Lateral Capillary Forces Measured by Torsion Microbalance

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(Received 9 May 1995)

The forces of capillary interaction between two thin cylindrical rods or two spherical particles placed at a liquid/air interface and immersed partially in the liquid are measured by a sensitive torsion microbalance. Cylindrical rods of radii 50, 165, and 365 μm are used. The spheres have radius 600 μm; they are modeling the lateral interaction between colloidal particles trapped in a thin liquid film. The measured forces range in magnitude between 10^{-4} and 10^{-9} N depending on the particle size and the interparticle distance. The experimental data agree well with the theory of capillary immersion forces.

PACS numbers: 47.17.+e, 07.10.Lw, 82.70.Dd

The overlap of the menisci surrounding two particles which are attached to a fluid interface leads to a lateral interaction between the particles. The latter can be either attraction for two similar particles or repulsion for two dissimilar particles [1]. A classical example for such interaction is the capillary flotation forces between two particles floating freely on a liquid surface [2]. Being important for many practical applications, these forces are significant only for relatively large particles (larger than a few microns) which are able to deform the liquid interface by their own weight. Very recently, a new type of lateral capillary force was reported concerning particles partially immersed in a liquid layer [3,4] where the deformation of the liquid surface is related to the wetting properties of the particle surface rather than to gravity [1]. Because of their different origin the immersion capillary forces can operate between much smaller particles (latex particles of micron [5] and submicron [6] diameters and even protein macromolecules of nanometer size [7]) which form two-dimensional arrays under the action of these forces. Capillary immersion forces between two vertical cylinders have been measured in Ref. [8] by means of a pressure sensor balance. Capillary immersion forces between relatively large spherical particles (of radius 1580 μm) were measured in Ref. [9] by means of a mechano-electrical balance; since theory of the immersion force was not available at that time the authors of Ref. [9] could not interpret their data. Unfortunately, quantitative interpretation of these data is not possible nowadays because important parameters of the system (surface tension, contact angle) are not given in Ref. [9]. Our aim here is to measure experimentally the immersion forces between model particles of micron size being as close as possible to these practical systems.

The theoretical description of the capillary immersion forces is attained by solving the Laplace equation of capillarity in two cases [3]: two interacting spheres, important for practical applications to spherical colloidal particles or biological cells, and two interacting vertical cylinders which can serve as a model system, simpler than the spheres. In both cases the theory gives the following approximate expression for the force of interaction F:

$$F(L) = 2\pi\sigma q Q_1 Q_2 K_1(qL). \qquad (1)$$

Here L is the center-to-center distance between particles; σ is the surface tension; Q_i is defined as

$$Q_i = R_i \sin\psi_i, \qquad i = 1,2, \qquad (2)$$

where R_i is the radius of the three-phase contact line and ψ_i is the meniscus slope angle at the particle surface; q is the reverse capillary length given by

$$q = \sqrt{\frac{\Delta\rho g}{\sigma}}$$

with $\Delta\rho$ being the density difference between two fluids and g being acceleration due to gravity; K_1 is the modified Bessel function of first order. Equation (1) is derived assuming particle radii much smaller than the capillary length and the separation distance ($R_i \ll q^{-1}$ and $R_i \ll L$). The form of this equation resembles other laws of classical physics considering Q_i as some sort of capillary "charges" [1]. The peculiar dependence on the distance comes from the fact that the capillary interaction is mediated by liquid menisci formed around the particles instead of any insubstantial field.

To prove the theoretical predictions we study experimentally the lateral capillary force between glass cylinders and spheres of micron size which are partially immersed in liquid. Since the interaction between such small particles is very weak, we measured the force by means of a specially constructed torsion balance. The classical torsion balance is known as one of the most sensitive tools for force detection [10]. Consider two couples of interacting particles (cylinders or spheres) immersed partially in the liquid as shown schematically in Fig. 1.

