

Mobility and In Situ Aggregation of Charged Microparticles at Oil–Water Interfaces

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Particle mobility, aggregate structure, and the mechanism of aggregate growth at the two-dimensional level have been of long-standing interest. Here, we use solid-stabilized emulsions as a model system to investigate the mobility of charged microparticles at poly(dimethylsiloxane) (oil)–water interfaces using confocal laser scanning microscopy. Remarkably, the rate of diffusion of the charged colloidal-sized polystyrene particles at the oil–water interface is only moderately slower than that in the bulk water phase. The ambient diffusion constant of solid particles is significantly reduced from $1.1 \times 10^{-9} \text{ cm}^2/\text{s}$ to $2.1 \times 10^{-11} \text{ cm}^2/\text{s}$ when the viscosity of the oil phase increases from 5 cSt to 350 cSt. In addition, we successfully observe the in situ structural formation of solid particles at the oil–water interface.

Particle mobility, aggregate structure, and the mechanism of aggregate growth at the two-dimensional level have been of long-standing fundamental as well as practical interest for diverse physical, chemical, and biological applications.^{1–7} An important consensus was reached which stated that the electrostatic repulsion was enhanced for charged particles at the interface between an aqueous phase and a low dielectric constant medium including air and oil.^{1,5,7} The enhanced repulsion usually resulted in a long-range ordered structure of charged solid particles at the interface, even at low solid concentrations.^{1,5,7,8} However, the existence of longer-range attraction between similarly charged colloids at the two-dimension or the three-dimension is controversial.^{9,10} The detailed mechanism of the aggregation of charged colloidal particles also remains unclear. Another unanswered fundamental question is the mobility of charged microparticles at the fluid–fluid interface. In this work, we use solid-stabilized emulsions as a model system to directly observe the mobility and in situ aggregation of charged microparticles at poly(dimethylsiloxane)–water emulsion interfaces.

Solid-stabilized emulsions (often referred to as Pickering emulsions and used hereafter), composed of droplets of one immiscible liquid in another liquid stabilized by solid particles, were discovered almost a century ago.¹¹ Recently, there has been a growing interest in Pickering emulsions because they open new avenues of emulsion stabilization and have numerous practical applications.^{8,12–15} For

example, in recent work, we reported that hydrophobic and hydrophilic polystyrene particles could simultaneously self-assemble to the same poly(dimethylsiloxane)–water emulsion interface.⁸ We also found that monodisperse colloidal-sized charged polystyrene solid particles, when included in the emulsions at low concentrations, were found to form small patches at the oil–water interface with local “hexagonal” order, separated by other particle-free domains.⁸

Pickering emulsions also provide a novel and convenient experimental model system for investigating particle mobility, aggregation, and the growth mechanism at the liquid–liquid interface. In Pickering emulsions, the motion of solid particles into either the water or the oil phase is restricted due to the high desorption energy. For instance, the average Gibbs free energy of desorption is calculated to be $1.43 \times 10^7 \text{ kT/particle}$ for poly(dimethylsiloxane) (oil, 5 cSt)-in-water Pickering emulsions containing sulfate-treated polystyrene particles of $1 \mu\text{m}$.⁸ The high desorption energy (conventional surfactants only have 10–20 kT/surfactant molecule¹⁶) indicates that the solid particles strongly adhere to the oil–water interface and the adsorption is almost irreversible. Thus, the assembled particles are confined at the oil–water interface and can only move laterally along the droplet contour, when the emulsion interface is partially covered with solid particles. The advantage of using Pickering emulsions as a model system to investigate particles at the liquid–liquid interface includes easily changeable interfacial properties such as curvature, tension, and rheology. It also provides direct fundamental understanding of Pickering emulsions for practical applications.

