

PH4211 Outline Solutions 2007

Question 1

a) S is the entropy. Ω is number of microstates in the macrostate. [2]

b) For an isolated system all microstates are equally probable. So probability of observing a macrostate is proportional to the number of microstates corresponding to it. State observed is the most probable one, so it is the state of greatest entropy. Upon removing a constraint the system will evolve to a more probable state – it will evolve to a state of greater (maximal) entropy. [2]

c) $\Omega_a(E_a)$ is no of microstates in system a when it has energy E_a . And $\Omega_b(E_b)$ is no of microstates in system b when it has energy E_b . Total number of microstates of the composite system is $\Omega = \Omega_a \Omega_b$. Let E_t be the total energy of the composite system, denote E_a by E and then E_b is $E_t - E$, so that

$$\Omega = \Omega_a(E_a) \Omega_b(E_b) = \Omega_a(E) \Omega_b(E_t - E).$$

Must maximise this by varying E . So differentiate and set equal to zero

$$\frac{d\Omega_a}{dE} \Omega_b - \Omega_a \frac{d\Omega_b}{dE} = 0.$$

or

$$\frac{d \ln \Omega_a}{dE} = \frac{d \ln \Omega_b}{dE}$$

but $S = k \ln \Omega$, so we get $T_a = T_b$, where

$$T = \frac{dE}{dS}.$$

Total derivatives here, since only heat energy is allowed to flow. [4]

Total energy of the composite system is fixed but energy can flow back and forth between the two. Probability of a energy partition is given by Ω . It will be sharply peaked at the equilibrium energy value. [1]

d) This is the square root of the average of the square of the deviations of E from its mean value. It has the dimensions of energy and measures the extent of the deviations from the mean. [2]

e)

$$\begin{aligned} \sigma_E^2 &= \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 - 2E \langle E \rangle + \langle E \rangle^2 \rangle \\ &= \langle E^2 \rangle - 2 \langle E \rangle^2 + \langle E \rangle^2 = \langle E^2 \rangle - \langle E \rangle^2 \end{aligned} \quad [2]$$

f)

$$P_j = \frac{1}{Z} e^{-E_j/kT}$$

is probability of E_j state. Here Z is the normalisation constant, known as the partition function – since probabilities must sum to unity.

Mean value given by summing over probabilities

$$\langle E \rangle = \frac{1}{Z} \sum_j P_j E_j = \frac{1}{Z} \sum_j E_j e^{-E_j/kT}. \quad [2]$$

g)

Starting from

$$\langle E \rangle = \frac{1}{Z} \sum_j E_j e^{-E_j/kT}$$

we see that we could get at $\langle E^2 \rangle$ by differentiating with respect to temperature so that another E_j comes down in the summation. It is simpler to get the Z on the left hand side first.

$$\langle E \rangle \sum_j e^{-E_j/kT} = \sum_j E_j e^{-E_j/kT}.$$

We differentiate this with respect to temperature (at constant volume):

$$\frac{\partial \langle E \rangle}{\partial T} \sum_j e^{-E_j/kT} + \frac{\langle E \rangle}{kT^2} \sum_j E_j e^{-E_j/kT} = \frac{1}{kT^2} \sum_j E_j^2 e^{-E_j/kT}.$$

This is then divided by the partition function, to give

$$\frac{\partial \langle E \rangle}{\partial T} + \frac{\langle E \rangle^2}{kT^2} = \frac{\langle E^2 \rangle}{kT^2},$$

or

$$\langle E^2 \rangle - \langle E \rangle^2 = kT^2 \frac{\partial \langle E \rangle}{\partial T}.$$

This may be written as

$$\langle E^2 \rangle - \langle E \rangle^2 = kT^2 C_V$$

so that

$$\sigma_E = \sqrt{kT^2 C_V}.$$

Or do it in terms of $\beta = 1/kT$. Easier. [3]

h) Since C_V is extensive, proportional to N , then *fractional* fluctuations

$$\frac{\sigma_E}{E} \propto \frac{\sqrt{N}}{N} = 1/\sqrt{N}.$$

So fractional fluctuations go to zero in the thermodynamic limit. [2]

Question 2

(a) Classical expression for partition function – integrating over p and q . Exponent is Hamiltonian / kT . Hamiltonian is total energy $T + V$, both expressed as functions of p and q . The powers of h are to specify the size of the cells in phase space. The $N!$ accounts for indistinguishable particles – multiple occupancy is not considered. [3]

(b) Ideal gas partition function is

$$Z_{\text{id}} = \frac{1}{N! h^{3N}} \int e^{-\left(\sum_i \frac{p_i^2}{2m}\right)/kT} d^{3N} p d^{3N} q$$

since here $U = 0$. But now can do integral over q , giving V^N :

$$Z_{\text{id}} = \frac{V^N}{N! h^{3N}} \int e^{-\left(\sum_i \frac{p_i^2}{2m}\right)/kT} d^{3N} p$$

So Z then factorises as $Z = Z_{\text{id}} Q_N$ where

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

The V^N thus arises from the integration over q . [4]

(c) $F = -kT \ln Z$ and $p = -\partial F / \partial V$. So $p = kT \partial \ln Z / \partial V$. Then

$$p = kT \left(\left. \frac{\partial \ln Z_{\text{id}}}{\partial V} \right|_{T,N} + \left. \frac{\partial \ln Q_N}{\partial V} \right|_{T,N} \right)$$

but first part gives ideal gas behaviour (or can show explicitly) so that

$$p = kT \left(\frac{N}{V} + \left. \frac{\partial \ln Q_N}{\partial V} \right|_{T,N} \right). \quad [4]$$

(d) Argument of exponential in partition function is either zero or infinity for $q > \sigma$ or $q < \sigma$. So there is no dependence on T . So partition function has no dependence on T .

