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Entrapment of charged, nonwetting colloids near oil-water interfaces

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Charged, nonwetting colloids with a contact angle $\theta = 180°$ are attracted to an oil-water interface due to image charge forces. Near the interface, the attractive image charge forces are balanced by repulsive van der Waals forces, and thus the colloids are trapped at a finite distance from the interface. Electrostatic and van der Waals pressure lead to a deformation of the interface in the equilibrium state. For parameters relevant to experiment, however, the effects of the deformed interface are negligible and thus the mutual interactions of such interfacially trapped colloids should be well characterized by electrostatic dipole repulsions.

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I. INTRODUCTION

Pattern formation and self-organization of colloids trapped at fluid interfaces offer new possibilities for manufacturing two-dimensional structures and templates. In this context it is desirable to have precise knowledge of the acting effective forces on the colloids in order to tune them in a controllable manner.

Partially wetting colloids trapped at the interface interact through various interface-induced interactions: electrostatic [1,2] and capillary [3] forces (which are longer ranged), van der Waals [4], and fluctuation [5–7] forces (which are shorter ranged). The complicated characteristics of these interactions arise mainly from the fact that the colloids intersect the interface. As an example, aspects of the effective interactions will be reviewed shortly in Sec. II, especially with regard to the factors which influence the relative magnitude of the capillary interactions with respect to the electrostatic ones.

On the other hand, it has been demonstrated quite recently [8] that nonwetting, charged colloids immersed in high-dielectric oils are attracted towards a water interface through image charge forces and become stabilized near the interface without intersecting it. Furthermore, an unusual depletion layer next to the layer of trapped colloids has been observed (for a possible explanation see Ref. [9]). In Sec. III we will discuss the nature of this entrapment near the interface, calculate the equilibrium position, and evaluate the deformation of the interface. The ensuing capillary interactions turn out to be small such that the longer-ranged lateral interactions between the colloids are described cleanly by electrostatic forces only. Section IV contains a short summary and some discussion of the results.

II. PARTIALLY WETTING COLLOIDS AT INTERFACES

Colloidal particles are trapped at an interface between water and a nonpolar medium if water wets the colloid only partially—i.e., if the contact angle θ is between 0° and 180°. This configuration is stable against thermal fluctuations due to the gain in interfacial energy which is of order γR^2 where γ is the surface tension of the interface and R is the radius of the colloid [1]. The effective interactions of such trapped colloids exhibit qualitatively new features when compared to the ones in colloidal bulk solutions; however, there appears to be little control in tuning them so far. In many applications, colloids are endowed with dissociable surface groups which lead to fairly large surface charge densities $\sigma_{\mathrm{water}} \sim 0.1\ \mathrm{C/m}^2$ when brought into contact with water. But also for colloids immersed in a nonpolar medium (dielectric constant ϵ_1) such as decane ($\epsilon_1 = 2$), there is partial evidence that the colloids possess surface charge densities $\sigma_{\mathrm{np}} \sim 10^{-5}\ \mathrm{C/m}^2$ [10]. Trapped at the interface, the colloid acquires a net electric dipole moment perpendicular to the interface, $p = p_{\mathrm{np}} + p_{\mathrm{water}}$, which is a consequence of both the charge on the nonpolar side, q_{np}, and the charge on the water side, q_{water}. For the charge on the nonpolar side, the water phase (dielectric constant $\epsilon_2 = 80$ and screening length $\kappa^{-1} < 1\ \mu\mathrm{m}$) is almost equivalent to a perfect conductor. Thus they attract an image charge of equal magnitude and opposite sign and the resulting dipole moment is $p_{\mathrm{np}} \sim q_{\mathrm{np}} R$. The dipole moment p_{water} is formed by the charges on the water side together with the asymmetric screening cloud, and it is strongly affected by charge renormalization [2]. The asymptotic electrostatic interaction energy $U_{\mathrm{el}}(d)$ between two colloids at lateral distance d is thus repulsive and given by

$$U_{\mathrm{el}}(d) = \frac{1}{8\pi\epsilon_1\epsilon_0} \frac{(p_{\mathrm{np}} + p_{\mathrm{water}})^2}{d^3} \quad (d \to \infty). \tag{1}$$

