液中AFMおよび接触過程の理論シミュレーション

Theoretical simulation of the contact mechanics for AFM in liquid

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ΣAAS 科学技術振興機構**研究成果展開**事業
【先端計測分析技術・機器開発】
「走査プローブ顕微鏡シミュレータ」

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学振ナノプローブ167委員会　第67研究会
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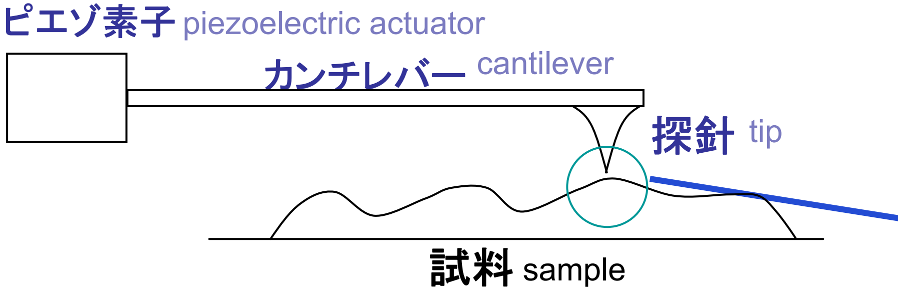
outline

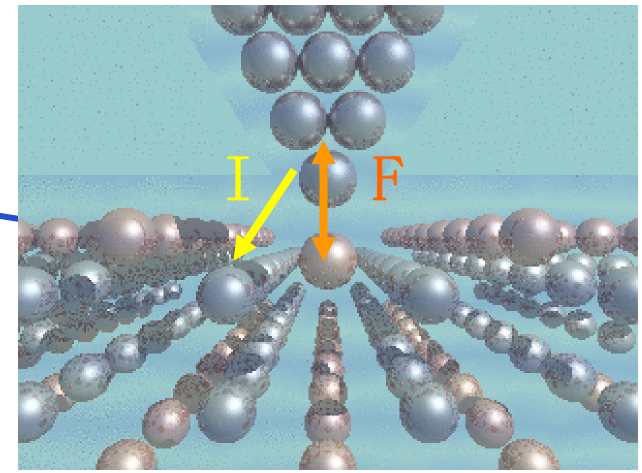
1. はじめに
   Introduction
2. SPM シミュレータの紹介
   比較型シミュレータ, 他
   Introduction of the SPM simulator
   A solver for comparing experimental and simulation results, and others
3. 液中におけるカンチレバー振動
   Vibration of cantilever in liquid
4. 水分子に媒介される探針ー試料間力
   Interactive force between the tip and the sample affected by solvent molecules
5. 接触問題
   Viscoelastic contact problem
6. 終わりに
   Concluding remarks

走査プローブ顕微鏡の理論

The theory of the scanning probe microscopy

STM/STS, AFM
KPFM, SNOM,….





What and how
Does SPM see the sample？

Why can the macro equipment obtain the information about each individual atom?

個々の原子レベルの情報が
マクロな装置でなぜ読み取れる？

ミクロな力と変位? The microscopic force and the displacement?
揺らぎと温度効果 The fluctuations and the thermal effects
量子効果? The quantum effect?
液中計測の機構？ The observation mechanism in liquid?

ナノ構造の生成と制御
Generation and control of the nanostructure

量子現象の観察と機能発現
Observation of quantum phenomena and emergency of functions

探針の原子構造・原子種の効果? The effect of the strucuture and the atomic species of the tip?

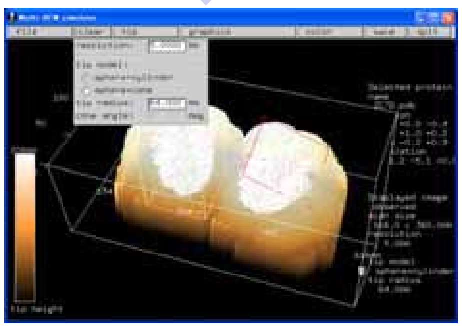
SPMシミュレーター
SPM simulator

科学技術振興機構研究成果展開事業
【先端計測分析技術・機器開発】
「走査プローブ顕微鏡シミュレータ」2004~2007, 2009~2011

1.Rapid AFM simulator for tip/sample/image

1A.Geometrical Mutual AFM Simulator (GeoAFM)
Rapid image estimation by the geometrical method

1B.Finite Element Method AFM simulator (FemAFM)
Complement GeoAFM by numerical calculations of finite element method

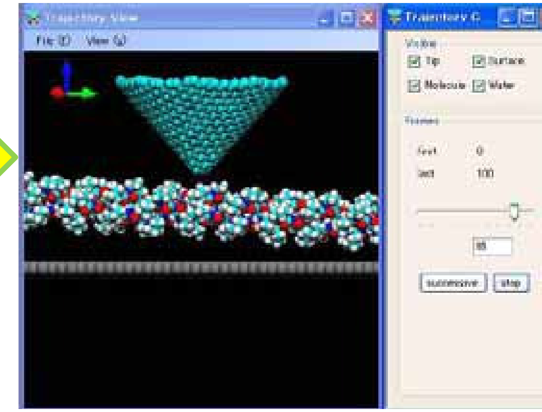


3. AFM image simulator for atoms/molecules/nanostructures

3A. Geometry Optimizing AFM Image Simulator
(classical force field method, Molecular Mechanics)

3B. Molecular Dynamics AFM Image Simulator
(the classical molecular dynamics)

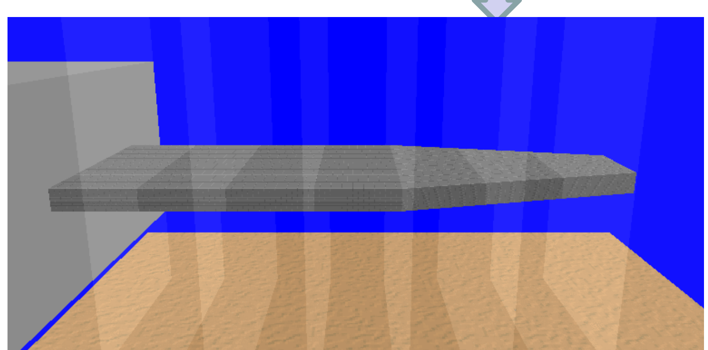
（古典分子動力学法）



2 液中ソフトマテリアル

2. Soft Material Liquid AFM Simulator (LiqAFM)
Oscillation analysis of cantilever in liquid,
AFM analysis of the visco-elastic sample,
High-speed mode AFM analysis
Analysis of the multiple-frequency excitation
Numerical calculation of the cantilever's elastic deformation and the fluid resistance using the mesh

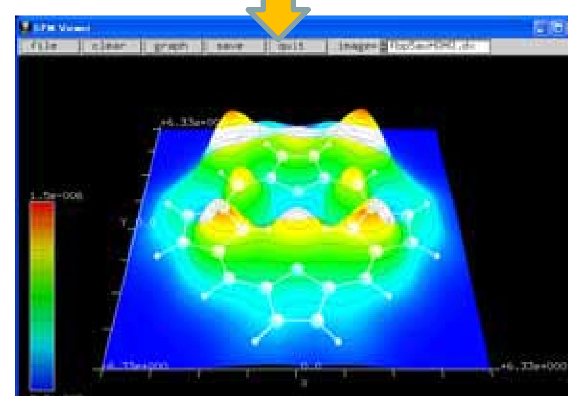
流体抵抗力のメッシュによる
数値計算



4 量子論的

4. Quantum mechanical AFM/STM/KPFM Simulator
High-precision image estimation by Quantum mechanics
DFTB method,
PR-DFTB method

DFTB法、
PR-DFTB法



Observed SPM image → Optimal Tip structure guess
Observed SPM image → Optimal Sample structure guess

"Observation-simulation" comparison type simulator

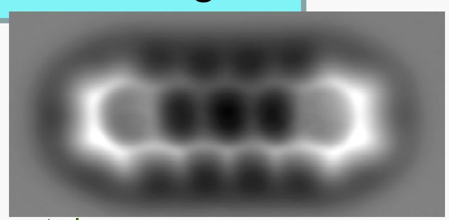
Inverse problem!

Observed SPM image → Optimal tip structure guess

Observed SPM image → Optimal sample structure guess

SPM experiment

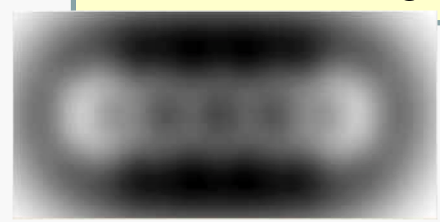
Observed image



L.Gross, et al,
SCIENCE, 325 (2009)1110

Modeling of simulation

Simulated image



Quantitative comparison

by the inner product method

New experiments

Improved models

Model reconstruction
with optimization/neural network approach

AFM images by the geometrical method and the force method

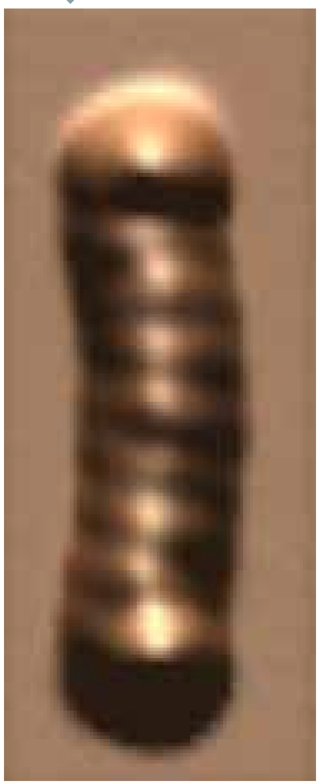
3. AFM image simulator for atoms/molecules/ nanostructures

1. Rapid AFM simulator for tip･sample･image

Calculated by

Interaction force

Geometrical condition

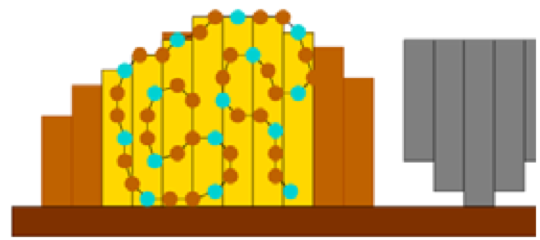


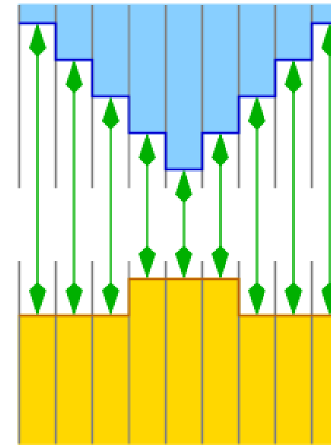
a few hours(WS)

less than 1 sec(PC)

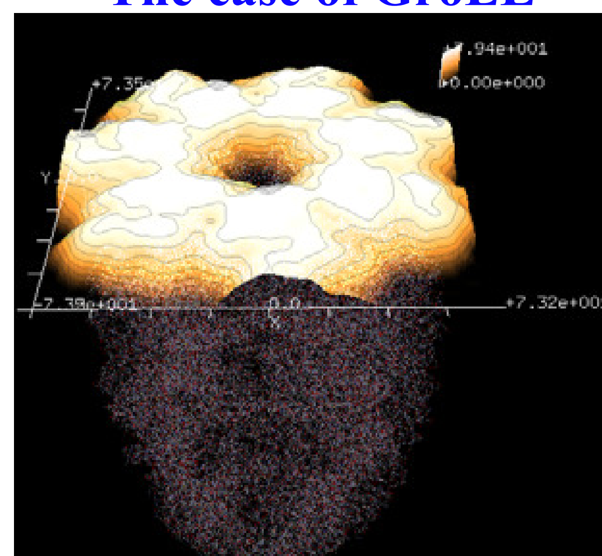
The case of collagen

Using only geometrical condition





The case of GroEL



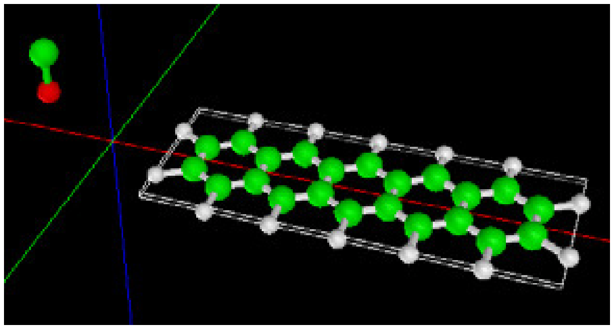
M.Tsukada, K.Tagami, Q.Gao, and N.Watanabe, Current nanoscience 3 (2007) 084005

Applications of the AFM simulator

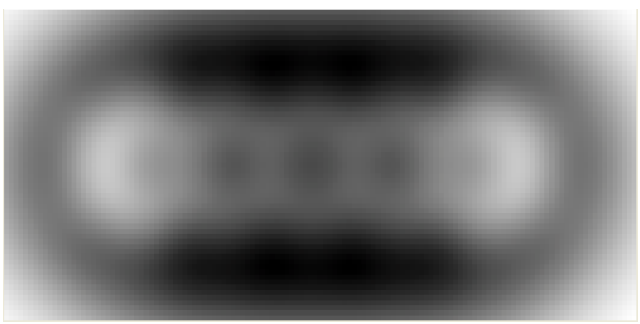
3. AFM image simulator for atoms/molecules/ nanostructures

AFM image of pentacene by a CO tip

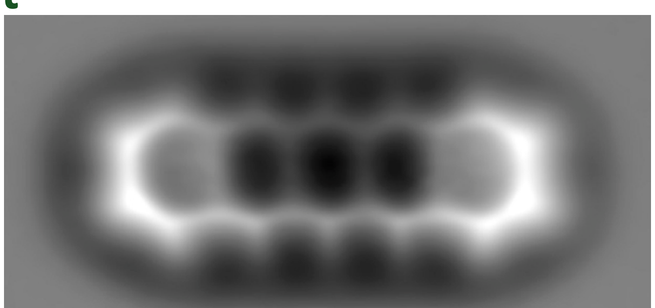
- fixed sample structure
- constant height
- calculation time
  20 min with PC



simulation



experiment



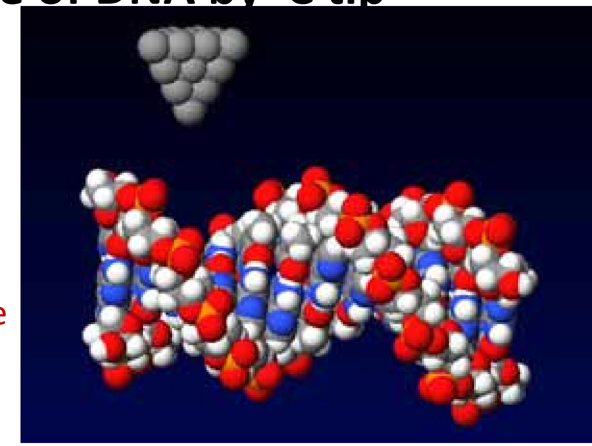
L.Gross, F.Mohn, N.Moll, P.Liljeroth, G.Meyer, SCIENCE, 325 (2009)1110

Using classical force field,

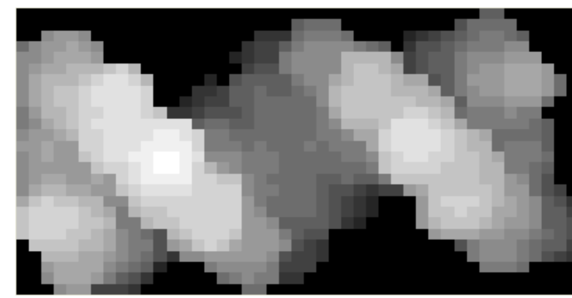
$$\Delta f = rf_0 = -\frac{f_0}{2kA\pi}\int_0^{2\pi} F(A\cos\theta + L)\cos\theta \, d\theta$$

AFM image of DNA by C tip

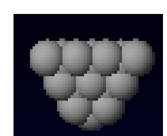
- DNA structure fixed
- constant frequency
- calculation time
  3 hours with PC

