

Scaling theory of polyelectrolyte adsorption on a repulsive charged surface

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We studied the problem of many-polyelectrolyte adsorption on a repulsive charged surface by scaling analysis. According to ratio of the dielectric constant between the medium and the substrate, the phase diagrams of the adsorbed layer are divided into two classes. Their phase diagrams are qualitatively different. The polyelectrolytes of low (high) fZ^2 are adsorbed for low (high) dielectric ratio, where f is the fraction of charged monomers and Z is the polyelectrolyte valency.

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Polyelectrolyte adsorption on an attractive surface has been well studied both theoretically and experimentally for several decades [1]. Recently the marcoion adsorption and the associated charge inversion acquires lots of attention [2]. Theoretical interest in the polyelectrolyte adsorption on an attractive surface is mainly due to its importance for understanding the multilayer formation by alternate deposition of positively and negatively charged polyelectrolytes on charged surface [3].

Basically the theoretical works dealing with many-chain polyelectrolyte adsorption on an attractive charged surface consists of two different approaches. One is the self-consistent field method, that is, to solve both the Edwards equation and the Poisson-Boltzmann equation simultaneously [4–6]. The Edwards equation describes the polyelectrolyte conformation fluctuation at the ground-state dominance limit [7] and the Poisson-Boltzmann takes care of the local electrostatic potential at mean-field level [8]. The other is scaling analysis [9]. It was predicted that the polyelectrolyte adsorbed on an attractive surface undergoes a transition from a compressed state to a undeformed state before the desorption [10]. The scaling behavior of the adsorption layer thickness with respect to the surface charge density is different from that obtained by the self-consistent field method in which the overall conformational changes is ignored.

Recently the possibility of a single chain adsorbed onto a high-dielectric substrate with repulsive surface charge was raised [11]. It shows that the polyelectrolyte under the Coloumb image attraction can overcome the slightly repulsive surface and is able to be adsorbed on the substrate. In this paper, we would like to investigate many-chain adsorption by scaling analysis.

Consider a polyelectrolyte chain with degree of polymerization N , fraction of charged monomers f , and bond length a in a solvent of dielectric constant ϵ . Below the solvent, there is a substrate of high dielectric constant $\epsilon' > \epsilon$. The surface charge density on the substrate is σ . At low ionic strength in which the bulk Debye screening length is much larger than the adsorption layer thickness, a single polyelectrolyte is still adsorbed when the charged substrate is slightly repulsive; that is, when the surface charge density σ does not exceed

some threshold value σ_r . The polyelectrolyte is going to desorb when the binding energy due to image charge attraction meets the potential barrier formed by repulsive surface [11].

When polyelectrolytes of multivalency $Z=fN \gg 1$ are adsorbed onto the repulsive surface, they form a two-dimensional (2D) Wigner liquid on the surface [12–16]. Poisson-Boltzmann theory fails because of strong correlation between polyelectrolytes. Dobrynin *et al.* developed the scaling theory to polyelectrolyte adsorption on an attractive surface [10]. In the following, we extend the scaling approach to the problem of a repulsive charged surface to take care of the strong correlation between the adsorbed polyelectrolytes. The monovalent counterions are then treated within the Poisson-Boltzmann theory since it is generally believed that mean-field theory is still valid for monovalent ions [2].

Suppose the surface Debye screening length $r_{s,0}$ is larger than the average distance between polyelectrolytes R ; otherwise, any two chains cannot feel each other and the problem is reduced to a single-chain adsorption [11]. Notice that the effective Debye screening length $r_{s,0}$ is not necessary equal to the bulk one $r_{s,\infty}$ because of nonuniform counterion distribution at different height from the charged surface.

