ENGINEERING TRIPOS PART IIB 2008

MODULE 4A9 – MOLECULAR THERMODYNAMICS

SOLUTIONS TO TRIPOS QUESTIONS

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ANSWERS

1 (a) $\beta = 1$

(b) $k = \dfrac{\rho \overline{C} \lambda}{2}\left[\beta \dfrac{3R}{2} + \left(c_v - \dfrac{3R}{2}\right)\right]$ with $\beta = \dfrac{5}{2}$

(c) $(T_0 - T_\mathrm{w}) = \lambda \dfrac{dT}{dy}$

2 (a) $\overline{C} = \left(\dfrac{8RT}{\pi}\right)^{1/2}$

(b) (i) 0.96 g/hr (ii) 17.0 g/hr

3 (c) 2.3×10^{28} 1.45×10^{22}

4 (a) 4/35, 9/35, 12/35, 2/7

(b) (i) $\Delta S_{\mathrm{sys}} = mc_\mathrm{v} \ln\left(1 + \dfrac{\Delta T}{T_\mathrm{o}}\right)$

(ii) $\Delta S_{\mathrm{res}} = -mc_\mathrm{v} \dfrac{\Delta T}{T_\mathrm{o}}$

(iii) $\dfrac{P(T)}{P(T_\mathrm{o})} = \exp\{-mc_\mathrm{v}\Delta T^2 / 2kT_\mathrm{o}^2\}$

(iv) 1.86×10^{-9} K

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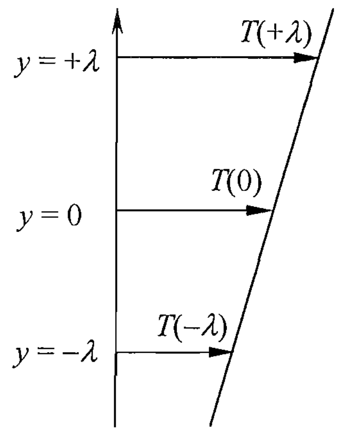
1. (a)

Assume molecules make their last collision one mean free path above or below the plane $y = 0$.



Flux of KE from below $= \dfrac{\rho \bar{C}}{4} c_v \left[T(0) - \lambda \dfrac{dT}{dy} \right]$

Flux of KE from above $= \dfrac{\rho \bar{C}}{4} c_v \left[T(0) + \lambda \dfrac{dT}{dy} \right]$

Net flux of KE in positive y-direction = heat flux $= q = \dfrac{\rho \bar{C} \lambda c_v}{2} \dfrac{dT}{dy}$

Thermal conductivity k is defined by $q = -k\dfrac{dT}{dy}$ and hence, $k = \dfrac{\rho \bar{C} \lambda c_v}{2}$.

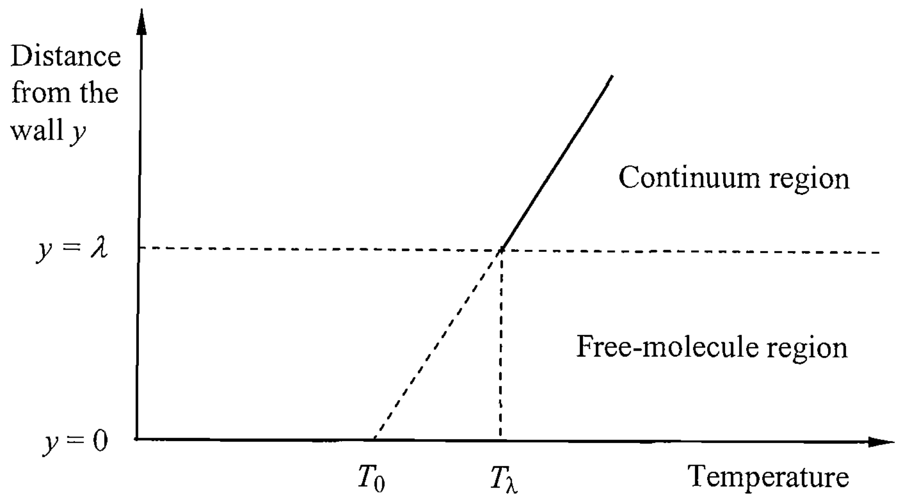
Thus $\beta = 1$. [35 %]

