Polymer 54 (2013) 6834–6842

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

The numerical study of the adsorption of bi-disperse flexible polyelectrolytes onto the surface of two charged objects

Guangyan Quan, Yuejin Zhu, Chaohui Tong*

Department of Physics, Ningbo University, Ningbo 315211, China

A R T I C L E I N F O

Article history:
Received 14 June 2013
Received in revised form
1 September 2013
Accepted 7 October 2013
Available online 18 October 2013

Keywords:
Self-consistent-field theory
Adsorption
Polyelectrolytes

A B S T R A C T

The continuum self-consistent-field theory (SCFT) is employed to study the adsorption of bi-disperse flexible polyelectrolytes (PEs) on two charged parallel columns. The effects of the bi-dispersity in terms of the average volume fractions and chain lengths of two kinds of chemically identical charged homo-polymers on the total amount of absorbed PE chains, the degree of charge compensation, and the total amount of the bridging chain conformation are investigated by numerically solving the SCF equations. The numerical study reveals that the longer PE chains are more effective than the shorter ones in charge compensating the opposite surface charges. The larger the relative chain length difference is, the more effective the longer PE chains in charge compensating the surface charges will be. The numerical results show different degrees of sensitivity of PE-adsorption to the screening-reduced salt effect for the constituents of the bi-disperse PE system. Moreover, how the dielectric contrast of the non-polar PE chains, the charged objects with respect to the polar solvent molecules impact the adsorption behaviors of mono-disperse PE chains is also examined.

1. Introduction

The adsorption of polyelectrolytes (PEs) onto oppositely charged surfaces is very interesting and important from both the fundamental and technological points of view [1–13]. PE adsorption has found a wide range of applications in industries, such as water treatment, paper-making. PE adsorption is also of crucial importance from the perspective of biology. For example, PE adsorption is involved in DNA wrapping in nucleosome core particles [14,15], and in RNA adsorption on the interior of viral capsids [16–18]. Due to the long range nature of Coulomb interaction and the multi-length scales in the PE systems, PE adsorption is much more complicated than the adsorption of neutral polymers onto neutral surfaces.

In the last several decades, PE adsorption has attracted considerable research attention, and has been the subject of various theoretical and computer simulation studies [19–35]. Important issues in PE adsorption, such as the charge inversion (the total amount of charges on adsorbed PE chains exceeds that of the surface charges of the object), the critical condition for adsorption, the thickness of the polymer layer, the addition of salt ions, and the difference between planar and curved (cylindrical, spherical) charged objects, and the interplay of PE-surface electrostatic and non-electrostatic interactions have been carefully investigated.

The presence of a polar solvent is indispensable for polyelectrolyte segments to dissociate and release counterions. The dielectric constants of organic polymers and the solvent could differ by 1 or 2 orders of magnitude. Furthermore, the dielectric constant of the substrates for PE adsorption could be much lower than that of the solvent. The effect of dielectric contrast between PE chains and the solvent was examined in the study of the one-dimensional interfacial properties of a phase-separated polyelectrolyte solution using the SCFT. It was found that a larger dielectric constant of the PE chains leads to a smaller miscibility of the PEs with the solvent and a longer decay length of the total charge density [36]. The influence of the low-dielectric substrates on PE adsorption has been examined theoretically and by computer simulations [37–47]. The electrostatic repulsion between the charges on the PE chains and the image charges of the same sign created beneath the substrate is shown to inhibit the adsorption of PEs onto the substrate.

In virtually all theoretical and simulation studies of PE adsorption, the PE chains are assumed to be monodisperse, that is, all of the chains are of the same length. However, in practice polydispersity is the rule rather than the exception for all the synthetic polymers, although much progress has been made in synthesizing polymers with very narrow molecular weight distribution through the so-called living polymerization technique [48]. Therefore, it is important to study the influence of polydispersity on PE adsorption.

---

* Corresponding author.
E-mail addresses: tongchaohui@nbu.edu.cn, ctong0@hotmail.com (C. Tong).

0032-3861/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymer.2013.10.017

In our previous studies, the adsorption of flexible PEs onto the surface of two oppositely charged columns immersed in a PE solution and the associated different chain conformations, the bridging chain conformation in particular, were examined by SCFT [49,50]. The polyelectrolyte mediated like-charge attraction between the two charged columns was revealed in the numerical study. In these works, the dielectric constants of the polymer chains and the substrate are assumed to be the same as that of the polar solvent. The effect of the PE chain length on the PE adsorption behaviors was investigated, but the influence of the chain length distribution was not considered. In this paper, the effect of the dielectric contrast of the PE chains and the substrate with respect to the solvent, and the influence of the PE molecular weight distribution on the adsorption of PEs onto two charged columns will be examined. For simplicity but without losing generality, the PE chains are assumed to be bidisperse, i.e., a mixture of two chemically identical polymers with different chain lengths. In the following, the theoretical model and numerical method are provided in Section 2. Results and discussions are presented in Section 3. Conclusions are summarized in Section 4.

