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Concentration measurement of particles by number fluctuation in dynamic light backscattering

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ABSTRACT

The noninvasive optical technique of dynamic light scattering (DLS) is routinely applied to the size measurement of particles undergoing Brownian motion. Theoretically, in addition to the mean particle size the concentration of the particles can be measured from an extra decay in the intensity autocorrelation function in the case of very low concentration. To the authors' knowledge, however, the experimental results of the concentration measurements are always unsatisfactory due to the practical difficulty of accurate definition of the scattering volume. In this paper, we propose a concentration measuring method using particle number fluctuation with Dynamic Light Back-Scattering (DLBS) technique. The DLBS technique can define the scattering volume very well. It is therefore promising for the particle concentration measurement.

1. Introduction

Dynamic light scattering (DLS), also known as Photon Correlation Spectroscopy (PCS), has become a mature and popular technique that is used to determine the size distribution profile of small particles in suspensions over the last decades [1–4]. It exploits the fact that light scattered by a (diluted) suspension, and the number fluctuation of the scattering volume changed within a characteristic time scale, which is inversely proportional to the particle diffusion constant. Traditional DLS, however, cannot be used to measure the concentration of particles in solution.

The first studies of the number fluctuations were made by microscopic observations of small volumes of a colloid system. Early measurements of the number fluctuations were made by Schaefer and Berne [5] who used the PCS technique to study the movement of motile microorganisms. Subsequently, the measurement of concentration and diffusion coefficients of fluorescent-labeled particles by use of fluorescence-correlation spectroscopy has become the main application of the PCS [6–9]. And the PCS technique has been applied in the measurement of size, concentration, and velocity of particles in flowing aerosol as well [10,11]. In 1996, Wuyckhuyse's group theoretically proposed that it was possible to measure the concentration of particles in suspension by number fluctuations owing to particles diffusing through the scattering volume that leads to an extra decay in the intensity autocorrelation function (ACF) [12]. Recently Nijman's group [13] carried out simulations and experiments on the measurement of particle concentration. The results, however, are not satisfactory because it is difficult to define accurately the scattering volume in the traditional DLS setup. As far as we know, there is not much information published in the field of how to define the scattering volume accurately.

In this paper, we measure the concentration by particle number fluctuation in the optic setup of Dynamic Light Back-Scattering (DLBS) which had been used to suppress the multiple scattering present in our previous work [14]. With this DLBS setup, the scattering volume is very well defined and the preliminary experiments are also carefully carried out for the concentration measurements.

2. Setup and theory

The schematic diagram of the DLBS optics setup is shown in Fig. 1. The incident linearly polarized laser beam is reflected by two mirrors, then passes through a spatial filter, and is focused into a sample cell by lens L3. The focal point of the lens L3 was designed to fall into a position which is several micrometers behind the cell fore-wall. The scattering volume is defined by the conjugate image of pinhole P1 through lens L2 and lens L3, which is shown in Fig. 2. The backscattered light from the particles in the scattering volume is collected by the lens L3. A Fourier spatial filter fixed between the sample cell and the photomultiplier tube (PMT) is used to filter out the scattered light that are not scattered from the scattering volume.

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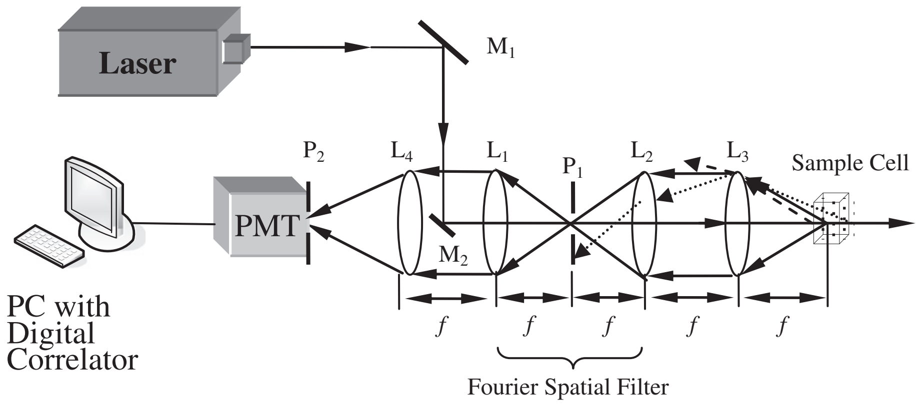

