II Interacting classical gas & van der Waals Eqn. of state

① partition function:

$$Q = \frac{1}{N!}\int \frac{\prod d^3k_i\, d^3f_i}{(2\pi)^{3N}} e^{-\beta\left[\sum \epsilon_{k_i} + V(f_i)\right]}$$

$$\frac{1}{N!}\int \frac{\prod d^3f_i}{h^{3N}}$$

replace $V(f_i)$ by $\langle V(f_i)\rangle$ mean-field

$$V(f_i) = \frac{1}{2}\sum_{i,j} U(f_i - f_j) = \frac{1}{2}\int d^3f\, d^3f'\, n^2\, U(f-f')$$

$$= \frac{1}{2} N \int d^3f\, U(f) = \frac{1}{2} N \bar{U} n$$

average potential: $\bar{U} = \int d^3f\, U(f)$

$$Q = \frac{1}{N!}\int \frac{\prod d^3k_i\, d^3f_i}{(2\pi)^{3N}} e^{-\beta\left[\sum \epsilon_k + \frac{1}{2}Nn\bar{U}\right]}$$

$$= \frac{1}{N!}\left[\int \frac{d^3k}{(2\pi)^3} e^{-\beta\epsilon_k}\right]^N e^{-\frac{\beta}{2}Nn\bar{U}} \qquad (V-b)^N$$

$$= \frac{1}{N!}\left(\frac{V-b}{\lambda^3}\right)^N e^{-\frac{\beta}{2}Nn\bar{U}}$$

b = excluded volume

$b \sim N\frac{4\pi}{3} r_0^3 = N v_0$ for hard balls

$$A = -k_B T \ln Q$$

$$= N k_B T\left(\ln \frac{N\lambda^3}{V-b} - 1\right) + \frac{1}{2} N n \bar{U}$$

$$= N k_B T\left(\ln \frac{N\lambda^3}{V - Nv_0} - 1\right) + \frac{1}{2}\frac{N^2\bar{U}}{V}$$

② Eqn. of state

$$P = -\frac{\partial A}{\partial V} = \frac{N k_B T}{V-b} + \frac{1}{2} N^2 \bar{v} / V^2$$

$$(V-b)\left(P - \frac{N^2 \bar{v}/2}{V^2}\right) = N k_B T$$

van der Waals eqn. of state

$$\boxed{(V-b)\left(P + \frac{a}{V^2}\right) = RT}$$

$$a = -\frac{1}{2} N^2 \bar{v}$$

$$R = N k_B$$

$$\boxed{A = N k_B T \left(\ln \frac{N\lambda^3}{V-b} - 1\right) - \frac{a}{V}}$$

Free energy for van der Waals model.

Virial expansion

$$\therefore P = P(V,T)$$

$$\Rightarrow \boxed{\frac{PV}{RT} = 1 + \frac{C_2(T)}{V} + \frac{C_3(T)}{V^3} \cdots}$$

$$C_2 = b - \frac{a}{RT} \qquad C_3 = b^2 \quad \cdots$$

if we ignore a then C_2 = excluded volume

For Fermi gas $C_2 = N \frac{\lambda^3}{2^{5/2}}$ Fermion ~

For hard ball $C_2 = N \frac{4\pi}{3} r_0^3$ hardball w/ $r_0 \sim \lambda$

(3) phase transition

∴ Knowing the free energy $A(T,V)$ allows us to know every thing

? Is there any phase transition?

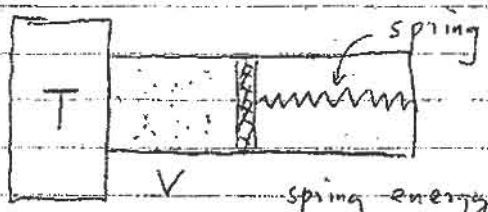
Is there any singularity in $A(T,V)$ as a function of T and V.?

singularity = phase Transition

We find on singularity in $A(T,V)$ seem no phase transition ×

Instead of examining phase Transition using the free energy, Let us examin it using Gibbs potential $G(T,P)$

