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STATISTICAL INVESTIGATION OF THE ULTRAFAST IMAGE-BASED DYNAMIC LIGHT SCATTERING TO MEASURE BIMODAL GAUSSIAN DISTRIBUTIONS OF NANOPARTICLES

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Abstract

In an ultrafast image-based dynamic light scattering (UIDLS) experiment, nanoparticles in Brownian motion in a solvent are illuminated by a focused Gaussian beam and scatter the light toward an ultrafast camera. The cross-correlation coefficients between pairs of pictures recorded by the camera permit to determine a size distribution of "equivalent spherical particles". In this abstract, an iterative UIDLS permit to retrieve characteristic information of a bimodal Gaussian particle size distribution (PSD) in the sample from the distribution of the equivalent spherical particles which has been measured by UIDLS. Satisfying agreements were achieved which indicates the validity of the method.

1 Introduction

In the conventional dynamic light scattering (DLS), nanoparticles are illuminated by a focused Gaussian beam and the scattered light is collected by a photo-detector such as a photomultiplier tube (PMT) [1]. The intensity autocorrelation function (ACF) of the light at the PMT is a multi-exponential function which is then used to extract the PSD by using, for instance a constrained regularization method [2]. The UIDLS is a technique extended from the conventional DLS to measure a PSD using an ultrafast camera [3]. The cross-correlation coefficients between the pairs of pictures recorded at times t and $t+\tau$ determine a PSD of "equivalent spherical particles", which are the monodisperse particles which scatter the same light fluctuations between times t and $t+\tau$ than the polydisperse particles in the measurement volume at time t. Recently, the UIDLS was extended to a polarized-depolarised UIDLS technique to measure characteristic information about size and shape of non-spherical particles [4, 5].

In this abstract, two statistical models are proposed to investigate the UIDLS for bimodal Gaussian distributions of spherical particles. The first model used to describe the direct problem is a statistical UIDLS simulation for a bimodal Gaussian distribution. The second model is a statistical prediction of the UIDLS for a bimodal sample where the variance of the Gaussian modes is $V_1 = V_2 = 0$, and where the Levenberg-Marquardt (LM) algorithm is applied to extract characteristic information of a bimodal Gaussian sample by fitting the PSD of equivalent spherical particles measured by UIDLS.

2 Theoritical treatement

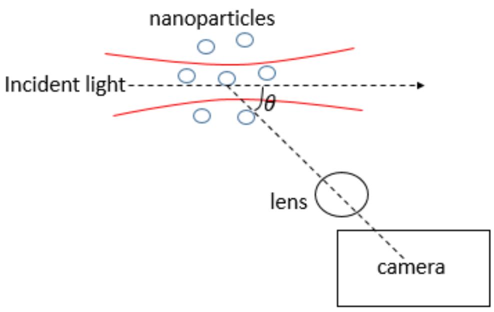

Figure 1 *UIDLS experimental set-up*

In an UIDLS experiment, nanoparticles are illuminated by a focused Gaussian beam. The experimental set-up of the UIDLS is shown in Figure. 1. The scattered light is recorded by a camera located at scattering angle θ. A lens between the sample and the camera permits to control the measurement volume. The cross-correlation coefficients between pairs of pictures are then measured to obtain information about the particles in the sample. To develop a way to measure Gaussian bimodal samples of spherical nanoparticles, two models are chosen to simulate the UIDLS experiment. The first model is the UIDLS simulation for a bimodal Gaussian sample of spherical particles. The second model is the UIDLS simulation for a bimodal sample of nanoparticles where the variance of both Gaussian modes is $V_1 = V_2 = 0$.

In the first model, named BG, the sizes of N particles are randomly generated according to the bimodal Gaussian PSD in the sample. In an UIDLS experiment, particles enter and exit the measurement volume. The cross-correlation coefficients between pair of pictures recorded by the camera at times t and $t+\tau$ are characteristics of the particles in the measurement volume at time t, assumed to be the same particles at time $t+\tau$. Figure. 2 shows an example of a bimodal Gaussian distribution by generating 1000 particles. The characteristic parameters of the bimodal Gaussian distribution are: (i) the average radii of the first Gaussian mode and that of the second Gaussian mode in the PSD, a_{1G} and a_{2G}, respectively (ii) the mixing proportion between both

Gaussian modes described by f_{1G}, the percentage frequency of particles in the first mode (iii) the variance of the first Gaussian mode, and that of the second Gaussian mode, V_1 and V_2, respectively.

