Self Assembly Modulated by Interactions of Two Heterogeneously Charged Surfaces

R. Brewster,1 P. A. Pincus,2 and S. A. Safran1

1Weizmann Institute of Science, Department of Materials and Interfaces, P.O. Box 26, Rehovot 76100, Israel
2Materials Research Laboratory, University of California at Santa Barbara, Santa Barbara, California 93106, USA

(Received 17 January 2008; published 16 September 2008)

Recent experiments have measured attractive interactions between two surfaces that each bear two molecular species with opposite charge. Such surfaces form charged domains of finite size. We present a theoretical model that predicts the dependence of the domain size, phase behavior and the interlayer forces as a function of spacing and salt concentration for two such interacting surfaces. A strong correlation between two length scales, the screening length and the surface separation, at the spinodal is shown. Remarkably, the first-order phase transition to infinite sized domains depends logarithmically on the ratio of the domain size to the molecular size. Finally, we fit the predicted pressure with experiments.

Measurements of the interactions between “patchy charged surfaces” have shown long-range attraction between surfaces bearing patches of both positive and negative charge [1]. In these experiments, each surface contains positively charged patches of bilayer and negatively charged patches of bare mica. The interactions of two such surfaces may be relevant to the interactions of proteins, which are known to be heterogeneously charged. Additionally, equilibrium domains are of interest in biology where small, mobile domains of particular lipids are believed to control a variety of cellular functions [2].

Theoretical predictions of the domain size and phase behavior of an isolated, patchy charged surface in water were previously reported [3,4]. When the salt concentration is increased so that the screening length is comparable to the equilibrium patch size, a first-order phase transition to a macroscopically separated state occurs [4]. Here, we predict and compare with experiment the equilibrium domain sizes of and interactions between two patchy charged surfaces across water. Our work differs from previous theories [5,6] of the interactions between heterogeneously charged surfaces in that the charged species are mobile and the charge distributions self-assemble to minimize the free energy of the system. Surprisingly, we find that increasing the salt concentration in the water increases the attraction between the surfaces, due to the increase in the equilibrium domain size. We also show that salt and interlayer spacing both induce a first-order phase transition to macroscopic phase separation (that depends logarithmically on the ratio of the domain size to the molecular size) in a similar manner; the opposite charges on one plate screen the charges on the other plate, acting much like a salt.

**Theoretical model.**—The system is modeled as two charged, infinite plates at \( z = \pm D \). We consider the simple case of charged stripes aligned parallel to the \( y \) axis with alternating sign; each plate has a surface charge density that varies in the \( x \) direction only [7]. In the strong segregation limit, the surface charge density is written,

\[
\rho = \sum_{n=0}^{\infty} \frac{4\sigma_0 \sin((2n+1)\pi x)}{\pi(2n+1)} \left[ \delta(z+D) - \delta(z-D) \right],
\]

where \( \sigma_0 \) is the magnitude of the surface charge density. The patches are assumed to be mobile and align with the positively charged stripes on one surface exactly opposite of the negatively charged stripes on the opposing surface and vice versa. This configuration is the minimum energy state and gives an upper bound to the attractive interaction. The opposite limit of a quenched disordered charge distribution has been studied by Naji and Podgornik [8]. The upper limit of the sum, \( n_m \), is related to the ratio of the domain size to the molecular size. Setting \( n_m = \infty \) results in a periodic set of uniform, alternating positive and negative domains with sharp boundaries, while \( n_m = 0 \) is the single mode approximation.

