King's College London

UNIVERSITY OF LONDON

B.Sc. EXAMINATION

CP/3212 Statistical Mechanics

Summer 2001

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

$$\text{Planck constant } h = 6.63 \times 10^{-34}\,\mathrm{J\,s}$$
$$\text{Boltzmann constant } k = 1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}}$$
$$\text{Mass of electron } m_e = 9.10 \times 10^{-31}\mathrm{kg}$$
$$\text{Unified atomic mass unit } m_u = 1.66 \times 10^{-27}\mathrm{kg}$$
$$1\,\mathrm{eV} = 1.60 \times 10^{-19}\,\mathrm{J}$$

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 $p(\omega)$. If the system has N states, what assignment of probabilities ensures that S has its maximum possible value, and what assignment gives the minimum possible value?

[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

$$S = k \log Z + k\gamma L \quad \text{and that} \quad dS = k\gamma dL.$$

[7 marks]

1.3) A system can exist in a number of energy states where $\lambda(\omega)$ is the energy of state ω. Using the principle of maximum entropy 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) A system consists of two atoms each of which can exist in a ground state with energy zero and an excited state with energy ϵ. The ground state is doubly degenerate and the excited state is singly degenerate. What is the partition function of the system using (a) Bose-Einstein statistics, (b) Fermi-Dirac statistics, and (c) Maxwell-Boltzmann statistics?

[7 marks]

1.5) A system consists of a single particle which can exist in a number of states with magnetic moment $m\sigma$ where σ is a continuous variable in the range $-\Delta \leq \sigma \leq \Delta$. Write down an expression for the partition function of the system, carefully explaining any new terms that you introduce.

[7 marks]

1.6) 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

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

A white dwarf star is composed of ^{4}He at a density of 10^9kg m^{-3} and a temperature of 10^9K and is completely ionised. Calculate the activity for the nuclear gas and that for the electron gas and explain the difference.

[7 marks]

1.7) The partition function of an ideal gas of fermions is

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

where z is the activity, β is an undetermined multiplier and $\lambda(\omega)$ is the energy of state ω. 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. Describe qualitatively how this explains the small contribution of the valence electrons to the heat capacity of metals.

[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 n are occupied by a defect species. Each defect species can exist in two electronic energy states with energies ϵ_1 and ϵ_2. Show that the partition function of the system is given by

$$Z = \left[1 + z(e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2})\right]^{\mathcal{N}} ,$$

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

[10 marks]

Calculate the mean number of defects N and show that

$$\frac{E}{N} = \epsilon_1 + \frac{\Delta\epsilon}{e^{\beta\Delta\epsilon} + 1} ,$$

where E is the mean energy and $\Delta\epsilon = \epsilon_2 - \epsilon_1$.

[10 marks]

Show that the heat capacity C_V of the system can be written in the form

$$\frac{C_V}{Nk} = \left(\frac{\beta\Delta\epsilon}{e^{\beta\Delta\epsilon} + 1}\right)^2 e^{\beta\Delta\epsilon} .$$

[10 marks]

3) The grand partition function Ξ for an ideal Fermi gas can be written in the form

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

where V is the volume, m is the mass of each particle, $\beta = 1/kT$ and z is the activity. Show that the entropy per particle of this system is given by

$$\frac{S}{Nk} = \frac{5 I_{3/2}(z)}{3 I_{1/2}(z)} - \ln z, \quad \text{where} \quad I_s(z) = \int_0^\infty \frac{ze^{-t} t^s dt}{1 + ze^{-t}}.$$

[14 marks]

Given that, for a highly-degenerate Fermi gas, that is $z \gg 1$,

$$I_s(z) = \frac{1}{s+1}(\ln z)^{(s+1)} + \frac{s\pi^2}{6}(\ln z)^{(s-1)} + O((\ln z)^{(s-3)}),$$

show that

$$\frac{S}{Nk} \sim \frac{\pi^2}{2}(\ln z)^{-1}.$$

[9 marks]

For this system the Fermi energy, λ_F is given by

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

Show that the entropy per particle is

$$\frac{S}{Nk} \sim \frac{\pi^2}{2}\frac{T}{T_F}, \quad T \ll T_F,$$

where T_F is the Fermi temperature. Considering, as an example, the case of electrons in metals, does this result make sense physically?

[7 marks]

4) Graphite has a layered structure in which the coupling of the motion of the atoms between layers is weak, especially at low temperatures. The thermal behaviour of graphite can therefore be considered as due to the motion of the atoms in a collection of layers within each of which the phonon spectrum is equal to $A\nu d\nu$, where ν is the frequency of a normal mode of oscillation and A is a constant. Adapt Debye theory to show that the partition function of the system is given by

$$\ln Z = -A \int_0^{\nu_m} \left(\beta h\nu/2 + \ln(1 - e^{-\beta h\nu})\right) \nu d\nu \,,$$

where $\beta = 1/kT$, and relate A to the constant ν_m.

[15 marks]

Thence show that at low temperatures the heat capacity due to each layer is proportional to $N_\ell T^2$, where N_ℓ is the number of atoms in each layer, and find the constant of proportionality in terms of the Debye temperature Θ_D.

[15 marks]

[You are given that

$$\int_0^\infty \frac{t^2 dt}{e^t - 1} \approx 2.404 \,. \quad]$$

5) Deduce that the condition for equilibrium at constant temperature and pressure of the reaction

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

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

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

where z_i is the activity of species i.

[8 marks]

The electrons evaporated from a heated metal filament can be treated as a perfect gas in equilibrium with the electrons in the metal. The electrons in the gas are at a higher potential energy χ with respect to those in the metal. Assuming that the chemical potential of the electrons in the metal is equal to the Fermi energy, λ_F, show that the number N_g of electrons in the gas is

$$N_g = 2V \left(\frac{2\pi m_e}{\beta h^2}\right)^{3/2} e^{-\beta(\chi - \lambda_F)} \,,$$

where $\beta = 1/kT$.

[14 marks]

If the difference $(\chi - \lambda_F) \approx 4\text{eV}$ and the system is heated to a temperature of 2500 K, show that the pressure of the free electron gas is about 0.18 Pa.

[8 marks]