King's College London

UNIVERSITY OF LONDON

B.Sc. EXAMINATION

CP/3212 Statistical Mechanics

Summer 2000

Time allowed: THREE Hours

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

Separate answer books must be used for each Section of the paper.

The approximate mark for each 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

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

SECTION A – Answer SIX parts of this section

1.1) A system can exist in a certain number of states, the set of which forms the state space Ω of the system. For each state ω belonging to Ω there is a probability $p(\omega)$ that the system is in state ω. Define the entropy of the system in terms of the set of probabilities $p(\omega)$. In a three horse race the bookmakers' odds are 1-1, 2-1, and 5-1. What is the entropy and how does it compare to the equally likely case?

[7 marks]

1.2) A certain system can exist in a number of energy states where $\lambda(\omega)$ is the energy of state ω. The principle of maximum entropy assigns, at equilibrium, the probability

$$p(\omega) = \exp(-\beta\lambda(\omega))/Z$$

to each state, where β is an undetermined multiplier and Z is the partition function. Write down an expression for Z and thence deduce the relation between the mean energy E and Z.

[7 marks]

1.3) A system (as in question 1.2) can exist in a number of energy states where $\lambda(\omega)$ is the energy of state ω. The probability assigned to state ω is

$$p(\omega) = \exp(-\beta\lambda(\omega))/Z$$

where β is an undetermined multiplier and Z is the partition function. Write down an appropriate expression for the fundamental equation of thermodynamics in this case, and thence relate the undetermined multiplier β to the temperature T.

[7 marks]

1.4) The energy eigenstates arising from 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 state is $(2J+1)$-fold degenerate. Deduce that the partition function for a system consisting of one such molecule can be written in the form

$$Z = \frac{T}{\Theta_R},$$

where T is the temperature and $T \gg \Theta_R$.

[7 marks]

1.5) A paramagnetic solid containing N spin-1/2 particles each with magnetic moment m, is placed in a uniform magnetic field B. Deduce that the partition function of the system is given by

$$Z = \left(2\cosh\frac{\gamma m}{2}\right)^N,$$

where γ is an undetermined multiplier. [You may assume that γ is related to magnetic field and temperature by $\gamma = -B/kT$.]

[7 marks]

1.6) A particle of mass m is attached to a spring with spring constant K. The particle undergoes simple harmonic motion in one dimension. The classical expression for the energy of the motion is

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

where p is the momentum and q is the position of the particle. Write down an expression for the partition function of the system, carefully explaining any new terms that you introduce.

[7 marks]

1.7) The partition function for a model of an ideal gas of bosons can be written in the form

$$\Xi = \prod_{\omega}\left(1 - ze^{-\beta\lambda(\omega)}\right)^{-1},$$

where z is the activity, $\beta = 1/kT$ and $\lambda(\omega)$ is the energy of state ω. Deduce an expression for $n(\omega)$, the number of particles in state ω, and sketch n as a function of λ.

[7 marks]

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

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

where σ is the Stefan-Boltzmann constant, c is the speed of light, 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 which is at a temperature of 2.735 K.

[7 marks]

SECTION B – Answer TWO questions

2) A system consists of three atoms and the macroscopic observable is the mean energy E. Each atom can exist in three energy states—the ground state chosen, by convention to have zero energy, and two excited states, one with energy ϵ and one with energy 2ϵ. The ground state is doubly degenerate ($g(0) = 2$) whereas the excited states are non-degenerate.

List the twenty possible states if the system obeys Bose-Einstein statistics.

[6 marks]

Letting $x = e^{-\epsilon/kT}$, write down expressions for the partition function of the system if it obeys (a) Bose-Einstein statistics (b) Fermi-Dirac statistics and (c) Maxwell-Boltzmann statistics.

[9 marks]

Show that, when the temperature $T \to \infty$, the mean energy $E = 9\epsilon/4$ in all three cases.

[9 marks]

Show that the entropy, S, in the Bose-Einstein case tends to $k \ln 4$ in the limit as $T \to 0$, and calculate the entropy in the same limit for the Fermi-Dirac case. What is the physical reason for the difference in the entropy between these two cases?

