1 Introduction

By the beginning of the 20th century, the evidence for the existence of atoms was mounting. It was known that atomic theory could explain the gas laws with the assumption \( \langle K \rangle = \frac{3}{2} k_B T \). Atomic theory was also helpful in understanding the periodic properties of the elements and the laws of chemical combinations. However, in 1905, the year of Einstein’s paper on Brownian motion, there were still a few reputable scientists, including two Nobel prize winners, who regarded the evidence for atoms as insufficient. Their view was that science should be based exclusively on concrete empirical facts. They thought that atoms could never be seen directly and therefore would always remain a hypothetical construct. As Einstein later wrote, “The prejudice … consists in the faith that facts by themselves can and should yield scientific knowledge without free conceptual construction.”

If the atomic hypothesis were to be more than a useful artifice, someone had to determine the size and mass of a single atom. Otherwise, it is just philosophical speculation, not exact science. As Lord Kelvin wrote: “When you can measure what you are speaking about and express it in numbers, you know something about it, and when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meager and unsatisfactory kind. It may be the beginning of knowledge, but you have scarcely in your thought advanced to a stage of science.”

To turn philosophy into science, we need to find the size of an atom, and from that we can find its mass and Avogadro’s number. Einstein knew this and set to work on the problem. The result was his paper on Brownian motion. It was this paper that finally stilled the voices of the atomic skeptics.

The so-called “Brownian movement” was described in 1828 by the botanist Robert Brown. (The phenomenon was first observed by Jan Ingenhousz in 1785, but was subsequently rediscovered by Brown in 1828.) He observed an irregular “swarming” motion of pollen in water. As the phenomenon repeated itself with all possible kinds of organic substances, he believed that he had found in these particles the “primitive molecule” of living matter. (He found later that the particles of every kind of inorganic substance exhibited the same motion.)

2 Theory

Einstein begins his paper with this sentence: “It will be shown in this paper that, according to the molecular-kinetic
theory of heat, bodies of microscopically visible size suspended in liquids must, as a result of thermal molecular motions, perform motions of such magnitude that these motions can easily be detected by a microscope."

The image is of many small particles constantly bombarding a large particle. In fact, the scale is enormous: if the water molecules were the size of baseballs, the diameter of the pollen particle would be half a mile. Fluctuations in the force due to these collisions cause the random, zig-zagging motion. Einstein’s theory involved some fundamental constants, including Avogadro’s number and Boltzmann’s constant. And he closed the paper with a specific prediction based on these constants: in water at 17 °C, particles with diameter of 1 micron would move an average horizontal distance of 6 microns in one minute. This measurement was performed by the French physicist Jean Baptist Perrin in 1908, and his result was consistent with Einstein’s theory. In 1949, Max Born wrote that Einstein’s theory of Brownian motion did “more than any other work to convince physicists of the reality of atoms and molecules, of the kinetic theory of heat, and of the fundamental part of probability in the natural laws.”

Einstein’s treatment was not simple, but over the years, physicists have developed easier (but not easy!) ways to derive the result. To find the average displacement, we start with Newton’s law, \( ma = F_{\text{ext}} - \Gamma v \), where \( \Gamma \) is the drag coefficient for spheres moving through the liquid. Focus on a single component (we’ll choose the \( x \)-component) and use derivatives to re-write the relationship:

\[
m \frac{d^2 x}{dt^2} = F_{\text{ext}} - \Gamma \frac{dx}{dt}.
\]

We’re trying to find an expression for \( d\langle x^2 \rangle/dt \); that is, the rate at which the mean squared displacement increases with time. This calculation requires a lot of steps, but none of the individual steps are terribly complicated. First multiply through by \( x \) and put all the terms on the same side of the equation:

\[
m x \frac{d^2 x}{dt^2} + \Gamma x \frac{dx}{dt} - x F_{\text{ext}} = 0.
\]

Now start with something that seems unrelated. Use the chain rule and the product rule to simplify the expression \( d^2(x^2)/dt^2 \):

\[
\frac{1}{2} \frac{d^2(x^2)}{dt^2} = \frac{1}{2} \frac{d}{dt} \left( \frac{d(x^2)}{dt} \right) = \frac{1}{2} \frac{d}{dt} \left( 2x \frac{dx}{dt} \right) = \frac{d}{dt} \left( x \frac{dx}{dt} \right) = \left( \frac{dx}{dt} \right)^2 + \frac{d^2 x}{dt^2}
\]

Substitute this result into the Brownian motion equation:

\[
m \left[ \frac{1}{2} \frac{d^2(x^2)}{dt^2} - \left( \frac{dx}{dt} \right)^2 \right] + \Gamma x \frac{dx}{dt} - x F_{\text{ext}} = 0.
\]

\[
\frac{m}{2} \frac{d^2(x^2)}{dt^2} - m \left( \frac{dx}{dt} \right)^2 + \Gamma x \frac{dx}{dt} - x F_{\text{ext}} = 0.
\]

