

Nano- and Submicron-particle Sizing in Concentrated Suspension by Dynamic Ultrasound Scattering Technique

Misaki Tani^{1‡}, Kana Kitao¹, Manami Yamane¹, and Tomohisa Norisuye^{1*} (¹ Grad. School of Sci. & Tech., Kyoto Institute of Technology)

1. Introduction

The dynamic ultrasound scattering (DSS) method is a nano-particle sizing technique which utilize information about the particle motion and can be used without dilution of sample for optically opaque media. However, because of ultrasound, particle motion was disturbed by excess acoustical energy, e.g., the acoustic radiation pressure exerted on diffusing nanoparticles. In the previous studies, this problem was avoided by preparing thin sample, where the effect of acoustic radiation force was fairly suppressed. Therefore, now one can utilize high-frequency, high-power (focused-beam) transducers at the higher pulse repetition time (PRT). As a result, nanoparticle sizing was achieved up to 30 nm in diameter in a short time and with high accuracy¹⁾.

Simulations and theoretical analyses have been performed on the diffusive motion in concentrated systems, and other electromagnetic wave scattering methods have been used in experiments^{2,3)}. The diffusion coefficient, D in concentrated systems depends on the volume fraction ϕ as well as the magnitude of scattering vector q , where q is a geometrical parameter related to the wavelength and scattered angle. This resulted in the break-down of so-called the Stokes-Einstein equation, which is a convenient relation to obtain the particle size from the single particle diffusion coefficient D_0 . The collective diffusion coefficient D_c of a concentrated system is expressed as $D_c(q, \phi) = D_0 H(q, \phi) / S(q, \phi)$ using the hydrodynamic factor H and the structure factor S . For short wavelengths and large q (i.e., the case for electromagnetic scattering), the q -dependence oscillates in a complicated manner. For ultrasonic waves with long wavelength with respect to the scatterer and small q , the q -dependence is expected to be relatively simple. In addition to the fact that DSS using ultrasonic waves can be used to measure even turbid or colored samples, where light cannot penetrate, it is believed that the diffusion coefficient can be evaluated up to high concentrations without the need for complex q -dependence.

In this study, DSS measurements were made with nano- to sub-micron particles ranging from tens to hundreds of nm, from 1wt% to 40wt%, and converted from diffusion coefficient to particle size.

2. Experiment

The time-correlation function of the back-scattered echoes during particle motion was calculated by the FD-DSS method⁴⁾ at a short time-window to evaluate D from the relaxation time τ . D may be converted to the particle size using an appropriate model as explained later. A spike-remote pulser BLP-12R manufactured by iSL, and focused transducers with center frequencies of 25, 30, and 40 MHz (Toray) were respectively used as the ultrasonic pulser and transducers. Received waveforms were recorded with a high-speed digitizer (GaGe Applied) with 3 Gs/s, and 12 bit vertical bit depth. Measurements were taken in a water tank controlled at $25 \pm 0.1^\circ\text{C}$. The sample cells were made of polymethylpentene (PMP) film (9 μm) and 1 mm-plates, with a liquid volume of 20 ~ 60 μL and a cell thickness of 0.2 ~ 0.5 mm.

Silica particles (ST-CM, ST-30L, ST-XL, MP4540M) manufactured by Nissan Chemical Co. were used as the samples. According to the manufacture, the DLS diameters obtained for dilute samples are 22 nm, 45 nm, 80 nm, and 450 nm, respectively. Ultrapure water and distilled water were used for sample dilution. The silica particles in the dry state were also observed by transmission electron microscopy (TEM).

3. Result

3.1 Time-correlation function

Fig. 1 shows the time correlation function $g^{(1)}(\tau)$ obtained for the silica particle with different diameters at (a) 5wt% and (b) 30wt%. To consider that the measurements were made at different frequencies, τ is multiplied by q^2 . The markers are experimental data, and the lines are fitting results. The black line is the result evaluated from the initial slope of $\ln g^{(1)}(\tau)$.

In the DSS analysis of nanoparticles, the decay rate Γ is obtained from the initial slope of $\ln g^{(1)}(\tau)$, and the diffusion coefficient is evaluated from $\Gamma = Dq^2$. From this method, a z-average diffusion coefficient D_z is obtained where weighting is performed according to the sixth power of the

E-mail: [‡]m3672011@edu.kit.ac.jp, ^{*}nori@kit.jp

particle size. Therefore, the presence of a small number of large particles has a significant effect on the correlation function, and then the resulting particle size may be evaluated to be larger.

