

Pickering emulsions stabilized by oppositely charged colloids: Stability and pattern formation

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A binary mixture of oppositely charged colloids can be used to stabilize water-in-oil or oil-in-water emulsions. A Monte Carlo simulation study to address the effect of charge ratio of colloids on the stability of Pickering emulsions is presented. The colloidal particles at the interface are modeled as aligned dipolar hard spheres, with attractive interaction between unlike-charged and repulsive interaction between like-charged particles. The optimum composition (fraction of positively charged particles) required for the stabilization corresponds to a minimum in the interaction energy per particle. In addition, for each charge ratio, there is a range of compositions where emulsions can be stabilized. The structural arrangement of particles or the pattern formation at the emulsion interface is strongly influenced by the charge ratio. We find well-mixed isotropic, square, and hexagonal arrangements of particles on the emulsion surface for different compositions at a given charge ratio. The distribution of coordination numbers is calculated to characterize structural features. The simulation study is useful for the rational design of Pickering emulsifications wherein oppositely charged colloids are used, and for the control of pattern formation that can be useful for the synthesis of colloidosomes and porous shells derived thereof.

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I. INTRODUCTION

Colloids and nanoparticles readily adsorb at fluid-fluid interfaces, leading to stable emulsion droplets and bubbles [1–6]. Though known for a long time, the approach was recently extended to use colloids of several kinds, such as polymeric latex [3,7–9], soft colloids [10,11], anisotropic colloids [12], proteins [13,14], Janus colloids [15,16], and patchy colloids [17]. The recent developments in the synthesis of these new types of colloids have broadened the applications, ranging from the preparation of stable emulsions and bubbles with an extended period of stability to the making of colloidosomes [18–21]. We recently reported experimental studies demonstrating the advantages of using oppositely charged colloids to stabilize water-in-oil (WO) emulsions [1,2]. It was shown that highly charged particles alone cannot stabilize emulsions because of the image-charge effect at the oil-water interface that prevents adsorption of particles [22]. Additives such as salt or oppositely charged surfactant or oppositely charged particles are needed to overcome the repulsive barrier and to enhance the adsorption of particles to the interface.

In using oppositely charged particles, the key is to first form aggregates of oppositely charged particles in water and then emulsify with oil, wherein the aggregates are transported to the interface, as these aggregates have low net charge. In such emulsion systems, the stability and size distribution of the emulsion droplets strongly depend on several factors such as charge ratio, number ratio, concentration of particles, and contact angles of the particles [2].

In a conventional emulsification process, tiny water droplets are first created in oil by providing mechanical energy externally. Therefore, the initial size distribution of the drops depends on the mixing process. If the adsorption of colloids at the interface is favored and instantaneous, and if a sufficient

number of colloids is available for the newly created oil-water interface, then all of the drops will be stable against further coalescence as the presence of particles at the interface offers steric stability. However, in practice, water drops that are initially formed are polydisperse and only a few of the particles or aggregates that overcome the image-charge effect can adsorb at the interface. This leads to partial coverage and further coalescence. In such cases, the final drop size distribution is governed by drop coalescence. Essentially, the drop size distribution is governed by the competition between the rates of adsorption of colloids versus the rate of coalescence of the drops [23,24].

When oppositely charged colloids are used, the ability of particles to adsorb on the WO interface depends on mutual interactions between the particles. For an emulsion drop to be stable, sufficient packing of particles at the interface is necessary to prevent coalescence leading to phase separation. In the present work, we ask the following questions relevant to experimental success in making stable emulsions: what is the range of the number ratio of oppositely charged colloids for a given charge density ratio that yields stable emulsion? How does this range of number ratio change when the charge density ratio is varied? What are the structural features of particles assembled at the emulsion surface? To answer these questions, we consider an isolated emulsion droplet with a particle coverage of 74%, and calculate the minimum energy per particle for a given number ratio and charge ratio using Monte Carlo simulations. In this approach, one can avoid the detailed kinetic mechanisms of adsorption of particles to the interface, which are limited by diffusion and adsorption kinetics. Thereby, we link the stability of emulsions to interparticle interactions, as the latter can be tuned experimentally.

