}{2} \int d\vec{r}_1 \, d\vec{r}_2 \, u(r_{12}) \underbrace{\frac{\int dr^{N-2} \, e^{-\beta U(r)}}{Z}}_{\frac{\rho^2}{N(N-1)} g^{(2)}(r_1, r_2)}$$

$$= \frac{\rho^2}{2} \int dr_1 \int dr_2 \, g^{(2)}(r_1, r_2) \, u(r_{12})$$

$$= 2\pi N\rho \underbrace{\int_0^{L \to \infty} dr\, r^2\, u(r)\, g(r)}_{\text{average potential energy}}$$

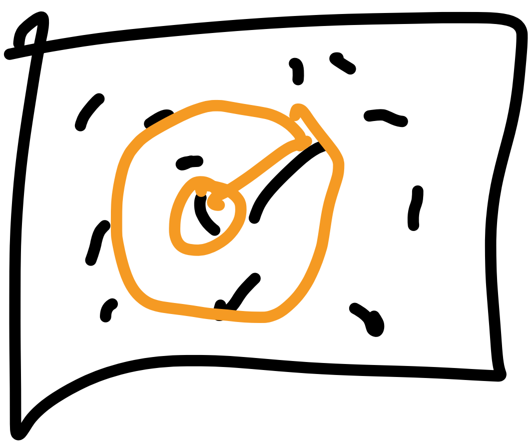
goes to zero

particles up to distance a

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

$u(r)$ × # molecules $\frac{N}{2}$

double counting



Pressure correction

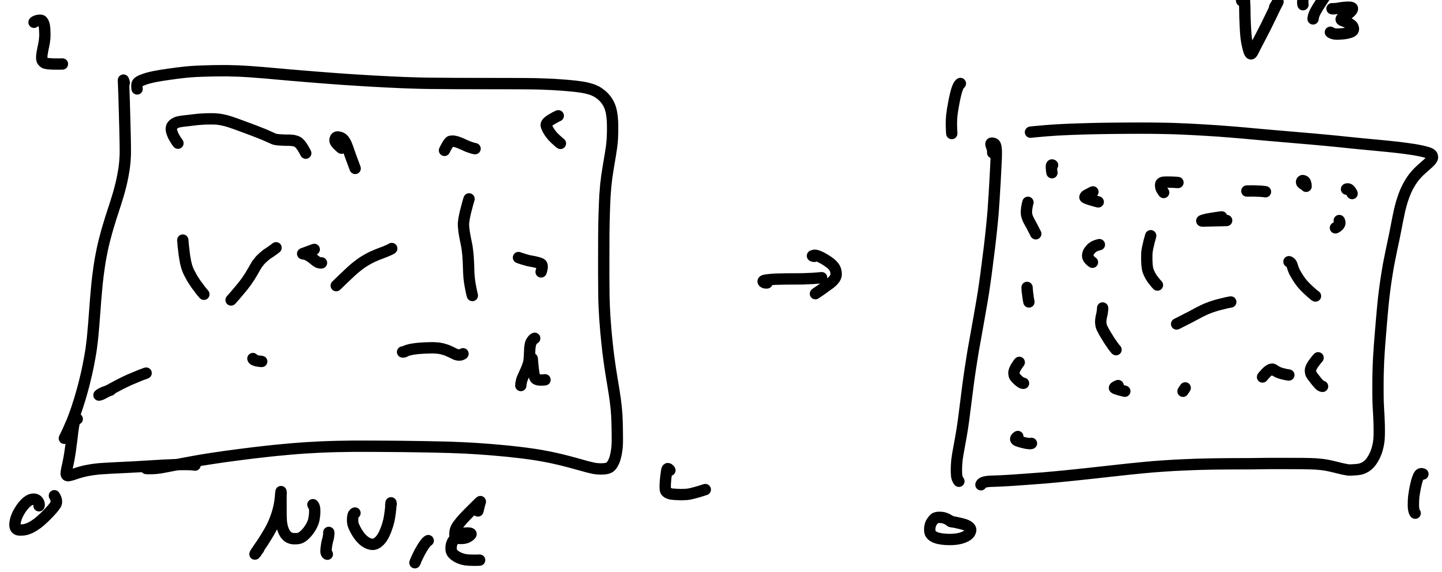
$A = -k_B T \ln Z$

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

$$Z = \int_V d\vec{r}^N e^{-\beta U(r)}$$

$$\int_0^L \int_0^L \cdots \int_0^L$$

Reduced coordinates $s_i = \frac{r_i}{V^{1/3}} \Rightarrow r_i = V^{1/3} \cdot s_i$