Fig. 1. Schematic diagram of the DLBS setup: M_1 and M_2 are mirrors; L_1, L_2, L_3 and L_4 are focusing doublets with focal length of 100 mm; P_1 is a diameter variable pinhole, and P_2 is 0.5 mm pinhole.

Finally the effective scattered light is gathered into the PMT by the lens L4, and the normalized intensity correlation function of the scattered light is calculated and can be written as:

$$g^{(2)}(\tau) = 1 + \beta \ \exp\left(-2D_T q^2 \tau\right) \tag{1}$$

where β is the coherence factor, D_T is the diffusion constant, and q is the scattering vector.

As theory predicts, when the number of particles in the scattering volume is small (<100), the normalized intensity autocorrelation function contains a term which describes the particle number fluctuation [15]:

$$\begin{aligned} g^{(2)}(\tau) &= g_D^{(2)}(\tau) + g_N^{(2)}(\tau) = \\ &1 + \beta \ \exp\left(-2D_T q^2 \tau\right) + \\ &\gamma \frac{1}{\langle N \rangle} \left(1 + \frac{4D_T \tau}{p^2}\right)^{-1} \left(1 + \frac{4D_T \tau}{a^2}\right)^{-1/2} \end{aligned} \tag{2}$$

where p and $2a$ are the radius and thickness of pinhole P1 respectively, the factor γ depends on the shape of the scattering volume.

From Eq. (2) we can get that the fluctuation $g^{(2)}(\tau)$ contains two parts: $g_D^{(2)}(\tau)$ and $g_N^{(2)}(\tau)$ which indicate diffusive and number fluctuation components respectively. In fact, these two terms are both generated from the Brownian motion of the particles. In the number fluctuation case when the number of particles in the scattering volume becomes small enough, any diffusion/Brownian motion of those particles means that they invariably move into/out of the (small) scattering volume giving rise to additional scattered light intensity fluctuations. Since the amplitude of the decay of $g_N^{(2)}(\tau)$ is proportional to the reciprocal average number of particles in the scattering volume <N>, the concentration of the particles can be calculated as <N> divided by the scattering volume.

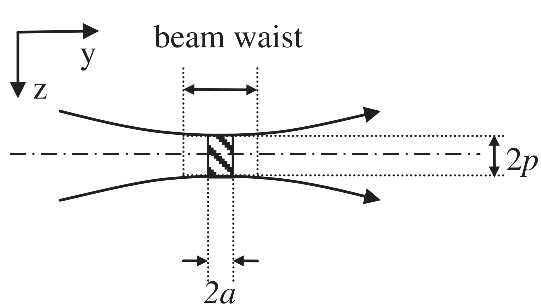

Fig. 2. Schematic diagram of the scattering volume: the shadow part is scattering volume which is defined by the pinhole 1 through two doublets. p and $2a$ are the radius and thickness of pinhole 1 respectively.

3. Data reduction

The important physical information hidden in the measured data is contained in the parameters β, D_T and <N> in Eq. (2). But, before these parameters are determined by a curve fitting process, an exact normalization is required to obtain Eq. (2).

Normalization and subsequent baseline error have long been a notorious problem in dynamic light scattering [16–19]. In our measurement, the baseline, which characterizes the square of the measured mean intensity, is independent of τ. It depends on the amplitude of the radiation flux density emitted by the laser, the solid angle of the detector, the mean particle number <N> in the scattering volume, and the particle size distribution, and it is also a function of the scattering angle and the refractive index of the particles. In fact the baseline subtraction is still biased, although it is rather small in most measurement. The estimation of bias and noise reduction due to baseline subtraction requires knowledge of the covariance matrix of the statistical errors in monitors and the covariance between monitors and correlation data [20]. To give an estimate of the uncertainty in baseline, we use the definition of normalization errors described by an analytical expression in terms of the relative baseline error $\Delta B/\hat{B}$ [21]. The $\Delta B/\hat{B}$ has an amplitude of about 10^{-4}, which is much smaller than the number fluctuation term with an amplitude of about 10^{-1}.

