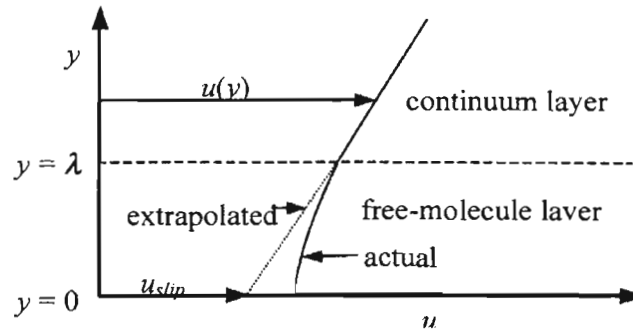


**ENGINEERING TRIPOS PART IIB 2014**  
**MODULE 4A9 – MOLECULAR THERMODYNAMICS**

**SOLUTIONS**

1. (a)



The slip velocity is defined by extrapolating the velocity profile through the free-molecule (or Knudsen) layer to the surface, keeping the velocity gradient  $du/dy$  the same. The ‘slip velocity’ is thus distinct from the actual velocity at the surface (which is of no real interest). [10%]

Assuming molecules make their last collision at  $y = \lambda$  before striking the plate :

$$x\text{-momentum flux incident on plate} = M_i = \frac{\rho \bar{C}}{4} \left( u_{slip} + \lambda \frac{du}{dy} \right)$$

Assuming molecules are reflected diffusely (*i.e.*, no preferential direction) :

$$x\text{-momentum flux reflected from plate} = M_r = 0$$

$$\text{Shear stress on the plate, } \tau = M_i - M_r = \frac{\rho \bar{C}}{4} \left( u_{slip} + \lambda \frac{du}{dy} \right)$$

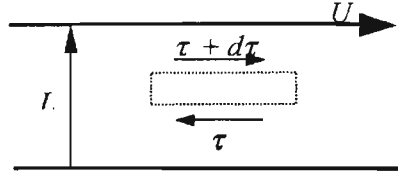
$$\text{In the continuum region } y > \lambda, \quad \tau = \mu \frac{du}{dy} = \frac{\rho \bar{C} \lambda}{2} \frac{du}{dy}$$

$$\text{Assuming the shear stress is uniform, } \frac{\rho \bar{C}}{4} \left( u_{slip} + \lambda \frac{du}{dy} \right) = \frac{\rho \bar{C} \lambda}{2} \frac{du}{dy}$$

$$\text{Hence, the slip velocity is given by, } u_{slip} = \lambda \frac{du}{dy} \quad [20\%]$$

This result is approximate because the transition from the free-molecule to the continuum layer actually occurs over a finite distance. To get an ‘exact’ result it would be necessary to solve the Boltzmann equation in the near-wall region. [5%]

(b)



The only force acting on the elementary control volume is the shear stress. Hence,

$$\left( \tau + \frac{d\tau}{dy} \delta y \right) \delta x - \tau \delta x = 0 \quad \rightarrow \quad \frac{d\tau}{dy} = 0 \quad \rightarrow \quad \tau = \text{constant}$$

This result is true for all flow regimes (continuum and non-continuum) because no specific model has been used for  $\tau$  ( $\tau = \mu du/dy$  only holds when the N-S equation is valid). [15%]

(c) The N-S equation is valid for  $0 < y < L$  so that,

$$\frac{du}{dy} = \frac{\tau}{\mu} \quad \rightarrow \quad u = \frac{\tau y}{\mu} + \text{const.} \quad \rightarrow \quad u = \frac{\tau y}{\mu} + u_{slip} \quad (u = u_{slip} \text{ at } y = 0)$$

At  $y = L$ ,  $u = U - u_{slip}$  and hence,

$$U - u_{slip} = \frac{\tau L}{\mu} + u_{slip} \quad \rightarrow \quad \tau = \frac{\mu U}{L} - \frac{2\mu u_{slip}}{L}$$

Now,  $u_{slip} = \lambda du/dy = \lambda \tau / \mu$ . For continuum flow,  $u_{slip} = 0$  and so  $\tau_0 = \mu U / L$ . Hence,

$$\tau = \tau_0 - \frac{2\lambda\tau}{L} = \tau_0 - 2\tau Kn \quad \rightarrow \quad \tau = \frac{\tau_0}{1 + 2Kn} \quad [20\%]$$

The mass flowrate is given by  $\dot{m} = \rho \bar{u} L$  where  $\bar{u}$  is the mean velocity. The velocity profile is linear from  $u = u_{slip}$  at  $y = 0$  to  $u = U - u_{slip}$  at  $y = L$ . Hence,  $\bar{u} = U/2$  and  $\dot{m} = \rho UL/2$ .

