

ENGINEERING TRIPOS PART IIB 2015
MODULE 4A9 – MOLECULAR THERMODYNAMICS
SOLUTIONS

1. (a) (i) The integral represents the mean value of $C_1^2/2$. Thus,

$$I = \frac{1}{n} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{C_1^2}{2} f dC_1 dC_2 dC_3 = \frac{\overline{C_1^2}}{2}$$

Kinetic temperature is defined in terms of the mean translational KE of a molecule by,

$$\frac{3RT}{2} = \frac{\overline{C^2}}{2}$$

Translational KE is equally partitioned at equilibrium so $\overline{C_1^2}/2 = RT/2$.

[10 %]

(ii) The flux per unit area of the quantity $mC_1^2/2$ carried by molecules with $C_1 > 0$ is given by the integral,

$$\dot{E}_1 = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} \frac{mC_1^2}{2} C_1 f dC_1 dC_2 dC_3$$

[5 %]

(iii) Substituting the Maxwell-Boltzmann expression for f ,

$$\dot{E}_1 = \int_{C_3=-\infty}^{\infty} \int_{C_2=-\infty}^{\infty} \int_{C_1=0}^{\infty} \frac{mC_1^2}{2} C_1 \frac{n}{(2\pi RT)^{3/2}} \exp\left[-\left(\frac{C_1^2 + C_2^2 + C_3^2}{2RT}\right)\right] dC_1 dC_2 dC_3$$

To carry out the integrations it is sensible to apply the transformations,

$$C_1 = \xi_1 \sqrt{2RT}, \quad C_2 = \xi_2 \sqrt{2RT}, \quad C_3 = \xi_3 \sqrt{2RT}.$$

Substituting into the integral and noting that $mn = \rho$ gives,

$$\dot{E}_1 = \frac{\rho}{2} \left(\frac{2RT}{\pi}\right)^{3/2} \int_{C_3=-\infty}^{\infty} \int_{C_2=-\infty}^{\infty} \int_{C_1=0}^{\infty} \xi_1^3 e^{-\xi_1^2} e^{-\xi_2^2} e^{-\xi_3^2} d\xi_1 d\xi_2 d\xi_3$$

Using the given definite integrals we have,

$$\int_{-\infty}^{\infty} e^{-\xi_3^2} d\xi_3 \int_{-\infty}^{\infty} e^{-\xi_2^2} d\xi_2 \int_0^{\infty} \xi_1^3 e^{-\xi_1^2} d\xi_1 = \sqrt{\pi} \times \sqrt{\pi} \times \frac{1}{2} = \frac{\pi}{2}$$

Hence,

$$\dot{E}_1 = \frac{\rho}{2} \left(\frac{2RT}{\pi}\right)^{3/2} \left(\frac{\pi}{2}\right) = \frac{\rho}{4} \left(\frac{8RT}{\pi}\right)^{1/2} (RT) = \dot{M}(RT)$$

where \dot{M} is the ‘one-sided’ mass flux per unit area through the plane (see given data).

Hence, the mean value of $C_1^2/2$ carried by molecules with $C_1 > 0$ is RT [and not $RT/2$ as in part (i), above]. This is because the equipartition principle does not apply – the KE flux (as opposed to the bulk average KE) is dominated by those molecules with higher values of C_1 .

(b) (i) Pressure = 1 Pa

Gas mass density at 350 K = $\rho = p/(RT) = 1.374 \times 10^{-6} \text{ kg/m}^3$

Mean molecular speed \bar{C} at 350 K = $(8RT/\pi)^{1/2} = 1361.6 \text{ m/s}$

Mean free path at 350 K = $\lambda = 2\mu/(\rho\bar{C}) = 2.35 \times 10^{-2} \text{ m}$

Knudsen number = $\lambda/L = 0.0235/0.002 = 11.8$

$Kn \gg 1$ so heat transfer is in the free-molecule regime.

