Simultaneous observation and analysis of sedimentation and floating motions of microspheres investigated by phase mode–dynamic ultrasound scattering

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(Received 17 October 2008; accepted 11 December 2008; published online 30 January 2009)

A high frequency dynamic ultrasound scattering technique was developed to evaluate the mean velocity and the velocity fluctuations of micron-sized beads in highly turbid suspensions. In contrast to the previous study, scattering phase was fully utilized to investigate the dynamics of mixtures consisting of settling and floating microspheres. The velocities of the particles moving upward and downward with respect to gravity were simultaneously measured by a single acquisition. Instantaneous velocities determined by the time derivative of the scattering phase were evaluated as functions of the evolution time and position of the scatterer. (1) The velocity analysis in the time domain, (2) the phase analysis without phase unwrapping, and (3) the effects of noise filtering were discussed. The results were compared with those derived from amplitude mode–dynamic ultrasound scattering. © 2009 American Institute of Physics. [DOI: 10.1063/1.3072687]

I. INTRODUCTION

In the previous studies,1,2 we demonstrated that high frequency dynamic ultrasound scattering, an acoustic analog of dynamic light scattering (DLS),3 allowed us to investigate the sedimentation dynamics of microspheres with the diameter ranging from several to several tens of micrometers. In addition to the potential of dynamics analysis in turbid solutions (where neither conventional optical velocimetry nor DLS does not work efficiently), there are further advantages on the fluid dynamics characterization, such as providing information on (1) velocity fluctuations and (2) spatial location of the scatterers associated with the time-dependent ultrasound field. For example, when ultrasound is emitted from the top of the sample, the sedimentation velocity can be probed by a backscattering setup, allowing the determination of the particle size via the Stokes relation.4 If settling is hindered by particle collision or other external force, the velocity fluctuations are simultaneously observed. On the other hand, the velocity fluctuations can be solely investigated from a horizontal setup because of the average component being zero. This enables us to investigate the long-range dynamic fluctuations originated from the size distribution and/or hydrodynamic interactions.5 While the average velocity of the sedimentation particles is well understood,4 its fluctuations are still of interests in the field of fluid dynamics. Spreading of the sedimentation front6,7 screening of hydrodynamic interactions,11–13 and hindered sedimentation14 are the examples. All these must be crucial for studying the velocity fluctuations observed by dynamic ultrasound scattering. Once the complicated hydrodynamics is elucidated, the technique may be utilized for characterization of soft matter such as surface modified microbeads, hollow spheres, metal-polymer hybrids, microbubbles, and so on.

The above advantages could be implemented thanks to the nature of ultrasound. In contrast to the simple photon counting in light scattering systems, the complete waveform of ultrasound can be captured repetitively by a latest digitizer with the optimal horizontal resolution and sufficient memory. This leads to versatile scattering techniques containing both amplitude and phase information of the scattered waves. When the backscattering amplitude is scanned parallel to the settling direction, the autocorrelation functions of the temporal amplitude along the evolution time T provide the particle velocity on the order of the pulse repetition time ΔT because the direction of the wave vector coincides with that of sedimentation. The correlation functions are obtained as many as the number of points along the field-time t within the allowance of the digitizer memory, providing the unique information corresponding to each sample position along the field-time. Here the field-time is defined as the propagation time of ultrasound. Such versatile applications are the inherent characteristic of ultrasound and are not possible for conventional optical techniques since the speed of light is too fast to be captured and resolved by currently available digitizers.

Besides the fascinating amplitude analysis, scattering phase contains rich information inherent in ultrasound scattering. The amplitude correlation function g(1)(τ) along the direction parallel to gravity provides quantitative mean velocity ⟨Vz⟩ and its variance ⟨δVz2⟩. However, the obtained data do not contain the information on the direction of the moving scatterer. Since the pulse field shifts forward or backward along the field-time depending on the displacement of the particles, the phase provides not only the information on the magnitude of the displacement but also the direction of the movement. Moreover, spurious pulses such as reflection from stationary walls and reverberated echoes could be eliminated if the ultrasound field is reconstructed from the amplitude and phase components, leading to more precise analysis of time-dependent ultrasound scattering.
field. In the present study, the time derivative of the scattering phase is evaluated to study the dynamics of microspheres involving settling, floating, or both together.

