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Particle-size measurements in a Micro-channel with Image Dynamic Light Scattering Method

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Abstract

Conventional dynamic light scattering (DLS) using a CCD camera as optical area detector (here we called Image Dynamic Light Scattering method, for the data acquired by images) has been developed successfully. We present a model experiment in a micro-channel to study flowing Brownian motion systems of polystyrene latex particles by using Image Dynamic Light Scattering method (IDLS). The modified correlation function proposed by Chowdhury et al., which is applied to the analysis of extracting the size and velocity of laminar flowing particulate dispersions, is used in the paper to obtain the particle size from the scattered light signals. The new method allows for much shorter measurement time compared to conventional DLS. As the inversion algorithm of polydisperse system is yet very complex, the measurement of the paper is for monodisperse polystyrene latex particles.

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1. Introduction

Since the concept of "nanofluids" was proposed by Choi et al from the U.S. Argonne National Laboratory in 1995, nanofluids as a new functional fluids has been attracting more and more attention[1]. Nanofluids is made by adding metal or metal oxide nanoparticles to the working fluid. The particle size is so small that nanoparticles can

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be well suspended in a liquid with greater stability than micrometer particles suspension. Since the 1990s, along with the natural sciences and engineering technology developing into Microminiaturization, microfluidic system such as the motion characteristics, heat exchange capability, and mass transfer performance etc. of nanofluids in a micro-channel has become a research hotspot \[2,3,4\]. The study of nanofluids in a micro-channel require knowledge of local properties that can provide information about the process and the optical in situ measurement methods is usually applied for the determination of the local properties such as particle size, fluid velocity and particle concentration.

Dynamic light scattering method (DLS), also known as photon correlation spectroscopy (PCS), is one of the most important means of measuring nanoparticle size, whose advantage is noninvasively, quickly, and accurate. DLS method is based on the Brownian motion of particles in suspension and traditionally applied to particle size measurement in the non-flowing systems \[5,6,7\]. The scattered light from small particles fluctuates rapidly and that from large particles fluctuates slowly. The particle diffusion coefficient can be determined by intensity autocorrelation function, from which we can obtain the particle size information. Meanwhile, the measurement method has also been used to characterize the fluid velocity in a flowing Brownian motion system \[8,9\]. Chowdhury et al has studied the application of DLS to a system of flowing Brownian motion particles and compare the results to a representative system of a suspension of polystyrene latex spheres in water flowing through a tube at known flow rate \[10\]. Alfred B. Leung has also measured the particle size and velocity in flowing conditions using DLS by receiving the backscattered light \[11\].

The traditional technology for measuring light intensity autocorrelation function comprises a laser, an optical system, a photomultiplier tube and a digital correlator. However, in order to obtain a sufficient amount of data, measurements in conventional DLS can be very time consuming, for the entire measurement process can take tens of seconds to more than hundreds of seconds. In order to achieve on-line particle size determination in-real time, the measurement time must be shortened. Dynamic light scattering using a CCD camera has been developed successfully \[12-18\]. The CCD camera is used as an area detector to capture the speckle pattern of the light intensity scattered by a dilute particle suspension in Image Dynamic Light Scattering (IDLS) method. As there are tens of thousands of pixels in a CCD chip, using a CCD camera allows us to measure a large number of signals simultaneously. Compared to the conventional technology, the measuring time for getting the same amount of data can be shortened to 1 second by using a high speed camera. Therefore, the intensity autocorrelation function can be measured in real time and on-line measurement of particle size and velocity can be achieved by IDLS method.

In this paper we present a model experiment in a micro-channel to study flowing Brownian motion systems of polystyrene latex particles by using Image Dynamic Light Scattering method (IDLS). As the inversion algorithm of polydisperse system is yet very complex, the measurement of this paper is for monodisperse polystyrene latex particles.

