

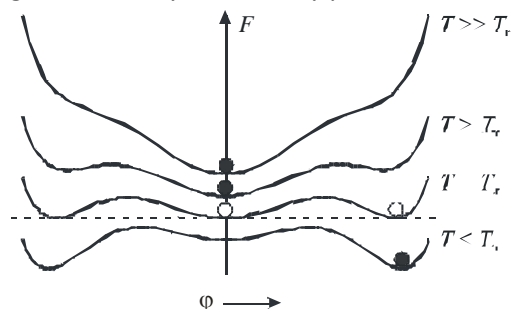
Question 1

Important points: Contrary to their stated views, much of Einstein's work was microscopic/reductionist in nature (quantum arguments), while much of Landau's work was macroscopic/phenomenological. Einstein – most quantum developments, Brownian motion etc. Landau – theory of phase transitions, Fermi liquid theory etc.

Unifying idea of emergence – while microscopic behaviour leads to macroscopic features, much that is macroscopic is robust against changes at the microscopic level. Classic example – Landau theory of phase transitions – macroscopic behaviour is essentially dependent on the nature of troughs in smooth curves.

Question 2

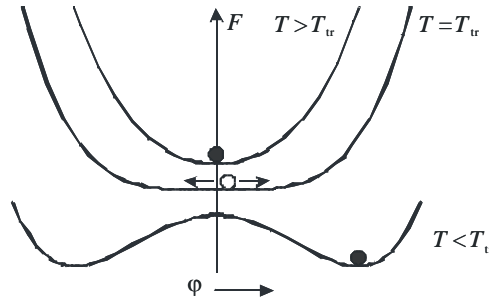
- a) Order parameter – a quantity that quantifies the amount of order in a system. Will be zero in a disordered phase and non-zero in an ordered phase. May be normalized to unity in a fully ordered state. [3]
- b) Termination ensures that the generic properties of the transition are brought out and unimportant details discarded. The point is that the generic behaviour can be described in terms of simple polynomials and the behaviour of their minima. Highest power must be even with positive coefficient (to ensure stability) [4]
- c) Odd terms are not used by considerations of symmetry. Ferromagnet order parameter is a vector, but free energy is a scalar. With no other vectors in the system we can only get a scalar by dotting the order parameter with itself. Thus no odd powers for the ferromagnet. The order parameter for the ferroelectric is the polarization along a given line. So it is Ising-like. Here inversion symmetry means that neither direction along the line is favoured so odd terms vanish. [2]
- d) Picture shows general sixth-order polynomial (odd powers only and coeff of 6th power positive). In general there are six roots, and five extrema. We have (in ordered state) three minima – one at the origin and two symmetrically placed either side. [2]



A first order transition is possible when the minima are at equal heights. Then the order parameter can jump (discontinuously) from the zero value to an outer minimum – or *vice*

versa. A discontinuous change in the order parameter signifies a first-order transition. [3]

- e) If the coeff of the 4th power is positive then there is no need for the sixth order term. Then in the vicinity of the transition the free energy looks like this:



In this case the minimum at non-zero order parameter evolves continuously from a minimum at zero order parameter as the system passes through the critical point. [5]

- f) The free energy is given by

$$F = F_0 + a(T - T_c)\varphi^2 + b\varphi^4$$

all the temperature dependence is in the second order term. The entropy is found by differentiating the free energy

$$S = -\frac{\partial F}{\partial T} = S_0 - a\varphi^2.$$

This shows the way the entropy drops as the ordered phase is entered. We see that the entropy is continuous at the transition

$$\begin{aligned} T > T_c, & \quad \varphi = 0 & \quad S = S_0(T) \\ T < T_c, & \quad \varphi = \pm \sqrt{\frac{a(T_c - T)}{2b}} & \quad S = S_0(T) + \frac{a^2}{2b}(T - T_c). \end{aligned}$$

The thermal capacity is given by

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

Thus we find

$$\begin{aligned} T > T_c, & \quad C = C_0 \\ T < T_c, & \quad C = C_0 + \frac{a^2 T}{2b}. \end{aligned}$$

At the transition there is a discontinuity in the thermal capacity given by

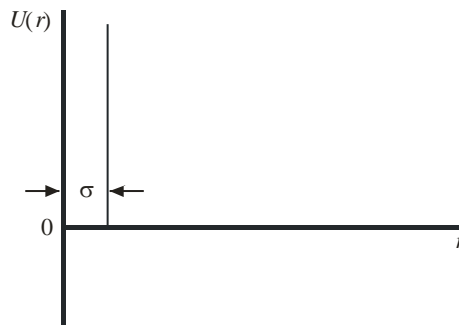
$$\Delta C = \frac{a^2 T_c}{2b}.$$

A discontinuity in φ means a discontinuity in S and therefore the existence of latent heat.

