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Attraction and Novel Phase Behavior between Like-Charged Polymer Layers

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Driving highly concentrated solutions of mesoscopic particles to self-assemble into ordered arrays, or colloidal crystals, has been the goal of a number of recent experiments.[1,2] Given the potential that these materials hold for fabricating novel optoelectronic devices, theoretical models are needed to highlight pathways for creating ordered colloidal arrays. Our work pinpoints one possible pathway. Here, we consider the interaction between two surfaces that are covered with identically charged polymers or polyelectrolytes. The interactions between these surfaces model the interactions between polymer-coated colloids in solution. When we immerse our system in a poor solvent and bring the layers into contact, we find conditions where similarly charged surfaces actually experience an attractive interaction. Furthermore, we find that the structure of the anchored polyelectrolyte layer can be abruptly altered by compressing the two surfaces. Namely, charged, stretched layers will collapse into distinct aggregates, or "pinned micelles",[3−5] when the chains are confined between the walls. This structural transformation constitutes a novel first-order phase transition. The resulting micelles effectively drive the surfaces into closer contact, despite the overall electrostatic repulsion between the interfaces. These findings provide new guidelines for creating colloidal crystals through self-assembly.

To carry out our investigations, we employ two complementary theoretical techniques, scaling theory and two-dimensional self-consistent field (2D SCF) calculations. Scaling theory yields explicit relationships between the structure of the anchored layer and the characteristics of chains and surrounding solvent. On the other hand, the 2D SCF calculations allow us to visualize these complex morphologies. Since the interactions between polymer-coated surfaces are commonly governed by the microstructure of the individual layers, we first use these methods to determine the equilibrium morphology of a polyelectrolyte layer on a single surface and then examine the effects associated with compressing two surfaces.

We consider homopolymers that are anchored by one end onto an inert, planar substrate. The chains are grafted at relatively low densities and the system is immersed in a poor solvent. The area per chain is given by the parameter s.[6] Each chain contains $N \gg 1$ segments and the unit of length is the diameter of a monomer, or a. The parameter τ is a measure of the relative deviation from the theta temperature, Θ, and is given by $\tau = (\Theta - T)/\Theta$. Here, we assume that $\tau N^{1/2} \gg 1$. The chains are flexible so that the Kuhn length $= a$. The degree of ionization per chain is specified by α. That is, each chain has $q = \alpha N$ immobilized charges and produces an equal number of q mobile counterions in the solution, which is assumed to be salt-free. We also assume that the Bijerrum length $l_B = e^2/\epsilon kT = a$, which is typical for flexible, water-soluble polymers. Here, e is the unit of elementary charge and ϵ is the dielectric constant of the solvent.

When neutral homopolymers ($\alpha = 0$) are sparsely grafted to a surface in a poor solvent, the chains self-assemble into pinned micelles to avoid the energetically unfavorable solution. The pinned micelles are composed of a dense core, whose radius is $R = (fN/\tau)^{1/3}$, and stretched "legs", which anchor the micellar core to the surface. The equilibrium characteristics of a pinned micelle containing f chains are determined by the balance of the surface free energy (per chain) of the core, ΔF_{surf}, and the free energy associated with the elastic stretching of a leg, ΔF_{leg}. The ΔF_{surf} term arises from the surface tension (which is proportional to τ^2) at the boundary between the core and the solvent, and is given by $\Delta F_{\mathrm{surf}} = \tau^2 R^2/f$. Since the lateral size of the micelles is $D = (fs)^{1/2}$, then $\Delta F_{\mathrm{leg}} = \tau D = \tau(fs)^{1/2}$. The free energies are measured in units of kT and all numerical coefficients have been omitted. Minimizing the sum of $\Delta F_{\mathrm{surf}} + \Delta F_{\mathrm{leg}}$ with respect to f yields the equilibrium dimensions of a neutral pinned micelle:[3,4]

$$f_o = N^{4/5}\tau^{2/5}/s^{3/5}; \quad R_o = N^{3/5}/(\tau^{1/5}s^{1/5}); \quad D_o = N^{2/5}\tau^{1/5}s^{1/5} \tag{1}$$

