Advanced Simulator for Scanning Probe Microscopy

Supported from **Japan Science and Technology Agency**

Introduction to the SPM simulators

Masaru Tsukada, Tohoku University

How to use Integrated GUI software, S. Shinohara, AA& S
Geometrical Mutual AFM Simulator/
Soft Material Liquid AFM Simulator N.Watanabe, Mizuho Inf.& Res. Inst.
Classical Force Field AFM Simulator K. Tsutsumi , AA& S
Quantum Dynamics SPM Simulator M. Shimizu, , AA& S

The aim of the project "Advanced simulator for SPM" is to develop a theoretical SPM simulator for analyses of AFM, STM, and KPFM images. The simulators are not only for specialists, but also for inexperienced SPM users.

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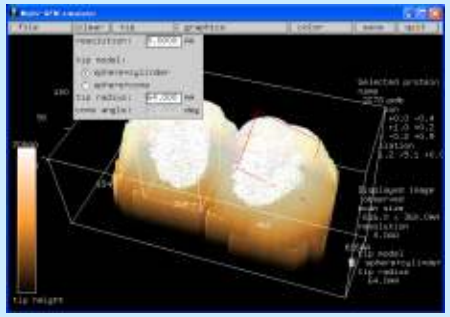
ADVANCED ALGORITHM & SYSTEMS

Luncheon Seminar at ncAFM 2010,
Kanazawa, 2010. 8. 1

Outline of SPM Simulators

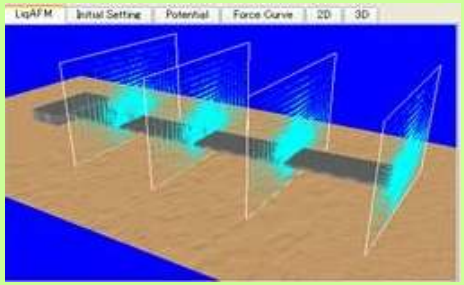
1. Geometrical Mutual AFM Simulator

- ✓ Estimate, within a second , one unknown item of 1)AFM image, 2)sample shape, or 3)tip shape based on the remaining two known items.

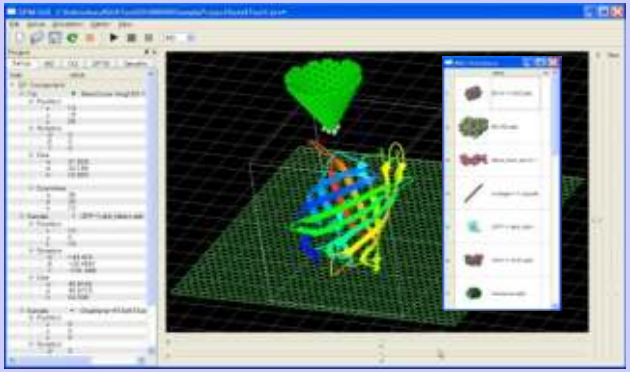


2. Soft Material Liquid AFM Simulator

- ✓ Simulate bending /twisting oscillation of a cantilever in liquid near the sample.
- ✓ Predict the tapping/dynamic mode AFM observables on soft materials in liquids.



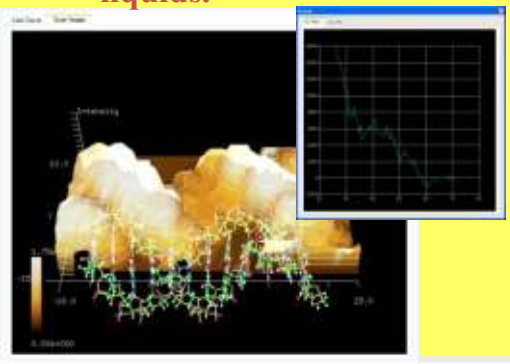
Integrated GUI software



- ✓ Provide a common platform for the SPM simulators.
  Manage and integrate tip/samples data, setup conditions and simulation results.

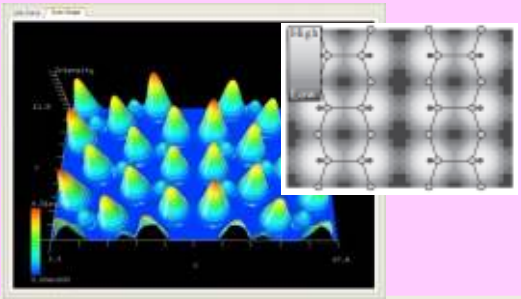
3. Classical Force Field AFM Simulator

- ✓ Calculate AFM images by the energy relaxation and the molecular dynamics method.
- ✓ Simulate AFM images for the dynamic AFM in liquids.



4. Quantum Dynamics SPM Simulator

- ✓ Based on the electronic state of the system, calculate AFM and STM/KPFM images and spectra.
- ✓ Adopt Density Functional based Tight Binding method , and perform much faster calculation than Density-functional-theory.



Contact information

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Integrated GUI System

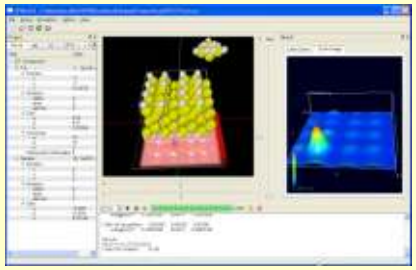
Features

1. **Provide a common platform for our SPM simulators.**
2. **Lump tip/samples data, setup conditions and simulation results by introducing *project files*.**

Roles

1. **To create/edit *project files*.**
2. **To display the calculated results by simulators.**

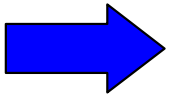
Integrated GUI software

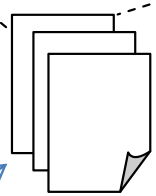


- Component(tip/samples) name
- Setup condition
- Parameter value
- Result file path

..... (XML format)

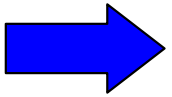
Create/Edit





Project files

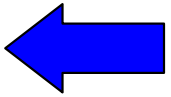
Input



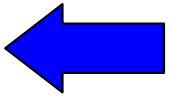
Simulators

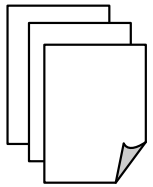
- Geometrical Mutual AFM
- Soft Material Liquid AFM
- Classical Force Field AFM
- Quantum Dynamics SPM

Display



Output

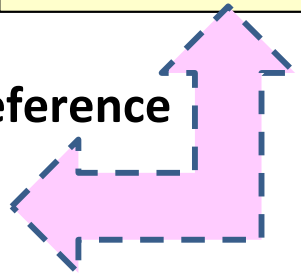




Result files

assist

Reference



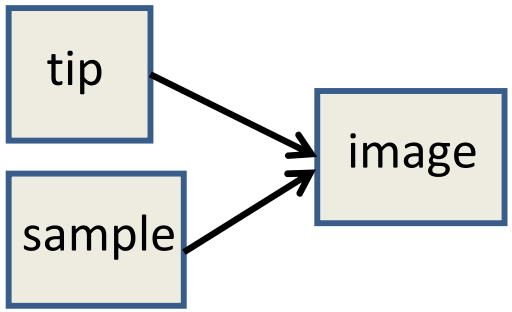
accumulation

Component Database (pdb,xyz…)

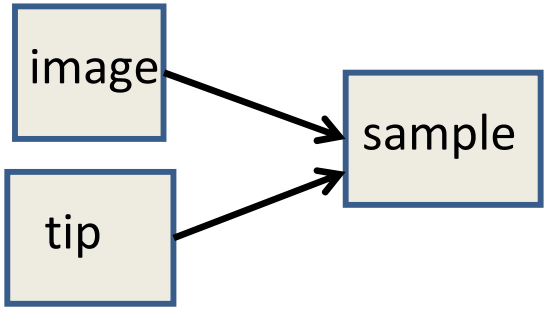
1. Geometrical Mutual AFM Simulator

Rapid calculation of AFM images by geometrical condition with meso-scale resolution

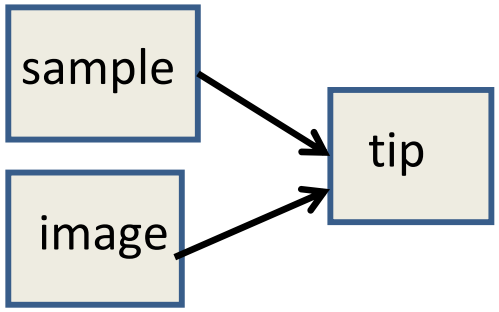
Correction to large deformation of the tip/sample by classical mechanical method



From models of tip and sample, AFM image is predicted



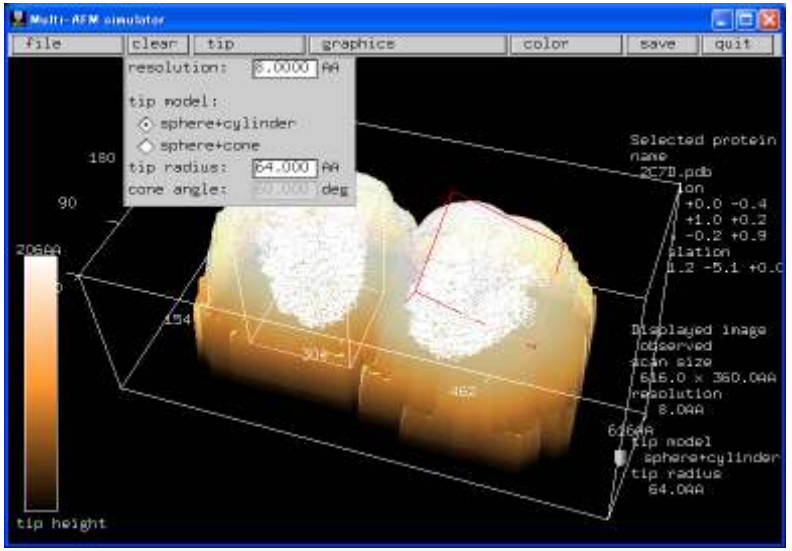
From image and tip model, structure of the sample is calculated



From the standard sample structure and its image, tip structure is calculated

Estimate one unknown item of
1)AFM image,
2)sample shape, or
3)tip shape
based on the remaining two known items.

A general 3D CG-GUI is used for the input and output



1. Geometrical Mutual AFM Simulator

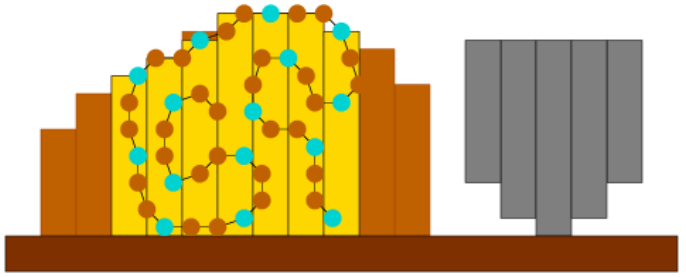
vs

3. Classical Force Field AFM Simulator

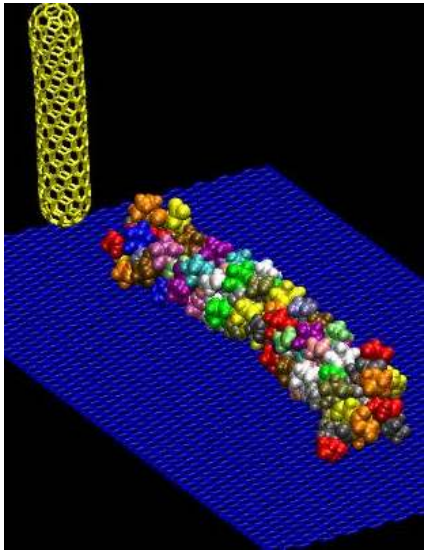
Calculation by Interaction force

Geometrical condition

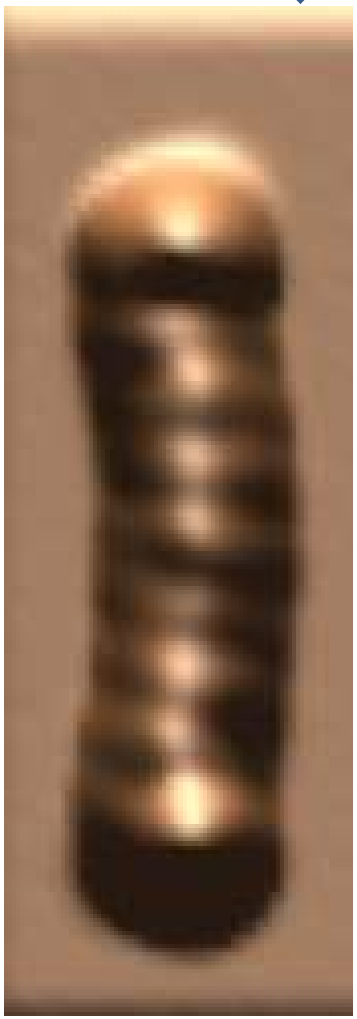
Rapid geometrical method



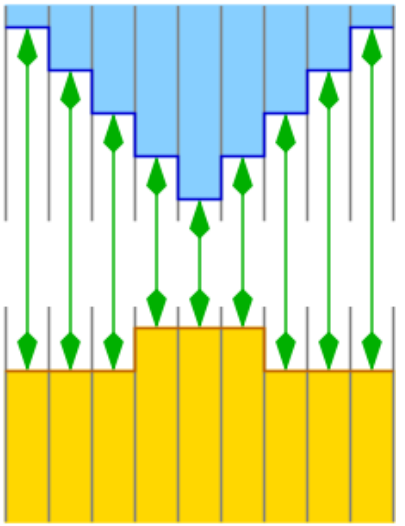
Example of collagen



2 weeks with WS



Less than 1 second with PC



Divide tip/sample into meshes
Assign the height of each mesh
By the top atom

2. Soft Material Liquid AFM Simulator

Oscillation analyses of cantilever in liquids, and dynamic AFM analyses of visco-elastic samples in liquids can be performed

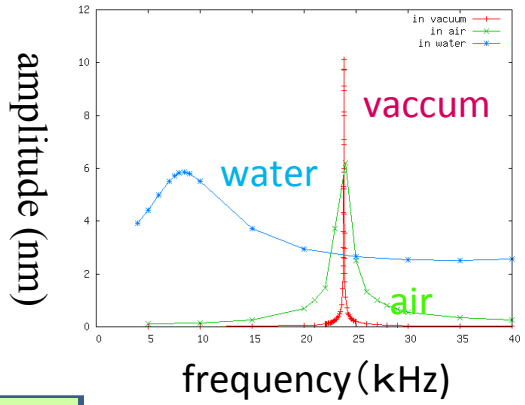
Various oscillation modes
Various cantilever shapes

Elastic oscillation of cantilever — Fluid dynamics of liquids

Collision with visco-elastic sample

Calculation of resonant curves

Noise analyses

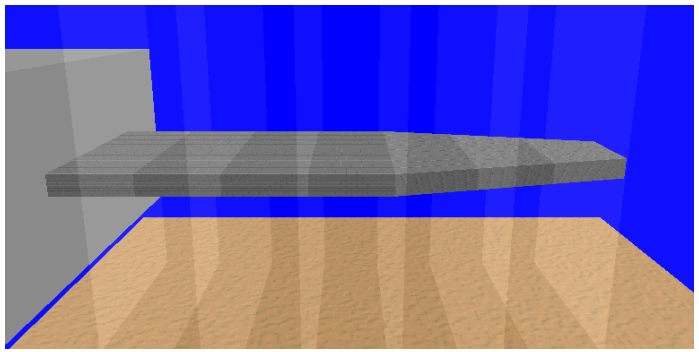


Coarse grained modeling of the sample

Design shape of the cantilever
Predict optimum oscillation modes

Simulation of (fast) dynamic AFM of soft(bio) materials in liquids

Frequency shift/phase images



2. Soft Material Liquid AFM Simulator

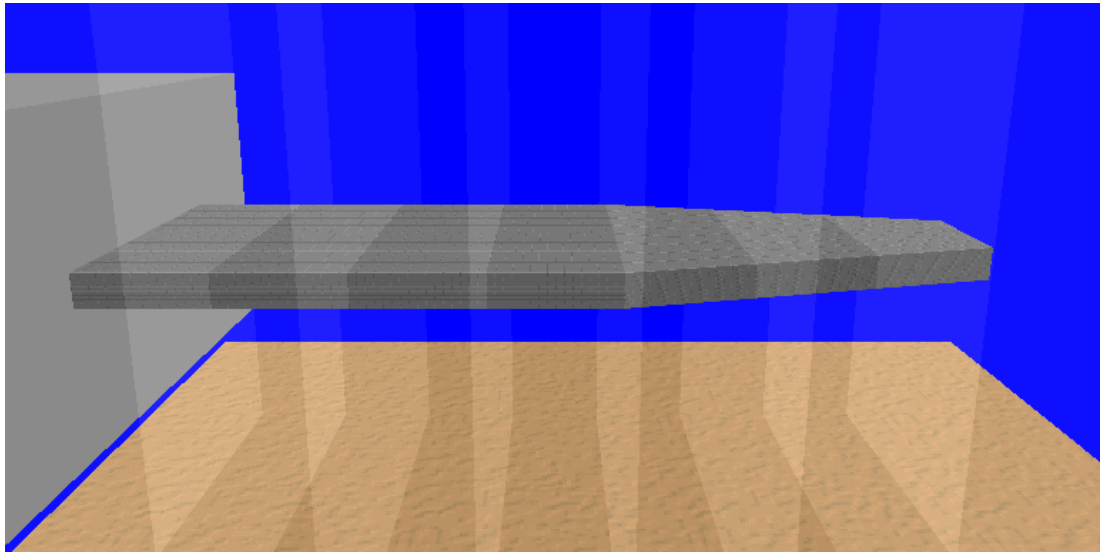
Numerical Analyses of the Cantilever Oscillation in Water

