

T-11

Condensed Matter & Statistical Physics

Self-Assembly of Organic Molecules

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While most interatomic potentials between components of organic molecules have been described with some success over the past decades by use of simple empirical noncovalent pair interactions, we have had little understanding of organic-inorganic interfaces, such as the thiol-gold interaction relevant for our studies. It has been widely assumed that thiols, having a binding energy to a gold-surface orders of magnitude larger than room temperature fluctuations, would be “pinned” at specific binding sites on the metal surface.

Self-assembled monolayers (SAMs) are a class of molecular assemblies that are prepared by spontaneous adsorption of lipid-like organic molecules from solution, or vapor, onto a solid substrate. Hence, SAMs provide a link between the science of organic surfaces and technologies that seek to exploit their adaptable character. Due to their dense and stable structure, SAMs have potential applications in corrosion prevention, wear protection, and more. In addition, the biomimetic and biocompatible nature of SAMs leads to promising applications in the area of chemical and biochemical sensors. Other applications are in electro-optic devices, and in the nanopatterning of semiconductor surfaces.

There are many classes of self-assembling systems; those most commonly studied include organosulfur/coinage

metal, organ-osilicon/oxide, and fatty acid/metal oxide systems. Of these varieties of SAMs, those involving organosulfur molecules absorbed on metal surfaces are the most studied, with alkanethiols on gold(111) usually taken as a model system.

Despite the amount of experimental and theoretical effort devoted to studying this system, many aspects of its structure and dynamical behavior are poorly understood, or subject to controversy. In particular, the majority of theoretical studies of alkanethiols on gold(111) have been forced to use oversimplified models to describe this system, due to its complexity and the lack of good experimental data on which to base their models. For example, most simulations have constrained sulfur headgroups to the locations of three-fold hollow sites on the gold surface.

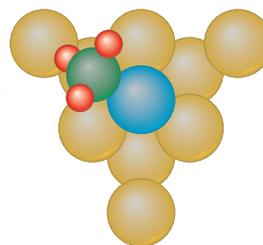
Recent advances in large scale computing and atomistic modeling has enabled us to address some of the fundamental questions necessary for realistic modeling of alkanethiols on gold(111).

While most interatomic potentials between atoms of organic molecules are well agreed upon, little consistent knowledge of the effective interactions of the sulfur interface between alkane and gold is known. This issue is critical for reliable modeling of self-assembly and dynamics of assembled structures as the surface mobility

Results

∂ Optimized structures.

	Site	180.0°	opt.
Energy	atop	11.3	0.0
Z_{AuS}		2.78	2.63
θ_{AuSC}		180.0	103.3
Energy	bridge	0.6	-5.5
Z_{AuS}		2.38	2.29
θ_{AuSC}		180.0	120.4
Energy	fcc	-2.4	-6.2
Z_{AuS}		2.25	2.35
θ_{AuSC}		180.0	122.5
Energy	hcp	-4.0	-3.8
Z_{AuS}		2.34	2.30
θ_{AuSC}		180.0	137.0



∂ Charges obtained by fits of dipole moments.

Site	S charge	Au charge	remainder
atop	-0.62	1×0.96	-0.34
bridge	-0.34	2×0.08	+0.18
fcc	-0.45	3×0.17	-0.06
hcp	-0.42	3×0.15	-0.04

Figure 1

of the molecules is uniquely related to the lateral binding energy. Lack of detailed knowledge about this interaction has lead much of the theoretical community to assume the sulfur headgroups to be restricted to the locations of the 3-fold hollow sites on the gold surface. To investigate this issue, we have produced a model of the S-Au interaction over the entire Au(111) surface, that incorporates realistic energies, energy barriers, and force constants, for use in molecular dynamics (MD) simulation. This has been incorporated in to an all-atom, long interaction range, parallel molecular dynamics code. The results of our simulations, include behavior that is precluded in the more restricted models previously used.

