Lecture 11 - Virial Expansion

$$P = \left(\frac{\partial A}{\partial V}\right)_{N,T} = -k_B T \left(\frac{\partial \ln Z}{\partial V}\right)_{N,T}$$

$$A(N,V,T) = -k_B T \ln Q(N,V,T)$$

$$U_{pair}(\vec{r}) = \frac{1}{2} \sum_{i,j} u(r_{ij})$$

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

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

$$g(r, \rho, T)$$

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

$$P/k_BT = \rho + \sum_{j=0}^{\infty} \left(B_{j+2}\right) \rho^{j+2}$$

$$B_{j+2}(T) = -\frac{2\pi}{3k_BT} \int_0^\infty r^3 \left(\frac{du}{dr}\right) g_j(r, T)$$

$$B_{j+2}(T) = -\frac{2\pi}{3k_BT}\int_0^\infty r^3 \left(\frac{du}{dr}\right) g_j(r,T)$$

$$g_0 = g(r)$$

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

at small ρ

$$\beta P \approx \rho + \rho^2 B_2 + \mathcal{O}(\rho^3)$$

One can show @ low ρ $g(r) \approx e^{-\beta u(r)}$

Tuckerman Prob 4.5

previously $g(r) = e^{-\beta W(r)}$

$$W(r) = -k_B T \ln g(r)$$

at low ρ $\quad W(r) \approx u(r)$

$$B_2 \approx -\frac{2\pi}{3k_BT}\int_0^\infty dr\, r^3 \,\underline{\frac{du}{dr}}\Big[\underline{e^{-\beta \overset{\approx g(r)}{u(r)}}}\Big]$$

$$\frac{d}{dr}\left[e^{-\beta u(r)}\right] = -\beta e^{-\beta u(r)} \frac{du}{dr}$$

$$= \frac{2\pi}{3}\int_0^\infty dr\, r^3 \,\frac{d}{dr}\left[e^{-\beta u(r)}\right]$$

$$B_2 \approx \frac{2\pi}{3}\int_0^\infty r^3 \,\frac{d}{dr}\left[\underset{\uparrow}{g}(r)\right] dr$$

$$\left(e^{-\beta u(r)}\right)$$

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

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

$$= u \cdot v - \int v\,du$$

$$= \frac{2\pi}{3}\left[\left(\cancelto{0}{r^3\left(g(r)-1\right)}\right)\Big|_0^\infty - \int_0^\infty 3r^2\left[g(r)-1\right] dr\right]$$

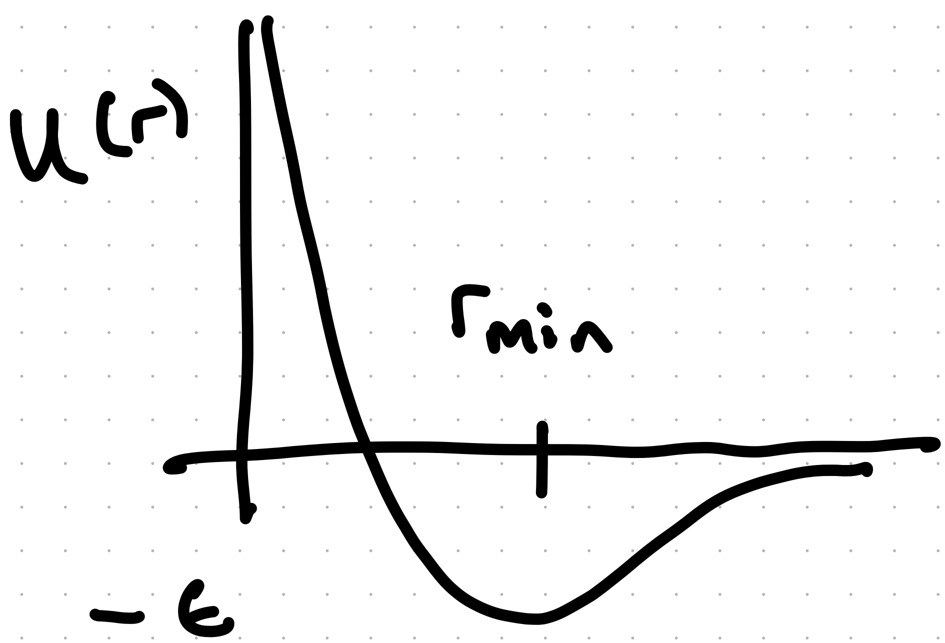
$$B_2 \approx -2\pi \int_0^\infty r^2 (g(r) - 1)\, dr$$

