

NOTE

Direct Measurement of Nanonewton Capillary Forces

We measured experimentally very weak interactions between microscopic particles by means of a torsion microbalance of sensitivity better than 10^{-9} N. The model system consists of two thin glass cylinders of radii $50\ \mu\text{m}$ immersed vertically in a liquid at the liquid/air interface. The cylinders attract each other by a capillary immersion force due to deformation of the liquid surface around them. The magnitude of the measured force ranges between 4×10^{-7} and 10^{-9} N, depending on the separation distance and the surface tension. At a fixed interparticle distance the force for solution of sodium dodecyl sulfate is about twice as small as that for pure water due to the lower surface tension. The experimental data are well described by the theory of lateral capillary forces. The presented results can be applied to the explanation of the interaction between spherical particles forming two-dimensional arrays on substrate. © 1996 Academic Press, Inc.

Key Words: force balance; capillary forces; two-dimensional arrays; platinum modulus.

INTRODUCTION

Surface forces are generally associated with the interaction of two condensed phases across an intermediate phase (1) modeling the interaction in bulk dispersions of particles. These are short-range forces because they are an integral result of the intermolecular interactions leading to an excess surface energy due to alteration of the bulk-phase properties in a vicinity of the interfaces. Surface forces are detected by a sensitive spring of known elastic constant which is the operational principle of the surface force apparatus (1). This apparatus is suitable for interactions between two opposite (solid) plates placed in liquid medium at a distance of about $10\text{--}100\ \text{\AA}$. On the same principle is based also the atomic force microscope (AFM) where a cantilever tip scans the surface relief, maintaining very low vertical force and separation distance (1, 2).

Another type of force are the lateral capillary forces between (solid) particles attached to a fluid boundary or liquid film. In this case the interaction is mediated by the liquid menisci due to deformation of the interfaces by the particles (3, 4). One can distinguish two types of capillary forces, flotation and immersion, depending on whether the interfacial deformation is created by the particles weight or by the wettability of their surfaces (4). In the latter case the lateral capillary forces are operative even between submicrometer colloidal particles and protein macromolecules (see below).

Since the spring balance is not suitable for horizontal applications the lateral capillary forces can be measured by other types of detection systems: galvanometer (5), pressure transducer (6), or torsion wire (7). Using these devices capillary forces are measured for interparticle separations ranging from 0.1 to $1.5\ \text{cm}$ (5–7).

The sensitivity of the force balances mentioned above is as follows: surface force apparatus, 10^{-8} N (1); atomic force microscope, 10^{-9} – 10^{-10} N (1, 2); and torsion force balance, 10^{-8} – 10^{-9} N (7). It is seen that the

torsion force balance has comparable sensitivity with the balances for surface forces, which makes it quite appropriate for measurement of small forces between distant microparticles.

To prove this possibility we apply here the torsion microbalance to measure very weak capillary interactions of two microscopic particles (very thin cylinders). The two cylinders are partially immersed in water as shown in Fig. 1 and are vertically immobilized. The menisci are formed due to the cylinders' wettability; hence, they interact via capillary immersion force (4). This leads to attraction between the cylinders when their menisci overlap.

The immersion force is much stronger than the flotation force acting on floating particles which deform the liquid interface by their own weight (4). Except for particles on the fluid interface, capillary immersion forces are important also for the formation of two-dimensional arrays of spherical particles in a wetting film on substrate (8–12). In this case the particles protrude from the water/air interface when the film thickness becomes less than the particle diameter. The menisci around the particles overlap, thus causing the particles to attract each other in order to arrange in a nucleus of hexagonal lattice. The nucleus can promote further the growth of two-dimensional crystal of particles on the substrate dominated by convective motion of the particles toward the crystal boundary (9, 10). This scenario seems quite universal for nucleation irrespective of the particle size and type of the substrate. It was observed already for latex particles and protein macromolecules on glass (9–11), mercury (8, 11), and fluorinated oil (12) as substrate. Since the capillary interaction cannot be measured directly with real colloidal particles of micron or submicron size we utilize here model particles (glass fibers) with radii of a few tens of microns. Thus the contact line at the cylinder surface in Fig. 1 mimics the contact line of a spherical particle protruding from the water surface in a wetting film (3, 4).

