Brownian Motion: Analysing Settling Time and Mean Squared Displacement Time of Silica Particles in Water

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1 Introduction

This lab aims to measure the mean squared displacement of microscopic silica particles suspended in doubly-ionized water and investigate possible systematic effects on the system being measured. First, we measure how the diffusion coefficient (D) changes with particle size, ranging from 1.04 to 4.15 micrometers. We then investigate how changing regions of the sample being recorded affects the diffusion coefficient. It is possible that the diffusion coefficient may differ throughout the sample if some areas of the sample are too saturated with particles, which could be caused by improper mixing. Other possible effects to consider may be the difference in temperature between regions, and settling of particles as more data videos are captured.

All videos of particle motion captured by the CCD camera were run through a Jupyter notebook using TrackPy, a python particle tracking code. The notebook prepared the videos and data in the following way: It first subtracted the background image of the video, where differences in intensities within the pixel array were static. The code then located the particles through differences in light intensity, and centered particles through a "mass" calculation. The darker the particle, the more certain the code is of its position. We then refine different parameters within the code to get rid of spurious features. Parameters include diameter of the particles, the separation between particle centers, and mass ratio. The python code then attempts to remove any overall particle drift, and plots trajectories, mean squared displacement (MSD) and gaussian fits on horizontal and vertical displacements.

All data regarding particle size were taken directly from the packaging bottle of the concentrated silica particles, and was not found experimentally through the python code.

2 Trial 1: 1.04 μm particles with 0 settling time.

We collected 300 frames of video using the CCD camera and ran the video in the TrackPy code. Below is a log-log graph demonstrating the MSD against lag time. Notice that all particles follow a power law. There are sudden dips in the displacement lines, since the statistics are poorer for large lag times. In order to counter this, more frames would be needed. We then average out the displacements for each time step of the MSD data

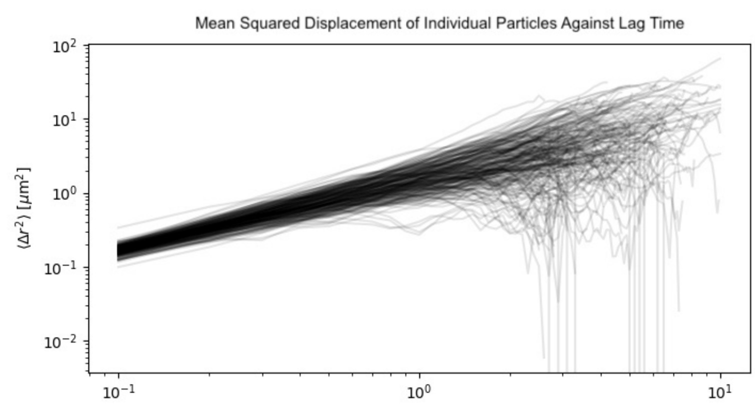


Figure 1: Mean Squared Displacement (MSD) of individual particles over lag time in seconds, plotted in a log-log plot.

displayed in figure 1 to illustrate information about the bulk data. This has been done using the TrackPy.emsd() function. Figure 2 demonstrates a power law, At^n, being fit to the data. we received $n = 1.057$ and $A = 1.446$, where n denotes the power law exponent. For water, we expect $n = 1$. $A = 4D$, where D represents particle diffusivity. Particles with a 1 μm diameter are expected to have an A value of $A = 1.66$ $\mu m^2/s$. This expected value is

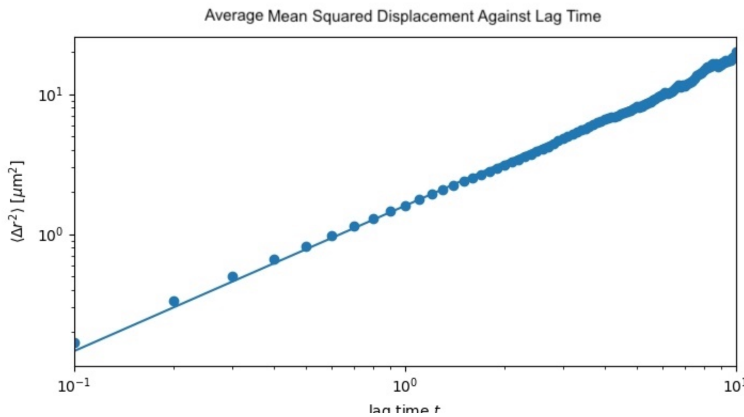


Figure 2: MSD averaged over each time interval in seconds, plotted in a log-log plot and fitted with a power law.

