

ENGINEERING TRIPOS PART IIB 2009
MODULE 4A9 – MOLECULAR THERMODYNAMICS
SOLUTIONS TO TRIPOS QUESTIONS
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1. (a) For the flux of x_1 -momentum in the x_1 direction, we set $Q = mu_1$ and $u_i = u_1$ to obtain, with the given expression for f (the flowing Maxwellian) :

$$\dot{M}_{11} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{nm u_1^2}{(2\pi RT)^{3/2}} \exp\left[-\left(\frac{(u_1 - V)^2 + u_2^2 + u_3^2}{2RT}\right)\right] du_1 du_2 du_3 \quad [10\%]$$

(b) We now introduce the given transformation in the form :

$$\begin{aligned} u_1 &= w_1\sqrt{2RT} + V, & u_2 &= w_2\sqrt{2RT}, & u_3 &= w_3\sqrt{2RT}, \\ du_1 &= dw_1\sqrt{2RT}, & du_2 &= dw_2\sqrt{2RT}, & du_3 &= dw_3\sqrt{2RT}. \end{aligned}$$

Substituting into the integral gives,

$$\dot{M}_{11} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{nm}{\pi^{3/2}} (w_1^2 2RT + 2V w_1\sqrt{2RT} + V^2) \exp(-w_1^2 - w_2^2 - w_3^2) dw_1 dw_2 dw_3 \quad [10\%]$$

(c) To evaluate the integral, we split it into three parts, note that $\rho = nm$, and use the results from Table 1 :

$$\begin{aligned} I_1 &= \frac{nm(2RT)}{\pi^{3/2}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} w_1^2 \exp(-w_1^2) \exp(-w_2^2) \exp(-w_3^2) dw_1 dw_2 dw_3 \\ &= \frac{nm(2RT)}{\pi^{3/2}} \frac{\sqrt{\pi}}{2} \sqrt{\pi} \sqrt{\pi} = \rho RT \end{aligned} \quad [10\%]$$

$$\begin{aligned} I_2 &= \frac{nm2V\sqrt{2RT}}{\pi^{3/2}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} w_1 \exp(-w_1^2) \exp(-w_2^2) \exp(-w_3^2) dw_1 dw_2 dw_3 \\ &= \frac{nm2V\sqrt{2RT}}{\pi^{3/2}} 0\sqrt{\pi}\sqrt{\pi} = 0 \end{aligned} \quad [10\%]$$

$$\begin{aligned} I_3 &= \frac{nmV^2}{\pi^{3/2}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp(-w_1^2) \exp(-w_2^2) \exp(-w_3^2) dw_1 dw_2 dw_3 \\ &= \frac{nmV^2}{\pi^{3/2}} \sqrt{\pi}\sqrt{\pi}\sqrt{\pi} = \rho V^2 \end{aligned} \quad [10\%]$$

Hence, $\dot{M}_{11} = I_1 + I_2 + I_3 = \rho RT + \rho V^2 = p + \rho V^2$

(d) If $L \gg \lambda$ we have free-molecule flow and the gas is undisturbed by the presence of the plate. Hence, the flux of x_1 -momentum to the plate (normal in the $-x_2$ -direction) is :

$$\dot{M}_{12} = \int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} \frac{n m u_1 u_2}{(2\pi RT)^{3/2}} \exp\left[-\left(\frac{(u_1 - V)^2 + u_2^2 + u_3^2}{2RT}\right)\right] du_1 du_2 du_3 \quad [10\%]$$

which becomes,

$$\dot{M}_{12} = \int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} \frac{nm}{\pi^{3/2}} (w_1 w_2 2RT + V w_2 \sqrt{2RT}) \exp(-w_1^2 - w_2^2 - w_3^2) dw_1 dw_2 dw_3 \quad [10\%]$$

Splitting the integral into two parts and using the results from Table 1 :

$$\begin{aligned} I_1 &= \frac{nm(2RT)}{\pi^{3/2}} \int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} w_1 \exp(-w_1^2) w_2 \exp(-w_2^2) \exp(-w_3^2) dw_1 dw_2 dw_3 \\ &= \frac{nm(2RT)}{\pi^{3/2}} 0 \frac{1}{2} \sqrt{\pi} = 0 \end{aligned} \quad [10\%]$$

$$\begin{aligned} I_2 &= \frac{nmV\sqrt{2RT}}{\pi^{3/2}} \int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} \exp(-w_1^2) w_2 \exp(-w_2^2) \exp(-w_3^2) dw_1 dw_2 dw_3 \\ &= \frac{nmV\sqrt{2RT}}{\pi^{3/2}} \sqrt{\pi} \frac{1}{2} \sqrt{\pi} = \rho V \sqrt{\frac{RT}{2\pi}} \end{aligned} \quad [10\%]$$