[3]

Question 3

a) Hard core potential



This gives a 'qualitative' treatment of the short-distance repulsion. But, of course, it doesn't have any long-distance attraction. [4]

b) Second virial coefficient given by

$$B_2(T) = -2\pi \int_0^{\infty} r^2 \left[e^{-U(r)/kT} - 1 \right] dr$$

so substituting for $U(r)$ only the interval $0 < r < \sigma$ contributes – outside this range the integral is zero. Thus

$$\begin{aligned} B_2(T) &= 2\pi \int_0^{\sigma} r^2 dr \\ &= \frac{2}{3} \pi \sigma^3. \end{aligned} \quad [4]$$

c) The virial expansion is

$$\frac{p}{kT} = \frac{N}{V} + v \left(\frac{N}{V} \right)^2 + \dots, \quad \text{where} \quad v = \frac{2}{3} \pi \sigma^3$$

Thus

$$pV \left(1 + v \frac{N}{V} \right)^{-1} = NkT.$$

So expand the binomial

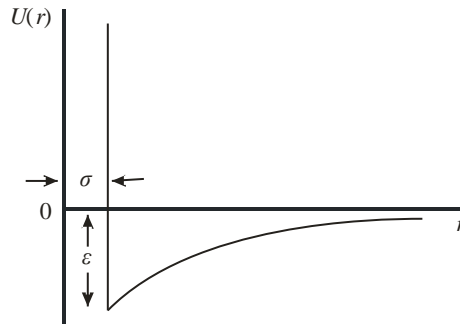
$$pV \left(1 - v \frac{N}{V} + \dots \right) = NkT$$

or

$$p(V - Nv) = NkT$$

and here we see that the effect of the v is to reduce the 'available' volume. Thus its interpretation as an excluded volume. [4]

d) Sutherland potential



This is 'as good as' the hard core potential at short distances; it gives a 'qualitative' treatment of the short-distance repulsion. However the attractive part is good. This is the correct $1/r^6$ form as expected for fluctuating electric dipoles and as used in the Lennard-Jones interaction potential. [3]

- e) The hard sphere second virial coefficient has a 'saturated' temperature-independent value (as indeed it must as the potential has no characteristic energy).
 All realistic forms for B_2 must go negative at low T as a consequence of the attraction at large distances. Both the Sutherland and the L-J are reasonable in this respect.
 At high T the Sutherland 'saturates' at the hard core value as the collisions become more energetic. However at high T the L-J shows a small drop as the most energetic collisions can cause particles to get even closer. (In reality the hard core is not quite so hard). [5]

Question 4

- a) Free energy of mixing is

$$F_m = Nsx(1-x)\epsilon + NkT \{x \ln x + (1-x) \ln (1-x)\}.$$

N – number of atoms in system

s – number of neighbours ('bonds') each atom has

x – concentration of 'A' atoms

ϵ – characteristic energy of interaction.

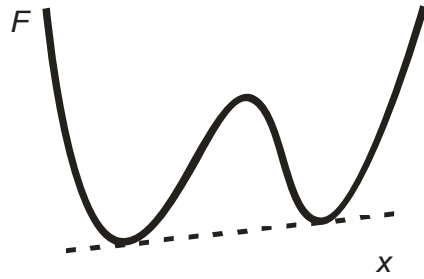
First term in the expression for F_m is the energy term – depends only on 'bonds and neighbours'.

Second term is the conventional 2-state entropy term (Ising form).

[3]

- b) i High temp state is a homogeneous mixture

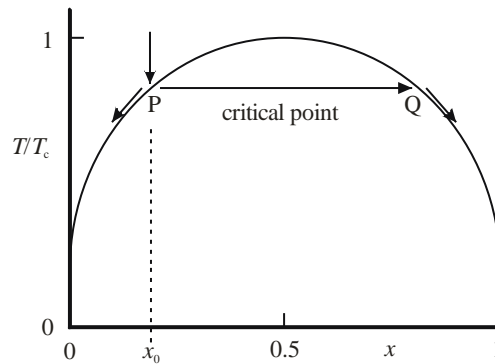
ii Low temp state is separated into A-rich regions and B-rich regions.
 Equilibrium state determined by double tangent construction.



