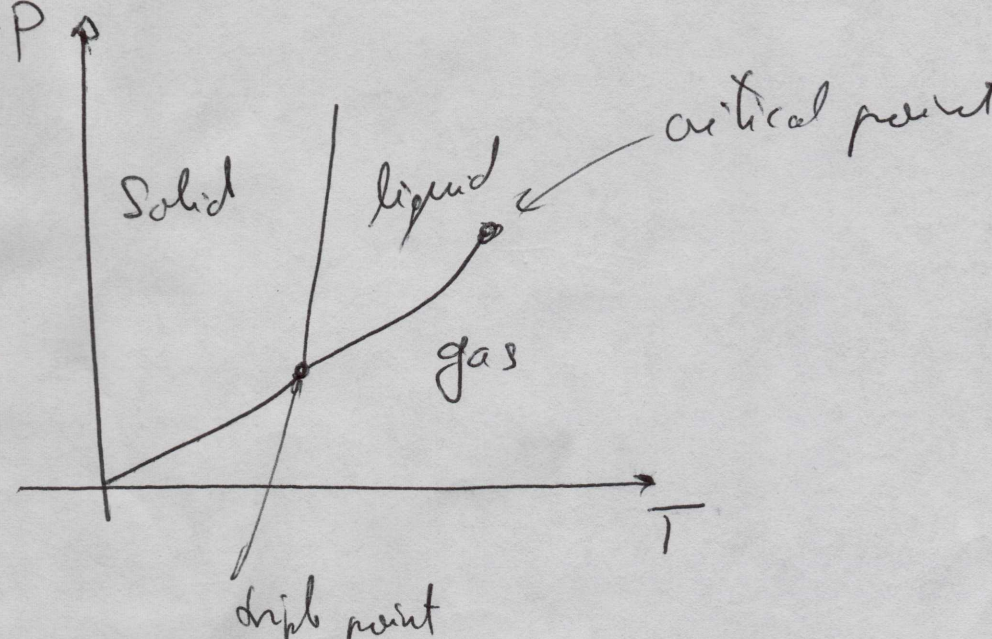
Phase transitions



Van der Waals eq. of state (non-ideal gas)