EXPERIMENT

The basic part of our torsion balance is an anchor of total weight $0.136\ \text{g}$ suspended on thin platinum wire and two particle holders. Using this system we measure the capillary force between two cylindrical glass capillaries of equal radii ($50\ \mu\text{m}$) immersed in liquid as shown in Fig. 1 (total capillary length $1\ \text{cm}$). As liquid phase we use either distilled water or a water solution of sodium dodecyl sulfate (SDS, Sigma) at a concentration of 8×10^{-2} mol/liter. One of the cylinders is attached to the anchor suspended on the platinum wire, whereas the other cylinder is stacked on a holder. There is a second pair of two identical cylinders of the same radii (not shown in Fig. 1) which are a counterpart of the first pair; one of the cylinders is on the opposite arm of the anchor, and the other one is on the second holder. The distance L between the particles in each pair can be varied by moving gently the cylinder attached to the holder. The force $F(L)$ is calculated from the torsion moment of the wire counterbalancing the moment of the couple of forces applied to the anchor (13),

$$F = \frac{f\phi}{2a}, \quad [1]$$

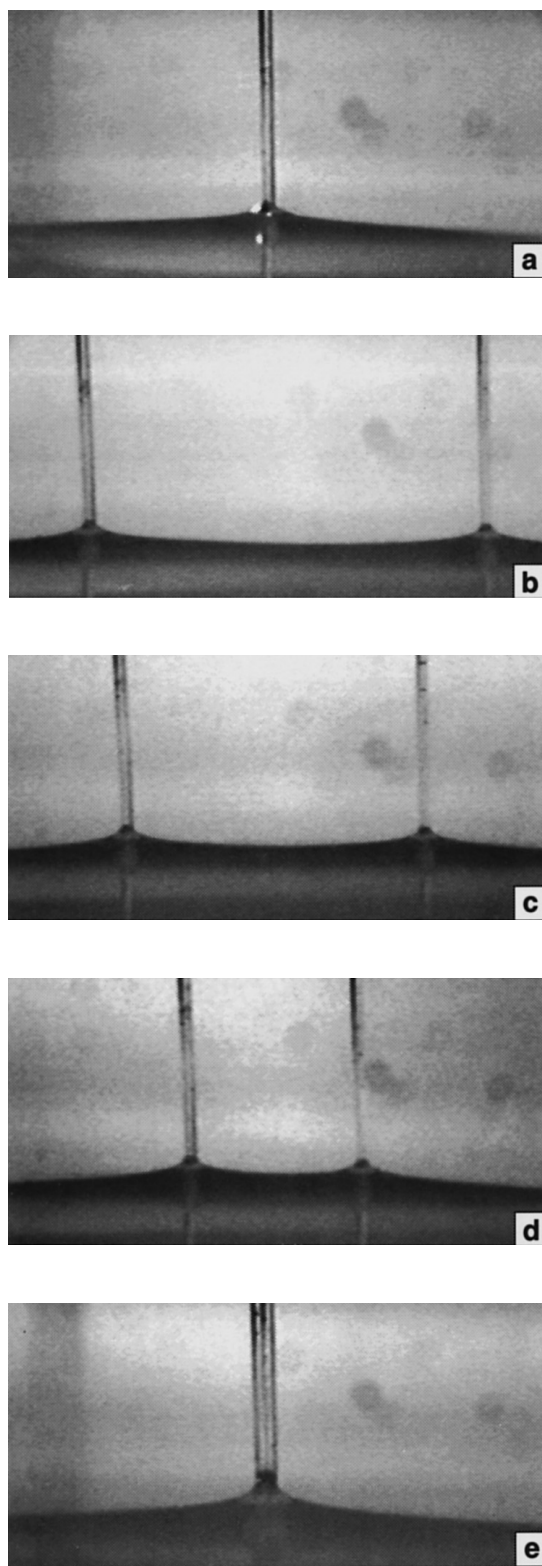


FIG. 1. Successive stages of interaction between two glass capillaries of radii $50\ \mu\text{m}$ immersed in a water solution of SDS: (a) $L = \infty$, $F = 0$; (b) $L = 0.317\ \text{cm}$, $F = 6.7 \times 10^{-8}\ \text{N}$; (c) $L = 0.273\ \text{cm}$, $F = 9.0 \times 10^{-8}\ \text{N}$; (d) $L = 0.126\ \text{cm}$, $F = 2.7 \times 10^{-7}\ \text{N}$; (e) $L = 0$, $F = \infty$.

where f is the torsion modulus of the wire, $\phi/2$ is the angle of torsion, and $a = 1\ \text{cm}$ is the length of the anchor arm. Experimentally we measured the angle of reflection $\phi(L)$ of a laser light beam from a mirror glued to the anchor.

The torsion modulus f was determined from the period of oscillations T of a brass cylinder of radius $0.4\ \text{cm}$, length $0.41\ \text{cm}$, and mass $1.698\ \text{g}$ suspended on the wire in air. In our measurements we used platinum wires of diameters 25 and $10\ \mu\text{m}$ (Nilaco, Japan) and lengths 5 – $10\ \text{cm}$. Figure 2a plots T for the $10\text{-}\mu\text{m}$ wire versus the square root of the wire length l , where each point is a mean value of 5 – 10 independent measurements. The period of oscillation is a linear function of \sqrt{l} (13); therefore, the torsion modulus f , calculated from the data in Fig. 2a, depends linearly on the reverse wire length $1/l$. From this dependence we estimated the elastic moduli of platinum wires shown in Fig. 2b, which are close to the values reported in the literature (14): $G = 5.884 \times 10^{11}$ – $7.1 \times 10^{11}\ \text{dyn/cm}^2$. At the same time G decreases with decreasing wire diameter d , which can be attributed to the different texture of the wire material compared to bulk platinum.

