Nano-Mechanics:
From Nanotechnology to Biology

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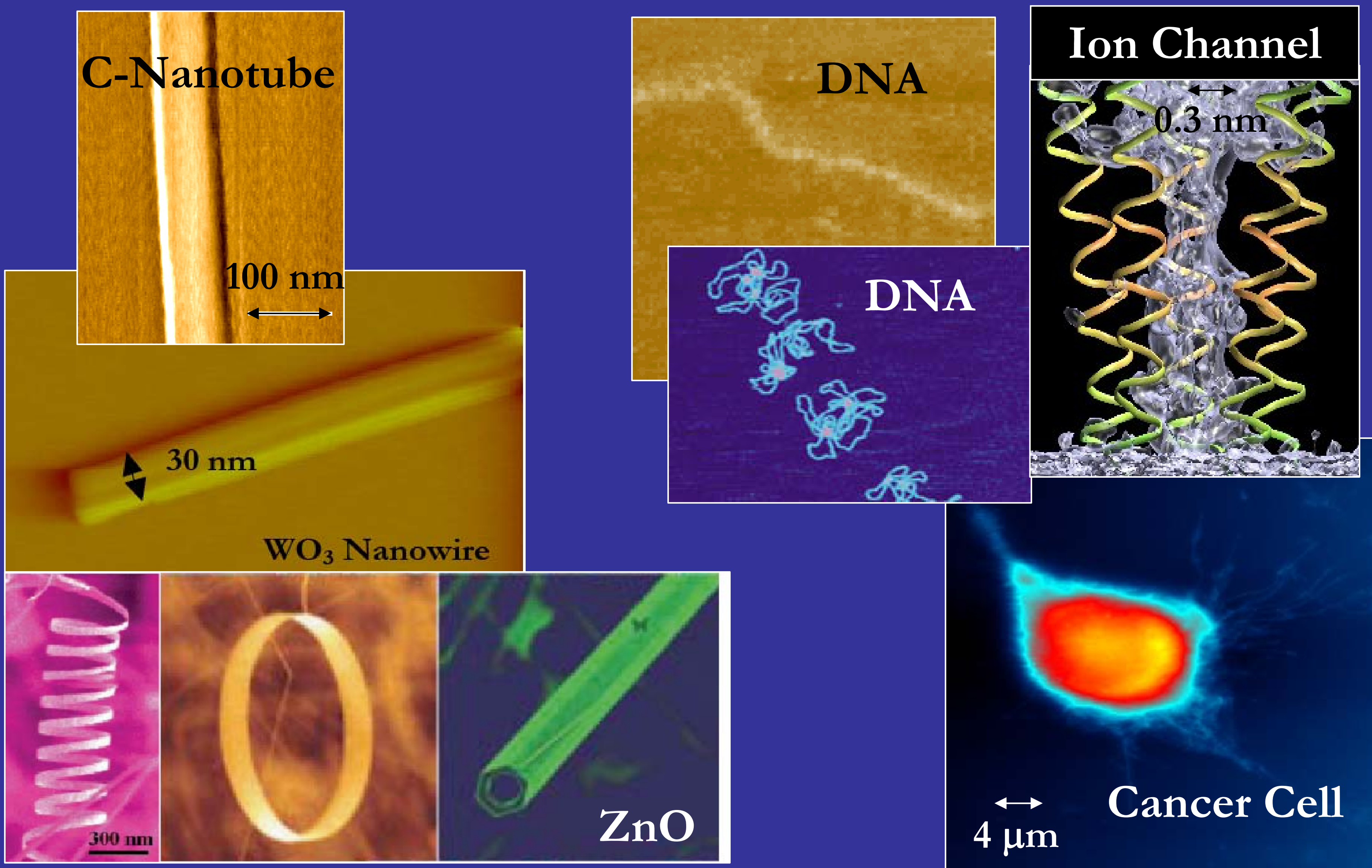
Outline:

- Motivations

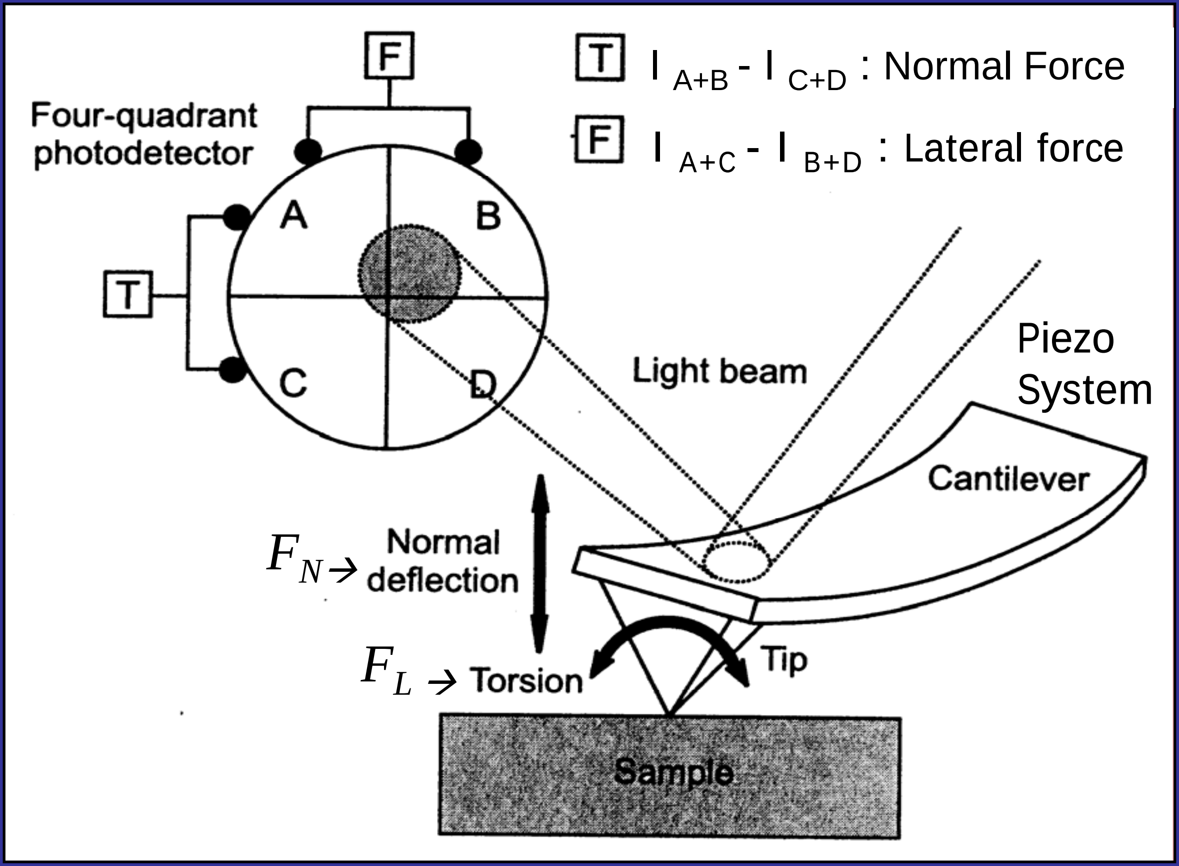
1. Radial elasticity of multiwalled carbon nanotubes
2. Axial elasticity of vertically aligned ZnO nanowires
3. Water in sub-nanometer gaps: a model system for biological ion channels
4. .. New project: Thermo-Chemical NanoLitography

Why NanoMechanics ?

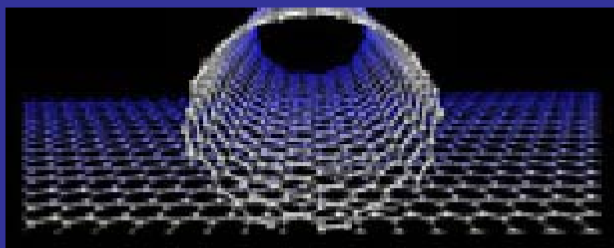


Atomic Force Microscope (AFM)

AFM system based on the beam-bounce detection method



1. Radial Elasticity of MultiWalled NanoTubes

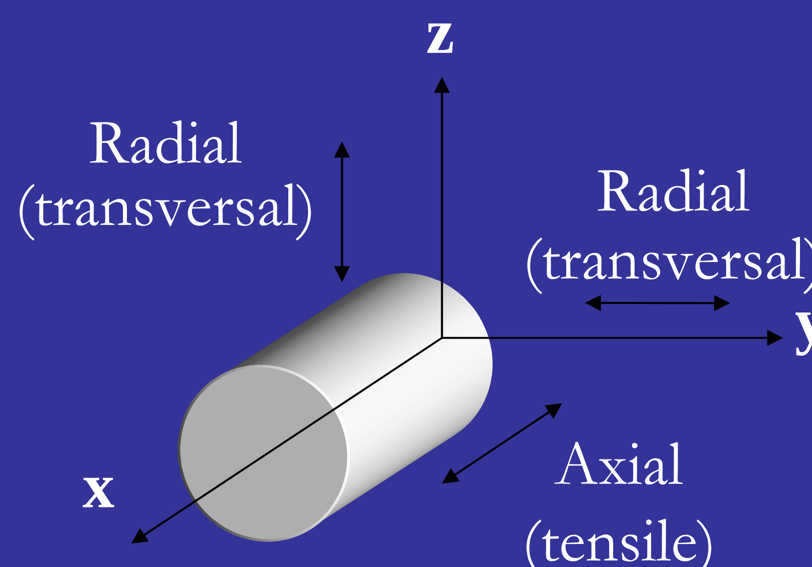


CNTs are made by enrolling graphite sheets

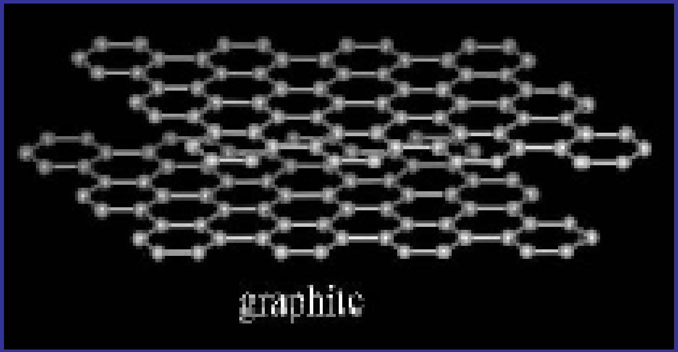
- They have cylindrical symmetry.
- Strong in plane covalent C-C bond

→ Extraordinary axial stiffness:

- Axial Young modulus ~ 1 TPa.



$C_{11} = 1.06$ TPa



$C_{33} = 36$ GPa.

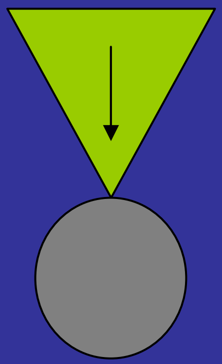
Similarly the radial Young modulus of CNTs is expected to be much smaller than the axial one.

