Multiscale analysis of adsorption-induced surface stress of alkanethiol on microcantilever

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Abstract
A multiscale scheme was developed to evaluate adsorption-induced surface stresses in an alkanethiol-passivated Au(1 1 1)-modified microcantilever surface using first-principle density-functional theory calculations. In particular, the effect of alkyl chain length on the generated surface stresses was considered in detail. It was found that the majority of the surface stress originated from re-organization of the first two Au atom layers that lie in close proximity to the adsorption site. The difference in the calculated surface stresses, which were consistent with experimental measurements, was determined to be approximately $-0.05 \text{ N m}^{-1}$ per two carbons added to the alkanethiol chain.

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(Some figures may appear in colour only in the online journal)

1. Introduction
Biosensor related research has gained much interest owing to its potential social and economic impact [1–3]. Biosensing offers an enticing opportunity for the innovation of theories and models that can be exploited to provide new insights for designing next-generation biosensor devices. Microcantilevers are one of the most promising mechanically enabled biosensors [4–7]. Such devices can be routinely fabricated with the micro/nano-electro-mechanical systems (MEMS) technology as shown from the scanning electron micrograph provided in figure 1(a).

Microcantilever-based biosensors support label-free molecular recognition measurements with ultra-high sensitivity. In particular, self-assembled monolayers (SAMs) have been established as sensing platforms to detect biomolecular interactions in both the gas-phase as well as in liquid environments [1–14]. Alkanethiol SAMs adsorbed on a gold-coated microcantilever surface have been commonly employed in such applications owing to their highly ordered structure and chemical stability [11]. Such alkanethiol SAMs can be readily synthesized with varying alkyl chain lengths and specific functional end-groups, the latter being capable as anchoring sites for biomolecules to the Au substrate.

Adsorbed alkanethiol SAMs induce surface stresses that consequently bend the microcantilever. The pioneering study by Berger et al [1] indicated that the surface stress generated by gas-phase self-assembly increased linearly with alkyl chain length. Recently, Godin et al [12] reported the effect of grain-size on the generated surface stresses in which the measured surface stress was $-6.3 \pm 0.2 \text{ N m}^{-1}$ for the gold substrate with a grain size of $500 \pm 400 \text{ nm}$.

Quantitative interpretation of this adsorption-induced chain length dependence remains a theoretical challenge to date. Moreover, a well-defined theoretical framework regarding the transduction principle of microcantilevers in biosensing is lacking. Recently, Dareing and Thundat [15] derived a theoretical model for calculating adsorption-induced surface stress based on atomic interactions. However, the model was restricted in that a simple Lennard-Jones potential was used and only a single atomic layer adsorption was considered. Extension of this approach for the analysis of the more complex molecular adsorption that typically occurs in biosensing applications is not straightforward. Moreover, the empirical interatomic potential limits its capacity to account for the complex charge transfer induced by adsorption.
a microcantilever. We consider the simple microcantilever model illustrated in figure 1(b) and assume a uniform curvature, \( \kappa \) for the entirety of the deflected microcantilever. From elementary beam theory, the displacement field for the microcantilever is given by

\[
\begin{align*}
    u_x &= -\kappa x z, \\
    u_y &= \text{constant}, \\
    u_z &= \frac{x^2}{2}.
\end{align*}
\] (1)

The bending deformation is the result of adsorption. The total energy of the model can thus be expressed as

\[
E_{\text{total}} = E_{\text{elastic}} + E_{\text{ads}},
\] (2)

where \( E_{\text{elastic}} \) corresponds to the bending elastic energy and \( E_{\text{ads}} \) the adsorption-induced energy. The equilibrium configuration of the microcantilever can be determined by minimizing the total energy with respect to the curvature \( \kappa \):

\[
\frac{dE_{\text{total}}}{d\kappa} = 0 \Rightarrow \frac{dE_{\text{elastic}}}{d\kappa} + \frac{dE_{\text{ads}}}{d\kappa} = 0,
\] (3)