In the presence of high dielectric substrate, the polyelectrolyte would feel a binding energy due to image charge attraction. Its layer thickness D can be determined by the balance between electrostatic attractive energy and conformational entropy

$$\frac{\Gamma(Ze)^2}{\epsilon D} \approx \frac{k_B T a^2 N}{D^2}, \quad (1)$$

where $\Gamma = (\epsilon' - \epsilon) / (\epsilon' + \epsilon)$ measures the coupling strength between the polyelectrolyte and its image. Equation (1) gives

$$D \approx a(l_B/a)^{-1} \Gamma^{-1} f^{-1} Z^{-1}, \quad (2)$$

where l_B is the Bjerrum length. The smaller fraction of charged monomers f , the larger conformational entropy and adsorbed layer thickness. Notice that, if the layer thickness derived above reaches the molecular size a , we should comment that the scaling theory is invalid in this regime. In general, we need $D \gtrsim a$, or $\Gamma f Z \lesssim 1$.

The binding energy is thus

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$$W_{\text{bind}} \approx -k_B T (l_B/a)^2 \Gamma^2 f Z^3 / R^2. \quad (3)$$

Because of the repulsive charged surface, we have repulsive energy from the surface

$$\begin{aligned} W_{\text{surf}} &\approx k_B T \frac{(1-\Gamma) Z l_B (\sigma/e)}{R^2} \int_0^\infty dr \exp\left(-\frac{r}{r_{s,0}}\right) \\ &= k_B T \frac{(1-\Gamma) Z l_B r_{s,0} (\sigma/e)}{R^2}. \end{aligned} \quad (4)$$

Repulsive energy from other polyelectrolytes

$$\begin{aligned} W_{\text{rep}} &\approx k_B T \frac{(1-\Gamma)^2 Z^2 l_B}{R^4} \int_R^\infty dr \exp\left(-\frac{r}{r_{s,0}}\right) \\ &= k_B T \frac{(1-\Gamma)^2 Z^2 l_B r_{s,0}}{R^4} \exp\left(-\frac{R}{r_{s,0}}\right). \end{aligned} \quad (5)$$

Since the bulk chemical potential of polyelectrolytes is in general small (its bulk density is small), the average distance between polyelectrolytes at the surface is determined by minimization of the total energy $W = W_{\text{bind}} + W_{\text{surf}} + W_{\text{rep}}$ with respect to R , which gives

$$\begin{aligned} \frac{\Gamma^2 f Z^2 l_B}{a^2} - (1-\Gamma) r_{s,0} (\sigma/e) &= \frac{2(1-\Gamma)^2 Z r_{s,0}}{R^2} \left(1 + \frac{R}{4r_{s,0}}\right) \\ &\times \exp\left(-\frac{R}{r_{s,0}}\right). \end{aligned} \quad (6)$$

In order to have a solution from Eq. (6) for $\sigma > 0$, one should have

$$\frac{\Gamma^2 f Z^2 l_B}{a^2} > (1-\Gamma) r_{s,0} (\sigma/e) \quad (7)$$

which determines the critical surface charge density

$$\sigma_c \approx e \frac{\Gamma^2 f Z^2 l_B}{(1-\Gamma) a^2 r_{s,0}} \quad (8)$$

σ_c decreases with increasing $r_{s,0}$. It is due to more repulsion from its neighbors and surface charge when the Debye screening length increases.

In the many-chain adsorption problem, we focus on the regime $r_{s,0} \gg R$. Expanding Eq. (6) in $R/r_{s,0}$, we get the surface polyelectrolyte density

$$n \approx R^{-2} \approx \frac{\sigma_c - \sigma}{2(1-\Gamma)Ze} + O\left(\frac{R}{r_{s,0}}\right). \quad (9)$$

As $\sigma \rightarrow \sigma_c^-$, the polyelectrolytes are going to desorb, its surface density decreases to zero. During the desorption, the average distance between polyelectrolytes can be arbitrary large so that the desorption happens as a single-chain desorption process. By comparing two length scales R and $r_{s,0}$, the problem is classified into two regimes. When $r_{s,0} \gg R$, it corresponds to many-chain adsorption

$$\sigma \lesssim \sigma_c - \frac{2(1-\Gamma)Ze}{r_{s,0}^2} \approx \sigma_c. \quad (10)$$

