

Direct Measurement of Depletion and Structural Forces in a Micellar System

P. Richetti^(a) and P. Kékicheff

*Department of Applied Mathematics, Research School of Physical Sciences, Australian National University,
G.P.O. Box 4, Canberra, Australian Capital Territory 2601, Australia*

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The force as a function of separation is measured between two mica surfaces coated with adsorbed bilayers of cetyltrimethylammonium bromide (CTAB) and immersed in aqueous ionic micellar solutions of CTAB. At low separations double-layer forces are observed and arise solely from the dissociated counterions and free CTA⁺. At large separations, the repulsion is reduced and a secondary minimum in the interaction potential deepens when the micellar concentration is increased. Finally, at higher concentrations, structural effects superimpose an oscillatory force profile at further separations.

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In colloid science the concept of depletion has been closely linked to nonadsorbing polymers [1]. Two mechanisms have been invoked to explain how stable colloidal dispersions may flocculate upon the addition of polymer. The first relies on adsorbing polymers bridging between particles resulting in demixing [2]. In the absence of adsorption two particles are attracted by the exclusion of macromolecules [3] as a region of solvent depleted in polymer will form around each particle due to a thermodynamically unfavorable configurational change of a nonadsorbing macromolecule when in close proximity to a surface. Indeed, flocculation occurs when the depleted regions of two approaching particles overlap as it causes the almost complete exclusion of macromolecules from between the surfaces; this in turn favors a closer approach of the particles because it results in a reduced depleted volume and the mixing of almost pure solvent with polymer solution. Depletion flocculation can also be seen from a mechanical interpretation [3,4] as the overall compressive osmotic pressure acting on the surface of one particle becomes imbalanced as soon as an overlap with the depleted layer of a second approaching particle occurs.

This concept, although developed for colloids in the presence of nonadsorbing polymers, is also valid for any spherical solute. Moreover, with a concentrated suspension of monodisperse spheres, in addition to depletion effects, structural contributions [5] to the interaction are expected in the same way that they appear in fluids [6]. Recently properties of fluids close to a wall and in thin films confined between two walls have been of considerable interest [7,8]. Structural effects give rise to an oscillatory distribution function of solvent in a narrow region near a surface. Similarly to the depletion induced by macromolecules, the break of the isotropy of the density profile around a spherical solute particle on the approach of a second one gives rise to an interaction between the solvated surfaces, i.e., the structural forces. According to Attard [8], the force between two hard-sphere solutes, of diameter d_1 , immersed in a solvent of hard spheres of diameter d_2 and separated by D is related to the density n_c of solvent spheres at contact around one of the solute

spheres:

$$f(D) = -\frac{1}{2} \pi k_B T (d_1 + d_2)^2 \int_0^\pi d\theta \sin\theta \cos\theta n_c(\theta, D), \quad (1)$$

where the angle θ positions the solvent spheres at contact relative to the axis linking the centers of the two solute particles. Note that the contact density n_c is a function both of position around the solute particles and of separation. The major difficulty is to determine $n_c(\theta, D)$ which in most cases is possible only by approximations or numerical calculations [8]. For sufficiently concentrated solutions of spheres (2) the force given by Eq. (1) has an oscillatory profile with a period close to d_2 and with a magnitude increasing on approach of the solute (1) surfaces. In the limit of high solute dilution, n_c is only a function of θ , independent of separation so that $n_c(\theta) = n_2^{\text{bulk}}$ when $\cos\theta < (d_1 + D)/(d_1 + d_2)$, and zero otherwise. Thus, Eq. (1) reduces to the classical expression for the depletion attraction given many years ago by different authors [3,4,9,10]:

$$f(D) = -\pi \left[\left(\frac{d_1 + d_2}{2} \right)^2 - \left(\frac{d_1 + D}{2} \right)^2 \right] n_2 k_B T, \quad D < d_2. \quad (2)$$

The attractive force between two particles (1) is proportional to the osmotic pressure $P_{\text{osm}} = n_2 k_B T$ times the area on one particle (1) inaccessible to the particles (2).

