Version AJW/3

EGT3
ENGINEERING TRIPOS PART IIB

Friday 29 April 2022    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. Throughout the question nitrogen may be treated as a perfect gas.*

Nitrogen gas flows in a nozzle whose axis is aligned with the $x_1$ direction. The width of the nozzle may be assumed large compared with any boundary layers. At a particular point $P$ on the centreline of the nozzle the temperature is 350 K, the pressure is 1 bar and the flow velocity is $100\,\mathrm{m\,s^{-1}}$ in the positive $x_1$ direction.

(a)    Calculate the average energy per molecule at point $P$ and determine what fraction of this energy is due to (i) random translational kinetic energy of molecules, (ii) bulk kinetic energy of the flow. [20%]

(b)    The molecular velocity distribution is denoted by $f$ and the cartesian components of the molecular peculiar velocity are denoted by $C_1$, $C_2$ and $C_3$. The corresponding absolute velocity components are $c_1$, $c_2$ and $c_3$ respectively.

Consider the integral

$$I = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} Q\, f\, \mathrm{d}C_1 \mathrm{d}C_2 \mathrm{d}C_3$$

for the cases where

(i)    $Q = m$, the mass of a molecule

(ii)    $Q = c_1/n$, where $n$ is the number density of molecules

(iii)    $Q = \frac{1}{2}C_3^2/n$

(iv)    $Q = mC_1C_2$

(v)    $Q = \frac{1}{2}mC_1C^2$, where $C^2 = C_1^2 + C_2^2 + C_3^2$

For each case give a physical interpretation of the quantity $I$ and determine its value at the point $P$. [40%]

(c)    An imaginary plane within the gas at $P$ is orientated such that the cartesian co-ordinate $x_3$ is normal to the plane. Write down an integral for the flux of the quantity $\frac{1}{2}mC_3^2$ through unit area of the plane transported by molecules with $C_3 > 0$. Evaluate this integral and hence obtain the mean value of $\frac{1}{2}C_3^2$ for molecules crossing the plane with $C_3 > 0$. How does this compare with the mean value of $\frac{1}{2}C_3^2$ at point $P$? Comment on any differences. [40%]

(cont.

## Information for Question 1

The 'one-sided' molecular mass flux per unit area through a plane for a gas of density $\rho$ and with specific gas constant $R$:

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

The Maxwellian velocity distribution function:

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

where $n$ is the number density of molecules.

Some definite integrals:

$$I(n) = \int_0^\infty x^n \exp\left(-x^2\right) \, dx$$

| $n$ | $I(n)$ |
|---|---|
| 0 | $\dfrac{\sqrt{\pi}}{2}$ |
| 1 | $\dfrac{1}{2}$ |
| 2 | $\dfrac{\sqrt{\pi}}{4}$ |
| 3 | $\dfrac{1}{2}$ |

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2    (a)    Define the Knudsen number, Kn, and explain its physical significance. Describe briefly the different flow regimes that occur at different Knudsen numbers, giving approximate ranges of Kn for each case.    [10%]

(b)    Argon gas at 300 K flows through a capillary tube of diameter $D$ and length $L \gg D$. The flow is driven by a pressure difference $\Delta p$ between the two ends of the tube. Information is sought on how, at low gas pressure, the velocity profile differs from that predicted by continuum theory.

(i)    If $D = 0.2$ mm estimate the range of pressures for which the flow is in the *slip regime*. Assume that the effective diameter of argon molecules is 0.37 nm.    [20%]

(ii)    Suppose from now on that the pressure lies within the range calculated in (i) and that $\Delta p$ is small compared with this range. With the aid of a suitable diagram, illustrate how the slip velocity at the tube wall, $u_{\text{slip}}$, is defined. Assuming that molecules are reflected diffusely from the wall, show that

$$u_{\text{slip}} \simeq -\lambda \left( \frac{\mathrm{d}u}{\mathrm{d}r} \right)_{r=D/2}$$

where $\lambda$ is the molecular mean free path and $r$ is the radial coordinate. It may be assumed without proof that the one-sided molecular mass flux per unit area is $\rho \bar{C}/4$ and that the dynamic viscosity $\mu$ is equal to $\rho \bar{C} \lambda / 2$, where $\rho$ is the density and $\bar{C}$ is the mean thermal speed of molecules.    [30%]

