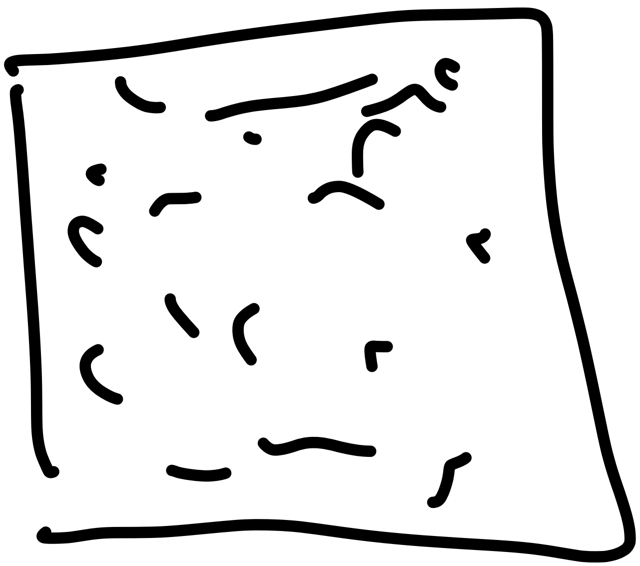
Lecture 15 - Non ideal gasses



N, V, T

$$Z = \int_V dx\, e^{-\beta U(x)}$$

$$U_{\text{ideal}}(x) = 0$$

$$U_{\text{total}}(x) = \sum_{i>j} u(r_{ij})$$

$$P = \frac{N k_B T}{V}$$

$$= \rho k_B T + \rho^2 (k_B T)^2 \cdot \frac{v}{2}$$

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

$$= \rho + B_2 \rho^2 + \dots$$

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

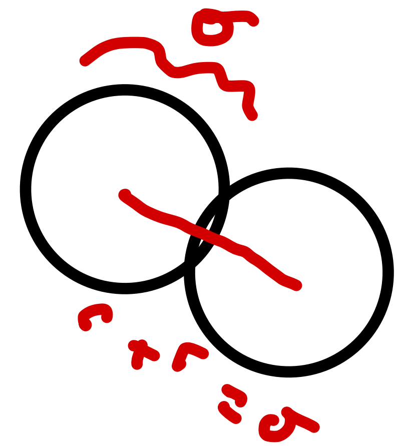
in same limit $g(r) \approx e^{-\beta u(r)}$

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

$$\mathcal{H} = \mathcal{H}_0 + V(x)$$

$$A = A_0 + \langle V(x) \rangle_0 \cancel{- \frac{\beta}{2} \mathrm{Var}_0(V)}$$