II. EXPERIMENTAL

A. Samples

Standard latex microspheres with the diameter \( d = 32 \ \mu m \) were supplied courtesy of Sekisui Chemical Co. Ltd. The diameter of the particles in the dry state was confirmed by Scanning Electron Microscope (SEM) micrographs (Hitachi S-3000N) where the coefficient of variation (CV) was found to be 0.11. The density of the particles \( \rho = 1.177 \ \text{g/cm}^3 \) was measured by a 25 ml Gay-Lussac pycnometer. Other latex particles with the average diameter of 45 \( \mu m \) were purchased from Duke Scientific Corporation. The density and CV were, respectively, 1.050 g/cm\(^3\) and 0.15. The code names d32 and d45 are used throughout the manuscript as the abbreviated name for the microspheres.

The density and CV were, respectively, 1.050 g/cm\(^3\) and 0.15. The code names d32 and d45 are used throughout the manuscript as the abbreviated name for the microspheres with \( d = 32 \) and 45 \( \mu m \), respectively. The particles were dispersed in deuterated water (99.9\%) containing 0.2\% sodium dodecyl sulfate to obtain a suspension with the particle concentrations \( c = 0.1\% - 1\% \) by weight, followed by a brief immersion in a low power ultrasonic bath prior to the experiments to avoid aggregation. Polystyrene rectangular vessels with the dimension of \( 10 \times 10 \times 40 \ \text{mm}^3 \) were used as the sample cells. The wall thickness was 1 mm. All the experiments were performed at (20.0 \pm 0.05) \(^\circ\)C.

B. Apparatus

A negative impulse emitted from a pulser/receiver (Olympus, model 5800PR) was transferred to a 10 MHz longitudinal plane wave transducer (Olympus, extratunrature transducer XMS-310B, bandwidth 74\%) immersed in a water bath to generate broadband ultrasound pulse. The wavelength \( \lambda \) and the magnitude of the scattering vector \( q = (4 \pi / \lambda) \sin(\theta / 2) \) were, respectively, 125 \( \mu m \) and 0.101 \( \mu m^{-1} \) at the central frequency of 11 MHz where the scattering angle \( \theta \) was 180°. The transducer diameter \( d_{TD} \) was 3 mm. The reflected or scattered ultrasound wave was received by the same transducer for the backscattering experiments (\( \theta = 180° \)). Note that the experiment with any scattering angle could be carried out if emitting and receiving transducers were placed separately at an appropriate angle. In the present study, an ultrasound transducer was placed parallel to gravity (z-direction) and the successive pulses were repetitively recorded to investigate the temporal displacement related to the sedimentation and/or floating motion of the microspheres. In most of the case, this experimental setup provides both the average velocity and its fluctuations. On the other hand, ultrasound waves were emitted to the sample normal to gravity (horizontal setup) when the direct monitoring of the velocity fluctuations was required. The transducer and the cell container were carefully aligned by using a custom-made stainless stage coupled with rotational and translational slides prior to the scattering experiments. The sample-to-detector distance was 15 mm. The obtained signals were then amplified by the receiver, followed by successive recording with a 14 bit high-speed digi-

![FIG. 1. Schematic presentation of the field amplitude as functions of the field-time \( t \) and the evolution time \( T \).](image)

