Depletion Forces in the Presence of Electrostatic Double Layer Repulsion

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We report direct measurements of the repulsive force-distance profiles between submicronic colloidal droplets stabilized by an ionic surfactant in the presence of the same surfactant micelles. We establish that the repulsive force profile may be described by a sum of two contributions. One is repulsive and arises from the presence of the droplets' double layers. The other originates in the depletion of charged micelles and is attractive. We conclude that the electrostatic repulsion between the micelles and the droplets enhances the depletion force. This effect is simply accounted for by considering an effective larger droplet diameter. We present the empirical relation between this extra thickness and the Debye length.

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Two colloidal particles may attract each other when surrounded by smaller ones. This attraction is an inherent consequence of the size asymmetry and is known as the depletion force [1–3]. Indeed, when the bigger particles approach, the smaller ones are expelled from the interspace, and their contribution to the osmotic pressure locally vanishes. This exclusion leads to an uncompensated pressure from which arises the attractive interaction. The depletion force develops at a separation equal to the effective size of the small component and monotonically increases up to the surface contact. The intensity is related to both the small component osmotic pressure and its size, which also governs the extension of the excluded range [4–7]. This attractive depletion force may coexist with other types of interactions and particularly the repulsive double layer one, which is mainly responsible for the stability of aqueous dispersions [8]. Such repulsion arises from the confinement of counterions which are thermally dissociated from surface charges within the diffuse double layer [9]. As an example, charged colloids mixed with neutral polymer coils would exhibit these two forces at the same time. Moreover, electrostatic repulsion between small particles and colloids may also superimpose; a mixture of identically charged colloidal particles and micelles or polyelectrolyte coils are one example. In that case the net interaction between colloids is certainly a combination of both the double layer repulsion and some depletion mechanisms. When acting together, the behavior of these two forces is still obscure. In previous experiments using the surface force apparatus [7,10], one of the two involved forces was always largely predominant with respect to the other, which precludes a reliable observation of their interplay. In this Letter we report direct measurements of the repulsive force distance profile between submicronic colloidal droplets stabilized by ionic surfactant in the presence of the same surfactant micelles.

Our system is made of a mixture of colloidal oil-in-water emulsion droplets (with a diameter of 0.2 μm) and surfactant micelles (with a diameter of about 5 nm). We use a cationic surfactant (CTAB: cetyltrimethylammonium bromide), which forms micelles above its critical micellar concentration (CMC $= 9 \times 10^{-4}$ M), and which adsorbs on the colloidal droplets. This ionic surfactant ensures that both species repel each other and that (big) droplets and (small) micelles also repel one another. The force profile between droplets is directly measured using the recently developed chaining technique [11]. A magnetic oil (ferrofluid) octane in which small grains (10 nm) of Fe_2O_3 are dispersed is used to create monodisperse emulsion droplets stabilized wiht CTAB. By imposing a magnetic field, polarized droplet chains align along the field and diffract the light, allowing their spacing to be measured precisely. Since a given field corresponds to an applied known attractive force between droplets [12], we deduce the opposing repulsive force at various separations. This force profile is measured from the onset of chaining up to the saturation of the ferrofluid magnetization which correspond to ratios F/R, where F is the force and R the droplet radius, that range from 10^{-6} to 10^{-4} N/m.

Figure 1 shows the force-distance profiles for four different surfactant concentrations $C_s = 1$, 5, 10, and 20 CMC, which correspond to micellar volume fracations (ϕ), equal to 0, 0.13%, 0.29%, and 0.62%, respectively. We plot the logarithm of the ratio F/R ($R = 98$ nm) versus droplet surface separation h. For the lowest surfactant concentration ($C_s =$ CMC), we observe a linear profile. Since a normal electrostatic repulsion is expected at $C_s =$ CMC where only free ions do contribute to the screening, we compare our data to the first order expansion of the double layer force derived from Poisson-Boltzmann equaiton [6,13]

$$F(h) = 2\pi\varepsilon\psi_{0,d}^2\kappa R\left[\frac{\exp(-\kappa h)}{1 + \exp(-\kappa h)}\right], \qquad (1)$$

where $\psi_{0,d}$ is the droplet effective surface potential, κ^{-1} the Debye length, and ε the dielectric constant of water. This expression is valid for particles having small charge densities and a thin double layer ($\kappa R > 5$) that allows the use of the Derjaguin approximation [14]. The surface

