UNIVERSITY COLLEGE LONDON

University of London

EXAMINATION FOR INTERNAL STUDENTS

For The Following Qualifications:-

B.Sc. *M.Sci.*

Physics 2B28: Statistical Thermodynamics and Condensed Matter Physics

COURSE CODE	:	**PHYS2B28**
UNIT VALUE	:	**0.50**
DATE	:	**28-MAY-03**
TIME	:	**10.00**
TIME ALLOWED	:	**2 Hours 30 Minutes**

03-C1071-3-110

TURN OVER

Answer ALL SIX questions from section A and THREE questions from section B.

The numbers in square brackets in the right-hand margin indicate the provisional allocation of marks per sub-section of a question.

Boltzmann's constant is k
Internal Energy is E and $\beta = 1/kT$
Planck's constant is h and $\hbar = \frac{h}{2\pi}$
Avogadro constant $N_A = 6.02 \times 10^{23}\text{mole}^{-1}$
Elementary charge $e = 1.6 \times 10^{-19}$C
All other thermodynamic symbols have their usual meaning
The Stirling approximation is $\ln n! = n \ln n - n$
Single particle density of momentum states $f(p)dp = \left(\frac{V}{h^3}\right) 4\pi p^2 dp$

SECTION A [Part marks]

1. A system is in contact with a large heat reservoir such that the pressure is constant throughout, and the final temperature following a process is the same as the initial temperature. Show that the maximum **useful** work done **by** the system W_u, is given by $W_u \leq -\Delta G$, where G, the Gibbs free energy is given by $G = E - TS + pV$. [4]

   In an electrolysis cell, the overall reaction is the dissociation of a water molecule with the transfer of two electrons across the cell. If the Gibbs free energy of the process is +237 kJ mol^{-1} determine the minimum EMF that must be applied to the cell for electrolysis to start, showing details of your reasoning. [3]

2. A rubber band in thermal equilibrium may be modelled by N freely pivoted inextensible links each of length d, which can point fowards or backwards along the band.

   If a band consists of 14 links of which 10 point forwards along the band, identify the macrostate, and determine the number of accessible microstates (or the statistical weight). [3]

   Use the fundamental equation of thermodynamics and the Boltzmann hypothesis to **qualitatively** explain the origin of the force required to extend the band. [3]

3. Write down the Boltzmann distribution of the probability p_r for a system to be in the r^{th} microstate with energy E_r. [2]

   If the energy levels of a hydrogen atom are given by $E_n = -\alpha/n^2$ eV and the degeneracy of the n^{th} level is $2n^2$ show that the probability of hydrogen atoms in thermal equilibrium, to be in the n^{th} level, is proportional to

   $$2n^2 e^{3\alpha/2n^2\bar{E}}$$

   where $\bar{E}$ is the average kinetic energy of the atoms. [3]

   What is the ratio of atoms in the state $n = 3$ to those in the state $n = 1$ for hydrogen atoms with mean energy $\bar{E}$ of 1 eV in a stellar gas, if α is 13.6 eV ? [1]

4. Show that allowed values of the momentum components p_x and p_y of a particle confined to move on a square surface of side L are given by

$$p_x = \frac{h}{2L} n_x \text{ and } p_y = \frac{h}{2L} n_y,$$

where n_x and n_y are positive integers. [3]

Obtain the single particle density of momentum states in two dimensions. [3]

5. Explain briefly what is meant by the term **photon** in the context of black-body radiation and the term **phonon** in the context of a crystalline solid. Why can such systems correctly be treated by the Boltzmann distribution? [3]

Show that the partition function Z_r and the occupation number n_r of the r^{th} microstate for photons are given by

$$Z_r = \frac{1}{1 - e^{-\beta\epsilon_r}} \text{ and } n_r = -\frac{1}{\beta}\frac{\partial}{\partial\epsilon_r}(\ln\ Z_r) = \frac{1}{e^{\beta\epsilon_r} - 1},$$

where $\epsilon_r = \hbar\omega_r$ is the energy and ω_r is the angular frequency of the r^{th} microstate. [2]

