Theoretical Approaches for the Analyses of Scanning Probe Microscopy

Masaru Tsukada
WPI-Advanced Institute for Materials Research, Tohoku Univ.

2009.12.06 ALC'09
Maui island, Hawaii

outline

1 Introduction

2 Theoretical methods for STM -1

Bardeen's Perturbation approach

Effect of the tip, some case studies of the results

3 Theoretical methods for STM -2

Non-equilibrium Green's Function and other methods

4 Coherent and Dissipating Tunnelling

tunneling current distribution, features of the resonant tunneling

energy loss spectral function, zero bias anomaly

5 Theory of dynamic AFM -1 in vacuum

derivation of the harmonic oscillator model,

dissipation image, tip effects, some case studies

6 Fast simulation methods

7 Nano-mechanics of protein molecules

8 Theory of dynamic AFM -2 in liquids

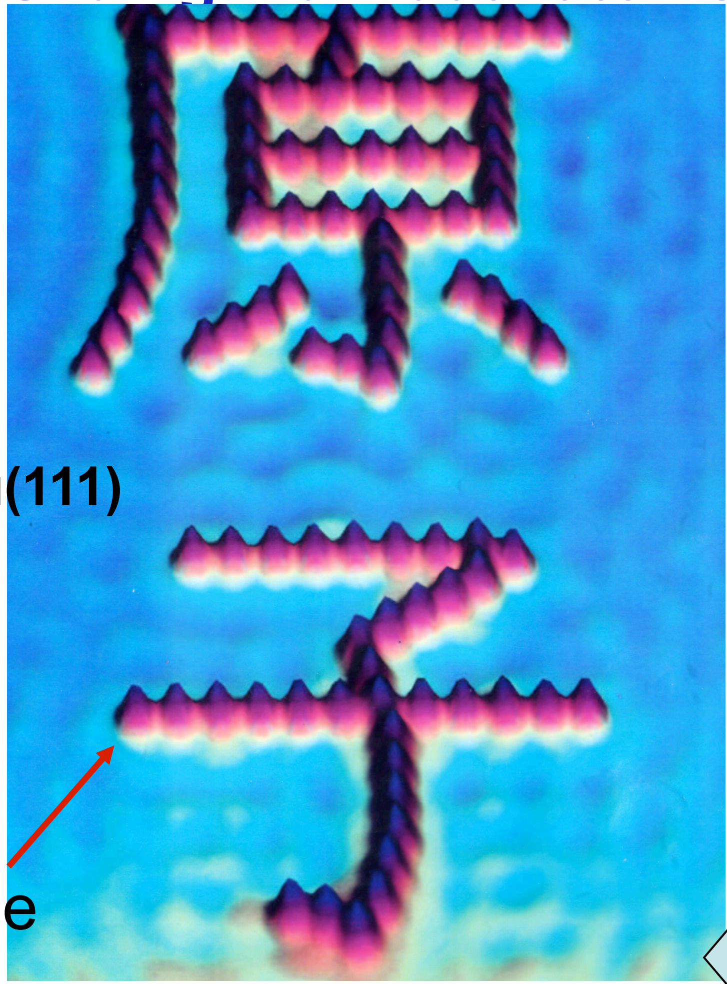
cantilever oscillation, oscillatory hydration force,

force mediated by water, case studies

9 Summary and outlook

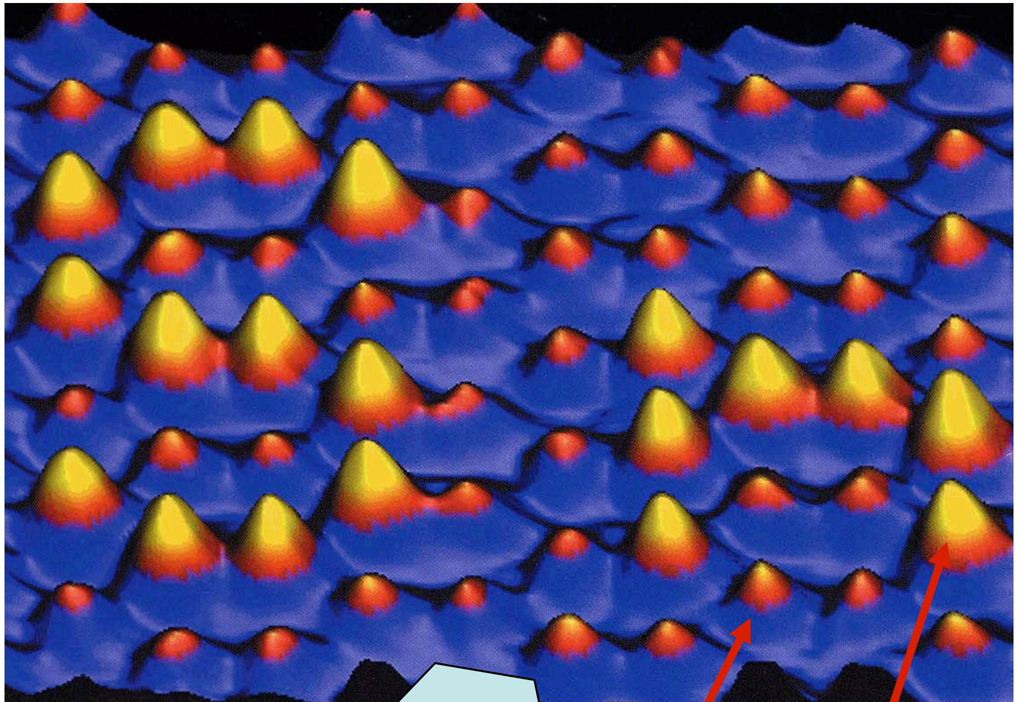
The letters written by atoms with SPM tip

Sliding individual atoms



Letters with Fe atoms on Cu(111), D.Eigler 1993

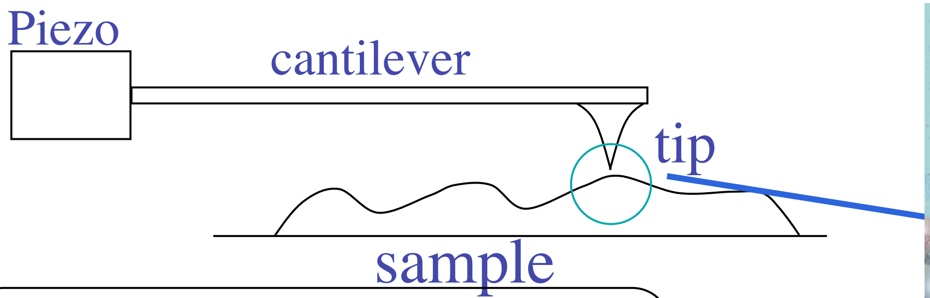
Interchanging atoms

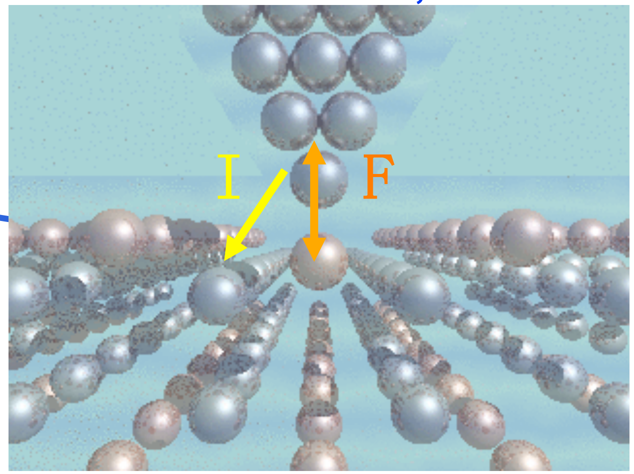


Y.Sugimoto, M.Abe, S.Hirayama, N.Oyabu, O.Custance and S.Morita, Nature Mterials 4 (2005) 156

Theory of Scanning Probe Microscopy

STM/STS, AFM
(contact, noncontact)
KFM, SNOM





What and how

Does SPM see the sample?

Effect of the tip atomic structure/ Atom kind?

Information transfer to macro-system

Formation and control of nanostructures

Observation of quantum Phenomena and functionalization

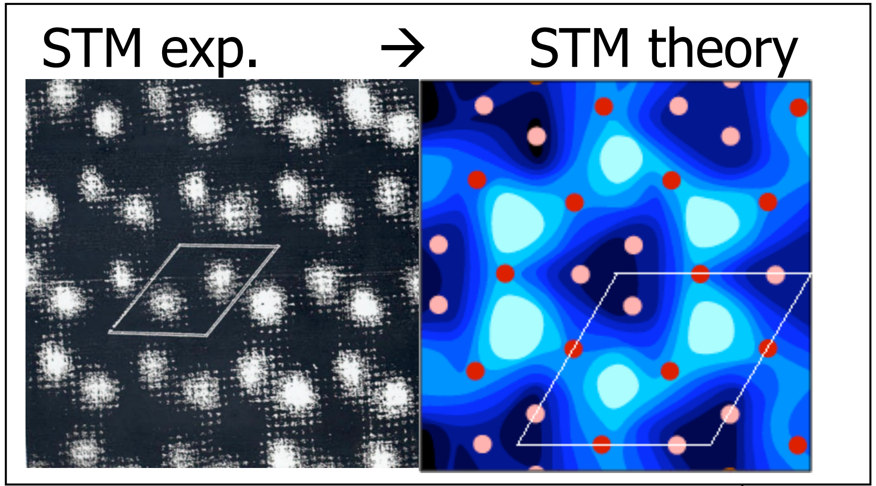
Atomic scale Observables

- Force? Displacement?
- Fluctuations and dissipations
- Influence of wave functions
- Quantum Coherence and de-cohenrence

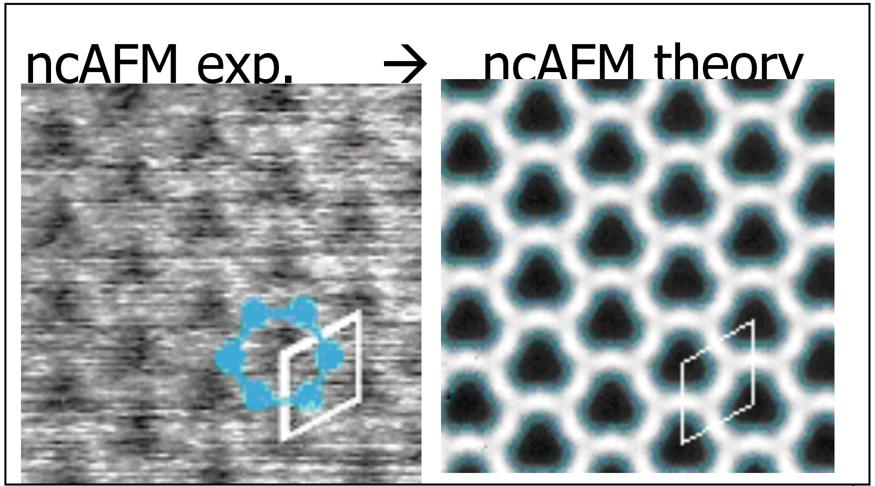
What can be seen by SPM？

From examples of the first-principles simulation

Si(111)√3× √3ーAg surface



S. Watanabe, M. Tsukada, Phys. Rev. B. 1991



N. Sasaki, S. Watanabe, M. Tsukada, Phys. Rev. Lett. 2002

Remarkably different images for the same surface by STM and ncAFM!

Bright spots in the STM image does not correspond atoms

→ Importance of quantum mechanical effect

Large temperature dependence of ncAFM images

→ reproduced by theoretical calculation

→ Very important role of Simulation!

Bardeen's Perturbation theory

Importance of the electron wave nature is clear from this expression!

Tunnel current

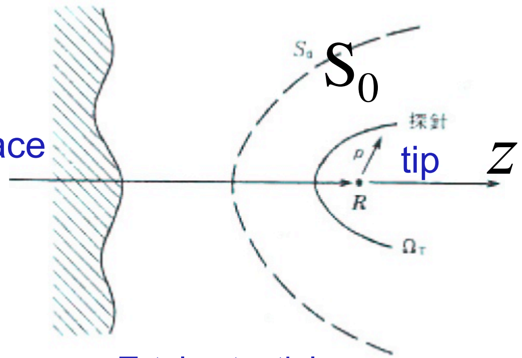
$$I = \frac{2\pi e}{\hbar} \sum \left\{ f(E_m) - f(E_n + eV) \right\} |M_{mn}|^2 \delta(E_m - E_n)$$

Sample side orbital

$$M_{\mu\nu} = \frac{\hbar^2}{2m} \int_{S_0} d\mathbf{S} \cdot \left(\phi_\mu^* \nabla \phi_\nu - \phi_\nu \nabla \phi_\mu^* \right)$$

tip side orbital

surface



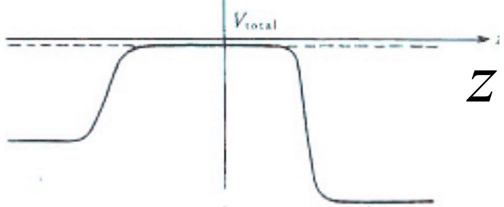
$$I(\mathbf{R}) = \frac{2\pi e}{\hbar} \int_{E_F}^{E_F + eV} A(\mathbf{R}, E, E - eV) dE$$

$$A(\mathbf{R}, E, E') = \int d\mathbf{r} \int d\mathbf{r}' V_T(\mathbf{r}) V_T(\mathbf{r}') \times G^T(\mathbf{r}', \mathbf{r}, E') G^S(\mathbf{r} + \mathbf{R}, \mathbf{r}' + \mathbf{R}, E)$$

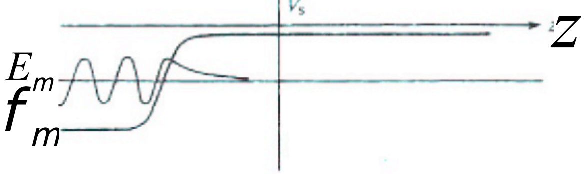
$$G^T(\mathbf{r}', \mathbf{r}, E') = \sum_\nu \phi_\nu^T(\mathbf{r}') \phi_\nu^{*T}(\mathbf{r}) \delta(E' - E_\nu)$$

$$G^S(\mathbf{r}, \mathbf{r}', E) = \sum_\mu \phi_\mu^S(\mathbf{r}') \phi_\mu^{*S}(\mathbf{r}) \delta(E - E_\mu)$$

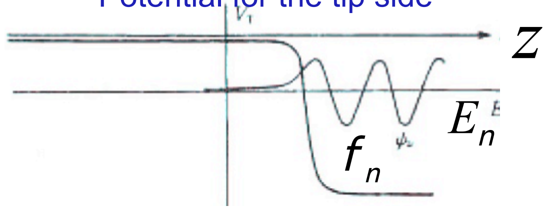
Total potential

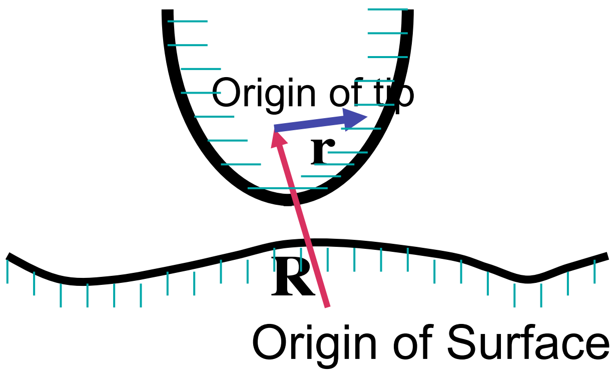


Potential for the surface side



Potential for the tip side





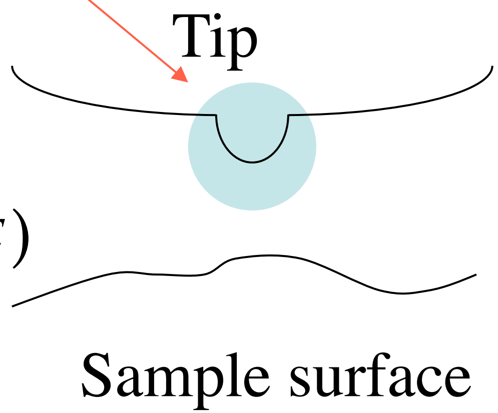
The relation to LDOS

$$I(\mathbf{R}) = \frac{2\pi e}{\hbar}\int_{E_F}^{E_F+eV} A(\mathbf{R},E,E-eV)\,dE$$

$$A(\mathbf{R},E,E') = \sum_{\nu\in Tip}\int_{Tip} d\mathbf{r}\,d\mathbf{r}'\,V_T(\mathbf{r})V_T(\mathbf{r}')\psi_\nu(\mathbf{r}')\psi_\nu^*(\mathbf{r})\delta(E'-E_\nu)$$
$$\times\tilde{G}^S(\mathbf{r}+\mathbf{R},\mathbf{r}'+\mathbf{R};E)\gamma(z;E)\gamma(z';E)$$

$$W(\mathbf{r},\mathbf{r}';E') \rightarrow \textit{weight function}$$

$$\tilde{G}^S = \frac{G^S}{\gamma(z;E)\gamma(z';E)} \qquad \gamma(z;E) = \exp\left(-z\frac{\sqrt{2m|E|}}{\hbar}\right)$$



Moment expansion

Surface DOS

$$A(\mathbf{R},E,E') = \sum_{\nu\in Tip}\left|\int_{tip} d\mathbf{r}\,V_T(\mathbf{r})\psi_\nu(\mathbf{r})\gamma(z,E)\right|^2\delta(E'-E_\nu)\times\rho(\mathbf{R},E)$$
$$+\sum_{m\geq1}\sum_{n\geq1}\mu_{mn}(E')\nabla\ldots\nabla\nabla'\ldots\nabla'\tilde{G}^S(\mathbf{r},\mathbf{r}';E)\Big|_{\mathbf{r}'=\mathbf{R},\mathbf{r}'=\mathbf{R}}$$

Moment of the weight function

$$\mu_{mn}(E') = \int \mathbf{r}\ldots\mathbf{r}\mathbf{r}'\ldots\mathbf{r}'W(\mathbf{r},\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}'$$

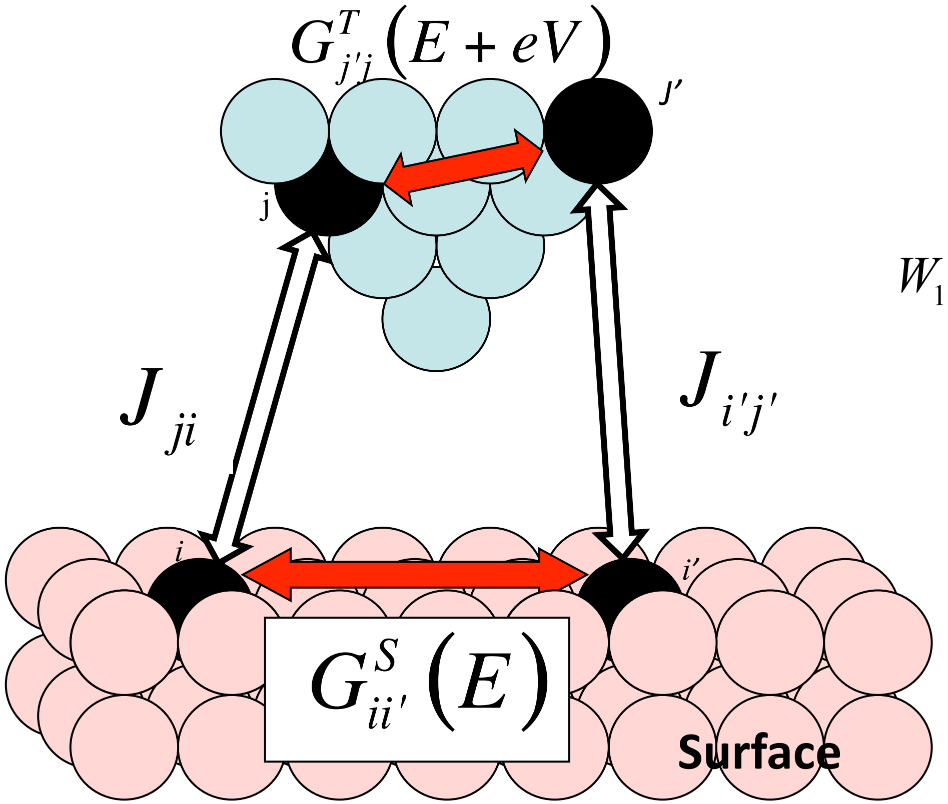
... Tersoff-Hamann

Taking only the first term, $\Longrightarrow$ $I(\mathbf{R}) \propto \rho_{surface}(\mathbf{R},E_F)V$

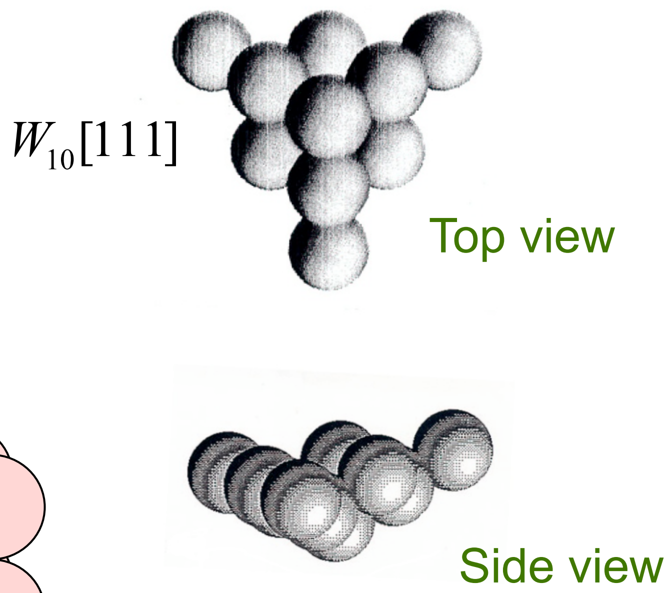
Tunneling current in the LCAO representation

Tunneling current at the tip position R and for the bias V is expressed as

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

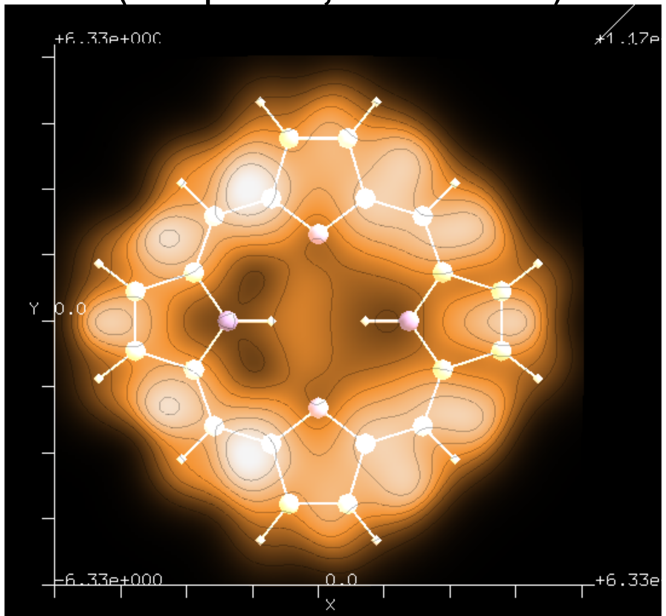


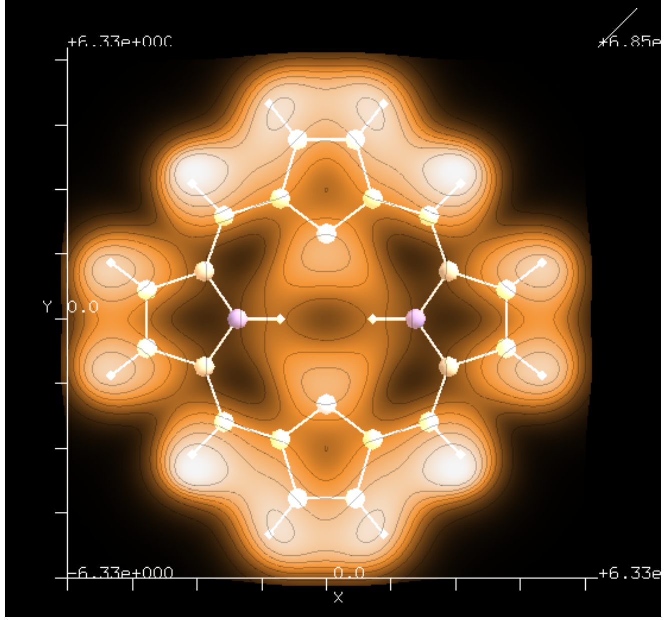
Cluster models for the tip



Simulation of STM image

STM image of porphyrin
(W tip : **6s,5d orbitals**)





(W tip: **6s orbital**)

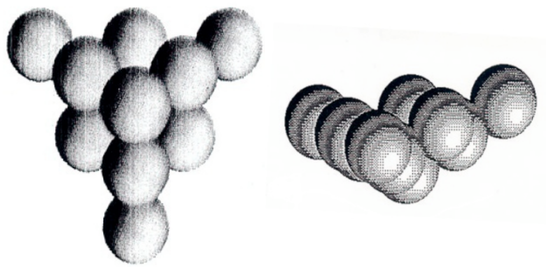
Energy density of
Tunnel current

$$I(\mathbf{R},V) \propto \sum_{ii'jj'} G^{S}_{ii'}(E) J_{i'j'} G^{T}_{j'j}(E+eV) J_{ji}$$

Green Function

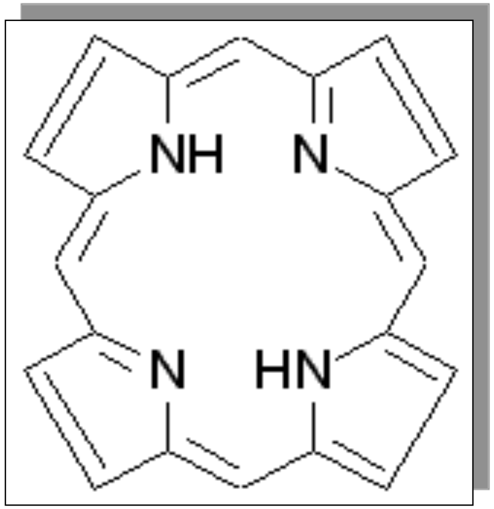
Tunnel matrix element

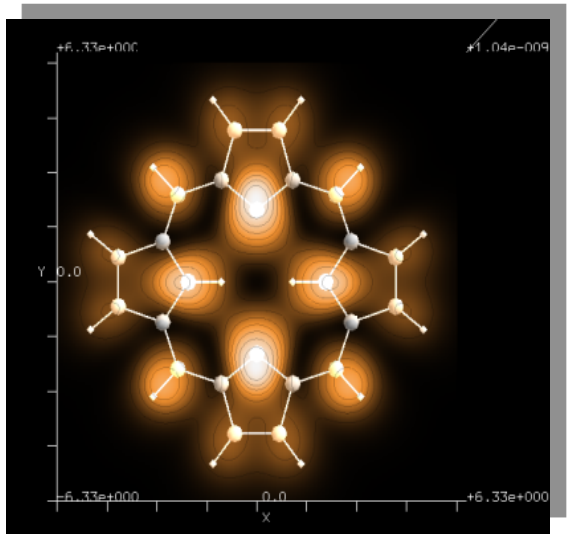
$W_{10}[111]$ tip model



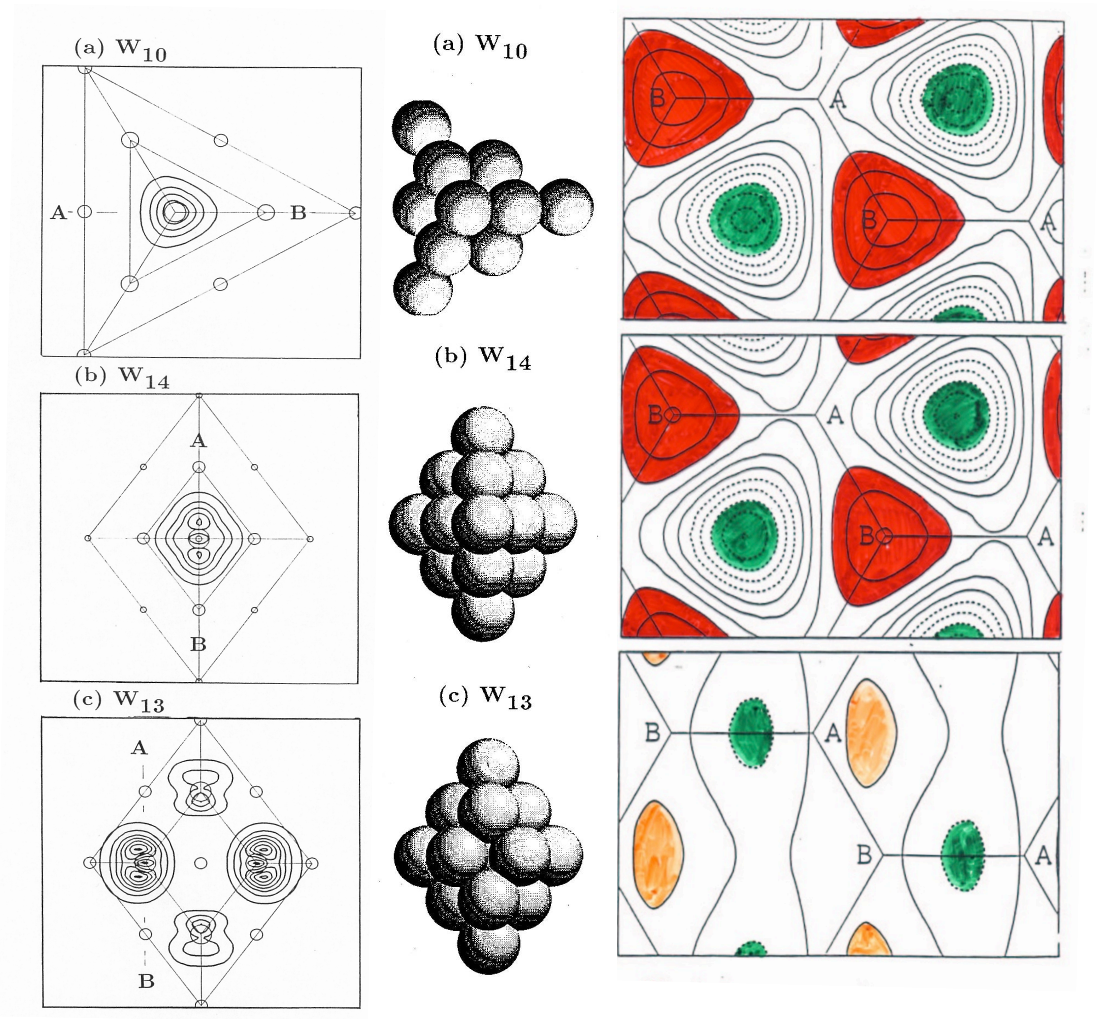
DVXα
calculation

LDOS of molecule

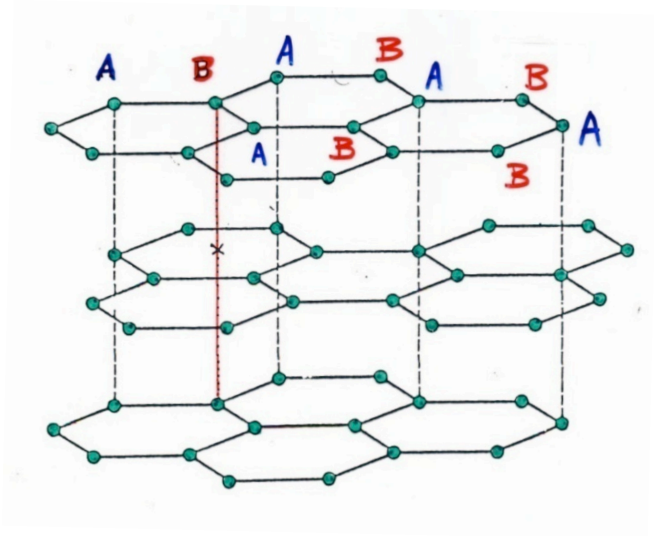




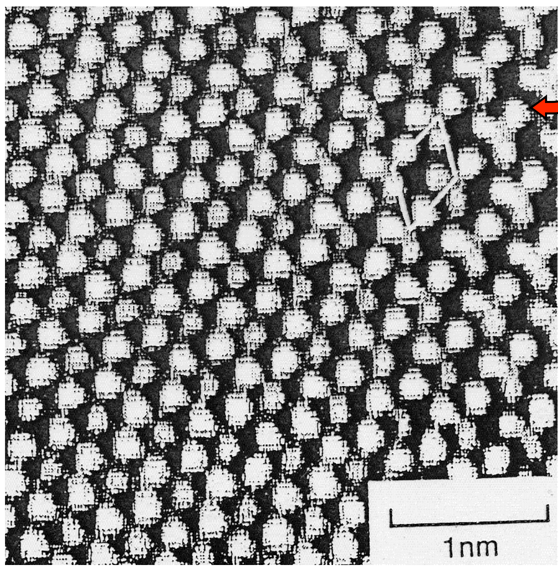
Simulation of the STM image of graphite



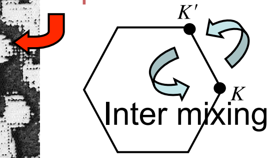
Isshiki,Kobayashi,Tsukada
J.Vac.Sci.Technol,B9(2)(1991)475