calculated through equation 1.

$$D = \frac{K_B T}{6\pi\eta r} \tag{1}$$

Our value for A was therefore 12.7 percent off the predicted. Next, we run a gaussian fit of our displacement data for both x and y axis displacements in pixels, as seen in figure 3. The y axis for the graphs demonstrated in figure 3 denotes the amount of particles found to have the given amount of displacement between frames. After fitting a gaussian fit to our data, we extract standard deviation values (σ_x and σ_y) from the graphs to use in our diffusion coefficient calculations. A conversion coefficient was found to calculate the real length from the pixel length presented in figure 3. The conversion coefficient (k) was found using equation 2.

$$k = \frac{0.01 \times 10^{-3}\, m}{61.0\, pxs} = 0.164 \frac{\mu m}{px} \tag{2}$$

We combine σ_x and σ_y by averaging the values and multiplying by the conversion coefficient to get an average sigma value in real length, demonstrated by equation 3.

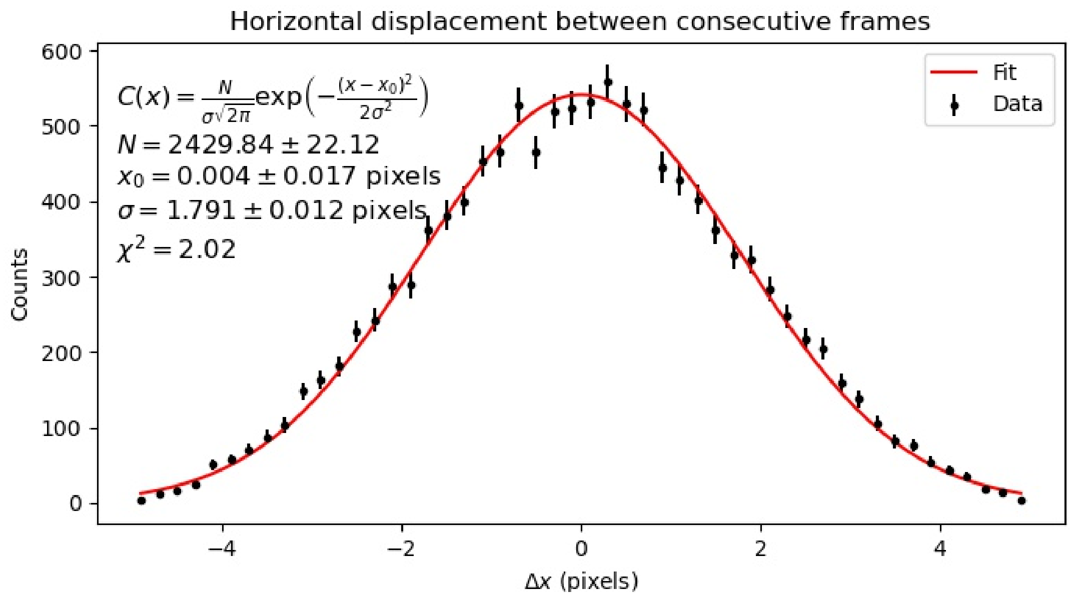
$$\sigma = \frac{\mid \sigma_x \mid + \mid \sigma_y \mid}{2} \times k. \tag{3}$$