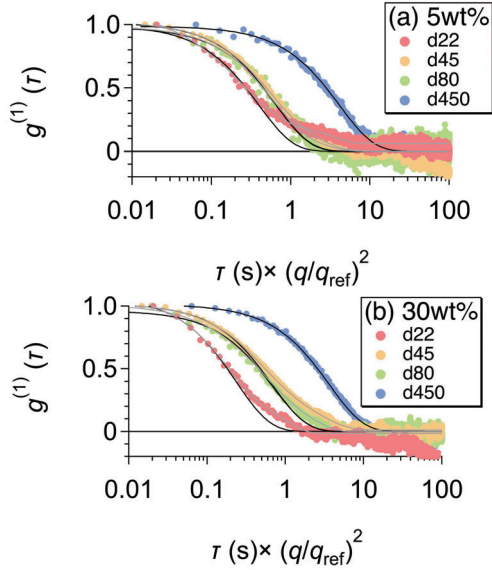


Fig. 1 $g^{(1)}(\tau)$ for the silica particle suspensions at (a)5wt% and (b)30wt%.

For smaller particle size, the correlation functions in **Fig. 1** exhibited a long-time decay. Due to this contribution, the average particle size was overestimated. This suggests that the sample contains a small number of agglomerates. Since two relaxations were clearly observed, the correlation function was fitted using equation (1) as the sum of the two relaxations, with the short-time relaxation as τ_f and the long-time relaxation as τ_s . In the following analysis, the diffusion coefficient of nanoparticles was obtained from the fast relaxation time. The result is shown by the gray line. This simultaneous analysis allowed us to evaluate the motion of nanoparticles and agglomerates respectively from the fast and slow modes.

$$g^{(1)}(\tau) = A \exp\left[-\left(\frac{\tau}{\tau_f}\right)^{\beta_f}\right] + (1 - A) \exp\left[-\left(\frac{\tau}{\tau_s}\right)^{\beta_s}\right] \quad (1)$$

3.2 Particle size measurement of concentrated systems

Fig. 2 shows the concentration dependence of hydrodynamic diameter obtained from τ_f for the silica particles with different particle diameters. The open circles are the results converted to the particle diameter using the conventional Stokes-Einstein equation, and the closed circle are corrected data with the hydrodynamic and structure factors. In this case, $H(0)$ is the sedimentation coefficient, K , and $S(0)$ is expressed using the Carnahan-Starling equation⁵. The solid line indicates the diameter

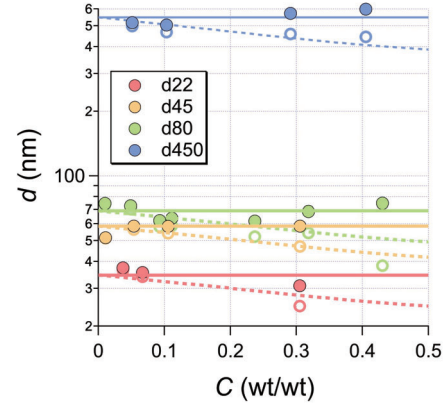


Fig. 2 Concentration dependence of d evaluated by the DSS method.

obtained by TEM and the dotted line is the non-corrected part guided for eye. Since D_c increases gradually with increasing the concentration, the apparent size becomes smaller with increasing the concentration. By correcting for the effect of concentration, the particle size could be evaluated to be constant irrespective of the concentration. In the case of dynamic light scattering, various effects, such as wavelength and scattered angle as well as the particle structure and friction coefficient must be considered. Now the nanoparticle sizing at the concentrated regime could be carried out without the concern of the complicated geometrical parameters.

4. Conclusions

Using the FD-DSS method with focused high frequency ultrasound pulse, nanometer to submicrometer silica particles up to 40wt% could be measured. A double exponential fitting analysis considering two relaxations enabled us to evaluate the particle size of nanoparticles containing a trace amount of aggregate. Furthermore, by correcting for the effect of concentration, it was possible to measure particle size at high concentrations. This broadens the range of samples that can be measured and is expected to be further utilized in the application field such as inks, cosmetics, and pharmaceuticals.

References

- 1) K. Kitao and T. Norisuye, *Ultrasonics* **126**, 106807 (2022).
- 2) A. J. Banchio, M. Heinen, P. Holmqvist and G. Nägele, *J. Chem. Phys.* **148**, 134902 (2018).
- 3) A. Martinez, J. H. J. Thijssen, F. Zontone, W. van Meegen and G. Bryant, *J. Chem. Phys.* **134**, 054505 (2011).
- 4) Konno, T. Norisuye, K. Sugita, H. Nakanishi and Q. Tran-Cong-Miyata, *Ultrasonics* **65**, 59 (2016).
- 5) J. Riest, T. Eckert, W. Richtering and G. Nägele, *Soft Matter* **11**, 2821 (2015).