

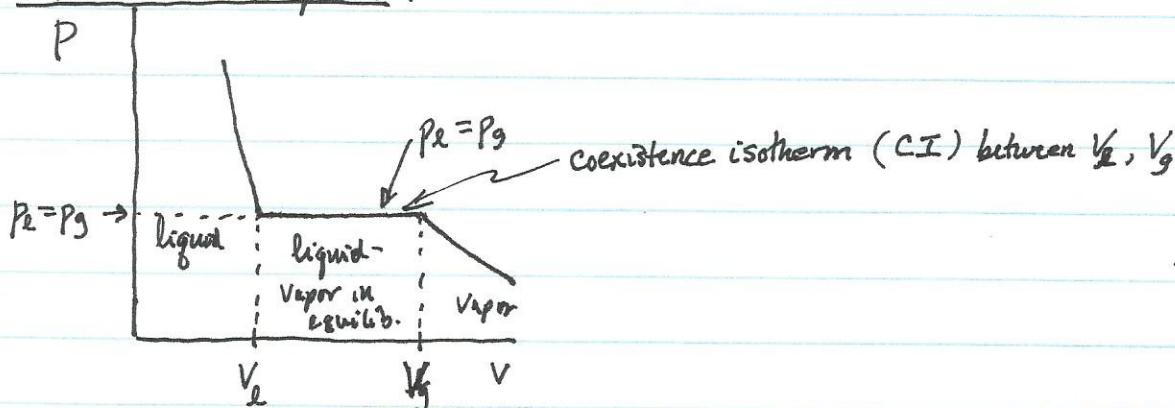
Phase Transformations

In phase transformations $N = \text{constant}$ $= N_g + N_l$

Coexistence of 2 phases in equilibrium (liquid (l), vapor (g))

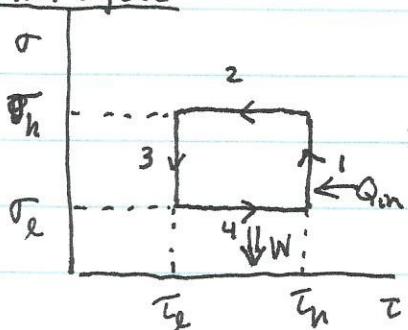
$$\tau_2 = \tau_g \quad p_2 = \mu_g \quad p_2 = p_g$$

Isotherm on P - V plane:



Vapor pressure equation

Carnot cycle

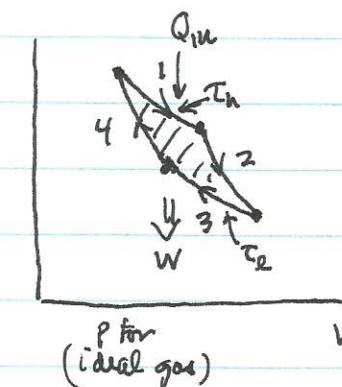


1: $T = T_h$ exp.

2: $T = T_h$ exp

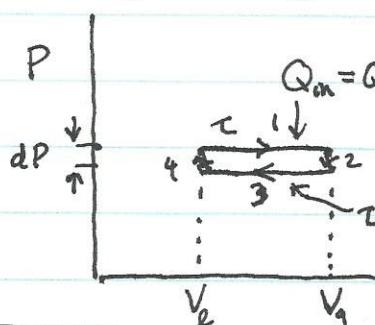
3: $T = T_L$ comp.

4: $T = T_L$ comp.



$$\frac{W}{Q_{in}} = \frac{T_h - T_L}{T_h} = \eta_C$$

$P \propto \text{const. of } V$ (not ideal gas!)



$$Q_{in} = Q_{evap} \quad W = dP(V_g - V_e)$$

$$\frac{W}{Q_{in}} = \frac{d\tau}{\tau} = \frac{dP(V_g - V_e)}{Q_{evap}}$$

$$\frac{dP}{d\tau} = \frac{Q_{evap}}{\tau(V_g - V_e)} = \frac{NL}{\tau(V_g - V_e)}$$

$$\boxed{\frac{dP}{d\tau} = \frac{L}{\tau(V_g - V_e)}}$$

2. Maxwell Relations

$$F = f(x, y)$$

$$df = adx + bdy = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

$$\left(\frac{\partial a}{\partial y}\right)_x = \left(\frac{\partial b}{\partial x}\right)_y \quad [\text{from } \left(\frac{\partial^2 f}{\partial y \partial x}\right)_x = \left(\frac{\partial^2 f}{\partial x \partial y}\right)_y]$$

Consider

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{dP}{dT} \quad \text{along coexistence curve, } P \underset{\text{isotherm}}{\text{independent}} \text{ of } V$$

P viewed as fn. of T, V

natural fn. of T, V is $F(T, V)$

$$dF = -\sigma dT - PdV$$

$$\therefore \left(\frac{\partial \sigma}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{dP}{dT}$$

Since P indep of V along coexistence curve, $\left(\frac{\partial \sigma}{\partial V}\right)_T$ is independent of V along this curve (line) $\therefore \sigma \propto V$ along coexistence isotherm (CI)

so σ has constant slope as fn. of V along CI $\therefore \left(\frac{\partial \sigma}{\partial V}\right)_T = \frac{Q_{\text{exp}}/T}{V_g - V_e}$

$$\text{and } \frac{dP}{dT} = \frac{Q_{\text{exp}}}{T(V_g - V_e)} = \frac{L}{T(V_g - V_e)}$$