The total free energy is the sum of the free energy due to the line tension between domains and the free energy due to the electrostatics. The free energy per unit area due to the line tension for long stripes in the strong segregation limit is simply \( f_s = \pi q \dot{\tau} \) where \( \tau \) is proportional to the line tension and \( q \) is the wave vector corresponding to the width of the stripes. The second contribution to the free energy is from the Coulomb interactions of the fixed charges on both surfaces and the mobile ions in solution as well as the entropy of the mobile ions. This free energy is written in terms of the dimensionless electrostatic potential [9], \( \phi = e\psi/k_BT \). All lengths are rescaled by the Gouy-Chapman length corresponding to a surface of uniform surface charge density \( \sigma_0 \), \( \mu = 1/2\pi\ell\sigma_0 \), where \( \ell = e^2/\varepsilon T \) is the Bjerrum length. The charge density, \( \rho \), is rescaled by \( \sigma_0/\mu \). Denoting rescaled quantities with a tilde, the free energy is,

\[
\tilde{F}_e = \int d^3 \tilde{r} \left[ \frac{1}{2}(\nabla \tilde{\psi})^2 + \tilde{r}^2(1 - \cosh \tilde{\psi}) + 2\tilde{\rho} \tilde{\psi} \right].
\]
where $\kappa$ is the inverse screening length and is related to the charge density, $n_0$, at the midplane ($z = 0$) by $\kappa^2 = 8\pi n_0 \ell$ and $\kappa = \kappa \mu$. The scaled and unscaled value of the free energy are related by, $F = 8\pi^2 \ell^2 \sigma_0 \bar{F}$ in units of $k_B T$. The rescaled line tension energy per area is $\bar{f}_L = \bar{\tau} \bar{q}$, where $\bar{\tau} = 4\pi \bar{q} \tau$. In the following, all quantities are in these rescaled units and tildes will be omitted.

Minimization of the scaled electrostatic free energy [Eq. (2)] leads to the Poisson-Boltzmann equation [10], $\nabla^2 \phi(f) = k^2 \sinh (\bar{q}) \bar{r}$. The boundary conditions for the case of two surfaces at $\pm D$ with the charge distribution of Eq. (1) fixes, $\partial \phi / \partial z = -\sum_8 8 \sin((2n + 1)qz)/(m \pi)$ at $z = \pm D$ when the charge distributions are exactly out of phase. We solve the Poisson-Boltzmann equation for $\phi$ and minimize the resulting total free energy to predict the equilibrium domain size $\sim q^{-1}$.

Zero salt.—In the case of zero salt, $\kappa = 0$ and the Poisson equation can be solved analytically. The surface, which is macroscopically neutral, does not require any counterions for charge neutralization which allows for counterions to be released to the reservoir, resulting in a considerable gain in entropy [11]. The total scaled free energy per unit area is the sum of the Coulomb interactions and the line tension,

$$f = 2\tau q + \sum_{n=0}^{n_m} \frac{32}{\pi^2} \left( \tanh \left( \frac{(2n + 1)qD}{2} \right) \right)$$

Minimizing Eq. (3) with respect to $q$ predicts the equilibrium condition as a function of $qD$ and $\tau/D^2$ for a particular value of $n_m$. The spinodal, found by setting $\partial^2 f / \partial q^2 = 0$, is the limit of stability of a phase with finite-size domains of alternating charge, to a phase with two, macroscopic plus and minus domains. Figure 1(a) shows the equilibrium value of $qD$ vs $\tau/D^2$ for $n_m = 0$ (lower black), 5 (middle red), $10^4$ (upper blue) plotted up to its minimal value at the spinodal (solid lines). Once the first few modes are included in the sum, the functional form of $\tau/D^2$ vs $qD$ does not change considerably as $n_m$ increases. However, the position of the spinodal (and binodal) points does depend on $n_m$. For the single mode approximation, using only $n = 0$, distinct binodal and spinodal points are found; this is the signature of a first-order transition between finite domain and macroscopic sized domain phases. As $n_m$ increases, both points recede toward $qD = 0$ and $\tau/D^2 = 0.69$. In an ideal case where the charge distribution is completely uniform over each patch, corresponding to $n_m = \infty$, the binodal and spinodal meet at $qD = 0$ and the system undergoes only a second order transition; such a transition was reported by Velichko and de la Cruz [12]. However, the approach of the spinodal and binodal to $qD = 0$ is extremely slow. The inset to Fig. 1(a) shows $qD$ at the spinodal vs $n_m$ (upper black solid line). In fact, an analytic solution for large $n_m$ gives $qD = \pi^2 / 2 \log(16\pi^2 n_m^2)$ (upper black dashed). In real systems, these domains are on order of tens of nanometers. Since the shortest wavelength oscillation of the charge is limited by the number of charged molecules in a domain, an upper cutoff on order of $10^{-2} - 10^{-3}$ is reasonable and the slow approach to a second order transition results in an effective first-order transition for any realistic situation. Furthermore, the steep plateau at $\tau/D^2 = 0.69$ suggests that any form of granularity in the experimental control of $D$ will cause the system to jump to $q = 0$ from a finite value; effectively, for any nonideal system, the phase transition to the separated state is first order. Remarkably, the value of $D$ at the spinodal (for fixed $\tau$) saturates very quickly and larger patches (increases in $n_m$) do not change the position of the transition; however, the patch size at the transition changes with $n_m$, but is logarithmically weak.

