

## Artifacts related to tip asymmetry in high-resolution atomic force microscopy and scanning tunneling microscopy measurements of graphitic surfaces

Berkin Uluutku and Mehmet Z. Baykara

Citation: *Journal of Vacuum Science & Technology B* **33**, 031802 (2015); doi: 10.1116/1.4915898

View online: <http://dx.doi.org/10.1116/1.4915898>

View Table of Contents: <http://scitation.aip.org/content/avs/journal/jvstb/33/3?ver=pdfcov>

Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

---

### Articles you may be interested in

[Different tips for high-resolution atomic force microscopy and scanning tunneling microscopy of single molecules](#)  
*Appl. Phys. Lett.* **102**, 073109 (2013); 10.1063/1.4793200

[High-percentage success method for preparing and pre-evaluating tungsten tips for atomic-resolution scanning tunneling microscopy](#)

*J. Vac. Sci. Technol. B* **30**, 033201 (2012); 10.1116/1.3701977

[Combined dynamic scanning tunneling microscopy and frequency modulation atomic force microscopy investigations on polythiophene chains on graphite with a tuning fork sensor](#)

*J. Appl. Phys.* **109**, 074320 (2011); 10.1063/1.3556437

[Application of the KolibriSensor® to combined atomic-resolution scanning tunneling microscopy and noncontact atomic-force microscopy imaging](#)

*J. Vac. Sci. Technol. B* **28**, C4E12 (2010); 10.1116/1.3430544

[Combined low-temperature scanning tunneling/atomic force microscope for atomic resolution imaging and site-specific force spectroscopy](#)

*Rev. Sci. Instrum.* **79**, 033704 (2008); 10.1063/1.2842631

---



**WE'RE SEARCHING FOR**  
**SKILLED ANTENNA, RF SYSTEMS AND MICROWAVE DESIGN ENGINEERS.**  
HELP US ENGINEER A BETTER TOMORROW. [LEARN MORE](#)

**LOCKHEED MARTIN**

# Artifacts related to tip asymmetry in high-resolution atomic force microscopy and scanning tunneling microscopy measurements of graphitic surfaces

Berkin Uluutku

Department of Mechanical Engineering, Bilkent University, Ankara 06800, Turkey

Mehmet Z. Baykara<sup>a)</sup>

Department of Mechanical Engineering and UNAM–Institute of Materials Science and Nanotechnology, Bilkent University, Ankara 06800, Turkey

(Received 29 December 2014; accepted 9 March 2015; published 20 March 2015)

The effect of tip asymmetry on atomic-resolution scanning tunneling microscopy and atomic force microscopy measurements of graphitic surfaces has been investigated via numerical simulations. Employing a three-dimensional, crystalline, metallic tip apex and a two-layer thick graphene sample as a model system, basic calculations of the tip–sample interaction have revealed a significant effect of tip asymmetry on obtained results, including artificial modulation of site-specific chemical interaction forces and spatial distortion of observed features. Related artifacts are shown to be enhanced for tips with low lateral stiffness values. Our results emphasize that potentially erroneous interpretations of atomic-scale surface properties via imaging and spectroscopy measurements can be caused or enhanced by tip asymmetry. © 2015 American Vacuum Society.

[<http://dx.doi.org/10.1116/1.4915898>]

## I. INTRODUCTION

The emergence of graphene—a *two-dimensional* material consisting of a single or few sheets of carbon (C) atoms arranged in a honeycomb lattice—in the last decade with its combination of outstanding electrical and mechanical properties has resulted in a renewed interest in graphitic materials, including highly oriented pyrolytic graphite (HOPG) as well as carbon nanotubes. Consequently, a significant amount of effort has been directed toward uncovering the physical properties of graphene as well as realizing potential applications in a number of fields.<sup>1,2</sup> While techniques such as Raman spectroscopy<sup>3</sup> and photoemission spectroscopy<sup>4</sup> provide useful information about the structure and electronic properties of this interesting material, successful implementation in functional applications requires a detailed and complete understanding of atomic-scale properties not delivered by the spectroscopic techniques mentioned above due to limitations on spatial resolution. On the other hand, atomic-resolution scanning probe microscopy (SPM) constitutes a powerful experimental tool with which structural, mechanical, physical, and chemical properties of surfaces can be investigated with true atomic resolution. Consequently, two members of the scanning probe microscopy family with atomic-resolution imaging and spectroscopy capabilities—scanning tunneling microscopy (STM) and atomic force microscopy operated in the *noncontact* mode (NC-AFM)—have been employed in recent years to study graphene samples obtained via various methods including mechanical exfoliation and epitaxial growth, as well as other graphitic materials.<sup>5–18</sup>

While scanning tunneling microscopy and atomic force microscopy have been proven to be indispensable in atomic-

scale imaging and spectroscopy of a large class of materials since their invention almost three decades ago, a major drawback associated with the methods is the ubiquitous effect of atomic-scale structural and chemical properties of the tip apex (such as tip asymmetry, elasticity, or elemental composition) on obtained experimental results.<sup>19–22</sup> In fact, data collected by various research groups on the same sample system often seem to be incompatible due to tip-related effects and repeatability of the experiments suffers as a consequence. Moreover, data sets featuring unexpected properties not immediately compatible with the sample structure are often discarded and more importantly, experimental results heavily affected by tip effects may form the basis for erroneous physical interpretation of surface properties.

