Competition of Particle Dynamics Accompanying Diffusion and Hydrodynamic Velocity Fluctuations Examined by Dynamic Ultrasound Scattering Method

Mayuko Hirano[1‡], Kana Kitao[1], and Tomohisa Norisuye[1] ([1]Grad. School of Sci. & Tech., Kyoto Institute of Technology)

1. Introduction

When longitudinal ultrasound pulses in the MHz frequency range are impinged on micron-sized particles with the particle diameter comparable with the wavelength, ultrasonic scattering is observed. Micron-sized particles exhibit sedimentation motion in addition to Brownian motion in liquid, and the scattering amplitude varies as a funciton of observation time since the particles are moving under both the thermal fluctuations and the hydrodynamic interactions. Such time-variation of the particle velocity, called velocity fluctuations, can be analyzed through the time correlation function of the scattering amplitude[1].

When the size of the particles is approximately less than 1 micrometer, Brownian motion becomes dominant and the hydrodynamic interaction is considerably weakened. Particularly in dilute systems, the size of particles can be determined from diffusion coefficient measurements using the Stokes-Einstein equation. On the other hand, for particles larger than a few micrometers, the hydrodynamic interactions play an important role. If an ultrasonic transducer is placed in the settling direction (Z-direction) of the particles, the settling velocity of the particles associated with the hydrodynamic interactions can be evaluated[1].

In our previous study, we have proposed a simple and accurate method for particle size distribution analysis, taking advantage of the ultrasonic phase detection[2]. This method enables us to obtain the particle size distribution by phase analysis of the sample position dependence of Stokes velocity and scattering intensity, where the particle size is evaluated from the Stokes velocity and the number of particle is determined by ratio of the scattered intensity to the given single particle intensity. In such measurements in the Z direction, the average sedimentation velocity component and its deviation can be analyzed, whereas in experiments in the horizontal (Y) direction, it is possible to measure the velocity deviation solely. This is because the horizontal beam is perpendicular to the sedimentation, so the average component does not contribute.

A model of velocity fluctuation of microparticles was proposed by Caflisch and Luke[3], but due to the inclusion of unknown proportional constants in this model, a methodology for calculating particle size from the measured velocity fluctuation has not yet been established. Therefore, in this study, quantitative analysis of sedimentation velocity fluctuations of various particles was performed by ultrasonic scattering analysis along the Y direction. The beauty of the dynamic ultrasonic analysis is that it can distinguish between Brownian motion, which is proportional to the first order of time, and hydrodynamic velocity fluctuations, which are proportional to the second order of time, in terms of the square displacement of the particle coordinates associated with particle motion[4]. Therefore, in this study, we simultaneously quantified the competing dynamics of diffusion and sedimentation velocity fluctuations.

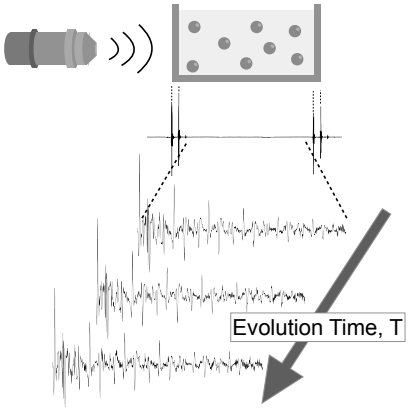

Fig. 1 Schematic representation of the dynamic ultrasound scattering (DSS) method.

2. Experimental section

Fig. 1 schematically shows the setup of the dynamic ultrasonic scattering method. Electrically excited pulses of –300 V spikes are irradiated to a 20 MHz or 30 MHz longitudinal ultrasonic transducer. Using the same transducer to receive echoes from a polystyrene cell with a path length of 10 mm and a thickness of 1 mm, particle scattering can be observed in addition to reflected waves from the cell. Unless otherwise stated, the sample height was 40 mm. Such scattered waves are acquired in pulse repetition time at 10 ms, for example. By analyzing the autocorrelation function for the observed time at a fixed pulse time, the particles motion at a pulse time, i.e., corresponding location in the sample, can be obtained.

