Long-Ranged Attraction between Disordered Heterogeneous Surfaces

Gilad Silbert,[1] Dan Ben-Yaakov,[2] Yael Dror,[1] Susan Perkin,[3] Nir Kampf,[1] and Jacob Klein[1,*]

[1]*Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot, 76100, Israel*
[2]*Department of Physics and Astronomy, Tel Aviv University, Ramat Aviv, Tel Aviv 69978, Israel*
[3]*Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, United Kingdom*

Interactions in aqueous media between uniformly charged surfaces are well understood, but most real surfaces are heterogeneous and disordered. Here we show that two such heterogeneous surfaces covered with random charge domains experience a long-range attraction across water that is orders of magnitude stronger than van der Waals forces, even in the complete absence of any charge correlations between the opposing surfaces. We demonstrate that such strong attraction may arise generally, even for overall neutral surfaces, from the inherent interaction asymmetry between equally and between oppositely charged domains.

The surfaces of most materials may become charged when immersed or dispersed in water. Often such surfaces, including surfactant and lipid monolayers or bilayers, or biological surfaces, are overall electrically "neutral," that is, have little or no net electric charge, but may consist of charged domains. Remarkably, as revealed and commented on in several recent studies [1–8], two surfaces each bearing such randomly distributed positive and negative charge patches, but which are overall close to neutral, may experience a long-ranged attraction—ca. 50 nm—across water which is orders of magnitude larger than expected from van der Waals (vdW) dispersion forces. This effect was attributed to the correlation of opposing charge domains: That is, as the surfaces approached, mobile positively charged domains on each of the surfaces were thought to move laterally (with velocities v_{domain}) so as to line up opposite the exposed negatively charged domains, driven by the lower free energy associated with such correlations. Theoretical studies of surfaces bearing patterned charge domains predict a long-range attraction as a result of such net correlations between the domains [8–13]. In the case of quenched disordered heterogeneous surfaces (i.e., random, and uncorrelated), Naji and Podgornik [14] showed that opposing charge domains which are small (relative to the surface separation) resulted in no interaction at the mean-field level.

But does the long-ranged attraction between initially random, opposing charge domains in fact arise from the development of charge correlations as above? Here we directly examine this question by measuring surface forces under conditions designed to frustrate any correlation arising from domain motion on the opposing surfaces. We find that such frustration makes little difference to the forces, showing clearly that domain correlation plays little role in the observed attraction between the surfaces. Rather, we demonstrate that long-ranged attractive forces may arise between random charge patches on opposing surfaces without any need for correlation, due to the unequal nature of repulsions and attractions between equally and between oppositely charged domains.

Heterogeneous surfaces with random positive and negative charge domains were created via the rearrangement with time of an initially uniform self-assembled surfactant monolayer, as shown in Fig. 1 by typical atomic force microscope micrographs. As observed previously with many other surfactants [3–7], the initially smooth monolayer breaks up with immersion time in water into a random mosaic of positively charged bilayers (mean thickness 3.2 ± 0.4 nm) on a background of negatively charged bare mica.
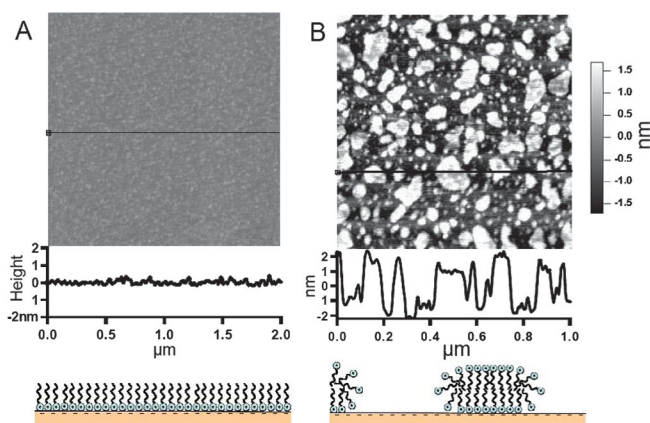

FIG. 1 (color). Surfaces with random charge domains. Atomic force microscope tapping-mode images (Asylum MFP 3D) of the model surfactant octadecyltrimethylammonium bromide $[CH_3(CH_2)_{17}N^+(CH_3)_3Br]$ (a) in air immediately after deposition and (b) after 22 h immersion time in pure water. The cartoons illustrate the breakup of the initially uniform monolayer into positively charged bilayer domains on a negatively charged substrate. For the micrograph shown, the bilayer domains (white, positively charged) cover some 45% of the total area in (b), while those with lateral dimensions >150 nm cover 7% of the total area.