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



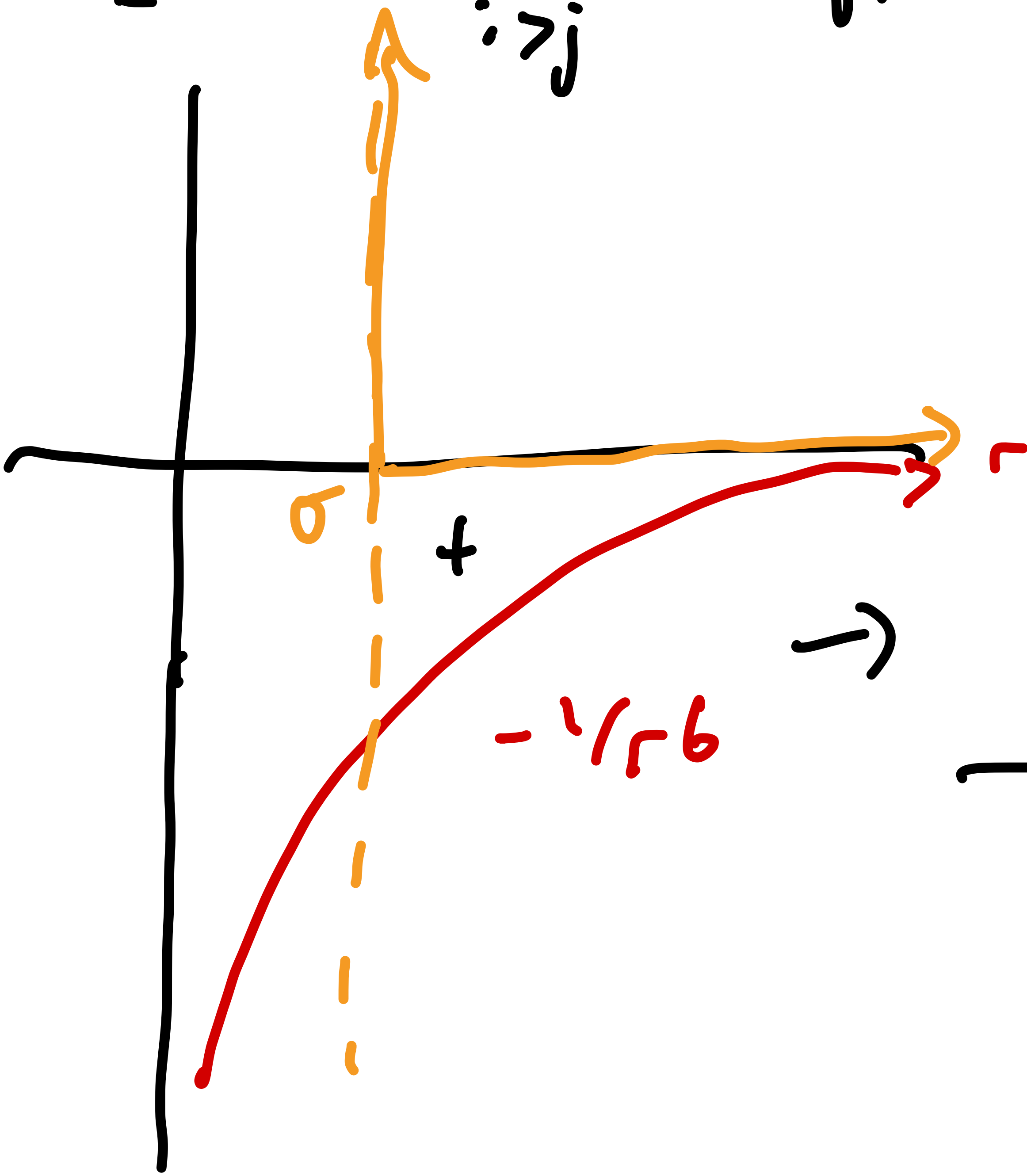
$$\mathcal{H}_0 = \sum_{i=1}^{N} p_i^2/2m_i + \sum_{i>j} u_0(r)$$

