

Nanomechanics

Herbstsemester 12

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Contents

Nanomechanics: Introduction

Cantilever: static and dynamic modes of force measurements
Limits of force measurements

Elastic properties of Nanotubes

Weighing single molecules?

Nanomotors

Nanodroplets and Superhydrophobicity

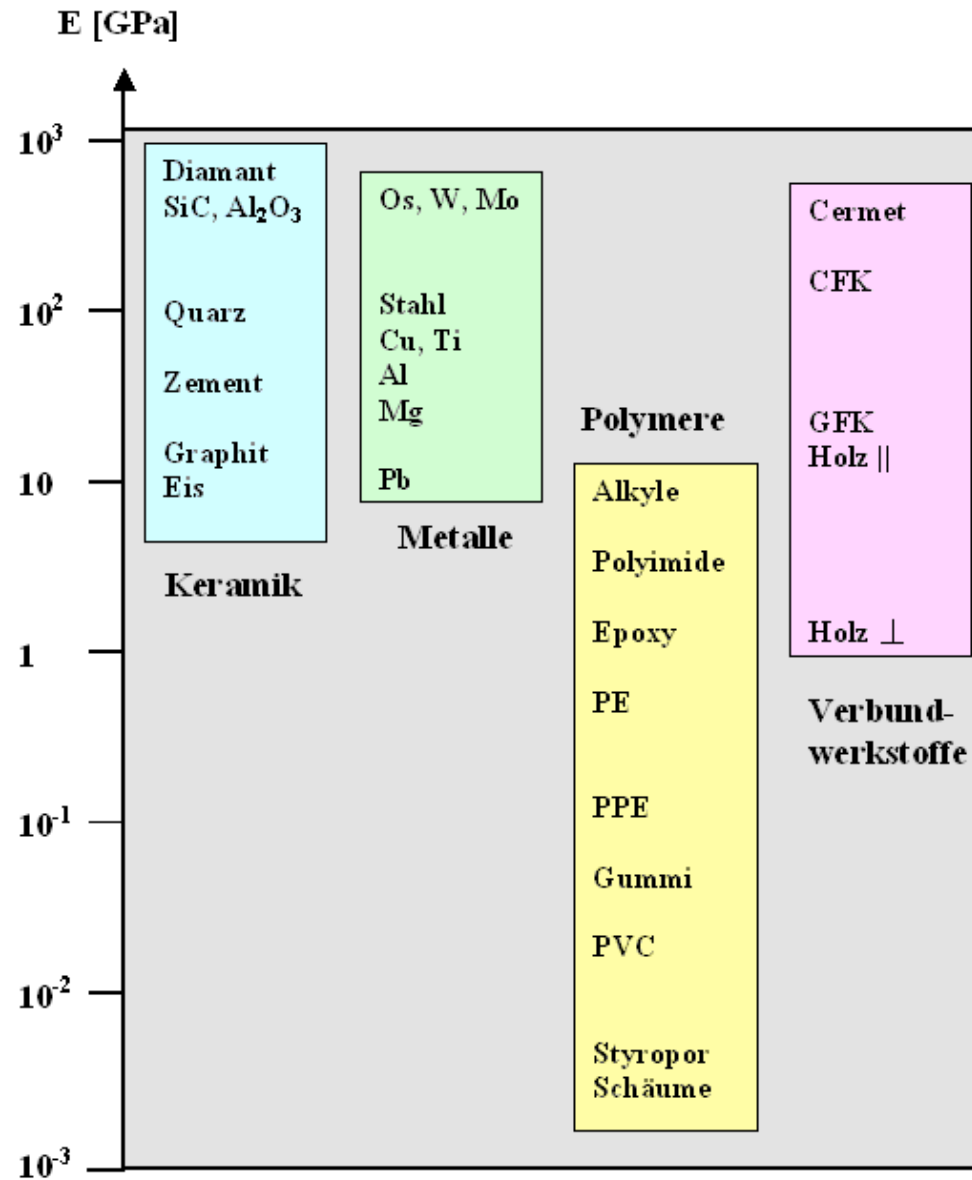
Small Forces

Dynamic Force Microscopy

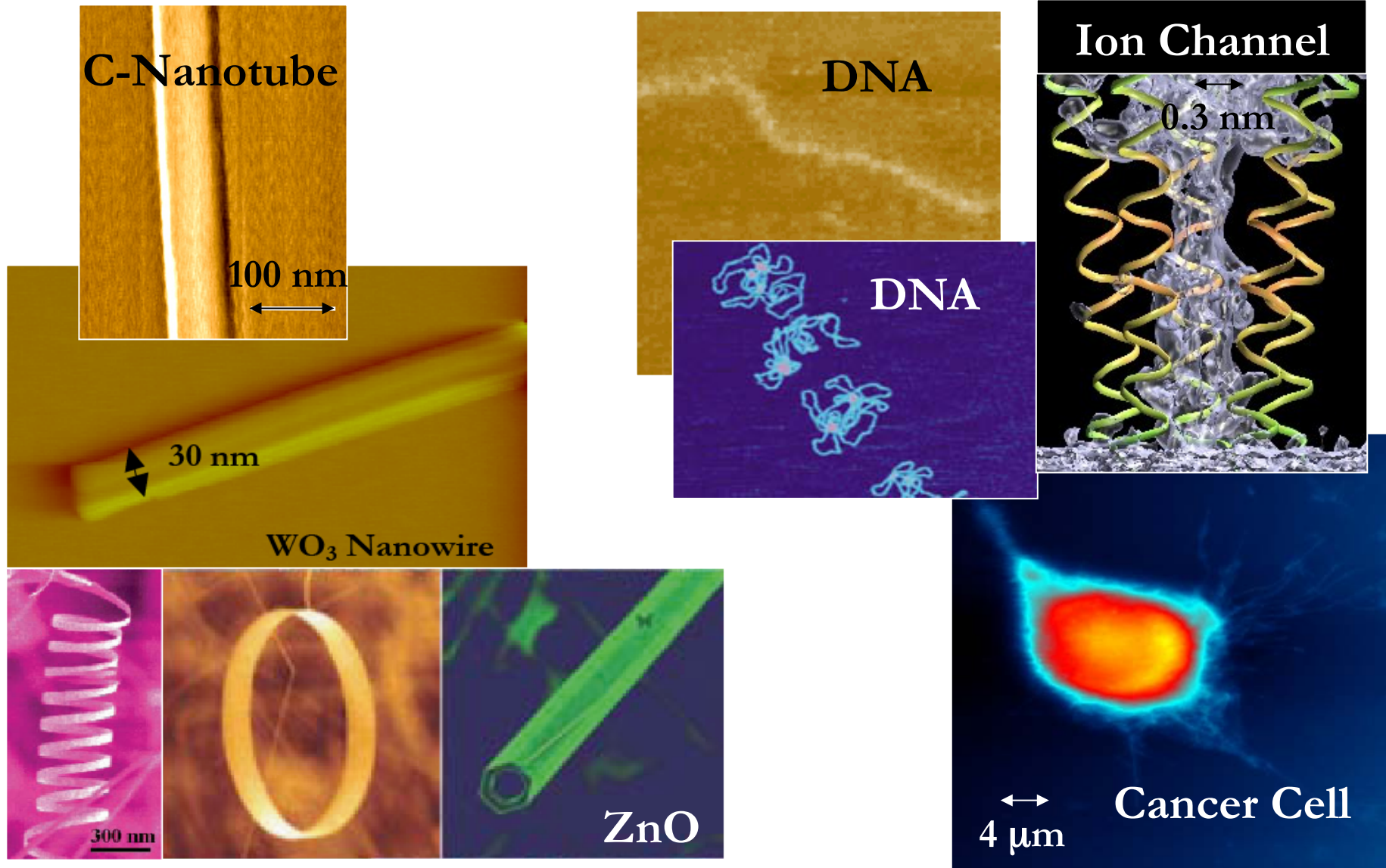
Mechanical detection of magnetic resonance

Superlubricity

Youngs modulus E

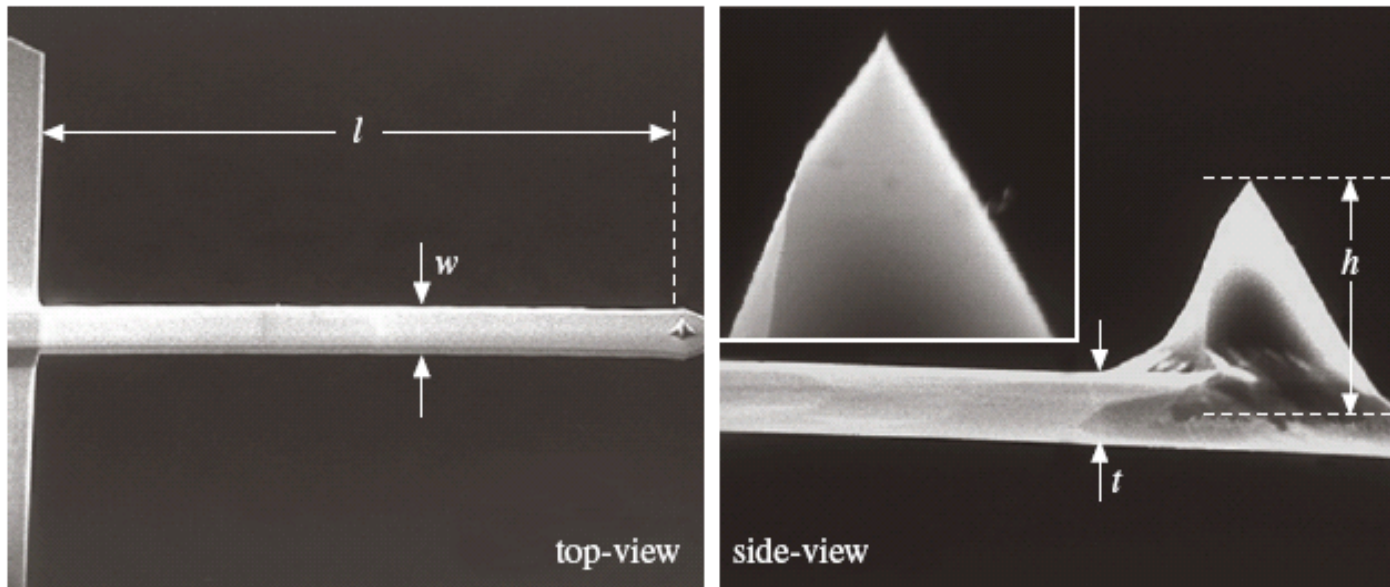


Why NanoMechanics ?

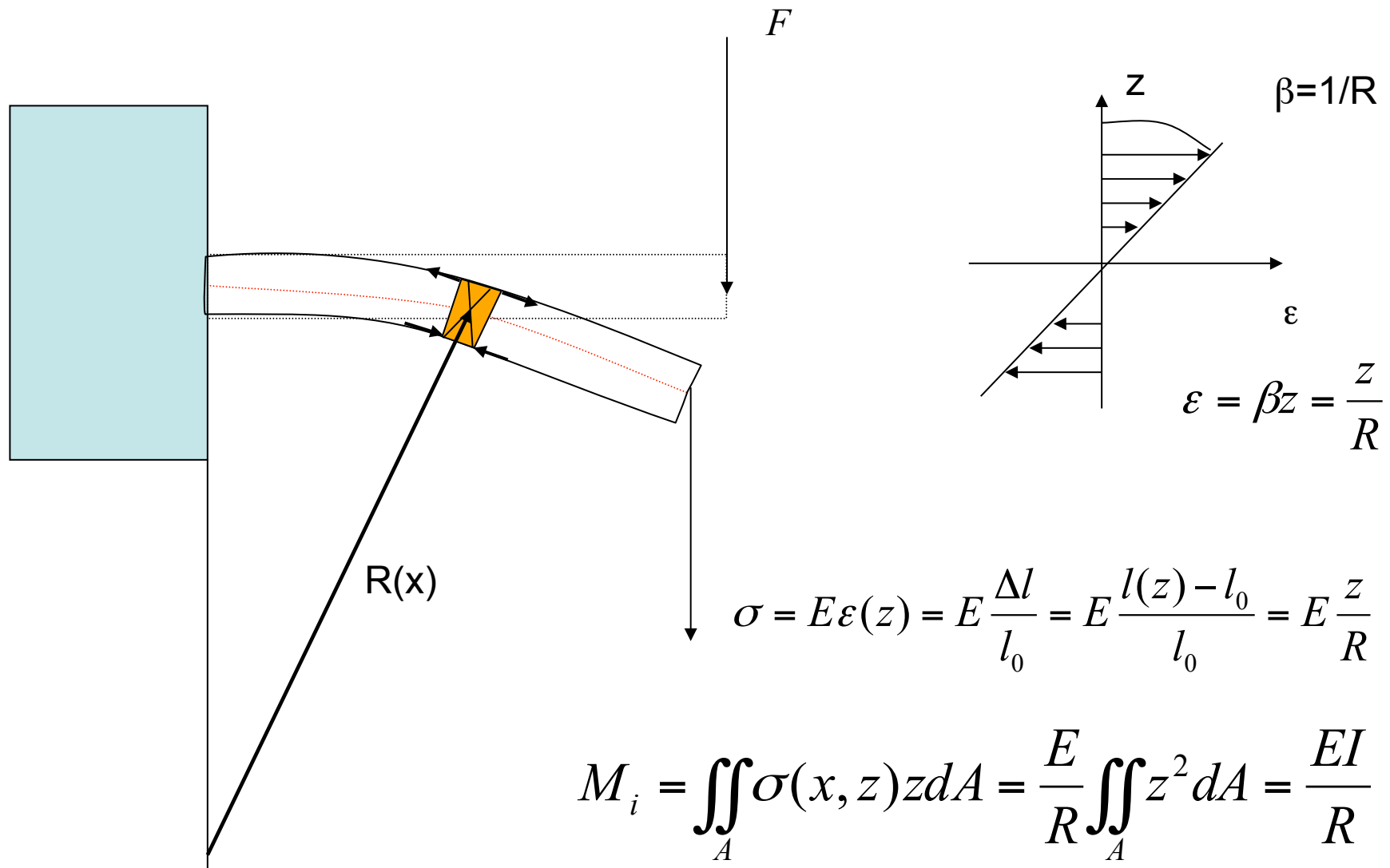


Cantilever

- Cantilever width w , thickness t and length l , tip height: from **SEM** pictures



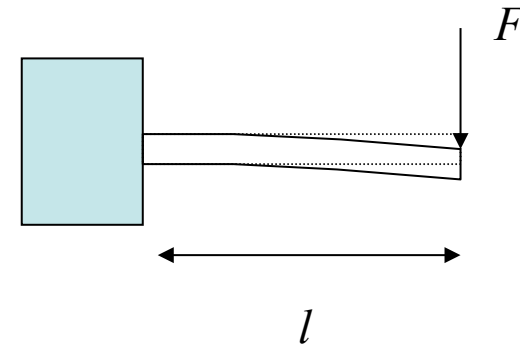
Deformations of beams



Deformations of beams

Flexure of Beams (Euler-Bernoulli-Theory)

$$\frac{1}{R} = -\frac{M_o}{EI} \quad I = \int_A z^2 dA$$



with $\frac{1}{R} \approx \frac{\partial^2 u}{\partial x^2} \Rightarrow \frac{\partial^2 u}{\partial x^2} = -\frac{M_o}{EI}$

with $M_o = F(l-x) \Rightarrow \frac{\partial^2 u}{\partial x^2} = \frac{F}{EI}(l-x)$

R: Radius of curvature
M: Torsional moment
E: Youngs modulus
I: Polar moment of inertia
(Flächenträgheitsmoment)
F: Force

$u(0)=0; u'(0)=0: \Rightarrow u(x) = \frac{F}{EI} \left(\frac{lx^2}{2} - \frac{x^3}{6} \right)$

Spring constant of a cantilever

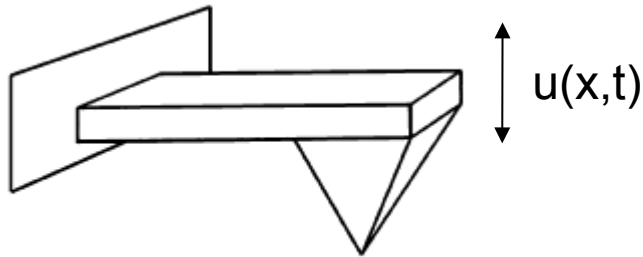
$$k = \frac{F}{u(l)} = \frac{EI}{\left(\frac{l^3}{2} - \frac{l^3}{6} \right)} = \frac{3EI}{l^3}$$

Rectangular cantilever:

$$I = wt^3/12$$

$$k = \frac{E}{4} \frac{wt^3}{L^3}$$

Cantilever dynamics



$$EI \frac{\partial^4 u(x,t)}{\partial x^4} + \mu \frac{\partial^2 u}{\partial t^2} = F(x,t)$$

E: Youngs Modulus

I: Moment of Inertia

μ : mass per unit length

F: Force

$$EI \frac{\partial^4 u(x,t)}{\partial x^4} + \mu \frac{\partial^2 u}{\partial t^2} + \gamma \frac{\partial u}{\partial t} = F(x,t)$$

γ : hydrodynamic coefficient

Cantilever dynamics: Free vibrations

$$\omega_i = \alpha_i^2 \sqrt{\frac{EI}{\mu}}$$

Rectangular cantilever:

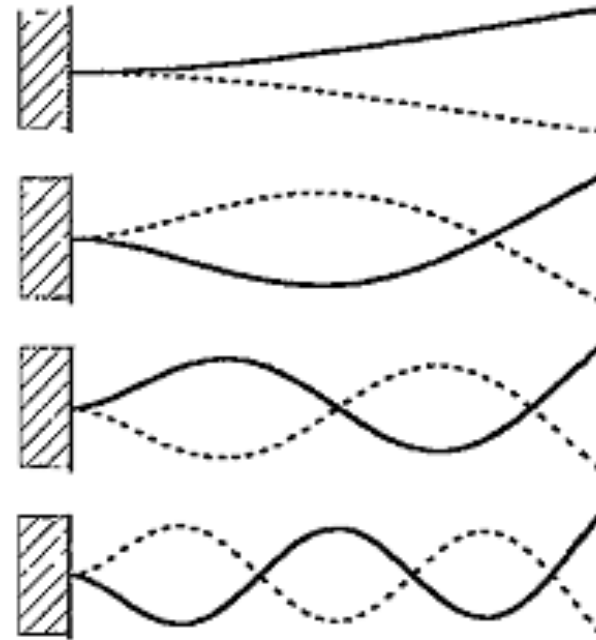
$$I = wt^3/12$$

$$\mu = \rho A = \rho wt$$

$$\omega_i = \alpha_i^2 t \sqrt{\frac{E}{12\rho}}$$

$$\alpha_1 l = 1.875, \alpha_2 l = 4.694, \alpha_3 l = 7.855, \alpha_4 l = 10.996 \dots$$

$$\text{Roots of } \cos(\alpha_n l) \cosh(\alpha_n l) + 1 = 0$$

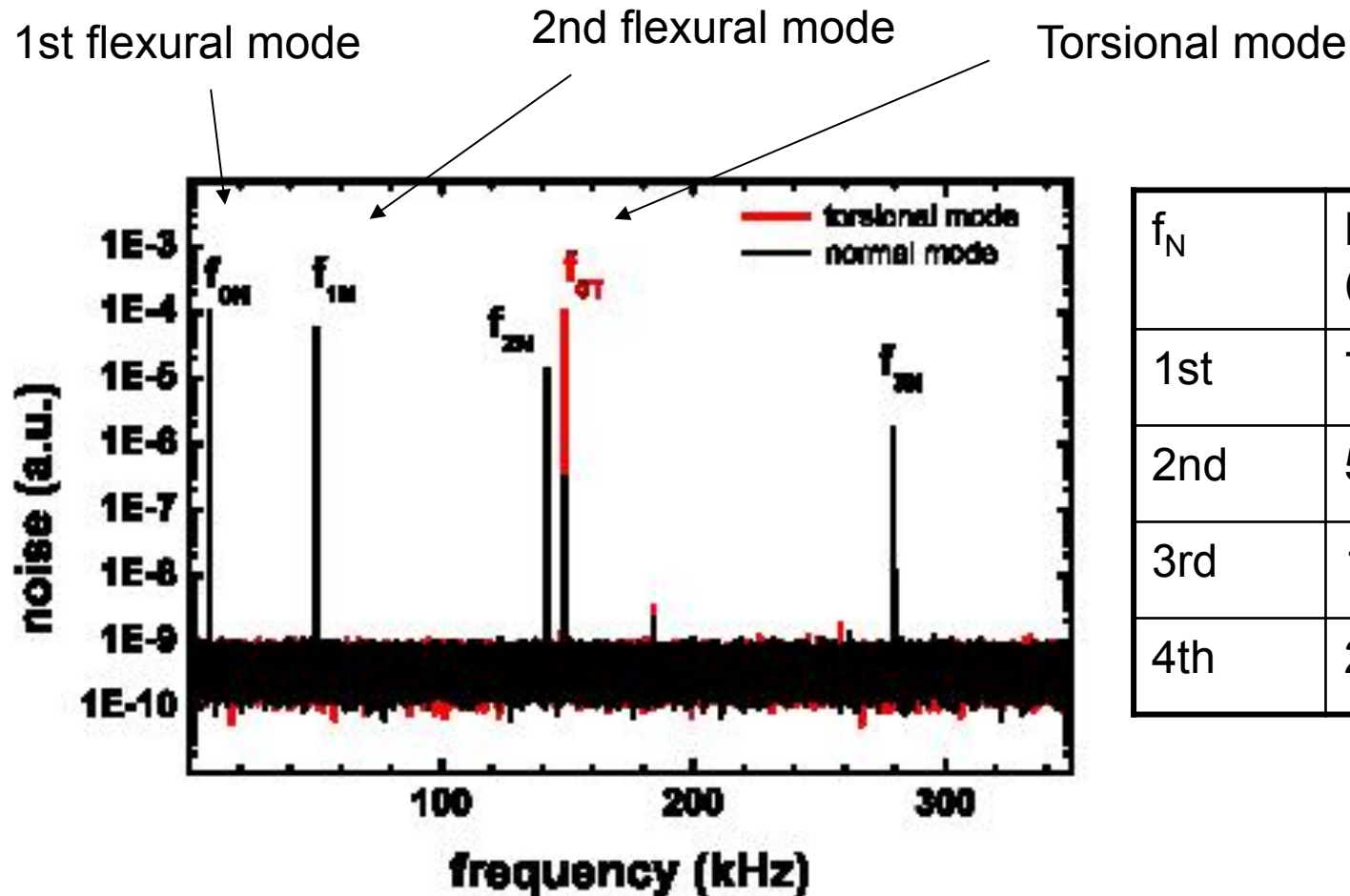


Silicon:

$$E = 1.69 \times 10^{11} \text{ N/m}^2$$

$$\rho = 2.33 \times 10^3 \text{ kg/m}^3$$

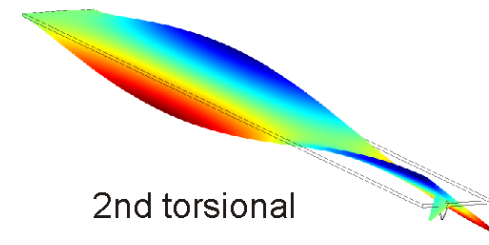
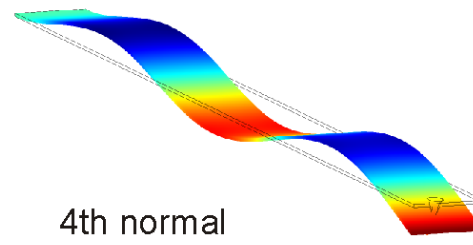
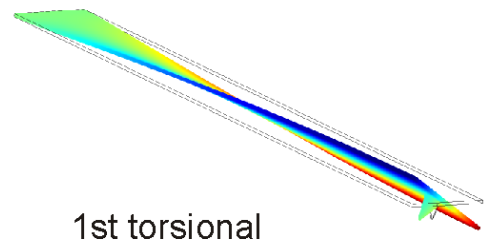
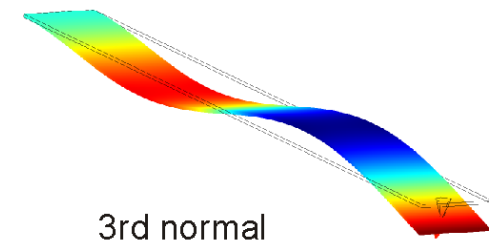
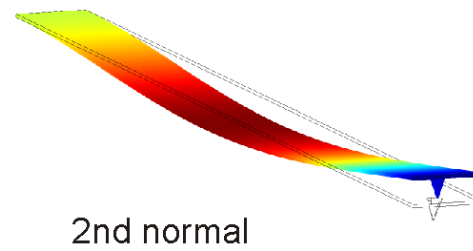
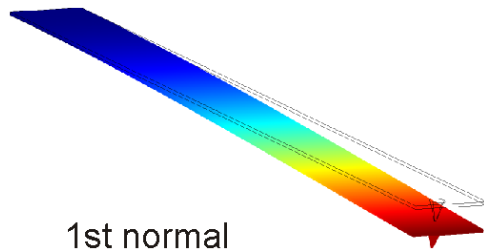
Thermal noise spectrum of a free cantilever



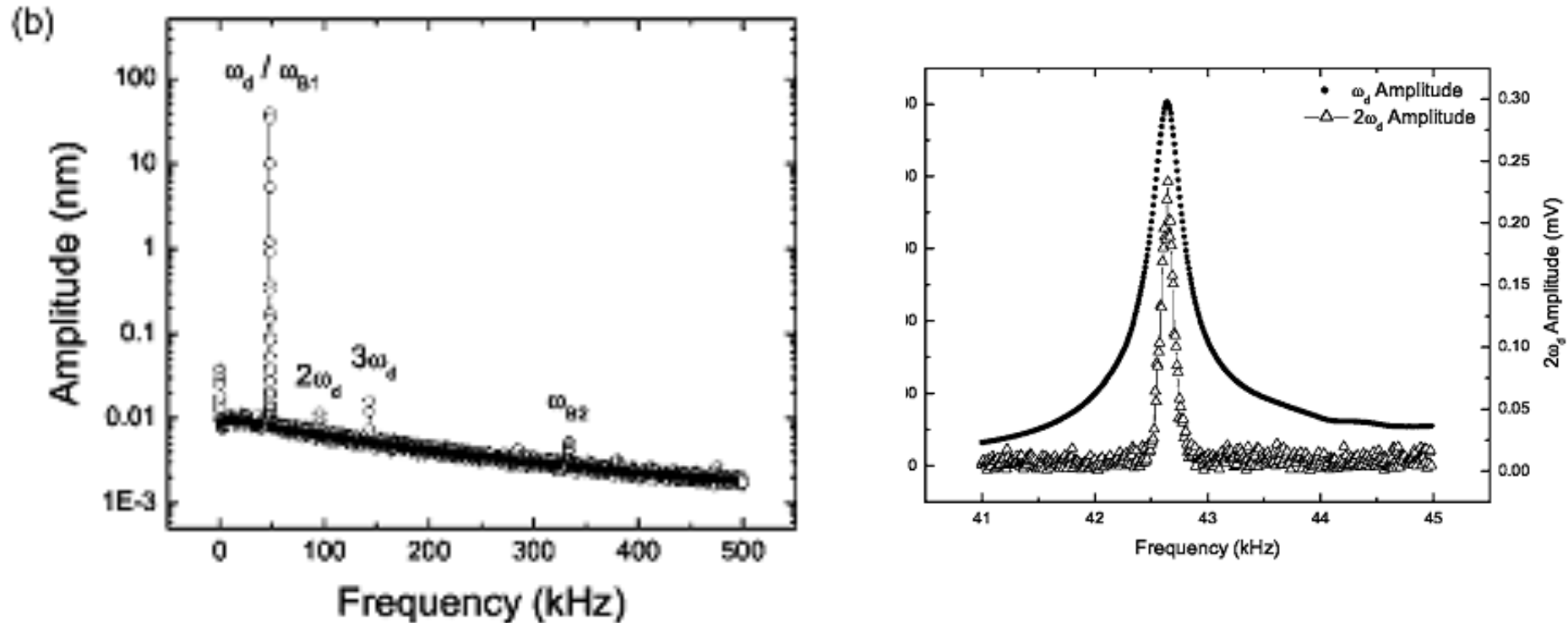
f_N	Exp. (kHz)	Model (kHz)
1st	7.97	
2nd	50.44	49.97
3rd	141.97	139.79
4th	279.62	274.09

The ratio between first and second flexural resonance frequency is about $(\alpha_2/\alpha_1)^2=6.26$ (depends on detailed geometry) Exp: 6-7

Oscillations modes of a free cantilever



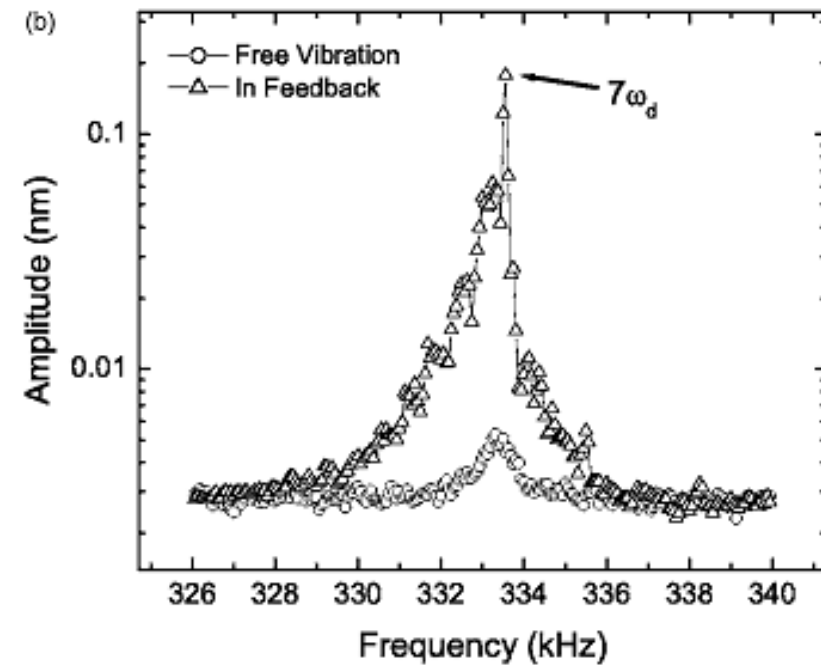
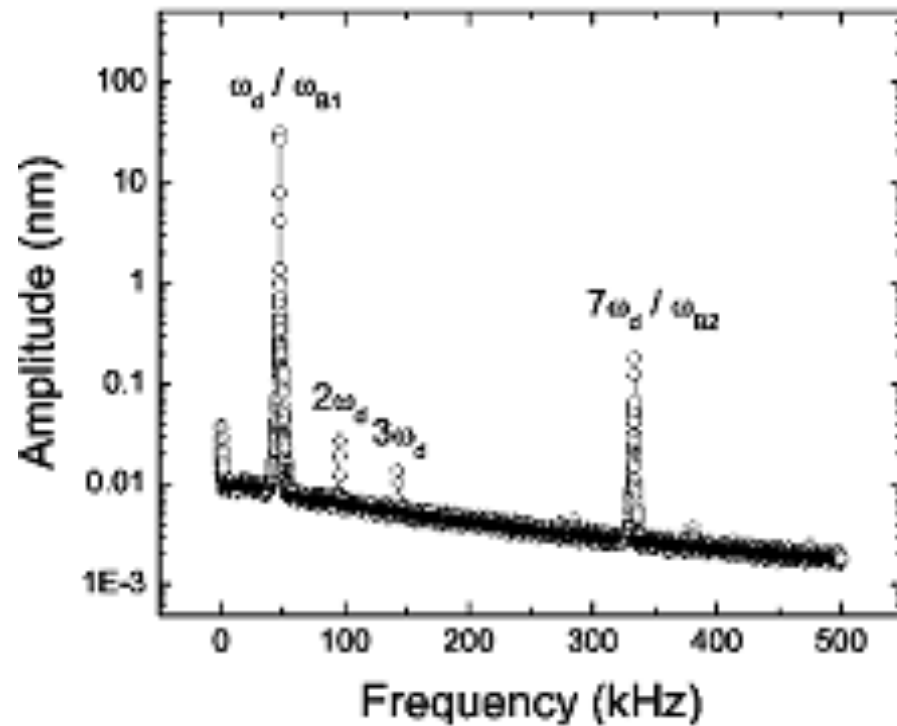
Measure non-linearities by the use of higher harmonic $n\omega_d$



Higher harmonics are sensitive to tip-sample interactions (e.g. van der Waals forces)

S. Crittenden, A. Raman and R. Reifenberger, Phys. Rev. B 72, 235422 (2005)

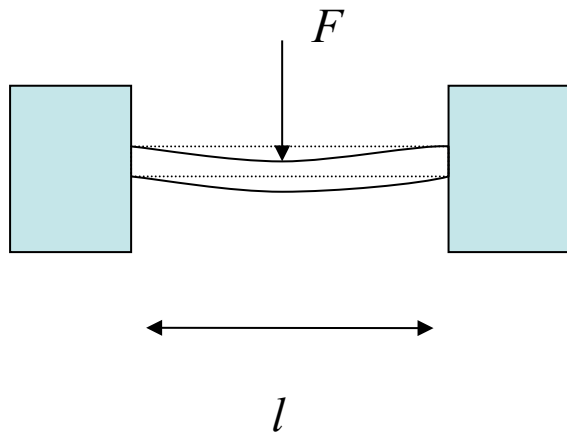
Enhance non-linearities by coupling higher harmonics to flexural modes



In the case of this cantilever: $7\omega_d \approx \omega_{B2}$; 7th harmonic coincides with 2nd flexural mode

S. Crittenden, A. Raman and R. Reifenberger, Phys. Rev. B 72, 235422 (2005)

Deflection of doubly-clamped beams



$$\frac{\partial^2 u}{\partial x^2} = \frac{Fl}{2EI} \left(\frac{x}{l} - \frac{1}{4} \right)$$

$$u(x) = \frac{Fl}{2EI} \left(\frac{x^3}{6l} - \frac{x^2}{8} \right)$$

$$u(0)=0; u'(0)=0;$$
$$u(l)=0; u'(l)=0;$$

$$u\left(\frac{l}{2}\right) = -\frac{F}{EI} \frac{l^3}{192}$$

Vibrations of doubly-clamped beam

$$EI \frac{\partial^4 u(x,t)}{\partial x^4} = -\mu \frac{\partial^2 u(x,t)}{\partial t^2}$$

Assuming a harmonic time dependence: $u(x,t)=u(x)e^{i\omega t}$

$$\frac{\partial^4 u(x)}{\partial x^4} = -\frac{\mu}{EI} \omega^2 u(x)$$

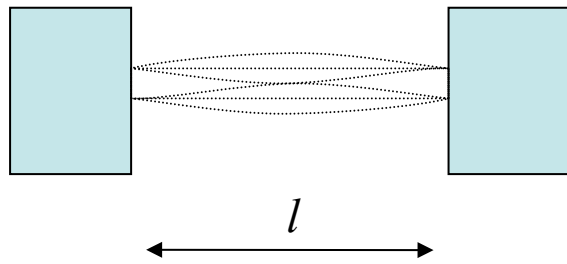
Solution: $u(x) = Ae^{i\beta x} + Be^{-i\beta x} + Ce^{\beta x} + De^{-\beta x}$

where $\beta = \left(\frac{\mu}{EI}\right)^{1/4} \omega^{1/2}$

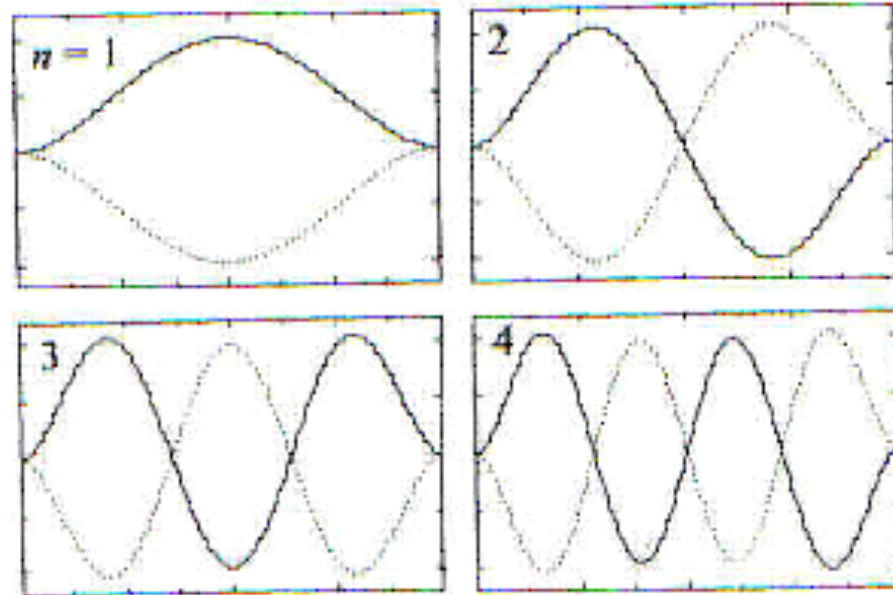
Boundary conditions: $u(0)=u(l)=u'(0)=u'(l)=0$

$$\Rightarrow \cos(\beta_n l) \cosh(\beta_n l) - 1 = 0 \Rightarrow \beta_1 l = 4.73, \beta_2 l = 7.8532, \beta_3 l = 10.9956, \beta_4 l = 14.1372 \dots$$

Vibrations of doubly-clamped beam



$$\omega_i = \beta_i^2 \sqrt{\frac{EI}{\mu}}$$



$$\beta_1 l = 4.73, \beta_2 l = 7.8532, \beta_3 l = 10.9956, \beta_4 l = 14.1372 \dots \quad \mu = \rho A$$

