Lecture 7: Maxwell Distribution & Brownian motion

- What does the Maxwell distribution look like?
- Extracting the probability
- Maxwell distribution in the limits of v
- Three characteristic velocities
- Maxwell distribution vs mass and temperature
- How can you measure the Maxwell distribution?
- A big beach-ball
- Brown's experiment pollen in water
- The drunken sailor problem
- Perrin's experiment
- The Tyndall effect





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Introduction

- You'll remember that we started out our analysis of pressure and temperature in the kinetic theory by looking at a single particle velocity *v*.
- We then generalised this result to a large number of particles by taking either the mean velocity $\langle v \rangle$ or more commonly the root-mean-square velocity $\langle v^2 \rangle^{\frac{1}{2}}$, which prevents the direction (either + vs for v_x or the direction in 3D space for a true vector v) from making our result zero.
- The use of this average masks the actual behaviour of the particles in the gas, and it's easy to think that they all travel at the average velocity, but this is absolutely not the case! The particles in the gas have a wide range of velocities from near zero to several times the average.

So a good logical question is:

Suppose I pick a particle at random in my gas, what is its velocity likely to be?

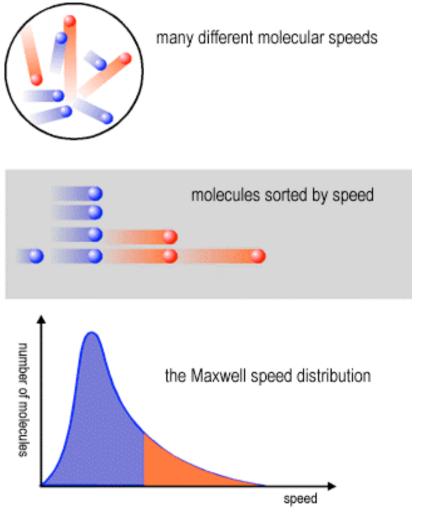
 This is a question that Maxwell looked at in 1866. He derived what is known as the Maxwell velocity distribution. It is sometimes also known as the Maxwell-Boltzmann distribution, because Boltzmann added some contributions to Maxwell's earlier work when he developed much of statistical mechanics.





What does the Maxwell distribution look like?

- The Maxwell velocity distribution (see below) is a plot of the probability density *D*(*v*) on the *y*-axis as a function of the particle speed *v* on the *x*-axis, for a particular gas at a particular temperature.
- The probability that a particle has a precisely given speed is zero. Since there are so many particles, their speed can vary continuously over infinitely many values, each particular speed has infinitesimal probability (i.e., zero).
- Hence, the actual value of a distribution function D(v) at a particular v isn't very meaningful by itself – it doesn't even have sensible units for a probability (i.e., none), its units are 1/v or s/m. The distribution function exists to be integrated – to turn it into a probability you need to integrate it over some range of velocities or interval dv.







Extracting the probability

• So, it's more correct to ask, what is the probability that a particle has a velocity between v_1 and v_2 , and this probability is then given by:

$$P(v_1...v_2) = \int_{v_1}^{v_2} D(v) dv$$
(7.1)

• This is equivalent to an area under the distribution curve as shown below. Note that you can make v_1 and v_2 arbitrarily close and for example integrate between v and v + dv, but in the limit where dv goes to zero (i.e., you ask for a precise velocity), you get back a zero (or infinitesimal) probability.

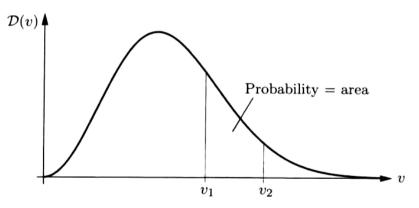


Figure 6.11. A graph of the relative probabilities for a gas molecule to have various speeds. More precisely, the vertical scale is defined so that the area under the graph within any interval equals the probability of the molecule having a speed in that interval.





So what is *D*(*v*)?

