

EGT3
ENGINEERING TRIPOS PART IIB

Wednesday 3 May 2017 2 to 3.30

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 A monatomic gas of molecular mass m and specific gas constant R is at equilibrium and has zero mean velocity. Consider a cartesian co-ordinate system (x_1, x_2, x_3) with corresponding molecular velocity components (C_1, C_2, C_3) .

(a) With reference to a suitable diagram, show that the flux per unit area and unit time of quantity Q (measured per molecule) in the positive x_3 direction is given by

$$F_3^+(Q) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} Q C_3 f(C_1, C_2, C_3) dC_3 dC_2 dC_1$$

where $f(C_1, C_2, C_3)$ is the molecular velocity distribution. [30%]

(b) Explain why the molecular speed distribution $g(C)$ is related to the molecular velocity distribution by

$$g(C) = 4\pi C^2 f(C)$$

where $C^2 = C_1^2 + C_2^2 + C_3^2$. [5%]

(c) By considering the case where $Q = m$ and converting the expression in (a) to spherical polar coordinates in velocity space (as shown in Fig. 1), show that the one-sided mass flux is given by

$$F^+(m) = \frac{\rho \bar{C}}{4}$$

where ρ is the gas density and \bar{C} is the mean molecular speed. [30%]

(d) A quantity of argon gas ($R = 208 \text{ J kg}^{-1} \text{ K}^{-1}$) is contained within a cubic box. The total mass of the box and gas is 0.5 kg. One wall of the box contains a large number of very small pores that have a total open area of 1 mm^2 . When the gas temperature and pressure inside the box are 300 K and 1 bar respectively, the box is released in outer space. Ignoring any gravitational effects, determine the initial acceleration of the box. [35%]

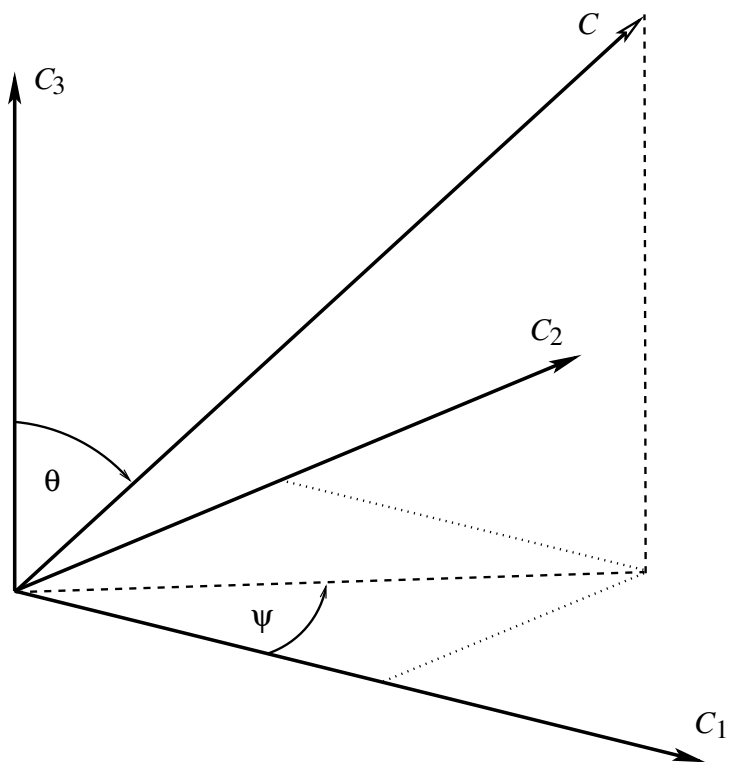


Fig. 1

2 With reference to Fig. 2, consider the laminar, incompressible, viscous flow of helium gas between two stationary parallel plates of length L separated by a small distance h . The flow is driven by a streamwise pressure drop Δp and the flow velocity u may be assumed to vary only with y . Information is required on how the pressure drop required to drive a given mass flow rate varies with Knudsen number, $\text{Kn} = \lambda/h$ (where λ is the molecular mean free path).

(a) Given that the gas temperature is 300 K and that the separation h is 0.1 mm, estimate the range of pressure for which the flow lies within the *slip regime*. Assume that helium molecules have a diameter of 0.26 nm. [20%]

(b) Suppose from now on that the slip-flow regime applies. An approximate kinetic theory model for this regime assumes *free-molecule* behaviour for the regions within one mean free path of the walls and *continuum* behaviour elsewhere. Sketch a u - y diagram to show how the slip velocity u_{slip} is defined. Assuming that molecules are reflected diffusely from the walls, show that on the lower wall

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

It may be assumed without proof that the mass flux of molecules incident on a surface per unit area is $\rho \bar{C}/4$ and that the dynamic viscosity μ is equal to $\rho \bar{C} \lambda / 2$, where ρ is the density and \bar{C} is the mean thermal speed of molecules. [30%]

(c) The analysis now proceeds as for continuum flow but with modified boundary conditions to account for the non-continuum layers at the walls. Starting from the force-momentum principle applied to a suitable control volume, derive an expression for the velocity profile $u(y)$ in terms of Δp , L , h , μ and Kn . Hence show that

$$\frac{\Delta p}{\Delta p_{\text{cont}}} = \frac{1}{1 + B \text{Kn}}$$

where Δp is the actual pressure drop and Δp_{cont} is the pressure drop (for the same mass flow rate) obtained assuming continuum theory to apply. Find also the value of the coefficient B . [50%]

