

Conformational properties of an adsorbed charged polymer

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The behavior of a strongly charged polymer adsorbed on an oppositely charged surface of a low-dielectric constant is formulated by the functional integral method. By separating the translational, conformational, and fluctuational degrees of freedom, the scaling behaviors for both the height of the polymer and the thickness of the diffusion layer are determined. Unlike the results predicted by scaling theory, we identified the continuous crossover from the weak compression to the compression regime. All the analytical results are found to be consistent with Monte Carlo simulations. Finally, an alternative (operational) definition of a charged polymer adsorption is proposed.

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Charged polymer (polyelectrolyte) adsorption on charged surfaces remains an interesting and important problem due to its influence to material science [1], colloidal science [2], and biological science [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 nonelectrostatic ones.

The problem of charged polymer adsorption on charged surfaces can be studied by many approaches [4]. By replacing the counterion effect by the Debye-Hückel potential within the linear mean-field theory, one solves the Edwards equation [5–7]. One can also solve both the Edwards equation and the Poisson-Boltzmann equation self-consistently [8–10] at a nonlinear mean-field level in which the effective screening length near the charged surface may not be equal to the bulk one. The scaling theory was also applied to the problem [11]. Even more, the effect of attractive image forces from a high-dielectric substrate [12–14], and repulsive image forces from a low-dielectric substrate [15–18] 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 *et al.* [13] 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 a dielectric constant ϵ . At $z = 0$ there is an impenetrable surface. Below the surface ($z < 0$), there is the substrate of a low-dielectric constant $\epsilon' < \epsilon$. Just above the substrate, there is a 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

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

where s is the variable to parametrize the chain and κ^{-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 the Debye-Hückel level. In particular, the longitudinal interaction decays algebraically rather than exponentially [17]. However, the conformational properties related to the adsorption behavior will not be affected. We shall focus on the case of a charged polymer adsorption in a low ionic strength medium.

The continuum Hamiltonian in Eq. (1) is discretized to

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perform MC simulation. The continuous curve $\vec{r}(s)$ is replaced by a chain of beads \vec{r}_i ($i=1, \dots, N$) with a hard-core excluded volume of finite radius a . The length and energy units are $2a$ and $q^2/2\epsilon a$, respectively. Runs up to 10^9 MC steps and up to $N=120$ are performed.

The partition function of the system is

$$\begin{aligned} Z &= \int \mathcal{D}[\vec{r}(s)] \exp \left[-\frac{3}{2a^2} \int_0^N ds \left(\frac{\partial \vec{r}(s)}{\partial s} \right)^2 - \beta \mathcal{H} \right] \\ &= \int \prod_{i=1}^N d(\Delta \vec{r}_i) \exp \left[-\frac{3}{2a^2} \sum_{i=1}^N (\Delta \vec{r}_i)^2 - \beta \mathcal{H} \right] \\ &= \int \prod_{i=1}^N d(\Delta \vec{r}_{\parallel i}) d(\Delta z_i) \exp \left[-\frac{3}{2a^2} \sum_{i=1}^N [(\Delta \vec{r}_{\parallel i})^2 + (\Delta z_i)^2] \right] \\ &\quad \times \exp[-\beta \mathcal{H}], \end{aligned} \quad (2)$$

where $\vec{r}_{\parallel}(s) = (x(s), y(s))$ is the xy -plane projection of the curve $\vec{r}(s)$. While the charged polymer is adsorbed, $|\Delta z_i| \ll |\Delta \vec{r}_{\parallel i}|$, and note that $\vec{r}_{\parallel}(s)$ should describe a two-dimensional (2D) polymer conformation. Hence we approximate