To examine the crucial issue of whether developing
charge correlations were leading to the long-ranged attrac-
tion, we carried out the following: Normal forces $F(D)$
between the two surfaces at closest distance D apart were
determined in a surface force balance in two different
modes, illustrated in the insets A and B in Fig. 2 [15,16].
The first, inset A, termed the straight-approach mode, is the
one used in all earlier studies of surface forces: The surface
separation D is progressively decreased by moving them
normally with respect to each other, to construct the force
vs separation profile $F(D)$. In the second mode, the shear
approach, the surfaces are again made to approach, but
now the sectored piezoelectric tube on which the upper
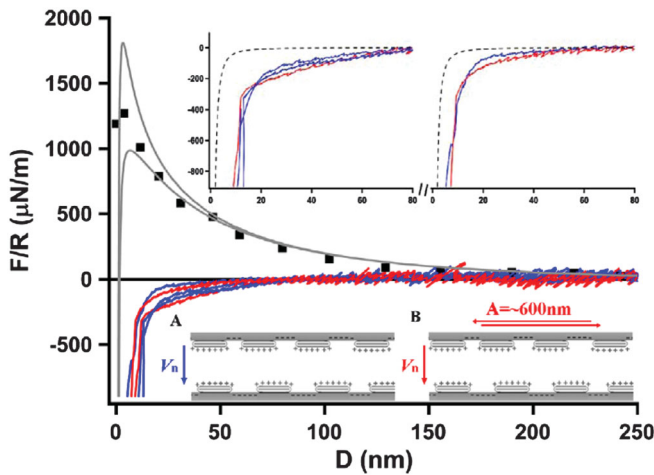surface is mounted is used, during this normal approach, to

FIG. 2 (color).   Normalized force vs distance profiles $F(D)/R$
(where R is the surface radius of curvature) between random
charge-domain-coated surfaces [arising as in Fig. 1(b)] on mica,
carried out both in the straight-approach mode (blue profiles) and
in the shear-approach mode (red profiles), obtained as in
Ref. [15]. Surfaces were immersed for 40 and 43 h in water,
and force profiles from two independent contact points are
shown (typical of many others); the upper insets show the
profiles on a magnified scale, where the broken curves are the
van der Waals interaction alone (Hamaker constant as below).
Consecutive force profiles alternating between shear approach
(red) and straight approach (blue) were carried out at each of the
contact points. Amplitudes of shearing during "shear approach"
were ca. 600 nm or more with frequencies up to 4 Hz resulting in
shear velocities of 3.8–5.1 μm/sec. First approach in both
contact points was carried out by using "straight approach"
(inset A), followed by a shear approach (inset B). A control
profile between two bare mica surfaces (prior to coating with
surfactant) across water is shown (■) and fitted to the solution of
Eq. (1) together with the vdW interaction (with Hamaker con-
stant $A = 2 \times 10^{-20}$ J) under limits of constant potential and
constant charge boundary conditions (lower and upper gray
curves, respectively). The corresponding parameters are surface
potential $\Psi_0 = -117$ mV, Debye length $\lambda_D = 75$ nm, and
surface-charge density $\sigma = e/70$ nm^2. The data points, inter-
mediate between the two curves, suggest boundary conditions
somewhere between these limits.