where \( \tilde{Y} \), \( t \), \( b \) and \( L \) correspond to the apparent Young’s modulus, thickness, width and length of the microcantilever, respectively. \( f_x \) and \( f_z \) represent the forces in the \( x \) and \( z \) directions of an atom \( i \) that arise from the interaction of the atoms (#atoms) between the surface of the microcantilever and the adsorbed molecules. The apparent Young’s modulus is given by \( Y/(1-\nu^2) \) and \( Y/(1-\nu) \) for uniaxial and biaxial bending, respectively, in which \( Y \) and \( \nu \) are Young’s modulus and Poisson’s ratio, respectively. By rearranging equation (3) we obtain

\[
\frac{\tilde{Y}k^2t^2}{6} = \frac{1}{bL} \sum_{i} \left( \frac{-2f_x x z + f_z x^2}{i} \right).
\] (4)

The left-hand side of equation (4) reduces to the well-known Stoney equation [24]. We can thus view equation (4) as a multiscale scheme allowing the calculation of the surface stress that arises directly from atomic interactions. These contributions include the atomic positions and atomic forces originating from local rearrangement of surface atoms as well as charge redistribution induced by ligand adsorption. Conceptually, the scheme presented herein belongs to a multiscale methodology where the atomic contributions are linked with the kinematics imposed by continuum mechanics. This approach can be extended to other MEMS devices representable by structural members, such as membranes, plates and shells.

The atomic contributions of surface stresses were rigorously obtained from DFT calculations. In this study, we used VASP 4.6 (Vienna Ab-initio Simulation Package) with a plane wave basis set [25, 26]. VASP, widely used in quantum chemistry, performed electronic structure calculations as well as quantum-mechanical molecular dynamics from first principles. The results of the DFT calculations were based on a 400 eV kinetic energy cutoff and a \( 10 \times 10 \times 1 \) k-point mesh in the Brillouin zone of the Au slab. The Brillouin
Figure 2. Structures of methanethiol (a) and butanethiol (b) adsorbed on Au (1 1 1) surface (top view). The adsorption sites of methanethiol and butanethiol are located at the fcc and hcp-bridge sites. The letters a to e indicate the five atoms that dominate resulting surface stresses. Yellow corresponds to the gold atom, purple to the sulfur atom, grey to the carbon atom and white to the hydrogen atom. (c) Electron density distribution differences in the absence and presence of the methanethiol adsorbed monolayer. Black circles indicate the atomic positions on a bare surface.

3. Results and discussion

Four different alkanethiols, i.e. methanethiol (SCH$_3$), butanethiol (SC$_4$H$_9$), hexanethiol (SC$_6$H$_{13}$) and octanethiol (SC$_8$H$_{17}$) adsorbed on a $\sqrt{3} \times \sqrt{3} R30^\circ$ Au(1 1 1)-coated microcantilever surface were analysed. From the optimized methanethiol-modified structure shown in figure 2(a), the adsorption site was face-centred-cubic (fcc). The adsorption energy was calculated to be 1.67 eV and the S–C bond at the gold surface was tilted 41.1° away from the surface normal. The calculated distance between the first gold layer and adsorbed methanethiol was 1.92 Å. The aforementioned results were in good agreement with previous studies [18–21]. The optimized butanethiol-modified structure is shown in figure 2(b). The adsorption site of butanethiol and hexanethiol on gold was hexagonal-closed-pack-bridge (hcp-bridge) whereas the site of octanethiol was bridge, significantly different from that of methanethiol. Calculated adsorption energies of butanethiol, hexanethiol and octanethiol were 1.54 eV, 1.59 eV and 1.32 eV, respectively. Additionally, the tilting angles between the S–C bonds of butanethiol, hexanethiol and octanethiol and the Au surface were 51.9°, 64.8° and 62.9°, respectively.

