PH4211 Outline Solutions 2005

Question 1

a) N: number of particles. k: Boltzmann's constant. T_c: critical temperature. s: number of nearest neighbours. ε_{aa}, ε_{bb}, ε_{ab}: energy of aa, bb and ab bond. [1]

Structure of eqn for F_m: first term is energy of system, found by counting bonds and their energies. Second term is entropy – has entropy of mixing form. Eqn for T_c – this compares energy of an 'unlike' bond with the arithmetic mean for the two types of 'like' bonds. [2]

Helmholtz free energy is minimised at constant T and V. I.e. the system is being considered at specified T and V. [1]

b) If the parameter is positive then aa and bb bonds are favoured over ab bonds at $T = 0$. Then get phase separation at low temperatures. If the parameter is negative then ab bonds are favoured over aa and bb bonds. In that case the low temperature phase will be a 'superlattice' structure. [2]

c) Upper curve is high temperature case and lower curve is lower temperature case. [2]

d) The curve corresponds to a homogeneous system. In regions where the curve is concave it is possible to lower the free energy by dropping below the curve – when the chord falls below the curve.
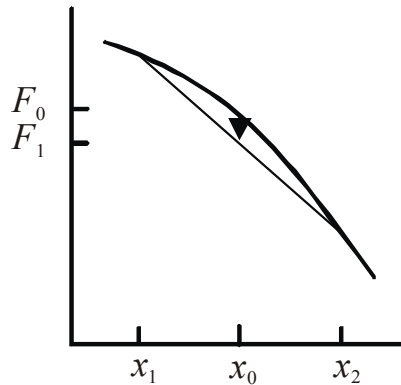
By dropping below the (homogeneous) curve the system of initial concentration x_0 can lower its free energy from F_0 to F_1. This happens when the system becomes inhomogeneous, comprising regions of concentration x_1 and regions of x_2.

Lowest free energy would correspond to double tangent drawn on curve. Conservation of numbers of particles gives mol-fractions of each phase in terms of the lever rule. [4]

e) Phase separation transition found from minima in F_m curve, so differentiate F_m and set equal to zero:

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

so

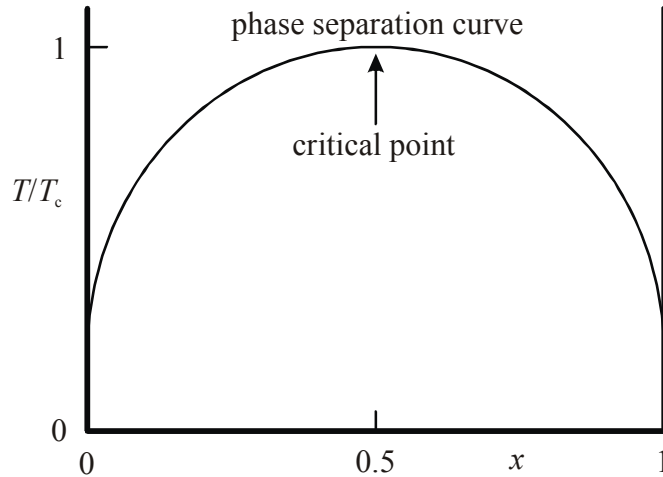$$\frac{dF_m}{dx} = Nk\left[2T_c(1-2x) + T\{\ln x - \ln(1-x)\}\right].$$

Set this equal to zero:

$$2T_c(1-2x) + T\{\ln x - \ln(1-x)\} = 0$$

and this may be solved for T as a function of x, giving

$$\frac{T}{T_c} = \frac{2(1-2x)}{\ln(1-x)/x}$$

as required. [2]

[2]

f) Substitute in values. For $x = 0.01$, $T = 0.427\ T_c = 128$ mK. [2]

Symmetry of phase curve about $x = \frac{1}{2}$ implies that the same transition temperature will apply for a concentration $x = 1 - 0.01 = 0.99$. [1]

Symmetry of the curve is a consequence of the regular solution model/assumption. So if the concentrations $x = 0.01$ and $x = 0.99$ have different transition temperatures, this means that the curve is not symmetric and so may be our specimen is not a regular solution. (In reality there are crystallographic transformations to consider – but the students are not expected to know that!) [1]

