Long-Range Attraction between Charge-Mosaic Surfaces across Water

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We have measured directly the forces across water between hydrophilic surfaces covered with a random mosaic of positive and negatively charged domains. We find a strong, long-ranged attraction between them. Analysis of the AFM micrographs reveals a series of irregular patches or rafts of uniform thickness ranging ca. 50–400 nm, and are surrounded by a continuous bilayer raft—due to an Euler-like spring instability driven by vdW attraction—from short range (ca. 4 nm, Table I) into adhesive contact [3,9]. Following this, the lens-mounted mica surfaces were removed and coated as described [5], remounted in the SFB, and forces between them were measured again at increasing immersion times. We consider first interactions across water with no added salt, Fig. 2(a) [10]. The interactions at short times between the initially smooth, hydrophobic layers [Fig. 2(a), open symbols] are, as expected, [11] long-ranged and strongly attractive, jumping from separation $D_j$ into contact at separation $D_0$.

Forces were subsequently measured following progressively longer immersion in water, as shown by the filled symbols in Fig. 2(a) and in part A of Table I. The remarkable feature of these profiles is that, despite the progressive breakup of the originally smooth monolayers into a hydrophilic mosaic of positive and negative charges [as in Fig. 1(c)], their interactions remain attractive and long ranged, indeed even slightly longer ranged than prior to

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the breakup. This is emphasized also in Table I which summarizes the separations $D_j$ from which jumps-in to contact occur. We note that the contact separation $D_0$ to which the surfaces jump under the long-ranged attraction is correlated with the state of the surfactant layer (Table I). $D_0$ values for jumps-in after short immersion of the surfaces in water, when the monolayers are still uniform and smooth, correspond to some twice the monolayer thickness, as expected for monolayer-monolayer contact. At later times, corresponding to the development of the raft-like bilayer structure as typified in Figs. 1(c) or 1(d), the $D_0$ values increase to some 4 times the monolayer thickness, as expected for bilayer-bilayer contact.

FIG. 1 (color online). (a) Advancing contact angle $\theta$ of a water droplet on the mica surface: $\triangle$—immersion in water; $\Delta$—immersion in aqueous 0.01 M NaCl; $\bullet$—immersion in water for mica incubated for 30 sec [rather than 2 h [5]] in the surfactant solution. Mica sheets were never reimmersed: each data point corresponds to a new mica sheet [7]. (b) Tapping-mode AFM images (fluid cell, Nanoscope III, Digital Instruments) of a coated mica surface under water [30 sec incubation in surfactant solution [5]], 5 min after coverage of the surface by the water. Dark areas are holes, 1.5 ± 0.2 nm deep, in the surfactant monolayer. (c) As (b), but following 30 min immersion in water. (d) Coated mica following 11 min immersion in 0.01 M NaCl, showing similar bilayer islands to (c), with cross section indicated below image. Bottom cartoon: the initially smooth monolayer [left, as in (b)] rearranges on immersion in water or 0.01 M NaCl to patches of bilayer [right, as in (c), (d)] which bear a net positive charge, surrounded by the negatively charged bare mica.

FIG. 2. SFB-measured force-distance profiles $F(D)/R$ vs $D$ between curved mica surfaces (mean radius of curvature $R$) a closest distance $D$ apart as described previously [8,9]. (a) Forces between bare (*) and coated (all other symbols) [5] mica surfaces across water [6], fitted by a DLVO model [[1,2], dot-dashed curves], using parameters of surface potential and effective ion concentration within the range of literature reports [24,27]. $\bigcirc$: profiles taken within 95 min of adding water to the cell [surfaces hydrophobic, Fig. 1(a)]. Filled symbols are recorded between 2 and 17 h after adding water [surfaces hydrophilic, Fig. 1(a)]. The dotted curve is the predicted vdW interaction between the surfaces according to Ref. [13]. The cartoon inset shows the negatively charged mica surface regions on one surface largely facing the positively charged bilayer rafts on the other. (b) As (a) but in aqueous 0.01 M NaCl. The shaded band shows the range of attractions measured in salt-free water from Fig. 2(a), while the data (\bigcirc, \bigtriangleup, \bigtriangledown) are for immersion periods of 40–90 min in the salt solution. The curves are the calculated DLVO double-layer profile for this salt concentration (offset by twice the thickness of a surfactant bilayer) and a surface potential 40 mV, indicating uncompensated charge on the mica surfaces. Inset: profiles in the vicinity of the jump on an expanded scale, showing the DLVO prediction up to the peak where vdW attraction overcomes the double-layer repulsion. The broken curve in the inset indicates the hydration repulsion observed between charged bare mica surfaces across NaCl solutions of similar concentrations [25,28].
The attractive forces near the point where the surfaces jump spontaneously into contact at surface separation, \( D = D_j \), may be evaluated from the condition at a jump instability (\( \partial F/\partial D_{D_j} = K \)), the normal spring constant. We approximate (\( \partial F/\partial D \)) by \( \delta F/\delta D = K \), where the mean value of \( |\delta D| \) is half the approaching step size \( \Delta D_0 \) (Fig. 2) at \( D = D_j \). Then, since the surfaces jump together from a point between \( D_j \) and \( (D_j - \delta D) \), \( \delta F = K \cdot |\delta D| \) is a lower limit on the magnitude of the attractive force \( F(D_j - \delta D) \) when the separation between the surfaces is \( D = (D_j - \delta D) \). Putting \( K = 160 \text{ N/m} \) and \( \delta D = (\Delta D_0/2) = ca.6 \text{ nm} \), we find \( F(D_j - \delta D) = -10^{-6} \text{ N} \). This is some 200 times larger than the expected nonretarded van der Waals attraction \( F_{vdw}(D_j - \delta D) = -(AR/6D_j^2 - \delta D^2) = -5 \times 10^{-9} \text{ N} \) [where \( A = 1.5 \times 10^{-20} \text{ J} \) is the Hamaker constant for hydrocarbon-coated mica surfaces across water [3]]. In practice the van der Waals forces at these values of \( D_j \) will be retarded [3], and therefore much lower still, so our measured attraction at \( D_j \) between the charge-mosaic surfaces is at least 3 or more orders of magnitude larger than the expected vdW forces at that separation.

