# Structure of Microparticles and Nanoparticles in Solid-Stabilized Emulsions

*Sowmitri Tarimala,[1] Chih-yuan Wu,[1] Renu Sharma,[2] and Lenore L. Dai,[1,]**

*[1] Department of Chemical Engineering, Texas Tech University, MS 3121, Lubbock, TX 79409*
*[2] Center for Solid State Science, Arizona State University, Temple, AZ 85287*

## Abstract

Emulsions of oil and water stabilized by adsorbed solid particles are known as solid-stabilized emulsions (often referred to as Pickering emulsions). Using confocal microscopy and environmental transmission electron microscopy, we have studied the self-assembly of colloidal-sized polystyrene particles and alkanethiol-capped silver nanopaticles in Pickering emulsions. Colloidal samples of monodisperse size, when exposed to the emulsion at low concentrations, were found to form small patches with local hexagonal order; these crystalline domains were separated by other particle-free domains. Polystyrene particles with different sizes (1 micron and 4 microns) and different wettability could simultaneously segregate to the emulsion interface and form mixtures on it. In contrast to microparticles that form monolayers, the dodecanethiol-capped silver nanoparticles of 1-5 nm form randomly distributed multilayers at the Pickering emulsion interface, with an interparticle distance varying from close contact to approximately 25 nm. Our work offers the first direct observation of nanoparticles in a liquid medium using the environmental transmission electron microscope (E-TEM).

About a century ago, Pickering discovered that fine solid particles could be used as stabilizers in emulsion technology.[1] Pickering emulsions, composed of droplets of one immiscible liquid in another liquid stabilized by solid particles, are often encountered in the recovery, separation, and cleaning of oil, in cosmetic preparation, and in wastewater treatment.[2] In Pickering emulsions, the solid particles are strongly adsorbed at the liquid-liquid interface, and the Gibbs free energy to remove one solid particle away from the interface is significantly higher than those of surfactants in conventional emulsions.[3,4] Recently, there has been growing interest in Pickering emulsions because they open new avenues of emulsion stabilization and have numerous practical applications. In addition, Pickering emulsions provide novel and simple templates for the self-assembly of solid microparticles[5] and nanoparticles.[6,7] Much relevant literature observes or assumes a monolayer of uniformly distributed spherical particles at the fluid-fluid interface in Pickering emulsions. It is also controversial whether or not a full coverage of solid at the oil-water interface is necessary to effectively stabilize Pickering emulsions.[8] Here, using confocal microscopy and environmental transmission electron microscopy (E-TEM) we have studied the structure of microparticles and nanoparticles at Pickering emulsion interfaces.

Oil-in-water Pickering emulsions containing solid particles were prepared using an ultrasonic processor, Sonics VibraCell, 500 watt model. The oil phase is either polydimethylsiloxane or trichloroethylene. The polydimethylsiloxane (Rhodorsil® Fluid 47V5, viscosity of 5 centiStokes at 25$^{o}$C) was purchased from Rhodia and the trichloroethylene (certified A.C.S. grade) and water (HPLC grade, residue after evaporation <1 ppm) were purchased from Fisher Scientific. In order to investigate the structure of the microparticles at Pickering emulsion interface, we purchased FluoSphere® fluorescent polystyrene microspheres from Molecular Probes. The nanoparticles used here are dodecanethiol-capped silver nanoparticles of 1-5 nm synthesized and size selected following well-established methods.[9,10] A confocal laser scanning microscope, Olympus FV 300 and an environmental transmission electron microscope (E-TEM), the Tecnai-20 FEG with upgraded environmental capability, have been employed to investigate the structure of microparticles and nanoparticles at the Pickering emulsion interfaces.