Otherwise, when $r_{s,0} \lesssim R$, it becomes single chain adsorption

$$\sigma \gtrsim \sigma_c - \frac{2(1-\Gamma)Ze}{r_{s,0}^2} \approx \sigma_c. \quad (11)$$

When σ increases, interchain distance R becomes larger, and then the system switches from many-chain to single-chain adsorption. σ_c is nothing but a surface charge density indicating the crossover. The threshold surface charge density is the same as the single chain case. The adsorption transition is still firstorder.

After the strongly correlated polyelectrolytes settled down on the surface, the effective surface charge felt by monovalent counterions varies. The new Gouy-Chapman length

$$\lambda \approx \frac{e}{2\pi(1-\Gamma)l_B(\sigma + Zen)} = \frac{e}{\pi l_B[(1-2\Gamma)\sigma + \sigma_c]}. \quad (12)$$

Naive thinking from the above expression, if the surface Debye screening length $r_{s,0}$ is fixed, the Gouy-Chapman length decreases (increases) with increasing surface charge density σ for $\Gamma < 1/2$ ($\Gamma > 1/2$). However, the naive picture does not necessarily hold since the counterions may condense on the surface, and the surface Debye screening length may be greatly reduced. Applying the Poisson-Boltzmann theory (see details in the Appendix), the problem is again divided into two cases according to the magnitude of the new Gouy-Chapman (GC) length.

Case (1). Small GC length; that is, $\lambda < (2\pi l_B c_\infty)^{-1/2}$, where c_∞ is the bulk counterion density. The surface counterion density

$$c_0 \approx \frac{1}{2\pi l_B \lambda^2} \approx \frac{\pi l_B}{2e^2} [(1-2\Gamma)\sigma + \sigma_c]^2 \quad (13)$$

which is much larger than the bulk value c_∞ . Surface Debye screening length

$$r_{s,0} \approx (4\pi l_B c_0)^{-1/2} \approx \frac{e}{\sqrt{2}\pi l_B [(1-2\Gamma)\sigma + \sigma_c]}. \quad (14)$$

Notice that the polyelectrolytes contribution to the ionic strength is ignored because the polyelectrolytes form a Wigner-crystal-like structure with its neighbors. It cannot provide significant contribution to mobile screening.

Eliminate σ_c from Eqs. (8) and (14),

$$r_{s,0} \approx \frac{1}{(1-2\Gamma)(\sigma/e)} \left(\frac{1}{\sqrt{2}\pi l_B} - \frac{\Gamma^2 l_B f Z^2}{(1-\Gamma)a^2} \right). \quad (15)$$

$r_{s,0}$ is a decreasing function with fZ^2 for fixed Γ . Fixing fZ^2 , when Γ is increased up to $1/2$, the prefactor in Eq. (15) turns to be negative. For high enough Γ , the bracket changes sign. Suppose we estimate the adsorption threshold for fZ^2 as $r_{s,0}$ approaching to zero, then the adsorption happens when

$$fZ^2 \lesssim \frac{1-\Gamma}{\Gamma^2} \frac{1}{\sqrt{2}\pi(l_B/a)^2} \quad (16)$$

for $\Gamma < 1/2$, and it happens when

$$fZ^2 \geq \frac{1-\Gamma}{\Gamma^2} \frac{1}{\sqrt{2\pi}(l_B/a)^2} \quad (17)$$

for $\Gamma > 1/2$.

