PH4211 Statistical Mechanics 2011
Outline Answers.

Q1 a) Λ is the deBroglie wavelength
corresponding to a free particle
of momentum p, corresponding
to a kinetic energy E
corresponding to the thermal
energy KT (— to within
a factor of π).

③

b) Since Z is the sum of Boltzmann
factors — i.e. it is related to
possibilities, then the probabilities
for independent events multiply,
so the Zs would multiply.   2
Since the free energy comes from
the __logarithm__ of Z, then to
be consistent with extensivity of
energy, the Zs must multiply.   2
So generally, for independent
systems: $Z = z_1 z_2 z_3 \cdots$.
And so if all N systems have
the same mathematical expression
for Z, then $Z = z^N$.   1   ③

c) $F = -KT \ln Z = -NKT \ln z$
$= -NKT \ln \left[V \left(\frac{MKT}{2\pi\hbar^2} \right)^{3/2} \right]$ ③

d) Although the N is needed for extensivity,
since it is saying that the total free
energy F is proportional to N,
this is not enough. The problem
is that the argument of the ln is

proportional to V. True, the argument is
dimensionless, but this is not
enough.
Extensivity requires
$$\frac{E}{N} \Rightarrow \text{limit } f \quad \text{as } N, V \to \infty$$
while $\frac{N}{V}$ remains constant.

In the existing form you don't get
a const value, instead $F \to \infty$!! ④

e) <u>Mathematically</u> the problem would be
solved by dividing the V in the ln
by a dimensionless quantity proportional
to N.
If we had some $\propto N$ then the α
would contribute an additive constant
to F. So not a problem classically. 2

From the quantum perspective the
particle indistinguishability leads to
a factor $\frac{1}{N!} \sim -(N\ln N - N)$ by
Stirling's approximation. This gives
the required correction to the answer
to the ln. Write $N = N \ln e$ 2
so that $\frac{1}{N!} \sim -N\ln(N/e)$.
giving
$$F = -NKT \ln\left[\frac{V}{N}\left(\frac{mKT}{2\pi\hbar}\right)^{3/2} e\right] \quad 1 \quad ⑤$$

Q2 a) Order parameter is a quantity giving a measure of the order in the ordered phase. It may be a scalar, vector, complex, tensor. 1
In a 1ˢᵗ order transition the order parameter goes to zero discontinuously at the transition 1
In a 2ⁿᵈ order transition the order parameter goes to zero continuously 1

ϕ ⌐ ϕ ⌐
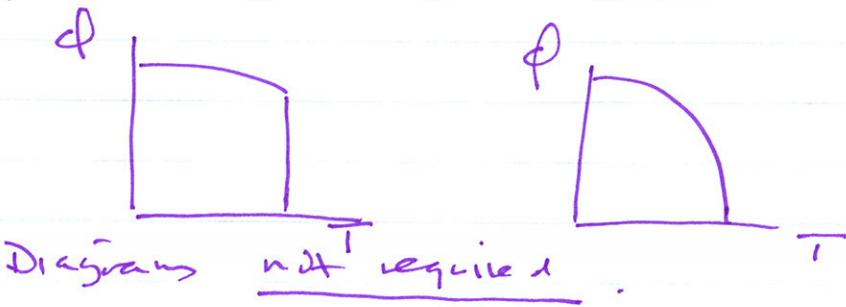
Diagrams not required. ③

b) Order parameter for ferroelectric transition is the electric polarization $\underset{\sim}{P}$, although it will only point along certain axes related to the crystal lattice structure. ②

c) Series is terminated at the lowest (even) power that is capable of exhibiting the correct generic behavior at the transition. It must be an even power so that the free energy is bounded, i.e. system is stable. 2
There are no odd powers in the expansion because of the symmetry — System has inversion symmetry — if we replace $\underset{\sim}{P}$ by $-\underset{\sim}{P}$ then the free energy must

be unchanged.

