PH4211 Statistical Mechanics 2022
Outline Answers

Question 1

(a) The order parameter is a measure of the *order* in a system. [2]

It is zero in the disordered state and it is non-zero in the ordered state. (It *might* be normalised to unity in the fully-ordered state. – not required.) [2]

In a first order transition the order parameter goes to zero *discontinuously* at the transition. In a second order transition the order parameter goes to zero *continuously* at the transition. [2]

Total part a [[6]]

(b) Order parameter is *magnetisation* / *magnetic moment*, (a vector). Total part b [[4]]

(c) Series is terminated to reflect the *generic* properties of the phase transition - (without extraneous features). It is terminated at the lowest (even) power that reflects the features of the transition. Must be even with positive coefficient for *stability* – so the order parameter is kept finite. [4]

No odd powers as free energy is a scalar so you must "dot" the magnetisation with itself. [4]

Total part c [[8]]

(d) Equilibrium state determined by minimising the Landau free energy with respect to the order parameter: $\partial F/\partial\varphi = 0$. Since

$$\frac{\partial F}{\partial\varphi} = 2F_2\varphi + 4F_4\varphi^3$$

the non-trivial root is

$$\varphi = \sqrt{\frac{-F_2}{2F_4}}.$$

[3]

Since F_4 must be positive, then F_2 must be negative in the ordered phase (i.e. $T < T_\mathrm{c}$), F_2 will change sign at $T < T_\mathrm{c}$, so simplest variation is

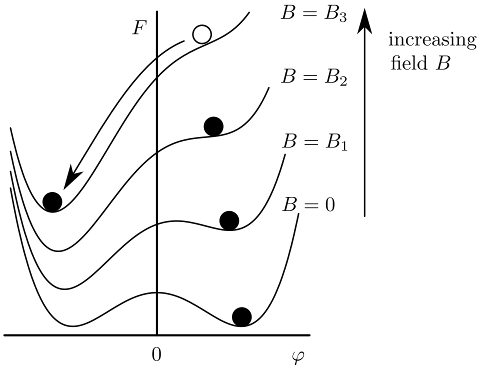
$$F_2 = a(T_\mathrm{c} - T), \quad F_4 = \text{const.}$$

Then as $T \to T_\mathrm{c}$ (from below) φ will go smoothly to zero: as *second order* transition. [5]

Total part d [[8]]

(e) Magnetic field will add a linear term to F, like $-B\varphi$. Total part e [[2]]

(f) In the Ising model φ is a scalar (it lies on the real line).



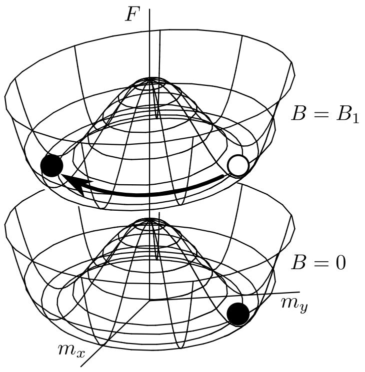
[3]

The field adds a "shear" to the free energy.

Must overcome the energy barrier to get, from the right, over to the lower (left) minimum. So B must increase to B_3. But then as B decreases it must go through zero to *minus* B_3 before the system can "slip" back to the right hand side. [3]

Total part f [[6]]

(g) With the Heisenberg magnet you can slide "round the side" of the free energy curve as the order parameter is a 3d vector (it is not constrained to a line).



[3]

The Ising model has a 1d order parameter (broken *discrete* symmetry); then there is nowhere to "slide". [3]

Total part g [[6]]

Total question 1 [[[40]]]

Question 2

Essay question (around 3 marks for mention of each bullet point)

- Macroscopic approach comes from the Laws of Thermodynamics.
- Zeroth Law leads to existence of equilibrium states/temperature – an ordering but no scale.

