

Odd-Even Effects in Self Assembly and Phase Transition of Alkanethiol Monolayers (SAMs) on Au (111) Surfaces

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ABSTRACT

This paper reports molecular dynamics simulations of thiol based $[\text{CH}_3(\text{CH}_2)_{n-1}\text{SH}]$ self assembled monolayers on a gold substrate. Here we examine the effects of molecular length on the structure of the monolayers. The effect of the temperature on the structure and how the phase transition temperature is varied with the molecular length have also been investigated. We find that for $n \leq 7$ the monolayer is liquid like and molecules show significant rotational mobility. For larger molecules ($n \geq 12$) the monolayers have a stable and well organized tilted structure. In the range of $12 \leq n \leq 15$ we find the tilt angle and tilt direction to be dependant on the number of carbon atoms being odd or even. For these systems, we find clear evidence that the odd alkanethiols show smaller gauche defects compared to even ones. For $n \geq 15$ we find the tilt angle to be independent of the molecular length. In agreement with experiments, we find melting phase transition takes place at temperatures which are significantly higher than those of corresponding bulk n-alkane systems. This enhancement is shown to be higher for odd alkanethiol systems. Overall, odd alkanethiols show better thermal stability and smaller structural defects compared to even ones.

Keywords: molecular dynamics simulations, SAMs, coating, thermal stability, phase transition, gold substrate

1 INTRODUCTION

Self assembled monolayers (SAMs) are important class of materials with enormous applications in many areas including nanotechnology. Miniaturization in the form of nano/micro electromechanical (NEMS/MEMS) devices requires working with extremely small parts whose adhesion/mass ratio is significantly larger than those in macroscale applications. SAMs are often used to coat such surfaces and modify their adhesion and frictional properties. Since such devices work at various environments, an understanding of the structural properties of SAMs and their response to temperature variations is very important. Alkanethiols, $[\text{CH}_3(\text{CH}_2)_{n-1}\text{SH}]$, are the simplest thiol-based SAMs consisting of a head, a thiol (SH) group with strong adsorption to the substrate; and a tail, an alkyl chain with varying number of carbon atoms where the methyl group acts as the functional terminal group. These self assembled systems on gold surfaces have

been widely studied by experimental and simulation methods.

Here we present molecular dynamics simulation results where alkanethiol systems of various lengths (both odd and even) have been studied. We show that structural and thermal properties of these systems not only depend on the molecules length but also on the number of carbon atoms being odd or even.

2 SIMULATION METHODS

Molecular dynamics simulation methods are used in this work to simulate the SAMs on (111) planes of exposed flat gold substrates. In this method, simulations are accomplished in three stages, developing a molecular model, calculating the molecular positions, velocities and trajectories, and finally collecting the desired properties from the molecular trajectories. Our system consists of a gold substrate and a layer of SAM attached to it. Au(111) surfaces are formed out of individual gold atoms which are placed in a crystalline structure with a lattice constant of 0.408 nm and the nearest neighbor distance of 0.288 nm. Dimensions of the gold surface depending on alkanethiol system, range from 5 to 9 nm in the lateral (xy) directions and each surface consists of 4 layers of (111) planes of gold atoms.

2.1 Modelling the SAMs

The thiol based chains $(\text{CH}_3(\text{CH}_2)_n\text{SH})$ are simulated with a united atom model in which CH_2 , SH and CH_3 groups are treated as single interaction sites. We have shown the capability of this united atom model [1] in the studies of n-alkane systems crystallization,[2],[3] confinement induced phase transitions,[4] and lubrication with gold surfaces [5]. Henceforth for brevity, in this paper we will refer to these alkanethiols by their number of carbon atoms (e.g. C12 for dodecanethiol) in each chain. The configuration of the SAM chains, at the start up is upright and all trans with sulphur group attached to the threefold position on gold surface atoms. As a result, the sulphur atoms form a hexagonal configuration giving a packing density of $21.6 \text{ \AA}^2/\text{chain}$. Periodic boundary conditions have been applied in the lateral (X and Y) directions. The interaction between sulphur atoms and gold substrate is governed by a harmonic potential with an equilibrium distance of $r_0=0.244 \text{ nm}$. Newtonian equations