$$\begin{aligned} Z &\simeq \int \prod_{i=1}^N d(\Delta \vec{r}_{\parallel i}) d(\Delta z_i) \exp \left[-\frac{1}{a^2} \sum_{i=1}^N (\Delta \vec{r}_{\parallel i})^2 \right] \\ &\quad \times \exp \left[-\frac{1}{2a^2} \sum_{i=1}^N (\Delta \vec{r}_{\parallel i})^2 + (\Delta z_i)^2 \right] \exp[-\beta \mathcal{H}] \\ &= \int \mathcal{D}[\vec{r}_{\parallel}(s), \vec{r}_{\perp}(s)] \exp \left[-\frac{1}{a^2} \int_0^N ds \left(\frac{\partial \vec{r}_{\parallel}(s)}{\partial s} \right)^2 \right. \\ &\quad \left. - \frac{1}{2a^2} \int_0^N ds \left(\frac{\partial \vec{r}_{\perp}(s)}{\partial s} \right)^2 - \beta \mathcal{H} \right], \end{aligned} \quad (3)$$

where $\vec{r}_{\perp}(s) = (\vec{r}_{\parallel}(s), z(s))$ is the side view of $\vec{r}(s)$ along the curve $\vec{r}_{\parallel}(s)$. 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 $|\vec{r}(s) - \vec{r}(s')| \simeq |\vec{r}_{\parallel}(s) - \vec{r}_{\parallel}(s')|$. 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 Γ' . Then the partition function becomes

$$\begin{aligned} Z &\simeq \int \mathcal{D}[\vec{r}_{\parallel}(s)] \exp \left[-\frac{1}{a^2} \int_0^N ds \left(\frac{\partial \vec{r}_{\parallel}(s)}{\partial s} \right)^2 \right. \\ &\quad \left. - \frac{\beta \Gamma}{2} \int_0^N ds \int_0^N ds' \frac{e^{-\kappa |\vec{r}_{\parallel}(s) - \vec{r}_{\parallel}(s')|}}{|\vec{r}_{\parallel}(s) - \vec{r}_{\parallel}(s')|} \right] \\ &\quad \times \int \mathcal{D}[\vec{r}_{\perp}(s)] \exp \left[\int_0^N ds \left\{ -\frac{1}{2a^2} \left(\frac{\partial \vec{r}_{\perp}(s)}{\partial s} \right)^2 \right. \right. \\ &\quad \left. \left. - \frac{\beta \Gamma'}{4} \frac{e^{-2\kappa \vec{r}_{\perp}(s) \cdot \hat{z}}}{\vec{r}_{\perp}(s) \cdot \hat{z}} + \beta \hbar \kappa^{-1} e^{-\kappa \vec{r}_{\perp}(s) \cdot \hat{z}} \right\} \right]. \end{aligned} \quad (4)$$

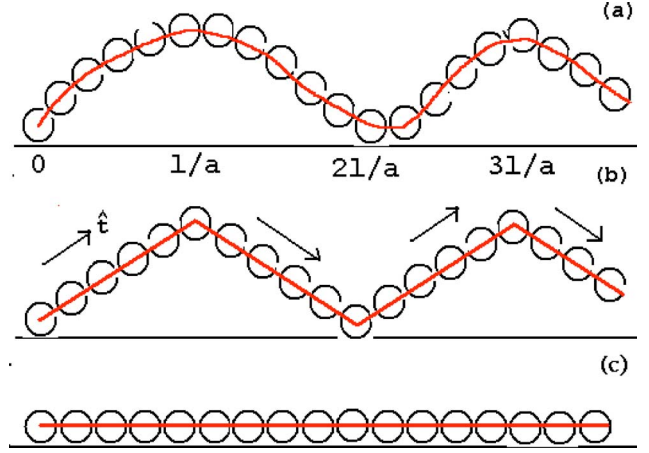


FIG. 1. Schematic diagram for the conformation of an adsorbed charged polymer. The degrees of freedom (entropies) of the polymer consists of three parts: the translation ($\vec{r}_{\perp c}$), the conformation [$\vec{r}(s)$], and the local fluctuation [$\delta \vec{r}_{\perp}(s)$]. The solid line represents the polymer orientation. The local fluctuation lies within the blobs. (a) The weakly compressed polymer (onset of adsorption) conformation in general. (b) The weakly compressed polymer conformation in our analytical approximation. (c) The compressed polymer (adsorption) conformation in which the conformational degree of freedom $\vec{r}(s)$ vanishes.