Enthalpy

Along CI, P is constant $\Rightarrow (dH)_p = \tilde{W}' + \tilde{Q}_p$

\tilde{W}' is volume-independent work since $\mu_e = \mu_g$ along CI and $\tilde{W}' = \mu_e dN_e + \mu_g dN_g$

$$dN = 0 = dN_e + dN_g \Rightarrow \tilde{W}' = 0 \text{ along CI } (\mu_e = \mu_g)$$

$$\therefore (dH)_p = \tilde{Q}_p \text{ along CI}$$

$$\int_{\text{CI}} (dH)_p = \int_{\text{CI}} \tilde{Q}_p = H_g - H_e = Q_{\text{exp}} = NL \quad C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

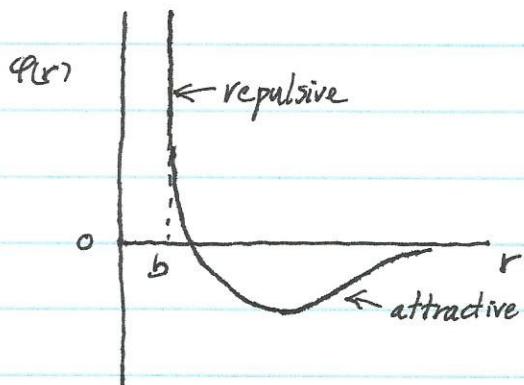
Van der Waals equation of state

ideal gas

$$F = -N\tau \left[\ln\left(\frac{V}{N}\right) + 1 \right]$$

Excluded volume: $V \rightarrow V - Nb$ b = volume per molecule

This comes from interaction between molecules:



$\varphi(r)$ = potential energy of interaction
between a molecule at $r=0$ and
one at r .

The attractive part of the interaction is treated as a mean field
experienced by one molecule.

$$\Delta V_{int} = \frac{1}{2} \sum_{i,j} \varphi(\vec{r}_i - \vec{r}_j) = \frac{1}{2} \sum_i \int d^3r' \varphi(\vec{r}_i - \vec{r}') \underbrace{\sum_j \delta(\vec{r}' - \vec{r}_j)}_{\rho(\vec{r}')} \quad (1)$$

$$\text{Replace } \rho(\vec{r}') \text{ by } \frac{N}{V}: \quad \approx \frac{1}{2} \sum_i \int d^3r' \varphi(\vec{r}_i - \vec{r}') \frac{N}{V} = \frac{1}{2} \frac{N}{V} \sum_i \underbrace{\int d^3r'' \varphi(\vec{r}'')}_{-2a} \quad (2)$$

$$\Delta V_{int} \approx -\frac{N^2 a}{V} \quad (a > 0) \quad (b > 0)$$

So

$$F = -N\tau \left[\ln\left(\frac{N(V-Nb)}{V}\right) + 1 \right] - \frac{N^2 a}{V} \quad (3)$$

$$\therefore P = -\frac{\partial F}{\partial V}_{TN} = \frac{N\tau}{V-Nb} - \frac{N^2 a}{V^2}$$

Define $v \equiv \frac{V}{N}$, then

$$P = \frac{\tau}{v-b} - \frac{a}{v^2}$$

2 phase stability

$$U = \tau\sigma - PV + \mu N$$

$$F = U - \tau\sigma = -PV + \mu N \quad (V = V_e + V_g, N = N_e + N_g)$$

Take 2 phases (e, g) to be in equilibrium where F is a minimum.

Change V_e, V_g , holding N constant, and holding $V = V_g + V_e$ constant.

$$F = F_e + F_g$$

$$\Delta F > 0 \quad \Delta F = \delta F + \delta^2 F + \delta^3 F + \dots$$

$$\delta F = \left(\frac{\partial F}{\partial V_e}\right)_{\tau, N} \delta V_e + \left(\frac{\partial F}{\partial V_g}\right)_{\tau, N} \delta V_g = -P_e \delta V_e - P_g \delta V_g = 0 \quad (P_e = P_g = P) \quad (\delta V_e = -\delta V_g)$$

$$\delta^2 F = \frac{1}{2} \left(\frac{\partial^2 F}{\partial V_e^2}\right)_{\tau, N} (\delta V_e)^2 + \frac{1}{2} \left(\frac{\partial^2 F}{\partial V_g^2}\right)_{\tau, N} (\delta V_g)^2 = \frac{1}{2} \left[\left(\frac{\partial P}{\partial V_e}\right)_{\tau, N} \delta V_e^2 - \left(\frac{\partial P}{\partial V_g}\right)_{\tau, N} \delta V_g^2 \right] \geq 0$$

$$-\left(\frac{\partial P}{\partial V_e}\right)_{\tau, N} \frac{1}{N_e} - \left(\frac{\partial P}{\partial V_g}\right)_{\tau, N} \frac{1}{N_g} \geq 0 \Rightarrow -\left(\frac{\partial P}{\partial V}\right) \geq 0 \quad \text{for each phase}$$

$\therefore -\left(\frac{\partial P}{\partial V}\right)_{\tau, N} \geq 0$ is required to assure that F increases when any change from equilibrium conditions is made, i.e. so that equilibrium is stable under such changes.

