Lecture 14: Non ideal gasses

Before considered

$$\beta P = \underbrace{\rho}_{\text{ideal gas}} + \sum_{j=0}^{\infty} B_{j+2}\, \rho^{j+2}$$

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

for low density, $g(r) \approx e^{-\beta u(r)}$

$$\Rightarrow \quad B_2 \approx -2\pi \int_0^{\infty} dr \left[e^{-\beta u(r)} - 1\right] r^2\, dr$$

If know $u(r)$, can plug in to get correction to pressure at second order

We will use a different approach to derive – perturbation theory (see exam!)

We showed on exam that if we have

$$\mathcal{H}(x) = \mathcal{H}_0(x) + \lambda V(x) \quad \text{that}$$

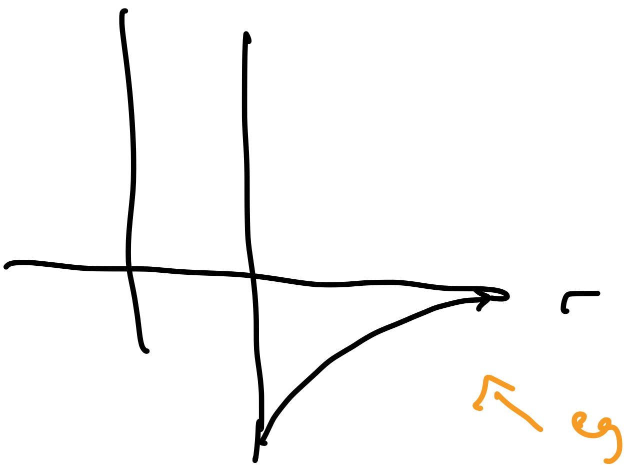
$$A = A_0 + \lambda \langle V(x) \rangle_0 - \beta \lambda^2/2 \; \mathrm{Var}(V)_0$$

to first order, $\lambda = 1$, $\Delta A \approx \langle V(x) \rangle_0$

If $\mathcal{H} = \sum_{i=1}^{\tilde{N}} p_i^2/2m_i + \mathcal{U}(x)$

← perturbation
interaction

Going to choose a $\mathcal{U}(x)$ - sticky hard spheres



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

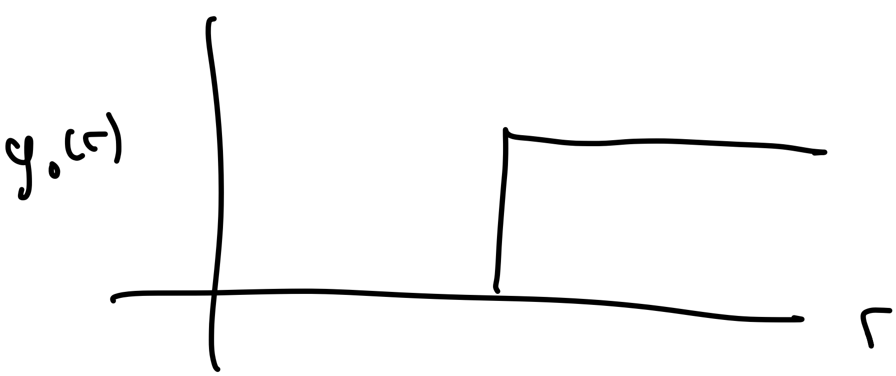
$u_1(r)$ is attractive pot

Remember for radially symmetric pair pot

$$\langle u \rangle = 2\pi N \rho \int_0^\infty r^2 u(r)\, g(r)\, dr$$

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

$$g_0(r) \approx e^{-\beta u_0(r)} \approx \begin{cases} 0 & \text{if } r < \sigma \\ 1 & \text{otherwise} \end{cases} = \Theta(r-\sigma)$$



low density

So $\Delta A = \langle U_1 \rangle_0 = 2\pi N\rho \int_0^\infty r^2 u_1(r)\, g(r)\, dr$

$$\approx 2\pi N\rho \int_0^\infty r^2 u_1(r)\, \Theta(r-\sigma)\, dr$$

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

$$\equiv -aN\rho$$

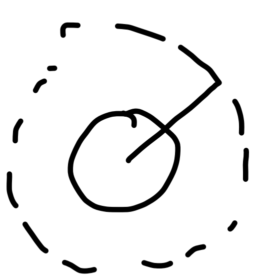
$a = -2\pi \int_\sigma^\infty r^2 u_1(r)\, dr \quad > 0$, total stickiness

