

## Adsorption of Polyelectrolytes at an Oppositely Charged Surface

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(Received 30 April 1999)

We develop a scaling theory of polyelectrolyte adsorption at an oppositely charged surface. At low surface charge densities, the thickness of the adsorbed layer is determined by the balance between electrostatic attraction to the charged surface and chain entropy. At high surface charge densities, it is determined by the balance between electrostatic attraction and short-range monomer-monomer repulsion. These different stabilizing mechanisms result in the nonmonotonic dependence of the layer thickness on the surface charge density.

PACS numbers: 61.20.Qg, 61.25.Hq

Macromolecules carrying electric charges, called polyelectrolytes [1,2], constitute one of the most interesting and least understood areas of polymer physics. Charged polymers are widely used in industry and are present in nature. The long-range Coulomb interactions are responsible for both the rich behavior of these systems and the difficulties in developing theory to describe them. While a coherent picture of polyelectrolyte solutions is beginning to emerge [3–6], the behavior of polyelectrolytes near charged surfaces and interfaces is far from being understood [7]. The progress in this direction will have a significant impact on different areas ranging from materials science to biophysics.

The significant fraction of theoretical works dealing with polyelectrolyte adsorption on a charged surface has been carried out within the framework of the self-consistent field method [7]. In these theories the polymer density distribution is coupled with the local electrostatic potential through the combination of the Poisson-Boltzmann equation and the diffusive equation describing the polymer conformations in the effective external potential. It was argued recently [8] that the Poisson-Boltzmann description of the electrostatic interactions is inapplicable to a system containing multivalent ions, the best examples of which are polyelectrolyte molecules. The major drawback of this approach is that it fails to capture the correlations between multivalent ions. These correlation effects can become so strong that the multivalent ions form a strongly correlated Wigner liquid [8,9]; the structure is impossible to obtain within the framework of the classical Poisson-Boltzmann approach. Thus, the newly emerging picture of electrostatic interactions in multivalent systems requires reinvestigation of polyelectrolyte adsorption. In this Letter we develop a scaling theory of polyelectrolyte adsorption at an oppositely charged surface from a dilute salt-free solution. In our model we used new ideas of the strong correlations in polyelectrolyte systems at low polymer concentrations and a related description at higher polymer concentrations in the adsorbed layer.

Consider a flexible polyelectrolyte chain with degree of polymerization  $N$ , fraction of charged monomers  $f$ , and bond length  $a$  in a solvent with Bjerrum length  $l_B =$

$e^2/\epsilon kT$ —the length scale on which the electrostatic interaction between two elementary charges  $e$  in the solvent with dielectric constant  $\epsilon$  is of the order of the thermal energy  $kT$ . In a dilute salt-free solution the charges on the chain interact via unscreened Coulomb potential. This electrostatic repulsion leads to chain stretching on length scales larger than the electrostatic blob size  $D_e$  [10,11]. The conformation of a chain inside the electrostatic blob is almost unperturbed by electrostatic interactions with the number of monomers in it being  $g_e \approx (D_e/a)^2$  for a  $\theta$  solvent for polymer backbone. The size of the electrostatic blob  $D_e$  containing  $g_e$  monomers can be found by comparing the electrostatic energy of a blob  $e^2 g_e^2 f^2 / \epsilon D_e$  with the thermal energy  $kT$ . This leads to the electrostatic blob size  $D_e \approx au^{-1/3} f^{-2/3}$  and the number of monomers in it  $g_e \approx u^{-2/3} f^{-4/3}$  (where  $u = l_B/a$  is the ratio of the Bjerrum length  $l_B$  to the bond size  $a$ ). In the absence of salt the polyelectrolyte configuration is that of a fully extended chain of  $N/g_e$  electrostatic blobs of length

$$L \approx D_e N / g_e \approx au^{1/3} f^{2/3} N. \quad (1)$$

However, the size of this chain in the transverse direction is still Gaussian,  $R_\perp \approx aN^{1/2}$ , due to decoupling of the longitudinal and transversal modes of a chain. The electrostatic self-energy of the polyelectrolyte chain  $W_{pe}$  is proportional to the thermal energy  $kT$  times the number of electrostatic blobs  $N/g_e$  in the polyelectrolyte chain

