

THERMAL CONDUCTIVITY OF AN IDEAL GAS

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Schroeder gives a rough derivation of the thermal conductivity of an ideal gas. I won't repeat the full derivation here; rather I'll summarize the key points.

The mean free path ℓ of a gas molecule is derived by freezing all molecules in place except for one, then doubling the radius of the moving molecule while reducing all other molecules to points. The mean free path is then taken to be the length of a cylinder swept out by the moving molecule, when the volume of that cylinder equals the average volume per molecule V/N in the gas. The result is

$$\ell = \frac{1}{4\pi r^2} \frac{V}{N} \quad (1)$$

where r is the radius of a gas molecule.

Next, we consider a box of molecules of width 2ℓ with a temperature gradient in the x direction. Imagine a partition across the middle of the box and consider the number of molecules that pass across this partition in each direction (that is, in the $+x$ and $-x$ directions). On average, half the molecules in each half of the box are moving towards the partition, and since the width of each half of the box is ℓ we expect about half the molecules in each half of the box to cross the partition. This means that half the energy in each half of the box is transported across the partition, so the net heat transfer is

$$Q = \frac{1}{2}(U_1 - U_2) = -\frac{1}{2}(U_2 - U_1) \quad (2)$$

The energy in the gas is the heat capacity times the temperature so

$$Q = -\frac{C_V}{2}(T_2 - T_1) \quad (3)$$

Assuming a linear temperature gradient, the temperature difference between the centres of the two halves of the box is

$$T_2 - T_1 = \ell \frac{dT}{dx} \quad (4)$$

so we get a formula for the heat transferred in time Δt by dividing both sides by Δt :

$$\frac{Q}{\Delta t} = -\frac{C_V \ell}{2\Delta t} \frac{dT}{dx} \quad (5)$$

Comparing this with the heuristic form of the Fourier heat conduction equation we had earlier, we get an expression for the thermal conductivity:

$$k_t = \frac{C_V \ell}{2A\Delta t} \quad (6)$$

where A is the area of the imaginary partition we inserted into the box. If Δt is taken to be the average time to travel the distance ℓ then

$$\bar{v} = \frac{\ell}{\Delta t} \quad (7)$$

is the average speed of the molecules. Further, if we take the volume of the box to be $V = A\ell$ (actually, given that the width of the box in Schroeder's derivation is 2ℓ I would think the volume should be $2A\ell$, but anyway...) we get

$$k_t = \frac{C_V \ell^2}{2A\ell\Delta t} = \frac{C_V}{2V} \ell \bar{v} \quad (8)$$

Given that the rms speed (which is roughly the same as \bar{v}) is

$$v_{rms} = \sqrt{\frac{3kT}{m}} \quad (9)$$

the heat capacity is

$$C_V = \frac{1}{2} f N k \quad (10)$$

where f is the number of degrees of freedom per molecule, we have, using 1,

$$k_t \propto \sqrt{T} \quad (11)$$

This relation agrees with measurements over a large temperature range for many gases.

Example 1. The mean free path in the air around us is very small. As given by Schroeder, using 1 this works out to around 1.5×10^{-7} m. Using the ideal gas law $PV = NkT$, we can find the pressure at which $\ell = 10$ cm at room temperature $T = 300$ K. We get

$$\ell = \frac{1}{4\pi r^2} \frac{kT}{P} \quad (12)$$

Taking $r = 1.5 \times 10^{-10}$ m we have

$$P = \frac{1}{4\pi r^2} \frac{kT}{\ell} \quad (13)$$

$$= 0.15 \text{ N m}^{-2} \quad (14)$$

Standard atmospheric pressure is around 10^5 N m^{-2} so this is a reasonable laboratory vacuum.

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