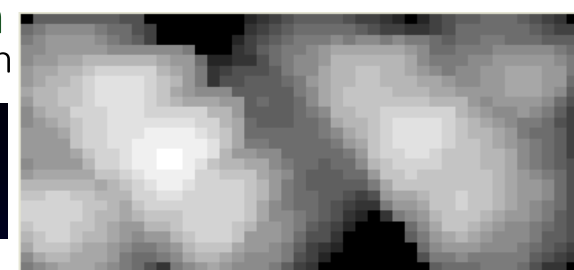


simulation
Tip C 1atom



simulation
Tip C 29 atom



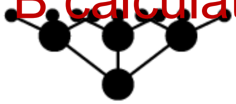


Non-Contact AFM image of methyl group on Si(100)/H

A. Masago et al, Jpn. J. Appl. Phys., 48, 025506 (2009)

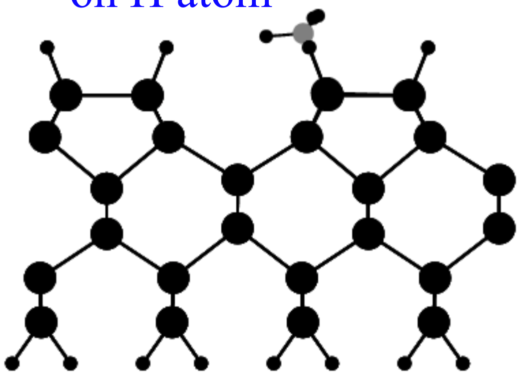
4. Quantum mechanical AFM/ STM /KPFM simulator

DFTB calculations



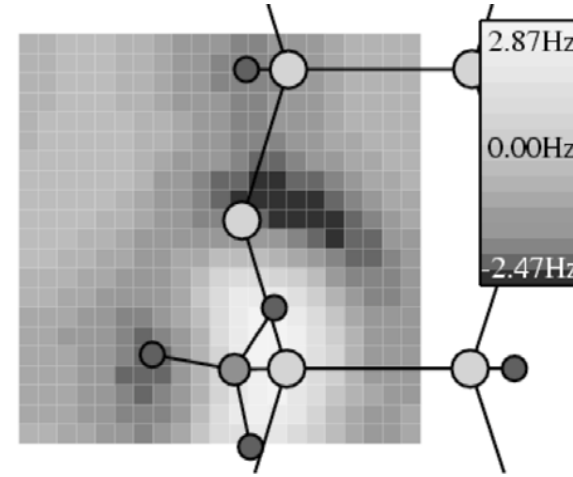
$$\Delta f = -\frac{f_0}{2kA\pi}\int_0^{2\pi} F(A\cos\theta + L)\cos\theta \, d\theta$$

on H atom



Frequency shift image

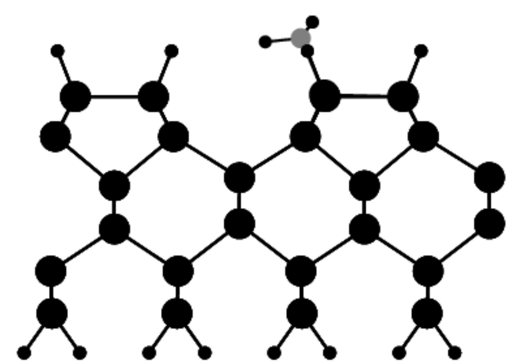
Constant height

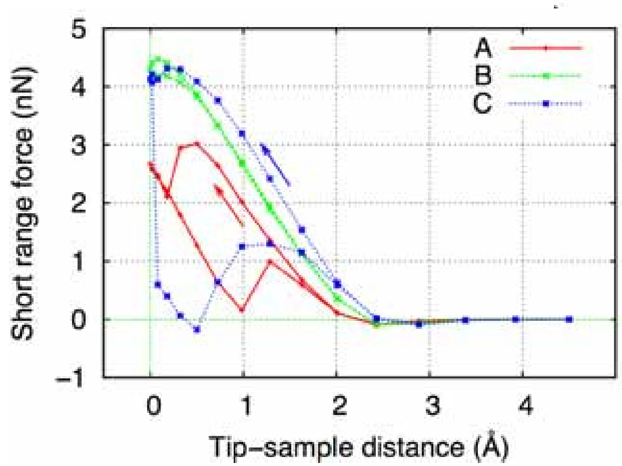


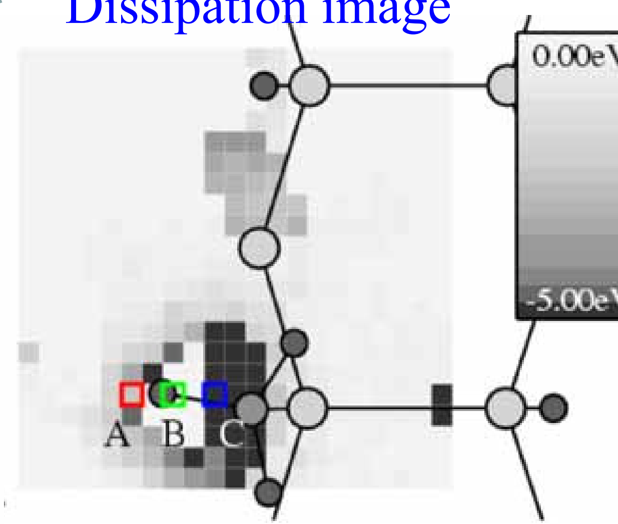
$$h = \frac{1}{\pi\omega_0}\int_0^{2\pi} \gamma(A\cos\theta + L)\sin^2\theta d\theta + \frac{1}{2kA\pi}\int_0^{2\pi} F(A\cos\theta + L)\sin\theta \, d\theta$$

Dissipation image

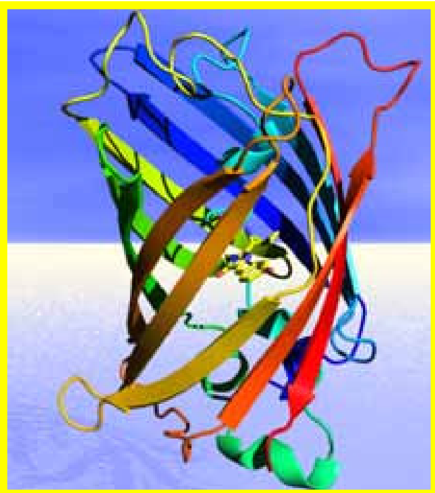
on methyl



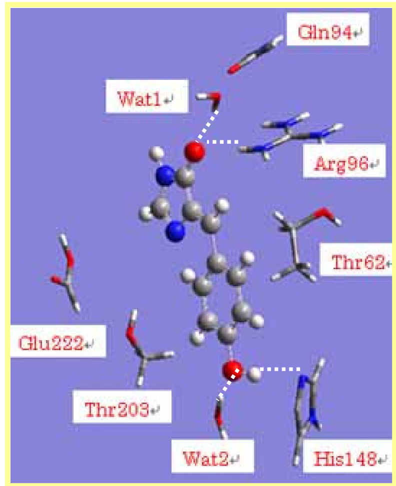




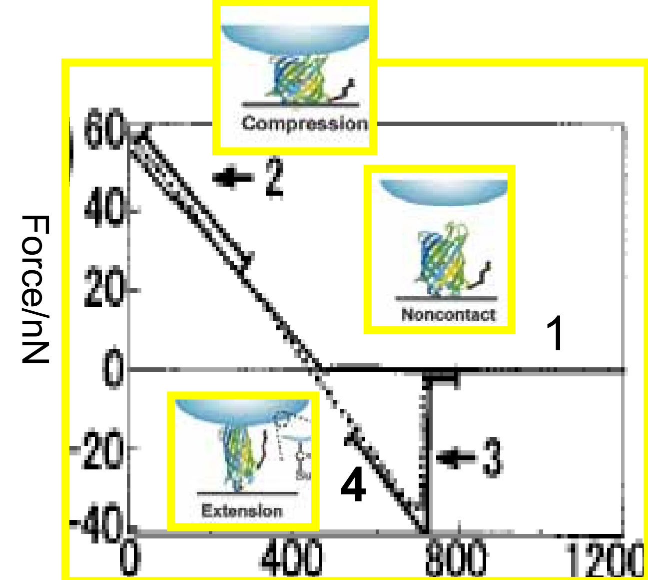
Nano-mechanical experiment on GFP (Green Fluorescent Protein)



Structure by X-ray



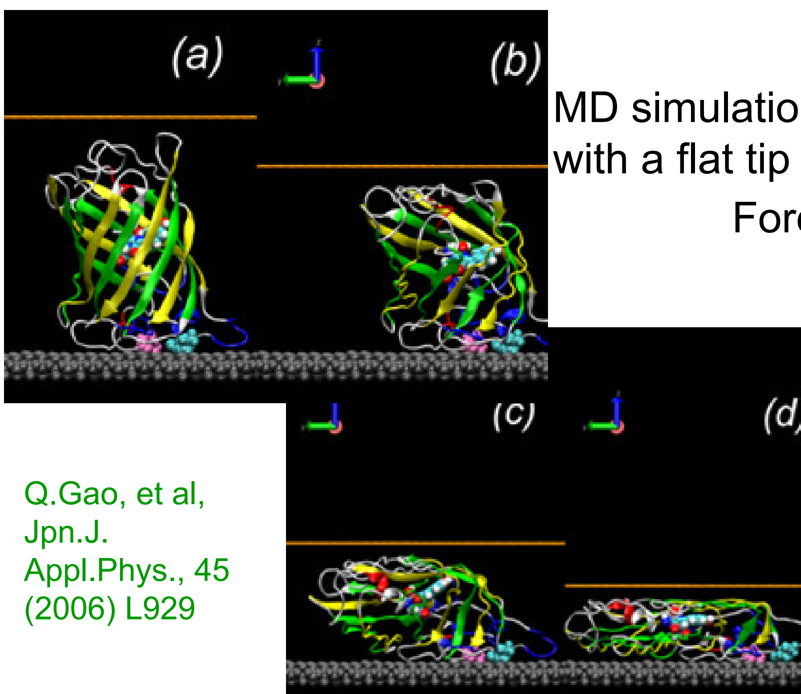
Cromophore



Tip height (nm)

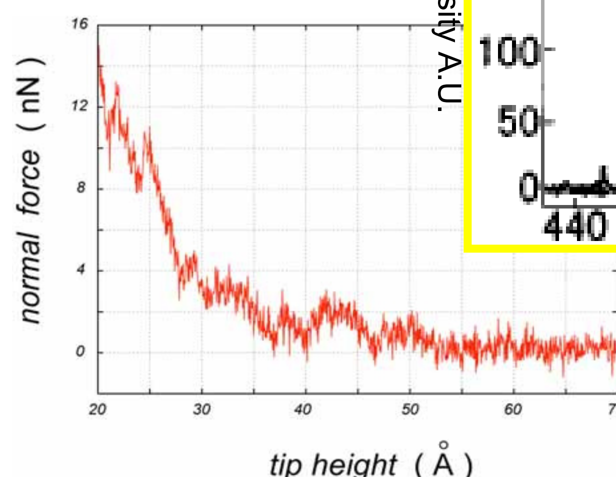
Remarkable quenching of fluorescence

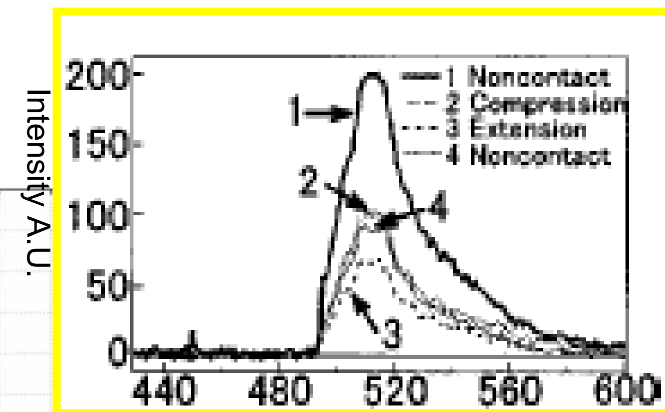
T。Kodama, H.Ohtani and A.Ikai, Appl. Phys. Lett. 86 043901(2005)



MD simulation of compression with a flat tip

Force-distance curve





Wavelength/nm

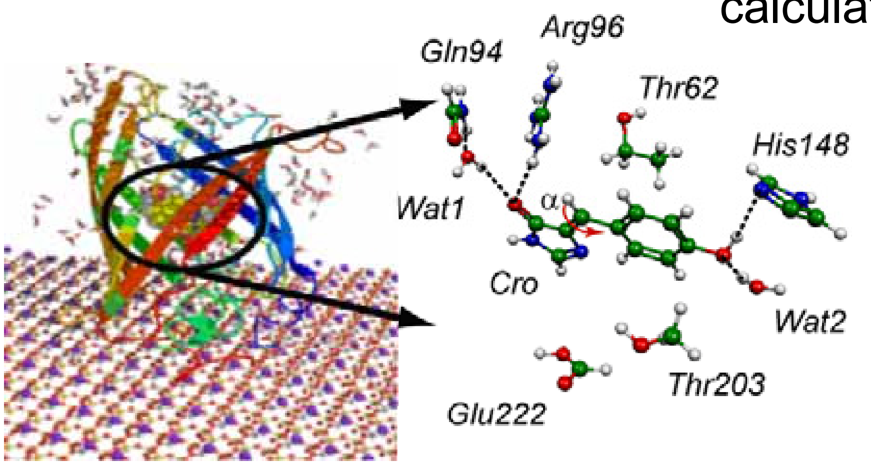
Q.Gao, et al, Jpn.J. Appl.Phys., 45 (2006) L929

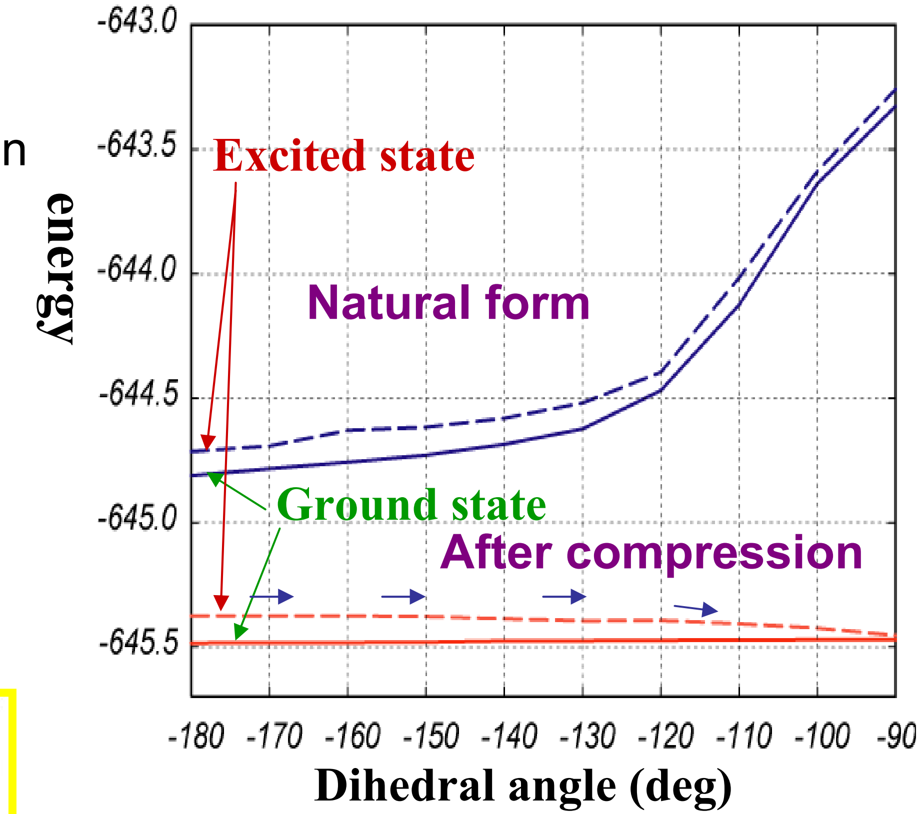
Mechanism of suppression of light emission