For high enough fZ^2 , when $r_{s,0}$ meets R , many-chain adsorption becomes a single-chain problem. By Eqs. (11) and (15), we have

$$fZ^2 \leq \frac{1}{2\sqrt{2\pi}\Gamma^2(l_B/a)^2} \quad (18)$$

for many-chain adsorption. Finally, for self-consistency, we need to check the condition $\lambda < (2\pi l_B c_\infty)^{-1/2}$, by Eq. (12), (14), and (15), where it gives

$$\frac{\sigma/(ea^{-2})}{(c_\infty a^3)^{1/2}} > \frac{2\sqrt{\pi}\Gamma^2(l_B/a)^{3/2}}{(1-2\Gamma)(1-\Gamma)} \left(\frac{1-\Gamma}{\sqrt{2\pi}\Gamma^2(l_B/a)^2} - fZ^2 \right). \quad (19)$$

The regime corresponds to high surface charge density or low bulk counterion density.

Case (2). Large GC length; that is, $\lambda > (2\pi l_B c_\infty)^{-1/2}$. According to Poisson-Boltzmann theory, the surface counterion density is almost the same as the bulk one under this condition. The surface Debye screening length

$$r_{s,0} \approx (4\pi l_B c_\infty)^{-1/2} \quad (20)$$

which is independent of σ . For many-chain adsorption, Eqs. (8) and (10) give

$$fZ^2 \geq \frac{1-\Gamma}{2\sqrt{\pi}\Gamma^2(l_B/a)^{3/2}} \frac{\sigma/(ea^{-2})}{(c_\infty a^3)^{1/2}}. \quad (21)$$

The self-consistent condition $\lambda > (2\pi l_B c_\infty)^{-1/2}$ requires

$$\frac{\sigma/(ea^{-2})}{(c_\infty a^3)^{1/2}} < \frac{2\sqrt{\pi}\Gamma^2(l_B/a)^{3/2}}{(1-2\Gamma)(1-\Gamma)} \left(\frac{1-\Gamma}{\sqrt{2\pi}\Gamma^2(l_B/a)^2} - fZ^2 \right). \quad (22)$$

In summary, according to the dielectric ratio ϵ'/ϵ (or the coupling strength Γ), the phase diagrams of the adsorbed layer are divided into two classes as shown in Figs. 1 and 2. When the surface charge density is low (or the bulk counterion density is high), the surface and the bulk counterion density are almost the same. Once the surface charge density is high enough [$\lambda < (2\pi l_B c_\infty)^{-1/2}$], counterions condense on the surface. In this regime, polyelectrolytes of lower valency $\{fZ^2 < 1/[2\sqrt{2\pi}\Gamma^2(l_B/a)^2]\}$ form a correlated many-chain state. As their valency is high enough, the state turns out to be single-chain because of stronger repulsion between neighboring chains.

The qualitative differences between the phase diagram of $\Gamma < 1/2$ (or $\epsilon'/\epsilon < 3$) and $\Gamma > 1/2$ (or $\epsilon'/\epsilon > 3$) is the following. Starting from the many-chain state with $c_0 \approx c_\infty$, it is expected the system transits to the single-chain state when the surface charge density increases. For $\Gamma < 1/2$, it happens for weakly charged polyelectrolytes $\{fZ^2 < 1/[2\sqrt{2\pi}\Gamma^2(l_B/a)^2]\}$; while for $\Gamma > 1/2$, strongly charged polyelectrolytes are needed. Another difference is their desorbed states. For $\Gamma < 1/2$, no adsorbed state exists for

