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Dynamics of micron-sized particles in dilute and concentrated suspensions probed by dynamic ultrasound scattering techniques

Tomoyuki Konno, Tomohisa Norisuye *, Kazuki Sugita, Hideyuki Nakanishi, Qui Tran-Cong-Miyata

Department of Macromolecular Science and Engineering, Graduate School of Science & Technology, Kyoto Institute of Technology Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

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ABSTRACT

A novel ultrasound technique called Frequency-Domain Dynamic ultraSound Scattering (FD-DSS) was employed to determine sedimentation velocities and the diameters of microparticles in a highly turbid suspension. The paper describes the importance of the scattering vector q for dynamic scattering experiments using broadband ultrasound pulses because q (or frequency) corresponds to the spatial length scale whereas the pulses involve inevitable uncertainty in the time domain due to the frequency distribution of broadband pulse. The results obtained from Stokes velocity of monodispersed silica and polydivinylbenzene (PDVB) particles were compared to those obtained by a Field Emission Scanning Electron Microscope (FE-SEM). A novel method to extract the particle size distribution is also demonstrated based on an ultrasound scattering theory.

1. Introduction

Dynamics of microparticles in fluid can be evaluated by dynamic light scattering (DLS) techniques via measurement of the decay rate of time-correlation function [1]. The concentration dependence of apparent diffusion constant provides information on the particle interactions and the particle diameter. Such information can be determined by extrapolating the diffusion coefficient to zero concentration, followed by calculation using the well-known Stokes–Einstein formula. On the other hand, as the particle size becomes larger, sedimentation becomes dominating the particle dynamics due to gravity. For this particular case, the particle diameter may be evaluated by the terminal velocity of a single particle [2]. Despite those advantages of the non-destructive techniques, DLS measurements are not available for most of the systems with micron-sized particles and concentrated suspensions because of multiple scattering and/or serious light attenuation.

In order to overcome the problem, we have developed a high-frequency Dynamic ultraSound Scattering (DSS) technique [3–7], which is an acoustic analog of DLS. Since the DSS technique employs ultrasound pulse instead of visible light, it can be applied to optically turbid systems. The DSS method was first proposed by Page and coworkers to investigate a complex dynamics of particle in fluids, such as velocity fluctuations in fluidized bed [8,9] or shared flow [10] using several megahertz ultrasound. On the other hand, the higher frequencies with the better spatial resolution were required in order to apply this technique to systems of micron- or nano-sized particles.

In our previous papers, we have shown that the high-frequency dynamic ultrasound scattering techniques enabled us to evaluate the dynamics and structure of microparticles [3–7,11]. When a micron-sized particle settles down, the motion of surrounding liquid is perturbed by the presence of the particle, resulting in a multi-body problem of particle dynamics. It leads to noticeable fluctuations of settling particle velocity, and is known to involve long-ranged hydrodynamic interactions [12]. The hydrodynamic interactions are also responsible for the unique and surprisingly large (in the order of millimeters) cooperative structures where the origin of velocity fluctuations is now believed to be fluctuations in the number of particle taking part in a cooperative domain structure called blob [13,14]. Therefore there exist dynamic structures in the velocity field in spite of the concentration profile being statistically random in both time and space. Such dynamic structures were visualized by temporal extraction of ultrasound phase by so called the phase-mode DSS technique [5,6].

Besides the advantages of the DSS techniques for many particle systems intractable by conventional optical techniques, the accuracy of the particle velocity still remained in about 10% [4]. Although "broadband" is crucial for probing the acoustic properties in a wide range of frequencies, and the corresponding short pulse in the time-domain could resolve the objects better in nondestructive testing, this drawback would be probably due to the frequency

* Corresponding author.
E-mail address: nori@kit.jp (T. Norisuye).

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distribution of the broadband pulse. Therefore, alternative DSS approaches were expected to overcome the problem. In this paper, we first address the importance of the scattering vector q for ultrasound scattering experiments using broadband ultrasound pulses because q is responsible for the spatial length scale in dynamic measurements while the pulses involve inevitable uncertainty in the time domain due to the frequency distribution of broadband pulse. We introduce a novel DSS technique, called Frequency-Domain Dynamic ultraSound Scattering technique (FD-DSS), which allows us to precisely determine the settling velocity and the corresponding particle diameter using broadband pulses having a wavelength distribution. As a result, the technique significantly improved the experimental accuracy compared to the previous studies. Second, the particle diameters converted from terminal velocities of sedimentation are quantitatively evaluated for mono-dispersed silica and polydivinylbenzene standard particles. Comparison of the results with those obtained by a scanning electron micrograph will be also made. Third, the effect of particle size distribution is addressed by probing two types of settling velocity: (1) the velocity of sedimentation front and (2) that of submerged particles in a suspension using the FD-DSS techniques. Finally, the dependence of the concentration profile of the sedimentation velocity on the Reynolds number, *Re*, will be compared to the data published by Richardson and Zaki (R–Z) [15], and Garside and Al-Dibouni [16].

