PHYSICAL REVIEW E **83**, 041606 (2011)

Role of particle inertia in adsorption at fluid-liquid interfaces

P. Singh,[1] D. D. Joseph,[2] I. S. Fischer,[1] and B. Dalal[1]
[1]*Department of Mechanical and Industrial Engineering, New Jersey Institute of Technology, Newark, New Jersey 07102, USA*
[2]*Department of Aerospace Engineering and Mechanics, University of Minnesota, Minneapolis, Minnesota 55455, USA*

(Received 22 December 2010; revised manuscript received 28 January 2011; published 14 April 2011)

It is shown that the inertia of a particle plays an important role in its motion in the direction normal to a fluid-liquid interface, and in determining its adsorption trajectory and orientation in the adsorbed state. Although the importance of inertia diminishes with decreasing particle size, on an air-water interface the inertia continues to be important even when the size is as small as a few nanometers. Furthermore, similar to an underdamped system, an adsorbed particle has characteristic linear and rotational frequencies that can be excited by an external forcing.

DOI: 10.1103/PhysRevE.83.041606 PACS number(s): 68.05.−n, 47.57.−s, 47.55.−t

In recent years, there has been much interest in the absorbed state of colloidal particles at fluid-liquid interfaces, i.e., their positions and orientations within the interface, because of their importance in a range of applications [1,2]. In these studies, the stable state is determined by a static analysis of the forces and torques that act on the particle. The momentum equation governing the motion in the direction normal to the interface and the angular-momentum equation governing the orientation, as well as the role of the particle inertia, are not considered. However, since nonspherical particles can have multiple stable states, a static analysis, as noted in Refs. [2] and [3], is not sufficient for determining which of these states are likely to be assumed by the particle. Furthermore, we have recently shown that the motion of particles in the direction normal to the interface while being adsorbed gives rise to a secondary lateral flow on the interface that causes newly adsorbed particles to disperse and those already present on the interface to move away (see Ref. [4]). This can influence the distribution as well as the state of particles on the interface.

In this paper, we show that, although the assumption that the inertia of small particles is negligible is justified in many problems involving colloidal particles because of their small mass, it may not be appropriate in the modeling of their adsorption at fluid-liquid interfaces. In fact, the motion of a particle in the direction normal to the interface is similar to that of an underdamped system in that it has characteristic linear and rotational frequencies that are excitable by an external forcing.

To show this, let us assume that the inertia is negligible. Then, the velocity V of the particle is determined by a balance of the capillary and drag forces, which gives $V = \frac{\gamma_{12}}{\mu}$. Here γ_{12} is the interfacial tension between the upper and lower fluids, and μ is the viscosity (which for simplicity is taken to be the larger of the upper-fluid or lower-fluid viscosity). The role of other forces such as gravity, as discussed below, is negligible for small particles. The kinetic energy E_k of the particle then becomes $E_k = \frac{1}{2}mV^2 = \frac{2\pi\rho_p R^3}{3}(\frac{\gamma_{12}}{\mu})^2$, where m is the particle mass, R is the particle radius, and ρ_p is the particle density. The adsorption energy W_a of a spherical particle is $W_a = \pi R^2\gamma_{12}(1+\cos\alpha)^2$, where α is the contact angle [1,2,4]. Assuming that the contact angle is 90°, the ratio of the kinetic and adsorption energies becomes

$$\frac{E_k}{W_a} = \frac{2\rho_p R\gamma_{12}}{3\mu^2}. \tag{1}$$

Clearly, $\frac{E_k}{W_a}$ must be *less* than 1 because the particle accelerates under the action of the capillary force and so its kinetic energy must be less than the interfacial work done on it. Furthermore, the inertia of the particle can be considered negligible only if its kinetic energy, a measure of the particle's inertia, is much smaller than the interfacial energy released during its adsorption, i.e., $\frac{E_k}{W_a} \ll 1$.

