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Simulations of emulsion stabilization by silica nanoparticles

Marina Yu. Koroleva,* Andrey M. Tokarev and Evgeny V. Yurtov

D. I. Mendeleev University of Chemical Technology of Russia, 125047 Moscow, Russian Federation.
Fax: +7 495 495 2116; e-mail: m.yu.kor@gmail.com

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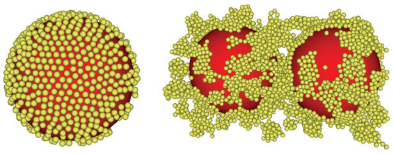
The Langevin dynamics simulation was used for studying the mechanisms of Pickering emulsion stabilization. The ranges of kinetically stable emulsions, unstable to coalescence, flocculated emulsions with silica nanoparticles bridging oil droplets, and emulsions with aggregated silica nanoparticle networks separating oil droplets were determined.



Oil droplet stabilized by SiO_2 nanoparticles

Nanoparticle gel in aqueous phase of emulsion

Methodologies for fabricating nano- and microcontainers as nanovehicles for drug delivery have been developed recently.[1] Emulsion-based delivery systems,[2,3] solid lipid particles[4,5] and organized systems based on amphiphiles[6] and oligosaccharides[7] are attractive for practical applications in pharmaceutical, food and cosmetic industries.

Surfactant-free emulsions stabilized by solid particles are known as Pickering emulsions. The stabilization of emulsions and foams by solid particles has been considered theoretically, assuming a liquid film between liquid droplets or bubbles stabilized by a bridging monolayer or bilayer of hexagonally close-packed particles.[8,9] The particles are required to adsorb at the oil–water interface and remain there forming a dense film around the dispersed droplets impeding coalescence.[10] If coalescence occurs, the film is ruptured *via* bilayer-to-monolayer transition in two steps: a particle rearrangement into a film with bridging monolayer followed eventually by its rupture.[11] If the particle rearrangement is difficult due to strong cohesion, the film could break *via* the formation of a void inside the bilayer followed by a rupture in the region unprotected by particles.[12]

In spite of these theoretical data on droplet coalescence mechanisms, there is no experimental evidence that strongly supports these positions. In general, a microscopic examination reveals that the droplets are covered with particle layers: hexagonally close-packed particles and regions of disturbed ordering with small gaps between particles.[13,14]

The available experimental data on the structures formed in the space between approaching droplets are limited. Two droplets bridged by a particle monolayer can be observed in freeze-fracture SEM micrographs of an emulsion of dodecane and isopropyl myristate stabilized by silica particles (radius, 430 nm).[15] Particle bridging proceeds through collisions occurring between partially coated droplets. The *in situ* microscopic observations of a water-in-octane emulsion[16] give evidence of the spontaneous accumulation of silica particles (3 µm in diameter) in a dense monolayer bridging the emulsion droplets sparsely covered with particles, thus preventing coalescence.

Computer simulations make it possible to gain insight into the mechanism of Pickering emulsion stabilization and to reveal information on nanoparticle adsorption onto the surface of droplets and structural changes in emulsions.

Nanoparticle aggregation can be simulated using stochastic and dynamic methods.[17] The Brownian and Langevin dynamics methods are most suitable for describing aggregation in disperse systems because the physical and chemical properties of these systems are used in simulations.[18]

In this study, Langevin dynamics simulations were used to construct the structures formed in oil-in-water emulsions with silica nanoparticles and to characterize the condition of emulsion stability. The motion of single silica nanoparticles, aggregates and oil droplets is described using the Langevin impulse integrator of the forms

$$v_{t+0.5\Delta t} = v_t + \frac{F_t}{2m}\Delta t \qquad (1)$$

$$x_{t+\Delta t} = x_t + \frac{m}{\mu}\left[1 - \exp\left(-\frac{\mu}{m}\Delta t\right)\right]v_{t+0.5\Delta t} + \frac{1}{\mu}\sqrt{2kT\mu}\,R_{2,t+\Delta t} \qquad (2)$$

$$v_{t+\Delta t} = v_{t+0.5\Delta t}\exp\left(-\frac{\mu}{m}\Delta t\right) + \frac{1}{m}\sqrt{2kT\mu}\,R_{1,t+\Delta t} + \frac{F_{t+\Delta t}}{2m}\Delta t, \qquad (3)$$

where v and x are the collections of velocity and position coordinates, respectively, as functions of time t; Δt is the time step; F is the collective interdroplet force vector; R_1 and R_2 are the stochastic Brownian force components; m is the droplet mass; T is the absolute temperature, and k is the Boltzmann constant.