3. Results

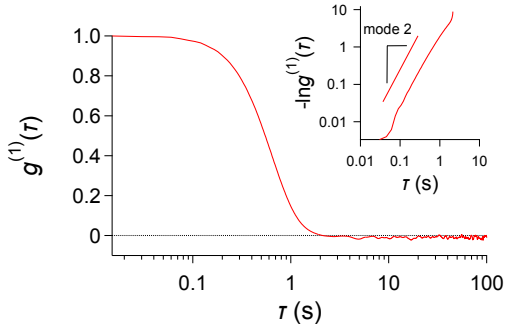

Fig. 2 An example of the correlation function obtained for the 1wt% polydivinylbenzene (PDVB) particle of 15 μm diameter.

Fig. 2 shows an example of the correlation function for a 1wt% polydivinylbenzene (PDVB) particle of 15 μm diameter. Taking the natural logarithm of the correlation function and plotting both logarithms, the exponent of the delay time was 2. This indicates that the particle motion is not a Brownian motion with $\langle x^2 \rangle = 2D\tau$, but a velocity fluctuation with hydrodynamic interaction of $\langle x^2 \rangle = \Delta V^2 \tau^2$. Analyzing such a measurement at all positions in the sample, i.e., at different pulse propagation time, one can quantify the standard deviation of the velocity depending on the position in the sample. Such velocity fluctuations were formulated by Caflisch and Luke (CF). However, unlike Brownian motion, velocity fluctuations take time to enter a steady state. Although not shown here, the experimental data decreased exponentially with observation time. Therefore, the volume fraction dependence of the velocity fluctuation after reaching the steady state was quantitatively evaluated by the CF theory. According to the CF theory, the velocity-derived ΔV can be described by using the volume fraction ϕ, sample path length L, and particle radius a in addition to the terminal velocity V_0 as follows:

$$\Delta V = C_y V_0 \sqrt{\frac{\phi L}{a}} \ .$$

Here, since the proportional constant C_y is unknown, in contrast to the measurement of the diffusion coefficient of Brownian motion, a particle size analysis cannot be easily performed. Therefore, in this study, the cell constant C_y was investigated by analyzing standard particles with known particle sizes.

Fig. 3 summarizes the results; C_y was a constant (C_y = 0.12) for relatively large particle diameter $d = 2a$ of 5 μm. On the other hand, C_y increased with decreasing d. Mucha et al.[5] predicted a value of 0.28, but C_y = 0.12 on the large particle size side was smaller than these values. In the presentation, more experiments will be conducted including the submicron region, where Brownian motion is more relevant.

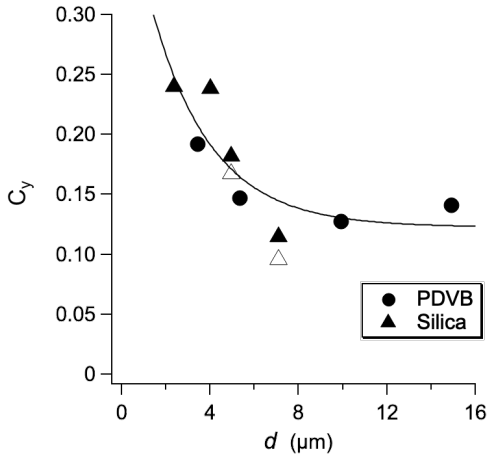

Fig. 3 d dependence of C_y obtained for the PDVB and silica particles. The silica particles of d = 5.5 and 7 μm were performed in a 40 mm high polystyrene cell (open triangles). On the other hand, a polyphenylenesulfide cell with a height of 80 mm was also used to verify the effect of height (solid triangles).

4. Conclusions

Measurement of nanoparticles in liquids can be easily performed by dynamic light scattering, but analysis of micron particles beyond the wavelength of light is not easy in terms of multiple scattering and complex scattering functions. In this study, we provide a methodology to easily evaluate the size of micron-sized particles in liquids using dynamic ultrasonic scattering. Micron-sized particles accompany significant hydrodynamic interactions even in dilute systems. We have shown how to take advantage of this fact to calculate the particle size from the velocity fluctuations. In this study, the unknown cell constant was determined to 0.12 at the large particle size limit (above 5 microns), which is larger than the values reported in the literature. In the future, we plan to investigate the submicron region and provide a methodology that supports a wide range of spatial regimes.

References

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