Phys 114

Seminar 12 Solutions

Problem 1) G+T prob 7.15

If a liquid boils at { 105°C at bottom of hill / 95°C at top of hill

and enthalpy of vaporizn is 1000 J/mol, what is height of hill?

Soln: Let height be h

We can use "vapour pressure eqn" from warmup prob 1, (Schroeder 5.35) that derives from Clausius-Clapeyron:

$$P(T) = e^{-L/RT}$$

$$\therefore \frac{P(368K)}{P(378K)} = e^{-\frac{L}{R}\left(\frac{1}{368} - \frac{1}{378}\right)}$$

$$= e^{\frac{-1000\ J/mol}{8.31\ J/mol\cdot K}\left(0.000719\right)}$$

$$\therefore \frac{P(368K)}{P(378K)} = 0.9914$$

1.2 kPa per 100 m

Now assuming the hill is not too high, we can use

$$\frac{P(368K) - P(378K)}{P(378K)} = \frac{-\rho g h}{1.01\times10^5\ Pa}$$

Where $\rho = 1.225\ kg/m^3$, $g = 9.81\ m/s^2$

$$\therefore 0.9914 - 1 = \frac{-\left(1.225\ \frac{kg}{m^3}\right)\left(9.81\ m/s^2\right)}{1.01\times10^5\ Pa}$$

$$\rightarrow \frac{0.0086\times10^5\ Pa}{\left(1.225\ \frac{kg}{m^3}\right)\left(9.81\ m/s^2\right)} = h = 72\ m$$

Problem 2

Schroeder 5.24

Want to verify diamond becomes more stable than graphite at about $P \approx 15$ kbar at room temp.

Soln: We need to show $G_g \approx G_d$ at this pressure $P = P^*$. We have Fig. 5.15 as a reference. Let's arbitrarily set

$G_g(P = 1\text{ bar}) = 0$

$G_d(P = 1\text{ bar}) = 2900\text{ J}$

Then reading the graph,

$G_g = C_1 P$; $G_d = 2900\text{J} + C_2 P$

C_1 + C_2 are constants ....

in fact since $\left(\frac{\partial G}{\partial P}\right)_{T,N} = V$, they are volumes ... $C_1 = V_g$; $C_2 = V_d$

Anyway, want intersection: $V_g P^* = V_d P^* + 2900\text{J}$

$\Rightarrow P^* = \frac{2900\text{ J}}{V_g - V_d} = \frac{2900\text{J}}{1.89 \times 10^{-6}\text{m}^3} = 1.53 \times 10^9\text{ Bar}$

$= 15.3 \times 10^8\text{ Bar}$

$= 15.3\text{ k Bar}$

V_g given as $5.31 \times 10^{-6}\text{ m}^3$

$V_g - V_d = 3.42 \times 10^{-6}\text{ m}^3$

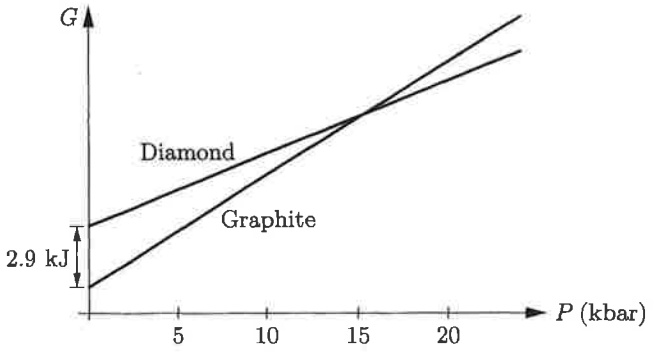
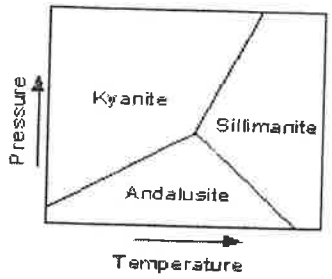


Figure 5.15. Molar Gibbs free energies of diamond and graphite as functions of pressure, at room temperature. These straight-line graphs are extrapolated from low pressures, neglecting the changes in volume as pressure increases.

Problem 3 — Schroeder Problem 5.29 parts (a), (b) + (c)



(a) To argue, at 298 K stable phase is Kyanite, regardless of pressure.

Well... on little plot above we do see that at very low P, Andalusite becomes stable. But this is not accounted for in table. That is, for fixed molar volume as seen in table, we assume $\left(\frac{\partial G}{\partial P}\right)_{T,N} = V = \text{const}$...

and $V_K < V_A$ or V_S. Thus, since $\Delta_f G$ is lowest for K at T = 298 K, P = 1 bar and $\frac{\partial G}{\partial P}$ is lowest, K must be most stable phase at T = 298 K

Al_2SiO_5 data from Schroeder (T = 298 K, P = 1 bar)

	ΔH_f (kJ)	ΔG_f (kJ)	S J/K	V cm^3
K	-2594.29	-2443.88	83.81	44.09
A	-2590.27	-2442.66	93.22	51.53
S	-2587.76	-2440.99	96.11	49.90

NB. 1 bar ≈ 1 atm = 0.9869 atm

b) Now fix P and let T vary.

