

Structuring of hydrophobic and hydrophilic polymers at interfaces

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ChE 210D Final Project

Abstract

In this work, a simplified Lennard-Jones (LJ) sphere model is used to simulate the aggregation, adsorption, and structure of interfacial layers of fully hydrophobic, fully hydrophilic, as well as block (hydrophobic-hydrophilic) polymers. The structure of the adsorbed polymers at hydrophobic and hydrophilic surfaces is determined by the equilibrium density profile as a function of the distance from the surface. Several interesting features of hydrophobic self assembly are captured, such as the segregation of hydrophobic moieties, and the ability of hydrophilic groups to effectively “shield” hydrophobic ones.

Introduction

The interplay of hydrophobic and hydrophilic interactions can determine the behavior and structure of many self-assembled biological and technological systems, such as proteins, peptides, lipid membranes, vesicles, and emulsifiers. These water-specific interactions arise largely due to water structuring effects: hydrophobic groups attract each other in water because water cannot satisfy its preferred hydrogen bonding network, while hydrophilic groups repel each other due to strong hydrogen bonding of surrounding waters. Advanced models can capture the subtleties of these two interactions, but for the purpose of this work a LJ polymer bead model is used as a simplified representation of a peptide or surfactant molecule. These polymers interact with a LJ surface in order to examine relevant physics and dynamics of hydrophobic self-assembly at interfaces.

Methods

A molecular dynamics simulation of short-chain polymeric beads was carried out using the dimensionless Lennard Jones chain model potential with the energy function U ,

$$U = \sum_{i < j, ij \text{ not bonded}} 4\epsilon_{ij}(r_{ij}^{-12} - r_{ij}^{-6}) + \sum_{i < j, ij \text{ bonded}} \frac{k}{2}(r_{ij} - r_0)^2 \quad (1)$$

where ϵ_{ij} is the non-dimensional energy, r_{ij} is the pairwise distance, k is the force constant between adjacent bonded atoms, and r_0 is the equilibrium bond distance. Literature values of $k = 3000$ and $r_0 = 1$ are used. When both atoms i and j are hydrophobic,

$$\epsilon_{ij} = \epsilon_{\text{hydrophobic-hydrophobic}} = 1.0, \quad (2)$$

otherwise,

$$\varepsilon_{ij} = \varepsilon_{\text{hydrophobic-hydrophilic}} = \varepsilon_{\text{hydrophilic-hydrophilic}} = 0.1 \quad (3)$$

In order to determine the behavior of these polymer chains as they adsorb and assemble at interfaces, an LJ wall potential of the form shown in equation 4 is used,

$$U(z) = \sum_i w_{i\text{-wall}1} \rho_s \sigma^3 \left(\frac{1}{15} z^{-9} - \frac{1}{2} z^{-3} \right) - w_{i\text{-wall}2} \rho_s \sigma^3 \left(\frac{1}{15} (z-L)^{-9} - \frac{1}{2} (z-L)^{-3} \right), \quad (4)$$

where crystalline close packing is used for the wall density, $\rho_s \sigma^3 = 0.74$, and $w_{i\text{-wall}}$ is the non-dimensional wall energy. Similarly to the case above, for a hydrophobic bead interacting with a hydrophobic wall, $w_{i\text{-wall}} = 150$, and for all other interactions (hydrophobic-hydrophilic and hydrophilic-hydrophilic), $w_{i\text{-wall}} = 15$. These values were chosen so that the magnitude of the attractive well in the potential energy is approximately equivalent for atom-wall and atom-atom interactions. The above equation accounts for a wall at $z = 0$ and $z = L$, and the combination of (1) and (4) allow for tuning the interaction strength, and thus structuring, of the “hydrophobic” and “hydrophilic” polymers at like and unlike interfaces.

For the simulations, 100,000 equilibration time steps were performed with the velocity Verlet algorithm, where the time step $dt = 0.001$. During the equilibration period, velocity rescaling was used as a thermostat to hold the temperature at T (dimensionless) = 1.0. After the equilibration period, a production run of 100,000 time steps was done in order to generate density histograms, $\rho(z)$. Simulations for different polymer and wall compositions were done for 500 total particles made up of 10-unit hydrophobic, hydrophilic, and block (5 units hydrophobic, 5 units hydrophilic) polymers with hydrophobic and hydrophilic walls. Periodic boundary conditions were implemented in the x and y directions, with a cubic simulation box with walls separated by the box length $L = 10$.

