UNIVERSITY OF BRISTOL

Examination for the Degrees of B.Sc. and M.Sci. (Levels 3 and M)

STATISTICAL MECHANICS 34

MATH M4500

(Paper Codes MATH-M4500)

May-June 2011, 2 hours 30 minutes

This paper contains **five** *questions*
A candidate's **FOUR** *best answers will be used for assessment.*

Calculators are **not** *permitted in this examination.*

You may wish to use Stirling's formula which for $N \gg 1$, gives

$$\ln N! \approx N \ln N - N \quad .$$

For small x,

$$\cosh x = 1 + \frac{x^2}{2} + \frac{x^4}{4!} + \dots \ ,$$

$$\sinh x = x + \frac{x^3}{3!} + \frac{x^5}{5!} + \dots \ ,$$

$$\coth x = \frac{1}{x} + \frac{x}{3} - \frac{x^3}{45} + \dots$$

Do not turn over until instructed.

1. Consider a gas of N particles in a volume V.

   (a) (**3 marks**)

   i. At pressure p, what is the differential work done in expanding an infinitesimal volume dV?

   ii. Use the 2nd law of thermodynamics to obtain expressions for

   $$\left(\frac{\partial S}{\partial V}\right)_{E,N} \quad \text{and} \quad \left(\frac{\partial E}{\partial V}\right)_{S,N} \quad ,$$

   where S is the entropy and E the internal energy of the gas.

   (b) (**7 marks**)
   Use the fact that the entropy, $S(E, V, N)$, of a gas composed of N molecules with energy E, volume V is *extensive* to show that

   $$S = E\left(\frac{\partial S}{\partial E}\right)_{V,N} + V\left(\frac{\partial S}{\partial V}\right)_{E,N} + N\left(\frac{\partial S}{\partial N}\right)_{E,V} \quad ,$$

   and hence that $E = TS - pV + \mu N$

   (c) Consider using a diatomic ideal gas composed of N molecules as the working substance of an engine whose reversible cycle (1→2→3→1) consists of three quasistatic steps: 1→2 is isobaric expansion (at constant pressure), 2→3 is a constant volume process (isochoric), 3→1 is isothermal compression (at constant temperature). The temperatures T_1 and T_2 at points 1 and 2 in the cycle are given.

   i. (**3marks**) Draw this cycle in $p - V$ coordinates.

   ii. (**5 marks**) For each step compute the work done *by* the gas and the heat added *to* the gas. Identify which steps have heat flowing into the gas.

   iii. (**3 marks**) What is the efficiency of the cycle in terms of T_1 and T_2?

   iv. (**4 marks**) Calculate the change in entropy *and* Helmholtz free energy at each step of the cycle.

2. (a) A simplified model of a magnet in a magnetic field $\mathbf{B}$ is a collection of N *distinguishable* spins which can each be characterised by a magnetic moment, a *three* dimensional vector of fixed magnitude μ and arbitrary orientation, $\mathbf{S}_i$, $i \in \{1, \ldots, N\}$. Due to its magnetic moment each 'spin' has lower energy when aligned with the field. The system is thus described by a Hamiltonian

$$\mathcal{H} = -\mu \sum_{i=1}^{N} \mathbf{B} \cdot \mathbf{S_i} \; , \quad |\mathbf{S}_i| = 1 \; ,$$

and the magnetization is given by $\mathbf{M} = \mu \sum_{i=1}^{N} \mathbf{S}_i$. Consider such a 'magnet' at a fixed temperature, T with the magnetic field $\mathbf{B} = B\,\hat{\mathbf{z}}$ (oriented along the $z-$axis).

i. (**3 marks**) Which ensemble is appropriate for this system ? What are the possible microstates?

ii. (**4 marks**) What is the probability of being in a particular microstate ?

iii. (**7 marks**) Calculate the Helmholtz free energy and the average magnetization, $\langle \mathbf{M} \rangle$. Hence obtain an expression for the susceptibility, $\chi(T)$ defined as $\chi(T) = \left(\frac{\partial}{\partial \mathbf{B}} \cdot \langle \mathbf{M} \rangle \right)_{B=0}$.

(b) A better model called the Heisenberg model, which takes account of interactions between the 'spins' and their d nearest neighbours (n.n) is described by a Hamiltonian

$$\mathcal{H} = -\mu \sum_{i=1} \mathbf{B} \cdot \mathbf{S}_i - \frac{J}{2} \sum_{i,j}^{\text{n.n.}} \mathbf{S}_i \cdot \mathbf{S}_j \quad , \quad |\mathbf{S}_i| = 1 \; , .$$

The second sum is over all d nearest neighbour (n.n.) pairs i, j.

A mean field (Weiss) approximation involves replacing the instantaneous magnetic field felt by each spin by its average. The instantaneous field on spin $\mathbf{S}_i$ is

$$\mathbf{B}_i = -\mu^{-1} \frac{\partial \mathcal{H}}{\partial \mathbf{S}_i} \quad .$$

i. (**2 marks**) Show that the average instantantenous effective field on spin i is

$$\langle \mathbf{B}_i \rangle = \mathbf{B} + \Delta \mathbf{B} \quad ; \quad \Delta \mathbf{B} = Jd \, \langle \mathbf{S}_i \rangle / \mu \; ,$$

and hence obtain the mean-field Hamiltonian.

ii. (**6 marks**) Show that the mean-field model gives rise to the self-consistent equation

$$m = \left(\coth\left(\beta \mu B + \beta d J m\right) - \frac{1}{(\beta \mu B + \beta d J m)} \right) \quad , \quad m = \frac{M}{\mu N} \quad , \quad \langle \mathbf{M} \rangle = \hat{\mathbf{z}}\, M \; .$$

iii. (**3 marks**) Show graphically or otherwise that at zero external field, ($B = 0$) the mean-field equation implies a phase transition from a state with $m = 0$ to one with $m \neq 0$ at a finite temperature T.

