

EGT3
ENGINEERING TRIPOS PART IIB

Friday 24 April 2015 9.30 to 11

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.*

*Write your candidate number **not** your name on the cover sheet.*

STATIONERY REQUIREMENTS

Single-sided script paper

SPECIAL REQUIREMENTS TO BE SUPPLIED FOR THIS EXAM

CUED approved calculator allowed

Engineering Data Book

10 minutes reading time is allowed for this paper.

You may not start to read the questions printed on the subsequent pages of this question paper until instructed to do so.

1 *Information relevant to this question can be found on the next page.*

A stationary monatomic perfect gas at equilibrium has molecular mass m , number density n , temperature T and gas constant per unit mass R . The cartesian components of the molecular peculiar velocity are denoted by C_1 , C_2 and C_3 .

(a) (i) Consider the integral,

$$I = \frac{1}{n} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{C_1^2}{2} f dC_1 dC_2 dC_3$$

where f is the Maxwell-Boltzmann velocity distribution. Without evaluating the integral, but explaining your reasoning, write down an expression for I in terms of R and T . [10%]

(ii) An imaginary plane within the gas is orientated such that the cartesian coordinate x_1 is normal to the plane. Write down an integral for the flux of the quantity $mC_1^2/2$ through unit area of the plane transported by molecules with $C_1 > 0$. [5%]

(iii) Evaluate the integral and hence obtain an expression in terms of R and T for the mean value of $C_1^2/2$ for molecules crossing the plane with $C_1 > 0$. Compare this result with that of part (i) and comment on any differences. [35%]

(b) Suppose the gas has $R = 2.08 \text{ kJ kg}^{-1} \text{ K}^{-1}$ and is confined between two parallel plates separated by a distance of 2 mm. The temperatures of the plates are 300 K and 400 K. The dynamic viscosity of the gas at 350 K is $2.2 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$ and its Prandtl number is 0.67. It may be assumed that molecules incident on the plates are reflected diffusely. Calculate the Knudsen number and estimate the heat flux per unit area between the plates when the gas pressure is,

(i) 1 Pa [25%]

(ii) 10,000 Pa [25%]

Information for Question 1

‘One-sided’ molecular mass flux per unit area through a plane for a gas of density ρ :

$$\frac{\rho \bar{C}}{4} = \frac{\rho}{4} \left(\frac{8RT}{\pi} \right)^{1/2}$$

Maxwell-Boltzmann velocity distribution function :

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

Dynamic viscosity μ in terms of the mean free path λ :

$$\mu = \frac{\rho \bar{C} \lambda}{2}$$

Some definite integrals:

$I(n) = \int_0^{\infty} x^n \exp(-x^2) dx$			
n	$I(n)$	n	$I(n)$
0	$\frac{\sqrt{\pi}}{2}$	1	$\frac{1}{2}$
2	$\frac{\sqrt{\pi}}{4}$	3	$\frac{1}{2}$
If n is even	$\int_{-\infty}^{\infty} x^n \exp(-x^2) dx = 2I(n)$		
If n is odd	$\int_{-\infty}^{\infty} x^n \exp(-x^2) dx = 0$		

2 A perfect diatomic gas has a molar mass of 42 kg kmol^{-1} . A crude model of the molecular velocity distribution for the gas 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 this '6-group gas' have absolute velocity components c_i ($i = 1, 2, 3$) in m s^{-1} as follows :

$$(480, 120, 0); \quad (50, 550, 0); \quad (50, 120, 430);$$

$$(-380, 120, 0); \quad (50, -310, 0); \quad (50, 120, -430).$$

- (a) (i) Calculate the temperature of the 6-group gas. [20%]
(ii) Stating any assumptions, calculate the contributions to the total energy per unit mass of the 6-group gas from the mean motion, the random translational motion and the internal molecular motion. [20%]
- (b) (i) Gas kinetic theory shows that the thermal conductivity k of a perfect monatomic gas of density ρ can be expressed as

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

where β is a constant, \bar{C} is the mean peculiar speed, λ is the mean free path and c_v is the constant volume specific heat capacity. Explain briefly why simple 'mean free path' theories give $\beta = 1$ whereas more exact theories give $\beta \cong 5/2$. Describe how the above expression can be modified to provide an approximation for the thermal conductivity of diatomic and polyatomic gases. [15%]

