Charged Particles on Surfaces: Coexistence of Dilute Phases and Periodic Structures on Membranes

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We consider a mixture of one neutral and two oppositely charged types of molecules confined to a surface. Using analytical techniques and molecular dynamics simulations, we construct the phase diagram of the system and exhibit the coexistence between a patterned solid phase and a charge-dilute phase. The patterns in the solid phase arise from competition between short-range immiscibility and long-range electrostatic attractions between the charged species. The coexistence between phases leads to observations of stable patterned domains immersed in a neutral matrix background.

Mixtures of cationic and anionic amphiphilic molecules can form thermodynamically stable structures such as micelles, membranes and multilamellar systems. These self-assembled structures have been studied as a function of the molar ratio of the oppositely charged molecules, their concentration in solution, and the ionic strength of the environment [1, 2, 3, 4]. In addition, the presence of other neutral components leads to a large variety of structures and the possibility of local organization on the surface of membranes and monolayers in emulsions. Such structures are important in diverse applications, such as the design bio-sensing devices [6]. Moreover, they serve as model systems for the understanding of cell membranes where structured domains are known to be crucial to cell signaling processes [5]. In multicomponent membranes periodic nanostructures can be immersed in a homogenous background. This letter discusses the possibility of this coexistence of periodic nanostructures with dilute phases of immiscible cationic and anionic molecules. Besides charges on biological membranes, the competition of short range immiscibility and long range attractions leads to the formation of periodic structures in a large variety of systems including lipid mixtures [7, 8, 9, 10, 11], two dimensional uni-axial ferromagnets [12], reaction controled phase segregating mixtures [13], and two dimensional electron gases in MOSFET’s [14].

Phase separation phenomena at surfaces is well known [15, 16, 17] and can be studied through simple models of immiscibility. On the other hand, several recent studies have shown that mixtures of immiscible oppositely charged molecules can form regular periodic nanostructures (or microphases) [18, 19, 20, 21]. To study the convergence of these two phenomena we use analytic techniques as well as off-lattice molecular dynamics simulations of a coarse-grained model with two immiscible charged molecular components. We assume that the membrane surface is in equilibrium and that fluctuations perpendicular to the surface are negligible. To begin with, we explore the phase behavior of this model analytically when the domains are well segregated and periodically ordered. We briefly describe the effect of different charge ratios of the molecules, but concentrate on the effects of the presence of the third neutral component and determine the conditions of coexistence between a microstructured solid and a dilute gas of charges. Secondly, we describe the results of molecular dynamics simulations for intermediate segregation regimes. Simulation results exhibit the expected microscopic phase behavior, but also indicate the limits of our theoretical analysis.

We consider only two possible phases for the system at low temperature. One phase consists of a dense, patterned solid formed by the charged components. Its free energy is computed by assuming the formation of regions of constant particle and charge density. We ignore the fluctuations in the charge density and the shape of the interface. The second phase is homogenous, has a low density of charged particles, and can be treated as a two dimensional charged gas. Its free energy can be calculated at low temperatures using linear response theory by means of the Random Phase Approximation (RPA). The resulting phase diagram is plotted in Fig. 1.

Consider first the calculation of the free energy of the solid phase. The average absolute value of the charge density in this phase is $\pm \psi$, (in electronic charges per unit area), and the line tension between microdomains is $\gamma$. As shown in previous work, the domains form a lamellar structure for near symmetric charge density ratios, while for highly asymmetric cases we have near-circular domains arranged in a hexagonal lattice. The periodicity of both of these possible structures defines a characteris-
tion of the free energy density at that point results on a

In the simulation, their Van der Waals interactions are

necessary to introduce a model of the individual molecules.

results of the molecular dynamics simulations, it is nec-

essary to compare energies with the more dilute ionic gas, and with

molecules from the neutral component. To be able to

expansive cohesive energy per unit area can then be written

in terms of $\epsilon$, with 6 favorable contacts with neighbors.

Using a similar approximation, the effective line tension

is $\sqrt{6}\epsilon/\sigma$. Inclusion of the cohesive energy, leads the final

result for the solid phase as:

$$
\frac{F_s(\rho_{\text{solid}})}{A} = -3\epsilon \rho_{\text{solid}} + 2(s_1 s_2)^{1/2} f_0 / L_0^2.
$$

Next, consider the free energy of the gas phase. RPA

[22] is used to calculate the free energy as a function of

the relative strength of the short range attraction and

the electrostatic interactions. The method involves an

expansion of the free energy of the system in terms of

density fluctuations, neglecting all terms of larger than

second order. For a general system of interacting $i, j$

charged monomers, the partition function is written as

$$
Z = Z_0 V^n \frac{N!}{N_1! \cdots N_n!} \exp \left( - \sum_{k \neq 0} \sum_{ij} \frac{(U_{ij}^{k} + \rho_i^{k-1} \delta_{ij}) \rho_k^{ij} \rho_l^{ij}}{2V} \right) \times \prod_{k > 0} \prod_i \frac{d\rho_k^i}{\pi \rho_k^i}.
$$

Here, $\rho_i$ represents the density of the $i$th component and

$\rho_k$ represents the Fourier transform of the component

densities. $Z_0$ includes the $k = 0$ and self energy terms.