For zero salt with $n_m = 0$, the equilibrium domain size of two surfaces with $D \to \infty$ is $q_s = (4/\pi)\sqrt{1/\tau}$. The normalized domain size $q/q_s$ depends only on the parameter $\tau/D^2$. This scaling is shown in Fig. 1(b) for several values of $n_m$. When $D$ is large, the equilibrium value of the domain size approaches $q_s$. It is also interesting to note that the domain size is only weakly dependent on $D$; as the surfaces approach each other, the equilibrium domain size increases by roughly a factor of 2 before undergoing an effective first-order transition to a macroscopically separated phase. This is reasonable since the free energy is simply that of two isolated surfaces with a correction that is only important when $qD = 1$.

In the case of an isolated surface, a first-order transition from a phase with finite-size domains to macroscopic phase transition is only predicted in the presence of a critical amount of salt; for zero-salt, the domain size increases smoothly with $\tau$. However, for the case of two, interacting layers, we find (for some critical value of the interlayer separation, $D$) a first-order transition to macro-

![Graph](128101-2)
scopic phase separation even at zero salt which varies only logarithmically with \( n_m \). This occurs because the two plates screen one another, similar to the role of salt in the case of an isolated layer. In fact, taking \( n_m = \infty \), the value of \( \tau / D^2 \) at the spinodal for zero salt is similar to the value of \( \tau \kappa^2 = 0.81 \) at the spinodal for the isolated surface in the high salt case, where \( \kappa \), the inverse screening length, is analogous to \( 1/D \) [4].

High salt.—We now consider high salt concentrations. Here, the fixed charges are well-screened by the salt ions in solution and the electric field is small. In this regime, we replace the cosh in Eq. (2) by \( \phi^2/2 \). Following the procedure above, the free energy per unit area is,

\[
f = 2\tau q + \sum_{n=0}^{\infty} \frac{32 \tanh(\kappa' D)}{\pi^2 (2n + 1)^2 \kappa'},
\]

where \( \kappa' = \sqrt{(2n + 1)^2 \kappa^2 + \kappa^2} \).

