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Dynamic ultrasound scattering analysis of nanoparticles using oblique incident ultrasound pulses

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1. Introduction

Dynamic ultrasound scattering (DSS) is a technique that uses megahertz frequency ultrasound to determine particle size from the diffusion and sedimentation motion of particles. It is an ultrasonic analog of dynamic light scattering, but the use of long wavelength ultrasound simplifies wavelength-dependent hydrodynamic interactions and allows particle size evaluation in concentrated suspensions.[1)]

In a previous study, we succeeded in measuring nanoparticles with high precision using a focused transducer.[2)] The use of high-power, high-speed pulsed ultrasound had the problem of unexpected acoustic flow which perturbs particle motion, but this effect could be eliminated by reducing the thickness of the cell. In order to reduce the effects further, it was necessary to use a cell thinner than 0.3 mm, but this will cause problems such as interference with the reflected echo signals in the analysis.

Fig. 1(a) shows the reflected waveform from a conventional 0.34 mm cell. Since the scattered wave of the particle suspension I_S exists between the two cell walls, the area indicated by the red line should be analyzed to evaluate the particle size. Here, if the path length is shortened, it will be easier to screen out the adverse effects of acoustic force even with stronger ultrasound. Thus, the thickness was further reduced to 0.11 mm as indicated in Fig. 1(b). However, the back scattered wave I_S is buried by the reflected wave R in front of the cell, and the signal unfortunately includes the unfavorable reflected echoes. Therefore, it is very difficult to analyze nanoparticles, especially those with weak scattering intensity.

Therefore, in this study, thin-film DSS measurements of about 0.1 mm were performed by positioning the cell at an angle so that the reflected echo (R) in front of the cell is reflected obliquely and do not enter the receiver as shown in Fig. 1(c). By making the cell thinner than before, we investigated whether it is possible to avoid unfavorable acoustic flow and to speed up and improve the accuracy of measurements of nano and submicron particles by the short pulse repetition time. The angular dependence of the tilt was also measured to demonstrate the validity of the oblique angle measurement.

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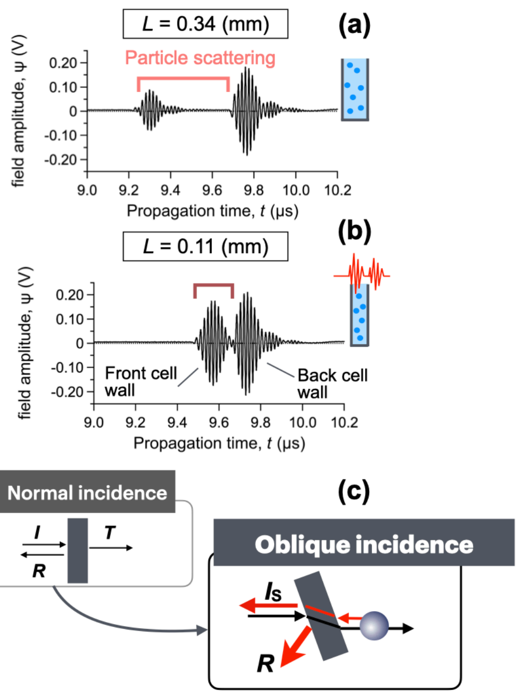

Fig. 1 Examples of reflected echoes from (a) a thick cell (L=0.34 mm) and (b) a thin cell (L=0.11 mm). (c) schematic figure of the oblique incidence setup employed in this study.

2. Experiments

Ultrasonic pulses are transmitted from the transducer and incident on the particle suspension using an iSL BLP-12R remote pulser. Backscattered waves from the particles were recorded with a high-speed digitizer at 3 Gs/s. A focus transducer with center frequency of 40 or 75 MHz was used. Measurements were taken in water controlled at 25°C. A 9 μm thick polymethylpentene (PMP) film was used as the window material. A PMP plate was used on the back of the cell. Between the film and the plate, 20 to 50 μl of sample was inserted to make a sample cell. The thickness of the cell was varied by adjusting the volume of liquid. For the measurement of angular dependence, a protractor was placed directly under the cell and the angle was varied from –30 to +30° in 5° increments.

Silica particles of the Sicaster series manufactured by Micromod were used as standard particles. The squared volume weighted TEM radius was 48.4 nm. Experiments were performed at a sample concentration of 5wt%. Styrene/acrylic acid copolymer (St-Ac) particles from Mitsubishi Chemical were used and diluted from the original solution to 1wt% with distilled water. The weighted radius was 130.4 nm. They were filtered through disposable syringe filters of 200 nm or 450 nm, respectively.