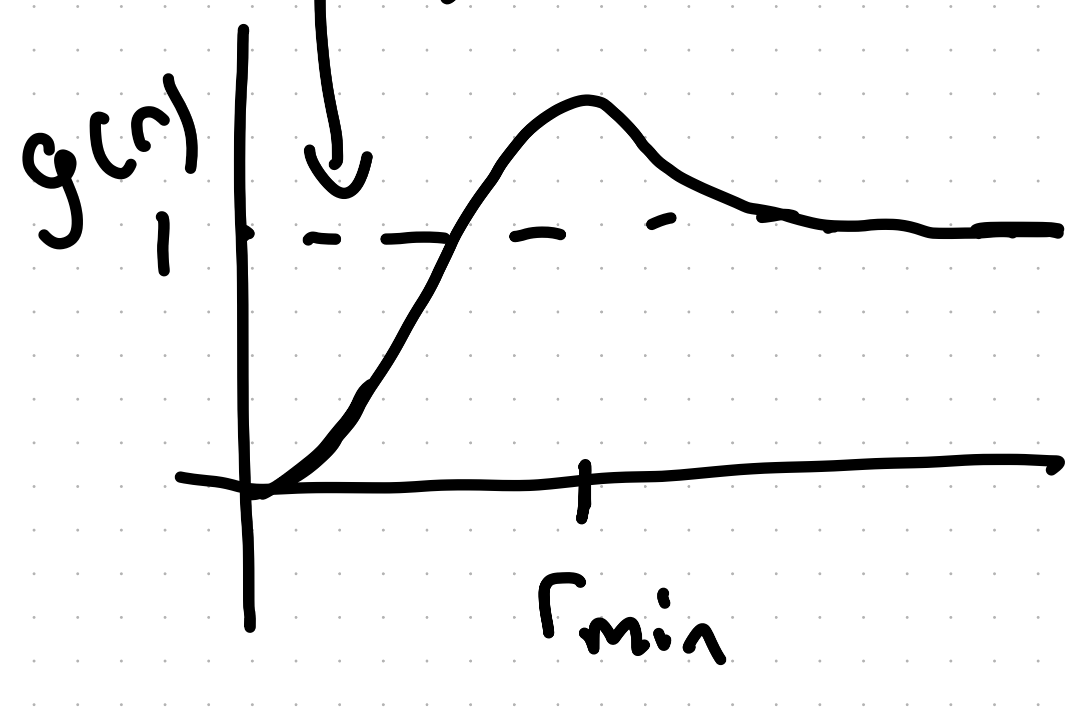
$$-2\pi \int_0^\infty r^2 \left(e^{-\beta u(r)} - 1\right) dr$$

