King's College London

UNIVERSITY OF LONDON

B.Sc. EXAMINATION

CP/3212 Statistical Mechanics

Summer 1998

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

$$
\begin{aligned}
\text{Planck constant } h &= 6.63 \times 10^{-34}\,\mathrm{J\,s} \\
\text{Boltzmann constant } k &= 1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}} \\
\text{Speed of light } c &= 3.00 \times 10^{8}\,\mathrm{m\,s^{-1}} \\
\text{Atomic mass unit } m_u &= 1.66 \times 10^{-27}\mathrm{kg} \\
\text{Mass of electron } m_e &= 9.1 \times 10^{-31}\mathrm{kg} \\
\text{Relative atomic mass of nitrogen } &= 14 \\
\text{Relative atomic mass of oxygen } &= 16 \\
1\mathrm{eV} &= 1.60 \times 10^{-19}\,\mathrm{J} \\
\text{Stefan-Boltzmann constant } \sigma &= 5.67 \times 10^{-8}\,\mathrm{J\,m^{-2}s^{-1}K^{-4}}
\end{aligned}
$$

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 $p(\omega)$. 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) The macroscopic observable M of a system corresponds to a set of microscopic properties $m(\omega)$ defined for each state ω of the system. The principle of maximum entropy assigns, at equilibrium, the probabilities

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

to each state of the system, where γ is an undetermined multiplier and Z is the partition function. Write down an expression for Z and thence deduce the relation between M and Z.

[7 marks]

1.3) A system consists of a single molecule of rubber. The macroscopic observable is the mean end-to-end length L of the molecule, and a state ω of the system corresponds to a configuration of the molecule. The internal energy of the system is constant. The probability that the molecule is in configuration ω is given by

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

where γ is an undetermined multiplier and Z is the partition function. Write down an expression for the fundamental equation of thermodynamics appropriate to this case, given that the molecule can be stretched by an external force F. Thence relate the undetermined multiplier γ to the external force.

[7 marks]

1.4) The partition function of an ideal gas of bosons is

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

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 Bose gas as a function of the energy λ. Describe qualitatively how this helps to explain the superfluid phase of liquid helium.

[7 marks]

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

[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 $10^9\,\mathrm{kg\,m^{-3}}$ 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 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) 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 system consists of a single molecule whose electronic configuration is such that it has a ground state with energy ϵ_0 and degeneracy g_0 and an excited state with energy ϵ_1 and degeneracy g_1. Write down an expression for the partition function of the system.

[4 marks]

Show that the heat capacity C is given by

$$\frac{C}{k} = \frac{\alpha x^2 e^{-x}}{(1 + \alpha e^{-x})^2} ,$$

where $\alpha = g_1/g_0$, $x = \Delta\epsilon/kT$ and $\Delta\epsilon = (\epsilon_1 - \epsilon_0)$.

[15 marks]

The heat capacity of this system has a maximum. Calculate the temperature at which this maximum occurs if $g_0 = 1, g_1 = 3$ and $\Delta\epsilon = 0.03\,\text{eV}$.

[11 marks]

[Note: The solution of

$$x = 2\left(\frac{1 + 3e^{-x}}{1 - 3e^{-x}}\right)$$

is $x \approx 2.845$.]

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

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

[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) Air is a mixture composed of N_2 (80% by mass) and O_2 (20% by mass). If air is at a temperature of 280 K and a mass density of $1.23\,\mathrm{kg\,m^{-3}}$, show that the nitrogen component of air can be treated as a non-degenerate perfect gas.

[8 marks]

Assuming a similar result for the oxygen component, deduce an expression for the partition function of air in terms of the single particle partition functions Q_N and Q_O of nitrogen and oxygen respectively. Show that the heat capacity is given by

$$C_V/k = \beta^2 \left(N_N \frac{\partial^2 \ln Q_N}{\partial \beta^2} + N_O \frac{\partial^2 \ln Q_O}{\partial \beta^2} \right),$$

where N_N and N_O are the number of molecules of nitrogen and oxygen respectively.

[10 marks]

By making reasonable assumptions about the distribution of energy between the various modes of motion of the system, calculate the contribution of translational, rotational and vibrational motion to the specific heat C_V/Nk, where $N = N_N + N_O$.

[12 marks]

[You are given that the characteristic temperature of rotational motion is about 5 K, and that for vibrational motion is about 2800 K for both molecules. You are also given that the energy eigenvalues for rotational motion are $\frac{\hbar^2}{2I}J(J+1)$, that each energy level is $(2J+1)$-fold degenerate, and that the energy eigenvalues for vibrational motion are $h\nu(n+1/2)$. Here $J = 0, 1, 2, \ldots$ and $n = 0, 1, 2, \ldots$.]

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

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

where $\beta = 1/kT$, z is the activity and $\sigma = +1$ for fermions and -1 for bosons. Given that

$$\ln(1+x) = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{x^n}{n} \quad \text{and} \quad \int_0^\infty x^{1/2} e^{-x} dx = \sqrt{\pi}/2$$

show that

$$\ln \Xi = V w \sum_{n \geq 1} (-\sigma)^{n+1} \frac{z^n}{n^{5/2}},$$

where $w = (2\pi m k T/h^2)^{3/2}$.

[10 marks]

Hence derive the virial expansion of the reduced pressure $\frac{P}{kT}$ in powers of the number density $\rho = N/V$ up to terms in ρ^2

[12 marks]

What is the physical significance of the parameter w in comparison with ρ? Sketch the behaviour of the second virial coefficient B_2 as a function of temperature in both the case of fermions and bosons and discuss its behaviour in comparison with the behaviour of B_2 for a non-ideal gas.

[8 marks]