We next evaluate this ratio for a neutrally buoyant particle at an air-water interface, i.e., $\mu = 0.001$ Pa s, $\rho_p = 1000$ kg/m^3, and $\gamma_{12} = 0.07$ N/m: $\frac{E_k}{W_a} \sim 10^8 R$. Thus, the inertia of a particle can be considered negligible only when R is *much smaller* than 10 nm. Furthermore, for $R \gtrsim 10$ nm, we erroneously obtain $\frac{E_k}{W_a} > 1$, which is a consequence of neglecting the inertia of the particle.

Momentum conservation: When a particle comes in contact with a fluid-liquid interface, or moves away from its equilibrium position in the interface, the component of the capillary force in the direction normal to the interface acts to bring it back to its equilibrium position (Fig. 1). The motion of the particle is given by the governing equations for the two fluids and the momentum equation for the particle, which are coupled, along with the interface stress condition and a condition for the contact-line motion. This is a formidable problem which can be solved analytically only in simple situations [4–7].

To quantify the role of various forces that act on a particle, let us consider the *decoupled* momentum equation in which the fluid forces that act on the particle are modeled [3,8]. The forces that act on the particle are the vertical capillary force (F_{st}), the buoyant weight (F_g), the Brownian force (F_{B}), and the viscous drag (F_{D}). The acceleration of a particle under the action of these forces can be written as

$$m\frac{dV}{dt} = F_{st} + F_{\mathrm{D}} + F_g + F_{\mathrm{B}}, \tag{2}$$

where m is the effective mass of the particle which includes the added mass contribution, and V is the velocity. The Brownian

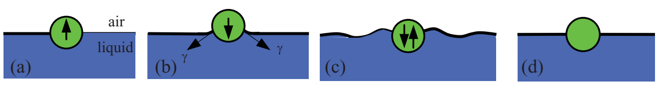

FIG. 1. (Color online) Vertical oscillation of a particle adsorbed at an air-liquid interface. The contact angle is assumed to be 90°, and so in equilibrium it floats with its center at the undeformed interface. (a) The particle is pushed up from its equilibrium position. (b) The particle is pulled downward by the interfacial force (γ). (c) The particle oscillates about the equilibrium height. (d) After oscillations subside, the particle assumes its equilibrium position.

force which is included here for completeness is negligible compared to the capillary force, as will be discussed below, and therefore need not be considered.

For a spherical particle, $F_{st} = 2\pi R\gamma_{12} \sin(\theta_c)\sin(\theta_c + \alpha)$ (see Fig. 2) [6]. We will assume that the drag force is given by $F_{\mathrm{D}} = 6\pi\mu R V f_D$, where μ is the viscosity of the lower liquid, and f_D is a coefficient which accounts for the fact that the particle is immersed in both upper and lower fluids. If $f_D = 1$, this expression reduces to Stokes law. Also, for simplicity, we will assume that the added mass is one half of the mass of the fluid displaced [8]. Although this result is for a particle fully immersed in a fluid and not for a particle on the interface, it is not likely to change the qualitative nature of results.

The angular velocity Ω of the particle is given by

$$\frac{d(I_p\Omega)}{dt} = T_{st} + T_D + T_g, \tag{3}$$

where I_p is the moment of inertia of the particle, T_{st} is the torque due to the interfacial tension, T_D is the torque due to the viscous resistance, and T_g is the torque due to gravity. Here we have assumed that the shape of the particle is symmetric, e.g., a rod or an ellipsoid, and therefore only one component of the angular-momentum equation needs to be considered.

