PH4211 Statistical Mechanics 2020
Outline Answers

Question 1

a)

S is the entropy [2], k is Boltzmann's constant [2] and Ω is the number of microstates in the macrostate [2].

part a: [[6]]

b)

For an isolated system all microstates are equally probable. [2]

So probability of observing a macrostate is proportional to the number of microstates Ω corresponding to it. [2]

The equilibrium state observed is the most probable one, so it is the state with the largest number of microstates. [2]

Since $S = k \ln \Omega$ it follows that the equilibrium state is that of maximal entropy. [2]

Upon removing a constraint the system will evolve to a more probable state it will evolve to a state of greater (maximal) entropy. [2]

part b: [[10]]

c)

We can work with S or Ω: we maximise either $S = S_1 + S_2$ or $\Omega = \Omega_1 \Omega_2$ with respect to the allowed variations.

$$\begin{aligned} E_0 &= E_1 + E_2 \quad \text{so} \quad E_2 = E_0 - E_1 \\ V_0 &= V_1 + V_2 \quad \text{so} \quad V_2 = V_0 - V_1 \\ N_0 &= N_1 + N_2 \quad \text{so} \quad N_2 = N_0 - N_1 \end{aligned}$$

Let's work with entropy:

$$\begin{aligned} S &= S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2) \\ &= S_1(E_1, V_1, N_1) + S_2(E_0 - E_1, V_0 - V_1, N_0 - N_1). \end{aligned}$$

Maximise S with respect to E interchange – vary E_1

$$\frac{\partial S}{\partial E_1} = \left.\frac{\partial S_1}{\partial E}\right|_{V,N} - \left.\frac{\partial S_2}{\partial E}\right|_{V,N} = 0 \quad \text{or} \quad \left.\frac{\partial S_1}{\partial E}\right|_{V,N} = \left.\frac{\partial S_2}{\partial E}\right|_{V,N}. \qquad \text{(X) [2]}$$

Maximise S with respect to V interchange – vary V_1

$$\frac{\partial S}{\partial V_1} = \left.\frac{\partial S_1}{\partial V}\right|_{E,N} - \left.\frac{\partial S_2}{\partial V}\right|_{E,N} = 0 \quad \text{or} \quad \left.\frac{\partial S_1}{\partial V}\right|_{E,N} = \left.\frac{\partial S_2}{\partial V}\right|_{E,N}. \qquad \text{(Y) [2]}$$

Maximise S with respect to N interchange – vary N_1

$$\frac{\partial S}{\partial N_1} = \left.\frac{\partial S_1}{\partial N}\right|_{E,V} - \left.\frac{\partial S_2}{\partial N}\right|_{E,V} = 0 \quad \text{or} \quad \left.\frac{\partial S_1}{\partial N}\right|_{E,V} = \left.\frac{\partial S_2}{\partial N}\right|_{E,V}. \qquad \text{(Z) [2]}$$

Now

$$\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$$

so

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}E + \frac{p}{T}\mathrm{d}V - \frac{\mu}{T}\mathrm{d}N$$

$\Longrightarrow$

$$\left.\frac{\partial S}{\partial E}\right|_{V,N} = \frac{1}{T}, \quad \left.\frac{\partial S}{\partial V}\right|_{E,N} = \frac{p}{T}, \quad \left.\frac{\partial S}{\partial N}\right|_{E,V} = -\frac{\mu}{T} \qquad [2]$$

Now (X) gives $T_1 = T_2$. [2]

Now (Y) gives $p_1/T_1 = p_2/T_2$. But since $T_1 = T_2$ by (X) it follows that $p_1 = p_2$. [2]

Now (Z) gives $\mu_1/T_1 = \mu_2/T_2$. But since $T_1 = T_2$ by (X) it follows that $\mu_1 = \mu_2$. [2]

part c: [[14]]

d)

Entropy *maximum* requires that

$$\frac{\partial^2 S}{\partial E^2} < 0.$$

[3]

But since $\partial S/\partial E = 1/T$ it follows that

$$\begin{aligned}\frac{\partial^2 S}{\partial E^2} &= \frac{\partial}{\partial E}\frac{1}{T} \\ &= -\frac{1}{T^2}\frac{\partial T}{\partial E} \\ &= -\frac{1}{T^2 C_v}.\end{aligned}$$

