Phys 232: Brownian Motion

Last Modified February 7, 2023

Introduction

In the first part of this lab, you will analyze the motion of microscopic spheres suspended in a solution. The quantitative analysis will result in a measurement of Avogadro's number N_A . The the second part of the lab, you will investigate the equilibrium distribution of the particle suspension to extract a second value for N_A . The key part of the experiment setup is the same for both parts of the experiment. As shown schematically in Fig. 1, the setup consists of a microscope slide with an indentation ground into it. The indentation is filled with a suspension of particles using an eyedropper and then covered with a coverslip (without trapping air bubbles). The suspension is latex spheres with a diameter of $d = (1.02 \pm 0.02) \,\mu\text{m}$ in a saline (saltwater) solution. The particles are viewed using a microscope equipped with a digital camera. You will record and analyze videos of the particle motion in part 1 of the experiment. In part 2, you will analyze digital images of the particle distribution. An example recording of the particle motion in the suspension has be posted to YouTube:

https://www.youtube.com/watch?v=iCaP9PCrr_k



Figure 1: Schematic diagram of the particle suspension loaded into a cell created using a ground glass slide and a coverslip.

You'll notice that some particles have sharp edges. These are particles that are within the microscope's depth of focus. Particles with blurry edges are outside the depth of focus. When analyzing particle motions from the videos that you record, you will want to work with particles that are in focus. A particle that is initially in focus may move out of focus at a later time as its vertical position changes. You'll also observe some clumps of two or more particles. You'll want to collect data from only isolated single particles.

When recording your videos for part 1, you'll want to ensure that the plane of focus and field of view are set to be approximately in the centre of the chamber formed by the glass slide and coverslip. This will help to prevent the inner walls of the chamber from influencing the particle motions.

In order to calibrate distances, you will place a calibration scale beneath the microscope and focus on the grid. Having an image of the grid at the end of your video will allow you to calibrate distances in the software that will be used to analyze the particle motion. An example calibration image is shown in Fig. 2.



Figure 2: Digital photograph of the calibration slide while using the $\times 40$ microscope objective. The distance between each division is 0.01 mm.

Theory – Part 1

Consider an isolated particle in the suspension. If it is a macroscopic particle (i.e. very large), then its motion in the x-direction is governed by the equation of motion $m\ddot{x} = -\Gamma\dot{x}$.¹ Here, like in the Millikan oil drop experiment, $\Gamma = 6\pi\eta a$ is the drag coefficient for a spherical particle of radius a moving through a viscous fluid with dynamic viscosity η . In this case, the time evolution of the particle's velocity follows $v(t) = v_0 e^{-t/\tau}$, where v_0 is the particle's initial velocity at t = 0and the time constant $\tau = m/\Gamma$. This result implies that, for any v_0 , the particle's velocity will exponentially approach zero and eventually come to rest.

If, on the other hand, the particle is microscopic we observe that its velocity does not decay to zero. The particle remains in constant motion and the direction of this motion is constantly randomized. This effect is due to the constant collisions that the particle has with the vast number of molecules that make up the solution. We attempt to model is effect by including a random force $F_{\rm R}$ that characterizes the complex interactions with the fluid molecules. In this case, the one-dimensional equation of motion becomes:

$$m\ddot{x} = -\Gamma\dot{x} + F_{\rm R},\tag{1}$$

which is known as the Langevin equation. We assume that $F_{\rm R}$ is independent of the position x of the particle and, because it is randomly fluctuating, we also assume that it averages to zero: $\langle F_{\rm R} \rangle = 0$. The goal is to use Eq. (1) to determine the average of square of the particle's displacement $\langle x^2 \rangle$ during a time interval t. We choose the square of the displacement because, due to the random nature of the particle motion, we expect $\langle x \rangle = 0$.

Multiplying Eq. (1) by x and reordering the terms results in:

$$mx\ddot{x} + \Gamma x\dot{x} - xF_{\rm R} = 0 \tag{2}$$

In the pre-lab assignment, you will use the chain rule to show that $x\ddot{x}$ can be rewritten as:

$$x\ddot{x} = \frac{1}{2}\frac{d^2(x^2)}{dt^2} - \dot{x}^2,\tag{3}$$

such that Eq. (2) becomes:

$$\frac{m}{2}\frac{d^2(x^2)}{dt^2} - m\dot{x}^2 + \Gamma x\dot{x} - xF_{\rm R} = 0.$$
(4)

¹Here, $\dot{x} = dx/dt$ and $\ddot{x} = d^2x/dt^2$.