Rectangular cantilever:

$$I = \frac{wt^3}{12}$$

Tube with inner and outer radii:

$$I = \pi \frac{r_2^4 - r_1^4}{4}$$

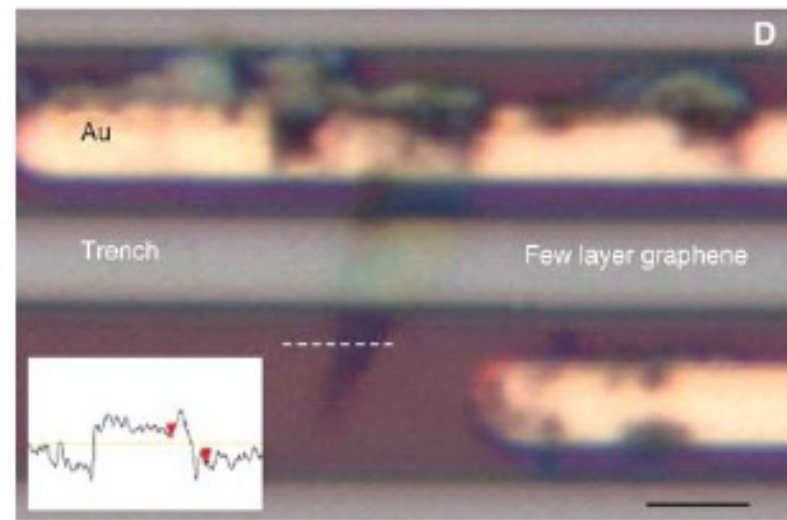
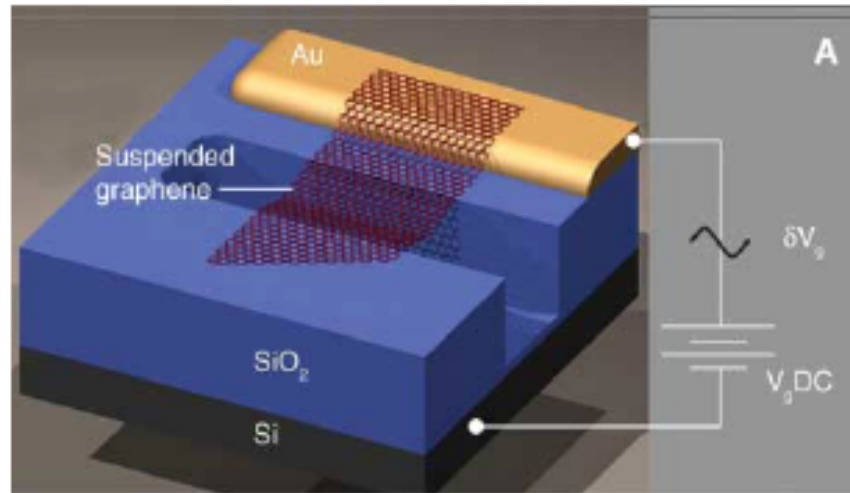
Short version:

Cantilever:
$$f_1 = \frac{1}{2\pi} \left(\frac{1.875}{l} \right)^2 \sqrt{\frac{EI}{\mu}} = \frac{1.875^2}{2\pi\sqrt{12}} \sqrt{\frac{E}{\rho}} \frac{t}{l^2} = 0.162 \sqrt{\frac{E}{\rho}} \frac{t}{l^2}$$

Doubly clamped beam:

$$f_1 = \frac{1}{2\pi} \left(\frac{4.73}{l} \right)^2 \sqrt{\frac{EI}{\mu}} = \frac{4.73^2}{2\pi\sqrt{12}} \sqrt{\frac{E}{\rho}} \frac{t}{l^2} = 1.03 \sqrt{\frac{E}{\rho}} \frac{t}{l^2}$$

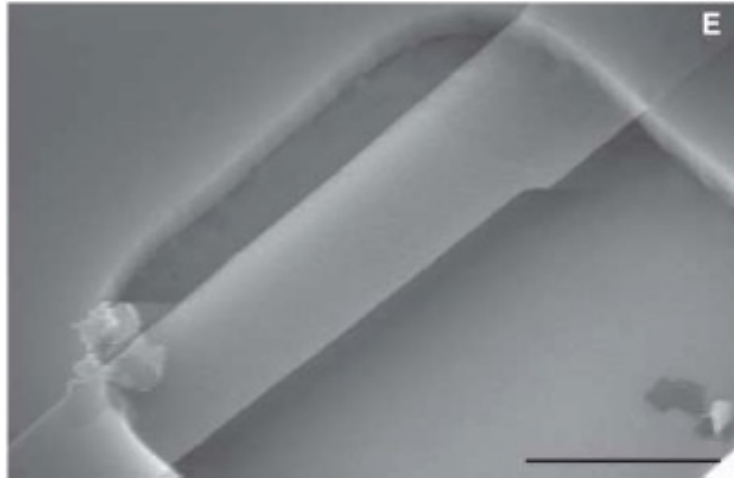
Electromechanical Resonators from Graphene Sheets



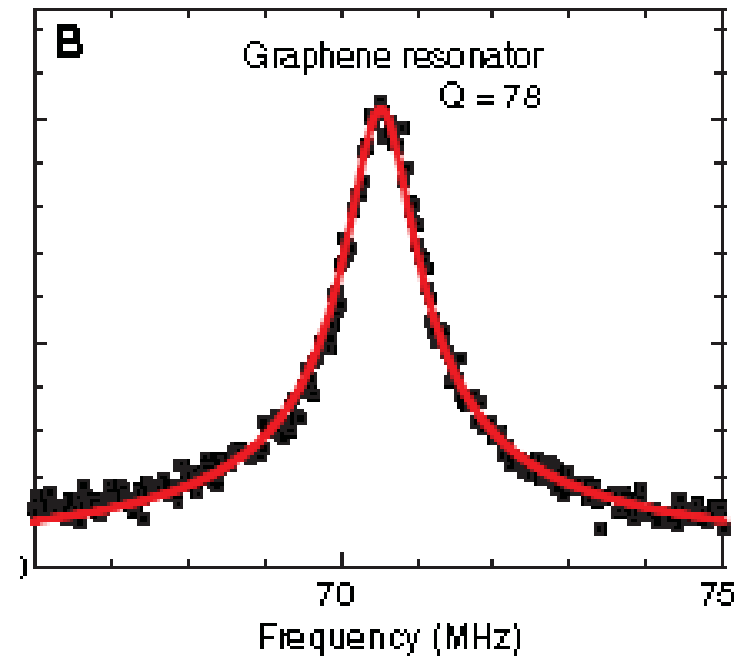
Suited for mass, force and charge sensors

J.S. Bunch, P.L. McEuen, Science 315, 490 (2007)

Electromechanical Resonators from Graphene Sheets



Few (2) layer graphene resonator



J.S. Bunch, P.L. McEuen, Science 315, 490 (2007)

Electromechanical Resonators from Graphene Sheets

$$f = \left(\left(A \sqrt{\frac{E}{\rho}} \frac{t}{l^2} \right)^2 + A^2 0.57 \frac{T}{\rho L^2 w t} \right)^{1/2}$$

Cantilever: $A=0.162$

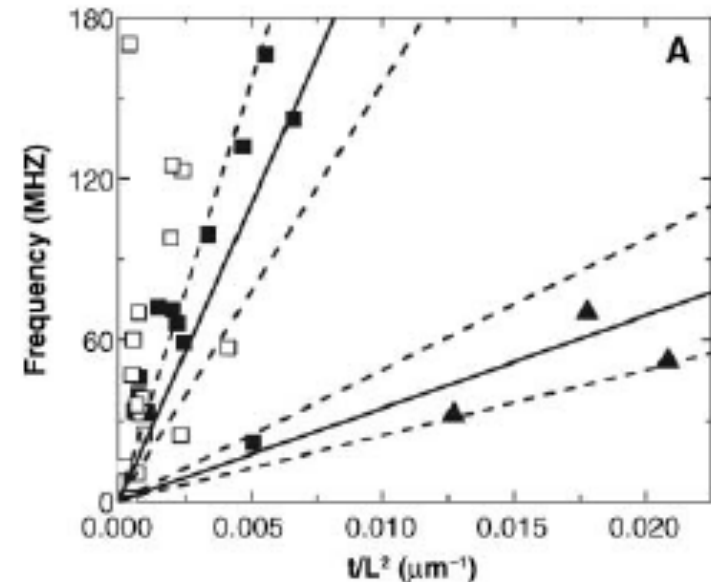
Doubly clamped beam: $A=1.03$

T : residual Tension (N)

$t < 0.7 \text{ nm}$: higher frequencies due to tension

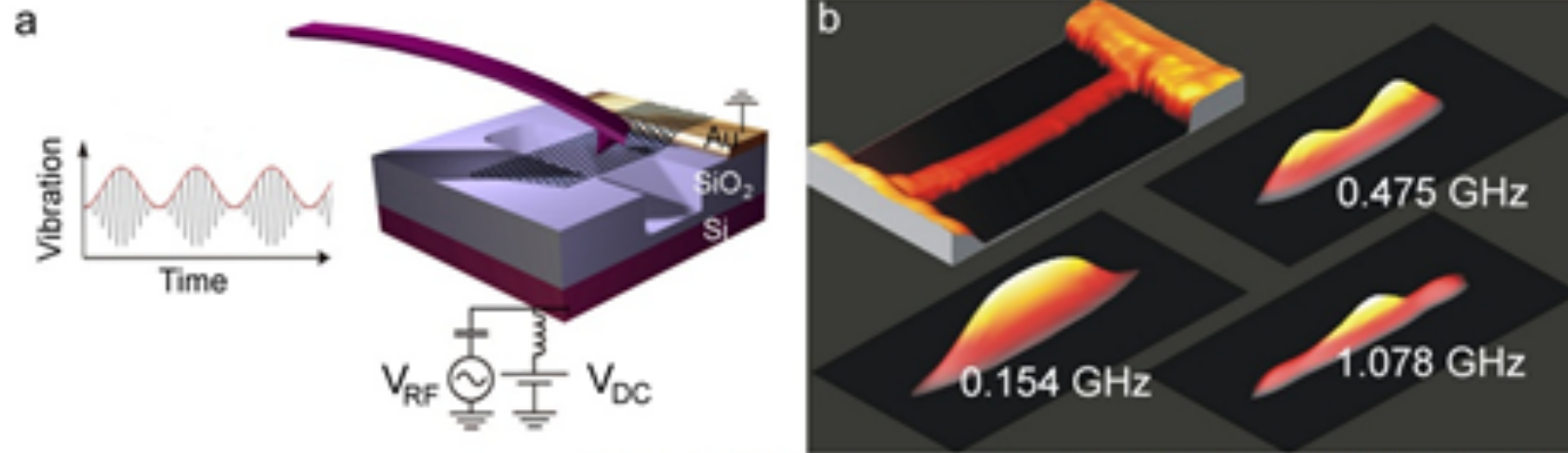
$t > 0.7 \text{ nm}$: $f \approx t / l^2$

$E=1 \text{ TPa}$ similar to nanotubes



J.S. Bunch, P.L. McEuen, Science 315, 490 (2007)

Bimodal AFM imaging of NEMS oscillations



A. San Paulo, A. Bachtold, PRL 99, 085501 (2007); Nano Lett. 8, 1399 (2008).

Swiss Cheese Method: Elasticity of Nanotubes

$$\delta = \delta_B + \delta_S = FL^3/192EI + f_s FL/4GA,$$

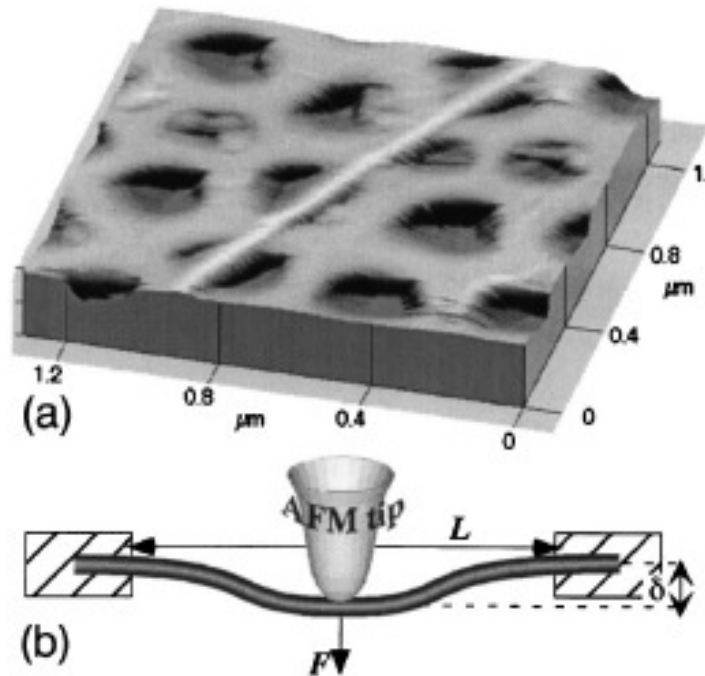


TABLE I. Diameter D , suspended length L , slope of the force-deflection curve $\Delta\delta/\Delta F$, as well as the calculated reduced modulus E_r and shear modulus G for the SWNT ropes studied in this work.

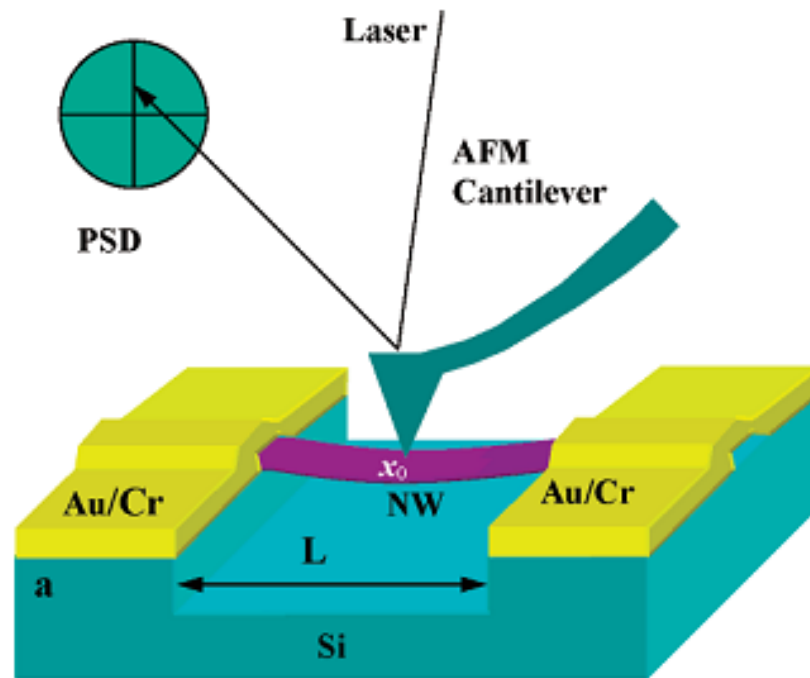
D (nm) ±0.5 nm	L (nm) ±10%	$\Delta\delta/\Delta F$ (m/N)	E_r (GPa) ±50%	G (GPa) ±50%
3.0	100	1.0	1310	...
3.0	140	4.0	899	...
4.5	285	9.3	642	...
4.5	180	3.0	503	6.5
6.0	200	1.8	369	2.9
6.0	230	3.0	332	1.7
9.0	180	0.5	189	2.3
13.5	360	0.5	298	2.8
13.5	360	1.0	149	0.9
20.0	370	0.5	67	0.7

$$\Rightarrow E_{\max} = 1310 \text{ GPa}, G = 6.5 \text{ GPa}$$

⇒ Bending plus shear of ropes

J.P. Salvetat et al., *Phys. Rev. Lett.* **82**, 944 (1999)

Elasticity of nanowires

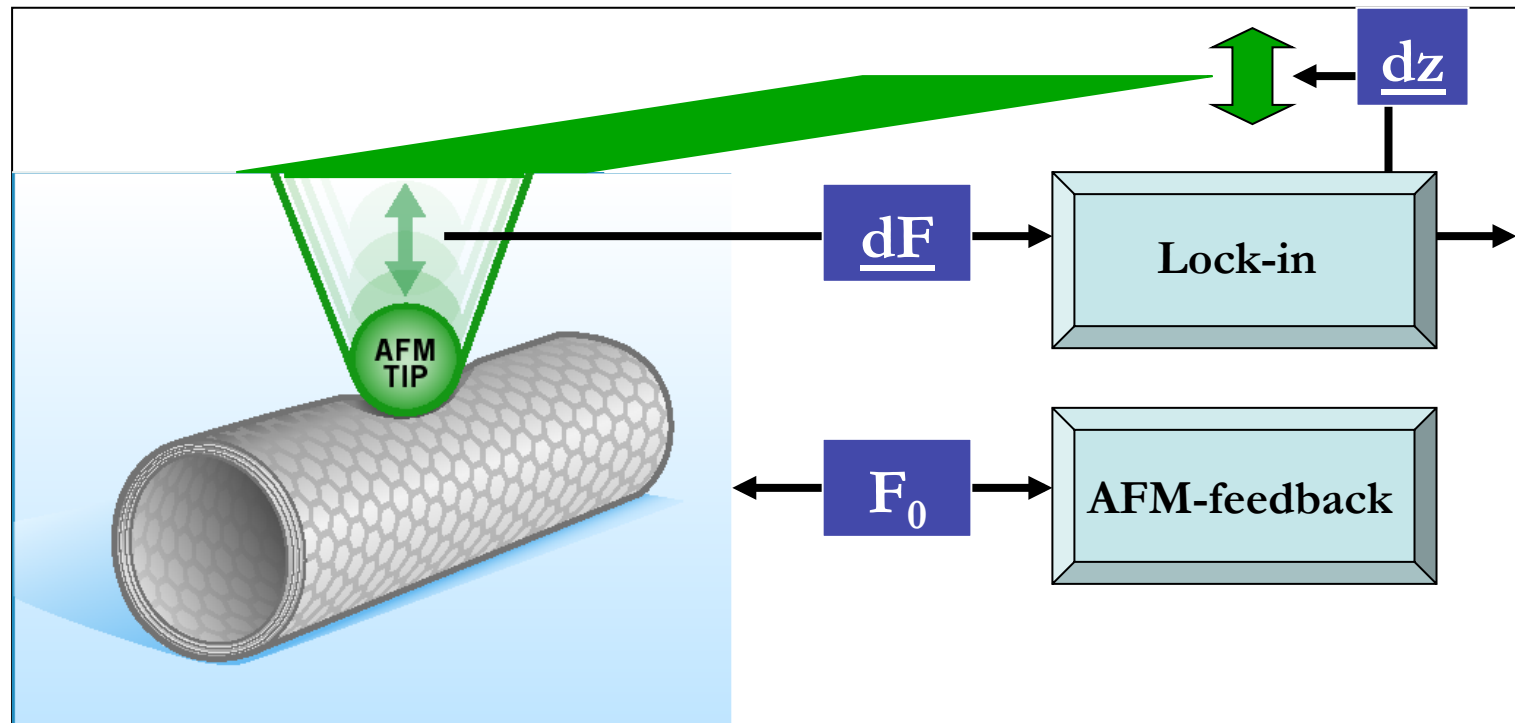


$$E = \frac{f}{\Delta Z} \frac{L^3}{192I}$$

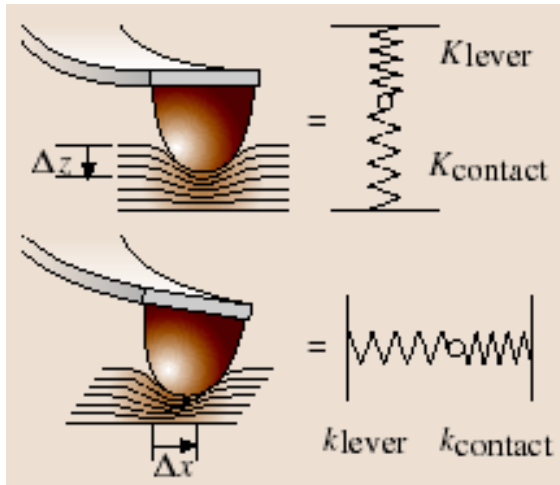
ZnS-Nanowires: $E=54\text{GPa}$

Xiong et al., *Nanoletters* **6**,1904 (2006)

Probing radial elasticity of MWNT



Normal contact stiffness



R. W. Carpick, D. F. Ogletree, M. Salmeron,
Appl. Phys. Lett. **70** 1548 (1997)

$$\left(\frac{dF}{d(z_{lever} + z_{indent})} \right)_{F=F_0} = k_{tot}(F_0) = \left(\frac{1}{k_{lever}} + \frac{1}{k_{cont}(F_0)} \right)^{-1}$$

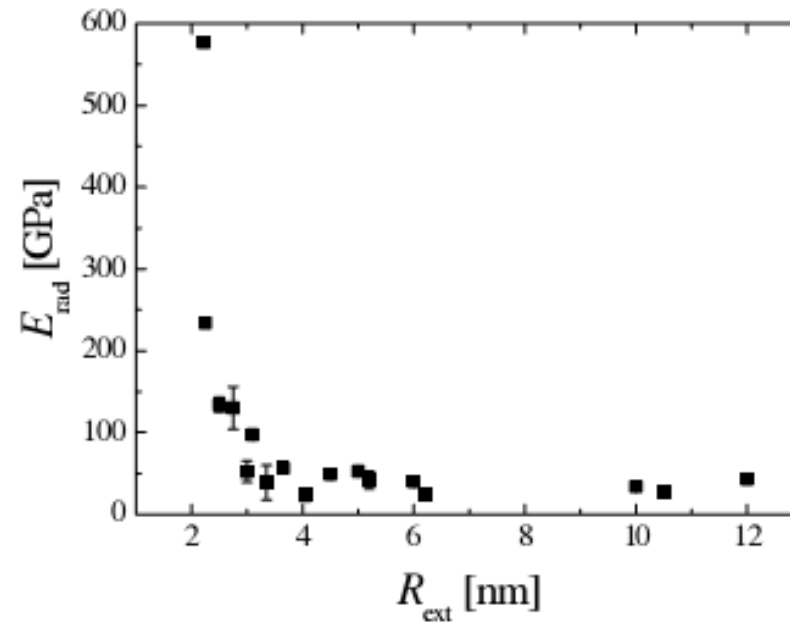
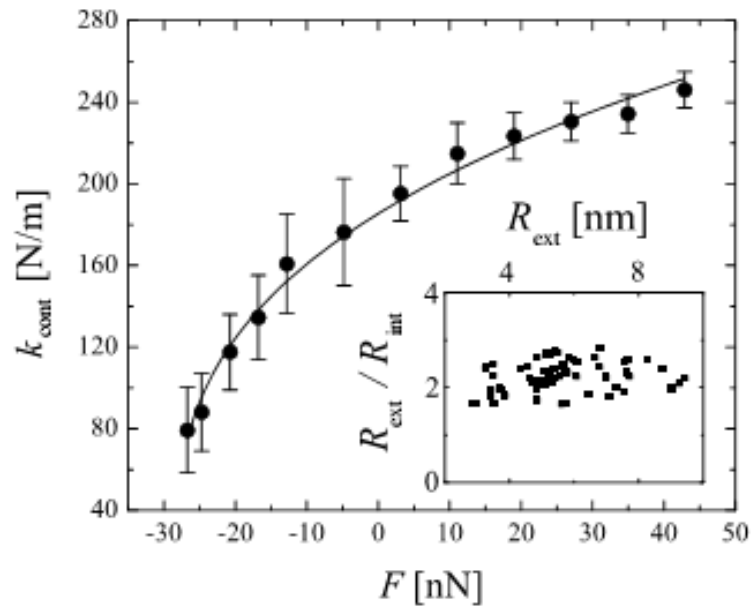
$$dF/dz_{tot}(F) \Rightarrow k_{cont}(F)$$

$$(1/k_{cont}(F)) dF = dz_{indent}$$

where z_{indent} is the indentation of the tip in the NT,

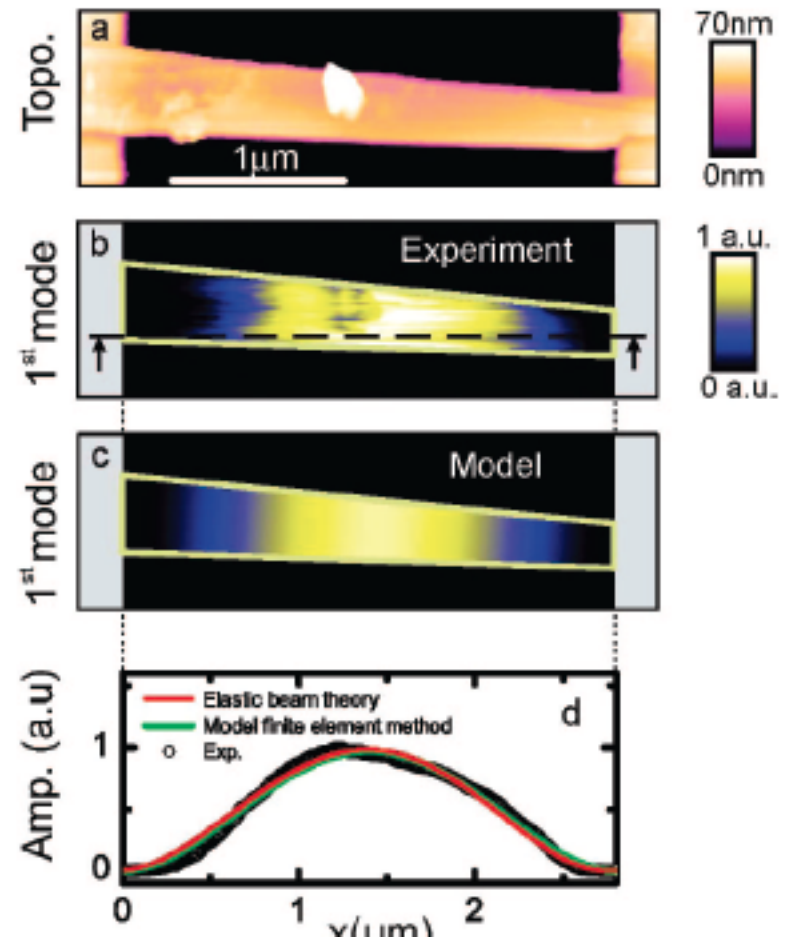
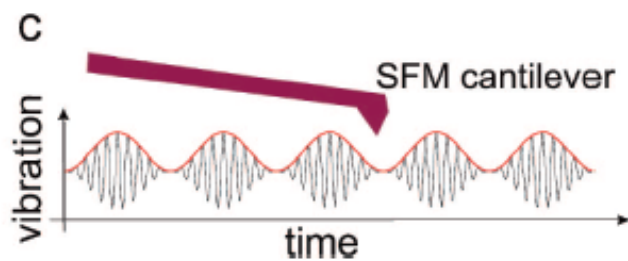
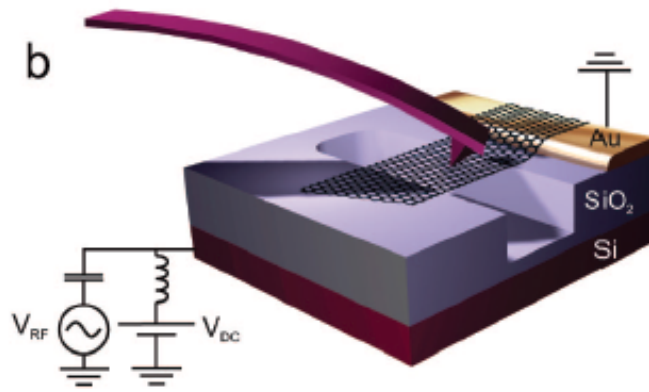
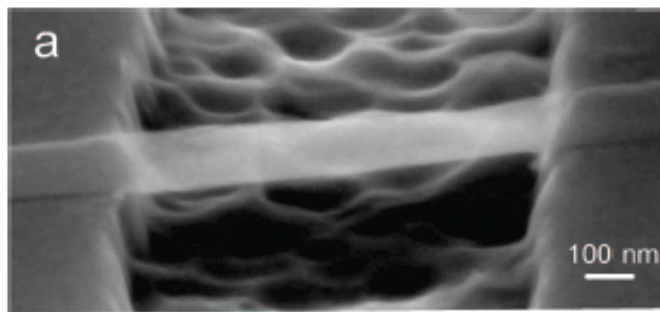
By integration we obtain $F(z_{indent})$ from the experimental $k_{cont}(F)$.

Contact stiffness of multiwalled Carbon nanotubes



Use of Hertz theory to extract E_{rad}

Imaging Graphene Resonators



Buckling of Graphene resonators

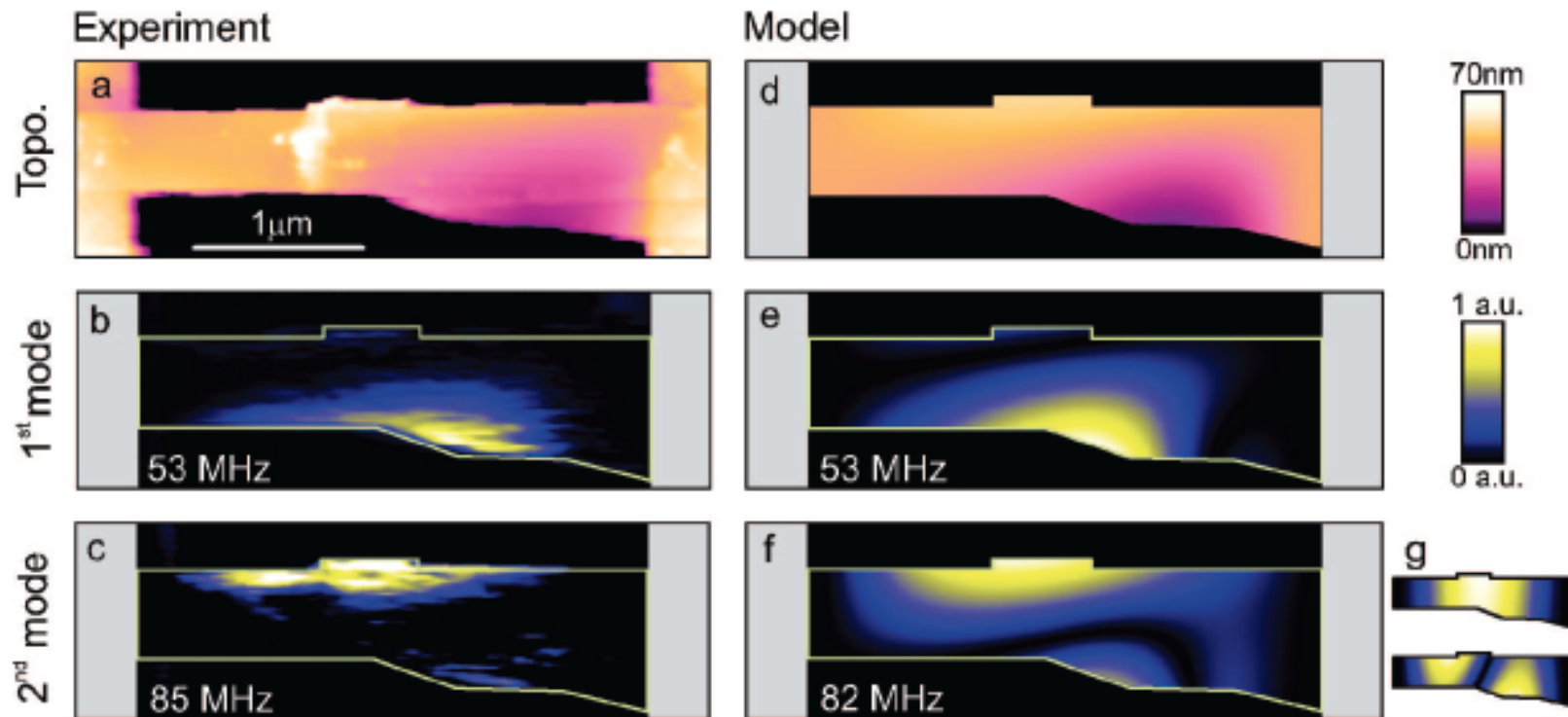
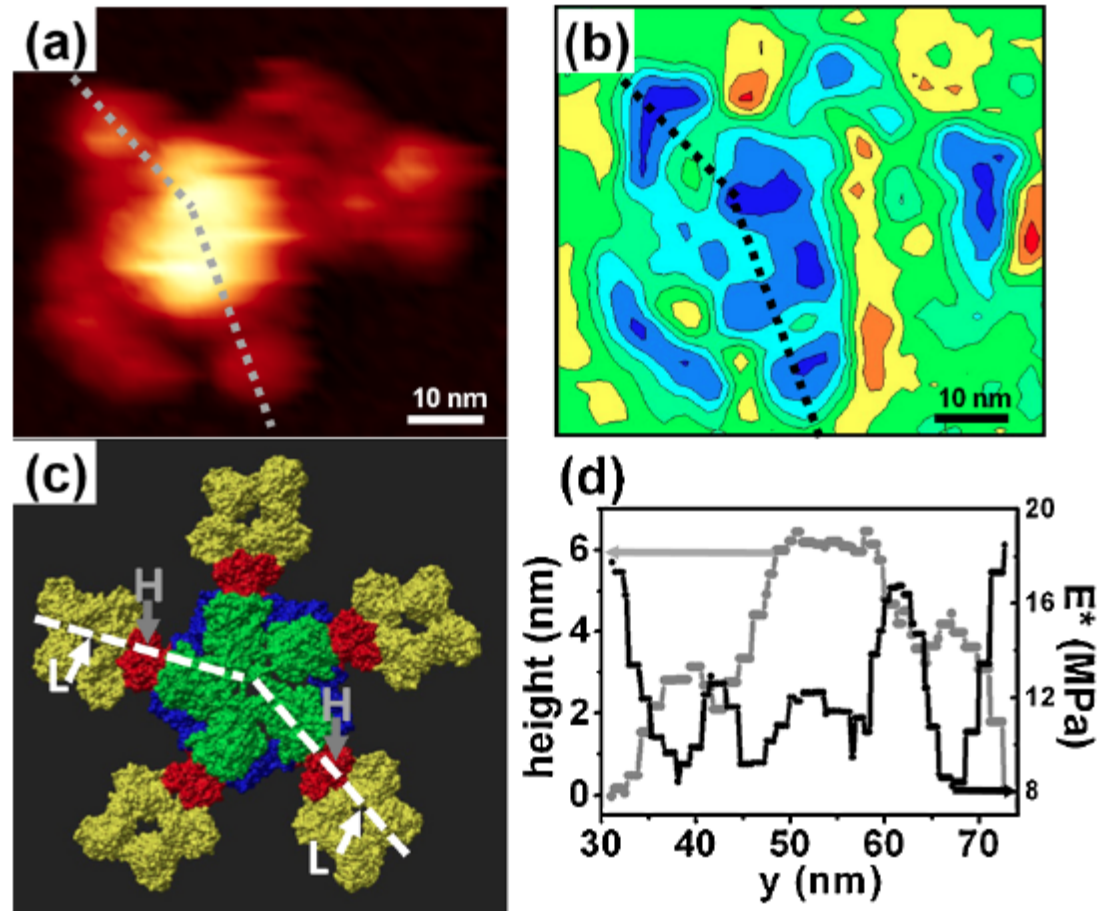


Figure 3. Graphene resonator with local buckling. (a) Measured topography. $t = 6$ nm, $l = 2.8$ μm , $w_{\text{min}} = 0.5$ μm , and $w_{\text{max}} = 0.8$ μm . The maximum out-of-plane displacement of the buckling is 37 nm. (b–c) Shape of the first and the second eigenmodes (raw data). $V_{\text{DC}} - \varphi = 3$ V and $V_{\text{RF}} = 40$ mV. The amplitude of vibration is in arbitrary units. (d) Topography obtained using FEM simulations on a stressed graphene sheet. The maximum displacement is 36 nm. See the text for the boundary conditions. (e–f) Shape of the first and the second eigenmodes using FEM simulations. (g) Shape of the two first eigenmodes using FEM simulations without any stress. The resonance frequencies are 17 and 46 MHz.

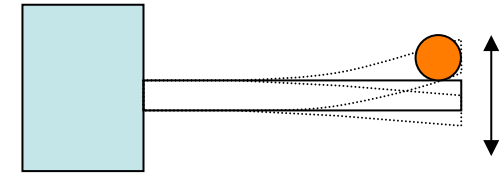
Local elasticity maps of antigene



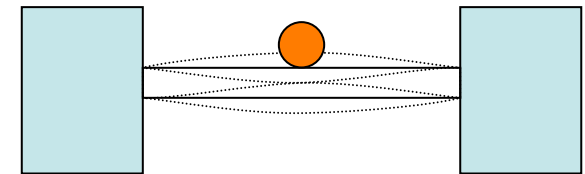
Topography and flexibility map of a single IgM antibody
(a) Bimodal AFM image (b) Flexibility map (c) structure (d) profiles
D. Martinez-Martin et al., *Phys.Rev. Lett.* 106, 125208 (2011).