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



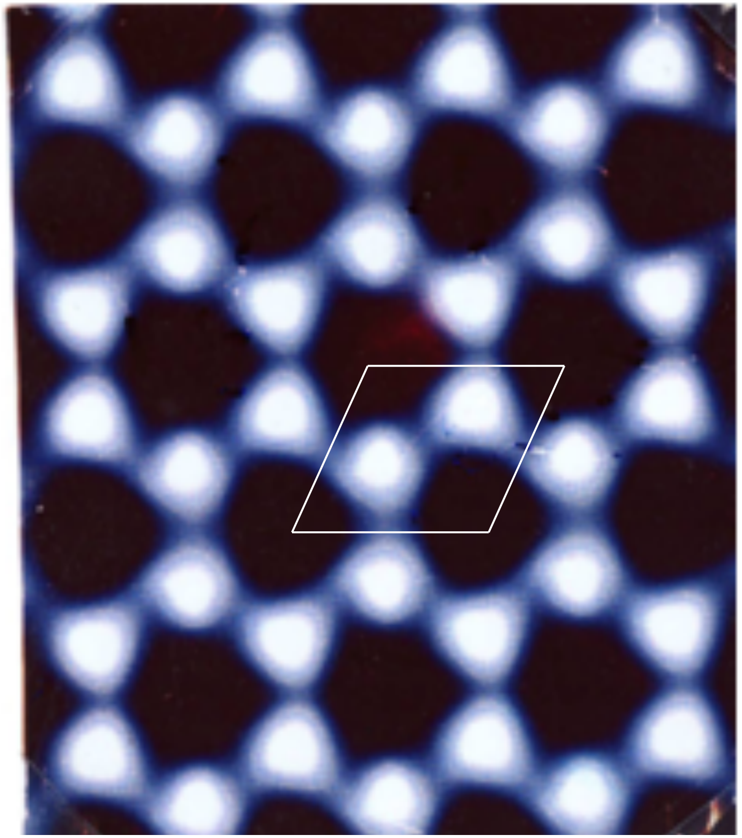
Super structure



Brilliouin Zone

Si(111)√3×√3-Ag 表面のSTM像　実験と理論

Theoretical Image for HCT model



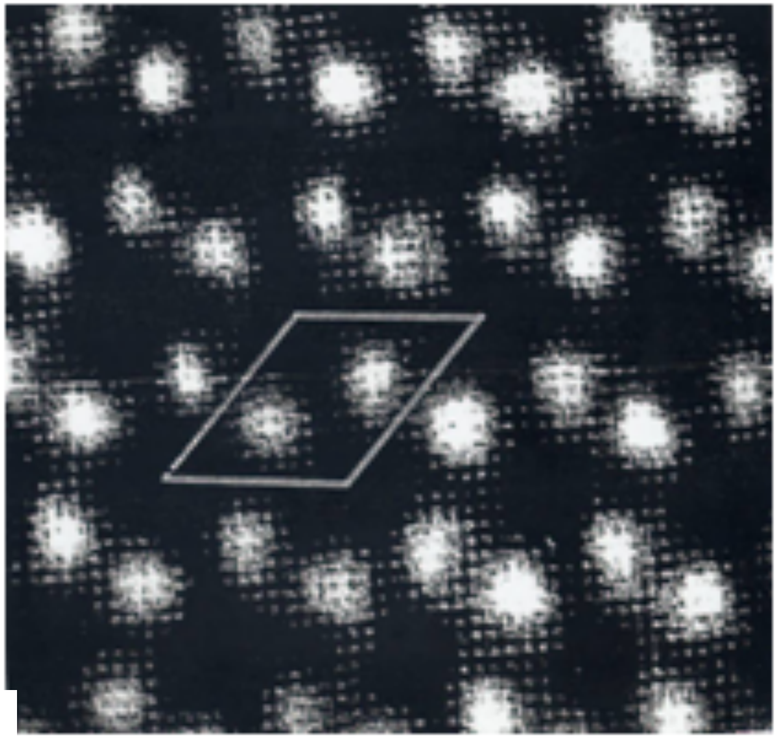
W [111] tip, tip height 3.6A

S.Watanabe, M.Aono and M.Tsukada
Phys. Rev. B44 ('91) 8330

Positive surface bias about 2eV

E.J.van Loenen, et al, PRL 58 (1987) 373

Experiment

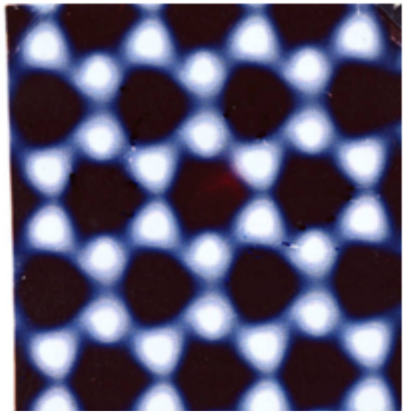


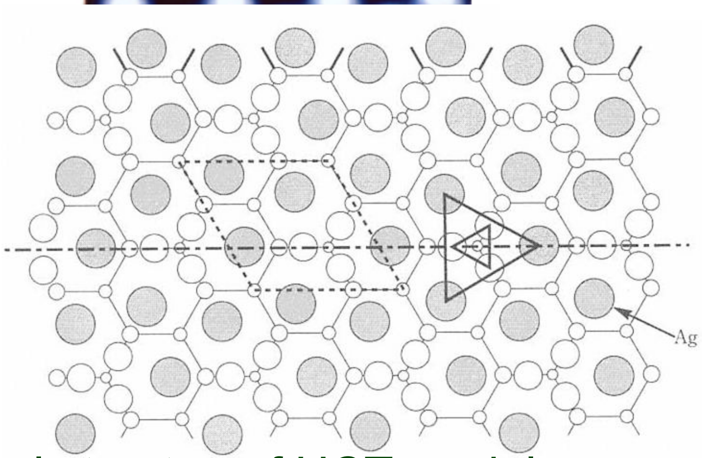
Si(111)√3X√3-Ag Surface(HCT model)

Wartanabe, Aono, Tsukada(1991) Phys.Rev.B44 (1991)8330

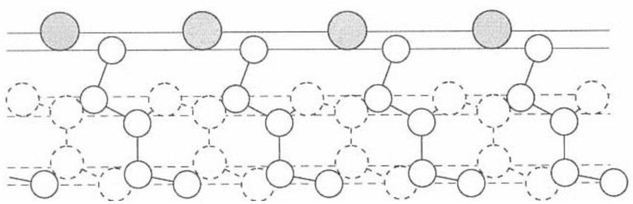
Bright spot located in the Ag triangle

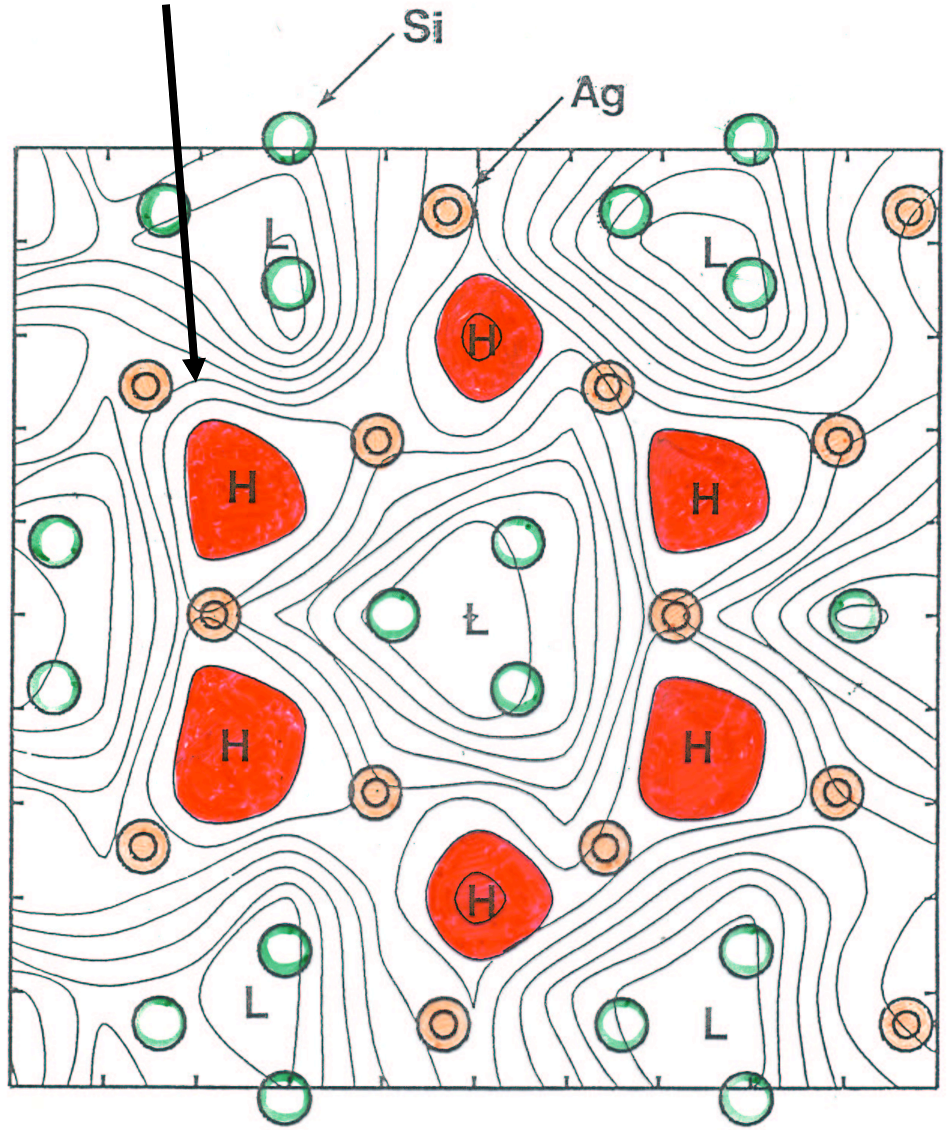
Theory HCT model





Actual structue of HCT model

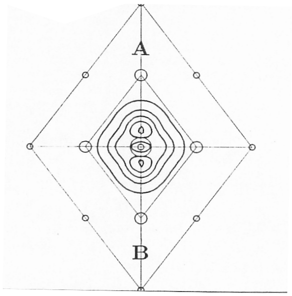


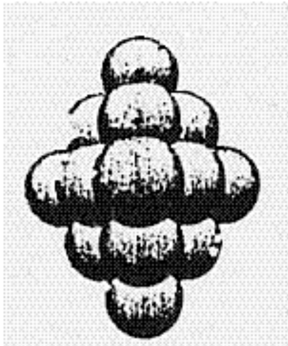


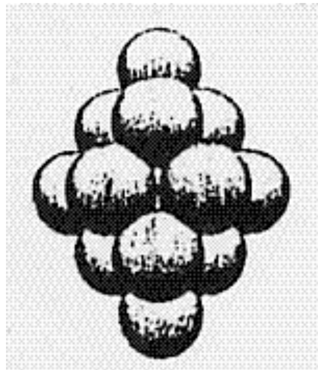
Effect of Tip Shape

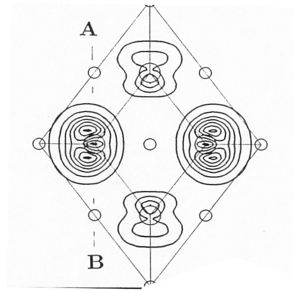
If the apex atom is removed

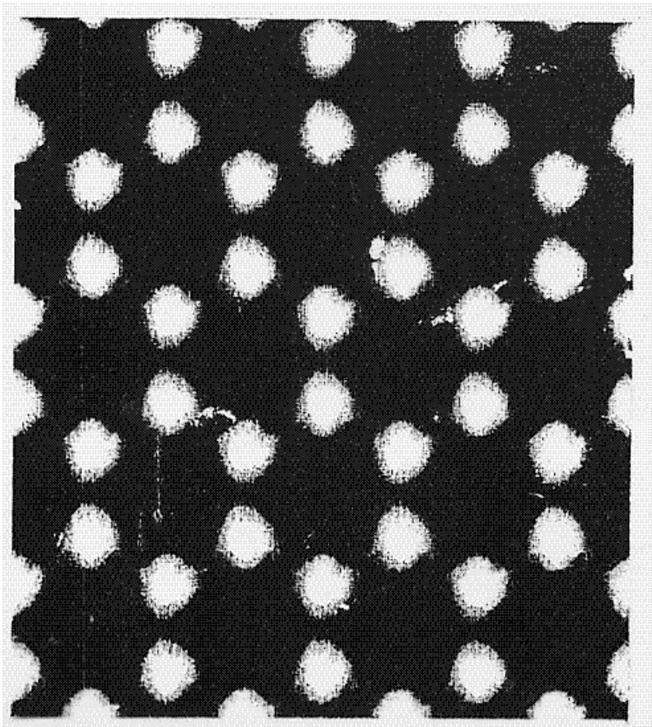
W tip [110]

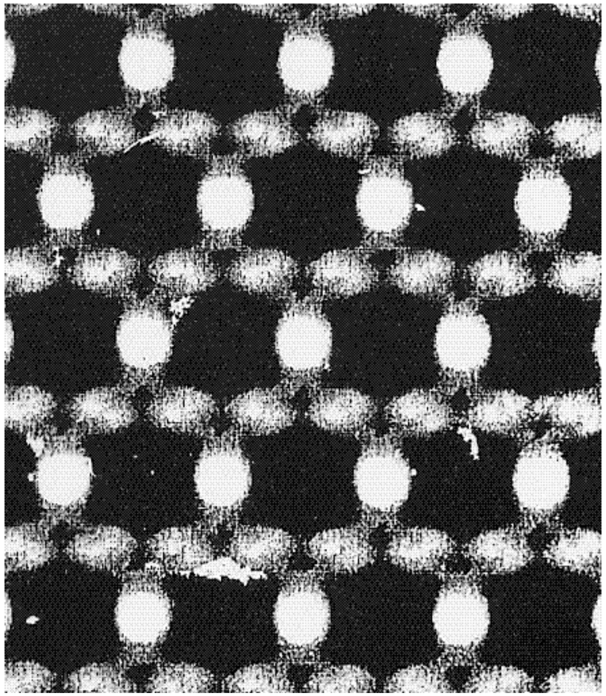








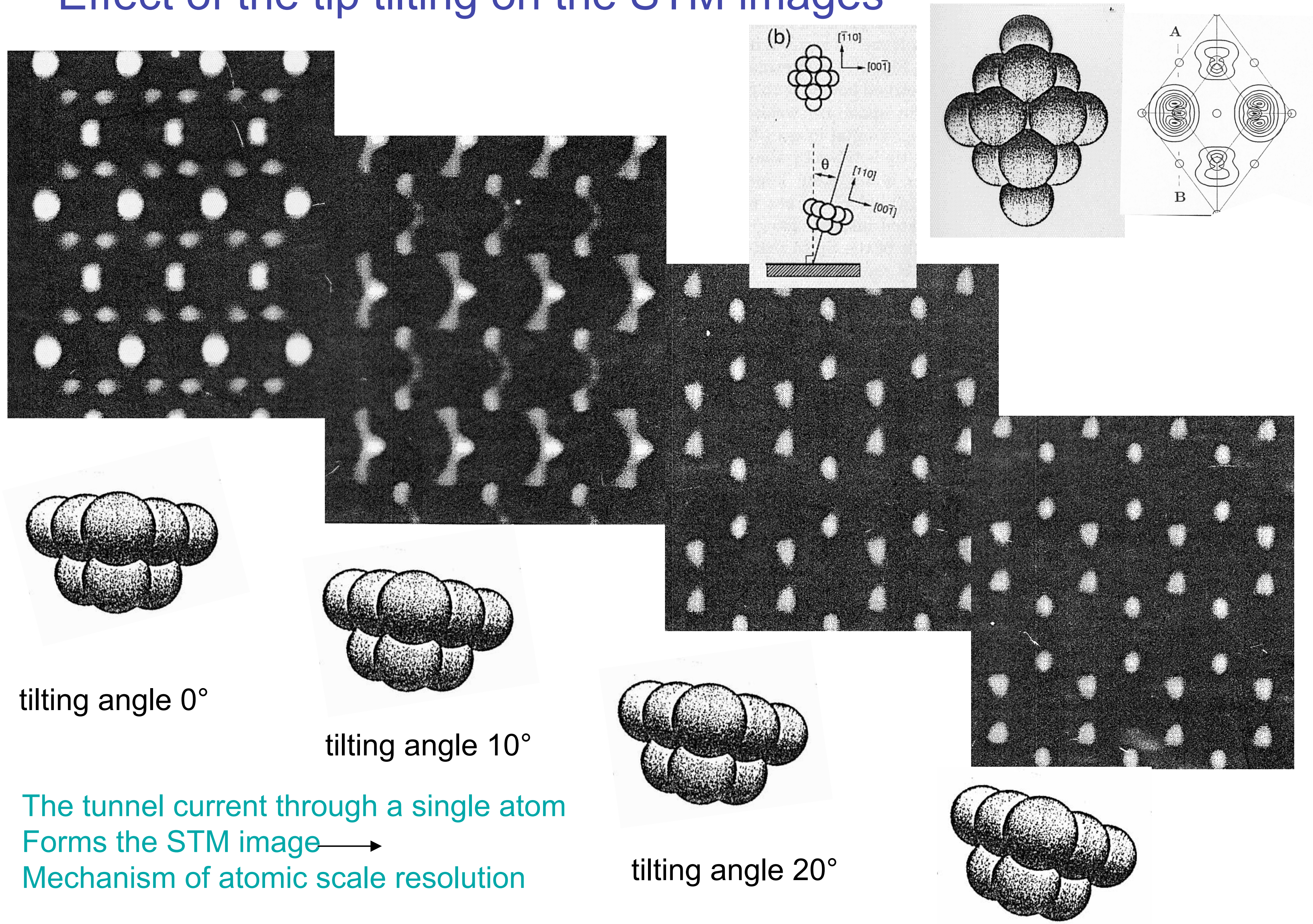




Abnormal image is obtained!

S.Watanabe, M.Aono and M.Tsukada, Jpn. J. Appl. Phys., 32 ('93) 2911

Effect of the tip tilting on the STM images



tilting angle 0°

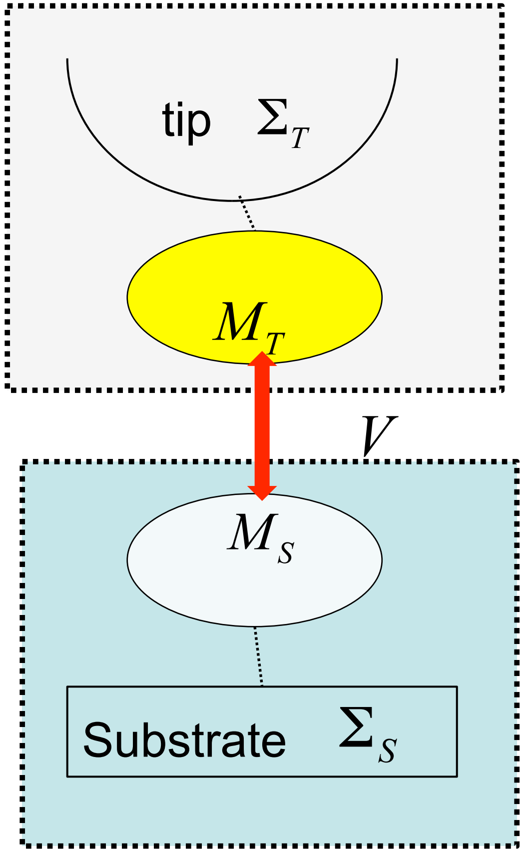
tilting angle 10°

tilting angle 20°

tilting angle 30°

The tunnel current through a single atom
Forms the STM image ⟶
Mechanism of atomic scale resolution

Tunnel current by a molecule adsorbed tip for molecular samples



Non-equilibrium Green's Function theory
- beyond Bardeen's Approximation

Green's function for the tip side

$$g^T = \left(E - i\eta - H_{M_T} - \Sigma_T\right)^{-1}$$

Green's function for the total system

Site of M_T Site of M_S

$$G_{ip}^{R/A} = \langle i | g^T V g^S + g^T V g^S V g^T V g^S + \ldots\ldots | p \rangle$$

$$= \langle i | g^T \Lambda g^S | p \rangle$$

Total interaction between the tip and the sample

$$\Lambda = V + V g^S V g^T V + V\left(g^S V g^T V\right)^2 + \ldots$$

$$= V\left(1 - g^S V g^T V\right)^{-1} \approx V$$

Tunnel current

$$I = \frac{2e}{h}\int \left(f_T - f_S\right)\bar{T}_{ip}(E)\,dE$$

$$\bar{T}_{ip} = Tr\left[\Gamma_i G^R \Gamma_p G^A\right] = Tr\left[\Gamma_i g^T \Lambda g^S \Gamma_p \bar{g}^S \Lambda \bar{g}^T\right]$$

$$\cong Tr\left[\Gamma_i g^T V g^S \Gamma_p \bar{g}^S V \bar{g}^T\right] = Tr\left[\bar{g}^T \Gamma_i g^T V g^S \Gamma_p \bar{g}^S V\right]$$

$$\rightarrow Tr\left[\mathbf{G}^T V \mathbf{G}^S V\right]$$

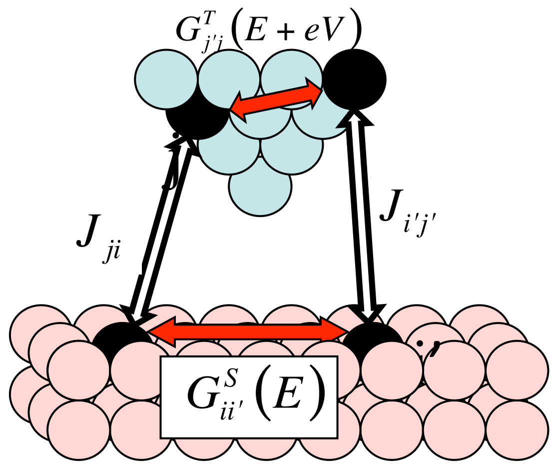
Green's function for the sample side

$$g^S = \left(E - i\eta - H_{M_S} - \Sigma_S\right)^{-1}$$

$$\Gamma_{i/p} = i\left(\Sigma_{i/p}^R - \Sigma_{i/p}^A\right) = t_{i/p}^{+}\left[i\left(g_{i/p}^R - g_{i/p}^A\right)\right]t_{i/p}$$

$$g^{R/A} = \left(E - i\eta - H_{M_T} - H_{M_S} - \Sigma_S^{R/A} - \Sigma_T^{R/A}\right)^{-1}$$

Correspondence to Bardeen's Approximation with cluster model approximation



$$I(\mathbf{R}) = \frac{2\pi e}{\hbar}\int_{E_F}^{E_F+eV} A(\mathbf{R},E,E-eV)\,dE$$

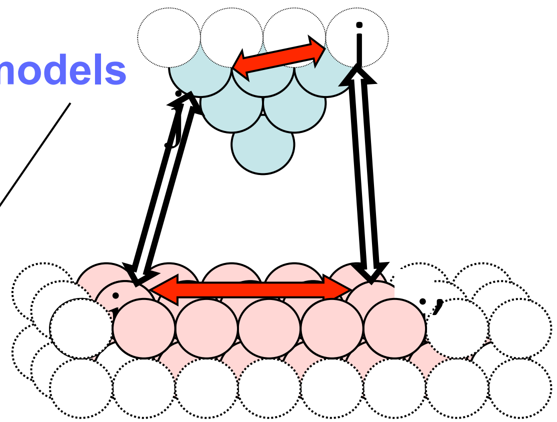
$$= \frac{2\pi e}{\hbar}\int_{E_F^L}^{E_F^R}\sum_{ii'jj'} G^S_{ii'}(E)J_{i'j'}(\mathbf{R})G^T_{j'j}(E+eV)J_{ji}(\mathbf{R})\,dE$$

With LCAO representation

$$\phi^T_n(\mathbf{r}) = \sum_i C^T_{ni}\varphi^T_i(\mathbf{r})$$

$$\phi^S_m(\mathbf{r}) = \sum_j C^S_{mj}\varphi^S_j(\mathbf{r})$$

Using cluster models



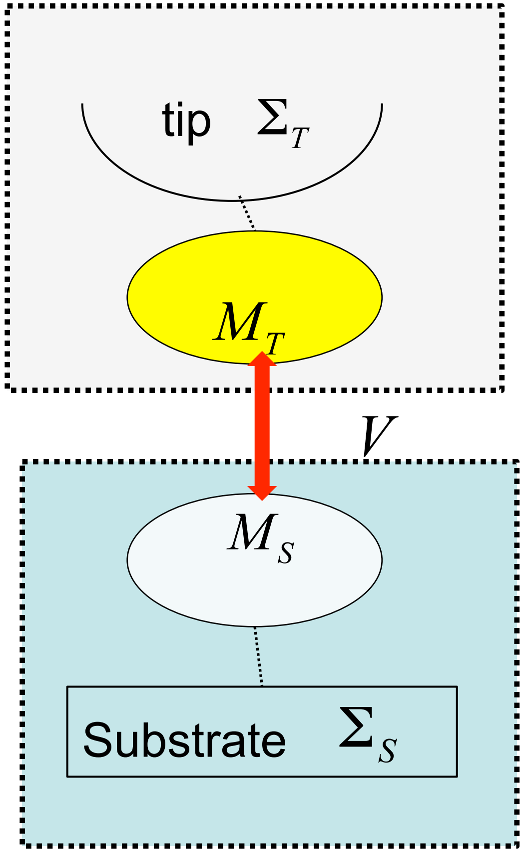
$$G^T_{j'j}(E') = \sum_n C^{T*}_{nj'}C^T_{nj}\,\delta(E'-E_n) \cong \sum_n C^{T*}_{nj'}C^T_{nj}\frac{\Gamma/\pi}{(E'-E_n)^2+\Gamma^2}$$

$$G^S_{ii'}(E) = \sum_m C^{S*}_{mi}C^S_{mi'}\,\delta(E-E_m) \cong \sum_m C^{S*}_{mi}C^S_{mi'}\frac{\Gamma/\pi}{(E-E_m)^2+\Gamma^2}$$

