

Question 1.

a) Want to minimise the free energy, but must be subject to any constraints imposed. In this case overall concentrations of A and B are fixed, implying a given value for x . So one can't 'explore' the x axis. Can only minimise the free energy by becoming inhomogeneous: mixture of regions at some x_1 and regions at some x_2 , so that overall concentration is original value – minimum F determined by double tangent construction. Constraint is conserved order parameter.

By contrast systems with non-conserved order parameter – can then vary order parameter 'at will' to minimise F . Then look for the true minimum in free energy curve.

[4]

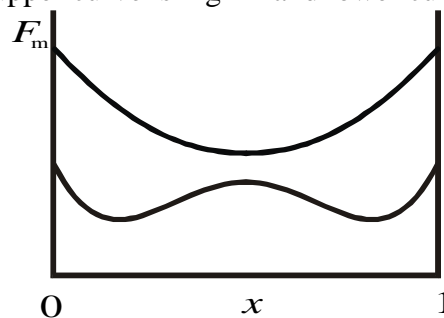
b)

$$F_m = Nk \left[2T_c x(1-x) + T \{ x \ln x + (1-x) \ln(1-x) \} \right]$$

Energy term $Nk 2T_c x(1-x)$, entropy $-Nk \{ x \ln x + (1-x) \ln(1-x) \}$

Energy term from counting a-a, a-b and b-b bonds. These energies go into T_c . Entropy is standard gibbs form for a collection of 2-state objects.

Free energy of mixing – upper curve is high T and lower curve is low T

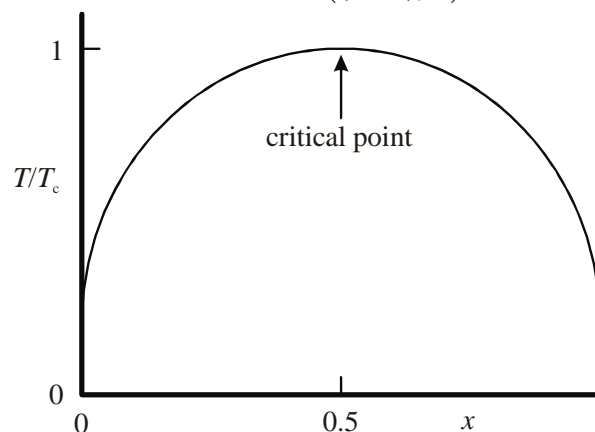


Curve is symmetrical with (both) minima at same level, do double tangent construction now means finding the tangent of the two minima – much easier.

[4]

c) $T = T_{ps}$ at the roots of $\partial F_m / \partial x = 0$. Find

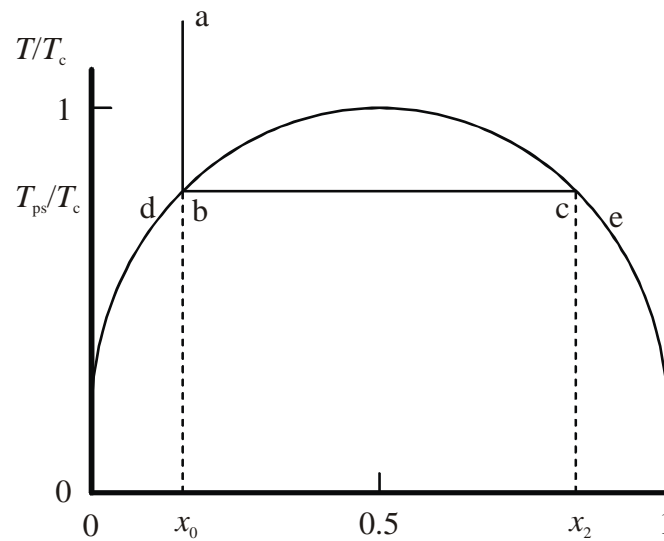
$$T_{ps} = \frac{2(1-2x)}{\ln((1-x)/x)} T_c.$$



Plot this

[4]

d)



Start at high temperature, $T > T_{ps}$. Initial homogeneous concentration is x_0 , so start at point a and drop down the line to b as temperature cools towards the phase separation temperature (at this concentration) T_{ps} . While this happens concentration remains constant at x_0 .

