

Adsorption Dynamics of Alkanethiol Self-Assembled Monolayers onto Gold Surfaces

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Abstract

Alkanethiol Self-Assembled Monolayers (SAMs) are a class of spontaneously adsorbing molecules—containing an adsorbing thiol head group and a (possibly end-functionalized) hydrocarbon tail—that are widely used to form dense, uniform, and sometimes functionalized monolayers in the surface science community. In this study, the effect of the hydrophobic tail length on the adsorption of alkanethiols onto gold surfaces was examined using Molecular Dynamics simulations. Head group and tail group density profiles—as functions of distance from the gold surface—were monitored during the simulations to show the time evolution of the monolayer adsorption. This study found that increasing the SAM hydrophobic tail length increased the hydrophobic interactions between the tail groups, and impeded head group adsorption.

Background

Alkanethiols are a group of amphiphilic molecules that readily form dense and uniform Self-Assembled Monolayers (SAMs) on gold surfaces. The molecule is composed of a thiol head group—which will strongly associate with a gold surface in solution through a dative bond—and a hydrocarbon tail—which may be end-functionalized with $-\text{OH}$, $-\text{NH}_2$, or $-\text{COOH}$ groups. Alkanethiols are facile and tunable way to alter the surface chemistry of a gold surface, and are routinely used as a precursor layer in the tethering of polymer chains or biomolecules to gold surfaces or nanoparticles. Alkanethiols are commercially available with tail lengths ranging from $-\text{C}_4\text{H}_8$ to $-\text{C}_{12}\text{H}_{26}$. This study considers the simple alkanethiol (without end-functional group) and examines the effect that increased hydrophobic tail length has on the adsorption dynamics of this molecule onto a gold surface.

Simulation

The molecular dynamics simulation was performed with a Verlet velocity algorithm at a dimensionless temperature $T^* = 1.0$, a time-step size $\Delta t = 0.001$, and using the following potential functions:

Head Group—Wall [9-3 Potential]

$$U(z^*) = \frac{4\pi\epsilon_{\text{HG-Wall}}\rho_s\sigma}{3} \left[\frac{1}{15}(z^*)^{-9} - \frac{1}{2}(z^*)^{-3} \right] + \frac{4\pi\epsilon_{\text{HG-Wall}}\rho\sigma}{3} \left[\frac{1}{15}(L-z^*)^{-9} - \frac{1}{2}(L-z^*)^{-3} \right] \quad [1]$$

$$\rho_s\sigma = 0.74$$

Tail Group—Wall [9 Potential, Purely Repulsive]

$$U(z^*) = \frac{4\pi\epsilon_{\text{TG-Wall}}\rho_s\sigma}{3} \left[\frac{1}{15}(z^*)^{-9} \right] + \frac{4\pi\epsilon_{\text{TG-Wall}}\rho\sigma}{3} \left[\frac{1}{15}(L-z^*)^{-9} \right] \quad [2]$$

Tail Group—Tail Group [“Hydrophobic” Lennard-Jones]

$$U(r_{ij}^*) = 4\epsilon_{\text{TG-TG}} \left[(r_{ij}^*)^{-12} - (r_{ij}^*)^{-6} \right] \quad [3]$$

$$\epsilon_{\text{HG-Wall}} = 10\epsilon_{\text{TG-TG}}$$

Head Group—Tail Group, Head Group—Head Group [“Soft” Lennard-Jones]

$$U(r_{ij}^*) = 2\epsilon_{HG-TG} \left[(r_{ij}^*)^{-12} - (r_{ij}^*)^{-6} \right] \quad [4]$$

$$\epsilon_{TG-TG} = 2\epsilon_{HG-TG}$$

The strength of the gold-thiol interaction and the strength of the hydrophobic interaction are $\sim 67\text{-}76 \text{ kT}^1$ and $\sim 3\text{-}7 \text{ kT}^2$, respectively. Accordingly, the potential energy well depth for the gold-thiol interaction, $\epsilon_{HG-Wall}$, was approximated to be 10x the potential energy well depth for the tail group-tail group interaction, ϵ_{TG-TG} . Both the head group-head group interaction, and the head group-tail group interaction were approximated to be $\frac{1}{2}$ of the hydrophobic interaction. All Lennard-Jones potentials were cut and shifted at a distance $r_c = 2.5$.

The system geometry was arranged so that the alkanethiols would adsorb between two identical gold surfaces, spaced a characteristic length $L = 10$ apart ($V_{\text{system}} = L^3$), and periodic boundaries were established in the x and y directions. A system size of 144 atoms (excluding the surface atoms) was used, and simulations were performed with tail lengths of 3, 5, and 7 hydrophobic atoms.

The alkanethiol molecules were first allowed to equilibrate in between the two surfaces, without the wall potentials (using only Lennard-Jones potentials) for 10,000 time steps, with velocity rescaling every 200 steps. After this equilibration, the wall potentials were turned on, and the molecules were allowed to adsorb for 80,000 time steps (with velocity rescaling), with periodic density histograms captured to analyze the time-dependence of adsorption. The average total energy was taken from the last 20,000 steps of this adsorption phase, and the velocity was rescaled to meet this average total energy. Velocity rescaling was then turned off, and the simulation was allowed to run at constant total energy for 100,000 time steps. Density histograms were taken periodically during this equilibrated stage.