apply a rapid lateral (shear) motion parallel to the lower
surface (inset B in Fig. 2), over a range of frequencies ν
and amplitudes A. The amplitude A of this lateral motion
(120–600 nm) is much larger than the characteristic size of
the charge domains (from ca. 10–200 nm, Fig. 1). The
lateral velocity $v_s = 2\nu A$ ranges to values (5.1 μm/sec)
that are up to 3 orders of magnitude larger than the esti-
mated value of v_{domain}, the velocity of the charge domains
during their assumed motion to correlation, at the onset of
attraction [4,17]. Such applied lateral motion $v_s \gg v_{domain}$
must thus frustrate any directed translation of the charge
domains on either surface to a correlated configuration
with the opposing charge regions. If indeed therefore it
was the charge correlations postulated earlier that were
leading to the long-ranged attraction in the straight-
approach mode, then the attractive normal interactions
measured by using the shear-approach mode should be
much weaker, and, in particular, they would onset at a
much shorter range. Likewise, as the surfaces come into
adhesive contact, any correlation between the opposing
charges—as on the straight approach—would lead to
larger adhesion energies than with the shear approach
where such correlation is absent.

Several typical surface interaction profiles using these
two modes are shown in Fig. 2, for surfactant-coated
surfaces that had been immersed in water for extended
periods. As clearly seen (and suggested also by an earlier
preliminary measurement [18]), there is no systematic
difference within the experimental scatter at a given con-
tact point between the straight-approach mode (as used in
all earlier studies) and the shear-approach mode designed
to frustrate any formation of a correlated (positive-faces-
negative) charge distribution: Both show the characteristic
long-ranged attraction reported earlier [3–7]. Likewise,
as shown in Fig. 3, there is no systematic difference in
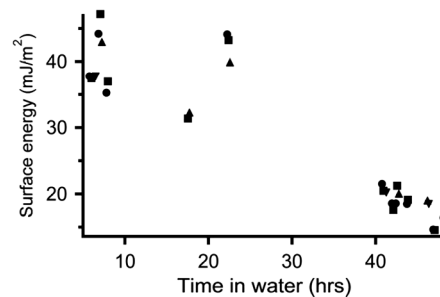

FIG. 3.   Surface energy of the random charge-domain-coated
surfaces (as in Fig. 1). Surface energies are shown as a function
of time in water and of multiple approaches at a given
contact point, for several different contact points and two inde-
pendent experiments, calculated by using the Johnson-Kendall-
Roberts model [33]. Consecutive approaches at a given contact
point are alternately in the straight- and shear-approach modes.
(●) First approach at a contact point. (■) Second entry at a
contact point. (△) Third entry at a contact point. (▼) Fourth
entry at a contact point.

the measured adhesion energy—as determined from the pull-off force—between the two modes of approach. We conclude, unambiguously, that the suppression of correlations does not result in the disappearance of the long-ranged attraction between the surfaces bearing randomly distributed charge domains. If, therefore, correlation is not the reason, what then is the origin of this attraction, which at its onset is a 100-fold larger than can be accounted for by dispersion forces alone?

We attribute the attraction to the asymmetry in the forces between equally and between oppositely charged surfaces across water. This is a counterintuitive observation which, as we show, may immediately lead to strong, long-ranged attraction between random, uncorrelated charge domains, an effect which has not earlier been remarked on. The interaction between two uniformly charged surfaces is well described by the Poisson-Boltzmann (PB) equation, which for a 1:1 electrolyte (in the configuration of our experiment) is given by [19–21] $\frac{d^2\psi(x)}{dx^2} = \frac{2c_0 e}{\varepsilon\varepsilon_0} \sinh\left[\frac{e\psi(x)}{k_B T}\right]$, where $\psi(x)$ is the potential at distance x from the surface, c_0 is the concentration of ions in the bulk solution, ε_0 is the permittivity of free space, ε is the dielectric constant, k_B is the Boltzmann constant, T is the absolute temperature, and e is the electronic charge. This mean-field model, developed for uniform surface-charge densities, has been extensively validated experimentally and has been extended in several directions [22–27]. The pressure between two approaching surfaces can be calculated by integration of the PB equation [28], yielding the net pressure Π after the subtraction of the bulk osmotic pressure:

$$\Pi = c_0 k_B T\left(e^{(-e\psi/k_B T)} + e^{(e\psi/k_B T)} - 2\right) - \frac{\varepsilon\varepsilon_0}{2}\cdot\left(\frac{d\psi}{dx}\right)^2. \tag{1}$$