Figure 1a presents a three-dimensional (3D) fluorescent image of a droplet of a polydimethylsioxane (oil)-in-water Pickering emulsion containing sulfate- treated polystyrene particles of 1 micron.[11] The sulfate-treated polystyrene particles are hydrophobic and have fluorescent excitation/emission wavelengths of 505/515 nm and average surface charge densities of $5.176\times10^{-2}$ C/m$^2$. The oil-water interface is only partially covered with solid particles, although there are excess particles in the water phase. The partial coverage does not seem to be dynamically affected by time since there was no noticeable change in particle concentration at the interface during a 3-day sample aging. At the oil-water interface, the particles form small patches with local hexagonal order; these domains were separated by other particle-free domains. Because of the relatively low surface concentration of the solid particles (~0.46) at the oil-water interface, the aggregation of particles and formation of islands are likely due to the diffusion-limited cluster aggregation (DLCA), which is analogous to colloidal suspensions.[12] However, it is intriguing to observe the local "hexagonal" order within the clusters. The average distance between particle centers in the ordered region is 1.6 μm, indicating the existence of long-range repulsive forces. We concluded, as shown in

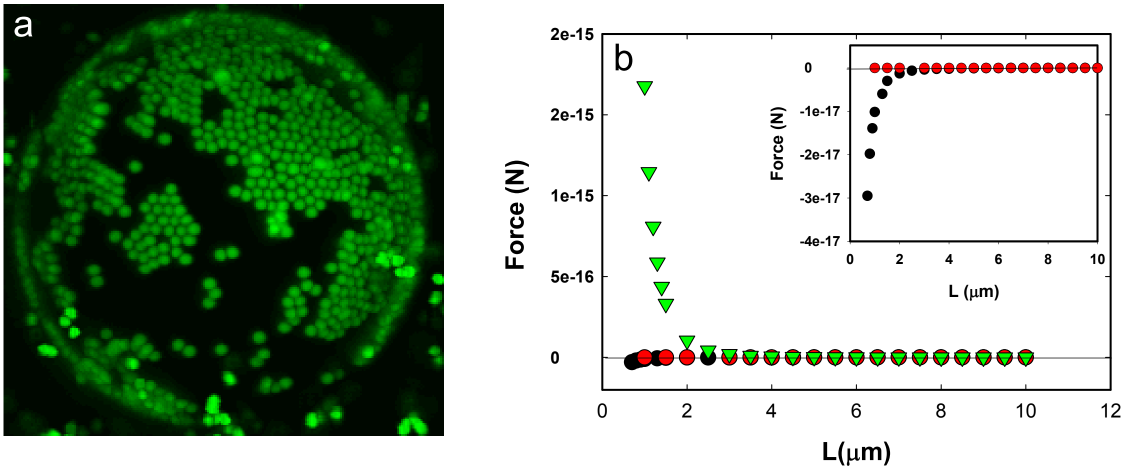

**Figure 1.** (a) A 3D image of a Pickering emulsion droplet; (b) Force-distance profiles of van der Waals force (black circles), electrostatic force (triangles), and capillary force (red circles). The insert is a replot of the van der Waals and capillary forces.

Figure 1b, that the electrostatic repulsion is the dominant force responsible for the "hexagonal" order. Figure 1b depicts the calculated force-distance profiles of the van der Waals, electrostatic, and capillary forces between two arbitrary particles at the oil-water interface. The van der Waals force was calculated using the equation, $F_{\text{van der waals}} = -A_{\text{eff}} * a * f(P)/12L^2$, where $A_{\text{eff}}$ is a modified effective Hamaker constant based on the immersion of particles at the oil-water interface, a is the radius of the solid particle, L is the distance between the two particles, and f(P) is an adjustable parameter which makes the van der Waals equation suitable for all distances.[13,14] The electrostatic force was calculated using, $F_{\text{electrostatic}} = 6\varepsilon_{\text{oil}} q_{\text{water}}^2/4\pi\varepsilon_0\varepsilon_{\text{water}}^2\kappa^2L^4$, where $\varepsilon_0$ is the permittivity of vacuum, $\varepsilon_{\text{oil}}$ and $\varepsilon_{\text{water}}$ are the relative permittivity of oil and water, $q_{\text{water}}$ is the charge of the water-immersed section of the particles, and $\kappa$ is the reciprocal of the Debye screening length.[15] Although the capillary interaction is expected to be minimal for small spheres, we included the calculated profile using the expressions developed by Chan et al for a complete comparison.[16]

The observed "hexagonal" order at the oil-water interface in the Pickering emulsion, resulting from the electrostatic repulsion, is consistent with the observation of the two-dimensional lattice structure formed by the polystyrene particles at the water/air planar interface.[17] There, the lattice order is due to the enhanced electrostatic repulsion originated from the asymmetry of the electrical double layers. In Pickering emulsions, the low permittivity of oil has a similar effect as air, and thus the electrostatic repulsion between the charged particles at the oil-water interface also increases.[15] It is also important to note that the electrostatic repulsion at the oil-water interface is insensitive to the ionic strength of the aqueous phase even with high electrolyte concentrations.[15]