Besides electrostatic interactions, long-ranged capillary interactions mediated by the deformation of the water interface may arise which asymptotically have the same d^{-3} dependence as the electrostatic interactions but are attractive [11],

$$U_{\mathrm{cap}}(d) \sim -\varepsilon_F U_{\mathrm{el}}(d) \quad (d \to \infty). \tag{2}$$

The dimensionless factor $\varepsilon_F = F/(2\pi\gamma R \sin\theta)$ is the ratio of the total vertical force acting on the colloid with a force scale set by surface tension. Thus the capillary attraction can only compete with the electrostatic repulsion if $\varepsilon_F \sim 1$ which appears to be possible only through the effect of the charges on the water side [11]. The contribution of the charges on the nonpolar side to ε_F is negligible. Asymptotically experimental results, obtained at air-water [12] and oil-water [10,13,14]

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interfaces, indicate that the electrostatic repulsion is larger than the capillary attraction ($\varepsilon_F \lesssim 0.1$). However, it is not clear yet how capillary interactions at closer distances affect the structure and pattern formation of colloidal monolayers at air-water interfaces (where $p_{\rm np} \approx 0$) where both effects of repulsion [1] and attraction [15] are seen which, however, need to be separated from the effect of surface impurities [16,17]. We emphasize that the difficulties in obtaining a complete picture for all distances between the colloids arise from the presence of the charges on the water side which requires a treatment incorporating renormalization in both direct electrostatic and interface-mediated capillary interactions.

III. NONWETTING COLLOIDS NEAR INTERFACES

In the experiments of Ref. [8], poly(methyl methacrylate) (PMMA) colloids with radius $R \approx 1$ μm and carrying $Z \approx 450$ elementary charges e were immersed in a high-dielectric oil ($\epsilon_1 \approx 5.6$). The charge corresponds to a surface charge density $\sigma_{\rm np} \approx 6 \times 10^{-6}$ C/m^2. They were attracted towards the surface of large water droplets through the image charge induced inside the water.[1] The pictures in Ref. [8] [see Figs. 2(a) and 2(b), below] indicate that the colloids become trapped near the interface without possibly being partially wetted by the water phase. Macroscopic contact angle measurements correspondingly yielded $\theta \approx 180°$ although it is not completely evident whether the colloids are fully hydrophobic. For $\theta < 180°$ we have the situation discussed in the previous section: the colloids penetrate the interface and the image charge force will be balanced by the surface tension acting on the three-phase contact line. If we assume $\theta = 180°$, the question arises how the image charge attraction is balanced such that the colloid is in equilibrium near the interface. This question is investigated in the next subsection.

A. Force balance for nonwetting colloids

For simplicity, we consider the water interface to be flat. The nature of the force balance can be understood by resorting to the effective interface potential $\omega(l)$ [18] which acts between two half spaces of PMMA and water, separated by a (thin) slab of oil with thickness l [see Fig. 1(a)]. The grand potential of such a configuration is given by

$$\Omega = \sum_{i=1}^{3} \Omega_{{\rm bulk},i} + A[\gamma_{12} + \gamma_{23} + \omega(l)]. \tag{3}$$

Here the index $i = 1$, 2, and 3 refers to water, oil, and PMMA, respectively. $\Omega_{{\rm bulk},i}$ is the bulk grand potential of phase i, γ_{ij} is the surface tension between phases i and j, and A is the area of the planar interface. In thermodynamic equilibrium, $\Sigma_i \Omega_{{\rm bulk},i} = -pV$ where p is the pressure and V the volume of the whole configuration. Then the surface tension between PMMA and water is given by