Using the equilibrium condition (\( \partial f / \partial q = 0 \)) to eliminate the \( q \) dependence of the spinodal, we plot the phase diagram using \( \tau / D^2 \) and \( \tau \kappa^2 \) in Fig. 2 for \( n_m = 0 \) (black dotted), 5 (red dashed), and \( 10^4 \) (blue solid). The regions of finite, equilibrium domains are marked “D” and the regions of macroscopic phase separation are marked “M.” When \( D \) is very large, such that \( \tau / D^2 \approx 0 \), the maximum amount of salt is required to observe a phase transition; above \( \tau \kappa^2 = 0.81 \), the transition occurs regardless of separation. As \( D \) decreases, less salt is required to cause separation until a critical value of \( \tau / D^2 \) (which depends extremely weakly on \( n_m \)), at which point no salt is required for the phase transition to occur. When \( \tau \kappa^2 = 0 \), the result from the zero-salt case is recovered for \( \tau / D^2 \) at the spinodal. It is important to note that while the zero-salt solution is recovered when \( \kappa = 0 \) in the Debye-Hückel approximation, the behavior at low salt may deviate when \( \kappa \) is small due to nonlinear effects. When \( \kappa = 0 \) (zero salt), \( \tau \propto D^2 \) along the binodal or spinodal; however, this is no longer the case at finite \( \kappa \). When salt is present, an increase in \( D \) requires a smaller increase in the line tension to remain on the spinodal. In the zero-salt limit, the transition occurs when the domain size is comparable to the separation between the plates. In the limit that \( D \to \infty \) (the one plate limit), the transition occurs when the domain size is comparable to the screening length. In between these two limits, the phase transition occurs when the domains are still smaller than both of these length scales. The relationship between \( \kappa^2 \) and \( 1/D^2 \) at the spinodal is approximately linear over a large portion of the range of \( \tau / D^2 \). As in the case of zero salt, we see a weak, logarithmic dependence of the domain size at the spinodal on \( n_m \) [see the inset of Fig. 1(a)]. The lower (red) solid line is the exact result and the dashed line is the analytic result for large \( n_m \) which is the solution of: \( (q / \kappa) 1/2 \exp [-\pi/(q / \kappa)] = (2^{5/2} \pi^n \kappa_m^2)^{-1} \).

Interactions.—The pressure between two patchy surfaces is, for both zero and high salt

\[
\Pi = \frac{1}{2} \frac{\partial f}{\partial D} = -\sum_{n=0}^{n_m} \left( \frac{n_m}{\pi (2n + 1)^2} \right) 2 \text{sech}^2(\kappa' D) \quad (5)
\]

For \( qD \gg 1 \), the \( \text{sech}^2 \) term can be approximated by an exponential and thus the range of interaction is \( \kappa'^{-1} \); in the zero-salt limit, the range is simply the patch size. Figure 3 (a) shows the pressure versus \( \tau / D^2 \) for varying salt concentrations. The (black) dotted and dash-dotted curves correspond to \( \tau \kappa^2 = 0 \) with \( n_m = 0 \) and \( n_m = 5 \), respectively. The subsequent lower (colored) curves correspond to increasing increments of \( \tau \kappa^2 \) by 0.2. For analytic convenience, we set \( n_m = 0 \) for fits with \( \tau \kappa^2 > 0 \); increasing \( n_m \) does not qualitatively change the results. The curves in Fig. 3(a) are plotted to the spinodal value of \( \tau / D^2 \). The spinodal point is proceeded by a binodal for \( n_m \neq \infty \);

![FIG. 2 (color online). Phase diagram in the high salt limit. The spinodal curve is shown for values of \( n_m = 0 \) (lower black), \( n_m = 5 \) (middle red), \( n_m = 10^4 \) (upper blue). In the region marked “D”, the charges on the plates form finite-sized domains. Above the spinodal, in the region marked “M”, the system is unstable to composition fluctuations and equilibrates to macroscopic phase separation (\( q = 0 \)).](image-url)
therefore, a discontinuous jump in the pressure as the system undergoes a phase transition to \( q = 0 \) and \( \Pi \propto \text{sech}^2kD \) is expected. However, experiments [1] measure an energy, rather than pressure, so this jump would appear as a “kink” in the data. In addition, we find that for fixed separation, as the salt concentration is increased, the force between the plates actually increases. This is counterintuitive; the interactions are electrostatic in nature and one expects higher salt concentrations to screen and hence decrease the interactions. However, this added screening also serves to increase the equilibrium size of the domains on each surface, which increases the attractive interaction between the plates. The pressure is proportional to \( \text{sech}^2(\kappa k^2)/(\tau/D^2) \). The inset to Fig. 3(a) shows that the factor in the numerator of the square root decreases (and the attractive pressure increases) as the salt increases; the decrease in \( (q_1^2) \) always dominates the increase in \( \kappa^2 \). However, this is critically sensitive to the assumption that the domains achieve their equilibrium size and orientation and that the surface remains net neutral. Some experiments observe long-range repulsion when salt is added [1]; this suggests that in these cases, a net residual charge is present which reduces the attractive interactions [6]. This net charge is more pronounced in salt solutions where the presence of salt ions allows the surfactant to desorb more readily into solution.