Hit the phase separation curve at point b. At this stage a new phase at concentration x_2 begins to appear. This is point c.

Further cooling gives two phases; a dilute phase as one slides down the curve from b past d, and a concentrated phase as one slides down the curve from c through e. The amount at the two concentrations is determined by the lever rule, to ensure mean concentration remains at x_0 .

[4]

e) In vicinity of critical point $x - x_c \sim (T - T_c)^\beta$, so determine β by fitting the curve in the vicinity of the maximum. Prediction from c) is $\beta = 1/2$, but experimentally it is closer to $1/3$. Explanation is the mean field result c) neglects fluctuations, which become important at the critical point.

[4]

Total 20

Question 2

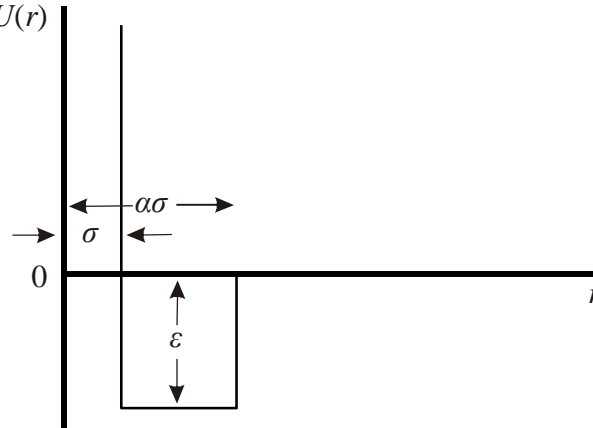
a) Virial expansion

$$\frac{p}{kT} = \frac{N}{V} + B_2(T) \left(\frac{N}{V} \right)^2 + B_3(T) \left(\frac{N}{V} \right)^3 + \dots$$

Valid at low densities.

[3]

b) Square well potential



Here σ is the hard core diameter, ϵ is the depth of the attractive potential and $\alpha\sigma$ is the range of the attractive potential.

[3]

c) Must evaluate

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

where, for this potential we have

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

So split the integral into three regions, to obtain the expression for $B_2(T)$ as

$$\begin{aligned} B_2(T) &= -2\pi \left\{ (-1) \int_0^{\sigma} r^2 dr + (e^{\epsilon/kT} - 1) \int_{\sigma}^{\alpha\sigma} r^2 dr \right\} \\ &= \frac{2}{3} \pi \sigma^3 \left\{ 1 - (\alpha^3 - 1) (e^{\epsilon/kT} - 1) \right\}. \end{aligned}$$

[6]

d) Expand the exponential and neglect the 1 in comparison with α^3 , to obtain

$$B_2(T) = \frac{2}{3} \pi \sigma^3 \left(1 - \frac{\alpha^3 \epsilon}{kT} \right).$$

[3]

e) Intercept of curve $\sim -7.0 \times 10^{-29} \text{ m}^3$, slope $\sim 2800 \times 10^{-29} \text{ m}^3 \text{ K}$

Intercept gives volume of an atom

$$\frac{2}{3} \pi \sigma^3 \sim 7 \times 10^{-29} \text{ m}^3,$$

corresponding to a hard core diameter of

$$\sigma \sim 3.2 \times 10^{-10} \text{ m}.$$

This is a reasonable size for the argon atom.

Slope \sim -intercept $\times \alpha^3 \varepsilon / k_B$, so that $\alpha^3 \varepsilon \sim 5.6 \times 10^{-21} \text{ J}$.

[5]

Total 20

Question 3

a) Third Law of Thermodynamics:

Entropy of a body tends to zero (or constant) as $T \rightarrow 0$. [3]

b) Boltzmann entropy $S = k \ln \Omega$, where Ω is number of microstates in macrostate. At $T = 0$ system will be in ground state. On the assumption that ground state is not degenerate, $\Omega = 1$ so that $S = 0$. In reality the ground state may well be degenerate, but the Law applies in the *thermodynamic limit*, so require that degeneracy of ground state increases slower than exponential with size/number.

