Molecular Structure Alters Apparent Height in nc-AFM Images of Alkanethiolate Embedded in Matrix

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The non-contact atomic force microscopy (nc-AFM) images of the single alkanethiolate molecules embedded in the bicyclo[2,2,2]octylmethylthiolate (BCO) self-assembled monolayer (SAM) are simulated using the all-atom empirical force field model. The tip is modeled by the chemically inactive and unpolarized carbon nanocone apex. When the alkyl chain is longer than the BCO matrix, the protruded chain is observed to be lower than its actual height. Even if the alkyl chain has a similar height to the BCO, the former is observed to be slightly lower than the latter. These findings indicate that even when the chemical and electrostatic interactions are not relevant for imaging, the nc-AFM images do not always give true topographical information of the molecules under the tip.

Keywords: Computer simulations; Semi-empirical models and model calculations; Molecular Dynamics; Atomic force microscopy; Alkanes; Nano-scale imaging, measurement, and manipulation technology; Inversion; Protrusion

I. INTRODUCTION

The non-contact atomic force microscopy (nc-AFM) has been widely used for imaging various materials with high resolutions. In particular, atomic resolutions have been obtained for the surfaces of inorganic materials, i.e., semiconductor (Si [1–7], GaAs [8–10], InAs [11]), alkali halide (KBr [12, 13]), metal oxide (TiO$_2$ [14]), and metal (Cu [15]) surfaces. These experiments promote theoretical studies concerning the tip-surface interactions and image contrasts based on the first-principles calculation [16–18], the density functional tight-binding model [19–21], and the phenomenological potential model [22–25]. They contribute to understating the mechanism of image contrast, tip-induced surface reconstruction [17, 19], multi-atom tip effect [20, 21], and so on.

For organic molecules, on the other hand, atomicly resolved images have not been obtained in experiments. At this stage molecular resolutions have been obtained for the self-assembled monolayers (SAMs) of hydrocarbons formed on the Au(111) surface [26–30], and the carboxylate molecules adsorbed on TiO$_2$ (110) surface [31, 32]. For the planar molecules, submolecular resolutions have been achieved in their crystallite/thin film phase or by isolating them on the substrate [33–35]. Correspondingly, theoretical simulations of nc-AFM images of the organic molecules have been reported only in a few articles [33, 36]. Due to these circumstances, it has not been clear what is observed and what can be observed in principle in the nc-AFM images of the organic molecules.

Our purpose in this work is to develop a method of theoretical simulation of nc-AFM images of organic molecules which are self-assembled on the substrates. Because of the large system size to be scanned for generating the nc-AFM images, we choose the phenomenological potential model in this article. To be specific, we assume the all-atom force field model called CHARMM whose parameters have been obtained by fitting to ab initio calculations, and simulate the nc-AFM images of the SAM of the bicyclo[2,2,2]octylmethylthiolate (BCO) [30] with a single alkyl chain molecule (1-pentanethiolate (C5) or 1-undecanethiolate (C11)) embedded in it.

As for the tip, we adopt the carbon nanocone which has a sharp apex structure and has a definite cone angle. In the point that the apex structure is clearly defined, this tip has an advantage in analyzing the tip-molecule interaction and achieved nc-AFM images, compared to the silicon-based tip. In a similar context, the nanotube tip has been used in imaging of the biomaterials [37, 38]. Although the nanocone tip has not been used in the AFM experiment, it is a candidate as a tip for achieving images with higher resolutions compared to the nanotube tip, as it has a sharper apex than the latter. In this work we treat the carbon nanocone tip as a chemically inactive and unpolarized tip. It directly means that not only the chemical interaction forces relevant for imaging the semiconductor surfaces but also the electrostatic forces relevant for imaging the polarized surfaces can be removed in the formation of image contrasts, which would make the analysis of images straightforward.

Although the SAM of the BCO molecules have been formed on the Au(111) surface in experiments, we treat the substrate surface only in an implicit manner. Namely, the anchoring S-Au bonds of all the molecules are substituted with the CH$_3$-CH$_3$ groups, and the heights of the bottom CH$_3$ groups are fixed on the virtual surface with the aid of the stiff harmonic springs. The whole calculations are performed using the program called NAMD 2.5 [39]. We found the following characteristic features by the simulations; 1) When the long alkane molecule such as C11 is protruded from the surrounding BCO matrix, it is observed to be lower than its actual height. Such a tendency agrees well with the finding in an experimentally observed image of the other organic molecule [40]. 2) When the C5 molecule is embedded in the BCO matrix, the former is observed to be slightly lower than the latter.