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

ideal gas

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



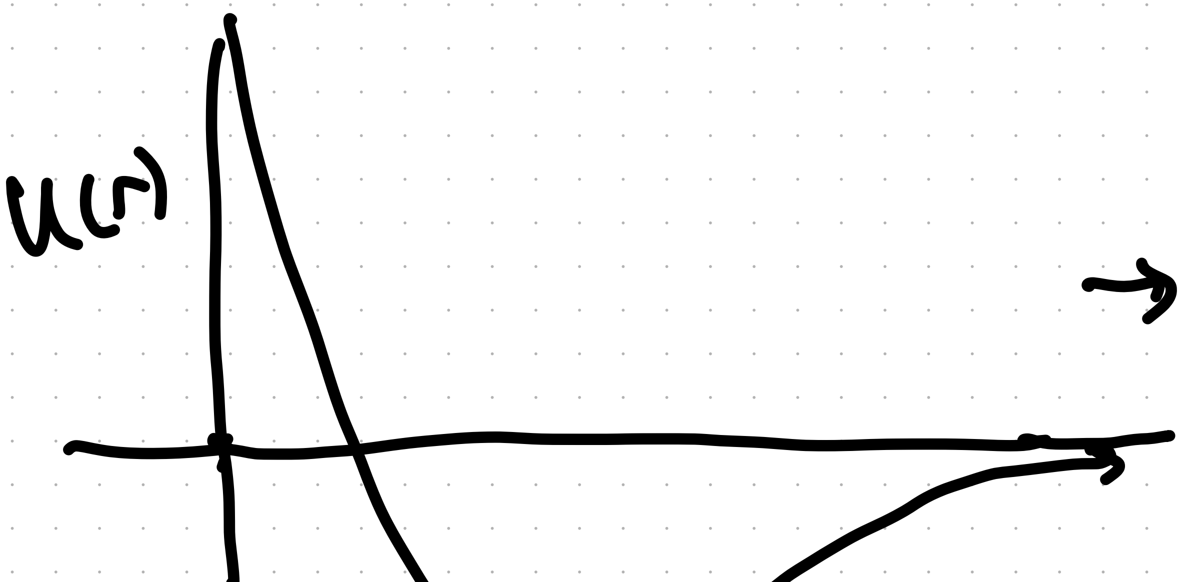


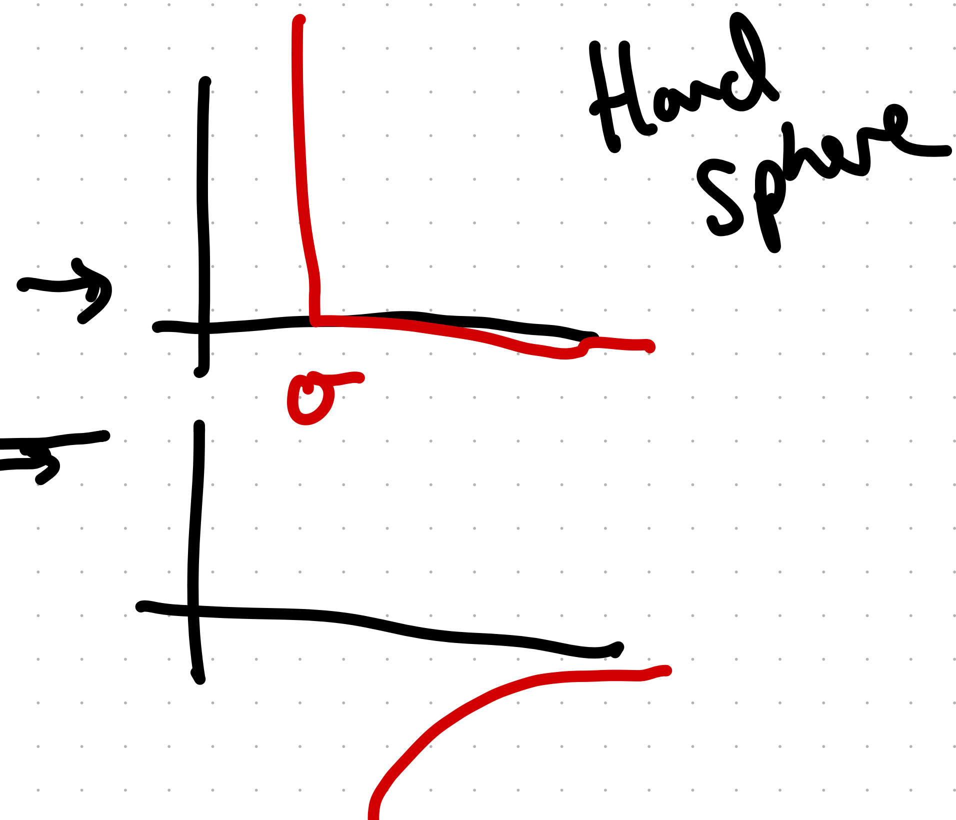
Perturbation Theory

$$U(r) = U_0(r) + U_1^{(\lambda)}(r)$$

solve a problem for $U_0(r)$

add corrections come from $U_1(r)$





$$Z = \int dx\, e^{-\beta U(r)} = \int dx\, e^{-\beta U_0(r)} \cdot e^{-\beta U_1(r)} \times Z_0 / Z_0$$

$$Z_0 = \int dx\, e^{-\beta U_0(r)}$$

$$Z = Z_0 \cdot \int dx\, e^{-\beta U_1(x)} \cdot \underbrace{\left[\frac{e^{-\beta U_0(r)}}{Z_0} \right]}_{P_0(x)}$$