• The distribution function *D*(*v*) is given by:

$$D(v) = \left(\frac{m}{2\pi k_{B}T}\right)^{3/2} 4\pi v^{2} \exp\left(-\frac{mv^{2}}{2k_{B}T}\right)$$
(7.2)

• The derivation is rather complex, but for those interested, pages 242-246 in DVS are a good place to start. One thing to note is that the factor at the front is a normalisation factor to ensure that the total area under the curve (i.e., the probability of the particle having *any* velocity) is equal to 1. In other words:

$$P(0...\infty) = \int_{0}^{\infty} D(v) dv = 1$$
(7.3)

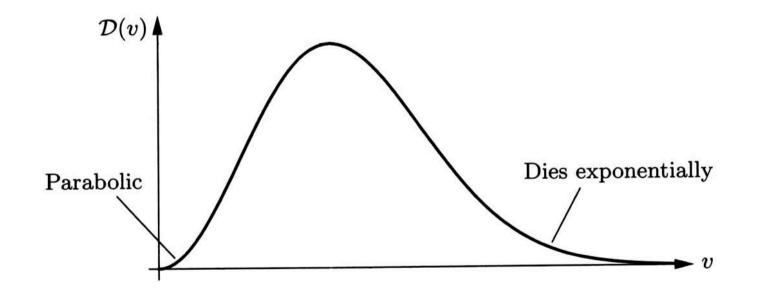
• The Maxwell distribution is actually rather difficult to use, mostly because the integral of the form $x^2 \exp(-x^2)dx$ cannot be solved analytically and requires instead either computational techniques, or in certain limits, you can take an approximation to make the integral analytical (for example, integrate $x \exp(-x^2)dx$ instead when $\exp(-x^2) > x^2$).





Maxwell distribution in the limits of *v*

Firstly, let's look the limits v → 0 and v → ∞. In both cases D(v) drops to zero. In the v → 0 limit, exp(-v²) << v² so the v² term dominates and the fall-off is roughly parabolic. In contrast, in the v → ∞ limit, exp(-v²) >> v² so the exp(-v²) term dominates and the fall-off is roughly exponential.

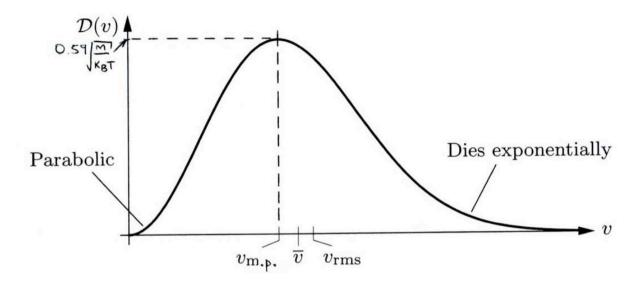






Three characteristic velocities

• We can also place three speeds on our distribution function.



- The first is the most probable speed $v_{m.p.} = (2k_B T/m)^{\frac{1}{2}}$, which you can obtain by setting the derivative of D(v) equal to zero and solving for v. The most probable speed $v_{m.p.}$ coincides with the peak in the Maxwell distribution, which lies at $D(v) = 0.59(m/k_B T)^{\frac{1}{2}}$.
- The second is the average speed v_{av} , which is the weighted average velocity:

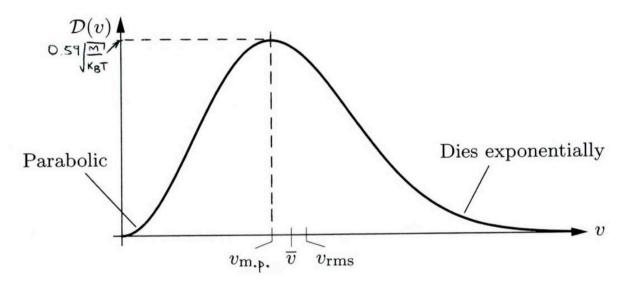
$$\overline{v} = v_{av} = \int_{0}^{\infty} v D(v) dv = \sqrt{\frac{8k_B T}{\pi m}}$$
(7.4)





Three characteristic velocities

• We can also place three speeds on our distribution function.