This expression is the same as for continuum flow. However, although  $U$  and  $L$  are the same, the density for slip-flow will be lower than for continuum flow and so  $\dot{m}$  will be lower. [15%]

(d) The approach for slip-flow [which is based on the result of part (a)] is not appropriate for transition flow because  $\lambda \approx L$  and so the Knudsen layer would occupy much of the channel. [15%]

2. (a) The energy of a diatomic molecule of mass  $m$  and absolute velocity  $(c_1, c_2, c_3)$  is

$$E = \frac{m(c_1^2 + c_2^2 + c_3^2)}{2} + E_{int}$$

where  $E_{int}$  is the molecular internal energy (*i.e.*, in this case due to rotation of the molecule).

The peculiar velocity of a molecule is defined by  $C_i = c_i - \bar{c}_i = c_i - u_i$  and hence,

$$E = \frac{m[(u_1 + C_1)^2 + C_2^2 + C_3^2]}{2} + E_{int} = \frac{mu_1^2}{2} + \frac{m(C_1^2 + C_2^2 + C_3^2)}{2} + mC_1 + E_{int}$$

Averaging over all molecules and noting that  $(C_1^2 + C_2^2 + C_3^2) = C^2$  and  $\bar{C}_i = 0$  gives,

$$\bar{E} = \frac{mu_1^2}{2} + \frac{m\overline{C^2}}{2} + \bar{E}_{int}$$

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

$$\frac{3kT}{2} = \frac{m\overline{C^2}}{2}$$

We assume that a diatomic molecule at around ambient temperature has 2 activated rotational, and zero activated vibrational, degrees of freedom. Hence, by the equipartition principle (an average energy of  $kT/2$  for each activated degree of freedom),  $\bar{E}_{int} = kT$ . Thus,

$$\bar{E} = \frac{mu_1^2}{2} + \frac{3kT}{2} + kT = \frac{mu_1^2}{2} + \frac{5kT}{2} \quad \rightarrow \quad f = 5 \quad [30\%]$$

(b) Assume molecules make their last collision at  $x_2 = \pm \lambda$  and that they acquire there, on average, the local mean molecular energy. At  $x_2 = \pm \lambda$ ,

$$T(\pm\lambda) = T(0) \pm \lambda \frac{dT}{dx_2} \quad u_1(\pm\lambda) = u_1(0) \pm \lambda \frac{du_1}{dx_2}$$

The mean molecular energy at  $x_2 = \pm \lambda$  is thus given by,

$$\bar{E}_{\pm\lambda} = f \frac{k}{2} \left[ T(0) \pm \lambda \frac{dT}{dx_2} \right] + \frac{m}{2} \left[ u_1(0) \pm \lambda \frac{du_1}{dx_2} \right]^2$$

The energy flux through unit area of the plane  $x_2 = 0$  from above (+) and below (-) is,

$$\frac{n\bar{C}}{4} \left\{ f \frac{k}{2} \left[ T(0) \pm \lambda \frac{dT}{dx_2} \right] + \frac{m}{2} \left[ u_1(0) \pm \lambda \frac{du_1}{dx_2} \right]^2 \right\}$$

The net energy flux per unit area in the positive  $x_2$  direction is therefore,

$$\frac{n\bar{C}}{4} \left[ -f k \lambda \frac{dT}{dx_2} - 2m\lambda u_1(0) \frac{du_1}{dx_2} \right]$$

Noting that  $nm = \rho$  and  $k = mR$  where  $R$  is the gas constant per unit mass,

$$\text{Energy flux per unit area} = -\frac{fR}{2} \frac{\rho\bar{C}\lambda}{2} \frac{dT}{dx_2} - \frac{\rho\bar{C}\lambda}{2} u_1(0) \frac{du_1}{dx_2}$$

Hence,

$$A = \frac{fR}{2} \frac{\rho\bar{C}\lambda}{2} \quad \text{and} \quad B = \frac{\rho\bar{C}\lambda}{2} u_1(0) \quad [40\%]$$

(c) The term  $fR/2$  is the constant volume specific heat capacity  $c_v$  and  $A$  is the simple hard sphere kinetic theory result for the thermal conductivity  $K$ . The kinetic theory result for the viscosity is  $\mu = \rho\bar{C}\lambda/2$  and  $\mu du_1/dx_2 = \tau_{12}$  where  $\tau_{12}$  is the shear stress. Hence,

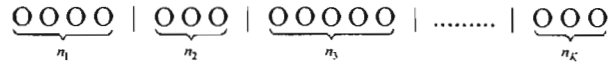
$$\text{Energy flux per unit area} = -A \frac{dT}{dx_2} - B \frac{du_1}{dx_2} = -K \frac{dT}{dx_2} - u_1(0) \tau_{12}$$

Macroscopically, the first term is the heat flux due to conduction and the second term is the work done by the shear stress against the mean velocity. [15%]