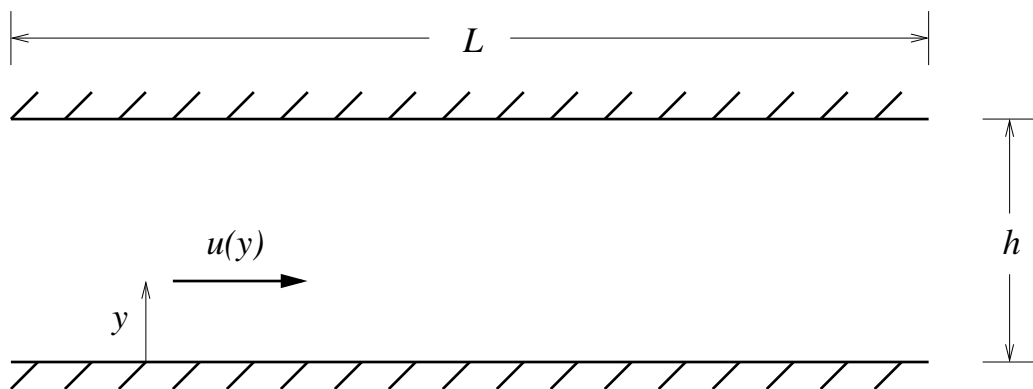


Fig. 2

- 3 (a) Provide one sentence answers to the following questions.
- (i) What is the fundamental postulate of statistical mechanics?
 - (ii) Which thermodynamic properties are held constant for microcanonical and canonical ensembles respectively?
 - (iii) In what order do the internal modes of energy typically become fully excited within a diatomic molecule?
 - (iv) What are the effects of heat addition *to* and work done *on* a system in terms of the energy level spacing and number of particles occupying each level? [20%]

(b) Sketch a canonical ensemble where two closed systems are in thermal contact with an infinite thermal reservoir. Explain why the probability of one system being in its i -th microstate, with energy E_i , must be of the functional form $P_i = C \exp(\beta E_i)$, where C and β are constants. Explain also why β must be related to temperature. [20%]

(c) A system contains one gram-mole of a diatomic ideal gas with a characteristic temperature of rotation of $\theta_r = 80$ K. The system is in contact with an infinite thermal reservoir at temperature $T = 40$ K.

- (i) The single-particle rotational partition function takes the form

$$Z_{\text{rot}} = \sum_{n=0}^{\infty} (2n+1) \exp\left(-\frac{n(n+1)\theta_r}{T}\right)$$

where n denotes the individual energy states. By considering only significantly populated energy states, estimate the rotational contribution to the internal energy of the system. You may use without proof the following expression for internal energy

$$U = kT^2 \frac{\partial}{\partial T} (\ln Q)$$

where Q is the system partition function and k is Boltzmann's constant. [35%]

- (ii) Taking the rotational component of the constant volume molar heat capacity as $\bar{C}_{v, \text{rot}} = 0.8 \bar{R}$, where \bar{R} is the molar gas constant, calculate the order of magnitude of the standard deviation in temperature fluctuations within the system. You may assume that the variance of system energy fluctuations is given by $\sigma_E^2 = \partial U / \partial \beta$, where $\beta = -1/kT$. [25%]

4 Consider an ideal gas at approximately ambient temperature, confined to a two-dimensional planar system. In the thermodynamic description of such systems, the area A plays a similar role to that of volume in three-dimensional systems, and the ‘surface pressure’ p_s replaces pressure. Thus, analogous to three-dimensional systems, the reversible work done by the system in increasing its area by dA is $\delta W = p_s dA$.

(a) Show that for an infinitesimal, reversible process the change in Helmholtz function for the system is given by

$$dF = -p_s dA - S dT$$

where $F \equiv U - TS$ and T and S are the temperature and entropy respectively. [15%]

(b) The energy levels of a free particle in a two-dimensional plane are given by the solution to the Schrödinger wave equation, resulting in

$$E(n_x, n_y) = h^2 \frac{2\pi}{m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right)$$

where n_x and n_y are integers taking values from 1 to ∞ , m is the particle’s mass, h is Planck’s constant, and L_x and L_y are the sides of the plane such that $A = L_x L_y$. Use this result to determine an expression for the two-dimensional system partition function Q in terms of m , h , A , T and Boltzmann’s constant, k .

You may use without proof the following integral

$$\int_0^\infty \exp(-x^2 \tau^2) dx = \frac{\sqrt{\pi}}{2\tau} \quad \text{where } \tau > 0 \quad [30\%]$$

(c) Using the partition function found in (b), develop a relationship for the entropy S of N monatomic molecules in terms of N , A , k , m , h , and T . Note that $F = -kT \ln Q$. [30%]

(d) Calculate the increase in available microstates as a ratio Ω_2/Ω_1 resulting from an isothermal expansion of 1 gram-mole of monatomic gas from $A_1 = 1 \text{ m}^2$ to $A_2 = 2 \text{ m}^2$. [25%]

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MODULE 4A9 – MOLECULAR THERMODYNAMICS

Answers

1. (d) 0.1 ms^{-2}

2. (a) ~ 0.02 to ~ 0.2 bar (c) $B = 6$

3. (c) (i) 66.5 J (ii) $3.4 \times 10^{-11} \text{ K}$

4. (b) $Q = \frac{mkT}{8h^2} A$ (c) $S = Nk \left(\ln T + \ln A + 1 - \frac{1}{N} \ln N! + \ln \left\{ \frac{mk}{8h^2} \right\} \right)$ (d) 2^{N_A}

AJW / AMB 2017