ENGINEERING TRIPOS PART IIB

Thursday 1 May 2008 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) Use a 'mean free path' kinetic theory model to show that the thermal conductivity k of a monatomic perfect gas can be expressed as

$$k = \beta \frac{\rho \overline{C} \lambda c_v}{2} ,$$

where β is a constant, ρ is the gas density, $\overline{C}$ is the mean molecular speed, λ is the mean free path and c_v is the specific heat capacity at constant volume. Obtain a value for the constant β and explain qualitatively why it is substantially different from the value $\beta = 5/2$ obtained from more detailed solutions of the Boltzmann equation. [40 %]

It may be assumed without proof that the 'one-sided' molecular mass incident on a surface of unit area per unit time is given by $\rho \overline{C}/4$.

(b) Explain Eucken's theory of how the above expression for the thermal conductivity can be modified so that it provides a reasonable approximation for diatomic and polyatomic gases. [20 %]

(c) Figure 1 shows a simple model for the temperature distribution in a stationary <u>monatomic</u> perfect gas near a solid wall. At distance $y = \lambda$ from the wall the gas temperature is T_λ and the temperature gradient is dT/dy. Extrapolating this temperature gradient down to the wall at $y = 0$ gives an <u>effective</u> gas temperature T_0 which may be different from the solid wall temperature T_w (*i.e.*, there may be a 'temperature jump' at the wall).

Develop a simple kinetic model for energy transport in the free-molecule ($y < \lambda$) and continuum ($y > \lambda$) regions, and match the energy fluxes to obtain a relation between the wall temperature jump ($T_0 - T_w$) and dT/dy. For simplicity, assume that molecules reflected from the wall are fully accommodated to the wall temperature T_w. [40 %]

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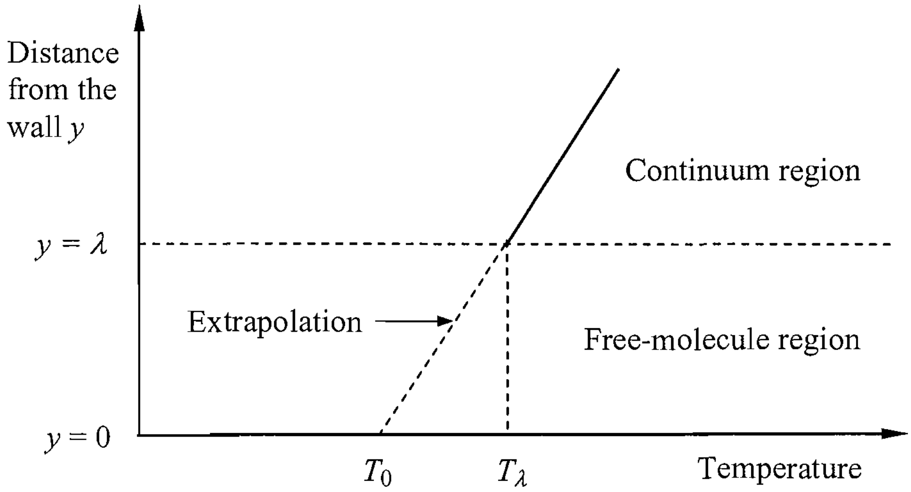

Fig. 1

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2 (a) For a stationary gas, the Maxwell-Boltzmann molecular speed distribution function $g_e(C)$ is

$$g_e(C) = \frac{4\pi C^2}{(2\pi RT)^{3/2}} \exp\left(-\frac{C^2}{2RT}\right),$$

where C is the molecular speed, R is the gas constant per unit mass and T is the temperature. Find an expression for the mean molecular speed $\overline{C}$ and show that its value for nitrogen at 300 K is about 477 m s^{-1}. [30 %]

You may use without proof the integral,

$$\int_0^\infty x^3 \exp(-x^2)\,dx = \frac{1}{2}.$$

(b) An experiment to investigate gas leakage due to small pressure differences in a vacuum system consists of two vessels A and B separated by a very thin, rigid partition. Both vessels contain nitrogen, the pressure in vessel A being $p_A = 5000$ Pa and that in vessel B being $p_B = 4800$ Pa. The temperature of the gas in both vessels is 300 K. The partition contains a large number of small circular holes each of diameter D through which leakage can occur, the total flow cross-sectional area being 1 mm^2. The dynamic viscosity of nitrogen at 300 K is 18.3×10^{-6} kg m^{-1} s^{-1}.