Figure 1 shows the results of a extensive series of *ab-initio* calculations, using Gradient Corrected Density Functional Theory (GC-DFT), to determine the energetics of the Au-S-C potential energy surface. The spheres represent gold (yellow), sulfur (blue), carbon (green), and hydrogen (red). The lateral motion of the sulfur on the gold surface can be described by a realistic empirical ‘eggbox’ potential function by fitting a suitable functional form to the *ab-initio* data. From Figure 2 (displaying the resulting surface potential), we find that the effective energy barrier, moving a sulfur from one hollow site to the next, is of order of kcal/mol, which is roughly the same as $k_B T$ at room temperature. Thus, contrary to most previous assumptions, thiols can diffuse easily on the Au(111) surface, suggesting that packing of the self-assembled structures appear independently of the detailed structure of gold.

We have implemented this empirical potential into a large scale, parallel, classical molecular dynamics code, with full summations of the long range Coulomb interactions,

to carry out simulations of this system; this code is currently run on the T3D in the Advanced Computing Laboratory.

Our initial focus has been to investigate how a surface, sparsely populated with alkane thiols, can accommodate diffusion of the molecules into assembled structures. Figure 3 shows the results of a simulation of a sparsely populated

surface, where only 2/3 of the maximum number of alkanethiols are present. Only the sulfur headgroups are shown — initial positions (large green), positions at every 0.5 ps (small green) and final positions at 7 ps (blue) of alkanethiols (sulfur). Imposing room temperature dynamics, Figure 3 demonstrates considerable diffusion of the molecules within times of the order of picoseconds—consequently, the results of our simulations show very different behavior when compared to those of previous studies where thiols were pinned at hollow sites.

The current simulations are also being used for calibration of partially and fully constrained stochastic models attempting to stretch temporal and spatial scales of the simulations through

time scale simplifications, and we are further generating simulation data for direct comparison with experiments being performed in CST/MST/MSL, probing the gold-sulfur interface, ordering of alkane chains, and tailgroup interface.

Ab-initio energy surfaces calculated for CH₃-S binding to Au(111)

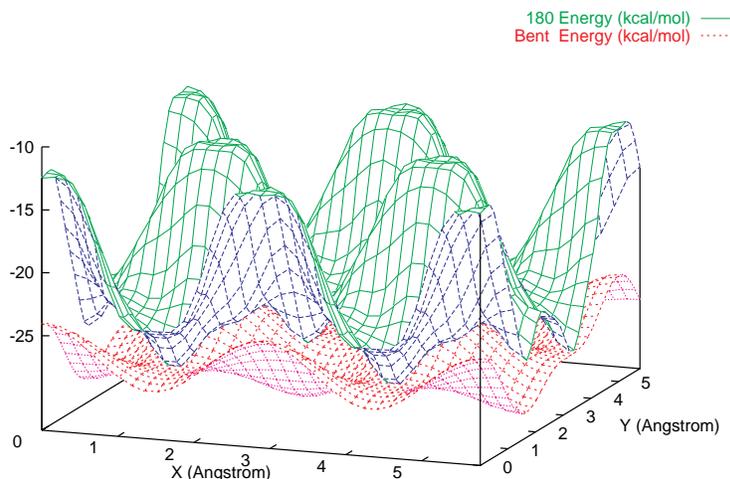


Figure 2

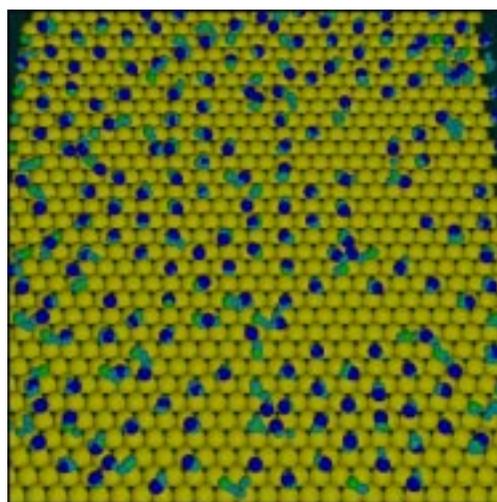


Figure 3