This allows the system to reduce its free energy by becoming inhomogeneous.

Free energy of mixing means *shearing* the free energy curve to make the minima at the same height. Shearing doesn't change the touching of the tangents. [5]

- c) The system starts at high temperatures (above the curve) with a homogeneous concentration x_0 .



Upon cooling one travels down the line until hitting the curve at point P. This is the transition point. At this temperature the new, concentrated, phase starts to appear at point Q. On further cooling one moves down the sides of the curve; on the left hand side the dilute phase becomes further depleted as its x reduces and on the right hand side the concentrated phase becomes further enriched as its x increases. [2]

- d) The phase separation curve is determined by the vanishing of the derivative of the free energy of mixing:

$$\frac{dF_m}{dx} = Ns\varepsilon(1-2x) - NkT \ln\left(\frac{1-x}{x}\right) = 0.$$

This gives the phase separation temperature as

$$T_{ps} = \frac{s\varepsilon(1-2x)}{k \ln(1-x)/x}.$$

Either by symmetry one infers that the maximum is at $x = \frac{1}{2}$ or by differentiating again and setting equal to zero one will find

$$T_c = \frac{s\varepsilon}{2k} \quad [4]$$

as required.

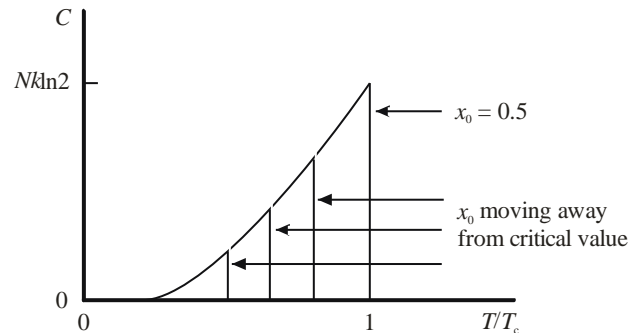
The critical concentration is $x_c = \frac{1}{2}$.

This point is called a critical point because the difference between the two coexisting phases (dilute and concentrated) disappears at this point and the discontinuity in the order

parameter vanishes at this point.

[2]

e) Heat capacity



There is a discontinuity in the heat capacity, but no *divergence*. That means there is no latent heat.

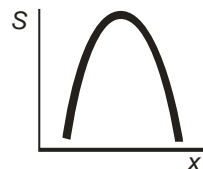
There is no latent heat involved because one is considering measurements at constant *volume*. To make the analogy with a fluid system one would need to make measurements at constant (osmotic) pressure. Then there would be a latent heat. [4]

Question 5

a) i) Start with the microcanonical $S = k \ln \Omega$. The probability of a macrostate is proportional to its number of microstates. Thus Einstein inverted the Boltzmann expression to obtain

$$P(x) \propto \Omega(x) = e^{S(x)/k}. \quad [3]$$

ii) Form for $S(x)$



S is a maximum at the mean value. This is a manifestation of the second law of thermodynamics. [3]

iii) Since S is peaked at the mean of x it follows that $\exp(S)$ will also be peaked. The probability has to go to zero (far) away from the peak. So $P(x)$ will be 'bell-shaped'. Then arguments of the Central Limit Theorem, together with the fact that the fluctuations observed are the sum of many smaller fluctuations, leads to the expectation of a normal distribution. [3]

b) i) The formula for $G(t)$ indicates an average over the fluctuations, where each contribution is weighted by its initial value. Thus positive fluctuations are weighted by a positive factor and negative fluctuations by a negative number. Thus we do not get cancellation and there will be an indication of the behaviour of the average regression. [4]

ii) The width of the autocorrelation function measures the time scale over which the fluctuations vary 'considerably'. We then have a formal definition of the width as the area

divided by the initial height. The width is known as the autocorrelation function. [4]

- c) The only unknown in the normal distribution is the mean square value of the fluctuation deviations. But this is precisely the zero-time value of the autocorrelation function. Thus we have

$$P(x) = \frac{1}{\sqrt{2\pi G(0)}} e^{-x^2/2G(0)}. \quad [3]$$