PH4211 Statistical Mechanics 2021
Outline Answers

Question 1

a)

Terms in the equation:

x is the concentration of one of the atomic species.

N is the total number of atoms.

k is Boltzmann's constant.

T is temperature

T_c is the critical temperature [4]

Structure of the expression

First term is the energy of mixing.

– The T_c incorporates the interaction energies

– .. *of mixing* means the terms in x and $1 - x$ are removed from the *total* internal energy.

– The factor $x(1 - x)$ gives symmetry about $x = \frac{1}{2}$ (regular solution).

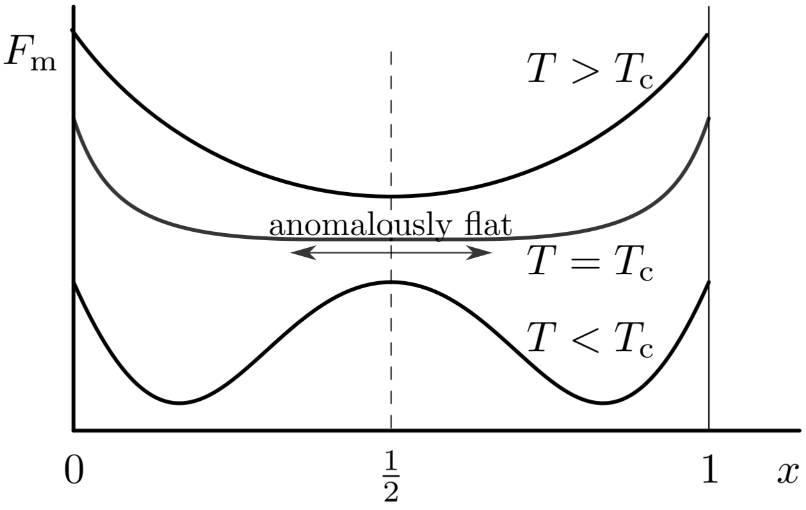
Second term is the entropy term (TS).

– Entropy characteristic of a two state system. [4]

part a: [[8]]

b)

Sketch of $F_m(x)$:



[4]

The curves are symmetrical about $x = \frac{1}{2}$.

(i) For $T > T_\mathrm{c}$ there is a single minimum (at $x = \frac{1}{2}$).

(ii) At $T = T_\mathrm{c}$ the minimum has become *anomalously broad*; the quadratic term has vanished.

(iii) For $T < T_\mathrm{c}$ there are two minima (spaced equally about $x = \frac{1}{2}$). [4]

part b: [[8]]

c)

In the $T < T_\mathrm{c}$ case the equilibrium state is determined by the *double tangent construction.* The curve indicates the free energy for the *homogeneous* system. But when the free energy is concave (from below) the system can lower its free energy by "dropping off" the curve and forming regions of lower x and regions of higher x – subject to the mean overall concentration remaining the same. The lowest free energy possible is when the x values are those at the two minima – hence the double tangent construction.

part c: [[6]]

d)

Expansion of $F_\mathrm{m}(x)$:

(i) Critical point is at $x = \frac{1}{2}$ (so $x - \frac{1}{2}$ is a sensible order parameter) and this is an expansion "at the critical point". [4]

(ii) In a first order phase transition you usually go to the 6th power of the order parameter – terminate at the third term. But here we terminate at the 4th power of the order parameter – the second term. This might seem surprising.

The explanation is that we are considering the *critical point.* And at the critical point the first order transition *goes second order*; the jump in the order parameter goes to zero. [4]

part d: [[8]]

e)

Write the order parameter $x - \frac{1}{2} = \varphi$. Then the (terminated) Landau free energy may be written

$$F = a(T - T_\mathrm{c})\varphi^2 + b\varphi^4$$

ignoring the F_0 term.

