Perfect Gases – Transport Phenomena

We have been able to relate quite a few macroscopic properties of gasses such as *P, V, T* to molecular behaviour on microscale. We saw how macroscopic pressure is related to the molecular motion in case of perfect gasses. Is there anything else interesting one can learn from the *kinetic theory* of perfect gasses? Indeed there is. So far we only considered macroscopic properties that can be termed as static. We shell now look at some properties that are not. Collectively they are termed *transport phenomena* and can be further subdivided in:

- *Diffusion* – molecular transport due to *concentration gradients*
- *Thermal* conduction – transport of *energy*
- *Viscosity* – transport of *momentum*

These are described by their corresponding coefficients: *D* for diffusion, *K* for thermal conduction and η for viscosity.

Mean free path

In order to consider the diffusion we must first look in details at molecular collision. We again suppose that all molecules are the same and collide elastically and also suppose σ to be an effective molecular diameter. We will follow the progress of a single molecule as it collides with others moving through the gas. For simplicity we assume that the rest of the molecules are frozen in their positions. Thus if our lonely molecule travels distance l it will sweep an element of volume $\pi\sigma^2 l$ and if there are n molecules per m^3 then our molecule will collide with $\pi\sigma^2 l\, n$ of them.
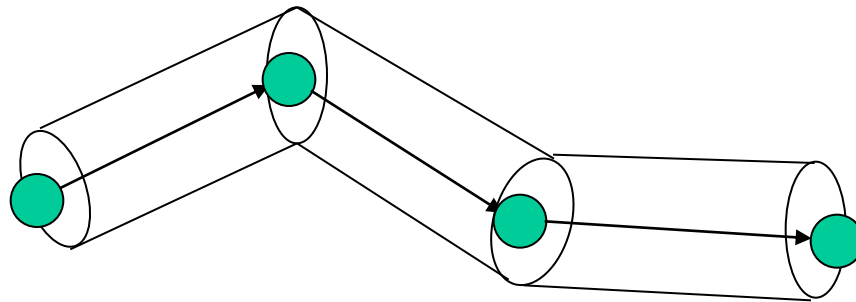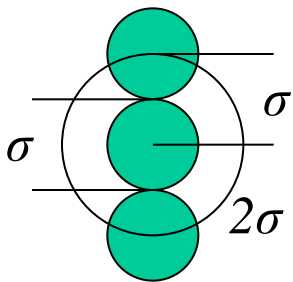
We can now define the mean distance between collisions or *mean free path* as (distance travelled)/(number of collisions):

$$\lambda = \frac{l}{\pi\sigma^2 nl} = \frac{1}{\pi\sigma^2 n} = \frac{k_B T}{P\pi\sigma^2}$$

Mean free path cntd.

We only considered the simplest approach, in reality other molecules will move too and if the speed distribution will be describe by that of Maxwell

$$P_M(v) = 4\pi \left[\frac{m}{2\pi k_B T} \right]^{3/2} v^2 e^{-mv^2/2k_B T} \Rightarrow \lambda = \frac{1}{\sqrt{2}\pi\sigma^2 n}$$

what a change!

We see that $\lambda \sim 1/n \sim 1/P$. For air ($\sigma$=0.3nm) at STP (standard temperature and pressure) $\lambda \approx$100nm, whilst mean distance between the molecules is of order $(1/n^3) \approx$3nm.

Number of collisions per unit area per second (*flux*)

Consider a volume of gas with concentration *n* and mean velocity *v* and lets see how many molecules will pass through an area *A* per unit time. We further split our velocity in three components one of which is perpendicular to area *A* (we done this before in kinetic theory). Then in time *t* about 1/6 of the molecules in the volume *vtA* will pass through *A* and hence flux *j*:

$$l = \bar{v}t$$

A

$$V = lA = \bar{v}tA$$

$$j = \frac{1}{6}\frac{n\bar{v}At}{At} = \frac{1}{6}n\bar{v}$$

1/6
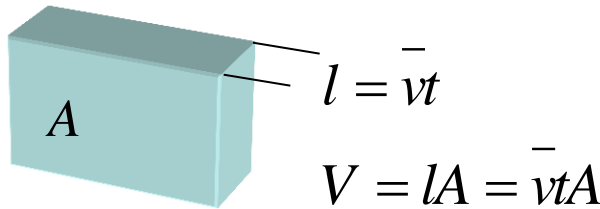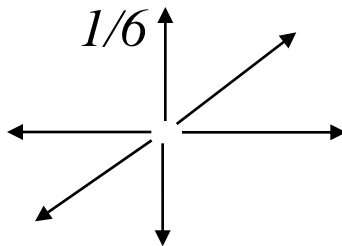
Diffusion