Designing optimum beam shape and oscillation modes

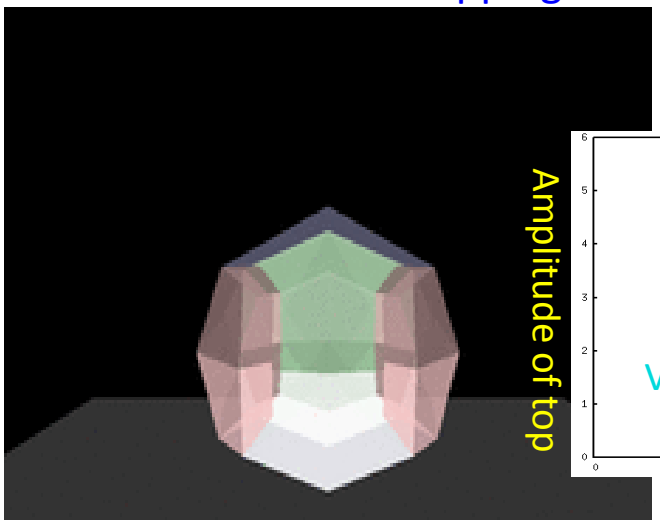
Numerical simulations of an elastic cantilever oscillation combined with fluid dynamics of water as well as the tip sample interaction force

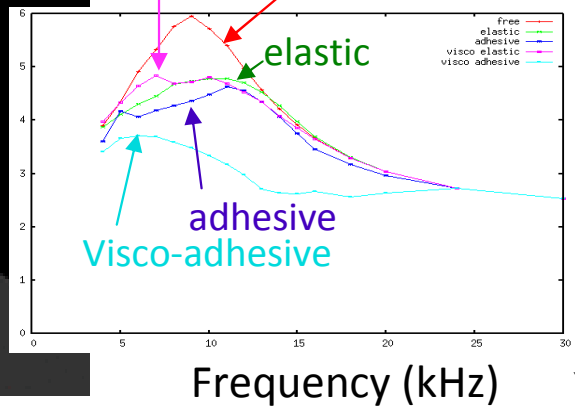
$$\rho S(z)\frac{\partial^2}{\partial t^2}h(z) = -\frac{\partial^2}{\partial z^2}EI(z)\frac{\partial^2}{\partial z^2}h(z) + F^{\mathrm{liq}}(z)$$

$$\frac{\partial \mathbf{v}}{\partial t} + \left(\mathbf{v}\cdot\vec{\nabla}\right)\mathbf{v} = -\vec{\nabla}P + \frac{1}{\mathrm{Re}}\Delta\mathbf{v}$$

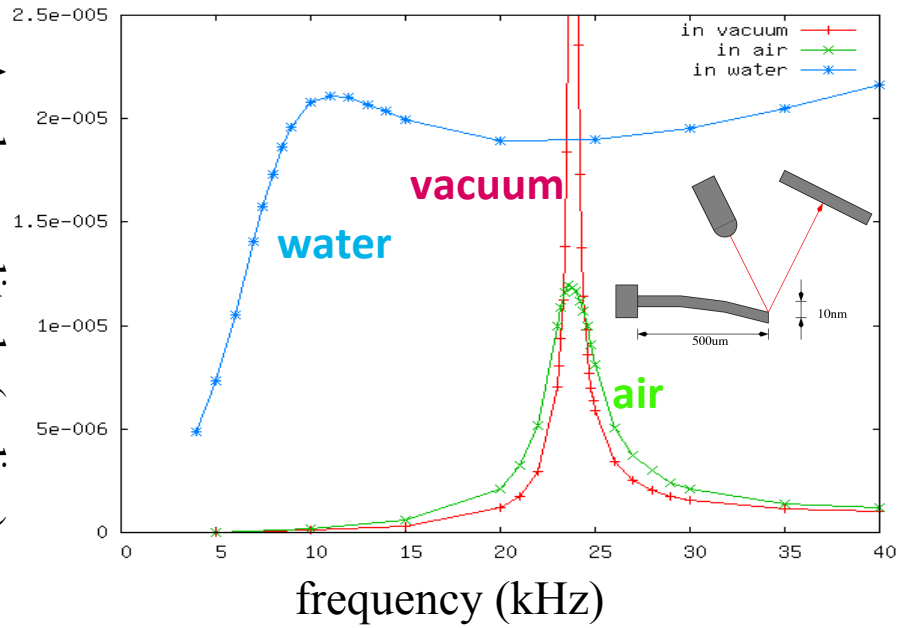


Resonant curves for tapping modes



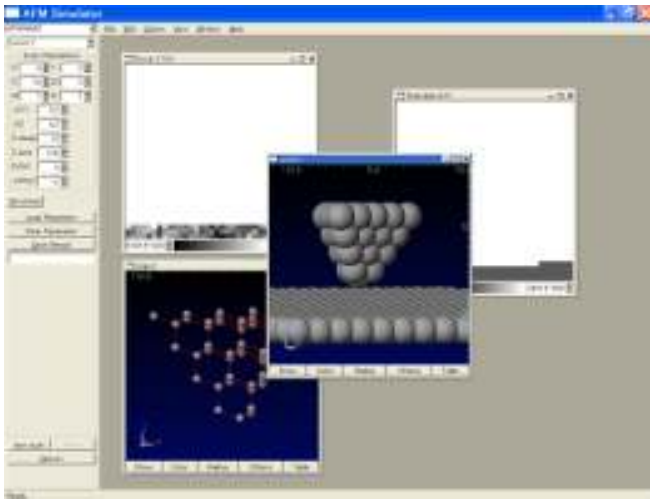


Resonant curves of Si beam cantilever in water



3. Classical Force Field AFM Simulator

AFM image simulations by classical MM/MD



Input/out put by GUI

Atomic model of tip

Sample initial structure

Deformation of tip/sample

4. Quantum Dynamics
SPM Simulator
Accurate initial structure

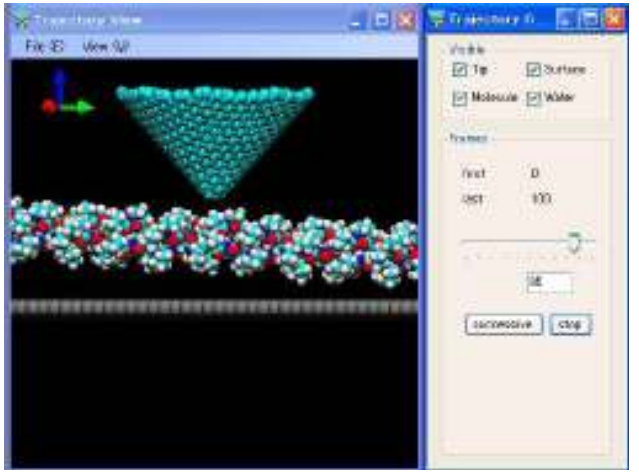
Van der Waals force

Classical MD

Classical MM

3D-RISM

tip-sample interaction force



Frequency shift image

Phase shift image

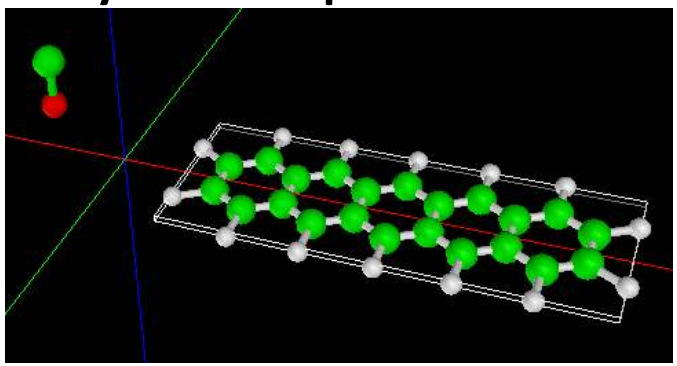
Dissipation image

Accumulation and consultation to data base

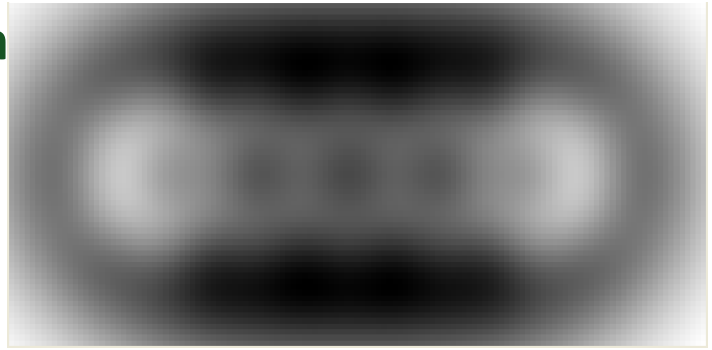
3. Classical Force Field AFM Simulator

-examples of molecules-

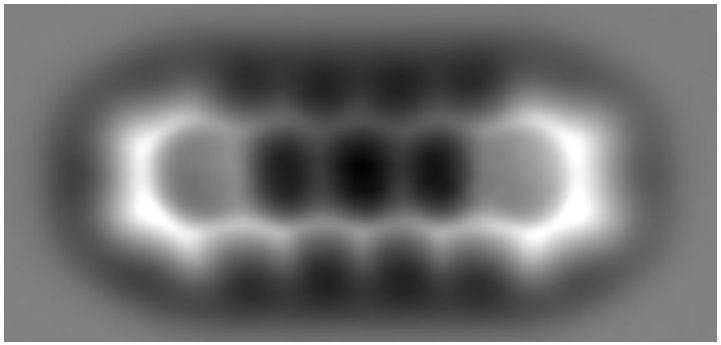
AFM image of pentacene by the CO tip



Simulation
（calc. 20 min on PC）



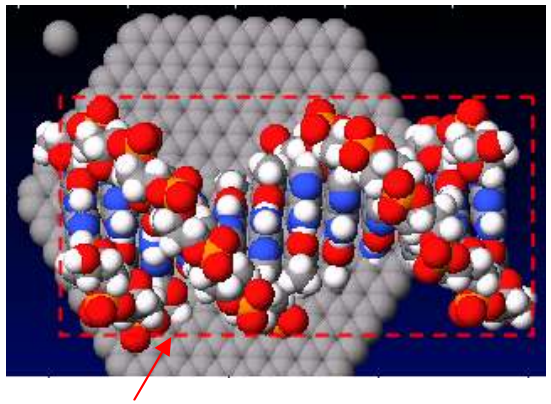
Experiment



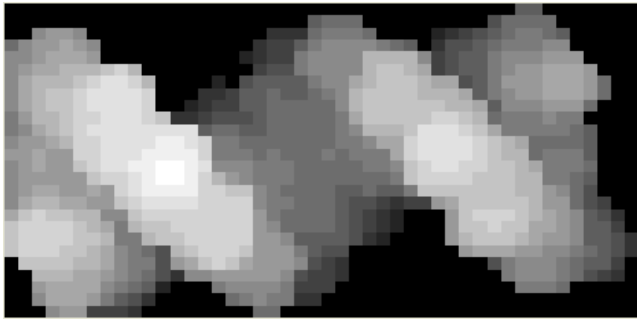
L.Gross, F.Mohn, N.Moll, P.Lilijeroth, G.Meyer, SCIENCE, 325 (2009)1110

AFM image of DNA

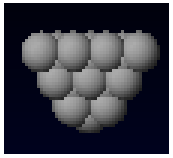
- DNA structure fixed
- constant Freq. shift
- calc. time 3hr. With PC

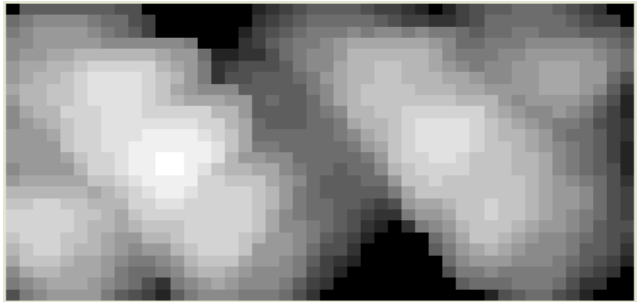


Tip C 1atom



Tip C 29 atom

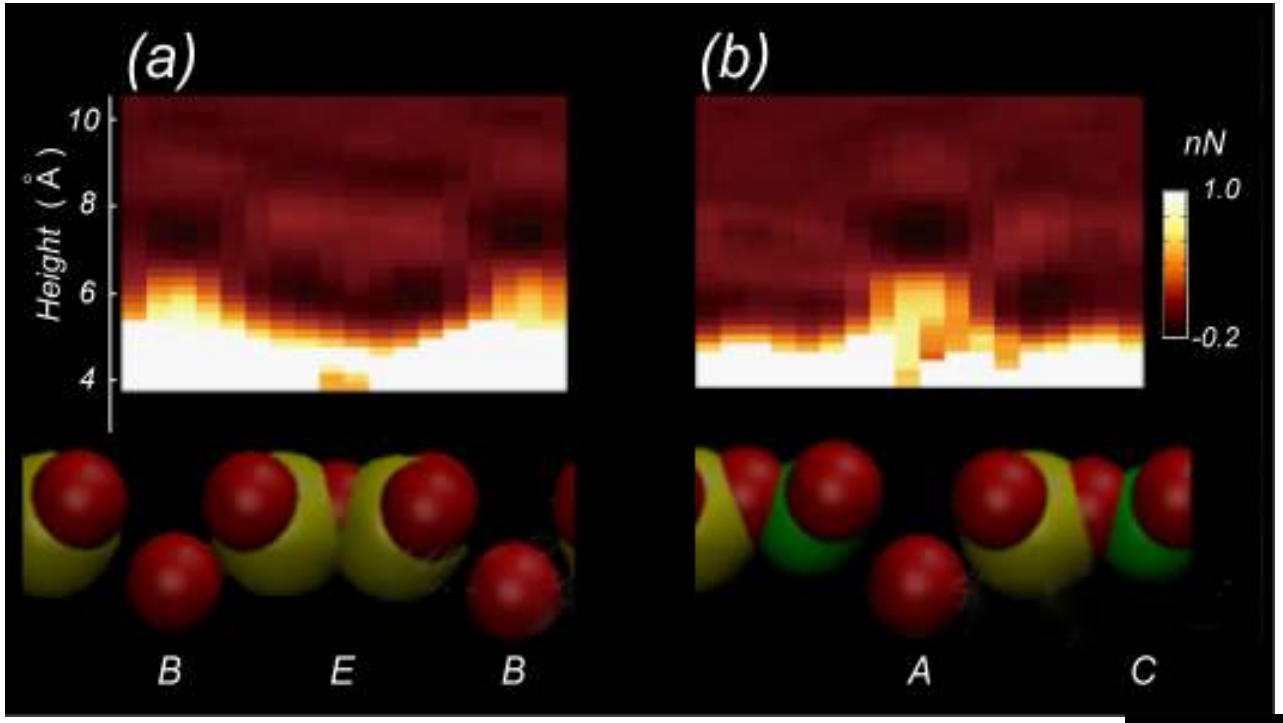




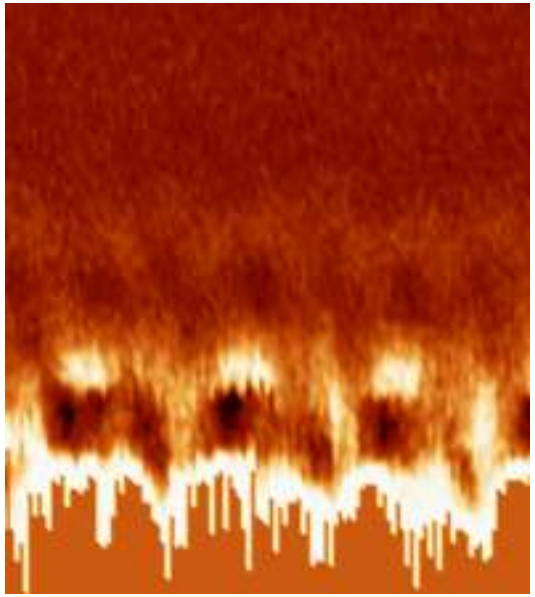
3. Classical Force Field AFM Simulator

based on MD

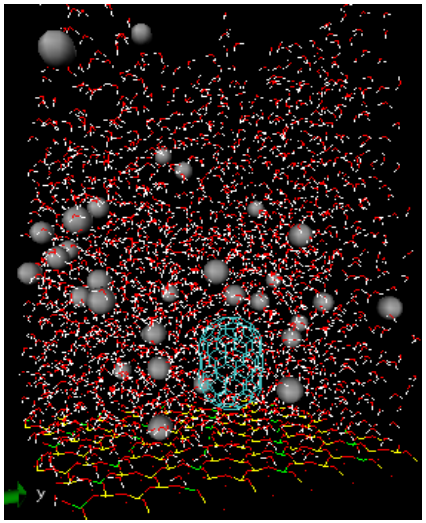
Simulation for dynamic AFM image of mica in water



