ENGINEERING TRIPOS PART IIB

Thursday 30 April 2009   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.

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 of molecular mass m, specific gas constant R, molecular number density n and temperature T is flowing with mean speed V in the x_1 direction. The absolute molecular velocity components are (u_1, u_2, u_3) and the molecular velocity distribution function $f(u_1, u_2, u_3)$ (which is uniform in space) is given by,

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

You may use the result that the net flux (*i.e.*, flow rate per unit cross-sectional area), in the x_i direction ($i = 1, 2$ or 3), of a molecular property $Q\,(u_1, u_2, u_3)$ is given by,

$$\int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} (Q\,u_i\,n\,f)\,du_1\,du_2\,du_3 \; .$$

(a)   Write down an integral expression for the net flux in the x_1 direction of molecular x_1-momentum.

[10 %]

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

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

[10 %]

(c)   Using the integrals of Table 1, show that, if ρ is the gas density, the net flux in the x_1 direction of molecular x_1-momentum is given by

$$p + \rho V^2 \; .$$

[30 %]

(d)   A flat plate having its length L aligned with the x_1-direction and its outward normal in the negative x_2-direction is placed in the gas. The mean free path of the gas molecules is very much greater than L. Write down an integral expression for the flux of molecular x_1-momentum incident on the plate. Evaluate this expression using the integrals of Table 1. Assuming that all incident molecules are reflected diffusely from the plate surface, find an expression for the drag force per unit width exerted by the gas on one side of the plate.

[50 %]

(cont.

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

$$\int_{0}^{\infty} x\exp(-x^2)\,dx = \frac{1}{2} \qquad\qquad \int_{-\infty}^{\infty} x\exp(-x^2)\,dx = 0$$

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

Table 1   Integrals for Question 1.

2   A <u>diatomic</u> perfect gas has a molar mass of 28 kg kmol^{-1} and a molecular diameter of 0.3 nm. In a certain thermodynamic state the gas density is 1.5 kg m^{-3}. A crude model of the molecular velocity distribution for the gas in this 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 m s^{-1}, as follows :

$$(590, 30, 0); \quad (40, 580, 0); \quad (40, 30, 550);$$

$$(-510, 30, 0); \quad (40, -520, 0); \quad (40, 30, -550).$$

In what follows, state your assumptions clearly. Calculations without comments will not secure the marks.

(a)   (i)   Calculate the gas temperature.

   (ii)   Explain why the temperature does not depend on whether the gas is in an equilibrium or non-equilibrium state.   [25 %]

(b)   (i)   Estimate the ratio of the specific heat capacities.

   (ii)   Estimate the internal molecular energy per kg of gas.   [15 %]

(c)   (i)   Derive a general expression for the mean free path of a gas molecule using a simple kinetic model.

   (ii)   Use this result to calculate the mean free path of the gas in question.   [20 %]

(d)   (i)   Derive a general expression for the thermal conductivity of a gas using a simple kinetic model.

   (ii)   Discuss the accuracy of this expression for monatomic and diatomic molecules.

   (iii) Estimate the thermal conductivity (due to all forms of energy transport) for the gas in question.   [40 %]

3   (a)   For a system in thermal contact with an infinite reservoir at temperature T, the relative frequency (or probability) of the i-th microstate is given by:

$$P_i = \frac{\exp(\beta E_i)}{Q}$$

where E_i is the energy of the microstate, $\beta = -(kT)^{-1}$ and Q is the system partition function. Derive an expression for the average energy of the system, U, in terms of β and Q.

[25%]

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

$$\varepsilon_n = nh\nu$$

where h is Planck's constant, ν is the classical oscillation frequency and n is a non-negative integer. Show that the partition function for a system composed of one such oscillator is:

$$Z = \frac{1}{1 - e^\tau}$$

where $\tau = \beta\nu h$.

[25%]

    (c)   In the Einstein model of a non-metallic crystal, the N atoms comprising the crystal are all assumed to behave as independent harmonic oscillators.

    (i)   Explain why the system partition function for a crystal obeying the Einstein model is given by:

$$Q = Z^{3N} \ .$$

    (ii)   Derive an expression for the crystal's internal energy, U, as a function of temperature.

    (iii)   Find the value of the crystal's specific heat capacity (in terms of appropriate quantities) in the high temperature limit and show that this is consistent with the equipartition principle.

[50%]

4   (a)   The Boltzmann relation is:

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

Use this relation to explain qualitatively how entropy changes may be interpreted in terms of molecular disorder and uncertainty for the following processes:

(i)   heat addition to an ideal gas at constant volume and,

(ii)   reversible, isothermal heat extraction from an ideal gas.   [25%]

(b)   A simple model for the volume dependence of the entropy of an ideal gas involves dividing the volume occupied by the gas into a number of identical boxes. The total number of boxes is denoted by M and the gas comprises N identical molecules, where $N < M$.

(i)   Assuming that no more than one molecule may occupy each box, show that the number of distinct arrangements of the N molecules amongst the M boxes is given by:

$$\Omega = \frac{M!}{(M-N)!N!} .$$ [15%]

(ii)   Making use of Stirling's approximation ($\ln(n!) \approx n \ln n - n$ for large n), show that the entropy of the gas is given approximately by:

$$S \approx Nk \ln\left(\frac{M}{N} - 1\right) - Mk \ln\left(1 - \frac{N}{M}\right) .$$ [25%]

(iii)   The size of the boxes may be chosen such that $M >> N$. Derive an expression for the change in entropy when the gas undergoes an adiabatic, unrestrained expansion from volume V_1 to V_2. Compare this with the result obtained from classical thermodynamics.   [25%]

(iv)   Comment on the assumption that no more than one molecule may occupy each box.   [10%]

END OF PAPER