Conformational Properties of an Adsorbed Charged Polymer

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Charged polymer (polyelectrolyte) adsorption on charged surface remains an interesting and important problem due to its influence to material science \textsuperscript{1}, colloidal science \textsuperscript{2}, and biological science \textsuperscript{3}. Hard substrates, and soft surfactant layers at interfaces can also be charged, due to the dissociation of ionic groups on the surfaces. Because the electrostatic force is strong and long-ranged, the electrostatic interaction between a charged polymer and a charged surface usually dominates over other non-electrostatic ones.

The problem of charged polymer adsorption on charged surface can be studied by many approaches \textsuperscript{4}. By replacing the counterion effect by the Debye-Hückel potential within the linear mean-field theory, one solve the Edwards equation \textsuperscript{5,6,7}. One can also solve both the Edwards equation and the Poisson-Boltzmann equation self-consistently \textsuperscript{5,6,7} at nonlinear mean-field level in which the effective screening length near the charged surface may not be equal to the bulk one. Scaling theory were also applied to the problem \textsuperscript{11}. Even more, the effect of attractive image forces from high-dielectric substrate \textsuperscript{12,13,14}, and repulsive image forces from low-dielectric substrate \textsuperscript{15,16,17,18} were also investigated by analytical methods or Monte-Carlo (MC) simulation.

However, the analytical approaches involving the Edwards equation usually impose zero monomer density at the charged surface in which the electrostatic boundary condition cannot be faithfully respected. It is only for the case of charged polymer adsorption on the high-dielectric substrate studied by Cheng \textit{et al.} \textsuperscript{12} that the surface monomer density is properly treated. The surface monomer density follows a linear relation with surface charge density at Debye-Hückel level. It indicates that the charged polymer is fully compressed on the high-dielectric substrate without any conformational change. For the low-dielectric substrate, due to the repulsive image forces, the polymer is not necessarily compressed on the substrate. Instead, the conformational degree of freedom plays an important role on the adsorption behavior.

In this paper, we study the conformational properties of charged polymer adsorbed on the low-dielectric substrate at Debye-Hückel level by both the functional integral methods and MC simulation. It is found that the usual Edwards equation is no longer valid to describe the non-Gaussian feature of polymer conformation. A new formulation by the functional integral method is proposed and compared with simulation results. Finally we give an operational definition of charged polymer adsorption.

A charged polymer carrying positive charges is immersed in a medium \((z > 0)\) of dielectric constant \(\epsilon\). At \(z = 0\) there is an impenetrable surface. Below the surface \((z < 0)\), there is the substrate of low dielectric constant \(\epsilon' < \epsilon\). Just above the substrate, there is an uniform surface charge density \(\sigma < 0\). The adsorbed charged polymer always stays above the surface charge layer. Denote the charge on a polymer segment \(ds\) by \(qds\), the Hamiltonian is

\[
H = \frac{1}{2} \int_0^N ds \int_0^N ds' \left( \frac{e^{-\kappa|\vec{r}(s)-\vec{r}(s')|}}{|\vec{r}(s)-\vec{r}(s')|} + \Gamma'(2 - \delta_{s,s'}) \right) \\
\times \frac{e^{-\kappa|\vec{r}(s)-\vec{r}(s')|}}{|\vec{r}(s)-\vec{r}(s')|} - h \int_0^N ds \kappa^{-1} e^{-\kappa\vec{r}(s)} \hat{z} \quad (1)
\]

where \(s\) is the variable to parametrize the chain and \(\kappa^{-1}\) the Debye screening length. \(\vec{r}(s) = (x(s), y(s), z(s))\), \(\vec{r}(s') = (x(s'), y(s'), -z(s'))\) are the positions of the monomers and their electrostatic images, respectively. \(\Gamma = q^2/\epsilon, \Gamma' = \Gamma(\epsilon - \epsilon')/(\epsilon + \epsilon') > 0\), and \(h = 4\pi q|\sigma|/(\epsilon' + \epsilon) > 0\) are the coupling parameters governing the strengths of Coulomb interactions among the monomers themselves, between the polymer and its image, and between the polymer and the charged surface, respectively. Note that the above Hamiltonian is not exact even at Debye-Hückel level. In particular, the long-
where \( \vec{r}_i(s) = (x_i(s), y_i(s)) \) is the \( xy \)-plane projection of the curve \( \vec{r}(s) \). While the charged polymer is adsorbed, \( |\Delta z_i| \ll |\Delta \vec{r}_i| \), and note that \( \vec{r}_i(s) \) should describe a 2D polymer conformation. Hence we approximate

\[
Z \approx \int \mathcal{D}[\vec{r}_i(s)] \exp\left[\frac{1}{a^2} \sum_{i=1}^{N} (\Delta \vec{r}_i)^2 \right] \times \exp\left[\frac{1}{2a^2} \sum_{i=1}^{N} (\Delta z_i)^2 \right] \exp[-\beta \mathcal{H}]
\]