We must show $\Delta_f G(T_2) = \Delta_f G(T_1) - \int_{T_1}^{T_2} \Delta_f S(T)\, dT$

Since (Gibbs Duhem)

$$dG = VdP - SdT + \mu dN$$

(V = 0 here; dN = 0)

It follows $\int dG = -\int S\,dT$ QED.

By the way, we must have $\Delta_f G$, $\Delta_f S$, ... refer to SAME standard state for all of A, K and S. These are all "polymorphs" of same "molecule" Al_2SiO_5. It is hoped that Schroeder's table got this right :)

(c) Now we are asked to assume $\Delta_f S$ is T-indep. What is range of temperatures over which each of K, A and S are stable at 1 bar.

This is best done by plotting, since we have

$$\Delta_f G(T_2) = \Delta_f G(T_1) - \int_{T_1}^{T_2} \Delta_f S\,dT$$

Want this to be lowest for stability

at $T_1 = 298K$

-2443.88×10^3 J K

-2442.66×10^3 J A

-2440.99×10^3 J S

$(T_2 - T_1)$ =

83.81 J/K K

93.22 J/K A

96.11 J/K S

Mathematica tells us that (next page)

at $T = 427.65$ K A becomes the stable phase

and at $T = 875.9$ K S becomes the stable phase

```
SK = 83.81 ; SA = 93.22; SS = 96.11
```

```
96.11
```

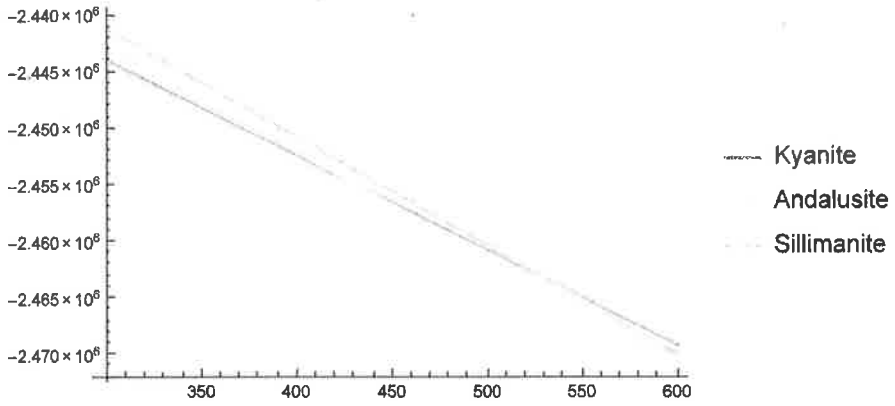
```
G1K = -2443.88 * 10^3; G1A = -2442.66 * 10^3; G1S = -2440.99 * 10^3
```

$$-2.44099 \times 10^{6}$$

```
T1 = 298
```

```
298
```

```
Plot[{G1K - (T - T1) * SK, G1A - (T - T1) * SA, G1S - (T - T1) * SS},
 {T, 298, 600}, PlotLegends → {"Kyanite", "Andalusite", "Sillimanite"}]
```




```
Solve[G1K - (T - T1) * SK == G1A - (T - T1) * SA, T]
```

```
{{T → 427.649}}
```

```
Solve[G1A - (T - T1) * SA == G1S - (T - T1) * SS, T]
```

```
{{T → 875.855}}
```

Problem 4 → Schroeder 5.34

This is about liquid-solid phase boundaries of ^4He and ^3He. See picture of phase diagram below.

for ^3He → (a) Since $\left(\frac{\partial G}{\partial P}\right)_T = V$, G must rise more quickly for a phase with a higher molar volume V ... hence less dense. Thus, the more dense phase will, at arbitrarily high pressures, always be the most stable one.

Since Clausius Clapeyron says $\frac{dP}{dt} = \frac{\Delta S}{\Delta V}$, the negative slope of P(T) at very low T tell us that signs are opposite for ΔS and ΔV. The phase with smaller V has larger S. Since this is solid phase (more dense) then below about 0.3K $S_{solid} > S_{liquid}$. Kooky! (This is due to multiplicity of spin alignments in solid, so I hear :))