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

Because of the repulsive image force from the low-dielectric substrate, the charged polymer may be at weak compression or compression in which their schematic diagrams are shown in Figs. 1(a) and 1(c), respectively. The terminology of weak compression (onset of adsorption) and compression (adsorption) are borrowed from Borisov *et al.* [15,16] for grafted polymers.

In order to distinguish between the weak compression and the compression in our formulation, and note that a slowly varying orientation of polymer conformation under weak compression, we decompose

$$\vec{r}_{\perp}(s) = \vec{r}_{\perp c} + \vec{r}(s) + \delta \vec{r}_{\perp}(s), \quad (5)$$

where $\vec{r}_{\perp c} = (1/N) \int_0^N ds \vec{r}_{\perp}(s)$ is the position of the center of mass, and $\vec{r}(s)$ is the orientation vector of the charged polymer. We also restrict

$$\vec{r}(s) \cdot \delta \vec{r}_{\perp}(s) = 0 \quad (6)$$

so that $\delta \vec{r}_{\perp}(s)$ represents the local fluctuation along $\vec{r}(s)$.

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

In general, it is hard to compute the effect from $\vec{r}(s)$. For simplicity but still capturing the qualitative picture of the

weak compression as shown in Fig. 1(a), we further make an approximation that

$$\vec{r}(s) \cdot \hat{z} = \begin{cases} (2as/l - 1)\vec{r}_{\perp c} \cdot \hat{z}, & 0 < s < l/a \\ -(3 - 2as/l)\vec{r}_{\perp c} \cdot \hat{z}, & l/a < s < 2l/a \end{cases} \quad (7)$$

and repeat for a period of $2l/a$. Its schematic diagram is shown in Fig. 1(b). Substituting Eqs. (5)–(7) into Eq. (4), and at the low-salt limit, we get

$$\begin{aligned} Z &= \mathcal{N}^{-1} \int d\vec{r}_{\perp c} \exp[N\beta h \vec{r}_{\perp c} \cdot \hat{z}] \int \mathcal{D}[\delta\vec{r}_{\perp}(s)] \\ &\times \exp \left[\int_0^N ds \left\{ -\frac{1}{2a^2} \left(\frac{\partial \delta\vec{r}_{\perp}(s)}{\partial s} \right)^2 - \beta h \delta\vec{r}_{\perp}(s) \cdot \hat{z} \right\} \right] \\ &\times \int \mathcal{D}[\vec{r}(s)] \exp \left[-\frac{\beta \Gamma'}{4} \int_0^N \frac{ds}{\vec{r}_{\perp}(s) \cdot \hat{z}} \right], \end{aligned} \quad (8)$$

where the integral of $\vec{r}(s)$ is absorbed into the normalization constant \mathcal{N} . Expand the following integral around small $\delta\vec{r}_{\perp}(s)$ up to quadratic order,

$$\begin{aligned} \int_0^N \frac{ds}{\vec{r}_{\perp}(s) \cdot \hat{z}} &= \frac{N}{l|\hat{f} \cdot \hat{z}|} \ln \frac{2\vec{r}_{\perp c} \cdot \hat{z} + l|\hat{f} \cdot \hat{z}|}{2\vec{r}_{\perp c} \cdot \hat{z} - l|\hat{f} \cdot \hat{z}|} \\ &- \int_0^N ds \left\{ \frac{\delta\vec{r}_{\perp}(s) \cdot \hat{z}}{(\vec{r}_{\perp c})^2} - \frac{(\delta\vec{r}_{\perp}(s) \cdot \hat{z})^2}{(\vec{r}_{\perp c})^3} \right\} \end{aligned} \quad (9)$$