This is equivalent to the new NEGF theory

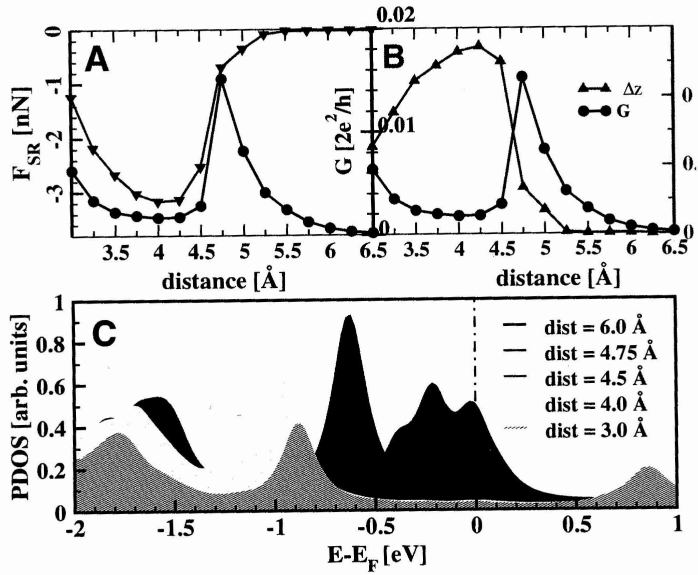
$$\bar{T}_{ip} = Tr\left[\bar{g}^T\Gamma_i g^T V g^S \Gamma_p \bar{g}^S V\right] = \sum_{ln}\frac{|\langle i|l\rangle|^2 V_{ln}|\langle n|p\rangle|^2 V_{nl}\Sigma^T_l\Sigma^S_n}{\left\{(E-\varepsilon^T_l)^2+(\Sigma^T_l)^2\right\}\left\{(E-\varepsilon^S_n)^2+(\Sigma^S_n)^2\right\}}$$

Reduction of tunnel current with the increase of the tip-sample interaction



$$\Lambda = V + Vg^S V g^T V + V\left(g^S V g^T V\right)^2 + \ldots$$
$$= V\left(1 - g^S V g^T V\right)^{-1} \approx V$$

$$I = \int_{-\infty}^{\infty} \left(f_T - f_S\right) tr\left[\Gamma_T \frac{g^T V g^S}{1 - g^S V g^T V} \Gamma_S \frac{\bar{g}^S V \bar{g}^T}{1 - \bar{g}^T V \bar{g}^S V}\right] dE$$

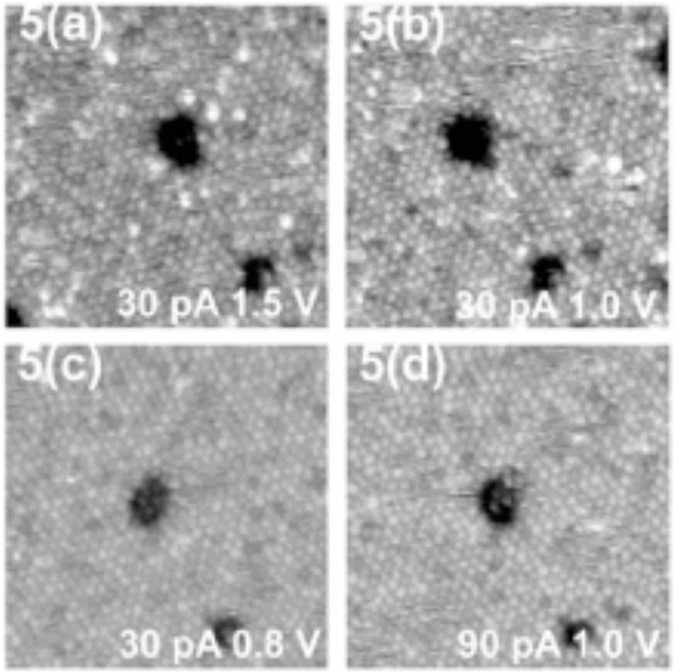


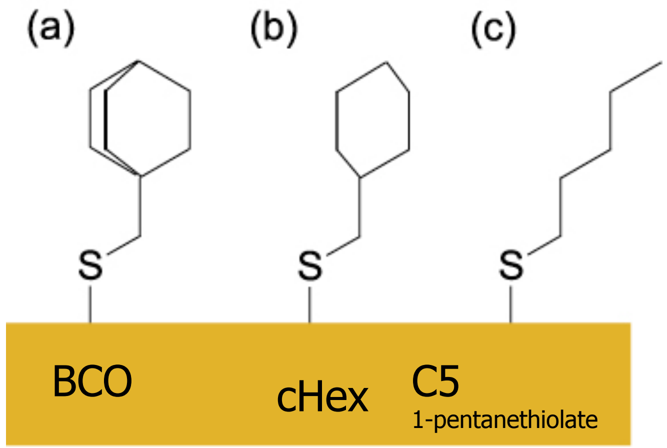
Jelinek et al,
Phys. Rev. Lett., 101 (2008)178101

Conduction Switching of Alkane Molecule on Au(111) by Conformation Change

STM images

M. Suzuki, et al.,
Nanotechnology 15, S150 (2004).

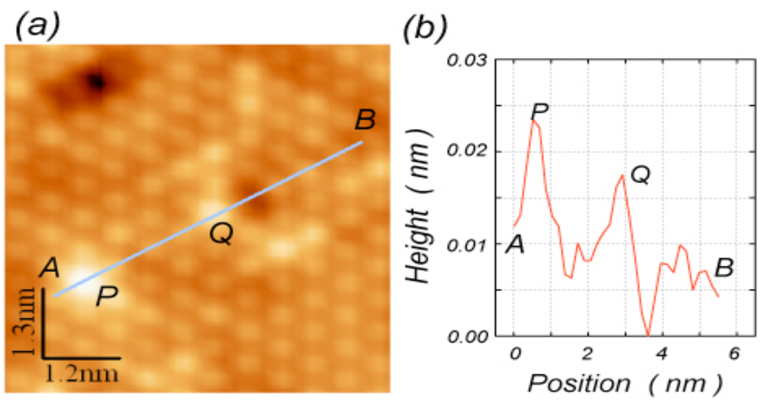




AFM image

Theoretical simulation

K.Tagami and M.Tsukada, E-J. Surf. Sci, and Nanotech., 4 (2006)299

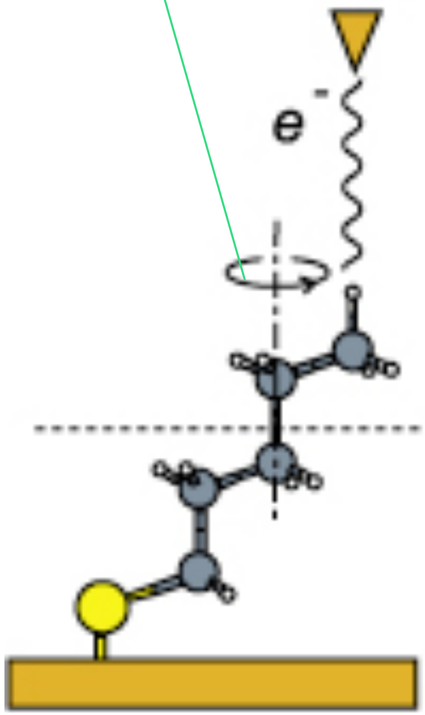


C5 molecules embedded in BCO-SAM Membrane are observed as bright spots.

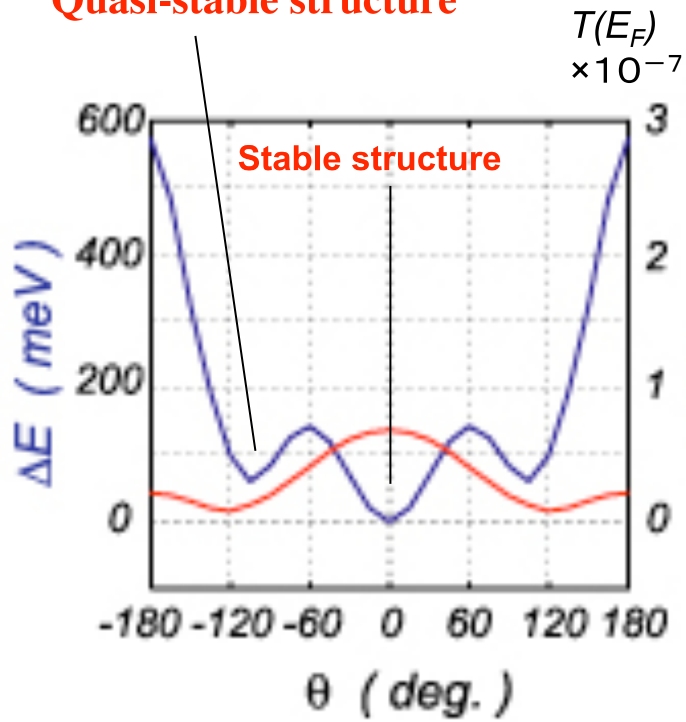
They are blinking!

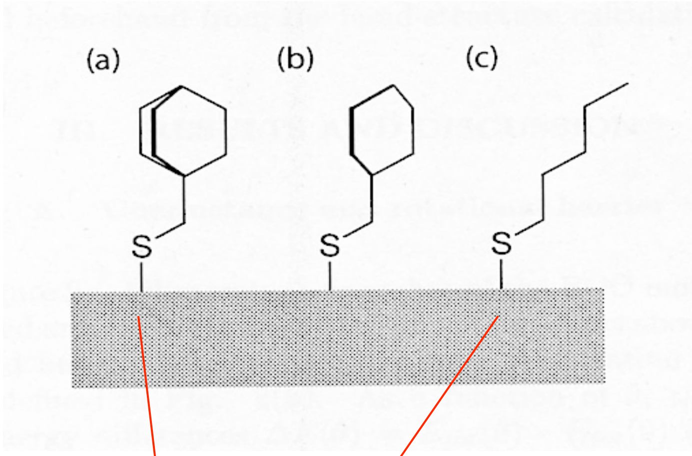
Conduction Switching of Alkane Molecule by Conformation change on Au(111)

1-pentanethiolate



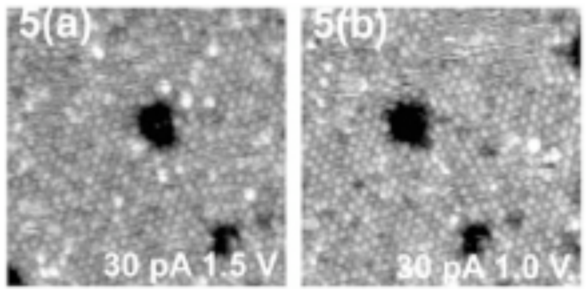
Quasi-stable structure





1-pentanethiolate

Bicyclo[2,2,2]octylmethylthiolate



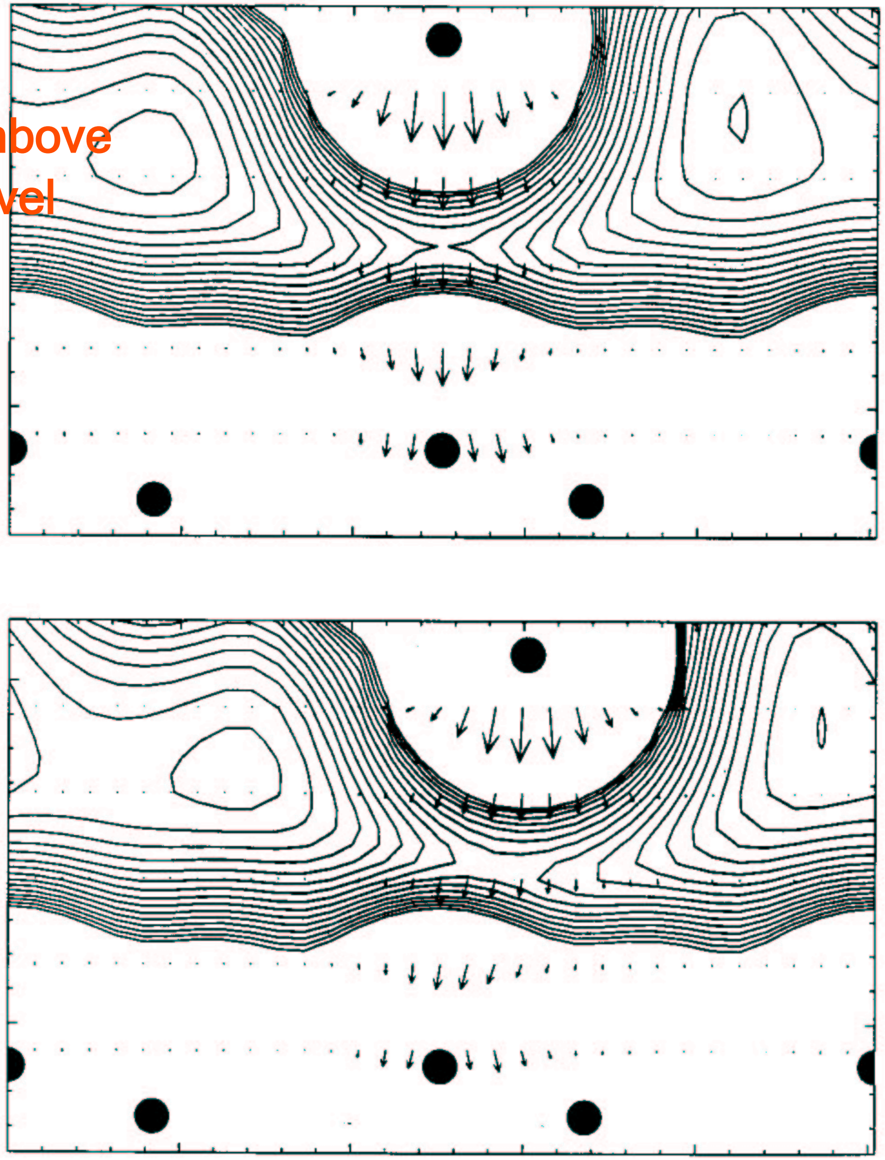
Bright stable structure And dark quasi-stable structure appears!

K.Tagami and M.Tsukada,e-J. Surface Sci. and Nanotech., 2 ('04) 186

Coherent Tunneling/Transport
vs
Dissipating Tunneling

Tunnel Current Density and Barrier

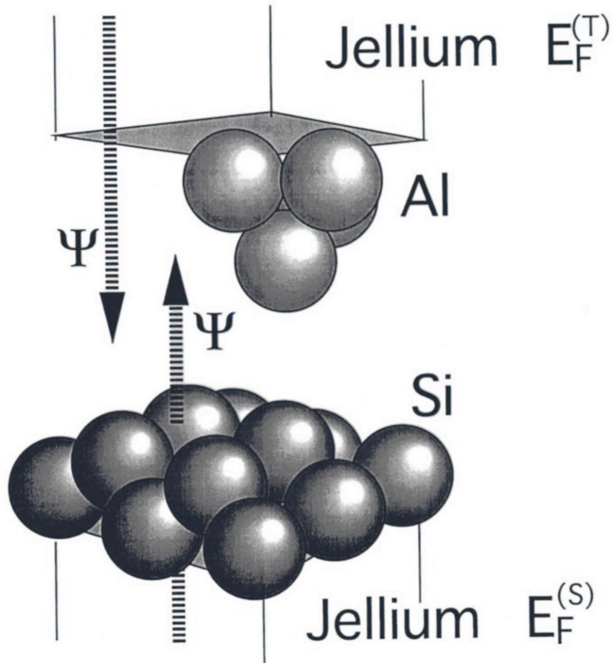
Barrier above
Fermi level



d=12au
V_s=2V

Calculation with
First principles RTM

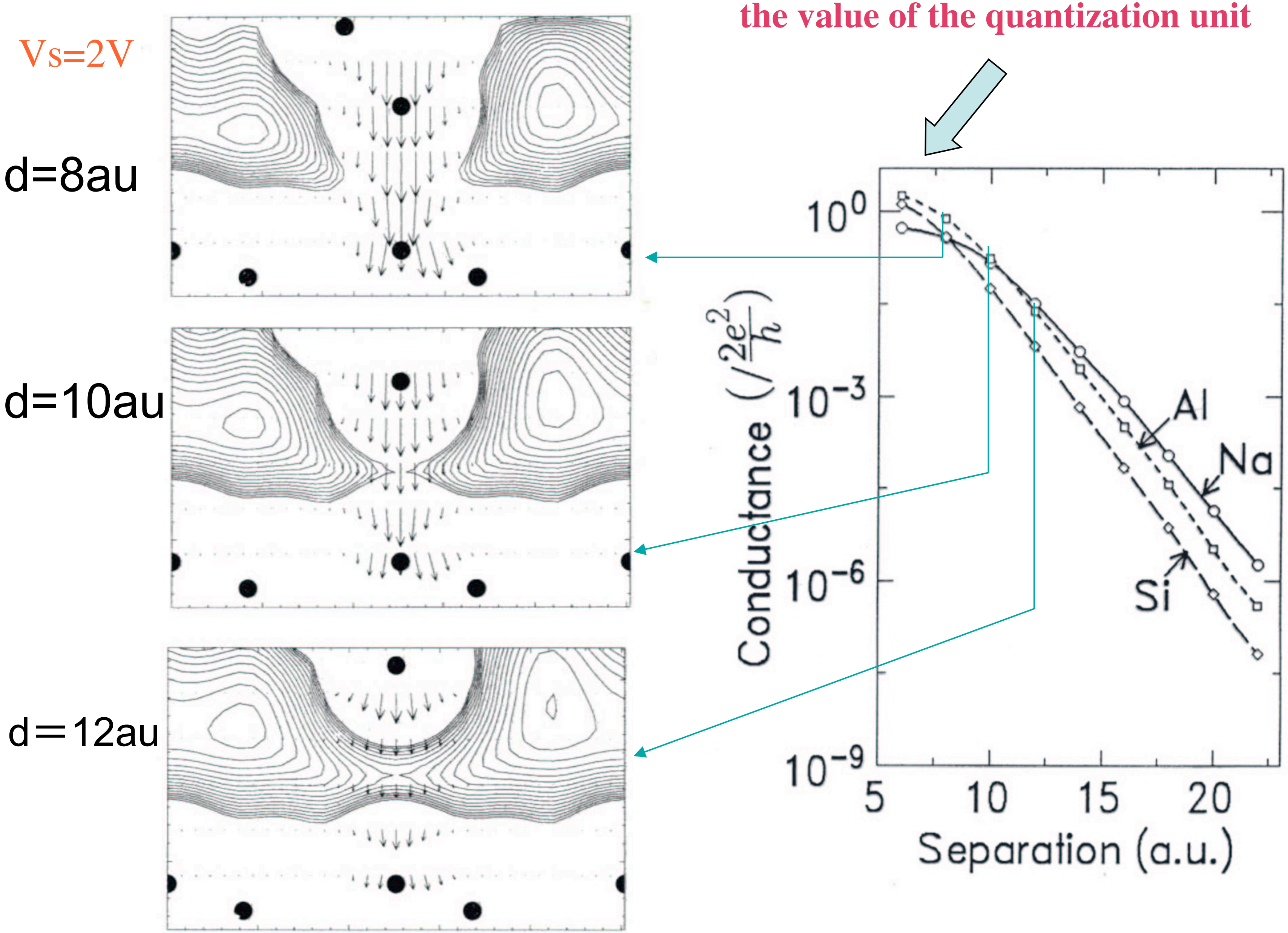
Current is confined
In a narrow channel !!



N.Kobayashi, K.Hirose and M.Tsukada,
J.J.Appl. Phys. 35(1996)3710

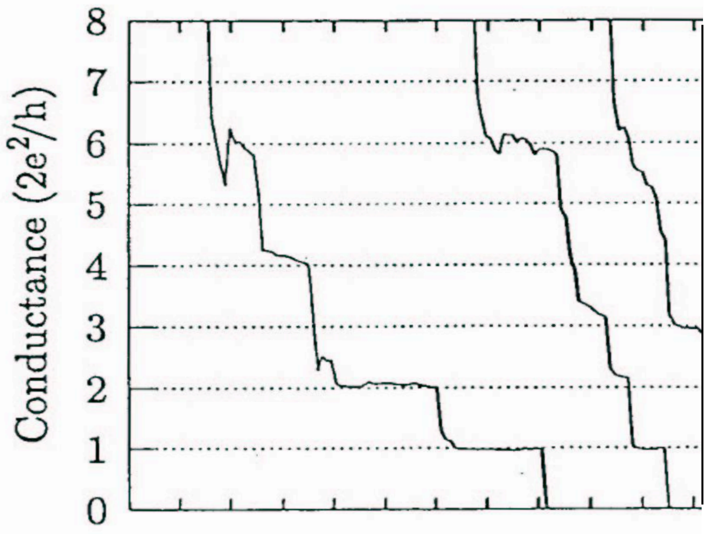
what happens at the atomic contact？

Conductance at the contact is close to the value of the quantization unit



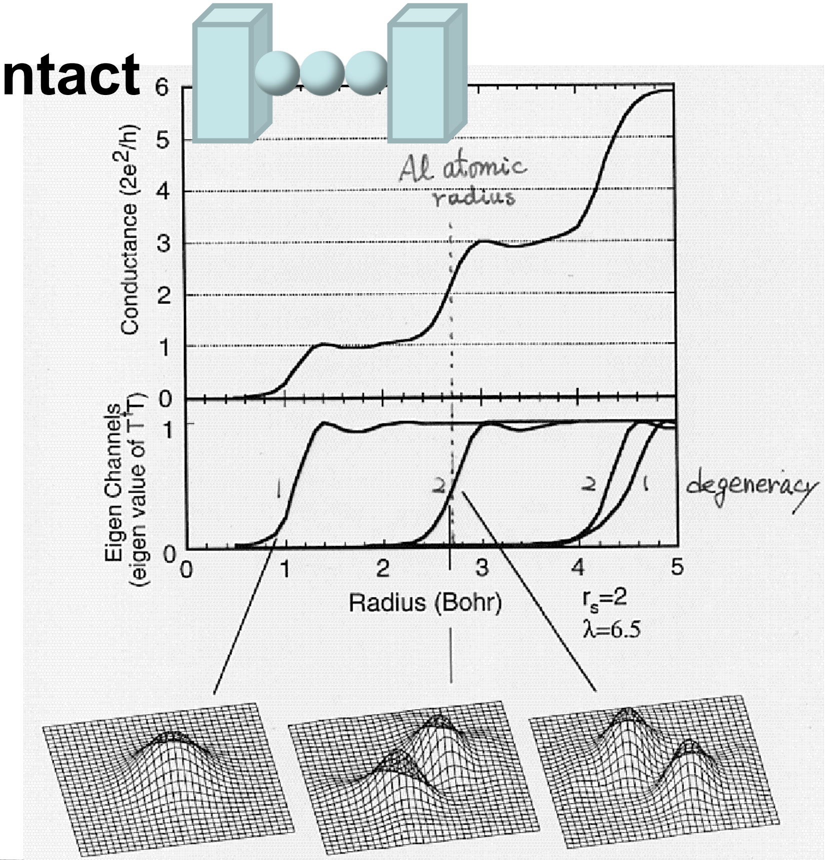
Quantum conductance of Au point contact

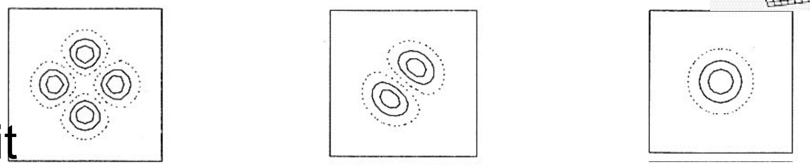
By Prof. Lars Olesen

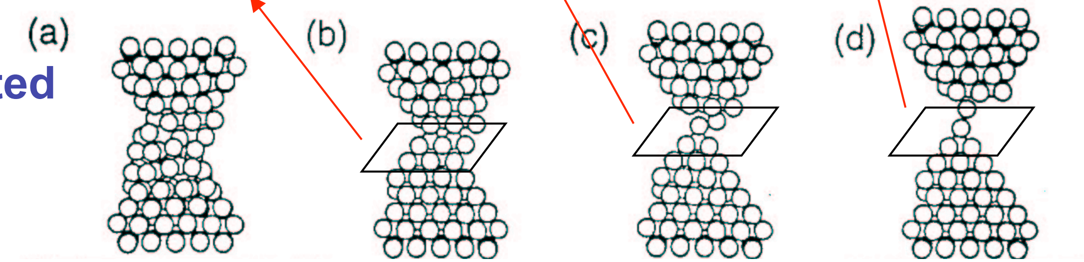


$$\frac{2e^2}{h} = \frac{1}{12.9k\Omega}$$

Quantization unit







W tip wetted with Au

Au surface

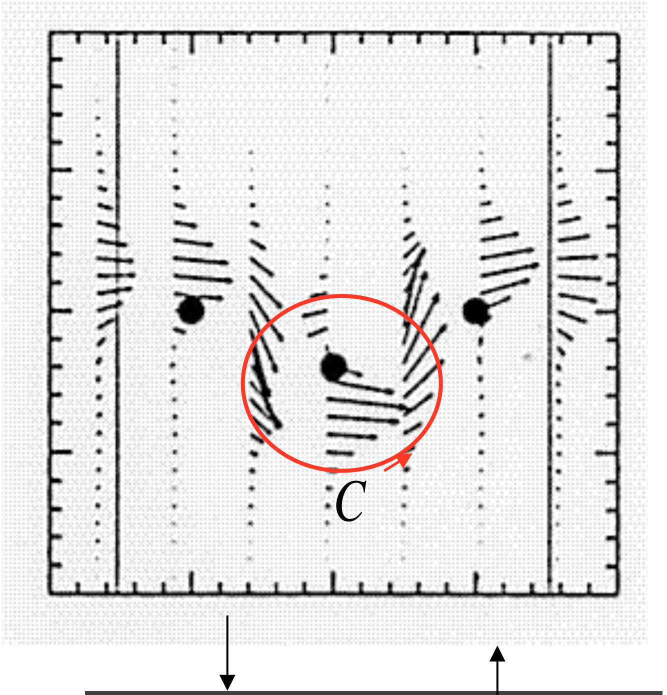
Retracting the tip from the gold surface

Electron behaves as a wave leading to quantum conductance

Simulation by Prof.M.Brandbyge

Loop current

through bent Al atomic wire



$$\oint_{loop\,C} R\mathbf{j}\cdot d\mathbf{r} \neq 0$$

⇩

Contradiction with Ohm's law !

⇩

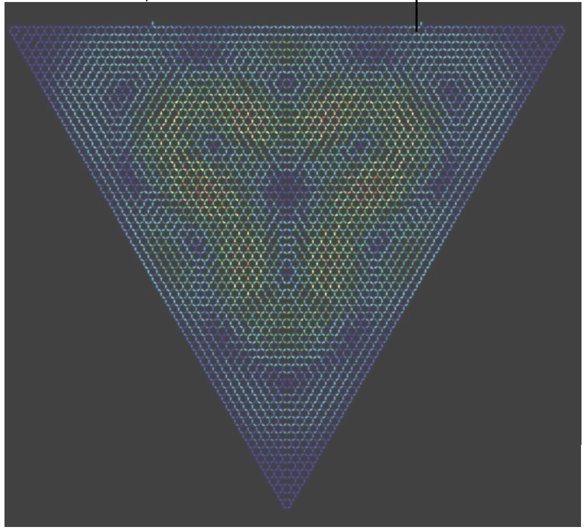
Without voltage drop, i.e., Without deriving electromotive Force, current flows.