More experimental details for the operation of the torsion balance are given in Ref. (7) where we measured the capillary force between larger particles (cylinders and spheres) using thicker platinum wire and a bigger anchor.

RESULTS AND DISCUSSION

The experimental results for the capillary force are plotted in Fig. 3a for glass cylinders immersed in pure water and in Fig. 3b for cylinders immersed in SDS solution. Each set of figures is obtained at a fixed length $l = 5.7\ \text{cm}$ for the wire of diameter $d = 10\ \mu\text{m}$ and $l = 11.3\ \text{cm}$ for $d = 25\ \mu\text{m}$. For certain interparticle distances L , the forces obtained at different experiments coincide within the experimental accuracy. Using the thinner wire of diameter $10\ \mu\text{m}$ one can measure much smaller forces than with the $25\text{-}\mu\text{m}$ wire, although the last wire is twice as long. Since the force increases appreciably when the cylinders come close to each other, large forces are measured using the thicker wire which has a much higher torsion strength. At very small separations, however, the capillary force goes beyond the torsion strength of platinum wire and the two capillaries stick to each other (Fig. 1e).

At a fixed distance between the cylinder axes, L , the force for pure water (Fig. 3a) is about two times larger than the force for SDS solution (Fig. 3b) because the surface tension of water is also twice as large (cf. Eq. [2] below). In both cases the uncertainty of force detection given by the error bars increases at small separations because the anchor becomes less stable close to the point of spontaneous sticking of capillaries. At a large distance L the capillary interaction, detected by the wire of diameter $10\ \mu\text{m}$, is so weak that it becomes comparable to the mechanical and thermal fluctuations in the system, which makes the experimental data scattered. To avoid this problem we close the system with a plastic cover prior to the reading of the angle ϕ and wait until the oscillations of the particles in a pair diminish. The distance L measured from video records of the pair is found to vary by about 1% around its mean value plotted in Fig. 3.