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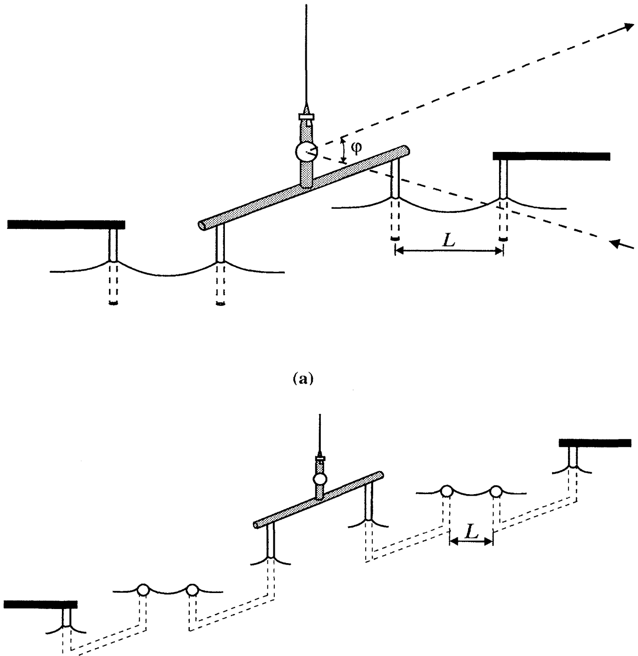

FIG. 1. Sketch of the basic part of the torsion balance with two pairs of particles experiencing capillary interaction on a liquid-air interface: (a) cylinders; (b) spheres. The immersed portions of the particles and holders are shown dashed. The torsion angle φ is measured by light beam reflection.

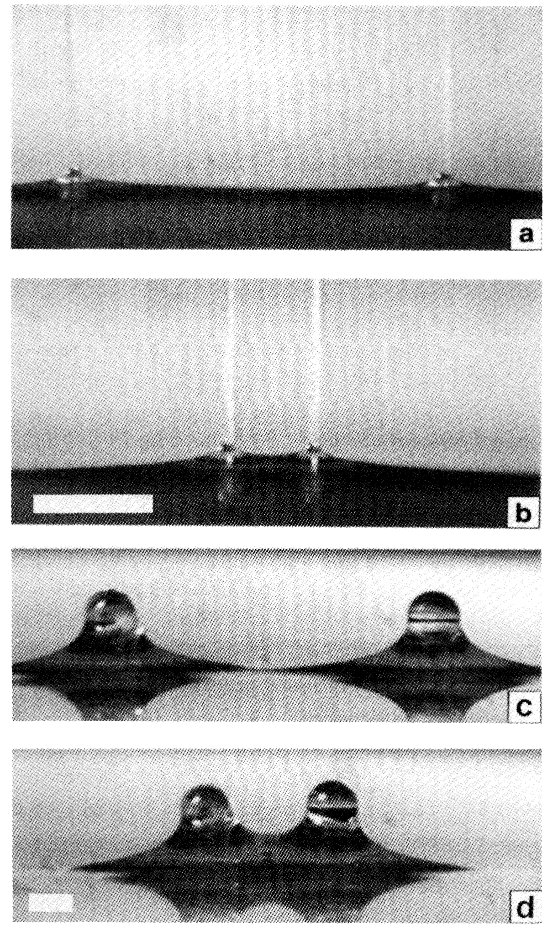

FIG. 2. Photographs of successive stages of capillary interaction: (a) two vertical cylinders of radii 50 μm immersed in water, $L = 0.328$ cm, $F = 1.6 \times 10^{-7}$ N; (b) the same capillaries, at close contact $L = 0.075$ cm; (c) two spheres of radii 600 μm immersed in water solution of surfactant at protrusion height 1000 μm, $L = 0.746$ cm, $F = 9.82 \times 10^{-7}$ N; (d) the same spheres, $L = 353$ cm, $F = 1.13 \times 10^{-5}$ N. The bars correspond to 1 mm.

Each particle is kept on the liquid surface by an individual support which plays the same role as the solid substrate in the experiments on two-dimensional crystallization [5–7]. A particle attached to the anchor suspended on a platinum wire of known strength forms a couple with the opposite particle attached to a holder. Photographs of couples of interacting particles are presented in Fig. 2. The force of interaction is measured by counterbalancing the moment created by the couple of forces applied to the anchor by the torsion moment of the wire. The latter can be determined from the angle of rotation of the anchor φ detected by reflection of a laser beam from a mirror attached to the anchor. The magnitude of accessible forces can be varied by several orders by using anchors of different size combined with wires of different diameter. For a given combination of anchor and wire the measured force can be varied additionally by varying the length of the wire. At fixed wire length we adjust the interparticle distance L by moving gently the holder and measure the respective force $F(L)$. Details about the experimental procedure will be published elsewhere [11].