The presence of charged groups within the chains leads to an additional free energy contribution, ΔF_{elec}, which arises from the electrostatic interactions between charges and the translational entropy of the mobile counterions. When α is small, the attraction between the charged core and the mobile counterions is insufficient to localize the ions in the vicinity of micelles; thus, the micelles are weakly charged. An increase in α leads to the localization of the ions near the cores and a partial screening of the Coulomb repulsion. The onset of counterion condensation occurs at $\alpha = \alpha_o$, the point at which the net charge of the core, $Q = \alpha fN$, equals the radius of the core, R, or $Q = R$.[7] At $\alpha \gg \alpha_o$, the majority of the counterions are trapped inside the cores and only a fraction of the counterions, $\approx R/Q$, are still found outside the micelles.

For significantly poor solvents, or $\tau \leq 1$, the charged micelles are still described by the scaling dependences in eq 1.[8] Thus, $\alpha_o = R_o/f_oN = s^{2/5}N^{-6/5}\tau^{-3/5}$, which is significantly less than 1. Consequently, the condensation threshold is quite low and the counterions are primarily localized within the pinned micelles.

The trapped counterions give rise to a contribution $\Delta F = N\alpha\ln(\alpha\tau)$ and create an osmotic pressure that partially swells the core. Eventually, the osmotic pressure produced by these trapped counterions disrupts the micelles and transforms the patterned layer into a laterally homogeneous swollen brush, which has a

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thickness[7,9] $H = N\alpha^{1/2}$. The point at which this transition occurs, α^*, is determined by equating the chemical potentials of the chains in a micelle, μ_c, and in a homogeneous layer, μ_s. In a micelle, the major contributions to μ_c arise from the polymer−polymer attractions and the translational entropy of the trapped counterions, yielding $\mu_c = -N\tau^2 + \alpha N \ln(\alpha\tau)$. In a swollen layer, μ_s is determined by the elastic stretching of the chains and the translational entropy of the mobile counterions, yielding $\mu_s = H^2/N + \alpha N \ln(\alpha N/sH)$. Substituting $H = N\alpha^{1/2}$ into the expression for μ_s, and equating μ_c and μ_s, we obtain[10] (neglecting logarithmic prefactors) $\alpha^* = \tau^2$ and thus, the height of the layer at α^* is $H^* = N\tau$.

The interaction between two such polyelectrolyte-coated surfaces is expected to be different for the $\alpha < \alpha^*$ and $\alpha > \alpha^*$ regimes. At $\alpha < \alpha^*$, the surfaces are covered with pinned micelles at all plate separations h. Since the counterions are predominantly condensed within the micelles, the initial repulsion between the surfaces due to noncondensed counterions is rather weak. As in the case of neutral polymers,[3,11] when the layers are brought into contact, micelles from the opposite surfaces merge at $h = D_o$, and this merger gives rise to an attractive minimum.

The situation is qualitatively different at $\alpha > \alpha^*$. Here, the surfaces are covered by swollen brushes at infinite plates separations. Compression of the layers leads to entropic losses with respect to the counterions. At a critical deformation h^*, the attractive polymer−polymer interactions will overwhelm the entropic contribution and the homogeneous, dilute layers abruptly transform into collapsed, pinned micelles. This transformation constitutes a first-order phase transition and is accompanied by a significant redistribution of the polymer segments and counterions (as will be seen in Figure 4). The value of h^*, the critical separation where the transition occurs, is obtained by equating the chemical potentials μ_s and μ_c. By introducing the reduced variable $\beta = h^*/H^*$, we can write $h^*(\alpha)$ in the following form

$$\alpha/\alpha^* = [\gamma - (1 - \beta^2)/2]/[\gamma + \ln(\beta)] \qquad (2)$$

where $\gamma = \ln(\tau^2 s) > 1$ and all the prefactors have been retained. Equation 2 determines the phase boundary between the two states of the system, pinned micelles vs a homogeneous layer, for both undeformed ($\beta = 1$) and compressed ($\beta < 1$) layers. As can be seen from eq 2, β is a decreasing function of α, i.e., a stronger compression is necessary to cause the formation of pinned micelles at higher values of α. When the layers are compressed further, micelles from the opposite surfaces again merge at $h = D_o$. (Note this merger also constitutes a first-order phase transition.) This behavior gives rise to a local minimum, which finally disappears with further increases in α (as can be seen in Figure 2 below).

