

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.

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

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 $J = 0, 1, 2, \dots$. 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 $T \rightarrow \infty$, 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 $T \rightarrow 0$, 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

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

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

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

[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 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

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

- 4) The energy eigenvalues of a simple harmonic oscillator of frequency ν are $(n + \frac{1}{2})h\nu$, where $n = 0, 1, 2, \dots$. 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 .

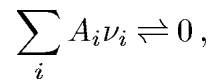
[2 marks]

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



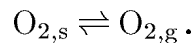
where A_i is the symbol of species i and ν_i is the stoichiometric coefficient. Deduce that the condition for equilibrium at constant temperature and pressure is

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

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,



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

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

[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

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

[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:

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