MOLECULAR SIMULATION METHODS FOR MODELING ORGANIC MATERIALS

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Molecular dynamics is a computational tool that is critical to modern methods of understanding materials across a wide range of applications. Molecular dynamics simulations calculate the motions of atoms through small time steps using Newton's laws of motion and potentials that approximate the forces. This allows for the prediction of a variety of physical properties with a fundamentally simple method. This method is used for the two main projects discussed here: the development of a genetic algorithm that parametrizes coarse-grain models and a framework to computationally probe the underwater adhesion of a range of molecules.

Deep neural networks have become popular model architectures for fitting coarse-grained molecular dynamics potentials (CGMD) owing to their ability to describe complex features and ease of training against large datasets. However, such architectures are much more complicated than traditional functional forms. This raises the question of whether a similar data-driven approach that used a simpler functional form would have any advantages. In in the first part of this defense, we develop a genetic algorithm that optimizes Lennard-Jones potentials for coarse-grained models of various crystal and liquid crystal forming materials based on both structural and thermodynamic information. A detailed description of the genetic algorithm, its loss function, and hyperparameters is presented. The models developed by the algorithm reproduce a much broader range of physical properties than achieved by simpler parametrization schemes used in more general methods, such as Martini. The models also show surprising transferability in reproducing properties that were not directly trained against. Simulations of larger systems with these models demonstrate stabilization of the reference crystal structure on long time scales, preserve melting-point trends, and reproduce liquid crystalline phase transitions, despite this information being absent from training. The genetic algorithm is then expanded to parametrize amorphous systems. The algorithm is used to parametrize a set of oligomers, originally modeled in all-atom simulations with developed machine learned interatomic potentials. The developed models show excellent performance in reproducing the radial distribution function, pressure, and interaction energy of these oligomers, showing that this parametrization methodology can be extended to a wide variety of systems. Despite the rush to adopt neural network potentials, these case-studies show that simpler functional forms retain untapped potential for CGMD when coupled with data-driven training algorithms.

Adhesives are critical materials across numerous applications, yet most commercial adhesives fail in aqueous environments. Catechol-based adhesives, inspired by marine mussels and other aquatic organisms, are distinctive in providing both strong surface adhesion and bulk cohesion underwater; however, the molecular mechanism enabling this performance remains poorly understood, limiting the rational design of improved materials. In the second part of this defense, steered molecular dynamics (SMD) simulations and density functional theory (DFT) calculations were used to systematically screen several hypothesis-driven series of candidate molecules for underwater adhesive performance on an alumina surface. Bidentate molecules consistently outperform unidentate molecules, and increasing hydroxyl substitution monotonically improves adhesion up to pentahydroxybenzene. Binding group geometry is also critical, with ortho-positioned groups outperforming meta and para isomers. Binding motif analysis revealed two mechanisms: direct

surface binding and binding to a surface-bound water layer, with the highest-performing molecules engaging in both simultaneously. Oxidation energy--a surrogate for crosslinking capacity--shows no correlation with adhesive performance, suggesting that adhesive and cohesive properties can be independently optimized. Alternative core groups were also studied, finding that 1,8-dihydroxynaphthalene can outperform the canonical benzene ring found in catechol. This framework was then extended to polymeric systems, where the adhesive small molecules are attached to a selection of experimentally known backbones and linkers. With the catechol binding group it was found that the best performing linkers tended to be less bulky or more hydrophobic, indicating that competing with water for physical space is a major limitation in underwater adhesion for the polymer case. When testing several of the small molecules with a consistent backbone and linker, it was found the attaching to polymers greatly exaggerated the existing trends in adhesive performance, and diminished some of the performance of higher substituted binding groups. These results establish structure-based design rules for underwater adhesives and identify promising candidates beyond catechol for future experimental validation.