

# Surfactant Self-Assembly on Nano-Structured Surfaces: Multi-Scale Computational Prediction and Design

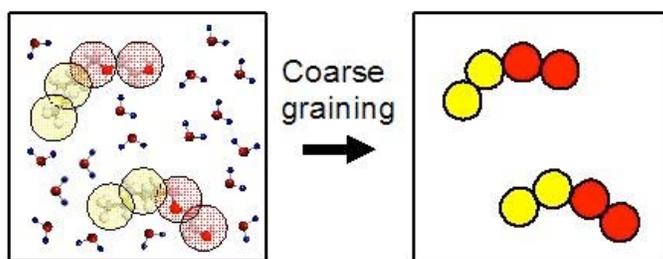
NSF NIRT GRANT CTS-0403633

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The long term goal of our project is to develop multi-scale (electronic, atomistic and meso-scale and continuum) computational methods for the prediction and design of nano-structures formed by the self-assembly of surfactants from aqueous solution onto solid surfaces and nano-porous media. Such processes are ubiquitous throughout nanoscale science. The central difficulty in such a program is that the length and time scales span many orders of magnitude, and one must construct a multi-scale protocol that preserves important aspects of the electronic and atomistic detail (e.g. H-bonding) while spanning these scales. In the first year of the program we have focused our efforts on (a) development of coarse graining procedures based as far as possible on rigorous statistical mechanics (atomistic and meso-scales), (b) initial studies of fluid flow through tethered polymer chains, self assembled on solid surfaces (atomistic and continuum scales), (c) studies of self-assembled monolayers of porphyrins on a Si (100) surface (electronic and atomistic scales), (d) studies of self-assembled systems of nanoparticles and polymer chains.

## Coarse Graining Procedures



**Figure 1.** The proposed coarse-graining procedure going from the fully atomistic surfactant system to a meso-scale model.

In coarse graining the large particles (surfactant molecules in our case) are treated as made up of ‘beads’, each of which contains a number of atoms (Fig. 1). In the simplest approach the coordinates of the solvent (water) molecules are integrated over to yield a well defined effective potential that is state dependent, and which is used in subsequent meso-scale dynamic simulations. As a first step towards our goal, we explored the *rigorous* coarse-graining approach where we match the partition function for the fully atomistic system of interest to that for the coarse grained meso-scale system. Such a procedure has the advantage that it maps the Hamiltonian of the meso-scale system onto the atomistic one, and leads to the reproduction of all the structural and thermodynamic properties of the atomistic system. Following the approach of Dijkstra *et. al.* [1], we have devised a procedure to calculate the rigorous effective 1,2,..N-body effective interactions using Widom’s particle insertion method [2]. We have first applied this procedure to find the effective 2-body potentials for a binary Ar/Kr system, where the degrees of freedom of Ar are integrated out [3]. We observed that the structure at the pair level is well reproduced by the effective system using only effective pair potentials and ignoring all higher multi-body contributions. However, we observe deviations in the

pressure for higher densities. These latter deviations are attributed to the neglect of three- and higher multi-body interactions. We are currently exploring the rigorous 3-body effective potentials and how they affect the structural and thermodynamic properties.

Since this rigorous approach is quite computer intensive, and is challenging for complex systems with Coulomb charges, we have also explored coarse-graining techniques where we find an effective potential which reproduces the property of interest. Since we are interested in exploring the nano-scale structures formed by these surfactant solutions on surfaces, we aim to find an effective potential which reproduces the structural properties such as the correlation functions. We are particularly interested in the nano-structures formed on surfaces and in pores by non-ionic surfactants, such as alkyl oligo (ethylene oxide) surfactants. We first explored the coarse-graining procedure for a system of ethanol molecules in water because ethanol resembles the structural units of the head groups of the polyethylene oxide surfactants [4]. In the coarse model each ethanol molecule is represented by one spherical bead and the water is coarse grained out completely. We have shown that an integral equation approach with hypernetted chain closure approximation works well up to quite high surfactant concentrations (50 wt%), while an iterative Boltzmann scheme works very well for even the highest concentrations studied (70wt%). We are now extending the iterative Boltzmann procedure for coarse-graining to realistic atomistic models of solutions of ethylene oxide surfactants, both in bulk and on surfaces.

### Fluid Flow through Tethered Polymer Chains

We are developing a multi-scale modeling procedure for describing fluid flow through polymer chains that are anchored to the inside of nano- and micron-scale pores. Of particular importance are systems in which the chains respond to environmental factors such as temperature or solvent pH that leads to smart materials with adjustable effective pore sizes. This class of material has important applications that include drug delivery, remote bioremediation, and remote sensing.

