Charged Colloidal Particles and Small Mobile Ions near the Oil-Water Interface: Destruction of Colloidal Double Layer and Ionic Charge Separation

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We study suspensions of hydrophobic charged colloids in a demixed oil-water solvent with salt by means of a modified Poisson-Boltzmann theory, taking into account image-charge effects and partitioning of the monovalent ions. We find that the ion's aversion for oil can deform the double layers of the oil-dispersed colloids, which qualitatively affects the colloidal density profiles. The same theory also predicts crystallization of colloid-free micron-sized water-in-oil droplets at water volume fractions as small as $\sim 10^{-3}$ in a narrow range of the oil-dielectric constant. These findings explain recent observations by M. E. Leunissen *et al.* [Proc. Natl. Acad. Sci. U.S.A. **104**, 2585 (2007)].

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Colloidal particles can strongly adsorb to an oil-water or an air-water interface, and hence form a monolayer. Since a pioneering study by Pieranski [1] a lot of attention has been devoted to the lateral structure and the lateral colloidal interactions of such monolayers [2,3]. This two-dimensional picture is often realistic because the ‘‘binding’’ potential of a single colloid to the interface can be very strong, typically of the order of 10^3–$10^6 k_BT$ for a micron-sized colloid due to surface-tension or image-charge effects [1,4,5]. Here k_B is the Boltzmann constant and T the temperature. However, in very recent experiments by Leunissen *et al.* [6], on systems of charged, micron-sized, hydrophobic poly-methylmethacrylate (PMMA) spheres dispersed in an oil-like mixture of cyclohexyl bromide and cis-decalin, the focus was not only on the in-plane structure of the adsorbed colloidal monolayer at the oil-water interface, but also on the out-of-plane structure in the direction normal to the interface. Striking observations of this three-dimensional study include (i) a dramatic increase of the lattice spacing of the oil-dispersed colloidal crystal up to 40 μm by bringing this dispersion in contact with water, (ii) strong colloidal adsorption to planar and spherical oil-water interfaces even for nonwetting colloids, (iii) an extremely large colloid-free zone between the adsorbed colloidal monolayer and the bulk crystal in the oil phase, in some cases with a thickness $d > 100$ μm, and (iv) the existence of micron-sized water-in-oil droplets that are sufficiently charged to crystallize into a lattice with a spacing of 10–15 microns, without any colloid presence in the system, provided the dielectric constant of the oil was in the narrow range $4 \lesssim \epsilon_o \lesssim 10$ [6]. In this Letter we develop a theory for a mixture of hydrophobic colloids, cations, and anions in an oil-water mixture, taking into account screening, image charges, and self energies. We do *not* focus on the lateral structure [1–3] but instead on the structure perpendicular to the interface, and *not* on a single colloid [5,7] but on a many-body system. We restrict the theory to be of Poisson-Boltzmann mean-field type, such that correlation-induced phenomena such as charge-inversion [8] are not taken into account. Key new mechanisms that we identify this way are (i) colloidal double-layer destruction, due to the preference of ions to reside in the water phase rather than in diffuse layers surrounding the oil-dispersed colloids, and (ii) ionic charge separation if the cation's and anion's aversion for oil differs, such that water-in-oil droplets can acquire a net charge. These phenomena explain essentially all observations of Ref. [6], and could be ingredients to further understand and manipulate systems involving charged species near liquid dielectric interfaces, e.g., Pickering emulsions [4,9–11], colloidozomes [12], or insulator-electrolyte interfaces [13].

