

Measurement of the diameter of polystyrene spheres using photon correlation spectroscopy

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Photon correlation spectroscopy (PCS) is used to determine the diameter of spherical polystyrene (standard value $d = 96 \pm 3.1\text{nm}$) in water. Assuming the sample exhibits Brownian motion and is dilute, an autocorrelation function of the intensity is used to measure the diffusion constant, which contains information about the polystyrene radii. Direct analysis through Brookhaven Instruments' software determines that the molecules have a diameter $d = 108.6 \pm 4.5\text{nm}$, which is within two standard deviations of the accepted value. Independent verification of this through other software determines the molecules to have diameters $d = 102 \pm 1.6\text{nm}$, which is also within two standard deviations of the accepted value.

INTRODUCTION & THEORY

Photon correlation spectroscopy (PCS) is a technique that utilizes the principles of Rayleigh scattering [1] to determine information about the particles within a scattering volume. Light waves strike molecules and as a result, electric field of the light induces an oscillating polarization of the electrons in the molecules [1]. The force of these induced polarizations accelerates the electrons, which re-radiate the light. Because of their motion, the measured intensity of scattered light from the particles will fluctuate in time. Information about the shape, size, motion and rates of reactions [1] can be determined.

The purpose of this experiment was to confirm the diameter of standard $d = 96 \pm 3.1\text{nm}$ spherical polystyrene molecules in a water suspension. We assumed that the suspension was dilute, that the molecules were exhibiting Brownian motion, and that the particles were uniformly dispersed in the solution and that they did not interact with each other.

An incident monochromatic electromagnetic beam can induce a dipole moment $\vec{\mu}$ in a single molecule which has an anisotropic polarizability described by the polarizability tensor $\vec{\alpha}$. The dipole moment varies in time like [1]

$$\vec{\mu}(t) = \vec{\alpha} \cdot \vec{E}(t). \quad (1)$$

This time-variant dipole moment will emit electromagnetic radiation that can be measured experimentally. The light beam has an electric field that can be described by the general form

$$\vec{E}_i(\vec{r}, t) = \vec{n}_i E_0 \exp \left[i \left(\vec{k}_i \cdot \vec{r} - \omega_i t \right) \right], \quad (2)$$

where \vec{n}_i is a unit vector in the direction of the electric field, E_0 is the magnitude of the electric field, \vec{k}_i is the propagation vector and ω_i is the angular frequency. This wave is assumed to be planar by the time it reaches the scattering medium, and impinges upon a medium with a local dielectric constant

$$\vec{\epsilon}(\mathbf{r}, t) = \epsilon_0 \vec{I} + \delta\vec{\epsilon}(\vec{r}, t), \quad (3)$$

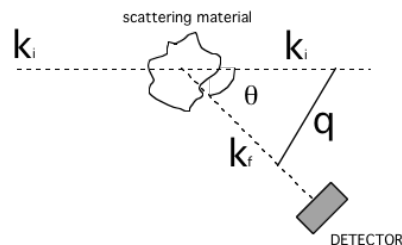


FIG. 1: The basic scattering geometry, where light travels toward the material with propagation vector \vec{k}_i , and scatters off with propagation vector \vec{k}_f .

where $\delta\vec{\epsilon}(\mathbf{r}, t)$ is the dielectric constant fluctuation tensor at a point \vec{r} and time t , and \vec{I} is the second-rank unit tensor [1]. The scattering vector \vec{q} is the difference between the vectors \vec{k}_i and \vec{k}_f as shown in Fig. 1, whose magnitudes are $2\pi n/\lambda_i$ and $2\pi n/\lambda_f$, respectively. It is usually the case that [1]

$$|\vec{k}_i| \cong |\vec{k}_f|, \quad (4)$$

which allows us to find an expression for the magnitude of \vec{q} :

$$q = 2k_i \sin \frac{\theta}{2} = \frac{4\pi n}{\lambda_i} \sin \frac{\theta}{2}. \quad (5)$$

This is the Bragg condition [1] which “specifies the wave vector component of the dielectric constant fluctuation that will give rise to scattering at an angle θ ”.

