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# Nanoparticle Sizing by High-Frequency Dynamic Ultrasound Scattering Techniques

高周波動的超音波散乱法によるナノ粒子サイジング

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## 1. Introduction

While modern science and nanotechnology are making great progress in highly functional materials, the in-situ analysis is an important research subject in pharmaceuticals, fuel cell electrode and electronics printing applications. Ultrasound methods, which have been utilized for fetal echocardiography and non-destructive testing, are now undergoing a major evolution in nanotechnology thanks to the latest high-speed technology.

The analysis of highly concentrated nanoparticles in liquids is about to realize by dynamic ultrasound scattering (DSS) [1], an acoustic analogue of dynamic light scattering (DLS). Along with the sophisticated technologies, such as low-coherence dynamic light scattering (LC-DLS) [2] and diffusing wave spectroscopy (DWS) methods [3], the analysis of optically turbid suspension gained a great attention. Among them, the DSS method has the potential to be utilized up to the close-packing concentration where transmission of visible light is not allowed. In this paper, we present a novel technique to enable analysis of nanoparticles with higher accuracy and small sample volume as low as 30 µl, while overcoming the problems of the previous DSS method.

## 2. Experimental section

In the DSS method, the backscattered ultrasonic pulse incident on a suspension is recorded by a high-speed digitizer. A remote pulsar BLP-12R manufactured by iSL was used as the spike-pulsar, and the data was recorded using a high-speed digitizer manufactured by GaGe Applied with a bit depth of 16 bits at 200 mega samples per second. For the analysis, we used the FD-DSS method[1], which provides more accurate nanoparticle analysis among the DSS methods. This method is based on the Fourier transform of the obtained pulse waveform to obtain the time correlation of the amplitude. For the transducer, we used a 40 MHz focused sensor from Toray or a 30 MHz composite sensor from KGK.

Silica standard particles with radius of 15 nm and 25 nm were obtained from micromod, and silica particles with radius of 50 nm and 250 nm were obtained from Nippon Shokubai. The former was used as is at 2.5 wt%, while the latter were used by dispersing the powder in ultrapure water at 1 wt%.

## 3. Results

In the previous studies, we have performed DSS analysis of the volume fraction $\varphi$~2.5% silica particles with a radius of about 30 nm [1]. However, due to the weak scattered intensity, it was necessary to record over night and accumulate a large number of data points. It is known that even the low-energy ultrasound waves can induce unexpected flow of microparticles due to the acoustic radiation force[4, 5]. Due to the effect, it was subject to perform DSS measurement with the lower ultrasonic frequency, lower pulse energy, and the longer pulse repetition time[6]. Because of the limitation, the DSS measurement of nanoparticles could not be performed at short time with good statistics.

### 3.1 Nanoparticle sizing using a novel method

**Fig. 1** shows the correlation function $g^{(1)}(\tau)$ obtained for the silica nanoparticle suspension at 2.5wt% (radius $a$ = 15 nm, 25 nm, 50 nm, 250 nm) measured using a 40 MHz focused transducer. The pulse repetition time is 10 ms and the number of recordings is 100,000 for a 15-minute measurement.

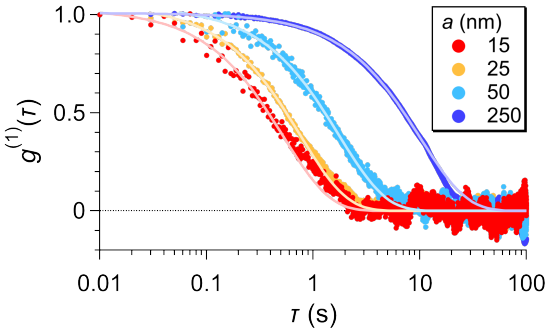


Fig. 1 Silica nanoparticles measured by the novel DSS method.

As a result of curve fitting, the hydrodynamic radii obtained from the diffusion coefficient $D$ could be calculated as 15.4 nm, 25 nm, 48.9 nm, and 247 nm, respectively. In the conventional method, the pulse repetition time had to be more than 100 ms, the frequency had to be less than 30 MHz, and plane waves had to be used instead of the focused type in

order to avoid the unexpected flow.