(4) Gibbs potential



Gibbs potential = free energy of combined system

spring energy $= PV + \text{const.}$

↳ sys + spring

Partition function of combined system: $Q_{com} = \sum_n e^{-\beta(E_n + V_n P)} = Q_{sys} e^{-\beta \bar{V} P}$

free energy of combined system: $A_{com} = -k_B T \ln Q_{com}$

is the Gibbs potential $= -k_B T \ln Q_{sys} + \bar{V} P$

$= A_{sys} + \bar{V} P = G_{sys}$

$$Q_{com} = \int dV \sum_n \delta(V - V_n) e^{-\beta(E_n + VP)}$$

$$= \int dV \underbrace{e^{-\beta(A(V,T) + VP)}}_{\bar{V} \text{ minimize this}} \approx e^{-\beta \underbrace{[A(\bar{V},T) + \bar{V}P]}_{G}}$$

↳ & Prob. distribution for V

> For fixed T, V system wants to minimize free energy A
> For fixed T, P system wants to minimize Gibbs potential G

From the relation $G = A + VP$

$$\Rightarrow dG = dA + dVP = -S dT - P dV + P dV + V dP$$

$$= -S dT + V dP$$

$$\Rightarrow \boxed{V = \frac{\partial G(T,P)}{\partial P}, \quad S = -\frac{\partial G(T,P)}{\partial T}}$$

(5) Phase Transition in gas of const. pressure

A gas with pressure P, what is V?