2. Experimental procedure

A series of standard polydivinylbenzene (PDVB) and silica microspheres were kindly provided by Sekisui Chemical Co. LTD. The silica or PDVB particles were dispersed in distilled water to obtain aqueous suspensions with desired concentrations in range $0.1 < C < 15\%$ in weight, followed by a brief immersion in a low power ultrasonic bath prior to ultrasound scattering experiments in order to avoid aggregation. In the case of the PDVB suspensions, 0.2 wt.% sodium dodecyl sulfate (SDS) was added to disperse the hydrophobic particles in water. Water was purified twice using 0.2 μm membrane filter after distillation. Polyphenylene sulfide (PPS) rectangular vessels with the dimension $10 \times 27.5 \times 30\ mm^3$ (width × depth × height) with the wall thickness of 1 mm were used as a sample cell. The effect of sample height (hindered settling) was carefully investigated prior to the experiments. The density of particle was determined to three places of decimals by a density matching method with calibrated aqueous solutions of sodium chloride (NaCl) or sodium polytungstate, SPT ($3Na_2WO_4 \cdot 9WO_3 \cdot H_2O$). The density of NaCl or SPT solutions was calibrated using a 25 mL Gay–Lussac pycnometer prior to the density matching experiments.

FE-SEM images (JEOL JSM-7600F) were taken to calibrate the particle size and its distribution. Prior to observation, the samples were dried *in vacuo* followed by a gold deposition by magnetron sputtering to enhance the quality of images. The obtained bitmap images were recorded with 2560×1920 pixels containing about 10 particles in each picture, followed by calculation of the diameter for at least 300 particles. Since the thickness of gold layer was much thinner (typically 50 nm) than the particle diameter (several tens of micrometers), further correction was not made. Examples of the SEM images and the corresponding particle size distribution obtained for the silica and PDVB particles are shown in Fig. 1. In the SEM images, both standard particles seemed to be mono-dispersed; however, it was found that the PDVB particles have a broader size distribution compared to those of silica. The quantitative information of the particle is summarized in Table 1 where d is the nominal particle size provided by the supplier, d_{SEM} is the average particle diameter calibrated by FE-SEM, CV is the coefficient of variation corresponding to the standard deviation of the particle size normalized to its average, ρ is the particle density, *Re* is the particle Reynolds number, *Pe* is the particle Peclet number, and N is the number of particle evaluated by the FE-SEM analysis.

An ultrasound pulse was generated using a broadband pulser/receiver (iSL BLP12R) connected to a longitudinal plane wave transducer. The energy of pulser was kept as low as possible to avoid unexpected flow induced by excess ultrasound energy [17]. Various water-immersion sensors such as, KGK B5K6I (diameter 6 mm, nominal frequency 5 MHz), B10K2I (2 mm, 10 MHz), B20K2I (2 mm, 20 MHz) and 25C6I (6 mm, 25 MHz), B30K1I (1 mm, 30 MHz) were employed to measure ultrasound signals with different frequency ranges. Although the FD-DSS technique described in this paper allows us to evaluate the frequency

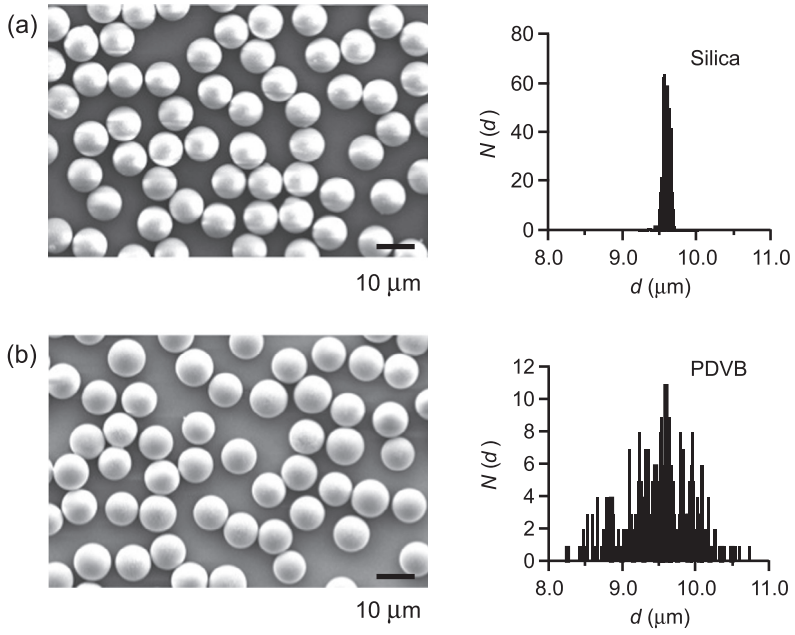

Fig. 1. Examples of SEM image and the corresponding particle-size distribution obtained for the (a) silica and (b) PDVB particles.