The first term corresponds to the net osmotic pressure in the gap (repulsive except when the potential vanishes), while the second term corresponds to the Maxwell stress which is always attractive. The equilibrium pressure between two similarly charged surfaces can be obtained by considering Eq. (1) at the midplane of the intersurface gap where the gradient of potential is equal to zero; thus, the only contribution to the pressure is the osmotic term. However, for two oppositely charged surfaces, the Maxwell stress never vanishes at finite separations. This result implies that two oppositely charged surfaces across water may attract more than two similarly charged ones will repel, for the same interacting areas, absolute surface-charge densities, and separations. This conclusion arises because of the qualitatively different mechanisms of repulsion and attraction across water between equally charged and oppositely charged surfaces, respectively. The former may be viewed as due to the osmotic pressure of trapped counterions at the midplane, while the latter may be seen as arising from the entropy gain upon release of counterion pairs from within the gap between the approaching surfaces [29].

To demonstrate that substantial long-ranged attraction between heterogeneous surfaces may be expected based on PB even without any correlation of opposing charges, we use a simple heuristic model, illustrated in the inset in Fig. 4, based on the following reasonable assumptions: randomly distributed charged domains on each surface; similar magnitudes of charge density $|\sigma|$ on oppositely charged domains; and a similar total area of the negatively and positively charged domains, for overall neutrality of each surface. We also assume for our model that all domains are substantially larger than the surface separation, enabling the neglect of domain edge effects and allowing us to treat the interactions as between flat uniform charge domains for which the PB equation applies (this is true only for some of the domains, and the relevance of this assumption is considered below).

In such a case—where charge-domain dimensions are much larger than other length scales in the system—the
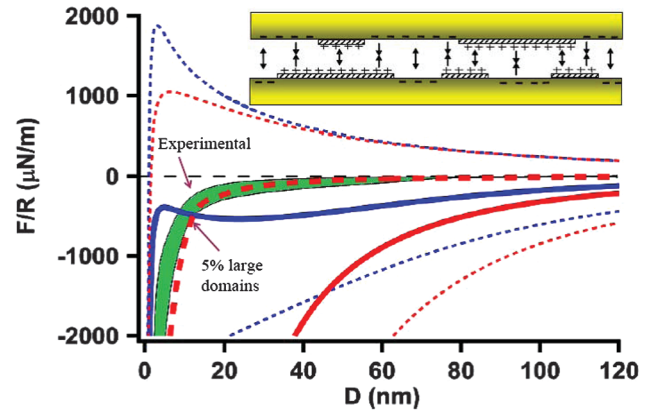

FIG. 4 (color). Numerical solutions for the interaction between two surfaces with uniform and with random charge domains. Results are based on the PB equation (1) combined with vdW attraction, under constant charge (blue curves) and under constant potential (red curves) boundary conditions. The upper (repulsive) broken curves show the interaction between two equally charged surfaces (symmetric interaction). The lower (attractive) broken curves show the interaction between two oppositely charged surfaces (antisymmetric interaction). The thicker smooth curves represent half the sum of both interactions (i.e., symmetric interaction/2 + antisymmetric interaction/2), which corresponds to that expected from our model of random charge domains described in the text. The green shaded region corresponds to the range of experimental attractions in Fig. 2. The inset cartoon illustrates the model, where outward pointing arrows indicate like-like repulsion, and inward pointing ones are like-unlike attraction. The calculations were carried out for a surface-charge density of $|\sigma_+| = |\sigma_-| = 1/70$ nm^2 (constant charge) or for $\Psi_0 = -117$ mV (constant potential), with Debye length $\lambda_D = 75$ nm and Hamaker constant $A = 2 \times 10^{-20}$ J for the van der Waals attraction. The thick broken red curve corresponds to the net interaction, where only 5% of the domains contribute to the interaction, as suggested from the relative areas of the large domains in Fig. 1 (calculated with constant potential BCs [31]).

average interactions per unit area become simply 25% (+ vs +, like/like, repulsive), 25% (− vs −, like/like, repulsive), and 50% (− vs +, like/unlike, attractive), as indicated schematically in the cartoon inset in Fig. 4 and also explained more fully in the Supplemental Material [16].