Mass detection by frequency detection

$$f = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad \Rightarrow \quad \Delta f = \frac{\partial f}{\partial m} \Delta m = -\frac{1}{2} \frac{\sqrt{k}}{m^{3/2}} \Delta m$$



$$\Rightarrow \quad \frac{\Delta f}{f} = -\frac{1}{2} \frac{\sqrt{k}}{m^{3/2}} \frac{\Delta m}{\sqrt{\frac{k}{m}}} = -\frac{1}{2} \frac{\Delta m}{m}$$

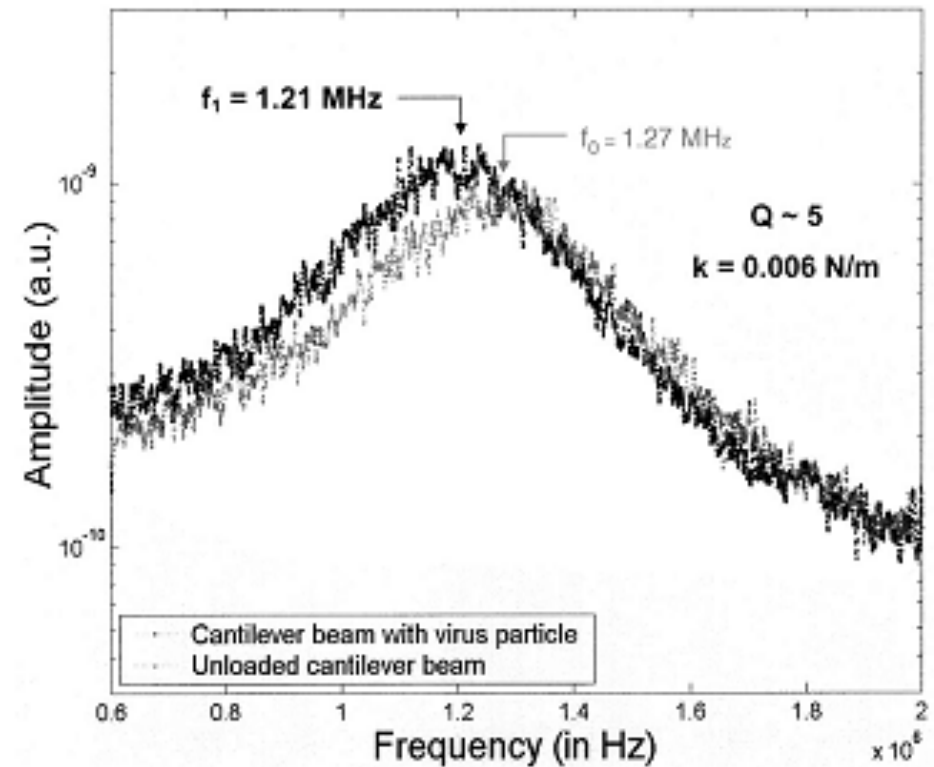
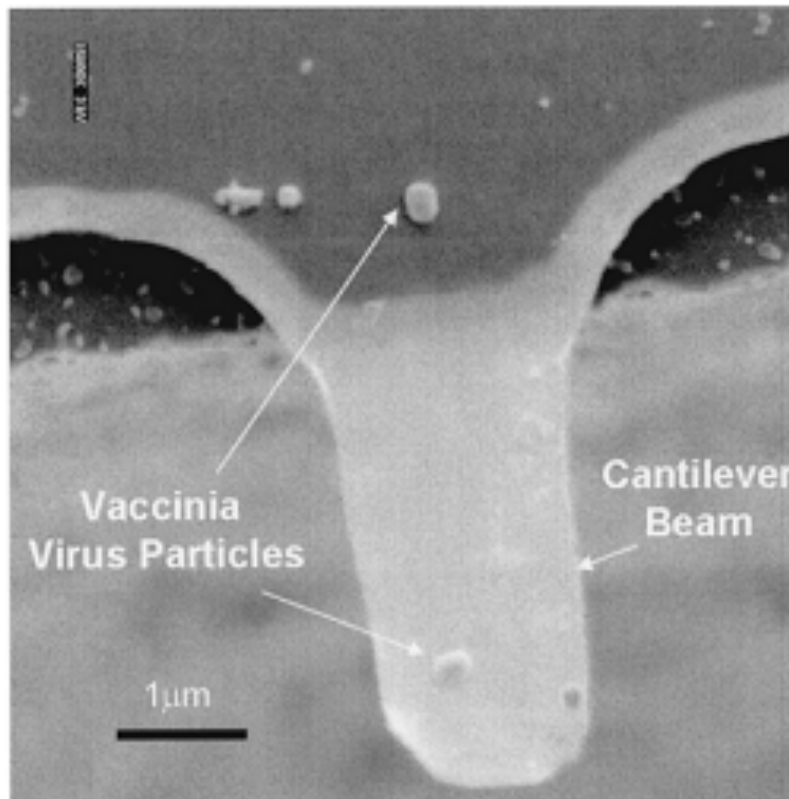


Typical Cantilever ($1 \times 10 \times 10 \mu\text{m}^3$) $\Rightarrow m = 2 \cdot 10^{-12} \text{kg}$

$\Rightarrow \Delta m = 4 \cdot 10^{-12} \text{kg} \cdot \Delta f / f$

\Rightarrow with $f = 137,5 \text{kHz}$; $\Delta f = 1 \text{mHz}$ $\Rightarrow \Delta m = 3 \cdot 10^{-20} \text{kg} = 3 \cdot 10^{-17} \text{g} = 30 \text{ag}$

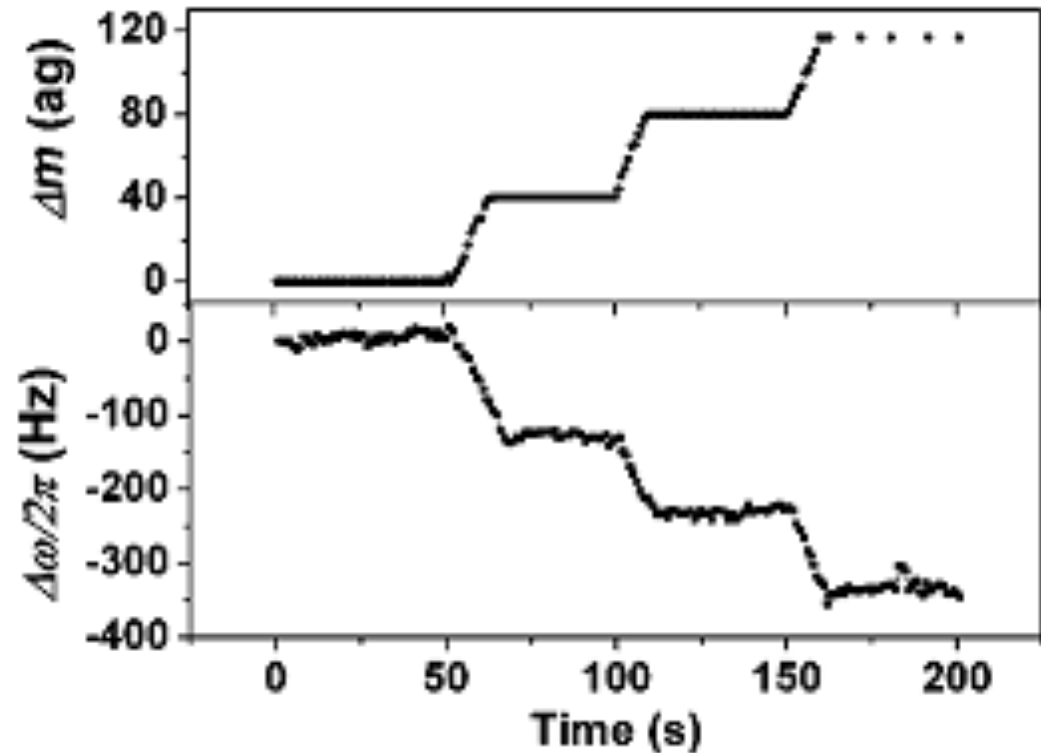
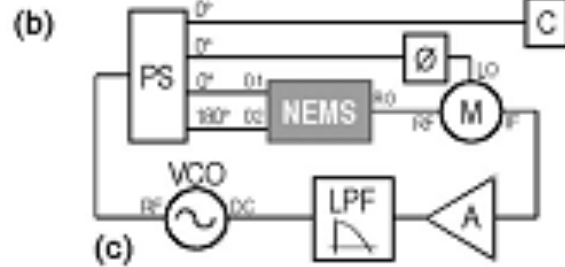
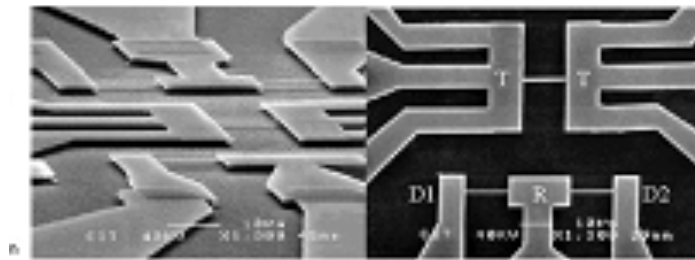
Single virus particle mass detection



$\Rightarrow 1 \text{ virus} = 9.5 \text{ fg}$

A. Gupta, D. Akin and R. Bashir, *Appl. Phys. Lett.* **84**, 1976 (2004)

Weighing single molecules?

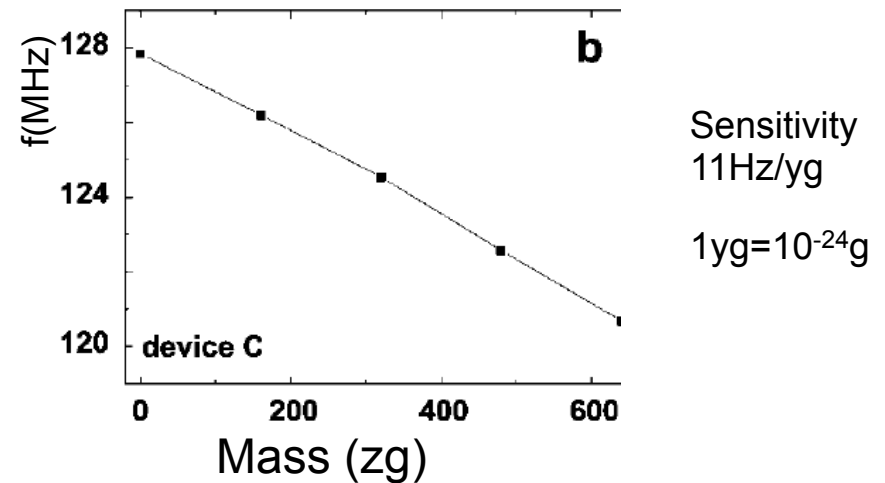
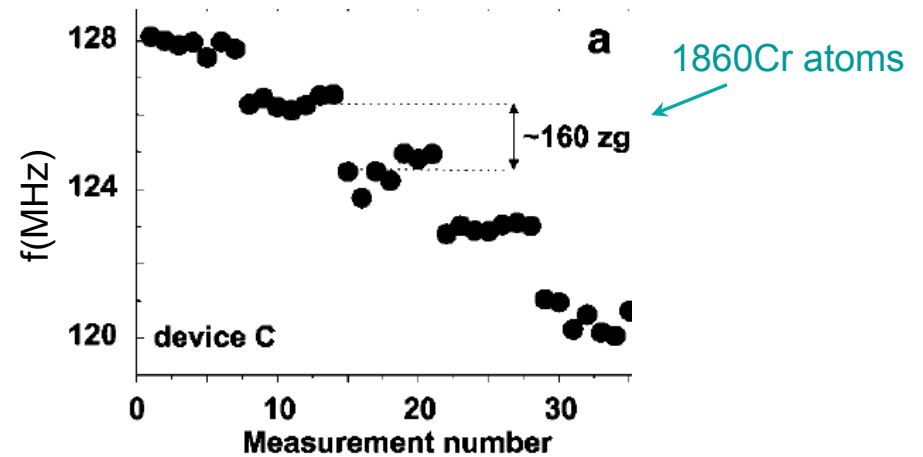
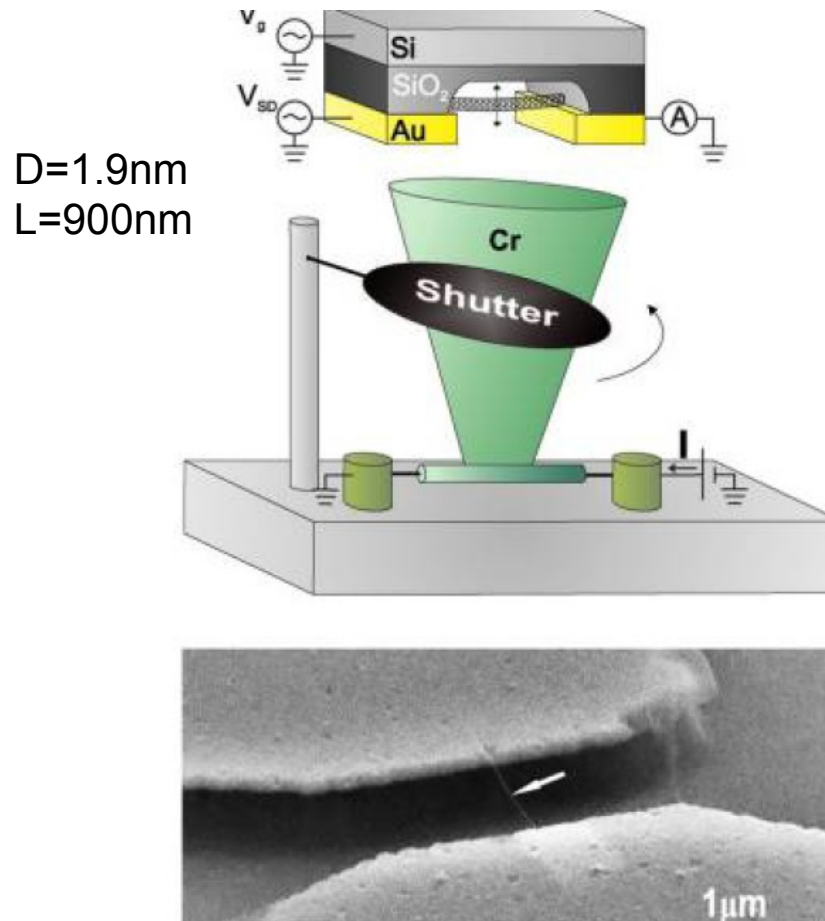


Detection of Attograms; Zeptograms ($=10^{-21}$ g) seems feasible

K.L. Ekinci, X.M.H. Huang and M.L. Roukes, *Appl. Phys. Lett.* **84**, 4469 (2004)

Carbon nanotubes to weigh zeptograms

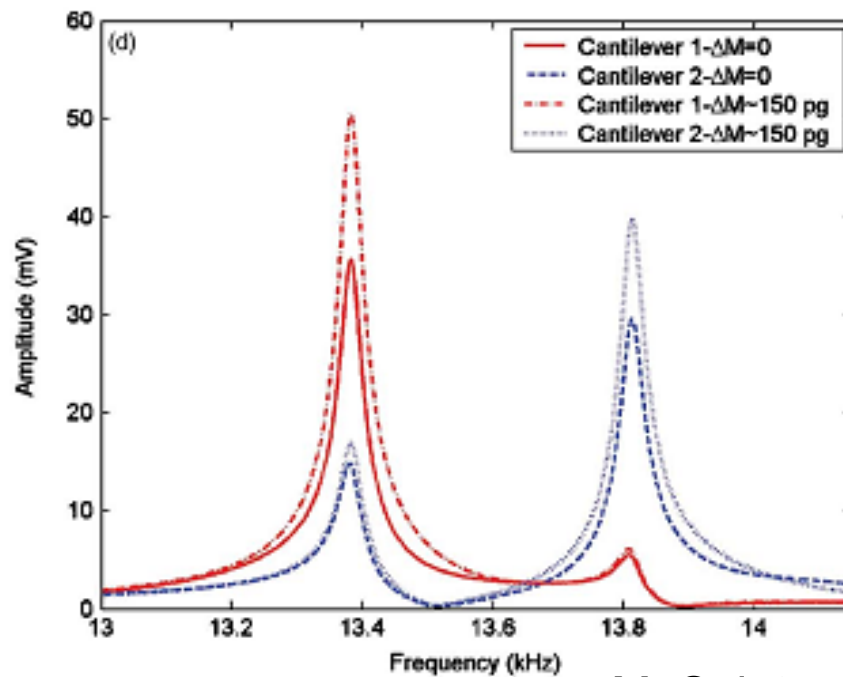
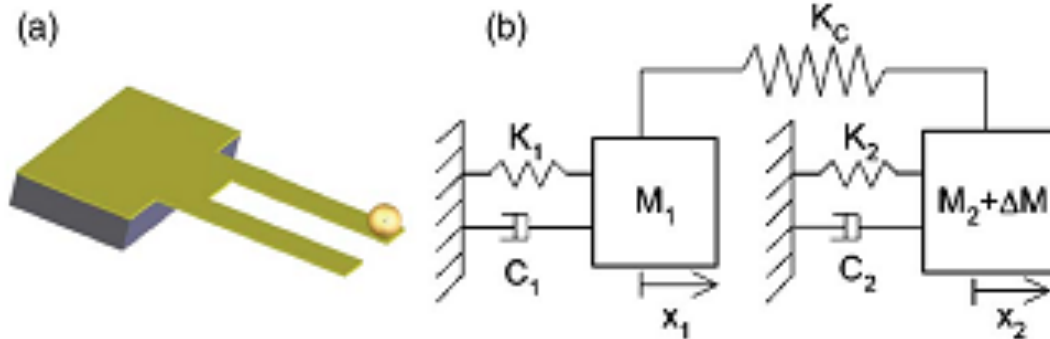
1.4zg at 4.2K



At present 1.4zg
 0.1zg=1Cr atom

B. Lassagne et al., *Nanoletters* 8, 3775 (2008).

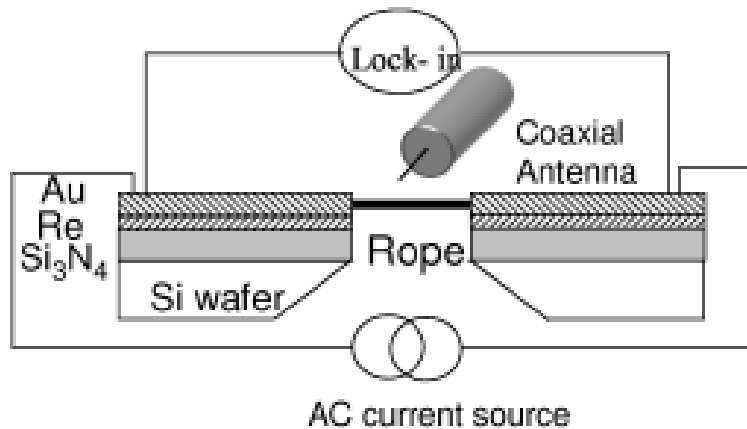
Mass detection with coupled oscillator



Relative change of amplitude of coupled modes is larger than relative frequency change

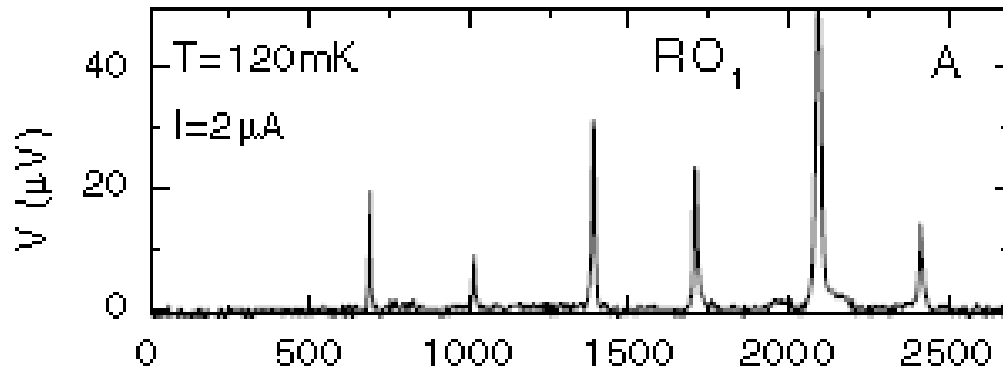
M. Spletzer, A. Ravan, A. Wu, X. Xu and R. Reifenberger, Appl. Phys. Lett. 88, 254102 (2006)

Excitation of carbon nanotubes due to rf-excitation



$$f_1 = \frac{22.4}{2\pi} \frac{R}{2L^2} \sqrt{\frac{Y}{\rho}}, \quad f_2 = 2.7f_1, \quad f_3 = 5.3f_1 \dots$$

But harmonics observed $f_2=2f_1, f_3=3f_1, f_4=4f_1 \dots$
 \Rightarrow Tubes under tension



Proximity superconductivity of nanowires (12nm x 1.7μm) is lost by heating due to resonant rf-excitation

Electron-sound coupling through two-level systems from adsorbates?

B. Reulet, H. Bouchiat, Phys. Rev. Lett. 85, 2829 (2000)

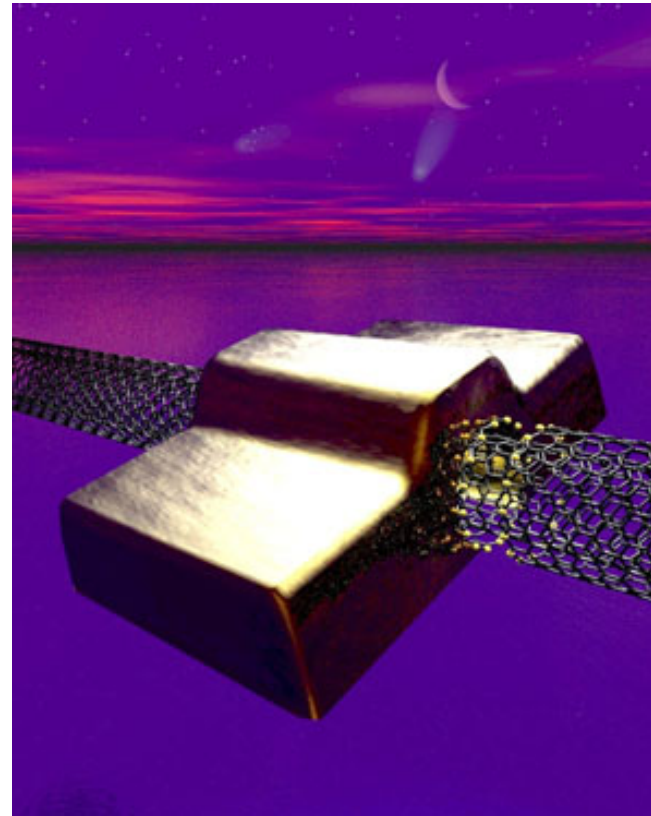
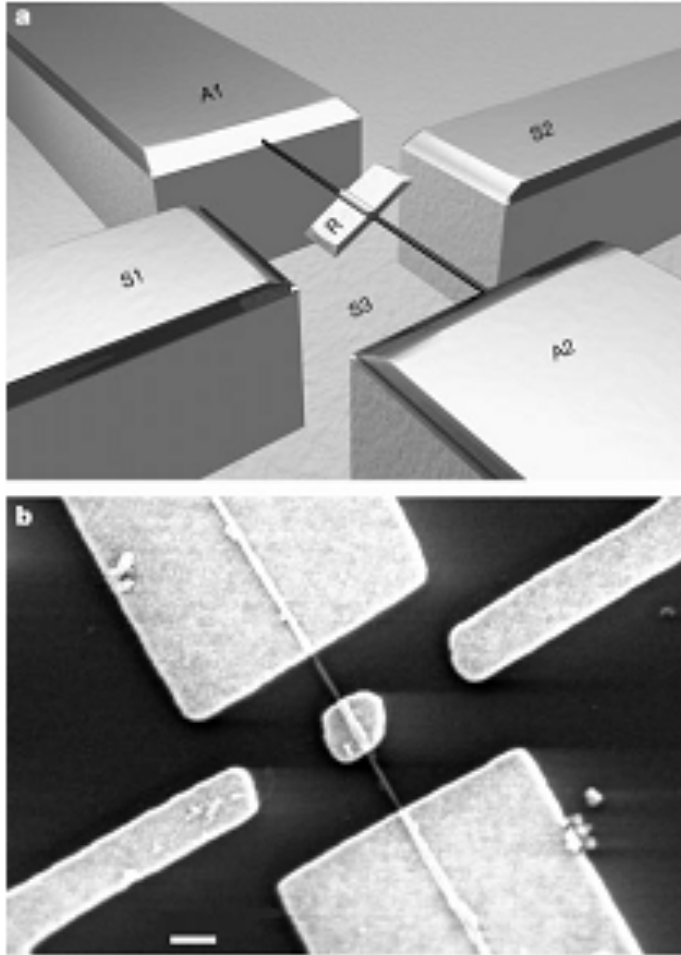
Nanomotors

Biological motors...

Here: artificial motors

Nanomotor with Multiwalled Carbon Nanotubes: Low friction and negligible wear

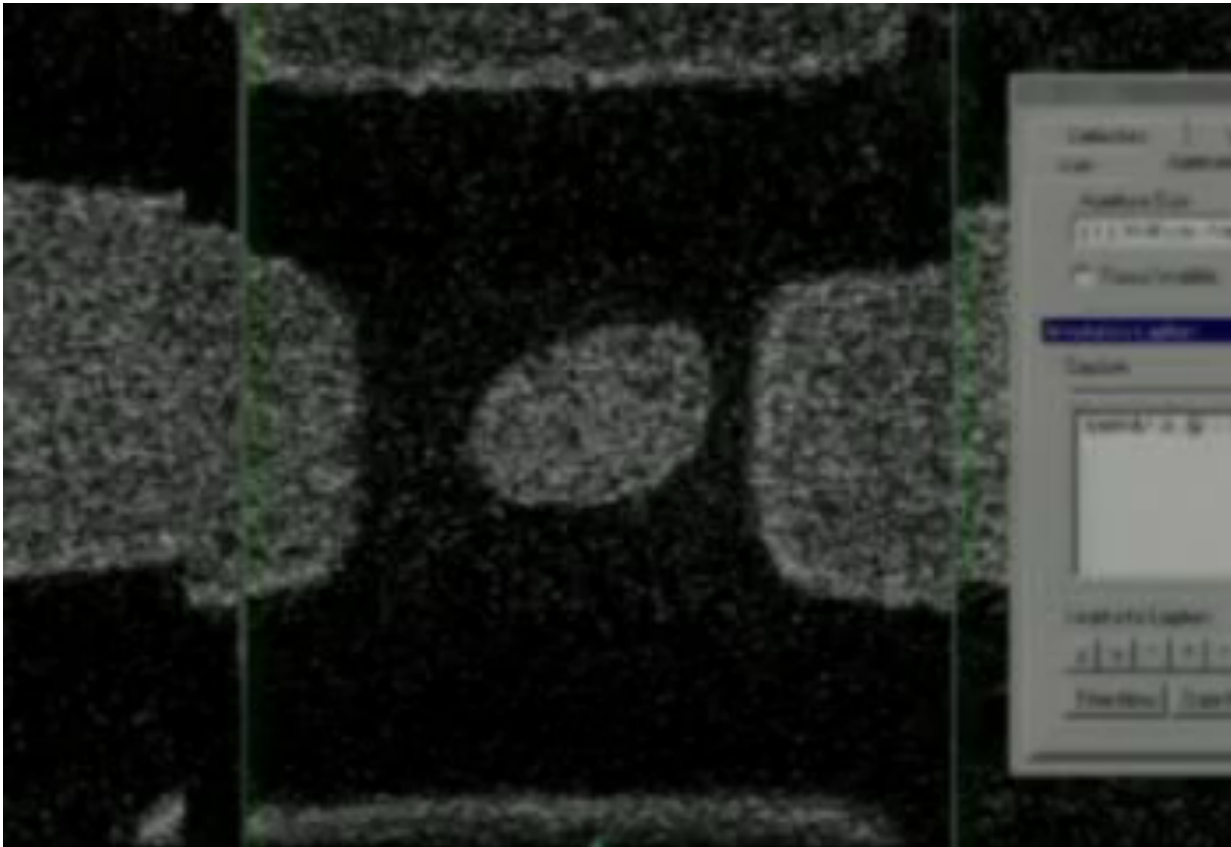
A. Zettl, University of California Berkeley



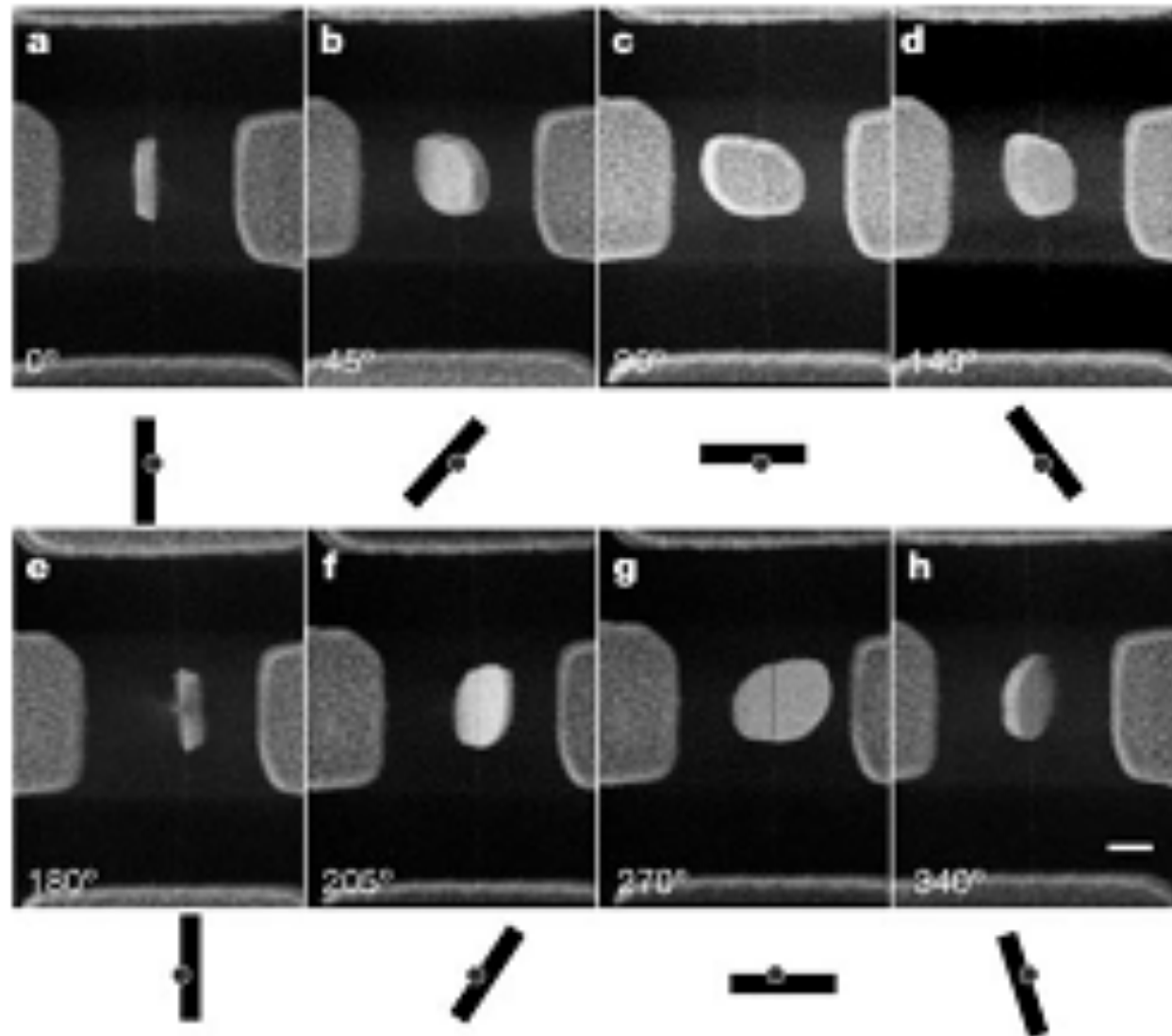
Sliding of incommensurate structures?

A. Fennimore et al., *Nature* **424**, 408 (2003).

Nano-Motor with CNTs

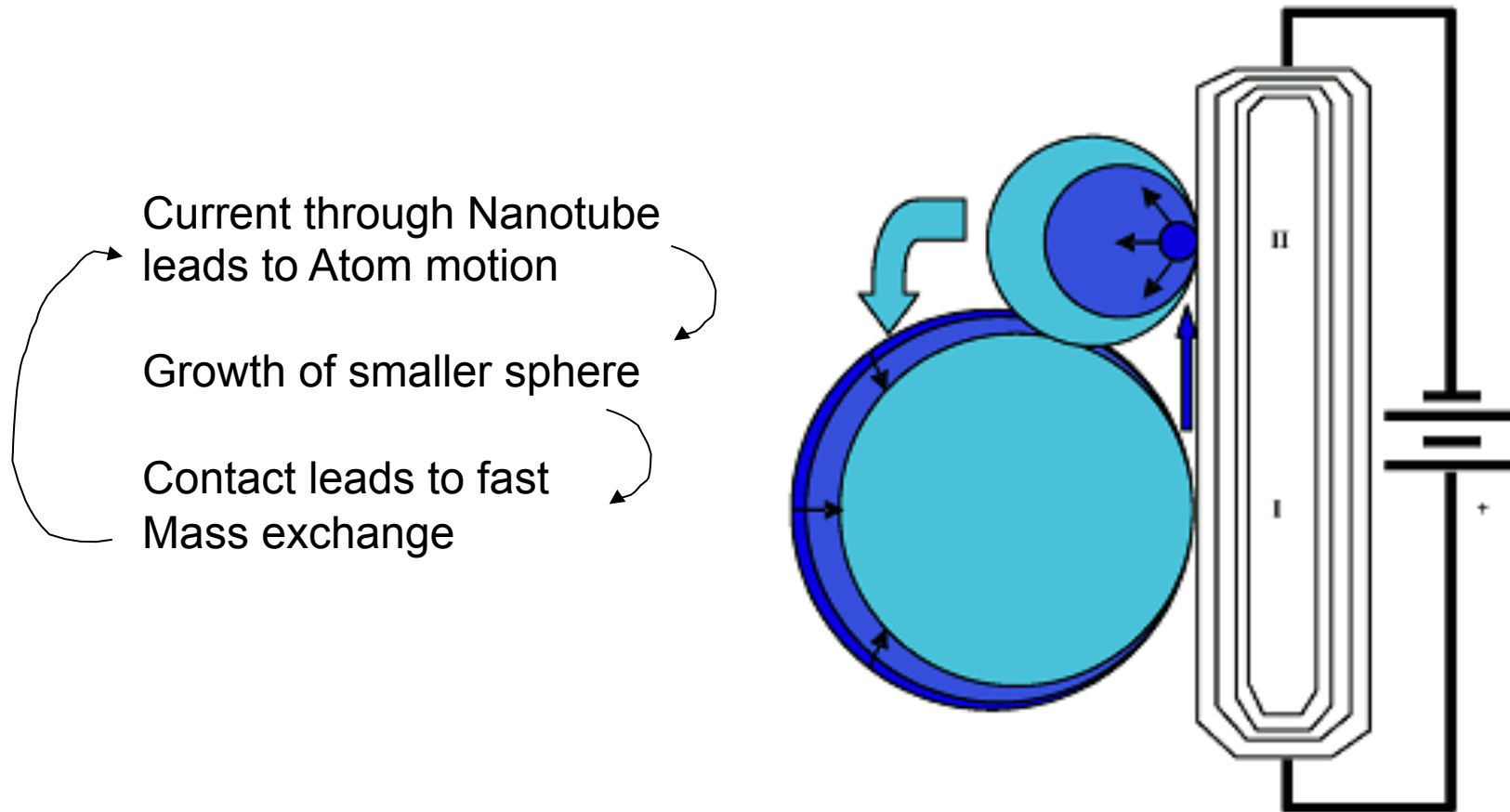


Nanomotor



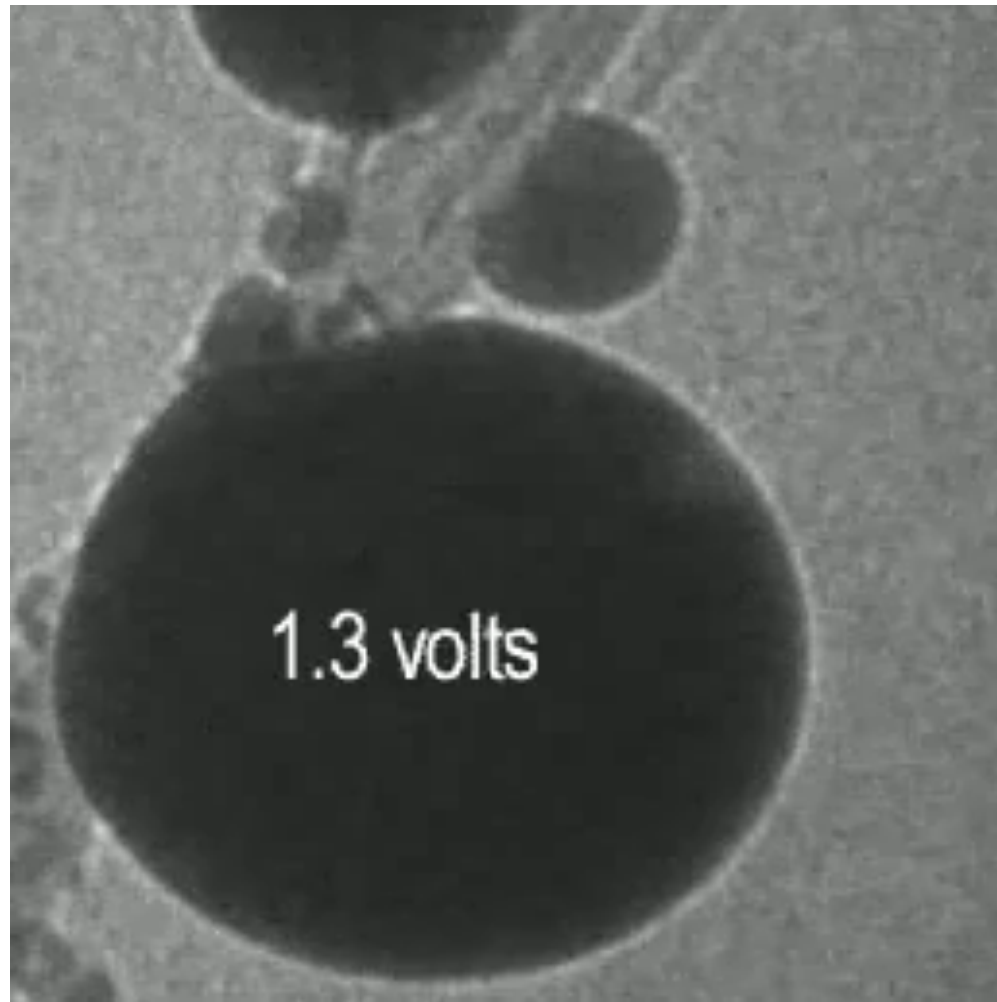
Application of gate voltage leads to rotation of the paddle
Friction and wear between walls of the nanotube are negligible