-Simulation of nano-mechanical experiments

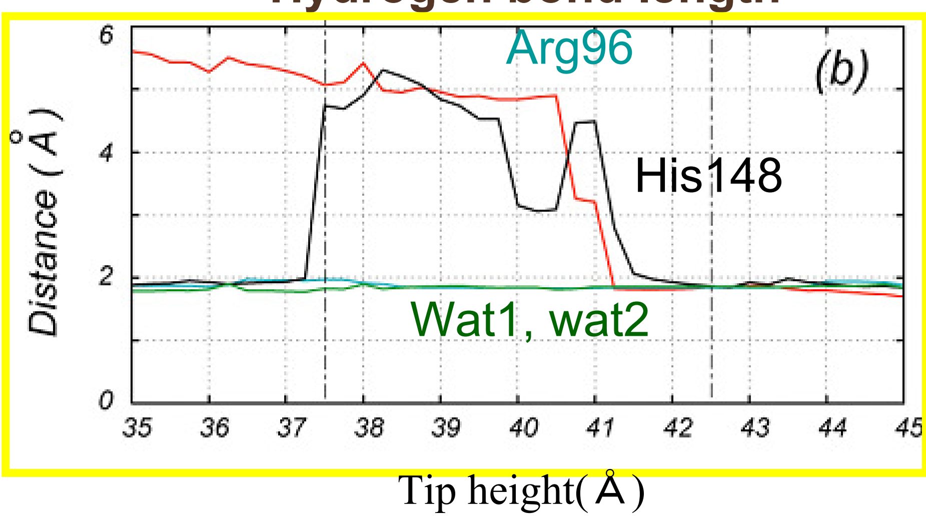
T. Kodama, H.Ohtani and A.Ikai, Appl. Phys. Lett. 86 043901(2005)

CM/MM
ONIOM
calculation





Hydrogen bond length



On the compression, rotation barrier disappears

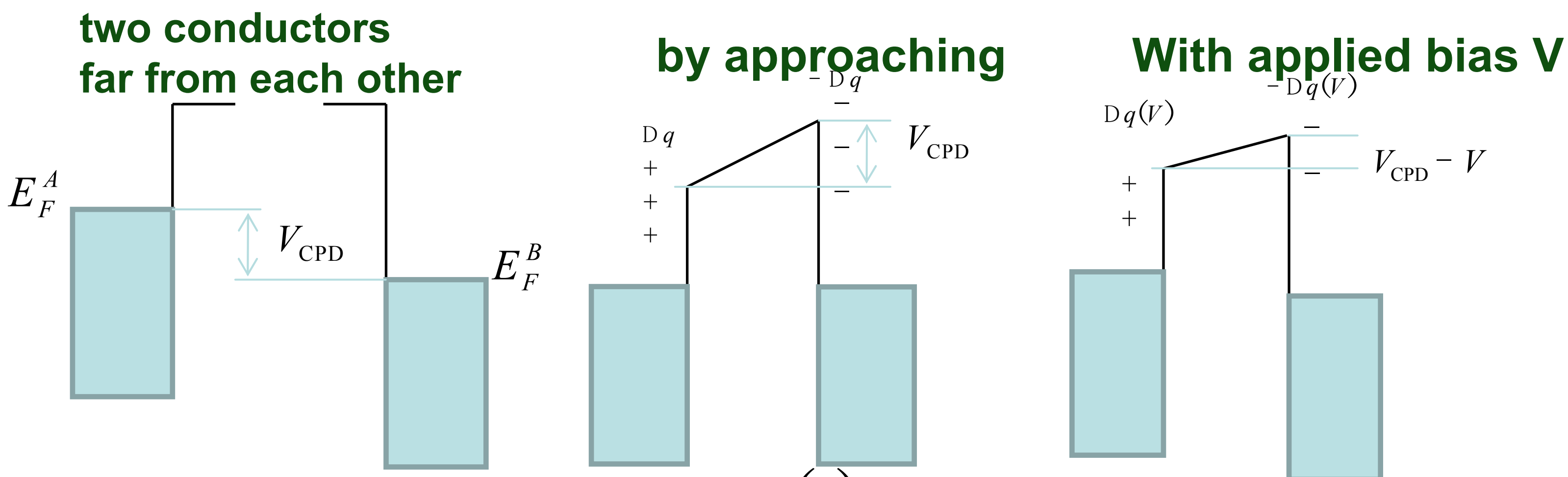
⇩

Non-radiative processes take place

⇨

Emission suppressed

Theory and simulation of Kelvin Probe Force Microscopy(KPFM)



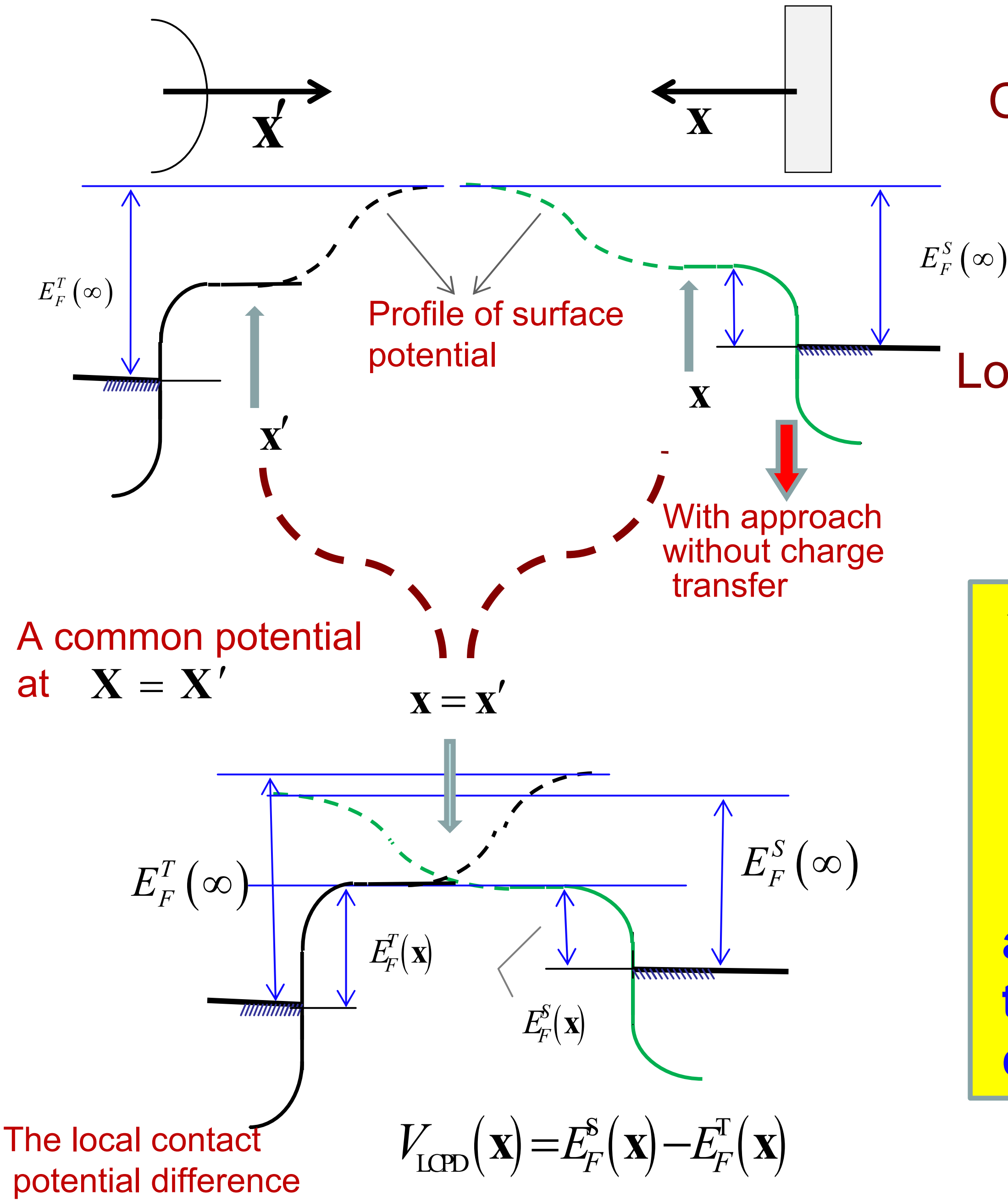
$$\Delta q = C(z)V_{CPD}$$

$$\Delta q(V) = C(z)(V_{CPD} - V)$$

Contact potential difference V_{CPD} is a global(averaged) quantity,
but in KPFM experiment, it depends on the tip position ?!
How is the local contact potential V_{LCPD} difference explained?

$$F = -\frac{1}{2}\frac{\partial C(z)}{\partial z}(V_{CPD} - V)^2$$

What is the Local Contact Potential Difference V_{LCPD}?



Contact Potential difference

$$V_{CPD} = E_F^S(\infty) - E_F^T(\infty)$$

Local Contact Potential Difference

$$V_{LCPD}(\mathbf{x}) = E_F^S(\mathbf{x}) - E_F^T(\mathbf{x})$$

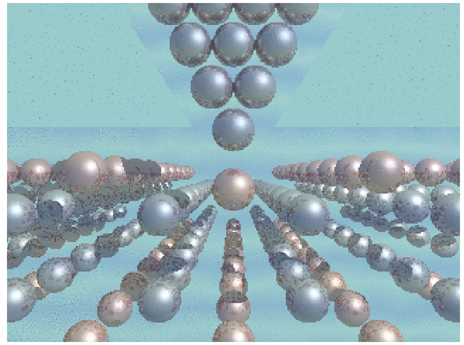
$V_{LCPD}(\mathbf{x})$ is determined by nano-scale surface potential governed by local charge distribution, but approach of the tip and the sample modifies the local charge distribution.

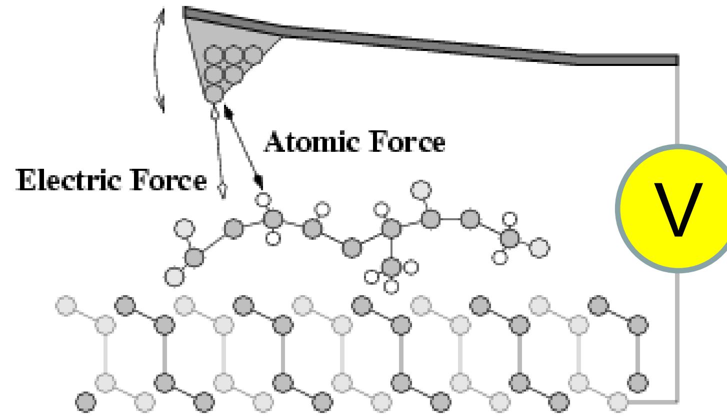
Simulation of KPFM Images

What is the "Local Contact Potential Difference"?

Partitioned real space
DFT based tight binding method

PR-DFTB method
+perturbation





For a given charge transfer $\mathrm{D}\,q$

Electronic state charge

$$\left\{\varphi_i^T\right\}, \rho_T(\mathbf{r})$$

solve electronic state of Tip with potential field of Sample

solve electronic state of Sample with potential field of Tip

$$\left\{\varphi_i^S\right\}, \rho_S(\mathbf{r})$$

Fermi level offset , i.e., applied bias and force are determined for this charge transfer, then

$$E_F^A(\mathrm{D}\,q) - E_F^B(\mathrm{D}\,q) = e\left(V(\mathrm{D}\,q) - V_{LCPD}\right)$$

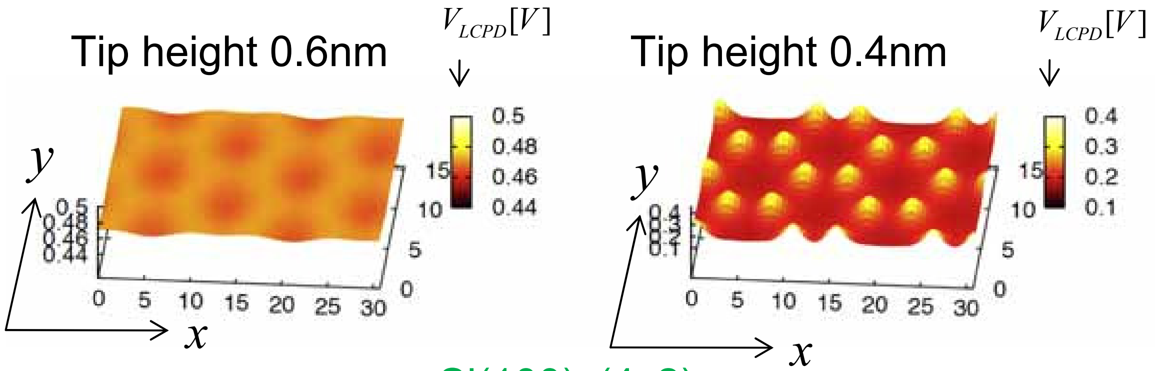
V_{LCPD} , local contact Potential difference determined

perturbation for the chemical force

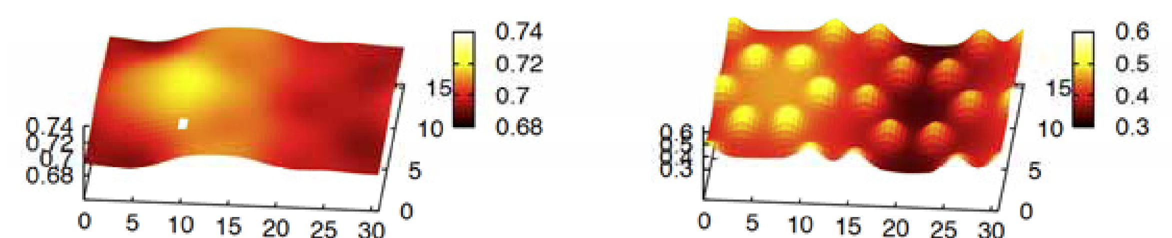
KPFM image of Si(001)-c(4x2)

-image of local contact potential differnce-

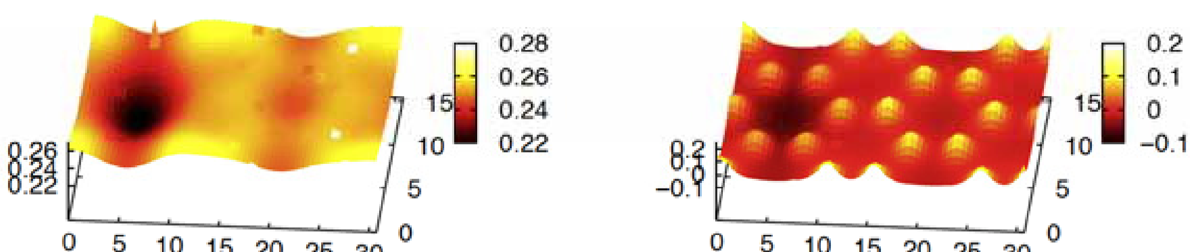
effect of embedded imturity atoms



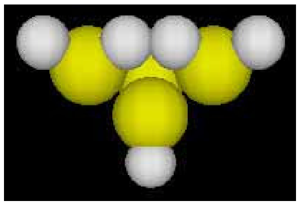
Si(100)c(4x2)



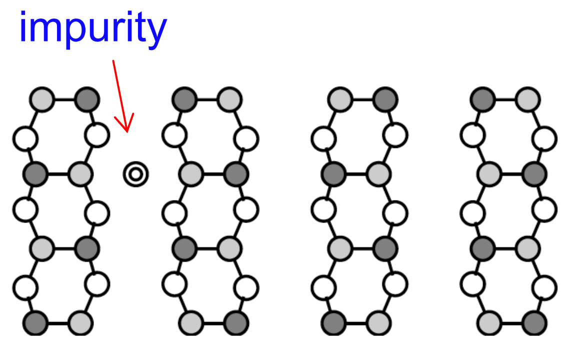
Al in Si(100)c(4x2)

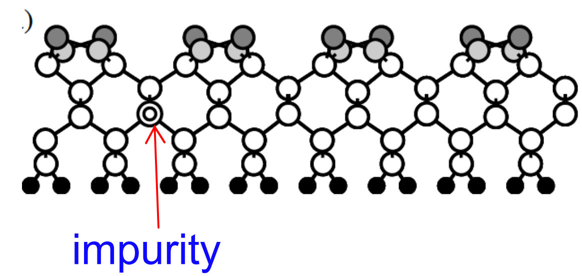


P in Si(100)c(4x2)



