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Characterizing Nanoparticle Size by Dynamic Light Scattering

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Running title: Characterizing Nanoparticle Size by Dynamic Light Scattering

Abstract

The Dynamic Light Scattering (DLS) Technique was used to determine the size, shape and diffusion coefficient of rod-like nanoparticles. The intensity auto-correlation functions of light scattered by particles in a solution were measured and analyzed to obtain the relaxation rates for decay of intensity correlations. These decay rates are related to the diffusion coefficients pertaining to the motion of the particle. In the case of nanorods, there are two types of motion - translational and rotational. By disentangling the relaxation rates, corresponding to these two types of motion, the shape and size of nanoparticles were characterized. These experiments, though limited in scope, demonstrate the promise of dynamical light scattering as an inexpensive and convenient technique for characterizing regular shaped nanoparticles in a fluid medium as well as the capability of DLS to distinguish nanoparticle shapes with smaller aspect ratios.

Introduction

Nanoparticles have a wide range of applications including those in the fields of cell and molecular biology, biomedical engineering, and electronic devices. Many properties of nanoparticles change with their size and shape. There are several techniques for measuring the particle size and shape, some of which are relatively expensive and not user friendly. Here we explore Dynamic Light Scattering Technique (DLS) (Chu 1991) as a relatively inexpensive and convenient technique for determining nanoparticle size and shape in a fluid medium. We compare and contrast it with other techniques to establish its advantages and limitations relative to them. In this research we measured the size and shape of three different rod-like nanoparticle samples using DLS. Two of the samples consisted of bare gold nanorods of different sizes and the third one of nanorods of gold copper alloy

(AuCu$_3$). A polystyrene nanosphere sample was used to calibrate the apparatus.

Theory

The theoretical models for light scattering by both nanosphere and nanorod particles are based on their polarizability tensor and its relation to scattered light intensity and polarization (Berne and Pecora 1976). In the case of nanospheres, only the translational motion contributes to the diffusion of nanoparticles. So the intensity of the scattered light is only related to translational diffusion. On the other hand, if the particle is a nanorod, both translational and rotational motion due to its anisotropic shape (different diameter and length) contribute to light scattering. The diffusion is then related to both translational and rotational motions and the model for light scattered by a nanorod particle involves its full polarizability tensor.
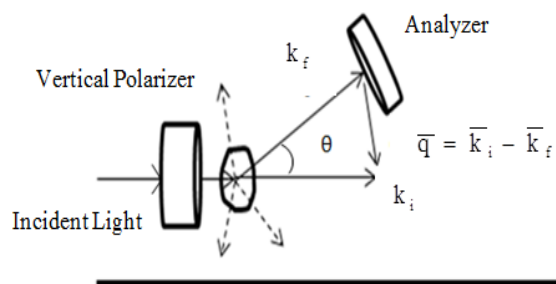
Figure 1: Light scattering geometry for a particle to be analyzed

To show the essentials of a theoretical model for diffusion of a nanorod, we consider a laser light beam illuminating a particle in a solution as shown in Figure 1. The electric field of the incident light is written as

$$\mathbf{E_i}(r,t) = \mathbf{n_i} E_o \exp i(\mathbf{k_i} \cdot \mathbf{r} - \omega_i t), \qquad (1)$$

where $\mathbf{n_i}$ is the polarization of the incident light wave, E_o is the amplitude of the electric field, $\mathbf{k_i}$ is the wave

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vector in the direction of propagation of incident light wave and ω_i is its angular frequency. The time and position dependent scattered electric field is then given by (Chu 1991)

$$E_s\left(R,t\right)=\frac{-k_f^2 A_o}{4\pi R\varepsilon_o}\exp i\left(k_f R-\omega_i t\right)\left[\mathbf{n_f}.\left(\delta\alpha_{if}\left(\mathbf{q},t\right).\mathbf{n_i}\right)\right]$$

(2)

where A_o the amplitude of the scattered electric field, $\mathbf{q}=\mathbf{k_i}-\mathbf{k_f}$ is the wave vector difference between incident and scattering wave vectors, which is also called the momentum transfer wave vector. The term $\mathbf{n_f}.\left(\delta\alpha_{if}\left(\mathbf{q},t\right).\mathbf{n_i}\right)$ is the component of the molecular polarizability tensor in the direction of the initial polarization $\mathbf{n_i}$ and the final polarization $\mathbf{n_f}$. This component is denoted by $\delta\alpha_{if}(\mathbf{q},t)$.