(ii) If the dynamic viscosity of the 6-group gas is $20 \times 10^{-6} \text{ kg m}^{-1} \text{ s}^{-1}$, estimate its thermal conductivity. [15%]

- (c) Consider the expression $\overline{c_i(c^2/2)}$ and explain what it represents physically. By writing $c_i = u_i + C_i$ (where u_i is the mean velocity and C_i is the peculiar velocity) decompose the expression into four terms. Identify the term representing the heat flux per unit mass q_i and calculate q_1 , q_2 and q_3 for the 6-group gas. [30%]

3 (a) Figure 1 shows a diatomic molecule that is constrained to rotate in the x - y plane. The orientation of the molecule at any instant is defined by the angle ϕ that its axis makes with the x -axis, as shown. The form of the Schrödinger equation appropriate to planar rotation is

$$\frac{d^2\psi}{d\phi^2} + \frac{8\pi^2 I \epsilon}{h^2} \psi = 0$$

where ψ is the wave function, h is Planck's constant, I is the molecule's moment of inertia about the z -axis and ϵ is its rotational kinetic energy. Obtain the general solution to the above equation and hence determine the possible values of ϵ . [20%]

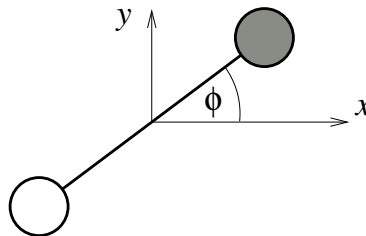


Fig. 1

(b) The molecules of a certain ideal, diatomic gas have translational, rotational and electronic energy modes only. The quantum energy levels of the electrons are such that only the ground state with zero energy and the first excited state with energy ϵ are significantly populated. Both states are non-degenerate.

(i) Write down an expression for the electronic partition function for a single molecule. [5%]

(ii) By considering the fraction of molecules in the electronically excited state, or otherwise, show that the electronic contribution to the constant volume specific heat capacity is given by

$$c_v^{\text{el}} = \frac{R\tau^2 e^\tau}{(1 + e^\tau)^2}$$

where R is the gas constant per unit mass and $\tau = -\epsilon/(kT)$, k being Boltzmann's constant and T being the temperature. [40%]

(iii) Stating your assumptions, show that the ratio of specific heat capacities $\gamma = c_p/c_v$ has a minimum when $\tau \approx -2.4$ and determine the minimum value. [35%]

4 The entropy of a stretched rubber band may be considered to comprise two independent components: a *configurational* component that depends on the band's length L , and a *thermal* component that depends on its temperature T . Figure 2 illustrates a simplified model for computing the configurational entropy. The rubber band is assumed to consist of a bundle of long chain polymers, each comprising N monomers of length a . One end of the chain is fixed at $x = 0$ and the other (at $x = L$) is subject to an externally applied tension τ . Each monomer of the chain may be aligned either parallel (+) or anti-parallel (−) to the x -axis such that there are N^+ and N^- monomers in the positive and negative x -directions respectively.

(a) Explain why the number of distinct arrangements for the orientations of the monomers in a single chain is given by

$$\Omega = \frac{N!}{(N^+)!(N^-)!} \quad [15\%]$$

(b) State what assumption is required for Boltzmann's relation ($S = k \ln \Omega$, where k is the Boltzmann constant) to apply to the configurational entropy and, assuming this is valid, show that the rate of change of entropy with length for a single polymer chain may be written in the form

$$\left(\frac{\partial S}{\partial L}\right)_{T,N} = A \ln \left(\frac{Na - L}{Na + L}\right)$$

Find an expression for the factor A in terms of quantities defined above.

Note that Stirling's formula states that $\ln(m!) \approx m \ln m - m$, for $m \gg 1$. [40%]

(c) With reference to the entropy, explain carefully what would happen to the temperature of the rubber band if it were stretched reversibly and adiabatically. [10%]

(d) By considering heat and work transfers to or from a polymer chain for a general (non-adiabatic) reversible process, show that infinitesimal changes are related by

$$\delta F = \tau \delta L - S \delta T$$

where $F = U - TS$ is the Helmholtz function and U is the internal energy. Hence determine what will happen to the tension in the rubber band if it is heated at fixed length.