The poly(dimethylsiloxane) (oil)–water type of Pickering emulsions containing sulfate-treated polystyrene solid particles were prepared using an ultrasonic processor (Sonics VibraCell, 500 W model). The oil (Rhodorsil Fluid, viscosity of 5–350 cSt at 25 °C) and water (HPLC grade, residue after evaporation <1 ppm) were purchased from Chemsil and Fisher Scientific, respectively. The interfacial tension of the oil–water interface, measured using a Krüss K100 tensiometer, varied from 40.4 mN/m to 42.7 mN/m when using oils with different viscosities (5–350 cSt). The

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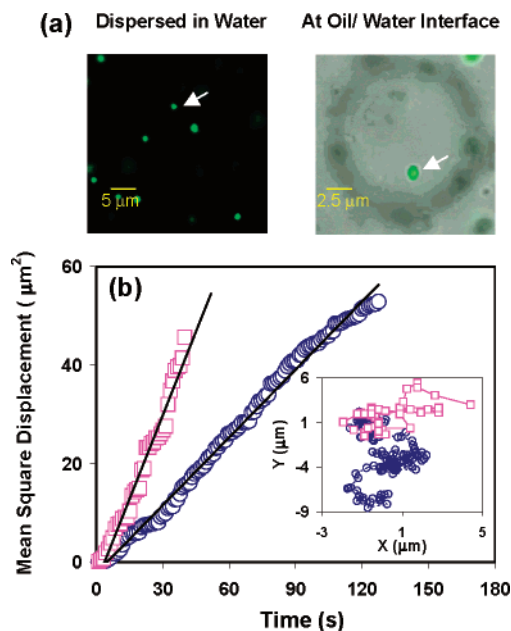


Figure 1. (a) Fluorescent image (left) of polystyrene particles dispersed in water and an overlay of a fluorescent image and a differential interference contrast image (right) of a polystyrene particle at the oil–water interface; the arrows point to the particles analyzed in part b. (b) Mean square displacement of the particle dispersed in water (squares) and the particle at the oil–water interface (circles). The solid lines represent the linear regression lines. The inset shows the trajectory of particle movement; the time between each point is 1 s. The initial positions were set to be at (0, 0).

sulfate-treated polystyrene particles were purchased from Molecular Probes, with diameters of $1.1 \pm 0.026 \mu\text{m}$ (hydrophobic, average surface charge densities of $5.176 \times 10^{-2} \text{ C/m}^2$). The low density of the sulfate-treated polystyrene particles, 1.055 g/cm^3 , is fairly close to those of water and oil and minimizes the gravity effect in the experiments. A confocal laser scanning microscope, the Olympus FV 300, was used to obtain detailed information on the mobility and in situ structural formation of solid particles at the oil–water interface under ambient conditions (with a typical temperature of 25.4°C). The possible effect of droplet rotation and fluctuation has been carefully addressed.¹⁷ We performed postimage analysis using the ImageJ program from NIH Image.

Figure 1 plots the mean square displacement, $\langle r^2 \rangle$, as a function of time, $\langle t \rangle$, for a single charged polystyrene particle at the oil (5 cSt)–water interface as well as for a charged polystyrene particle dispersed in water. Displacement was recorded every second. The mean square displacement was calculated by following the movement of the particles in each frame. The inset in Figure 1b is the trajectory of particle movement. The ambient diffusion constant, calculated from the particle dispersed in water and from $\langle r^2 \rangle = 4D\langle t \rangle$ (although the particle was moving three-dimensionally, we only recorded the two-dimensional trajectories), is $2.8 \times 10^{-9} \text{ cm}^2/\text{s}$. This value is reasonably close to the value, $4.4 \times 10^{-9} \text{ cm}^2/\text{s}$, calculated from the Stokes–Einstein relationship, $D = kT/6\pi\eta a$, where k is the Boltzman constant, η is the viscosity of the