After normalization, the unknown parameters β, D_T and <N> in Eq. (2) can be calculated from the measured $g^{(2)}(\tau)$ by a non-linear least square fitting.

4. Scattering volume

Generally there are three kinds of collecting optics setups in the traditional DLS, which are shown in Fig. 3 [22]. The dimension of the scattering volume in these setups, however, cannot be exactly defined. Because the laser beam profile at the waist and the collecting optics which is controlled by the pinholes and the scattering angle are both Gaussian profile. The scattering volume is determined by the cross-section between the laser beam and the collecting optics.

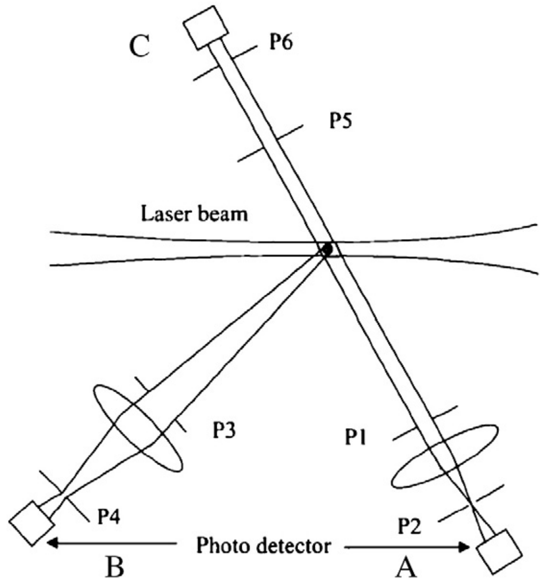

Fig. 3. Schematics of the scattering volume in traditional DLS optics setups.

In the DLS setup, it is almost impossible to calculate the cross part precisely for the absolute error from any tiny deviation in the optics setup.

In the DLBS setup, as shown in Figs. 1 and 2, the scattering volume and the pinhole P1 are conjugate image of lens L2 and lens L3. Therefore the effective scattering volume can be well defined by the radius p and thickness a of the pinhole as shown below:

$$V = \pi p^2 a. \tag{3}$$

For a spherical scattering volume with the radius of σ, the characteristic time of the number-fluctuation decay is in the order of σ^2/D_T [12,14]. Therefore, the measurement of the number-fluctuation decay is time dependent which is related to the dimension of the scattering volume. Theoretically we can shorten the measuring time by reducing the scattering volume. In practice, however, to avoid the diffraction from the decrease of the diameter of the pinhole, the diameter of the pinhole should be at least 5 times larger than the wave length of the incident light. Furthermore, another practical issue with decreasing the diameter is the requirement in the higher accuracy in the manufacture of the pinhole, which, at the end, may result in a larger error of the estimation of the scattering volume.

5. Experiments

To evaluate whether the DLBS technique is suitable for concentration measurement, we chose two different types of latex suspensions for the concentration measurement. The original suspensions we used were aqueous dispersions of spherical latex particles (Duke Scientific), both were monodispersed with the particle diameters of 100 nm (5010 A) and 500 nm (5050 A) respectively. The original latex suspensions have a volume fraction of 10%. For the measurement two series samples with different concentrations were prepared by diluting the original suspensions with filtered water, which are listed in Table 1.