The torque on a spherical particle due to the interfacial tension is zero [9], and thus the rotational motion is not important for spherical particles. To illustrate the role of inertia in the rotational motion, we will consider a rod of length L and radius R, which in equilibrium floats on a liquid surface with its axis parallel to the surface (see Fig. 3). We will assume that the contact angle is 90°, and that it floats such that one half of it is immersed in the liquid below. When the angle between the axis of the rod and the undeformed liquid surface is θ, an interfacial torque of $\gamma L^2(\frac{L}{6R} + 2\frac{R}{L})\sin\theta$ acts on the rod to bring it back to its equilibrium horizontal orientation. In addition, a frictional torque $T_D = -\frac{\pi\mu L^3}{3}\ln(\frac{L}{2R})\Omega$ acts on a rotating rod [10]. The moment of inertia of a rod about a direction normal to its axis is $\frac{mL^2}{12}$, where m is the mass of the rod.

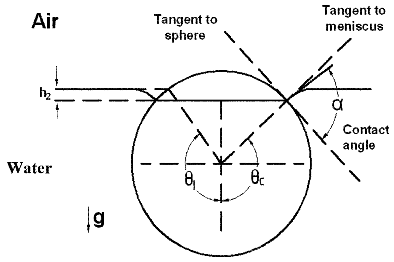

FIG. 2. Schematic of a heavier-than-liquid hydrophilic (wetting) sphere hanging on the contact line at θ_c. The point of extension of the flat meniscus on the sphere determines the angle θ_1 and h_2.

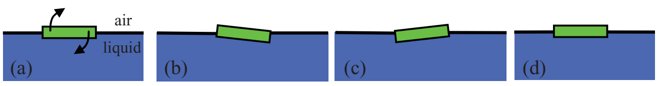

FIG. 3. (Color online) Rotational oscillation of a cylindrical rod adsorbed at an air-liquid interface. The contact angle is assumed to be 90°, and so in equilibrium the rod floats with its center at the undeformed interface and axis parallel to the interface. (a) The rod is rotated clockwise from its equilibrium orientation. (b) The rod rotates in the direction of the torque, but is pulled back by the interfacial torque toward its equilibrium orientation. (c) The rod oscillates about the equilibrium orientation. (d) After the oscillations subside, the rod assumes equilibrium orientation.

Brownian forces: The Brownian force in Eq. (2) is negligible compared to the capillary force. To show this, we note that the Brownian force cannot cause a particle to move away from its equilibrium position within the interface or deadsorb when W_a is larger than kT, i.e., $\frac{W_a}{kT} = \frac{\pi R^2\gamma_{12}}{kT} > 1$. Here we have assumed α to be 90°. The same result can be obtained from the Peclet number, defined to be the ratio of the capillary and Brownian forces, $\mathrm{Pe} = \frac{RU}{D_{\mathrm{B}}} = \frac{6\pi R^2\gamma_{12}}{kT} > 1$, where $U = \frac{\gamma_{12}}{\mu}$ is the characteristic velocity and $D_{\mathrm{B}} = \frac{kT}{6\pi\mu R}$ is the Brownian diffusion coefficient [10,11]. This is the same condition except for a constant factor of 6 in the definition of the Peclet number. On an air-water interface, for $R = 1\ \mu$m, $\mathrm{Pe} \approx 10^8$, and for $R = 10$ nm, $\mathrm{Pe} \approx 10^4$. Therefore, for $R \gtrsim 10$ nm, the Brownian force is several orders of magnitude smaller than the capillary force (in the direction normal to the interface), and thus can be neglected.

Governing dimensionless parameters: Assuming that the characteristic velocity, length, and time are $U = \gamma_{12}/\mu$, R, and R/U, respectively, Eq. (2) can be nondimensionalized to give (see Ref. [6])

$$\mathrm{We}\, m'\frac{\rho_p}{\rho}\frac{dV'}{dt'} = \sin(\theta_c)\sin(\theta_c + \alpha) + 3V' f_D + \frac{2}{3}B\frac{\rho_p - \rho_c}{\rho} f_b\left(\frac{\rho_a}{\rho}, \frac{\rho_p}{\rho}, \theta_c, \frac{h_2}{R}\right). \tag{4}$$

