

Kinetic Theory II

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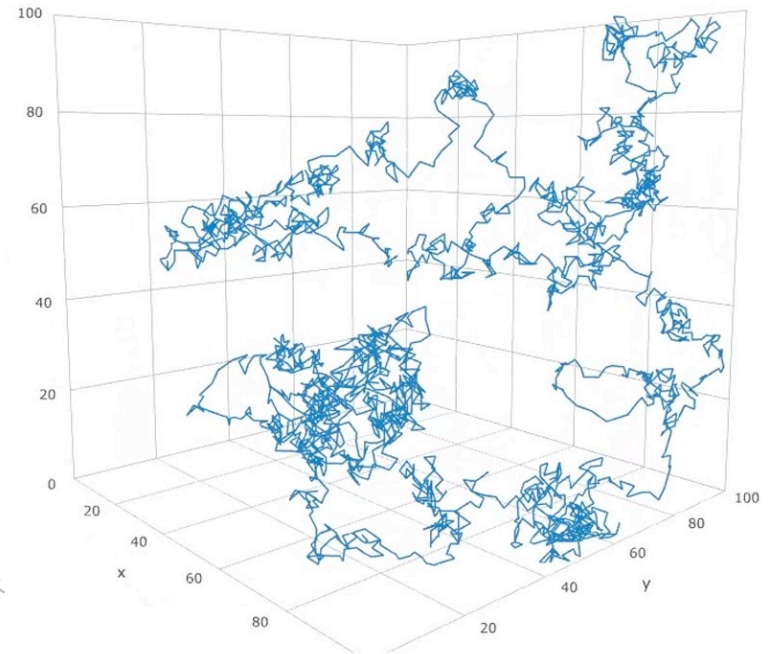
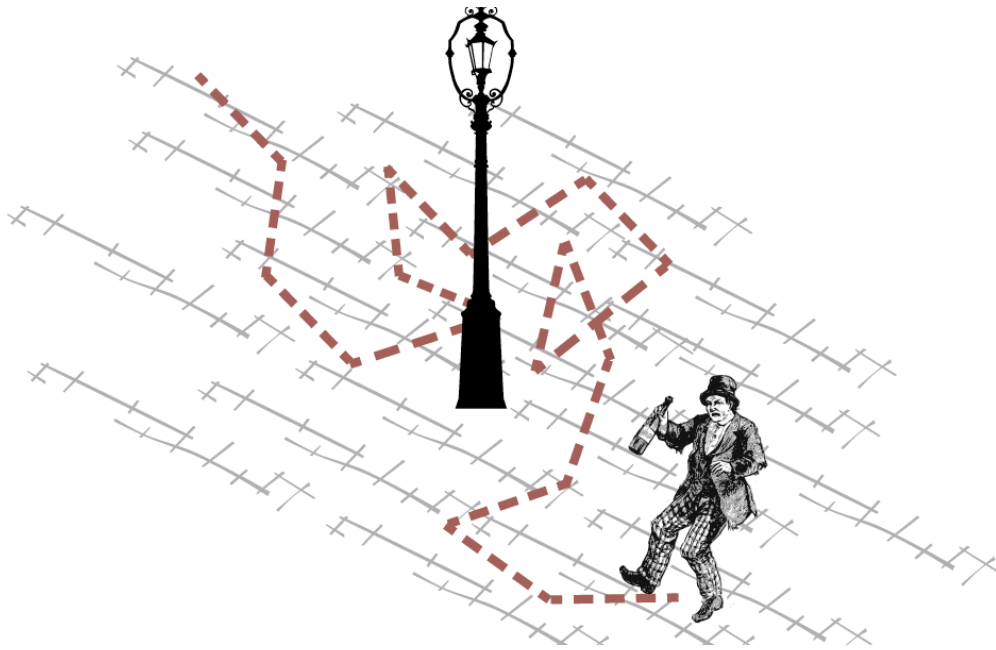
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The paths of isolated molecules in a gas paths are called **random walks**.

- how far molecules travel on average **over given intervals of time**?
- how far do they travel **before a collision** occurs?

Before a collision we can describe a gas as if composed of many individual molecules.

When collisions occur, we need to consider a gas as composed of interacting molecules (the density will be a critical parameter).

3.1 The Mean Free Path

Molecules collide, travel freely, collide and so on.

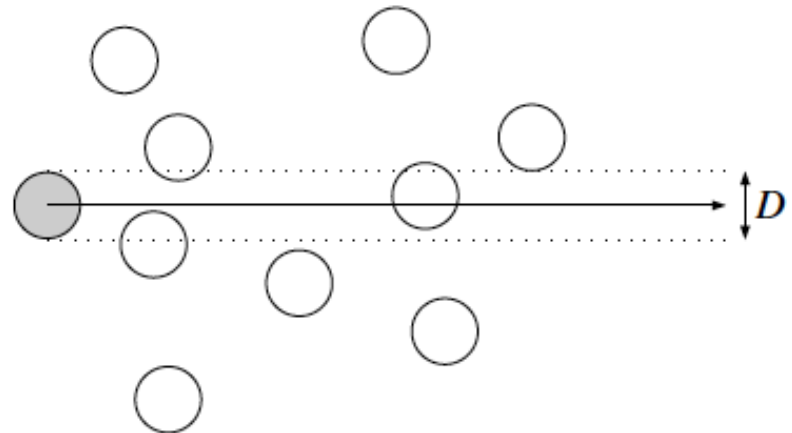
The **mean distance between collisions** is the **mean free path** usually denoted by λ

To estimate λ

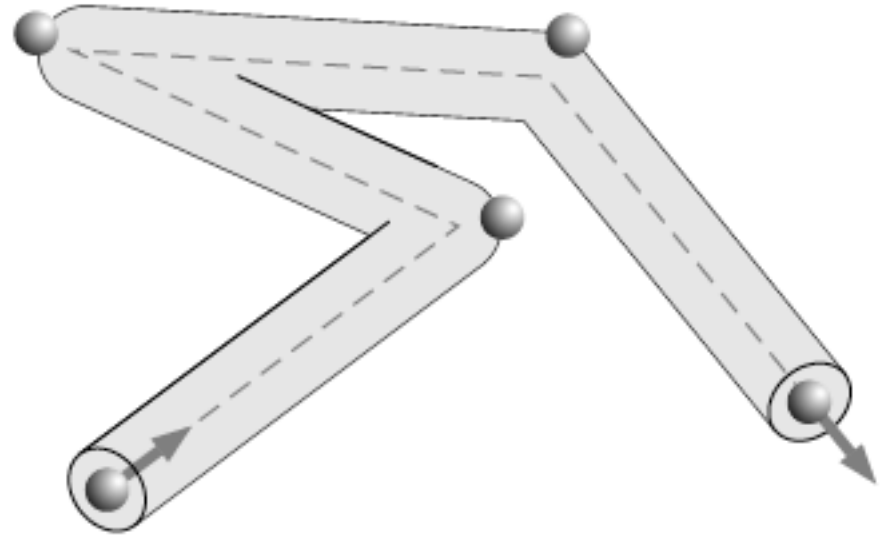
we consider N stationary molecules and a molecule travelling from left to right, all with radius R and diameter $D = 2R$.

