ABSTRACT

Title of Dissertation: Atomistic Description of Cationic Polyelectrolyte Brushes Using Molecular Simulations and Machine Learning

Raashiq Ishraaq, Doctor of Philosophy, 2025

Dissertation directed by: Professor Siddhartha Das, Department of Mechanical Engineering, University of Maryland.

Densely grafted polymer and polyelectrolyte (PE) brushes, owing to their significant abilities to functionalize surfaces for a plethora of applications such as sensing, diagnostics, current rectification, surface-wettability modification, drug delivery, and oil recovery, have attracted significant attention over the past several decades. Unfortunately, most of the attention has primarily focused on understanding the properties of the grafted polymer and the PE chains with little attention devoted to studying the behavior of the brush-supported ions (counterions needed to screen the PE chains) and water molecules. Over the past few years, our group has been at the forefront of addressing this gap: we have employed all-atom molecular dynamics (MD) simulations for studying a wide variety of polymer and PE brush systems with specific attention to unraveling the properties and behavior of the brush-supported water molecules and ions. Our

findings have revealed some of the most fascinating properties of such brush-supported ions and water molecules, including the most remarkable control of nanofluidic transport afforded by the specific ion and water responses induced by the PE brushes grafted on the inner walls of the nanochannel.

The present dissertation is devoted towards employing all-atom molecular dynamics (MD) simulations, quantum MD simulations, and machine learning (ML) techniques to explore the water microstructure, ion dynamics, and hydration behavior of a very commonly used *cationic brush*, namely, poly(2-(methacryloyloxy)ethyl trimethylammonium chloride) (PMETAC). First, we investigate the hydration shells and the ion behavior within the PMETAC brush system, identifying that the $\{N(CH_3)_3\}^+$ and C═O groups of the PMETAC brushes respectively demonstrate apolar and hydrophillic hydration. Also the Cl^- counterions have high mobilities inside PMETAC brushes due to the mismatch of hydration strength of $\{N(CH_3)_3\}^+$ and Cl^-. Next, we extend our simulations to study the impact of different halide counterions ($I^–$, $Br^–$, $Cl^–$, and $F^–$ ions) on brush behavior, revealing trends in ion binding, brush compression, water structuring, and halide mobility due to the prevalence of chaotropic effects (demonstrated by iodide and bromide ions) and kosmotropic effects (demonstrated by chloride and fluoride ions). Next, we introduce an unsupervised machine learning framework to identify two hydration states around the $\{N(CH_3)_3\}^+$ group, showing that increased brush grafting density leads to a shift towards less structured water molecules. This combined ML-MD approach offers valuable insights into the role of hydration in soft matter systems and highlights the complex interplay between polyelectrolytes, water, and ions. Building on our understanding of equilibrium behavior and complex ion pairing, we further explored the system's response to an electric field by examining the electroosmotic (EOS) flow within a PMETAC-grafted nanochannel. Our observations revealed that the loose ion pairing

enabled PMETAC chains to adopt a specific configuration, enhancing ion concentration at the brush-nanochannel bulk interface which resulted in a nonlinearly large EOS flow. A bottleneck for this EOS study was the extent of analysis that we needed to do in order to identify the appropriate physical factors that drive such non-linear EOS transport. To address this challenge, we came up with another ML algorithm (driven by Linear Discriminant Analysis) that enabled us to quickly identify the necessary variables that one needs to study to analyze the EOS transport (or any generic perturbation-driven phenomenon). Finally, in a completely new genre of contribution, we developed a combined all-atom and quantum MD framework to analyze the interaction pattern between the PMETA brushes and a multi-atom counterion (SCN^- ion): our analysis revealed which atom of the SCN^- ion interact to what extent with the different atoms of the $\{N(CH_3)_3\}^+$ group and what is the chemical nature (covalent or electrostatic) of such interactions.