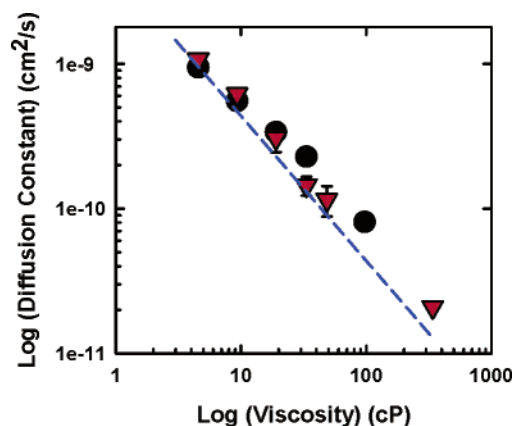


Figure 2. Effect of poly(dimethylsiloxane) (oil) viscosity on the diffusion coefficient of single polystyrene particles at the interfaces in oil-in-water type (triangles) and water-in-oil type (circles) Pickering emulsions. The dashed line is calculated on the basis of the Stokes–Einstein relation if the particles were dispersed in the bulk oil phase.

medium, and a is the radius of the particle. The comparable values support the hypothesis of the applicability of the Stokes–Einstein relationship to electrically charged particles.¹⁸ In addition to the dispersed particle in water, we also quantified the diffusion for the single particle at the oil–water interface in Figure 1. Remarkably, the ambient diffusion constant of the particle at the oil–water interface ($D_{\text{oil–water interface}} = 1.1 \times 10^{-9} \text{ cm}^2/\text{s}$) is only moderately smaller compared to that in the bulk. This suggests that the Brownian motion of charged solid particles at the two-dimensional oil–water interface is surprisingly fast.

We have changed the oil phase with oils of different viscosities and found that it has a significant influence on the diffusion of charged solid particles at the oil–water interface, as shown in Figure 2. The interfacial tension of the oil–water interface remains relatively constant, measured to be $41.6 \pm 1.1 \text{ mN/m}$. The ambient diffusion constant drops rapidly from $1.1 \times 10^{-9} \text{ cm}^2/\text{s}$ to $2.1 \times 10^{-11} \text{ cm}^2/\text{s}$ by increasing the viscosity of the oil phase to 350 cSt (339.5 cP). By comparing with the values calculated from the Stokes–Einstein relationship (the dashed line in Figure 2) if the particles were dispersed in the bulk oil phase, our work suggests that the hindrance of the diffusivity at the liquid–liquid interface is significantly influenced by the characteristics of the phase with higher viscosity. It needs to be noted that we performed experiments on both the oil-in-water type and water-in-oil type Pickering emulsions; the emulsion type seems to have a minor influence on the particle diffusion in these systems. We are also trying to address the influence of interfacial curvature on the mobility of particles, but the result is inconclusive due to the limited amount of data.

We also compared the ambient diffusion constants of a single particle and a five-particle cluster confined at the oil (5 cSt)–water emulsion interface. The diffusion constant of the cluster is significantly hindered compared to that of a single particle (lowered by a factor of 2); however, the hindrance in diffusivity is not linearly proportional to the cluster size, as concluded from the above and other data series.

Aggregation and structural formation of solid particles in two dimensions are of tremendous interest and im-

(17) The possible effect of droplet rotation and fluctuation has been carefully addressed. We have focused on Pickering emulsion droplets partially attached to the substrate or cover slip to prevent any rotational effect. We also included a fixed reference point to take into account any horizontal fluctuation effect of the droplets. In addition, we have compared the diffusion constants of 1.1 and $4 \mu\text{m}$ solid particles at the oil–water emulsion interface, and the difference is roughly on the order of 4.