Then

$$\frac{p}{kT} = \frac{N}{V} + \left. \frac{\partial \ln Q_N}{\partial V} \right|_N$$

and the rhs is independent of temperature. This means that the only free variables for the rhs are V, N . The lhs is intensive; V/N is the only intensive combination.

So $p/kT = \text{fn}(N/V)$ [3]

(e)
$$\frac{pV}{NkT} = 1 + \frac{V}{N} \left. \frac{\partial \ln Q_N}{\partial V} \right|_N.$$

Clearly $\partial \ln Q_N / \partial V$ depends on σ and can depend on N/V . Overall we require that

$\frac{V}{N} \partial \ln Q / \partial V$ be dimensionless so σ and N/V must combine as $N\sigma^3/V$.

-- Virial expansion, Padé approximants, molecular dynamics. [3]

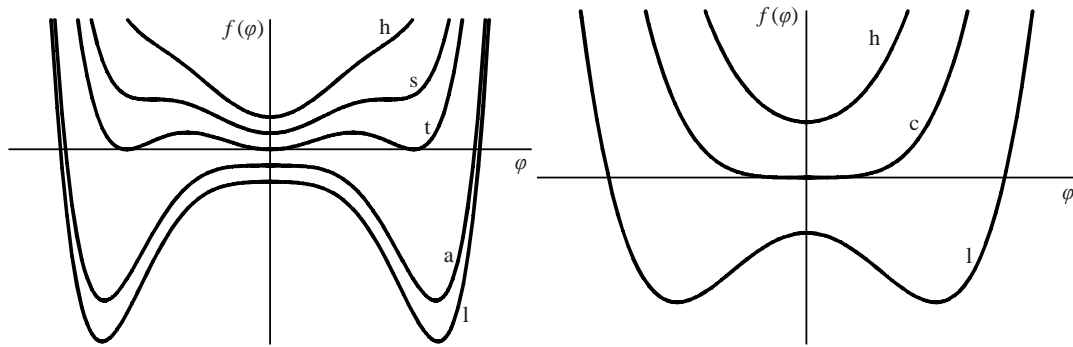
(f) No transition to a liquid since the fluid can't be self-bound as there is no attractive part to the interaction. But could be a solid phase; molecular dynamics indicate so. [3]

Question 3

(a) Order parameter – measure of the order in the system, zero in disordered phase. Order parameter varies discontinuously in a first-order transition and continuously in a second-order transition. [3]

(b) Order parameter is polarisation \mathbf{P} . Odd terms in the free energy expansion vanish if the lattice has inversion symmetry (or because \mathbf{P} is a vector while F is a scalar). Expansion terminated at 6th order. Need the 6th term because the 4th term may be negative, while we require the system to be stable / φ bounded. [3]

(c)



h: high temp. t: transition temp. c: critical temp. l: low temp.

First order

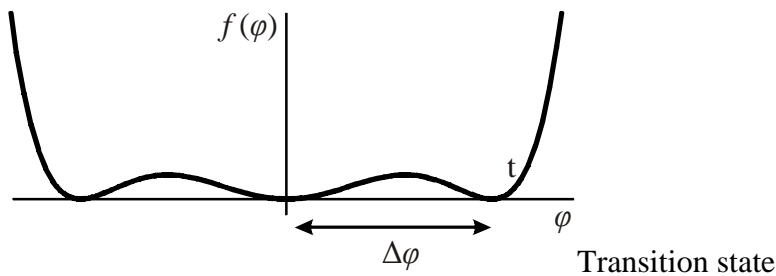
Second order

[4]

(d) If F_4 coefficient is negative then we need the F_6 term (with a positive coefficient) so that φ is bounded. The sextic curve is the first-order form above. If F_4 coefficient is positive then since φ is assumed small the F_6 term can be neglected and the system will be stable. And the quartic curve is the second-order form above.

[3]

(e)



At the transition temperature the three minima are level. Write:

$$F = F_2\varphi^2 + F_4\varphi^4 + F_6\varphi^6$$

The transition point is characterised by the conditions

$$F(\varphi) = 0 \quad \text{and} \quad \frac{dF}{d\varphi} = 0$$

or

$$F_2\phi^2 + F_4\phi^4 + F_6\phi^6 = 0$$

$$2F_2\phi + 4F_4\phi^3 + 6F_6\phi^5 = 0.$$

We know we have the $\phi = 0$ solution; this can be factored out. The others are found from solving the simultaneous equations

$$F_2 + F_4\phi^2 + F_6\phi^4 = 0$$

$$F_2 + 2F_4\phi^2 + 3F_6\phi^4 = 0.$$

The solution to these is

$$\phi^2 = -\frac{F_4}{2F_6}$$

or

$$\phi = \sqrt{\frac{-F_4}{2F_6}}$$

as we know that F_4 is negative.