Figure 1a shows an example of sulfate-treated polystyrene particles non-uniformly assembled (with local "hexagonal" order) at the oil-water interface. Pickering emulsions

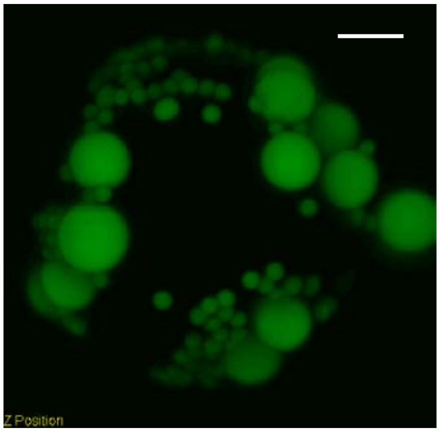

**Figure 2.** Self-assembled heterogeneous particles with diameters of 1 μm and 4μm at the oil-water interface. The scale bar is 5 μm.

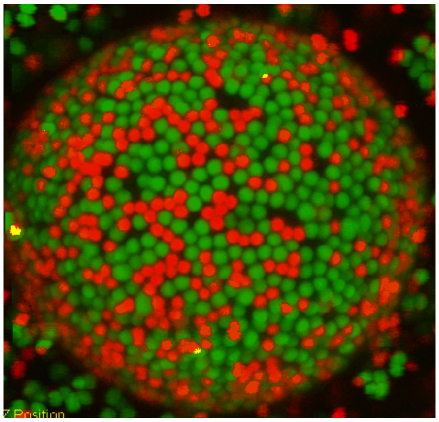

**Figure 3.** Simultaneously self-assembled hydrophobic (green) and hydrophilic (red) particles with diameters of 1 μm. Color print is needed to illustrate effect.

also provide a meaningful way to assemble heterogeneous solids with different sizes. Figure 2 shows a mixture of the sulfate-treated polystyrene particles with diameters of 1 micron and 4 microns that are simultaneously assembled at the oil-water interface. The solids particles were assembled from the equal bulk concentration of 0.15% by weight of each particle type in the liquid phase. It appears that the inclusion of 4-micron solid particles destroys the ordered packing resulting from the electrostatic repulsion discussed previously, although more experiments are needed to quantify the observation.

The most intriguing result that we report for microparticles, is the fact that hydrophobic and hydrophilic microparticles can simultaneously assemble at the oil-water interface. As it is known, the amphiphilic nature of molecules is a key element in the self-assembly of surfactants or polymer chains in the absence of electrostatic interactions. Similarly, the wettability of solid particles in Pickering emulsions has been reported as a key controlling factor, with hydrophilic particles tending to stabilize oil-in-water Pickering emulsions and hydrophobic particles tending to stabilize water-in-oil Pickering emulsions.[2,8,18] Figure 3 shows the sequential scanning result of a three-dimensional (3D) fluorescent image of an polydimethylsiloxane (oil)-in-water Pickering emulsion droplet containing both sulfate-treated (hydrophobic, in green) and carboxylate-treated (hydrophilic, in red) polystyrene particles of 1 micron. Figure 3 is the result of the simultaneous self-assembly of hydrophobic and hydrophilic particles from equal bulk concentration of 0.15% by particles. We hypothesize that this is due to the amphiphilic nature of the oil-water interface. We have made efforts to investigate the three-phase contact angles of the particles in Figure 3 and to comment on whether the hydrophobic and hydrophilic particles form a monolayer or semi-double layers across the oil-water interface. However, the results are inconclusive. Calculations for electrostatic stabilization are not presented here due the uncertainty of the three-phase contact angles of this system. We are in the process of further investigating this phenomenon.