The solid lines in Fig. 3 represent the theoretical computation of the force by using (4)

$$F(L) = 2\pi\sigma R^2 q K_1(qL), \quad [2]$$

where σ is the surface tension, R is the cylinder radius, K_1 is the modified Bessel function of the second kind, first order, and $q = \sqrt{\Delta\rho g/\sigma}$ is the reverse capillary length ($\Delta\rho = 1\ \text{g/cm}^3$, $g = 981\ \text{cm/s}^2$). Equation [2] was obtained by solving the Laplace equation of capillarity in superposition approximation. The theory describes very well the experimental data, especially for the SDS solution. The coincidence between theory and experiment

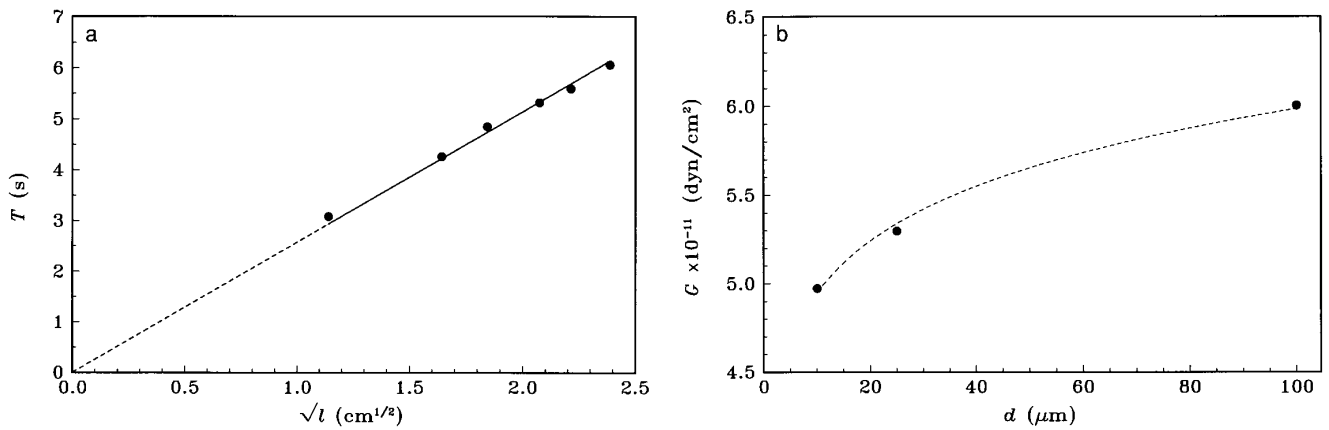


FIG. 2. Determination of the torsion modulus of platinum wire: (a) period of oscillations of standard brass cylinder suspended on a wire of diameter $d = 10 \mu\text{m}$; (b) elastic modulus G of platinum wires of different diameters d .

in the present study seems much better than that with glass capillaries of sufficiently larger radii (165 or 365 μm) used previously (7). The reason is that the capillaries of radii 50 μm better satisfy the assumptions made when deriving Eq. [2]: $R \ll q^{-1}$ and $R \ll L$. The deviation between theory and experiment for pure water at small separations is most probably due to contamination of the water surface which decreases the actual surface tension σ throughout the measurement. To lessen this effect we suck out the water surface prior to the immersion of the glass capillaries. It was not possible, however, to clean the water surface during the measurement, which took in some cases more than 1 h.

The discrepancy between theory and experiment for pure water at small L can be due also to contact angle hysteresis at the glass cylinder surface caused by its roughness and/or impurities. Hence, the addition of surfactant stabilizes the system by keeping a constant surface tension and a constant slope angle $\psi = 0$ during the course of measurement.

In view of the results in Fig. 3 one can conclude that our torsion balance allows one to study very small lateral forces at separation distances between 0.1 and 1 cm. The maximum sensitivity in the detection of the force is 10^{-9} N, obtained with platinum wire of diameter 10 μm . This value is one order of magnitude smaller than the one reported for the balance for lateral forces with a galvanometer detection system (5). Compared with the balances for surface forces the sensitivity of our balance seems intermediate

between that of the surface force apparatus (1) and that of the AFM (2). To improve it one can use thinner wire for detection of the force, e.g., quartz wire, and minimize the fluctuations in the system by improving the construction of the balance.

