King's College London

UNIVERSITY OF LONDON

This paper is part of an examination of the College counting towards the award of a degree. Examinations are governed by the College Regulations under the authority of the Academic Board.

BSc EXAMINATION

CP/3212 Statistical Mechanics

SUMMER 2002

Time allowed: **THREE** HOURS

Candidates must answer any SIX parts of SECTION A, and TWO questions from SECTION B.

The approximate mark for each question or part of a question is indicated in square brackets.

You must not use your own calculator for this paper. Where necessary, a College calculator will have been supplied.

TURN OVER WHEN INSTRUCTED

$$\begin{aligned}
\text{Planck constant } h &= 6.63 \times 10^{-34}\,\mathrm{J\,s} \\
\text{Boltzmann constant } k &= 1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}} \\
\text{Mass of electron } m_e &= 9.10 \times 10^{-31}\mathrm{kg} \\
\text{Unified atomic mass unit } m_u &= 1.66 \times 10^{-27}\mathrm{kg} \\
1\,\mathrm{eV} &= 1.60 \times 10^{-19}\,\mathrm{J} \\
\text{Speed of light } c &= 3.00 \times 10^{8}\,\mathrm{m\,s^{-1}} \\
\text{Stefan-Boltzmann } \sigma &= 5.67 \times 10^{-8}\mathrm{J\,m^{-2}s^{-1}K^{-4}}
\end{aligned}$$

SECTION A — answer any SIX parts of this section

1.1) A system can contain a variable number of particles and the only macroscopic observable is the mean number of particles N. The system can exist in a number of position states such that there are $g(n)$ states with exactly n particles. At equilibrium, the principle of maximum entropy assigns the probability

$$p(n) = \exp(-\eta n)/Z$$

to each state of the system with exactly n particles, where η is an undetermined multiplier and Z is the partition function. Write down an expression for Z and deduce the relations between N and Z, and between the entropy S and N and Z.

[7 marks]

1.2) For the system as defined in question 1.1, write down an appropriate expression for the fundamental equation of thermodynamics, and hence relate the undetermined multiplier η to the chemical potential μ. The free energy in this case is given by $F = -TS - \mu N$. Deduce the relation between the free energy F and the partition function Z.

[7 marks]

1.3) A system consists of a one-dimensional simple harmonic oscillator of mass m and force constant K. The state of the system is described classically by the instantaneous values of the momentum p and position q. The energy of the oscillator is given by

$$\frac{1}{2m}p^2 + \frac{1}{2}Kq^2,$$

and the macroscopic observable is the mean energy E. Show that the partition function of the system is given by

$$Z \propto kT\sqrt{\frac{m}{K}},$$

and find the constant of proportionality.
[Note:

$$\int_{-\infty}^{\infty} e^{-ax^2}\,dx = \sqrt{\pi/a}\,. \qquad]$$

[7 marks]

1.4) A system consists of a single simple harmonic oscillator whose energy eigenvalues are $h\nu(n + 1/2)$ with $n = 0, 1, 2, \ldots$. Show that the specific heat is

$$C = k\frac{x^2 e^x}{(e^x - 1)^2} \ ,$$

where $x = \beta h\nu$.

[7 marks]

1.5) The partition function Z for blackbody radiation can be written in the form

$$\ln Z = \frac{4\sigma}{3kc} V T^3 \ ,$$

where V is the volume and T is the temperature. Estimate the entropy density, S/kV, of the universe due to the cosmic microwave background radiation whose temperature is 2.735 K.

[7 marks]

1.6) Using Maxwell-Boltzmann statistics, derive an expression for the partition function of a mixture of two ideal gases in terms of the activities z_1 and z_2, and the single particle partition functions Q_1 and Q_2, of the two species.

[7 marks]

1.7) For an ideal gas composed of N particles of mass m the activity, in the classical limit, is related to the number density and temperature T by

$$z = \frac{N}{V}\left(\frac{2\pi mkT}{h^2}\right)^{-3/2} = \frac{N}{V}V'.$$

What is the physical significance of the term V'? Calculate V/N and V' for a plasma containing a mixture of protons and electrons in equal numbers with a mass density of $10\,\mathrm{kg\,m^{-3}}$ and a temperature of 2×10^4K, and comment on the results.

[7 marks]

1.8) The Van der Waals equation of state for an imperfect gas can be written in the form

$$\frac{P}{kT} = \frac{\rho}{1 - c\rho} - \frac{d}{kT}\rho^2,$$

where ρ is the number density and c and d are constants. What is the physical significance of the terms involving c and d? Write down the virial expansion of the pressure, and give a physical explanation of the temperature behaviour of the second virial coefficient.

[7 marks]

SECTION B — answer TWO questions

2) A solid contains $\mathcal{N}$ lattice sites. Most of these sites are occupied by one chemical species but a variable number are occupied by magnetic ions. Each magnetic ion can exist in a number of states with magnetic moment $m\sigma$ where σ is a continuous variable in the range $-\Delta \leq \sigma \leq \Delta$. The macroscopic observables are the mean number of magnetic ions N and the bulk magnetic moment M. Write down an expression for the partition function Z.