For VdW gas

$$P = \frac{\tau}{v-b} - \frac{a}{v^2}$$

$$-\left(\frac{\partial P}{\partial v}\right)_{\tau, N} = \frac{\tau}{(v-b)^2} - \frac{2a}{v^3} \geq 0 \quad \text{is required for stability}$$

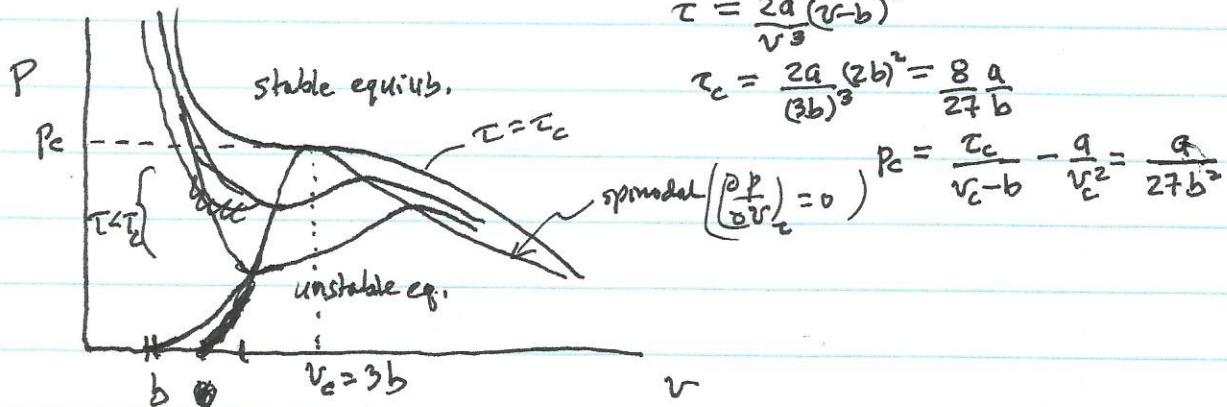
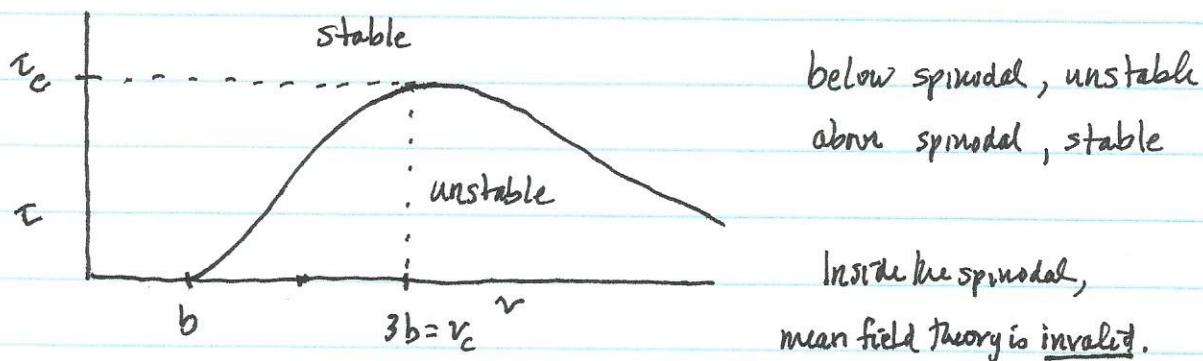
Clearly, for τ small enough, VdW eqn of state violates stability!

In $\tau-v$ plane, boundary of stability is given by

$$\tau = \frac{2a}{v^3}(v-b)^2 \quad \leftarrow \tau(v) is a low - "spinodal line" on \tau-v plane.$$

$$\frac{d\tau}{dv} = 0 = 2a \left[2\frac{(v-b)}{v^3} - \frac{3(v-b)^2}{v^4} \right] = 2a\frac{(v-b)}{v^3} \left[2 - \frac{3(v-b)}{v} \right]$$

$$\therefore \text{get maximum in } \tau-v \text{ at } v=3b \equiv v_c \text{ at } \tau=\tau_c = \frac{8}{27} \frac{a}{b}.$$



What do we do about these thermodynamically unstable regions?

Consider $G = F + pV = \mu N$ $dG = -\sigma d\tau + Vdp + \mu dN$

$$\mu = \frac{G}{N} \Rightarrow \left(\frac{\partial \mu}{\partial p}\right)_{CN} = \left(\frac{\partial(G/N)}{\partial p}\right)_{CN} = \frac{V}{N} = v$$

$$\therefore (d\mu)_{CN} = \left(\frac{\partial \mu}{\partial p}\right)_{CN} (dp)_{CN} = v(p/dp) = d(vp) - pdv$$

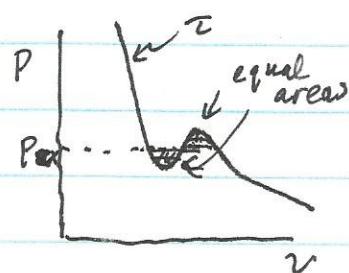
$$\int_v^g d\mu = \int_v^g vp dp = vp \Big|_v^g - \int_v^g pdv = p_g v_g - p_e v_e - \int_v^g pdv$$