It is assumed that Brownian forces predominate over hydrodynamic ones, and μ is the friction coefficient determined from Stokes' law ($\mu = 6\pi\eta r$), r is the droplet radius, and η is the dynamic viscosity of the oil phase of emulsion.

The attraction energy (U^{w}) between two droplets is[19]

$$U^{\mathrm{w}} = -\frac{32}{3}A\frac{r_1^3 r_2^3 (D + r_1 + r_2)}{D^2(D + 2r_1)^2(D + 2r_2)^2[D + 2(r_1 + r_2)]^2}, \qquad (4)$$

where r_1 and r_2 are droplet radii, and s is the distance between the centers of the spheres. The distance between the surfaces is $D = s - r_1 - r_2$. A is the Hamaker constant.

The electrostatic repulsion between droplets (U^{el}) is calculated by the following expression:[19]

$$U^{\mathrm{el}} = \pi\varepsilon\varepsilon_0\frac{r_1 r_2}{r_1 + r_2}\times$$
$$\times[(\psi_1 + \psi_2)^2\ln(1 + \mathrm{e}^{-\kappa D}) + (\psi_1 - \psi_2)^2\ln(1 - \mathrm{e}^{-\kappa D})], \qquad (5)$$

where ψ_1 and ψ_2 are the surface potentials, ε is the relative dielectric permittivity, ε_0 is the vacuum permittivity, and κ is the inverse Debye length.

The attraction and repulsion forces are found by differentiating the equations of potential energy with respect to the coordinate. The force of gravity is also taken into account. The Brownian motion is modelled as a random force applied to each droplet in every step.[20]

The interdroplet forces in aggregates were calculated by the Rattle algorithm[21] that iteratively optimizes the distances between neighbouring particles in an aggregate to prevent them from overlapping.

The energy needed for the detachment of particles from the surface of emulsion droplets is much greater than the thermal energy.[22] Therefore, adsorbed nanoparticles are being trapped at the droplet surface; the lateral motion of adsorbed nanoparticles on the droplet surface is permitted in the calculations. Nanoparticle aggregation is assumed to be reversible.

The diameters of oil droplets and SiO_2 nanoparticles are 1 μm and 50 nm, respectively. The generation of nanoparticles is performed randomly. The number of silica nanoparticles N varies between 1000 and 5000. A minimum distance between silica nanoparticles and between silica nanoparticles and oil droplets is 10 nm. The initial distance between oil droplets is 200 nm. The ζ-potentials of SiO_2 nanoparticles and oil droplets are –50 and –10 mV, respectively.

The Hamaker constants A for silica and hydrocarbon oil across water are 6.7×10^{-21} and 3.9×10^{-21}, respectively. The Hamaker constant between silica and hydrocarbon oil across water is calculated as the square root of A for silica multiplied by A for hydrocarbon oil.

An aqueous phase of emulsions is modeled as NaCl solution with a viscosity of 0.001 Pa s. The densities of oil phase and silica nanoparticles are 870 and 2648 kg m^{-3}, respectively. The temperature is 298 K.

Figure 1 shows the typical kinetic curves of interdroplet distance in emulsions with various N . According to the evolution of the interdroplet distances, the next states are considered:

– coalescence is assumed if the distance between the oil droplets becomes less than 1 nm (C);

– flocculation occurs if the distance between oil droplets becomes 50 or 100 nm, *i.e.*, one or two silica nanoparticle diameters (F_1 and F_2);

– emulsion is kinetically stable if the distance between the drops increases with time and does not become smaller than the distance in the generation (S).

The snapshots of simulated emulsions are depicted in Figure 2. Different well-distinguished stability domains are found depending on the operating variables. At low ionic strengths of aqueous phase and amounts of SiO_2 nanoparticles insufficient for dense droplet coverage, oil droplets flocculate and do not coalesce. A tenuous layer of nanoparticles is formed on the surface of oil droplets; SiO_2 nanoparticles are separated from each other [Figure 2(*a*)]. If the amounts of SiO_2 nanoparticles are insufficient for dense droplet coverage and the ionic strengths are high, oil droplet flocculation also takes place, and coalescence is absent. In this case, nanoparticles are arranged in two-dimensional clusters with a well-ordered hexagonal structure [Figure 2(*b*)]. Such structures are very similar to dense monolayer domains observed in the oil film between touching water droplets that prevented coalescence, although the droplets were barely covered with particles outside the contact region.[16] Note that only a bridging monolayer is formed in a simulated emulsion stabilized by silica nanoparticles. Flocculation across a nanoparticle bilayer (F_2) was not observed at any simulation variables.