$$W_{pe} \approx kTu^{2/3} f^{4/3} N. \quad (2)$$

*Multivalent Gouy-Chapman regime.*—Polyelectrolyte chains replace counterions at the oppositely charged surface. The density  $\rho$  of polyelectrolyte chains is almost constant ( $\rho \approx l_B \sigma^2$ , where  $\sigma$  is the surface charge number density) inside the Gouy-Chapman length [12]  $\lambda \approx (l_B f N \sigma)^{-1}$ , for polyions with valency  $fN$ , and decays as  $z^{-2}$  on larger length scales. The thickness  $\lambda$  of the Gouy-Chapman layer of polyions is larger than the average distance between polyions  $R \approx \rho^{-1/3} \approx l_B^{-1/3} \sigma^{-2/3}$  for the surface charge density lower than

$$\sigma_{WC} \approx l_B^{-2} f^{-3} N^{-3}. \quad (3)$$

The classical Poisson-Boltzmann approach works well only in this regime (for  $\sigma < \sigma_{\text{WC}}$ ). The average repulsive energy  $W_{\text{rep}}$  between neighboring polyions

$$W_{\text{rep}} \approx kT l_B f^2 N^2 / R \approx kT (\sigma / \sigma_{\text{WC}})^{2/3} \quad (4)$$

is less than  $kT$  for  $\sigma < \sigma_{\text{WC}}$ .

*Two-dimensional Wigner liquid: Undeformed polyelectrolytes.*—For the surface charge densities  $\sigma > \sigma_{\text{WC}}$  the distance between polyions  $R$  becomes larger than their average distance to the surface  $D \approx \lambda$ . In this regime the strong electrostatic repulsion  $W_{\text{rep}} \gg kT$  between chains forces them to organize into a two-dimensional strongly correlated Wigner liquid [8,9] at the charged surface. To estimate the adsorption energy of a polyion, one can consider an elementary Wigner-Seitz cell of size  $R$  which is determined by the electroneutrality condition  $\sigma R^2 \approx fN$ . The attraction energy of the polyelectrolyte chain with the center of mass located at distance  $z$  ( $z \ll R$ ) from the surface can be estimated as the energy of electrostatic attraction between a charged disk of radius  $R$  and a charge of valency  $fN$ ,

$$W_{\text{att}}(z) \approx -kT (\sigma / \sigma_{\text{WC}})^{1/2} (1 - z/R), \quad (5)$$

where  $\sigma_{\text{WC}}$  is given by Eq. (3). The polyelectrolyte chains are strongly attracted to the surface with the binding energy  $|W_{\text{att}}(0)| \gg kT$  as long as the surface charge density  $\sigma$  is larger than the adsorption threshold value  $\sigma_{\text{WC}}$ . The electrostatic attraction of a polyelectrolyte chain to the charge surface  $W_{\text{att}}(z)$  affects only translational and orientational degrees of freedom of the chain but does not deform the chains in this regime. The polyelectrolytes are localized within the layer of the thickness

$$D \approx (l_B f N \sigma)^{-1}, \quad (6)$$

inside which (for  $z < D$ ) the change of the attraction energy [Eq. (5)] is of the order of the thermal energy  $kT$ . The probability of finding a polyelectrolyte molecule beyond this distance  $D$  is exponentially low [8]. It is interesting to note that this length scale  $D$  is proportional to the Gouy-Chapman length  $\lambda$ .

*Two-dimensional Wigner liquid: Compressed polyelectrolytes.*—Polyelectrolytes lay flat on the surface when the layer thickness  $D$  becomes comparable with the transverse size of a chain  $aN^{1/2}$ . This happens when the surface charge density  $\sigma$  reaches the value

$$\sigma_{\text{def}} \approx a^{-2} u^{-1} f^{-1} N^{-3/2}. \quad (7)$$

At higher surface charge densities  $\sigma > \sigma_{\text{def}}$ , the electrostatic attraction of the charged monomers to the surface perturbs the conformations of the chain. The thickness of a chain in the direction perpendicular to the surface is determined by balancing its confinement entropy  $kT a^2 N / D^2$  inside the layer of thickness  $D$  with its electrostatic attraction  $W_{\text{att}}(D)$  [see Eq. (5)] to the charged surface. This gives the equilibrium thickness of the chain

$$D \approx a^{2/3} l_B^{-1/3} f^{-1/3} \sigma^{-1/3} \quad (8)$$

that is independent of the degree of polymerization  $N$ . A similar power-law dependence of the thickness of the adsorbed layer  $D$  on the surface charge density  $\sigma$  was recently obtained by Borukhov *et al.* [13] in the framework of the Flory-like consideration of polyelectrolyte adsorption and by Borisov *et al.* [14] for polyelectrolyte brushes. Because of strong electrostatic repulsion between chains, they are localized in the centers of the Wigner-Seitz cell separated by distance  $R \gg L$ .

