PH4211 Outline Solutions 2006

Question 1

(a) Λ is the de Broglie wavelength corresponding to the momentum corresponding to the kinetic energy corresponding to the temperature:

$\Lambda \sim h/p$ where $p \sim \sqrt{2mE}$ where $E \sim kT$ [2]

(b) For *distinguishable* objects one multiplies the individual partition functions so that $Z = z^N$. For *indistinguishable* objects one must take account of permutations, which result in identical states. Thus we would have

$$Z = \frac{n_1! n_2! \ldots}{N!} z^N$$

where N is the number of particles, n_1 is the number of particles in state 1 etc.

When multiple occupancy may be ignored then

$$Z = \frac{1}{N!} z^N,$$

as required.

So the $N!$ takes account of indistinguishability and the expression is valid when multiple occupancy may be ignored – when its probability is very small. [5]

(c) Helmholtz free energy F:

$$F = -kT \ln Z$$

But

$$\ln Z = N \ln z - \ln N!$$
$$= N \ln z - N \ln N + N \ln e$$
$$= N \ln (ze/N)$$

using Stirling's approximation.
Now use

$$z = V/\Lambda^3$$

so that

$$\ln Z = N \ln (Ve/N\Lambda^3)$$

and then

$$F = -NkT \ln (Ve/N\Lambda^3).$$ [5]

(d) If the $N!$ term were ignored then we would have

$$\ln Z = N \ln z$$

so that

$$F = -NkT \ln (V/\Lambda^3).$$

This expression is unacceptable because the argument of the logarithm is *extensive*. This means that F would increase with volume in a strange way; F would not be extensive.

(e) given

$$\Lambda = \sqrt{\frac{2\pi\hbar^2}{mkT}}$$

Substitute values in to get

$$\Lambda(T = 3K) = 5.02 \times 10^{-10}\,\text{m}$$
$$\Lambda(T = 300K) = 5.02 \times 10^{-11}\,\text{m}$$

Mean distance between atoms is

$$\lambda \sim (kT/p)^{1/3}$$

Use 1 bar $= 10^5$ N m^{-2} so that

$$\lambda(T = 3K) = 7.45 \times 10^{-10}\,\text{m}$$
$$\lambda(T = 300K) = 3.46 \times 10^{-9}\,\text{m}$$

So at 300K the interparticle spacing is much greater than Λ so quantum effects can be ignored (and multiple occupancy is not a problem). But at 3K λ and Λ are similar and so quantum effects become important.

[4]
Total [20]

Question 2

Points that should be made include:
- Connection with Second Law [2]
- Reversibility appearing to occur at the microscopic level [2]
- But irreversibility appearing to occur at the macroscopic level [2]
- Need for a statistical description [2]
- Discussion of a macrostate as a region in phase space [2]
- Evolution of the region determined by equations of motion [2]
- Liouville's theorem saying that 'volume' in phase space is constant [2]
- Boltzmann's H theorem arguing that 'volume' in phase space increases [2]
- Nature of the 'flow' in phase space [2]
- Resolution of paradox in terms of coarse graining. [2]
- Possible mention of cosmological connections.

Total [20]

Question 3

(a) Equation looks like ideal gas equation of state but pressure increased by $a N^2/V^2$ and volume decreased by Nb. The a term relates to the long-distance attractive tail of the inter-particle interaction. This has the effect of decreasing the pressure on the walls of the container. The b term relates to the repulsive hard core of the inter-particle interaction. This has the effect of reducing the allowed volume the particles can occupy. [3]

(b)
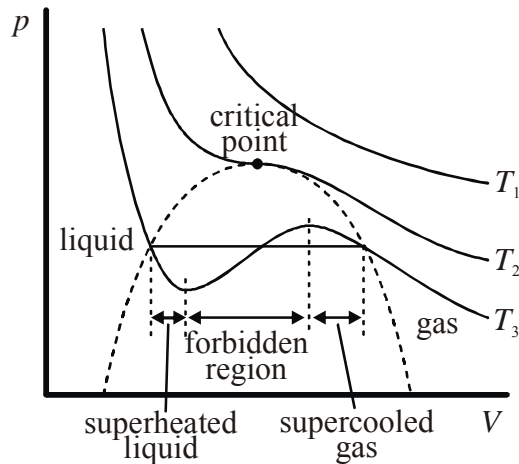
    Curves out of the coexistence region are *stable*
    Superheated and supercooled regions are *metastable*
    Forbidden region is *unstable* [3]

