

ENGINEERING TRIPOS PART IIB 2006

MODULE 4A9 – MOLECULAR THERMODYNAMICS

SOLUTIONS TO TRIPOS QUESTIONS

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1 (a) (i) Along the nozzle centre-line the flow is near-isentropic. With respect to the local flow velocity, the molecular velocity distribution will be very close to M-B and the N-S equations will hold locally. In terms of the streamwise molecular velocity component C_1 the distribution will be symmetrical around the speed V . [10 %]

(ii) A point in the wall BL where the velocity is $0.1V$ will be many mean-free paths from the wall and the flow there will be in the continuum regime. The viscous shear stress associated with the wall-normal velocity gradient is equivalent to a transport of streamwise molecular momentum towards the wall. To generate this momentum flux, the velocity distribution will be perturbed from M-B. The perturbation will not be too great and the N-S equations will be locally valid. In terms of the wall-normal molecular velocity component C_2 the distribution will be slightly skewed. The mean value of C_2 will be zero. [10 %]

(iii) Very close to the wall, the velocity distribution will deviate strongly from M-B and the N-S equations will not hold locally. Molecules coming from the bulk of the gas (negative C_2) will have a distribution similar to that described in (ii), while reflected molecules (positive C_2) will have a 'half-Maxwellian' distribution if the reflection is diffuse. In terms of the wall-normal molecular velocity component C_2 the distribution will be discontinuous. The mean value of C_2 will be zero. [10 %]

(b) (i) Making the substitution,

$$X^2 = \frac{mC^2}{2kT} \quad \rightarrow \quad dC = dX \left(\frac{2kT}{m} \right)^{1/2}$$

gives,

$$\int_0^{C_0} g_e(C) dC = \frac{4}{\sqrt{\pi}} \int_0^{C_0} C^2 \left(\frac{m}{2kT} \right)^{3/2} \exp\left(-\frac{mC^2}{2kT}\right) dC = \frac{4}{\sqrt{\pi}} \int_0^{X_0} X^2 \exp(-X^2) dX \quad [10 \%$$

The mean translational kinetic energy of a molecule is then given by,

$$\overline{\text{KE}} = \int_0^{\infty} \left(\frac{mC^2}{2} \right) g_e(C) dC = \frac{4kT}{\sqrt{\pi}} \int_0^{\infty} X^4 \exp(-X^2) dX = \frac{4kT}{\sqrt{\pi}} \frac{3\sqrt{\pi}}{8} = \frac{3kT}{2}$$

where the $3\sqrt{\pi}/8$ comes from the Table of Integrals for $n = 4$. [10 %]

(ii) Fraction of molecules with translational KE less than the mean is given by,

$$\begin{aligned}
 F &= \frac{4}{\sqrt{\pi}} \int_0^{X_0} X^2 \exp(-X^2) dX && \text{with } X_0^2 = \frac{mC_0^2}{2kT} = \frac{3kT}{2kT} = \frac{3}{2} \\
 &= \frac{4}{\sqrt{\pi}} \left[\frac{X e^{-X^2}}{(-2)} \Big|_0^{X_0} - \int_0^{X_0} \frac{e^{-X^2}}{(-2)} dX \right] \\
 &= -\frac{2X_0 e^{-X_0^2}}{\sqrt{\pi}} + \text{erf}(X_0) && \text{[Definition of erf in second Table]} \\
 &= -0.3084 + 0.9155 && \text{[erf}(\sqrt{1.5}) = 0.9155 \text{ by interpolation]} \\
 &= 0.6071 && \text{[Fraction of molecules with translational KE less than } 3kT/2 \text{]} \quad [30 \%]
 \end{aligned}$$

(iii) The mean square deviation of the KE from the mean value is given by,

$$\overline{(\text{KE} - \overline{\text{KE}})^2} = \overline{(\text{KE})^2} - 2\overline{(\text{KE})(\overline{\text{KE}})} + (\overline{\text{KE}})^2 = \overline{(\text{KE})^2} - (\overline{\text{KE}})^2$$

