

EGT3
ENGINEERING TRIPOS PART IIB

Wednesday 25 April 2018 2 to 3.40

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.

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

(a) Define kinetic temperature and calculate its value for a sample of helium that has an RMS molecular speed of 1250 ms^{-1} . Under what circumstances is the kinetic temperature equal to the thermodynamic temperature? [15%]

(b) Consider a cartesian coordinate system (x_1, x_2, x_3) . A perfect monatomic gas flows such that at a particular point its density is ρ and the mean velocity components are (u_1, u_2, u_3) . The peculiar velocity component C_i ($i = 1, 2, 3$) is defined by $C_i = c_i - u_i$ where c_i is the corresponding absolute molecular velocity component.

(i) Starting from the integral expression for the net flux of a general quantity Q , derive an expression in terms of ρ , u_i , u_j , C_i and C_j for the net flux per unit area and unit time of x_i -direction momentum through a surface normal to the x_j direction. Describe the physical significance of each term in your expression. [15%]

(ii) Consider the averaged quantity $\overline{C_i^n C_j^m}$, where m and n are integers. Determine the conditions on m and n that make this quantity zero if the velocity distribution is Maxwellian. Distinguish between cases when $i = j$ and $i \neq j$. [10%]

(iii) Explain clearly why, in general, the molecular velocity distribution within a laminar boundary layer cannot be Maxwellian. [5%]

(iv) By considering the normal stresses, show that the gas pressure may be written in the form

$$p = \frac{2}{3} E_{tr}$$

where E_{tr} is the translational thermal kinetic energy per unit volume. [10%]

(c) Helium (specific gas constant R) flows through an adiabatic converging nozzle. At a particular point on the nozzle centre line the speed of the flow is V and the temperature is T . Using a kinetic theory approach, show that at this point the flowrate of molecular energy in the streamwise direction per unit cross-sectional area is given by

$$\rho V \left(BRT + \frac{V^2}{2} \right)$$

and determine the value of the coefficient B . Explain from a macroscopic viewpoint why B is not equal to $3/2$. [45%]

Information for Question 1

The net flux per unit area and unit time of quantity Q (measured per molecule) in the x_j direction is given by

$$F_Q = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} Q c_j f(c_1, c_2, c_3) dc_3 dc_2 dc_1$$

where c_1 , c_2 and c_3 are the absolute molecular velocity components.

The Maxwellian velocity distribution for a gas at temperature T and with specific gas constant R is given by

$$f(c_1, c_2, c_3) = \frac{n}{(2\pi RT)^{3/2}} \exp \left\{ -\frac{(c_1 - u_1)^2 + (c_2 - u_2)^2 + (c_3 - u_3)^2}{2RT} \right\}$$

where n is the number density of molecules and u_i ($i = 1, 2, 3$) is the average value of c_i .

2 (a) Use a 'mean free path' kinetic theory model to show that the thermal conductivity k of a monatomic perfect gas can be expressed as

$$k = \beta \rho \bar{C} \lambda R$$

where β is a constant, ρ is the gas density, \bar{C} is the mean peculiar molecular speed, λ is the mean free path and R is the specific gas constant. Obtain a value for the constant β and explain how and why it differs from the value that would be obtained from more detailed solutions of the Boltzmann equations.

It may be assumed that the number of molecules incident per unit time on one side of a plane surface of unit area is given by $n\bar{C}/4$ where n is the number density of molecules. [35%]

(b) For argon gas the measured value of k at 1 bar and 300 K is $0.0178 \text{ Wm}^{-1}\text{K}^{-1}$. Explaining clearly your reasoning, estimate its value at 0.1 bar and 400 K. [20%]

(c) With the aid of a suitable sketch, describe how you would expect the mean free path to be affected by intermolecular forces. Hence explain whether the real value of k for argon at 0.1 bar and 400 K is likely to be higher or lower than your estimate in part (b). [15%]

(d) Two parallel plates of infinite extent are placed a distance 1 mm apart. One plate is maintained at 300 K and the other at 500 K. The space between the plates is filled with stationary argon gas at 0.1 bar. The approximate Knudsen number for these conditions is $\text{Kn} \approx 0.001$. Using an appropriate theory, giving your answers to three significant figures, determine the heat transfer rate per unit area between the plates for the following cases:

(i) assuming a constant value of k as determined by your estimate in part (b); [10%]

