Hydrophobicity at a Janus Interface

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Water confined between adjoining hydrophobic and hydrophilic surfaces (a Janus interface) is found to form stable films of nanometer thickness whose responses to shear deformations are extraordinarily noisy. The power spectrum of this noise is quantified. In addition, the frequency dependence of the complex shear modulus is a power law with slope one-half, indicating a distribution of relaxation processes rather than any dominant one. The physical picture emerges that whereas surface energetics encourage water to dewet the hydrophobic side of the interface, the hydrophilic side constrains water to be present, resulting in a flickering, fluctuating complex.

The role of water as a solvent or lubricant in physical situations from biology to geology is almost universally thought to be important, but the details are disputed (1–19). In proteins, for example, the side chains of roughly half the amino acids are polar whereas the other half are hydrophobic; the nonmixing of the two is a particularly, it is an everyday occurrence to observe the beading-up of raindrops, on raincoats or the leaves of plants. Moreover, it has been observed theoretically and experimentally that when the gap between two hydrophobic surfaces becomes critically small, water is spontaneously ejected (10, 15–19), whereas water films confined between symmetric hydrophilic surfaces are stable at comparable spacings (3). It is then interesting to consider the antisymmetric situation, with a hydrophilic surface on one side to contain the water and a hydrophobic surface on the other to force it away. This Janus situation is shown in Fig. 1.

The main result of this experimental study is that when water is confined between these two competing tendencies, the result is neither simple wetting nor dewetting. We observe instead giant fluctuations (of the dynamical shear response) around a well-defined mean. This noise and fluctuation are peculiar to water and are not observed with nonpolar fluids (20) or with a polar fluid such as ethanol. Aqueous films in the confined, symmetrically hydrophilic situation also give stable dynamical responses (21). The implied spatial scale of fluctuations is enormous compared to the size of a water molecule and lends support to the theoretical prediction that an ultrathin gas gap forms spontaneously when an extended hydrophobic surface is immersed in water (5, 10, 12).

The atomically smooth clay surfaces used in this study—muscovite mica (hydrophilic) and muscovite mica blanketed with a methyl-terminated organic self-assembled monolayer (SAM) (hydrophobic)—allowed the surface separation to be measured by multiple beam interferometry. Pairs of hydrophilic-hydrophobic surfaces were brought to the spacings described below by means of a surface forces apparatus (3) modified for dynamic oscillatory shear (22, 23). A droplet of water was placed between the two surfaces oriented in crossed cylinder geometry. Piezoelectric bimorphs were used to produce and detect controlled shear motions. The deionized water was previously passed through a purification system, Barnstead Nanopure II (control experiments with water containing dissolved salt were similar). In experiments using degassed water, the water was either first boiled, then cooled in a sealed container, or was subjected to vacuum for 5 to 10 hours in an oven at room temperature. The temperature at which the measurements were taken was 25°C.

In order to firmly determine that the findings did not depend on the details of surface preparation, three methods were used to render one surface hydrophobic. In order of increasing complexity, these were (i) atomically smooth mica coated with a SAM of condensed octadecyltrihexysiloxane (OTE), according to methods described previously (23); (ii) mica coated by means of Langmuir-Blodgett methods with a monolayer of condensed OTE; and (iii) a thin film of silver sputtered onto atomically smooth mica, then coated with a self-assembled thiol monolayer. In method (i), the monolayer quality was improved by distilling the OTE before self-assembly. In method (ii), OTE was spread onto aqueous HCl (pH 2.5), 0.5 hour was allowed for hydrolysis, the film was slowly compressed to the surface pressure π = 20 mN m⁻¹ (3 to 4 hours), and the close-packed film was transferred onto mica by the Langmuir-Blodgett technique at a creep-up speed of 2 nm min⁻¹. Finally the transferred films were vacuum-baked at 120°C for 2 hours. In method (iii), 650 Å of silver were sputtered at 1 Å s⁻¹ onto mica that was held at room temperature, then octadecanethiol was deposited from 0.5 mM ethanol solution. In this case, atomic force microscopy (AFM) (with a Nanoscope II) showed the root mean square roughness to be 0.5 nm. All three methods led to the same conclusions. The contact angle of water with the hydrophobic surface was θ = 110° ± 2° (OTE surfaces) and θ = 120° ± 2° (octadecanethiol). In shear experiments, the sheared plate held the hydrophobic alkane monolayer.

