Determining Sizes of Suspended Microspheres Using Dynamic Light Scattering

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March 2022

Abstract

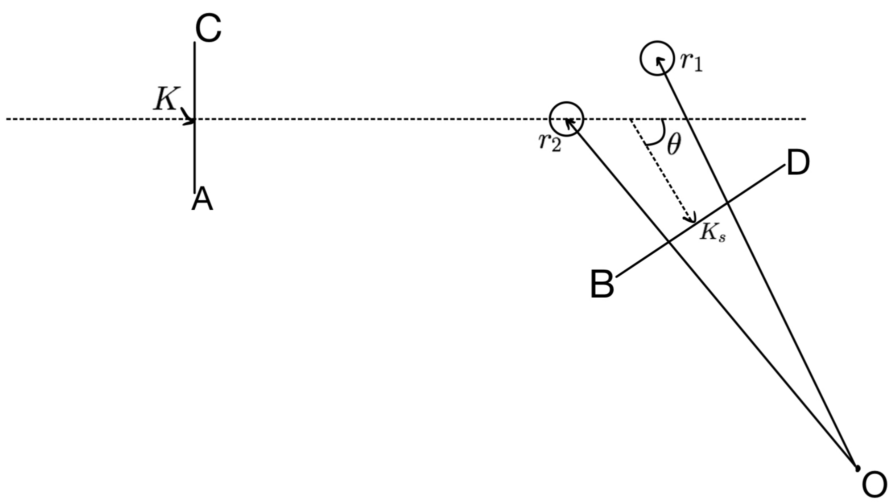
We report a technique for determining the size of microspheres suspended in a liquid sample by measuring fluctuations in the intensity of laser light scattered off the sample and applying a model for light scattering by a statistical medium. Using this technique on a sample of latex microspheres in water, we found the size of these microspheres to be 181.2 $\pm$ 1.8 nm, which agrees approximately with the manufacturer's specifications (1.9σ).

1 Introduction

Microscopic particles in a liquid medium experience a random motion caused by impingement of molecules of the medium. To study this Brownian motion, we investigate its consequence on how light scatters off of the microscopic particles, and demonstrate how studying time dependence of the scattered light intensity can determine the physical size of these microspheres.

First, consider how light scatters off of a single pair of spheres, seen in figure 1.

Figure 1:



An observer sensitive to light intensity, a photomultiplier tube (PMT), is located at an origin distant from the two particles. The amplitude of the light that reaches the PMT depends on the amplitude of the incident light E_0, the amplitude of the light scattered in the θ direction by each sphere $f(\theta)$, and the relative phase of the light when incident on each sphere. The incident light, with wavevector $\mathbf{k}$ and plane wave front AC, is scattered by particles at $\mathbf{r}_1$ and $\mathbf{r}_2$ through angle θ. The plane wave front BD is focused on the PMT, with wavevector $\mathbf{k}_s$.

The wave incident on particles $i = 1, 2$ at time t is

$$E = E_0 \cos (\omega t - \mathbf{k} \cdot \mathbf{r}_i) \tag{1}$$

The light striking the PMT at time t then accumulates an additional phase $\mathbf{k}_s \cdot \mathbf{r}_i$ in travelling the additional distance $\mathbf{r}_i$. This obtains a total amplitude of the light striking the detector

$$e = f(\theta)E_0 \sum_{i=1}^{2} \cos\left(\omega t - (\mathbf{k} - \mathbf{k}_s) \cdot \mathbf{r}_i\right) \tag{2}$$

The PMT power output is proportional to the time average of this amplitude over many optical periods, which evaluates to

$$I_{out} \propto \langle e^2 \rangle = |f^2(\theta)| E_0^2 \left[1 + \cos\left(\Delta\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)\right)\right] \tag{3}$$

where $\Delta\mathbf{k} = \mathbf{k} - \mathbf{k}_s$ is the difference between the incident and scattered wave vectors. By a simple geometric argument, this difference can also be written in terms of the scattering angle,

$$\Delta\mathbf{k} = (4\pi/\lambda)\sin(\theta/2) \tag{4}$$

Notice that equation (3) depends on the relative distance between particles 1 and 2. As the particles move randomly through their medium, the PMT power output will fluctuate in response. If the spheres produce a maximum in the scattered intensity at one time, we can assume that the following decay in intensity is exponential (as a more careful derivation that extends to $N- > \infty$ particles would reveal), with correlation time τ_c defined so that the intensity decays like

$$I(t) \propto e^{-t/\tau_c} \tag{5}$$

up to a constant background of noise.