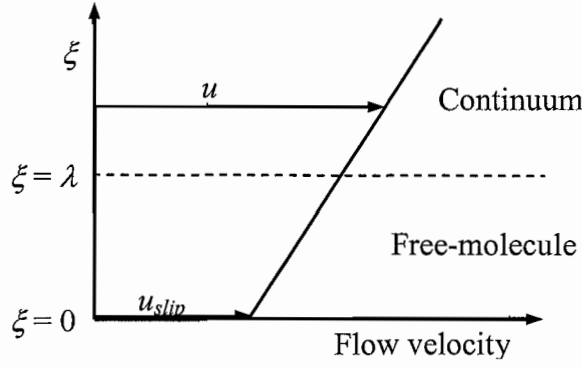
The mean of the square of the translational kinetic energy is given by,

$$\begin{aligned}
 \overline{(\text{KE})^2} &= \int_0^{\infty} \left(\frac{mC^2}{2} \right)^2 g_e(C) dC = \frac{4(kT)^2}{\sqrt{\pi}} \int_0^{\infty} X^6 \exp(-X^2) dX \\
 &= \frac{4(kT)^2}{\sqrt{\pi}} \frac{15\sqrt{\pi}}{16} = \frac{15(kT)^2}{4}
 \end{aligned}$$

where the $15\sqrt{\pi}/16$ comes from the Table of Integrals for $n = 6$. Hence,

$$\begin{aligned}
 \overline{(\text{KE} - \overline{\text{KE}})^2} &= \overline{(\text{KE})^2} - (\overline{\text{KE}})^2 = \frac{15(kT)^2}{4} - \left(\frac{3kT}{2} \right)^2 = \frac{3(kT)^2}{2} \\
 \sqrt{\overline{(\text{KE} - \overline{\text{KE}})^2}} &= \sqrt{\frac{3}{2}} kT && [20 \%]
 \end{aligned}$$

2 (a)



Assume molecules make their last collision at $\xi = \lambda$ before striking the wall. The velocity is extrapolated through the strongly non-equilibrium F-M region and the velocity gradient is therefore constant. Hence, the x -momentum flux incident on the wall is,

$$M_i = \frac{\rho \bar{C}}{4} \left(u_{slip} + \lambda \frac{du}{d\xi} \right)$$

Assuming diffuse reflection, the x -momentum flux reflected from the wall is $M_r = 0$, and so the net x -momentum flux to the wall is,

$$M_i - M_r = \frac{\rho \bar{C}}{4} \left(u_{slip} + \lambda \frac{du}{d\xi} \right)$$

In the continuum region the net momentum flux is equal to the shear stress. Hence,

$$\tau = \mu \frac{du}{d\xi} = \frac{\rho \bar{C} \lambda}{2} \frac{du}{d\xi}$$

Equating the momentum fluxes gives,

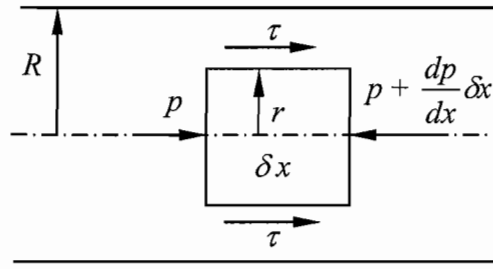
$$\frac{\rho \bar{C}}{4} \left(u_{slip} + \lambda \frac{du}{d\xi} \right) = \frac{\rho \bar{C} \lambda}{2} \frac{du}{d\xi}$$

From which (as $\xi = R - r$),

$$u_{slip} = \lambda \left(\frac{du}{d\xi} \right)_{\xi=0} = -\lambda \left(\frac{du}{dr} \right)_{r=R}$$

[40 %]

(b)



