

# Session 17

## Transport Properties

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# Welcome

Welcome to session 17.

In this session we'll look at transport properties in fluids. By transport properties we mean the flows that restore a system to equilibrium, so for example, the flow of heat to eliminate a temperature gradient.

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# Learning Objectives

- Brownian motion
- Mean free path
- Random walk
- Diffusion,
- Fick's law,
- Fluctuations,
- Viscosity
- Einstein relation

# The Problem

The sequence shows the dispersal in water of an ink drop (arrowed)



If we could follow the paths of the ink particles, which are readily displaced by impacts with the atoms of the water, we would see them disperse quickly through the surrounding medium. We call this diffusion. We're all familiar with this diffusion of a coloured blob of ink through a glass of water. The process is irreversible – you can't get the blob of ink back again from the uniform mixture that eventually forms.

In the following images, we see a coloured blob being stirred and then reformed by reversing the motion. It's not recovered exactly because the stirring motion isn't exactly reversed, but it certainly doesn't diffuse like the ink blot in water. Given long enough it might do so, but why is it so slow?



To answer this question we need to understand how diffusion arises from the microscopic motion of atoms and molecules. This motion is apparent in a phenomenon known as Brownian motion which we'll turn to next.

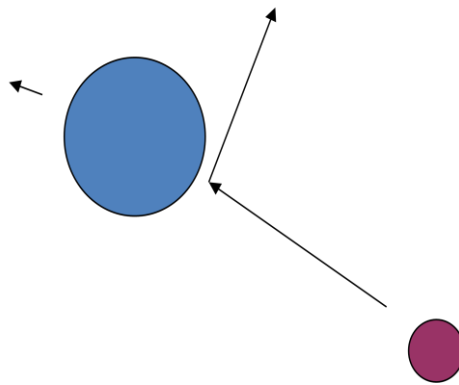
# Brownian Motion

If you observe a substance such as milk under a microscope, you can observe small globules of fat suspended in the liquid. These globules are very small, and as you observe them you can see them 'jiggle'.

This jiggling motion of the particles was first observed in a different context by the Scottish botanist Robert Brown and is known as 'Brownian Motion'. Brown found the same effect in pollen grains suspended in water. His first thought was that it showed the pollen grains to be alive in some way. We now know this isn't the case – the fat particles in milk aren't alive – so the motion must reflect the buffeting being received from the environment.

## Can we explain Brownian motion in terms of the impact of atoms?

What is the speed of a molecule of water?



If a molecule of mass  $m$  has speed  $v$  its kinetic energy is  $\frac{1}{2}mv^2$ . The mean energy of a molecule of a gas at a temperature  $T$  is  $\frac{3}{2}kT$  where  $k$  is Boltzmann's constant. Equating these two expressions gives equation 1.

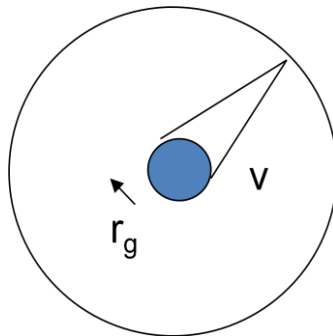
$$\frac{1}{2}m\langle v^2 \rangle = \frac{3}{2}kT \quad (1)$$

The typical speed of a gas molecule is therefore given by equation (2).

$$v = \langle v^2 \rangle^{1/2} = \sqrt{\frac{3kT}{m}} \approx 10^3 \text{ m s}^{-1} \quad (2)$$

Let's use this as a rough estimate of the speed of a water molecule, even though water is far from a perfect gas. If this collides with a pollen grain, what is the speed of the grain?

A pollen particle is roughly 1  $\mu\text{m}$  in diameter, roughly 10,000 times larger than a water molecule, so let's take it to be at least 10,000 times more massive. By conservation of momentum this means that the speed of the pollen grain is around 0.2 metres a second. It's probably quite difficult to measure the speed of the pollen grain. So let's see how far it moves before another collision changes its direction.



The number of collisions with water molecules per second is given by the number of water molecules moving towards the grain within a sphere of radius  $v$ , since these are the ones that can reach the grain in 1 second. The result is equation (3).

$$\left(\frac{r_g}{v}\right)^2 \frac{1}{4\pi} n \left(\frac{4}{3}\pi v^3\right) \approx 10^{19} \text{ s}^{-1}$$

