ENGINEERING TRIPOS   PART IIB   2013

MODULE 4A9 – MOLECULAR THERMODYNAMICS

SOLUTIONS

1. (a) (i) In the freestream the distribution function will be Maxwellian if it is written in terms of the peculiar velocity components, $C_1 = c_1 - V$, $C_2 = c_2$, $C_3 = c_3$. Technically, the Navier-Stokes equation is valid although, as the viscous shear stress is zero, it actually takes the form of the Euler equation.   [1]

(ii) A point in the BL where the flow speed is $0.1V$ will be many mean free-paths from the plate surface and the flow there will be in the continuum regime. The molecular velocity distribution function will be perturbed from Maxwellian in order to generate the wallwards flux of streamwise momentum which is described macroscopically as the viscous shear stress. The perturbation will be modest, however, and the Navier-Stokes equation will be valid.   [2]

(iii) At a point on the plate surface the molecular velocity distribution function will be far from Maxwellian. The mean wall-normal velocity will be zero ($\bar{c}_2 = 0$) so $C_2 = c_2$. Molecules coming from the bulk of the gas ($C_2 < 0$) will have a distribution similar to those in (ii) while molecules emitted from the plate ($C_2 > 0$) will have a half-Maxwellian distribution because the reflection is diffuse. The distribution function will thus be discontinuous at $C_2 = 0$. The Navier-Stokes equations will not be valid.

[2]

(b) (i) For the x_1 flux of molecular energy, we set $Q = m(c_1^2 + c_2^2 + c_3^2)/2$, $c_i = c_1$ and use the given expression for f to obtain,

$$\dot{E} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} c_1 \frac{m(c_1^2 + c_2^2 + c_3^2)}{2} \frac{n}{(2\pi RT)^{3/2}} \exp\left[-\left(\frac{(c_1 - V)^2 + c_2^2 + c_3^2}{2RT}\right)\right] dc_1\, dc_2\, dc_3$$

We now introduce the given transformation in the forms,

$$c_1 = V + w_1\sqrt{2RT}, \qquad c_2 = w_2\sqrt{2RT}, \qquad c_3 = w_3\sqrt{2RT}.$$

$$dc_1 = dw_1\sqrt{2RT}, \qquad dc_2 = dw_2\sqrt{2RT}, \qquad dc_3 = dw_3\sqrt{2RT}.$$

Substituting into the integral gives,

$$\dot{E} = \int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} \frac{nm}{\pi^{3/2}} (V + w_1\sqrt{2RT}) \left(\frac{V^2 + 2Vw_1\sqrt{2RT} + 2RT(w_1^2 + w_2^2 + w_3^2)}{2} \right)$$

$$\times e^{-w_1^2} e^{-w_2^2} e^{-w_3^2} \, dw_1 dw_2 dw_3 \qquad [3]$$

(ii)   To evaluate the integral, we first note that any odd functions of w_1, w_2 or w_3 integrate to zero. Using $\rho = nm$ this leaves us with,

$$\dot{E} = \int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} \frac{\rho}{\pi^{3/2}} \left(\frac{V^3 + 2VRT(w_1^2 + w_2^2 + w_3^2) + 4VRTw_1^2}{2} \right) e^{-w_1^2} e^{-w_2^2} e^{-w_3^2} \, dw_1 dw_2 dw_3$$

$$= \rho V \int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} \left(\frac{V^2 + 2RT(w_1^2 + w_2^2 + w_3^2) + 4RTw_1^2}{2\pi^{3/2}} \right) e^{-w_1^2} e^{-w_2^2} e^{-w_3^2} \, dw_1 dw_2 dw_3$$

From the given integrals,

$$\int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} e^{-w_1^2} e^{-w_2^2} e^{-w_3^2} \, dw_1 dw_2 dw_3 = \sqrt{\pi}\sqrt{\pi}\sqrt{\pi} = \pi^{3/2}$$

$$\int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} w_i^2 e^{-w_1^2} e^{-w_2^2} e^{-w_3^2} \, dw_1 dw_2 dw_3 = \frac{\sqrt{\pi}}{2}\sqrt{\pi}\sqrt{\pi} = \frac{\pi^{3/2}}{2} \quad \text{(for } i = 1, 2 \text{ or } 3)$$

Hence,

$$\dot{E} = \rho V \left(\frac{V^2}{2} + \frac{3RT}{2} + RT \right) = \rho V \left(\frac{5RT}{2} + \frac{V^2}{2} \right) \qquad [8]$$

(iii)   For a monatomic gas $c_v = 3RT/2$. The energy of the gas per unit mass is thus,

$$\left(\frac{3RT}{2} + \frac{V^2}{2} \right) = c_v T + \frac{V^2}{2} = e + \frac{V^2}{2}$$

where e is the specific thermal energy. This is as expected from macroscopic considerations. For a perfect gas $RT = p/\rho$ and so the microscopic energy flux can be written,

$$\dot{E} = \rho V \left(e + \frac{p}{\rho} + \frac{V^2}{2} \right) = \rho V \left(h + \frac{V^2}{2} \right)$$

where h is the specific enthalpy. This also is expected from macroscopic considerations. The extra contribution arises in the macroscopic analysis because of the flow work term. At the microscopic level this term is simply absorbed into the total energy flux.