A diode pumped solid state laser (RGB Lasersystems) operating at 532 nm with a nominal power output of 300 mW and diameter of 1 mm is used as the coherent source. The focal-length of the lens is 100 mm. According to basic optics, the waist of a focused beam is:

$$D_w \approx 2.44 \lambda f / d = 130 \mu\mathrm{m}. \tag{4}$$

To filter out the over-scattering light from the outside of the focal point, the diameter of the pinhole P1 should be smaller than the waist of a focused beam. In this case pinhole P1 with diameter of 100 μm and thickness of 4 μm was used. Therefore the effective scattering volume is about $\pi \cdot 10^4 \mu\mathrm{m}^3$ calculated by Eq. (3). And γ equals to 0.5 which is the result of the fact that the effective volume defined by Eq. (3) decreases when it is squared [13,23].

A photomultiplier tube (Hamamatsu, Model H6240-01) is used to detect the scattered light and the resulting photo-electron TTL pulses are processed by a digital correlator (Brookhaven Instruments, BI-9001) to calculate the ACF.

6. Results and discussion

In the first experimental series, the experiments on the number-fluctuation decay as a function of the measurement time are carried out in order to compare the results by the DLBS technique with those by traditional Photon Correlation Spectroscopy (TPCS) technique. The suspension of 100 nm in diameter and 3×10^{-4}% in particles volume fraction is used, and the result is shown in Fig. 4. It is obvious that the measured amplitude increases as we increase the measurement time, and a saturated amplitude of 0.59 is obtained by the DLBS system, at the time of 1000 s. The TPCS measurement, however, is not saturated even when the measuring time exceeds 10,000 s. This is because the relaxation time depends on the geometry (for a given concentration). For the TPCS setup the scattering volume was larger in which case the fluctuation time would be longer and the fluctuation amplitude would be smaller. If measurements were made for long enough, the TPCS number fluctuation amplitude would also eventually plateau.

In the second experimental series, the particle numbers in the scattering volume of the different concentration samples are measured by DLBS, and the saturated values (at 1000 s) are shown in

Table 1
Particle concentration range and corresponding particle number applied in this work.

Diameter	100 nm								
Volume fraction (‰)	1.5×10^{-4}	3×10^{-4}	6×10^{-4}	1.2×10^{-3}	1.5×10^{-3}	1.8×10^{-3}	2×10^{-3}	2.5×10^{-3}	3×10^{-3}
Particle number	9	19	35	71	91	102	110	130	145
Diameter	500 nm								
Volume fraction (‰)	0.01	0.03	0.05	0.10	0.20	0.25	0.32	0.38	0.42
Particle number	6	11	25	46	97	112	132	154	162

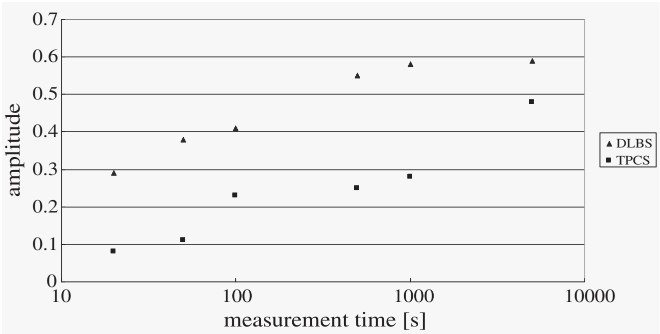

Fig. 4. Measured amplitude of the number-fluctuation decay increases with the measurement time; triangle, results by Dynamic Light Back-Scattering (DLBS); square, results by traditional Photon Correlation Spectroscopy (TPCS).

Fig. 5. It is clear that the increase of the mean particle number <N> in the scattering volume is approximately linear with the increase of the particle concentration when the <N> is less than 100. The dashed lines in Fig. 5 are the expected mean number concentrations. In addition, since the intensity autocorrelation function contains diffusive and number fluctuation components as:

$$G^{(2)}(\tau) = G_D^{(2)}(\tau) + G_N^{(2)}(\tau) = \langle N\rangle^2\left[1+\beta\ \exp\left(-2D_Tq^2\tau\right)\right] + \gamma\langle N\rangle\left(1+\frac{4D_T\tau}{p^2}\right)^{-1}\left(1+\frac{4D_T\tau}{a^2}\right)^{-1/2}. \quad (5)$$

