The Effect of Particle Size, Liquid Viscosity and Temperature on the Time Dependence of Brownian Motion

Guy Pelc and Tomer Greenberg

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Abstract

We examined how small particles move in a viscouous liquid under a random force created by frequent collisions with molecules. We have demonstrated that the relation between the square of a particle's from its initial location, on average, can be described as linearly dependent on time, given appropriate treatment of the overall drift of individual layers of the liquid, and taking into account technical limitations such as the number of pixels.

Introduction and Theoretical Background

Brownian motion is the movement of small particles due to collisions with individual molecules when submergred in a liquid. Its properties have been used to describe a wide range of systems operating under random forces, from intercellular transportation of organic molecules to the motion of stars in a galaxy. Apart from being one of the first scientific evidence in history suggesting the discrete nature of matter, it is also closely connected with the concept of diffusion, which has overreaching implications on the study of transform phenomena, such as osmosis in biological systems. The accurate description of Brownian motion influences major technologies in the engineering of metals, pharmaceutical products and semiconductors.

The theory of Brownian Motion regards small particles in a uniform liquid as moving under a force that is random in time and is independent of location. It is also assumed that the force from collisions with individual molecules is small compared to the damping viscuous force, which means we can use Stoke's Law. In one dimension, this leads to an equation of motion of the type:

$$m\frac{dv}{dt} = -6\pi\eta av + F_{random}(t) \tag{1}$$

where v is the velocity in one dimension, η is the viscosity constant and a is the particle's radius. Because of the random force, the only meaninful description would be that of the average location and velocity of a particle undergoing brownian motion. Taking the average of equation (1), together with the equipartition theorem which relates particles' mean velocity in each dimension to the temperature, we can obtain the following formula, which relates the motion of the particle in two dimensions to the temperature:

$$m\frac{d^2 < r^2 >}{dt^2} + 6\pi\eta a\frac{d < r^2 >}{dt} = 4kT \tag{2}$$

Where T is temperature, k is the Boltzman constant, and $< r^2 >$ is the mean distance-squared of the particle from the origin. In two dimensions, this can be solved to obtain the following formula, which relates a spherical particle's distance from its original location to the time from the beginning of the motion:

$$< r^2 >= \frac{2kT}{3\pi\eta a}t \tag{3}$$

Where $< r^2 >$ is the mean distance-squared in two dimensions from the particle's location at $t = 0$.

Our goal in the experiment was to verify formula (3) empirically. This consists of demonstrating a linear relation between $< r^2 >$ and time for individual particles, and by observing the motion of particles with various sizes, in solutions with various viscosities and under various temperatures, to validate that the linear coefficient fits the theoretical value.

Experiment Setup and Measurement Technique

Our goal in the experiment was to verify formula (1) by observing the motion of particles with various sizes, in solutions with various viscosities and under various temperatures. In each measurement cycle, we used a droplet of a solution of water and glycerol, mixed with a smaller droplet of water which contains plastic spheres with typical radii between 2 and 10 μm. We will from now on call these spheres the "particles". Every such mixture is characterized by a certain viscosity, which we calculated by looking up the resulting proportion of water and glycerol in literature tables. Each droplet of mixure was placed under a microscope using a level to prevent the effect of gravitational force on two-dimensional motion. In measurements where we varied the temperature, we heated the base on which the droplet was placed using an electric heater pad. In other cases, the room temperature was measured. We then focused the microscope on a set of particles in an area of $\sim 1.3mm^2$ and took a video of that area. Across all measurements, we obtained 38 such videos, taken over between 1 and 2 minutes.

Data Analysis

We then used the Python object detection library "trackpy" to obtain a raw data set for each with the particle's x and $y$coordinates at each time t. This enabled us to automatically filter particles with strange trajectories, and then manually select particles and measure their correct radius. Particles were initially selected according to the following criteria:

1. The particle must have a roughly spherical shape, so that Stoke's Law will be applicable.

2. The tracking algorithm must be able to track the particle over at least 100 nearly-consequtive frames, or 5 seconds, under strict limitations on tracking accuracy.

3. The particle must stay in focus for the majority of the length of the video. This implies that the particle stayed roughly in the same layer of liquid throughout the video, and therefore is unlikely to have drifted under changing current in the liquid. It also means that we were able to measure the particle's radius accurately.

4. The track of the particle must be roughly a straight line. Some particles, for example, were close to the edge of the droplet, and were affected by streams generated by its surface tension.