Here the primed variables are dimensionless. f_b is the dimensionless buoyancy which is $O(1)$ but depends on the profile of the deformed interface. θ_c and h_2 are defined in Fig. 2. ρ and ρ_a are the densities of the lower and upper fluids, ρ_c is the effective density of the volume displaced by the particle, and ρ_p is the particle density. The dimensionless parameters in the above equation are the Weber number $\mathrm{We} = \frac{2}{3}\frac{\rho R\gamma_{12}}{\mu^2}$, the Bond number $B = \rho R^2 g/\gamma_{12}$, the density ratio $\frac{\rho_p}{\rho}$, and the contact angle α. The Weber number is the ratio of the fluid's inertia and surface tension, and the Bond number is the ratio of gravity and surface tension forces. As the characteristic velocity is the capillary velocity, the capillary number is unity (see Ref. [6]). Thus, the Reynolds number (Re), which is a product of the We and capillary number, becomes the same as We, i.e., Re = We.

Similarly, assuming that the characteristic angular velocity, length, and time are $\frac{\gamma_{12}}{\mu L}$, L, and $\frac{\mu L}{\gamma_{12}}$, respectively, Eq. (3) can nondimensionalized to give

$$\frac{\pi}{8}\frac{R}{L}\frac{\rho_p}{\rho}\mathrm{We}\frac{d\Omega'}{dt'} = \sin\theta\left(\frac{L}{6R}+2\frac{R}{L}\right) - \frac{\pi}{3}\ln\left(\frac{L}{2R}\right)\Omega' - \frac{1}{6}B\frac{L}{R}\frac{\rho_p-\rho_c}{\rho}\sin\alpha\,\tan\theta\,\cos\theta. \quad (5)$$

The dimensionless parameters in this equation are $\frac{R}{L}$, and those in Eq. (4): We, B, $\frac{\rho_p}{\rho}$, and α.

To illustrate our results, we consider the case of a particle on an air-water interface, assuming the parameters to have the values $\mu = 0.001$ Pa s, $\rho = \rho_p = 1000\ \mathrm{kg/m^3}$, $\frac{\rho_p-\rho_c}{\rho} = 0.1$, and $\gamma_{12} = 0.07$ N/m, and $\mu_a = \rho_a = 0$, $m' = 1.5$, $f_d = 0.5$, and $f_b = 1$. Therefore, for an air-water interface, We $\sim 10^8 R$ and $B \sim 10^5 R^2$.

The role of particle inertia becomes negligible only when We $\ll 1$ or R is *much smaller* than 10 nm. The influence of gravity on an air-water interface becomes negligible when B is small or $R \lesssim 1$ mm in the sense that such small particles float so that the interfacial deformation is negligible [1,4–6]. However, even a negligibly small deformation of the interface gives rise to attractive lateral capillary forces which, even though small, cause floating particles to cluster. This happens because a particle floating on a liquid surface is *free* to move laterally. The only resistance to its lateral motion is the hydrodynamic drag that can slow its motion but *cannot* stop it.

Therefore, only very small particles, for which lateral capillary forces are smaller than Brownian forces, do not cluster. For example, on an air-water interface, lateral capillary forces become smaller than Brownian forces when $R \lesssim 10\ \mu$m, and so micrometer and smaller sized particles undergo Brownian motion on the interface and do not cluster [4–6]. Meanwhile, the capillary force which acts vertically to pull the particle back toward its equilibrium position in the interface remains much stronger than the Brownian force, even for nanoparticles.