(d) The kinetic theory result for the viscosity is quite close to the Chapman-Enskog value and so we would expect the shear stress work term to be quite accurate. The simple theory for the thermal conductivity does not agree well with the Chapman-Enskog result because the calculation of the translational energy flux ignores the fact that molecules with higher velocities tend to come from greater distances. The result could be improved by including the Eucken modification. [15%]

3. (a) (i) The oscillators are independent so the total energy is  $E = (n_1 + n_2)h\nu$  and therefore  $(n_1 + n_2) = 5$ . Thus,  $n_1$  can take on six possible values (0 to 5) for each one of which  $n_2$  will be fixed at  $5 - n_1$ . There are therefore six microstates. [2]

(a) (ii) The quantum numbers  $n_1, n_2 \dots n_K$  must sum to  $M$  so we consider  $M$  balls and  $K - 1$  partitions, as shown:



There are therefore  $(M + K - 1)$  things, but the  $M$  balls are indistinguishable and the  $(K - 1)$  partitions are also indistinguishable. Thus,

$$\Omega = \frac{(M + K - 1)!}{M!(K - 1)!} \quad \text{whence } A = (M + K - 1), B = M \text{ and } C = (K - 1). \quad [6]$$

(b) (i) Assume that the entropy is equal to the statistical analog of entropy and that both  $M$  and  $K$  are  $\gg 1$ . Thus,

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

with  $M = E / h\nu$  and  $K = 3N$  (three oscillators per atom corresponding to three directions). In the high temperature limit we can also assume that  $M \gg K$  so

$$\begin{aligned} S &\approx k \left\{ M \ln \left( 1 + \frac{K}{M} \right) + K \ln \left( \frac{M}{K} \right) \right\} \\ &= 3Nk + 3Nk \ln \left( \frac{E}{3N h\nu} \right) \end{aligned} \quad [7]$$

(b) (ii) For a closed system,  $TdS = dE + pdV$  and therefore:

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_V = \frac{3Nk}{E} \Rightarrow E = 3NkT = 3mRT \Rightarrow c_v = 3R \quad (m \text{ total mass, } R = k/m_{\text{atom}})$$

This gives an  $R/2$  contribution to each squared term (PE and KE) associated with oscillations for each of the three directions, i.e.,  $c_v = 6 \times R/2$ , consistent with the equipartition principle. [5]

4.(a) In the ground state all  $n_i = 1$ , so for 4 times the ground state energy,  
 $n^2 = \sum n_i^2 = 4 \times 3 = 12$ . Possible states are therefore as shown below:

$n_1$	$n_2$	$n_3$	$n^2$	Degeneracy, $g_n$
1	1	1	3	1
1	1	2	6	3
1	2	1		
2	1	1		
1	2	2	9	3
2	1	2		
2	2	1		
1	1	3	11	3
1	3	1		
3	1	1		
2	2	2	12	1

[4]

(b) (i) 
$$N = \frac{pV}{kT} = \frac{10^6 \times 10^{-3}}{1.38 \times 10^{-23} \times 400} = \underline{1.81 \times 10^{23} \text{ molecules}}$$

(ii) The number of states with energy less than or equal to  $\epsilon$  is given by 1/8 of the volume of a sphere of radius  $n$ :

$$\Gamma(\epsilon) = \frac{1}{8} \times \frac{4\pi}{3} \left( \frac{8mV^{2/3}\epsilon}{h^2} \right)^{3/2} = \frac{4\pi V}{3h^3} (2m\epsilon)^{3/2}$$

The average energy of a molecule is  $\bar{\epsilon} = \frac{3kT}{2}$ , hence

$$\Gamma(\epsilon) = \frac{4\pi V}{3h^3} (3mkT)^{3/2} = \frac{4\pi \times 10^{-3}}{3 \times (6.626 \times 10^{-34})^3} \left( \frac{3 \times 1.38 \times 10^{-23} \times 400 \times 4}{6.023 \times 10^{26}} \right)^{3/2} = \underline{1.66 \times 10^{28} \text{ states}}$$

There are approximately  $10^5$  states for each molecule so most states are empty and the probability of finding two or more molecules in the same states is negligible.

[8]

(c) Writing  $\epsilon = mC^2 / 2$  gives  $\Gamma(C) = \frac{4\pi V}{3h^3} (mC)^3$  (no. of states with speed  $\leq C$ )

Thus,

$$\underline{g(C) = \frac{d\Gamma}{dC} = \frac{4\pi V m^3 C^2}{h^3}}$$

[5]

(d) The term  $\frac{\exp(-mC^2/2kT)}{Z}$  is the probability that a molecule is in a particular energy state that has a speed  $C$ . To obtain the probability that a molecule has a speed in the range  $C$  to  $C + dC$  then we multiply this term by the number of states in this speed range,  $g(C) dC$ , but this will only be correct if the probability of there being more than one molecule in the same state is vanishingly small. From the answers to part (b) the expression therefore becomes inaccurate when  $p$  is high and (especially) when  $T$  is low.

[3]

AJW / JBY