1P2-3

Dynamics of Concentrated Nanoparticle Suspensions Probed by Frequency-Domain Dynamic Ultrasound Scattering Techniques
周波数ドメイン動的超音波散乱法による濃厚系ナノ粒子懸濁液のダイナミクス

Masashi Fujisawa[1 ‡], Tomohisa Norisuye[1], Hideyuki Nakanishi[1] and Qui Tran-Cong-Miyata[1] ([1]Grad.School of Sci. & Tech., Kyoto Institute of Technology)
藤澤　雅[1 ‡], 則末　智久[1], 中西　英行[1], 宮田　貴章[1]　([1]京工繊大院工)

1. Introduction

The Frequency-Domain Dynamic ultraSound Scattering (FD-DSS) technique[1], [2] has been developed to evaluate the dynamics and the size distribution of microparticles in liquid. The technique is an acoustic analog of Dynamic Light Scattering (DLS), and are utilized to study the motion of particle by the time-dependence of the particle displacement. On the other hand, the Ultrasonic Spectroscopy (US) technique[3] provides the mechanical properties as well as the particle-size distribution via the frequency spectra of ultrasound attenuation coefficient. However, since the elastic modulus obtained by the US technique provides the information on the mechanical properties at the megahertz regime, thus acquired properties are not compatible with that obtained by rheological experiments but represent the local dynamics of the material. Therefore, in this study, we attempted to explore the possibility to evaluate the dynamics of concentrated suspension at the time-scale accessible by rheological experiment.

According to Stokes-Einstein relation $D=k_BT/6\pi\eta R$, the viscosity, $\eta = G''(\omega)/\omega$, of suspensions could be obtained by the apparent diffusion coefficient, D, of the particles provided that the particle size is given. For suspensions exhibiting a yield stress, the real part of the complex shear modulus, $G'(\omega)$, can be also obtained by the dynamic measurements. Such quantities are accessible by the DLS measurements. For the concentrated suspensions, the Diffusing Wave Spectroscopy (DWS) technique, which utilizes diffusion of light, is employed to evaluate microrheology in the long-path limit. Here we show the FD-DSS technique can be used to investigate the dynamics of concentrated suspension using ultrasound at the rheological time-scale. The advantage of the technique is that it can be used in any scattering path and optically opaque system, and even if it is the case of multiply scattered system of ultrasound, the number of scattering events can be determined by the phase analysis, allowing us to evaluate the relaxation time without assuming the diffusion approximation of the source wave.

2. Experiments

Silica nanoparticles were synthesized by the hydrolysis and condensation of alkoxide in the presence of a base catalyst, so-called the Stöber method[4], [5]. After the purification, the particles were calibrated by a Transmission Electron Microscopy (TEM; JEOL JEM-2100), followed by an image analysis to extract the particle size distribution.

The calibration resulted in the average radius $R_{TEM} = 38$ nm, the standard deviation of particle size obtained by TEM σ=4.94 nm, and the coefficient of variation $CV \equiv \sigma/R_{TEM}$ =0.13.

The synthesized particles were dispersed in distilled water, and the concentration dependence of the silica suspensions was examined in range φ = 0.0053 - 0.19, where φ is the volume fraction of particles in suspensions.

The motion of particles in suspension may be analyzed by a time-correlation function of the scattering amplitude given by,

$$g^{(1)}(\tau) = \exp\left(-\frac{1}{6}q^2\langle\Delta r(\tau)^2\rangle\right) \qquad (1)$$

where, $\langle\Delta r(\tau)^2\rangle$ is the mean-square displacement and τ is the time lag. $\langle\Delta r(\tau)^2\rangle$ of nanoparticle in suspensions is given by

$$\langle\Delta r(\tau)^2\rangle = 6D\tau \qquad (2).$$

$\langle\Delta r(\tau)^2\rangle$ is converted to the complex shear modulus, $G^*(\omega)$, by the so-called generalized Stokes-Einstein relation,

$$G^*(\omega) = k_BT/\pi Ri\omega F\langle\Delta r(\tau)^2\rangle \qquad (3)$$

where k_BT is the Boltzmann energy, R is the particle radius, $i=\sqrt{-1}$, ω is the angular frequency, and $F\langle\Delta r(\tau)^2\rangle$ is the Fourier transformation of $\langle\Delta r(\tau)^2\rangle$.

3. Results

Fig. 1 shows a series of time-correlation functions obtained for the silica nanoparticles in water with φ= 0.0053 - 0.19 observed at 31 MHz. The decay time of the correlation functions became longer with increasing the volume fraction. D was evaluated by eq. (2). **Fig. 2** shows the volume

fraction dependence of D. The drastic decrease in D was observed at about φ= 0.10.