We consider a water-oil interface in the plane $x = 0$, characterized by a macroscopic surface-tension $\gamma_{\rm wo}$. The interface separates two semi-infinite continuous bulk phases of water ($x < 0$) and oil ($x > 0$). This system is a medium for a three-component mixture of hydrophobic colloids (radius a, charge Ze in oil), cations (radius a_+, charge e), and anions (radius a_-, charge $-e$), where the ions stem both from the colloid surfaces (counterions) and from salt added to the solvents. Here e is the elementary charge. The strongly hydrophobic character of the colloids is described here phenomenologically through the colloid-water and colloid-oil surface tensions $\gamma_{\rm cw} = 10$ mN/m and $\gamma_{\rm co} = 1$ mN/m, respectively. Note that these tensions do *not* incorporate electrostatic contributions. Following Pieranski's geometric argument [1] a colloidal particle with its center at $x \in (-a, a)$ is therefore subject to the external potential

$$V(x) = 2\pi a^2(\gamma_{\rm cw} - \gamma_{\rm co})\left(1 - \frac{x}{a}\right) - \pi a^2 \gamma_{\rm wo}\left(1 - \frac{x^2}{a^2}\right), \quad (1)$$

while a particle completely immersed in water ($x < -a$) or oil ($x > a$) has $V(x) = 4\pi a^2(\gamma_{\rm cw} - \gamma_{\rm co}) \simeq 10^6 k_BT$ for $a \simeq 1$ μm and $V(x) = 0$, respectively. Note that we shifted the potential of Ref. [1] by an arbitrary constant. The potential $V(x)$ has a deep minimum at $x = x^* = a(\gamma_{\rm cw} - \gamma_{\rm co})/\gamma_{\rm wo} \equiv a\cos\theta$ with θ the wetting angle, provided $|\gamma_{\rm cw} - \gamma_{\rm co}| < \gamma_{\rm wo}$. Otherwise, $V(x)$ is monotonic and we speak of nonwetting. Below we consider the wetting case $\gamma_{\rm wo} = 9.2$ mN/m, such that $\cos\theta = 0.987$ and $V(x^*) \simeq -10^3 k_BT$, from which strong adsorption of micronsized colloids at $x \simeq x^*$ is expected. We also consider the nonwetting case $\gamma_{\rm wo} = 9$ mN/m such that $\cos\theta = 1$, where no strong adsorption is to be expected because $V(x)$ is monotonic.

The planar water-oil interface also generates an external potential for the ions due to the dielectric discontinuity, which leads to different electrostatic self energies in the two solvents. We write the self-energy in medium $i = w, o$, as the Born energy $e^2/(2\epsilon_i a_\pm) \equiv f_\pm(\epsilon_i)$. Denoting the local dielectric constant by the step function $\epsilon(x) = \epsilon_w$ for $x < 0$ and ϵ_o for $x > 0$, this self-energy effect can be accounted for in terms of (conveniently shifted) ionic external potentials $V_\pm(x) = f_\pm(\epsilon(x)) - f_\pm(\epsilon_w)$, which vanishes in water and is of the order of (1–20)k_BT for realistic $\epsilon_o \simeq 4$–20, i.e., the ions prefer to be in water.

Now that we have specified the external potentials $V(x)$ and $V_\pm(x)$ for the colloids and the monovalent ions, respectively, we employ the framework of density functional theory to calculate the equilibrium density profiles $\rho(x)$ and $\rho_\pm(x)$ [14–16]. The grand-potential functional $\Omega[\rho, \rho_+, \rho_-]$ is written, per unit lateral area A, as

$$\begin{aligned}\frac{\Omega}{A} = \sum_{\alpha=\pm}\int dx\rho_\alpha(x)\bigg[k_BT\bigg(\ln\frac{\rho_\alpha(x)}{\rho_s} - 1\bigg) + V_\alpha(x)\bigg]\\ + \int dx\rho(x)\bigg[k_BT\bigg(\ln\frac{\eta(x)}{\eta_0} - 1\bigg) + V(x)\bigg]\\ + k_BT\int dx\bigg(\rho(x)\Psi(\bar{\eta}(x)) + \frac{1}{2}Q(x)\phi(x)\bigg),\end{aligned} \qquad (2)$$