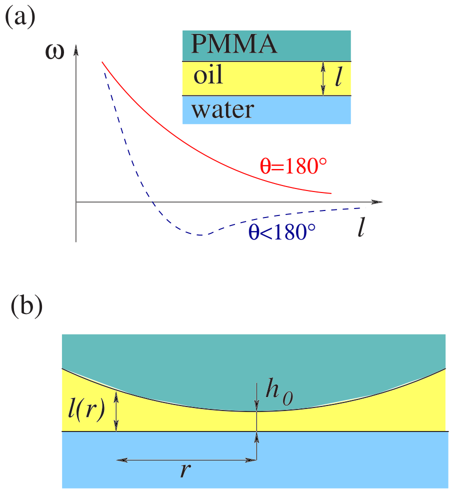

FIG. 1. (Color online) (a) Schematic behavior of the effective interface potential for partially wetting and nonwetting colloids. (b) Definitions used in the Derjaguin approximation for the total repulsive force acting on the colloid.

$$\gamma_{13} = \gamma_{12} + \gamma_{23} + \min_l \omega(l) \tag{4}$$

and the contact angle is

$$\cos\theta = \frac{\gamma_{23} - \gamma_{13}}{\gamma_{12}} = -1 - \frac{1}{\gamma_{12}} \min_l \omega(l). \tag{5}$$

Quite generally, in the presence of dispersion forces $\omega(l)$ takes the form

$$\omega(l) = \frac{a}{l^2} + \frac{b}{l^3} + \cdots, \tag{6}$$

where $a = A_H/12\pi$ is related to the Hamaker constant A_H of the three-phase slab configuration which has a typical magnitude of several $k_{\rm B}T$. $\theta = 180°$ implies that $\min_l \omega(l) = 0$ which is only consistent with $a > 0$ and $\omega(l) \geqslant 0$. Microscopic arguments [18] show that the magnitude of b is $O(l_0|a|)$ where l_0 is a molecular length scale. Thus for $l \gg l_0$ we may safely assume

$$\omega(l) \approx \frac{A_H}{12\pi l^2} \quad (l \gg l_0, A_H > 0). \tag{7}$$

This repulsive interface potential is responsible for keeping the colloids away from the water interface. The total repulsive force on the colloid located at a distance $h_0 \ll R$ from the interface can be found via the Derjaguin approximation [see Fig. 1(b)]

$$F_{\rm rep} \overset{R/h_0 \to \infty}{\approx} 2\pi \int_0^R r\, dr \omega'(l(r)) \tag{8}$$

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[1] Since the water droplets themselves carried a net charge of the same sign as the colloids, there was a repulsive barrier repelling far-away colloids from the surface. However, near the surface the image charge attraction always dominates this repulsion.

$$\overset{R/h_0\to\infty}{\approx} \frac{A_H}{3}\int_0^\infty \frac{r\,dr}{[h_0+r^2/(2R)]^3} = A_H\frac{R}{6h_0^2} \tag{9}$$

($\omega' = d\omega/dl$). On the other hand, the image charge force on the colloid opposed to the flat water interface is given by

$$F_{\text{im}} = -(k_{\text{B}}T)\frac{\epsilon_2-\epsilon_1}{\epsilon_2+\epsilon_1}Z^2\frac{\lambda_B}{4(R+h_0)^2} \approx -(k_{\text{B}}T)Z^2\frac{\lambda_B}{4(R+h_0)^2}, \tag{10}$$

where $\lambda_B = e^2/(4\pi\epsilon_1\epsilon_0 k_{\text{B}}T)$ is the Bjerrum length of oil ($\lambda_B \approx 10$ nm for the above parameters). The equilibrium position of the colloid is given by $F_{\text{rep}}+F_{\text{im}}=0$ and for $A_H/k_{\text{B}}T \ll Z^2\lambda_B/R$ we find that $h_0 \ll R$ and

$$\frac{h_0}{R} \approx \frac{1}{Z}\sqrt{\frac{2}{3}\frac{A_H}{k_{\text{B}}T}\frac{R}{\lambda_B}}. \tag{11}$$