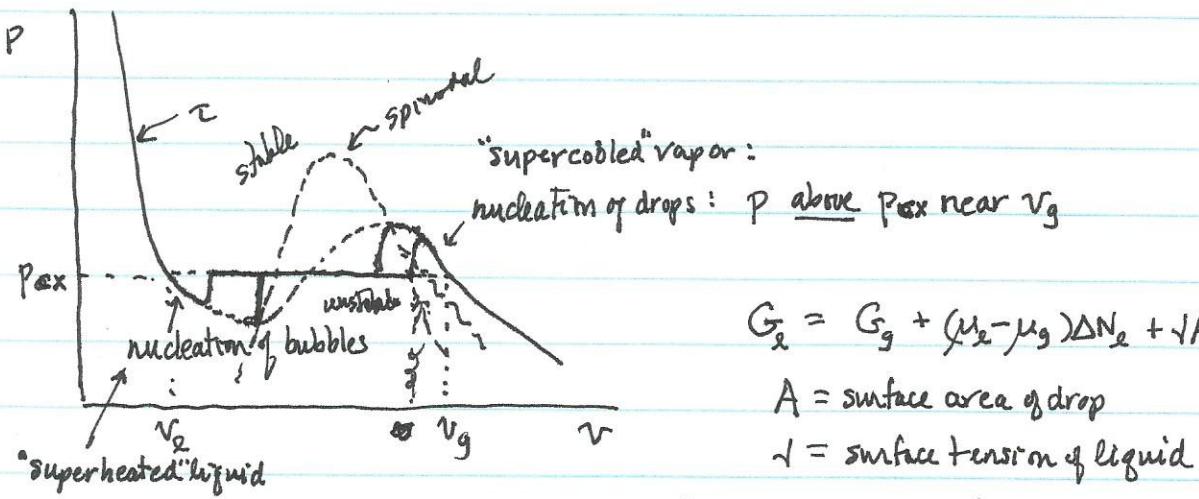
\uparrow isotherm

$$p_e = p_g = p_{ex} \Rightarrow p_{ex} = p_{ex}(\tau) \quad (\tau \leq \tau_c) \\ p_e = p_{ex}(\tau_c) \quad (\tau > \tau_c) = - \int_v^g (p - p_{ex}) dv$$

$$\therefore \mu_g - \mu_e = 0 = - \int_{v_e}^{v_g} (p - p_{ex}) dv$$

("maxwell construction" of C-I)





$$G_e = G_g + (\mu_e - \mu_g) \Delta N_e + \gamma A$$

A = surface area of drop

γ = surface tension of liquid

$$G_e = G_g - (\Delta \mu) \frac{4}{3} \pi R^3 n_e + 4\pi \gamma R^2$$

$$\Delta \mu = \mu_g - \mu_e \approx \tau \ln\left(\frac{P}{P_0}\right)$$

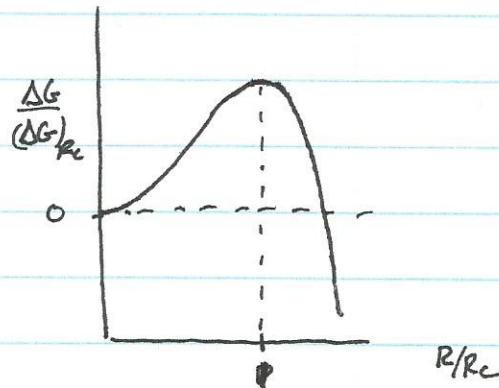
$G_e - G_g$ has max. at $R = R_c$:

$$\left(\frac{d(G_e - G_g)}{dR} \right)_{R_c} = 0 \Rightarrow R_c = \frac{2\gamma}{n_e \Delta \mu}$$

$$(G_e - G_g)_{R_c} = \frac{4\pi \gamma R_c^2}{3} \quad \text{free energy "barrier"}$$

$$\frac{G_e - G_g}{(G_e - G_g)_{R_c}} = -2\left(\frac{R}{R_c}\right)^3 + 3\left(\frac{R}{R_c}\right)^2$$

Thermal fluctuations in energy must be large enough to overcome this barrier



$$\text{pg 83, eqn (89)} \quad \langle (\varepsilon - \langle \varepsilon \rangle)^2 \rangle = \tau^2 C_v \quad (\sim N \tau^3)$$

$$\therefore \text{need } \tau \sim (G_e - G_g)_{R_c} / C_v^{1/2} = \frac{1}{C_v^{1/2}} \frac{4\pi \gamma R_c^2}{3} = \frac{1}{C_v^{1/2}} \frac{4\pi}{3} \left(\frac{2\gamma}{n_e \Delta \mu} \right)^2 \frac{1}{\ln(P/P_0)}$$

$$\frac{A}{V} = \frac{1}{L}$$

$$\ln(P/P_0) = \left[\frac{4\pi}{3} \left(\frac{2\gamma}{n_e \Delta \mu} \right)^2 \frac{1}{L} \right]^{1/2} = \frac{2\gamma}{n_e} \left(\frac{4\pi}{3} \frac{1}{L^2 \Delta \mu} \right)^{1/2} N^{-1/4}$$

$$P = P_{ex} + \Delta P$$

$$\Delta P \approx \frac{2\gamma}{n_e N^{1/4}} \left(\frac{4\pi}{3} \frac{1}{L^2 \Delta \mu} \right)^{1/2}$$

$$C_v \sim N \tau$$

Ferromagnetism - Mean Field Theory

Mean field assumption

Magnetic dipoles interact

Each "sees" an effective field $B_E = \lambda M$

$$M = n\mu \tanh(\mu B/c) \rightarrow M = n\mu \tanh(\mu \lambda M V/c)$$

$$m \equiv \frac{M}{n\mu} \quad \text{dimensionless magnetization}$$

$$m = \tanh(n\mu^2 \lambda m/c) = \tanh(m/t)$$

t = reduced temperature

$$\text{critical temp : } m \downarrow 0 \Rightarrow m = \frac{m}{t} \xrightarrow{t \downarrow t_0} 1 = \frac{1}{t_0} \Rightarrow t_0 = 1 =$$
$$\therefore M \approx \frac{n\mu^2}{t_0} M \quad t_0 = n\mu^2 \lambda$$

Landau Theory of Phase Transitions

Mean field theory of phase transitions

At constant V, c , F is a minimum

min wrt what variables?

