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Strong capillary attraction between spherical inclusions in a multilayered lipid membrane

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Strong attraction has been experimentally observed between two spherical latex particles, which are included into the membrane of a giant spherical phospholipid vesicle. We interpret this attraction as a capillary force resulting from the overlap of the menisci formed around each of the two encapsulated particles. A theory is proposed to describe films containing large inclusions, i.e. when the particles are much greater than the natural film thickness. First theoretical results for the capillary forces are in line with the experimentally observed trends.*

1. INTRODUCTION

The attachment of colloid particles to a fluid interface, or their confinement in a liquid film, is often accompanied with interfacial deformations, i.e. appearance of menisci around the separate particles. The overlap of the menisci around such two particles gives rise to a lateral capillary force between them which is attractive for similar particles, see e.g. Ref. [1]. Depending on the physical origin of the interfacial deformations, two types of lateral capillary forces can be distinguished. In the case of *flotation* force the meniscus is due to the weight of floating particles, including the buoyancy force [1-5]. This force causes two-dimensional aggregation of floating particles [6,7]; its magnitude is proportional to R^6 (R = particle radius). For that reason the flotation capillary force strongly decreases with the decrease of R and becomes immaterial for R smaller than c.a. 5 μm.

The other type of capillary force, the *immersion* force, appears between particles that are confined in a liquid film with one or two deformable surfaces [8], see Fig. 1a,b. In this case the deformation is related to the wetting properties of the particle surfaces (contact angles, edges), rather than to gravity. It turns out that the immersion force can be significant between particles of radius larger than a few nanometers [1,4]. It has been found to promote the growth of two dimensional crystals from colloid particles, viruses and globular proteins, see Ref. [9].

The theoretical description of the lateral capillary forces is based on the Laplace equation which determines the shape on the liquid meniscus, $z = \zeta(x,y)$. In general, it is a second order

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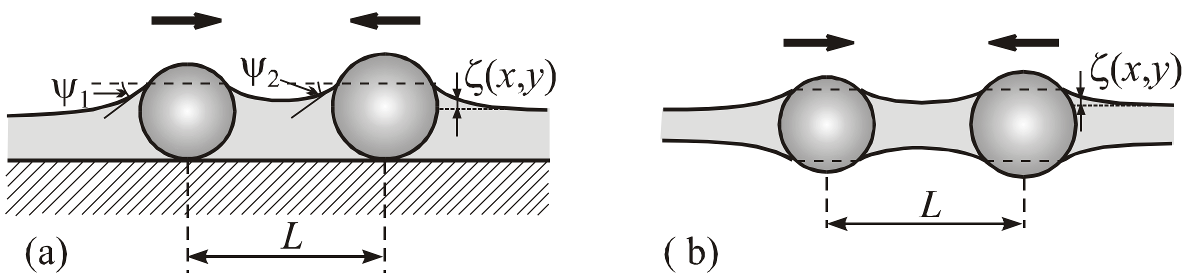


Fig. 1. The capillary "immersion" force is due to the overlap of the menisci formed in a vicinity of colloidal particles confined in liquid films. (a) Two particles in a wetting film on a solid substrate. (b) Two particles in a free film; $z = \zeta(x,y)$ describes the meniscus shape (deviation from planarity).

nonlinear partial differential equation. However, when the particles only slightly deform the interfaces, i.e. when slopes are small ($|\nabla_{\mathrm{II}}\zeta|^2 \ll 1$), the Laplace equation simplifies into the linear form [1,8,9]:

$$\nabla_{\mathrm{II}}^2\zeta = q^2\zeta\,, \qquad\qquad \nabla_{\mathrm{II}} \equiv \mathbf{e}_x\frac{\partial}{\partial x} + \mathbf{e}_y\frac{\partial}{\partial y} \tag{1}$$

∇_{II} is the two-dimensional gradient operator in the x,y plane. When gravity drives the deformation, q^{-1} is the usual capillary length. In the case of a thin film of thickness h, Eq.(1) holds when $\zeta/h \ll 1$. Then the characteristic length, q^{-1} , is given by:

$$q^2 = -\frac{(\partial\Pi/\partial h)_{h=h_0}}{\sigma} \tag{2}$$

where Π is the disjoining pressure and σ is the surface (membrane) tension. h_0 is the thickness of the non-perturbed film.