Figure 3(b) shows a comparison of theory with the experimental data. The black points are data from Meyer et al. [1] which are compared to (i) Poisson-Boltzmann theory for two equal and oppositely charged surfaces as in Ref. [11] (red dotted), (ii) the theoretical result from Eq. (5) with the domain size fixed at \( q = q_s \) (black solid), and (iii) Eq. (5) with equilibrated domains; i.e., \( q \) varies with \( D \) as in Fig. 1(b) (green dashed). The screening length is set to match experimental conditions; in (i) the screening length is \( \kappa^{-1} = 1000 \text{ Å} \) appropriate for water at \( \text{pH} = 5 \) and in (ii) and (iii) we use \( k = 0 \). In each of these fits the Gouy-Chapman length, \( \kappa \), is 16 Å which corresponds to a charge density of one charge every 7 nm\(^2\). This value allows the theory and experimental data to match at small \( D \). However, this value for \( \kappa \) is reasonable; the nominal, fully ionized charge density of mica corresponds to \( \kappa = 0.9 \text{ nm} \); however, some experiments on bare mica-mica interactions indicate the regulated charge density can be 2 orders of magnitude lower, corresponding to \( \kappa = 90 \text{ nm} \) [13]. Additionally, for (ii) and (iii) the line tension is 0.3\( k_BT/\text{nm} \). This small value for the line tension is corroborated by the observed irregular shapes and sizes of domains in experiment. It is encouraging that the fit parameters (\( \kappa \) and \( \tau \)) are the correct order of magnitude; however, the uncertainties in these parameters prevent definitive conclusions. Regardless, several important conclusions can be reached from Fig. 3(b). First, the Poisson-Boltzmann theory for two uniform but oppositely charged surfaces cannot describe the observed behavior. This is true even if one attempts a fit for unequal, but opposite surface charges as in Ref. [14]; this is shown in the inset to Fig. 3(b) for \( \mu_+ = 16 \text{ Å} \) and \( \mu_+ / \mu_- = 5 \) (black solid) and \( \mu_+ = 60 \text{ Å} \) and \( \mu_+ / \mu_- = 2 \) (red dashed), where \( \mu_+ / \mu_- \) is \( \mu \) for the positive or negative surface. For these uniform-charge models, the decay length of the pressure, \( \kappa^{-1} = 1000 \text{ Å} \), is far too long. To fit the data requires an increase in \( k \) by an order of magnitude (corresponding to a 2 order of magnitude increase in the salt concentration). In our theory we have shown how finite-sized patches can provide this additional screening. Finally, because the equilibrated domains data [fit (iii)] do not conform well to the experimental data compared to the fixed domains [fit (ii)], it seems reasonable to conclude that the time scale for rearrangement of the domains is large in comparison with the experimental time scale. Future experiments in which the time scale of approach is reduced may show, at slow enough rates, our predicted first-order transition to macroscopic domains.

We are grateful for discussions with N. Kampf, J. Klein, D. Andelman, and D. Ben-Yaakov. The authors acknowledge support from the US-Israel Binational Science Foundation, ISF converging technologies grant, NSF DMR 0503347 and 0710521 and the Perlman foundation.

[7] The extension of this stripe model to patches with charge modulation in two dimensions is straightforward and does not change the derived scaling relations.