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Capillary-induced interactions between colloids at an interface

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Abstract

Within a general framework we study the effective, deformation-induced interaction between two colloids trapped at a fluid interface. As an application, we consider the interface deformation owing to the electrostatic field of charged colloids. The effective interaction is attractive and overcomes the direct electrostatic repulsion at large separations if the system is not mechanically isolated. Otherwise, a net attraction seems possible only for large enough colloidal charges.

1. Introduction

In view of various basic and applied issues (two-dimensional melting [1], mesoscale structure formation [2], engineering of colloidal crystals [3]), the self-assembly of sub-micrometre colloidal particles at water–air or water–oil interfaces has gained significant interest in recent years. These particles are trapped at the interface if water wets the colloid only partially; in this case the trapped configuration is stable against thermal fluctuations [4]. For charge-stabilized colloids at interfaces, the *repulsive* part of their mutual interaction is well understood and behaves as a dipole–dipole interaction at large separations due to the screening of the colloidal charge [5, 6] (see (12) below). Nonetheless, charged colloids at interfaces apparently also exhibit *attractive* interactions far beyond the range of van der Waals forces. According to the experimental studies listed in [7], polystyrene spheres (radii $R = 0.25\text{--}2.5\ \mu\text{m}$) on flat water–air interfaces spontaneously form complicated metastable mesostructures. They are consistent with the presence of a minimum in the effective intercolloidal potential at separations $d/R \approx 3 \dots 20$ with a depth of a few $k_B T$. Reference [8] provides a direct measurement of the effective potential for PMMA spherical particles of radius $R = 0.75\ \mu\text{m}$ at the surface of a water droplet immersed in oil: a surprisingly steep minimum has been found at a separation $d/R = 7.6$ with a depth $>4 k_B T$.

A theoretically sound mechanism for the appearance of an attractive minimum in the intercolloidal potential at μm separations has not been found yet⁴. Electrostatic forces can deform the interface and thus a capillary-mediated effective attraction appears as a possible explanation. The conclusions reached in the literature, however, are varied and contradictory [8, 10–14]. In a systematic theoretical study of the effective potential induced by the interfacial deformation, we first considered the case of an asymptotically flat interface and calculated the effective colloid–colloid potential within a superposition approximation [13]. While reliable for systems under the action of external forces, this approximation is insufficient for mechanically isolated systems [14]. Recently, we have started to analyse the relevance of finite-size effects [15] (related, for example, to the finite droplet size in the experiment reported in [8], and to the finite thickness of a nematic layer on top of which colloidal patterns provide some experimental evidence [16] for a capillary-mediated attraction as well).

2. Deformation of an asymptotically flat interface

The shape of a piece \mathcal{S} of the interface is determined by the condition of mechanical equilibrium under the common action of a pressure field $\Pi(\mathbf{r})$ acting on the fluid interface and the line force acting at the boundary \mathcal{C} of \mathcal{S} :

$$\int_{\mathcal{S}} dA \mathbf{e}_n \Pi + \gamma \oint_{\mathcal{C}} d\ell \mathbf{e}_t \times \mathbf{e}_n = \mathbf{0}, \quad (1)$$

where γ is the surface tension, \mathbf{e}_n is the local unit vector normal to \mathcal{S} and \mathbf{e}_t is the local unit vector tangent to \mathcal{C} (such that $\mathbf{e}_t \times \mathbf{e}_n$ points outwards). We apply this equation to the configuration of a single spherical colloid trapped at a fluid interface which approaches asymptotically the plane $z = 0$: \mathcal{C}_0 is the projection on this plane of the colloid–interface contact line of radius r_0 , \mathcal{C}_r is a circle of radius $r > r_0$, and \mathcal{S}_r is the region between \mathcal{C}_0 and \mathcal{C}_r . When the distance r from the colloid is large enough ($r \gg r_0$), the (rotationally symmetric) vertical height $u(r)$ of the interface, measured from the plane $z = 0$, is small and the line force exerted at \mathcal{C}_r can be treated in linear approximation: $\mathbf{e}_n = \mathbf{e}_z - \mathbf{e}_r(du/dr) + \mathcal{O}(u^2)$, where \mathbf{e}_r is the radial vector pointing away from the colloid. Projection of (1) onto the vertical direction \mathbf{e}_z then yields

$$-2\pi\gamma r \frac{du}{dr} = \int_{\mathcal{S}_r} dA (\mathbf{e}_n \cdot \mathbf{e}_z) \Pi + \gamma \oint_{\mathcal{C}_0} d\ell (\mathbf{e}_t \times \mathbf{e}_n) \cdot \mathbf{e}_z. \quad (2)$$

