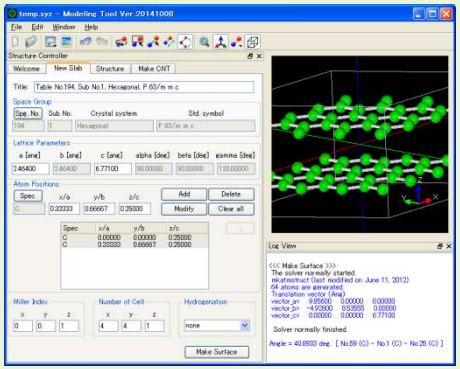
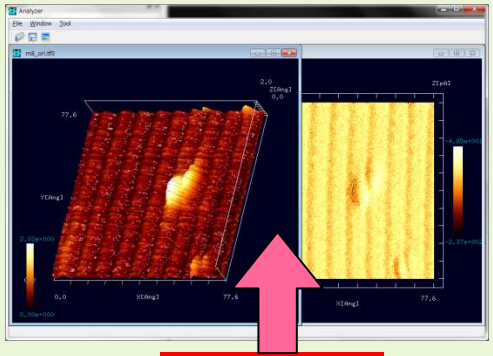
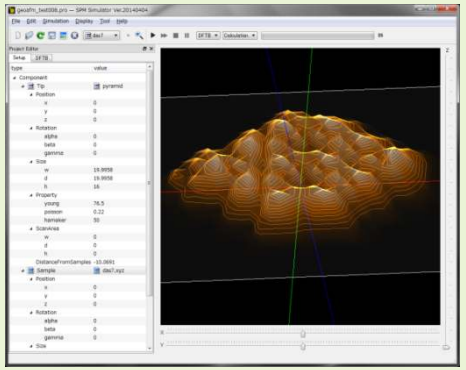
SPM Case Examples of Calculation



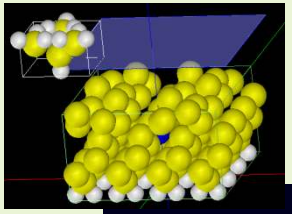


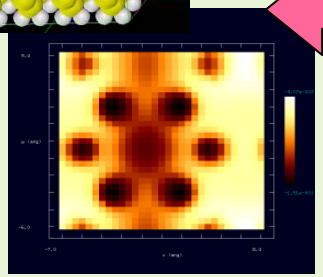


Analyzer
The Experimental Image Data Processor

SetModel
Atomic Structure Modeling Tool

GeoAFM
Geometrical Mutual AFM Simulator

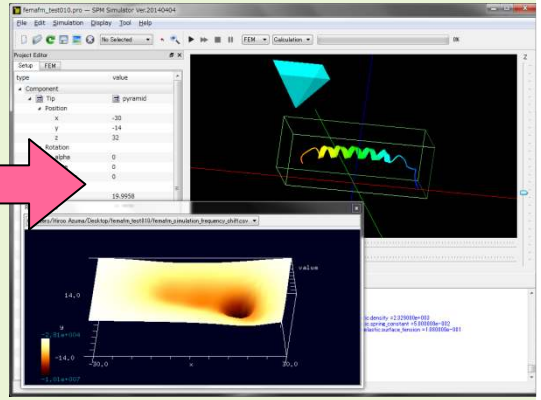




DFTB
Quantum Mechanical SPM Simulator

SPM Simulator

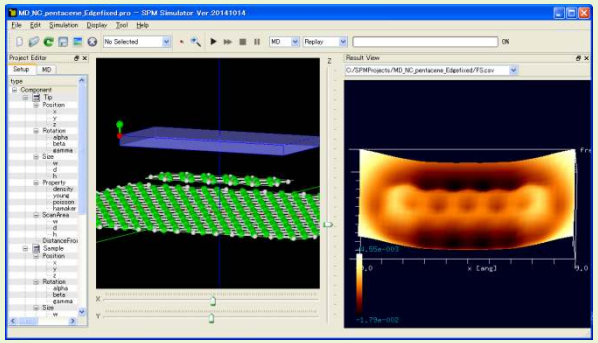
FemAFM
Finite element method AFM simulator

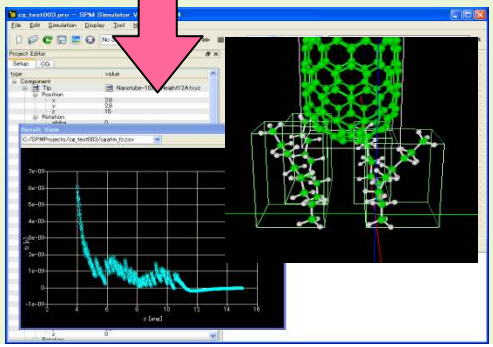


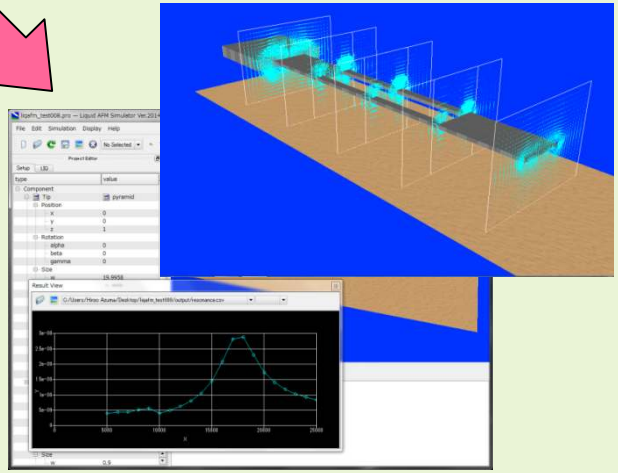
MD
Molecular Dynamics AFM Image Simulator

CG
Geometry Optimizing AFM Image Simulator

LiqAFM
Soft Material Liquid AFM Simulator



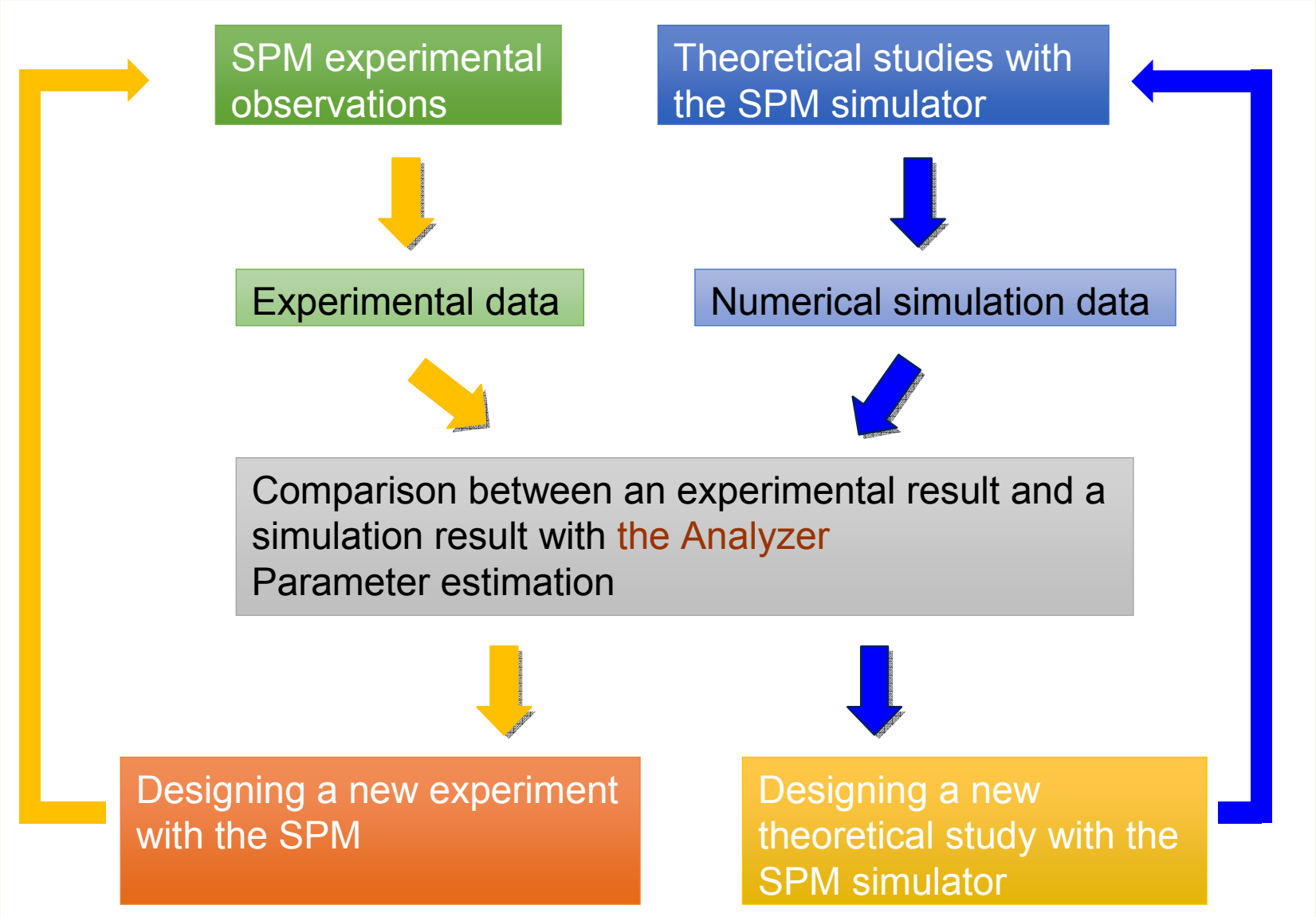




Comparison and Verification Function between the Experimental Image and the Simulated Image

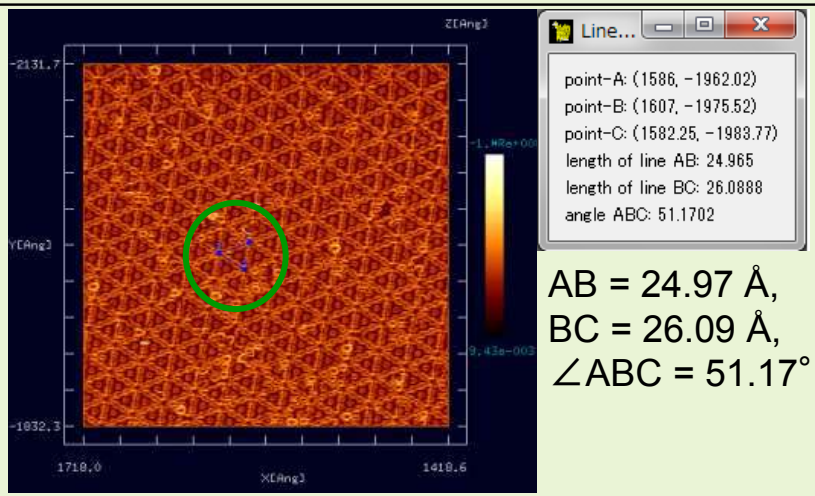
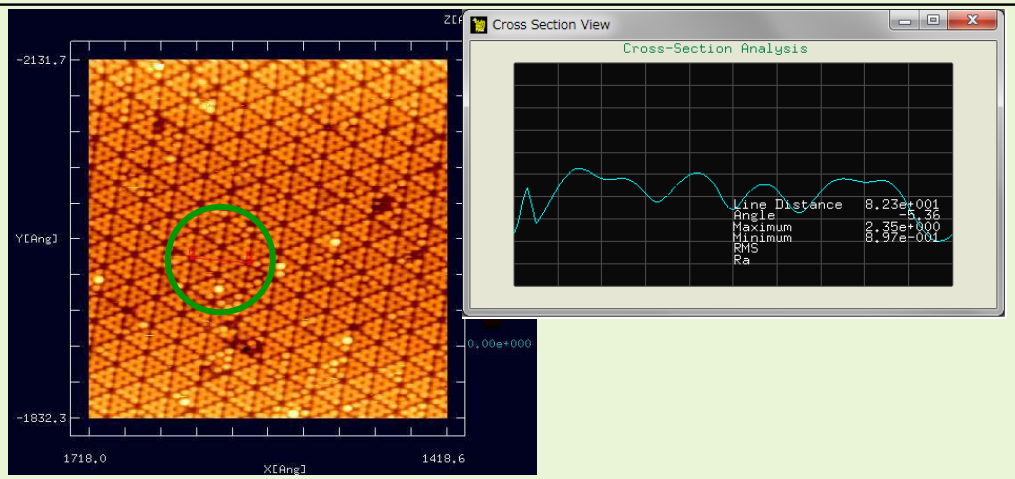
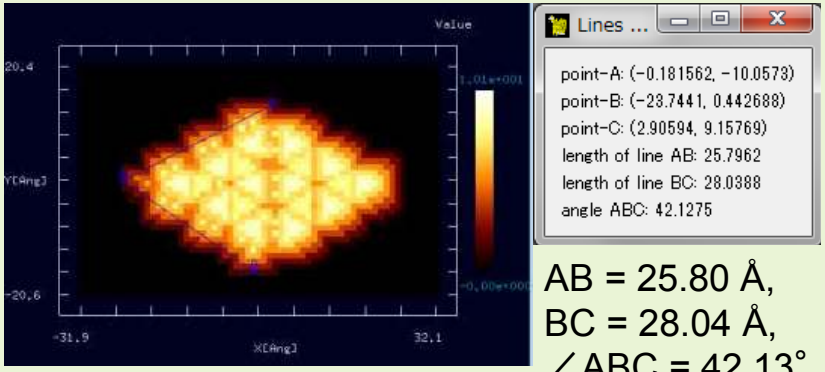
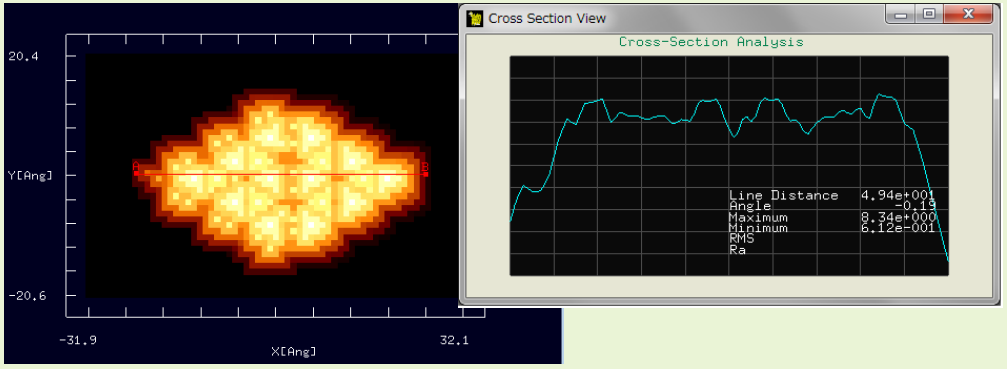
Analyzer

It handles the SPM experimental data and the simulated image data uniformly.



Example of the Comparison Between an AFM Experiment and a Simulation of Si(111)-(7x7) DAS

Analyzer

	Comparison and measurement of the length and the angle of the lattice	Comparison of the cross sections of the SPM images
Experimental image	 AB = 24.97 Å, BC = 26.09 Å, ∠ABC = 51.17°	 (The original image is provided by Professor Hiroyuki Hirayama, Nano-Quantum Physics at Surfaces and Interfaces, Department of Materials and Engineering, Tokyo Institute of Technology.)
Simulation result obtained with the GeoAFM	 AB = 25.80 Å, BC = 28.04 Å, ∠ABC = 42.13° (loaded the simulation result obtained with the GeoAFM)	 (loaded the simulation result obtained with the GeoAFM)

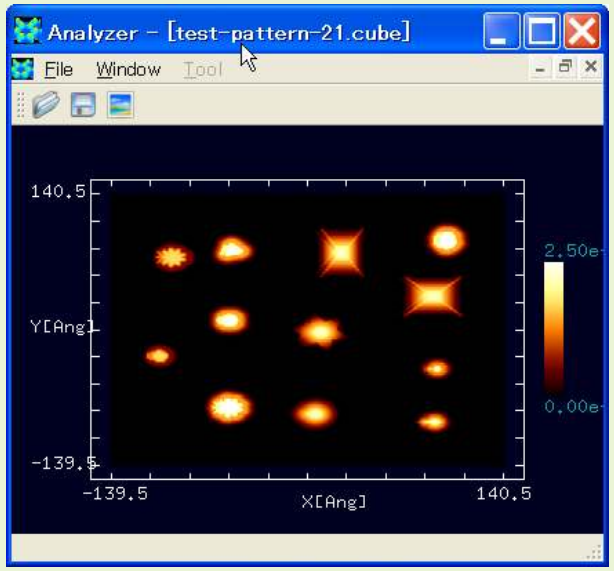
All these can be done on the same platform.
The comparison gives us a plan to simulate better.

The Blind Tip Reconstruction Method & Removing the Artifacts from Experimental Images (1)

Analyzer

The blind tip reconstruction method

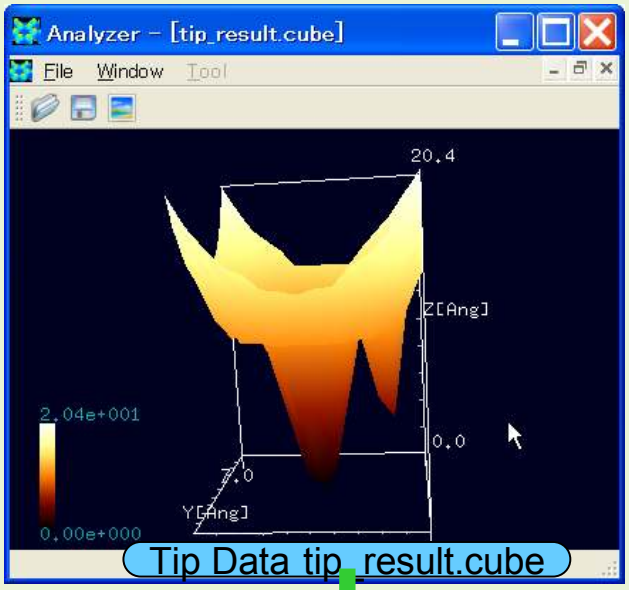
The blind tip reconstruction and removal of the artifacts, for an artificial AFM image by a broken double-tip.



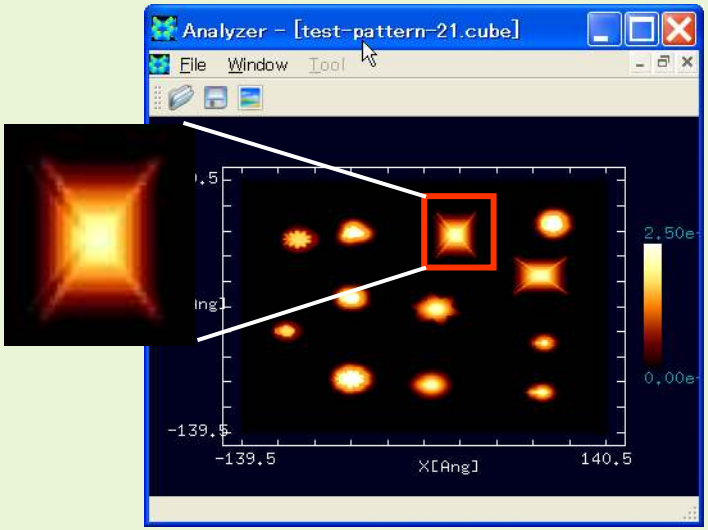
Estimation with the blind tip reconstruction method using the parameter you set (0.0~1.0)

0.0 : the maximum blind tip

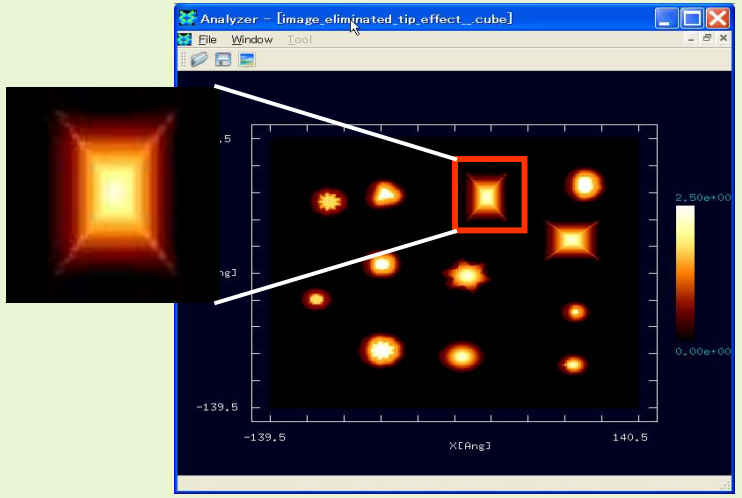
1.0 : the minimum blind tip



Removing the artifacts from experimental images



Removing the artifacts with the specified tip data

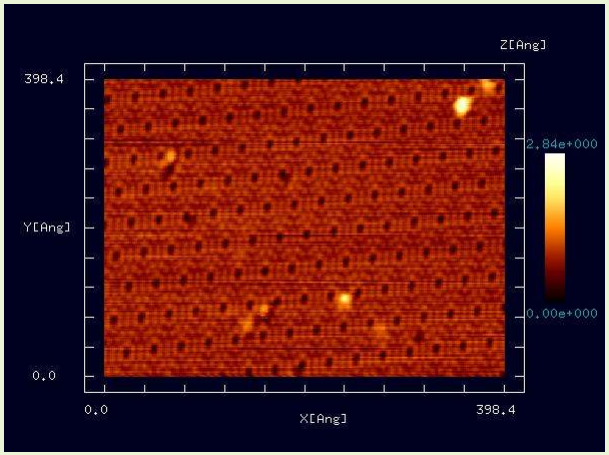


The Blind Tip Reconstruction Method & Removing the Artifacts from Experimental Images (2)

Analyzer

The blind tip reconstruction method

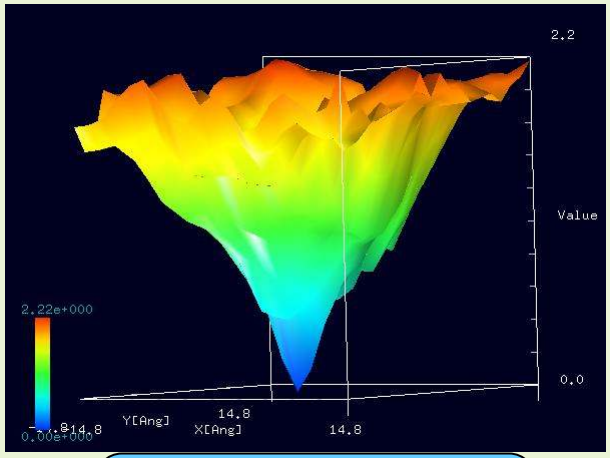
The blind tip reconstruction and removal of the artifacts, for an original SPM image by an unknown tip.



Estimation with the blind tip reconstruction method using the parameter you set (0.0~1.0)

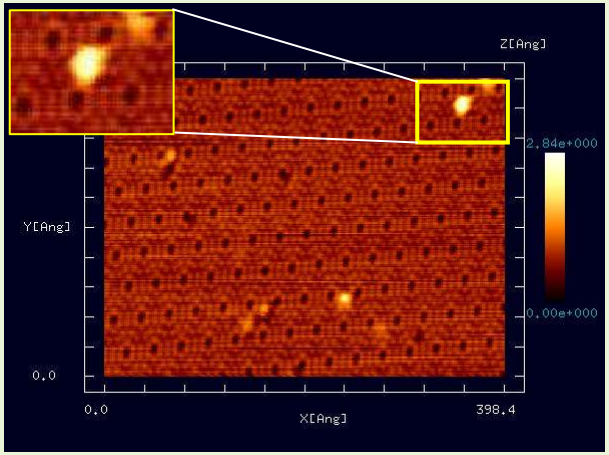
0.0 : the maximum blind tip

1.0 : the minimum blind tip

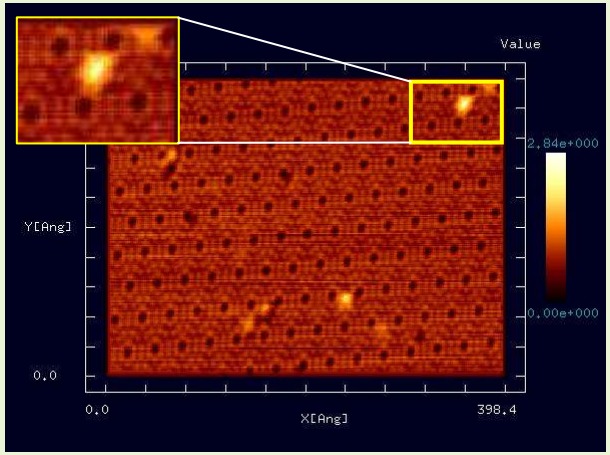


Tip Data tip_result.cube

Removing the artifacts from experimental images



Removing the artifacts with the specified tip data

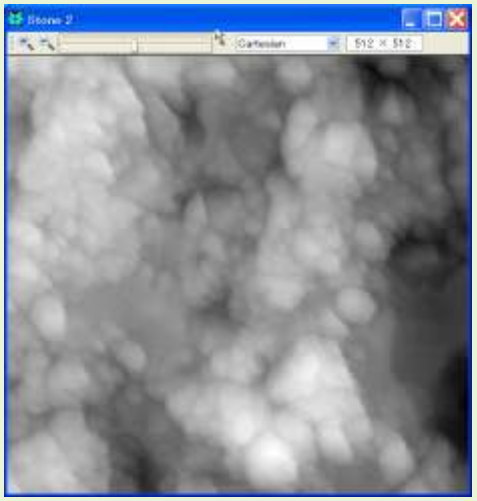


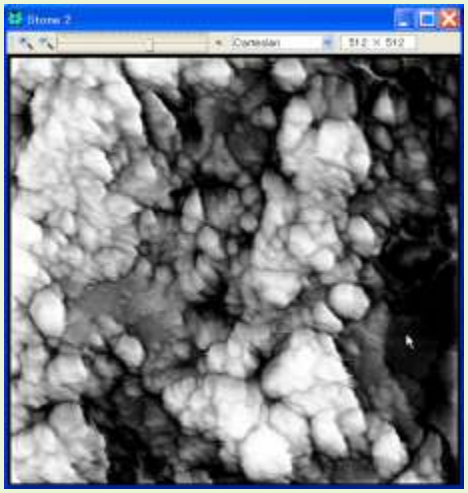
(The original image is provided by Professor Katsuyuki Fukutani, Vacuum and Surface Physics, Institute of Industrial Science, The University of Tokyo.)

Fourier Analysis of the Image

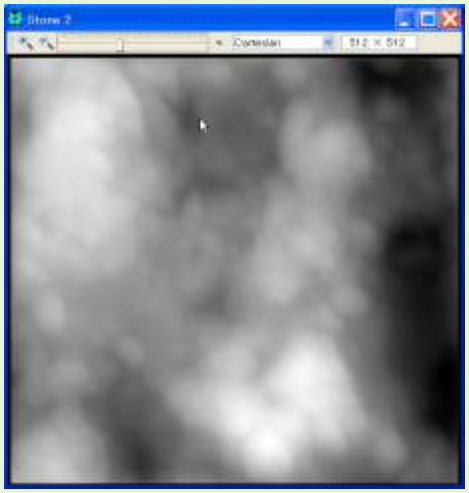
Analyzer

Fourier analysis of the image

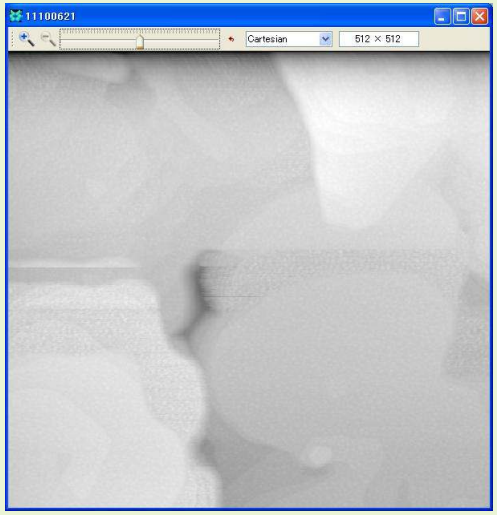


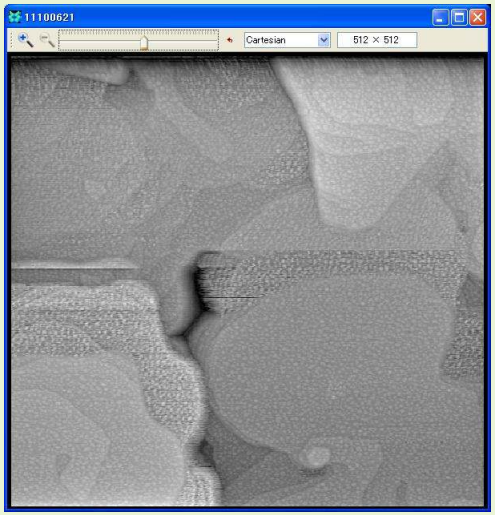


Emphasize high frequencies



Emphasize low frequencies

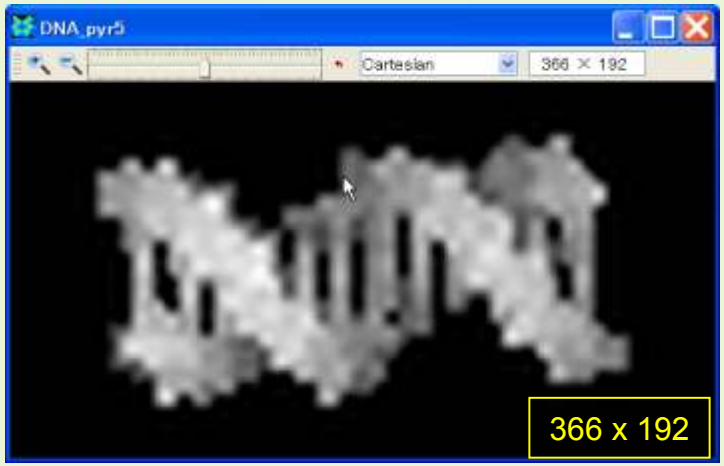


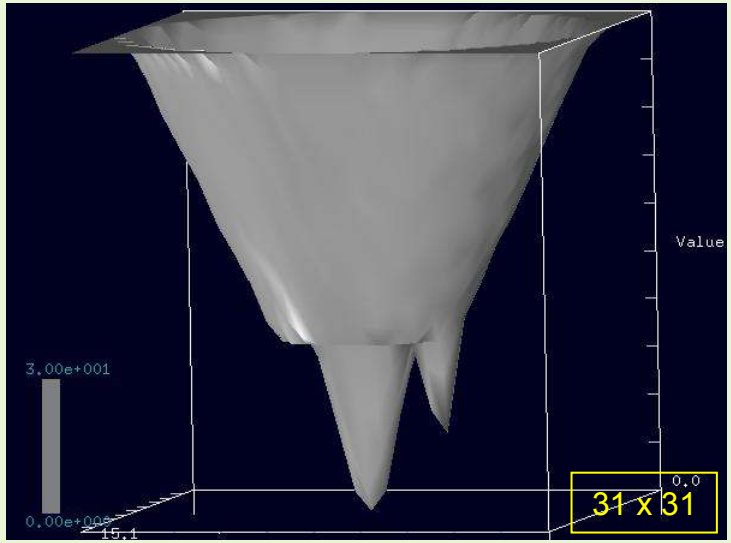


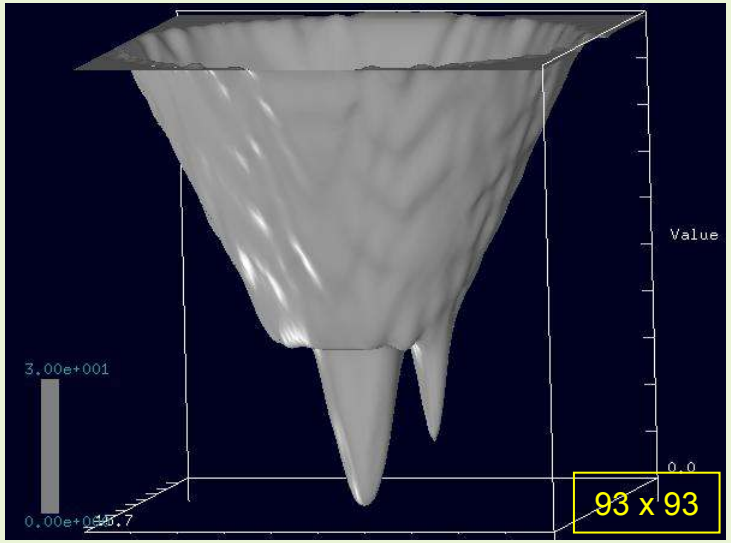
Improvement of the Subjective Quality of the Image

Analyzer

Improvement of the subjective quality of the image



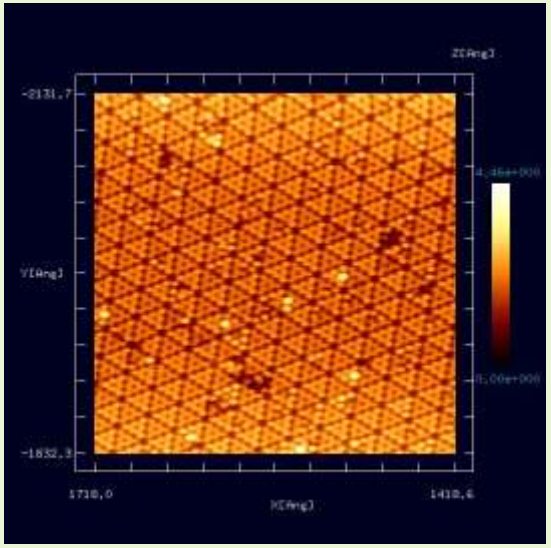




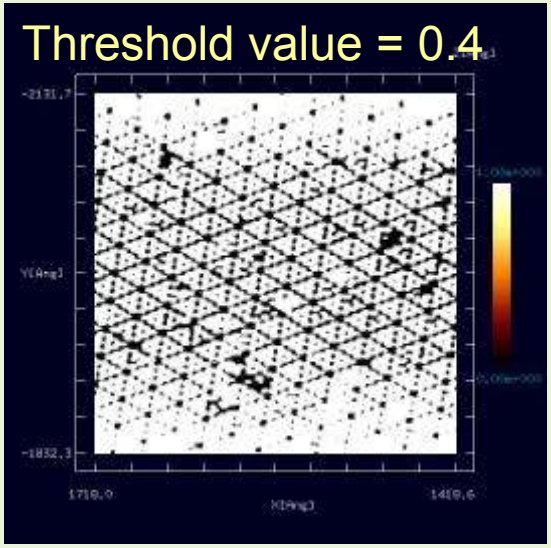
Digital Image Processings Function (1)

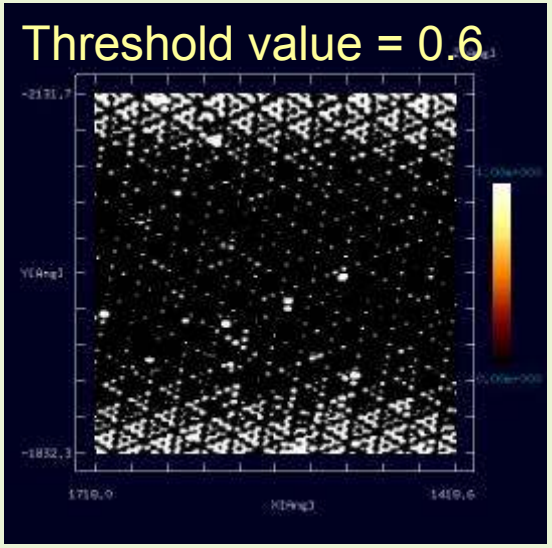
Analyzer

Thresholding for creating binary images



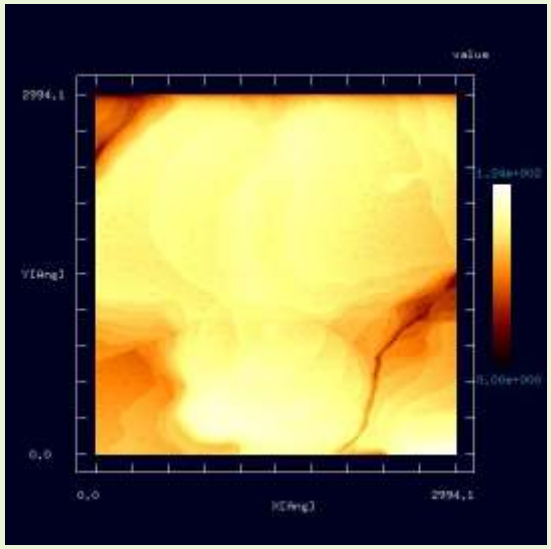
Changing the original image into a black-and-white image using the threshold value you set (from 0.0 and 1.0)



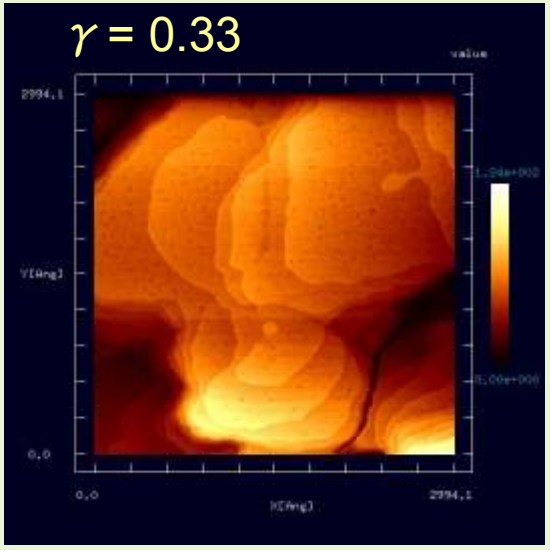


(The original image is provided by Professor Hiroyuki Hirayama, Nano-Quantum Physics at Surfaces and Interfaces, Department of Materials and Engineering, Tokyo Institute of Technology.)