Vertical oscillation of a sphere: Our experiments and direct numerical simulations show that when a particle being adsorbed reaches the equilibrium height for the first time, its velocity is nonzero, and so it continues to move downward [4]. However, when the particle center moves below the equilibrium height, the vertical capillary force changes direction and acts upward to bring the particle back to the equilibrium height. This suggests that the motion of the particle in the direction normal to the interface is inertia dominated. This can be also seen by linearizing Eq. (4) about the particle's equilibrium position. It can be shown that the behavior of the particle depends on the sign of $D = 9R^2\mu^2[1 - \frac{8}{9}We\frac{\rho_p}{\rho}[2 + B(\frac{\rho_p-\rho_c}{\rho})]]$. Here we have assumed that the contact angle is 90°. When $D < 0$, the particle undergoes underdamped oscillations about the equilibrium height, and when $D > 0$, its displacement from the equilibrium height decays exponentially with time (see Ref. [4]). For small particles, B is small, and thus D is zero for We $= \frac{9}{16}\frac{\rho}{\rho_p}$. Above this critical value of We (or R), D is negative and the particle motion is underdamped.

The dimensionless frequency of oscillation $\omega\prime$ for $D < 0$ is given by

$$\omega' = \omega\frac{R\mu}{\gamma_{12}} = \frac{3}{8\pi\ \mathrm{We}}\frac{\rho}{\rho_p}\sqrt{-1 + \frac{8}{9}\mathrm{We}\frac{\rho_p}{\rho}\left[2 + B\left(\frac{\rho_p-\rho_c}{\rho}\right)\right]}. \quad (6)$$

The frequency ω increases with decreasing R (or We). For an air-water interface for $\frac{\rho_p}{\rho} = 1$, for $R = 1$ mm, $\omega = 51.6$ Hz; for $R = 10\ \mu$m, $\omega = 5.2 \times 10^4$ Hz; and for $R = 100$ nm, $\omega = 4.8 \times 10^7$ Hz.

The above results imply that for a particle adsorbed on an interface there is a characteristic frequency which can be excited by an external forcing. To show that this is indeed the case, we conducted experiments in which a particle floating on a water surface was subjected to an oscillatory magnetic field of variable frequency generated by an electromagnet mounted directly above the interface and the particle (see Fig. 4) [12]. The particles used in this study were steel or plastic beads that contained a smaller magnetizable particle inside. When

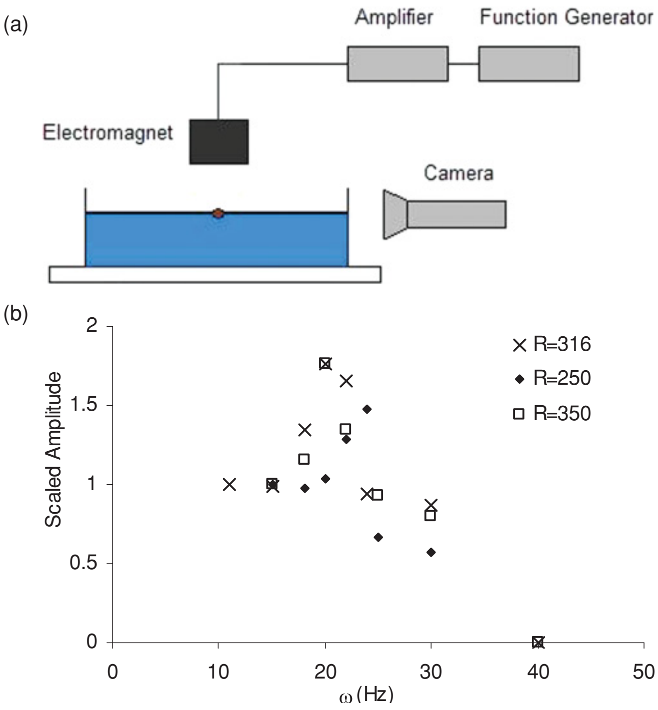

FIG. 4. (Color online) (a) Schematic of the experimental setup used to study the forced oscillations of a steel bead floating on a liquid surface. An oscillating voltage from a function generator was amplified and then applied to an electromagnet mounted directly above the interface to produce an oscillating magnetic field. The bead was subjected to an oscillating magnetic force in the direction normal to the interface. The vertical oscillations of the bead were recorded using a high-speed camera. (b) The scaled amplitude of oscillation for three spherical steel beads floating on the surface of water is shown as a function of the forcing frequency. The radii of the beads were 250, 316, and 350 μm. The amplitude is scaled by a constant factor so that it has a value of unity at the smallest measured frequency. The amplitude of forced oscillation for the 350-μm bead was maximal around ~20 Hz and for the 250-μm bead around ~24 Hz.