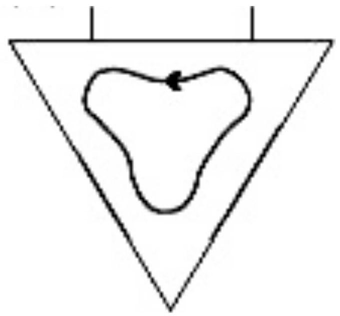
⇩

Remarkable quantum effect

Loop current

through triangle graphene



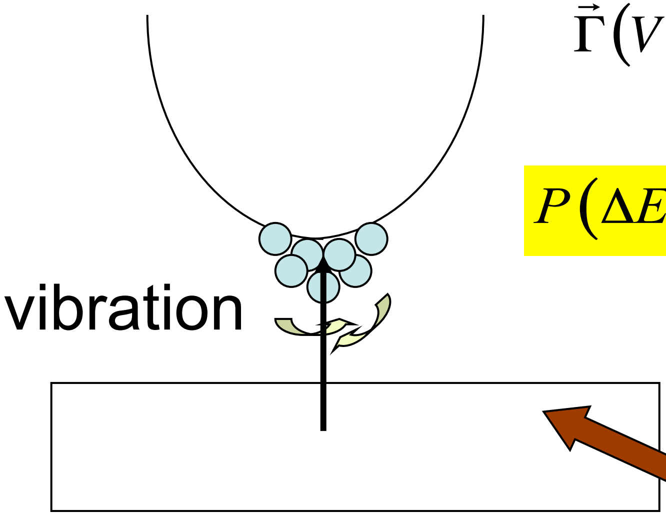


From coherent to dissipating electron transport

$\delta(E-E')$ for elastic tunneling

Electron transition rate

$$\vec{\Gamma}(V)=\frac{1}{R}\int dE\int dE' f(E)\{1-f(E'+eV)\}P(E-E')$$



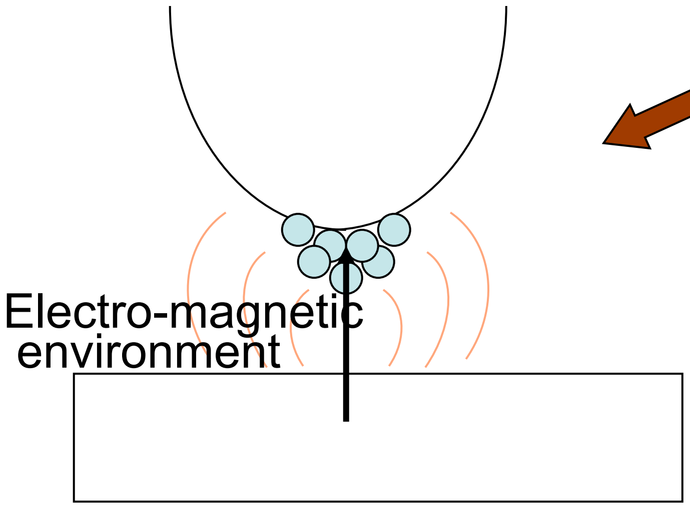
$$P(\Delta E)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dt\exp\left[J(t)+\frac{i}{\hbar}\Delta E t\right]$$

energy loss spectral function

$$J(t)\equiv\langle(\varphi(t)-\varphi(0))\varphi(0)\rangle$$

$$=\sum_{\lambda}\gamma_{\lambda}^{2}\left\{\coth\left(\frac{\beta\hbar\omega_{\lambda}}{2}\right)(\cos\omega_{\lambda}t-1)-i\sin\omega_{\lambda}t\right\}$$

$$=\frac{2e^{2}}{h}\int_{0}^{\infty}\frac{d\omega}{\omega}\mathrm{Re}\,Z_{t}(\omega)\left\{\coth\left(\frac{\beta\hbar\omega}{2}\right)(\cos\omega t-1)-i\sin\omega t\right\}$$



Electron-Vibration Coupling strength

$$\gamma_{\lambda}=\frac{\eta_{\lambda}}{\hbar\omega_{\lambda}}=\sqrt{\frac{\pi e^{2}\alpha_{\lambda}}{hC\omega_{\lambda}^{3}}}$$

Normal mode intensity of electro-magnetic environment

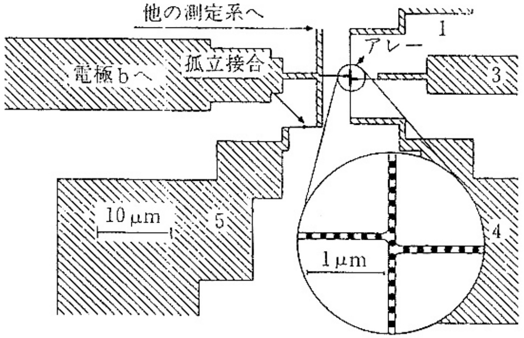
$$\frac{d^{2}I}{dV^{2}}=\frac{e}{R}P(eV)$$

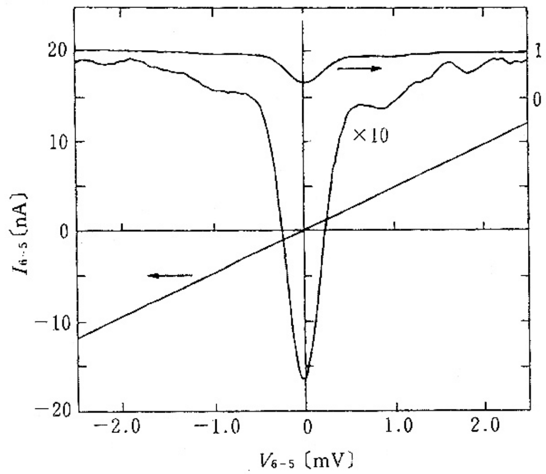
Inelastic tunneling spectroscopy

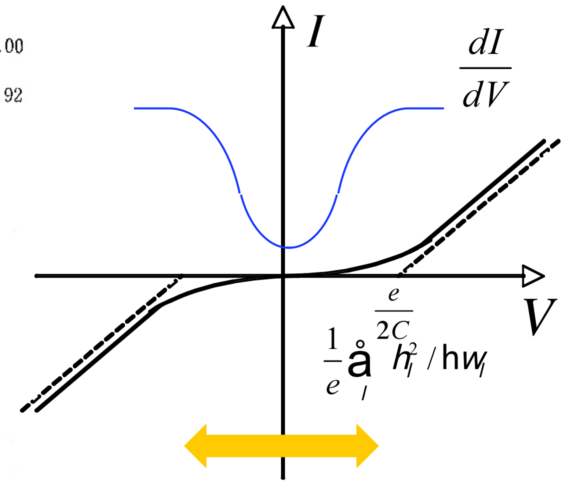
$$\frac{dI}{dV}=\frac{1}{R}\int_{0}^{eV}P(\Delta E)\,d\Delta E$$

Zero bias anomaly

The integrated energy loss spectral function and zero bias anomaly







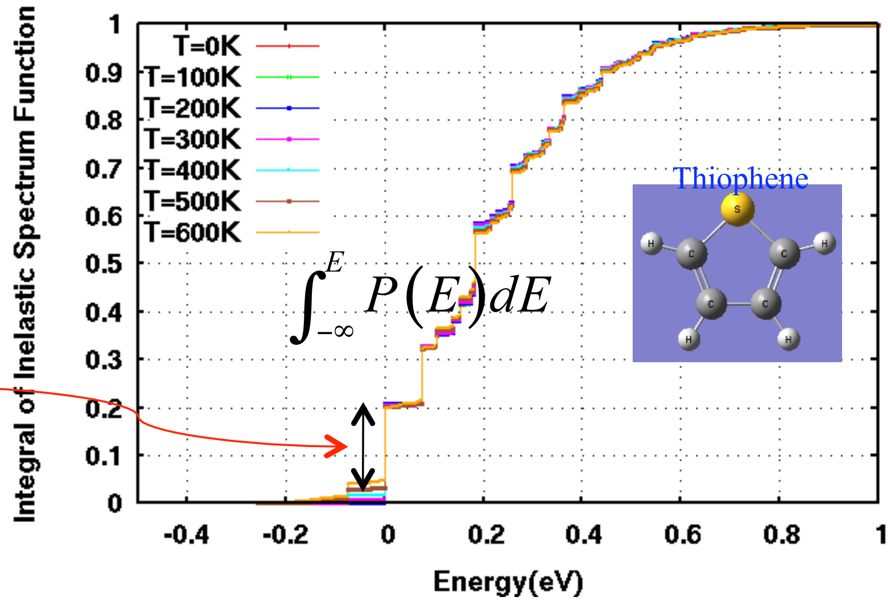
Small gap of the conductance is opened between the unoccupied and the occupied sates;
this is zero bias anomaly

$$\frac{d^2 I}{dV^2} = \frac{e}{R} P(eV)$$

$$\frac{dI}{dV} = \frac{1}{R}\int_0^{eV} P(E)dE$$

$V \to \infty$: $\frac{dI}{dV} = \frac{1}{R}$

$V \to 0$: $\frac{dI}{dV} = 0$



The step height at origin corresponds to the prob. of coherent process

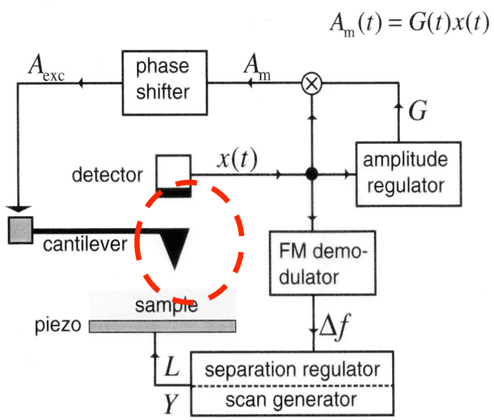
$$G(0) = \exp\left[-2\sum_\lambda \gamma_\lambda^2 k_B T / \hbar\omega_\lambda\right] G^{(0)}$$

Branching ratio to the coherent process

Theory of dynamic AFM

Dynamics of cantilever as an elastic body

What does the conventional harmonic oscillator model imply?



Equation of motion for **a harmonic oscillator**

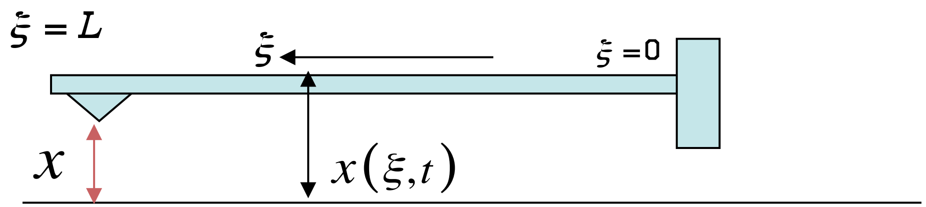
$$\frac{d^2x}{dt^2} + \gamma\frac{dx}{dt} + \omega_c^2 x = F_{driv}(t) + F_{TS}(x)$$

Friction Coefficient | Cantilever Resonant Freq. | Deriving force Of cantilever | Tip-Surface Interaction force

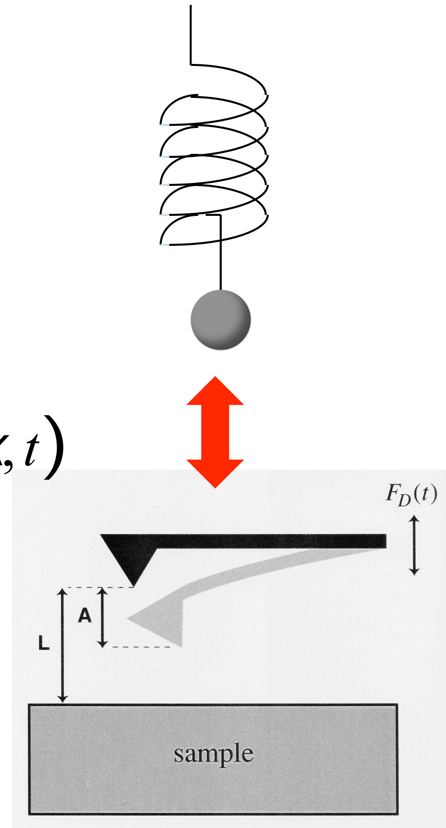
?

Equation of motion for continuum elastic body

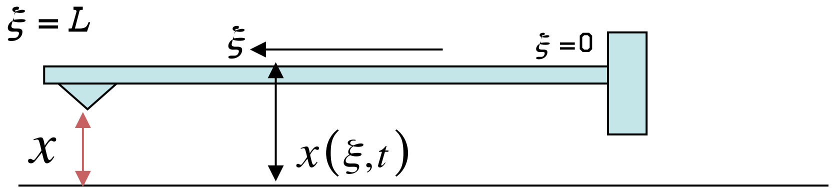
$$EI\frac{\partial^4 x(x,t)}{\partial x^4} + \gamma\frac{\partial x(x,t)}{\partial t} + \rho\frac{\partial^2 x(x,t)}{\partial t^2} = \tilde{F}_{driv}(x,t) + \tilde{F}_{TS}(x,t)$$



The meaning of the parameters??



Projection onto a normal mode



$$EI\frac{\partial^4 x(\xi,t)}{\partial \xi^4} + \gamma\frac{\partial x(\xi,t)}{\partial t} + \rho\frac{\partial^2 x(\xi,t)}{\partial t^2} = \tilde{F}_{driv}(\xi,t) + \tilde{F}_{TS}(\xi,t)$$

$$x(\xi,t) = \sum_n x_n(t)\phi_n(\xi)$$

Eigen functions (Normal modes waves) obtained by

The coefficients satisfy the equation of motion of harmonic oscillator !!

$$\frac{d^2}{dt^2}x_n(t) + \gamma\frac{d}{dt}x_n(t) + \omega_n^2 x_n(t)$$

$$= F_{driv}(t) + F_{TS}(t)$$

$$F_{driv}(t) = \frac{\int_0^L \tilde{F}_{driv}(\xi,t)\phi_n(\xi)d\xi}{\rho S_n}$$

$$F_{TS}(t) = \frac{\int_0^L \tilde{F}_{TS}(\xi,t)\phi_n(\xi)d\xi}{\rho S_n}$$

$$S_n = \int_0^L |\phi_n|^2 d\xi$$

$$EI\frac{d^4\phi_n(\xi)}{d\xi^4} - \rho\omega_n^2\phi_n(\xi) = 0$$

with $\omega_n = \frac{C_n^2}{L^2}\sqrt{\frac{EI}{\rho}}$

$$\phi_n(\xi)\big|_{\xi=L} = \frac{d\phi_n(\xi)}{d\xi}\bigg|_{\xi=L} = \frac{d^2\phi_n(\xi)}{d\xi^2}\bigg|_{\xi=0} = \frac{d^3\phi_n(\xi)}{d\xi^3}\bigg|_{\xi=0}$$

For uniform beam case

$$f_n(x) = \left(\cos(C_n\tilde{x}) - \cosh(C_n\tilde{x})\right) + \frac{\cos(C_nL) + \cosh(C_nL)}{\sin(C_nL) + \sinh(C_nL)}$$

$$\cdot\left(\sin(C_n\tilde{x}) - \sinh(C_n\tilde{x})\right)$$

Parameters are given by $\cos(C_nL)\cosh(C_nL) + 1 = 0$

Analysis of the forced harmonic oscillator model

Standard Theory

amplitude

frequency

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

Resonance curve

Frequency shift

Tip-surface interaction force

$$\Delta f = rf_0 = -\frac{f_0}{2kA\pi}\int_0^{2\pi} F(A\cos\theta + L)\cos\theta \, d\theta$$

Friction coefficient

Width of the resonant curve

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

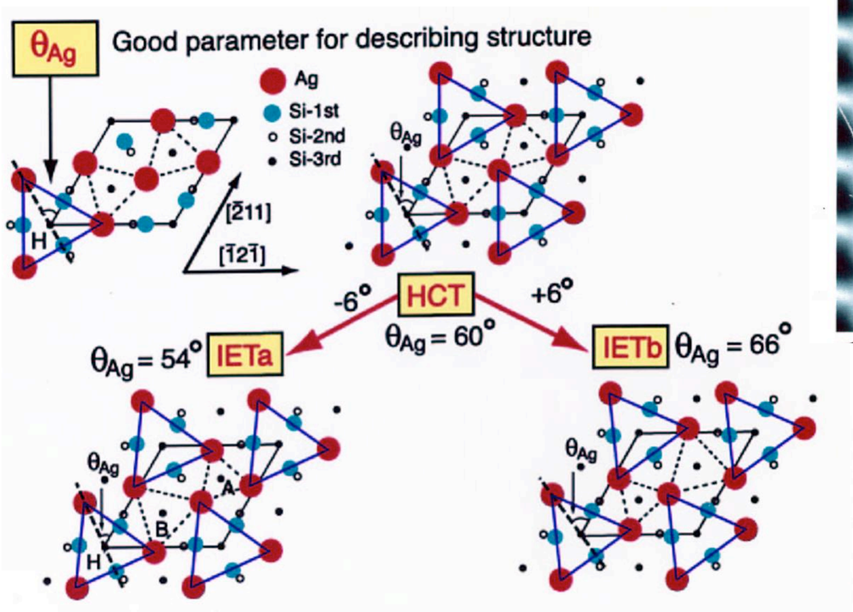
$$+\frac{1}{2kA\pi}\int_0^{2\pi} F(A\cos\theta + L)\sin\theta \, d\theta$$

Hysteresis Force

(First-Principles) Calculation with atomisitic models

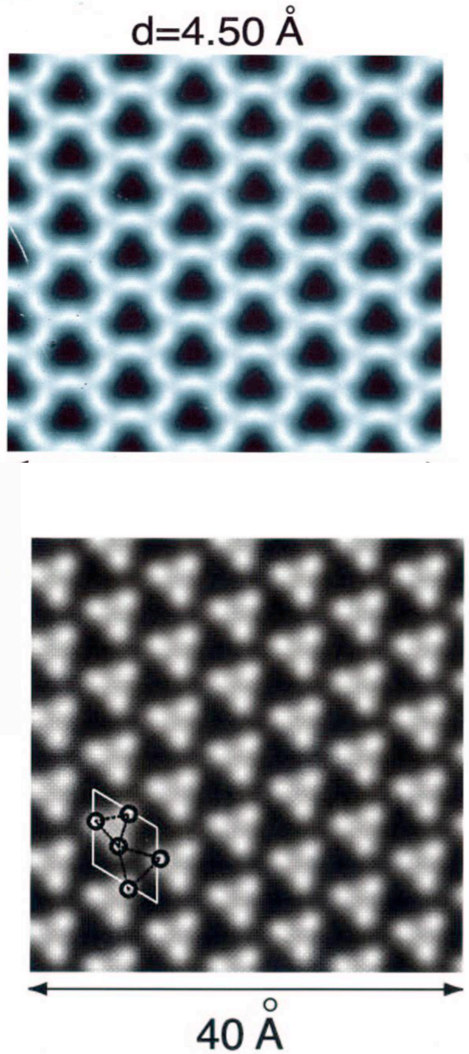
Temperature dependence of NC-AFM image of $Si(111)\sqrt{3}\times\sqrt{3}-Ag$

Model of fluctuating
Surface structure



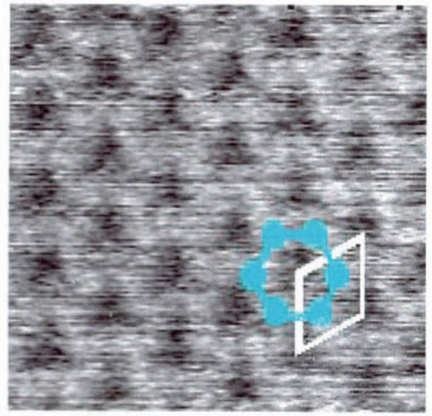
Remarkable temperature dependence is caused by the thermal adatom fluctuation Influenced by the tip

Theory

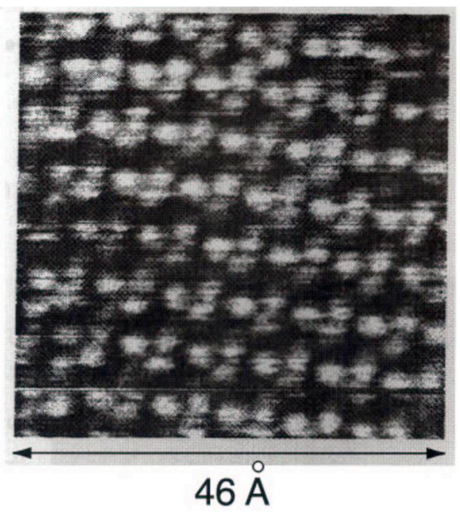


Experiment *T=300K*

By Morita/Sugawara



T=6.2K

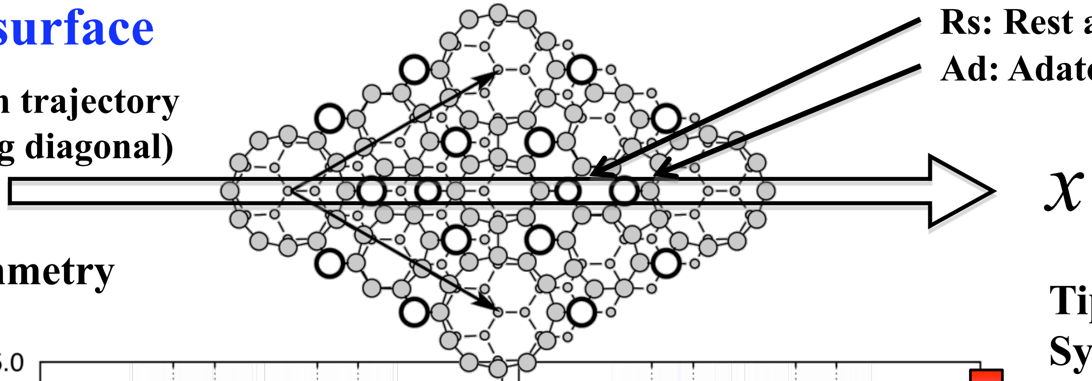


N.Sasaki,S.Watanabe and M.Tsukada,PRL 88(2002)046106 ncAFM

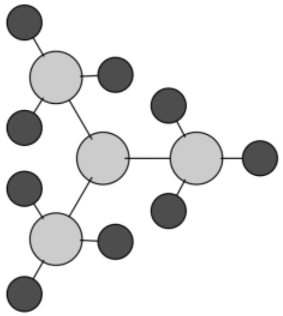
Effect of tip structure on the 3D force map

Si(111)-(5x5)-DAS surface

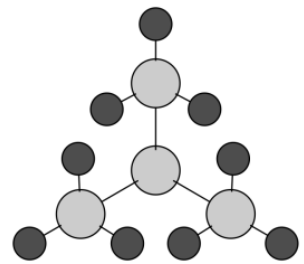
DFTB method

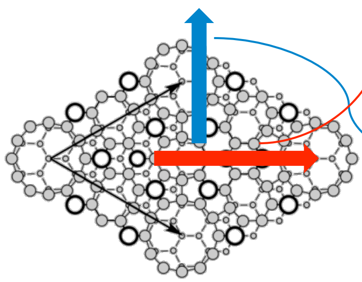


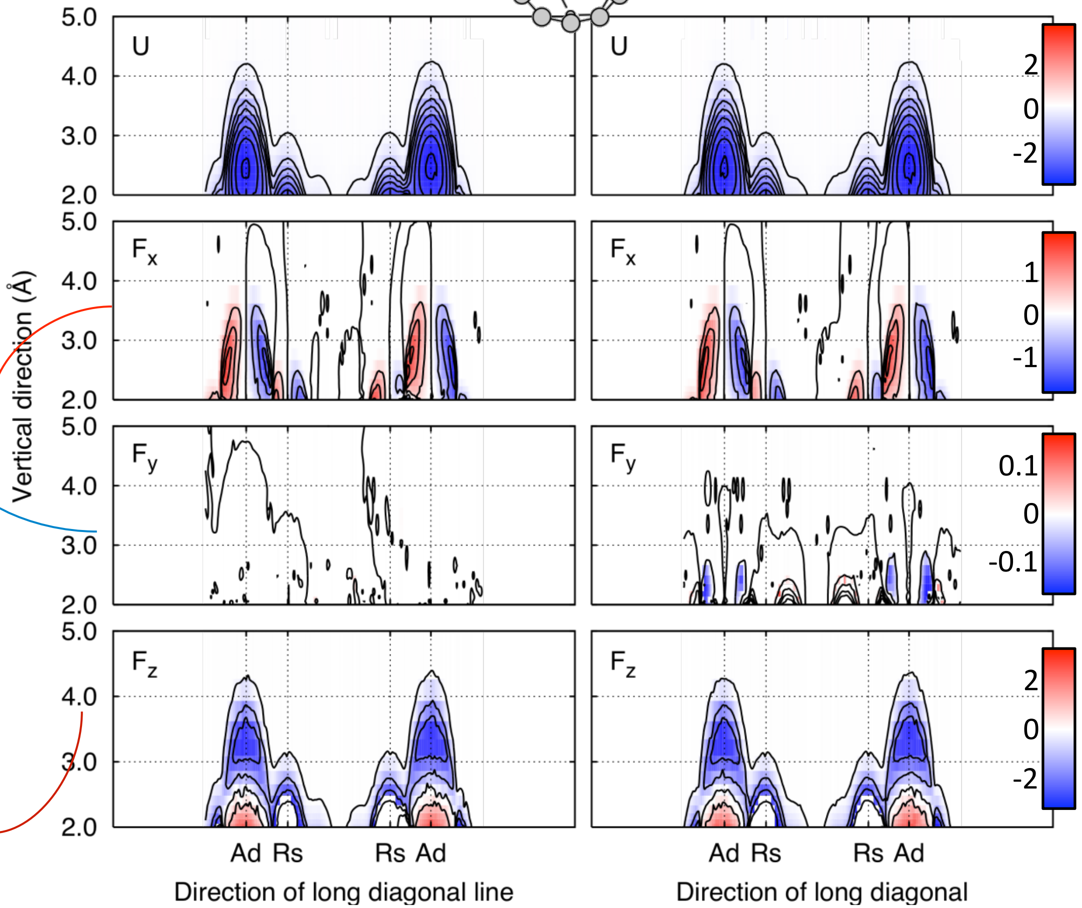
Tip with the mirror symmetry to x-axis



Tip without mirror Symmteryto x-axis







Vertical force To the surface

Ad: atom
Rs: Rest atom

Frequency shift image and dissipation image

NaCl island on Cu(111)

Topography by $\Delta\nu$ Dissipation image

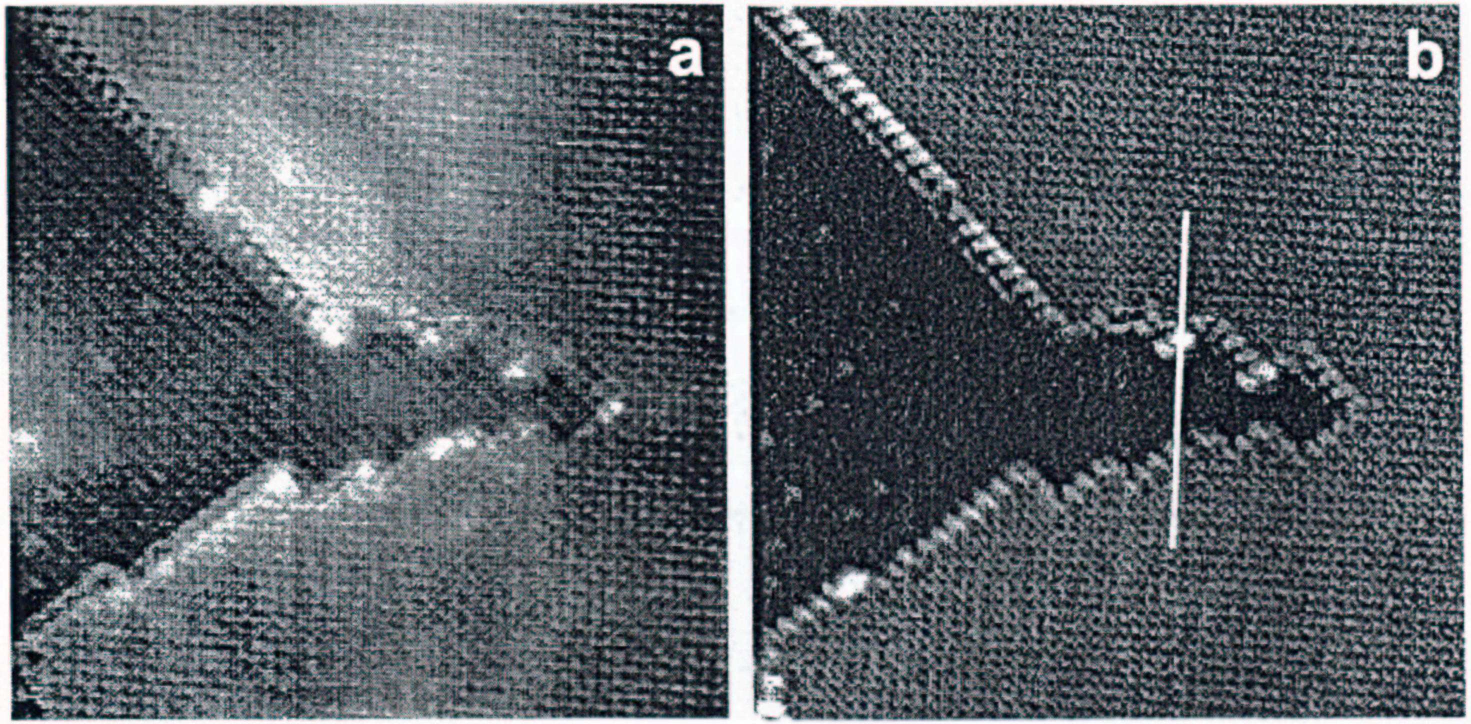


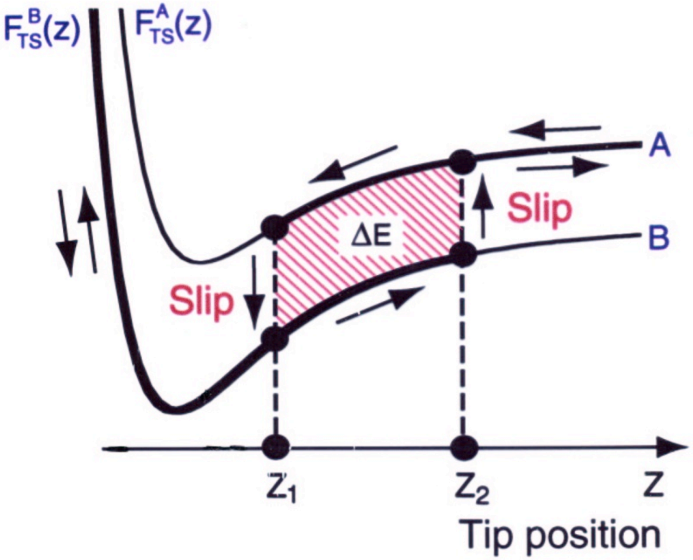
Figure 2: (a) Enlarged topography and (b) A_{exc} images of the area mapped in Fig.1. Image size 18×18 nm.