Now if we consider gas with a concentration gradient it should be clear that molecules will move from the more concentrated to the less concentrated regions via a process of collision/random walk. This is diffusion process. If over distance dx concentration change is dn the concentration gradient is dn/dx. The number of molecules crossing A normal to gradient per second can then be written as:

$$\frac{dN}{dt} = -D\frac{dn}{dx}A \qquad \left(j = \frac{dN}{Adt} = -D\frac{dn}{dx}\right) \quad \text{Fick's Law}$$

Where D is called the coefficient of self-diffusion and the negative sign implies flow in the direction of smaller concentration.

Consider the following situation:
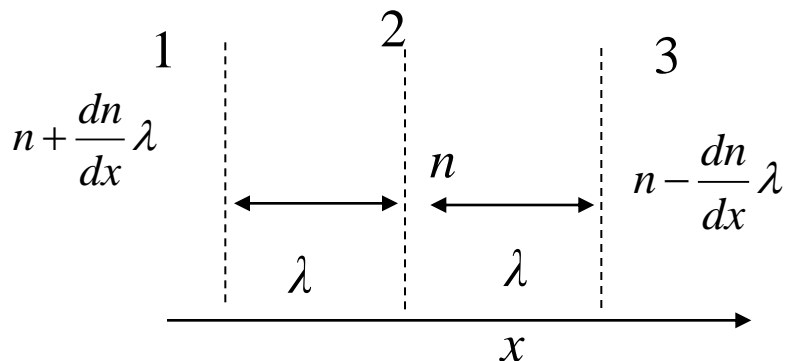
Diffusion contd.

We would then have the number of molecules per second crossing from 1

$$= \frac{1}{6}\left(n + \frac{dn}{dx}\lambda\right)\bar{v}A$$

and from 3

$$= \frac{1}{6}\left(n - \frac{dn}{dx}\lambda\right)\bar{v}A$$

There will also be molecules leaving on each side of 2 of number $= \frac{1}{6}n\bar{v}A$

So the net transfer is then

$$-\frac{1}{6}\left(n + \frac{dn}{dx}\lambda\right)\bar{v}A + \frac{1}{6}\left(n - \frac{dn}{dx}\lambda\right)\bar{v}A - \frac{1}{6}n\bar{v}A + \frac{1}{6}n\bar{v}A = -\frac{1}{3}\frac{dn}{dx}\lambda\bar{v}A = -D\frac{dn}{dx}A$$

hence

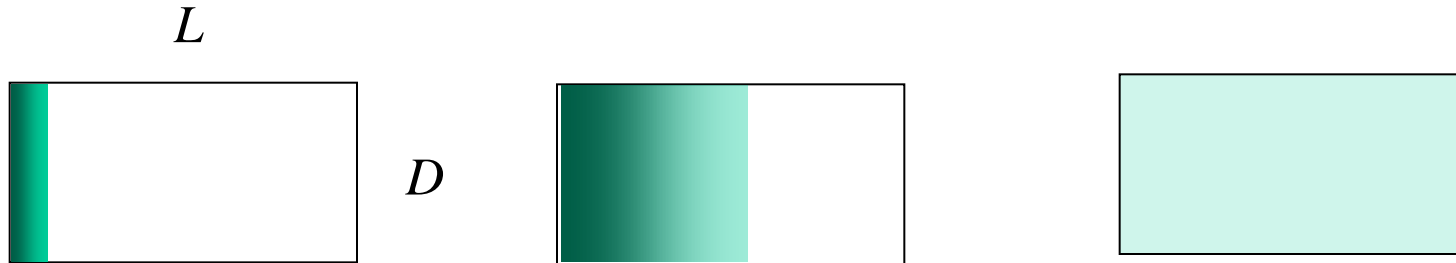$$\boxed{D = \frac{\lambda\bar{v}}{3} = \frac{\bar{v}}{3\pi n\sigma^2}}$$

For air at STP $\sigma=0.3$nm, $\lambda\approx100$nm, $v=450$m/s, n $\approx3*10^{25}$m^{-3}

which gives D of order 10^{-2} m^2/s

also

$$\bar{v} = \left(\frac{8k_BT}{\pi m}\right)^{1/2}$$

hence D can be related with macroscopic T and also P and V through n

Diffusion contd.