Assume system can be described by a single order parameter (e.g., M)

In equilibrium, order parameter $\xi = \xi_c(c)$

Take

$$F \Rightarrow F_L(\xi, c) = U(\xi, c) - c \sigma(\xi, c)$$

In equilibrium

$$F_L(\xi_c, c) = F(c) \leq F(\xi, c) \quad \xi \neq \xi_c$$

Expand (assume $\xi, -\xi$ equally likely, assume F analytic in ξ near $\xi=0$)

$$F_L(\xi, c) = g_0(c) + \frac{1}{2} g_2(c) \xi^2 + \frac{1}{4} g_4(c) \xi^4 + \frac{1}{6} g_6(c) \xi^6 + \dots$$

Example: $g_2(c) = (c - c_0)\alpha$ c near c_0

$$g_4 > 0 \quad g_6, g_8, \dots \approx 0$$

$$F_L(\xi, c) = g_0(c) + \frac{1}{2} \alpha (c - c_0) \xi^2 + \frac{1}{4} g_4 \xi^4$$

Find ξ_0 , equilibrium value of ξ :

$$\left(\frac{\partial F_L}{\partial \xi}\right)_{\xi_0} = 0 = \alpha(\tau - \tau_0)\xi_0 + g_4 \xi_0^3 \quad \text{and: } \left(\frac{\partial^2 F_L}{\partial \xi^2}\right)_{\xi_0} = \alpha(\tau - \tau_0) + 3g_4 \xi_0^2 > 0$$

$$\xi_0 = 0 \quad \tau > \tau_0$$

$$\xi_0^2 = \frac{\alpha}{g_4} (\tau_0 - \tau) \quad \tau \leq \tau_0$$

For $\tau < \tau_0$, the thermodynamic free energy is:

$$F_L(\xi_0, \tau) = F(\tau) = g_0(\tau) + \frac{1}{2} \alpha(\tau - \tau_0) \frac{(\xi_0 - \tau)^2}{g_4} + \frac{1}{4} g_4 \left(\frac{\alpha(\tau_0 - \tau)}{g_4} \right)^2$$

$$= g_0(\tau) - \frac{1}{4} \frac{\alpha^2}{g_4} (\tau_0 - \tau)^2 < g_0(\tau)$$

Landau theory of ferromagnetism = mean field theory of ferromagnetism

Take $\xi = M$

For convenience (since $V = \text{constant}$) take $g_0(\tau) \rightarrow V g_0(\tau)$

$g_2(\tau) \rightarrow V g_2(\tau)$

etc...

$$F_L(M, \tau) = V \left(\underset{\substack{\uparrow \\ \text{energy/vol.}}}{u(M, \tau)} - \tau s(M, \tau) \right) = V \left[-\frac{1}{2} \lambda M^2 + \frac{1}{4} g_4 M^4 - \tau s_0 + \frac{M^2}{2n\mu^2} \tau \right]$$

$$= V \left[\frac{1}{2} \left(\frac{\tau}{n\mu^2} - \lambda \right) M^2 + \frac{1}{4} g_4 M^4 - \tau s_0 \right]$$

$$\tau_0 = n\mu^2 \lambda :$$

$$= V \left[\frac{1}{2} \left(\frac{\tau_0 - \tau_0}{n\mu^2} \right) M^2 + \frac{1}{4} g_4 M^4 - \tau s_0 \right]$$

[For $\tau < \tau_0$, need the M^4 term, since otherwise $M \rightarrow \infty$ would give minimum.]

Note: $\alpha = \frac{1}{n\mu^2}$ here. Also, the transition temperature is the same as in mean field theory: $\tau_0 = n\mu^2 \lambda$.

$$\text{We get } \xi_0^2 = \frac{\alpha}{g_4} (\tau_0 - \tau) \rightarrow M^2 = \frac{1}{n\mu^2 g_4} (\tau_0 - \tau) \quad \tau < \tau_0$$

This also agrees with mean field theory. To see this, take

the mean field theory equation

$$M = n\mu \tanh\left(\frac{\mu\lambda M}{T}\right)$$

and evaluate to lowest order in $(T - T_0)/T_0$:

$$\frac{\mu\lambda M}{T} \approx \mu\lambda M \left[\frac{1}{T_0 + (T - T_0)} \right] \approx \frac{\mu\lambda M}{T_0} \left[1 - \frac{(T - T_0)}{T_0} \right]$$

$$M \approx n\mu \tanh\left(\frac{\mu\lambda M}{T_0} \left[1 - \frac{(T - T_0)}{T_0} \right]\right)$$

$$\approx \frac{n\mu^2}{T_0} M \left[1 - \frac{(T - T_0)}{T_0} \right] - \frac{n\mu}{3} \left(\frac{\mu\lambda M}{T_0} \left[1 - \frac{(T - T_0)}{T_0} \right] \right)^3 + \dots$$

$$\approx M - \frac{(T - T_0)}{T_0} M - \frac{1}{3} n\mu \left(\frac{\mu\lambda M}{T_0} \right)^3 \left[1 - 3 \frac{(T - T_0)}{T_0} \right]$$

or

$$0 = -\frac{(T - T_0)}{T_0} - \frac{1}{3} n\mu \left(\frac{\mu\lambda}{T_0} \right)^3 M^2 \left[1 - 3 \frac{(T - T_0)}{T_0} \right]$$

$$\Rightarrow M^2 \approx \frac{3}{n\mu} \frac{T_0^3}{(\mu\lambda)^3} \frac{(T_0 - T)}{T_0} = \frac{3 T_0}{(\mu\lambda)^2} (T_0 - T)$$

with $n\mu^2 g_4 = (\mu\lambda)^2 / 3 T_0$ i.e. $g_4 = \frac{\lambda^2}{3nT_0}$, this agrees with the Landau theory.