R.Bennewitz, A.S.Foster, L.N.Kantorovich, M.Bammerlin, Ch.Loppacher, S.Schar, M.Guggisberg, E.meyer and A.L.Shluger, Phys. Rev. B 62 (2000) 2074

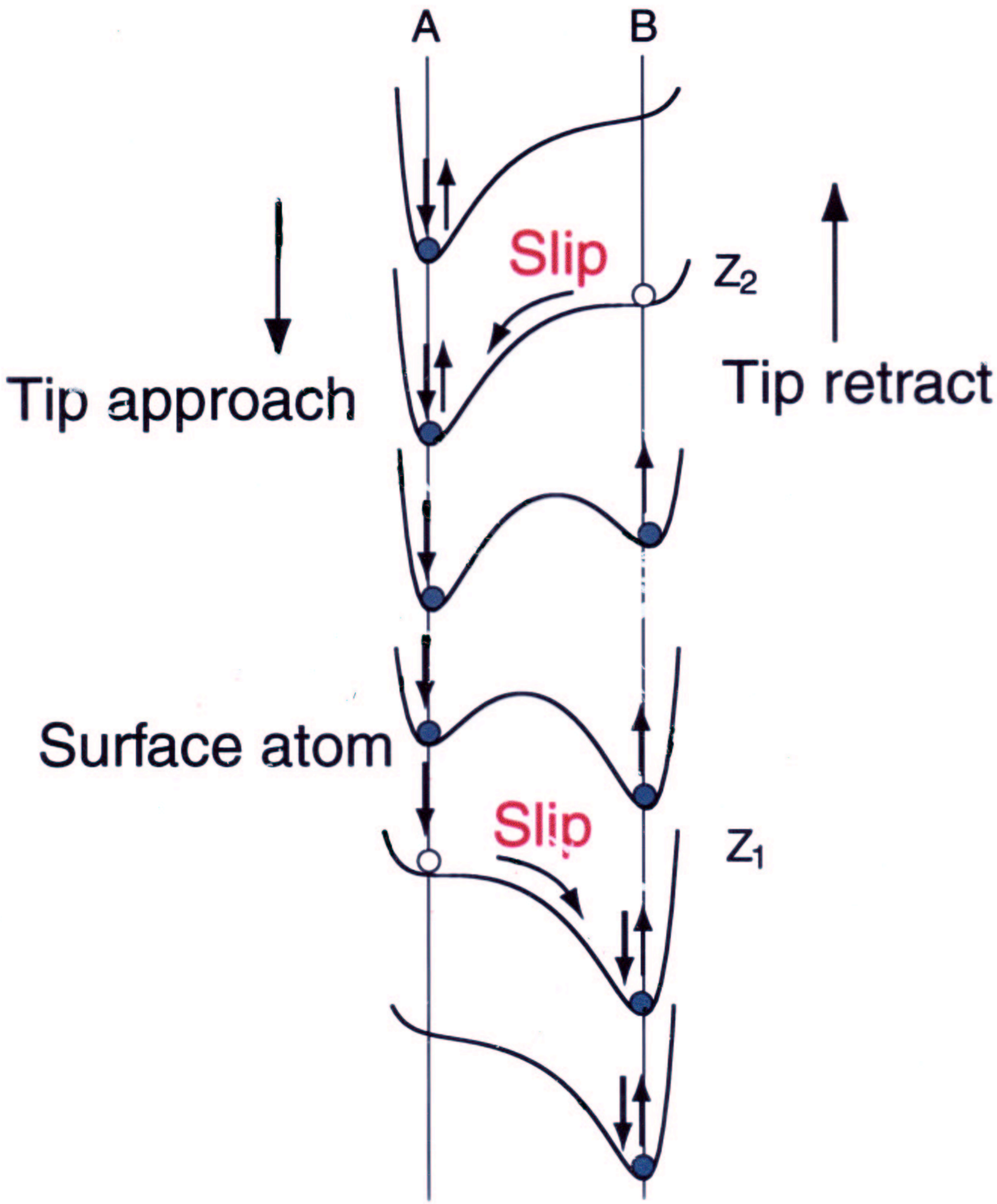
Origin of dissipation

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

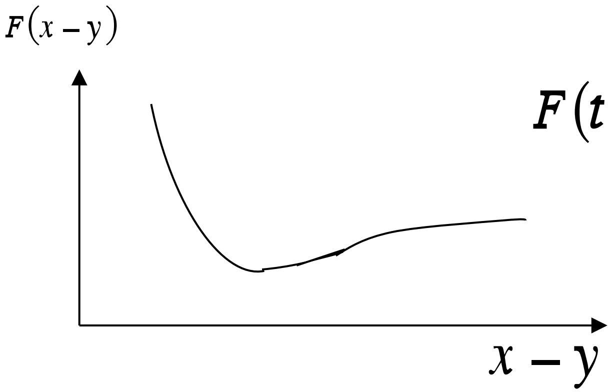
$$+\frac{1}{2kA\pi}\int_0^{2\pi}F(A\cos\theta + L)\sin\theta d\theta$$



Potential energy surface



Dissipation force microscopy



Thermal Fluctuation

$$F(t) = \bar{x} - \bar{y} + \frac{\partial F}{\partial x}\delta x + \frac{\partial F}{\partial y}\delta y$$

Brawnian motion of the tip/sample atoms

$$\langle \delta F(0)\delta F(t)\rangle = \left(\frac{\partial F}{\partial x}\right)^2 \langle \delta x(0)\delta x(t)\rangle + \left(\frac{\partial F}{\partial y}\right)^2 \langle \delta y(0)\delta y(t)\rangle$$

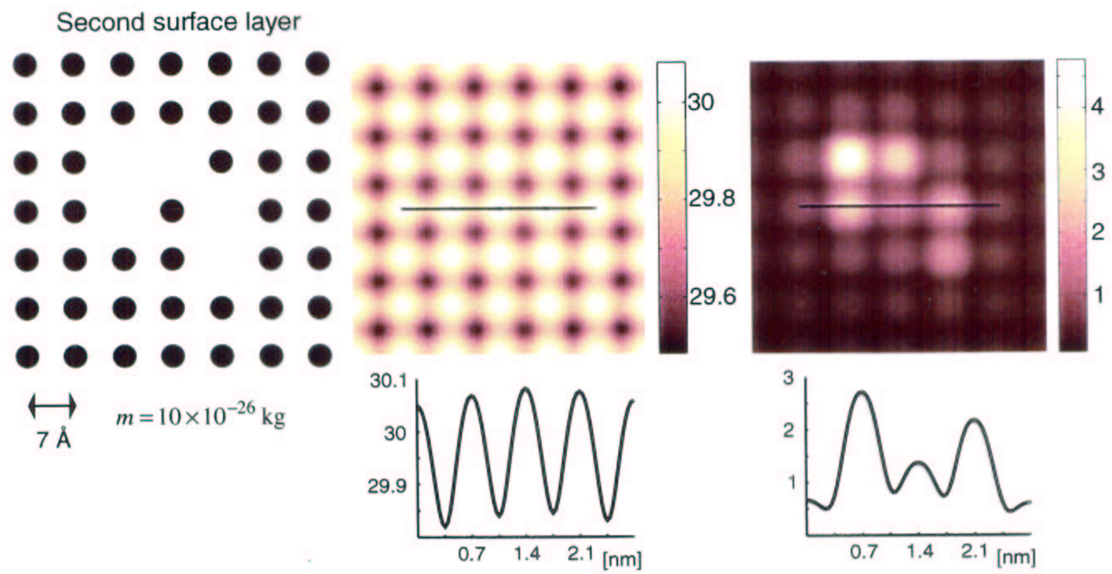
Fluctuation-Dissipation Theorem

$$\gamma = \frac{1}{Mk_B T}\int_0^\infty \langle \delta F(0)\delta F(t)\rangle dt$$

Detecting the stochastic motion of sample atoms with AFM?

M.Gauthier and M.Tsukada Phys.Rev.Lett. 85(2000)5348

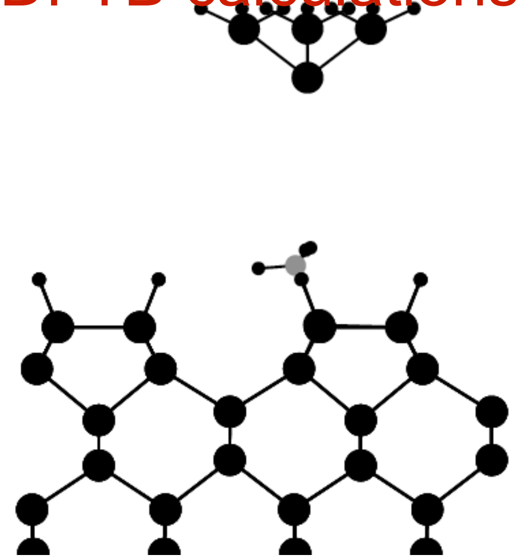
M.Gauthier and M.Tsukda Surface Sci. 495(2001)204-210



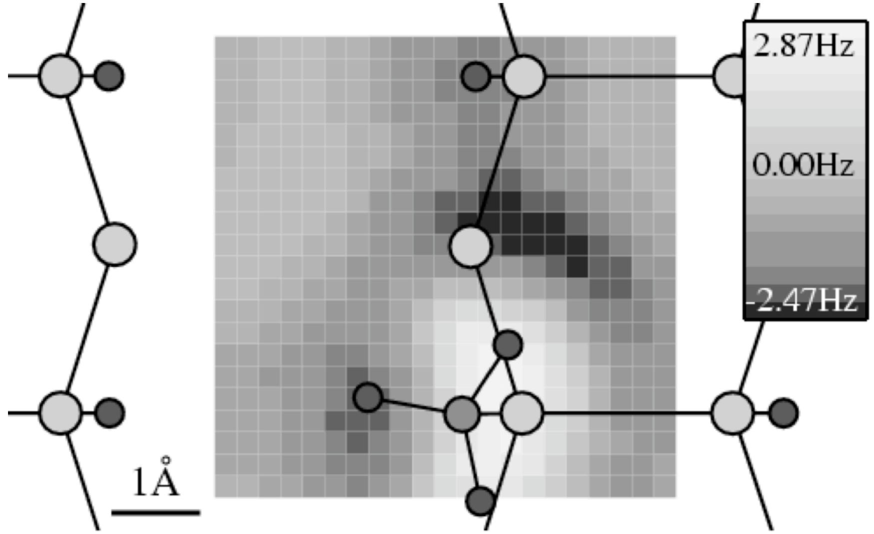
Non-Contact AFM image of methyl group on Si(100)/H

DFTB calculations

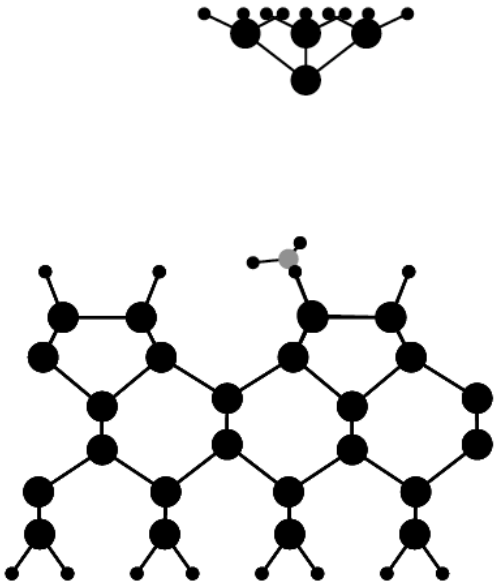
Frequency shift image Constant height



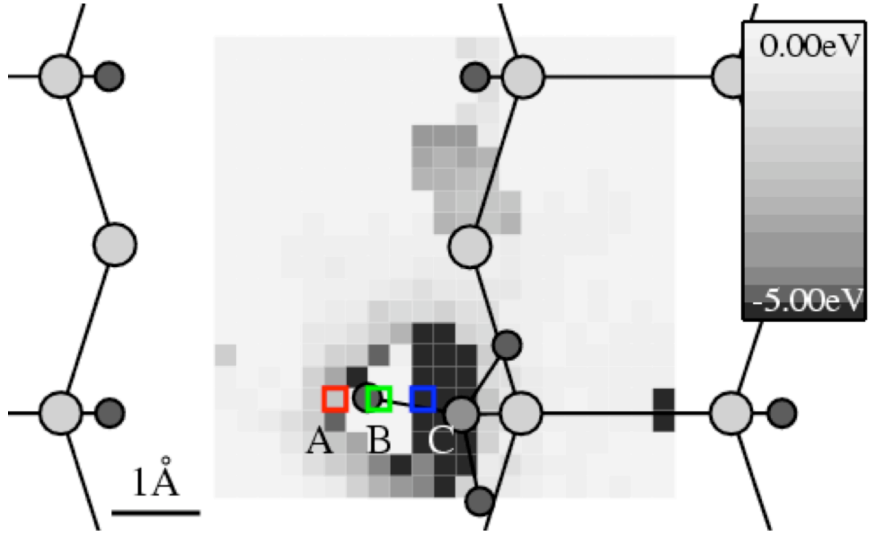
on H atom



Dissipation image

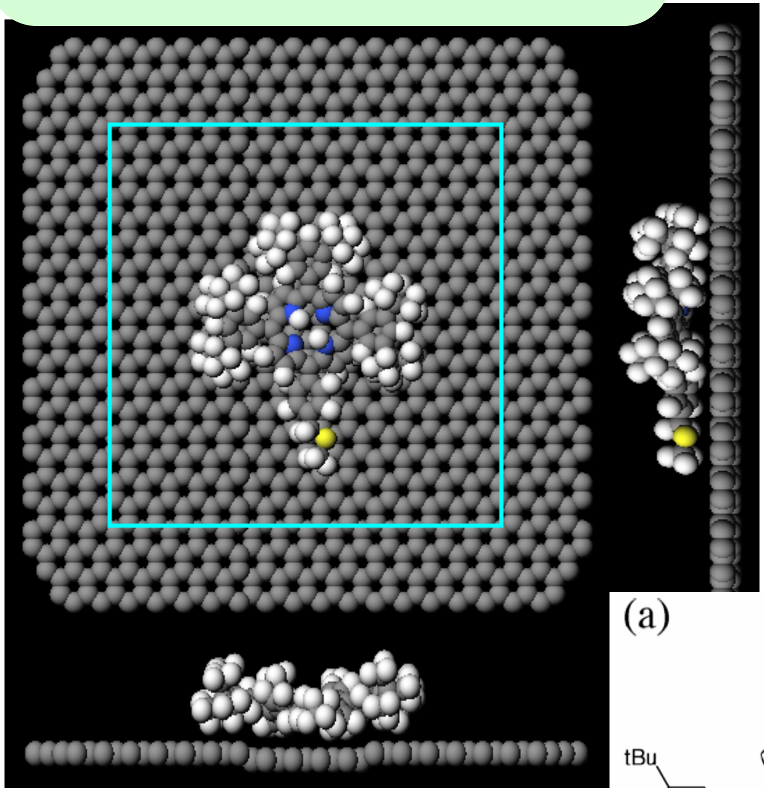


on methyl



Molecular mechanics calculation

AFM image of MSTBPP

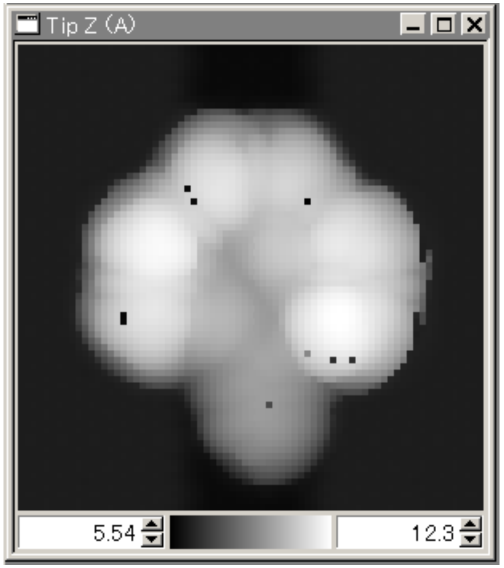


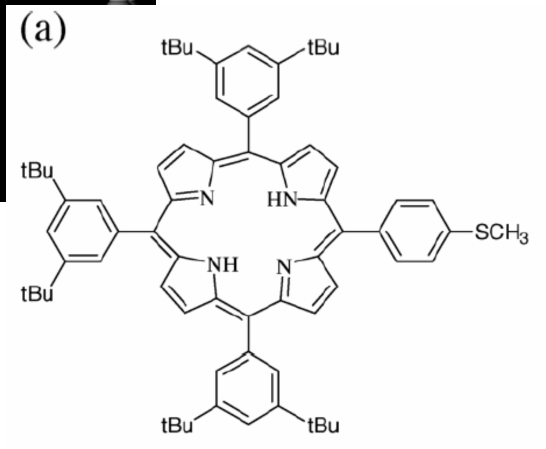
Depth = 0.5Å

Simulated constant force image

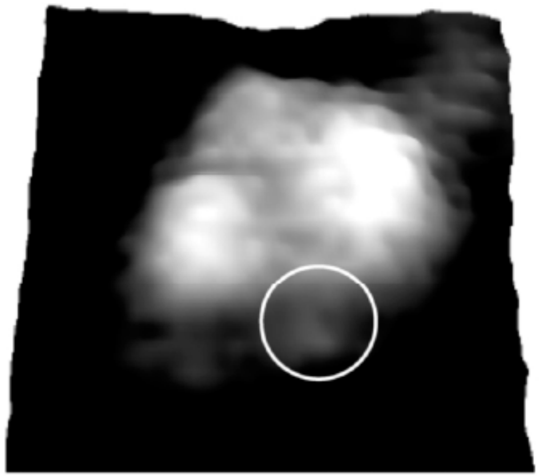
Hydrogen atom tip
Fz = - 0.0005nN
36Å×36Å（pixsize=0.5Å）

For fixed shape of molecule



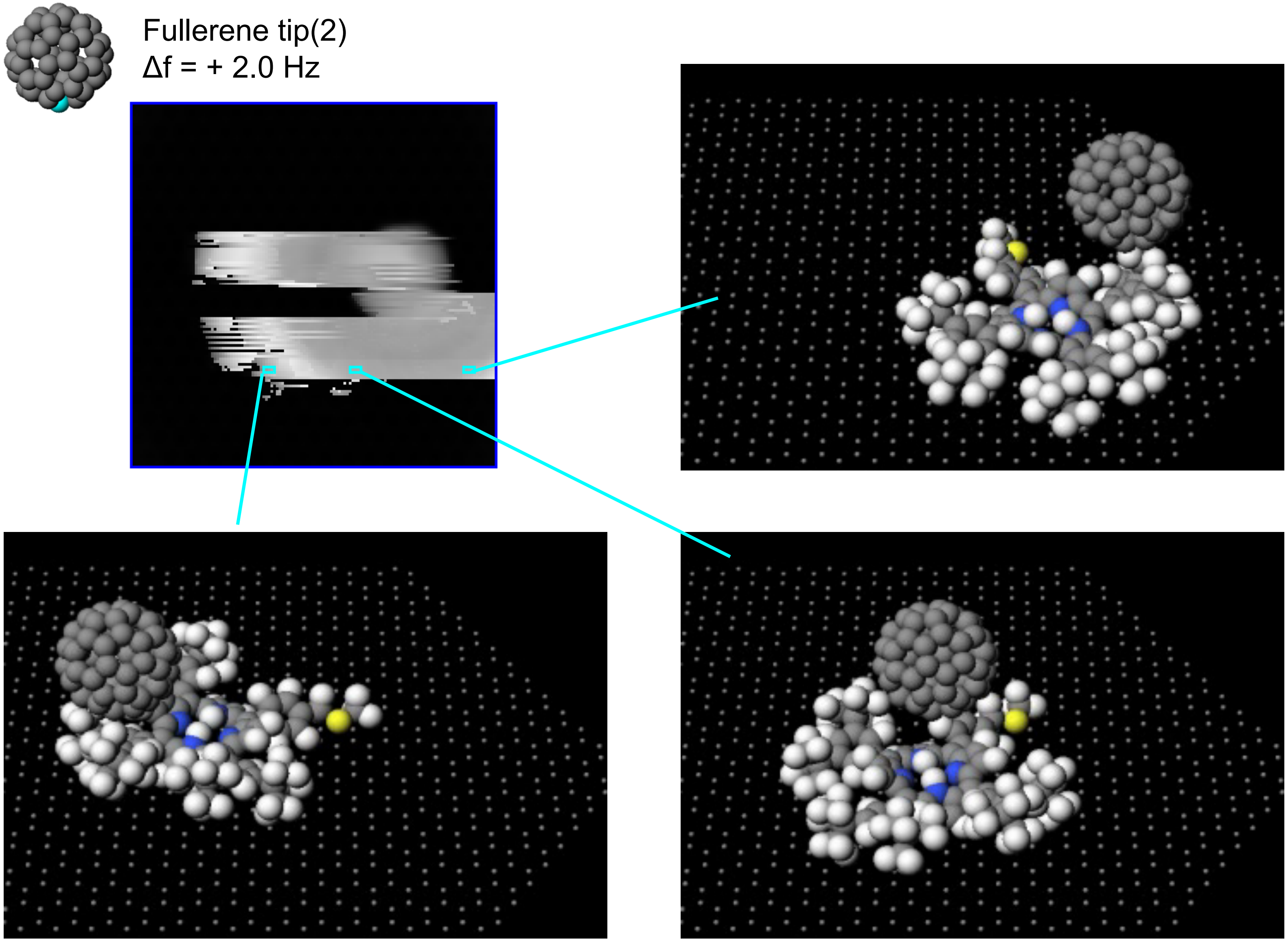


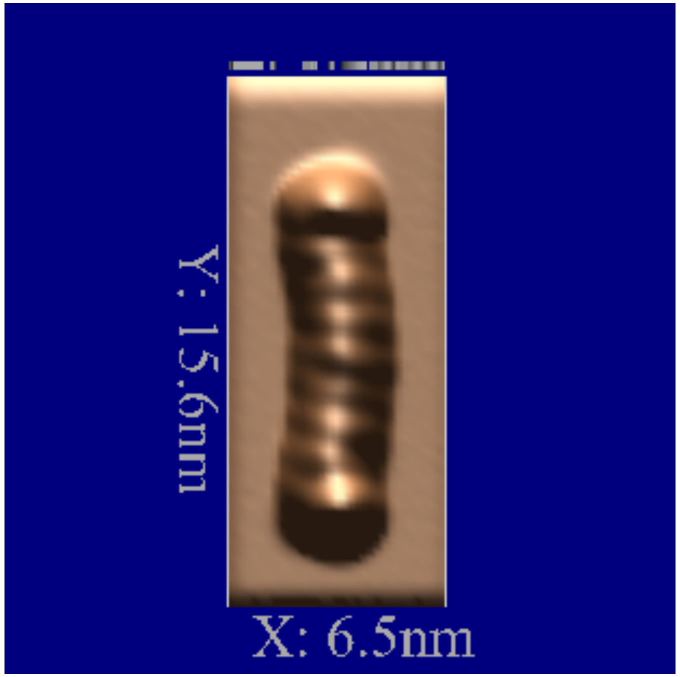
Experimental image

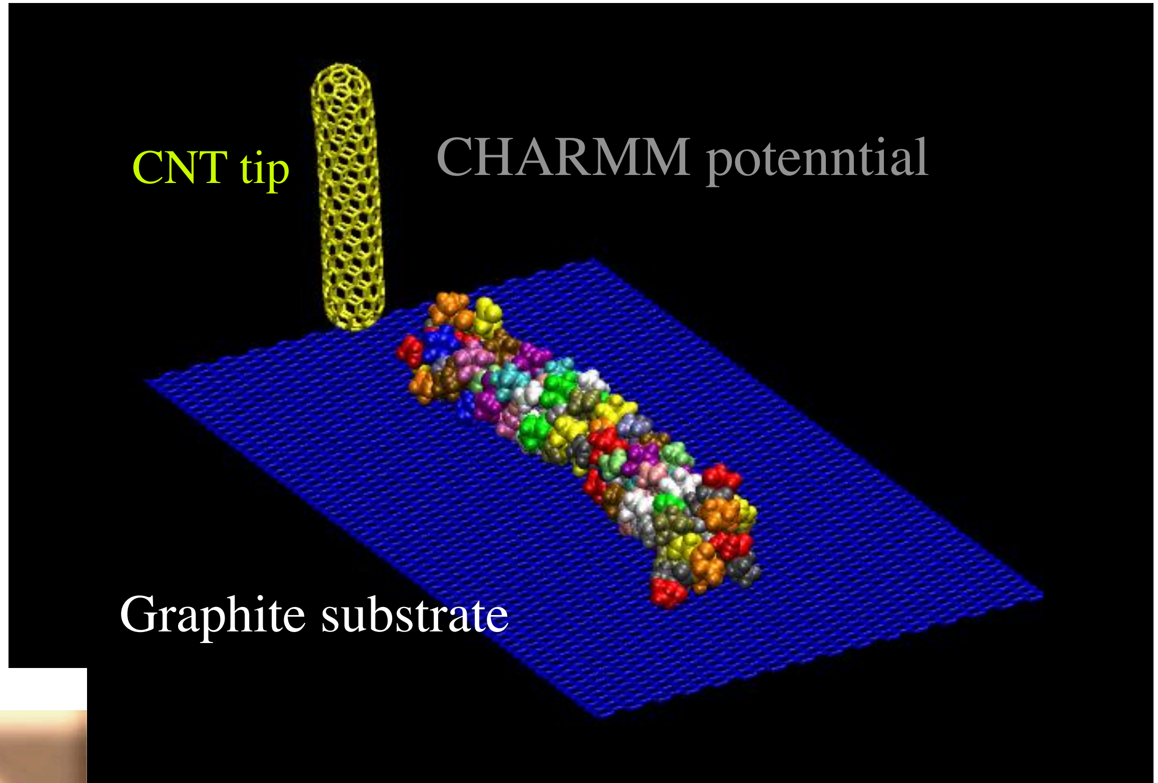


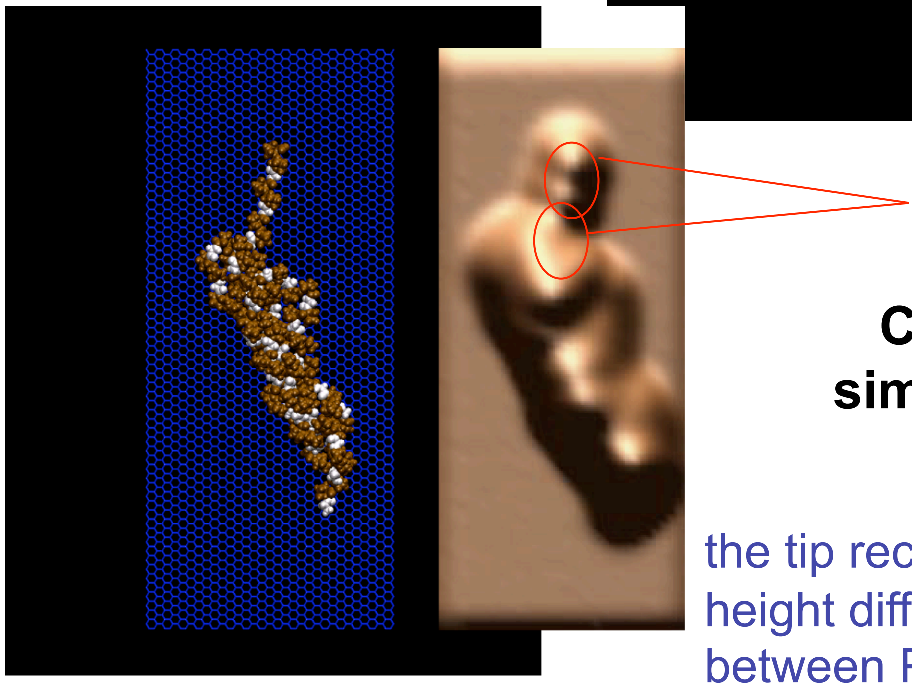
NC-AFM image of methylthiophenyl-tris-t-buthylphenyl-porphyrin（MSTBPP）molecule observed by S.Tanaka’ group

NC-AFM image simulation with C60 tip for MSTBPP molecule、Constant frequency mode～Motion of the Molecule～









proline

Constant mode AFM image simulation of a model collagen

the tip recognizes height difference between PRO and GLY.

Good correspondence with experiments!