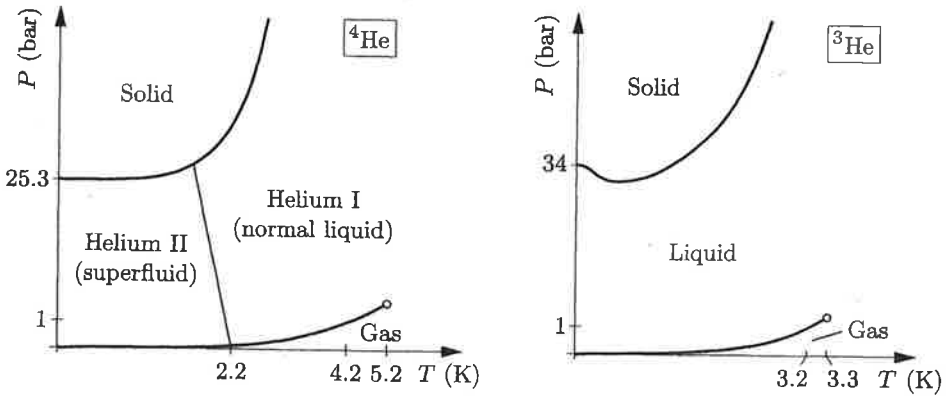
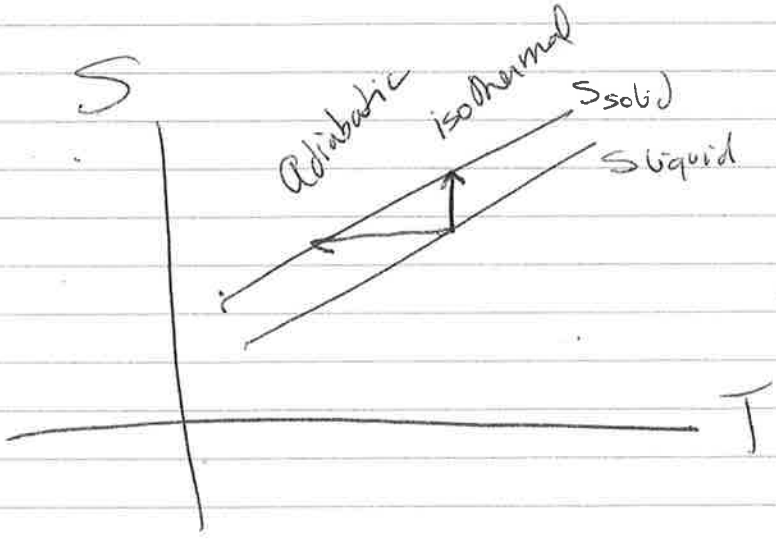


Figure 5.13. Phase diagrams of ^{4}He (left) and ^{3}He (right). Neither diagram is to scale, but qualitative relations between the diagrams are shown correctly. Not shown are the three different solid phases (crystal structures) of each isotope, or the superfluid phases of ^{3}He below 3 mK.

(b) Why does slope of phase boundary vanish at $T=0$? This is because by the third law, $\Delta S \to 0$. We assume $\Delta V \neq 0$ between liquid ↔ solid or liquid ↔ gas. ($\nexists$ critical point at $T=0$.)

(c) Part a) indicates that solid at same temp would have higher entropy ... $\Delta_f S|_{T,s} > \Delta_f S|_{T,l}$

If we want $\Delta_f S|_s = \Delta_f S|_l$ the only way is for T to drop ..... ⇒ This is a way of cooling ^3He.



Problem 5 → G&T 7.10 Law of Corresponding States

(a) WTS $\tilde{P}_c = \tilde{T}_c = \tilde{\rho}_c = 1$ where

$$P = \frac{a}{27b^2}\tilde{P}\,; \quad kT = \frac{8a}{27b}\tilde{T}\,; \quad \rho = \frac{1}{3b}\tilde{\rho}$$

Soln → With these definitions, the vdW eqn of state:

$$P = \frac{NkT}{V-Nb} - \frac{aN^2}{V^2} = \frac{\rho kT}{1-\rho b} - a\rho^2$$

becomes...

$$\tilde{P}\frac{a}{27b^2} = \frac{\tilde{\rho}\,8a\tilde{T}}{3b\cdot 27b} - \frac{a}{9b^2}\tilde{\rho}^2$$

$$\Rightarrow \tilde{P} = \frac{8}{3}\frac{\tilde{\rho}\tilde{T}}{1-\tilde{\rho}/3} - \frac{\tilde{\rho}^2}{9}\cdot 27$$

or

$$\tilde{P} = \frac{8\tilde{\rho}\tilde{T}}{3-\tilde{\rho}} - 3\tilde{\rho}^2 .$$

Given this eqn. we now want to assert that the critical point is where

$$\left(\frac{\partial \tilde{P}}{\partial \tilde{\rho}}\right)_{\tilde{T}_c} = 0 = \left(\frac{\partial^2 \tilde{P}}{\partial \tilde{\rho}^2}\right)_{\tilde{T}_c}$$

Now, $\left(\frac{\partial \tilde{P}}{\partial \tilde{\rho}}\right)_{\tilde{T}_c} = \frac{8\tilde{T}_c}{3-\tilde{\rho}} + \frac{8\tilde{\rho}\tilde{T}_c}{(3-\rho)^2} - 6\tilde{\rho}$

$$= \frac{24\tilde{T}_c - 8\rho\tilde{T}_c + 8\tilde{\rho}\tilde{T}_c - 6\tilde{\rho}(3-\tilde{\rho})}{(3-\tilde{\rho})} = 0$$

$$\Rightarrow 24\tilde{T}_c = 6\tilde{\rho}(3-\tilde{\rho})^2$$

Similarly $\left(\frac{\partial^2 \tilde{P}}{\partial \tilde{\rho}^2}\right)_{\tilde{T}_c} = \frac{8\tilde{T}_c}{(3-\tilde{\rho})^2} + \frac{16\tilde{\rho}\tilde{T}_c}{(3-\rho)^3} + \frac{8\tilde{T}_c}{(3-\rho)^2} - 6$

$$= \frac{16\tilde{T}_c}{(3-\tilde{\rho})^2} + \frac{16\tilde{\rho}\tilde{T}_c}{(3-\tilde{\rho})^3} - 6 = 0$$

great check... $\Rightarrow \quad 0 \overset{?}{=} \frac{16}{4} + \frac{16}{8} - 6 = 4+2-6 = 0$ ✓ ☺

$\tilde{T}_c = 1$

$\tilde{\rho}_c = 1$

(b) Now asked to back-substitute & show

$\frac{V_c}{N} = 3b, \quad P_c = \frac{a}{27b^2}, \quad kT_c = \frac{8a}{27b}$.