*Two-dimensional Wigner liquid crystals.*—The effects of the anisotropic shape of polyelectrolyte chains become important when the correction to the adsorption energy due to the chain anisotropy becomes of the order of the thermal energy  $kT$ . Because of the symmetry of the problem, the orientation-dependent part of the electrostatic interaction between two neighboring Wigner-Seitz cells starts with quadruple-quadruple interactions. The orientational transition to a herringbone structure (see, for review, Ref. [15]) occurs at the surface charge density

$$\sigma_{\text{orient}} \approx a^{-2} u^{-14/13} f^{-13/15} N^{-7/5}. \quad (9)$$

In the mean-field approximation this is a second order phase transition.

As the surface charge density  $\sigma$  increases further, the size of the Wigner-Seitz cell  $R \approx (fN)^{1/2} \sigma^{-1/2}$  decreases and reaches the size of the polyelectrolyte chain  $L$  at the surface charge density

$$\sigma_L \approx a^{-2} u^{-2/3} f^{-1/2} N^{-1}. \quad (10)$$

The crossover from a dilute to semidilute adsorbed layer at  $\sigma \approx \sigma_L$  does not affect the surface charge density dependence of the layer thickness; it is still given by Eq. (8). At the surface charge density  $\sigma \approx \sigma_L$  the electrostatic self-energy of a chain  $W_{pe}$  [Eq. (2)] becomes of the order of its attraction to the charged surface  $W_{\text{att}}(0)$  [Eq. (5)]. The size of the Wigner-Seitz cell  $R$  is determined by the distance between sections of neighboring chains  $\sigma R^2 \approx f g_R$  with the number of monomers in it  $g_R$  related to its size  $R$  by the equation analogous to Eq. (1),  $R \approx a u^{1/3} f^{2/3} g_R$ . The resulting size of the Wigner-Seitz cell is  $R \approx f^{1/3} / u^{1/3} \sigma a$ . In this regime the adsorbed polyelectrolytes arrange into a two-dimensional layered structure, for which surface charge density  $\sigma$  plays a role of the effective temperature. We will discuss this regime in details in a separate publication. The crossover to the isotropic two-dimensional polyelectrolyte layer occurs at the surface charge density

$$\sigma_{D_e} \approx f a^{-2}, \quad (11)$$

when the size of the Wigner-Seitz cell  $R$  becomes of the order of the electrostatic blob size  $D_e \approx a u^{-1/3} f^{-2/3}$ . In fact, at that point the electrostatic self-energy of the polyelectrolyte chain, its electrostatic attraction to the charged surface, and its confinement energy are of the same order of magnitude ( $W_{pe} \approx kT u^{2/3} N f^{4/3}$ ).

*Self-similar adsorbed layer.*—If the surface charge density increases further ( $\sigma > \sigma_{D_e}$ ), the electrostatic

attraction becomes strong enough to deform a chain on the length scales smaller than the electrostatic blob size  $D_e$ . In this regime ( $\sigma > \sigma_{D_e}$ ) the electrostatic attraction between polyelectrolytes and charged surface is stabilized by the short-range repulsion between monomers. For a polymer chain in a  $\theta$  solvent for uncharged backbone, these interactions can be approximated by the three-body repulsion  $kTa^6c^3(z)$ . The monomer density  $c(z)$  in the adsorbed layer can be obtained by equilibrating the density of the electrostatic energy  $\varepsilon E^2(z)$  with polymeric osmotic pressure

$$\varepsilon E^2(z) \approx kTa^6c^3(z), \quad (12)$$

where the local electric field  $E(z)$  at distance  $z$  from the surface is

$$E(z) \approx e/\varepsilon \left( \sigma - f \int_0^z c(z) dz \right). \quad (13)$$

Substitution of the expression for the electric field [Eq. (13)] into Eq. (12) results in the integral equation for the monomer density in the adsorbed layer

$$\sigma - f \int_0^z c(z) dz \approx l_B^{-1/2} a^3 c^{3/2}(z). \quad (14)$$

The solution of this integral equation gives a parabolic density profile

$$c(z) \approx uf^2(z_{\max} - z)^2 a^{-5}, \quad (15)$$

where we have introduced  $z_{\max} \propto a^{5/3} u^{-1/3} f^{-1} \sigma^{1/3}$ . The thickness of the adsorbed layer  $D$  is determined from the electroneutrality condition, which gives

$$D \approx z_{\max} \approx a^{5/3} u^{-1/3} f^{-1} \sigma^{1/3}. \quad (16)$$

The thickness of the adsorbed layer increases with increasing surface charge density.

