ONE HOUR THIRTY MINUTES

A list of constants is enclosed.

UNIVERSITY OF MANCHESTER

Statistical Mechanics

[redacted] 2024, [redacted] - [redacted]

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

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The use of calculators is permitted, as long as they cannot store text and have no graphing capability.

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} , $\hbar c = 1973$ eV Å, and one atomic mass unit is 9.315×10^5 eV/c^2.

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 $N \gg 1$.

$\sum_{n=0}^{\infty} (n+1)\, x^n = (1-x)^{-2}$ 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 an example which makes clear how they are related.

[5 marks]

b) From the following, list the true expressions:

$$P = -\left.\frac{\partial F}{\partial V}\right|_{TN}, \quad \frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_{TN}, \quad P = -\left.\frac{\partial \Phi_G}{\partial V}\right|_{T\mu}, \quad E = T\left.\frac{\partial S}{\partial T}\right|_{VN},$$

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{VN}, \quad \mu = -\left.\frac{\partial \Phi_G}{\partial N}\right|_{TV}, \quad S = -\left.\frac{\partial \Phi_G}{\partial T}\right|_{P\mu}, \quad \frac{\mu}{T} = \left.\frac{\partial S}{\partial N}\right|_{EV}.$$

[4 marks]

c) A single particle of a classical ideal gas in a volume V has partition function Z_1. What is the partition function of N identical particles? Explain your answer, including any restrictions on N that apply for its validity. Show that the Helmholtz free energy derived from this partition function is extensive.

[6 marks]

d) Write down the Fermi-Dirac distribution function and define all relevant terms. Explain the meanings of a "degenerate Fermi gas" and its "Fermi Temperature", T_F. Sketch the distribution as a function of energy for two temperatures, T_1 and T_2, where $T_1 \ll T_F$ and $T_1 < T_2 < T_F$.

[6 marks]

e) A pioneering experiment on Bose-Einstein condensation involved 5×10^5 atoms of ^{23}Na in a volume of 500 μm^3. Estimate the condensation temperature.

[4 marks]

2. i) Explain the statistical basis of entropy and of its increase in spontaneous processes.

[6 marks]

ii) A paramagnetic solid consists of N spin-$\frac{1}{2}$ non-interacting magnetic dipoles, of magnetic moment μ. These can orient themselves in either of two directions, parallel or antiparallel to the external magnetic field B. What is the energy of the system if n dipoles are oriented parallel to the field? Give an expression for the statistical weight $\Omega(n, N)$ of this macrostate.

[4 marks]

iii) Two such systems each with $N = 20$ dipoles are initially isolated from each other and from the surroundings, and have internal energies $E = -16\mu B$ and zero respectively. How many of the spins are parallel and antiparallel to the magnetic field in each system? Show that the systems have entropies $5.25k_B$ and $12.13k_B$ respectively. (Do not use Stirling's approximation.)

[6 marks]

iv) The systems are brought into thermal contact so that energy can flow freely between them. What is the total energy of the combined system? Calculate the statistical weight of the combined system, and hence find the increase in entropy of the universe as a result of bringing the two systems into contact.

[4 marks]

v) A solid with a macroscopic number of dipoles is in a magnetic field. It is found that when 0.01 J of heat is added, the entropy increases by 3.33×10^{-5} J/K. What is the temperature of the solid?

If the internal energy is changed by the same amount by changing the magnetic field instead (without heat transfer), what happens to the entropy? Does the field need to increase or decrease for this to happen?

[5 marks]

3. i) Write down the Boltzmann distribution for the probability of a system at temperature T being in a microstate with energy E. Briefly and without detailed derivation, say how this distribution arises.

[7 marks]

ii) A particle has evenly spaced energy levels, 0, ε, 2ε .... These levels have degeneracies which increase with the energy so that the first state is non-degenerate and the state with energy $n\varepsilon$ has degeneracy $n+1$. Show that the one-particle partition function is

$$Z_1 = \frac{1}{\left(1 - \exp\left(-\varepsilon\beta\right)\right)^2} \quad .$$

[4 marks]

iii) Hence show that the average energy of the particle at temperature T is

$$E = \frac{2\varepsilon}{\exp(\varepsilon\beta) - 1} \quad .$$

Find and explain the low-temperature limit of this expression. Show that the high temperature limit is $2k_BT$.

[8 marks]

iv) For a particular system the level spacing ε is 0.54 eV. Can 300 K be considered as the low or high temperature limit? Find the heat capacity at this temperature in units of k_B.

[6 marks]

4. i) Sketch the heat capacity of diamond as predicted by the Einstein and Debye models, making clear where they agree and how they differ, and explaining the principal difference in the assumptions that enter each.

[7 marks]

ii) In diamond, phonons have an approximately linear dispersion relation $\omega = v_s k$, and we will assume that the speed v_s is the same for all modes of vibration. Given that the density of diamond is 3.52 $\mathrm{g\,cm^{-3}}$, and $v_s = 1.4 \times 10^4$ $\mathrm{m\,s^{-1}}$ find the Debye temperature. Comment on the implications of this for the room temperature heat capacity of diamond.

[8 marks]

iii) At low temperatures, there are three types of phonons in graphene. For two modes the vibration is in-plane with a linear dispersion relation $\omega = v_s k$, and for the third it is out-of-plane with a quadratic dispersion relation, $\omega = \alpha k^2$. For simplicity we will take v_s to be equal for the two in-plane modes. All modes propagate in a plane (i.e. in two dimensions).

By first calculating the average energy at low temperatures, show that the heat capacity per unit area, ignoring the electronic contribution, has the form

$$c = PT + QT^2$$

where the first term is due to the out-of-plane mode and the second to the in plane modes, and P and Q are constants, involving α and v_S respectively, which you should determine. Which term will dominate at sufficiently low temperatures?

[10 marks]

END OF EXAMINATION PAPER