 The third is the root-mean-squared velocity v_{rms}, which we can obtain as the squareweighted average:

$$v_{rms} = \int_{0}^{\infty} v^2 D(v) dv = \sqrt{\frac{3k_B T}{m}}$$
 (7.5)

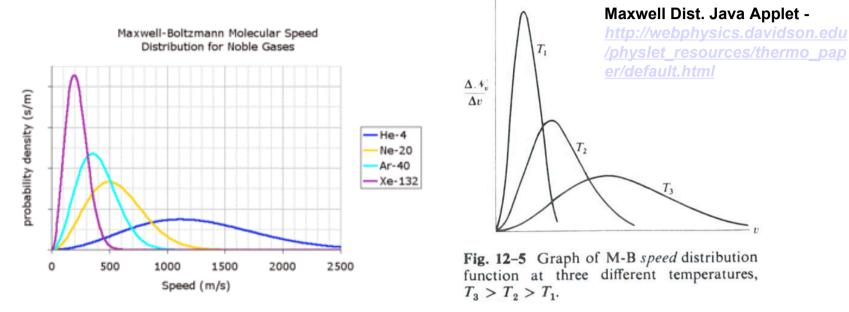
Note that this is the same result we got from the equipartition of energy, which is reassuring, and is the average velocity of the particles in our gas. We find that v_{av} is 13% larger than v_{m.p.}, and v_{rms} is 22% larger than v_{m.p.}.





Maxwell distribution vs mass and temperature

• There is one final thing to consider, and that is how *D*(*v*) varies with the two parameters that we can control *m* and *T*.



- The behaviour of D(v) with m at constant T is shown above left we find that increasing m squashes the distribution to the left, raising the peak and lowering the most probable, average and rms speeds.
- The behaviour of *D*(*v*) with *T* at constant *m* is shown above right reducing *T* pushes the distribution to the left, raising the peak and lowering the most probable, average and rms speeds.





How can you measure the Maxwell distribution?

• The Maxwell distribution can be measured using a molecular beam deposition technique, as done by Zartman and Ko in 1930-1934 using the apparatus below.

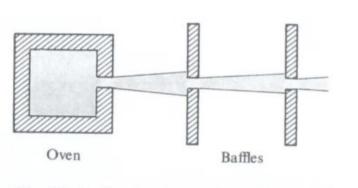


Fig. 12–9 Production of a beam of neutral particles.

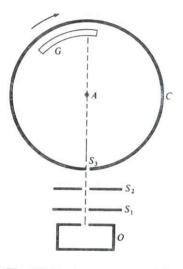


Fig. 12-10 Apparatus used by Zartman and Ko in studying distribution of velocities.

- The concept is fairly simple, the faster the molecule the closer to the clockwise side of the glass slide that it is deposited, you can then use the deposition on the glass slide to tell you the distribution of velocities of the molecules in the gas.
- For a more extended discussion of experimental measurement of the Maxwell distribution, see pages 362 366 of SS.





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Introduction

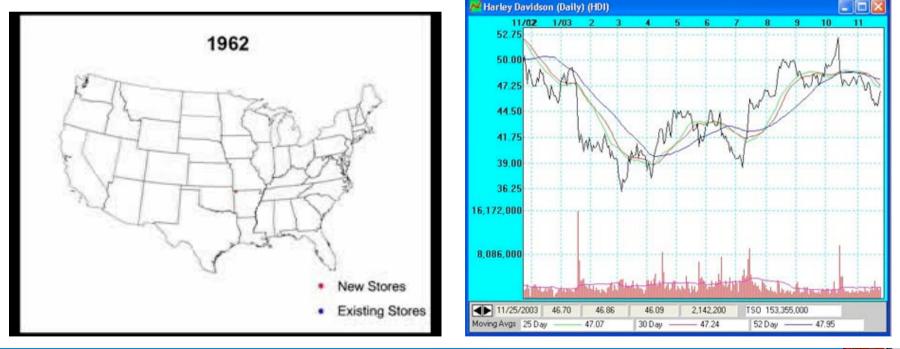
- We've now discussed kinetic theory to the point of understanding the force of the particles against a wall (pressure), their average kinetic energy (temperature), their various excitations (equipartition of energy), and in the last lecture, the likely velocity of a particle chosen at random (the Maxwell Distribution).
- In this lecture we're going to start looking at the trajectories of a particle in a gas.
- While so far we've always assumed that the particles travel very long distances between collisions in a straight line, this typically only happens at very low pressures (i.e., at high vacuum *P* << 1 millionth of an atmosphere).
- At most normal pressures, a particle will travel a very short distance between collisions with other particles in the gas. This leads to a number of interesting behaviours, which will be the subject of the next 2 lectures. The first one that we'll talk about is the Brownian motion of larger particles suspended in liquids or gases.





