Measuring the hydrodynamic radius of polystyrene spheres in water

Joseph G. Theiss
Basement, Physics Department, The College of Wooster, Wooster, Ohio 44691, USA

(Dated: August 6, 2018)

PCS was used on small polystyrene spheres of radius (53.5 ± 2)nm in a water solution, to measure the sphere's radius experimentally. A He-Ne laser was used and shone through a vial containing the spheres. A PMT was at an angle of 90^o to catch light scattered off of the spheres. Due to the small size of the spheres when compared to the wavelength generated by the He-Ne laser (632.58 nm), Rayleigh Scattering was used. A computer program recorded the intensity values from the PMT and saved them for later review. Autocorrelation was used on this stochastic data set to relate it to the underlying mechanism. After fitting an exponential to multiple trails of varying concentration, an average error of 1.8% was found with a minimum error of 0.5% and a maximum error of 3.1%. No measured values were outside one standard deviation from the known value of the spheres.

INTRODUCTION

Brownian motion is used to describe the random movements of small particles in liquids or gasses. This random motion was first observed by its namesake Brown in 1827. He was observing particles of pollen grains in water. This motion was concluded to be random as Brown had trouble figuring out the underlying mechanism driving this movement.

As with many things, Einstein helped figure out this problem. The idea of molecules and their building blocks, atoms, were not well understood. In 1905 Einstein published a paper on Brownian motion and showed evidence that the pollen was being pushed by water molecules. This was the cause of the random movement, collisions off of water molecules.

The random walk motion is seen in Fig. 1. The distance from the center of the immersed molecule to where the molecules interact with each other is called the hydrodynamic radius. This is an important distinction because the actual radius of a molecule or atom isn't "touched"[1], what is "touched" is the radius where water can interact and repel the molecule or atom.

A laser can be used as in Fig. 2 to measure the size of the immersed molecules or atoms in our solutions. Those caught in the path of the laser reflect its intensity. As the particles move in and out of the path of the laser, the laser's reflected intensity will fall and rise. These fluctuations are a time series which can be measured and correlated to their diffusion into and out of the laser's path.

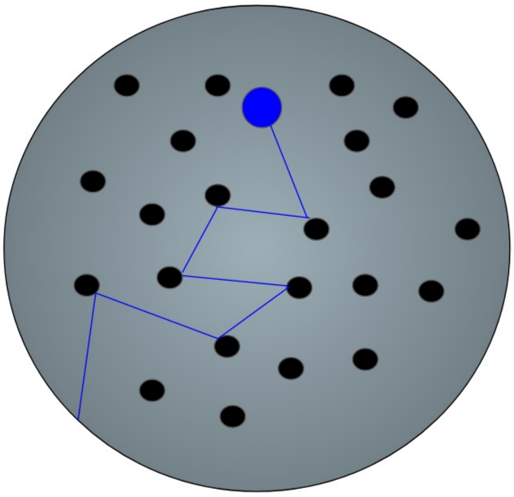

FIG. 1: The immersed molecule - blue - is seen walking along a random path caused by the interactions with the water molecules - black.

This whole process is an already well-defined study call PCS - Photon Correlation Spectroscopy[2]. The scattering from these small particles was described in a paper by Rayleigh in 1871 and is referred to as Rayleigh scattering, but large particle scattering is described by Mie scattering. PCS uses Raleigh scattering for simplification and the diffusion from Brownian motion to find the hydrodynamic radius.

THEORY

Finding the value of q

As seen in Fig. 3, the wavefront of light from the laser approaches the test chamber with wave vector $\vec{K}_i$

---

[1] There are many ways one could describe the moment when two atoms are considered touching. This is obvious as nuclei in everyday life stay well apart from each other, less in extreme conditions not conducive to human life; therefore, we need other definitions of touching. Here the radius of touch is simply the edge of interaction for water molecules.

[2] The first name, now outdated in some circles, is Quasi-elastic light scattering - QELS.

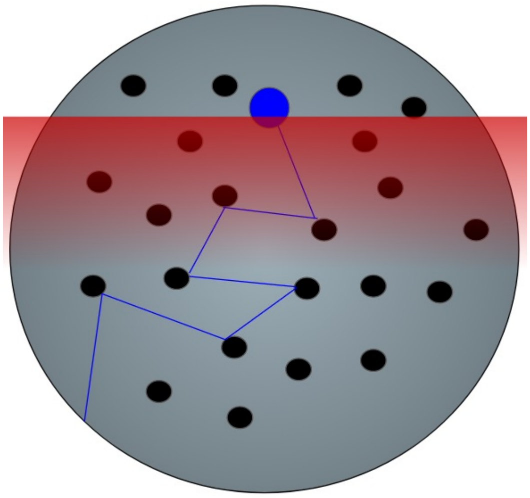

FIG. 2: The section that the laser scatters off of is shown in red. The immersed molecule - blue - can be seen making its normal Brownian motion into and out of the laser's path. This is the diffusion that Einstein described.

