ONE HOUR THIRTY MINUTES

A list of constants is enclosed.

UNIVERSITY OF MANCHESTER

Statistical Mechanics

1st June 2022, 9.45 a.m. - 11.15 a.m.

Answer **ALL** parts of question 1 and **TWO** other questions

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Electronic calculators may be used, provided that they cannot store text.

The numbers are given as a guide to the relative weights of the different parts of each question.

Information which may be used in this paper:

The density of states for a spinless particle in two dimensions is $g(k) = \dfrac{Ak}{2\pi}$.
The symbol β is defined as $\beta = 1/(k_B T)$.

You may use $k_B = 8.6173 \times 10^{-5}$ eV K^{-1}

The symbol n_Q is defined as $n_Q = \left(\dfrac{mk_B T}{2\pi\hbar^2}\right)^{3/2}$.

The translational partition function for a single non-relativistic particle in a box is $Z_1 = V g_s n_Q$, where g_s is the spin degeneracy.

In the classical limit, the chemical potential for an ideal gas is given by $\mu = -k_B T \ln\left(\dfrac{g_s n_Q}{n}\right)$.

The Planck formula for the energy density of black-body radiation is

$$u(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{\mathrm{e}^{\hbar\omega\beta} - 1}.$$

Stirling's approximation is $\ln N! \approx N \ln N - N$ for $N \gg 1$.

$$\sum_{n=0}^{\infty} (n+1)\, x^n = (1-x)^{-2} = \text{for } |x| < 1.$$

The following integrals may be useful (note $n!! \equiv n(n-2)(n-4)\ldots 1$ for odd n.)

$$\int_0^\infty \frac{x^{1/2}}{\mathrm{e}^x + 1}\mathrm{d}x = 0.678094 \qquad \int_0^\infty \frac{x^{1/2}}{\mathrm{e}^x - 1}\mathrm{d}x = 2.31516$$

$$\int_0^\infty \frac{x}{\mathrm{e}^x + 1}\mathrm{d}x = \frac{\pi^2}{12} \qquad \int_0^\infty \frac{x}{\mathrm{e}^x - 1}\mathrm{d}x = \frac{\pi^2}{6}$$

$$\int_0^\infty \frac{x^{3/2}}{\mathrm{e}^x + 1}\mathrm{d}x = 1.15280 \qquad \int_0^\infty \frac{x^{3/2}}{\mathrm{e}^x - 1}\mathrm{d}x = 1.78329$$

$$\int_0^\infty \frac{x^2}{\mathrm{e}^x + 1}\mathrm{d}x = 1.80309 \qquad \int_0^\infty \frac{x^2}{\mathrm{e}^x - 1}\mathrm{d}x = 2.40411$$

$$\int_0^\infty \frac{x^{5/2}}{\mathrm{e}^x + 1}\mathrm{d}x = 3.08259 \qquad \int_0^\infty \frac{x^{5/2}}{\mathrm{e}^x - 1}\mathrm{d}x = 3.74453$$

$$\int_0^\infty \frac{x^3}{\mathrm{e}^x + 1}\mathrm{d}x = \frac{7\pi^4}{120} \qquad \int_0^\infty \frac{x^3}{\mathrm{e}^x - 1}\mathrm{d}x = \frac{\pi^4}{15}$$

$$\int_0^\infty x^n \mathrm{e}^{-x/a}\mathrm{d}x = n!\, a^{n+1} \qquad \int_0^\infty x^n \mathrm{e}^{-x^2/a^2}\mathrm{d}x = \frac{(n-1)!!\sqrt{\pi}a^{n+1}}{2^{(n/2+1)}} \quad \text{for even } n.$$

1. a) Distinguish between the microstates and macrostates of a many-particle system, giving examples.

[5 marks]

b) The internal energy of a certain gas of volume V and entropy S is given by

$$E = CS^{4/3}V^{-1/3},$$

where C is a constant. Find the relationship between the energy density and the temperature T. What might the gas be?

[5 marks]

c) A system has two energy states of 0 eV and 1 eV. It is in thermal equilibrium with a heat bath, and the average energy of the particle is 0.25 eV. What is the temperature of the heat bath?

[5 marks]

d) For an ideal, non-relativistic gas of spin-$\frac{1}{2}$ particles of mass m, show that the Fermi energy at zero temperature is given by

$$\varepsilon_F = Cn^{2/3} \ ,$$

where n is the particle number density. You should determine the constant C.

