Van der Waal's Perturbation theory & intro to Sampling

Last time:

Showed that the pressure depends on density formally as:

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

with

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

So that at low density

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

with

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

Also, said that

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

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

$$= Z_0 \cdot \int dr\, e^{-\beta U_1(r)} \left[\frac{e^{-\beta U_0(r)}}{Z_0} \right] \leftarrow P_0(r)$$

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

$$\langle a \rangle_0 = \int dr\, a(r) \frac{e^{-\beta U_0(r)}}{Z_0}$$

Suppose u_1 is small compared to u_0

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

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

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

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

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

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

cumulant expansion [pg 171]

So what is $\langle u_1 \rangle_0$?

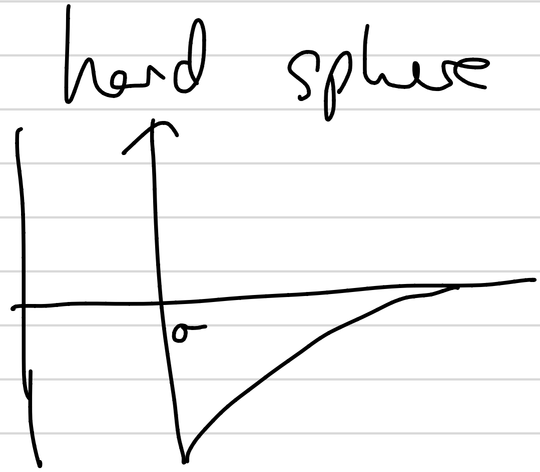
Remember $\langle u_0 \rangle_0 = 2\pi N \rho \int_0^\infty dr\, r^2\, u_0(r)\, g_0(r)$

where $g_0(r)$ is $g(r)$ when $u_1 = 0$

same analysis gives $\langle u_1 \rangle_0 = 2\pi N \rho \int_0^\infty dr\, r^2\, u_1(r)\, \underline{g_0(r)}$

Now know A_1 to low order

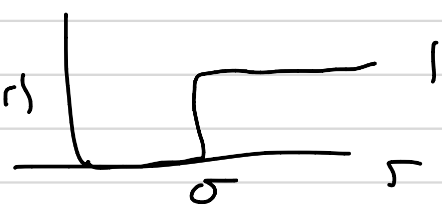
Simple potential is hard sphere + attraction



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

in low density limit, for unperturbed $g_0(r) \approx e^{-\beta u_0(r)} = \begin{cases} 0 & r < \sigma \\ 1 & r \geq \sigma \end{cases}$

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



$$A^{(1)} \approx 2\pi N \rho \int_0^\infty r^2 u_1(r) g_0(r)\, dr = 2\pi N \rho \int_\sigma^\infty r^2 \underbrace{u_1(r)}_{<0} dr$$

$= -aN\rho = -aN^2/V$

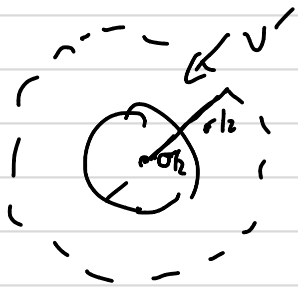
$$a \equiv -2\pi \int_\sigma^\infty r^2 u_1(r)\, dr > 0$$

To get A^0, need $Z^{(0)}$. for ideal gas $Z = V^N$

for low density ideal gas, $Z_0 = V_{\text{available}}^N$

$V_{available} = V - V_{excluded}$

What is $V_{excluded}$ for a hard sphere particle



no particle can be closer than $R = \sigma$, so $V' = \frac{4}{3}\pi\sigma^3$

Not obvious, But this double counts exclusion b/c particle i excludes j & vice versa, so

$$V_{excluded} = N \cdot \frac{1}{2} \cdot \frac{4}{3}\pi\sigma^3 = Nb \leftarrow \frac{2}{3}\pi\sigma^3$$

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

$$A \approx -k_BT \log\left[\frac{(V-Nb)^N}{N!\,\Lambda^{3N}}\right] - aN^2/V$$

$$P = -\left(\partial A/\partial V\right) = +k_BTN \cdot \frac{1}{V-Nb} - aN^2/V^2$$

$$= \frac{Nk_BT}{V-Nb} - aN^2/V^2$$

or $\beta P = \frac{\rho}{1-\rho b} - a\rho^2\beta$ ✱ Van der Waal's eqn of state

$$\frac{1}{1-x} = -\frac{d}{dx}\log(1-x) = 1 + x + x^2 + \cdots$$

$$\beta P \approx \rho(1 + \rho b + \rho^2 b^2 + \cdots) - a\rho^2\beta \approx \rho + \underbrace{(b - a\beta)}_{B_2}\rho^2 + \underbrace{b^2}_{B_3}\rho^3 + \cdots$$

Note, Van der Waals eqn of state has a change in behavior corresponding to a critical point. Can predict some "critical behavior" (see pg 175-177) but we will discuss more w/ phase transitions

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These were actually some of the first things people tried to compute with simulations, either to solve problems impossible by hand or to give as inputs to theories [eg equations depending on $g(r)$]

E.g. do system of disks crystallize? first shown on a computer by Alder & Wainright 1957. Crystal actually has more entropy!

How do we do these simulations?

we want to compute quantities like

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

$P(\vec{x})$ might be something like $e^{-\beta \mathcal{H}(\vec{x})} \Big/ \int d\vec{x}\, e^{-\beta \mathcal{H}(\vec{x})}$

If we know the prob. func., then we can do this integral by "quadrature" (discritization)

$$\langle A \rangle \approx \sum_{i=1}^{N} A(\vec{x}_i) P(\vec{x}_i) \Delta x$$

Eg

Prob of being on left is $A(x) = \begin{cases} 1 & x < x_1 \\ 0 & x > x_1 \end{cases}$

χ_A, indicator function

however, this does not work in higher dimensions b/c num points is $\left(L/\Delta x\right)^d \sim e^{d \log (L/\Delta x)}$