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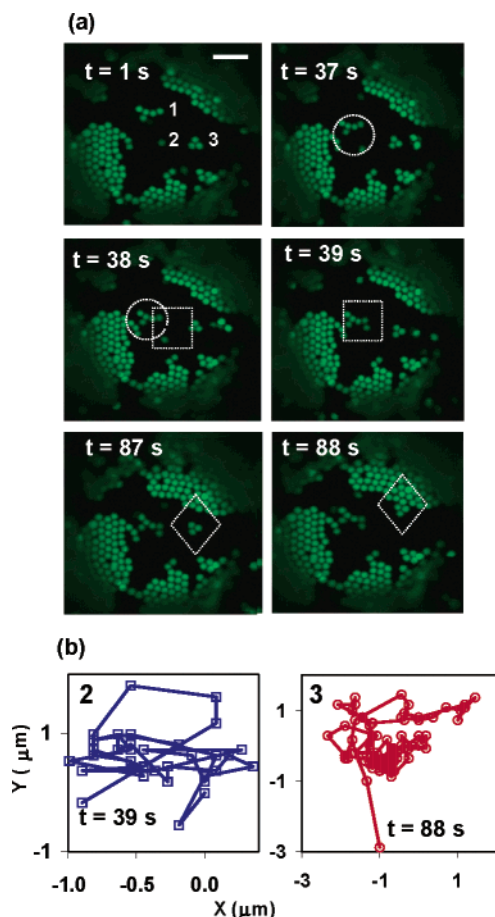


Figure 3. (a) Fluorescent images showing the aggregation of polystyrene particles at the poly(dimethylsiloxane) (5 cSt)-in-water Pickering emulsion interface. The circles, squares, and diamonds highlight locations before and after particle attachment. The scale bar is $5\ \mu\text{m}$. (b) Trajectories of the single particle (2) and the three-particle cluster (3) before aggregation. At $t = 0$, the positions were set to be at $(0, 0)$.

portant to various processes.^{19–21} Here, we report the in situ aggregation of charged solid particles at the oil–water interface in Pickering emulsions. Figure 3 shows a single particle, a three-particle cluster, and a five-particle cluster (in Figure 3a, $t = 1\ \text{s}$, designated as 2, 3, and 1, respectively) confined between already formed large cluster domains. The particle and the clusters initially went through “random walks” (here, we only show the trajectory plots of the single particle and the three-particle cluster) and then eventually attached to the large domains. Since every collision of the particles at the oil–water interface leads to aggregation of particles, the observed structural formation is likely due to diffusion-limited cluster aggregation (DLCA).^{21,22} Another example of the in situ structural formulation is shown in Figure 4. There was no noticeable structural change after 56 s. We are in the process of quantifying the kinetics and growth mechanism of the aggregates at Pickering emulsion interfaces. For example, by analyzing the trajectories and noticing some large steps right before aggregation, as shown in Figure 3b for the single particle and the three-particle cluster, our preliminary results suggest the existence of attraction (longer-

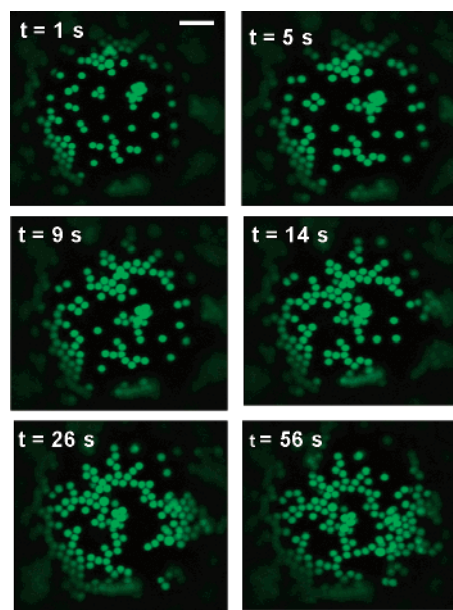


Figure 4. In situ structural formation of polystyrene particles at the poly(dimethylsiloxane) (20 cSt)-in-water Pickering emulsion interface. The scale bar is $5\ \mu\text{m}$.

range compared to the range of the repulsion) between similarly charged polystyrene particles at the oil–water interface.

This work, using confocal microscopy, studied the mobility of colloidal-sized charged polystyrene particles at the oil–water interface in Pickering emulsions. Remarkably, the rate of diffusion of the charged particles at the interface is only moderately slower than that in the bulk water phase. Increasing the viscosity of the oil phase significantly reduces the ambient diffusion constant of charged solid particles. We also successfully observed the in situ structural formation of charged solid particles at the oil–water interface in Pickering emulsions.

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