The starting point was to measure the force-distance profile. The inset of Fig. 1 shows force, normalized by the mean radius of curvature of the crossed cylinders (R = 2 cm), plotted against surface separation (D). Each datum refers to an equilibrium of 5 to 10 min. Attrac-
force-distance attraction was nearly proportion-
ally to the spring constant of the force-measuring
spring. This indicated, according to well-known
arguments (3), that the measurements repre-
sented points of instability at which the force
gradient exceeded the spring constant of the
force-measuring device, although these attrac-
tive forces were very slow to develop (24). The
opposed surfaces ultimately sprang into contact
from $D \sim 5$ nm and when the surfaces were
pulled apart, an attractive minimum was ob-
erved at $D = 5.4$ nm. The surfaces could be
squeezed to lesser thickness. Knowing that the
linear dimension of a water molecule is $\sim 0.25$
nm (3), the thickness of the resulting aqueous
films amounted to on the order of 5 to 20 water
molecules, although it is not clear that mole-
cules were distributed evenly across this space.
In our shear measurements, the sinusoidal shear
deformations were gentle, the signifi-
cance of the resulting linear response being that
the act of measurement did not perturb the
equilibrium structure (linear responses were
verified from the absence of harmonics). Using
methods that are well known in rheology,
from the phase lag and amplitude attenuation,
these were decomposed into one component in
phase (the elastic force, $f''$), and one compo-
ent out of phase (the viscous force, $f'$) (25).
The main portion of Fig. 1 illustrates responses at
a single frequency and variable thickness. The
shear forces stiffened by more than an order of
magnitude as the films were squeezed. When
molecularly thin aqueous films are confined
between clay surfaces that are symmetrically
hydrophilic, deviations from the response of
bulk water appear only at lesser separations
(21); evidently the physical origin is different
here. Moreover, at each separation, the elastic
and viscous forces were nearly identical. Again,
this contrasts with recent studies of molecularly
thin water films between surfaces that are sym-
metrically hydrophilic (21). The equality of
elastic and viscous forces proved to be general,
not an accident of the shear frequency chosen.

Physically, these shear responses reflected
the efficiency of momentum transfer between the
moving (hydrophobic) surface and the ad-
joining water films. Figure 2 illustrates the un-
usual result that the in-phase and out-of-phase
shear forces scaled in magnitude with the same
power law: the square root of excitation fre-
quency. This behavior, which is intermediate
between “solid” and “liquid,” is often associat-
ed in other systems with dynamical heteroge-
enity (26, 27). According to known arguments,
it indicates a broad distribution of relaxation
times rather than any single dominant one. In
Fig. 2, shear forces have been normalized in
two alternative ways. The right-hand ordinate
scale shows viscous and elastic forces with
units of spring constant, force per nanometer of
sinusoidal shear motion. Additional normaliza-
tion for film thickness and estimated contact
gave the effective loss modulus $G''(\omega)$, out
of phase with the drive, and the elastic
modulus $G'(\omega)$ (left ordinate), in phase with
the drive, where $\omega$ denotes radian frequency.
The slope of 1/2 is required mathematically by
the Kramers-Kronig relations if $G'(\omega) = G''(\omega)$
(25); its observation lends credibility to the
measurements. The main portion of Fig. 2 il-
ustrates this scaling for an experiment in which
data were averaged over a long time. The inset
shows that the same was observed when other
methods were used to produce a hydrophobic
surface. In all of these instances, $\omega^{1/2}$ scaling
was observed regardless of the method used to
render the surface hydrophobic, but required
extensive time averaging.