Using the chain rule again, we note that:

$$\frac{d\left(x^{2}\right)}{dt} = 2x\dot{x}.\tag{5}$$

Therefore, we have:

$$\frac{m}{2}\frac{d^2(x^2)}{dt^2} - m\dot{x}^2 + \frac{\Gamma}{2}\frac{d(x^2)}{dt} - xF_{\rm R} = 0.$$
(6)

We now imagine taking an average of Eq. (6). It is called an *ensemble* average which is commonly used in statistical mechanics. In an ensemble average, we imagine preparing many replica systems with identical initial conditions. We then watch the time-evolution of the system and average the results from all the replica systems. Using angle brackets to represent the ensemble average, we have:

$$\frac{m}{2} \left\langle \frac{d^2 \left(x^2 \right)}{dt^2} \right\rangle - m \left\langle \dot{x}^2 \right\rangle + \frac{\Gamma}{2} \left\langle \frac{d \left(x^2 \right)}{dt} \right\rangle - \left\langle x F_{\rm R} \right\rangle = 0.$$
(7)

First, we consider the last term on the left-hand side (lhs) of Eq. (7). Because $F_{\rm R}$ is independent of position, $\langle xF_{\rm R}\rangle = \langle x\rangle \langle F_{\rm R}\rangle = 0$ since $\langle F_{\rm R}\rangle = 0$. The $m\langle \dot{x}^2\rangle$ term can be related to the particle's average kinetic energy $\langle K\rangle$:

$$\langle K \rangle = \frac{m}{2} \left(\langle \dot{x}^2 \rangle + \langle \dot{y}^2 \rangle + \langle \dot{z}^2 \rangle \right). \tag{8}$$

Note, however, that there is nothing to distinguish the x, y, and z directions from one another. Therefore, $\langle \dot{x}^2 \rangle = \langle \dot{y}^2 \rangle = \langle \dot{z}^2 \rangle$ such that $\langle \dot{x}^2 \rangle + \langle \dot{y}^2 \rangle + \langle \dot{z}^2 \rangle = 3 \langle \dot{x}^2 \rangle$. This implies that $\langle K \rangle = 3 \langle \dot{x}^2 \rangle / 2$. Finally, from thermodynamics, the internal energy per particle (which is all kinetic energy) of a monatomic dilute gas is $3k_{\rm B}T/2$ where $k_{\rm B}$ is Boltzmann's constant and T is temperature in Kelvin. Together, these results imply that $m \langle \dot{x}^2 \rangle = k_{\rm B}T$.

Therefore, Eq. (7) becomes:

$$\frac{m}{2}\frac{d^2\langle x^2\rangle}{dt^2} = -\frac{\Gamma}{2}\frac{d\langle x^2\rangle}{dt} + k_{\rm B}T,\tag{9}$$

where the averages have been taken inside the derivatives and the terms have been reordered.

Now, define $u = d\langle x^2 \rangle/dt$ such that:

$$\frac{m}{2}\frac{du}{dt} = -\frac{\Gamma}{2}u + k_{\rm B}T.$$
(10)

In the pre-lab assignment you will show that the solution to Eq. (10) is:

$$u = \frac{d\langle x^2 \rangle}{dt} = Ce^{-t/\tau} + \frac{2k_{\rm B}T}{\Gamma},\tag{11}$$

where the time constant $\tau = m/\Gamma = m/(6\pi\eta a)$. In the pre-lab assignment, you will also show that,

for our experimental conditions, τ is very small. Therefore, for all practical time intervals, $t \gg \tau$ and the exponential term on the right-hand side (rhs) of Eq. (11) is small compared to $2k_{\rm B}T/\Gamma$. As a result, we have:

$$\frac{d\langle x^2\rangle}{dt} \approx \frac{2k_{\rm B}T}{\Gamma}.$$
(12)

Finally, integrating Eq. (12) with respect to time, we have our desired result for the mean displacement of the particle during time interval t:

$$\langle x^2 \rangle = \frac{2k_{\rm B}Tt}{\Gamma} = \frac{k_{\rm B}Tt}{3\pi\eta a}.$$
 (13)