$$= Z_0 \cdot \left\langle e^{-\beta U_1} \right\rangle_0$$

$$Z = Z_0 \cdot \langle e^{-\beta U_1} \rangle_0$$

$$A = -k_B T \ln Q = -k_B T \ln \left[\frac{Z}{\lambda^{3N} N!} \right]$$

$$= \underbrace{-k_B T \ln \left(\frac{Z_0}{\lambda^{3N} N!} \right)}_{A^0} \underbrace{- k_B T \ln \left(\langle e^{-\beta U_1} \rangle_0 \right)}_{A'}$$

$$\langle a \rangle_0 = \int a(x) e^{-\beta U_0(x)} dx \Big/ Z_0$$

$$A_1 = -k_BT \ln \langle e^{-\beta U_1} \rangle_0$$

U_1 is "small" compared to U_0

$$e^{-\beta U_1} \approx 1 - \underbrace{\beta U_1 + \beta^2/2\, U_1^2 + \cdots}_{x}$$

$$A_1 \approx \langle U_1 \rangle_0 - \beta/2 \left[\langle U_1^2 \rangle_0 - \langle U_1 \rangle_0^2 \right]$$

$\mathrm{Var}(U_1) + \cdots$

Cumulant expansion [pg 171]

$$A_1 \approx \langle u_1 \rangle_{\underline{0}} - \beta/2 \, \mathrm{Var}_{\underline{0}}(u_1)$$

$$\langle u_{pair} \rangle_0 = 2\pi N \rho \cdot \int_0^\infty dr\, r^2 u_0(r) g_0(r)$$

$$\Updownarrow$$

$$\langle u_1 \rangle_0 = 2\pi N \rho \int_0^\infty dr\, r^2 u_1(r) g_0(r)$$

$$u_0(r) = \begin{cases} \infty & r \leq \sigma \\ 0 & r > \sigma \end{cases}$$

hard sphere

$$g_0(r) \approx e^{-\beta u(r)} \approx \begin{cases} 0 & r \leq \sigma \\ 1 & r > \sigma \end{cases}$$

$$\equiv \Theta(r - \sigma)$$

$$\langle u_1 \rangle_0 = 2\pi N \underset{\uparrow \atop \frac{N}{V}}{\rho} \int_\sigma^\infty r^2 \underbrace{u_1(r)}_{<0} \, dr$$

$$= -a N^2/V \quad , \quad a > 0$$

$$a = -2\pi \int_\sigma^\infty r^2 u_1(r) \, dr$$

$$P = \frac{\partial A}{\partial V} = \frac{\partial}{\partial V}\left(A^0 + A^1\right)$$

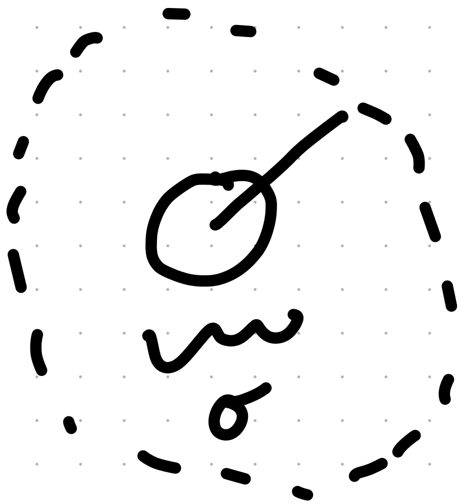
$$A^{o} = -k_B T \ln\left(\frac{Z^{o}}{\lambda^{3N} N!}\right)$$

What is Z_o for hard sphere system?

$$Z_o = \int dx\, e^{-\beta U_o(x)} \qquad U_o(x) = \begin{cases} \infty & r \le \sigma \\ 0 & r > \sigma \end{cases}$$

If ideal gas $Z_o = V^N$

$$Z_o^{\text{Hard sphere}} = (V - V_{\text{excluded}})^N$$



No other particle can get closer than σ

$$V_{excluded} = \frac{4}{3}\pi\sigma^3$$

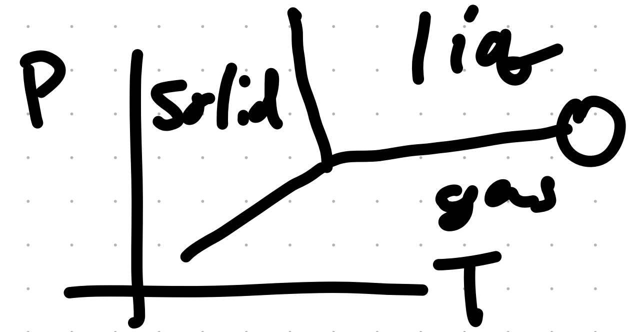
$$V_{excluded\text{-}total} = \frac{N}{2} V_{excluded}$$

