Calculating Deflection of Micro-Cantilever with Self-Assembled Monolayer Molecules Using Molecular Dynamics Simulations

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Abstract

By evaluating the change of Gibbs free energy of the Self-Assembled Monolayer (SAM) molecules on the surface of the micro-cantilever, the deflection of the micro-cantilever can be calculated according to the Stoney's equation. All computations of the free energy changes were performed isothermally with periodic boundary conditions (PBC) by the commercial Molecular Dynamics (MD) simulation software CHARMM in associated with the specific molecular topology and force fields for alkanethiolic molecules $(HS)(CH_2)_7CH_3$. The alkanethiolic molecules are respectively arranged in squared 4x4 and 8x8 array formats adsorbed on the Au atoms coated on the surface of the micro-cantilever. The effects of the seeding density of the adsorbed molecules are taken into consideration by different separations between Au atoms.

Keywords: Molecular Dynamics (MD) Simulation, Self-Assembled Monolayer (SAM), CHARMM, Stoney's Equation, Dupre Relation.

1. Introduction

Self-Assembled Monolayer (SAM) by spontaneous adsorption of molecules on microscale substrates has attracted a huge interest due to their scientific importance and potential use in technological applications and health care industry [1-4]. Diverse selections of SAM in accompanying with various bio-molecules to form biological probes on the substrate surface have made the micro-cantilever an excellent device for studies of interactions between solid surfaces and biological systems, such as molecular recognition, selective binding of enzymes to surfaces, chemical force microscopy, corrosion protection, and pH-sensing. It has been shown [5] that intermolecular interactions resulting from absorption of SAM molecules and probe molecules on the surface of a micro-cantilever induce the changes in surface stresses, which directly contribute to the deflection of the micro-cantilever. Therefore, the deflection of micro-cantilever can, in principle, be expressed in terms of the properties mentioned above like:

δ = δ (topology, number density, configuration, conformation, thickness and patterns...)

In present study the deflection of the micro-cantilever is analyzed, which is coated on the upper surface an Au (111) layer adsorbed with $(HS)(CH_2)_7CH_3$ as SAM molecules. The deflection is calculated by the Stoney's equation [6, 7], which is related to the change of Gibbs free energy according to the Dupré relation [7] by the thermodynamics laws [5]. The change of Gibbs free energy is obtained by the MD simulation by the commercial software CHARMM [8, 9].

2. Formulations

2.1 Thermodynamics relation and mechanical analysis

According to the thermodynamics laws, the change of Gibbs free energy can be expressed as [5]

$$dG = -SdT + dW + \mu dN \quad (1)$$

where S is the entropy, T the temperature, W the work done on the system, μ the chemical potential, N the number of particles, respectively. Suppose that the process is isothermal and no net particle flux through the boundary, Eq.(1) can be simplified by setting $dT = dN = 0$:

$$dG = dW \quad (2)$$

On the other hand, from experiments one can assume that the work dW on the molecular system is done by the micro-cantilever from the adsorption of the molecules on the micro-cantilever surface. Thus the work can be expressed as the scalar product of the tangential stress σ_e along the surface and the surface deformation dA_e (extension or contraction), which is caused by the micro-cantilever deflection resulted from adsorption:

$$dW = \sigma_{\parallel} \cdot dA_{\parallel} \quad (3)$$

Substituting (3) into (2) and follows the Dupré relation [7]:

$$N_a \Delta \bar{G} = \Delta\sigma \quad (4)$$

where $\Delta\sigma$ stands for the surface tension and N_a and $\Delta\bar{G}$ are the number of adsorbed molecules and the change of Gibbs free energy per unit surface area, respectively.