Molecules are reflected diffusely from each plate (accommodation coefficients = 1) and make no collisions with other molecules before impacting the other plate. The mass flux emitted from plate 1 is $\rho_1\bar{C}_1/4$ and from plate 2 is $\rho_2\bar{C}_2/4$. These must be equal as the net mass flux between the plates must be zero. Hence, $\rho_1\sqrt{T_1} = \rho_2\sqrt{T_2}$. However, although we know T_1 and T_2 it is not obvious how to find ρ_1 and ρ_2 . To circumvent this problem, a good approximation is to calculate the one-sided mass flux using average values of ρ and T . Hence, the rate of heat transfer per unit area is approximately given by:

$$\dot{q} = \frac{\rho\bar{C}}{4}(2RT_1 - 2RT_2) = \frac{1.374 \times 10^{-6} \times 1361.6}{4} \times 2 \times 2080.0 \times (400 - 300) = 194.6 \text{ W/m}^2 \quad [25 \%]$$

Note that the mean translational KE per unit mass appropriate to the energy flux is $2RT$ rather than $c_v T = 3RT/2$ which is the mean value in the bulk. The extra $RT/2$ comes from the calculation in part (a) (iii) above. Candidates were not penalised for missing this detail.

(ii) Pressure = 10,000 Pa

Gas mass density at 350 K = $\rho = p/(RT) = 1.374 \times 10^{-2} \text{ kg/m}^3$

Mean molecular speed \bar{C} at 350 K = $(8RT/\pi)^{1/2} = 1361.6 \text{ m/s}$

Mean free path at 350 K = $\lambda = 2\mu/(\rho\bar{C}) = 2.35 \times 10^{-6} \text{ m}$

Knudsen number = $\lambda/L = 2.35 \times 10^{-6}/0.002 = 0.00118$

$Kn \ll 1$ so heat transfer is in the continuum regime.

The thermal conductivity can be calculated from the Prandtl number and the viscosity.

Thermal conductivity = $k = c_p\mu/\text{Pr} = (3R/2 + R)\mu/\text{Pr} = 0.171 \text{ W/m}^2\text{K}$

Rate of heat transfer per unit area is given by,

$$\dot{q} = -k \frac{(T_2 - T_1)}{L} = -0.171 \frac{(300 - 400)}{0.002} = 8550 \text{ W/m}^2 \quad [25 \%]$$

Examiner's comment:

This question was very well done. It was gratifying to see that almost all candidates had absorbed the course material very well and knew exactly what they were doing. The only real difficulties occurred at the end when trying to derive expressions for the heat flux under free molecule and continuum conditions. Some candidates got into a mess here by mistakenly trying to include the Knudsen layer in the analysis.

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

$$\begin{aligned} & (480, 120, 0); & (50, 550, 0); & (50, 120, 430); \\ & (-380, 120, 0); & (50, -310, 0); & (50, 120, -430). \end{aligned}$$

The components of the mean velocity u_i are thus :

$$\begin{aligned} u_1 &= (480 - 380 + 50 + 50 + 50 + 50) / 6 = 50 \text{ m/s} \\ u_2 &= (120 + 120 + 550 - 310 + 120 + 120) / 6 = 120 \text{ m/s} \\ u_3 &= (0 + 0 + 0 + 0 + 430 - 430) / 6 = 0 \text{ m/s} \end{aligned}$$

The thermal or peculiar velocity components are given by $C_i = c_i - u_i$:

$$\begin{aligned} & (430, 0, 0); & (0, 430, 0); & (0, 0, 430); \\ & (-430, 0, 0); & (0, -430, 0); & (0, 0, -430). \end{aligned}$$

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

$$\frac{3}{2}RT = \frac{\overline{C^2}}{2} \rightarrow T = \frac{(6 \times 430^2 / 6)}{3 \times (8314.3 / 42)} = 311.3 \text{ K} \quad [20 \%$$