The equilibrium state is determined by $\partial F/\partial\varphi = 0$; so differentiate

$$\frac{\partial F}{\partial \varphi} = 2a(T - T_\mathrm{c})\varphi + 4b\varphi^3 = 0.$$

We discard the $\varphi = 0$ term, giving

$$a(T - T_\mathrm{c}) + 2b\varphi^2 = 0.$$

This has solution

$$\varphi = \pm\sqrt{\frac{a}{2b}}\,(T_\mathrm{c} - T)^{1/2}.$$

So the critical exponent β is $\frac{1}{2}$. [8]

Mean field / Landau treatment ignores fluctuations at the critical point. The observed behaviour is closer to $\beta = \frac{1}{3}$. [2]

part e: [[10]]

question total: [[[40]]]

Question 2

Essay question

Isolated → open:

Isolated system – all microstates equally likely.

Extend to open system by considering open system + "reservoir" as an isolated system – so to *that* composite system one applies the fundamental postulate. Thus for open systems the probability of a microstate is given by a Boltzmann factor, Gibbs factor etc.

In the process one needs to generalise the Boltzmann entropy to the Gibbs entropy. Done ny considering an *ensemble* of open systems, but where the ensemble itself is isolated.

Arguments apply if one allows just thermal interaction with the outside (Boltzmann factor), or particle exchange as well (Gibbs factor), or indeed any more general interaction. [[20]]

Equilibrium → non-equilibrium:

Basic point is the *Onsager hypothesis*, that the average regression of a fluctuation is the same whether it arises as an equilibrium fluctuation or following a disturbance from equilibrium.

Fluctuations are a "microscopic" phenomenon, whereas "equilibrium" is a macroscopic phenomenon: at the microscopic level the system doesn't "know" whether it is in equilibrium or not.

(These ideas have their origin in Onsager's reciprocity theorem, but that is not part of the course.)

Justification for Onsager hypothesis is in *linear response theory*. The notes/book (but not the lectures/recordings) use the approach whereby a nonequilibrium intital condition may be regarded as an equilibrium state of a system with a *different* hamiltonian. Students might have studied this – it is not expected/required, but some bonus marks would be awarded for this. [[20]]

question total:[[[40]]]

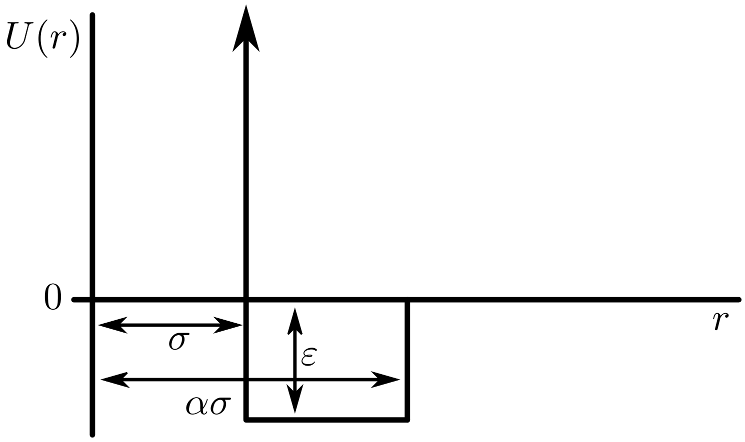
Question 3

a)

Validity: low density. part a: [[3]]

b)

Sketch potential



[3]

σ: hard core diameter

ε: depth of attractive well

α: factor for attractive well extent [3]

part b: [[6]]

c)

For this potential

$$\begin{aligned} e^{-U(r)/kT} &= 0 \qquad & 0 < r < \sigma \\ &= e^{\varepsilon/kT} \qquad & \sigma < r < \alpha\sigma \\ &= 1 \qquad & \alpha\sigma < r < \infty \end{aligned}$$

[3]

so do integral for the three separate regions:

$$\begin{aligned} B_2(T) &= -2\pi \left\{ (-1) \int\limits_0^{\sigma} r^2 \mathrm{d}r + \left(e^{\varepsilon/kT} - 1\right) \int\limits_{\sigma}^{\alpha\sigma} r^2 \mathrm{d}r \right\} \\ &= \frac{2}{3}\pi\sigma^3 \left\{ 1 - \left(\alpha^3 - 1\right)\left(e^{\varepsilon/kT} - 1\right) \right\} \end{aligned}$$

as required. [6]

part c: [[9]]

d)

When $T \to \infty$ then $e^{\varepsilon/kT} \to 1$. So in this limit $B_2(T) \to \frac{2}{3}\pi\sigma^3$. [4]