L

D

The difference from the previous consideration ($j_{in} = j_{out}$, *dn/dt=0*) is that now *n=n(x,t)*, and *dn/dt≠0* so we arrive to another relationship:
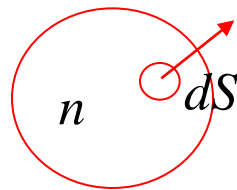
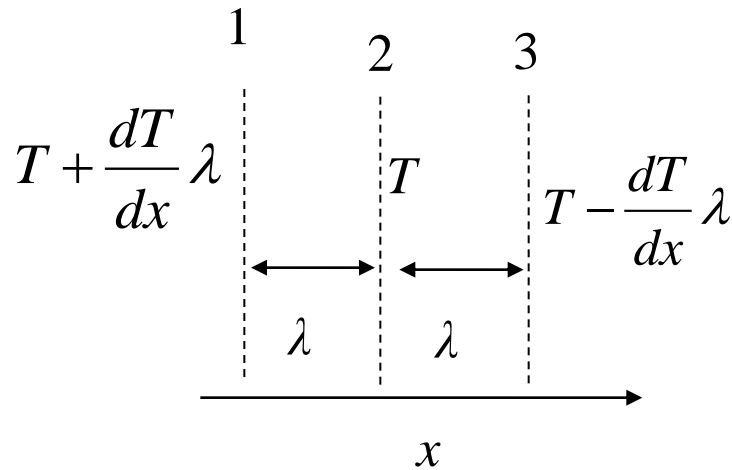$$\int_V \frac{\partial n}{\partial t} d^3x = -\int_S \vec{j} d\vec{S} = -\int_V \nabla \vec{j} d^3x$$

hence

$$\frac{\partial n}{\partial t} + \nabla \vec{j} = 0$$

$$\frac{dn}{dt} = D \frac{d^2n}{dx^2}$$

With the solution (for *L>>D*):

$$n(x,t) = \frac{N_0}{A(\pi Dt)^{1/2}} e^{-x^2/4Dt}$$

N_0 is the initial number of molecules, *A* is the area across which gas expands.

Thermal conductivity

1   2   3

$$T + \frac{dT}{dx}\lambda \qquad T \qquad T - \frac{dT}{dx}\lambda$$

$$\lambda \qquad \lambda$$

x

$$\boxed{Q = -KA\frac{dT}{dx}}$$

where K is the thermal conductivity

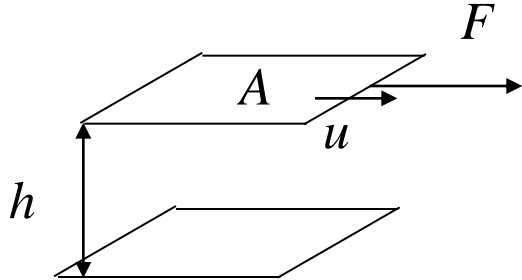Now the rate of transport, this time of thermal energy ($dQ = C_V dT$), is from 1

$$\frac{\overline{nv}A}{6}c_V\left(T + \frac{dT}{dx}\lambda\right)$$

from 3 $\quad \dfrac{\overline{nv}A}{6}c_V\left(T - \dfrac{dT}{dx}\lambda\right)$ so the net transfer at 2 is $\quad \dfrac{\overline{nv}A}{3}c_V\left(\dfrac{dT}{dx}\lambda\right)$