In general, in order to obtain a statistically valid measurement for $< r^2 >$ after a certain time Δt, we would have to perform the same measurement for identical particles several times, and average their r^2 after Δt time from the beginning of their motion. However, since the particle is moving under forces that are random in time and independent of location, this is equivalent to measuring the r^2 for the same particle during non-overlapping intervals of Δt, and taking the average of r^2 across the intervals. This means that for each particle, the number of samples decreases inversly with the interval size. However, since we are only interested in an accurate linear fit for each particle, and since the frequency of particle collisions under brownian motion is much higher than the number of frames per second in our videos, we chose to limit the size of time intervals to 1.5 seconds, so we can ensure each measurement averages over at least 6 intervals, and that every linear fit is over 15 data points. From now onward throughout the report, we will regard $< r^2 > (t)$ for a certain particle as the average squared distance over time intervals of size t.

We now needed to isolate the effect of Brownian motion on the particle's trajectory, and cancel other factors that might influence it. We first eliminated the effect of drift caused by movement of liquid in the droplet. Since layers of liquid in the droplet travel in different velocities, and since the particles we selected from a certain video might be positioned in different layers, we needed to treat each particle individually, rather than eliminating the average drift of all particles in the video. We did this by first assuming that the particle's drift is constant throughout the motion. If it isn't, then the particle was under net force other than that caused by collision with molecules, and its data is useless. We treated these cases separately, as described in a following section. To counter the effect of a particle's drift, we calculated the its mean velocity throughout its trajectory $\overline{v}$, and subtracted $\overline{v}t$ from each data point.