Significance is that when $T \to \infty$, the B_2 will *saturate* at the hard core value. [4]

part d: [[8]]

e)

At $T = T_\mathrm{B}$ we have

$$\left(\alpha^3 - 1\right)\left(e^{\varepsilon/kT} - 1\right) = 1$$

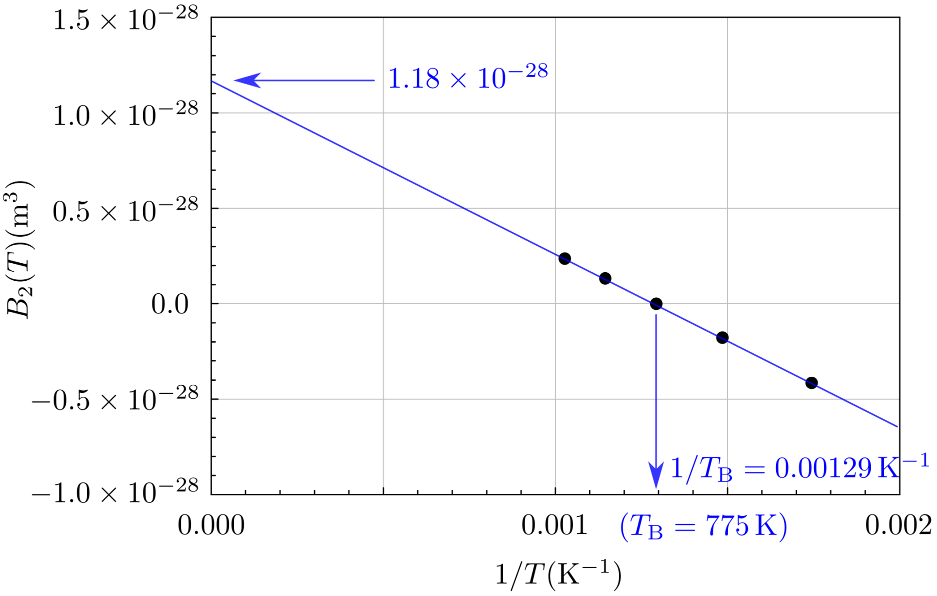
so that

$$T_\mathrm{B} = \frac{\varepsilon/k}{\ln\left(\frac{\alpha^3}{\alpha^3 - 1}\right)}\,.$$

part e: [[4]]

f)

Data points fall reasonably well on a straight line.



(i) The zero of $B_2(T)$ falls at $1/T_\mathrm{B} = 0.00129\,\mathrm{K}^{-1}$, corresponding to a Boyle temperature of 775 K. We are given that $\alpha = 1.6$. So

$$T_\mathrm{B} = \frac{\varepsilon/k}{\ln\left(\frac{\alpha^3}{\alpha^3 - 1}\right)} = \frac{\varepsilon/k}{\ln\left(\frac{4.10}{3.10}\right)} = 3.57\varepsilon/k\,.$$

And then

$$\varepsilon/k = T_\mathrm{B}/3.57.$$

But since $T_\mathrm{B} = 775\,\mathrm{K}$, it follows that

$$\boxed{\varepsilon/k = 217\,\mathrm{K}} \quad \text{or} \quad \boxed{\varepsilon = 2.99 \times 10^{-21}\,\mathrm{J}}$$

[5]

(ii) We saw the $T \to \infty$ limit of $B_2(T)$ is $\frac{2}{3}\pi\sigma^3$. Extrapolating the line through the data points gives $B_2(T \to \infty) = 1.18 \times 10^{-28}\,\mathrm{m}^3$.