The uncertainty in sigma, dσ, was found using

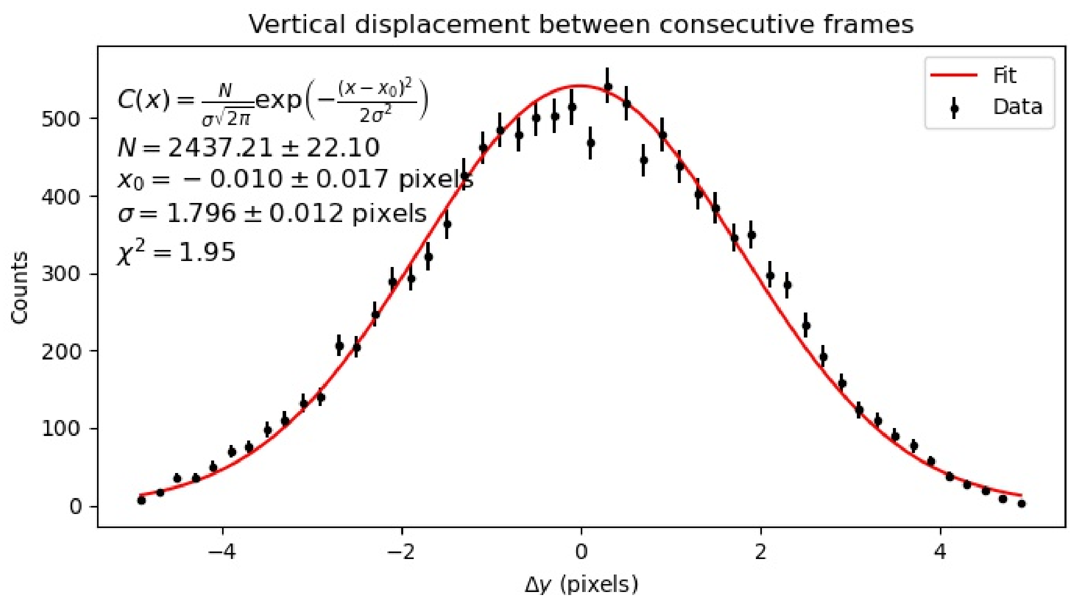
$$d\sigma = \frac{\sqrt{\sigma_x^2 + \sigma_y^2}}{2} \times k. \tag{4}$$

The uncertainty in frame rate is calculated using equation 5.

$$dt = \frac{1}{\text{frame rate}} = 0.1 \text{ s/frame} \tag{5}$$



(a) Gaussian fit of displacements in x-axis



(b) Gaussian fit of displacements in y-axis

Figure 3: Fits used to find the mean displacement in two dimensions.

We calculate the uncertainty in sigma, since the likely primary cause of uncertainty is caused by sampling error. To calculate the diffusion coefficient we use

$$D = \frac{\sigma^2}{2} * \frac{1}{dt}. \tag{6}$$

Appropriately, we find the uncertainty in the diffusion coefficient, dD, using

$$dD = D\frac{d\sigma}{\sigma}. \tag{7}$$

The calculated diffusion constant is demonstrated in table 1. This was within 5 percent of the

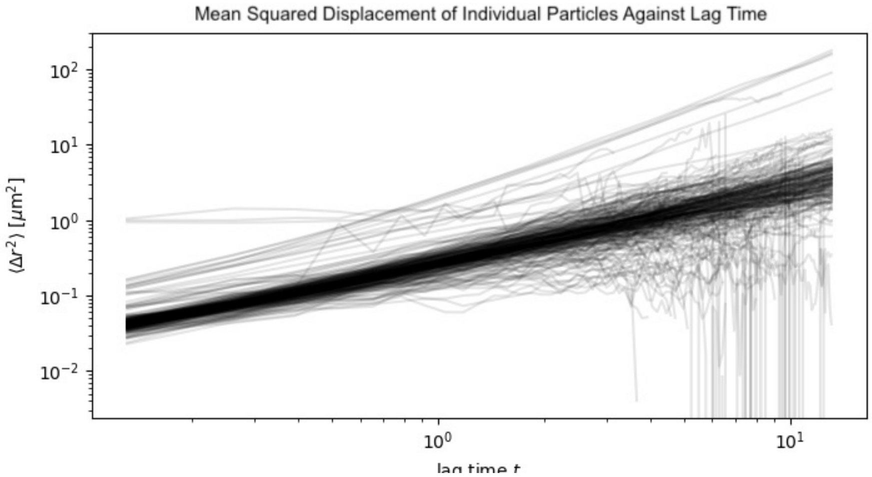
Particle Size (μm)	Predicted D ($10^{-13} m^2$/s)	Measured D ($10^{-13} m^2$/s)	Uncert. in pred. D ($10^{-13} m^2$/s)	Uncert in meas. D ($10^{-13} m^2$/s)
1.05	4.7003	4.6215	0.0496	0.0210

Table 1: Diffusion coefficient and associated uncertainties for the 1.04 micrometer particle sample

