



A numerical study of spherical polyelectrolyte brushes by the self-consistent field theory



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ABSTRACT

The self-consistent field theory (SCFT) is employed to numerically study the scaling laws of brush height and the amount of counter-ions trapped inside a spherical polyelectrolyte (PE) brush immersed in a good solvent with no added salt ions. In particular, the curvature effect of the grafting substrate on the brush height and the amount of counter-ions trapped inside the PE brush is carefully examined. It is found that the brush height shows a non-trivial dependence on the radius of the grafting substrate. The numerical result reveals that the brush height scales linearly with respect to the grafting density and the average degree of ionization of PE chains in the planar surface limit, but not in the opposite limit. The numerical results show that, in a salt-free solution, about 96% of the counter-ions are trapped within the range of extension of grafted PE chains in the planar surface limit, irrespective of other system parameters. On the contrary, for the grafting substrate with high curvature, i.e., the radius of the grafting substrate is much smaller than the brush height, the amount of counter-ions trapped inside the PE brush approaches zero in the large system size limit. The underlining mechanisms governing the curvature effect of the grafting substrate on the brush height and the amount of counter-ions trapped inside PE brushes are elucidated.

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1. Introduction

Polyelectrolyte (PE) brushes comprise charged polymer chains densely grafted onto planar or curved surfaces by covalent bonds or physical adsorption [1–3]. PE brushes play a crucial role in modifying and regulating material surface properties. In the last decades, PE brushes have been extensively used in many technological applications such as surface modification [4], colloidal stabilization [5], oil recovery [6], lubrication [7,8], smart materials [9], etc. Thus, it is not surprising that PE brushes have been studied intensively by theories [10–16], simulations [17–30], and experiments [31–35].

Due to the presence of charged monomers and counter-ions in PE brushes, the characteristics and properties of PE brushes are quite different from neutral polymer brushes. Due to the Coulomb interaction and quite a few new length scales associated with PE brushes, a deep and thorough understanding of PE brushes is much more challenging than the neutral counterpart. One focal point of the physics of PE brushes is the dependence of the brush height on various relevant physical parameters, such as the chain length, the grafting density, the average charge fraction of the PE chains. From scaling arguments [10–12], in the so-called osmotic brush regime

where almost all the counter-ions are trapped inside the brush, by balancing the chain elasticity with the counter-ion osmotic pressure, the equilibrium brush height is found to be linearly proportional to the chain length, but independent of the grafting density. However, recent experimental as well as simulation works show a weak increase of the brush height with the grafting density [19,32,33]. A so-called non-linear osmotic brush regime has been proposed [13,33], in which the brush height scales linearly with the grafting density. Nevertheless, in most of the theoretical and computational studies of PE brushes, the grafting substrates are assumed to be planar surfaces. Using the self-consistent field theory (SCFT), Qu and coworkers numerically studied the scaling laws of the brush height of cylindrical PE brushes [20]. Non-trivial dependences of the brush height on the grafting density and charge fraction of PE chains were found in their study. However, the radius of the grafting substrate in their study, i.e., the cylinder, is rather small compared to the brush height and it is fixed throughout the study. Therefore, it is interesting and imperative to study the effect of curvature (spherical or cylindrical PE brushes) on the scaling laws of brush height, which is one main focus of the present study.

Another important issue regarding PE brushes is the distribution of counter-ions inside PE brushes. The amount of counter-ions trapped inside PE brushes has rarely been systematically investigated before. For planar osmotic PE brushes, the scaling theory simply assumes a nearly 100% trapping of the counter-ions inside

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the PE brushes. Moreover, how the dimensionality of the grafting substrate impacts the distribution of counter-ions inside PE brushes has received little attention.

In this paper, we employ a continuum self-consistent field theory (SCFT) to numerically study the scaling laws of the brush height and the distribution of counter-ions inside a spherical PE brushes immersed in a good solvent with no added salt ions. In particular, the effect of radius of the grafting substrate on the scaling laws of the brush height and the total amount of counter-ions inside PE brushes is carefully examined. As is well-known, the SCFT offers computational advantages over molecular simulations. The paper is organized as follows. In Section II, the theory and methods used in the present paper are described. In Section III, results and discussions concerning the brush height, the curvature effect as well as the amount of counter-ions trapped inside the brushes, are presented. In Section IV, the main results are summarized.

2. Theory, model equations, and numerical methods

In the system considered in this work, there are n_p PE chains with the smeared charge distribution and a chain length of N uniformly grafted onto a neutral sphere with a radius of R_p . The grafting density is denoted as σ_g (in unit of number of chains per unit area). Thus, we have $n_p = 4\pi R_p^2 \sigma_g$. The PE chains are confined in a much bigger concentric sphere of radius R_s than the neutral sphere and the bigger sphere has a neutral inner hard wall. Then the system volume is $V = 4\pi(R_s^3 - R_p^3)/3$. Similar to what has been shown in our previous study of the adsorption of polyelectrolytes onto a spherical oppositely charged object [39,40], it is expected that, the spherical geometry of the system and the neutral hard wall adopted in this study, instead of a spherical PE brush in the center of a cube with the periodic boundary condition, should exert no influence on the physics of spherical PE brush as long as the system size, i.e., the radius of the sphere in which the spherical PE brush is enclosed, is large enough.