The Hamaker constant is unknown for the particular combination of materials used in Ref. [8]. However, from typical literature values we may put $A_H/k_{\text{B}}T \lesssim 10$ which results in $h_0 \lesssim 50$ nm for the experimental parameters. This equilibrium distance is large enough for the coarse-grained interface potential description to be valid; on the other hand, it is small enough on the scale of the colloid for the Derjaguin approximation to be valid as well. Indeed this offers an explanation why the colloids appear to be localized quite near the interface in the experiment of Ref. [8]. Since $h_0 \ll R$, the depth of the potential well V_{min} in which the particle is trapped is given by the image charge potential only:

$$\frac{V_{\text{min}}}{k_{\text{B}}T} \approx Z^2\frac{\lambda_B}{2R}. \tag{12}$$

For the parameters used above, $V_{\text{min}} \approx 1000 k_{\text{B}}T$.

B. Interface deformation and capillarylike interaction

Both the image charge effect (through an electric stress field π_{el}) and the interface potential (through a disjoining pressure π_{dis}, evaluated with the Derjaguin approximation) exert forces on the interface which deform it and may affect the effective interaction between the trapped colloids. Acting on the flat interface, these stresses are given by

$$\pi_{\text{el}}(r) = \left.\frac{\epsilon_1\epsilon_0}{2}E_z^2(r)\right|_{z=0} \approx \frac{k_{\text{B}}T}{2\pi}Z^2\frac{\lambda_B R^2}{(r^2+R^2)^3}, \tag{13}$$

$$\pi_{\text{dis}}(r) = -\omega'(l(r)) \approx -\frac{A_H}{6\pi}\frac{1}{[h_0+r^2/(2R)]^3}. \tag{14}$$

Here, $h_0 \ll R$ has been used in the expression for the electric stress. Of course, for the equilibrium position of the colloid given by Eq. (11) the total force on the interface is zero:

$$2\pi\int_0^\infty r\,dr(\pi_{\text{el}}+\pi_{\text{dis}}) = 0. \tag{15}$$

Since there is no net force acting on the colloid, this is equivalent to the condition that in mechanical equilibrium the total force on the system "colloid+interface" be zero. According to Refs. [19,20] this furthermore implies that there will be no long-ranged, logarithmic deformations of the interface (otherwise, these logarithmic deformations would need to be balanced by external means such as walls of a container).

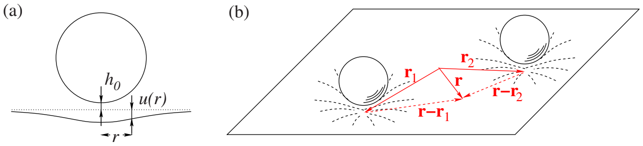

FIG. 2. (Color online) (a) One colloid near the interface. (b) Deformations around two colloids near the interface.

The interface deformation $u(r)$ can be treated as a small perturbation from the flat interface [see Fig. 2(a) for some definitions]. The free energy of the deformed interface is given by

$$\mathcal{F}[u] = \int d^2r\left[\frac{\gamma}{2}(\nabla u)^2 - (\pi_{\text{el}}+\pi_{\text{dis}})u\right]. \tag{16}$$

Minimization of this free energy leads to the condition that locally the stress on the interface given by Eqs. (13) and (14) needs to be balanced by the capillary pressure ($\gamma=\gamma_{12}$),

$$\gamma\Delta u_{\text{eq}} + \pi_{\text{el}}(r) + \pi_{\text{dis}}(r) = 0, \tag{17}$$

and the solution to this inhomogeneous Laplace equation, consistent with the boundary condition $u(r\to\infty)=0$, is given by

$$u_{\text{eq}}(r) = -\frac{1}{\gamma}\int_r^\infty s\,ds[\pi_{\text{el}}(s)+\pi_{\text{dis}}(s)]\ln\frac{s}{r}. \tag{18}$$