Another avenue for the importance of Pickering emulsion is that they have been increasingly used as a template for the synthesis of colloidosomes. With a binary mixture of particles, as in the present case, such emulsion drops can be

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used to make colloidosomes with multifunctionality. Further, by selective removal of one of the types of particles, pores of selective size can be made, leading to application in controlled drug delivery using colloids. Such porous colloidosomes have potential use in size and shape selective transport. To this end, it is imperative to study the structural patterning of oppositely charged particles on the emulsion surface and how it is influenced by the charge ratio and number ratio. We address these aspects from our simulations. Structural features on colloidosomes stabilized by polarizable hard spheres were shown to be dependent on particle density [25]. On flat two-dimensional interfaces consisting of oppositely charged surfactant species, the structural transition from lamellae to hexagonal ordering has been reported [26,27]. A rich phase behavior of binary mixtures of uncharged particles with different size ratios and compositions to study random metal alloys and metallic glasses has been reported [28–33]. Binary mixtures of like-charged colloids [34] and dipolar colloids [35] have been shown to exhibit a diverse variety of crystalline phases in two dimensions at zero temperature. The role of interparticle interactions on the stability of colloidosomes has been studied for colloids with competing interactions [36]. In this context, our work addresses the role of interparticle interactions on the pattern formation of oppositely charged colloids at emulsion surfaces. These results can be of use in screening emulsions that mimic the target structure of desired colloidosomes.

II. MODEL AND SIMULATION

A. Effective interaction

In the formulation of the problem, an isolated water-in-oil emulsion droplet of radius R with a total number N_t of oppositely charged colloids adsorbed on its surface is considered. The role of water, oil, and oil-water interface is considered via an effective interaction potential between oppositely charged colloids at the interface. It is known that charged particles at the interface behave like dipoles because of the asymmetric distribution of charges across the interface [37–40]. The chargeable groups on the part of the particle immersed in water dissociate. Due to this charge asymmetry about the oil-water interface, the particle acts as an electric dipole (see Fig. 1). As the system consists of oppositely charged colloids, there are attractive dipolar interactions between unlike-charged colloids and repulsion between like-charged colloids. The strength of interactions depends on the charge density, dielectric constant of water, and Debye screening length. We use the pair potential of the form that depends

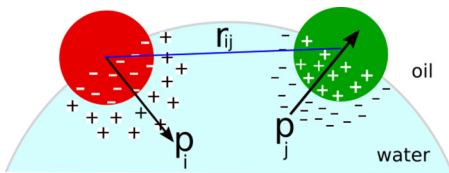


FIG. 1. (Color online) A schematic of oppositely charged colloids at the water-in-oil emulsion drop interface.

on the relative orientation of the dipoles as

$$U(r_{ij}) = \begin{cases} \infty, & \text{if } r_{ij} < \sigma \\ \frac{p_i \cdot p_j - 3(\hat{r}_{ij} \cdot p_i)(\hat{r}_{ij} \cdot p_j)}{4\pi\epsilon\epsilon_0 r_{ij}^3}, & \text{otherwise,} \end{cases} \quad (1)$$

where p_i and p_j are the electric dipole moment of particles i and j , respectively, ϵ is the dielectric constant of water (where particles were initially present), ϵ_0 is the permittivity of vacuum, r_{ij} is the interparticle separation distance, and \hat{r}_{ij} is the unit vector along the vector connecting the two particles. For $r_{ij} < \sigma$, i.e., the diameter of the particle, we use the hard-sphere potential. The dipole moments can be related to the number of charges as $p_i = z_i q_i e \hat{u}_i / \kappa$ [37]. The parameter $1/\kappa$ is the Debye screening length, e is the elementary charge, q_i is the number of charges per particle, z_i is the sign of the charge ($z_i = -1$ for negatively charged particles and $z_j = +1$ for positively charged particles), and \hat{u}_i is the unit vector in the direction of the dipole moment of particle i . It is the outward unit normal drawn from the center of mass of particle i . All of the particles are constrained such that the center of mass of the particles lies on the spherical surface. Equation (1) can now be written as

$$U(r_{ij}) = \frac{z_i z_j q_i q_j e^2 [\hat{u}_i \cdot \hat{u}_j - 3(\hat{n} \cdot \hat{u}_i)(\hat{n} \cdot \hat{u}_j)]}{4\pi\epsilon\epsilon_0 \kappa^2 r_{ij}^3}. \quad (2)$$