$$\boxed{(V-b)\,\underbrace{(p+a/V^2)}_{P_{kinetic}} = RT}$$

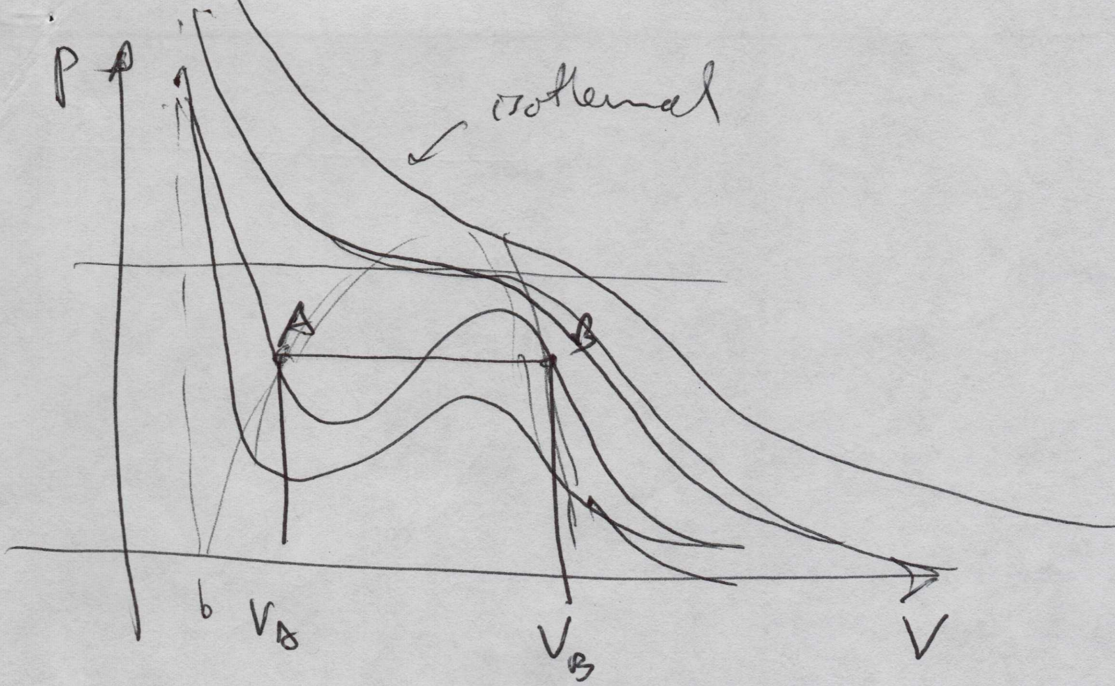
less volume

pressure on wall

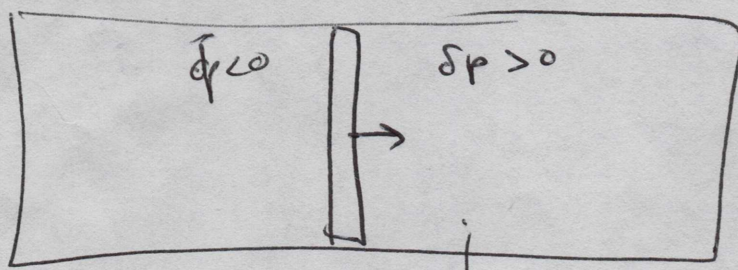
$V \to \infty$ $\boxed{pV = RT}$ ✓ T fixed

$p \to \infty$ $(V-b)\,p = RT$

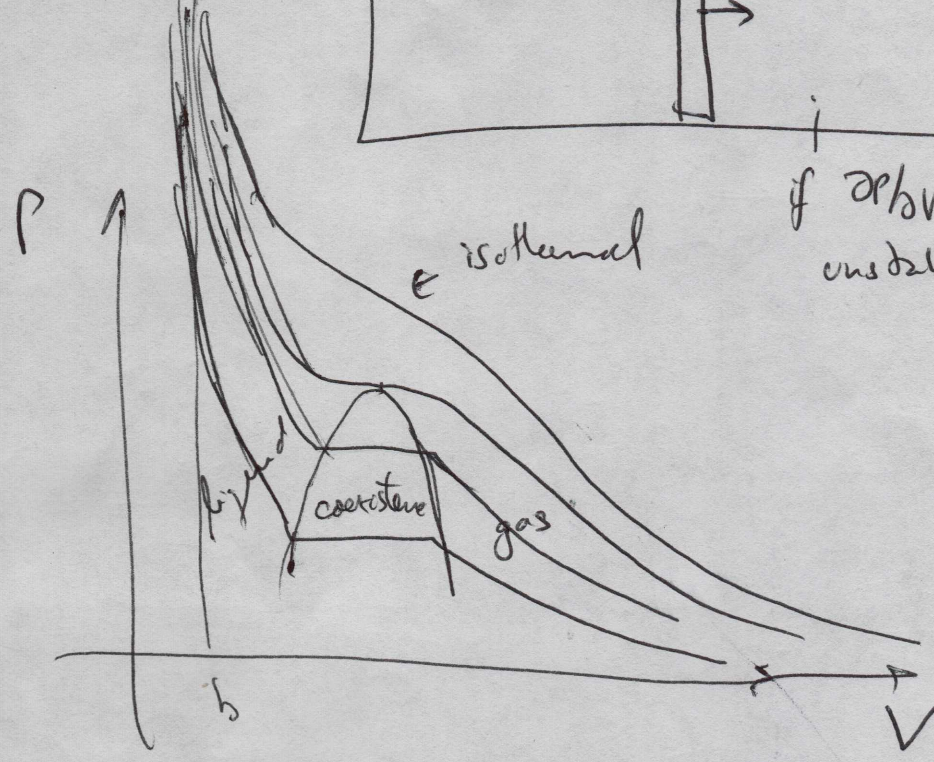
$\boxed{V \to b}$ incompressible.



$$\frac{\partial p}{\partial V} < 0$$



if $\partial p / \partial V > 0$
unstable.