Despite the fact that the precise characterization of the atomic-scale structure and chemistry of tip apices remains extremely challenging, several research groups around the world have now achieved notable success in tip property standardization via the controlled adsorption of single molecules such as CO on the apex prior to imaging and spectroscopy experiments.<sup>15,23</sup> However, the application of the method usually requires highly specialized microscopy equipment operated at low temperatures and ultrahigh vacuum conditions as well as involved recipes for tip preparation. As such, most atomic-resolution STM and NC-AFM experiments are still performed with insufficiently characterized tip apices.

A major source of imaging and spectroscopy artifacts in STM and NC-AFM experiments as well as the resulting inconsistencies between data sets is *tip asymmetry*.<sup>20,24</sup> Most tip apices used in STM and NC-AFM experiments—whether they are obtained by electrochemical etching of thin metallic wires or are in the form of micromachined cantilevers—feature a certain degree of atomic-scale asymmetry at the

<sup>a)</sup>Electronic mail: mehmet.baykara@bilkent.edu.tr

very apex with respect to the surface, leading to notable changes in obtained imaging contrast and/or force/tunneling current spectroscopy data.<sup>20,24</sup> Within that context, high-resolution measurements of vertical and lateral forces on the surface of graphite have previously revealed a significant effect of tip asymmetry on NC-AFM measurements, confirming that experimental results truly represent a convolution of surface properties and those of the probe.<sup>16</sup>

Based on the discussion above, we have analyzed in this contribution the effect of tip asymmetry on high-resolution STM and NC-AFM measurements via numerical simulations. A two-layer graphene sample has been chosen as the model surface due to: (1) The scientific and technological relevance of the material and the associated recent increase in atomic-scale SPM measurements and (2) The fact that the existence of the second layer allows us to make comparisons with previously obtained results on HOPG. While effects associated with tip-induced elastic deformations of the surface and the specific electronic structure at the tip apex have also been shown to lead to various unusual features observed in high-resolution STM and AFM experiments reported in the literature,<sup>25,26</sup> our results reveal that tip asymmetry *by itself* has a measurable effect on imaging and spectroscopy data obtained via NC-AFM and STM on graphitic materials, which might potentially result in erroneous evaluation of surface properties.

## II. MODELING

In order to investigate the effect of tip asymmetry on high-resolution STM and NC-AFM measurements performed on graphitic sample surfaces, numerical simulations of Lennard–Jones interactions, as well as the STM contrast for a model tip and sample surface have been performed [Fig. 1(a)]. A three-dimensional model of a metallic tip apex consisting of ten platinum (Pt) atoms arranged in a triple-layer, close-packed configuration has been employed in the simulations [Fig. 1(b)]. Based on the fact that high-resolution NC-AFM/STM experiments are frequently performed using tuning fork based sensors<sup>27</sup> employing electrochemically etched Pt/Ir tips, the choice of Pt as the model tip material is reasonable and also consistent with previous simulation work.<sup>20,21</sup> To evaluate the effect of substantial tip asymmetry on NC-AFM/STM imaging and spectroscopy, the model tip apex is rotated by an angle of  $56^\circ$  around the front-most atom, in line with previous efforts [Fig. 1(c)].<sup>20</sup> While effects related to tip asymmetry discussed in Sec. III are valid for tips featuring lower degrees of asymmetry, the results are demonstrated for the present tip apex model to better emphasize the associated artifacts. For reasons outlined in Sec. I of this contribution, the sample system used in the numerical simulations comprises two layers of graphene, consisting of  $50 \times 50$  unit cells each. Every other C atom in the top layer has a direct neighbor underneath and thus one can distinguish between A-type (those with a neighboring C atom in the bottom layer) and B-type (those without a neighboring C atom in the bottom layer) atoms in the top layer. The two-layer graphene sample is taken to be *suspended* in