Using $F(T) = Vg_0(T) - \frac{1}{4} \frac{\alpha^2}{g_4^2} (T_0 - T)^2$ with $\alpha = \frac{1}{n\mu^2}$, $g_0(T) = -TS_0$ we get the ~~thermodynamic~~ free energy

$$F(T) = V(-TS_0 - \frac{1}{4} \frac{1}{g_4 n\mu^2} (T_0 - T)^2)$$

$$\sigma = -\frac{\partial F}{\partial T} = V(S_0 + \frac{1}{2g_4 n\mu^2} (T - T_0)) < V S_0 \quad (T < T_0)$$

the ordered state has lower entropy, as expected.

$$\sigma = VS_0 \quad T > T_0$$

1. σ is continuous at $T = T_0$

$$2. C_V = T \left(\frac{\partial \sigma}{\partial T} \right)_V = \begin{cases} T V \left(\frac{1}{2g_4 n\mu^2} \right) & T < T_0 \\ 0 & T > T_0 \end{cases}$$

so $C_V = T \left(\frac{\partial^2 F}{\partial T^2} \right)$ has a discontinuity at $T_0 \rightarrow$ 2nd order $\left(\frac{\partial^2 F}{\partial T^2} \right)$ phase transition.

First order phase transition ($\sigma = -\frac{\partial F}{\partial \tau}$ discontinuous at τ_c)

$$g_2 = \alpha(\tau - \tau_0)$$

$$g_4 = -|g_4| < 0$$

$$g_6 > 0$$

$$F_L(\xi, \tau) = g_0(\tau) + \frac{1}{2}\alpha(\tau - \tau_0)\xi^2 - \frac{1}{4}|g_4|\xi^4 + \frac{1}{6}g_6\xi^6$$

minimize:

$$\left(\frac{\partial F_L}{\partial \xi}\right)_{\xi_{eq}} = 0 = \alpha(\tau - \tau_0)\xi_{eq} - |g_4|\xi_{eq}^3 + g_6\xi_{eq}^5 \quad (1)$$

$$\left(\frac{\partial^2 F_L}{\partial \xi^2}\right)_{\xi_{eq}} > 0 \text{ (for minimum)}$$

$$\Rightarrow \alpha(\tau - \tau_0) - 3|g_4|\xi_{eq}^2 + 5g_6\xi_{eq}^4 > 0 \quad (2)$$

Solve (1):

$$\xi_{eq} = 0 \text{ violates (2) for } \tau < \tau_0, \text{ so only holds for } \tau > \tau_0.$$

$$\xi_{eq}^2 = \frac{|g_4| \pm \sqrt{|g_4|^2 - 4g_6\alpha(\tau - \tau_0)}}{2g_6} \quad \tau < \tau_0$$

Which sign? From (1), $\alpha(\tau - \tau_0) = |g_4|\xi_{eq}^2 - g_6\xi_{eq}^4$

so (2) becomes

$$(4g_6\xi_{eq}^2 - 2|g_4|)\xi_{eq}^2 > 0$$

or

$$(\pm \sqrt{|g_4|^2 - 4g_6\alpha(\tau - \tau_0)})^2 \xi_{eq}^2 > 0$$

This shows that the $-$ sign is for a maximum, hence the minimum of F_L is for

$$\xi_{eq}^2 = \frac{|g_4| + \sqrt{|g_4|^2 - 4g_6\alpha(\tau - \tau_0)}}{2g_6} \quad \tau < \tau_0 \quad (3)$$

Find τ_c :

$$F_L(0, \tau_c) = F_L(\xi_{eq}, \tau_c) \quad (\xi_c \text{ is value of } \xi_{eq} \text{ at } \tau_c)$$

$$\begin{aligned} g_0(\tau) &= g_0(\tau_0) + \frac{1}{2}\alpha(\tau_c - \tau_0)\xi_c^2 \Rightarrow \frac{1}{2}|g_4|\xi_c^4 + \frac{1}{6}g_6\xi_c^6 \\ \text{or} \end{aligned}$$

$$\alpha(\tau_c - \tau_0) - \frac{1}{2}|g_4|\xi_c^2 + \frac{1}{3}g_6\xi_c^4 = 0 \quad (4)$$

From (1) with $\xi_{eq} = \xi_c$:

$$\alpha(\tau_c - \tau_0) = |g_4|\xi_c^2 - g_6\xi_c^4$$

so (4) becomes

$$\frac{1}{2}|g_4|\xi_c^2 - \frac{2}{3}g_6\xi_c^4 = 0 \quad \text{or} \quad \xi_c^2 = \frac{3}{4} \frac{|g_4|}{g_6}$$

Using (3) with $\xi_{eq} = \xi_c$, $\tau = \tau_c$:

$$\xi_c^2 = \frac{|g_4| + \sqrt{|g_4|^2 - 4g_6\alpha(\tau_c - \tau_0)}}{2g_6} = \frac{3}{4} \frac{|g_4|}{g_6}$$

Solve for $\tau_c - \tau_0$:

$$\frac{3}{2} |g_4| = |g_4| + \sqrt{\quad}$$

$$\frac{1}{2} |g_4| = \tau \Rightarrow \frac{1}{4} |g_4|^2 = |g_4|^2 - 4g_6\alpha(\tau_c - \tau_0)$$

$$\boxed{\tau_c - \tau_0 = \frac{3}{16} \frac{|g_4|^2}{g_6 \alpha}}$$

Find discontinuity in $\sigma = -\frac{\partial F}{\partial \tau}$:

$$F(\tau) = g_0(\tau) + \frac{1}{2} \alpha(\tau - \tau_0) \xi_{eq}^2 - \frac{1}{4} |g_4| \xi_{eq}^4 + \frac{1}{6} g_6 \xi_{eq}^6$$

