Boundary condition of polyelectrolyte adsorption

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The modification of the boundary condition for polyelectrolyte adsorption on charged surface with short-ranged interaction is investigated under two regimes. For weakly charged Gaussian polymer in which the short-ranged attraction dominates, the boundary condition is the same as that of the neutral polymer adsorption. For highly charged polymer (compressed state) in which the electrostatic interaction dominates, the linear relationship (electrostatic boundary condition) between the surface monomer density and the surface charge density needs to be modified.

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I. INTRODUCTION

Polyelectrolyte adsorption on neutral (due to short-ranged interaction) and charged (due to electrostatic interaction) surfaces is still active and important in recent years [1–3]. The theoretical approach on solving the continuum theory (Edwards equation and its derivatives) [4] on the adsorption problem requires a proper boundary condition.

The boundary condition for a pure short-ranged attraction was first given by de Gennes [5]. Later, the same boundary condition was adopted for problems with both short-ranged and electrostatic interaction between the polymer and the surface [6–10]. The treatment implicitly assumes that the short-ranged interaction between the polymer and the surface dominates over the electrostatic ones. However, it is still a question for the validity of this assumption.

On the other hand, it was recently identified that the boundary condition for a highly charged polymer adsorbed on the charged surface is governed by the electrostatic boundary condition, and it can simply be expressed in a linear form between the surface monomer density and the surface charged density in the adsorption regime (compressed state) [11,12]. With an extra perturbed short-ranged interaction, although the interaction is also dominated by the electrostatic one, it is still a puzzle whether the form of the boundary condition remains unchanged or its modification is needed.

In this paper, we are going to fill the above two gaps in the literature. We show that for a weakly charged polymer adsorption due to short-ranged attraction, an perturbed electrostatic interaction in general does not modify the boundary condition. For a highly charged polymer adsorption (compressed state) due to electrostatic interaction, a perturbed short-ranged interaction would induce a nonlinear correction to the original boundary condition expressed in a linear form between the surface monomer density and the surface charge density.

II. SHORT-RANGED ATTRACTION REVISED

Before our main investigation, we first revise a Gaussian polymer adsorbed on the surface with short-ranged attraction. Suppose the short-ranged attraction between the monomers and the hard-wall surface is modeled by the δ potential $-\gamma\delta(z-b)$ located just above the hard wall at $z=0$.

The continuum equation describing the density profile $\rho(z)=\psi_0^2(z)$ is determined by the Edwards equation

$$\left(-\frac{a^2}{6}\frac{d^2}{dz^2}-\beta\gamma\delta(z-b)\right)\psi_0(z)=\varepsilon_0\psi_0(z), \tag{1}$$

where a is the bond length, $\beta=1/(k_BT)$, and ε_0 is the ground state eigenvalue. The boundary condition imposed is $\psi_0(0)=0$ and $\psi_0(+\infty)=0$. Similar to the usual eigenproblem appearing in quantum mechanics [13],

$$\psi_0(z)=\begin{cases}\sinh(z/d_0), & 0\leqslant z\leqslant b,\\ A\exp(-z/d_0), & z\geqslant b,\end{cases} \tag{2}$$

up to a normalization constant. d_0 describes the length scale of the diffusion layer of the adsorbed polymer. By fitting the boundary condition at $z=b$, we have

$$\frac{b}{d_0}\left[1+\coth\left(\frac{b}{d_0}\right)\right]=\frac{6\beta\gamma b}{a^2}. \tag{3}$$

The binding energy (in units of k_BT) or the eigenvalue $\varepsilon_0=-a^2/6d_0^2$.

The idea suggested by de Gennes [5] to absorb the δ potential into the surface (by taking sufficiently small b) is to modify the boundary condition at the surface and to match with the asymptotic behavior away from the surface by identifying the same binding energy (eigenvalue). That is, we are looking at the profile

$$\psi_1(z)=A\exp(-z/d_1),\quad 0<z<+\infty, \tag{4}$$

in which it is the solution of the eigenproblem

$$-\frac{a^2}{6}\frac{d^2}{dz^2}\psi_1(z)=\varepsilon_0\psi_1(z) \tag{5}$$

with the boundary condition

$$\left.\frac{1}{\psi_1}\frac{d\psi_1}{dz}\right|_{z=0^+}=-\frac{1}{d_1}, \tag{6}$$

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$$\psi_1(+\infty) = 0, \tag{7}$$

which is adopted on neutral polymer adsorption. The binding energy (in units of k_BT) $\varepsilon_0 = -a^2/6d_1^2$. Hence $d_1 = d_0$. Notice that the microscopic parameters γ and b are now replaced by the macroscopic quantity d_0.