The spectral density of scattered light can be measured from the scattered electric field through its time correlation function which is proportional to the polarizability fluctuations. The Fourier spectral density of the scattered field is proportional to

$$\mathbf{I}_{if}^{\alpha}\left(\mathbf{q},\omega\right)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}dt\exp i\left(\omega_f t-\omega_i t\right)\mathbf{I}_{if}^{\alpha}\left(\mathbf{q},t\right)$$

(3)

where $\mathbf{I}_{if}^{\alpha}\left(\mathbf{q},t\right)=\left\langle\delta\alpha_{if}^*\left(\mathbf{q},0\right)\delta\alpha_{if}\left(\mathbf{q},t\right)\right\rangle$,

$$\delta\alpha_{if}\left(\mathbf{q},t\right)=\sum_{j=1}^{N}\alpha_{if}^j\left(t\right)\exp\left(i\mathbf{q}.\mathbf{r}(t)\right),$$

and N is the total number of particles illuminated by laser light.

If both incident light and scattered light are vertically polarized, the scattered light spectral density or autocorrelation in term of polarizability tensor depends on the molecular polarizability α_{zz}^j. On the other hand if incident light is vertically polarized and scattered light is horizontally polarized, the scattered light spectral density depends on molecular polarizability component α_{yz}^j. These two scattered light spectral density equations are given below:

$$I_{VV}^{\alpha}\left(\mathbf{q},t\right)=\left\langle N\right\rangle\left\langle\alpha_{zz}^j\left(t\right).\alpha_{zz}^j\left(0\right)\right\rangle\mathbf{F}_s\left(\mathbf{q},t\right)$$

(4)

$$I_{VH}^{\alpha}\left(\mathbf{q},t\right)=\left\langle N\right\rangle\left\langle\alpha_{yz}^j\left(t\right).\alpha_{yz}^j\left(0\right)\right\rangle\mathbf{F}_s\left(\mathbf{q},t\right)$$

(5)

where $F_s\left(\mathbf{q},t\right)=\exp\left(-q^2 D\right)$ and D is the diffusion coefficient (Einstein 1926).

In the molecule-fixed coordinate system, the above equations can be expressed in terms of second order spherical harmonics. After rotational diffusion analysis these autocorrelation functions can be finally expressed in terms of translational (Γ_{tr}) and rotational relaxation (Γ_{rot}) rates (Glidden and Muschol 2012) which are related to the corresponding diffusion coefficients D_{tr} and D_{rot} via

$$I_{VV}^{\alpha}\left(\mathbf{q},t\right)=A\exp\left(-\Gamma_{tr}t\right)+B\exp\left[-(\Gamma_{tr}+\Gamma_{rot})t\right],$$

(6)

$$I_{VH}^{\alpha}\left(\mathbf{q},t\right)=C\exp\left[-(\Gamma_{tr}+\Gamma_{rot})t\right],$$

(7)

where $A=\left\langle N\right\rangle\alpha^2$, $B=\left\langle N\right\rangle\left(\frac{4}{45}\right)\beta^2$ $C=\left\langle N\right\rangle\left(\frac{1}{15}\right)\beta^2$,

$\Gamma_{tr}=q^2 D_{tr}$, $\Gamma_{rot}=-6D_{rot}$ and α, β are the isotropic and anisotropic parts of the polarizability tensor, respectively.

The relation between translational diffusion coefficient and length of the nanorod is (Glidden and Muschol 2012)

$$D_{tr}=\frac{k_B T}{3\pi\eta L}F\left(AR\right),$$

(8)

where F(AR) is a model dependent function of the aspect ratio (AR)

$$F\left(AR\right)=\ln\left(AR\right)+0.312+\frac{0.565}{AR}-\frac{0.1}{AR^2}.$$

(9)

Another relation for length of the nanorod and rotational diffusion coefficient is

$$D_{rot}=\frac{3k_B T}{\pi\eta L^3}G\left(AR\right),$$

(10)

where G (AR) is another model dependent function of the aspect ratio

$$G\left(AR\right)=\ln\left(AR\right)-0.662+\frac{0.917}{AR}-\frac{0.05}{AR^2}.$$

(11)

By combining these two equations, the length of nanorods can be expressed in terms of translational and rotational relaxation rate,

$$L=\frac{1}{q}\sqrt{54\frac{\Gamma_{tr}}{\Gamma_{rot}}H(AR)}$$

(12)

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where H(AR)= G(AR)/F(AR). The value of H(AR) is approximately 0.5 for our experiment. To determine the aspect ratio of the nanorod, the length, obtained from Eq. (12) is used in the model-dependent aspect ratio function.