Figure 3 shows experimental results for the force between two cylinders of equal radii: 50, 165, and 365 μm, respectively. Distilled water is used as a liquid phase. Data points corresponding to certain interval of distances L are obtained with different wire lengths not specified in the figure. With decreasing separation distance the force increases due to a stronger overlap of the menisci around the particles (cf. Fig. 2). When the capillary attraction overcomes the strength of the platinum wire the particles stick to each other, which is the reason for the absence of experimental points at separations smaller than about 0.15 cm. The force between cylinders of given radii (Fig. 3) ranges within one to three orders of magnitude. In our measurements we varied the sensitivity of the registration system by using platinum wires of different diameters: 10, 25, and 100 μm. Since the respective intervals of accessible forces overlap, one can extend the force to larger or smaller values simply by increasing or decreasing the wire diameter. The forces for the largest cylinders of radii 365 μm are in quantitative agreement with the

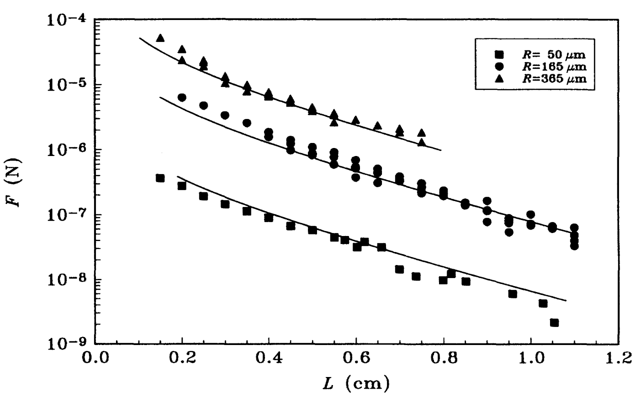

FIG. 3. Force of capillary interaction between two glass cylinders immersed in water ($\sigma = 72.4$ dyn/cm, $q^{-1} = 0.272$ cm. The triangles represent data obtained by an anchor of weight 8.9 g suspended on platinum wire of diameter 100 μm, the circles—by anchor 0.14 g on platinum wire 25 μm, and the squares—by anchor 0.14 g suspended either on wire 25 μm or on wire of diameter 10 μm (smallest detected force). The solid lines are predicted by Eq. (1); no adjustable parameters.

data for similar system obtained by pressure sensor balance [8]. By increasing the wire diameter above 100 μm we can extend sufficiently the upper limit of forces accessible experimentally, but the basic advantage of our force balance is the possibility to detect extremely weak interactions. The lower limit of forces was obtained with cylinders of radii 50 μm using platinum wire of diameter 10 μm (the last 10 data points from the respective curve in Fig. 3). The scattering of these data is caused by mechanical and thermal fluctuations in the system which can be minimized by covering the whole balance and adding of surfactant.

The solid lines in Fig. 3 are theoretical curves drawn in accordance with Eq. (1) without any adjustable parameter. As seen from the photographs, the contact angle between the liquid-air surface and the cylinder-liquid interface is almost zero, which assures slope angle $\psi_i \approx \pi/2$. Hence, in view of Eq. (2), the capillary "charges" Q_i in Eq. (1) can be replaced simply by the cylinder radii R_i. The agreement between theory and experiment looks fairly good, especially at large separation distance L. At small distance the measured force for the two thicker capillaries is systematically larger than the theoretical prediction since the assumption of small meniscus slope in the linearized theory is no longer valid. To improve the theory in this case, one should solve numerically the nonlinear Laplace equation. Better coincidence with the experiment at small separation distance is observed for the thinnest cylinders whose radii (50 μm) satisfy the requirements of the linearized theory.

Similar trends were observed also for the force between cylinders immersed in an aqueous solution of surfactant (sodium dodecyl sulfate with concentration 8×10^{-3} mol/l). In this case, however, the force is about two times lower than the force shown in Fig. 3 for pure water, in agreement with Eq. (1) because the surface tension σ is approximately twice smaller (for details see Ref. [11]).

The measured force of capillary interaction between two spheres of radii 600 μm shown in Fig. 4 exhibits similar trends as for two cylinders. The data points in this figure are obtained at constant height of sphere protrusion (elevation of the top of a particle above the horizontal liquid surface far from the particles) about 0.11 cm, see Fig. 2. Lowering of the protrusion height decreases the capillary force since the meniscus becomes less steep [11]. The magnitude at small separation distance is close to the magnitude of the force between two cylinders of radii 365 μm. At large distance the force between two spheres decreases to much lower values than the respective force between two cylinders (see Fig. 3). To compare the theory with the experimental results, one needs the contact angle at the sphere surface which was found to be 16°. Another complication is that the contact line radius R_i varies when the spheres approach each other (for calculation of Q_i see Ref. [11]). The solid line drawn by Eq. (1) in Fig. 4 agrees satisfactorily with the experimental data, bearing in mind that the menisci on the two spheres do not satisfy well the requirements of the linearized theory. Again, the theoretical fit can be improved by numerically solving the nonlinear Laplace equation of capillarity in the respective geometry. The data about capillary forces between spherical particles [9] cannot be compared with ours because the particles radii (1580 μm) are much larger and, moreover, parameters like surface tension and contact angle are not given in Ref. [9].