More detailed solutions of the Boltzmann equation give $\beta = 5/2$. This is because molecules with higher velocity (and therefore higher KE) tend to come from further away and this correlation is not accounted for in the simpler mean-free-path theories. [5 %]

(b) Eucken suggested that the effect of the high velocity molecules leading to $\beta = 5/2$ should only be applied to the contribution from the translational KE and that the contribution from the rotational and vibrational energies should be treated as in the simple theories. The contribution of the translational KE to c_v is equal to $3R/2$ by the equipartition principle (there are 3 translational degrees of freedom and each contributes $RT/2$ per unit mass to the total energy). This leaves $(c_v - 3R/2)$ to represent the rotaional and vibrational contributions to the specific heat. Hence, the Eucken expression for the thermal conductivity of a diatomic or polyatomic gas is,

$$k = \frac{\rho \bar{C} \lambda}{2} \left[\beta \frac{3R}{2} + \left(c_v - \frac{3R}{2} \right) \right] \quad \text{with} \quad \beta = \frac{5}{2}.$$ [20 %]

(c)



For the free-molecule region :

KE flux carried to the wall by incident molecules $= \dfrac{\rho \overline{C}}{4} c_v T_\lambda$

KE flux carried from the wall by reflected molecules $= \dfrac{\rho \overline{C}}{4} c_v T_w$

(The latter expression assumes complete thermal accommodation to the wall temperature.)

Hence, net KE flux in the positive y-direction $= \dfrac{\rho \overline{C}}{4} c_v (T_w - T_\lambda)$

For the continuum region :

Net KE flux in the positive y-direction $= q_y = -k \dfrac{dT}{dy}$

Matching the fluxes gives :

$$\frac{\rho \overline{C}}{4} c_v (T_w - T_\lambda) = -k \frac{dT}{dy} = -\frac{\rho \overline{C} \lambda c_v}{2} \frac{dT}{dy}$$

where the final expression comes from the result of part (a) with $\beta = 1$.

Substituting $T_\lambda = T_0 + \lambda \dfrac{dT}{dy}$ gives the required expression for the temperature jump :

$$(T_0 - T_w) = \lambda \frac{dT}{dy}$$ [40 %]

Note : If $\beta = 5/2$ is used when substituting for k then the free-molecule fluxes probably ought to be modified similarly (although the theory doesn't really stand up to this level of detailed analysis).

2. (a) The mean molecular speed is given by,

$$\bar{C} = \int_0^\infty C g_e(C)\,dC = \int_0^\infty \frac{4\pi C^3}{(2\pi RT)^{3/2}} \exp\left(-\frac{C^2}{2RT}\right) dC$$

Defining $x = \dfrac{C}{\sqrt{2RT}}$ and hence $dx = \dfrac{dC}{\sqrt{2RT}}$ the integral is transformed to,

$$\bar{C} = \frac{4\pi (2RT)^{3/2} (2RT)^{1/2}}{(2\pi RT)^{3/2}} \int_0^\infty x^3 \exp(-x^2)\,dx$$

Using the given integral, $\int_0^\infty x^3 \exp(-x^2)\,dx = \dfrac{1}{2}$, we obtain,

$$\bar{C} = \left(\frac{8RT}{\pi}\right)^{1/2}$$ [25 %]

The molar mass of N_2 is 28 kg/kmol so $R_{N2} = 8314.3/28 = 298$ J/kg K. Hence,

$$\bar{C}_{N2} = \left(\frac{8 \times 298 \times 300}{\pi}\right)^{1/2} = 477 \text{ m/s}$$ [5 %]

(b) (i) $D = 0.1$ μm. The Knudsen number is defined by $Kn = \lambda/D$ where λ is the mean free path. λ can be estimated using the approximate formula $\mu = \rho \bar{C} \lambda/2$. Hence,

$$\lambda = \frac{2\mu}{\rho_A \bar{C}} = \frac{2\mu RT}{p_A \bar{C}} = \frac{2 \times 18.3 \times 10^{-6} \times 298 \times 300}{5000 \times 477} = 1.38 \times 10^{-6} \text{ m} = 1.38\ \mu\text{m}$$

$$Kn = \frac{\lambda}{D} = \frac{1.38}{0.1} = 13.8 \gg 1 \quad \text{(Free molecule regime)}$$ [10 %]

