SOLUTIONS TO 4A9 Molecular Thermodynamics 2022

Examiners' comments:

Q1. Relatively few candidates got part (a) completely correct, with many forgetting the rotational energy for N_2. Part (b) (calculating and interpreting various molecular averages and fluxes for a Maxwellian distribution) was done well, and many students made good attempts at computing the one-sided kinetic energy flux in part (c), though few got exactly the correct result.

Q2. Although not especially popular, most candidates that attempted this question showed a good knowledge and understanding of Knudsen effects and were able to apply the flux-matching method to find the slip velocity. The greatest difficulties were in applying the momentum equation to the flow in a circular tube (1B material).

Q3. A significant fraction of those attempting this question were able to derive the ideal gas relations from the Helmholtz function and partition function, and to correctly identify the statistical equivalents of heat and work transfers. The last section, relating to the changes in molecular distribution over different energy states for an isentropic process, was not done well, with few candidates making much headway.

Q4. Most candidates had a good grasp of the different constraints applying to the canonical and microcanonical ensembles, and many were able to apply Lagrange multipliers to maximise the (statistical) entropy. Fewer were able to apply similar analysis to determine the distribution of microstates for a system in contact with a thermal reservoir. There were nonetheless several perfect or near-perfect attempts at this question.

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Q1. (a) Per molecule, $\varepsilon = F\frac{kT}{2} + \frac{1}{2}mV^2$

$$= 5\frac{kT}{2} + \frac{1}{2}\frac{k}{R}V^2$$

$$= \left(\frac{5\times 350}{2} + \frac{100^2}{2\cdot 297}\right)k = \underline{1.23\times 10^{-20}}\ \mathrm{J}$$ [2]

(i) Fraction as molecular translational KE $= \frac{3/2 \times 350}{891.8} = \underline{0.59}$ [1]

(ii) fraction as bulk flow KE $= \frac{1/2\ 100^2 \times \frac{1}{297}}{891.8} = \underline{0.0189}$ [1]

(b) (i) $I = nm = \rho$ the density $= \frac{p}{RT} = \frac{10^5}{297\cdot 350} = \underline{0.962\ \mathrm{kg\,m^{-3}}}$ [1]

(ii) $I = \bar{c}_1$ the average velocity $= \underline{100\ \mathrm{ms^{-1}}}$ [1]

(iii) $I = \frac{1}{2}\overline{C_2^2}$ the average KE per unit mass associated with random translational motion in the x_2 direction. By equipartition this is $RT/2 = \frac{297\times 350}{2} = \underline{51.98\ \mathrm{kJ/kg}}$. [2]

(iv) $I = \rho\overline{C_1C_2}$ this is the negative of the viscous stress, σ_{12}. On the centreline of the nozzle the velocity distribution is Maxwellian so C_1 & C_2 are uncorrelated (there is no shear stress). Thus $\underline{I=0}$ [2]

(v) $I =$ the net flux of random translational KE in the x_1 direction due to molecular motion. This is proportional to the heat flux, q_1. It is zero due to the symmetry of f. [2]

(c) $F = \int_0^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{1}{2} m c_3^2 c_3 f \, dc_1 dc_2 dc_3$

$$= \frac{\rho}{2\beta^3\pi^{3/2}} \int_0^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} c_3^3 \, e^{-(c_1^2+c_2^2+c_3^2)/\beta^2} \, dc_1 dc_2 dc_3$$

where $\beta = \sqrt{2RT}$; put $x_i = c_i / \beta$.

$$\Rightarrow \quad F = \frac{\rho\beta^3}{2\pi^{3/2}} \int_0^{\infty} x_3^3 e^{-x_3^2} dx_3 \int_{-\infty}^{\infty} e^{-x_2^2} dx_2 \int_{-\infty}^{\infty} e^{-x_1^2} dx_1$$

$$= \frac{\rho\beta^3}{2\pi^{3/2}} I_3 (2I_0)^2 = \frac{\rho\beta^3}{2\pi^{3/2}} \times \frac{1}{2} \times \pi$$

$$= \frac{\rho}{4} \cdot 2RT \cdot \sqrt{\frac{2RT}{\pi}} = \left(\frac{\rho\bar{c}}{4}\right) RT = F_M^+ \cdot RT$$

The mean value of $c_3^2/2$ carried by the one-sided mass flux is thus RT ($\simeq 104$ kJ/kg) which is twice the mean value evaluated in part (b)(iii). This is because the KE flux (as opposed to the average value of KE) is dominated by higher values of c_3.