[6 marks]

3) The grand partition function Ξ for an ideal Fermi gas of particles of mass m and g internal degrees of freedom can be written in the form

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

where z is the activity, V is the volume and $\beta = 1/kT$. Deduce the condition for non-degeneracy, namely

$$z = \frac{N}{gV} \left(\frac{\beta h^2}{2\pi m}\right)^{3/2} \ll 1.$$

[6 marks]

Show that, when the gas is highly degenerate, the equation of state can be written in the form

$$PV = \frac{2}{5} N \lambda_F \,,$$

where

$$\lambda_F = \left(\frac{3N}{4\pi g V}\right)^{2/3} \left(\frac{h^2}{2m}\right) .$$

[12 marks]

A white dwarf star, which is electrically neutral, consists solely of completely ionised silicon (atomic number 14, relative atomic mass 28, $g = 1$) and free electrons ($g = 2$). The star has a uniform mass density of $10^9 \,\mathrm{kg\,m^{-3}}$ and is at a temperature of 10^9 K. Show that the silicon ions contribute about 10% to the total internal pressure of the star.

[12 marks]

[Note:

$$I_s(z) = \int_0^\infty \frac{ze^{-t}}{(1 + ze^{-t})} t^s dt \approx \frac{(\ln z)^{s+1}}{s+1} \quad \text{when } z \gg 1,$$

and

$$\int_0^\infty t^{1/2} e^{-t} dt = \sqrt{\pi}/2 \,. \qquad]$$

4) The energy eigenvalues of a simple harmonic oscillator of frequency ν are $(n + \frac{1}{2})h\nu$, where $n = 0, 1, 2, \ldots$. The eigenvalues are non-degenerate. Derive an expression for the partition function of the system.

[6 marks]

Given that the number of normal modes of blackbody radiation with frequencies between ν and $\nu + d\nu$ in a cavity of volume V is

$$g(\nu) = \frac{8\pi V}{c^3}\nu^2 d\nu\,,$$

where c is the speed of light, deduce the Planck radiation formula for the spectral density $\rho(\nu, T)$ namely,

$$\rho(\nu, T)d\nu = \frac{8\pi}{c^3}\frac{h\nu^3}{e^{h\nu/kT} - 1}d\nu\,.$$

[10 marks]

Sketch ρ as a function of ν.

[2 marks]

The cosmic microwave background radiation is blackbody radiation for which the spectral density as a function of frequency has a maximum at $\nu_m = 1.6 \times 10^{11}\mathrm{s}^{-1}$. Calculate the temperature of the radiation.

[12 marks]

[Note: $x_m = 2.82144$ is the solution of the equation $x_m = 3\,(1 - e^{-x_m})$.]

5) Consider the reaction

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

where A_i is the symbol of species i and ν_i is the stoichiometric coefficient. Deduce that the condition for equilibrium at constant temperature and pressure is

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

where z_i is the activity of species i.

[7 marks]

Oxygen is enclosed in a container of volume V, and the conditions of temperature and density are such that it behaves as an ideal, non-degenerate gas. Some of the molecules are adsorbed on the surface of the container, so that there are N_s adsorbed molecules and N_g molecules in the gas. There is interchange between the gas molecules and adsorbed molecules so that, at equilibrium,

$$\mathrm{O}_{2,\mathrm{s}} \rightleftharpoons \mathrm{O}_{2,\mathrm{g}}\,.$$

At equilibrium what is the relation between the activity z_g in the gas phase and the activity z_s of the adsorbed molecules?

[2 marks]

Given that the classical expression for the translational energy of each molecule in the gas phase is

$$\frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)\,,$$

where p_x, p_y, p_z are the components of the momentum and m is the mass, show that the grand partition of the gas phase can be written in the form

$$\ln \Xi_g = V \left(\frac{2\pi mkT}{h^2}\right)^{3/2} z_g\,.$$

[7 marks]

Suppose that for the adsorbed molecules there are $\mathcal{N}$ possible adsorption sites and there is a binding energy $-\epsilon$ associated with each adsorbed molecule. Show that the grand partition function for the adsorbed molecules is given by

$$\Xi_s = \left(1 + z_s e^{\beta\epsilon}\right)^{\mathcal{N}}\,.$$

[7 marks]

Thence show that

$$\frac{N_s}{\mathcal{N}} = \frac{\beta P}{\beta P + \left(\frac{2\pi m}{\beta h^2}\right)^{3/2} e^{-\beta\epsilon}}\,,$$

where P is the pressure in the gaseous phase.

[7 marks]

[Note:

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