Energy Dissipation Mechanism of Non-Contact Atomic Force Microscopy for Movable Objects

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The energy dissipation in non-contact atomic force microscopy (NC-AFM) caused by the hysteresis loop of the potential energy between a tip and a sample with respect to the tip height is investigated in detail by the case studies for models of a graphite flake with a diamond tip. One of the models is made up of a graphite flake on a graphite surface. In this case, the hysteresis is caused by the difference of the lateral positions of the flake during the upward and the downward motion of the tip. The other model is made up of a graphite flake edge. In this model, the hysteresis is caused by the difference of the vertical positions of the flake edge during the upward and the downward motion of the tip. [DOI: 10.1380/ejssnt.2008.1]

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I. INTRODUCTION

The energy of the cantilever oscillation is dissipated in the operation of the non-contact atomic force microscopy (NC-AFM). The magnitude of the dissipation per cycle relative to the total oscillation energy is the inverse of the Q-value of the resonance, and measured by NC-AFM with enough accuracy. This quantity can be used as the NC-AFM image which has the atomic resolution, sometimes better resolution than the usual image formed by the resonant frequency shift. For the soft materials like organic or bio-molecules, the information of the dissipation provides important nano-mechanical properties of the samples. In spite of its crucial role in NC-AFM, the microscopic mechanism of the energy dissipation has not been well understood either from experiment or from theoretical analyses. Roughly speaking, two main mechanisms are generally thought of.

One of them is due to the effect of microscopic thermal fluctuation of atoms of the tip and the sample, which causes the randomly oscillating force between the tip and the sample. Due to the fluctuation-dissipation theorem of the statistical mechanics, such a random force acting on a small body causing the Brownian motion inevitably accompany a systematic friction force to the body. The energy loss by this friction balances the enhancement of the microscopic random motion of the sample and the tip atoms by the movement of the body. This means that some kinetic energy of the tip is transformed into the microscopic thermal motions of the atoms on sample and the tip. This energy transformation is irreversible and the tip loses its energy. The mechanism of energy dissipation due to the thermal random motion of the sample atoms was investigated in details by Gauthier et al. [1–5].

The other mechanism is caused by the hysteresis loop of the potential energy between a tip and a sample with respect to the tip height. If the tip feels the force from the sample which depends only on its vertical position, but not on its moving direction, some kinetic energy of the tip is transformed into the potential energy during its downward motion (Fig. 1) and the potential energy is transformed back again into the kinetic energy of the tip during its upward motion (Fig. 1). So, the tip does not lose any energy. But if there is a hysteresis and the amount of the energy transformed back during the upward motion of the tip is smaller than the energy transformed during the downward motion of the tip, the difference of the energy is observed as the energy dissipated in one cycle of a cantilever oscillation. This mechanism is not related to the tip velocity [6–9].

Compared with the mechanism related to the hysteresis loop, the mechanism related to the thermal random motion is not so important because the velocity of lattice vibrations or the movements of individual atoms or molecules on the surface is much faster than the speed of the vertical motion of the tip. The experimental result by Schimeisen et al. [10] shows that the energy dissipation on a graphite surface with a Si tip is determined mainly by the hysteresis mechanism, and not by the thermal fluctuating force mechanism. In this report, we therefore focus on the energy dissipation caused by the hysteresis loop.

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FIG. 1: Tip motion of NC-AFM.
We introduce two models of a graphite flake and a diamond tip to estimate the energy dissipation by the hysteresis mechanism.

II. SIMULATION METHOD

A. Model

Simulations of the constant height mode of NC-AFM are performed for two models. One of them is composed of a graphite flake on a graphite surface. The other model is made up of a graphite flake edge.

The former 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 made up of 432 carbon atoms and iii) graphite flake made up of 96 carbon atoms, as seen in Fig. 2.