The moving molecule can potentially hit any molecule located within a distance D from its projected path.

The moving molecule sweeps out a cylinder of radius D and any molecule within this cylinder can be hit.



after each collision, the direction of the moving molecule changes.



The moving molecule sweeps out a volume $\pi D^2 v$ per unit time
giving a collision rate $\pi D^2 n v$ where $n=N/V$

If we now consider that the other molecules can move,
the **collision rate** becomes:

$$\sqrt{2}\pi D^2 n v$$

Example:

If we consider air at STP, $P = nkT_1$,

$$n = \frac{P}{kT_1} = \frac{1.01 \times 10^5 \text{ Pa}}{1.38 \times 10^{-23} \text{ JK}^{-1} \times 273 \text{ K}} = 2.7 \times 10^{25} \text{ m}^{-3}$$

Taking $D = 0.3 \text{ nm}$ and $v = 477 \text{ ms}^{-1}$

then the collision rate $\sqrt{2}\pi D^2 n v \approx 5.1 \times 10^9 \text{ s}^{-1}$.

The mean free path is the speed divided by the collision rate

speed = v

collision rate $\sqrt{2}\pi D^2 n v$



mean free path

$$\lambda = \frac{1}{\sqrt{2}\pi D^2 n}$$

For air at STP, $\lambda \approx 10^{-7}$ m

Exercise:

Electrons travel 3 km along the SLAC linear collider at Stanford in California.

To reduce scattering losses, the electrons need to have a mean free path of at least 50 km.

What is the maximum allowed pressure inside the collider's beam pipe at $T_1 = 20\text{C}$?

We know that:

$$\lambda_{\text{electron}} = \frac{1}{\sqrt{2}\pi D^2 n} \quad P = nkT_1$$



$$P = \frac{kT_1}{\sqrt{2}\pi D^2 \lambda_{\text{electron}}} = \frac{1 \times 1.38 \times 10^{-23} \text{ J K}^{-1} \times 293 \text{ K}}{\sqrt{2} \pi (1 \times 10^{-10} \text{ m})^2 \times 50 \times 10^3 \text{ m}} = 1.8 \times 10^{-6} \text{ Pa.}$$

We have taken the gas molecules to have a diameter $D = 0.2 \text{ nm}$, appropriate for diatomic molecules.

This pressure is about $2 \times 10^{-11} \text{ atm}$.

3.1.1 What is the distribution of molecular path lengths?

The mean free path tells us how far a molecule travels on average

what is the probability that a molecule travels a distance r without collision?



The probability of colliding in a small distance dr equals the time taken multiplied by the collision rate:

$$\frac{dr}{v} \times (\text{collision rate}) = \frac{dr}{\lambda}$$

The probability of NOT colliding in a small distance dr is: $\left(1 - \frac{dr}{\lambda}\right)$

We consider the probability of traveling a distance r , defined as $P(r)$
the probability of traveling a distance $r+dr$, defined as $P(r+dr)$

We can write $P(r+dr)$ as the probability of getting to r multiplied by
the chance of surviving (i.e., not being hit) within the next short
interval dr :

$$P(r + dr) = P(r) \left(1 - \frac{dr}{\lambda} \right)$$

$$\frac{P(r + dr) - P(r)}{dr} = -\frac{P(r)}{\lambda}$$

$$\frac{dP}{dr} = -\frac{1}{\lambda} P. \quad \Rightarrow \quad P(r) = P(0)e^{-r/\lambda}$$

$P(0)$ is the probability of not hitting any molecules for a zero travelled distance, which is clearly unity $\rightarrow P(0)=1$



$$P(r) = e^{-r/\lambda}$$

exponential probability distribution

typical for random events

3.1.2 Distance travelled

How far will a molecule have travelled after a time t ?

If there are no collisions, the answer is vt , where v is the speed of the molecule

If there are collisions the distance travelled will be different.

We consider the total path travelled by the molecule to be composed by N steps.

We can then write the position vector \mathbf{r} as:

$$\mathbf{r} = \mathbf{s}_1 + \mathbf{s}_2 + \mathbf{s}_3 + \dots$$

where s_i is the displacement of the i -th step.

Let us now consider the square modulus of \mathbf{r} :

$$r^2 = \mathbf{r} \cdot \mathbf{r} = s_1^2 + s_2^2 + s_3^2 + \dots + \mathbf{s}_1 \cdot \mathbf{s}_2 + \mathbf{s}_1 \cdot \mathbf{s}_3 + \mathbf{s}_2 \cdot \mathbf{s}_1 + \dots$$

The cross terms can be written as:

$$\mathbf{s}_i \cdot \mathbf{s}_j = s_i s_j \cos \theta_{ij}$$

for $i \neq j$, where θ_{ij} is the angle between step i and step j

while $s_i^2 = s_i^2$

If we assume that the angle between the steps is random, the average value of $\langle \cos \theta_{ij} \rangle = 0$.

Therefore, the mean squared distance can be written as:

$$\bar{r}^2 = \sum_{i=1}^N \bar{s}_i^2 \approx N\lambda^2$$

Mean square distance:

$$\bar{r}^2 = \sum_{i=1}^N \bar{s}_i^2 \approx N\lambda^2$$

$$\bar{s}_i^2$$

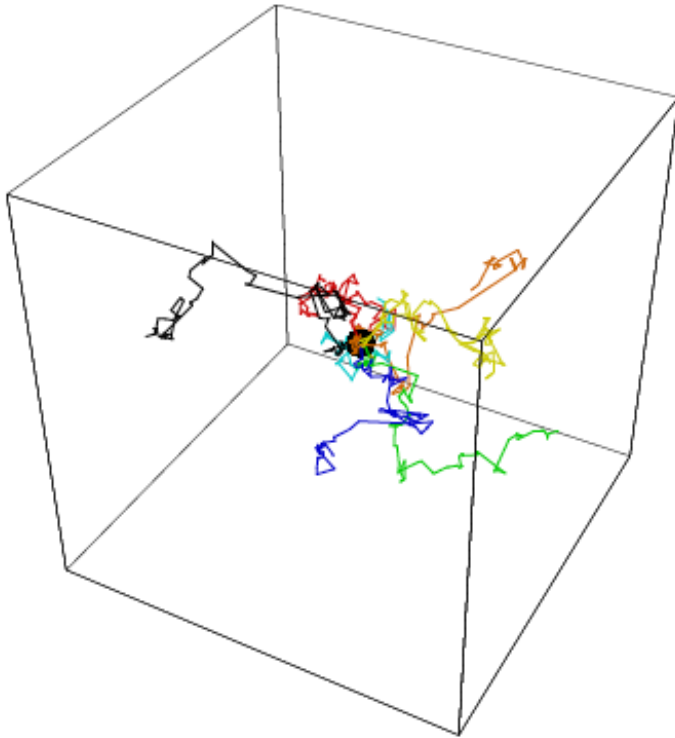
is the **mean squared steplength**
which we have approximated with λ