We introduce reduced lengths $\tilde{u}_{\text{eq}}=u_{\text{eq}}/R$, $\tilde{h}_0=h_0/R$ and $x=r/R$, $y=s/R$, and by exploiting the equilibrium condition (11) the reduced meniscus solution is

$$\tilde{u}_{\text{eq}}(x) = -\tilde{u}_0\int_x^\infty y\,dy\left[-\frac{\frac{\tilde{h}_0^2}{2}}{\left(\tilde{h}_0+\frac{y^2}{2}\right)^3} + \frac{1}{(1+y^2)^3}\right]\ln\frac{y}{x},$$

$$\tilde{u}_0 = \frac{Z^2}{2\pi}\frac{k_{\text{B}}T}{\gamma R^2}\frac{\lambda_B}{R}. \tag{19}$$

The integral can be solved explicitly:

$$\tilde{u}_{\text{eq}}(x) = \frac{\tilde{u}_0}{8}\left(\ln\frac{2\tilde{h}_0+x^2}{1+x^2} + \frac{x^2(1-2\tilde{h}_0)}{(1+x^2)(2\tilde{h}_0+x^2)}\right) \tag{20}$$

$$\overset{x\to\infty}{\approx} -\tilde{u}_0\frac{1-4\tilde{h}_0^2}{16x^4}. \tag{21}$$

The asymptotic behavior $u_{\text{eq}}(r\to\infty) \propto r^{-4}$ could have been guessed immediately from Eq. (17) and the asymptotic behavior of the stress fields $\propto r^{-6}$. In Fig. 3 the reduced meniscus deformation $\tilde{u}_{\text{eq}}(x)$ is plotted for several choices of the

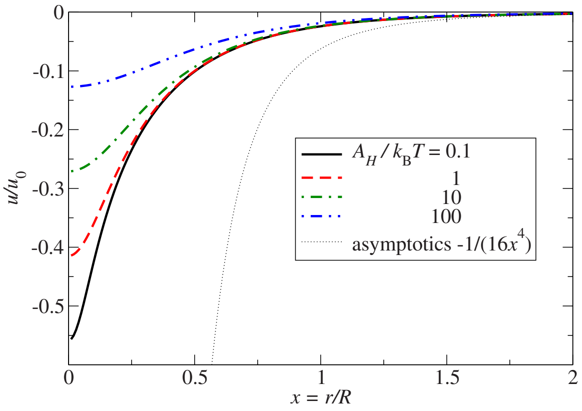

FIG. 3. (Color online) Normalized meniscus deformation $u(x=r/R)/u_0$ for several choices of the Hamaker constant A_H and the experimental parameters of Ref. [8]. While the equilibrium distance $h_0 \propto \sqrt{A_H}$ varies between 6 nm ($A_H/k_B T=0.1$) and 180 nm ($A_H/k_B T=100$), the meniscus deformation appears to be rather insensitive with respect to changes in A_H.

Hamaker constant (which determines $\tilde{h}_0$). Note that for the experimental parameters of Ref. [8] (we additionally assumed $\gamma \approx 0.05$ N/m), $\tilde{u}_0 \sim 2.6 \times 10^{-5}$, and thus the total meniscus deformation is tiny, less than 1 Å.

The capillary interaction energy between two colloids placed at lateral positions $\mathbf{r}_1$ and $\mathbf{r}_2$ at distance $d=|\mathbf{r}_1 - \mathbf{r}_2|$ is found by again minimizing the surface free energy, Eq. (16), now in the presence of two colloids. The treatment is very similar to the case of two partially wetting colloids which has been discussed in Refs. [11,21]. The total stress acting on the interface has again a disjoining and an electric part. For $d \gg R$, the disjoining pressure can be safely assumed to be additive:

$$\hat{\pi}_{\rm dis} = \pi_{{\rm dis},1} + \pi_{{\rm dis},2} = \pi_{\rm dis}(|\mathbf{r} - \mathbf{r}_1|) + \pi_{\rm dis}(|\mathbf{r} - \mathbf{r}_2|). \quad (22)$$