2.2 The Stoney's equation

The geometry of the micro-cantilever is shown in Figure 1. The deflection δ of the micro-cantilever can be calculated by the Stoney's equation [6,7]:

$$\delta = \frac{3l^2}{t_m^2}\frac{1-\upsilon}{E}\Delta\sigma \qquad (5)$$

where E and υ are the Young's modulus and Poisson's ratio, respectively; and their values are given in Table 1. Combining (4) and (5) gives the relation for the deflection of the micro-cantilever and the change of Gibbs free energy:

$$\delta = \frac{3l^2}{t_m^2}\frac{1-\upsilon}{E}N_a\Delta\bar{G} \qquad (6)$$

2.3 Molecular Dynamics simulation

All computations were performed by the commercial software CHARMM [9]. The MD simulations follow the trajectories of the alkanethiolic molecules $(HS)(CH_2)_7CH_3$ adsorbed on the Au(111) surface and with applied Periodic Boundary Conditions (PBC) at a temperature of 300K with a time step of 1fs (femto second) = 0.001ps (pico second) are specified in present work. Starting from the 4x4 and 8x8 arrays of alkanethiolic structures with the separation distances between sulfur atoms of 5, 6, 7, 8, and 9Å. The sulfur atoms of each alkanethiol molecular structure have been fixed with the bond constraints using the SHAKE algorithm [10]. A cut-off ratio of 14Å has been used for Lennard-Jones function. The setting of Periodic Boundary Condition was applied as the cubic box covering the entire molecular system with additional 2Å on each spatial direction. The minimization of potential energy for the alkanethiolic structures has been carried out with a combination of two algorithms: 20ps with steepest descent, 80ps with adopted basis Newton-Ralphason minimization. The heating procedure of the molecular system ranges from 240K to 300K with increments of 3K over 0.2ps. An equilibration process of system was performed with 50ps. The simulation process of the molecular system was performed with 4.5ns and 5.5ns for 4x4 and 8x8 arrays of alkanethiolic structures, respectively.

The bond lengths are constrained by the SHAKE algorithm [10] with the Au-S, S-H, S-C, C-C and C-H bonds held fixed at $d_{Au\text{-}S}$ = 2.531Å, $d_{S\text{-}H}$ = 1.325Å, $d_{S\text{-}C}$ = 1.836Å, $d_{C\text{-}C}$ = 1.531Å and $d_{C\text{-}H}$ = 1.111Å, respectively. The intramolecular potentials contain the bending $V_b(\theta)$ and dihedral $V_d(\phi)$; while the van der Waals effects are represented by the Lennard-Jones potential $V_{LJ}(r_{ij})$ with a cut-off ratio of 14 Å, as defined below [11,12,13]:

$$V_b(\theta) = \frac{1}{2}k_\theta(\theta-\theta_0)^2 \qquad (7)$$

$$V_d(\phi) = k_d[1+\cos(n\phi-\phi_0)] \qquad (8)$$

$$V_{LJ}(r_{ij}) = \varepsilon_{ij}\left[\left(\frac{r_{\min}}{r}\right)_{ij}^{12} - 2\left(\frac{r_{\min}}{r}\right)_{ij}^{6}\right] \qquad (9)$$

where θ is, for example, the C-C-C or S-C-C angle, with corresponding force constant k_θ and equilibrium angle θ_0; while ϕ is the torsion angle in associated with the constants k_d , n and equilibrium angle ϕ_0; and $(r)_{ij}$ is the distance between the i-th and j-th atoms. Note that the ε_{ij} and $(r_{min})_{ij}$ in (9) are defined as

$$\begin{aligned}\varepsilon_{ij} &= \sqrt{\varepsilon_i\varepsilon_j}\\ (r_{\min})_{ij} &= \frac{1}{2}\left[(r_{\min})_i + (r_{\min})_j\right]\end{aligned} \qquad (10)$$

The parameters used for calculating $V_{LJ}(r_{ij})$ are listed in Table 2, where the atoms connected to the considered atoms are represented in the parentheses.

