EGT3
ENGINEERING TRIPOS PART IIB

Monday 29 April 2024 9.30 to 11.10

Module 4A9

MOLECULAR THERMODYNAMICS

Answer not more than ***three*** *questions.*

All questions carry the same number of marks.

The ***approximate*** *percentage of marks allocated to each part of a question is indicated in the right margin.*

Write your candidate number ***not*** *your name on the cover sheet.*

STATIONERY REQUIREMENTS
Single-sided script paper

SPECIAL REQUIREMENTS TO BE SUPPLIED FOR THIS EXAM
CUED approved calculator allowed
Engineering Data Book

10 minutes reading time is allowed for this paper at the start of the exam.

You may not start to read the questions printed on the subsequent pages of this question paper until instructed to do so.

You may not remove any stationery from the Examination Room.

1 Nitrogen has a molar mass of 28 kg kmol^{-1}. A crude model of the molecular velocity distribution of nitrogen gas in a certain low-pressure state divides the molecules into six groups. Each group contains the same number of molecules and each molecule within a group has the same velocity. The absolute velocity components c_i (i = 1, 2, 3) in m s^{-1} for the six groups are as follows:

$$(548, 40, -10); \qquad (23, 565, -10); \qquad (23, 40, 515);$$

$$(-502, 40, -10); \qquad (23, -485, -10); \qquad (23, 40, -535).$$

(a) (i) Calculate the temperature of the gas. [20%]

(ii) Stating any assumptions, calculate the contributions to the total energy per unit mass of the gas from the mean motion, the random translational motion and the internal molecular motion. [25%]

(b) The Lennard-Jones potential for the interaction between two molecules may be written in the form

$$V(r) = A\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\}$$

where A and σ are constants and r is the separation between the molecules.

(i) Sketch on the same axes $V(r)$ and the corresponding force of interaction between two molecules. Take repulsive forces as positive. [15%]

(ii) For nitrogen $A = 5.30 \times 10^{-21}$ J and $\sigma = 0.372$ nm. Determine the separation between two nitrogen molecules for which the intermolecular force is zero. [10%]

(iii) Using the data from (ii), estimate the critical temperature of nitrogen. [15%]

(iv) Consider nitrogen gas at the same temperature as in part (a) but now at a pressure of 200 bar. Estimate the energy of a single molecule due to potential interaction with its nearest neighbours. Compare this with its other components of internal energy and comment on the result. [15%]

2 (a) The Boltzmann 'master equation' describing the evolution of the molecular velocity distribution function, f, may be expressed in the form

$$\frac{\partial f}{\partial t} + c_j \frac{\partial f}{\partial x_j} = \left[\frac{\partial f}{\partial t}\right]_{\text{coll.}}$$

where c_j is the absolute molecular velocity component in the x_j direction and the term on the right-hand side is due to molecular collisions. Note that the Einstein summation notation has been adopted for this equation.

(i) Give a full definition of the molecular velocity distribution function f. [10%]

(ii) Consider some molecular quantity Q (measured per molecule). Starting from the Boltzmann equation, and explaining the steps in your derivation, show that

$$\frac{\partial}{\partial t}\left(n\overline{Q}\right) + \frac{\partial}{\partial x_j}\left(n\overline{c_j Q}\right) = \text{RHS}$$

where n is the number density of molecules. Determine the right-hand side term (RHS) in terms of quantities defined above. [20%]

(iii) By making appropriate choices for Q and, where appropriate, writing $c_j = u_j + C_j$ (where u_j is the mean velocity and C_j is the peculiar velocity), derive equations for the conservation of mass and the conservation of momentum. To obtain full marks your momentum equation should show explicitly terms corresponding to viscous stresses and pressure forces. [40%]

(b) Consider the quantity $F_j = \overline{\rho c_j (c^2/2)}$ (where ρ is density) for a monatomic gas. Explain what this quantity represents physically. By writing $c_j = u_j + C_j$, decompose F_j into four terms. Provide a physical interpretation for each term with reference to macroscopic quantities. [30%]

3 *Information relevant to this question can be found on the next page.*

(a) Show that the de Broglie wavelength for a particle of mass m and with translational kinetic energy ϵ is given by

$$\lambda = \frac{h}{(2m\epsilon)^{1/2}}$$

where h is Planck's constant. [10%]

(b) Estimate the De Broglie wavelength for:

(i) a car on the motorway;

(ii) a typical helium atom within a gas at $T = 300$ K (base λ in this case on the RMS velocity component in a single coordinate direction);

(iii) an electron accelerated across a potential difference of 100 V.