Some history behind Brownian motion

- The discovery of 'Brownian motion' is attributed to the botanist Robert Brown. In 1827, Brown noticed the irregular motion of pollen particles suspended in water, and was able to rule out the motion being due to the pollen being 'alive' by repeating the experiment using suspensions of dust in water. However, at the time, the origin of this Brownian motion could not be explained.
- The first explanation of the mathematics behind Brownian motion was made by Thorvald Thiele in 1880 (the mathematics of Brownian motion is important in fields ranging from fractals to economics).







Some history behind Brownian motion

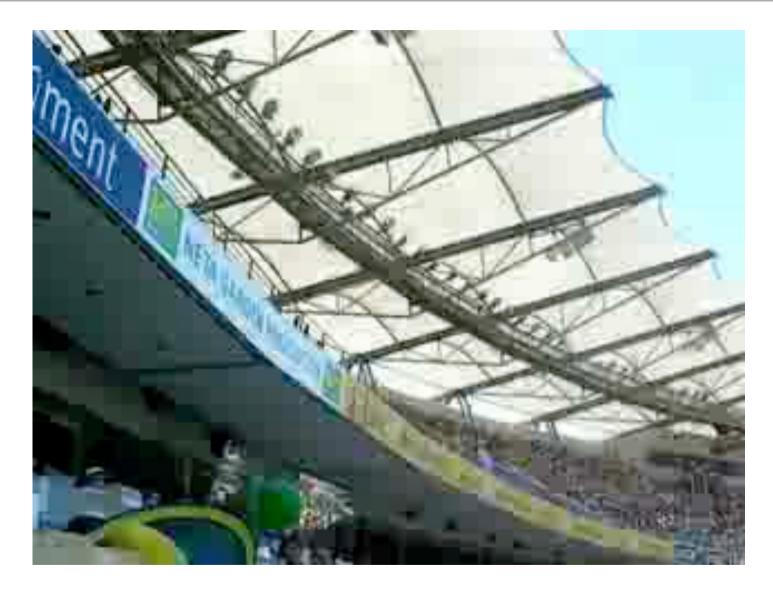
- However, it was Albert Einstein who is widely acknowledged for putting together the first physical understanding of Brownian motion in 1905. At the time, the atomic nature of matter was still controversial, so understanding that Brownian motion was due to the kinetic motion of particles was an important result. In fact, it was one of two results that earned Einstein the Nobel Prize in 1921, and one of Einstein's three great discoveries in 1905.
- Finally, Jean Perrin carried out the first experiments to test the new mathematical and theoretical models for Brownian motion, as we'll see later. The results of this ended a 2000-year-old dispute (beginning with Democritus and Anaxagoras in ~500 B.C.) about the reality of atoms and molecules.
- Brownian motion is also very important in biology, where you have a lot of small molecules and structures immersed in water at ~300K, and is even used by biological entities to move things around. If you're interested, see this week's reading "Making molecules into motors" by R. Dean Astumian from Scientific American.