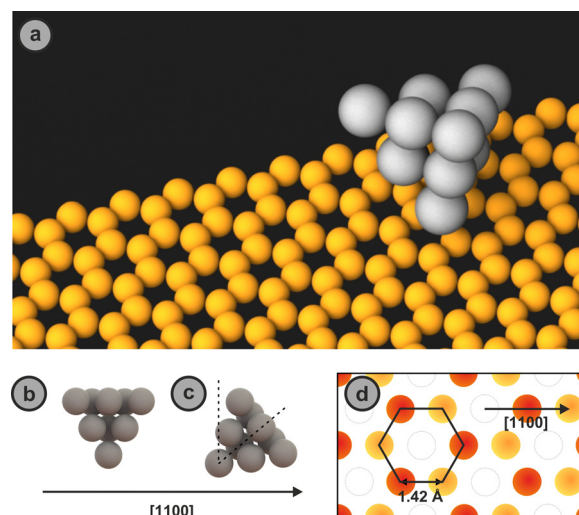


FIG. 1. (Color online) (a) Representative illustration describing the model tip–sample system used for the numerical simulations of AFM and STM imaging. The model tip apex consisting of ten close-packed Pt atoms is raster-scanned in a three-dimensional mesh over the sample surface comprising C atoms arranged in a honeycomb lattice. Please note that the second layer of C atoms has not been shown for clarity. (b) Symmetric tip apex configuration. The [1100] direction of the surface [detailed in part (d)] is drawn as a guide to the eye. (c) Asymmetric tip configuration obtained by a  $56^\circ$  rotation around the front-most atom. (d) Schematic drawing of the sample surface region used for the results presented in Figs. 2 and 4. A-type carbon atoms are drawn bright and B-type carbon atoms dark, while the dotted circles represent the positions of the bottom layer carbon atoms. The [1100] crystallographic direction as well as a honeycomb unit cell are depicted.

the simulations, in order to eliminate potential effects of an underlying substrate on the tip–sample interaction and thus study the influence of tip asymmetry in an isolated fashion.

The total interaction force acting between the tip and the sample surface at each point of a three-dimensional mesh with 3 pm resolution above the sample surface is calculated by summing up the individual interaction forces acting between each tip and surface atom utilizing the well-known 12–6 Lennard–Jones model and appropriate parameters for Pt and C atoms.<sup>28</sup> On the other hand, in accordance with literature,<sup>5,29,30</sup> STM images are calculated based on the tunneling currents acting between the individual atoms of the tip apex and the sample surface, which are directly related to the local density of states at the Fermi level ( $\rho_{\text{Fermi}}$ ) at respective tip–sample distances. It should be mentioned that the  $\rho_{\text{Fermi}}$  employed in our simulations have been calculated according to Ref. 30, as it has previously been done to compare experimental STM results to theoretical expectations on HOPG.<sup>5</sup> Calculated STM images for graphite for the investigated height regime result in triangular patterns, reflecting the concentration of charge density at every other C atom (B-type).<sup>5,30</sup> It should be noted that the simulated STM images in this contribution simply represent the spatial evolution of  $\rho_{\text{Fermi}}$  as the tip is scanned over the surface (rather than representing actual tunneling current values) and are thus utilized only for qualitative comparison purposes to investigate the effect of tip asymmetry and elasticity on STM contrast patterns.

To estimate the effect of elastic relaxations of the tip apex on calculated AFM and STM images, the lateral force acting

on the apex at each ( $x$ ,  $y$ , and  $z$ ) location is computed and the associated lateral deflection of the apex based on lateral stiffness  $k$  is determined, in accordance with previous work.<sup>21</sup>

Despite the fact that the model calculations performed here involve certain simplifications of the actual physical mechanisms responsible for tip-sample interactions (such as the assumption of a basic Lennard-Jones type interaction between Pt and C atoms as well as neglecting tip-induced changes on the charge density distribution of the surface<sup>31</sup>), the obtained results do provide valuable insight into the potential effect of tip asymmetry on experimental measurements reported in the literature, as detailed in Sec. III. While more detailed numerical simulations based on, e.g., *density functional theory* (DFT) are successfully used to simulate NC-AFM and STM operation,<sup>19,25,26,32,33</sup> the basic advantages of the analytical simulation method utilized here and in previous work are the ability to work with a larger number of atoms and more rapid calculations.<sup>20,21</sup> Moreover, a comparison of simulated interaction forces for the carbon atoms and hollow sites on the sample surface with experimental results obtained via Pt-terminated tip apices<sup>13,34</sup> reveals that the calculated and experimentally measured atomic-scale force contrasts agree very well ( $\sim 40$  and  $\sim 80$  pN, respectively) for the immediate distance regime before the point of maximum force interaction is reached. Additionally, let us indicate that calculations for larger tip clusters are not expected to change our main conclusions regarding the effect of tip asymmetry and elasticity on AFM/STM imaging on graphitic surfaces, since it is well-known in the SPM

community that the atomic-scale contrast obtained in experiments is due to the atomic structure/chemistry of the last few atomic layers of a given tip apex.<sup>24</sup> On the other hand, a larger tip cluster would lead to an increase in the absolute values of total interaction forces, especially if long-range effects such as van der Waals interactions were included in the calculations.