From ①

$$\begin{aligned} F(\tau) &= g_0(\tau) + \frac{1}{2} \xi_{eq}^2 [|g_4| \xi_{eq}^2 - g_6 \xi_{eq}^4] - \frac{1}{4} |g_4| \xi_{eq}^4 + \frac{1}{6} g_6 \xi_{eq}^6 \\ &= g_0(\tau) + \frac{1}{4} |g_4| \xi_{eq}^4 - \frac{1}{3} g_6 \xi_{eq}^6 \\ &= g_0(\tau) + \left[\frac{1}{4} |g_4| - \frac{1}{3} g_6 \xi_{eq}^2 \right] \xi_{eq}^4 \end{aligned}$$

$$\sigma = -\frac{\partial F}{\partial \tau} = -\frac{\partial g_0}{\partial \tau} + \left[-\frac{1}{2} |g_4| \xi_{eq}^2 + g_6 \xi_{eq}^4 \right] \frac{d \xi_{eq}^2}{d \tau} \quad (\text{neglecting } \frac{\partial |g_4|}{\partial \tau} \text{ and } \frac{\partial g_6}{\partial \tau})$$

$$= -\frac{\partial g_0}{\partial \tau} + \left[2g_6 \xi_{eq}^2 - |g_4| \right] \frac{1}{2} \xi_{eq}^2 \frac{d \xi_{eq}^2}{d \tau}$$

$$= -\frac{\partial g_0}{\partial \tau} + \sqrt{\frac{1}{2} \xi_{eq}^2 \frac{d \xi_{eq}^2}{d \tau}}$$

At τ_c^+ :

$$\xi_{eq}^2 = \xi_c^2 = \frac{3}{4} \frac{|g_4|}{g_6} \quad \frac{d \xi_{eq}^2}{d \tau} = \frac{1}{2g_6} \frac{(-2g_6 \alpha)}{\sqrt{\quad}}$$

$$\therefore (\sigma)_{\tau=\tau_c^-} = -\frac{\partial g_0}{\partial \tau} + \sqrt{\frac{1}{2} \xi_c^2 \frac{(-2g_6 \alpha)}{\sqrt{\quad}}} = -\frac{\partial g_0}{\partial \tau} - \frac{\alpha}{2} \xi_c^2$$

$$(\sigma)_{\tau=\tau_c^+} = -\frac{\partial g_0}{\partial \tau}$$

$$\sigma_{\tau_c^-} - \sigma_{\tau_c^+} = -\frac{\alpha}{2} \frac{3|g_4|}{4g_6}$$

$\therefore \frac{\partial F}{\partial \tau}$ discontinuous \Rightarrow 1st order PT

(e.g. entropy of liquid lower than entropy of gas)

$\tau > \tau_c$ gas, $\tau < \tau_c$ liquid

Bose-Einstein Condensation - The phase transition

$$U = \frac{3}{2} N_e(\tau) \tau \frac{g_{3/2}(\lambda)}{\zeta(3/2)} \quad \lambda \equiv e^{\mu/\tau}$$

$$P = \frac{N_e(\tau)}{V} \frac{g_{3/2}(\lambda)}{\zeta(3/2)} \quad N_e(\tau) \equiv N \left(\frac{\tau}{\tau_E} \right)^{3/2}$$

$$\Gamma = \frac{5}{2} N_e(\tau) \frac{g_{3/2}(\lambda)}{\zeta(3/2)} - N \ln \lambda$$

λ equation (μ):

$$g_{3/2}(\lambda) = \begin{cases} \frac{n}{n_a} = \left(\frac{\tau_E}{\tau} \right)^{3/2} \zeta(3/2) & \tau > \tau_E, \lambda < 1 \\ \zeta(3/2) & \tau \leq \tau_E, \lambda = 1 \end{cases}$$

$$g_{3/2}(\lambda) = \sum_{m=1}^{\infty} \frac{\lambda^m}{m^{3/2}} = \frac{1}{\Gamma(3/2)} \int_0^{\infty} dx \ x^{1/2} \frac{1}{\lambda^{-1} e^x - 1}, \ g_{3/2}(1) = \zeta(3/2)$$

Want to find μ for τ just above τ_E , with $\lambda^{-1} \ll 1$.

$$g_{3/2}(\lambda) - g_{3/2}(1) = \frac{n}{n_a} - \zeta(3/2) = \frac{1}{\Gamma(3/2)} \int_0^{\infty} dx \ x^{1/2} \left[\frac{1}{\lambda^{-1} e^x - 1} - \frac{1}{e^x - 1} \right]$$

For $\lambda^{-1} \rightarrow 0$, small values of x contribute most to the integral:

$$\lambda^{-1} e^x - 1 = \lambda^{-1} + \lambda^{-1} x \approx 1 + x = x - \mu/\tau = x + |\mu|/\tau$$

$$e^x - 1 \approx x$$

So

$$\frac{n}{n_a} - \zeta(3/2) \approx \frac{1}{\Gamma(3/2)} \int_0^{\infty} dx \ x^{1/2} \frac{(-\mu/\tau)}{x(x + |\mu|/\tau)}$$

$$\text{set } x = \frac{|\mu|}{\tau} y^2 \quad dx = \frac{|\mu|}{\tau} 2y dy$$

$$= \frac{1}{\Gamma(3/2)} \int_0^{\infty} \frac{|\mu|}{\tau} 2y dy \frac{1}{(\sqrt{\frac{|\mu|}{\tau}} y) \frac{|\mu|}{\tau} (y^2 + 1)} (-\mu/\tau)$$

$$x^{1/2} = \sqrt{\frac{|\mu|}{\tau}} y \quad x + \frac{|\mu|}{\tau} = \frac{|\mu|}{\tau} (y^2 + 1)$$

$$= -2 \sqrt{\frac{|\mu|}{\tau}} \int_0^{\infty} dy \frac{1}{y^2 + 1} = -\frac{\pi \sqrt{\frac{|\mu|}{\tau}}}{\Gamma(3/2)}$$