For the investigation of the tip height dependency, tip heights are chosen as 5.5 and 5.9 Å from the substrate surface. 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. In this simulation the scan area is 7×7 Å² square centered at the hollow site of the substrate graphite seen in the right of Fig. 2 and the pixel size is chosen as 0.2×0.2 Å².

The second model we adapt as a case study of the energy dissipation is a model of a graphite edge as shown in Fig. 3. This model is constructed with the two parts, \( i.e. \), i) a diamond flat head tip with (111) axis made up of 25 carbon atoms and ii) 2 layers of graphite substrate made up of 300 carbon atoms. White atoms of the graphite flake seen in Fig. 3 are fixed and the other atoms are free to move along all directions. Simulations were performed at the tip height of 3.5 Å in the constant height mode of NC-AFM. The scan area is 8×4 Å² square shown in Fig. 3 and the pixel size is 0.5×0.5 Å².

For this simulation, the strong attractive force between the tip and the graphite flake was necessary to pull up the flake so that energy dissipation could be obtained, and this is the reason why we used the flat head tip (Fig. 4(a)). The flat head diamond tip is obtained by removing 4 atoms at the tip apex from the normal sharp diamond tip (Fig. 4(b)). The force curves are calculated at the lower left corner of the scan area using the rigid flat head tip (a) and the rigid normal sharp tip (b). As shown in Fig. 4(c), the maximum attractive force of tip (a), −0.231 nN, is larger than that of normal diamond tip, −0.138 nN. Therefore the flat head tip is appropriate to see clearly the pull up process of graphite flake.

B. Potential

The total potential energy of the system is expressed as follows:

\[
V = V_T + V_S + V_TF + V_{TS} + V_{SF},
\]

where \( V_T \), \( V_S \) and \( V_TF \) 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.

For \( V_T \), \( V_S \) and \( V_{TS} \), we use the same potential model as the theoretical simulation by Sasaki and Tsukada [11]. Since graphite is used as a flake as well as a substrate, \( V_T \) and \( V_{TF} \) were chosen to have the same expression as \( V_S \) and \( V_{TS} \) respectively. We summarize those potential models as follows. Please see Ref. [11] and references cited in the report for more details.

\[
V_T = \frac{1}{2} \sum \lambda_i (r_{ij} - r_0)^2 + \frac{1}{2} \sum \lambda_\theta r_\theta^2 (\theta_{ijk} - \theta_0)^2
\]

\[
\left( r_0 = 1.5445 \text{ Å}, \lambda_i = 29.512 \text{ eV/Å}, \lambda_\theta = 3.5213 \text{ eV/Å}^2, \theta_0 = \cos^{-1}( -1/3 ) \text{ rad} \right)
\]

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 \( \theta_0 \).


\[ V_S = V_F = \frac{1}{2} \sum \mu_i (r_{ij} - r_0)^2 + \frac{1}{2} \sum \mu_r \eta_j^2 (\theta_{ijk} - \theta_0)^2 + \frac{1}{2} \sum \mu_d (d_{ij} - d_0)^2 + \frac{1}{3} \sum \mu_p \left[ \frac{\delta z_i - (\delta z_j + \delta z_k + \delta z_l)}{3} \right]^2 \]

(3)

\[ r_0 = 1.4210 \, \text{Å}, \quad \mu_r = 41.881 \, \text{eV/Å}^2, \quad \theta_0 = 2\pi/3 \, \text{rad}, \quad \mu_\theta = 2.9959 \, \text{eV/Å}^2, \quad \mu_d = 0.34765 \, \text{eV/Å}^2, \quad d_0 = 3.3539 \, \text{Å}, \quad \mu_p = 18.225 \, \text{eV/Å}^2 \]

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 \( l \); \( \delta z_i \) 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:

\[ V_{TS} = V_{TF} = \sum_{i,j} 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right] \]

(4)

\( \epsilon = 0.87381 \times 10^{-2} \, \text{eV}, \quad \sigma = 2.4945 \, \text{Å} \).