Finally, despite the fact that a *cross-over* between the force-distance curves on carbon atoms and hollow sites has been previously calculated for metallic (W) tips via a DFT-based approach (which corresponds to a sign change in the difference of the chemical interaction magnitudes measured on the two sites during force-distance spectroscopy),<sup>33</sup> several experimental results<sup>13,34</sup> do *not* feature such a cross-over, but rather a *smooth* separation between the force interactions for carbon atoms and hollow sites with decreasing tip-sample distance, with hollow sites monotonously representing a more attractive behavior than C atoms, as predicted by our simulations.

### III. RESULTS AND DISCUSSION

A straightforward method for evaluating the effect of tip asymmetry on NC-AFM and STM imaging involves the comparison of constant height images of interaction force and charge density calculated via the methods discussed in Sec. II on a certain region of the sample surface [Fig. 1(d)] using symmetric [Fig. 1(b)] and asymmetric [Fig. 1(c)] tip configurations. As one can see in Fig. 2, tip asymmetry has a significant effect on simulated images, resulting in contrasts

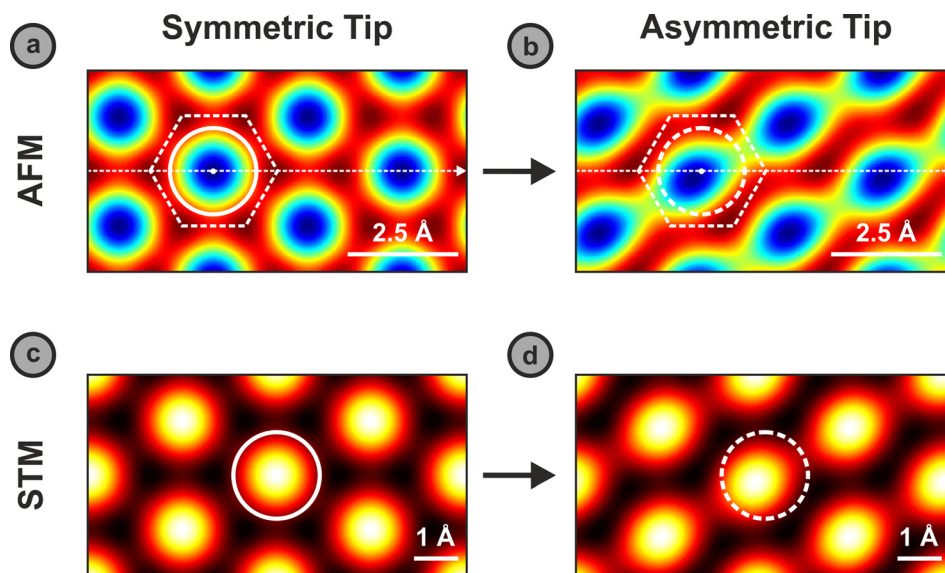


Fig. 2. (Color online) (a) Constant height ( $z = 3 \text{ \AA}$ ) image of interaction forces calculated for a symmetric tip apex on the surface region depicted in Fig. 1(d). The location of the dashed hexagon directly corresponds to the position of the hexagon depicted in Fig. 1(d) for both parts. The color-scale reflects the corrugation of interaction force at that height ( $\sim 0.25$  nN), with sites of maximum attraction located on the hollow sites of the lattice. (b) Calculated image of interaction forces for an asymmetric tip apex on the same surface region. Note the spatial distortion affecting all lattice sites, as well as the lateral shift associated with the carbon atoms and the hollow sites [where the actual position of a representative hollow site is indicated by the straight and dashed circles in parts (a) and (b), respectively]. Further, interaction forces exhibited by the two carbon atoms now differ, breaking the honeycomb symmetry observed in part (a) in favor of triangular symmetry. (c) Constant height ( $z = 3 \text{ \AA}$ ) STM image for a symmetric tip apex on the same surface region. B-type C atoms are imaged as round and isolated maxima, as highlighted by the circle. (d) Simulated STM image for an asymmetric tip apex. The maxima corresponding to B-type carbon atoms are now imaged as elongated and are connected by faint bridges of tunneling current, in accordance with published experimental results (Ref. 5). The associated lateral shift in position is indicated by the straight and dashed circles in parts (c) and (d), respectively.