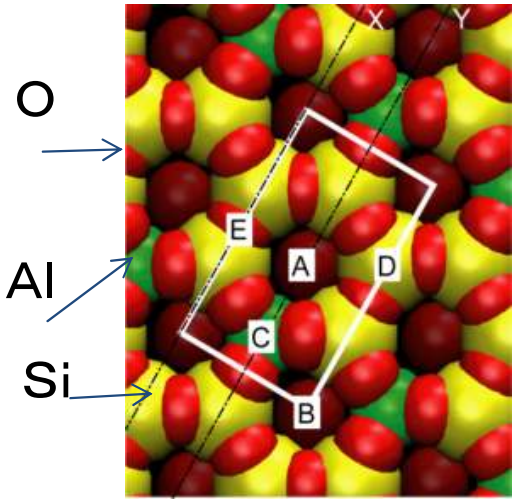
Exp. By Prof. Yamada



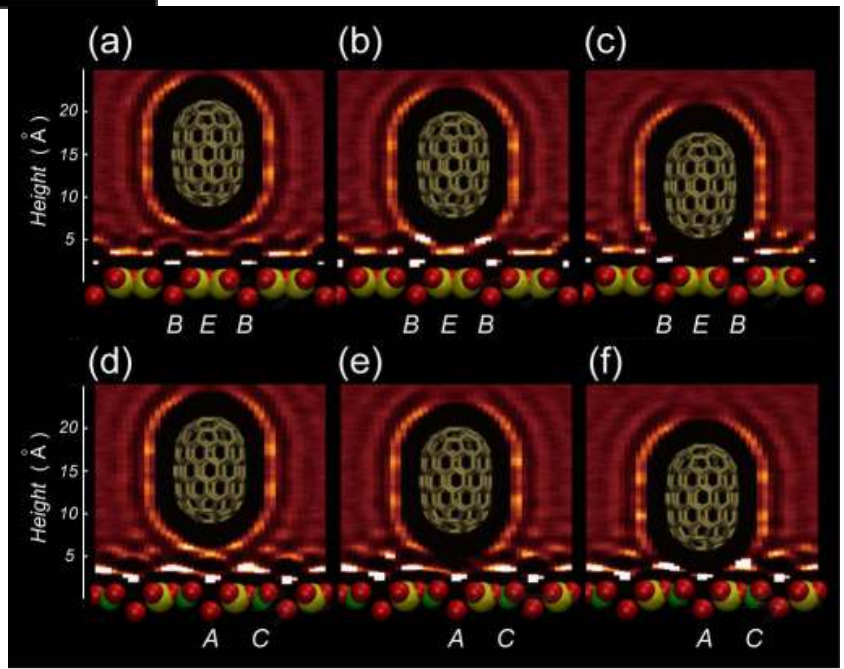
A snap shot of MD



Model of mica in water



Distribution of water



4. Quantum Dynamics SPM Simulator

Accurate SPM image simulation by the quantum mechanical calculation

3. Classical Force Field AFM Simulator

DFT

DFTB

PR-DFTB

Electronic states

Initial tip model

Initial sample model

Chemical/electro-static interaction

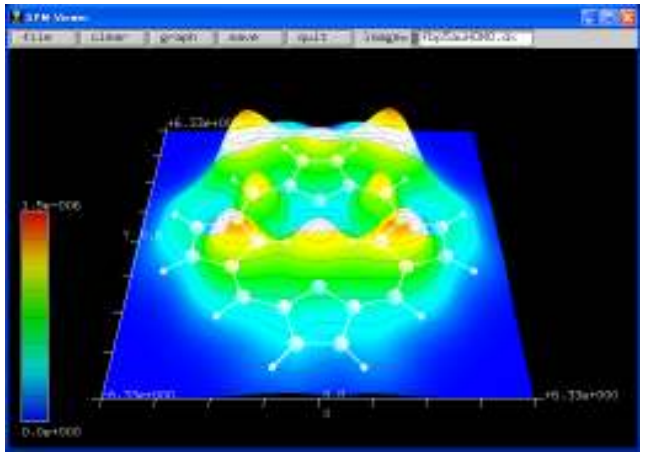
Decorated tip By molecules

Tunnel current

Realistic tip models

STM image・STS spectra

AFM・KPFM images ・force curve

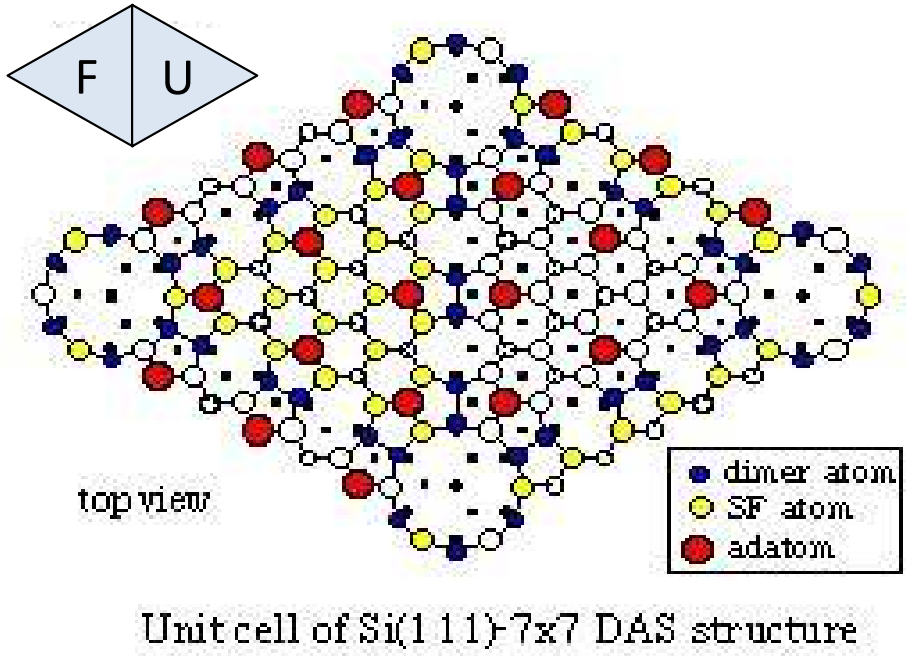


Sample manipulation

Accumulation of Data base and search

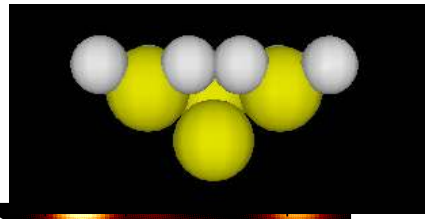
4. Quantum Dynamics SPM Simulator

-example : STM image of Si(111)-7x7 DAS surface

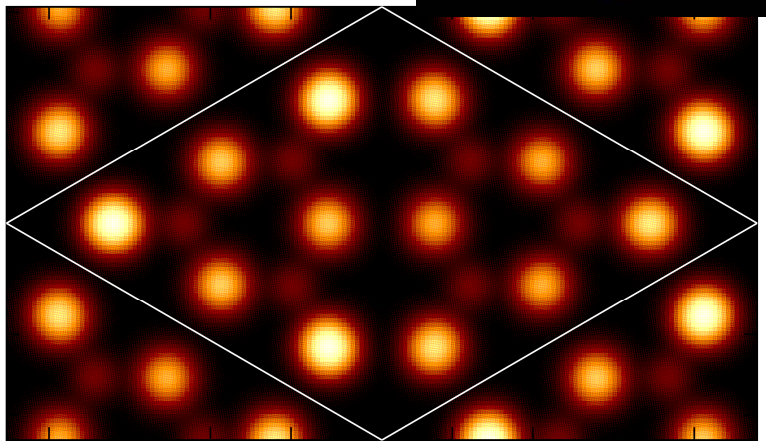


Unit cell of Si(111)-7x7 DAS structure

Tip model Si_4H_9

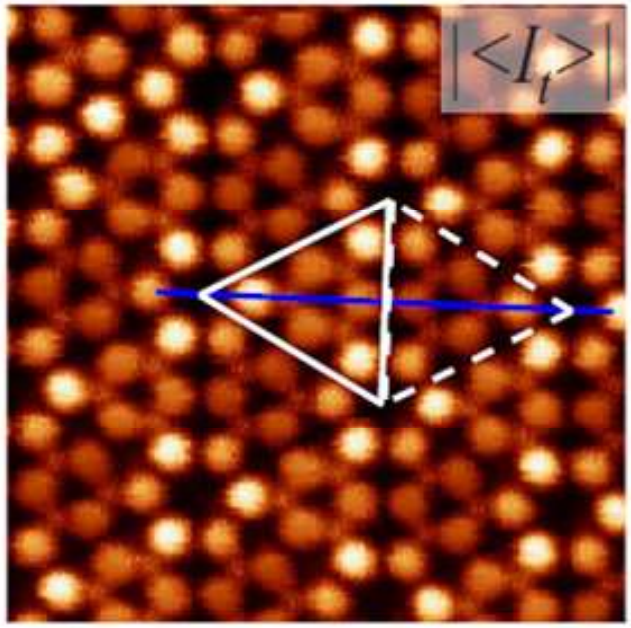


simulation



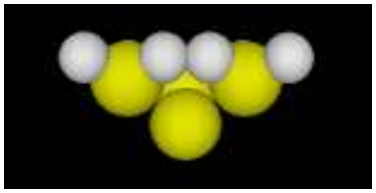
Experiment

by Sawada
et al. (2009)



- calc. time on PC 1.5 hour
  (172x100 pixels)
- tip height = 4.0 Å
- order of brightness
  corner adatoms >center adatoms
  faulted half> unfaulted half
- Rest atoms can be observed !

4. Quantum Dynamics SPM Simulator



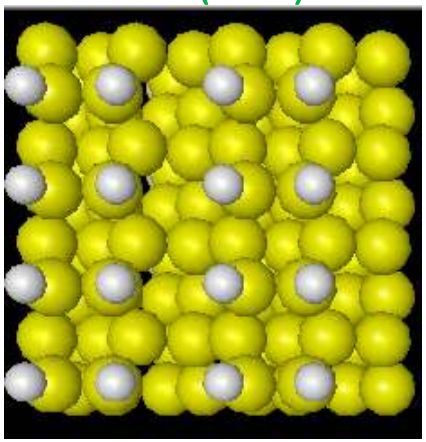
Tip height 6Å

KPFM (V_{LCPD}) images of H-Si(100) based surfaces

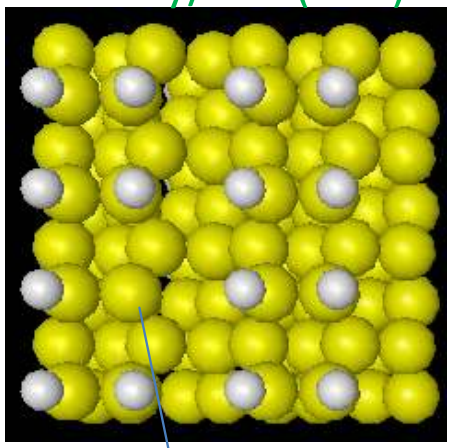
PR-DFTB method was used

Substituted by N

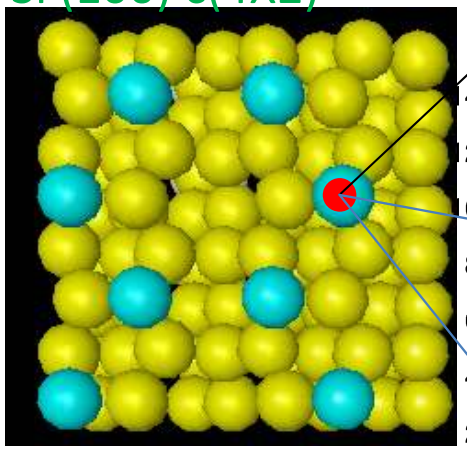
H-Si(100)

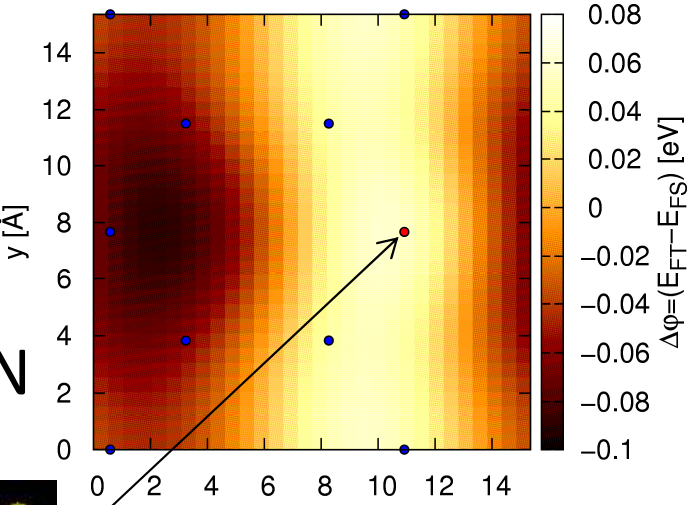


Vacancy/H-Si(100)

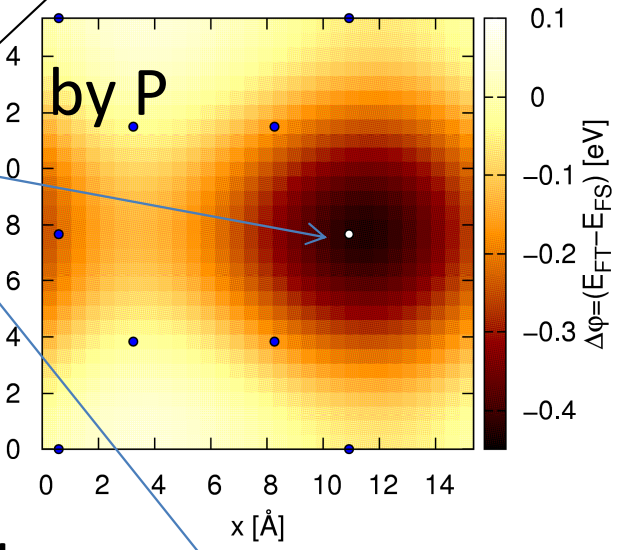


Si (100) c(4X2)

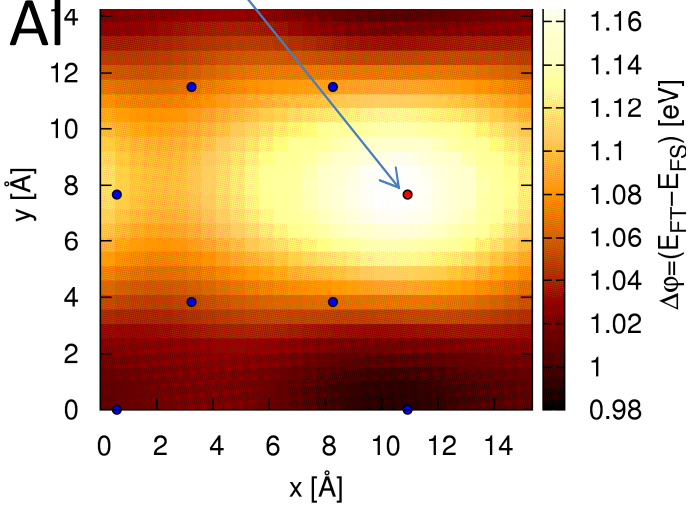


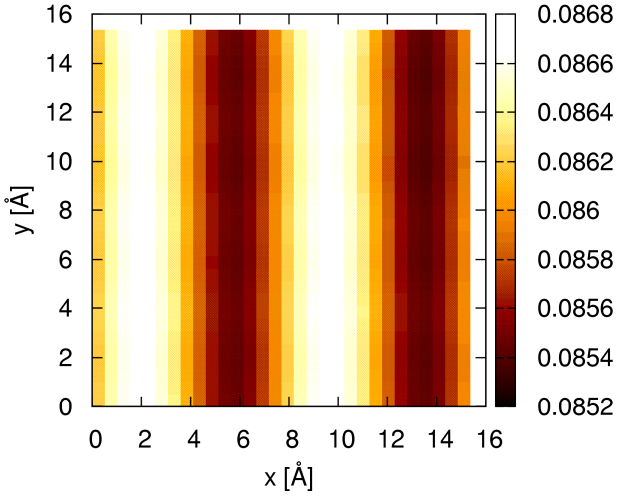


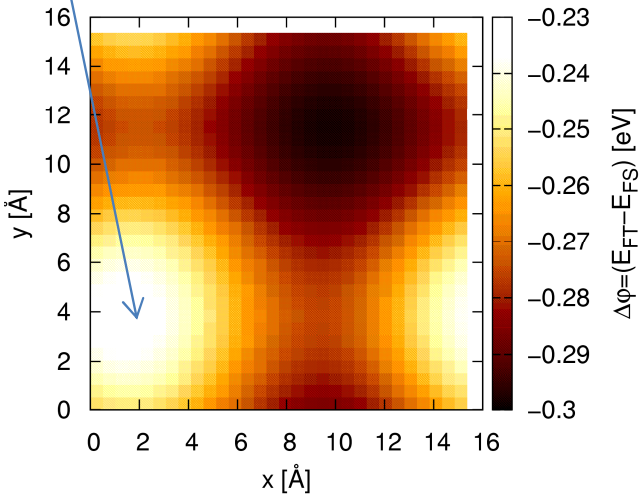
by P



by Al







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How to use Integrated GUI software

Shuji Shinohara
(Advanced Algorithm & Systems Co., Ltd.)

Luncheon Seminar at ncAFM, August 1, 2010.

