Very-Long-Range Nature of Capillary Interactions in Liquid Films

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Micron-sized objects confined in thin liquid films interact through forces mediated by the deformed liquid-air interface. These capillary interactions provide a powerful driving mechanism for the self-assembly of ordered structures such as photonic materials or protein crystals. We demonstrate how optical micro-manipulation allows the direct measurement of capillary interactions between mesoscopic objects. The force falls off as an inverse power law in particles separation. We derive and validate an explicit expression for this exponent whose magnitude is mainly governed by particle size. For micron-sized objects we found an exponent close to, but smaller than 1, making capillary interactions a unique example of strong and very long ranged forces in the mesoscopic world.

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It is a well-known fact that small objects floating on a liquid surface cluster together. Bubbles on the surface of a soap solution [1] or cereals in a bowl of milk [2] attract each other with long range forces arising from the interface deformation under particles weight (or buoyancy for bubbles). Close packed configurations for such macroscopic objects are found to minimize gravitational potential energy. Shrinking lengths to the mesoscopic scale, particle weight soon becomes too weak to produce any significant deformation and hence attraction. However, if the particles are confined in thin liquid films, a deformation of the interface is unavoidable. This is the case, for example, of a colloidal suspension drying on a solid substrate, or dispersed in a freestanding thin film. When the thickness of the liquid film becomes smaller than the bead diameter, the interface has to deform with an increase in surface energy. The liquid interface will then react on the particles with forces aiming to reach a minimum surface (energy) configuration, usually corresponding to close packed two dimensional crystals [3]. Such phenomena, already observed by Perrin in 1909 [4], have attracted considerable interest in recent times due to their relevance for the engineering of photonic materials [5] and protein crystallography [6]. Consequently, a strong effort has been devoted to the theoretical analysis of the involved forces, resulting in a long series of papers reviewed in [7]. Prediction for macroscopic objects have been confirmed by experiments on immersed cylinders [8] or particles attached to holders [9]. However, no experiment so far has been able to directly measure capillary forces between an isolated pair of mesoscopic objects, although it is in the mesoscopic and nanoscopic realm that this effect finds the most interesting applications. Any physical contact with the particles would inevitably produce a significant deformation of the liquid-air interface and dramatically affect the interaction. On the other hand, due to the long-ranged hydrodynamic interactions in thin films, particle mobility is very sensitive to interparticle distances and force measurements are difficult to deduce from trajectories. A static, highly noninvasive method is required for a direct and reliable measurement of these interactions.

In this Letter we demonstrate how optical micromanipulation [10] allows the precise measurement of capillary interactions between 2 μm-sized spheres confined in a freestanding thin liquid film. Working in a freestanding liquid film is essential for accurate capillary force determinations since no particle-substrate interactions have to be taken into account. Holographic optical trapping [11] is used to scan the distance between particles while gauging the attractive interaction with the optical restoring forces.

The force law can be anticipated by calculating the surface tension forces acting on a pair of spherical objects confined in a thin liquid film. Kralchewsky *et al.* [12] derived the shape of the meniscus around the two particles using the method of matched asymptotic expansions. An implicit expression for the force law was obtained, whose evaluation requires the numerical solution of a system of nonlinear equations in the accessible system parameters. Confining ourselves here to mesoscopic objects, we show that Kralchewsky solution for the force can be very well approximated by an inverse power law whose parameters have an explicit expression in terms of the system's physical properties. We assume complete wetting (zero contact angle) with the liquid surface departing from a contact ring of radius r_c with continuous slope angle ψ_c [Fig. 1(a)]. Surface tension will exert a force on the contact ring whose resultant is orthogonal to the ring plane and has a modulus

$$F = \gamma 2\pi r_c \sin\psi_c, \tag{1}$$

where γ is the liquid-air surface tension ($\gamma \simeq 35$ mN/m in our experiment). For small gradients $r_c = a\sin\psi_c \sim a\psi_c$, $z_c = a(1 - \cos\psi_c) \simeq a\psi_c^2/2$, and the force $F \simeq 4\pi\gamma z_c$ is then proportional to z_c with a strength of order 1 nN/nm. The order of magnitude of other forces into play is 1 pN for particle's weight and 100 pN for the maximum optical force exerted by our trap. The interface is supposed to be