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although the actual height order is opposite. This can be explained by the difference of the molecular shape, i.e., the BCO molecule has more atoms due to its cage structure, which enhances the van der Waals force contribution in the normal force. These findings indicate that even at the moderate condition where only the van der Waals interactions are relevant for imaging, the nc-AFM images do not always give true topographical information of the molecules under the tip.

The rest of the paper is organized as follows. In §II the computational model and simulation method will be described. In §III the results of our calculations will be presented. In §IV the paper will be summarized.

II. MODEL AND METHOD

A. Model structure of SAM

We consider the SAM of the BCO molecules with a single C5 or C11 molecule embedded in it. Figure 1(a) schematically illustrates the system in consideration in the case of C5. The molecules at the left and right correspond to the BCO molecules, and the molecule at the center corresponds to the C5. In experiments, these molecules are anchored to the Au(111) surface by the bottom Au-S bonds. However, at room temperature, they have been known to move around on the surface. It indicates that the hopping across the adsorption sites such as the fcc-hollow, bridge sites can be realized with a low energy cost. In addition, the BCO has been observed to form the matrix on the Au(111) surface irrespective of the incommensurateness between the intermolecular distance and the lattice length of the Au(111) surface [30]. This indicates that the intermolecular interaction plays the dominant role in the formation of the BCO matrix.

Taking these experimental facts into account, we model the system in a rather simplified way by treating the S-Au bonds implicitly. First, the S-Au groups at the bottom of the molecules are substituted with the CH$_2$-CH$_3$ groups (see Fig. 1(b)). Then, the virtual harmonic springs [41] are connected to all of the four atoms at the bottom CH$_3$ groups, in order to suppress unrealistic oscillation along the normal direction. The strength of the spring constant $\alpha$ is commonly assumed to be $10^4$ kcal/mol/nm$^2$. In contrast, no constraints are imposed on the dynamics of the molecules along the lateral directions. Thus, the rotation along the molecular axis is allowed in this treatment. Hereafter, we call the modeled molecules after the actual molecules, although the chain lengths differ between the former and the latter. For example, we call the molecule depicted at the left and right in Fig. 1(b) BCO, and the molecule at the center C5.

The structures of the modeled SAM are prepared in the following way. We assume the supercell whose dimensions are $6.24 \times 6.60$ nm$^2$ along the lateral directions. Initially, at the bottom of the supercell, the BCO molecules are arranged to form the close packed structure with the intermolecular spacing of 0.56 nm, which is a typical distance obtained in the simulations with free boundary conditions. Then, one of the BCO molecules is substituted with a C5 or C11 molecule which has the all-trans conformation. Namely, the supercell is occupied by 131 BCO molecules and a single C5 or C11 molecule. The total number of atoms amounts to 4,084 and 4,102 in the case of C5 and C11, respectively.

Next, the molecular dynamics simulations are performed at $T = 300$ K for 0.65 ns (325,000 steps) with the constraint on the bond length of the hydrogen atoms, using the package NAMD 2.5 [39] with the all-atom empirical force field CHARMM. The periodic boundary conditions are imposed and the Particle Mesh Ewald (PME) sum method is used for calculating the electrostatic interaction. The size of the PME grids is assumed to be 32, 32, and 32 for the corresponding directions. The van der Waals interactions are smoothly cut off beyond 1.2 nm. The temperature control is performed by the LANGEVIN method. Then, the successive MD simulation is performed for 0.3 ns with the temperature lowered by 25 K. This procedure is repeated until the temperature
FIG. 3: (a) Top view of C11 embedded in BCO matrix. The green and cyan colored molecules correspond to the BCOs which form the different domains from each other. The purple colored molecule at the center corresponds to the C11. The topmost hydrogen atoms whose heights are beyond 0.732 nm are marked by the orange color with the VDW representation. Among the marked hydrogen atoms, the highest atoms in each of the BCOs and C11 are marked by the red color. (b) Closeup of the area enclosed by the white square in (a).

FIG. 4: (a) Top view of C5 embedded in BCO matrix. The green and cyan colored molecules correspond to the BCOs which form the different domains from each other. The purple colored molecule at the center corresponds to the C5. The topmost hydrogen atoms whose heights are beyond 0.732 nm are marked by the orange color with the VDW representation. Among the marked hydrogen atoms, the highest atoms in each of the BCOs and C5 are marked by the red color. (b) Closeup of the area enclosed by the white square in (a) viewed from the right side.

gets 0 K. In the following calculations of the force curves, we adopt the final molecular configuration obtained at $T = 0$ K.