Contrast adjustment (Gamma correction)



You set γ value (0.25~4.0)

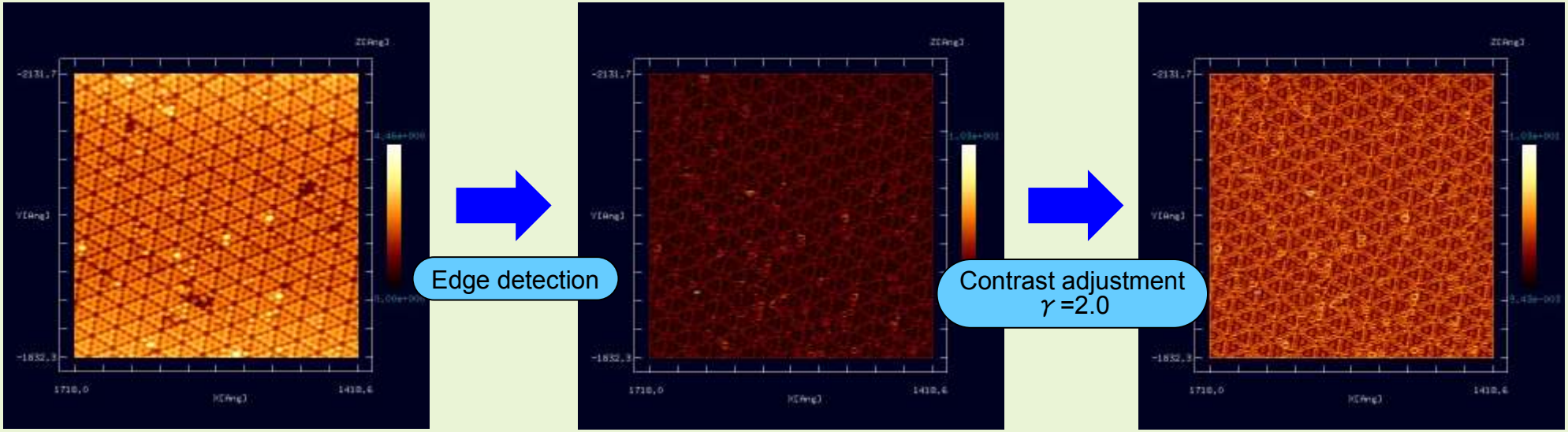


(The original image is provided by Professor Ken-ichi Fukui, Surface/Interface Chemistry Group, Department of Materials Engineering Science, Osaka University.)

Digital Image Processings Function (2)

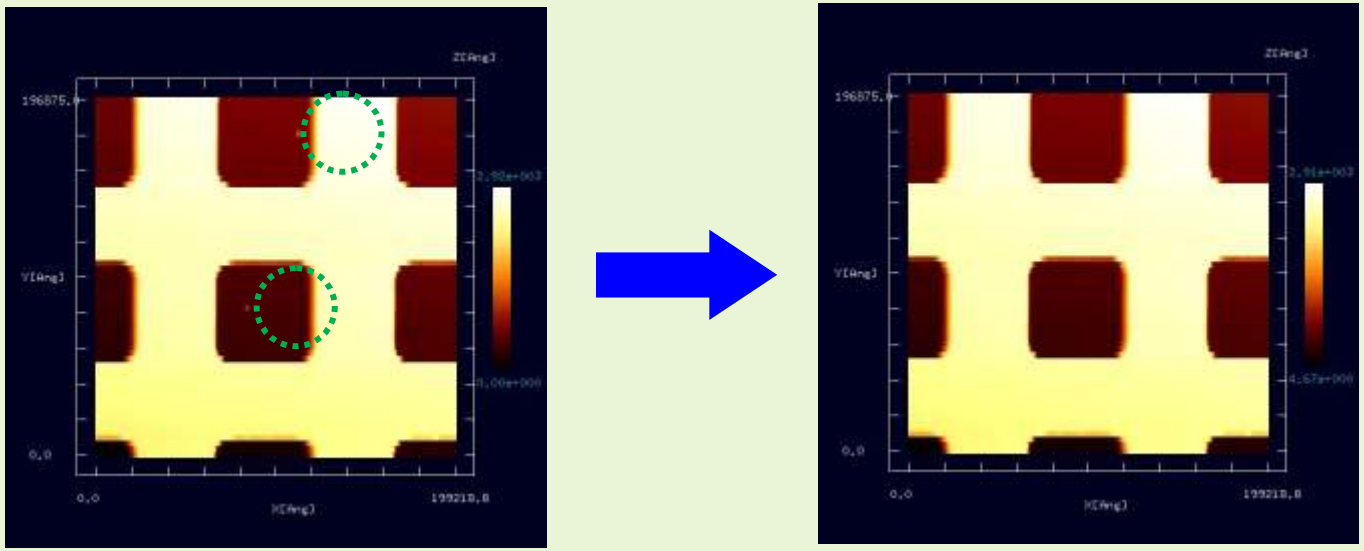
Analyzer

Edge detection with the Sobel filter



(The original image is provided by Professor Hiroyuki Hirayama, Nano-Quantum Physics at Surfaces and Interfaces, Department of Materials and Engineering, Tokyo Institute of Technology.)

Noise reduction with the median filter

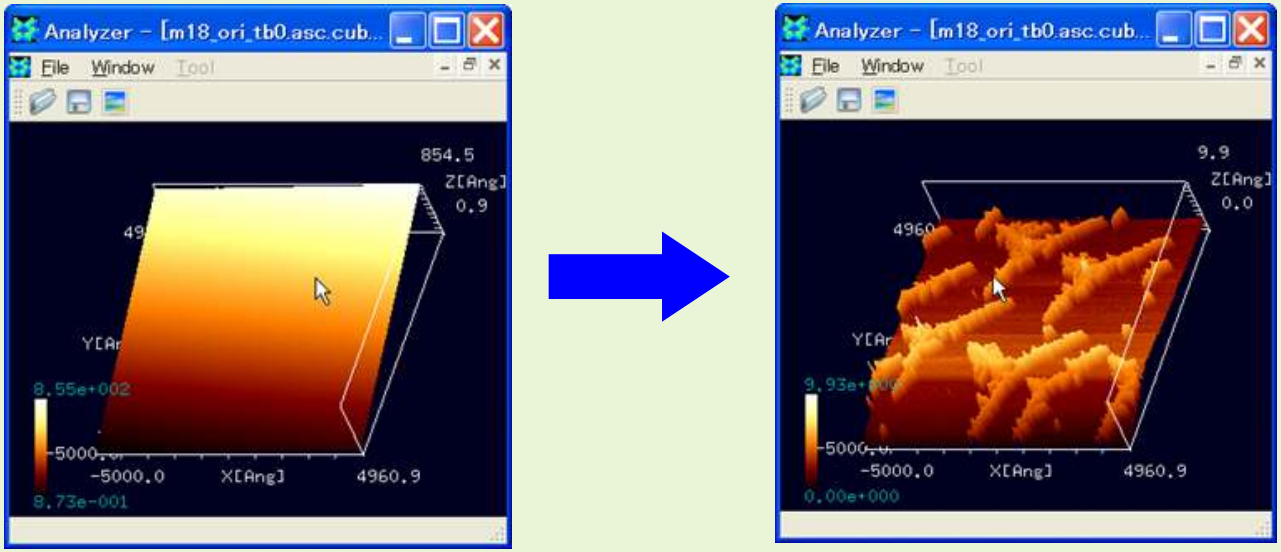


(The image is provided by Professor Katsushi Hashimoto, Solid-State Quantum Transport Group, Department of Physics, Graduate School of Science, Tohoku University.)

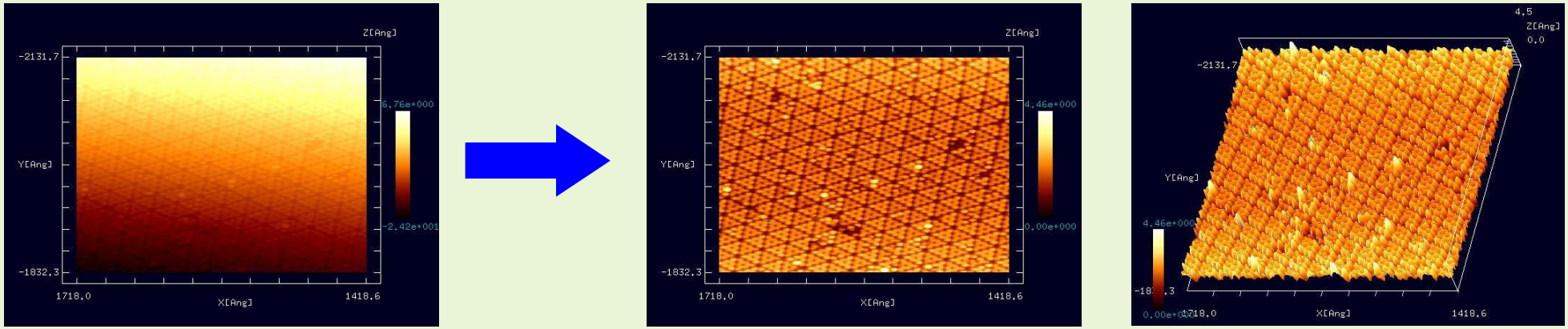
Digital Image Processings Function (3)

Analyzer

Correcting a tilt



(The original image is provided by the laboratory of the Professor Fukutani, Institute of Industrial Science, the University of Tokyo.)

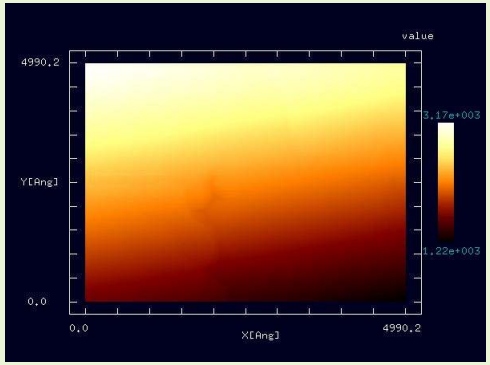


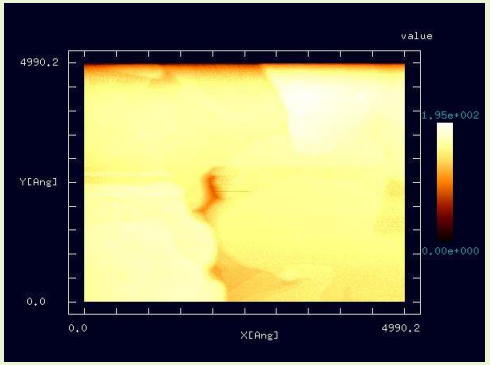
(The original image is provided by the laboratory of the Professor Hiroyuki Hirayama, Nano-Quantum Physics at Surfaces & Interfaces, Department of Materials & Engineering, Tokyo Institute of Technology.)

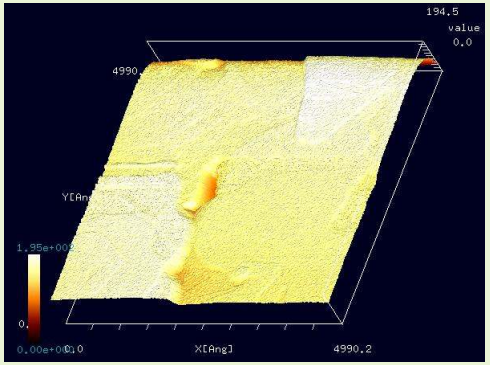
Digital Image Processings Function (4)

Analyzer

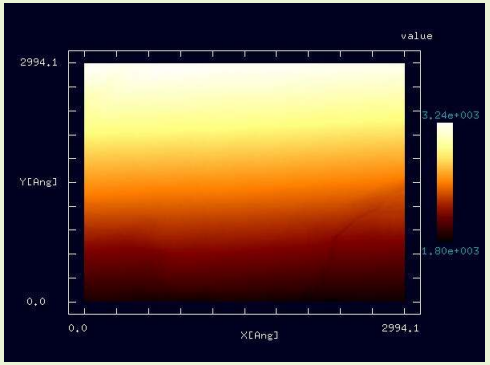
Correcting a tilt

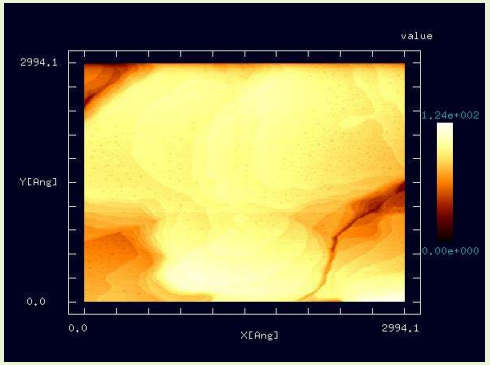


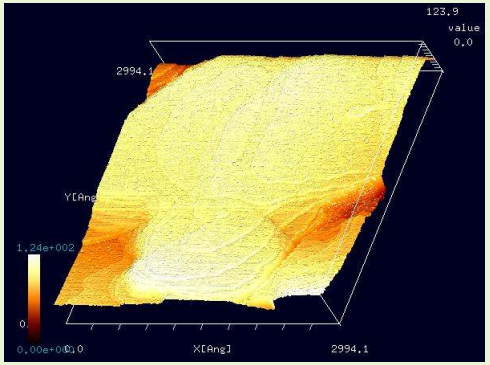




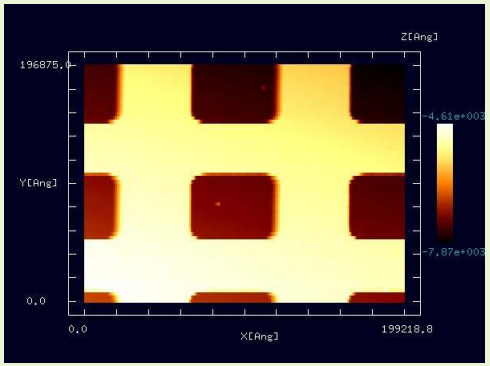
(The original image is provided by Professor Ken-ichi Fukui, Division of Chemistry, Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University.)

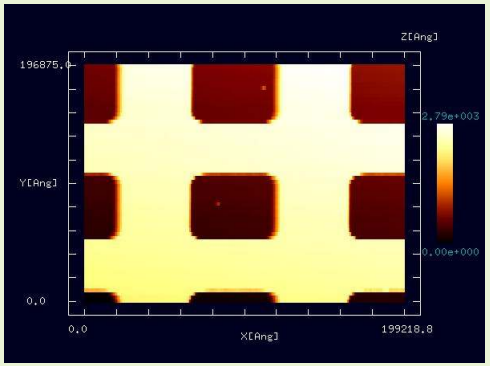


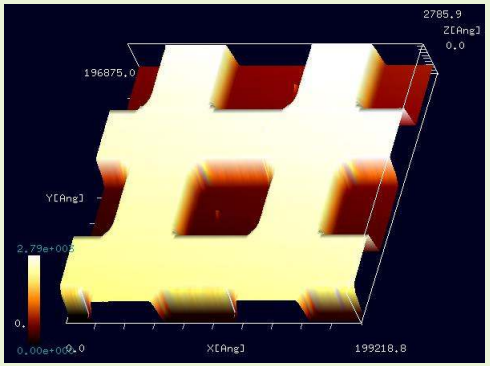




(The original image is provided by Professor Ken-ichi Fukui, Division of Chemistry, Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University.)





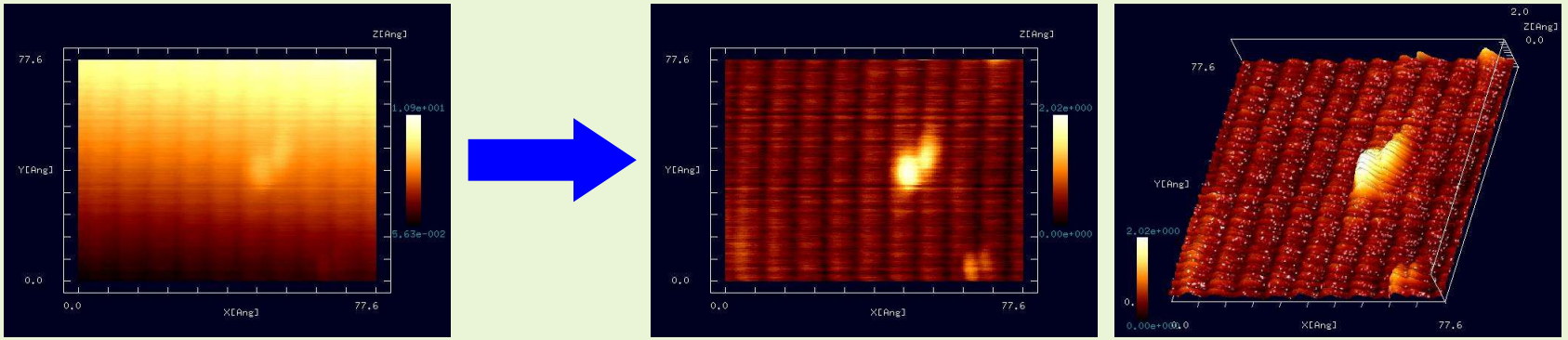


(The original image is provided by Dr. Katsushi Hashimoto, Solid-State Quantum Transport Group, Department of Physics, Tohoku University.)

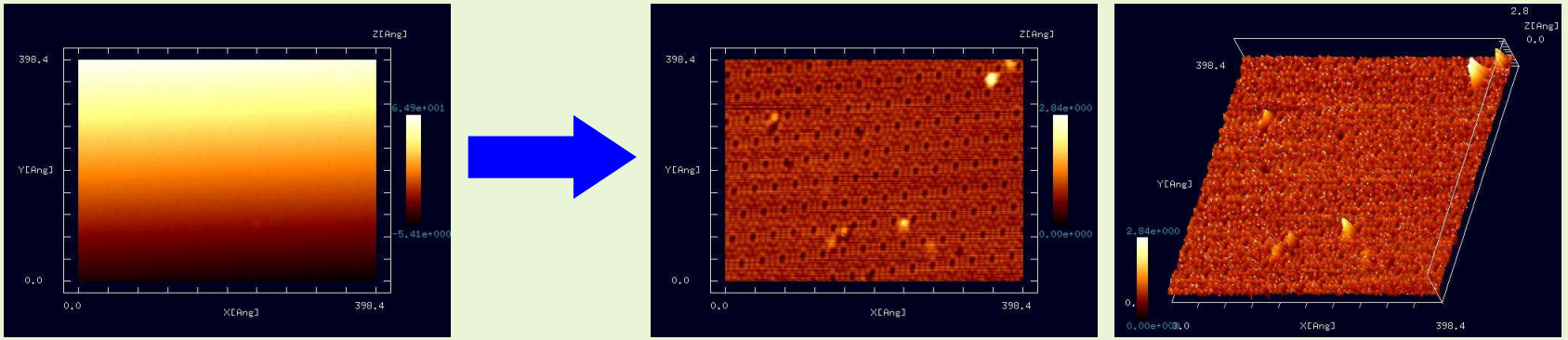
Digital Image Processings Function (5)

Analyzer

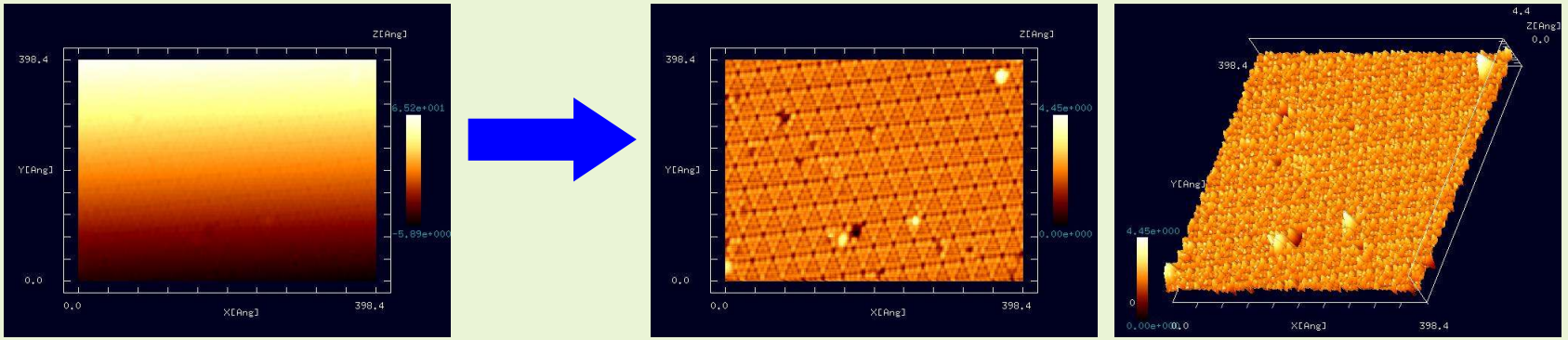
Correcting a tilt



(The original image is provided by Professor Katsuyuki Fukutani, Vacuum and Surface Physics, Institute of Industrial Science, The University of Tokyo.)



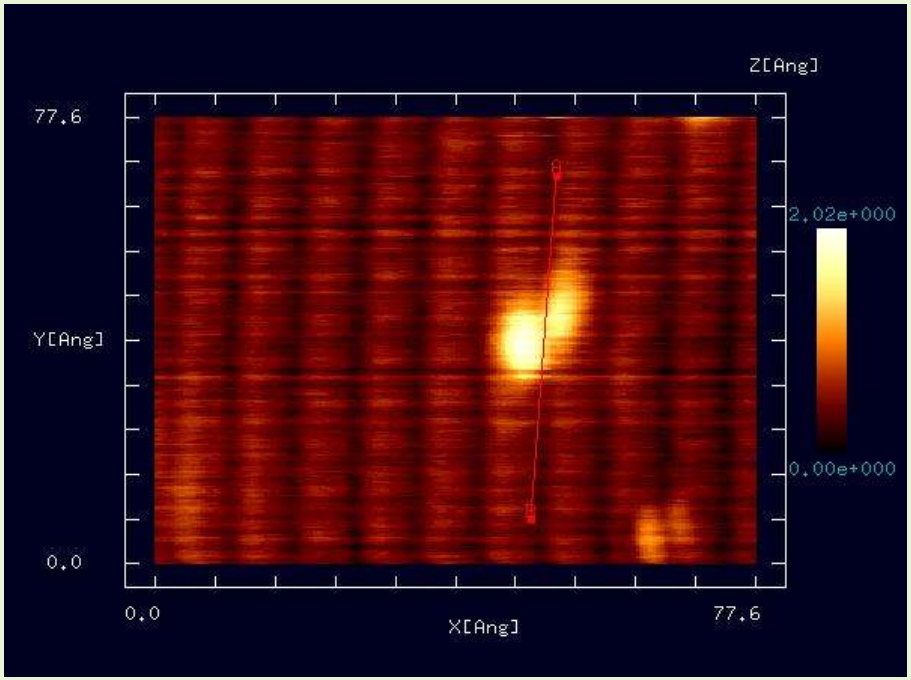
(The original image is provided by Professor Katsuyuki Fukutani, Vacuum and Surface Physics, Institute of Industrial Science, The University of Tokyo.)

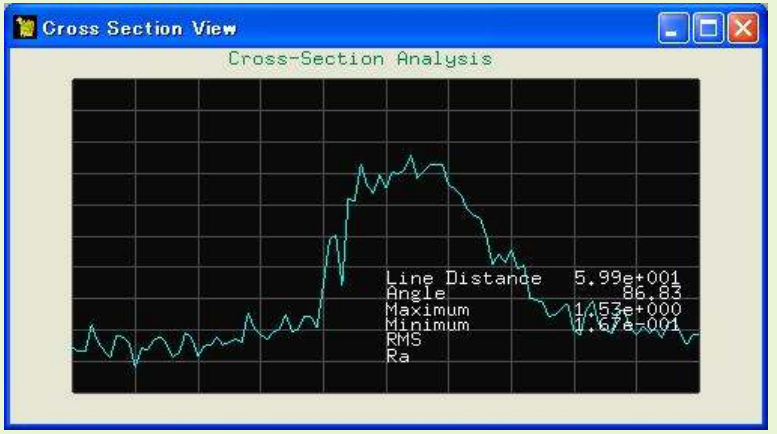


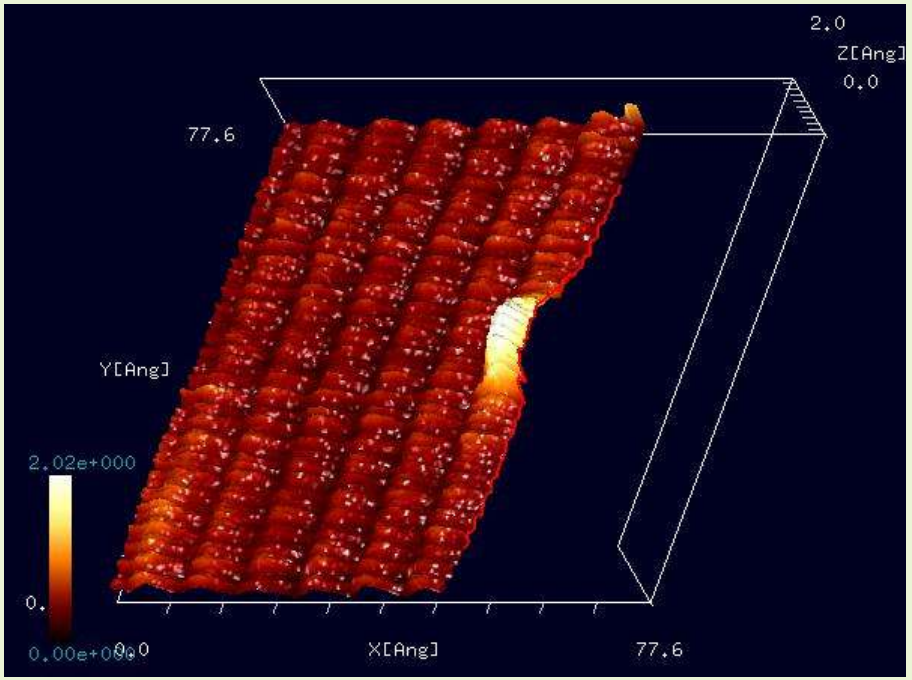
(The original image is provided by Professor Katsuyuki Fukutani, Vacuum and Surface Physics, Institute of Industrial Science, The University of Tokyo.)

Display the cross section

Display the cross section



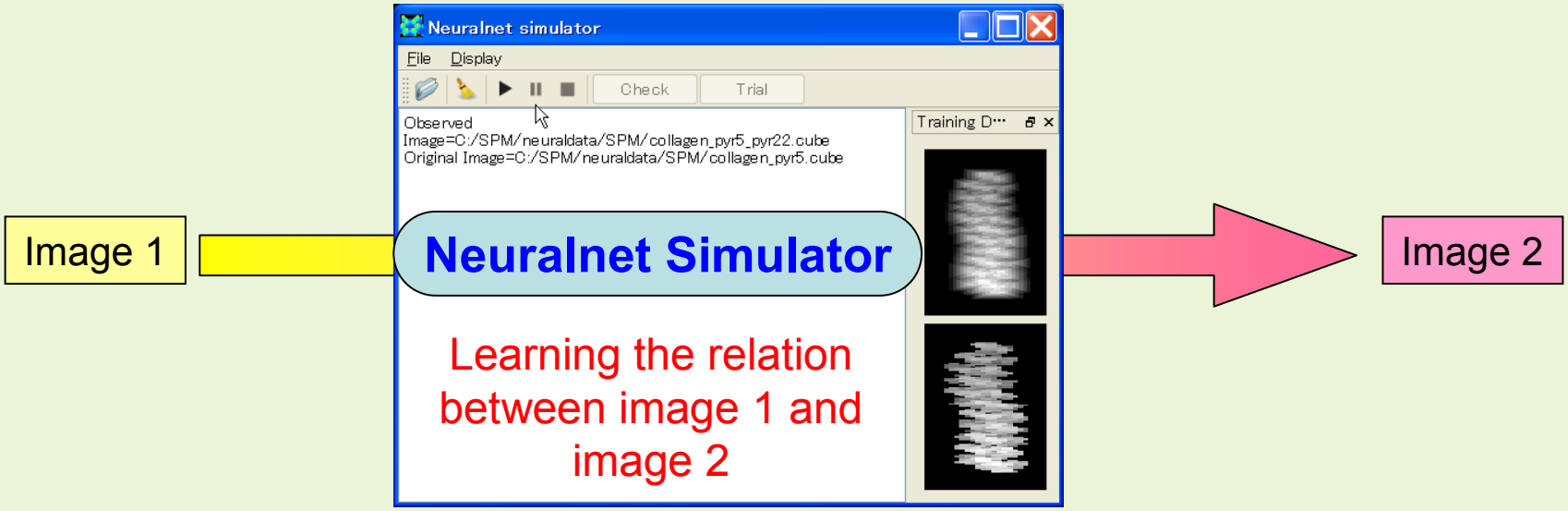




(The original image is provided by Professor Katsuyuki Fukutani, Vacuum and Surface Physics, Institute of Industrial Science, The University of Tokyo.)

Neural Network Simulator

Analyzer

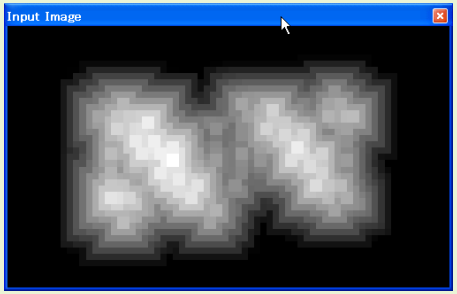


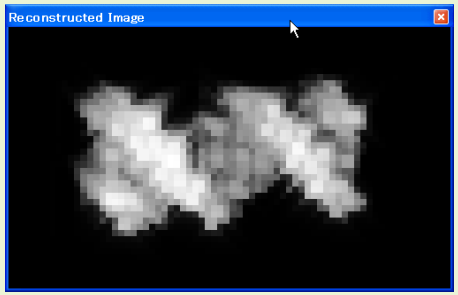
Observation process: The sample → The tip → The SPM image

Learning process: The SPM image of the known sample → Neural network → The known sample

Applying the results of the learning

Estimating process: The SPM image of any sample → Neural network → The estimated sample



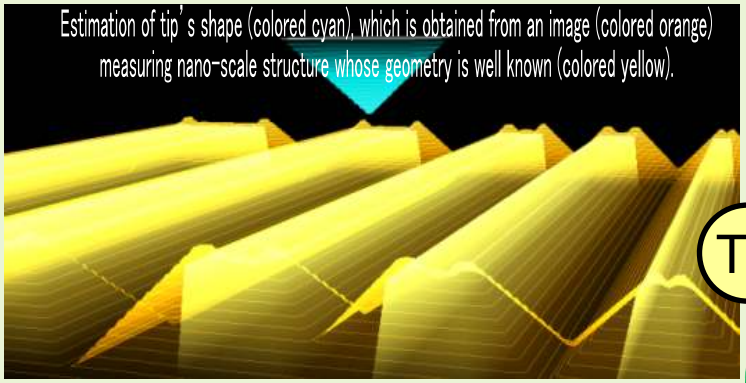


We can obtain the image from which the artifacts are removed.

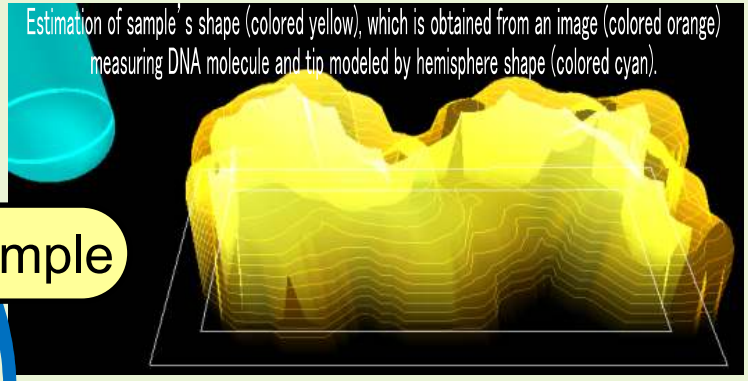
GeoAFM

Geometrical Mutual AFM Simulator

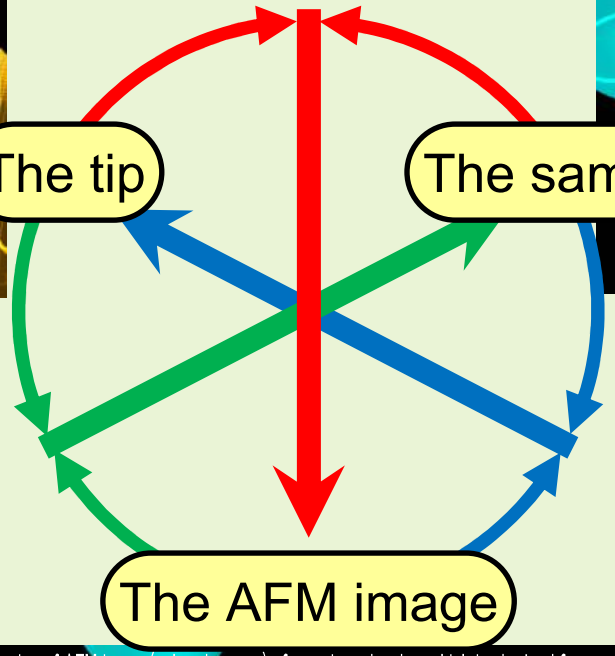
Geometrical Mutual AFM Simulator (GeoAFM) provides users with a kind of a three-way data processor, so that it reconstructs the one out of the other two among three geometrical elements, a tip, a sample material and its AFM image. The GeoAFM produces a result from only the information of the geometry of the tip, the sample material and the AFM image.

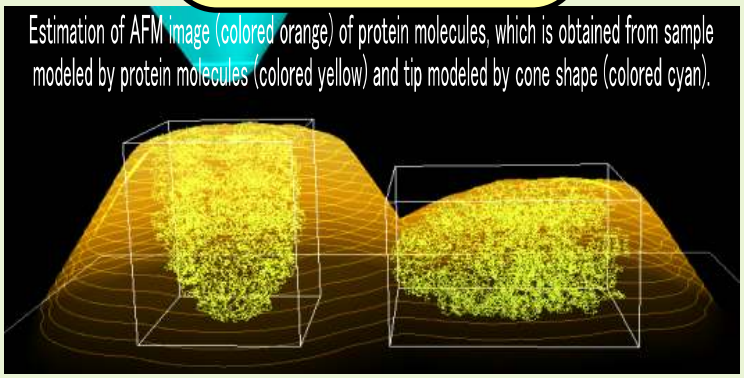


Estimation of Tip's shape from sample's structure and its image.



Estimation of Sample's shape from tip model and image observed.





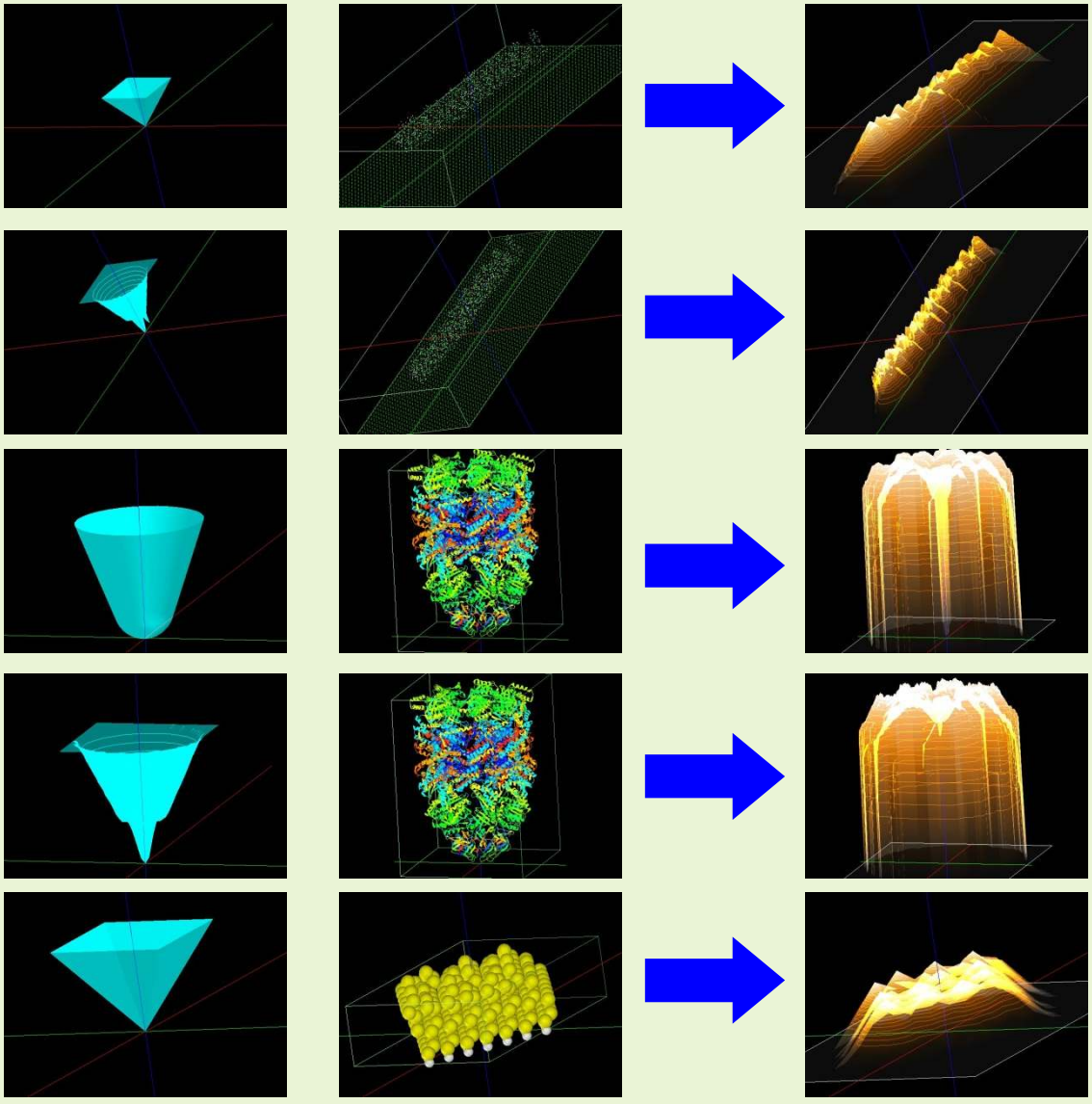
Estimation of AFM Image from tip model and sample model.