What is $A_0 = -k_B T \ln Z_0$

Z_0 is partition for volume excluding ideal gas

Z_0 ideal gas $= V^N$

For volume exclusion, argue that less space is available by Nb



minimum dist for another mc is σ

so V_{excl} here is $\frac{4}{3}\pi\sigma^3$

But this double counts area from other particle so

$V' = V - Nb$ where $b = \frac{2}{3}\pi\sigma^3$

diameter

$$A = -k_BT \ln\left[(V-Nb)^N\right] + (-aN\rho)$$

$$= -Nk_BT \ln[V-Nb] - aN^2/V$$

$$P = -\left(\partial A/\partial V\right)_{N,T} = \frac{Nk_BT}{V-Nb} - aN^2/V^2$$

$$\cancel{\mathcal{A}}\ \beta P = \frac{N}{V-Nb} - a\beta\rho^2$$, not quite in virial form

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

$$\frac{1}{1-b\rho} \approx 1 + b\rho + b^2\rho^2 \qquad \frac{1}{1-x} \approx 1 + x + x^2 + \cdots$$

$$\Rightarrow \beta P \approx \rho + [\underbrace{b - a\beta}_{B_2}]\rho^2 + \underbrace{b^2}_{B_3}\rho^3 + \cdots$$

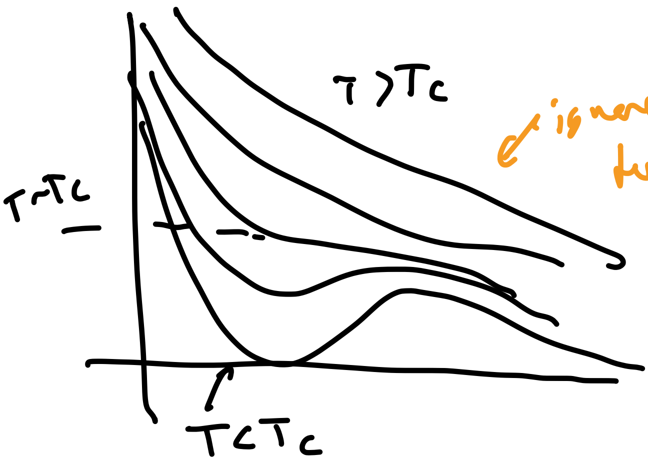
For just first term

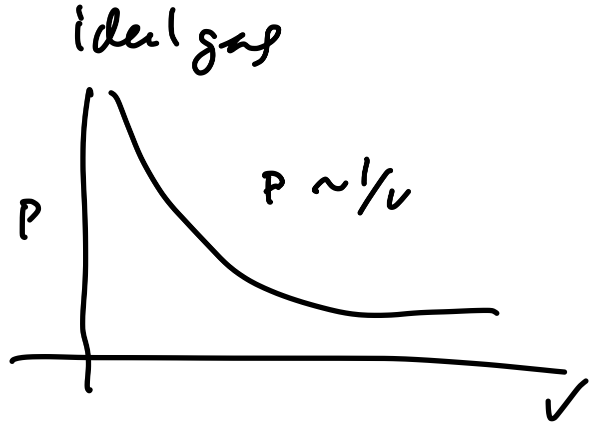
$$P = \frac{Nk_BT}{V} + \frac{N^2}{V^2}(k_BTb - a)$$

$$\Rightarrow PV - \underbrace{\frac{N^2}{V}k_BTb}_{Nb\,P_{\text{ideal}}} + \frac{N^2}{V}a = Nk_BT$$

Often written $\left(P + an^2/V^2\right)(V - nb) = nRT$, not quite same what does this look like

$$\beta P = \frac{N}{V-Nb} - a\beta\frac{N^2}{V^2}$$





when flat? consider

$$dP/dV = d^2P/dV^2 = 0$$

$$\frac{d}{dV}P = Nk_BT\frac{\partial}{\partial V}\left[V-Nb\right]^{-1} - a\,N^2\frac{d}{dV}\left[V^{-2}\right]$$