Ultrasound scattering is observed when ultrasound pulse propagates through a suspension consisting of microspheres whose diameter is comparable with the wavelength of ultrasound.\(^{15,16} \) The pulse wave \( \psi \) for the main scattering component may be written as

\[
\psi(t) = A(t) \cos[2\pi f_c t + \Phi(t)],
\]

where \( t \) is the field-time, \( f_c \) is the central frequency, and \( A \) and \( \Phi \) are, respectively, the amplitude and phase of the temporal pulse. In the case of the backscattering geometry, \( t \) contains the spatial information of the scatterers along the beam direction as explained below. The amplitude \( \psi(t, T) \) may vary with the evolution time \( T \) depending on the particle concentration and the position in the scattering volume, as demonstrated in Fig. 1. Because the whole pulse amplitude fluctuates with the evolution time \( T \), the temporal amplitude can be independently evaluated at different \( t \). The pulses are repetitively captured by a digitizer with an interval \( \Delta T \) (approximately millisecond) which is much longer than the pulse duration time (approximately microsecond) along the field-time axis but sufficiently short compared with the characteristic time (approximately second) of the microsphere dynamics. The amplitude fluctuations appeared at an intermediate field-time between reflected pulses from the stationary cell walls. Therefore the evolution time dependence of \( \psi(t, T) \) for the smaller \( t \) provides the near wall properties, while that at the intermediate time \( t \) corresponds to the dynamics of the sample at the center.

Accessible information depends on the beam direction with respect to gravity. For example, if the beam is emitted from the sample top (z-direction), the average displacement and its fluctuations contribute to the time-dependent backscattering. On the other hand, when the beam direction is
perpendicular to that of the sedimentation (y-direction), only the velocity fluctuations are probed by dynamic ultrasound scattering since the average displacement due to sedimentation along the direction is zero. In order to quantitatively evaluate the velocity and its fluctuations, a field correlation function defined below was evaluated.\textsuperscript{17,18}

\[
g^{(1)}(\tau) = \frac{\langle \psi(t,T) \psi^*(t,T+\tau) \rangle}{\langle \psi(t,T) \psi^*(t,T) \rangle}.
\]

The correlation functions for z- and y-components are, respectively, given by\textsuperscript{1,19,20}

\[
g_{z}^{(1)}(\tau) = \cos(q\langle V_z \rangle) \exp\left(-\frac{1}{2}q^2\langle \delta V_z^2 \rangle \tau^2\right)
\]

and

\[
g_{y}^{(1)}(\tau) = \exp\left(-\frac{1}{2}q^2\langle \delta V_y^2 \rangle \tau^2\right),
\]

where \(\langle V_z \rangle\) is the average velocity along the z-axis, and \(\langle \delta V_z^2 \rangle\) and \(\langle \delta V_y^2 \rangle\) are, respectively, the variance for the z- and y-components. The bracket indicates the evolution time average. In the present study, ultrasound waves are emitted from the top or bottom of the sample to investigate the settling or floating of the microspheres.

Figure 2 shows the field correlation functions obtained for d32 and d45 dispersed in D\(_2\)O. Since the densities of d32 and d45 were, respectively, higher and lower than the density of D\(_2\)O, these could be the model systems for studying sedimentation and floatation. The ultrasound pulse was emitted from the bottom of the sample. The data were fitted to Eq. (3), leading to the quantitative determination of \(\langle V_z \rangle=0.055\) and \(\langle \delta V_z^2 \rangle^{1/2}=0.013\) for d45 and \(\langle V_z \rangle=0.030\) and \(\langle \delta V_z^2 \rangle^{1/2}=0.016\) mm/s for d32. Although the fitting was quite successful, the information on the moving direction, i.e., settling or floating, could not be extracted from the result. Therefore, in an attempt to satisfy this demand, the extraction of phase from the field matrix was carried out. As described in the previous papers,\textsuperscript{1,2} the particle sizing would be possible if the concentration dependence is systematically examined.

