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A Classical Potential for the Gold(111)-Alkanethiols Interface

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Abstract: *We present a classical potential for self-assembled monolayers of alkanethiols on gold(111) (Au-SR, in our case R is hydrogen to simplify the system, in general R is* C_nH_{2n+1}*), which has been parameterized using the forces and energies extracted from ab initio calculations. We use this classical potential to investigate the dynamics of the Au(111)-SH interface using classical molecular dynamics. We compare the results of simulations with this potential both to the experiment and to the result of ab initio molecular dynamics simulations.*

Key Words: *Classical Potential, Self-assembled monolayers (SAMs), ab initio.*

Introduction

Self-assembled monolayers (SAMs) of alkanethiols on metal surface have many potential applications in molecular electronics [1] biosensors [2], and nanopatterning [3]. For this reason its structural and dynamic properties have been extensively studied both experimentally and by means of simulation [4] [5] [6] [7] [8]. Recent *ab initio* studies of intermediate length alkyl sulfides on Au(111) shows the presence of RS-Au-SR motif in Au-thiol interface [4] [5], which have been proved by X-ray diffraction experiment [4]. The molecular dynamics simulation was performed in [4] with four hexanethiols SAMs having two initial vacancies both at 300K and 500K. The result shows that (i) hexanethiol chains retained a well-ordered hexagonal array with a tilt angle of about 30º with respect to the surface normal (Figure 1B) (ii) ad-atoms and vacancies should be present at the surface in similar concentrations (iii) sulfur atoms should be located in either the bridge or RS-Au-SR configurations in roughly equal proportions (iv) the alkyl chains should retain a well-ordered hexagonal array with a height corrugation of about 0.6 Å.

Computer simulations are done in the hope of understanding the properties of assemblies of molecules in terms of their structure and the microscopic interactions between them. This serves as a complement to conventional experiments, enabling us to learn something new, something that cannot be found in other ways. Molecular Dynamics (MD) simulation requires the definition of a potential function or a description of the terms by which the particles in the simulation will interact with each other. The atomistic approaches to calculate the potential of the system may be divided into two distinct categories: *ab initio* and empirical approaches.

In the *ab initio* approach potentials by which atoms in a system interact with each other are determined almost exactly by solving the Schrödinger equation of the system. *Ab initio* calculations provide a large amount of information, such as density of electronic states or other electronic properties. But for *ab initio* MD, one is generally confined to a system of around 100 atoms and simulation times of ~10 picoseconds, and so the precision with which many macroscopic properties may be calculated, is poor.

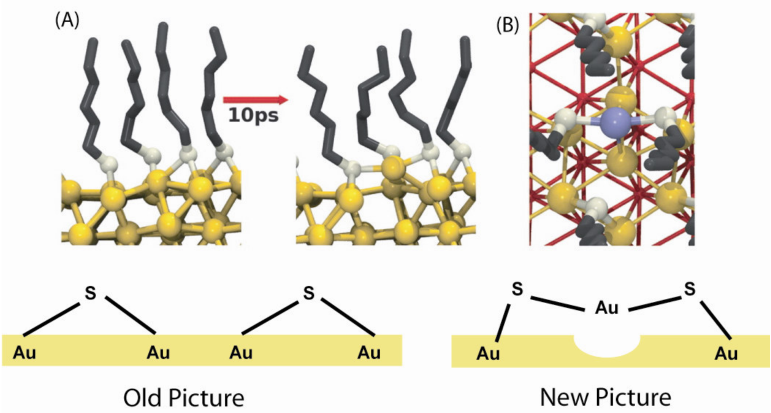

Figure 1: (A) MD snapshots (10ps at 500K) from hexanethiol (HT) [R=$(CH_2)_5CH_3$] cell, formation of HT-Au-HT species (gray(large), S; black, C; gray(small), Au); (B) Average structure positions from 16-HT cell; ad-atom labeled in blue and second Au layer marked in red. HT SAM exhibits hexagonal packing of the chains that are tilted off the normal by 30º, irrespective of the binding site. Au-S bond lengths are 2.45 Å for the bridge configuration, whereas lengths of 2.33 Å are found between the S and ad-atom in RS-Au-SR; S atoms display different heights of 2.0 Å and 2.6 Å above the surface for bridge and S-Au-S structures, respectively. This height corrugation is preserved in the height of chains [4].