In the Brownian motion images that you will analyze, you will observe particle motion in a 2-D plane, say the x-y plane. The calculation of $\langle y^2 \rangle$ is identical to the calculation we just completed for $\langle x^2 \rangle$ and yields the same result. Therefore, the mean 2-D displacement of the particle in time t is given by:

$$\left\langle \Delta r^2 \right\rangle_{2\mathrm{D}} = \left\langle x^2 \right\rangle + \left\langle y^2 \right\rangle = \frac{2k_{\mathrm{B}}Tt}{3\pi\eta a}.$$
 (14)

We have used the Δr notation to emphasize that we are interested in the *change* in position of the particle during time *interval t*. In part 1 of this lab, you will determine $\langle \Delta r^2 \rangle_{2D}$ of the latex spheres for different values of t.

Boltzmann's constant can be expressed in terms of the universal gas constant and Avogadro's constant via $k_{\rm B} = R/N_{\rm A}$ such that:

$$\left\langle \Delta r^2 \right\rangle_{\rm 2D} = \frac{2RTt}{3\pi N_{\rm A}\eta a}.\tag{15}$$

Equation (15) shows that a measurement of $\langle \Delta r^2 \rangle_{2D}$ as a function of t should yield a straight line whose slope can be used to determine an experimental value for N_A .

Pre-lab Assignment

1. (a) By evaluating $d(x\dot{x})/dt$, show that:

$$x\ddot{x} = \frac{d}{dt}\left(x\dot{x}\right) - \dot{x}^2.$$

(b) Next, by evaluating $d(x^2)/dt$, show that:

$$x\dot{x} = \frac{1}{2}\frac{d\left(x^2\right)}{dt}$$

(c) Combine the results from (a) and (b) to show that:

$$x\ddot{x} = \frac{1}{2}\frac{d^2(x^2)}{dt^2} - \dot{x}^2.$$

2. Starting from Eq. (10) in the theory section, make the substitution:

$$w = \frac{\Gamma}{2}u - k_{\rm B}T,$$

and show that the solution to Eq. (10) is:

$$u = Ce^{-t/\tau} + \frac{2k_{\rm B}T}{\Gamma},$$

where C is a constant and $\tau = m/\Gamma$.

3. For latex spheres of radius $a \approx 0.5 \,\mu\text{m}$ and density $\rho \approx 1000 \,\text{kg/m}^3$, estimate the value of τ . You may assume a dynamic viscosity of $\eta \approx 1 \times 10^{-3} \,\text{Pa} \cdot \text{s}$ for the saline solution.

💽 Camera List 🏾 🕆			
SCMOS05000KPA			
Capture & Resolution 🏦			
Snap Record			
Live:	640 × 480		~
Snap:	640 × 480		\sim
Format:	RGB24		~
🜠 Exposure & Gain 🔗			
Auto Exposure			
Low Light Compensation			
Exposure Time:			31.250ms
Gain:			46
Defaults			

Figure 3: ToupView settings. Click on the text in the "Camera List" box to open a live video feed. Change the resolution to 640×480 and, if necessary, adjust the Exposure Time and Gain to achieve the necessary frame rate.

Procedure – Part 1

- Start by preparing your slide. Place two drops of the particle suspension into the indentation of a clean slide. Cover the suspension with a clean coverslip without trapping air inside the particle suspension chamber.
- Place the slide in the slide holder of the microscope. Use the ×40 objective (40/0.65) to view the particles. Turn on the microscope light, connect the USB camera to the computer and open ToupView. Click on the camera from the "Camera List" to see a live view of the particle suspension in ToupView. See Fig. 3
- In order to get a reasonably high frame rate (in frames per second or fps), change the resolution to 640×480. A frame rate of 15 fps or greater is desirable. If necessary, adjust the illumination of the suspension using the light below the glass slide and/or adjust the Exposure & Gain (Fig. 3) to achieve a frame rate > 15 fms.
- Allow the particle suspension to reach a steady state before starting your recording. The particle motion should be random without any net drift in any one direction. Avoid bumping the microscope or table. When ready, record your video using the "mp4 (H264)" format. A recording of approximately 10 minutes should be sufficient.
- The free Tracker Video Analysis and Modeling Tool (https://physlets.org/tracker/) will be used to analyze the data. Tracker already installed on the computers in SCI 241. Import

your video into Tacker.