Method

The main part of the experimental set up is a scattering chamber mounted on a goniometer (BI-200SM) shown in Figure 2. A collimated and vertically polarized He:Ne laser beam is focused into the center of the scattering chamber that holds the scattering sample. Light scattered at 90 degrees to the direction of incident light is collected and guided to a photomultiplier tube (PMT). The output from the photomultiplier is used to measure the two-time intensity auto-correlation function of the scattered light. The analysis of the measured correlation function is carried out by the light scattering software included with the DLS instrument (Brookhaven BI-9000AT digital correlator with 9KDLSW software). A temperature controller is also included in the set up to record measurements at different temperatures by changing the sample temperature, if desired. The sample holder test tube was cleaned with isopropyl alcohol, acetone and de-ionized water. As the particles to be measured were in the nanometer range, the solvent medium was filtered by 20 nm syringe filters.
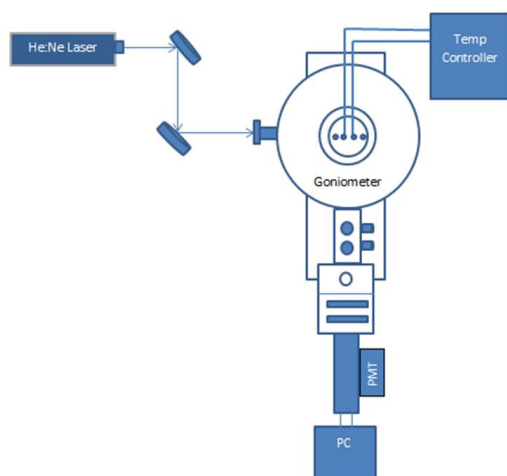

Figure 2: An outline of the experimental setup. Vertically polarized light from a laser is focused into a sample cell at the center of the goniometer. Light scattered at 90 degrees from forward direction is detected by a photomultiplier tube.

Results

The size of nanorods and nanospheres was determined by analyzing the measured correlation functions using the software package that came with the correlator. The software allows several different approaches to analyzing the data to determine particle size and shape. The cumulant data fitting method was used for nanospheres. In the case of nanorods, a double exponential fit was used to separate translational and rotational diffusion constants as these two types of motion are governed by different relaxations rates. This was reflected in the auto-correlation function of the scattered light. By using these relaxation rates and scattering wave vector, the length and diameter of the nanorods were determined using Eqs. (8) - (12).

Both polarized (VV) and depolarized (VH) light experiments were carried out for the three samples labeled as 001, RPD700D and RPD235AD. The polarized scattered light was used to obtain the size through translational and mixed relaxation rates. The mixed relaxation rate was also independently confirmed by depolarized light scattering measurements.
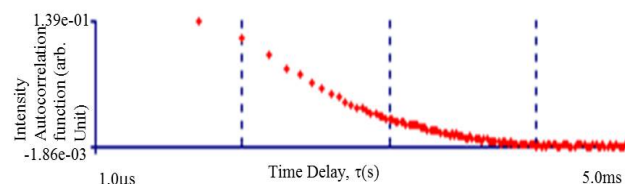

Figure 3: Autocorrelation function of vertically polarized light (VV) experiment for sample RPD235AD

The first experiment was with vertically polarized scattered light (VV). A typical experimentally measured autocorrelation for sample RPD235 is shown in Figure 3. A double exponential fitting of the measured auto-correlation function gave the relaxation rate vs relaxation rate intensity graph is sown in Fig. 4. The measured translational relaxation rate was 2.3 kHz and mixed relaxation rate was 31 kHz. The rotational relaxation rate is the (positive) difference between mixed and translational relaxation rates. So the calculated rotational relaxation rate was 28.8 kHz.