of motion were integrated to calculate the new positions and velocities at each time step. The initial random velocity for each atom was assigned to give a Maxwell-Boltzman distribution corresponding to the target temperature of 300K which is kept constant unless stated otherwise. To study the effects of the temperature on the structure and phase transition of the monolayers, the equilibrated configuration at 300 K for each alkanethiol-Au system was used as the starting point, and the temperature was gradually increased to 420 K. MD simulations were carried out for 6 ns as the temperature was raised at a rate of 1 K per 47 ps from 300 to 420 K.

The equations of motion were integrated using the velocity Verlet algorithm with a time step of 2.35 fs. A parallel algorithm [6] with link cell and neighbor list methods was used in order to reduce the computational time and effort. The model included stretching, bond angle, and dihedral potentials given by equations 1, 2 and 3. The van der Waals interactions were modelled via a 6-12 Lennard-Jones potential, given by eq. 4, cut off at $r_c=1$ nm.

$$\phi(r) = \frac{1}{2}k(r - r_0)^2 \quad (1)$$

$$\phi(\theta) = \frac{1}{2}k_\theta(\cos\theta - \cos\theta_0)^2 \quad (2)$$

$$\phi(\varphi) = \sum_i^5 C_i(\cos\varphi)^i \quad (3)$$

$$\phi_{LJ}(r) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right] - \phi_{shift}, \quad (4)$$

$$\phi_{shift} = 4\epsilon \left[\left(\frac{\sigma}{r_c} \right)^{12} - \left(\frac{\sigma}{r_c} \right)^6 \right]$$

The potential parameters are given elsewhere [1], [6], [7] and [8].

2.2 Modelling the Gold Surface

The substrate is modelled by using an explicit atomic structure of gold. Crystalline surface of gold is made from four layers of (111) faces of fcc (face centred cubic) lattice structure. Gold has a density of 19.32 g/cm³ and an atomic weight of 196.97 amu. The interactions of the gold atoms and alkanethiol united atoms are also governed by the 6-12 Lennard Jones potential (eq. 4). The interaction parameters of Au are chosen by fitting the calculated and experimental desorption data of alkanes from metal surfaces [9]. These values are ($\epsilon_s/k_B=939$ K) and $\sigma_s=0.2655$ nm, which yield energy and length parameters for the interaction of CH₂ and Au of about four times that of CH₂-CH₂, LJ interactions. So that substrate-CH₂ interaction parameters $\epsilon_{sf} = 1.795$ kJ/mol= $4.59\epsilon_{CH_2}$.and $\sigma_{sf} = 0.328$ nm. In Figure 1 a typical alkanethiol-Au system is shown, where molecules are organized with their backbone tilted in a certain direction.

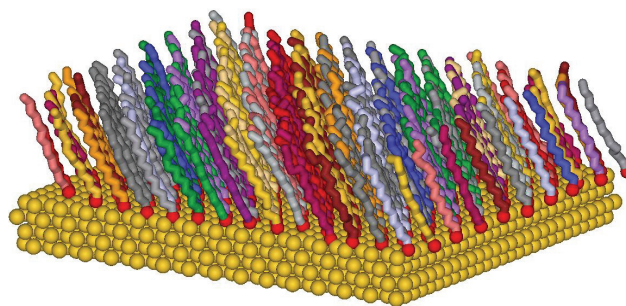


Figure 1 A snapshot taken from an equilibrated tetradecanethiol (C14) SAM attached on a (111) surface of a gold substrate. The sulphur groups are shown in red and arranged in a hexagonal pattern which produces packing density of 21.6 Å²/chain. The lateral dimensions of the gold substrate are 7.790×7.495 nm. The alkyl chains are shown with various colors to enhance the visualization.