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Overview

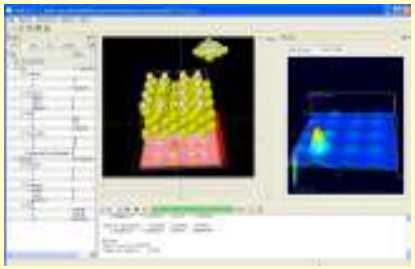
Features

1. **Provide a common platform for our SPM simulators.**
2. **Lump all of the information used in each simulator as a *project file*.**

- Component(tip/samples) name
- Setup condition
- Parameter value
- Result file path

….. (XML format)

Integrated GUI software



Create/Edit

Input

Project files

Simulators

- Geometrical Mutual AFM
- Soft Material Liquid AFM
- Classical Force Field AFM
- Quantum Dynamics SPM

Display

Output

Result files

Reference

Component Database (pdb,xyz…)

Roles

1. **To create/edit *project files*.**
2. **To display the calculated results by simulators.**

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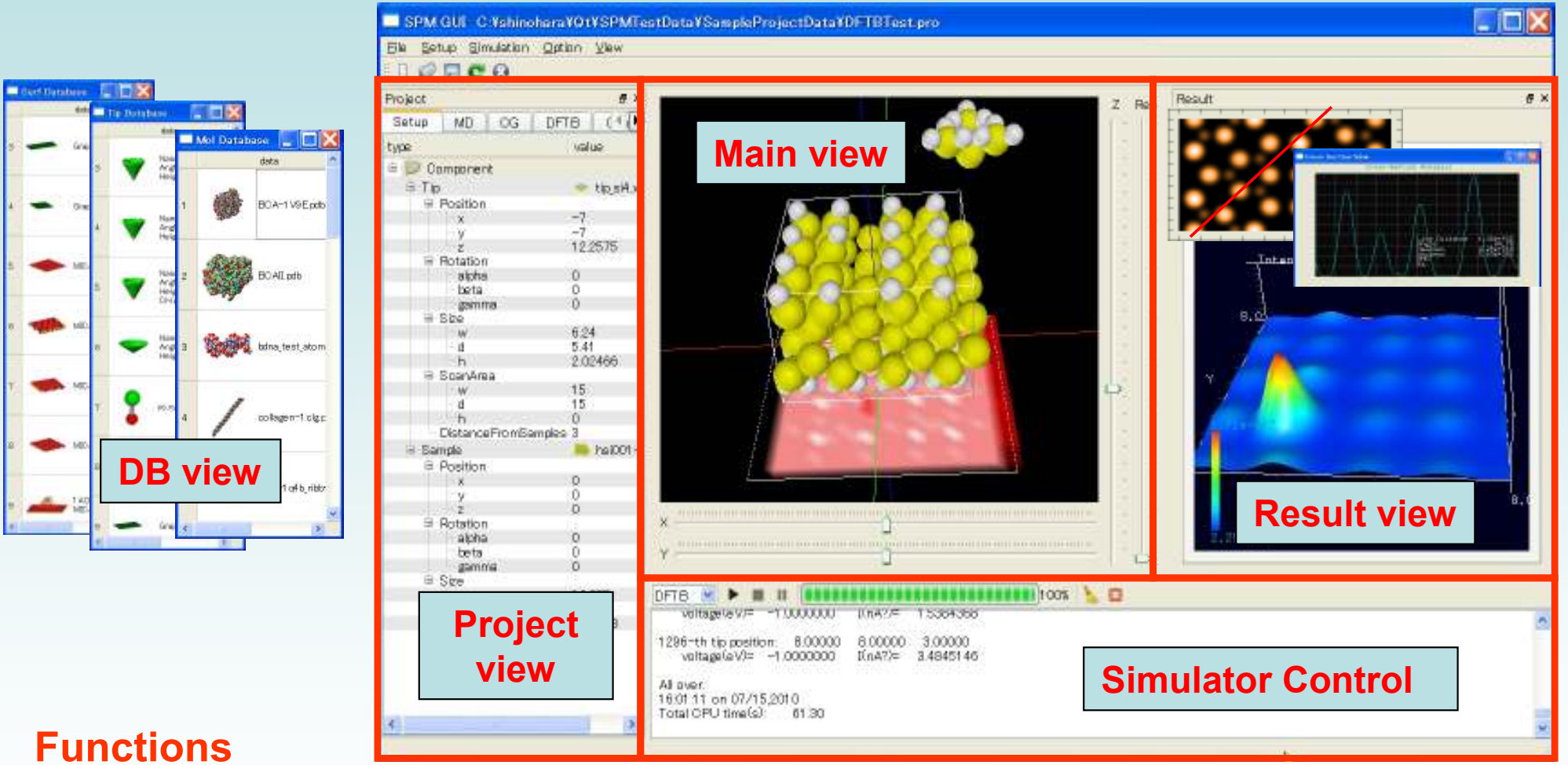
Part names and functions



Functions

1. **Main view : visualizes the setup condition written in a project file. User can change the layout of the components by manipulating mouse/keyboard.**
2. **Project view: shows the content of project file as tree-view. User can create a new project file and edit existing ones.**
3. **Simulator Control: user can select a simulator , start/stop calculation and monitor the progress of the calculation.**
4. **Result view: visualizes the results calculated by our simulators as 2D and 3D images.**
5. **DB view: displays tip/sample data stored in database, from which user can select interesting components by clicking mouse.**

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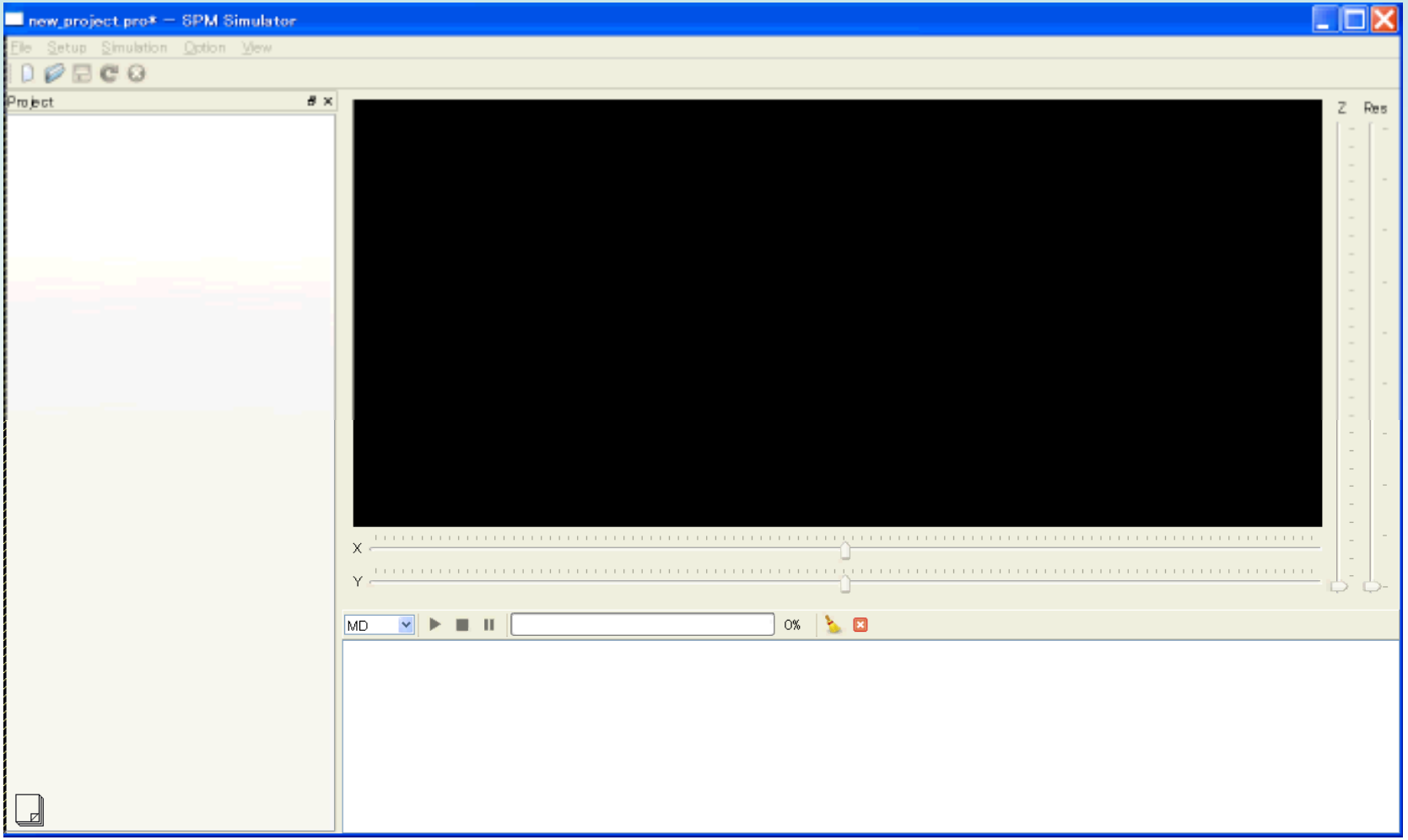
Simulation using “Quantum Dynamics SPM Simulator”



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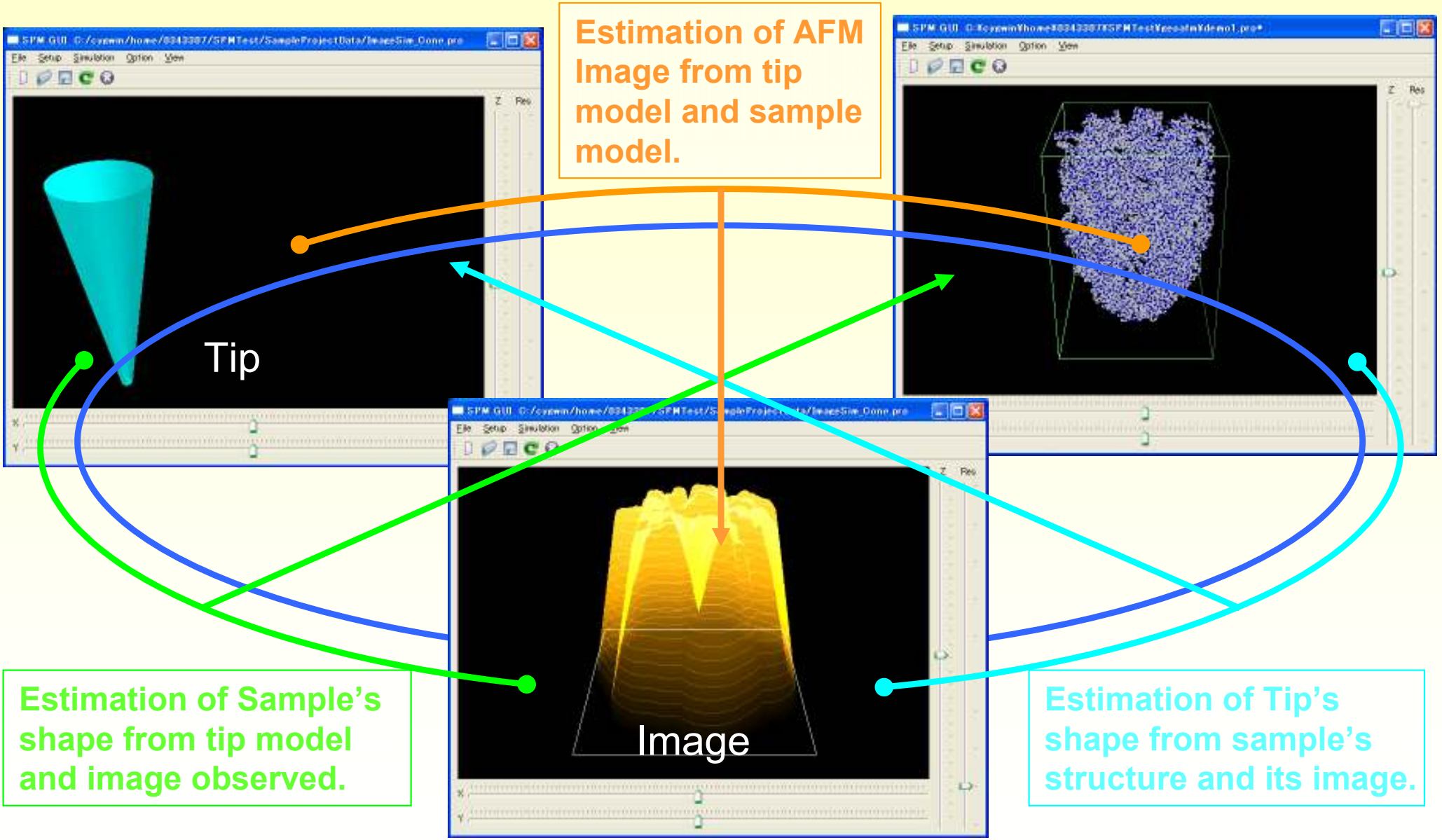
Geometrical Mutual AFM Simulator

Naoki Watanabe

Mizuho Information & Research Institute, Inc

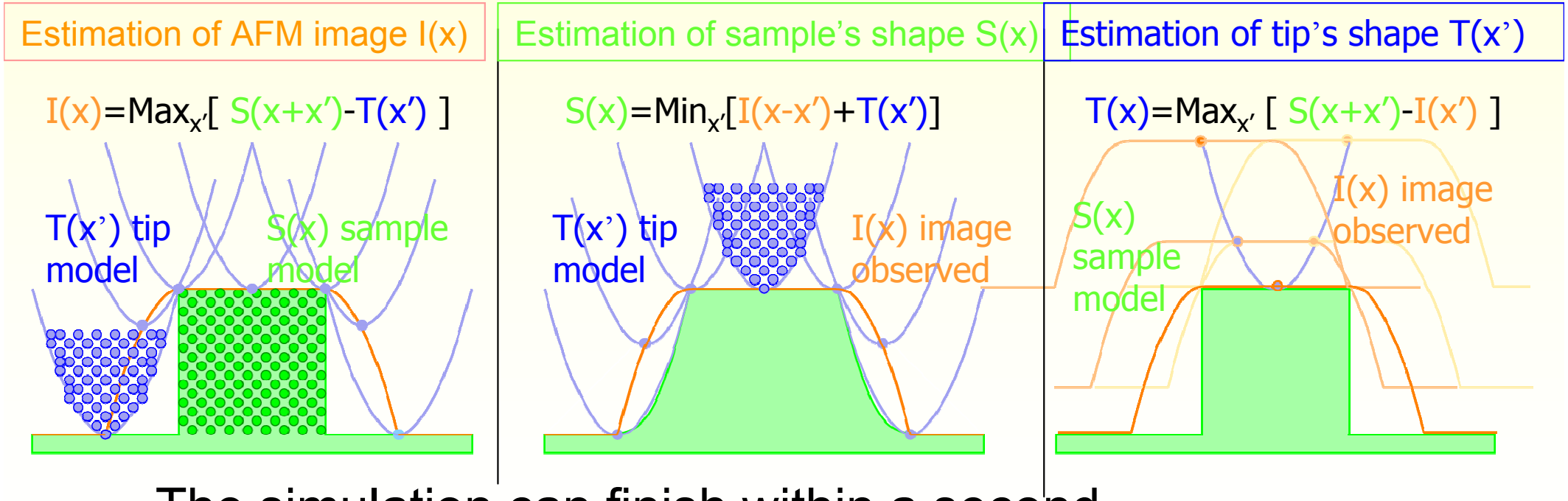
Three functions of this software



Mutual estimation of one unknown object from other two known objects

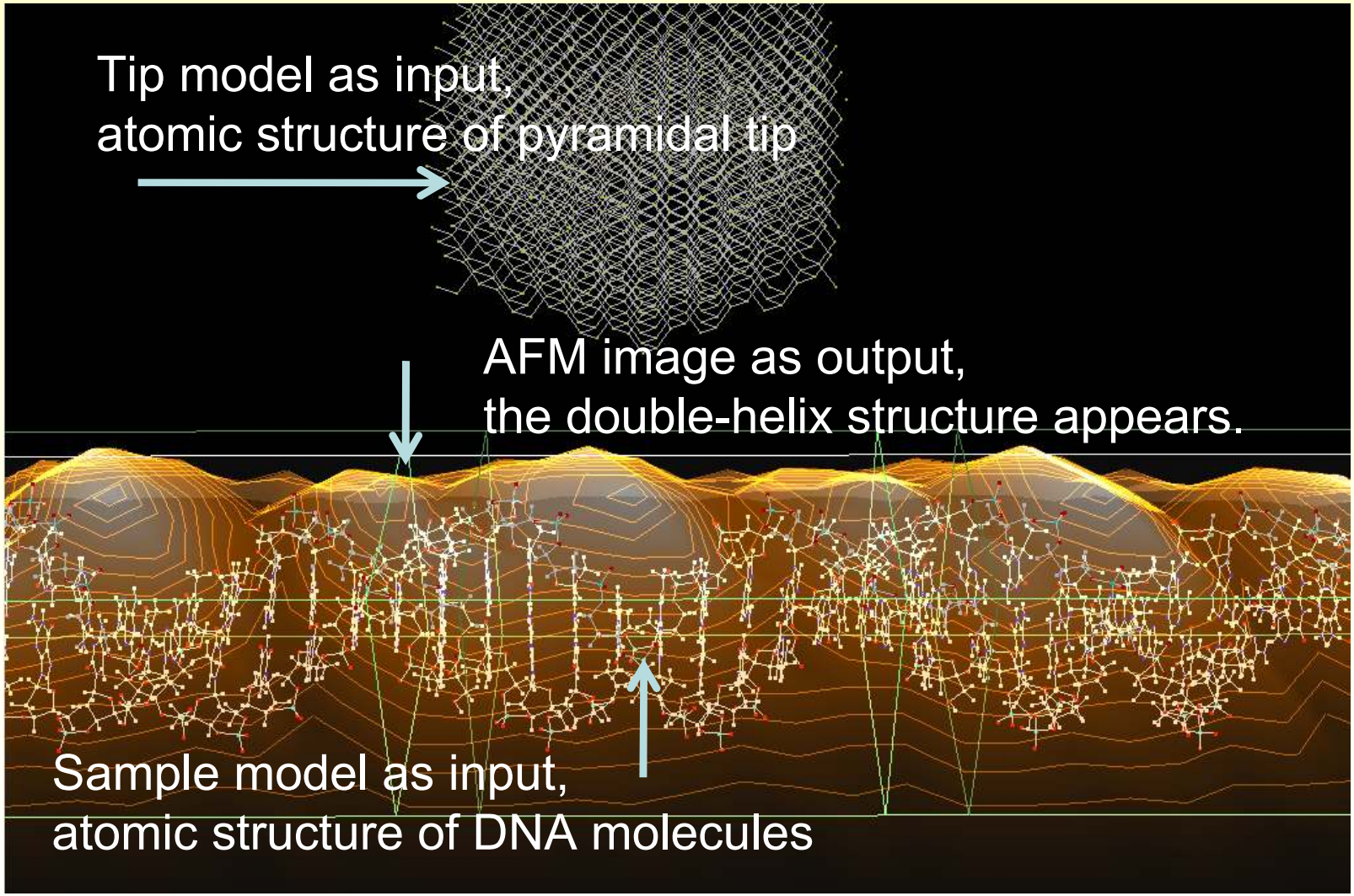
Geometrical Method, simplified approximation

1. Converts atomic structures into continuous rigid materials.
2. Expresses the materials by their shape of the surface.
3. Calculates the contact height of these surfaces.
4. Estimates surface of unknown material as below.