The free energy is a scalar. If we take $\underset{\sim}{P}$ as the order parameter and if there are no other directions in the problem then the only way to make a scalar out of a $\underset{\sim}{P}$ is to dot it with itself. So we only have powers of P^2

d)
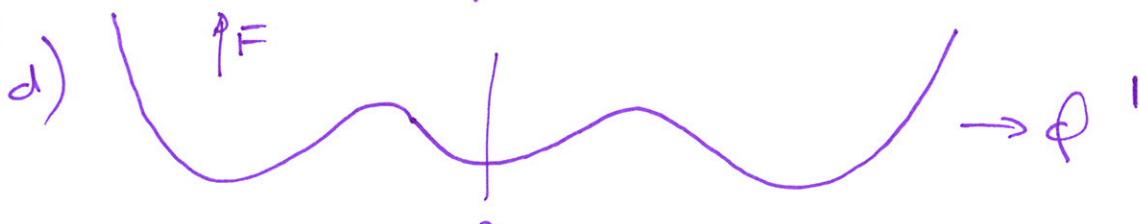
This is the general form for a 6th order even polynomial.

When the central minimum is below the other two we are in the disordered (High-T) state.

But when the side minima fall below the central one there will be a discontinuous jump in P — i.e. a 1st order transition.

High T (disordered)

Transition point
Jump in P.

Low T (ordered)
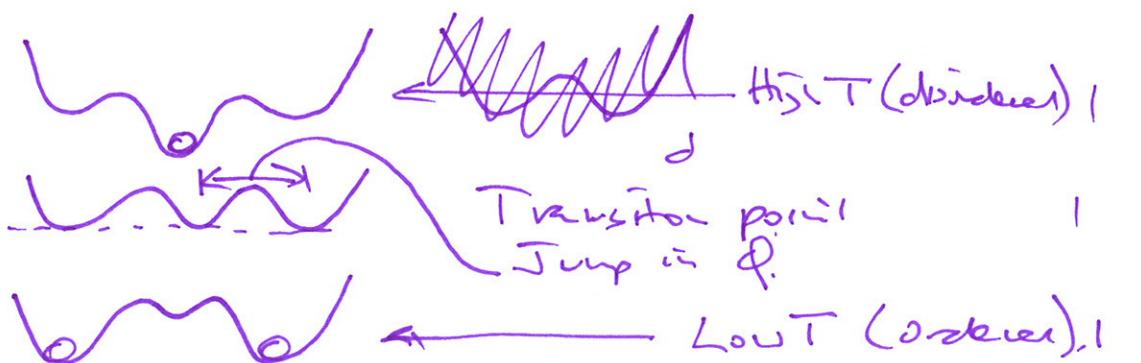
e) For the transition to be 1st order

we require $F_4 < 0$ as $F_6 > 0$

If F_4 becomes positive then

we no longer need the F_6 term.

When $F_4 > 0$ the transition is 2nd order.   ③

f) At the transition the three minima are

at the same height. Let

us put $F_0 = 0$ so the central

minimum is at $F = 0$ as so the

other two are zero as well.

Then $F_2 \phi^2 + F_4 \phi^4 + F_6 \phi^6 = 0$

The fact that these are also minima

means that $\dfrac{dF}{d\phi} = 0$. i.e. $2F_2 \phi + 4F_4 \phi^3 + 6F_6 \phi^5 = 0$

So $\phi = 0$ or $F_2 + 2F_4 \phi^2 + 3F_6 \phi^4 = 0$

the Simultaneous eqns: $F_2 + F_4 \phi^2 + F_6 \phi^4 = 0$

$F_2 + 2F_4 \phi^2 + 3F_6 \phi^4 = 0$

Eliminate F_2

$\to \quad F_4 + 2F_6 \phi^2 = 0$ or $\phi = \sqrt{-\dfrac{F_4}{2F_6}}$

B/c F_6 is +ve. F_4 is −ve.

as this gives the $\phi \ne 0$ roots.

So the jump in ϕ is from 0 to $\sqrt{\dfrac{-F_4}{2F_6}}$

or $\Delta\phi = \sqrt{\dfrac{-F_4}{2F_6}}$ 3

F_4 goes to zero as the transition becomes

2nd order. So from the expression

for $\Delta\phi$ we see that $\Delta\phi \to 0$ as expected.   ④

3 a) Virial expansion is an expansion in density $\frac{N}{V}$ — so high order terms may be increasingly neglected as the density gets smaller.