Hence, $\dot{M}_{12} = \rho V \sqrt{\frac{RT}{2\pi}} = \frac{pV}{\sqrt{2\pi RT}}$

If the molecules are reflected diffusely, they carry zero x_1 -momentum away from the plate so the drag force per unit width on one side of the plate is,

$$\rho VL \sqrt{\frac{RT}{2\pi}} = \frac{pVL}{\sqrt{2\pi RT}} \quad [10\%]$$

2. (a) The six groups have velocity components in m/s as follows :

$$(590, 30, 0); \quad (40, 580, 0); \quad (40, 30, 550);$$

$$(-510, 30, 0); \quad (40, -520, 0); \quad (40, 30, -550).$$

(i) The components of the gas mean velocity are:

$$U_1 = (590 - 510 + 40 + 40 + 40 + 40) / 6 = 40 \text{ m/s}$$

$$U_2 = (30 + 30 + 580 - 520 + 30 + 30) / 6 = 30 \text{ m/s}$$

$$U_3 = (0 + 0 + 0 + 0 + 550 - 550) / 6 = 0 \text{ m/s}$$

[5 %]

The thermal or peculiar velocity components are therefore :

$$(550, 0, 0); \quad (0, 550, 0); \quad (0, 0, 550);$$

$$(-550, 0, 0); \quad (0, -550, 0); \quad (0, 0, -550).$$

Temperature is defined in terms of the mean translational KE by,

$$\frac{3}{2}RT = \frac{\overline{C^2}}{2} \rightarrow T = \frac{550^2}{3 \times (8314.3/28)} = 339.6 \text{ K}$$

[15 %]

(ii) The kinetic temperature is defined in terms of the mean translational KE of the gas. This is a well-defined quantity irrespective of the state of the gas. Hence, it does not matter whether the gas is in an equilibrium or a non-equilibrium state – it has the same temperature.

[5 %]

(b) (i) As the gas is diatomic, there are 3 translational, 2 rotational and 2 vibrational (1 KE + 1 PE) degrees of freedom. However, at 339.6 K the vibrational states will be inactive. Hence, assuming the equipartition of energy to apply,

$$\overline{C_v} = (3 + 2) \frac{\overline{R}}{2}, \quad \overline{C_p} = \overline{C_v} + \overline{R} = (3 + 2 + 2) \frac{\overline{R}}{2}, \quad \gamma = \frac{\overline{C_p}}{\overline{C_v}} = \frac{7}{5} = 1.4$$

[5 %]

(ii) The internal molecular energy is due to the 2 rotational degrees of freedom. Assuming the equipartition of energy to apply,

$$e_{int} = 2 \left(\frac{RT}{2} \right) = \frac{8.3143}{28} \times 339.6 = 100.8 \text{ kJ/kg}$$

[10 %]

- (c) (i) When two molecules collide, the distance between centres is d . Consider a test molecule moving at \bar{C} and all other molecules stationary. The test molecule sweeps out a cylinder of diameter $2d$ and cross-sectional area πd^2 . It collides with any stationary molecule whose centre lies in this cylinder. In unit time the test molecule moves a distance \bar{C} and the swept volume is $\pi d^2 \bar{C}$. If the number density of molecules is n then the number of collisions is $n\pi d^2 \bar{C}$ and the mean free path is,

$$\lambda = \frac{1}{\pi n d^2} \quad [15\%]$$

- (ii) For the gas in question,

$$\lambda = \frac{1}{\pi n d^2} = \frac{m}{\pi \rho d^2} = \frac{(28/6.023 \times 10^{26})}{\pi \times 1.5 \times (0.3 \times 10^{-9})^2} = 1.10 \times 10^{-7} \text{ m} \quad [5\%]$$

- (d) (i) Consider a temperature gradient dT/dy in a gas. Assume molecules make their last collision before crossing the plane $y=0$ at $y = \pm \lambda$.

