Studies on the sedimentation dynamics of silica suspensions by means of dynamic ultrasound scattering method
動的超音波散乱法によるシリカ系懸濁微粒子溶液の沈降ダイナミクスに関する研究

Kazuki Sugita[1†], Tomohisa Norisuye[1], and Qui Tran-Cong-Miyata[1] ([1]Kyoto Institute of Technology)
杉田　一樹[1†]，則末　智久[1]，宮田　貴章[1] ([1]京都工芸繊維大学　工芸科学研究科)

1. Introduction

Dynamic sound scattering method, DSS has been developed to investigate the dynamics of micron-sized particles during sedimentation. The technique has several advantages compared to the conventional optical techniques, such as applicability to highly turbid solutions, sensitivity to the depth information, and so on. In the previous studies, hydrophobic particles, such as polystyrene microparticles, were dispersed in water with a surfactant where the effects of electrostatic interactions were not taken into account[1]. In this study, the effect was investigated by using silica colloids in order to elucidate the role of the electrostatic interactions as well as the hydrodynamic interactions.
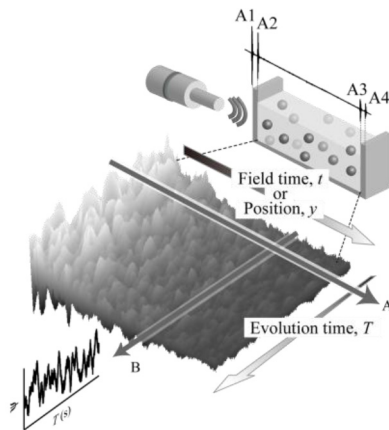
2. Theory

Fig. 1 Schematic illustration of DSS setup

As an ultrasound pulse propagates through a cell containing a suspension of microspheres, four reflected echoes A1, A2, A3, A4 from the cell walls are observed as shown in Fig. 1. If there are noticeable scattering contributions from the microspheres, the complicated scattering patterns could be observed between A2 and A3 as well. The pulse wave ψ for the scattering component may be written as:

$$\psi(t) = A(t)\cos[2\pi f_c t + \Phi(t)] \qquad (1)$$

where t is the field-time, f_c is the central frequency, A and Φ are respectively the amplitude and phase of the temporal pulse. In the case of the backscattering geometry, t contains the spatial information of the scatters along the beam direction enabling us to obtain the information about the location of the particles as indicated by the line A in Fig. 1. Since the time difference between A2 and A3 is fairly short, c.a. 13.5 µs for the round trip in a cell with the size $L = 10$ mm, the time-evolution of the pulse can be visualized as an image of the sound field by successive recording of pulses at an interval $\Delta T(\sim\text{ms})$. As the results, we obtain the time fluctuations of the scattered signals along the axis of the evolution-time, T, as indicated by the line arrow B. The characteristic time of the fluctuations may be evaluated[1] by the time correlation function $g^{(1)}(\tau)$ defined by:

$$g^{(1)}(\tau) = \frac{\langle\psi(t,T)\psi^*(t,T+\tau)\rangle_T}{\langle\psi(t,T)\psi^*(t,T)\rangle_T}$$
$$= \exp\langle[-iq\cdot\Delta r(\tau)]\rangle_T \qquad (2)$$

where Δr is the displacement of the microspheres during the lag time τ, q is the magnitude of the scattering vector, and asterisk indicates complex conjugate. The bracket indicates the average over the evolution time T. After trivial calculation, the standard deviation of the horizontal component of velocity $\langle\delta V_y^2\rangle^{1/2}$ can be obtained as:

$$g_y^{(1)}(\tau) = \exp\left(-\frac{1}{2}q^2\langle\delta V_y^2\rangle\tau^2\right) \qquad (3)$$

since the average velocity for horizontal direction is zero and:

$$\langle(\Delta r)^2\rangle = \langle\delta V_y^2\rangle\tau^2 \qquad (4)$$

3. Experimental

3.1 Samples

Mono-disperse silica and polystyrene microspheres with particle diameter of 4.84 μm and 4.75 μm, respectively, purchased from Sekisui Chemical Co. Ltd were used. Three types of suspensions were prepared: (1) polystyrene particles in distilled water containing 0.2% sodium dodecyl sulfate (SDS), (2) silica particles in distilled water without any surfactant and (3) silica particles in 1mM sodium chloride aqueous solution. Disposable polystyrene rectangular vessels with the dimension 10 x 10 x 40 mm^3 and the wall thickness 1mm were used as the sample cells.