This follows trivially from $\tilde{\rho}_c = \tilde{T}_c = \tilde{P}_c = 1$

c) At what T does κ become negative? This will be when κ^{-1} becomes negative as well ....

Thus when $\left(\frac{\partial \tilde{P}}{\partial \tilde{\rho}}\right) = 0$. So

$\tilde{T} = \frac{\tilde{\rho}}{4}(3-\tilde{\rho})^2$ is temperature ....

This is the boundary in $\tilde{T}$-$\tilde{\rho}$ space of the spinodal wire.

d) What is $\frac{P_c}{\rho_c k T_c}$?

Answer: It is $\frac{a/27b^2}{\frac{1}{3b}\frac{8a}{27b}} = \frac{3}{8} = 0.375$

Expt gives 0.29. Not bad!

Background for Prob 6

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

or

$$P = \frac{\rho kT}{1-\rho b} - a\rho^2 \qquad \text{vdW eqn of state}$$

In reduced units* (a la G & T Prob 7.10)

This eqn is

$$\tilde{V} = V/V_c \qquad V_c = 3b$$

$$\tilde{\rho} = 1/\tilde{V}$$

$$\tilde{P} = P/P_c \qquad P_c = \frac{a}{27b^2}$$

$$\tilde{T} = T/T_c \qquad kT_c = 8a/27b$$

*

Free energy?

One way to find it:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$\Rightarrow F = -NkT\ln(V-Nb) - \frac{aN^2}{V} + Nf(T)$$

where $f(T)$ is indep, explicitly, of V

Now $G = F + PV$ so

$$G = -NkT\ln(V-Nb) - \frac{aN^2}{V} + PV + Nf(T)$$

and in reduced units

$$\tilde{g} = \frac{G}{3NkT_c} = -3\tilde{\rho} - \frac{8}{3}t\ln\left(\frac{3}{\tilde{\rho}} - 1\right) + \frac{\tilde{\rho}}{\tilde{\rho}} + \text{terms indep of } \tilde{\rho} \text{ or } \tilde{P}$$

Note: This is not a G in terms of its natural variables, $G(T, P, N)$. But we can use vdW eqn of state to recast G as a function of T, P & N; or $g(T, \tilde{\rho})$ see plot that follows!

Problem 6 i) Schroeder 5.52

To Plot: vdW isotherm for $T/T_c = 0.95$ in terms of reduced variables.

To Do: Maxwell construction to get $P(V)$ at this temperature.

To Plot further: $\frac{G}{NkT_c}(P)$ for $T/T_c = 0.95$ & predict it gives same shape as book figure (G+T 7.6) *

Answer: vdW eqn. in reduced units is

$$\frac{8\tilde{T}}{3\tilde{V}-1} - \frac{3}{\tilde{V}^2} = \tilde{P}$$

where $\tilde{V} = 1/\tilde{\rho}$ when we are talking about one mole.

This is a pain to write ... so we will let $\tilde{T} \equiv t$; $\tilde{V} \equiv v$; $\tilde{P} \equiv p$.

Thus vdW eqn/isotherm is given by

$$\frac{8t}{3v-1} - \frac{3}{v^2} = p$$

* Note that these units are $\tilde{P} = \frac{P}{P_c}$, $\tilde{V} = \frac{V}{V_c}$, $\tilde{T} = \frac{T}{T_c}$

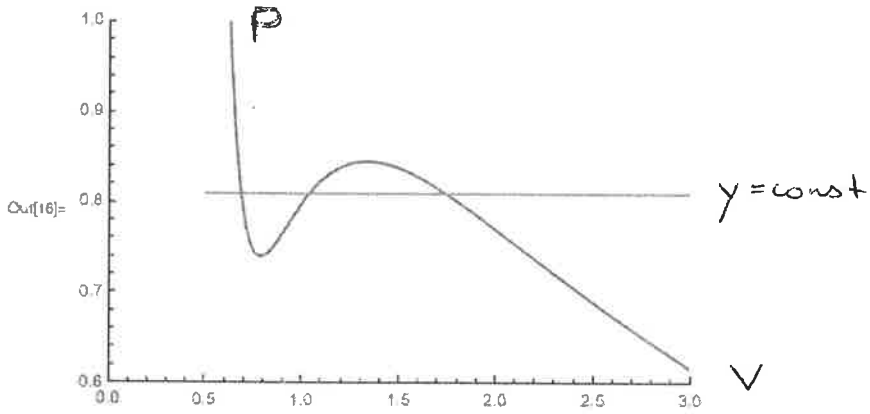
We will set $t = 0.95$.