A rapid simulation method of AFM images

Calculation by

Interaction force

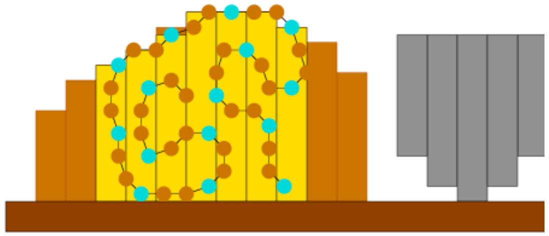
Geometrical condition

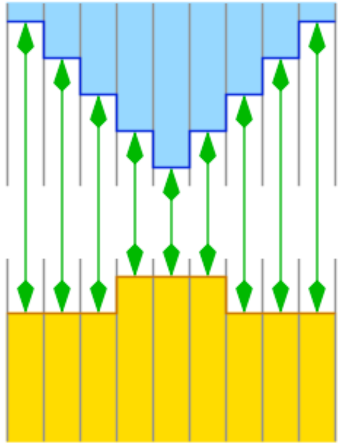
Computation time 2 weeks with the usual WS

Computation time 1 sec the usual PC

Secret of rapid calculation

Using only geometrical condition

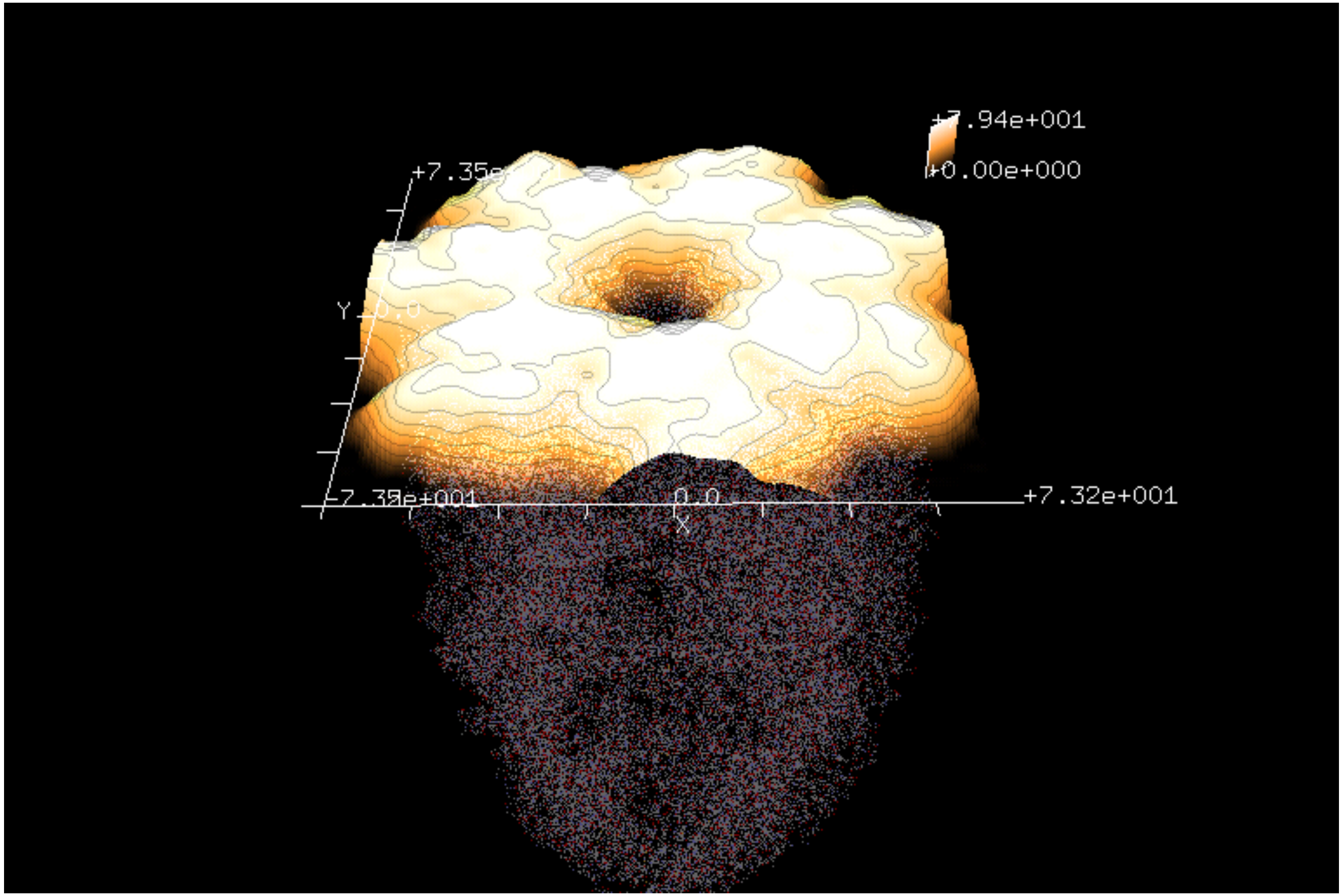




1. Divide each of the tip and the sample into fine meshes.
2. The highest atom in the mesh defines its height
3. Approach the tip vertically to the sample, until they touch each other.
4. The height of the tip at the touch defines the sample shape.

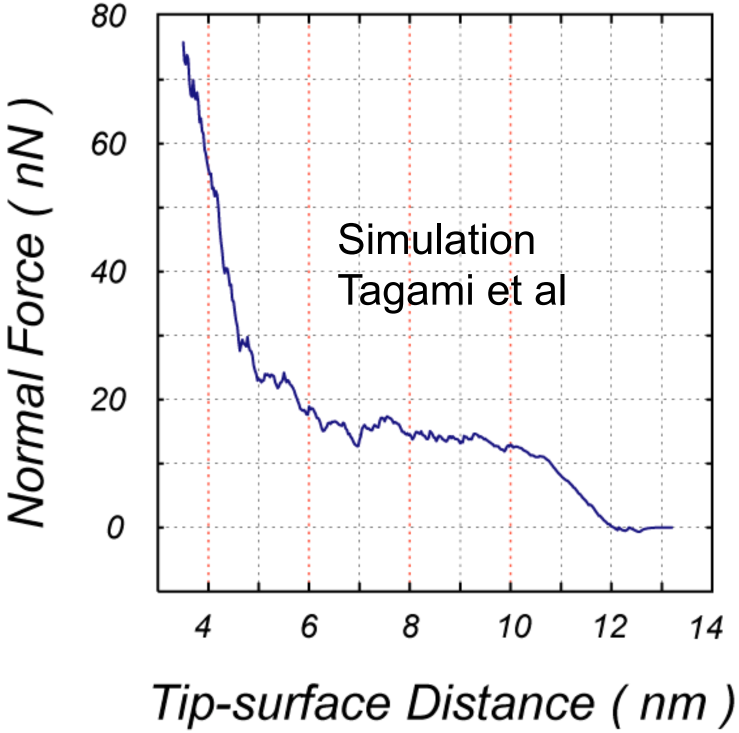
Fast AFM image simulator for protein molecules

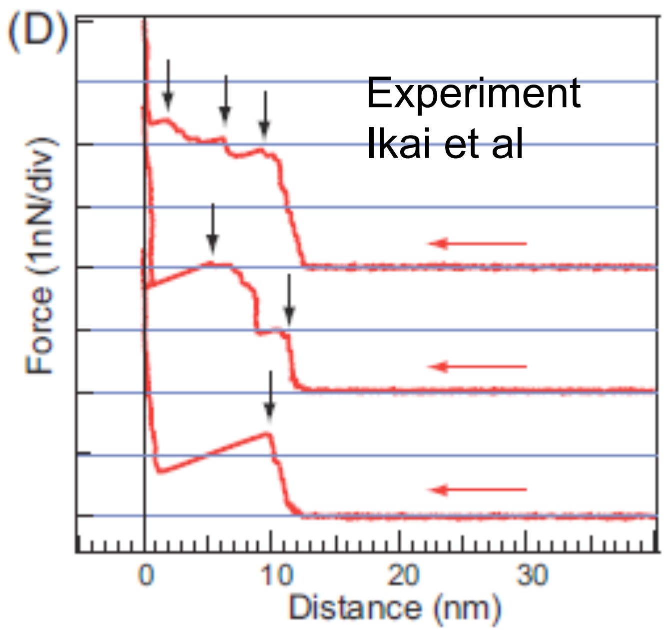
The case of GroEL

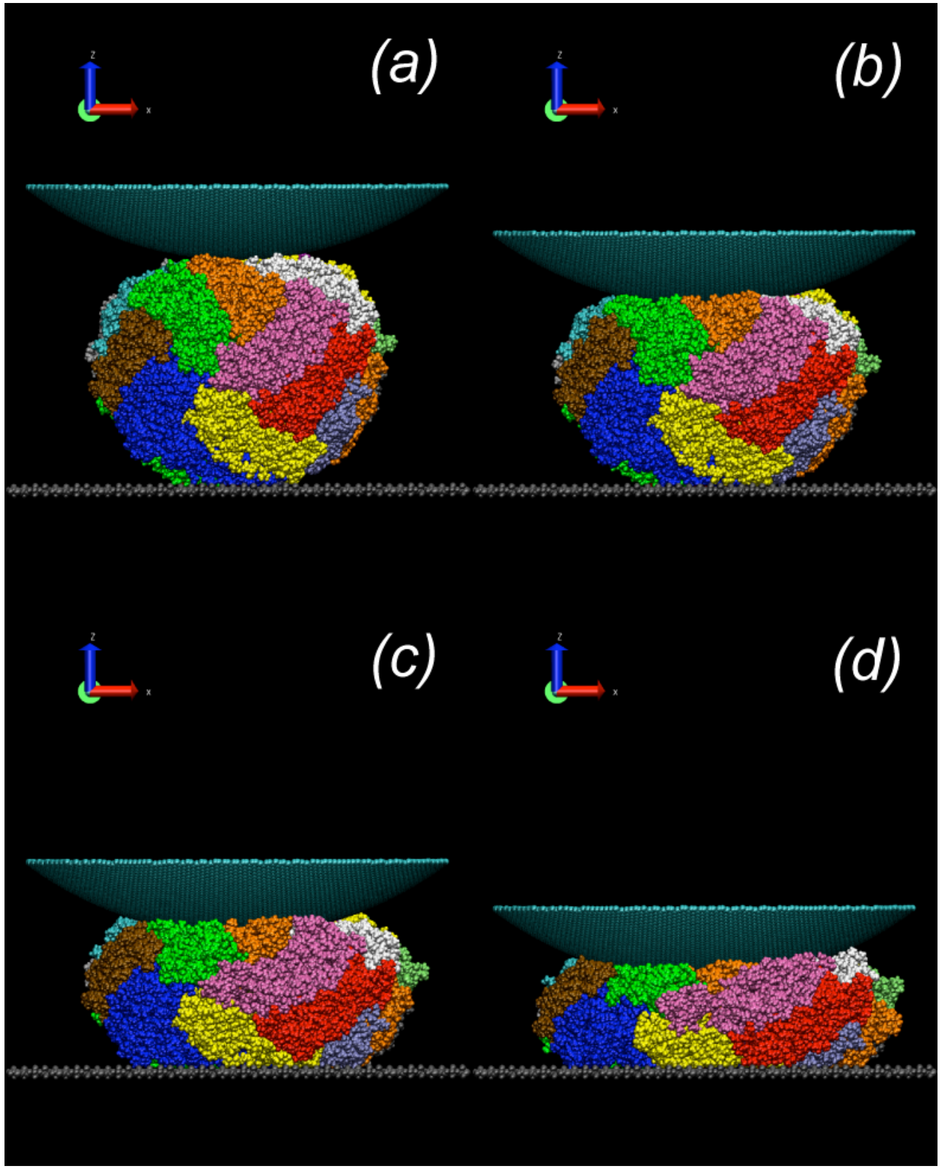


Theory of nano mechanics of protein molecules

Compression of apo-ferritin

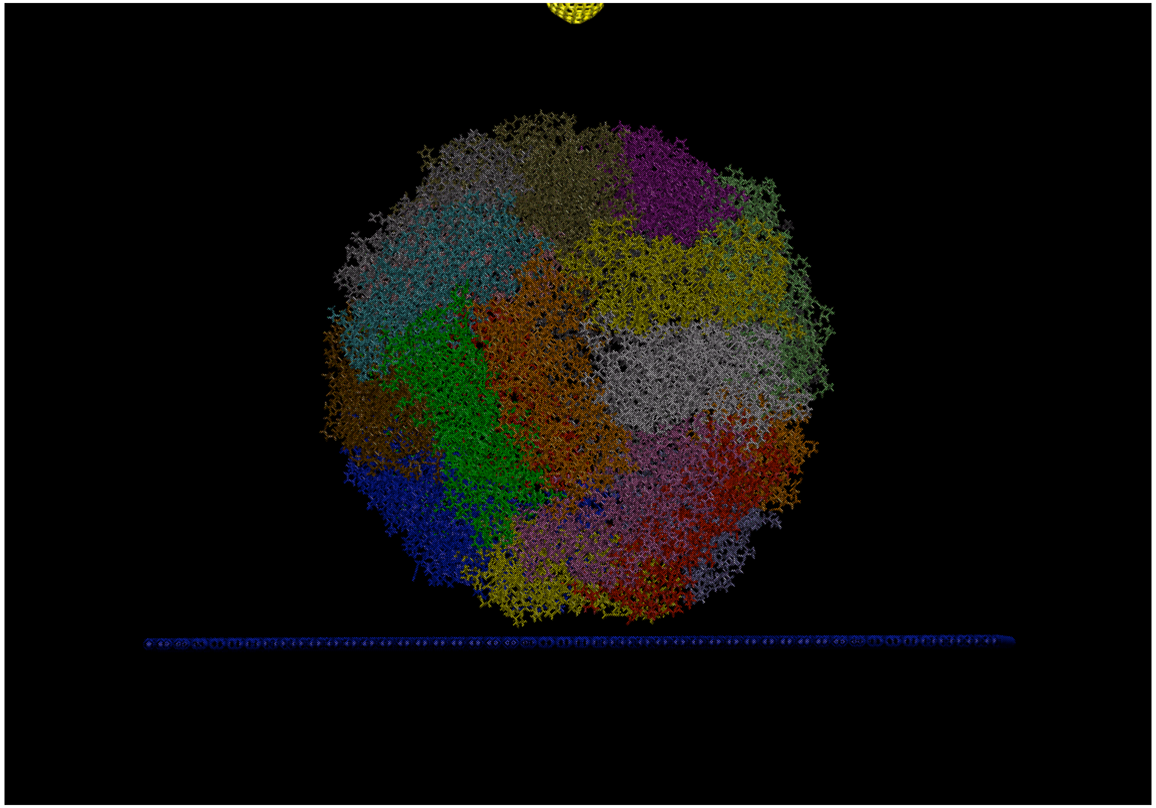






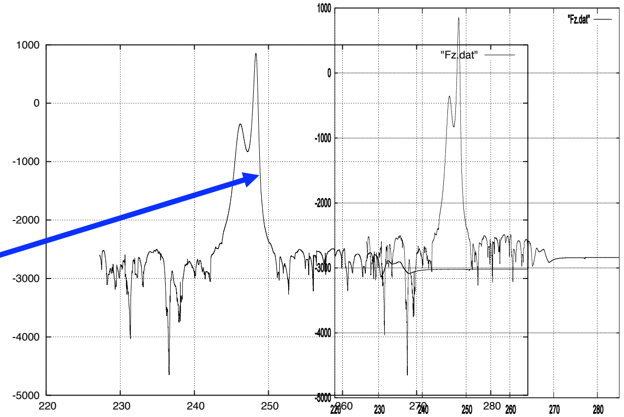
Penetration of CNT tip through apo-ferritin

A simulation of nano-mechanical experiment on protein molecule



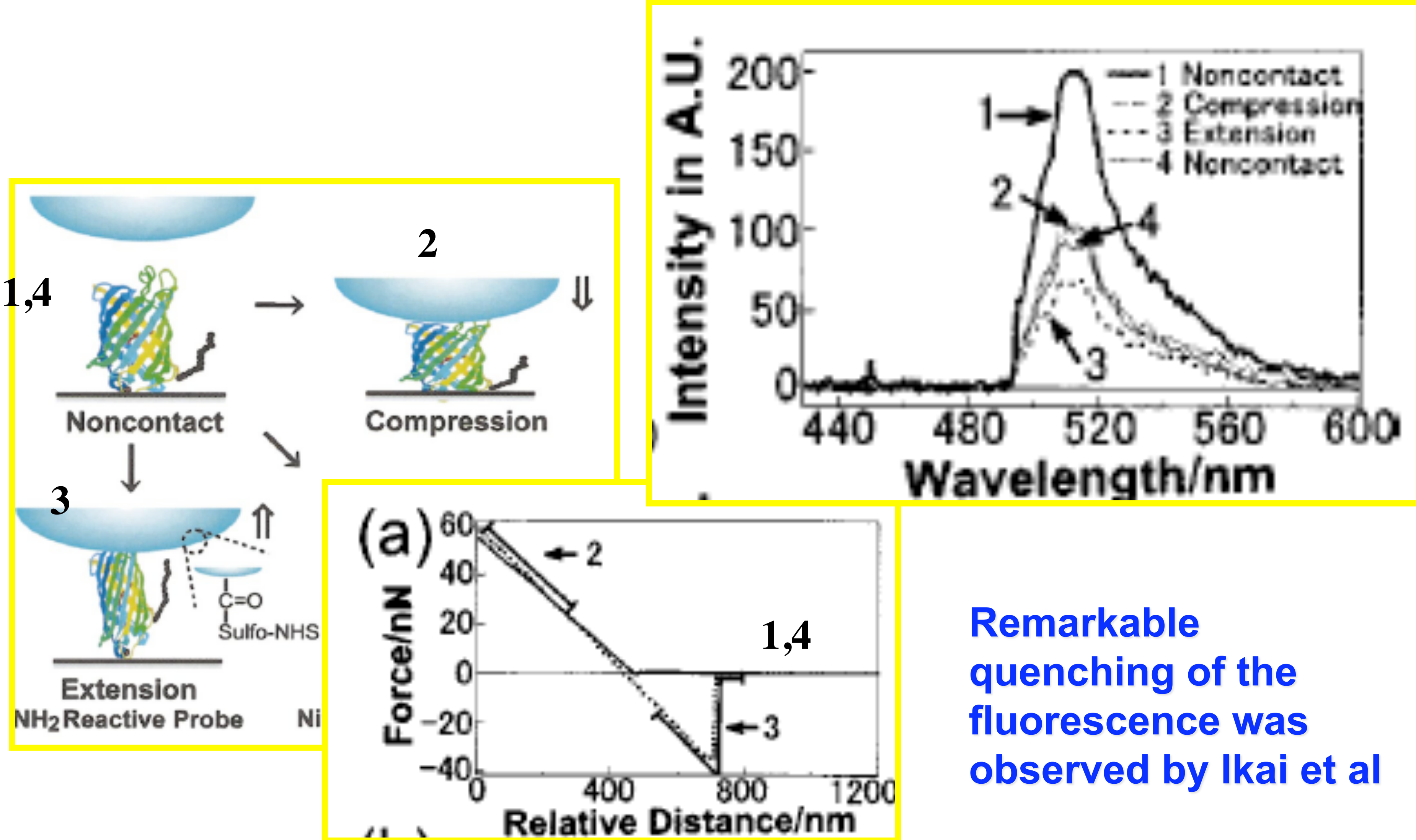
Tip velocity is 0.125A/ps
(Steered MD, T=0K)

Force is calculated by MD with Langevin method



Large force at the instance of the penetration

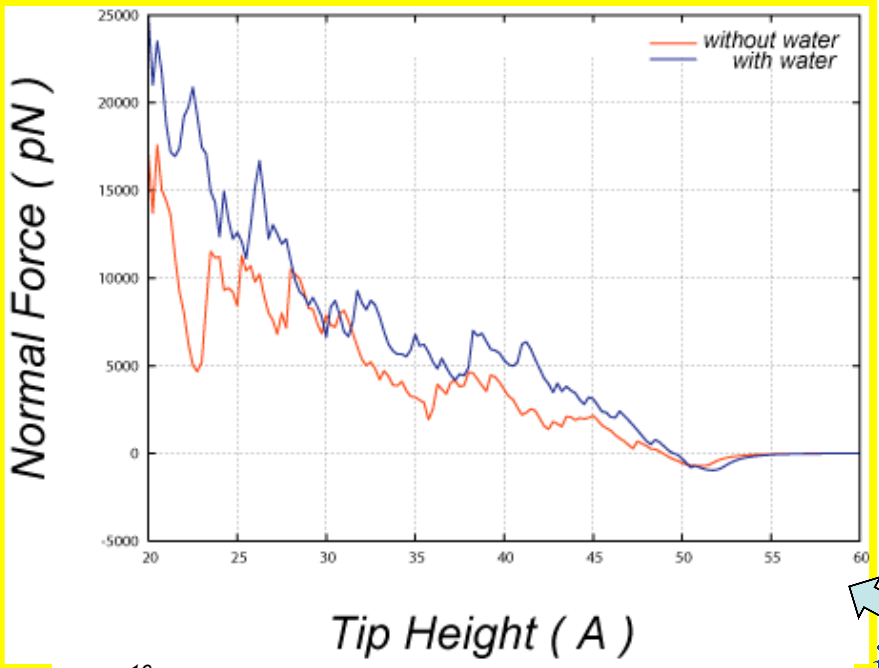
The effect of compression/elongations on the fluorescence of GFP



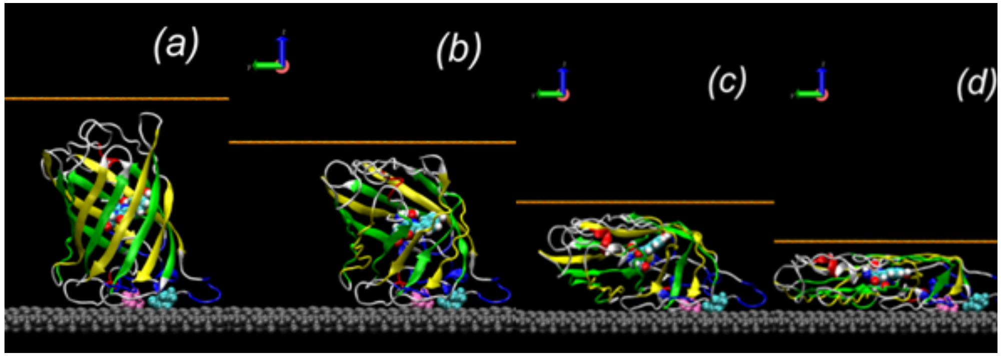
Remarkable quenching of the fluorescence was observed by Ikai et al

T。Kodama, H.Ohtani and A.Ikai, Appl. Phys. Lett. 86 043901(2005)

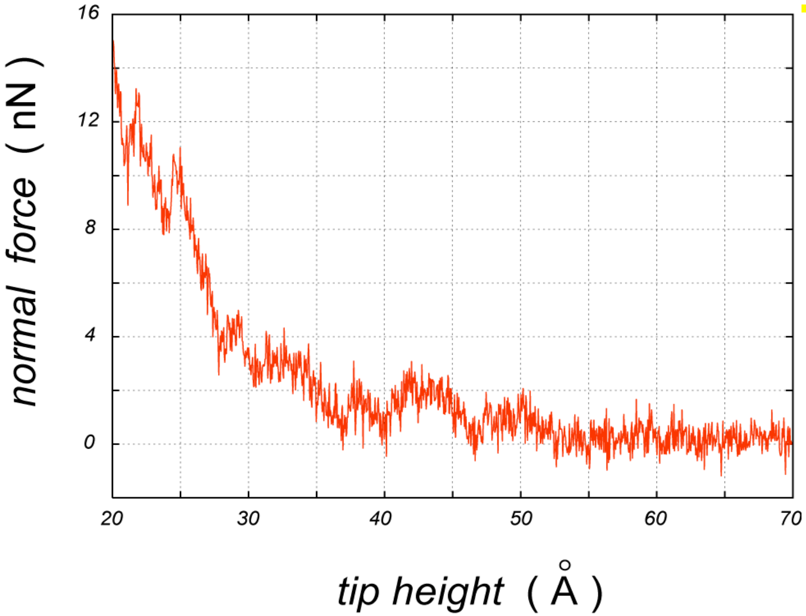
Simulation of compression of GFP by a flat tip



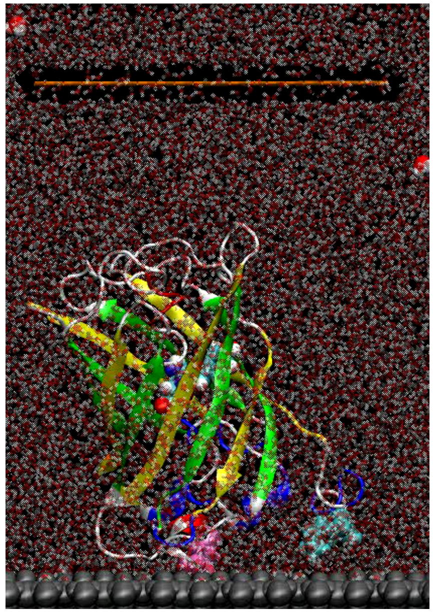
- Tip model ; graphite   substrate :mica
- At each height, structure and the force are
- Calculated by CG and MD method



in vacuum



in water

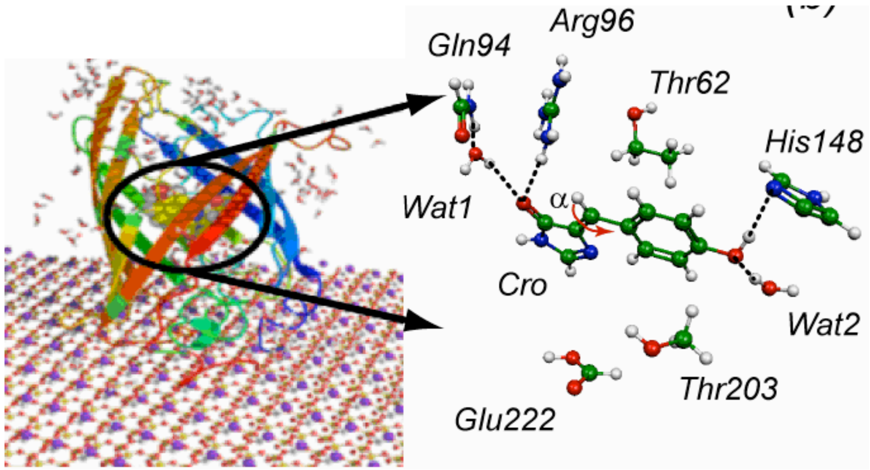


What happens at Compression of GFP

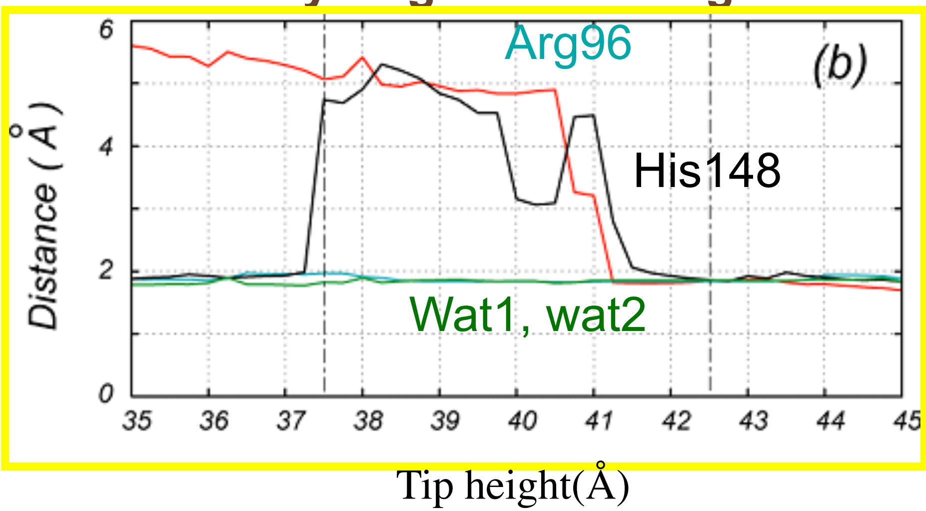
Vertical excitation energy:
calculated 455nm
(observed:465nm)

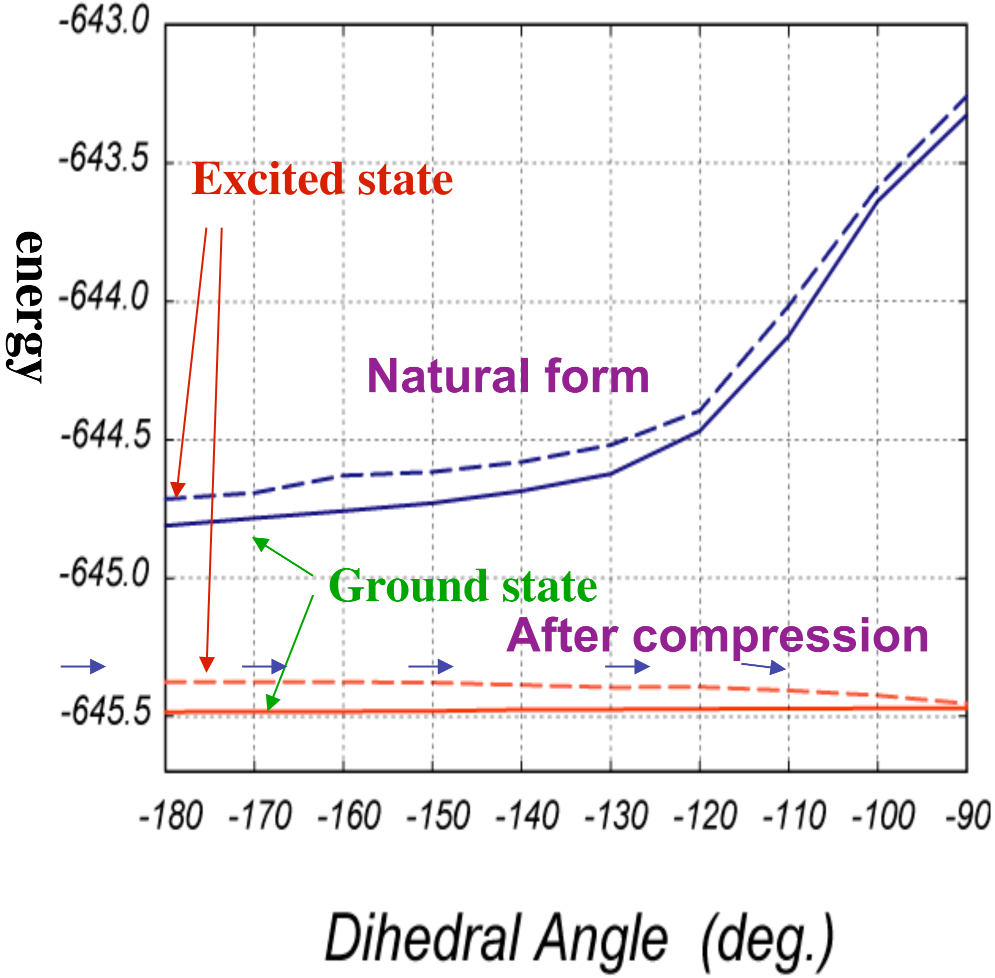
On the comprssion Barrier of the Rotation dissappears

