

ENGINEERING TRIPOS PART IIB

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Thursday 29 April 2010 2.30 to 4

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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.*

*There are no attachments.*

STATIONERY REQUIREMENTS

Single-sided script paper

SPECIAL REQUIREMENTS

Engineering Data Book

CUED approved calculator allowed

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

1 A monatomic perfect gas flows steadily with mean velocity  $u = u(y)$  in the  $x$ -direction. In the  $y$ -direction  $u$  varies according to:

$$u = u_0 + y \frac{du}{dy}$$

where  $u_0$  is the value of  $u$  at  $y = 0$  and the velocity gradient  $du/dy$  is constant. In what follows it may be assumed without proof that the one-sided molecular mass flux incident on a surface per unit area is given by  $\rho \bar{C}/4$  where  $\rho$  is the gas density and  $\bar{C}$  is the mean molecular speed.

(a) Using simple kinetic theory, derive an approximate expression for the viscous shear stress  $\tau$  at the plane  $y = 0$  in terms of  $\rho$ ,  $\bar{C}$ ,  $du/dy$  and  $\lambda$  (the molecular mean free path). State clearly the two main assumptions of the theory. [25%]

(b) Based on the above result, how would you expect the dynamic viscosity of a perfect gas to vary with pressure and temperature? How does the viscosity vary in reality and why? [20%]

(c) Noting that the flow is isothermal and there is no temperature gradient, consider the transport of molecular translational kinetic energy due to the velocity gradient  $du/dy$ . Show that the molecular translational kinetic energy flux per unit area in the positive  $y$ -direction across the plane  $y = 0$  is given by:

$$-A \frac{du}{dy}$$

and find the coefficient  $A$  in terms of  $\rho$ ,  $\bar{C}$ ,  $\lambda$  and  $u_0$ . [35%]

(d) Give a macroscopic interpretation of the expression for the molecular translational kinetic energy flux derived in part (c), explaining how it relates to the First Law of Thermodynamics. Hint: make use of the expression for  $\tau$  derived in part (a). [20%]

2 Two parallel plates, 1 and 2, of infinite extent are placed a distance  $L$  apart and are maintained at temperatures  $T_1$  and  $T_2$  respectively ( $T_1 > T_2$ ). The intervening space contains a stationary monatomic perfect gas. The Knudsen number  $Kn$  is defined by  $Kn = \lambda/L$  where  $\lambda$  is the molecular mean free path. In what follows, it may be assumed without proof that the one-sided molecular mass flux to a surface is given by  $\rho \bar{C}/4$  where  $\rho$  is the gas density and  $\bar{C}$  is the mean molecular speed. It may also be assumed that the gas thermal conductivity  $k$  is given by the uncorrected result from mean free path theory,  $k = \rho \bar{C} \lambda c_v/2$ , where  $c_v$  is the specific heat capacity at constant volume.

(a) Suppose the gas pressure is such that  $Kn \ll 1$ . Derive an expression (in terms of the quantities defined above) for  $q_0$  the conduction heat transfer rate per unit area between the plates. [10%]

(b) The gas pressure is now lowered to such an extent that  $Kn \gg 1$ . If all molecules incident on a plate are reflected diffusely with thermal accommodation coefficient  $\alpha$ , show that  $q_\infty$  the heat transfer rate per unit area is given by:

$$\frac{q_\infty}{q_0} = \left( \frac{\alpha}{2 - \alpha} \right) \frac{1}{A Kn}$$

and obtain a value for the constant  $A$ . The coefficient  $\alpha$  is defined by  $\alpha = (E_{ref} - E_{inc}) / (E_{eqm} - E_{inc})$ , where  $E_{inc}$  and  $E_{ref}$  are the energy fluxes of incident and reflected molecules respectively, and  $E_{eqm}$  is the reflected energy flux were the molecules to achieve thermal equilibrium with the plate. [40%]

