

PH4211 Statistical Mechanics 2018

Outline Answers

Question 1

a)

The order parameter is a quantity that measures the extent of the order. It is zero in the disordered phase and it will have finite values in the ordered phase. It might be normalized to unity in the fully ordered state. The order parameter may be a scalar, a complex number, a vector or a tensor of higher degree. part a: [[6]]

b)

The Landau expansion is terminated in order that it gives the *generic* features of the phase transition, unencumbered by extraneous detail. The highest power must be even with positive coefficient so that the system is stable (order parameter bounded). One takes the lowest power, consistent with this, that will give a transition. So if the coefficient of ϕ^4 is positive we will stop there, but if it is negative we will need to go to ϕ^6 or possibly higher. part b: [[8]]

c)

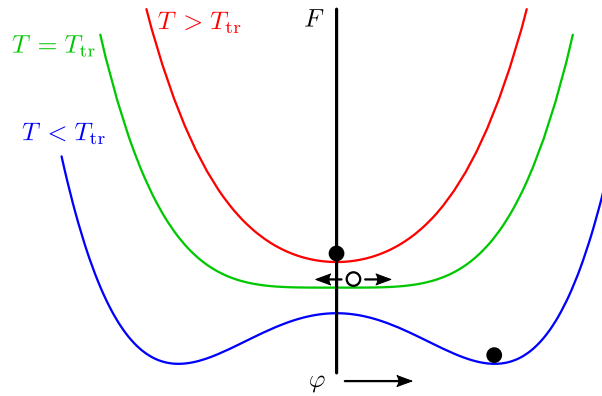
In the ferromagnetic transition the order parameter, the magnetization, is a *vector*. The free energy is a scalar. The only way of getting a scalar is by ‘dotting’ a vector with another. So in the absence of an external field the magnetization must be dotted with itself and so only even powers of the order parameter will be present. [3]

In the ferroelectric case, strictly speaking, the order parameter is a scalar: it is the electric polarization *along* the displacive direction. In this case we appeal to *inversion symmetry*. There is no difference between displacements in either direction. So in this case, also, there can be no odd powers. [3]

part c: [[6]]

d)

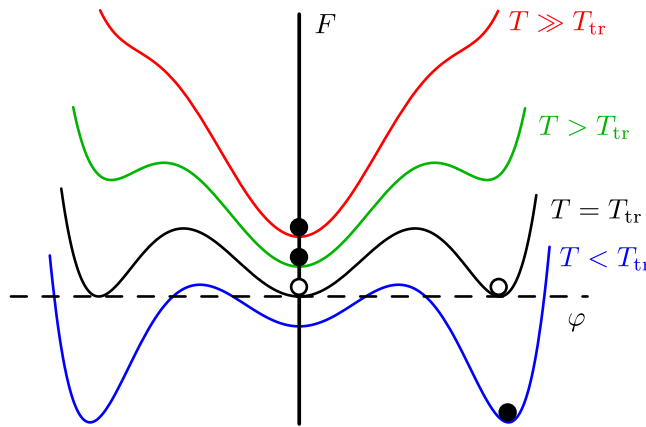
Ferromagnetic case:



At high temperatures (red line) there is a single minimum at $\varphi = 0$ and so there is no magnetization. Upon cooling through the transition two minima emerge from the single minimum together with a maximum. The minima indicate possible equilibria and we see they emerge *continuously* from the high temperature minimum. *Thus* the transition is second order. part d: [[6]]

e)

Ferroelectric case



At high temperatures (red line) there is a single minimum at $\varphi = 0$ and so there is no magnetization. Upon cooling (green line) extra minima appear, but the $\varphi = 0$ minimum is the favourable one. At the transition (black line) the other minima drop to the $\varphi = 0$ value. And at lower temperatures (blue line) the new minima are favourable. So at $T = T_{tr}$ there will be a *jump* in the order parameter from the middle to one of the outer minima. In this case there is a *jump* in the order parameter. *Thus* the transition is first order. part e: [[6]]

f)

In the Landau expansion

$$F = a + b\varphi^2 + c\varphi^4 + d\varphi^6$$

we have the first order case when c is negative and d is positive. However if c is positive, then we can terminate there and we have a second order transition. So the transition changes from first order to second order when c changes from negative to positive. part f: [[8]]

Total Q1: [[40]]

Question 2

a)

For an isolated system all microstates are equally probable. [3]

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. [3]

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 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:

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

Maximise S with respect to E interchange – vary E_1

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

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

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

\Rightarrow

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

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)

Entropy *maximum* requires that

$$\frac{\partial^2 S}{\partial E^2} < 0. \quad [3]$$

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

$$\begin{aligned} \frac{\partial^2 S}{\partial E^2} &= \frac{\partial}{\partial E} \frac{1}{T} \\ &= -\frac{1}{T^2} \frac{\partial T}{\partial E} \\ &= -\frac{1}{T^2 C_v}. \end{aligned} \quad [5]$$

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. [4]

part c: [[12]]

Total Q2: [[[40]]]

Question 3

a)

N : number of particles

T : temperature

T_c : critical temperature

x : concentration of one species

[2]

First term is the internal energy (of mixing).