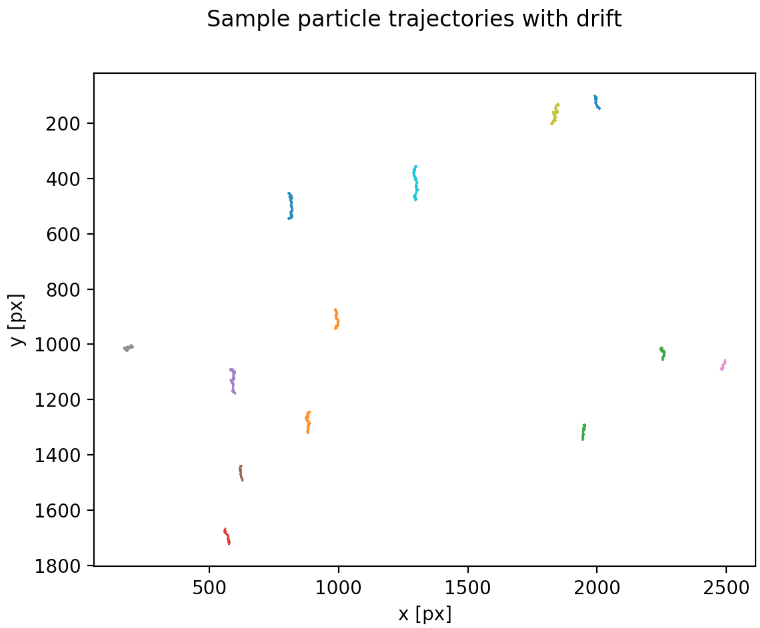

Figure 1 - Particle trajectories in one video without constant drift elimination

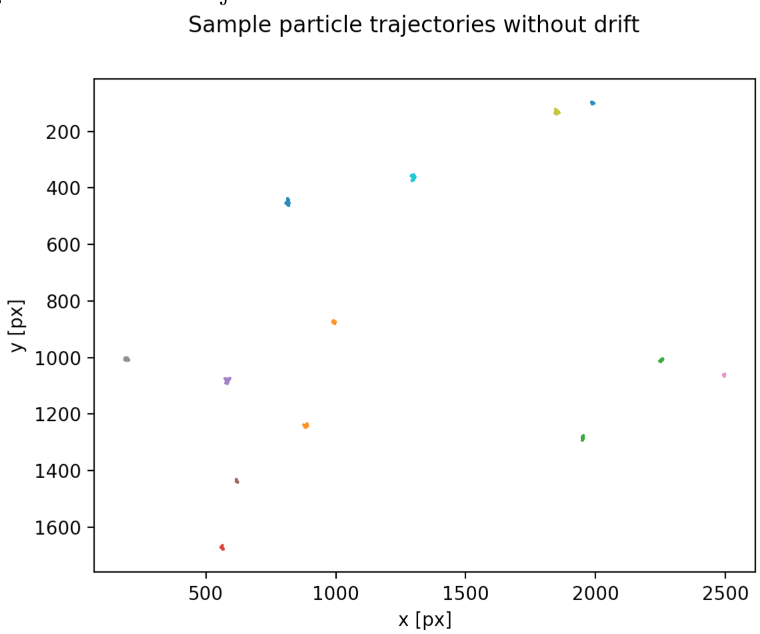

Figure 2 - Particle trajectory in one video with constant drift elimination

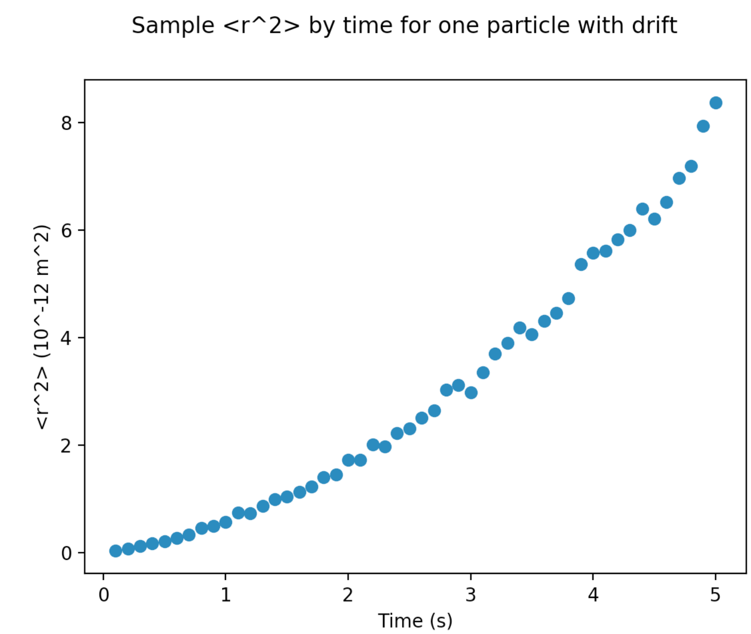

Figure 3 - <r^2> by time data for one particle with constant drift. The relation is clearly non-linear.

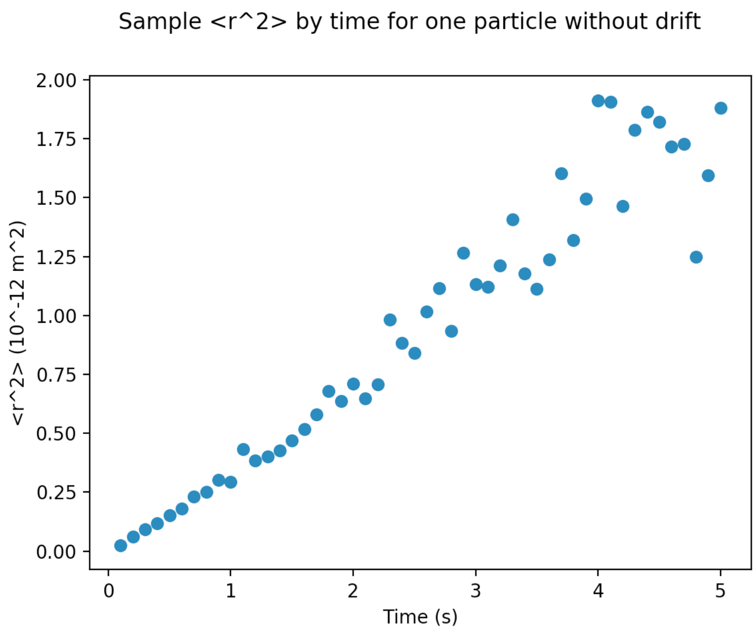

Figure 4 - <r^2> by time data for one particle after eliminating constant drift

We then needed to regard for forces that might have been unaccounted for. These include gravitational force along the measurement plane as a result of the microscope plate being slightly unlevel, or the particle moving perpendicular to the measurement plane and therefore under non-constant drift. Since this type of motion is not strictly brownian, we had to be able to detect it and filter out these particles completely. We did this by automatically filtering out particles by the quality of the linear fit for their $< r^2 > (t)$ data, and by examining the residuals from a linear fit. Since the residuals of individual particles are often not very informative, we looked at the mean residual across all particles for an entire video. If the mean residual by time for a video is not randomly distributed like a around 0, it might indicate gravitational force from an unlevel microscope plate, or non-constant drift currents caused by the droplet sticking to the edge of the plate. This kind of analysis is especially helpful in our case since these forces are still small in comparison to the viscuous force in the liquid, so they might only slightly skew the linear relation between $< r^2 > (t)$, but they are easily detectable if the residuals are clearly time-dependent. What we found is that in almost all videos, the average residuals are positive for small time intervals and decreasing for larger ones, until they are slightly negtaive. While these residuals are comparatively small on average (from 10% to -5% of actual $< r^2 >$ values), they appear consistently across videos. Of course, looking at these residuals without our drift elimination reflects the convex trend we see for drifting particles, but after eliminating drift, we were not able to counter the slightly concave trend of $< r^2 > (t)$ that these residuals imply. Our best hypothesis is that they are the result of jittering of the tracking algorithm's positioning of the particles, and the rounding of the displacement to an integer number of pixels, both of which take effect mainly over shorter periods when the actual motion is miniscule - typically, a displacement of 3 pixels per second. To support this hypothesis, we were able to steadily decrease the relative residuals up to some point by fitting for only longer time intervals. However, we could not completely rule out the possibility that this slight concave arching of the generally-linear $< r^2 > (t)$ trend is the result of small net forces like the ones mentioned above, when their effects are distorted by our drift elimination. Viewing this, we decided to disregard time intervals smaller than 0.4 seconds, so we would minimize the impact of this effect on the linear fit, while still have 12 data points per particle for each fit.