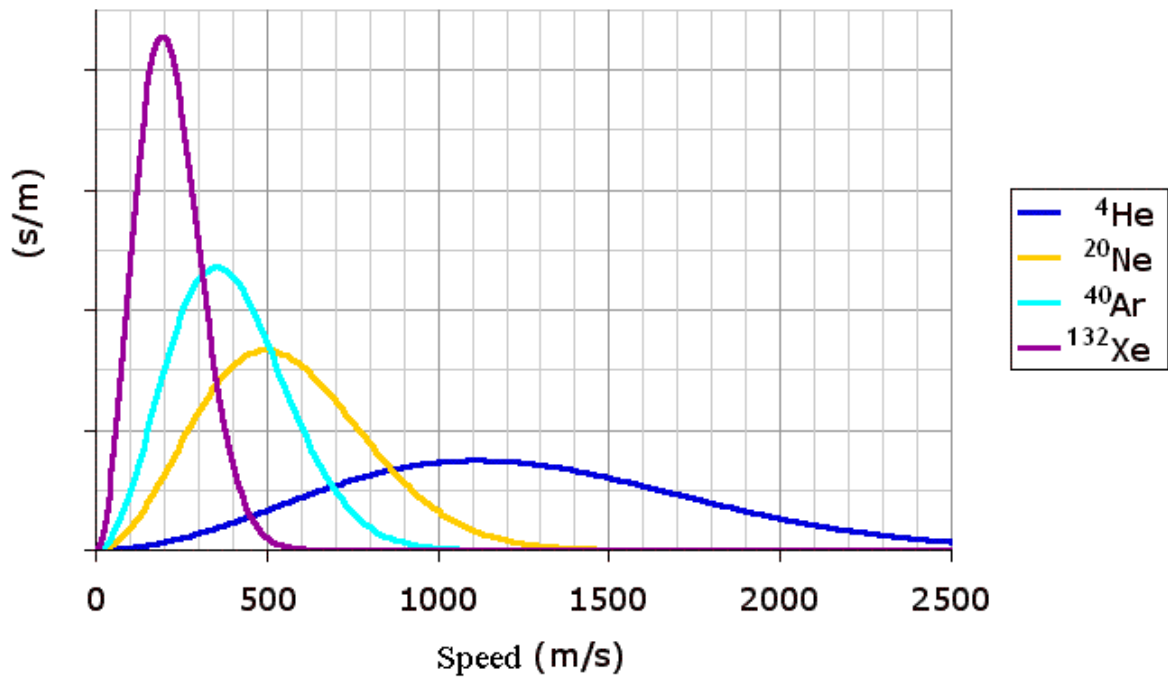
Looking at the factors in this expression we have: the fraction of  $4\pi v^2$  into which the water molecule must be moving to hit the target, the number of water molecules per unit volume  $n$  times the volume. Of course, molecules nearer the grain will have a greater chance of striking it, so this is an underestimate.

The result is about  $10^{19}$  per second. So the grain moves  $10^{-19} \times 10^{-2}$  m between collisions – an amount that is quite imperceptible.

Could we appeal to impacts not with the average water molecule, which individually have negligible effect, but to the fastest moving ones? For this we need to know how the speeds are distributed amongst the molecules – that is, how probable is it that a molecule will have a speed a specified amount greater than the norm. For a gas in thermal equilibrium at temperature  $T$  this is given by the Maxwell Boltzmann distribution. The graph shows this distribution of particle velocities for atoms of various masses.



Probability  
Density



Image<sup>1</sup>

Because the Maxwell Boltzmann distribution is not symmetrical, the mean and the peak are not quite the same, but they are both of order of magnitude  $\sqrt{3kT/m}$ . You can see that once the speed is more than a few times the mean, the number of atoms with that speed becomes very small. For example at 10 times the mean the number is  $e^{-100}$  times smaller, which is around  $10^{-50}$ .

$$N \propto v^2 \exp\left(-\frac{mv^2}{kT}\right) \approx \left(\frac{v}{v_0}\right)^2 \exp\left(-\frac{v^2}{v_0^2}\right)$$

$V_0 =$  mean speed

This leaves us with the alternative that it is not single impacts that are important in Brownian motion, but clusters of impacts. Let's see how that works.

<sup>1</sup> Adapted from Maxwell-Boltzmann molecular speed distribution for noble gases, Choihei, as posted on commons.wikimedia.org. Creative Commons Licensed.

## Random events

Consider writing down a sequence of 0s and 1s randomly. How could we check if the sequence you write down is truly random?

We can do this by checking on the distribution of sequences of the same digit. How often would you expect a run of  $k$  1's in a sequence of  $N$  digits? The answer is that on average  $k$  consecutive 1s should appear about  $(1/2)^{k+2}N$  times. The  $N$  comes from the fact that we can start off the sequence in any of  $N$  positions. In each slot we have a probability of  $1/2$  that we will choose a 1 so you might expect a probability of  $(1/2)^k$  that we choose  $k$  1s. The actual probability is  $(1/2)^{k+2}$ . Can you see where the extra two powers of  $1/2$  come from? Think about the digit before the sequence starts and the one after it ends.

The example illustrates the fact that in a long series it's not at all unusual to find long sequences of 1s or 0s.

Does this now enable us to explain Brownian motion? Is it the occasional occurrence of large imbalances of impacts from different directions that displaces the pollen grain? If there are  $10^{19}$  impacts per second then what is the likely length of the largest run of hits from one direction in this time? We require that the probability of a run of  $k$  identical outcomes in  $10^{19}$  trials,  $p_k = (1/2)^{k+2}N$ , should be of order 1. That is,  $2^{k+2} = 10^{19}$ . It will be sufficient to evaluate this only very approximately: 10 is roughly  $2^3$  so we need  $2^{k+2} = 2^{57}$  or  $k = 55$ . This is still an insignificant excess as far as observing Brownian motion is concerned. What's the problem?

In fact, it's not necessary that the imbalance should be created by successive impacts in the same direction: only that there should be a persistent imbalance over an observable time interval. To find out if this can be achieved we need to investigate the probability of getting imbalances of different sizes. This is the subject of the random walk, which we'll turn to in the next section.

## Summary

Brownian motion is the random motion of a macroscopic particle suspended in a fluid.

It cannot be explained in terms of individual impacts of atoms of the fluid, but by excess impacts from one side in a random sequence.

## SAQs

- (i) Suppose that a pollen grain is hit either from the left or the right. If we were to need an excess of 100 successive hits from one side in order for the effect to be observable, how long would it be before this happens? Which of the following is nearest?

(a)  $10^{13}$  years   (b)  $10^{-17}$  seconds   (c) 2 seconds

(ii) Why do we not need to wait this long for imbalances to be observed?

(a) we see the pollen grain responding between individual impacts

(b) the pollen grain responds to the overall imbalance, not just to strings of impacts from one side

(c) the pollen grain has its own thermal motion
- Cross section for photon scattering off of a charged particle of mass  $m$  is  $1/m^4$ . Is it (a) more or (b) less likely that a photon will be impeded by an electron than by a proton?