Write down an expression, without simplification, for the energy density $u(\omega_r, T)$ of black body radiation, clearly identifying the component parts of your expression. [3]

6. A system containing a quantal gas, is in contact with a heat bath with which it can exchange particles as well as heat. Show that the Gibbs distribution (or the grand canonical distribution) for a state with N_r particles, $N_r = \sum_i n_i$ where the n_i are the occupation numbers, and an energy E_{N_r} where $E_{N_r} = \sum_i n_i\epsilon_i$, factorises into the product of probabilities

$$p_i(n_i) = \frac{\exp(\beta(\mu - \epsilon_i)n_i)}{Z_{Gi}}$$

where μ is the chemical potential. [4]

Show that for quantal statistics, the mean occupation number is given by

$$\bar{n}_i = kT\frac{\partial \ln\ Z_{Gi}}{\partial\mu}$$

and obtain $\bar{n}_i$ for Fermi-Dirac statistics. [3]

SECTION B

7. Starting with the fundamental equation of thermodynamics and using the third Maxwell equation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$ show that

$$\left(\frac{\partial E}{\partial V}\right)_T = \left(T\left(\frac{\partial p}{\partial T}\right)_V - p\right).$$ [4]

A mole of gas obeys the van der Waals equation $\left(p + \frac{a}{V^2}\right)(V - b) = RT$ where a and b are constants. Show that $\left(\frac{\partial E}{\partial V}\right)_T = \frac{a}{V^2}$. [3]

By considering $E(T, V)$ obtain an expression for E, the internal energy of a mole of van der Waals gas. [4]

By considering $S(T, V)$ show that

$$dS = \frac{C_V}{T}dT + \frac{R}{V - b}dV$$

and obtain an expression for the entropy. [4]

Obtain the relation between the temperature and volume for the ideal adiabatic expansion of the van der Waals gas. [5]

8. Write down the Boltzmann equation relating the entropy S to the number of microstates (or statistical weight) Ω of an isolated system, and state the condition of equilibrium. [3]

An isolated system of volume V, containing N particles is partitioned by a diathermal wall into two subsystems 1 and 2. Derive the equilibrium condition

$$\left(\frac{\partial S_1}{\partial E_1}\right)_{N,V} = \left(\frac{\partial S_2}{\partial E_2}\right)_{N,V}, \text{ and justify the relation } \frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V}.$$ [4]

Spin 1/2 magnetic dipoles in a paramagnetic solid align in a magnetic field B such that dipoles aligned parallel to the field have energy $-\mu B$ and those antiparallel have energy $+\mu B$, where μ is the dipole moment. Determine the number of microstates of the macrostate of N dipoles, with n dipoles aligned parallel to the field, and show using the above equilibrium condition that

$$n = \frac{N}{1 + e^{-x}} \text{ and } E = N\mu B\left(1 - \frac{2}{1 + e^{-x}}\right) \text{ where } x = \frac{2\mu B}{kT}.$$

Comment on the physical interpretation of the internal energy E at $x = 0$ and $x = \infty$. [8]

Suppose now that the paramagnetic solid is made of spin J particles where the magnetic interaction energy $-\mu \cdot \mathbf{B}$ is given by $-g_J\mu_B m_J B$, where g_J is the Lande g factor, μ_B the Bohr magneton and $m_J, -J \leq m_J \leq J$, the magnetic quantum number. Explain why this system is treated by the Boltzmann distribution and obtain the partition function. [5]

9. By considering a system containing N particles and of volume V in contact through diathermal walls with a large heat bath, show that the probability p_r of the system being in its r^{th} microstate with energy E_r is given by the Boltzmann distribution [4]

$$p_r = \frac{e^{-\beta E_r}}{Z}, \text{ where the partition function } Z = \sum_r e^{-\beta E_r}.$$