Until now the lack of direct measurements of the interaction potentials has limited any theoretical comparisons so crucial in the understanding of the stability of large colloids in a suspension of smaller particles. Such interaction may be directly measured using a surface force apparatus [11]. This device relies on two crossed cylinders (mean radius R) of molecularly smooth mica surfaces which is geometrically equivalent to two spheres of radius $2R$ approaching each other when the separation D is much smaller than the radii ($D \ll R$). Under this approximation, the two mica surfaces, which may be regarded as a special case of two bodies of type (1) immersed in a solution of particles (2), should experience a

force due to the latter. Notably, the force at contact would be $f(0)/R \approx -12k_B T \Phi_2/d_2^2$, where $\Phi_2 = \pi d_2^3 n_2/6$ is the volume fraction. In a typical dilute regime ($\Phi_2 \approx 0.01$) the amplitude of this interaction would be just beyond experimental resolution (≈ 0.005 mN/m) where the characteristic size of the dispersion is $d_2 \approx 10$ nm. Use of smaller particles would emphasize the effect but would reduce the interaction range accordingly. Moreover, superposition of any other fundamental attractive interactions such as dispersion forces may complicate and obscure the observation of a depletion or structural effect.

Although the extent of the ever-present dispersion forces cannot be easily controlled, it is possible to shift the position of the depletion effect away from its influence. This is easily achieved in ionic dispersions, where the addition of a diffuse double layer surrounding the charged interfaces effectively increases the mean diameters. Although such systems are qualitatively distinct from the theoretical hard-sphere systems considered, a comparison is still possible in terms of effective hard-sphere size. Among various colloidal systems, ionic micellar solutions have been shown to induce some fluid-solid phase transitions by depletion in stabilized colloids [12] and also emulsions [13]. In addition, the small size and spherical shape of a micelle with a reasonable polydispersity over a large range in concentration conspires to make ionic micellar solutions a good system for study with the surface force apparatus.

Cetyltrimethylammonium bromide (CTAB, from Kodak) was used without further purification and water was double distilled. All the experiments were carried out at 25°C above the Krafft temperature of the surfactant with the latest version of the surface force apparatus [14]. Comparison of the contact position at equilibrium in micellar solutions with that of bare mica indicates that both mica surfaces have an adsorbed CTAB bilayer, the thickness of which is independent of micellar concentration and in direct agreement with previous observations [15]. In these highly asymmetric electrolytes the measured double-layer decay lengths κ_0^{-1} appear to be due entirely to the dissociated bromide and free surfactant ions CTA^+ , with no apparent contribution from charged micelles as observed before [15,16], and are well described by the following equation [15]:

$$\kappa_0^2 = \frac{4\pi q^2}{\epsilon k_B T} \left[2\rho_{\text{cmc}} + \frac{\rho_s - \rho_{\text{cmc}}}{N} (N - Q) \right], \quad (3)$$

where ρ_s is the surfactant concentration, ρ_{cmc} that at the c.m.c., N the aggregation number, and $N - Q$ the effective charge of the micelle.

Over the micellar concentration studied by Pashley and Ninham no depletion effect was noticed [15], even at the highest CTAB concentration studied ($\Phi_2 \approx 0.006$). Force-distance measurements at higher micellar volume fractions ($\Phi_2 = 0.009, 0.019$, and 0.073) are reported