[8]

Q2. (a) $Kn = \lambda/L$ where λ is the molecular mean free path and L is a suitable length scale for the flow. It characterises departures from continuum flow. Approximate regimes are:

Continuum ($Kn \ll 1$). Continuum (Navier-Stokes) equations apply, with no-slip at solid boundaries.

Slip regime ($0.01 < Kn < 0.1$). Continuum equations may be assumed to occur throughout most of the flow, but with velocity slip at boundaries.

Transition ($Kn \sim 1$). Continuum equations no longer apply, but there are still significant collisions between molecules. Difficult to analyse!

Free-molecule ($Kn \gg 1$). There are very few collisions between molecules, compared to collisions with boundaries. [2]

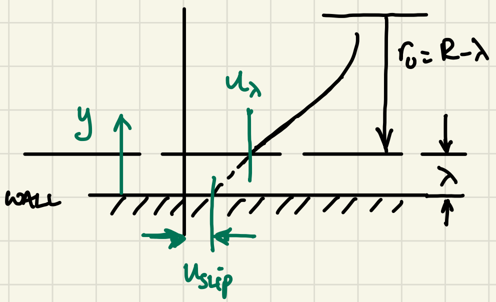
(b) (i) The mean free path is given approximately by $n\pi d^2 \lambda = 1$

More precisely $\lambda = \dfrac{1}{n\pi d^2\sqrt{2}}$

$$\therefore \; Kn = \frac{\lambda}{D} = \frac{kT}{D\,p\,\pi d^2\sqrt{2}} = \frac{1.38\times10^{-23}\times300}{\pi\sqrt{2}\,(0.37\times10^{-9})^2\;0.0002}\;\frac{1}{p} = \frac{34}{p}$$

For Kn in range 0.01 to 0.1, p is in range 340 Pa to 3.4 kPa [4]

(ii)



u_{slip} defined by extrapolation to wall from $y=\lambda$

Thus $\quad u_\lambda = u_{slip} + \lambda\left(\dfrac{du}{dy}\right)_w$

Momentum flux to wall $= (2\pi r_0)\,\dfrac{\rho\bar{c}}{4}\,u_\lambda$ [per unit length of tube]

Momentum flux from wall $= 0$ (diffuse reflection)

Net momentum flux to wall $= (2\pi r_0)\,\dfrac{\rho\bar{c}}{4}\,u_\lambda$

$=$ shear force at $y=\lambda$

$= (2\pi r_0)\,\mu\left(\dfrac{du}{dy}\right)$

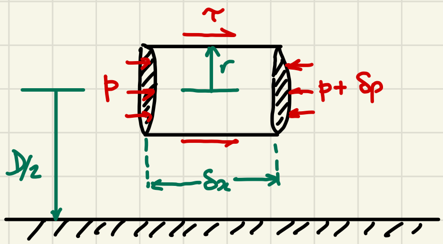
$$\therefore \quad \cancel{(2\pi r_0)}\, \frac{\rho \bar{c}}{4}\, u_\lambda = \cancel{(2\pi r_0)}\, \frac{\rho \bar{c}}{2}\, \lambda \left(\frac{du}{dy}\right)_w$$

$$u_\lambda = u_s + \lambda \left(\frac{du}{dy}\right)_w = 2\lambda \left(\frac{du}{dy}\right)_w .$$

$$\therefore \quad u_s = \lambda \left(\frac{du}{dy}\right)_w = -\lambda \left(\frac{du}{dr}\right)_{wall} \qquad (y = R - r)$$

[6]

(iii)



Flow is "fully developed" so u is only $fn(r)$

$$\pi r^2 \delta p = 2\pi r\, \delta x\, \tau$$

$$\Rightarrow \quad \tau = \frac{r}{2}\frac{dp}{dx}$$

$$\therefore \quad \frac{du}{dr} = \frac{r}{2\mu}\frac{dp}{dx} = -\frac{r}{2\mu}\frac{\Delta p}{L}$$

$$u = C - \frac{r^2}{4\mu L}\Delta p \qquad (1)$$

$$u_{slip} = C - \frac{R^2}{4\mu L}\Delta p$$

but $$u_{slip} = -\lambda \left(\frac{du}{dr}\right)_R = \frac{\lambda 2 R \Delta p}{4\mu L}$$

$$\therefore \quad u(r) = \frac{\Delta p}{4\mu L}\left\{R^2 - r^2 + 2\lambda R\right\} = \frac{\Delta p R^2}{4\mu L}\left(1 + \frac{2\lambda}{R} - \left(\frac{r}{R}\right)^2\right)$$