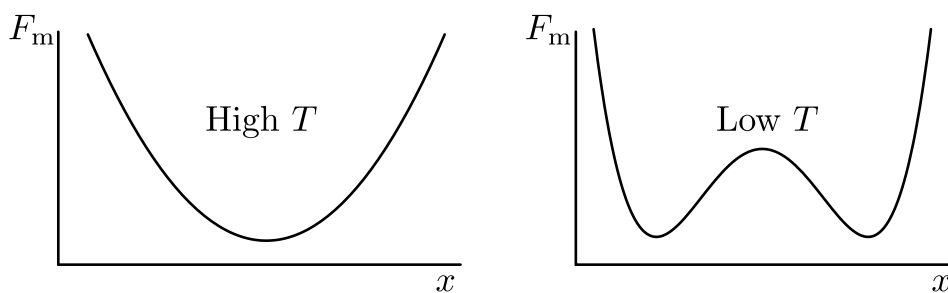
[2]

Second term is the entropy ($\sum P_j \ln P_j$ of a 2-state system).

[2]

part a: [[6]]

b)



[3+3]

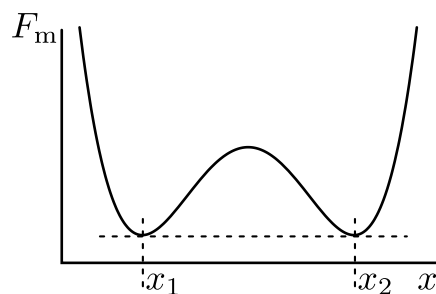
Important point that the curves are symmetrical. For the low T curve the minima are at the same level.

part b: [[6]]

c)

At high T there is no choice – state is determined by the concentration x .

At low T the state is determined by the *double tangent construction*:



there is a coexistence of regions at concentration x_1 and concentration x_2 .

part c: [[6]]

d)

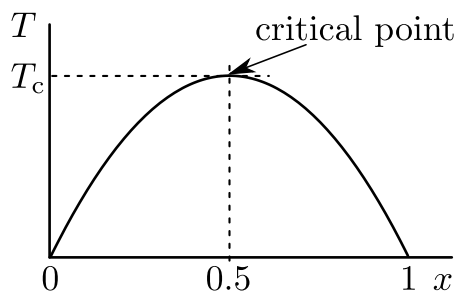
For the minima of the double tangent construction we have $\partial F_m / \partial x = 0$. So

$$\begin{aligned} \frac{\partial F_m}{\partial x} &= 2NkT_c(1 - 2x) + NkT[1 + \ln x - 1 - \ln(1 - x)] \\ &= 0 \end{aligned}$$

giving

$$T = \frac{2(1 - 2x)}{\ln[(1 - x)/x]} T_c. \tag{A}$$

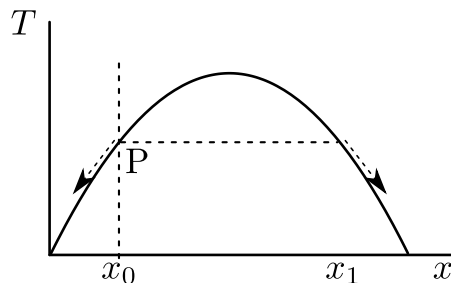
[3]



[3]

part d: [[6]]

e)



The initial concentration is x_0 .

As you cool, the system remains homogeneous until you hit the curve at point P. [2]

Then you nucleate concentrated regions with concentration x_1 . [1]

Then as you cool further the dilute phase at x_0 becomes depleted (left arrow) and the concentrated phase at x_1 becomes more concentrated (right arrow). [2]

You travel down the two curves to the concentrations 0 and 1 at $T = 0$. [1]

part e: [[6]]

f)

At this point the distinction between the two phases (the concentrated and the dilute) disappears. Upon cooling through this point (both) new phases emerge *continuously*. We may say that at this point the 1st order transition becomes 2nd order. [4]

part f: [[4]]

g)

Critical exponent β is defined from $(x - x_c) \propto (T_c - T)^\beta$ (where $x_c = \frac{1}{2}$) close to the transition. Expansion of Eq. (A) above gives $\beta = \frac{1}{2}$. But experiment gives more like $\beta = 1/3$. The difference lies in the limitations of mean field theory and its neglect of fluctuations in the vicinity of the critical point. part g: [6]

