

ABSTRACT

Title of Dissertation: Atomistic Exploration of Water and Salt
 Confined in Sub-Nanometer and
 Nanometer Wide Boron-Nitride
 Nanotubes.

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In my dissertation, I will use atomistic simulations to study the behavior of water and salt solutions confined in sub-nanometer and nanometer wide boron nitride nanotubes (BNNTs). This study will provide fundamental insight into the effect of nanoconfinement on a) the structure of water-in-salt electrolytes (WiSEs) inside nanometer-wide BNNTs, b) structure, filling thermodynamics, and hydrogen bond (HB) kinetics and strength for water confined in BNNTs of various diameters.

For the past few decades, nanoconfined fluids are being actively researched by scientists and engineers due to their interesting properties that are absent in their bulk counterparts. Such fluids could play a crucial role in developing novel nanofluidic devices for application in the fields of energy storage, membrane separation, and bioengineering. In the context of nanoconfined

fluids, nanotubes are a very popular choice as structures used for confining these fluids. Among them, carbon nanotubes (CNTs) and boron nitride nanotubes (BNNTs) are two of the most well-studied nanotubes. They exhibit outstanding mechanical properties, chemical stability, and thermal conductivity. However, their electronic properties are dissimilar. CNTs are known to be semiconducting materials, while BNNTs are regarded as electrical insulators. These properties make each of these nanotube types quite unique. Also, due to the polar nature of the B-N bonds, the behavior of the fluid confined inside the BNNT is distinctly different compared to the fluid confined inside the CNT.

In chapter 2, I use all-atom molecular dynamics (MD) simulations to report a novel non-covalent endohedral nanotube-salt-water hybrid formed by confining a 10 molal (m) LiTFSI aqueous solution inside a (7, 7) BNNT that has an internal diameter comparable to the size of the TFSI anion. The simulation reveals that TFSI⁻ ions and hydrated Li⁺ ions form axially non-overlapping periodic blocks inside the (7, 7) BNNT. Also, the TFSI anions are immobile inside the hybrid, and as a result, traps the water encapsulated in between them. These circumstances lead to an interesting scenario where the entrapped water is confined in all directions resulting in zero-dimensional water blocks. Further, water exists in a liquid state in these zero-dimensional blocks. Finally, it is demonstrated (by detailed free energy curves) that this hybrid is stable against increasing temperature and the change of the surrounding chemical composition.

In chapter 3, I use all-atom MD simulations to show that water free localization of a TFSI⁻ ion at the negative electrode is possible for a moderately concentrated LiTFSI based WiSE confined inside a 1-nm diameter BNNT. I explain this possibility as a combined effect of the affinity of the TFSI⁻ ion to enter an empty nanometer-wide BNNT prior to other electrolyte molecules, and the size of the TFSI⁻ being comparable to the diameter of the BNNT.

In chapter 4, I use ReaxFF MD simulations to study the water structure and thermodynamics inside BNNTs of various diameters. This study shows that water is thermodynamically more stable when confined inside BNNTs compared to bulk water. Also, entropic favorability is found to be the predominant factor in stabilizing BNNT-confined water despite the mild hydrophilicity of hexagonal boron nitride. Further, the factors dictating the entropic favorability varies with the BNNT diameter due to significant changes in water structure.

In chapter 5, I explore the effect of BNNT based confinement on the water hydrogen bond kinetics and strength. First, appropriate water HB definitions were devised for BNNT-confined water systems (with varying degrees of confinement). Using these definitions, pairs of water molecules with HB configurations are identified and the corresponding HB kinetics and strengths are quantified.