We choose to identify τ_c by how long it takes the phase factor in (3) to change by one radian. In particular, this is the time necessary for the spheres to change their relative distance by

$$|\mathbf{r}_1 - \mathbf{r}_2| = 1/\Delta\mathbf{k} = \lambda/4\pi\sin(\theta/2) \tag{6}$$

The Brownian motion of the spheres can be modelled by the random walk problem. Properties of the particles and the medium they move in become absorbed into and described by a diffusion constant D, defined such that the mean square displacement after time t is given by $\langle x^2 \rangle = 2Dt$. Relating this to equation (6) by squaring that displacement allows us to determine a correlation time that's given in terms of a diffusion constant as

$$\tau_c = 1/(2D\Delta\mathbf{k}^2) = \frac{\lambda^2}{32\pi^2\sin^2(\theta/2)D} \tag{7}$$

We finish by making use of the Stokes-Einstein relation to relate D to the geometry of the particles and the properties of the fluid. For the turbulence-free diffusion of spherical particles through a liquid, the diffusion constant is given by

$$D = \frac{K_bT}{3\pi\eta d} \tag{8}$$

where k_b is Boltzmann's constant, η is the fluid viscosity, and d is the diameter of the microspheres. Now, comparison with equation (7) gives a connection between the geometry of the microspheres, their motion through their medium, and the response of scattered light intensity to their relative configurations, by the unified equation

$$d = \frac{32\pi n^2}{3\lambda^2\eta}\sin^2(\theta/2)K_bT\tau_c \tag{9}$$

remembering that the laser wavelength λ in air must be corrected by the index of refraction of water, $n = 4/3$.

Now we have achieved a method for determining the size of particles suspended in water. By looking for large spikes in received intensity, recording the intensity decay that immediately follows, and averaging over the results of sufficiently many such spikes, we should find exponential behavior from which we can extract the correlation time for a given scattering angle. The diameter of the particles then follows immediately from known properties of the solution, the scattering angle, and temperature (which is effectively constant and in equilibrium with the surrounding environment).

Section 2 will describe our apparatus and procedures for studying the fluctuations of scattered light intensities, in two parts; Section 2.1 will describe the apparatus and the procedures for acquiring data from this equipment, section 2.2 will describe the procedures for extracting our microsphere sizes from the data. Section 3 will present the information obtained from the time dependence of all observed fluctuations, and section 4 will conclude by reporting one value for the size of our suspended microspheres and the validity of this model for dynamic light scattering.

2 Procedures

2.1 Apparatus

Figure 2: A simplified diagram of the experimental setup.

Figure 2 provides a block diagram of the experimental setup. A He-Ne laser provides a monochromatic and steady beam of red light, with wavelength 632.8 nm. The incident laser beam is focused onto the sample, a cylindrical glass vial containing a suspension of latex microspheres in water. This vial is at the center of rotation of the detector rail. The detector rail and its light sensitive equipment is mounted on a goniometer, and can be rotated and locked to angles in a range of $10°$ to $170°$. Fixing an angle on the goniometer is effectively equivalent to fixing a scattering angle for investigation. At the end of the detector rail is a photomultiplier tube (PMT), a device sensitive to light that outputs a voltage proportional to its received intensity $I(t)$.

The PMT then outputs to an amplifier. To minimize leakage of 60Hz line voltage onto the signal, the amplifier is powered by a battery, not by AC. The amplifier in turn outputs into channels 1 and 2 of a digitizing oscilloscope. Channel 2 triggers the scope on the largest voltage fluctuations, and channel 1 averages and records the signals. We then transfer the data to a PC for data analysis.

When the fluctuating voltage crosses some threshold, we observe an exponential decay in the signal immediately following this maximum.

$$\langle V(t)\rangle = V_0 e^{-t/\tau_c} + B \tag{10}$$

This decay physically corresponds to the scattering particles randomly moving out of maximum alignment for the set scattering angle. To observe the exponential decay, the scope's trigger level must be high relative to B such that the signal fluctuation is physical. We set the trigger level by gradually raising the trigger level until the scope only triggers one time per second, a heuristic that we found reliably avoids background fluctuations while still consistently triggering on high signal fluctuations.

2.2 Analysis Procedures

For each angular setting we measure the temperature using a thermometer, record the trigger threshold, and collect a time averaged signal. Figure 3 shows one of these time averaged signals.