This gives the discontinuity in the order parameter at the transition since ϕ will jump from zero to this value at the transition. Thus we can write

$$\Delta\phi = \sqrt{\frac{-F_4}{2F_6}}.$$

$\Delta\phi \rightarrow 0$ as $F_4 \rightarrow 0$ as expected. [4]

(f) F_2 vanishes at the critical point since the free energy is then a pure quartic. Linear temperature dependence is simplest and F_2 must be +ve in the high-temp disordered phase.

$$F = a(T - T_c)\phi^2 + F_4\phi^4 + F_6\phi^6.$$

Entropy:

$$S = -\frac{\partial F}{\partial T},$$

so that

$$S = -\frac{\partial F_0}{\partial T} - a\phi^2.$$

The latent heat is

$$L = -T_r\Delta S$$

$$= aT_r\Delta\phi^2.$$

So that latent heat as

$$L = aT_r \frac{|F_4|}{2F_6}.$$

$L \rightarrow 0$ as $F_4 \rightarrow 0$ and transition becomes 2nd order. [3]

Question 4

- (a) i Order parameter is magnetisation \mathbf{M} .
 ii Order parameter is non-conserved
 iii Rotational symmetry broken
 iv Continuous symmetry broken
 v Transition is 2nd order. [5]

(b) $B = B_{\text{ext}} + b$, so that

$$\frac{M}{M_0} = \tanh\left(\frac{M_0}{N} \frac{B_{\text{ext}} + b}{kT}\right)$$

but $b = \lambda M$ and we want the spontaneous magnetisation in the absence of the external B_{ext} . Then

$$\frac{M}{M_0} = \tanh\left(\frac{M_0}{N} \frac{\lambda M}{kT}\right)$$

which can be written as

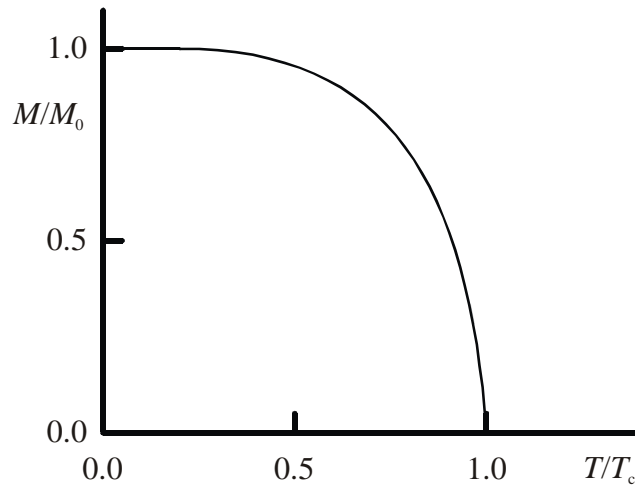
$$\frac{M}{M_0} = \tanh\left(\frac{M}{M_0} \frac{T_c}{T}\right)$$

where

$$T_c = \lambda M_0^2 / Nk.$$

T_c is the transition temperature / Curie temperature. [9]

(c)



M is continuous at the T_c so the transition is 2nd order. [2]

(d) $\lambda = NkT_c / M_0^2$ so $b = NkT_c M / M_0^2$. Put $M/M_0 \sim 1$.

Then $b \sim NkT_c / M_0$. $M_0 = 2N\mu_B$ - here μ_B is Bohr magneton. So

$$b \sim \frac{kT_c}{2\mu_B} = \frac{1.4 \times 10^{-23} \times 1043}{2 \times 9.27 \times 10^{-24}} = 788 \text{ T}.$$

Dipole field is many orders of magnitude less than this. Explanation is Heisenberg exchange interaction. [4]

Question 5

Essay question.

Must cover microscopic and macroscopic description of states. Very large number of microstates compatible with a macrostate necessitates the adoption of a statistical approach.

Microcanonical – Isolated system – Boltzmann entropy $S = k \ln \Omega$ – all microstates equally likely.

Canonical – thermal contact with a reservoir (T replaces E as proper variable) – Gibbs entropy $S = -k \sum_j P_j \ln P_j$ – probability of microstate $\propto \exp -E_j/kT$.

Can obtain canonical from microcanonical by regarding (canonical) system plus reservoir as isolated (microcanonical).

Partition function $Z = \sum_j \exp -E_j/kT$. Helmholtz free energy $F = -kT \ln Z$.
 $F = E - TS$, so $dF = -SdT - pdV + \mu dN$. From this we obtain S, p, μ from
$$S = -\partial F / \partial T, \quad p = -\partial F / \partial V, \quad \mu = \partial F / \partial N.$$

So we can obtain all thermodynamic properties from the partition function – and that just needs knowledge of the microscopic energy levels.