Leakage in the free molecule regime is by effusion. If the total flow area is A :

$$\text{Molecular mass flowrate from A to B} = \frac{\rho_A \bar{C} A}{4} = \frac{p_A \bar{C} A}{4RT}$$

$$\text{Molecular mass flowrate from B to A} = \frac{\rho_B \bar{C} A}{4} = \frac{p_B \bar{C} A}{4RT}$$

$$\text{Net mass flowrate A to B} = \frac{(p_A - p_B)\bar{C} A}{4RT} = \frac{(5000 - 4800) \times 477 \times 1.0 \times 10^{-6}}{4 \times 298 \times 300}$$

$$= 0.267 \times 10^{-6} \text{ kg/s} = 0.96 \text{ g/hr}$$ [25 %]

(ii) $D = 50\ \mu m$. The mean free path $\lambda = 1.38\ \mu m$ as before

$$Kn = \frac{\lambda}{D} = \frac{1.38}{50} = 0.028 \ll 1 \quad \text{(Continuum regime)}$$ [5 %]

Leakage in the continuum regime is calculated using conventional fluid mechanics (estimation of the mass flowrate through an orifice). Assuming inviscid flow (actually a poor assumption because the Reynolds number is very low) the velocity V at the hole is obtained by applying Bernoulli's equation from the stagnation pressure p_A to the plane of the hole where the static pressure will approximately p_B. The density can be assumed constant at ρ_A because the pressure drop is small and the flow essentially incompressible. Thus,

$$p_A = p_B + \frac{1}{2}\rho_A V^2$$

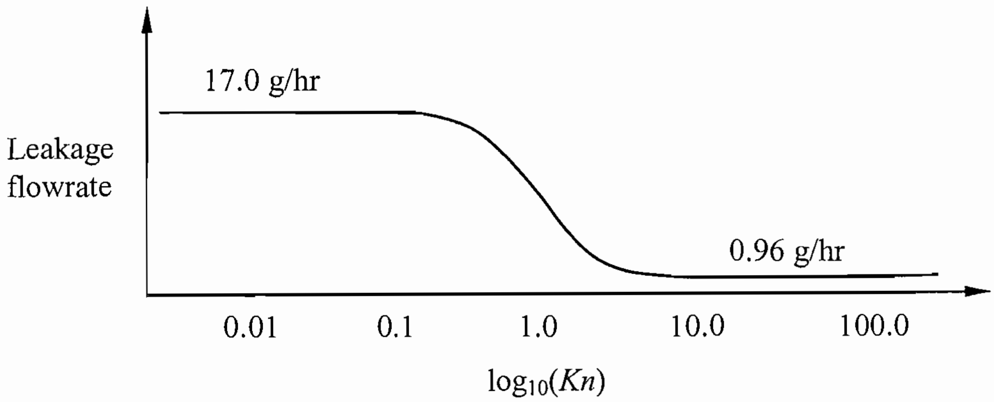
$$V = \left[\frac{2(p_A - p_B)}{\rho_A}\right]^{1/2} = \left[\frac{2RT(p_A - p_B)}{p_A}\right]^{1/2} = \left[\frac{2\times 298\times 300\times(5000-4800)}{5000}\right]^{1/2}$$

$= 84.6$ m/s (Mach number = 0.24 so incompressible assumption is OK)

$$\text{Leakage mass flowrate} = \rho_A VA = \frac{p_A VA}{RT} = \frac{5000\times 84.6\times 1.0\times 10^{-6}}{298\times 300}$$

$= 4.73\times 10^{-6}$ kg/s $=$ 17.0 g/hr [20 %]

(iii) A graph of leakage mass flowrate versus $\log_{10}(Kn)$ will look something like this :



[10 %]

3 **(a)** ε - total energy of the particle

ε_p - potential energy of the particle

ψ - the wave function, defined such that $|\psi|^2$ dV is the probability of finding the particle within the elemental volume dV.