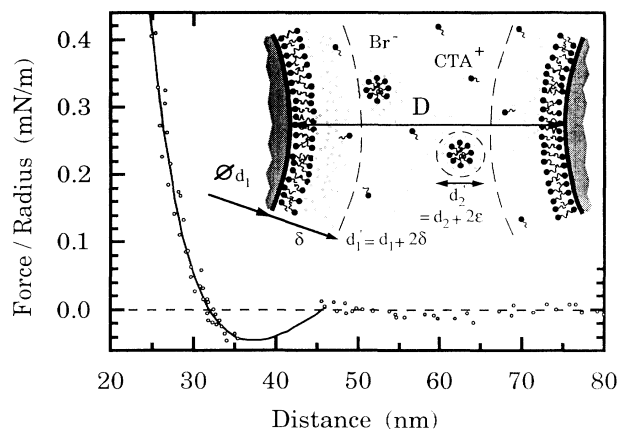


FIG. 1. Measured force F (normalized by the mean radius of curvature R of the surfaces) as a function of surface separation D between crossed cylinders, each coated with an adsorbed bilayer of CTAB (thickness of about 3.2 nm), and immersed in a micellar solution of CTAB (volume fraction $\Phi_2 \approx 0.009$). The attractive minimum around 38 nm is due to depletion in micelles, while the exponential repulsion at smaller separations arises from double-layer forces. The solid line is the best-fit numerical solution (see text and Table I).

here.

At low concentration ($\Phi_2 \approx 0.009$) the force profile exhibits two distinct regimes (Fig. 1). At small surface separations the interaction is exponentially repulsive as expected for a double-layer interaction, while at large separations a weak attraction characterized by a shallow well is revealed (Fig. 1). Note that for this concentration the experimental limitation in accuracy precludes the observation of an eventual repulsive maximum before this secondary minimum. On the other hand, this maximum is seen clearly at higher surfactant concentrations whereas the secondary minimum, located at shorter separations, becomes deeper [Fig. 2(a)]. A further increase in CTAB concentration emphasizes this effect with the appearance of many other structural oscillations (Fig. 3) with a nearly constant period (≈ 10 nm), being rapidly damped as separation is increased. Since one surface is suspended at the end of a spring [11] (stiffness K), note the occurrence of intrinsic unstable regimes without data when $\partial F/\partial D \geq K$ (Figs. 1-3).

The emergence of the secondary minimum cannot result from the attractive dispersion forces as the contribution would be only 0.025 mN/m at a surface separation of 10 nm (Hamaker constant of $\approx 1.5 \times 10^{-20}$ J), dropping by an order of magnitude at 30 nm. The interpretation given by Pashley and Ninham [15] that highly charged micelles between two charged walls behave as co-ions expelled from the region of close double-layer overlap is consistent with a depletion mechanism. The range of this latter interaction can be generalized from the situation of a system of uncharged particles and walls. In this

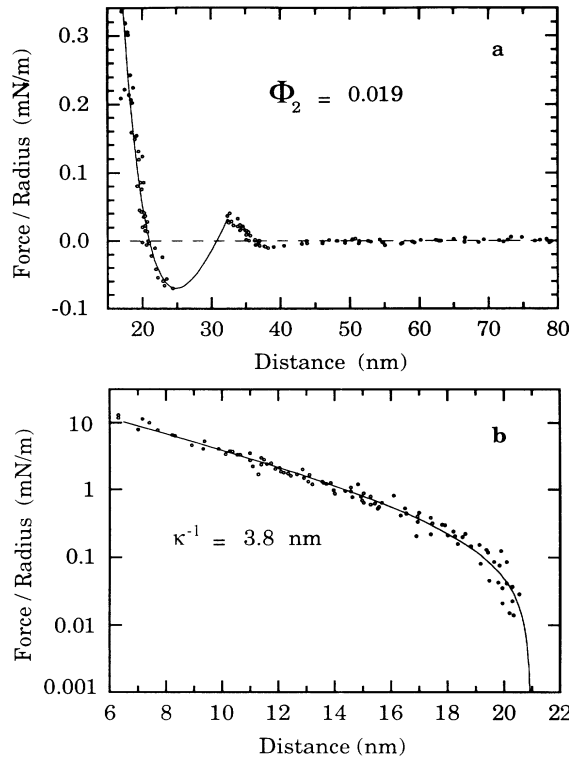


FIG. 2. Same as in Fig. 1 but for $\Phi_2 \approx 0.019$. (a) Linear scale: Note the occurrence of one oscillation at large separations beyond the depletion minimum. This structural effect is not described by the numerical fit. (b) Semilogarithmic scale: The deviation from the exponential double-layer repulsion indicates the competition with the attractive depletion.