Thus the **root-mean-square (rms) distance travelled**, measuring in a straight line from the point of origin is

$$r \approx \sqrt{N}\lambda$$

for a random walk
of N steps

Random walks



Seven random walks of a particle. Each walk comprises 100 steps with steplengths distributed according to the exponential distribution

$$P(r) = e^{-r/\lambda}$$

The distance travelled (displacement from the starting point) and the path length can be hugely different,

$$r \approx \sqrt{N}\lambda$$

since $\sqrt{N} \ll N$ for large N

Examples:

1. How far on average does an air molecule travel in 1 second?

We had found that the collision rate for air at STP was $\approx 5.1 \cdot 10^9 \text{ s}^{-1}$
(see previous example).



in 1 second we will have $5.1 \cdot 10^9$ collisions

We saw that for air at STP, the mean free path $\lambda \approx 10^{-7} \text{ m}$



$$\text{So } r = \sqrt{N} \lambda = 6.7 \text{ mm}$$

This compares to 477m of actual total path length travelled.

2. The mean free path of a photon inside the Sun before it is absorbed and re-emitted in a random direction is about 0.01 m.

a. **How many steps** will photons take to travel from the centre of the Sun to its surface, a distance of 7×10^8 m?

The number of steps is equal to the number of collisions N , using

$$r = \sqrt{N}\lambda \quad \text{we obtain}$$

$$N = (r/\lambda)^2 = (7 \times 10^8 \text{ m}/0.01 \text{ m})^2 = 4.9 \times 10^{21}$$

b. **How long** will this take if the time between absorption and re-emission can be neglected?

Photons will travel at speed c , therefore the time that each step takes is λ/c , the total time will be $N \lambda/c$

$$\frac{N\lambda}{c} = \frac{r^2}{\lambda c} = \frac{(7 \times 10^8 \text{ m})^2}{0.01 \text{ m} \times 3 \times 10^8 \text{ m s}^{-1}} = 1.6 \times 10^{11} \text{ s} = 5200 \text{ years}$$

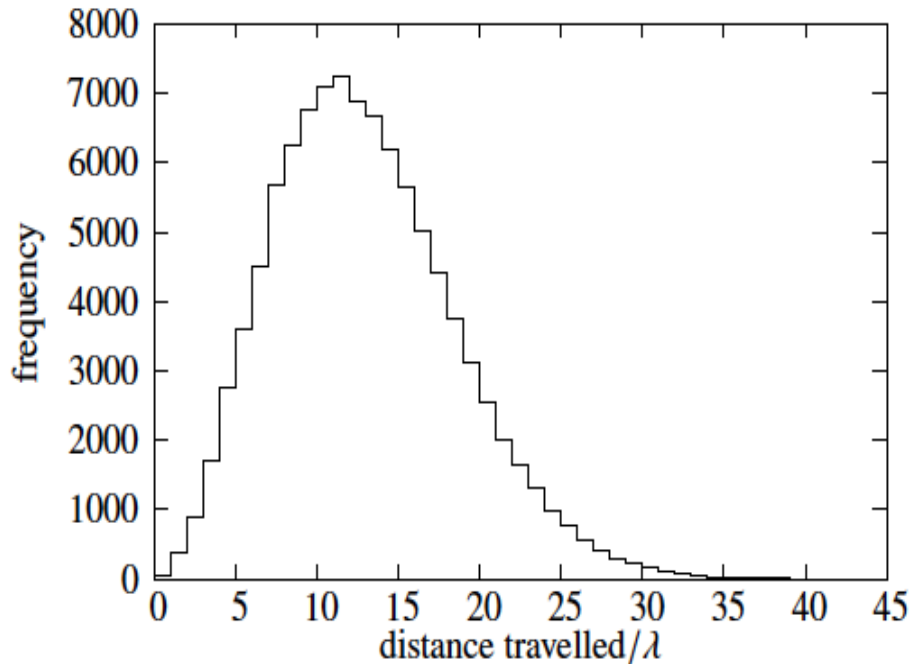
Without scattering it would take 2.3s instead!

Since the number of collisions increases with time, $N \propto t$,
and

$$r = \sqrt{N}\lambda$$

the distance travelled from the origin by a molecule scales
with $t^{1/2}$.

The distance is in reality best described by a distribution
rather than simply a mean.



Frequency distribution of the distance
travelled in 100 000 random walks,
each of 100 steps, with the step-
lengths themselves distributed
according to an exponential
distribution with mean λ .

3.2 Transport

Transport processes apply when there is a departure from equilibrium

if a temperature gradient is set up, then energy will be transported.
If a concentration gradient of one type of molecule is set up, then there will a flow of that type of molecule from high to low concentration (diffusion).

We can consider three cases:

- different identity: *diffusion*
- different energy: *thermal conduction*
- different momentum: *viscosity.*

We consider molecules that are free to move in all directions in space $+x, -x, +y, -y, +z, -z$.

We will make the following assumptions to develop our models:

- $1/6$ of the molecules travel in each of the directions $\pm x, \pm y, \pm z$ at speed \bar{v} .
- Molecules have the average properties of the position of their last collision, λ away from the surface through which the property of interest is being transported.

We are ignoring correlations between the energy, speed and mean free path of molecules
but we will capture the main features of the processes under study.

3.2.1 Diffusion

Diffusion is the movement of a substance driven by a gradient in its concentration.

The flow rate across area A in terms of a number of molecules N per unit time is governed by an equation known as Fick's Law:

$$\frac{dN}{dt} = -DA \frac{dn}{dx}$$

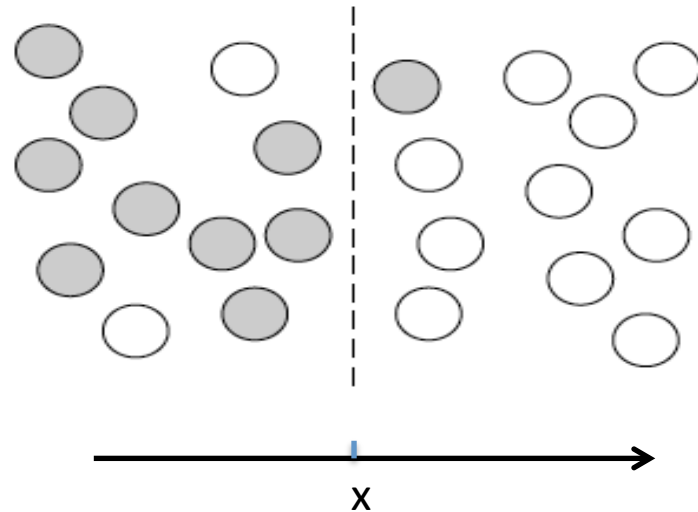
where D is the diffusion coefficient (defined by this equation).

The term dn/dx is the gradient in the number density ($n=N/V$) of the substance of interest.

The minus sign indicates that diffusion causes a flow from high towards low concentrations.

The diffusion coefficient has units of $[m^2 s^{-1}]$.