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On the other hand, in classical or empirical approaches the system is described by an effective potential, the so-called force field. Classical potentials are explicit function of the atomic coordinates, with certain tunable parameters. The reliability of classical potential depends on how good it is to capture the phenomenon under study and on the method by which that has been parameterized. Force fields may be parameterized either by fitting to experimental data, or by fitting to *ab initio* calculations or both. The limitation of the classical potential is its transferability in different physical situations to predict different properties. In order to be able to confidently transfer a potential from the physical situation in which it is parameterized to the situation in which it is to be used, one needs to be confident that the model is flexible enough in terms of its representation of the relevant electronic effects to extend between the two situations. The reliability of an empirical force field can be increased dramatically by restricting both the fitting procedure and the domain of application of the force field itself to a well-defined physical situation [9].

The goal of the present work is to construct a classical potential, that is, to find suitable functional forms of potentials with suitable parameters for the Au(111)-SR (R=C_nH_{2n+1}) interface, which will be able to describe the system exactly as known from *ab initio* calculations and X-ray diffraction experiment [4]. The potential may be used to predict unknown properties of a system of larger size. The dynamics of the system can also be studied for a longer time scale. The potential may also be used to study properties of nanoclusters, in which case *ab initio* calculations are extremely expensive. For this purpose we have started with a very simple system, where we have replaced the real alkene thiol (SR) by SH. This is because, the *ab initio* calculations that we have performed in parameterizing the classical potential do not take into account the Van der Waals interaction, which is important for systems with large carbon chains. The system we have studied has 16 sulfur-hydrogen (SH) molecules on the top of 192 Au atoms in four (111) gold layers, totaling 224 atoms.

Fitting Empirical Potentials to *Ab Initio* Data

Since our purpose was to find a classical potential, we chose molecular dynamics simulation method. MD simulation consists of the numerical, step-by-step solution of the classical equations of motion, which for a simple atomic system may be written as:

$$m_i \boldsymbol{r}_i = \boldsymbol{f}_i \qquad\qquad \boldsymbol{f}_i = -\frac{\partial U}{\partial \boldsymbol{r}_i}$$

For this purpose we need to be able to calculate the forces $\boldsymbol{f}_i$ acting on the atoms, and these are usually driven from a potential energy, $U(\boldsymbol{r}_i)$, where $\boldsymbol{r}^N=(\boldsymbol{r}_1,\boldsymbol{r}_2,. \quad . \quad . \quad ,\boldsymbol{r}_N)$ represents the complete set of 3N atomic coordinates. U can be calculated using density functional theory (DFT) or can also be given by classical potential. Because of the computational limitation of performing *ab initio* MD for large system in longer time scale, which in most of the cases requires understanding the dynamics of the system, we use classical potentials, which allows us to do the simulation for a large enough system in longer time scale to understand its actual behavior. We have fitted our classical potentials to the DFT forces and energies.