As the flow is incompressible, the momentum fluxes entering and leaving the control volume are equal. Applying the force-momentum principle gives,

$$2\pi r \tau \delta x - \pi r^2 \frac{dp}{dx} \delta x = 0 \quad \rightarrow \quad \tau = \frac{r}{2} \frac{dp}{dx}$$

We now make the continuum approximation for the shear stress giving,

$$\mu \frac{du}{dr} = \frac{r}{2} \frac{dp}{dx}$$

This is valid across the tube if we apply the slip boundary condition (compensating for the Knudsen layer near the wall). Hence, integrating with respect to r subject to $u = u_{slip}$ at $r = R$,

$$u = u_{slip} + \left(-\frac{dp}{dx} \right) \left(\frac{R^2 - r^2}{4\mu} \right)$$

At the tube wall,

$$u_{slip} = -\lambda \left(\frac{du}{dr} \right)_{r=R} = \lambda \frac{R}{2\mu} \left(-\frac{dp}{dx} \right) = Kn \frac{R^2}{2\mu} \left(-\frac{dp}{dx} \right)$$

Thus, the velocity distribution is given by,

$$u = \left[\frac{(1+2Kn)R^2 - r^2}{2\mu} \right] \left(-\frac{dp}{dx} \right) \quad [40 \%]$$

If ρ is the density, the mass flowrate is,

$$\begin{aligned} \dot{m} &= \int_0^R 2\pi r \rho u \, dr = \frac{2\pi \rho}{2\mu} \left(-\frac{dp}{dx} \right) \int_0^R [(1+2Kn)R^2 r - r^3] \, dr \\ &= \frac{\pi \rho}{\mu} \left(-\frac{dp}{dx} \right) \left[\frac{(1+2Kn)R^4}{2} - \frac{R^4}{4} \right] = (1+4Kn) \frac{\rho \pi R^4}{4\mu} \left(-\frac{dp}{dx} \right) \end{aligned}$$

The continuum result is obtained by setting $Kn = 0$. Hence,

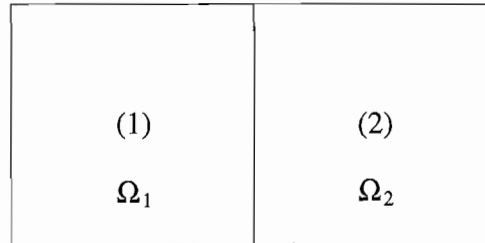
$$\frac{\dot{m}}{\dot{m}_{cont}} = (1+4Kn) \quad [20 \%]$$

Q3

(a) S is the entropy of a system in J/K (or units consistent with k)

k is Boltzmann's constant, 1.38×10^{-23} J/K

Ω is the number of microstates of the system consistent with the constraints.



Consider a system composed of two subsystems (1) and (2) as shown above. The total number of microstates available to the composite system is:

$$\begin{aligned} \Omega &= \Omega_1 \times \Omega_2 \\ \therefore S &= k \ln \Omega = k \ln(\Omega_1 \times \Omega_2) \\ &= k \ln \Omega_1 + k \ln \Omega_2 \\ &= S_1 + S_2 \end{aligned}$$

i.e., the entropy of the composite system is the sum of the entropies of the two [25%] subsystems: *extensive*.

(b) Let ΔS be the entropy change (which will be -ve) in going from the equilibrium to the perturbed state. Then,

$$\begin{aligned} \Delta S &= c_C \ln \left(1 + \frac{\Delta T_C}{T} \right) + c_F \ln \left(1 + \frac{\Delta T_F}{T} \right) \\ &= c_C \left\{ \frac{\Delta T_C}{T} - \frac{1}{2} \left(\frac{\Delta T_C}{T} \right)^2 + \dots \right\} + c_F \left\{ \frac{\Delta T_F}{T} - \frac{1}{2} \left(\frac{\Delta T_F}{T} \right)^2 + \dots \right\} \end{aligned}$$