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

$$\begin{aligned} Z &= \mathcal{N}^{-1} \int_0^{\infty} dz_c z_c \exp \left[-N\beta \left(h z_c + \frac{\Gamma'}{4z_c} \right) \right] \\ &\times \int \mathcal{D}[\delta z(s)] \exp \left[\int_0^N ds \left\{ -\frac{1}{2a^2} \left(\frac{\partial \delta z(s)}{\partial s} \right)^2 \right. \right. \\ &\left. \left. - \beta \left(h - \frac{\Gamma'}{4z_c^2} \right) \delta z(s) - \frac{\beta \Gamma'}{4z_c^3} [\delta z(s)]^2 \right\} \right]. \end{aligned} \quad (10)$$

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

Without the effect from $\vec{r}(s)$ and $\delta\vec{r}_{\perp}(s)$, 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

$$\langle \delta z(s) \rangle = \frac{z_c}{2} \left(1 - \frac{4h z_c^2}{\Gamma'} \right). \quad (11)$$

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 for $\delta z(s)$ is linear rather than the harmonic. The result for the case of a 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 $\delta z(s)$

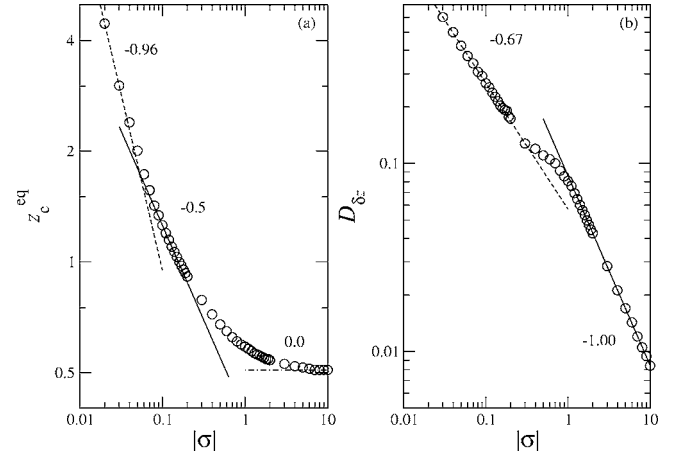


FIG. 2. (a) Simulation results for the equilibrium height of the polymer, z_c^{eq} (in units of $2a$), as a function of surface charge density, $|\sigma|$ (in units of $q/4a^2$), in logarithmic scale at $\epsilon'/\epsilon = 0.01$ and $\kappa^{-1} = 25$. It shows the scaling exponents decrease continuously from -0.96 (weak compression) to 0 (compression) with the surface charge density. The scaling exponent of -0.5 indicates the crossover (analytically predicted) occurs at $|\sigma| \approx 0.11$. (b) The thickness of the diffusion layer, $D_{\delta z}$, as a function of surface charge density, $|\sigma|$, in logarithmic scale. It shows the scaling exponents are -0.67 and -1.00 for weak compression and compression, respectively. The crossover occurs at $|\sigma| \approx 0.11$.

under the ground-state dominance (large- N limit), there leaves only the variable z_c in the partition function that determines the effective probability density distribution for the height of the center of mass,

$$\begin{aligned} \rho(z_c) &= z_c \exp \left[-N\beta \left\{ \left(h z_c + \frac{\Gamma'}{4z_c} \right) + \frac{z_c^3}{\Gamma'} \left(h - \frac{\Gamma'}{4z_c^2} \right)^2 \right. \right. \\ &\left. \left. - \frac{a}{2} \left(\frac{\Gamma'}{2\beta z_c^3} \right)^{1/2} \right\} \right], \end{aligned} \quad (12)$$