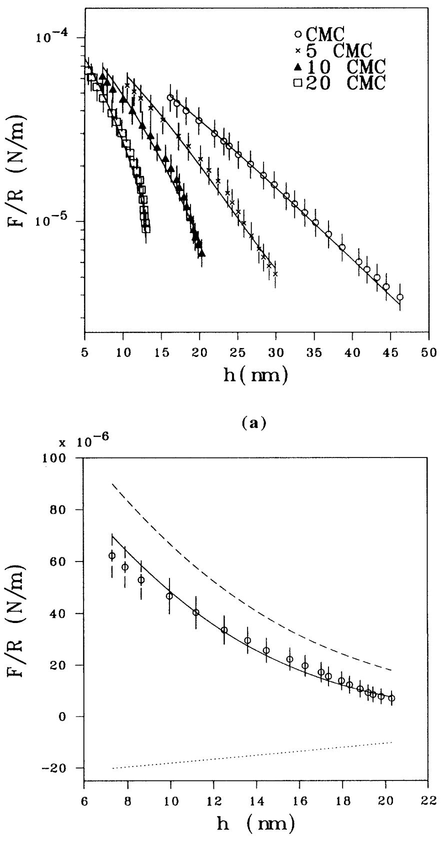

FIG. 1. (a) At $C_s = \text{CMC}$, the force profile is purely exponential and the continuous line is the best one parameter fit obtained with Eqs. (1) and (2) defined in the text ($\psi_{0,d} = 25.5$ mV). Above CMC, in the presence of charged micelles, the profiles are no longer purely exponential and a deviation appears at large distance. The continuous lines are the best fits obtained with Eqs. (1), (3) (double layer repulsion), and (4) (depletion attraction), defined in the text; $\psi_{0,d}$ and δ are free parameters (5 CMC: $\delta = 16.6$ nm, $\psi_{0,d} = 24.49$ mV; 10 CMC: $\delta = 14.3$ mm, $\psi_{0,d} = 23.5$ mV; 20 CMC: $\delta = 11.2$ nm, $\psi_{0,d} = 22.3$ mV). (b) Force distance profile at $C_s = 10$ CMC. The repulsive (positive dashed line) and the attractive (negative dashed line) contributions as well as the summed interaction (continous line) are presented separately ($\delta = 14.3$ nm, $\psi_{0,d} = 23.5$ mV).

potential $\psi_{0,d}$ is assumed to remain constant when h is decreasing. As previously observed [11], the slope is in perfect agreement with the experimentally controlled Debye length expressed as [6]

$$\kappa^{-1} = \left(\frac{1}{4\pi}\right)(2L_b^2 C_s)^{-1/2}, \tag{2}$$

where L_b is the Bjerrum length $L_b = 0.708$ nm). κ^{-1} is then equal to 10.1 nm. The surface potential $\psi_{0,d}$ is deduced from the best fit to our data using Eq. (1) and is found to be 25.5 mV (see the continuous line in Fig. 1). At C_s larger than CMC (Fig. 1), the behavior is no longer linear; instead, it exhibits a larger slope at larger separation. This curvature suggests that micelles contribute to an attractive force that becomes comparatively more pronounced at large distance. This bahavior is in qualitative agreement with previous data [7,10]. Indeed, since the surfactant concentration C_s exceeds the CMC, micelles are present and should be expelled from the gap when droplets are brought close enough to each other. Therefore some depletionlike mechanism is expected, which might be superimposed on the double layer repulsion and would account for the increasing observed slope.

Let us first recall some aspects of the repulsive electrostatic force in the presence of charged micelles that are already established: Using the surface force apparatus, a highly repulsive regime was observed at short separation and was shown to follow the classical double layer theory [7,10,15]. However, the screening length is found larger than that expected from the total amount of charged surfactant. Instead, the Debye length is empirically deducible from the amount of free ions only and does not include the presence of charged micelles [10]

$$\kappa^{-1} = \left(\frac{1}{4\pi}\right)L_b^2[2\text{CMC} + (C_s - \text{CMC})Q]^{-1/2}, \tag{3}$$

where Q is the fraction of dissociated CTAB molecules in a micelle ($Q = 25\%$ [10]). In that limit the presence of micelles is only affecting the Debye length [see Eq. (3)] and still allows the classical double layer theory to apply. The deviation already mentioned at large separation was attributed to the depletion force, which is superimposed on the previously reported asymptotic repulsive regime [7,10]. However, in the net repulsive regime the double layer repulsion was always largely predominant with respect to the depletion force, which precluded a reliable observation of their interplay.

To account for our data, we hypothesize that these two forces simply add and that the repulsion between micelles and droplets increases the effective diameter of the droplets (or micelles). This diameter is involved in the hard sphere depletion force description. This force is derived by integrating the osmotic pressure P_0 over the accessible zone for micelles of diameter $2r_m$ ($r_m = 2.35$ nm [16]) from $\theta = \pi$ to $\theta = \pi - \theta_1$ with θ_1 defined in Fig. 2(a). The distance at which the small micelles are excluded from the gap between droplets is evidently influenced by the electrostatic micelle-droplet repulsion. To account for this repulsion, we consider that droplets (or micelles) enter the depletion mechanism as particles of radius $(R + \delta)$ [or micelles of radius $(r_m + \delta)$] where 2δ is the extra distance at which micelles are excluded from the gap [see Fig. 2(a)]. From

$$F(h) = -2P_0\pi(R + r_m + \delta)^2 \int_{\pi}^{\pi-\theta_1} \sin\theta \cos\theta \, d\theta$$