3. (a) Consider a dilute gas of N particles in three dimensions with positions $\mathbf{q}_i(t)$ and momenta $\mathbf{p}_i(t)$, $(1 \leq i \leq N)$, which satisfy *Hamilton's equations* of motion. Its *microstate* is defined by the $6N$-dimensional *phase space* $(\boldsymbol{p}, \boldsymbol{q})$ where $\boldsymbol{p} = (\mathbf{p}_1, \cdots, \mathbf{p}_N), \boldsymbol{q} = (\mathbf{q}_1, \cdots, \mathbf{q}_N)$ with Hamiltonian $\mathcal{H}(\boldsymbol{p}, \boldsymbol{q})$.

i. (**3 marks**) What is the phase space density $\rho(\boldsymbol{p}, \boldsymbol{q}, t)$?

ii. (**8 marks**) Show that a consequence of Liouville's theorem is that the phase space density, $\rho(\boldsymbol{p}, \boldsymbol{q}, t)$ satisfies the equation

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \{\rho, \mathcal{H}\} = 0 \tag{1}$$

and explain the meaning of the **Poisson bracket** $\{A, B\}$.

(b) *Non Hamiltonian dynamics in molecular dynamics simulations:* consider a system of N particles in three dimensions with Hamiltonian, $\mathcal{H}$:

$$\mathcal{H}(\{\mathbf{p}_i, \mathbf{q}_i\}) = \sum_{i=1}^{N} \frac{1}{2m} |\mathbf{p}_i|^2 + \sum_{i \neq j} U(\mathbf{q}_i - \mathbf{q}_j) ,$$

where the equation of motion is modified by a friction term to

$$\dot{\mathbf{q}}_i = \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} \quad ; \quad \dot{\mathbf{p}}_i = -\frac{\partial \mathcal{H}}{\partial \mathbf{q}_i} - \lambda \mathbf{p}_i$$

i. (**7 marks**) Given that $\lambda(\boldsymbol{p})$ is function of momenta only, show that the Liouville theorem can be written in the form

$$\frac{\partial \rho}{\partial t} + \{\rho, \mathcal{H}\} = -C\lambda\rho + \boldsymbol{D} \cdot \frac{\partial \rho}{\partial \boldsymbol{p}} ,$$

and give the value of $C, \boldsymbol{D}$ in terms of λ and $\boldsymbol{p}$.

ii. (**7 marks**) If $U(\mathbf{r}) = A|\mathbf{r}|^{-12} - B|\mathbf{r}|^{-6}$, what value of friction, $\lambda(\boldsymbol{p}, \boldsymbol{q})$ must be chosen for the kinetic energy to remain constant?

4. (a) (**4 marks**)
Write down expressions for the classical and quantum partition functions in the *canonical ensemble* for a set of N particles with momentum p_i and position q_i and Hamiltonian $\mathcal{H}(\{p_i, q_i\})$. Explain why Planck's constant appears in the classical formula.

(b) (**5 marks**)
The Hamiltonian for a *classical* harmonic oscillator of frequency ω is

$$\mathcal{H}(\{q, p\}) = \frac{p^2}{2m} + \frac{m\omega^2\, q^2}{2} \, .$$

Calculate the free energy F , entropy S and internal energy E for the *classical* harmonic oscillator at temperature T.

(c) i. (**5 marks**) Write down an expression for the energy levels of a *quantum* harmonic oscillator of frequency ω. Briefly explain how it is obtained.

ii. (**6 marks**) Hence calculate the free energy F , entropy S and internal energy E for the *quantum* harmonic oscillator at temperature T.

(d) (**5 marks**)
Compare and contrast the specific heat capacity obtained from the classical and quantum calculations. Comment on what happens as $T \to 0$ and at high temperatures.

5. (a) Consider a *classical* system in the *grand canonical ensemble.*

i. (**3 marks**) Write down the expression for the *classical* grand partition function. How is this related to the grand potential?

ii. (**5 marks**) Calculate the mean number of particles $\langle N \rangle$ and the mean square fluctuations $\langle \Delta N^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2$ and hence obtain the relative mean-square fluctuation $\dfrac{\langle \Delta N^2 \rangle}{\langle N \rangle^2}$ in the thermodynamic limit.

(b) An ideal gas of *indistinguishable* classical particles of mass m is in a uniform attractive potential $U(\mathbf{r}) = -\varepsilon$ where $\varepsilon > 0$ in *three* dimensions and in contact with a reservoir at fixed chemical potential μ and temperature T. The gas is in a rectangular box of height h and base area A. There

i. (**3 marks**) Write down the Hamiltonian of the system.

ii. (**5 marks**) Evaluate the grand partition function $\mathcal{Z}$ and hence the grand potential, $\mathcal{G}$ of the system.

iii. (**5 marks**) Calculate the pressure, p and density, ρ and hence obtain a relationship between ρ , p and T.

iv. (**4 marks**) What happens as $\varepsilon \to \infty$?

End of examination.