Using cylindrical coordinates (r,φ) in Eq. (1) one can determine the shape of the meniscus around a single particle in the form $\zeta(r) = A\,\mathrm{K}_0(qr)$, where K_0 is the modified Bessel function of the second kind and zeroth order and A is a constant of integration. Next, one can apply the superposition approximation [2], i.e. assume that the interfacial deformation caused by two particles (Fig. 1) is equal to the sum of the deformations caused by the separate particles in isolation. Then, in view of the expression for $\zeta(r)$, the energy of lateral capillary interaction between the two particles can be expressed in the form [1,3,9]

$$\Delta W \approx -\,2\pi\sigma Q_1 Q_2 \mathrm{K}_0(qL) \tag{3}$$

where L denotes the distance between the two particles, $Q_i \equiv r_i \sin\psi_i$ (i = 1,2) are the so called "capillary charges", r_i and ψ_i are the radius of the contact line and the slope angle at the contact line of the respective particle. ΔW represents a variation in the gravitational energy or in the energy of wetting, for floatation or immersion forces, respectively. For a recent review see Ref. [9].

It is worthwhile noting that Eq. (1) is not valid for all physically possible cases. Indeed, the relationship $\zeta/h_0 << 1$ corresponds to comparable magnitudes of the particle diameter and the film thickness. However, it is possible the particle size to be much greater than the film thickness, $\zeta/h_0 >> 1$, see Fig. 2. Then, instead of Eq. (1), the meniscus profile obeys the equation

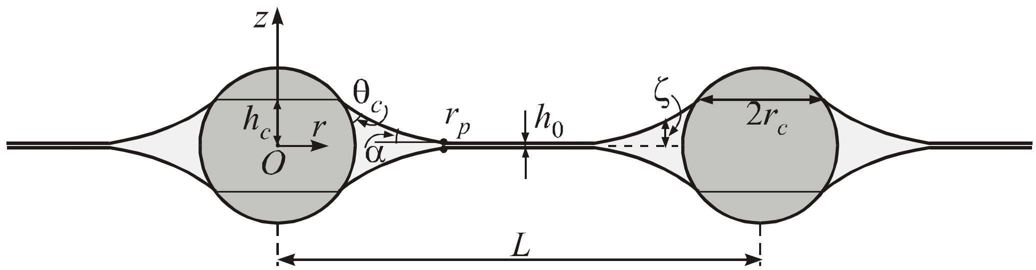


Fig. 2. Two colloidal spheres entrapped in a free liquid film, whose thickness h_0 is much smaller than the particle diameter. "Plateau borders" of outer radius r_p and peripheral contact angle α are formed around each sphere; θ_c is a solid-liquid-fluid contact angle.

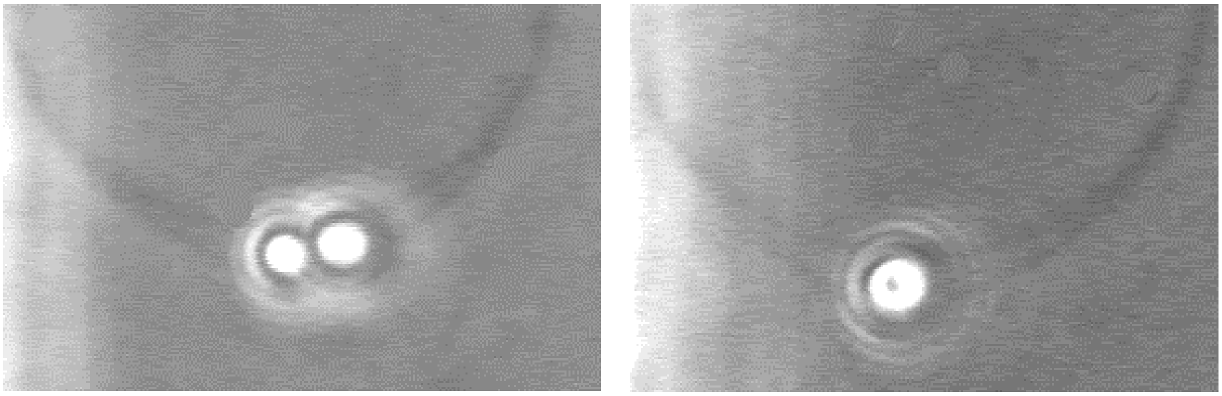
$$\sigma\nabla_{\mathrm{II}}^{2}\zeta = \Delta P = \mathrm{const.} \qquad (\zeta/h_0 >> 1) \qquad (4)$$

Here ΔP is the pressure jump across the meniscus; ΔP is constant if the effect of the gravitational hydrostatic pressure is negligible. Note, that mathematically Eq. (1) is a Helmholtz-type equation, whereas Eq. (4) is a Laplace-type equation. Consequently, unlike Eq. (1), equation (4) has no solutions which are finite at infinity. The latter fact implies that the meniscus around each particle must end at a *peripheral contact line* (of radius r_p), out of which the film is plane-parallel ($\zeta \equiv 0$), see Fig. 2. In this case the overlap of the menisci, and the interaction between the particles, begins when they come at a distance $L < 2r_\mathrm{p}$ from each other; such type of interaction is obviously different from that described by Eq. (3).