description, double-layer and depletion forces are considered as purely additive interactions with opposing effects, in a similar fashion that the Derjaguin-Landau-Verweg-Overbeek theory considers the summation of electrostatic and dispersion forces. Thus, just as the addition of salt may destabilize a charged suspension, the addition of charged micelles may induce flocculation, reflecting the occurrence of a secondary minimum in the interaction potential between two colloids.

To describe our experimental data the Asakura-Oosawa [3] type of approximation is used; that is, the enhancement of the contact density in the wedges that remain between the two curved walls outside the depletion overlap is considered as negligible. This assumption is reasonable at low micellar concentrations according to numerical simulations [8]. The charged walls (mica surfaces) and particles (micelles) behave as a soft system with effective hard-sphere diameters $d'_1 = d_1 + 2\delta$ ($d_1 = 4R$, see above) and $d'_2 = d_2 + 2\varepsilon$ (see inset in Fig. 1). In the limit where $d_1 = 4R \gg d_2, \delta, \varepsilon$, the attractive depletion contribution [Eq. (2)] to the total interaction is linear in separation D :

$$f(D)/R = -2\pi(d'_2 + 2\delta - D)an_2k_B T, \quad (4)$$

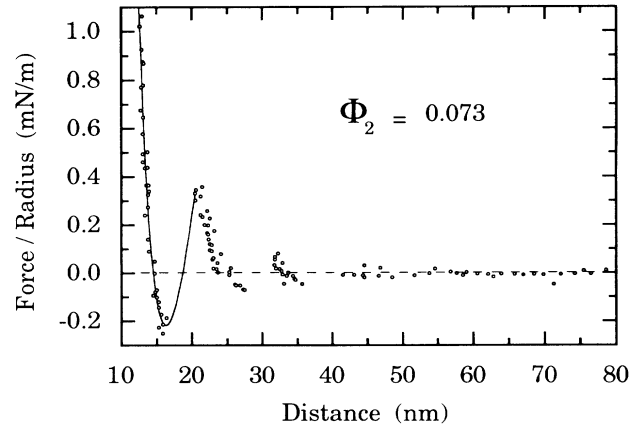


FIG. 3. Same as in Figs. 1 and 2 (linear scale) but at higher micellar volume fraction ($\Phi_2 \approx 0.073$) where two oscillations due to structural forces turn up.

where the osmotic coefficient α is introduced for the osmotic pressure. The structural contribution adds a concentration-dependent constant to Eq. (4) since the free energy is no longer necessarily zero when the depletion attraction first occurs at $D = d'_2 + 2\delta$ (note that this is the new range of the interaction) as was assumed previously in the ideal solution description.

Consequently, if the observed deviation from the pure double-layer repulsion is due to the depletion the force-distance profile would be described by a law $f(D)/R = A_1 \exp(-\kappa D) + A_2 D + A_3$, where the electrostatics is treated by a linearized Poisson-Boltzmann contribution. This is a three-independent-parameter fit since the magnitude of the force where the surfaces jump inwards (secondary minimum) is imposed on the calculation. For the three concentrations this modeling force is in remarkable agreement with the measured profile (Table I). More precisely, the decay lengths extracted from the fits agree well with the values calculated by Eq. (3) except for the highest concentration. Furthermore, for the two lowest concentrations where the structural effects are weak, the fits give 46.6 and 31.5 nm for $-A_3/A_2 \approx d'_2 + 2\delta$, which are in close agreement with the measured values 45.9 and 32.3 nm, respectively. Finally, from $A_2 = 2\pi an_2 k_B T$ and using an aggregation number of 90 and a micelle diameter around 4.7 nm [17], the osmotic coefficient α is estimated to be 2.38, 3.01, and 7.96, respectively, for the three concentrations. Conversely, an

TABLE I. Parameters of the fits (Figs. 1-3) and decay-screening length κ_0^{-1} calculated with Eq. (3).