Results

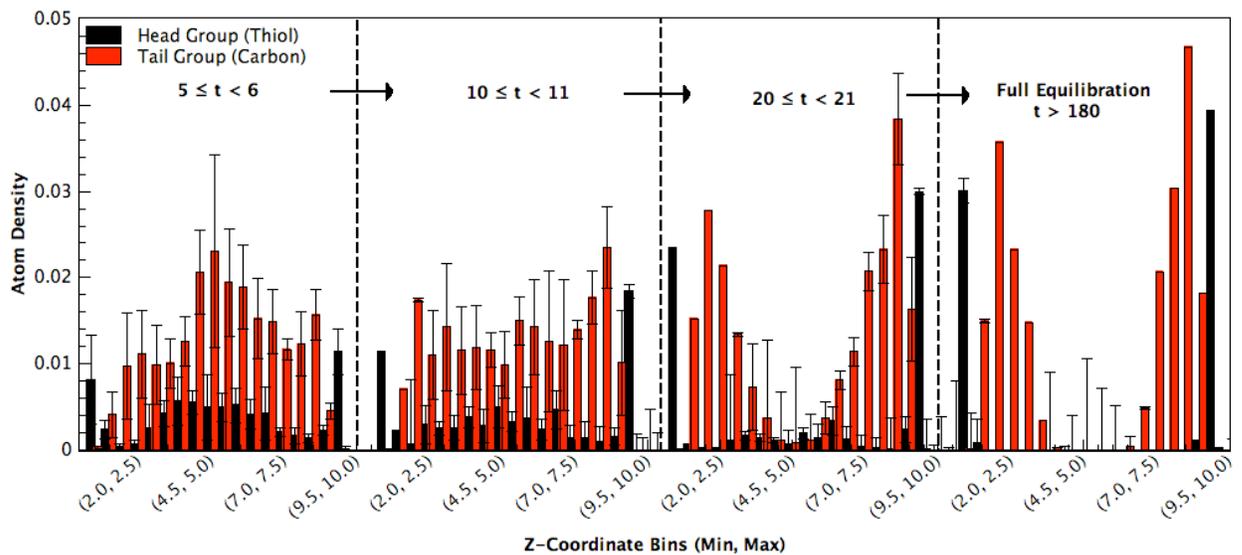


Figure 1: Time evolution of adsorbing alkanethiols with a 3-carbon tail. This figure displays atom density histograms as a function of the z-coordinate for selected times, t . Gold surfaces are located at $z = 0$ and $z = 10$. The data presented is the average over 5 trials, with the error bars representing the standard deviation of the trials.

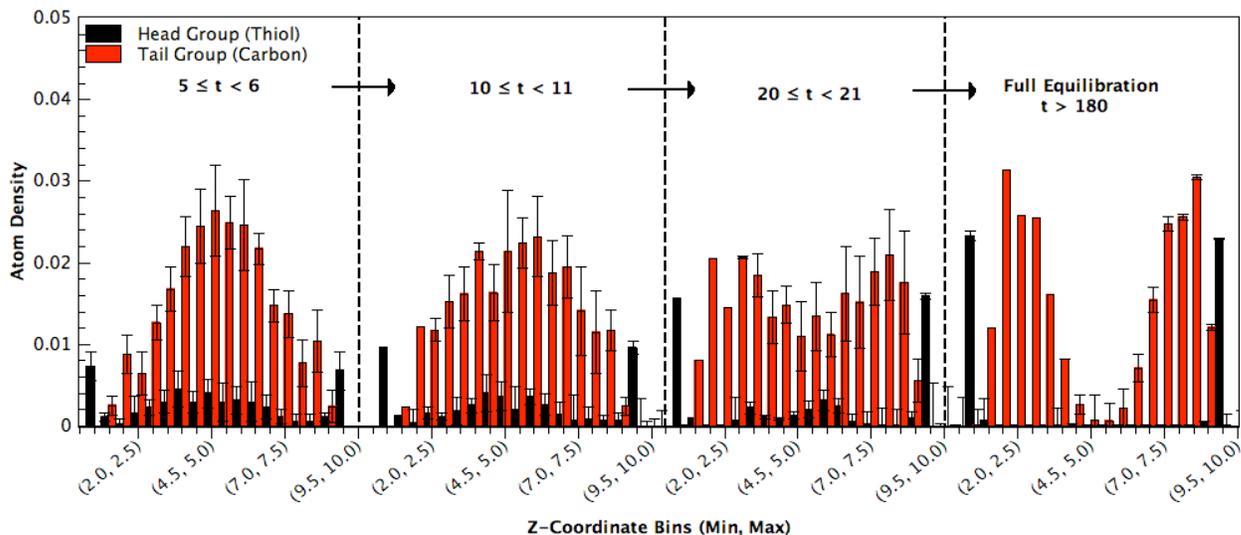


Figure 2: Time evolution of adsorbing alkanethiols with a 5-carbon tail. This figure displays atom density histograms as a function of the z-coordinate for selected times, t . Gold surfaces are located at $z = 0$ and $z = 10$. The data presented is the average over 5 trials, with the error bars representing the standard deviation of the trials.