GeoAFM

Geometrical Mutual AFM Simulator

Estimation of AFM Image from tip model and sample model.

The tip | The sample | The AFM image



•Simulation of the AFM image of a Glycoprotein (1clg) on HOPG (Highly Oriented Pyrolytic Graphite) by the use of a quadrilateral pyramid probe tip.

•Simulation of the AFM image of a Glycoprotein (1clg) on HOPG (Highly Oriented Pyrolytic Graphite) by the use of a broken double tip.

•Simulation of the AFM image of a GroEL (chaperonin) by the use of a cone probe tip. The chaperonin is a basket-shaped polymer of 140 Å width, 140 Å depth and 200 Å height. The simulated AFM image reproduces a hole on the top of the basket shape.

•Simulation of the AFM image of a GroEL (chaperonin) by the use of a broken double tip. The chaperonin is a basket-shaped polymer of 140 Å width, 140 Å depth and 200 Å height. The simulated AFM image reproduces a hole on the top of the basket shape.

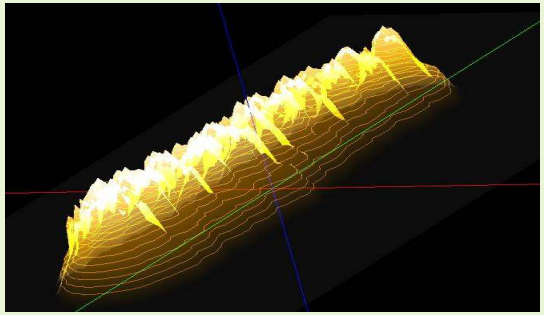
•Simulation of the AFM image of a Si(111)-(7x7) DAS surface by the use of a quadrilateral pyramid probe tip.

GeoAFM

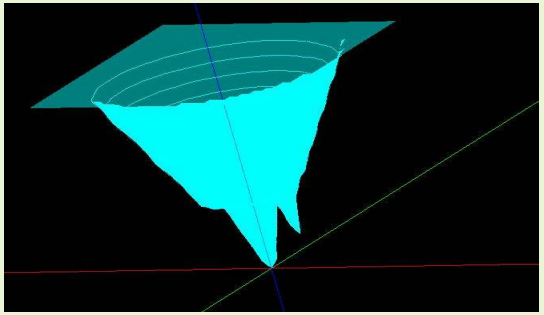
Geometrical Mutual AFM Simulator

Estimation of Sample's shape from tip model and image observed.

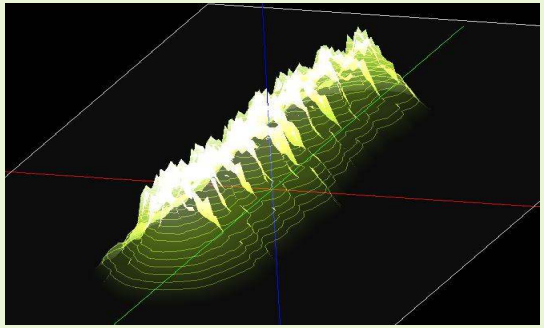
The AFM image



The tip



The sample



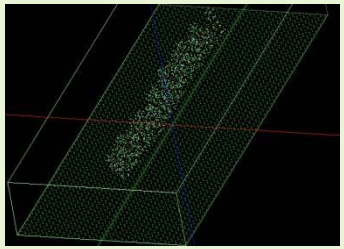
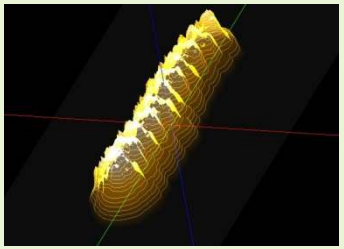
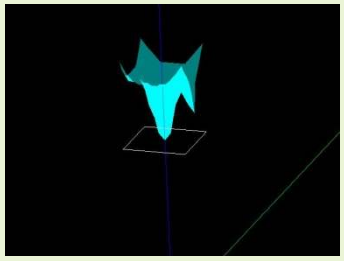
•Simulation of the sample surface by removing the artifacts from an AFM image of a Glycoprotein (1clg) on HOPG (Highly Oriented Pyrolytic Graphite) by the use of a broken double tip.

GeoAFM

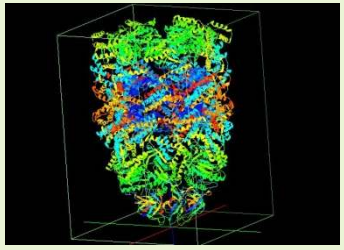
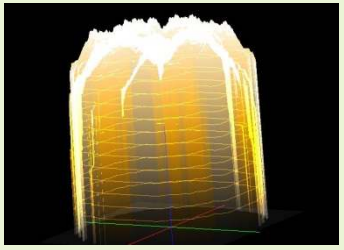
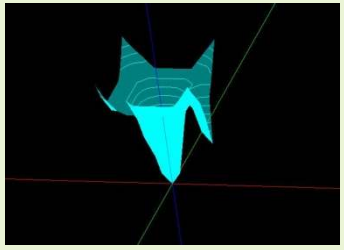
Geometrical Mutual AFM Simulator

Estimation of Tip's shape from sample's structure and its image.

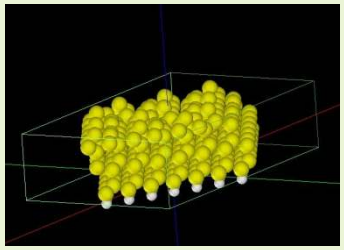
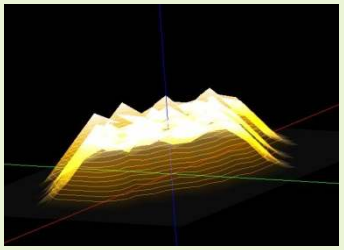
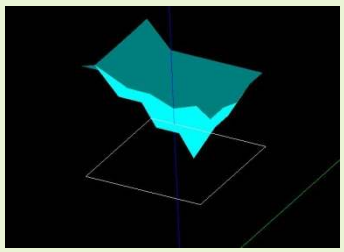
The sample | The AFM image → The tip

•Simulation of the tip shape from an AFM image of a Glycoprotein (1clg) on HOPG (Highly Oriented Pyrolytic Graphite) by the use of a broken double tip, and from a sample surface data constructed by a molecule structure.

•Simulation of the tip shape from an AFM image of a GroEL (chaperonin) by the use of a broken double tip, and from a sample surface data constructed by a molecule structure. The chaperonin is a basket-shaped polymer of 140 Å width, 140 Å depth and 200 Å height.

•Simulation of the tip shape from an AFM image of a Si(111)-(7x7) DAS surface, and from a sample surface data constructed by the atomic structure of a crystal surface.

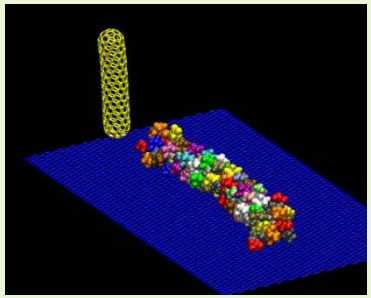
The Comparison between Normal method and GeoAFM

Calculation by
Interaction force
2 weeks by a WS

Calculation by
Geometrical condition
1 second by a PC

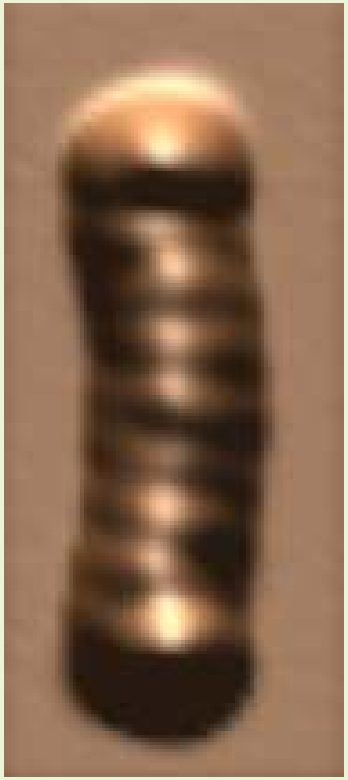
MD

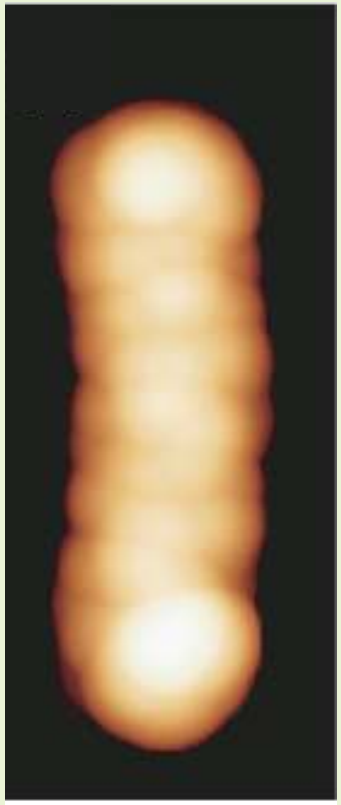
GeoAFM



Geo AFM reproduces an AFM image observed by an experiment well.

The tip recognize the difference in height of the Pro and the Gly.

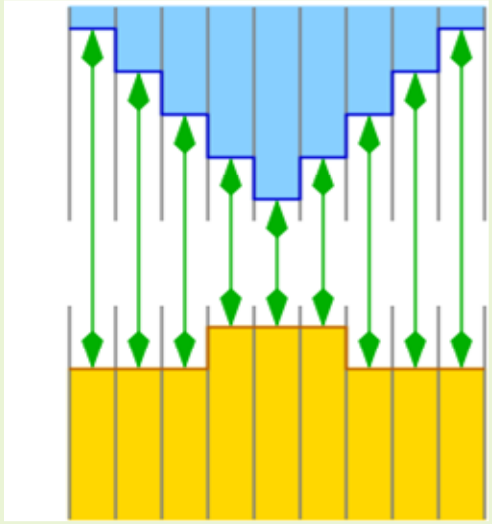


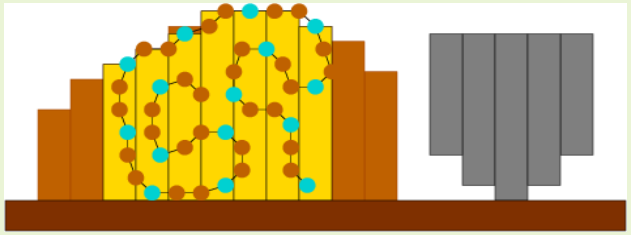


Collagen image

By 2 x 10^{-8} shorter !!

Rapid geometrical method



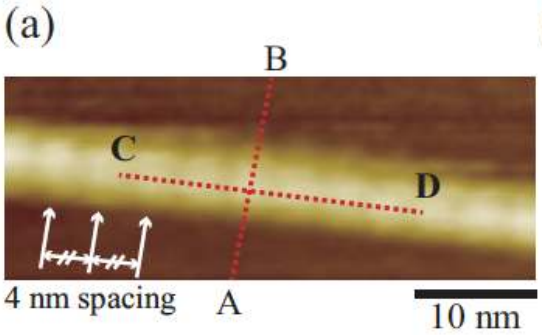


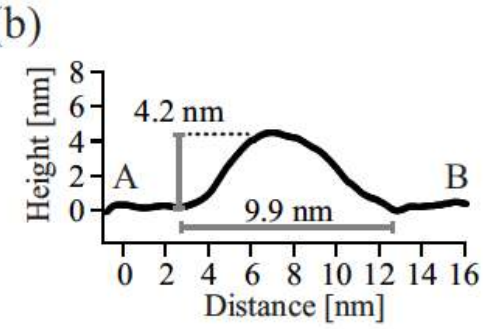
Divide tip/sample into meshes assign the height of each mesh by the top atom, and measure the difference in height. It is a geometrical method, so the computational complexity is little.

FM-AFM observation and AFM simulation of tubulin in liquid

H.Asakawa, K.Ikegami, M.Setou, N.Watanabe, M.Tsukada, T.Fukuma.
Biophysical Journal 101(5), 1270-1276 (2011).

Experimental AFM image

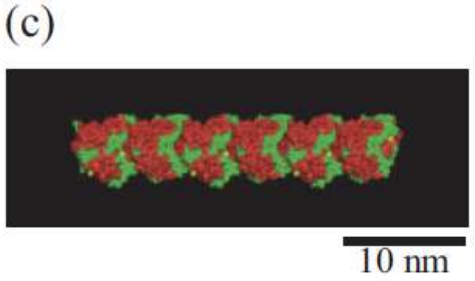


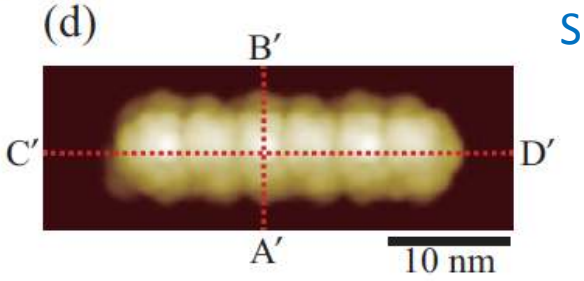


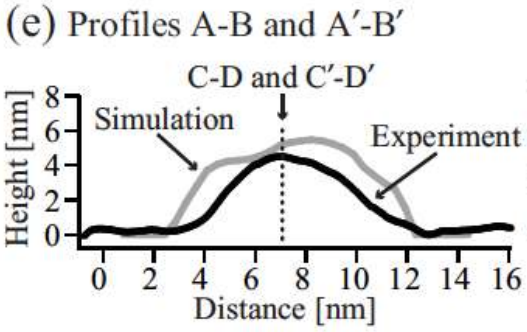
Simulated AFM image

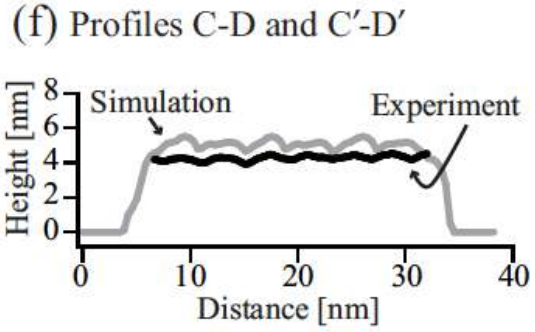
GeoAFM

The Comparison between the Experimental Image and Simulated Image









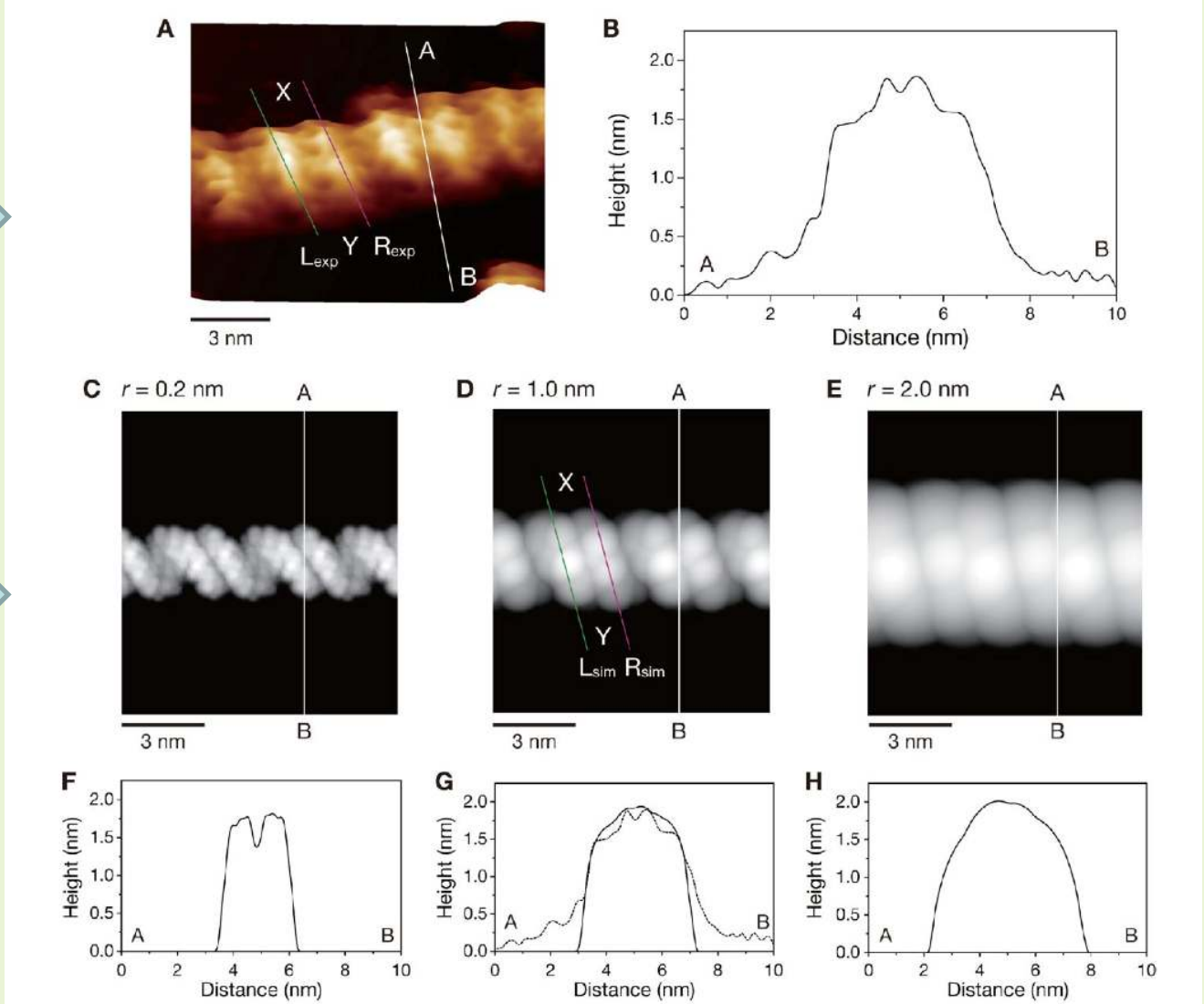
Direct observation and Simulation of the DNA in aqueous solution

S. Ido, K. Kimura, N. Oyabu, K. Kobayashi, M. Tsukada, K. Matsushige and H. Yamada, ACS Nano 7(2), 1817-1822 (2013). DOI: 10.1021/nn400071n

FM-AFM experiments

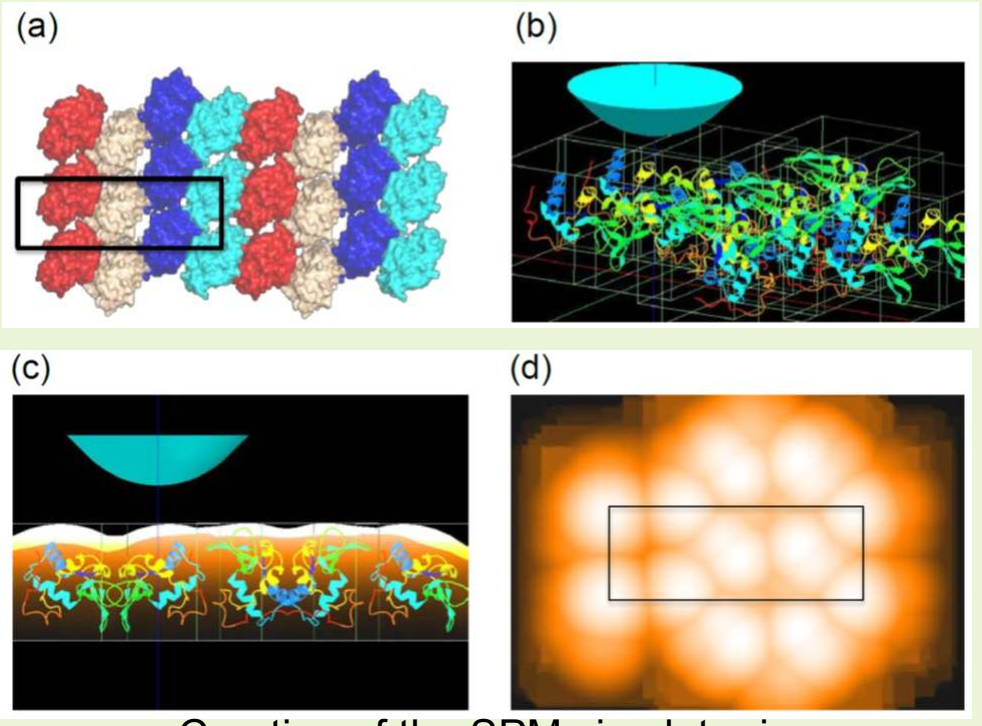
The theoretical simulation

GeoAFM



Decision of the (110) face of tetragonal lysozyme single crystal in liquid

The (110) face of tetragonal lysozyme single crystal has two possibilities that the surface structure is a (110) a face or a (110) b face.



Creation of the SPM simulator image

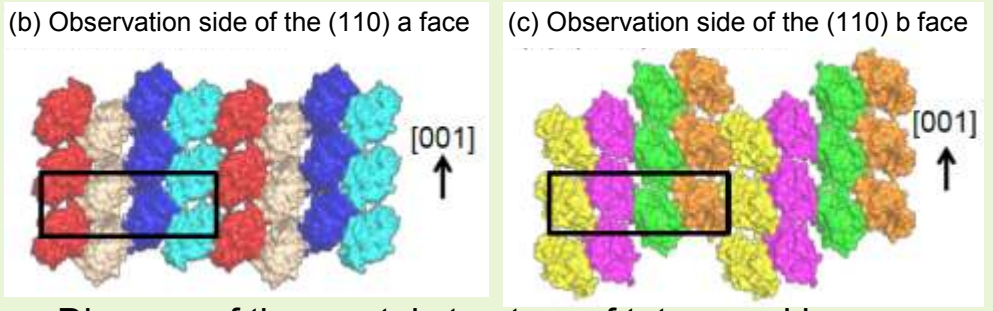
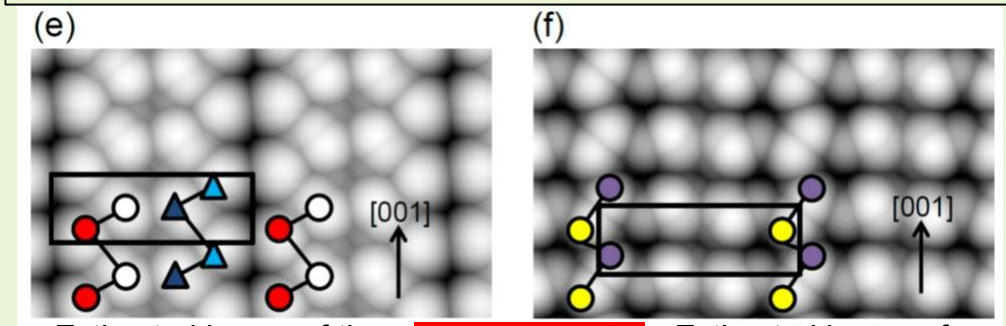


Diagram of the crystal structure of tetragonal lysozyme



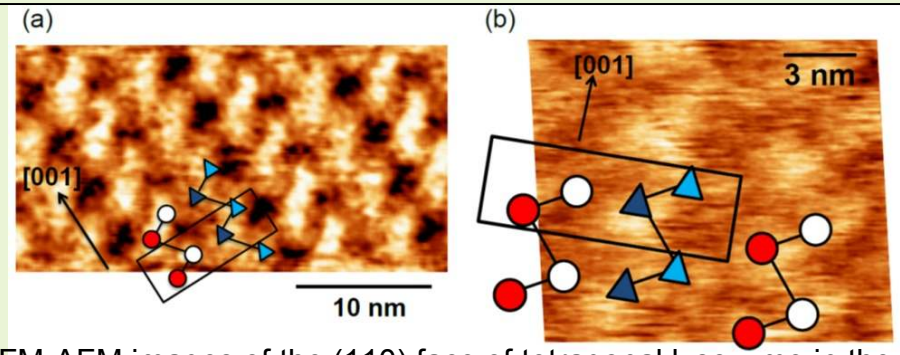
Estimated image of the (110) a face

GeoAFM

Estimated image of the (110) b face

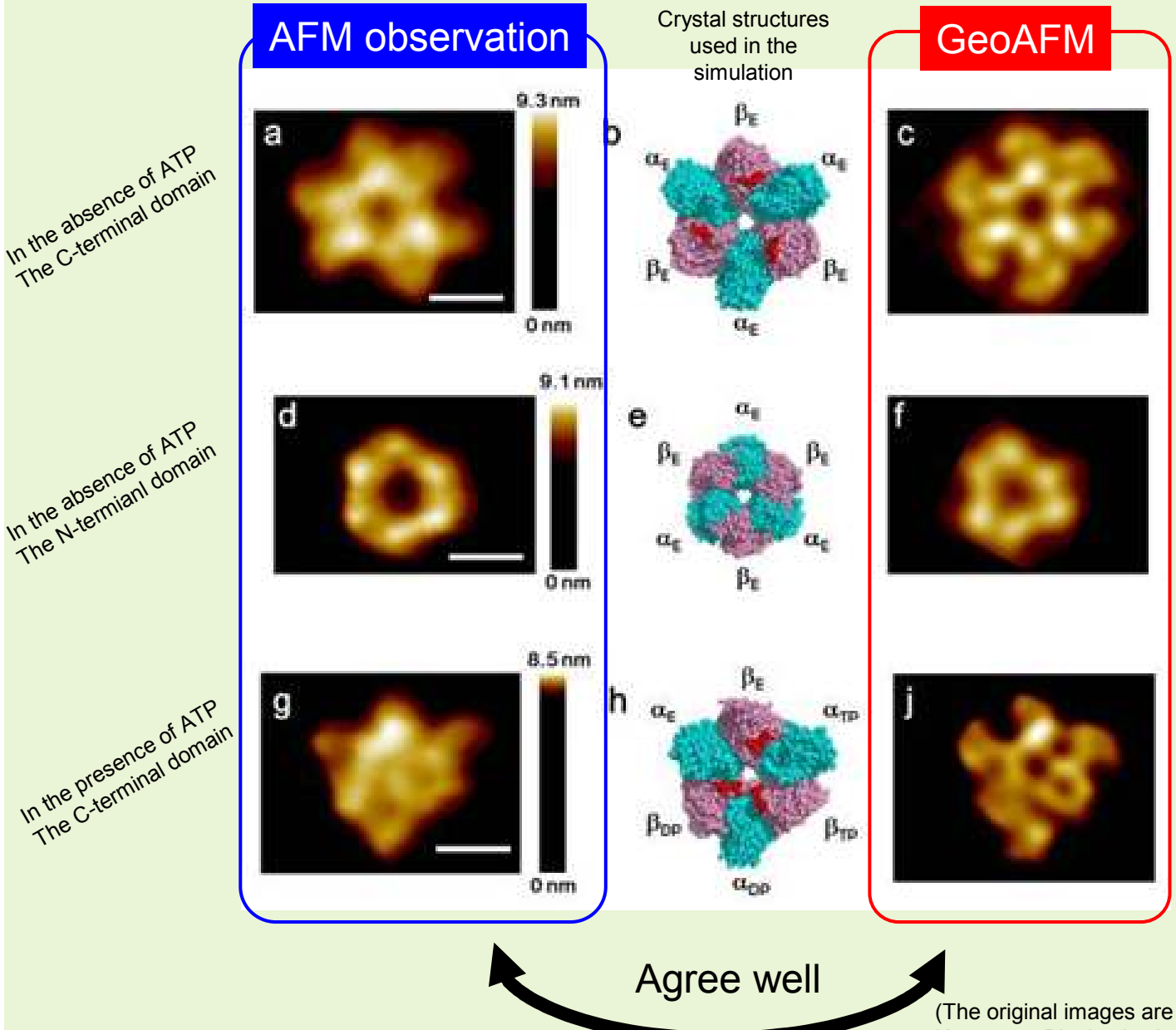
Comparing between the observed AFM image and the simulated image, the (110) face of tetragonal lysozyme single crystal is a (110)a surface structure.

(The original images are provided by Assistant Professor Ken Nagashima, Phase Transition Dynamics Group, Frontier Ice and Snow Science Division, Institute of Low Temperature Science, Hokkaido University)



FM-AFM images of the (110) face of tetragonal lysozyme in the solution (actual survey)

AFM observation and simulation of rotating molecular motor F_1-ATPase



F_1-ATPase:

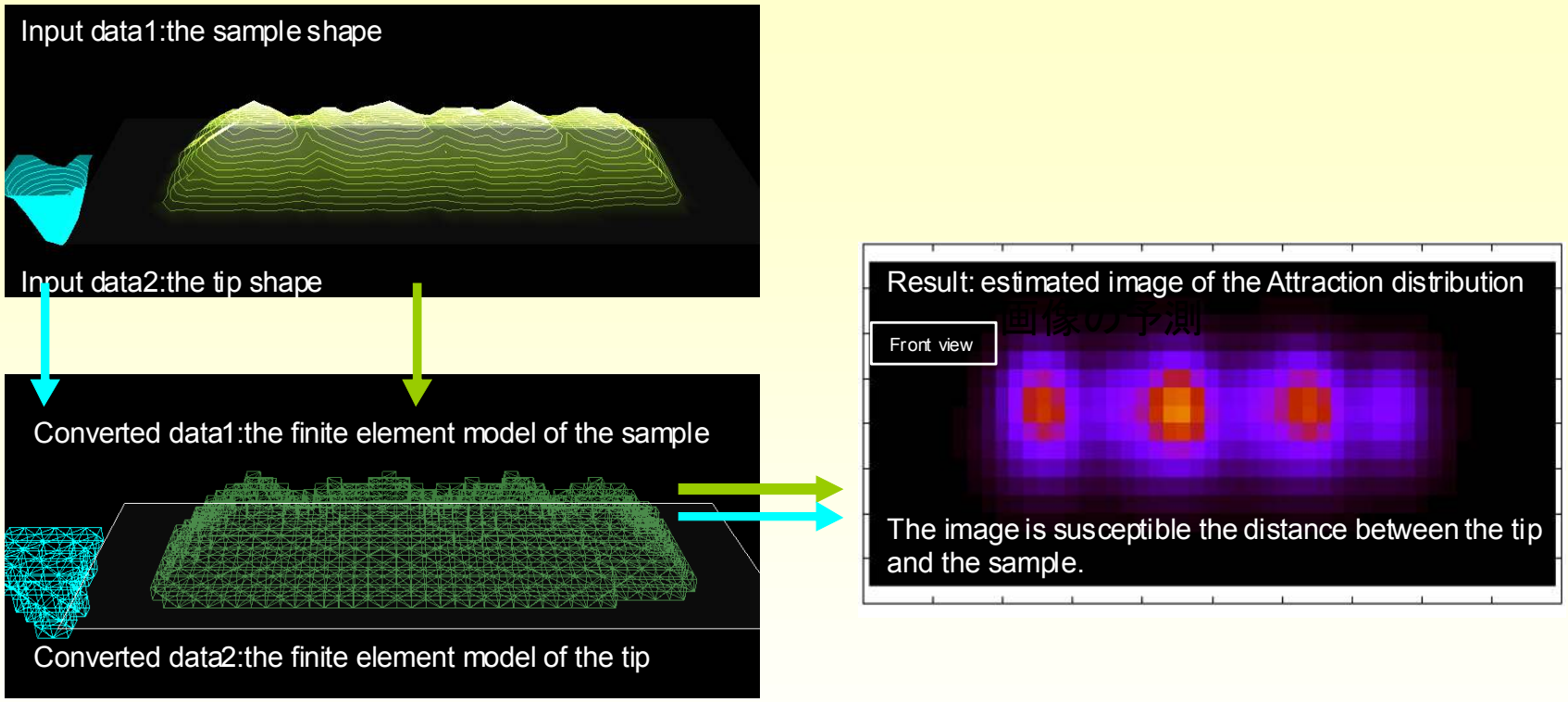
The rotary moleculer motor which turns a subunit using hydrolysis energy of the ATP in one direction.

The Comparison between the observed and the simulated images corroborated the reliability of the experiment.

(The original images are provided by Associate Professor takayuki Uchibashi, Kanazawa Biophysics Lab, Department of Physics, Bio-AFM Frontier Research Center, Kanazawa University)

Estimation of the measured image which was deformed by the interaction from the sample model.

FemAFM

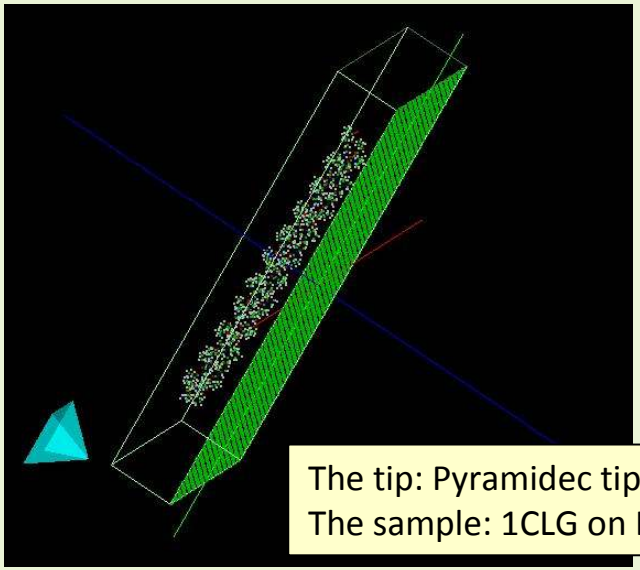


Convert shape of the tips and the samples into continuum of the finite element which have the modulus of elasticity and the van der Waals force.
Calculate the interaction and the elastic deformation.
Imaging the attraction distribution suffered by the tip.

Finite element method AFM simulator (FemAFM) simulates the AFM image using the finite element method.
It is different from Geometrical Mutual AFM Simulator (GeoAFM), it treats a deformation of the shape of the sample and the tip.

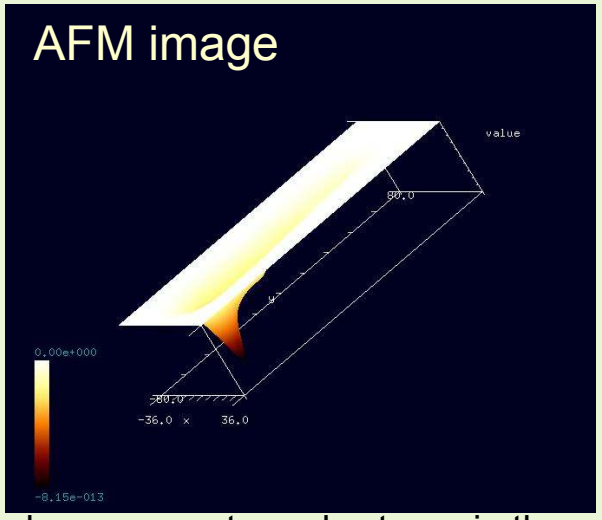
An AFM simulation of a single molecule of Glycoprotein (1clg)

FemAFM



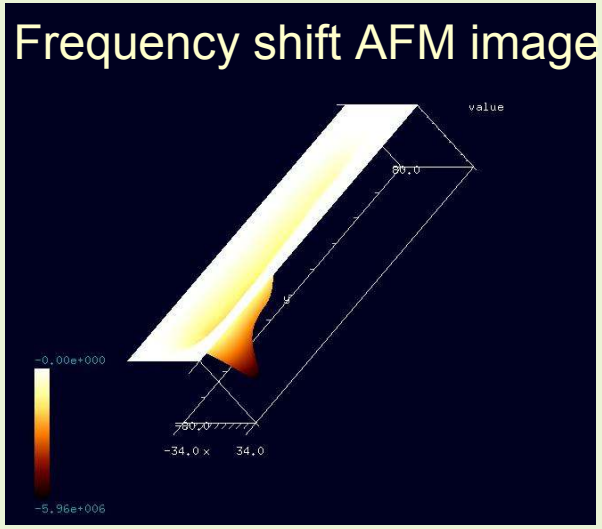
HOPG: Highly Oriented Pyrolytic Graphite
1CLG:Glycoprotein(CLG：ε -caprolacton・(L)lactide・glycolide copolymer)

Non-contact mode



The van der Waals force becomes extremely strong in the area where the tip is quite close to the sample surface, due to the law of inverse power of six.

Femafm_frequency_shift mode

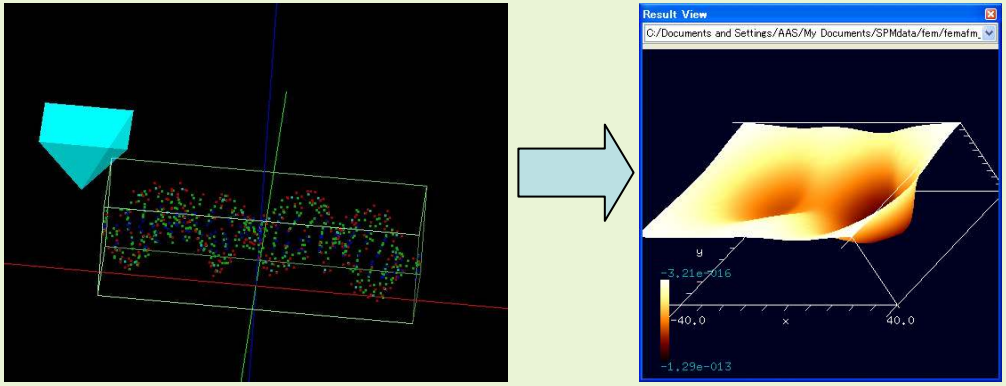


The cantilever oscillates at 500[MHz]. The maximum value of the frequency shift is about 5.96[MHz].