Since the colloidal particle is also in mechanical equilibrium, the contact line force at \mathcal{C}_0 must be balanced by the vertical force F exerted on the colloid by sources other than surface tension (gravitational, electrostatic, hydrostatic . . .):

$$F - \gamma \oint_{\mathcal{C}_0} d\ell (\mathbf{e}_t \times \mathbf{e}_n) \cdot \mathbf{e}_z = 0. \quad (3)$$

We define the dimensionless parameters

$$\varepsilon_F := -\frac{F}{2\pi\gamma r_0} \quad (\text{force on the colloid}), \quad (4)$$

$$\varepsilon_\Pi := \frac{1}{2\pi\gamma r_0} \int_{\mathcal{S}_\lambda} dA (\mathbf{e}_n \cdot \mathbf{e}_z) \Pi \quad (\text{force on the whole interface}), \quad (5)$$

⁴ As a matter of fact, in [9] the effective attraction is attributed to oil contaminations of the water–air interface.

where λ is a length determined by a boundary condition far from the colloid, for example, the size of the vessel containing the system [13]. Using these definitions, equations (2) and (3) combined yield

$$r \frac{du}{dr} = r_0(\varepsilon_F - \varepsilon_\Pi) + \frac{1}{\gamma} \int_r^\lambda ds s \Pi(s), \quad (6)$$

because the linearization $\mathbf{e}_n \cdot \mathbf{e}_z = 1 + O(u)$ applies in the integral of Π over the range $s > r \gg r_0$. This equation can be integrated immediately with the boundary condition $u(\lambda) = 0$ (pinned interface):

$$u(r) = r_0(\varepsilon_\Pi - \varepsilon_F) \ln \frac{\lambda}{r} - \frac{1}{\gamma} \int_r^\lambda ds s \Pi(s) \ln \frac{s}{r} \quad (r_0 \ll r). \quad (7)$$

We note that $\varepsilon_\Pi - \varepsilon_F$ is the (dimensionless) net force acting on the system ‘colloidal particle + interface’. Assuming the asymptotic decay $\Pi(r \gg r_0) \sim r^{-n}$ with $n > 2$, the following two qualitatively different cases arise.

- (i) Mechanical non-isolation ($\varepsilon_\Pi \neq \varepsilon_F$): the interface deformation varies asymptotically as a logarithm, $u(r) \sim \ln r$, and the net force is balanced by the line force exerted at the system boundary determined by λ .
- (ii) Mechanical isolation ($\varepsilon_\Pi = \varepsilon_F$): the asymptotic decay of the interface deformation is faster than logarithmic, $u(r) \sim r^{2-n}$, and the limit of large system sizes ($\lambda \rightarrow \infty$) is finite.

We emphasize the generality of the results contained in equation (7). In particular, the equation holds also even if Π and the meniscus deformation *near* the colloid are too large to allow the small-deformation approximation (linearization) everywhere.

