ENGINEERING TRIPOS PART IIB

Thursday 3 May 2007 2.30 to 4

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) State briefly how temperature is defined in gas kinetic theory. [10 %]

(b) Nitrogen N_2 has a molar mass of 28 kg kmol^{-1}. A crude model of the molecular velocity distribution for the gas in a certain state divides the molecules into six groups. Each group contains the same number of molecules and each molecule in a group has the same velocity. The molecules in the six groups have velocity components in the x_1, x_2 and x_3 directions, measured in ms^{-1}, as follows :

(1250, 120, 0); (50, 1320, 0); (50, 120, 1200);

(−1150, 120, 0); (50, −1080, 0); (50, 120, −1200).

(i) Calculate the temperature of the gas.

(ii) Assuming the principle of the *equipartition of energy* to apply, and all rotational and vibrational states to be active, calculate the internal energy per kg of the gas. [40 %]

(c) The molecular velocity distribution function at a point in a monatomic gas flowing with mean speed V in the x_1 direction is given by

$$f(u_1, u_2, u_3) = \frac{1}{(2\pi RT)^{3/2}} \exp\left[-\left(\frac{(u_1 - V)^2 + u_2^2 + u_3^2}{2RT}\right)\right],$$

where u_i is the molecular velocity component in the x_i direction (i = 1, 2, 3), R is the specific gas constant and T is the temperature.

(i) Write down an integral expression in terms of f for the mean kinetic energy of a molecule.

(ii) Transform the expression to new variables w_1, w_2 and w_3 defined by,

$$w_1 = \frac{(u_1 - V)}{\sqrt{2RT}}; \qquad w_2 = \frac{u_2}{\sqrt{2RT}}; \qquad w_3 = \frac{u_3}{\sqrt{2RT}}.$$

(iii) Using the integrals on the next page, show that e, the energy per unit mass of the gas, is given by,

$$e = \frac{3}{2}RT + \frac{V^2}{2}.$$ [50 %]

(cont.

$$\int_{-\infty}^{\infty} \exp(-x^2)\, dx = \sqrt{\pi}$$

$$\int_{-\infty}^{\infty} x \exp(-x^2)\, dx = 0$$

$$\int_{-\infty}^{\infty} x^2 \exp(-x^2)\, dx = \frac{\sqrt{\pi}}{2}$$

Integrals for Question 1.

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2 (a) Using a 'mean free path' kinetic theory model, show that the dynamic viscosity μ of a perfect gas can be approximated by,

$$\mu = \beta \rho \overline{C} \lambda \ ,$$

where β is a constant, ρ is the gas density, $\overline{C}$ is the mean molecular speed and λ is the mean free path. Obtain a value for the constant β. [35 %]

(b) As shown in Fig. 1, two parallel plates of infinite extent are placed a distance L apart. The top plate has velocity U in the x-direction and the bottom plate is stationary. The intervening space contains a perfect gas which is set in motion by the movement of the top plate. The flow velocity u varies only with y and the pressure is uniform. By considering the forces acting on an elementary control volume, show that the shear stress τ is independent of y irrespective of the value of the Knudsen number, $Kn = \lambda / L$. [15 %]

(c) A simple model of the flow, valid for $Kn < 0.1$, is based on the assumption that the non-continuum layers adjacent to the plate surfaces can be modelled simply by changing the wall boundary conditions to allow for a slip velocity of magnitude,

$$u_{wall} = \lambda \left(\frac{du}{dy} \right)_{wall} ,$$

where λ is the mean free path. Using this model show that the shear stress on the upper plate τ is related to the shear stress τ_0 (corresponding to the limit $Kn \to 0$) according to,

$$\tau = \frac{\tau_0}{(1 + 2Kn)} \ .$$

[30 %]

(d) Suppose the plate spacing L is 2 mm and the upper plate velocity is 50 ms^{-1}. If the gas is air at a pressure of 0.001 bar and a temperature of 300 K estimate the value of Kn. If you cannot remember any required kinetic theory expression, make an 'educated estimate'. [20 %]

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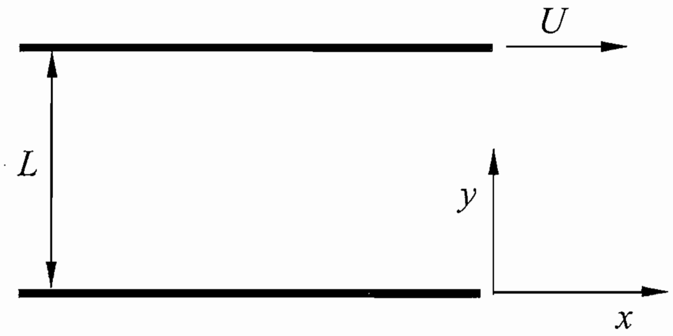