②

b) Re-arrange vdW eqⁿ

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

or

$$\frac{P}{kT} = \frac{N}{V}\left(\frac{1}{1-\frac{N}{V}b}\right) - \frac{a}{kT}\frac{N^2}{V^2}$$

$$= \frac{N}{V}\left(1 + \frac{N}{V}b + \cdots\right) - \frac{a}{kT}\frac{N^2}{V^2}$$

$$= \frac{N}{V} + \left(\frac{N}{V}\right)^2\left(b - \frac{a}{kT}\right) + \cdots$$

So $\quad B_2 = b - \frac{a}{kT}$

④

c) From the plot the $1/T = 0$ intercept is approx $17\ cm^3/mol$. So $b = 17\ cm^3/N_A$ or $2.8 \times 10^{-23}\ cm^3 = \frac{2}{3}\pi\sigma^3$ so

or $\sigma^3 = 1.35 \times 10^{-23}\ cm^3$ so $\sigma = 2.38 \times 10^{-8}\ cm$

$$= 2.38 \times 10^{-10}\ m$$

Slope of plot is $\sim 100\ b$

c) From the plot of the B_2 data
the $1/T = 0$ intercept gives $b = 17 \text{ cm}^3/\text{mol}$
i.e. $b = 17 \text{ cm}^3/N_A = 2.8 \times 10^{-23} \text{ cm}^3$

or $b = 2.8 \times 10^{-29} \text{ m}^3$ 2

Slope of curve $= -a/k = -100 b$

So $a = 100 b \times k = 2.8 \times 10^{-23} \times 1.4 \times 10^{-23}$
$a = 3.9 \times 10^{-50} \text{ J m}^3$ 2

Important approximation/assumption is
to draw the line through the
high-temp data where the quantum
~~effects~~ are negligible.   2   ⑥

d) ε is the depth of the attractive
well (energy) and σ is
the hard-core diameter.   ②

e) b comes from the hard-core volume
so it is related to $\frac{4}{3}\pi\sigma^3$
a comes from $a\frac{N^2}{V^2} = N\frac{\partial\langle E\rangle}{\partial V}$
and $\langle E\rangle \sim \frac{1}{V}\int_\sigma^\infty 4\pi r^2 U(r)\,dr$
which then gives us $a = \frac{4}{3}\pi\sigma^3\varepsilon$
for the L-J 6-12 potential for $U(r)$.   3

$\sigma = \left(\frac{3b}{2\pi}\right)^{1/3} \longrightarrow 2.38 \times 10^{-8} \text{ cm}$ or $2.38 \times 10^{-10} \text{ m}$

$\varepsilon = \frac{a}{2b} = 7 \times 10^{-22} \text{ J} \quad \left(\frac{\varepsilon}{k} \approx 50 \text{ K}\right)$ 3   ⑥

4 a) Minimize Helmholtz @ const T, V !
       Minimize Gibbs @ const T, p ! ②

   b) Order parameter must be <u>conserved</u> !

       If free energy is concave.
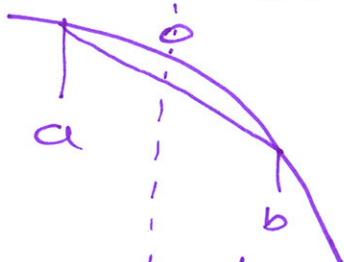
       Then can drop off curve to
       the straight line. So have
       reduced the free energy and
       have some material in state a
       and some in state b rather
       than all in state 0.
       Populations determined by matching the
       mean value A the order parameter
       what it is specified (conserved) to be.

                                    2 ③

   c) Equilibrium state is determined by
       minimizing the free energy
       so must continue dropping below
       the curve until you can go
       no further. — Ultimately the
       free energy must look like
       this!