3. Capillary-induced potential on an asymptotically flat interface

We consider two colloidal particles a distance d apart at an asymptotically flat interface. (By symmetry, we consider just one of the colloids and \hat{S} will denote the region in the corresponding half-plane outside C_0 .) $\hat{\Pi}(\mathbf{r})$ denotes the pressure field and \hat{F} the force on this colloid, both evaluated in the reference configuration corresponding to $\hat{\varepsilon}_F = \hat{\varepsilon}_\Pi = 0$: the interface is flat and the colloid is positioned vertically such that at three-phase contact Young’s law holds in terms of the contact angle $\theta \in (0, \pi)$.⁵ A configuration is then described by the deformation $\hat{u}(\mathbf{r})$ and the height $\Delta\hat{h}$ of the colloid centre with respect to the unperturbed reference height. The free energy of a configuration contains contributions from the change of area of the two-phase interfaces and from work done by the forces $\hat{\Pi}$ and \hat{F} upon displacements with respect to the reference configuration [13]. Assuming $|\hat{\varepsilon}_F|, |\hat{\varepsilon}_\Pi| \ll 1$, so that the interface deformation is small everywhere (see (6)), one obtains the following free energy functional:

$$\hat{\mathcal{F}} = \int_{\hat{S}} dA \left[\gamma |\nabla \hat{u}|^2 - 2 \hat{\Pi} \hat{u} \right] + \frac{\gamma}{r_0} \oint_{C_0} d\ell [\Delta\hat{h} - \hat{u}]^2 - 2 \hat{F} \Delta\hat{h}, \quad (8)$$

up to corrections of $O(\hat{\varepsilon}_F, \hat{\varepsilon}_\Pi)^3$. Without loss of generality, we write $\hat{u} =: u_1 + u_2 + \hat{u}_m$ and $\hat{\Pi} =: \Pi_1 + \Pi_2 + 2\hat{\Pi}_m$, where u_1 (u_2) is the solution of the single-colloid configuration

⁵ Thus the radius of the three-phase contact circle is $r_0 = R \sin \theta$, where R is the radius of the colloid.

centred at the first (second) colloid (cf equation (7)) and Π_1 (Π_2) is the corresponding single-colloid pressure field. The equilibrium state minimizing $\hat{\mathcal{F}}$ is obtained by solving the following equations:

$$\begin{aligned} \Delta \hat{h} &= \langle \hat{u}_m + u_1 + u_2 \rangle - \hat{\varepsilon}_F r_0, & \langle \cdot \rangle &:= \frac{1}{2\pi r_0} \oint_{\mathcal{C}_0} d\ell(\cdot), \\ \gamma \nabla^2 \hat{u}_m &= -2\hat{\Pi}_m, & \mathbf{r} &\in \hat{\mathcal{S}}, \\ \mathbf{e}_r \cdot \nabla(\hat{u}_m + u_1 + u_2) &= \frac{1}{r_0}[\hat{u}_m + u_1 + u_2 - \Delta \hat{h}], & \mathbf{r} &\in \mathcal{C}_0. \end{aligned} \quad (9)$$

Additionally, the asymptotic boundary condition $\hat{u}_m(r \rightarrow \infty) = 0$ holds, i.e., \hat{u}_m does not contain logarithmic terms⁶. The effective interaction potential induced by the meniscus deformation, depending on the separation d , is defined as $V_{\text{men}}(d) := \hat{\mathcal{F}}_{\text{eq}}(d) - \hat{\mathcal{F}}_{\text{eq}}(d \rightarrow \infty)$, where the free energy for $d \rightarrow \infty$ corresponds to the free energy of two isolated single-colloid configurations. If the system ‘interface + colloids’ is *not* mechanically isolated ($\hat{\varepsilon}_F \neq \hat{\varepsilon}_\Pi$), one obtains asymptotically using equation (7) [13]

$$V_{\text{men}}(d) \approx -2\pi\gamma r_0(\varepsilon_\Pi - \varepsilon_F)u(d) \approx -2\pi\gamma r_0^2(\varepsilon_\Pi - \varepsilon_F)^2 \ln \frac{\lambda}{d} \quad (r_0 \ll d), \quad (10)$$

which describes a long-ranged attractive force, irrespective of the precise form of the (single-colloid) pressure field $\Pi(r)$. Physically, $V_{\text{men}}(d)$ represents the work done by the net force $2\pi\gamma r_0(\varepsilon_\Pi - \varepsilon_F)$ in the single-colloid configuration as this configuration as a whole is shifted vertically by an amount $u(d)$ due to the meniscus deformation induced by the second colloid. This effect is captured by the superposition approximation, defined by $\hat{u}_m = 0 = \hat{\Pi}_m$ [17, 18, 13].