Question 2

a)

	ferromagnet	ferroelectric	
Order parameter	Magnetisation	Polarisation	[2]
Cons / non-cons	Non-conserved	Non-conserved	[2]
symmetry	rotational / time rev.	inversion	[2]
Cont / discrete	continuous	discrete	[2]
order	2nd order	1st or 2nd order	[2]

b) $H = -J \sum_{\substack{i,j \\ \text{neighbours}}} \mathbf{S}_i \mathbf{S}_j$ looks like $H = -\sum_i \mathbf{S}_i . \mathbf{B}_i$, in other words, where each spin

sees a magnetic field: $B_i = J \sum_{\substack{j:\text{neighbours} \\ \text{of } i}} S_j$. However each spin sees a different field. In

the mean field approximation we take the field to be the same at each site, being the mean value. Then $\mathbf{b} \propto \langle \mathbf{S} \rangle$ and so $\mathbf{b}$ is proportional to the magnetisation so we can write $\mathbf{b} = \lambda \mathbf{M}$. [4]

c) $\dfrac{M}{M_0} = \tanh\left(\dfrac{M_0}{N}\dfrac{B}{kT}\right)$ and $B = \lambda M$ as there is no external field. Thus
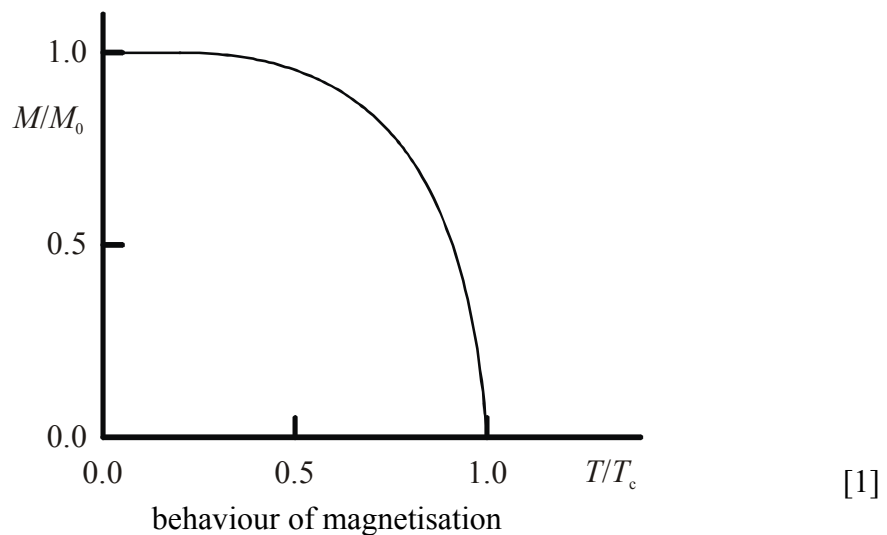
$$\frac{M}{M_0} = \tanh\left(\frac{M_0}{N}\frac{\lambda M}{kT}\right),$$

which we can write as

$$\frac{M}{M_0} = \tanh\left(\frac{M}{M_0}\frac{T_c}{T}\right) \qquad [3]$$

where $T_c = \lambda M_0^2 / Nk$. Here T_c is the critical temperature. [1]

d)

behaviour of magnetisation [1]

The transition is second order – the magnetisation goes to zero *continuously* at the critical point. [1]

Question 3

a) Law of corresponding states: equation of state takes similar 'universal' form if p, V, T are scaled by their values at the critical point. [2]

If the variables of the van der Waals equation are scaled in this way then the equation of state does indeed take on a universal form – the a and b parameters vanish (but behaviour not in quantitative agreement with reality). [1]

On assumption that the law of interaction between molecules takes a universal form: $V(r) = \varepsilon f(r/\sigma)$ – here f is a universal function and ε and σ scaling parameters, different for different molecules, then in terms of reduced variables the partition function, and thus all thermodynamic properties, would have universal form. This is independent of the van der Waals equation of state. [2]

b)   Apart from the heliums, the data do fall reasonably well on a single curve – this supports the law of corresponding states.