The answers appear on the following page

## Answers

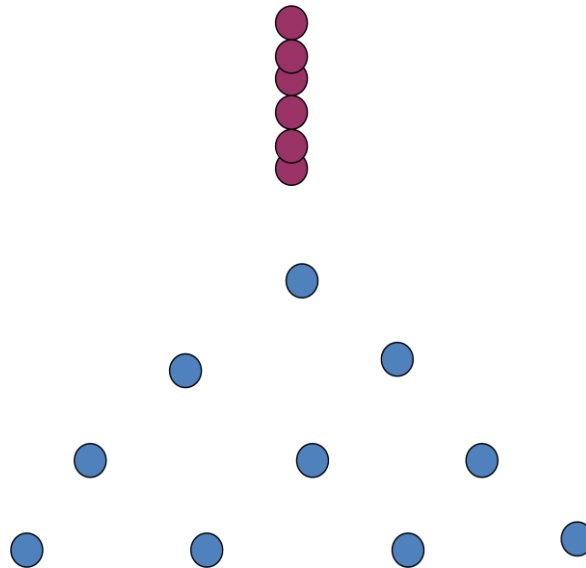
1. (i)
  - (a) Correct: Require  $N = 2^{k+2} = 2^{100} = 10^{30}$ . So we have to wait  $10^{30}/10^{19}$  seconds =  $10^{21}$  s =  $3 \cdot 10^{13}$  years!!!!
  - (b) Incorrect: this is the time for 100 hits, which will be a mixture of impacts from left and right, not the excess
  - (c) Incorrect You may have argued from the calculation in the lecture that if the excess in 1 second is 55 then the excess in 2 seconds will be 110. This is quite wrong: large excesses are increasingly unlikely: we'll see the probabilities in the next section.
- (ii)
  - (a) Incorrect: the time between impacts is too short for this to be the case
  - (b) Correct
  - (c) Incorrect: thermal motions always arise from the interaction with the environment
2. (a) Correct: the scattering cross section is larger for the electron than the proton because the electron has a smaller mass
- (b) Incorrect: the scattering cross section is inversely proportional to the mass of the target to the power 4 so the probability of scattering goes down as the mass of the target goes up.

# Random Walks

## Galton's Board

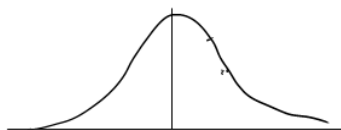
We've seen that the pollen grain fluctuates in position and velocity – but the fluctuations to the left are balanced by those to the right. So you might think that the pollen grain on average remains where it started. If we are to explain diffusion we need to understand why this is not true.

Let's start with a simulation of Galton's board.

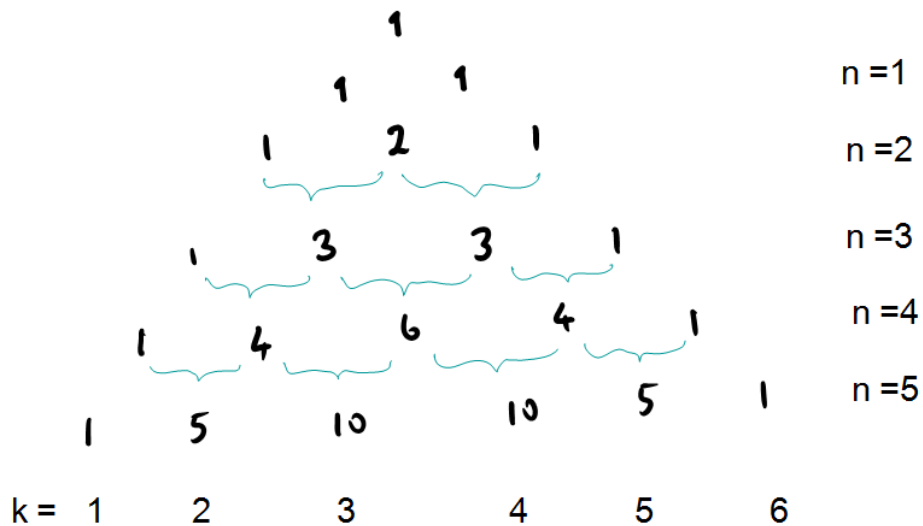


The blue circles represent fixed pins that the purple circles bounce off as they fall either to the left or the right with equal probability. At the bottom of the heap the balls are collected and counted. Where do you expect the majority of the balls to fall – in the centre or at the edge? Where do you expect the least number? Can you construct a verbal argument to explain your answer before going on?

We expect the distribution to peak in the centre because there are less paths leading to the extreme positions.



Below we show the calculation of the outcomes.



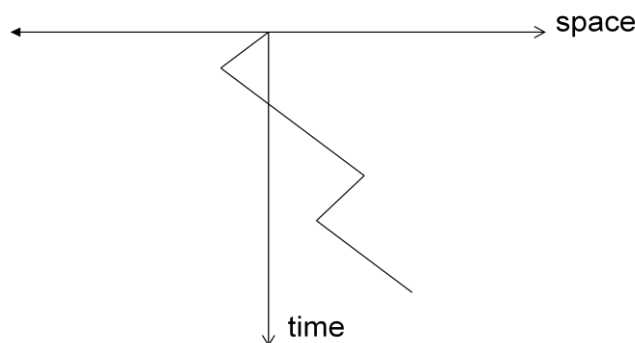
Let's focus on the 2 in the line labelled  $n=2$ . This is the number of ways on which one can get from the top 1 as starting point to this point, namely the sequence of moves LR or RL. The 1's at the edges arise because there is only one way to get to these points, namely the sequence of moves LLL and so on or RRR and so on.