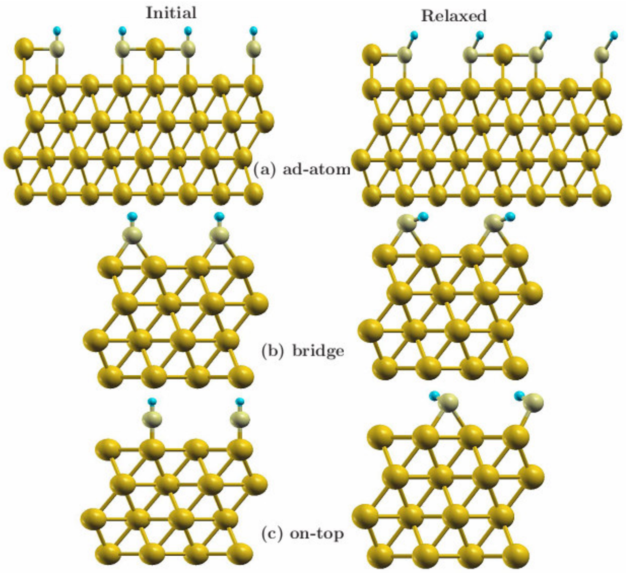

Figure-2: Structure of Au-S interface

Ab Initio Calculation

We performed DFT calculation as employed in the quantum espresso [10] to study the adsorption of H_2S on Au(111) surfaces. For all calculations we used Vanderbilt ultrasoft pseudopotentials (US-PP) and Perdew-Becke-Ernzerhoff exchange correlation. For the surfaces, a vacuum of 20 Å was used to avoid a spurious inter-image interaction. The plane wave cutoff was set to 45 Ryd. Different (ad-atom, bridge, on-top) sites were considered to study the adsorption of H_2S on the Au(111) surface. We considered the H_2S concentration to be 0.3 monolayer (ML) for bridge and on-top sites. For the ad-atom case, we considered cases where there were one and two ad-atoms on the surfaces. In case of one ad-atom, we further varied the concentration of H_2S by attaching only one H_2S to the ad-atom (this is the case of 0.15 ML) and two H_2S to the ad-atom (this corresponds to 0.3 ML). For the two ad-atom cases, each ad-atom had only one H_2S, which corresponded to 0.25 ML of H_2S. All the geometries considered in this work are shown in Figure-2. The geometries were relaxed using BFGS algorithm. The adsorption energy (Ea) of the H_2S was calculated using the following expression:

$$E_a = E_{slab}^{Au(111)} + nE^{H_2S} - E_{slab}^{(Au(111)+n[H_2S])}$$

Classical Potential

Classical potentials, which is also known as force fields describe the system in an effective way. These potentials contain free parameters such as atomic charge, Van der Waals parameters reflecting estimates of atomic radius, and equilibrium bond length, angle and dihedral; these are obtained by fitting against detailed quantum mechanical simulations or experimental physical properties such as elastic constants, lattice parameters and spectroscopic measurements. There have been a large number of classical potentials proposed. However to describe our system we started with three well known potentials to describe different types of interactions present in the system. We used harmonic potential to specify the S-H chemical bond. Gupta type metal potential was used to describe Au-Au and Au-S interactions. The three body interaction in Au-S-H was represented by truncated harmonic potential. The functional forms of the potentials are given below with parameters in square brackets

(A) Harmonic potential [k, r_0]:

$$U(r) = \frac{1}{2}k\left(r_{ij} - r_0\right)^2$$

(B) Truncated harmonic potential [k, θ_0, ρ]:

$$U(\theta) = \frac{1}{2}k(\theta - \theta_0)^2 \exp\left[-\frac{r_{ij}^8 + r_{jk}^8}{\rho^8}\right]$$

(C) Gupta type potential [11] [A, B, p, r_0, q_{ij}]:

$$U_i(r) = \frac{1}{2}A \exp\left[-\frac{p\left(r_{ij} - r_0\right)}{r_0}\right] - B\left\{\sum_{j\neq i} \exp\left[2q_{ij}\left(r_{ij} - r_0\right)/r_0\right]\right\}^{1/2}$$

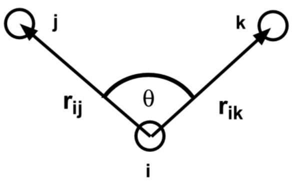

Figure-3: The valence angle and associated vectors for potentials (A) and (B)

Potential Parameterization

It has been shown for a number of systems that a very high level of accuracy may be achieved by parametrizing an effective potential by fitting to forces, stresses and energies in selected atomic configurations obtained from first principles by using quantum mechanical method, such as DFT [12] [13] [14] [15]. In the fitting it is assumed that if one achieves a perfect fit to *ab initio* data he or she gets an extremely accurate effective potential. However, as one moves away from this limit, the relationship between the fit to the *ab initio* data and the quality of the effective potential clearly weakens.

