

Study of polyelectrolyte adsorbent theory on a repulsive charged surface

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Received 5 August 2013; Accepted (in revised version) 10 November 2013
Published Online 28 February 2014

Abstract. Applying scaling theory of polyelectrolyte adsorption, and according to ratio of the dielectric constant between the medium and the substrate, and taking into account strong interaction between polyelectrolytes of multivalency adsorption, we proposed a scaling theory of the approximation method on a repulsive charged surface. It is divided into two kind phase diagrams that one is qualitatively different. This shows 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, counterions condense on the surface. In this regime, polyelectrolytes of lower valency 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.

PACS: 73.20.-r, 61.30.Jf, 68.43.Nr

Key words: dielectric constant, polyelectrolyte, charged of surface, adsorbent theory

1 Introduction

Over the past decade, lots of researches have been done on polyelectrolytes on induced surfaces both theoretically and experimentally [1]. By applying Van der Waals Force based on Lifshitz quantum electrodynamics established the general theory, Chen and Li researched on the attractive potential between same dielectric molecules in the vacuum,

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hoping to get their (including atoms) equivalent interaction potential [2]. Through analysis of the dielectric constant on a material surface for granular film, Ge and Zheng calculated the dielectric constant of granular film, based on the relative dielectric constant of the substrate material and the distance between polar molecules. In their paper, they also found out that the interaction between molecules and the material surface plays the solo role when the molecular size is close to the molecular critical size; while the local-field interaction plays the major role when the two values differ largely [3]. Recently, Grosberg's research on the physics of strong interaction of water at room temperature leading to the discovery of abnormal charge inversion of charged macromolecules has aroused great attention [4]. Theories on polyelectrolyte absorption on induced surfaces focus on analyses of multilayer forms of the charge inversion on surfaces. They fall into two categories involving combinations of multi-chain polyelectrolyte absorption on two different charged surfaces. One is the self-consistent field theory (SCFT), also known as Edwards's equation and Poisson-Boltzmann equation [5-7]. The former describes the conformation fluctuation of polyelectrolytes within the ground state limit [8]; while the latter is concerned with the local electrostatic potential at the mean-field level [9]. The other is scaling theory, which predicts that polyelectrolytes on induced surfaces will go through the transformation from the compressed state to the invisible metamorphosis state before desorption [10-11]. When conformational changes are ignored, the scaling of absorbing layer of surface charge density is different from that of SCFT.

The single-stranded absorption on high dielectric substrate which repels surface charge is protruding; indicating polyelectrolytes can overcome slight surface repelling with the Coulomb attraction and be absorbed by the substrate. This paper tends to further study the strong correlation between multi-valent dielectrics absorption, so as to establish an approximate scaling theory on surface repelling charge. Poisson-Boltzmann equation can be applied to explain the absorption of monovalent ions with opposite charge, because mean-field theory is still valid for their general behavior.

2 Theoretical models and results

Polymer dielectric chain will be related to polymerization number N , charged monomers fraction f , bond length a , if it is in the solution whose dielectric constant is ϵ . In the solution which bases the high dielectric chain ϵ' , its base's surface charge density is σ . In low ionic strength, Debye screening length is much larger than the adsorbed layer thickness. When the charge level is slightly repulsive, simple polymerization dielectric is still adsorbed. In other words, when the surface charge density does not exceed the critical value, polymer dielectric will release the potential barrier formed by repulsive surface, the outcome of the encounter of the image charge [12].

When the multivalent polymerization is adsorbed on the electric exclusion surface, forming a two-dimensional surface (2D) Wigner liquid [13-16], the Poisson Boltzmann theory will fails due to the strong interaction between polymer dielectric.

Assuming that the surface Debye screening length is larger than the average distance between polymer dielectric, mutual contact between any two chains doesn't exist and adsorption is a single chain, we will note that the effective Debye screening length does not have to equal the quantity of $r_{S,\infty}$ of the block, because the ions with opposite charges are not evenly distributed in different depth-charge.