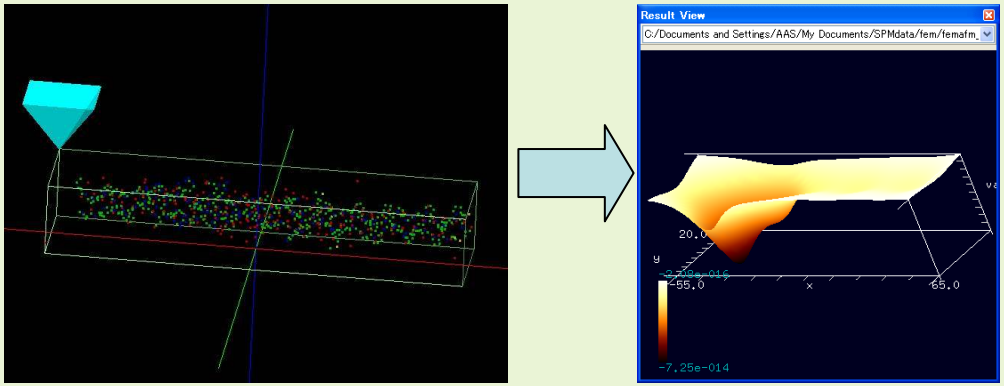
FemAFM

Non-contact mode

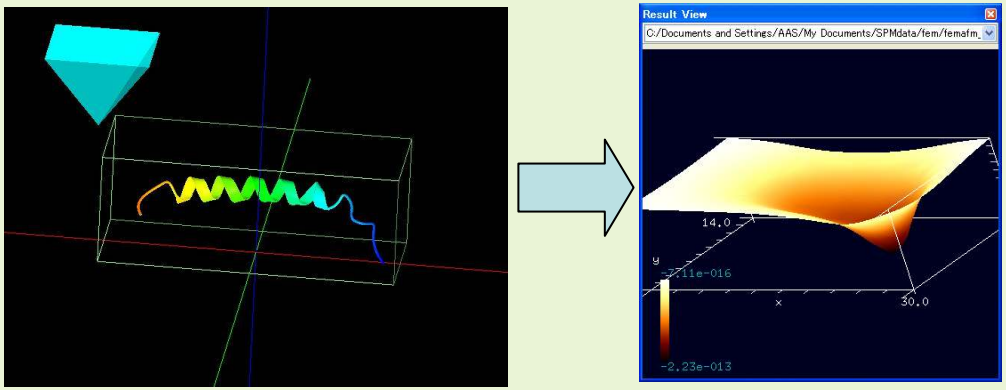
A probe tip attached to the front edge of the cantilever scans the surface of the sample material, keeping the distance around a few angstroms.



•Simulation of the AFM image of a DNA (Self-assembled Three-Dimensional DNA).



•Simulation of the AFM image of a collagen (collagen alpha-1(III) chain).

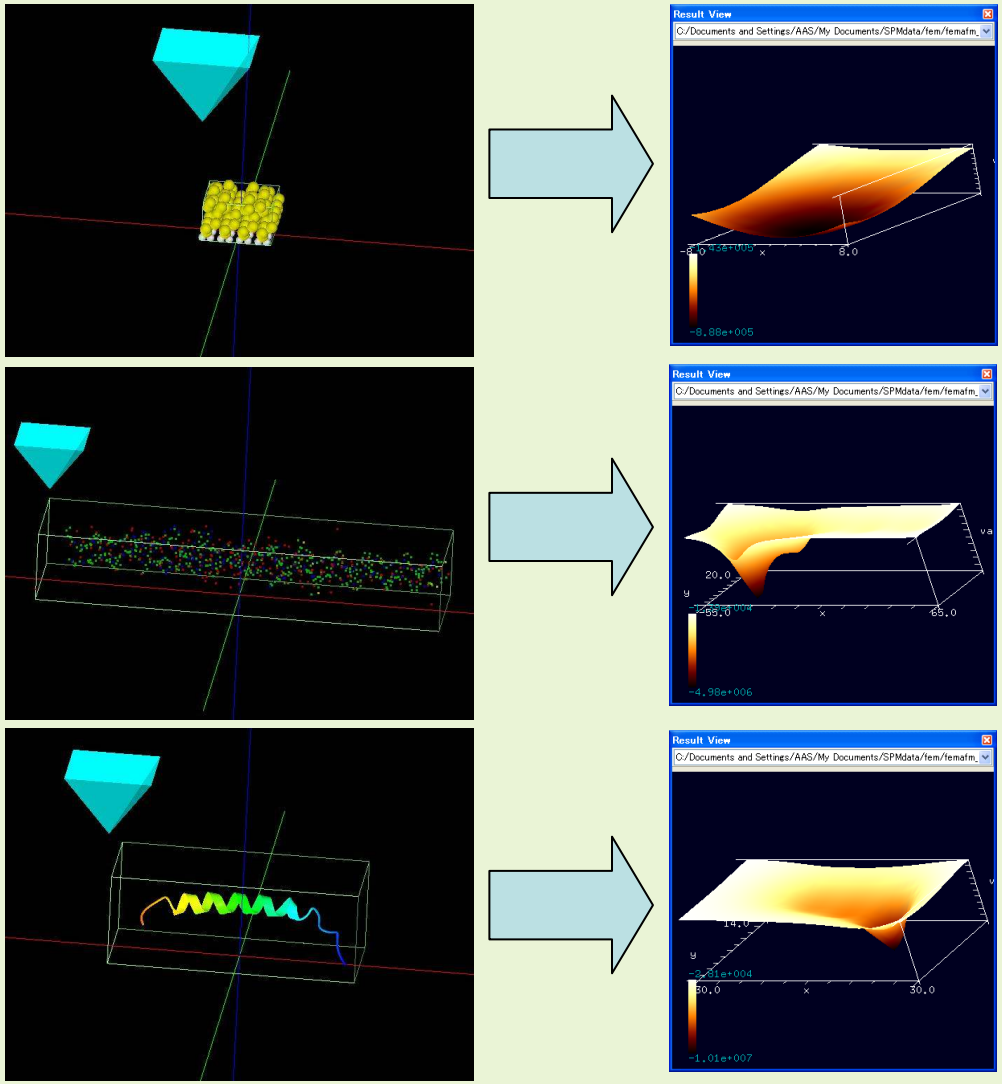


•Simulation of the AFM image of a collagen (COLLAGEN ALPHA 1).

FemAFM

Frequency shift image mode

A cantilever, which is oscillated by an external force with a constant frequency, approaches a sample surface but does not contact with it. A frequency shift caused by an interaction between a tip and a sample is calculated.



•Simulation of the frequency shift AFM image of a Si(111)-(7x7) DAS surface.

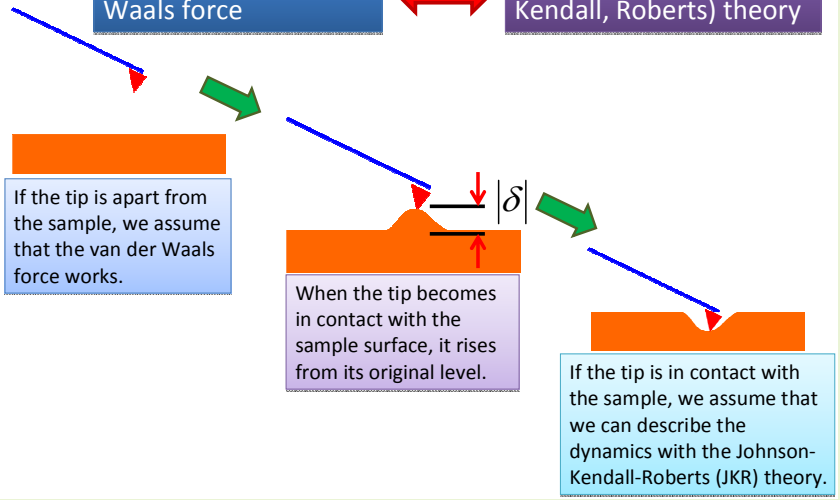
•Simulation of the frequency shift AFM image of a collagen (collagen alpha-1(III) chain).

•Simulation of the frequency shift AFM image of a collagen (COLLAGEN ALPHA 1).

Principle of a Method for Investigating Viscoelastic Contact Analysis

Model of the visoelastic contact between the tip and the sample

Model of the van der Waals force ⟷ The JKR (Johnson, Kendall, Roberts) theory

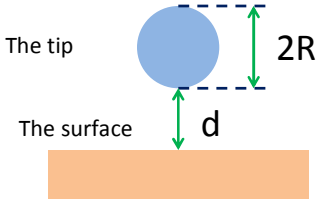


If the tip is apart from the sample, we assume that the van der Waals force works.

When the tip becomes in contact with the sample surface, it rises from its original level.

If the tip is in contact with the sample, we assume that we can describe the dynamics with the Johnson-Kendall-Roberts (JKR) theory.

Van der Waals force



$$F \cong \frac{A}{12}\frac{D}{d^2}$$

Where $D = 2R$, $A = \sqrt{H_1 H_2}$

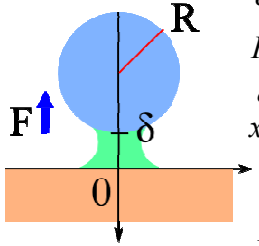
H_1 , H_2 :Hamaker constant

The tip ⟶ elastic body with no viscous characteristic

The sample ⟶ viscoelastic ➡ Introduction of surface tension

➡ We assume that the dynamics can be described by the JKR theory.

The JKR theory



F :The force between the tip and the sample. (It is positive in the vertical upward direction.)

δ :The length between the tip and the sample. (It is positive in the vertical downward direction.)

$$F = 4F_c(x^3 - x^{3/2})$$

$$\delta = \delta_0(3x^2 - 2\sqrt{x})$$

x :The dimensionless quantity which is in proportion to a contact area of the tip and the sample.

$$6^{-2/3} \le x \le 1$$

$$F_c = 3\pi\gamma R \quad (\ \gamma \text{ :surface tension of the sample})$$

$$\delta_0 = \frac{a_0^{\,2}}{3R}\ , \quad a_0 = \left(\frac{9\pi\gamma R^2}{E^*}\right)^{1/3}\ , \quad \frac{1}{E^*} = \frac{1-\sigma_1^{\,2}}{E_1} + \frac{1-\sigma_2^{\,2}}{E_2}$$

E_1 , E_2 Young's modulus σ_1 , σ_2 :Poisson's ratio

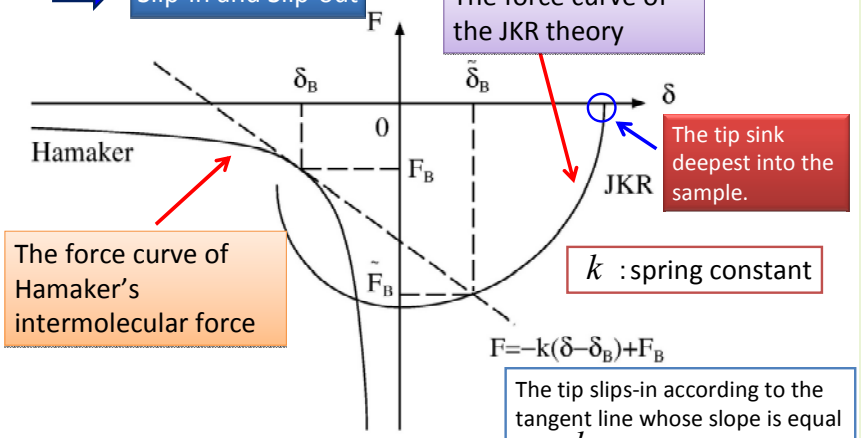
a_0 : The contact area at a zero load. When the tip goes down below the surface of the sample, and the adhesive force of the surface tension and the repulsive force of the elasticity cancel each other out with the tip, the area of their contact is equal to a_0.

$a = a_0 x$:contact area

Transition between a state where van der Waals force works and a state where the JKR theory is effective.

Slip-in and Slip-out

The force curve of the JKR theory



The tip sink deepest into the sample.

The force curve of Hamaker's intermolecular force

k :spring constant

The tip slips-in according to the tangent line whose slope is equal to $-k$.

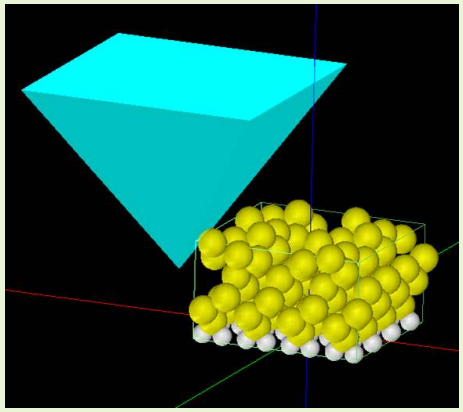
Transition from the theory of van der Waals force to the JKR theory

A Method for Investigating Viscoelastic Contact Analysis

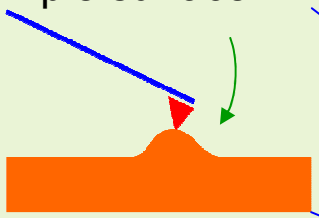
FemAFM

A Method for Investigating Viscoelastic Contact Analysis Mode

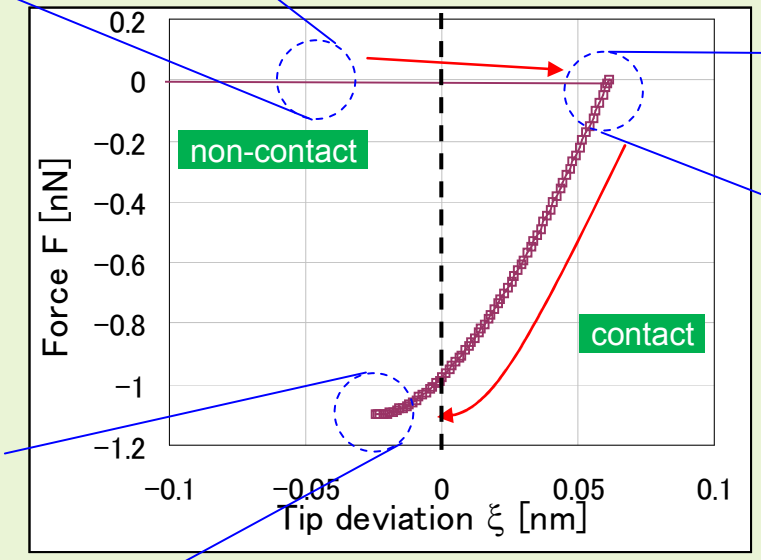
We let a cantilever vibrate at constant frequency by external force. We can simulate successive processes such as making the tip become in contact with the sample surface, making the tip be stuck with the sample by the adhesive force, letting the tip be pushed back upwards outside the sample, and letting the tip leave the sample surface.

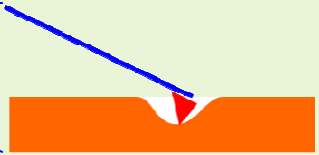


The tip: Pyramidec tip (SiO_2)
The sample: Si(001)

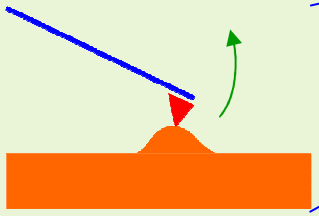


The tip came in contact with the sample above the surface.





The tip is pushed into the interior of the sample.



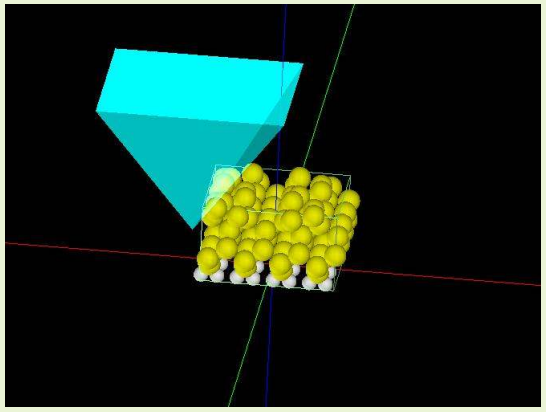
Till the tip leaves the sample.

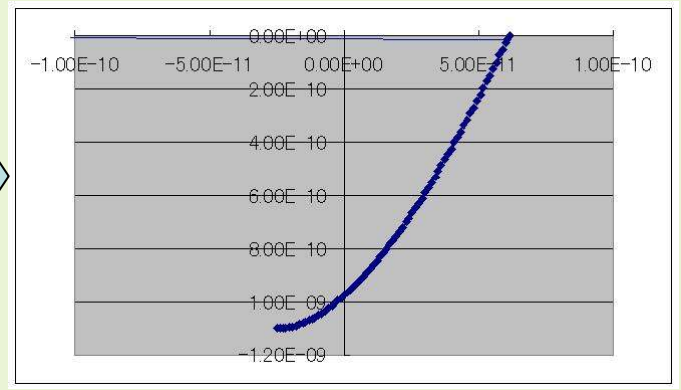
Direction of the force that the tip experienced is positive in the vertical upward direction.

FemAFM

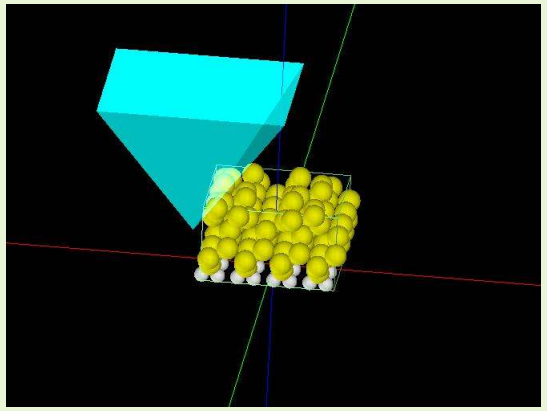
Viscoelastic dynamics mode

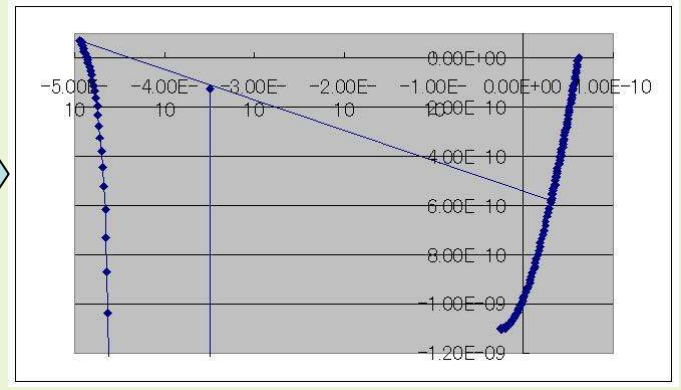
A cantilever is oscillated by an external force with a constant frequency at a single point on the sample surface. A sequential motion of the tip is calculated; the tip contacts to a sample, pushes a sample, and detaches from a sample.





Simulation of the time evolution of the displacement of the tip and the interaction force between the tip and the sample, when the tip contacts to a sample, pushes a sample, and detaches from a sample; in case of a small spring constant.





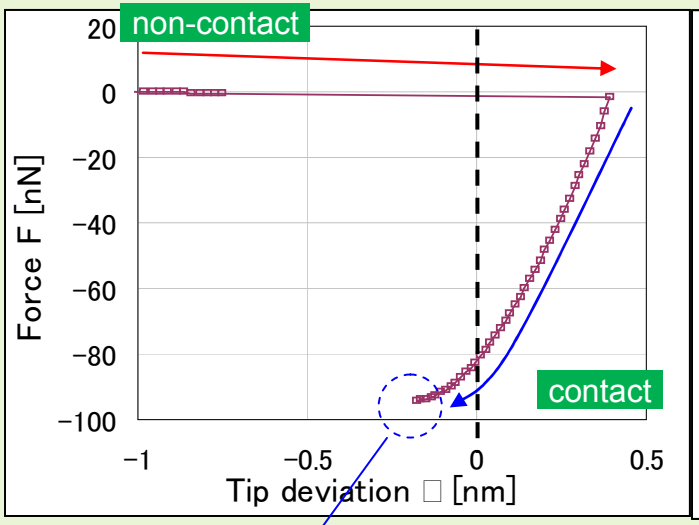
Simulation of the time evolution of the displacement of the tip and the interaction force between the tip and the sample, when the tip contacts to a sample, pushes a sample, and detaches from a sample; in case of a large spring constant.

A Method for Investigating Viscoelastic Contact Analysis

LiqAFM A Method for Investigating Viscoelastic Contact

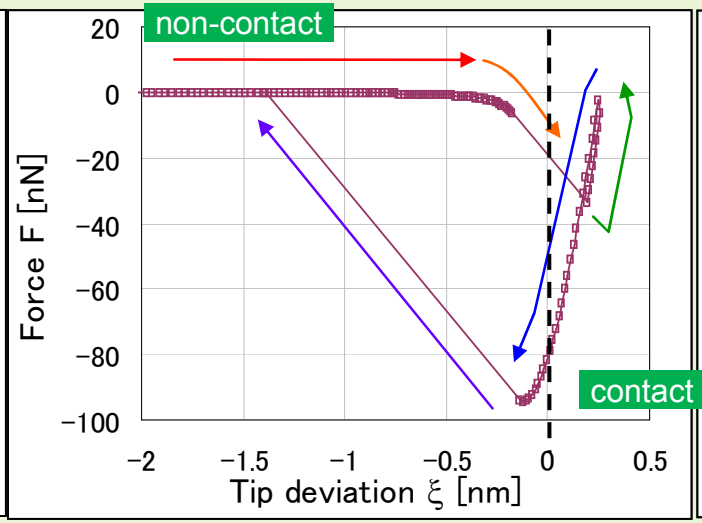
We can simulate a contact between a viscoelastic sample and a tip, and can compute a force curve.

In the case of a cantilever of a small spring constant in vacuum

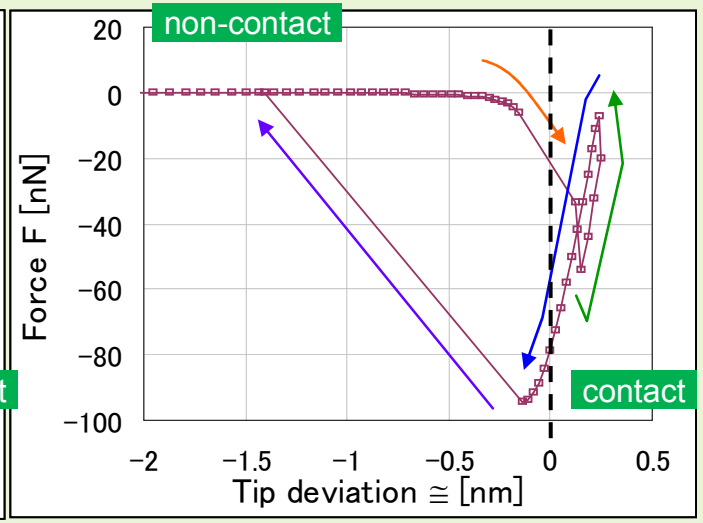


The spring constant is too small that the tip can not overcome adhesion and can not leave the sample.

In the case of a cantilever of a large spring constant in vacuum



In the case of a cantilever of a large spring constant in liquid



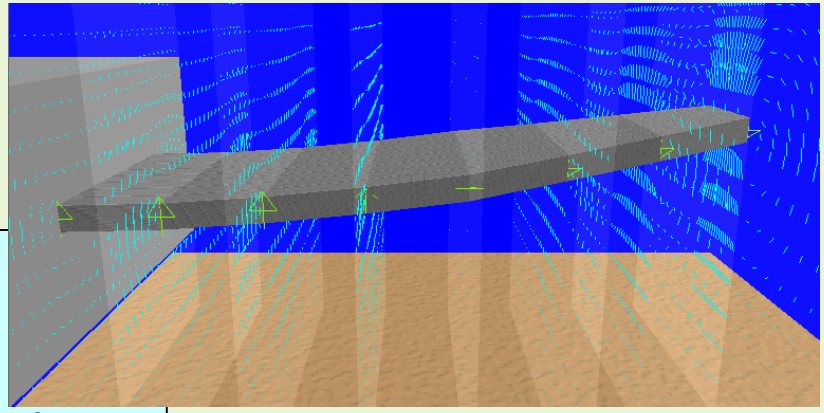
1. The tip moves downwards.
2. The tip becomes in contact with the sample above the surface, and it sinks into the sample.
3. The tip sinks into the sample deepest and the adhesion force become equal to zero.
4. The tip moves upwards.
5. The tip leaves the sample surface.

It is observed that motion of the tip is influenced by fluid in the process of contact between the tip and the sample.

Theory and simulation of dynamic AFM in liquid

LiqAFM

Problem of AFM Theory



Nonlinear effect
Multimode
vibrational
excitation

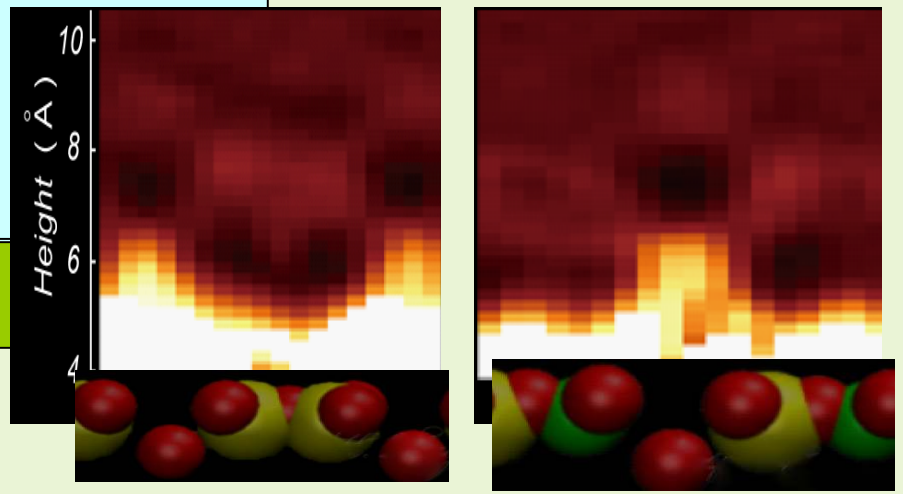
Cantilever oscillation in liquid

Adhesive force
Electric double-
layer

The force affected by
liquid molecules
The structuring of
water

Soft material
Effect of the
viscoelastic
response

AFM image of water on mica
It shows the structuring of water.

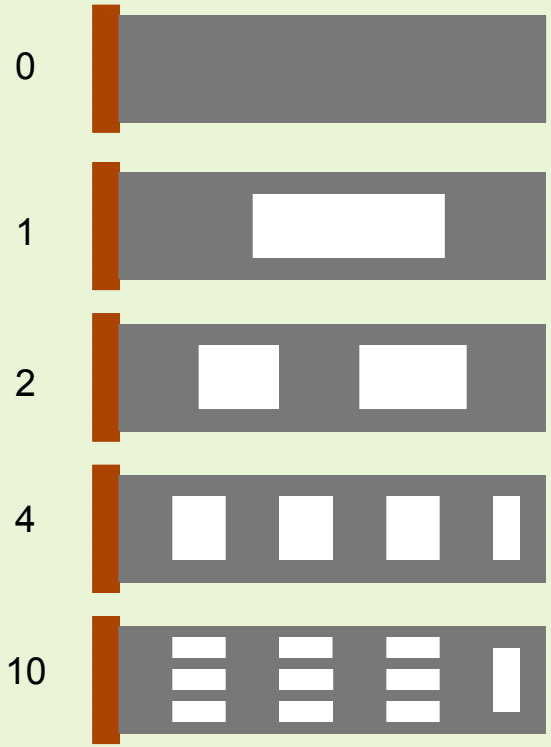


A characteristic oscillation analysis of a cantilever in liquid

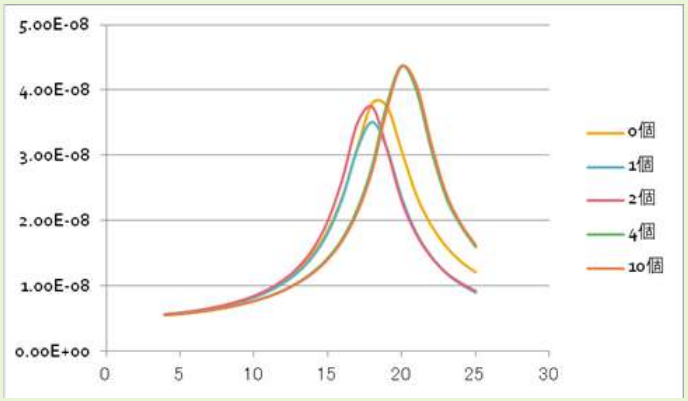
LiqAFM

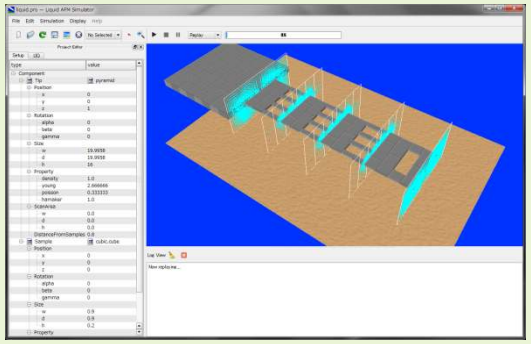
Oscillation of a tabular cantilever in liquid

Making holds on a cantilever



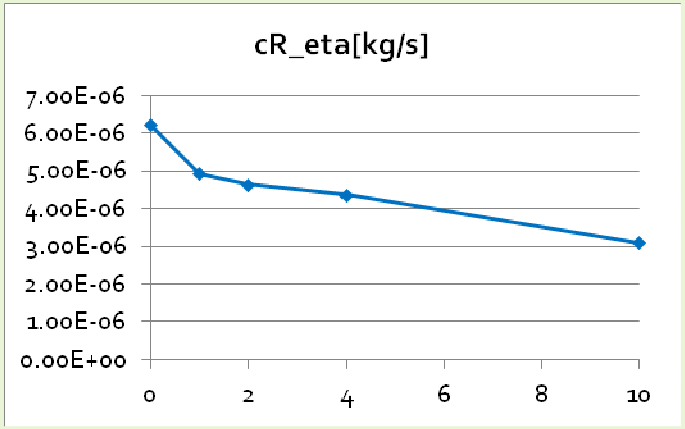
The cantilever is vibrated in liquid. The convergence value of cantilever's amplitude with respect to frequency of forced vibration of the cantilever is calculated.





GUI on which the vibration of a cantilever is simulated.

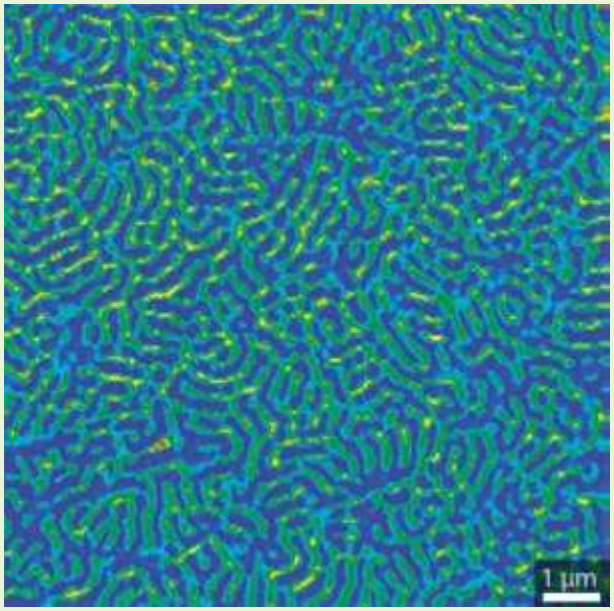
The coefficient of viscous resistance force is gained.



It is understood that the coefficient of viscous resistance force decreases as holes increase.

The prospect to soft material based materials

- In the field of nanobio connection, experiment analysis by the AFM is a tendency to increase.
- The AFM experiments image of biological material such as DNA is measured chronologically.
- The viscoelastic of polymer is measured by AFM measurement.
- Etc.



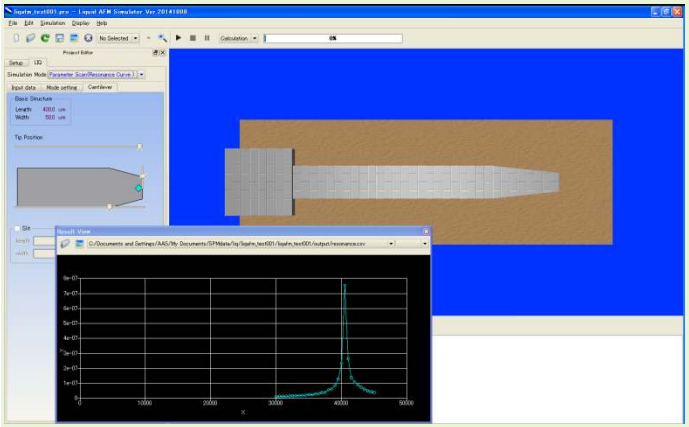
The polymer thin film is observed by AFM,
And its viscoelastic is visualized.
D. Wang et al., Macromolecules 44, 8693–8697 (2011).

The development of our simulator which has a function of the viscoelastic contact analysis become able to simulate such examples.

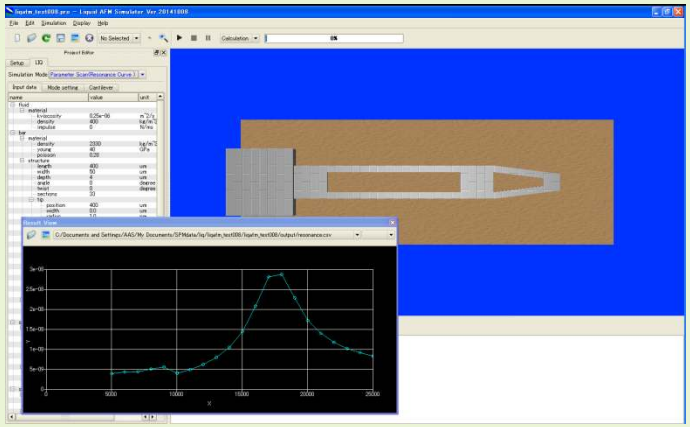
Parameter scan mode

LiqAFM

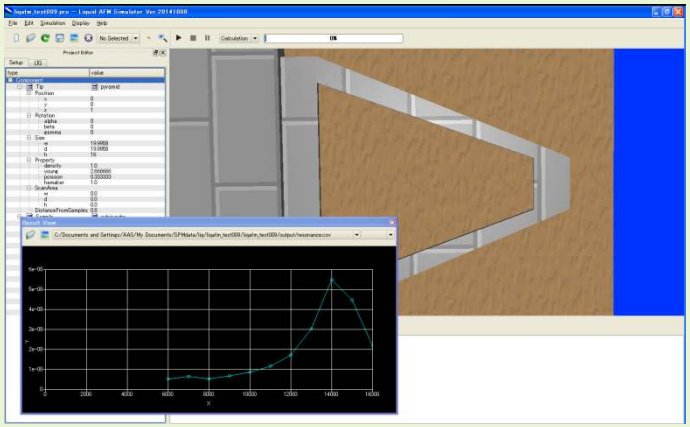
We examine the resonance frequency of the cantilever. At first, we calculate the time evolution of the cantilever motion for a sequence of frequencies, and obtain saturated amplitudes for their frequencies. We then estimate a resonance frequency from a frequency spectrum which is the amplitude of the cantilever vs. the frequency.



We obtain a resonance frequency by simulating a frequency spectrum of a cantilever. **In case of a rectangular cantilver with a single hole in vacuum.**



We obtain a resonance frequency by simulating a frequency spectrum of a cantilever. **In case of a rectangular cantilver with two holes in liquid.**

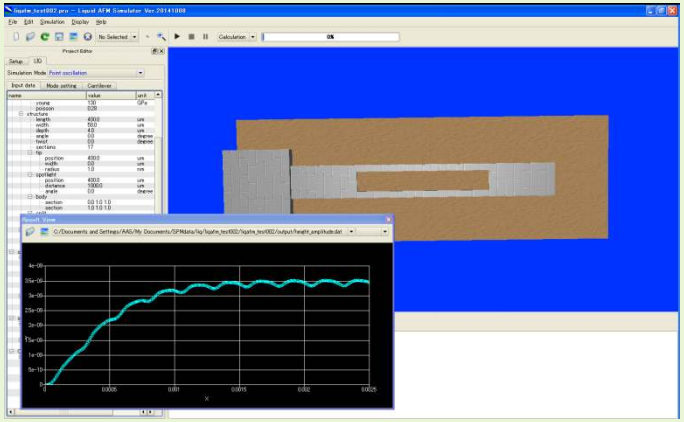


We obtain a resonance frequency by simulating a frequency spectrum of a cantilever. **In case of a triangle cantilver with no hole in liquid.**

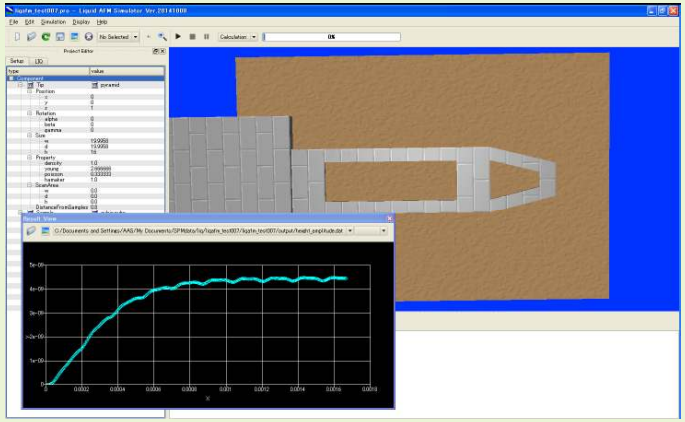
Non-viscoelastic dynamics mode

LiqAFM

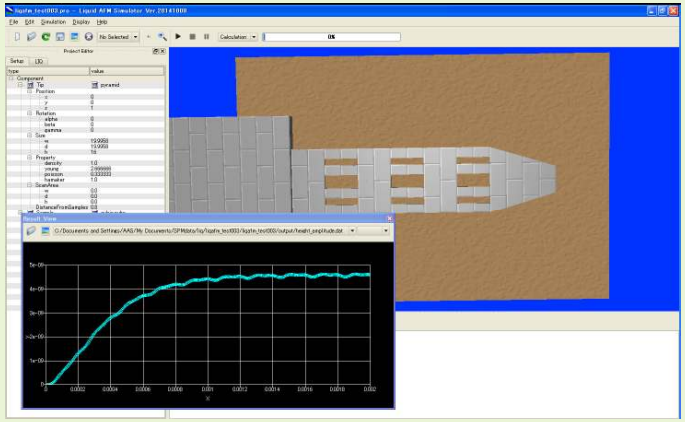
A cantilever is oscillated by an external force with a constant frequency at a single point on the sample surface. A sequential motion of the tip is calculated provided that there is no viscoelasticity of the sample.