Achieving a fundamental understanding of the radial deformability of CNTs is important for applying them in nanoelectromechanical and nanoelectronic systems.

For example, the radial deformation of CNTs may strongly affect their electrical properties.

How do we measure Radial Elasticity?

Indenting a tip in the NT and
<u>measuring Force vs. Indentation</u>
remaining in the elastic regime



Very challenging →
To stay in the elastic regime, we have to measure
<u>Forces of a few nN vs Indentations of a few Å</u>

Previous work:

So far :

Plastic regime or

Semi-quantitative results

Studies performed on only one tube

With an unknown number of layers

M. F. Yu, T. Kowaleweski, and R. S. Ruoff,
Phys. Rev. Lett. **85**, 1456 (2000).

W. Shen, B. Jiang, B. S. Han, and S. S. Xie,
Phys. Rev. Lett. **84**, 3634 (2000).

Our work:

Now:

Elastic regime and

Quantitative results

Many tubes

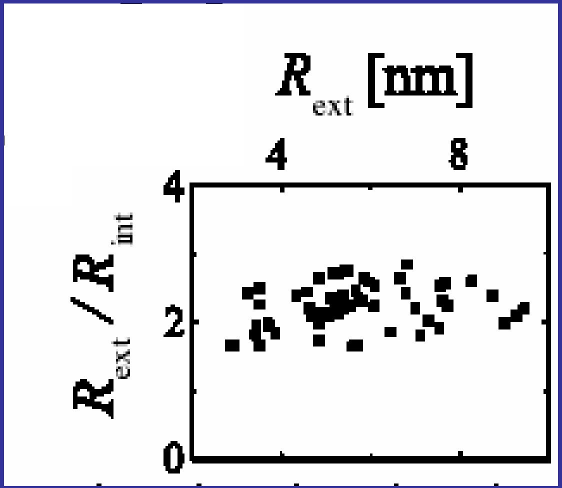
Control of # layers and radius

Palaci, S. Fedrigo, H. Brune, C. Klinke,
M. Chen and E. Riedo,
Phys. Rev. Lett. 94, 175502, (2005)

Control of radius and # Layers

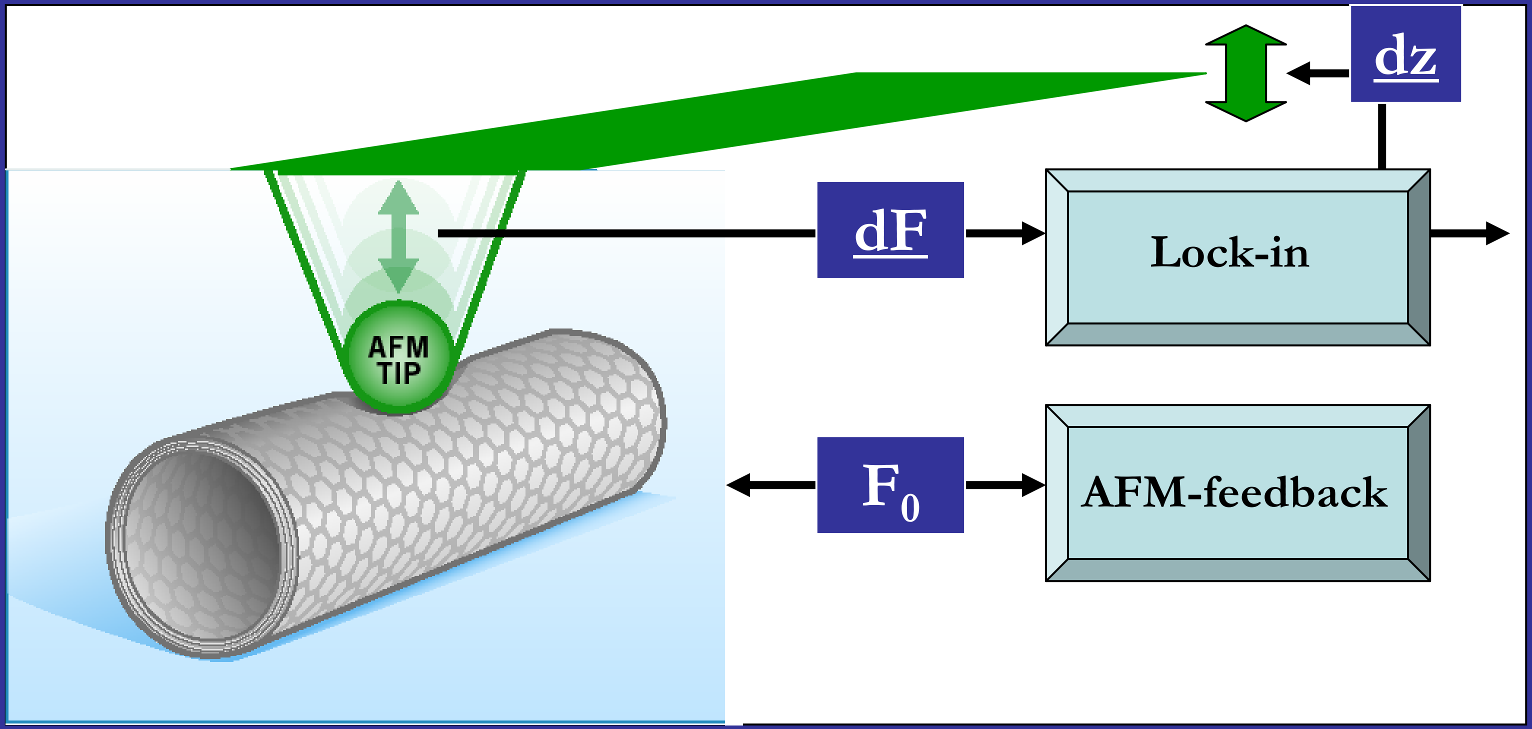
- 40 CNT with R_{ext} from 0.2 to 12 nm
- CNT grown by CVD
- CNT deposited on a Si substrate
- R_{ext}/R_{int} = 2.2 as seen from TEM

TEM measurement

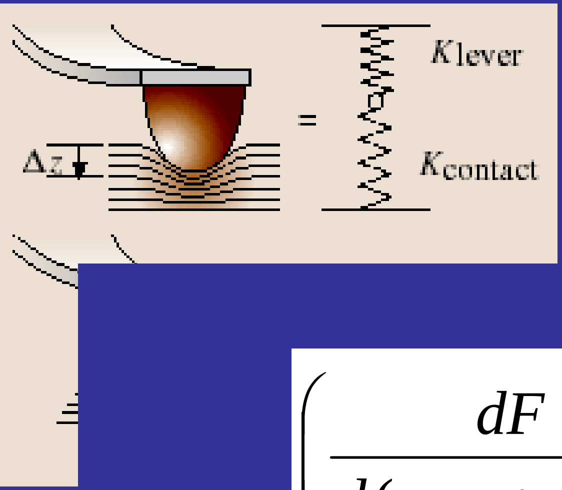


AFM Modulated NanoIndentation:

Indenting an AFM tip in a sample up to a fixed $\boldsymbol{F_0}$
while small oscillations (1.3 Å) are applied to the cantilever holder.
We measure dF/dz around fixed F_0 instead of F(z)



Normal contact stiffness



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

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

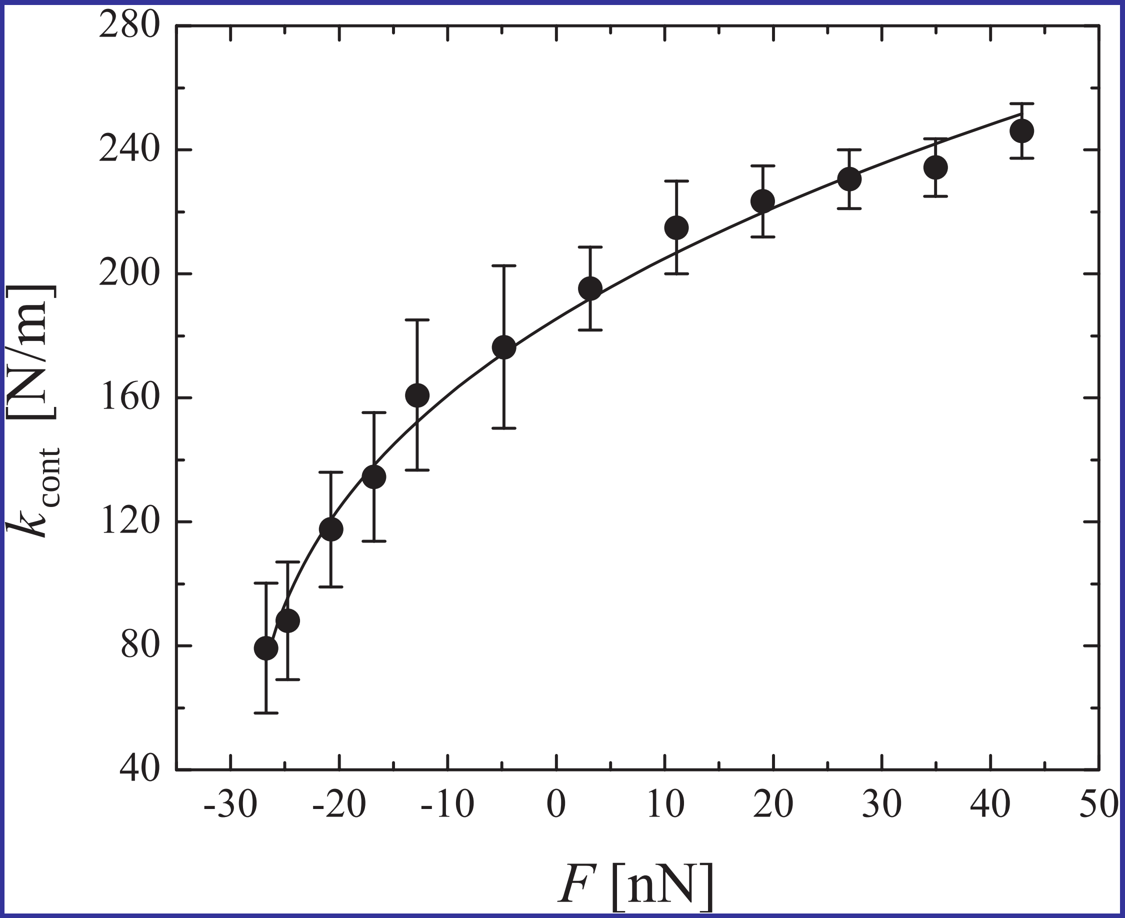
We measure $dF/dz_{tot}(F)$ **→ We obtain** $k_{cont}(F)$