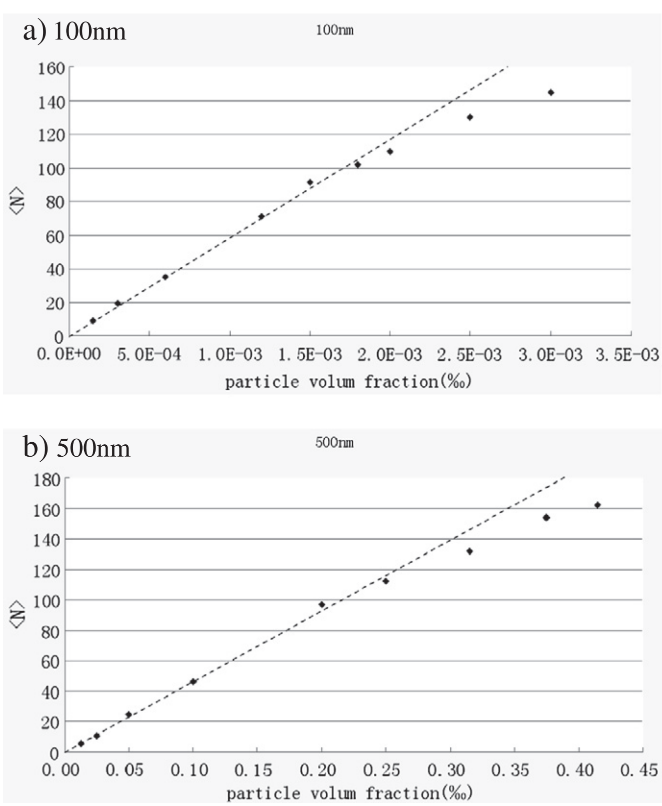

Fig. 5. Relationship between the mean particle number in the scattering volume and the particle volume fraction, (a) 100 nm, and (b) 500 nm polystyrene spheres.

The number fluctuation component which is in the latter term of Eq. (5) is only linearly dependent on <N>. With increasing particle concentration, its amplitude decreases relatively to that of the diffusive component, which results in the decrease of the measured values at higher particle volume.

For the samples of narrow size distributions, with the cumulants method Eq. (2) can be rewritten as:

$$g^{(2)}(\tau) = 1+\beta\ \exp\left(-2D_Tq^2\tau+\mu\tau^2\right) + \gamma\frac{1}{\langle N\rangle}\left(1+\frac{4D_T\tau}{p^2}\right)^{-1}\left(1+\frac{4D_T\tau}{a^2}\right)^{-1/2} \quad (6)$$

where μ is a measurement of the dispersion of the reciprocal relaxation time around the average value. The particle number <N> as well as β, D_T and μ can be calculated from Eq. (6) by a non-linear least square fitting. It can easily achieve a reproducibility of 2–3% for the number fluctuation component.

For polydisperse samples, since the characterization of the size distribution of the sample is far from satisfactory, there is still a long way for the measurement of the concentration of polydispersity samples by number fluctuation.

7. Conclusion

In this work, as a modification of the PCS technique, we have demonstrated a DLBS setup to measure the concentration of particles in suspensions by monitoring the number fluctuation in a well-defined scattering volume. With this new DLBS technique, the experimental results match with the pre-known sample concentration quite well. The measuring time is decreased compared with the previous work [13]. The proposed DLBS technique exhibits a promising future in applications for particle concentration measurement as further improvement can be made to decrease the measuring time.

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Glossary

a: thickness of pinhole
B: the exact baseline value
d: the diameter of incident laser
D_T: the diffusion constant
D_w: the waist of a focused beam
f: the focal-length of the doublets
$g^{(2)}(\tau)$: Normalized Auto Correlation Function
$<N>$: average number of particles in the scattering volume
p: the radius of pinhole
V: the effective scattering volume
β: coherence factor
γ: a factor depends on the shape of the scattering volume
λ: wavelength
μ: a measure of the dispersion of the reciprocal relaxation time around the average value.