[35%]

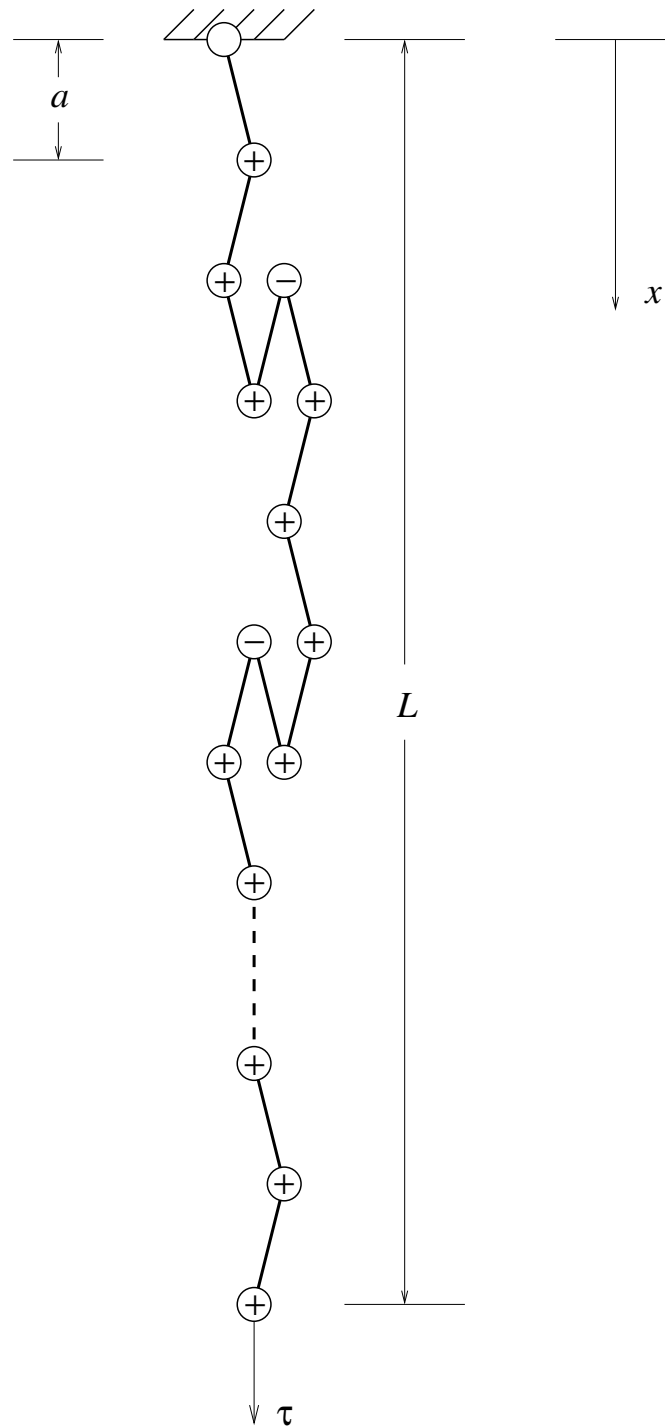


Fig. 2

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ENGINEERING TRIPOS PART IIB 2015
MODULE 4A9 – MOLECULAR THERMODYNAMICS

ANSWERS

1. (a) (i) $RT/2$
(ii) RT
(b) (i) 195 W/m^2 (depending on assumptions)
(ii) 8550 W/m^2
2. (a) (i) 311.3 K
(ii) 8.45 kJ/kg (mean), 92.45 kJ/kg (random translational), 61.63 kJ/kg (rotational)
(b) (ii) $0.019 \text{ W m}^{-1}\text{K}^{-1}$
(c) $q_i = C_i(C^2/2)$; $q_1 = q_2 = q_3 = 0$
3. (a) $\epsilon = \frac{n^2 h^2}{8\pi^2 I} \quad n = 0, 1, 2 \dots$
(b) (i) $Z = 1 + e^{-\epsilon/kT}$
(iii) $\gamma_{\min} = 1.340$
4. (b) $A = k/2a$

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