$$\text{Energy transfer rate, below to above} = \left(\frac{\rho \bar{C}}{4} \right) c_v \left(T_0 - \lambda \frac{dT}{dy} \right)$$

$$\text{Energy transfer rate, above to below} = \left(\frac{\rho \bar{C}}{4} \right) c_v \left(T_0 + \lambda \frac{dT}{dy} \right)$$

$$\text{Net energy transfer rate, below to above} = - \left(\frac{\rho \bar{C} \lambda c_v}{2} \right) \frac{dT}{dy} \rightarrow k = \frac{\rho \bar{C} \lambda c_v}{2} \quad [15\%]$$

- (ii) For monatomic molecules this expression is inaccurate because the derivation ignores the fact that fast molecules make their last collisions at greater distances from the plane $y=0$. More accurate calculations suggest the expression should be multiplied by a factor $\beta = 5/2$. For polyatomic molecules this correction factor should be applied to the translational contribution only (and not to the rotational and vibrational contributions). [10 %]

- (iii) From the above considerations,

$$\begin{aligned} k &= \beta \frac{\rho \bar{C} \lambda}{2} \left(\frac{3R}{2} \right) + \frac{\rho \bar{C} \lambda}{2} \left(c_v - \frac{3R}{2} \right) = \frac{\rho \bar{C} \lambda}{2} \left(\frac{3}{2} \beta + \frac{c_v}{R} - \frac{3}{2} \right) R \\ &= \frac{1.5 \times 550 \times 1.10 \times 10^{-7}}{2} \left(\frac{3}{2} \times \frac{5}{2} + \frac{5}{2} - \frac{3}{2} \right) \frac{8314.3}{28} = 0.064 \text{ W/m K} \quad [15\%] \end{aligned}$$

$$3 \quad (a) \quad U = \sum P_i E_i = \frac{1}{Q} \sum E_i \exp(\beta E_i)$$

where $Q = \sum \exp(\beta E_i)$.

Thus, $\frac{\partial Q}{\partial \beta} = \sum E_i \exp(\beta E_i) = QU$

$$\therefore \underline{\underline{U = \frac{1}{Q} \frac{\partial Q}{\partial \beta} = \frac{\partial}{\partial \beta} \ln Q}}$$

$$(b) \quad Z = \sum \exp(\beta \epsilon_n) = \sum \exp(n\beta h\nu) = \sum \exp(n\tau) = 1 + e^\tau + e^{2\tau} + \dots$$

Now τ is negative (since $\beta = -1/kT$) so $e^\tau < 1$, and the terms follow a G.P.

Thus, Z is the sum to infinity of a G.P. with common ratio e^τ .

$$\therefore \underline{\underline{Z = \frac{1}{1 - e^\tau}}}$$

(c) (i) For 2 independent oscillators, the total energy would be:

$$\epsilon_n = \epsilon_i^{(1)} + \epsilon_j^{(2)} .$$

The partition function for 2 oscillators would therefore be:

$$\begin{aligned} Q &= \sum_n \exp(\epsilon_n) = \sum_i \sum_j \exp \beta(\epsilon_i^{(1)} + \epsilon_j^{(2)}) = \sum_i \exp \beta \epsilon_i^{(1)} \times \sum_j \exp \beta \epsilon_j^{(2)} \\ &= Z^{(1)} \times Z^{(2)} \\ &= Z^2 \end{aligned}$$

and similarly for 3 and 4 oscillators, and so on. For the crystal there are $3N$ oscillators, because each atom may vibrate in three spatial dimensions.

$$\therefore \underline{\underline{Q = Z^{3N}}}$$

(Note, the atoms are distinguishable by their location in the crystal.)

(ii) Using the results from (a) and (b):

$$\begin{aligned} U &= \frac{\partial}{\partial \beta} \ln Q = 3N \frac{\partial}{\partial \beta} \ln Z = -3N \frac{\partial}{\partial \beta} \ln(1 - e^\tau) \\ &= \frac{3Ne^\tau}{1 - e^\tau} \frac{d\tau}{d\beta} = \underline{\underline{\frac{3N h \nu e^{-h\nu/kT}}{1 - e^{-h\nu/kT}}}} \end{aligned}$$

(iii) In the high temperature limit, $\tau \rightarrow 0$, so:

$$U \rightarrow \frac{3N\hbar\nu}{1-(1+\tau+\dots)} \approx \frac{-3N\hbar\nu}{\tau} = \frac{-3N\hbar\nu}{\beta\hbar\nu} = \frac{-3N}{-1/kT} = 3NkT$$

$$\therefore c_v = \frac{\partial}{\partial T} \left(\frac{U}{Nm} \right) \rightarrow \frac{3k}{m} = 3R$$

This is consistent with the equipartition principle which states that each "squared term" in the energy contributes $R/2$ to c_v (there are six squared terms corresponding to potential and kinetic energies in each of the 3 directions).