The scattering phase was obtained by fast Fourier transformation of the ultrasound pulse along the field-time \(t\). The effects of truncation points on the pulse shape were carefully investigated to eliminate the contributions from the spurious signals. The phase \(\Phi(f,T)=\arg\{P(f,T)\}\) obtained by this way at a frequency \(f\) will vary as a function of the evolution time \(T\) according to the particle displacement. Figure 3 shows the time evolution of the scattering phase obtained for (a) d45 and (b) d32 at and near the central frequency \(f_c\), where \(\Phi(T)\) was normalized by \(q\) to obtain \(\langle V_z \rangle\) from the slope of the plots. The solid lines were reproduced by \(\langle V_z \rangle\) estimated from Fig. 2. As shown in the figures, the phase evolution was approximately superimposed on a single curve independent of the frequencies. \(\Phi(T)\) for d45 and d32, respectively, provided the negative and positive slopes, which indicated the average settling and floating velocity for the microspheres. Unexpected jumps in the phase were sometimes observed due to the failure of unwrap operation, which was very sensitive to the presence of the small amount of noise. \(\langle V_z \rangle\) obtained by the phase evolution roughly agreed with that of the correlation function in spite of the limiting range of the phase evolution \(\Phi(f,T)\).

![Figure 2](image_url)

**FIG. 2.** The field correlation functions obtained for (a) d45 and (b) d32 dispersed in D\(_2\)O.

![Figure 3](image_url)

**FIG. 3.** The time evolution of the cumulative phase normalized by \(q\) obtained for (a) d45 and (b) d32 dispersed in D\(_2\)O with different frequencies. The solid lines were reproduced by \(\langle V_z \rangle\) estimated from Fig. 2. The scattering phase was extracted in the frequency domain.

Furthermore, \(\Phi(f,T)\) at or near the central frequency is free from noise of high frequency or undulation with low frequency, resulting in the plausible calculation of velocity. However, the extracted phase in the frequency domain no longer contains the position dependent information. This fact
restricts the advantages of ultrasound in providing versatile information, such as the effect of the cell wall, convection, or dynamic inhomogeneities. Therefore the attempt to extract the phase information in the time domain was made in the next step.

Equation (1) contains the ac components in the cosine term. Therefore a sine and cosine wave at $f_\text{c}$ is multiplied to Eq. (1), followed by low-pass filtering to extract the phase components $S(t)$ and $C(t)$,

\[
S(t) = \mathcal{F}^{-1}[\mathcal{F}[\phi(t)\sin(2\pi f_\text{c} t)] \times H(f)],
\]

\[
C(t) = \mathcal{F}^{-1}[\mathcal{F}[\phi(t)\cos(2\pi f_\text{c} t)] \times H(f)],
\]

where $\mathcal{F}$ and $\mathcal{F}^{-1}$ denote the forward and inverse Fourier transformations and $H(f)$ is the filter function. In the present study, a Fermi–Dirac type function

\[
H(f) = \frac{1}{1 + \exp[(f - f_\text{c})/a]},
\]

was employed with $a=0.1f_\text{c}$. As a result, we obtain

\[
A(t) = 2 \sqrt{(C(t) - \langle C(t) \rangle)^2 + (S(t) - \langle S(t) \rangle)^2},
\]

\[
\Phi(t) = \tan^{-1}\left[-\frac{S(t) - \langle S(t) \rangle}{C(t) - \langle C(t) \rangle}\right],
\]

with

\[
S(t) = -\frac{A(t)}{2}\sin \Phi(t),
\]

\[
C(t) = \frac{A(t)}{2}\cos \Phi(t),
\]

where the bracket denotes the evolution time average which represents the dc offset originated from stationary reflected waves or transducer specific artifacts.

As a particle moves a distance $\Delta r$ during a time interval $\Delta T$, the corresponding scattering phase shift is $\Delta \Phi = q \Delta r$, resulting in an instantaneous velocity given by

\[
V = \frac{1}{q} \frac{d \Phi}{d T}.
\]

Because the phase is wrapped around $\pm \pi$ by definition, appropriate addition of $2 \pi$, i.e., unwrap operation, is generally required to obtain the cumulative phase.\(^{21}\) This can be done by integrating the phase derivative; however, the number of $2 \pi$ becomes ambiguous if the noise contribution is not negligible. Instead of using Eq. (10), the following equation based on the derivative of arctangent is proposed to obtain the velocity without phase unwrapping:

\[
V = \frac{d S(t)}{d t} \left(\langle C(t) - \langle C(t) \rangle\rangle - \frac{d C(t)}{d t} \langle S(t) - \langle S(t) \rangle\rangle\right).\]