On the surface of high polymer dielectric substrate, due to the generation of binding energy from polymer dielectric by attraction of the image charge, the thickness of layer D is balanced between the relationship of the energy of static electronic and the conformational entropy, which can be expressed by the formula

$$\frac{\Gamma(Z_e)^2}{\varepsilon D} \approx \frac{k_B T a^2 N}{D^2} \quad (1)$$

Here $\Gamma = (\varepsilon' - \varepsilon) / (\varepsilon' + \varepsilon)$ is the coupling strength measured between polymer dielectric and its image which can be worked out by the Eq. (1)

$$D \approx \frac{a}{(l_B/a)\Gamma f Z} \quad (2)$$

Here $l_B = e^2 / 4\pi\varepsilon - 0\varepsilon_r k_B T$ is the Bjerrum length, the monomer fraction f of negative charge is small, while the conformational entropy and the thickness of adsorbed layer are bigger. Note: if the layer thickness is more than that of molecular scale, under the circumstances here, the theory in question is invalid, in General, the prerequisite is $D \geq a$ or $T f z \leq 1$. At this point the total energy of the polymer dielectric is $W = W_{bind} + W_{surf} + W_{rep}$.

Among them, the binding energy is

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

Due to the exclusive charge on the surface, so the exclusive energy W_{surf} is

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

Exclusive energy from other polymer dielectric is

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

It is generally said that the chemical potential of polymer dielectric block is smaller (less bulk density), so the average distance between polymer dielectric on the surface is determined by the minimum value of r in the equation of total energy ($W = W_{bind} + W_{surf} +$

W_{rep}), the relationship between them can be expressed by the formula

$$\frac{\Gamma^2 f Z^2 l_B}{a^2} - (1-\Gamma)r_{S,0}(\sigma/e) = \frac{2(1-\Gamma)^2 Z r_{S,0}}{R^2} \left(1 + \frac{R}{4r_{S,0}}\right) \exp\left(-\frac{R}{r_{S,0}}\right) \quad (6)$$

In order to get the solution, for $\sigma > 0$ in the case of Eq. (6), there will be

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

So the charge density on critical surface is

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

in which σ_c reduces with the increase of $r_{S,0}$. When the screening length increases, its immediate neighbors' and surface charge is more exclusive. As for the problem of multiple chain adsorption, for the $r_{S,0} \gg R$ area, the Eq. (6) can be used to get the surface density of polymer dielectric at the nearby of $R/r_{S,0}$ which is

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

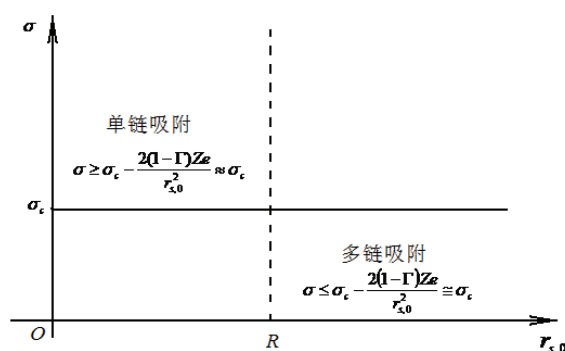


Figure 1: Two regimes of sing-chain and many-chain adsorption.

Polymer dielectric will release the absorption content to make the surface density decreased to zero when $\sigma \rightarrow \sigma_c^-$, the average distance between polymer dielectric during desorption can arbitrarily be large that desorption occur as single desorption process. The comparison of these two length scales, R and $r_{S,0}$, can classify them into two regimes. As shown in Figure 1, for $r_{S,0} \geq R$, the corresponding many-chain absorb, thus

$$\sigma \leq \sigma_c - \frac{2(1-\Gamma)Ze}{r_{S,0}^2} \cong \sigma_c \quad (10)$$

In addition, for $r_{S,0} \leq R$, it becomes single-chain adsorption, thus

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

When σ increases, the chain distance R will become very large, the system of many-chain adsorption will invert into that of single-chain, and at this point σ_c is just a logo of charge density on transverse surface. The charge density on surface is the same as the case of single-chain from the start, i.e. absorption still invert into the initial situation. Then, with strong polymer electrolyte of the interrelationships fixing on the surface, the effective surface charge are bonded by the monovalent charge with opposite changes, the new (Gouy-Chapman) GC length becomes

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

From the above expression it can be imagined, if the surface Debye screening distance is determined, (GC) length will decrease with the increase of surface charge density (or it will increase with the decrease of density) [for $(\Gamma < 1/2)$ and $(\Gamma > 1/2)$]. In any case, ions with opposite charges on the surface may be concentrated (condensed) and surface Debye screening length can be quickly reduced.