When the system is mechanically isolated, however, $V_{\text{men}}(d)$ does depend on the functional form of $\Pi(r)$, and the superposition approximation is no longer sufficient [13–15], because $V_{\text{men}}(d)$ is dominated by the work done by the additional pressure $\hat{\Pi}_m$ and the ensuing additional vertical shift \hat{u}_m . Motivated by the experiments with charged colloids, we consider the case that $\hat{\Pi}$ and \hat{F} are due to the electrostatic force acting on the charged colloid and the counterions accumulated at the fluid interface and the external surface of the colloids⁷. Far from a colloid, the electric field is normal to the interface and within the Debye–Hückel approximation the electric fields from the individual colloids are additive, and thus $\hat{\Pi}_m = \sqrt{\Pi_1 \Pi_2}$. The single-colloid electric field decays dipole-like, so the associated stress field $\Pi(r) \propto (\gamma\varepsilon_F/r_0)(r_0/r)^6$ and $\varepsilon_F > 0$ [5, 12, 14]. Equation (9) can be solved analytically in the asymptotic limit $d \rightarrow \infty$ leading to an attractive capillary-induced interaction [14],

$$V_{\text{men}}(d) \propto -\varepsilon_F^2 \gamma r_0^2 \left(\frac{r_0}{d}\right)^3 \quad (r_0 \ll d). \quad (11)$$

The direct dipolar repulsion between the colloids is given asymptotically by [14]

$$V_{\text{rep}}(d) \propto \varepsilon_F \gamma r_0^2 \left(\frac{r_0}{d}\right)^3 \quad (r_0 \ll d), \quad (12)$$

so the total potential $V_{\text{rep}} + V_{\text{men}}$ is asymptotically repulsive in the regime $\varepsilon_F \ll 1$, and an attraction is only possible for $\varepsilon_F = \mathcal{O}(1)$.

In order to study $V_{\text{tot}}(d)$ for closer separations d , we have calculated [14] $\Pi(r)$ within the Debye–Hückel approximation assuming that all the charge of the colloid is concentrated at its centre (so the results are not quantitatively reliable at distances $d \approx r_0$), and (9) was solved numerically. It is found (see figure 1) that $V_{\text{tot}}(d)$ can exhibit a shallow minimum provided that

⁶ As can be easily checked by generalizing the argument of section 2, this is also true in the absence of mechanical isolation provided the net external force is additive: $2\hat{\varepsilon}_F - \hat{\varepsilon}_\Pi = 2(\varepsilon_F - \varepsilon_\Pi)$.

⁷ Note that there is also the osmotic pressure on the interface exerted by the counterions [11, 12, 14].

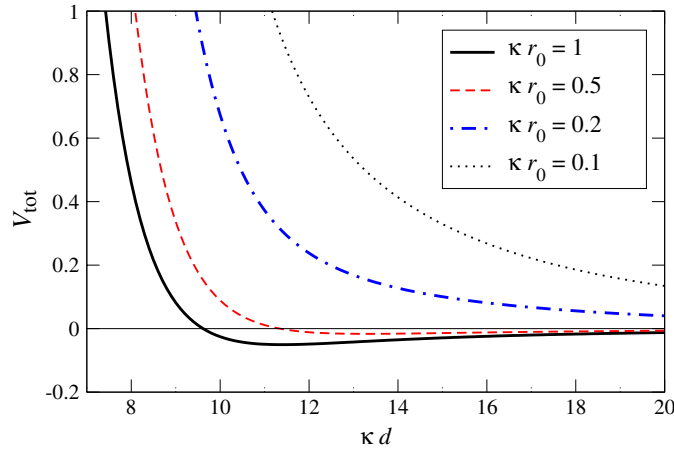


Figure 1. Total intercolloidal potential as function of the separation, in units of $10^3 q^2 \kappa^2 r_0 / 2\pi \epsilon_2$, where q is the total charge of a colloid and ϵ_2 is the dielectric constant of one fluid phase (for the other fluid phase we took $\epsilon_1 = \epsilon_2/81$ so that we have, for example, air and water). The curves correspond to $\epsilon_F = 0.6$.