The dominant electrostatic interactions are then symmetric repulsive (+ vs + and − vs −, with resulting pressures $\Pi_{+/+}$) or antisymmetric attractive (+ vs −; $\Pi_{+/-}$): It may readily be shown analytically that, in the conditions of our experiments, $|\frac{\Pi_{+/-}}{\Pi_{+/+}}| \cong \frac{4}{\pi^2}\ln^2(\frac{D}{8\lambda_D})$ [16,28,30], where $\lambda_D = \sqrt{\varepsilon\varepsilon_0 k_B T/2c_0 e^2}$ is the Debye screening length. This expression was derived under constant charge boundary conditions (BCs), but—as seen in the numerical solutions below (and [16])—the ratio of attractive to repulsive pressure is even higher when constant potential BCs are used.

This is shown in Fig. 4, where the force vs distance profile in our model (inset) is plotted from numerical solutions of the PB equation, under either constant charge or constant potential BCs, incorporating also vdW attraction, using parameters typical for mica in water with no added salt, as for our experiments (Fig. 2). Also plotted (green band) is the spread of experimental profiles from Fig. 2. We see clearly that our model—where there is no charge correlation and repulsive and attractive interactions cover equal areas—does indeed predict a net long-ranged attraction in the absence of any charge correlation (red and blue solid curves), though its range and magnitude are larger than our measured attractions (see below).

Our heuristic PB-based treatment demonstrates clearly the strong long-ranged attraction between opposing, uncorrelated charge domains arising from the $\Pi_{+/-}$ vs $\Pi_{+/+}$ asymmetry detailed above. This general conclusion is quite robust with respect to the assumption of the model [16]. The weaker measured attraction (green band in Fig. 4) relative to the prediction of our model (red curve in Fig. 4) is due, we believe, to the following: As clearly seen in Fig. 1, most of the surfaces are covered by charge patches that are smaller than the surface separation over much of the range of attraction $D < 50$ nm, while in our model all patches are assumed much larger. Such small patches, equivalent to quenched disorder of small charge domains, have been shown to have no effect on the overall interaction at the PB level [14]. Thus the effective area of the charge domains contributing to the attraction (domains larger than ca. 150 nm, say) is much smaller than the full coverage assumed in Fig. 4 (solid red and blue curves); this explains qualitatively the much smaller measured attraction compared to the calculated one. When this is taken into account from the relative area of large domains, Fig. 1, we find a far closer fit to the data (broken red curve in Fig. 4 [31]). The essential point evident from Fig. 4, however, is that there is no need for correlation of opposing charges to explain the strong attraction between randomly charged surfaces that we (and many others [3–7]) earlier have

observed: It can be readily accounted for by using the well-tested PB model [32].

In conclusion, long-ranged attractions between surfaces bearing random charge domains across water, measured under conditions designed to frustrate correlated motion of charges on the opposing surfaces, suggest that these attractions are not the result of correlations developing on approach, as first proposed several years ago. We demonstrate rather that such attractions, between patches large compared with D, arise naturally as the consequence of the Poisson-Boltzmann equation even when the charge domains on the opposing surfaces are disordered and uncorrelated. Our results have clear implications for understanding long-ranged attractions between the large class of surfaces made hydrophobic by surfactant monolayers that subsequently rearrange into positive and negative charged domains (e.g., Refs. [3–8]), but the implications are much broader: They apply wherever interactions between heterogeneously charged surfaces occur, including those ubiquitous in biological systems and in colloid science.

*Jacob.klein@weizmann.ac.il

[1] P. Ball, Chem. Rev. **108**, 74 (2008).

[2] M. U. Hammer, T. H. Anderson, A. Chaimovich, M. S. Shell, and J. Israelachvili, Faraday Discuss. **146**, 299 (2010).

[3] E. E. Meyer, Q. Lin, T. Hassenkam, E. Oroudjev, and J. N. Israelachvili, Proc. Natl. Acad. Sci. U.S.A. **102**, 6839 (2005).