where $\eta(x) = 4\pi a^3\rho(x)/3$ is the colloidal packing fraction, and where the first and second line are the ideal-gas grand-potential functionals of the ions and the colloids in their external fields, respectively, and the third line describes the hard-core and Coulomb interactions. The colloid-colloid hard-core interactions are taken into account by the Carnahan-Starling excess free energy per particle $\Psi(\bar{\eta}) = (4\bar{\eta} - 3\bar{\eta}^2)/(1-\bar{\eta})^2$ with the weighted packing fraction $\bar{\eta}(x) = \int_{x-2a}^{x+2a} dx' w(x-x')\eta(x')$ with the (low-density) weight function $w(x) = \frac{3}{32}(4a^2 - x^2)/a^3$ [15]. Such a nonlocal treatment of the hard-core interactions is only included to quasirealistically describe the close-packed colloidal monolayer in the case of wetting; by comparison with simpler local descriptions we checked that it hardly affects other features of the profiles to be discussed below. The electrostatic interactions between all species are described in Eq. (2) at a mean-field level in terms of the total local charge number density $Q(x) = Z\rho(x) + \rho_+(x) - \rho_-(x)$ and the yet unknown electrostatic potential $k_BT\phi(x)/e$ that must satisfy the Poisson equation and boundary conditions

$$\begin{aligned}&\epsilon(x)\phi''(x) = -4\pi\beta e^2 Q(x), && (x \neq 0);\\ &\lim_{x\uparrow 0}\epsilon_w\phi'(x) = \lim_{x\downarrow 0}\epsilon_o\phi'(x); && \lim_{x\to\pm\infty}\phi'(x) = 0.\end{aligned} \qquad (3)$$

Here a prime denotes a derivative with respect to x, and $\beta = 1/(k_BT)$. Note that the second line of (4) describes the image-charge effects (first term) and global charge neutrality (second term). Minimizing Eq. (2) gives

$$\begin{aligned}\eta(x) &= \eta_0\exp[-\beta V(x) - Z\phi(x) - \beta\mu(x)];\\ \rho_\pm(x) &= \rho_s\exp[-\beta V_\pm(x) \mp \phi(x)],\end{aligned} \qquad (4)$$

with $\beta\mu(x) = \Psi(\bar{\eta}(x)) + \int_{x-2a}^{x+2a} dx' w(x-x')\eta(x') \times \Psi'(\bar{\eta}(x'))$, where $\Psi'(\eta) = d\Psi(\eta)/d\eta$. Note that the strongly hydrophobic character of the colloids leads to a vanishing colloid-density at $x \to -\infty$, such that $\phi(-\infty) = 0$ and $\rho_\pm(-\infty) = \rho_s$ for electroneutrality reasons, i.e., the bulk water phase acts as a salt reservoir with a total ion concentration $2\rho_s$ such that its Debye screening length is $\kappa_w^{-1} = (8\pi\beta e^2\rho_s/\epsilon_w)^{-1/2}$. In the bulk oil suspension, $x \to \infty$, the average colloid packing fraction $\eta(\infty) \equiv \eta_b$ can be imposed by tuning η_0 appropriately. Equations (3) and (4) also imply, for $x > 0$, that $\phi''(x) = \kappa_o^2\sinh(\phi(x) - \phi_c) - 4\pi\beta e^2 Z\rho(x)/\epsilon_o$, with the Debye screening length κ_o^{-1} in the oil phase defined by $\kappa_o^2 = \kappa_w^2(\epsilon_w/\epsilon_o) \times \exp[-\beta(V_+(\infty) + V_-(\infty))/2]$ and $\phi_c = \beta(V_-(\infty) - V_+(\infty))/2$.

Equations (3) and (4) form a closed set for the four unknown profiles $\rho(x)$, $\rho_\pm(x)$, and $\phi(x)$, and can be solved numerically on an x grid by standard iterative methods on desktop PC's. Typically we need $\sim 10^3$ nonequidistant grid points, with a relatively small spacing close to $x = 0$ and, in the wetting case, also close to $x = x^*$.