Critical point

$$p = -\frac{a}{V^2} + \frac{RT}{V-b}$$

$$\frac{\partial p}{\partial V} = \frac{2a}{V^3} - \frac{RT}{(V-b)^2} = 0 \quad \Rightarrow \quad \frac{2a}{V_c^3} = \frac{RT_c}{(V_c-b)^2}$$

$$\frac{\partial^2 p}{\partial V^2} = -\frac{6a}{V^4} + \frac{2RT}{(V-b)^3} = 0 \quad \Rightarrow \quad \frac{3a}{V_c^4} = \frac{RT_c}{(V_c-b)^3}$$

$$\frac{2\cancel{a}}{\cancel{V_c^3}} = \frac{3a}{V_c^4}(V_c - b) = \frac{\cancel{3}a}{V_c^3} - \frac{3ab}{V_c^4}$$

$$3\cancel{a}b = \cancel{a}V_c \qquad \boxed{V_c = 3b}$$

$$RT_c = \frac{2a}{V_c^3}(V_c-b)^2 = \frac{2a}{27b^{\cancel{3}}}4\cancel{b^2} = \frac{8}{27}\frac{a}{b}$$

$$p_c = -\frac{a}{9b^2} + \frac{\cancel{8}^{\,4}}{27}\frac{a/b}{\cancel{2}b} = \left(\frac{4}{27} - \frac{1}{9}\right)\frac{a}{b^2}$$

$$\boxed{p_c = \frac{1}{27}\frac{a}{b^2}}$$

$$\left(V - \frac{V_c}{3}\right)\left(p + \frac{27 P_c b^2}{V^2}\right) = RT$$

$$P_c V_c \left(\frac{V}{V_c} - 1/3\right)\left(p/p_c + 3 V_c^2/V^2\right) = R \frac{T}{T_c} T_c$$

$$V/V_c = \bar{V} \qquad p/V_c = \bar{p} \qquad T/T_c = \bar{T}$$

$$P_c V_c = \frac{3}{27}\frac{a}{b} = \frac{a}{9b} = \frac{1}{9}\frac{27}{8} RT_c = \frac{3}{8} RT_c$$

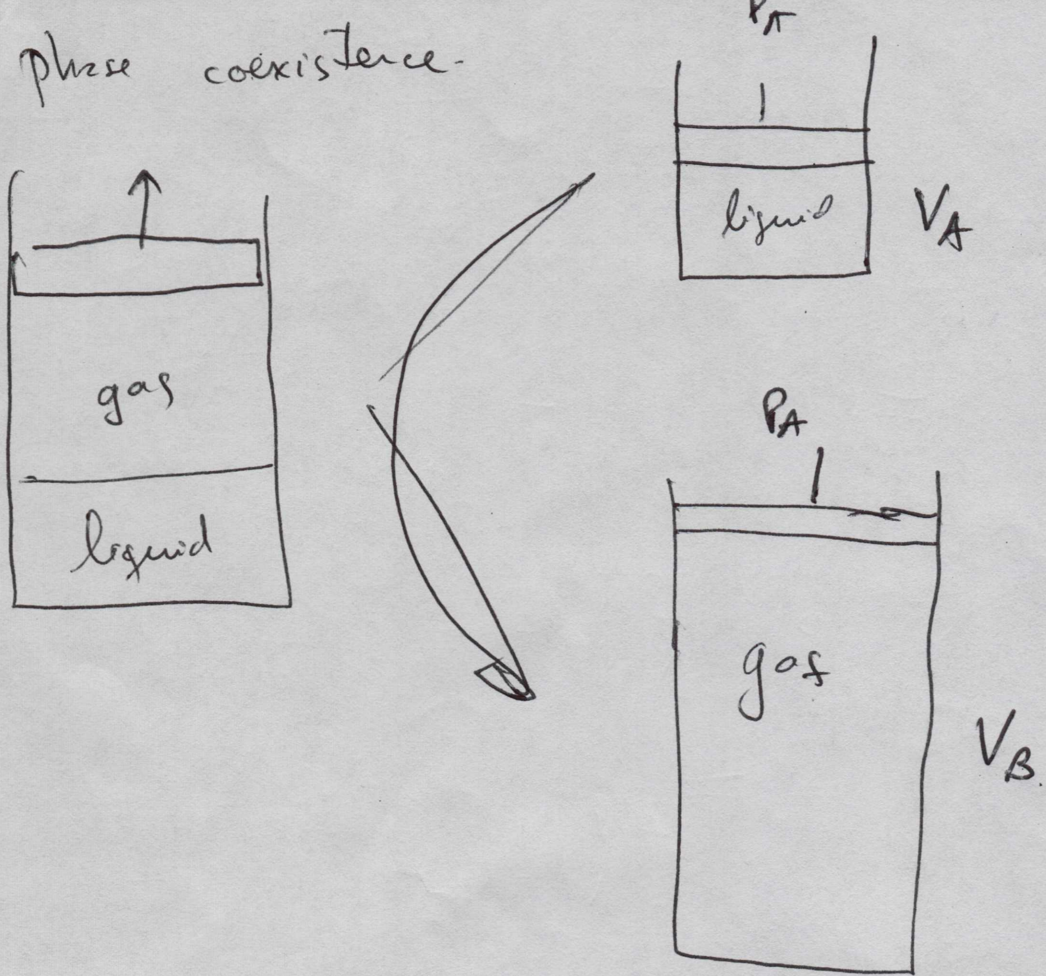
$$\frac{3}{8}\left(\frac{V}{V_c} - 1/3\right)\left(\bar{p} + \frac{3}{\bar{V}^2}\right) = \bar{T}$$