B. Calculation of force curves

The AFM tip is modeled by the apex of the carbon nanocone which has a disclination angle of 120 degrees and has a cone angle $\alpha$ of 41.8 degrees [42, 43], as illustrated in Fig. 2. The figure is drawn using the program VMD [44]. The bottom of the tip apex is composed of a four membered ring. The length of the tip is 1.98 nm in the normal direction, and the number of tip atoms amounts to 628. First, this tip is set on the height $z = 2.1$ and 2.2 nm in the case of C5 and C11 molecules, respectively. Here the tip height $z$ is defined to be the height difference between the tip apex atoms (four-membered ring) and the carbon atoms of the bottom CH$_3$ group of the molecules. Then, $z$ is varied by pulling up/down the virtual springs attached to the CH$_3$ groups of the BCO/alkane molecules along the normal directions simultaneously. Pulling up/down of the springs corresponds to approach/retraction of the tip. The pulling velocity is as-
III. RESULTS

A. Domain and gauche structure

Figure 3(a) shows the top view of the C11 molecule embedded in the surrounding BCO matrix. The green and cyan colored molecules correspond to the BCO molecules which form the different domains from each other. Namely, the cage structures of the BCOs in the former domain are rotated by 60 degrees around the normal axis compared to those in the latter domain. Here we will make a brief comment on the formation of these domains. During the MD simulations, the minor ribbon-like domain (green color) is observed to grow and decrease along a certain direction on the BCO molecules. In addition, the existence of the alkane molecule C11 (purple color) is found to work as a source of such a domain. In fact, one of the domain boundaries is observed at the site of the C11 molecule. Although the length of the one-dimensional ribbon-like domain is found to depend on the initial orientation of the molecules and the speed of cooling of the system temperature, a similar feature is also observed in the simulations with the alkane molecules of different chain lengths. Thus, it might be a general feature in the mixed SAM of these two molecular species. We expect that such domain dynamics will be investigated from experimental studies.

The topmost hydrogen atoms whose heights are beyond 0.732 nm are marked by the orange color with the van der Waals (VDW) representation. Here the atomic height \( h = 0 \) is defined to be the height of the carbon atoms of the bottom \( \text{CH}_3 \) group of the molecules. As seen, inside the BCO matrix, the molecular heights do not take a constant value, and rather it ranges from 0.710 to 0.753 nm. Such non-uniform molecular heights are originated from the differences in the bending angle \( \theta \) and the dihedral angle \( \phi \) defined in Fig. 1(b). Namely, the values of \( \theta \) and \( \phi \) range from 111.3 to 115.1 and from 164.2 to 179.9 degrees, respectively. Among the marked hydrogen atoms, the highest atoms in each of the BCOs and C11 are marked by the red color, whose heights are \( h = 0.753 \) and 1.120 nm, respectively. Figure 3(b) shows the closeup of the area enclosed by the white square in Fig. 3(a). The C11 molecule is found to take a gauche structure, i.e., it bends at the point over the height of the surrounding BCO matrix and extends its chain over one of the BCO...

FIG. 5: Force curves in the case of C11 molecule. The curves with the blue and red color are calculated on top of the highest hydrogen atoms of the BCOs and C11, respectively. The solid and dotted curves correspond to the approach and retraction curves, respectively.

FIG. 6: Dihedral angle of BCO molecule B defined in Fig. 3(b) plotted against the tip height. The solid and dotted curves correspond to the approach and retraction curves, respectively.
FIG. 7: Force curves in the case of C5 molecule. The curves with the blue and red color are calculated on top of the highest hydrogen atoms of the BCOs and C5, respectively. The solid and dotted curves correspond to the approach and retraction curves, respectively.

molecules labeled A.

In a similar manner, Fig. 4(a) shows the top view of the C5 molecule embedded in the surrounding BCO matrix. The green and cyan colored molecules correspond to the BCO molecules which form the different domains from each other, as previously mentioned. The purple colored molecule at the center corresponds to the C5 molecule. The topmost hydrogen atoms whose heights $h$ are beyond 0.732 nm are marked by the orange color with the VDW representation. In addition, the highest atoms in each of the BCOs and C5 are marked by the red color, whose heights are $h = 0.758$ and 0.777 nm, respectively. Figure 4(b) shows the closeup of the area enclosed by the white square in Fig. 4(a), which are viewed from its right side. The C5 molecule is found to take the gauche structure under the influence of the surrounding BCO matrix.

