

PH4211 Statistical Mechanics 2017

Outline Answers

Question 1

a)

Boltzmann entropy defined by $S = k \ln \Omega$ where Ω is the number of microstates in the macrostate (for an isolated system). [3]

Fundamental postulate of Statistical Mechanics: *In an isolated system all microstates in the macrostate are equally likely.* [3]

\implies Most probable macrostate is the one with the largest number of microstates. [3]

— I.e. the macrostate with the largest entropy. [3]

part a: [[12]]

b)

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.

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

Let's work with entropy:

$$S = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2).$$

Maximise S with respect to E interchange – vary E_1

$$\frac{\partial S}{\partial E_1} = \frac{\partial S_1}{\partial E} \Big|_{V,N} - \frac{\partial S_2}{\partial E} \Big|_{V,N} = 0 \quad \text{or} \quad \frac{\partial S_1}{\partial E} \Big|_{V,N} = \frac{\partial S_2}{\partial E} \Big|_{V,N}. \quad (\text{X}) [3]$$

Maximise S with respect to V interchange – vary V_1

$$\frac{\partial S}{\partial V_1} = \frac{\partial S_1}{\partial V} \Big|_{E,N} - \frac{\partial S_2}{\partial V} \Big|_{E,N} = 0 \quad \text{or} \quad \frac{\partial S_1}{\partial V} \Big|_{E,N} = \frac{\partial S_2}{\partial V} \Big|_{E,N}. \quad (\text{Y}) [3]$$

Maximise S with respect to N interchange – vary N_1

$$\frac{\partial S}{\partial N_1} = \frac{\partial S_1}{\partial N} \Big|_{E,V} - \frac{\partial S_2}{\partial N} \Big|_{E,V} = 0 \quad \text{or} \quad \frac{\partial S_1}{\partial N} \Big|_{E,V} = \frac{\partial S_2}{\partial N} \Big|_{E,V}. \quad (\text{Z}) [3]$$

Now

$$dE = TdS - pdV + \mu dN$$

so

$$dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$$

$$\implies \quad \frac{\partial S}{\partial E} \Big|_{V,N} = \frac{1}{T}, \quad \frac{\partial S}{\partial V} \Big|_{E,N} = \frac{p}{T}, \quad \frac{\partial S}{\partial N} \Big|_{E,V} = -\frac{\mu}{T} \quad [1]$$

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 b: [[16]]

c)

i)

Condition (Y) gives

$$\frac{p_1}{T_1} = \frac{p_2}{T_2} \quad (P)$$

upon maximising the entropy.

If you forbid E interchange then you will *not* get $T_1 = T_2$ by (X); in other words $T_1 \neq T_2$.

But mechanical equilibrium requires

$$p_1 = p_2 \quad (Q)$$

See that (P) and (Q) are incompatible if $T_1 \neq T_2$. This is the paradox. [3]

ii)

Simple answer:

If you don't allow exchange of E then you *cannot* achieve thermodynamic equilibrium. So then the maximization of S (or Ω) prescription is not applicable. [3]

So then $p_1/T_1 = p_2/T_2$ is not a valid inference. [3]

Further points:

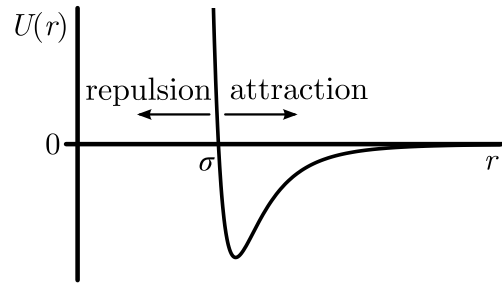
The 'mechanical' condition $p_1 = p_2$ is a 'stronger' condition. You expect it to apply in the absence of thermodynamic equilibrium. BUT if you release a piston in a cylinder then in the *absence of dissipation* the piston would oscillate and not even the mechanical equilibrium would be reached. [3]

part c: [[12]]

question total: [[[40]]]

Question 2

a)



The repulsive and the attractive parts are taken into account differently:

- The ‘hard’ repulsion effectively prevents particles approaching closer than σ . Thus a certain volume is unavailable and the approximation is simply to exclude this volume from the partition function

$$\frac{V}{\Lambda^3} \rightarrow \frac{V - V_{\text{ex}}}{\Lambda^3}. \quad [3]$$

- The ‘weak’ attraction is treated in ‘mean field’, by adding a mean field energy ε to the (free particle) energies in the partition function: $e^{-E_i/kT} \rightarrow e^{-(E_i+\varepsilon)/kT}$ so that

$$z \rightarrow ze^{-\varepsilon/kT}. \quad [3]$$

(Note ε will be $-ve$ for attraction).