Results and Discussion

To determine the behavior of the weaker hydrophilic interaction, simulations are performed with hydrophilic polymers and varying wall configurations. Figure 1 displays an overall average of 5 simulation runs of hydrophilic polymers; 3 runs with hydrophilic walls, 1 run with hydrophobic walls, and 1 run with asymmetric (hydrophobic vs. hydrophilic) walls. The hydrophilic polymers clearly preferentially adsorb to the interfaces at $z = 0$ and $z = L = 10$. The adsorption causes peaks in the density distribution, corresponding to weaker structuring as the density decreases away from the wall, until the bulk value is approached near the middle of the box. Hydrophobic polymers were also simulated to determine how the structure is influenced for a stronger interaction.

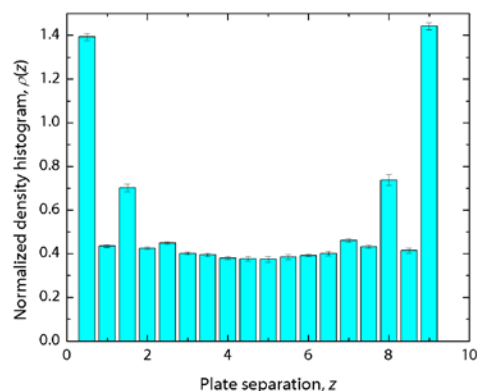


Figure 1. Normalized density histogram of the z -direction for simulations of *hydrophilic polymers* and varying plate composition separated by $z = L$. The results shown are an average of 5 simulations: 3 simulations with hydrophilic plates and 2 simulations with hydrophobic plates. The interaction with the plate is the same regardless of the plate composition for these hydrophilic polymers, and the error bars shown are the standard deviations for each of the bins over the 5 simulation trials.

Extreme differences are observed when examining hydrophobic polymers, as shown in Figure 2. Figure 2A shows the density distribution for hydrophobic polymers interacting with hydrophilic plates, while Figure 2B shows the density profile for hydrophobic polymers interacting with hydrophobic plates. Several interesting features are observed. Enhanced attractions between the polymer molecules lead to more pronounced aggregation and the 2nd and 3rd adsorbed layers are easily observable. Interestingly, asymmetry in the density profiles was observed, which is likely the result of the initial energy minimized configuration. Polymers

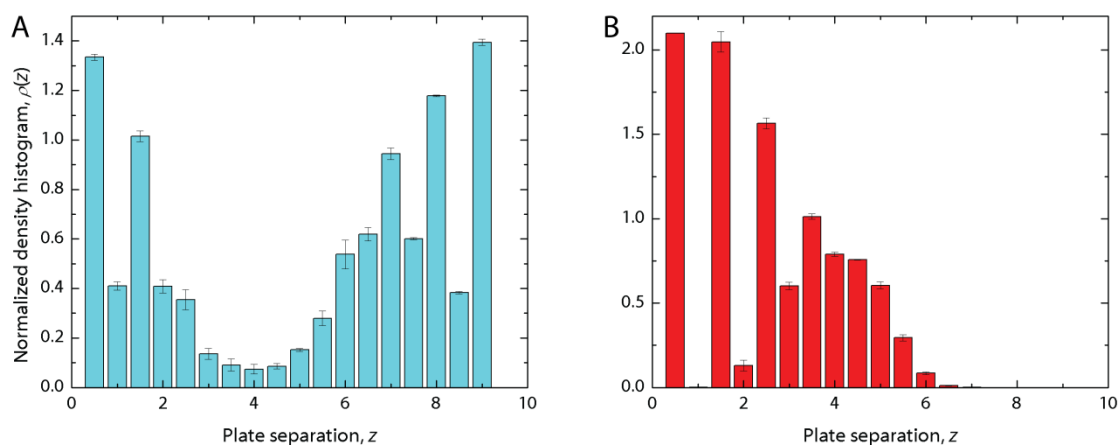


Figure 2. Equilibrium density profiles for *hydrophobic polymers* near (A) *hydrophilic* walls and (B) *hydrophobic* walls. Each histogram was averaged over 3 trials and the error bars represent the standard deviation for each bin for the 3 trials.

that initially have more molecules closer to one of the walls will migrate preferentially towards that wall due to enhanced attraction of both the wall and the surrounding particles, as

observed for the hydrophilic wall at $z = L$ in Figure 2A and additionally for the hydrophobic wall at $z = 0$ in Figure 2B. Also, the strong adsorption of the hydrophobic polymers at a hydrophobic interface results in a configuration in which the first layers are actually laying down on the surface in a somewhat ordered manner, as indicated by the first two peaks in the density profile of Figure 2B.