2.3 Structural properties

The structure of a well ordered alkanethiol SAM is often characterised by two parameters, tilt angle which is the angle of the molecular backbone with respect to the substrate normal, and the tilt orientation angle, which is the angle between the projection of the molecular backbone onto the substrate and an arbitrary direction. We have used the unit vector along the longest axis of an inertially equivalent ellipsoid to calculate the orientation of each molecule [10] and the resulting tilt (θ) and tilt direction (φ) angles. Torsional angle represents the rotation of the bonds from *trans* position. We define the *trans* and *gauche* as the torsion angle being within $\pm 60^\circ$ of respectively 0° and $\pm 120^\circ$. A molecule with larger *gauche* defects represents a more disordered structure or distortion at certain segments of the molecule.

3 RESULTS

3.1 Effect of chain length on the tilt angle, θ

We have calculated the tilt angle for various alkanethiol systems on gold. Time average of the ensemble average values of the tilt angle was calculated over 1.8 ns for all the systems and the results versus the number of carbon atoms (chain length) are shown in Figure 2. Here we can see that the average tilt angle initially increases with the length of molecule as we go from C4 to C12. C4 and C7 show the lowest average tilt angle. For $12 \leq n \leq 15$, we can see odd-even effect, where the odd alkanethiols showing larger tilt angles than even ones. For alkanethiols with $n \geq 15$, tilt angle shows no noticeable dependence on the chain length or n being odd or even. Here our calculated tilt angle of $\sim 30^\circ$ is consistent with reported experimental values.

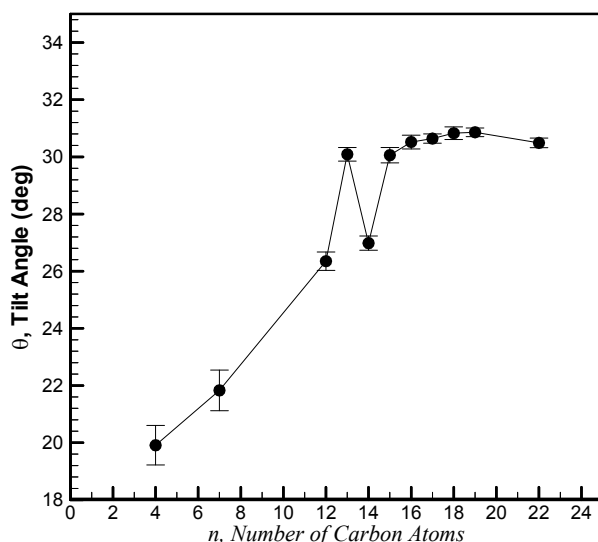


Figure 2 Tilt angle versus the number of carbon atoms for alkanethiols SAMs on Au(111) substrates at T=300 K.

3.2 Effect of chain length on tilt orientation ϕ

The tilt orientation angle (ϕ) is defined as the angle between the projection of the unit vector along the backbone of the molecule (as described in section 2.3) on the XY plane and an arbitrary direction. Here we have calculated ϕ with respect to the [100] direction of the gold substrate. Monitoring the tilt orientation angle over the time of the simulation, we find the smaller systems C4 and C7 show large variations in ϕ . This is an indication of large rotational freedom for these smaller systems. This fluid behaviour is consistent with our observations for tilt angle for C4 and C7. For $n \geq 12$ we find all systems show very stable tilt direction over time.

Since the Au(111) surface has six fold symmetry (60° symmetry), the possible orientation of the molecules, relative to the underlying gold lattice, can be represented with respect to the neighbouring sulphur groups. Thus, the possible orientation of the molecules are shown by NN ($\pm 30^\circ, \pm 90^\circ, \pm 150^\circ$), NNN ($0^\circ, \pm 60^\circ, \pm 120^\circ, \text{ and } 180^\circ$) and NNNN ($15^\circ, 75^\circ, 135^\circ, 195^\circ, 255^\circ, 315^\circ$) directions, which respectively are the nearest neighbour, next nearest neighbour and next next nearest neighbour of a sulphur group.

