Introduction:
Water / oil interfaces are ubiquitous in our natural environment. They are extremely important in biological systems and have significant industrial applications. It is surprising, then, that some of the fundamental molecular-level aspects of these interfaces remain unexplored.

Goals:
Our goal in this research is to better understand specific properties of water / oil interfaces, such as density, molecular orientation, and hydrogen bonding. We wish to understand how the presence of surfactants affects those properties. Our approach is to use molecular dynamics software to simulate an interface which includes water, hexane, and sodium lauryl sulfate. We anticipate that results obtained from this simulation can be applied to similar non-polar substances, such as oils, interacting with water.

Classical Molecular Dynamics:
Molecular dynamics (MD) is a branch of computational chemistry concerned with predicting the motion of atoms and molecules over time. In ab-initio MD, quantum mechanics is used to do the computation. In classical MD, Newtonian physics is used. Classical MD and is the only approach which can model extremely large numbers of atoms with adequate efficiency. The figure below shows some intra-molecular bond force calculations performed by MD software.

Intra-Molecular Bond Force Calculations
Clockwise from upper left: bond stretching, dihedral angles, improper dihedral angles (out-of-plane bending), and simple bond angles.

We use AMBER v. 11 software for our simulations. In addition to the forces shown above, AMBER calculates inter-molecular forces, including coulombic interactions, Van der Waals forces, and polarizability.

Density Profiles
One of the distinguishing characteristics of a liquid-liquid interface is its density profile: a graph of the density of each interfacial liquid vs. its position along an axis perpendicular to the interface. The vertical red line indicates the zero-point of the interface, which roughly corresponds to where the place where the two liquids meet.

The division between the two liquids is quite sharp, indicating very little “mixing.” In future work, we plan to compensate for localized fluctuations of interface position.

Surfactants:
Surfactants (surface-active agents) are compounds that lower the surface tension and surface energy of a liquid. In so doing, they can change the solubility of another substance in the liquid. For example, the surfactants in soap cause dirt and oil to diffuse more easily into the wash water. Surfactants have many other applications, including in the manufacture of adhesives, extracting oil from water, and the environmental remediation of oil spills. Sodium lauryl sulfate (also called sodium dodecyl sulfate) is an ionic surfactant. Surfactants include it in soap, shampoo, and toothpaste because it makes a thick foam when agitated.

Hydrogen Bonding
Many of water’s unique properties result from the exceptionally strong hydrogen bonds that can form between adjacent water molecules. To computationally analyze hydrogen bonding in water, we need a precise definition of exactly which intermolecular interactions qualify as a “hydrogen bond.” For our calculations, a hydrogen bond was defined to be a proximity of less than 2.2Å between an oxygen and a hydrogen on distinct water molecules. The angle of the bond is not yet considered.

\[ \text{d} \leq 2.2\text{Å} \]
\[ \theta \text{ not yet considered} \]

Hydrogen Bond Criteria
Roughly speaking, there are a total of nine ways in which an individual water molecule can bond with the others in its environment. These are referred to as bonding modes. The following nomenclature is used for bonding modes: each “O” indicates a bond to oxygen, and each “H” a bond to hydrogen. For our calculations, a hydrogen bond was defined to be a proximity of less than 2.2Å between an oxygen and a hydrogen on distinct water molecules. The angle of the bond is not yet considered.

Orientation Histograms
Interestingly, the values of θ and ϕ change with depth into the bulk of the water. If we plot the cosines of each angle on a histogram vs. interface depth, trends appear. The following graphs are for a water / hexane interface without surfactant.

Taken together, these results suggest that the water molecules lie flat on the very edge of the water / hexane interface, as shown in the illustration at right.

Orientation histograms for water / vacuum interfaces are very similar, but have slightly more variation in tilt and twist values. This suggests that water molecules at the interface with a vacuum have slightly more freedom of motion. Water / hexane tilt values are also more negative than water / vacuum values at the interface. This suggests that the negatively charged water oxygen is attracted to the partially positive hexane hydrogen atoms, and tilts toward them a bit.

References