It is worth emphasizing that the magnitudes

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Fig. 1. Deionized water confined between a hy-
drophilic surface (A) on one side and a hydro-
phobic surface (B) on the other. The cartoon
is not to scale, because the gap thickness is
nanometers at closest approach and the drop-
let size ($\sim 2$ nm on a side) vastly exceeds the
contact zone ($\sim 10$ μm on a side). The main
figure shows the time-
averaged viscous (circles) and elastic
(squares) shear forces measured at $1.3$ Hz and
$0.3$ nm deflection, plot-
ted semi-logarithmically
against surface sepa-
ration for deionized water
confined between OTE deposited onto mica by means of the Langmuir-
Blodgett technique (shear impulses were applied to this hydrophobic surface). The inset shows the static
force-distance relations. Force, normalized by the mean radius of curvature ($K \sim 2$ cm) of the crossed
cylinders, is plotted against the thickness of the water film ($D = 3$ refers to contact in air) as the spacing
was decreased. The pull-off adhesion at $D \sim 5.4$ nm is indicated by a star. The straight line with slope $K_{eff}/R$
indicates the onset of a spring instability when the gradient of attractive force exceeds the spring
constant ($K_{eff}$), $930$ N m$^{-1}$. After this “jump” into contact, films of stable thickness resulted, whose
thickness could be varied in the range $D = 1$ to $4$ nm by the application of compressive force.

Fig. 2. For the situa-
tion depicted in Fig. 1,
the frequency depen-
dence of the momen-
tum transfer between the
moving surface (hydrophobic) and the
aqueous film with ad-
joining stationary (hy-
drophilic) surface is plotted on log-log
scales. Time-averaged quantities are plotted.
On the right-hand ordinate scale are the
viscous, $g''$ (circles), and
elastic, $g'$ (squares), spring
constants. On the left-
hand ordinate are the equi-
valent loss moduli,
$G''(\omega)$ (circles), and
elastic moduli, $G'(\omega)$ (squares). All measurements were made just after the jump into contact shown
in Fig. 1; that is, at nearly the same compressive pressure, $\sim 3$ MPa. The main panel, representing
Langmuir-Blodgett—deposited OTE, shows $\omega^{1/2}$ scaling after long-time averaging. 0.5 to 1 hour per
data point. The inset shows comparisons with other methods used to produce a hydrophobic surface.
In those experiments, the thickness was generally $D = 1.5$ to $1.6$ nm but was occasionally as large
as $2.5$ nm when dealing with octadecanethiol monolayers. Symbols in the inset show data averaged
over only 5 to 10 min with hydrophobic surfaces prepared with (i) a SAM of OTE (half-filled
symbols), (ii) Langmuir-Blodgett deposition of OTE (crossed symbols), or (iii) deposition of
eptadecanethiol on Ag (open symbols). As in the main figure, circles denote viscous forces and
squares denote elastic forces. Scatter in this data reflects shorter averaging times than in the main
part of this figure (compare Fig. 3).
of the shear moduli in Fig. 2 are “soft,” something like those of agar or jelly. They were considerably softer than for molecularly thin aqueous films confined between surfaces that are symmetrically hydrophobic (21). In repeated measurements at the same frequency, we observed giant fluctuations around a definite mean, as illustrated in Fig. 3, A through C, although water confined between symmetric hydrophilic-hydrophobic surfaces (Fig. 3D) did not display this.

It is extraordinary that fluctuations did not average out over the large contact area (∼10 μm on a side) that far exceeded any molecular size. The structural implication is that the confined water film comprised some kind of fluctuating complex, seeking momentarily to dewet the hydrophobic side by a thermal fluctuation in one direction, but unable to do so because of the nearby hydrophilic side: seeking next to dewet the hydrophobic side by a thwarted fluctuation in another direction; and so on. Indeed, as Weissman emphasizes (28), nearby hydrophobic and hydrophilic surfaces may produce a quintessential instance of competing terms in the free energy, to satisfy which there may be many metastable states that are equally bad (or almost equally bad) compromises (29, 30). This suggests the physical picture of flickering capillary-type waves, sketched hypothetically in Fig. 3E. These proposed long-wavelength capillary fluctuations would differ profoundly from those at the free liquid-gas interface, because they would be constricted by the nearby solid surface.