$U_{ij}^k$ is the sum of the interaction energies, consisting of

the short range interactions due to the excluded volume

and hydrophobic interaction, as well as the long range

contributions due to the electrostatic energy. The elec-

trostatic contribution to the internal energy matrix uses

the two dimensional Fourier transform of the screened

Coulomb interaction, $F_{ci}^{ij} = 2\pi z_i z_j L_B (k^2 + \kappa^2)^{-1/2}$. The free energy is then

$$
F = \sum_{ij} \frac{N_i (N_j - \delta_{ij})}{2V} U_{ij}^{0} + \sum_i N_i \ln \frac{\rho_i}{e} + \sum_{k > 0} \left[ \ln \frac{\det[U_{ij}^{k}] + \rho_i^{k-1} \delta_{ij}}{\det[\rho_i^{k-1} \delta_{ij}]} - \sum_i \rho_i U_{ik}^{ii} \right].
$$

The first sum (the $k = 0$ terms) vanishes due to charge

neutrality. The second term is a constant entropic term.
The third term is the electrostatic contribution due to density fluctuations, which is calculated by integrating over the possible values of $k$ from 0 to $2\pi/a$, where $a$ is the molecular size. We neglect terms arising from excluded volume interactions, as the calculation is dominated by the electrostatic terms. We only consider the limit of no screening due to ions in the surrounding solution (matching the conditions of the calculation for the solid phase and for the molecular dynamics simulations).

The electrostatic contribution is found to be,

$$F_{el} = \frac{1}{4\pi} \left[ 2\pi^2 \ln(1 + \frac{a^2}{\pi^2}) + \pi k_t^2 \rho \right]$$

where $k_t^2 = 2\pi l_B(\rho_+ z_+^2 + \rho_+ z_-^2)$. The above equations simplify when considering the charge neutrality constraint, $z_+ \rho_+ = z_- \rho_-$. The total free energy per unit area for the gas phase, in terms of $\rho$ where $\rho = \rho_+ + \rho_-$, is then

$$F_{\text{gas}} = \frac{\rho}{\alpha} \ln \left[ \frac{\rho}{\alpha \rho} \right] + \frac{\rho}{\beta} \ln \left[ \frac{\rho}{\beta \rho} \right] + \frac{F_{el}}{k_B T}$$

where $\alpha = 1 - \frac{2}{\pi} z_+$ and $\beta = 1 - \frac{2}{\pi} z_-$. The virial terms are $\nu_{ij} = -\int e^{-U_{ij}/k_B T} - 1$ where $U_{ij}$ is a hard core potential from $0 < r < \sigma$ and a classic 6-12 Lennard Jones potential from $\sigma < r < 2.5\sigma$.

To determine the phase coexistence of the solid, patterned phase and the dilute gas, we use the common tangent rule. Since the density of the solid phase is assumed fixed, the equation

$$F_S \left( \frac{\rho_{\text{solid}}}{A} \right) = F_{\text{gas}} \left( \frac{\rho_{\text{solid}}}{A} \right) + (\rho_{\text{solid}} - \rho) \frac{\partial F_{\text{gas}}}{\partial \rho}$$

is solved for the gas phase density $\rho$. We plot the two phase coexistence line calculated in this way, for low temperatures, in Fig. 1. The figure refers to the case of equal charge density $z_+ / z_- = 1$. The phase diagram shape depends on course of the relative strengths of the Coulomb interaction (through the charge density) and on cohesive/immiscibility parameter $\epsilon$. With increasing strength of the electrostatics, the transition points occurs at lower temperatures, while increasing values of the short range interaction increase those temperatures. At higher values of the density, nonlinear corrections to RPA including short range correlations and ion association [24, 25]. Fig. 1 sketches an extrapolation of the results to higher temperatures when the solid phase retains its near constant density.