Finally, a more complex simulation is performed with block (hydrophobic-hydrophilic) polymers for the hydrophilic and hydrophobic walls, the results of which are shown in Figure 3A and 3B, respectively. Both density profiles for the block polymers display obvious segregation and aggregation of hydrophilic and hydrophobic moieties. The hydrophobic moieties once again show more structuring in general, as expected. The profile shown in Figure 3B, for hydrophobic plates, has several exciting and interesting characteristics. There are clear segregated regions: at $z = 0$, hydrophobic residues have adsorbed to the surface, while extending their hydrophilic groups away from the surface. Interestingly, hydrophilic groups have adsorbed at $z = L$ (likely because their initial configuration was closer to this surface), and blocked the hydrophobic atoms from adsorbing at the hydrophobic interface. While the physics are likely different than those shown by this simple model, the hydrophilic atoms appear to quench the local hydrophobicity, an idea captured by recent experimental and theoretical work. Instead of adsorbing at the hydrophobic interface, the hydrophobic polymer beads are content to aggregate into a central region between the hydrophilic groups, similar to a self-assembled bilayer.

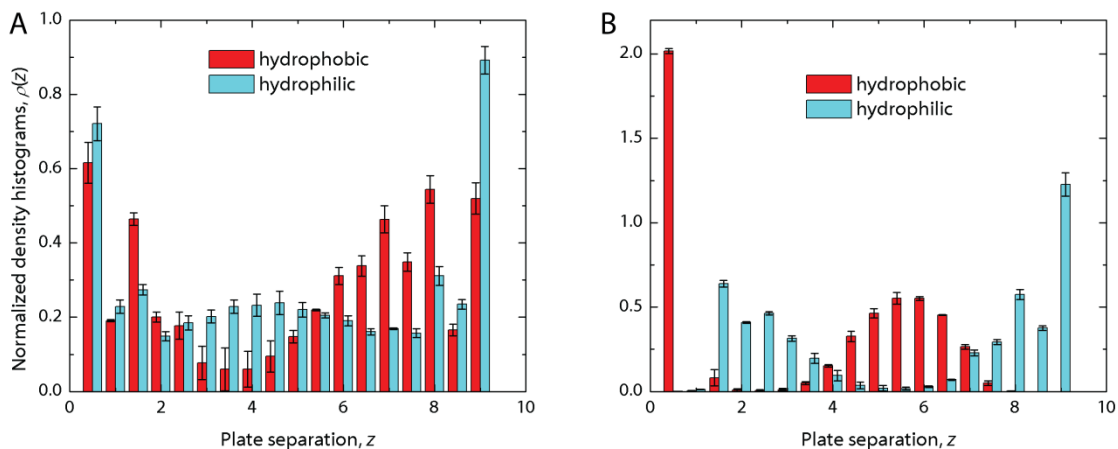


Figure 3. Equilibrium density profiles for block copolymers (5 hydrophobic units bonded to 5 hydrophilic units) near (A) hydrophilic walls and (B) hydrophobic walls. Each histogram was averaged over 3 trials and the error bars represent the standard deviation for each bin for the 3 trials.

While the simple LJ model can capture some of the features of hydrophobic self-assembly, many important details are lost. Many aspects of the hydrophobic interaction arise

from the detailed and specific water structure near an interface, so improvements of increasing complexity could be made, such as inclusion of a specific explicit water model that might better capture water's hydrogen bonding (or lack thereof) and proton hopping capabilities. The polymer model could be improved as well to apply to i.e. proteins by including charges or hydrogen bonding motifs in the backbone. The complexity of the problem calls for multi-scale methods; the results presented here indicate that even the simplest coarse-grained molecular dynamics model can capture some of the essential physics of an extremely complex phenomenon.

Movie caption

This movie shows the evolution with time of block copolymer molecules consisting of 5 "hydrophobic" and 5 "hydrophilic" atoms in each polymer, with 500 total atoms. Hydrophobic groups quickly adsorb to the bottom interface, exposing their hydrophilic groups, while the hydrophilic groups that begin near the top surface adsorb, causing aggregation of the hydrophobic groups in the middle of the box.