$$= \underbrace{\frac{2}{3}\pi\sigma^3}_{b} N$$

$$Z_0 = (V - Nb)^N$$

$$A = -k_B T \ln\left[\frac{(V - Nb)^N}{\lambda^{3N} N!}\right] - aN^2/V$$

$$P = -\left(\partial A/\partial V\right)_{N,T}$$



Pg 175-177

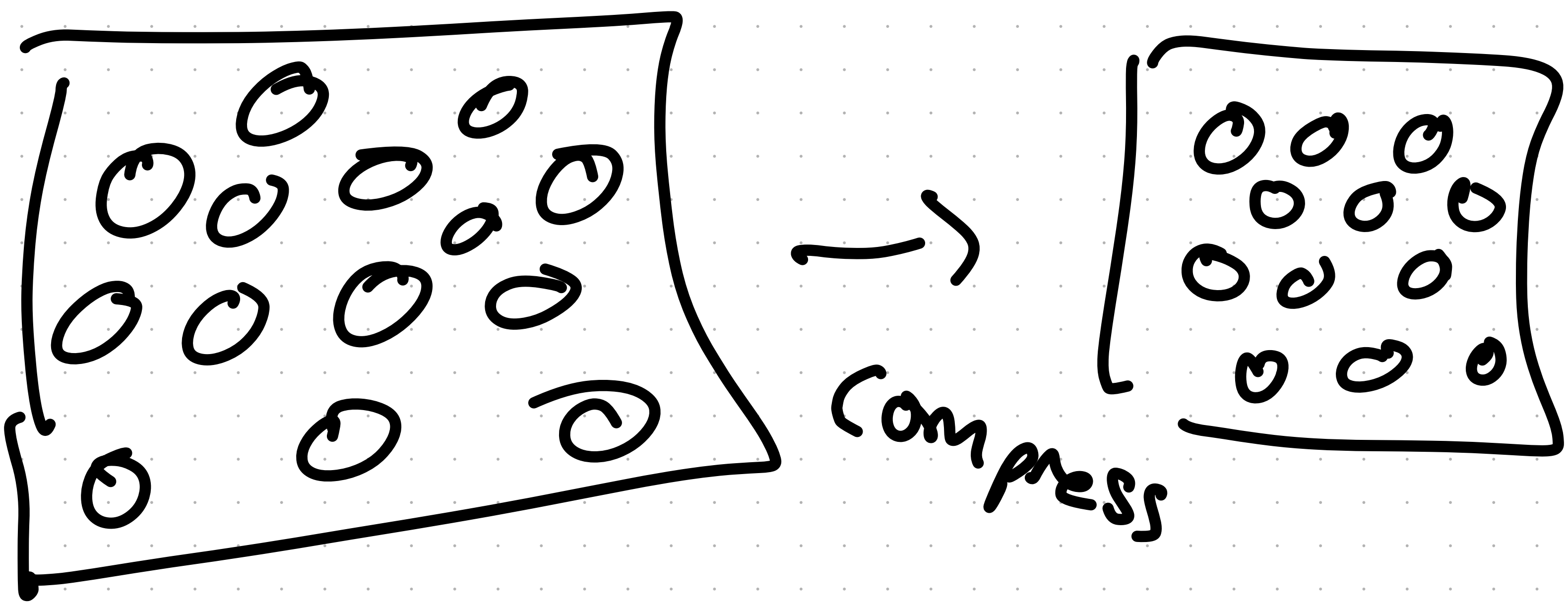
can get Vdw equation of state

or approximate B_2

"a" stickyness "b" repulsion

See Eg. talk by Sharon Glozer

1957, Alder-Wainright



$$A = \underset{0}{\cancel{E}} - TS$$

Computer Simulations

Compute quantities like

$$\langle A \rangle = \int d\vec{x}\, A(\vec{x})\, P(\vec{x})$$

where $P(x) = e^{-\beta \mathcal{H}(x)} / \int dx\, e^{-\beta \mathcal{H}(x)}$