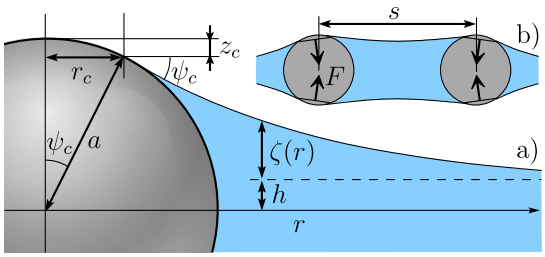

FIG. 1 (color online). Wetting geometry. The liquid film wraps the particle inside a spherical cap of radius r_c. For $r > r_c$ the liquid-air interface is freestanding and slowly falls to the large distance height h. The local height of the interface measured from h is indicated by the function $\zeta(r)$, whose gradients are assumed to be small everywhere ($\psi_c \ll 1$).

flat and horizontal far from the particle and we indicate with $\zeta(r)$ the local vertical displacement of the interface from this reference surface. In the small gradient approximation, Laplace equation for the pressure drop across the freestanding portion of the upper surface ($r > r_c$) reads [13]

$$\gamma \nabla^2 \zeta(r) = \rho g \zeta(r), \tag{2}$$

where ρ is the liquid density and g the acceleration due to gravity. The only axisymmetric solution to (2) vanishing at infinity takes the form [14]:

$$\zeta(r) = -\frac{\tan\psi_c}{q} \frac{K_0(qr)}{K_1(qr_c)}, \tag{3}$$

where $K_i(x)$ is the modified Bessel function of ith order [15] and $q^{-1} = \sqrt{\gamma/\rho g}$ is the capillary length. This is the length scale below which gravitational forces play no role in determining the interface shape and its about a few millimeters for typical solvents. Therefore, we can safely replace $K_0(x)$ and $K_1(x)$ with their small argument expansion and write for small gradients

$$\zeta(r) = -2z_c[\log(qr/2) + \gamma_e], \tag{4}$$

where γ_e is the Euler-Mascheroni constant. At the micron scale gravitational energy will be negligible and the bottom surface will have a symmetrical shape to the top one. Therefore two opposite and equally strong capillary forces will act on the top and bottom contact rings of an isolated particle but they will cancel out, giving no net force. When a second particle is introduced in the film at a distance s, it will in turn contribute to the interface deformation producing a tilt of the contact lines around the first particle [Fig. 1(b)]. Within the superposition approximation by Nicolson [14], the amount of tilt would simply be given by the gradient of the surface deformation produced by an isolated particle at the location of the second one. According to (4) the interface height around an isolated particle is expected to decay logarithmically with the distance producing a tilt of the contact lines that falls off as the inverse interparticle distance. The capillary forces F acting on the contact rings will not be balanced anymore but a net attractive force would appear whose intensity is given by the projections of F on the film reference plane

$$f(s) = 2F(s) \frac{\partial \zeta(r)}{\partial r}\bigg|_{r=s} = 16\pi\gamma z_c^2(s) \frac{1}{s}. \tag{5}$$

The resulting force is than proportional to the square of z_c and inversely proportional to the distance separating the particles. In analogy with Coulomb electrostatic force in 2D, the quantity z_c is usually called the "capillary charge" of the particle [16]. However, the capillary charge is not an intrinsic constant property but a slowly varying function of particle separation. This function can be calculated by imposing the continuity and differentiability of the interface across the contact ring.

$$\zeta(r_c) + \zeta(s) + h = a - z_c, \tag{6}$$

$$r_c = a \sin\psi_c \sim \sqrt{2az_c}, \tag{7}$$

where we rely on the superposition approximation [14] to express the interface vertical displacement, as the sum of two single particle displacement fields (4). We are also assuming in (6) that the deformation field $\zeta(s)$ produced by one particle is constant over the contact line of the other. Eqs. (6) and (7) can be solved analytically giving

$$z_c(s) = \frac{a - h}{-W[-q^4 s^2 a(a-h)C]}, \tag{8}$$

where W is the Lambert-W function [17] diverging logarithmically for small negative argument, $W(-\epsilon) \sim \log\epsilon - \log(\log\epsilon)$, and C is the numerical factor $\exp[4\gamma_e - 1]/8 = 0.46\ldots$. The above expression for z_c is a slowly varying function of s and it can be well approximated by its logarithmic expansion about close contact $s = 2a$:

$$z_c(s) \sim z_0 (s/2a)^{\alpha}, \tag{9}$$

$$z_0 = z_c(2a) = \frac{a - h}{-W[-4q^4 a^3 (a-h)C]}, \tag{10}$$

$$\alpha = \frac{d\log z_c}{d\log s}\bigg|_{s=2a} = \frac{2}{-W[-4q^4 a^3(a-h)C] - 1}. \tag{11}$$