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

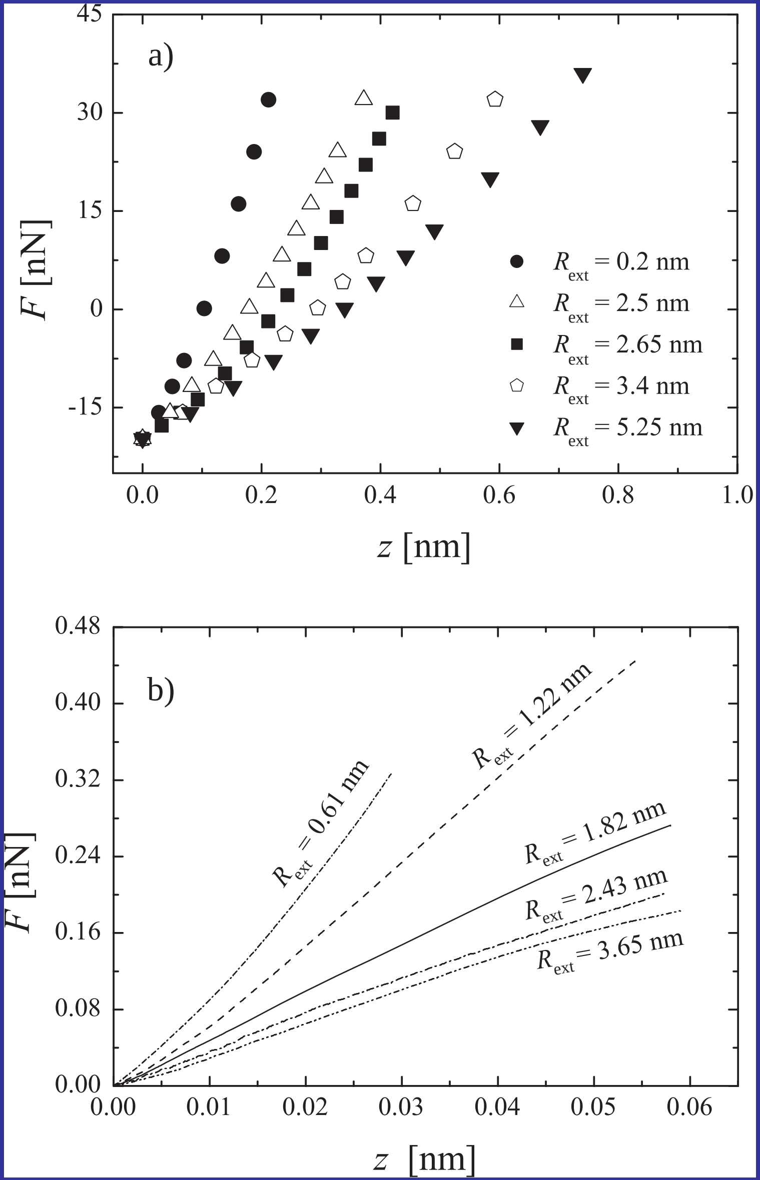
where z_{indent} is the indentation of the tip in the NT,

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

Radial Contact Stiffness



Normal Force versus Indentation



Experiments

MD simulations

How we can now extract the Young Modulus?

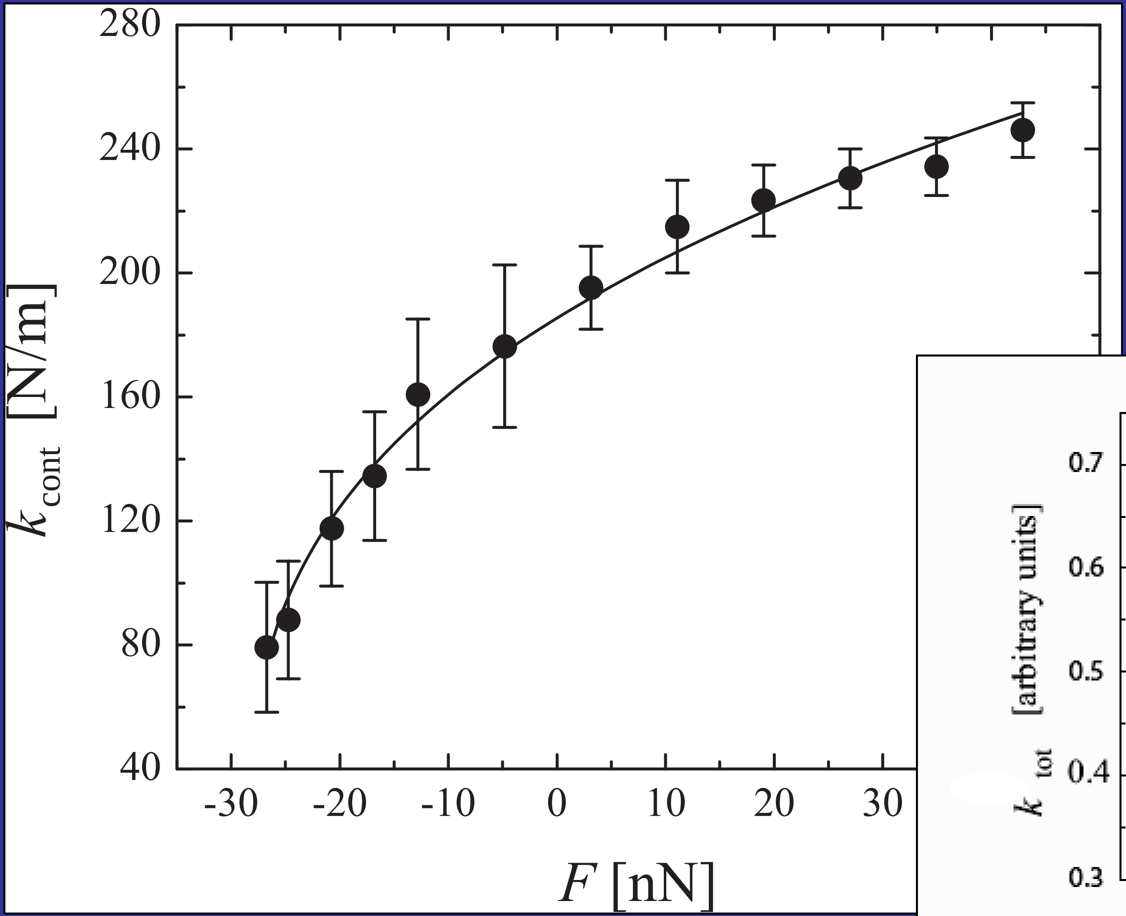
→ we need to calculate the Area of Contact

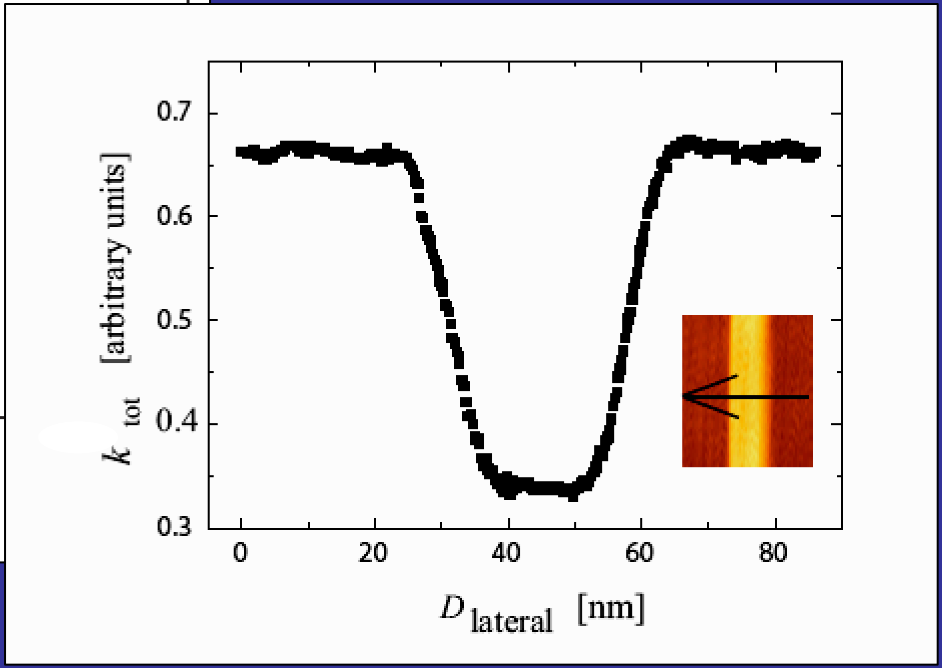
→ Hertz Theory

$$k_{\mathrm{cont}} = \beta\left(\frac{R(F + F_{\mathrm{adh}})}{\tilde{K}^2}\right)^{1/3}, \qquad (2)$$

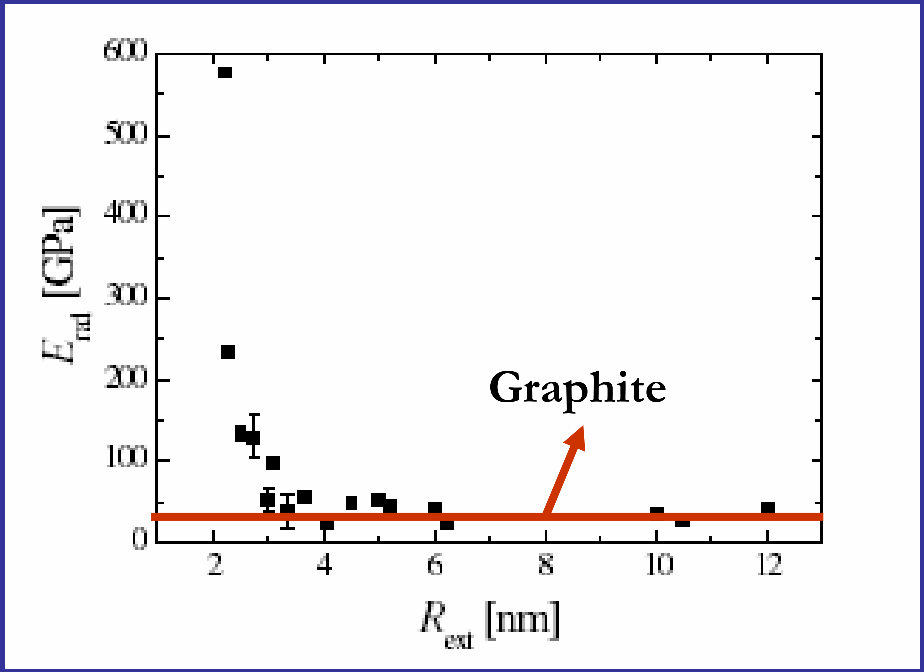
with $\frac{1}{R} = \frac{1}{R_{\mathrm{tip}}} + \frac{1}{2R_{\mathrm{NT}}}$ and $\tilde{K} = \frac{3}{4}\left(\frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2}\right)$, where $\nu_{1,2}$ and $E_{1,2}$ are, respectively, the Poisson ratios and radial Young moduli of the tip and NT. β depends on R_{tip} and R_{NT}