The calculated average orientation angle, ϕ , as a function of chain length for alkanethiols in the range of C12-C22 is shown in Figure 3. Here, the orientation angle is calculated within $0\text{--}30^\circ$ with NNN and NN forming the boundaries of our measurements. The results clearly show for $12 \leq n \leq 15$ there is an odd-even effect with the even alkanethiols being closer to NNN direction by $7\text{--}8^\circ$. For alkanethiols with $22 > n \geq 15$ there is not much dependence on the chain length or n being odd or even and most systems are tilted $\sim 10^\circ$ relative to NNN direction. For C22, the longest system we examined here the tilt orientation is clearly pointing towards NN direction.

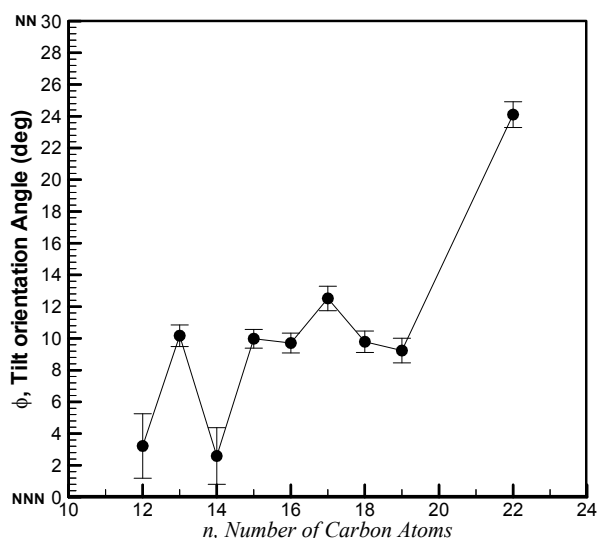


Figure 3 Tilt orientation angle, ϕ , versus the number of carbon atoms, n , for alkanethiols SAMs on Au(111) substrates at T=300 K. The orientation angle is shown in the range of 0 (NNN direction) and 30° (NN direction).

3.3 Effect of chain length on gauche defects

We have calculated time averaged gauche defect for all system and have plotted the results in Figure 4. For smaller systems C4 and C7 the gauche defects are significantly larger and this is consistent with their fluid and mobile nature as we observed earlier. For C12 and larger systems the overall gauche defects are much smaller consistent with their organized structure. For $12 \leq n \leq 15$ there is an odd-even effect where even alkanethiols show slightly larger gauche defects than that of their odd counterparts. For $n \geq 15$ no odd-even effects or noticeable dependence on the chain length could be seen.

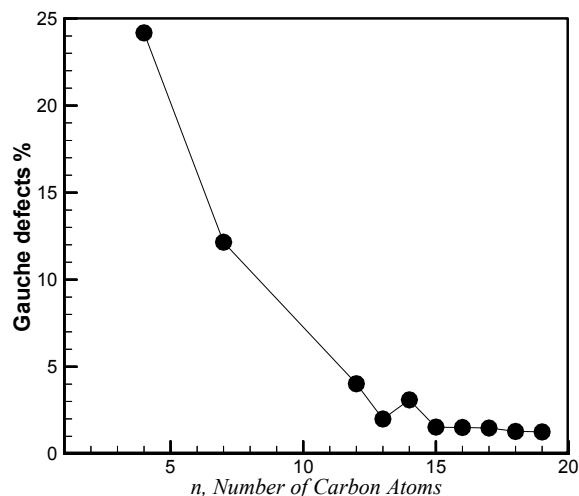


Figure 4 Percentage of gauche defects along the chain backbone, versus the number of carbon atoms, n , for alkanethiols SAMs on Au(111) substrates at T=300 K.