Accounting for the s dependence of z_c the attractive force (5) will still display a power law behavior but with an exponent smaller than 1,

$$f(s) = \frac{16\pi\gamma z_0^2}{2a} \left(\frac{2a}{s}\right)^{1-2\alpha}, \tag{12}$$

where α is an explicit function of the three characteristic lengths: particle size, film thickness, capillary length of the solvent. It is natural to choose h as the free parameter in the theory being the only parameter in our experiment which is difficult to control. The force switches on when the film

thickness is smaller than particle diameter ($h < a$) and its intensity then grows roughly quadratically with a-h (5) and (8). On the other hand, the exponent $1–2\alpha$ is equal to 1 for vanishing a-h but then quickly drops to a fairly constant value as soon as a-h is large enough to produce significant forces (~1 pN). This constant value depends practically only on the particle size and varies very little with typical solvent properties (q). Changing particle size from 10 nm to 10 μm produces a corresponding exponent variation in the range 0.92 to 0.82. For our particle size we predict an exponent of 0.86.

A schematic view of the experimental setup is reported in Fig. 2(a). Latex beads (5.7 μm diameter) are dispersed in a 2/3 water–1/3 glycerol mixture with added 0.2% wt surfactant (SDS). A thin film is obtained by sweeping the solution on a square frame (6 mm side) of nylon wires (60 μm thickness). Special care has to be devoted to sample preparation and handling to avoid dust and other particles which may distort the film interfaces. We used very low concentrated samples and trapped particles in the central part of the film, far away from menisci. Flow currents at the beginning tend to move free floating particles towards the borders and the central part remains clear when the currents disappear. Increasing the solvent viscosity plays an important role in stabilizing the film by reducing drainage but has no direct role in determining static capillary interactions. The freestanding liquid film is enclosed in a humidity chamber and placed over the 40x objective of an inverted optical microscope (Nikon TE2000-U). The same objective is used to focus the laser beam ($\lambda = 532$ nm) reflected off a spatial light modulator (Holoeye LCR-2500) into two, dynamically reconfigurable, optical traps [11,18]. Axial confinement is guaranteed by the normal components of capillary forces. We can also access the thickness variations around an isolated particle by viewing the film under reflected monochromatic light. To this end a red diode laser beam ($\lambda = 657$), overlapped to the trapping green beam, is focused by the same microscope objective far from the film surface. The observed portion of the red beam wave front is approximately plane and the film reflectance than varies with $\cos[4\pi\zeta(r)n/\lambda]$ ($n = 1.37$). The distorted film will then show ring shaped interference fringes centered on the trapped particle [Fig. 3(b)]. Thickness variations can be extracted from the fringe pattern and are reported in Fig. 3(a). A clean logarithmic shape is found up to 200 μm, in perfect agreement with (4).

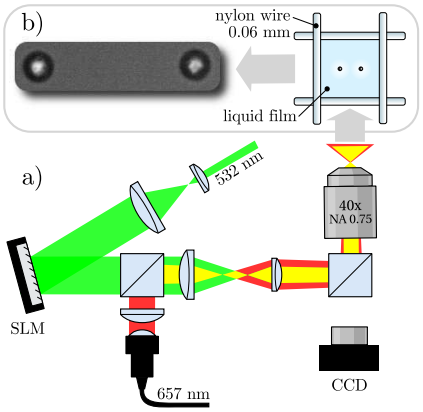

FIG. 2 (color online). Schematic view of the experimental setup described in text.

To extract the force law one of the two traps is held fixed while the other is continously scanned through different distances with a step of 2 μm. Because of liquid drainage, the film is slowly but constantly thinning. By recording the intensity of the focused laser spot at the two film interfaces while scanning the microscope focus we estimate a thinning rate dh/dt below 5 μm/h. When the thickness is so small that optical forces cannot balance the capillary interaction, one of the two particles jumps out of the trap and collapses onto the other. Until that time we can extract the attractive capillary force from the interparticle distance. Calling k_1 and k_2 the two trap elastic strengths, each particle will be displaced towards the other by a distance $\Delta x_i = f/k_i$. The observed interparticle separation will be then smaller than trap separation by an amount: $\Delta s = (\Delta x_1 + \Delta x_2) = f(1/k_1 + 1/k_2) = f/k'$. Particle distance will actually fluctuate due to Brownian motion with a mean squared value given by [19]: $\langle \Delta d^2 \rangle = k_B T/k'$ which can be used to experimentally determine k'. Particle positions can be measured by image analysis with an accuracy better than 10 nm [20]. On the other hand SLM allows very precise and reproducible particles relative positioning (beam pointing stability may only affect absolute positions). Brownian motion is then the most important source of uncertainty in measuring the distance. We observe $\langle \Delta d^2 \rangle = 12$ nm [21] and deduce a trap stiffness of $k' = 29$ pN/μm. For each of the 25 relative distances in a scan,