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 is nearly the same as the inter layer distance of the substrate, 3.3539 Å. The second criterion is not based on any theoretical or experimental background. Based on these, we chose the same expression as Eq. (4) for \( V_{SF} \), except that the \( \sigma = 3.4923 \, \text{Å} \) is different from that of \( V_{TS} \) and \( V_{TF} \), 2.4945 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. Although this distance is different from the inter layer distance of the substrate, 3.3539 Å, it is closer than the calculated distance using the sigma of \( V_{TS} \) or \( V_{TF} \), 2.4945 Å. Adjusting the \( \sigma \) more precisely is not easy because the distance between the flake and the substrate is sensitive to the \( \sigma \) and it depends on flake size, substrate size and flake position. So we did not adjust the \( \sigma \) any further and adopted 3.4923 Å as the typical value.

C. Method of the Calculation

The conjugate gradient (CG) method [12] 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 1.0\( \times \)10\(-4 \) nN. This criterion is weaker than that used in Ref. [11]. 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 and energy dissipation during one cycle of the tip oscillation is calculated by the same formula as that by Sasaki et al. [6–9] as follows:

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

(5)

\[ E_{\text{disp}} = A \int_0^{2\pi} F_z(\theta) \sin \theta d\theta. \]

(6)

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. 5. We chose 300.0 kHz, 40.0 N/m and 100.0 Å for \( \nu_0, k \) and \( A \), respectively. It should be noted that the Eq. (6) does not include the viscosity effect but only include the hysteretic effect.

III. RESULT

A. Graphite Flake on Graphite Surface

Frequency shift images of the flake for two tip heights of 5.5 Å and 5.9 Å in the constant height mode of NC-AFM are shown in Figs. 6(a) and (b), respectively. In the case of the tip height, 5.9 Å, the flake starts to move to a horizontal 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.

In frequency shift image (Fig. 6(b)), 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. Black areas correspond to hollow sites. Because of Eq. (5), less negative frequency shift 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 onttop 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 of the flake which is seen when the tip is near to a hollow site becomes larger than the case of 5.9 Å. 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, after 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 at the new stable position. The same process repeats at every bridge or atom site of the tip position. In the frequency shift image (Fig. 6(a)), the stripe patterns are seen at the scan positions where the flake moves from a stable position to another. This is due to the fact that the initial geometry of the flake relative to the substrate differs depending on the scan direction; in the simulation the scan direction is reversed between the neighboring scan lines.

The calculated energy dissipation for this model are shown in Figs. 6(c) and (d). A larger energy dissipation is seen at the tip height of 5.5 Å, and no energy dissipation is seen at the height of 5.9 Å. Compared with the results of the frequency shift, positions where a large energy dissipation is seen are consistent with those where the discontinuities of the frequency shift are seen. From this fact, we can say that the energy dissipation is related to the slipping motions of the flake between its local stable positions.

The detailed mechanism of the energy dissipation is analyzed at the scan position, where the frequency shift is −2.78 Hz and the energy dissipation is 0.101 eV, as indicated in Figs. 6(a) and (c). At this scan position, the slipping motion of the flake in y-direction is seen as shown in Fig. 7(left). In Fig. 7(right), the calculated potential energy contour is shown in the parameter space of the tip height and the relative flake position in y-direction. The potential energy, which is stored while the tip is approaching to the surface indicated by the path from point ① to ② in Fig. 7(right), is released at the 5.51 Å tip height by the slipping motion of the flake indicated by the path from point ② to ③.

**B. Graphite Edge**

The images of the frequency shift and the energy dissipation for the model of the graphite edge are shown in Fig. 8. We analyzed the mechanism of the energy dissipation by tracing the force during one cycle of the tip motion at the scan position indicated by the arrow in Fig. 8 where the frequency shift is −16.2 Hz and the energy dissipation is 0.156 eV. The result is shown in Fig. 9(a). We can see the hysteresis loop at the tip heights between 3.9 and 5.0 Å.