the magnetic field was switched on, the particle was subjected to an oscillatory magnetic force in the direction normal to the interface. The amplitude of oscillation of the particle due to this forcing was measured by analyzing high-speed video recordings of the particle's vertical motion. Figure 4(b) shows the amplitude of oscillation for three steel beads as a function of the frequency. For $R = 350$ μm, the amplitude was maximal at the frequency of ~20 Hz; for $R = 316$ μm, at ~20 Hz; and for $R = 250$ μm, at ~24 Hz. The latter is approximately the smallest size for which such measurements could be made using our present experimental setup.

This behavior of a particle adsorbed at the interface is similar to that of an underdamped mass-spring-dashpot system subjected to forced oscillations. The frequency at which the amplitude is maximal is comparable to that given by Eq. (6) for this system. Also, the frequency increases with decreasing particle radius, in agreement with Eq. (6). The approximate agreement is noteworthy considering that Eq. (6) contains only the fluid and particle properties, and that there are *no* adjustable parameters.

Rotational oscillation of a rod: Similarly, Eq. (5) can be linearized about the equilibrium orientation to show that the rotational behavior of a rod when disturbed from equilibrium orientation depends on the sign of

$$D_r = \left[\frac{\pi}{3}\ln\left(\frac{L}{2R}\right)\right]^2 \left\{1 - \frac{9}{2\pi}\frac{\mathrm{We}}{\left[\ln\left(\frac{L}{2R}\right)\right]^2}\frac{\rho_p}{\rho} \times \left[\frac{1}{6} + 2\left(\frac{R}{L}\right)^2 - \frac{1}{6}\frac{\rho_p - \rho_c}{\rho}B\right]\right\}.$$

The contact angle has been assumed to be 90°. The rod undergoes underdamped rotational oscillations about the equilibrium orientation when $D_r < 0$. The dimensionless rotational frequency ω_r' of the rod for $D_r < 0$ is given by

$$\omega_r' = \omega_r \frac{\mu L}{\gamma_{12}} = \frac{4}{3}\frac{L}{R}\ln\left(\frac{L}{2R}\right)\frac{1}{\mathrm{We}}\frac{\rho}{\rho_p}\sqrt{\left(-1 + \frac{9}{2\pi}\frac{We}{\left[\ln\left(\frac{L}{2R}\right)\right]^2}\frac{\rho_p}{\rho}\left[\frac{1}{6} + 2\left(\frac{R}{L}\right)^2 - \frac{1}{6}\frac{\rho_p - \rho_c}{\rho}B\right]\right)}. \quad (7)$$

Notice that the rotational frequency ω_r' depends on We, B, the density ratios and the aspect ratio $\frac{L}{R}$, and that it is different from the characteristic frequency with which a rod oscillates vertically. The frequency ω_r increases with decreasing R (or We), and decreases with increasing aspect ratio $\frac{L}{R}$. For example, for an air-water interface for $\frac{L}{R} = 4$, $\frac{\rho_p}{\rho} = 1$, for $R = 1$ mm, $\omega_r = 568.6$ Hz; for $R = 10$ μm, $\omega_r = 5.9 \times 10^5$ Hz; and for $R = 100$ nm, $\omega_r = 4.9 \times 10^8$ Hz. For $\frac{L}{R} = 8$, $\frac{\rho_p}{\rho} = 1$, for $R = 1$ mm, $\omega_r = 323.8$ Hz; for $R = 10$ μm, $\omega_r = 3.6 \times 10^5$ Hz; and for $R = 1$ μm, $\omega_r = 9.5 \times 10^6$ Hz. For this larger value of the aspect ratio, when R is $O(100$ nm) the rotational motion of the rod becomes overdamped.

