

ENGINEERING TRIPOS PART IIB 2010

MODULE 4A9 – MOLECULAR THERMODYNAMICS

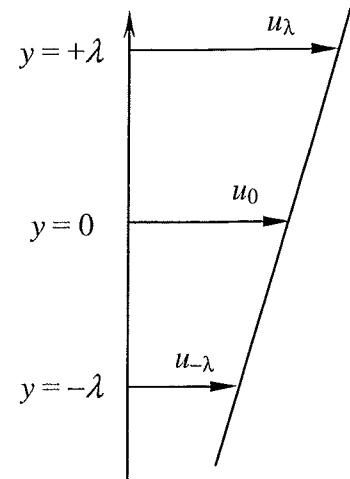
SOLUTIONS TO TRIPOS QUESTIONS

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

- 1 (a) Consider the fluxes of x_1 -momentum across the plane $x_2 = 0$.

$$\text{Flux of } x\text{-momentum from below} = \frac{\rho \bar{C}}{4} \left[u_0 - \lambda \frac{du}{dy} \right]$$

$$\text{Flux of } x\text{-momentum from above} = \frac{\rho \bar{C}}{4} \left[u_0 + \lambda \frac{du}{dy} \right]$$



$$\text{Net flux of } x\text{-momentum in negative } y\text{-direction} = \text{shear stress} = \tau = \frac{\rho \bar{C} \lambda}{2} \frac{du}{dy} \quad [20 \%]$$

The main assumptions of the theory are,

- i) Molecules make their last collision one mean free path above or below the plane $y = 0$.
- ii) At this collision, molecules acquire the local mean velocity. [10 %]

(b) Dynamic viscosity μ is defined by $\tau = \mu \frac{du}{dy}$ and hence $\mu = \frac{\rho \bar{C} \lambda}{2}$

λ is inversely proportional to ρ and \bar{C} is proportional to $T^{1/2}$. Hence, the above result suggests that μ should be independent of p and vary with $T^{1/2}$. [10 %]

In reality, μ is almost independent of p but tends to vary with $T^{0.7} \sim T^{0.8}$. This is because molecules do not behave as hard spheres but are 'softer' depending on the inter-molecular force. As a result, λ is slightly temperature-dependent. [10 %]

- (c) Now consider the translational KE flux.

$$\text{Flux of translational KE from below} = \frac{\rho \bar{C}}{4} \left[\frac{u_0^2}{2} - \lambda \frac{d(u^2/2)}{dy} \right]$$

$$\text{Flux of translational KE from above} = \frac{\rho \bar{C}}{4} \left[\frac{u_0^2}{2} + \lambda \frac{d(u^2/2)}{dy} \right]$$

$$\begin{aligned} \text{Net flux of translational KE in positive } y\text{-direction} &= -\frac{\rho \bar{C} \lambda}{2} \frac{d(u^2/2)}{dy} \\ &= -\frac{u \rho \bar{C} \lambda}{2} \frac{du}{dy} \end{aligned}$$

At the plane $y = 0$,

$$\text{Net flux of translational KE in positive } y\text{-direction} = -\frac{u_0 \rho \bar{C} \lambda}{2} \frac{du}{dy}$$

Hence,

$$A = \frac{u_0 \rho \bar{C} \lambda}{2} \quad [30 \%$$

(d) We now substitute

$$\tau = \frac{\rho \bar{C} \lambda}{2} \frac{du}{dy}$$

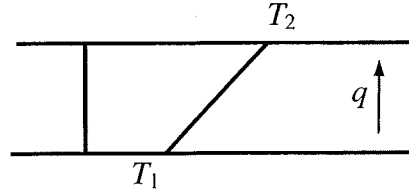
Hence, net flux of translational KE in the positive y -direction = τu_0 [10 %]

At a macroscopic level this is the rate at which work is done by the viscous shear stress at the plane $y = 0$. Thus, at a microscopic level, the work transfer is simply a flux of translational KE (just as one might expect from the First Law of Thermodynamics). [10 %]

Examiners' comments

Every candidate knew the kinetic theory of viscosity in (a), but not all were able to deduce how the dynamic viscosity varied with pressure and temperature in (b). The calculation of the kinetic energy flux was surprisingly well done (c), although not everyone was able to relate this microscopic energy flux to the macroscopic rate of work done by the shear force.

2. (a)



For $Kn \ll 1$ (continuum regime), Fourier's law of heat conduction applies. Hence, using the uncorrected expression from mean free path theory $k = \rho \bar{C} \lambda c_v / 2$, we obtain,

$$q_0 = -k \frac{dT}{dy} = -\frac{\rho \bar{C} \lambda c_v}{2} \frac{(T_2 - T_1)}{L} \quad [10 \%$$