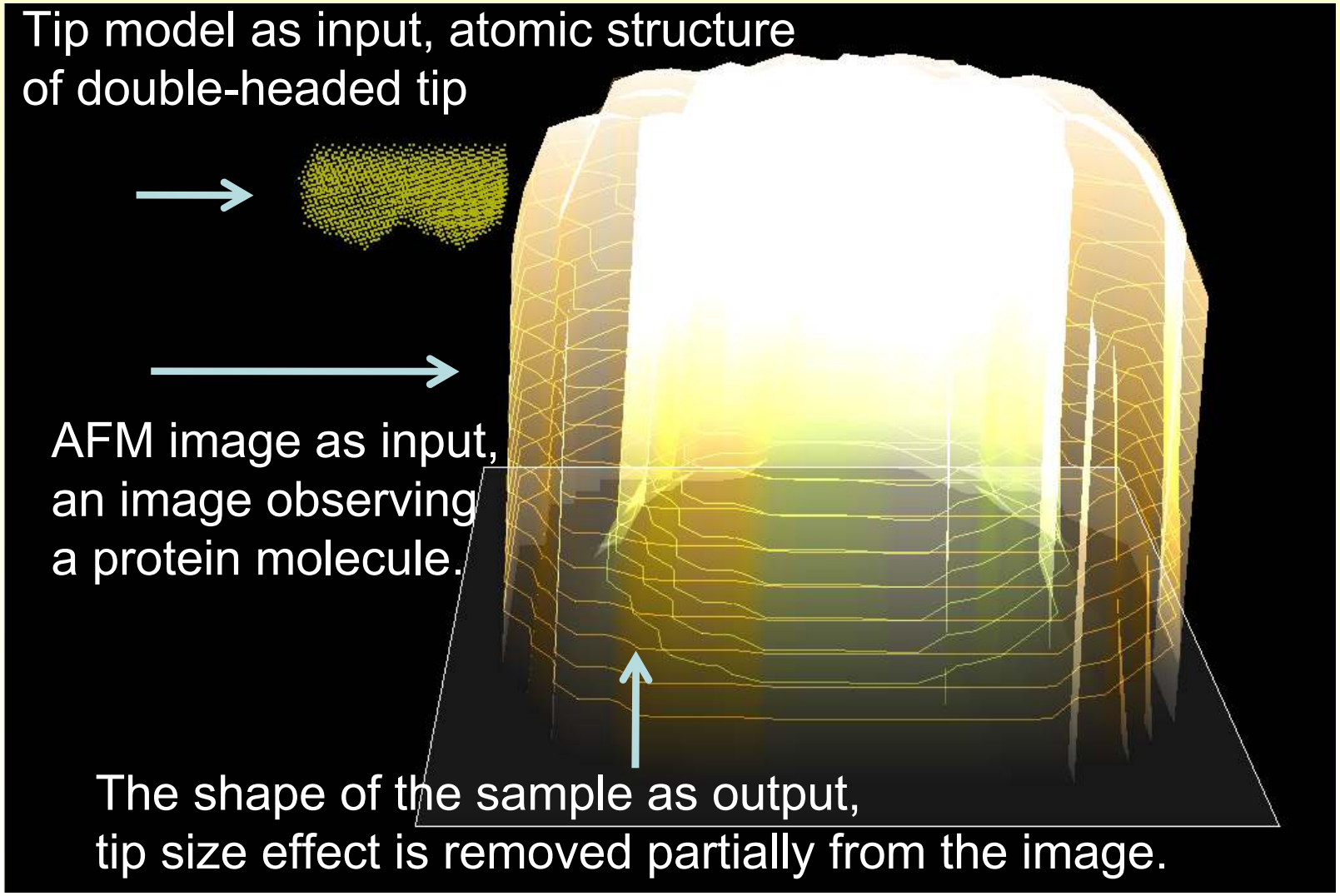
The simulation can finish within a second.
Very useful for a rough estimation/analysis of AFM.

The 1st function: Estimation of AFM image.



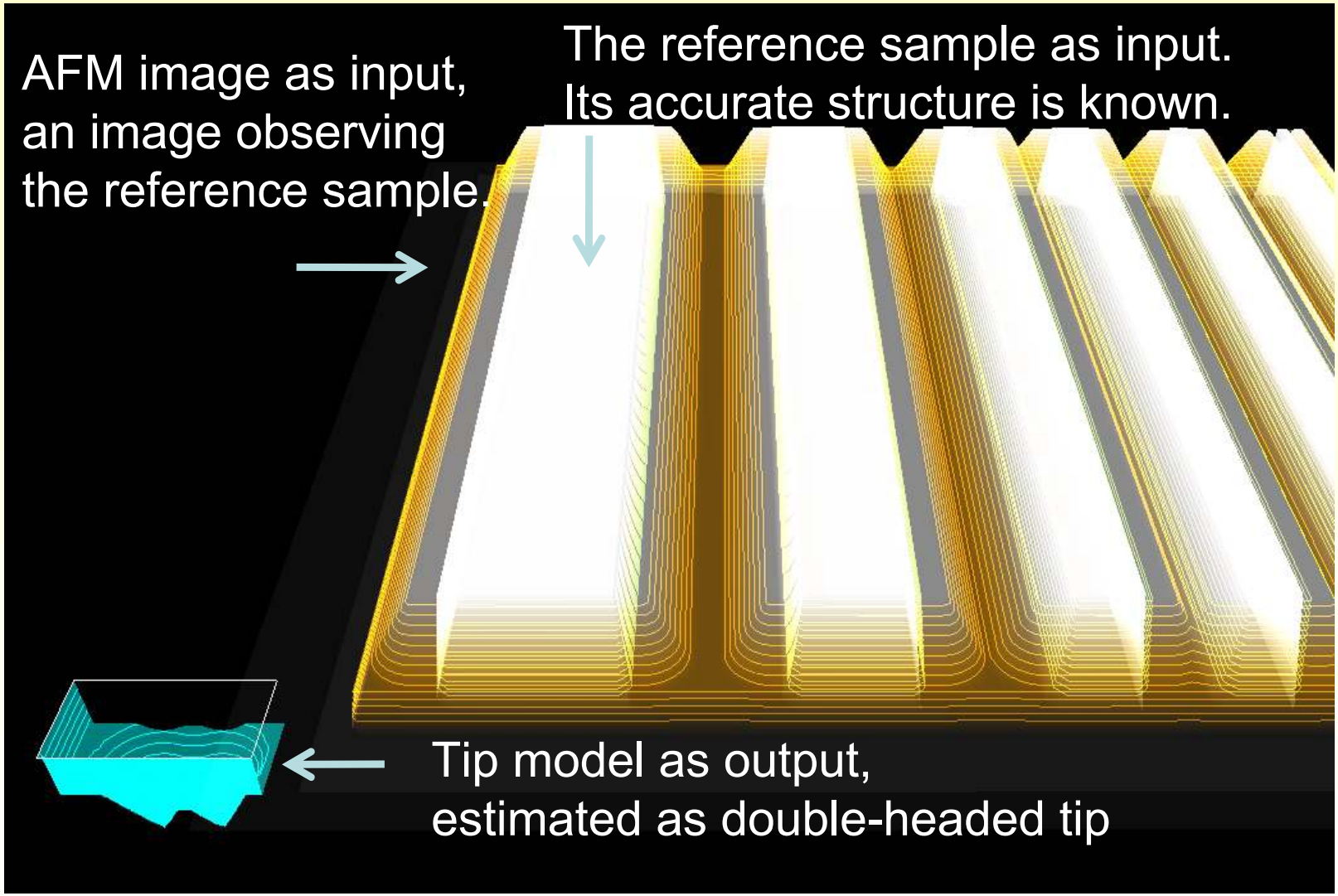
We can estimate the AFM image in advance of experiments.

The 2nd function: Estimation of sample's shape.



We can estimate a shape of the sample we have observed in the experiments

The 3rd function: Estimation of tip's shape.



We can estimate a shape of the tip observing the AFM image in the experiments.

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Soft material Liquid AFM Simulator

Naoki Watanabe

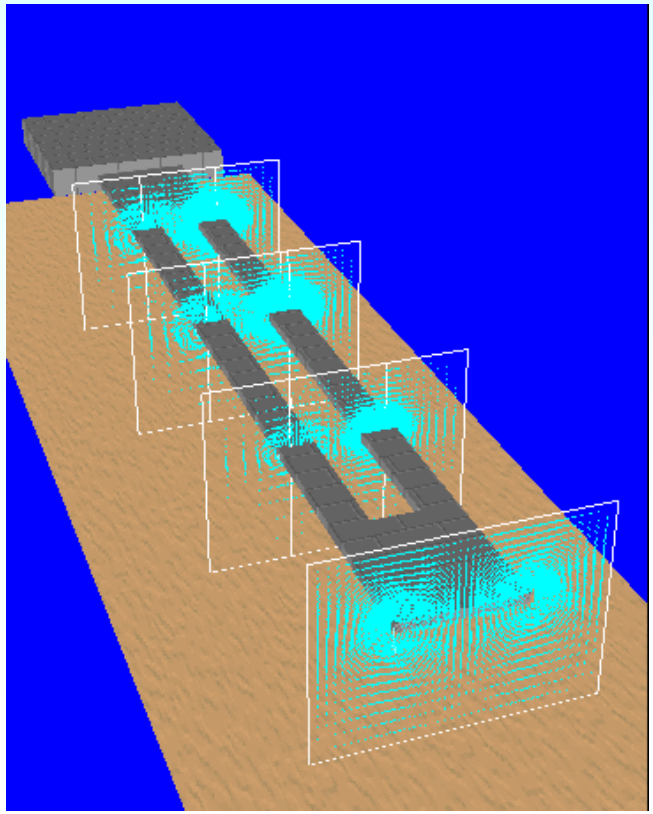
Mizuho Information & Research Institute, Inc

Background of this software

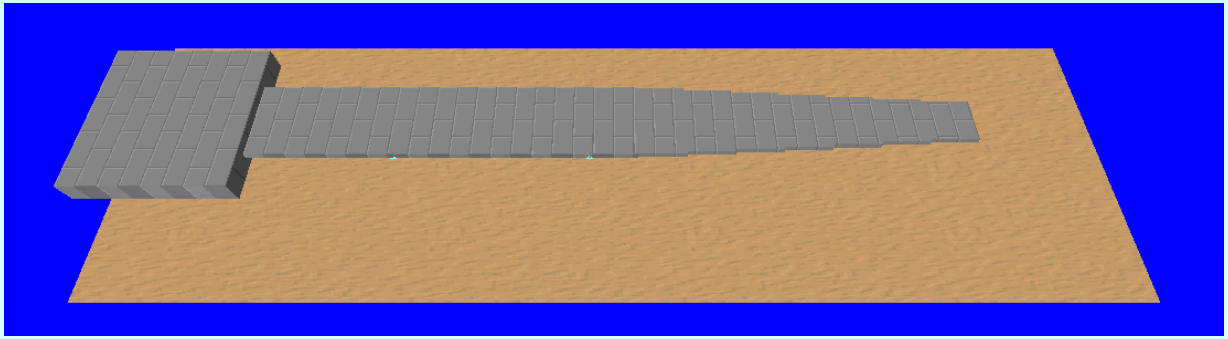
- Bio molecules has been observed by AFM.
- The sample and the cantilever are embedded in water.
- The cantilever feels strong fluid force during oscillation.
- Also it taps soft material samples with its probe tip.
- It elastically bend or twist in during the oscillation.

Purpose of this software

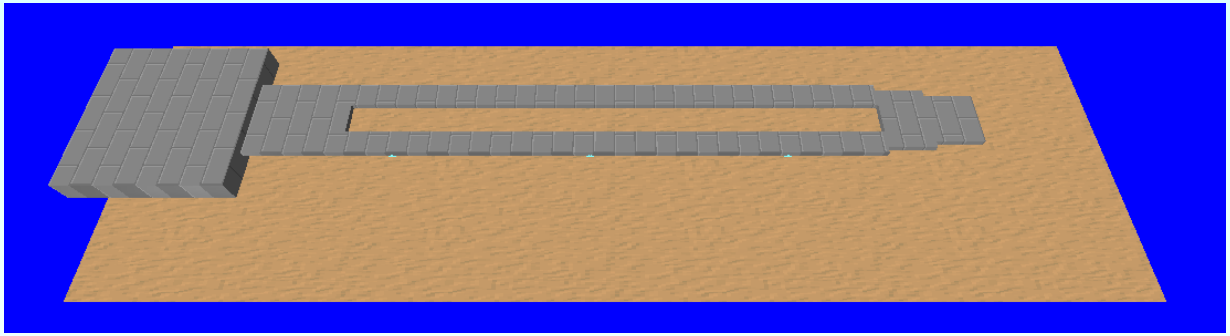
- Simulate the complicated motion.
- Finds oscillation property of cantilever in liquid, with tapping soft materials.
- Design a good cantilever for liquid.
- Analyze the motion of the cantilever.



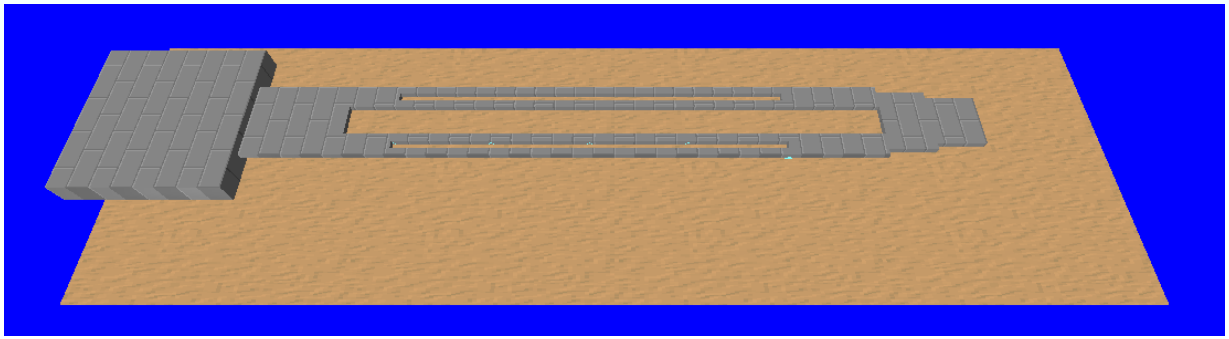
Cantilever shapes for simulation



Beam structure, rectangle in base end, trapezoid in tip end.



Beam structure, with a single hole to reduce fluid force.



Beam structure, with multiple holes to reduce fluid force.

Numerical simulation of cantilever dynamics

1D elastic beam, bending oscillation, vertical motion. Equation of motion:

$$\rho S(z)\frac{\partial^2}{\partial t^2}h(z) = -\frac{\partial^2}{\partial z^2}\left[EI(z)\frac{\partial^2}{\partial z^2}h(z)\right] - \gamma\rho S(z)\frac{\partial}{\partial t}h(z) + F^{\text{liq}}(z)$$

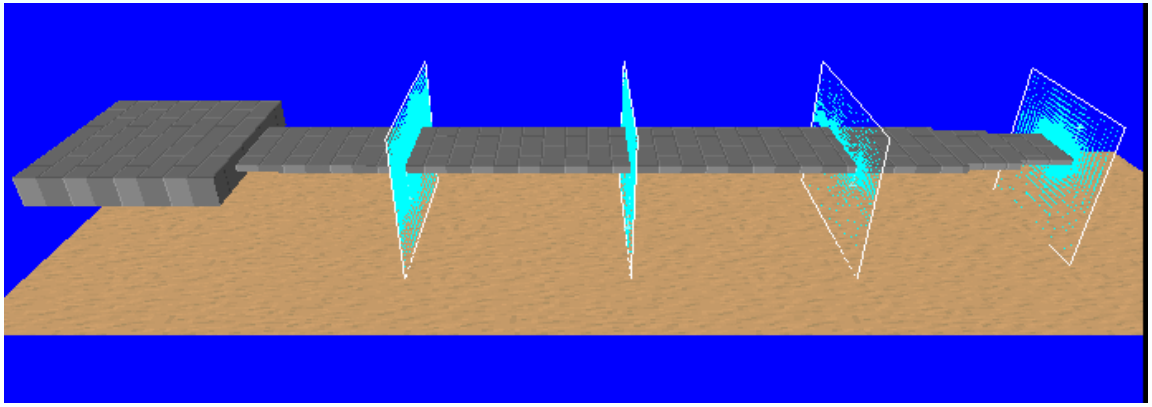
1D elastic beam, twisting oscillation, rotational motion. Equation of motion:

$$\rho I(z)\frac{\partial^2}{\partial t^2}\theta(z) = -GI(z)\frac{\partial^2}{\partial z^2}\theta(z) + T^{\text{liq}}(z)$$

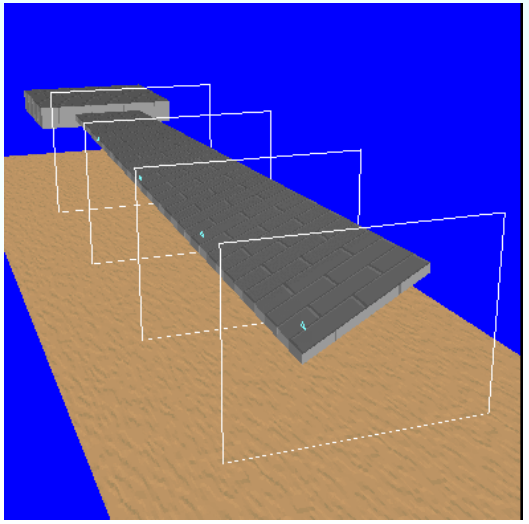
Numerical simulation of fluid dynamics

2D Viscous fluids in some sections. Equation of motion:

$$\frac{\partial\omega}{\partial t} = \mu\left[\frac{\partial^2\omega}{\partial x^2} + \frac{\partial^2\omega}{\partial y^2}\right] \qquad \left[\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2}\right] = -\omega$$



Bending oscillation and fluid dynamics

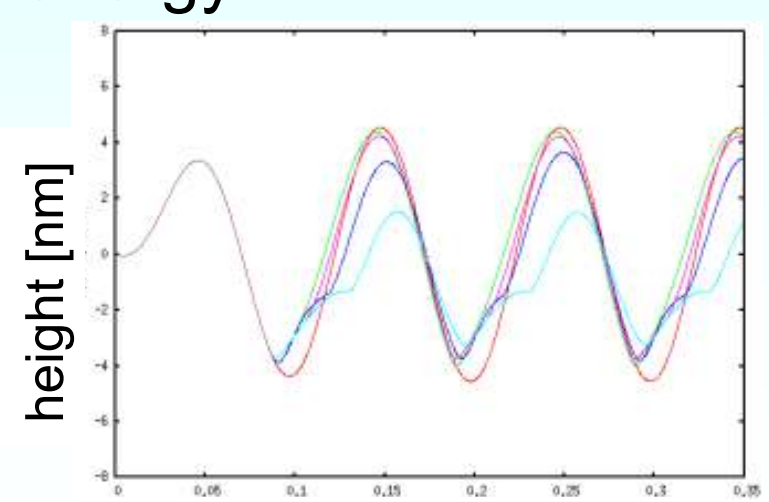


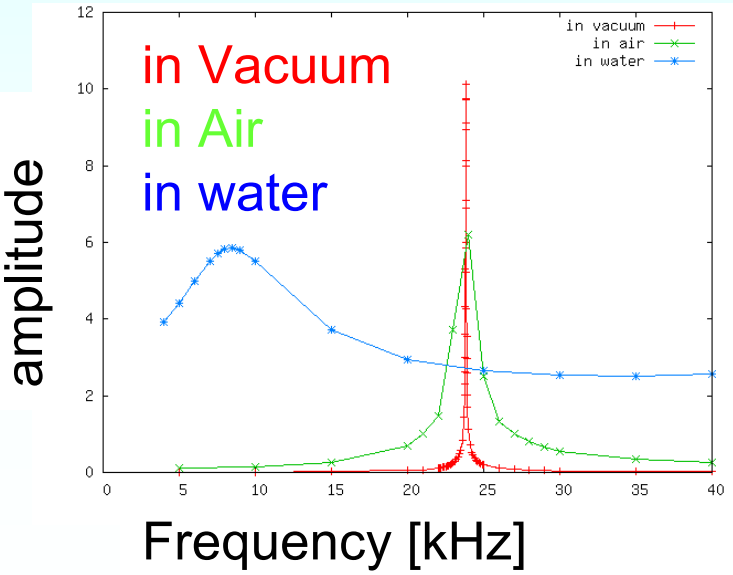
Dumped twisting oscillation and fluid dynamics

Output data this software can produce.