The electric part is proportional to the square of the perpendicular electric field, E_z [see Eq. (13)]. Since the two electric fields from the single colloids add up, the electric stress acquires an additional, mixed component (this is why a naive superposition approximation for the deformation around two colloids fails; see Refs. [11,21]):

$$\begin{aligned}\hat{\pi}_{\rm el} &= \pi_{{\rm el},1} + \pi_{{\rm el},2} + 2\pi_{{\rm el},m}\\ &= \pi_{\rm el}(|\mathbf{r} - \mathbf{r}_1|) + \pi_{\rm el}(|\mathbf{r} - \mathbf{r}_2|) + \epsilon_1 \epsilon_0 E_z(|\mathbf{r} - \mathbf{r}_1|) E_z(|\mathbf{r} - \mathbf{r}_2|).\end{aligned} \quad (23)$$

The equilibrium position of each colloid above the interface will shift slightly to $h_0 + \Delta h_0$ since it experiences also an additional attraction from the image charge of the other colloid. Thus the disjoining pressure can be Taylor expanded:

$$\pi_{{\rm dis},i}(h_0 + \Delta h_0) \approx \pi_{{\rm dis},i}(h_0) + \Delta h_0 \pi'_{{\rm dis},i}(h_0) \quad (i=1,2). \quad (24)$$

Force balance determines the shift Δh_0 through

$$\Delta h_0 = - \frac{\int d^2 r \pi_{{\rm el},m}}{\int d^2 r \pi'_{{\rm dis},1}(h_0)}. \quad (25)$$

The two-colloid equilibrium solution $\hat{u}_{\rm eq}$ can be decomposed similarly to the pressures

$$\hat{u}_{\rm eq} = u_{1,{\rm eq}} + u_{2,{\rm eq}} + 2u_{m,{\rm eq}}, \quad (26)$$

with the single colloid solutions fulfilling $\gamma \Delta u_{i,{\rm eq}} + \pi_{{\rm el},i} + \pi_{{\rm dis},i}(h_0) = 0$ and the mixed solution obeying

$$\gamma \Delta u_{m,{\rm eq}} + \Pi_m = 0, \quad (27)$$

with

$$\Pi_m = \pi_{{\rm el},m} + \frac{\Delta h_0}{2} \sum_{i=1}^{2} \pi'_{{\rm dis},i}(h_0).$$

The effective capillary potential is defined as the difference in free energy of the two-colloid equilibrium solution $\hat{u}_{\rm eq}$ and of the two single colloid solutions $u_{\rm eq}$:

$$U_{\rm cap} = \mathcal{F}[\hat{u}_{\rm eq}] - 2\mathcal{F}[u_{\rm eq}]. \quad (28)$$

The leading contributions to $U_{\rm cap}$ reside in the mixed terms Π_m and $u_{m,{\rm eq}}$ defined above since ($\tilde{d}=d/R$)

$$\int d^2 r \pi_{{\rm el},m} \sim \gamma R \tilde{u}_0 \tilde{d}^{-3}, \quad \frac{\Delta h_0}{h_0} \sim \tilde{d}^{-3}. \quad (29)$$

A longer calculation yields

$$\begin{aligned} U_{\rm cap} &\approx - \int d^2 r \left[\Pi_m \sum_{i=1}^{2} u_{i,{\rm eq}} + u_{m,{\rm eq}} \sum_{i=1}^{2} (\pi_{{\rm el},i} + \pi_{{\rm dis},i}) \right] \\ &\sim - \gamma R^2 \tilde{u}_0^2 \tilde{d}^{-3}. \end{aligned} \quad (30)$$

The direct electrostatic interaction between the two trapped colloids is given by the dipole-dipole repulsion where each dipole is formed by the colloidal charge together with its image charge:

$$U_{\rm el} \approx \frac{1}{4\pi \epsilon_1 \epsilon_0} \frac{(2ZeR)^2}{d^3} \sim \gamma R^2 \tilde{u}_0 \tilde{d}^{-3}. \quad (31)$$

Thus we recover the capillary potential law already found for partially wetting colloids [see Eq. (2), with $\varepsilon_F \to \tilde{u}_0$]:

$$U_{\rm cap} \approx - \tilde{u}_0 U_{\rm el} \quad (d \to \infty). \quad (32)$$

Indeed, $\tilde{u}_0$ can also be viewed (apart from a numerical factor) as a quotient of the electrostatic force scale $k_B T \lambda_B Z^2 / R^2$ with the capillary force scale γR.