- (ii) It is easy to show that, in general, $\overline{c^2/2} = \overline{u^2/2} + \overline{C^2/2}$. For the 6-group gas,

$$\frac{u^2}{2} = \frac{50^2 + 120^2}{2} = 8450 \text{ J/kg} = 8.45 \text{ kJ/kg}$$

$$\frac{\overline{C^2}}{2} = \frac{430^2}{2} = 92450 \text{ J/kg} = 92.45 \text{ kJ/kg}$$

For a diatomic gas at 311.3 K only the 2 rotational states will be activated. If the energy is partitioned equally, the rotational energy per unit mass is,

$$e_{rot} = 2 \left(\frac{RT}{2} \right) = 2 \times \frac{92.45}{3} = 61.63 \text{ kJ/kg} \quad [20 \%$$

- (b) (i) Simple theories of thermal conduction give $\beta \cong 1$ because they assume that all molecules make their last collision about one mean free path distance from the plane of interest and acquire there the local average kinetic energy. In fact, molecules with higher kinetic energies tend to come from further away. Taking this into account (as in the Chapman-Enskog theory) gives $\beta \cong 5/2$.

The Eucken model for diatomic and polyatomic gases adopts a factor $\beta = 2.5$ for the translational part of the heat flux while $\beta = 1$ is used for the internal (rotational and vibrational) part. Thus,

$$k = \frac{\rho \bar{C} \lambda}{2} \left[\frac{5}{2} \left(\frac{3R}{2} \right) + \left(c_v - \frac{3R}{2} \right) \right] \quad [15 \%$$

- (ii) The dynamic viscosity is $\mu \cong (\rho \bar{C} \lambda) / 2$ (this is pretty obvious from the expression for k even if it hasn't been memorised). Hence, for the 6-group gas,

$$k = \mu \left[\frac{5}{2} \left(\frac{3R}{2} \right) + \left(c_v - \frac{3R}{2} \right) \right] = 20 \times 10^{-6} \left[\frac{15}{4} + \left(\frac{5}{2} - \frac{3}{2} \right) \right] \times \frac{8314.3}{42} = 0.019 \text{ W.m}^{-1}\text{K}^{-1} \quad [15 \%]$$

- (c) The term $\overline{c_i(c^2/2)}$ is the i -direction flux of translational KE per unit mass of gas. It is decomposed by substituting $c_i = u_i + C_i$. Adopting the summation convention :

$$\begin{aligned} \frac{\overline{c_i c_j c_j}}{2} &= \frac{\overline{(u_i + C_i)(u_j + C_j)(u_j + C_j)}}{2} = \frac{\overline{(u_i + C_i)(u_j u_j + 2u_j C_j + C_j C_j)}}{2} \\ &= \frac{\overline{u_i u_j u_j + 2u_i u_j C_j + u_i C_j C_j + u_j u_j C_i + 2u_j C_j C_i + C_j C_j C_i}}{2} \\ &= \frac{u_i u^2}{2} + \frac{u_i \bar{C}^2}{2} + \overline{C_i C_j} u_j + \frac{\bar{C}_i C^2}{2} \quad (\text{using } \bar{C}_i = 0) \end{aligned} \quad [15 \%]$$

The i -direction heat flux per unit mass is $q_i = \overline{C_i(C^2/2)}$.

For the 6-group gas $C = 430$ m/s for all groups. We therefore find,

$$q_1 = q_2 = q_3 = \left(\frac{430 - 430 + 0 + 0 + 0 + 0}{6} \right) \frac{430^2}{2} = 0$$

Thus, the heat flux is zero in all directions. Actually, this is obvious because the 6-group peculiar velocity distribution function is symmetric. [15 %]

Examiner's comment:

This question was very well done. It was gratifying to see that almost all candidates had absorbed the course material very well and knew exactly what they were doing. The only serious problem occurred right at the end where most candidates identified $u_i(C^2/2)$ as the heat flux (u_i being the mean velocity and C_i being the peculiar velocity) instead of $C_i(C^2/2)$.

