EGT3

ENGINEERING TRIPOS PART IIB

Friday 30 April 2021   9.00 to 10.40

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 and at the top of each answer sheet.*

STATIONERY REQUIREMENTS
Write on single-sided paper.

SPECIAL REQUIREMENTS TO BE SUPPLIED FOR THIS EXAM
CUED approved calculator allowed.
You are allowed access to the electronic version of the Engineering Data Books.

10 minutes reading time is allowed for this paper at the start of the exam.

The time taken for scanning/uploading answers is 15 minutes.

Your script is to be uploaded as a single consolidated pdf containing all answers.

1   Consider an ideal gas and let $\bar{Q}$ be some mean molecular quantity (measured per molecule) which varies only in the x_2 direction, as shown in Fig. 1. Molecules crossing an arbitrary plane $x_2 = x_{20}$ may be assumed to transport a value of $\bar{Q}$ corresponding to a location $\beta_Q \lambda$ from the plane, where λ is the molecular mean free path and β_Q is a constant that depends on the nature of $\bar{Q}$. It may also be assumed that the one-sided flux of molecules crossing the plane (per unit area and per unit time) is given by $n\bar{C}/4$, where n is the number density of molecules and $\bar{C}$ is the average molecular (peculiar) speed.

(a)   Stating any other assumptions, show that the net flux F_Q of $\bar{Q}$ transported through the plane in the positive x_2 direction (per unit area and per unit time) is given by

$$F_Q = -D_Q \frac{\mathrm{d}\bar{Q}}{\mathrm{d}x_2}$$

and find an expression for D_Q in terms of the quantities defined above.   [25%]

(b)   Experiments show that for the transport of x_1-direction momentum $\beta_Q \simeq 1$, whereas for the transport of the random (thermal) component of kinetic energy $\beta_Q \simeq 5/2$. Explain briefly the reason for the difference in these two values and determine expressions for the dynamic viscosity μ and thermal conductivity k valid for ideal monatomic gases. Hence estimate the Prandtl number for helium.   [30%]

(c)   The value of μ for helium at 1 bar and 300 K is $19.9 \times 10^{-6}\,\mathrm{kg\,m^{-1}s^{-1}}$. Estimate its value at 2 bar and 600 K on the basis of the above model.   [15%]

(d)   In reality, intermolecular forces of attraction 'soften' the molecules such that their effective diameter d_{eff} depends on the temperature T. It may be shown that, to a good approximation

$$d_{\mathrm{eff}}^2 = d^2 \left(1 + \frac{\chi}{T}\right)$$

where d is the actual molecular diameter and χ is a constant.

     (i)   With the aid of a sketch, explain whether χ is positive or negative. Explain also the consequent trend in d_{eff} with temperature.

     (ii)   For helium $|\chi| = 101$ K. Obtain a revised estimate for μ at 2 bar and 600 K.   [30%]
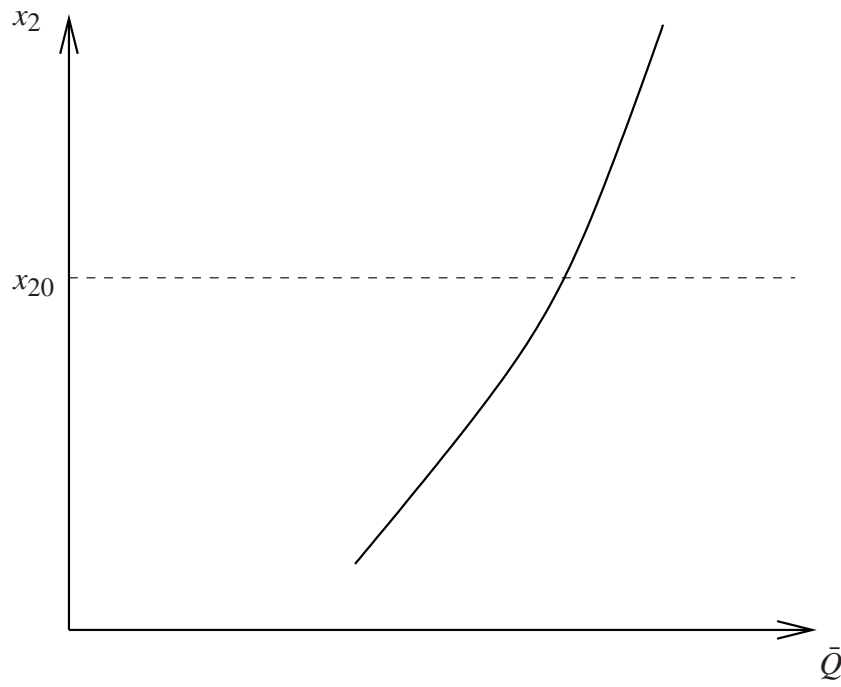
Fig. 1

