Version AJW/3

EGT3
ENGINEERING TRIPOS PART IIB

Friday 28 April 2023   9.30 to 11.10

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 at the start of the exam.

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

You may not remove any stationery from the Examination Room.

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

(a) Starting from the Maxwellian molecular velocity distribution function and stating carefully your arguments, derive an expression for the molecular speed distribution function for a stationary gas at equilibrium. Find also an expression for the most probable speed in terms of the specific gas constant R and temperature T. [20%]

(b) An equimolar mixture of helium and argon is contained within a stationary cubic box at 300 K and 1 bar. One face of the box, F, is oriented relative to a coordinate system x_i ($i = 1, 2, 3$) such that x_1 points normally outward from the box through F.

(i) Sketch on the same set of axes the molecular speed distributions, distinguishing between the curves for helium and argon. [10%]

(ii) For helium molecules striking F, calculate the flux per unit area and per unit time of the quantity mC_1, where m is the mass of a helium molecule and C_1 is the molecular velocity component in the x_1 direction. Include the units in your result. [25%]

(iii) Calculate the average value of C_1 for helium molecules striking F. [25%]

(c) A small hole is now made in the face F of the box described in part (b). The diameter of the hole is much smaller than the mean free path of the molecules within the box, and the face of the box may be assumed infinitesimally thin. Molecules of gas effuse through the hole into an evacuated space. Determine the fraction of helium molecules leaving the box for which $C_1 > 670\,\mathrm{m\,s^{-1}}$. [20%]

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Information for Question 1

The Maxwellian velocity distribution for a stationary gas at temperature T and with specific gas constant R is given by

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

where n is the number density of molecules.

Some definite integrals of the form:

$$I(n) = \int_0^\infty x^n \exp\left(-x^2\right)\,\mathrm{d}x$$

n	$I(n)$	n	$I(n)$
0	$\frac{\sqrt{\pi}}{2}$	2	$\frac{\sqrt{\pi}}{4}$
1	$\frac{1}{2}$	3	$\frac{1}{2}$

Tabulated values of the error function:

$$\mathrm{erf}\,(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-x^2)\,\mathrm{d}x$$

x	erf (x)	x	erf (x)	x	erf (x)
0.0	0.0000	1.0	0.8427	2.0	0.9953
0.2	0.2227	1.2	0.9103	2.2	0.9981
0.4	0.4284	1.4	0.9523	2.4	0.9993
0.6	0.6039	1.6	0.9763	2.6	0.9998
0.8	0.7421	1.8	0.9891	2.8	0.9999

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2 (a) Mean free path analysis for the dynamic viscosity μ of an ideal gas gives

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

where ρ is the density, λ is the molecular mean free path and $\bar{C} = \sqrt{8RT/\pi}$ is the mean molecular speed, (R being the specific gas constant and T the temperature).

(i) Show that μ is independent of pressure. [10%]

(ii) Given that the dynamic viscosity of nitrogen at 300 K is 1.79×10^{-5} Pa s, estimate the diameter of nitrogen molecules. [15%]

(b) Low-pressure gas is contained within the space between two concentric circular cylinders, as shown in Fig. 1. The inner cylinder has radius a and is stationary. The outer cylinder has radius $2a$ and moves with speed V parallel to the common axis. The pressure is uniform and the axial velocity u within the gas depends only on the radial location r. The value of the Knudsen number ($\mathrm{Kn} = \lambda/a$) is such that the flow is in the *slip* regime.

(i) Draw a sketch of the velocity profile in the vicinity of the inner cylinder to show how the slip velocity u_s is defined. Using a flux matching model and assuming molecules are reflected diffusely from the surface, show that

$$u_s \simeq \lambda \left(\frac{\mathrm{d}u}{\mathrm{d}r}\right)_{r=a}$$

It may be assumed without proof that the one-sided molecular mass flux per unit area is given by $\rho\bar{C}/4$. [30%]

(ii) Obtain an expression for how the shear stress varies with r and explain why this is valid for both continuum and non-continuum flow. Hence determine the velocity profile $u(r)$ in terms of V, a, λ and r. [30%]

(iii) Show that the axial force F on the outer cylinder is given by

$$F = \frac{F_0}{1 + B\,\mathrm{Kn}}$$

where F_0 is the axial force in the continuum limit and B is a constant. Determine the value of B. [15%]

