

Studies on Nanoparticle Suspensions Probed by Frequency-Domain Dynamic Ultrasound Scattering Techniques 周波数ドメイン動的超音波散乱 (FD-DSS) 法による懸濁溶液中のナノ粒子解析

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1. Introduction

Recently, dynamic ultrasound scattering (DSS) technique, which is an acoustic analog of dynamic light scattering (DLS) method, opened a new route to investigate the dynamics of highly turbid suspension of nanoparticles^[1]. It has several advantages compared to DLS. First, since the field time-correlation function can be directly evaluated by the fluctuations of the pressure amplitude, the conversion from the intensity to field correlation function is unnecessary. Second, the technique can be applied to a highly turbid suspension, motivating us to utilize it for studying concentrated suspensions, which is difficult to be observed by conventional optical techniques. Third, the frequency dependence of the relaxation time can be obtained by a single acquisition. Therefore, the measurement of the angular dependence is unnecessary to obtain the average particle size. Furthermore, this fact gives a new insight into understanding the dynamics over a wide range of the length scales by a single step acquisition. Thus, the DSS technique is considered to be a useful technique to probe particles in liquid in a range from several tens of nanometers to several tens of micrometers. On the other hand, since the wavelength of ultrasound is still considerably long compared to visible light, it is important to study the sensitivity and reliability of the technique. For example, the dependence of particle-concentration and of the salt-concentration have not explored yet. In the previous papers^{[1][2]}, while the nanometer-sized silica particles were investigated, the particle concentration was fixed at 5wt%. In addition, increasing the salt concentration could lead to screening of the electrostatic interactions. As the results, the particle size could be affected by the presence of the electric double layer. Therefore, in this study, silica nanoparticle suspensions in a dilute regime were studied by the DSS technique to systematically investigate the effect of salt on the hydrodynamic radius, R_h .

2. Experiments and Results

Silica nanoparticles were synthesized by the hydrolysis and condensation of alkoxide in the presence of base catalyst, so-called a Stöber method^{[3][4]}. After the purification, the particles were calibrated by Field-Emission Scanning Electron Microscopy (FE-SEM; JEOL JSM-7600F) followed by an image analysis to extract the particle size distribution.

The calibrated results were summarized in **Table I**, where R_{SEM} , σ and CV, respectively, represent the average radius, standard deviation of the particle size obtained by FE-SEM and the coefficient of variation defined by $CV \equiv \sigma/R_{SEM}$.

Table I Calibrated data of the average radius R_{SEM} , the standard deviation σ , and the coefficient of variation CV by FE-SEM.

R_{SEM} (nm)	σ (nm)	CV
43	6.47	0.15
53	7.52	0.15

Two series of silica suspension having different particle concentration, C , and salt concentration, C_{NaCl} , were prepared in this study. Among them, only the result of $R_{SEM} = 43$ nm will be demonstrated in this paper. The synthesized particles were dispersed in the distilled water, and the C dependence of the silica suspensions was examined in range 0.1 - 1wt%.

The motion of particles in suspension may be analyzed by a time-correlation function. For monodisperse particles, it is given by,

$$g^{(1)} = \exp(-\Gamma\tau) \quad (1)$$

for the diffusive nanoparticles where Γ is the decay rate, and τ is the time lag. If the sample is polydisperse, the first cumulant is evaluated by an initial slope of the correlation function to give the decay rate expressed by,

$$\Gamma = Dq^2(1 + k_D C + \dots) \quad (2)$$

where q is the magnitude of the scattering vector, D is translational diffusion coefficient, and k_D is the second virial coefficient of the DSS data.

Fig. 1 shows a series of time-correlation functions obtained for the silica particle in water with $C = 0.1, 0.5$ and $1\text{wt}\%$ observed at 31 MHz . Although the data are more or less noisy at the lowest concentration of $0.1\text{wt}\%$, it is rather surprising that the DSS experiments with the wavelength of $50\ \mu\text{m}$ allow us to probe the nanoparticle in such a low concentration regime. This is because of the improved algorithm of the Frequency-Domain (FD) DSS analysis and the good transducer response employed in this study.