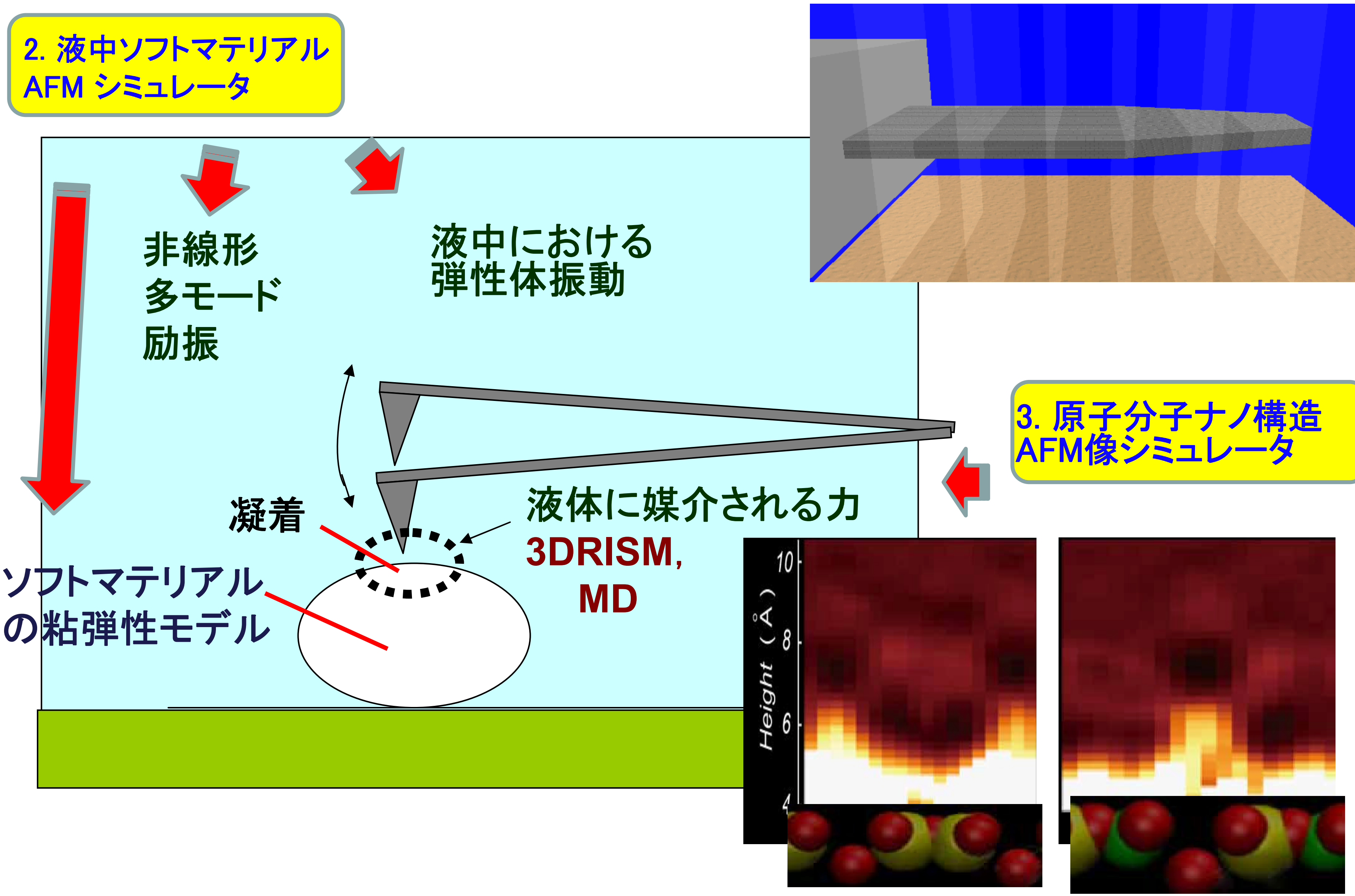
Si4H9 tip



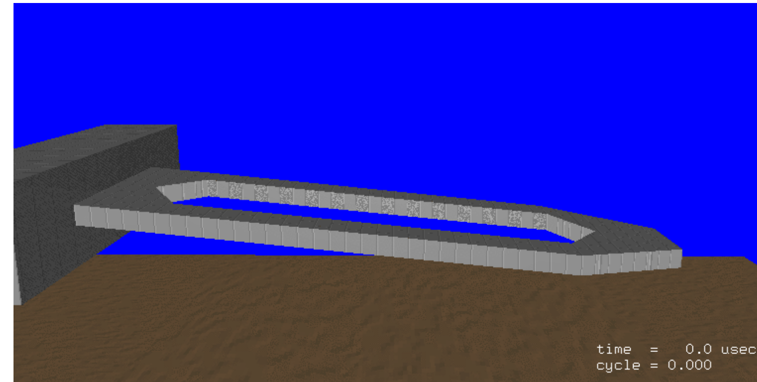


A.Masago et al, Phys. Rev. B 82 (2010)195433

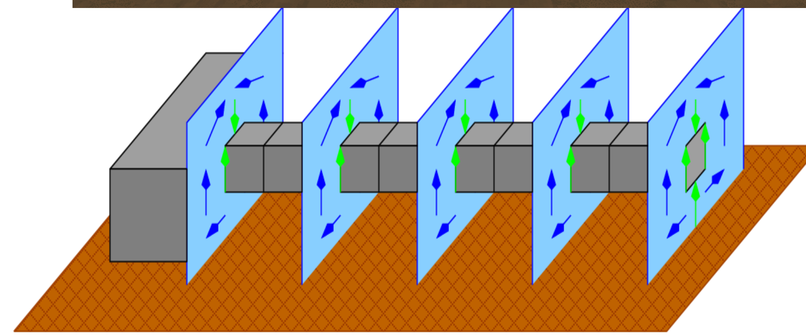
液中ncAFMの理論シミュレーション



液中カンチレバー振動の解析理論



1)共鳴曲線は?
2)非線形効果は?
3)基盤からの高さの影響？
4)探針の受ける力の効果？



カンチレバー:
一方向に長い構造

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

→ 液体からの力

h; カンチレバーの高さ

E; ヤング率modulus

I; 断面の幾何学的能率

液体:
各断面で2次元の 非圧縮流体

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

Navier-Stokes 方程式

Re; レイノルズ数

Method for fluid dynamics on 2D

Flow function $\Psi \Rightarrow v_x = +\frac{\partial \psi}{\partial y} \quad v_y = -\frac{\partial \psi}{\partial x}$ **Velocity component of fluid**

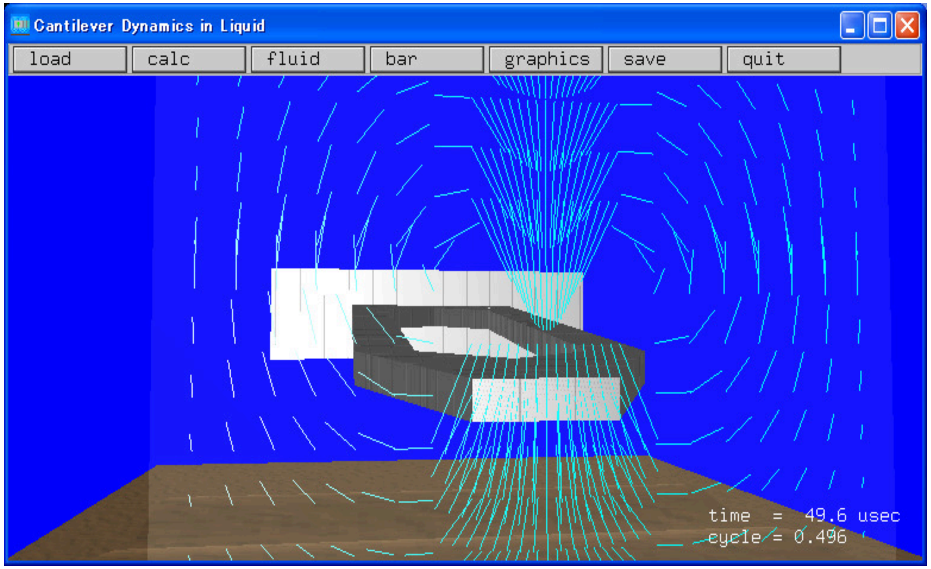
vorticity $\omega \Rightarrow \omega = \partial_x v_y - \partial_y v_x \Rightarrow \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = -\omega$

From Navier-Stokes eq.

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

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

negligible

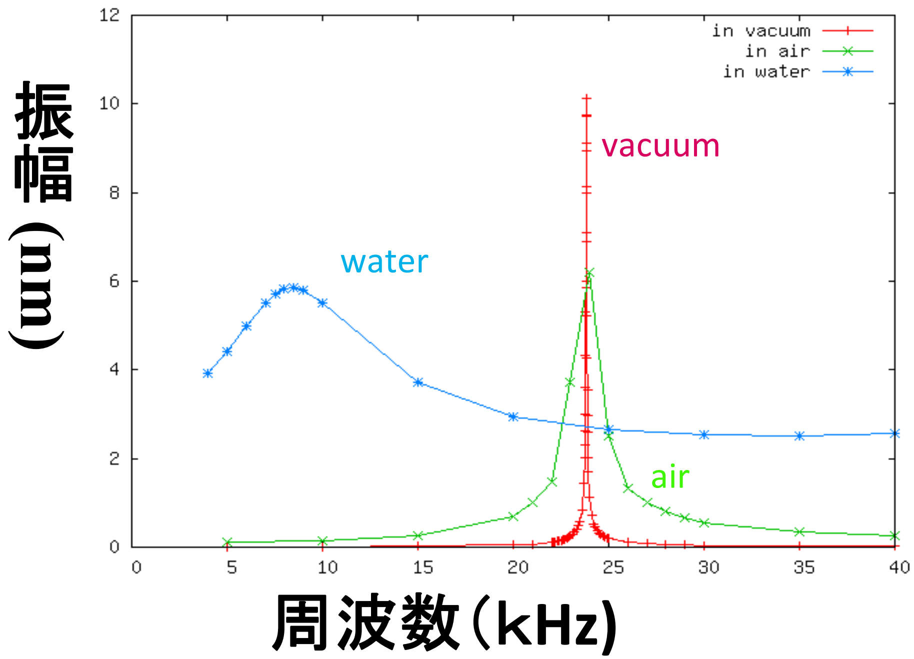


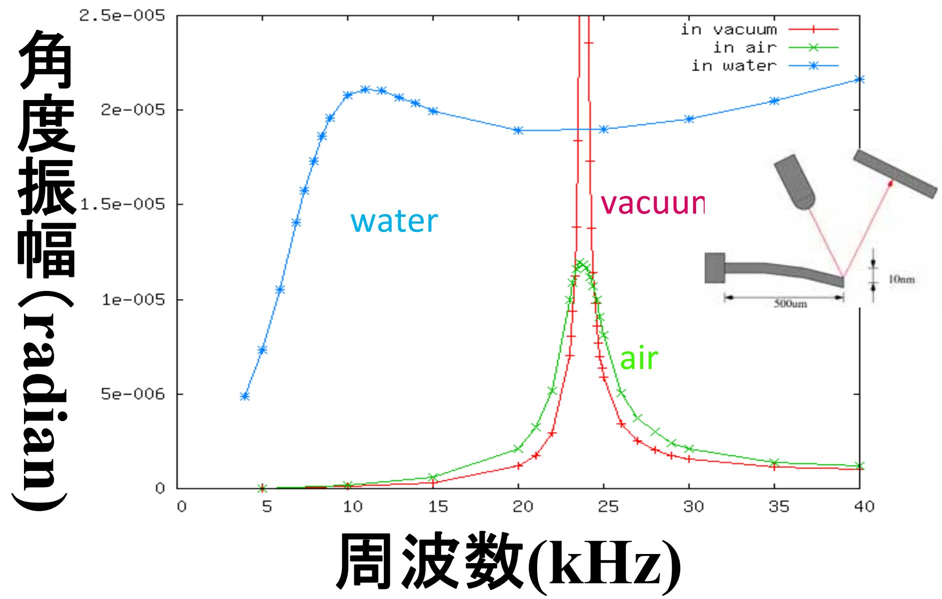
Closed equation of ω solved by FEM

Force felt by cantilever is given by

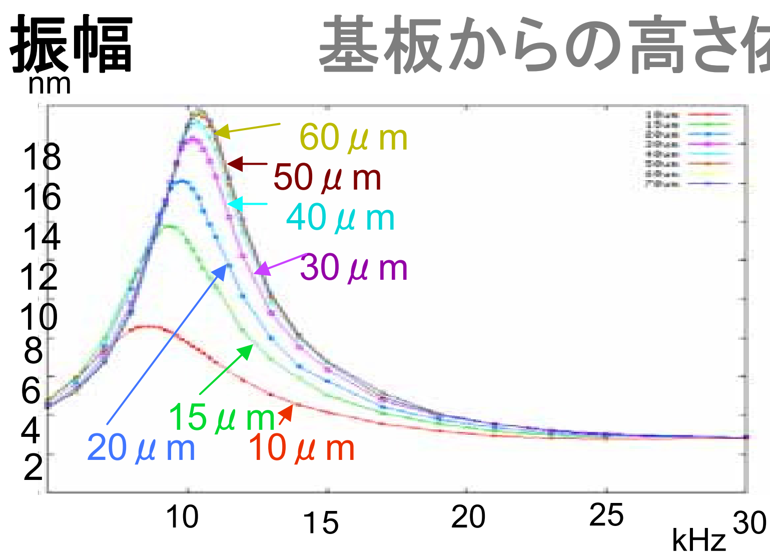
$$F_s = \oint \left(P + \frac{\omega}{\mathrm{Re}} \right) dl$$