- Start a new "Point Mass" track control using the "Track" menu. See Fig. 4. Hold the shift button the use left mouse clicks to track the position of a particle as a function of time. As you click, the video will advance a specified number of frames. You can use the Zoom control to zoom into the particle to make it easier to track its position. The software will also tabulate the particle's coordinates as a function of time. The data in the table can be copied in Excel (or another spreadsheet) for further processing.
- Use the data to calculate the average displacement of the particle $\langle \Delta r^2 \rangle_{2D}$ for the given time step t. $\langle \Delta r^2 \rangle_{2D}$ and t are related by Eq. (15).
- Determine (Δr²)_{2D} for many different values of t. This can be done to adjusting the number of frames Tracker advances the video after each click. To make this adjustment, click on the number next to the "Advance by N frames" arrow in Fig. 4. Use the data you collect and Eq. (15) to determine N_A from a weight least-squares linear fit.

Theory – Part 2

The goal of the next part of this experiment is to examine how the particle number density n varies with height within the suspension. Due to the effects of gravity, the number density is expected to increase as the bottom of the suspension cell shown in Fig. 1 is approached. This experiment was inspired by Ref. [1]. In that paper, the particle number density is given by:

$$n(z) = n_0 \exp\left[-\frac{N_{\rm A}V\left(\rho - \rho_0\right)gz}{RT}\right],\tag{16}$$

where n_0 is the particle number density at the bottom of the cell and n(z) is the number density a height z above the cell's bottom. $V = 4\pi a^3/3$ is the volume of a single particle, ρ is the density of a single latex sphere, ρ_0 is the density of the suspending fluid, T is temperature in Kelvin, and g is the gravitational acceleration. A measurement of n as a function of z can, therefore, be used to determine $N_{\rm A}$.

Procedure – Part 2

• Prepare a suspension in the same was as was done for part 1. This time, however, use the bottle that produces a suspension with a higher density of particles. For this measurement, it is important that the suspension be allowed to reach equilibrium before taking the measurements. This can take up to 12 hours. You'll need to prepare your suspension the day before your lab so that it can settle overnight. Please make suitable arrangements with your lab instructor or TA.



Figure 4: ToupView settings. Click on the text in the "Camera List" box to open a live video feed. Change the resolution to 640×480 and, if necessary, adjust the Exposure Time and Gain to achieve the necessary frame rate.

- Use ToupView to take a series of photos of the suspension at many different heights above the bottom of the cell. Use the highest resolution images available. You'll need to know the change in height between successive images which cannot be obtained directly from the microscope. To measure changes in height of the microscope platform, we will use a Starrett dial indicator (Last Word, Fig. 5) with 0.0005 inch (0.0127 mm) divisions. Please use care when using the dial indicator. Its total range of motion is only ± 0.015 inches (0.38 mm)! You should be able to measure half a division (0.00025 inches or 6.35 μ m).
- Note that, due to water's refractive index of 1.333, the change of height of the microscope platform does not correspond directly to the change in observation height within the suspension. If z' is the height measured using the dial indicator, the observation height in the suspension is given by z = 1.333z' [1].



Figure 5: The Starrett Last Word dial indicator with 0.0005 inch divisions.

- You will need to count the number of particles in each photo. You can count them in any way you want, but you will need to make a judgment about when to include particles in your count and when to exclude them (due to being too out of focus). One convenient method for counting particles is to use ImageJ a free image processing software (https://imagej.nih.gov/ij/). To count particles in ImageJ, first open your photo and then select the "Multi-point" tool shown in Fig. 6(a). Then, simple click on each particle you wish to include in the count. ImageJ will mark each particle you click on with cross and a number. A partial count of the particles in an example photo is shown in Fig. 6(b).
- Use you counts and measured heights in combination with Eq. (16) to determine $N_{\rm A}$ from a weight least-squares linear fit.

References

 M. Horne, "An experiment to measure Boltzmann's constant," Am. J. Phys. 41, 344–348 (1973).



Figure 6: (a)The "Multi-point" tool in ImageJ. (b) A partial count of the number of particles in an image.