What is the origin of this behavior, where hydrophilic surfaces covered by domains of positive and negative charges experience a strong, long-ranged attraction for each other across water? We attribute the attractive forces to a correlation between oppositely charged domains on the interacting surfaces as they face each other. Such a correlation, we believe, may develop as the charged bilayer rafts on each surface adjust their position when they approach [12], driven by the lower free energy associated with such a configuration, so that positively charged regions on one surface face mostly negatively charged bare mica surface regions on the other [cartoon inset to Fig. 2(a)]. We note that strong attraction across aqueous media has long been known between hydrophobic surfaces [as for the open symbols in Fig. 2(a)], often hydrophobized with self-assembled layers of amphiphilic surfactant molecules in a solution of the surfactant [11]. Explanations of the hydrophobic attraction have ranged from an adsorption-instability model [13] of surface attractions within surfactant solutions [14,15], to conjectures that it may be associated with electrostatic attraction [16,17] between surfaces with mixed charges [15,18–22]. Our mosaic-charge surfaces are clearly hydrophilic rather than hydrophobic and so differ conceptually from the earlier work [11]: the present study unambiguously demonstrates the strong, long-ranged attraction that is possible between surfaces covered by domains of mixed charge.

Models of interactions between mixed charge domains in salt solutions indicate an attraction whose range depends on both domain size and the Debye screening length [19–21,23]. A configuration quite similar to ours was treated in Ref. [23], evaluating the interaction between two overall-neutral surfaces bearing positively and negatively charged domains of radius \( P \) (with positive domains on one surface facing negative domains on the other). The resulting predicted long-ranged attraction across water has a magnitude at large surface separations \( D \) decreasing exponentially as \( e^{-D/\delta} \), with a decay length \( \delta = [k^2 + (C/P^2)]^{-1/2} \), where \( k^{-1} \) is the Debye screening length across the aqueous medium between the surfaces, and \( C \) a constant of order unity (depending on the precise shape of the charged domains). The range of the attraction is then determined largely by the shorter of \( k^{-1} \) or \( P \). In our experiments the charge domains [Figs. 1(c) and 1(d)] vary in size and shape, so that \( P \) is not precisely defined, but it is noteworthy that the range \( 50 \pm 20 \text{ nm} \) (Table I) of the attraction between the charge-mosaic-covered surfaces across water with no added salt, Fig. 2(a), is comparable with the lower size range \( 2P = 50–100 \text{ nm} \) of the positive charge domains, Figs. 1(c) and 1(d). The magnitude of the attraction at the jump positions \( D = D_j \) [Fig. 2(a)] is also comparable with that predicted by this model [23].

To get further insight we measured forces between our charge-mosaic surfaces in 0.01M aqueous NaCl solution, as shown in Fig. 2(b). The surface forces, after immersion times long enough to hydrophilize the surfaces [Figs. 1(a) and 1(d)], are weakly repulsive at larger separations due to a small net residual surface charge, but as they approach, a strong attraction causes the surfaces to jump into contact. Such attraction is very different to the monotonic hydration repulsion (due to trapped hydrated counterions) observed between bare charged mica surfaces across 0.01M NaCl [25,26]. Its range and magnitude, though much stronger and longer ranged than expected from vdW forces [inset in Fig. 2(b)], is strikingly smaller than for the case of the salt-free water [Fig. 2(a), summarized as gray-shaded zone in Fig. 2(b)]. The jump distances \( (D_j \) to \( D_o \), Table I), characteristic of the range of the attractive interaction, are of order \( 6–7 \text{ nm} \), compared with \( k^{-1} \approx 3 \text{ nm} \) in 0.01M NaCl and compared with the attraction range of \( 50 \pm 20 \text{ nm} \) in the salt-free water and with the (lower) values of \( P = 25–50 \text{ nm} \) [Figs. 1(c) and 1(d)]. This crossover of the range of the attraction, from a value similar to the charge domain size \( P \) in salt-free water, to much smaller values compa-
rable with $\kappa^{-1}$ at the higher salt concentration, is in line with expectations [19,23].