So

$$\frac{2}{3}\pi\sigma^3 = 1.18 \times 10^{-28}\,\mathrm{m}^3$$

or

$$\sigma = \left(\frac{3}{2\pi} \times 1.18 \times 10^{-28}\right)^{1/3}\,\mathrm{m}$$

or

$$\boxed{\sigma = 3.83 \times 10^{-10}\,\mathrm{m}}$$

[5]

part f: [[10]]

question total: [[[40]]]

Question 4

a)

A system in thermal contact with a reservoir can exchange energy with the reservoir. It is assumed the *sum* of the system energy and the reservoir energy is fixed. But different partitions of the energy between system and reservoir are possible with different probabilities. One can talk about the *mean* energy of the system, but there will bw fluctuations about this mean. In general a system at fixed temperature will have fluctuations in its energy and a system at fixed energy will have fluctuations in its temperature. part a:[[6]]

b)

This is the square root of the mean of the square of the deviation of the energy from its mean value: root mean square. The point is that there will be an instantaneous deviation of the energy from its mean: this is $E - \langle E \rangle$. This quantity will sometimes be positive and sometimes negative; indeed its mean is zero. So if we square it we get something that is positive for both positive and negative fluctuations. It has a non-zero mean with the dimensions of energy squared. The square root of this, σ_E, has the dimensions of energy: it is the 'typical' magnitude of an energy fluctuation. part b: [[6]]

c)

From the expression for σ_E we have

$$\sigma_E^2 = \left\langle (E - \langle E \rangle)^2 \right\rangle .$$

Expand the square:

$$\begin{aligned}\sigma_E^2 &= \left\langle E^2 - 2E \langle E \rangle + \langle E \rangle^2 \right\rangle \\ &= \left\langle E^2 \right\rangle - 2 \langle E \rangle \langle E \rangle + \langle E \rangle^2 \\ &= \left\langle E^2 \right\rangle - \langle E \rangle^2 .\end{aligned} \qquad [4]$$

d)

The mean value of a quantity A is the sum of all possible values A_j multiplied by the probability p_j of the occurrence:

$$\langle A \rangle = \sum_j A_j p_j . \qquad [2]$$

A system at temperature T will be found in the microstate of energy E_j with a probability $p_j = e^{-E_j/kT}/Z$. This is the Boltzmann probability distribution function.

And so the mean energy is

$$\langle E \rangle = \frac{1}{Z} \sum_j E_j \, e^{-E_j/kT} . \qquad [2]$$

Z is the partition function. [2]

part d: [[6]]

e)

By argument similar to the previous section

$$\left\langle E^2 \right\rangle = \frac{1}{Z} \sum_j E_j^2 \, e^{-E_j/kT}. \qquad [2]$$

Use the 'beta trick': put $\beta = 1/kT$. Then since $\frac{\partial}{\partial\beta} e^{-\beta E_j} = -E_j e^{-\beta E_j}$ we have

$$\frac{\partial Z}{\partial \beta} = -\sum_j E_j \, e^{-\beta E_j} = -Z \left\langle E \right\rangle \qquad \text{(P) [2]}$$

and differentiating again:

$$\frac{\partial^2 Z}{\partial \beta^2} = +\sum_j E_j^2 \, e^{-\beta E_j} = Z \left\langle E^2 \right\rangle. \qquad \text{(Q) [2]}$$

But the derivative of the right-most expression of (P) gives

$$\frac{\partial^2 Z}{\partial \beta^2} = -\frac{\partial Z}{\partial \beta} \left\langle E \right\rangle - Z \frac{\partial \left\langle E \right\rangle}{\partial \beta}.$$

Equating this with the right-most expression of (Q) gives

$$Z \left\langle E^2 \right\rangle = -\frac{\partial Z}{\partial \beta} \left\langle E \right\rangle - Z \frac{\partial \left\langle E \right\rangle}{\partial \beta}$$

or

$$\left\langle E^2 \right\rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} \left\langle E \right\rangle - \frac{\partial \left\langle E \right\rangle}{\partial \beta}.$$

But $\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\left\langle E \right\rangle$ and so

$$\left\langle E^2 \right\rangle = \left\langle E \right\rangle^2 - \frac{\partial \left\langle E \right\rangle}{\partial \beta}$$

or

$$\sigma_E^2 = -\frac{\partial \left\langle E \right\rangle}{\partial \beta}. \qquad \text{(R) [3]}$$

Now we convert from β back to T:

$$\frac{\partial}{\partial \beta} = \frac{\partial}{\partial T} \Bigg/ \frac{\mathrm{d}\beta}{\mathrm{d}T}$$

and $\mathrm{d}\beta/\mathrm{d}T = -1/kT^2$. Then

$$\begin{aligned} \frac{\partial \left\langle E \right\rangle}{\partial \beta} &= -kT^2 \frac{\partial \left\langle E \right\rangle}{\partial T} \\ &= -kT^2 C_V. \end{aligned}$$