The transported property in the case of diffusion is the type of molecule (different identity).



Consider the **flow rate** (number of molecules per unit time) from left to right across area A of the dashed line at x :

$$\frac{1}{6}n(x - \lambda)A\bar{v}$$

We are only considering molecules moving along $+x$, hence $1/6$
 The number density is evaluated a distance λ from the reference line (molecules a mean free path away can scatter and cross the surface at x)
 The flow rate will depend on the molecule mean velocity.

Molecules on the right-hand side of x can bounce to the left and cross A , thus contributing to the flow rate with the term:

$$\frac{1}{6}n(x + \lambda)A\bar{v}$$

The total flux is therefore given by:

$$\frac{1}{6}[n(x - \lambda) - n(x + \lambda)]A\bar{v}$$

Since λ is small, we now expand each of the terms to the first order as follows:

$$n(x - \lambda) \approx n(x) - \frac{dn}{dx}\lambda \quad \text{and} \quad n(x + \lambda) \approx n(x) + \frac{dn}{dx}\lambda$$

so the net flow rate is

$$-\frac{1}{3}\lambda\bar{v}A\frac{dn}{dx}$$

Given that Fick's law defined the diffusion coefficient D as:

$$\frac{dN}{dt} = -DA \frac{dn}{dx}$$

net flow rate is $-\frac{1}{3} \lambda \bar{v} A \frac{dn}{dx}$



The kinetic theory estimates the diffusion coefficient to be:

$$D = \frac{1}{3} \lambda \bar{v}$$

we have a **relation between**
a macroscopic constant (the diffusion coefficient),
and microscopic properties of a gas
(the mean free path and mean velocity)

Example 3.4 How fast does water in a test-tube evaporate?**Answer 3.4** The question is very brief, so we have to make some assumptions:

1. The water vapour has its saturated density, n_s , at the water surface.
2. The number density drops to zero at the mouth of test-tube, a height h above the water surface.
3. There are no air currents within the tube.
4. Water vapour can be described as an ideal gas.

In equilibrium, the concentration gradient is constant along the tube, so $dn/dx = n_s/h$. Therefore the loss rate/unit area is

$$\frac{\lambda \bar{v} n_s}{3h} = \frac{\lambda \bar{v} P_s}{3hkT_1},$$

using the ideal gas equation, $n_s = P_s/kT_1$. Therefore the rate of reduction in water level is the loss rate in molecules per unit time multiplied by the mass of each molecule m and divided by the density of water ρ :

$$\frac{m\lambda\bar{v}P_s}{3hkT_1\rho} = \frac{m_{\text{mole}}\lambda\bar{v}P_s}{3hRT_1\rho}.$$

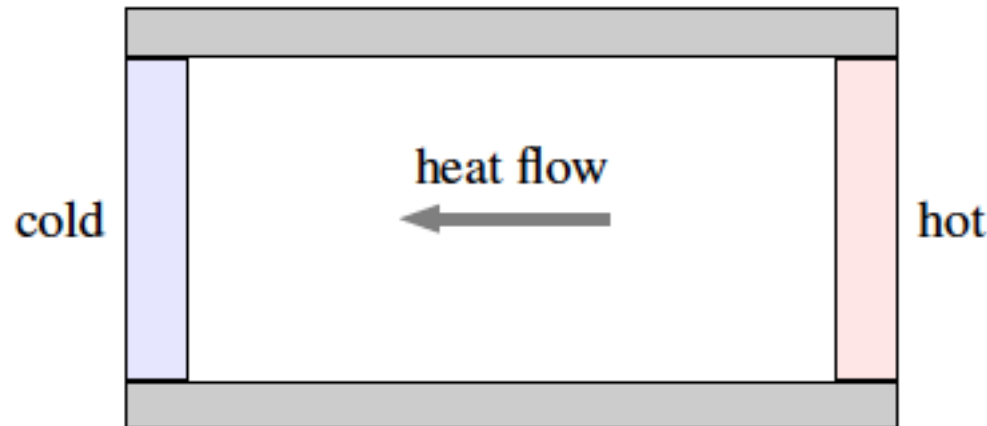
In the last step, top and bottom were multiplied by Avogadro's number, N_A , to express the result in terms of the mass of a mole, $m_{\text{mole}} = N_A m$, and $R = N_A k$.

For example, at $T_1 = 293$ K, the saturated vapour pressure is $P_s = 1710$ N m⁻² and the density of water is $\rho = 10^3$ kg m⁻³. Assuming $h = 0.1$ m and taking $\lambda = 10^{-7}$ m, $\bar{v} = 650$ m s⁻¹ (water molecules are less massive and move faster than those of air, $m_{\text{mole}} = 0.018$ kg), then the evaporation rate is

$$\begin{aligned} \frac{0.018 \text{ kg} \times 10^{-7} \text{ m} \times 650 \text{ m s}^{-1} \times 1710 \text{ N m}^{-2}}{3 \times 0.1 \text{ m} \times 8.314 \text{ J K}^{-1} \times 293 \text{ K} \times 10^3 \text{ kg m}^{-3}} &= 2.7 \times 10^{-9} \text{ m s}^{-1} \\ &= 0.24 \text{ mm per day.} \end{aligned}$$

3.2.2 Thermal conduction

Thermal conduction is the transfer of energy as heat that occurs when there is a temperature gradient



The fundamental equation of heat conduction is Fourier's Law:

$$\frac{dQ}{dt} = -KA \frac{dT}{dx}$$

where dQ/dt is the energy flow rate across area A because of a temperature gradient of dT/dx .

This equation defines the **thermal conductivity K** , which has units of $[Wm^{-1} K^{-1}]$.

The kinetic theory estimates K as for diffusion, but we are here transferring energy.

Let the energy/molecule at position x be $E(x)$, then the energy flow rate from left to right is

$$\frac{1}{6}nA\bar{v}E(x - \lambda)$$

then the energy flow rate from right to left is

$$\frac{1}{6}nA\bar{v}E(x + \lambda)$$

Their difference gives the net energy flow from left to right:

$$-\frac{1}{3}nA\bar{v}\lambda\frac{dE}{dx}$$

After applying the same expansions as for the diffusion case, we obtain:

$$\frac{dE}{dx} = \frac{dE}{dT} \frac{dT}{dx}$$

We can define $(n dE/dT)$ as the rate of increase of energy/volume with temperature

that we call **specific heat capacity per unit volume c**

Given Fourier's law:

$$\frac{dQ}{dt} = -KA \frac{dT}{dx}$$

The net energy flow from left to right:

$$-\frac{1}{3}nA\bar{v}\lambda \frac{dE}{dx}$$

And the relation:

$$\frac{dE}{dx} = \frac{dE}{dT} \frac{dT}{dx} \quad \text{and} \quad c = n \frac{dE}{dT}$$

We can write:

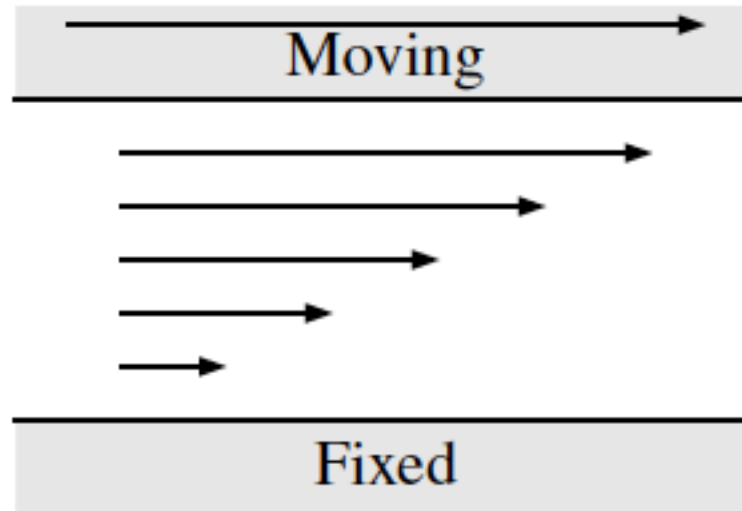
$$\frac{dQ}{dt} = -\frac{1}{3}Ac\bar{v}\lambda \frac{dT}{dx}$$

and we can define

$$K = \frac{1}{3}\lambda\bar{v}c$$

heat capacity here is per unit volume and hence **density dependent**

3.2.3 Viscosity



The phenomenon of viscosity is seen in its simplest form when considering two parallel surfaces, with one moving relative to the other

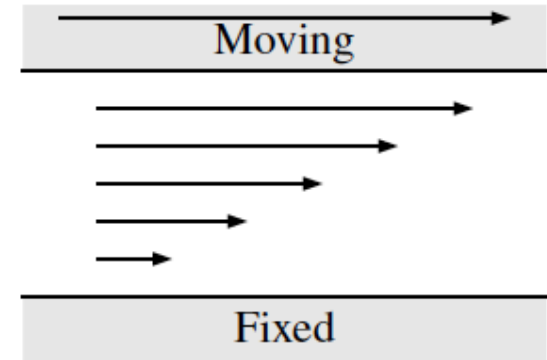
We consider that when molecules hit each surface they stick briefly before leaving

In doing so they acquire the mean velocity of the surface.

If one surface moves with respect to the other, there must therefore be a velocity gradient.

This produces a **drag force** on each surface given by

$$F_x = -\eta A \frac{dv_x}{dy}$$



where F_x is the force in the x-direction (left to right)
 dv_x/dy is the velocity gradient, i.e. the change in v_x with y-position
 A is the area of the surface

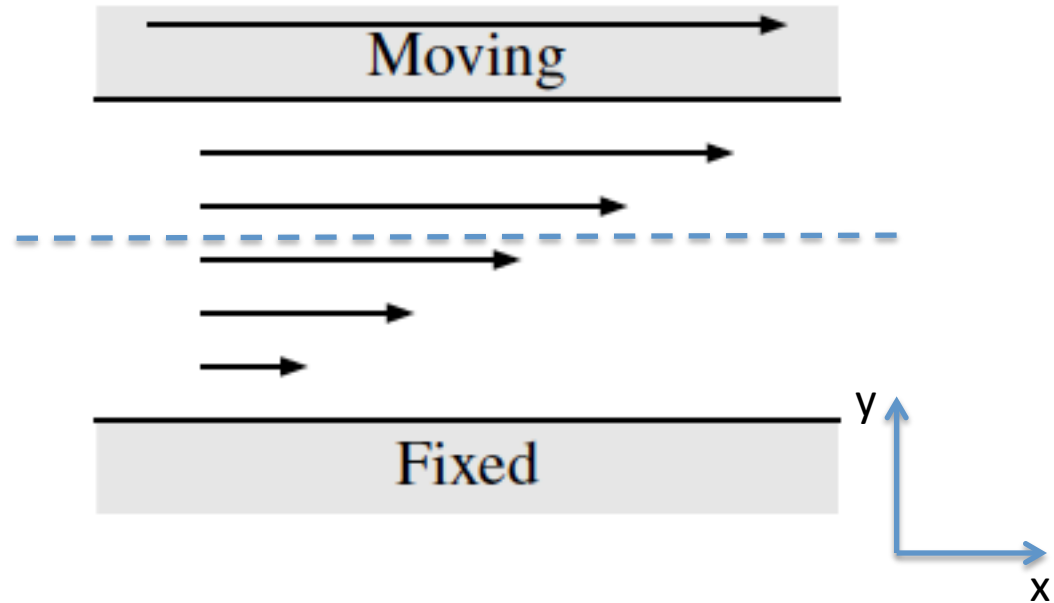
This equation defines the constant η , the **viscosity coefficient** with units of $[\text{Nm}^{-2} \text{s}^{-1}]$.

The minus sign means that the force is a drag force.

Viscosity is the transport of momentum, in this case the x-component of momentum transported in the y-direction.

Let's consider a surface in the fluid parallel to the upper and lower surfaces

The mean
x-momentum/molecule at y
will be $mv_x(y)$



the momentum per unit time carried from bottom to top across the surface is:

$$\frac{1}{6}nA\bar{v}mv_x(y - \lambda)$$

And the rate from top to bottom is:

$$\frac{1}{6}nA\bar{v}mv_x(y + \lambda)$$

Therefore, the net flow rate is:

$$-\frac{1}{3}nA\bar{v}\lambda m \frac{dv_x}{dy}$$

Given that $n*m$ is the mass/unit volume, i.e. the density ρ , we deduce that:

