

ENGINEERING TRIPOS PART IIB

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Monday 7 May 2012 9 to 10.30

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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 With reference to Fig. 1, consider the laminar, incompressible, viscous flow of a perfect gas through a capillary tube of radius  $R$ . The flow is driven by a streamwise pressure gradient  $dp/dx$ , and  $\tau$  is the shear stress. The flow velocity  $u$  varies only with radius  $r$ . The Knudsen number of the flow is defined by  $Kn = \lambda/(2R)$  where  $\lambda$  is the molecular mean free path.

(a) Non-continuum fluid mechanics recognises several regimes for the capillary tube flow. For each regime, give the approximate range of  $Kn$  over which the description applies and state whether or not the Navier-Stokes equation is valid for analysing the flow. [20%]

(b) Suppose the flow is in the *slip-flow regime*. If  $y$  is the distance measured from the wall, an approximate kinetic theory model assumes *free-molecule* behaviour for the region  $0 < y \leq \lambda$  and *continuum* behaviour for  $y > \lambda$ . Sketch a  $u$ - $y$  diagram to show how the slip velocity at the wall  $u_{slip}$  is defined. Assuming that all molecules are reflected diffusely from the wall, show that

$$u_{slip} = \lambda \left( \frac{du}{dy} \right)_{y=0}$$

It may be assumed without proof that the mass flux of molecules incident on a surface per unit area is  $\rho \bar{C}/4$  where  $\bar{C}$  is the mean thermal speed of the molecules, and that the dynamic viscosity  $\mu$  is equal to  $\rho \bar{C} \lambda / 2$ . [25%]

(c) The analysis to find the velocity profile  $u(r)$  proceeds as for continuum flow but with a modified wall boundary condition. Starting from the force-momentum principle applied to the control volume shown in Fig. 1, show that

$$u = -\frac{dp}{dx} \left[ \frac{(1 + 4Kn)R^2 - r^2}{4\mu} \right]$$

[35%]

(d) If  $\dot{m}$  is the actual mass flow rate and  $\dot{m}_{cont}$  is the mass flow rate obtained assuming continuum theory to apply, find an expression for  $\dot{m}/\dot{m}_{cont}$  in terms of  $Kn$  only. [20%]

(cont.)

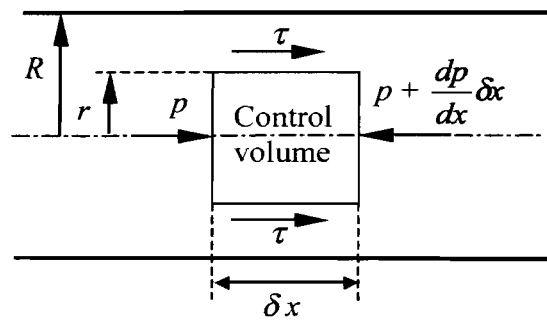


Fig. 1

2 (a) (i) How is the kinetic temperature of a monatomic gas defined in the kinetic theory of gases?

(ii) How is the kinetic temperature of a diatomic gas defined? [10%]

(b) A mixture of 0.01 kmol of nitrogen and 0.03 kmol of helium is at equilibrium in a container. The root mean square (rms) velocity of the nitrogen molecules is  $500 \text{ m s}^{-1}$ .

(i) Calculate the rms velocity of the helium molecules. [15%]

(ii) 50 kJ of heat is added to the mixture while maintaining the volume constant. Stating your assumptions and approximations clearly, and using kinetic theory only (not tabulated data), estimate the final rms velocity of the helium molecules. [35%]

(c) Consider a monatomic ideal gas in a rigid container. If  $Q$  is a molecular property depending on the molecular velocity components  $C_1$ ,  $C_2$  and  $C_3$ , then the mean value  $\bar{Q}$  is defined by

$$\bar{Q} = \frac{1}{n} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} Q f(C_1, C_2, C_3) dC_1 dC_2 dC_3$$

where  $n$  is the number density of molecules. If the gas is at equilibrium then  $f$  is the Maxwell-Boltzmann velocity distribution function