$$Z(N,V,T) = \int d\vec{r}^{\,N} \, e^{-\beta U(r_1 \cdots r_N)}$$

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

$$dr_i = V^{1/3} ds_i$$

$$= \underbrace{V^N}_{A} \int \underbrace{d\vec{s}^{\,N} \, e^{-\beta U[V^{1/3}s_1, V^{1/3}s_2 \cdots, V^{1/3}s_N]}}_{B}$$

$$\frac{\partial \ln Z}{\partial V} = \frac{1}{Z}\left[N V^{N-1} [B] + V^N \frac{\partial}{\partial V}[B] \right]$$

$$\times \frac{V}{V}$$

$$= \frac{1}{Z}\left[\frac{N}{V} \cdot Z + V^N \frac{\partial}{\partial V}[B] \right]$$

$$\frac{\partial}{\partial V}[B] = \int ds^N \left[-\beta \frac{\partial U}{\partial V} e^{-\beta U[\;]} \right]$$

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

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

$$= \frac{1}{3V} \sum_{i=1}^{N} (-F_i)(V^{1/3} s_i)$$

$$= \underbrace{\frac{-1}{3V} \sum_{i=1}^{N} F_i \cdot r_i}_{\text{Virial}}$$

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

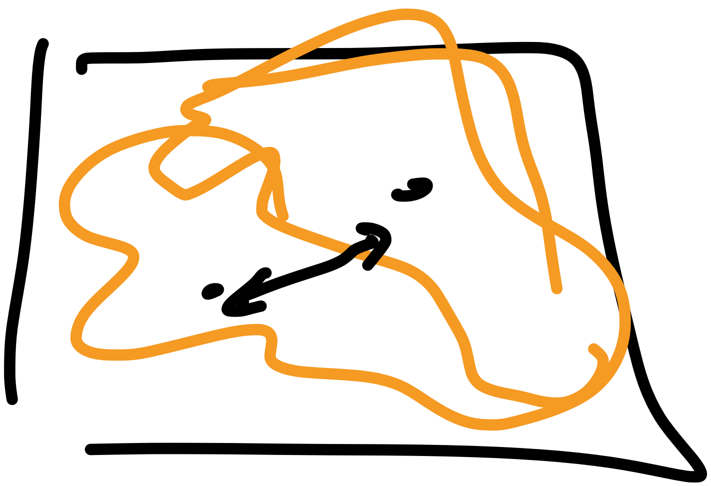
$$= k_B T \left[\frac{N}{V} + (-\beta) V^N \int d\vec{s}^{\,N} \left(-\frac{1}{3V} \sum F_i \cdot r_i \right) e^{-\beta U} \right]$$

$$= k_B T \left[\frac{N}{V} + \frac{(-\beta)}{Z} \int d\vec{r}^{\,N} \left(-\frac{1}{3V} \sum F_i r_i e^{-\beta U(x)} \right) \right]$$

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

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

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



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

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

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

$$\vec{r}_i \vec{f}_{ij} + \vec{r}_j \underbrace{\vec{f}_{ji}}_{-f_{ij}} = \vec{r}_{ji} \vec{f}_{ij}$$

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

$$= \frac{N(N-1)}{2 \cdot 3 \cdot V} \cdot \int dr_1 dr_2\, \vec{r}_{21} \vec{f}_{12} \overbrace{\int dr^{N-2} e^{-\beta U(r)} / Z}^{g(r)\, \rho^2 / N(N-1)}$$

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

$$R = \frac{\vec{r}_1 + \vec{r}_2}{2}$$

$$r = \vec{r}_1 - \vec{r}_2$$

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

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

$$P = P_{ideal} +$$

$$P_{ideal} = \rho k_B T$$

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

note $g(r)$ depends on ρ, T

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

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

Virial Expansion, B_{j+2} are virial coefficents at low ρ

$$\beta P = \rho + \rho^2 B_2$$

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

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

Can show [HW prob 4.5]

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

low density limit

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

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

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

u du

$$= \frac{2\pi}{3}\left[r^3(g(r)-1)\right]_0^\infty$$

[Theory of simple Liquids]

$$- \frac{2\pi}{3}\int dr\,(g(r)-1)\,3r^2$$

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

computational check

$$= -2\pi\int dr\,[\underbrace{e^{-\beta u(r)}-1}_{\text{mayer f function}}]\,r^2 \quad \star$$

We will show

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

Vander waal's equation of state