Theoretical Simulations of Atomic Force Microscopy of Graphite Flake on Graphite Surface

Masanori Harada* and Masaru Tsukada
Department of Nanoscience and Nanotechnology, Graduate School of Science and Engineering, Waseda University, 513 Waseda Tsurumaki-cho, Shinjuku-ku, Tokyo 162-0041, Japan

Naruo Sasaki
Department of Materials and Life Sciences, Faculty of Science and Technology, Seikei University, 3-3-1 Kichijoji-Kitamachi, Musashino-shi, Tokyo 180-8633, Japan

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We present results of theoretical simulations of atomic force microscopy (AFM) for the systems consisting of a graphite flake on a graphite substrate with a diamond tip. How are atomic sliding motions of the sample reflected on AFM images? This central issue was investigated by changing tip height and size of the flake which was located on the substrate surface and placed in a vacancy on the surface. When the tip height becomes higher, the flake motion induced by the tip changes from the swinging motion centered at one local potential minimum to the slipping motion between local potential minima. At the same time, the image changes from the one reflecting flake feature to the one reflecting surface feature. When the flake size changes, the inverse of image contrast is seen. When the flake is in a small vacancy, a ring shaped image is seen, which reflects the rotational motion of the flake induced by the tip motion. When the flake is in a large vacancy, the image is a combination of a ring shaped one and a noisy ribbon like one caused by the lateral movement of the flake. [DOI: 10.1380/ejssnt.2007.126]

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I. INTRODUCTION

Since its invention [1] the enormous ability of atomic force microscopy (AFM) has been widely recognized and the fields of its application have been extended remarkably. As an example, AFM is broadening its scope to the organic molecular systems and the bio-nano systems. AFM images not only of static organic molecules but also of sliding organic molecules have been obtained. Deformation properties of organic molecules have been measured by AFM. Atom manipulations of inorganic surface, which can selectively pick up an individual atom and move it to the desired location, is another example of new applications. The common feature of these new AFM applications is that the target objects are movable on a substrate surface.

On the other hand, most of the AFM simulations performed so far have targeted the system of inorganic crystal surface and their models consist only of a tip and a surface. In some results, however, there are quantitative gaps between experimental data and simulation results which are thought to be caused by some movement of the sample on a surface [2, 3]. Theoretical simulation of AFM image for the system including movable substances like flake or molecule on surface is crucial [4, 5]. Such simulations are also helpful to understand the mechanism of friction and lubrication.

In this report we present the results of theoretical simulations of AFM for the systems consisting of a graphite flake on a graphite surface with a diamond tip, which is a simplified model of a movable object on a surface. How are atomic motions of the sample reflected on AFM images? This central issue was investigated by changing tip height and flake size when the flake is put on the substrate surface and placed in a vacancy on the surface. After explaining the simulation methods, we show simulation results for various cases and clarify the relation between atomic motions and simulated AFM images.

II. SIMULATION METHOD

A. Model and Scan Mode

Simulations are performed to investigate three issues, i.e., A) the tip height dependency in the constant height mode of NC-AFM, B) the flake size dependency in the constant height mode of contact AFM and C) the dependency of the size of the vacancy trapping the flake in the constant height mode of contact AFM. The constant height mode of NC-AFM is the mode which measures the frequency shift and the energy dissipation as the data constructing the image keeping the tip height a constant value at all the scan positions. Here and hereafter the tip height of NC-AFM means the lowest tip atom position at the closest turning point of the tip oscillation.

The model is constructed with the three parts, i.e., i) the diamond tip with (111) axis made up of 54 carbon atoms, ii) 2 layers of graphite substrate including a vacancy made up of 432 or 588 carbon atoms and iii) graphite flake made up of 6 or 96 carbon atoms (FIGs. 1, 2 and 3).