Contact Stiffness





Multiwalled Nanotubes Radial Young Modulus



- For $R_{ext} < 4$ nm → E_{rad} increases sharply by decreasing R_{ext}
- For $R_{ext} > 4$ nm → $E_{rad} \sim 30 \pm 10$ GPa → Graphite C_{33} constant (36 GPa)
- $R_{ext}/R_{int} = 2.2$ and distance between layers is 0.34 nm → $R_{ext} \propto R_{int} \propto N_{layers}$

→ for small R_{int}, E_{rad} is controlled by R_{int}, while N_{layers} plays a minor role

2. Axial elasticity of vertically aligned nanorods :

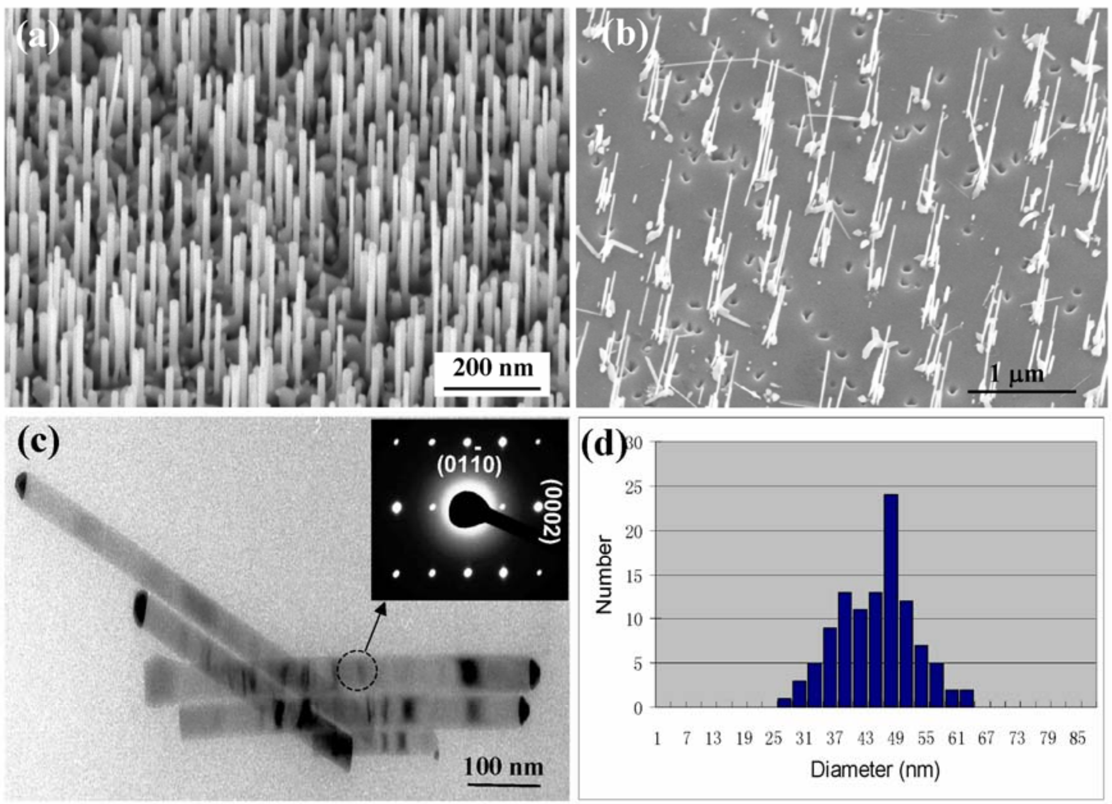


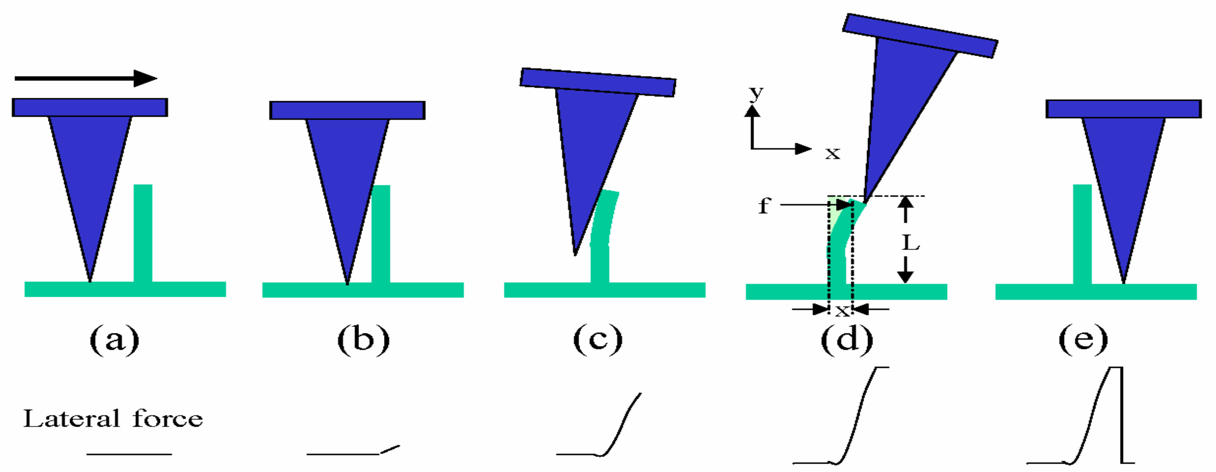
Figure 1

- The aligned ZnO NR arrays were grown using gold as catalyst by a vapor-liquid-solid method (VLS) process. On a α–Al_2O_3, substrate
- Applications: sensors, optoelectronics and field emission

Axial elasticity

- How to measure the axial Young Modulus of these wires quickly and without destroying the sample ?

We propose an AFM based method



J.H. Song, X.D. Wang, E. Riedo and Z.L. Wang, *Nano Letters* 12, 1954 (2005).

Axial elasticity

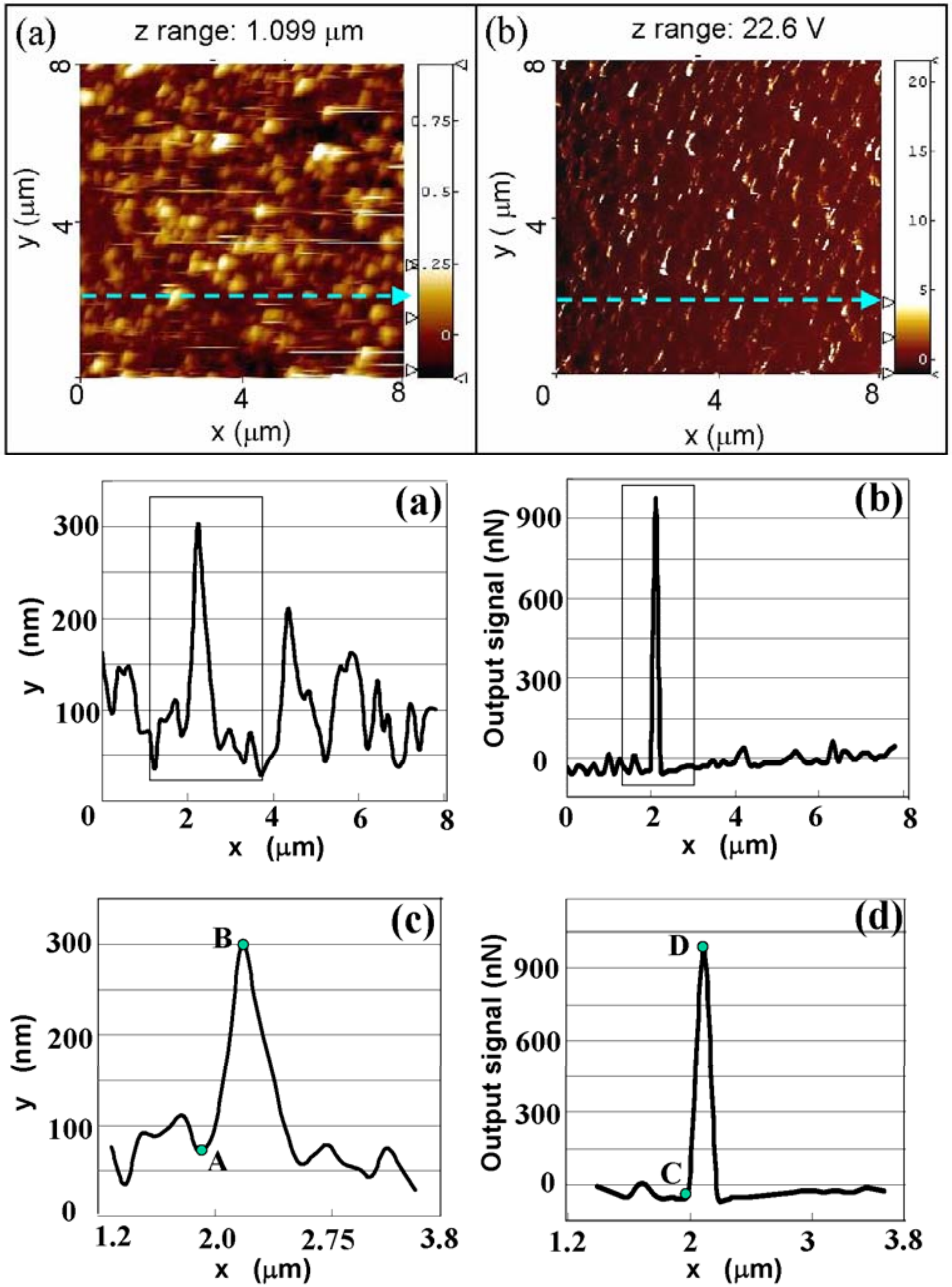
$$EI\frac{d^4x}{dy^4} = (f_0 + f)\delta(y - L)$$

f_0 is the friction force between the tip and the NW
E is the elastic modulus of the NW
I is the momentum of inertia of the NW
x is the lateral displacement perpendicular to the NW
y is the distance from the fixed end (root) of the NW to the point where the lateral force is applied
L is the length of the NW

