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Short communication

Fast nanoparticle sizing by image dynamic light scattering☆

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ABSTRACT

In this paper, an image dynamic light scattering method for nanoparticle sizing is introduced. The spatial distribution of the scattered lights from nanoparticles undergoing Brownian motion was captured at a high frame rate by a digital camera within one second, which is considerably faster than the conventional photon correlation spectroscopy method. The captured series of photographs were meshed into thousands of small units for calculating the intensity autocorrelation functions in parallel. Experimental results from the measurements of three reference nanoparticle samples (27, 80, and 352 nm in diameters) demonstrated the feasibility of this method.

Principle of image dynamic light scattering (IDLS)

The dynamic light scattering (DLS) due to particles' Brownian motion is widely applied in nanoparticle sizing. Several measurement techniques have been developed (Schärtl, 2007). Among them, photon correlation spectroscopy (PCS) is the main method and has been applied in subjects as chemistry, biology, and physics (Berne & Pecora, 1976). In PCS, a photon multiplier tube (PMT) or avalanche photodiode is employed to measure signals of scattered light at one point. Then, the measured signals are processed by digital correlators to obtain the time intensity autocorrelation functions (ACFs). In order to guarantee an accurate result, long acquisition time is needed to collect enough data, usually from tens of seconds to several minutes, depending on the size of measured nanoparticles (Allen, 2003; Brown, 1993). However, such a long acquisition time is far from real-time nanoparticle sizing. Furthermore, Brownian motion is sensitive to the viscosity of the suspending medium, and viscosity is related to the temperature. A temperature control unit is necessary to stabilize the sample temperature during the long acquisition time in PCS (Linsinger et al., 2012). This leads to a complex structure of the system and it is not suitable for on-line and in situ measurements of nanoparticles, especially in such fields as nanofluids in microchannels, synthesis of nanoparticles, and chemical reaction processes. For those reasons, a fast IDLS method with a compact structure is studied to explore the possibility of real-time and in situ nanoparticle sizing.

For spherical particles undergoing Brownian motion, the Stokes-Einstein equation relates the particles' translational diffusion coefficient D_T to the particle's hydrodynamic diameter d as follows:

$$D_{\mathrm{T}} = \frac{k_{\mathrm{b}}T}{3\pi\eta d} \tag{1}$$

where k_b is Boltzmann's constant, T is the absolute temperature, and η is the dynamic viscosity of the suspending medium. When a focused laser beam travels through the sample cell, the suspended nanoparticles scatter the incident laser beam in all directions. The intensities of the scattered lights fluctuate with time due to particles' Brownian motion. The intensity fluctuation signals are processed with the autocorrelation function:

$$G(\tau) = \left\langle I(t)I(t+\tau)\right\rangle = \lim_{T\to\infty}\frac{1}{T}\int_0^T I(t)I(t+\tau)dt. \tag{2}$$

The decay rate of the autocorrelation function is related to the particle's diffusion coefficient D_T. Using the Siegert relation to fit the autocorrelation function of monodisperse nanoparticles, the normalized autocorrelation function is written as

$$g^{(2)}(\tau) = \frac{\left\langle I(t)I(t+\tau)\right\rangle}{\left\langle I(t)\right\rangle^2} = 1 + \beta\,\exp\left(-2\Gamma\tau\right), \tag{3}$$

where β denotes the coherence factor, and the decay rate

$$\Gamma = \mathbf{q}^2 D_{\mathrm{T}}, \tag{4}$$

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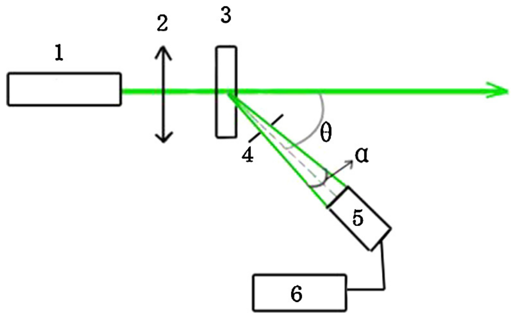

Fig. 1. Schematic diagram of IDLS apparatus (1 – laser; 2 – lens; 3 – sample cell; 4 – aperture; 5 – camera; 6 – computer).

where $\mathbf{q}$ is the scattering wave vector, given as

$$|\mathbf{q}| = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right), \tag{5}$$

where θ is the scattering angle, n is the refractive index of the medium, and λ is the wavelength of the beam. As shown in Fig. 1, the spatial distribution of the scattered lights is captured by a digital camera in IDLS, rather than using a PMT to collect signals at one point. Millions of pixels on the imaging chip are equivalent to a large number of sensors, collecting different light speckles simultaneously. This approach can shorten the acquisition time to milliseconds, less than 1% of the time that PCS would take. Apart from the possibility to achieve real-time acquisition, there are still other advantages, such as reducing the thermal impact caused by heat convection (Schaertl & Roos, 1999) when the laser beam is focused into the sample cell, and simplifying the structure of the system with no need to have a temperature control unit.