Surface-tension driven motor



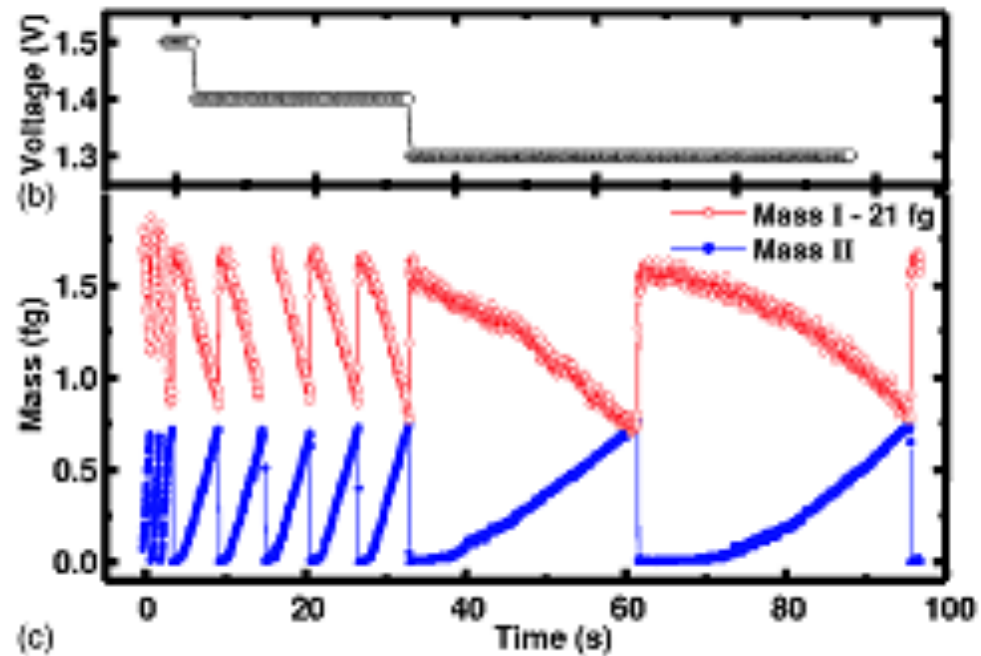
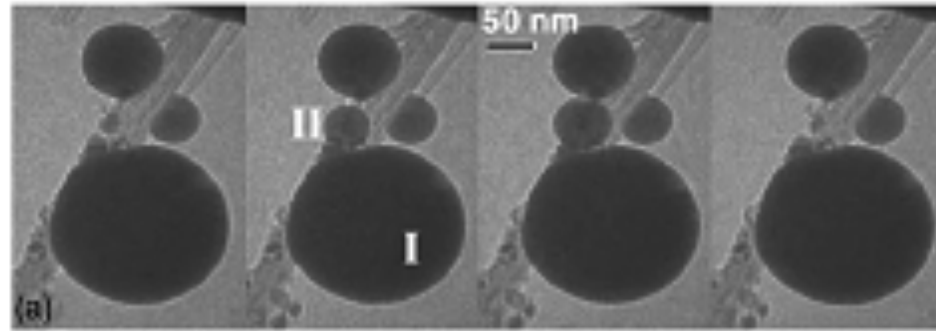
B.C. Regan, S. Aloni, K. Jensen and A. Zettl, Appl. Phys. Lett. 86, 123119 (2005)

Surface tension driven motor



B.C. Regan, S. Aloni, K. Jensen and A. Zettl, Appl. Phys. Lett. 86, 123119 (2005)

Surface-tension driven motor



Frequency depends on applied voltage (current through tube)

Surface tension driven devices

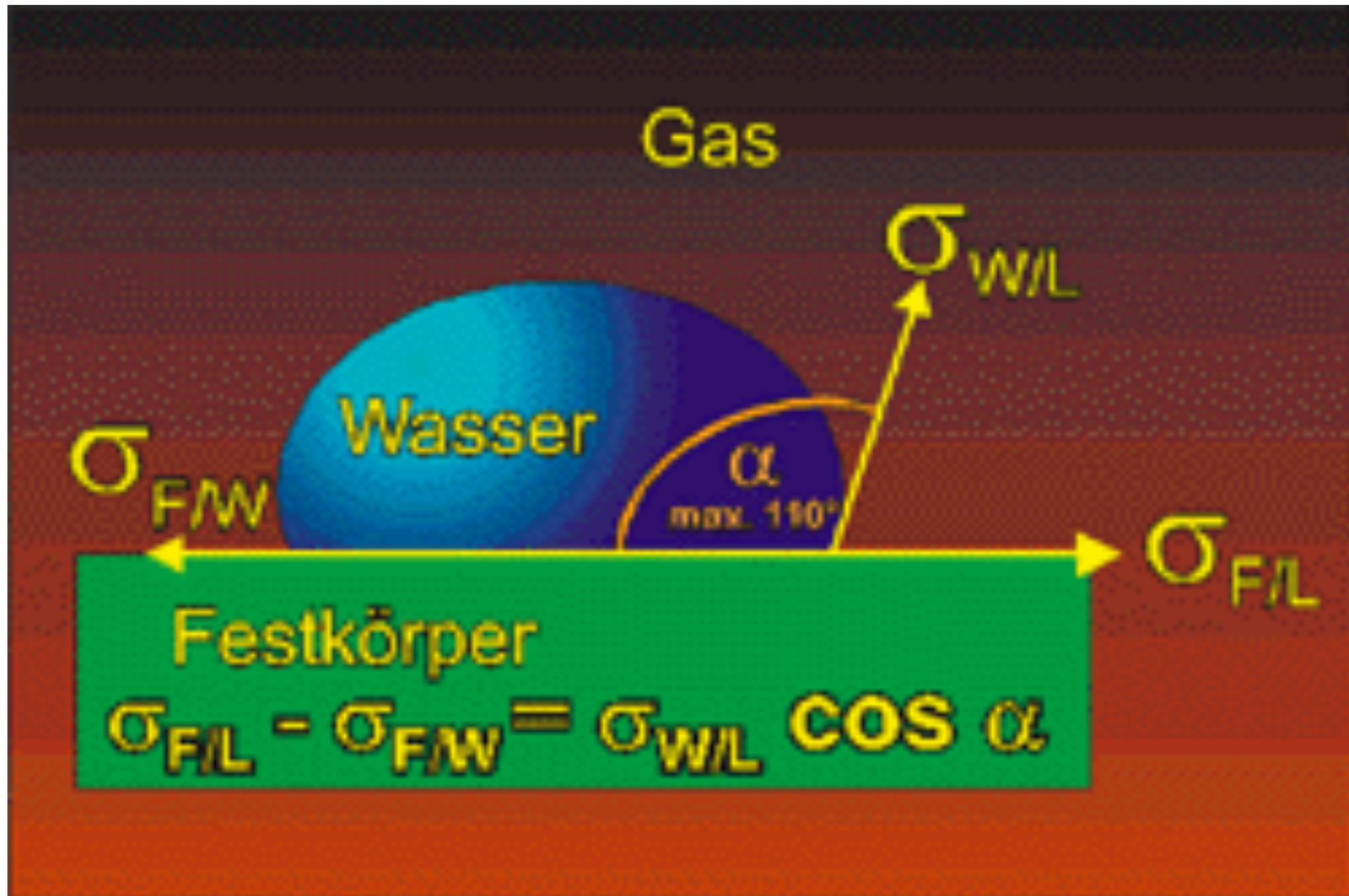


B.C. Regan, S. Aloni, K. Jensen and A. Zettl, Appl. Phys. Lett. 86, 123119 (2005)

Nanodroplets and Superhydrophobicity

How do nanodroplets behave, compared to macroscopic droplets?
What is the influence of roughness on contact angles?

Young's Equation



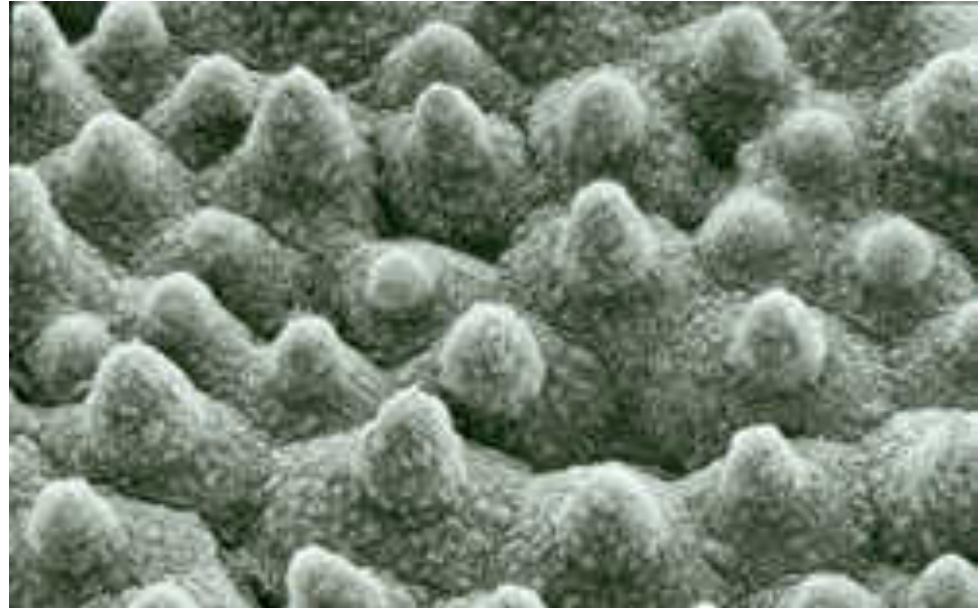
Lotus-Effect



Lotus-Effect

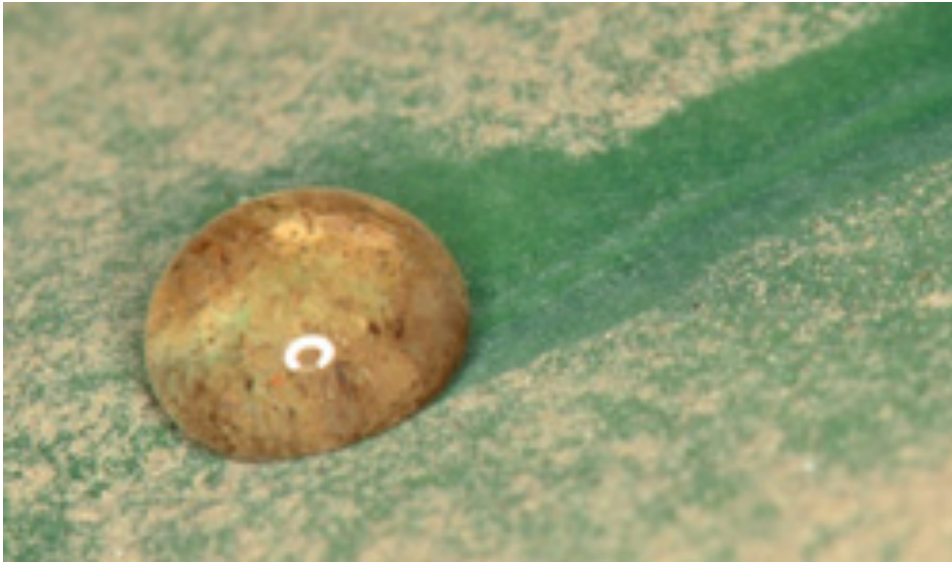


Lotus Flower

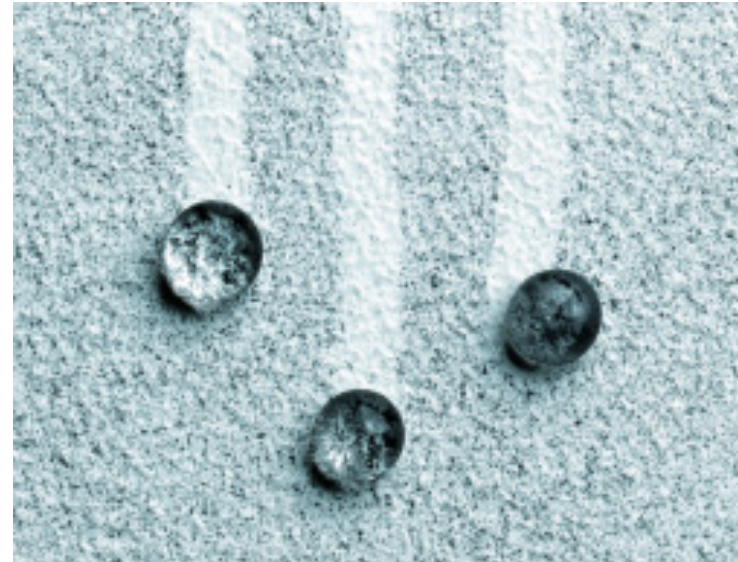


Surface of the Lotus Flower

Lotus-Effekt



Dust particles are swept away



Self-cleaning paint

Superhydrophobicity

$$\gamma_{SL} + \gamma_{lv} \cos \Theta = \gamma_{sv}$$

Youngs Equation

$\Theta=0^\circ \Rightarrow$ hydrophilic

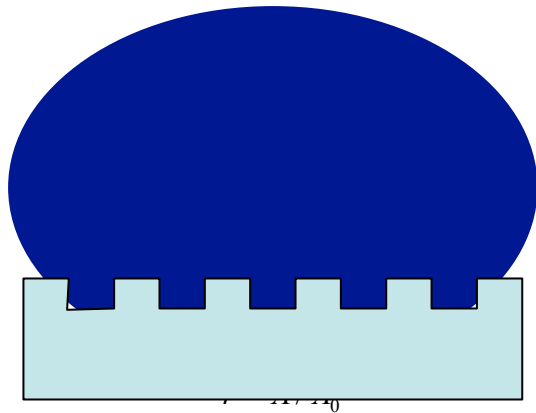
$\Theta>90^\circ \Rightarrow$ hydrophobic

$\Theta>150^\circ \Rightarrow$ superhydrophobic

Experimental evidence:

Roughness increases contact angles from 100-120 °
to 150-175 ° !

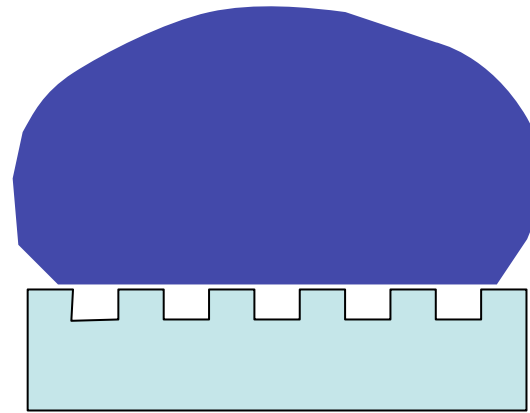
Wenzel vs. Cassie Model



Wenzel

$$\cos \Theta_0 = r \cos \Theta$$

$$r = A / A_0$$

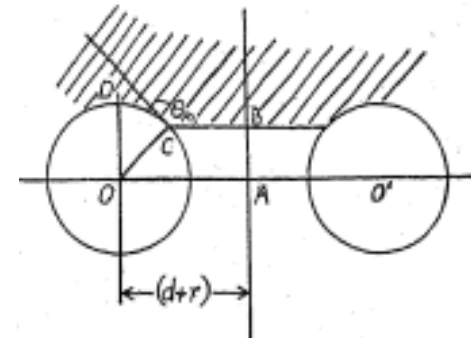
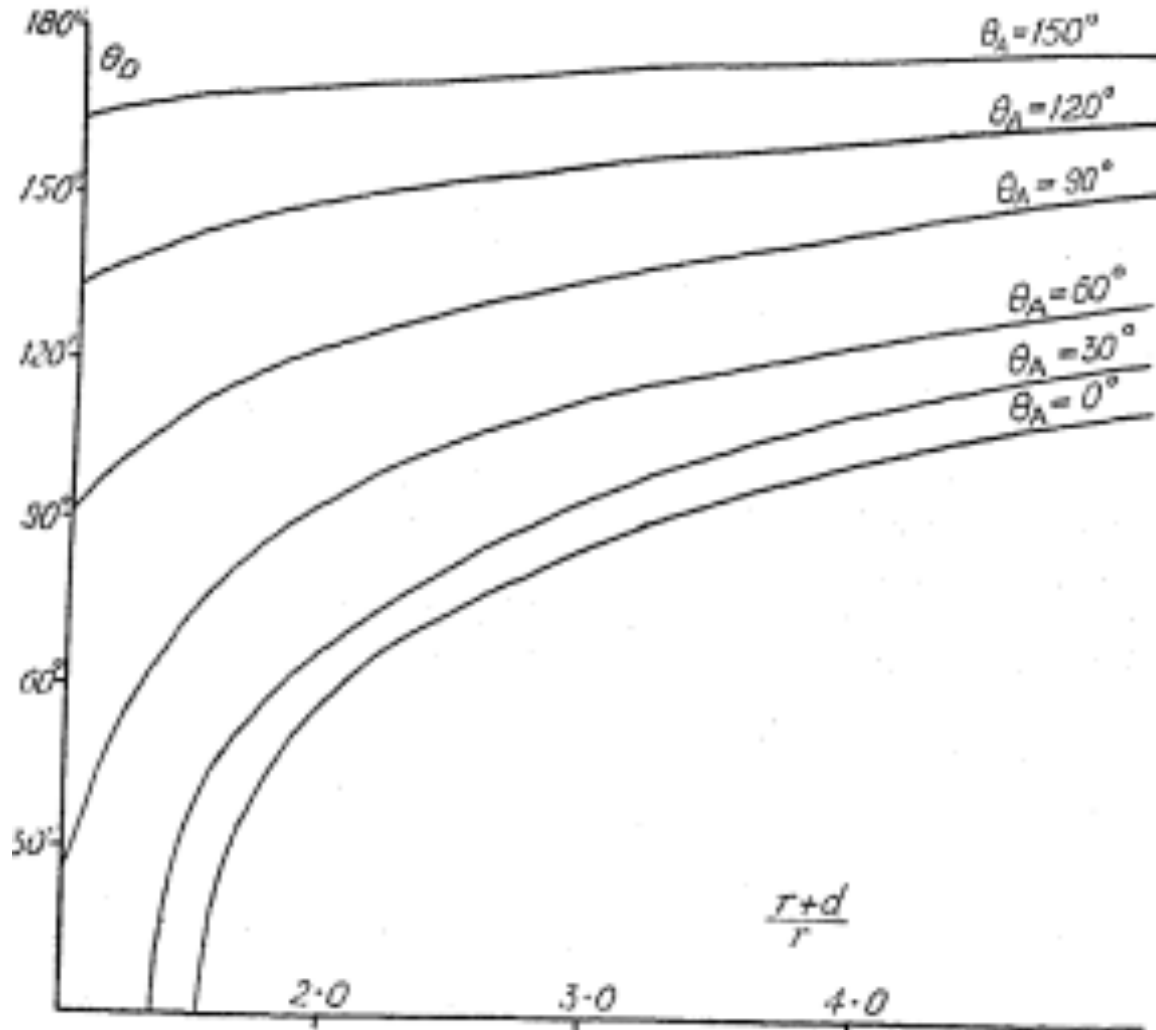


Cassie

$$\cos \Theta_0 = -1 + \Phi(1 + \cos \Theta)$$

$$A = \Phi A_0$$

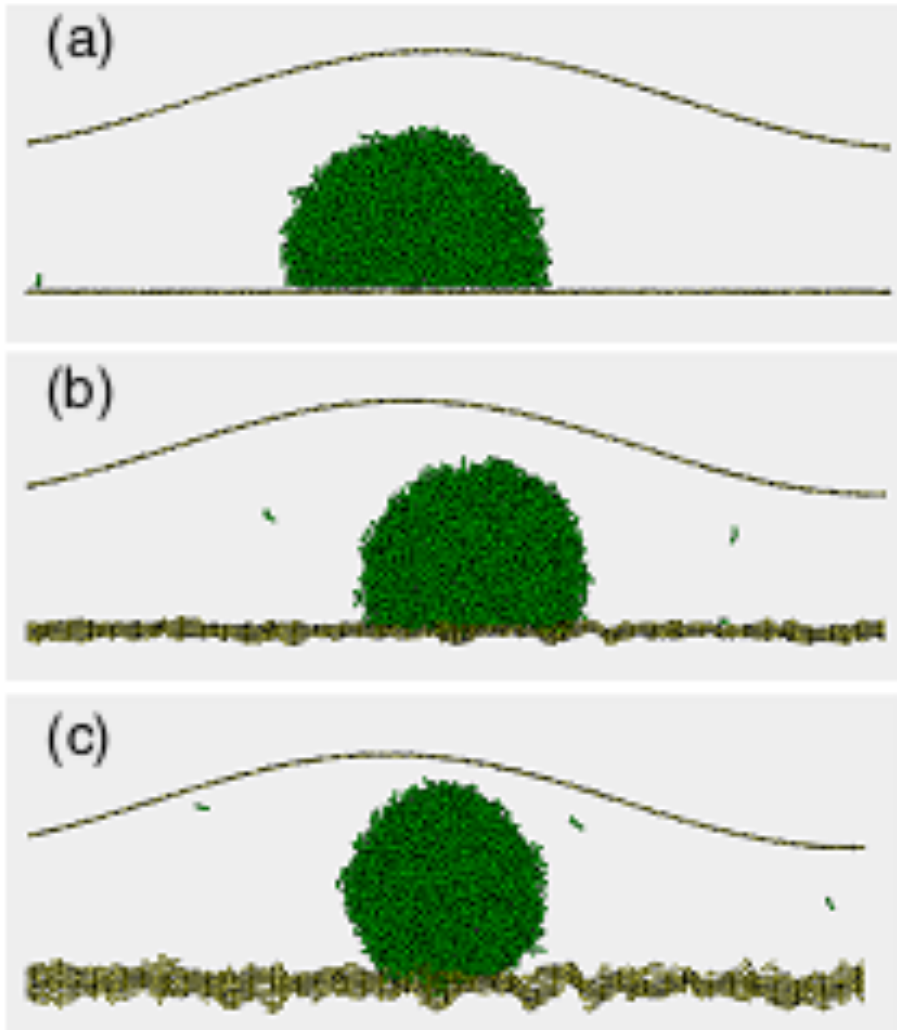
Cassie-Modell



Fibers with radius r

FIG. 3.—
Apparent ad-
vancing con-
tact angle.

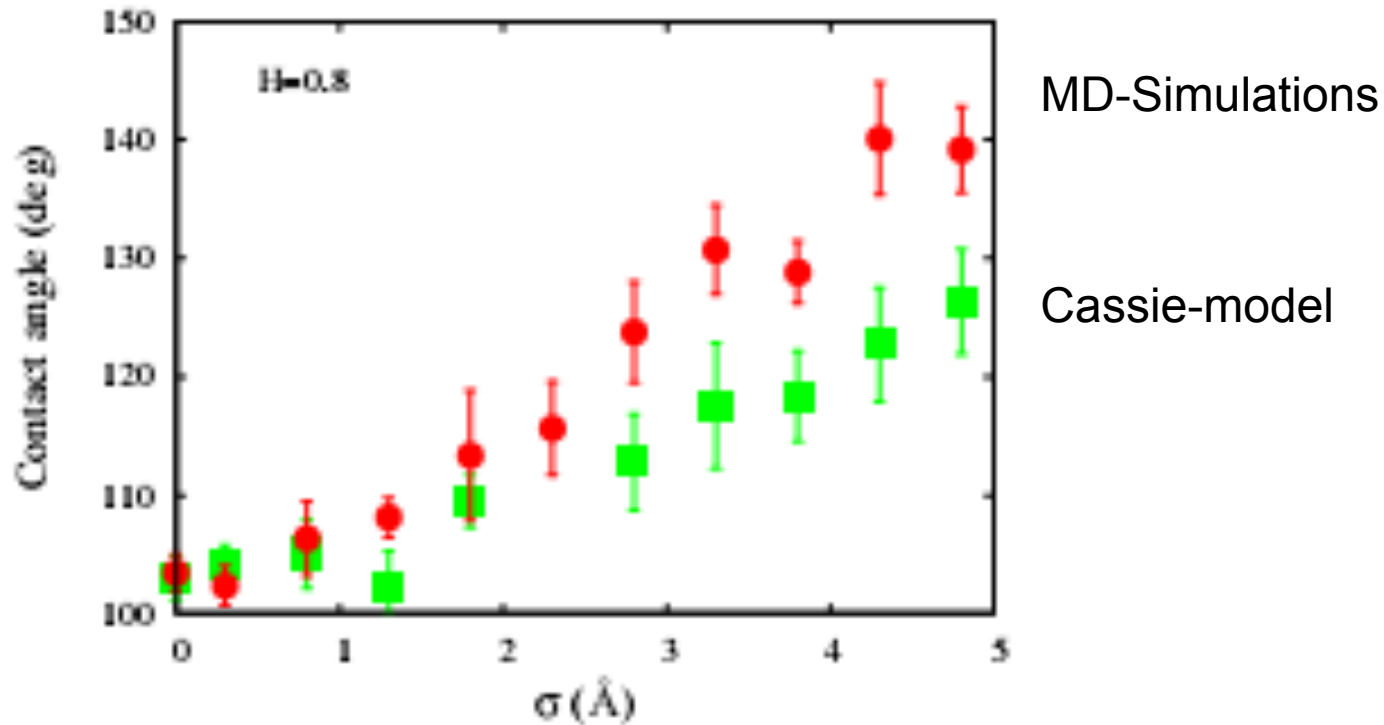
Nanodroplets: Wetting and Roughness



MD-Simulations of Octane nanodroplet on a flat surface (a) and rough surface rms= 2:3 Å and rms=4:8 Å

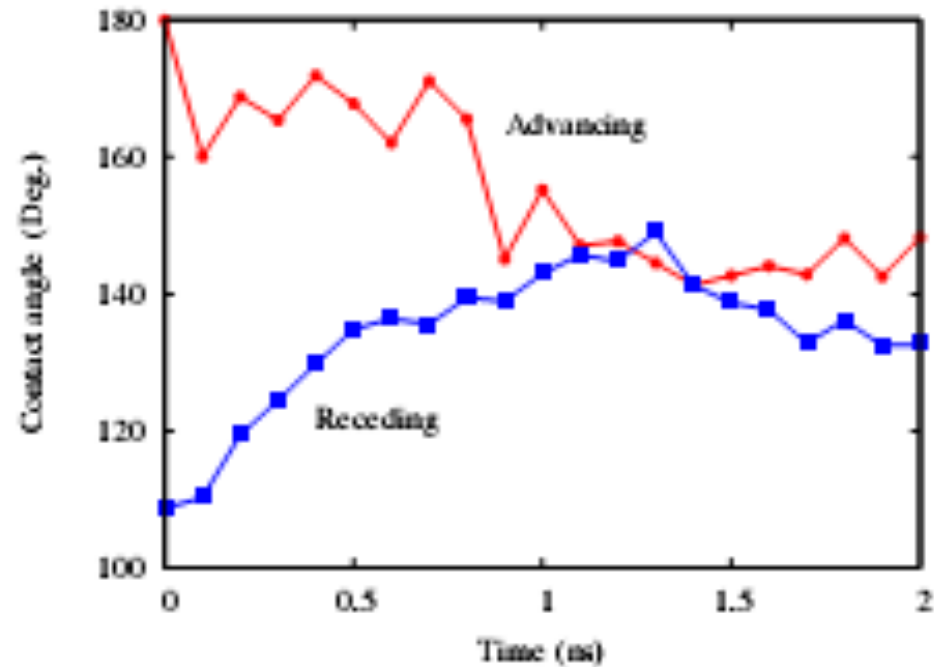
C. Yang et al., Phys. Rev. Lett. 97, 116103 (2006)

Comparison of MD-simulations with models



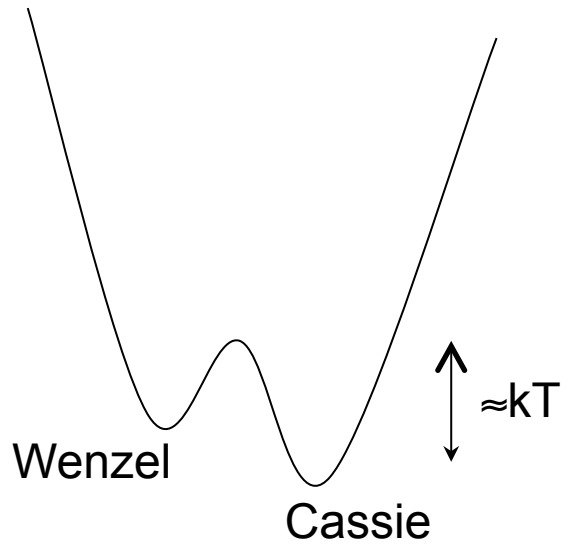
Contact angle increases with rms-roughness but not with fractal dimension
⇒ Agreement with Cassie-model

Advancing and Receding contact angle are equal after 1ns

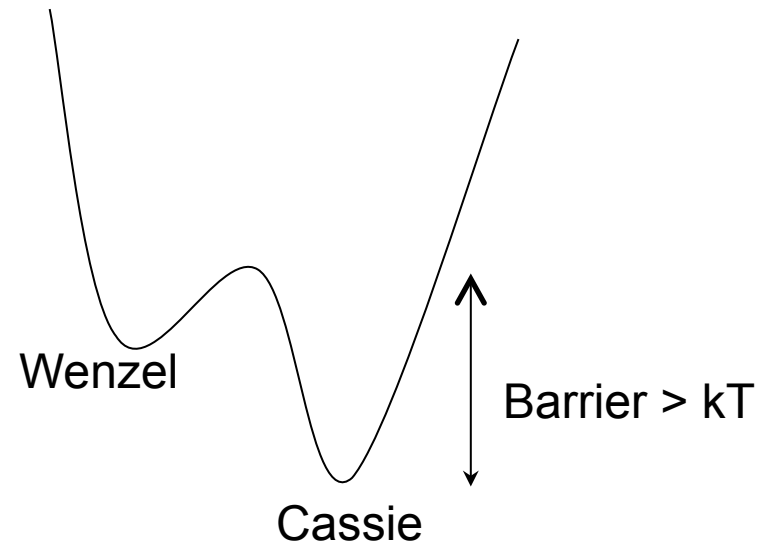


Thermal activation between Wenzel-state and Cassie-state is Possible for nanodroplet; not for macroscopic droplet! Hysteresis

Transition between Cassie-state and Wenzel-state

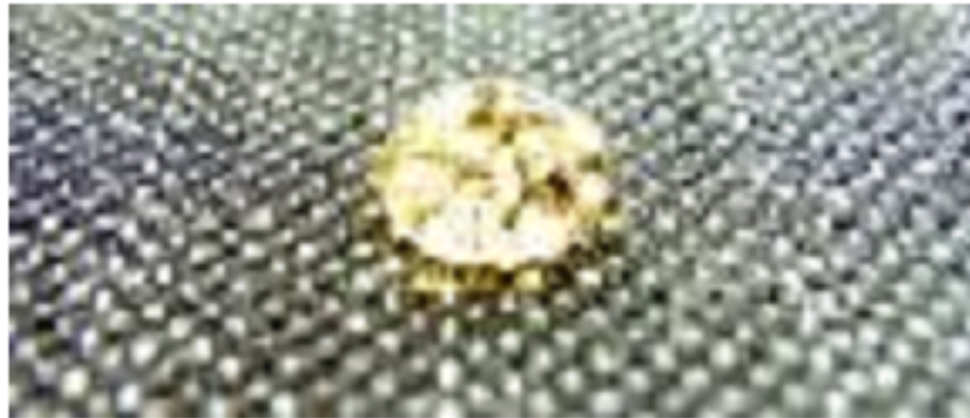


Nanodroplet
⇒ Transition by thermal activation
⇒ No hysteresis



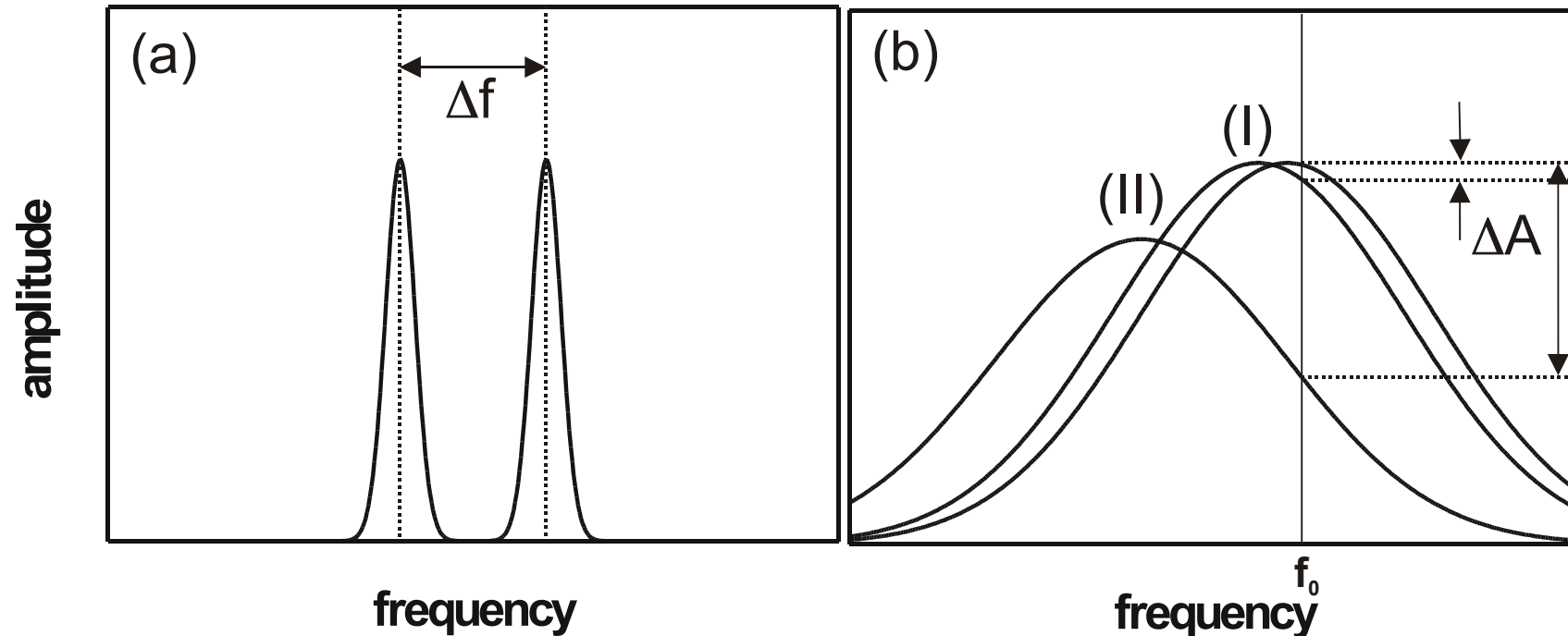
Macroscopic droplet
⇒ If droplet is pushed into Wenzel
it is an irreversible transition
⇒ hysteresis

Nanotech Business Suit



Using ultra-fine processing technologies, Miyuki Keori Co. has developed a business suit that repels water and even oil and stays comfortable. The suit is difficult to stain with wine or olive oil. The maker processed the suit by spraying extremely small chemical particles on its surface, each as small as 30 nanometers.