If we consider that $f_0 << f$ then:

$$f = 3EI\frac{x}{L^3}$$

$$I = \frac{5\sqrt{3}}{16} \cdot a^4$$

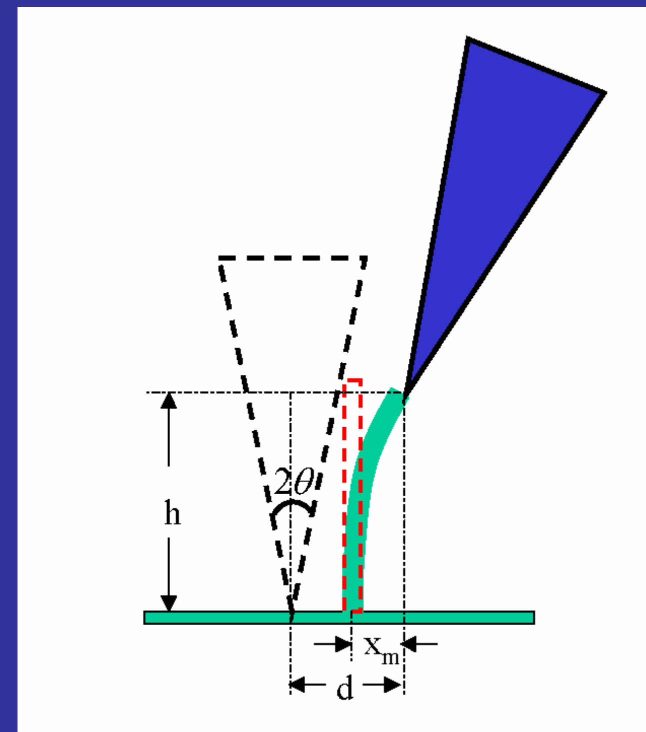


Topography

Lateral Force

$$L \approx \sqrt{h^2 + x_m^{\ 2}}$$

$$x_m = d - h\tan\theta$$



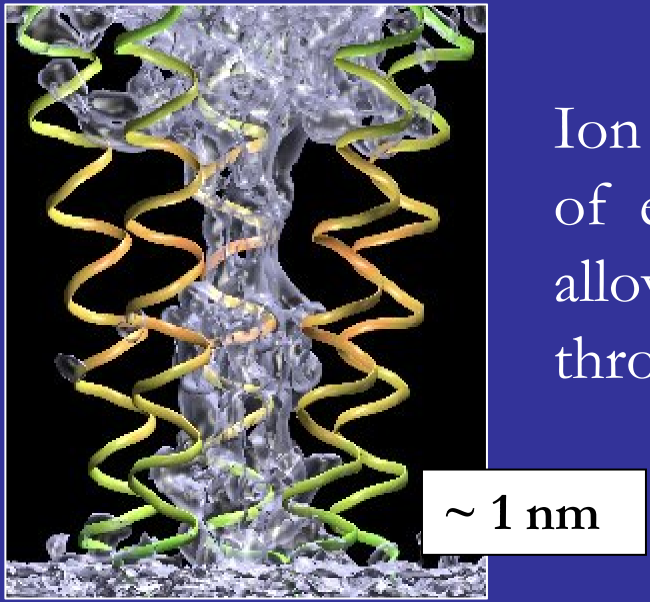
$$f = E\left(3I\frac{1}{L^3}\right)x$$

Results:

Nanowire	Length (μm)	Elastic modulus (GPa)
1	0.277	20
2	0.281	22
3	0.452	20
4	0.211	36
5	0.301	42
6	0.640	36
7	0.683	47
8	0.209	35
9	0.168	15
10	0.209	35
11	0.194	22
12	0.285	28
13	0.631	21
14	0.328	31
15	0.641	20

3. Water in sub-nanometer gaps: a model system for ion channels

Dr O. Beckstein and M.S.P. Sansom



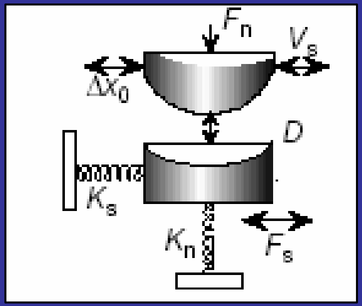
Ion channels play a central role in the physiology of e.g. neurons, muscle, and heart cells. They allow rapid (~10^7 ions s^{-1}) flux of selected ions through a transmembrane pore.

In order to understand the fundamental physical mechanisms of ion channel processes, including permeation, selectivity and gating, <u>it is crucial to know what is the behavior of water in sub-nanometer gaps</u>

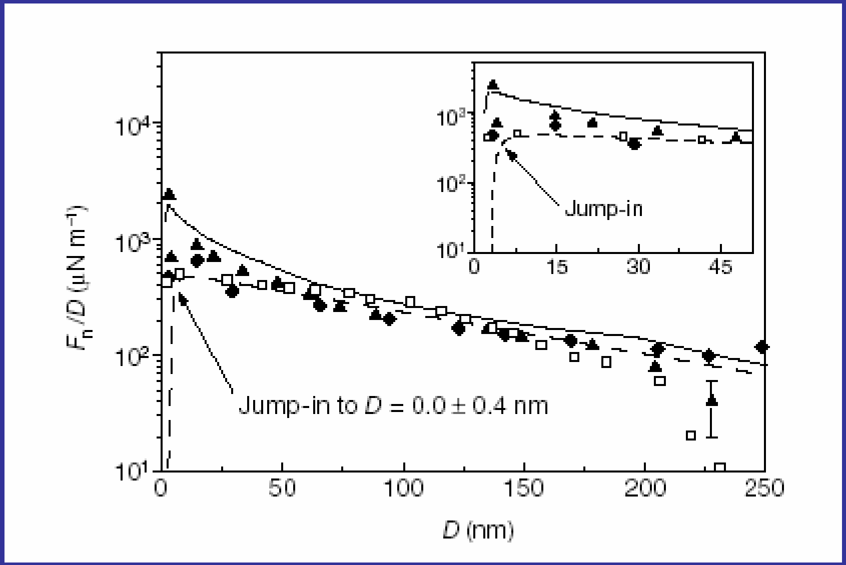
State of the Art:

The key question:

Is water liquid or solid-like when it is confined in less than 1 nm?



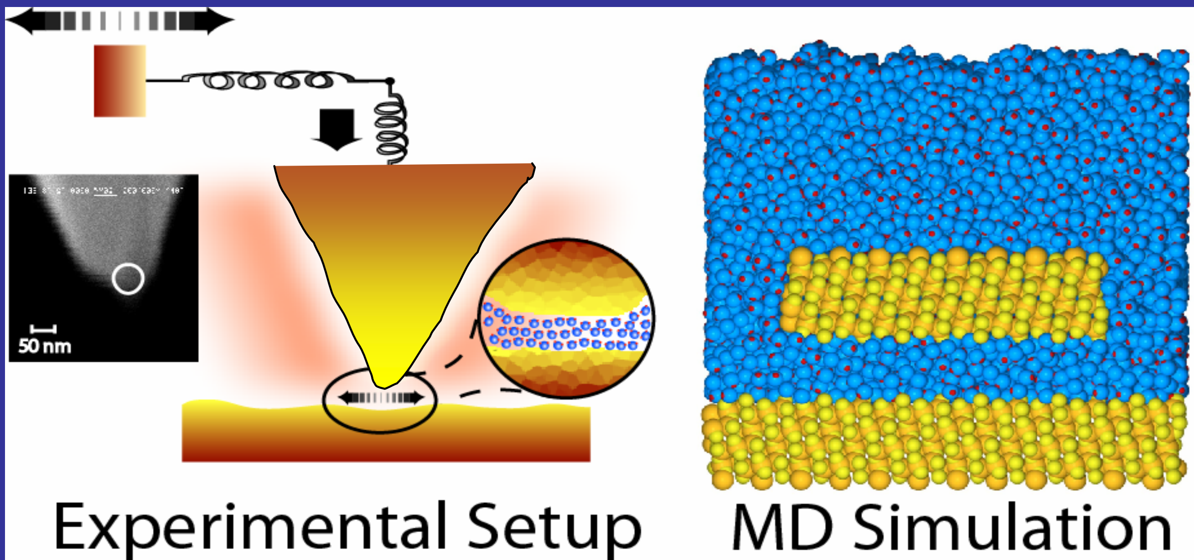
Pioneering studies of the forces between two macroscopic mica cylinders immersed in water, showed that **<u>water is fluid</u>** for gap sizes >2.4 nm



Raviv, U., Laurat, P., and Klein, J. Nature 413, 51 (2001)

Our study:

Water confined between and AFM tip and a solid surface (mica, glass and graphite)



T.-D. Li, J. Gao, R. Szoszkiewicz, U. Landman and E. Riedo, submitted

We have studied experimentally and theoretically the **normal and shear forces** encountered by a nano-sized tip when it approaches a solid surface in water.

We are able to investigate, with sub-Angstrom resolution, tip-surface distances from 2 nm down to 0.4 nm.

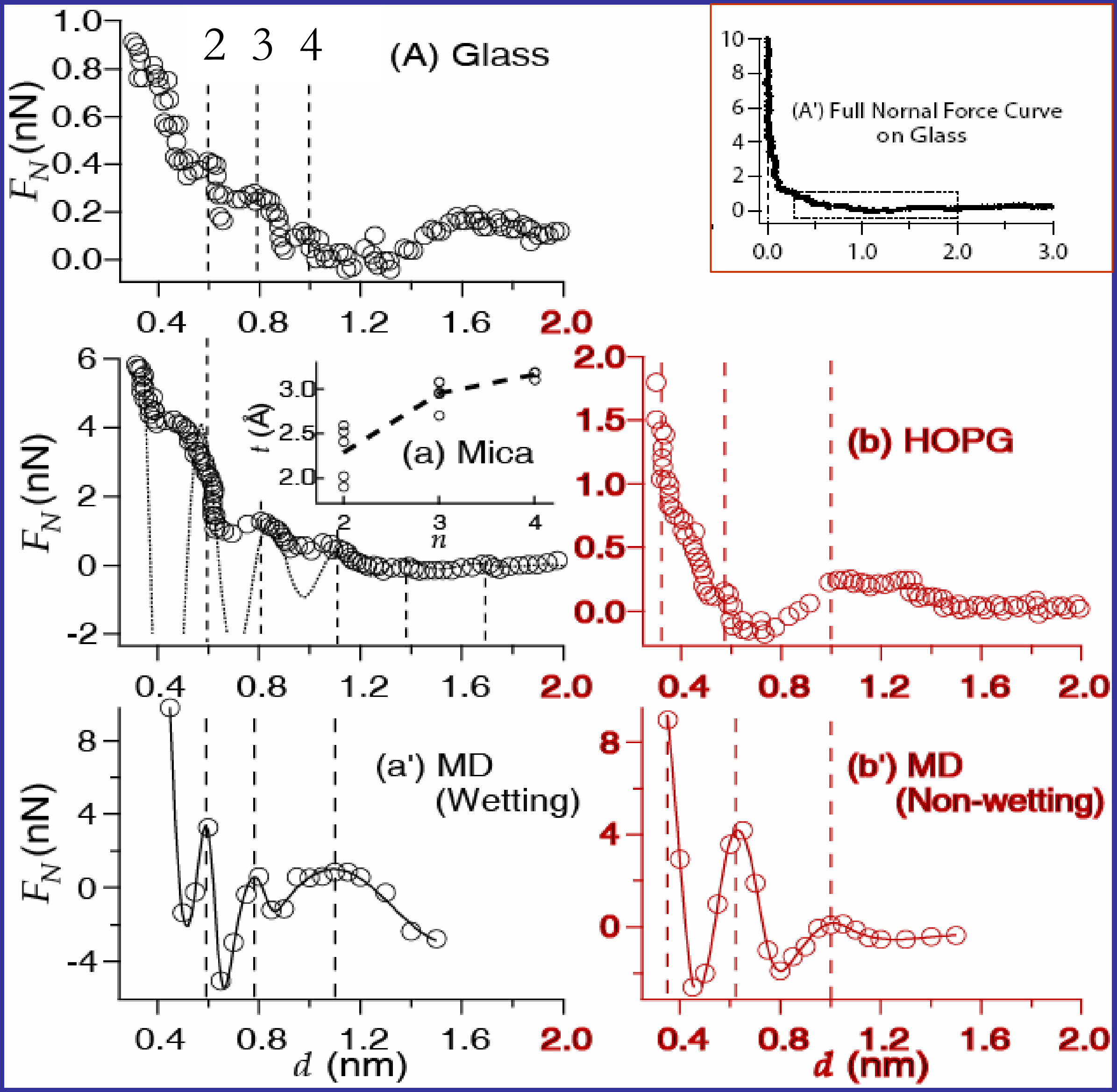
Comparison of Solid Surface Samples

Mica	Glass	Graphite (HOPG)
Hydrophilic (Wetting)	Hydrophilic (Wetting)	Hydrophobic (Non-wetting)
Atomically Smooth	Nanometer Rough	Atomically Smooth