(c) The critical point is characterised by   (2 marks for this)
$$\partial p/\partial V = 0 \quad and \quad \partial^2 p/\partial V^2 = 0$$
So write the equation of state as
$$p = \frac{NkT}{V - Nb} - a\frac{N^2}{V^2}$$
and differentiate (twice), set equal to zero and solve the equations. Working through the algebra will give
$$T_c = \frac{8a}{27kb}, \quad V_c = 3Nb.$$
[4]

Alternative derivation (following H E Stanley): write the equation of state as
$$V^3 - N\left(b + \frac{kT}{p}\right)V^2 + N^2\frac{a}{p}V - N^3\frac{ab}{p} = 0.$$
In general the solutions to this equation give three values for V (possibly two are complex). At the critical point the three values coalesce – the 3 roots of
$$V^3 - N\left(b + \frac{kT_c}{p_c}\right)V^2 + N^2\frac{a}{p_c}V - N^3\frac{ab}{p_c} = 0$$
are equal. Then this equation must be equivalent to the cubic
$$(V - V_c)^3 = 0$$

or
$$V^3 - 3V_c V^2 + 3V_c^2 - V_c^3 = 0.$$

So equate coefficients of the two equations to get
$$3V_c = N\left(b + \frac{kT_c}{p_c}\right), \quad 3V_c^2 = N^2 \frac{a}{p_c}, \quad V_c^3 = N^3 \frac{ab}{p_c}.$$

Then these are easily solved to give
$$T_c = \frac{8a}{27kb}, \quad V_c = 3Nb.$$

(d) To do this one write the equation of state as
$$\frac{p}{kT} = \frac{N}{V}\left(1 - b\frac{N}{V}\right)^{-1} - \frac{a}{kT}\left(\frac{N}{V}\right)^2$$

and then expand the first term using the binomial series
$$\frac{p}{kT} = \frac{N}{V}\left(1 + b\frac{N}{V} + \dots\right) - \frac{a}{kT}\left(\frac{N}{V}\right)^2$$
$$= \frac{N}{V} + \left(b - \frac{a}{kT}\right)\left(\frac{N}{V}\right)^2 + \dots$$

thus we identify the second virial coefficient as
$$B_2(T) = \left(b - \frac{a}{kT}\right).$$

[3]

(e) From the above equation we find the parameters a and b as
$$a = kT_1 T_2 \frac{B_2(T_2) - B_2(T_1)}{T_1 - T_2}, \quad b = \frac{T_2 B_2(T_2) - T_1 B_2(T_1)}{T_1 - T_2}$$

and from the given data calculate
$$a = 3.86 \times 10^{-49} \text{ J m}^3, \quad b = 6.48 \times 10^{-29} \text{ m}^3$$

Then using $T_c = 8a/27kb$, this gives a T_c of 127.6.

[3]

(f) The 'calculated' value is 128K to 3 sig. figs, whereas the experimental value is 126K. This small discrepancy is related to the fact that the van der Waals equation is only an approximation to the behaviour of a real gas. The fact that the discrepancy is indeed small is an indication that the van der Waals equation is quite good. [2]

(g) This corresponds to moving along the curve of the 'superheated liquid' in the figure above, rather than joining the (equilibrium) coexistence line. The *curve* is described by the van der Waals equation of state. The limit of superheating (the minimum pressure) is at the minimum of the isotherm. So knowing the parameters a and b of the equation of state, one can find the pressure at which the derivative is a minimum. (the algebra is a bit messy). [2]

Total [20]

Question 4

(a) History: Brown's observation. Other examples. Randomness of the Brownian motion. Equipartition applies to a Brownian particle. Langevin equation – friction proportional to velocity – fluctuation-dissiation relation. Diffusive motion – expressions for diffusion coefficient.   [10]