In Mathematica output which follows, we add a horizontal line "by eye" to do Maxwell construction - but we also check numerically:

```
In[10]:= p[v_] := 8 * t / (3 * v - 1) - 3 / v^2

In[14]:= y[v_] := 0.81

In[16]:= Plot[{p[v], y[v]}, {v, 0.5, 3}, PlotRange → {{0, 3}, {.6, 1}}]
```



Let's find the two volumes that these correspond to, and also really check that $\tilde{p} = 0.81$

```
Clear[x]

Solve[p[x] == .81, x]

{{x → 0.685149}, {x → 1.0353}, {x → 1.74045}}
```

OK we are going to now find that p = 0.81 by looking above and below

```
t

0.95

pIntegral[v_] := (8 / 3) * t * Log[3 * v - 1] + 3 / v

AreaDiff[p0_, v1_, v2_] :=
 pIntegral[v2] - pIntegral[v1] - p0 * (v2 - v1)

Clear[y]
```

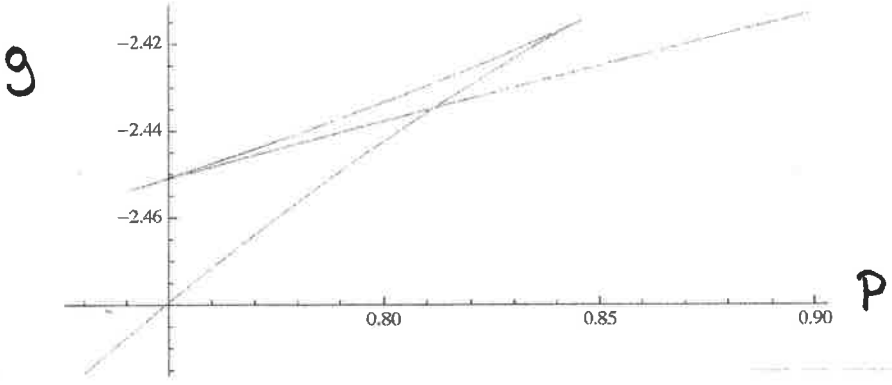
```
AreaDiff[.81, .685149, 1.74045]
0.0019716
Above ...
Solve[p[x] == 0.79, x]
{{x → 0.697574}, {x → 0.968089}, {x → 1.87442}}
AreaDiff[.79, 0.6975743530399708`, 1.874421178403473`]
0.0243193
Below ...

Solve[p[x] == 0.82, x]
{{x → 0.679902}, {x → 1.0762}, {x → 1.66667}}
AreaDiff[.82, .679902, 1.6666666666666659`]
-0.00824481
```

Ok so $p \approx 0.81$ was a pretty good pressure that obeyed Maxwell construction

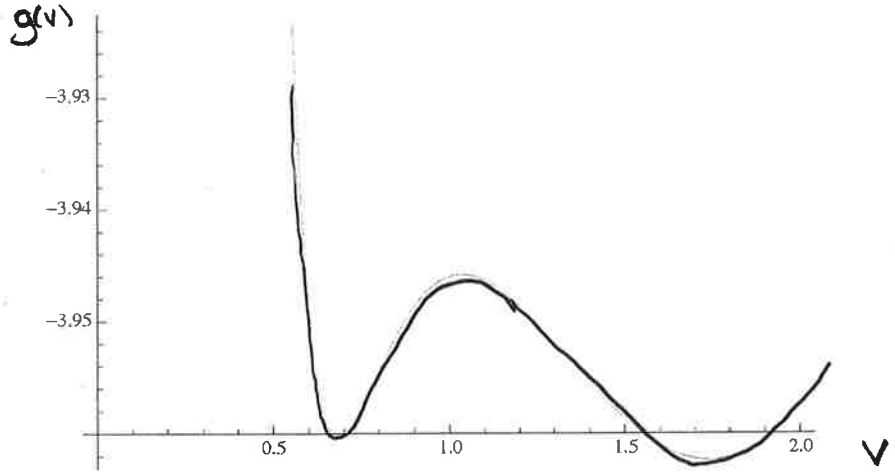
Now do G / NkT_c ... start with Schroeder Eq. 5.56 and neglect function c(T)

```
g[v_] := -t * Log[3 * v - 1] + t / (3 * v - 1) - 9 / (4 * v)
ParametricPlot[{p[v], g[v]}, {v, .65, 2.25}]
```



ii) Now, using expression for $g(v)$ as in G&T 7.59, so we are holding P fixed at $p = 0.81$, we look to see that we have two local minima. We do ☺

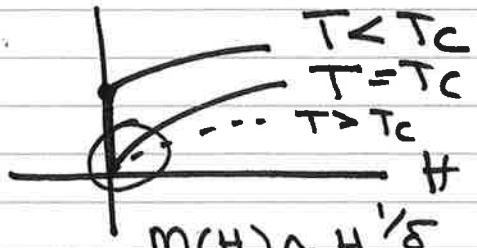
```
gGT[v_] := -3 / v - (8 / 3) * t * Log[3 * v - 1] + 0.81 * v
Plot[gGT[v], {v, 0, 2.0}]
```