[4]

c) Third law gives $\partial S / \partial T \rightarrow 0$ as $T \rightarrow 0$. But $C_v = T \partial S / \partial T$, so this goes to zero as $T \rightarrow 0$. Equipartition is a *classical* result; the Third Law depends on quantum mechanics.

[3]

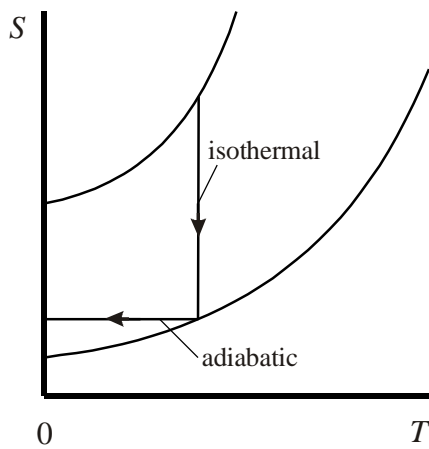
d) If $T \partial S / \partial T = \text{const}$, then $\partial S / \partial T = \text{const} / T$, so integrating this up gives $S \sim \ln T$. This would imply that as $T \rightarrow 0$, $S \rightarrow -\text{infinity}$.

[3]

e) Classically, smaller and smaller volume of phase space would be accessible (volume $\rightarrow 0$) as $T \rightarrow 0$. This would give $S \rightarrow -\text{infinity}$. But QM says the region of phase space cannot be smaller than h^3 (Boltzmann ensemble) – equivalent to one state. I.e. Ω cannot be less than 1, so Third Law recovered.

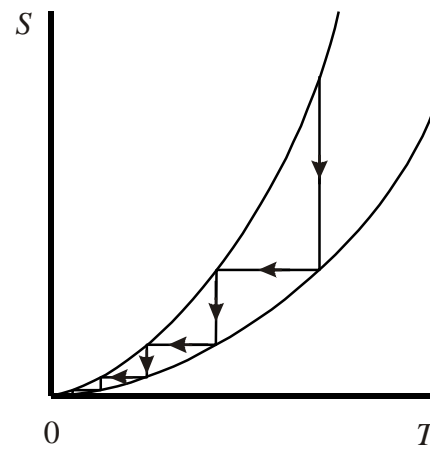
[3]

f)



System not obeying Third Law

can get to $T = 0$ in two steps



System obeying Third Law

cannot get to $T = 0$ in a finite number of steps

Taking a sequence of adiabatics and isothermals between two values of some external parameter we see that the existence of the Third Law implies that you cannot get to $T = 0$ in a finite number of steps.

[4]