3.4 The effect of temperature on the SAM structure

In order to examine the response of the monolayers to temperature changes we studied their structural changes under varying temperature. The temperature was increased from 300K to 420 K at a rate of 1K per 47 ps. We monitored the structural properties as a function of time. We have displayed this in Figure 5 for C13 on Au(111). We can see from this graph that as the system temperature is increased from 300K to 354K, the tilt angle almost linearly decreases from $\sim 30^\circ$ to about 26.4° . Here the tilt orientation angle is shown in the range of ± 180 with respect to [100] direction, so that variations in the tilted structure can be detected. Up to this temperature (355 K) the tilt orientation angle remains very stable. At this point there is a sudden sharp decrease in the tilt angle by as much as $\sim 5^\circ$. This coincides with significant instability seen in the tilt orientation angle (ϕ). This instability is a signature of melting phase transition where significant rotational mobility is unlocked and system starts to behave more fluid. As the temperature increases further to 420 K, the tilt angle continues to drop further and reaches to $\sim 10^\circ$ at 420K. The melting temperature of corresponding bulk alkane, tridecane $C_{13}H_{28}$, is about 269K. Thus, the calculated melting point for C13 SAM is about 87 K above its corresponding bulk alkane. For C12, an even alkanethiol, we calculate the melt transition temperature of ~ 330 K, which is in close agreement with reported experimental [11] result of 323K. Bulk dodecane has a melting point of ~ 263 K. That means, for C12 SAM, the enhancement in the melt transition temperature is ~ 67 K. For C14 SAM our calculated melting point is ~ 357 K only slightly higher than C13. That is C14 despite being longer than C13 shows smaller enhancement, of about 78 K, over the bulk melting point of tetradecane $C_{14}H_{30}$. This is an indication that odd alkanethiols have larger enhancement in their melt transition temperatures than that of their even counterparts. We find this trend to be consistent over the range of alkanethiols we examined here ($12 \leq n \leq 19$).

CONCLUSIONS

In this paper we reported molecular dynamics simulations of alkanethiols SAMs on gold substrates. The results showed the effect of the chain length and temperature on the structure. At $T=300$ K, for alkanethiols in the range of $12 \leq n \leq 15$ we found odd-even effects in the monolayer tilt angle and tilt direction angle. For $n > 15$ the tilt angle and tilt orientation angle is almost independent from the chain length or being odd or even. All SAM systems respond to increasing temperature by untilting. At phase transition temperature the stable structure gives way to large rotational mobility and loss of order, signified by abrupt fluctuations in the tilt orientation angle and sharp decrease in the tilt angle. We find this phase transition temperature to be well above that of their bulk alkane system. The enhancement in the phase transition temperature was larger for odd alkanethiols.

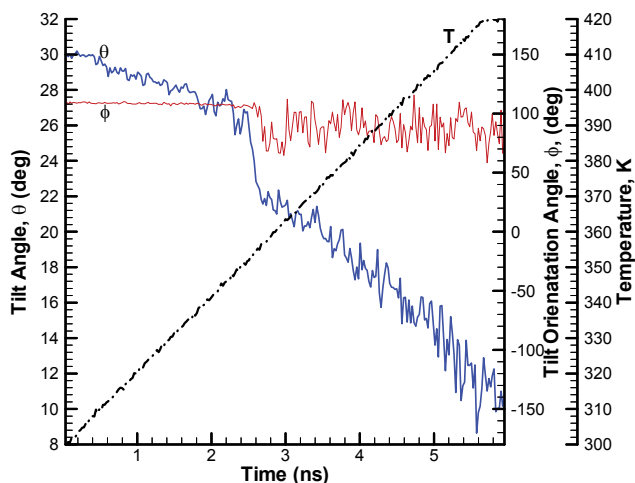


Figure 5 Temperature (T), tilt angle (θ) and tilt orientation angle (ϕ) as a function of time as the temperature is ramped up from 300 to 420 K for C13 alkanethiols on Au(111) surface.

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