(b) $\varepsilon = \frac{1}{2}m(u_1^2 + u_2^2 + u_3^2)$ $\varepsilon_p = 0$

$$\therefore \quad \nabla^2\psi + \frac{4\pi^2 m^2}{h^2}(u_1^2 + u_2^2 + u_3^2)\psi = 0$$

$$\therefore \quad \psi_2\psi_3\frac{d^2\psi_1}{dx_1^2} + \psi_1\psi_3\frac{d^2\psi_2}{dx_2^2} + \psi_1\psi_2\frac{d^2\psi_3}{dx_3^2} + \frac{4\pi^2}{h^2}(p_1^2 + p_2^2 + p_3^2)\psi_1\psi_2\psi_3 = 0$$

$$\therefore \quad \frac{1}{\psi_1}\frac{d^2\psi_1}{dx_1^2} + \frac{1}{\psi_2}\frac{d^2\psi_2}{dx_2^2} + \frac{1}{\psi_3}\frac{d^2\psi_3}{dx_3^2} + \frac{4\pi^2}{h^2}(p_1^2 + p_2^2 + p_3^2) = 0$$

Each of the first three terms is a function only of x_1 , x_2 and x_3 respectively and must therefore be constant. It is also evident that ψ_1 must depend only on the momentum in the x_1 direction etc. It therefore holds that

$$\frac{1}{\psi_1}\frac{d^2\psi_1}{dx_1^2} + \frac{4\pi^2 p_1^2}{h^2} = 0$$

and similarly for directions x_2 and x_3 .

The solution is:

$$\psi_1 = A\sin\left(\frac{2\pi|p_1|}{h}x_1\right) + B\cos\left(\frac{2\pi|p_1|}{h}x_1\right) \quad \text{with } \psi_1(0) = \psi_1(a) = 0 .$$

The b/c's give $B = 0$ and $\frac{2\pi|p_1|a}{h} = n_1\pi$, where n_1 is a positive integer. The momentum is thus quantized, such that $|p_1| = n_1\,(h / 2a)$ and n_1 is the number of half DeBroglie wavelengths that fit inside the box in the x_1 direction.

The kinetic energy is thus given by:

$$\varepsilon = \frac{p_1^2 + p_2^2 + p_3^2}{2m} = \frac{h^2}{8ma^2}\left(n_1^2 + n_2^2 + n_3^2\right)$$

(c) The number of energy states with energy less than or equal to ε is given by the volume of the octant of a sphere in n-space.

i.e., $\Gamma(\varepsilon) = \frac{1}{8}4\pi n^3/3 = \frac{4\pi V}{3h^3}(2m\varepsilon)^{3/2}$ with $\varepsilon = \frac{3}{2}kT$

$$\therefore \quad \Gamma(\varepsilon) = \frac{4\pi V}{3h^3}(3mkT)^{3/2} = \frac{4\times\pi\times10^{-3}}{3\times h^3}\left(3\times\frac{4}{6.023\times10^{26}}\times k\times 500\right)^{3/2} \approx \underline{2.3\times10^{28}}$$

The number of molecules is given by:

$$pV = NkT$$

$$\therefore \quad N = \frac{pV}{kT} = \frac{10^5.10^{-3}}{1.38\times10^{-23}.500} = \underline{1.45\times10^{22}}$$

Comment: there are about a million times as many energy states as particles, so most energy states are unoccupied.

4 **(a)** Let Y be the sum of scores on the yellow dice, P be the sum on pink dice.

Y	**$Y_1Y_2Y_3$**	**No. of Y permutations**	**P**	**P_1P_2**	**No. of P permutations**	**Total permutations**
18	6,6,6	1	**9**	6,3 5,4	2 2	**4**
17	6,6,5	3	**10**	6,4 5,5	2 1	**9**
16	6,5,5 6,6,4	3 3	**11**	6,5	2	**12**
15	6,6,3 6,5,4 5,5,5	3 6 1	**12**	6,6	1	**10**

Total number of outcomes = 4+9+12+10 = 35

∴ Relative frequencies for P = 9, 10, 11, 12 are 4/35, 9/35, 12/35 and 2/7 respectively.