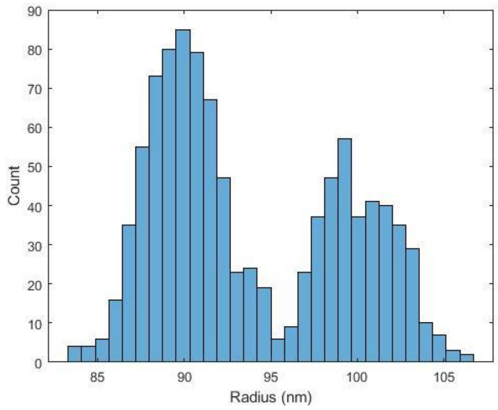

***Figure 2** Example of a bimodal Gaussian distribution where 1000 particles are generated, a_{1G}=90 nm, a_{2G}=100nm, f_{1G}=0.60, $V_1 = V_2 = 5$ nm^2*

We describe a distribution of cross-correlation coefficients from the PSDs in the measurement volume which have been randomly simulated. For a total of N_G cross-correlation coefficients N*N_G random radii are determined. The cross-correlation coefficient G(τ) between a pair of pictures recorded at times t and t + τ is [3]:

$$G(\tau) = g^{(2)}(\tau) - 1 = \beta\left[g^{(1)}(\tau)\right]^2, \quad (1)$$

where $g^{(2)}(\tau)$ is the normalized ACF of the intensity scattered by the particles in the measurement volume, $g^{(1)}(\tau)$ is the normalized ACF of the electric field, τ is the time interval, β is an instrumental constant [3]. From the N*N_G random radii, N_G values of cross-correlation coefficients are determined. From a PSD in the measurement volume randomly determined, the normalized ACF of the electric field [2] is:

$$g^{(1)}(\tau) = \sum_{i=1}^{N} h(a_i)\exp\left(-q^2 D_t(a_i)\tau\right) \quad (2)$$

where **q** is the scattering vector which depends on the scattering angle θ and the wavelength λ of the incident light in the surrounding medium [1]. $D_t(a_i)$ is the translational diffusion coefficient [1] of the i-th particle. The coefficient $h(a_i)$ is the fraction of the light intensity scattered by the i-th particle in the measurement volume.

In summary, from a randomly determined PSD in the measurement volume, a normalized electric field ACF can be obtained, from which the cross-correlation coefficient is determined. The distribution of cross-correlation coefficients is then used to determine a PSD of equivalent spherical particles.

In the present abstract, a way is proposed to get characteristic information about the bimodal Gaussian PSD in the sample by using UIDLS simulations for bimodal samples where the variances are $V_1 = V_2 = 0$, associated with the LM algorithm.

The second model of UIDLS simulation, named "BV0" model, is based on the statistical prediction of the cross-correlation coefficients corresponding to a bimodal sample where the variance of the Gaussian modes are $V_1 = V_2 = 0$ (the parameters which describe the PSD are the radii a_1 and a_2, and f_1 the percentage frequency of particles of radius a_1 in the sample). In this model, the particle size is the radius a_1 or the radius a_2. The number of cross-correlation coefficients N_k corresponding to a PSD in the measurement volume with k particles of radius a_1 and N-k particles of radius a_2 among N particles is described as:

$$N_k = N_G \frac{N!}{k!(N-k)!} f_1^N (1-f_1)^{N-k}, \quad (4)$$

where all the coefficients N_k from k=0 to k=N are described from the probability $P(k)=N_k/N_G$. As in the BG model, the values of the cross-correlation coefficients are described from the PSDs in the measurement volume, and the PSD of equivalent spherical particles is determined from the distribution of the cross-correlation coefficients.

3 Numerical results and disscussion

The direct problem is simulated using the BG model, for a given bimodal Gaussian distribution. The corresponding cross-correlation coefficients are computed and then the PSD of equivalent spherical particles is obtained. Figure. 3. shows an example of PSD of equivalent spherical particles simulated using the BG model.