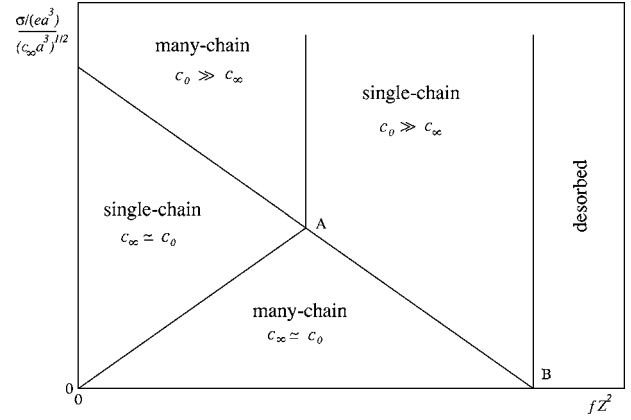


FIG. 1. Phase diagram of the adsorbed layer for $\Gamma < 1/2$ (or $\epsilon'/\epsilon < 3$). The corresponding fZ^2 at points A and B are $1/[2\sqrt{2\pi}\Gamma^2(l_B/a)^2]$ and $(1-\Gamma)/[\sqrt{2\pi}\Gamma^2(l_B/a)^2]$, respectively. For strongly charged polyelectrolytes such that $fZ^2 > (1-\Gamma)/[\sqrt{2\pi}\Gamma^2(l_B/a)^2]$, no adsorbed state exists. $\Gamma fZ \leq 1$ for the validity of scaling analysis.

strongly charged polyelectrolytes $\{fZ^2 > (1-\Gamma)/[\sqrt{2\pi}\Gamma^2(l_B/a)^2]\}$; while weakly charged polyelectrolytes are all desorbed for $\Gamma > 1/2$.

We emphasize that our treatment of multivalent polyelectrolytes interaction within the Gouy-Chapman layer is preliminary, in which it is still subtle [17,18], and the mean-field treatment of the counterion distribution ignores the effect from the inhomogeneity of the surface charge density. The qualitative prediction of the phase diagram should not be altered and could be tested experimentally.

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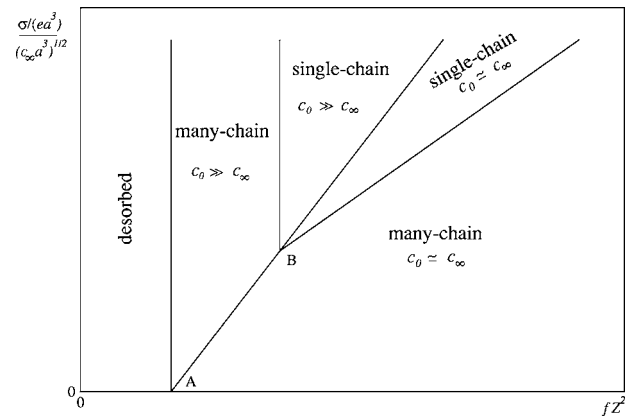


FIG. 2. Phase diagram of the adsorbed layer for $\Gamma > 1/2$ (or $\epsilon'/\epsilon > 3$). The corresponding fZ^2 at point A and B are $(1-\Gamma)/[\sqrt{2\pi}\Gamma^2(l_B/a)^2]$ and $1/[2\sqrt{2\pi}\Gamma^2(l_B/a)^2]$, respectively. For weakly charged polyelectrolytes such that $fZ^2 < (1-\Gamma)/[\sqrt{2\pi}\Gamma^2(l_B/a)^2]$, no adsorbed state exists. $\Gamma fZ \leq 1$ for the validity of scaling analysis.

**APPENDIX: POISSON-BOLTZMANN THEORY
FOR HIGH-Z**

Suppose the surface charge density at the surface $\sigma > 0$. The polyion distribution of valency Z carrying charge Ze is $\rho(z)$, and its counterion distribution of monovalency is $c(z)$. Neglecting the ion correlation in Poisson-Boltzmann theory, we have

$$\rho(z) = \rho_\infty \exp[-\beta Ze\psi(z)], \quad (\text{A1})$$

$$c(z) = c_\infty \exp[\beta e\psi(z)]. \quad (\text{A2})$$

$c_\infty = Z\rho_\infty$ neutralizes the whole system. The Poisson-Boltzmann equation becomes

$$\frac{d^2\psi}{dz^2} = \frac{4\pi e c_\infty}{\epsilon} [\exp(\beta e\psi) - \exp(-Z\beta e\psi)]. \quad (\text{A3})$$