In what follows, a discussion of the relationship between volume density c_∞ with opposite charge and surface density $c=0$ with opposite charge is presented. Given the (GC) critical length being $\lambda = e/(2\pi l_B \sigma)$, by the magnitude order of (GC) length, Poisson-Boltzmann theory can be used to make a simple note that assuming that on the surface, for the surface charge density $\sigma > 0$, polymerization ion distribution with valency Z and charge Ze is $\rho(z)$, and the distribution of single-Valence ions with opposite charges is $c(z)$. In Poisson-Boltzmann theory, if the ionic interactions are ignored, there are

$$\begin{aligned} \rho(z) &= \rho_\infty \exp[-\beta z e \Psi(z)] \\ c(z) &= c_\infty \exp[\beta z \Psi(z)] \end{aligned} \quad (13)$$

Of the system as a whole, where, $c_\infty = Z\rho_\infty$, second-order Poisson-Boltzmann equation of the solution of potential function on space can be further derived to get distribution function of single Valence ion for $Z \gg 1$, when $Z \rightarrow \infty$ and $c_\infty/c_0 \leq 1$, the application condition for self-consistent, and the boundary condition $\Psi'(z)|_{z=0}$ for $z=0$ are considered.

For $\lambda < (2\pi l_B c_\infty)^{-1/2}$, the relationship will be

$$c(z) \cong \frac{1}{2\pi l_B (z + \lambda)^2} [1 - (2\pi l_B c_\infty)^{Z+1} \lambda^{2Z} z^2] \quad (14)$$

Therefore, for $z \ll \lambda$, it is indicated that the surface ions with opposite charges will be concentrated by $c_0 \approx 1/(2\pi l_B \lambda^2) \gg c_\infty$. However, for $\lambda > (2\pi l_B c_\infty)^{-1/2}$, the formula can be expressed as

$$c(z) \cong \frac{c_\infty \lambda^2}{(z + \lambda)^2} (1 - 2\pi l_B c_\infty z^2) \quad (15)$$

So the equation $c_0 \approx c_\infty$ can be derived when $z \ll (2\pi l_B c_\infty)^{-1/2}$.

3 Discussion

In what follows, a discussion of two cases above will be presented. In the first case, GC is smaller which is shown as $\lambda < (2\pi l_B c_\infty)^{-1/2}$, here c_∞ is the bulk density of opposite charges, and the surface density with opposite charges is

$$c_0 \approx \frac{1}{2\pi l_B \lambda^2} \approx \frac{\pi l_B}{2e^2} [(1-2\Gamma)\sigma + \sigma_c]^2 \quad (16)$$

The quantity is much larger than that of bulk density, in such a way that the surface Debye length is

$$r_{S,0} \approx (4\pi l_B c_0)^{-1/2} \approx \frac{e}{\sqrt{2}\pi l_B [(1-2\Gamma)\sigma + \sigma_c]} \quad (17)$$

Note: the dielectric is characterized by the crystal lattice structure which is similar as Wigner, so the polymer (molecular) dielectric's contribution to the ionic strength can be ignored. Upon making use of Eq. (8) and Eq. (17) to eliminate σ_c , Debye screening length can be obtained in the following formula

$$r_{S,0} \approx \frac{1}{(1-2\Gamma)(\sigma/e)} \left(\frac{1}{\sqrt{2}\pi l_B} - \frac{\Gamma^2 l_B f Z^2}{(1-\Gamma)a^2} \right) \quad (18)$$