Dynamic force detection



Cantilever is excited to oscillate, frequency shift and amplitude are measured for force detection

(a) high Q-factor (vacuum)

sharp resonance, detection of frequency shift: non-contact mode, Dynamic Force Microscopy

(b) low Q-factor (air, liquid)

fast amplitude response, detection of amplitude: intermittent contact or tapping mode

How to measure small forces?

$$F_{\min} = \sqrt{\frac{2k_{\text{B}}T\Gamma\Delta\omega}{\pi}}$$

$$\Gamma = \frac{k}{\omega_0 Q}$$

$$Q=10^6$$

$$\omega_0=10^4\text{Hz}$$

$$k=1\text{mN/m}$$

$$T=4\text{K}$$

$$\Delta\omega=1\text{Hz}$$

$$\Rightarrow F_{\min}\approx 10^{-18}\text{N}=1\text{aN}$$

k_{B} : Boltzmann constant

T: Temperature

B: Bandwidth

k: spring constant

Q: Q-factor

ω_0 : Resonance frequency

Γ : Damping coefficient

High Q

Low temperature

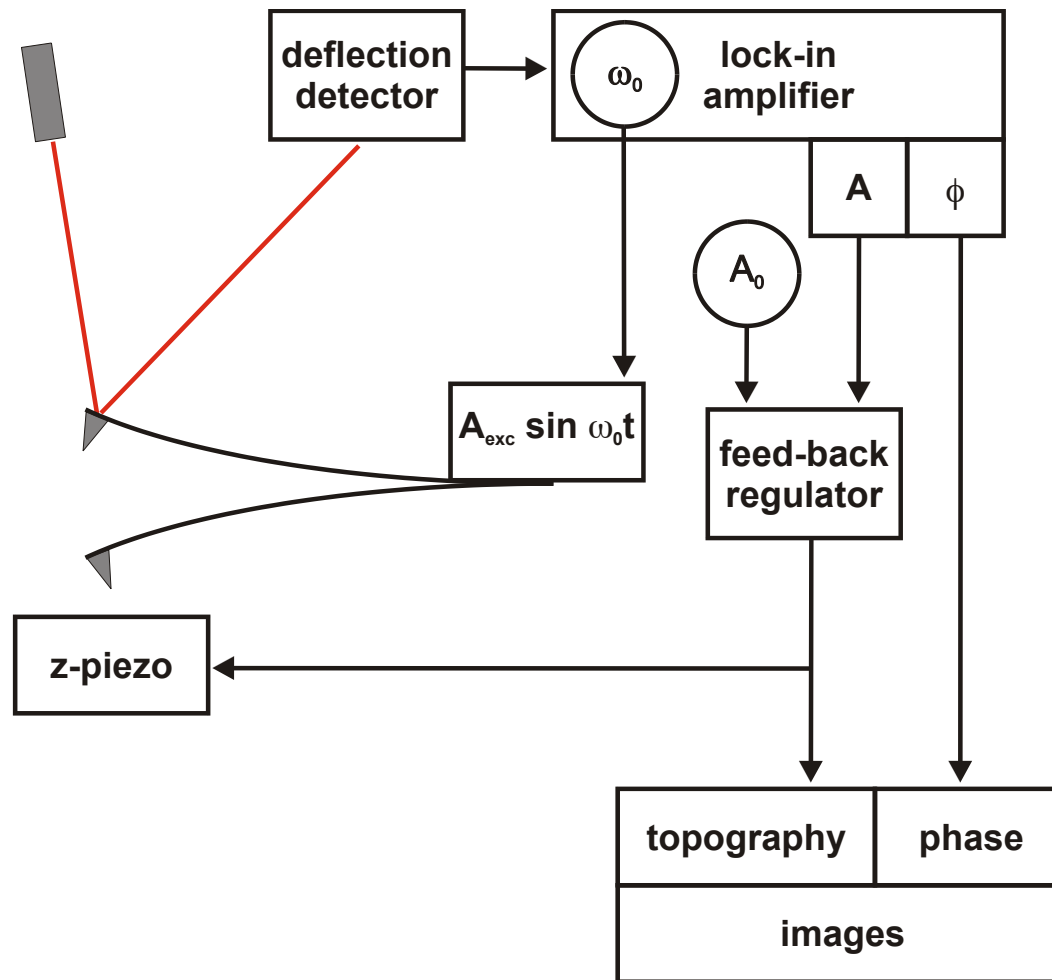
Low spring constant k

Advantages of Dynamic Force Microscopy

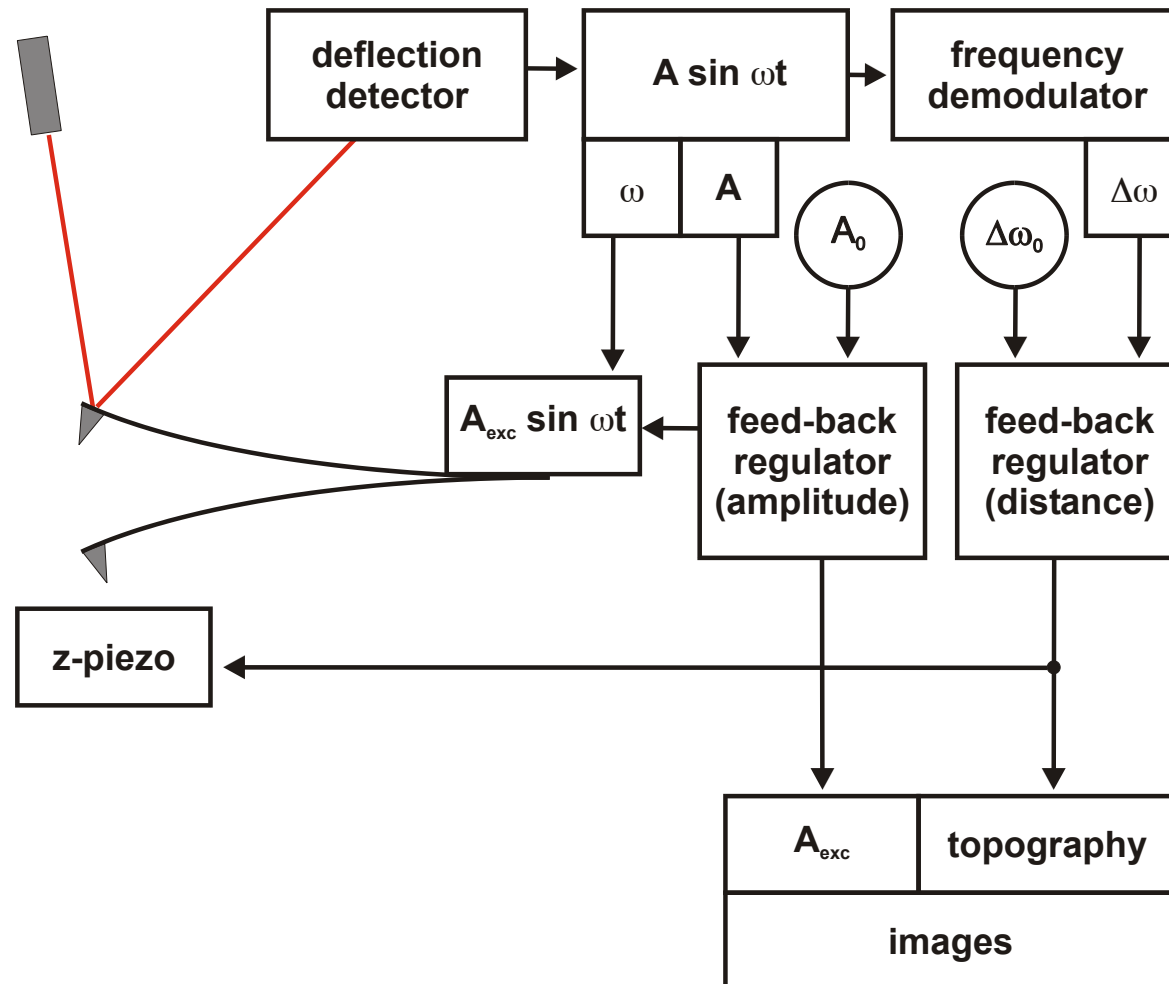
- Avoid jump into contact
 - Spring constants $k > 10$ N/m
 - Rather large amplitudes $kA > F_{adh}$ ($A=2-60$ nm)
- Reduced damage of the surface due to lateral forces
- Preparation of probing tips (similar to STM)
- Atomic resolution in non-contact modes
- Differentiation of force contributions
- High force sensitivity:

$$F_{\min} = \sqrt{\frac{4kk_B T B}{Q\omega_0}} \approx 10^{-15} \frac{\text{N}}{\sqrt{\text{Hz}}}$$

Setup for tapping mode



Setup for Dynamic Force Microscope



How to measure forces in dynamic force microscopy

For **small amplitudes** A , compared to the interaction length,

The frequency shift Δf is related to **force gradients** $k_{ts} = dF_{ts}/dz$

$$\Delta f(z_c) = \frac{f_0}{2k} k_{ts}(z_c)$$

The tip-sample force can be determined by integration

Forces in nc-AFM

Frequency modulation: $f_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m^*}}$ $\Delta f = -\frac{f_0}{2k} \frac{\partial F_{tot}}{\partial z}$

⇒ measured topography = surface of constant $\frac{\partial F}{\partial z}$

$$F_{tot} = F_{chem} + F_{mag} + F_{el} + F_{vdW}$$

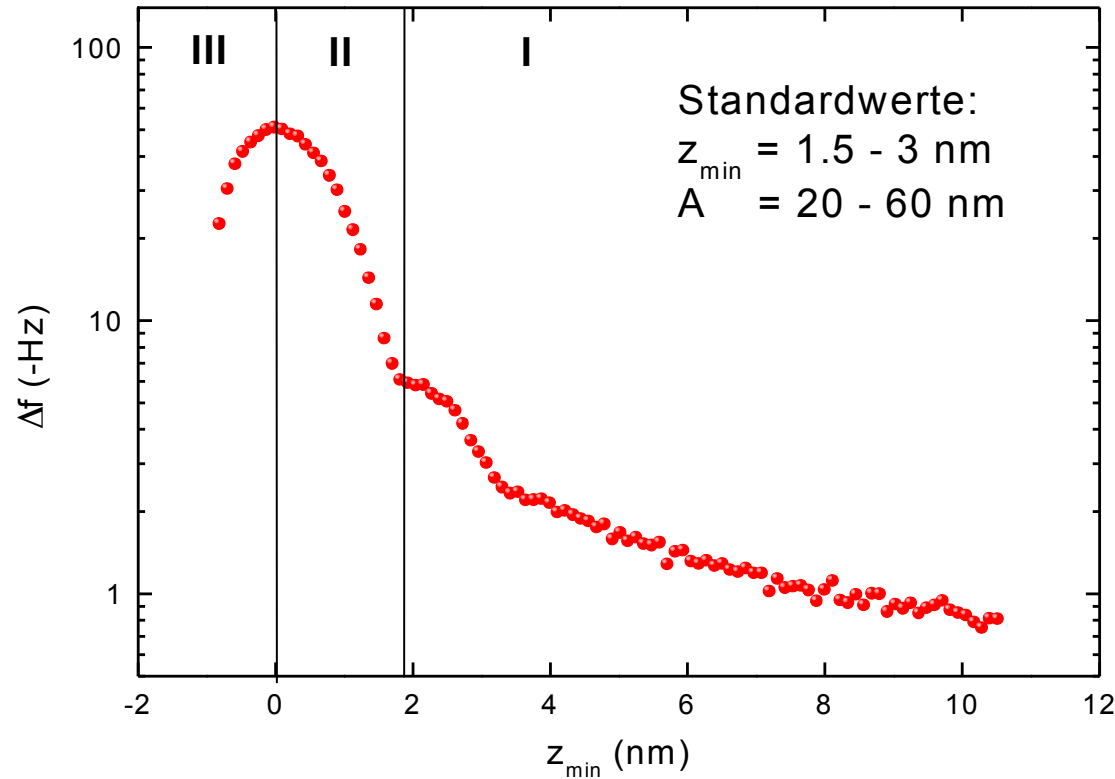
bonding between
tip and sample
atoms
(only for $d < 5 \text{ \AA}$)

only for
magnetically
sensitive tips

$$F_{el} = -\frac{1}{2} \frac{\partial C}{\partial z} V^2$$

$$F_{vdW} = -\frac{HR}{6d^2}$$

Dynamic Mode, non-contact



region I:

attractive forces
non-contact mode

region II:

attractive forces
atomic resolution

region III:

repulsive forces
tapping mode

Perturbation approach for the large amplitude case

The motion of the tip can approximately be described as a harmonic oscillator, where internal damping is compensated by the driving force:

$$m\ddot{z} = -kz + F_{tip-sample}$$

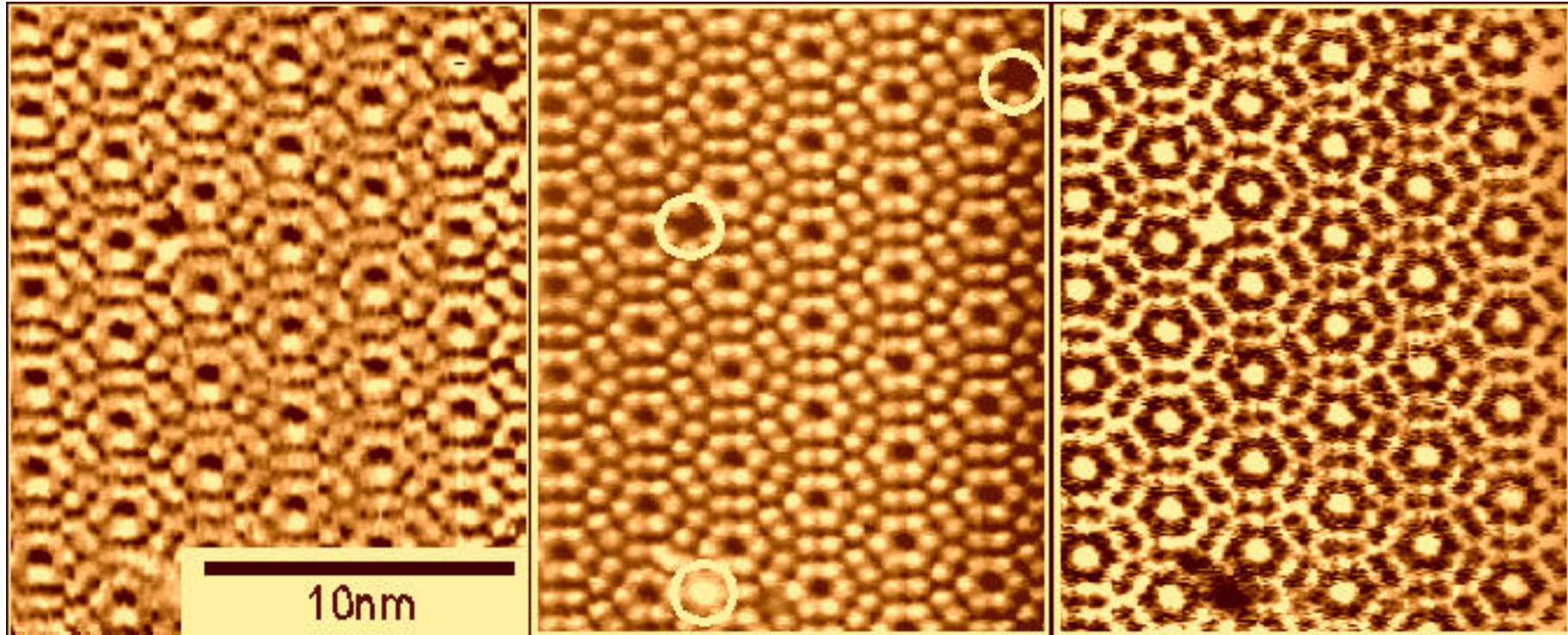
For large amplitudes, the motion is nearly harmonic and the frequency shift is given by :

$$\frac{\Delta f}{f} kA = \frac{1}{\pi} \int_0^{\frac{2\pi}{\omega}} \sin \omega t F_{tip-sample}(z(t)) dt$$

The force law can be reconstructed from the $\Delta f(z)$ -curve.

Non-contact AFM on Si(111)7x7

(Constant frequency mode)



Topography
 $\Delta f = \text{const.}$ $\Delta z \approx 1 \text{ \AA}$

Tunneling Current
 $\overline{\Delta I_t} \approx 20 \text{ pA}$

Damping
 A_{exc}

$f_0 = 156710 \text{ Hz}$ $k = 27 \text{ N/m}$ $Q = 16500$ $A = 16.9 \text{ nm}$ $\Delta f = -122 \text{ Hz}$ $(\Delta f/f)kA = -0.35 \text{ nN}$

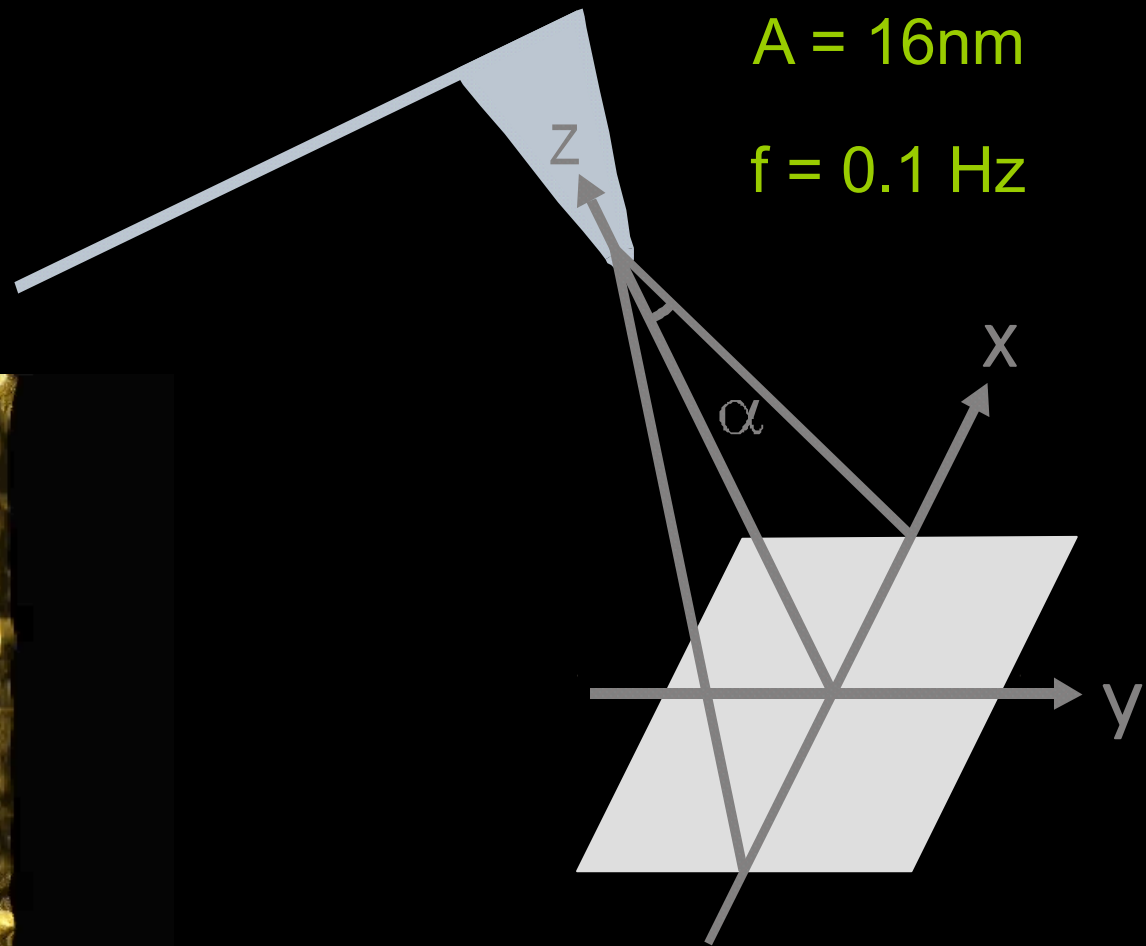
R. Lüthi et al. *Surf. Rev. Lett.* 4, 1025 (1997)

Simulation of oscillating tip

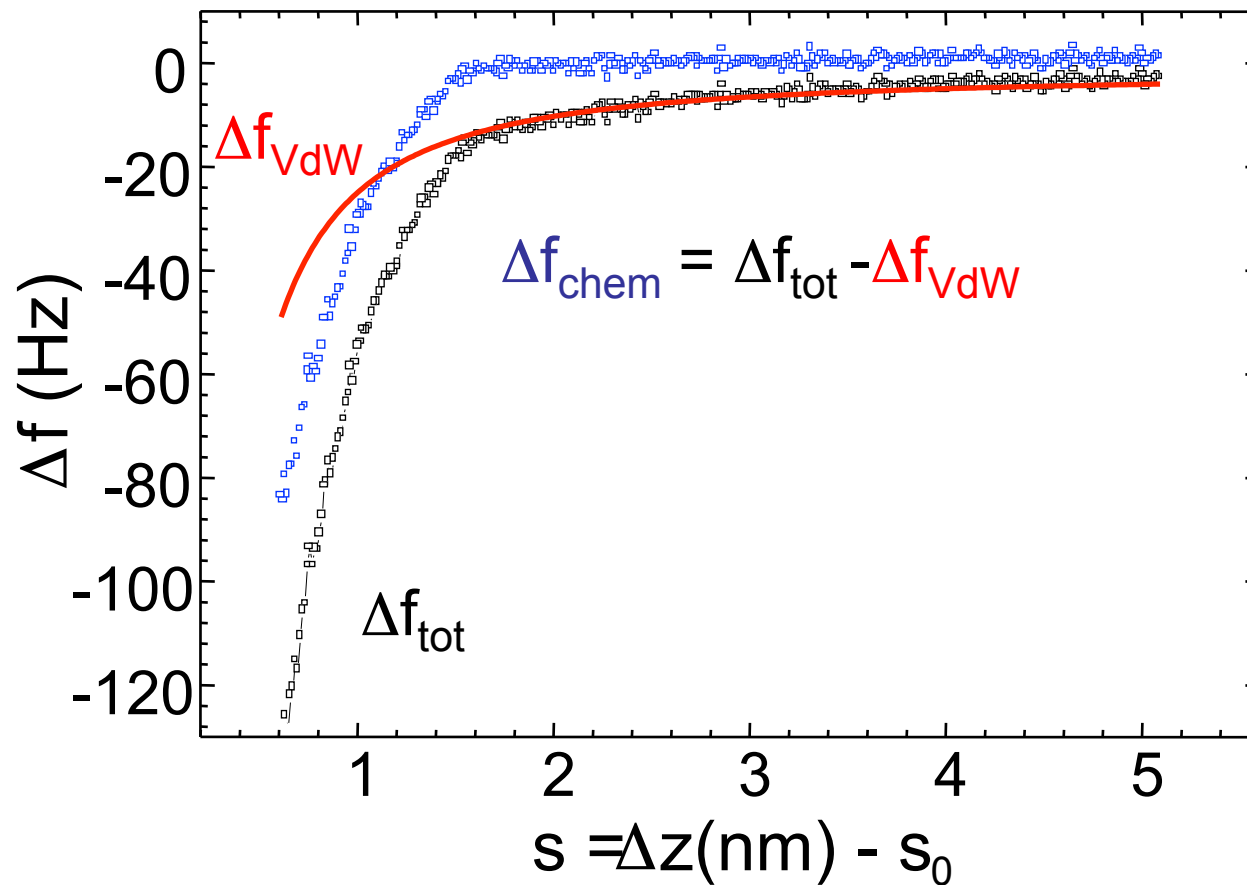
$$\alpha = 6.6^\circ$$

$$A = 16\text{nm}$$

$$f = 0.1\text{ Hz}$$



Short range interaction

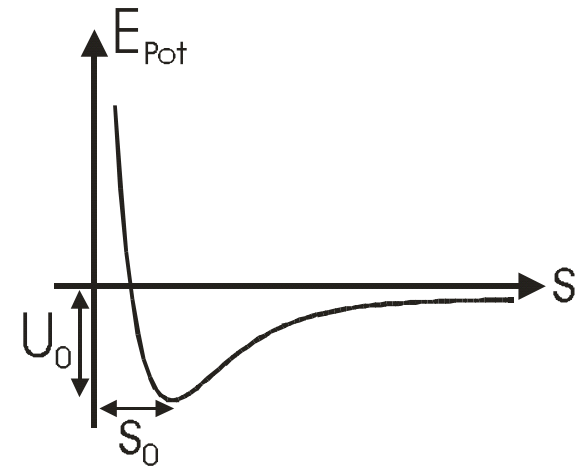


$$\Delta f_{\text{chem}} = \frac{f_0}{kA} \frac{U_0}{\sqrt{2\pi A \lambda}} e^{-\Delta z / \lambda}$$

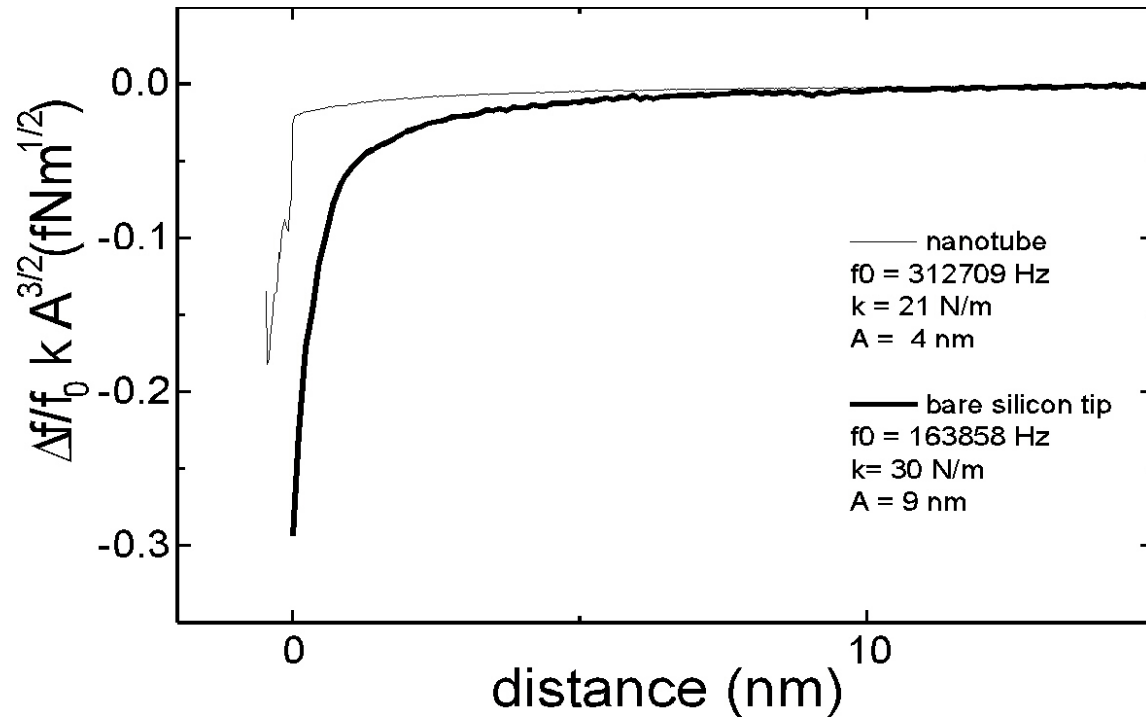
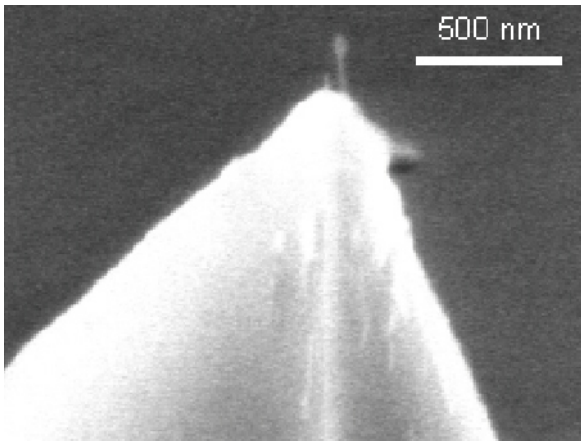
$$\lambda = 0.35 \text{ nm}$$

$$U_0 = -4.7 \text{ eV}$$

$$s_0 = 0.45 \text{ nm}$$



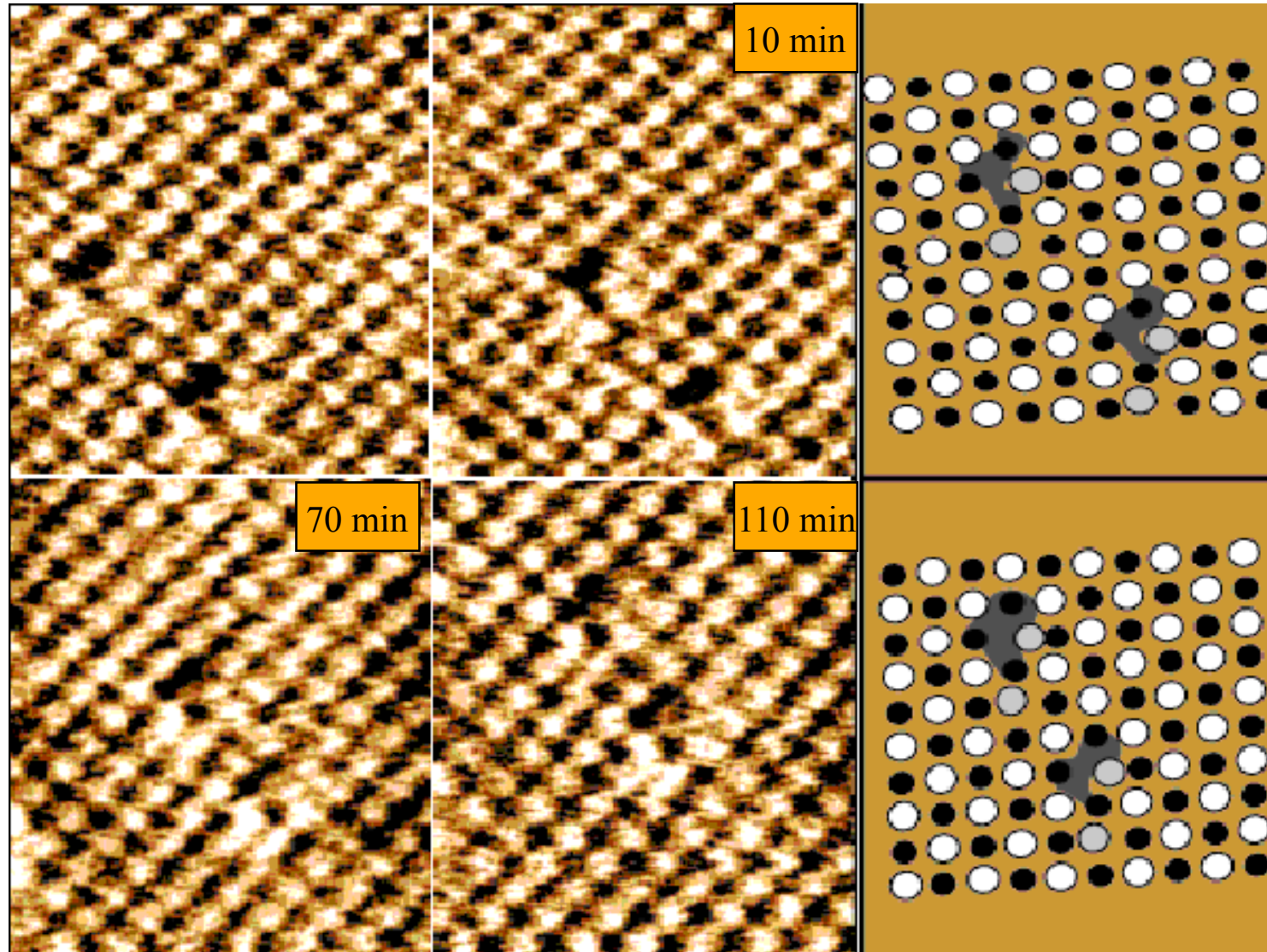
Carbon nanotubes as probing tips for nc-AFM



⇒ Long-range forces are reduced

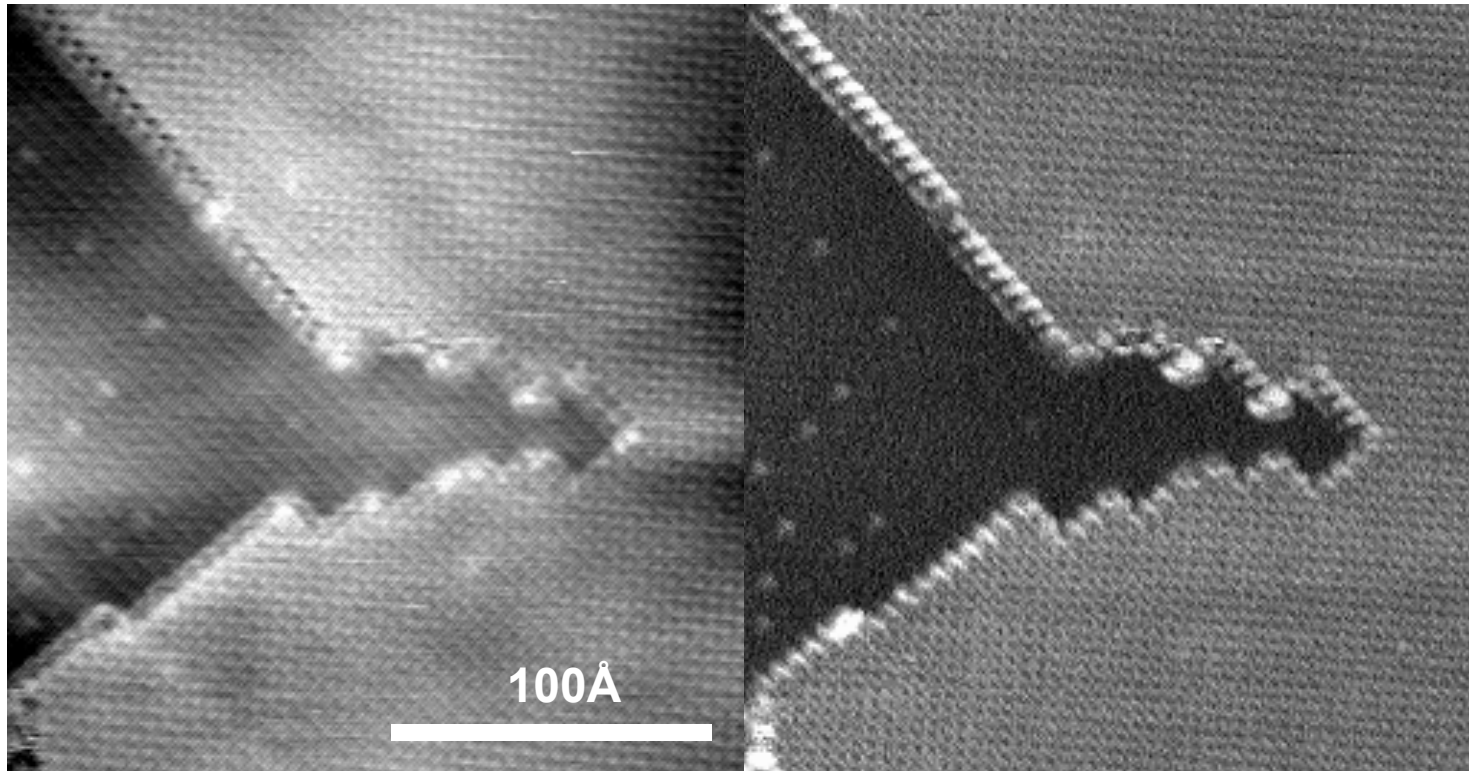
True atomic resolution on NaCl(001)

(Insulator surface with point defects)



M. Bammerlin et al., *Probe Microscopy* 1, 3 (1997)

True-atomic resolution at step edges of NaCl(001)-thin films on Cu(111)



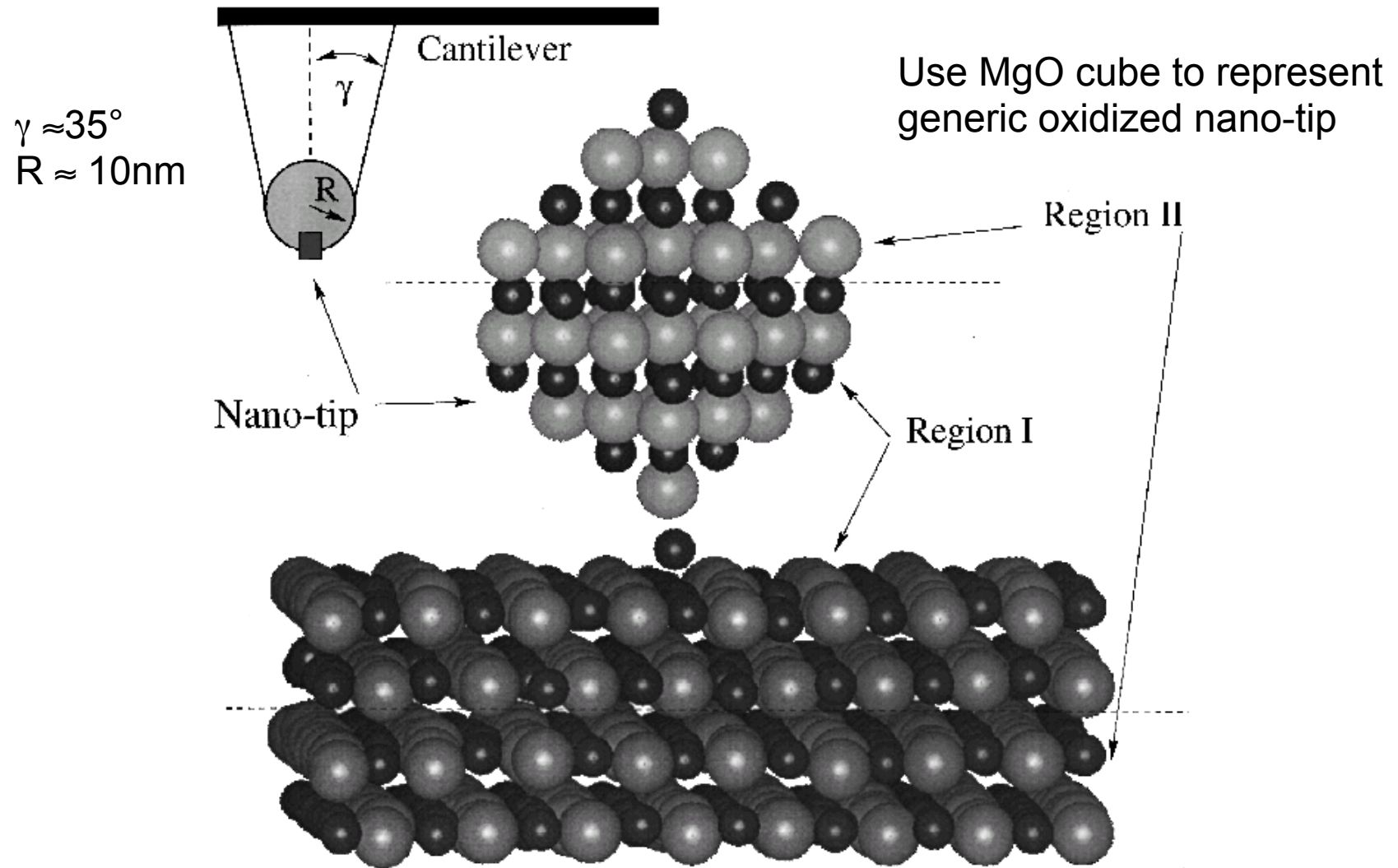
Topography

Excitation Amplitude (A_{exc})

$k=26\text{N/m}$ $f_0=158.3\text{kHz}$ $A=0.7\text{nm}$ $\Delta f=-185\text{Hz}$ $(\Delta f/f)kA = -0.02\text{nN}$

⇒ Step atoms and kink sites give different contrast

Theory of nc-AFM on Ionic Surfaces



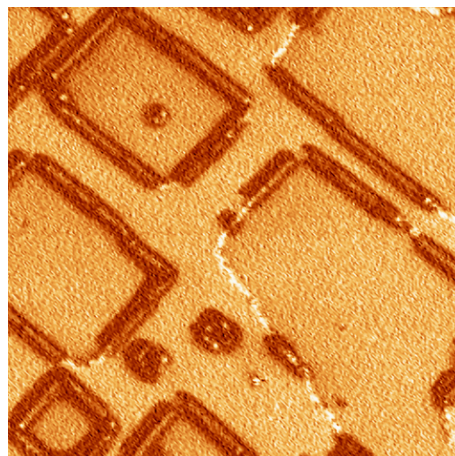
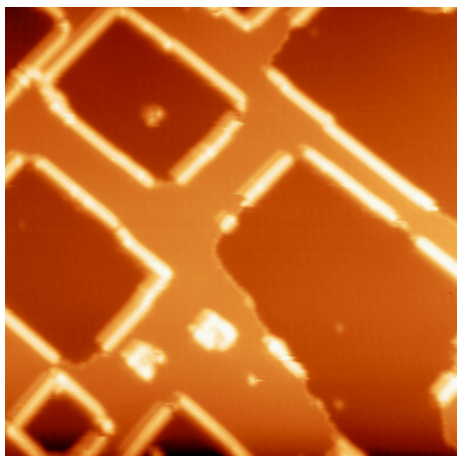
R. Bennewitz et al., Phys. Rev. B 62 (2000) 2074

Molecular nanowires on KBr

Topography

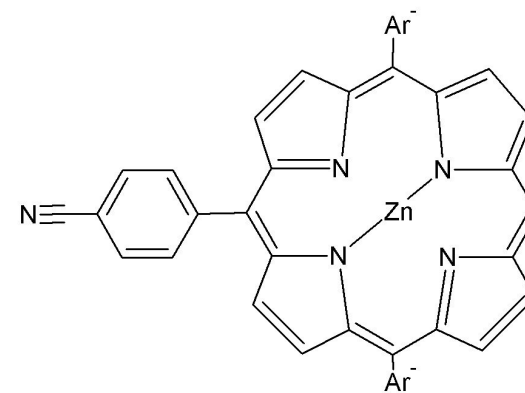
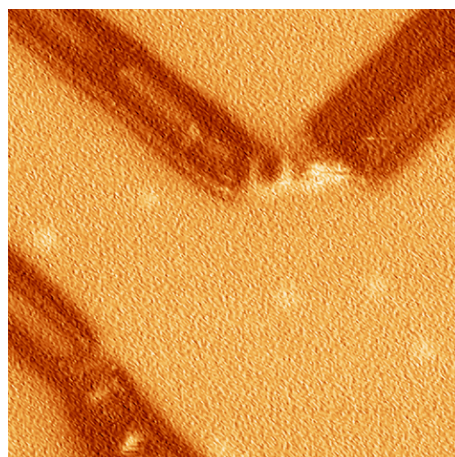
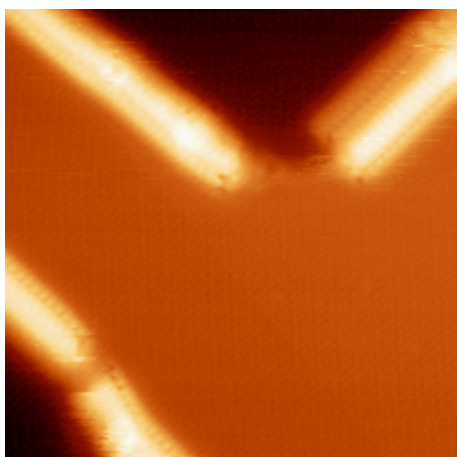
Damping

100 nm

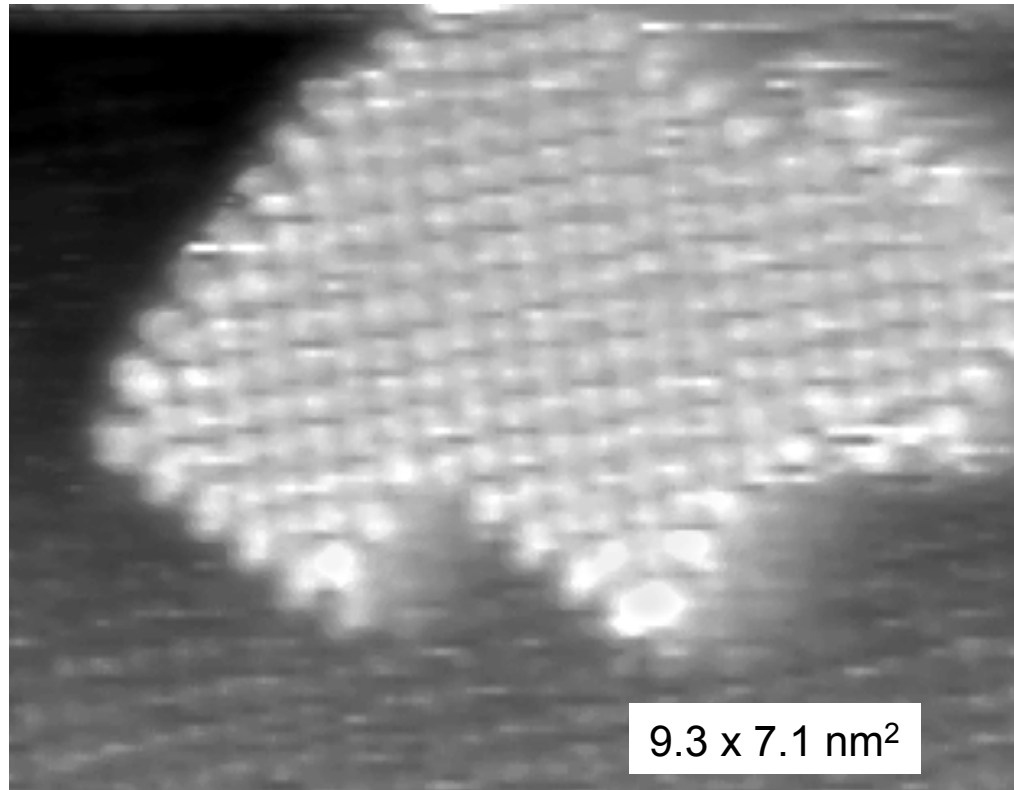


- “Asymmetric” porphyrins on KBr with pits
- Straight edges are decorated
- Image height approx 1nm, Single molecules ?

