Cooperative and self-diffusion dynamics of highly concentrated bimodal particle suspensions by Dynamic Ultrasound Scattering method

Manami Yamane^{1‡}, Kana Kitao¹, Misaki Tani¹and Tomohisa Norisuye^{1*} (¹ Grad. School of Sci. & Tech., Kyoto Institute of Technology)

1. Introduction

The particle size distribution of nanoparticles in Brownian motion can be calculated from the diffusion coefficient at relatively low concentration. However, at higher concentrations, inter-particle interactions must be taken into account. Recently, in addition to dynamic light scattering (DLS) method, Dynamic ultraSound Scattering (DSS) method is now also available for particle sizing of nanoparticles.¹⁾

Here, diffusive motion may exhibit cooperative diffusion and self-diffusion depending on the relation between the diameter of particle and Particularly, the wavelength. at higher concentrations, difference between cooperative diffusion and self-diffusion is more pronounced. A schematic diagram on cooperative diffusion and selfdiffusion is shown in Fig. 1 For monodisperse nanoor submicron particles, cooperative diffusion which reflects the collective nature of particle motion is observed at the wavelength of ultrasound, i.e., macroscopic spatial scales.²⁾ On the other hand, at wavelength of light or x-ray, i.e., microscopic scales, self-diffusion may be observed.³⁾ This difference is not observed in dilute systems but is specific to samples in concentrated system.



Fig. 1 A schematic diagram on cooperative diffusion and self-diffusion

However, in a polydisperse case, selfdiffusion can be observed even in the ultrasonic wavelength range, because of coherence of moving particles is not maintained in the case of samples with a distribution of particle size. This study focuses

E-mail: [‡]m4672033@edu.kit.ac.jp, *nori@kit.jp

on bimodal particle suspensions of two types of silica particles, 100 nm and 200 nm. Then, it was examined whether it is possible to extract information of two types of particles, taking into account both cooperative diffusion and self-diffusion.

2. Experiment

2.1. DSS Experiment

To emit longitudianl ultrasound pulse, a polymer transducer with a nominal frequency of 75 MHz, manufactured by Toray Japan was employed. The incident spike voltage of -275 V was applied to the transducer by a remote pulser BLP-12R manufactured by iSL Japan. Subsequently, back scattered waves were recorded with a GaGe 12-bit high speed digitizer at 3Gs/s as voltage waves. Pulse repetition time (PRT) was set at 25 ms and number of multiple record was 100,000 times. DSS measurements were conducted in water at 25 °C. About 20 µL of suspension was sandwiched between a polymethylpentene (PMP) film with a thickness of 9 µm and a sheet of PMP with a thickness of 1 mm. The region between the two reflected waveforms was analyzed after taking fast Fourier transformation. The temporal amplitude at a fixed frequency fluctuates a function of observation time. Thus, the time-correlation function $q^{(1)}(\tau)$ was employed to evaluate the diffusion coefficient.

2.2 Sample

Silica particles with nominal diameters d of 90 nm (MP1040) and 190 nm (MP2040) provided by a courtesy of Nissan Chemical were used. By transmission electron microscopy, it was found that the number mean diameter of MP1040 was 119.6 nm and that standard deviation normalized by the mean diameter CV was 0.089. It was also found that the number mean diameter of MP2040 was 211.2 nm and that CV was 0.053 by TEM. MP1040 and MP2040 are hereafter abbreviated as d100 and d200 respectively. Prior to the experiment, d100 were purified thorough optical disposal syringe filters with appropriate mesh size (e.g. 200 nm, 450 nm, 1.2 μ m and 5 μ m). d100 and d200 were mixed to obtain a scattering intensity ratio of 5:5.5 mM NaCl was used as a solvent.

3. Result

For dilute suspensions, Time-correlation function $g^{(1)}(\tau)$ may be described as $g^{(1)}(\tau) = \exp(-Dq^2\tau)$, where *D* is diffusion coefficient and *q* is the magnitude of the scattering vector. In monodisperse particles case, the natural logarithm plot of the time-correlation function gives a straight line. **Fig. 2** shows the natural logarithm plot of the time-correlation functions for (A) d100 and d200, and (B) the mixed suspensions of d100 and d200 with different volume fractions.



Fig. 2 Natural logarithm plot of the time-correlation functions for (A) d100 and d200 and (B) the mixed suspensions of d100 and d200 with different volume fractions.

The decay time was found to be shorter at the higher concentrations. This means that cooperative diffusion is dominant. On the other hand, in case (B), the relaxation is slower at higher concentrations. This means that the dynamics is dominated by selfdiffusion, which is inherent in polydisperse system. Cooperative diffusion coefficient increases with concentration, while self-diffusion coefficient decreases. Subsequently, the decomposition analysis of cooperative diffusion and self-diffusion was carried out by using four exponential functions for cooperative diffusion and self-diffusion of d100 and d200 (5:5 mixture).

The correlation function was fitted using the two particle diameters as unknowns. The equation used is expressed by the following formula.

$$g^{(1)}(\tau) = X[A_{cA} \exp(-D_{cA}q^{2}\tau_{c}) + (1 - A_{cA})\exp(-D_{sA}q^{2}\tau_{s})] + (1 - X)[A_{cB}\exp(-D_{cB}q^{2}\tau_{c}) + (1 - A_{cB})\exp(-D_{cB}q^{2}\tau_{s})]$$
(1)

where D_c and D_s are cooperative diffusion coefficient and self-diffusion coefficient respectively, X = 0.5 is the intensity ratio of two kinds of particle, τ_c and τ_s are decay time for cooperative diffusion and selfdiffusion, A_c and A_s are amplitude ratio of cooperative diffusion and self-diffusion, which are calculated as known constants if the concentration is known.⁴⁾ The following polynomial expressions on ϕ for D_c/D_0 and D_s/D_0 could be also used.⁵⁻⁷⁾ $D_c/D_0 = 1/(1 - 1.368\phi - 1.178\phi^2 + 49.848\phi^3)$

$$D_c/D_0 = 1/(1 - 1.368\phi - 1.178\phi^2 + 49.848\phi^3 - 387.68\phi^4 + 1478\phi^5 - 2679.2\phi^6 + 1818.8\phi^7)$$
(2)

$$D_{\rm s}/D_0 = 1 - 1.8315\phi - 0.21978\phi^2 + 1.28205\phi^3 \quad (3)$$

Using these relations, the only unknowns are D_{0A} and D_{0B} , which are translational diffusion coefficient of particle A and B.

Fig. 3 shows concentration dependence of D/D_0 for (A) D_{cA}/D_0 and D_{sA}/D_{0A} and (B) D_{cB}/D_{0B} and D_{sB}/D_{0B} . Note that the orange and green solid markers are D_c/D_0 and D_s/D_0 from result of analysis. The orange and green solid lines are calculated curves using Eqs. (2) and (3). The diameters for particle A and particle B were 98.1 nm and 173 nm respectively.



Fig. 3 Concentration dependences of D/D_0 (A) D_{cA}/D_0 , D_{sA}/D_{0A} and (B) D_{cB}/D_{0B} , D_{sB}/D_{0B}

4. Conclusion

In the mixed suspensions of silica particles with diameters of 100 nm and 200 nm at ratio 5:5, concentrated particle suspensions up to the volume fraction $\phi = 0.20$ are measured by DSS. The timecorrelation function obtained from the DSS experiments were fitted by a 4-exponential function with some conditions related to the cooperative diffusion coefficient D_c and self-diffusion coefficient D_s , enabling us to successfully extract diameters of two particles.

References

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