- Zeroth Law leads to idea of temperature – an ordering but no scale.
- Second Law leads to absolute temperature scale in terms of heat in and heat out of a heat engine.
- Macroscopic approach predates microscopic, and conception/feel of temperature predates thermodynamic specification.
- Microscopic approach comes from considering the most likely macrostate as that with the largest number of microstates. (Entropy maximisation – from the microscopic perspective).
- When two systems exchange (thermal) energy, without exchanging work then the maximal entropy state (most probable) or "equilibrium" state is that which equalises the temperatures.
- Entropy / probability maximisation leads to $\partial S/\partial E|_{V,N}$ being equalised for the two systems. This is identified as $1/T$.
- Consistency of macroscopic and microscopic approach may be demonstrated by considering the ideal gas in both approaches, noting that the equation of state is the same when statistical temperature is identified with thermodynamic temperature.
- It may be done in a more "abstract" way by taking $1/T = \partial S/\partial E|_{V,N}$ looked at from a macroscopic and a microscopic viewpoint, and identifying the S and E in both cases.
- The importance of "equilibrium" states is that we can use (macro)states with a small number of variables rather than (micro)states with an impossibly large number of variables.
- The existence of equilibrium states (as stated by the Zeroth law) is a phenomenological property of the real world. It cannot be "derived".
- Equilibrium states are characterised by properties such as temperature , pressure, chemical potential etc. These are defined in terms of derivatives of the entropy.
- Equilibrium states "emerge" as an initial non-equilibrium state moves towards its most probable state. The path is one of increasing probability (entropy for an isolated system).

Question 3

(a) For *distinguishable* systems 1,2,3 . . . the partition function is $z_1 z_2 z_3 \ldots$ essentially since energies are additive in $e^{-E/kT}$. If all z have the same mathematical form then we would have $Z = z^n$. [3]

Indistinguishability means that if two particles are swapped then that corresponds to the *same* (micro)state. So in the product z^n we have *over-counted* the number of contributing states. Number of ways of re-arranging N objects is $N!$ (neglecting multiple occupancy - which we can do in the classical case). So $Z = z^N/N!$. [3]

Total part a [[6]]

(b) $\mathrm{d}F = \mathrm{d}E - T\mathrm{d}S - S\mathrm{d}T = -S\mathrm{d}T - p\mathrm{d}V$, so

$$p = -\left.\frac{\partial F}{\partial V}\right|_T$$

[3]

Then since $F = -kT \ln Z$, then

$$P = kT \left.\frac{\partial \ln Z}{\partial V}\right|_T .$$

[3]

(I'm not too fussed about keeping the N constant) Total part b [[6]]

(c) $\ln Z = N \ln z + \ldots$ and $\ln z = \ln V + \ldots$ So $\ln Z = N \ln V + \ldots$, [4]

and then

$$\frac{\partial \ln Z}{\partial V} = \frac{N}{V}$$

so that $p = NkT/V$, or $pV = NkT$ as required. [4]

Total part c [[8]]

(d) Kinetic energy $p^2/2m$ means that thermal energy kT corresponds to a momentum $\sqrt{2mkT}$. Since the de Broglie wavelength is $\lambda = 2\pi\hbar/p$, the momentum corresponds to $\lambda = 2\pi\hbar/\sqrt{2mkT} = \sqrt{2\pi^2\hbar^2/mkT}$. (A clear explanation in words, without equations would be OK). [3]

To within a factor of order unity this is Λ. So that the thermal de Broglie wavelength is the wavelength corresponding to the momentum corresponding to the kinetic energy corresponding to the thermal energy. [3]

Total part d [[6]]

(e) Treat the hard core short-distance repulsion and the weak attractive tail separately.

The hard core excludes a region from the spatial integration in the partition function. So V is replaced by $V - V_{\text{ex}}$ in the free-particle PF. [3]

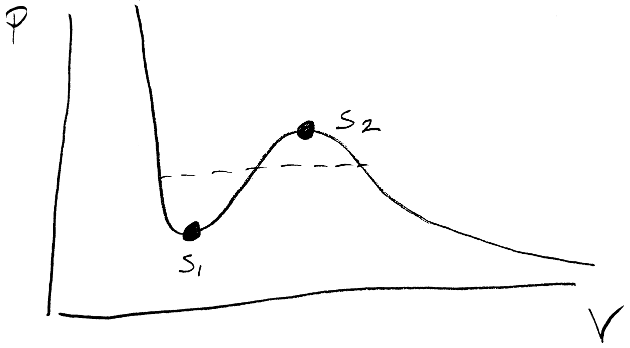
The weak attractive tail is approximated by a (small) constant potential $\langle E \rangle$. This adds to all the energies in the PF so the free-particle PF is multiplied by a factor $e^{-\langle E \rangle/kT}$ [3]

Total part e [[6]]

(f) Interacting particles are approximated by *free particles* immersed in a field – same field for all particles. This is called the "mean field" as it is an average of the fields the particles see.