(This figure is in colour only in the electronic version)

the Debye length $\kappa^{-1} \sim r_0$ ($\kappa^{-1} \approx 1 \mu\text{m}$ in ultrapure water) and $\epsilon_F \gtrsim 0.3$, which is at the limit of validity of our calculations. The presence of a minimum can be traced back to a crossover in $\Pi(r)$ at $\kappa r \sim 7$ from being dominated by the normal electric field to being dominated by the tangential electric field and the ionic osmotic pressure, as the colloid is approached and the charge looks less screened. For experimentally relevant values of the parameters ($\gamma = 0.07 \text{ N m}^{-1}$, $\theta = \pi/2$, $R = 0.5 \mu\text{m}$, $\kappa^{-1} = 1 \mu\text{m}$), the condition $\epsilon_F = 0.6$ implies a total colloidal charge $q \approx 2 \times 10^5$ elementary charges (consistent with the typical values quoted in the literature [7]). This yields a minimum at $d \approx 13 \mu\text{m}$ and a depth $\approx 32 k_B T$ at room temperature. These numbers suggest that the effect just described may be experimentally relevant. Thus more refined calculations relaxing some of the present assumptions (pointlike charge distribution and Debye–Hückel approximation) are called for.

4. Outlook and conclusions

The finite size of the experimental system may be of importance. As considered in [13], an external electric field violates mechanical isolation of the system ‘colloid + interface’. This can be relevant for the experiment of [8], where the particles are trapped at the interface of a water droplet of a relatively small radius $R_{\text{drop}} \approx 32R$. The ions can accumulate at the far side of the droplet if the system is not properly grounded. The argument of section 2 can be generalized for the deformation of a quasi-spherical interface and one obtains [15]

$$u(r) = r_0(\epsilon_F - \epsilon_\Pi) \left[1 + \cos\left(\frac{r}{R_{\text{drop}}}\right) \ln \tan\left(\frac{r}{2R_{\text{drop}}}\right) \right] + \dots \quad (r_0 \ll r). \quad (13)$$

If the droplet is grounded, $\epsilon_F = \epsilon_\Pi$ and there is no curvature-induced logarithmic deformation in the intermediate asymptotics $r_0 \ll r \ll R_{\text{drop}}$. (This corrects a corresponding opposite remark made in [13].) The case of a non-grounded, charged droplet is currently under investigation.

Another example for the relevance of finite size corrections may be found in analysing the experiment reported in [16]. There colloidal droplets have been observed to self-assemble on top of a nematic layer into patterns which are consistent with an effective intercolloidal potential which besides short-range repulsion features an attractive minimum at intermediate distances. The repulsive contribution in the effective potential can be understood by analysing the nematic distortions around the colloids (being equivalent to the direct electrostatic repulsion considered above). Capillary-mediated interactions arise through the presence of a net force on the colloid exerted by the substrate onto which the nematic layer is deposited. Essential for the occurrence of such a net force are the hybrid alignment boundary conditions: the director is anchored parallel at the substrate and perpendicular at the upper interface of the nematic film. This gives rise to a spatially varying director field (background field) even in the absence of the colloids; in the presence of the colloids oscillatory solutions for the director field around the background field appear which lead to a net force on the colloid. This net force is absent if uniform alignment is imposed at the substrate and at the upper interface.

In conclusion, we have demonstrated that a logarithmic attractive potential is possible only if the system is not mechanically isolated, confirming the conclusions in [10, 11] and refuting those in [8, 12]. If mechanical isolation holds, we have shown that the capillary-induced effective potential $V_{\text{men}}(d)$ decays as $\sqrt{\Pi(d)}$ and cannot be computed within the superposition approximation (which predicts a decay $\propto \Pi(d)$). This corrects the results in [10, 11]. Under the condition of mechanical isolation, our calculations suggest that a minimum in the total potential $V_{\text{tot}}(d)$ can exist if the colloidal charge is large enough.

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