The data do not fall on the van der Waals curve so this is not a good model for describing the data. Thus corresponding states is not reliant on van der Waals.
[2]

Van der Waals is a mean field theory; thus the mean field β critical exponent of ½. If the data exhibit a β critical exponent of ⅓, this is an indication of the inapplicability of mean field theory.   [3]

c) In the vicinity of the critical point the helium data should fall on the common curve of the other data. This is because the critical behaviour is universal, not depending on quantum effects.   [3]

Thus the β critical exponent of for the helium data is expected to be ⅓.   [2]

d) This is (essentially) the wavelength corresponding to the momentum corresponding to the kinetic energy (of a free particle) kT. It represents the 'quantum size', the extent of delocalisation of a particle due to quantum effects.   [2]

The importance of this quantity is that when the mean inter-particle spacing is comparable to or less than Λ then quantum effects are important. Then it is not adequate to use classical mechanics in discussing such systems. This is true for the helium liquids (and to a marginal extent to liquid neon – as can be seen in the data).
[2]

Data on right hand side are for liquids – there density is high, so if quantum effects are important it will be there. Data on left hand side are for gas. There density is low so quantum effects are not significant; data fall on universal curve.   [1]

Question 4

a) A Brownian particle stationary in the centre of mass frame of the fluid experiences random impacts from all directions; it experiences a random force of mean value zero. A Brownian particle moving with respect to the centre of mass frame of the fluid experiences impacts from the front which are more energetic than the ones from behind. These have a greater momentum transfer. So in addition to the random force there will be a mean force depending on the velocity of the Brownian particle (with respect to the centre of mass frame of the fluid). Simple argument shows force proportional to the velocity.   [5]

b) Simple application of Newton's law $M\dot{v} = F$, and using $F = f - v/\mu$.   [2]

c)

$$v^2(t) = \left[v(0)e^{-t/M\mu} + \frac{1}{M}\int_0^t e^{(u-t)/M\mu} f(u)\,du \right]^2$$

$$= v^2(0)e^{-2t/M\mu} + \frac{2}{M}v(0)e^{-t/M\mu}\int_0^t e^{(u-t)/M\mu} f(u)\,du$$

$$+ \frac{1}{M^2}\int_0^t du_1 \int_0^t du_2 \; e^{(u_1-t)/M\mu} e^{(u_2-t)/M\mu} f(u_1) f(u_2).$$

Now take average:

$$\langle v^2(t)\rangle = \langle v^2(0)\rangle e^{-2t/M\mu} + \frac{2}{M}e^{-t/M\mu}\int_0^t e^{(u-t)/M\mu} \langle v(0)f(u)\rangle\,du$$

$$+ \frac{1}{M^2}\int_0^t du_1 \int_0^t du_2 \; e^{(u_1-t)/M\mu} e^{(u_2-t)/M\mu} \langle f(u_1) f(u_2)\rangle.$$

[2]

First term is mean transient response; this dies to zero at long times. In second term $v(0)$ is uncorrelated with $f(t)$ so this term vanishes. So we are left with

$$\langle v^2(t)\rangle = \frac{e^{-2t/M\mu}}{M^2}\int_0^t du_1 \int_0^t du_2 \; e^{(u_1+u_2)/M\mu} \langle f(u_1) f(u_2)\rangle.$$

Assumption of short correlation time: $\langle f(u_1) f(u_2)\rangle = f^2\delta(u_1 - u_2)$, where

$f^2 = \int_{-\infty}^{\infty}\langle f(0)f(t)\rangle\,dt$. This assumption forces $u_1 = u_2$ when the integral is done:

$$\langle v^2(t)\rangle = \frac{f^2 e^{-2t/M\mu}}{M^2}\int_0^t du_1 e^{2u_1/M\mu}$$

$$= \frac{\mu}{2M}f^2 e^{-2t/M\mu}\left(e^{2t/M\mu} - 1\right)$$

$$= \frac{\mu}{2M}f^2\left(1 - e^{-2t/M\mu}\right).$$

So at long times the equilibrium value is

$$\langle v^2\rangle = \frac{\mu}{2M}f^2$$

or

$$\langle v^2\rangle = \frac{\mu}{2M}\int_{-\infty}^{\infty}\langle f(0)f(t)\rangle\,dt.$$

[2]

Now equipartition gives $\langle v^2\rangle = kT/M$ so that

$$\frac{kT}{M} = \frac{\mu}{2M}\int_{-\infty}^{\infty}\langle f(0)f(t)\rangle\,dt$$

or

$$\frac{1}{\mu} = \frac{1}{2kT}\int_{-\infty}^{\infty}\langle f(0)f(t)\rangle\,dt.$$

[1]

d) Left hand side is a dissipation coefficient. Right hand side involves fluctuations. So this is an equation relating fluctuations and dissipation. Generalisation called the fluctuation-dissipation theorem.

