

ABSTRACT

Title of Dissertation: ATOMISTIC EXPLORATION OF DENSELY-GRAFTED POLYELECTROLYTE BRUSHES: EFFECT OF APPLIED ELECTRIC FIELD AND MULTIVALENT SCREENING COUNTERIONS

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Polyelectrolyte (PE) or charged polymers are ubiquitous under biological and synthetic conditions, ranging from DNA to advanced technologies. PE chains can be grafted on a surface and they extend into solution to form a "brush"-like configuration if the grafting density is high. PE brushes respond to external stimuli by changing their conformation and chemical details, which make them very attractive for numerous applications. Multivalent counterions (neutralizing PE charges) and external electric fields are known to significantly affect the brush behavior. Obtaining fundamental insights into PE brush's response to ions and electric field is of utmost importance for both industrial and academic research. In this dissertation, we use atomistic tools to improve our understanding of the PE brushes grafted on a single surface and two inner walls of a nanochannel under these two stimuli.

We start by developing an all-atom molecular dynamics simulation framework to test the behavior of the PE brushes (grafted on a single surface) in the presence of externally applied electric fields. It is discovered that the charge density of PE monomers can have significant influence on their response; a smaller monomer charge density helps the brush to tilt along the electric field, while the PE brush with higher monomer charge density bends and shrinks. We

found that counterion condensation to PE chains has a substantial impact in controlling these responses.

In the subsequent study we discuss the effect of counterion size and valence in dictating counterion mediated bridging interaction of two or more negative monomers. By examining the solvation behavior, we identify that bridging interactions are not a sole function of the counterion valence. Rather, it depends on the counterion condensation on the PE chain, as well as the size of the counterion solvation shell. We also test the dynamic properties of the counterions and associated bridges.

Later, we proceeded to simulate PE brush-grafted nanochannels to explore equilibrium and flow behavior in presence of nanoconfinement. We identify the onset of overscreening: there are a greater number of coions than counterions in the bulk liquid outside the brush layer. This specific ion distribution ensures that the overall electroosmotic flow is along the direction of the coions. Furthermore, for a large electric field, some of the counterions leave the PE brush layer into the bulk, resulting in disappearance of overscreening. If the number of counterions is greater than coions, electroosmotic flow reverses its direction and follows the motion of counterions. Finally, we discover that counterion-monomer interactions control the ion distribution. As a result, a diverse range of electroosmotic flow is found for counterions with different valence and size.