Density Functional Theory for Polyelectrolytes near Oppositely Charged Surfaces

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We report a nonlocal density functional theory of polyelectrolyte solutions that faithfully accounts for both short- and long-range correlations neglected in a typical mean-field method. It is shown that for systems with strong electrostatic interactions, the long-range correlations are subduced by direct Coulomb attractions, thereby manifesting strong local excluded-volume effects. The theory has also been used to describe the influence of the polyion chain length and small ion valence on charge inversion due to the adsorption of polyelectrolytes at an oppositely charged surface.

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The structural and thermodynamic properties of polyelectrolytes have been extensively studied, but theoretical predictions remain challenging because of the complex interplay of the excluded-volume effects, chain connectivity, and long-range electrostatic interactions. The incomplete knowledge of the physicochemical properties of polyelectrolyte solutions has been a major hurdle in understanding a variety of natural phenomena occurring in biological systems and in applications of polyelectrolytes to technologically important problems [1–4]. A number of theoretical methods have been proposed for polyelectrolyte systems, including those based on the Poisson-Boltzmann equation [5–7], polymer scaling laws [8,9], self-consistent-field theories [10–16], integral-equation theories [17–21], and, most recently, classical density functional theory (DFT) [22]. While a typical mean-field approach is useful to describe various aspects of weakly charged polyelectrolyte solutions, it is often inadequate for strongly charged systems where both short- and long-range correlations are important. The strong electrostatic interactions in polyelectrolyte systems may make any attempts to neglect either the excluded-volume effects or long-range correlations necessarily unsuccessful. In this Letter, we present a nonlocal density functional theory (NLDFT) for polyelectrolytes that accounts for, along with the bond potentials, the excluded-volume effects, long-range electrostatic interactions, and intramolecular correlations due to the chain connectivity in a self-consistent manner. By comparison with Monte Carlo simulations, we demonstrate that the NLDFT provides accurate density distributions of both polyelectrolytes and small ions. Theoretical predictions are also discussed concerning the effects of small ion valence and polyion chain length on the adsorption of polyelectrolytes.

We consider a primitive model of polyelectrolyte solutions where the polyions are represented by freely jointed chains of charged hard spheres, the small ions by individual charged hard spheres, and the solvent by a continuous dielectric medium. For convenience, all polymer segments and small ions are assumed to have the same diameter \( \sigma \). The total bond potential \( V_B(R) \) for a polyion with \( M \) spherical segments satisfies \( \exp[-\beta V_B(R)] = \prod_{i=1}^{M} \delta(|r_{i+1} - r_i| - \sigma)/4\pi \sigma^2 \), where \( \beta = (k_B T)^{-1} \) with \( k_B \) being the Boltzmann constant and \( T \) the absolute temperature, \( \delta \) stands for a one-dimensional Dirac delta function, and \( R = (r_1, r_2, \ldots, r_M) \) denotes a set of coordinates describing the segmental positions. The pair potential between nonbonded segments consists of a hard-sphere repulsion, i.e., \( \beta u_{ij}(r) = \infty \) for \( r < \sigma \), and a Coulomb interaction, \( \beta u_{ij}(r) = l_B Z_i Z_j/r \) for \( r \geq \sigma \). Here \( r \) is the center-to-center distance, \( Z_i \) is the particle valence, and \( l_B = \beta e^2/e \) is the Bjerrum length with \( e \) being the dielectric coefficient of the solvent and \( e \) the unit charge. Near a charged surface with a uniform charge density \( Q \), the external potential for each charged sphere is given by \( \beta \varphi_{i}(z) = \infty \) for \( z < \sigma \) and \( \beta \varphi_{i}(z) = -2\pi l_B Z_i Q z/e \) for \( z \geq \sigma \) with \( z \) being the perpendicular distance from the surface.

The intrinsic Helmholtz energy can be expressed as the sum of an ideal-gas term that preserves the bond connectivity and an excess that takes into account all nonbonded interactions:

\[
\beta F = \sum_i \int dR \rho_i(R) [\ln \rho_i(R) - 1 + \beta V_{h_i}(R)] + \frac{l_B}{2} \sum_{i,j} \int \int dR dR' \frac{Z_i Z_j \rho_i(R) \rho_j(R')}{|R - R'|} + \int \int dR dR' [-n_0 \ln(1 - n_3) + \frac{n_1 n_2 - n_{v1} n_{v2}}{1 - n_3}]
\]