$$= -Nk_BT(V-Nb)^{-2} + 2aN^2V^{-3} = 0$$

2 eqns, solve for V_c & T_c where the

$$\frac{d^2P}{dV^2} = 2Nk_BT\cdot\frac{1}{(V-Nb)^3} - 6aN^2\cdot V^{-4}$$

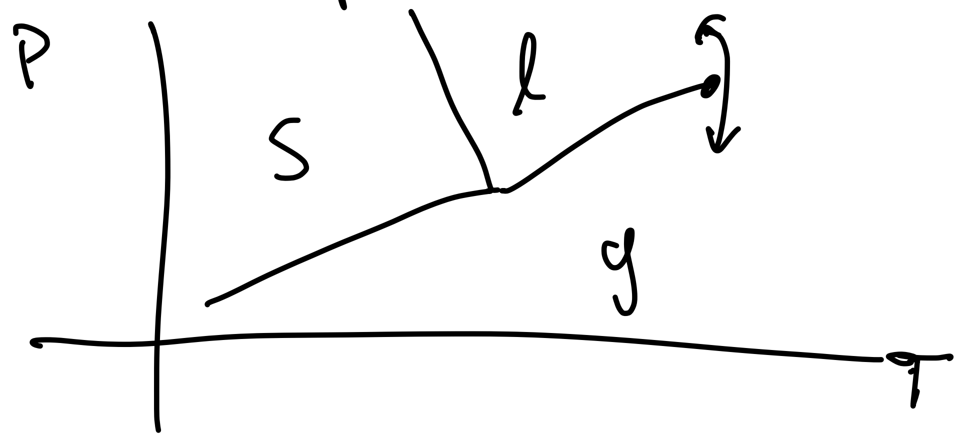
$$\times\frac{3}{V} \text{ \& add} \Rightarrow 2Nk_BT\cdot\frac{1}{(V-Nb)^3} - \frac{3Nk_BT}{V}\cdot\frac{1}{(V-Nb)^2} = 0$$

$$= \frac{2V}{3} = V-Nb \Rightarrow V_c = 3Nb \quad ✱$$

$$k_BT_c = \frac{2aN^2}{NV_c^3}\cdot(V_c-Nb)^2 = \frac{2aN}{(3Nb)^3}\cdot(2Nb)^2 = \frac{8a}{27b} \quad ✱$$

$$P_c = \frac{Nk_BT_c}{V_c-Nb} - a\frac{N^2}{V_c^2} = \frac{N\left(\frac{8a}{27b}\right)}{2Nb} - a\frac{N^2}{(9N^2b^2)} = \frac{1}{27}\frac{a}{b^2}$$

Critical points have strange behavior



(sec 4.7.55)

isothermal compressibility

$$K_T = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right) = \frac{1}{V(\partial P/\partial V)} \sim (T_c - T)^{-1} \quad \text{diverges}$$

$$\propto \mathrm{Var}(V)$$

Exponent is typical for a certain class of systems

$$C_V \sim |T - T_c|^{-\alpha}$$

$$P - P_c \sim |\rho - \rho_c|^{\delta} \, \mathrm{sign}(\rho - \rho_c)$$

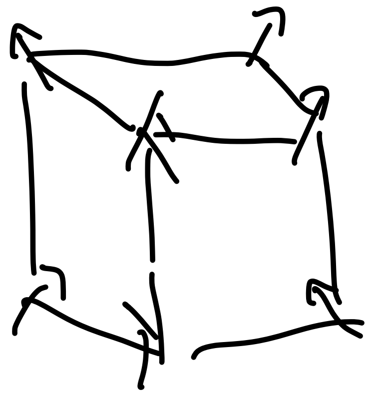
$$\rho_L - \rho_G \sim |T_c - T|^{\beta}$$

VdW theory gives

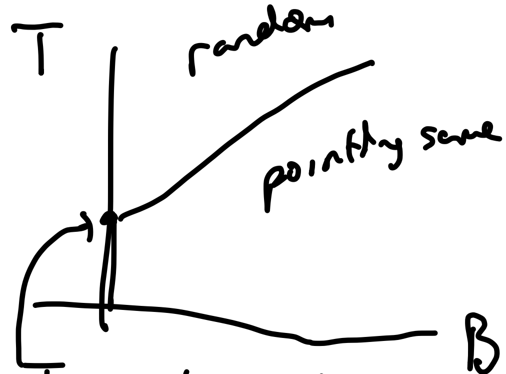
$\alpha = 0, \ \beta = 1/2, \ \gamma = 1, \ \delta = 3$

Expt $\alpha = 0.1$ $\beta = 0.34$ $\gamma = 1.35$ $\delta = 4.7$

Next, will learn about ising model, prototypical model for phase transitions



← real magnet



T_c, does this exist or only at 0

Full hamiltonian just up or down

$$\mathcal{H} = -J \sum_i \sum_j s_i \cdot s_j - h \sum_i s_i$$

field

make neighbor approx

$$\mathcal{H} = -J \sum_{\langle ij \rangle} s_i s_j - h \sum_i s_i$$

like 2J from above

in 1d $$\mathcal{H} = -J \sum_{i=1}^{N} s_i s_{i+1} - h \sum_{i=1}^{N} s_i$$

can have periodic $S_{N+1} = S_1$ to reduce boundary effects

No J, independent : $Z = (Z_0)^N = \left(e^{-\beta h/2} + e^{\beta h/2}\right)^N$

(not indisting) $E = -\partial \ln Z / \partial \beta = -N \dfrac{h/2\left[-e^{-\beta h/2} + e^{\beta h/2}\right]}{e^{-\beta h/2} + e^{\beta h/2}}$