To complement our scaling predictions and illustrate the above findings, we use a 2D SCF model extended to charged polymers.[12] Our SCF method is derived from the theory developed by Scheutjens and Fleer.[13] In this treatment, the phase behavior of polymer systems is modeled by combining Markov chain statistics with a mean field approximation for the free energy. Given the probability of finding a single monomer at a particular site and the fact that all the monomers in a chain are connected, the statistics for chains of arbitrary length can be obtained through a series of recursion relations. These recursion relations involve the potential of mean-force acting at a site **r**. This potential, in turn, is determined from the local distribution of all the components at the point **r**, as well as the Flory−Huggins interaction parameters, or χ's, between the different components. For charged polymers, an additional contribution to the potential arises from the electrostatic interactions between different species.[12] Solving this series of equations numerically and self-consistently yields the equilibrium profiles for all the components in the system.[13] In the 2D SCF theory, the equations are written explicitly in terms of both the vertical (Z) and lateral (Y) directions. We assume that all the quantities are translationally invariant in the **X** direction. As a consequence, the pinned micelles assume a cylindrical geometry. Though the micelles are roughly spherical in three dimensions, it is anticipated that the SCF theory will nonetheless capture the qualitative, as well as certain quantitative, features of the 3D system.

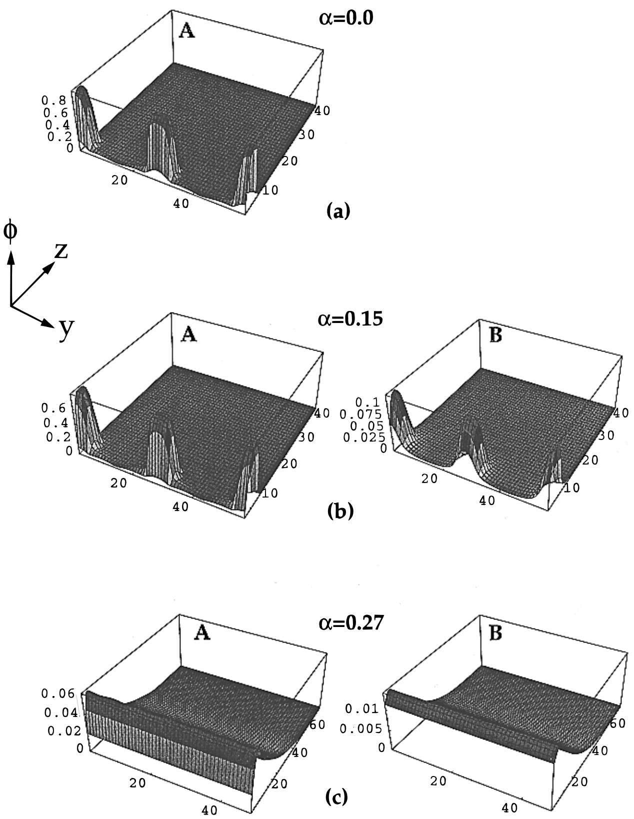

Figure 1. Three dimensional SCF density profiles for the polymer and counterions showing the effect of increasing the degree of ionization, α, for $N = 100$, $s = 100$, and $\chi = 2$. The chains are grafted in the XY plane, the Z direction lies perpendicular to the surface, and ϕ denotes the polymer (A) or counterion (B) density. In part a, $\alpha = 0.0$, b, $\alpha = 0.15$, and c, $\alpha = 0.27$.