This software can output quantities below.

- Time-evolution of the cantilever's head.
- Frequency spectrum of the oscillation.
- Modulation of the amplitude of the oscillation.
- Shift of the phase of the oscillation.
- Dispersion of energy.
- AFM signals.
- AFM image.





- We aim to make an integrated cantilever simulation software.

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Classical Force Field AFM Simulator

Kazuma Tsutsumi
(Advanced Algorithm & Systems Co., Ltd.)

Luncheon Seminar at ncAFM, August 1, 2010.

Outline

- Features of this simulator.
- Three examples of simulation using this simulator.
  - ✓Frequency shift image of pentacene.
  - ✓Compression of GFP.
  - ✓Tip-substrate interaction in water.
- Simulation principles of AFM imaging and Calculation method of tip-sample interaction force.

1. Feature of this simulator (Difference from other simulators)

AFM imaging by the classical mechanics method using force field.

This simulator

■Classical mechanics method

Statics or dynamics simulation using classical mechanics.

■Atom scale simulation

Classical force field is assigned to all atoms.

⇔ Quantum Dynamics SPM Simulator

Quantum mechanical method

⇔ Geometrical Mutual AFM Simulator

Geometrical method

Application range

- ●Substance

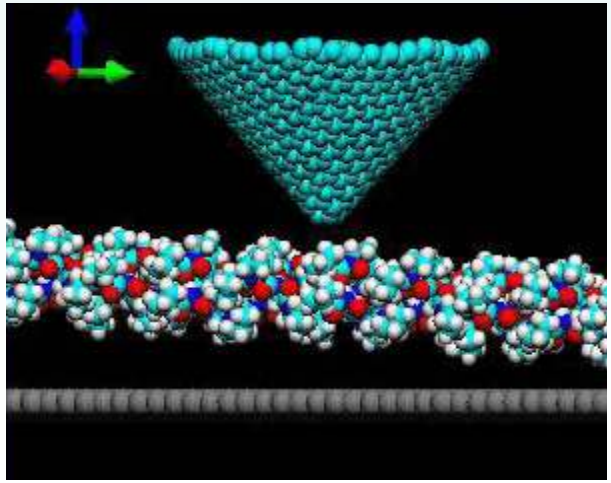
  Organic molecular, Inorganic material, Protein etc.

- ●Environment

  In vacuum or in water.

- ●Spaciotemporal scale

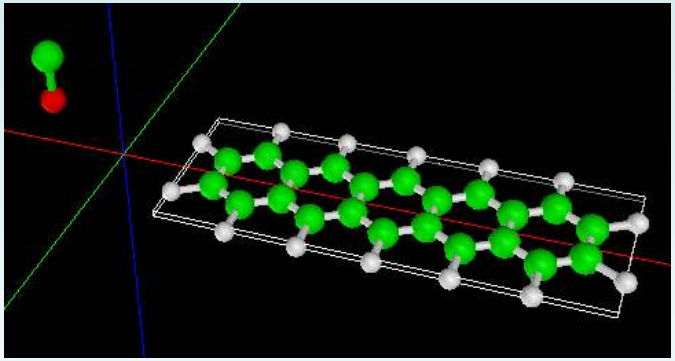
  Nano meter and μ-ns scale.



2.1 Example of simulation (1)

Frequency shift imaging of pentacene by MM.

pentacene molecule and CO-probe

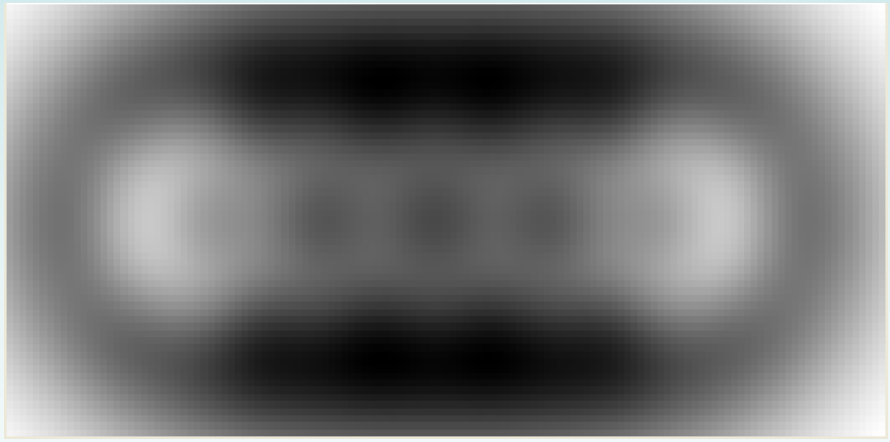


Please enjoy the demonstration movie.

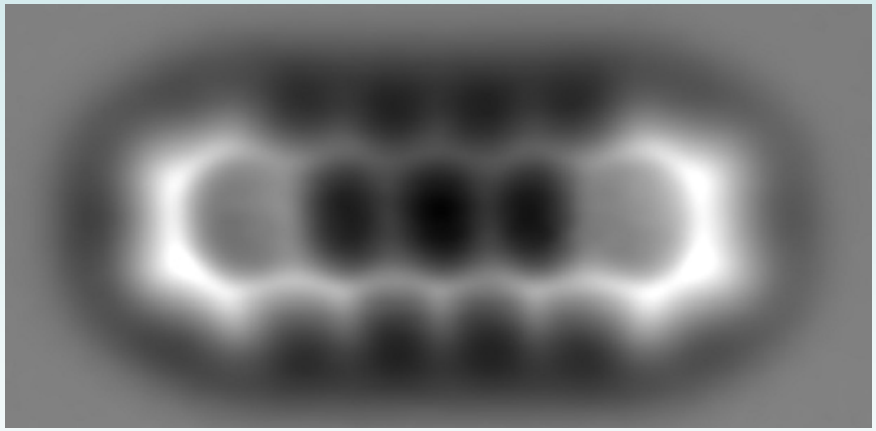
2.1 Example of simulation (1)

Comparison of experiment and simulation of pentacene AFM imaging.

Simulation result



Experimental result

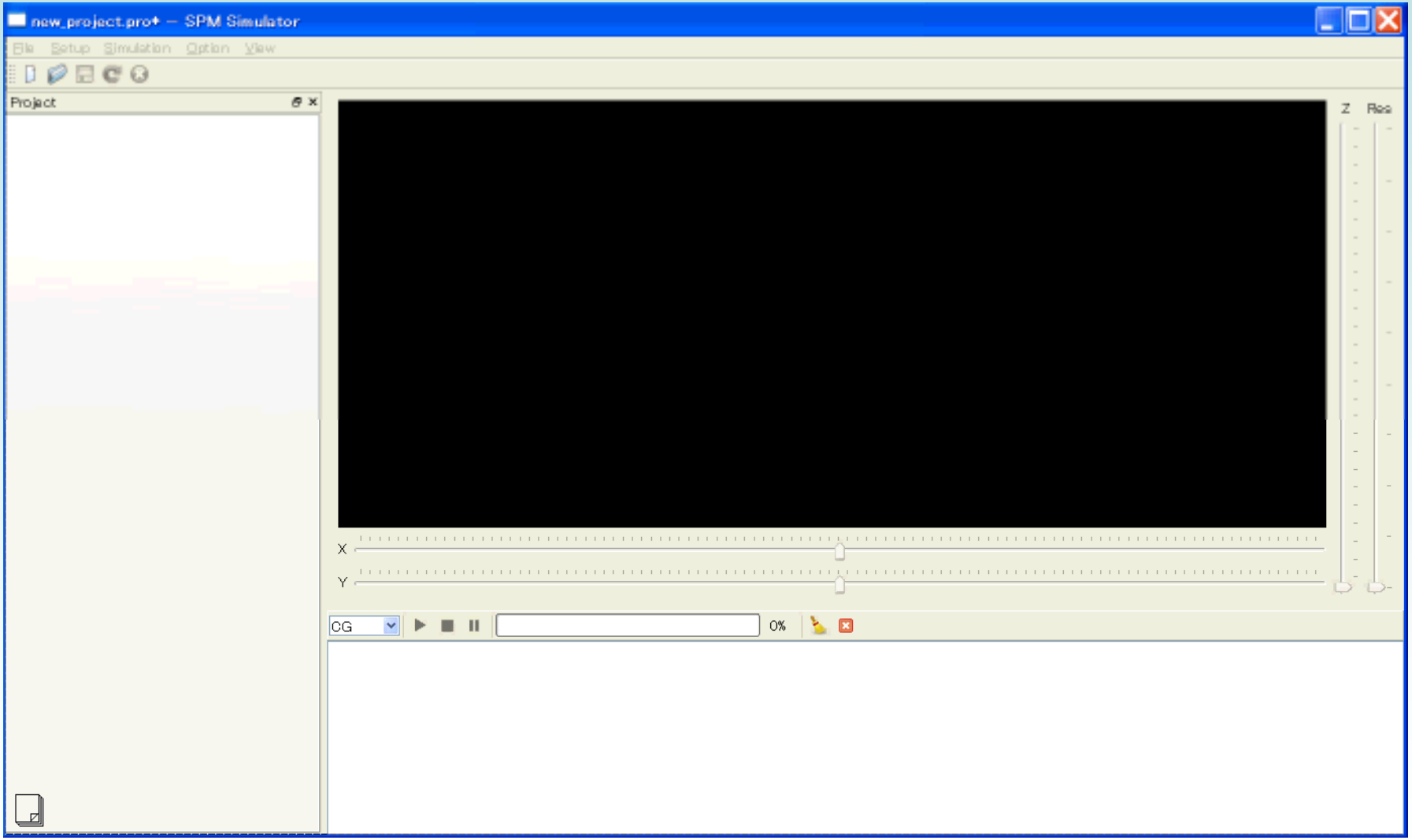


SCIENCE, **325** (2009) pp.1110-1114.

Both results are resemble.

2.2 Example of simulation (2)

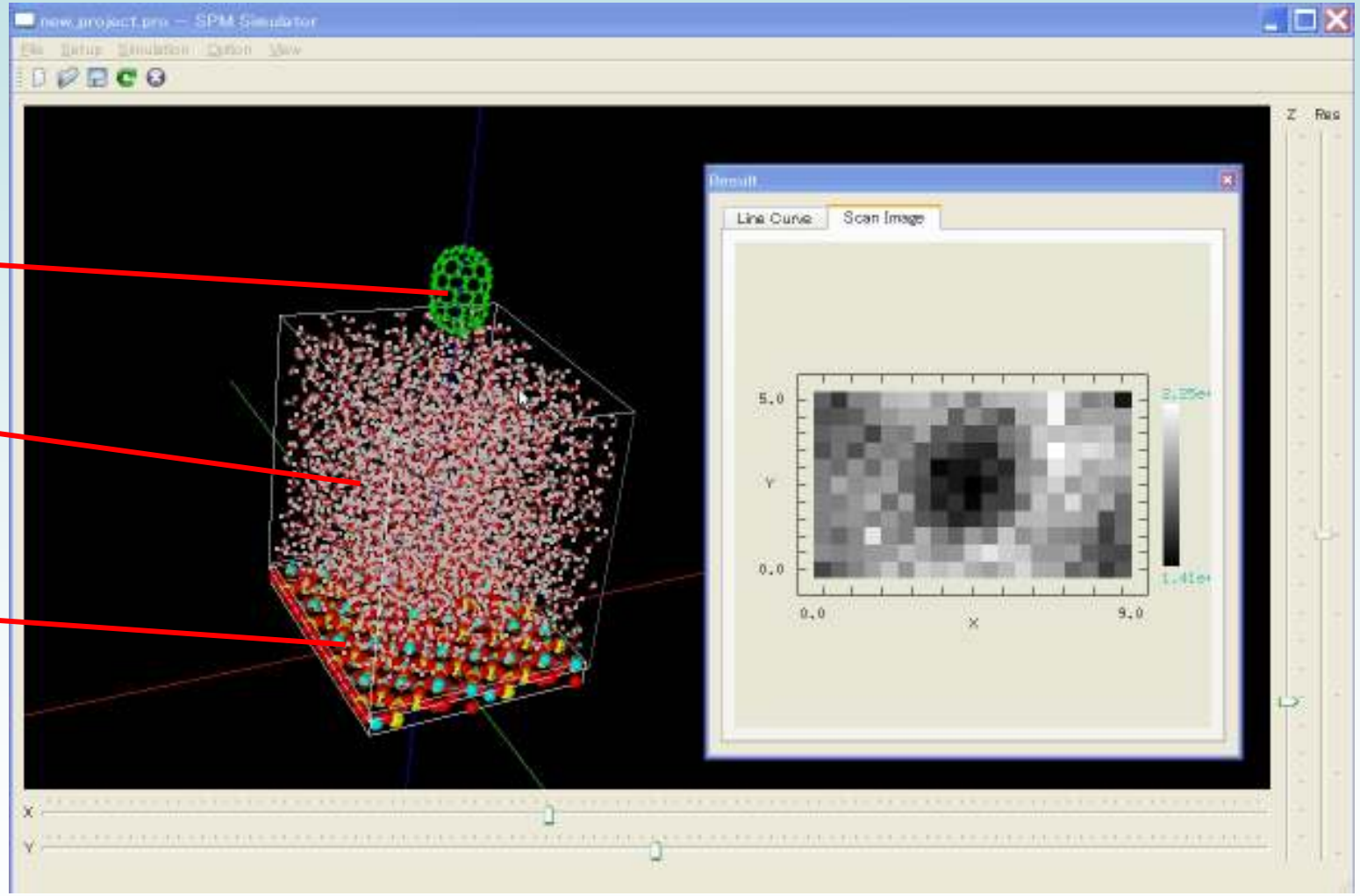
Compression simulation of protein:Green Fluorescent Protein (GFP), by MD.



Our simulator will be able to make you observe the force curve and the corresponding deformation behavior of molecules.

2.3 Example of simulation result (3)

Simulation example of muscovite mica surface in liquid water by MD.

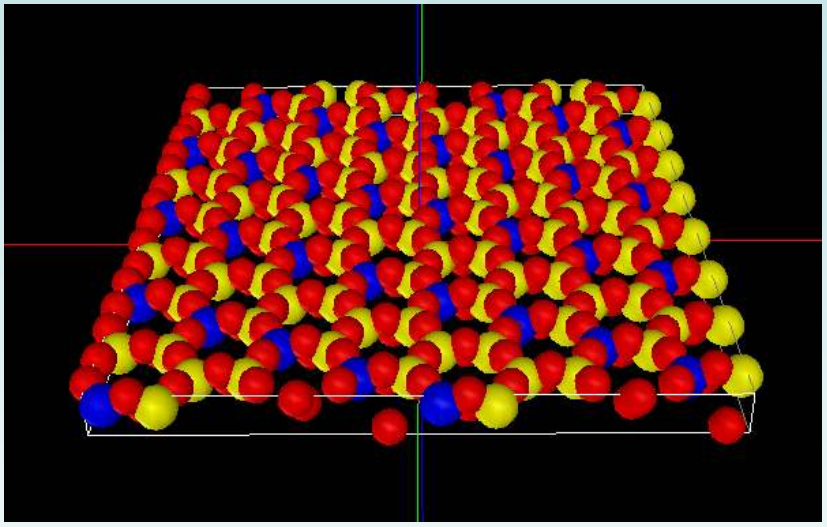


Calculating the force acting on the carbon nanotube probe that sank in water.