(c) Suppose the gas pressure is such that  $0 < Kn < 0.1$ . A simple model of heat transfer in this regime assumes that Fourier's law of heat conduction applies everywhere but there is a temperature jump  $\Delta T$  at each plate surface given (for  $\alpha = 1$ ) by  $\Delta T = (\lambda/L) dT/dy$ , where  $dT/dy$  is the temperature gradient in the bulk of the gas. For  $\alpha = 1$ , show that  $q_s$  the heat transfer rate per unit area is given by:

$$\frac{q_s}{q_0} = \frac{1}{1 + B Kn}$$

and obtain a value for the constant  $B$ . Explain why this result is unlikely to give good results in the transition regime where  $Kn = O(1)$ . [50%]

- 3 (a) A statistical analogue of entropy is given by:

$$S' = -k \sum_{i=1}^{\Omega} P_i \ln P_i$$

- (i) Explain the meaning of each of the quantities in this expression and compute  $S'$  for a system having only one possible microstate. [15%]

- (ii) Using the method of Lagrange multipliers or otherwise, show that  $S'$  attains a maximum value when all of the  $P_i$  are equal. Hence find an expression for  $S'$  involving only  $k$  and  $\Omega$  which is valid for isolated systems at equilibrium. [35%]

- (b) A quantity of helium gas is contained within an insulated vessel as shown in Fig. 1. The vessel is divided into two parts, A and B, by a copper piston which is initially held in place by a locking pin. The initial pressures in A and B are  $P_A = 1$  bar and  $P_B = 2$  bar respectively. The initial volumes are  $V_A = 0.2 \text{ m}^3$  and  $V_B = 0.3 \text{ m}^3$  for A and B respectively. The temperature is uniform throughout and equal to 300 K. The locking pin is removed and the system attains a new equilibrium. Calculate the ratio of the number of microstates in the initial state to the number of microstates in the final state. Does this ratio depend on the type of gas? Explain your answer. [50%]

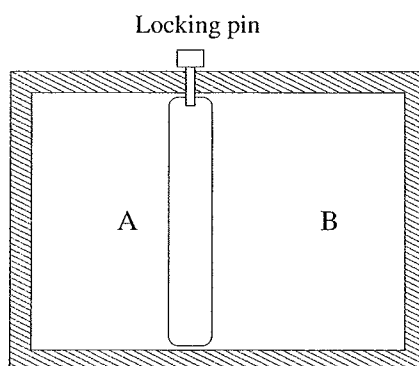


Fig. 1

4 For a monatomic gas, the energy of a single translational energy state is given by:

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

where  $h$  is Planck's constant,  $m$  is the mass of one molecule,  $V$  is the volume of the system and  $n_1$ ,  $n_2$  and  $n_3$  are the translational quantum numbers.

(a) Derive an expression for the number of energy states with energy less than or equal to  $\epsilon$ . [25%]

(b) A cylinder with a volume of 2.0 litres contains neon gas (molar mass  $20 \text{ kg kmol}^{-1}$ ) at 300 K. Calculate the number of energy states available to a molecule within this cylinder travelling no faster than the RMS molecular speed. [20%]

(c) Stating your assumptions, show that the system partition function for a monatomic gas is given by:

$$Q = \frac{1}{N!} Z_1^{3N}$$

where  $N$  is the number of molecules and  $Z_1$  is given by:

$$Z_1 = \sum_{n_1=1}^{\infty} \exp\left[-\frac{h^2}{8mV^{2/3}kT} n_1^2\right]$$

$T$  being the temperature and  $k$  the Boltzmann constant.

Show also that this expression for  $Q$  leads to the ideal gas equation of state. [55%]

You may use the following without proof:

$$\int_0^{\infty} \exp(-n_1^2 \tau^2) dn_1 = \frac{\sqrt{\pi}}{2\tau} \quad \text{and} \quad p = kT \frac{\partial}{\partial V} \ln Q$$

where the symbols have their usual meanings.

**END OF PAPER**

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**MODULE 4A9 – MOLECULAR THERMODYNAMICS**

**ANSWERS**

1. (c)  $A = \frac{u_0 \rho \bar{C} \lambda}{2}$

2. (b)  $A = 2$       (b)  $B = 2$

3. (a) (i) 0      (ii)  $S = k \ln \Omega$       (b)  $\Omega_1 / \Omega_2 = \exp(-9.63 \times 10^{23})$

4. (a)  $\Gamma(\epsilon) = 4\pi V (2m\epsilon)^{3/2} / 3h^3$       (b)  $2.42 \times 10^{29}$  states

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