Dynamics of Nanoparticles in Concentrated Suspension Examined by Focused-Beam Dynamic Ultrasound Scattering Method

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1. Introduction

Dynamic ultraSound Scattering (DSS) technique is a particle analysis method based on the analogy between visible light and ultrasound, which enables the evaluation of particle size from the diffusion coefficient[1]. The Dynamic Light Scattering (DLS) method is suitable for the analysis of nanoparticles, while the DSS method can be applied for the analysis of submicron to micron particles. Nevertheless, recently, we have achieved the analysis of nanoparticles with a diameter of 30 nm by the DSS method using focused-ultrasound[2]. This method utilizes a high-frequency focused transducer with a high pulse repetition rate to increase the temporal resolution. In general, when such high-energy ultrasound is used, the acoustic radiation pressure accelerates the particle motion[3]. Thus, the DSS method underestimates the particle size because of the overestimation of the diffusion motion of the particles[4]. To overcome the problem, the thickness of the sample was reduced to a few hundred micrometers. Then, the unexpected acoustic flow was suppressed, thereby achieving the non-destructive diffusion measurement without external acoustic flow. The DSS method produces the correlation function of particles, which further allows us to evaluate the collective diffusion coefficient from its decay rate. A microparticle in Brownian motion accompanying thermal fluctuations can be represented by the Stokes-Einstein translational diffusion coefficient D_0 in the infinite dilution state. The diffusion behavior of nanoparticles in concentrated systems has been discussed from simulations, theoretical analysis, and experiments using the DLS and dynamic X-ray scattering methods[5, 6]. Compared to light and x-rays, ultrasound, which has a longer wavelength, has the potential to access high concentrations at the long wavelength regime. This may make discussion and analysis easier to interpret the scattering behavior and the collective diffusion. In this study, the focused-DSS method was used to measure charged silica nanoparticles with volume fractions from 0.03 - 28.3% and the concentration dependence of their diffusion coefficient was investigated.

2. Experimental section

Ultrasonic pulses were irradiated into a suspension from a focused 40 MHz transducer (Toray) placed in water at 25±0.1°C. A remote pulser BLP-12R manufactured by iSL was used as the spike pulser, and backscattered waveforms were recorded with a 16 bit high-speed digitizer (GaGe Applied) with 200 mega samples/sec, followed by time-correlation analysis by the FD-DSS method[7]. 9 µm thick-polymethylpentene (PMP) film was used as the cell window. The sample thickness was 400 - 600 µm. The silica particles of 30, 50 and 100 nm diameter were purchased from micromod, and those of 500 nm diameter was purchased from Nippon Shokubai. The concentration of particles of 30 and 50 nm diameter was 2.5wt%, and 100 and 500 nm diameter was 1wt%. For concentration-dependent experiments, silica particles (ST-XL) from Nissan Chemical were employed. The volume fractions ϕ were varied from 0.03 to 28.3%.

3. Results

The DSS method has been used to detect 55 nm-silica particles at ϕ=2.5%[1]. However, due to the weak scattering intensity of the nanoparticles, it was necessary to perform the measurement at least for 24 hours and accumulate the data. **Fig. 1** shows the correlation functions $g^{(1)}(\tau)$ of silica nanoparticles (and submicron particles) with nominal diameters of 30, 50, 100, and 500 nm, measured using a 40 MHz focused transducer. The solid markers are experimental data and the solid lines are fitted results. The pulse repetition time was 10 ms and the number of recordings was 100,000 times for 15 minutes.
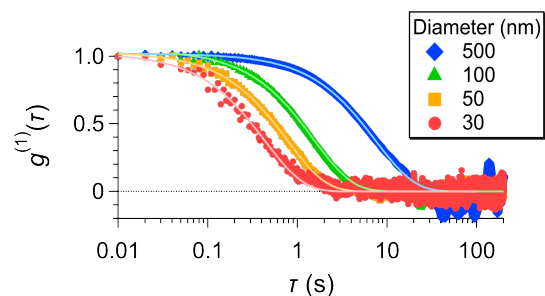

Fig. 1 Correlation functions obtained for the silica particles at 30, 50, 100, and 500 nm.