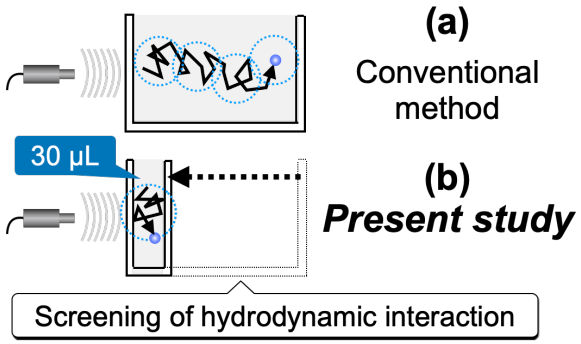


Fig. 2 Schematic representation of (a) conventional and (b) new sample setup.

To achieve this novel result, we made the sample as thin as possible to avoid this effect as schematically illustrated in **Fig. 2**. In addition, this may screen the long-ranged hydrodynamic interaction [7], as discussed below.

### 3.2 Analysis of submicron-particle: Screening of hydrodynamic interactions

In the submicron size regime, the sedimentation velocity fluctuations compete with the diffusion mode originating from Brownian motion [1]. In DLS measurements with short wavelengths, only the diffusion mode is detected. In contrast, in DSS measurements, the two modes contribute to $g^{(1)}(\tau)$;

$$g^{(1)}(f,\tau) = \exp\left[-Dq^2\tau - \frac{1}{2}\Delta V^2 q^2 \tau^2\right] \quad (1)$$

where $q$ is the magnitude of the scattering vector, $\Delta V$ is the standard deviation of the velocity and is given by [8],

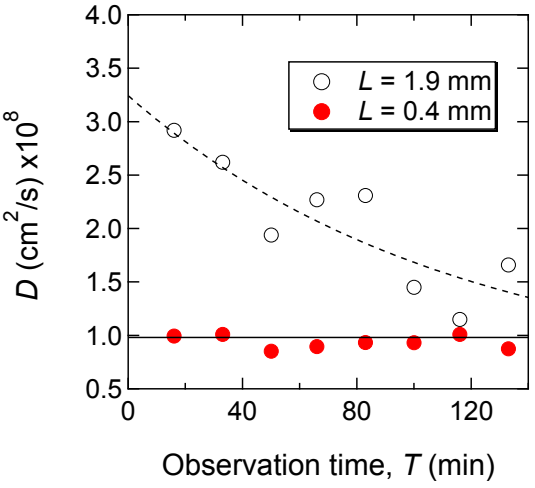


Fig. 3 Observation time dependence of the $D$ obtained for the 250 nm silica particle, revealing the advantage of using thinner sample cell.

$$\Delta V = CV_0\sqrt{\frac{\phi L}{a}} \quad (2)$$

$V_0$ is the terminal velocity. One may notice that the $\Delta V$ is a function of the sample thickness $L$, so that it can be eliminated by $L \to 0$. The effect of the velocity fluctuation varies with time until it enters its steady state. Therefore, previous measurements had to wait for the equilibrium state [1].

**Fig. 3** shows the results of 1 wt% silica particles with the radius of 250 nm. When the sample thickness was 1.9 mm, the $D$ was overestimated even after 2 hours of measurement. On the other hand, when the cell thickness was 0.4 mm, the correct particle size could be calculated regardless of the measurement time. The good agreement between the experimental data (solid circles) and the theoretical value of $D$ (solid line) was confirmed.

## 4. Conclusions

Nanoparticle sizing with a hydrodynamic radius of 15 nm was achieved by using a 40 MHz focused transducer. By reducing the sample thickness, the acoustic streaming could be highly suppressed. Thus, high power, high precision and high-speed measurements were achieved. In the ultrasonic wavelength regime, in addition to Brownian motion, particle dynamics accompanying hydrodynamic interaction dominate the dynamics. By simply reducing the sample thickness, we were able to screen the effect and successfully capture the Brownian motion of submicron particles solely. This makes it possible to immediately evaluate particles accompanying hydrodynamic interaction without waiting for their hydrodynamic steady state.

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