Problem 7 intro

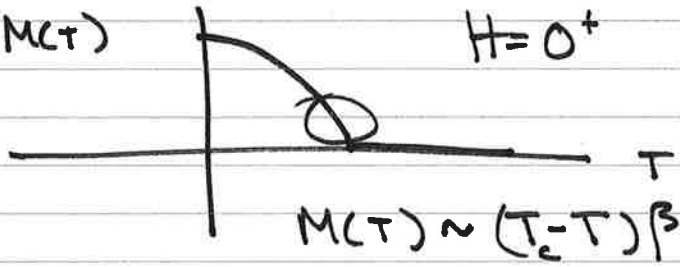
MFTy and Ferromagnets

$M(H)$



$M(H) \sim H^{1/\delta}$

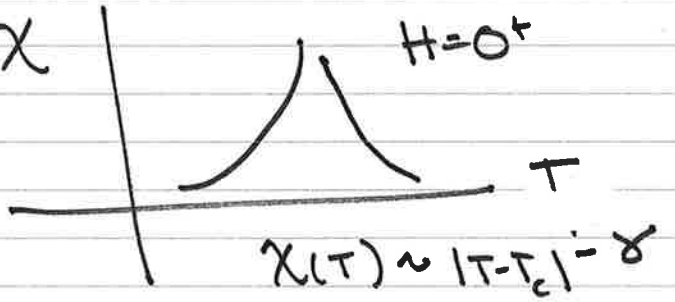
$M(T)$ $\quad H=0^+$



$M(T) \sim (T_c - T)^{\beta} \sim \epsilon^{\beta}$

$$\chi = \left.\frac{\partial m}{\partial H}\right|_T$$

χ $\quad H=0^+$



$\chi(T) \sim |T - T_c|^{-\gamma}$

How do we know those exponents via mean field Thy?

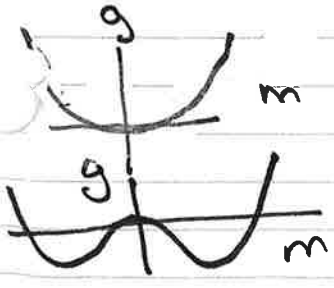
Way 1 Believe: $g(T,m) = a(T) + b\left(\frac{T-T_c}{T}\right)m^2 + \frac{c(T)}{4}m^4 - Hm$

Then $\frac{\partial g}{\partial m} = 0$ defines physical m

When $H=0$ have either $m=0$ if $T>T_c$

or $T<T_c$: $m=0$ or $m^2 \sim (T_c - T)$

$\Rightarrow m \sim (T_c - T)^{\beta} \sim \epsilon^{\beta}$



If $T>T_c$, $m=0$ is minimum

If $T<T_c$, nonzero m's are minima

Way 2 Don't believe ... remember ...

ch 5 $f = -kT \ln Z_1$

m-f theory $= -kT \ln\left[2\cosh\left(\frac{Jqm+H}{kT}\right)\right]$

$\therefore \quad m = \frac{-\partial f}{\partial H} = \tanh\left[\frac{Jqm+H}{kT}\right]$

small m ... expand $\quad m \approx \frac{Jqm}{kT} - \frac{1}{3}\left(\frac{Jqm}{kT}\right)^3$

Solutions? $\quad m = 0$ if $\frac{Jq}{kT} < 1$

but if $\frac{Jq}{kT} > 1 \quad m = 0$ or $1 = \frac{Jq}{kT} - \frac{1}{3}\left(\frac{Jq}{kT}\right)^3 m^2$

$\Rightarrow m^2 \propto \frac{Jq}{kT} - 1$

$m^2 \propto \frac{T_c}{T} - 1$

if $T_c \equiv \frac{Jq}{k} \quad m^2 \propto T_c - T$

Extension of Way 2 G+T prob 5.17

extended the mean field theory to a Landau theory. For $H = 0$

$f \equiv g = \frac{1}{2} Jqm^2 - kT \ln\left[2\cosh\left(\frac{Jqm+H}{kT}\right)\right]$

impt new term

$g \approx a + b\left(1 - \frac{qJ}{kT}\right)m^2 + cm^4$ ☺

$\uparrow \frac{T_c}{T}$

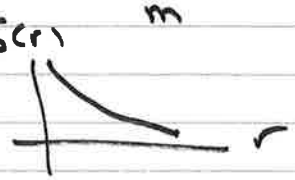
There is one more quantity we might discuss...

correlation length, ξ

Ch. 5

$$G(r) = \overline{S_k S_{k+r}} - \underbrace{\bar{S}_k \bar{S}_{k+r}}_{m^2}$$

In 1D $G(r) = (\tanh \frac{J}{kT})^r$



$G(r, T_c)$?