Since the laser scanning confocal microscope does not provide sufficient resolution to show the detailed self-assembled structure of nanoparticles of 1-5 nm at the Pickering emulsion interface, we have employed the environmental transmission electron microscope (E-TEM) technique. The E-TEM has opened a new way to study, with a high resolution, hydrated materials in their natural states. The principle of E-TEM involves leaking a gas, for example, water vapor, up to certain pressures in the specimen area but restricting its leak to the rest of the column, especially the gun area.[19]

Figure 4a shows several droplets of a trichloroethylene-in-water Pickering emulsion containing dodecanethiol-capped silver nanoparticles of 1-5 nm recorded using the E-TEM; a portion of a droplet is shown in Figure 4b.[20] The Pickering emulsion contains nano-sized droplets, for example, the droplets (labeled with circles) with diameters less than 100 nm in Figure 4a, as well as large diameter droplets. The interface is nanoparticle-rich and the nanoparticles form randomly distributed multilayers, as shown in Figure 4b. From the imaged area, the inter-particle distance varies approximately from 0 (close contact) to 25 nm at the trichloroethylene-water interface. It is worthwhile to note that the images in Figures 4a and 4b are projected on emulsion droplets or a portion of the droplet suspended in the bulk water phase; they are representative and about ten similar images are obtained from different spots of the Pickering emulsion. They are not dried emulsion droplets that are pinned at the substrate.

Our preliminary work does not show any preferable adsorption of nanoparticles to either the water or the trichloroethylene, although the nanoparticles are hydrophobic by nature. The observed randomly distributed multilayers of the nanoparticles at the trichloroethylene-water interface is in sharp contrast to the hexagonal ordered monolayer of the dodecanethiol-capped 5 nm silver nanoparticles on solid substrates after solvent evaporated.[10] The variable inter-particle distance suggests that the nanoparticles do not experience consistently balanced attractive and repulsive forces at the interface that will lead to ordered arrays. Finally, one possible hypothesis for the multilayers is that the size of the nanoparticles is much smaller compared to the "sharpness" of the trichloroethylene-water interface. In this case, the trichloroethylene-water interface seems to have a thickness of approximately 85 nm with unclear chemical composition. Future experiments will be performed on dodecanethiol-capped silver nanoparticles at interfaces with other pairs of liquids.

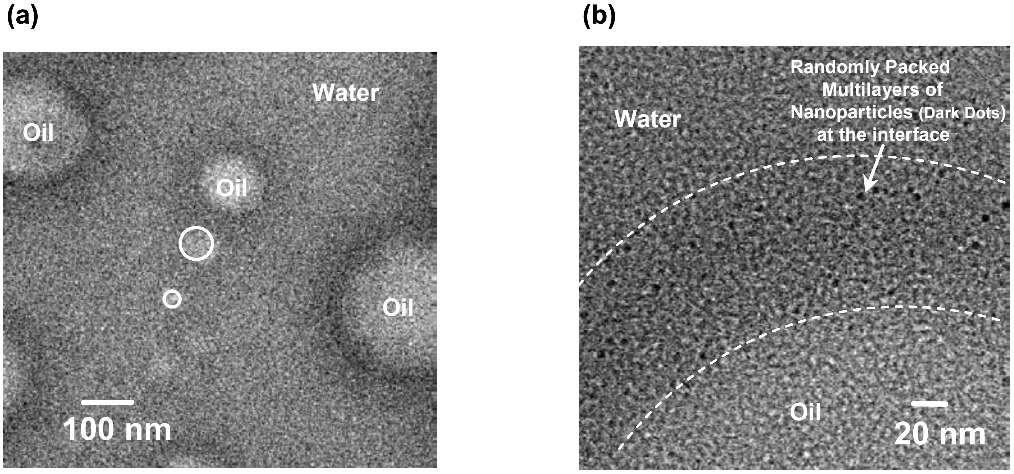

**Figure 4.** A trichloroethylene-in-water Pickering emulsions containing dodecanethiol-capped nanoparticles imaged by the E-TEM. (a) on a relatively large area (b) a portion of an emulsion droplet showing details at the interface.

This work, using confocal microscopy and environmental transmission electron microscopy, studied the structure of polystyrene microparticles and dodecanethiol-capped silver nanoparticles in Pickering emulsions. The polystyrene microparticles were found to aggregate and form a monolayer with small patches with local "hexagonal" order at low interfacial concentrations. Polystyrene particles with different sizes and different wettability could simultaneously segregate to the emulsion interface and form mixtures on it. In contrast to microparticles that form monolayers, the dodecanethiol-capped silver nanoparticles of 1-5 nm form randomly distributed multilayers at the liquid/liquid interface, with an interparticle distance varying from close contact to approximately 25 nm.

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