In the simulation, the energy is scaled in units of $k_B T$ (k_B is Boltzmann constant and T is temperature), and length is scaled by σ . The scaled potential then becomes

$$\bar{U}(\bar{r}_{ij}) = \frac{A z_i z_j q_i q_j e^2 [\hat{u}_i \cdot \hat{u}_j - 3(\hat{n} \cdot \hat{u}_i)(\hat{n} \cdot \hat{u}_j)]}{\bar{r}_{ij}^3}, \quad (3)$$

where the prefactor A is defined as

$$A = \frac{\lambda_B}{\bar{\kappa}^2 \sigma}. \quad (4)$$

The parameter λ_B , i.e., the Bjerrum length, is defined as

$$\lambda_B = \frac{e^2}{4\pi\epsilon\epsilon_0 k_B T}. \quad (5)$$

The Debye screening length κ^{-1} is defined as

$$\kappa^{-1} = \sqrt{\frac{\epsilon\epsilon_0 k_B T}{2N_A e^2 I}}. \quad (6)$$

In this equation, N_A is the Avogadro number and I is the ionic strength due to counterions released to water depending upon the number ratio of oppositely charged particles. Note that the value of the prefactor A changes with Debye screening length, which in turn changes as the composition of charged colloids is varied. To generate initial positions (coordinates) of the colloids on a spherical surface, we create N_t particles with diameter of unity on a spherical surface of radius \bar{R} using an icosadeltahedral configuration [41]. Of the total N_t particles, the N_+ number of positively charged and N_- number of negatively charged colloids are of equal size. They are randomly positioned on the surface of the sphere. We fix $N_t = 1092$ particles and study total area coverage (ϕ) of 74%, corresponding to the radius of the sphere (\bar{R}) of 9.6 (assuming the particles at the oil-water interface make a contact angle of 90°).

N_t , \bar{R} , and ϕ are related by the geometric relation

$$\phi = \frac{N_t a}{S} = \frac{N_t}{16\bar{R}^2}, \quad (7)$$

where a is the cross sectional area of the particles at the interface and S is the surface area of emulsion drop.

B. Monte Carlo simulation

In the Monte Carlo simulation, a particle is randomly chosen and moved with a constraint that it remain on the spherical surface after the move. This step mimics the motion of colloids at the water-oil interface. The total interaction energy, defined as the sum of all pairwise interactions, is calculated before (E_o) and after (E_n) the move. Because the potential is long ranged [Eq. (3)], in calculating total energy, each particle interacts with all of the other particles. If $E_n < E_o$, the new position is accepted and continued, otherwise the new position is accepted with a probability of $e^{-(E_n - E_o)/k_B T}$. The simulation is continued until the total energy converges to equilibrium value. To speed up the equilibration of the system, we also perform swap moves along with local moves using the long-range Kawasaki exchange method [42], wherein two particles are randomly chosen and their positions are interchanged. The exchange is accepted with the probability

$$P = \frac{e^{-(\Delta E/k_B T)}}{1 + e^{-(\Delta E/k_B T)}}. \quad (8)$$

Swap moves are done only during the equilibration cycle with a probability of 0.1.

A constant number-volume-temperature (NVT) MC simulation is carried out for 21 different charge ratios in the range of 1 to 5 with an interval of 0.2. The charge ratio is defined as $R_c = q_-/q_+$. q_+ is fixed at 2000. q_- is varied according to the charge ratio. Table I shows the values of parameter A for different compositions ratios at $R_c = 1$. Similarly the parameter A is calculated for other charge ratios from Eq. (4). Composition of the particles on the spherical surface is expressed as the number fraction $\phi_+ = N_+/(N_+ + N_-)$. Compositions in the range of 15–98% are studied for each of the charge ratios. The simulation box size is kept at 40σ . Interaction between emulsion drops is neglected. The simulation was carried out for two million MC cycles for equilibration and another two million MC cycles to sample averages. After reaching equilibration, the structural arrangement of particles on the

TABLE I. Parameters used in the simulation. Nondimensional parameter A is obtained from Eq. (4) with $\lambda_B = 0.702$ nm, $\sigma = 1$ μ m, $q_+ = 2000$. The values are given for $R_c = 1$.

ϕ_+	$A \times 10^7$
0.45	0.98
0.50	1.02
0.55	1.05
0.6	1.09
0.65	1.13
0.70	1.17
0.75	1.22

surface is characterized by calculating coordination number distributions.