3. Results

The upper panel of **Fig. 2** shows the correlation functions $g^{(1)}(\tau)$ measured with a cell thickness of

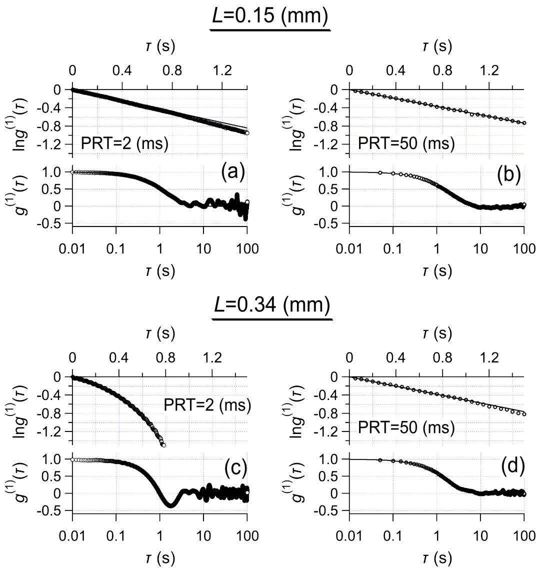

Fig. 2 $g^{(1)}(\tau)$ for (upper) a thick cell (L=0.15 mm) and (lower) a thin cell (L=0.34 mm).

0.15 mm and pulse repetition times PRT= (a) 2 ms and (b) 50 ms. The lower panel shows $g^{(1)}(\tau)$ for a cell thickness of 0.34 mm with PRT= (c) 2 ms and (d) 50 ms. A sample of 1wt% St-Ac particles with a radius of 130.4 nm was used for the measurements. In general, a shorter PRT improves the temporal resolution of the correlation, but also increases the unexpected acoustic flow effects. Fig. 2(a) shows the results of the oblique incidence method with a cell thickness of 0.15 mm. The effect of acoustic force is reduced and concentrated corrected R_h was 111.1 (nm). This method also allows the short measurement time of only 3 minutes. On the other hand, at PRT=2 ms in Fig. 2(c) with a conventional cell thickness of 0.34 mm, adverse effect was observed due to acoustic force, resulting in oscillations in the observed correlation function. When the PRT was set to 50 ms, R_h = 123.6 (nm) and R_h was 119.1 (nm), respectively, were not adversely affected by acoustic flow, although the measurement took a long time as shown in Figs 2(b) and 2(d).

Fig. 3(a) shows R_h measured at various angles of incidence. 5wt% silica particles with a radius of 46.5 nm with concentration correction were used. From Fig. 3(b), at an angle of 0°, R_h evaluated by the conventional method was significantly smaller (15.6 nm) (×). On the other hand, the correct particle size could be measured when the cell was inclined in the range of ±5 to 30°. Fig. 3(b) shows the angular dependence of the Fourier amplitude of the reflected wave in front of the cell. The maximum amplitude was observed at an angle of 0°, and the reflected wave became smaller as the angle increased.

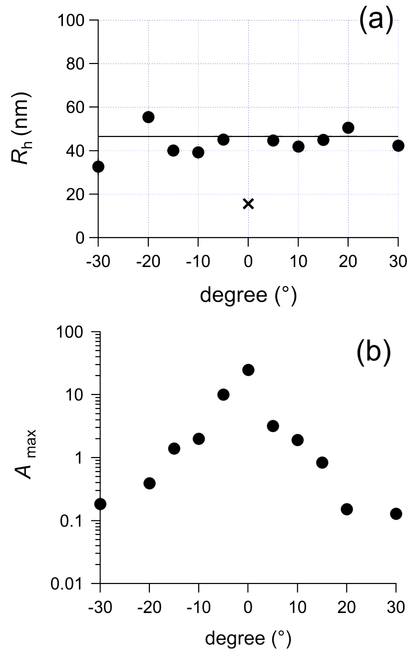

Fig. 3 Angular dependence of (a) apparent hydrodynamic radius R_h and (b) amplitude of the reflected wave on the front cell wall.

4. Conclusions

The disturbance of particle motion due to acoustic radiation force can be shielded by reducing the cell thickness. On the other hand, the cell thickness has so far been limited to 0.3 mm because the cell reflected waves overlap the analysis range in the conventional parallel setup. This time, by making the cell surface oblique in the range of ±5 to 30°, it was possible to receive only the scattered wave without allowing the reflected wave to participate in the detector. As a result, further shielding of acoustic force was successfully achieved by using a thinner cell. In addition, by reducing the effect of reflected waves, the correct particle size could be determined.

References

1) K. Kitao, M. Tani, M. Yamane, S. Inui, M. Yamada and T. Norisuye, Colloids Surf. A: Physicochem. Eng. Asp. **690**, 133807 (2024).
2) K. Kitao and T. Norisuye, Ultrasonics **126**, 106807 (2022).