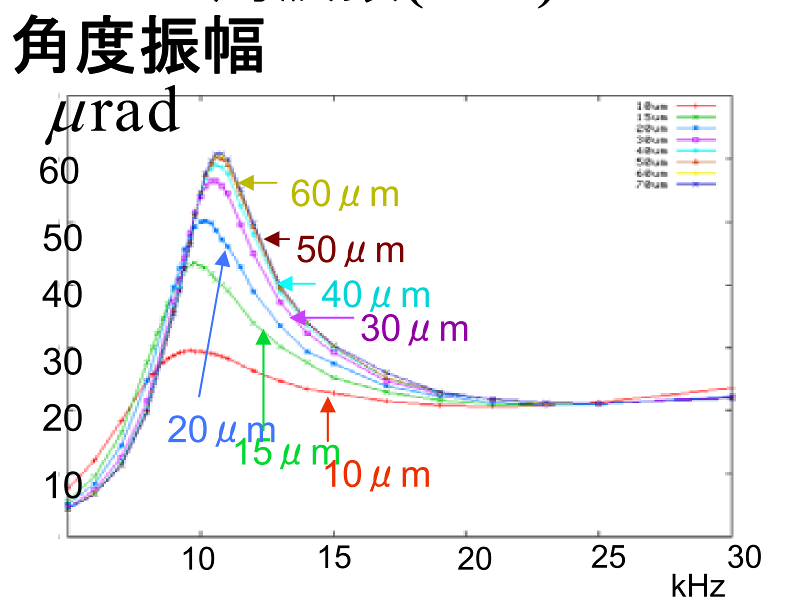
水中のSi矩形薄板カンチレバーの共鳴曲線





基板からの高さ依存性



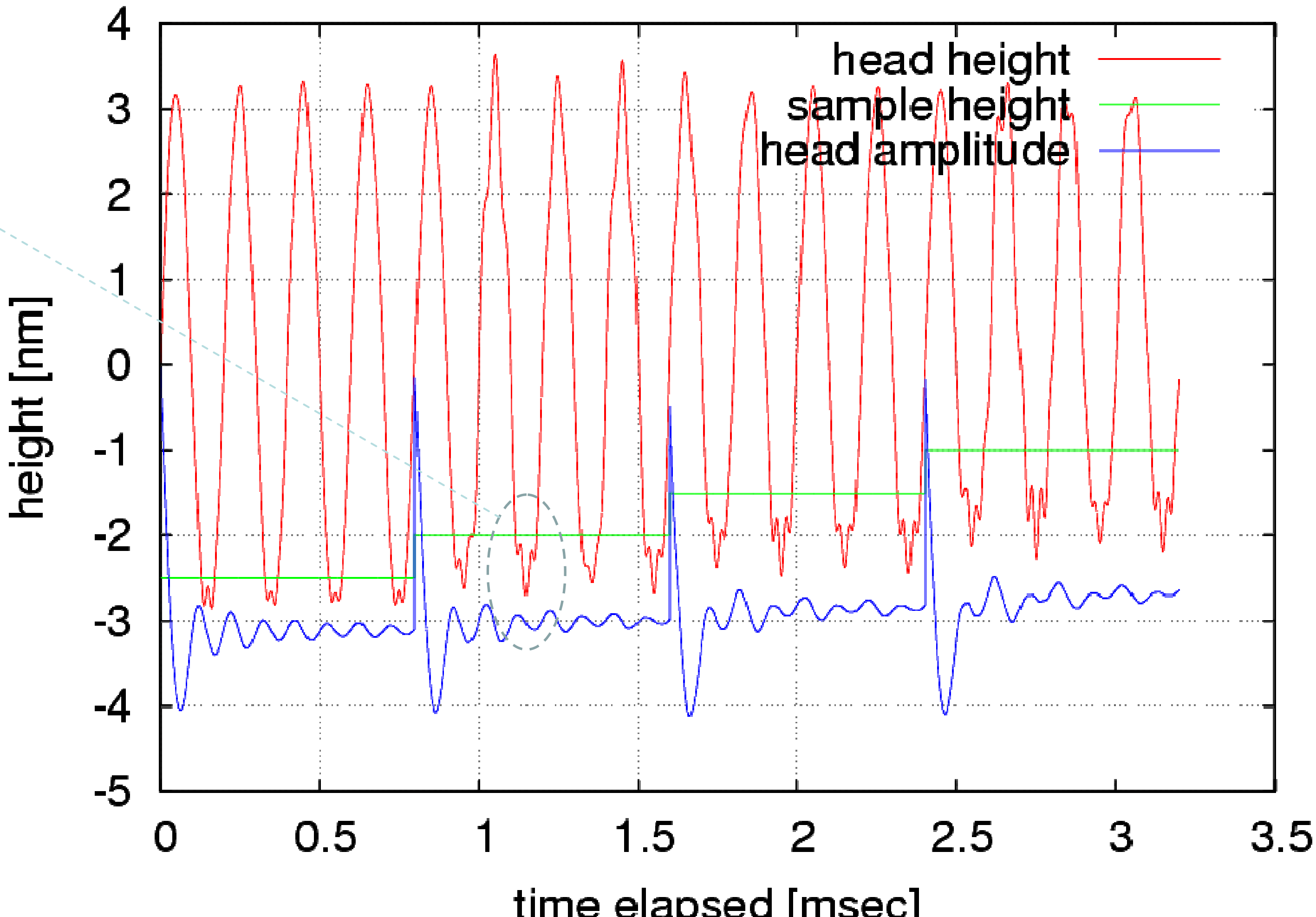


M.Tsukada, N.Watanabe, Jpn.J.Appl.Phys. 48 (2009) 035001

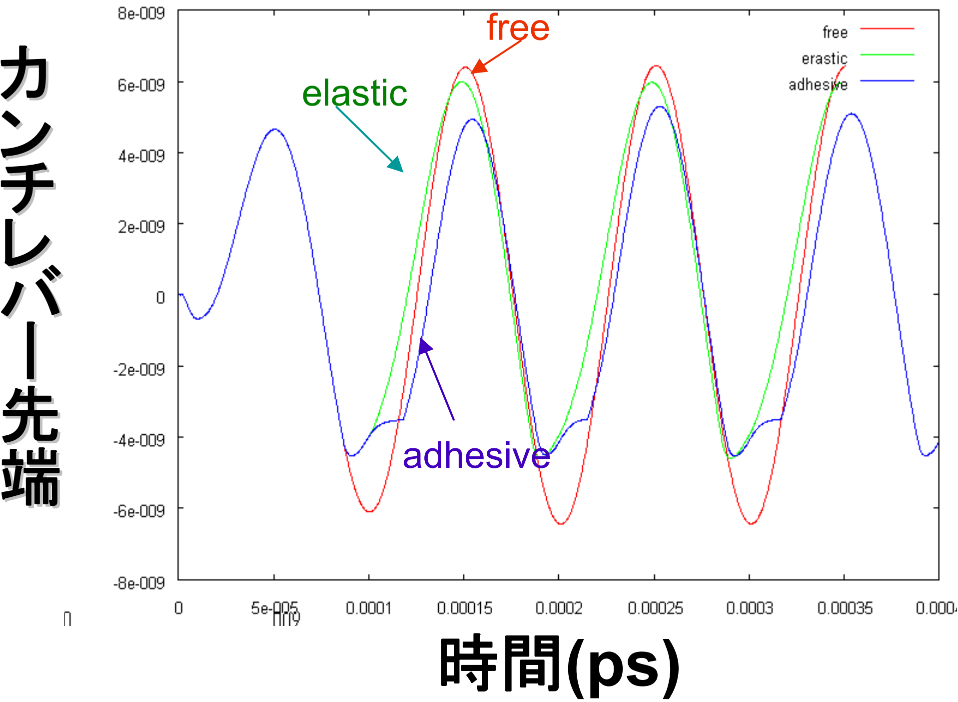
探針から受ける力の影響　1

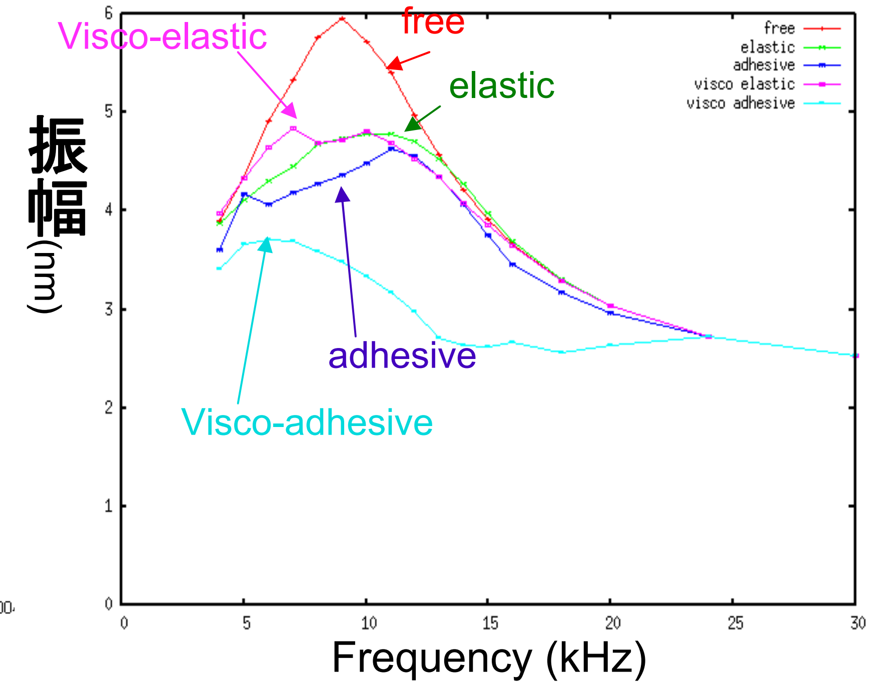
-ステップ列上の高速スキャンと多重モード -

高調波モード
の励起



探針の受ける力の影響　２　ー水中タッピングモードー



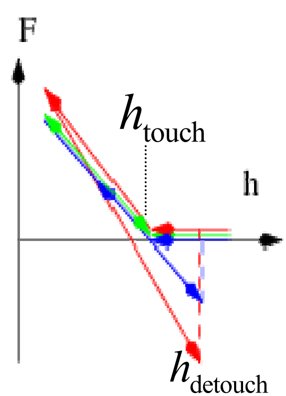


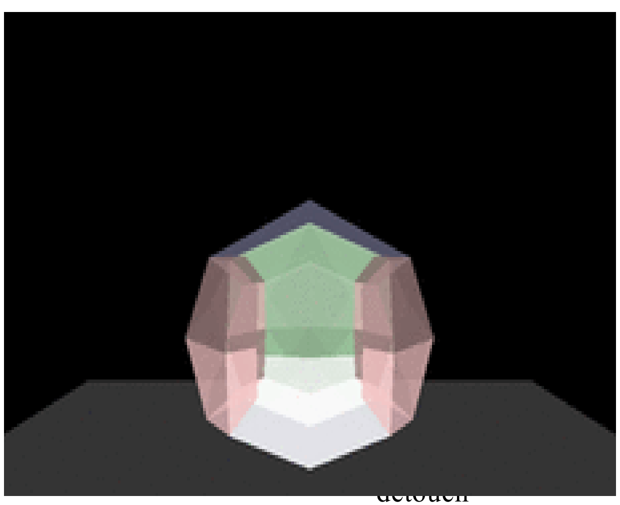
elastic $f(h) = -k(h - h_{touch}) \quad h < h_{touch}$