SCFT for PEs treats the many-chain problem as an effective single flexible charged chain in a mean-field which is to be determined self-consistently. Compared with SCFT for neutral polymers, inside the Hamiltonian for PEs, the electrostatic contribution in the form $\int d\vec{r} [\psi(\vec{r}) \hat{\rho}_e(\vec{r}) - \epsilon |\vec{\nabla} \psi(\vec{r})|^2 / 2]$ with ϵ , ψ , $\hat{\rho}_e$ respectively denoting the dielectric permittivity of the medium, the electric potential and the total charge density, is included [36–38]. The partition function in the form of standard many-dimensional integral representation over the particle degrees of freedom is transformed into a functional integral representation over the auxiliary field functions. It is not possible to evaluate the functional integral exactly. 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 SCF equations. Within SCFT, the dimensionless mean-field free energy per chain of length N is

$$f = \frac{Na^3 F}{k_B T V} = \frac{1}{V} \int d^3 \vec{r} [\chi_{PS} N \phi_P(\vec{r}) \phi_S(\vec{r}) - \frac{1}{V} \int d^3 \vec{r} [\omega_P(\vec{r}) \phi_P(\vec{r}) + \omega_S(\vec{r}) \phi_S(\vec{r}) + \frac{\epsilon(\vec{r})}{2} |\vec{\nabla} \psi(\vec{r})|^2 + \eta(\vec{r}) [1 - \phi_P(\vec{r}) - \phi_S(\vec{r})]] - \left[\bar{\phi}_P \ln \left(\frac{Q_P}{\bar{\phi}_P} \right) + N \bar{\phi}_S \ln \left(\frac{Q_S}{\bar{\phi}_S} \right) + N \bar{\phi}_+ \ln \left(\frac{Q_+}{\bar{\phi}_+} \right) + N \bar{\phi}_- \ln \left(\frac{Q_-}{\bar{\phi}_-} \right) \right] \quad (1)$$

where k_B is the Boltzmann constant and T the absolute temperature, $\phi_j(\vec{r})$ with $j = P, S$ and \pm are the dimensionless volume fractions of PE chains, solvent molecules and mobile ions, $\eta(\vec{r})$ is the Lagrange multiplier to enforce the incompressibility condition, χ_{PS} denotes the Flory–Huggins interaction parameter between monomers and solvent molecules, $\omega_j(\vec{r})$ denotes the conjugate potential field within the SCFT formalism. The volume-averaged densities $\bar{\phi}_P = n_p N / (\rho_0 V)$, $\bar{\phi}_M \equiv n_M / (\rho_0 V)$ with n_M representing total number of species M ($M = S, +, -$) and ρ_0 denoting the same density of PE segments and the solvent molecules. $\epsilon(\vec{r})$ denotes the dielectric permittivity, $Q_P = \int d\vec{r} q(\vec{r}, 1) / V$, $Q_M = \int d\vec{r} \exp[-\omega_M / N] / V$. In the present study, we scale all the 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 propagator $q(\vec{r}, s)$ and $q^*(\vec{r}, s)$ represent the probability of finding the segment s at the position \vec{r} starting from two distinct ends of a grafted PE chain, which both satisfy the following modified diffusion equation:

$$\frac{\partial q(\vec{r}, s)}{\partial s} = \nabla^2 q(\vec{r}, s) - [\omega_P(\vec{r}) + N \alpha_P \nu_P \psi(\vec{r})] q(\vec{r}, s) \quad (2)$$

with the initial condition $q(r = R_p, 0) = 1$, $q(r > R_p, 0) = 0$, $q^*(r = R_p, 0) = 0$, $q^*(r > R_p, 0) = 1$, and the boundary condition $d\psi(r)/dr|_{r=R_p} = 0$, $d\psi(r)/dr|_{r=R_s} = 0$, $q(r = R_p, s) = 0$ for $s \neq 0$, $q(r = R_s, s) = 0$, $q^*(r = R_p, s) = 0$, $q^*(r = R_s, s) = 0$.

The dimensionless mean-field SCF equations are

$$\phi_P(\vec{r}) + \phi_S(\vec{r}) - 1 = 0, \quad (3)$$

$$\omega_P(\vec{r}) = \chi_{PS} N \phi_S(\vec{r}) + \eta(\vec{r}), \quad (4)$$

$$\omega_S(\vec{r}) = \chi_{PS} N \phi_P(\vec{r}) + \eta(\vec{r}), \quad (5)$$

$$\omega_{\pm}(\vec{r}) = N \nu_{\pm} \psi(\vec{r}), \quad (6)$$

$$\phi_P(\vec{r}) = \frac{\bar{\phi}_P}{Q_P} \int_0^1 ds q(\vec{r}, s) q^*(\vec{r}, 1 - s), \quad (7)$$

$$\phi_M(\vec{r}) = \frac{\bar{\phi}_M}{Q_M} \exp[-\omega_M(\vec{r}) / N], \quad (8)$$

$$\vec{\nabla} \cdot [\epsilon(\vec{r}) \vec{\nabla} \psi(\vec{r})] = -N [\alpha_P \nu_P \phi_P(\vec{r}) + \nu_+ \phi_+(\vec{r}) + \nu_- \phi_-(\vec{r})], \quad (9)$$

In Eqs. (2) and (9), α_P denotes the average degree of ionization or charge fraction of PE chains with the smeared charge distribution, $\nu_P = -1$, $\nu_{\pm} = \pm 1$ are for the charge valences of PE chains and the mobile ions, respectively. As can be seen from Eqs. (8) and (9), the electrostatics of SCFT is on the Poisson–Boltzmann level.

In numerically solving the SCF equations, it is convenient to employ a spherical coordinate system (r, θ, ϕ) where the origin is placed at the center of the two concentric spheres. Because SCFT as a mean-field theory neglects density fluctuations and is only applicable in the weak electrostatic coupling regime [41], it is very reasonable to assume that all physical quantities are independent of the two angular coordinates θ, ϕ , and vary only along the radial direction. Therefore, the dimensionality of the problem is reduced to one. Accordingly, the volume element is transformed to $dV \equiv d^3 \vec{r} = 4\pi r^2 dr$.

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