AFM Tip: Silicon Oxide, Hydrophilic

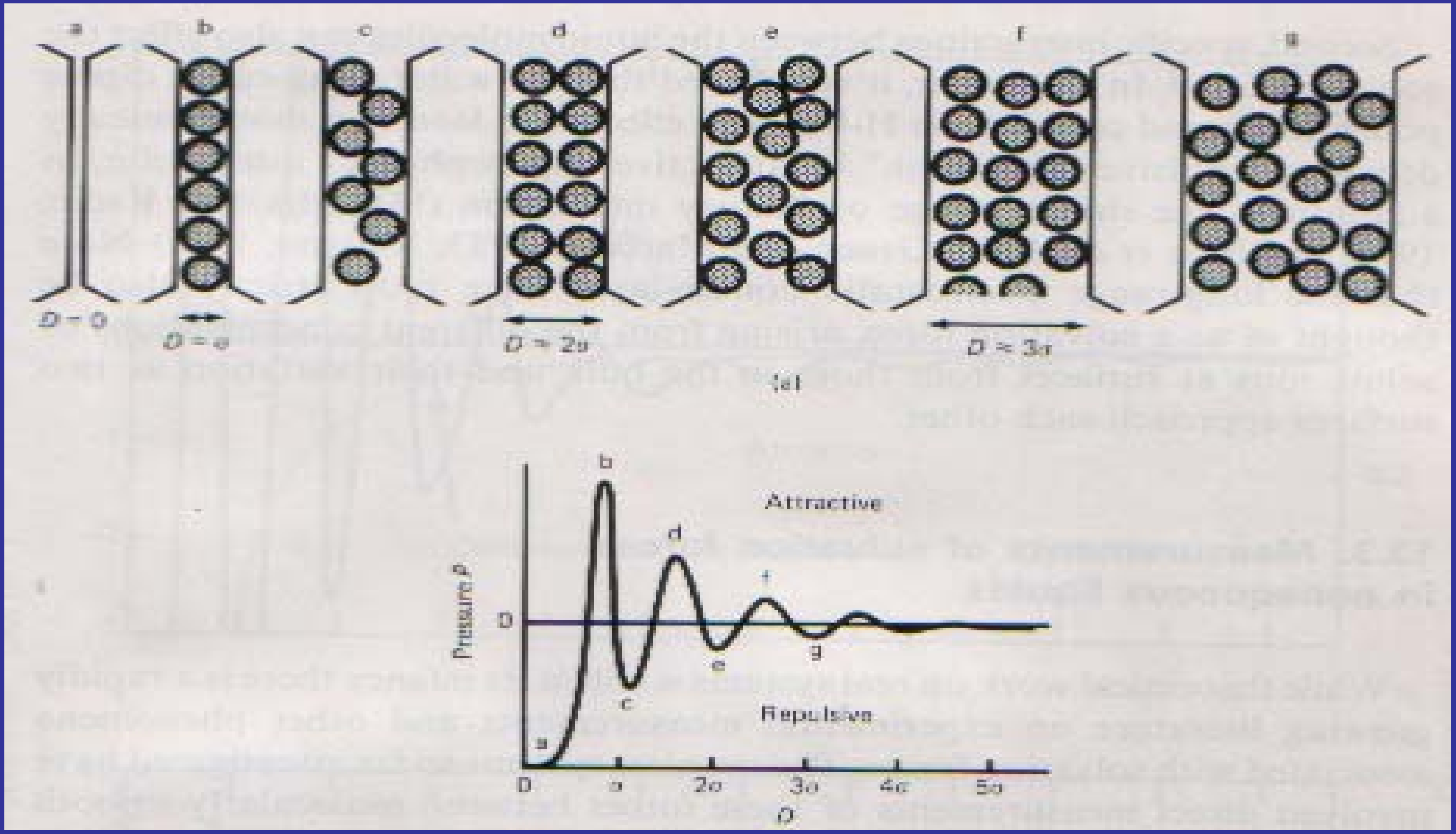
Normal Forces

wetting non-wetting



- Oscillations
- Periodicity: ~3Å, Water molecule
- Oscillations more marked on wetting surfaces