[4]

So since we require $\partial^2 S/\partial E^2 < 0$ and, of course, $T^2 > 0$, we see that

$$C_v > 0$$

as required. [3]

part d: [[10]]

Total Q1: [[[40]]]

Question 2

a) Virial expansion

$$\frac{P}{kT} = \frac{N}{V} + B_2(T)\left(\frac{N}{V}\right)^2 + B_3(T)\left(\frac{N}{V}\right)^3 + \cdots$$ [3]

This is an expansion in density N/V.
So validity for truncation is low density [3]

[[6]]

b) Re-write vdW eq^n as

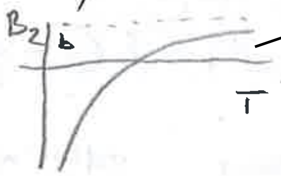
$$\frac{P}{kT} = \frac{N}{V-Nb} - \frac{aN^2}{kTV^2}$$

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

expand 1st term →

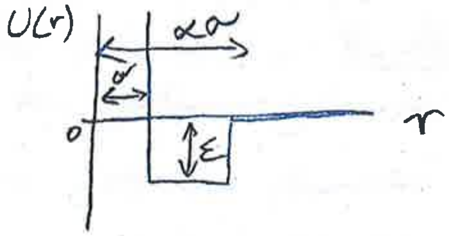
$$\frac{P}{kT} = \frac{N}{V} + \left(\frac{N}{V}\right)^2\left(b - \frac{a}{kT}\right) + \cdots$$ [1]

So $$B_2(T) = b - \frac{a}{kT}$$ [1]



[[4]]

c)



[3]

σ: hard core diameter [1]
ε: depth of attractive well [1]
α: factor for attractive well range [1]

[[6]]

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d) Split integral into 3 regions:

$$e^{-U(r)/kT} = 0 \qquad 0 < r < \sigma$$ [4]
$$= e^{\varepsilon/kT} \qquad \sigma < r < \alpha\sigma$$
$$= 1 \qquad \alpha\sigma < r < \infty$$

So $B_2(T) = -2\pi\left\{(-1)\int_0^\sigma r^2 dr + (e^{\varepsilon/kT}-1)\int_\sigma^{\alpha\sigma} r^2 dr\right\}$ [4]

$= \frac{2}{3}\pi\sigma^3\left\{1-(\alpha^3-1)(e^{\varepsilon/kT}-1)\right\}$ [4]

[[12]]

e) Expand exponential: $e^{\varepsilon/kT}-1 \rightarrow \varepsilon/kT$ [2]

α is large so $\alpha^3-1 \rightarrow \alpha^3$ [2]

So $B_2(T) \rightarrow \frac{2}{3}\pi\sigma^3\left(1-\frac{\alpha^3\varepsilon}{kT}\right)$ [2]

[[6]]

f) vdW: $B_2(T) = b\left(1-\frac{a}{bkT}\right)$ — sq well limit: $B_2T = \frac{2}{3}\pi\sigma^3\left(1-\frac{\alpha^3\varepsilon}{kT}\right)$ [2]

Can say vdW model corresponds to sq well model in limit of small attraction of infinite range. (or more generally, of general interaction of small attraction and infinite range. [4]

Also identify $b \leftrightarrow \frac{2}{3}\pi\sigma^3$ hard core 'excluded' volume [[6]]

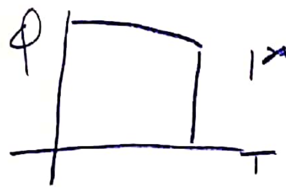
Total Q2 [[[40]]]

Question 3

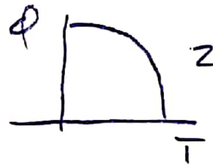
a) <u>Order Parameter</u> is a quantity giving a measure of the <u>order</u> in the ordered phase.
It may be a scalar, vector, complex, tensor. [2]

In a 1st order transition the order parameter goes to zero <u>discontinuously</u> at the transition [2]

In a 2nd order transition the order parameter goes to zero <u>continuously</u> at the transition [2]



1st order



2nd order.

