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ENGINEERING TRIPOS   PART IIB   2007

MODULE 4A9 – MOLECULAR THERMODYNAMICS

SOLUTIONS TO TRIPOS QUESTIONS

(A.J. WHITE & J.B. YOUNG)

1. (a) Kinetic temperature is defined as being proportional to the mean thermal (or peculiar) <u>translational</u> kinetic energy of a molecule through the equation,

$$\frac{3}{2}kT = \frac{1}{2}m\overline{C^2} \qquad \left[\text{or} \quad \frac{3}{2}RT = \frac{1}{2}\overline{C^2} \right]$$

where k is Boltzmann's constant, m is the mass of a molecule, $R = k/m$ is the gas constant per unit mass and $\overline{C^2}$ is the mean square thermal speed.   [10 %]

(b) The six groups have velocity components in m/s as follows :

$$(1250, 120, 0); \qquad (50, 1320, 0); \qquad (50, 120, 1200);$$
$$(-1150, 120, 0); \qquad (50, -1080, 0); \qquad (50, 120, -1200).$$

(i) The components of the gas mean velocity are obviously (50, 120, 0) m/s. The thermal or peculiar speed is the same for each group (as it should be by the equipartion principle) and is equal to 1200 m/s. Hence, the temperature is,

$$T = \frac{\overline{C^2}}{3R} = \frac{1200^2}{3 \times (8314.3/28)} = 1616 \text{ K} \qquad\qquad \text{[20 %]}$$

(ii) As the gas is diatomic, there are 3 translational, 2 rotational and 2 vibrational (1 KE + 1 PE) degrees of freedom. If all these are active then, according to the equipartition principle, the internal energy per unit mass will be,

$$(3 + 2 + 2)\frac{RT}{2} = \frac{7 \times (8.3143/28) \times 1616}{2} = 1679 \text{ kJ/kg} \qquad \text{[20 %]}$$

(c) (i) The mean translational KE of a molecule is given by,

$$\int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} \frac{m(u_1^2 + u_2^2 + u_3^2)}{2} f(u_1, u_2, u_3)\, du_1\, du_2\, du_3$$

where m is the mass of a molecule. Introducing the expression for f gives,

$$\int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} \frac{m(u_1^2 + u_2^2 + u_3^2)}{2} \frac{1}{(2\pi RT)^{3/2}} \exp\left[-\left(\frac{(u_1 - V)^2}{2RT} + \frac{u_2^2}{2RT} + \frac{u_3^2}{2RT} \right) \right] du_1\, du_2\, du_3 \qquad \text{[10 %]}$$

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(ii)   Define new variables,

$$w_1 = \frac{(u_1 - V)}{\sqrt{2RT}} \; ; \quad w_2 = \frac{u_2}{\sqrt{2RT}} \; ; \quad w_3 = \frac{u_3}{\sqrt{2RT}} \; .$$

Hence, the energy per unit mass e is (divide by m),

$$e = \frac{2RT}{2\pi^{3/2}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left[\left(w_1 + \frac{V}{\sqrt{2RT}} \right)^2 + w_2^2 + w_3^2 \right] e^{-w_1^2} e^{-w_2^2} e^{-w_3^2} \, dw_1 \, dw_2 \, dw_3$$

$$= \frac{RT}{\pi^{3/2}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left[w_1^2 + \frac{2w_1 V}{\sqrt{2RT}} + \frac{V^2}{2RT} + w_2^2 + w_3^2 \right] e^{-w_1^2} e^{-w_2^2} e^{-w_3^2} \, dw_1 \, dw_2 \, dw_3 \qquad [20\%]$$

(iii)   Integrating over w_3 using the given integrals :

$$e = \frac{RT}{\pi^{3/2}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left[\left(w_1^2 + \frac{2w_1 V}{\sqrt{2RT}} + \frac{V^2}{2RT} \right) \sqrt{\pi} + w_2^2 \sqrt{\pi} + \frac{\sqrt{\pi}}{2} \right] e^{-w_1^2} e^{-w_2^2} \, dw_1 \, dw_2$$

Integrating over w_2 :

$$e = \frac{RT}{\pi^{3/2}} \int_{-\infty}^{\infty} \left[\left(w_1^2 + \frac{2w_1 V}{\sqrt{2RT}} + \frac{V^2}{2RT} \right) \pi + \frac{\pi}{2} + \frac{\pi}{2} \right] e^{-w_1^2} \, dw_1$$

Integrating over w_1 :

$$e = \frac{RT}{\pi^{3/2}} \left[\frac{\pi^{3/2}}{2} + 0 + \frac{V^2 \pi^{3/2}}{2RT} + \frac{\pi^{3/2}}{2} + \frac{\pi^{3/2}}{2} \right]$$

Finally,

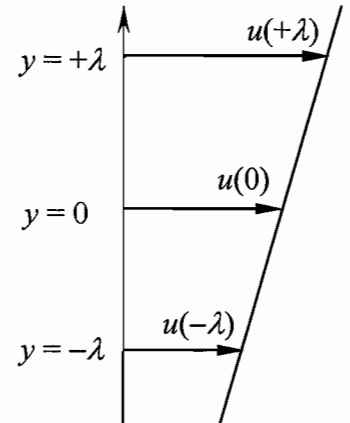$$e = \frac{3}{2} RT + \frac{V^2}{2} \qquad [20\%]$$

(The first term is the internal energy per unit mass of a monatomic gas ($c_v = 3R/2$) and the second term is the KE per unit mass based on the mean velocity V.)

