The questions below focus on the following topics: the Maxwell-Boltzmann distribution, equipartition of energy, and heat conduction in gases and solids.

Q1. Rewrite the Maxwell-Boltzmann distribution for molecular speeds in terms of a new variable, $s = v/v_{mp}$ where v_{mp} is the most probable molecular speed. Hence, using Table I below, estimate the percentage of O_2 molecules which, at a temperature of 273 K, have speeds between 190 ms^{-1} and 565 ms^{-1}

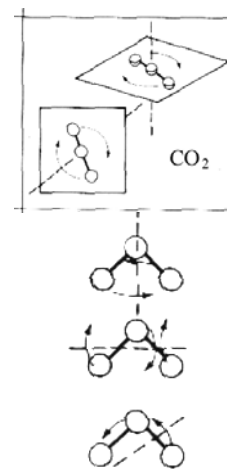| x	$\dfrac{4}{\sqrt{\pi}} \int_0^x z^2 e^{-z^2}\, dz$
0.1	7.48 x 10^{-4}
0.2	5.88 x 10^{-3}
0.3	0.019
0.4	0.044
0.5	0.081
0.6	0.132
0.7	0.194
0.8	0.266
0.9	0.345
1.0	0.438
1.5	0.788
2.0	0.954

Table I

Fig Q3. Rotational axes for CO_2 and H_2O

Q2. Staring from the Maxwell-Boltzmann speed distribution function, show that the fraction of molecules with kinetic energies between E and $E + dE$ is given by:

$$2\pi\left(\frac{1}{\pi kT}\right)^{\frac{3}{2}} E^{\frac{1}{2}} \exp\left(-\frac{E}{kT}\right) dE$$

Q3. Both H_2O and CO_2 have three atoms per molecule yet they do not have the same heat capacities. Considering Figure Q3 and using classical equipartition of energy theory, determine the heat capacity at constant volume for each molecule.

Q4. Heat conducts through He gas trapped between two plates 1 cm apart and 1.5 m^2 in area. Treating He as an ideal gas what is the rate of heat conduction at 300K if the temperature difference is 10 K?
[σ_0 for a helium atom = 1.2 x 10^{-19} m^2, mass of He atom = 6.68 x 10^{-27} kg, k = 1.38 x 10^{-23} JK^{-1}]

Q5. The cavity wall of a house consists of two 10 cm thick brick walls separated by a 15 cm air gap. If the temperature inside the house is 25°C and outside is 0°C, calculate the rate of heat loss by conduction per unit area.
[For this temperature range, k$_{brick}$ = 0.8 Wm^{-1}K^{-1} and k$_{air}$ = 0.023 Wm^{-1}K^{-1}]

SOLUTIONS

Q1. If we wish to determine the fraction of molecules, *F,* travelling with speeds smaller than some speed, *c*, then the following integral should be evaluated:

$$F = \int_o^c 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 \exp\left(-\frac{mv^2}{2kT}\right) dv$$

As stated in the question, rewrite this integral in terms of $s = v_{mp}/v$.

As derived in Set 2 of the coursework, $v_{mp} = \sqrt{\dfrac{2kT}{m}}$.

Express *T* in terms of v_{mp} and the integral above can be rewritten as:

$$F = \int_0^c 4\pi \left(\frac{2km}{2\pi mkv_{mp}^2}\right)^{\frac{3}{2}} v^2 \exp\left(-\frac{2kmv^2}{2kmv_{mp}^2}\right) dv$$

$$\Rightarrow F = \int_0^c 4\pi \left(\frac{1}{\pi v_{mp}^2}\right)^{\frac{3}{2}} v^2 \exp\left(-\frac{v^2}{v_{mp}^2}\right) v_{mp} d(\frac{v}{v_{mp}})$$

$$\Rightarrow F = \frac{4}{\sqrt{\pi}} \int_0^{s=v/v_{mp}} s^2 \exp(-s^2) ds$$

We now have an integral in terms of *s* (the ratio of speed to the most probable speed).

For O_2 at 273 K, use formula for v_{mp} given above to get $v_{mp} = 375$ ms^{-1}.

The percentage of molecules which have speeds below 190 ms^{-1} may be estimated from the table by setting x = 190/375 (i.e. approximately 0.5). This corresponds to 8.1% of the molecules. In a similar manner, the percentage of molecules with speeds below 565 ms^{-1} is approximately 78.8%. Hence, the percentage of molecules with speeds between 190 ms^{-1} and 565 ms^{-1} is approximately 70.7%.

Q2.

The Maxwell-Boltzmann distribution for speeds is:

$$f(v)dv = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 \exp\left(-\frac{mv^2}{2kT}\right) dv$$

$E = \frac{1}{2} mv^2 \Rightarrow dE = mv\, dv$

Thus,

$$f(v)dv = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v \exp(-\frac{E}{kT}) v dv$$

$$\Rightarrow f(E)dE = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \sqrt{\frac{2E}{m}} \exp(-\frac{E}{kT}) \frac{dE}{m}$$

$$\Rightarrow f(E)dE = 2\pi \left(\frac{1}{\pi kT}\right)^{\frac{3}{2}} E^{\frac{1}{2}} \exp\left(-\frac{E}{kT}\right) dE$$

It is worthwhile – from the perspective of both the *Thermal & Kinetic* module and the *Spacetime and Matter* module – to point out to the students that the distribution function comprises a density of states factor (proportional to $\sqrt{E}$) and a factor that gives the probability of a state being occupied.