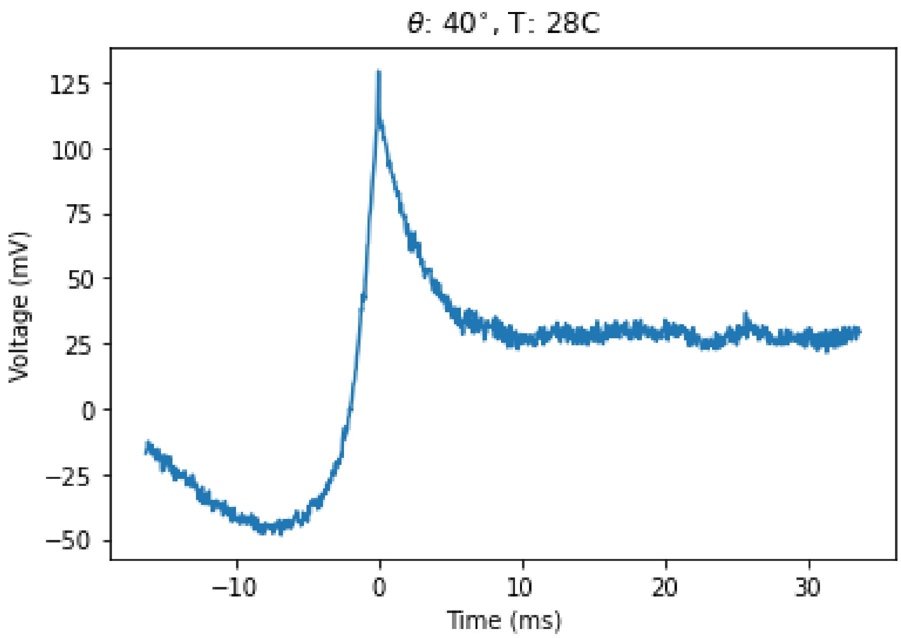


Figure 3: An example data set. Note the buildup to a large peak that decays away exponentially. Only the signals measured after this peak correspond to the physical behavior that equation (9) describes.

To prepare the data sets for analysis, we remove the intensity data measured before the peak, and trim down any large region of flat background toward the end if necessary. To this prepared data set, we fit an exponential function plus background (10), with fit parameters V_0, τ_c, and B, using the Trust Region Reflective algorithm as a nonlinear least squares optimization method. The optimization algorithm is given initial estimates for the fit parameters, and an estimate of the error on the voltage points. We estimated the voltage errors by calculating the standard deviation of the last 200 values, where the curve is flattest and received intensities should only deviate from the background due to random fluctuations and not from the dynamics of the latex spheres. We chose the initial fit parameter estimates by observing the signals and guessing that to within an order of magnitude, the signal peaks at 0.03 Volts above background, the background is 0.02 Volts, and the correlation time is 0.01 seconds. Obtaining τ_c then allows us to calculate particle sizes using equation (9).

3 Results

We collected a total of 22 averaged signals from a range of 10 angles between 20 and 65 degrees, in increments of 5 degrees. Figure 4 demonstrates one of our results of fitting data sets to exponential functions according to equation (10), and extracting the particle size from its correlation time. The goodness of fit, given by a reduced Chi-squared test, is provided, and so is our estimated uncertainty on the voltage values.

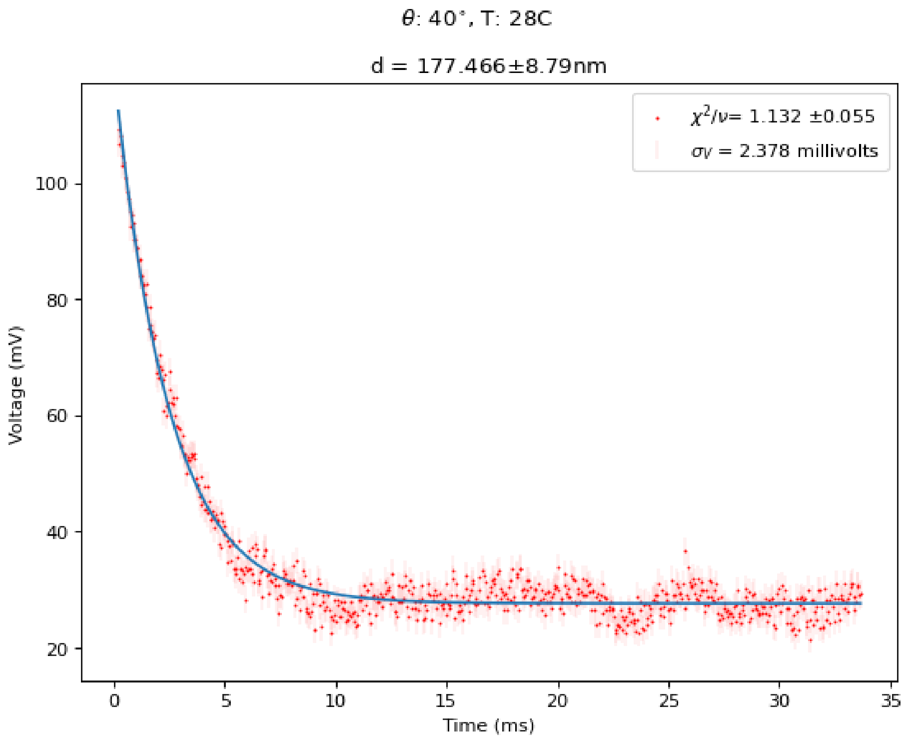


Figure 4: Example of fitted data.