The adsorbed layer can be considered as being built of the blobs with gradually increasing size  $\xi(z)$ . The number of monomers  $g(z)$  in a blob is determined from the fact that these blobs are space-filling,  $g(z) \approx c(z)\xi^3(z)$ , and the statistics of a chain inside a blob is Gaussian,  $\xi^2(z) \approx a^2 g(z)$ . This gives the dependence of the blob size,

$$\xi(z) \approx a^3 u^{-1} f^{-2} (D - z)^{-2}, \quad (17)$$

and the number of monomers in them,

$$g(z) \approx a^4 u^{-2} f^{-4} (D - z)^{-4}, \quad (18)$$

on the distance  $z$  from the surface. These blobs are multi-valent sections of polyions with the valency  $q(z) = fg(z)$ .

The divergence of the blob size  $\xi(z)$  and the number of monomers  $g(z)$  at the edge of the adsorbed layer ( $z \approx D$ ) is due to the fact that we have neglected the polymer entropy term [10]. This term suppresses the large variations of monomer density at the edge of the adsorbed layer. The entropic effects begin to dominate over the three-body repulsion at the distances  $z$  from a surface larger than  $D - D_e$ . The effective surface charge density  $\Delta\sigma$  "felt" by the last layer of the thickness  $D_e$  is of the order

of the threshold value  $\sigma_{D_e} \approx fa^{-2}$ . The structure of this layer is a two-dimensional melt of electrostatic blobs for which the electrostatic attraction to the surface is of the same order of magnitude as the electrostatic self-energy, the confinement energy, and the thermal energy  $kT$ .

*Counterion screening.*—The number of monomers  $g(0) \approx a^{-8/3} u^{-2/3} \sigma^{-4/3}$  in a blob inside the first adsorbed layer decreases with increasing surface charge density. There will be, on average, one charged monomer per such a blob at the surface charge density

$$\sigma_{\text{ion}} \approx f^{3/4} a^{-2} u^{-1/2}. \quad (19)$$

At this surface charge density the monomer concentration at the surface reaches its maximum possible value  $c_{\max} \approx a^{-3} f^{1/2}$ . Further increase of polymer density is unfavorable due to the high cost of the short-range monomer-monomer repulsive interactions. For the higher surface charge densities  $\sigma > \sigma_{\text{ion}}$ , surface counterions start to dominate the screening of the surface potential inside the layer of thickness  $h$ . A counterion pays of the order  $kT$  of the translational entropy when it is localized at a surface inside the layer of thickness  $h$ , while it will cost more than  $kT$  of the repulsive energy between monomers to produce a similar screening effect by increasing concentration above  $c_{\max}$ . The polymer density  $c$  inside this layer is almost constant (up to logarithmic corrections) and is equal to  $c_{\max} \approx a^{-3} f^{1/2}$ . The thickness of the counterion layer  $h$  can be found by matching the counterion density [12]  $c_{\text{ion}}(h) \approx \sigma^2 l_B / (1 + \sigma l_B h)^2$  with the density of the charged monomers  $fc_{\max} \approx a^{-3} f^{3/2}$ ,

$$h \approx au^{-1/2} f^{-3/4} - 1/l_B \sigma. \quad (20)$$

The counterions effectively screen the surface charge in the layer of thickness  $h$ , reducing the effective surface charge density at the distance  $h$  from the surface down to the crossover value  $\sigma_{\text{ion}}$ . At length scales  $z > h$  the screening of the surface charge is dominated by charged monomers which results in a self-similar structure of polyelectrolyte chains with the parabolic density profile described above [see Eq. (15)]. At very high surface charge densities, the thickness of the polymer layer saturates at  $au^{-1/2} f^{-3/4}$ .

In summary, we have presented a scaling analysis of polyelectrolyte adsorption at oppositely charged surfaces. We have identified six different regimes of chain adsorption. The thickness of the adsorbed layer as a function of the surface charge density is plotted in Fig. 1.