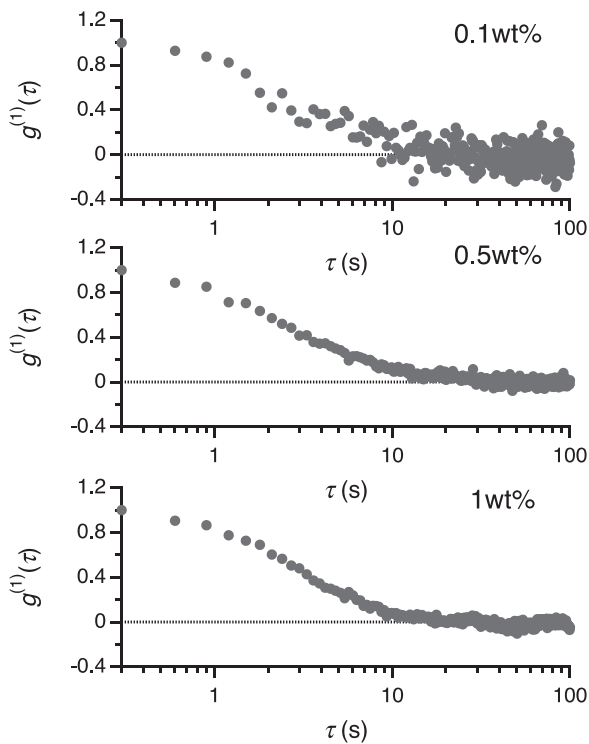


Fig. 1 A series of time-correlation functions obtained for the silica particle in water with $C = 0.1, 0.5$ and $1\text{wt}\%$ observed at 31 MHz .

Fig. 2 shows the C dependence of D with different C_{NaCl} where the dashed line is the value of D expected from the SEM analysis for $R_{\text{SEM}} = 43\text{ nm}$. While D decreased with C for $C_{\text{NaCl}} = 0\text{ mM}$, D increased with C_{NaCl} at a fixed C . Although the electrostatic interaction could lead to increase or decrease of D with C , depending on the sign of the second order coefficient of the osmotic compressibility, the data clearly indicated that the D obtained by DSS approached the dashed line of $R_{\text{SEM}} = 43\text{ nm}$. The R_h can be obtained by the so-called Stokes-Einstein relation,

$$D = k_B T / 6\pi\eta R_h \quad (3)$$

where $k_B T$ is the Boltzmann energy and η is the solvent viscosity of the surrounding liquid. Therefore, an increase in D with C_{NaCl} corresponds to a decrease in the apparent radius of the silica particles. It was deduced from the above results that the electrostatic interaction was screened out with

C_{NaCl} , and the thickness of the electric double layer decreased by addition of salt.

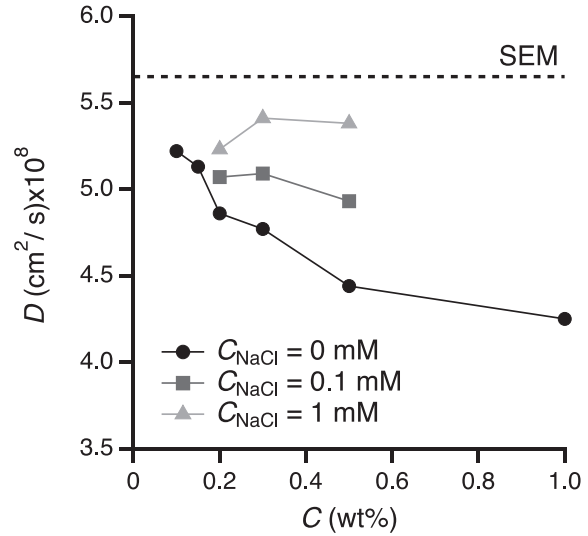


Fig. 2 The concentration dependence of diffusion coefficient under different NaCl concentration.

3. Conclusions

The FD-DSS experiments were carried out at a low concentration regime of the silica nanoparticles to test the potential of the DSS techniques. The apparent particle radius decreased with increasing the salt concentration, suggesting that the effect of electrostatic interactions is screened out to have a thinner electric double layer.

4. References

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