For the investigation of the tip height dependency, tip heights are chosen as 5.5, 5.7 and 5.9 Å from the substrate surface. The flake which is made up of 96 atoms is used. To investigate the flake size dependency on flake motions and images for constant height mode AFM, we choose the flakes made up of 6 atoms, 24 atoms and 96 atoms. The tip height is fixed at 5.5 Å. In this simulation the scan area is 7×7 Å² square centered at the hollow site of the

*Corresponding author: harada@cms.nano.waseda.ac.jp

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is expressed as follows: $T_{\text{S}}$ and $V_{\text{S}}$ denote the normal displacement of the $i$th atom from the plane made of the three neighboring atoms $j$, $k$ and $l$; $d_{ij}$ denotes the normal displacement of the $i$th atom from the initial positions.

The tip-substrate interaction $V_{TS}$ and the tip-flake interaction $V_{TF}$ are expressed by the 6-12 Lennard-Jones potential as follows:

$$V_{TS} = V_{TF} = 4\epsilon \left( \frac{\sigma}{r_{ij}} \right)^{12} - 2\epsilon \left( \frac{\sigma}{r_{ij}} \right)^{6} \quad (\epsilon = 0.87381 \times 10^{-2} \text{ eV}, \sigma = 2.4945 \text{ Å}).$$

Since graphite is used as a substrate, the intra-flake potential was chosen to be the same as the one between the tip and the substrate (eq. (2)). For the same reason, the potential between the tip and the flake was determined to be the same as the one between the tip and the substrate (eq. (3)). On the other hand, the potential between the substrate and the flake $V_{\text{SF}}$ was determined by two criteria. One of them is that the potential is given by the 6-12 Lennard-Jones type. The other is that the distance between the flake and the top layer of the graphite substrate becomes similar to the interlayer distance of the substrate, 3.3539 Å. The selection of the distance in the vacuum trapping the flake.

FIG. 1: Model of a graphite flake on a graphite surface (left) and the scan area (right) to investigate A) the tip height dependency and B) the flake size dependency.

substrate graphite, as seen in the right of FIG. 1. The pixel size is chosen as 0.2×0.2 Å$^2$.

To investigate the effect of the flake motion and the image of a flake in a vacancy for constant height mode AFM, we use a 6 atom flake at the tip height of 2.2 Å. Two types of vacancy are introduced on a graphite surface. One of them is a 24-atom size hexagonal vacancy caved on a 432-atom graphite substrate seen in FIG. 2. The scan area for the simulation is 14×6 Å$^2$ and the pixel size is 0.2×0.2 Å$^2$. The other is a 77-atom size rectangular vacancy caved on a 588-atom graphite substrate seen in FIG. 3. The scan area is 20×7 Å$^2$ and the pixel size is 0.2×0.2 Å$^2$.

B. Potential

We use the same potential model and calculation method as the theoretical simulation by Sasaki and Tsukada [6]. The total potential energy of the system is expressed as follows:

$$V = V_T + V_S + V_F + V_{TS} + V_{TF} + V_{SF}, \quad (1)$$

where $V_T$, $V_S$, and $V_F$ represent the potential energy of the tip, the substrate and the flake respectively and $V_{TS}$, $V_{TF}$ and $V_{SF}$ represent the tip-substrate, tip-flake and substrate-flake interactions respectively.

First, $V_T$ is expressed as the sum of two harmonic terms as follows:

$$V_T = \frac{1}{2} \sum \lambda_r (r_{ij} - r_0)^2 + \frac{1}{2} \sum \lambda \theta \delta^2 (\theta_{ijk} - \theta_0)^2 \quad (2)$$

Here the first term means the bond-stretching energy due to the change of each nearest-neighbor bond length $r_{ij}$ from the equilibrium one $r_0$. The second term represents the bond-bending energy corresponding to the change of each bond angle $\theta_{ijk}$ from the equilibrium one $\theta_0$.