$$\boxed{\left(\bar{p} + 3/\bar{V}^2\right)\left(\bar{V} - 1/3\right) = \frac{8}{3}\bar{T}}$$

law of corresponding states

$$\boxed{f(\bar{p}, \bar{V}, \bar{T}) = 0}$$

phase coexistence



$$dA = -SdT - pdV$$

$dT = 0$ (along isothermal)

$$dA = -pdV$$

$$A_B - A_A = -\int_A^B p\,dV = -P_A (V_B - V_A)$$

$\boxed{\text{I, II same area}}$ Maxwell's construction.

$$\left(\frac{\partial U}{\partial V}\right)_T = -p + T\left(\frac{\partial p}{\partial T}\right)_V$$

Van der Waals gas.

$$(V-b)\left(\frac{\partial p}{\partial T}\right)_V = R$$

$$\left(\frac{\partial U}{\partial V}\right)_T = -p + \frac{RT}{V-b} = \cancel{-p} \cancel{+p} + a/V^2$$

$$\left(\frac{\partial U}{\partial V}\right)_T = a/V^2$$

$$U = -\frac{a}{V} + f(T)$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{R}{V-b}$$

$$S = R \ln\left(\frac{V-b}{b}\right) + g(T)$$

$$A = U - TS = -\frac{a}{V} - RT\ln\left(\frac{V-b}{b}\right) + f - Tg$$

units

$$\boxed{A = -\frac{a}{V} + C_v T - RT\ln\left(\frac{V-b}{b}\right) - C_v T \ln\frac{T}{T_0} - S_0 T}$$

?

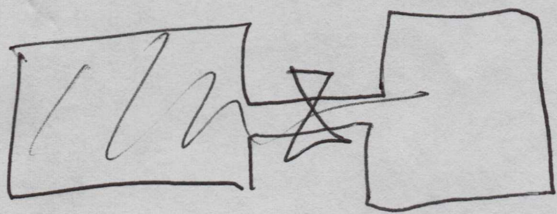
✓

if $C_v = \left(\frac{\partial U}{\partial T}\right)_V =$ const. $\Rightarrow U = -\frac{a}{V} + C_v T + U_0$

$C_v = T\left(\frac{\partial S}{\partial T}\right)_V =$ const. $\quad S = C_v \ln T/T_0 + f(V)$

$$S = R\ln\left(\frac{V-b}{b}\right) + C_v \ln(T/T_0) + S_0$$

✓



expansion

U conserved

$$-\frac{a}{V_f} + C_v T_f = -\frac{a}{V_i} + C_v T_i$$

$$C_v (T_f - T_i) = -\frac{a}{V_i} + \frac{a}{V_f} = \frac{a}{V_i V_f}(-V_f + V_i)$$