In the depolarized scattered light (VH) experiment, the relaxation rate extracted from the measurements was 29.2 KHz which was in reasonable agreement with that derived from the measurements of mixed relaxation rates in polarized light (VV) experiment. A

typical intensity auto-correlations function of this experiment is shown in Figure 5.
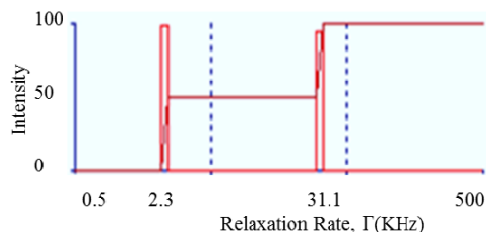

Figure 4: Relaxation rate intensity (weight) vs relaxation rate graph for sample RPD235AD
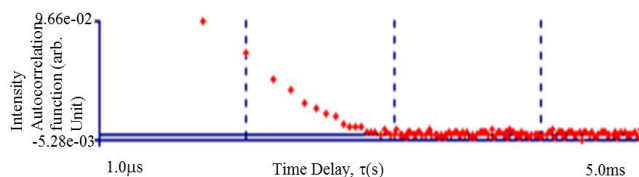

Figure 5: Typical autocorrelation function of depolarized light (VH) for sample RPD235AD

The scattering angle of the experiment was 90 degrees, refractive index of solvent (toluene) is 1.496 and incident laser light wavelength was 633nm. The calculated scattering wave vector was

$$q = \frac{4\pi\eta}{\lambda}\sin\left(\frac{\theta}{2}\right) = \frac{4 \times 3.14 \times 1.496}{633nm}\sin\left(\frac{90}{2}\right) = 0.021 / nm$$

Finally, by using equation (12), the calculated length, L of the nanorod was 93.3nm. The aspect ratio found from the equation (10) was 4.4 which gave the diameter of the nanorod to be 21.2 nm. In this way two others sample were also characterized. Table 1 shows a comparison of length and diameter determined by dynamic light scattering technique with those obtained from transmission electron microscopy (TEM). The TEM image of sample 001 was supplied by the manufacturer (Chen et al. 2013) and the TEM images of other two samples were taken at the University of Arkansas Nanoscience Center. In the case of sample RPD007 and RPD235AD, the DLS experiment was repeated 25 times which allowed us to extract average length and diameter along with standard deviations. On the other hand, due to limited amount of sample 001,

the experiment could be repeated only thrice from which only average length and diameter were obtained.

Discussion

The purpose of this research was to explore the viability of dynamic light scattering technique for determining nanorod size and shape in a fluid medium. We demonstrated the viability of the technique by successfully measuring three nanorod samples. In the case of sample RPD235AD both polarized and depolarized scattered light were intense enough to allow measurement of nanorod size and shape. For the other two smaller size samples, polarized and depolarized scattered light intensities were low because light scattering is directly proportional to the ratio of the fourth power of particle size to wavelength ratio. The particle size determination of these two samples could still be done by polarized scattered light (VV). However, the depolarized scattered light intensity was even smaller because of the smaller aspect ratio and could not be used to confirm measurements of mixed decay rate obtained from polarized light experiments for these two samples.

From Table 1, we find that our measurements have pushed the limits of DLS for size and shape determination to lower AR values than previous studies, where the same technique was used for comparatively bigger aspect ratio particles (Rodrigue-Fernandez et al. 2007). We also find that, especially for biological applications, the light scattering technique is better suited than, for example, TEM, as DLS allows measurements of nanoparticle shape and size in life-like conditions in a fluid medium.

Table 1: Comparison of DLS and TEM results

Sample Name	Length (nm)		Diameter (nm)	
	DLS	TEM	DLS	TEM
001	18.2	24 ± 4	9.2	10 ± 1
RPD700D	27 ± 8	23 ± 8	13 ± 3	10 ± 2
RPD235AD	95 ± 1	80 ± 8	32 ± 3	25 ± 3

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Conclusion

The experiments described here show that dynamic light scattering is an inexpensive and effective technique for analyzing particle shapes and sizes down to a few nanometers and aspect ratios as small as 1.9 for certain types of particles. For more complicated shapes or aspect ratios close to one, it may yield only average size information. To realize the full potential of DLS and fully characterize its limitations as a technique for determining shape and size will require further studies.

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