[4]

2. (a)

Nitrogen with trace impurities — Small hole of diameter a — $N dx$ holes in length dx — x — dx
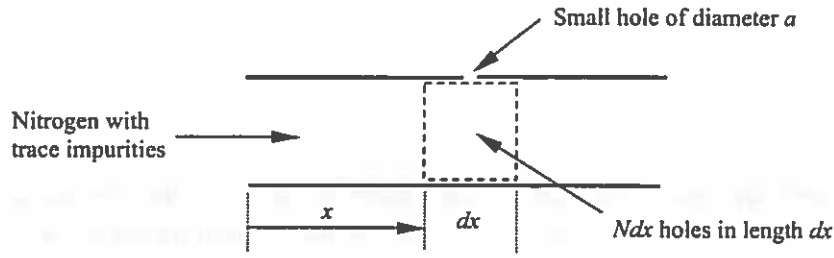
Under free-molecule conditions (*i.e.*, collisions between molecules can be neglected compared to collisions with the walls of the pore), the leakage mass flowrate $\dot{M}_i$ of impurity gas i through a single pore is given by,

$$\dot{M}_i = \frac{\pi a^2}{4}\frac{m_i n_i \overline{C}_i}{4} = \frac{\pi a^2 \rho_i \overline{C}_i}{16} = \frac{\pi a^2 \rho Y_i \overline{C}_i}{16}$$

where, for impurity i, m_i is the mass of a molecule, $\overline{C}_i$ is the mean molecular speed and ρ_i is the mass density. The nitrogen molecules are not involved because the pressure outside the tube is the same as inside. There is no 'return' flux of i-molecules because the gas outside the tube is effectively pure nitrogen (*i.e.*, the impurity concentration is negligible).

Applying conservation of mass of impurity i to the control volume of length dx gives,

$$\frac{\pi D^2}{4}\rho_i V = \frac{\pi D^2}{4}\rho_i V + \frac{d}{dx}\left(\frac{\pi D^2}{4}\rho_i V\right)dx + N\dot{M}_i dx$$

Noting that $\rho_i = Y_i \rho$ and using the expression for $\dot{M}_i$ derived above gives,

$$\frac{\pi D^2}{4}\rho V \frac{dY_i}{dx} = -N\frac{\pi a^2}{4}\frac{\rho \overline{C}_i}{4}Y_i \qquad \rightarrow \qquad \frac{dY_i}{dx} = -\frac{a^2}{4D^2}\frac{N\overline{C}_i}{V}Y_i$$

But $\overline{C}_i = (8\overline{R}T/\pi M_i)^{1/2}$ and hence,

$$\frac{dY_i}{dx} = -A\frac{Y_i}{\sqrt{M_i}} \qquad \text{with} \qquad A = \frac{a^2 N}{D^2 V}\left(\frac{\overline{R}T}{2\pi}\right)^{1/2}$$

[7]

(b) Integrating this equation subject to $Y_i = Y_{i,0}$ at $x = 0$, gives,

$$\ln\left(\frac{Y_i}{Y_{i,0}}\right) = -\frac{Ax}{\sqrt{M_i}}$$

As A does not depend on any property of the impurity gas, we therefore have,

$$-Ax = \sqrt{M_1}\ln\left(\frac{Y_1}{Y_{1,0}}\right) = \sqrt{M_2}\ln\left(\frac{Y_2}{Y_{2,0}}\right)$$

[5]

3

(c)   To estimate the mean free path of an i-molecule we consider the collision with nitrogen molecules of a single i-molecule moving at the mean speed for i-molecules. We can neglect collisions with other impurity molecules because their concentrations are very small. For simplicity we assume that all the nitrogen molecules are stationary.
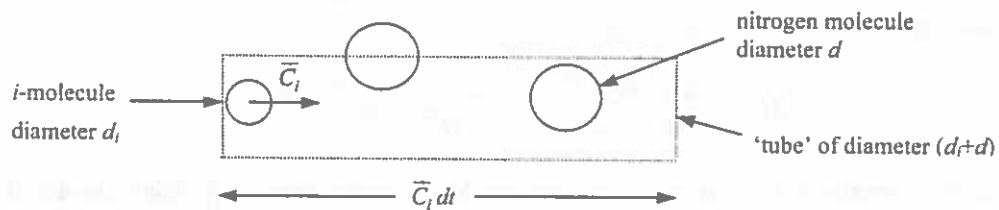
In time dt the i-molecule collides with all nitrogen molecules having their centres in the 'tube' of diameter $(d_i + d)$ and length $\overline{C}_i dt$. If the number density of nitrogen molecules is n then the number of collisions in time dt is,