$V_S$ and $V_F$ have the same form and consist of four different types of harmonic terms as follows:

$$V_S = V_F = \frac{1}{2} \sum \mu_r (r_{ij} - r_0)^2$$
$$+ \frac{1}{2} \sum \mu \theta (\theta_{ijk} - \theta_0)^2 + \frac{1}{2} \sum \mu d (d_{ij} - d_0)^2$$
$$+ \frac{1}{2} \sum \mu p \left[ \delta_{ij}^2 - \delta_{ij}^3 + \delta_{ij}^4 + \delta_{ij}^3 + \delta_{ij}^2 - \delta_{ij}^4 \right] \quad (3)$$

Similar to $V_T$, the first and second terms correspond to the bond-stretching and the bond-bending energy, respectively. $\theta_{ijk}$ denotes the angle between the bond $i$-$j$ and the bond $j$-$k$ within the same honeycomb net plane. The third term is the deformation energy of the interlayer spacing $d_{ij}$ from the equilibrium distance $d_0$. The fourth term is the bending energy of the local planar structure due to the normal displacement of the $i$th atom from the plane made of the three neighboring atoms $j$, $k$ and $l$; $\delta_{ij}$ denotes the normal displacement of the $i$th atom from the initial positions.

The tip-substrate interaction $V_{TS}$ and the tip-flake interaction $V_{TF}$ are expressed by the 6-12 Lennard-Jones potential as follows:

$$V_{TS} = V_{TF} = 4\epsilon \left( \frac{\sigma}{r_{ij}} \right)^{12} - 2\epsilon \left( \frac{\sigma}{r_{ij}} \right)^{6} \quad (4)$$

Since graphite is used as a flake as well as a substrate, the intra-flake potential was chosen to be the same as the intra-substrate one (eq. (3)). For the same reason, the potential between the tip and the flake was determined to be the same as the one between the tip and the substrate (eq. (4)). On the other hand, the potential between the substrate and the flake $V_{SF}$ was determined by two criteria. One of them is that the potential is given by the 6-12 Lennard-Jones type. The other is that the distance between the flake and the top layer of the graphite substrate becomes similar to the interlayer distance of the substrate, 3.3539 Å. The selection of the distance in
the second criterion is not based on any theoretical background. Based on these, we expressed the potential between the substrate and the flake $V_{SF}$ in the same formula as eq. (4), but with the different $\sigma$, 3.4923 Å. The calculated distance between the flake and the substrate using this potential was 3.4737 Å when a 24-atom flake was on a 2-layer 432-atom substrate.

To make a vacancy region, we simply remove atoms inside the vacancy and no special parameter setting was added for the rest of atoms even for ones surrounding the vacancy.

C. Method of the Calculation

The conjugate gradient (CG) method [7] is used to determine the optimized structure at each scan position and at each tip height. The criterion for the completion of the optimization is that forces for all movable atoms are less than 1.0E-4 nN. This criterion is weaker than that used in Ref. [6]. But we confirmed that the same quality image can be obtained even when the weaker criterion is adopted.

In the non-contact atomic force microscopy (NC-AFM), the frequency shift during one cycle of the tip oscillation is calculated by the same formula as that by Sasaki et al. [8–11] as follows:

$$\Delta \nu = -\frac{\nu_0}{2\pi k A} \int_0^{2\pi} F_z(\theta) \cos \theta d\theta.$$  

In this equation, $\nu_0$ and $k$ correspond to the resonance frequency of the cantilever and the cantilever stiffness. $A$, $\theta$ and $F_z(\theta)$ correspond to the oscillation amplitude, phase of the oscillation and the vertical force at the phase of $\theta$ which are seen in FIG. 4. We chose 300.0 kHz, 40.0 N/m and 100.0 Å for $\nu_0$, $k$ and $A$, respectively.

Frequency shift images of the flake for three tip heights in the constant height mode of NC-AFM are shown in FIG. 5. The motion and the image for the case of the tip height, 5.7 Å, has the same common features of the images for both tip heights, 5.5 Å and 5.9 Å. So, first we explain the cases of the tip heights, 5.5 Å and 5.9 Å, in the followings.