The flow rate of water through a cylindrical pore containing grafted poly-glutamic acid has been estimated as a function of pH. Modeling this system fully atomistically is too computationally intensive to be practical; therefore we have developed a methodology combining continuum and atomic modeling. The equilibrium conformation of a single poly-glutamic acid chain in water with a pH of 7 and a pH of 3 was simulated using molecular dynamics. These simulations were used to estimate via free energy model chain configurations and associated densities for a grafted brush as a continuous function of pH. Fluid flow was then calculated by numerically solving the continuum Brinkman equation for flow through a porous medium using the chain densities to define the local fluid permeability. The fully protonated structure forms a dense helix, while the neutral structure forms a lower density random coil. The former creates a more open pore that exerts less drag on solvent flow and results in more fluid flow compared to the neutral structure, in agreement with literature experimental data.

In current work, we are using the same approach to calculate how fluid flow depends on the pore size and the chain length, with the goal of extending our nanopore results to membranes with micron-scale pores. As a first step we are using simplified bead-spring models with Lennard-Jones non-bonded interactions.

## Self-Assembly of Porphyrins on Silicon Surfaces

In the future molecular electronics might emerge as a viable alternative to semiconductor-based technology. Already, prototypical memories based on self-assembled monolayers (SAMs) of porphyrins on Si surfaces have been demonstrated experimentally. The specific redox properties of the porphyrin molecule enable its use as a charge storage device – a molecular capacitor – and therefore as a memory element. In this work we have studied the structural and electronic properties of porphyrin molecules adsorbed on a Si(100) surface reconstruction using Ab-initio Density Functional Theory methods. The calculated structural parameters include optimization of bond lengths, the adsorption energy, the angles between the molecule and surface, and the upper limit for the surface density of adsorbed molecules in a monolayer. The electronic structures of the free molecule, the free surface, and the molecule plus the surface were calculated. It was shown that the molecule preserves

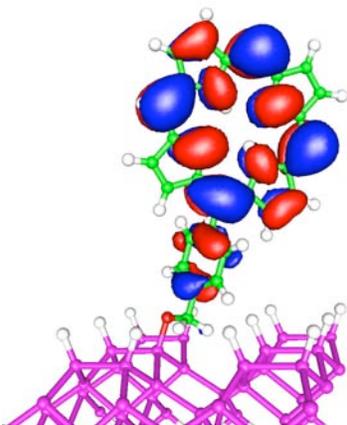


Fig 2: Calculated HOMO state of a porphyrin molecule attached to a Si (100) surface. The redox active HOMO state is preserved upon adsorption.

its essential electronic character, specifically, the HOMO state – shown in Fig.1 - from which charge is removed for information storage. It was also shown that no significant charge transfer occurs between the porphyrin and the surface. Further work is currently under way concerning the electronic transport properties of a porphyrin molecule between two Si electrodes.

## Tethered Nanoparticles

Further crystallization. This method of nanoparticle synthesis has created a wide range of polyhedral shapes and highly anisotropic branched particles, including tetrapods and Y-junctions. In addition, the surfactant layer on the nanoparticle surface provides a means of tailoring nanoparticle interactions if the surfactant assembly on the surface can be controlled. We are using dissipative particle dynamics (DPD) to study small molecules and surfactants physically or chemically bound to spherical nanoparticle and cylindrical nanorod surfaces. The code treats surfactant molecules using a coarse-grained bead-spring model, and permits the investigation of an arbitrary number of surfactant species. We have carried out initial investigations of binary mixtures and block copolymers. Our next step will be to investigate the behavior of multicomponent surfactant mixtures on spherical surfaces to ascertain how the molecules self-organize under various thermodynamic conditions. In addition, we plan to incorporate the more rigorous coarse grained potentials being developed in part (1) above into our DPD codes when these are available.

Nanoparticles today are often grown as nanocrystals in solution, their growth stabilized at nanometer scales by the addition of surfactant molecules that physisorb on the surface and arrest

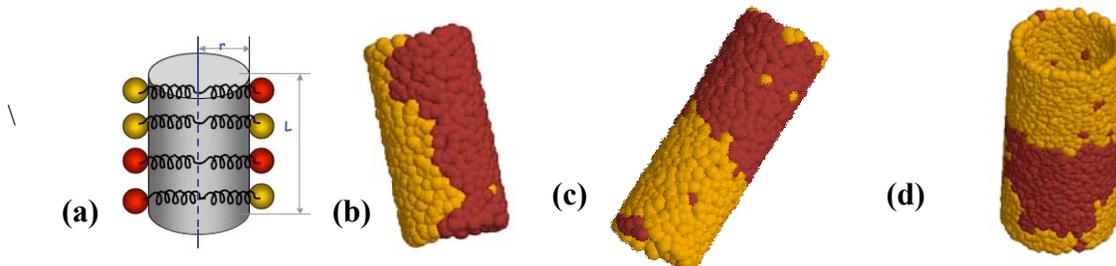


Figure 3: DPD simulations of phase separation of a binary mixture on a cylindrical surface, for different ratios of cylinder radius to length. Model is shown in (a).

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