Figure 1

(TURN OVER

3 (a) The Boltzmann relation is:

$$S = k \ln \Omega \ .$$

Use this relation to explain how entropy increases may be interpreted in terms of molecular disorder and uncertainty, with reference to:

(i) adiabatic unrestrained expansion of an ideal gas and,

(ii) heat addition to an ideal gas at constant volume. [25%] 5

(b) Figure 2 shows a system composed of two rows of boxes. There are C boxes in each row. N white balls and N black balls (where $N < C$) are distributed amongst the boxes, with a maximum of one ball permitted in each box.

(i) Show that if the black balls are constrained to the lower row and the white balls to the upper row, the total number of distinct arrangements is given by:

$$W = \left\{ \frac{C!}{(C-N)!N!} \right\}^2 \ .$$

Derive a similar expression for the case where the constraint is removed, such that black and white balls are permitted in both rows. [25%] 5

(ii) Use the result of (i) to show that the "entropy of mixing" when C and N are very large is given by:

$$\Delta S = 2Nk \ln 2 \ .$$ [25%] 5

You may use without proof Stirling's formula: $\ln x! \cong x \ln x - x$.

(iii) By considering the limiting case of C = 1, show that the same result is obtained for the entropy of mixing when the restriction of only one ball per box is relaxed, provided N remains large. (Note that the condition $N < C$ no longer applies.) Comment on the analogy with the mixing of two ideal gases. [25%] 5

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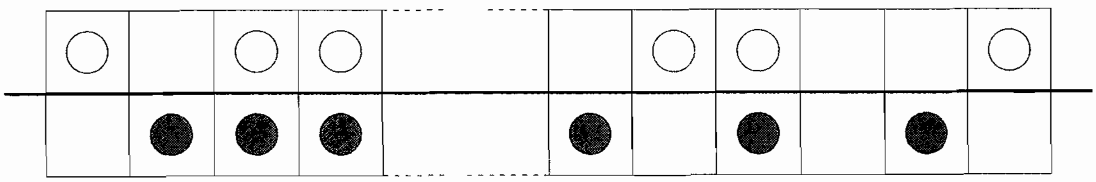

Figure 2

(TURN OVER

4 (a) The Boltzmann distribution is:

$$\frac{N_j^*}{N} = \frac{C_j \exp\{-\varepsilon_j / kT\}}{Z} .$$

Briefly give the meaning of each of the quantities in this expression and, by summing over all possible values of j, derive an expression for Z. [15%]

(b) Show that the average molecular energy is given by:

$$\bar{\varepsilon} = kT^2 \frac{\partial}{\partial T}(\ln Z) ,$$

and that the mean of the square of the molecular energy is given by:

$$\overline{\varepsilon^2} = \frac{kT^2}{Z} \frac{\partial}{\partial T}\left(kT^2 \frac{\partial Z}{\partial T} \right) ,$$

where the partial derivatives are at constant volume. [40%]

(c) For a certain gas at room temperature,

$$Z = Z_{tr} = V\left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} ,$$

where the symbols have their usual meanings.

(i) Suggest, giving reasons, what type of gas this is. You may find the following expression for pressure useful:

$$p = NkT \frac{1}{Z}\left(\frac{\partial Z}{\partial V} \right)_T .$$ [10%]

(ii) Show that the root mean square deviation of the translational kinetic energy of a molecule from the mean value is equal to $kT\sqrt{3/2}$. Does this suggest that there are temperature fluctuations of the order of $T\sqrt{3/2}$ within the gas? Explain your answer. [35%]

END OF PAPER

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MODULE 4A9 – MOLECULAR THERMODYNAMICS

ANSWERS

1 (b) (i) 1616 K (ii) 1679 kJ/kg

(c) (i) $$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{m(u_1^2+u_2^2+u_3^2)}{2}\,f(u_1,u_2,u_3)\,du_1\,du_2\,du_3$$

2 (d) $Kn = 0.045$

3 (b) (i) $$W=\frac{(2C)!}{(2C-2N)!N!N!}$$

4 (a) $Z=\sum C_j \exp\{-\varepsilon_j/kT\}$

(c) (i) Ideal, monatomic.

(ii) No.

A.J. White & J.B. Young