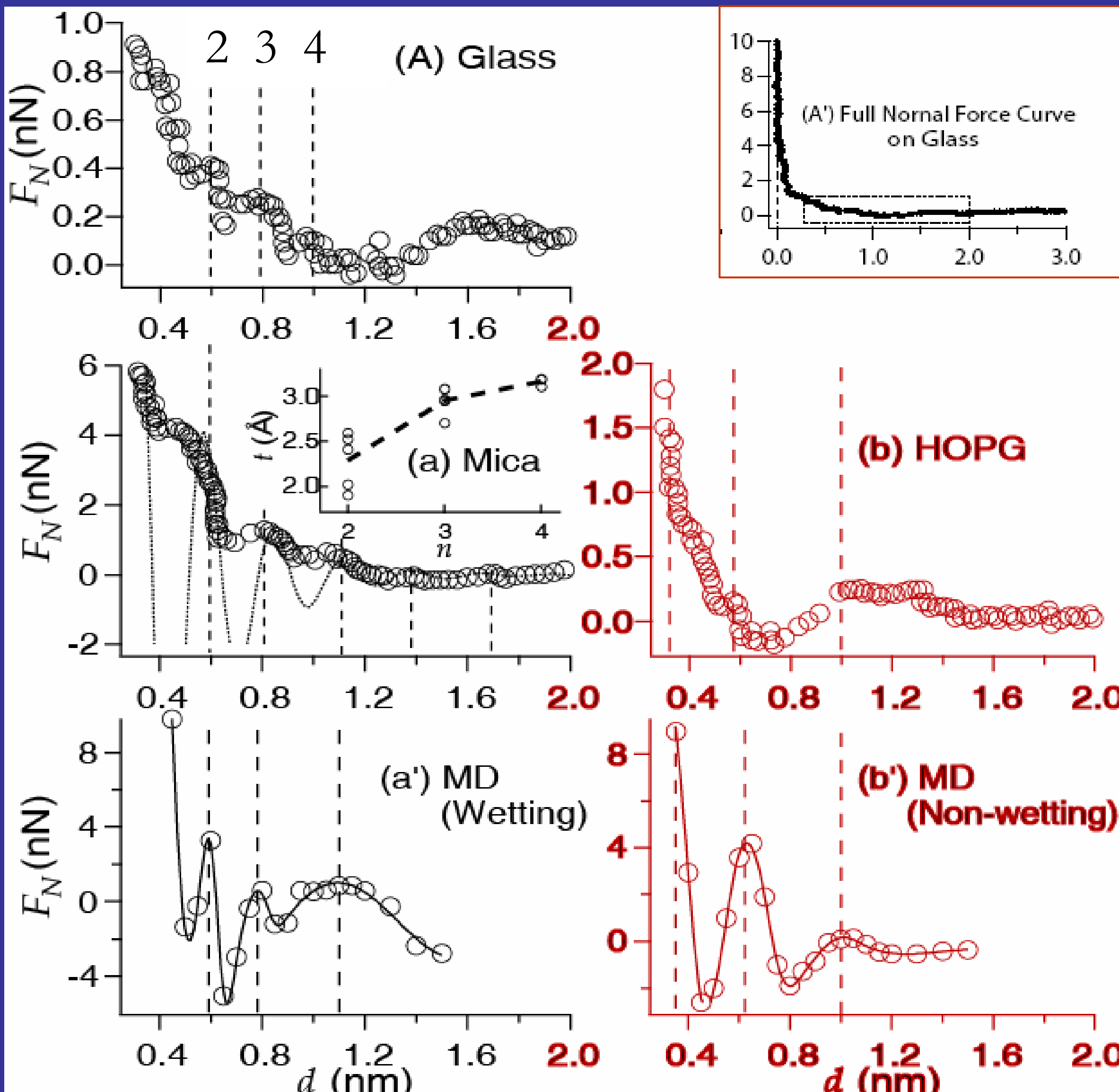
On the Nanometer Scale



Israelachvili, *Intermolecular and Surface Forces* 1991

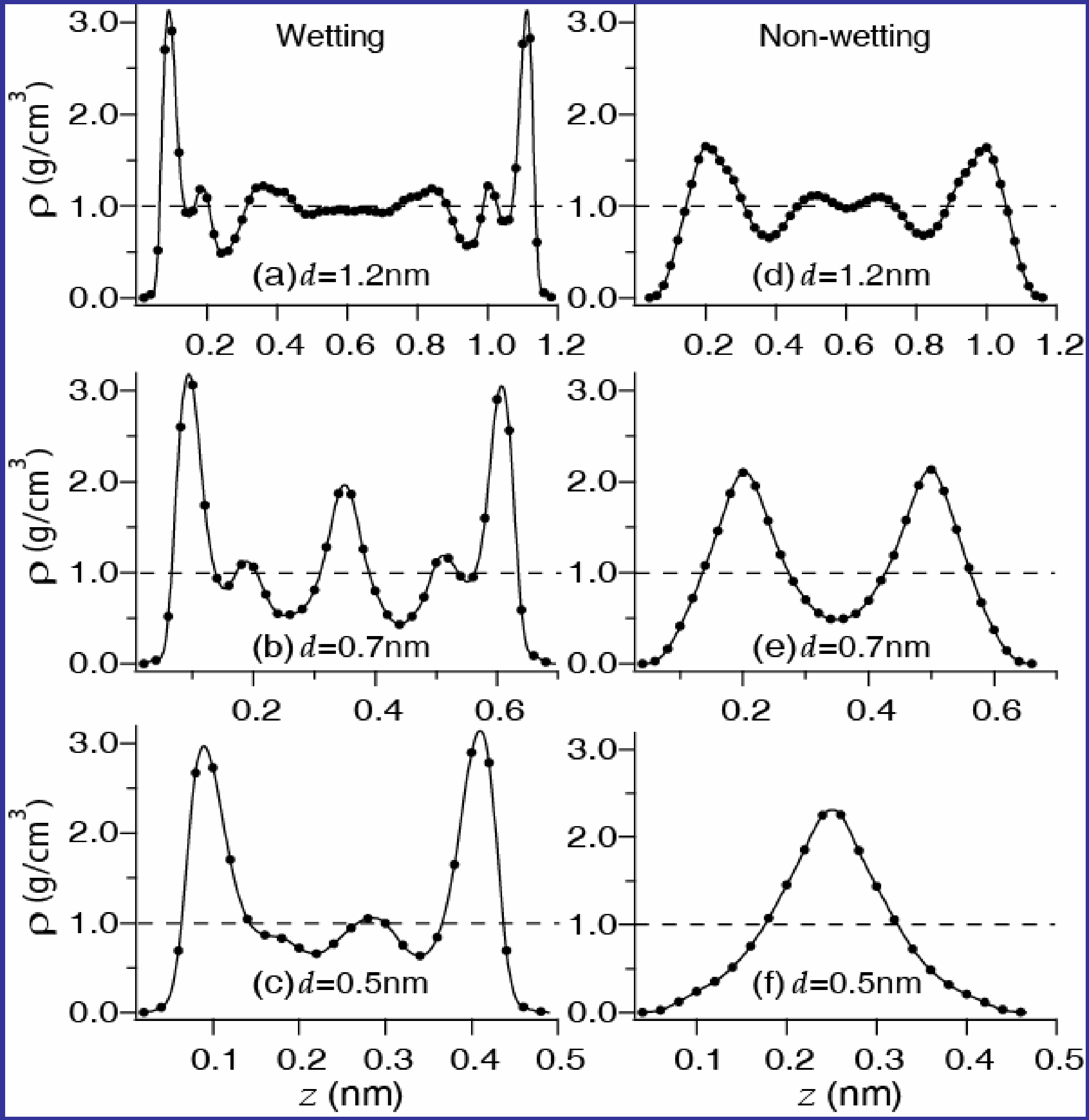
Normal Forces

wetting non-wetting

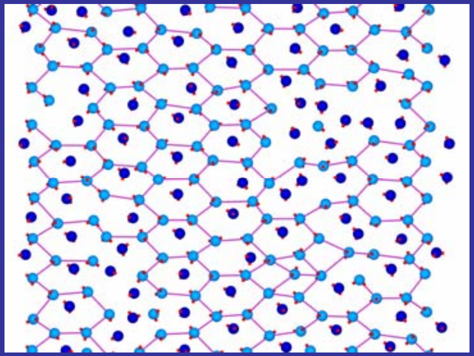


- Oscillations
- Periodicity: ~3Å, Water molecule
- Oscillations more marked on wetting surfaces

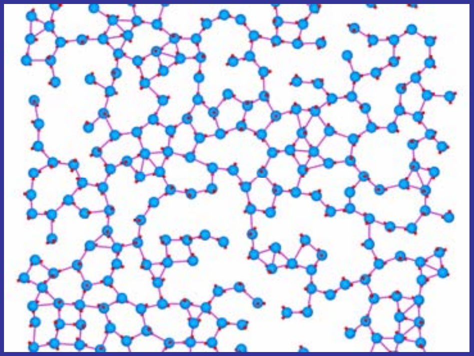
Density Profiles → High-Low density Transitions



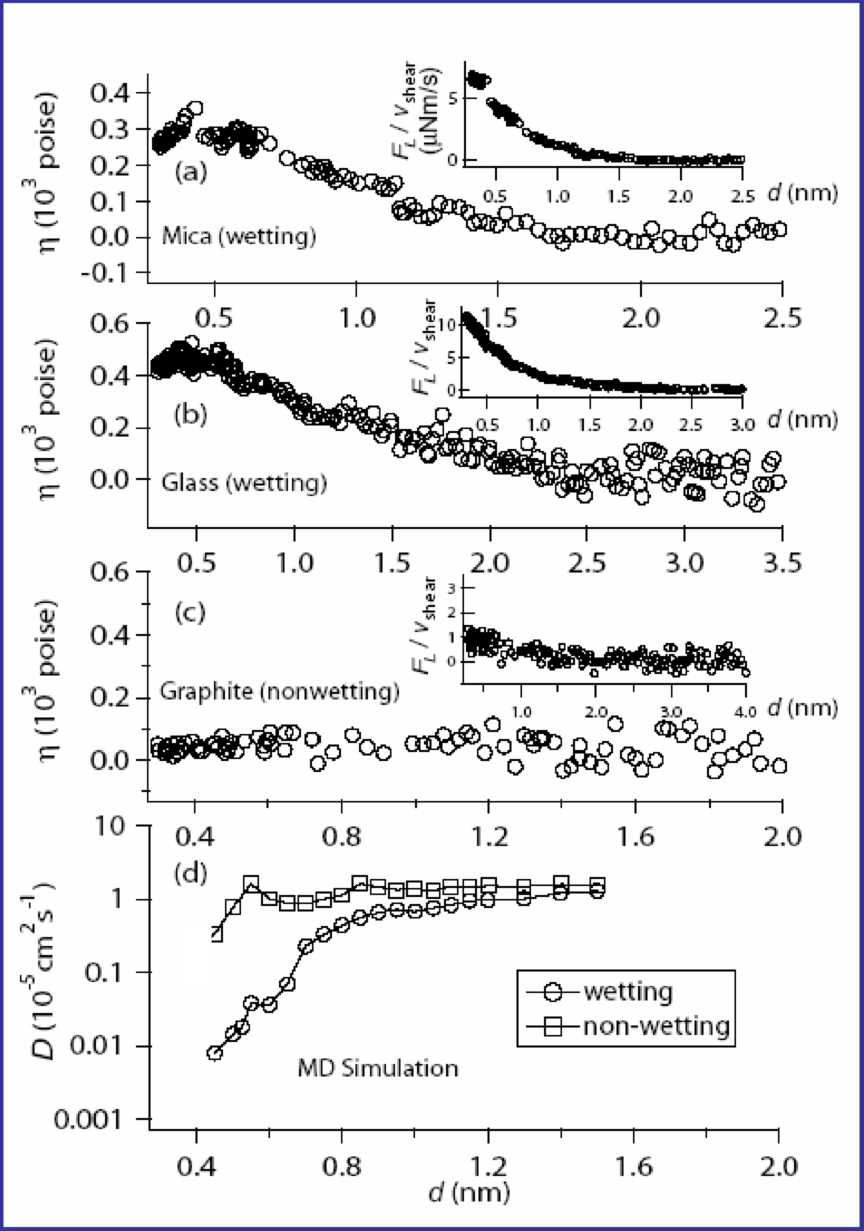
wetting
d = 0.7 nm, z = 0.1 nm



non-wetting
d = 0.7 nm, z = 0.2 nm



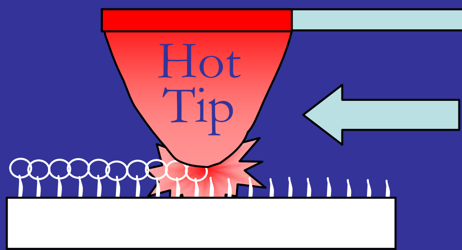
Dynamic Viscosity and Diffusion Constant



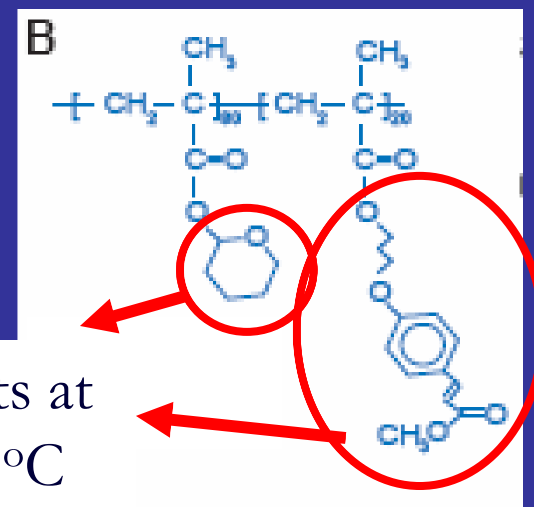
- η (bulk H_2O)= 0.01 poise
- η (nano-confined H_2O)~ 10^2 poise