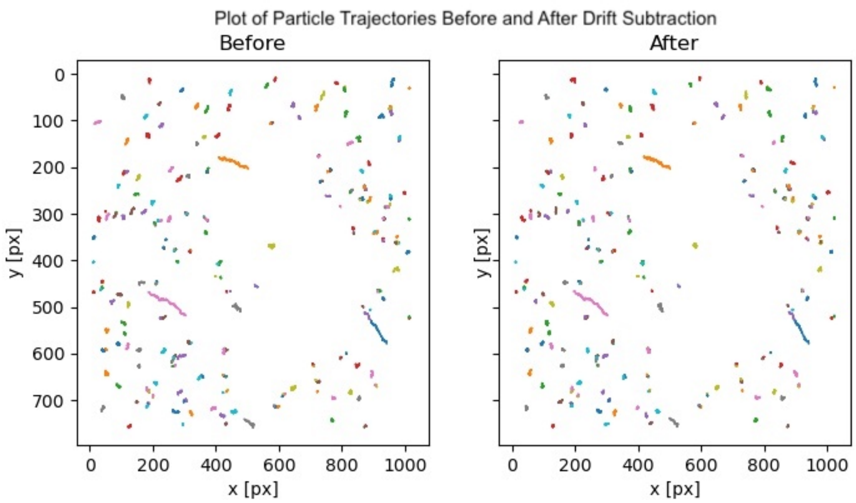
predicted value of the diffusion coefficient for the given particle size, suggesting a relatively good fit with theory. The Gaussian proved to be a good fit, with a reduced chi-squared of 2.02 and 1.95 for x and y displacements respectively.

3 Trial 2: 4.15 μm particles with 0 settling time.

For this measurement, 600 frames were captured at a rate of 7.63 fps. This would help with the accuracy of the MSD data for larger lag time, which is where we expected the movement of the larger particles to be more pronounced due to their size. Upon examination of the overall trajectories, as well as the mean square displacement graph over lag time, it is clear that several particles exhibited motion that could not be explained by Brownian motion alone. This is because their trajectories were much longer than the average particles, and because their MSDs seemed to be increasing exponentially with lag time. This led to inaccurate results regarding the diffusion coefficient. Observing the longer trajectories more closely, one can notice that the particles all travel in the same south-eastern direction relative to the center of the graph. This is suggestive of a current or drift, which seems to be affecting some particles more than others. It is possible that the particles in question are slightly above or below the focal plane, and thus are influenced by a different kind of drift.



(a) MSD Against Lag Time for 4.15 micrometer samples



(b) Trajectories of individual 4.15 micrometer particles in two dimensions

Another source of error might be with the python code and parameterization. It is clear that the choice of parameters for the software to use in order to filter particles has a very significant effect on the data. We noticed that some circles localizing the particles within the frames would instantaneously and significantly change positions while the particle itself exhibit small changes in motion. This could have led to more exaggerated motion and influenced results. At first it was believed that this occurred due to improper parameterization of particle diameter, however after changing diameter parameters the issue would still sometimes occur within the code. Overall, the average MSD over bulk data gave value $n = 1.137$ and $A = 0.0306$, an A value that does not conform with expected value.

Additionally, we observe behavior in y-displacement that cannot be accurately fitted with a gaussian. We notice that most of the counted displacements are very small, leading to a very large peak, and narrow spread around the mean. This can potentially be explained by the

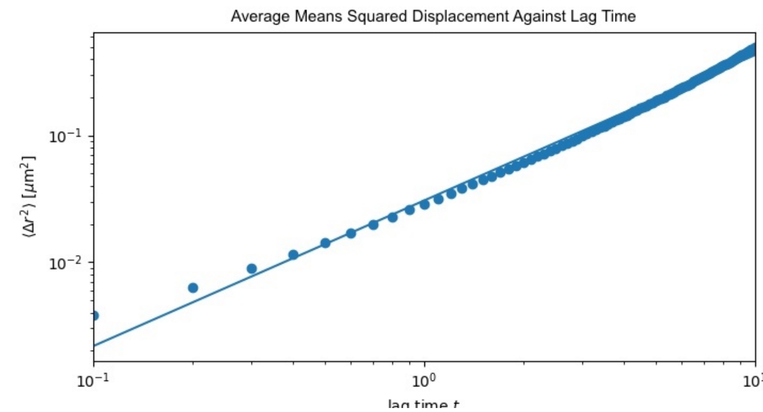
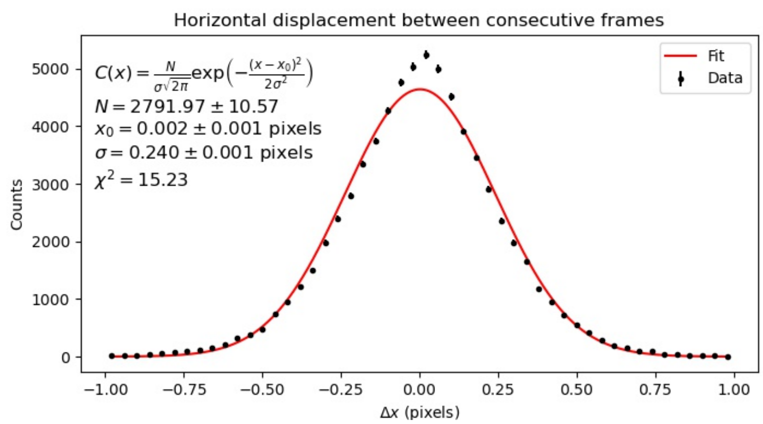
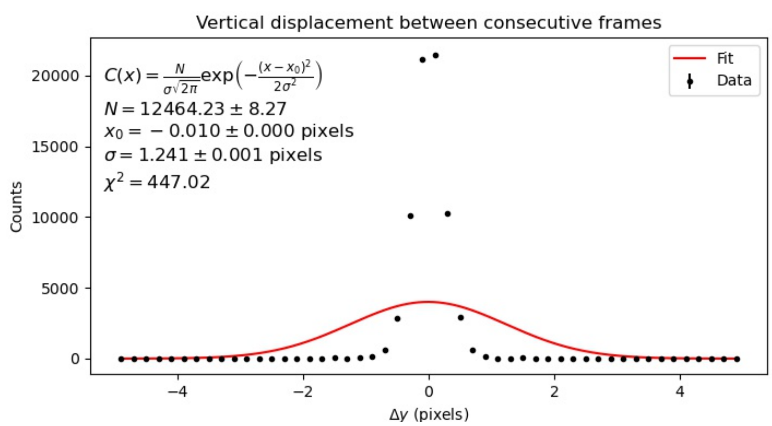