The concept







The concept

- Imagine you are at the cricket. The crowd gets a bit bored so they pull out a large beach ball and start bouncing it around. As you know, assuming someone isn't deliberately aiming it in some direction (like away from security), it will take a random path through the crowd.
- If the ball is a few seat-areas away, it may seem that the ball never seems to make it over to you. Instead, it just wanders 'around in circles' near where it started, travelling a long path but not travelling very far from its origin.
- This is very similar to Brownian motion, but here the ball only takes one hit at a time with some long interval in between. In Brownian motion, the hits are more frequent, so let's extend our analogy a little further.



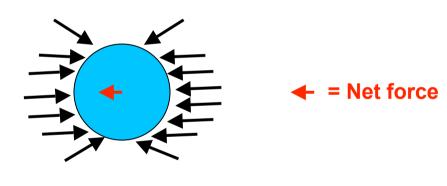




A big beach-ball

- Imagine that the beach-ball is actually *really* big, say 20 m in diameter (not 1 m in diameter like the one in the picture last slide). This ball will be so big that many people in the crowd can hit it all at once.
- If we now consider the force on it, 20 people might be pushing it to the left and 21 people might be pushing it to the right, so the forces to the left and right are almost balanced and there is a small net force to the right, and the ball will take a small step right. Next time, it might go another direction.





 The motion will be even more random now, one person might want to send it some direction, but on average that will be cancelled out by all the other directions that people are pushing it in, and so at each point the net force on the ball will be random, and the strength and direction of the net force will depend entirely on the balance of all the little pushes that it receives.



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Brown's experiment – Pollen in water

- Returning to Robert Brown's experiment in 1827 the motion of pollen in water the physics is pretty much the same.
- A liquid is just a gas where the potential energy between the particles is comparable to the kinetic energy of those particles (in contrast a gas has negligible potential energy compared to the kinetic energy and the particles travel around freely between collisions).
- So the particles of the liquid are all bouncing around (just very close to each other and making lots of collisions with one another) and if we stick a piece of pollen in, we get something very close to our beach ball analogy – a lot of water particles smacking against the pollen particle and randomly pushing it around.
- The water particles are ~1 nm in size, and our pollen particle is ~ 1μm, about 1000 times bigger (given a fist is about 10 cm in diameter, this would mean a beach-ball around 100 m in diameter!). So the pollen particle would receive a massive quantity of little pushes (about 10¹⁴ per s) from all the water molecules bouncing against it, and at any time the net force would be the balance of all these little pushes.





Brown's experiment – Pollen in water

• The experiments can be tricky (watching tiny particles for long periods under a microscope) but we can quite easily see the behaviour of a particle undergoing Brownian motion using simulations:

http://www.chm.davidson.edu/ChemistryApplets/KineticMolecularTheory/Diffusion.html

and

http://mutuslab.cs.uwindsor.ca/schurko/animations/brownian/gas2d.htm

- In the simulations, the pollen particle wanders about randomly, and each time, the path is completely random and different. The one consistent thing is that as the particle wanders around, the 'spread' of its path away from the starting point slowly increases with time.
- It's also clear that the particle travels a much smaller distance than we'd expect if it was just travelling along at its velocity.
- So a very useful question to ask at this point is: After a given length of time, how far away from its starting point is the particle likely to be? This is exactly the question that Einstein and Smoluchowski asked in 1905.



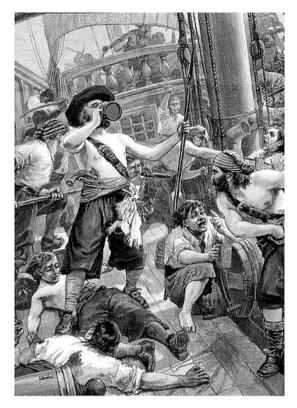


The drunken sailor problem

 This something commonly known as the 'drunken sailor problem', which is where we'll start our analysis, and it goes like: A drunk sailor comes out of a bar, but he is so drunk that as he staggers around, each step at some arbitrary angle relative to the last step, as shown below.



Fig. 41-6. A random walk of 36 steps of length *l*. How far is S_{36} from B? Ans: about 6*l* on the average.