Rather than counting we can derive a formula: to get to position  $k$  at the  $n$ th level we have to make  $k$  right moves out of  $n$ . The number of ways of doing this is the number of ways of choosing  $k$  objects from  $n$  without regard to order, which is  $n \times (n-1) \times \dots \times (n-k+1)$  divided by  $k!$ .

The entries are equal to 
$$\frac{n!}{(n-k)!k!} \quad n! = n(n-1)\dots 2.1$$

### Interpretation as a random walk

Instead of watching the balls fall down the pin board we can think of a body moving to the left or the right along a straight line at each step.



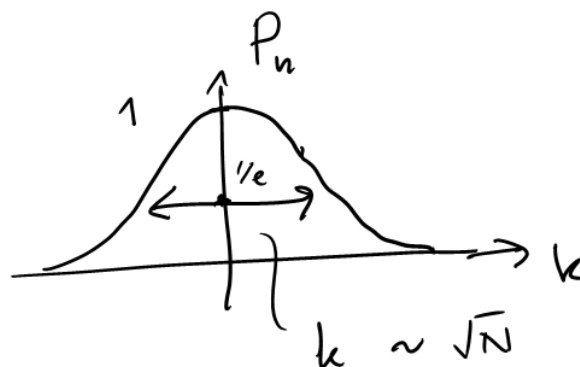
The body starts at the origin but as time goes on the probability of finding it a given distance from the origin increases. At each step there is a probability of 1/2 of moving to the left or right. The average displacement, counting left and right as opposite signs, is zero, but that's because the digressions to the left are balanced over time by digressions to the right. As time goes on the probability grows of long sequences in which one direction dominates over the other.

To see how far we expect the body to drift away from the origin as a function of time we need the mean square displacement or standard deviation. This can be derived from the probability distribution, but this involves some complicated maths so we'll omit the derivation and go straight to the result.

## Probability distribution after N steps

We now address the problem of how the excess impacts are distributed, that is, the probability of getting an excess of  $k$  impacts in one direction after  $N$  steps. This probability is the exponential of  $-k^2/N$ .

$$P_k \approx e^{-k^2/N}$$



From the probability distribution we can find the mean distance from the origin. The figure shows us immediately that the mean is zero! The mean distance is therefore not a useful measure of how far a random walker strays from the origin. Instead we want a quantity that doesn't average over positive and negative displacements. The simplest such quantity is the mean of the square of the displacement.

We can see from the figure that the probability that the particle is  $k = \sqrt{N}$  steps from the origin after  $N$  steps overall is  $e^{-1}$  or  $1/e$ . This means that typically the probability of finding the particle much further away than this is declining rapidly, so we expect the mean

distance to the right or left to be about  $\sqrt{NL}$  from the origin after  $N$  steps of length  $L$ . The mean square distance is therefore  $NL^2$  and the root mean square displacement is of order  $\sqrt{NL}$ .

$$\langle x_N^2 \rangle = NL^2$$

This now gives us a complete account of Brownian motion: it tells us where on average the pollen grain will be after  $N$  impacts, even though we do not see the effect of individual impacts. And it also tells us the distribution about this average.

## Summary

- We can model Brownian motion as a random walk with equal probability of steps of equal length to the right or the left.
- This enables us to calculate the probability of an excess of  $k$  steps in one direction after  $N$  steps in total; this probability is Gaussian.
- This tells us the distribution of the Brownian particle with time.



## SAQs

1. A particle undergoes a random walk with step length  $L$ . After  $N$  steps it has travelled along a path of length  
(a)  $N^{1/2}L$  (b)  $NL$  (c)  $NL^{1/2}$
2. The distribution of distances from the origin in a random walk arises  
(a) because the particles have different step lengths  
(b) because particles on the edge make are more likely to collide with the larger number of particles at smaller distances and hence more likely to be pushed out.  
(c) all paths are equally likely so the end points with the most paths leading to them are more highly populated.
3. An epidemic diffuses 3 miles in 1 week; how far in 4 weeks?  
(a) 12 miles (b) 4.7 miles (c) 8.2 miles (d) 6 miles

The answers appear on the following page

## Answers

- (a) Incorrect: this is the root mean square distance from the origin, not the length of the path

(b) Correct: all particles travel the same distance of the number of steps times the step length. It is the fact that some of these steps are back towards the origin that leads to an average distance from the origin of  $N^{1/2}L$ .

(c) Incorrect: After  $N$  steps the length of path is  $NL$
- (a) Incorrect: the distribution is related to the mean step length

(b) Incorrect: the particle distribution, and hence the probability of collision, is symmetrical about the diffusing particle.

(c) Correct
- (a) Incorrect. This would be the distance at constant speed, but diffusion spreads the epidemic at a rate proportional to the square root of time

(b) Incorrect This answer arises if you add  $\sqrt{3}$  to the original 3 miles; but the epidemic is not starting from a point at a distance of 3 miles and the diffusion rate is not unity.

(c) Incorrect; It is not just the additional time over which the epidemic diffuses from a point 3 miles out, but over the whole time from a point at the origin.

(d) Correct. Since it diffuses 3 miles in 1 week,  $D = 3 \text{ miles (week)}^{1/2}$  and so after 4 weeks the distance is  $3 \times (4)^{1/2} = 6$  miles.

# Diffusion

So now let's apply what we've learnt to diffusion in a gas assuming that the gas atoms undergo random walks in their collisions with each other. We'll assume that the step length of the random walk is a constant, the mean free path of the molecules. Although in practice there would be a distribution of path lengths between collisions this does not affect the conclusions.