Figure 5: Average MSD against lag time of 4.15 micrometer particles



(a) Gaussian fit of 4.15 micrometer particle displacements in x-axis



(b) Gaussian fit of displacements of the same particles in y-axis

travelling particles, which could be contributing to the fit through very small displacements in the y-axis as they travel.

The uncertainties and expected values were all calculated in the same manner as in the measurements for the 1.04 μm particles. The calculated diffusion coefficient is demonstrated in table 2.

Particle Size (μm)	Predicted D ($*10^{-13}m^2$/s)	Measured D ($*10^{-13}m^2$/s)	Uncert. in pred. D ($*10^{-13}m^2$/s)	Uncert in meas. D ($*10^{-13}m^2$/s)
4.15	1.1779	0.7368	0.0124	0.0004

Table 2: Diffusion coefficient and associated uncertainties for the 4.15 micrometer particle sample

4 Trial 3: 1.5 μm particles with 0 settling time.

This trial captured 300 frames at 10fps. Some traced particles were observed to have a mean square displacement (MSD) that is below the expected trend, with a tendency to have an exponential increase in MSD as lag time increases. In addition to the reasons mentioned in the 4.15 micrometer trial, this could suggest a contamination of the sample, as some particles being tracked clearly behave differently through time, in ways that is not governed by Brownian motion, due to presence of an exponential increase in MSD.

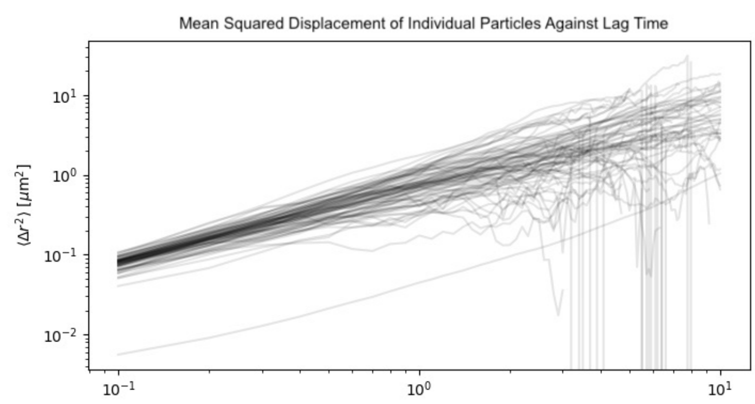


Figure 7: MSD against lag time of 1.5 micrometer particles

This issue is similar to the results we found for the 4.15 micrometer particle size. It has been observed that many particles stuck together, or seemed to be influenced by each other's motions. This is clear when we observe the graphed trajectories. The particles seem to be looping near each other, with frequent collisions. This could be due to some unknown potential within the sample, or perhaps due to an electric charge picked up by the particles during preparation. In order to counter this, we decreased the density of the samples, by