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2   Consider a monatomic ideal gas for which the molecular velocity distribution f is a function of time t, the spatial coordinates x_i ($i = 1, 2, 3$) and the corresponding absolute molecular velocity components c_i.

(a)   Describe how f is defined and determine integral expressions for the following quantities at a fixed point in space and time:

   (i)   the gas (mass) density, ρ;

   (ii)   the mean molecular (bulk) velocity components, u_i;

   (iii)   the kinetic temperature, T.   [20%]

(b)   The Boltzmann equation for the evolution of f may be written in the form

$$\frac{\partial f}{\partial t} + c_j \frac{\partial f}{\partial x_j} = \left[\frac{\partial f}{\partial t} \right]_{\text{coll.}}$$

where the term on the right-hand side is due to molecular collisions. Starting from this equation, derive an expression for the evolution of the mean value $\bar{Q}$ of some general molecular quantity Q (measured per molecule). Hence, with a suitable choice of Q, and by splitting the absolute molecular velocity into its mean and peculiar components (i.e., $c_i = u_i + C_i$), show that the momentum equations take the form

$$\frac{\partial}{\partial t}(\rho u_i) + \frac{\partial}{\partial x_j}(\rho u_i u_j) = \text{RHS}$$

where the RHS (right-hand side) comprises terms to be determined. Find these terms and provide their physical interpretations, distinguishing cases for which $i = j$ and $i \neq j$.   [40%]

(c)   A similar analysis to that of part (b) leads to the energy equation

$$\frac{\partial}{\partial t}\left\{ \frac{\rho}{2}(u^2 + \overline{C^2}) \right\} + \frac{\partial}{\partial x_j}\left\{ \frac{\rho u_j}{2}(u^2 + \overline{C^2}) \right\} = -\frac{\partial}{\partial x_j}\left\{ \rho u_k \overline{C_j C_k} + \frac{\rho \overline{C_j C^2}}{2} \right\}$$

where $u^2 = u_1^2 + u_2^2 + u_3^2$ and $C^2 = C_1^2 + C_2^2 + C_3^2$. Show that if the flow is steady and the molecular velocity distribution is Maxwellian this equation simplifies to constant h_0 along streamlines, where $h_0 = h + u^2/2$ and h is the specific enthalpy.   [40%]

3   (a)   The vibrational energy of a molecule with w independent vibrational energy modes, relative to its ground state, is given by

$$\epsilon_n = (n_1 + n_2 ... + n_w)\, h\nu$$

where h is Planck's constant, ν is the classical oscillation frequency and $\{n_1, n_2, ... \, n_w\}$ is a set of non-negative quantum numbers that characterise the molecule's vibrational state. Determine an expression for the j-th vibrational energy *level* ϵ_j, where $j = 0, 1, 2, ...$ etc., and the levels are ordered such that $\epsilon_j > \epsilon_{j-1}$. By analogy with the distribution of balls into boxes show that the degeneracy of this energy level is given by

$$g_j = \frac{(w + j - 1)!}{j!(w - 1)!}$$ [25%]