Φ_2	κ_0^{-1} (nm)	κ^{-1} (nm)	A_2 (10^5 N/m ²)	A_3 (mN/m)
0.009	4.9	4.8	0.10096	-0.470115
0.019	3.6	3.8	0.24814	-0.782655
0.073	1.9	2.4	2.58577	-5.081037

effective volume fraction $\Phi_2' = 0.21, 0.25$, and 0.42 is derived from

$$\alpha(\Phi) = P_{\text{osm}}/nk_B T = (1 + \Phi + \Phi^2 - \Phi^3)/(1 - \Phi)^3$$

according to the Carnahan-Starling [18] approximation and by use of the geometric limit of planar walls (since $d_1 \gg d_2$). The effective concentration can also be extracted from the periodicity of the oscillatory force profile. At the intermediate concentration (Fig. 2) only one oscillation due to structural effects is observed, occurring between 43.5 and 32.4 nm, and indicates an effective diameter $d_2' \approx 11.1$ nm. This corresponds to an effective volume fraction $\Phi_2' \approx 0.23$, again in close agreement with 0.25 obtained from the fit. Nevertheless, at the highest concentration where two oscillations are observed (Fig. 3), $\Phi_2' \approx 0.58$ (from $d_2' \approx 10.0$ nm) departs from the fitted value of 0.42 . This discrepancy can be due to several effects. First, the overlap of the structured regions in the wedges outside the depletion volume reduces the net interaction between the walls; consequently, the Asakura-Oosawa approximation used here is invalid as underlined by Attard [8]. In addition, the particular experimental geometry of crossed cylinders [11] may complicate the effect. Furthermore, the polydispersity of the micelles may reduce the interaction.

Direct force measurements between charged CTAB bilayers in micellar solutions at large volume fractions indicate that depletion and structural contributions superimpose on top of classical double-layer interactions. Structural forces, which have also recently been observed in an uncharged reversed micellar system [19], reflect some particle packing effects favoring an integral number of particle layers between the two interacting walls, as occurs in a pure solvent despite the dynamic structure and short lifetime of such aggregates. For the first time, a force profile owing to a depletion mechanism has been directly measured. The quantitative information extracted from this profile is in good agreement with theory. The addition of an oscillatory potential to the depletion minimum suggests the possibility of several metastable states for a dispersion of particles in highly concentrated micellar solutions, leading to a reentrant phase transition sequency. At some concentrations, the repulsive barrier preceding the depletion minimum might be high enough to prevent any destabilization, while at higher concentrations the preceding well due to structural effects might be deep enough to favor a new flocculation.

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- ^(a)Permanent address: Centre de Recherche Paul Pascal, CNRS, Château Brivazac, Avenue Schweitzer, 33600 Pessac, France.
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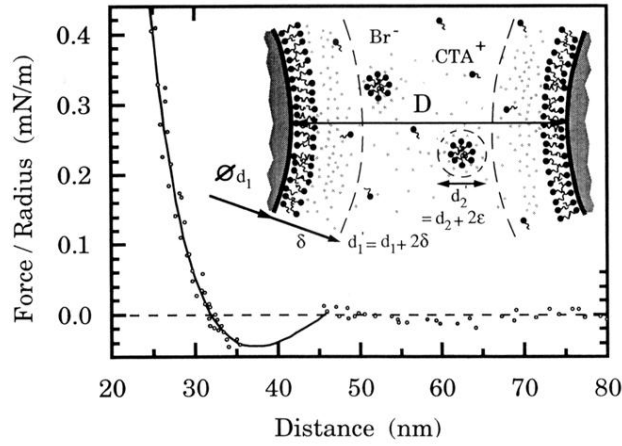


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