We began the procedure performing *ab initio* calculation to have energies and forces for a number of uncorrelated configurations with different bond geometry and topology. Then a molecular dynamics trajectory was generated for the system of interest starting with an initial guess of effective potentials. Those potentials had well defined functional form with certain tunable parameters, which were tuned to fit with *ab initio* data. In the calculation the potential was parameterized by minimizing the function

$$\Gamma(\{\eta_i\}) = w_f \Delta F + w_e \Delta E$$

with respect to the parameters $\{\eta_i\}$, where weighting factors w_f and w_e determine which quantity has how much contribution in fitting and

$$\Delta F = \frac{1}{0.1}\sqrt{\sum_{k=1}^{n_c}\sum_{I=1}^{N}\sum_{\alpha}|F^{\alpha}_{cl,I}(\{\eta_i\}) - F^{\alpha}_{ai,I}|^2}$$

$$\Delta E = \frac{1}{0.1}\sqrt{\sum_{k=1}^{n_c}|E_k^{cl}(\{\eta_i\}) - E_k^{ai}|^2}$$

Here $F^{\alpha}_{cl,I}$ is the αth component of the force on atom I as calculated with the classical potential, $F^{\alpha}_{ai,I}$ is the force component calculated by *ab initio* method. E_k^{cl} and E_k^{ai} are the energies of kth configuration calculated using classical potential and *ab initio* respectively. n_c is the number of atomic configurations used to fit the classical potential to the *ab initio* calculations. Forces are expressed in units of Ry/Bohr and energies in units of Ry. Once a parameter set has been found, a new molecular dynamics trajectory is generated by classical molecular dynamics, from which a new set of configurations are extracted. Then forces and energies of these configurations are calculated by *ab initio*. A new set of parameters is obtained using *ab initio* forces and energies of those configurations. This process is repeated until the difference in the values of $\Gamma\{\eta_i\}$, from successive minimizations converge to a small enough value.

Results

Classical potentials are empirical, that is these functions are based on or characterized by observations and experiences. They may have any form with a number of tunable parameters, different values of which make the potentials capable to explain different physical conditions. We fitted the classical potentials at 300 K, and used different functional form to describe different type of interactions in the system, which usually very useful for a system having different types of atoms. We began with Harmonic Potential which we used to describe the two body interaction between hydrogen and sulfur. The three body interaction between hydrogen-sulfur-gold (H-S-Au) is described by Truncated Harmonic Potential. This allows S-H part to rotate up to a certain angle with respect to Au. Parameters of both the functions are presented in table 1.

Table 1: Parameters of Harmonic potential and Truncated Harmonic potential

Potential	Parameters
Harmonic Potential	k = 0.100 kCal Å^{-2}
	r_0= 1.36 Å
Truncated Harmonic Potential	k = 8.8235 kCal degree^{-2}
	ρ = 1.36 Å
	θ_0= 100.91°

The Gupta type pair potential is used to describe S-Au, Au-Au, Au-Aub interactions, which is usually very useful for systems having different types of interactions. Aub represents lowest gold layer, which is kept fixed during fitting. The system is periodically repeated in all three directions. A gap of 20 Å is introduced in the z-direction in the purpose of having a two dimensional bulk, which is almost twice of the thickness of the bulk. Parameters of Gupta type potential are given in Table 2.

Table 2: Parameters of Gupta type potential for different interaction

Interaction	A (kCal)	p	r_0 (Å)	B (kCal)	q_{ij}
Au-S	299.70	3.666	1.6177	185.20	1.981
Au-Au	7.788	10.84	2.884	32.29	3.613
Au-Aub*	9.667	9.706	2.884	25.23	3.593

* Aub represents lowest gold layer, which is kept fixed during fitting

In order to check the reliability of our parameterized potential, we performed classical molecular dynamics using the parameterized potentials. The system consisted of 16 SH molecules on the top of 192 Au atoms in four Au(111) layers at a temperature of 300K and at zero pressure. The system also initially contained adatom and vacancy in the gold layer. For this purpose we used DL_POLY_2 classical MD simulation package. We used Verlet integration algorithm. Though we fitted the Harmonic Potential for S-H, during MD we kept S-H as a rigid molecule.

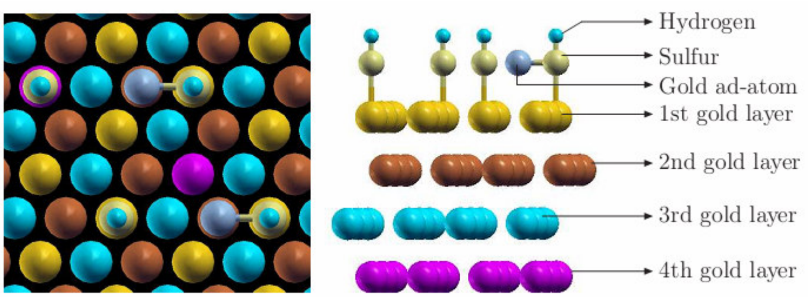

Figure 4: Top and side view of the configuration which is used at the beginning of classical MD, different colors have been used to indicate different gold layers.