In conclusion, we have measured the forces of capillary interaction between two particles of very small size: glass cylinders of different radii (365, 165, and 50 μm) and

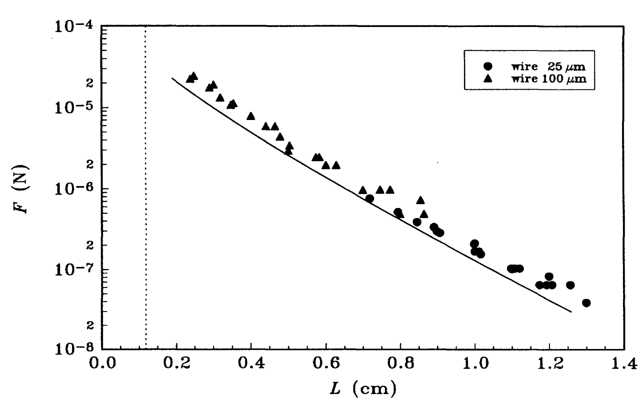

FIG. 4. Force of capillary interaction between two glass spheres of radii 600 μm immersed in surfactant solution ($\sigma = 36.8$ dyn/cm, $q^{-1} = 0.194$ cm). The data are obtained either by the anchor 0.14 g suspended on platinum wire of diameter 25 μm or by the anchor 8.9 g on wire 100 μm. The solid line is a prediction of Eq. (1). The dotted line shows the position of closest contact between the two spheres.

glass spheres of radii 600 μm. For this purpose we utilized a torsion microbalance to detect forces from 10^{-4} N down to 10^{-9} N. The magnitude of the force depends on both the particle size and the separation distance between the particles. This balance is comparable in sensitivity with the best devices for studying intermolecular and surface forces [12] and even with the atomic force microscope. The force laws established experimentally agree well with the predictions of the linear theory of capillary immersion forces especially at small particle size and large separation distance. Our results can contribute to a better understanding of the forces governing the formation of two-dimensional arrays of fine colloidal particles and biological species.

We are indebted to V. Paunov for carrying out the numerical computation of the force between two spherical particles. The financial support of the Research and Development Corporation of Japan (JRDC), ERATO program, is gratefully acknowledged.

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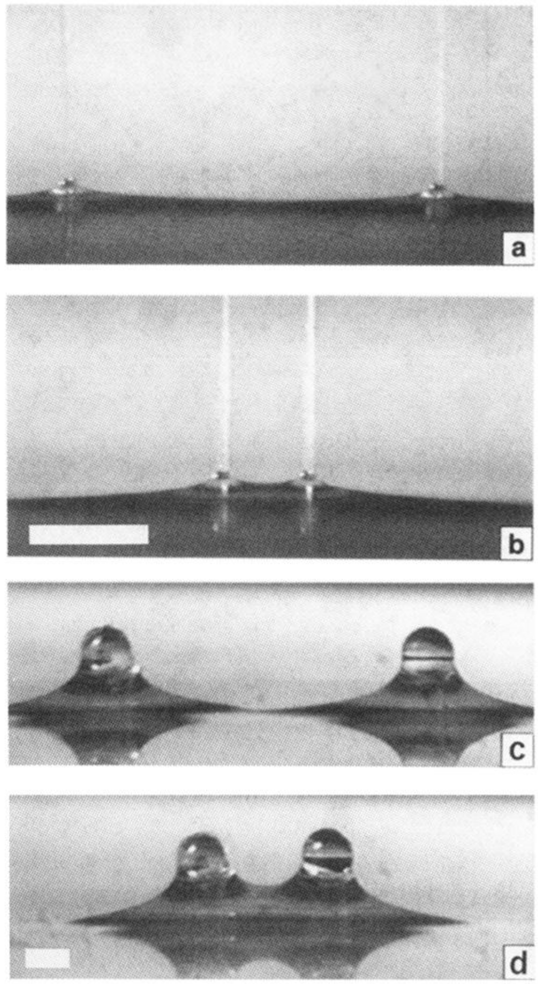

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