

EGT3  
ENGINEERING TRIPOS PART IIB

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Monday 28 April 2014 9.30 to 11

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**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

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

1 (a) A perfect gas flows steadily over a flat plate, the flow velocity  $u$  varying with the normal distance  $y$  from the plate. With the aid of a diagram, explain how the ‘slip velocity’ at the plate surface is defined. Assuming that molecules incident on the plate are reflected diffusely, use a simple kinetic model to show that the slip velocity is given by

$$u_{\text{slip}} \approx \lambda \frac{du}{dy}$$

where  $\lambda$  is the molecular mean free path and  $du/dy$  is the velocity gradient close to the wall. Explain why this result is approximate.

*It may be assumed that the mass flux of molecules incident on one side of a plane surface of unit area is given by  $\rho\bar{C}/4$  where  $\rho$  is the mass density and  $\bar{C}$  is the mean thermal speed of the molecules, and that the dynamic viscosity of a perfect gas is given by  $\mu = \rho\bar{C}\lambda/2$ . [35%]*

(b) Figure 1 shows two parallel plates of infinite extent. The lower plate is stationary and the upper plate at  $y = L$  moves with speed  $U$  in the  $x$  direction. The intervening channel contains a perfect gas that is in steady motion due to the movement of the upper plate. The pressure is uniform. By considering the forces acting on an elementary control volume (and not otherwise), show that the shear stress  $\tau$  is independent of  $y$ . State, giving reasons, for which flow regimes (continuum and non-continuum) this result is valid. [15%]

(c) Suppose the flow is in the slip-flow regime. In this regime the flow can be modelled using the Navier–Stokes equations in the region  $0 < y < L$  but with the boundary conditions at  $y = 0$  and  $y = L$  modified to allow for the slip velocity  $u_{\text{slip}}$  as calculated in part (a). Find an expression for the shear stress  $\tau$  in terms of the shear stress for continuum flow  $\tau_0$  and the Knudsen number  $Kn = \lambda/L$ . Also, find an expression for the mass flowrate in terms of  $\rho$ ,  $U$  and  $L$ . How does the mass flowrate in the slip-flow regime relate to the mass flowrate for continuum flow? [35%]

(d) Explain briefly why the method of part (c) for calculating the shear stress and mass flowrate would be inappropriate if the flow were in the non-continuum transition regime. [15%]

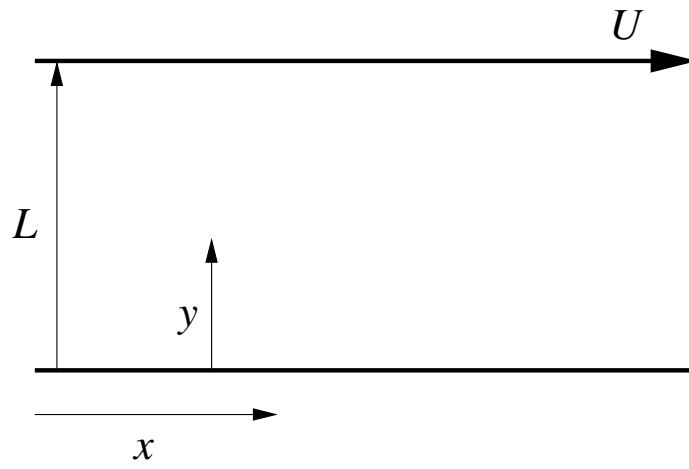


Fig. 1

2 (a) Consider a cartesian co-ordinate system  $(x_1, x_2, x_3)$ . A perfect diatomic gas flows uniformly in the  $x_1$  direction with mean velocity  $u_1$ . The temperature  $T$  of the gas is around ambient. Starting from an expression for the energy of an individual molecule of mass  $m$  moving with absolute velocity  $(c_1, c_2, c_3)$ , show that the average energy per molecule is given by an expression of the form

$$f \frac{kT}{2} + \frac{mu_1^2}{2}$$

where  $k$  is Boltzmann's constant. Estimate the value of the coefficient  $f$ .

*To secure the marks for this part of the question, all steps in your derivation, including any definitions, principles and assumptions used, must be stated clearly and correctly.* [30%]

(b) Suppose now that  $u_1$  and  $T$  vary with  $x_2$  and that near the plane  $x_2 = 0$  the gradients  $du_1/dx_2$  and  $dT/dx_2$  are constant. Using a simple 'mean free path' kinetic model show that the flux per unit area of molecular energy across the plane  $x_2 = 0$  in the positive  $x_2$  direction can be expressed in the form

$$-A \frac{dT}{dx_2} - B \frac{du_1}{dx_2}$$

Find expressions for the coefficients  $A$  and  $B$  in terms of the mean peculiar molecular speed  $\bar{C}$ , the mean free path  $\lambda$  and other flow properties.