Chains of length $N = 100$ units are tethered at $s = 100$. We model a significantly poor solvent by setting χ, the polymer−solvent interaction parameter, equal to 2. (This χ value corresponds to $\tau \approx 1$ in our scaling model, and here, $\alpha_o \approx 0.01$.) Figure 1 reveals the equilibrium profiles of the polymer and mobile ions at various α values for the single surface case. At $\alpha = 0$ (neutral chains), the polymers form well-defined pinned micelles with dense cores (ϕ, the polymer density, $\approx$0.9). At $\alpha = 0.15$, the counterions are predominantly condensed into the micellar core, resulting in the partial swelling of the core. (The volume fraction of polymer in the cores diminishes, and the total size of the micelle

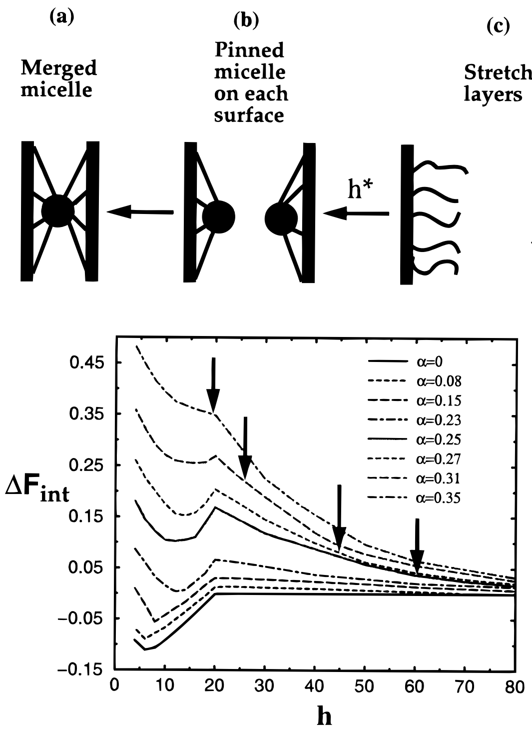

Figure 2. Free energy of interaction as a function of surface separation for $N = 100$, $s = 100$, and $\chi = 2$ and values of α ranging from 0 (no charge) to 0.35 (approximately one charge per three monomers). The vertical arrows in the plot pinpoint the transition from a homogeneous layer to pinned micelles, the transition from (c) to (b) in the scheme above the figure. This transition occurs at h^*. With further compression of the layers, the plots reveal minima, which indicate the merging of the micelles. In other words, the minima represent the transition from (b) to (a) in the schematic.

increases slightly.) At $\alpha = 0.27$, the micelles have been destroyed, and the laterally homogeneous layer is swollen by counterions. (The transition occurs at $\alpha^* = 0.23$ and is accompanied by a drastic change in the polymer concentration.)

Figure 2 shows the interaction free energy, $\Delta F_{\rm int}$, as the two surfaces are brought into contact for various values of α. For small α's, there is an initial increase in $\Delta F_{\rm int}$, which is caused by the osmotic pressure of the noncondensed counterions; this is followed by a pronounced attractive minimum that arises from the merging of micelles from opposite surfaces. This merging is energetically favored since expulsion of the solvent between the two layers prevents polymer−solvent contact at the outer edges and thus gives rises to an attraction at this surface separation.

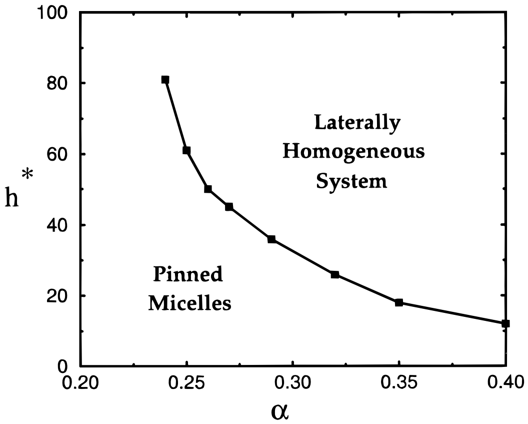

Figure 3. Phase boundary for the first-order phase transition separating the homogeneous layers from the inhomogeneous layer of pinned micelles. For a fixed α and $h < h^*$, the inhomogeneous system is favored over the homogeneous layer.