4 (a) Ω is the number of microstates that the system may exist in. 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 heat addition at constant volume, the temperature of the gas will increase and so the molecular velocity distribution 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.

(ii) For reversible, isothermal heat extraction, the volume of the gas must decrease in order to maintain a constant temperature (i.e., this is really isothermal compression). The molecular velocity distribution is unchanged (since T is constant), but we are more certain about the location of each molecule (since V decreases). Thus, the entropy decreases in accord with $dS = \delta Q / T$, with δQ being negative in this case.

(b) (i) The number of distinct arrangements is just the number of ways of choosing N things from M . There are M possible locations for the first molecule, for each of which there are $M-1$ locations for the second, and so on. However, the molecules are not distinguishable, so the result must be divided by $N!$. Thus,

$$\Omega = \frac{M(M-1)(M-2)\dots(M-N+1)}{N!} = \frac{M!}{(M-N)!N!}$$

(ii) The 'entropy' is given by:

$$\begin{aligned} S/k &= \ln \Omega = \ln M! - \ln(M-N)! - \ln N! \\ &= M \ln M - (M-N) \ln(M-N) - N \ln N - M + (M-N) + N \\ &= M \ln M - (M-N) \ln(M-N) - N \ln N \\ &= N \{ \ln(M-N) - \ln N \} - M \{ \ln(M-N) - \ln M \} \\ &= \underline{\underline{N \ln \left(\frac{M}{N} - 1 \right) - M \ln \left(1 - \frac{N}{M} \right)}} \end{aligned}$$

(iii) For $M/N \gg 1$:

$$\begin{aligned} S/k &\approx N \ln \left(\frac{M}{N} \right) - M \left(\frac{N}{M} + \dots \right) \\ &\approx N \ln \left(\frac{M}{N} \right) - N \end{aligned}$$

Thus, when the number of boxes increases from M_1 to M_2 , the change in entropy is:

$$\underline{\underline{S_2 - S_1 = Nk \ln \frac{M_2}{M_1} = Nk \ln \frac{V_2}{V_1}}}$$

For adiabatic, unrestrained expansion, T is constant, so from the data book:

$$S_2 - S_1 = mR \ln \frac{V_2}{V_1} = Nk \ln \frac{V_2}{V_1}$$

i.e., the two expressions are identical.

(iv) The assumption is valid because, when $M \gg N$, the probability of having more than one molecule in each box becomes vanishingly small, so the number of overlooked arrangements is negligible.

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ANSWERS

$$1. \quad (a) \quad \dot{M}_{11} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{n m u_1^2}{(2\pi RT)^{3/2}} \exp\left[-\left(\frac{(u_1 - V)^2 + u_2^2 + u_3^2}{2RT}\right)\right] du_1 du_2 du_3$$

$$(d) \quad \dot{M}_{12} = \int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} \frac{n m u_1 u_2}{(2\pi RT)^{3/2}} \exp\left[-\left(\frac{(u_1 - V)^2 + u_2^2 + u_3^2}{2RT}\right)\right] du_1 du_2 du_3$$

$$\text{Drag force per unit width} = \frac{pVL}{\sqrt{2\pi RT}}$$

2. (a) (i) 339.6 K

(b) (i) 1.4 (ii) 100.8 kJ/kg

(c) (ii) 1.10×10^{-7} m

(d) (iii) 0.064 W/m K

3. (a) $U = \frac{1}{Q} \frac{\partial Q}{\partial \beta} = \frac{\partial}{\partial \beta} \ln Q$

(c) (ii) $U = \frac{3Nh\nu e^{-h\nu/kT}}{1 - e^{-h\nu/kT}}$ (iii) $c_v \rightarrow \frac{3k}{m} = 3R$

4. (b) (ii) $S_2 - S_1 = Nk \ln \frac{M_2}{M_1} = Nk \ln \frac{V_2}{V_1}$