Analogy with the canonical ensemble: P represents energy of system, Y represents energy of reservoir. Total energy, $P + Y$, is constant. As with the canonical ensemble, each "microstate" of the composite system (i.e., system plus reservoir) is equally probable, but probability of microstates of the system alone depends on the system energy.

(b) (i) $\Delta S_{\text{sys}} = \int_{T_o}^{T} \frac{dQ}{T} = mc_{\text{v}} \int_{T_o}^{T} \frac{dT}{T} = mc_{\text{v}} \ln\left(1 + \frac{\Delta T}{T_{\text{o}}}\right)$

(ii) $\Delta S_{\text{res}} = -\int \frac{dQ}{T_{\text{o}}} = -mc_{\text{v}} \frac{\Delta T}{T_{\text{o}}}$

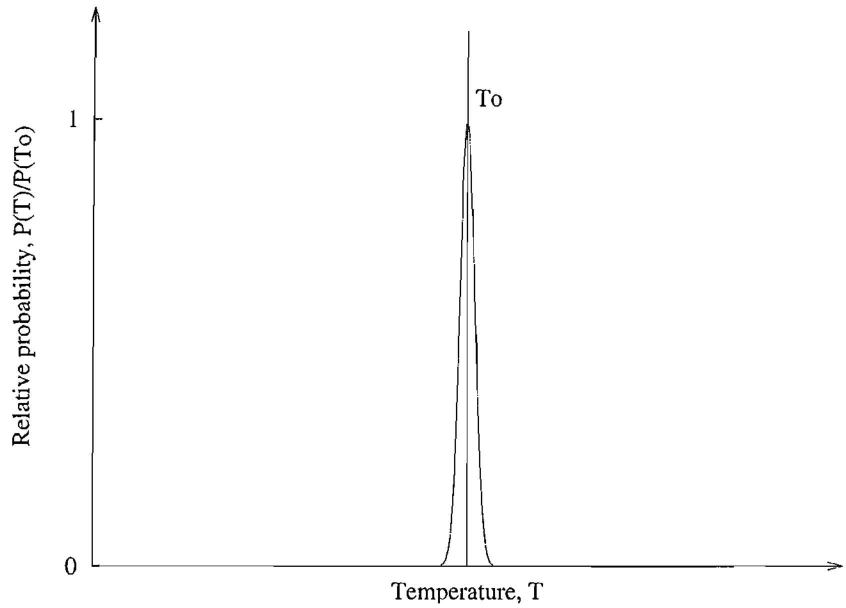
$$\Delta S_{\text{tot}} = mc_{\text{v}} \ln\left(1 + \frac{\Delta T}{T_{\text{o}}}\right) - mc_{\text{v}} \frac{\Delta T}{T_{\text{o}}}$$

$$\therefore \quad = mc_{\text{v}} \left\{ \frac{\Delta T}{T_{\text{o}}} - \tfrac{1}{2}\left(\frac{\Delta T}{T_{\text{o}}}\right)^2 + \ldots - \frac{\Delta T}{T_{\text{o}}} \right\}$$

$$\approx -\tfrac{1}{2} mc_{\text{v}} \left(\frac{\Delta T}{T_{\text{o}}}\right)^2$$

(iii) $\Delta S_{\text{tot}} = S(T) - S(T_{\text{o}}) = k \ln \frac{\Omega_{\text{tot}}(T_{\text{sys}} = T)}{\Omega_{\text{tot}}(T_{\text{sys}} = T_{\text{o}})} = \frac{P(T)}{P(T_{\text{o}})}$

$$\therefore \quad \frac{P(T)}{P(T_{\text{o}})} = \exp\{\Delta S_{\text{tot}} / k\} = \exp\{-mc_{\text{v}} \Delta T^2 / 2kT_{\text{o}}^2\}$$



From the form of $P(T)$, the standard deviation (RMS) of temperature fluctuations is:

$\text{RMS} = T_{\text{o}}\sqrt{k / mc_{\text{v}}} = 500 \times \sqrt{1.38 \times 10^{-23} / (10^{-3}.10^{3})} = \underline{1.86 \times 10^{-9} \text{ K}}$