2   (a)

Assume molecules make their last collision one mean free path above or below the plane $y = 0$.

Flux of x-momentum from below $= \dfrac{\rho \overline{C}}{4}\left[u(0) - \lambda \dfrac{du}{dy} \right]$

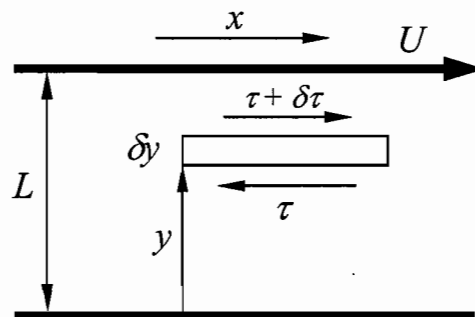Flux of x-momentum from above $= \dfrac{\rho \overline{C}}{4}\left[u(0) + \lambda \dfrac{du}{dy} \right]$

Net flux of x-momentum in negative y-direction $=$ shear stress $= \tau = \dfrac{\rho \overline{C} \lambda}{2} \dfrac{du}{dy}$

Macroscopically, dynamic viscosity μ is defined by $\tau = \mu \dfrac{du}{dy}$ and hence, $\mu = \dfrac{\rho \overline{C} \lambda}{2}$.

Thus $\beta = \dfrac{1}{2}$.   [35%]

(b)

Applying the force-momentum equation to the control volume of length δx gives,

$$\left(\tau + \frac{d\tau}{dy} \delta y \right) \delta x - \tau \delta x = 0 \qquad \rightarrow \qquad \frac{d\tau}{dy} = 0 \qquad \rightarrow \qquad \tau = \text{constant}$$

This is valid for any flow regime as no model for the shear stress has been introduced.   [15 %]

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(c)   In the central region, momentum transport is described by continuum theory so,

$$\tau = \mu\frac{du}{dy} = \text{constant} \qquad \rightarrow \qquad u = \frac{\tau y}{\mu} + C$$

The slip boundary conditions to model the two non-continuum layers are,

$$u(0) = \lambda\frac{du}{dy} ; \qquad u(L) = U - \lambda\frac{du}{dy} .$$

du/dy is constant across the duct because τ is constant and hence,

$$\lambda\frac{du}{dy} = C ; \qquad U - \lambda\frac{du}{dy} = \frac{\tau L}{\mu} + C .$$

Thus,

$$\tau = \frac{\mu U}{L} - 2\frac{\lambda}{L}\mu\frac{du}{dy} = \frac{\mu U}{L} - 2Kn\tau \qquad \rightarrow \qquad \tau = \frac{\tau_0}{(1 + 2Kn)}$$

where $\tau_0 = \mu U/L$ is the shear stress for $Kn \rightarrow 0$ (*i.e.*, the continuum flow solution).   [30 %]

(d)   The density ρ and mean molecular speed $\overline{C}$ are given by,

$$\rho = \frac{p}{RT} = \frac{0.001\times10^5}{287.5\times373.15} = 9.321\times10^{-4} \text{ kg/m}^3$$

$$\overline{C} = \left(\frac{8RT}{\pi}\right)^{1/2} = \left(\frac{8\times287.5\times373.15}{\pi}\right)^{1/2} = 522.7 \text{ m/s}$$

From the Thermofluids Data Book, for air at 100 °C and 1 atm, $\mu = 22\times10^{-6}$ kg/m s. This is also valid for 0.001 bar because μ is independent of pressure. Hence, the mean free path and Knudsen number are,

$$\lambda = \frac{2\mu}{\rho\overline{C}} = \frac{2\times22\times10^{-6}}{9.32\times10^{-4}\times522.7} = 90.32\times10^{-6} \text{ m} \quad \rightarrow \quad Kn = \frac{\lambda}{L} = \frac{90.32\times10^{-6}}{2\times10^{-3}} = 0.045 \qquad [20 \%]$$

3 **(a)** Ω is the number of microstates that the system may exist in. For an isolated system, the basic postulate is that these are equally probable. If the entropy increases, there are more microstates available to the system and hence we are less certain about which state it will be in at any time. (i) For the unrestrained expansion of an ideal gas, there is no work or heat transfer, so the temperature will remain constant, and hence the level of certainty in molecular velocities is unchanged. The volume has increased, however, so we are less certain about the location of each molecule, consistent with the increase in entropy associated with irreversibility. (ii) For heat addition, the temperature of the gas will increase and so the molecular velocity distributions will broaden. We are therefore less certain about the momentum of each molecule. The certainty in location remains unchanged (since the volume is constant) so there is a net increase in uncertainty, consistent with the entropy increase associated with heat addition.