Comment on the significance of these values. [20%]

(c) For a thermodynamic system with length scale ℓ a dimensionless parameter Π may be formed by normalising ℓ with the de Broglie wavelength, i.e., $\Pi = \ell/\lambda$.

(i) Explain the physical significance of the parameter Π. [10%]

(ii) For an ideal monatomic gas contained within a cubic box show that, provided $\Pi \gg 1$, the single-particle partition function may be written

$$Z = \alpha \Pi^q$$

and determine values for the constants α and q. Explain the significance of the constraint on Π in terms of the spacing of energy states. [30%]

(iii) For a system with d degrees of freedom the number of microstates may be estimated from

$$\Omega \simeq \Pi^d$$

Use this to determine an expression for the entropy S of a system comprising N molecules of an ideal monatomic gas contained within a volume V at temperature T. Compare your result with that obtained from

$$S = k\left(\frac{\partial(T \ln Q)}{\partial T}\right)_{V,\,N}$$

where Q is the system partition function and k is Boltzmann's constant. Comment on any difference. [30%]

Information for Question 3

Mass of an electron, m_e	:	9.11×10^{-31} kg
Charge on an electron, e	:	1.60×10^{-19} C

The translational energy states for a particle of mass m confined within a volume V have quantised energies

$$\epsilon_i = \frac{h^2}{8mV^{2/3}}(n_1^2 + n_2^2 + n_3^2)$$

where h is Planck's constant and n_1, n_2 and n_3 are the quantum numbers corresponding to translational modes in the three coordinate directions.

The single particle partition function is defined by

$$Z = \sum_i \exp(-\epsilon_i/kT)$$

where k is Boltzmann's constant and T is temperature.

You may find the following definite integral useful

$$\int_0^\infty \exp(-\tau^2 x^2)\,\mathrm{d}x = \frac{\sqrt{\pi}}{2\tau}$$

4 By separation of variables, the time-independent Schrödinger wave equation for a particle possessing only translational kinetic energy may be expressed in the ordinary differential form

$$\frac{\mathrm{d}^2\psi_i}{\mathrm{d}x_i^2} + \left(\frac{2\pi p_i}{h}\right)^2 \psi_i = 0$$

where x_i ($i = 1,\ 2,\ 3$) are the spatial coordinates and h is Planck's constant.

(a) Explain fully what p_i and ψ_i represent and give units for each of these quantities. [15%]

(b) Determine a general solution to the above equation for a single dimension, x_1. [15%]

(c) Consider a single particle of mass m confined to move within a field-free square plane of side L. The plane is oriented such that its normal is in the x_3 direction.

(i) Write down the boundary conditions for ψ and hence determine the quantised energies of the particle, ϵ_k, in terms of quantities introduced above and two suitably defined quantum numbers, n_1 and n_2. [20%]

(ii) Derive an expression for the function $g(C)$, defined such that $g(C)\,\mathrm{d}C$ is the number of energy states for which the speed of the particle is in the range C to $C + \mathrm{d}C$. State any restrictions on the range of validity of your expression. [30%]

(d) Consider now the hypothetical situation in which argon molecules at $T = 300$ K are confined to a two-dimensional plane of area $100\,\mathrm{cm}^2$. Calculate the number of quantum states (for a single molecule) that have energy less than that corresponding to the RMS molecular speed. [20%]

END OF PAPER

ANSWERS

1

(a) 309.4 K; 1.115 kJ/kg; 137.8 kJ/kg; 91.9 kJ/kg

(b) 0.418 nm; 96 K; 9×10^{-22}J/molecule ~ 10%

2

3

(a)

(b) 1.1×10^{-38} m; 1.26×10^{-10} m; 1.23×10^{-10} m

4

(a)

(b)

(c)

(d) 3.94×10^{19} states