2. Theory

DLS method is based on the Brownian motion of particles in suspension. For spherical particles, relationship between particle diffusion coefficient $D_T$ and hydrodynamic diameter $D$ can be described by the Stock-Einstein relationship:

$$D_T = \frac{K_B T}{3\pi\eta D}$$ \hspace{1cm} (1)

Here $K_B (1.38 \times 10^{-23} \text{JK}^{-1})$ is the Boltzmann constant, $T$ is the absolute temperature of the scattering medium, and $\eta$ is the viscosity of suspending liquid. DLS technology characterizing the particle motion by measuring the light intensity fluctuation can be understood with reference to Fig.1. Scattering vector is defined as a difference between scattered light and incident light: $\mathbf{q} \equiv \mathbf{K}_S - \mathbf{K}_I$, the magnitude of the scattering wave vector is given by:

$$q = \frac{4\pi n}{\lambda} \sin \left( \frac{\theta}{2} \right)$$ \hspace{1cm} (2)

Here $\theta$ is the scattering angle, $n$ is the refractive index of the solvent, and $\lambda$ is the wavelength of the incident light in vacuum. The light intensity seen by the detector is a randomly fluctuating signal as shown in Fig.2, and the time
autocorrelation function (ACF) in normalized form is used to characterize the time scale of the fluctuation:

\[
\begin{align*}
g^{(2)}(\tau) &= \frac{\langle (I(t)I(t+\tau)) \rangle}{\langle I(t)^2 \rangle} \\
g^{(1)}(\tau) &= \frac{\langle E(t)E^*(t+\tau) \rangle}{\langle |E(t)|^2 \rangle}
\end{align*}
\]

(3a) (3b)

Here, the angle brackets indicate a time average, \( \tau \) is the time delay between the samples. Eq.(3a) is the intensity ACF, and Eq.(3b) is the electric filed ACF. For homodyne detection, in the usual case of Gaussian statistics, \( g^{(2)}(\tau) \) and \( g^{(1)}(\tau) \) are simply related by the Siegert relation:

\[
g^{(2)}(\tau) = A[1 + \beta g^{(1)}(\tau)]
\]

(4)

Here, \( A \) is the baseline of the autocorrelation function, \( \beta \) is an empirical experimental constant. For a dilute suspension of monodisperse spheres, \( g^{(1)}(\tau) \) is a simple exponential:

\[
g^{(1)}(\tau) = \exp(-\Gamma\tau)
\]

(5)

Here, \( \Gamma = D_T q^2 \) is the decay constant. Thus \( g^{(2)}(\tau) \) can be written as:

\[
g^{(2)}(\tau) = A[1 + \beta \exp(-2\Gamma\tau)]
\]

(6)

However, when a flow is induced, the position vector of the particles involves two items: the diffusional motion and the translational motion of the particles. In the nondilute limit, the experimental homodyne autocorrelation function will be \( [10] \):

\[
g^{(2)}(\tau) = A \left[ 1 + \beta \exp(-2\Gamma\tau) \exp \left( -\frac{\nu^2 \tau^2}{\omega^2} \right) \right]
\]

(7)

Here, \( \nu \) is the flow velocity, \( \omega \) is the focused beam waist radius, and \( \omega/\nu \) is the beam transit time equal to the pass time of the particle through the laser beam. The diffusional and translational information are included within the two exponential. And the particle size and velocity can be derived respectively from the two exponential. And from Gaussian optics, the focused beam waist can be given by:

\[
\omega = \frac{\lambda}{\pi \omega_0 f}
\]

(8)

Here, \( \omega_0 \) is the radius of the laser beam, \( f \) is the lens focus length.
3. Data analysis

As mentioned above, the photomultiplier tube is replaced by an image sensor used as an area detector in IDLS method. Fig.3 shows the schematic diagram, where the sensor chip acts as an array of detectors. Thus, a set of multiple DLS measurements is carried out simultaneously. As shown in Fig.4, for each data set, the intensity autocorrelation is calculated and the value of particle size and velocity will be obtained. Then we take the ensemble average to obtain the final result. Here approximately, we assume all of the scattering vectors are from the same scattering angle. One can control the angular resolution by changing the size of the pinhole. However, after calculating the ensemble average of all the grids, $\Delta \theta \approx \pm 1^\circ$ at scattering angle of 45°C can be allowed. While there is one final issue to note: how many pixels can represent the size of the coherence area in the speckle pattern. For the situation shown in Fig.3, assuming the diameter of the scattering volume is $d$ and the distance away from the detector is $R$, the size of the coherence area will be:

$$A_{coh} = \frac{\lambda^2 R^2}{\pi d^2}$$

Thus, the number of the pixels for one coherence area is:

$$n = \frac{A_{coh}}{a}$$

where $a$ is the area of one pixel.
4. Experimental

The experimental setup, as shown in Fig. 5, comprises a laser, two lenses, a high speed camera, a micro flow cell, a syringe pump (LSP02-1B), an iris diaphragm, and a personal computer. The light source was a 5-mW He-Ne laser operating at the wavelength $\lambda = 632.8$ nm. As shown in Fig. 6, the micro flow cell with a 0.5 mm optical path length is made of quartz. The plastic hoses connected the syringe, the micro flow cell and the sample bottle. The flow was generated by a syringe pump (running in perfusion or extraction mode). The syringe pump can completely meet the requirements of flow velocities by providing a wide flow rate range (e.g., 109.83μL/hr to 47.59ml/min with a 30ml syringe). The diaphragm determines the effective scattering volume and also the range of scattering angles covered by the image sensor. The first lens with $f = 50$mm focal length focused the laser beam inside the flow cell. The second lens mapped the scattered light onto a number of pixels on the image sensor. The image detector was a MotionProX3 high speed camera featuring a CMOS sensor with 8-bit pixel depth. The sensor had an active area of $15.4 \times 12.3$ mm divided into $1280 \times 1024$ pixels. The dimension of each pixel was $12 \times 12 \mu m^2$. The maximum speed can reach 1000 fps (frames per second) at $1280 \times 1024$ resolution and 64000 fps at $1280 \times 8$ resolution. The dynamic range of the sensor is 59 dB. USB 2.0 was used to acquire the images from the camera into the computer.

For our system, the diameter of the diaphragm was 1mm. The distance from the beam center to the sensor matrix was 11 cm. As a consequence, the speckle size estimated by Eq.(9) and Eq.(10) was approximately $14 \mu m^2$ or 4 pixels corresponding to one coherence area. As the incident beam was measured to be with $\omega_0 = 1$mm in this study, the average beam radius was calculated to be 20μm. All the measurements were at the same resolution $700 \times 128$, and the scattering angles are approximately in the range of $45^\circ \pm 1^\circ$. We collected images of the speckle pattern respectively at 2000fps, 3000fps, 5000fps. The samples studied were suspensions of two different sized particles: 79nm and 352nm diam latex spheres diffusing in filtered distilled water. The concentrations of these dispersions are chosen to minimize the effects of multiple scattering. Only the low velocities (0~1cm/s) were considered in this study. The experiment was carried out at room temperature 20 °C$\pm 0.5$ °C. Fig. 7 presents the speckle pattern of 352nm as monitored by the CMOS sensor.
5. Results and Discussion

5.1. Results at different frame rates with zero velocity

Table 1 Results at different frame rates with zero velocity

| Nominal value | Frame Rate | 2000fps(Δt=0.5ms) | 3000fps(Δt=0.33ms) | 5000fps(Δt=0.2ms) |
|---------------|------------|--------------------|--------------------|-------------------|
|               | diameter   | deviation          | diameter           | deviation         | diameter           | deviation         |
| 352nm         | 376nm      | 6.8%               | 373nm              | 5.9%              | 361nm              | 2.56%             |
| 79nm          | 85nm       | 7.5%               | 72nm               | 8.8%              | 81nm               | 2.53%             |

Table 1 shows the extracted particle sizes at different frame rates with zero velocity. At 2000fps and 3000fps, the measurement error averaged at about 7% for the two sized particles. However, at 5000fps, the measurement error is significantly reduced. As can be seen, the error for 352nm particles was 2.56%, and for 79nm particles was 2.53%, which is quite pleasing since the time interval of 0.2ms is much longer compared with the conventional DLS.

5.2. Results at different velocities with 5000fps
Fig. 8 shows the results at different velocities at 5000fps. The particle sizes remain constant for the initial flow velocity (0–0.1 mm/s), but with the increases in velocity, the extracted particle size is decreasing. The main reason for the decreasing trend is that, with the increases in velocity, the scattered light intensity fluctuates more and more rapidly, and our camera speed is too slowly to cover the time scale of the particle motion. That’s also why the velocities we studied in this paper is so small.

6. Conclusion

Successful application of this method is demonstrated. Measurement of nanoparticle size under directional flow conditions in a micro-channel by using image DLS, has the following advantages: (1) measurement time is significantly reduced within 1 second; (2) the measure device is simple and handy; (3) on-line monitoring of dispersions under flowing conditions in a micro-channel is realized.

However the main limitation of a CCD sensor is its reduced dynamic range and the long exposure time. Our future purpose is the in situ determination of the particle size distributions of a polydisperse fluid-particle system that flows laminarily in a micro-channel, and so there are still a lot of work to do for us.

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