- Let's bring some maths to bear on this. The sailor's position after *N* steps is given by the vector R_N , which is the vector sum of all his individual vector steps *L*.
- This problem is much like you would have done for interference of light in 1st year we take a series of vectors, one for each step, line them up head to tail and work out the vector sum of them all, which is R_N .



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The drunken sailor problem

• Now the relationship between the R_N and R_{N-1} is given by $R_N = R_{N-1} + L$, where L is the vector for the *N*th step. So if we calculate R_N squared, we get:

$$\mathbf{R}_{N} \cdot \mathbf{R}_{N} = {R_{N}}^{2} = {R_{N-1}}^{2} + 2\mathbf{R}_{N-1} \cdot \mathbf{L} + L^{2}$$
 (7.6)

• Each time the system is different, so again our response is to average, and when we do we get:

$$\left\langle R_{N}^{2}\right\rangle = \left\langle R_{N-1}^{2}\right\rangle + \left\langle 2R_{N-1}L\cos\theta\right\rangle + L^{2} = \left\langle R_{N-1}^{2}\right\rangle + L^{2}$$
(7.7)

because the angle between R_{N-1} and L is random and so $\langle \cos \theta \rangle = 0$ and therefore $\langle R_{N-1} L \rangle = 0$. And so by induction, we get:

$$\left\langle R_N^2 \right\rangle = NL^2 \tag{7.8}$$

• Since the number of steps is proportional to time in this problem, the mean square distance is also proportional to the time, so we can also write $\langle R_N^2 \rangle = \beta t$, where β is a constant that in part, will depend on the particle and the fluid it is in.





The square here is important!

• Something important to note here is that we're talking about the mean square distance, not the mean distance, being proportional to time.

If the mean distance was proportional to time then it would mean that the drifting is a nice uniform velocity. Certainly not very drunken.

While the sailor is making sensible headway, he's walking a lot further than he has to because of the randomness of his walk. The mean square distance being proportional to time is the key characteristic of what is called a 'random walk' – something that is common from biology right through to economics.

• So what I'd like to do now is calculate β , because this is clearly the key to being able to put numbers to how *fast* our particle moves due to the Brownian motion since $\beta = \langle R_N^2 \rangle / t$.

We will do this with something called the Langevin equation.





The Langevin equation

 What we have to do now, is something that we do a lot in physics (you will all have done this many times in the mechanics course last session) – cook up an 'equation of motion' and solve it to work out the dynamical behaviour. For example, with the harmonic oscillator, the equation of motion is:

$$m\frac{d^2x}{dt^2} = -kx \tag{7.9}$$

and we solve it to get $x = x_0 \cos(\omega t + \phi)$. The first step in doing this is to consider the various forces and motions involved in this new problem.

- Firstly, we're going to start by considering this problem in 1D (i.e., $\langle x^2 \rangle = \beta t$) and work our way up to the 3D answer (i.e., $\langle R_N^2 \rangle = \beta t$). We do this quite commonly in physics, it's a standard approach.
- To come up with the equation of motion for this system, we need to think about how the particle will react to an external force F_{ext} . In this problem, there are two factors involved.





The two factors

Inertia: First, there is the usual inertia term m(d²x/dt²). Even though it won't appear explicitly, the mass m isn't the mass as we'd normally think of it (i.e., the mass m obtained by dividing the weight W by g). It's an 'effective' mass that accounts for the interaction between the particle and the fluid around it. You can see this as the mass corrected so that the effect of the liquid moving around our pollen particle is buried in the mass itself (this is separate from the drag, which we'll deal with below).

This is a very similar concept to the effective mass of electrons in solids, where for example, an electron in Si behaves like it has a mass $\sim 1/4$ of the free electron mass due to its interaction with the Si crystal. In the limit of the fluid being a gas, the mass *m* is the real mass of the real particle though. All that said, we don't have to care too much about *m*, it cancels out anyway.