Combine this with Eq. (R) gives

$$\sigma_E^2 = kT^2 C_V$$

or

$$\sigma_E = \sqrt{kT^2 C_V}. \qquad [3]$$

part e: [[12]]

f)

Since C_V is extensive: i.e. $C_V \propto N$ it means that

$$\sigma_E \propto \sqrt{N}. \qquad [2]$$

So the size of the fluctuations does increase with the size of the system – and indeed tends to infinity as $N \to \infty$.

BUT it is the *fractional* fluctuations, $\sigma_E / \langle E \rangle$, that are important. And since E, also, is extensive it follows that

$$\frac{\sigma_E}{\langle E \rangle} \propto \frac{1}{\sqrt{N}}.$$

So in the thermodynamic limit ($N \to \infty$) we see that the fractional fluctuations vanish. [2]

part 4: [[4]]

g

An exception is the fluctuation in the order parameter at the critical point of a phase transition. Here the free energy minimum of the equilibrium state becomes anomalously broad. Then one can have diverging fluctuations in the order parameter at negligible free energy cost. Since this is accompanied by a diverging heat capacity, there is no contradiction with the discussion of the previous part. [2]

part g: [[2]]

question total: [[[40]]]

Question 5

a)

Ordinate (vertical axis) is temperature divided by the critical temperature for the atom/molecule. Abscissa (horizontal axis) is density divided by the critical density for the atom/molecule.

This is a *coexistence* plot; the left side shows the gas phase and the right side shows the liquid phase. part a: [[8]]

b)

The essential assumption is that the inter-particle potential is a *universal* function, scaled (vertically) by an energy parameter ε, and (horizontally) by a distance parameter σ: $U(r) = \varepsilon f(r/\sigma)$. (Like the Lennard-Jones 6–12 potential.)

It follows, from this, that the partition function will be a universal function, when its arguments are scaled by the appropriate powers of ε and σ. – For example, temperature is scaled by ε/k, density is scaled by σ^{-3}. Similarly for $F(T, V, N) = -kT \ln Z$, so that $F/N = f(kT/\varepsilon, V/\sigma^3)$

The same scaling is applied to the points in the Guggenheim plot. Thus, the essential assumption leads to the collapse of the data on the plot: $T/T_\mathrm{c} = t(\rho/\rho_\mathrm{c})$, since $kT_\mathrm{c} = \mathrm{const} \times \varepsilon$ and $\rho_\mathrm{c} = \mathrm{const} \times N/\sigma^3$.

part b: [[9]]

c)

i) The order parameter for the liquid–gas transition is the difference between the density and the critical density: $\rho - \rho_\mathrm{c}$. So this is the series expansion for the order parameter. The $1/3$ is the exponent in the singular part of the expansion; thus it is critical exponent for the order parameter.

[5]

ii) Quantum effects are important for helium. Thermal de Broglie wavelength becomes comparable with or greater than the particle size. Effect is greater as the mass is smaller. So we see a *slight* deviation for liquid Ne, a significant effect for ^{4}He and an even greater effect for ^{3}He.

[5]

iii) The critical point of the liquid-gas transition is of the Ising universality class – scalar order parameter. This applies to helium as to other liquids. You need to be *very close* to T_c to observe this – effect of fluctuations. So if you were to plot the Guggenheim plot *very close* to the critical point, *then* the helium points will collapse onto the other points. [5]

part c: [[15]]

d)

Universality really means same behaviour for *different* systems (in the vicinity of the critical point). – For example Ising magnet and liquid–gas system.

So whereas the Guggenheim plot indicates collapse of all the plotted gases (except the heliums) the real reason for the Guggenheim behaviour is the "universality" of the interaction – discussed in

b) above. It is *not* universality in the critical point sense. Moreover, the Guggenheim fit formula holds over a wide range – not just in the vicinity of $T_{\rm c}$

One might argue, if the data were available, that the helium behaviour close to $T_{\rm c}$ *would* be an indication of universality if it collapsed.

part d: [[8]]

question total: [[[40]]]