(ii) accounting for variations in k , but neglecting the effect of intermolecular forces. [20%]

3 (a) The Helmholtz function is defined as $F = U - TS$, where U , T and S are the internal energy, temperature and entropy respectively. Derive a partial differential relationship between S , F and T for a system at constant volume. [15%]

(b) Given that $F = -kT \ln Q$, where k is Boltzmann's constant and Q is the system partition function, show that the internal energy of a system is given by

$$U = kT^2 \left(\frac{\partial}{\partial T} \ln Q \right)_V \quad [15\%]$$

(c) A small system comprises a single particle that can access two energy levels with energies $\epsilon_0 = 0$ and $\epsilon_1 = \epsilon$, and corresponding degeneracies g_0 and g_1 . This system is in thermal contact with a reservoir at constant temperature T .

(i) Derive an expression for the entropy of the system in terms of the quantities k , T , ϵ , g_0 and g_1 . [20%]

(ii) Derive an expression for the mean internal energy \bar{U} of the system in terms of the same quantities and sketch (\bar{U}/ϵ) versus (kT/ϵ) for $(g_1/g_0) = 0.1$ and $(g_1/g_0) = 10$. [25%]

(iii) Derive an expression for the constant volume heat capacity c_V of the system in terms of k , T , ϵ , g_0 and g_1 . What is the limiting behaviour of c_V at very low and at very high temperatures? Sketch the heat capacity versus temperature. [25%]

4 (a) Four different systems, A , B , C and D , can each exist in one of four states. The probabilities of each of the states are given by the matrix

$$\begin{pmatrix} P_{A1} & P_{A2} & P_{A3} & P_{A4} \\ P_{B1} & P_{B2} & P_{B3} & P_{B4} \\ P_{C1} & P_{C2} & P_{C3} & P_{C4} \\ P_{D1} & P_{D2} & P_{D3} & P_{D4} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & \frac{1}{12} & \frac{1}{3} & \frac{1}{12} \\ 0 & 1 & 0 & 0 \\ \frac{1}{4} & 0 & \frac{1}{2} & \frac{1}{4} \\ \frac{1}{10} & \frac{1}{10} & \frac{7}{10} & \frac{1}{10} \end{pmatrix}$$

where, for example, P_{Ai} is the probability of system A being in its i -th state. A fifth system E is an isolated system at equilibrium and has N possible states.

- (i) Rank the systems A to D from highest to lowest entropy. [15%]
(ii) Find the value of N (to the nearest whole number) for which system E would have the same entropy as system A . [10%]

(b) A system that has Ω microstates with individual energies E_i ($i = 1, 2, \dots, \Omega$) and corresponding probabilities P_i is in thermal contact with an infinite reservoir at temperature T . The Helmholtz function of the system is defined by $F = \bar{U} - TS$, where \bar{U} is the average energy of the system and S is its entropy. Use the method of Lagrange multipliers to show that minimising F results in

$$E_i + kT(1 + \ln P_i) + \lambda = 0 \quad (i = 1, 2, \dots, \Omega)$$

where k is Boltzmann's constant and λ is the undetermined multiplier. Hence determine how P_i varies with E_i when the system is at thermal equilibrium with the reservoir. [25%]

(c) A particular system has $\Omega = 5$ possible microstates with individual energies given by $E_1 = E_2 = \varepsilon$ and $E_3 = E_4 = E_5 = 2\varepsilon$. The system is in thermal equilibrium with an infinite reservoir such that its average energy is $\bar{U} = (6\varepsilon/5)$.

- (i) Calculate the probabilities of the five individual states and determine the temperature of the reservoir in terms of ε and Boltzmann's constant, k . [30%]
(ii) Calculate the RMS fluctuation in system energy and express this as a fraction of the average energy \bar{U} . Comment on the result. [20%]

END OF PAPER

MODULE 4A9 – MOLECULAR THERMODYNAMICS

Answers

1. (a) 250.6 ms^{-1} (c) $B = 5/2$
2. (a) $\beta = 5/4$ (b) $0.0206 \text{ Wm}^{-1}\text{K}^{-1}$ (d) i) 4.11 kW m^{-2} ii) 4.10 kW m^{-2}
4. (a) ii) $N = 3$ (c) i) $P_1 = P_2 = 2/5$; $P_3 = P_4 = P_5 = 1/15$ ii) $\sigma_E / \bar{U} = 1/3$

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