One more trick: Use the chain rule once again, but backwards. We know \( d (x^2)/dt = 2x (dx/dt) \). Use this fact to rewrite the third term in the expression. And, at the same time, substitute \( v_x = dx/dt \) in the second term:

\[
\frac{m}{2} \frac{d^2(x^2)}{dt^2} - m v_x^2 + \Gamma \frac{d(x^2)}{dt} - x F_{\text{ext}} = 0.
\]
What we’re really interested in is average values of all these quantities:
\[
\frac{m}{2} \langle \frac{d^2(x^2)}{dt^2} \rangle - m \langle v_x^2 \rangle + \frac{\Gamma}{2} \langle \frac{d(x^2)}{dt} \rangle - \langle x F_{\text{ext}} \rangle = 0.
\]

Now, finally, the equation starts to simplify. We recognize that the second term is related to the kinetic energy.
\[
\langle K \rangle = \frac{1}{2} m \langle v^2 \rangle
\]
\[
\frac{3}{2} k_B T = \frac{1}{2} m \left( \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle \right)
\]
\[
\frac{3}{2} k_B T = \frac{3}{2} m \langle v_x^2 \rangle
\]
\[
k_B T = m \langle v_x^2 \rangle.
\]

Next consider the term \( \langle x F_{\text{ext}} \rangle \). Unlike, for example, a spring force, this force is not correlated with position. When the particle is displaced to the right, the force is equally likely to push it further to the right as back to the left, and therefore \( x F_{\text{ext}} \) averages to zero.

Finally, note that because \( \frac{d}{dt}(f + g) = \frac{df}{dt} + \frac{dg}{dt} \), the averages can be moved inside the derivatives, yielding:
\[
\frac{m}{2} \left( \frac{d^2(x^2)}{dt^2} \right) - k_B T + \frac{\Gamma}{2} \frac{d(x^2)}{dt} = 0.
\]

Re-arranging:
\[
\frac{d^2\langle x^2 \rangle}{dt^2} = -\frac{\Gamma}{m} \frac{d\langle x^2 \rangle}{dt} + 2k_B T.
\]

This equation has the familiar form
\[
\frac{dy}{dt} = -A y + B
\]
with \( y = \frac{d\langle x^2 \rangle}{dt} \); \( A = \Gamma/m \); and \( B = 2k_B T/m \). The solution is \( y = C e^{-At} + B/A \), or
\[
\frac{d\langle x^2 \rangle}{dt} = C e^{-\Gamma t/m} + \frac{2k_B T}{\Gamma}.
\]

For typical experiments, \( m/\Gamma \sim 10^3 \text{ s} \). At times \( t << 10^3 \text{ s} \), the exponential term is small, and we’re left with:
\[
\frac{d\langle x^2 \rangle}{dt} = \frac{2k_B T}{\Gamma}
\]
which integrates to
\[
\langle x^2 \rangle = \frac{2k_B T t}{\Gamma}.
\]

There’s nothing special about the \( x \)-direction, so \( \langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle \) and \( \langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle = 3\langle x^2 \rangle \), which yields Einstein’s result:
\[
\langle r^2 \rangle = \frac{6k_B T t}{\Gamma} = \frac{6RT t}{\Gamma N_A}.
\]

\( \Gamma \) is the drag force on a particle, which is measurable, as are all the other constants besides \( N_A \). This means that a measurement of Brownian motion can be used to measure \( N_A \). All we do is observe a particle drifting around and measure its average squared displacement over a set period of time. From Avogadro’s number, we can find the mass and size of a molecule. So, now the concept of atoms is no longer just a construct, and their existence is accepted by all scientists.

What Einstein did was particularly important because he managed to make this testable quantitative prediction, that the average squared displacement would scale linearly with time. Others had already suggested that the explanation of Brownian motion might be the motion of molecules. However, they were not able to formulate a theory that made a testable prediction. Any physicist (including you!) can look at a particle under a microscope and measure how far it has moved from its original position as a function of time, and thus test Einstein’s prediction.
3 Procedure

You will be observing Brownian motion of a collection of small polystyrene spheres with diameter equal to 1.01 µm using a microscope with an LCD display that can transfer the images to your computer.

3.1 Creating a calibration image

You may need to calibrate your system. If so, your instructor will provide a calibration slide. Insert this slide into your microscope, sliding it underneath the two small arms. You should see a series of parallel lines. You may find it easiest to start with the 4x magnification and gradually increase it to 40x, adjusting the focus after each increase.

3.2 Taking photos

If your microscope already has saved pictures on it, you’ll want to clear them. Use the “escape” button to scroll through the options. If you see a screen full of photos, clear them by pressing “menu” then following the steps to “delete all.” Then set your microscope to take a photograph (again, by using the “escape” button to scroll through the options). A camera icon will appear in the upper right hand corner of the display when it is set for photographs. Press “snap” to take a photograph.