but since the system is isolated, $c_C \Delta T_C + c_F \Delta T_F = 0$. Thus,

$$\begin{aligned} \Delta S &\approx -\frac{1}{2} c_C \left(\frac{\Delta T_C}{T} \right)^2 (1 + c_C / c_F) \\ &= -0.5 \times 380 \times (0.001/300)^2 \times (1 + 19/22) \\ &= -3.93 \times 10^{-9} \text{ J/K} \end{aligned}$$

$$\begin{aligned}\Delta S &= S_2 - S_1 \\ \text{Now} \quad &= k \ln \Omega_2 - k \ln \Omega_1 = k \ln \frac{\Omega_2}{\Omega_1}\end{aligned}$$

where subscript 2 denotes the perturbed state and subscript 1 the equilibrium state. The relative probability of the system being found in state 2 is thus:

$$\begin{aligned}\frac{\Omega_2}{\Omega_1} &= \exp(\Delta S / k) \\ &= \exp(-2.85 \times 10^{14})\end{aligned}$$

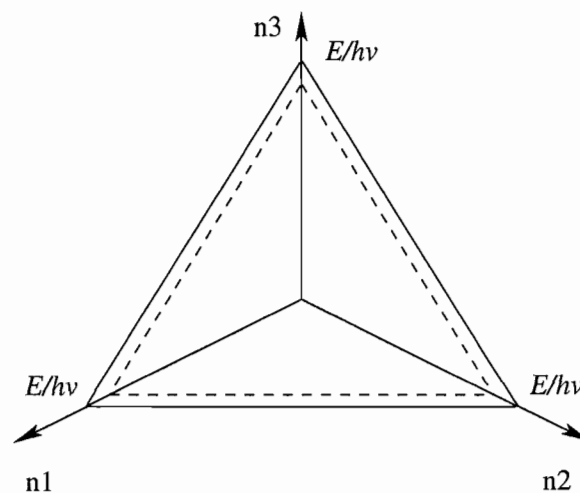
i.e., very small.

Even such a small fluctuation is vanishingly improbable.

[45%]

(c) $n_1 + n_2 + n_3 = E / h\nu$

i.e., a plane normal to $(1,1,1)^T$



No. of available states = volume contained between two planes

$$\begin{aligned}&= (1/6) \times \{(E_2/h\nu)^3 - (E_1/h\nu)^3\} \\ &= (1/6) \times \{(1.001 \times 10^{-6} / 6.626 \times 10^{-20})^3 - (1 \times 10^{-6} / 6.626 \times 10^{-20})^3\} \\ &= \underline{1.72 \times 10^{36} \text{ states.}}\end{aligned}$$

[30%]

Q4

- (a) (i) For H_2 , the characteristic temperature of rotation is relatively high (87.5K) due to the low moment of inertia of hydrogen molecules. Thus at very low temperatures, only the translational energy modes are excited. Assuming the Boltzmann limit still applies to these modes (doubtful) the specific heat capacity is $c_v = 3R/2$ in this region (3 translational degrees of freedom). The rotational energy modes become excited once the temperature is of the order of the characteristic temperature, so c_v increases and tends towards $5R/2$ at around room temperature (3 translational + 2 rotational degrees of freedom). At very high temperatures, the vibrational energy modes become excited such that c_v tends towards $7R/2$ (3 translational + 2 rotational + 2 vibrational degrees of freedom), though dissociation becomes significant at such temperatures.

(ii) At low temperature: $c_v = 3R/2 = 1.5 \times 8315 / 2 = 6.24 \text{ kJ/kgK}$

$$\gamma = (c_v + R) / c_v = 5/3 = 1.67$$

At room temperature: $c_v = 5R/2 = 2.5 \times 8315 / 2 = 10.4 \text{ kJ/kgK}$

$$\gamma = (c_v + R) / c_v = 7/5 = 1.40$$

At high temperature: $c_v = 7R/2 = 3.5 \times 8315 / 2 = 14.6 \text{ kJ/kgK}$

$$\gamma = (c_v + R) / c_v = 9/7 = 1.29$$

- (iii) For O_2 , the characteristic temperature of rotation is very much lower (2.08K) so the low temperature plateau does not exist. (The vibrational temperature is also much lower, but this is not required in the answer). The two constant c_v regimes for O_2 will be at $5R/2$ and $7R/2$, though of course R will be much lower.