[6 marks]

e) Classify the following as bosons or fermions, giving your reasoning: protons, photons, hydrogen atoms, ^{7}Li atoms.

[4 marks]

2. i) For a gas of N indistinguishable non-interacting molecules in the classical limit, write down the partition function Z_N in terms of the single-particle partition function, here denoted z. Explain how the entropy and pressure can be obtained from Z_N via the Helmholtz free energy F.

[5 marks]

ii) For a particular gas, around room temperature, $z = aVT^{5/2}$, where a is a constant. Find expressions for the entropy, pressure and energy. What might the gas be?

[7 marks]

iii) Now consider the case where there are two different kinds of molecule present, N_a of one type and N_b of another, with single-particle partition functions z_a and z_b respectively. The $N_a + N_b$ particle partition function is the product of the partition functions for the two gases separately. Show that the pressures, entropies and energies add. Hence show that if $z_a = z_b$ and both have the form given in part (ii), the pressure and energy are the same as if all particles were indistinguishable, but that there is an extra term S_{mixing} in the entropy, where

$$S_{\text{mixing}} = k_B(N \ln N - N_a \ln N_a - N_b \ln N_b).$$

[6 marks]

iv) From your results in part (ii), write down an expression for the Gibbs free energy of the gas, and hence for the chemical potential.

[2 marks]

v) Consider the case where the two gases can react to make a third gas, also with the same z:

$$\mathrm{A} + \mathrm{B} \rightleftharpoons 2\mathrm{C}.$$

Initially there are twice as many molecules of gas A present as gas B, with none of C. What will be the ratios of the gases at equilibrium?

[5 marks]

3. a) A system consists of four distinguishable spin-1 atoms. The z-component of the magnetic moment of each can be $\pm\mu$ or 0. State how many microstates there are there with total magnetic moment 4μ, 3μ, 2μ and 0 respectively.

[7 marks]

b) In a three-dimensional crystal of magnetic atoms in a strong magnetic field, collective excitations of the atoms' spins are called magnons. Each magnon contributes $2\mu_B$ to the magnetic moment of the crystal. Magnons behave like free spin-1 bosons in a box with a quadratic energy spectrum $\varepsilon = \alpha k^2$, where α is a constant and k is the wave number.

i) Explain why the chemical potential of magnons is zero.

[1 marks]

ii) Write down an expression for the number of magnons in the system with wave numbers between k and $k + \mathrm{d}k$, and hence show that the change in magnetisation of the crystal due to the magnons is

$$M_m = 0.352\mu_B \left(\frac{k_B T}{\alpha}\right)^{3/2} .$$

[9 marks]

iii) Will the magnons exhibit Bose-Einstein condensation? Briefly explain your answer.

[3 marks]

iv) Now consider a crystal with a magnon gas pumped by microwave radiation in such a way that an additional number of magnons ΔN is created, independent of temperature. Write down an implicit equation for the chemical potential of the pumped magnon gas. State whether the pumped magnon gas can exhibit the phenomenon of Bose-Einstein condensation. (Note that the lowest energy state of a magnon is slightly above zero for a finite crystal.)

[5 marks]

4. i) Briefly describe the external constraints that lead to the use of the microcanonical, canonical and grand canonical distributions, and state the relevant probability distributions and the key thermodynamic potentials used in each case.

[9 marks]

ii) Consider an adsorbent surface that has sites which can adsorb up to two gas molecules. A single molecule can be adsorbed in two different states, but there is only one way of adsorbing two molecules. An adsorbed molecule has binding energy ϵ compared to one in a free state. The surface is in contact with a classical spinless ideal gas with chemical potential μ, pressure P and temperature T.

Derive an expression for the mean occupancy per site, $\overline{n}$, in terms of ϵ, T and μ. Is this valid for arbitrary binding energy?

[6 marks]

iii) Hence show that $\overline{n}$ is related to the gas pressure, P, via the equation

$$P = P_0 \left(\frac{\overline{n}}{2 - \overline{n}} \right) \exp(-\epsilon/k_B T),$$

and determine P_0 in terms of the temperature.

[6 marks]

iv) For an ideal gas which is slightly too cold or dense to be in the classical regime, the equation of state is

$$PV = Nk_B T \left(1 \pm \frac{N}{4\sqrt{2} g_s n_Q V} \right).$$

State what determines whether we take the plus or minus sign, and explain the origin of the deviation in each case.

[4 marks]

END OF EXAMINATION PAPER