• Drag: Second, if we put a steady pull on the object, there would be a drag on it, a retarding force proportional to its velocity. In other words, besides the inertia, there is a resistance to flow due to the fluid's viscosity. This is a very important. *It is absolutely essential that there be some irreversible losses (called dissipation), something like resistance, in order that there be random fluctuations.* This is something called the fluctuation-dissipation theorem. The origin of this drag force is beyond this course, but it appears as $\alpha(dx/dt)$, where α is a constant that depends on the particle and the fluid.





• Bringing these two terms together, we get the total external force on our particle as:

$$F_{ext} = m\frac{d^2x}{dt^2} + \alpha\frac{dx}{dt}$$
(7.10)

This is our equation of motion and it's something known as the Langevin equation. The Langevin equation occurs quite a lot in fluid dynamics (due to the inertia and drag terms) usually with variations of F_{ext} and occasionally additional terms to account for other forces.

We now need to solve the Langevin equation for (x²), which we will then generalise to 3D to get (R²).



Solving the Langevin equation for $\langle x^2 \rangle$ (Advanced)

- So if we have $\langle x^2 \rangle = \beta t$, then our goal will be to show that $d\langle x^2 \rangle / dt = \beta$ (i.e., a constant).
- How do we do this from the equation of motion (Eqn. 7.10)? If we realise that d(x²)/dt = 2x (dx/dt), then it's clear that we can get somewhere if we multiply Eqn. 7.10 by x, to get:

$$xF_x = mx\frac{d^2x}{dt^2} + \alpha x\frac{dx}{dt}$$
(7.11)

and then get the time average of x(dx/dt) by averaging the whole equation and looking at the three terms individually.

• xF_x : We can kill this term by direction. This is a 1D problem right now, so both x and F_x can be positive or negative. If the particle has just travelled x, since the force is completely irregular then there is no reason why the force should be positive or negative (and likewise if we travelled -x), and so the average will be the sum of an equal number of $x \times F_x$, $-x \times F_x$, $x \times -F_x$, $-x \times -F_x$, which is just zero. Physically, this just tells us that the impacts from all the water particles don't drive the pollen in any particular direction, as we would expect from observing it experimentally.





Solving the Langevin equation for $\langle x^2 \rangle$

• $mx(d^2x/dt^2)$: We have to be a little more sophisticated here, and rewrite $mx(d^2x/dt^2)$ as:

$$mx\frac{d^2x}{dt^2} = m\frac{d\left[x(dx/dt)\right]}{dt} - m\left(\frac{dx}{dt}\right)^2 = m\frac{d}{dt}xv - mv^2$$
(7.12)

and then consider the average of the two terms. Starting with m d/dt(xv), xv has an average that doesn't change with time, because when it gets to some position, the particle has no memory of where it was before, so this term is zero on average.

The other term is $\langle mv^2 \rangle$ and it certainly isn't zero because v is always parallel to itself. Furthermore, we know from equipartition that $\frac{1}{2} \langle mv^2 \rangle = \frac{1}{2} k_B T$ (n.b., it's a half here because our problem is 1D! The factor of three will appear when we convert to 3D).

x(dx/dt): We can rewrite (x dx/dt) as ½ d/dt(x²), and so now we are in reach of our final result. Eqn. 7-11 becomes:

$$\left\langle mx \frac{d^2 x}{dt^2} \right\rangle + \alpha \left\langle x \frac{dx}{dt} \right\rangle = \left\langle x F_x \right\rangle$$
 (7.13)

Substituting our new terms:

$$-\left\langle mv^{2}\right\rangle + \frac{\alpha}{2}\frac{d}{dt}\left\langle x^{2}\right\rangle = 0$$
(7.14)





Solving the Langevin equation for $\langle x^2 \rangle$

• We can rewrite Eqn. 7.14 as:

$$\frac{d}{dt}\left\langle x^{2}\right\rangle = 2\frac{k_{B}T}{\alpha}$$
(7.15)

and then integrating:

$$\left\langle x^{2}\right\rangle = 2\frac{k_{B}T}{\alpha}t$$
 (7.16)

The same displacement will occur for the y- and z-directions, so $\langle R^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle$, and we get:

$$\left\langle R^2 \right\rangle = 6 \frac{k_B T}{\alpha} t$$
 (7.17)

which gives $\beta = k_B T / \alpha$, and so now we can actually now determine how far our particles go.