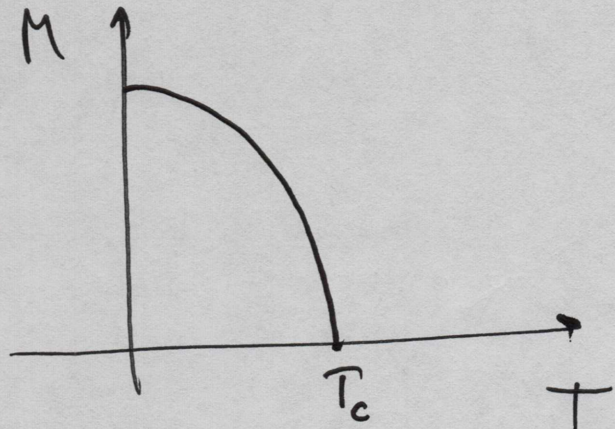
$$= -\frac{a}{V_i V_f}(V_f - V_i)$$

$$C_v \Delta T = -\frac{a}{V_i V_f} \Delta V$$

$$\boxed{\Delta T = -\frac{a}{C_v V_i V_f} \Delta V}$$

$\underline{\Delta T < 0}$ gas cools down.

Critical exponents



$$M = -\frac{\partial G}{\partial H}$$

$$\chi = \frac{1}{V}\frac{\partial M}{\partial H}$$

$$U = G - T\frac{\partial G}{\partial T}\left[+p\frac{\partial G}{\partial p}\right]$$

$$C = T^2\frac{\partial^2 G}{\partial T^2}$$

$$C_v \sim |t|^{-\alpha} \qquad t = \frac{T - T_c}{T_c}$$

$$M \sim |t|^{\beta}$$

$$\chi \sim |t|^{-\gamma}$$

$$M \sim H^{1/\delta} \qquad t = 0$$

$$\Gamma(r) = \langle m(r)\, m(0)\rangle - \langle m(r)\rangle\langle m(0)\rangle$$

$$\Gamma(r) \underset{t \to 0}{=} \frac{e^{-r/\xi}}{r^p} \qquad \xi \sim t^{-\nu}$$

$$p = d - 2 + \eta$$

$$\gamma = \nu(2-\eta)$$

$$\alpha + 2\beta + \gamma = 2$$

$$\gamma = \beta(\delta - 1)$$

$$\nu d = 2 - \alpha.$$

$$G = U - TS + pV$$

$$dG = -S\,dT + V\,dp$$

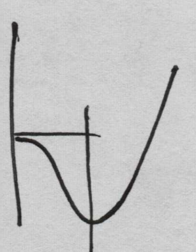
$$\frac{\partial G}{\partial T} = -S \qquad \frac{\partial G}{\partial p} = V$$

$$U = G + TS - pV$$

$$\boxed{U = G - T\frac{\partial G}{\partial T} + p\frac{\partial G}{\partial p}}$$

$$A = \int d^d x \; (\nabla M_a)(\nabla M_a) + \cancel{t}\, M_a^2 + \lambda (M_a^2)^2 - HM$$

$$0$$



$$t + 2\lambda M_a^2 = 0 \qquad M_a^2 = -t/2\lambda$$

$$|M| = \sqrt{\frac{-t}{2\lambda}} \qquad \boxed{\beta = 1/2}$$

$$\cancel{t + 2\lambda M^2 - H = 0.}$$

$$t M^2 + \lambda M^4 - HM = 0.$$

$$2tM + 4\lambda M^3 - H = 0.$$

$$M = \frac{1}{2t} H$$

$$\chi = \frac{\partial M}{\partial H} = \frac{1}{2t} \qquad \boxed{\gamma = 1}$$

$$t = 0 \qquad 4\lambda M^3 = H$$

$$M = \left(\frac{H}{4\lambda}\right)^{1/3} \qquad \boxed{\delta = 3}$$

$$A = -t^2/2\lambda + \lambda \frac{t^2}{4\lambda^2} = -\frac{t^2}{4\lambda}$$

$$\frac{\partial A}{\partial t} = -S = \frac{2t}{4\lambda} = \frac{t}{2\lambda}$$

$$C_V = T\frac{\partial S}{\partial t} = \frac{T}{2\lambda}. \qquad (\alpha = 0)$$

finite discontinuity.