B. Force curves

Figure 5 shows the force curves obtained in the case of the C11 alkane molecule. The curves with the blue and red color are calculated on top of the highest hydrogen atoms of the BCOs and C11, respectively, i.e., the red atom enclosed by the white circle in Fig. 3(a) and the atom enclosed by the red circle in Fig. 3(b). The solid and dotted curves correspond to the approach and retraction curves, respectively. On the BCO molecule, the approach and retraction force curves are similar to each other, apart from the region $z < 1.06$ nm. In contrast, on top of the C11, the strong repulsive force regions is observed at $1.071 < z < 1.366$ nm in the approach curve, while it is not observed in the retraction curve. These indicate that a significant conformational change occurs in the latter case. Indeed, at around the small saw-tooth peak at $z = 1.27$ nm, the protruded chain of the C11 molecule slides from the above of the BCO molecule labeled A (see Fig. 3(b)) to the above of the molecule labeled B. Pushing the C11 molecule further by the tip induces the structural change of the molecule B.

Figure 6 shows the dihedral angle $\phi$ (defined in Fig. 1(b)) of the molecule B plotted against the tip height $z$. The solid and dotted curves correspond to the approach and retraction curves, respectively. By comparing this figure to Fig. 5, the rapid decrease of $\phi$ at $1.0 < z < 1.1$ nm is found to bring about the abrupt decrease of the normal force. In addition, the values of $\phi$ in the retraction curve do not retrieve the values prior to the approach, which indicates that the molecule B is kept to be rotated. However, we have to point out that the bottom of the molecule B also slides along the lateral directions which amounts to 0.22 nm at $z = 1.0$ nm. Such a sliding motion may not occur when the BCO molecule is anchored by the Au-S bond on the surface. Thus, in order to investigate whether the rotation of the BCO molecule denoted above is actually realized in experiments, a more careful modeling with an accurate calculation method would be required.

In a similar manner, Fig. 7 shows the force curves obtained in the case of the C5 alkane molecule. The curves
FIG. 9: (a) Simulated nc-AFM image of C11 molecule embedded in BCO matrix. The color scale range is adjusted to be about 0.02 nm (see text). (b) The line profile across the highest BCO molecule A and the C11 molecule labeled P.

FIG. 10: (a) Simulated nc-AFM image of C5 molecule embedded in BCO matrix. (b) The line profile across the highest BCO molecule labeled P and the C5 molecule labeled Q.

with the blue and red color are calculated on top of the highest hydrogen atoms of the BCOs and C5, respectively, which are depicted by the red atom enclosed by the white circle in Fig. 4(a) and the atom enclosed by the red circle in Fig. 4(b). Again, the solid and dotted curves correspond to the approach and retraction curves, respectively. In this case, the approach and retraction curves resemble each other, apart from the region, $z < 1.09$ nm, which indicates that no significant structural change occurs during the oscillation cycle of the tip.

The inset shows the closeup of the force curves at $1.08 < z < 1.18$ nm and gives a significant information. Namely, at the same value of the normal force, the tip height is evaluated to be higher on top of the BCO molecule than on top of the C5 molecule, while the actual physical height of the topmost hydrogen atom is higher by 19 pm on the latter molecule, as denoted in the previous subsection. The origin of such an inverted height order is considered to be the difference of the molecular shape. Namely, the BCO molecule has three carbon atoms at similar atomic height due to the cage structure which does not exist in the C5 molecule. Note that as we assume no charge distribution inside the nanocone tip, the electrostatic forces do not contribute to the normal
force. Thus, the excess atoms enhance the van der Waals attractive force between the molecule and the tip, which shows up as the increase of the normal force.

C. Constant frequency shift images

Hereafter, in order to simulate the nc-AFM images under the condition in which the AFM tip causes no significant structural change on the SAM, we only consider the attractive force regions in the approach curve. The frequency shift curves are calculated using the formula [19]

\[
\frac{\Delta \nu}{\nu_0} = -\frac{1}{2\pi Ak} \int_0^{2\pi} F_z (z_0 + A \cos \varphi) \cos \varphi \, d\varphi,
\]

where \(\Delta \nu\) and \(\nu_0\) is the frequency shift and the resonance frequency of the cantilever. The quantities of \(A\) and \(k\) are the oscillation amplitude and spring constant of the cantilever whose values are set to be 10 nm and 30 N/m, respectively. The variable \(z_0\) represents the center of the oscillation. In this work the uniform background van der Waals interactions are not added to the normal force, because they do not contribute to the lateral resolution.