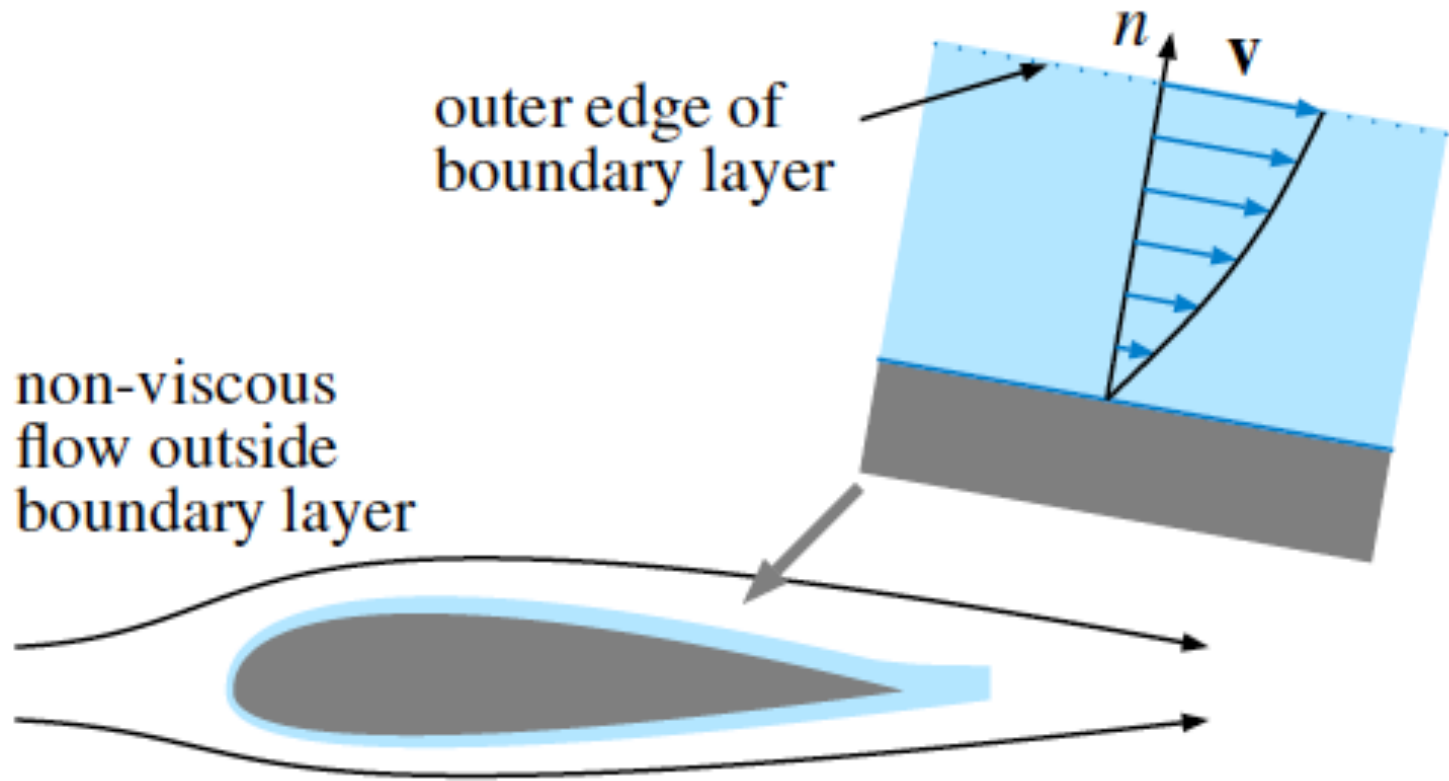
$$\eta = \frac{1}{3}\lambda\bar{v}\rho$$

Viscosity is important in the boundary layer near the surface of a body moving through a fluid.

Outside this layer the flow can be taken as non-viscous.

Example:

Fluid flow past a wing



the flow velocity \mathbf{v} changes, as a function of the normal distance n ,
from zero at the surface to the full non-viscous flow value at the outer edge of the layer.

Transport coefficients

| | transported quantity | macroscopic law | kinetic theory estimate |
|--------------------|------------------------------|---|---|
| diffusion | number density or 'identity' | $\frac{dN}{dt} = -DA \frac{dn}{dx}$ | $D = \frac{1}{3} \lambda \bar{v}$ |
| thermal conduction | thermal energy | $\frac{dQ}{dt} = -KA \frac{dT}{dx}$ | $K = \frac{1}{3} \lambda \bar{v} c$ |
| viscosity | momentum | $\frac{dp_x}{dt} = F_x = -\eta A \frac{dv_x}{dy}$ | $\eta = \frac{1}{3} \lambda \bar{v} \rho$ |

3.2.4 Avogadro's number

The kinetic theory of transport led to the first reliable estimate of Avogadro's number, provided by Maxwell in 1865.

We cannot measure the flow rate of molecules directly, but we can measure it in terms of the mass flow rate, and hence we can measure:

$$D_m = mD = \frac{1}{3}\lambda\bar{v}m.$$

from kinetic theory, the ratio of the viscosity coefficient to the mass diffusion coefficient is expected to be

$$\frac{\eta}{D_m} = \frac{\rho}{m} = n$$

the number of molecules per unit volume.

If we now measure the volume of one mole, the molar volume V_m , then $N_A = V_m n$, and therefore:

$$N_A = \frac{V_m \eta}{D_m}$$

All the quantities are [measurable experimentally](#)

although Maxwell found that there were no existing measurements of the viscosity of gases and had to devise methods to carry them out.

3.2.5 Temperature dependence of transport coefficients

If we consider the temperature dependence of the mean speed:

$$\bar{v} \propto T_I^{1/2}$$

At constant pressure, the number of molecules per unit volume is:

$$n = P/kT_I$$

the quantities c and ρ are both proportional to n and hence decrease with T_I

However, this is compensated by a matching increase of

$$\lambda \propto 1/n.$$

Overall **all transport coefficients of gases** are expected to **increase with temperature**.

This is observed, although not necessarily in good agreement with $T_i^{1/2}$ (or $T_i^{3/2}$ for diffusion) because of the inaccuracy of the hard sphere approximation.

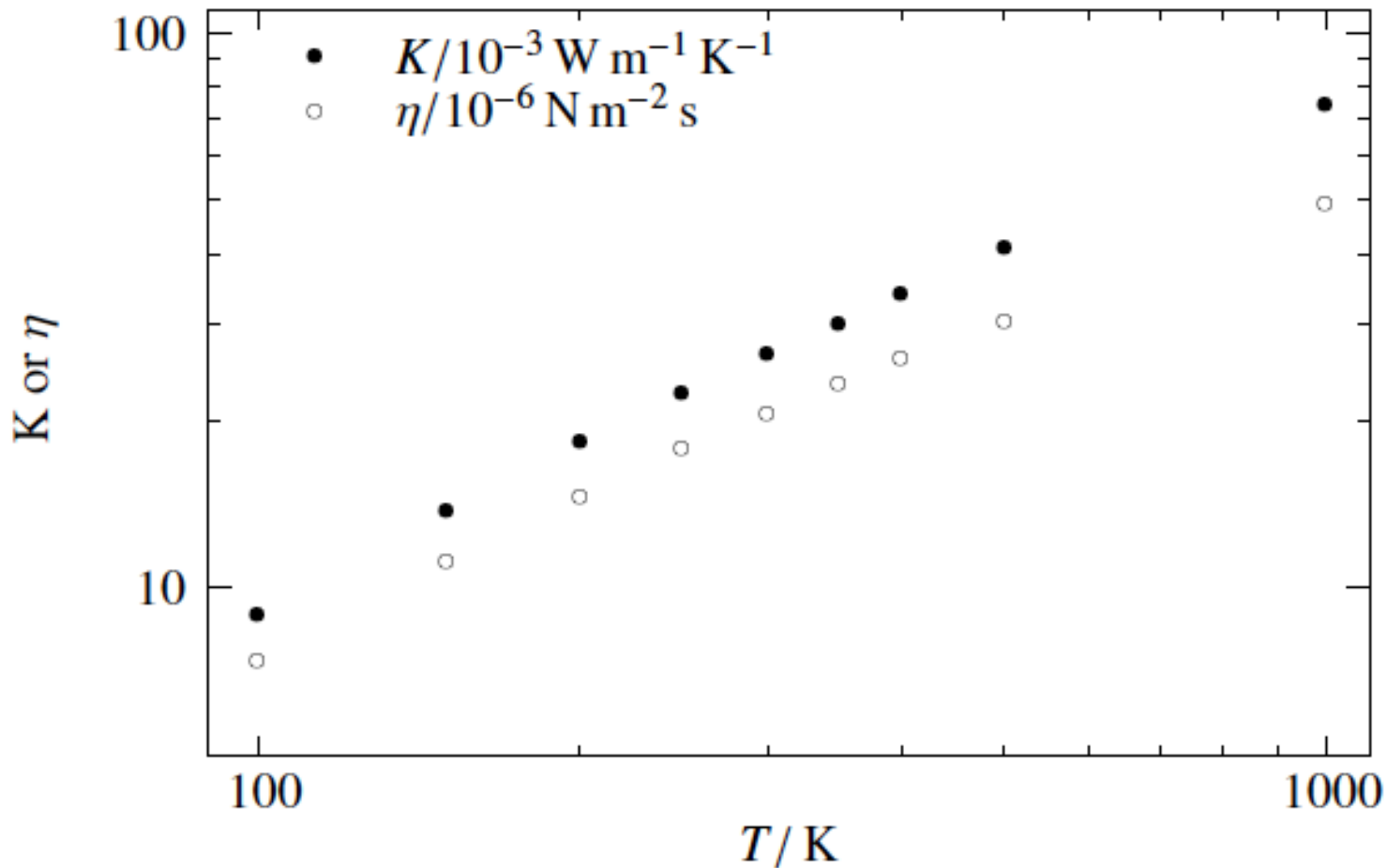
By contrast, the **viscosity of liquids decreases with T**.