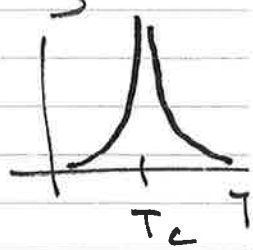
Say $G(r) \equiv e^{-r/\xi}$

Then $\xi = \frac{-1}{\ln(\tanh \frac{J}{kT})} = \frac{1}{2} e^{\frac{2J}{kT}}$

So $\xi \to \infty$ as $T \to 0$

But no phase transition

Higher dimension $\xi \sim |T - T_c|^{-\nu}$



G & T Landau-Ginzburg theory pp. 462-463

$$g(r) = a + \underbrace{b(T)}_{\propto (T-T_c)} m^2(r) + \frac{c(T)}{4} m^4(r) + \frac{\lambda}{2}\left[\nabla m(r)\right]^2 - m(r) H$$

$\lambda > 0$

Math math math

$$\xi(T) = \begin{cases} \left[\frac{\lambda}{b(T)}\right]^{1/2} & T > T_c \\ \left[\frac{-\lambda}{2b(T)}\right]^{1/2} & T < T_c \end{cases}$$

$b(T) \propto (T - T_c)$

$\Rightarrow \xi \sim T - T_c^{-\frac{1}{2}}$

$\nu = \frac{1}{2}$

Problem 7 — Critical exponents for VdW fluid

i) G&T 7.18

Want to find the critical exponent δ predicted by the VdW eqn of state.

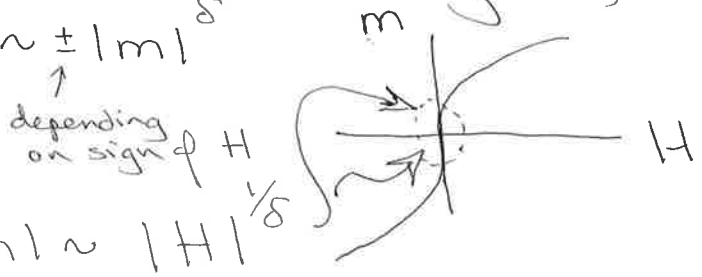
- What's δ again?

For a ferromagnet, it is for $T = T_c$

$$H \sim \pm |m|^{\delta}$$

↑ depending on sign of H

or $|m| \sim |H|^{1/\delta}$



- What's the VdW equation again?

Let's write it in reduced units as problem suggests: At $T = T_c$

$$\tilde{P} - \tilde{P}_c = \frac{8\tilde{\rho}\tilde{T}_c}{3 - \tilde{\rho}} - 3\tilde{\rho}^2 - 1 \qquad (1)$$

Now, $\tilde{P}_c = 1$ but we'll leave it as $\tilde{P}_c$

b/c ultimately, we are going to find δ s.t. $\tilde{\rho} - \tilde{\rho}_c \sim (\tilde{P} - \tilde{P}_c)^{1/\delta}$

- We will use $\tilde{T}_c = 1$, $\tilde{\rho}_c = 1$ (2)

We further assume we are a bit above the critical density so

$$\tilde{\rho} = \tilde{\rho}_c + \Delta = 1 + \Delta \qquad (3)$$

- Here we go .... Starting with Eq. (1) & utilizing Eqs (2) & (3)

$$\tilde{P} - \tilde{P}_c = \frac{8(1+\Delta)\cdot 1}{2-\Delta} - 3(1+\Delta)^2 - 1$$

so $$\tilde{P} - \tilde{P}_c = \frac{8(1+\Delta) - 3(1+\Delta)^2(2-\Delta) - (2-\Delta)}{2-\Delta}$$

Thus .... expanding out in powers of Δ

$$\tilde{P} - \tilde{P}_c = \frac{0 + \Delta(0) + \Delta^2(0) + 3\Delta^3}{2-\Delta}$$

$$\approx \frac{3\Delta^3}{2}(1+\Delta) \approx \frac{3}{2}\Delta^3 + \text{ord}(\Delta^4)$$

$\therefore$ Since $\Delta = \rho - \rho_c$ ....

$$\rho - \rho_c \sim (\tilde{P} - \tilde{P}_c)^{1/3} \Rightarrow \underline{\delta = \frac{1}{3}}$$

The mean field theory value

Problem 7 B&B 26.1

ii) Compressibility of the VdW gas...

Want to show $K_T = \frac{4b}{3R}(T-T_c)^{-1}$ at $V=V_c$

- Start with VdW eqn. where (in B&B fashion ☺) we let $V \equiv V_m$, the molar volume. Thus VdW eqn looks like

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad (1)$$

$$\Rightarrow K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \equiv -\frac{1}{V}\frac{1}{\left(\frac{\partial P}{\partial V}\right)_T} \quad (2)$$

rule of partial derivatives

Thus subbing (1) into (2):

$$K_T = -\frac{1}{V}\left(\frac{1}{\frac{-RT}{(V-b)^2} + \frac{2a}{V^3}}\right)$$

- Now, at $V = V_c = 3b$,

$$K_T = \frac{1}{\frac{3bRT}{4b^2} - \frac{6a}{9b^3}} = \frac{4b}{3R}\frac{1}{T - \frac{8a}{27Rb^2}}$$

$$= \frac{4b}{3R}(T-T_c)^{-1}$$

with $T_c = \frac{8a}{27Rb^2}$ QED

Note: This has been calculated with the tacit assumption that there is only one value of V, not two ... this is only true for $T > T_c$.

There is a tougher calculation that is Schroeder problem 5.55 which asks us to do $T < T_c$ & show that $K_T \sim |T - T_c|^{-\gamma}$ for both $T \gtrsim T_c$ and $T \lesssim T_c$.