(b)   The binomial expansion formula for a negative integral power is

$$(x + y)^{-m} = \sum_{r=0}^{\infty} \frac{(m + r - 1)!}{r!(m - 1)!}(-1)^r x^r y^{-(m+r)} \qquad \text{(valid for } |x| < y\text{)}$$

Making use of this expression, or otherwise, show that the partition function for a single molecule with w vibrational energy modes in contact with a thermal reservoir at temperature T is given by

$$Z_w = \frac{1}{(1 - e^{-\theta_v/T})^w}$$

where $\theta_v = h\nu/k$ and k is Boltzmann's constant.   [40%]

(c)   The molecules of a particular ideal gas possess $w = 3$ independent vibrational energy modes. Assuming that these modes are also independent of any translational and rotational energy modes, determine the vibrational contribution to the constant volume specific heat capacity of the gas as a function of temperature. Find the value of this contribution in terms of the specific gas constant R when $T \gg \theta_v$ and show that this value is consistent with the equipartition principle.

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

$$U = kT^2 \left(\frac{\partial}{\partial T} \ln Q\right)_{V, N}$$

where Q is the system partition function, V the volume and N the number of molecules. [35%]

4   (a)   The statistical analogue of the 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 Ω is the number of possible microstates.

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

(ii)   Derive the conditions that maximise S' for a system that has three microstates and determine this maximum value.   [20%]

(iii)   Show that S' is an extensive property.   [20%]

(iv)   What can be said about the values of P_i for an isolated system at equilibrium? Simplify the expression for S' for such a system.   [10%]

(b)   A closed system comprising a gas is maintained within a cylinder and piston arrangement, as shown in Fig. 2. The cylinder walls are perfectly conducting and the piston is light and frictionless such that the gas remains in thermal and mechanical equilibrium with the surrounding atmosphere. Under these conditions it may be shown that fluctuations in gas volume are given by

$$\sigma_V^2 = \left\langle (V - V_0)^2 \right\rangle = kT \left\{ \left(\frac{\partial^2 U}{\partial V^2} \right)_T - T \left(\frac{\partial^2 S}{\partial V^2} \right)_T \right\}^{-1}$$

where V_0 is the equilibrium volume of the gas and U, S and T are its internal energy, entropy and temperature respectively.

(i)   Starting from the Gibbs' relation for a closed system $T dS = dU + p dV$, show that, irrespective of the type of gas, the above expression simplifies to

$$\sigma_V^2 = -kT \left(\frac{\partial V}{\partial p} \right)_T$$

where p is the pressure.   [25%]

(ii)   Calculate the normalised volume fluctuation σ_V / V_0 for a system comprising 0.1 g of helium. Take the atmospheric conditions as $T_0 = 300\,\text{K}$ and $p_0 = 1\,\text{bar}$.   [20%]

(cont.

atmosphere
at p_0 and T_0

light piston

conducting
walls

gas
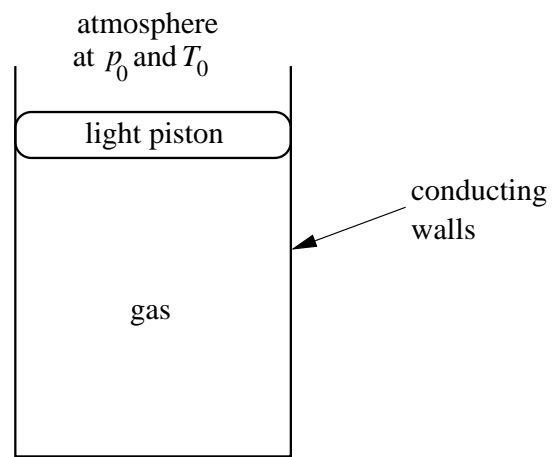
Fig. 2

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ANSWERS

Q1. (b) 2/3

(c) 28.1×10^{-6} kg m^{-1} s^{-1}

(d) 32.2×10^{-6} kg m^{-1} s^{-1}

Q4. (b) (ii) 8.15×10^{-12}