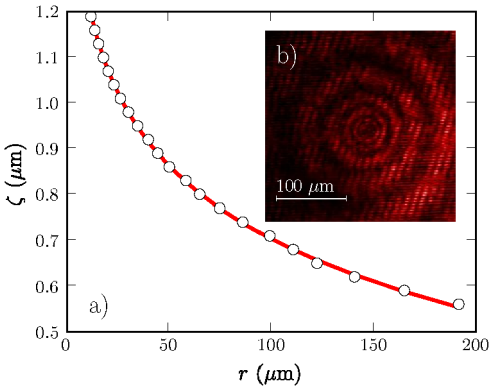

FIG. 3 (color online). Film thickness profile around an isolated particle. (b) Monochromatic light reflected off the film displays interference fringes centered around an isolated trapped particle. A period in the fringe pattern corresponds to 240 nm thickness variation. (a) Film height $\zeta(r)$ versus distance from particle center r (open circles), red line is a logarithmic fit.

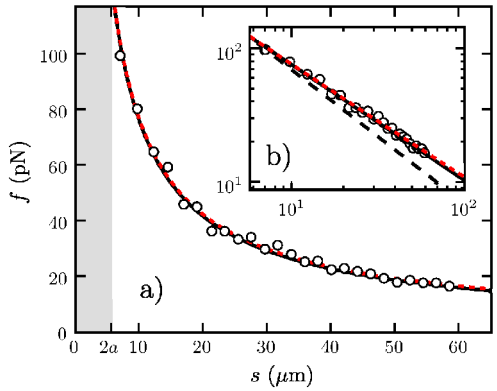

FIG. 4 (color online). Capillary force law. (a) Open circles are experimental determinations and black solid line represents a fit to the predicted power law (12). Red dashed line is the full Kralchewsky theory. (b) Same plot on a double-log scale. A $1/s$ law is added for reference, as a black dashed line.

we acquired 40 frames at 200 fps, resulting in a full scan time of about 5 s. Equilibrium distances are averaged over the last 10 frames, after the particles have settled in to the new trap positions, and compared to the distances between non interacting particles ($h > a$). From the time series of frames we can also check that the force is constant in time and that film thinning is negligible during a scan.

As already discussed, the logarithmic film shape in Fig. 3 would lead, in the Nicolson approximation, to an attractive force decaying roughly as the inverse of interparticle distance. More precisely we would expect to find the power law in (12). Indeed a clean power law is found experimentally as evidenced by the double log insert in Fig. 4. The overall behavior is very well fitted by (12) leaving the film thickness at large distance h as the only free parameter. We find $h = 2.2\ \mu\text{m} = 0.8a$ that makes an average gradient $\psi_c = 0.12$, confirming the small gradient assumption. For this fitted h value we get from (10) and (11) a power law exponent $1–2\alpha = 0.86$ and $z_0 = 20$ nm. The full Kralchewsky prediction for the same parameter values, also reported in Fig. 4(b), is almost completely overlapped to our power law expansion, confirming the goodness of our approximations. The force law was derived for particles of identical size, however, inspection of particle images reveals a size difference not exceeding 20 nm. Thought it is easy to generalize (6) and (7) for spheres of different size, we could not obtain an explicit analytical solution for that case. However, numerical solutions show that (12) (with a the average radius) remains valid within 1% when size differences are below 3% of a-h, as in our case.

In conclusion, we have shown how optical micromanipulation provides an unprecedented tool for investigating capillary forces governing the self-assembly of colloids in liquid films. We provide a static measurement of the capillary force law between an isolated colloidal pair and perform a direct test of the theoretically predicted power law. The exponent of the power law is found to be close to, but smaller than 1, making capillary forces a quite unique example of very long ranged interactions in the mesoscopic world. The experiment opens the way to a variety of further developments addressing the role of many body-effects, membrane elasticity, wetting properties, surfactant dynamics, hydrodynamic interactions in 2D. A deep insight into the nature of interface-mediated forces at the mesoscopic scale could suggest new routes to self-assembly of meso- and nanostructures [22]. Optical trapping of colloidal particles bound to lipid membranes [23] could also provide new insights in the dynamics of biomembrane inclusions [24].

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