We fix as many parameters as possible in accordance with those in the experiments described in Ref. [6], such that $Z = 450$, $a = 1$ μm, $\eta_b = 5 \times 10^{-5}$, $\epsilon_w = 80$, $\epsilon_o = 5.2$. For simplicity we take in most cases equal ionic sizes $a_+ = a_- = 0.3$ nm such that $V_\pm(x) = 17k_BT$ for $x > 0$. This leads to $1 \leq \kappa_o^{-1}/a \leq 40$ if one varies ρ_s from 0.07 to 26 mM. Figure 1 shows the resulting colloidal packing fractions $\eta(x)$ for $\kappa_o^{-1}/a = 4, 8, \cdots, 40$, in (a) for $\cos\theta = 1$ and in (b) for $\cos\theta = 0.987$. In all cases the colloids are so hydrophobic that $\eta(x)$ is vanishingly small for $x < 0$. In Fig. 1(a) $\eta(x)$ increases by up to several orders of magnitude near the interface at $a < x \lesssim 5a$, more so for lower salinity. This effect is, however, extremely sensitive to small positive deviations of $\xi \equiv \frac{a_-}{a_+}$ from unity. The dotted curves in (a) show $\eta(x)$ for $\kappa_o^{-1}/a = 8$ and $\xi = 1.004$, 1.006, 1.01; the larger cationic preference for water gives the water a positive surface charge (see below) that pushes the positive colloids away from the interface, while for $\xi < 1$ (not shown) the opposite takes place such that $\eta(x)$ resembles those curves shown in Fig. 1(a) for $a_+ = a- = 0.3$ and $\kappa_o^{-1}/a > 8$. By contrast, the partial wetting of (b) is very *insensitive* to details of $a_\pm$ because its electrostatics is completely dominated by a densely packed monolayer of

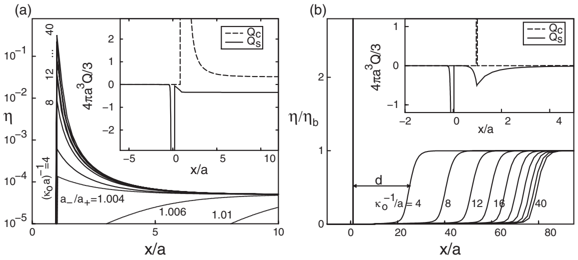

FIG. 1. The packing fraction profile $\eta(x)$ of strongly hydrophobic, oil-dispersed colloidal spheres (radius $a = 1\ \mu$m, charge $Z = 450$) in the vicinity of a planar interface at $x = 0$ between water ($x < 0$, dielectric constant $\epsilon_w = 80$) and oil ($x > 0$, $\epsilon_o = 5.2$), for a colloidal bulk packing fraction $\eta_b = \eta(\infty) = 5 \times 10^{-5}$, in (a) for nonwetting colloids ($\cos\theta = 1$) for oil screening lengths $\kappa_o^{-1}/a = 4 - 40$ from bottom to top, and in (b) for weakly wetting colloids ($\cos\theta = 0.987$) for $\kappa_o^{-1}/a =$ 4–40 from left to right. The insets show, for $\kappa_o^{-1} = 40a$, the salt and colloidal charge distributions, revealing the complete (a) and partial (b) deformation of the double layer around the adsorbed colloidal layer. In all cases the ionic radii are equal, $a_+ = a_- =$ 0.3 nm, except for the dotted curves in (a) where a_- is slightly increased (for $\kappa_o^{-1}/a = 8$).

colloids at $x = x^*$, separated from the bulk by a colloid-free zone of thickness d of the order of several κ_o^{-1}.