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

$$h(z_c^{\text{eq}})^2 + \frac{a}{4} \left(\frac{\Gamma'^3}{2\beta(z_c^{\text{eq}})^5} \right)^{1/2} = \frac{\Gamma'}{4} \quad (13)$$

at the large- N limit. For a high enough surface charge density that z_c^{eq} is low, Eq. (13) gives $z_c^{\text{eq}} \sim |\sigma|^0$. 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_c^{eq} is high, Eq. (13) reduces to the scaling $z_c^{\text{eq}} \sim |\sigma|^{-1/2}$. 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 $z_c^{\text{eq}} \sim |\sigma|^{-1}$. It predicts a continuous crossover from the compressed state to the weakly compressed state. It is different from that obtained by scaling analysis for grafted polymer, predicting a discontinuous jump [15]. Our analytical result is consistent with MC simulation as shown in Fig. 2(a).

Besides the position of the center of mass, we also calcu-

late the thickness of the diffusion layer, which is defined as the characteristic length scale of the exponential decay of monomer density. We first determine the saddle-point z_c^* from Eq. (10) (equivalent to integrating out the variable z_c at the large- N limit), which is given by

$$h(z_c^*)^3 - \frac{\Gamma'}{4} z_c^* + \Gamma' \langle \delta z(s) \rangle = 0. \quad (14)$$

The above equation is then solved self-consistently with Eq. (11) in which z_c is replaced by z_c^* . The solution is

$$z_c^* = \sqrt{\Gamma'/4h} \sim |\sigma|^{-1/2}. \quad (15)$$

The effective partition function for $\delta z(s)$ becomes

$$Z = \int \mathcal{D}[\delta z(s)] \exp \left[\int_0^N ds \left\{ -\frac{1}{2a^2} \left(\frac{\partial \delta z(s)}{\partial s} \right)^2 - \frac{\beta \Gamma'}{4(z_c^*)^3} [\delta z(s)]^2 \right\} \right], \quad (16)$$

which gives the diffusion layer thickness

$$D_{\delta z} \sim (z_c^*)^{3/4} \sim |\sigma|^{-3/8}. \quad (17)$$

The scaling exponent does not depend on the surface charge density. It means that the local fluctuation $\delta z(s)$ is independent of the polymer conformation, which is consistent with its definition expressed in Eqs. (5) and (6). However, simulation results in Fig. 2(b) 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 Figs. 2(a) and 2(b), both the simulation results of z_c^{eq} and $D_{\delta z}$ 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. Figure 3 shows the simulation data follow the linearity at high enough $|\sigma|$, and start to deviate from the linearity at

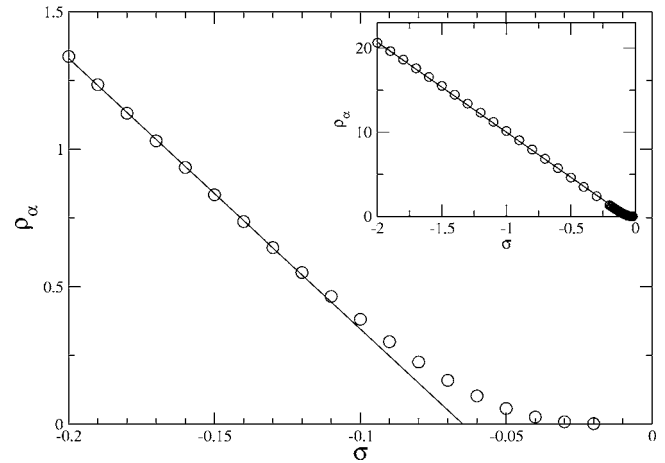


FIG. 3. Monte Carlo results for the normalized monomer density at the surface, ρ_s , as a function of surface charge density, σ (in units of $q/4a^2$), at $\epsilon'/\epsilon=0.01$ and $\kappa^{-1}=25$. The straight line is linearly fit to the data of higher $|\sigma|$. It shows the data starts to deviate from the linearity when $\sigma \approx -0.11$. Inset: More results to cover a larger range of surface charge density σ . It shows the data follows the linearity at higher $|\sigma|$.

$\sigma \approx -0.11$. 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_c^{eq} and $D_{\delta z}$. 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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