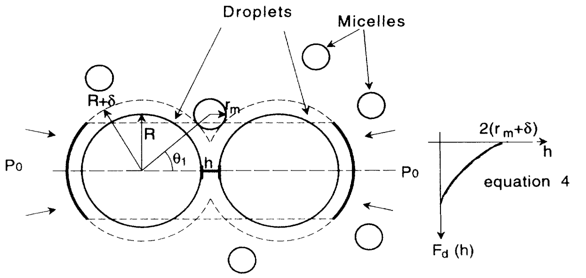

FIG. 2. Schematic representation of the depletion mechansim: Because micelles are excluded from the gap, a depletion force takes place and is computed by integrating the uncompensated osmotic pressure over the accessible surface (see bold line). The force is described by Eq. (4) and continuously increases from $h = 2(r_m + \delta)$ to $h = 0$.

we obtain

$$F(h) = -P_0\pi(R + r_m + \delta)^2\left[1 - \left(\frac{R + h/2}{R + r_m + \delta}\right)^2\right]. \tag{4}$$

This depleiton force increases form the distance where micelles start to be excluded $[h = 2(r_m + \delta)]$ to the droplets' surface contact where $F(0) = -P_0\pi(r_m + \delta)[2R + r_m + \delta]$.

We directly compare our data to the summation of Eqs. (4) and (1). κ^{-1} is given by Eq. (3) and is equal to 4.5 nm. The osmotic pressure P_0 is given by $P_0 = \alpha nkT$ where α is the osmotic coefficient arising from micelle-micelle interaction, n being the micelle concentration related to C_s [$n = (C_s - \mathrm{CMC})N_a/N$, where N is the aggregation number, equal to 90 [16], and N_a the Avogadro number], kT being the thermal energy. The osmotic coefficient α is taken to be equal to 1 since the effective micellar volume fraction is never larger than approximately 5% [7,8]. The comparison of the data and the theoretical curve is shown in Fig. 1 (continuous line) for three surfactant concentrations above the CMC. The unknown parameters are $\psi_{0,d}$ and δ. δ is found equal to 16.6, 14.3, and 11.2 nm, respectively. $\psi_{0,d}$ slightly decreases as the surfactant concentratin is increased above the CMC (25.5 to 22.3 mV). It is evident that the sum of a screened electrostatic force where κ^{-1} is set by free ions only [Eqs. (1) and (3)] and a depletion force that includes the role of the micelles' free zone around droplets [extra thckness δ; Eq. (4)] fits the experimental data properly. Hence, the net repulsive regime is properly described by this simple model as previously proposed for the net attractive regime [7].

On the basis of this description we empirically establish the relation between the two lengths δ and κ^{-1}. By gradually increasing the amount of micelles and fitting the force profiles we deduce the values of δ. In Fig. 3, we show the evolution of δ as a function of the calculated Debye length κ^{-1}. The thickness δ increases linearly with κ^{-1} or decreases linearly when increasing the micellar volume fraction (or the corresponding osmotic pressure). From the plot of Fig. 3, we deduce a slope of about 2 (see the continuous line which is the best fit to our data). The inherent coupling between the two forces is reflected by this empirical linear relation. The linear relation is a consequence of the microscopic origin of this coupling. Indeed, the repulsion between droplets and micelles leads to the existence of this extra thickness that enhances the depletion force. The repulsive energy between droplets and micelles may be written as

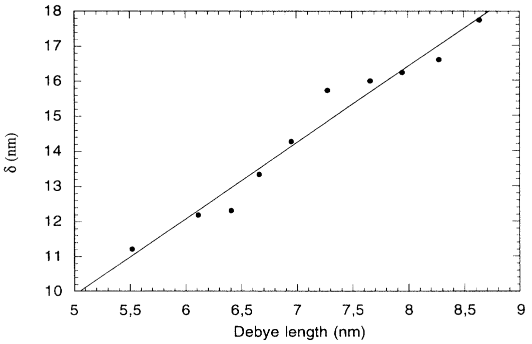

FIG. 3. Evolution of the parameter δ as a function of the Debye length κ^{-1}. δ is obtained from the best fit to the force-distance profiles obtained for 10 different surfactant concentrations from 4 to 20 CMC. κ^{-1} is calculated with Eq. (3). The continuous line is the best fit to our data and leads to $\delta = 2.03\ \kappa^1$.

$$V(h) = A(h)\exp(-\kappa h),$$

where $A(h)$ takes into account the nonexponential dependence, which is esentially constant. As a consequence, in the dilute regime, the thickness δ may be conceptually defined by the identity

$$A(h)\exp(-\kappa\delta) = B,$$

where B is a threshold energy of the order of the thermal energy kT. From this assumption we deduce that $\kappa\delta$ scales as $\log[B/A(h)]$ which may be considered as a constant. Hence, κ^{-1} and δ should be linearly related as observed experimentally. The slope is a nonuniversal quantity that mainly depends upon the surface potentials and respective diameters. Finally, it is remarkable to note that this simple picture involving only a second specific length δ (in addition to the Debye length) is sufficient to account for both the previously explored attractive regime and the repulsive one which is probed here.

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