(i) If $D = 0.1$ μm calculate the Knudsen number based on D to confirm that the flow is in the free-molecule regime. Using a suitable theory estimate the total leakage mass flowrate in g hr^{-1}. [35 %]

(ii) If $D = 50$ μm calculate the Knudsen number based on D to confirm that the flow is in the continuum regime. Assuming that the flow is inviscid, estimate the total leakage mass flowrate in g hr^{-1}. [25 %]

(iii) Sketch a graph showing how the leakage mass flowrate might vary with the logarithm of the Knudsen number (for fixed p_A and p_B). [10 %]

It may be assumed without proof that the 'one-sided' molecular mass incident on a surface of unit area per unit time is given by $\rho\overline{C}/4$ where ρ is the gas density. It may also be assumed that the dynamic viscosity μ is given by $\mu = \rho\overline{C}\lambda/2$ where λ is the mean free path of a gas molecule.

3 (a) For a particle of mass *m*, the time-independent form of the Schrödinger wave equation may be written as

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(\varepsilon - \varepsilon_p)\psi = 0 \ .$$

Explain what each of ψ, ε and ε_p represent, giving a quantitative definition for ψ. [10%]

(b) A particle possessing only translational kinetic energy is confined to a field-free cubic box of side *a*. By writing $\psi = \psi_1(x_1)\psi_2(x_2)\psi_3(x_3)$ show that the above equation reduces to the three ordinary differential equations:

$$\frac{d^2\psi_i}{dx_i^2} + \left(\frac{2\pi p_i}{h}\right)^2 \psi_i = 0 \qquad i = 1, 2, 3$$

where p_i is the particle's momentum in the direction x_i. Hence show that the particle's momentum in each of the three directions is quantised and that

$$\varepsilon = \frac{h^2}{8ma^2}\left(n_1^2 + n_2^2 + n_3^2\right) \ .$$

What is the physical significance of the numbers n_1, n_2 and n_3? [50%]

(c) 1 litre of helium is contained within a cubic container at 1 bar and 500 K. Calculate the number of energy states available to molecules that have speeds in the range zero to the RMS molecular speed. Calculate also the total number of molecules in the container and comment on the comparison between the two results. [40%]

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4 (a) Three yellow dice and two pink dice are thrown together repeatedly. Each time the total score on all five dice is 27, the sum of the scores on the two pink dice is recorded. By drawing up a table, or otherwise, determine the relative frequency of the possible values of P, where P is the sum of the scores on the pink dice. Comment briefly on the analogy with the canonical ensemble. [45%]

(b) Figure 2 shows a closed system of fixed volume in thermal contact with an infinite thermal reservoir at temperature T_0. The system has mass m and is composed of a material that has a constant specific heat capacity at constant volume of c_V.

(i) Derive an expression for the increase in entropy of the system when its temperature is increased from T_0 to $T = T_0 + \Delta T$. Your expression should be in terms of T_0, ΔT, m and c_V.

(ii) Determine also the corresponding reduction in entropy of the reservoir, assuming the system and reservoir together constitute an isolated system. Hence, if $\Delta T \ll T_0$, show that the total change in entropy for the reservoir plus system is given approximately by:

$$\Delta S \approx -\tfrac{1}{2} m c_V (\Delta T / T_0)^2 \ .$$

(iii) Use the Boltzmann relation to determine the ratio of the probability of the system being at temperature T to that of it being at temperature T_0. Sketch this ratio as a function of T.

(iv) If $m = 0.001$ kg, $c_V = 1000$ J kg^{-1} K^{-1} and $T_0 = 500$ K, estimate the RMS temperature fluctuations of the system. [55%]

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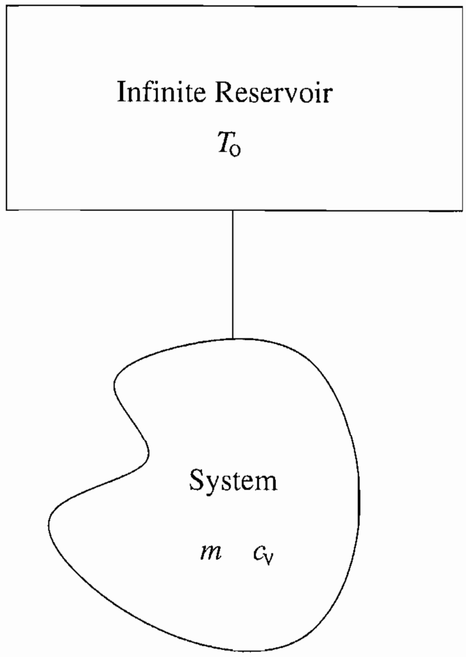

Fig. 2

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