Hydrodynamic Interaction of Surfaces in Electrolyte Solution. A New Method of Investigation of Surface Forces using a Capacitor Ultradynamometer

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A new electromechanical instrument, developed to investigate the interaction of surfaces and enabling high resolution simultaneous displacement and force measurement with an electrical capacitor as a sensor, has been used to study the viscous resistance of thin interlayers of a liquid medium (10^{-1} mol dm^{-3} aqueous NaCl) between molten glass spheres.

The last decade was marked by significant progress in studies of the interaction between solid surfaces, mainly due to a new surface force apparatus based on measuring the distance between mica sheet samples by multiple beam interferometry.[1,2] Alternative approaches were also proposed, notably one using a piezoelectric sensor.[3] We have reported previously[4] on the development of a new experimental method for the investigation of surface forces, based on the use of an electrical capacitor as a high resolution sensor.[5] In the new instrument described below the sensor (capacitor), which is separated from the samples, is situated outside the measuring cell; this leads to significant simplification of the measurements and allows freedom of choice of samples for investigation, of conditions and experimental regimes and also of the scope for applications. This work presents the results of an investigation of the hydrodynamic effects arising on the approach and on the removal of molten silica glass spheres in electrolyte solution, in conditions under which static interaction of the surfaces is negligible.

The instrument used is shown schematically in Fig. 1. One of the samples 2 is positioned, using micro drive unit 4, with respect to the other sample 1, which is installed on the bicantilever spring 3 (spring stiffness $k = 10^2$ N m^{-1}). A magnetoelectrical system[6,7] enables to apply external force to sample 1.[6] If the variation of this loading force in time t occurs at a given rate α, the equation of balance of the forces is given by eqn. (1),

$$\alpha \cdot \Delta t - k \cdot \Delta z + F = 0 \qquad (1)$$

where F is the force of interaction of the samples. The dis-

placement Δz of sample 1 is measured using electrical capacitor 5, the plates of which (one of the plates constitutes part of the construction of spring 3) are separated by an air gap. Electrical signals taken from the capacitor and the magnetoelectrical system pass through the electronic unit and finally arrive at the recorder, which produces plots of the force of interaction of the samples, F, against the displacement, Δz. Calibration was achieved in the ordinary way using a microscope, weights and a quartz filament (deformations of all parts of the device other than the dynamometric spring are included in the calibration but contribute less than 1%).

The effective mass of the spring carrying sample 1 was in the region of several fractions of a gram. The instrument is protected from the convective motion of air in the room by a box and is installed on a vibration protecting suspension possessing typical mechanical frequencies of the order of 1 Hz. Measurements were performed under normal laboratory conditions at room temperature (20 ± 2 °C), displacement and force amplitudes of the residual noise were within 0.5 nm and 5×10^{-8} N, accordingly.

Spherical glass samples about 7 mm in diameter were melted at the ends of silica glass tubes immediately before installation in the instrument. The whole preparation procedure for the experiment, from melting the samples to the beginning of the measurements, occupied only a few minutes.

Test measurements in air reveal strong adhesion forces typical for molecularly smooth surfaces of molten glass.[7] In measurements taken in twice-distilled water electrical double
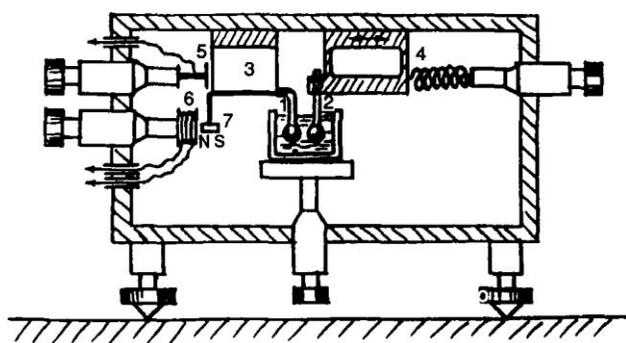
Fig. 1 Schematic diagram of ultradynamometer showing (1, 2) the samples; (3) dynamometer (bicantilever) spring; (4) micropositioning unit; (5) capacitor (sensor); (6, 7) magnetoelectrical (loading) system

layer repulsion is seen, decaying exponentially with the distance (according to the DVLO), in full agreement with previously reported data for glass[8] and quartz.[9] The addition of electrolyte (10^{-1} mol dm^{-3} NaCl) prevents the repulsion and enables immediate observation of hydrodynamic (viscous) forces, which are significant at sufficiently high external force loading rates.

The results of measurements in salt solution are shown in Fig. 2(a–c). The experimental curves are generally reproducible within the limits determined by the noise. At low loading rates (quasistatic regime) a small attraction ($F < 0$) is observed at distances of the order of a few nm [Fig. 2(a)], indicative of weak molecular forces. The curves for approach ($\alpha < 0$) and separation ($\alpha > 0$) virtually coincide. At high loading rates α [Fig. 2(c)] viscous resistance results in a force, directed against the direction of movement of the sample ($F > 0$ on approach, $F < 0$ on separation). On approach the force increases monotonously (under a given loading regime $\alpha = $ const. < 0), on separation ($\alpha = $ const. > 0) the curve possesses a minimum (viscous 'adhesion'); the depth of the minimum at sufficiently high α exceeds by many times the depth of the minimum observed under quasistatic conditions. The viscous force on separation of the surfaces is independent of the pre-history, *i.e.* of the magnitude and duration of action of the preliminary compression force.