Although the instantaneous velocity was given by the above equation, the experimental noise could significantly affect the derivative data. Figure 4 demonstrates commonly available filters and their performance. First, a test data consisting of a sine and its derivative were, respectively, shown in Figs. 4(a) and 4(b). A randomly generated Gaussian noise with the normalized standard deviation $s=0.1$ was added to the test data. As indicated in Fig. 4(b), the derivative was significantly affected by the presence of the small noise in the original form. Subsequently, median, binomial, and
LOESS filters\textsuperscript{22} were applied where the smoothing factor was set as high as possible. As shown in Fig. 4(c), the median filter was not sufficient to reproduce the original sine curve and further increase in the smoothing factor resulted in distortion of the original shape. While the binomial filter moderately filtered the noise, a locally weighted regression method, such as LOESS (Ref. 22) or LOWESS (Ref. 23) filter, was found to be more effective to smooth our data. In the LOESS algorithm, subset of data within the smoothing window was weighted by a tricube weighting function and fitted with a local polynomial, which can be constant, linear, or quadratic, to obtain the smoothed data. LOWESS, a robust version of LOESS, is a similar technique, which would be very useful if the data contain a strong spike due to the unexpected shot noise. Figure 4(d) demonstrates the performance of the LOESS filter with a quadratic polynomial function. The time evolution of $S(t)$ with $2 \times 10^4$ points calculated by Eq. (5) was presented. When the smoothing window increased from $p=15$ to 51 points, clear improvement was confirmed from the smoothed curve. However, as evidence from the figure, too much filtering led to the shape distortion. Therefore $p=51$ or less depending on the data quality was set to carry out the analysis utilizing the LOESS filter. While the effect of the filter value was carefully investigated, the subsequent phase analysis with the velocity histogram was insensitive to the filter value unless $p$ was not too high. In most of the case, $p$ was set to $11–51$.

Let us now demonstrate the velocity imaging of settling and floating microspheres. The velocity was calculated from the scattering phase in the \textit{time domain} with efficient noise filtering by using the LOESS algorithm. Figure 5(a) shows the image of the velocity $V(t, T)$ for d45 where the particles are buoyant in D$_2$O and was observed from the sample bottom. The velocity has the negative sign since the position of the particles became farther from the transducer with the evolution time. On the other hand, the sedimentation of d32 was imaged, as shown in Fig. 5(b). The histograms of d45 and d32 were, respectively, exhibited in Figs. 5(c) and 5(d). It is worthwhile to address that the peak value agreed well with $\langle V \rangle$ evaluated by the correlation function approach using Eq. (3) as indicated by the solid arrows.

Since Eq. (3) produces only the average and its standard deviation, it is not straightforward to understand the shape of velocity distribution from the correlation function analysis. For the analysis of DLS data, there are several procedures to extract the distribution function or its moment, e.g., CONTIN,\textsuperscript{24} cumulant expansion,\textsuperscript{25} and so on. On the contrary to these analyses, one can assume a symmetrical distribution for the velocity data due to the following reasons. First, the exponential decay in Eq. (3) represents essentially time-squared dependence. The odd order term with respect to $\tau$ vanished by definition. This suggests that the skewness of the velocity distribution is zero (symmetrical distribution). Therefore assume that a normal distribution is a good starting point to compare the velocity distribution obtained by the phase analysis with $\langle V \rangle$ and $(\delta V_{\tau}^2)$. Figure 6 demonstrates the velocity distributions of d32 and d45, respectively, evaluated by the phase analysis and the normal distribution reconstructed by the average $(\langle V \rangle)$ and width $(\langle \delta V_{\tau}^2 \rangle)^{1/2}$. As shown in the figure, the agreement between two results is fairly satisfactory.