So combining these two parts gives

$$z = \frac{V - V_{\text{ex}}}{\Lambda^3} e^{-\varepsilon/kT}. \quad [2]$$

part a: [[8]]

b)

$$\begin{aligned} F &= -kT \ln Z \\ &= -kT \ln \left(\frac{1}{N!} z^N \right) \\ &= -NkT \ln z + kT \ln N! \end{aligned} \quad [4]$$

but, from Stirling’s approximation

$$\ln N! \approx N \ln N - N = N \ln(N/e). \quad [2]$$

So

$$F = -NkT \ln \left(\frac{ze}{N} \right). \quad [2]$$

part b: [[8]]

c)

We need to use

$$p = - \left. \frac{\partial F}{\partial V} \right|_{T,N}.$$

So actually we need only the parts of Z that depend on V . Then let us write

$$\begin{aligned} \ln \left(\frac{ze}{N} \right) &= \ln z + \dots \\ &= \ln(V - V_{\text{ex}}) - \varepsilon(V)/kT + \dots \end{aligned}$$

since ε depends on volume.

So differentiating:

$$\frac{\partial(ze/N)}{\partial V} = \frac{1}{V - V_{\text{ex}}} - \frac{1}{kT} \frac{d\varepsilon}{dV}$$

or

$$\begin{aligned} p &= NkT \left(\frac{1}{V - V_{\text{ex}}} - \frac{1}{kT} \frac{d\varepsilon}{dV} \right) \\ &= \frac{NkT}{V - V_{\text{ex}}} - N \frac{d\varepsilon}{dV} \end{aligned} \tag{4}$$

or

$$\left(p + N \frac{d\varepsilon}{dV} \right) (V - V_{\text{ex}}) = NkT. \tag{2}$$

And this is equivalent to

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

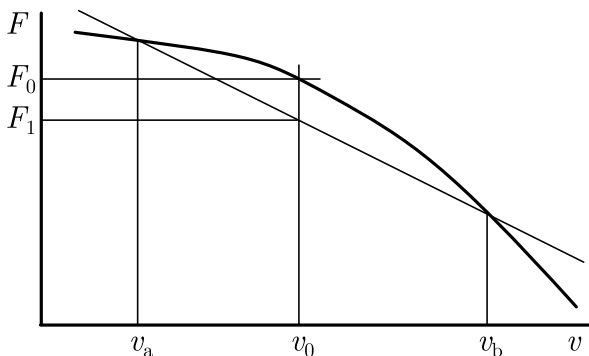
when

$$a = \frac{V^2}{N} \frac{d\varepsilon}{dV} \quad \text{and} \quad b = \frac{V_{\text{ex}}}{N}.$$

part c: [[8]]

d)

The curve gives the free energy of a *homogeneous* system.

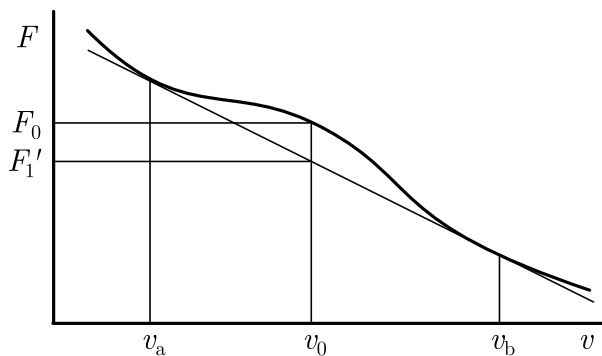


So, from the figure, if the specific volume (volume per particle) is v_0 , the free energy of the homogeneous system will be F_0 .

But if the system were *inhomogeneous* with a fraction (higher density: liquid) at specific volume v_a and a fraction (lower density: gas) at v_b , subject to the *mean* specific volume remaining v_0 , the free energy would drop to F_1 . We have a straight line because the volume is extensive / additive.

Then with the free energy curve above (concave function) it is preferable for the system to go inhomogeneous. [4]

It would be preferable for the free energy to go lower and lower, with v_a and v_b getting further and further apart. The lowest F could go is shown on the diagram below.



This is the *double tangent* construction. The free energy has dropped to F'_1 , the lowest possible (subject to the v_0 constraint). [4]

part d: [[8]]

e)

At the critical point the distinction between the liquid and gas disappears: $v_a - v_b \rightarrow 0$. The concavity just vanishes. The two tangent points become degenerate; the double tangent becomes a simple tangent. part e: [[8]]

question total: [[[40]]]

Question 3

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 be 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. [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. [6]

c)

From the expression for σ_E we have

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

Expand the square:

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

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:

$$\langle A \rangle = \sum_j A_j p_j. \quad [3]$$

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

$$\langle E \rangle = \frac{1}{Z} \sum_j E_j e^{-E_j/kT}. \quad [3]$$

part d: [[6]]

e)

By argument similar to the previous section

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

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

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

and differentiating again:

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

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

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

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

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

or

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

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

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

or

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

Now we convert from β back to T :

$$\frac{\partial}{\partial \beta} = \frac{\partial}{\partial T} \bigg/ \frac{d\beta}{dT}$$

and $d\beta/dT = -1/kT^2$. Then

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

Combine this with Eq. (R) gives

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

or

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

part e: [[6]]

f)