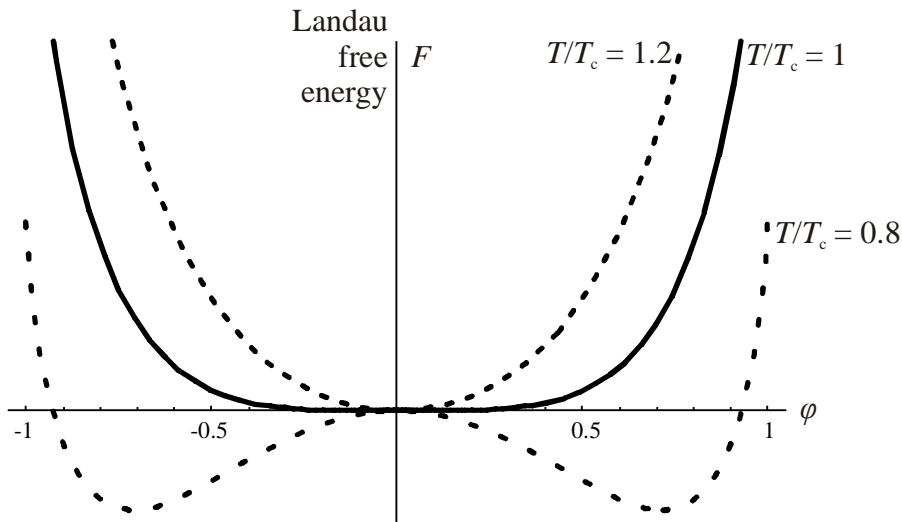
Total 20

Question 4

a) In the Ising model the spins can point either up or down; the order parameter is a scalar – the magnetisation along this special direction. In the Heisenberg model the spins can point in any direction; the order parameter is a vector in 3d space – the magnetisation. In the ordered phase (say $T = 0$) the Ising magnetisation can only be $+M_0$ or $-M_0$. The Heisenberg magnetisation will have *magnitude* M_0 , but it can point in *any* direction. So one ordered state can be continuously rotated into another. By contrast the Ising magnetisation has only two possible states and you cannot change one continuously into the other. This is a discrete symmetry.

[4]

b) (i)



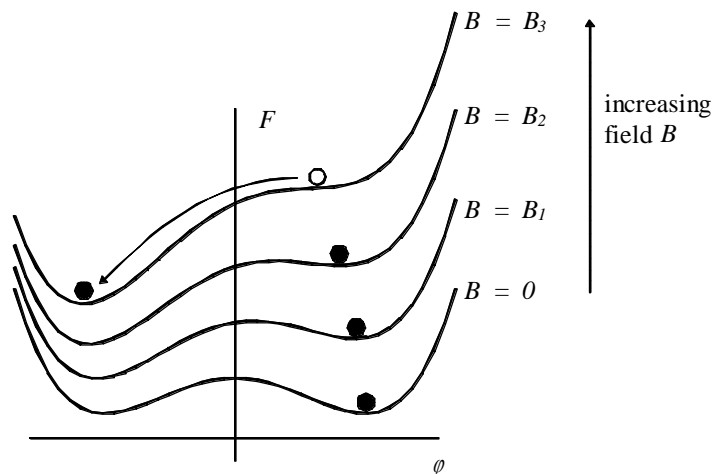
(ii) Here T_c is the critical temperature (Curie temperature).

[4]

c) In the presence of an external field must add a term *linear* in ϕ .

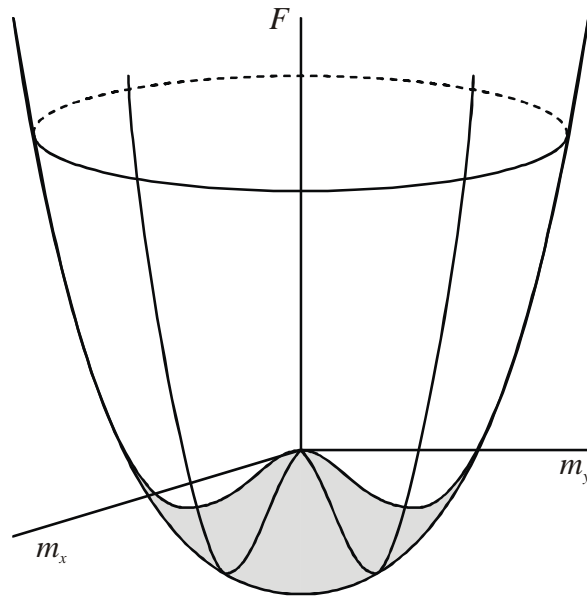
[2]

d) Field ‘shears’ the free energy curve.



In case of a discrete symmetry you cannot go smoothly from one minimum to the other so you have to wait until ‘the ball is tipped out’ the spinodal point.

But in the case of a continuous symmetry there is a whole continuum of states as shown:



[6]

e) The last diagram but one shows the limits of stability. So you need to find the points of inflection of the curve – need the values of B to *get* points of inflection.

[4]

Total 20

Question 5

Must include:

Common description of phase transition phenomena – order parameter.

Constrained free energy, expansion in powers of order parameter, T dependence of coefficients. Application to both second order and first order transitions; weakly first order transitions. Fluctuations – critical exponents.

Total 20