3. (a) The solution is simply,

$$\psi = A \cos \omega \phi + B \sin \omega \phi = \psi_0 \cos \omega (\phi - \phi_0)$$

where
$$\omega^2 = \frac{8\pi^2 I \epsilon}{h^2}$$

In order for ψ to be single-valued at $\phi - \phi_0 = 0, 2\pi, 4\pi$ etc., ω must be an integer. Thus,

$$\frac{8\pi^2 I \epsilon}{h^2} = \omega^2 = n^2 \quad \Rightarrow \quad \epsilon = \frac{n^2 h^2}{8\pi^2 I} \quad n = 0, 1, 2, \dots \quad [4]$$

(b) (i) $Z = \sum g_j \exp(-\epsilon_j / kT) = 1 \times e^0 + 1 \times e^{-\epsilon/kT} = 1 + e^\tau$

(ii) The terms in Z give the relative probabilities of a molecule's being in each of its electronic states, so the fraction of molecules in the electronically excited state is

$$f = \frac{e^\tau}{1 + e^\tau}$$

hence the internal energy associated with electronic excitation is

$$U_e = Nf\epsilon = N\epsilon \frac{e^\tau}{1 + e^\tau} \quad \Rightarrow \quad u_e = \frac{U_e}{Nm} = \frac{\epsilon}{m} \frac{e^\tau}{1 + e^\tau}$$

The electronic component of specific heat capacity is thus

$$\begin{aligned} c_v^e &= \left(\frac{\partial u_e}{\partial T} \right)_v = \frac{\epsilon}{m} \frac{d}{d\tau} \left(1 - \frac{1}{1 + e^\tau} \right) \frac{d\tau}{dT} \\ &= \frac{\epsilon}{m} \frac{e^\tau}{(1 + e^\tau)^2} \frac{\epsilon}{kT^2} = \left(\frac{\epsilon}{kT} \right)^2 \frac{k}{m} \frac{e^\tau}{(1 + e^\tau)^2} = \underline{\underline{R\tau^2 \frac{e^\tau}{(1 + e^\tau)^2}}} \end{aligned} \quad [8]$$

(iii) The required assumption is that the translational and rotational energy modes are fully excited. (This is reasonable as electronic excitation requires large energy jumps and is therefore only significant at elevated temperatures.) Together, the fully excited modes contribute $5R/2$ to c_v in accordance with the equipartition principle. Thus

$$\gamma = \frac{c_p}{c_v} = \frac{c_v + R}{c_v} = 1 + \frac{1}{5/2 + c_v^e / R}$$

Hence γ will have a minimum value when the electronic contribution to c_v is a maximum.

Taking logs (for convenience) and differentiating the expression in (ii):

$$\ln \frac{c_v^e}{R} = \tau + 2 \ln \tau - 2 \ln(1 + e^\tau)$$

$$\therefore \frac{1}{c_v^e} \frac{dc_v^e}{d\tau} = 1 + \frac{2}{\tau} - \frac{2e^\tau}{1+e^\tau}$$

$$\Rightarrow 1 + \frac{2}{\tau} = \frac{2e^\tau}{1+e^\tau} \quad \text{when } c_v^e \text{ is max.}$$

Substituting the value of $\tau = -2.4$ gives 0.1667 on the LHS and 0.1663 on the RHS. At this value of τ , the expression for electronic c_v gives

$$c_v^e / R = 2.4^2 \frac{e^{-2.4}}{(1+e^{-2.4})^2} \approx 0.43923$$

$$\therefore \gamma_{\min} = 1 + \frac{1}{5/2 + 0.43923} \approx \underline{\underline{1.340}} \quad [7]$$

Examiner's comment:

This was a relatively straightforward question and the majority of candidates demonstrated a reasonable understanding of the material. Most candidates were able to find the correct general solution to the Schrodinger equation for a diatom constrained to rotate in a plane, and also correctly identified and implemented the boundary condition so as to find the possible rotational energy states. (The only minor error was that many assumed the 'ground state' was $n=1$ rather than the correct $n=0$). In the second part of the question, most attempts at deriving the expression for the electronic component of specific heat capacity were acceptable, but many derivations contained errors that somehow disappeared to reveal the given expression. In attempting to obtain the minimum value of γ , several candidates forgot about the translational and rotational energy modes, and many others made a mess of the algebra.