[7 marks]

Calculate the mean number of magnetic ions N and show that

$$M = Nm\Delta\left(\frac{1}{\gamma m\Delta} - \coth\gamma m\Delta\right),$$

where γ is an undetermined multiplier.

[11 marks]

Write down the fundamental equation of thermodynamics appropriate for this model and by comparing with the statistical mechanical expression for dS, where S is the entropy, relate γ to the applied magnetic field B and the temperature T.

[6 marks]

Deduce an expression for the isothermal susceptibility $(\partial M/\partial B)_T$ in the limit $B \to 0$.

[6 marks]

[Note: when $x \ll 1$

$$\coth x = \frac{1}{x} + \frac{1}{3}x + O(x^3) \quad]$$

3) A system consists of three indistinguishable particles each of which can exist in three possible energy states. The ground state is doubly degenerate and has, by convention, zero energy. The two excited states are singly degenerate and have energies ϵ and 2ϵ respectively. List the twenty states allowed using Bose-Einstein statistics. Write down expressions for the partition function using (a) Bose-Einstein statistics, (b) Fermi-Dirac statistics and (c) Maxwell-Boltzmann statistics.

[12 marks]

Deduce expressions for the mean energy E in each case and show that $E \to 9\epsilon/4$ at very high temperatures in all cases.

[8 marks]

Calculate the entropy for the Fermi-Dirac and Bose-Einstein cases and show that, at very low temperatures, the entropy tends to zero in the Fermi-Dirac case whereas the mean energy is finite, but when using Bose-Einstein statistics the mean energy is zero whereas the entropy is finite. Give a rational explanation of this apparent paradox.

[10 marks]

4) The grand partition function Ξ for an ideal gas of indistinguishable particles of mass m can be written in the form

$$\ln \Xi = 2\pi\sigma V \left(\frac{2m}{\beta h^2}\right)^{3/2} \int_0^\infty \ln(1 + \sigma z e^{-t})\, t^{1/2} dt,$$

where V is the volume, $\beta = 1/kT$, z is the activity and $\sigma = -1$ for bosons and $+1$ for fermions. Show that in both cases the pressure P is related to the energy density E/V by

$$P = \frac{2E}{3V}\,.$$

[8 marks]

The behaviour of the valence electrons in a metal can be modelled, reasonably successfully, as that of an ideal gas of fermions. The grand partition function Ξ_e for an ideal Fermi gas of particles with two internal degrees of freedom can be written in the form

$$\ln \Xi_e = 2 \ln \Xi\,,$$

where $\ln \Xi$ is given above with $\sigma = 1$. Show that

$$\frac{\beta PV}{N} = \frac{2}{3}\frac{I_{3/2}(z)}{I_{1/2}(z)}\,.$$

Then show that, when the gas is highly degenerate, the pressure of the electron gas is

$$P = \frac{2}{5}\frac{N}{V}\lambda_F\,,$$

where the Fermi energy λ_F is given by

$$\lambda_F = \left(\frac{3N}{8\pi V}\right)^{2/3} \left(\frac{h^2}{2m_e}\right)\,.$$

[15 marks]

Calculate the pressure of the electron gas in copper, whose mass density is $9000\,\mathrm{kg\,m^{-3}}$ and relative atomic mass is 64, on the assumption that there is one conduction electron per copper atom.

[7 marks]

[Note: when $z \gg 1$

$$I_s(z) = \int_0^\infty \frac{z e^{-t}}{(1 + z e^{-t})} t^s dt \approx \frac{(\ln z)^{s+1}}{s+1}\,. \qquad]$$

5) A gas consists of a mixture of n chemical species and is at sufficiently high temperature and low density for it to obey Maxwell-Boltzmann statistics. Show that the mean number N_i of particles of species i is related to the single-particle partition function $\mathcal{Q}_i$ and the activity z_i of the species i by

$$N_i = \mathcal{Q}_i z_i .$$

[6 marks]

The condition for equilibrium for the ideal gas reaction

$$\sum_i A_i \nu_i \rightleftharpoons 0,$$

where A_i is the chemical symbol of species i and ν_i is the stochiometric coefficient, is

$$\prod_i z_i^{\nu_i} = 1 \ .$$

The energy levels for the rotational motion of a diatomic molecule are $k\Theta_R J(J+1)$ where Θ_R is a characteristic temperature and $J = 0, 1, 2, \ldots$. Each level is $(2J+1)$-fold degenerate.

Describe why a gas of molecular hydrogen is considered as a mixture of two species, ortho-hydrogen and para-hydrogen.

[10 marks]

Write down the single particle partition function appropriate for each species.

[4 marks]

Given that for molecular hydrogen $\Theta_R = 85.4$K, show that the equilibrium ratio of the number of molecules of para-hydrogen to those of ortho-hydrogen, in the presence of charcoal, at 30 K is 33:1.

[10 marks]