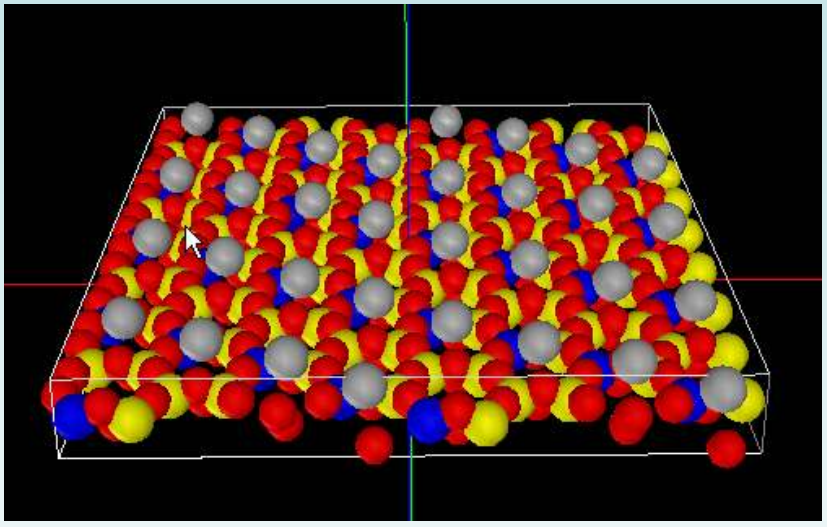
2.3 Example of simulation result (3)

Modeling of simulation system.

① Potassium ions are not placed.



② Potassium ions are placed.

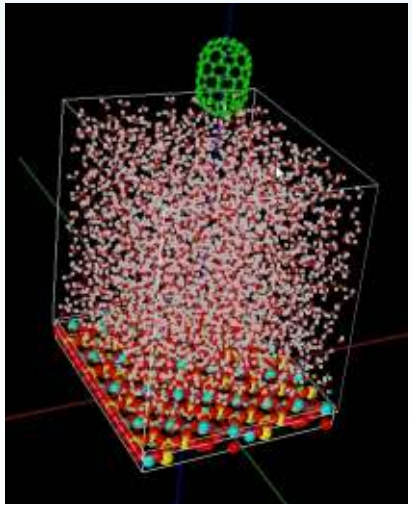


Red: oxygen

Yellow: silicon

blue : aluminum

Gray: potassium ion



Water and probe molecular are placed on the substrate.

And, probe is sank in water.

2.3 Example of simulation result (3)

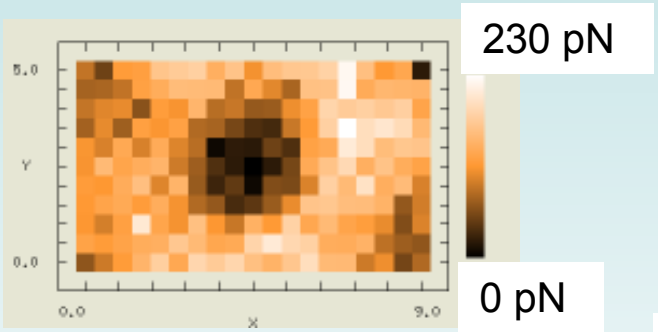
AFM imaging

Force distribution of horizontal plane (parallel to the substrate).

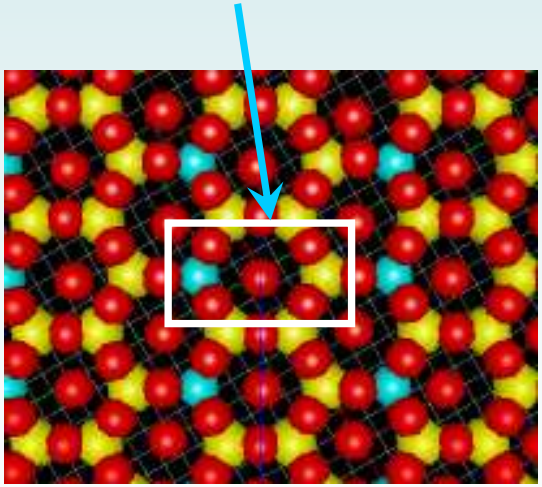
Potassium ions are not placed on outermost surface of mica.

d : probe-substrate distance

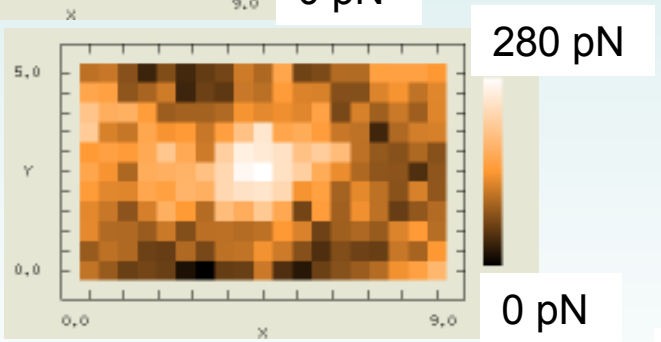
d=7.8 Å



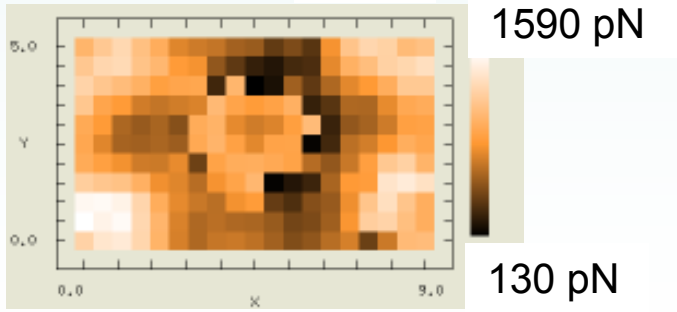
Scanning area



d=6.8 Å



d=5.0 Å



(By taking the time to calculate more, you can get a higher resolution.)

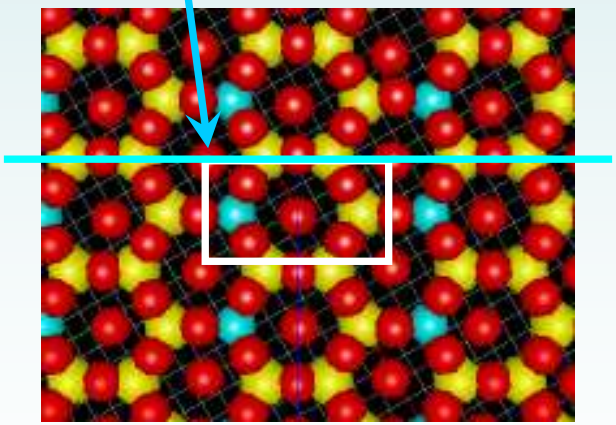
2.3 Example of simulation result (3)

AFM imaging　　Difference in the presence of potassium ions.

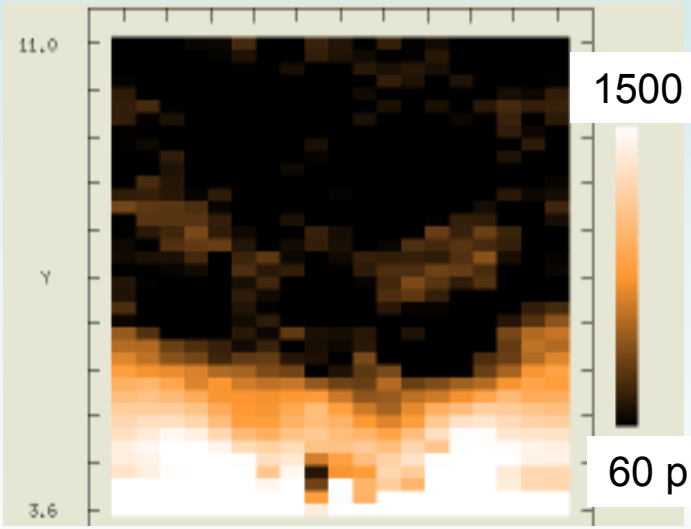
Force distribution of vertical plane.

Potassium ions are placed on outermost surface of mica or not placed.

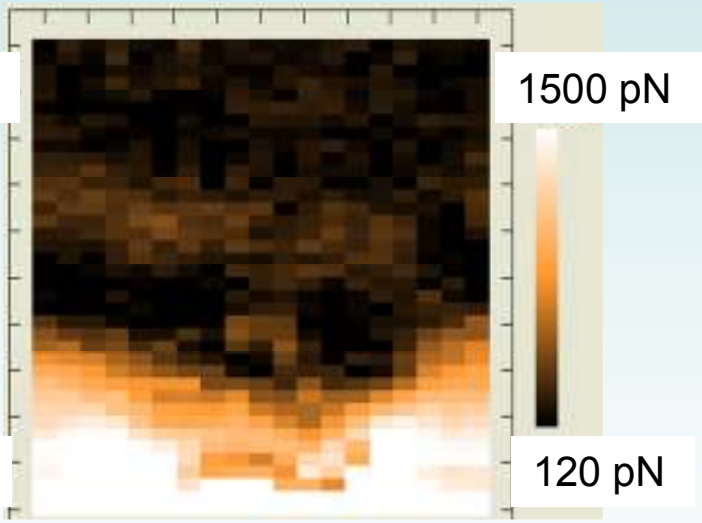
Slice position

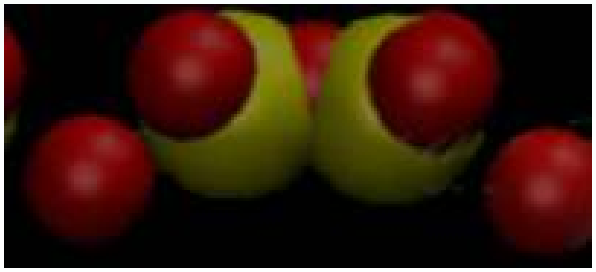


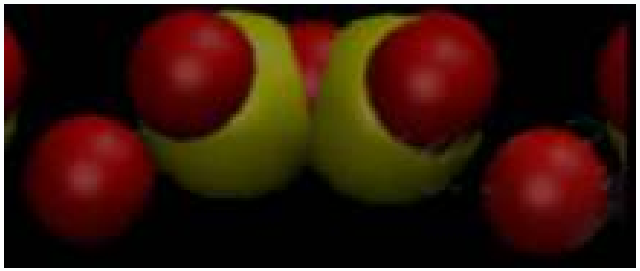
① not placed



② placed







3.1 Calculation principles of dynamic AFM imaging

Resonance curve

$$A = \frac{1}{2\sqrt{(f/f_0 - 1 + r)^2 + h^2}}$$

Frequency shift : tip-sample interaction

$$\Delta f = r f_0 = -\frac{f_0}{2kA\pi}\int_0^{2\pi} F(A\cos\theta + L)\cos\theta \, d\theta$$

Resonance width : friction + hysteresis term

$$h = \frac{1}{\pi\omega_0}\int_0^{2\pi} \gamma(A\cos\theta + L)\sin^2\theta \, d\theta$$

$$+\frac{1}{2kA\pi}\int_0^{2\pi} F(A\cos\theta + L)\sin\theta \, d\theta$$

By calculating the frequency shift and the resonance width for each tip position, you can obtain AFM images.

3.2 Calculation method of AFM tip-sample interaction force

■Energy relaxation method (MM: Molecular Mechanics method)

Calculating the most stable atomic structure on the classical force field potential by conjugate gradient method (CG).

■Molecular dynamics method (MD)

Equations of motion of all the atoms in the simulation system are solved.

Comparison of two methods of calculation

Calculation method	Property	Temperature Effect	Output
MM	Static	Not considered	Force Energy dissipation Frequency shift
MD	Dynamic	considered	Trajectory of atoms

You can choose the appropriate method for your purpose

Summary

■You can simulate simple but realistic cases by using this simulator.

■You can observe the behavior of atoms by visualization. So you will be able to get some useful information.

Thank you for your kind attention.

ADVANCED ALGORITHM & SYSTEMS

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World Premier International Research Center Initiative

Quantum Dynamics SPM Simulator

Mamoru Shimizu

(Advanced Algorithm & Systems Co., Ltd.)

Supervised by Prof. Tsukada and Dr. Masago

(WPI-AIMR, Tohoku Univ.)

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STM (1/3)

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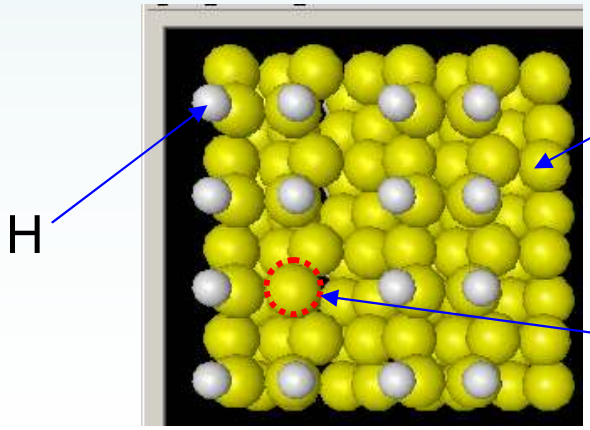
use the formula by Bardeen's perturbation theory

- tip and sample: so distant
- calculation of electronic states: only once
- image calculation is fast !

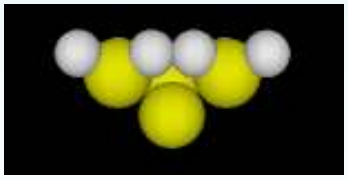
H-Si(001)-(2x1) with one defect : **a few min.** (60x60 pixels)

(You can experience at our exhibition booth.)

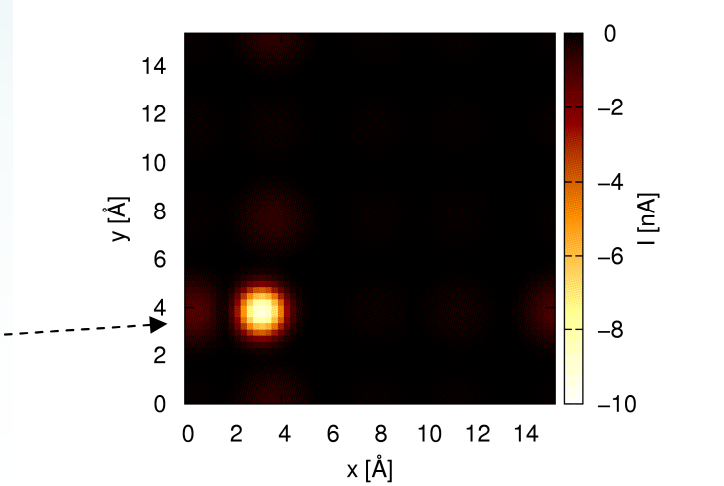
Surface



Tip

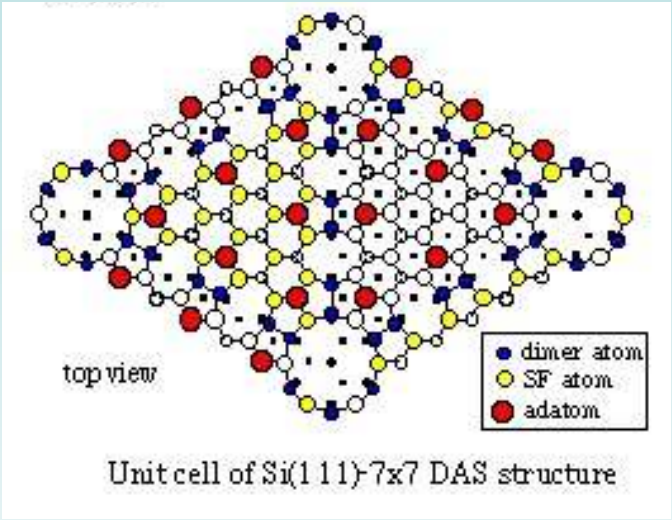


Sim. Tip height 4.2 Å



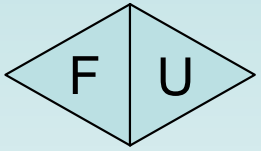
STM (2/3)

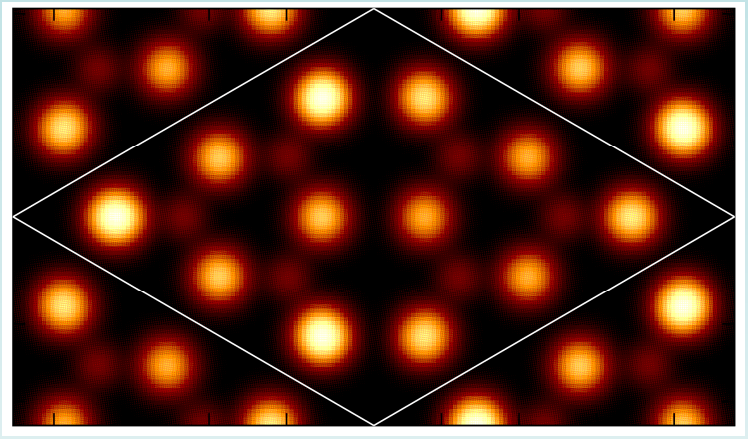
Si(111)-7x7 DAS structure



(strct. fig. http://www.ohdomari.comm.waseda.ac.jp/)

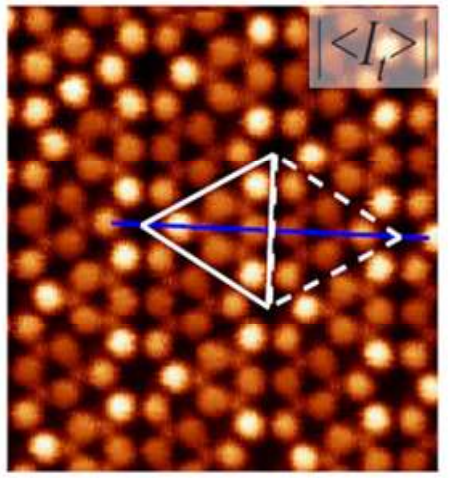
Sim.