Define $Kn = \lambda / D$: $$\boxed{u(r) = \frac{\Delta p D^2}{16 \mu L}\left(1 + 4Kn - \left(\frac{2r}{D}\right)^2\right)} \qquad (2)$$

$$\frac{u_{slip}}{u_{max}} = \frac{u(R)}{u(0)} = \frac{4Kn}{1 + 4Kn} \quad \Rightarrow \quad B = 4$$

[8]

Q3 (a) $F = U - TS$

$$\therefore dF = dU - TdS - SdT$$
$$= dU - (dU + pdV) - SdT$$
$$= -pdV - SdT$$
$$\Rightarrow p = -\left(\frac{\partial F}{\partial V}\right)_T$$

Now $F = -kT \ln Q = -kT \ln\left(\frac{Z^N}{N!}\right)$

$$\therefore p = NkT \frac{\partial}{\partial V} \ln Z = NkT \frac{\partial}{\partial V}\{\ln V + f(T)\} = \frac{NkT}{V}$$

ie, $pV = NkT$ $\boxed{5}$

(b)
$$U = \sum_j N_j \varepsilon_j$$
$$\therefore dU = \underbrace{\sum_j \varepsilon_j dN_j}_{\delta Q} + \underbrace{\sum_j N_j d\varepsilon_j}_{-\delta W}$$

The first term is due to a redistribution of the numbers of molecules over the energy levels. It thus affects the number of microstates of the system and hence the entropy and may therefore be identified with heat transfer for a reversible process. The second term is due to a change in the energy levels. It does not affect the entropy and may therefore be identified as a reversible work transfer. $\boxed{3}$

(c) (i) The question gives a strong hint we should work in terms of T & V

Thus,
$$s_B - s_A = c_v \ln\left(\frac{T_B}{T_A}\right) + R \ln\left(\frac{V_B}{V_A}\right) = 0 \quad \left[\begin{array}{c}\text{reversible,}\\ \text{adiabatic}\end{array}\right]$$

$$\Rightarrow T_B V_B^{R/c_v} = T_A V_A^{R/c_v} = \text{const} \quad \text{or} \quad TV^{2/3} = \text{const}$$

(Also available directly from data book for isentropic process)

Now $\quad \dfrac{N_j}{N} \simeq \dfrac{g_j \exp(-\varepsilon_j / kT)}{Z} \quad$ and $\quad \varepsilon_j \propto V^{-2/3}$

$\therefore \quad \varepsilon_j / kT \quad \propto \quad 1/(TV^{2/3}) \quad = \text{const}$

Hence the exponential terms are unchanged. Z is also unchanged (because $Z = \sum_j g_j \exp(-\varepsilon_j / kT)$ or directly from expression for Z given)

$\therefore \quad \dfrac{N_j}{N}$ is unchanged between states A & B.

This is consistent with all δN_j being zero, as required for constant S. $\boxed{6}$

(c) (ii) 1ST LAW:

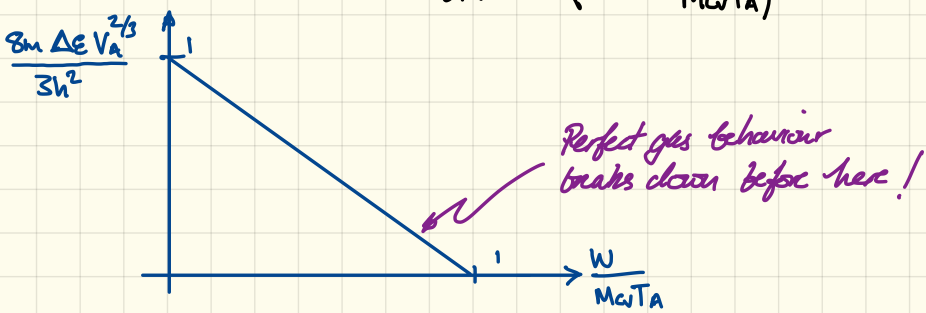
$$\begin{aligned} W &= -\Delta U \\ &= Mc_v(T_A - T_B) \quad \text{or} \quad \frac{3NkT_A}{2}\left(1 - \frac{T_B}{T_A}\right) \\ &= \frac{3NkT_A}{2}\left(1 - \left(\frac{V_B}{V_A}\right)^{-2/3}\right) \end{aligned} \qquad (1)$$