Although the increase of $\eta(x)$ up to $10^3\eta_b$ close to the interface in Fig. 1(a) is significant, it is weaker than to be expected on the basis of the attractive image-charge potential $W(x) = ZZ'e^2/(4\epsilon_o x) \simeq -500ak_BT/x$ that a single colloid (without cations and anions) would experience at $x > a$ for the present parameters, with $Z' = -Z(\epsilon_w - \epsilon_o)/(\epsilon_w + \epsilon_o) = -395$ the image charge [5]. At first sight one would attribute this relatively modest colloidal adsorption to the mutual repulsion between adsorbed colloids, which in the present many-body description is included through the mean-field Coulombic term in Eq. (2). However, in that case one would expect a stronger (longer-ranged) colloid-colloid repulsion and hence a weaker colloidal adsorption for increasing κ_o^{-1}, whereas Fig. 1(a) shows the opposite trend. This implies that another mechanism is at work here. The mechanism that we identify involves the salt and colloidal charge distributions $Q_s(x) = \rho_+(x) - \rho_-(x)$ and $Q_c(x) = Z\rho(x)$, respectively, shown in the insets of Fig. 1 for $\kappa_o^{-1}/a = 40$. These insets show an accumulation of negative counterions in water, in a very thin layer $-\kappa_w^{-1} < x < 0$, and a net positive colloidal charge for $a < x < 5a$ in (a) and at $x = x^*$ in (b). The compensating ion cloud, usually in the direct vicinity of several Debye lengths from a charged surface, is shown here to be deformed completely (a) or partially (b): a fraction of the compensating ionic charge prefers to reside in the water phase "further away" rather than close to the colloidal surface. Since the length scale for local charge separation is set by the Debye length, this fraction, and hence the net charge in the thin layer $-\kappa_w^{-1} < x < 0$ in the water, will increase with increasing κ_o^{-1}. This accumulated charge attracts the oppositely charged colloids at $x > a$ in Fig. 1(a), and hence the adsorption of colloids increases with κ_o^{-1}. In an oversimplified dynamic sense one could envisage a colloid with a spherical double layer approaching the water-oil interface from the oil side, then being stripped from (part of) its ionic cloud if it gets too close, such that it cannot diffuse back to the bulk as a neutral entity and hence adsorbs. Colloidal double-layer deformation also takes place in the wetting case of Fig. 1(b); a close-packed monolayer of colloids at $x = x^*$ is formed by the deep well of $V(x)$ at $x = x^*$, driving a large fraction of the screening ions into a narrow layer in the water phase. Because of colloid-colloid repulsions this monolayer strongly repels the colloids in bulk, giving rise to the colloid-depleted zone of a thickness d that increases with κ_o^{-1}, as expected. The observations of d decreasing from about 100 to 20 μm upon adding salt to the water [6] [and hence varying κ_o^{-1} over the parameter regime of Fig. 1(b)] is in agreement with our theoretical values.

One problem in the comparison between the results of Fig. 1 and the experiments of Ref. [6] is that the colloid-depleted zone was observed in combination with a dense monolayer for nonwetting colloids, whereas Fig. 1(b) holds for the case of wetting colloids, $\cos\theta = 0.987$. One could, on the one hand, of course argue that the wetting angle of the experimental system is smaller than the resolution of its measurement, such that the experimental system would actually be (extremely weakly) wetting. On the other hand, there could be sources of electrostatic attraction to the interface beyond the accuracy of the present theory, e.g., due to charge regulation or correlations [8]. It is not entirely straightforward, however, to quantify the importance of correlations in this system: both in the colloidal bulk ($x \to \infty$) and in the colloidal monolayer ($x \simeq a$) the pressure and electrostatic energy are overestimated by ignoring the colloid-colloid correlations, with competing effects on d, and the presence of mobile ions at *both* interfacial sides is an additional complication. We note, however, that our results are robust with respect to lowering Z, e.g., taking $Z = 150$ (not shown) yields very similar results.

