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Why is graphite so slippery? Gathering clues from three-dimensional lateral forces measurements

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Why is Graphite so Slippery?
Gathering Clues from 3D Lateral Force Microscopy

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The Structure of Graphite
Atomic Scale Movement of the Atoms at the Interface during FFM Experiments

Example: Silicon tip/graphite sample

$F_x$  Image size: 20 Å $\times$ 20 Å  $F_y$
Atomic Scale Movement of the Atoms at the Interface during FFM Experiments

Example: Silicon tip/graphite sample

$F_x$  
Image size: 20 Å × 20 Å
Atomic Scale Movement of the Atoms at the Interface during FFM Experiments

Example: Silicon tip/graphite sample

$F_x$  Image size: 20 Å $\times$ 20 Å
Atomic Scale Movement of the Atoms at the Interface during FFM Experiments

Example: Silicon tip/graphite sample

$F_x$ - Experiment

Image size: 15 Å × 15 Å

Path of the tip
Atomic Scale Movement of the Atoms at the Interface during FFM Experiments

Example: Silicon tip/graphite sample

Probability density

Image size: 15 Å × 15 Å

Path of the tip

Measurement of Lateral Forces with Picometer and Piconewton Resolution

How do we not jump over parts of the tip-sample interaction potential?

OUR APPROACH:

- Employ noncontact atomic force microscopy with atomic resolution
- Measure full 3D force field
Imaging of Individual Atoms with „Traditional“ AFM (Contact, Tapping)?
Imaging of Individual Atoms with „Traditional“ AFM (Contact, Tapping)?
Imaging of Individual Atoms with Atomically Sharp Tip in Noncontact Mode (Vacuum)

Attractive interaction, noncontact operation

=> *Atomic resolution possible!*
Principle of Noncontact Atomic Force Microscopy (NC-AFM) in Vacuum
Atomic Resolution Results:
HOPG(0001) Imaged with NC-AFM

$1.0 \times 1.0 \text{ nm}^2$, $\Delta f = -2.9 \text{ Hz}$, $f_0 = 29529 \text{ Hz}$, Amplitude = 0.25 nm
How do I get force information in NC-AFM?

Atomic resolution images reflect **PLANES OF CONSTANT $\Delta f$**!

Silicon tip on graphite surface

$F_{ad}$

$z_0$ $D$ [Å]

force [nN]

$-10$ $-5$ $0$ $5$ $10$ $15$

$-8$ $-4$ $0$ $4$ $8$

How do I get force information in NC-AFM?

Publications with either 2D or 3D force/energy maps:

- M. Heyde et al., APL 89, 263107 (2006)
- A. Schirmeisen et al., PRL 97, 136101 (2006)
- M. Abe et al., APL 90, 203103 (2007)
- M. Ternes et al., Science 319, 1066 (2008)
- M. Ashino et al., Nanotechnology 20, 264001 (2009) *(41 x 41)*
- L. Gross et al., Science 325, 1110 (2009) *(80 x 40)*
Low Temperature Ultrahigh Vacuum NC-AFM/STM for 3D-AFM Imaging

3D-AFM: Measuring Full \((x, y, z, F)\) Arrays on Graphite

Grid of 119 \times 256 force curves = 30464 force curves, \(T = 6\) K acquisition time 40 hours, average force for each height subtracted

“True” Force Imaging with Atomic Resolution on Graphite

Example: Force image recorded at constant height

\[ F_{av} = -2.306 \text{ nN}, \text{ force corrugation} \approx 70 \text{ pN}, \ T = 6 \text{ K} \]
3D-AFM: Plotting the Force for Every z Distance

Grid of $119 \times 256$ force curves = 30464 force curves, $T = 6$ K
acquisition time 40 hours, average force for each height subtracted
“True” Force Imaging with Atomic Resolution on Graphite

Height dependent forces on graphite

Height range covered: 180 pm
Total force range covered: -2.35 nN - -1.40 nN

Schwarz Group at Yale University
3D-AFM: Plotting the Force for $yz$ Planes
3D-AFM: Plotting the Force for $yz$ Planes

Vertical force on graphite [nN]
$x: 0$ pm

$z$ [pm]

$y$ [pm]

-0.03
-0.02
-0.01
0
0.01
0.02
0.03

Schwarz Group @ Yale
Characterization of Site-Specific Interactions

Interactions at A-, B-, and H-sites

\[ F_{av} = -2.306 \text{ nN}, \text{ force corrugation } \approx 70 \text{ pN}, z = 12 \text{ pm}, T = 6 \text{ K} \]
Characterization of Site-Specific Interactions