[2]

e) By direct analogy $M \to L$ (not needed), $v(t) \to I(t)$, $1/\mu \to R$, $f(t) \to V(t)$. [2]

Then

$$R = \frac{1}{2kT} \int_{-\infty}^{\infty} \langle V(0)V(t) \rangle \, dt.$$ [2]

f) Can observe as the hiss (as opposed to the hum) from a loudspeaker when there is no input connected to a hi-fi amplifier. [2]

Question 5

a) Ensemble: a collection of identically-prepared systems that can be used for probabilistic calculations. The systems are envisaged as all manifesting the same *macrostate*, while being in different *microstates*. [4]

b) Boltzmann regarded a gas as being an ensemble of single particles. Gibbs regarded the gas as being one element of the ensemble. To Gibbs the ensemble was a collection of boxes of the gas. Boltzmann view breaks down when the interactions between the particles becomes significant. The Gibbs approach is the more general and it does not suffer from this limitation. Thus for Boltzmann the ensemble is real; for Gibbs it is imaginary. [4]

c) Phase space is a space of (generalised) position and momentum coordinates. A microstate is specified as a point in phase space and its time evolution is specified as a curve in phase space. According to the Boltzmann view a gas of N particles would be specified by N points in a 6-dimensional phase space. According to the Gibbs view the gas would be specified by a single point in $6N$-dimensional phase space. An ensemble would then be represented by a collection of points in the phase space. [4]

d) Assumption that goes into Liouville's theorem is that the dynamics are governed by Classical (Hamiltonian)mechanics – although an analogous result may be obtained in quantum mechanics. Restriction on the flow of points in phase space is that no two curves can intersect. [2]

e) Boltznann's H theorem: Essentially Boltzmann's H theorem says that the density of points in phase space decreases as time evolves. Strictly it is specified in terms of $\rho \ln \rho$ which, when integrated gives the mean value of $\ln\rho$ – connection with entropy. [2]

The paradox is that while Liouville's theorem states that ρ remains constant, the H theorem states that ρ decreases. [2]

Paradox may be resolved by considering the dendritic nature of the flow in phase space and coarse-graining:
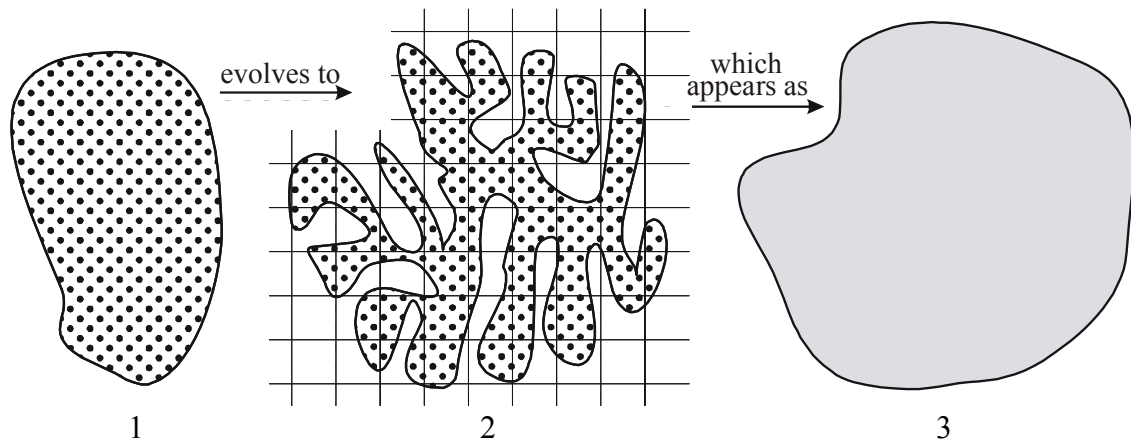
Initial state represented by picture 1. Some time later this has evolved to picture 2. The density of points in the enclosed 'volume' has remained the same – in accordance with Liouville's theorem. One erects a grid; the reasoning is that one cannot practically discern detail in phase space on a scale finer than the grid. Thus one considers the mean density in each cell– called coarse-graining. And then the *apparent* density is as in picture 3; the density ρ appears to have reduced and the volume occupied appears to have increased. Ultimately the Uncertainty Principle would provide an appropriate scale for coarse-graining. [2]