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

excluded volume

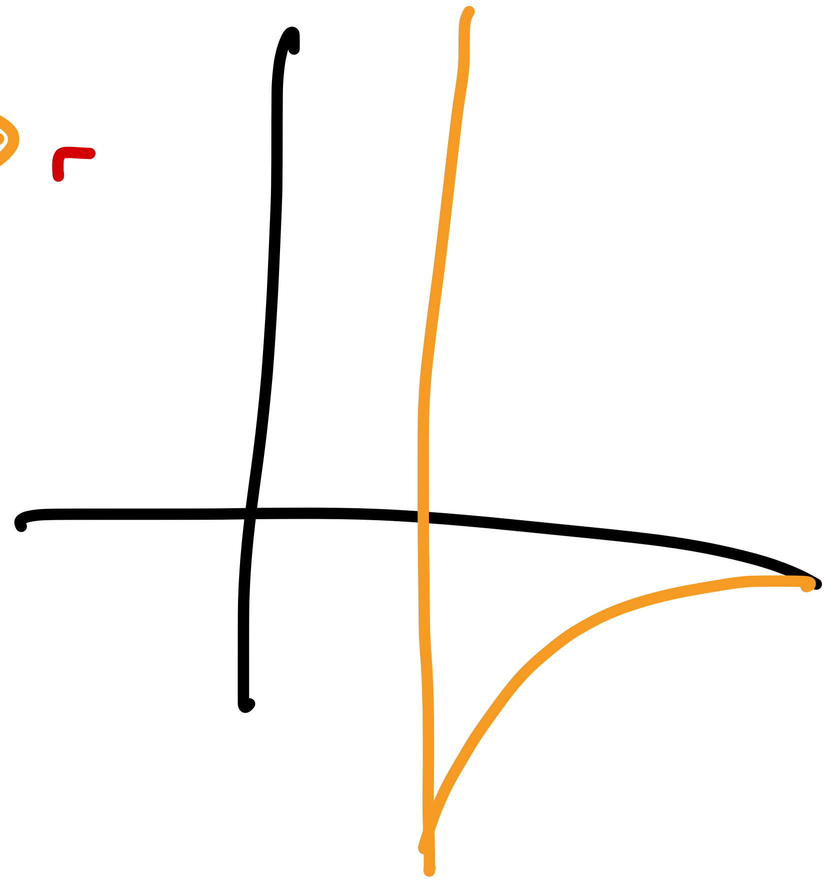
$u_1(r)$ attractive

$$V(\underline{x}) = \sum_{i>j} u_1(r_{ij})$$



u_1 example

$$u_1(r) = -\varepsilon/r^6$$



$$\langle U_{total} \rangle^{\text{pairwise}} = 2\pi N \rho \int_0^\infty r^2 u(r)\, g(r)\, dr$$

pairwise, radially symmetric

$$\langle O \rangle = \int dx\, O(x)\, e^{-\beta U(x)} \Big/ \int dx\, e^{-\beta U(x)}$$

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

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

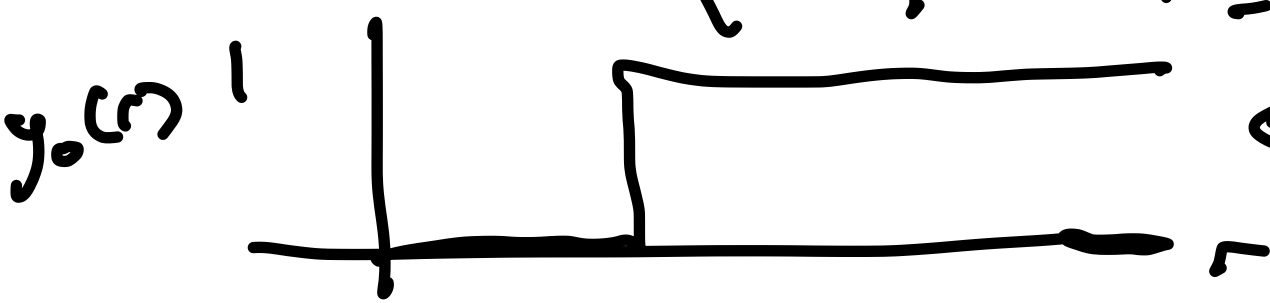
$$U_0^{total} = \sum_{i>j} u_0(r_{ij})$$

low density limit

$$g_0(r) \approx e^{-\beta u_0(r)}$$

$$g_0(r) = \begin{cases} 0 & r < \sigma \\ 1 & r \geq \sigma \end{cases}$$

Heaviside function



$\Theta(r-\sigma)$

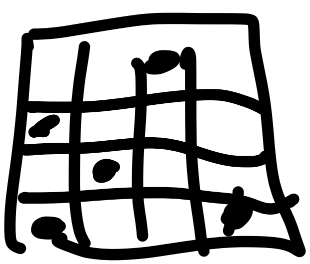
$$\frac{d\Theta(\alpha)}{d\alpha} = \delta(\alpha)$$

$$\Delta A = \langle V \rangle_0 = 2\pi N\rho \int_0^{\infty} r^2 u_1(r) \underbrace{g_0(r)}_{\Theta(r-\sigma)} dr$$

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

$$\equiv -aN\rho$$

$$a = \underbrace{-2\pi \int_{\sigma}^{\infty} r^2 u_1(r) dr}_{\text{total stickiness}} > 0$$



$$A_0 = -k_B T \ln Z_0 :$$

for an ideal gas: $Z_0 = V^N \longrightarrow \underbrace{(V-Nb)^N}$ volume exclusion

$$V_{excluded} = \frac{4}{3}\pi\sigma^3 \times \frac{1}{2}$$

Van der Waals equation of state

$$A \approx A_0 + \langle V \rangle$$

$$= -k_BT \ln (V-Nb)^N - aN \cdot N/V$$

$$P = -\frac{\partial A}{\partial V} = NkBT/(V-Nb) - aN^2/V^2$$

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

4.7

(.35)

