ABSTRACT

$\pi-\pi$ stacking interactions are pervasive non-covalent forces that play a central role in determining the structure and dynamics of a wide range of chemical and biological systems. These interactions influence molecular organization in aromatic liquids, contribute to the stability of nucleic acid architectures in aqueous environments, and shape the local structuring of interfacial and ionic liquid systems. Despite their apparent simplicity, π–stacking interactions arise from a subtle interplay of dispersion, electrostatics, hydrogen bonding, and solvation effects, making their behavior highly sensitive to molecular environment and electronic structure. In this thesis, molecular dynamics simulations are utilized to investigate π–stacking across chemically diverse condensed-phase systems, ranging from pure aromatic molecular liquids and solvated nucleobase pairs to liquid–vapor interfacial systems and aromatic ionic liquids. A combined *ab initio* molecular dynamics and classical molecular dynamics framework is used to capture both electronic structure-driven effects and long-time statistical behavior. *Ab initio* simulations provide an accurate description of π-electron interactions, polarization, and hydrogen bonding in aqueous and interfacial environments, while classical simulations enable systematic exploration of larger systems and extended time scales. Structural and dynamical properties are analyzed using radial and spatial distribution functions, distance–angle correlations, hydrogen-bond statistics, and energetic descriptors to characterize stacking motifs and their evolution under different conditions. The results show that π–stacking persists in aqueous environments but is continuously affected by solvent-mediated interactions, while at liquid–vapor interfaces aromatic ions display distinct orientational preferences, with benzoate ions displaying a clear tendency to form stacked arrangements at the interface. In aromatic ionic liquids, π–stacking between aromatic cations and anions contributes to local structural organization and

influences transport properties, as captured through validated classical force-field simulations. Overall, this work highlights the environment-dependent nature of π–stacking interactions and demonstrates the importance of combining *ab initio* and classical molecular dynamics approaches to achieve a coherent molecular-level understanding of aromatic interactions in realistic condensed-phase systems.