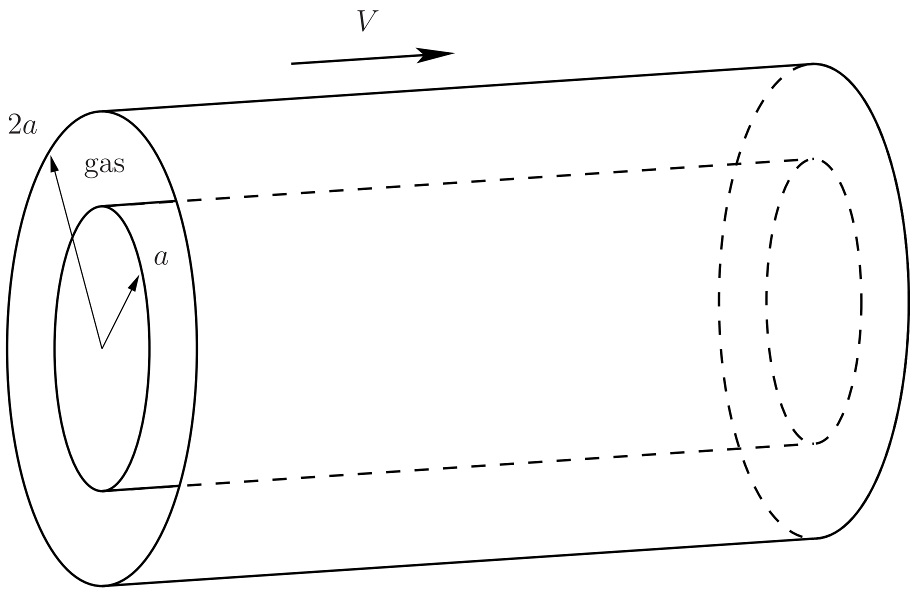

Fig. 1

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3 For a particle of mass m confined to a cubic box of volume V, the quantised translational energy is given by

$$\epsilon_{tr} = \frac{h^2}{8mV^{2/3}}(n_1^2 + n_2^2 + n_3^2)$$

where h is Planck's constant and n_1, n_2 and n_3 are the translational quantum numbers.

(a) Define the term *degeneracy* and calculate the energy of the first energy level with a degeneracy greater than 3 for a helium molecule confined to a cubic box of side 1 mm. [20%]

(b) Derive an expression for the function $\Gamma(\epsilon_{tr})$ representing the number of translational energy states with energy less than ϵ_{tr}. Hence determine the number of translational energy states which have energy less than the average value for helium molecules at temperature $T = 300\,\mathrm{K}$ confined to a cubic box of side 1 mm. [25%]

(c) Starting from your expression for $\Gamma(\epsilon_{tr})$, derive an expression for the function $g(C)$, defined such that $g(C)\,\mathrm{d}C$ is the number of translational energy states corresponding to molecular speeds in the range C to $C + \mathrm{d}C$. [25%]

(d) The (single-particle) translational partition function is given by

$$Z_{tr} = \sum_j g_j \exp(-\epsilon_j/kT) = V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

where g_j and ϵ_j are the degeneracy and energy respectively of the j-th translational energy level and k is Boltzmann's constant.

By considering the fraction of molecules in the j-th energy level and relating $g(C)$ to the degeneracy g_j, find an expression for $\zeta(C)$ defined such that $\zeta(C)\,\mathrm{d}C$ is the fraction of molecules with molecular speeds in the range C to $C + \mathrm{d}C$. Your answer should be in terms of C, R and T, where R is the specific gas constant. [30%]

4 (a) Consider the statistical analogue of entropy

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

(i) Define each of the quantities on the right-hand side of this equation. [10%]

(ii) Show that S' is an extensive property. [25%]

(iii) Stating carefully your arguments, show that S' reaches a maximum value for an isolated system at equilibrium. Explain how this relates to the classical thermodynamic concept of entropy, and determine a simplified expression for the maximum value of S'. [25%]

(b) A system comprising a fixed volume V of nitrogen gas is in thermal equilibrium with a large thermal reservoir at temperature T, which is close to normal room temperature. Determine the number N of nitrogen molecules present if the RMS fluctuation in the energy of the system equates to 0.001% of its average energy, $U = Mc_vT$, where M is the system mass and c_v is the specific heat capacity at constant volume. You may use without proof the following relationships:

$$U = kT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{V,N} \qquad \text{and} \qquad Q = \sum_{i=1}^{\Omega} \exp(-E_i/kT)$$

where Q is the system partition function and E_i is the energy of the i-th microstate. [40%]

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