(b) (i) Considering first the white balls. The number of locations for placing the first white ball is C. For each of these, there are $C-1$ locations for the second ball, then $C-2$ for the third, and so on. The number of possible arrangements for the white balls assuming them to be distinguishable is thus $C(C-1)(C-2)\ldots(C-N+1) = C! / (C-N)!$ However, the balls are not distinguishable, and so we must divide by $N!$ (the number of ways of arranging the N balls on their own), giving $C! / (C-N)!\ N!$ The same computation applies to the black balls, so the total number of arrangements is $W_1 = \{C! / (C-N)!\ N!\}^2$.

When the partition is removed, there are now $2N$ balls to distribute between $2C$ boxes, but the N black balls and N white balls are indistinguishable. Thus,

$$W_2 = \frac{(2C)!}{(2C-2N)!\,N!\,N!}$$

(ii) The entropy of mixing is given by

$$\Delta S / k = \ln\left(\frac{W_2}{W_1}\right) = \ln(2C)! + 2\ln(C-N)! - 2\ln C! - \ln(2C-2N)!$$
$$= 2C\ln 2C - 2C + 2(C-N)\ln(C-N) - 2(C-N) - 2C\ln C + 2C$$
$$\qquad -2(C-N)\ln(2C-2N) + 2(C-N)$$
$$= 2C\ln 2 - 2(C-N)\ln 2$$
$$= 2N\ln 2$$

(iii) With $C=1$ and unrestricted balls per box, there is clearly only one arrangement, $W_1=1$, in the unmixed state. When mixed, there are 2 boxes and $2N$ balls. It is best to consider this as $2N$ balls and one partition. Thus,

$$W_2 = \frac{(2N+1)!}{N!\,N!}$$

so
$$\Delta S / k = (2N+1)\ln(2N+1) - (2N+1) - 2N\ln N + 2N$$
$$= 2N\ln(2+1/N) + \ln(2N+1) - 1$$
$$\approx 2N\ln 2$$

The process is analogous to the mixing of equal volumes of two ideal gases at the same pressure and temperature. The volume doubles for each gas, so the entropy increase for each gas is $mR\ln 2 = Nk\ln 2$, giving the same result as above.

4. (a) N = Total number of particles.

N_j^* = The number of particles in the j-th group for the most probable macrostate.

C_j = The number of energy states in the j-th energy group.

ε_j = The (average) energy of the j-th energy group

k = Boltzmann's constant (1.38×10^{-23} J/K).

T = The temperature.

Z is the (single particle) partition function and can be found by summing over all groups:

$$\sum \frac{N_j^*}{N} = 1 = \frac{1}{Z}\sum C_j \exp\{-\varepsilon_j/kT\} \qquad \Rightarrow \qquad Z = \sum C_j \exp\{-\varepsilon_j/kT\}$$

(b)

$$\frac{\partial Z}{\partial T} = \sum \frac{\varepsilon_j}{kT^2} C_j \exp\{-\varepsilon_j/kT\}$$

$$= \frac{Z}{NkT^2}\sum N_j^*\varepsilon_j$$

$$= \frac{Z}{kT^2}\frac{E}{N} = \frac{Z}{kT^2}\overline{\varepsilon}$$

$\therefore \qquad \overline{\varepsilon} = kT^2 \frac{\partial}{\partial T}\ln Z$

$$\frac{\partial}{\partial T}\left(kT^2 \frac{\partial Z}{\partial T}\right) = \frac{Z}{NkT^2}\sum N_j^*\varepsilon_j^2 = \frac{Z}{kT^2}\overline{\varepsilon^2}$$

$\therefore \qquad \overline{\varepsilon^2} = \frac{kT^2}{Z}\frac{\partial}{\partial T}\left(kT^2 \frac{\partial Z}{\partial T}\right)$

(c) (i) Clearly $pV = NkT$, so the gas is ideal, and since there is only a translational contribution to the partition function it is likely that it is monatomic.

(ii)

$$Z = V\left(\frac{2\pi mkT}{h^2}\right)^{3/2} = AT^{3/2}$$

$\therefore \qquad \overline{\varepsilon} = kT^2 \frac{3}{2}\frac{1}{T} = \frac{3kT}{2}$ $\qquad$ (quoting this is fine)

and

$$\overline{\varepsilon^2} = \frac{kT^2}{AT^{3/2}}\frac{\partial}{\partial T}\left(kT^2 \frac{3}{2}AT^{1/2}\right) = \frac{15}{4}k^2T^2$$

RMS of deviations in translational kinetic energy is given by:

$$RMS = \sqrt{\overline{\varepsilon^2} - \overline{\varepsilon}^2} = \sqrt{\frac{15k^2T^2}{4} - \frac{9k^2T^2}{4}} = kT\sqrt{3/2}$$

This is the root mean square deviation of the translational KE for a single <u>molecule</u>. The temperature is proportional to the mean KE averaged over the (many) molecules, so fluctuations in this will be very much less.