(iii)    Starting from the force-momentum principle applied to a suitable control volume, derive an expression for the velocity profile $u(r)$ in terms of $\Delta p$, $L$, $D$, $\mu$, Kn and $r$. Hence show that

$$\frac{u_{\text{slip}}}{u_{\text{max}}} \simeq \frac{B\,\text{Kn}}{1 + B\,\text{Kn}}$$

where $u_{\text{max}}$ is the maximum velocity at the centreline of the tube and $B$ is a constant. Find the value of $B$.    [40%]

3    A closed system comprises $N$ molecules of a monatomic gas of molecular mass $m$. When the volume of the system is $V$ the energies of the molecular translational quantum states, $\epsilon_i$, and the corresponding single-particle partition function, $Z$, are given by

$$\epsilon_i = \frac{h^2}{8mV^{2/3}}(n_1^2 + n_2^2 + n_3^2) \qquad \text{and} \qquad Z = V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

where $k$ is Boltzmann's constant, $h$ is Planck's constant, $n_1$, $n_2$ and $n_3$ are the three translational quantum numbers and $T$ is the temperature.

(a)    Starting with the definition of Helmholtz free energy, $F = U - TS$ (where $U$ is the internal energy and $S$ is the entropy), derive the ideal gas relationship. You may use without proof the relation $F = -kT \ln Q$, where $Q$ is the *system* partition function.    [25%]

(b)    Write down an equation for $U$ in terms of $\epsilon_j$ and $N_j$, where $\epsilon_j$ is the energy of the $j$-th energy *level* and $N_j$ is the average number of molecules within that energy level. Hence determine an expression for an infinitesimal change in $U$ in terms of $\epsilon_j$ and $N_j$. Give, with justification, physical interpretations to the different terms in this expression.    [15%]

(c)    The system expands reversibly and adiabatically from state $A$ (temperature $T_A$ and volume $V_A$) to state $B$ (temperature $T_B$, volume $V_B$) whilst doing work $W$.

(i)    Starting from thermodynamic relations for the entropy of a perfect gas, show that the values of $N_j$ do not change between these states. Explain how this result relates to your answer to part (b). You may use without proof the relation

$$\frac{N_j}{N} \simeq \frac{g_j \exp(-\epsilon_j/kT)}{Z}$$

where $g_j$ is the degeneracy of the $j$-th energy level.    [30%]

(ii)    Derive expressions for the spacing between the first and second energy levels, $\epsilon_2 - \epsilon_1$, and between the second and third energy levels, $\epsilon_3 - \epsilon_2$, in terms of the work transfer $W$ and other appropriate quantities. Sketch on the same axes how these spacings vary with $W$.    [30%]

4 (a) State whether each of the following applies to the microcanonical ensemble (M), the canonical ensemble (C), neither (N) or both (B):

   (i) fixed energy;

   (ii) fixed temperature;

   (iii) fixed number of particles;

   (iv) allows for heat transfer.

In each case provide a brief justification for your answer. [20%]

(b) The statistical analogue of 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 that the system is in its $i$-th microstate and $\Omega$ is the total number of possible microstates.

   (i) What constraint applies to the $P_i$? [5%]

   (ii) Using the method of Lagrange multipliers, show that $S'$ is maximised when all microstates are equally probable. Hence determine a simplified expression for the statistical analogue of entropy valid for isolated systems. [25%]

(c) A closed system of fixed volume is in thermal contact with a large thermal reservoir at temperature $T$. The energy and probability of the system microstates are denoted by $E_i$ and $P_i$ respectively, and the (thermodynamic) internal energy by $U$.

   (i) By minimising $F' = U - TS'$ (the statistical analogue of Helmholtz free energy), determine how $P_i$ depends on $E_i$ when the system is at equilibrium. [20%]

   (ii) Show that $F' = -kT \ln Q$, and find an expression for $U$ in terms of $k$, $T$ and $Q$, where $Q$ is the system partition function. [30%]

**END OF PAPER**

**ANSWERS**

Q1. (a)   $1.23 \times 10^{-20}$ J        (i) 0.589    (ii) 0.0189

    (b)   (i) 0.962 kgm$^{-3}$   (ii) 100 ms$^{-1}$        (iii) 52.0 kJkg$^{-1}$   (iv) 0 Nm$^{-2}$        (v) 0 Wm$^{-2}$

    (c)   Mean value = 104 kJkg$^{-1}$


Q2. (b)   (i) 340 Pa to 3.4 kPa    (iii) $B = 4$