King's College London

UNIVERSITY OF LONDON

B.Sc. EXAMINATION

CP/3212 Statistical Mechanics

Summer 1999

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

$$\text{Planck constant } h = 6.63 \times 10^{-34}\,\text{J s}$$
$$\text{Boltzmann constant } k = 1.38 \times 10^{-23}\,\text{J K}^{-1}$$
$$\text{Mass of electron } m_e = 9.10 \times 10^{-31}\text{kg}$$
$$1\text{eV} = 1.60 \times 10^{-19}\,\text{J}$$
$$\text{Stefan-Boltzmann constant } \sigma = 5.67 \times 10^{-8}\,\text{J m}^{-2}\text{s}^{-1}\text{K}^{-4}$$

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 $p(\omega)$. If the system has N states and each state is equally likely, what then is the entropy?

[7 marks]

1.2) A certain 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 states such that there are $g(n)$ states with exactly n particles. The principle of maximum entropy assigns at equilibrium, 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 thence deduce the relation between N and Z.

[7 marks]

1.3) For the system as defined in question 1.2, write down an appropriate expression for the fundamental equation of thermodynamics, and hence relate the undetermined multiplier η to the chemical potential μ.

[7 marks]

1.4) A system consists of two indistinguishable dice. What are the total number of allowed states of the system using Bose-Einstein statistics, Fermi-Dirac statistics and Maxwell-Boltzmann statistics?

[7 marks]

1.5) 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]

1.6) The quantum-mechanical energy eigenvalues for a simple harmonic oscillator of frequency ν are non-degenerate and equal to $(n + 1/2)h\nu$, where $n = 0, 1, 2, \ldots$. Derive an expression for the partition function of the system and hence calculate the mean energy.

[7 marks]

1.7) 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

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

[7 marks]

1.8) What are the main assumptions on which the Debye theory of the heat capacities of solids is based?

[7 marks]

SECTION B – Answer TWO questions

2) A solid contains $\mathcal{N}$ lattice sites most of which 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 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 for an ideal Fermi gas of particles with two internal degrees of freedom can be written in the form

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

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

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

[20 marks]

Thence derive an expression for the compressibility of a metal due to that of the electron gas.

[10 marks]

[Note: when $z \gg 1$

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

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

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

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

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

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 0.12 Pa.

[8 marks]