

ENGINEERING TRIPOS PART IIB  
ELECTRICAL AND INFORMATION SCIENCES TRIPOS PART II

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Saturday 3 May 2003 2.30 to 4.00

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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*

**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**

(TURN OVER

1 (a) In gas kinetic theory, the one-sided flux (per unit area) of a molecular property  $Q$  across a surface with normal in the  $x_3$  direction is given by

$$Flux = \int_0^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} Q C_3 n f dC_1 dC_2 dC_3 ,$$

where all symbols have their usual meaning. If  $f$  is the Maxwellian distribution

$$f = (2\pi RT)^{-3/2} \exp\left(-\frac{C_1^2 + C_2^2 + C_3^2}{2RT}\right) ,$$

show that the one-sided molecular mass flux is given by the expression

$$\rho \left(\frac{RT}{2\pi}\right)^{1/2} .$$

The following integral may be assumed without proof:  $\int_{-\infty}^{\infty} \exp(-ax^2) dx = (\pi/a)^{1/2}$ . [40%]

(b) Nitrogen with trace amounts of two different gases flows through a tube of diameter  $d$ . The tube wall has a large number of very small circular pores of diameter  $a$ , there being  $N$  pores per unit length of tube. The gas outside the tube is pure nitrogen at the same pressure, and the temperature is uniform everywhere. The gases leak out through the pores so that the mass fractions  $Y_i$  ( $i = 1, 2$ ) decrease along the length of the tube. It may be assumed that, at any distance  $x$  along the tube, the  $Y_i$  and other properties are uniform across the tube. Diffusion along the tube may be neglected.

(i) Set up a control volume of length  $dx$  and derive an expression for  $dY_i/dx$  in terms of  $N$ ,  $a$ ,  $d$ ,  $G_i$  and  $G$ , where  $G_i$  is the mass flux of gas  $i$  through a pore and  $G$  is the mass flux of nitrogen along the tube. [30%]

(ii) Assume now that  $a$  is much smaller than the molecular mean free path, and that the tube wall is of negligible thickness. Using the result from part (a), show that  $Y_1$  and  $Y_2$  are related at any value of  $x$  by,

$$\sqrt{M_1} \ln\left(\frac{Y_1}{Y_{1,0}}\right) = \sqrt{M_2} \ln\left(\frac{Y_2}{Y_{2,0}}\right) ,$$

where  $M_i$  is the molar mass and  $Y_{i,0}$  is the value of  $Y_i$  at the tube inlet. [30%]

2 Consider a Cartesian co-ordinate system  $(x_1, x_2, x_3)$ . A perfect gas flows steadily with bulk velocity  $\bar{u}_1$  in the  $x_1$ -direction.  $\bar{u}_1$  varies in the  $x_2$ -direction such that

$$\bar{u}_1(x_2) = \bar{u}_1(0) + x_2 \frac{d\bar{u}_1}{dx_2} ,$$

where  $\bar{u}_1(0)$  is the value of  $\bar{u}_1$  at  $x_2 = 0$  and the velocity gradient  $d\bar{u}_1/dx_2$  is constant.

(a) Using a 'mean free path model', consider the transport of molecular momentum across the plane  $x_2 = 0$ . If  $\lambda$  is the mean free path of a gas molecule and  $\bar{C}$  is the mean molecular speed, show that the macroscopic viscous shear stress  $\tau_{12}$  at the plane  $x_2 = 0$  is given by the expression

$$\tau_{12} = \beta \rho \bar{C} \lambda \frac{d\bar{u}_1}{dx_2} ,$$

and obtain an estimate for the value of the constant  $\beta$ . State your assumptions clearly.

It may be assumed without proof that the one-sided molecular mass flux incident on a surface is given by  $\rho \bar{C}/4$ . [35%]

(b) Without undertaking any more analysis, explain why the dynamic viscosity of a perfect gas is independent of the pressure. [15%]

(c) Consider now the transport of molecular kinetic energy (KE) across the plane  $x_2 = 0$ . Show that the molecular KE flux (per unit area) across this plane in the positive  $x_2$ -direction is given by an expression of the form

$$\text{molecular KE flux} = -A \frac{d\bar{u}_1}{dx_2} ,$$

and find an expression for the coefficient  $A$  in terms of  $\rho$ ,  $\bar{C}$ ,  $\lambda$  and  $\bar{u}_1(0)$ . [35%]

(d) Give a macroscopic interpretation of your expression for the molecular KE flux. [15%]

(TURN OVER

3 (a) The energy levels associated with rotation of a diatomic molecule are given by

$$\varepsilon_m^{rot} = \frac{h^2}{8\pi^2 I} m(m+1) \quad ,$$

while the degeneracy of each level is,

$$g_m = \frac{1}{\sigma} (2m+1) \quad .$$

- i) Explain the physical meaning of each symbol in these equations.
- ii) Write down an expression for the contribution to the partition function  $Z_{rot}$  arising from rotation.
- iii) Write down an expression for the characteristic temperature of rotation  $\theta_r$ . [50%]

(b) If  $\theta_r \ll T$  the rotational contribution to the partition function may be written

$$Z_{rot} = \frac{T}{\sigma \theta_r} \quad .$$

A general expression for the thermodynamic internal energy  $U$  in terms of the overall partition function  $Z$  is

$$U = NkT^2 \left[ \frac{\partial}{\partial T} \ln(Z) \right]_V \quad .$$

Show that for nitrogen gas at room temperature the ratio of specific heats  $\gamma$  is equal to 1.4. [35%]

(c) Describe briefly how the partition function may be extended to account for vibration of the molecule (lengthy analysis is not required). Explain why vibrational modes do not contribute to the specific heat capacity at room temperature. [15%]

- 4 (a) Show that the momentum of a photon of wavelength  $\lambda$  is given by

$$p = \frac{h}{\lambda} ,$$

where  $h$  is Planck's constant (having the value  $6.6262 \times 10^{-34}$  Js).

[15%]

- (b) Estimate the De Broglie wavelength of,
- (i) a student cycling to lectures,
  - (ii) a tennis ball in flight,
  - (iii) a hydrogen atom at room temperature.

Hence explain why quantum effects are important at atomic scales but are not observed at macroscopic scales.

[35%]

(c) An isolated system contains 3 particles and has a total of 8 units of energy. The available energy levels have energies of 0, 2, 4 and 6 units, and have corresponding degeneracies of 1, 2, 1 and 1. The volume of the system is constant.

Evaluate all of the possible microstates and macrostates available to the system, and calculate the thermodynamic probability of each macrostate, assuming that

- (i) the particles are bosons,
- (ii) the particles are fermions.

[50%]

**END OF PAPER**