This is just another example of the inapplicability of kinetic theory to liquids and solids.

| Temperature K | η $10^{-6} \text{ N m}^{-2} \text{ s}$ | K $10^{-3} \text{ W m}^{-1} \text{ K}^{-1}$ | K/η $\text{m}^2 \text{ s}^{-2} \text{ K}^{-1}$ |
|------------------|--|--|--|
| 100 | 7.400 | 8.960 | 1211 |
| 150 | 11.18 | 13.85 | 1237 |
| 200 | 14.65 | 18.35 | 1253 |
| 250 | 17.80 | 22.49 | 1263 |
| 300 | 20.68 | 26.38 | 1276 |
| 350 | 23.34 | 30.10 | 1289 |
| 400 | 25.83 | 33.79 | 1308 |
| 500 | 30.41 | 41.13 | 1352 |
| 1000 | 49.05 | 74.32 | 1515 |

Experimental measurements of the **thermal conductivity and viscosity** of oxygen as a function of temperature

they **increase with temperature**



Thermal conductivity and viscosity of oxygen as a function of temperature. This is a log-log plot, so both lines should be straight with the same slope if the kinetic theory prediction that K and η are proportional to $T^{1/2}$ holds.

Remembering the formulae:

$$K = \lambda \bar{v} n C_m / 3 \quad \eta = \lambda \bar{v} n m / 3$$

where C_m and m are the heat capacity and mass per molecule, then we expect

$$\frac{K}{\eta} = \frac{C_m}{m} = \frac{5k}{2m}$$

for a diatomic molecule.

We therefore expect from kinetic theory that the ratio of thermal conductivity to viscosity should be independent of temperature.

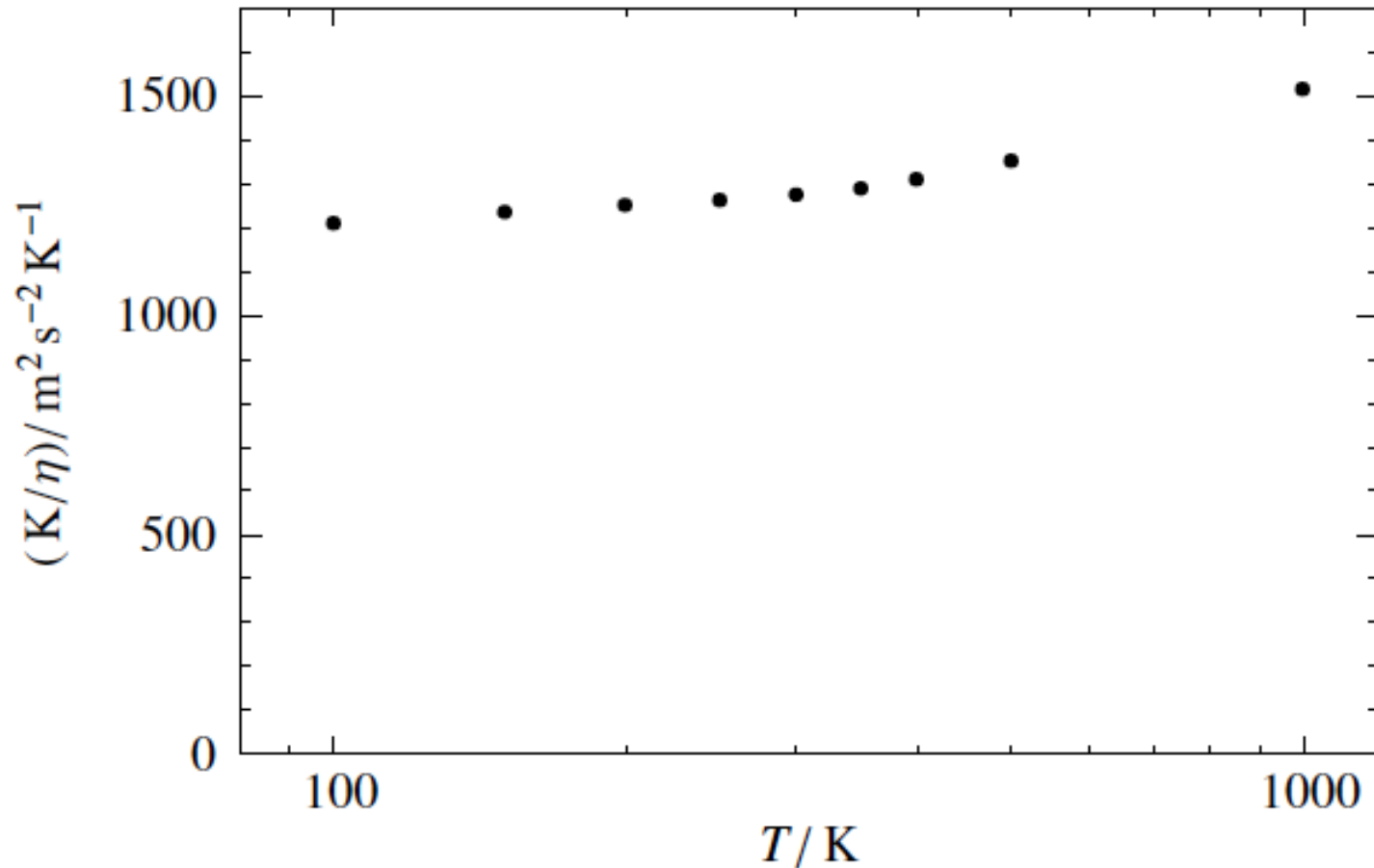
| Temperature K | η $10^{-6} \text{ N m}^{-2} \text{ s}$ | K $10^{-3} \text{ W m}^{-1} \text{ K}^{-1}$ | K/η $\text{m}^2 \text{ s}^{-2} \text{ K}^{-1}$ |
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$$\frac{K}{\eta} = \frac{C_m}{m} = \frac{5k}{2m}$$

it does rise, partly as a result of the excitation of vibrations in the oxygen molecule.