24 nm

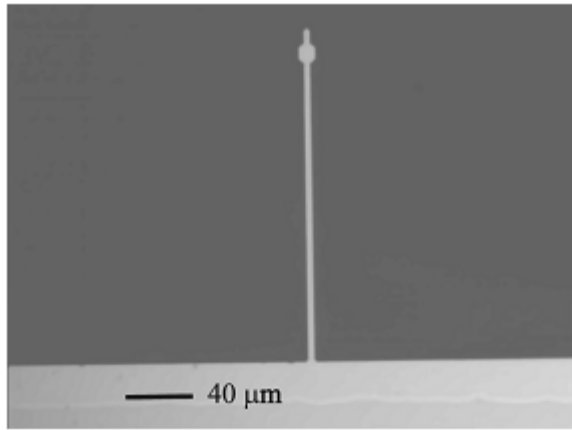


Nano-Switzerland

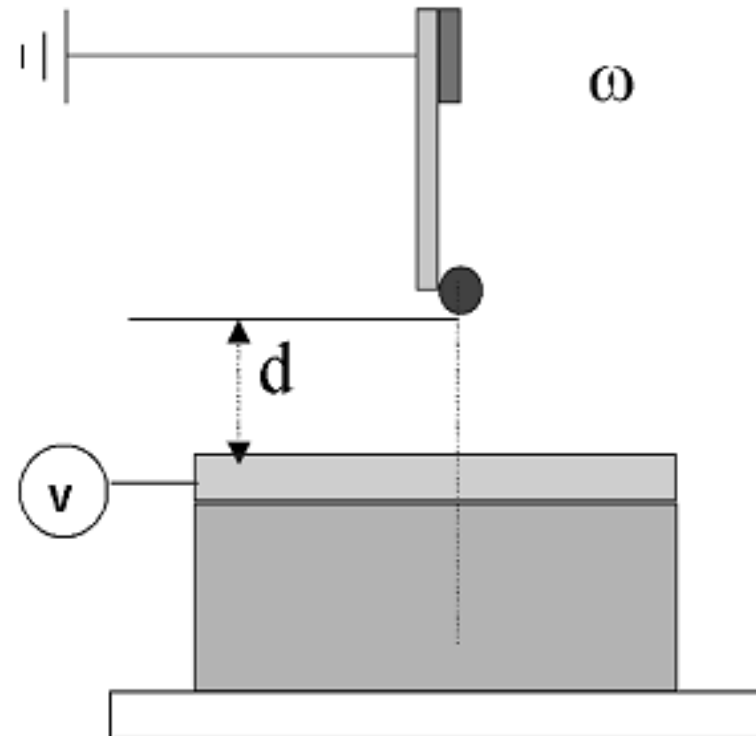


NaCl-Islands consisting of 120 atoms

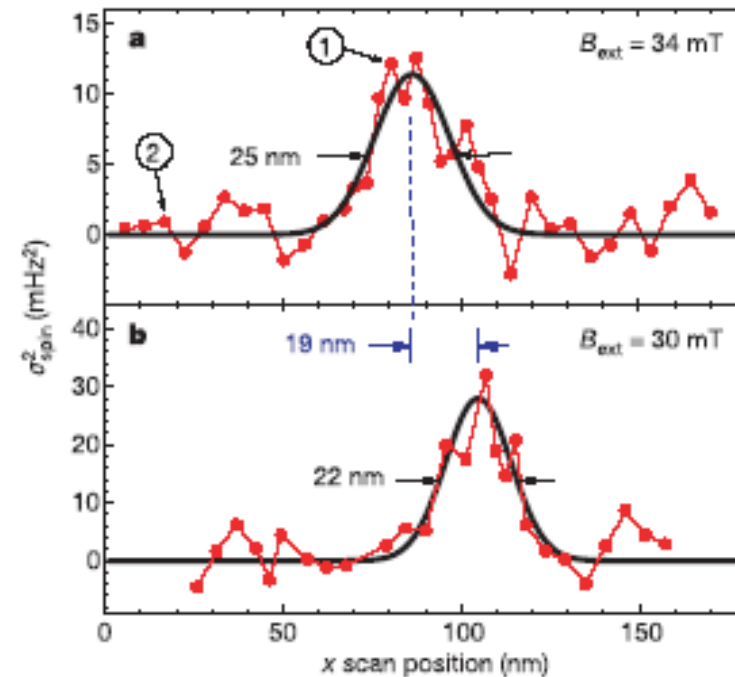
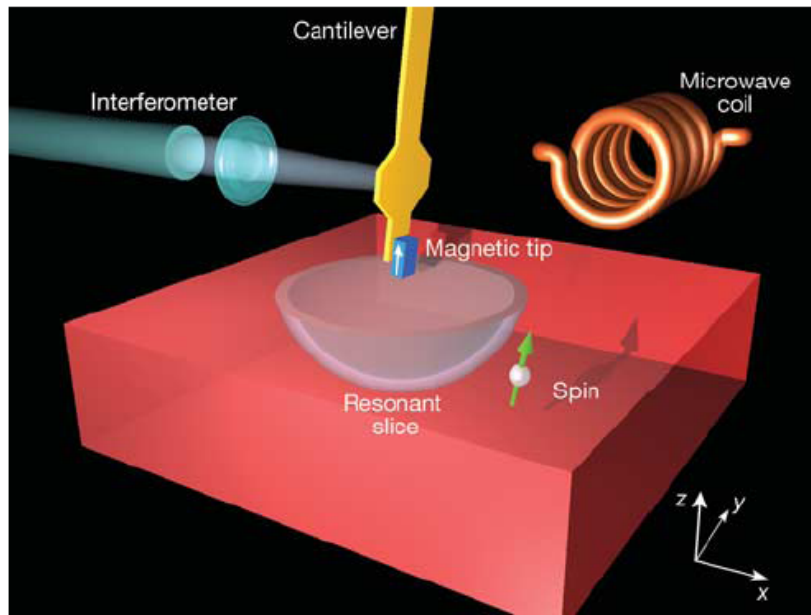
Pendulum geometry



$k \approx \text{mN/m}$
No snap in to contact!



Magnetic Resonance Force Microscopy: Detection of single electron spins vertically mounted cantilevers (pendulum)



D. Rugar et al., Nature 430, 329 (2004)

Atomare Reibung und Kontrolle von Reibung

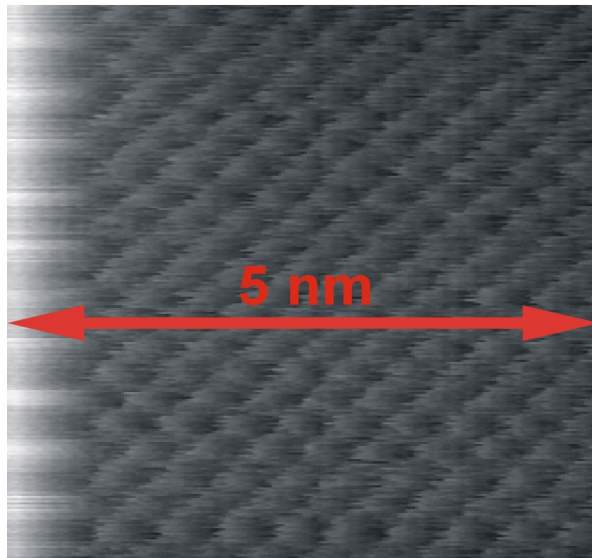
How to understand atomic friction?

Can we avoid atomic friction?

Can we control friction?

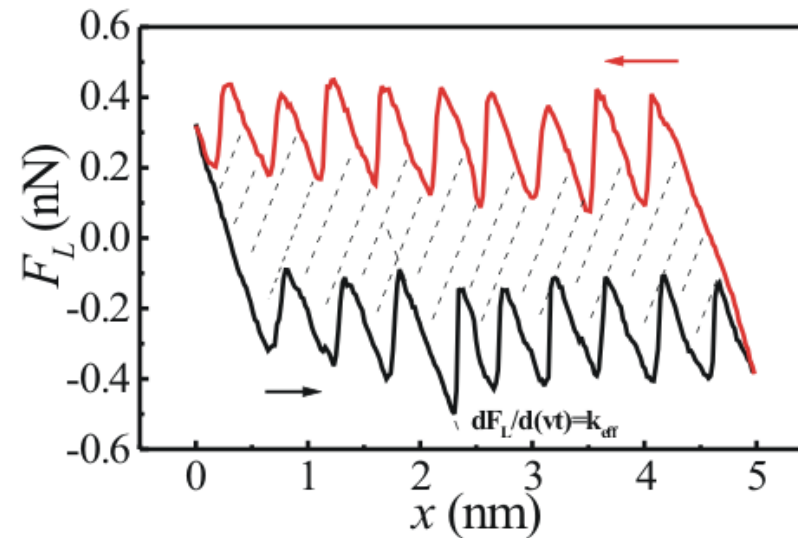
Friction on the Nanometer-scale: Atomic-Stick Slip

Atomic stick-slip



KBr(001)-crystal

Friction loop

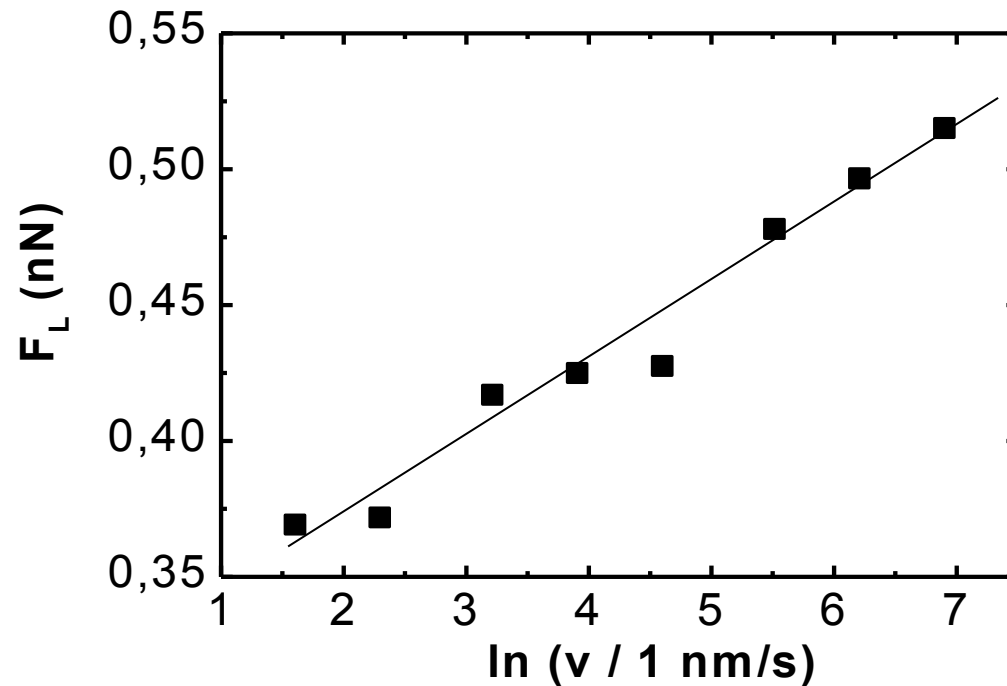


$$F_N = 0.44 \text{ nN}$$

$$E_{\text{diss}} = 1.4 \text{ eV}$$

(per slip)

Velocity dependence of atomic friction

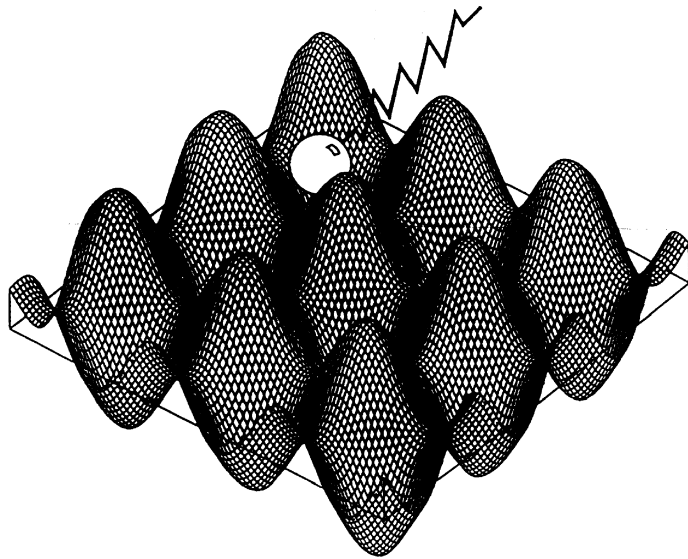


- Friction increases with the logarithm of velocity
- The slope of the curve increases with the applied load

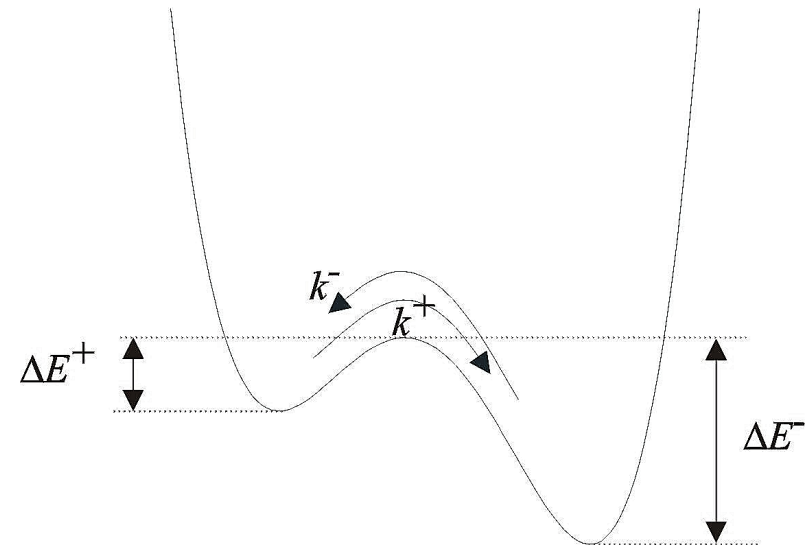
E. Gnecco et al., *Phys. Rev. Lett.*, **84**, 1172 (2000)

Interpretation of velocity dependence

Tomlinson model:



thermal activation:

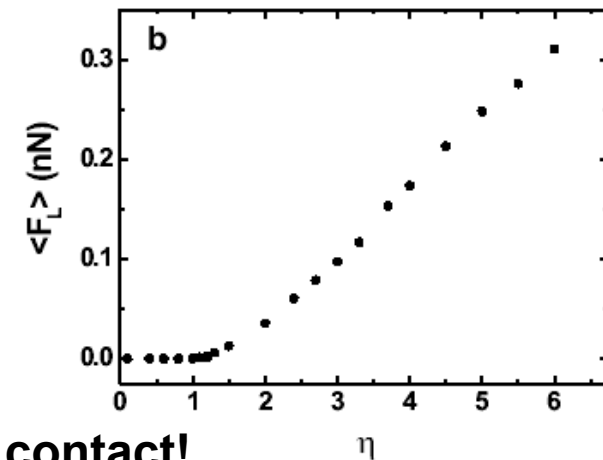
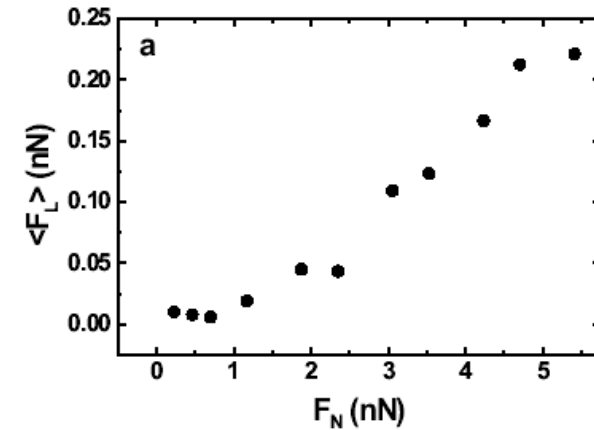
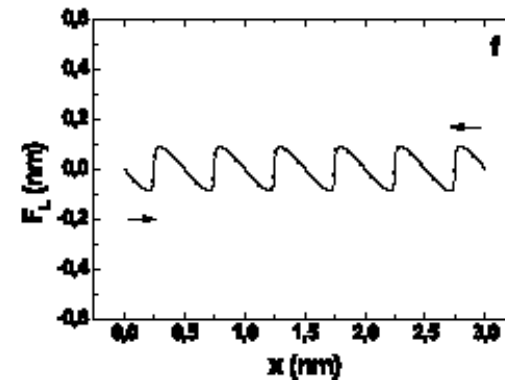
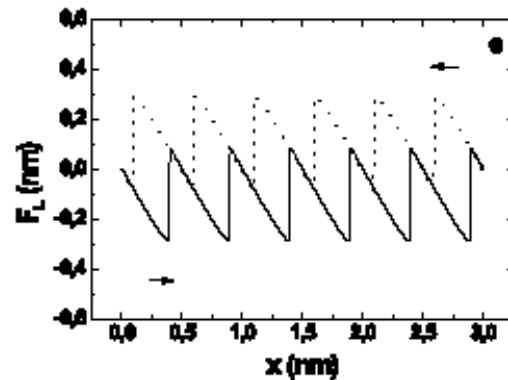
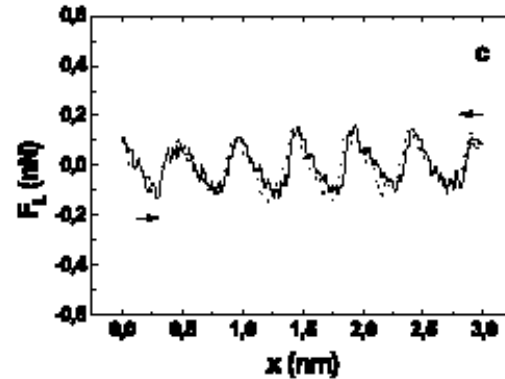
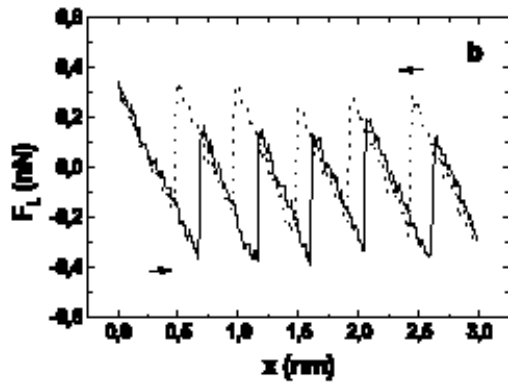


$$F_L(v) = F_L + \frac{k_B T}{\lambda} \ln \frac{v}{v_1}$$

Transition to Ultralow Friction on NaCl(001)

UHV FFM with sharp tip vs. Prandtl-Tomlinson model

$k_x = 29 \text{ N/m}$, $k_z = 0.05 \text{ N/m}$, $v_x = 3 \text{ nm/s}$, const. z
 Scans along [100] showing maximum variation



Stick-slip

$$\eta > 1$$

A. Socoliuc et al., *Phys. Rev. Lett.* **92**, 134301 (2004)

Continuous sliding in contact!

$$\eta < 1$$

$$\text{mean load } F_N = F_z + 0.7 \text{ nN}$$

1d-Prandtl-Tomlinson-Model

Potential energy:

$$U = -\frac{E_0}{2} \cos\left(2\pi \frac{x_t}{a}\right) + \frac{1}{2} k(x_t - x_s)^2$$

Stability criterion:

$$\frac{\partial U^2}{\partial x_t^2} = \frac{2\pi^2}{a^2} E_0 \cos\left(2\pi \frac{x_t}{a}\right) + k > 0$$

$$\eta = \frac{2\pi^2 E_0}{ka^2} = \pi^2 \frac{E_0}{ka^2/2}$$

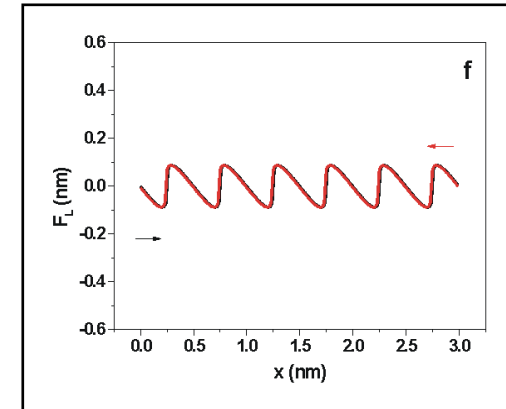
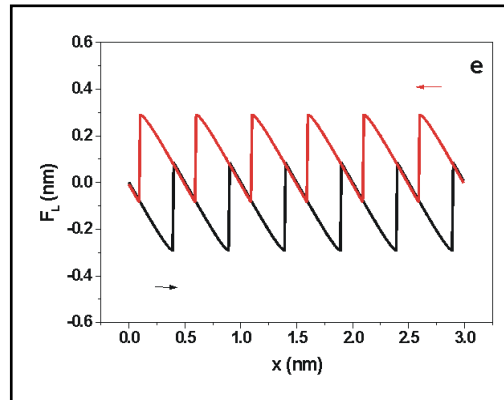
$\eta > 1$

$\eta < 1$

$\eta = 3$

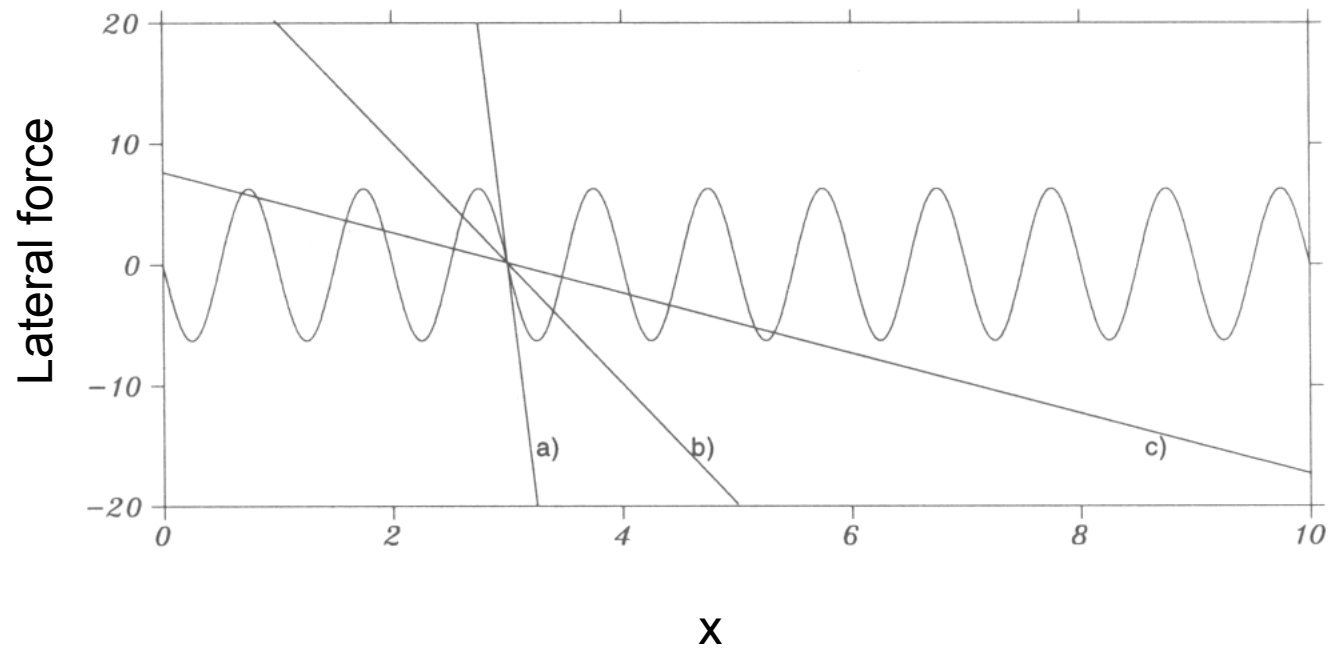
$\eta = 1$

$\eta < 1$: unique sliding solution
 $\eta > 1$: instabilities

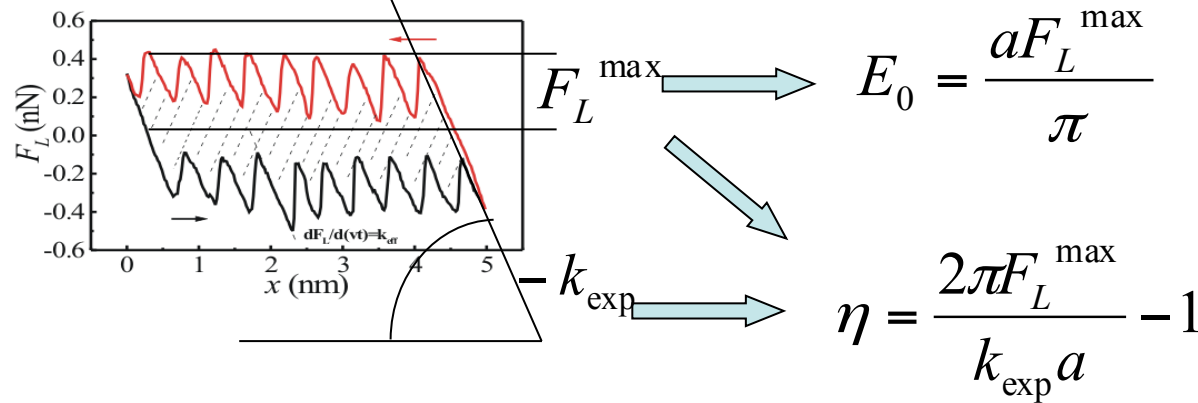


Instability Criterium

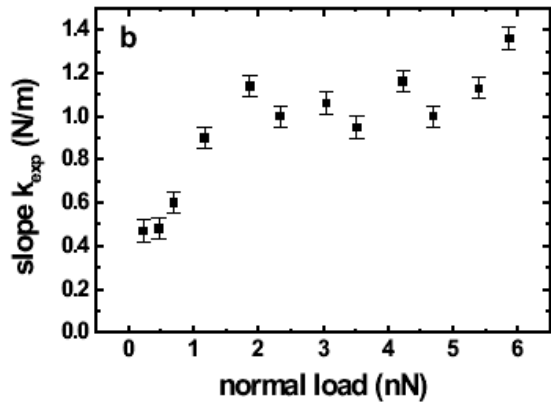
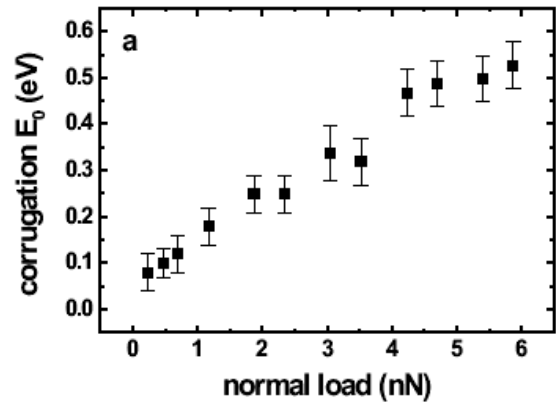
1d: Effective spring constant equals 2nd derivative of adiabatic potential between tip and sample



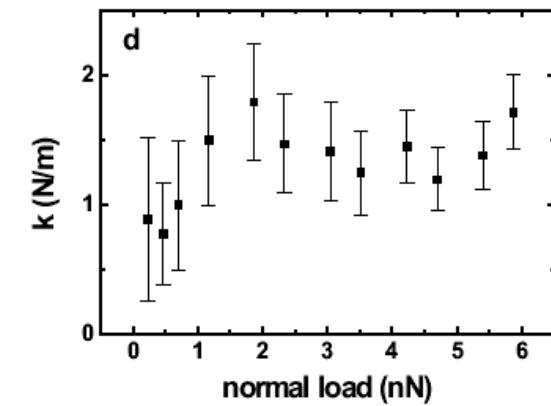
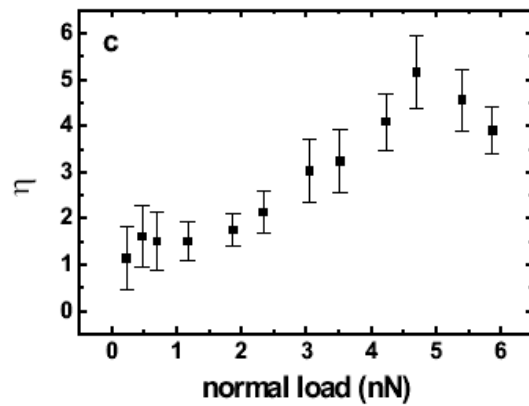
Dependence of Tomlinson Parameters



$$k = \frac{\eta + 1}{\eta} k_{\text{exp}}$$

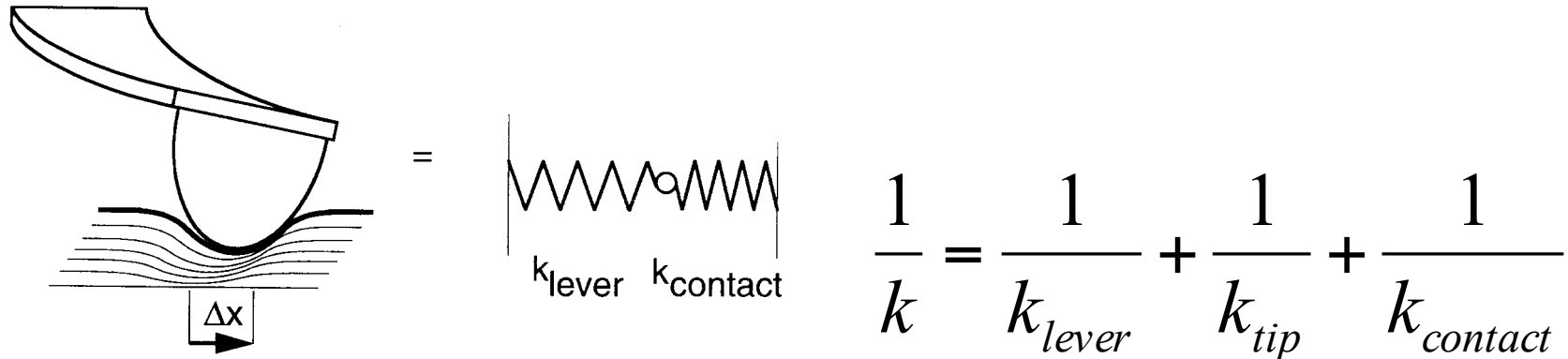


E_0 : linear increase with normal forces



k : rather independent (contact area const.?)

Lateral contact stiffness



R. Carpick et al, Appl. Phys. Lett. 70, 1548-1550 (1997)

Here: $k_{\text{lever}} = 29 \text{ N/m} \gg k \Rightarrow k_{\text{contact}} \approx 1\text{-}2 \text{ N/m}$

Continuum model :

$k_{\text{contact}} = 8 a G \Rightarrow a < 1 \text{ \AA} ?$

\Rightarrow Atomistic model needed

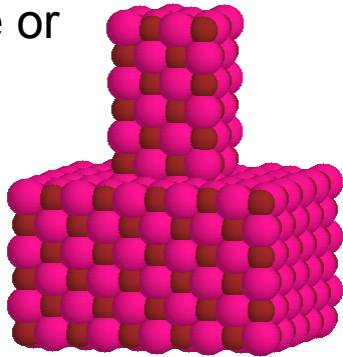
Simulations: KBr cluster tips against KBr(001)

10x10x6 slab (fixed boundaries), SciFi code (L.N. Kantorovich et al.)