When Γ is fixed, $r_{S,0}$ is a decreasing function that changes with fZ^2 , when fZ^2 is fixed and Γ is increased to more than 1/2, the former factor in the Eq. (18) changes into a negative one (Γ can't be equal to 1/2 and 1). The parentheses changes symbol with large enough quantity of Γ . It is assumed that the quantity of fZ^2 and $r_{S,0}$ is approximately zero at the beginning of adsorption, so the occurrence of adsorption can be assured by above equation, it is when

$$fZ^2 \leq \frac{1-\Gamma}{\Gamma} \frac{1}{\sqrt{2}\pi (l_B/a)^2} \quad (\Gamma < 1/2) \quad (19)$$

$$fZ^2 \geq \frac{1-\Gamma}{\Gamma} \frac{1}{\sqrt{2}\pi (l_B/a)^2} \quad (\Gamma > 1/2) \quad (20)$$

that adsorption starts.

When fZ^2 is large enough and $r_{S,0}$ is almost equal to R ($r_{S,0}$ is greater than but close to R), many-chain adsorption changes into a state of a single-chain adsorption. Making use of Eq. (11) and Eq. (18) leads to the following relation

$$fZ^2 \leq \frac{1-\Gamma}{\Gamma} \frac{1}{2\sqrt{2}\pi (l_B/a)^2} \quad (21)$$

The above equation shows a state of many-chain adsorption. Finally, the conditions $\lambda < (2\pi l_B c_\infty)^{-1/2}$ should be examined for self-consistent by making use of Eq. (12), Eq. (17)

and Eq. (18), leading to the following relation

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

This area is a response of high surface charge density or of low body charge density with opposite charges.

In the second case, with longer GC length, according to Poisson-Boltzmann theory, ion density with opposite charges on the surface is almost the same as volume density. Surface Debye screening length is

$$r_{S,0} \approx (4\pi l_B c_{\infty})^{-1/2} \quad (23)$$

which is irrelevant to σ , as for the many-chain adsorption, the relationship can be expressed by the use of Eq. (8) and Eq. (10) as follows

$$fZ^2 \geq \frac{1-\Gamma}{2\sqrt{\pi}\Gamma^2(l_B/a)^{3/2}} \frac{\sigma/(ea^{-2})}{(c_{\infty}a^3)^{1/2}} \quad (24)$$

The self-consistent condition $\lambda > (2\pi l_B c_{\infty})^{01/2}$ requires

$$\frac{\sigma/(ea^{-2})}{(c_{\infty}a^3)^{1/2}} < \frac{2\sqrt{\pi}\Gamma^2(l_B/a)^{3/2}}{(1-2\Gamma)(1-\Gamma)} \left(\frac{1-\Gamma}{2\sqrt{\pi}\Gamma^2(l_B/a)^2} - fZ^2 \right) \quad (25)$$

Now according to the previous discussion, the phase diagram of adsorbed factor $\frac{\sigma a^3}{\epsilon\sqrt{c_{\infty}}}$ and that of fZ^2 can be respectively made for $\Gamma < 1/2$ or $\Gamma > 1/2$, as shown in Fig. 2. Fig. 2 (a) is the phase diagram of the adsorbed layer for $\Gamma < 1/2$ or $\epsilon'/\epsilon < 3$, fZ^2 at the point of A and of B is $\frac{1}{2\sqrt{2\pi}\Gamma^2(l_B/a)^2}$ and $\frac{1}{\sqrt{2\pi}\Gamma^2(l_B/a)^2}$ respectively.

For $fZ^2 > (1-\Gamma)/[\sqrt{2}\Gamma^2(l_B/a)^2]$, the strong charged polymer dielectric is not in the state of adsorption with $\Gamma fz \leq 1$ here. Fig. 2 (b) is the phase diagram of the adsorbed layer for $\Gamma > 1$ or $\epsilon'/\epsilon > 3$, fZ^2 at the point of A and of B is $\frac{1}{\sqrt{2\pi}\Gamma^2(l_B/a)^2}$ and $\frac{1}{2\sqrt{2\pi}\Gamma^2(l_B/a)^2}$ respectively.

For $fZ^2 < (1-\Gamma)/[\sqrt{2}\Gamma^2(l_B/a)^2]$, the weak charged polymer dielectric is not in the state of adsorption with $\Gamma fz \geq 1$ here.