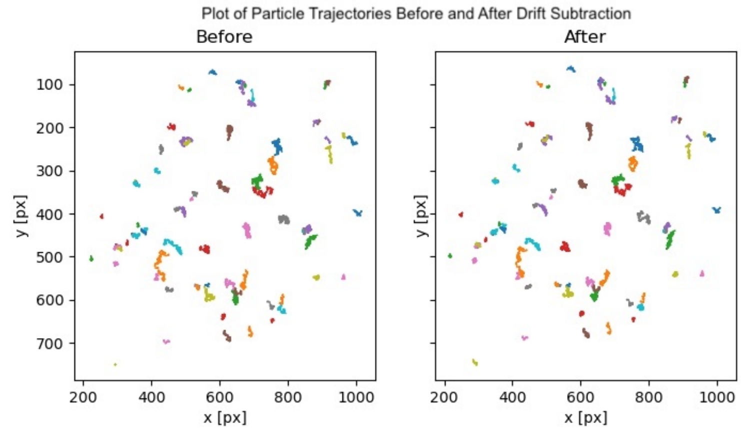


Figure 8: Trajectories of 1.5 micrometer particles plotted in two dimensions

inserting less droplets of particles as well as diluting more thoroughly. This approach was done for the 2.07 micrometer trials.

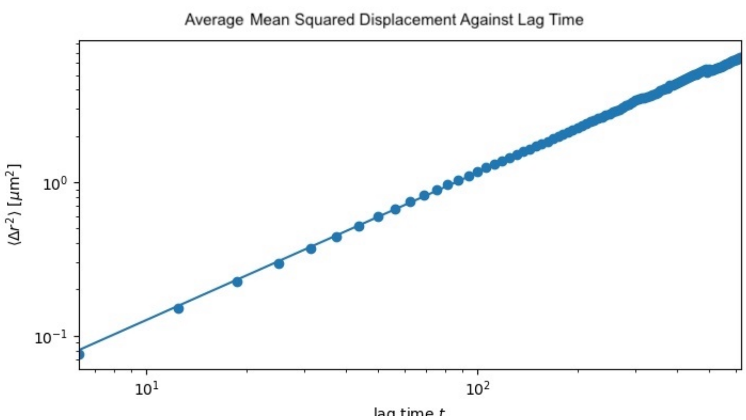
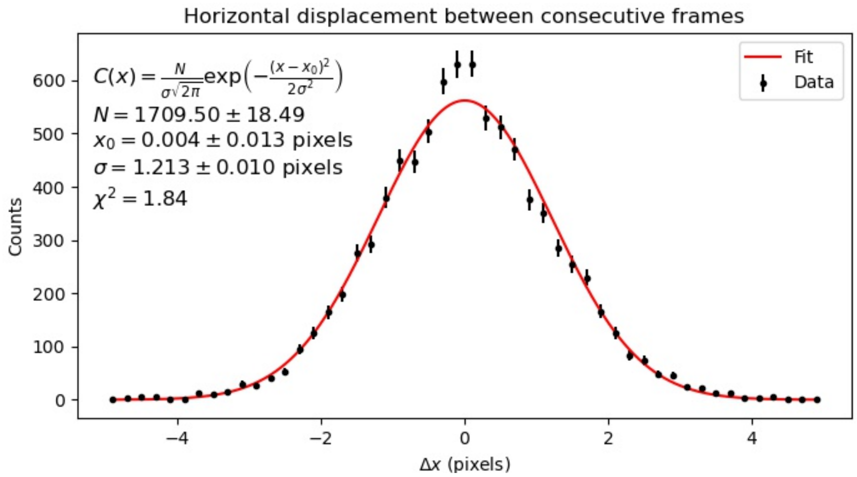


Figure 9: Average MSD against lag time of 1.5micrometer particles with a power fit.