For menisci of *finite extent*, whose shape is described by Eq. (4), the problem about the lateral capillary force has not yet been addressed theoretically. This problem deserves to be investigated insofar as the experiment provides evidence about the existence of capillary interaction between particles surrounded by such menisci. For example, Velikov et al. [10] observed a strong attraction between latex particles of diameter $2R \approx 7$ μm entrapped in a foam film of thickness $h_0 \approx 0.07$ μm. In the next section, we further illustrate this point by similar observations with micron-sized latex spheres encapsulated within the multi-lamellar membrane of a giant lipid vesicle. As we will see, these experiments neatly reveal the film deformation caused by the particles and the related attraction. In Section 3, we briefly report some results of the theory, essentially in relation to the experiments of interest in Section 2. A complete presentation of the theory will be the matter of a forthcoming article [11].

2. EXPERIMENTS WITH LATEX PARTICLES ATTACHED TO LIPID VESICLES

Phospholipids in water self assemble into bilayers about 4 nm in thickness. Different preparation procedures allow to produce vesicles, whose membranes are constituted of one or a few such lipid bilayers [12]. In our experiments, we use so-called "giant vesicles", grown by electroformation [13]. The method produces a cluster of vesicles on the surface of a platinum electrode. The vesicles at the outer boundary of the cluster are approximately spherical, with diameters in the 10–100 micrometers range. On their "rear" sides (towards the electrode), they are connected to neighboring vesicles by a few contact points, sometimes by a small adhesion area. Their outer sides are free of contacts.



(a) (b)

Fig. 3. Photos of a couple of latex beads trapped between two detached lipid membranes composing a multilamellar spherical vesicle. Each photo is an equatorial cut of the vesicle. (a) The two beads are side by side in the same equatorial plane. (b) Section perpendicular to the line that goes through the centers of the beads: the two beads are still present, but one is just on top of the other.

Electroformation is a nice method to produce unilamellar giant vesicles; nevertheless, multilamellar specimens can be found in the cluster, in proportions that subtly depend on the used lipid and on the parameters of the procedure.

The experiment of interest here is one of many which were carried out [13,14] to study the interactions of polystyrene latex particles with the membranes of giant lipid vesicles. We use an optical trap to manipulate single particles and bring them in contact with vesicles. It is generally observed that simple latex spheres (whose surfaces bear sulfate groups) spontaneously adhere to neutral lipid vesicles [13]. The membranes in the photographs below (Fig. 3) were in fact positively charged, but similar behaviors, in terms of particle encapsulation and capillary interactions, were observed with neutral vesicles.

When a particle gets in contact to a lipid membrane, different scenarios may happen, leading to a partial wetting of the particle surface by the lipids or to a complete encapsulation [13]. The photos in Fig. 3 reveal that the vesicle was bi-lamellar. Each particle was incorporated between two lipid lamellae and pushed them apart, creating a water gap in between. Below we will call "Plateau border" this narrow region filled with water, making analogy with the similar formations in foams. At the present stage, the dynamics of particle incorporation and membrane delamination is poorly understood [13], but this is not the important point here, in as much as we are interested only in the final configuration. Indeed, the experiment is a physical realization of the configuration sketched in Fig. 2, i.e. a film with 2 solid inclusions whose diameters, about 4.3 micrometers, are considerably greater that the equilibrium film thickness (a few nanometers).

The optical setup can be operated in a double trap configuration (2 pairs of laser beams, see Ref. 15), which allowed us to catch each particle and to vary the interparticle separation. For instance, starting with the configuration of Fig. 3a, i.e. with both particles in the vesicle equatorial plane, we pulled them apart. When the particles were separated, we switched off the beams and noticed that the particles would move back towards contact, proving the existence of a long range (micrometers) attraction. The observation could be repeated at will. Interestingly, we found that the capillary attraction would reach a maximum not when the particles were in contact but when they were separated by a distance comparable to their diameter (about 4 microns). We estimated the maximum force to be of the order of 10 pico-Newtons.

As we mentioned, the observation was repeatable. This does not mean that the experiment can be systematically reproduced with any vesicle and any couple of particles. In fact, we observed capillary attractions only sporadically among hundreds of different systems. This is not surprising, because the simultaneous occurrence of a bi- or multi-lamellar membrane and of a proper encapsulation of both particles is a rare event. We observed the attraction first with small particles, about 2 microns in diameter [16]. In this case, we estimated the interaction energy at contact on the order of $k_B T$ (the thermal energy). Conversely, the attraction energy of large (15 microns) particles turned out enormous. By "enormous", we mean a value well beyond 10^5 k_BT, which is about the maximum optical trapping energy in these experiments. Apparently, the attraction drastically increases with the particle size.