[[6]]

(Diagrams <u>not</u> required)

b) Order parameter for ferroelectric is the electric polarization $\underset{\sim}{P}$. [2]
But it can point only along a given axis related to the crystal structure.
So strictly the order parameter is a scalar - not a vector. [2]

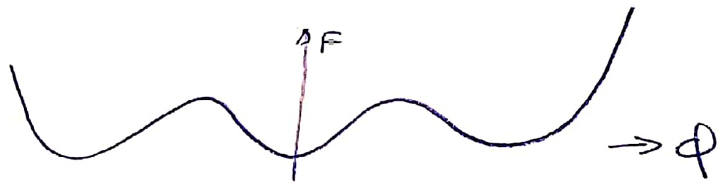
[[4]]

c) Series is terminated at the lowest even power that is capable of exhibiting the correct generic behaviour at the transition. It must be an even power with positive coefficient so that the energy is bounded — i.e. the system is stable. [4]

There are no odd powers in the expansion because of inversion symmetry. — If we replace P by $-P$ then the free energy must be unchanged. [2]

And the free energy is a scalar, so the only way of making a scalar from inversion-symmetric P is to have [2] powers of P^2

[[8]]

d)  [2]

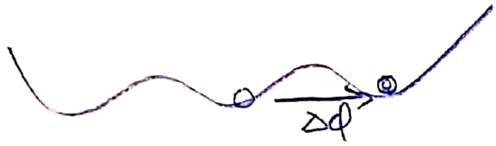
This is the general form of a 6^{th} order polynomial.

When the central minimum is below the other two, we are in the $\phi = 0$ disordered (high-T) state. [2]

But when the side minima fall below the central one then we will have a discontinuous jump of ϕ to a non-zero value. [2]

— i.e a 1^{st} order transition

← high T (disorder) [2]



Transition point [2]
Jump in ϕ

Low T (order). [2]

[[8]]

e) For the transition to be 1st order

We require $F_4 < 0$ & $F_6 > 0$.

If F_4 becomes positive then we

no longer need the F_6 term.

When $F_4 > 0$ the transition is 2nd order. [[6]]

f) At the transition the minima are at the

same height. Let us put $F_0 = 0$ so

the central minimum is at $F = 0$ and

so the outer ones 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 $\frac{dF}{d\phi} = 0$ – i.e. $2F_2\phi + 4F_4\phi^3 + 6F_6\phi^5 = 0$

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

Have simultaneous equations

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

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

Eliminate F_2

$\rightarrow$ $F_4 + 2F_6 \phi^2 = 0$ or $\phi = \sqrt{-\frac{F_4}{2F_6}}$

<u>But</u> F_6 is +ve , F_4 is −ve

and this gives the $\phi \neq 0$ roots.

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

or $\Delta\phi = \sqrt{\frac{-F_4}{2F_6}}$ [6]

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 [2]

[[8]]

Total Q4 [[[40]]]

Q4

Landau - Einstein Views:

* The L+L book on Statistical Physics derives all of macroscopic thermodynamics from microscopic first principles
* Einstein, in his debates with others on the fundamentals of Quantum Mechanics, often used purely thermodynamic arguments.
* The Landau view is pure reductionism. This was exemplified by much of Boltzmann's work on thermodynamics — and, of course, strongly criticised by Ernst Mach.
* Arguments from pure classical Thermodynamics relate physical phenomena that are independent of microscopic structure. In this respect one may say that the properties that can be related using classical thermodynamics are universal, independent of the microscopic, whereas those which cannot are system-specific. An elegant example is Onsager's rule for the reciprocity of transport coefficients - such as for thermoelectricity.

'Perverse' behavior

* Einstein was much alarmed by Quantum Mechanics - an ultimate in microscopics
* The Einstein model of heat capacity is a good example of this.
* BEC is also a possible example
* Landau was the great 'Model builder' — nothing could be further from the reductionist approach.
* The Landau theory of Phase Transitions is a great example where one specifically eschews the microscopics.
* He used the concept of the "effective hamiltonian": an up-front statement that he was not interested in the ultimate microscopic description.