➡ **Non-radiative processes**



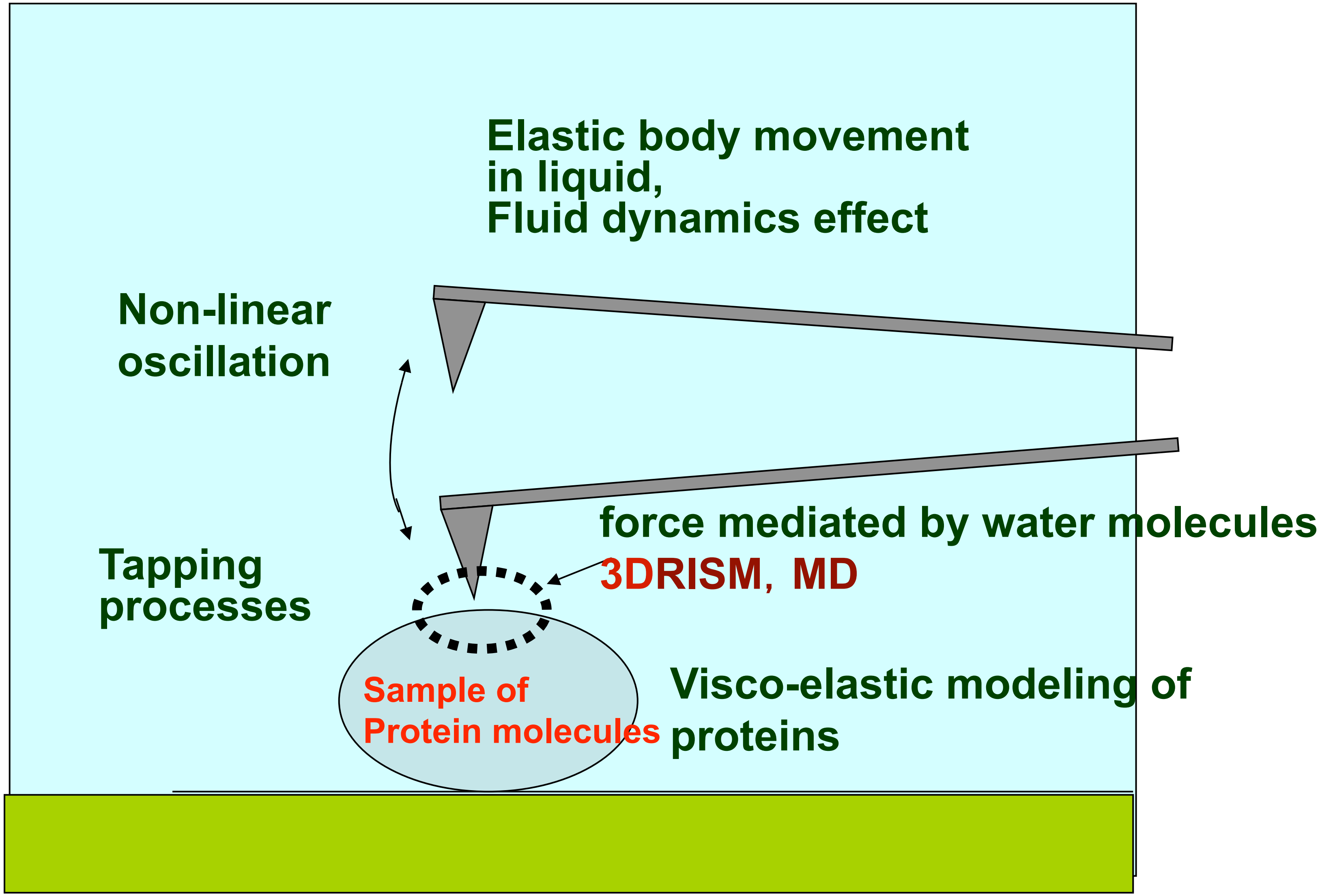
Hydrogen bond length





Theory of dynamic AFM in liquids

Problems of the simulation methods for the tapping mode AFM in liquids

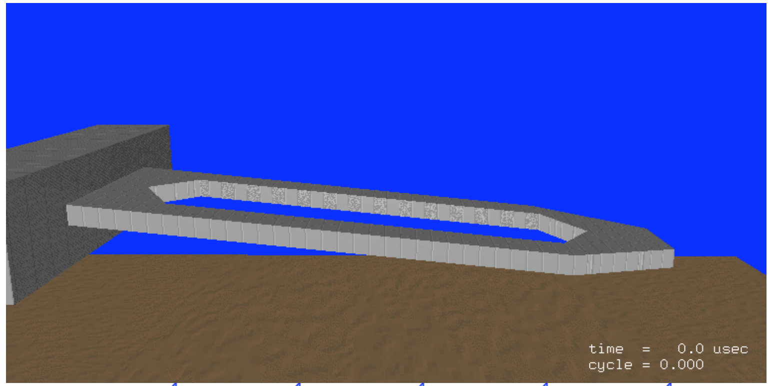


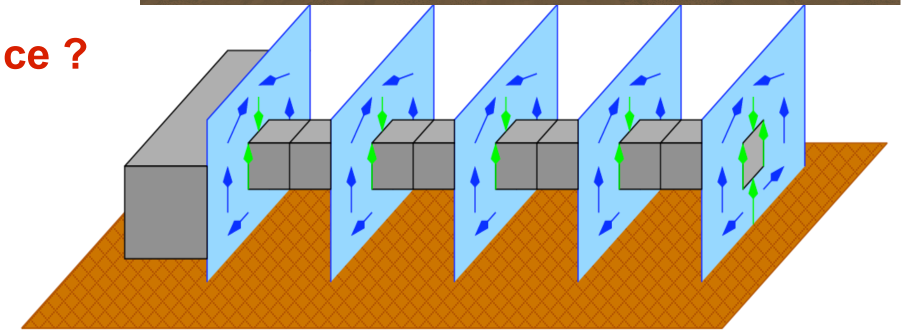
A simplified model of 3D elastic-body/fluid combined system

1)Resonant Curve?

2)Nonlinear Effect?

3)Effect of the tip substrate distance ?





Cantilever:
1D elastic beam

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

E; Young's modulus
I; moment of the cross section

Water:
2D incompressible viscous fluid for each 2D cross section

Navier-Stokes equation

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

Re; Reynolds number

Method for fluid dynamics on 2D

Flow function $\Psi \Longrightarrow v_x = +\dfrac{\partial \psi}{\partial y} \quad v_y = -\dfrac{\partial \psi}{\partial x}$

vorticity $\omega \Longrightarrow \omega = \partial_x v_y - \partial_y v_x \Rightarrow \dfrac{\partial^2 \psi}{\partial x^2} + \dfrac{\partial^2 \psi}{\partial y^2} = -\omega$

From Navier-Stokes eq. $\dfrac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \vec{\nabla})\mathbf{v} = -\vec{\nabla} P + \dfrac{1}{\mathrm{Re}} \Delta \mathbf{v}$

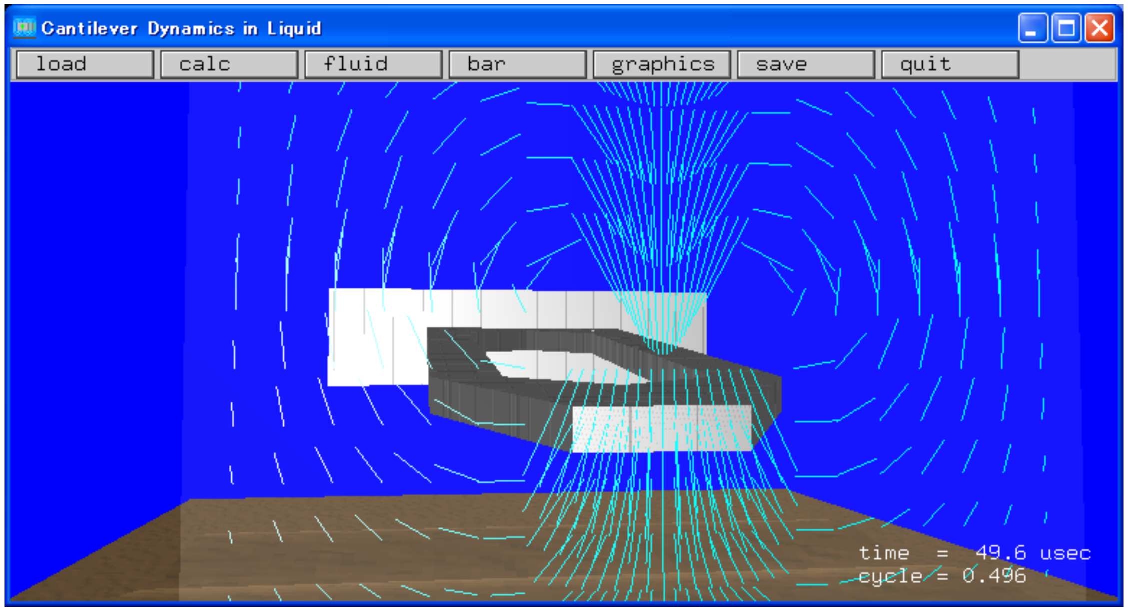
$$\frac{\partial \omega}{\partial t} = \left[\frac{\partial \psi}{\partial x}\frac{\partial \omega}{\partial y} - \frac{\partial \psi}{\partial y}\frac{\partial \omega}{\partial x} \right] + \frac{1}{\mathrm{Re}} \left[\frac{\partial^2 \omega}{\partial x^2} + \frac{\partial^2 \omega}{\partial y^2} \right]$$

negligible

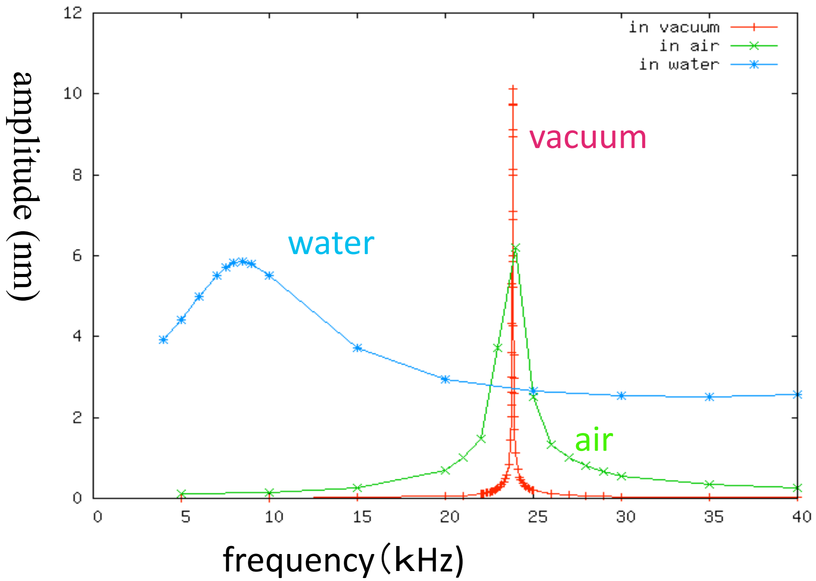
ω Is solved by FEM

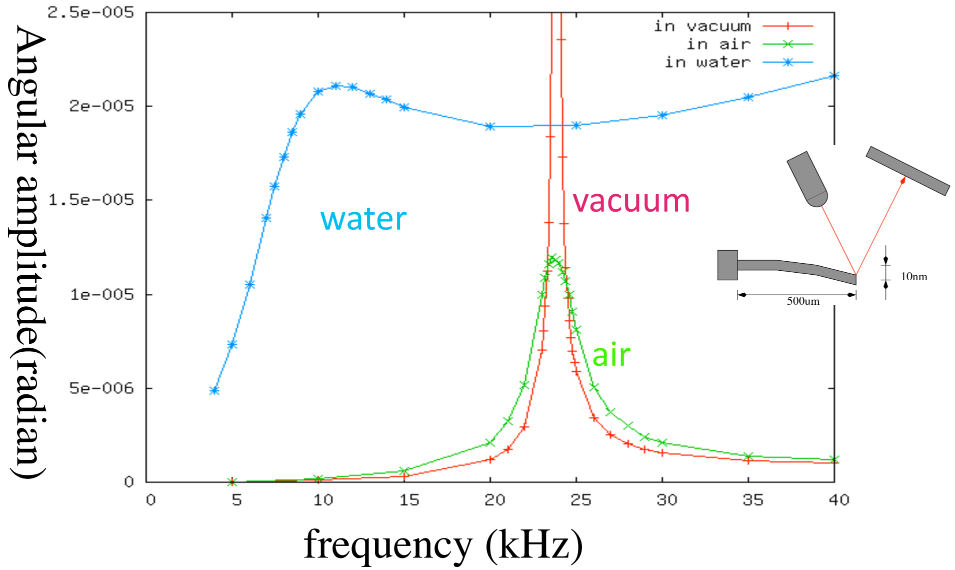
Force felt by cantilever is
Given by

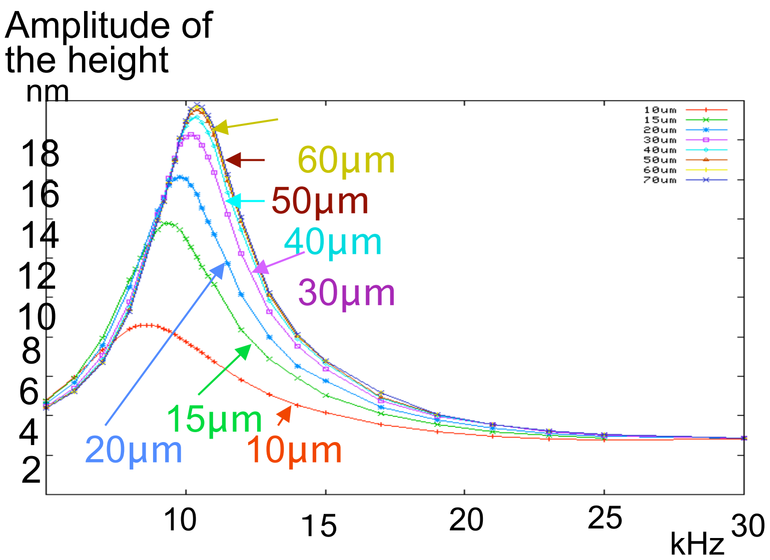
$$F_s = \oint \left(P + \frac{\omega}{\mathrm{Re}} \right) dl$$

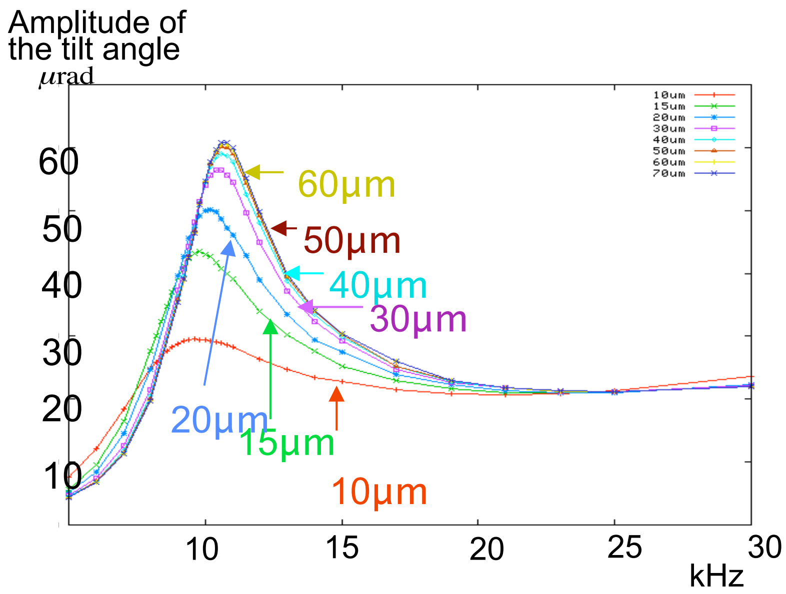


Calculation methods of the cantilever motion in liquids



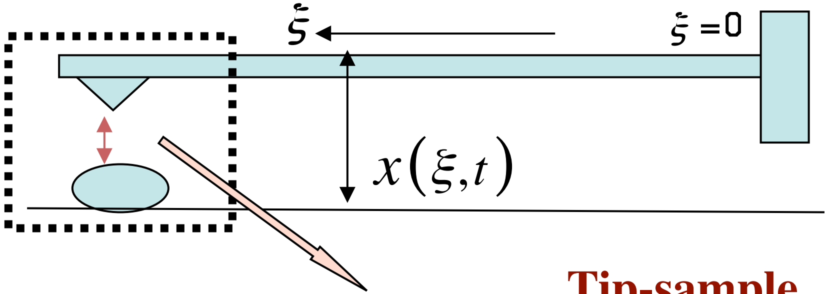






Simulation of tapping mode AFM in liquid

$$x(\xi,t) \cong \sum_n x_n(t)\phi_n(\xi)$$



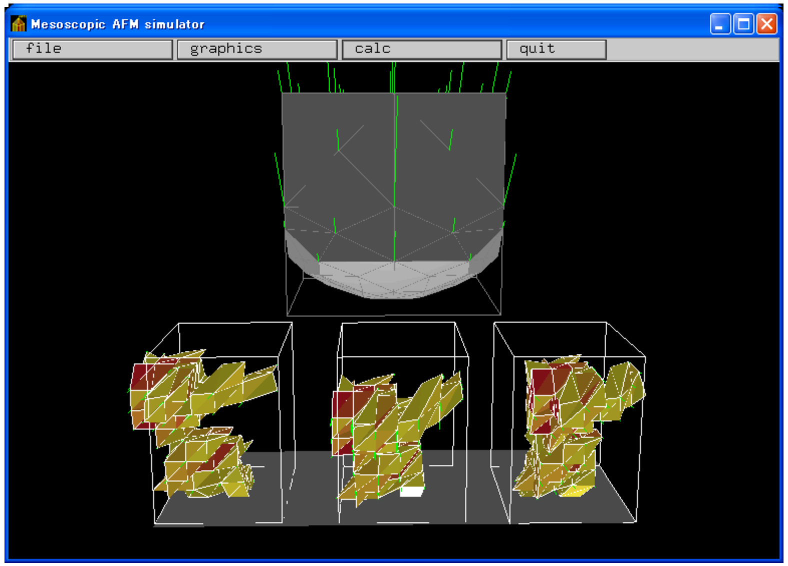
Projecting onto a certain mode

$$(1+\kappa)\frac{d^2x}{dt^2} + (\tilde{\gamma} + \gamma_{liq} + \gamma_{diss})\frac{dx}{dt} + \omega_0^2 x = F_{driv}(t) + F_{TS}(x)$$

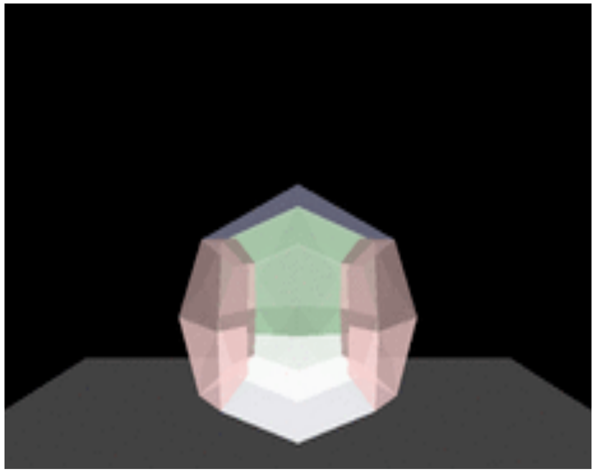
Tip-sample force

Coarse graining of protein molecules

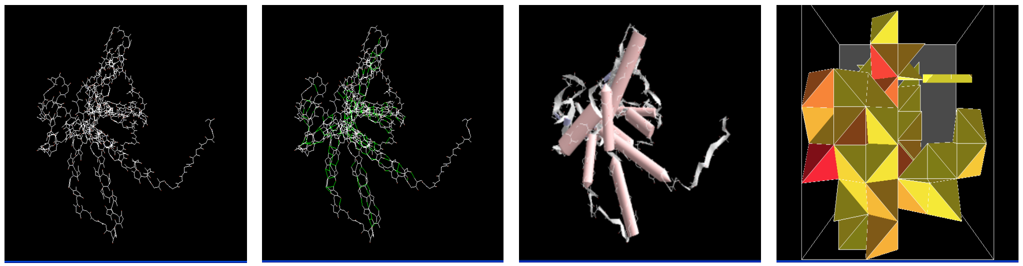
Visco-elastic model



Coarse graining of the sample

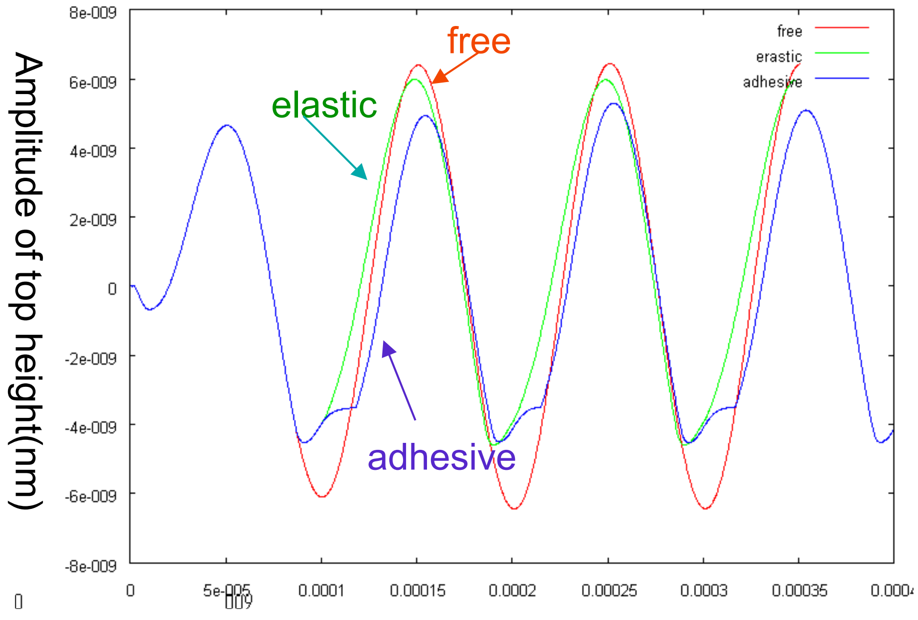


Tapping process

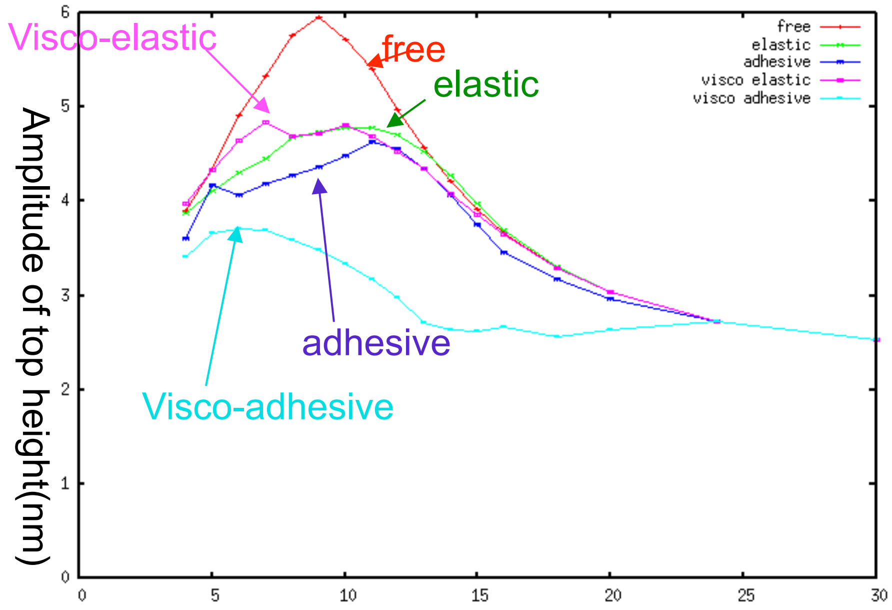


Analyses of cantilever oscillation in the tapping mode AFM in water

Height of the cantilever top



Resonant curves for various collisions

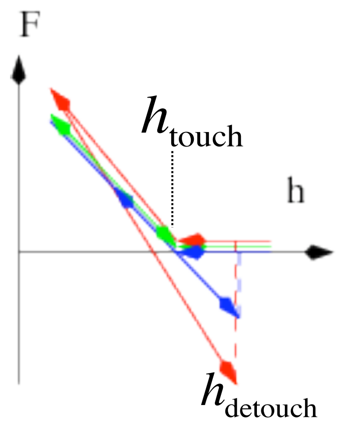


elastic $f(h) = -k(h-h_{touch}) \quad h < h_{touch}$

adhesive $f(h) = -k(h-h_{touch}) \quad \begin{cases} h < h_{touch} \\ h < h_{detach} \end{cases}$

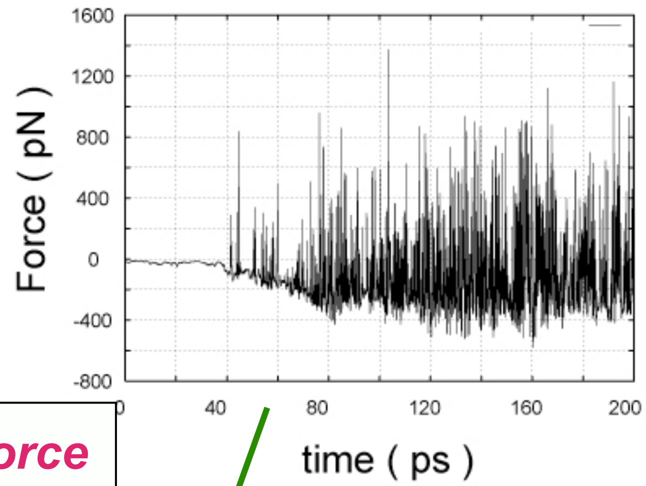
Visco-elastic $f(h) = -k(h-h_{touch}) - \gamma v \quad h < h_{touch}$

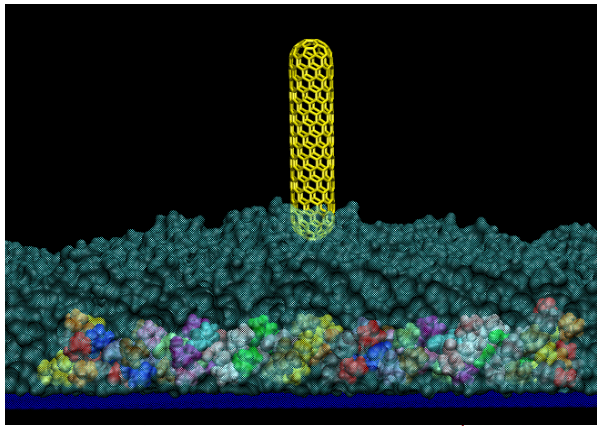
Visco-adhesive $f(h) = -k(h-h_{touch}) - \gamma v \quad \begin{cases} h < h_{touch} & v < 0 \\ h < h_{detach} & v > 0 \end{cases}$