Fitting all of our data sets to exponential functions in the same manner gives the following results for particle sizes, in table 1.

Table 1: Fitted Particle Sizes by Individual Signal

Angle (Degrees)	Size (nm)	Goodness of Fit (χ^2/ν)
$20°$	217.975 ± 22.884	0.558 ± 0.055
$20°$	161.892 ± 16.389	1.0719 ± 0.055
$25°$	186.609 ± 14.912	0.9131 ± 0.055
$25°$	193.300 ± 15.478	1.3793 ± 0.055
$30°$	153.961 ± 10.685	0.6341 ± 0.041
$35°$	195.013 ± 10.990	1.0755 ± 0.055
$35°$	187.443 ± 10.543	2.7358 ± 0.055
$35°$	195.022 ± 11.021	1.0601 ± 0.055
$40°$	177.466 ± 8.790	1.1320 ± 0.055
$40°$	168.453 ± 8.326	1.1585 ± 0.055
$40°$	179.747 ± 8.876	1.4637 ± 0.055
$45°$	190.289 ± 8.355	1.4609 ± 0.055
$45°$	169.189 ± 7.583	1.1052 ± 0.055
$45°$	203.376 ± 9.112	1.0924 ± 0.055
$50°$	241.960 ± 9.691	1.2861 ± 0.055
$50°$	188.644 ± 7.535	1.3270 ± 0.055
$55°$	165.743 ± 6.190	1.4154 ± 0.055
$55°$	175.902 ± 6.463	1.0215 ± 0.055
$60°$	190.689 ± 6.880	0.7879 ± 0.055
$60°$	163.490 ± 5.961	1.0525 ± 0.055
$65°$	182.875 ± 6.762	1.0921 ± 0.055
$65°$	179.693 ± 6.353	0.9527 ± 0.055

Finally, we categorize these results by angle by calculating a weighted mean (and weighted uncertainty) for each set of angles. Figure 5 shows the average particle size determined for each scattering angle.

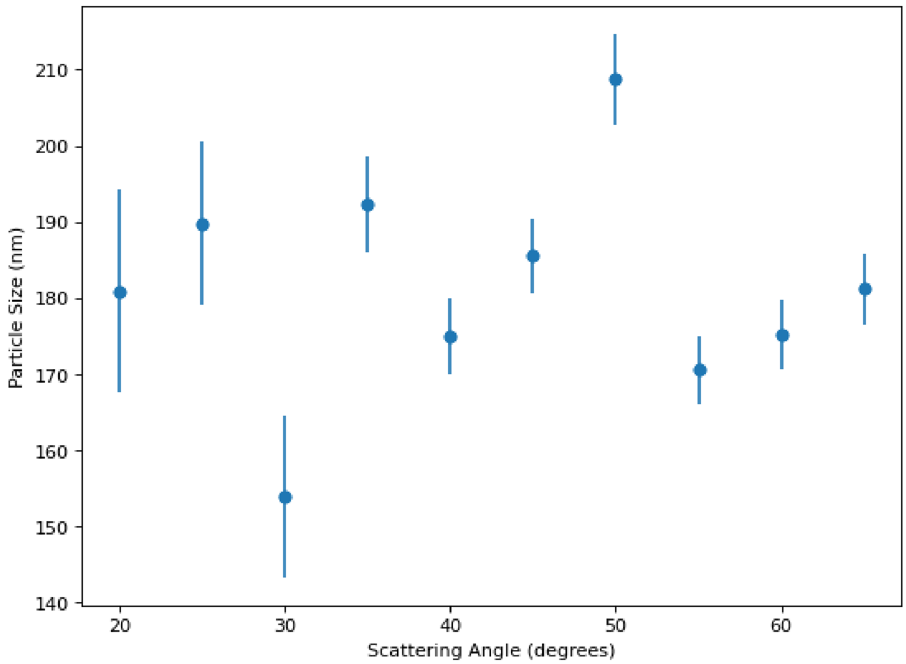


Figure 5: Calculated values of the particle size from scattering at angles between 20 and 65 degrees.

4 Conclusions

The results from figure 3 do not suggest any nontrivial dependence of determined particle size on angle for which measurements are made; the microspheres have one definite size, about which our measurements fluctuate. Taking one final weighted mean of these different sizes, we conclude that the microspheres in this solution have a diameter of 181.2 ± 1.8 nanometers. For comparison, this sample when supplied came with a manufacturer's specification that the microspheres have a diameter of 200 $\pm$ 10 nanometers. Our derived measurement agrees with this specification to within 2 standard deviations. Therefore we conclude that Brownian motion appropriately models microsphere movement through water, and that dynamic light scattering accurately determines the sizes of these suspended particles.

5 References

1) Light Scattering, B. Luokkala