Emergence

* The basic idea of Emergence is that different descriptions are appropriate for different scales.

* Thus one talks of the temperature of a collection of electrons, but the temperature of a single electron is meaningless.

* The behaviour at the macroscopic level must be consistent with the microscopic — but not necessarily derivable from it.

* Indeed one expects the macroscopic description to be robust against microscopic changes.

* Example: thermal equilibrium requires interactions but the nature of the thermal equilibrium does not depend on the precise nature of the (small) interactions.

3 marks for each bullet point
to maximum of 40

Question 5

a) For <u>distinguishable</u> particles $Z = z^N$
Since we multiply the PFs for different systems — probabilities must multiply and extensive quantities are additive.

Indistinguishable particles can be interchanged without changing the state. So then z^N overcounts the number of distinguishable states. Since N particles can be re-arranged in $N!$ ways so the $\frac{1}{N!}$ is required to remove the overcounting. [6]
(Assuming negligible multiple occupancy).

b) $F = E - TS$ so $dF = dE - TdS - SdE$
but $dE = TdS - pdV + \mu dN$
so $dF = -SdT - pdV + \mu dN$
and $p = -\left.\frac{\partial F}{\partial V}\right|_{T,N}$.

Since $F = -kT \ln Z$
it then follows that $p = kT \left.\frac{\partial \ln Z}{\partial V}\right|_{T,N}$ [6]

c) $Z = \frac{1}{N!} z^N$

So $\ln Z = N \ln z - \ln N!$

$$P = kT \frac{\partial \ln Z}{\partial V} = NkT \frac{\partial \ln z}{\partial \ln V}$$

as $\ln z = \ln V + \ln \left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2}$

so $$\frac{\partial \ln z}{\partial V} = \frac{\partial \ln V}{\partial V} = \frac{1}{V}$$

so $P = \frac{NkT}{V}$ which is the ideal gas eqn of state [[6]]

d) Temperature → Thermal energy kT

→ kinetic energy $\frac{1}{2}mv^2$

→ velocity $v = \sqrt{\frac{2kT}{m}}$

→ momentum $p = \sqrt{2mkT}$

→ Wave number $k = \sqrt{\frac{2mkT}{\hbar^2}}$

→ Wave length $\lambda = \frac{2\pi}{k} = 2\pi\sqrt{\frac{\hbar^2}{2mkT}}$

Which is almost Λ [[6]]

e) Split interaction into
hard core repulsion
weak long range attraction

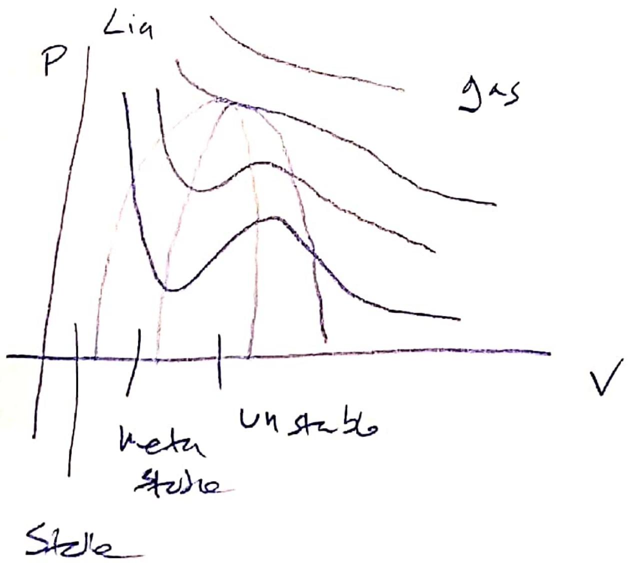
* Account for repulsion by simply excluding the volume from the PF calculation (V_{ex})

* Account for attraction by small mean energy $\langle E \rangle$ thus

$$Z = \frac{V}{\Lambda^3} \longrightarrow \frac{V - V_{ex}}{\Lambda^3} e^{-\langle E \rangle / kT}$$ [[6]]

f) Many-body problem reduced to a single-particle immersed in a "mean field". [[4]]

g)



[[6]]

Question 5 total [[[40]]]