4 Conclusion

Thereby, we can infer that the phase diagram of adsorbed layer is divided into two parts, as shown in Figs. 1 and 2, in accordance with dielectric ratio ϵ'/ϵ or the coupling strength. When the surface charge density is low (or oppositely charged ion density is high), the surface and bulk of oppositely charged ion density is almost the same. Once the surface charge density is high enough $\lambda < (2\pi l_B c_{\infty})^{-1/2}$, it will condense the

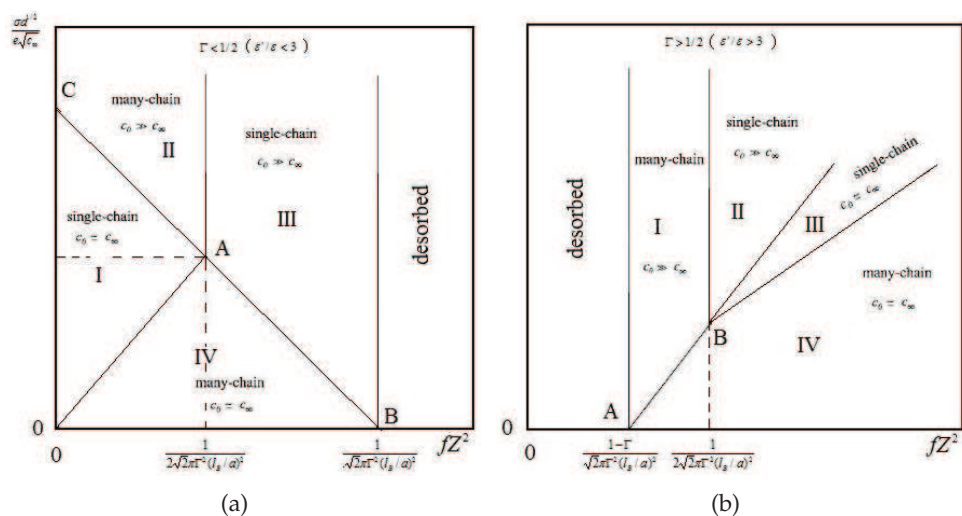


Figure 2: (a) Phase diagram of the adsorbed layer for $\Gamma < 1/2$ or $\epsilon'/\epsilon < 3$; (b) Phase diagram of the adsorbed layer for $\Gamma > 1/2$ or $\epsilon'/\epsilon > 3$.

oppositely charged ions on the surface. In this area, low valence polymeric dielectric $\{fZ^2 < 1/[2\sqrt{2}\pi\Gamma^2(l_B/a)^2]\}$ forms an associated chain state. When their valence is high enough, the rejection between the neighbor chains enhance, changing the state into a single chain.

The phase diagram of $\Gamma < 1/2$ ($\epsilon'/\epsilon < 3$) and $\Gamma > 1/2$ ($\epsilon'/\epsilon > 3$) has two qualitative differences. On the one hand, when $c_0 \approx c_\infty$, the surface charge density increases, and the system is expected to be a single chain. When $\Gamma < 1/2$, the result is $fZ^2 < 1/2\sqrt{2}\pi\Gamma^2(l_B/a)^2$, a weak charge polyelectrolyte; when $\Gamma > 1/2$, they are strong charge polymeric dielectrics. On the other hand, another difference is their desorption state. When $\Gamma < 1/2$, there is not the existence of strong adsorption of dielectric charge polymerization, $fZ^2 > (1 - \Gamma)/\sqrt{2}\pi\Gamma^2(l_B/a)^2$; when $\Gamma > 1/2$, it is on the contrary.

We emphasize that multivalent interactions involved in polymeric dielectric in the range of GC is preliminary. Considering the inhomogeneity of the surface charge density and the ignorance of the oppositely charged ions distribution, we can use the average field processing. Prediction and experiments on the nature of the phase diagram turn out to be the same [17, 18].

Acknowledgments. Proje supported by the National Natural Science Foundation of China (Grant No. 11205022) and the Natural Science Research Program of Chongqing Educational Committee (Grant Nos. KJ061305 and KJ081307).

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