The possible role of dissolved gas is clear in the context of our proposed physical explanation. Indeed, submicrometer-sized bubbles resulting from dissolved air have been proposed to explain the anomalously long range of the hydrophobic attraction observed between extended surfaces (15–19) and have been visualized by AFM (17, 18). To test this idea, first we performed control experiments using degassed water. The power spectrum (in Fig. 3F) showed the same threshold Fourier frequency when the drive frequency was raised from 1.3 to 80 Hz, and therefore it appears to be a characteristic feature of the system. It defines a characteristic time for rearrangement of some kind of structure, ∼10−2 s; we tentatively identify this with the lifetime of bubble or vapor. The subsequent decay of the power spectrum as roughly 1/10 suggests that these fluctuations reflect discrete entities, because smooth variations would decay more rapidly (28). Noise again appeared to become “white” but with amplitude 104 times smaller at f > 0.1 Hz, but the physical origin of this is not evident at this time. It did not reflect instrumental response, because the power spectrum for water confined between symmetrically hydrophilic surfaces was much less. Whether the fluctuations we observed were actually created by the drive or are also present at equilibrium has not been determined unequivocally, but the linearity of the shear moduli suggests the latter, and theoretical ideas support this (10, 12). The noisy response appears to represent some collection of long-lived metastable configurations whose free energies are similar.

From recent theoretical analysis of the hydrophobic interaction, the expectation of dewetting emerges: it is predicted that an ultrathin gas gap, with thickness on the order of 1 nm, forms spontaneously when an extended hydrophobic surface is immersed in water (5, 10, 12). The resulting capillary wave spectrum does not appear to have yet been considered theoretically, but for the related case of the free water-vapor interface, measurements confirm that capillary waves with a broad spectrum of wavelengths up to micrometers in size contribute to...
Beta-Diversity in Tropical Forest Trees

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The high alpha-diversity of tropical forests has been amply documented, but beta-diversity—how species composition changes with distance—has seldom been studied. We present quantitative estimates of beta-diversity for tropical trees by comparing species composition of plots in lowland terra firme forest in Panama, Ecuador, and Peru. We compare observations with predictions derived from a neutral model in which habitat is uniform and only dispersal and speciation influence species turnover. We find that beta-diversity is higher in Panama than in western Amazonia and that patterns in both areas are inconsistent with the neutral model. In Panama, habitat variation appears to increase species turnover relative to Amazonia, where unexpectedly low turnover over great distances suggests that population densities of some species are bounded by as yet unidentified processes. At intermediate scales in both regions, observations can be matched by theory, suggesting that dispersal limitation, with speciation, influences species turnover.

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Beta-diversity is central to concepts about what controls diversity in ecological communities. Species turnover can reflect deterministic processes, such as species’ adaptations to differences in climate or substrate, or it can result from limited dispersal coupled with speciation, delayed response to climate change, or other historical effects. Perhaps more important, beta-diversity is as important as alpha-diversity for conservation, because species turnover influences diversity at large scales. Recently, Hubbell (7) and Harte et al. (2, 3) have derived theories relating species turnover with distance to species-area relations and total species richness. In very rich forests of the neotropics, these theories may allow us to interpolate species turnover and estimate species distributions and diversity at scales relevant to conservation even with the sparse data from forest plots that are currently available.

To measure beta-diversity and test factors influencing it, we identified all trees in 34 plots near the Panama Canal, 16 plots in Ecuador’s Yasuní National Park, and 14 plots in Peru’s Manu Biosphere Reserve (4–7). All plots were in terra firme, or unlogged, forests. Over 50,000 trees ≥10-cm stem diameter were tagged, measured, and sorted to morphospecies. The similarity between two plots was measured three different ways: Sørensen’s and Jaccard’s measurements of the fraction of species shared and the probability F that two trees chosen randomly, one from each plot, are the same species (8). The Sørensen and Jaccard indices weight all species equally; F is influenced primarily by common species. We used the overall decay of similarity in species composition with distance as a measure of beta-diversity (9).

References and Notes

24. As reviewed by E. Kokkoli and C. F. Zukoski, J. Colloid Interface Sci. 230, 176 (2000), equilibrium force-distance interactions between opposed hydrophobic and hydrophilic surfaces have also been studied, in other systems by other researchers.
31. X. Zhang, Y. Zhu, S. Granick, data not shown.
33. M. Grünze, personal communication.
34. R. K. Thomas, personal communication.
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