So, let's look at a Brownian particle moving through the gas. It performs  $N$  steps between collisions in a time  $t$  each of length  $L$ . We saw that the mean square displacement from the origin is then as  $\langle x_N^2 \rangle = NL^2$ .

If we let the time between collisions be  $\Delta t$  then

$$t = N\Delta t = \frac{N\lambda}{v}$$

We can then write equation (1)

$$\langle x_t^2 \rangle = 2Dt \quad (1)$$

which defines the diffusion coefficient  $D$ , and  $D$  is given by equation (2) by direct comparison.

$$D = \frac{L^2}{2\Delta t} = \frac{\lambda^2}{2\frac{\lambda}{v}} = \frac{1}{2}\lambda v \quad (2)$$

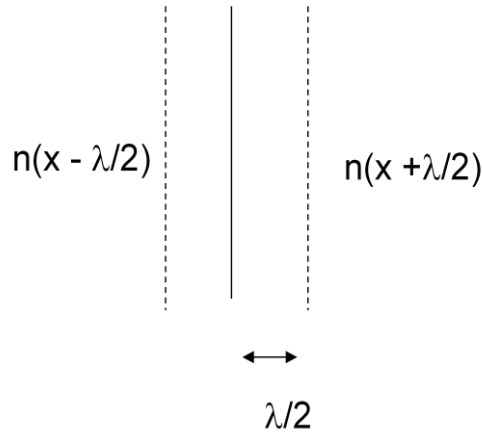
## What does this say about the flow of particles?

We now know that the distance a diffusing particle moves in time  $t$  is proportional to  $t^{1/2}$ . But we don't yet know the rate at which particles diffuse.

In this section we derive Fick's law which answers this question.

We imagine a gas of particles in random motion moving freely between collisions. The gas is in thermal equilibrium, so has the same temperature everywhere, but the density is not uniform. On average, particles in this gas move a distance  $\lambda$  between collisions.  $\lambda$  is called the mean free path. To begin the derivation we imagine a surface in the gas at some location

x. The density of gas particles here is  $n(x)$ . Particles are crossing this surface from the left and right moving freely on average within a distance  $\lambda$ . So typically particles travel freely from  $\lambda/2$  on the right to  $\lambda/2$  on the left and vice-versa.



The net flux is therefore as given in equation (1). The particles from the left provide a flux  $\frac{1}{2} n(x - \lambda/2)v$  times the average velocity  $v$  per unit area per unit time; those from the right,  $\frac{1}{2} n(x + \lambda/2)v$ . The factor of a half comes from the fact that  $\frac{1}{2}$  the particles are moving to the left and  $\frac{1}{2}$  to the right at each point. Notice that the distribution of speeds is the same everywhere because we are assuming that the gas is in thermal equilibrium at some fixed temperature. Expanding  $n(x \pm \lambda/2)$ , assuming that  $\lambda$  is small, gives equation (2), and hence (3).

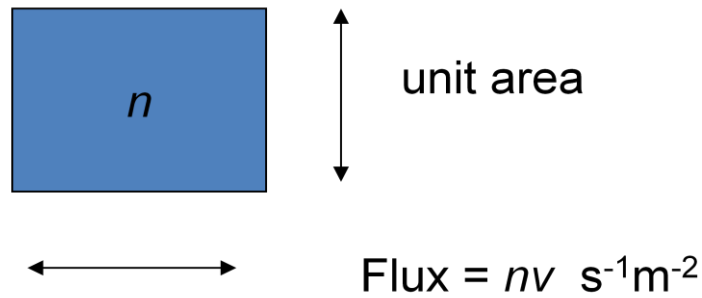
$$F = \frac{1}{2} n(x - \lambda/2)v - \frac{1}{2} n(x + \lambda/2)v \quad (1)$$

$$= \frac{1}{2} n(x)v - \frac{\lambda v}{4} \frac{dn}{dx} - \frac{1}{2} n(x)v - \frac{\lambda v}{4} \frac{dn}{dx} \quad (2)$$

$$= -\frac{\lambda v}{2} \frac{dn}{dx} \quad (3)$$

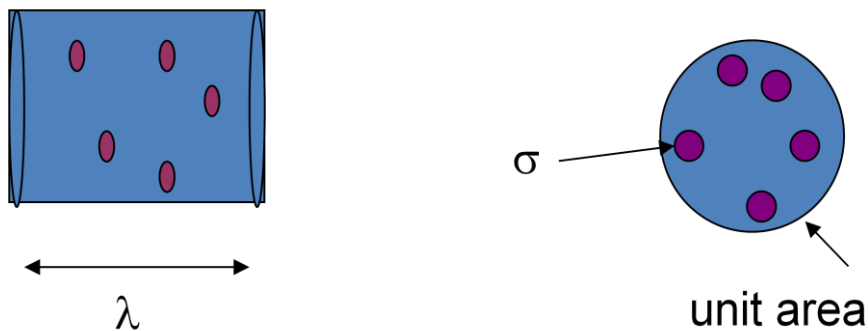
$$= -D \frac{dn}{dx}$$

Notice the minus sign which tells us that particles diffuse down a gradient in density. The diffusion rate is proportional to the gradient in density. The diffusion constant  $\lambda v/2$  is usually written as  $D$ .



## Kinetic theory

Kinetic theory relates the diffusion constant  $D$  or  $\lambda v$  to the properties of the gas. The mean free path can be written in terms of the collision cross section  $\sigma$ . Consider a cylinder of unit area. Each target in this cylinder has area  $\sigma$ . If the cylinder has length  $\lambda$ , then viewed end there must be enough of the areas  $\sigma$  to fill the view, because we know that on average a particle entering the cylinder must make a collision within it.