Problem 8 i) The BE Critical temp

Schroeder 7.65

Want to show integral in Eq. 7.124:

$$N = \frac{2}{\sqrt{\pi}} \left(\frac{2\pi mkT}{h^2}\right)^{3} V \int_0^\infty \frac{\sqrt{x}}{e^x - 1}\, dx$$

evaluates to right number (numerically) 2.315, so that $N = 2.612 \left(\frac{2\pi mkT}{h^2}\right)^{3} V$.

Answer: We could just do Mathematica: NIntegrate[Sqrt[x]/(Exp[x]-1), {x, 0, Infinity}] & we get 2.31516.

Alternatively, we can see Appendix C.4 and C.5 of B&B. There ... we learn that

$$\int_0^\infty \frac{x^{1/2}\, dx}{e^x - 1} = +\Gamma(3/2)\, \underbrace{Li_{3/2}(1)}_{\zeta(3/2)}$$

($z = 1$)

$$\equiv I_B(1/2)$$ Bose Integral

Look at Table C.2 to see $\zeta(3/2) \approx 2.612$

$$\Gamma(3/2) = \frac{\sqrt{\pi}}{2}$$

This $\Gamma(3/2)$ just cancels prefactor in N ☺

$$\therefore \quad N = 2.612 \left(\frac{2\pi mkT}{h^2}\right)^{3} V$$

Problem 8

ii) G+T 6.39 → WTS $\lambda_c \approx a$

where a is interparticle spacing,

when $\lambda_c = \sqrt{\frac{h^2}{2\pi m k T_c}}$. Implications?

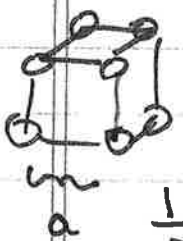
Since $kT_c = \frac{1}{(2.612)^{2/3}} \frac{2\pi\hbar^2}{m} \rho^{2/3}$

We can write

$$\lambda_c = \sqrt{\frac{h^2 (2.612)^{2/3} m}{2\pi m \cdot 2\pi\hbar^2 \rho^{2/3}}}$$

$$= \sqrt{(2.612^{2/3})\, \rho^{-1/3}}$$

$$\approx 1.38 \rho^{-1/3} = \underline{1.38\, a}$$



$\frac{1}{\rho} = \frac{V}{N} = a^3$

$\Rightarrow \rho^{-1/3} = a$

The implication is that the particle's extent is roughly the distance to the next particle. Dense.. Not surprising that quantum effects dominate and particles are able to "coordinate" & collapse into ground state.

Problem 9 BE condensate ... Behavior of Pressure

G+T Problem 6.40

(a) Start with $PV = NkT$, let $N = \bar{N}_\epsilon$ (which is number in non-ground, hence excited states) and give argument as to why $P \propto T^{5/2}$ at low temperatures.

Answer ... $N_\epsilon = N\left(\frac{T}{T_c}\right)^{3/2}$ $T<T_c$

From eqn. (6.215). Thus

$$PV = N\left(\frac{T}{T_c}\right)^{3/2} kT \propto T^{5/2}$$

There are fewer particles to participate in pressure ... the ones in ground state make no contribution ... or very little .. see (b)

(b) To show: Ground state particles contribute pressure $P_0 = \frac{kT}{V}\ln(\bar{N}_0 + 1)$. Also explain why P_0 is essentially zero, and why pressure for Bose gas at $T<T_c$ is volume-independent.

Answer: Go back to definition of pressure from the grand canonical thermodynamic potential: $\Omega = -PV$

$$\Omega = kT\sum_k \ln\left[1 - e^{-\beta(\epsilon_k - \mu)}\right]$$

For g.s.: $k=0$; $\epsilon_k = 0$: $\Omega_0 = kT\ln\left[1 - e^{\beta\mu}\right]$

What is connection with $\bar{N}_0$?

$$\bar{N}_0 = \frac{1}{e^{-\beta\mu} - 1} \iff 1 - e^{\beta\mu} = \frac{1}{\bar{N}_0 + 1}$$

$$\Rightarrow \quad \Omega_0 = kT \ln\left(\frac{1}{\bar{N}_0 + 1}\right)$$

$$\therefore \quad P_0 V = kT \ln\left(\bar{N}_0 + 1\right)$$

Since V is extensive, and RHS is not, only way this can happen is if $P_0 \approx 0$.

Reason $P(T < T_c)$ is volume indep?

Not sure I understand question.

I guess b/c it only comes from particles in excited state ... but according to

$$PV = NkT^{5/2}/T_c^{3/2}$$

$$\propto \frac{NkT^{5/2}}{\left(\left(\frac{N}{V}\right)^{2/3}\right)^{3/2}} \qquad (6.210)$$

$$PV \propto V^1$$

$$P \propto V^0 \qquad \text{for fixed } N$$

So for {normal / classical} gas, fixed N

$$P \propto V^{-1}$$

It is weaker... though not V indep.

When we increase V, for fixed $T < T_c$ * we do draw more particles out of ground state...

This lowers T_c slightly but still $T < T_c$

* This is $T_c(V)$ so imagine we start with a certain volume, find T_c, go to $T < T_c$ + then increase volume slightly.