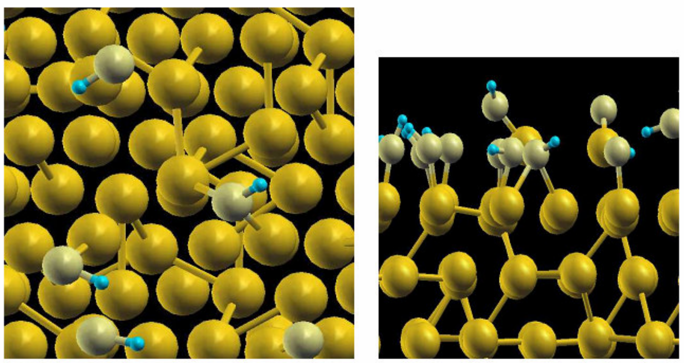

Figure 5: Top and side view of two different classical MD snapshots showing the presence of Au-S-Au bridge structure.

First, we have performed MD simulation for 50 ps in a time step of10^{-4} ps treating the system as isothermal-isobaric (NPT) ensemble to relax the geometry. This allowed the atoms in the super cell to find their minimum energy position. Then constant tem-perature molecular dynamic simulation was done for 500 ps again in a time step of 10^{-4} ps, where the system was considered as a canonical ensemble (NVT). In the Au-S interface we found Au-S-Au, bridge structures were formed which is shown in Figure 5. We also found adatom-vacancy configurations in the interface, though we could not see any RS-Au-SR type structure. During our simulation we found that the system did not contain bridge type configuration all the time, but bridge type configurations formed and vanished time to time.

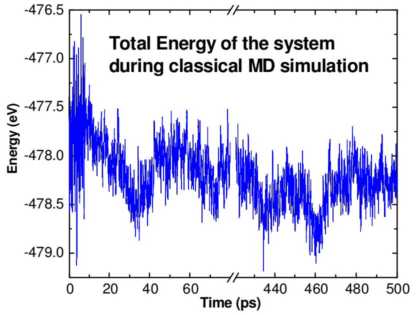

Figure 6: Total energy of the system during MD simulation.

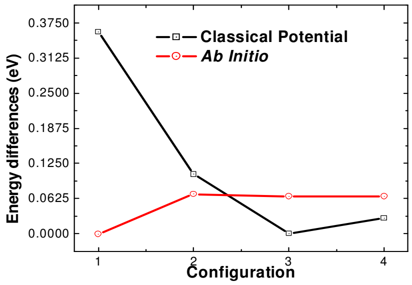

Figure 7: Comparison of the total energy difference for 4 different con-figurations both calculated from *ab initio* and from classical potential. The values in the Y-axis are for per sulfur atom.

A time vs total energy plot is shown in Figure 6. Since experimental results were not available for the system that we studied, to check our classical molecular dynamics result we calculated total energy of the system for four different representative configurations taken from classical molecular dynamics trajectory. We found the configuration which contained bridge type structure had the lowest energy if calculated from our potential (configuration number 3 in Table 3), while that had second lowest energy value if calculated by *ab initio*. Total energy differences from the minimum value for each type of calculations are plotted in Figure 7. In all the cases total energy of the system is almost same.

Table 3: Energies of four representative configurations

Configuration number	Total energy calculated from classical potential (eV)	Total energy calculated from from *ab initio* (eV)
1	-481.70795	-864.45613
2	-485.75113	-864.45250
3	-487.43814	-864.45272
4	-487.00023	-864.45271

From our results we come to the conclusions that the fitted potential is able to reproduce the feature known from *ab initio* calculations. We could not find any RS-Au-SR type structure. May be that type of structure is not energetically favorable for this kind of over simplified system. The value of total energy of the system during molecular dynamics simulation indicates that the system may be at dynamic disorder at 300 K. As there is no experimental result for such kind of system we could not compare our results with any experiment. Further fitting of the parameters may give a better picture of the dynamics of the studied system. This will also justify our achievement from molecular dynamics simulation.

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