• The one missing piece is α , which can be determined experimentally. For example we can drop a large particle in the fluid and watch it fall under gravity and since we know the force is mg, then α is just mg divided by the particle's terminal velocity. Or if the particle is charged, we can put it in a field and measure how fast it moves (remember this next week) – but ultimately α isn't something artificially cooked up, it's something real that we can actually measure.



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(Advanced)

Perrin's experiment

• Perrin provided the experimental confirmation of Eqn 8-12 by looking at how dust suspended in water behaved under a microscope. At the time, this was a very significant experiment because it allowed one of the first measurements of Boltzmann's constant k_B . Aside from knowing k_B , this was important because in the ideal gas law PV = nRT, we can measure R, and since this is equal to Avogadro's number N_A times k_B , we can kill two birds with one stone – we get k_B and we get N_A .

 Both may seem to be trivial constants, you've known them for a while and you even get to measure k_B in the 2nd year lab, but in the early 1900s, this was nothing to be sneezed at. The existence of atoms was still a hypothesis and N_A was only roughly known (i.e., to order of magnitude at best). Perrin managed to obtain a very accurate number for N_A and prove beyond doubt the existence of atoms, and for this won he the 1926 Nobel prize in Physics.







The Tyndall effect

 At this point it might seem that Brownian motion is all about small light particles in liquids. But if the particles are light enough, it can also happen in gases. Some of you will have seen this as light rays through a hazy or dusty sky, and if you see it inside a building where the air is very calm (e.g., the OMB corridor around mid-morning in mid-spring is ideal) you might even be able to see little dust particles 'floating' around randomly as we'd expect.





 In the 1860s, another Irishman, John Tyndall was investigating light scattering in liquids and gases. He was the first to explain why the sky is blue, which is due to Rayleigh scattering of shorter wavelength light by particles. He used this knowledge to develop a technique for distinguishing between solutions and suspensions based on their optical scattering.



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Maxwell Distribution - Summary

• The Maxwell distribution provides the probability density D(v) as a function of velocity for a particular gas and takes the form:

$$D(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi v^2 \exp\left(-\frac{mv^2}{2k_B T}\right)$$

- The distribution itself isn't too meaningful it exists to be integrated and the probability of having a velocity between v_1 and v_2 is given by the integral of D(v)dv over v_1 and v_2 , and graphically is the area under D(v) between v_1 and v_2 .
- The distribution tails off parabolically as $v \rightarrow 0$ and exponentially as $v \rightarrow \infty$.
- The weighted average velocity and r.m.s. velocity are 13% and 22% larger than the most probable velocity, which coincides with the peak of the distribution function.
- As we increase *m* or decrease *T*, the Maxwell distribution 'squashes' to the left, raising the peak and lowering the most probable, average and rms speeds.

In the next lecture we will begin to think about the dynamics of the particles in our gas a little more. We will talk about Brownian motion, which explains the motion of a particle in a gas (or liquid) and how far it can 'diffuse' as a function of time.





Brownian Motion - Summary

- Brownian motion is the random motion of a particle in a gas or liquid due to the force imparted by collisions with the gas/liquid particles.
- The path of the particle is known as a 'random walk' and it is characterised as having a mean squared displacement that is not only proportional to time, it is also proportional to the square root of the number of steps taken up to that time.
- The equation of motion for this system is called the Langevin equation, it contains an inertial term and a dissipative drag term, which is essential for obtaining random fluctuations.
- The mean square fluctuation goes as $\langle R^2 \rangle = 6(k_B T/\alpha)t$. The term α can be measured experimentally, and Perrin used observations of Brownian motion to make the first accurate measurements of k_B and N_A .
- The Tyndall effect is the scattering of light by particles suspended in a gas or liquid.

In the next lecture we will look further at collisions between particles in a gas or liquid, but with more of a focus on how this is a mechanism for taking a system out of equilibrium back to equilibrium.