$$\sqrt{\frac{U}{\tau}} = -\frac{\Gamma(3/2)}{\pi} \left[\frac{n}{n_a} - S(3/2) \right] = -\frac{\Gamma(3/2) S(3/2)}{\pi} \left[\left(\frac{\tau_E}{\tau}\right)^{3/2} - 1 \right]$$

$$\therefore \mu = - \left[\frac{S(3/2)}{2\sqrt{\pi}} \right]^2 \tau \left[\left(\frac{\tau_E}{\tau}\right)^{3/2} - 1 \right]^2$$

$$\frac{\tau - \tau_E}{\tau_E} \ll 1 : \left[\left(\frac{\tau_E}{\tau}\right)^{3/2} - 1 \right]^2 = \left[\left(\frac{\tau_E}{\tau_E + (\tau - \tau_E)}\right)^{3/2} - 1 \right]^2 \approx \left[\left(1 - \left(\frac{\tau - \tau_E}{\tau_E}\right)\right)^{3/2} - 1 \right]^2$$

$$\approx \left[1 - \frac{3}{2} \left(\frac{\tau - \tau_E}{\tau_E} \right) - 1 \right]^2 = \frac{9}{4} \left(\frac{\tau - \tau_E}{\tau_E} \right)^2$$

$$\therefore \mu \approx - \frac{9}{16\pi} \left[S(3/2) \right]^2 \frac{(\tau - \tau_E)^2}{\tau_E^2} \quad \left(\frac{\tau - \tau_E}{\tau_E} \ll 1 \right) \quad (\tau > \tau_E)$$

Note: $\mu, \frac{\partial \mu}{\partial \tau} \rightarrow 0$ as $\tau \rightarrow \tau_E$ but $\left(\frac{\partial^2 \mu}{\partial \tau^2} \right)_{\tau_E} = -\frac{9}{8\pi} [S(3/2)]^2 \frac{1}{\tau_E}$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{15}{4} N_e(\tau) \frac{g_{5/2}(\lambda)}{S(3/2)} + \frac{3}{2} N_e(\tau) \tau \frac{1}{S(3/2)} \frac{\partial g_{5/2}(\lambda)}{\partial \lambda} \frac{\partial \lambda}{\partial \tau}$$

$$\lambda \frac{\partial g_{5/2}(\lambda)}{\partial \lambda} = \lambda \frac{\partial}{\partial \lambda} \left(\sum_{m=1}^{\infty} \frac{\lambda^m}{m^{5/2}} \right) = \lambda \sum_{m=1}^{\infty} \frac{\lambda^{m-1}}{m^{3/2}} = g_{3/2}(\lambda) = \left(\frac{\tau_E}{\tau} \right)^{3/2} S(3/2)$$

$$\therefore C_V = \begin{cases} \frac{15}{4} N_e(\tau) \frac{g_{5/2}(\lambda)}{S(3/2)} + \frac{3}{2} N_e(\tau) \frac{\partial (U/\tau)}{\partial \tau} & \tau > \tau_E \\ \frac{15}{4} N_e(\tau) \frac{S(3/2)}{S(3/2)} & \tau < \tau_E \end{cases}$$

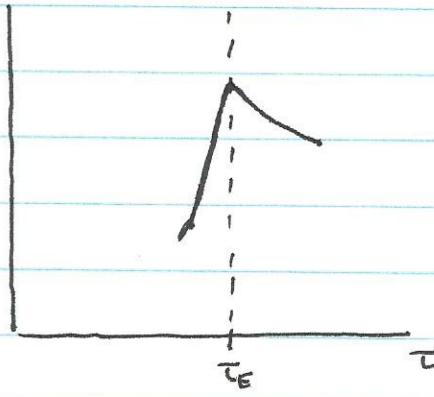
$$\left(\frac{\partial C_V}{\partial \tau} \right)_{\tau_E} = \begin{cases} \frac{45}{8} \frac{N}{\tau_E} \frac{S(5/2)}{S(3/2)} + \frac{3}{2} N \tau_E \left(\frac{\partial^2 (U/\tau)}{\partial \tau^2} \right)_{\tau_E} & \tau > \tau_E \\ \frac{45}{8} \frac{N}{\tau_E} \frac{S(5/2)}{S(3/2)} & \tau < \tau_E \end{cases}$$

$$\Delta \left(\frac{\partial C_V}{\partial \tau} \right)_{\tau_E} = \frac{3}{2} N \left(\frac{\partial^2 \mu}{\partial \tau^2} \right)_{\tau_E} = -\frac{27}{16\pi} \left(S(3/2) \right)^2 \frac{N}{\tau_E}$$

$$\text{Slope of } C_V \text{ vs. } \tau \text{ above } \tau_E : \left(\frac{45}{8} \frac{S(5/2)}{S(3/2)} - \frac{27}{16\pi} [S(3/2)]^2 \right) \frac{N}{\tau_E} = -0.85 \frac{N}{\tau_E}$$

$$\text{Slope of } C_V \text{ vs. } \tau \text{ below } \tau_E : \frac{45}{8} \frac{S(5/2)}{S(3/2)} \frac{N}{\tau_E} = 2.8125 \frac{N}{\tau_E}$$

C_V



" λ transition"

(λ = Lambda)

BE condensation: 3rd order phase

transition since discontinuity

is in $\left(\frac{\partial^3 F}{\partial T^3}\right)_{T_E}$ at T_E :

$$\begin{aligned} \left(\frac{\partial C_V}{\partial T}\right)_{T_E} &= \frac{\partial(T_E)}{\partial T} \frac{\partial \sigma}{\partial T} \\ &\approx -T_E \left(\frac{\partial^3 F}{\partial T^3}\right)_{T_E} \end{aligned}$$

In He^4 due to interactions, transition is sharper.

C_V