3. THEORETICAL CALCULATION OF THE CAPILLARY FORCE

To calculate the capillary force for the configurations in Fig. 2 and 3 we solved the Laplace equation (4), which governs the shape of the capillary menisci (of the Plateau borders). We applied bipolar coordinates (u,v) in the plane xy, see Ref. [17]:

$$x = g \sinh u \,, \qquad y = g \sin v \,, \qquad g = a/(\cosh u - \cos v) \tag{5}$$

$$\frac{\partial^2 \zeta}{\partial u^2} + \frac{\partial^2 \zeta}{\partial v^2} = g^2 \frac{\Delta P}{\sigma} \tag{6}$$

where a is a parameter related to the radius of the contact line and the distance between the two particles. To determine ΔP, which is equivalent to determining the pressure of the inner liquid (captured between the two detached menisci, Fig. 2), we used the assumption that the total volume of the captured liquid is constant:

$$V = 4 \iint \zeta(u,v)\, g^2 \, du\, dv = \text{const.} \tag{7}$$

Equation (6) was solved by numerical integration, using Eq. (7) and a combination of boundary conditions at the peripheral line (fixed peripheral line or fixed peripheral angle α) and at the contact line on the particle surface (fixed contact line or fixed contact angle θ_c), see Fig. 2 for the notation. Thus the meniscus shape $\zeta(u,v)$ was determined. Next, from the calculated shape we computed the capillary force **F** exerted on each particle. The latter is a sum of contributions due to the pressure, integrated over the particle surface, and the surface tension, integrated along the contact line, see Ref. [9] for details. Due to the symmetry of the system, **F** is directed along the x-axis, passing through the centers of the two particles.

Figure 4 shows a plot of the dimensionless force, $F_x/(\sigma r_c)$, vs. the surface-to-surface distance between the two particles, scaled with the radius of the contact line, r_c (see Fig. 2); here $F_x = \mathbf{e}_x \cdot \mathbf{F}$. For typical experimental values ($r_c \geq 2$ μm, $\sigma \geq 0.1$ mN/m), the calculated capillary force is greater than the lateral force of the optical trap and can explain the observed spontaneous "escape" of the particles from the trap and their sticking together. In consonance with the experimental observations, the calculated attractive force exhibits a local maximum (maximum negative F_x) at a certain intermediate value of the interparticle separation.

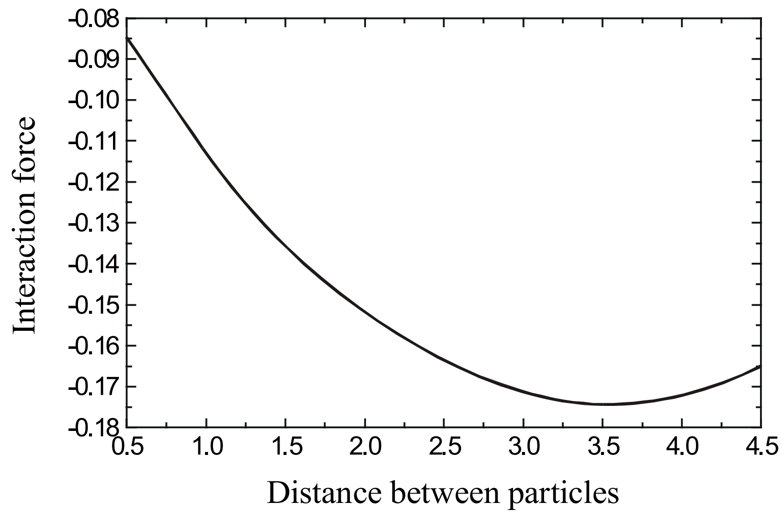


Fig 4. Calculated plot of the dimensionless force $F_x/(\sigma r_c)$ vs. the surface-to-surface distance between two identical particles, scaled with the contact line radius, r_c. The contact line at the particle surface is fixed at h_c/r_c = 1, whereas the peripheral contact line is movable at peripheral contact angle α = 0; the total volume of the liquid in the two Plateau borders is $V/(\pi r_c^3)$ = 2, see Fig. 2 for the notation.

It should be noted that Eq. (7) and the boundary condition at the peripheral contact line lead to a nonlinear *boundary* problem, despite the fact that the differential equation (6) is linear. For that reason we had to use a numerical solution. Moreover, the nonlinearity of the boundary problem forbids the application of the superposition approximation [2]. A detailed description of our experiments and theoretical considerations can be found in Ref. [11].

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