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



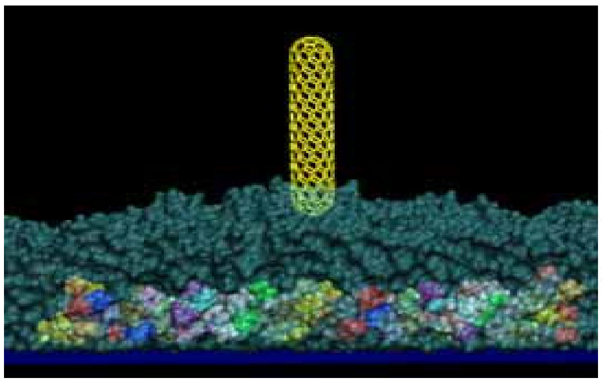


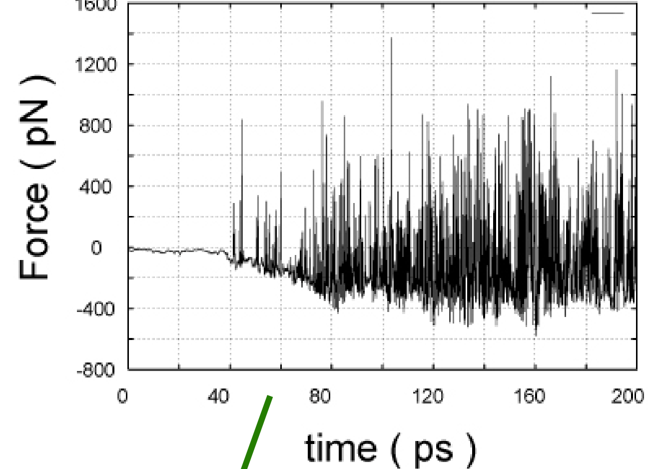
液体分子に媒介される
探針-試料間相互作用力

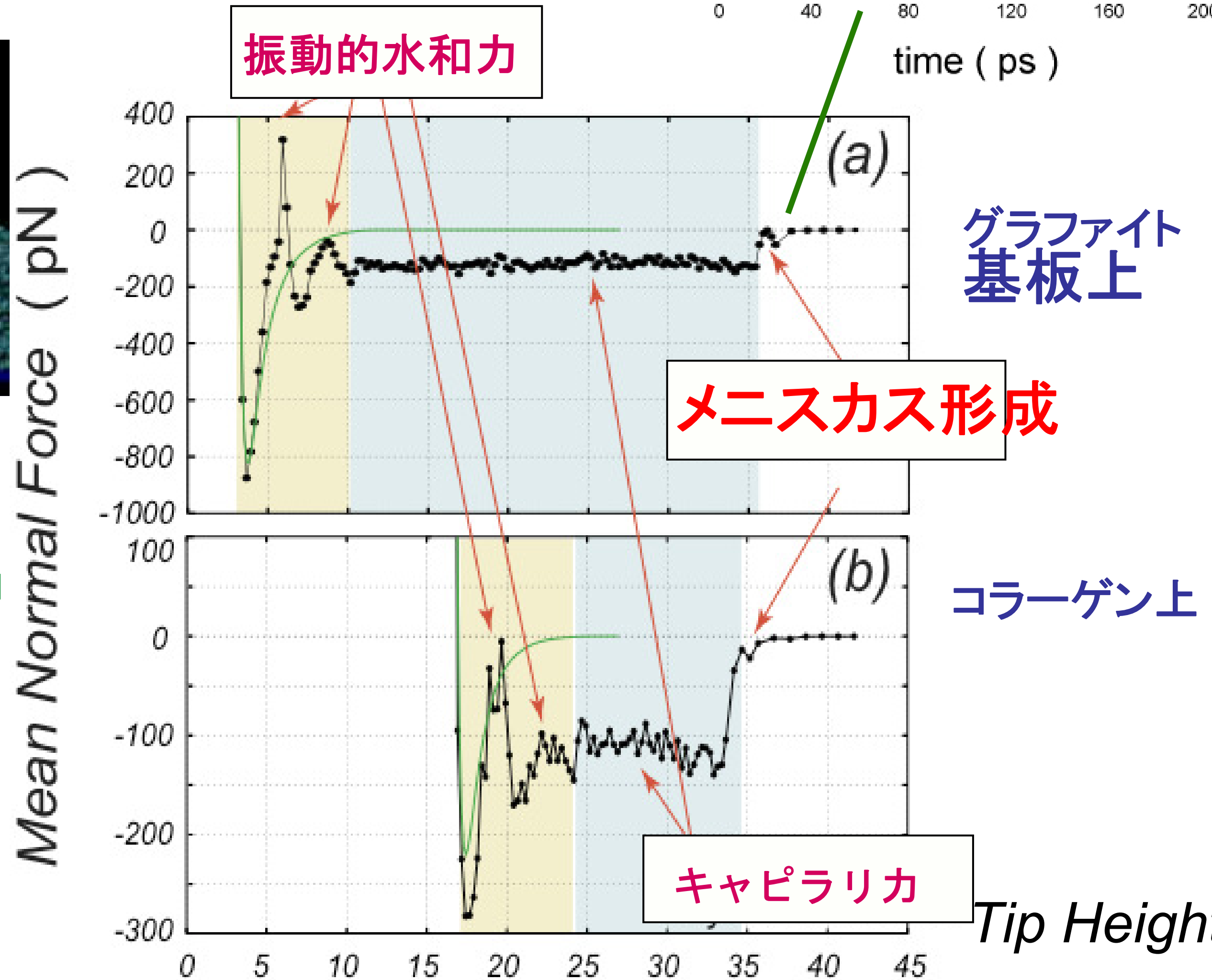
水分子に媒介される
探針ー試料間相互作用力

古典分子動力学法による AFMシミュレーション ；

水中のCNT 探針とコラーゲン試料







K.Tagami and M.Tsukada,

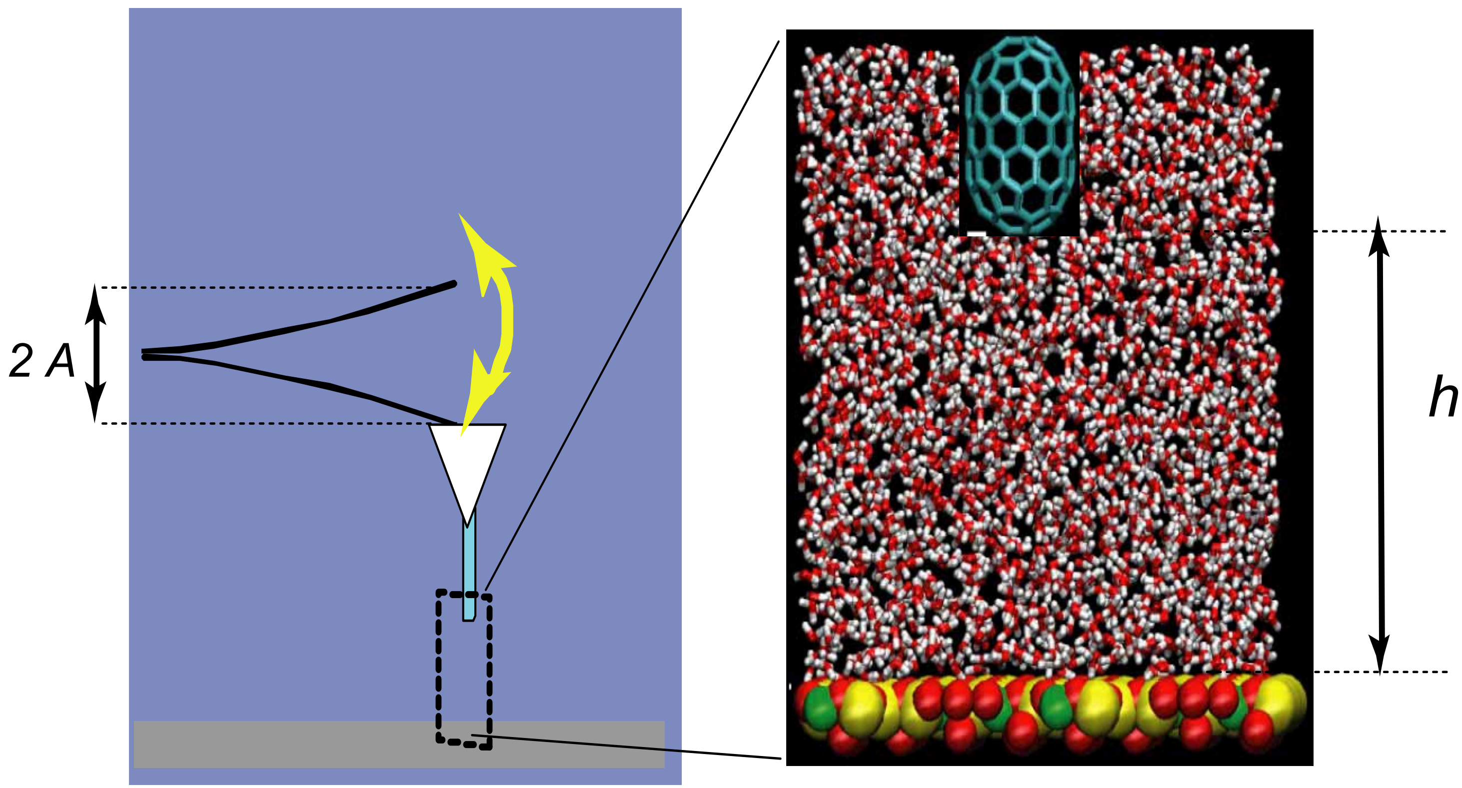
e-J. Surf.Sci.Nanotech. 4 (2006)311

水中マイカについてのnc-AFM シミュレーション -古典 MD 法

MD計算条件

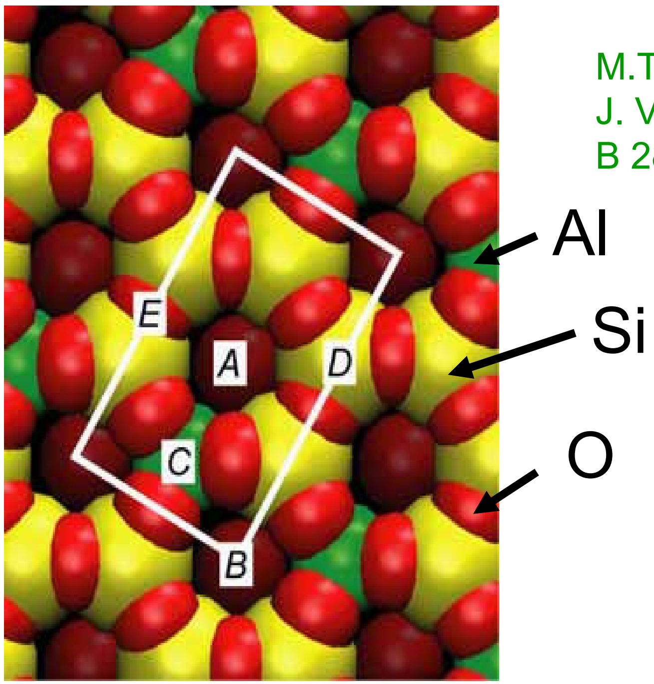
マイカ表面サイズ：36A×42A
探針模型：(10,0)CNT
水分子ポテンシャル ：TIP3P
全原子数：6,338

力場: *CHARMM 22 + CLAY (modified)*
プログラム: *NAMD2.5 and 2.6*
温度: *300 K*
時間メッシュ: *2fs*



M.Tsukada, N.Watanabe, M.Harada and K.Tagami, J. Vac. Sci. and Techn. B28 (2010) c4c1

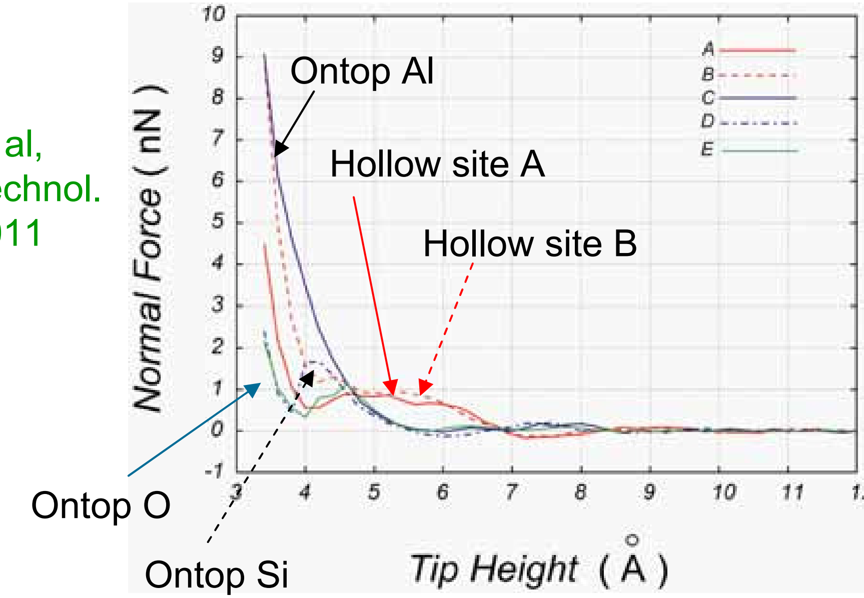
Force-distance curve by MD simulation; mica in water by a CNT tip



M.Tsukada, et al, J. Vac. sci,. Technol. B 28, C4C1 2011

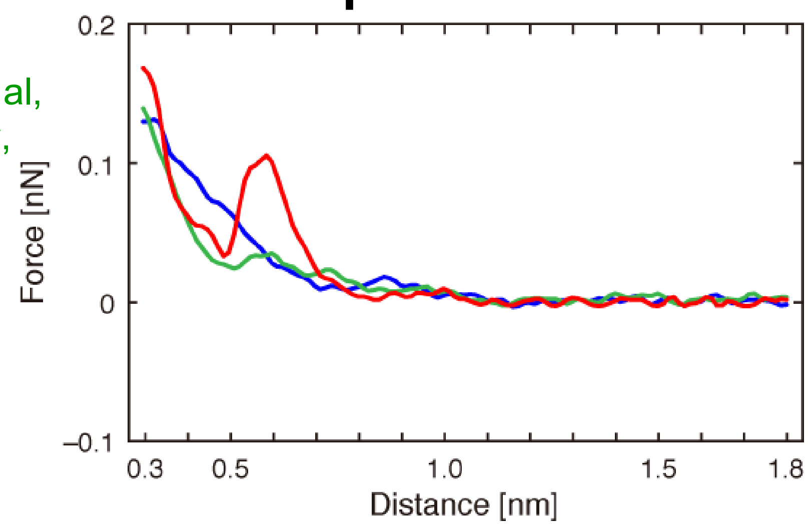
A, B: ontop of hollow site
C: ontop of Al atom
D: ontop of Si atom
E: ontop of O atom

MD simulation



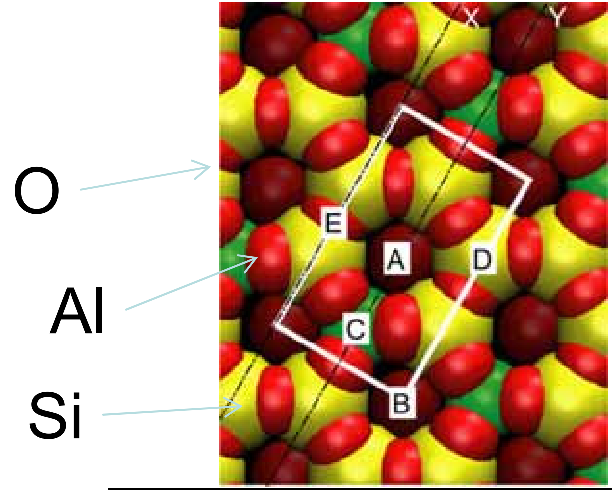
Experiment

K.Kobayashi, et al, Nanotechnology, submitted



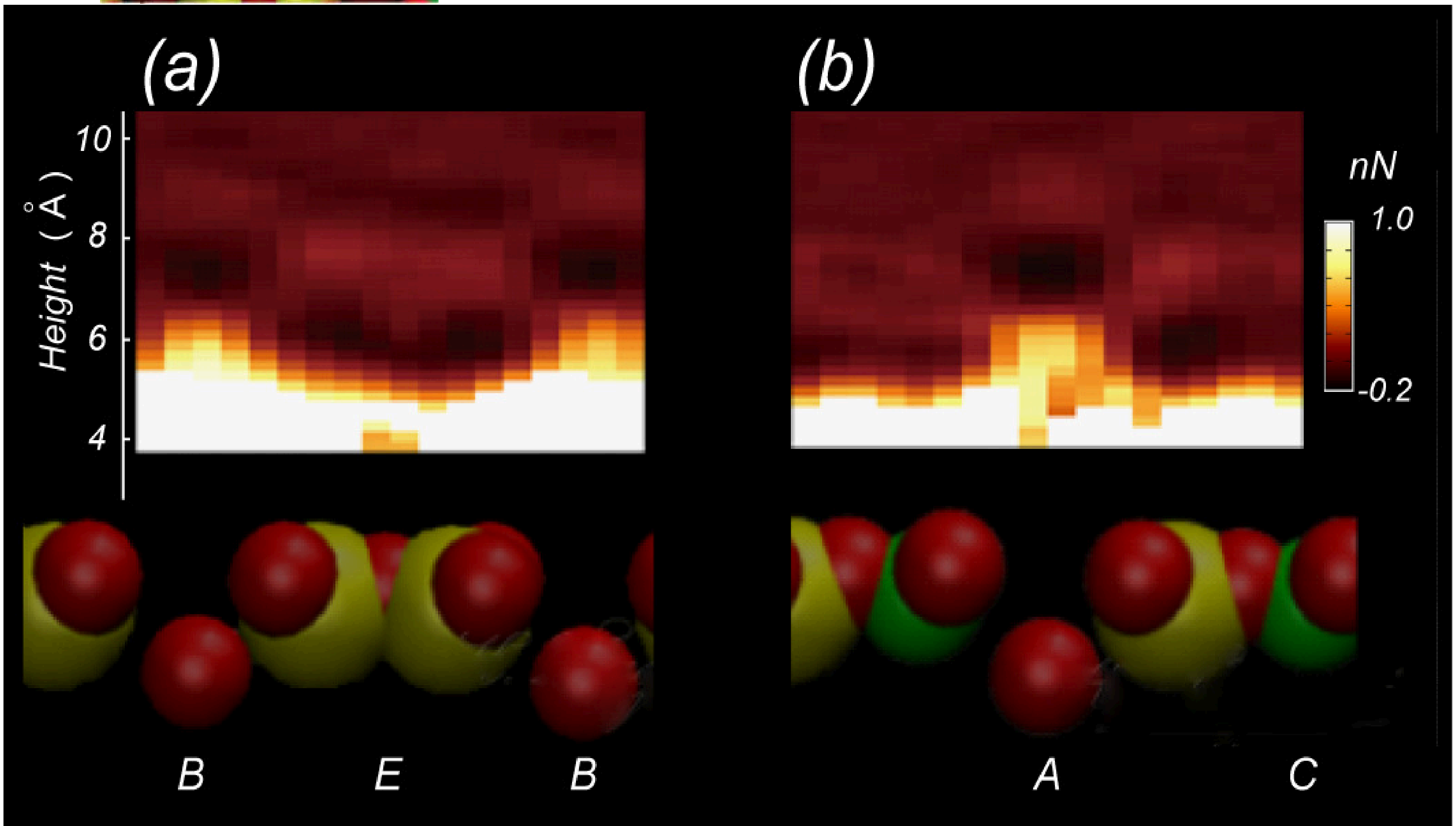
水中マイカの 3D力分布の断面像
（SWCNT 探針によるMDシミュレーション結果）

M.Tsukada et al, J. Vac. Sci. B28 (2010) c4c1



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

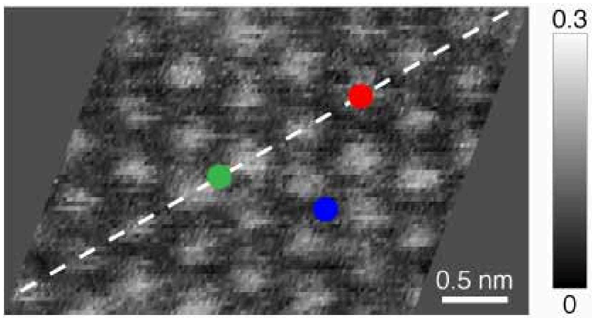
D: ontop of Si atom *E: ontop of O atom*

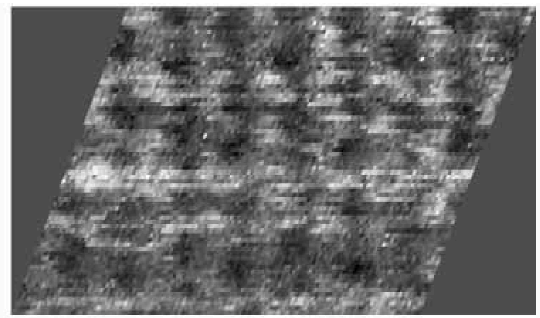


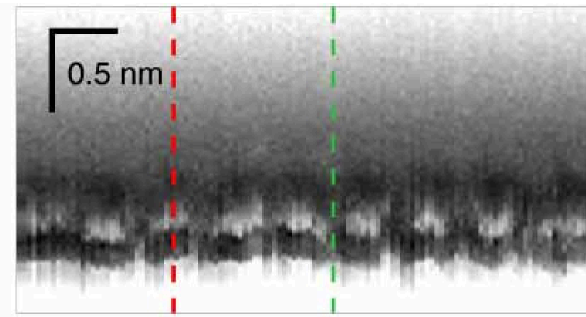
Comparison between the theory and the experiment

Experiment

K.Kobayashi, et al, Nanotechnology, submitted



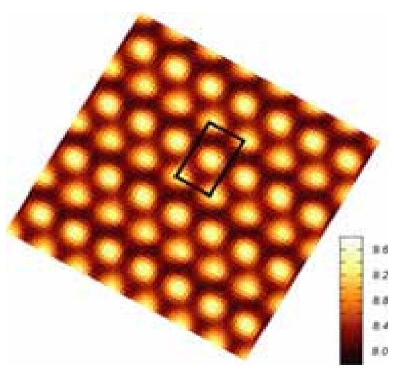


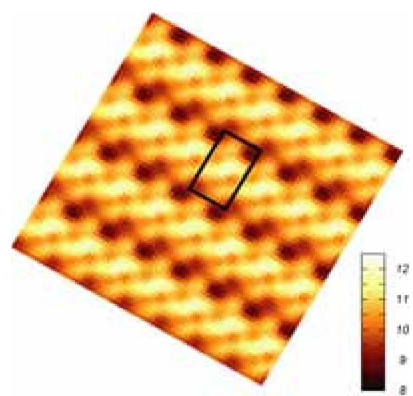


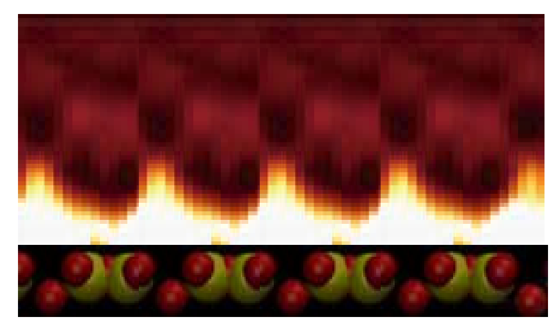
Force map
at a horizontal plane
with a certain height