In the case of the tip height, 5.9 Å, the flake starts to move to some X-Y direction feeling a force from the tip when it goes down approaching to the flake in its oscillation motion. In the case where the scan position of the tip is above the hollow site of the flake, the motion of the flake is small and returns to the initial position when the tip goes up away from the flake. In other words, the flake swings horizontally centering on a stable position during a cycle of the tip oscillation motion. And when the tip scan position becomes nearer to an ontop atom site or a bridge site, the motion of the flake becomes larger. Frequency shift image is shown in FIG. 5(c). White and black areas represent the regions of least and most negative frequency shift respectively. White areas in the image correspond to ontop atom sites or bridge sites. The difference between A sites, the atom sites under which a 2nd layer atom exists, and B sites, the atom sites under which no 2nd layer atom exists, can be seen as the difference of the brightness of white spots. Black areas correspond to hollow sites. Because of eq. (5), less negative frequency means the overall force during one cycle of the tip oscillation shifts to the positive side. In this simulation, the tip feels repulsive force when it approaches to ontop atom sites or bridge sites. Here it should be mentioned that we did not include the van der Waals attraction force contributed from a very wider range of the system, since such a force is not sensitive to the atomistic details of the scan position. For a realistic system, the van der Waals force from the long range area contributes to a uniform back ground negative force, and frequency shift values shift to the negative side.

In the case of the tip height, 5.5 Å, the swing motion which is seen when the tip is near to a hollow site becomes larger than the 5.9 Å case. And when the tip scan position becomes nearer to an atom site or a bridge site, the motion of the flake is much enhanced. Moreover, when the motion becomes the largest at some scan position of the tip, the flake moves from the original stable position to another stable position at a certain instance.
of swinging motion. After that event, the flake swings centering the new stable position. The same process repeats every bridge or atom site of the tip position. The frequency shift image is shown in FIG. 5(a). The noise of the frequency shift image is generated when the flake moves from a stable position to another. In this simulation, lateral scan direction of the tip alternates left-to-right and right-to-left. This is seen as the difference of the lateral position of the noise. We obtained two force curves, the force in z-direction (FIG. 5(b)) and the force in y-direction (FIG. 5(a)), at point 1 of FIG. 5. The noise of the frequency shift image is generated when the flake moves from a stable position to another. In this simulation, lateral scan direction of the tip alternates left-to-right and right-to-left. This is seen as the difference of the lateral position of the noise. We obtained two force curves, the force in z-direction (FIG. 5(b)) and the force in y-direction (FIG. 5(a)), at point 1 of FIG. 5 where the stable position of the flake changes in y-direction. When the tip moves down from tip height 6.0 Å to 5.9 Å, the stable position of the flake changes into another stable position. When the tip moves up, the stable position of the flake does not change. This motion of the flake is related to the energy dissipation. The analysis for the energy dissipation will be reported in another paper by the same author.

B. Flake Size dependency

Features in the motions of the flakes in the constant height mode of contact AFM are similar for all the three sizes of flakes. The flakes often adhere to the bottom of the tip and rotate around a vertical axis of the tip while moving with the tip. The vertical force images at the constant tip height of 5.5 Å are shown in FIG. 7. The vertical forces at all the pixel positions are repulsive for the three flake sizes, though they might change negative with the inclusion of the long range van der Waals force. Large white spots in FIGS. 7(a) and (c) correspond to the hollow sites of the graphite substrate in the cases of the 6-atom and 96-atom flakes respectively, while large black spots in FIG. 7(b) correspond to the hollow sites in the case of the 24-atom flake.

The periodicity of the images, which is consistent with the periodicity of the lateral positions of substrate surface atoms, and the reverse of the image contrasts between the 24-atom flake and the others are easily understood. Because the flakes cling to the bottom of the tip, the distance between the tip and the flake does not change as much as the one between the tip and substrate during the scanning. Namely, we can regard the tip and the flake as a combined tip. So, the periodicity of the force images is consistent with the one of the substrate surface atom position, and not of the flake atom position. Generally, in repulsive force regimes, the tip atom and the substrate atom which approaches closest each other dominate the entire force. Consequently, the Z force is dominated by the interaction between the substrate and the flake not by the one between the substrate and the tip. So, the reverse of the contrast among three images reflects the reverse of the lateral positions of the minimum and maximum forces among three flake sizes.