The total area of the  $n \times \lambda$  targets is  $n \lambda \sigma$  and if this fills the view it must have unit area. Thus  $n \lambda \sigma = 1$ , which is equivalent to equation (1).

$$\lambda = \frac{1}{n\sigma} \quad (1)$$

We already know that the root mean square speed is:

$$v = \left( \frac{3kT}{m} \right)^{1/2} \quad (2)$$

which gives us equation (3) for the diffusion constant:

$$D = \frac{\lambda v}{2} = \frac{1}{2n\sigma} \left( \frac{3kT}{m} \right)^{1/2} \quad (3)$$

Can you explain the diffusion constant is larger at higher temperatures?

## Summary

- In a diffusion process the mean square displacement of a particle after a time  $t$  satisfies  $\langle x_t^2 \rangle = 2Dt$  where  $D$  is the diffusion constant.
- The rate of diffusion is described by Fick's law:  $F = -D \frac{dn}{dx}$  relating the flux of particles to the density gradient.
- The mean free path is given by  $\lambda = \frac{1}{n\sigma}$  where there are  $n$  targets per unit volume of cross-section  $\sigma$ .

## SAQs

- In outer space the particle density is  $1 \text{ cm}^{-3}$  and the temperature is 3K.
  - What is the mean free path in metres of a hydrogen atom, assuming that its cross section is the Bohr radius,  $10^{-8} \text{ cm}$ ?
  - What is time between collisions in years? Give your answers as the power of 10 to the nearest integer.
- $D_{\text{air}} \sim 10000 D_{\text{water}}$  and  $n(\text{water}) = 1000 n(\text{air})$  What does this tell us about the relative cross sections?
  - they are the same;
  - the collision cross section for water molecules is 10 times that for air molecules;
  - the collision cross section for air molecules is 10 times that of water
- The units of  $D$  are (a)  $\text{m s}^{-1}$  (b)  $\text{m}^2 \text{ s}^{-1}$  (c)  $\text{m s}^{-1/2}$

The answers appear on the following page

## Answers

- 14 (i.e.  $10^{14}$  m)
  - 3 (i.e. 1000 years)
- $D \propto \lambda \propto 1/n\sigma$  so  $n\sigma$  (water) =  $10^4 \times n\sigma$  (air) and hence  $\sigma$  (water) /  $\sigma$  (air) =  $10^4 n$ (air) /  $n$ (water) = 10; (One molecule of water is about 0.1 to 0.2 nm)
- Incorrect:  $D$  is not a velocity since it's the ratio of  $\langle x^2 \rangle$  to  $t$ , not  $\langle x^2 \rangle^{1/2}$  to  $t$ .
  - Correct:  $D$  is the ratio of  $\langle x^2 \rangle$  to  $t$  so has the units of distance<sup>2</sup> / time
  - Incorrect: this would be true if  $D$  were defined as the coefficient relating the root mean square displacement to  $(\text{time})^{1/2}$ , but it in fact related  $\langle x^2 \rangle$  to  $t$ .



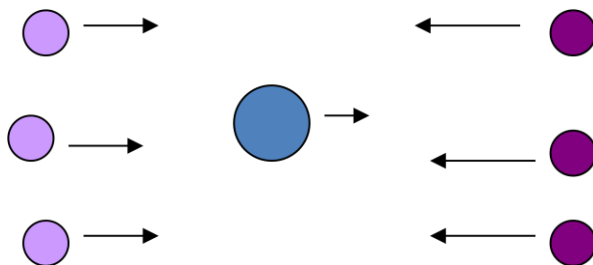
# Fluctuations and dissipation

## Fluctuations and drag

Einstein's original 1905 paper describes the connection between the diffusion constant, which is related to the fluctuations in the displacement of a fluid particle, and the drag that the fluid exerts on a body moving through it.

We can get some idea of why this connection comes about by considering again our Brownian particle, but this time not in terms of its changing position, but its changing velocity. Suppose that the particle suffers an excess of hits from the left; it will therefore be moving to the right. From the point of view of the particle, the medium will therefore appear to be moving towards it, so the particles of the medium now striking from the right will transfer a greater momentum than those from the left. The Brownian particle will therefore slow down – in other words the medium will appear to possess a viscosity.

$D$  = fluctuation in  $x^2$  is related to drag in medium:



## Viscosity

Let's see if we can make this argument quantitative. We know that as a body moves through a viscous medium it eventually reaches a terminal speed. This occurs when the viscous force balances the applied force. For example a body falling through the air will reach a speed at which gravity balances the drag from air resistance.

Viscous forces have a particular form: the force is proportional to the speed of the body with the coefficient of proportionality being the coefficient of viscosity, written here as  $\zeta$  (*zeta*) in equation (1):

$$\zeta v = f \quad (1)$$

↙
↘

coefficient of viscosity
applied force

When

$$v = \frac{\lambda}{\Delta t}$$

$$\lambda = \frac{1}{2} \frac{f}{m} (\Delta t)^2$$

$$v = \frac{1}{2m} (\Delta t) f \quad (2)$$

So

$$\zeta = \frac{2m}{\Delta t} \quad (3)$$

The terminal velocity of our Brownian particles is the average speed with which they move through the medium, namely  $\lambda / \Delta t$ . Immediately after a collision the Brownian particle is just as likely to be travelling in the direction of the applied force as against it. So on average, just after a collision the particle starts with zero speed. Between collisions the applied force accelerates a particle of mass  $m$ , according to Newtonian mechanics, with an acceleration  $f/m$ . Using the constant acceleration formula for distance and time we see that by the time of the next collision,  $\Delta t$  later, the distance covered  $\lambda$  must be  $\frac{1}{2} f/m \Delta t^2$ .