Force map at the
horizontal plane
by 0.2nm closer
from the left

Force map
at a vertical plane
Including the dots
of the left







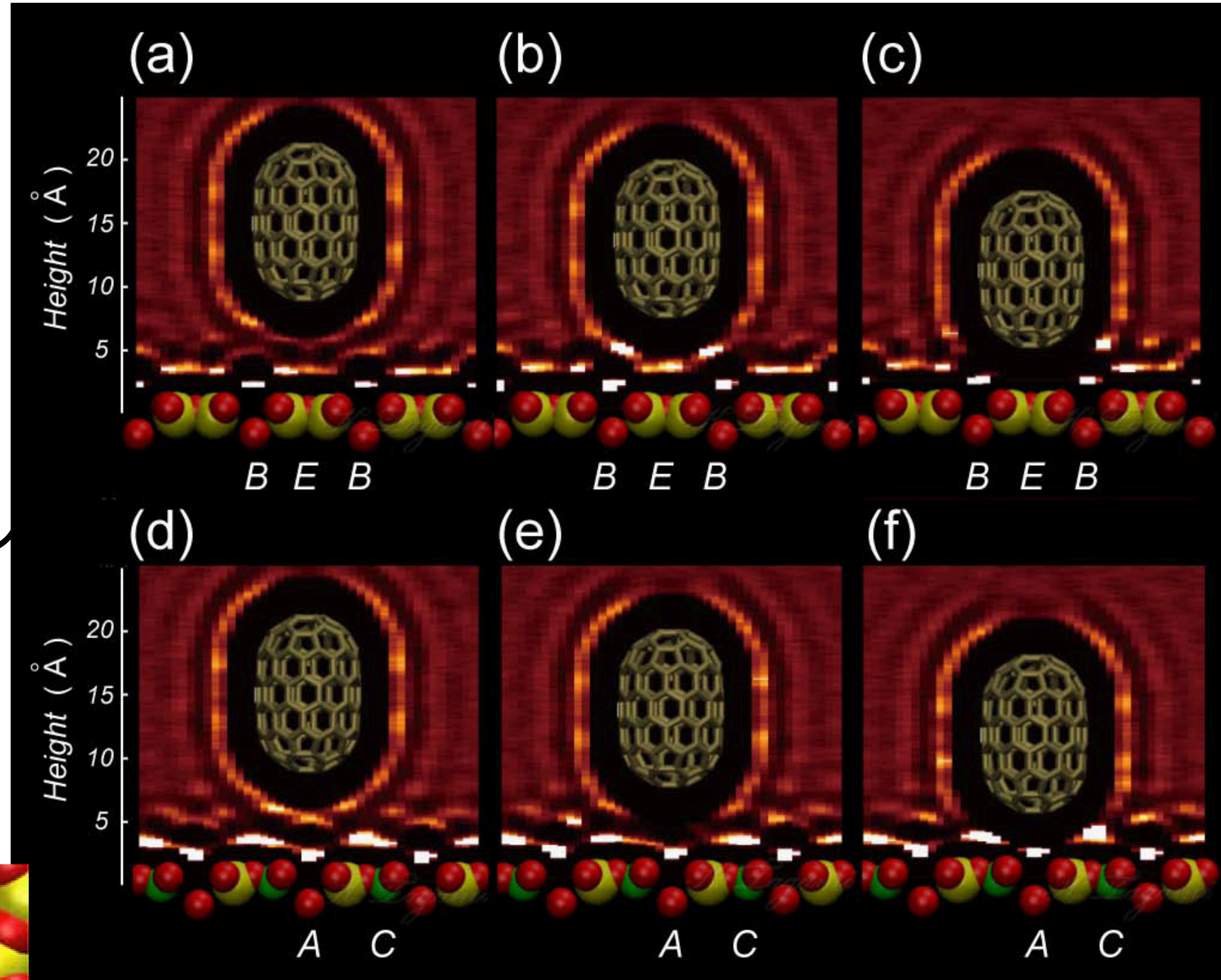
Theoretical Simulation

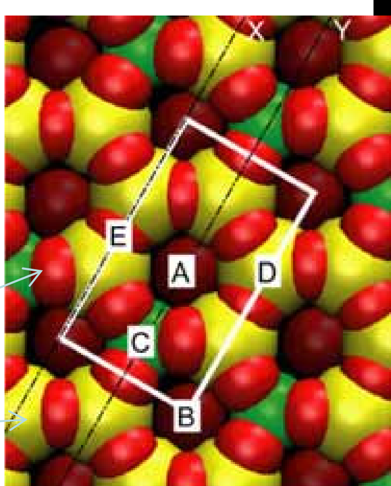
M.Tsukada et al, J. Vac. Sci. B28 (2010) c4c1

水中マイカとCNT探針間の

水分子の分布
（O原子）

MDシミュレーション結果

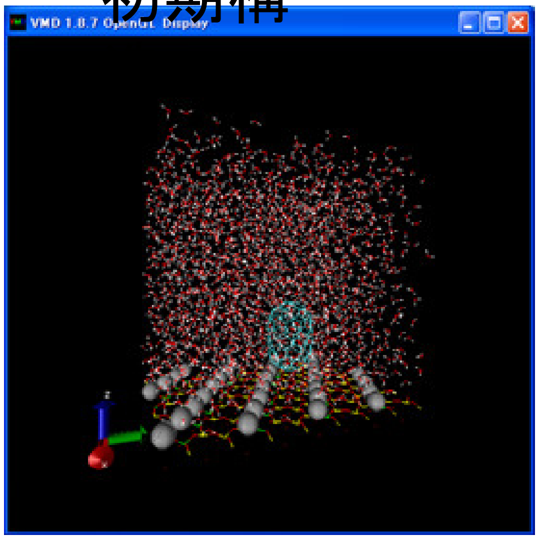




A, B:　ontop of hollow site　C:　ontop of Al atom
D:　ontop of Si atom　E：ontop of O atom

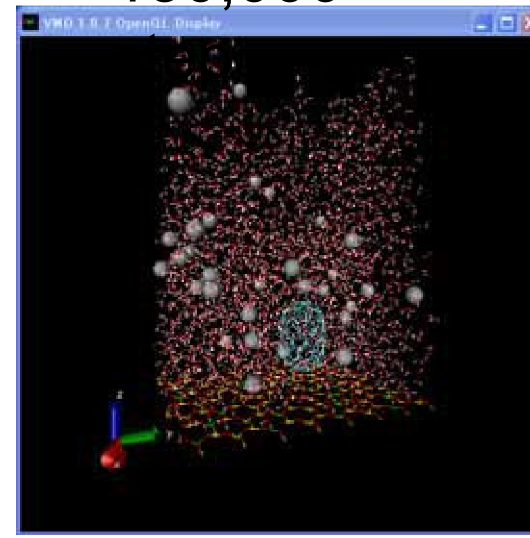
シミュレーション初期におけるK イオンの挙動

初期構



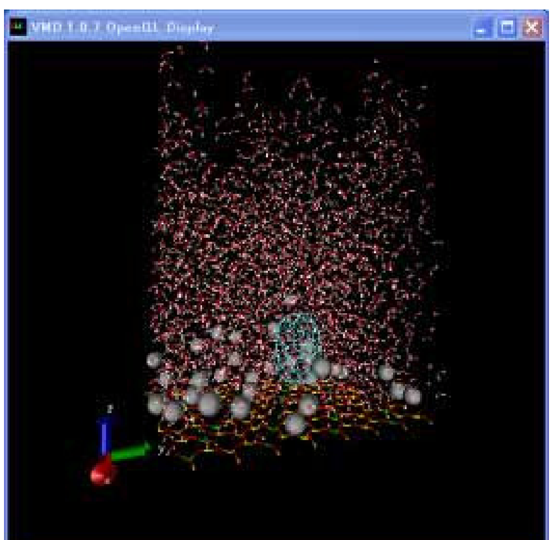
50,000 step

150,000

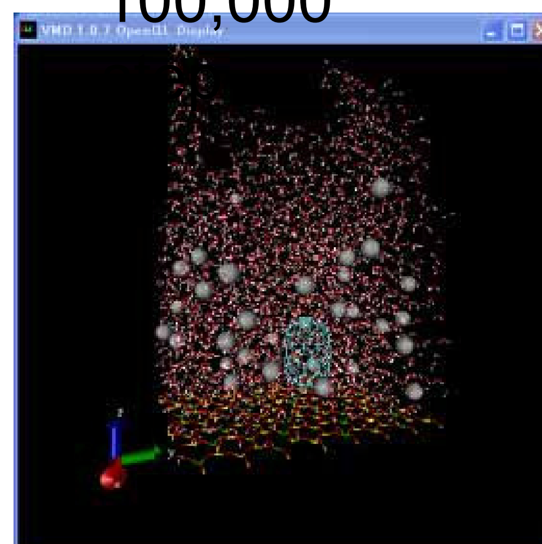


1step=2fs

20,000
step



100,000



水中AFMの力計算のための
(3D)- RISM法

$\mathbf{h}, \mathbf{c}, \omega \Longrightarrow N \times N$ 行列

$N =$ 非等価な原子の数

$$\omega_{ij}^{\alpha\beta} = \delta_{\alpha\beta} \sin\left(kl_{ij}\right) / kl_{ij}$$

分子間全相関関数 → $\mathbf{h}$

分子間直接相関関数 → $\mathbf{c}$

分子内原子相関関数 → ω

原子分布関数 → ρ

$$\mathbf{h} = \omega * \mathbf{c} * \omega + \omega * \mathbf{c} * \rho \mathbf{h}$$

convolution → $*$

短距離相互作用 → βu_{ij}^{0}

長距離相互作用 → $\beta \phi_{ij}$

$$c_{ij} = \exp\left(-\beta u_{ij}^{0} + t_{ij} - \beta \phi_{ij}\right) - 1 - t_{ij}$$

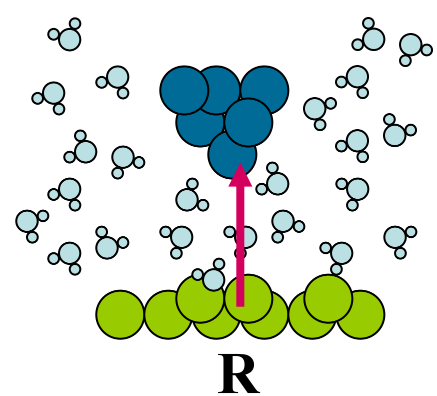
$$\beta = \frac{1}{k_B T}$$

$$\mathbf{t} \equiv \mathbf{h} - \mathbf{c}$$

自由エネルギー

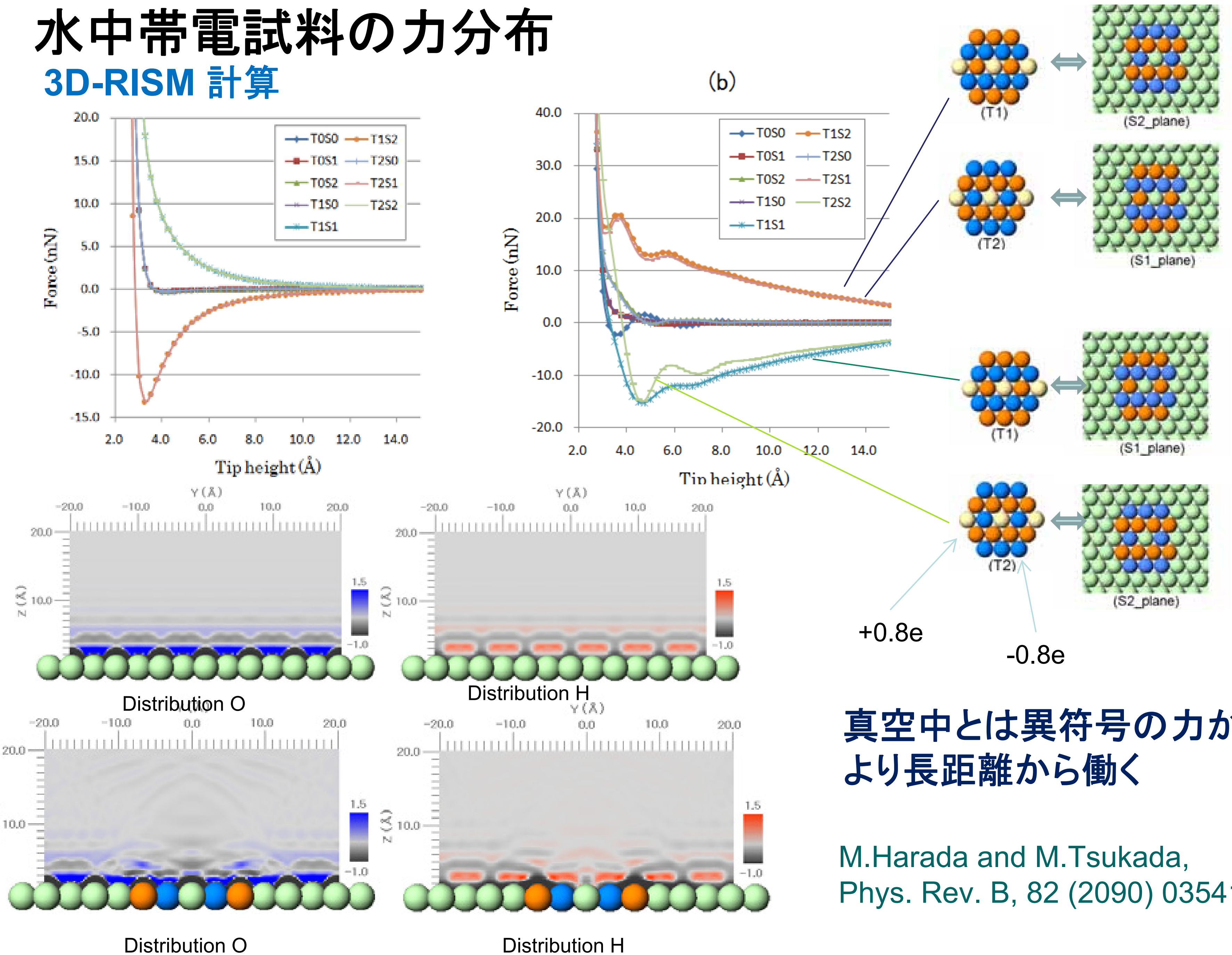
$$W(\mathbf{R}) = \rho k_B T \sum_{ij} \int d\mathbf{r} \left\{ \frac{1}{2} \left[h_{ij}(r) \right]^2 - c_{ij}(r) - \frac{1}{2} h_{ij}(r) c_{ij}(r) \right\}$$

探針力 $\quad F(\mathbf{R}) = -\dfrac{\partial W(\mathbf{R})}{\partial \mathbf{R}}$



水中帯電試料の力分布

3D-RISM 計算

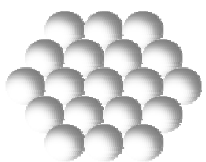


真空中とは異符号の力が
より長距離から働く

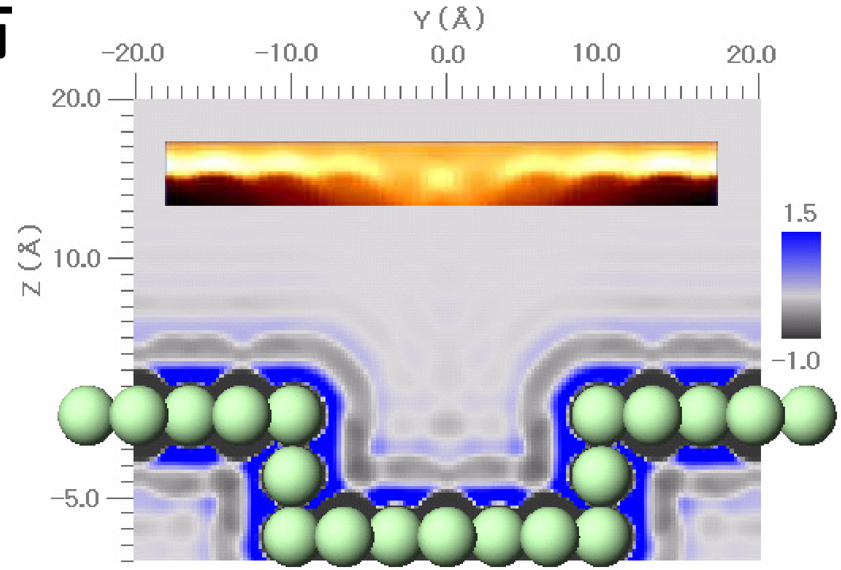
M.Harada and M.Tsukada,
Phys. Rev. B, 82 (2090) 035414