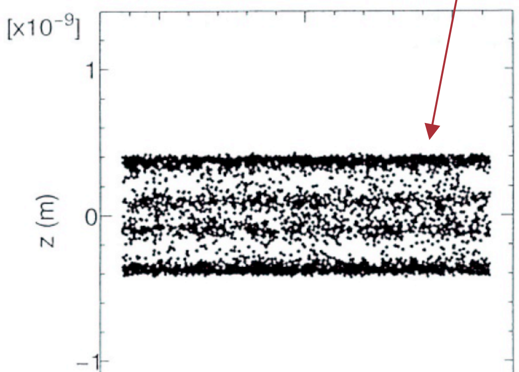


Tip-sample interaction force
Mediated by water

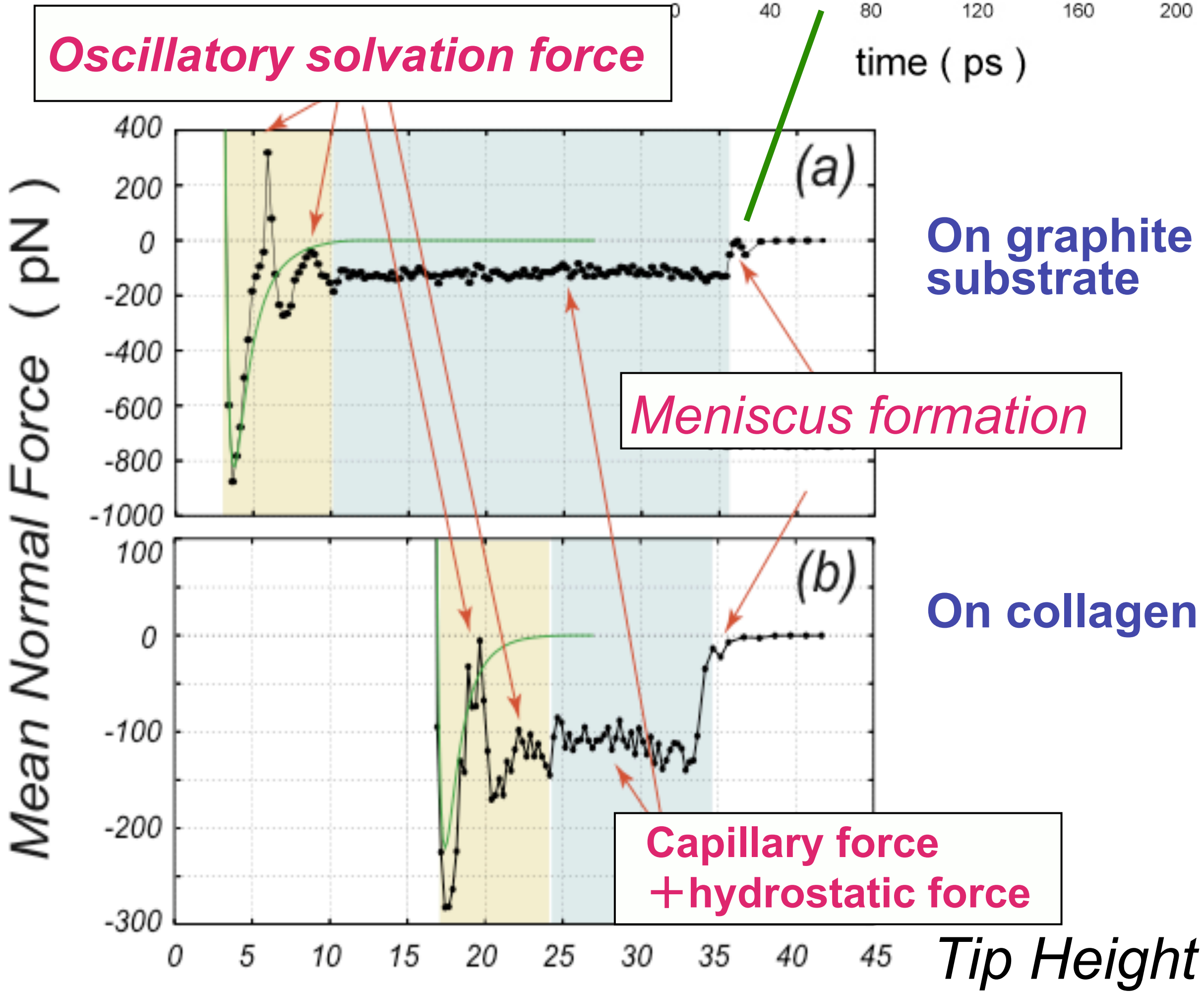
AFM simulation by MD in liquids







Oscillatory solvation structure of water



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

Simulation of nc-AFM of mica in water-classical MD method

MD condition

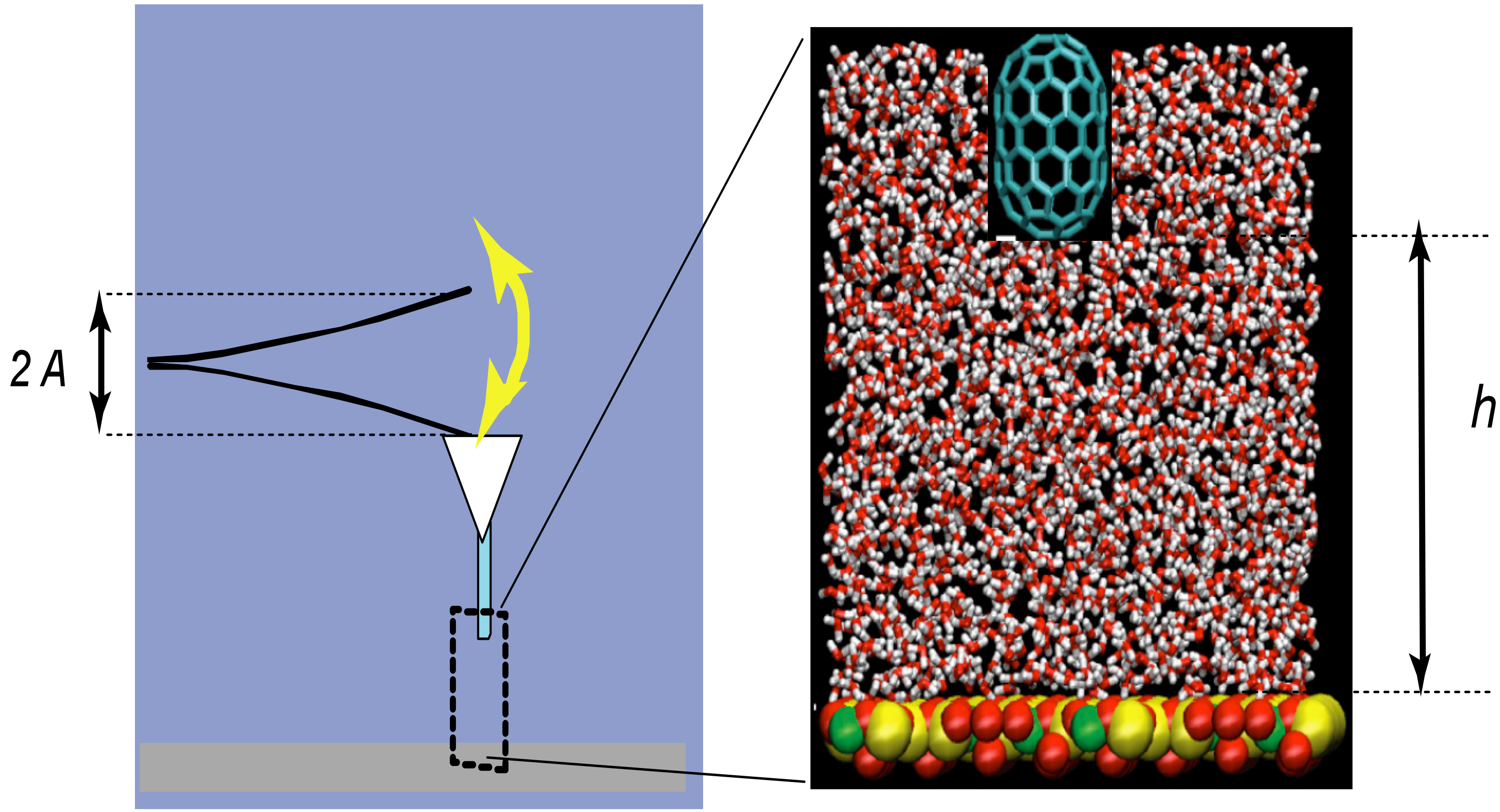
Size of mica surface： 36A×42A
Tip model： (10,0)CNT
Potential of water molecules： TIP3P
Total numer of atoms： 6,338

Force field: ***CHARMM 22 + CLAY (modified)***

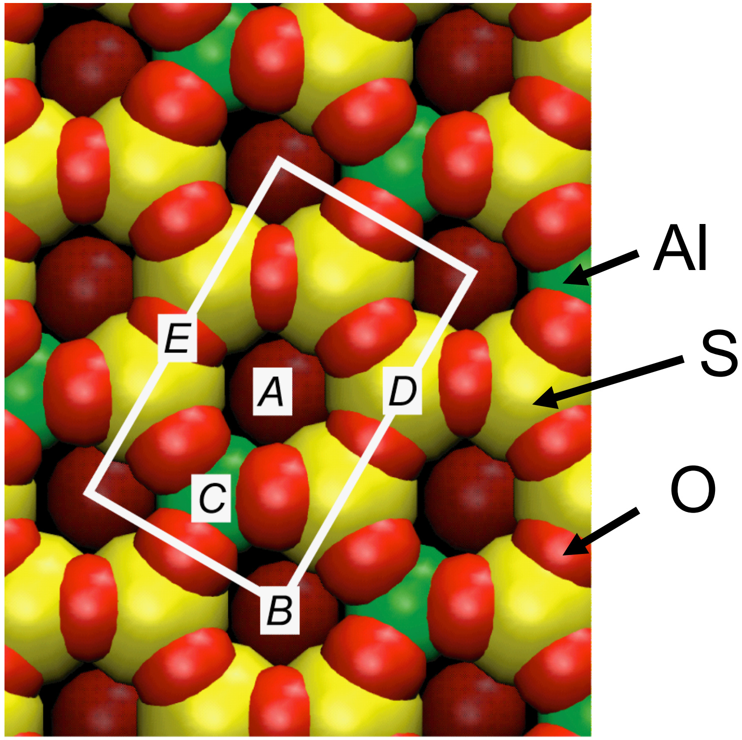
Program: ***NAMD2.5 and 2.6***

Temperature: ***300 K***

Time mesh***: 2fs***

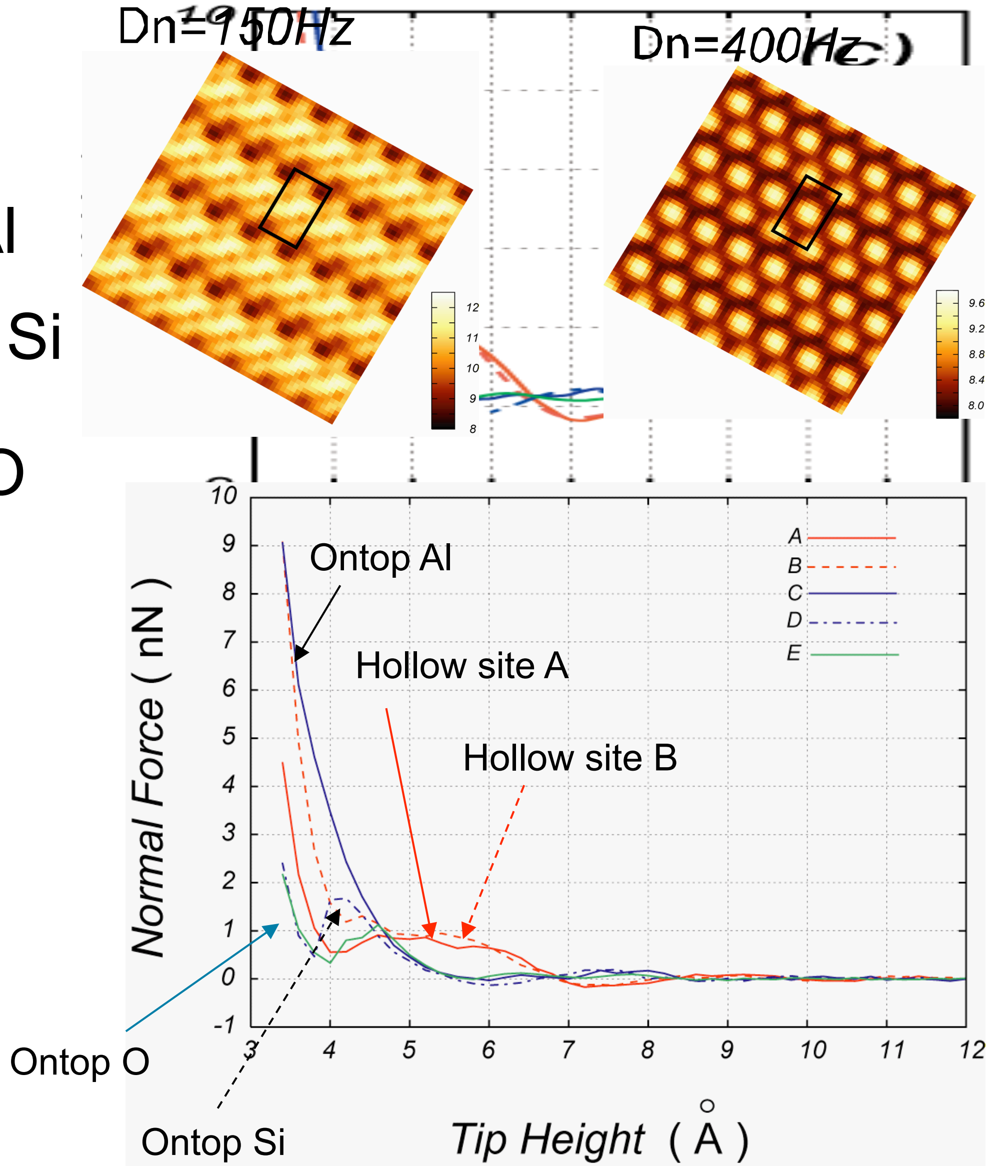


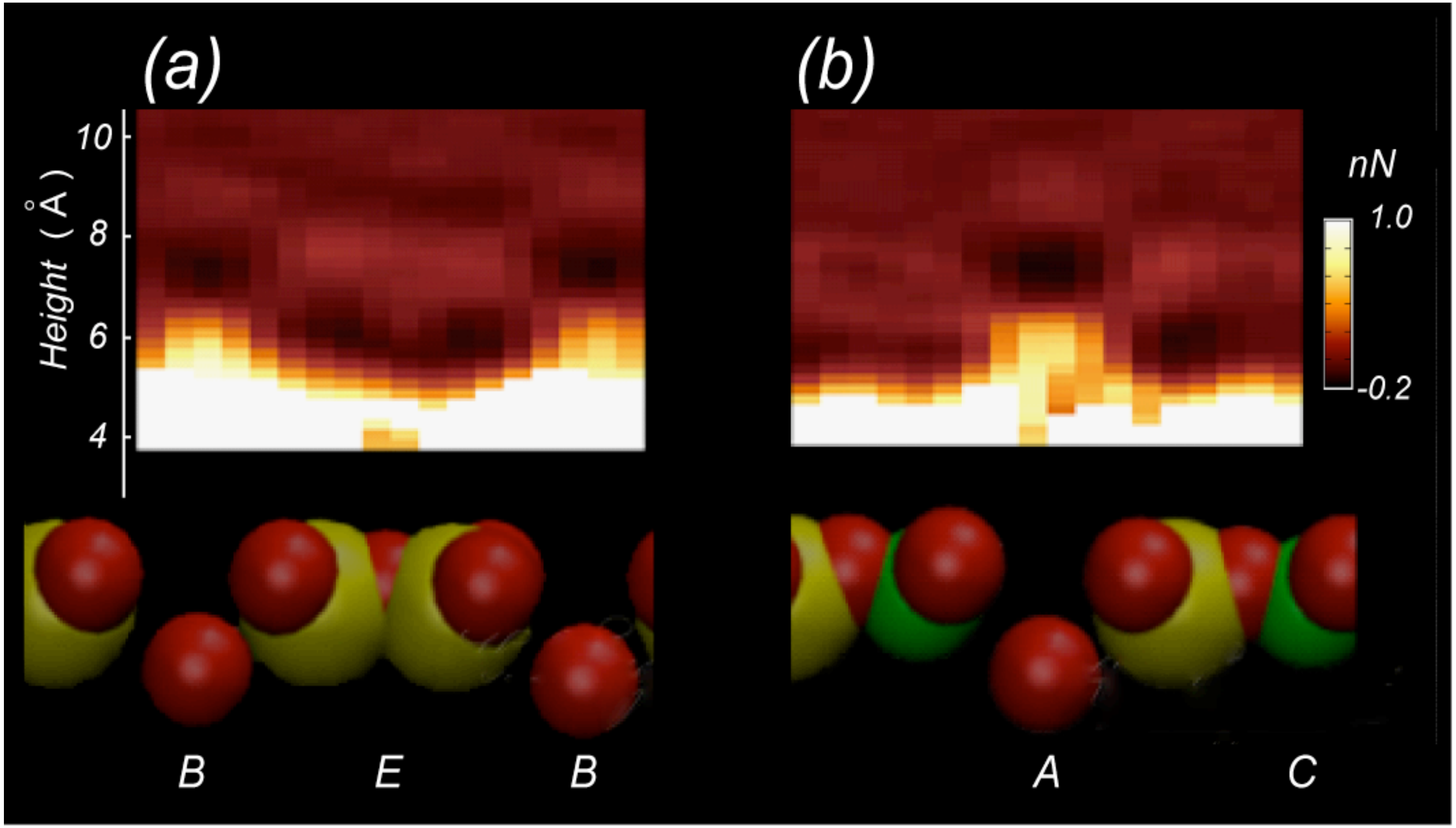
Simulated dynamic AFM image of mica in water

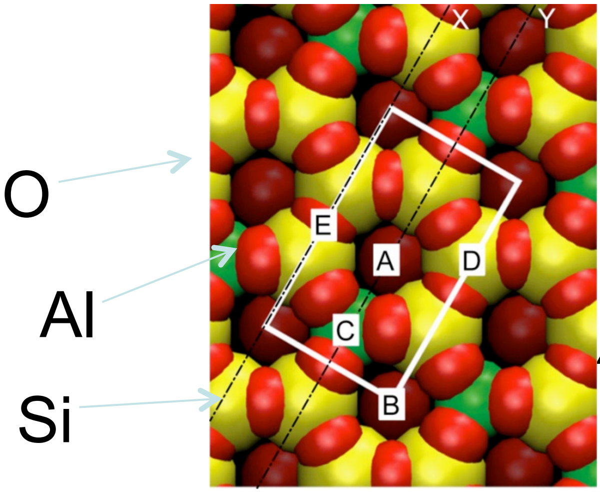


Mica surface in water

A, B: ontop of hollow site
C: ontop of Al atom
D: ontop of Si atom
E: ontop of O atom





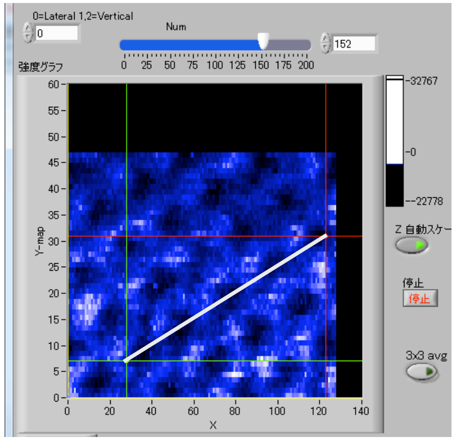


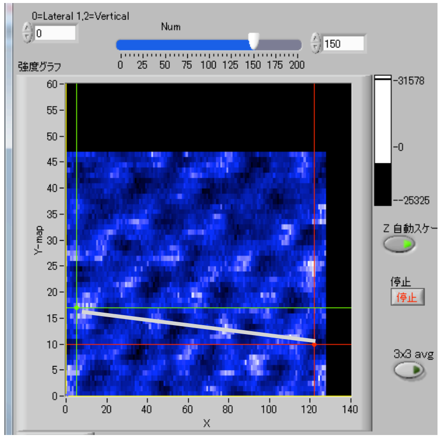
Cross section of 3D force map of mica surface in water (SWNT tip)

A, B: ontop of hollow site C: ontop of Al atom
D: ontop of Si atom E : ontop of O atom

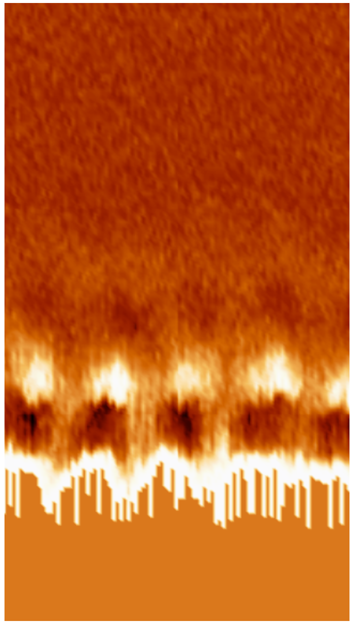
Comparison between the theory and the experiment

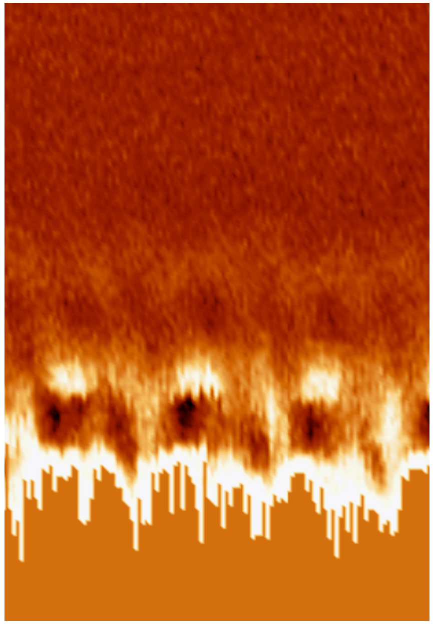
Experiments H.Yamada, et al





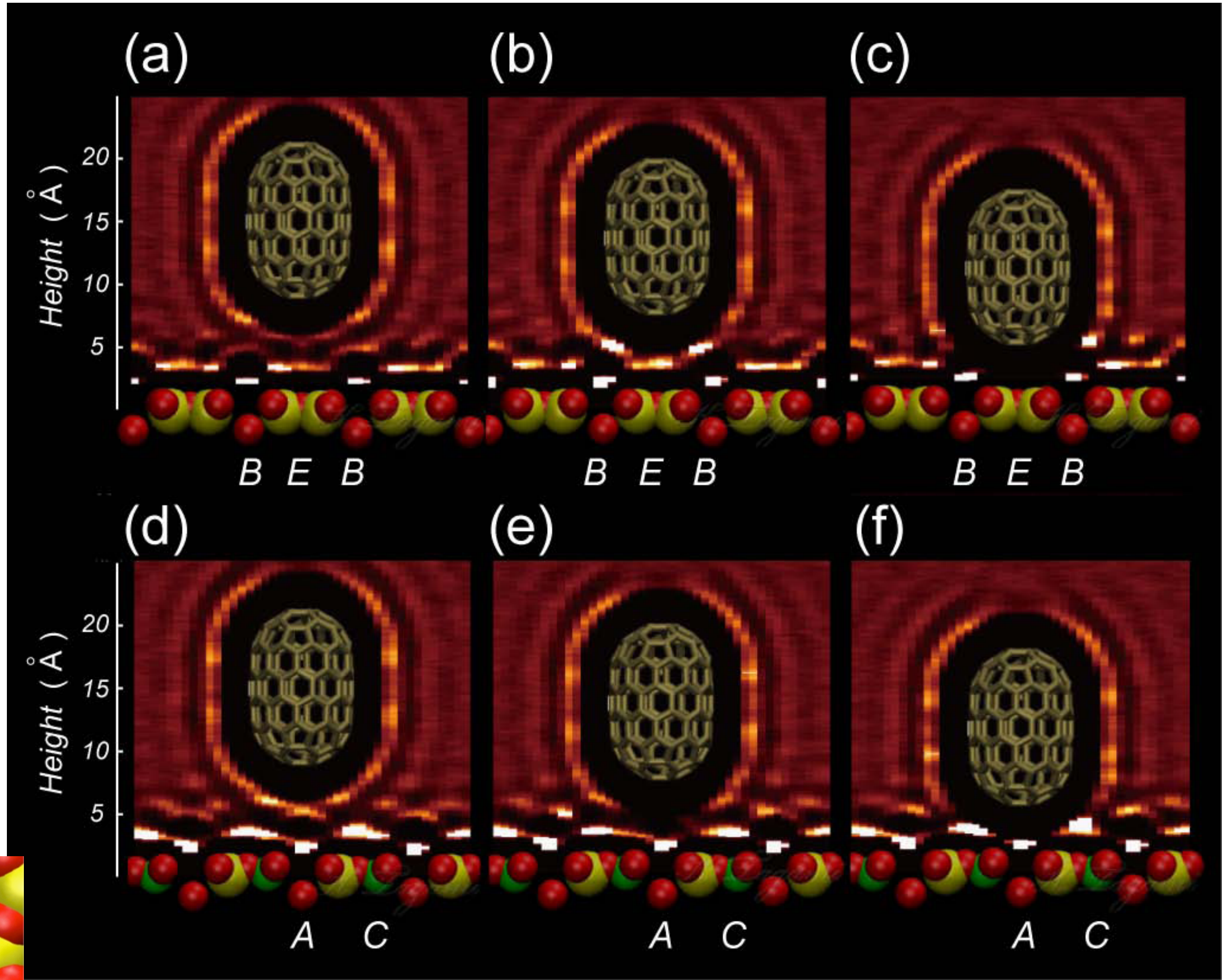
Results of theoretical simulation reproduced fairly well the experimental observation of nc-AFM images of mica surface in water.

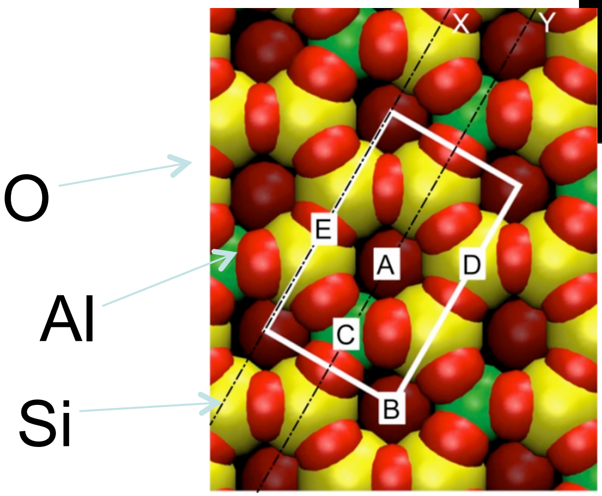




Theoretical Simulation

Distribution function of water molecules





A, B: ontop of hollow site C: ontop of Al atom

D: ontop of Si atom E: ontop of O atom

Summary and outlook

1 Theoretical methods for STM such as
Bardeen's Perturbation theory, NEGF method, RTM are reviewed
are presented. Problems discussed are
Effect of the tip, decorated tip, weak to strong interaction

2 Coherent and Dissipating Tunnelling in the STM systems
are discussed including
tunneling current distribution, features of the coherent
current in the nano-structures, from the coherent to dissipative
tunneling, zero bias anomaly

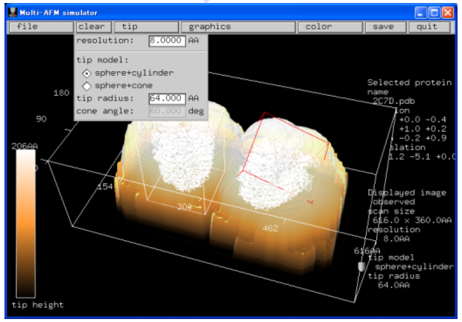
3 Theories of dynamic AFM in vacuum and in water are presented as
derivation of the harmonic oscillator model,
dissipation image, tip effects, cantilever oscillation,
oscillatory hydration force, force mediated by water

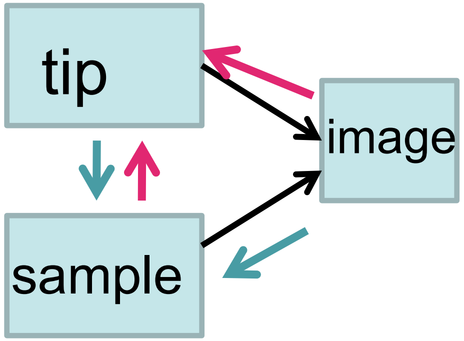
4 Simulations of Nano-mechanics of protein molecules

SPM Simulator Project

1.Rapid AFM simulator for tip･sample･image

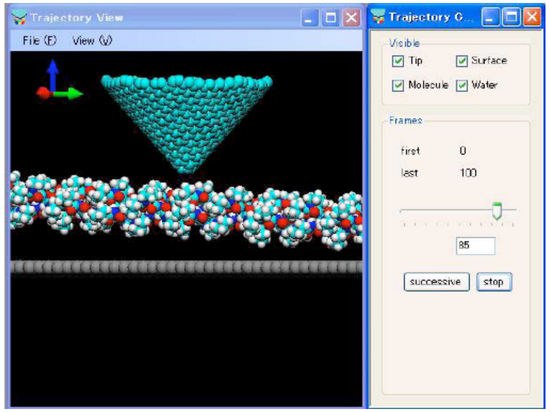
Utilizing the geometrical relation reinforced by the continuum mechanics





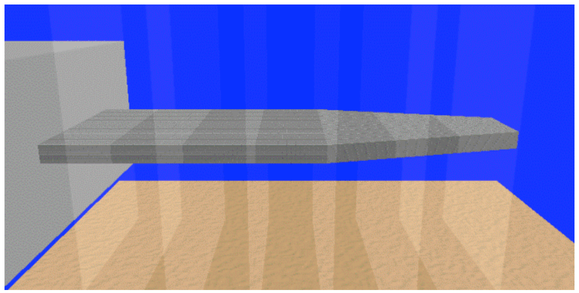
3. AFM image simulator for atoms/molecules/ nanostructures

Using classical MD
Molecular field
3D-RISM



2. AFM simulator for soft materials in liquids

Cantilever oscillation in liquids
Analyses of AFM for visco-elastic sample models



4. Quantum mechanical AFM/STM /KFM simulator

Using DFT, DFTB, DVXα method