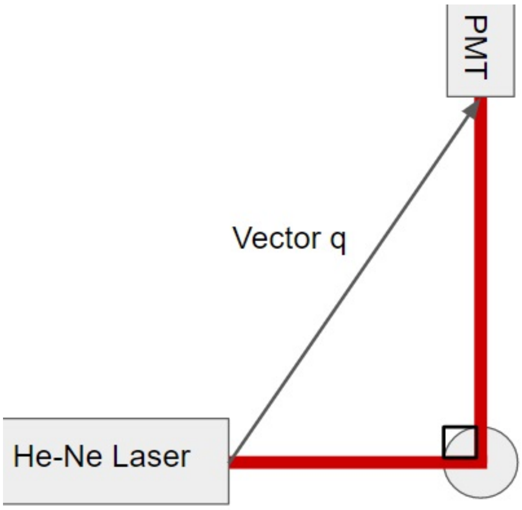

FIG. 3: The laser lights path can be seen as the wavefront approaches our sample and scatters at our angle of 90^o. This is then superimposed into the imaginary triangle to determine the two vectors difference q.

and, after the scattering event, leaves the test chamber with wave vector $\vec{K}_f$. These two wave vectors can be approximated to have the same wave vector magnitude as little energy is left with the particles. We can use the definition of wave vectors to relate the magnitude to the wavelength λ and the refractive index n as seen in

$$|\vec{K}_f| = |\vec{K}_i| = \frac{2\pi n}{\lambda}.$$

Since the scattered light is always measured at a fixed angle of 90^o we can imagine a right triangle with legs of $\vec{K}_f$ & $\vec{K}_i$ as shown in Fig. **??**. This triangle would have a hypotenuse $\vec{q}$ whose magnitude q would be the magnitude of the difference between the wave vectors. Using the Pythagorean theorem, we find that

$$|\vec{q}| = \sqrt{2}|\vec{K}_i| = \frac{2\sqrt{2}\pi n}{\lambda} = q.$$

Correlation

A time series function can be made up of random noise or more hopefully, useful data. Autocorrelation is done by comparing a point of the time series with another point at some time τ away. If the time series consisted of only random noise, then it would be obvious that any-one point compared to any other will also be random in their correlation. If however, the data had an underlying mechanism for how the time series evolved, there would be a pattern in how two points in time were related, see Fig. 5. This pattern turns into random noise at larger values of τ, which makes conceptual sense as the further in time two points are, the less they weigh on each other's outcome.

This decay of the two points' correlation asymptotes to one as time increases as seen in Fig. 5. This is because no past data in the time series is completely useless, just less relevant to new data. This relation is drawn on a graph called a correlogram and shows how correlation decreases with time. Mathematically this relation is

$$C(\tau) =< I(0)I(\tau) >,$$

where the brackets indicate a time average and I is our intensity function which was experimentally measured. Normalizing this function gives

$$C_n(\tau) = \frac{< I(0)I(\tau) >}{< I(0) >^2}.$$

Scattering

Consider a probability density $\Psi(\vec{r}, t)$ which is the probability of a particle moving through the laser light due to fluctuations of $\vec{r}$ at thermal equilibrium. It follows then that the spatial diffusion properties D can be related to the temporal fluctuations by the diffusion equation

$$\frac{\partial \Psi(\vec{r}, t)}{\partial t} = D\nabla^2\Psi(\vec{r}, t). \tag{1}$$

This equation parallels the time-dependent Schrodinger equation very well. This makes sense as both are relating temporal fluctuations with spatial fluctuations but at different proportions. Solving Eq. (1) gives the needed first order solution

$$\frac{\partial \Psi^*(\vec{q},t)}{\partial t} = Dq^2 \Psi^*(\vec{q},t)$$

$$\Psi^*(\vec{q},t) = e^{-Dq^2 t}, \tag{2}$$

where $\Psi^*(\vec{q},t)$ is the 3D spatial Fourier transform of $\Psi(\vec{r},t)$ such that it is also equal to the ensemble [3] average seen below as

$$\Psi^*(\vec{q},t) = \int_V \Psi(\vec{r},t) e^{iq\vec{r}(t)} d\vec{r} = < e^{iq\vec{r}(t)} > .$$

Eq. (2) is used with the Siegert relationship to relate our data to the normalized intensity function we measure[3],

$$C_n(\tau) = 1 + e^{-2Dq^2 t}.$$

Solving for the hydrodynamic radius R

Once a normalized correlogram is made, an exponential fit can be made to it. This fit will return a value for the exponent seen in Eq. (2). We don't want the whole $2Dq^2$ from the fit F. We are looking for the hydrodynamic radius, whose measurement has not been mentioned yet.