4. (a) A single arrangement of the monomers may be written as a series of “-”s and “+”s, e.g., ++-++++-+...+-+ etc. There are N objects in this series which if they were all distinct could be arranged in $N!$ ways. However, the N^+ “+”s and the N^- “-”s are indistinguishable, so the total number of distinct arrangements is

$$\Omega = \frac{N!}{(N^+)!(N^-)!} \quad [3]$$

(b) The Boltzmann relation ($S = k \ln \Omega$) will apply to the configurational component of entropy if each of the arrangements is equally probable. This really requires that the energy of the “microstates” is independent of whether the monomers are oriented in the +ve or -ve directions. Writing $S = S_c + S_t$ (i.e., configurational and thermal components),

$$\begin{aligned} S_c &= k \ln \Omega = k \{ \ln N! - \ln N^+! - \ln N^-! \} \\ &= k \{ N(\ln N - 1) - N^+(\ln N^+ - 1) - N^-(\ln N^- - 1) \} \\ &= k \{ N \ln N - N^+ \ln N^+ - N^- \ln N^- \} \quad (\text{since } N^+ + N^- = N) \end{aligned}$$

But,

$$\begin{aligned} N^+ + N^- &= N & \therefore & & N^+ &= \frac{1}{2}(N + L/a) \\ N^+ - N^- &= L/a & & & N^- &= \frac{1}{2}(N - L/a) \end{aligned}$$

Hence,

$$\begin{aligned} \left(\frac{\partial S}{\partial L} \right)_{T,N} &= \left(\frac{\partial S_c}{\partial L} \right)_N = -k(1 + \ln N^+) \frac{dN^+}{dL} - k(1 + \ln N^-) \frac{dN^-}{dL} \\ &= \frac{k}{2a} \ln \left(\frac{N^-}{N^+} \right) = \frac{k}{2a} \ln \left(\frac{Na - L}{Na + L} \right) \end{aligned} \quad [8]$$

Thus, $A = k/2a$.

(c) The above result shows that the configurational entropy decreases with length. If the band is stretched adiabatically and reversibly then its entropy remains constant. Since S_c goes down the thermal component must go up, implying an increase in temperature.

$$\begin{aligned} (d) \quad \delta Q &= T\delta S & \text{and} & & \delta W &= -\tau\delta L \\ \therefore \delta U &= \delta Q - \delta W = T\delta S + \tau\delta L \end{aligned} \quad [2]$$

$$\text{Hence:} \quad \delta F = \delta U - T\delta S - S\delta T = T\delta S + \tau\delta L - T\delta S - S\delta T = \underline{\underline{\tau\delta L - S\delta T}}$$

From the theory of partial derivatives,

$$\frac{\partial^2 F}{\partial T \partial L} = \frac{\partial^2 F}{\partial L \partial T} \quad \Rightarrow \quad \left(\frac{\partial \tau}{\partial T} \right)_L = - \left(\frac{\partial S}{\partial L} \right)_T$$

Since S decreases with L this implies the tension increases with temperature (i.e., as it is heated), contrary to “normal” expectation. [7]

Examiner's comment:

The techniques required for this question were quite standard, but the physical application (i.e., the model of a rubber band) had not appeared in previous papers. This is probably why so few candidates attempted the question. Most explanations of the expression for the number of configurational microstates were loosely correct, but only one candidate gave a clear and thorough explanation. Part (b) (deriving an expression for the rate of change of entropy with length of the band) was not well done, although most candidates were able to make a start. Not a single candidate used the 'cross derivatives' in the given expression for changes in Helmholtz function to determine the effect of temperature on tension, though a few identified the correct trend with plausible physical explanations.

AJW / JBY

May 2015