King's College London

UNIVERSITY OF LONDON

B.Sc. EXAMINATION

CP/3212 Statistical Mechanics

Summer 1997

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

$$\text{Planck constant } h = 6.63 \times 10^{-34}\,\mathrm{J\,s}$$
$$\text{Boltzmann constant } k = 1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}}$$
$$\text{Speed of light } c = 3.00 \times 10^{8}\,\mathrm{m\,s^{-1}}$$
$$\text{Atomic mass unit } m_u = 1.66 \times 10^{-27}\,\mathrm{kg}$$
$$\text{Mass of electron } m_e = 9.11 \times 10^{-31}\,\mathrm{kg}$$
$$\text{Stefan-Boltzmann constant } \sigma = 5.67 \times 10^{-8}\,\mathrm{J\,m^{-2}s^{-1}K^{-4}}$$

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 $p(\omega)$, and state the principle of maximum entropy.

[7 marks]

1.2) A molecule of rubber can be characterised by the end-to-end length $\ell(\omega)$ of each configuration ω. The macroscopic observable of the system is the mean end-to-end length L. The principle of maximum entropy assigns to each configuration ω, a probability

$$p(\omega) = \exp[-\gamma \ell(\omega)]/Z,$$

where Z is the partition function, and γ is an undetermined multiplier. Show that the entropy S of the system is given by

$$S = k \log Z + k\gamma L$$

and that

$$dS = k\gamma dL.$$

[7 marks]

1.3) Sketch the graph of the number of particles per energy state, $n(\lambda)$, of a degenerate Fermi gas as a function of the energy λ. Explain qualitatively why each electron does not contribute $\frac{3}{2}$k to the heat capacity of metals at room temperature.

[7 marks]

1.4) 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 $\rho = N/V$, is the number density, and c and d are constants. Deduce the virial expansion of the equation of state and explain the physical significance of the terms involving c and d.

[7 marks]

1.5) The grand partition function for an ideal gas of fermions or bosons of mass m enclosed in a volume V can be written in the form

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

where z is the activity, $\beta = 1/kT$, and $\sigma = \pm 1$, depending on whether the particles are fermions or bosons. Deduce the condition that the gas is non-degenerate, namely

$$z = \left(\frac{N}{V}\right) \left(\frac{2\pi mkT}{h^2}\right)^{-3/2} \ll 1.$$

[7 marks]

[Note:

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

1.6) Describe qualitatively the assumptions underlying the Debye theory of the vibrational states of a solid.

[7 marks]

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

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

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 whose temperature is 2.735 K.

[7 marks]

1.8) 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 Q_i and the activity z_i of the species i by

$$N_i = Q_i z_i.$$

[7 marks]

SECTION B – Answer TWO questions

2) Consider 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. The condition for equilibrium is

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

Use the results of question 1.8 to show that the equilibium constant K is related to the number of particles N_{A_i} by

$$K = \prod_i N_{A_i}^{\nu_i}$$

[5 marks]

and relate K to the single particle partitions of the species.

[3 marks]

The energy levels for the rotational motion of a diatomic molecule are $(\hbar^2/2I)J(J+1)$ where I is the moment of inertia of the molecule and $J = 0, 1, 2, \ldots$. Each level is $(2J+1)$-fold degenerate.

Describe qualitatively how the behaviour of the heat capacity of molecular hydrogen is explained in terms of para-hydrogen and ortho-hydrogen.

[8 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 40 K is 7.95.

[14 marks]

3) The grand partition function for a model of a gas consisting of N indistinguishable, non-interacting fermions of mass m and two internal degrees of freedom enclosed in a volume V can be written in the form

$$\log \Xi = 4\pi V \left(\frac{2m}{\beta h^2}\right)^{3/2} \int_0^\infty \log\left(1 + ze^{-t}\right) t^{1/2} dt \ ,$$

where z is the activity and $\beta = 1/kT$.

When the gas is highly degenerate show that

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

where

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

[20 marks]

Calculate separately the pressures due to the electron gas and the nuclear gas in a star composed of equal numbers of protons and electrons with a mass density of 10^9kg m^{-3} and at a temperature of 10^9K.

[10 marks]

[Note: When $z \gg 1$

$$\int_0^\infty \frac{t^s ze^{-t}}{1 + ze^{-t}} dt = \frac{(\log z)^{s+1}}{s+1} + \cdots \ . \qquad]$$

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

[5 marks]

The number of normal modes of oscillation of a continuous, isotropic, elastic solid with frequencies between ν and $\nu + d\nu$ is

$$8\pi V\left(\frac{1}{c_\ell^3}+\frac{2}{c_t^3}\right)\nu^2 d\nu,$$

where V is the volume of the solid and c_ℓ is the speed of longitudinal waves and c_t is the speed of transverse waves.

Use Debye theory to show that, at low temperatures, the energy of a solid containing N atoms is given by

$$E = \frac{9}{8}Nk\Theta_D + \frac{3\pi^4}{5}Nk\frac{T^4}{\Theta_D^3}$$

where T is the temperature and Θ_D is the characteristic Debye temperature.

[12 marks]

Relate the Debye temperature to the speeds of sound in the solid.

[6 marks]

Discuss the behaviour of the total heat capacity of a *metal* at low temperatures.

[7 marks]

[Note:

$$\int_0^\infty \frac{t^3 e^{-t}}{1-e^{-t}}dt = \frac{\pi^4}{15} \qquad]$$

5) Blackbody radiation in a volume V can be treated as a gas of photons with energies $h\nu$, $0 \leq \nu < \infty$, where a state of the system is specified by the momentum $\mathbf{p} = (h\nu/c)\mathbf{n}$, where $\mathbf{n}$ is the direction of motion, and the position $\mathbf{r}$ of each photon of frequency ν. The partition function for a gas of bosons with two internal degrees of freedom and with energy $\lambda(\omega)$ in state ω is given by

$$Z = \prod_{\omega} \left(1 - ze^{-\beta\lambda(\omega)}\right)^{-2},$$

where z is the activity and $\beta = 1/kT$. Show that the partition function for blackbody radiation can be written in the form

$$\log Z = -\frac{8\pi V}{c^3} \int_0^\infty \log\left(1 - ze^{-\beta h\nu}\right) \nu^2 d\nu \ .$$

[10 marks]

The energy E is related to the spectral density $\rho(\nu)$ by

$$E = \int_0^\infty \rho(\nu) d\nu \ .$$

Deduce the Planck expression for the spectral density.

[6 marks]

Show that the number density of photons is given by

$$\frac{N}{V} = 60.422 \left(\frac{kT}{hc}\right)^3 \ .$$

[7 marks]

Calculate the number density of photons in the universe due to the cosmic microwave background radiation which has a temperature of 2.735 K. If matter in the universe is composed of 75% H and 25% He by mass, and the mean mass density of the universe is $6 \times 10^{-28}\,\mathrm{kg\,m^{-3}}$, show that there are approximately 10^9 photons for every material particle.

[7 marks]

[Note:

$$\int_0^\infty \frac{x^2 e^{-x}}{1 - e^{-x}} dx = 2.40412\ldots \qquad]$$