that differ substantially for the two tip configurations. Evaluating first the simulated AFM image for the symmetric tip ( $z = 3 \text{ \AA}$ ), the following observations are made: As expected from previous work, simulations indicate that the model tip exhibits the most attractive interaction with the hollow site of the honeycomb lattice ( $\sim 0.75 \text{ nN}$ ), due to the close separation of the C atoms ( $\sim 142 \text{ pm}$ ) on the surface [Fig. 2(a)].<sup>7,13</sup> Moreover, the two C atoms are indistinguishable from each other in terms of interaction forces, despite the fact that high-resolution NC-AFM measurements have been able to detect a slight difference in chemical interaction forces associated with the two types of carbon atoms in a few experiments performed on HOPG in the past, while uneven interaction forces exhibited by the C atoms of a graphene sample epitaxially grown on Ir(111) were attributed to substrate effects.<sup>5,13,18</sup>

Switching over to the simulated AFM image for the asymmetric tip apex, a significant change in contrast becomes apparent involving the following aspects [Fig. 2(b)]:

- (1) The honeycomb symmetry associated with the C atoms on the surface is broken in favor of a triangular arrangement, with the two C atoms now exhibiting detectable differences ( $\sim 50 \text{ pN}$ ) in terms of interaction forces.
- (2) The location of the observed force maxima shift laterally by about  $25 \text{ pm}$  when compared to the actual locations of the hollow sites on the underlying lattice of the sample surface.
- (3) Despite the fact that the hollow sites appeared completely round and isolated from each other in AFM images simulated for the symmetric tip, they now appear to be *elongated* and *connected* via bridges of attractive interaction regions along a preferred crystallographic direction on the surface [Fig. 2(b)].

Before switching to a discussion of the observed contrast changes in the simulated force images and published experimental results, constant height STM images based on site-specific  $\rho_{\text{Fermi}}$  calculations simulated for the two types of tip apices should be discussed [Figs. 2(c) and 2(d)]. As expected from previous theoretical and experimental work conducted on HOPG as well as few-layer graphene,<sup>5,9,30,35</sup> the STM data highlight every other C atom of the sample surface, based on the uneven distribution of charge density indicated earlier [Fig. 2(c)]. Following the same procedure for simulated AFM images, the following changes in image contrast are observed based on the utilization of asymmetric tip apices [Fig. 2(d)]:

- (1) Similar to the observation made for the AFM images, the simulated appearance of the C atoms observed in STM images changes from round and isolated to *elongated* and *connected* along the same crystallographic direction as for the AFM image.
- (2) Additionally, the location of the observed current maxima shift laterally by about  $25 \text{ pm}$  when compared to the STM image simulated for the symmetric tip, thus resulting in a slight shifting of the observed STM contrast with respect to the underlying lattice of the sample surface.

A major advantage of NC-AFM when compared to other members of the SPM family is its capability to perform site-specific measurements of chemical interaction forces and energies as a function of the three spatial dimensions above the sample surface, in addition to atomic-resolution imaging.<sup>13,32,34,36</sup> As such, the effect of tip asymmetry on site-specific force spectroscopy has been estimated in our simulations via the calculation of two-dimensional, vertical slices ( $x, z$ ) of interaction forces along the  $[1100]$  crystallographic direction on the sample surface [shown with the dashed arrows in Figs. 2(a) and 2(b)] that includes both types of C atoms, as well as the hollow site (Fig. 3). As already discussed, the symmetric tip apex interacts most attractively with the hollow sites on the surface ( $\sim 0.75 \text{ nN}$ ), while interactions measured on both types of C atoms are virtually equal ( $\sim 0.50 \text{ nN}$ ) [Fig. 3(a)]. When the same interaction force *slice* is simulated for the asymmetric tip apex, it is clearly observed that the two C atoms now exhibit differences in interaction force, breaking the expected symmetry of force interactions for this sample surface, leading to potential complications in data interpretation in actual experiments aimed at recovering site-specific chemical interactions [Fig. 3(b)].