Two of the primary methods used in light scattering techniques are the homodyne and heterodyne methods. The homodyne method directly detects scattered light in a photomultiplier tube, then sends the information through an autocorrelator or spectrum analyzer. The heterodyne method detects un-scattered light and scattered light simultaneously in a photomultiplier, then sends the information to an autocorrelator or spectrum analyzer. The quantities measured in these scattering techniques are the time-correlation functions of either

the scattered electric field or intensity. The intensity I is defined to be the square of the electric field such that $I_0 \equiv |E_0^2|$. For heterodyne and homodyne detection, we define the spectral intensity self-correlation functions to be, respectively:

$$I_1(\tau) \equiv \langle E_0^*(t)E_s(t+\tau) \rangle \quad (6)$$

$$I_2(\tau) \equiv \langle |E_s^*(t)|^2 |E_s(t+\tau)|^2 \rangle, \quad (7)$$

where $E_s^*(t)$ is the complex conjugate of $E_s(t)$ and the correlation function looks at the electric field at time t and a later time $t + \tau$. The two intensity correlation functions are related by

$$I_2(\tau) = |I_1(t)|^2 + |I_1(t+\tau)|^2. \quad (8)$$

Brownian motion

If a molecule was observed for a time τ , the path would be seemingly random because of collisions. Over time, the total displacement would be $\Delta\vec{R}(\tau)$. Assuming this displacement distribution can be modeled as a random walk, the probability that a particle would be displaced within the scattering volume d^3R is the Gaussian distribution function [1]

$$G_s = \left[\frac{2\pi}{3} \langle \Delta\vec{R}^2(\tau) \rangle \right]^{-3/2} \exp[-3R^2/2\langle \Delta R^2(\tau) \rangle], \quad (9)$$

where $\langle \Delta R^2(\tau) \rangle$ is the mean-square displacement of the particle in time τ . It is convenient to create an intermediate scattering function that is dependent upon the scattering vector \vec{q} , so the spatial Fourier transform is performed on the Gaussian distribution function and gives [1]

$$F_s(\vec{q}, \tau) = \exp[-q^2 \langle \Delta R^2(\tau) \rangle / 6]. \quad (10)$$

For a diffusing particle [1], $\langle \Delta\vec{R}^2(\tau) \rangle = 6D\tau$, where D is the self-diffusion coefficient whose value, according to the Einstein relation, is

$$D = \frac{k_B T}{6\pi\eta a}. \quad (11)$$

By multiplying Eq. 10 by the number of particles inside the scattering volume, the number-density self-correlation function for heterodyne scattering is found to be

$$F_1(\vec{q}, \tau) = \langle N \rangle \exp[-q^2 D \tau]. \quad (12)$$

The self-correlation function for heterodyne scattering F_1 is proportional to the spectral density correlation function I_1 by the relation

$$I_1(\tau) = (\vec{n}_i \cdot \vec{n}_f)^2 \alpha^2 F_1(\vec{q}, \tau), \quad (13)$$

where α is the magnitude of the molecular polarizability tensor $\vec{\alpha}$ along \vec{n}_i and \vec{n}_f .

Spectral and numerical density functions

From Eqs. 13 and 8, we can state that the homodyne spectral density correlation I_2 is proportional to

$$I_2(\tau) = \langle N \rangle^2 + \langle N \rangle^2 \exp(-2Dq^2\tau), \quad (14)$$

where

$$Dq^2 = \frac{1}{a} \frac{8k_b T \pi n^2}{3\lambda^2 \eta} \sin^2 \frac{\theta}{2}, \quad (15)$$

where n is the refractive index of the scattering particles. The radius of the particles a can be calculated from the slope of a linear plot between Dq^2 and $\sin^2 \theta/2$.

EXPERIMENT

A suspension of polystyrene was created for this experiment. One drop of concentrated polystyrene spheres in water was dropped into a vial containing about 20mL of distilled water inside a glass vial (index of refraction $n = 1.5$), which was placed into the goniometer, where it was in contact with an index-matched decahydronaphthalene solution. This was temperature controlled by a circulating water bath using the Brinkman RM6 water heater, set to 25°C. The decahydronaphthalene was not sealed in a container, so it was necessary to filter it through a Brookhaven Instruments filtering unit. The filtering process eliminated any large dust particles that could have affected the scattered light measurement.