Buckingham short-range + shell model Coulomb pair potentials

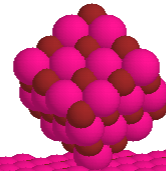
U. Wvder. A. Baratoff, E. Gnecco. T. Trevethan and L. N. Kantorovich

cube or
stub



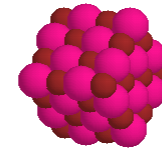
[111]

single



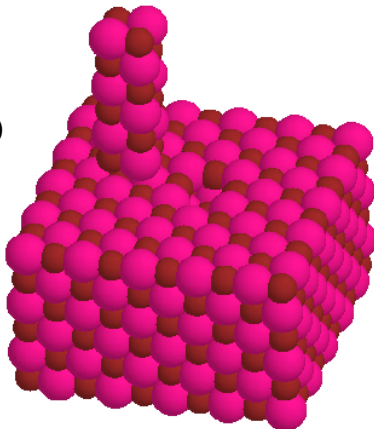
ion

[100]



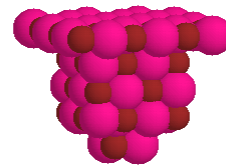
edge

stab



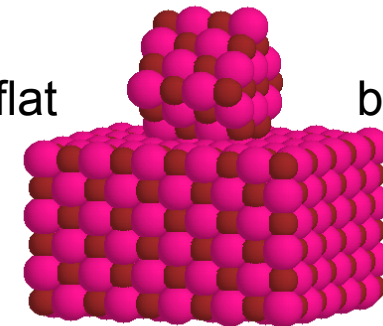
[001]

pyramid



[011]

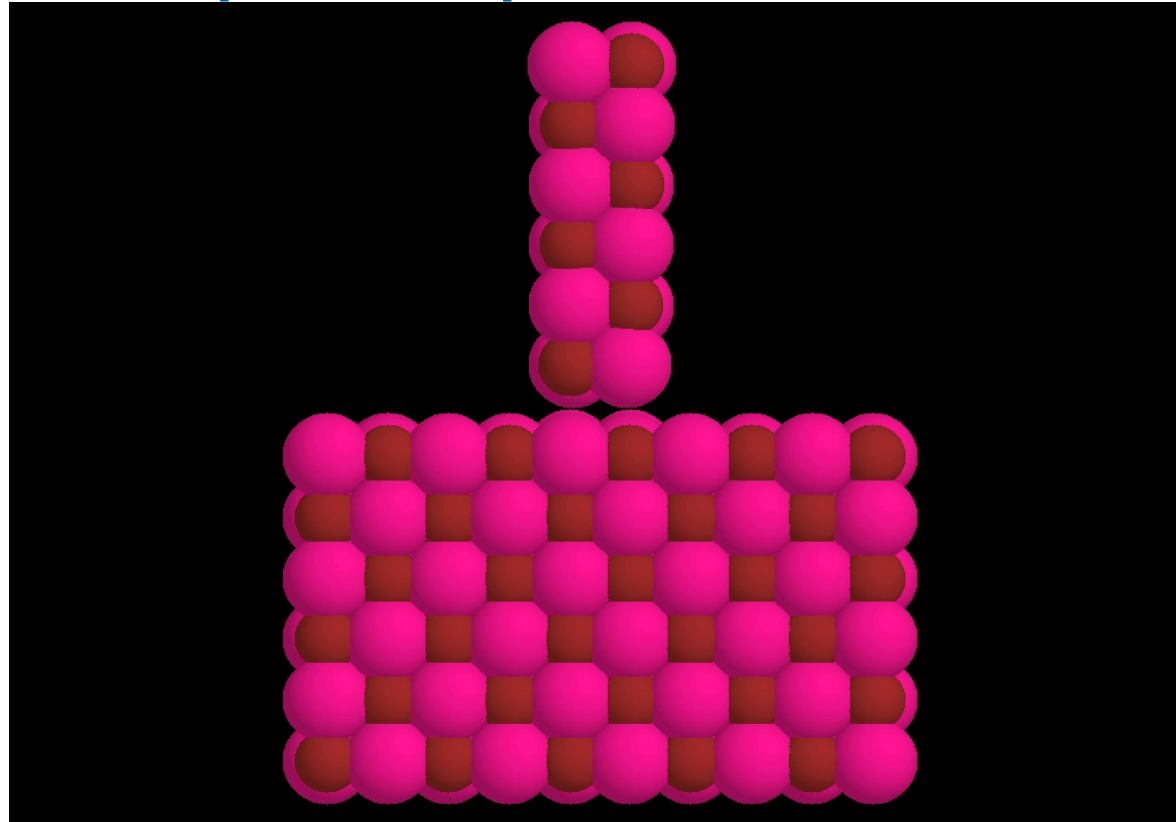
flat



bottom

Tip top layer(s) frozen; $\langle 100 \rangle$ scans at constant z (corrugation unaffected by van der Waals attraction which, together with soft cantilever k_z causes jump to/from contact in experiment)

Atomistic Simulation of the Tip-Sample Interaction

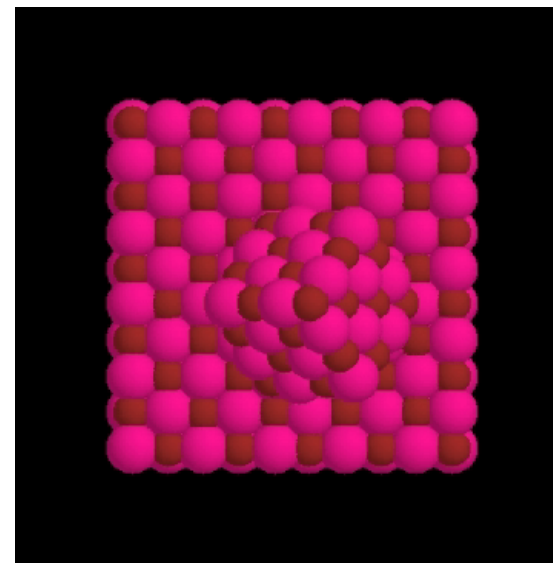
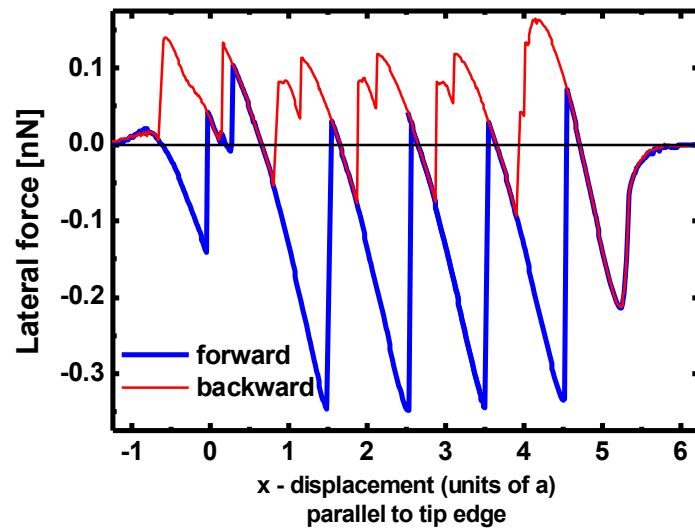
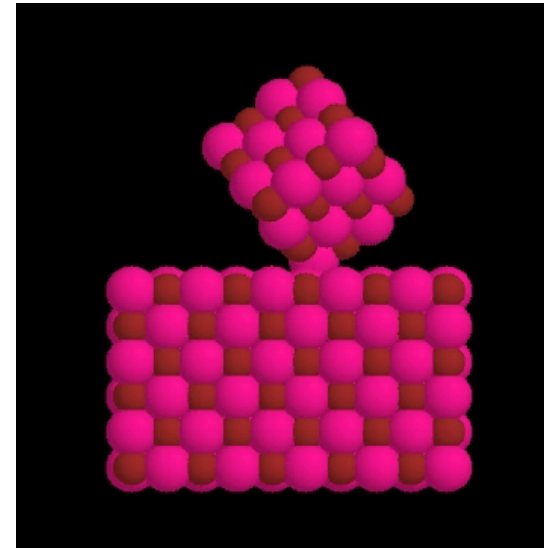
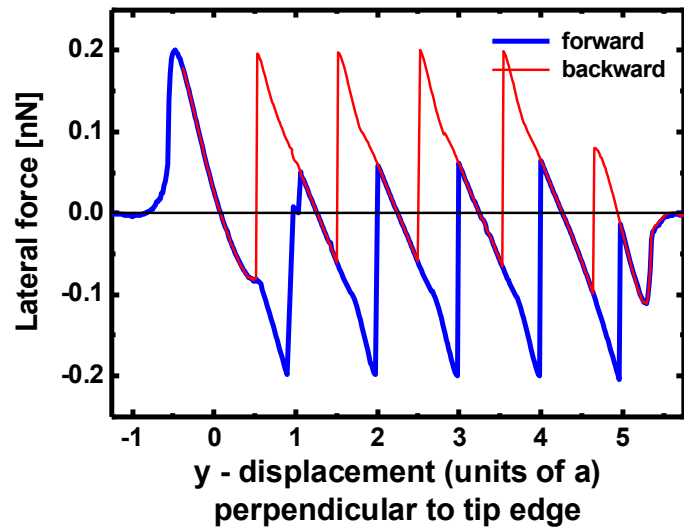


Quasi-static atomistic simulation using pair potentials

L. Kantorovich, T. Trevethan, King's College London

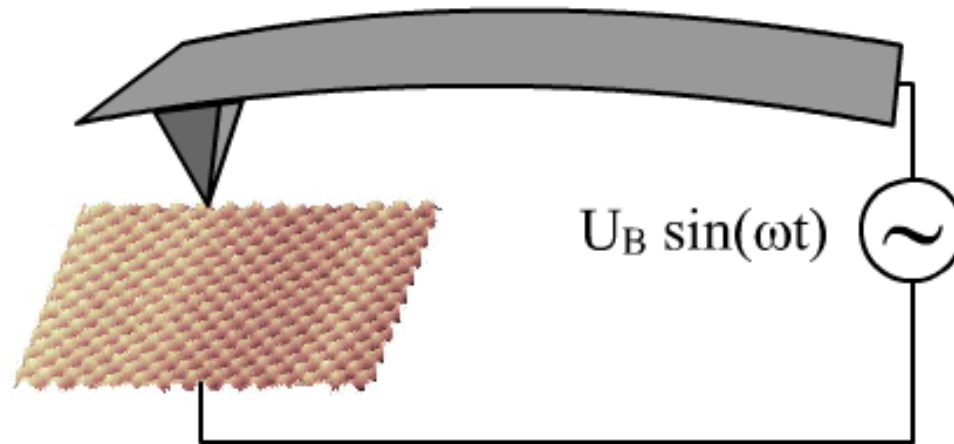
U. Wyder, A. Baratoff, University Basel

[111] K-terminated Tip



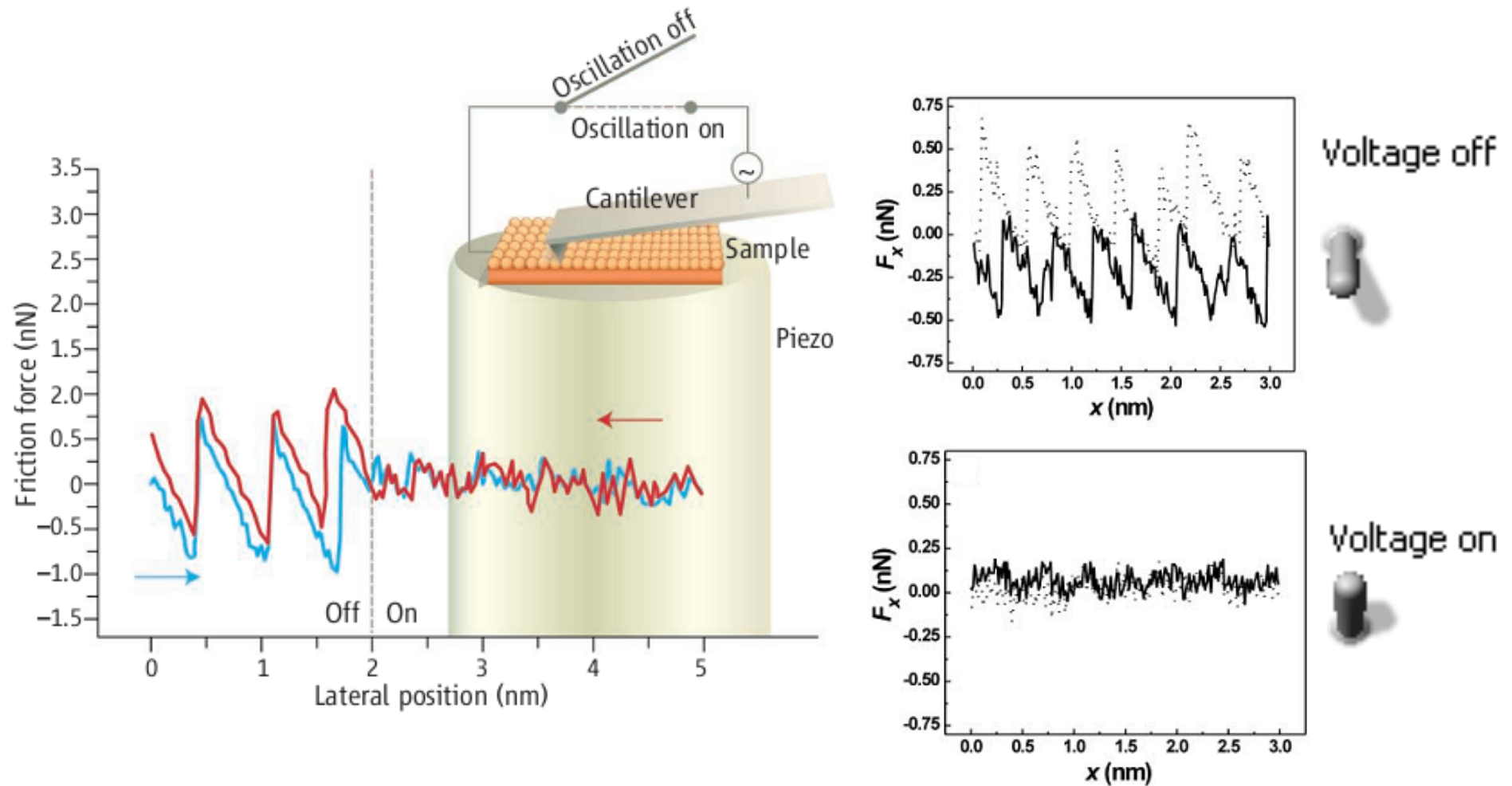
Can we switch friction on and off?

AC voltages were applied across thin KBr and NaCl crystals:



- Capacitive interaction between lever and sample holder $\propto U_B^2$
- Coulomb interaction $\propto U_B$

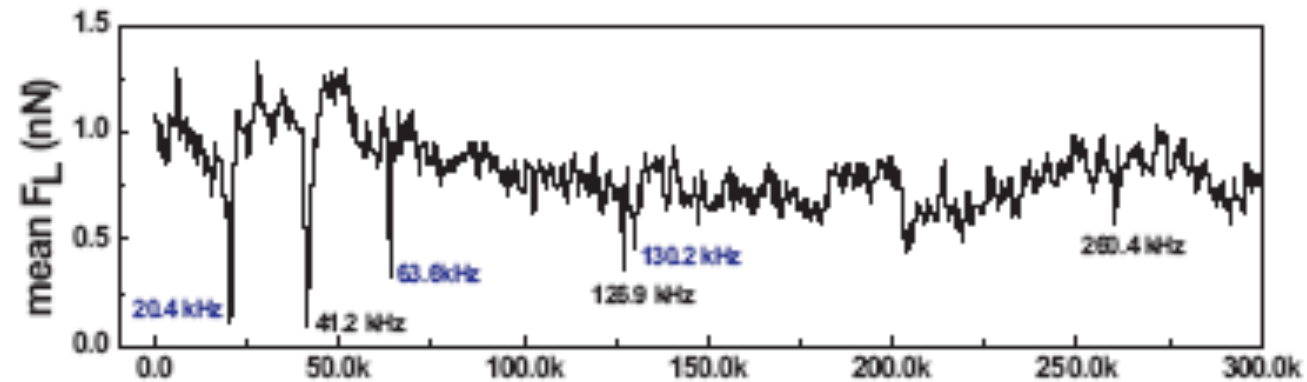
Controlling Friction: Actuation of Nanometer-Sized Contacts



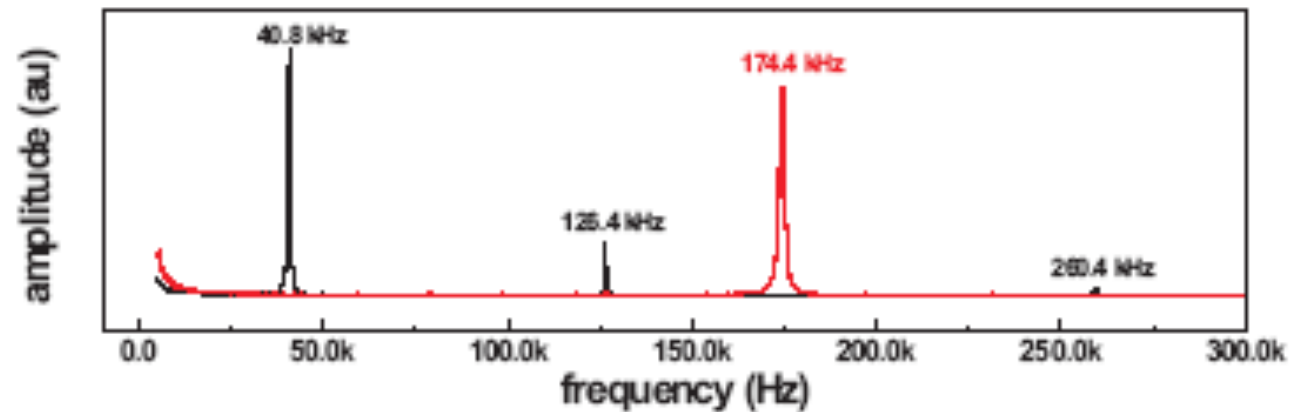
A. Socoliuc, E. Gnecco, S. Maier, O. Pfeiffer, A. Baratoff, R. Bennewitz, E. Meyer,
Science **313**, 207 (2006)

Frequency dependence of friction

Friction:

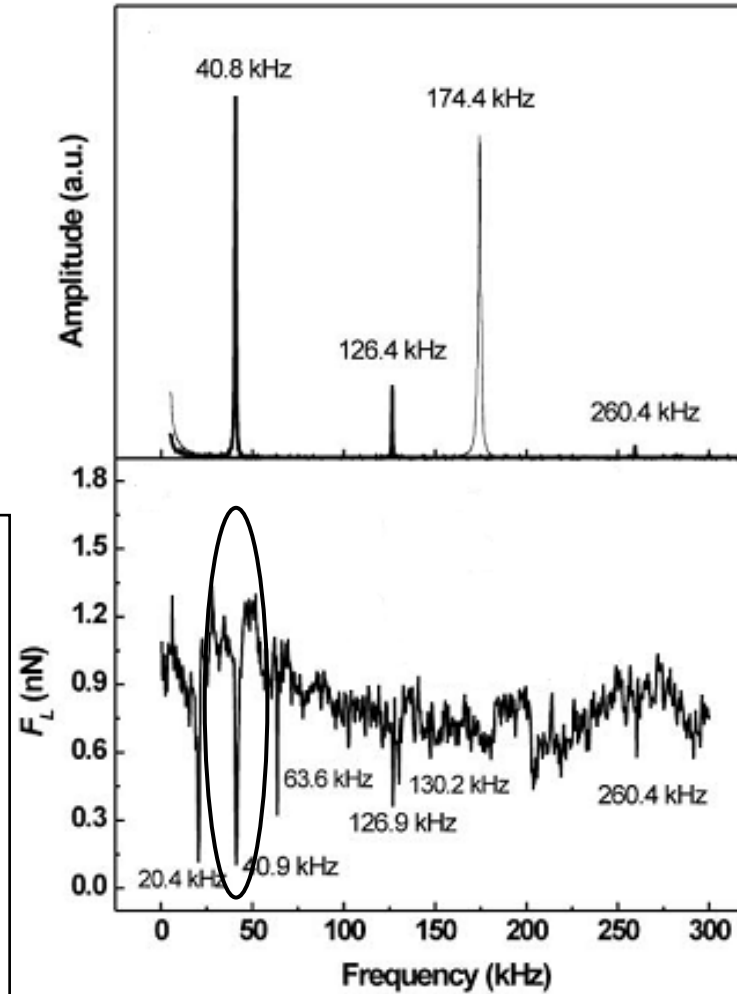
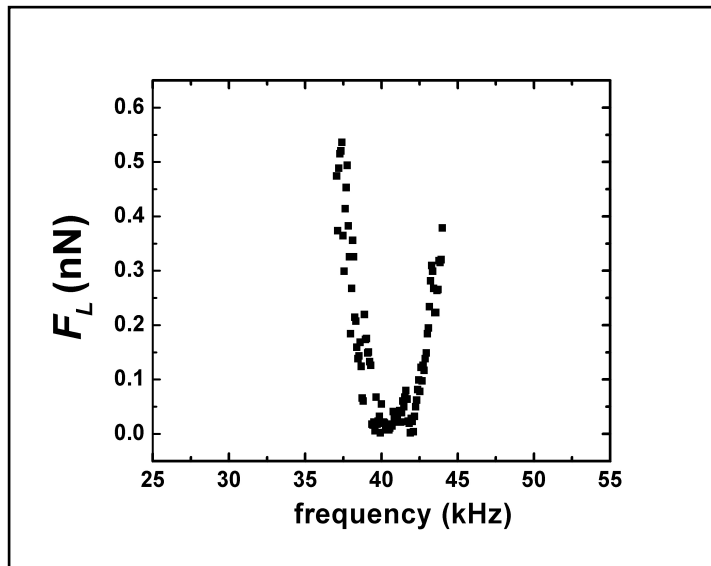


Thermal noise:



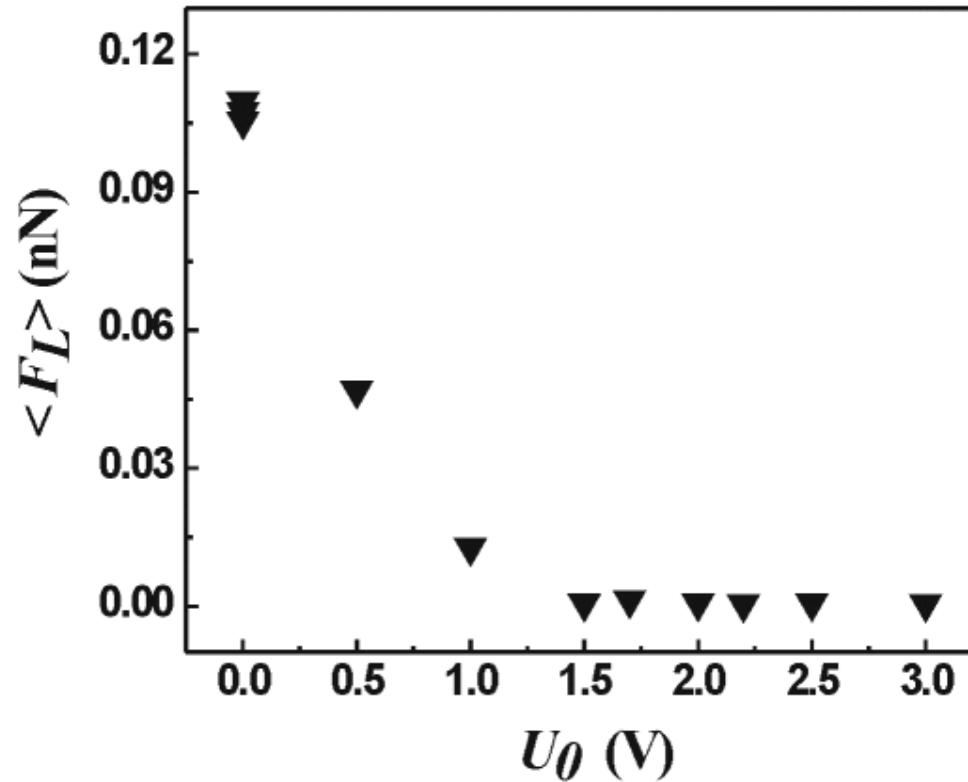
- Friction is “switched off” only if $f_{\text{exc}} = f_{\text{norm}}$ or $(1/2) f_{\text{norm}}$
- No effect when $f_{\text{exc}} = f_{\text{tors}}$!

Frequency dependence of friction



Reduction of friction at and resonance
Frequencies of the the bending modes f and $f/2$

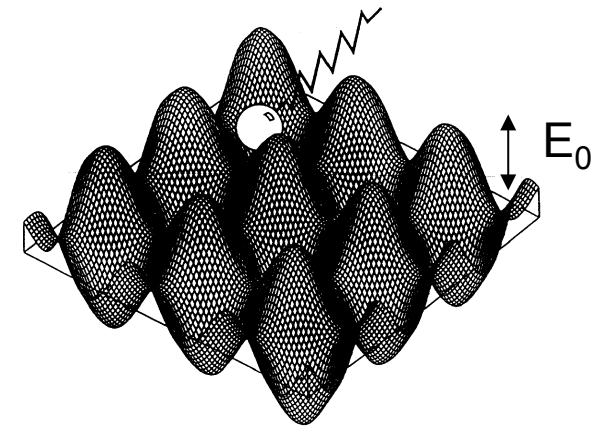
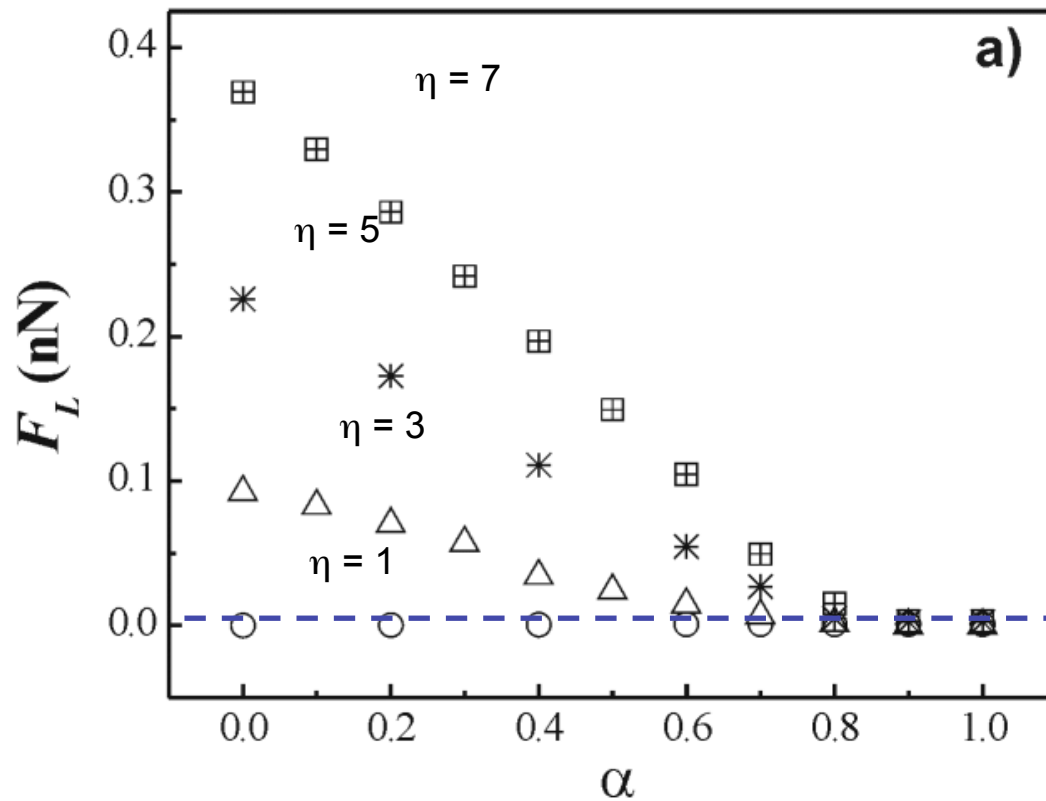
Voltage dependence of friction



- Friction goes down to zero increasing the excitation amplitude !

Interpretation of Dynamic Superlubricity

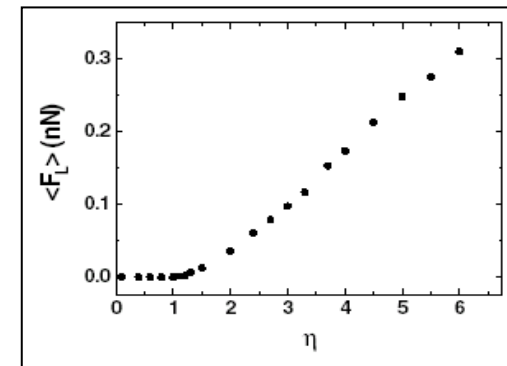
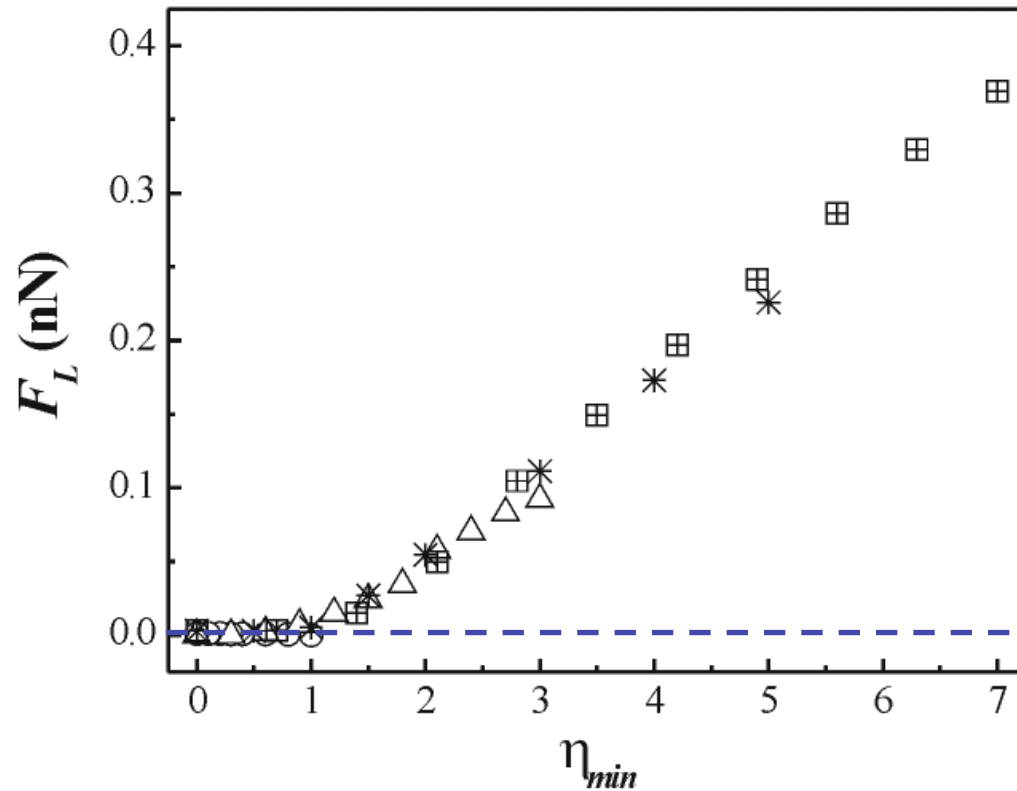
- In the Tomlinson model: We replace E_0 with $E_0 (1 + \alpha \cos \omega t)$
- The parameter α increases with the applied voltage



Friction decreases
when $\alpha \rightarrow 1$

New parameter η_{min}

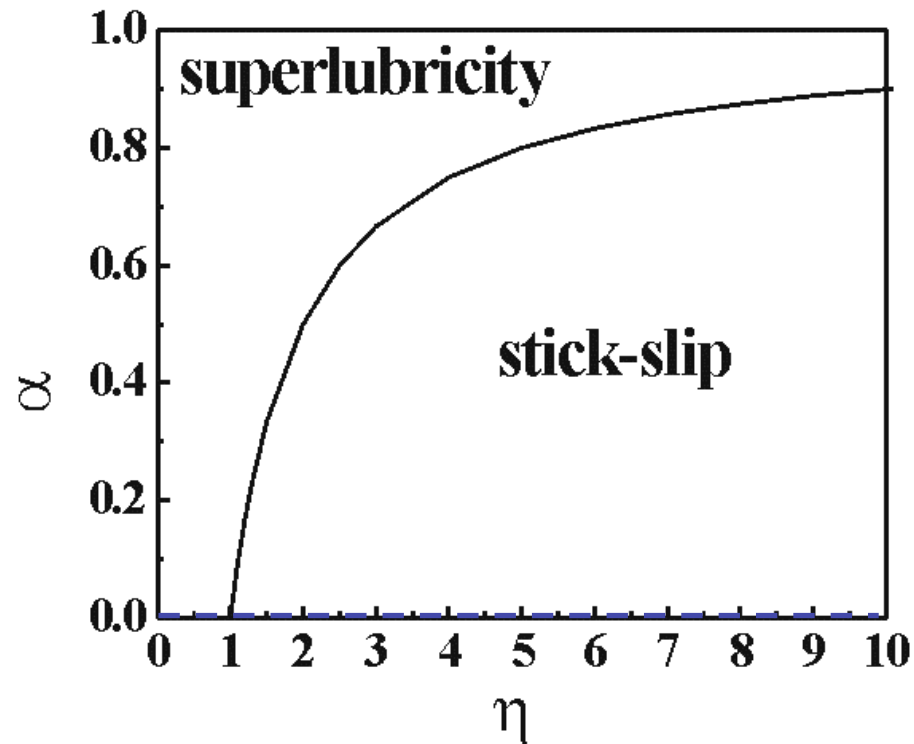
- The parameter $\eta_{min} = \eta (1-\alpha)$ determines superlubricity



“Static” case

„Phase“ diagram of friction

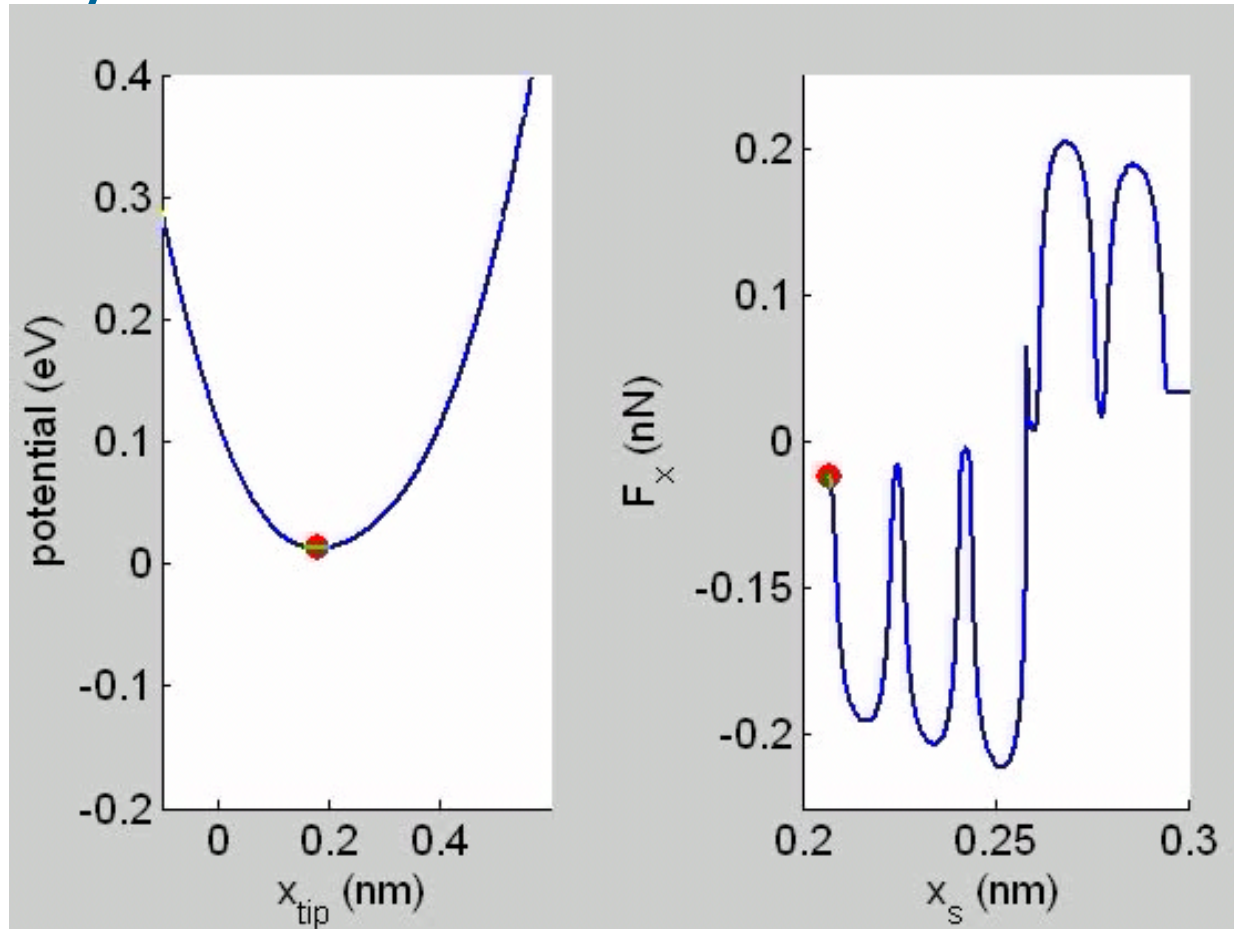
- A "phase diagram" in the η - α plane can be drawn:



$$\alpha_{\text{cr}} = 1 - \frac{1}{\eta}$$

"Static" SL

Modulation of the Energy barrier by actuation of the nano-contact

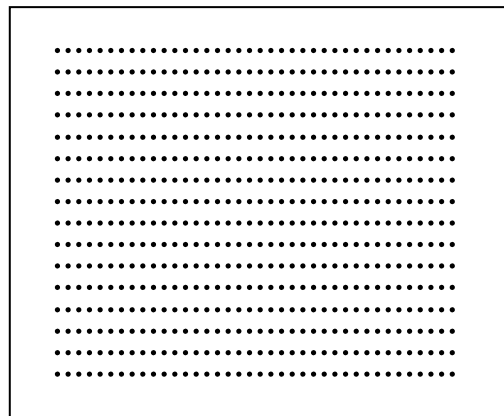


**Standard parameters for the Tomlinson model with excitation:
0.5 times critical damped**

Parameters: $\eta=4$, $\alpha=0.9$, $f=567\text{Hz}$, $v=10\text{e-}9\text{m/s}$, $\gamma=1\text{e-}6\text{kg/s}$,
 $m=8\text{e-}13\text{kg}$, $a=0.5\text{e-}9\text{m}$, $c=1\text{N/m}$

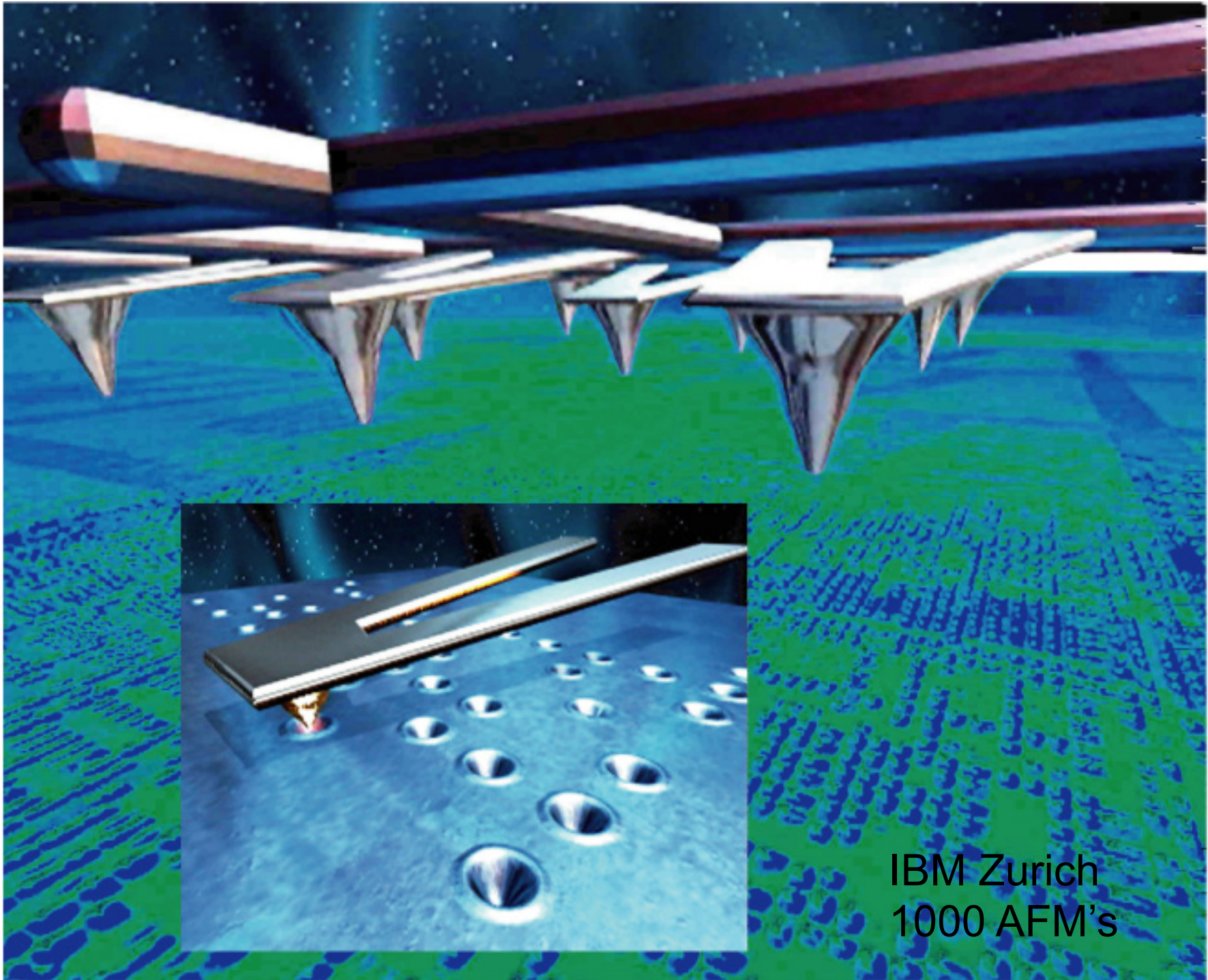
Ultralow friction on the macroscopic scale?