\[
= \int \mathcal{D}[\vec{r}_{\parallel}(s), \vec{r}_{\perp}(s)] \exp\left[-\frac{1}{a^2} \int_0^N ds \left( \frac{\partial \vec{r}_{\parallel}(s)}{\partial s} \right)^2 \right] \times \exp\left[-\frac{1}{a^2} \int_0^N ds \left( \frac{\partial \vec{r}_{\perp}(s)}{\partial s} \right)^2 \right] - \beta \mathcal{H}
\]

where \( \vec{r}_{\parallel}(s) = (\tilde{r}_i(s), z(s)) \) is the side-view of \( \vec{r}(s) \) along the curve \( \tilde{r}_i(s) \). Note that the coefficients of the entropy terms of \( \vec{r}_{\parallel}(s) \) and \( \vec{r}_{\perp}(s) \) are \(-1/a^2\) and \(-1/2a^2\), respectively, which are different from that of \( \vec{r}(s) \), \(-3/2a^2\).

For the case of charged polymer adsorption, the self-electrostatic interaction takes almost no effect in \( \vec{r}_{\perp}(s) \) since \( |\vec{r}_{\parallel}(s) - \vec{r}'_{\parallel}(s')| \approx |\vec{r}_i(s) - \vec{r}_i(s')| \). The repulsion from the images of the monomers can be effectively approximated by the interaction between each monomer and its image only. The residual repulsion is absorbed by renormalizing \( \Gamma' \). Then the partition function becomes

\[
Z \approx \int \mathcal{D}[\vec{r}_{\parallel}(s)] \exp\left[\frac{1}{a^2} \int_0^N ds \left( \frac{\partial \vec{r}_{\parallel}(s)}{\partial s} \right)^2 \right] \times \int \mathcal{D}[\vec{r}_{\perp}(s)] \exp\left[\int_0^N ds \left( -\frac{1}{2a^2} \left( \frac{\partial \vec{r}_{\perp}(s)}{\partial s} \right)^2 \right) - \frac{\beta \Gamma'}{2} \int_0^N ds \int_0^N ds' e^{-\kappa|\vec{r}_i(s) - \vec{r}_i(s')|} \right] \\
\times \int_0^N ds \left( -\frac{1}{2a^2} \left( \frac{\partial \vec{r}_{\perp}(s)}{\partial s} \right)^2 \right) - \beta \hbar \kappa \left[ e^{-\kappa \vec{r}_{\perp}(s) \cdot \hat{z}} \right]^{N} \]

The system is decoupled into two independent degrees of freedom, \( \vec{r}_i(s) \) and \( \vec{r}_{\parallel}(s) \). Since the above functional integral with respect to \( \vec{r}_i(s) \) does not affect the adsorption behavior, we investigate only the conformational properties of \( \vec{r}_{\perp}(s) \) in the following.

\[
\vec{r}_{\perp}(s) = \vec{r}_{\perp}(s) + \vec{l}(s) + \delta \vec{r}_{\perp}(s) \]

where \( \vec{r}_{\perp}(s) \) is the position of the center of mass, and \( \vec{l}(s) \) is the orientation vector of the charged polymer. We also restrict

\[
\vec{l}(s) \cdot \delta \vec{r}_{\perp}(s) = 0
\]
so that $\delta r_{\perp}(s)$ represents the local fluctuation along $\vec{l}(s)$.

The adsorbed polymer is now characterized by translational ($\vec{r}_{\parallel}$), conformational ($\vec{r}(s)$), and local fluctuational ($\delta r_{\perp}(s)$) degrees of freedom. Under the compression regime, $\vec{l}(s)$ vanishes.

In general, it is hard to compute the effect from $\vec{l}(s)$. For simplicity but still capturing the qualitative picture of the weak compression as shown in Fig. 1a, we further make an approximation that

$$
\vec{l}(s) \cdot \hat{z} = \begin{cases} 
(\frac{2as}{l-1})\vec{r}_{\perp} \cdot \hat{z}, & 0 < s < l/a \\
-(3-2as/l)\vec{r}_{\perp} \cdot \hat{z}, & l/a < s < 2l/a
\end{cases}
$$

(7)

and repeat for a period of $2l/a$. Its schematic diagram is shown in Fig. 1b. Substituting Eqs. (5)-(7) into Eq. (4),

$$\frac{\delta \vec{r}}{\delta l}$$

so that $\delta z(s)$ makes an approximation that

$$\delta z(s) \ll 1.$$ (8)

(9)

and then integrate out the variable $\vec{l}(s)$ under the condition that $|\vec{l} \cdot \hat{z}| \ll 1$, the partition function becomes

$$Z = \mathcal{N}^{-1} \int d\vec{r}_{\perp} \exp[N\beta h\vec{r}_{\perp} \cdot \hat{z}] \int D[\delta r_{\perp}(s)]$$

$$= \mathcal{N}^{-1} \int d\vec{r}_{\perp} \cdot \hat{z} \int D[\vec{r}_{\perp}(s), \vec{l}(s)]$$

and $\hat{z}$ is a normalizing factor.