Subsequently, the volume fraction dependences of $G'(\omega)$ and viscosity of suspension were examined as shown in **Fig. 3(a)** and **(b)**. $G'(\omega)$ drastically increased at φ= 0.10, representing the solid-like behavior of the silica nanoparticle suspensions. It was found that the viscosity of suspension diverged at a critical concentration presumably attributed to the jamming transition[6],[7]. Note that the dotted and dashed lines represent the line calculated by the models by Moony et.al. [8] and Simha et.al. [9]

In the case of silica nanoparticle suspensions, the electrostatic repulsion due to negatively charged surface, reduced the mobility of silica particles. Therefore, the drastic increase in η is expected to occur at the lower volume fraction compared with those without electrostatic interactions.

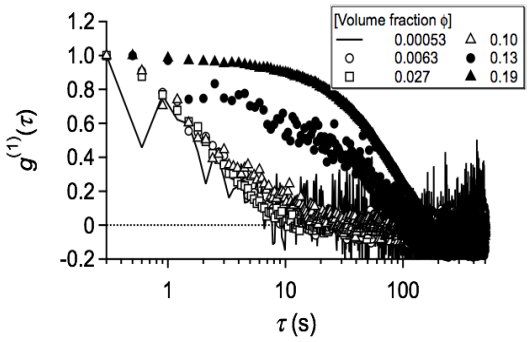

Fig. 1 A series of time-correlation functions obtained for the silica nanoparticle in water with φ= 0.0053 - 0.19 observed at 31 MHz.

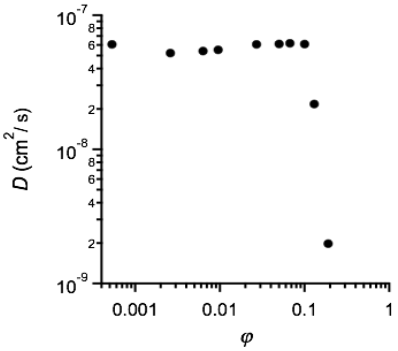

Fig. 2 The volume fraction dependence of D.

4. Conclusions

We showed that the FD-DSS technique had a potential to evaluate the complex shear moduli of the concentrated suspensions. The complex shear moduli showed drastic change around φ= 0.10 for the silica particles without salt. Further investigation will be carried out for the suspension in the presence

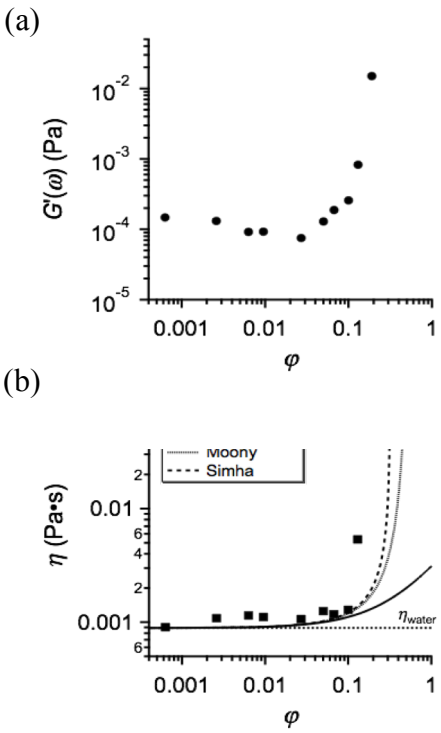

Fig. 3 The volume fraction dependence of (a) $G'(\omega)$ and (b) η.

of salt to elucidate the effect of electrostatic interaction of the particle on the jamming transition of the silica nanoparticle at the time-scale of rheological measurement.

References

[1] K. Igarashi, T. Norisuye, K. Kobayashi, K. Sugita, H. Nakanishi and Q. Tran-Cong-Miyata, *J. Appl. Phys*., 2014, **115**, 203506.
[2] K. Kobayashi, T. Norisuye, K. Sugita, H. Nakanishi and Q. Tran-Cong-Miyata, *J. Appl. Phys.*, 2017, **122**, 045106.
[3] K. Kubo, T. Norisuye, T.N. Tran, D. Shibata, H. Nakanishi and Q. Tran-Cong-Miyata., Ultrasonics, 2015, **62**, 186.
[4] W. Stöber, A. Fink and E. Bohn, *J. Colloid Interface Sci*., 1968, **26**, 62.
[5] R. Sato-Berrú, J. M. Saniger, J. Flores-Flores and M. Sanchez-Espíndola, *J. Mater. Sci.*, 2013, A **3**, 237.
[6] R. Pal, *the Canadian journal of chemical engineering*, 2017, **95**, 1605.
[7] R. Niu, S. Heidt, R. Sreij, R.I. Dekker, M. Hofman and T. Palberg, *Science Reports*, 2017, **7**, 17044.
[8] M. Moony, *J Colloid Sci.*, 1951, **6**, 162.
[9] R. Simha, *J. Appl. Phys.*, 1952, **23**, 1020.