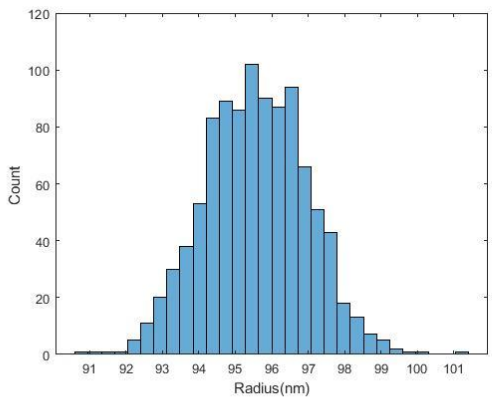

***Figure 3** Example of a PSD of equivalent spherical particles measured for a bimodal Gaussian distribution in the sample (simulation using the BG model)*

The particles are immerged in water at temperature 298 K. The number of particles in the measurement volume is N=1000. The number of cross-correlation coefficients is N_G=1000. The time interval is the same for all the cross-correlation coefficients: $\tau = 10^{-3}$s . The wavelength of the incident beam is 532 nm. The scattering angle θ is

$\pi/4$ rad. The instrumental constant β equals 1. The parameters of the bimodal Gaussian PSD are: same variance $V_1 = V_2 = 5$ nm^2 for both Gaussian modes, and average radii a_{1G}=90 nm and a_{2G}=100 nm. A white noise $\delta G = 10^{-3} \times R$, where $R \in [-1,1]$ is a uniform random number, has been added to the cross-correlation coefficients. From the PSD of equivalent spherical particles, the LM algorithm associated with the BV0 model is used to get characteristic information of the bimodal Gaussian PSD. It determines two radii a_1 and a_2, and the percentage frequency f_1. Table. 1. shows a comparison of the bimodal Gaussian PSD set in the simulation and the bimodal PSD of variances $V_1 = V_2 = 0$ obtained by fitting the PSD of equivalent spherical particles using the LM algorithm associated with the BV0 model.

	Bimodal Gaussian PSD in the sample	Fit of the PSD of equivalent spherical particles (using BV0 model and LM algorithm)
Example 1	a_{1G}=90.0 nm	a_1=91.2 nm
	a_{2G}=100.0 nm	a_2=101.3 nm
	f_{1G}=60%	f_1=65.5 %
Example 2	a_{1G}=80.0 nm	a_1=88.8 nm
	a_{2G}=100.0 nm	a_2=98.4 nm
	f_{1G}=60%	f_1=55.5%

Table 1 *A comparison of the bimodal Gaussian PSD set in the simulation (BG model) and the result of the fit of the PSD of the equivalent spherical particles based on simulations for bimodal samples of variances $V_1 = V_2 = 0$ (BV0 model associated with LM algorithm)*

In Table. 1, we can see that for the first example, both radii a_{1G} and a_{2G} agree with the radii of the bimodal sample of variance $V_1 = V_2 = 0$ that fit the PSD of equivalent spherical particles, but for the second example, a_{1G} = 80.0 nm has been overestimated, which is due to the Rayleigh scattering of the particles: the intensity scattered by a particle is proportional with the 6th power of its size. Our numerical results show that the LM algorithm associated with the BV0 model has the potential to measure characteristic information about the bimodal Gaussian PSD, and our next step is to validate it in the UIDLS experiment with bimodal Gaussian PSDs in the sample. However, the BV0 model cannot permit to measure the variances V_1 and V_2 of the Gaussian modes in the sample. Thus, one of our purposes is to extend our model of iterative UIDLS in order to measure information about the variances. The LM algorithm associated with UIDLS simulations could also permit to measure the distributions of characteristic parameters of the size and the shape of non-spherical particles.

4 Conclusion and perspectives

Two different models of simulation of the UIDLS experiment and an iterative UIDLS to measure characteristic information of a bimodal Gaussian PSD of spherical nanoparticles have been proposed. The following work are in the tray: (i) To develop a new model of UIDLS simulation where the Brownian motion and the light scattered by the particles are computed to describe the cross-correlation coefficients, which will permit us to investigate the influence of the characteristics of the camera and the measurement volume on the measurement of the PSD in the sample (ii) the experimental validation of our numerical simulations by the measurement of bimodal Gaussian samples of spherical nanoparticles (iii) to investigate the measurement of the variances of the Gaussian modes in the bimodal sample, which is not possible to determine with the BV0 model described in the present abstract, and extend the measurement of bimodal distributions to other kinds of polydisperse PSDs in the sample (iv) to extend our models of simulation to measure the distributions in the sample of characteristic parameters of the size and the shape of non-spherical particles.

5 Acknowledgement

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