The DNA molecule may be modelled as a zip fastener where one end of the fastener is always closed. From the open end, s links are open with total energy $s\epsilon$ where ϵ is the energy of an open link, and $N - s$ links are closed. Show that the partition function Z is given by

$$Z = \frac{1 - x^N}{1 - x} \text{ where } x = e^{-\beta\epsilon}.$$

[5]

Prove that the mean number of open links $\bar{s}$ is given by

$$\bar{s} = x\frac{\partial \ln Z}{\partial x} = N\frac{x^N}{x^N - 1} - \frac{x}{x - 1}$$

[6]

By considering the behaviour of $\ln Z$ as $x \to 1$ show the $\bar{s} = N/2$ when $x = 1$. Under what conditions of degeneracy can $x = 1$ be reached? [5]

10. For Bose-Einstein statistics the mean occupation number $\bar{n}_r$ of a single particle state of energy ϵ_r is given by

$$\bar{n}_r = \frac{1}{(e^{\beta(\epsilon_r - \mu)} - 1)}, \text{ and for the lowest energy state } \bar{n}_1 = \frac{1}{(Be^{\beta\epsilon_1} - 1)}$$

where ϵ_1 is extremely close to zero energy and $B = e^{-\beta\mu}$. Explain why B is expected to be just greater than one at low temperatures. [4]

Using the density of states factor in terms of the momentum, and the integral given at the end of this question, show that at high temperature B is proportional to $T^{\frac{3}{2}}$ for N bosons in a volume V. [5]

Show that the appropriate density of states factor for N non-relativistic spinless ideal bosons in a volume V, each of mass m and kinetic energy ϵ is given by

$$f(\epsilon)d\epsilon = 2\pi\frac{V}{h^3}(2m)^{\frac{3}{2}}\epsilon^{\frac{1}{2}}d\epsilon.$$

[5]

Obtain an expression for the internal energy E of an ideal boson system below T_c where T_c is the temperature at which B becomes just greater than one and μ close to zero. [4]

What is the temperature dependence of the heat capacity C_V of the above system where $T < T_c$? [2]

In this question you may use

$$\int_0^\infty x^2 e^{-\alpha x^2} dx = \frac{1}{4}\left(\frac{\pi}{\alpha^3}\right)^{\frac{1}{2}}.$$

11. The energy levels E_n of a particle of mass m moving in a one dimensional box of length L are given by

$$E_n = \frac{\hbar^2\pi^2 n^2}{2mL^2}$$

Show that the partition function of a particle in a three dimensional cubic box of side L, assuming that summations are replaced by integrals and that $\int_0^\infty e^{-\alpha x^2}dx = \frac{1}{2}\left(\frac{\pi}{\alpha}\right)^{\frac{1}{2}}$, is given by

$$Z(1,T) = \left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2} L^3$$ [5]

Write down the classical partition function for a monatomic gas of N identical particles, explaining the factors in the expression. [3]

Assuming, without proof that the above yields the Sackur-Tetrode equation for the entropy S,

$$S = Nk\left[\ln\frac{V}{N} + \frac{3}{2}\ln\left(\frac{mkT}{2\pi\hbar^2}\right) + \frac{5}{2}\right]$$

use $\mu = -T\left(\frac{\partial S}{\partial N}\right)_V$ to show that the chemical potential μ is given by

$$\mu = kT\ln\frac{n}{n_Q} \text{ where } n = \frac{N}{V} \text{ and } n_Q = \left(\frac{mkT}{2\pi\hbar^2}\right)^{\frac{3}{2}}.$$ [5]

Oxygen circulating in the blood stream is absorbed by the myoglobin (Mb) molecule to form MbO_2 which has an energy ϵ with respect to the Mb molecule. Assuming that the oxygen in the blood can be treated as an ideal classical gas, and that the grand canonical partition function is of the usual form $Z_{Gi} = \sum_{n_i} e^{\beta(\mu-\epsilon_i)n_i}$, show that the ratio f of the oxygenated molecules to those unoxygenated molecules is given by

$$f = \frac{p}{(n_Q kT e^{\epsilon/kT} + p)}$$

where p is the partial pressure of the oxygen. [7]