C. Stability criterion

Interfacial tension and bending modulus of the particle-coated interface are important parameters in the stability of emulsions. However, in some cases, the self-energy of the interface due to interparticle interactions can be used as a criterion to define stability. Emulsion drops destabilize and lead to phase separation because of coalescence. Pickering emulsion drops are usually stable against coalescence because, as they come rather close to each other, the particles at the interface offer steric hindrance [43]. There are studies which show that poorly covered emulsions are also stable against coalescence [44]. There seems to be a range of coverage depending upon the type of emulsion, type of particles, and their interactions that corresponds to stable emulsions. We fix a coverage of 74% in our studies. Once we fix the required particle coverage, then the question of stability is whether or not such a coverage is thermodynamically feasible. To this end, we can write the free energy change due to adsorption as

$$\Delta f = \frac{2\phi S}{N_t}(\gamma_{pw} + \gamma_{po} - \gamma_{ow}) + e_s. \quad (9)$$

Here, Δf is the Helmholtz free energy per particle in the units of $k_B T$, γ is the interfacial tension, with suffix p , o , and w denoting particle, oil, and water, respectively. The term e_s refers to the self-energy of the interface per particle due to interparticle interactions. In our simulations, we have taken the contact angle of particles as 90° . From the Young-Dupré equation, this means $\gamma_{pw} = \gamma_{po}$. Hence, for $\theta = 90^\circ$ and $\gamma_{pw} + \gamma_{po} = \gamma_{ow}$, Eq. (9) becomes

$$\Delta f = e_s. \quad (10)$$

Note that we have neglected the entropy of mixing of particles as it gives a negative contribution in the free energy (discussed later) and that we set an upper bound for the stability criterion. Therefore, if the free energy is negative, it is thermodynamically favorable to pack oppositely charged particles at the interface, leading to steric stabilization of emulsion drops. In the special case considered here, the interfacial energy change due to adsorption of the particle is zero. Therefore, the sign of the interaction energy due to interparticle interaction then becomes the important factor in determining stability. To be precise, we are considering here a *conditional stability* because of an imposed particle coverage and contact angle.

III. RESULTS AND DISCUSSION

A. Emulsion stability

We consider emulsion drops with particle coverage of 74%, and calculate the energy per particle at equilibrium for several number fractions of oppositely charged particles. Figure 2 shows the energy per particle as a function of composition for several charge ratios (R_c) at equilibrium. The energy per particle varies steeply with composition as the charge ratio increases from 2 to 5. We see that for every charge ratio,

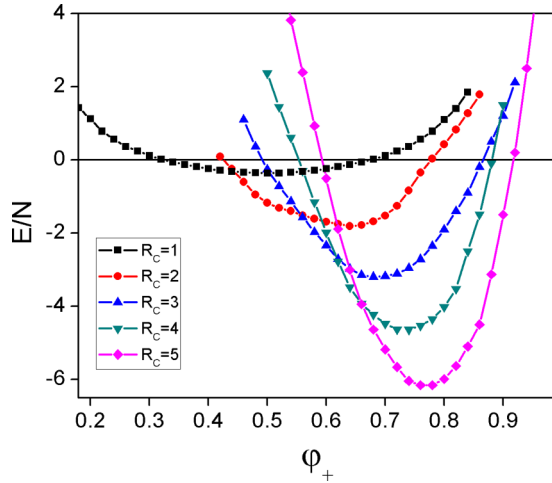


FIG. 2. (Color online) Energy per particle as a function of fraction of ϕ_+ for different ratios of charge density.

there is a minimum in the energy per particle, leading to an optimum composition. The optimum composition can be correlated to the most stable state of the emulsion drop, leading to better stability. The optimum composition shifts to higher compositions as the charge ratio increases. This is because as the charge ratio is increased, a larger number of positively charged particles is required to minimize the energy. If an emulsion drop should be stable, then the energy per particle should be zero or negative at a given coverage. According to this definition of stability, we can find that the curves given in Fig. 2 dictate a range of compositions where emulsions will be stable. This stability region is denoted in Fig. 3 as the stability diagram. The region between the two connected lines corresponds to stable emulsions.