In conclusion, it is shown that the behavior of particles adsorbed at fluid-liquid interfaces in the direction normal to the interface is different from that in the lateral direction to the interface. This is a consequence of the fact that particles are free to move laterally on the interface just as when they are fully immersed in a fluid, but in the direction normal to the interface the capillary force keeps them at their stable positions in the interface. Consequently, although inertia can be usually neglected for a colloidal particle fully immersed in a fluid, this may not be case for a particle trapped at a fluid-liquid interface even when its size is as small as a few nanometers. Furthermore, for an adsorbed particle there are characteristic linear and rotational frequencies that can be excited by an external forcing. This latter behavior of particles is similar to that of an underdamped mass-spring-dashpot system.

[1] W. H. Binder, Angew. Chem. Int. Ed. **44**, 5172 (2005); *Colloidal Particles at Liquid Interfaces: An Introduction*, edited by B. P. Binks and T. S. Horozov (Cambridge University Press, Cambridge, UK, (2006); C. Zeng, H. Bissig, and A. D. Dinsmore, Solid State Commun. **139**, 547 (2006); B. Madivala, J. Fransaer, and J. Vermant, Langmuir **25**, 2718 (2009).

[2] F. Bresme and M. Oettel, J. Phys. Condens. Matter **19**, 413101 (2007); J. Faraudo and F. Bresme, J. Chem. Phys. **118**, 6518 (2003).

[3] J. de Graaf, M. Dijkstra, and R. van Roij, Phys. Rev. E **80**, 051405 (2009); J. Chem. Phys. **132**, 164902 (2010).

[4] P. Singh, D. D. Joseph, S. K. Gurupatham, B. Dalal, and S. Nudurupati, Proc. Natl. Acad. Sci. **106**, 19761 (2009); P. Singh, D. D. Joseph, and N. Aubry, Soft Matter **6**, 4310 (2010).

[5] M. M. Nicolson, Proc. Cambridge Philos. Soc. **45**, 288 (1949); H. M. Princen, *Surface and Colloid Science*, edited by E. Matijevie (Interscience, New York, (1969); V. N. Paunov, P. A. Kralchevsky, N. D. Denkov, and K. Nagayama, J. Colloid Interface Sci. **157**, 100 (1993); P. A. Kralchevsky, and N. D. Denkov, Curr. Opin. Colloid Interface Sci. **6**, 383 (2001).

[6] P. Singh, and D. D. Joseph, J. Fluid Mech. **530**, 31 (2005).

[7] P. Singh, D. D. Joseph, T. I. Hesla, R. Glowinski, and T. W. Pan, J. Non-Newtonian Fluid Mech. **91**, 165 (2000); P. Singh, T. I. Hesla, and D. D. Joseph, Int. J. Multiphase Flows **29**, 495 (2003).

[8] C. Crowe, *Multiphase Flows with Droplets and Particles* (CRC, Boca Raton, FL, 1998); L. S. Fan and C. Zhu, *Principles of Gas-Solid Flows* (Cambridge University Press, Cambridge, UK, 1988); I. G. Currie, *Fundamentals Mechanics of Fluids* (McGraw-Hill, New York, 1974).
[9] P. Singh and T. I. Hesla, J. Colloid. Interface Sci. **280**, 542 (2004).
[10] J. K. G. Dhont, *An Introduction to Dynamics of Colloids* (Elsevier, Amsterdam, 1996).
[11] K. Tsujii, *Surface Activity: Principles, Phenomena, and Applications* (Academic, New York, 1998).
[12] B. Dalal, S. K. Gurupatham, Md. Hossain, I. Fischer, P. Singh, and D. D. Joseph (unpublished).