(b) For $Kn \gg 1$ (free-molecule regime), we assume that molecules do not collide with each other, only with the plates. From the definition of the thermal accommodation coefficient α we have,

$$E_{ref} = (1 - \alpha) E_{inc} + \alpha E_{eqm}$$

Let q_{12} and q_{21} be the energy fluxes from 1 \rightarrow 2 and 2 \rightarrow 1 respectively (*i.e.*, $q_\infty = q_{12} - q_{21}$). Hence, from the above equation,

$$q_{12} = (1 - \alpha) q_{21} + \alpha \frac{\rho \bar{C}}{4} c_v T_1$$

$$q_{21} = (1 - \alpha) q_{12} + \alpha \frac{\rho \bar{C}}{4} c_v T_2$$

Subtracting the second equation from the first gives,

$$(q_{12} - q_{21}) = (1 - \alpha)(q_{21} - q_{12}) + \alpha \frac{\rho \bar{C}}{4} c_v (T_1 - T_2)$$

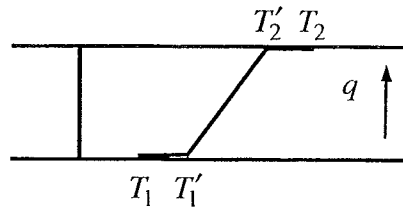
$$(2 - \alpha)(q_{12} - q_{21}) = (2 - \alpha) q_\infty = \alpha \frac{\rho \bar{C}}{4} c_v (T_1 - T_2)$$

$$q_\infty = \left(\frac{\alpha}{2 - \alpha} \right) \frac{\rho \bar{C}}{4} c_v (T_1 - T_2)$$

Combining with the expression for q_0 gives,

$$\frac{q_\infty}{q_0} = \left(\frac{\alpha}{2 - \alpha} \right) \frac{L}{2\lambda} = \left(\frac{\alpha}{2 - \alpha} \right) \frac{1}{2Kn} \quad \rightarrow \quad A = 2 \quad [40 \%$$

(c) In the slip regime, we allow for a temperature jump at the surface of each plate, while Fourier's law is assumed to apply everywhere else :



$$q_s = -k \frac{dT}{dy} = -\frac{\rho \bar{C} \lambda c_v}{2} \frac{(T_2' - T_1')}{L}$$

Hence,

$$\frac{q_s}{q_0} = \frac{(T_2' - T_1')}{(T_2 - T_1)}$$

The surface temperature jumps are,

$$T_1' - T_1 = \frac{\lambda}{L} (T_2' - T_1') \quad T_2 - T_2' = \frac{\lambda}{L} (T_2' - T_1')$$

Adding these equations gives,

$$(T_2 - T_1) - (T_2' - T_1') = 2 \frac{\lambda}{L} (T_2' - T_1')$$

$$(T_2 - T_1) = (1 + 2Kn) (T_2' - T_1')$$

Hence,

$$\frac{q_s}{q_0} = \frac{(T_2' - T_1')}{(T_2 - T_1)} = \frac{1}{1 + 2Kn} \quad \rightarrow \quad B = 2 \quad [40 \%]$$

This is unlikely to give good results in the transition regime where $Kn = O(1)$ because the Knudsen layers adjacent to the plates occupy a significant fraction of L . Inter-molecular collisions and collisions between molecules and the plates are of comparable significance and this is very difficult to model theoretically. Although the correct free-molecule limit ($Kn \rightarrow \infty$) is obtained, this does not necessarily mean that the interpolation in the transition regime is accurate. [10 %]

Examiners' comments:

With hindsight, this unpopular question was rather challenging and a hint or two would not have been out of place. Nevertheless, several candidates managed to work through all three parts using essentially the correct theoretical approach in each case. The main problems were in deploying the definition of the thermal accommodation coefficient in the free-molecule calculation and in introducing the temperature jump expression correctly in the slip-flow calculation.

- 3 (a) (i) k Boltzmann's constant
 P_i the probability (or relative frequency) of the i -th microstate
 Ω number of accessible microstates of the system.

If $\Omega = 1$ then $P_i = P_1 = 1$ so $S' = 0$. [15%]

- (ii) We wish to maximize S' subject to the constraint $P = \sum_i P_i = 1$.

Using Lagrange multipliers, the turning point will be attained when:

$$\frac{\partial S'}{\partial P_i} + \lambda \frac{\partial P}{\partial P_i} = 0 \quad \text{or} \quad -k \left(\frac{P_i}{P_i} + \ln P_i \right) + \lambda \times 1 = 0 .$$

Rearranging gives:

$$P_i = \exp \left(\frac{\lambda}{k} - 1 \right) = \text{const.}$$

i.e., turning point is when all P_i are equal.

(This turning point must be a maximum because S' is clearly positive, except when one of the $P_i = 1$ and the rest are zero, in which case $S'=0$).