Now $\quad \varepsilon_n^B = \dfrac{h^2}{8m}(n_1^2 + n_2^2 + n_3^2) V_B^{-2/3}$

FIRST TWO LEVELS, $(\varepsilon_2 - \varepsilon_1) = \dfrac{h^2 V_B^{-2/3}}{8m}\left[(4+1+1) - (1+1+1)\right] = \dfrac{3h^2 V_B^{-2/3}}{8m}$

SECOND TWO LEVELS, $(\varepsilon_3 - \varepsilon_2) = \dfrac{h^2 V_B^{-2/3}}{8m}\left[(4+4+1) - (4+1+1)\right] = \dfrac{3h^2 V_B^{-2/3}}{8m}$

From (1), both spacings are $\dfrac{3h^2}{8m} V_A^{-2/3}\left(1 - \dfrac{W}{Mc_v T_A}\right)$



$\boxed{6}$

Q4. (a)

(i) M only (M is isolated; C in contact with a reservoir)

(ii) B (C in contact with reservoir at fixed T; M isolated and T is $\propto$ average translational KE per molecule)

(iii) B (M & C closed)

(iv) C only (M is isolated)

NOTE: either C or B would be acceptable here

[4]

(b) (i) $G = \sum P_i = 1$ [1]

(ii) $S' = -k \sum P_i \ln P_i$

Minimise S' at constant G $\Rightarrow$ $\nabla S' + \lambda \nabla G = 0$

$$\Rightarrow \frac{\partial S'}{\partial P_i} + \lambda \frac{\partial G}{\partial P_i} = 0$$

$$\therefore \quad -k\frac{P_i}{P_i} - k\ln P_i + \lambda \times 1 = 0$$

$$\Rightarrow \ln P_i = \frac{\lambda}{k} - 1 \Rightarrow P_i = e^{(\lambda/k - 1)} = \text{const} = c$$

$$\sum P_i = 1 \Rightarrow c\Omega = 1$$

$$\therefore \quad \underline{P_i = \frac{1}{\Omega}}.$$

Isolated system: entropy is maximised at equilibrium.

$$\therefore \quad S' = S'_{max} = -k\sum \frac{1}{\Omega}\ln\left(\frac{1}{\Omega}\right) = \underline{k\ln\Omega}$$ [5]

(c) (i) $F' = U - TS' = \sum P_i E_i + kT \sum P_i \ln P_i$

$$\therefore \quad F' = \sum P_i \left(E_i + kT \ln P_i \right)$$

Minimise subject to $G = \sum P_i = 1$

$$\therefore \quad \nabla F' + \lambda \nabla G = 0$$

$$\Rightarrow \quad E_i + kT + kT \ln P_i + \lambda \times 1 = 0$$

$$\Rightarrow \quad \ln P_i = -\frac{\lambda}{kT} - 1 - E_i / kT$$

$$\Rightarrow \quad P_i = \mathrm{fn}(T, V)\, e^{-E_i / kT}$$

But $\sum P_i = 1 \Rightarrow \mathrm{fn}(T, V) = \dfrac{1}{\sum e^{-E_i/kT}} = \dfrac{1}{Q}$.

$$\therefore \quad P_i = \frac{e^{-E_i/kT}}{Q}$$

[4]

(ii) $F' = \sum P_i \left(E_i + kT \ln P_i \right) = \sum P_i \left(\cancel{E_i} - kT \dfrac{\cancel{E_i}}{kT} - kT \ln Q \right)$

$$= -kT \ln Q \sum P_i = -kT \ln Q$$

$$U = \sum E_i P_i = \frac{1}{Q} \sum E_i \exp\left(-E_i / kT\right)$$

$$Q = \sum \exp\left(-E_i / kT\right) \Rightarrow \left(\frac{\partial Q}{\partial T} \right)_{V,N} = \sum \frac{E_i}{kT^2} \exp\left(-E_i / kT\right)$$

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

[6]

These are needed to keep E_i const. and apply to the given system.