From experimental data, it was found that the stable region for decane in water emulsions stabilized by a mixture of oppositely but equally charged $0.5 \mu\text{m}$ polystyrene particles ranges from 0.3–0.7 [2]. The simulations shows this range to be 0.34–0.66 with a corresponding charge ratio of 1. Although

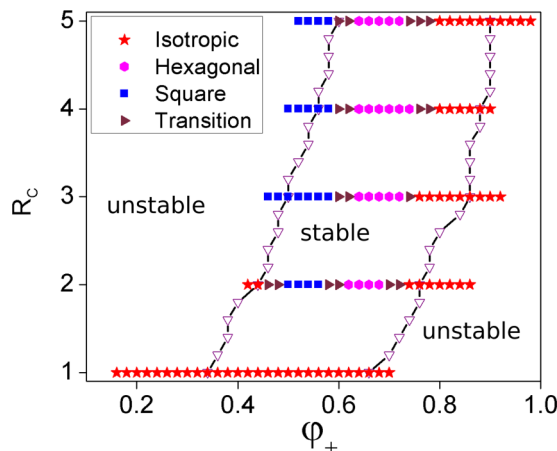


FIG. 3. (Color online) Stability diagram of emulsions stabilized by oppositely charged particles based on energy per particle. The connected lines are the boundaries at which the energy per particle changes its sign. The markers denote different structural patterns.

the model and stability criterion used in our simulations are simplified, the comparison of the simulation data with experiments is in reasonable agreement. Note that in our simulations, we have considered the contact angle of particles as 90° , and the present simulation results are valid for both OW and WO emulsion types. Outside the stable region, it is unlikely that an emulsion would be stable because in these cases the energy per particle becomes positive. Therefore, the limit on stability in terms of the charge ratio can be useful for the rational design of emulsion stabilized by oppositely charged colloids.

To verify if the entropy of mixing affects the value of optimum composition, we calculate entropy from

$$S = k_B \ln \Omega, \quad (11)$$

where Ω is the total number of configurations obtained by mixing N_+ positive colloids and N_- negative colloids. Assuming full coverage of the emulsion surface (i.e., 90.6%, although simulations correspond to a maximum coverage of 74%), we find that

$$\Omega = \frac{N!}{N_+!N_-!}. \quad (12)$$

Using Stirling's approximation [$\ln(x!) \approx x \ln(x) - x$] in Eq. (12) and substituting in Eq. (11), entropy per particle becomes

$$s(\phi_+) = -k_B \phi_+ \ln \phi_+ - k_B (1 - \phi_+) \ln(1 - \phi_+). \quad (13)$$

Since the actual coverage of particles is 74%, the excess area available for particles contributes to entropy as $k_B \ln(0.906/0.74)$, and hence the entropy of mixing is given by

$$s(\phi_+) = -k_B [\phi_+ \ln \phi_+ + (1 - \phi_+) \ln(1 - \phi_+) - \ln(0.906/0.74)]. \quad (14)$$

Then Helmholtz free energy per particle is given by

$$f(\phi_+) = u(\phi_+) - Ts(\phi_+). \quad (15)$$

Note that the change of interfacial energy due to particle adsorption is considered to be zero, as discussed earlier in Sec. II C.

As shown in Fig. 4, the effect of mixing entropy is negligible compared to interaction energy in determining the optimum composition for a given charge ratio of colloids. The optimum composition is primarily influenced by the dipolar interaction energy. However, the range of stability is slightly affected by entropic contributions. This additional entropic part slightly increases the window of stability.

B. Patterning of oppositely charged colloids at the interface

For the imposed coverage, the binary mixture of particles exhibits interesting patterns on the surface of the emulsion drop as a function of composition. We classify these patterns into three distinct classes: (i) isotropic, (ii) square, and (iii) hexagonal patterns. In Fig. 3, these patterns are marked for different charge ratios. A snapshot of these phases is shown in Fig. 5 for $R_c = 3$. For $R_c = 1$, the particles are in a completely mixed state, which we call an isotropic phase due to the absence of any structural order in the arrangement of particles.

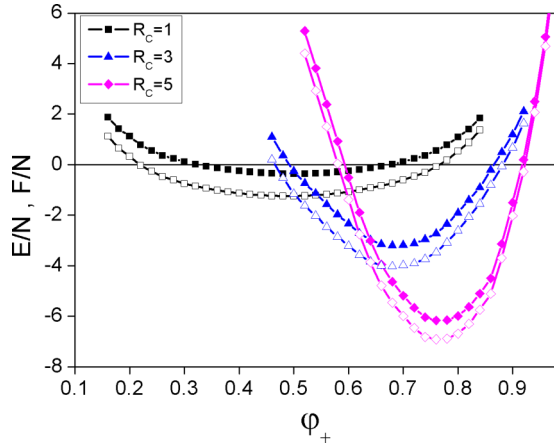


FIG. 4. (Color online) Energy (filled markers) and free energy (open markers) per particle as a function of composition ϕ_+ for different charge ratios.