Figure 8 illustrates the frequency shift curves plotted against the variable \(z_0\) which are calculated on top of the C11 (red curve), C5 (green), and BCO (blue) molecules. Here, the values of the normal forces are taken from Fig. 5 and Fig. 7. This indicates that the C11 and C5 molecules can be imaged in the frequency shift range where \(\Delta \nu/\nu_0 > -1.38 \times 10^{-5}\) and \(-2.85 \times 10^{-5}\), respectively. In addition, the intersection between these curves and the horizontal lines such as the dot-dashed lines give the observable heights of the molecules in the constant frequency shift mode. Although such intersections may have more than one solutions, we choose the highest value among the possible solutions in generating the nc-AFM images, because we focus on the attractive force region.

The nc-AFM images with wide area are obtained as in the followings. First, the force curves as seen in the previous subsection are calculated with the lateral spacings of 0.15 nm. Then, the frequency shift curves as denoted above are calculated at every lateral positions. Finally, the images in the constant frequency shift mode are obtained by mapping the highest values of the intersections. Figure 9 (a) shows the simulated image in the case of C11 obtained with \(\Delta \nu/\nu_0 = -1.25 \times 10^{-6}\). The bright circle at the center labelled P corresponds to the C11 molecule. We have to comment here on the shape of this bright spot. Originally the bright spot takes an elliptical shape which appears around the protruded chain of the C11 molecule, while no contrast is seen on the BCO matrix. In order to display not only the C11 but also the BCO molecules at the same time, the color scale range is adjusted to be about 0.02 nm, which artificially enlarges the radius of the bright spot and makes its shape round.

The bright spot labelled A corresponds to the highest BCO molecule which is marked by the white circle in Fig. 3(a). The darkest area at the upper left corresponds to the domain boundary formed on the BCO matrix where the intermolecular distance is slightly increased ( see Fig. 3 ). The line profile across the two points A and P illustrated in Fig. 9(b) indicates that the height difference between these two points is about 0.275 nm, which is smaller than the actual physical height difference, 0.367 nm, as presented in the previous subsection. Such a feature agrees well with the findings in the nc-AFM experiment of the other organic molecule protruded from the surrounding molecules [40].

Figure 10(a) shows the simulated image in the case of C5 obtained with \(\Delta \nu/\nu_0 = -2.50 \times 10^{-5}\). In this case, the BCO molecules are clearly recognized individually. The non-uniform brightness in the BCO matrix is originated from the height differences among the BCO molecules, as previously denoted. In experiment, a similar feature has been observed in the scanning tunneling microscopy (STM) [45] and nc-AFM images [30] of the BCO matrix, although the authors have not discussed its origin. The brightest spot labeled P corresponds to the highest BCO molecule which is marked by the white circle in Fig. 4(a). The slightly bright spot labeled Q corresponds to the C5 molecule. Again, the darkest area at the upper left corresponds to the domain boundary of the BCO matrix ( see Fig. 4 ). The line profile across the two points in Fig. 10(b) indicates that the BCO molecule is observed to be about 6 pm higher than the C5 molecule. However, as denoted previously, the actual height of the former is lower by 19 pm than the latter.

These two images indicate that the nc-AFM images do not always give true topographical information of the organic molecules under the tip, even at the moderate condition where the strong chemical and electrostatic interactions are not relevant for the image contrast. When a molecule is protruded from the surrounding matrix, it is observed to be lower than its actual height. Even when the molecule has an almost similar height to the surrounding molecules, the observable height order can be inverted reflecting the shape of the molecular species.

IV. SUMMARY

Using the all-atom empirical force field, the nc-AFM images of single alkane molecules embedded in the BCO matrix are simulated in the constant frequency shift mode. The tip is modeled by the carbon nanocone apex which has a sharp apex and has no charge distribution inside it. When a long alkane molecule such as C11 is protruded from the matrix, it is observed to be lower than its actual physical height. When the C5 molecule, which is slightly higher than the BCO matrix, is embedded, the former is observed to be slightly lower than the latter. This can be explained by the difference of the molecular shape, i.e., the BCO molecule has more atoms due to its cage structure, which enhances the van der Waals force contribution in the normal force. These findings indicate that even at the moderate condition where only the van der Waals interactions are relevant for imaging, the nc-AFM images do not always give true topographical information of the molecules under the tip.
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