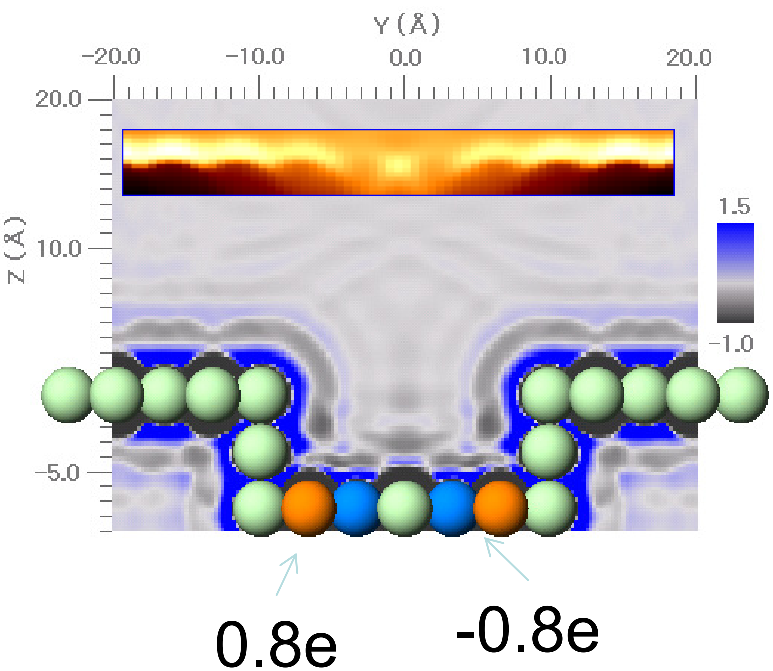
ナノピット周辺の水分子の分布

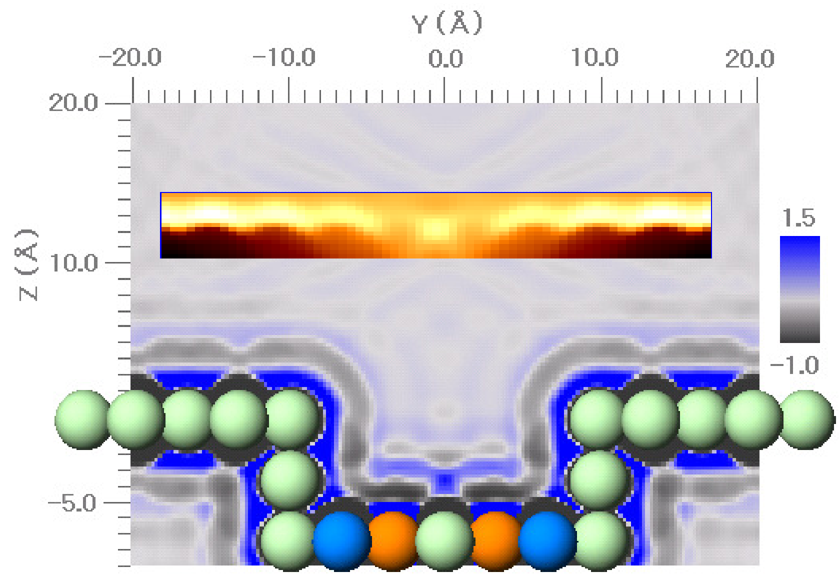
O分子密度分布
3D-RISM法による計算



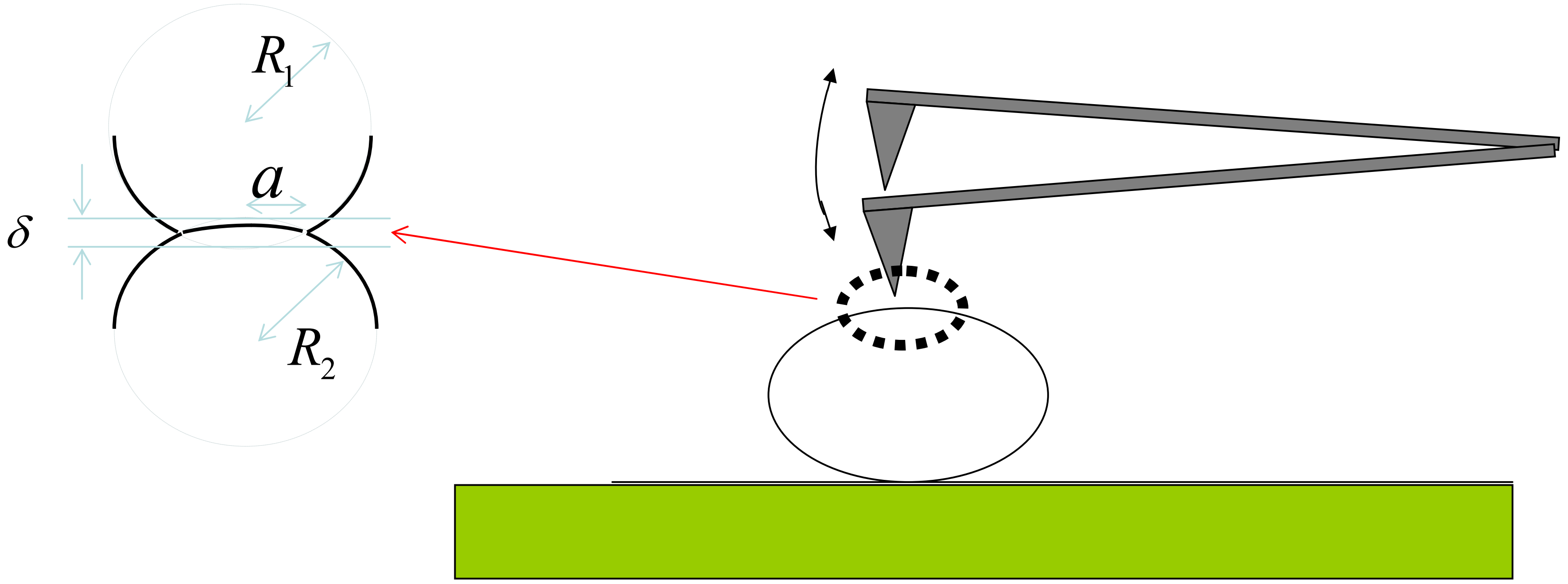
tip







接触問題



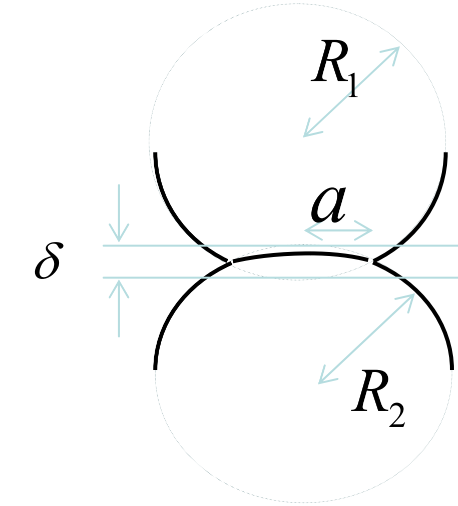
粘弾性試料のAFM計測シミュレーション

接触問題のJKR　理論

力　接触半径　実効ヤング率

$$F=\frac{4E^*}{3R}a^3-\sqrt{16\pi\gamma E^* a^3}$$

$$\frac{1}{E^*}=\frac{1-\nu_1^2}{E_1}+\frac{1-\nu_2^2}{E_2}$$



凝着エネルギー

$$U_S=-2\gamma\pi a^2\left(=U_{12}-U_1-U_2\right)$$

変位

$$\delta=\frac{a^2}{R}\left\{1-\sqrt{\frac{4\pi\gamma R^2}{E^* a^3}}\right\}$$

有効半径

$$\frac{1}{R}=\frac{1}{R_1}+\frac{1}{R_2}$$

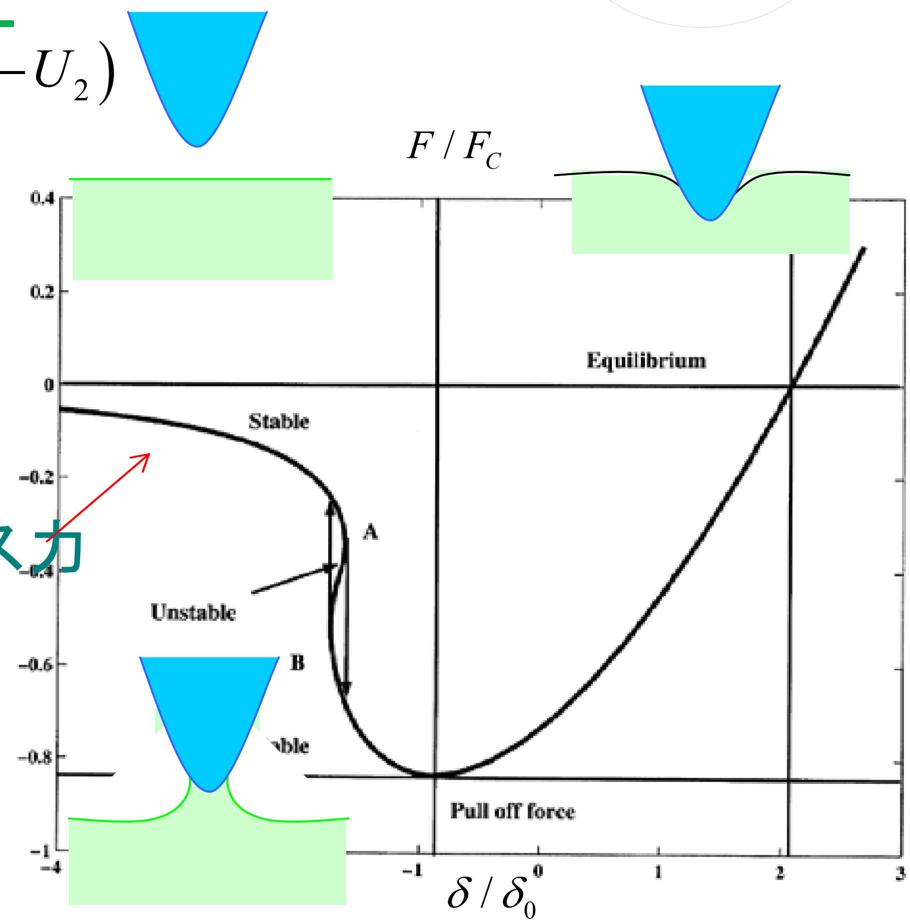
$$a_0=\left(\frac{9\pi\gamma R^2}{E^*}\right)^{1/3}$$

$$\delta_0=\frac{a_0^2}{3R}$$

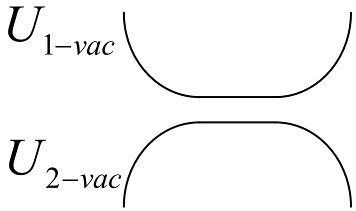
$$F_c=3\pi\gamma R$$

ファンデアワールス力

$$f_{\mathrm{vdW}}=-\frac{A_{\mathrm{H}}R}{6z^2}$$



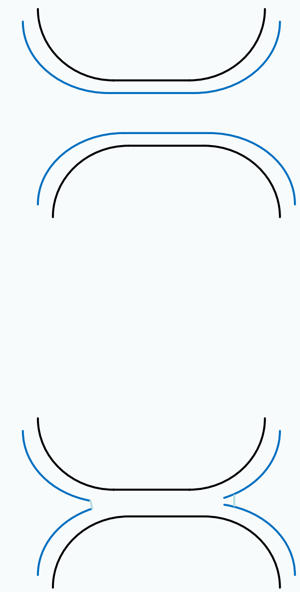
凝着エネルギー: γ

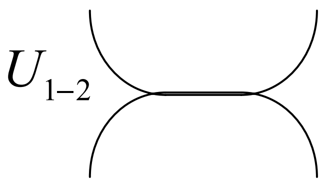


Surface energy for the detached state

$$U_{ditach} = U_{1-vac} + U_{2-vac}$$

For the case of wetting





Surface energy for the atached state

$$U_{tach} = U_{1-2}$$

Adhesion energy

$$U_{adhesion} = U_{ditach} - U_{tach}$$
$$= U_{1-vac} + U_{2-\mathrm{det}ach} - U_{1-2}$$

$$U_{adhesion}$$
$$= 2A \times u_{water\_surf\_tension} - A \times u_{water\_surf\_tension}$$
$$= A \times u_{water\_surf\_tension}$$

ソフトマテリアルの粘弾性的性質

西一中嶋 による高分子表面の計測

D.Wang et al, Macromolecules, (2010) 43, 3169

理論シミュレーションの方法

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

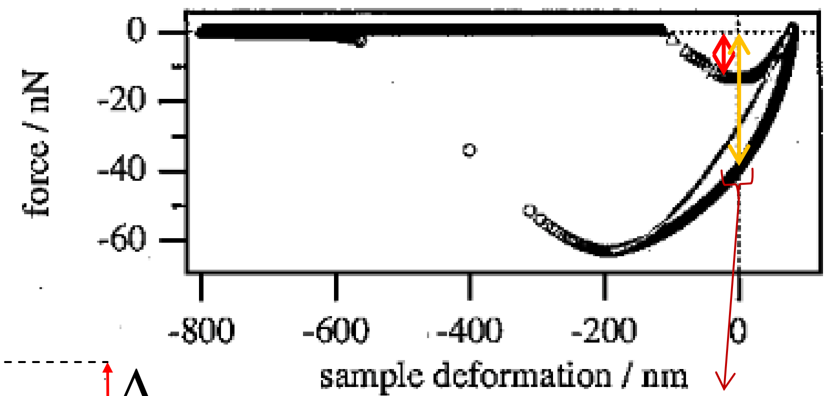
$\mathrm{Si\_Cantilever:\_}400\mu m\times 40\mu m\times 0.4\mu m$

$R=20nm$ $\nu=0.01k\mathrm{Hz}$ amplitude: 200nm

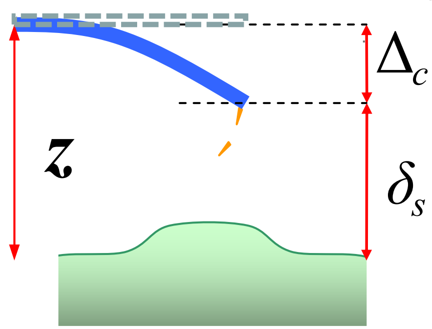
Sample(tip)YoungModulous:

60.0MPa(130GPa)

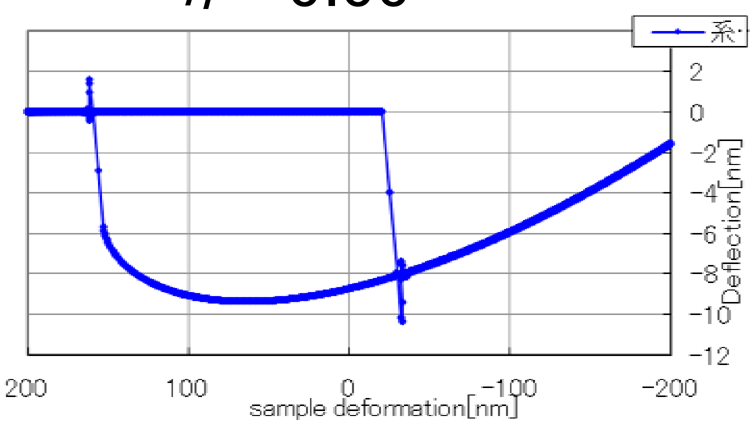
$\mathrm{adhesive\_energy}(\gamma)=10\mathrm{J/m^2}$



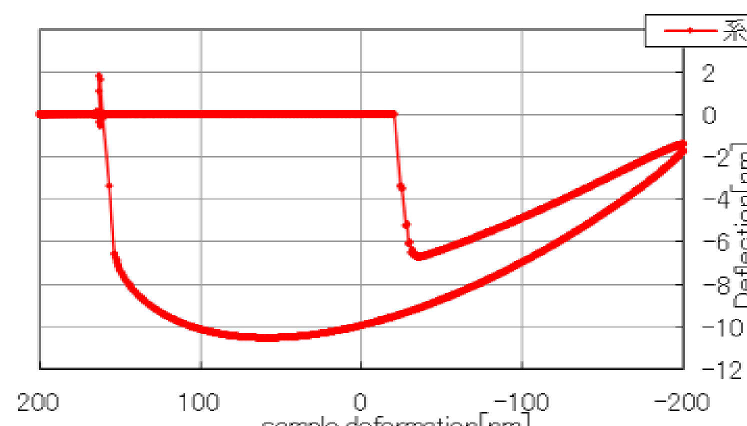
Visco-elastic effect?



η = 0.00



η = 0.02



研究協力者

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吾妻広夫	Advanced Algorithm & Systems
橋本直樹	Advanced Algorithm & Systems
清水守	Advanced Algorithm & Systems

ΣAAS

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