                                       3²
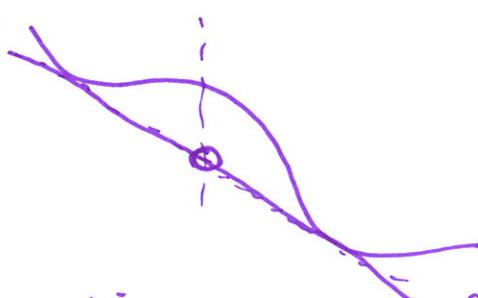
       then the line gives the lowest free
       energy — equilibrium state.

d) Critical point is the "coalescence" of the two phases. — When the a and the b phase go together.

This is when the "wiggle" in the free energy disappears.
It corresponds to the highest temperature of the transition. ②

e) N: n° of particles/site
S: n° of neighbours
x: Concentration of one species
k: Boltzmann's const
T: temperature. │

First term is energy term
Second term is entropy of 2-state system. ②

f) Coexistence curve corresponds to minimizing free energy:

$$\frac{dF}{dx} = NS\varepsilon(1-2x) - NkT\ln\left(\frac{1-x}{x}\right) = 0$$

So
$$T_{PS} = \frac{S\varepsilon(1-2x)}{k\ln\left(\frac{1-x}{x}\right)}$$

Symmetry $\Rightarrow x_c = \frac{1}{2}$
take limit of T_{PS}
$$\Rightarrow T_c = \frac{1}{2}\frac{S\varepsilon}{k}$$ ③

g) $x_c = \frac{1}{2}$ by $\overline{\text{symmetry}}$ ②

h) Similar shape — but alloy curve is symmetric while fluid curve's skewed.
β critical exponent for both is 1/3 ③

3. (a) The virial expansion for a gas is given by

$$\frac{p}{kT} = \frac{N}{V} + \left(\frac{N}{V}\right)^2 B_2 + \left(\frac{N}{V}\right)^3 B_3 + \ldots;$$

here the B_n are the virial coefficients and the other symbols have their usual meaning. Under what conditions may the higher-order terms be ignored?

[2]

(b) The van der Waals equation of state is written, in conventional form, as

$$\left(p + a\frac{N^2}{V^2}\right)(v - Nb) = NkT.$$

Show that the second virial coefficient corresponding to this equation of state is

$$B_2 = b - \frac{a}{kT}.$$

[4]

(c) Measurements of the second virial coefficient of neon are shown in the figure below.

intercept = 17 cm³/mol

slope = − 1700 cm³/mol K
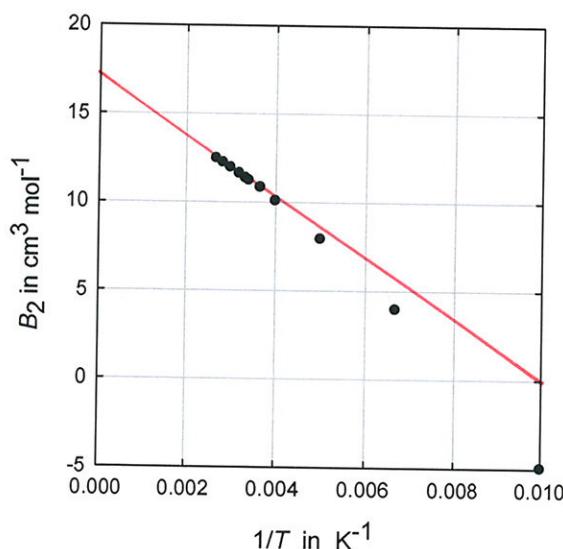
Estimate the values of the van der Waals parameters a and b. Be sure to state your units. Explain any approximations or assumptions.

[6]

(d) The interaction between neon atoms is conventionally represented by the Lennard-Jones 6-12 potential

$$U(r) = \varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\};$$

what are ε and σ in this expression?

[2]

(e) Outline briefly the arguments by which one makes the identification

$$a = \frac{4}{3}\pi\sigma^3\varepsilon \quad \text{and} \quad b = \frac{2}{3}\pi\sigma^3$$

and hence estimate ε and σ for argon.

[6]