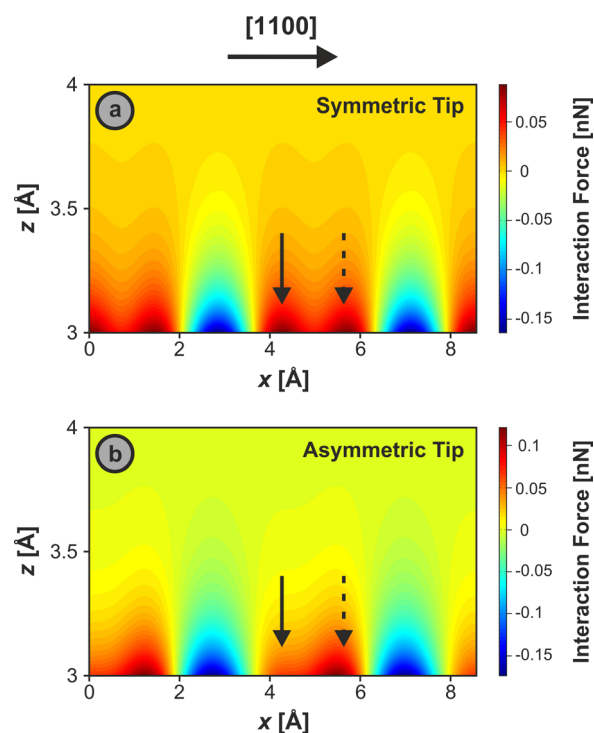


Fig. 3. (Color online) (a) Vertical slice of interaction forces calculated along the  $[1100]$  direction indicated by the dashed arrow in Fig. 2(a) for a symmetric tip apex. The average force for each height has been subtracted for improved contrast. As such, the color-scale reflects the *corrugation* of interaction forces (negative numbers mean more attractive forces). The straight arrow indicates the position of a B-type carbon atom, whereas the dashed arrow indicates the position of an A-type carbon atom next to it. (b) The same force slice calculated for an asymmetric tip apex. As indicated by the straight and dashed arrows, the two types of carbon atoms now exhibit  $\sim 50 \text{ pN}$  difference in interaction force, potentially complicating interpretation of high-resolution force spectroscopy experiments due to convolution of tip and surface properties.

It has been recently shown that in addition to structural asymmetry in the tip apex, the lateral stiffness of individual probe tips used in high-resolution SPM imaging and spectroscopy experiments influence obtained results by distorting the structural symmetry of observed features on the atomic scale.<sup>21</sup> In order to evaluate the combined effect of asymmetry and elasticity, we have performed representative calculations of STM imaging using a relatively *soft* asymmetric tip apex [Fig. 1(c)] with a lateral stiffness of  $k = 5$  N/m. As it can be clearly inferred from the comparison presented in Fig. 4, observed maxima in tunneling current images for our model sample (corresponding to B-type C atoms) are further distorted due to elastic relaxations of the tip apex toward hollow sites during imaging caused by lateral interaction forces, resulting in an *elongated* and *triangular* appearance [Fig. 4(b)], helping to explain the variety of shapes reported in the literature for maxima observed in STM imaging of graphitic materials (e.g., elongated and elliptical<sup>5,6,10</sup> as well as semitriangular<sup>9</sup>).

The results of AFM and STM imaging simulations described above clearly indicate that structural asymmetries associated with the tip apex likely lead to detectable artifacts in actual experiments, potentially resulting in erroneous and/or exaggerated interpretation of atomic-scale surface properties. In particular, the simulation results indicated here imply that apparent differences in chemical interaction forces for different lattice sites may be induced or enhanced by tip asymmetry, a fact that needs to be carefully taken into account

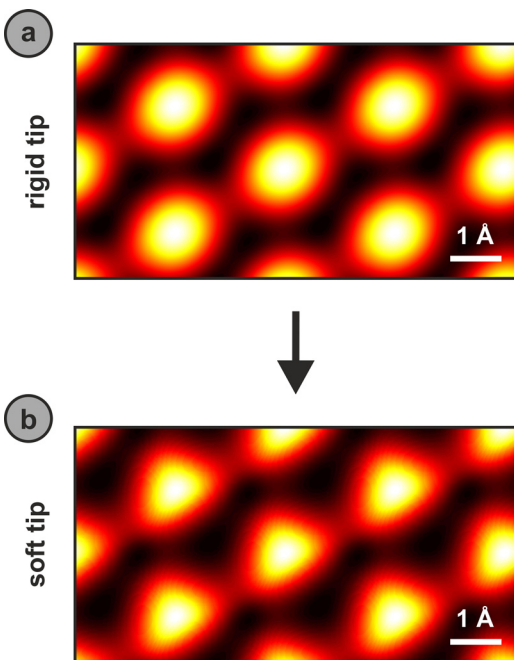


FIG. 4. (Color online) Constant height ( $z = 3$  Å) STM images calculated for the asymmetric tip apex in Fig. 1(c). (a) Simulated STM image for an ideally rigid tip where the lateral stiffness  $k$  is taken to be infinite. (b) Simulated STM image for a soft tip with lateral stiffness  $k = 5$  N/m. Note that the shape of observed maxima in the calculated images has changed considerably (more *triangular* than *elliptical*) due to the lateral relaxation of the tip apex toward the hollow sites of the sample lattice, reproducing some features associated with published experimental images of few-layer graphene samples (Ref. 9).