The diffusion D for this particular application was found by Einstein in 1905[2].

$$D = \frac{k_B T}{3\pi\eta d}. \tag{3}$$

Here k_B is the Boltzmann constant, T is the temperature in Kelvin, η is the viscosity of the solvent, and d is twice the hydrodynamic radius.

Substituting what we know as D and what was earlier shown to be q into fit F gives

$$F = 2Dq^2$$

$$F = 2\frac{k_B T}{3\pi\eta d}\left(\frac{2\sqrt{2}\pi n}{\lambda}\right)^2 .$$

We can solve for our diameter d which readily yields our hydrodynamic radius R as

$$R = \frac{8}{3}\left(\frac{k_B T n^2 \pi}{\eta\lambda^2 F}\right). \tag{4}$$

PROCEDURE

A He-Ne laser is used with a PMT. A test chamber was also provided whose purpose is to prevent unwanted light from entering the aperture to the PMT. This test chamber was filled with Decahydronaphthalene; the choice of this specific chemical is essential as it has a refractive index near glass. Sodium Azide is also added to the test chamber to avoid scum buildup which could impede the light of the laser from reaching our sample.

The sample prep begins with an empty glass vial. This vial is filled with distilled water and then a known size of polystyrene sphere solution - (53.5 ± 2)nm in radius - is added via a single drop. The exact concentration of the polystyrene spheres in this test solution is not known. This vial is capped off to avoid spillage, mixed with the thermolyne, and wiped of fingerprints. This step is crucial to avoid bad data as fingerprints could cause the laser light to be obstructed and throw off intensity measurements. The sample is placed into the test chamber, and then the test chamber is covered from above to avoid stray light.

The laser is mounted on a metal guide rail which is used to stabilize the beam path. A small aperture on the side of the test chamber allows the beam to enter, pass through our sample and scatter off of it. The scattered light goes off in many directions, but our PMT was fixed at 90^o. To help protect the PMT from accidents, there is a filter placed in front of it that allows only a fraction of the total light hitting it to pass through. After that filter is another filter which only allowed 633 nm light through. The positioning of all the instruments are shown in Fig 3.

The last step was to pump the Decahydronaphthalene with a BIC BI-FC 1070 pump so that the possibilities of air bubbles in solution were low. These could change the direction of light and could potentially throw off intensity measurements. After the pump ran for 15 minutes, it was turned off, and the trail was ready to be ran. This was done with the program BIC Dynamic Light Scattering software which read and graphed the intensity as kilocounts of photons per period - 100ms. The data collection device took two constant minutes of data.

To up the concentration, the instruments were all turned off. The PMT was protected from light by closing its filter to allow no light through. The vial was pulled out of the test chamber and cleaned. Another drop of polystyrene sphere solution was added and remixed with

---

[3] This is a very difficult average to explain in a meaningful way shortly. Should one want to learn more about this special type of averaging for stochastic processes I recommend Prof. Gabriel Popescu's Spring 2018 class ECE 564 Modern Light Microscopy. [1]

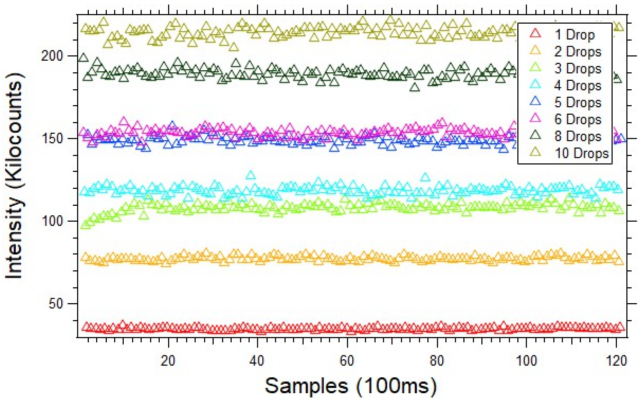

FIG. 4: The seemingly random data is plotted for all trails. As concentration increases so does the kilo counts per sample which makes sense.