Adsorption of the alkanethiols on gold led to gold surface reconstruction. Binding of the sulfur atom altered the atomic positions as well as charge distribution of the gold atoms in a few surface layers. Electron density distribution differences between a bare and SAM-modified gold surface are shown in figure 2(c). In addition, non-uniform surface coverage of the monolayer resulted in localized charge distribution around the adsorption site as previously demonstrated [29]. Furthermore, we found that alkanethiol SAMs with different alkyl chain lengths yielded different charge redistribution on gold. The charge redistribution induced interaction forces and surface rearrangement of the uppermost three layers of the gold slab.
The multiscale scheme in equation (4) allows surface stresses to be evaluated directly from the DFT calculations. The thickness, width and length of the microcantilever were set to the same values used by Berger et al [1]. We found that the atomic contributions from the first three layers of the Au slab, listed in table 1, dominated the generated surface stresses. In addition, a majority of contributions came from the five atoms labelled in figures 2(a) and (b). Atoms a, b and c were located in the first layer and were thus in close proximity to the sulfur atom. The positions of atoms d and e were in the second layer and the atom f was just below the hcp-bridge or fcc site. A drastic change in surface stress contributions was observed at atoms b and d when the geometry of the adsorption site shifted from fcc to hcp-bridge.

Useful deductions can be obtained by comparing our calculations to experimental measurements. We regulated the comparison by the difference of surface stress between the calculated and measured surface stresses resulting from adsorption of different alkyl chain lengths are plotted in figures 3(a) and (b). Our results showed that the longer the chain length, the larger the generated compressive surface stresses (figure 3(a)), which agreed well with the findings of Berger et al [1]. The difference of the calculated surface stresses for hexanethiol and octanethiol-modified Au(1 1 1) was about $-0.05 \text{ N m}^{-1}$ in comparison with the $-0.04 \text{ N m}^{-1}$ reported by Berger et al [1]. We also compared our calculated results with those of Godin et al [12] in figure 3(b). Although Godin et al [12] reported that the measurement of surface stresses was independent of the carbon chain length, a careful re-examination of the data revealed that the mean difference in their measured surface stress for hexanethiol and octanethiol-modified Au(1 1 1) was approximately $-0.07 \text{ N m}^{-1}$. Our predicted surface stress values thus agreed remarkably well with two independent experimental measurements.

It should be noted that this study only examined SAMs adsorbed on Au(1 1 1) surfaces. The microstructural effect, such as the grain size of gold films [30], was not considered. Since atomic forces and positions will be influenced by the varying surface structures of different gold substrates, proper homogenization is required to effectively capture the effects of grain size and orientation. Furthermore, the displacement field of the multiscale scheme developed herein has been limited to the pure bending of beams since our primary focus is on deflected microcantilevers bearing uniform curvature $\kappa$. We could extend our approach to the pure bending of plates in which displacement fields with a non-constant $u_s$ could be included in the scheme. As a result, pure bending of plates will in general lead to two curvatures, $\kappa_x$, $\kappa_y$ and a twist $\kappa_{xy}$ for total energy minimization. Although this theoretical extension is interesting, direct correlation with surface stress measurements is expected to pose a significant challenge.

The present multiscale scheme only considers the charge distribution of a single microcantilever but in practice, a biosensing chip often consists of an array of several...
microcantilevers. If the microcantilevers are electrically connected, the collective charge distribution will be different from that of a single microcantilever. Therefore, one interesting study would involve extending our scheme to calculate charge distribution in a microcantilever array. The resulting atomic forces and positions could then be utilized to predict the surface stresses and curvatures generated in each microcantilever.

4. Conclusions

We have presented a multiscale scheme to calculate surface stresses of a microcantilever using DFT calculations. We found that the surface stresses were primarily contributed from the Au atoms in the first two layers that were in close proximity to the adsorption site. The difference in calculated surface stress was approximately $-0.05 \text{ N m}^{-1}$ for every two carbons in the alkyl chain of the surface-bound ligand. The observed trend quantitatively agreed with the experimental measurements reported by Berger et al [1] as well as Godin et al [12]. In the future, it is expected that the multiscale scheme described herein will find use in the treatment of the adsorption-induced bending in systems containing other organic molecules such as proteins. In addition, the scheme presented herein belongs to a multiscale framework of linking atomic contributions with the assumed kinematics imposed by continuum mechanics. The predictive power offered from the multiscale scheme will help us to design next-generation mechanical-based biosensors.

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