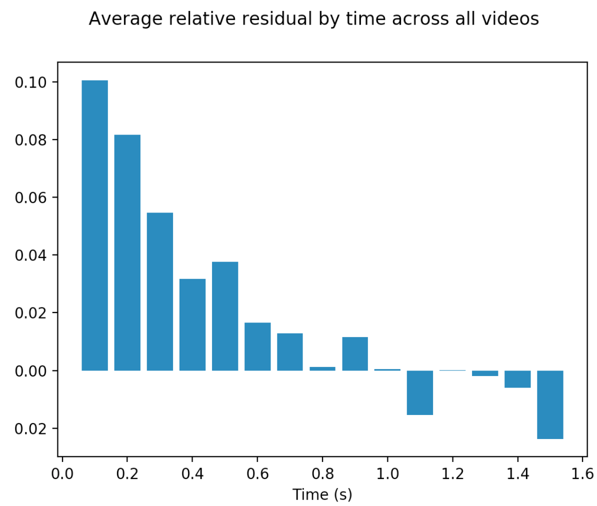

Figure 5 - Relative residual (divided by actual value of $< r^2 >$) from linear fit by time, averaged for all particles. Notice how the trend ceases to exist after ~0.8 seconds.

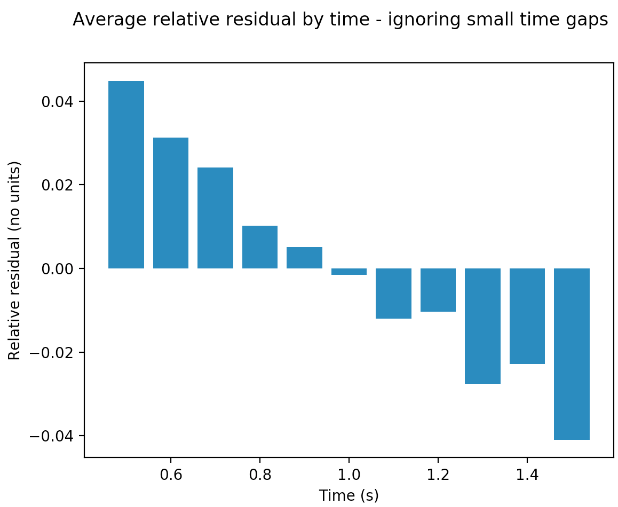

Figure 6 - Same figure when only fitting for time intervals of between 0.6 and 1.5 seconds. The concave trend is still present, but has been reduced in magnitude.

After performing a linear fit in this manner on 161 particles, we were able to reach an average R^2 fitting value of 0.981, and conclude that we have validated a strong linear fit for $< r^2 > (t)$ for a single particle.

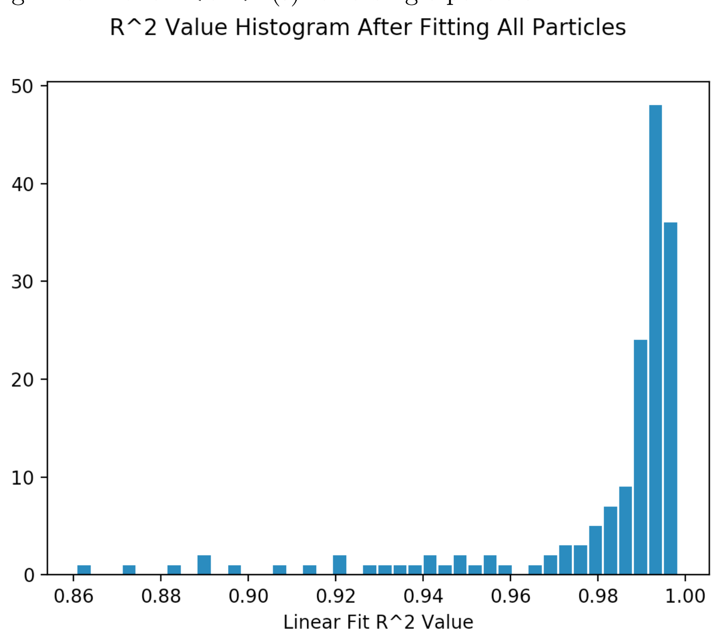

Figure 7 - a histogram of R^2 values for 161 particles

Once we had the slope for each linear fit, we could compare it to theoretical values derived from $< r^2 >= \frac{2kT}{3\pi\eta}t$..... (Now your part)