CONCLUSION

We succeeded in measuring very weak capillary forces of interaction between two vertical glass cylinders of radii 50 μm immersed in water or in surfactant solution. For this purpose we utilized a torsion microbalance where the capillary force is counterbalanced by the torsion strength of ultrathin platinum wire. The magnitude of the forces is between 10^{-7} and 10^{-9} N, which makes the torsion balance comparable in sensitivity with the most precise balances for measurement of surface forces known in the literature. The capillary immersion forces measured by us are of great importance for the formation of two-dimensional arrays of ordered colloidal particles on substrate, which are a sort of monolayer crystals of hexagonal packing. Such monolayers are expected to find various practical applications as media for storage of information, coating, coloring, etc. (15).

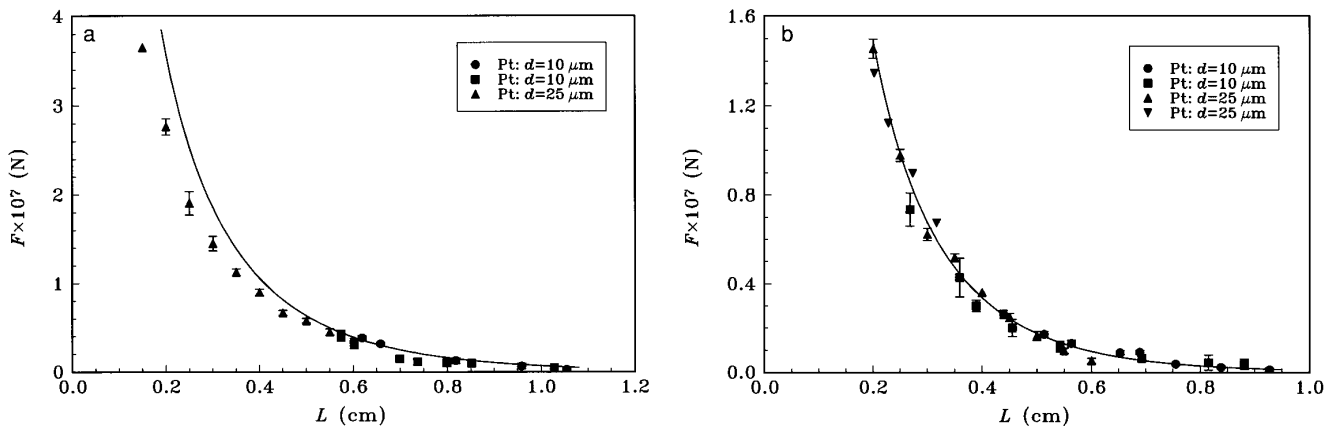


FIG. 3. Capillary immersion force between two glass capillaries of radii 50 μm immersed in (a) distilled water or (b) a $8 \times 10^{-2} M$ solution of SDS. The experimental data are obtained by using platinum wires of diameters 10 or 25 μm . Different figures correspond to different runs; error bars show deviations of two repeated measurements. The solid lines are drawn by the theory without any adjustable parameter.

ACKNOWLEDGMENTS

This work was supported by the Research and Development Corp. of Japan (JRDC), ERATO Program. The authors are indebted to Dr. P. Kralchevsky for discussion of the experimental results.

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CECO D. DUSHKIN*¹
HIDEYUKI YOSHIMURA†
KUNIAKI NAGAYAMA†

*Laboratory of Thermodynamics and Physicochemical Hydrodynamics
University of Sofia
Sofia 1126, Bulgaria
†Protein Array Project
ERATO, JRDC
Tsukuba 300-26, Japan

Received May 23, 1995; accepted February 12, 1996

¹ To whom correspondence should be addressed.