\[
+ \frac{1}{36 \pi} \left( n_1 \ln(1 - n_3) + \frac{n_3^2}{(1 - n_3)^2} \right) \frac{n_1^2 - 3 n_2 n_{v2} n_{v2}}{n_3^3} \right] + \beta F_{el}^{\text{ex}}(\rho^e) - \int \int dR \sum_i \Delta C_{i}^{(\text{leq})}[\rho_i(R) - \rho_i^e] + \frac{1}{M} \int dR n_0 u_{ij}(1 - n_{v2}^e n_{v2}^e / n_{v2}^e) \ln(\sigma, n_{\alpha}) .
\]
where $\rho_i(R)$ denotes the number density of molecule $i$ (a polyelectrolyte or a small ion) with configuration $R$, $n_a(R)$, $\alpha = 0, 1, 2, 3, V_1, V_2$, are the scalar and vector weighted densities from the fundamental measure theory (FMT) [23], $y(\sigma_p, n_a)$ stands for the contact value of the cavity correlation function of polyelectrolyte segments in an inhomogeneous fluid of charged particles where all polymer chains are disconnected [24], $\Delta C_{ij}^{\text{el}}$ and $\Delta C_{ij}^{\text{el}}(r)$ represent, respectively, contributions of electrostatic interactions to the first- and second-order direct correlation functions of charged particles with uniform number density $\rho^e_i$, and $\beta F_{\text{el}}(\rho^e_i)$ is the corresponding reduced Helmholtz energy due to electrostatic correlations. Equation (1) accounts for multibody correlations by using a modified FMT for hard-sphere repulsions [25,26], a quadratic functional expansion (or hypernetted-chain approximation) for the electrostatic interactions [27,28], and the first-order thermodynamic perturbation theory (TPT1) for intrachain connectivity [29,30]. Similar expressions of the free-energy functionals have been used in our previous work for confined associating fluids [31], polymeric fluids [29,32], and electrolyte solutions [27,33]. Neglect of the size effects and intersegment correlations would reduce the Helmholtz energy to that used in the polyelectrolyte Poisson-Boltzmann approximation [5] or equivalently, in terms of the continuous Gaussian model for the chain connectivity, to that used in the self-consistent-field theory for polyelectrolytes [11]. The free-energy functional given in Eq. (1) also differs from that used in an earlier version of DFT for polyelectrolytes [22] where the contributions from the hard-sphere repulsion and chain connectivity are represented by a simple choice of the weight function [34,35] and the electrostatic correlation is ignored. Unlike alternative versions of DFT for hard spheres, the FMT is built upon firm physical and mathematical foundations rather than on empirical approximations for the weight function [36]. As indicated by others [37], FMT represents the best available DFT for strongly inhomogeneous hard-sphere fluids.

The numerical performance of the NLDFT is tested with Monte Carlo simulations for the polymer density profiles and small ion distributions for polyelectrolytes near an oppositely charged hard surface [22,38], because the solvation force can be directly derived from the density profiles through the contact-value theorem [5], a successful representation of the density profiles implies that the theory will also be accurate for predicting the solvation forces. For direct comparison, all parameters used in NLDFT are the same as those used in simulations [22,38]. Specifically, each polyelectrolyte chain consists of $M = 10$ segments and each segment bears a negative unit charge, i.e., $Z_p = -1$. All small ions are monovalent ($Z_+ = -Z_- = 1$). As in the simulations, the diameters of polymer segments and small ions are rather arbitrarily assumed the same as the Bjerrum length for water at 298.15 K (i.e., $\sigma = l_B = 0.714$ nm). The segmental densities in the bulk vary from $\rho_{p,b}\sigma^3 = 0.01$ to 0.2 and the surface charge density is fixed at $Q\sigma^2/e = 0.125$. All systems considered are at the salt-free condition; i.e., the influence of the salt concentration can be neglected.

Figure 1(a) presents the segment density profiles near an oppositely charged surface at five polyelectrolyte concentrations. In contrast with the prediction of a polymer-field theory that gives zero polyelectrolyte density at the contact [13], both NLDFT and Monte Carlo simulation [22,38] show significant accumulations of polyelectrolyte segments near the surface ($z = \sigma$) and a monotonic increase of the contact density with the bulk concentration. At high concentration, the polyelectrolyte density exhibits a secondary peak at approximately $z = 2\sigma$, signifying the layering of polyelectrolyte chains at the oppositely charged surface. Such a layering effect resembles that shown in the adsorption of neutral polymers and disappears at low polymer density, suggesting that the secondary peak at $z = 2\sigma$ is due to the local packing effect and chain connectivity [29]. The layering effects were not captured in an early version of DFT. Far from the surface, the NLDFT faithfully reproduces the oscillatory distributions of polyelectrolytes due to the long-range electrostatic interactions (the Debye length due to the screening of small ions varies from $l_{\text{Debye}}/\sigma = 2.8$ for $\rho_{p,b}\sigma^3 = 0.01$ to $l_{\text{Debye}}/\sigma = 0.631$ for $\rho_{p,b}\sigma^3 = 0.2$) that were not shown in previous theoretical investigations [5,11,13,22]. Figure 1(b) shows that at low polyelectrolyte concentration, the small cations are slightly depleted from the positively charged surface. At high concentration of polyelectrolytes, however, the contact densities of cations can be significantly higher than the corresponding bulk densities due to the adsorption of polyelectrolytes and excluded-volume effects.