•While the external force oscillates the cantilever's tail in liquid, we examine the time evolution of the amplitude of the cantilever's head. The tip is quite far from the sample surface so that the tip does not contact to the sample. **In case of a rectangular cantilver with a single hole.**



•While the external force oscillates the cantilever's tail in liquid, we examine the time evolution of the amplitude of the cantilever's head. The tip is quite far from the sample surface so that the tip does not contact to the sample. **In case of a rectangular cantilver with two holes.**

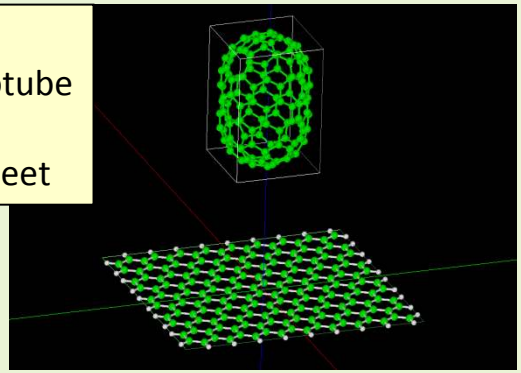


•While the external force oscillates the cantilever's tail in liquid, we examine the time evolution of the amplitude of the cantilever's head. The tip is quite far from the sample surface so that the tip does not contact to the sample. **In case of a rectangular cantilver with a lot of holes.**

The energy curve and the force curve of the system in vacuum / liquid

CG　CG-RISM

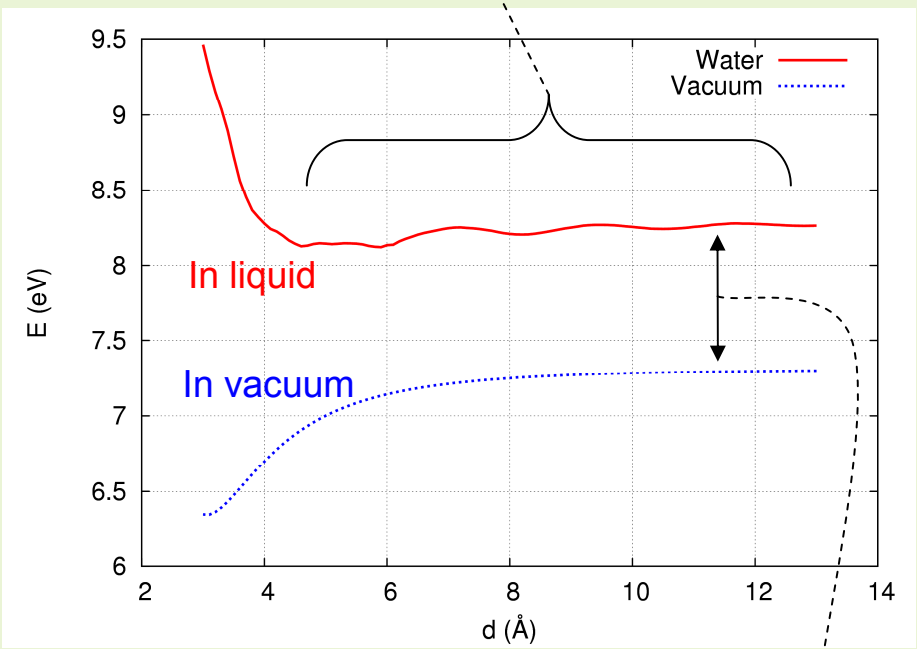
The tip :
　Carbon nanotube
The sample:
　Graphene sheet



Energy of a system

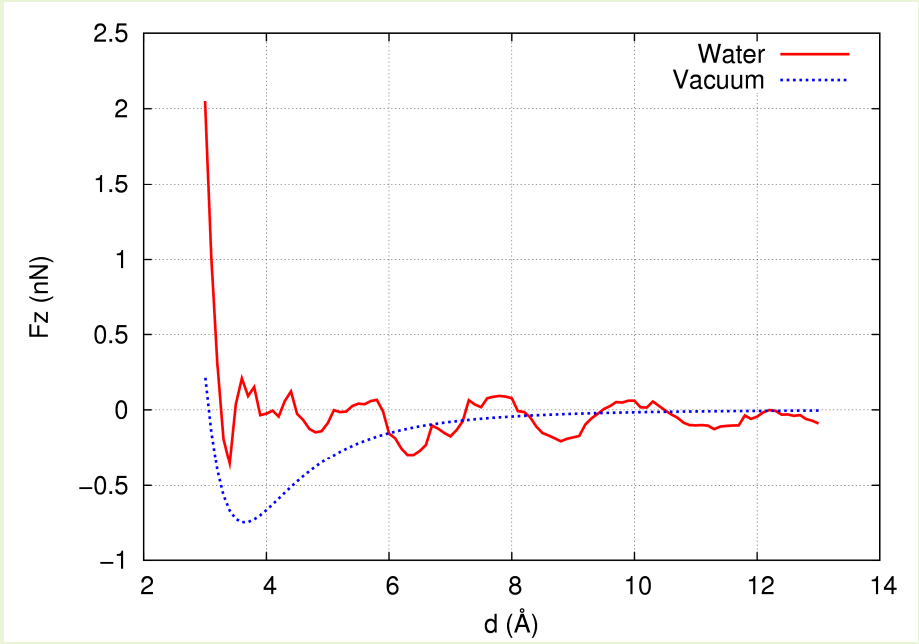
The distance d between the tip and the sample is varied, and the energy of a system is calculated.

Vibration behavior by the hydration structure



Offset by the underwater environment

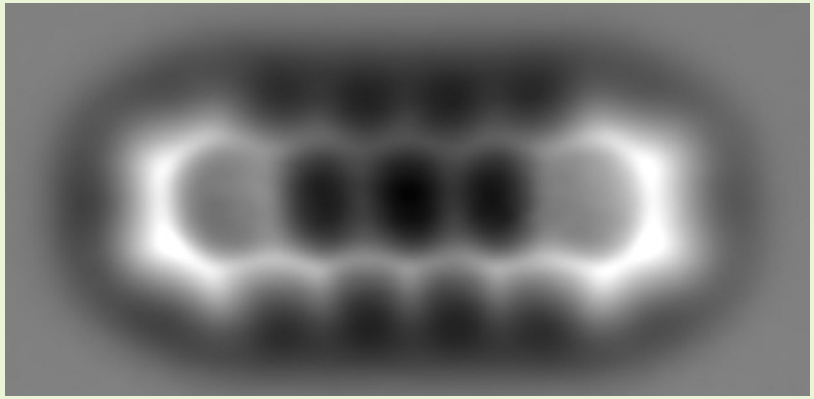
Force curve



(The case of the under the aquatic environment (red line) is a simple numerical differentiation.)

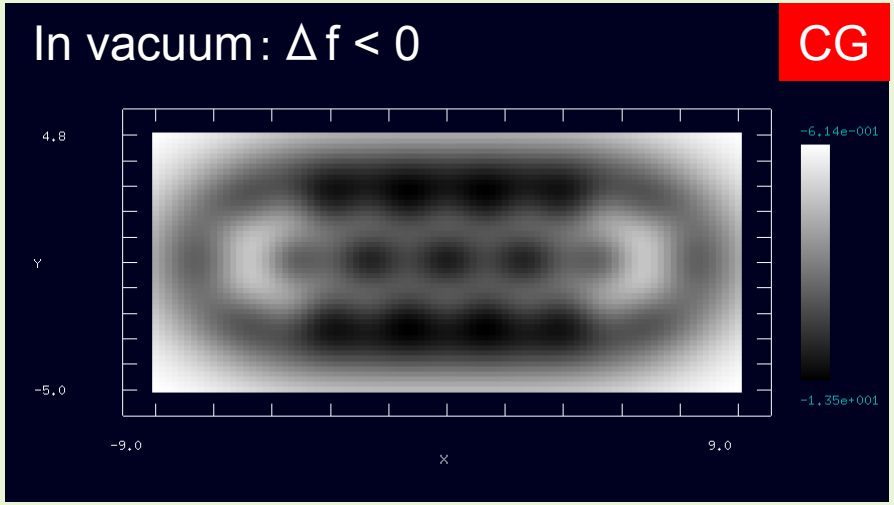
Observation and simulation of AFM frequency shift image of pentacene

The observation of the frequency shift image

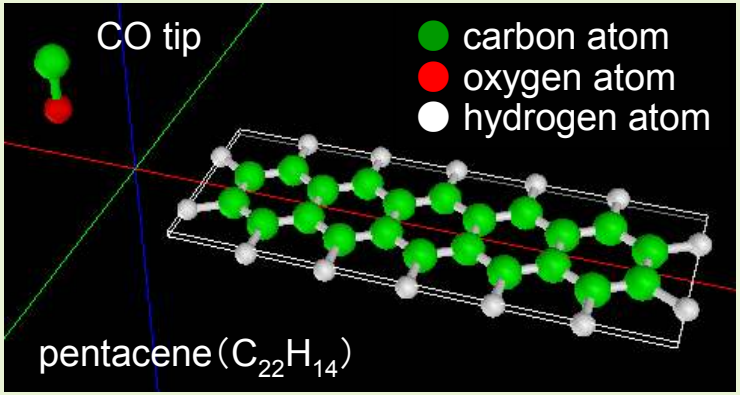


L. Gross *et al.*, Science **325**, 1110-1114 (2009).

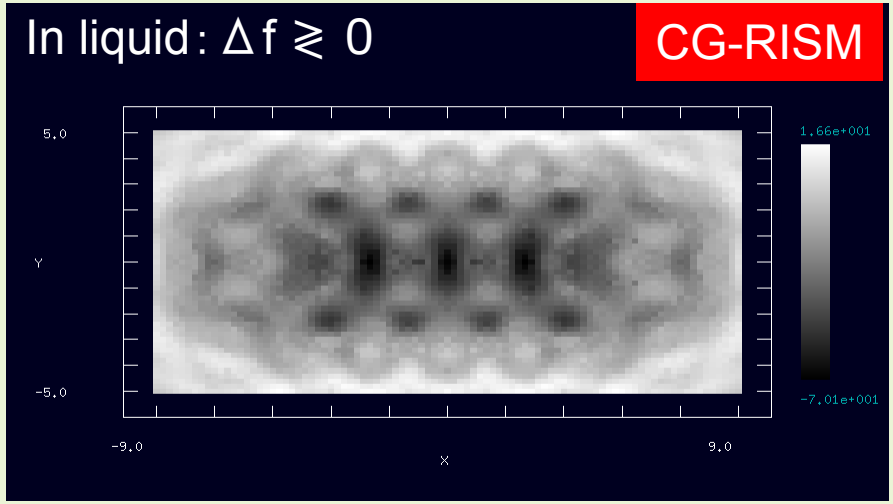
The simulation of the frequency shift image



Good agreement

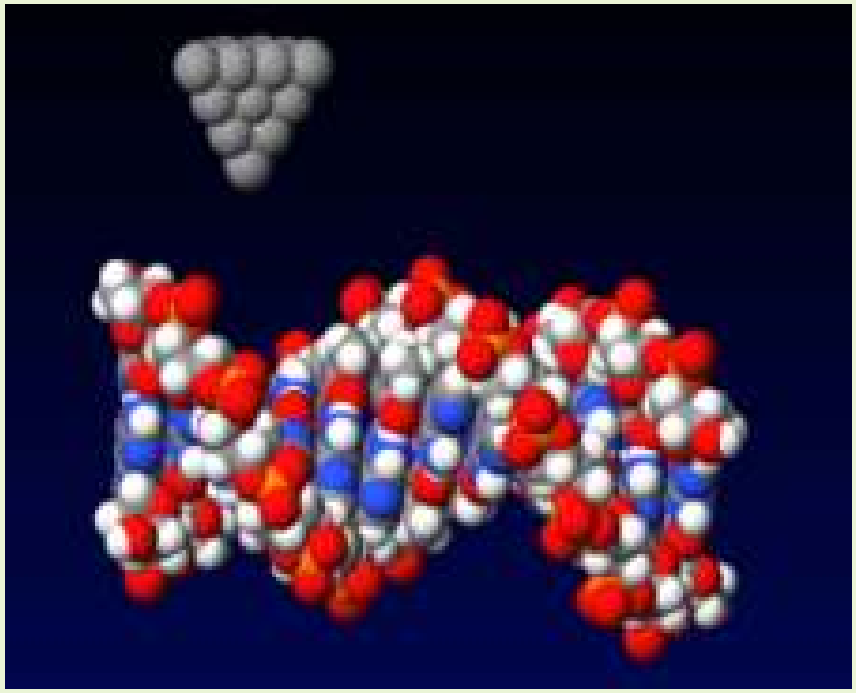


It can also simulate in the case of in water.

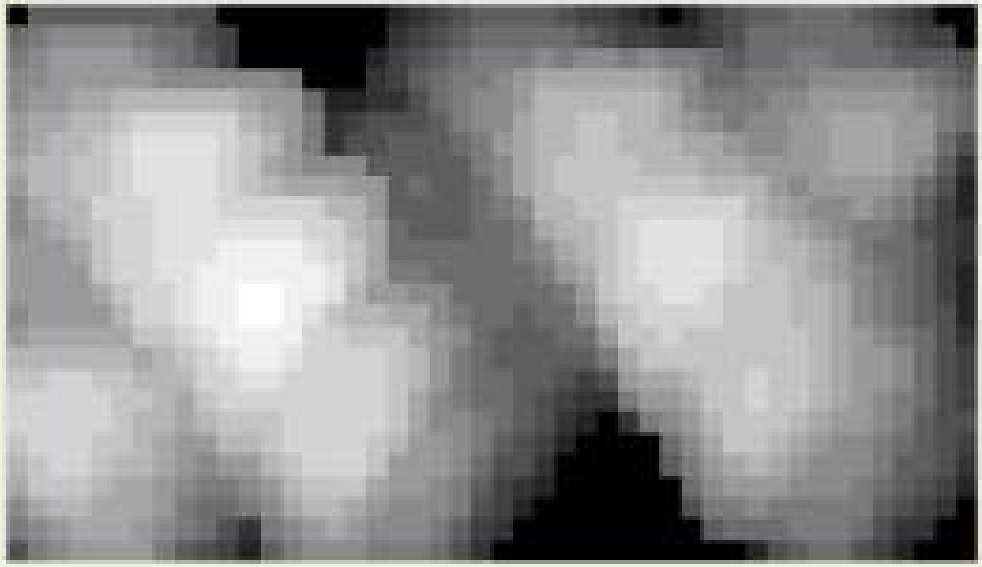


Example of NC-AFM topography image

DNA model

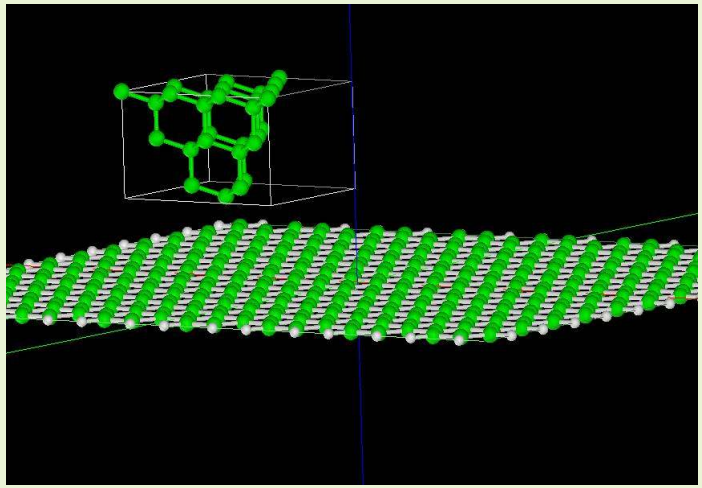


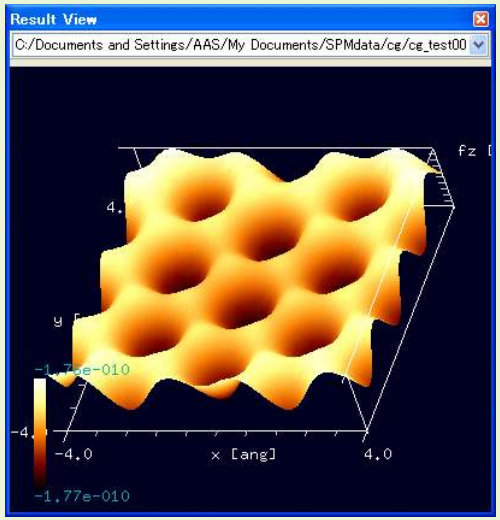
Simulation result



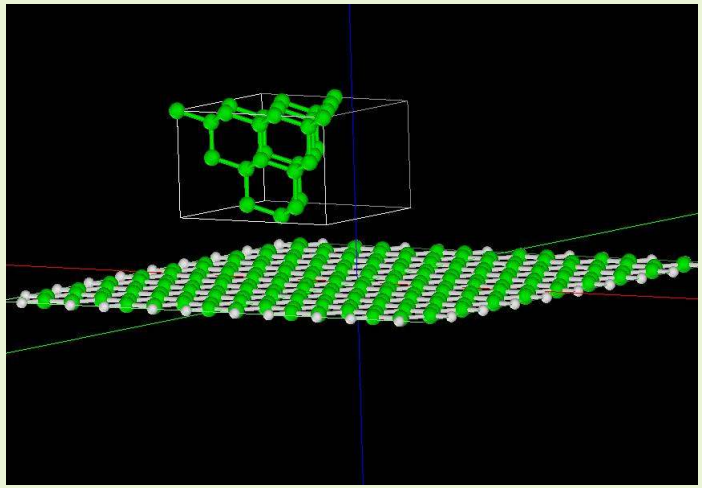
Constant-height mode

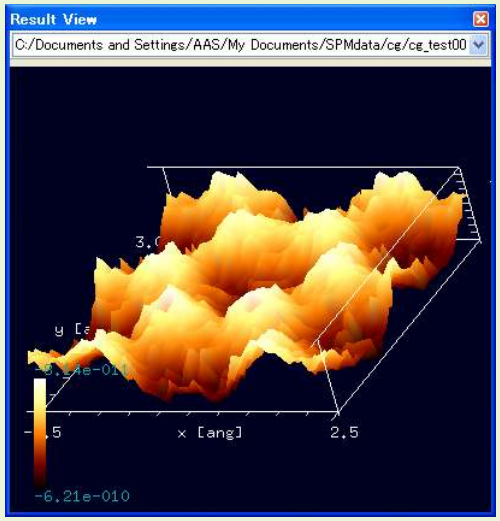
CG CG-RISM We derive the forces to the tip which scans on the sample surface at a constant height.





•The AFM simulation of a graphene sheet by a diamond tip in the constant-height mode; **in vacuum**.



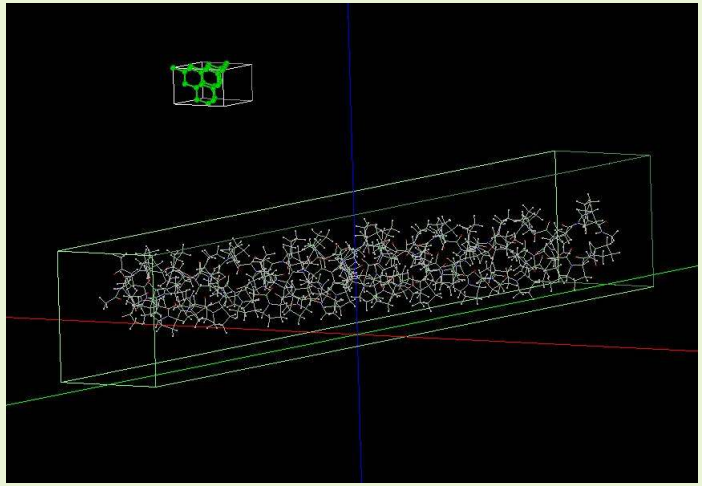


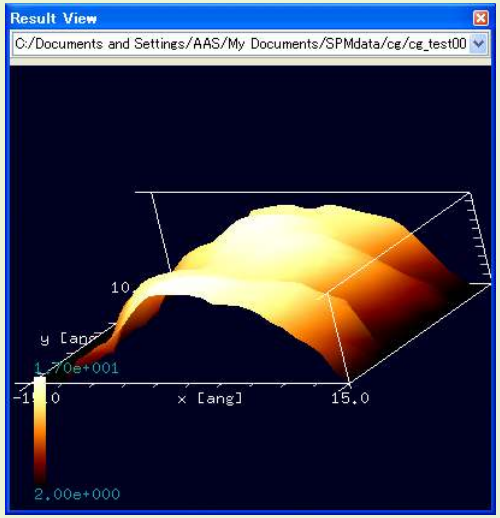
•The AFM simulation of a graphene sheet by a diamond tip in the constant-height mode; **in water**.

Constant-force mode

CG

We search the tip heights on the sample surface where the force to the tip is equal to the specified value. (Not available for a calculation in water)

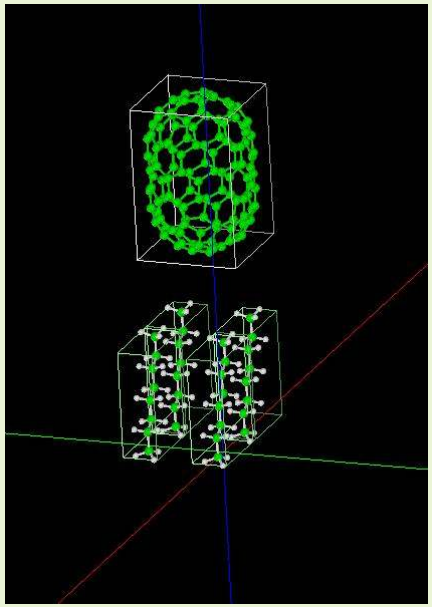


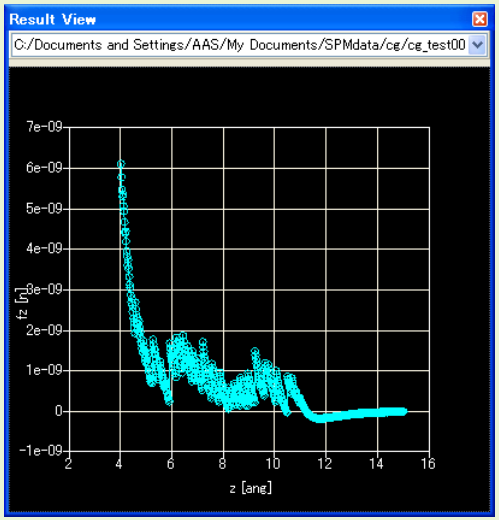


•The simulation of a collagen by a diamond tip in the constant-force mode in vacuum.

Force curve measurement mode

CG CG-RISM We derive the forces to the tip which comes up to the sample at a specified position on the sample surface.

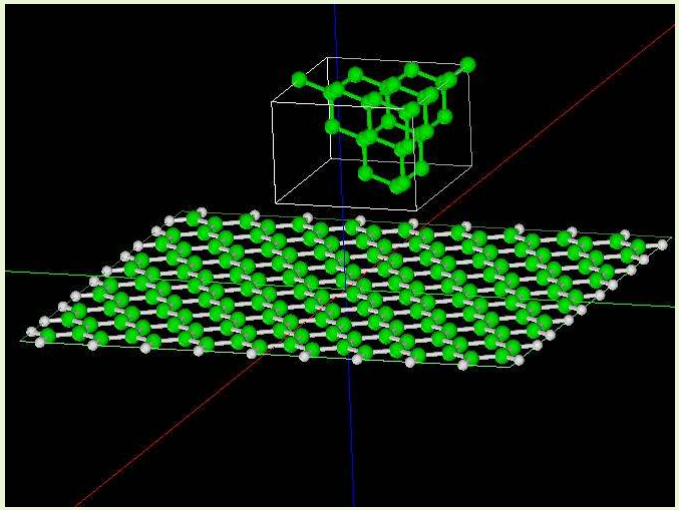


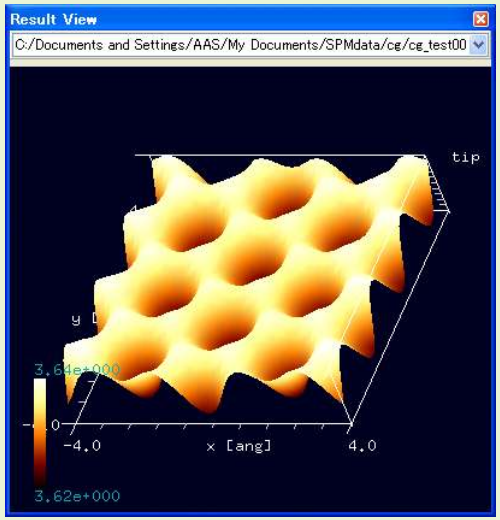


•The force curve simulation of a set of four octance chains by a carbon nanotube tip in the force curve measurement mode in vacuum, considering that the deformation of the atomic configuration in the sample molecules.

Minimum power mode

CG We search the tip heights on the sample surface where the force to the tip may be minimum. (Not available for a calculation in water)





•The simulation of a graphene sheet by a diamond tip in the minimum power mode in vacuum.

Case study of Classical Force Field AFM Simulator

MD

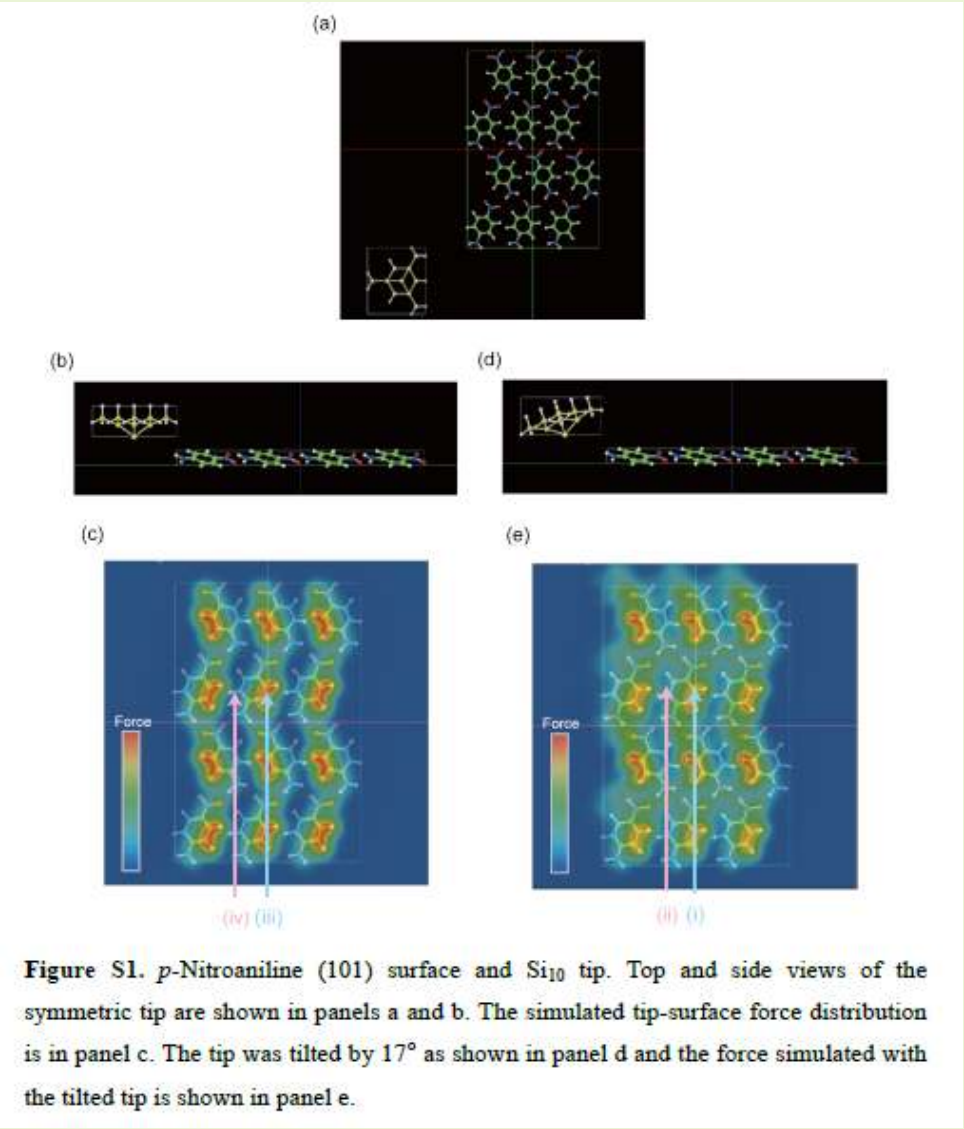


Figure S1. *p*-Nitroaniline (101) surface and Si_{10} tip. Top and side views of the symmetric tip are shown in panels a and b. The simulated tip-surface force distribution is in panel c. The tip was tilted by 17° as shown in panel d and the force simulated with the tilted tip is shown in panel e.

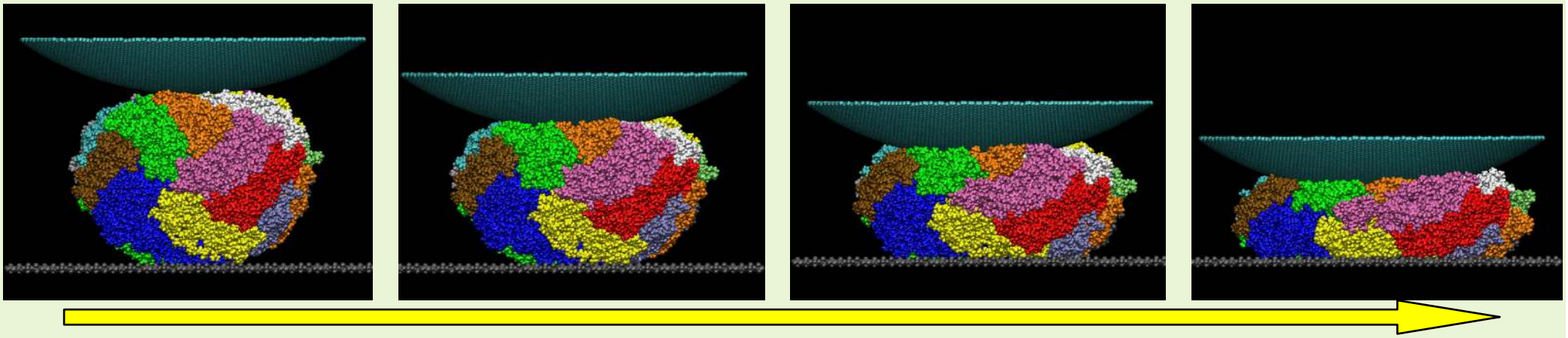
The simulator was utilized in Onishi Laboratory, Department of Chemistry, Kobe University.
（Nishioka et al., J. Phys. Chem. C 117, 2939-2943 (2013).）

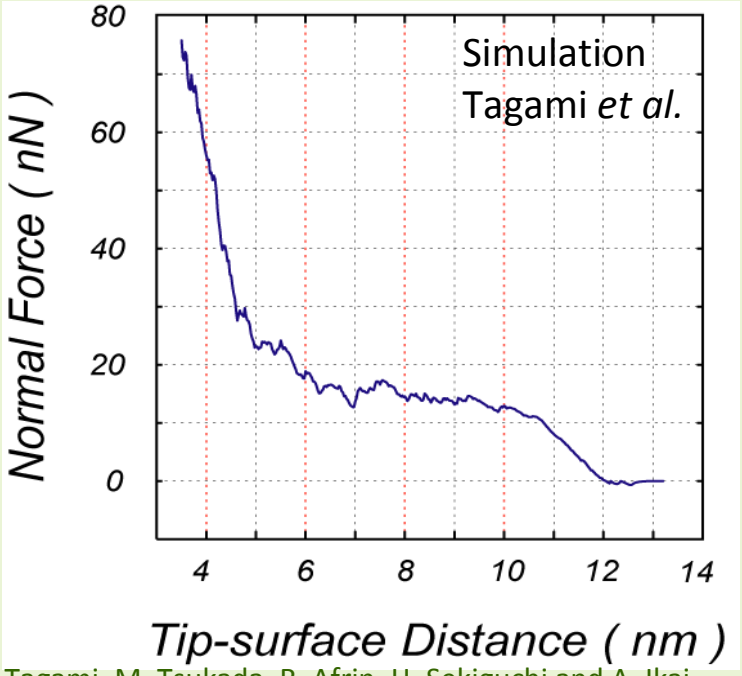
Lower left: the force map of the surface of p-nitroaniline crystal by our "Molecular Dynamics AFM Image Simulator (MD)"
(It appears on Supporting Information of the above thesis.)

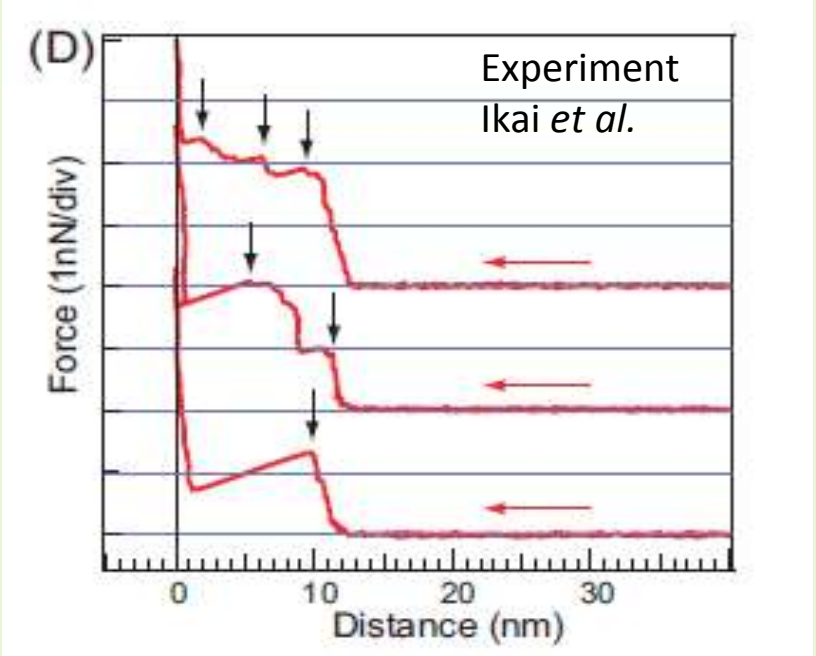
It was used for interpreting of the observed constant frequency shift topography, and it gave a theoretical support on the consideration that the main reason for significantly changing the topography is due to the tilted tip.

Compression simulation of apo-ferritin

MD **Nano-mechanical experiments of protein molecule**







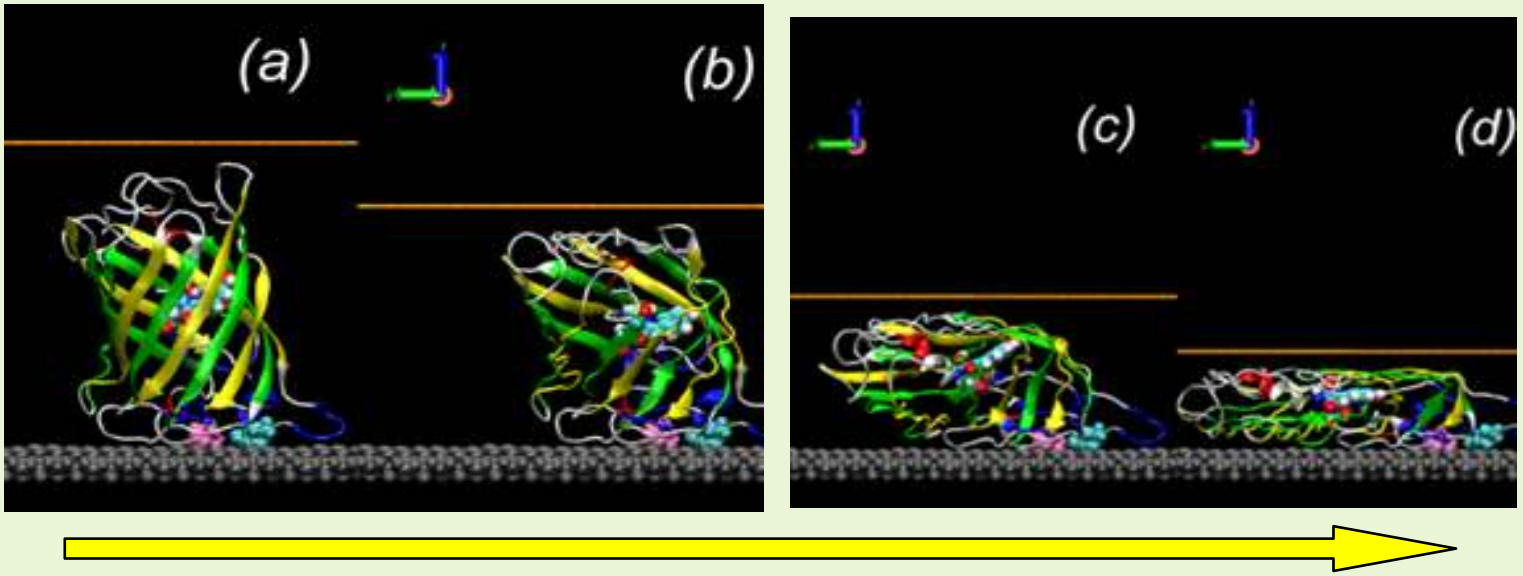
K. Tagami, M. Tsukada, R. Afrin, H. Sekiguchi and A. Ikai,
e-J. Surf. Sci. Nanotech. 4, 552-558 (2006).