- Normal force per asperity is limited to 1nN
- Macroscopic weight of 1g \approx 10mN has to be distributed to 10^7 mini-tips (\approx array of 3'000 x 3'000 tips)



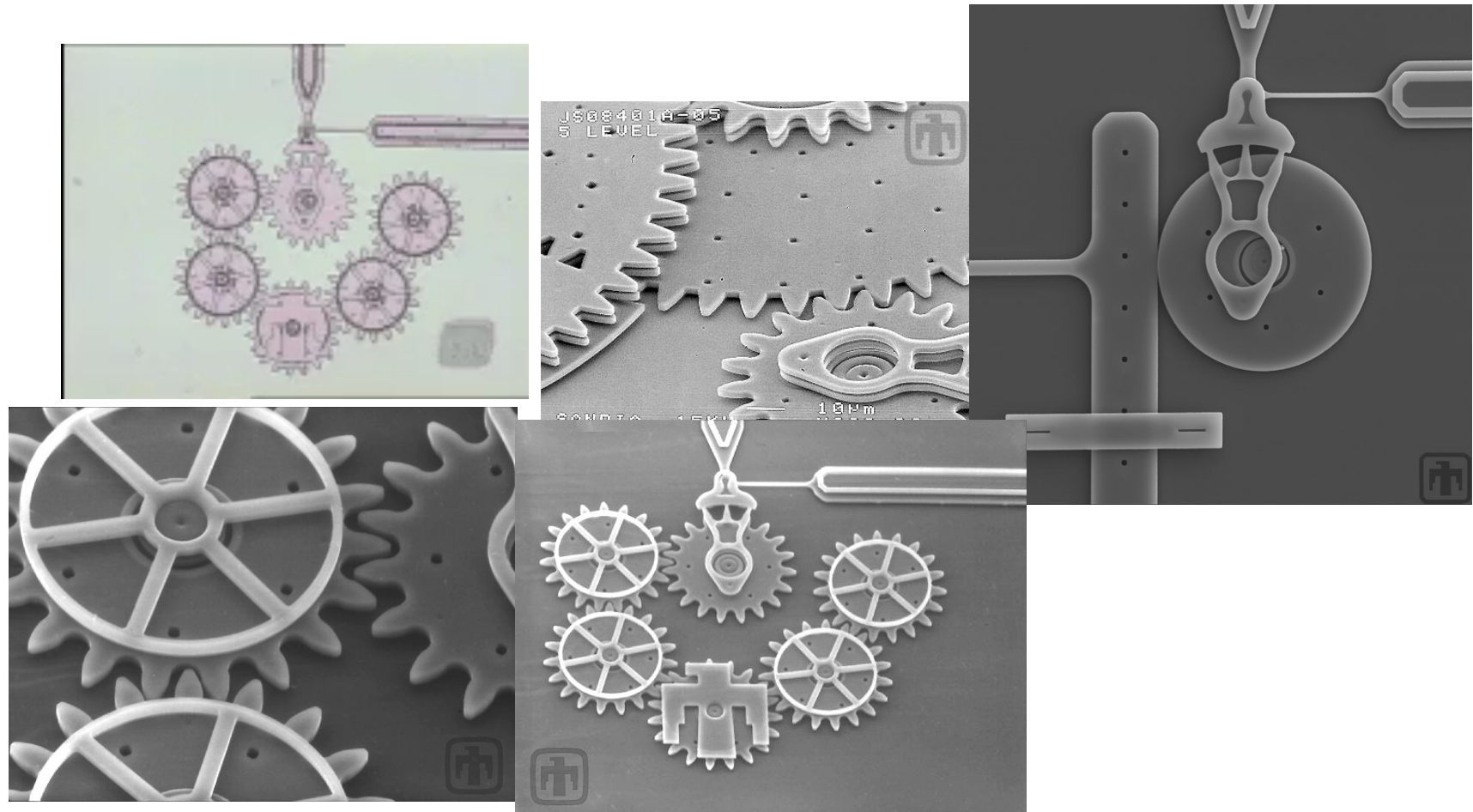
10mm

Tips with a
spacing of $3\mu\text{m}$



IBM Zurich
1000 AFM's

MEMS-Devices



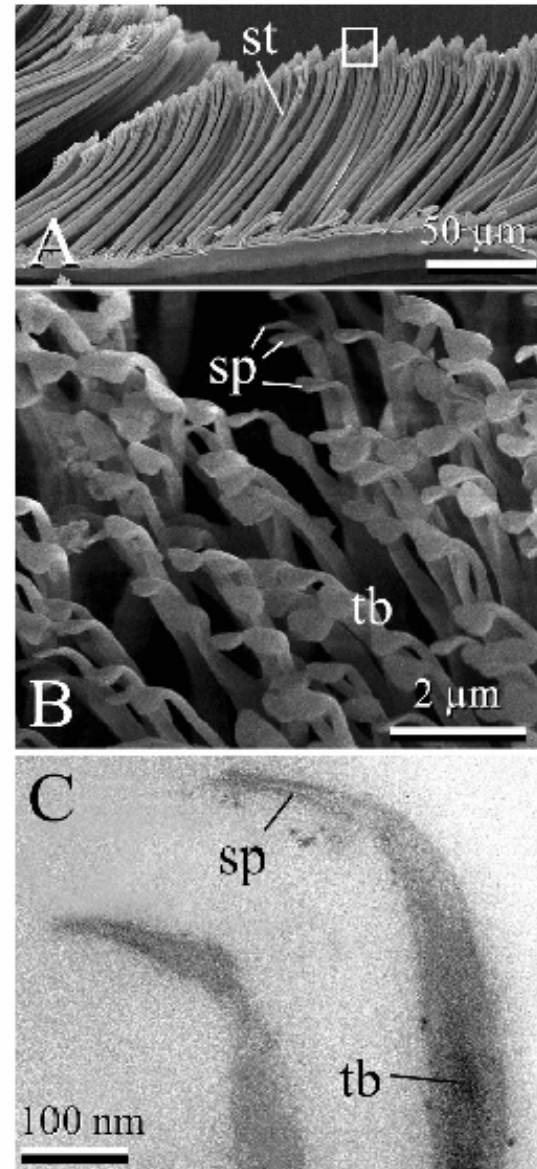
Courtesy of Sandia National Laboratories, SUMMiTTM Technologies,
www.mems.sandia.gov"

Gecko uses nanometer-sized contacts to climb walls



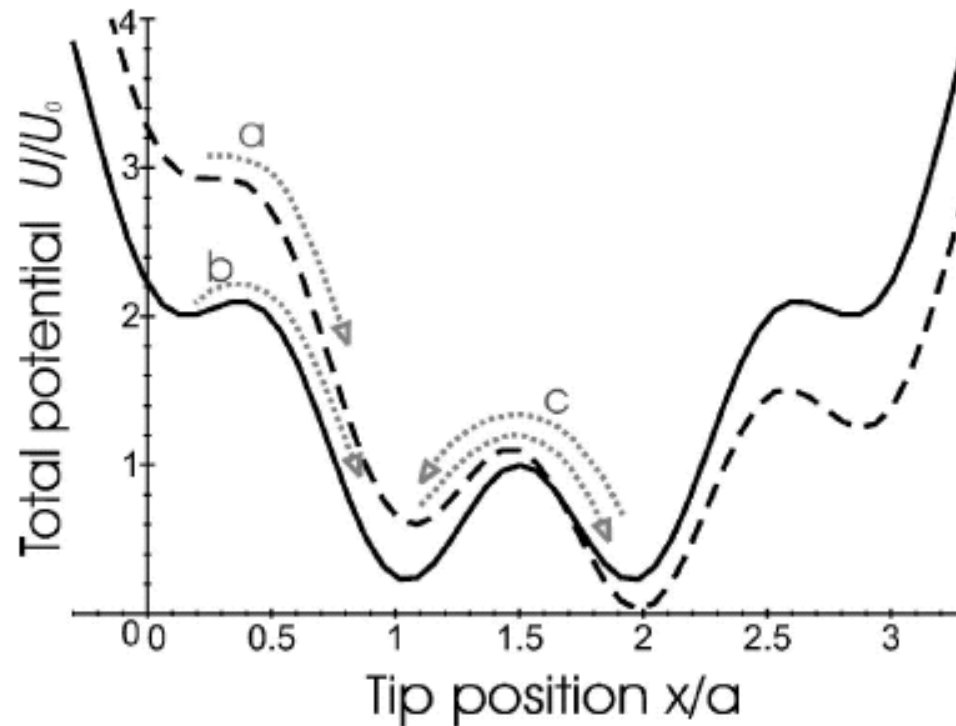
Gecko is able to control the contact area on all length scales

From B. Persson and S. Gorb
JCP, 119, 11437 (2003)



Other forms of "superlubricity"

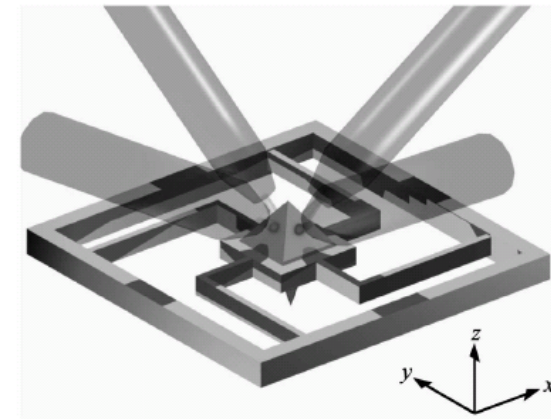
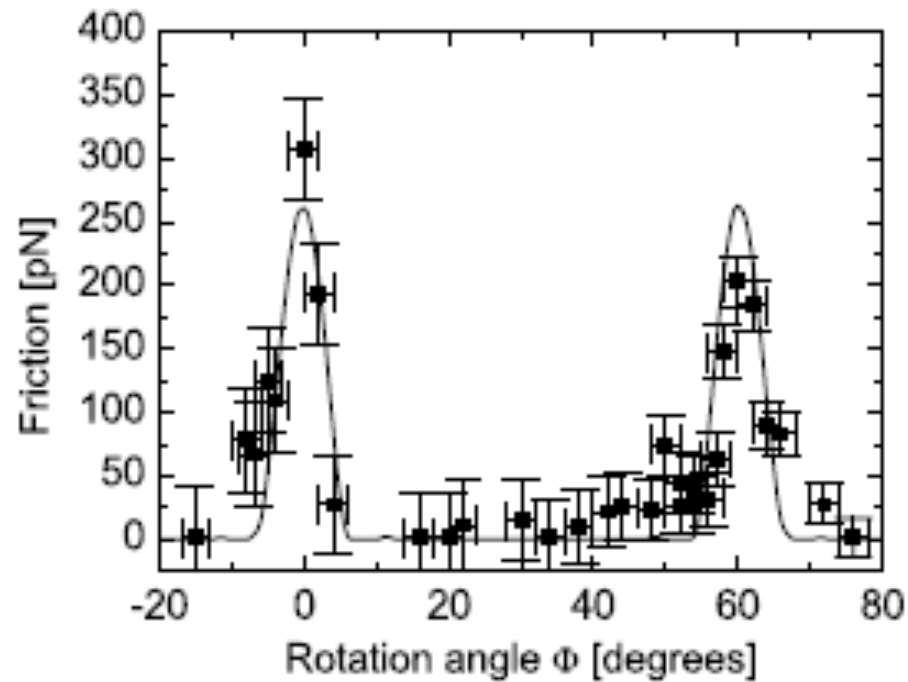
- **Thermolubricity** (Krylov et al., PRE 2005):



(taking "backjumps" into account \rightarrow friction vanishes at low speed)

Other forms of "superlubricity"

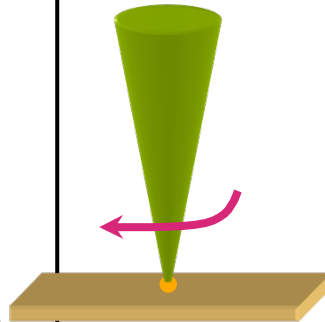
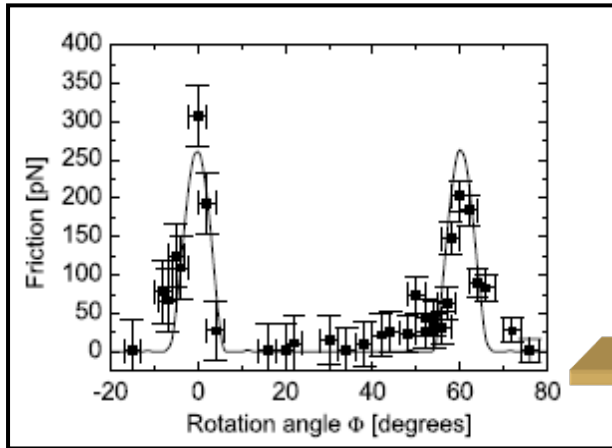
- **Structural lubricity** (Dienwiebel et al., PRL 2004):



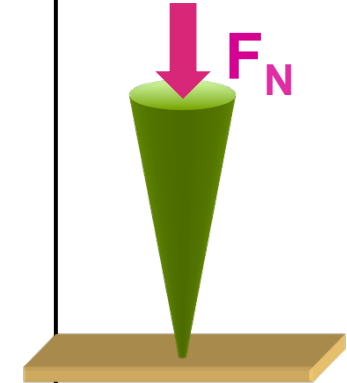
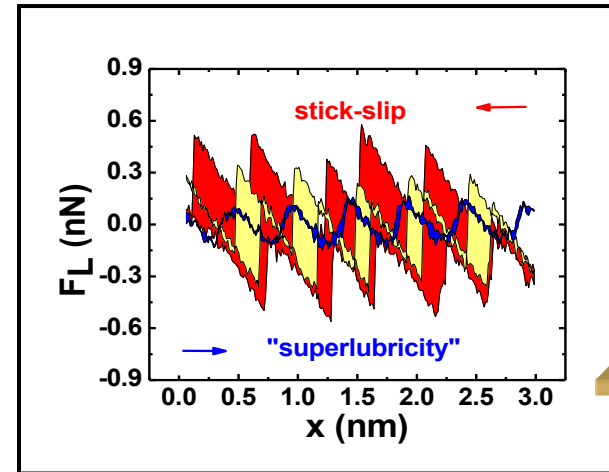
(two mismatched graphite flakes sliding past each other)

Transitions to negligible friction in different dry contacts

Graphite against rotated flake picked up by tip



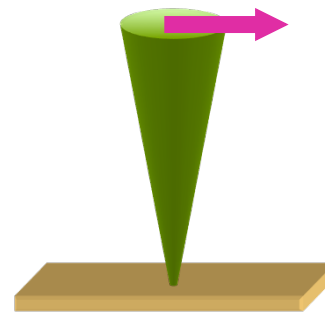
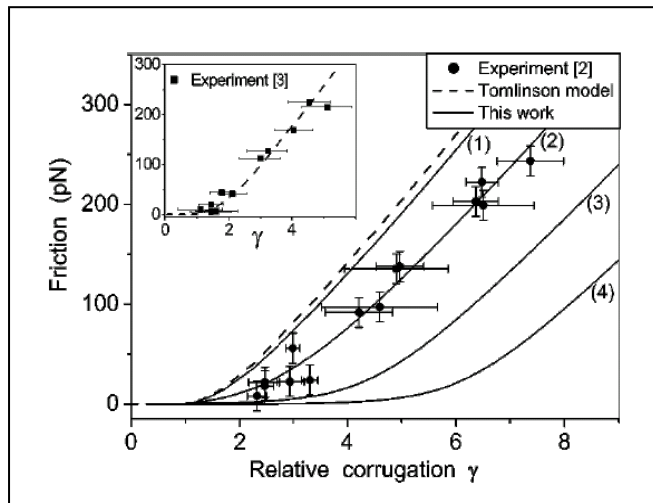
NaCl(001) cleaved in UHV



M. Dienwiebel et al. PRL 92, 126101 (2004)

A. Socoliuc et al. PRL 92, 134301 (2004)

Effective corrugation on graphite reduced at low velocities at fixed room T



Thermal activation:
small velocity ~ high temperature

Like creep of dislocations
or vortices in type II superconductors

S.Yu Krylov et al. PRE 71, 065101(R) (2005)

Appendix: Calibration of lateral forces

Force calibration (2)

- Cantilever **thickness** also from the **resonance frequency**:

$$t = \frac{2\sqrt{12}\pi}{1.875^2} \sqrt{\frac{\rho}{E}} f_0 l^2$$

- ρ , E : density and Young modulus

(Nonnenmacher et al., JVSTB 1991)

- For pure silicon:

$$\rho = 2.33 \cdot 10^3 \text{ kg/m}^3$$

$$E = 1.69 \cdot 10^{11} \text{ N/m}^2$$

Force calibration (3)

- **Normal and lateral spring constants of cantilever:**

$$c_N = \frac{Ewt^3}{4l^3}$$

$$c_L = \frac{Gwt^3}{3h^2l}$$

- G: shear modulus
- For pure silicon:

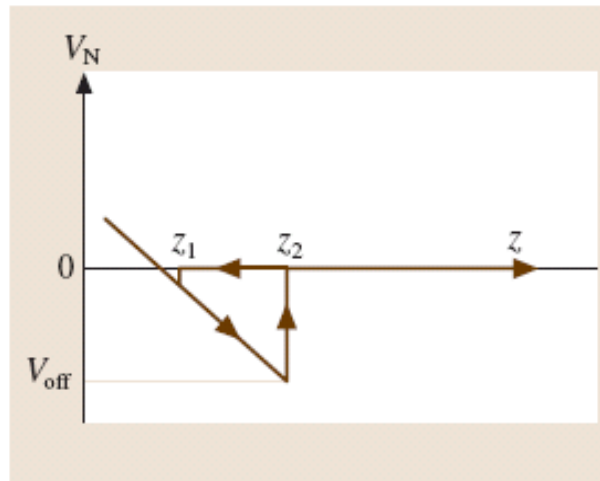
$$\rho = 2.33 \cdot 10^3 \text{ kg/m}^3$$

$$E = 1.69 \cdot 10^{11} \text{ N/m}^2$$

$$G = 0.5 \cdot 10^{11} \text{ N/m}^2$$

Force calibration (4)

- Next step: **sensitivity of photodetector**
- Force-distance curves on hard surfaces (e.g. Al_2O_3):



- Scanner movement = cantilever deflection
- Slope \rightarrow sensitivity

Force calibration (5)

- **Normal and lateral forces:**

$$F_N = c_N S_z V_N$$

$$F_L = \frac{3}{2} c_L \frac{h}{l} S_z V_L$$

(if the light beam is above the probing tip!)

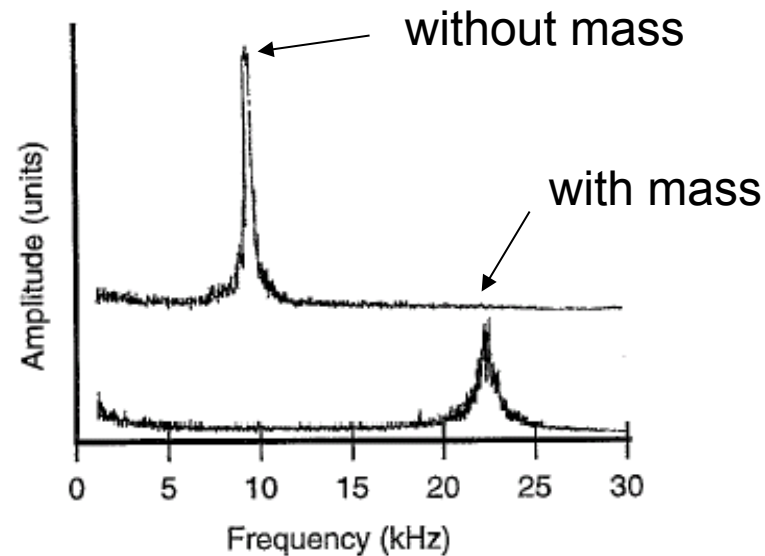
- V_N , V_L : normal and lateral signals

Force calibration (6)

- Alternative method #1: Tungsten **spheres attached to the tip** (Cleveland et al., RSI 1993)
- Frequency shift:

$$f_0 = \frac{1}{2\pi} \sqrt{\frac{c_N}{M + m^*}}$$

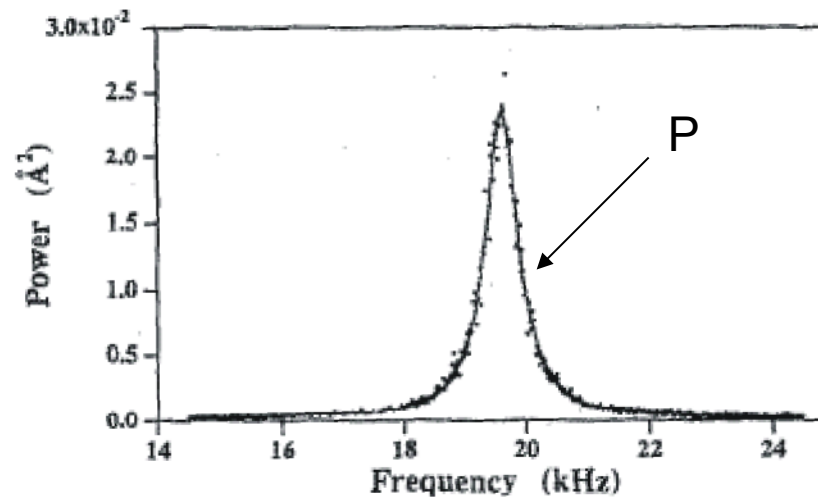
- M, m*: added mass and effective mass of the cantilever



Force calibration (7)

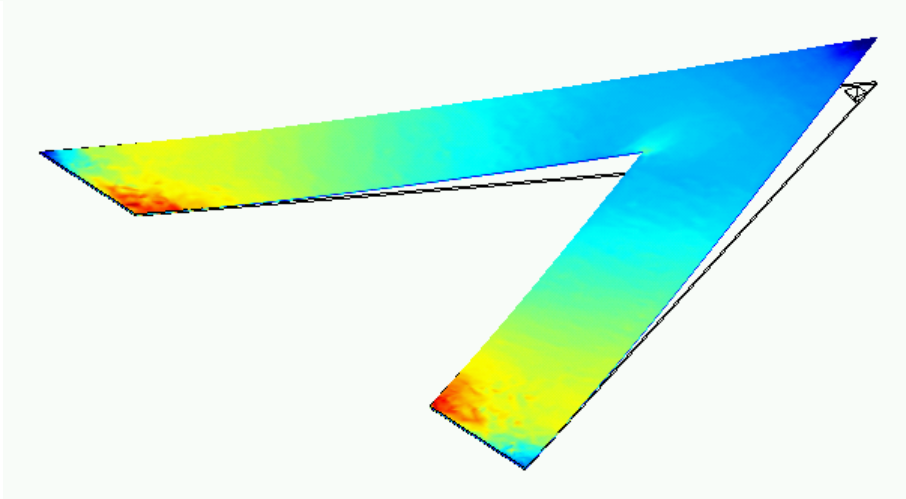
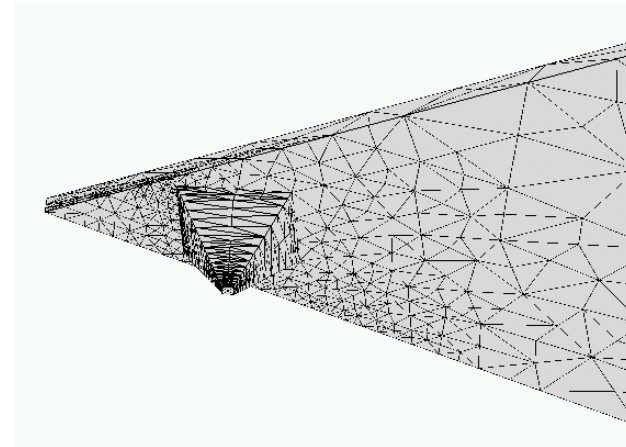
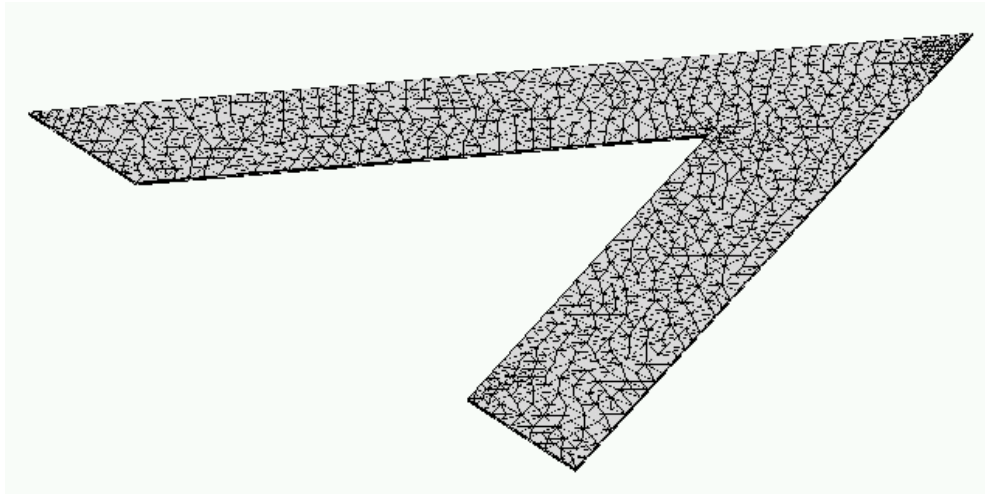
- Alternative method #2: Spring constant **from thermal power spectrum** (Hutter et al., RSI 1993)
- Correct relation (Butt et al., Nanotech. 1995):

$$c_N = \frac{4k_B T}{3P}$$



Force calibration (8)

- Different shapes → **Finite elements analysis** (alternative method #3)

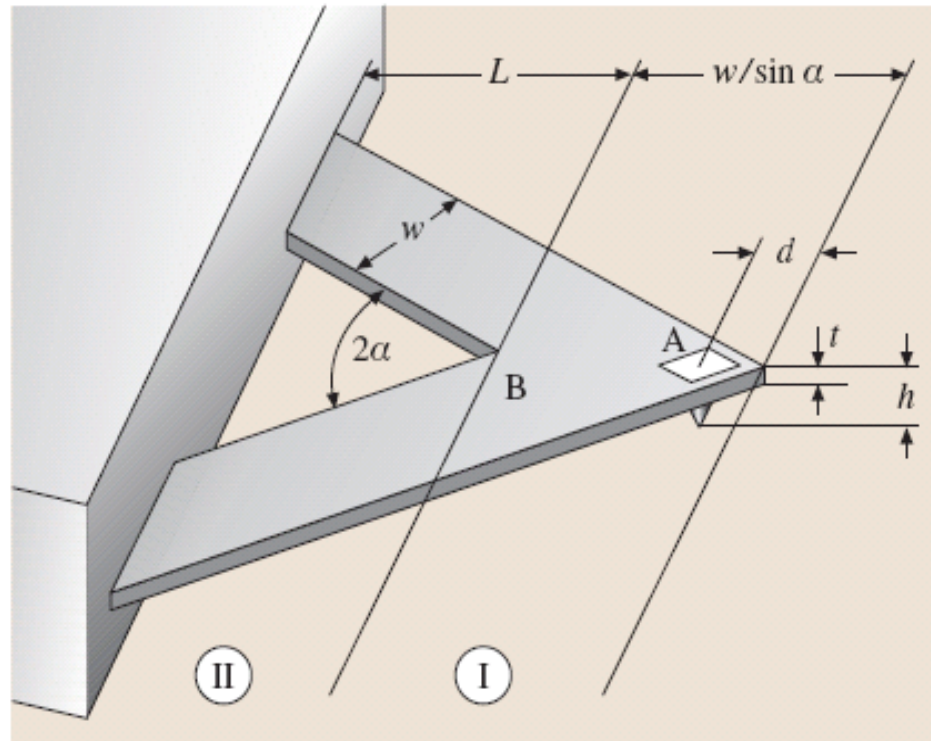


(Femlab™ 3.0)

Force calibration (9)

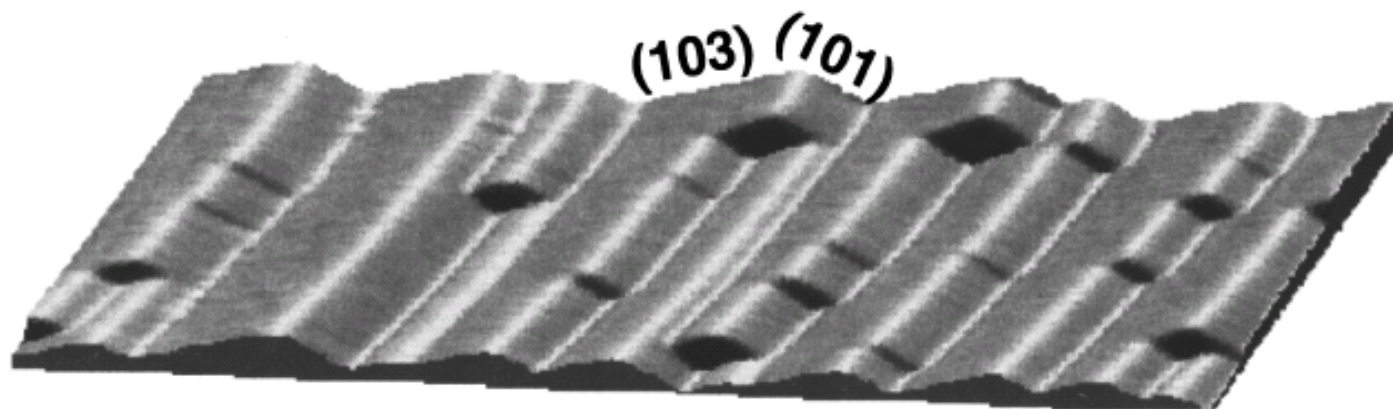
- Approximate relations hold for **V-shaped cantilevers** (Neumeister et al., RSI 1994):

$$c_L = \frac{Et^3}{3(1+\nu)h^2} \left(\frac{1}{\tan \alpha} \ln \frac{w}{d \sin \alpha} + \frac{L \cos \alpha}{w} - \frac{3 \sin 2\alpha}{8} \right)^{-1}$$

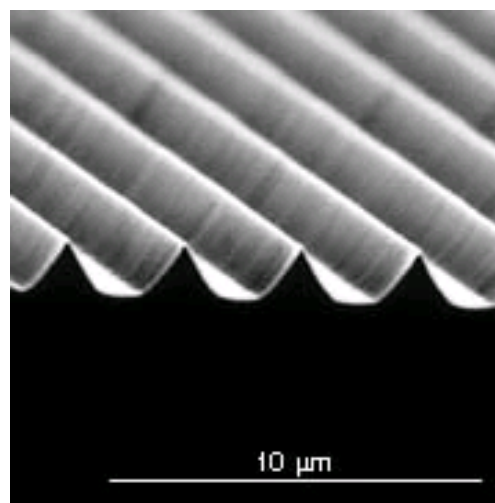


Force calibration (10)

- Alternative method #4: Scanning over profiles with **well-defined slope** (Ogletree et al., RSI 1996)

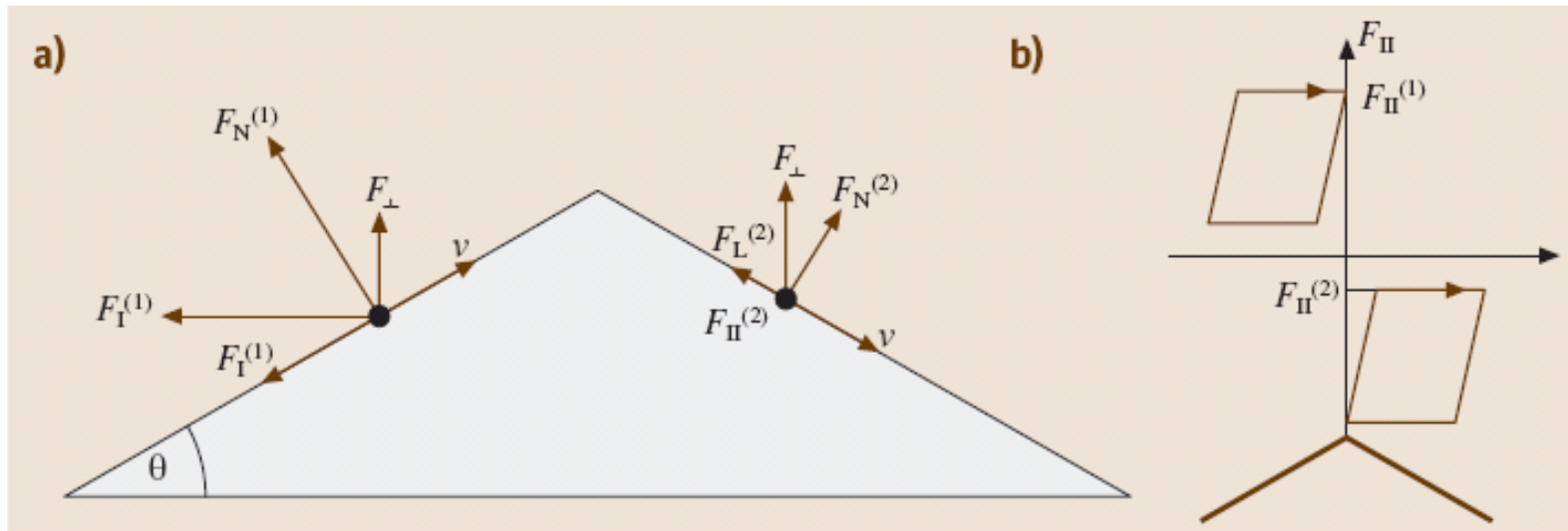


Commercially available grating:



(TGG01, NT-MDT,
Moscow)

Force calibration (11)



$$F_{//} = \frac{\mu + \tan \theta}{1 - \mu \tan \theta} F_{\perp}$$

$$F_{\perp} = \text{const.}$$



$$F_{+} \equiv F_{//}^{(1)} + F_{//}^{(2)} = \frac{2\mu(1 + \tan^2 \theta)}{1 - \mu^2 \tan^2 \theta} F_{\perp}$$

$$F_{-} \equiv F_{//}^{(1)} - F_{//}^{(2)} = \frac{2(1 + \mu^2) \tan \theta}{1 - \mu^2 \tan^2 \theta} F_{\perp}$$

(E. Gnecco, PhD Thesis, 2000)