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

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

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

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 ($N \rightarrow \infty$) we see that the fractional fluctuations vanish. [2]

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 f: [[6]]

question total: [[[40]]]

Question 4

a)

Helmholtz free energy is $F = E - TS$. In zero external field energy E will be the ‘self energy’ term ($\propto -mb$) of the Weiss mean field ($b \propto m$). So the E term will be proportional to m^2 and it comes out as

$$E = -\frac{Nk}{2}T_c m^2.$$

The entropy S is that of a two state system (assuming spin $S = 1/2$). This will be expanded as an (even) power series in m . In accordance with the Landau prescription we terminate at the fourth power. [4]

T is temperature

T_c is the critical temperature

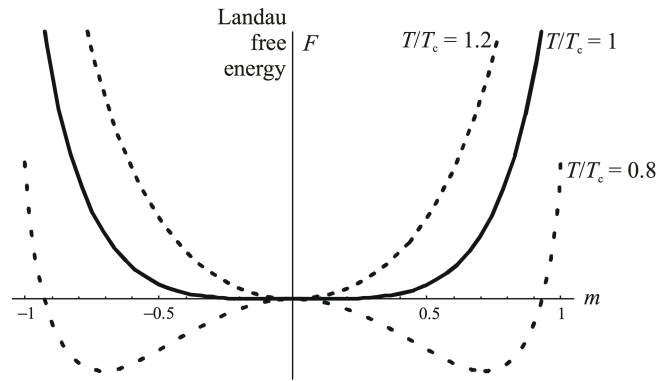
N is the number of magnetic spins

m is the order parameter – magnetization normalized to the saturation magnetization

k is Boltzmann’s constant. [4]

part a: [[8]]

b)



At high temperature there is one minimum at $m = 0$ so the order parameter is zero; no spontaneous magnetization.

At low temperature there are minima at non-zero m ; there is a spontaneous magnetization.

As the system is cooled through T_c the single minimum gradually evolves into the single maximum and two minima. The magnetization gradually grows from zero. [6]

At $T = T_c$ the free energy minimum is anomalously broad so variations in m can occur at no energy cost: divergent fluctuations. [2]

part b [[8]]

c)

Equilibrium state found by minimizing F with respect to m . Differentiate and set equal to zero

$$\frac{\partial F}{\partial m} = Nk(T - T_c)m + \frac{1}{3}NkT_c m^3 = 0.$$

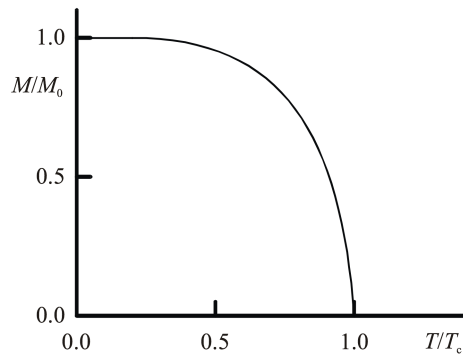
We have the trivial root at $m = 0$; can factorize this out. So

$$Nk(T - T_c) + \frac{1}{3}NkT_c m^2 = 0$$

or

$$m = \pm \sqrt{\frac{3(T_c - T)}{T_c}}. \quad [8]$$

This is plotted below



[2]

part c [[10]]

d)

The transition is second order because m goes to zero continuously as T goes to T_c from below: as we have shown, $m \propto \sqrt{T - T_c}$. part d: [[6]]

e)

Entropy is given by

$$S = -\frac{\partial F}{\partial T}$$

so differentiating the given F :

$$S = -\frac{Nk}{2}m^2$$

and since m^2 is given by

$$m^2 = \frac{3(T_c - T)}{T_c}$$

it follows that

$$S = \frac{3}{2}Nk\frac{T - T_c}{T_c}. \quad [6]$$

(This is an 'extra' (negative) contribution to S arising from the non-zero m .)

We express the heat capacity as

$$C = T\frac{\partial S}{\partial T}$$

so the jump in heat capacity is

$$\Delta C = \frac{3}{2}Nk$$

since we evaluate the derivative at $T = T_c$. [2]

part e: [[8]]

question total: [[[40]]]

Question 5

Essay question – important points are:

- Classical mechanics \implies Liouville's theorem \implies density of points in phase space ρ is *constant*. [5]
- Entropy is proportional to $-\langle \ln \rho \rangle$. [5]
- So Liouville's theorem \implies S is constant, but [5]
- Second Law says that S increases. [5]
- Discuss the nature of time evolution in phase space. [5]
- Dendritic flow gives the *appearance* of a reduction in ρ . [5]
- Uncertainty principle gives an ultimate resolution of regions of phase space. [5]
- Possible connection between quantum mechanics and the Second Law. [5]

question total: [[[40]]]