In Ref. [6], and very recently also in Ref. [17], it was reported that water-in-oil droplets could be stable *without* any colloids or any other additives in the system. This observation goes against the common believe that emulsions require "emulsifiers" in order to be stable [18]. The stabilization mechanism proposed in Ref. [6] is based on the asymmetry between the cations and anions as regards their self-energy in oil and water, such that the droplets spontaneously acquire a net charge. Moreover, it was observed that a system of water-in-oil droplets could actually even crystallize, but only if $4 \lesssim \epsilon_o \lesssim 10$. The present theory as formulated in Eqs. (3) and (4) can be employed to underpin and further understand these recent surprising observations. The absence of any colloids is

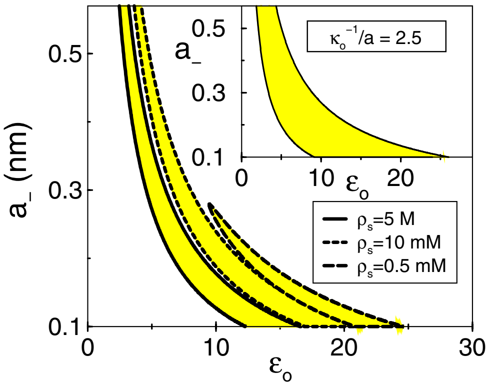

FIG. 2 (color online). Predicted crystallization regime (filled area) for water-in-oil droplets (see text) as a function of the oil-dielectric constant ϵ_o and the anion radius a_-, for a cation radius $a_+ = a_-/2$, in the main figure for several salt concentrations ρ_s in the water phase, and in the inset for a fixed Debye length κ_o^{-1} in the oil phase.

modeled by setting $\rho(x) \equiv 0$ throughout, and the alleged asymmetry of the cations and anions is taken into account by setting their size ratio $\xi > 1$, such that $V_+(x) = \xi V_-(x)$, i.e., the aversion of the cations for oil is larger than that of the anions. For $\xi = 2$ and $\epsilon_w = 80$, we solved Eqs. (3) and (4) on an x grid to obtain the equilibrium profiles $\rho_\pm(x)$, for a range of ϵ_o and a_-, keeping either ρ_s or κ_o fixed. The net (positive) charge in the water phase (per unit area, in units of e) follows as $\sigma = \int_{-\infty}^{0} dx(\rho_+(x) - \rho_-(x))$. It is reasonable to presume that a spherical water-in-oil droplet of radius R has a total charge number $Z = 4\pi R^2\sigma$, and that two of these droplets repel each other by a potential of the form $v(r) = (Ze)^2 \times \exp(\kappa_o(2R - r))/[\epsilon_o(1 + \kappa_o R)^2 r]$ [16]. Given that it is empirically known from point-Yukawa simulations [19] that crystallization occurs when the coupling parameter $\Gamma \equiv \beta v(\rho^{-1/3})(1 + k + k^2/2) > 106$, with ρ the number density and $k = \kappa_o \rho^{-1/3}$, we can investigate straightforwardly for which parameters crystallization of water-in-oil droplets is to be expected. We indicate in the (ϵ_o, a_-) plane of Fig. 2 the regime where $\Gamma > 106$, for the experimental parameters $R = 1.5\ \mu$m and $\rho^{-1/3} = 10R$ [6], in the main figure for several ρ_s and in the inset for a fixed κ_o. The narrow ϵ_o-bands separate a large-ϵ_o regime where the screening in the oil is too strong for crystallization (given ρ and R) from a low-ϵ_o regime where the droplet charge is too small. The crystallization that we predict in the narrow ϵ_o-bands in Fig. 2 is in fair agreement with the experiments [6]. Note, however, that the thermodynamic stability of the crystal, e.g., the optimal R for a given ρ, is not studied here.

In conclusion, we have presented a theory for charged colloids, anions, and cations near a water-oil interface, taking into account colloidal wetting properties, ionic self-energies, electrostatic image effects, and screening. We identified the destruction of colloidal double layers and the separation of ionic charge as important mechanisms, with which we can describe several recent observations of hydrophobic charged colloids, most notably the large colloid-depleted zone in between the adsorbed colloidal monolayer and the bulk oil-dispersed colloidal phase, the spontaneous self-charging of water-in-oil droplets, and their crystallization in a narrow band of ϵ_o [6]. The theory can be applied to general systems of charged particles near a dielectric interface, where similar double-layer effects are expected.

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