Cumulant analysis revealed that the hydrodynamic diameters d calculated from the diffusion coefficients D of the particles are 24.6, 43.6, 100.4, and 496 nm, respectively.

Fig. 2 shows the correlation functions obtained for the silica particles with ϕ=0.06, 3.26, 16.5, 25.9%. As indicated by the dotted arrow, the relaxation time decreased from 0.06 to 16.5vol%, followed by increase up to 25.9vol% (solid arrow).
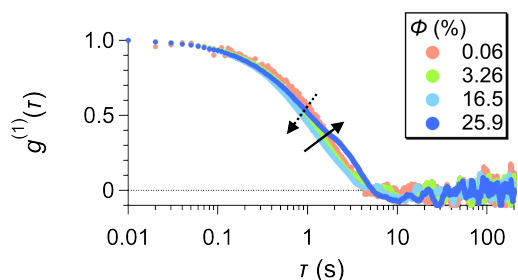

Fig. 2 Correlation functions obtained for the silica particles (ST-XL) with ϕ=0.06, 3.26, 16.5, 25.9%.

Fig. 3 shows the ϕ dependence of D obtained for the silica particles with ϕ of 0.03 - 28.3% (solid markers). The silica particles in the dried-condition were also observed by electron microscopy (TEM). The resultant number average diameter was 66.7 nm according to the particle counting analysis. Since the DSS technique measures the time variation of the ultrasonic scattered intensity, which is proportional to d^6, the evaluated D is intensity weighted. Thus, D ($\propto 1/d$) is weighted by the fifth power of d, which is called the z-average diffusion coefficient. The corresponding diameter was 87.5 nm. The D expected from TEM was 5.61×10^{-8} (cm²/s) which is shown by the dashed line in Fig. 3. At the low ϕ, D seemed to be a constant although the values are larger than that expected from the TEM analysis. This means the hydrodynamic diameter obtained by the DSS method is smaller than that expected from TEM. Then, D increased with ϕ up to ϕ=19.8%. D is known to be determined by the ratio of the hydrodynamic factor $H(q)$ and structure factor $S(q)$.
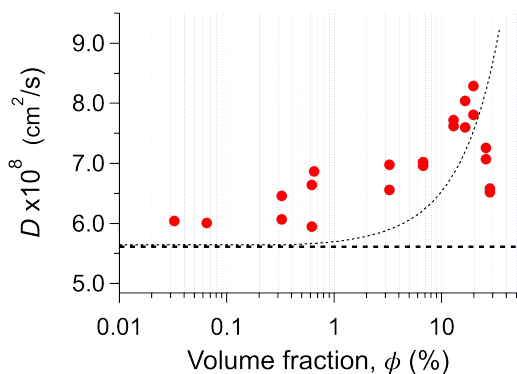
That is, $D=D_0 H(q)/S(q)$ where q is the magnitude of the scattering vector. At the low ϕ, D was reported to increase due to the dominant decrease in $S(q)$ rather than the gradual decrease in $H(q)$. The expected curve for uncharged particles, $D=D_0(1+1.4\phi+0.91\phi)$[8] was shown in Fig. 3 as the dotted curve. The equation considers the 3-body interactions and valid up to 50vol% for uncharged particles. Experimentally, above 19.8vol%, the effect of $H(q)$ may become dominant, resulting in a significant decrease in D. While the experimental maximum was observed at 19.8vol%, the theoretical maximum indicated by the dotted lines are far higher concentration than the presented concentration range of abscissa in this figure. The diffusion of silica particles obtained in the experiment is considered to have a greater osmotic modulus due to the influence of the charge, and the maximum are represented at lower concentrations than uncharged particles.

4. Conclusions

The newly developed focused-DSS method enables measurement of a wide range of particle-size from 30 to 500 nm. D for the silica particle was measured up to 28.3vol% where maximum of D was observed at 19.8vol%. Unlike the DLS method, the frequency dependence is expected to be rather simple (no q-dependent oscillations in both $S(q)$ and $H(q)$) for ultrasound with longer wavelengths. In the future, we will directly measure the friction coefficient and osmotic modulus of particles and attempt to calculate these correction factor, as well as the particle size from the diffusion coefficient at arbitrary concentration.

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Fig. 3 ϕ dependence of D obtained for the silica particles (ST-XL).