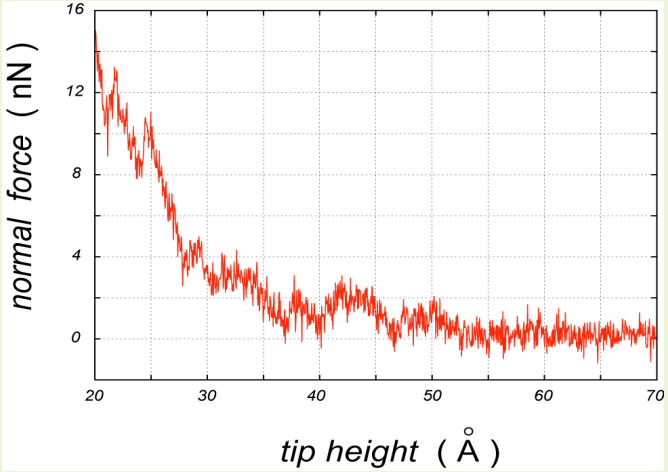
Compression simulation of GFP

MD **Nano-mechanical experiments of protein molcule**

GFP = Green Fluorescent Protein

MD simulation of compression

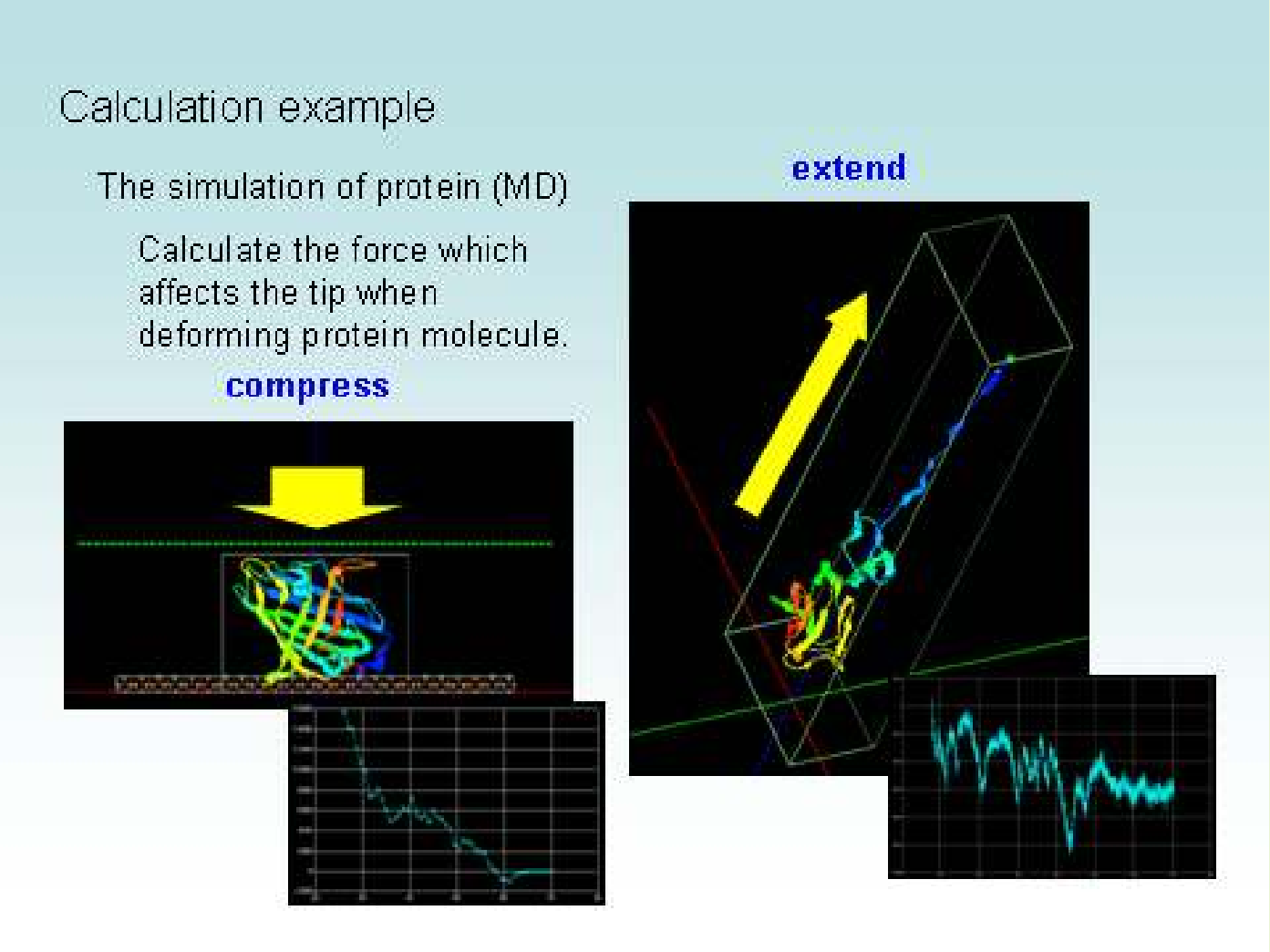




Q. Gao, K. Tagami, M. Fujihira and M. Tsukada, Jpn. J. Appl. Phys., 45, L929 (2006).

Compression and extension experiments of protein molecules by MD

MD **Nano-mechanical experiments of protein molecule**

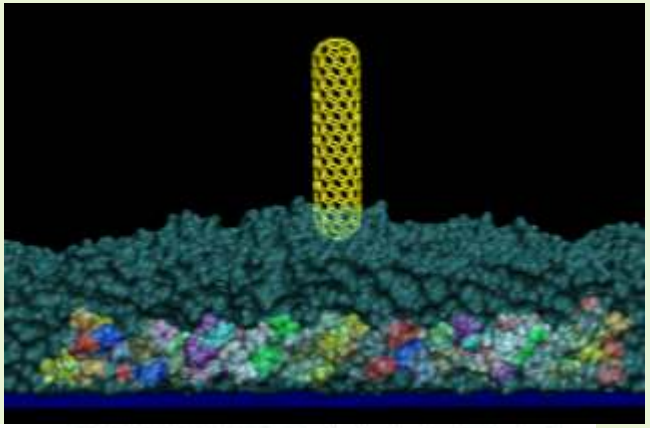


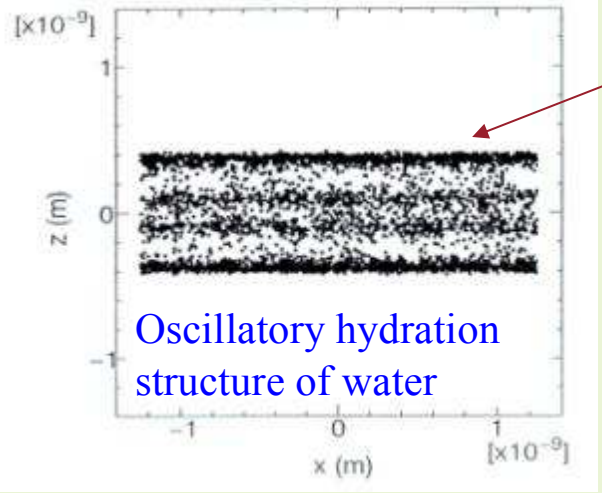
MD can calculate the force curve of simulation which is the compression/extension of protein molecules by the graphite tip.

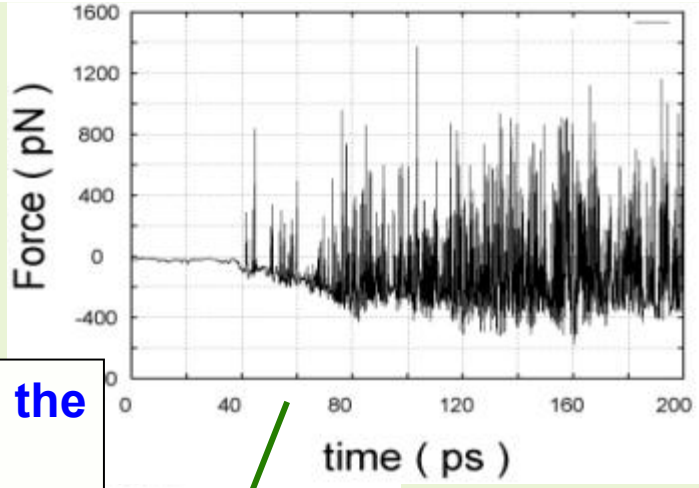
Microscopic structures of water in the vicinity of the object

MD **In the case of Collagen @ graphite**

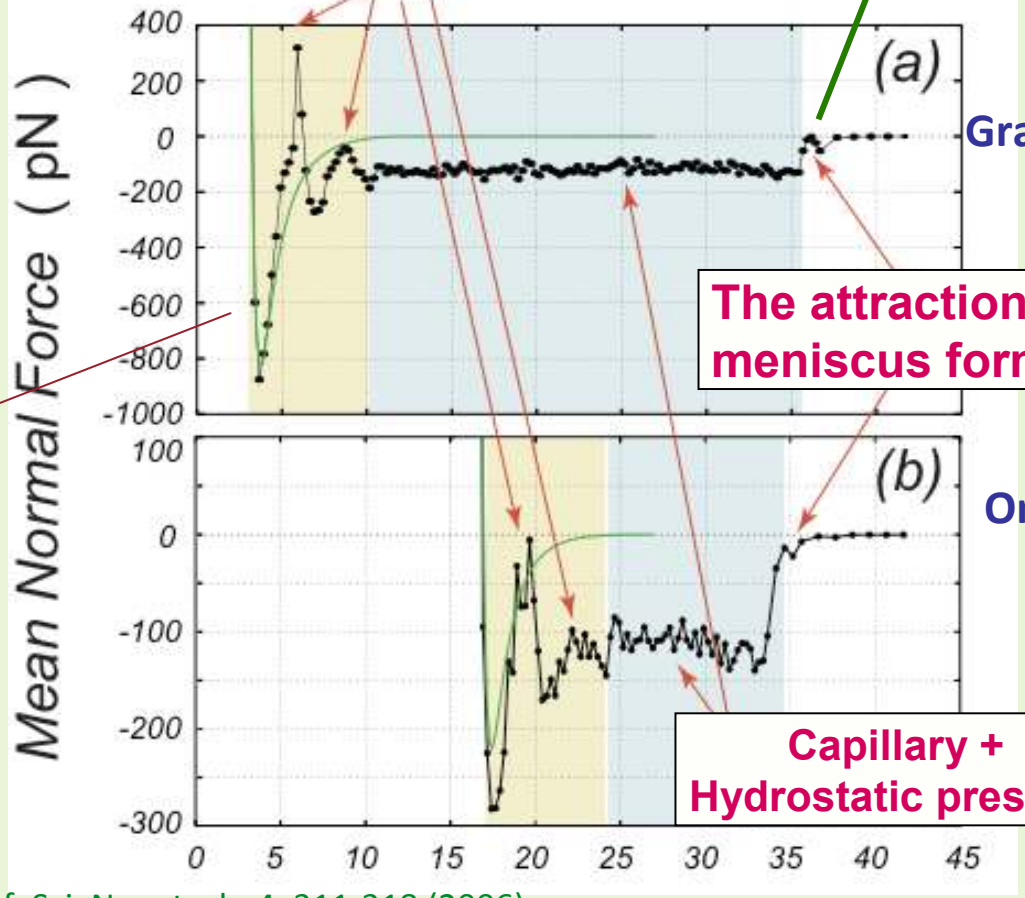
AFM simulation by classical molecular dynamics method (CNT tip)







Oscillatory force reflects the hydration structure



Graphite substrate

The attraction by meniscus formation

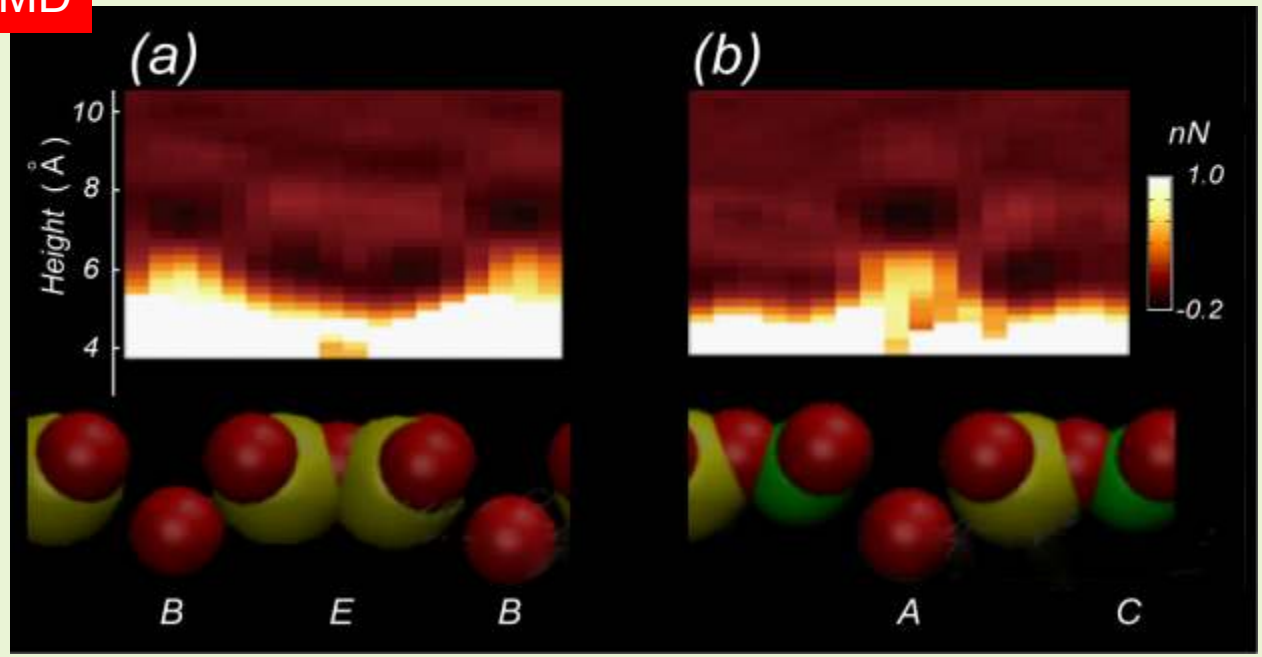
On Collagen

Capillary + Hydrostatic pressure

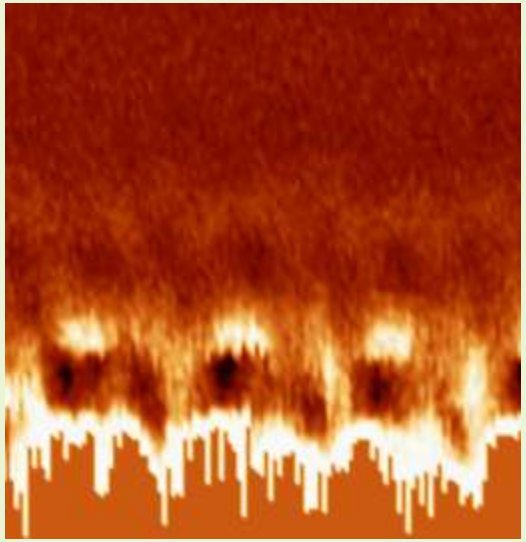
K. Tagami and M. Tsukada, e-J. Surf. Sci. Nanotech. 4, 311-318 (2006).

Interfacial structure of mica surfaces and water

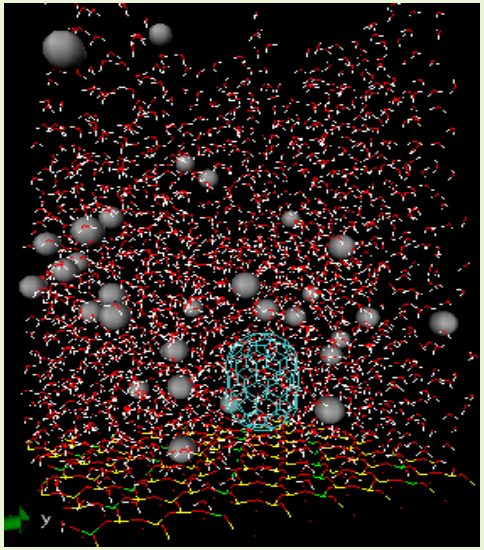
MD **Aspect of force distribution** **Hydration structure is in 3D basis.**



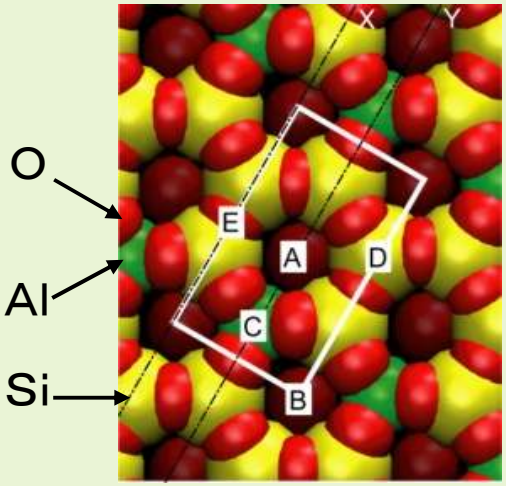
AFM experiment
(The original image is provided by Professor Yamada, Kyoto University.)



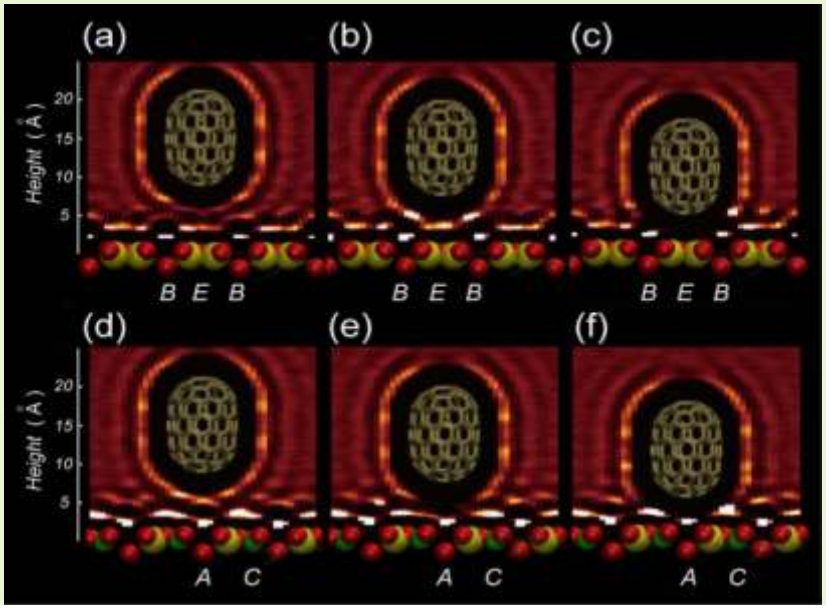
Snapshot in MD



Mica sample model



Distribution of water molecules

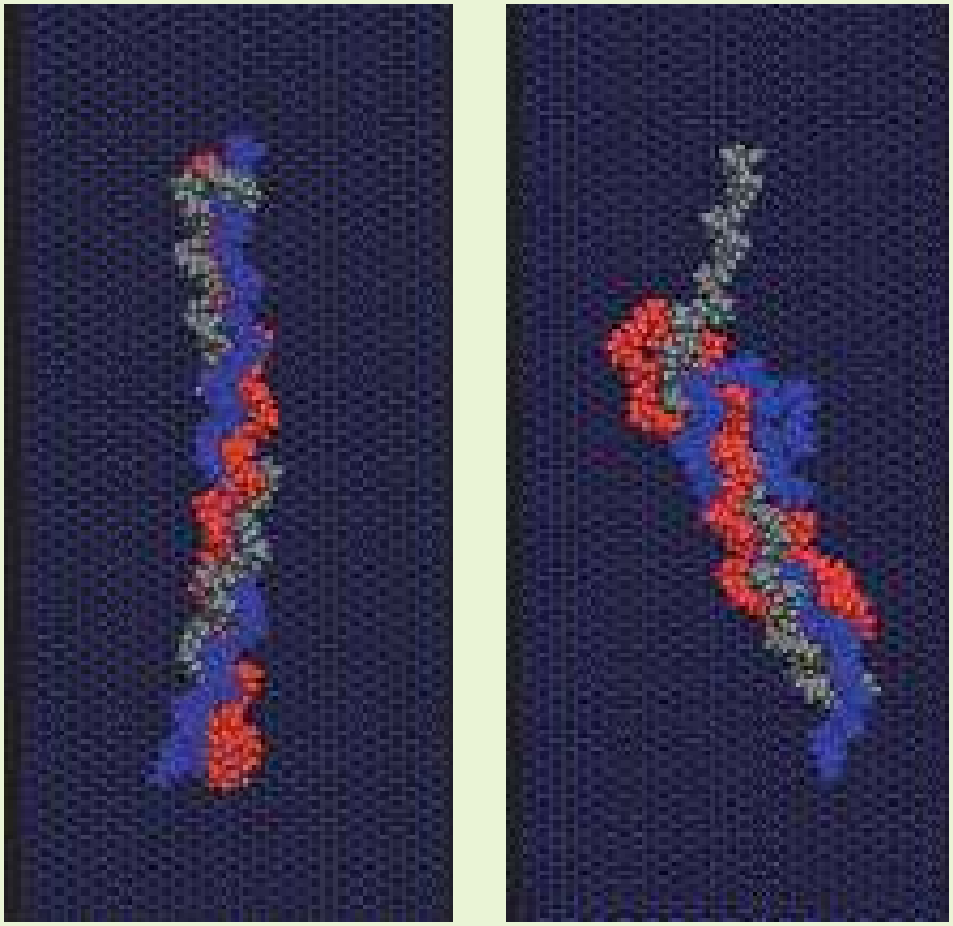


AFM imaging simulation of collagen on the HOPG substrate

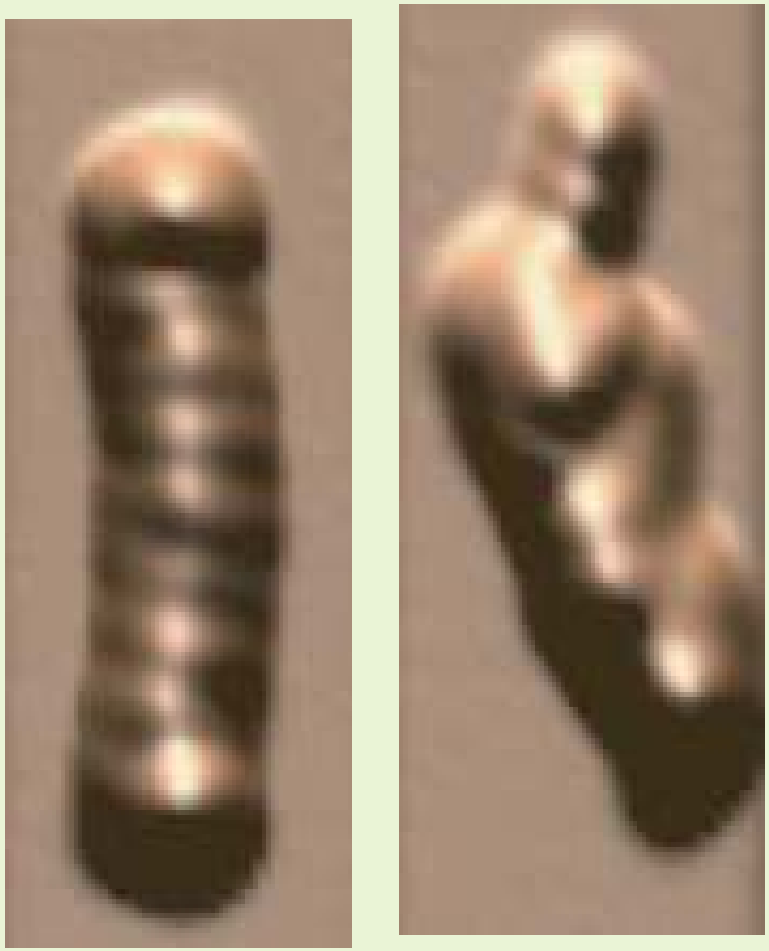
Example of AFM imaging simulation

AFM imaging of collagen adsorbed to the HOPG substrate

Molecular model



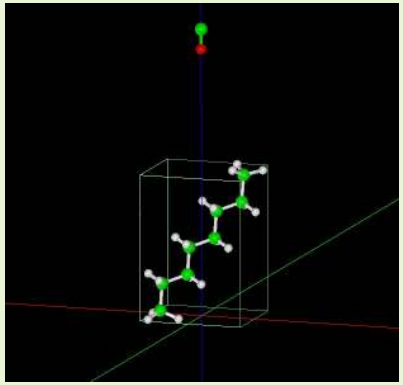
Simulation result

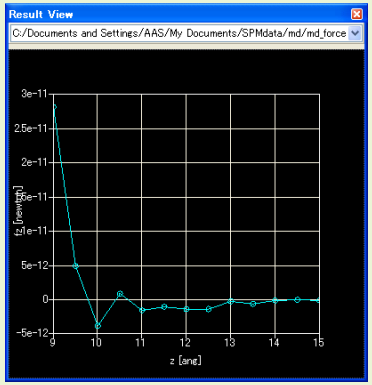


Katsunori Tagami and Masaru Tsukada, e-J. Surf. Sci. Nanotech. Vol. 4 (2006) 294-298.

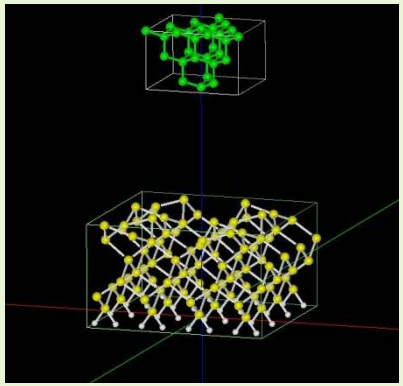
Force curve measurement mode

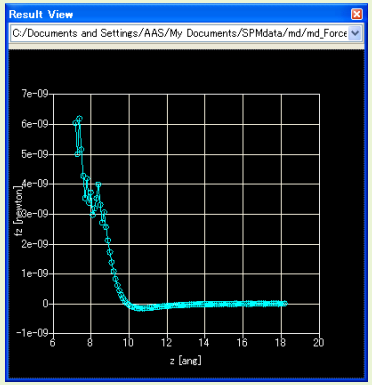
MD We derive the forces to the tip which comes up to the sample at a specified position on the sample surface.



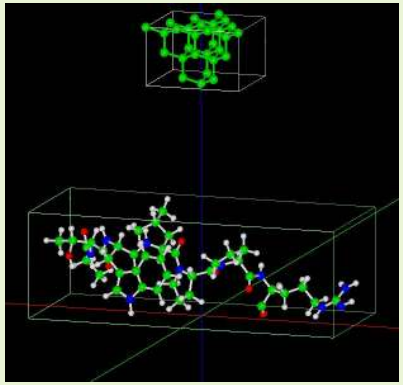


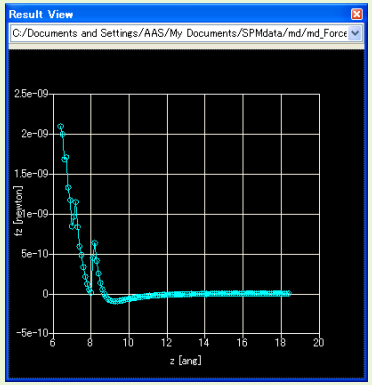
•The force curve of an octane molecule.





•The force curve of a Si(001) surface.

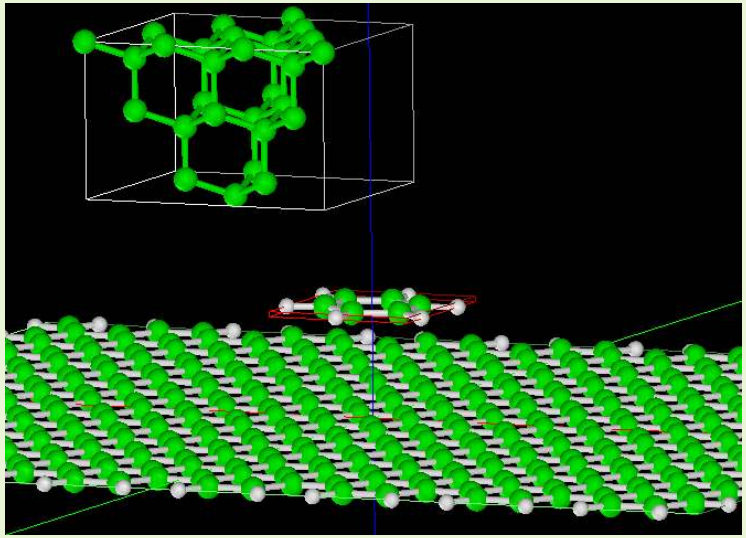


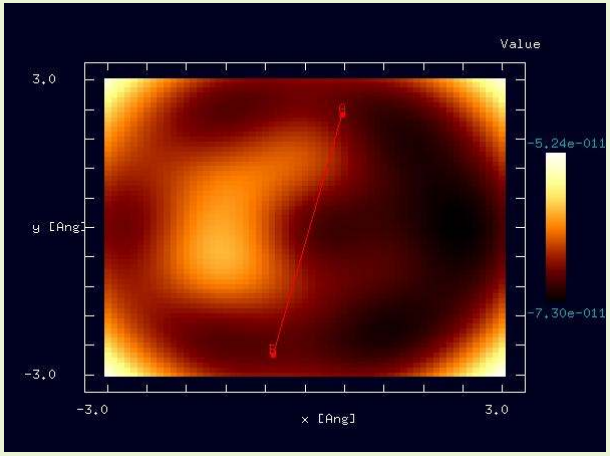


•The force curve of the antiangiogenic ATWLPPR peptide.

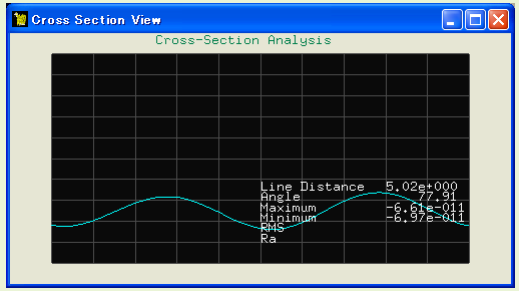
Constant-height mode

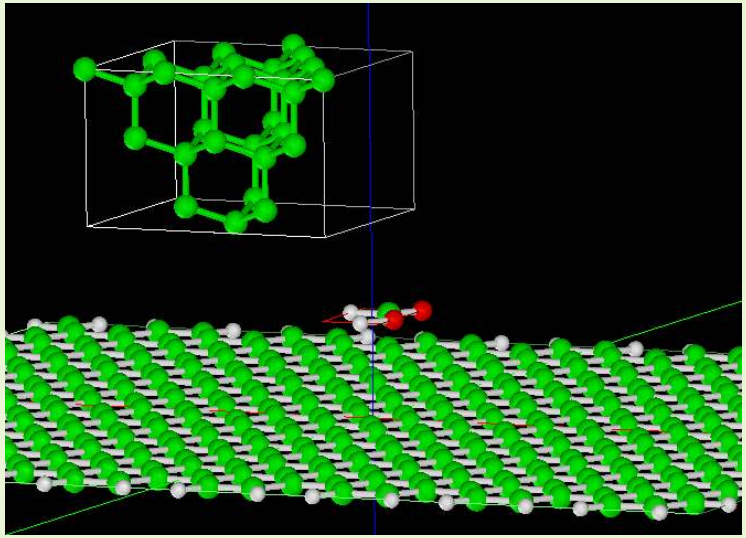
MD We derive the forces to the tip which scans on the sample surface at a constant height.

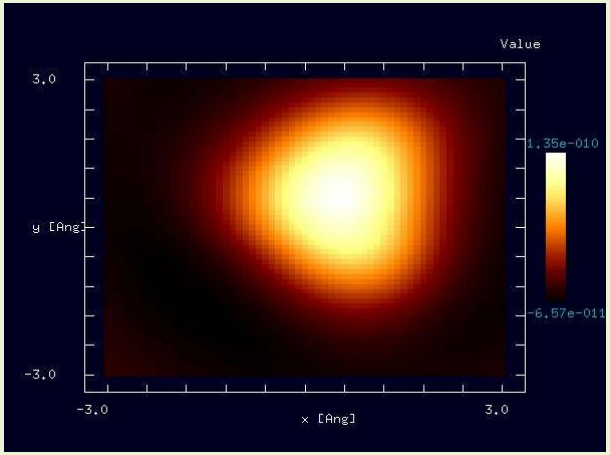




•The simulation of the forces to the tip on a benzene on HOPG in constant-height mode.





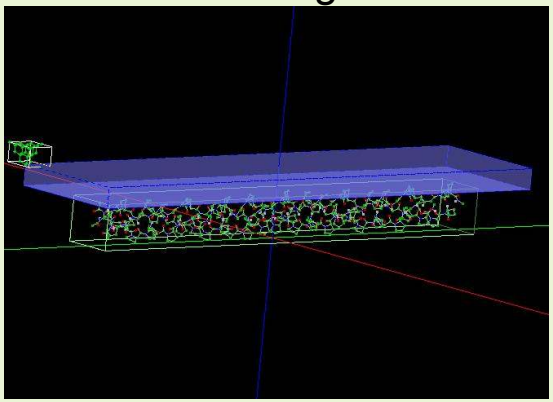


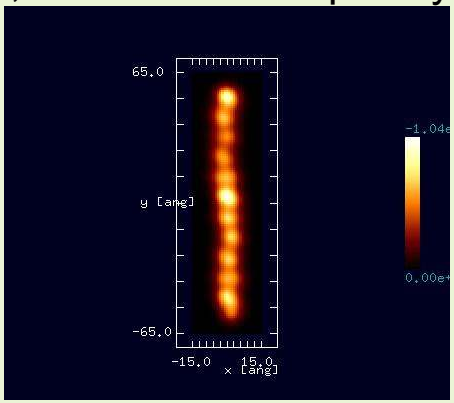
•The simulation of the forces to the tip on a formic acid on HOPG in constant-height mode.

Non-contact mode height constant

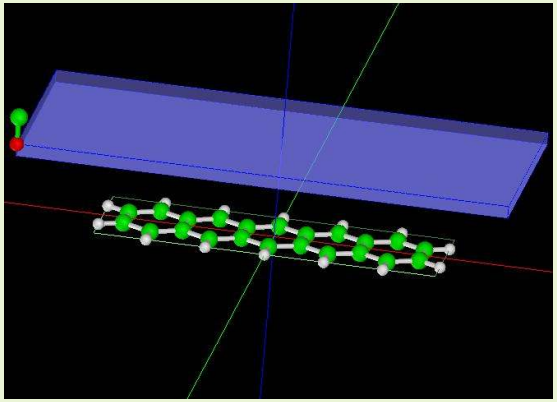
MD

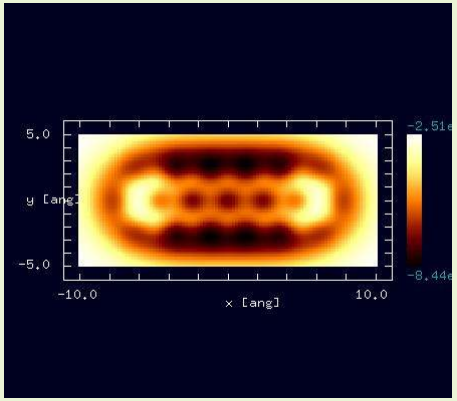
We derive the forces to the tip which scans on the sample surface while oscillating around a constant height. As a result, we obtain a frequency shift image and an energy dissipation image.



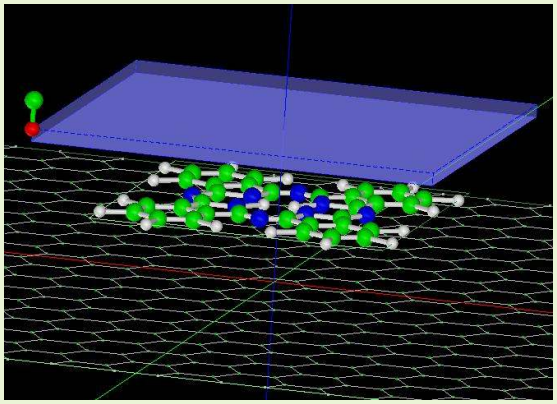


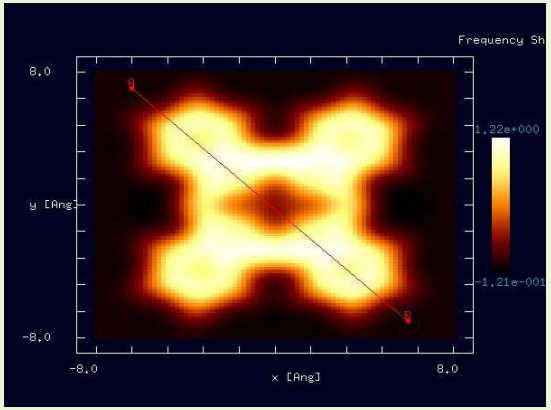
•The simulation of the frequency shift image of a **collagen** in the non-contact mode.



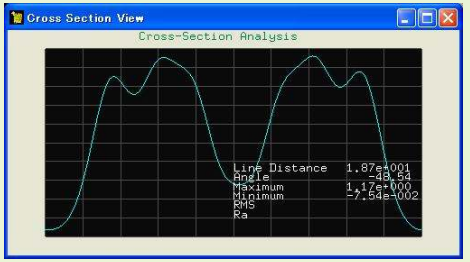


•The simulation of the frequency shift image of a **benzene** in the non-contact mode.





•The simulation of the frequency shift image of a **phthalocyanine** in the non-contact mode.