III. SHORT-RANGED ATTRACTION WITH PERTURBED ELECTROSTATIC INTERACTION

Suppose the weakly charged polymer can still keep its Gaussian features when a perturbed local electrostatic interaction $V(z)$ from the charged surface is considered. In general the local potential $V(z) = V_0$ at $z=0$ becomes linear at $z \gtrsim 0$ and saturates to zero at large $z \gtrsim r_s$ (r_s is the Debye screening length). The Edwards equation is

$$\left(-\frac{a^2}{6}\frac{d^2}{dz^2} - \beta\gamma\delta(z-b) + \beta V(z)\right)\psi_0(z) = \varepsilon_0\psi_0(z) \tag{8}$$

with the boundary condition $\psi_0(0) = \psi_0(+\infty) = 0$. Following the same spirit as in previous section, we absorb the δ potential into the surface such that the eigenproblem becomes

$$\left(-\frac{a^2}{6}\frac{d^2}{dz^2} + \beta V(z)\right)\psi_1(z) = \varepsilon_0\psi_1(z) \tag{9}$$

with the boundary condition the same as in Eqs. (6) and (7). The binding energy ε_0 in both Eqs. (8) and (9) can be estimated by the first-order perturbation theory [13] to the solution in Eqs. (2) and (4), respectively. In Eq. (8), its corresponding eigenvalue

$$\begin{aligned}\varepsilon_0 &= -\frac{a^2}{6d_0^2} + \left(\int_0^b + \int_b^\infty\right) dz\,\psi_0^2(z)\beta V(z)\\ &\simeq -\frac{a^2}{6d_0^2} + \int_b^\infty dz\,\psi_0^2(z)\beta V(z)\end{aligned} \tag{10}$$

at sufficiently small b. The eigenvalue in Eq. (9) shares the same form

$$\varepsilon_0 = -\frac{a^2}{6d_1^2} + \int_0^\infty dz\,\psi_1^2(z)\beta V(z) \tag{11}$$

except d_0 is replaced by d_1. Hence, by identifying the same eigenvalue in both Eqs. (10) and (11), we get $d_1 = d_0$. Both the neutral and weakly charged Gaussian polymers share the same boundary condition due to the short-ranged attractive surface. Notice that the discussion of the boundary condition was also made by Joanny in which the coupling of the monomer density to a further electrostatic equation of Poisson-Boltzmann type is considered. The effective d_1 would then be different from d_0 [7].

In order to investigate the validity of the Gaussian feature, we choose the local potential of the Debye-Hückel form $V(z) = V_0\exp(-z/r_s)$, where $V_0 = 4\pi l_B\tau\sigma r_s$, with the Bjerrum length l_B, line charge density of polymer τ, and surface charge density of the surface σ. Substituting this $V(z)$ into Eq. (11),

$$\varepsilon_0 = -\frac{a^2}{6d_0^2} + \frac{2\beta V_0 r_s}{2r_s + d_0} \tag{12}$$

The first term is the binding energy due to short-ranged attraction whereas the second term is the electrostatic interaction. The condition for perturbed electrostatic interaction requires

$$\frac{a^2}{6d_0^2} \gg \frac{2\beta|V_0|r_s}{2r_s + d_0} \tag{13}$$

where it becomes $|V_0| \ll k_BTa^2/6d_0^2$ for low ionic strength $r_s \gg d_0$. For high ionic strength $r_s \ll d_0$, it requires $|V_0| \ll k_BTa^2/12r_sd_0$. Equation (13) is a necessary condition to identify whether the electrostatic interaction is still perturbatively small. If the surface charge density becomes strong such that $|V_0|$ no longer satisfies Eq. (13), the Gaussian polymer undergoes conformational changes. The corresponding boundary condition would deviate from Eq. (6) very much.

IV. ELECTROSTATIC BOUNDARY CONDITION WITH PERTURBED SHORT-RANGED INTERACTION

In another regime where the polymer is highly charged such that the adsorbed polymer is in a compressed state on the substrate, the boundary condition is determined by the electrostatic boundary condition across the dielectric [11,12]. The continuum theory is described also by the Edwards equation

$$\left(-\frac{a^2}{2}\frac{d^2}{dz^2} + \beta V(z)\right)\psi_0(z) = \varepsilon_0\psi_0(z), \tag{14}$$

where the coefficient of the entropic term is $-a^2/2$ instead of $-a^2/6$ [12]. The boundary condition imposed is $\psi_0(0) = C_0$ and $\psi_0(+\infty) = 0$. $C_0 \neq 0$ because the electrostatic boundary condition for a compressed adsorbed polyelectrolyte needs to be satisfied [11],

$$C_0^2 = -\frac{2K}{\epsilon'/\epsilon - 1}\left(\sigma + \frac{\epsilon'/\epsilon + 1}{2}\sigma_p\right) \tag{15}$$

where ϵ and ϵ' are the dielectric constant of the medium and the substrate, respectively. σ is the surface charge density just above the substrate. σ_p is the polarization surface charge density induced by the polymer only. It depends on ϵ'/ϵ but not on σ. K is the proportional constant depending only on ϵ'/ϵ. Both K and σ_p are model dependent; in other words, they depend on the microscopic details of the system. Similar to the diffusive layer thickness d appearing in the previous sections, the microscopic details are absorbed into these two macroscopic quantities K and σ_p.