[40%]

(b) (i) $Z_{el} = \sum g_n \exp(-\epsilon_n / kT) = 1 + g \exp(-\epsilon / kT)$

$$U = NkT^2 \frac{\partial}{\partial T} \ln Z = NkT^2 \frac{\partial}{\partial T} (\ln Z_{tr} + \ln Z_{el}) = U_{tr} + U_{el}$$

$$\frac{\partial Z_{el}}{\partial T} = \frac{g\epsilon}{kT^2} \exp(-\epsilon / kT)$$

$$\therefore U_{el} = \frac{Ng\epsilon \exp(-\epsilon / kT)}{1 + g \exp(-\epsilon / kT)} = \frac{Ng\epsilon}{\exp(\epsilon / kT) + g}$$

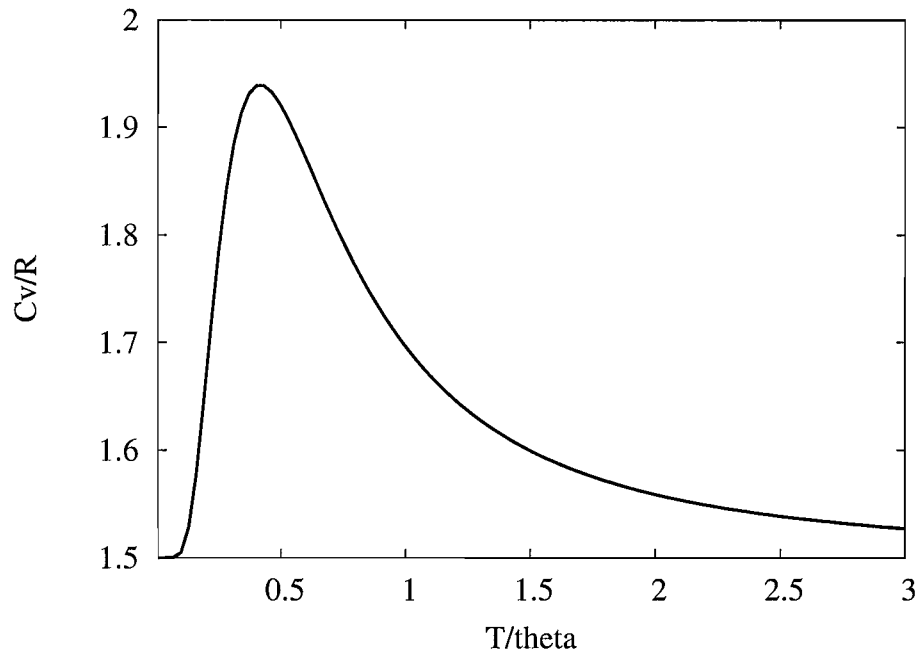
$$C_{v,el} = \frac{\partial U_{el}}{\partial T} = \frac{Ng\epsilon^2}{kT^2} \frac{\exp(\epsilon / kT)}{(\exp(\epsilon / kT) + g)^2}$$

per unit mass: $c_v = C_v / Nm = c_{v,tr} + c_{v,el} = R \left\{ \frac{3}{2} + \left(\frac{\theta}{T} \right)^2 \frac{g \exp(\theta/T)}{(\exp(\theta/T) + g)^2} \right\}$

[45%]

where $\theta = \epsilon/k$ is a characteristic temperature for electronic excitation.

(ii) A detailed plot is not required. The main points to include are that the contribution to c_v from electronic excitation disappears at low and high temperature and that there is thus a maximum in between. These points are evident from the expression for Z .



[15%]

Variation of c_v for $g=1$

