Relaxation Time of Confined Aqueous Films under Shear

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The many special physical properties of water have been obvious for many years.[1,2] We are interested here in shear relaxation dynamics at solid surfaces—a topic directly relevant to electrochemistry and corrosion,[3−5] soil science,[6] geophysics,[7] and colloidal suspensions,[8] and with possible ramifications for understanding vicinal water at lipids and proteins.[9] Previous studies of sheared molecularly-thin films had emphasized nonpolar fluids[10−14] (though "low friction" in molecularly-thin aqueous films has been noted[15]), primarily for reasons of drifts of piezoelectric circuity in a humid environment and the complexities of computer simulations to model a molecule so complicated as water at a charged surface. Here we report the Brownian relaxation time of aqueous films confined between clay (mica) surfaces. Aqueous confined films are found to be spectacularly more fluid than nonpolar fluids of comparable thickness. The data presented here are restricted to linear response. Behavior with large driving amplitude resulted in a yield point but only when the frequency of motion exceeded the inverse Brownian relaxation time described below.[16]

Modification of a surface force apparatus to measure dynamic oscillatory shear forces by use of piezoelectric elements was described previously.[10,17] The piezoelectric circuity was sensitive to the humid environment, which made these measurements difficult. To minimize drifts, the piezoelectric elements were incubated in a saturated water atmosphere for at least 24 h before measurements, and calibrations were repeated at least hourly in the course of taking measurements.

Briefly, the aqueous salt solutions were confined between two atomically smooth mica crystals glued onto two crossed cylindrical lenses whose separation was controlled using a surface forces apparatus. With compression the two mica cylinders became flattened at the apex, simplifying the geometry to flat parallel plates. To apply shear motion, with amplitudes of 0.1−10 nm, sinusoidal shear forces were applied with voltage on the order of millivolts to one piezoelectric bimorph and the resulting displacement was monitored by the voltage induced in a symmetrically-placed second piezoelectric bimorph.[10,17] Water was distilled, passed through a purification system (Barnstead), and mixed with analar grade salts (Aldrich). The temperature was 27 °C. To make contact with known *equilibrium* behavior, it was verified that static force−distance profiles were in good agreement with literature values.[2,18]

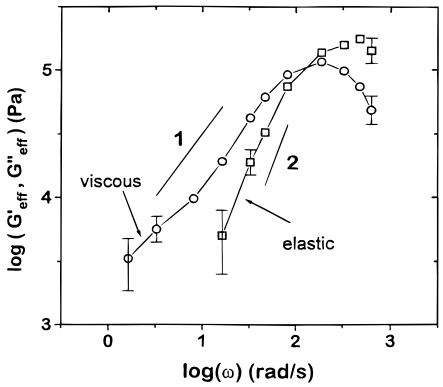

Figure 1. Effective shear moduli, in the linear response regime, of aqueous $MgCl_2$ (100 mM) confined between mica surfaces at a thickness of 0.6 ± 0.2 nm. The elastic modulus, G'_{eff} (squares), and loss modulus, G''_{eff} (circles), are plotted against radian frequency (ω) on log−log scales. The logarithmic slopes of +1 and +2 are the classical response of a fluid whose effective viscosity is $\eta_{eff} \equiv G''_{eff}/\omega \approx 10^5$ P.

The initial linear viscoelastic experiments involved aqueous $MgCl_2$ (100 mM). These films presented the advantage that, since repulsive hydration forces overwhelmed van der Waals attraction, films of near-molecular yet stable thickness could be prepared. The components of sinusoidal force, in-phase and out-of-phase with the drive, were normalized by deflection amplitude, film thickness, and contact area to give the effective elastic and dissipative shear moduli, $G'_{eff}(\omega)$ and $G''_{eff}(\omega)$, respectively.[19] Here ω is radian frequency. Note that normalizations affected neither the relative magnitudes of the moduli nor their locations on the frequency scale. Though these films were surely inhomogeneous in the direction from one solid surface to the other,[2] the effective shear modulus notation provided a convenient way to present the data and to compare the findings with known behavior[19] of bulk systems.