3.3 Uploading photos

Upload the photographs onto your computer, using the cable provided. The connection port on your microscope is located just under the display area. Your microscope will go dark once you connect the cable—don’t worry about that. (You’ll find that when you disconnect the cable, you’ll need to turn the microscope back on.) The computer will automatically pop up a window asking what you’d like to do. Choose “Copy pictures to a folder on my computer.” You’ll probably want to put them in a folder on your desktop.

3.4 Using ImageJ to calibrate distance

Open “ImageJ” from the “all programs” listing under the “start” menu. Within ImageJ, open the calibration photo. Then use the line tool to draw a line from center-to-center of one or two sets of black and white lines. The center-to-center distance between pairs of white or black lines is 60 µm. To get the most accurate calibration, draw a line that covers as many stripes as you can. Then, under the “analyze” menu, choose “set scale.” In the window that pops up, choose the appropriate value for the “known distance.” You may have to use “um” for the length, unless you find a way to input “µm.” ImageJ should tell you that the scale is set to roughly 4 pixels per µm. Check the box “global” so that this calibration will be used in all your measurements.

3.5 Making images of Brownian motion

Your instructor will help you prepare a slide containing a droplet of spheres suspended in saline solution. Insert this slide into your microscope and adjust the focus...
until you see the small spheres jiggling around. If you have trouble finding the right focus, try moving the slide so that you can focus on the edge of the cover slip, then center the slide and slowly lower the focus through the cover slip into the solution. Once you’ve found the spheres, check that what you see appears to be random jiggling, and not collective drift of all the particles in the water.

Einstein’s equation describing Brownian motion gives an average behavior. For accuracy, you’ll need to make a lot of measurements and take their average. Plan to take 50–100 snapshots of the position of the spheres, separated by a fixed amount of time (3 or 4 s).

3.6 Analyzing images

Upload the series of snapshots onto the computer into a single folder. (See the “Uploading photos” directions for connecting the microscope to the computer.) In ImageJ, choose “Import” “Image sequence.” Select the first photo in the folder, then press “open.”

You might start by scrolling through the whole set of images to see if all the spheres seem to be drifting in the same direction. If you estimate that the conglomeration moves by more than about half the width of the window, you’ll want to take a new set of images once the drift has settled down. (If it doesn’t seem to be settling, prepare a new microscope slide.)

By scrolling through the images, you can also select a promising sphere to trace. Ensure it is a single sphere, and not a clump. ImageJ will record the coordinates of sphere using the “point tool.” Double-click on the point tool to open a dialog box, and select “auto-next slice” so that it will automatically scroll between photos. Then click on the sphere you wish to trace. Its position will be recorded in the “Results” window and the next image will be displayed. Try to follow the same sphere between images. If you can’t, then note the image number and choose a new sphere, preferably much farther away than the sphere would move in a single jump. Continue until you have ~ 200 data points.

You instructor can help you open the “Results” file in MATLAB, calculate the squared displacement, $r^2$, between steps, and find the average squared displacement. If you switched to a different sphere during the sequence, you’ll need to eliminate that value when computing the average.

Determine a way to use the data to determine Avogadro’s number. Describe your analysis method clearly. Remember that you are only measuring displacement in two dimensions, but the spheres are moving in three dimensions. You will also need the following facts:

1. The viscosity of the saline solution in which the spheres are suspended is

   \[
   \begin{align*}
   1.14 \times 10^{-3} \text{ Pa-s at } 15 \degree C \\
   1.02 \times 10^{-3} \text{ Pa-s at } 20 \degree C \\
   0.89 \times 10^{-3} \text{ Pa-s at } 25 \degree C \\
   0.80 \times 10^{-3} \text{ Pa-s at } 30 \degree C.
   \end{align*}
   \]

2. The drag coefficient $\Gamma$ for the spheres is $6\pi \eta a$, where $\eta$ is the viscosity of the solution and $a$ is the radius of the sphere. The diameter of the spheres is 1.01 $\mu$m.

Remember that Einstein’s relationship says that $\langle r^2 \rangle \propto t$. You used a fixed $t$
to collect your data. But, through clever analysis, you can use the same data to find $\langle r^2 \rangle$ for different values of $t$ and learn how $\langle r^2 \rangle$ depends on $t$. Think about it, and ask for help if needed.

Throughout this experiment, we’re sure you have been thinking about the uncertainty of your measurements, but now that you are using them to calculate Avogadro’s number, you’ll want to think more deeply about the uncertainty and quantify different contributions to it. You may, for example, need to repeat some measurements or repeat your analysis by tracing a different sphere in the photographs. In the end, you should be able to report whether your data are consistent with Avogadro’s number within your uncertainty.