Interactions at A-, B-, and H-sites

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Characterization of Site-Specific Interactions

Interactions at A-, B-, and H-sites

- B atom
- A atom
- H site

A atom curve separates
H site curve separates

force [nN] vs. tip-sample distance [nm]
3D-AFM:
Measuring Full \((x, y, z, E)\) Arrays on Graphite

Grid of \(119 \times 256\) energy curves = 30464 energy curves, \(T = 6\) K
acquisition time 40 hours, average energy for each height subtracted

B. J. Albers et al.,
Interaction Energy Imaging with Atomic Resolution on Graphite

Example: Energy image recorded at constant height

$E_{av} = -5.47 \text{ eV}$, energy corrugation $\approx 38 \text{ meV}$, $z = 12 \text{ pm}$, $T = 6 \text{ K}$

Darker colors mean lower (i.e., higher negative) potential energies
Potential Energy Well on a Hollow Site
Measured with 3D-AFM at 6 K in UHV
Potential Energy Well with Lateral Forces
Measured with 3D-AFM at 6 K in UHV
Lateral Force Image of Graphite

Lateral force corrugation $\approx 100$ pN, $T = 6$ K

3D-AFM: Lateral Force Mapping
Local Lateral Forces on Graphite
Measured with 3D-AFM at 6 K in UHV
Local Lateral Forces on Graphite
Measured with 3D-AFM at 6 K in UHV
3D-AFM: Lateral Force Contour Along [1100]

![3D-AFM Contour Plot](image)

- **Fl [nN]**
- **x [pm]**
- **z [pm]**
- **B atom**
- **H site**
- **A atom**
- **B atom**
- **H site**
- **A atom**

**F_l [nN]**

- Color scale from 0 to 0.1
3D-AFM: Lateral Force Mapping

Lateral Force Image of Graphite

Lateral force corrugation $\approx 100$ pN, $T = 6$ K
Lateral Forces for Constant Load: Paths of Least Resistance

Lateral Force Image of Graphite for constant normal force \( \sim 2.31 \text{ nN} \)

Lateral force corrugation \( \approx 100 \text{ pN}, \ T = 6 \text{ K} \)
Transitioning to “Attractive Static Friction”: $F_{\text{friction}}$ vs $F_{\text{load}}$ along Paths of Least Resistance

Maximum Lateral Force vs. Load Curves along path (I)

Curve averaged over all paths (I) of inset map

Curve along path (I) as given in inset map
Transitioning to “Attractive Static Friction”: $F_{\text{friction}}$ vs $F_{\text{load}}$ along Paths of Least Resistance

Maximum Lateral Force vs. Load Curves along path (I)

Curve averaged over all paths (I) of inset map

Curve averaged over all paths given in inset map
Transitioning to “Attractive Static Friction”: \( F_{\text{friction}} \) vs \( F_{\text{load}} \) along Paths of Least Resistance

Maximum Lateral Force vs. Load Curves along path (I)

Curves acquired at the arbitrary points (i), (ii), and (iii) of inset map

Curve averaged over all paths given in inset map
3D-AFM:
Plotting the Dissipation for Every z Distance

Grid of 119 x 256 force curves = 30464 force curves, $T = 6 \text{ K}$

total height covered = 180 pm, average force for each height subtracted
Height-Dependent Image Contrast in Dissipation Signal

$z = 12 \text{ pm}$
$E_{\text{diss}} = 272 \, \mu\text{eV/cycle}$
$E_{\text{corr}} = 43 \, \mu\text{eV/cycle}$

$z = 97 \text{ pm}$
$E_{\text{diss}} = 98 \, \mu\text{eV/cycle}$
$E_{\text{corr}} = 26 \, \mu\text{eV/cycle}$
Characterization of Site-Specific Interactions

Interactions at A-, B-, and H-sites

Distance along [\overline{1}00] direction

Tip-sample distance [pm]

B atom A atom H site B atom A atom
Different Interaction Mechanisms in Dissipation and Force Signals?

Top row: Force images; bottom row: dissipation images
Left column: Height $z = 12$ pm, Right column: $z = 97$ pm
Conclusions

3D-AFM:
An ideal tool for the high-resolution investigation of local lateral forces!
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