Effective potential for $\delta z(s)$ is linear rather than the harmonic. The result for the case of low-dielectric substrate cannot be analytically continued to the case of same dielectric constants. If $\Gamma' < 0$ (high dielectric substrate), the system is unstable. It implies that the decomposition in Eq. (5) is inadequate in high-dielectric case.

Hence, after integrating out the fluctuation variable $\delta z(s)$ under the ground state dominance (large-$N$ limit), there leaves only the variable $z_c$ in the partition function which determine the effective probability density distribution for the height of the center of mass,

$$\rho(z_c) = z_c \exp[-N\beta((h z_c + \Gamma') + \hat{z})]$$

(10)

Note that $l$ is related to $\vec{l}(s)$ via Eq. (7), and will be integrated out inside the functional integral of $\vec{l}(s)$.

Without the effect from $\vec{l}(s)$ and $\delta r_{\perp}(s)$ which expressed in the effective potential of $\delta z(s)$, the polymer acts as a rigid rod. Its equilibrium height is at $z_c = \sqrt{\Gamma'/4h}$. The ensemble average

$$\langle \delta z(s) \rangle = \frac{z_c}{2}(1 - \frac{4h z_c^2}{\Gamma'})$$

(11)

The entropic force points upward (downward) when the height of center of mass of the polymer is lower (higher) than $\sqrt{\Gamma'/4h}$. If $\Gamma' = 0$ (same dielectric constants), the effective potential of $\delta z(s)$ is linear rather than the harmonic. The result for the case of low-dielectric substrate cannot be analytically continued to the case of same dielectric constants. If $\Gamma' < 0$ (high dielectric substrate), the system is unstable. It implies that the decomposition in Eq. (5) is inadequate in high-dielectric case.

Hence, after integrating out the fluctuation variable $\delta z(s)$ under the ground state dominance (large-$N$ limit), there leaves only the variable $z_c$ in the partition function which determine the effective probability density distribution for the height of the center of mass,

$$\rho(z_c) = z_c \exp[-N\beta((h z_c + \Gamma') + \hat{z})]$$

(12)

up to a normalization constant. The new equilibrium including the effect from conformational changes is calculated by “force balance”, $\partial z_c \log \rho(z_c) = 0$, which gives

$$\Gamma' + \frac{z_c^3}{4}(h - \frac{\Gamma'}{4z_c^2})^2 - \frac{a}{2}(\frac{\Gamma'}{2\beta z_c^2})^2 = \frac{\Gamma'}{4}$$

(13)

at large-$N$ limit. For high enough surface charge density that $z_{eq}^c$ is low, Eq. (13) gives $z_{eq}^c \sim |\sigma|^{0}$. The polymer is compressed in which the center of mass is independent of the surface charge density. When the surface charge density is lowered such that $z_{eq}^c$ is high, Eq. (13) reduces to the scaling $z_{eq}^c \sim |\sigma|^{-1/2}$. If the surface charge density is further lowered so that the polymer basically behaves as a colloid (undeformed state), Eq. (12) becomes...
\(\rho(z_c) = \exp[-N/\beta h z_c]\), and hence \(z^{*}\) is independent of the polymer conformation, which is consistent with its definition expressed in Eqs. (16). However, simulation results in Fig. 2 show that the scaling exponent is -0.67, a quite large deviation from our analytical result, -0.375. The deviation may be due to the approximation of the effective potential up to the quadratic order only. As shown in Fig. 2a and 2b, both the simulation results of \(z^{*}\) and \(D_{s}\) exhibit the crossover between the weak compression and compression regimes occurring at \(\sigma \approx -0.11\).

Finally, we also examine the relation between the surface monomer density and surface charge density by MC simulation. Fig. 3 shows the simulation data follows the linearity at high enough \(|\sigma|\), and start to deviate from the linearity at \(\sigma \approx -0.11\). The linear relation implies the compression regime \([13]\). The deviation from linearity tells that the polymer starts to be weakly compressed, which is also consistent with the MC results of both \(z^{*}\) and \(D_{s}\). Since it is hard to characterize the polymer conformation in MC simulation by the original definition as shown in Fig. 1, we would like to propose an alternative (operational) definition for charged polymer adsorption - the linearity between the surface monomer density and the surface charge density.

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\[\delta z \sim (z^*)^\frac{1}{2} \sim |\sigma|^{-\frac{1}{2}}\]
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