Total part f [[3]]

(g) Sketch isotherm . . . . S_1 and S_2 are the spinodal points, corresponding to $\partial p/\partial V = 0$.



[2]

Spinodal points indicate the *limit of stability.* Region between S1 and S2 is *forbidden.* On left and right side the regions between the dotted (equilibrium coexistence) line and spinodal points are metastable - (superheating and supercooling.) [3]

Total part g [[5]]

Total Question 3 [[[40]]]

Question 4

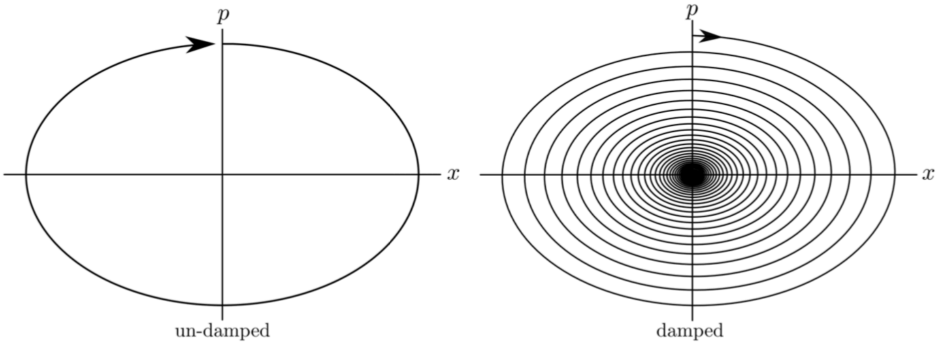
(a) Phase space is the space of generalised coordinates (q's) and generalised momenta (p's) of a system (classical description). A (micro)state is specified by a point in phase space; its time evolution is specified by a path in phase space. [2]

In the Gibbs picture an N-particle system will have $3N$ p's and $3N$ q's. So the phase space will have $6N$ dimensions – very large indeed. The microstate of such a system is described by a *single point* in the phase space. [2]

In the Boltzmann picture the state of each particle will be represented by a point in a 6-dimensional phase space. So then a system of N particles is represented by a "cloud" of N points in the 6-dimensional space. [2]

Total part a [[6]]

(b)Harmonic oscillator



[4]

The damping causes the phase point to spiral in to the origin. [2]

Total part b [[6]]

(c) $S \propto -\int \rho \ln \rho \, \mathrm{d}^N p \, \mathrm{d}^N q$ or $S \propto -\langle \ln \rho \rangle$ (This hides the question of the "size" of the "cells" in phase space that will need Planck's constant in order to get the correct classical–quantum correspondence). Total part c [[5]]

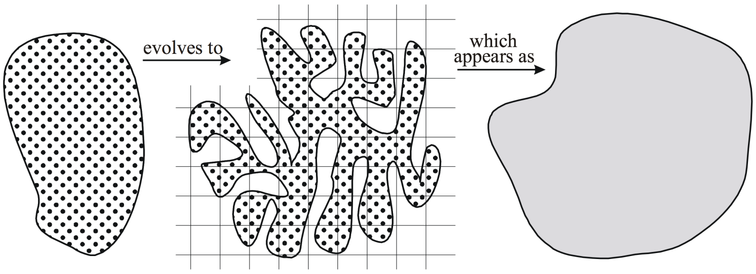
(d) Liouville $\Longrightarrow$ $\rho =$ const. – follows from the laws of mechanics. [3]

2nd. Law $\Longrightarrow$ $\rho =$ decreases – as the entropy increases. [3]

Explanation is in the nature of the flow of the cloud of points in phase space. [1]

Total part d [[7]]

(e) Flow of points in phase space



[4]

One cannot discern details of phase space on a scale finer than some limit. So one erects a grid at this limiting scale (coarse graining). Then it *appears* that the system occupies a *larger* region of phase space – i.e. the density appears to have decreased. [2]

The Uncertainty Principle of Quantum Mechanics would give limiting scale for discerning details of phase space. [2]

Total part e [[8]]

(f) Third Law says $S \to 0$ when $T \to 0$.