For molecular oxygen, $m = 32 \text{ u}$, and the ratio is expected to be 650.

This is too low, but is at least the correct order of magnitude, which is all one can expect given the simple assumptions made.



Ratio of thermal conductivity and viscosity of oxygen as a function of temperature.

This should be a constant if the kinetic theory prediction that K and η are both proportional to $T^{1/2}$ holds.

3.2.6 Pressure dependence of transport coefficients

The viscosity and thermal conductivity coefficients:

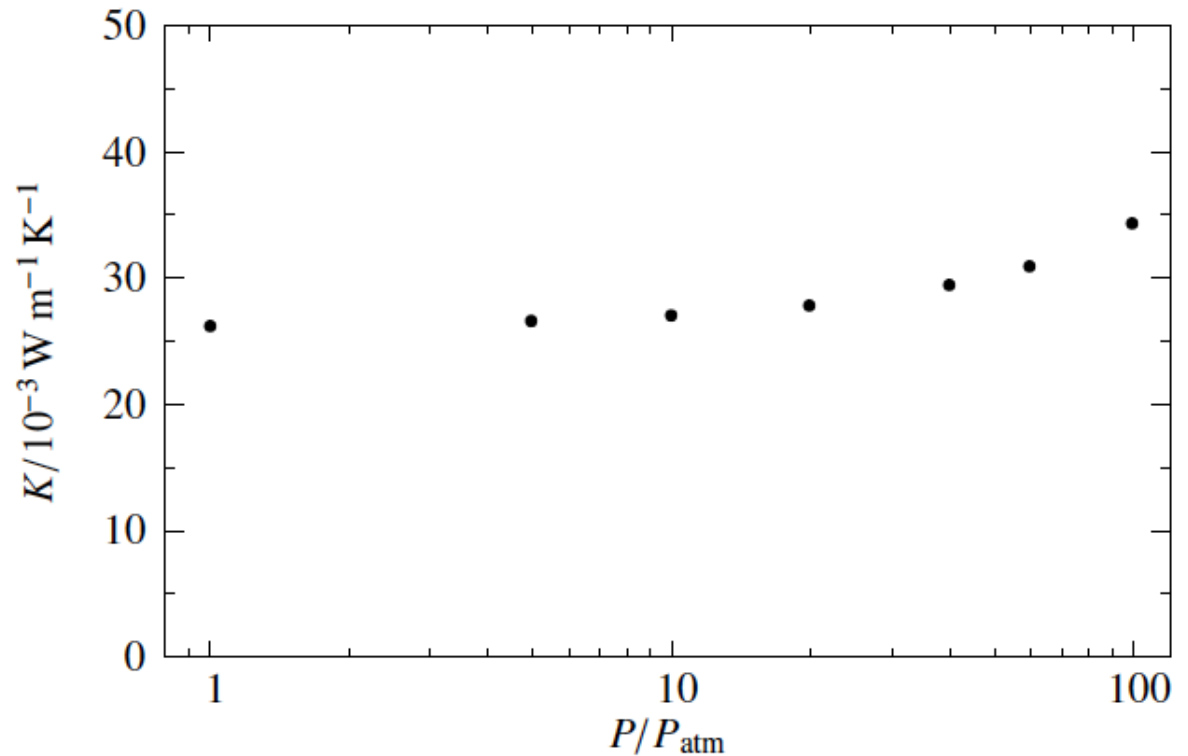
$$\eta = \frac{1}{3}\lambda\bar{v}\rho,$$
$$K = \frac{1}{3}\lambda\bar{v}C.$$

both ρ and C scale with n , while $\lambda \propto n^{-1}$

Therefore:

kinetic theory predicts that η and K are independent of pressure!

| Pressure atm | K $10^{-3} \text{ W m}^{-1} \text{ K}^{-1}$ |
|-----------------|--|
| 1 | 26.2 |
| 5 | 26.6 |
| 10 | 27.0 |
| 20 | 27.8 |
| 40 | 29.4 |
| 60 | 31.0 |
| 100 | 34.3 |



Thermal conductivity of oxygen as a function of pressure at 300K

- At low pressures, the mean free path does get larger, but eventually it will become similar in size to the dimensions of the apparatus.

It then ceases to increase and the transport coefficients start to drop. This is known as the Knudsen regime of pressures, and is difficult to treat accurately since results start to depend upon details of the apparatus.

- At high pressures, other problems set in as interatomic forces becomes significant.

Example 3.5 Estimate the power per unit area carried by conduction between two plates differing in temperature by 10 K and separated by a 1 mm thick air gap at pressures of 10^5 N m^{-2} and 0.1 N m^{-2} at $T = 298 \text{ K}$.

Answer 3.5 For $P = 10^5 \text{ N m}^{-2}$ (1 bar), $\lambda = 10^{-7} \text{ m} \ll d$, so we use

$$K = \frac{1}{3} \lambda \bar{v} c. \quad (3.39)$$

with $\bar{v} = 500 \text{ m s}^{-1}$. Estimate c , the heat capacity *per unit volume*, using the equipartition theorem for a diatomic gas with no vibrations:

$$c = \frac{5}{2} kn = \frac{5}{2} \frac{P}{T_1}, \quad (3.40)$$

Hence,

$$K = \frac{10^{-7} \times 500 \times 5 \times 10^5}{3 \times 2 \times 298} = 0.014 \text{ W m}^{-1} \text{ K}^{-1}. \quad (3.41)$$

For $\Delta T = 10 \text{ K}$, $\Delta x = 0.001 \text{ m}$, $dT/dx = 10^4 \text{ K m}^{-1}$ and so the conduction rate is 140 W m^{-2} .

For $P = 0.1 \text{ N m}^{-2}$, $\lambda = 0.1 \text{ m} \gg d$, where d is the thickness of the air gap, so we expect the rate to be $d/\lambda = 150$ times smaller, very roughly.

3.2.7 Variation with nature of gas

large mean free paths will lead to good conduction



small molecules will conduct better

small molecules are often low mass molecules



they move faster at a given temperature



higher conductivity

Therefore we expect hydrogen and helium to be better heat conductors than carbon dioxide for instance.

Remember: for fixed P and T , n is the same for all ideal gases!

3.3 Limitations of kinetic theory

Kinetic theory is successful in explaining, for instance, the pressure exerted by a gas, but it fails to describe:

- phase changes (boiling, melting),
- the existence of liquids and solids,
- deviations from the ideal gas law.

It is the neglect of interatomic forces which is most important (without them there could be no liquids).

We will now follow a more utilitarian approach in which we take some measured (macroscopic) properties and try to extrapolate physical (microscopic) theories from these.

This is the subject of **classical thermodynamics**.