By the way, in the image of 24-atom flake, 6 smaller gray spots can be seen around a larger black spot, the positions of which are consistent with the positions of atoms of substrate surface. However, regarding each gray spot as the reflection of the surface atom underneath the tip is not correct. As mentioned above, the vertical force image is mainly determined by the interaction between the substrate and the flake. So, when the flake size is larger, the one pixel of the image reflects wider area of substrate surface. This can be confirmed by the image simulations of a one atom vacancy on the substrate surface shown in FIG. 8(a). FIGS. 8(b) and (c) show the images for the case of 6-atom flake and 24-atom flake respectively. In the 6-atom flake image, the position of the vacancy can be recognized. In the 24-atom flake image, however, not only can the position of the vacancy not be clearly recognized, but the influence of the vacancy can be seen spread over at least 7×7 Å² area, which is the size of the image.

C. Flake in Vacancy

In the case where the flake is located in the small vacancy in the constant height mode of contact AFM, the rotating motion of the flake can be seen when the tip is near to the flake. The driving force of this motion is the repulsive force between the tip and the flake. At the tip
FIG. 9: (a), (b) and (c) are the Fx, Fy and Fz images when the movable flake is in the small vacancy, and (d), (e) and (f) are corresponding images when all the atoms are fixed.

height of 2.2 Å, at which the calculation is performed, the potential energy between the tip and the flake has its maxima when the tip is just above one of the flake atoms. So when the tip passes through above the flake, the flake rotates in order for flake atoms to avoid tip apex atom. Since the barrier between the potential energy minima of the flake-substrate interaction is relatively small, the flake sometimes moves from a potential minimum to the nearest one. The images of Fx, Fy and Fz are shown in FIGs. 9(a), (b) and (c). The circular shapes in the images reflect the rotating motion. For comparison, images (d), (e) and (f) are for the case where all atoms are fixed. Individual atoms can be observed in contrast to images (a)-(c).

In the case of the large vacancy, the combination of the rotating motion and the straight sliding motion along scanning direction can be seen. The rotating motion is similar to the motion of small vacancy case. The straight motion is similar to the motion of the 6-atom flake case of model B. The images are combinations of circle shapes and straight band shapes as seen in FIGs. 10(a), (b) and (c). We find also irregular noise like stripes, which are similar to the noisy patterns often observed in experimental images. From this result, some of noises seen in general experimental images might be caused by movable objects on a surface, and not by the mechanical or electrical vibration of the apparatus. For comparison, images (d), (e) and (f) are for the case where all atoms are fixed. Individual atoms can be observed.

IV. SUMMARY

The atomic motions and AFM images are investigated when a graphite flake is on a graphite surface. For the investigation of the tip height dependency, the motion of the flake changes qualitatively from the swinging motion at the same position to the combined motion of the swinging and sliding motions when the tip is closer to the surface. The frequency shift image also changes from reflecting the periodicity of the surface to reflecting the flake itself. In the investigation of the flake size dependency, no qualitative change of the motion of the flake is confirmed for different flake size. However, image contrast reverses depending on the flake size. And although image reflects substrate periodicity, its resolution is determined by the flake size, that is, when the flake is smaller the resolution of the image increases. When the flake is located in a small vacancy, the circle shape instead of the atomic structure of the flake can be seen because of the rotating motion induced by the tip. The combination of circle shapes and straight band shapes can be seen as the force image when the flake is in a large vacancy.

It is also possible to have the viewpoint whether a movable object is the part of the substrate or the part of the tip. The cases of the 5.9 Å tip height are categorized in the former examples. The cases of the 5.5 Å tip height are later examples.

Most experimental images which include noises or blurred area may have been thought not as appropriate to analyze as images which have better continuity and resolution. As we can see in this paper, however, various information of nanometer scale dynamics exist in such images, and not in atomic resolution images. And those images can be analyzed with theoretical simulations for movable objects.

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FIG. 10: (a), (b) and (c) are the Fx, Fy and Fz images when the movable flake is in the large vacancy, and (d), (e) and (f) are corresponding images when all the atoms are fixed.
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