A Brookhaven Instruments 900AT digital correlator fed information directly into a computer, a process which was controlled by Brookhaven Instruments' Dynamic Light Scattering Software. The software automatically determined the size of the polystyrene particles based upon a few experimental parameters: the viscosity of the solvent $\eta = 1.002$ cP, the refractive index of the particles $n = 1.59$, and the wavelength of light $\lambda = 632.8$ nm. The values τ and I_1 were saved for some of the experiments, and were imported into Igor Pro. The correlation function I_1 was plotted as a function of the time displacement τ in a log-log plot, and an exponential function of the form

$$A + B \exp[-2Dq^2\tau] \quad (16)$$

was fit to the data. Each set of data represents a two minute sampling time where the digital correlator would measure the light intensity every 5 μ sec. Four data runs were taken, with the scattering angle ranging from 50 to 110 degrees in 20 degree intervals.

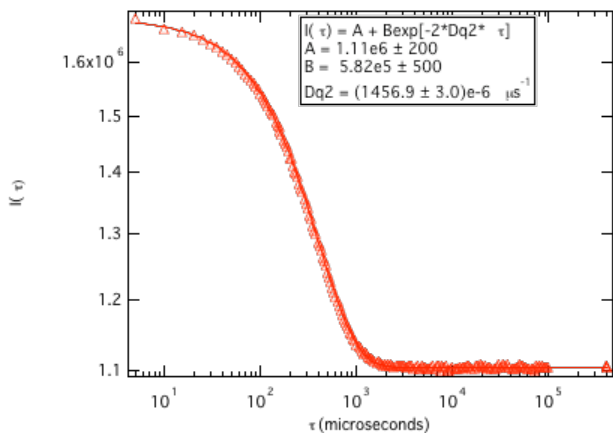


FIG. 2: A log-log plot of the correlation function taken from an experiment with temperature $T = 293\text{K}$ and scattering angle 90° . This data is well fit by a decaying exponential function, whose values are shown in the legend.

RESULTS AND ANALYSIS

The data was fit to Eq. 16, and the calculated values for Dq^2 were set equal to the expanded form

$$Dq^2 = \frac{16\pi k_B T n^2}{6\eta \lambda^2 r} \sin^2 \frac{\theta}{2} \quad (17)$$

and solved for r , the radius of the spherical molecules. Figure 2 shows data taken from a two minute sampling time, where $T = 273\text{K}$ and $\theta = 90^\circ$.

The value of Dq^2 for this sample is $(1456.9 \pm 3.0) \times 10^{-6}(\text{time})^{-1}$. It is necessary that the value be in terms of seconds. A simple change in units shows

$$Dq^2 = 1456.9 \times 10^{-6} \frac{\text{time}}{1 \mu\text{sec}} \times \frac{10^6 \mu\text{sec}}{\text{sec}} = 1457 \text{ sec}^{-1}. \quad (18)$$

The radius for each molecule is then

$$r = \frac{16\pi k_B T n^2}{6\eta \lambda^2 (Dq^2)} \sin^2 \frac{\theta}{2} \quad (19)$$

$$= 51\text{nm}. \quad (20)$$

The calculated diameter of the polystyrene spheres is $d = 102 \pm 1.6\text{nm}$. This is within two standard deviations of the standard value of the diameter, $d = 96 \pm 3.1\text{nm}$. The Brookhaven software calculated the diameter of the polystyrene spheres to be $d = 108.6 \pm 4.5\text{nm}$, which is also within two standard deviations of the supplier's standard value $d = 96 \pm 3.1\text{nm}$.

DISCUSSION AND CONCLUSION

This experiment successfully validated the theoretical predictions for finding the diameter of spherical particles with the photon correlation spectroscopy technique. The calculated value for the diameter of standard $d = 96 \pm 3.1\text{nm}$ spheres was $d = 102 \pm 1.6\text{nm}$, which is within two standard deviations of the accepted value. The Brookhaven software determined the size of the molecules to be $d = 108.6 \pm 4.5\text{nm}$, which is within two standard deviations of the accepted value.

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