when performing high-resolution NC-AFM experiments on sample surfaces.<sup>5,13,34</sup> Moreover, the results presented here suggest a certain degree of misalignment of observed features in atomic-resolution SPM experiments compared to the underlying lattice of the graphitic sample surface, as previously predicted for ionic crystal and metallic surfaces.<sup>20</sup>

Most importantly, the observed elongations and other distortions of the experimental atom images in previously published high-resolution NC-AFM and STM imaging experiments on graphitic materials<sup>5,6,9,10,16</sup> are correctly predicted by our images, pointing to the possibility of the utilization of asymmetric and potentially soft tip apices in the mentioned experiments. Consequently, while effects such as those attributed to the specific orbital structure of an assumed tip termination<sup>5</sup> may still be responsible for unusual features observed in NC-AFM and STM images, the possibility of a strongly asymmetric and/or soft tip apex should not be ignored before definite conclusions can be made regarding surface properties.

#### IV. SUMMARY AND CONCLUSIONS

In summary, we have presented numerical simulations aimed at evaluating the role of tip asymmetry in high-resolution NC-AFM/STM experiments performed on graphitic materials. Our results point toward several artifacts associated with the utilization of asymmetric tips in such experiments, including an artificial but detectable modulation of chemical interaction forces on individual lattice sites, as well as spatial distortions in the appearance of individual features in acquired images and inconsistencies in the alignment of observed features with the underlying lattice of the sample surface. Moreover, the additional effect of tip elasticity has been shown to enhance related artifacts. Overall, our calculations help to explain certain unexpected features of high-resolution STM and NC-AFM experiments reported in the literature. In particular, while DFT-based simulations have been successful in evaluating the contribution of effects associated with, e.g., the electronic structure of the tip apex<sup>26</sup> and elastic surface displacements<sup>25</sup> on SPM measurements on graphitic surfaces, our simulation results point toward separate artifacts associated with tip asymmetry as well as elasticity. Taking into account that a fundamental, atomic-scale understanding of surface properties is required for the successful implementation of emerging materials such as graphene in actual applications, our simulations underline that the role of the tip in high-resolution SPM experiments should be carefully evaluated in individual experiments before definitive conclusions are made about surface properties.

#### ACKNOWLEDGMENT

This work was financially supported by TÜBİTAK (The Scientific and Technological Research Council of Turkey) via the 2209/A program.

<sup>1</sup>A. K. Geim and K. S. Novoselov, *Nat. Mater.* **6**, 183 (2007).

<sup>2</sup>K. S. Novoselov, V. I. Fal'ko, L. Colombo, P. R. Gellert, M. G. Schwab, and K. Kim, *Nature* **490**, 192 (2012).

<sup>3</sup>A. C. Ferrari *et al.*, *Phys. Rev. Lett.* **97**, 187401 (2006).