Total Q3: total [[[40]]]

Question 4

Essay on Brownian motion. Should include the following points

- Brown's observations on pollen powder suspended in/on water. [5]
- Erroneous deduction that particles are alive. [5]
- He saw same thing with stone dust and other "inert" matter powder!! [5]
- Einstein interpreted Brownian motion as movement of a *macroscopic* object through bombardment of microscopic atoms. [5]
- I.e. the effect of a *single* atomic bombardment is unobservable, but. . . [5]
- One sees the slight imbalances of many impacts. [5]
- This provides evidence of the atomic nature of matter. [5]
- Nice connections with equipartition. [5]

Total Q4: [[[40]]]

Question 5

a)

The integral for Z may be factorized into an integral over the p and an integral over the q :

$$Z = \frac{1}{N!h^{3N}} \int e^{-\sum_i \frac{p_i^2}{2m}/kT} d^{3N}p \int e^{-\sum_{i<j} U(q_i, q_j)/kT} d^{3N}q.$$

We note that if $U(q_i, q_j)$ were zero we would have the ideal (non-interacting) partition function

$$\begin{aligned} Z_{\text{id}} &= \frac{1}{N!h^{3N}} \int e^{-\sum_i \frac{p_i^2}{2m}/kT} d^{3N}p \int d^{3N}q \\ &= \frac{V^N}{N!h^{3N}} \int e^{-\sum_i \frac{p_i^2}{2m}/kT} d^{3N}p \end{aligned}$$

upon performing the q integrals.

We substitute this expression into the factorized Z expression, giving

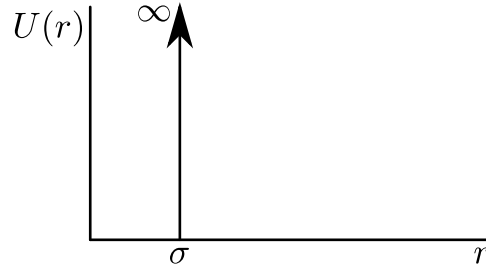
$$Z = Z_{\text{id}} \frac{1}{V^N} \int e^{-\sum_{i<j} U(q_i, q_j)/kT} d^{3N}q,$$

as required. [6]

We note that the V^N factor emerges from the integral over the q in the expression for Z_{id} . [2]

part a: [[8]]

b)



Here σ is the *diameter* of an atom since the closest distance between two atoms is the sum of the hard core radii of each. [4]

part b: [[4]]

c)

This expression for Z is like the ideal gas partition function, except that V is replaced by $V - Nb$. This is like the van der Waals incorporation of the repulsive part of the interaction, and it follows if one regards the atomic hard core as simply excluding available volume from the system. In other words we are saying that the integral in Eq. 5.1 is approximated by $(V - Nb)^N$.

part c: [[6]]

d)

Write the equation of state as

$$\begin{aligned} \frac{p}{kT} &= \frac{N}{V - Nb} \\ &= \frac{N}{V} \left(1 - \frac{Nb}{V}\right)^{-1} \end{aligned}$$

and then perform a binomial expansion

$$\begin{aligned} \frac{p}{kT} &= \frac{N}{V} \left\{ 1 + \frac{Nb}{V} + \left(\frac{Nb}{V}\right)^2 + \left(\frac{Nb}{V}\right)^3 + \dots \right\} \\ &= \frac{N}{V} + b \left(\frac{N}{V}\right)^2 + b^2 \left(\frac{N}{V}\right)^3 + b^3 \left(\frac{N}{V}\right)^4 + \dots \end{aligned}$$

[5]

From this we identify directly

$$B_2 = b \quad \text{and} \quad B_3 = b^2.$$

[2]

For the general case we would have

$$B_n = b^{n-1}.$$

[1]

part d: [[8]]

e)

In the configuration integral $\int e^{-\sum_{i<j} U(q_i, q_j)/kT} d^{3N}q$ the potential energy U is either infinite or it is zero. In both cases the temperature scale is immaterial and so T cannot appear in the evaluation of this integral. This means the right hand side of the virial expansion cannot depend on temperature and thus the hard sphere virial coefficients will not depend on temperature.

part e: [[6]]

f)

We see that B_2 has the “correct” value. However while B_3 and the higher order virial coefficients depend on the expected power of b – as indeed they must on purely dimensional grounds, but the numerical coefficients are different from those calculated from the so-called Clausius equation of state. The reason for this is that in the nested integrals for the configuration integral, that arise in the hard sphere case, it is *not* appropriate simply to replace the system volume V by $V - Nb$. The correct integral is much more complicated.

part f: [[8]]

Total Q5: [[[40]]]