- calc. takes about 1.5 hours
  (172x100 pixels)
- Contrast of current from the adatoms are reproduced.
- tip height = 4.0 Å

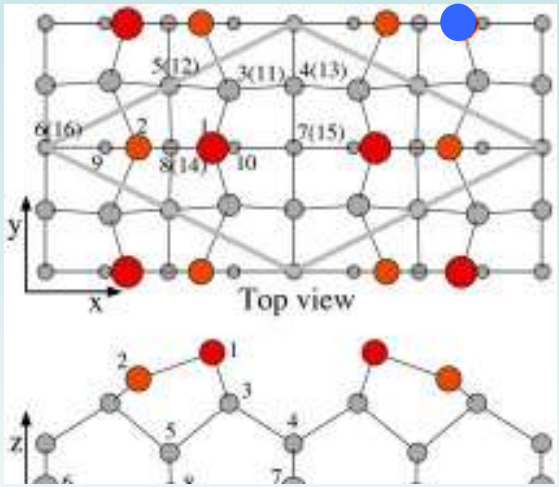
Exp. by Sawada et al. (2009)



STM (3/3)

one impurity on Si(001)-c(4x2) surface

an up dimer atom replaced



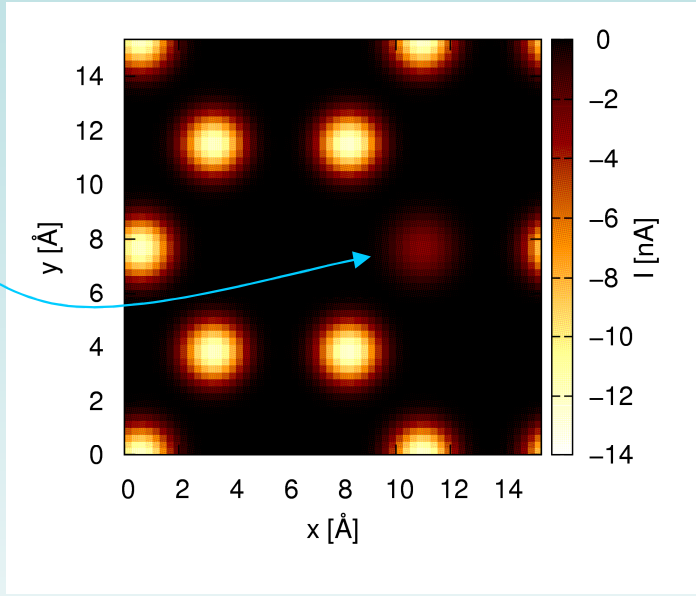
tip height = 5.5 Å

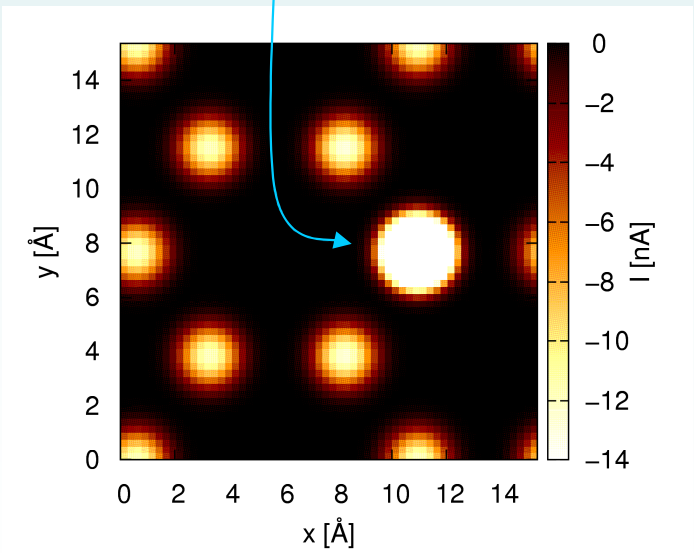
V_{Surf} = +1.0 V

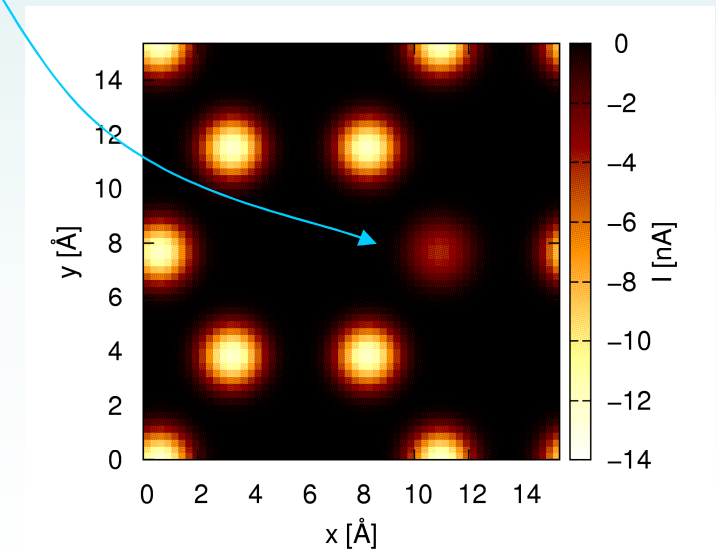
N

P

Al







(structure fig. : http://leed4.mm.kyushu-u.ac.jp/surface/)

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Features of this simulator

- Based on the electronic state of the system
  - ➢ STM / KPFM images
  - ➢ precise AFM images ⇒ Dr. Masago's poster (P2-3-4)

- Density Functional based Tight Binding method
  [Elstner et al.(1998)]
  - ➢ self-consistent calculation
  - ➢ much faster than the DFT simulators
  - ➢ We prepare the Tight Binding parameters (e.g. Hij, Sij).

Next: KPFM simulation

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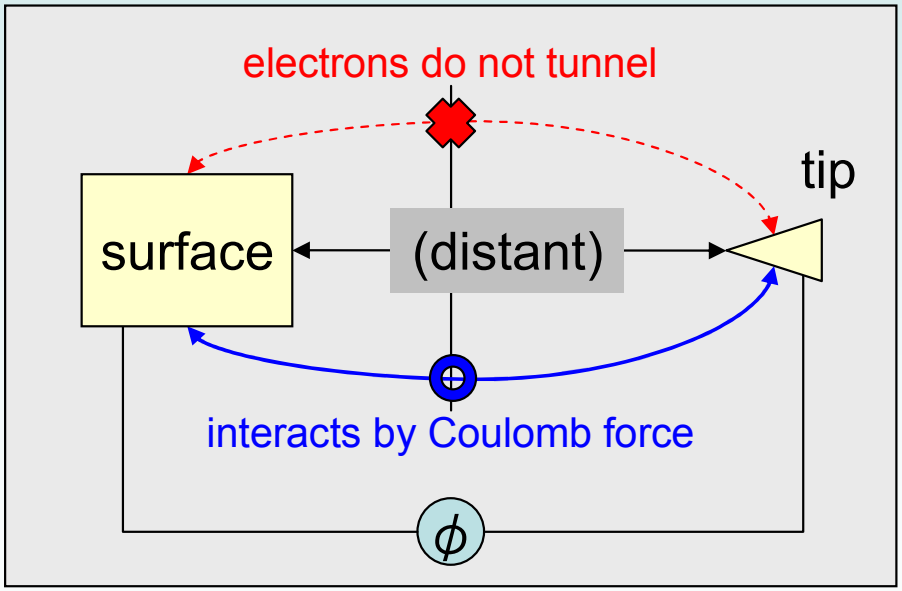
KPFM image calculations

Precisely, Prof. Tsukada's talk (**Today**, 16:30-)

Adopt the concept of the Partitioned Real-space Density Functional model [Nakaoka et al.(2001)]

overview

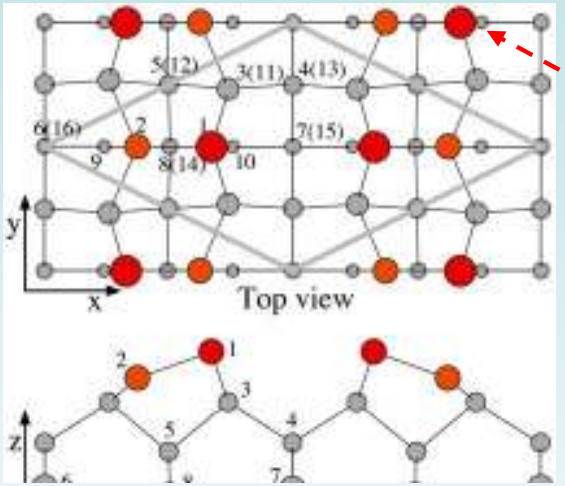


under the bias, $E^{T}_{F} \neq E^{S}_{F}$, in general

Find local contact potential difference: $\phi \equiv E^{T}_{F} - E^{S}_{F}$ when the tip force has extremum.

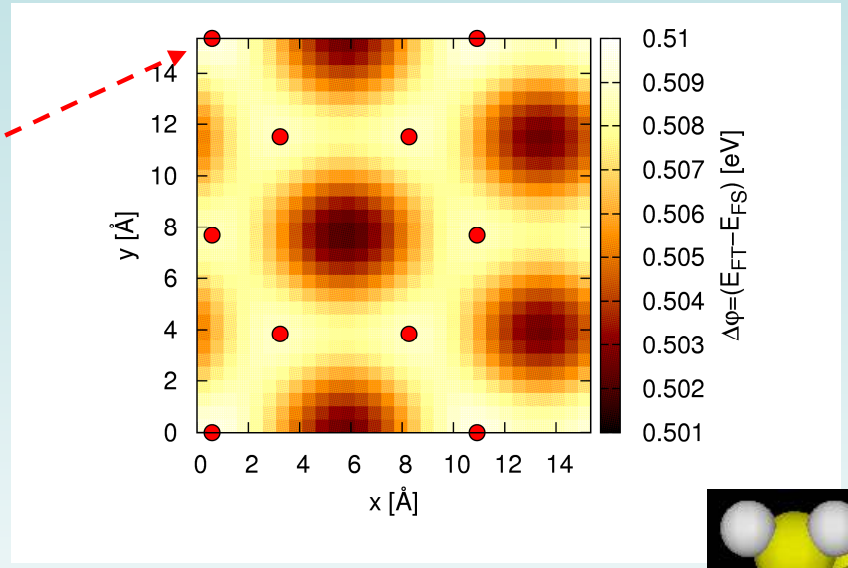
KPFM: example (1/2)

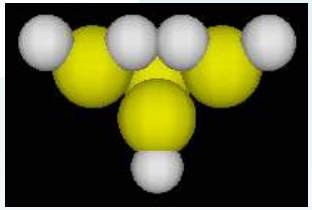
Si(001)-c(4x2) surface



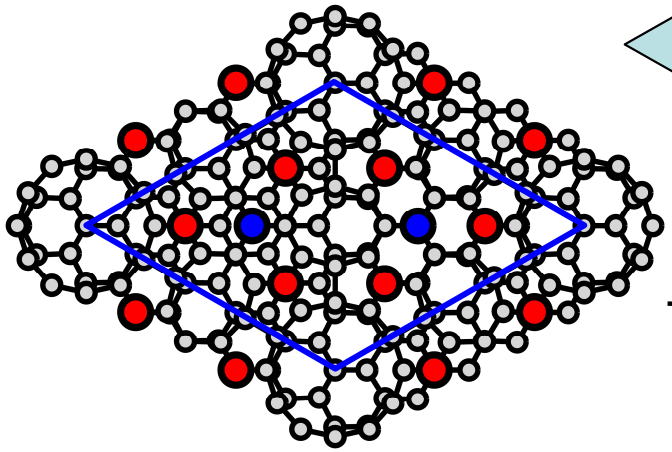
up dimer
Si atoms

Tip height
6.0 Å

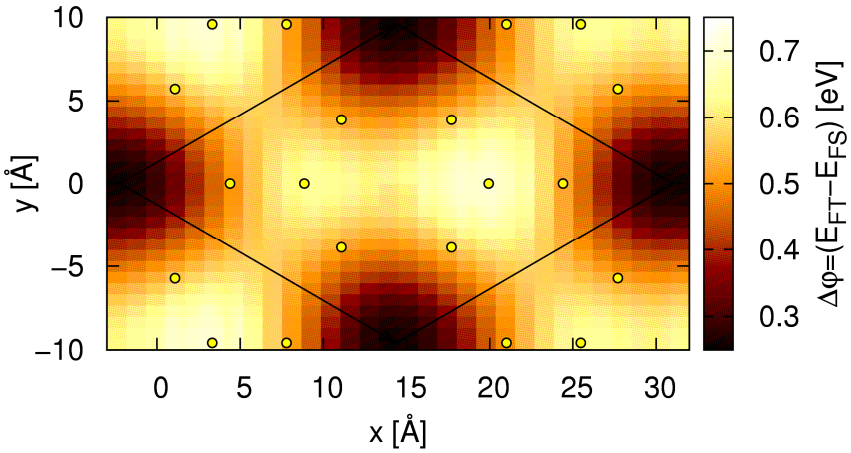




Si(111)-5x5 DAS structure



Tip height
5.5 Å



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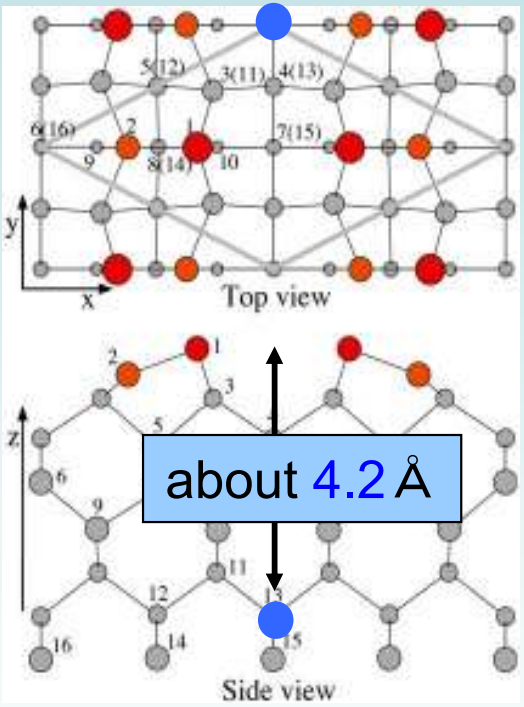
KPFM: example (2/2)

one dopant in Si(001)-c(4x2) surface



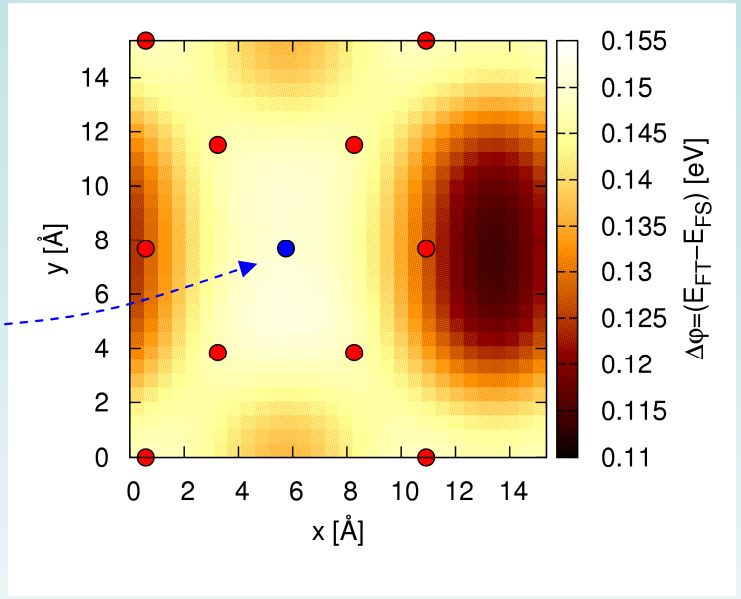
tip height = 6.0 Å

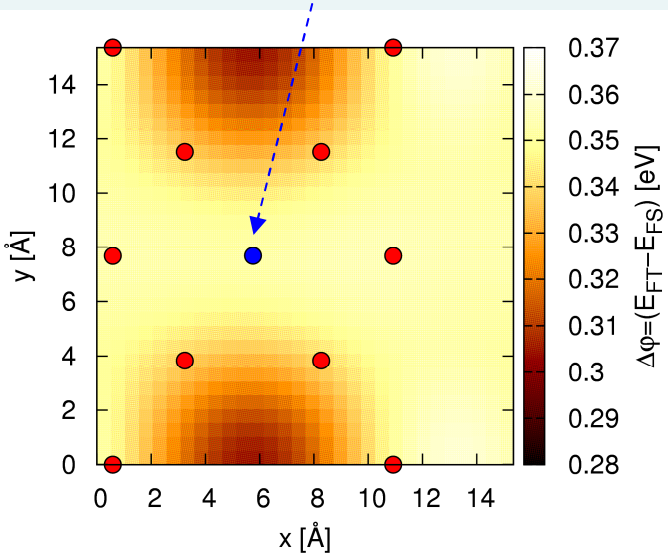
Map patterns change **drastically!**

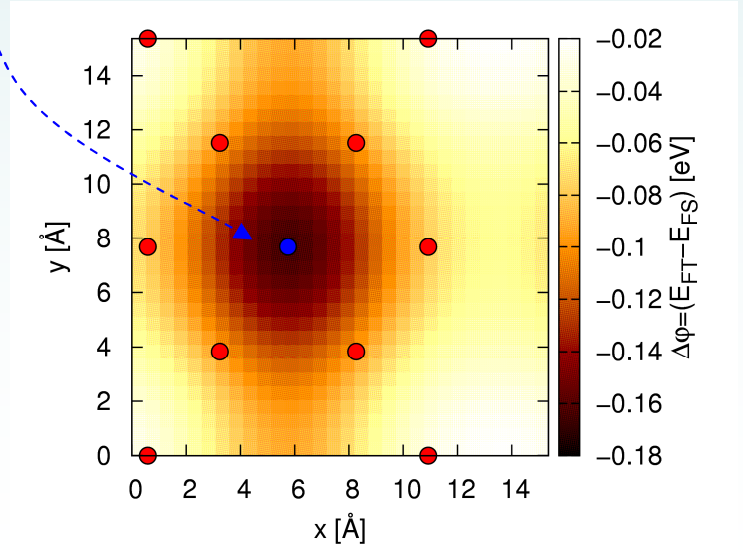
N

P

Al







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Summary of Quantum Dynamics SPM Simulator

- Calculate precise AFM/STM/KPFM images
- KPFM image simulator

  The first one in the world !

  can observe an unique properties of the local polarizability of the materials in nano-scale
- future plan

  develop another simulator for simulating simultaneous imaging of AFM/STM/KPFM measurements

ADVANCED ALGORITHM & SYSTEMS

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Thank you for your kind attention.

Please visit our booth!

This development was supported by SENTAN, Japan Science and Technology Agency (JST).