Quantum case: at $T = 0$ the system is in the ground state. Ignoring degeneracy this is a *single* state – i.e. $\Omega = 0$. Then from $S = k \ln \Omega$ this means $S = 0$, in accordance with the Third law. [4]

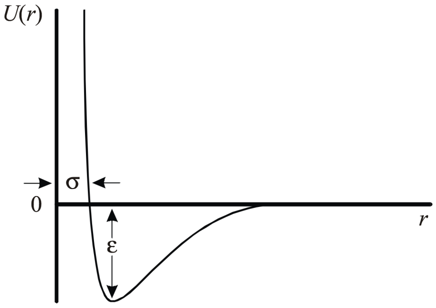
If the world were truly classical then the ground state would correspond to a *single point* in phase space. The density there would be *infinite* so the entropy would be minus infinity. (As given by the Sackur-Tetrode equation). [4]

Total part f [[8]]

Total Question 4 [[[40]]]

Question 5

Sketch of $U(r)$



Here σ is $\sim$ the distance of closest approach and ε is the depth of the attractive well.

Total part a [[4]]

(b) i. The interaction potential has the form of a “universal” function, scaled with a horizontal distance parameter σ and a vertical energy parameter ε. This means that distances are measured in terms of σ and energies in terms of ε then calculated properties would be the sane for different substances. [6]

(b) ii. Put $r = \sigma\rho$, so that $\mathrm{d}r = \sigma \mathrm{d}\rho$ and write $U(r) = \varepsilon f(r/\sigma)$. [3]

Then

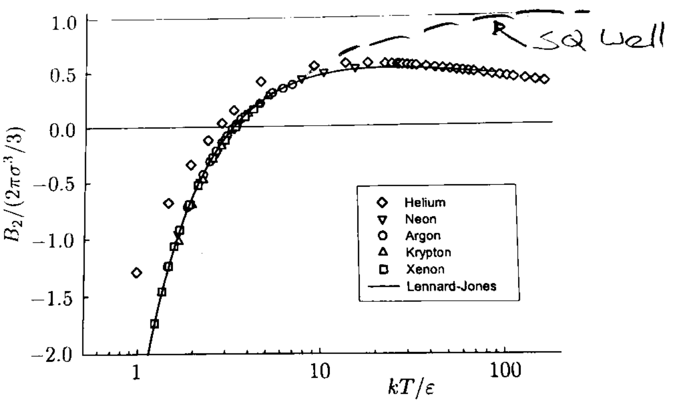
$$B_2(T) = -2\pi\sigma^3 \int_0^\infty \rho^2 \left(e^{-\varepsilon f(\rho)/kT} - 1\right) \mathrm{d}\rho.$$

[3]

The integral is a function of kT/ε only. So B is a function of kT/ε only. So then if B is plotted as a function of kT/ε then all points should collapse onto a common curve. [4]

Total part b [[16]]

(c) i. Sketch:



The square well $B_2(T)$ saturates at high temperature at the hard core value. By contrast the Lennard-Jones $B_2(T)$ turns over and reduces. [6]

(c) ii. The hard core of the square well potential means that two particles can never approach closer than a distance σ, no matter how "energetic" the collision. There is a certain "softness" of the Lennard-Jones potential at short distances. The $1/r^{12}$ variation means that very energetic collisions (high temperatures), the thermal energy can be enough to rise up the repulsive potential and the particles get (a little) closer together. By equating kT and $U(r)$ we can estimate how this "closest" r varies with increasing T. This may be regarded as an "effective" temperature-dependent hard core. [4]

Observed reduction of $B_2(T)$ at high temperatures may thus give information about the short-distance repulsive part of the interaction potential. [4]

Total part c [[14]]

(d) Quantum effects for helium are important – both statistics and delocalisation, but mainly delocalisation. This is more important at low temperatures where the thermal de Broglie wavelength becomes comparable with the size of the particle. [3]

The effect can be interpreted as the particles averaging the interaction potential over the delocalisation distance, resulting in an effective interaction potential, which does not obey the scaling property described above. [3]

Total part d [[6]]

Total Question 5 [[[40]]]