In general, only a few solution can be expressed in a closed form e.g., $Z=1,2$ [19]. For $Z \rightarrow \infty$, the above equation is reduced to

$$\frac{d^2\psi}{dz^2} = \frac{4\pi e c_\infty}{\epsilon} \exp(\beta e\psi) \quad (\text{A4})$$

with the boundary condition $\psi'|_{z=0} = -4\pi\sigma/\epsilon$. Near the surface $z=0$, it gives the Gouy-Chapman form

$$c(z) = \frac{A}{(z+\lambda)^2}, \quad (\text{A5})$$

where $\lambda = e/(2\pi l_B \sigma)$ and A is an undetermined constant. In the usual Gouy-Chapman solution, $A = 1/(2\pi l_B)$ because we restrict $c(z \rightarrow \infty) = 0$. In our case $c(z \rightarrow \infty) = c_\infty > 0$ and hence the Gouy-Chapman form is only valid near the surface.

In term of the variable $c(z)$, Eq. (A3) can be written as

$$\frac{1}{c} \frac{d^2c}{dz^2} - \frac{1}{c^2} \left(\frac{dc}{dz} \right)^2 = 4\pi l_B \left[c - c_\infty \left(\frac{c_\infty}{c} \right)^Z \right]. \quad (\text{A6})$$

In order to consider the solution at the limit of $Z \rightarrow \infty$, we need self-consistency condition $c_\infty/c_0 \leq 1$. Substitute Eq. (A5) into Eq. (A6) and restrict $z \approx 0$, one gets $A \approx 1/(2\pi l_B)$ if $\lambda < (2\pi l_B c_\infty)^{-1/2}$, and $A \approx c_\infty \lambda^2$ otherwise.

The above result are derived from the high- Z limit. Now we are going to look at the next order contribution from finite Z^{-1} . Write the electric potential into $\psi = \psi_0 + \psi_1$ such that ψ_0 is the solution shown above, and ψ_1 is the next order correction subject to the following boundary condition $\psi_1|_{z=0} = \psi_1'|_{z=0} = 0$. Expand in ψ_1 and around $z=0$,

$$\begin{aligned} \frac{d^2\psi_1}{dz^2} &= -\frac{4\pi e c_\infty}{\epsilon} [e^{-Z\beta e\psi_0} - (e^{\beta e\psi_0} + Z e^{-Z\beta e\psi_0})\beta e\psi_1] \\ &\approx -\frac{4\pi e c_\infty}{\epsilon} \left(\frac{A}{c_\infty \lambda^2} \right)^Z \end{aligned} \quad (\text{A7})$$

if we keep only the leading order. Solving for ψ_1 gives

$$\begin{aligned} c(z) &= c_\infty \exp[\beta e(\psi_0 + \psi_1)] \\ &\approx \frac{A}{(z+\lambda)^2} \left[1 - 2\pi l_B c_\infty \left(\frac{c_\infty \lambda^2}{A} \right)^Z z^2 \right] \end{aligned} \quad (\text{A8})$$

In summary, for $Z \gg 1$, when $\lambda < (2\pi l_B c_\infty)^{-1/2}$,

$$c(z) \approx \frac{1}{2\pi l_B (z+\lambda)^2} [1 - (2\pi l_B c_\infty)^{Z+1} \lambda^{2Z} z^2] \quad (\text{A9})$$

at $z \ll \lambda$. Hence $c_0 \approx 1/(2\pi l_B \lambda^2) \gg c_\infty$ implying that counterions condense on the surface. On the other hand, when $\lambda > (2\pi l_B c_\infty)^{-1/2}$

$$c(z) \approx \frac{c_\infty \lambda^2}{(z+\lambda)^2} (1 - 2\pi l_B c_\infty z^2) \quad (\text{A10})$$

at $z \ll (2\pi l_B c_\infty)^{-1/2}$. Then $c_0 \approx c_\infty$.

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