Q3. For a molecule, the total number of degrees of freedom is $3N$ where N is the number of atoms comprising the molecule. Both CO_2 and H_2O are associated with three translational degrees of freedom. However, as shown in the figure associated with the question, CO_2 has two rotational degrees of freedom whereas H_2O has three. Hence, there are 4 (i.e. 9-3-2) vibrational degrees of freedom for CO_2 whereas there are 3 for H_2O.

Each translational and rotational degree of freedom contributes ½ RT. However, each vibrational degree of freedom contributes RT to the thermal energy (make sure the students know why this is the case).

Therefore, the total thermal energy per mole for CO_2 is $(13/2)RT$ which corresponds to $C_v = (13/2)R$.
C_v for H_2O is 6R.

[Notes for tutors:
(i)   Although I have made the point in the lectures, it is worthwhile explaining to the students that the reason a diatomic or linear polyatomic molecule is not associated with a third rotational degree of freedom about the line joining the atoms is that we assume that the atoms are point masses. The moment of inertia about this axis is zero.
(ii)   It is useful to make a link between the vibrational degrees of freedom of the CO_2 molecule and the normal modes of vibration covered in the *Vibrations and Waves* module. The four vibrational degrees of freedom for CO_2 are: symmetric stretch, antisymmetric stretch, in-plane bending, and out-of-plane bending.]

Q4

Thermal conductivity of gas given by:

$$K = \frac{1}{3}\frac{N}{V} <v> C_V \lambda \frac{1}{N_A}$$

Molar heat capacity $= 3R/2 = 3(N_A k/2)$ (ideal gas with three degrees of freedom).

$$K = \frac{n'}{3}\sqrt{\frac{8kT}{\pi m}}\frac{3k}{2}\frac{1}{\sqrt{2}n'\sigma_0}$$

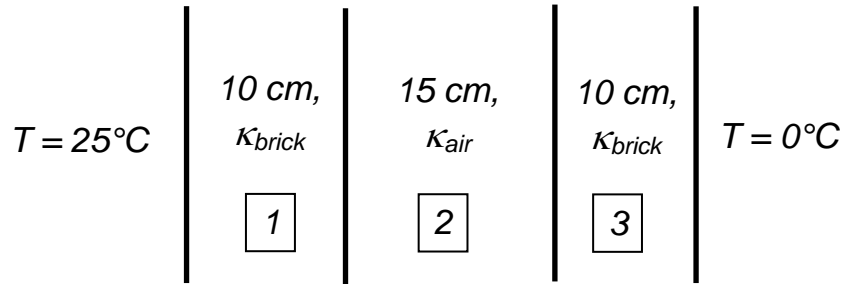$$K = \frac{k}{2\sqrt{2}\sigma_0}\sqrt{\frac{8kT}{\pi m}}$$

$\Rightarrow$ K = 0.051 Wm^{-1}K^{-1}

Rate of heat flow given by: $\dfrac{dQ}{dt} = KA\dfrac{\Delta T}{\Delta x}$

Plugging in following values, A = 1.5 m^2, ΔT = 10 K, Δx = 0.01 m.

$\Rightarrow \dfrac{dQ}{dt} = 1.5 \times 0.051 \times 1000 = 76.5$ Wm^{-2}

Q5.

$T = 25°C$ | 10 cm, κ_{brick} [1] | 15 cm, κ_{air} [2] | 10 cm, κ_{brick} [3] | $T = 0°C$

Note that heat current must be <u>*conserved*</u> as we pass from brick to air to brick.

$$\left(\frac{dQ}{dt}\right)_1 = \left(\frac{dQ}{dt}\right)_2 = \left(\frac{dQ}{dt}\right)_3$$

$$\left(\frac{dQ}{dt}\right)_1 = \kappa_{brick} A \frac{25 - T_1}{0.1}$$

$$\left(\frac{dQ}{dt}\right)_2 = \kappa_{air} A \frac{T_1 - T_2}{0.15}$$

$$\left(\frac{dQ}{dt}\right)_3 = \kappa_{brick} A \frac{T_2 - 0}{0.1}$$

Solve to get T_1 and T_2. $dQ/dt = 3.7$ Wm^{-2}

Alternatively (and somewhat more elegantly):

Make analogy with electrical circuit. Consider:

- I equivalent to *dQ/dt*,
- V equivalent to temperature difference
- R equivalent to *thermal resistance*

$$R_T = \frac{\Delta x}{kA}$$

$R_{TOTAL} = R_1 + R_2 + R_3$

In analogy with $V = IR$, $dQ/dt = (\Delta T)/R_{TOTAL}$