The accumulation of polyelectrolytes at an oppositely charged surface is strengthened by the charge correlations and excluded-volume effects but weakened by the chain connectivity. A balance of these correlations leads to the curvature change in the polyelectrolyte density profile near the surface ($z/\sigma < 2$). Because the NLDFT describes the electrostatic correlations and excluded-volume effects rather well, the slightly overpredicted contact densities of polyelectrolyte segments shown in Fig. 1(a) are probably due to the use of TPT1 for chain connectivity. As for bulk polymeric fluids, TPT1 ignores the correlations beyond the nearest neighbors and thereby underestimates the intrachain correlations. This oversimplified approximation for the intrachain correlations is also responsible for the different curvatures of the polyelectrolyte density near the surface ($z/\sigma < 2$) predicted by NLDFT and by simulations at some intermediate polyelectrolyte densities ($\rho_{p,b}\sigma^3 = 0.06$ and 0.1). As a result, the theoretically predicted local packing effect at $z = 2\sigma$ is slightly more distinctive than the simulation results.

We now investigate the effects of polymer chain length and small ion valence on the adsorption of polyelectrolytes. For simplicity, the polyelectrolyte segments and small ions still have the same size ($\sigma = 0.425$ nm), but they are no longer equal to the Bjerrum length $l_B = 0.714$ nm. As before, each polymer segment carries one negative charge
(Z_p = -1), and the system remains at the salt-free condition. The polyion segment density in the bulk is fixed at $\rho_{p,b} \sigma^3 = 0.1$. Figure 2(a) shows the predicted density distributions of the polyions and small ions in contact with a planar surface of reduced charge density $Q\sigma^2/e = 0.125$. Here the polyion chain length is $M = 100$, significantly higher than that used in the simulations ($M = 10$). Three valences of small ions, $Z_+ = 1, 2, 3$, are considered. The polymer density profiles exhibit noticeable layering effects, and a weak minimum appears around $z = 3\sigma$. As the valence of small ions increases, we observe a magnified oscillation of small ion distributions, accompanied by less adsorption of polyions. In all cases, the polyions form a primary and a secondary layer near the oppositely charged surface, beyond which the polyion density essentially reduces to its bulk value. In other words, the long-range electrostatic and intrachain correlations are suppressed by the strong Coulomb attraction between the long-chain polyions and the oppositely charged surface.

Figure 2(b) presents the corresponding local mean electrostatic potentials and integrated charge distribution functions predicted by the NLDFT. The local mean electrostatic potential is calculated from the density profiles of polyions and small ions,

$$\psi^*(z) = 4\pi l_B \int_z^\infty dz' (z - z') \sum_k Z_k \rho_k(z'),$$

and the integrated charge distribution function, defined as

$$P(z) = \int_0^z dz' \sum_k Z_k \rho_k(z') + \frac{Q}{e},$$

specifies the net charge per unit area within distance $z$ from the surface. Figure 2(b) shows a strong oscillatory distribution of the local mean electrostatic potential. It declines sharply near the positively charged surface and exhibits a negative minimum approximately at $z = 2\sigma$, coinciding with the position of the secondary polyion layer. This negative electrostatic potential is responsible for the charge inversion of highly charged colloidal particles and plays an important role in the formation of polyelectrolyte multilayer structure. As the valence of small ions increases from +1 to +3, the minimum value of the electrostatic potential is slightly increased, but little variation is observed at the contact. The integrated charge distribution follows closely the mean electrostatic potential. The negative minimum in the integrated charge also reflects the charge inversion or overcharging effect. Interestingly, the minimal integrated charge varies little with the valence of small ions, suggest-
ing that the adsorption of polyelectrolytes at an oppositely charged surface is dominated by the direct Coulomb interactions with the surface.

To investigate the influence of the polyion chain length on charge inversion, we use the minimum value of the integrated charge distribution as an effective measure of overcharging. Figure 3 presents the minimal integrated charge versus the polyion chain length of polyelectrolytes at different surface charge densities. In all cases, the valence of small ions is fixed at $Z_{\pm} = 1$. Because of the relatively high concentration of polyions in the bulk, charge inversion occurs even when $M = 1$, i.e., in a simple electrolyte solution. As the chain length increases from $M = 1$ to 100, the magnitude of overcharging is also increased, in particular, at high surface charge densities. However, the chain length has a diminishing effect beyond $M = 100$, suggesting that the results obtained in this work are also applicable to very long polyelectrolytes. As expected, the charge inversion becomes more distinctive as the surface charge density increases, and such variation is most noticeable for polyelectrolytes with long-chain lengths.

In summary, we have shown that the NLDFT faithfully captures the layering and charge-inversion effects that cannot be reproduced by a typical mean-field method. It predicts that the adsorption of polyelectrolytes near an oppositely charged surface is dominated by the direct Coulomb attraction from the surface and the excluded-volume effects while the valences of small ions and long-range intrachain and electrostatic correlations play only a minor role. Charge inversion becomes more significant as the surface charge density or polyelectrolyte chain length increases, but it is relatively insensitive to the valences of small ions. Because of the versatility of the Helmholz energy functional, we expect that the NLDFT will be useful for more realistic models of polyelectrolytes including those containing nuclear acids or charged dendrimers.

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[38] A. Yethiraj and C. N. Patra (private communication).