3. Results and Discussions

The free energy change is obtained by the MD simulations in the sampling rate of 0.1 ns, i.e., the results are averaged for every 10^5 time steps. The potential of the mean force (PMF) is calculated by the Weighted Histogram Analysis Method (WHAM) [14, 15] and the results are shown in Figure 2. The deflection δ of the micro-cantilever is calculated by (6) and the results are shown in Figure 3.

As shown in the results, the calculated Gibbs free energy change, and the deflection as well, for both cases decrease as the separations between the adsorbed molecules increase. This can be interpreted as that the micro-cantilever is deflected by the adsorbing molecules through the work done on the Au atoms coated on the micro0cantilever surface. The applying work is related to the Gibbs free energy change according to the thermodynamics laws under constant (N, T) condition. On the other hand, the contribution to the Gibbs free energy change of the entire molecular system is diminishing as the seeding density becomes lower. Therefore, the micro-cantilever will be flatten-out as the seeding density of the adsorbing molecules is getting dilute.

4. Conclusion

As shown by the results the deflection of the micro-cantilever can be calculated by the Gibbs free energy change obtained by the MD simulation, whose results will be improved as the magnification of the simulated region, i.e., increasing the seeding density, and the application of more accurate interaction models.

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Table 1. Parameters of micro-cantilever.

$E(Nt/\mu m^2)$	0.15
t_m (μm)	0.6
l (μm)	180
υ	0.26

Table 2. Parameters for the Lennard-Jones potential.

	ε_{ij} (*kcal/mole*)	$(r_{min})_i/2$(Å)
S	-0.47	2.20
C(S)	-0.11	2.20
H(S)	-0.10	0.45
H(C)	-0.022	1.32

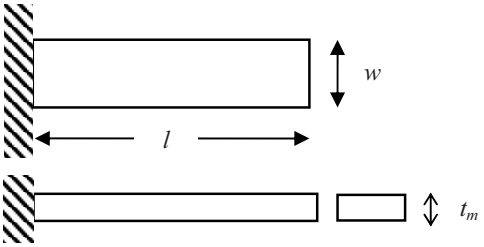
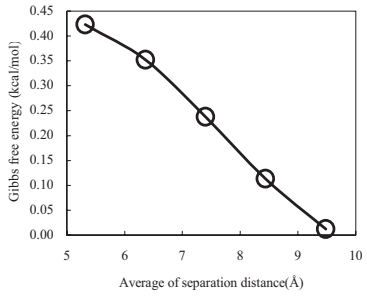
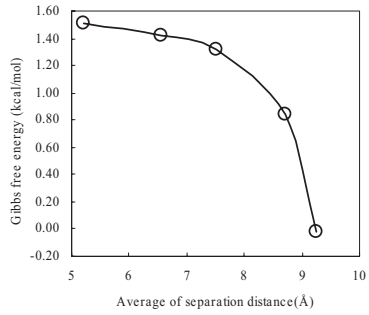


Figure1. Geometry of micro-cantilever.

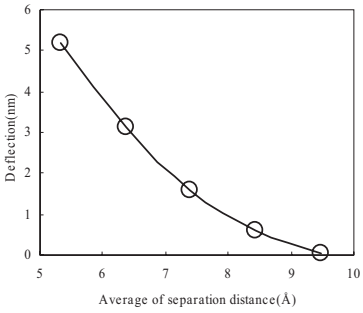


(a)

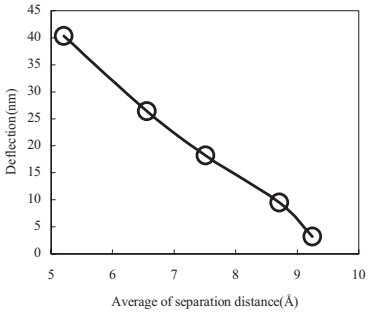


(b)

Figure 2. Potential of mean force (PMF): (a) 4x4 case; (b) 8x8 case.



(a)



(b)

Figure 3. The deflection δ of micro-cantilever: (a) 4x4 case; (b) 8x8 case.