$$\frac{n\pi(d_i + d)^2 \overline{C}_i\, dt}{4}$$

The distance moved by the i-molecule in time dt is $\overline{C}_i\, dt$. Hence, the mean free path is,

$$\lambda_i = \frac{4}{n\pi(d_i + d)^2}$$

But the mean free path of a nitrogen molecule is,

$$\lambda = \frac{4}{n\pi(d + d)^2}$$

Hence,

$$\lambda_i = 4\lambda\left(1 + \frac{d_i}{d}\right)^{-2}$$

If the flow through the leakage hole is under free-molecule conditions then,

$$Kn = \frac{\lambda_i}{a} \gg 1$$

where Kn is the Knudsen number. From the data in the question we have, for pure nitrogen, $\mu \approx \rho\overline{C}\lambda/2$. Hence, the condition for free-molecule flow through the hole can be written,

$$a \ll \lambda_i = 4\lambda\left(1 + \frac{d_i}{d}\right)^{-2} = \frac{8\mu}{\rho\overline{C}}\left(1 + \frac{d_i}{d}\right)^{-2} = \frac{8\mu\overline{R}T}{pM}\left(\frac{\pi M}{8\overline{R}T}\right)^{1/2}\left(1 + \frac{d_i}{d}\right)^{-2} = B_i\frac{\mu}{p}\left(\frac{8\pi\overline{R}T}{M}\right)^{1/2}$$

where $B_i = \left(1 + \frac{d_i}{d}\right)^{-2}$.

[8]

3. (a)

$$Z_{vib} = \sum_{n=0}^{\infty} e^{-nh\nu/kT} = 1 + e^{-\tau} + e^{-2\tau} + \ldots \qquad \text{where } \tau = h\nu/kT = \theta_v/T$$

This is just the sum of a GP with common ratio $e^{-\tau}$ (which has modulus less than 1)

$$\therefore \qquad Z_{vib} = \frac{1}{1-r} = \frac{1}{1-e^{-\theta_v/T}} \qquad [5]$$

(b) Let the K-th state be the last in the series, so $K \approx \varepsilon_d/h\nu$. Then,

$$Z_{vib} = \sum_{n=0}^{K-1} e^{-nh\nu/kT} = \sum_{n=0}^{\infty} e^{-nh\nu/kT} - \sum_{n=K}^{\infty} e^{-nh\nu/kT}$$

$$= \frac{1}{1-e^{-\theta_v/T}} - (e^{-K\tau} + e^{-(K+1)\tau} + \ldots) \qquad \text{(or use sum of } K-1 \text{ terms)}$$

$$= \frac{1}{1-e^{-\theta_v/T}} - e^{-K\theta_v/T}(1 + e^{-\tau} + e^{-2\tau} + \ldots) = \frac{1-e^{-K\theta_v/T}}{1-e^{-\theta_v/T}}$$

but $\quad K\theta_v = \dfrac{\varepsilon_d}{h\nu}\dfrac{h\nu}{k} = \dfrac{\varepsilon_d}{k} = \theta_d \qquad$ (this defines θ_d)

$$\therefore \qquad Z_{vib} = \frac{1-e^{-\theta_d/T}}{1-e^{-\theta_v/T}} \qquad [8]$$

(c) $\quad u_{vib} = RT^2 \dfrac{\partial}{\partial T} \ln Z = RT^2 \dfrac{\partial}{\partial T}\left\{\ln(1-e^{-\theta_d/T}) - \ln(1-e^{-\theta_v/T})\right\}$

Given the form of $c_{v,\,vib}$ when there is no dissociation, it follows that with dissociation,

$$\frac{c_{v,vib}}{R} = \left(\frac{\theta_v}{T}\right)^2 \frac{e^{\theta_v/T}}{(e^{\theta_v/T}-1)^2} - \left(\frac{\theta_d}{T}\right)^2 \frac{e^{\theta_d/T}}{(e^{\theta_d/T}-1)^2}$$

For $\theta_v/T = 1$ and neglecting the second term,

$$\frac{c_{v,vib}}{R} = (1)^2 \frac{e}{(e-1)^2} = \underline{\underline{0.921}}$$

Now $\theta_d / T = (\theta_d / \theta_v)\theta_v / T = 8 \times 1$

$$\therefore \qquad \frac{c_{v,vib}}{R} = 0.921 - (8)^2 \frac{e^8}{(e^8-1)^2} = 0.921 - 0.0215 = \underline{\underline{0.899}}$$

i.e., a 2.3 % reduction in vibrational specific heat capacity .