This gives us a second formula (2) for the velocity in terms of the force  $f$ , from which we can deduce a value for  $\zeta$  in equation (3)

## Results so far

We have a formula for the diffusion coefficient  $D$ , and for the viscosity coefficient.

$$D = \frac{\lambda^2}{2\Delta t} \qquad \zeta = \frac{2m}{\Delta t}$$

We're not yet home though because  $\Delta t$  and  $L$  are both microscopic properties that cannot be obtained from macroscopic measurements, that is measurements of the bulk properties rather than the atomic properties of the gas. So we need one more connection.

This is the relation between the speed of gas molecules and their temperature. For a perfect gas, that is one where the particles interact only when they collide and move freely in between collisions, we know that  $v^2 = kT/m$  (remember this is a one dimensional random walk so there is no factor of 3!)

$$\left(\frac{\lambda}{\Delta t}\right)^2 = v^2 = \frac{kT}{m} \quad (\text{for a perfect gas})$$

The product  $\zeta D$  can now be expressed directly in terms of the temperature  $T$ . We end up with Einstein's relation. This connects the fluctuations in position seen in Brownian motion and expressed here through the diffusion constant with the dissipative properties of viscosity (or friction).

$$\zeta D = m \left(\frac{\lambda}{\Delta t}\right)^2 = kT \quad (\text{Einstein fluctuation-dissipation relation})$$

This then answers the problem we posed at the start: large diffusion implies small viscosity and small diffusion implies large viscosity. The application to liquids which are not perfect gases is not exact, because we would have to take account of the stickiness of the molecules, but the same principle is followed.

## Now explain observations:

We can now return to our original problem of the diffusion of ink in different fluids and explain what we saw.

Ink diffuses freely through non-viscous liquid, but not through viscous one.

The Einstein relation tells us that the rate of diffusion in a fluid, as given by  $D$  the diffusion coefficient, and its viscosity are inversely related: rapid diffusion corresponds to low viscosity and vice-versa. Treacle has a viscosity about  $10^5$  times higher than water, hence a rate of diffusion 100 000 times slower. We should guess therefore that the fluid in original images was something like treacle – in fact it was golden syrup.

## Another example: frictional forces

We end with another example of the Einstein relation connecting fluctuations and dissipation. It is very easy to get into a muddle thinking about frictional forces. The muddle usually arises from forgetting that friction is a dissipative process that arises from fluctuations, just like viscosity. We illustrate that here.



Image<sup>2</sup>

A boat is towed along a canal by a constant force just sufficient to resist the frictional drag of the water. Clearly energy is required to keep the boat moving at constant speed. Where does this energy come from? Clearly from the machine doing the towing. But how can the energy be transmitted down the rope if the force and hence the extension is constant? If nothing is changing in the rope, how can energy be flowing? The answer is that friction cannot be a constant force on a microscopic level, even if it appears constant averaged over macroscopic time intervals. The motion of the boat must be fluctuating, hence the extension of the rope is changing and elastic waves propagate down it carrying the energy to the boat.

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<sup>2</sup> Where is the Horse?, by Dave Hamster, as posted on [www.flickr.com](http://www.flickr.com). Creative Commons Licensed.

## SAQs

1. At constant density the rate of diffusion is expected to (a) increase (b) decrease with temperature?
2. At constant temperature the diffusion rate in a perfect gas is expected to (a) increase (b) decrease with pressure?
3. The viscosity of a fluid tends to (a) increase (b) decrease with temperature?

The answers appear on the following page

## Answers

- (a) Correct: Kinetic theory gives  $D$  proportional to  $T^{1/2}/n$ ; the increase in temperature implies that molecules move faster hence diffusion is more rapid.

(b) Incorrect: Kinetic theory gives  $D$  proportional to  $T^{1/2}/n$  so increases with temperature; the increase in temperature implies that molecules move faster hence diffusion is more rapid.
- (a) Incorrect: Since the density  $n$  is proportional to  $P/T$ , we have that  $D$  is proportional to  $T^{3/2}/P$ . The mean free path is smaller at higher pressure.

(b) Correct: Since the density  $n$  is proportional to  $P/T$ , we have that  $D$  is proportional to  $T^{3/2}/P$  so the diffusion rate decreases as the pressure increases. The mean free path is smaller at higher pressure.
- (a) Incorrect: Viscosity is inversely related to diffusion: since  $D$  increases with increasing temperature the viscosity must go down.

(b) Correct: Viscosity is inversely related to diffusion: since  $D$  increases with increasing temperature the viscosity must go down.

# Additional Problems

## Problem 1: Photons from the Sun's centre

The Sun shines as a result of nuclear energy released in its centre and transported to the surface by radiation and convection. If the nuclear reactions were turned off, how long would it go on shining for?

Our first guess might be the time it takes light to travel from the centre to the surface. This would be a solar radius, around  $10^9\text{m}$ , divided by the speed of light, or about 3 seconds. How do we know this is wrong? Think for a moment before listening to the answer.

If light were to travel directly from the centre to the surface, and then on to the Earth, we should be able to see into the centre of the Sun. Since we can't we know that light from the centre must be scattered through the solar interior. In fact, it is also absorbed and re-emitted many times.