In the following, with the perturbed short-ranged interaction (attractive or repulsive) modelled by a δ potential located just above the substrate, we are going to investigate how this perturbed term is absorbed into the boundary condition. That is, we consider the Edwards equation

$$\left(-\frac{a^2}{2}\frac{d^2}{dz^2}+\beta V(z)\right)\psi_1(z)=\varepsilon_1\psi_1(z) \tag{16}$$

with the boundary condition $\psi_1(0)=C_1$ and $\psi_1(+\infty)=0$. Notice that ε_0 in Eq. (14) (without δ potential) is not equal to ε_1 in Eq. (16) (with δ potential). In fact, the binding energy ε_1 can be related to ε_0 by perturbation theory [13] up to first order, in which

$$\begin{aligned}\varepsilon_1&=\varepsilon_0+\int_0^\infty dz\psi_0^2(z)[-\beta\gamma\delta(z-b)]\\&=\varepsilon_0-\beta\gamma\psi_0^2(b)\to\varepsilon_0-\beta\gamma C_0^2\end{aligned} \tag{17}$$

for sufficiently small b. The change of the surface monomer density due to the perturbed interaction can be further estimated by applying the WKB approximation [13]. Near the surface, we have

$$\begin{aligned}\psi_0(z)&=\frac{A}{[\varepsilon_0-V(z)]^{1/4}}\sin\left(\frac{\sqrt{2}}{a}\int_0^z dz\sqrt{\varepsilon_0-V(z)}+\alpha\right)\\&\simeq\frac{A}{(\varepsilon_0-V_0)^{1/4}}\sin\left(\frac{\sqrt{2(\varepsilon_0-V_0)}}{a}z+\alpha\right),\end{aligned} \tag{18}$$

where $\alpha\neq 0$ related to

$$C_0=\frac{A}{(\varepsilon_0-V_0)^{1/4}}\sin\alpha. \tag{19}$$

Notice that, in the usual case of quantum mechanics [13], because of the hard-wall boundary condition $C_0=0$, α is set to be zero.

Similarly, we can also write

$$\psi_1(z)\simeq\frac{A}{(\varepsilon_1-V_0)^{1/4}}\sin\left(\frac{\sqrt{2(\varepsilon_1-V_0)}}{a}z+\alpha\right), \tag{20}$$

where the coefficients A and α are assumed unchanged. Hence

$$C_1=\frac{A}{(\varepsilon_1-V_0)^{1/4}}\sin\alpha. \tag{21}$$

From Eqs. (19) and (21), we got the relation $(\varepsilon_0-V_0)C_0^4=(\varepsilon_1-V_0)C_1^4$, and hence

$$C_1\simeq C_0-\frac{C_0}{4(\varepsilon_0-V_0)}(\varepsilon_1-\varepsilon_0)=C_0+\frac{\beta\gamma}{4(\varepsilon_0-V_0)}C_0^3 \tag{22}$$

by applying Eq. (17). Remind that $\varepsilon_0-V_0>0$. Equation (22) is consistent with our picture that short-ranged attraction (repulsion), $\gamma>0(<0)$, increases (decreases) the surface monomer density. The next higher order correction for C_1 is $O(C_0^3)$ [14]. The linear relation between the surface monomer density and the surface charge density is no longer valid after including the short-ranged interaction effect. However, the violation of the linear relation implies that part of the surface monomer density is not due to the electrostatic interaction in which the electrostatic boundary condition does not apply [15].

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[14] The author have tried several different "variational wave functions" $\psi(z)$ to determine the next higher-order correction, and it was found that the orders are different among those different variational wave functions. It seems that the order depends on the details of the potential $V(z)$. However, the main point is that the correction should be at higher order, and hence the simple linear form of the boundary condition no longer holds after including the short-ranged interaction.
[15] Another way to understand it is as follows. The part of the adsorbed monomers due to short-ranged interaction $-\gamma\delta(z-b)$ is adsorbed at $z=b$, and it is counted into the surface monomer density after taking sufficiently small b.