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

By making a suitable choice for  $Q$ , prove that the molecular energy of a monatomic gas in an equilibrium state is partitioned equally between the three translational degrees of freedom. [40%]

The following integrals may be used without proof:

$$\int_{-\infty}^{\infty} e^{-x^2} dx = \pi^{1/2} \qquad \int_{-\infty}^{\infty} x^2 e^{-x^2} dx = \frac{\pi^{1/2}}{2}$$

3 (a) For a diatomic molecule constrained to rotate in a plane, the solution of the Schrödinger equation may be written

$$\psi = \psi_0 \cos \left\{ \left( \frac{8\pi^2 I \epsilon}{h^2} \right)^{1/2} (\phi - \phi_0) \right\}$$

where  $\psi$  is the wave function,  $\phi$  is the angular displacement,  $I$  is the moment of inertia,  $\epsilon$  is the rotational kinetic energy and  $h$  is Planck's constant ( $\psi_0$  and  $\phi_0$  are constants). Use this solution to show that  $\epsilon$  is quantised. Find an expression for its possible values. [20%]

(b) When the rotation is *not* constrained to a plane, the rotational energy levels for a diatomic molecule are given by

$$\epsilon_m = \frac{h^2}{8\pi^2 I} m(m+1) \quad \text{where } m = 0, 1, 2, \dots$$

while the degeneracy of each level is

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

- (i) What does  $\sigma$  signify and what values can it take?
- (ii) Write down an expression for the contribution to the (single molecule) partition function  $Z_{rot}$  arising from rotation.
- (iii) Hence write down an expression for the characteristic temperature of rotation,  $\theta_{rot}$ . [20%]

(c) Determine an expression for  $Z_{rot}$  in terms  $\sigma$ ,  $\theta_{rot}$  and the temperature  $T$  for the case where  $\theta_{rot} \ll T$ . Hence show that, in the high temperature limit, the rotational energy modes for diatomic gases contribute  $R$  to the constant volume specific heat capacity, where  $R$  is the specific gas constant. State whether you would expect this result to be accurate for (i) nitrogen at 250 K, and (ii) hydrogen at 250 K. Give qualitative justifications for your answers. [60%]

You may use without proof the expression for the internal energy

$$U = NkT^2 \left( \frac{\partial}{\partial T} \ln Z \right)_v$$

where the symbols have their usual meanings.

4 (a) For each of the following, specify whether the statement is true or false, giving brief but full justifications for your answers. Give also the corrected, true statement for each case that you believe to be false.

(i) A system comprising 1 kg of helium gas undergoes a reversible, isothermal expansion. At the end of the process the number of possible microstates of the system has increased.

(ii) The molecules of a certain monatomic, ideal gas have one electronic excitation mode. At high temperature, the specific heat capacity at constant volume is given by  $c_v = 2R$ , where  $R$  is the specific gas constant. [25%]

(b) A statistical analogue of the entropy of a system is given by

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

where  $k$  is Boltzmann's constant,  $P_i$  is the probability of the  $i$ -th microstate and  $\Omega$  is the number of microstates of the system. For a system with only three possible microstates, show that the maximum value of  $S'$  is  $k \ln 3$ . When is this achieved? [35%]

(c) Consider a system undergoing a reversible process while exchanging work and heat with an environment at temperature  $T$ . Write down an expression for an infinitesimal change in the average energy of the system in terms of the energies and probabilities of its microstates. Identify the terms in your expression with the corresponding terms in the First Law of Thermodynamics and show that the heat transfer terms are consistent with the classical expression for reversible heat exchange

$$\delta Q = TdS \quad [40\%]$$

You may use without proof the following expression for the probability of the  $i$ -th microstate

$$P_i = \frac{\exp(-E_i / kT)}{Q}$$

where  $Q$  in the above expression is the system partition function and the other symbols have their usual meanings.

**END OF PAPER**