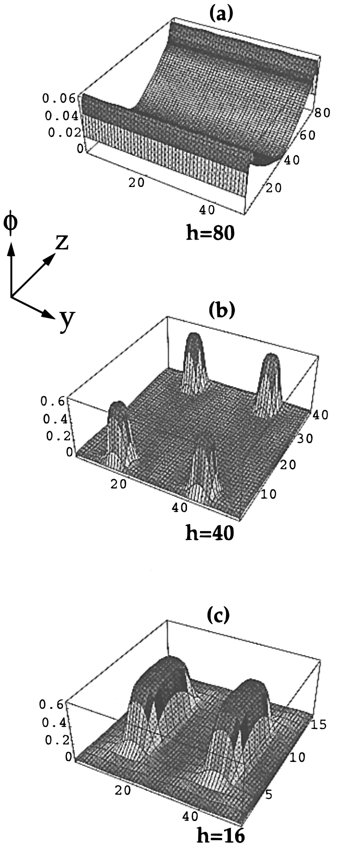

Figure 4. Three-dimensional SCF plots showing the effect of decreasing the surface separation for $N = 100$, $s = 100$, $\chi = 2$, and $\alpha = 0.27$. The parameter ϕ denotes the polymer density. Here, the shape of the profiles for the counterions are qualitatively the same as those for the polymers. (a) At surface separation $h = 80$, the grafted chains form homogeneous layers. (b) At $h = 40$, micelles form on each of the surfaces. (c) At $h = 16$, compression causes the micelles from the surfaces to merge.

An increase in α leads to a corresponding increase in the osmotic pressure of the noncondensed part of the counterions and a decrease in the attractive minimum. However, a nonmonotonic dependence of $\Delta F_{\rm int}$ on h is still evident at rather high values of $\alpha \gg \alpha^*$, where each layer forms a laterally homogeneous, swollen brush. The nonmonotonic behavior is due to a novel effect noted above: the compression of these swollen brushes leads to the formation of the pinned micelles at both surfaces.[14] The region where the pinned micelles appear, as a function of surface separation and α, is marked in Figure 3. Above the boundary, the system forms a laterally homogeneous layer, while below this line, the chains collapse into pinned micelles. This curve was obtained from the SCF calculations and is in agreement with the scaling prediction that h^*, the critical separation where the micelles appear, is a decreasing function of α.

These different morphologies can be visualized from the density profiles obtained through the SCF calculations. The profiles in Figure 4 reveal the laterally homogeneous layer (Figure 4a) at large separations, and the appearance of distinct pinned micelles on each surface as the layers are compressed (Figure 4b). Further compression of the surfaces drives the micelles to merge into larger structures between the plates

(Figure 4c); this merger gives rise to the minimum in the curves for higher values of α.

The positions of the various minima are not affected by the value of α (see Figure 2). For both $\alpha > \alpha^*$ and $\alpha < \alpha^*$ the location of the minimum is determined by the lateral periodicity of the system, D, since the merging of the micelles occurs at $h \approx D$. For values of the parameters examined here, D is not affected by α and, within reasonable accuracy, equals D_o (see Figure 1).

The appearance of the minima in Figure 2 has important practical implications. Our results are applicable to a system of polyelectrolyte-coated colloidal particles; this system will exhibit a similar free energy profile. The relatively sharp minima indicate that there is an optimal separation between the coated particles, and thus, these colloids could form an ordered array. (While the minimum for $\Delta F_{\text{int}} > 0$ represents metastable states, they are nonetheless experimentally accessible and may be long lived.) Thus, our results indicate that by increasing the concentration of these colloids in solution, and thus effectively decreasing the surface separation h, the system can be driven into an ordered state.

Our analysis also indicates that the position of the minimum is governed by the lateral periodicity of the system, D_o, (i.e., by the parameters N and s), while the depth is predominantly affected by the value of α. An additional means of manipulating the depth of the minima is to vary the ionic strength of the solution. Our results demonstrate that attractive and metastable states are expected even in salt-free solutions, where the electrostatic interactions are not significantly screened. By varying the ionic strength, one can effectively decrease the strength of the electrostatic interactions and additionally tailor the interactions between the particles.

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(10) The same scaling dependence applies to the collapsed-to-stretched transition in laterally homogeneous charged brushes; see ref 9.

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(14) In our SCF calculations in Figure 2, the changes in free energy as a function of h are so small that a discontinuity in the slope, which characterizes this first-order transition, is not evident in the figure.

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