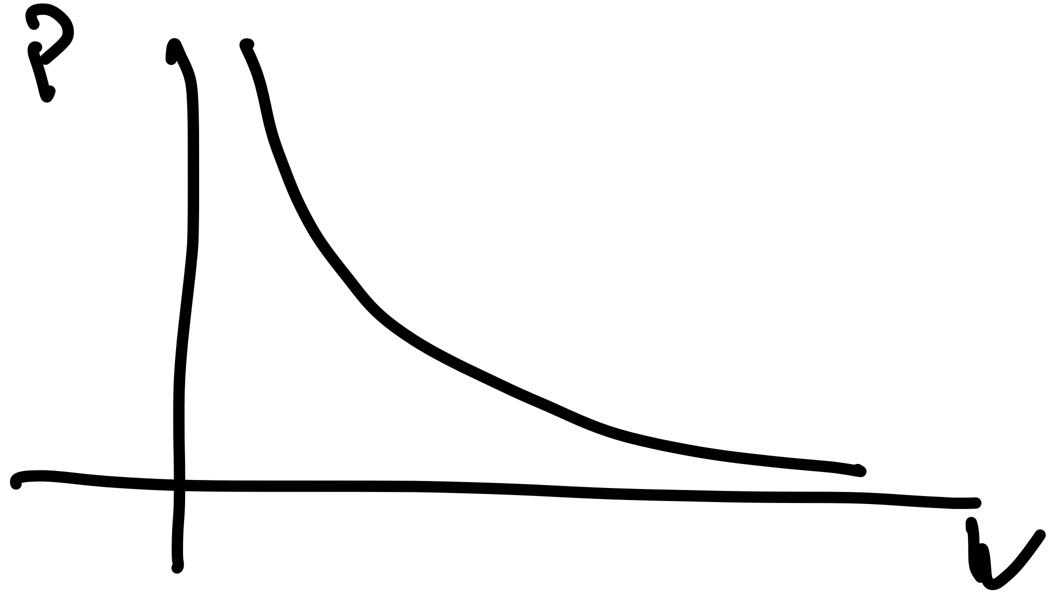
$$= \rho \cdot \frac{1}{1 - b\rho} - a\beta\rho^2$$

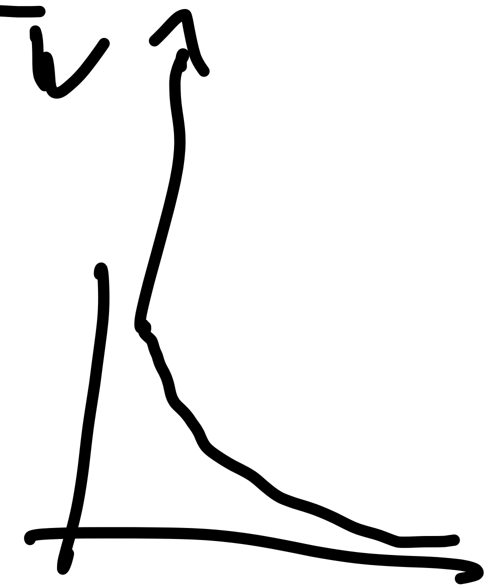
$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \cdots$$

$$\approx \rho\left(1 + b\rho + b^2\rho^2 + \cdots\right) - a\beta\rho^2$$

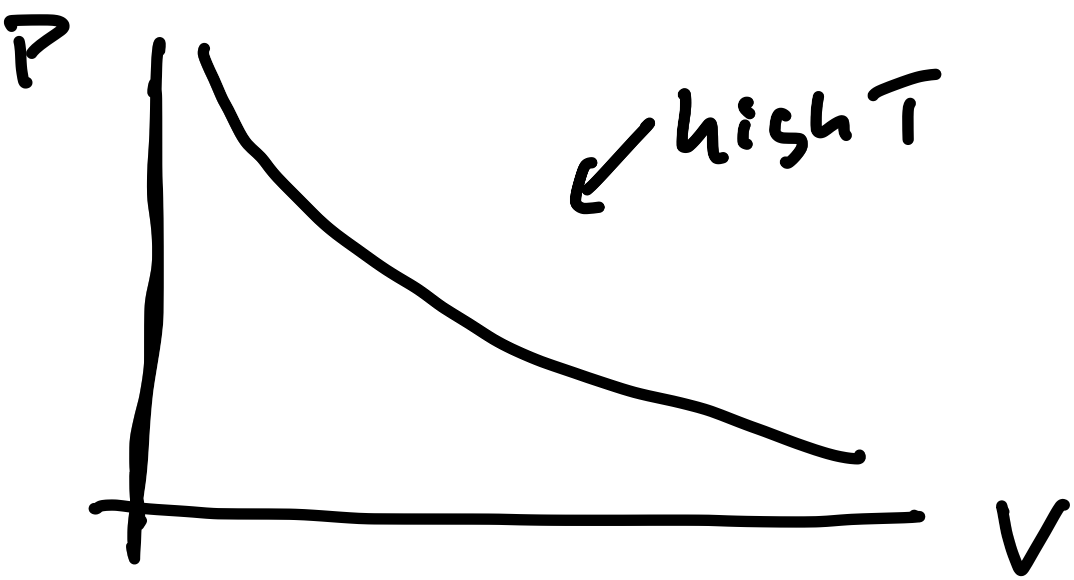
$$= \rho + \underbrace{[b - a\beta]}_{B_2}\rho^2 + \underbrace{b^2}_{B_3}\rho^3 + \underbrace{b^3}_{B_4}\rho^4 + \cdots$$