[7]

4. (a) For an isolated system at equilibrium, all microstates are equally probable, so $P_i = 1/\Omega$.

$$\therefore \quad S = -k\sum_1^\Omega \frac{1}{\Omega}\ln\frac{1}{\Omega} = \frac{k}{\Omega}\ln\frac{1}{\Omega}\sum_i^\Omega 1 = \underline{\underline{k\ln\Omega}}$$

Consider a system initially at equilibrium. By inserting a rigid, insulating partition it is possible to divide the system into two isolated subsystems A and B, each at equilibrium. The systems are independent of each other so the total number of microstates is

$$\Omega = \Omega_A \times \Omega_B$$
$$\therefore \quad S = k\ln\Omega = k\ln(\Omega_A \times \Omega_B) = k\ln\Omega_A + k\ln\Omega_B = S_A + S_B$$

Evidently, no change in state will take place when the partition is removed (since A and B were initially at equilibrium with each other), so the total entropy is the sum of the entropies of the constituent parts, as is required of an extensive property.   [6]

(b) (i) Reversible and adiabatic implies isentropic, so no change in entropy and hence the number of microstates remains as Ω_0.

(ii) $$\Delta S = mR\ln\frac{V}{V_0} = m\frac{\bar{R}}{M}\ln\frac{V}{V_0} = 0.001\frac{8314}{20}\ln\frac{1}{1.25} = -0.09276 \text{ J/K}$$

$$\frac{\Omega}{\Omega_0} = \exp((S - S_0)/k)$$
$$\therefore \quad \Omega = \Omega_0\exp(-.09276/1.38\times10^{-23})$$
$$= \Omega_0\exp(-6.72\times10^{21})$$ [6]

(c) The probability that the system has energy E (corresponding to temperature, T) is:

$$P(E) = \Omega_E P_E$$

where P_E is the probability of being in a microstate with energy E and Ω_E is the number of microstates with this energy. Ω_E can be obtained if we assume that the system entropy can be calculated from

7

$$S - S_0 = mc_v \ln \frac{T}{T_0}$$

Thus,

$$\frac{\Omega(T)}{\Omega_0} = e^{(S-S_0)/k} = \left(\frac{T}{T_0}\right)^{mc_v/k}$$

Now

$$P_E = \frac{e^{-E/kT_0}}{Q} = \frac{e^{-(mc_v/k)(T/T_0)}}{Q}$$

$$P(T) = \frac{\Omega_0}{Q}\left(\frac{T}{T_0}\right)^\alpha \exp(-\alpha T/T_0)$$

hence

$$P(T_0) = \frac{\Omega_0}{Q}(1)^\alpha \exp(-\alpha)$$

so

$$\frac{P(T)}{P(T_0)} = \left(\frac{T}{T_0}\right)^\alpha \exp(\alpha\{1 - T/T_0\}) \quad ; \quad \alpha = \frac{mc_v}{k} = \frac{.001 \times 1.5 \times 8314}{1.38 \times 10^{-23} \times 20} \approx 4.52 \times 10^{22}$$

$P(T)$ is the product of two terms, one that rises extremely rapidly and one that falls extremely rapidly. Since α is so large (for finite systems) the result is effectively a delta function, so the probability of significant departures from the average temperature is very small.
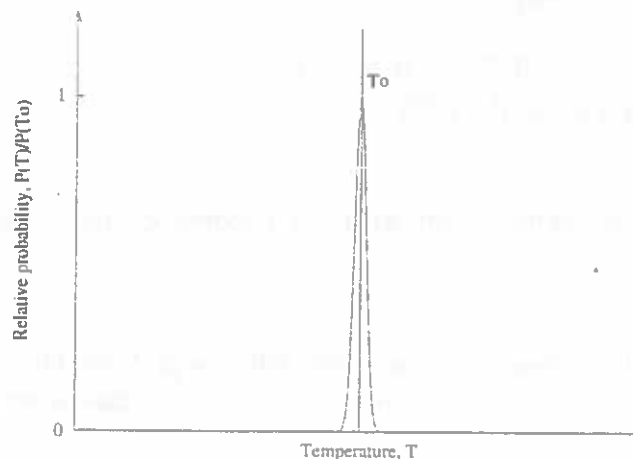
[8]

[Note that writing $(T/T_0) = 1 + x$ and expanding gives $\exp(-\alpha\{(T-T_0)/T_0\}^2/2)$ for the above expression. This could be derived by instead considering the total entropy of combined system + reservoir, as in the 2008 paper.

AJW / JBY