hence $\quad Q = -\dfrac{\overline{nv}A}{3}c_V\lambda\dfrac{dT}{dx} \Rightarrow \boxed{K = \dfrac{\overline{nv}\lambda}{3}c_V}$
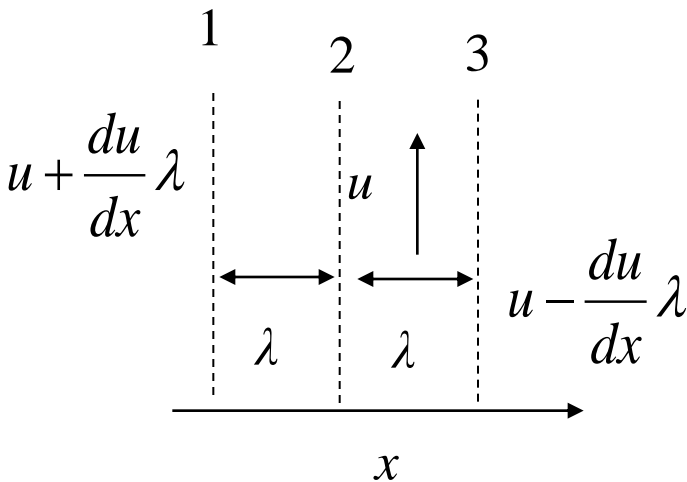
Viscosity

F must be applied to maintain constant flow. F is proportional to A and u/h.

$$F = \eta A \frac{du}{dx}$$

We further assume: (i) $u \ll v$, (ii) the only molecules reaching 2 are those that just made their collision at a distance λ. Thus the number of molecules crossing A is $\frac{1}{6} n \bar{v} A$ per second and from 3 this molecules bring to 2 net horizontal momentum

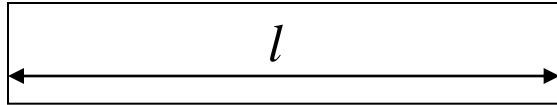$$m \left(u - \frac{du}{dx} \lambda \right) \frac{n\bar{v}}{6} A$$

Similarly fro 1 to 2 $\quad m \left(u + \frac{du}{dx} \lambda \right) \frac{n\bar{v}}{6} A$

But 2 sends $\frac{1}{6} n\bar{v} A$ both ways too

Thus the total momentum transfer per second (i.e. force) is

$$F = \frac{m \lambda n \bar{v}}{3} A \frac{du}{dx} \Rightarrow \eta = \frac{1}{3} m \lambda n \bar{v} = \frac{1}{3} \frac{m\bar{v}}{\pi \sigma^2}$$
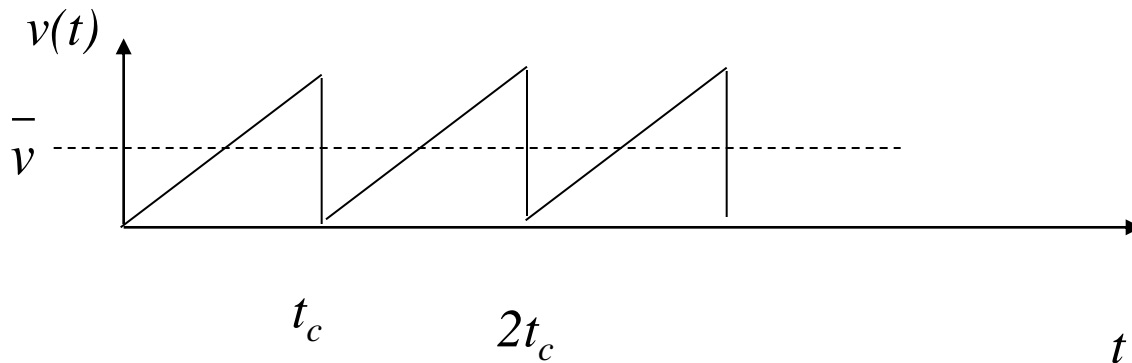
Electrical conductivity

l

Electric field $E = V/l = const$

V- voltage difference

A charge e subject to constant E experiences a constant force $F=e(V/l)=ma$ and the drift velocity is then

$$v(t) = at = \frac{eV}{ml}t$$

and grows linearly with time. Now lets consider that a collision takes v to 0

$v(t)$

$\bar{v}$

t_c $\quad$ $2t_c$ $\quad\quad\quad\quad$ t

$$\bar{v} = \frac{1}{2}\frac{eV}{ml}t_c$$

Electrical conductivity cntd.

The current density is then

$$j = en\bar{v} = \frac{e^2 V n}{2ml} t_c = \frac{e^2 n t_c}{2m}\left(\frac{V}{l}\right) = \sigma E$$

$$\boxed{\sigma = \frac{e^2 n t_c}{2m}}$$