$$\beta P \propto \frac{1}{V}$$

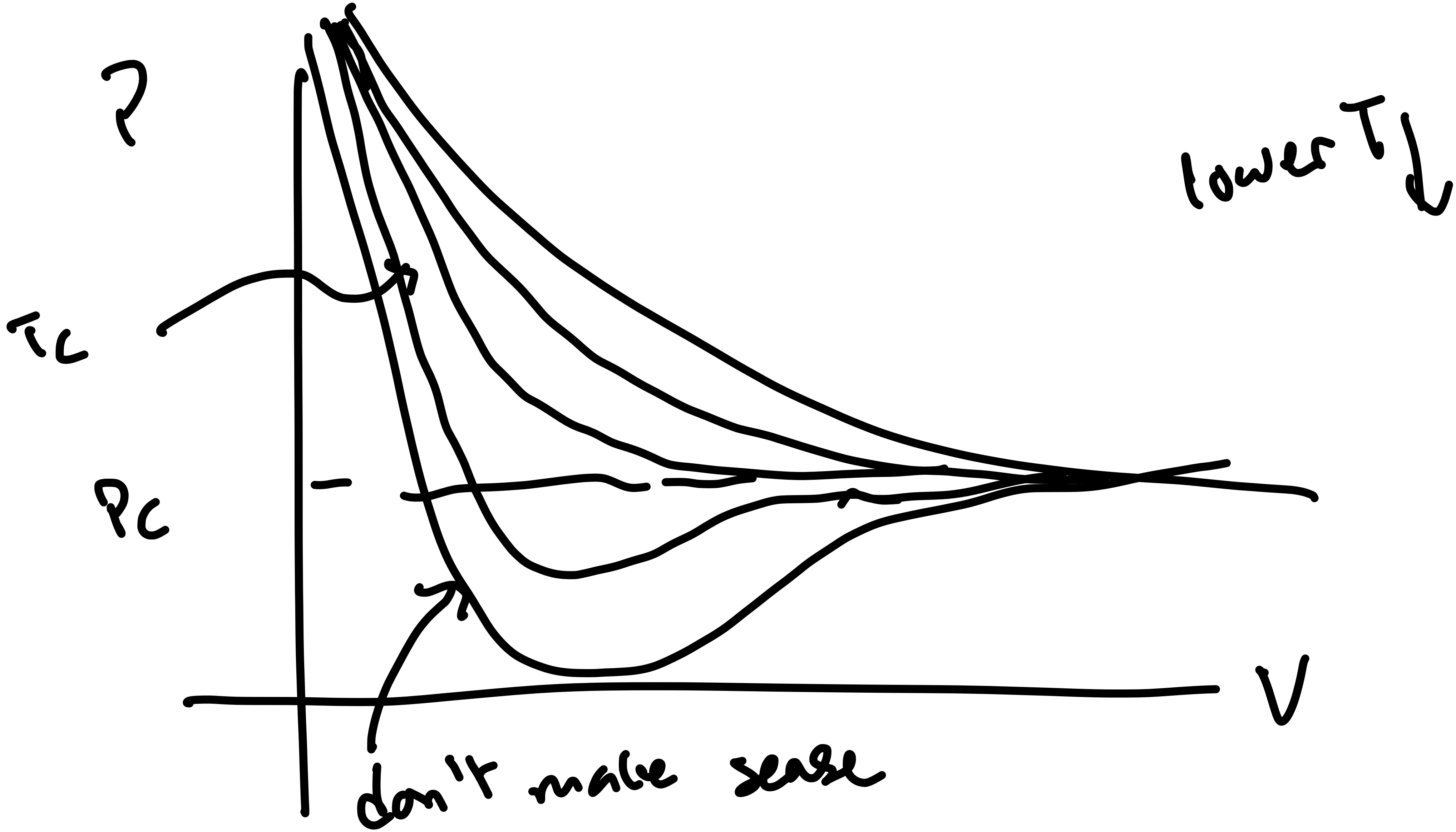


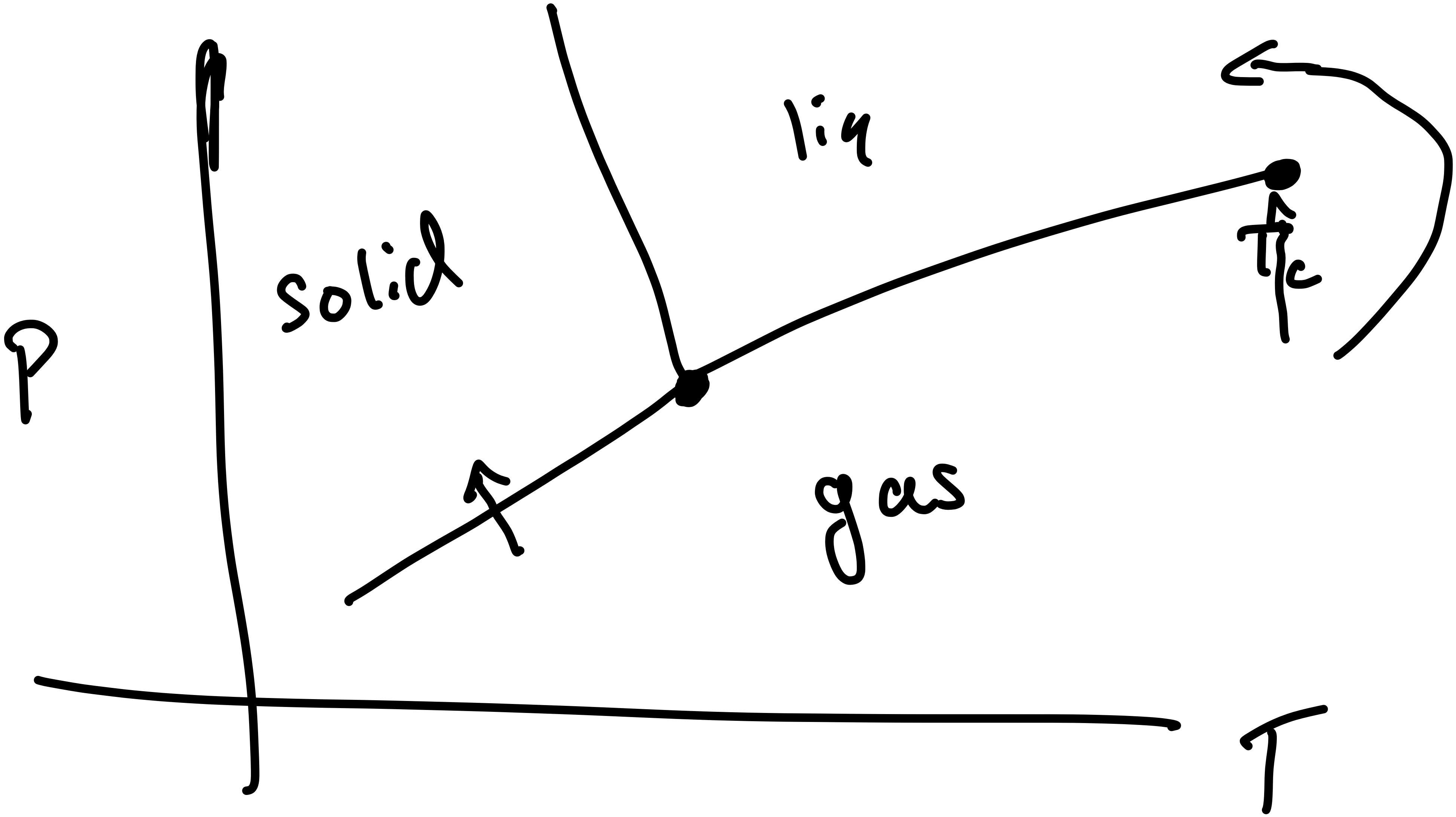


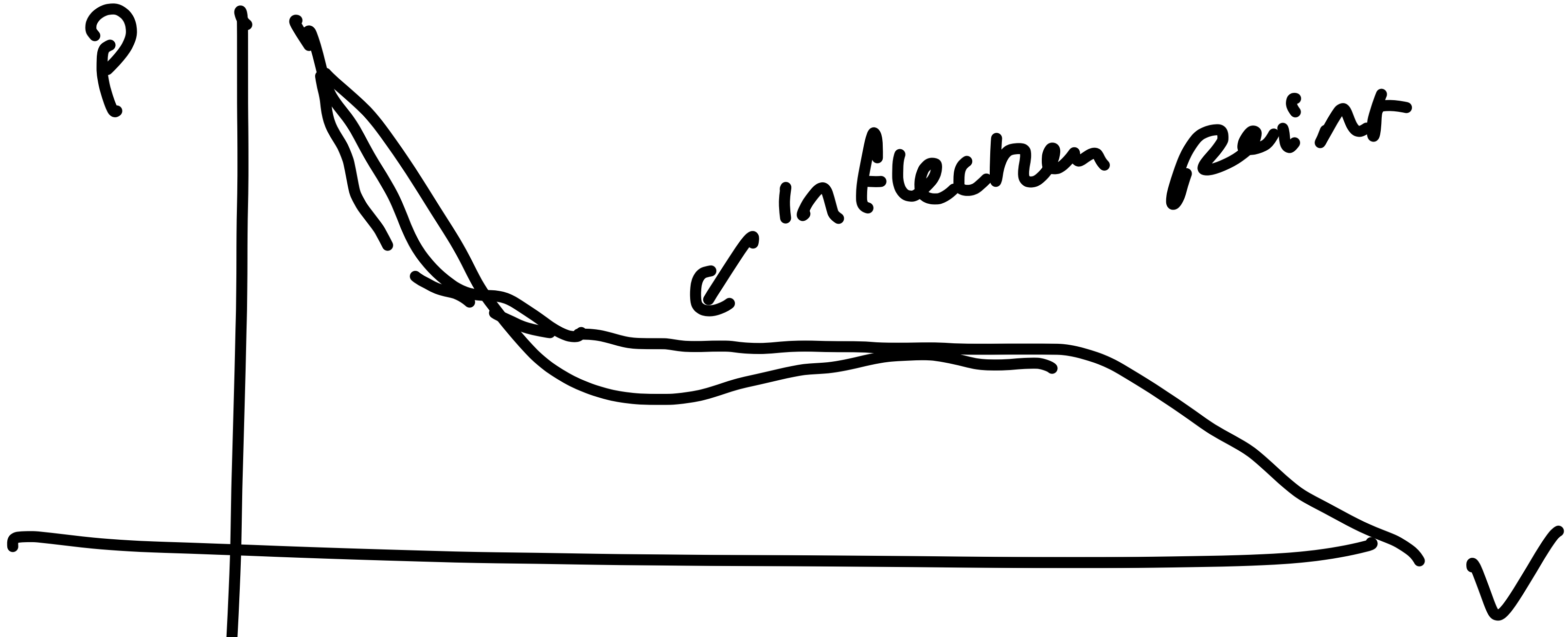
$$\beta P = \frac{N}{V-Nb} - a\beta \frac{N^2}{V^2}$$



high T


P
lower T
Tc
Pc
V
don't make sense


P
solid
liq
gas
T_c
T



$$\frac{dP}{dU} = 0 \qquad \frac{d^2P}{dV^2} = 0$$

2 equations, 2 unknowns

V_c, T_c

$$V_c = 3Nb \qquad k_B T_c = 8a/27b \qquad P_c = \frac{1}{27} a/b^2$$

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right) = \frac{1}{V\left(\partial P/\partial V\right)}$$

isothermal compressibility $\sim \frac{1}{T_c - T}$ $\Rightarrow$ density has div. density fluc

diverges as T_c is approached

$\mathrm{Var}\, N \propto \frac{\partial \langle N \rangle}{\partial \mu}$ $\qquad$ $\mathrm{Var}\, V \propto \frac{\partial \langle V \rangle}{\partial P}$

Critical opalescence

$K_T \sim (T_c - T)^{-\gamma}$ $\qquad$ $\gamma = 1$

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

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

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

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

Expt: $\alpha = 0.1$, $\beta = 0.34$
$\gamma = 1.35$, $\delta = 4.2$