[4] E. E. Meyer, K. J. Rosenberg, and J. Israelachvili, Proc. Natl. Acad. Sci. U.S.A. **103**, 15 739 (2006).

[5] S. Perkin, N. Kampf, and J. Klein, J. Phys. Chem. B **109**, 3832 (2005).

[6] S. Perkin, N. Kampf, and J. Klein, Phys. Rev. Lett. **96**, 038301 (2006).

[7] J. Zhang, R.-H. Yoon, M. Mao, and W. A. Ducker, Langmuir **21**, 5831 (2005).

[8] Y. S. Jho, R. Brewster, S. A. Safran, and P. A. Pincus, Langmuir **27**, 4439 (2011).

[9] R. Brewster, P. A. Pincus, and S. A. Safran, Phys. Rev. Lett. **101**, 128101 (2008).

[10] D. F. Evans and H. Wennerström, *The Colloidal Domain* (Wiley, New York, 1999).

[11] S. J. Miklavic, D. Y. C. Chan, L. R. White, and T. W. Healy, J. Phys. Chem. **98**, 9022 (1994).

[12] Y. H. Tsao, D. F. Evans, and H. Wennerstrom, Science **262**, 547 (1993).

[13] Y. S. Mamasakhlisov, A. Naji, and R. Podgornik, J. Stat. Phys. **133**, 659 (2008).

[14] A. Naji and R. Podgornik, Phys. Rev. E **72**, 041402 (2005).

[15] N. Kampf, D. Ben-Yaakov, D. Andelman, S. A. Safran, and J. Klein, Phys. Rev. Lett. **103**, 118304 (2009).

[16] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.109.168305 for details of surface force balance measurements, surfactant coating, and analytical and numerical results of our model for different salt and surface potential conditions.

[17] S. Perkin, L. Chai, N. Kampf, U. Raviv, W. Briscoe, I. Dunlop, S. Titmuss, M. Seo, E. Kumacheva, and J. Klein, Langmuir **22**, 6142 (2006).

[18] G. Silbert, J. Klein, and S. Perkin, Faraday Discuss. **146**, 309 (2010).

[19] B. V. Derjaguin, N. V. Churaev, and V. M. Muller, *Surface Forces* (Plenum, New York, 1987).

[20] J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic, London, 1992).

[21] J. Lyklema, *Fundamentals of Interface and Colloid Science* (Elsevier, Amsterdam, 1991).

[22] D. Ben-Yaakov, D. Andelman, D. Harries, and R. Podgornik, J. Phys. Condens. Matter **21**, 424106 (2009).

[23] J. Gregory, J. Colloid Interface Sci. **51**, 44 (1975).

[24] B. W. Ninham and V. Yaminsky, Langmuir **13**, 2097 (1997).

[25] L. Onsager and N. T. N. Samaras, J. Chem. Phys. **2**, 528 (1934).

[26] R. Kjellander and S. Marcelja, J. Chem. Phys. **82**, 2122 (1985).

[27] E. Ruckenstein and D. Schiby, Langmuir **1**, 612 (1985).

[28] D. Andelman, in *Handbook of Physics of Biological Systems*, edited by R. S. E. Lipowsky (Elsevier Science, Amsterdam, 1995).

[29] S. A. Safran, Europhys. Lett. **69**, 826 (2005).

[30] D. Ben-Yaakov, Y. Burak, D. Andelman, and S. A. Safran, Europhys. Lett. **79**, 48 002 (2007).

[31] While the BCs are likely to lie between constant potential and constant charge (e.g., square symbols in Fig. 2), the very much larger attraction predicted at small separations between the antisymmetric surfaces for constant potential BCs will swamp the smaller attraction predicted for the constant charge BC. Thus using the constant potential BC is likely to provide an approximately correct prediction even if the actual BCs are mixed. A further indication for this is that at small separations the intersurface forces are largest, and charge regulation—which suppresses potential changes—is more likely.

[32] Our model immediately accounts also for the long-ranged attractions between a *single* surface covered with disordered charge patches and a uniformly charged surface, observed both by us (data not shown) and by others [3].

[33] K. L. Johnson, *Contact Mechanics* (Cambridge University Press, Cambridge, England, 2004).