We also plotted the position of the flake by summing up the Z positions of all the flake atoms by the function of the tip height (Fig. 9(b)). The hysteresis loop is clearly seen in this graph. The flake edge moves up and sticks to the bottom of the tip at a certain height A of the tip during its downward motion. After the sticking the flake moves with the tip, and on the retracting way it is detached from the tip at a certain height B, and finally it moves down to its initial height. The height A is smaller than the height B.

To analyze the detail mechanism of the energy dissipation, we calculated the potential energy contour in the parameter space of the tip height and the flake edge height in Fig. 10. We can see the energy dissipation at two steps in the motion of a tip oscillation. For the first step, potential energy, 0.08 eV, is dissipated when the flake edge sticks to the bottom of the tip, namely it moves from point ② to ③. For the second step, potential energy, 0.07 eV, is dissipated when the flake edge is detached from the tip, namely it moves from point ⑤ to ⑥. Total energy dissipation of 0.15 eV is consistent with one obtained in
FIG. 7: Left: initial position of the slipping flake at the scan position where the energy dissipation of 0.101 eV is obtained. The X marks the position of the tip apex. The arrow shows the distance of the flake motion in y-direction. Right: potential energy contour in the parameter space of the tip height and the relative y-position of the flake. The initial y-position of the flake is 0.62 Å and the final y-position of the flake is -0.62 Å.

FIG. 8: Simulated (a) frequency shift image and (b) energy dissipation image of the graphite edge.

FIG. 9: (a) the vertical force and (b) the vertical position of the flake by the function of the tip height.

This model is different from the one in the previous subsection in the sense that the hysteresis is generated by the vertical motion of the flake, and not by the lateral motion of the flake. We predict that the hysteresis generated by the vertical motion of the sample is more likely to happen in the condition that the sample is smaller and the binding energy to the substrate is smaller or in the condition that the attractive force between the tip and the sample is strong. We can check this by the simulation in which we reduce the attractive force by using the original tip structure shown in Fig. 4(b). In this simulation, we could not see any energy dissipation. If the attractive force is by chemical interaction as in the experiment of atom manipulation [13–15], energy dissipation explained in this model is easy to be observed.

The energy dissipation is larger at the positions near to the edge than the inner positions, though we cannot say it for a scale as small as the width of the scan area.
used in this report (Figs. 3 and 8). This was confirmed by the fact that the energy dissipation becomes smaller when we change the position of the scan area toward the fixed atoms by the distance which is larger than the width of the scan area. This is observed experimentally. In the paper by Hembacher et al. [16], they show the experimental energy dissipation image of a graphite edge. It is larger at the area nearer to the edge than the inner area.

From above result, we can generally say that the energy dissipation is larger when the range of the motion of the sample is larger. This is consistent with the result of the simulation in the previous subsection. When the slipping motion of the flake is larger, the energy dissipation is larger. This is because the difference of potential energy at an initial and a final position is generally larger when the motion is larger.

IV. SUMMARY

We investigated the energy dissipation of NC-AFM generated by the hysteretic potential energy between a tip and a sample with respect to the tip height using the two models of graphite flake. The hysteresis of the first model is caused by the lateral motion of the graphite flake. The shift of the lateral position of the flake is seen when the tip is approaching to the flake. Some potential energy between the tip and the flake which is transformed from the energy of the tip during the downward motion of the tip dissipates to the surroundings when the flake slips into a lower potential minimum. The hysteresis of the second model is caused by the vertical motion of the graphite flake edge. The flake moves up with the tip and the potential energy increases. When the flake is detached from the tip and returns to the initial height, some potential energy dissipates to the surroundings. Of course these two models are just examples of the energy dissipation mechanism generated by the hysteretic potential energy. There must be more types of motion which generate energy dissipation by hysteresis loop in real systems [16]. But the basic concept of the dissipation must be similar to the two models.

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