ENGINEERING TRIPOS PART IIB

Thursday 4th May 2006 2.30 to 4.00

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) An ideal gas flows through an adiabatic converging nozzle. Consider the state of the gas at the following positions:

(i) A point on the nozzle centre-line where the flow velocity is **V**;

(ii) A point in the laminar viscous boundary layer on the nozzle wall where the flow velocity is 0.1**V**;

(iii) A point extremely close to the nozzle wall where the flow velocity is effectively zero.

For each case, explain briefly how you would expect the molecular velocity distribution at the point in question to deviate from the Maxwell-Boltzmann distribution and state whether or not you would expect the Navier-Stokes equations to be valid locally. [30 %]

(b) An ideal gas at temperature T is composed of identical molecules of mass m. The Maxwell-Boltzmann molecular *speed* distribution function $g_e(C)$ is defined by,

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

where C is the speed of a molecule and k is Boltzmann's constant. In answering the following questions you may make free use of the tables of integrals on the next page.

(i) Using a suitable substitution prove that,

$$\int_0^{C_0} g_e(C)dC = \frac{4}{\sqrt{\pi}} \int_0^{X_0} X^2 \exp(-X^2)dX .$$

Hence show that the mean translational kinetic energy of a molecule is equal to $3kT/2$. [20 %]

(ii) Find the fraction of molecules with translational kinetic energies less than the mean value. [30 %]

(iii) Show that the root mean square deviation of the translational kinetic energy of a molecule from the mean value is equal to $kT\sqrt{3/2}$. [20 %]

(cont.

$$\mathrm{I}(n) = \int_0^\infty X^n \exp(-X^2)\,dX$$

n	$\mathrm{I}(n)$	n	$\mathrm{I}(n)$
0	$\frac{\sqrt{\pi}}{2}$	1	$\frac{1}{2}$
2	$\frac{\sqrt{\pi}}{4}$	3	$\frac{1}{2}$
4	$\frac{3\sqrt{\pi}}{8}$	5	1
6	$\frac{15\sqrt{\pi}}{16}$	7	3

$$\mathrm{erf}(X_0) = \frac{2}{\sqrt{\pi}} \int_0^{X_0} \exp(-X^2)\,dX$$

X_0	$\mathrm{erf}(X_0)$	X_0	$\mathrm{erf}(X_0)$
0	0	1.6	0.9763
0.2	0.2227	1.8	0.9891
0.4	0.4284	2.0	0.9953
0.6	0.6039	2.2	0.9981
0.8	0.7421	2.4	0.9993
1.0	0.8427	2.6	0.9998
1.2	0.9103	2.8	0.9999
1.4	0.9523	∞	1.0000

Tables of Integrals for Question 1.

(TURN OVER

2 Consider the laminar incompressible viscous flow of a perfect gas through a capillary tube of diameter $2R$. The flow is driven by a streamwise pressure gradient dp/dx and the flow velocity u varies with radius r. Conditions are such that the flow is in the *slip regime* and information is required on how the mass flowrate varies with the Knudsen number, Kn. ($Kn = \lambda/R$ where λ is the molecular mean free path.)

(a) In order to estimate u_{slip} (the effective slip velocity at the tube wall), a simple kinetic theory model is used. If ξ is distance measured from the wall, the model assumes 'free-molecule' behaviour for $0 < \xi \le \lambda$ and 'continuum' behaviour for $\xi > \lambda$. Assuming that all molecules are reflected diffusely from the wall show that,

$$u_{\text{slip}} = -\lambda \left(\frac{du}{dr} \right)_{r=R} .$$

It may be assumed without proof that the mass flux of molecules incident on a wall is $\rho \overline{C}/4$ where $\overline{C}$ is the mean thermal speed of the molecules, and that the dynamic viscosity of the gas μ is equal to $\rho \overline{C} \lambda / 2$. [40 %]

(b) The analysis now proceeds as for continuum flow but with a modified wall boundary condition to compensate for the non-continuum layer near the wall. Starting from the force-momentum principle applied to a cylindrical control volume of radius r and length δx, derive an expression for the flow velocity $u(r)$ in terms of R, Kn and dp/dx. Hence show that,

$$\frac{\dot{m}}{\dot{m}_{\text{cont}}} = 1 + 4Kn ,$$

where $\dot{m}$ is the actual mass flowrate and $\dot{m}_{\text{cont}}$ is the mass flowrate obtained assuming continuum theory to apply. [60 %]

3 (a) The Boltzmann relation is:

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

Explain briefly the meaning of S, k and Ω, and show that this relationship is consistent with entropy being an extensive property. [25%]

(b) Figure 1 shows an isolated system comprising a 1 kg block of iron (specific heat capacity, c_v = 440 $\mathrm{Jkg^{-1}K^{-1}}$) in thermal contact with a 1 kg block of copper (specific heat capacity, c_v = 380 $\mathrm{Jkg^{-1}K^{-1}}$). At equilibrium the temperature of both blocks is 300 K. Calculate the probability of the system existing in a state where the temperature of the copper block is increased by 0.001 K due to random fluctuations. Comment briefly on the result. [45%]