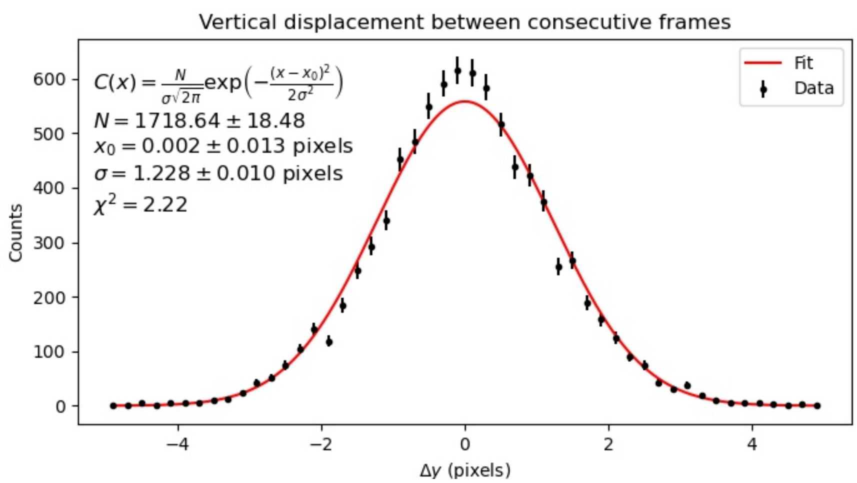
Note that all uncertainties were calculated using the method highlighted under the first experiment (1.04 μm). Notice that the Gaussian fit seems to fit the data accurately, due to reduced chi-squared values of 1.84 and 2.22 for x and y displacements respectively.

Particle Size (μm)	Predicted D ($*10^{-13}m^2$/s)	Measured D ($*10^{-13}m^2$/s)	Uncert. in pred. D ($*10^{-13}m^2$/s)	Uncert in meas. D ($*10^{-13}m^2$/s)
1.5	3.2529	2.0018	0.0344	0.0113

Table 3: Diffusion coefficient and associated uncertainties for the 1.5 micrometer particle sample



(a) Gaussian fit of 1.5 micrometer particle displacements in x-axis



(b) Gaussian fit of displacements of the same particles in y-axis

5 Comparison of all three trials regarding particle size

We see that, as the average size of the particles increases, the diffusion coefficient decreases. This is expected. Two forces are assumed to contribute to the random motion of the particle, one of which is the time-independent dissipative frictional force μ, which itself is affected by the radius of the particle. The relationship between particle radius and the frictional force can be expressed as

$$\mu = 6\pi\eta r. \tag{8}$$

The relationship between D and particle radius becomes

$$D = \frac{K_B T}{6\pi\eta r}, \tag{9}$$

where η is the viscosity of water, and r is the radius particles, K_B is the Boltzmann constant, and T is the overall temperature. The bigger the particle, the greater the frictional force it experiences. From the equations we see that a greater frictional force would lead to less movement of the particle, and thus a lower coefficient. However, only one of the trials reaches a measured coefficient which is within a 5 percent deviation from the expected value. For reasons mentioned above (large sample densities, unexplained single particle behaviors, particle groupings, and large particle diameters), the 1.5 and 4.15 micrometer trials have questionable significance due to systematic influences, even though the uncertainties of these measurements still allow us to infer that a negative correlation between particle size and the diffusion coefficient exists.

6 Trial 4-6: 2.07 μm particles in different physical regions of the sample.

The second part of our experiment focused on measuring the effect of potential systematic influences on the samples, and thus the experimental system. Other influences on the system have been averaged out by the gaussian distribution. Thus, we decided to measure how differences in location of the sample may affect the diffusion coefficient. It is expected that, if the sample has uniform density, uniform temperature and is pure, then the diffusion coefficient should be the same for all measurements of the same sample, irrespective of location. We chose a 2.07 μm diameter for the particles, since we noticed the python code responded to diameters closer to 1 μm more effectively. We noticed differences in the diffusion coefficient as we changed locations under observation within the sample, illustrated in table 4. All of the diffusion coefficients and uncertainties were found using the same method as the one illustrated in the 1.05 μm trial. It was noted that there seemed to be no particles that

Sample Region Number	Predicted D	Measured D	Unct. Pred. D	Unct. in Meas. D	Percentage Diff.
Region 1	2.3615	2.6738	0.0249	0.0210	113.2
Region 2	2.3615	2.4593	0.0249	0.0122	104.1
Region 3	2.3615	2.9716	0.0249	0.0148	125.8

Table 4: Diffusion coefficients and measured uncertainties for all trials of 2.07 micrometer particles

behaved more erratically upon investigation of MSD graphs and trajectory plots. It is also unlikely that overall drift caused differences in diffusion coefficients, since it is subtracted out by the python code. Therefore, it is likely that the reason for the differences in diffusion coefficients is caused by two things:

1. Differences in regional densities of the sample,
2. Settling time as the sample was left to rest.

6.1 Settling Time

The time between measurements of the regions was not recorded, however it would be reasonable to estimate an average time of about 2 minutes per measurement. This is the time taken to record and save 300 frames of footage, as well as recalibrate the microscope to a new region. This means that the final region was settling for around 4 minutes before a measurement was taken. The settling velocity of the silica particles can be expressed as

$$V_m = 5.448 \times 10^{-5}(\rho - 1)d^2. \tag{10}$$

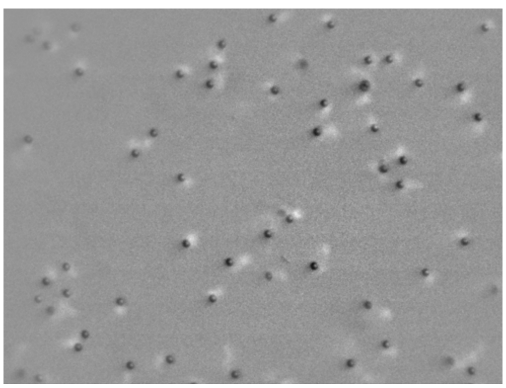
V_m in equation 10 is the drift velocity (in cm/s), ρ is the sphere density (g/cm^3) and d is the diameter of the sphere (μm). The observed drift velocity was 3.1×10^{-4} cm/s. The numerical value for the density of silica was extracted from Wikipedia, and the diameter of the particles was extracted from the containers of the concentrated silica solution. From this velocity we can calculate the settling time as

$$t = h/V_m = 0.3/3.1 \times 10^{-4} = 97.4s. \tag{11}$$

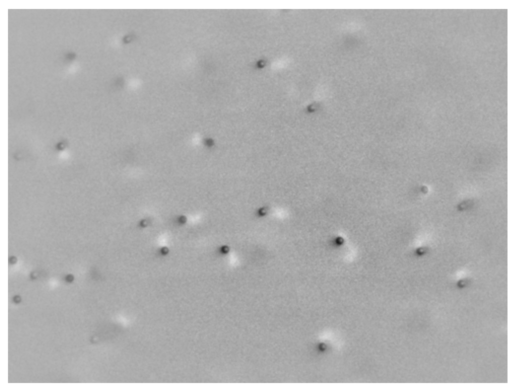
The observed settling time is significant, meaning the particles were given enough time to settle on the same focal plane. Settling on the same focal plane would lead to greater density at that plane, which could negatively impact the diffusion coefficient. This is because if density of the sample increases, the particles will have less room to exhibit Brownian motion and are more likely to influence each other's movement. Potentially, movement at larger densities could be caused by collisions between the particles, or attraction between the molecules if they accidentally picked up some electric charge during preparation of the sample. However, between trial 1 and 2 for 2.07 micrometer sample, the diffusion coefficient decreased before increasing again for third trial. Therefore, we cannot infer that the difference in diffusion coefficients was caused by settling time, since the differences do not follow a specific trend. This in turn suggests that there might be specific differences within the regions being examined, which leads to the next point in the analysis.

6.2 Differences in the regional densities of the sample

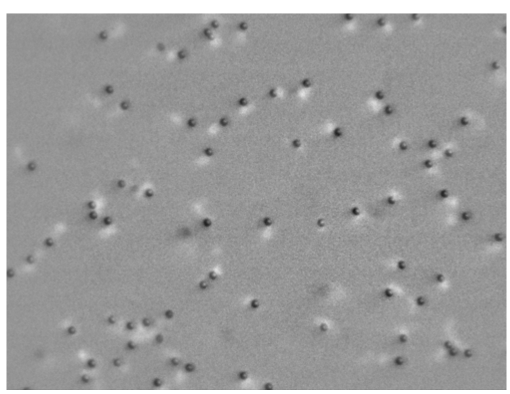
Upon inspection of the captured videos, it is clear that there are noticeable differences in particle densities between regions of the sample. The second trial exhibited the lowest density, while the third trial exhibited the highest particle density within the frame. This suggests that the differences in diffusion coefficients are caused by non-uniformity in particle density throughout the sample. This could suggest that there is some density threshold after which the particles do not exhibit Brownian motion. However, we cannot rule out other potential regional effects, such as differences in sample temperature between trials and potential regional contamination. We also potentially risk exposing the trials to particle settling if trials are done in succession. Potential improvements to the method would thus be monitoring temperature, or studying the effects of particle settling through trials were particles were left to settle for a known period of time.



(a) Frame demonstrating the density of the particles in the sample for region 1.



(b) Frame demonstrating the density of the particles in the sample for region 2.



(c) Frame demonstrating the density of the particles in the sample for region 3.

Figure 11: Frames from the CCD camera recording.