ABSTRACT

Title of Dissertation:	ATOMISTIC AND THEORETICAL DESCRIPTION OF LIQUID FLOWS IN POLYELECTROLYTE-BRUSH-GRAFTED NANOCHANNELS
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Polyelectrolyte (PE) chains grafted in close proximity stretch out to form a "brush"-like configuration. Such PE brushes can represent a special class of nanomaterials that are capable of exhibiting stimuli-responsive behavior. They can be manipulated as needed by changing the environmental conditions like pH, solvent quality, salt concentration, temperature, etc. This responsiveness renders them very useful for a plethora of applications such as lubrication, emulsion stabilization, current rectification, nanofluidic energy conversion, drug delivery, oil recovery, etc. Therefore, gaining fundamental insights into PE brush systems is of utmost importance for both industrial as well as academic research. In this dissertation, we make use of theoretical and computational tools to improve our understanding of planar PE brushes and then use this understanding to probe flows in PE brush-grafted nanochannels.

We begin our quest by conducting all-atom Molecular Dynamics (MD) simulations to probe the microstructure of planar PE brushes with an unprecedented atomistic resolution. This allows us to not only investigate the properties of the PE chains but also the local structure and arrangement of the counterions and water molecules trapped within the brushes. Next, we use our atomistic model to probe the effects of variation in charge density on the microstructure of weak polyionic brushes. Such a variation in the charge density is typically enforced by a change in the surrounding pH and is a characteristic behavior of pH-responsive (annealed) PE brushes.

Furthermore, we go on to develop the most exhaustive theoretical model for pH-responsive PE brushes known as the augmented Strong Stretching Theory (SST). Our model is an improvement over the existing state-of-the-art as it considers the effects of the excluded volume interactions and an expanded form of the mass action law. We further improve this model by including several non-Poisson Boltzmann effects, especially relevant at high salt concentrations. This improved model is in excellent agreement with the results of our all-atom MD simulations.

Next, we use our augmented SST to model pressure-driven transport in backbone-charged PE brush-grafted nanochannels. Our results are an improvement over previous electrokinetic studies that did not consider a thermodynamically self-consistent description of the brushes. Finally, we conduct all-atom MD simulations to probe the pressure-driven transport of water in PE brush-grafted nanochannels using an all-atom framework. The nanoscale energy conversion characteristics obtained from our simulations are in reasonable agreement with the predictions of our continuum framework and lie within the range of values reported by a prior experimental study.