V is obtained by minimize Gibbs energy

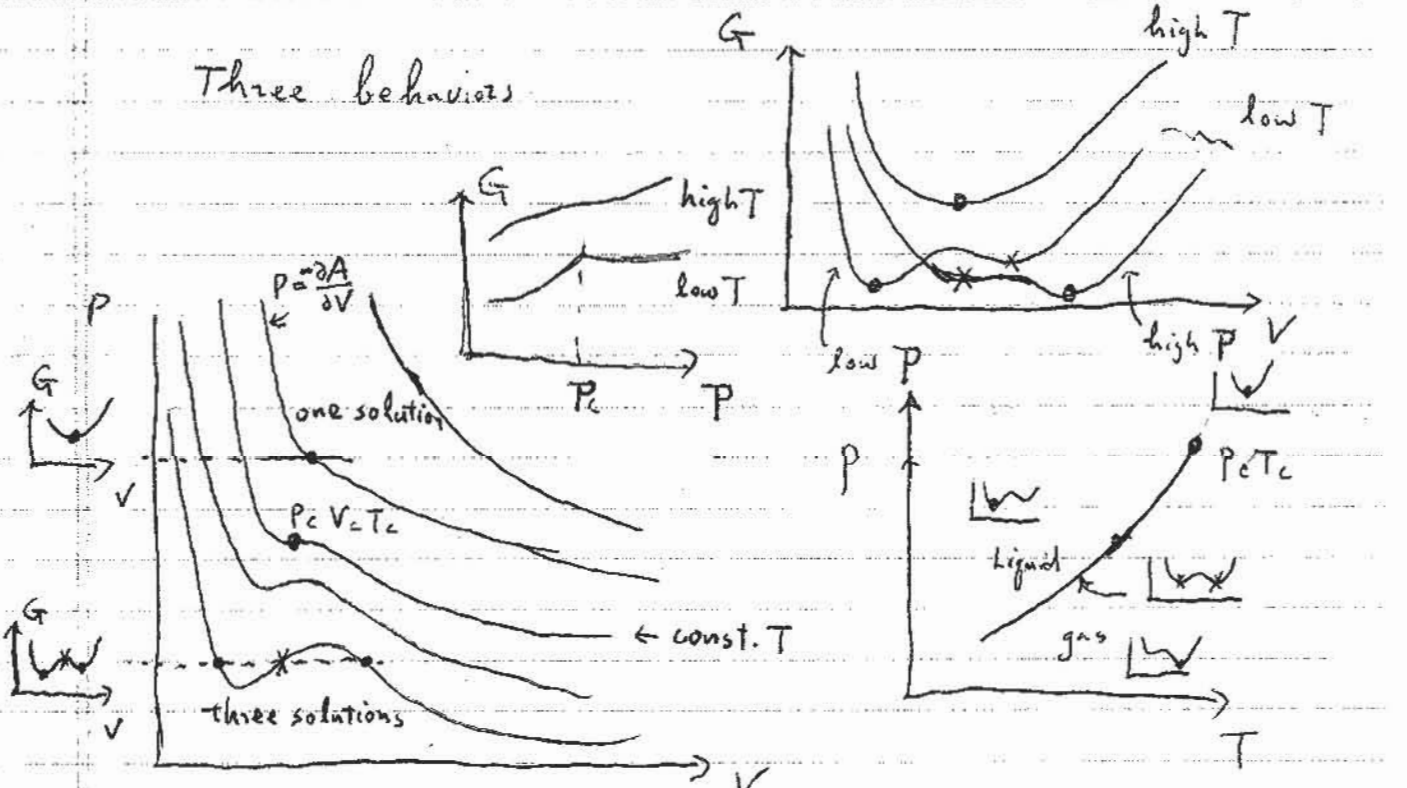
$$G = A + PV$$

van der Waals model

$$G = N k_B T \left(\ln \frac{N\lambda^3}{V-b} - 1 \right) - \frac{a}{V} + PV$$

$$= -N k_B T \ln (V-b) - \frac{a}{V} + PV + \text{terms indep. of } V$$

Three behaviors



Eq. of state: $\left[V^3 - \left(b + \frac{RT}{P}\right) V^2 + \frac{a}{P} V - \frac{ab}{P} = 0 \right] = (V - V_c)^3$

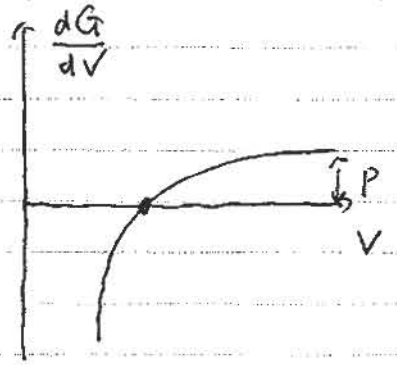
at critical point. $\left[3V_c = b + \frac{RT_c}{P_c}, \quad 3V_c^2 = a/P_c, \quad V_c^3 = ab/P_c \right]$ ↑ critical condition: three degenerate solutions.

$$\left[T_c = \frac{8a}{27bR} \qquad P_c = \frac{a}{27b^2} \qquad V_c = 3b \right]$$