In the interval of low surface charge densities ( $\sigma_{\text{WC}} < \sigma < \sigma_{D_e}$ ), polyelectrolytes substitute surface counterions and form a two-dimensional strongly correlated Wigner liquid and Wigner liquid crystal at the charged surface. The size of the corresponding Wigner-Seitz cell is determined by the electroneutrality condition of the cell. The chains are localized inside the layer of thickness  $D \approx (l_B f N \sigma)^{-1}$  for surface charge densities smaller than  $\sigma_{\text{def}}$ . For higher surface charge densities,  $\sigma > \sigma_{\text{def}}$ , the thickness of an adsorbed chain  $D$  is determined by the balance of the energy

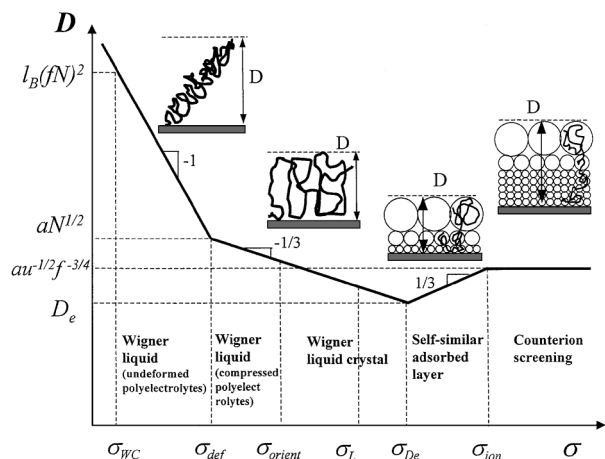


FIG. 1. Dependence of the thickness of the adsorbed layer  $D$  on the surface charge density  $\sigma$  (logarithmic scales).

gain due to electrostatic attraction and the confinement entropy loss due to chain localization. The equilibrium chain thickness  $D$  decreases with increasing surface charge density as  $\sigma^{-1/3}$ . The orientational transition in the adsorbed layer at  $\sigma \approx \sigma_{\text{orient}}$  has no effect on the layer thickness (see Fig. 1).

If the surface charge density increases further ( $\sigma_{D_e} < \sigma < \sigma_{\text{ion}}$ ), the equilibrium density profile in the adsorbed layer is determined by the balance between electrostatic attraction of charged monomers to the surface and short-range monomer-monomer repulsion. On length scales  $z < D - D_e$  the polyelectrolytes form a self-similar carpet with polymer density decaying as  $(D - z)^2$  in a  $\theta$  solvent for polymer backbone [as  $(D - z)^8$  in a good solvent]. The thickness of the adsorbed layer  $D$  increases with surface charge density as  $\sigma^{1/3}$  in a  $\theta$  solvent (see Fig. 1) (as  $\sigma^{1/9}$  in a good solvent).

For very high surface charge densities ( $\sigma > \sigma_{\text{ion}}$ ) the surface counterions dominate the screening of the surface potential inside the layer of thickness  $h$  and reduce the effective surface charge density at  $z \approx h$  to the crossover value  $\sigma_{\text{ion}}$ . The polymer density within this layer of thickness  $h$  is almost constant,  $c \approx c_{\text{max}}$ , with one elementary charge per correlation blob. On length scales between  $h$  and  $h + au^{-1/2}f^{-3/4}$ , adsorbed polyelectrolytes form a self-similar structure as described above. In this regime the thickness of the adsorbed layer saturates at  $au^{-1/2}f^{-3/4}$  in a  $\theta$  solvent for polymer backbone (see Fig. 1) (at  $au^{-1/2}f^{-9/10}$  in a good solvent).

It is useful to estimate typical  $\sigma$  values for the boundaries between different regimes in the adsorption diagram (Fig. 1). Consider polyelectrolyte chains consisting of  $N \approx 10^2$  Kuhn segments with size  $a \approx 4A$  and with 10% ( $f \approx 0.1$ ) of these segments charge adsorbing from an aqueous solution with the Bjerrum length  $l_B = 7A$ . In this case, the boundaries between regimes in the adsorption diagram are  $\sigma_{\text{WC}} \approx 2 \times 10^{-5} A^{-2}$ ,  $\sigma_{\text{def}} \approx \sigma_{\text{orient}} \approx 10^{-3} A^{-2}$ ,  $\sigma_{D_e} \approx 6 \times 10^{-3} A^{-2}$ , and  $\sigma_{\text{ion}} \approx 10^{-2} A^{-2}$ . These regimes are within the experimental range for polyelectrolyte adsorption on glass and mica substrates.

We hope this paper will inspire experimentalists to test the predictions of the proposed model.

The authors are grateful to B. Shklovskii for valuable discussions and to the National Science Foundation for financial support under Grant No. DMR-9730777.

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