- <sup>4</sup>A. Bostwick, T. Ohta, T. Seyller, K. Horn, and E. Rotenberg, *Nat. Phys.* **3**, 36 (2007).
- <sup>5</sup>S. Hembacher, F. J. Giessibl, J. Mannhart, and C. F. Quate, *Proc. Natl. Acad. Sci. U. S. A.* **100**, 12539 (2003).
- <sup>6</sup>S. Hembacher, F. J. Giessibl, J. Mannhart, and C. F. Quate, *Phys. Rev. Lett.* **94**, 056101 (2005).
- <sup>7</sup>M. Ashino, A. Schwarz, H. Holscher, U. D. Schwarz, and R. Wiesendanger, *Nanotechnology* **16**, S134 (2005).
- <sup>8</sup>M. Ishigami, J. H. Chen, W. G. Cullen, M. S. Fuhrer, and E. D. Williams, *Nano Lett.* **7**, 1643 (2007).
- <sup>9</sup>E. Stolyarova, K. T. Rim, S. M. Ryu, J. Maultzsch, P. Kim, L. E. Brus, T. F. Heinz, M. S. Hybertsen, and G. W. Flynn, *Proc. Natl. Acad. Sci. U. S. A.* **104**, 9209 (2007).
- <sup>10</sup>P. Lauffer, K. V. Emtsev, R. Graupner, T. Seyller, L. Ley, S. A. Reshanov, and H. B. Weber, *Phys. Rev. B* **77**, 155426 (2008).
- <sup>11</sup>A. T. N'Diaye, J. Coraux, T. N. Plasa, C. Busse, and T. Michely, *New J. Phys.* **10**, 043033 (2008).
- <sup>12</sup>M. Ashino, D. Obergfell, M. Haluska, S. H. Yang, A. N. Khlobystov, S. Roth, and R. Wiesendanger, *Nanotechnology* **20**, 264001 (2009).
- <sup>13</sup>B. J. Albers, T. C. Schwendemann, M. Z. Baykara, N. Pilet, M. Liebmann, E. I. Altman, and U. D. Schwarz, *Nat. Nanotechnol.* **4**, 307 (2009).
- <sup>14</sup>Z. X. Sun, S. K. Hamalainen, J. Sainio, J. Lahtinen, D. Vanmaekelbergh, and P. Liljeroth, *Phys. Rev. B* **83**, 081415 (2011).
- <sup>15</sup>M. P. Boneschanscher, J. van der Lit, Z. X. Sun, I. Swart, P. Liljeroth, and D. Vanmaekelbergh, *ACS Nano* **6**, 10216 (2012).
- <sup>16</sup>M. Z. Baykara, T. C. Schwendemann, B. J. Albers, N. Pilet, H. Monig, E. I. Altman, and U. D. Schwarz, *Nanotechnology* **23**, 405703 (2012).
- <sup>17</sup>S. K. Hamalainen, M. P. Boneschanscher, P. H. Jacobse, I. Swart, K. Pussi, W. Moritz, J. Lahtinen, P. Liljeroth, and J. Sainio, *Phys. Rev. B* **88**, 201406 (2013).
- <sup>18</sup>Y. Dedkov and E. Voloshina, *Phys. Chem. Chem. Phys.* **16**, 3894 (2014).
- <sup>19</sup>P. Pou, S. A. Ghasemi, P. Jelinek, T. Lenosky, S. Goedecker, and R. Perez, *Nanotechnology* **20**, 264015 (2009).
- <sup>20</sup>M. Z. Baykara, O. E. Dagdeviren, T. C. Schwendemann, H. Monig, E. I. Altman, and U. D. Schwarz, *Beilstein J. Nanotechnol.* **3**, 637 (2012).
- <sup>21</sup>B. Uluutku and M. Z. Baykara, *J. Vac. Sci. Technol. B* **31**, 041801 (2013).
- <sup>22</sup>L. P. Biro, G. I. Mark, and E. Balazs, in *Nanophase Materials, Nato Advanced Study Institute Series E*, edited by G. C. Hadjipanayis and R. W. Siegel (Kluwer, Dordrecht, 1994), Vol. 260, pp. 205–208.
- <sup>23</sup>L. Gross, F. Mohn, N. Moll, P. Liljeroth, and G. Meyer, *Science* **325**, 1110 (2009).
- <sup>24</sup>H. Mönig, M. Todorovic, M. Z. Baykara, T. C. Schwendemann, L. Rodrigo, E. I. Altman, R. Perez, and U. D. Schwarz, *ACS Nano* **7**, 10233 (2013).
- <sup>25</sup>H. S. Wong and C. Durkan, *Nanotechnology* **23**, 185703 (2012).
- <sup>26</sup>G. Teobaldi, E. Inami, J. Kanasaki, K. Tanimura, and A. L. Shluger, *Phys. Rev. B* **85**, 085433 (2012).
- <sup>27</sup>F. J. Giessibl, *Appl. Phys. Lett.* **76**, 1470 (2000).
- <sup>28</sup>S. Y. Liem and K. Y. Chan, *Surf. Sci.* **328**, 119 (1995).
- <sup>29</sup>J. Tersoff and D. R. Hamann, *Phys. Rev. Lett.* **50**, 1998 (1983).
- <sup>30</sup>H. A. Mizes, S. Park, and W. A. Harrison, *Phys. Rev. B* **36**, 4491 (1987).
- <sup>31</sup>I. P. Batra and S. Ciraci, *J. Vac. Sci. Technol. A* **6**, 313 (1988).
- <sup>32</sup>M. Z. Baykara, M. Todorovic, H. Mönig, T. C. Schwendemann, Ö. Ünverdi, L. Rodrigo, E. I. Altman, R. Perez, and U. D. Schwarz, *Phys. Rev. B* **87**, 155414 (2013).
- <sup>33</sup>M. Ondracek, P. Pou, V. Rozsival, C. Gonzalez, P. Jelinek, and R. Perez, *Phys. Rev. Lett.* **106**, 176101 (2011).
- <sup>34</sup>M. Z. Baykara, T. C. Schwendemann, E. I. Altman, and U. D. Schwarz, *Adv. Mater.* **22**, 2838 (2010).
- <sup>35</sup>I. P. Batra, N. Garcia, H. Rohrer, H. Salemkink, E. Stoll, and S. Ciraci, *Surf. Sci.* **181**, 126 (1987).
- <sup>36</sup>S. Fremy, S. Kawai, R. Pawlak, T. Glatzel, A. Baratoff, and E. Meyer, *Nanotechnology* **23**, 055401 (2012).