2. Theory, model equations, and numerical methods

In this paper, we consider a system of volume V comprising two infinitely long charged columns with square cross-sections immersed in an oppositely charged polymer solution. The surface charge density of the columns is denoted as σ. There are two kinds of chemically identical homo-polymer chains A, B with chain lengths of N_A, N_B, respectively. Let's denote $\alpha = N_B/N_A$, and write $N_A \equiv N$. The size of the square cross-sections of the two columns is denoted as L_0, and the width of the gap between the two columns is labeled as H. For simplicity, the system is assumed to be translationally invariant along the axial direction (z direction).

The self-consistent field theory treats the many-chain problem as an effective single polymer chain in a mean-field which is to be determined self-consistently. The first step in deriving SCFT is writing down the partition function in the form of standard many-dimensional integral representation over the particle degrees of freedom. Next, by using the delta function transformation, the partition function is transformed into a functional integral representation over the auxiliary field functions. The exact evaluation of the functional integral is not possible. With the mean-field approximation, the functional integral can be evaluated by the saddle-point technique. The minimization of the free energy functional with respect to the field variables leads to a set of self-consistent field equations. The details of SCFT for weakly charged flexible PE chain systems can be found in Refs. [34,36]. Within the SCF theory, the auxiliary fields and the electric potential field are denoted by $\omega_j (j = A, B, S)$ and $\psi(\overrightarrow{r})$, respectively. The dimensionless free energy F is as follows:

$$\begin{aligned}\frac{Na^3F}{k_\mathrm{B}TV} = & \frac{1}{V}\int \mathrm{d}^2\overrightarrow{r}[\chi_{PS}N\phi_A(\overrightarrow{r})\phi_S(\overrightarrow{r}) + \chi_{\mathrm{PS}}N\phi_B(\overrightarrow{r})\phi_S(\overrightarrow{r})] \\ & -\frac{1}{V}\int \mathrm{d}^2\overrightarrow{r}\Big[\omega_A\phi_A(\overrightarrow{r}) + \omega_B\phi_B(\overrightarrow{r}) + \omega_S\phi_S(\overrightarrow{r}) \\ & +\frac{\varepsilon(\overrightarrow{r})}{2}|\vec{\nabla}\psi(\overrightarrow{r})|^2 + \eta(\overrightarrow{r})[1-\phi_A(\overrightarrow{r}) - \phi_B(\overrightarrow{r}) \\ & -\phi_S(\overrightarrow{r})]\Big] - \left[\overline{\phi}_A\ln\left(\frac{Q_A}{\overline{\phi}_A}\right) + \frac{\overline{\phi}_B}{\alpha}\ln\left(\frac{Q_B}{\overline{\phi}_B}\right) + N\overline{\phi}_S\ln\left(\frac{Q_S}{\overline{\phi}_S}\right)\right. \\ & \left. + N\overline{\phi}_+\ln\left(\frac{Q_+}{\overline{\phi}_+}\right) + N\overline{\phi}_-\ln\left(\frac{Q_-}{\overline{\phi}_-}\right)\right]\end{aligned} \tag{1}$$

where k_B is the Boltzmann constant and T denotes the absolute temperature, $\phi_j(\overrightarrow{r})$ with $j = A, B, S$ and $\pm$ are the dimensionless volume fractions of PE chains, solvent molecules and mobile ions, $\eta(\overrightarrow{r})$ is the Lagrange multiplier to enforce the incompressible condition, χ_{PS} denotes the Flory–Huggins interaction parameter between monomers and solvent molecules. In the above equation, the volume-averaged densities $\overline{\phi}_A \equiv n_A N/(\rho_0 V)$, $\overline{\phi}_B \equiv n_B \alpha N/(\rho_0 V)$ and $\overline{\phi}_M \equiv n_M/(\rho_0 V)$ with n_A, n_B and n_M representing, respectively, the total number of PE chains with a chain length N, αN and species $M(M = S, +, -)$, and $Q_A = \int \mathrm{d}\overrightarrow{r} q_A(\overrightarrow{r}, N)/V$, $Q_B = \int \mathrm{d}\overrightarrow{r} q_B(\overrightarrow{r}, \alpha N)/V$, $Q_M = \int \mathrm{d}\overrightarrow{r} \exp[-\omega_M/N]/V$. ρ_0 denotes the same density of PE segments and the solvent molecules, and $\varepsilon(\overrightarrow{r})$ denotes the dielectric permittivity. In the present study, we scale all lengths in the system by the Gaussian radius of gyration $R_g \equiv a\sqrt{N/6}$ with a the monomer statistical Kuhn length. The propagators $q_A(\overrightarrow{r}, s_A)$ and $q_B(\overrightarrow{r}, s_B)$ represent the probability of finding the segment $s_{A(B)}$ at the position $\overrightarrow{r}$, which respectively satisfy the following modified diffusion equations:

$$\frac{\partial q_A(\overrightarrow{r}, s_A)}{\partial s} = \nabla^2 q_A(\overrightarrow{r}, s_A) - [\omega_A(\overrightarrow{r}) + N\alpha_P\nu_A\psi(\overrightarrow{r})]q_A(\overrightarrow{r}, s_A), \tag{2}$$

$$\frac{\partial q_B(\overrightarrow{r}, s_B)}{\partial s} = \nabla^2 q_B(\overrightarrow{r}, s_B) - [\omega_B(\overrightarrow{r}) + N\alpha_P\nu_B\psi(\overrightarrow{r})]q_B(\overrightarrow{r}, s_B), \tag{3}$$

with the initial condition $q_{A(B)}(\overrightarrow{r}, 0) = 1$ outside the solid charged objects and the boundary condition $q_{A(B)}(\overrightarrow{r}, s) = 0$ on the surfaces of the objects. The SCF equations are summarized as following:

$$\phi_A(\overrightarrow{r}) + \phi_B(\overrightarrow{r}) + \phi_S(\overrightarrow{r}) - 1 = 0, \tag{4}$$

$$\omega_A(\overrightarrow{r}) = \chi_{PS}N\phi_S(\overrightarrow{r}) + \eta(\overrightarrow{r}), \tag{5}$$

$$\omega_B(\overrightarrow{r}) = \chi_{PS}N\phi_S(\overrightarrow{r}) + \eta(\overrightarrow{r}), \tag{6}$$

$$\omega_S(\overrightarrow{r}) = \chi_{PS}N\phi_A(\overrightarrow{r}) + \chi_{PS}N\phi_B(\overrightarrow{r}) + \eta(\overrightarrow{r}), \tag{7}$$

$$\omega_\pm = N\nu_\pm\psi(\overrightarrow{r}), \tag{8}$$

$$\phi_A(\overrightarrow{r}) = \frac{\overline{\phi}_A}{Q_A}\int_0^1 \mathrm{d}s_A q_A(\overrightarrow{r}, s_A)q_A(\overrightarrow{r}, 1 - s_A), \tag{9}$$

$$\phi_B(\overrightarrow{r}) = \frac{\overline{\phi}_B}{\alpha Q_B}\int_0^\alpha \mathrm{d}s_B q_B(\overrightarrow{r}, s_B)q_B(\overrightarrow{r}, \alpha - s_B), \tag{10}$$

$$\phi_M(\overrightarrow{r}) = \frac{\overline{\phi}_M}{Q_M}\exp[-\omega_M(\overrightarrow{r})/N], \tag{11}$$

$$\begin{aligned}\vec{\nabla}\cdot\Big[\varepsilon\Big(\overrightarrow{r}\Big)\vec{\nabla}\psi\Big(\overrightarrow{r}\Big)] = -N\Big[\alpha_P\nu_A\varphi_A\Big(\overrightarrow{r}\Big) + \alpha_P\nu_B\varphi_B\Big(\overrightarrow{r}\Big) \\ + \nu_+\varphi_+\Big(\overrightarrow{r}\Big) + \nu_-\varphi_-\Big(\overrightarrow{r}\Big)\Big],\end{aligned} \tag{12}$$

In Eqs. (2), (3) and (12), α_P denotes the average degree of ionization of PE chains with the smeared charge distribution, $\nu_A \equiv \nu_B \equiv \nu_P = -1$, $\nu_\pm = \pm 1$ are for the charge valences of PE chains and the mobile ions, respectively. Because the system is assumed to be translationally invariant in the z direction, each physical quantity can be viewed as a two-dimensional one on a per unit length in the z direction basis. Thus in the above and the following equations, the 3D position vector $\overrightarrow{r}$ is reduced to a 2D one.

When considering the dielectric contrast between the nonpolar polyelectrolyte chains, the substrate (the charged columns)