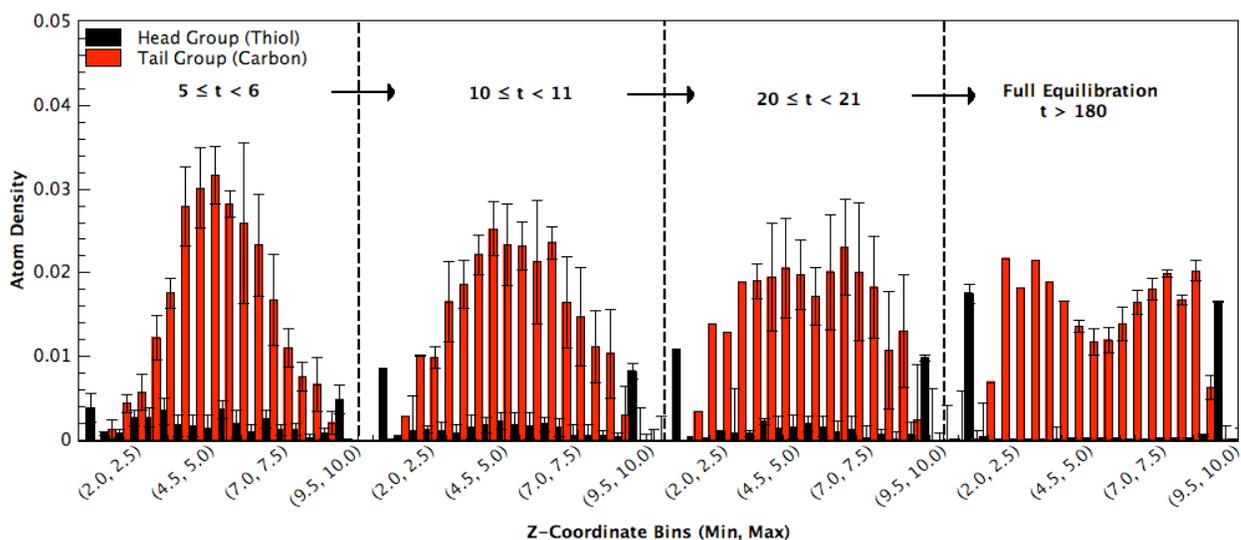


Figure 3: Time evolution of adsorbing alkanethiols with a 7-carbon tail. This figure displays atom density histograms as a function of the z-coordinate for selected times, t . Gold surfaces are located at $z = 0$ and $z = 10$. The data presented is the average over 5 trials, with the error bars representing the standard deviation of the trials.

Discussion

Figures 1, 2, and 3 display the time evolution of adsorbing alkanethiols with tail lengths of 3, 5, and 7 carbons, respectively. The histogram series in each figure display the same general trend: (1) at $5 < t < 6$, a few head groups have adsorbed, however the high density of tail groups in the center suggests a significant hydrophobic interaction/entanglement in the tail groups, (2-3) from $10 < t < 20$ the head groups continue to adsorb and the tail groups spread out from the center, (4) by $t > 180$, the system has fully equilibrated, with nearly all head groups adsorbed to the surface, and there is a marked decrease (or total vacancy) of tail groups in the center of the surfaces. The average thickness of the adsorbed monolayer can be seen in the fully equilibrated profile where the tail density falls to zero; in the case of the 7-carbon tail, there is a slight overlap in the monolayers between the top and bottom surface. (Note: the number of total atoms was kept constant throughout the trials, so that increasing the tail length decreases the total number of alkanethiol molecules, and leads to a density profile of lower magnitude for longer tail lengths.)

Comparisons between Figures 1, 2, and 3 indicate that increasing the hydrophobic tail length impedes the adsorption process. In Figure 1, after $t > 20$, the shortest tail length alkanethiol system already approaches the fully equilibrated density profile. This trend is less apparent in Figure 2 for the 5-carbon tail length, and hardly apparent at all in Figure 3 for the 7-carbon tail length. This trend indicates that as the tail length is increased, the favorable hydrophobic interaction between the tails begins to compete against the gold-thiol interaction; the hydrophobic interactions entangle the tails in the center of the system and slow the adsorption process of the head group to the surface.

While this series of MD simulations have returned decent results, there are several key deficiencies in this simplistic model. Firstly, velocity rescaling was used, which does not allow for the correct energy fluctuations in the system. Additionally, the molecules did not account for bending potentials, or for differences in atomic radius between the head group and tail group. Finally, the adsorption of SAM molecules from a bulk solution in reality occurs over both a much larger length scale and much larger time scale than this model permits.

References

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2. Valtiner, M. *J. Am. Chem. Soc.* **2012**, 3, 134