IV. DISCUSSION

We have shown that charged, nonwetting colloids become trapped near an interface between a nonpolar medium (oil) and water due to a balance of attractive image charge forces with repulsive dispersion forces. This result lends support to the observations of Ref. [8] where μm-sized colloids (observed by video microscopy) in high-dielectric oil seem to be stabilized at a mesoscopic distance near large water droplets without penetrating the interface. The interfacial stability (depth of the trapping potential) is mainly determined by the image charge potential; for the parameters of Ref. [8], it is about 1000 $k_B T$. This is in contrast to the case of partially wetting colloids where the stability is of order γR^2 which for μm-sized colloids is $>10^6\, k_B T$. This difference stems from the comparably small surface charge density which the colloids possess when immersed in a nonpolar medium. The smallness of the surface charge density is also the reason why the capillary deformations due to electric and dispersion forces are tiny and the ensuing capillary potential is negligible compared to the lateral electrostatic interactions of the trapped colloids. This is also in contrast to the case of partially wetting colloids where the charge density on the colloid-water interface is several orders of magnitude larger which may lead to capillary effects in colloidal interactions.

How do these phenomena depend on the colloid size? If one assumes that the charge density in the nonpolar medium of differently sized colloids stays approximately equal (i.e., the number of charges $Z \propto R^2$), then the trapping distance $h_0 \propto R^{-1/2}$ [Eq. (11)] and the dimensionless capillary amplitude $\tilde{u}_0 \propto R$ [Eq. (19)] are influenced only moderately. However, the well depth $V_{\min} \propto R^3$ indicates that nonwetting colloids with radius $R \sim 100$ nm would be trapped by the water interface very loosely, with binding energies around $1 k_B T$ since particles of that size would be charged with a few elementary charges only. Also the dipolar repulsion ($\propto R^4$) between the trapped colloids becomes small quickly with lowering the colloid size. Therefore the stability of a colloidal monolayer near an interface is size sensitive, a fact which might be of use in working with polydisperse samples.

Finally, we remark that a two-dimensional model system of magnetically doped colloids trapped *near* an air-water interface with tunable lateral interactions (undisturbed by capillary effects) has already been used successfully (for a review see Ref. [22]). There, fully wetting colloids ($R = 2.35$ μm, mass density $\rho = 1.7$ g/cm^3) immersed in a suspended cylindrical drop sedimented onto the interface until the gravitational force $F_{\text{grav}} = 4/3\pi R^3(\rho - \rho_{\text{water}})g$ is balanced (see Ref. [23] for the first realization of this system). Both the repulsive interface force [Eq. (9)] and an electrostatic force repelling the colloid from the air-water interface [24] counteract the gravitational force. If the salt concentration in the water phase is chosen such that the screening length is small, $\kappa^{-1} \lesssim 10$ nm, then the electrostatic force is small compared to the interface force at colloidal distances from the interface beyond a few screening lengths. The balance of the gravitational force with the interface force results in an equilibrium distance from the interface of

$$h_0 = \frac{1}{R}\sqrt{\frac{A_H}{8\pi(\rho - \rho_{\text{water}})g}}. \tag{33}$$

For $A_H / k_B T \lesssim 10$, the trapping distance from the interface in this case is $h_0 \lesssim 200$ nm, quite comparable to the case of charged colloids. Thus the colloids are trapped at such a distance from the interface that lateral electrostatic interactions (through the small screening length) and capillary interactions are negligibly small [the capillary deformation, evaluated using Eq. (17) with $\pi_{\text{el}} = 0$, turns out to be tiny]. The tunable lateral interactions are achieved by the magnetic dipole interactions between the colloids in the presence of an external magnetic field.

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