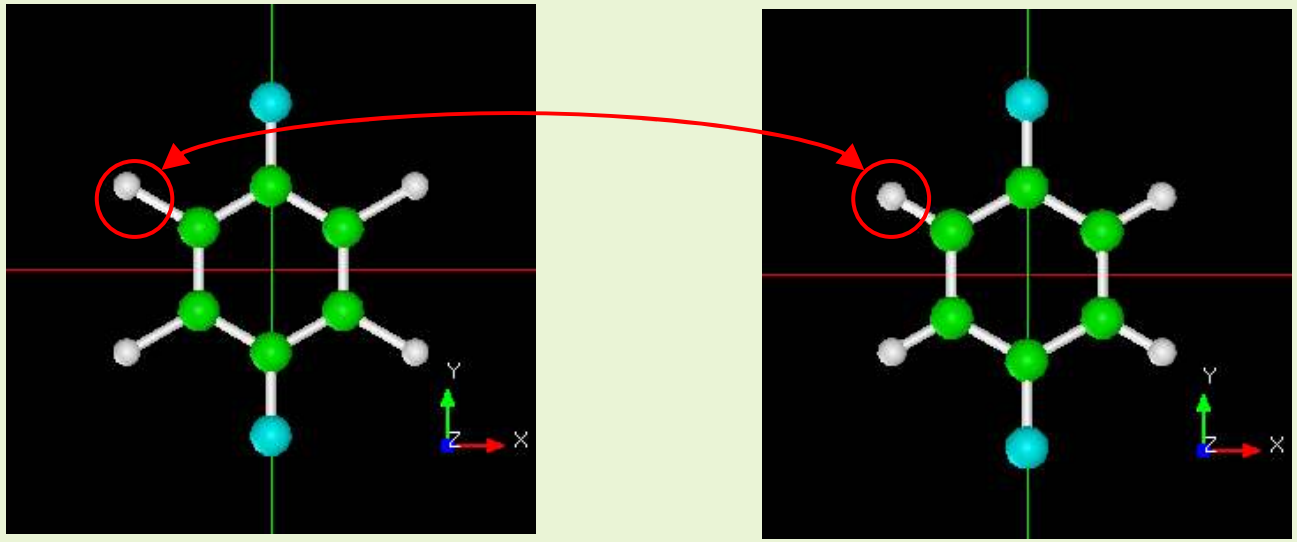


Relaxation

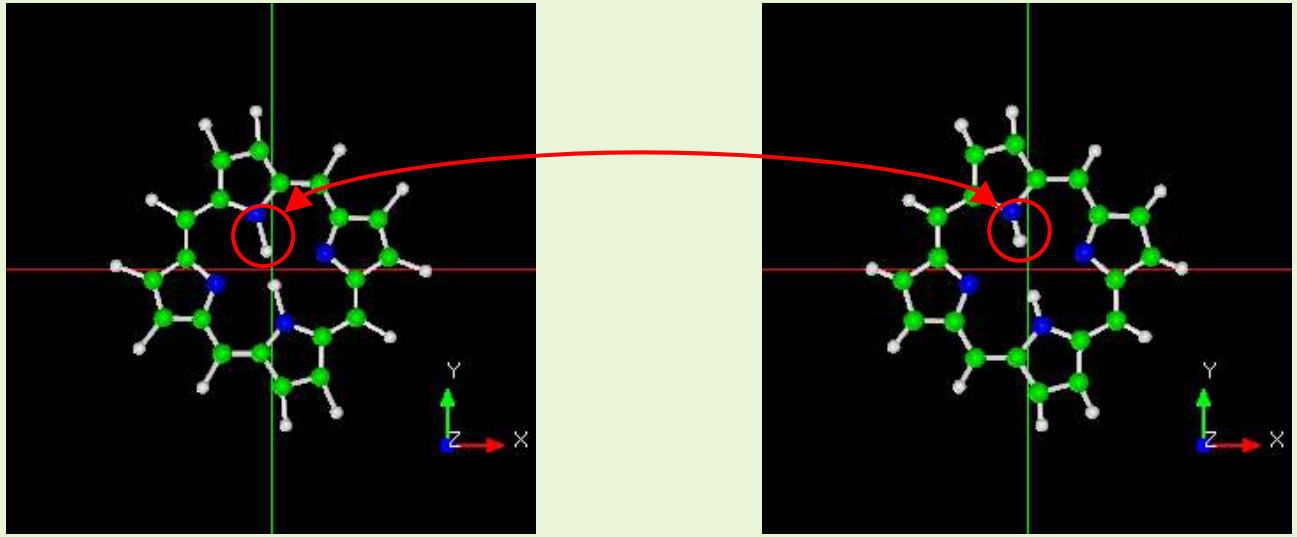
MD We calculate the structural relaxation of a sample molecule as a preparation for a simulation.

Before

After



The structural relaxation of a **dichlorobenzene**



The structural relaxation of a **porphyrin**

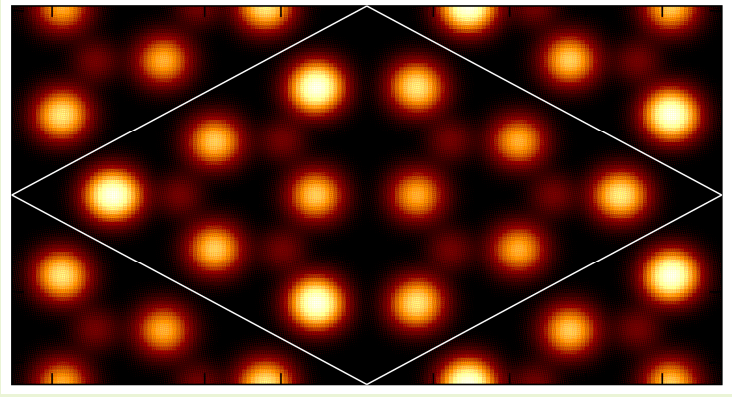
Simulation of STM by Bardeen's perturbation method and DFTB method

-Calculation of the tunneling current-

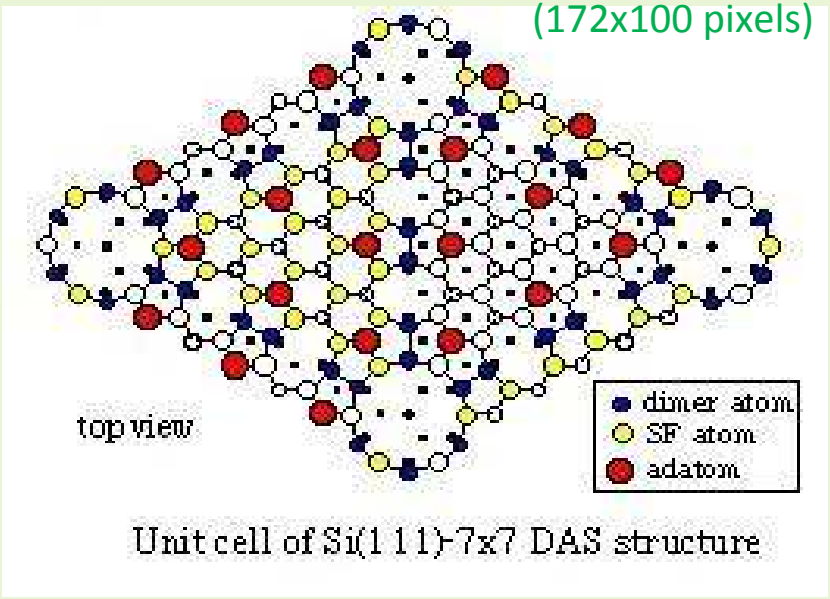
DFTB **STM simulation**

Si_4H_9 tip; tip height = 4.0 Å

$$I(\mathbf{R},V)=\frac{2\pi e}{\hbar}\int_{E_F^L}^{E_F^R}\sum_{ii'jj'}G_{ii'}^{S}(E)J_{i'j'}(\mathbf{R})G_{j'j}^{T}(E+eV)J_{ji}(\mathbf{R})dE$$

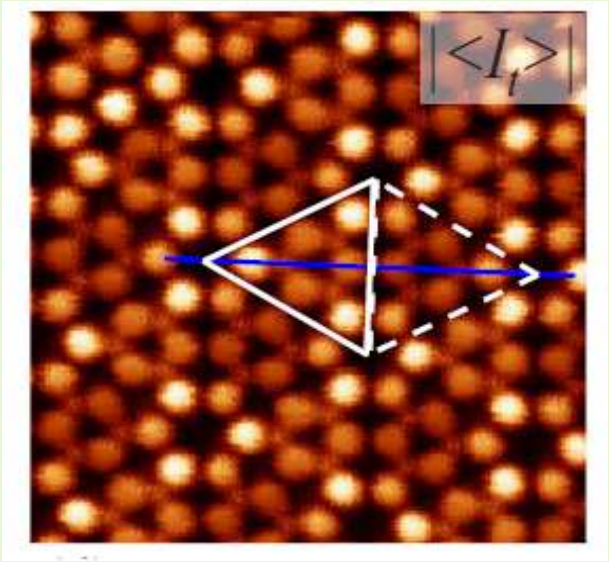


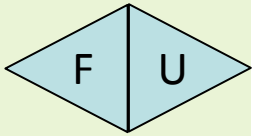
Si(111)-7x7 DAS structure Computation time 1.5 hours (172x100 pixels)



Unit cell of Si(111)-7x7 DAS structure

experiment by Sawada et al. (2009)

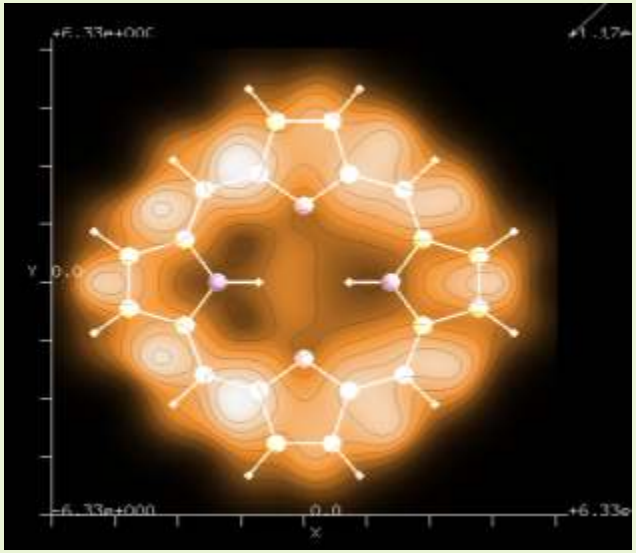


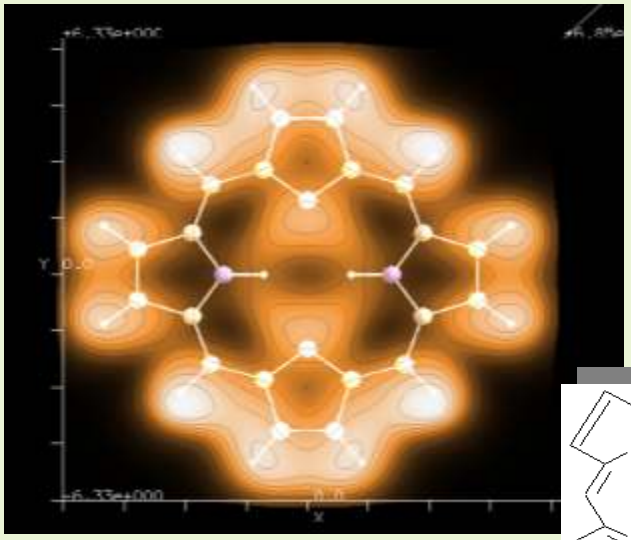


It reproduces the difference in brightness between region F and region U.
It reproduces that looks slightly restatom.

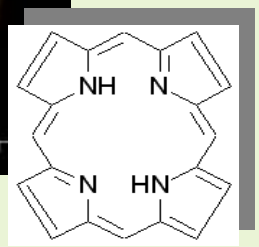
STM image of Porphyrin

DFTB (W tip : 6s,5d orbitals)





(W tip: 6s orbital)



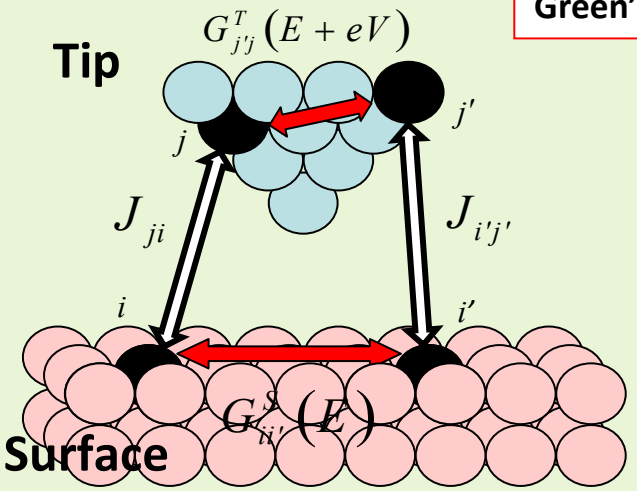
Simulation of STM image

$$I(\mathbf{R},V)=\frac{2\pi e}{\hbar}\int_{E_F^L}^{E_F^R}\sum_{ii'jj'}G_{ii'}^{S}(E)\,J_{i'j'}(\mathbf{R})\,G_{j'j}^{T}(E+eV)\,J_{ji}(\mathbf{R})\,dE$$

Green's function

The tunneling matrix element

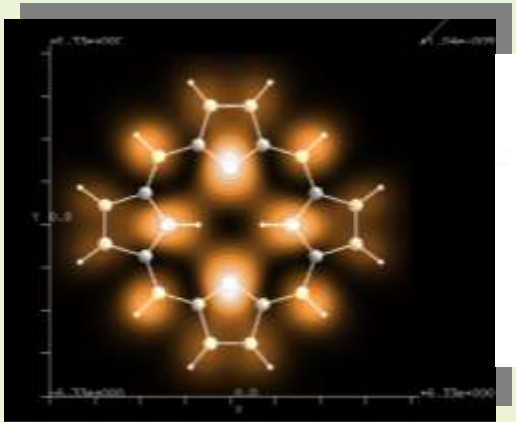
DFTB Calculation



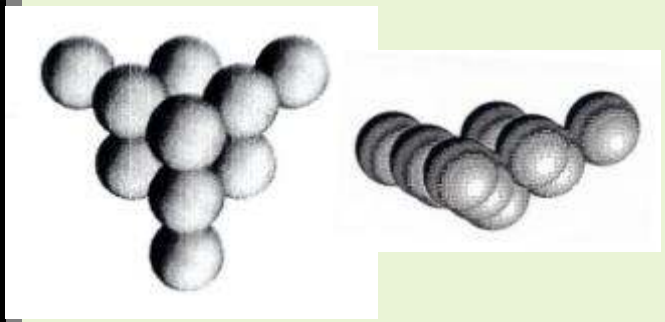
$$G_{ii'}^{S}(E)=\sum_{\nu}C_{\nu}{}^{S}C_{\nu}^{S*}\delta(E-E_{\nu})$$

$$G_{j'j}^{T}(E)=\sum_{\mu}C_{j'}{}^{T}C_{j}^{T*}\delta(E-E_{\mu})$$

LDOS



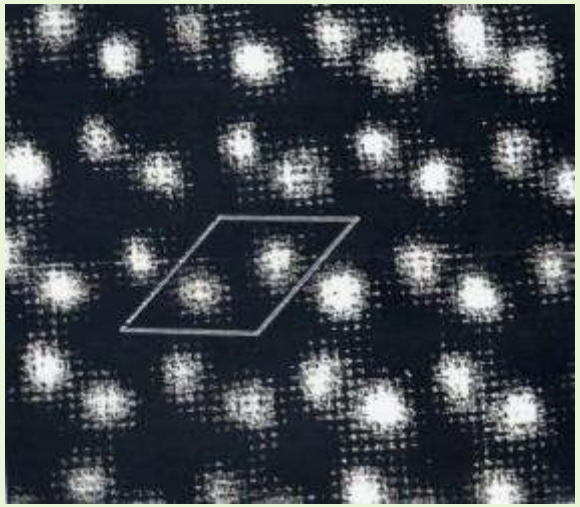
$W_{10}[111]$ tip model



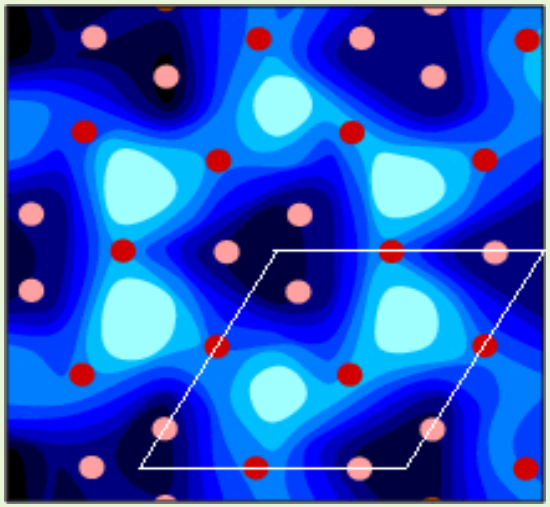
What does SPM see and how does SPM see.

In the case of the surface of Si $\sqrt{3} \times \sqrt{3}$-Ag

STM experiment



STM theory



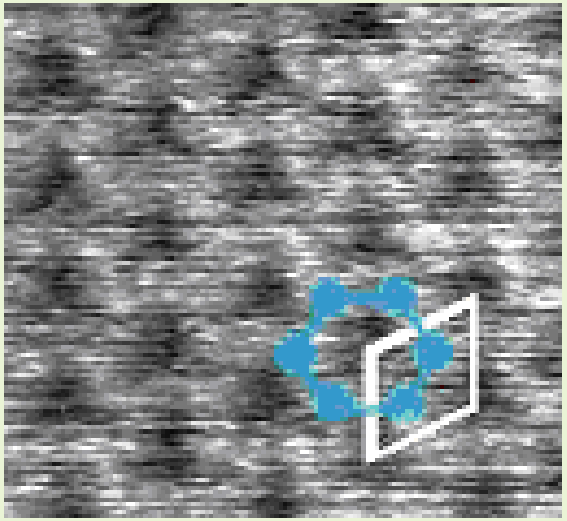
S. Watanabe, M. Aono and M. Tsukada,

Phys. Rev. B. 44, 8330 (1991)

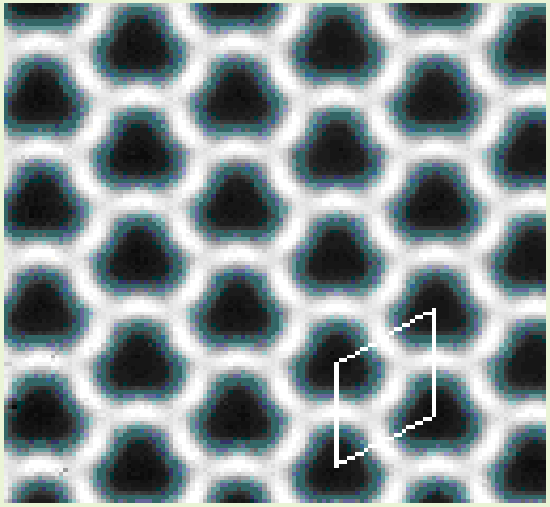
STM image and AFM image are obtained from same surface, but these are quite different.

STM image is composed of the amplitude of the unoccupied wave function.

ncAFM experiment



ncAFM theory



N. Sasaki, S. Watanabe, M. Tsukada,

Phys. Rev. Lett. 88, 046106 (2002).

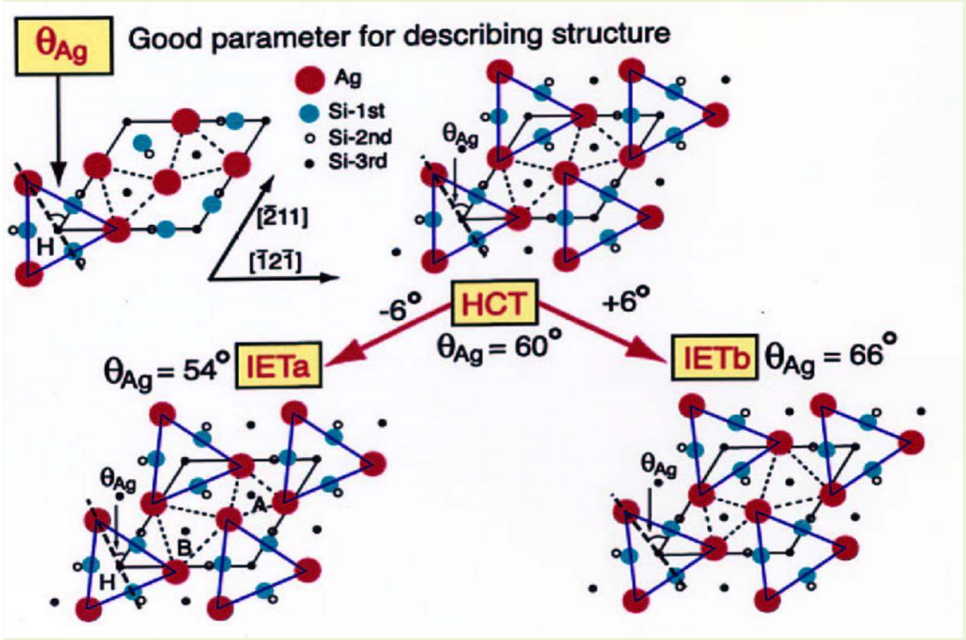
Reproduction of the AFM image is reproduced by theoretical calculation.

But...

The temperature dependability of ncAFM image of surface of Si(111)$\sqrt{3}\times\sqrt{3}$

N. Sasaki, S. Watanabe, M. Tsukada,

Phys. Rev. Lett. 88, 046106 (2002).

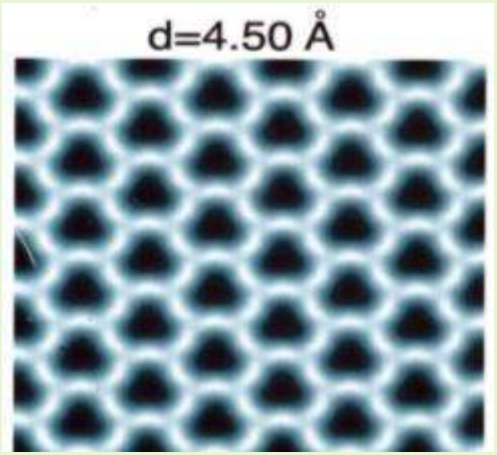


The temperature dependability can be explained by the structural fluctuation of the silver atoms in the outermost layer.

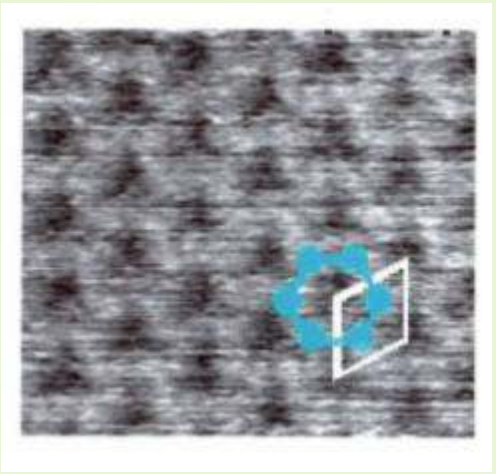
⇒

Good agreement between the experiment and the theory

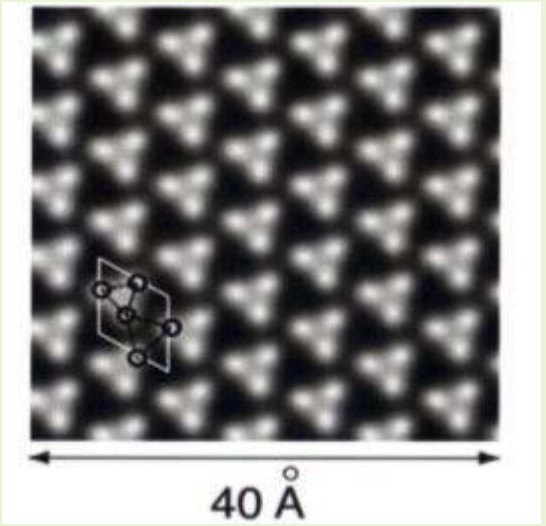
Theory



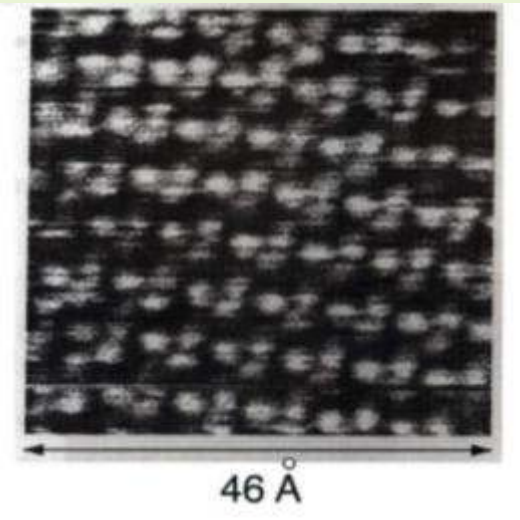
Experiment
By Prof. Morita ***T=300K***



Theory

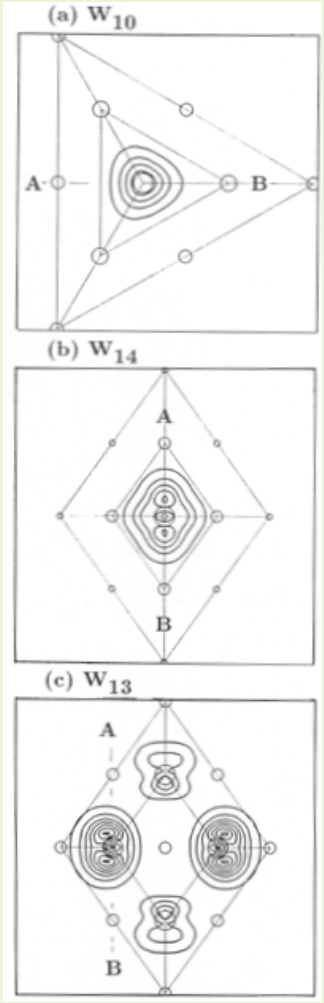


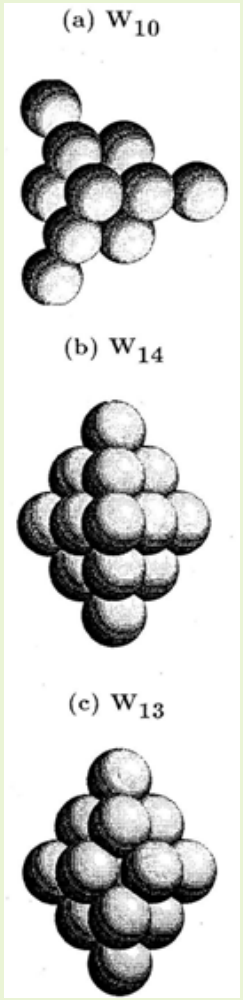
Experiment
By Prof. Morita ***T=6.2K***

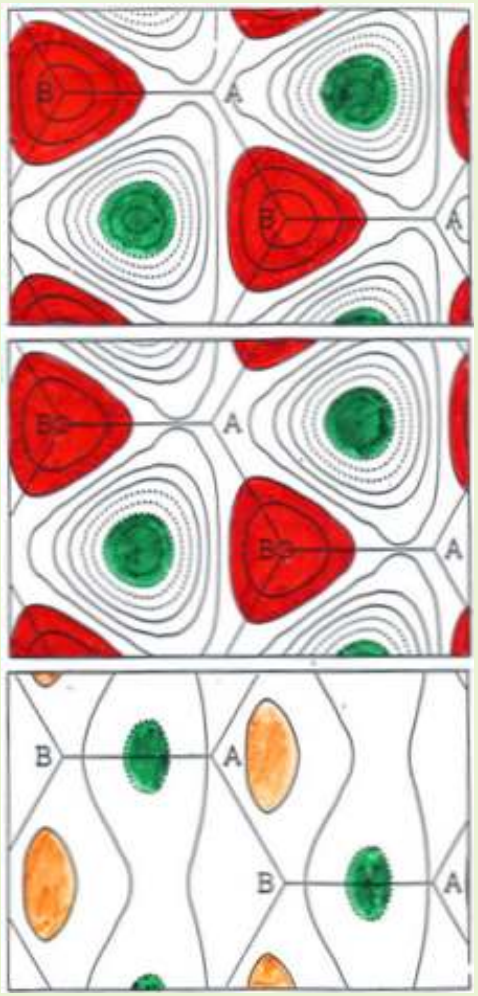


The tip-shape influence

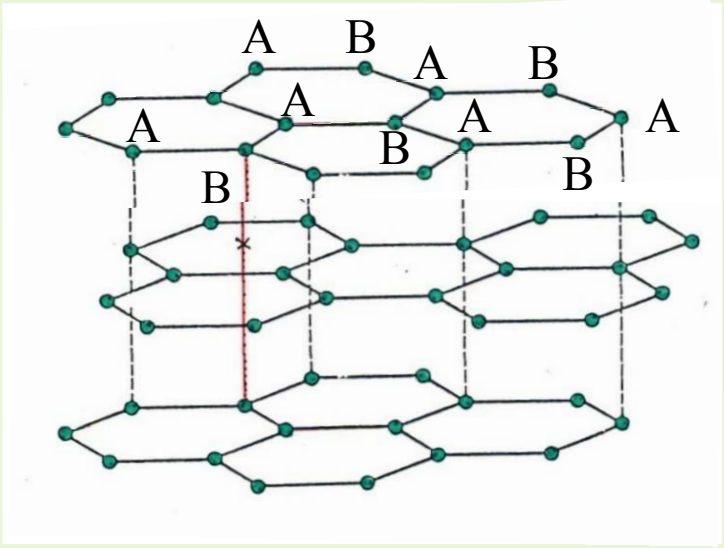
In the case of STM image of graphite



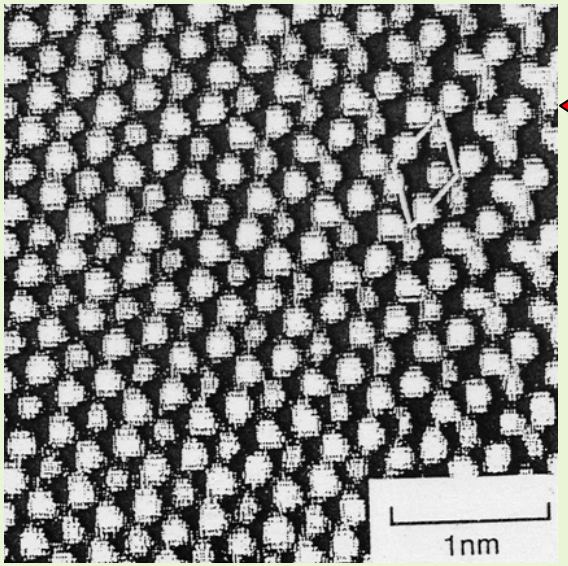


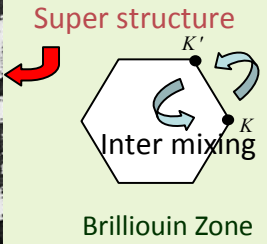


N. Isshiki, K. Kobayashi, M. Tsukada,
J. Vac. Sci. Technol. B 9(2), 475 (1991).



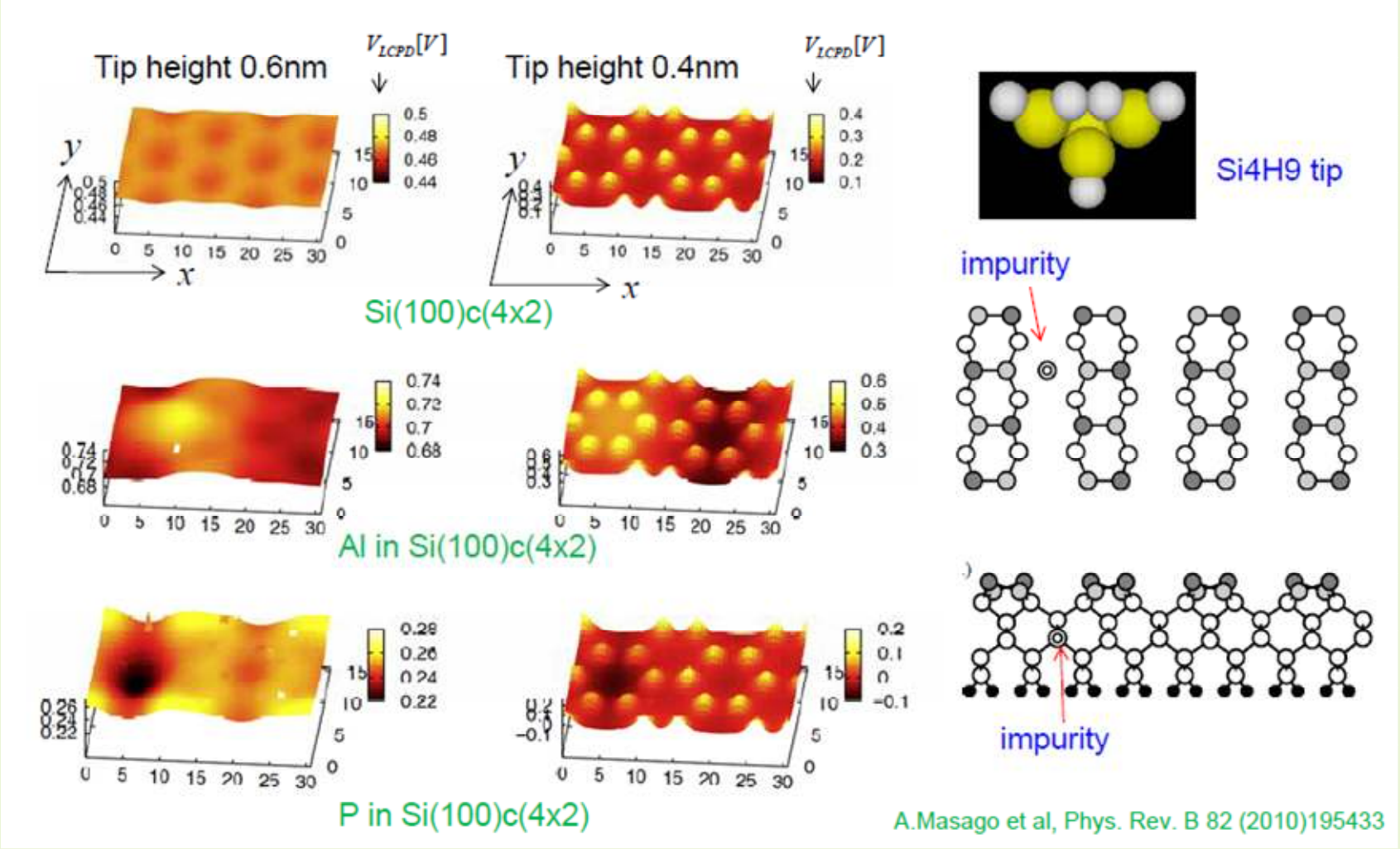
Nakagawa et al., Proc. Ann. Meeting of
The Phys. Soc. Jpn, (1989) 374





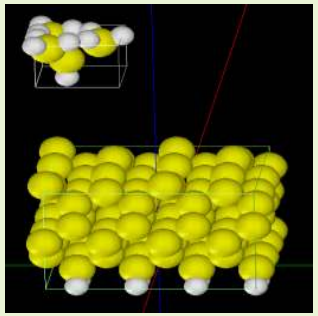
KPFM image of impurity embedded Si(001)-c(4x2) surface

DFTB -Image of distribution of local contact potential difference-



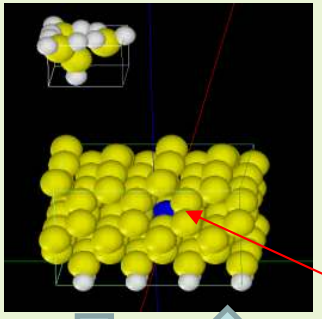
This is a result of simulation that KPFM scans the Si sample surface with an impurity. Slightly larger bright spot than the atomic scale is appeared on the surface position of the impurity, and also it can be confirmed the spot which was caused by an atom on the sample surface.

KPFM image of impurity(nitrogen atom) embedded Si(001)-c(4x2) surface



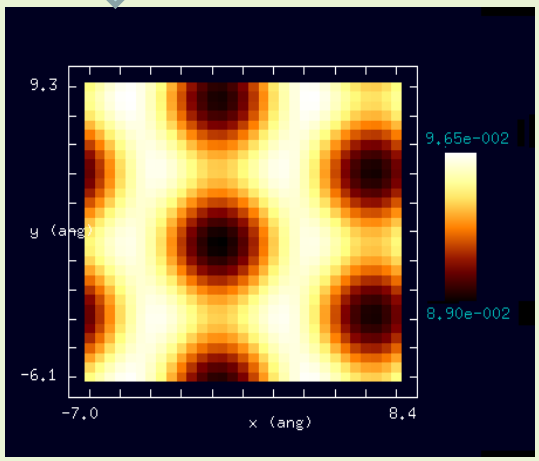
The tip: H-Si_4H_{10}
The sample surface: Si(001)-c(4x2)

Tip-surface distance: 6 Å

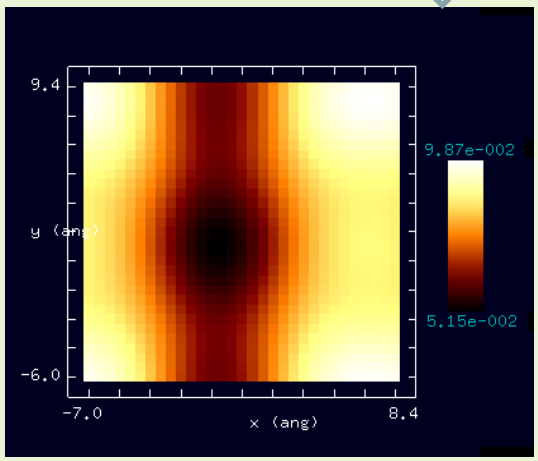


The tip: H-Si_4H_{10}
The sample surface:
Nitrogen atom is doped
Si(001)-c(4x2)

Nitrogen atom

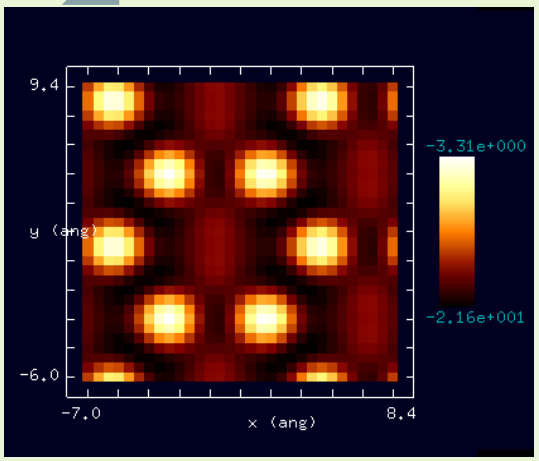


KPFM image of a local contact potential difference
Nitrogen atom is not doped.