For an isolated system at equilibrium, the entropy reaches a maximum

(and all the P_i are equal, and since $\sum_{i=1}^{\Omega} P_i = 1$, $P_i = \frac{1}{\Omega}$).

$$\therefore S' = -k \sum_{i=1}^{\Omega} \frac{1}{\Omega} \ln \frac{1}{\Omega} = \underline{\underline{k \ln \Omega}} \quad [35\%]$$

- (b) The final temperature must be uniform (implied by the copper piston) and, since the overall system is isolated, must be the same as the initial temperature. The processes for A and B are therefore isothermal. At equilibrium, the pressures on either side of the piston are obviously equal.

$$\therefore p_2(V_A + V_B) = p_A V_A + p_B V_B \Rightarrow p_2 = 1.6 \text{ bar}$$

$$\text{Now, } S_2 - S_1 = k \ln \frac{\Omega_2}{\Omega_1}$$

$$S_2 - S_1 = m_A R \ln \frac{p_2}{p_A} + m_B R \ln \frac{p_2}{p_B}$$

$$\begin{aligned} \text{But } &= \frac{p_A V_A}{T} \ln \frac{p_2}{p_A} + \frac{p_B V_B}{T} \ln \frac{p_2}{p_B} \\ &= \frac{10^5 \times 0.2}{300} \ln 1.6 + \frac{2 \times 10^5 \times 0.3}{300} \ln 0.8 = 13.30 \text{ J / K} \end{aligned}$$

$$\therefore \frac{\Omega_1}{\Omega_2} = \exp(\Delta S / k) = \exp(-9.63 \times 10^{23}) \quad \text{i.e., extremely small.}$$

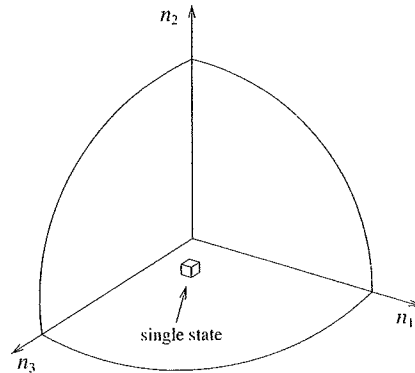
Provided the gas behaves as an ideal gas, the above shows that the ratio does not depend on R so it is independent of the gas. This is really because the entropy changes (and hence the change in the number of microstates) depends only on the change in uncertainty in position of the constituent molecules.

[50%]

Examiners comment: Many students had difficulty with the Lagrange multipliers in part (a) and very few calculated the correct final pressure in part (b).

The question had a straightforward introduction for which most students scored full marks. However, few students managed to apply Lagrange multipliers correctly to maximize the expression for entropy. The last part of the question involved using 1A material: only 1 out of the 10 M.Eng students got it right!

4. (a)



Number of microstates $\Gamma(\epsilon) = \text{volume of octant}$

$$\begin{aligned} \Gamma(\epsilon) &= \frac{1}{8} \times \frac{4\pi}{3} \times n^3 \\ \therefore &= \frac{4\pi V}{3h^3} \times (2m\epsilon)^{3/2} \end{aligned} \quad [25\%]$$

(b) At RMS speed, $\epsilon = \frac{3kT}{2}$

$$\begin{aligned} \therefore \Gamma(\epsilon) &= \frac{4\pi \times 0.002}{3 \times (6.626 \times 10^{-34})^3} \times \left(2 \times \frac{20}{6.022 \times 10^{26}} \times \frac{3}{2} \times 1.381 \times 10^{-23} \times 300 \right)^{3/2} \\ &= \underline{\underline{2.415 \times 10^{29} \text{ states}}} \end{aligned} \quad [20\%]$$

(c) The single particle partition function is:

$$Z = \sum_i \exp(-\epsilon_i / kT) = \sum_{n_1} \sum_{n_2} \sum_{n_3} \exp \left[-\frac{h^2}{8mV^{2/3}kT} (n_1^2 + n_2^2 + n_3^2) \right] = Z_1^3$$

Assuming particles are weakly interacting, the **system** partition function for N **distinguishable** particles would be:

$$Q = Z^N = Z_1^{3N}$$

Taking account of indistinguishability,

$$Q \approx \frac{Z^N}{N!} = \frac{Z_1^{3N}}{N!}$$

The 'approximately equals' sign stems from the fact that dividing by $N!$ is not correct in cases where more than one particle is in the same quantum state. This, however, is extremely rare at moderate temperatures for which most quantum

states are empty. Writing $\tau^2 = \frac{h^2}{8mV^{2/3}kT}$ gives:

$$Z_1 = \sum_{n_1=1}^{\infty} \exp(-n_1^2 \tau^2) \times 1 = \sum_{n_1=1}^{\infty} \exp(-n_1^2 \tau^2) \times dn_1 \approx \int_0^{\infty} \exp(-n_1^2 \tau^2) dn_1$$

is The approximation is very good because (at least at moderate temperatures), τ^2 very small, so the summation becomes an integral with the lower limit of zero.

Thus,

$$Q = \frac{Z_1^{3N}}{N!} = \left(\frac{\sqrt{\pi}}{2\tau} \right)^{3N} = \text{fn}(N, T, m) \times V^N$$

$$\therefore p = kT \frac{\partial}{\partial V} \ln Q = kT \frac{\partial}{\partial V} (N \ln V) = \frac{NkT}{V}$$

or $pV = NkT$

[55%]

Examiners' comments:

There were several near-perfect solutions to this question but also a few very poor attempts which brought the average down. Most students derived the correct expression for the number of energy states and applied it correctly in the numerical section. Deriving the expression for the partition function and showing this led to the ideal gas equation of state was done less well.