

Normal Electric Fields Bifurcate Polyelectrolyte Brushes

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Introduction

Surface modification by grafting (or otherwise associating) polymer chains to interfaces offers a well-developed path for nanoengineering “smart” surfaces that can respond to external stimuli and resemble biological systems. Polyelectrolyte coatings are particularly sensitive to environmental factors. Applying an electric field is an obvious and convenient method for impacting the state of the polyelectrolyte brush. When a field is oriented parallel to the surface, counterions move under the action of an external electric field and drag the surrounding solvent causing electro-osmotic flow but does not significantly alter the brush conformation. When the field is applied normal to the grafting surface a predicted [1,2] transition between extended/collapsed states is experimentally observed [3]. Such a swelling/de-swelling response may be the ideal behaviour for a controllable gate, limiting the passage of flowing fluid or ions [2,4] through MEMS devices.

We will discuss the case of a normal, external electric field since knowing that a brush is simply swollen or collapsed is not sufficient for determining its potential efficacy as a controllable gate. Before such responsive brushes can be deployed in microfluidic devices, the detailed structure of polyelectrolyte brushes subject to normal electric fields determined. In this talk, we will present simulations of low, intermediate and high grafting density polyelectrolyte brushes in the zero salt limit subject to normal electric fields that elucidate the conformational structure of polyelectrolytes and their associated counterions within brushes.

Materials and Methods

We use a typical Langevin dynamics scheme [5] in which monomers and counterions interact through purely repulsive Lennard-Jones and long-ranged Coulombic potentials. Monomers are bonded by finitely extensible nonlinear elastic bonds to form linear polyelectrolyte chains. The Bjerrum length is set to $\lambda_B = 3\sigma$ (where σ is the monomer diameter).

The polymer brush system is modeled as an ensemble of $M = 16$ flexible coarse-grained polyelectrolyte chains each composed of $N = 96$ negatively charged monomers. Each monomer dissociates one monovalent counterion (there is no added salt). The system dimensions are set in order to achieve the desired grafting densities $\sigma_g = M/(L_x L_y)$. The chains are grafted to a lower wall by a neutral grafting monomer. The grafting points are fixed and arranged in a hexagonal lattice of 4 rows with 4 lattice points on each row.

Results

At low grafting density, each chain is isolated occupying a volume characterized by $R_{g,0}$, the radius of gyration of a single grafted chain in zero field. The “mushroom regime” occurs for $\Sigma = \sigma_g/R_{g,0} < 1$. At $\Sigma \approx 1$ the chains start to overlap. This leads to the “true brush regime” in which $\Sigma > 1$. The set of densities used in this study cover the entire range of regimes.

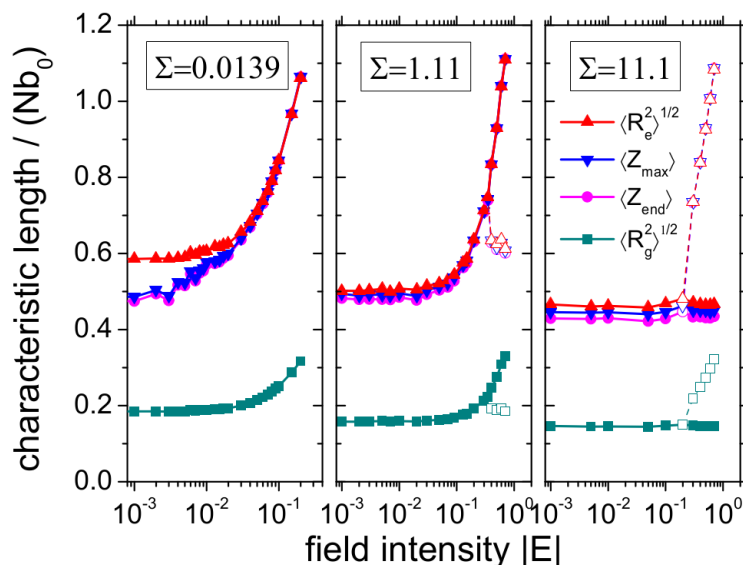
We will demonstrate that below a critical field $|E^*|$, local electroneutrality fails to be an adequate description for low grafting densities. Below $|E^*|$ the brush height remains relatively constant but above it there is significant charge redistribution due to polarization by the electric field. The brush height increases with field intensity. Figure 1 shows this behaviour for the low grafting density of Σ

= 0.0139 by considering the average of four separate metrics of the brush height: (i) the end-to-end distance $\langle R_e^2 \rangle^{1/2}$; (ii) the distance of the monomer furthest from the substrate $\langle Z_{max} \rangle$; (iii) the distance of the last monomer from the substrate $\langle Z_{end} \rangle$; (iv) the radius of gyration $\langle R_g^2 \rangle^{1/2}$. We will discuss monomer and counterion distributions and how the fraction of condensed counterions decreases. We will explain that the critical field scales as $1/3$ with grafting density.

At moderate and high grafting densities, a novel phenomenon is seen to occur: the population of grafted polyelectrolytes bifurcates into sub-populations of stretched and collapsed chains. At intermediate grafting densities the brush first swells and then above a second critical field $|E^{**}|$ bifurcates. The majority of chains are stretched, while the minority are non-stretched as seen in Figure 1. At high grafting densities bifurcation and swelling occur simultaneously and most chains remain non-stretched.

Discussion

We have explored polyelectrolyte brushes subject to external fields normal to the grafting substrate and discovered that under certain conditions the ensemble of chains bifurcates into two distinct populations. The conformational states are intimately tied to the counterion distributions. At low fields and high densities, brushes are roughly locally neutral and heights do not vary significantly. Above $|E^*|$ the brush heights rise as the counterions are pushed against the substrate by leaving the polyelectrolytes less screened. The film is thus polarized. Above $|E^{**}|$ a fraction of the polyelectrolytes rise above the counterion sea that is confined to be near the substrate. These bare ends feel the full force of the electric field and are significantly stretched. Their neighbours gain entropically and so collapse into the counterion sea where the counter-charge of the free ions protects them from the external field. The result is a bifurcation of the population into stretched and non-stretched chains. We predict that a third critical field $|E^{***}|$ exists above which the two subpopulations must remerge into a single fully stretched brush, although this value is predicted to be large and is not observed within the limits of our computational simulations.



References

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