- **4 orders** of magnitude increase on wetting surfaces

4. Thermo-Chemical NanoLitography (TCNL)

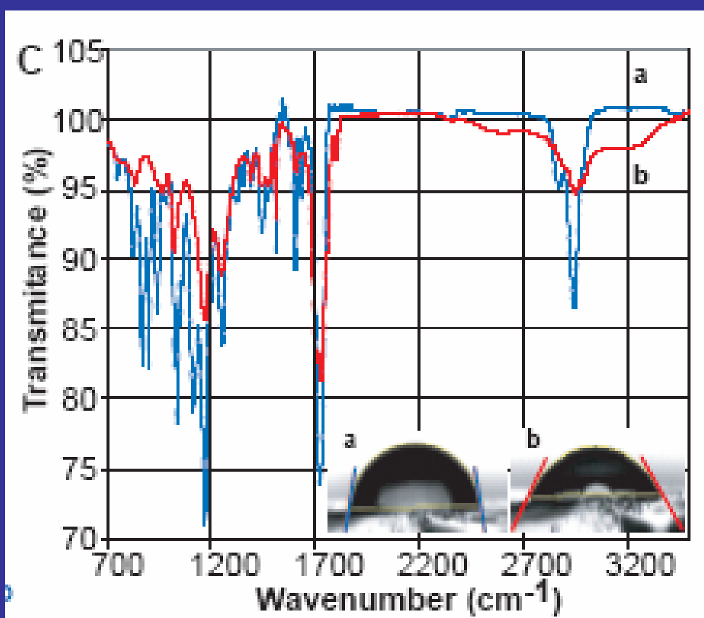


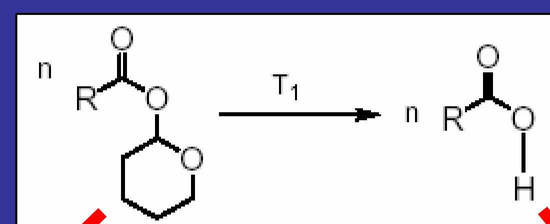
Tip movement direction



Deprotects at
T > 125 °C

$p(THP\text{-}MA)_{80}\ p(PMC\text{-}MA)_{20}$



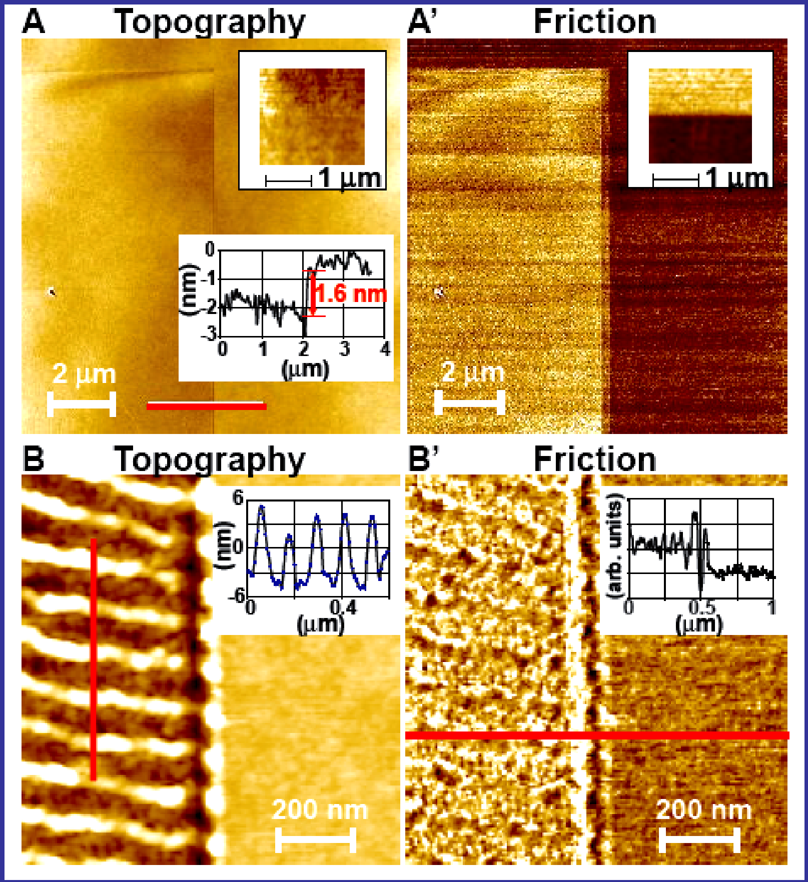


Hydrophobic

Hydrophilic

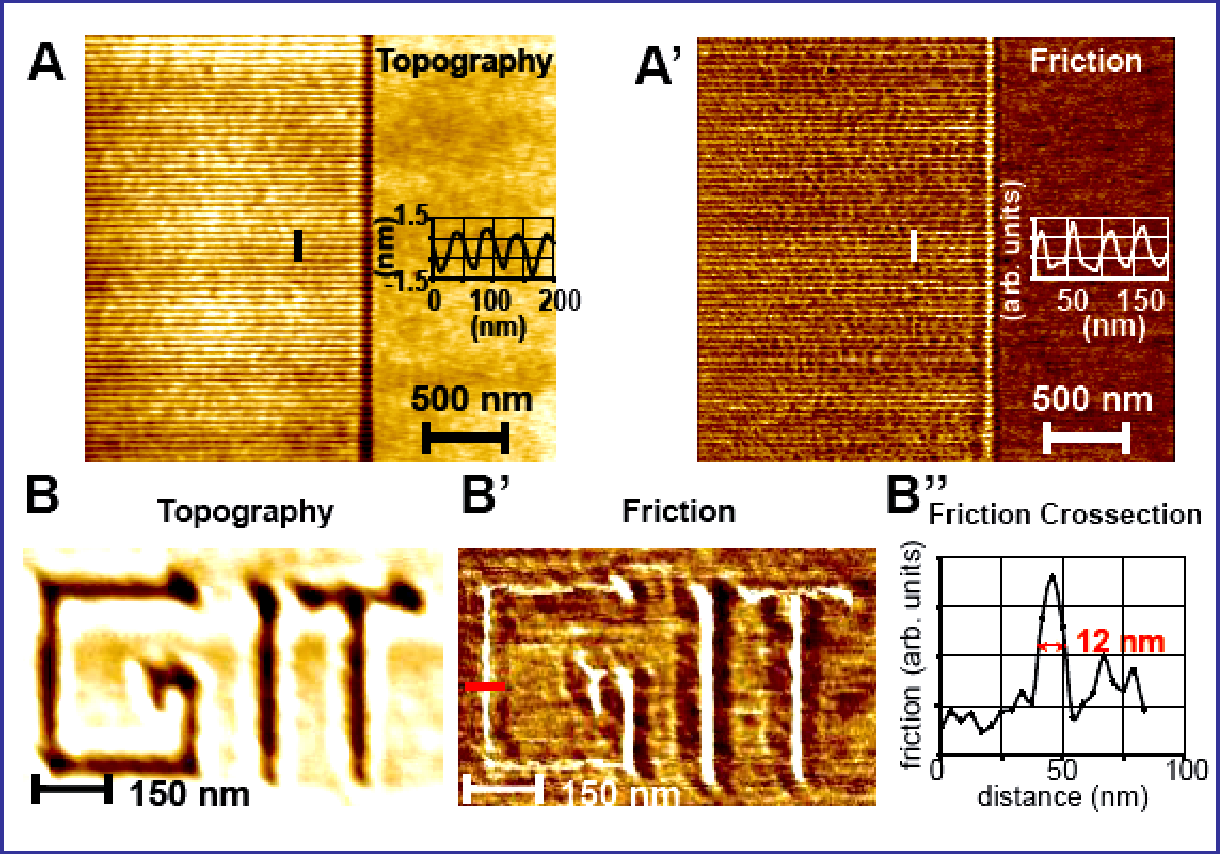
R. Szoszkiewicz, T. Okada, S. C. Jones, T.-D. Li, W. P. King, S. R. Marder, and E. Riedo
Submitted

TCNL at work…



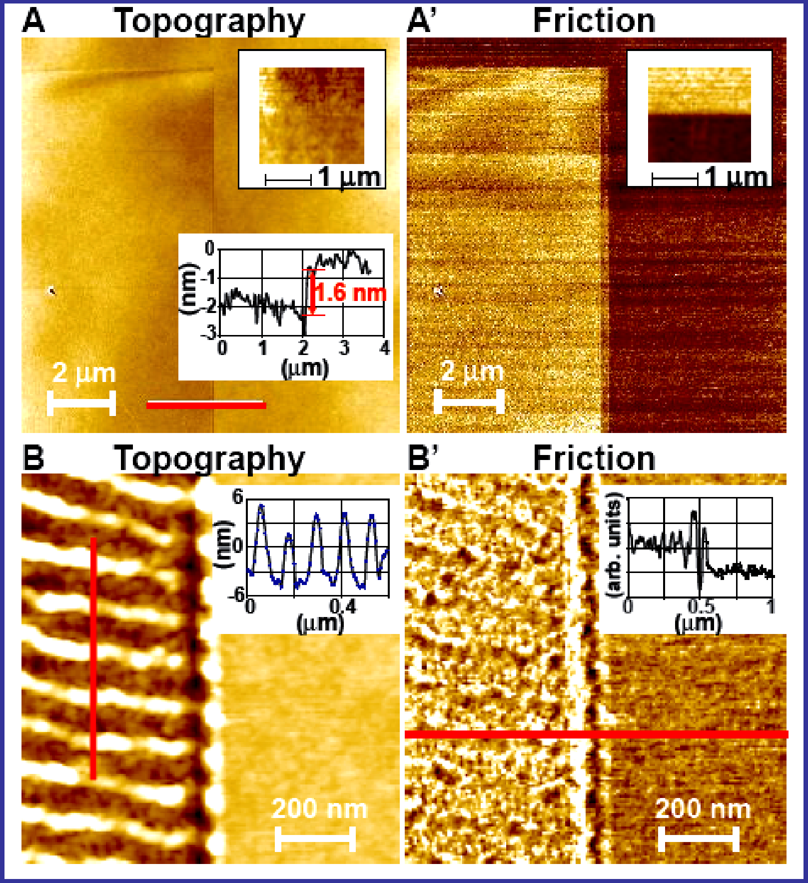
- Writing Speeds faster than 1 mm/s
- Working in a range of environments
- Possibility to control Surface Energy AND Topography
- Possibility to create hydrophilicity/hydrophobicity gradients
- Extendable to Many other systems

TCNL at work…



- Line density of 2×10^7 lines/meter (260 Gbit /inch^2)
- Sub-15 nm feature size – (single molecule patterns?)

TCNL at work…



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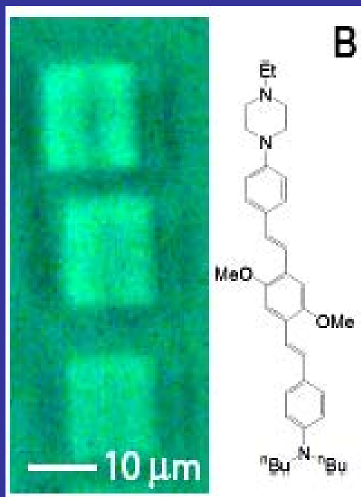
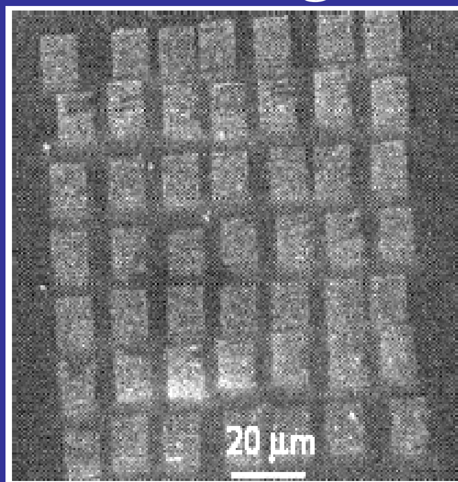
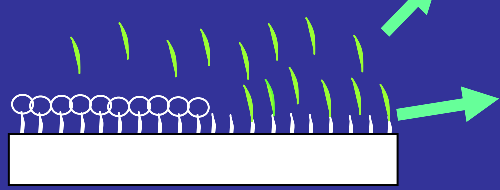
Functionalization of Chemical Modified Areas…

Fluorescence image



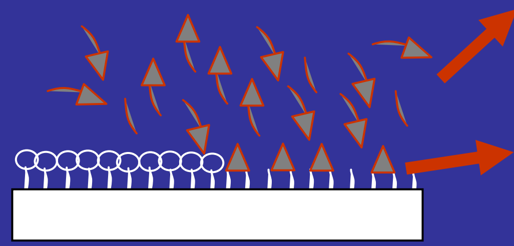
SEM image





Fluorescent Dye

Acid-Base Reaction on the AFM modified areas



Pb^{2+} (acetylacetonate)$_2$

Pb^{2+} bound to two deprotonated carboxylic acid groups on AFM modified areas

Thanks For your attention.

Undergraduate Students:

Anna Pavlova

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Jonathan Diaz

Stephen Medina

Special Problems Students:

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Dr. Robert Szoszkiewicz

Dr. Marcel Lucas

Visiting Scientists:

Ismael Palaci

Lucel Sirghi

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T. Okada

S. Jones

W. King

J. Gao

U. Landman

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