In summary, we have shown that two (hydrophilic) surfaces covered by domains of positive and negative charge may attract each other strongly across water: the magnitude of this attraction is at least 3 or more orders of magnitude greater than the van der Waals attraction at surface separations of some tens of nm, a range comparable to the lateral domain mobility of each domain, we estimate (to be published) a lateral domain velocity $v_1 \approx A(\sigma/e)D_1/k_BT f_1(\theta, D)$, where $\sigma$ is the domain area, $A$ is the net charge, $e$ the electron charge, $D_1$ the domain diffusion coefficient of a surfactant molecule on the substrate, and $f_1 = \langle \cos^2 \theta \rangle (4\pi\sigma_0D^4)(-15\cos^2 \theta \sin^2 \theta + 3\cos^2 \theta \sin \theta)$ is the lateral attraction between two dipoles each of moment $\mu$, where $\theta$ is the angle subtended between the dipoles and the surface normal. For typical values of the present configuration we find, for patches of extent 50 nm at surface separation $D = D_1 \approx 50$ nm and $\theta = 450^\circ$, $v_1 \approx O(10)$ nm/sec, which is ample for domain correlation to occur over the jump into contact.

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Note added in proof.—An attractive interaction between charge mosaic surfaces, similar to that published earlier by S. Perkin et al. [11], was reported by E. Meyer et al. [29].

[5] Freshly cleaved mica surfaces were incubated for 2 h in a 0.1% w/w solution of cetyltrimethylammonium bromide (CH$_3$(CH$_2$)$_{14}$N$^+$ (CH$_3$)$_2$Br$^-$) [CTAB; Fluka Puriss, >99%], in water, to emerge smooth, dry, and hydrophobic [Figs. 1(a) and 1(b)].
[6] Tap water was passed through a ROIs$^\text{TM}$ reverse-osmosis stage followed by purification in a Milli-Q Gradient$^\text{TM}$ system: it had a resistivity $\geq 18.2$ M$\Omega$ and total organic content $\leq 4$ ppb. The NaCl used (Aldrich, 99.999%) was UV irradiated for 60 min before dissolution in the water.
[7] Withdrawal from water of the mica sheets removes the upper monolayer of the bilayer rafts, exposing the hydrophobic alkyl tails of the lower layer, resulting in finite contact angles at long immersion times [Fig. 1(a)]. The immersed surfaces fully covered by charged patches are expected to be completely wetted by water.
[10] Interactions between surfaces where monolayers were formed following 30 sec incubation were qualitatively similar to those shown in Fig. 2(a), though of somewhat shorter range [S. Perkin, N. Kampf, and J. Klein, J. Phys. Chem. B 109, 3832 (2005)].
[12] By evaluating the lateral attraction between two oppositely charged domains (effectively dipole domains) together with the lateral mobility of each domain, we estimate (to be published) a lateral domain velocity $v_1 \approx A(\sigma/e)D_1/k_BT f_1(\theta, D)$, where $\sigma$ is the domain area, $A$ is the net charge, $e$ the electron charge, $D_1$ the domain diffusion coefficient of a surfactant molecule on the substrate, and $f_1 = \langle \cos^2 \theta \rangle (4\pi\sigma_0D^4)(-15\cos^2 \theta \sin^2 \theta + 3\cos^2 \theta \sin \theta)$ is the lateral attraction between two dipoles each of moment $\mu$, where $\theta$ is the angle subtended between the dipoles and the surface normal. For typical values of the present configuration we find, for patches of extent 50 nm at surface separation $D = D_1 \approx 50$ nm and $\theta = 450^\circ$, $v_1 \approx O(10)$ nm/sec, which is ample for domain correlation to occur over the jump into contact.
[22] Note, however, that the attraction between opposing domains of mixed charge predicted in Refs. [19,20] is—within the parameters accessible to these studies—comparable to van der Waals attraction, and very much weaker than that measured in our study at separations corresponding to the onset of attraction, Fig. 2(a).
[24] The screening length $\kappa^{-1}$ for interactions between bare mica across purified water with no added salt has been measured in the range up to $120 \pm 20$ nm [e.g., U. Raviv et al., Langmuir 20, 5322 (2004)], corresponding to an effective 1:1 salt concentration $6 \times 10^{-6}$ M, though smaller values have also been measured, as in Fig. 2(a).