More recently there are extensive studies on the velocity fluctuations of the particles in suspensions.\textsuperscript{7,10,13,26–28} While the average settling velocity is well understood,\textsuperscript{4} the fluctuations accompanying long-range hydrodynamic interactions\textsuperscript{5,29,30} are still not fully elucidated. The sedimentation front represents interesting broadening and self-sharpening\textsuperscript{32} behavior depending on the concentration of the particles. The theory and simulation suggested that one of the main driving forces of the velocity fluctuations is the density fluctuation of the particles with the Poisson statistics.\textsuperscript{29} The velocity fluctuations obtained by the phase analysis may be described by such characteristics. However, the shape of the distribution function shown in Fig. 6 is not much altered even if the Poisson distribution was employed.

Since the instantaneous velocity was successfully extracted from the phase analysis of the ultrasound scattering
data, it is possible to measure simultaneously two types of particles moving oppositely if the two velocities can be correctly discriminated by this technique. Figure 7 shows the velocity image of a mixture of d45 and d32. The concentrations were, respectively, set at 0.1 wt % for d45 and 0.2 wt % for d32. The velocities of the floating and settling particles can be identified by positive and negative values as indicated in red and blue, respectively. In the earlier evolution time, most of the particles exhibited buoyancy (blue) in all the field-time because of the higher scattering contrast of the larger particles where the positive velocity (red) observed in the field-time region $t < 4 \, \mu s$ was due to the experimental lag time of the sample setting. As the buoyant particles move away from the smaller $t$ region, the heavier particles began to settle as seen by the red color. Figure 7(b) shows the histogram obtained from Fig. 7(a). The velocity distribution of the mixture clearly indicated that the distribution was bimodal, where the two peaks, respectively, agreed well with the individual components obtained in Fig. 6. Near zero velocities were also observed between the two peaks. Since the buoyant particles collide with the settling particles, the positive and negative velocities are more or less canceled similar to the hindered sedimentation.4 Nevertheless, each component in the bimodal distribution well preserves the characteristic feature for the pure component.

Ultrasound Doppler velocimetry33,34 has essentially the same basis with dynamic ultrasound scattering in terms of utilization of the time-dependent phase evolution. However, most of the studies were carried out at relatively low frequencies and were not intended to apply for studying of microparticles. As for the higher frequency study, one can find literatures based on a cross-correlation technique for ultrasound field data acquired by oriented beam setups.35–37 This is similar to the autocorrelation function approach, but the cross-correlation technique requires determination of an area to be analyzed prior to the data analysis. Furthermore, averaging over several wave numbers was required to obtain the satisfactory result. In contrast, the method demonstrated in this study provides instantaneous velocity not only with the evolution time but also with each field-time containing the scattering path information.

IV. CONCLUSIONS

A phase mode–high frequency dynamic ultrasound scattering technique has been developed to investigate the sedimentation dynamics. The results were compared with those obtained by the amplitude mode in dynamic ultrasound scattering reported previously. The extracted phase quantitatively agreed with the data obtained by the amplitude mode. In order to apply the phase technique to investigate the time evolution of the sedimentation dynamics, the time derivative of the scattering phase was analyzed where the phase derivative was successfully evaluated without phase unwrapping. Since the phase derivative was strongly affected by the experimental noise, a locally weighted regression method was applied to obtain plausible phase data. The validity was discussed by comparing the data obtained by amplitude mode in the dynamic ultrasound scattering method. Finally, settling and floating microspheres were measured simultaneously to investigate the validity of the average and fluctuations of the velocity for each component. All the ultrasound scattering data were evaluated in the time domain rather than in the frequency domain so that the spatial information of the target scatterers could be obtained without averaging the adjacent points.

ACKNOWLEDGMENTS

This work was supported by Grant-in-Aid Contract No. 20750178 and Grant-in-Aid for Scientific Research on Priority Area “Soft Matter Physics” (Contract No. 463/19031018) from the Ministry of Education, Science, Sports, Culture, and Technology.

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