To get an estimate of the time we can make some simple approximations. First of all we ignore absorption and re-emission of photons and suppose that they are just scattered. So a photon maintains its identity. The actual scattering takes place in three dimensions, but we'll approximate the motion as a one dimensional random walk. We'll also assume that the photons scatter off of free electrons only. To calculate the mean free path we need to know the number of such electrons per unit volume. We'll assume that the Sun is made of hydrogen, that the hydrogen is fully ionised throughout the solar interior, and that the density is uniform. These assumptions sound fairly drastic, but they give some idea of the order of magnitude one might expect.

$$\text{Solar Radius} \quad R = 7 \times 10^8 \text{ m}$$

$$\text{Solar Mass} \quad M = 2 \times 10^{30} \text{ kg}$$

*Thomson Cross-section (for photons scattering off of free electrons)*

$$\sigma = 6 \times 10^{-29} \text{ m}^2$$

Start by thinking about how you would calculate the mean free path, and then how you would use this to calculate the time taken to random walk the distance of the solar radius.

Answer:

The mean free path of the photons can be found from equation (1), where  $n$  is the number density of electrons. From our assumptions the number of electrons is the same as the number of hydrogen atoms which is just the mass of the Sun divided by the mass of a hydrogen atom. To get the density we divide by the volume, giving us equation (2).

$$\text{Find the m.f.p.} \quad \lambda = \frac{1}{n\sigma} \quad (1)$$

$$n = \frac{(M / m_H)}{V} = \frac{M}{\frac{4}{3}\pi R^3 m_H} \quad (2)$$

$$\text{Random Walk} \quad R = N^{1/2} \lambda \quad (3)$$

$$\text{Time} = \frac{\text{distance}}{\text{speed}} \quad t = N\lambda / c \quad (4)$$

$$= \frac{R^2 \sigma}{c} \frac{M}{\frac{4}{3}\pi R^3 m_H}$$

$$= \frac{3}{4\pi} \frac{M}{m_H} \frac{\sigma}{R^2} \frac{R}{c}$$

$$\left. \begin{array}{l} M = 2 \times 10^{30} \text{ kg} \\ m_H = 2 \times 10^{-27} \text{ kg} \\ R = 7 \times 10^8 \text{ m} \\ \sigma = 6 \times 10^{-29} \text{ m}^2 \\ c = 3 \times 10^8 \text{ m s}^{-1} \end{array} \right\} \approx \frac{1}{4} \times \frac{2 \times 10^{30}}{2 \times 10^{-27}} \times \frac{6 \times 10^{-29}}{7 \times 10^8} \times \frac{1}{3 \times 10^8} \approx 3000 \text{ years}$$

Next we use what we have learnt about random walks, namely that after  $N$  steps a photon will have on average diffused a distance  $N^{1/2}$  times its mean free path. To escape from the centre a photon must diffuse a distance equal to the radius of the Sun; so equation (3) tells us how many steps of length  $\lambda$  are required. We convert this into a time in equation (4) and then substitute for  $N$  and  $\lambda$  from the earlier equations. From the given data we get a time of about 3000 years. As a result of our rather simple assumptions this is in fact too small by several orders of magnitude.



## Problem 2: Life in the Galaxy

The centre of our Milky Way galaxy is a relatively crowded place and that makes it an unlikely place to search for signs of life. The density of stars in the central region is of the order of  $3 \times 10^4$  per cubic light year and their speeds are around  $200 \text{ km s}^{-1}$ . So why are inhabited planets unlikely to be found at the centre of the Galaxy?

The answer lies in the frequency of stellar collisions. In order for life to emerge we can assume that a planet must be subject to fairly stable conditions over an extended time period. At the very least, it needs to be in an orbit round a star. A collision between a planetary system and another star will disrupt the system and send the planets off into space. So the way to answer this question is to calculate the time interval between collisions in the Galactic Centre. This involves calculating the mean free path. To do this we need an appropriate cross-section. One might guess that this would be the area of a star, but stars do not actually have to collide to disrupt a planetary system. Let's say it would be sufficient for stars to come within a distance of the orbit of Jupiter, which is  $8 \times 10^{11} \text{ m}$ . See if you can calculate the time between collisions from this before reading any further.

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Answer:

The mean free path is  $1/n\sigma$ , and so if the average speed of a star is  $v$ , the average time between collisions is  $1/n\sigma v$ . Taking  $\sigma = \pi R^2$ , where  $R$  is the radius of Jupiter's orbit round the Sun and a light year as about  $10^{16} \text{ m}$ , we get about 2 million years between collisions. Life on Earth arose within a period of 300 million years, which suggests that the process would be disrupted many times in the Galactic Centre. So this is an unlikely place to find life.

## Overall Summary

- Brownian motion is explained in terms of the multiple impacts of molecules on a macroscopic particle
- A particle undergoing a random walk diffuses a distance proportional to the square root of time:  $\langle x^2 \rangle^{1/2} = (2Dt)^{1/2}$
- The probability of finding a particle  $k$  steps from the origin after  $N$  steps of a random walk is proportional to  $\exp(-k^2/N)$
- Fick's law relates the diffusive particle flux to the density gradient:  $F = -\frac{dn}{dx}$
- Einstein's fluctuation-dissipation relation connects diffusion and viscosity:  $\zeta D = kT$

## Meta tags

Author: Derek Raine.

Owner: University of Leicester

Title: Enhancing Physics Knowledge for Teaching – Transport properties

Keywords: Brownian motion; Random walks; Diffusion; Fluctuations; Dissipation; sfoer; ukoer

Description: In this session we'll look at transport properties in fluids. By transport properties we mean the flows that restore a system to equilibrium, so for example, the flow of heat to eliminate a temperature gradient.

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Language: English

Version: 1.0



## Additional Information

This pack is the Version 1.0 release of the module. Additional information can be obtained by contacting the Centre for Interdisciplinary Science at the University of Leicester.

<http://www.le.ac.uk/iscience>