*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.* [40%]

(c) Give a macroscopic physical interpretation of both terms in the expression for the molecular energy flux. [15%]

(d) Explain briefly whether you would expect the expressions for the coefficients  $A$  and  $B$  resulting from your kinetic model to give good numerical accuracy. [15%]

- 3 (a) The quantum energy levels of a simple harmonic oscillator are non-degenerate and have energies relative to the ground state given by

$$\varepsilon = nh\nu$$

where  $h$  is Planck's constant,  $\nu$  is the classical oscillation frequency and  $n$  is a non-negative integer.

- (i) How many microstates does a system consisting of two such oscillators have if its total energy is  $E = 5h\nu$ ?

*Assume that the oscillators are distinguishable and that their quantum states are independent.* [10%]

- (ii) For a system comprising  $K$  independent harmonic oscillators with total energy  $E = Mh\nu$ , the number of microstates may be written in the form

$$\Omega = \frac{A!}{B! C!}$$

where  $A$ ,  $B$  and  $C$  are integers. By considering an analogy with arrangements of appropriate numbers of 'balls' and 'partitions' (or otherwise), determine  $A$ ,  $B$  and  $C$  in terms of  $K$  and  $M$ . [30%]

- (b) In the Einstein model of a non-metallic crystal, the  $N$  atoms of the crystal are assumed to behave as independent harmonic oscillators in a 3D lattice.

- (i) Making use of Stirling's formula ( $\ln(m!) \approx m \ln m - m$ , for  $m \gg 1$ ) and stating clearly your assumptions, show that in the high temperature limit the entropy of the crystal is given by

$$S \approx 3Nk + 3Nk \ln \left( \frac{E}{3Nh\nu} \right)$$

[35%]

- (ii) Determine an expression for the specific heat capacity of the crystal in the high temperature limit and show that its value is consistent with the principle of equipartition of energy. [25%]

4 The translational kinetic energy of a single particle of mass  $m$  confined to a cubic box of volume  $V$  is given by

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

where  $n_1$ ,  $n_2$  and  $n_3$  are quantum numbers corresponding to motion in the  $x_1$ ,  $x_2$  and  $x_3$  directions respectively.

(a) Tabulate all possible energy states (i.e., the permutations of the quantum numbers) for a particle that has energy less than or equal to four times its ground state energy. Specify also the degeneracy of each energy level. [20%]

(b) One litre of helium gas (atomic mass 4) is maintained at a pressure of 10 bar and a temperature of 400 K in a rigid cubic vessel. Calculate:

- (i) the number of helium molecules;
- (ii) the number of energy states for a single helium molecule with energy less than or equal to the average molecular energy.

What can be deduced by comparing your answers to (i) and (ii)? [40%]

(c) Determine an expression for  $g(C)$  defined such that  $g(C)dC$  is the number of energy states available to a molecule with speed in the range  $C$  to  $C + dC$ . [25%]

(d) The fraction of molecules in the speed range  $C$  to  $C + dC$  may be written

$$\phi(C)dC \approx \frac{\exp(-mC^2/2kT)}{Z}g(C)dC$$

where  $Z$  is the single particle partition function. Explain why this expression is approximate and under what conditions it becomes inaccurate. (Note that a qualitative answer only is required. You do not need to derive the above expression for  $\phi(C)$ .) [15%]

**END OF PAPER**

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1. (c)  $\tau = \frac{\tau_0}{(1+2Kn)}$ ,  $\dot{m} = \frac{\rho UL}{2}$
2. (a)  $f = 5$
- (b)  $A = \frac{fR}{2} \frac{\rho \bar{C} \lambda}{2}$ ,  $B = \frac{\rho \bar{C} \lambda}{2} u_1(0)$
3. (a) (i) 6 (ii)  $A = (M + K - 1)$ ;  $B = M$ ;  $C = (K - 1)$
- (b) (ii)  $c_v = 3R$
4. (b) (i)  $1.81 \times 10^{23}$  molecules (ii)  $1.66 \times 10^{28}$  states
- (c)  $g(C) = \frac{4\pi V m^3 C^2}{h^3}$