(b) Critical exponents – behaviour in the *vicinity* of the critical point. Scaling arguments – a single length parameter. Law of corresponding states. Discussion of the Ehrenfest classification of phase transitions and the idea that it is not really appropriate/useful.   [10]

(c) Ising model as a description of magnetic phenomena. Has non-conserved order parameter in this case. Mention of a *scalar* order parameter. Binary mixture can also be expressed in this form. And lattice gas model of fluid systems. But both of these have conserved order parameter.   [10]

Total [20]

Question 5

(a) The order parameter is a measure of the order on the ordered phase. It is taken to be zero in the disordered phase. The order parameter may be a real scalar, a complex scalar, a vector or a tensor – depending on the nature of the order.   [3]

(b) First order transition – order parameter is *discontinuous* at the transition. In a second order transition the order parameter is *continuous.*   [3]

(c) Symmetry might require odd terms to vanish. For instance if the order parameter is a vector then you must take the dot product of it with itself to make the (scalar) free energy.

The highest order term must be an even term and its coefficient must be positive so the system is stable – the order parameter must be bounded; it can't go off to infinity.

The order of the expansion must be sufficiently high that the free energy curve exhibits the phenomena under investigation.

But the expansion must not go to *higher* order than strictly needed – the Landau free energy is supposed to describe *generic* behaviour. And higher order terms would just add superfluous detail.   [3]

(d) Plot of free energy….
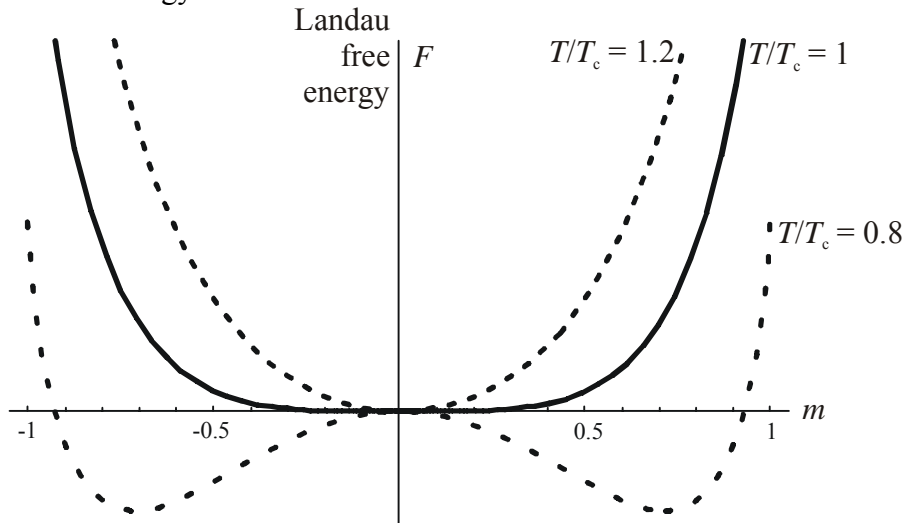
[3]

(e) Write free energy as
$$F = F_2\varphi^2 + F_4\varphi^4 .$$
Equilibrium states found by finding minima of F:
$$\frac{dF}{d\varphi} = 2F_2\varphi + 4F_4\varphi^3 = 0$$

so that

$$\varphi = 0 \qquad \text{or} \qquad \varphi = \pm\sqrt{\frac{-F_2}{2F_4}} .$$

We know that F_4 is positive. So when $F_2 < 0$ there are three stationary points while when $F_2 > 0$ there is only one. The critical point is where the roots coalesce – so this means the vanishing of F_2 at the critical point. Simplest assumption is a linear variation

$$F_2 = a(T - T_c)$$

while F_4 is a constant b. Then in the vicinity of the critical point

$$\varphi = \pm\sqrt{\frac{a(T - T_c)}{2b}} \ .$$

Thus the order parameter critical exponent has the value $^1/_2$. [6]

(f) Real systems often have a beta closer to 1/3. Importance of the role of fluctuations. [2]

Total [20]