For $R_c > 1$, however, we find that all three phases exist. In the square phase, each particle is surrounded by four other types of particles. In the hexagonal phase, minority particles (negatively charged) assemble themselves in a hexagonal lattice, and are surrounded by nearly six positively charged particles. If we consider only the stable region, for $R_c = 1$, all configurations are in the isotropic phase. For $2 \leq R_c \leq 4$, all three phases are attainable, and for $R_c = 5$, only the hexagonal and isotropic phases are attainable. Between the ordered phases, and between the ordered and isotropic phases, there are transition phases. For instance, in the transition phase between the square and hexagonal phases, both phases coexist on the emulsion surface. Due to the curvature of the interface, the two-dimensional crystal lattices develop many defects and grain boundaries. These imperfections can be minimized if we consider higher coverages close to the close-packing limit.

Figure 6 shows the number of positively charged particles distributed around a negatively charged particle. These data correspond to the optimum composition for each charge ratio (see Fig. 2). The average number of neighbors increases from 3.5 to 5.7 as the charge ratio is increased from 1 to 5, although all of the simulations correspond to the same coverage. For a charge ratio of 3–5, the peak at $Z = 6$ clearly indicates the particle’s self-assembly into a hexagonal order. Therefore, for the synthesis of colloidosomes with a square or hexagonal pattern, emulsions can be prepared by choosing the right set of

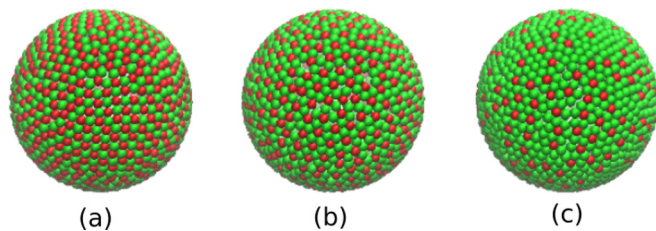


FIG. 5. (Color online) Pattern formation on the emulsion surface for $R_c = 3$: (a) square patterning for $\phi_+ = 0.52$, (b) hexagonal patterning for $\phi_+ = 0.64$, and (c) isotropic phase for $\phi_+ = 0.82$.

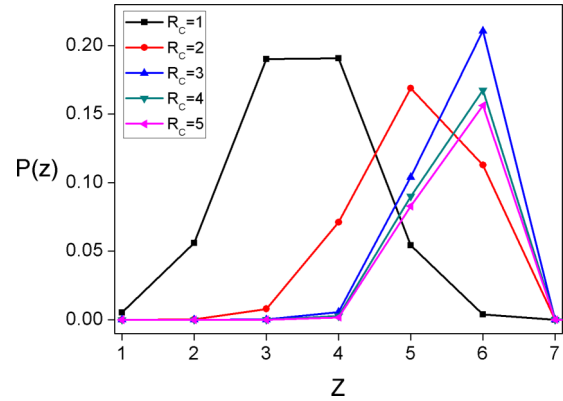


FIG. 6. (Color online) Neighbor distribution at optimum compositions for several charge ratios. The compositions correspond to 0.5, 0.64, 0.68, 0.74, and 0.76 for R_c from 1 to 5, respectively.

experimental conditions (charge ratio and composition) from Fig. 3. Note that a colloidosome with a square lattice cannot be made with single type particles, and the use of oppositely charged colloids opens up this possibility.

IV. CONCLUSION

The use of oppositely charged colloids offers various possibilities to stabilize water-in-oil or oil-in-water emulsions by means of controlling the charge ratio and number of particles on their surfaces. From Monte Carlo simulations, we trace a range of composition of particle mixture to stabilize emulsion, and report the optimum composition corresponding to the most stable state. We find that the charge ratio is an important parameter that controls emulsion stability. Additionally, it is seen that the spatial distribution (patterns) of colloids on the emulsion surface can be modulated with the charge density ratio. The simulation study can help the experimentalist design optimum parameters to stabilize emulsions. Further, our approach can, in principle, be extended to several studies that have shown the unusual role of charged colloids at interfaces, such as two-dimensional alloys [39], colloidal gels [45], and bridging or bilayer formation at interfaces [46]. When Pickering emulsion stabilized by oppositely charged particles is used to synthesize colloidosomes, the crystalline phases exhibited at the interface can be used for systematic functionalization and for creating ordered pores.

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