The significance of linear response, obtained with deflection amplitudes less than 0.1−0.2 nm, was to probe the dynamical structure of the film structure unperturbed by the measurement itself. In Figure 1, the linear viscoelastic moduli are plotted on log−log scales against radian frequency for a film of thickness 0.6 ± 0.2 nm (roughly 2−3 times the size of a water molecule). The inverse frequency where G'_{eff} and G''_{eff} cross defines the longest relaxation time, τ_1. In Figure 1, one sees that $\tau_1 \approx 0.01$ s—enormously slower than for bulk water. At frequencies less than $1/\tau_1$, the logarithmic slopes of +1 for G''_{eff} and +2 for G'_{eff} demonstrate that the film was fluid and that the Kramers−Kronig relations were obeyed, in turn supporting the validity of the measurements.[19] Stated otherwise, the films relaxed shear stress in the manner of viscous liquids when the rate of deformation was sufficiently low, less than $1/\tau_1$. At frequencies less than $1/\tau_1$ the effective viscosity was $\eta_{eff} \equiv G''_{eff}(\omega)/\omega \approx 10^5$ P, or $\approx 10^7$ times larger than for water in the bulk.

Much attention has previously been given to the origins of slow relaxation in confined films of single-component nonpolar liquids such as alkanes. For nonpolar films, the hypotheses of confinement-induced crystallization[12,13] and vitrification[14,20] have been advanced. The present situation involving water and ions is obviously more complex.

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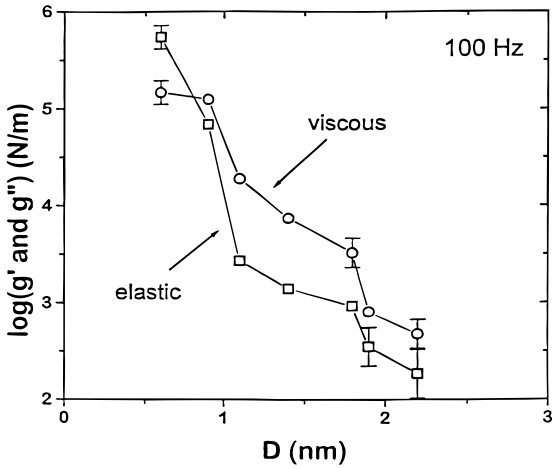

Figure 2. Elastic and viscous spring constants for shear at 100 Hz (squares, g', and circles, g'', respectively), measured in the linear response regime, plotted logarithmically against film thickness for the experiment in Figure 1. Here g' and g'' are elastic and viscous forces (respectively) normalized by displacement amplitude.

What of the thickness dependence−the transition between thin-film and bulk rheological response? At larger thicknesses than for Figure 1, the setup presented a crossed cylinder rather than parallel plate geometry, and it was not possible to normalize for the area of contact to obtain in effective shear modulus. Instead, the viscous and elastic forces were normalized by displacement amplitude to give the viscous and elastic shear spring constants (g' and g'', respectively). In Figure 2, g' and g'' at fixed frequency are plotted semilogarithmically against thickness (D). With increasing D, the spring constants quickly fell below the apparatus resolution and extrapolated to the value for bulk water at ≈3 nm thickness, roughly 10 diameters of the water molecule, with decay length 0.3-0.5 nm. These data show unambiguously that the change of viscoelastic response with thickness was gradual rather than the hypothetical first-order freezing that could be imagined.

Quantification of a well-defined single relaxation time, so much slower than for bulk water, is our central result. To interpret the observation is more difficult, as the actual structure of water at surfaces is still under debate.[1−9] At any rate the frozen ("ice-like") structure, sometimes postulated for water at surfaces, appears unlikely in this system.

The measurement is unambiguous; definitive explanation comprises a challenge for theoretical understanding. It may seem tempting to suppose that the negative lattice sites on mica should be balanced by localized Mg^{2+} counterions, but unfortunately the mechanism of charge compensation in this system is not known. Continued computer simulations of the clay−water interface[21] will shed light on the distribution of ions, on the ratio of ions to water molecules within the narrow gap, and on related matter such as the hydration of confined ions and the interaction of the electric fields of the opposing surfaces. We tentatively attribute slow relaxation in part to the packing and crowding of molecules in a space comparable to their own size[10,14] and in part to exchange of water with hydrated ions and discrete charges at the solid surface. Hydrogen bonding may also be altered.

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