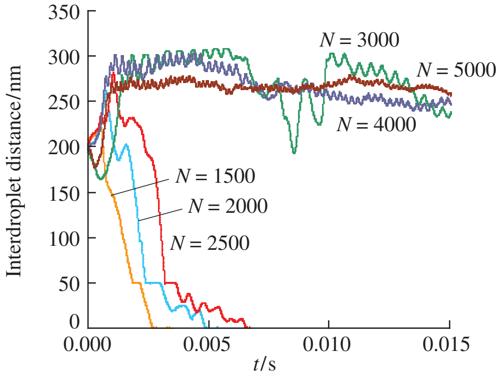


Figure 1 Time evolution of the distance between oil droplets in model emulsions with different numbers of SiO_2 nanoparticles and the ionic strength I = 10 mol m^{-3} of an aqueous phase.

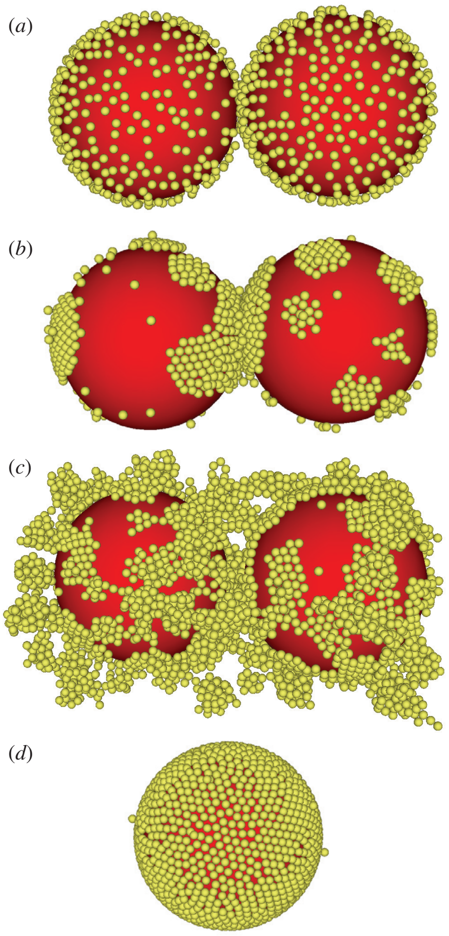


Figure 2 The snapshots of flocculated droplets in emulsions with (*a*) $N = 2000$, $I = 100$ mol m^{-3}, (*b*) $N = 2000$, $I = 2000$ mol m^{-3}, (*c*) $N = 4000$, I = 2000 mol m^{-3} and (*d*) a droplet in the kinetically stable emulsion with $N = 3000$, $I = 50$ mol m^{-3}.

Gel is formed from silica nanoparticles in an aqueous phase at high ionic strengths and the number of SiO_2 nanoparticles that exceeds the amount necessary for a dense nanoparticle layer [Figure 2(*c*)]. The network of the connected assemblies of aggregated SiO_2 nanoparticles separates oil droplets, and this can prevent droplet approaching.[17,23] Such a gel is long-lived compared with the simulation timescale of about 1 s.

Emulsions are kinetically stable if the ionic strengths are low and the amounts of SiO_2 nanoparticles are sufficient or exceed those necessary for emulsion droplet coverage. Oil droplets are separated from each other and are coated with an almost dense nanoparticle layer [Figure 2(*d*)].

Emulsions are unstable to flocculation and subsequent coalescence at a very low amount of silica nanoparticles (Table 1).

Thus, the mechanisms of Pickering emulsion stabilization can be studied by computer simulations using the Langevin dynamics

Table 1 Simulated emulsion stability.

N	Ionic strength/mol m^{-3}							
	10	20	50	100	500	1000	2000	3000
1000	C	C	C	C	C	C	C	C
2000	C	C	C	F_1	F_1	F_1	F_1	F_1
3000	S	S	S	F_1	F_1	F_1	Gel	Gel
4000	S	S	F_1	F_1	F_1	F_1	Gel	Gel
5000	S	F_1	F_1	F_1	F_1	F_1	Gel	Gel

method. This simulation procedure can provide a description of phenomena observed in emulsions with solid particles and predict emulsion stability, as applied to Pickering emulsions.

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