KPFM image of a local contact potential difference
Nitrogen atom is doped.

Nitrogen by doping,local contact potential is shifted negative.



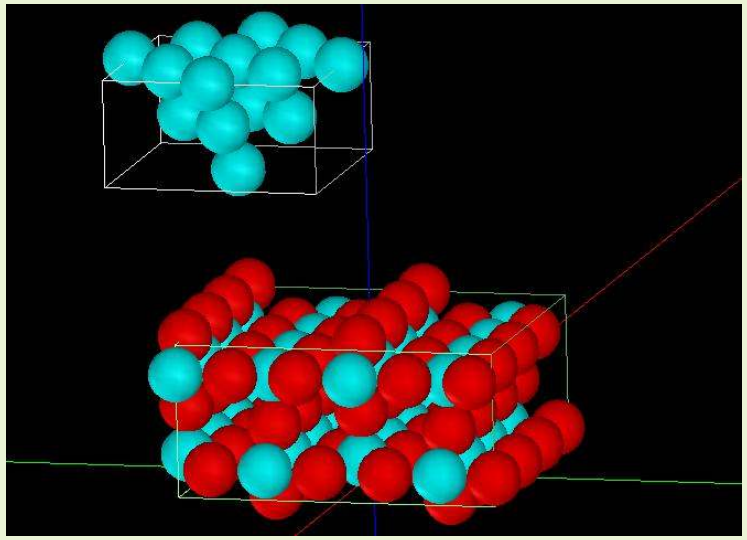
AFM frequency shift image
Nitrogen atom is doped.

Frequency shift image reflects the height of atoms.

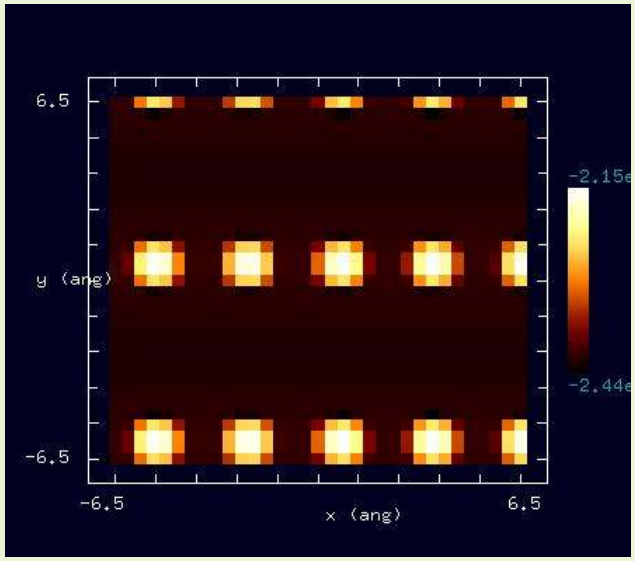
The LCPD image of a TiO_2(110) surface

DFTB The simulation of the LCPD image of a TiO2(110) surface by the KPFM.

The tip:	Pt_{14}
The sample surface:	TiO_2(110)



The tip model and the sample model

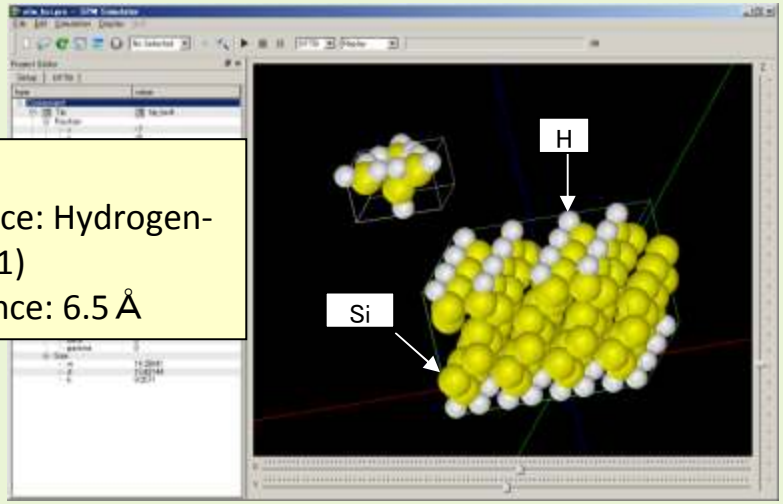


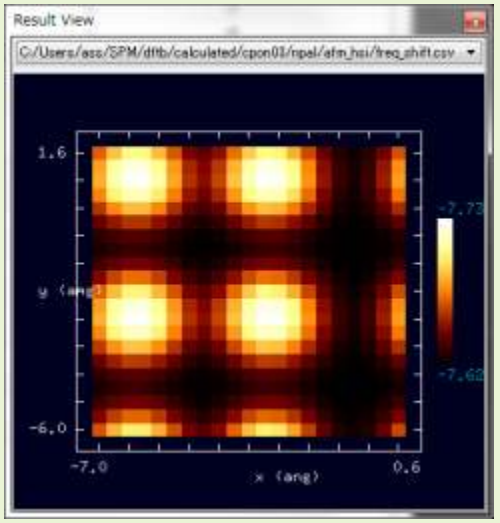
Result of the simulation of the LCPD image

The case examples of frequency shift AFM image and KPFM image

DFTB Simulation of frequency shift image

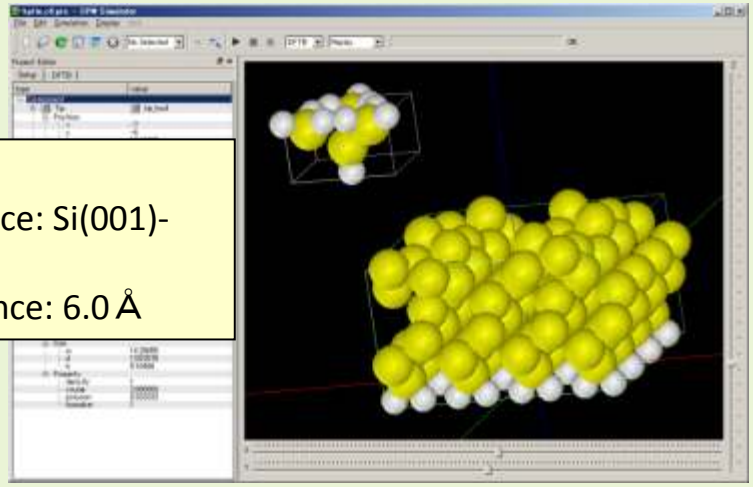
The tip: Si_4H_{10}
The sample surface: Hydrogen-terminated Si(001)
Tip-sample distance: 6.5 Å

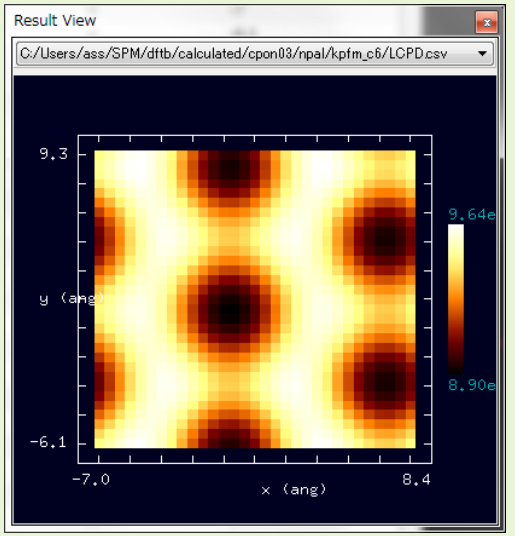




DFTB Simulation of contact potential difference image

The tip: Si_4H_{10}
The sample surface: Si(001)-c(4x2)
Tip-sample distance: 6.0 Å





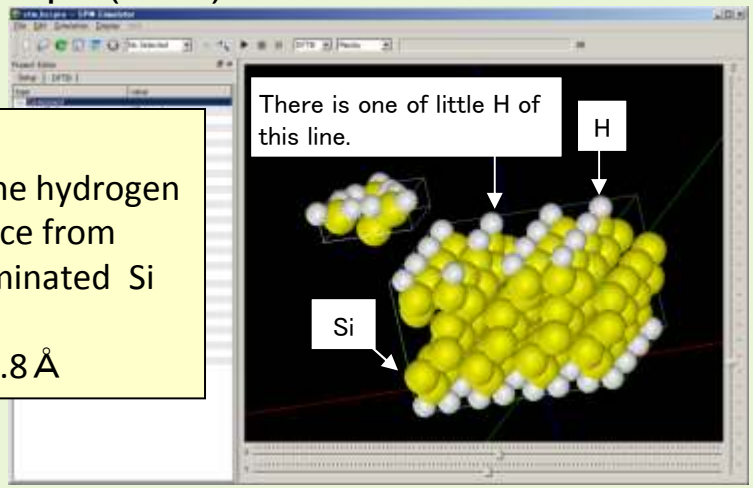
We can see the region with the large potential difference. This region coincides with the lines connecting the up dimer Si atoms.

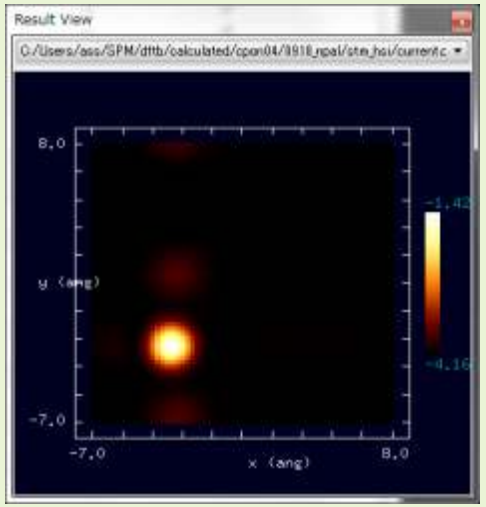
The case examples of the Scanning Tunneling Microscope and the Scanning Tunneling Spectroscopy

DFTB

Simulation of Scanning Tunneling Microscope (STM)

The tip: Si_4H_9
The sample surface: one hydrogen eliminated surface from Hydrogen- terminated Si (001) surface
Tip-surface distance: 3.8 Å



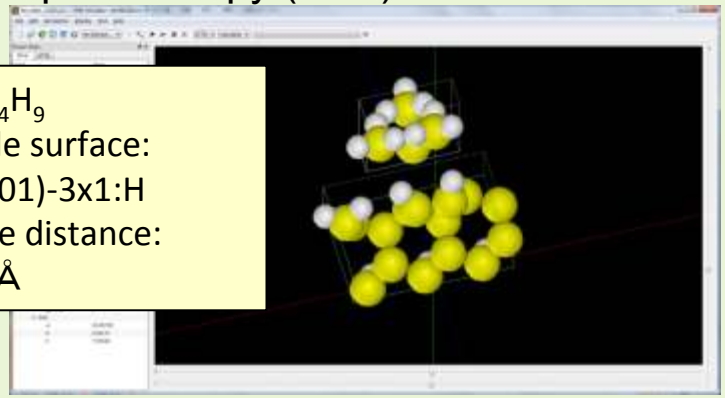


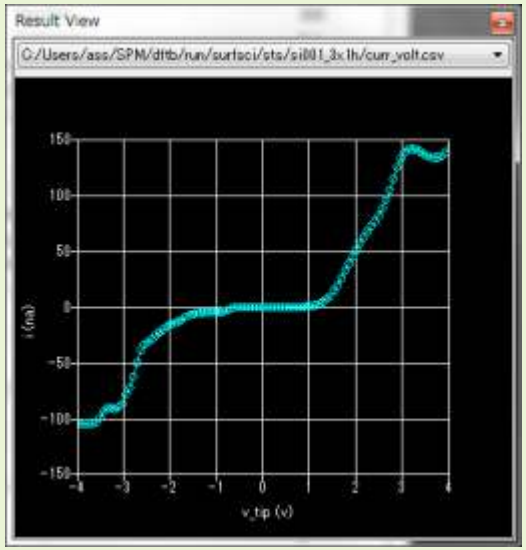
There is a dangling bond at the hydrogen- eliminated position, then this is read that a large current flows.

DFTB

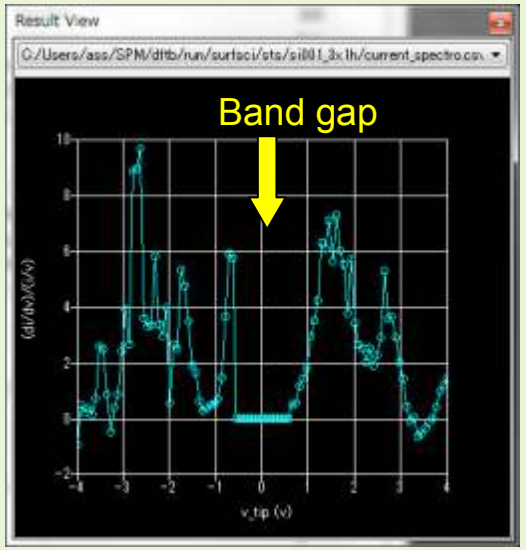
Simulation of Scanning Tunneling Spectroscopy (STS)

The tip: Si_4H_9
The sample surface: Si(001)-3x1:H
Tip-surface distance: 3.4 Å





I-V characteristic curve



(dI/dV)/(I/V) vs. V

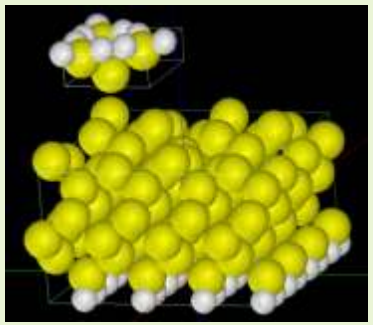
The voltage V of the horizontal axis is the tip bias compared to the sample one.

The observation and the simulation of Si(001)-c(4x2) surface by STM

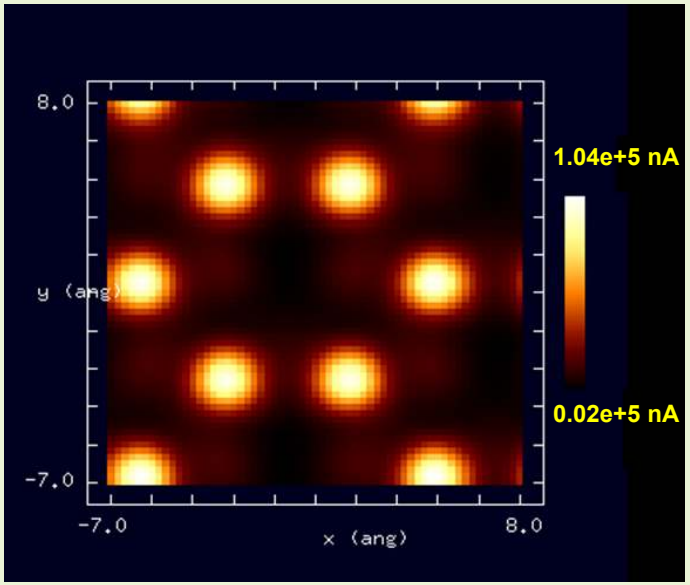
DFTB

The tip/sample model

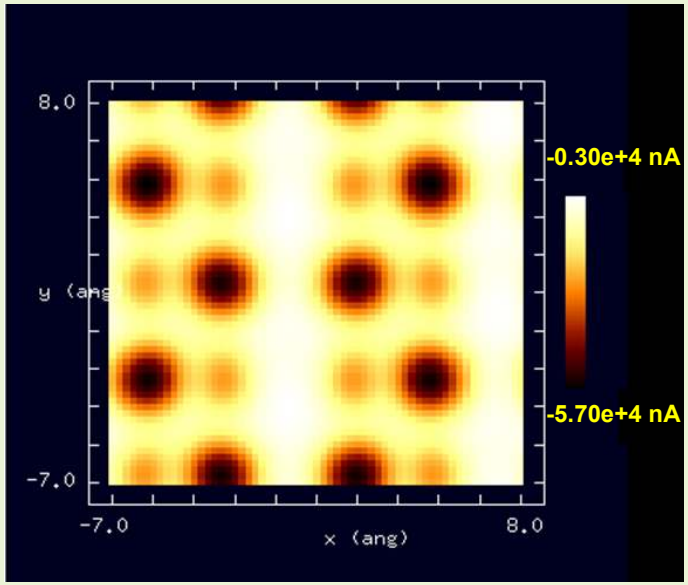
Tip: Si_4H_9
The sample surface:
Si(001)-c(4x2)
Tip-sample distance: 2.32 Å



Computed result of STM image



Bias voltage +1.0V



Bias voltage -1.0V

Honeycomb structure is inverted by the bias.

experiment

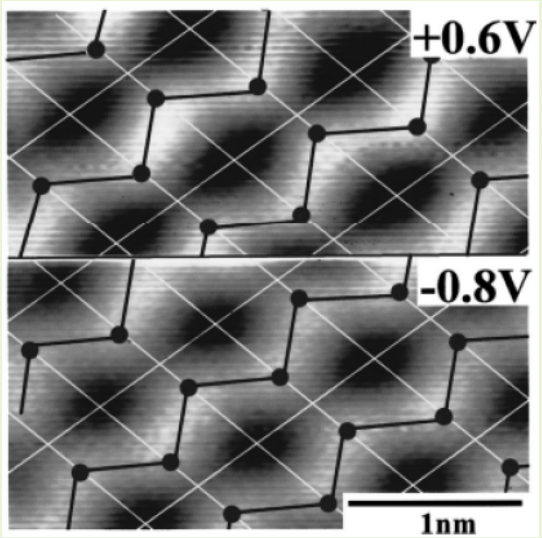


Image of tunneling current of Si(001) surface

It is known that the honeycomb structure is inverted by the sign of the bias.

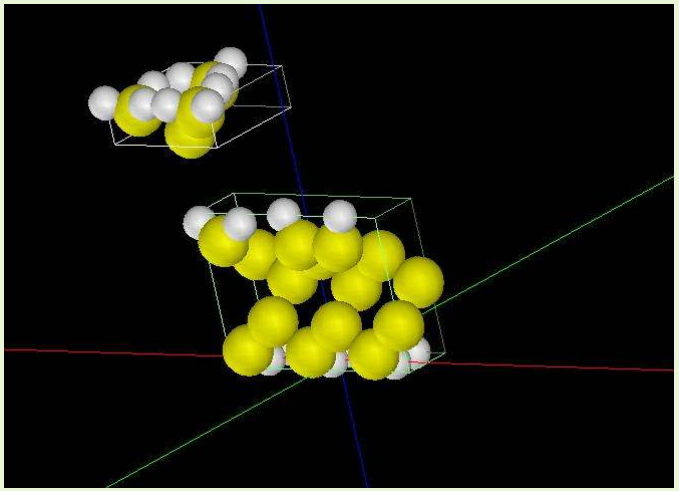
K. Hata, S. Yasuda, and H. Shigekawa, Phys. Rev. B **60**, 8164 (1999).

similarity

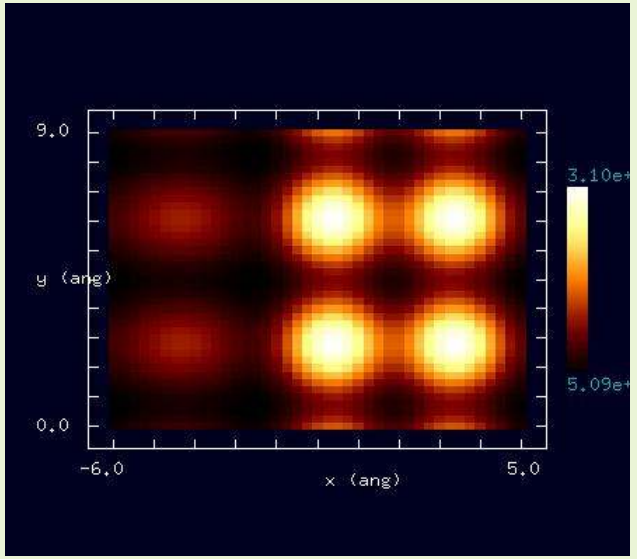
The tunneling current image of a Si(001)-3x1:H surface

DFTB The simulation of the tunneling current image of a Si(001)-3x1:H surface by the STM mode.

The tip:	Si_4H_9
The sample surface:	Si(001)-3x1:H
Tip-surface distance:	3.4 Å



The tip model and the sample model



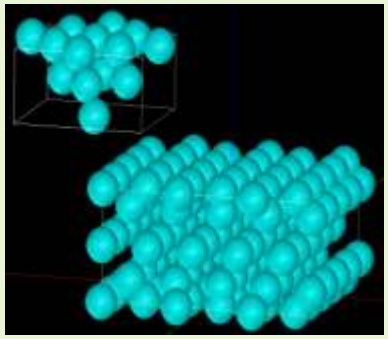
Result of the simulation of the tunneling current image

The observation and simulation of Au(001) reconstructed surface by STM

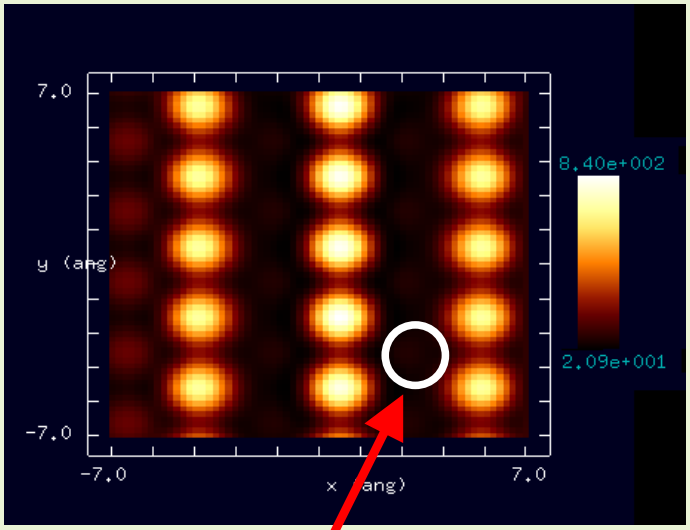
DFTB

The tip/sample model

The tip: Au_{14}
The sample surface: Au(001)-5x1 reconstructed
Tip-surface distance: 4 Å
Bias voltage (tip voltage): +0.7 V



Computed result of STM image

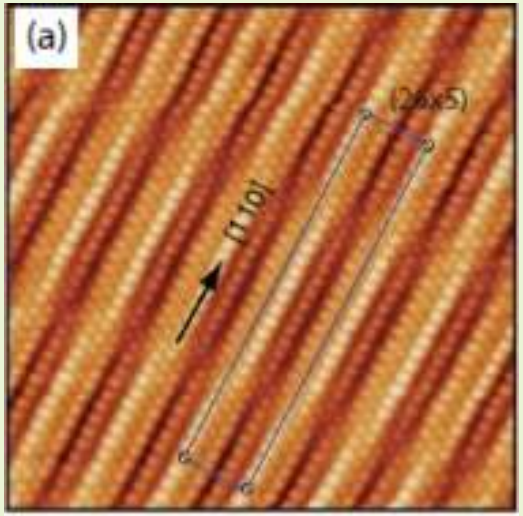


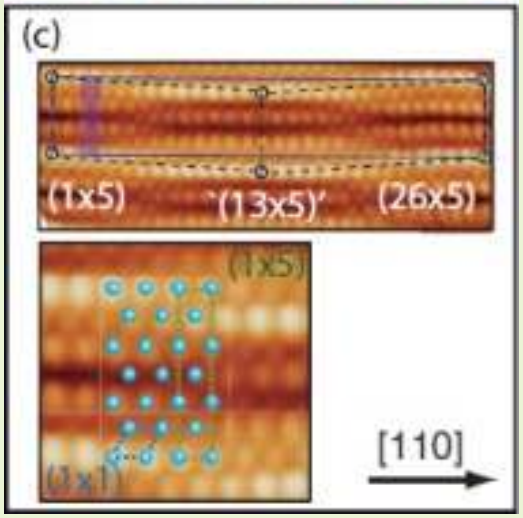
In spite of the existence of an atom, current does not flow so much.

Charge transfer occurs.

similarity

Experiment



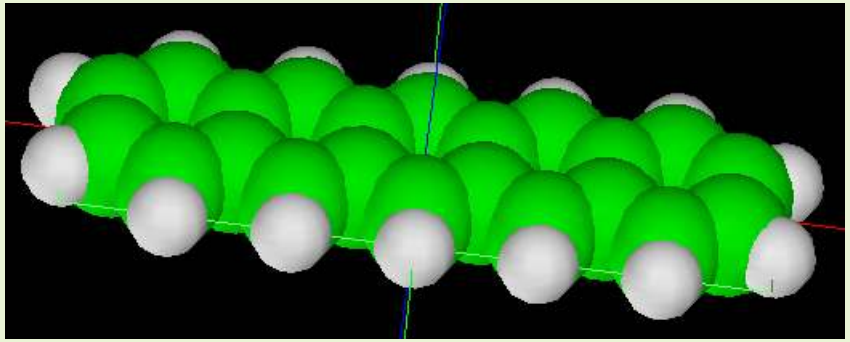


S. Bengió *et al.*, Phys. Rev. B **86**, 045426 (2012).
Au(100)-26x5 reconstructed

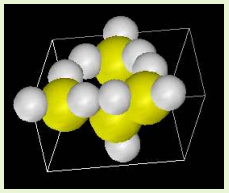
The observation and the simulation of pentacene molecules by AFM and STM

The tip:
- Si_4H_{10} (for AFM, KPFM)
- or Si_4H_9 (for STM)

The sample:
- Pentacene molecule

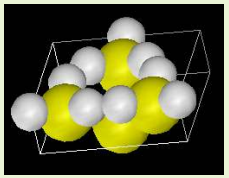


Pentacene



Si_4H_{10}

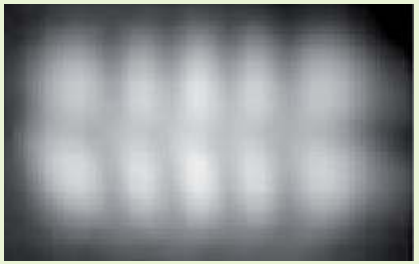
The tip for AFM, KPFM



Si_4H_9

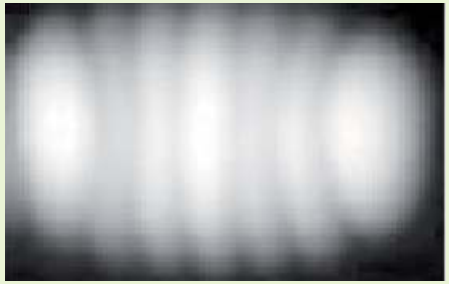
The tip for STM

Measured images



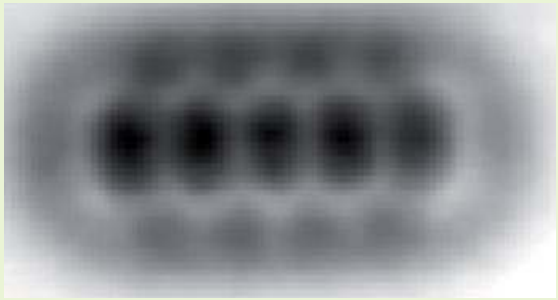
STM HOMO

Phys. Rev. Lett. 94, 026803 (2005)



STM LUMO

Same as on the left

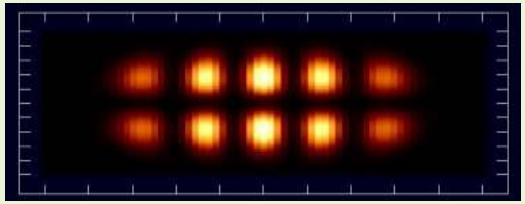


NC-AFM

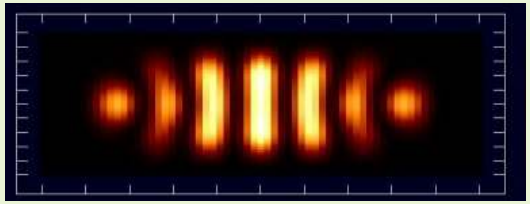
Science 325, 1110–1114 (2009)

DFTB

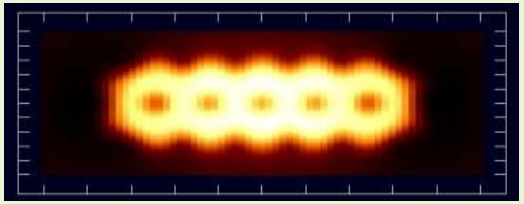
Simulated images



STM tip-sample distance: 4.0 Å
The tip bias voltage: +1.0V



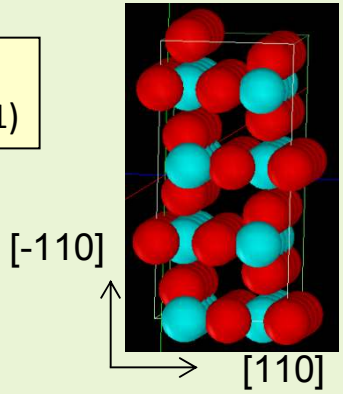
STM tip-sample distance: 4.0 Å
The tip bias voltage: -1.0V



AFM tip-sample distance: 4.0 Å

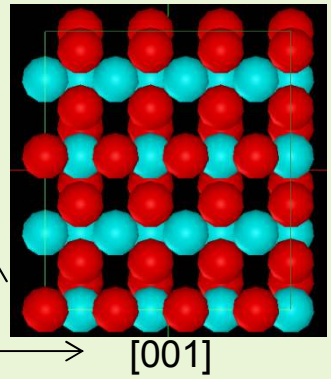
The observation and the simulation of TiO_2(110) surface by AFM and KPFM

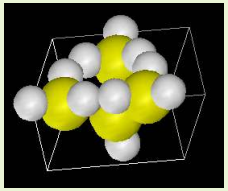
The tip: Si_4H_{10}
The sample: TiO_2(110)-(1x1)



$TiO_2(110)-(1\times1)$

Oxygen of the highest position

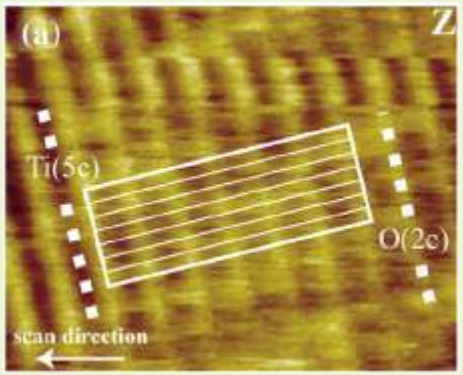




Si_4H_{10}

The tip

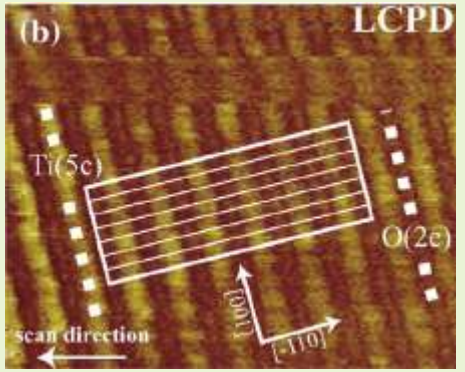
Measured images



AFM

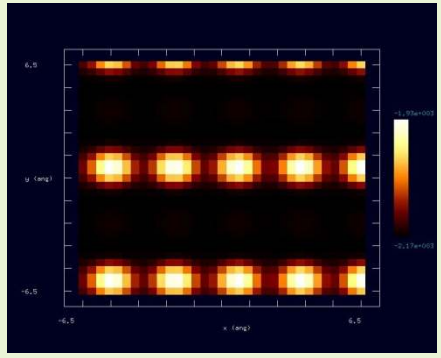
Surface Science Reports, 66, (2011),1-27

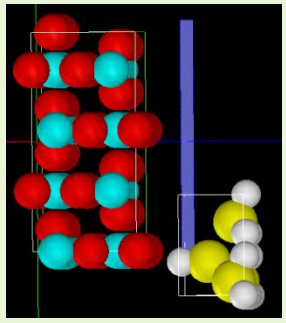
KPFM

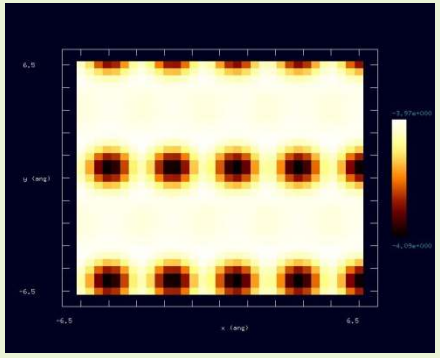


DFTB

Simulated images







AFM Tip-sample distance: 3.5 Å

KPFM Tip-sample distance: 2.5 Å

Sample Modeling

SetModel

Inputting crystal data, create a sample model of any size

↓

Remove, copy, move an atom and change the element.

↓

Hydrogenate, generate of MM3 force field parameters.

↓

Save as the suitable format for each solvers.

How to make a graphite thin film with a defect.

Crystal data

The space group number: 194

The lattice constants:

a = 2.464 Å

b = 6.711 Å

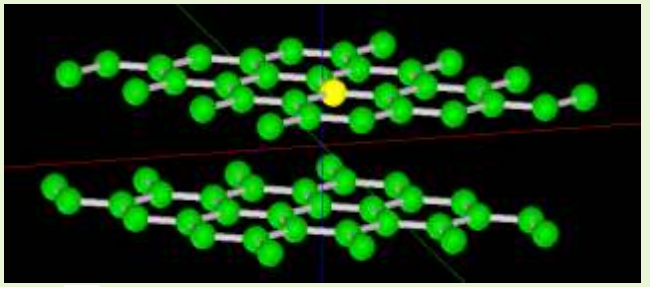
Fractional coordinate: C (0, 0, 1/4)

C (1/3, 2/3, 1/4)

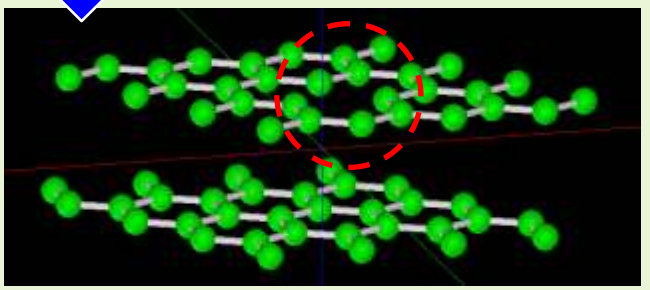
Direction and size

Miller index: (0 0 1)

Size of lattice: (4, 4, 1)



Select an atom and remove it.



Create MM3 force field parameters

Save as txyz format

Save as xyz format

CG MD GeoAFM FemAFM DFTB

Sample Modeling

SetModel

Inputting crystal data, create a sample model of any size

Remove, copy, move an atom and change an element.

Hydrogenate, generate of MM3 force field parameters.

Save as the suitable format for each solvers.

How to make a tip model of a silicon cluster.

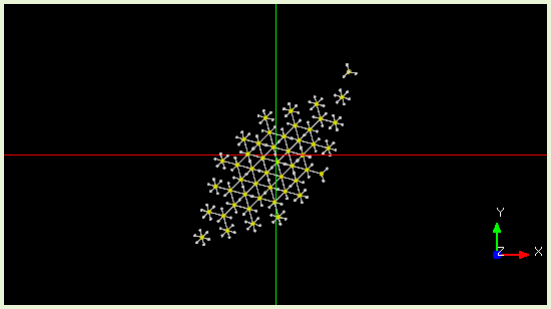
Crystal data

The space group number: 227
The lattice constants:
a = 5.4 Å
Fractional coordinate:
Si (0, 0, 0)

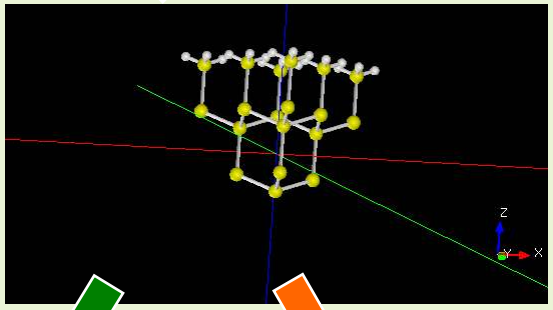
Direction and size

Miller index: (1 1 1)
Size of lattice:(2, 2, 3)

Hydrogenate the dangling bounds



Cut off the useless parts to make an apex structure with a sharp top.



Create MM3 force field parameters

Save as txyz format

Save as xyz format

CG MD GeoAFM FemAFM DFTB

Sample Modeling

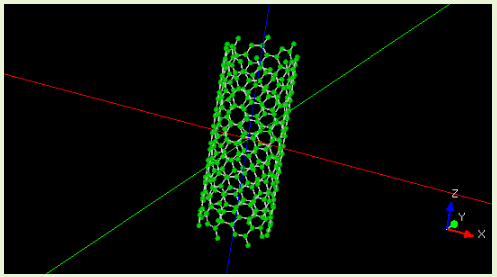
SetModel

How to make a carbon nanotube or its derivatives.

Single-wall nanotube

Input data

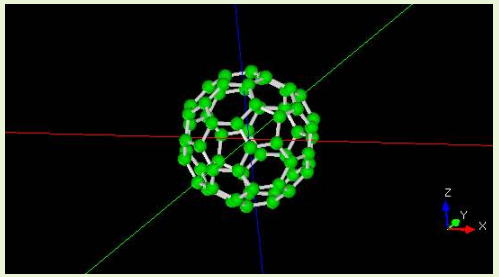
mode: swcnt
Chiral index: (8, 6)
Number of unit cell: 1



Fullerene

Input data

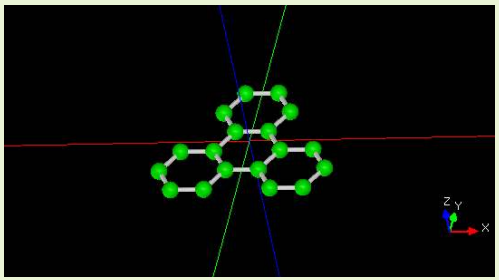
mode: fuller
Chiral index: (5, 5)
Number of unit cell: 1



Graphene sheet

Input data

mode: sheet
Chiral index: (20, -10)
Number of unit cell : 1



Capped carbon nanotube

Input data

mode: capped
Chiral index: (10, -5)
Number of unit cell: 8