The force of interaction between two spherical (geometrical) surfaces having radius r, resulting from the viscous resistance of an interlayer having thickness z of continuous uniform medium having viscosity η is given by a known[10,11] limiting ($z \ll r$) expression [eqn. (2)].

$$F = - 3/2\ \pi\eta r^2(1/z)\mathrm{d}z/\mathrm{d}t \qquad (2)$$

Dynamic terms and electroviscous effects[11] are negligible under the experimental conditions. The speed $v = \mathrm{d}z/\mathrm{d}t$ according to eqn. (1) for the movement can be expressed as eqn. (3).

$$v = \alpha/k\{1 - [(1/k)(\mathrm{d}F/\mathrm{d}z)]\} \qquad (3)$$

Substitution of eqn. (3) into eqn. (2) for the hydrodynamic model results in eqn. (4), where $a = 3/2\ \pi\eta r^2$. In particular,

$$F(z) = - a\alpha/zk\{1 - [(1/k)(\mathrm{d}F/\mathrm{d}z)]\} \qquad (4)$$

when $\mathrm{d}F/\mathrm{d}z = 0$ (which is true for 'infinite' separation and that corresponding to the minimum arising in the surfaces separation regime) eqns. (3) and (4) are reduced to $v_* = \alpha/k$ and eqn. (5) respectively.

$$F_*z_* = - a(\alpha/k) \qquad (5)$$

Numerical integration of eqn. (4), for spheres having $r = 3.5 \times 10^{-3}$ m approaching each other under a constant loading rate $\alpha = - 2.5 \times 10^{-6}$ N s^{-1} regime starting from sufficiently large distances to allow $F = 0$ ($\mathrm{d}F/\mathrm{d}z = 0$ and corresponding to the given value of α initial speed $v_* = \alpha/k = 25$ nm s^{-1}), gives curve 1 in Fig. 2(d). Integration of eqn. (4) with positive (separation) value $\alpha = + 2.5 \times 10^{-6}$ N s^{-1} and with $F_* = - 1.25 \times 10^{-6}$ N
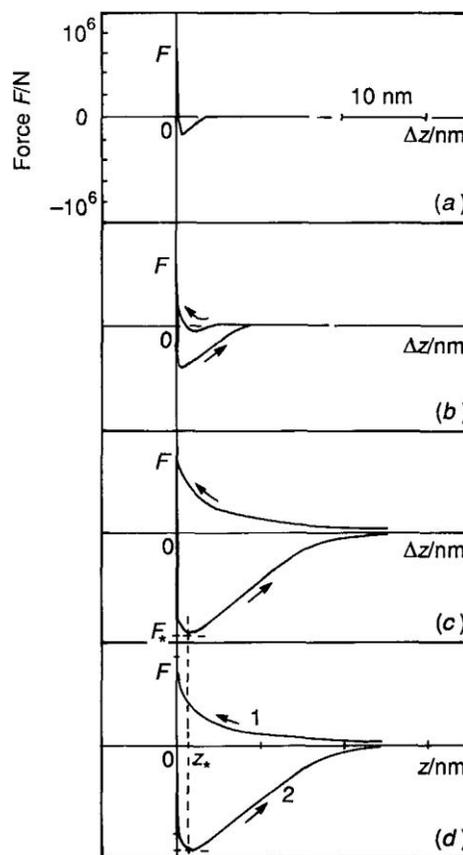

Fig. 2 Plots of force of interaction F *vs.* displacement Δz for glass spheres ($r = 3.5 \times 10^{-3}$ m) in 0.1 mol dm^{-3} aqueous NaCl obtained during approach and separation at different loading rates: $\alpha/\text{N s}^{-1} = \pm 2.5 + 10^{-8}$ (a) $\pm 2.5 \times 10^{-7}$ (b) and $\pm 2.5 \times 10^{-6}$ (c); (d) plots of theoretical force F *vs.* distance z, for $\alpha = \pm 2.5 \times 10^{-6}$ N s^{-1}, $\eta = 10^{-3}$ Nm^{-1} s (for curves 1 and 2, see text). The scale is the same for all the curves and is indicated in Fig. 2(a).

(experimental value for the minimum) gives curve 2 in Fig. 2(d) for which, in accordance with eqn. (5), $z_* = 1.2$ nm.

It follows from comparison of the data in Figs. 2(c) and 2(d) that the experimental curves for both approach and separation of the surfaces coincide (within the accuracy of the measurements) with the theoretical curves based on the approximation of a continuous medium with the bulk viscosity of water. This provides further support for the conclusions made previously,[9,12] according to which water in interlayers as thin as a few nm retains its bulk value of viscosity. At smaller thicknesses (a few molecular layers) the continuous medium approximation is definitely inapplicable. For a detailed analysis of the behaviour of such interlayers, the molecular structure of the medium as well as the surface structure, elasticity of the samples and other factors should be taken into account. Additional experiments need to be done at greater distance resolution (on reduction of the noise this is quite possible using the capacitor method). It should be noted, however, that at any displacement (Δz) resolution the question of the 'absolute' distance (z) between the solid surfaces is open to debate.

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