To explore higher temperatures and the effects of fluctuations, we carried out a set of molecular dynamics simulations. The model systems used are composed, in the symmetric case, of a mix of $N_+ = 1000$ positively charged and $N_- = 1000$ negatively charged units in a simulation box of size $D^3$, with $D = 66\sigma$. In the asymmetric case we used $N_+ = 900$ and $N_- = 300$ units with charge (-3). The molecules are confined to a plane perpendicular to the $Z$ axis, with periodic boundary conditions in the $X$ and $Y$ directions. The molecular dynamics simulations, with constant $N, V, T$ were performed using the Espresso simulation code of the MPPI-Mainz group of Polymer Theory and Simulation [22]. We explored regions of the phase diagram at surface densities of $\rho = \frac{(N_+ + N_-)\pi^2}{4D^2} = 0.36$. The potential between charges is a Coulomb potential, $U_C = \frac{l_B}{4\pi\epsilon_0}\frac{q_+ q_-}{r}$. Further parameters are as described in detail in previously published work [22]. Late-time snapshots of the simulations are shown in Fig. 2. To compare the behavior observed in the simulations to our theoretical results, we point out that the simplest extrapolation of the results from the strong segregation limit to higher temperatures, consist on identifying the characteristic length scale of system (the size of microdomains), up to a constant, with the form $L = (\gamma/(l_B \psi^2))^{1/2} \sim (\epsilon/(l_B \psi^{3/2}))^{1/2}$. To use this expression for extrapolation, we abandon the assumption of a solid phase density fixed by the molecular radius, but take $\psi$ as the density determined by the simulation at finite temperatures. All our simulations exhibit the same expected behavior. At small values of $\epsilon$ or low Bjerrum lengths (high temperature), positive and negative regions develop on the surface and as the temperature decreases the domains increase in size. In all the simulations, the individual molecular components exhibit a hexagonally close-packed structure (as was assumed in our analytical approach), with density fluctuations dependent on the temperature. For asymmetric charge ratios, $z_+ / z_- = 1/3$, we show in Fig. 2a the formation of a
hexagonally patterned 'island' at $\rho = 0.10$. For larger densities, as in Fig. 2b, the solid phase occupies a larger fraction of the space, but exhibits more clearly the ordering.

Next, as shown in Fig. 2c-d, for symmetric charge ratios, $\frac{z^+}{z^-} = 1$ the preferred microstructure is lamellar. At the values of the parameters used, we observe as well the phase separation between solid patterned and neutral regions. The temperature decrease from snapshot $c$ to $d$, clearly modifies the fluctuations of both types of interfaces: between charged regions, and between the solid and neutral phases. At lower temperatures (Fig. 2d) the interfaces are much sharper and exhibit lower shape fluctuations. In these simulations, a note and an interesting feature of the solid-gas interface: the orientation of the lamella is perpendicular to the interface. While the charged domains have symmetric interactions with the neutral region, the alignment must be a result of minimization of the local electrostatic energy. To some extent, this feature also appears in the asymmetric case, Fig. 2a-b, where both charged domains appear at the interface with the neutral domain.

For symmetric charge ratios, but for weaker electrostatic interactions, Fig. 2e-f show the transition from a solid to a solid-gas coexistence phase. At low values of the cohesive energy $\epsilon$ the system shows the lamellar patterning but has large voids between the charged domains; the neutral component is attracted to the interfaces where it can reduce the effective line tension between domains. On further increase in the cohesive parameter, the coexistence region is reached, and the neutral regions segregate to form their own phase, as shown in Fig. 2f. The lower values of the Bjerrum length in these cases produce larger lamellar sizes, compared with those of Fig. 2c-d.

To study the behavior of the domain size (lamellar width) in the symmetric case, we have determined the structure factor $S(\vec{k}) = \langle \rho \rho_{-\vec{k}} \rangle$, the Fourier transform of the correlation function of the charged components, for the late stages of a number of simulations with different values of the interaction parameters. $S(\vec{k})$ displays a peak at values $k^*$ corresponding to the inverse lamellar spacing in the direction perpendicular to the lamellas, and thus must scale as $k^* \sim (\epsilon/(l_B\psi^{3/2}))^{-1/2}$. Indeed, in our simulations, we find that the position of the structure factor peak can be fit through a line of slope $-0.47 + /-0.02$ when plotted against the group $\epsilon/(l_B\psi^{3/2})$, as shown in Fig. 3.

By use of analytic techniques, combining RPA and strong segregation theory, as well as off-lattice molecular dynamics simulations we have demonstrated the clear possibility of coexistence of structured regions, made of charged components, in a matrix rich in neutral components. The competition between immiscibility tendencies between molecules, against the attractive interactions between oppositely charged species, provides a method to generate well-controlled, self-assembled surface patterns. Furthermore, suitable extensions of the results from the strong segregation limit to higher temperatures provide a clear way to quantitatively address the properties of these materials in practical regimes.

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