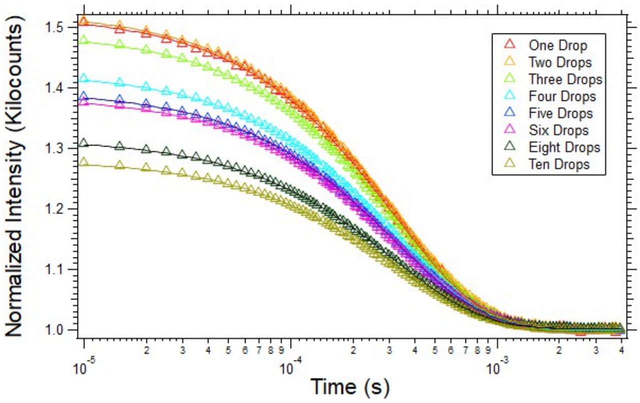

FIG. 5: A semi-log plot of the normalized intensity vs. Time for all the trails. The exponential fits are lines while data points are hollow triangles.

thermolyne. All the previous steps were repeated until ten drops were added to the vial, a 10x concentration increase.

RESULTS & ANALYSIS

The seemingly random data was taken and was then autocorrelated. Show in Fig. 4 is the untouched data, but after autocorrelation, we see a large change, see Fig. 5. What may not be intuitive is that the spread of a data set in Fig. 4 weighs more to its normalization than the total counts. See Fig. 5 for how one and two drops follow the same path, and in Fig. 4 they have the same spread but different counts.

We can now fit exponentials to each of the concentration runs. Using the results from this fit and Eq. (4) we can form Table I which shows the experimental value, the known value of the polystyrene spheres - (53.5 ± 2) nm, and the percent difference.

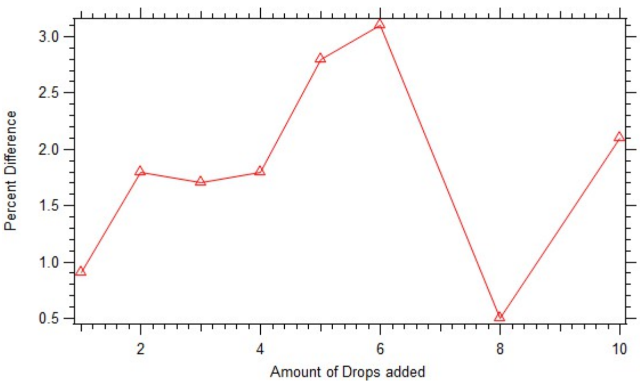

FIG. 6: A simple look to see how as concentration changes so does the error. The theory put forward does not take into account multiple scattering

TABLE I: Tabulation of the individual data points and their values for Fig. 6

Drops	Measured (nm)	Expected	Percent difference
1	54.0	53.5 ± 2 nm	0.9
2	54.5		1.8
3	54.4		1.7
4	54.5		1.8
5	55.0		2.8
6	55.2		3.1
8	53.8		0.5
10	54.6		2.1

The measurements are low and all well within the one standard deviation - deviation. The error from the percent difference can also be graphed to see how error increases with concentration, see Fig. 6. This is not as rigorous as the rest of the experiment however due to the definition of a drop, which is a very imprecise way to describe a volume. This should provide a general idea of a trend should it be better tested in the future.

A unique measurement was taken at eight drops. This measurement breaks the previous upwards trend dramatically. This could be explained by a complete theory or could be random variance as at these small error differences dust in solution can make a difference.

The mechanism that is causing this inflation of error is most likely multiple scatterings off of each other particle. As concentration rises the chance that a scattered beam of light will hit another particle increases. The current theory does not account for this self-scattering and would need to be corrected to test concentration's effect.

CONCLUSION

PCS can offer an excellent idea of the size of a solute in a solvent on some conditions. Concentration has a substantial effect on PCS but at low concentrations can be ignored. Scaling of the theory is needed to include cases of self-scattering between particles. For the cases tested in this experiment the maximum percent error seen was 3.1% and the lowest was 0.5%. The average error was 1.8%. This is an excellent approximation considering the time needed for sample prep which was around one minute. Testing took another 17 minutes, but this was time in which other work could be done, and so a solution for testing product in an industry setting this does well.

[1] Gabriel Popescu, *ECE 564 Modern Light Microscopy*, http://light.ece.illinois.edu/ECE564/ (2018).

[2] HORIBA, *Dynamic Light Scattering* http://www.horiba.com/scientific/products/particle-characterization/technology/dynamic-light-scattering/, (2018).

[3] Malvern Instruments, *Dynamic Light Scattering: An Introduction in 30 Minutes* (2018).