3.2 Apparatus

Negative impulse emitted from a pulser/receiver (iSL Pulser) was transferred to a 20MHz-longitudinal plane wave transducer (B20K2I-M) immersed in a water bath to generate broadband ultrasound pulses. The same transducer received the reflected or scattered ultrasound waves. The obtained signals were then amplified by the receiver, followed by successive recording with a 14bit high-speed digitizer (Compuscope CS14200) at the sampling rate 200Ms/s.
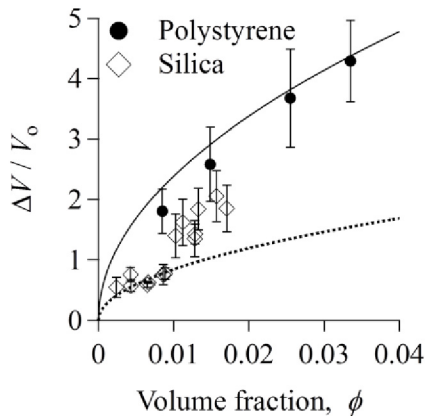
4. Results and discussions

Fig. 2 Volume fraction dependence of the normalized velocity fluctuations.

Fig. 2 shows the volume fraction dependences of the velocity fluctuations for the polystyrene (solid circle) and the silica particles (open diamond) where the standard deviation of the horizontal velocity is abbreviate as $\langle \delta V_y^2 \rangle^{1/2} \equiv \Delta V$, and V_0 is the terminal velocity. In the previous studies, the volume fraction dependence of ΔV has been well reproduced by the Caflisch-Luke(CL) theory[2]. However, in the case of the silica particles in water, the results were significantly different from those expected from the CL theory. While the velocity fluctuations followed the CL theory at relatively

low volume fraction, i.e. $\phi < 1\%$, an anomalous upturn in the velocity fluctuations was observed at the higher volume fraction. This behavior may be ascribed to the electrostatic interactions. In order to confirm the hypothesis, effects of salt to the velocity fluctuations of the silica suspensions were investigated.
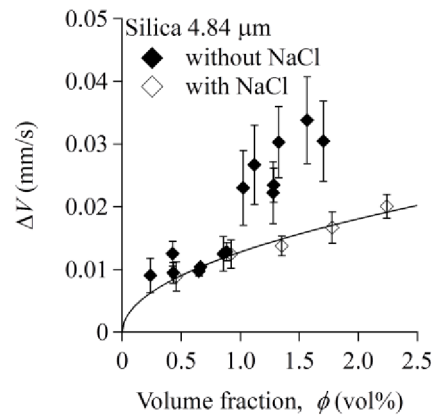

Fig. 3 Effects of salt on the volume fraction dependence of the velocity fluctuations

Fig. 3 shows the dependence of velocity fluctuations obtained for the silica particles dispersed in 1 mM sodium chloride aqueous solution. Addition of salts resulted in the reduction of the velocity fluctuations. Now the data was well reproduced by the CL theory. It was found that the electrostatic interactions as well as the hydrodynamic interactions played an important role for the analysis of sedimentation dynamics.

5. Conclusions

Sedimentation dynamics of the suspensions of silica particles was investigated by means of DSS. The dynamics significantly differed from the polystyrene suspensions. However, when the electronic interactions were screened out, the velocity fluctuations were still reproduced by the Caflisch-Luke theory. The present study demonstrated the importance of the electrostatic interactions which were neglected in the previous studies.

References
1. M. Kohyama, T. Norisuye, and Q. Tran-Cong-Miyata: *Macromolecules*, **42** (2009) 752-759.
2. R. E. Caflisch and J. H. C. Luke: *Phys. Fluids* **28** (1985) 759-760.