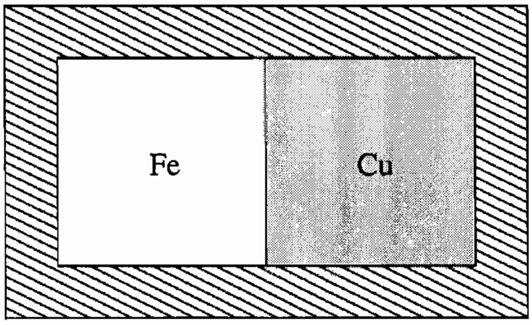

Fig. 1

(c) The quantum energy of a simple harmonic oscillator relative to its ground state is given by:

$$\varepsilon = nh\nu \ ,$$

where h is Planck's constant, ν is the oscillation frequency and n is a non-negative integer. Draw a state-space diagram showing the permissible quantum states for a system that comprises three such oscillators and has a total energy E. Determine the number of states for this system having energy in the range 1.0 μJ to 1.001 μJ if the oscillation frequency is 10^{14} Hz. [30%]

Data: $h = 6.626\times10^{-34}$ Js $\qquad k = 1.381\times10^{-23}$ $\mathrm{JK^{-1}}$

4 (a) Figure 2 shows the variation with temperature of the constant volume specific (not molecular) heat capacity, c_v, for hydrogen gas, H_2.

(i) Explain the shape of the curve.

(ii) Give theoretical values for c_v and the ratio of specific heat capacities, γ, at very low, very high and room temperatures.

(iii) Explain how the curve would differ for oxygen gas, O_2. [40%]

(b) The atoms of a certain monatomic gas have translational and electronic energy modes only. The quantum energy levels of the electrons are such that only the ground state (with degeneracy $g_0 = 1$ and energy $\varepsilon_0 = 0$) and the first excited energy level (with degeneracy $g_1 = g$ and energy $\varepsilon_1 = \varepsilon$) are significantly populated.

(i) Write down an expression for the electronic partition function and hence derive the relationship between the constant volume specific heat capacity, c_v, and temperature, assuming that the translational energy modes are fully excited. [45%]

(ii) Sketch and annotate a graph of c_v against T. (Detailed quantitative information is not required.) [15%]

You may use without proof the following expression for the internal energy:

$$U = NkT^2 \frac{\partial}{\partial T}(\ln Z)_V \quad ,$$

where $Z = \sum g_n \exp(-\varepsilon_n / kT)$ is the partition function and other symbols have their usual meanings.

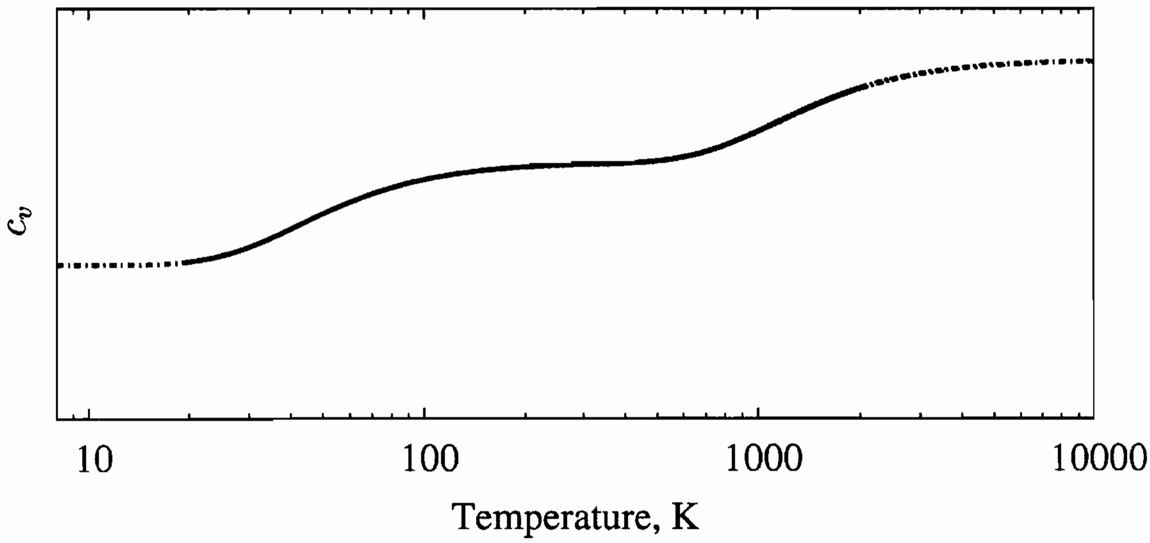

Fig. 2

END OF PAPER

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ANSWERS

1 (b) (ii) 0.607

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

3 (b) $\exp(-2.85\times 10^{14})$

(c) 1.72×10^{36}

4 (a) (ii) Low Temperature: 6.24 kJ/kgK, 1.67;
High Temperature: 14.6 kJ/kgK, 1.29;
Room T: 10.4 kJ/kgK, 1.4.

(b) (i) $c_v = R\left\{\dfrac{3}{2} + \left(\dfrac{\theta}{T}\right)^2 \dfrac{g\exp(\theta/T)}{(\exp(\theta/T)+g)^2}\right\}$ where $\theta=\varepsilon/k$

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