To obtain the maximum signal-to-noise ratio of the light intensity fluctuation signal, the measurement should be carried out in a coherence area that is calculated with the following equation (Pusey & Vaughan, 1975)

$$A_{\text{coh}} = 4\frac{\lambda^2 R^2}{\pi w^2}, \tag{6}$$

where λ is the wavelength, R is the distance between the detector and the scattering volume, and w is the diameter of the scattering volume. If the detected area $A_d \gg A_{\text{coh}}$, the coherence factor β of the measurement will decrease to zero (Pecora, 2000); the signals will be uncorrelated. Set $\lambda = 532$ nm, $R = 0.18$ m and $w = 1$ mm, the coherence area A_{coh} is equal to 11,681 μm^2, approximately 108 μm × 108 μm. To guarantee such a small area, a detector aperture (pinhole) is necessary in PCS (Thomas, 1991). In IDLS, this is realized by the pixel itself with its tiny size. The smallest area for a pixel is only approximately 5 μm × 5 μm. The coherence factors of our experiments are around 0.7 after the dark count is subtracted. The gray value of the picture is not solely caused by the scattered light signals, due to the existence of CCD dark count and sometimes stray lights. Fig. 2 is the captured image of the scattered light signals.

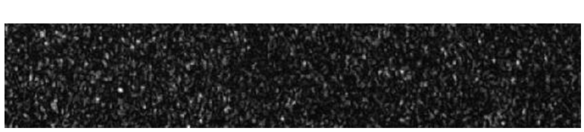

Fig. 2. Photograph of scattered lights (352 nm latex spheres) captured by IDLS apparatus.

Table 1
The calculated diameters of latex spheres in water.

Nominal diameter (nm)	Mean measured value (nm)	Deviation (%)
27	31	14.8
80	86	7.5
352	340	3.4

$n = 1.33$, $\eta = 0.00089$ Pa s, $T = 298$ K, and frame rate = 8290 fps.

Table 2
The calculated diameters of latex spheres in 75% (v/v) glycerol solution.

Nominal diameter (nm)	Mean measured value (nm)	Deviation (%)
27	28	3.7
80	79	1.3
352	357	1.4

$n = 1.44$, $\eta = 0.02773$ Pa s, $T = 298$ K, and frame rate = 1000 fps.

Experiments and discussions

In the experiments, a high-speed camera (Redlake's MotionPro X3, 8-bit monochrome) was placed at the scattering angle θ of 45°. Frame rate can be set from 1000 frames per second (fps) at full resolution (1280 × 1024 pixels) to over 64,000 fps at reduced resolution. Three kinds of standard polystyrene latex spheres (27, 80, 352 nm) produced by Beijing Haianhongmeng Reference Material Technology Co., Ltd. and China University of Petroleum, Beijing, were measured. During each measurement, 2000 frames of the

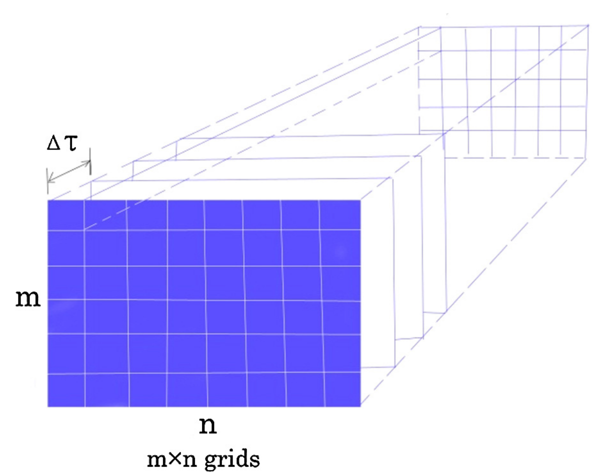

Fig. 3. Grid division for frames captured.

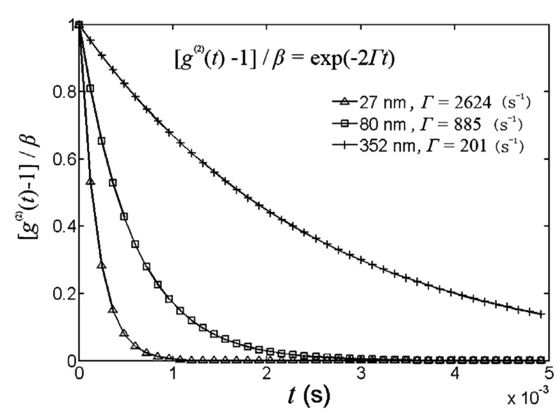

Fig. 4. Fitting results of the normalized autocorrelation functions for latex spheres in water with $T = 298$ K, and frame rate = 8290 fps.