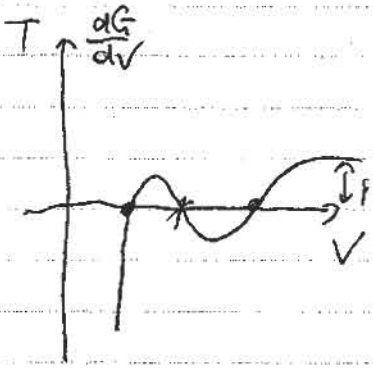
* $a > 0$ attraction $b > 0$ hard

$$\frac{dG}{dV} = -\frac{N k_B T}{V - b} + \frac{a}{V^2} + P$$

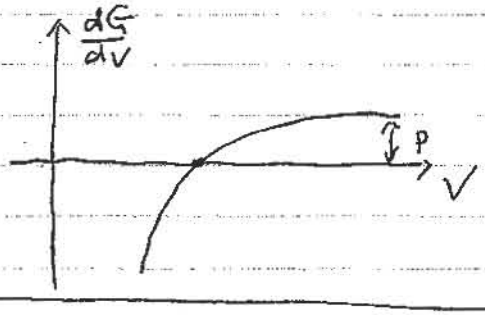
Large T

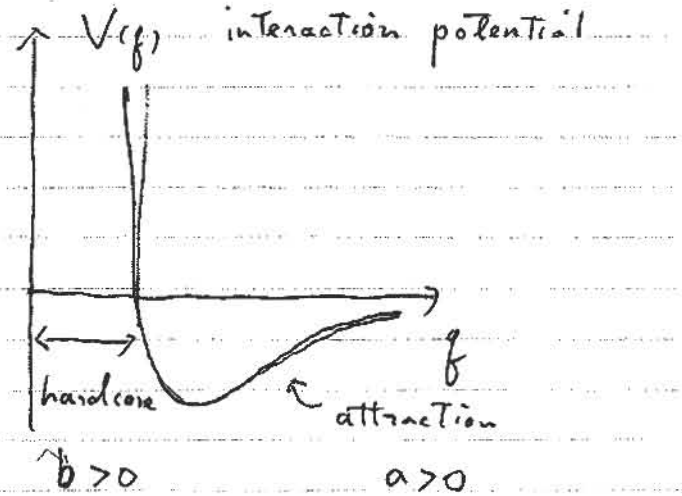


small T

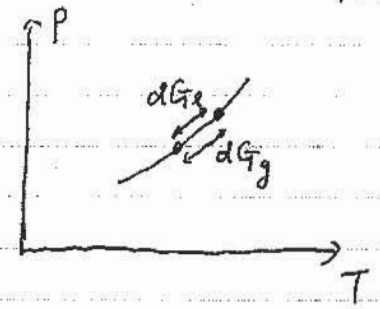


* $a < 0$ replusion $b > 0$





(6) Clapeyron equation:



$G_{liquid}(P,T)$ and $G_{gas}(P,T)$ are equal along the phase transition line.

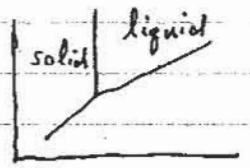
$$dG_\ell = V_\ell\, dP - S_\ell\, dT$$
$$= dG_g = V_g\, dP - S_g\, dT$$

$$\Rightarrow \quad \frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T\Delta V} \qquad L = T\Delta S$$

latent heat.

liquid solid transition

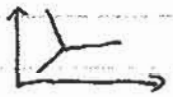
$\Delta V \simeq 0 \quad \Rightarrow$



from solid → liquid: $\Delta S > 0$

if $\Delta V > 0$

$\Delta V < 0$



water.

(7) Scaling and equation of state near critical point

Introduce dimensionless quantities

$$\bar{P} = \frac{P}{P_c} \qquad \bar{V} = \frac{V}{V_c} \qquad \bar{T} = \frac{T}{T_c}$$

van der Waals equation of state

$$\left(\bar{V} - \frac{b}{V_c}\right)\left(\bar{P} + \frac{a}{\bar{V}^2 P_c V_c^2}\right) = \frac{R T_c}{P_c V_c}\,\bar{T}$$

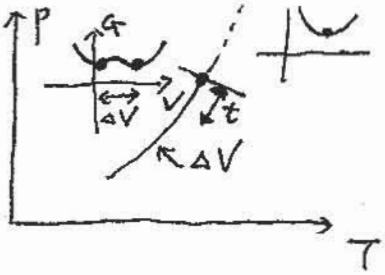
$$\Rightarrow \boxed{\left(\bar{V} - \frac{1}{3}\right)\left(\bar{P} + \frac{3}{\bar{V}^2}\right) = \frac{8}{3}\,\bar{T}}$$

same for all gases near critical point

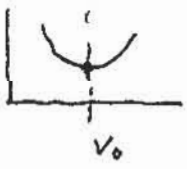
$\Rightarrow$ "universality"

Volum jump near the critical point

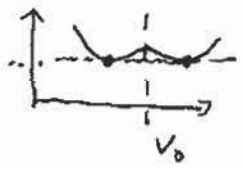
$$G(t, V) = C_1 t\,(V - V_0)^2 + C_2 (V - V_0)^4 + \text{const.}$$



$t > 0$



$t < 0$



$$\frac{dG}{dV} = 2C_1 t\,(V - V_0) + 4C_2 (V - V_0)^3 = 0$$

$$\Rightarrow (V - V_0) = \pm\sqrt{-\frac{C_1 t}{2C_2}}$$

$$\Rightarrow \Delta V = \sqrt{\frac{-2C_1 t}{C_2}} \propto |t|^{1/2}$$

experiment: $\Delta V \propto |t|^{\beta}$ $\qquad \beta \simeq \frac{1}{3}$

Universality: does not depend on what atom that form the ga