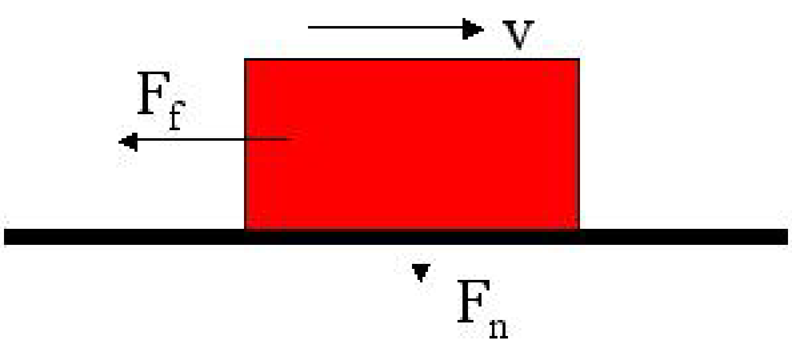
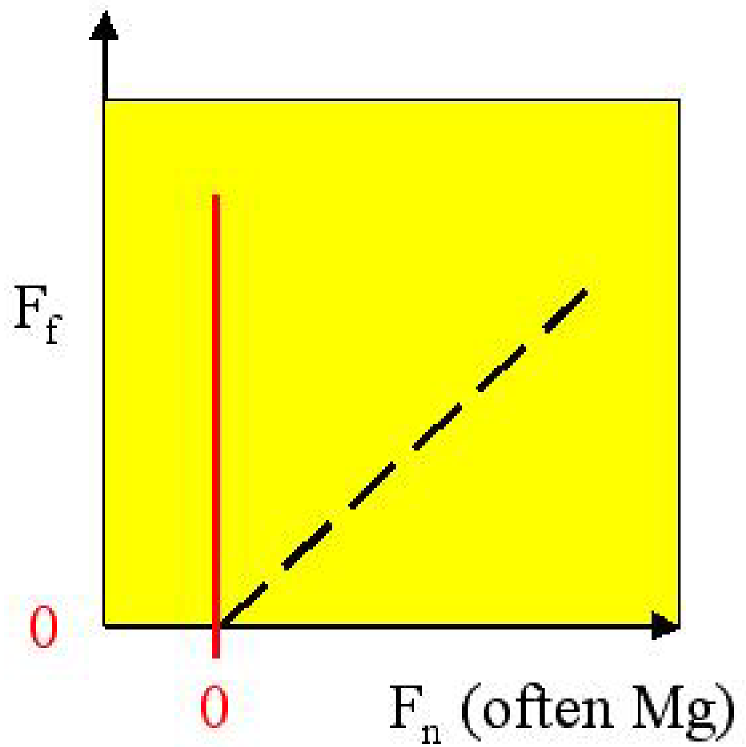
**adhesion/friction:**

Macroscopic scale (Amontons law)

$F_f$: friction force at constant speed
$F_n$: normal load

Slope: $\mu$=friction coefficient



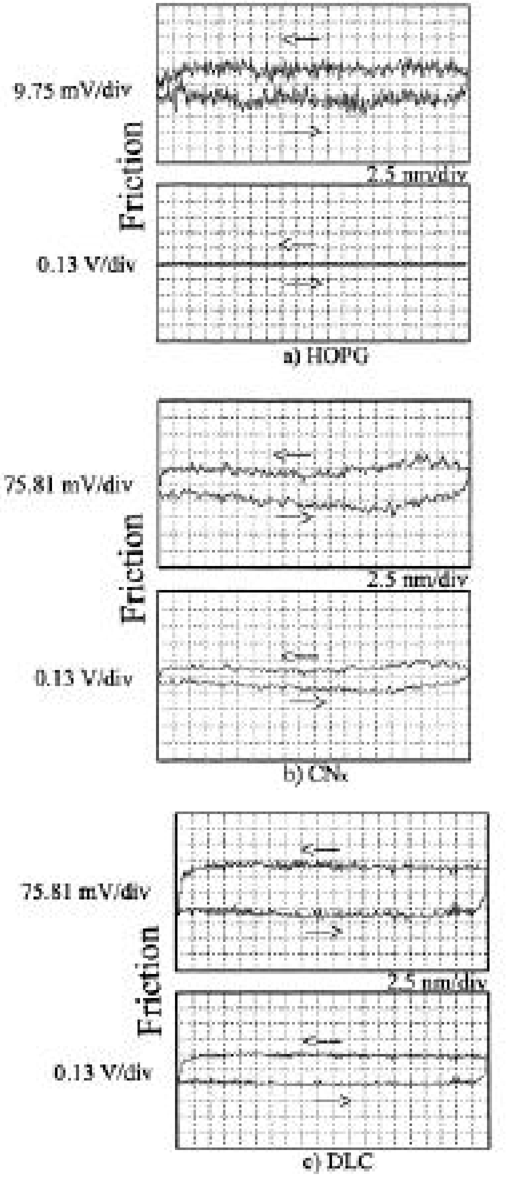
# adhesion/friction:

## Nanoscale

Surface Science 477 (2001) 25–34

### Nanotribology of carbon based thin films: the influence of film structure and surface morphology

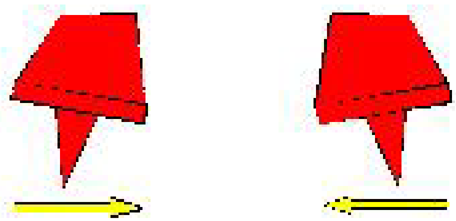
E. Riedo [a,c,*], J. Chevrier [a,b], F. Comin [a], H. Brune [c]
[a] ESRF, BP220, F-38043 Grenoble Cedex, France
[b] LEPES CNRS, F-38043 Grenoble, France
[c] EPFL, CH-1015 Lausanne, Switzerland

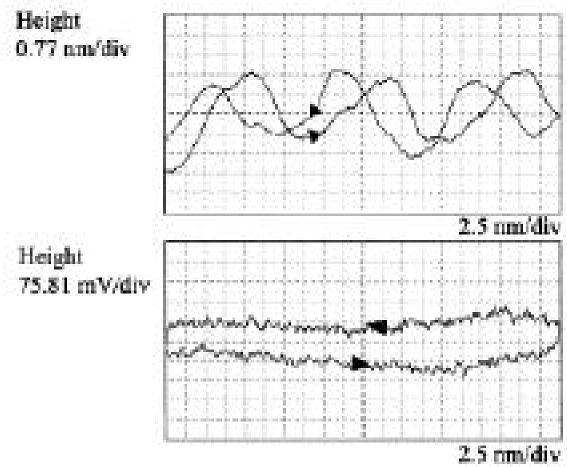



. Each graph presents a scan width of 50 nm

. Simultaneous profiles of friction and topography

on a 50 nm scan width for a $CN_{0.23}$ film.






Dêposition by
pulsed laser deposition

# Nanoscale: large influence of adhesion on solid friction

E. Riedo [a,c,*], J. Chevrier [a,b], F. Comin [a], H. Brune [c]

Surface Science 477 (2001) 25–34

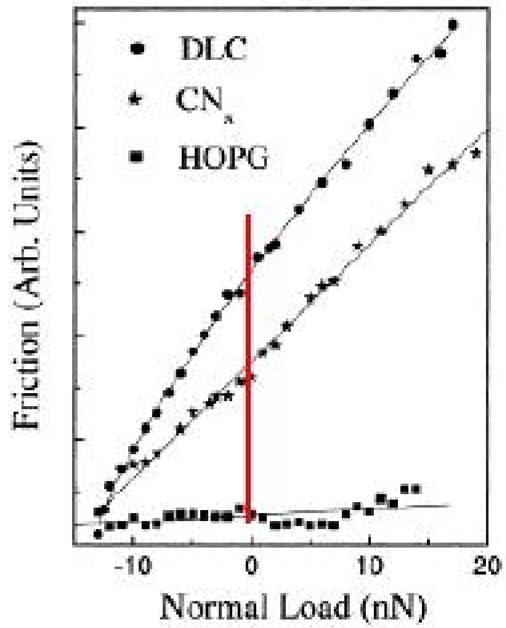
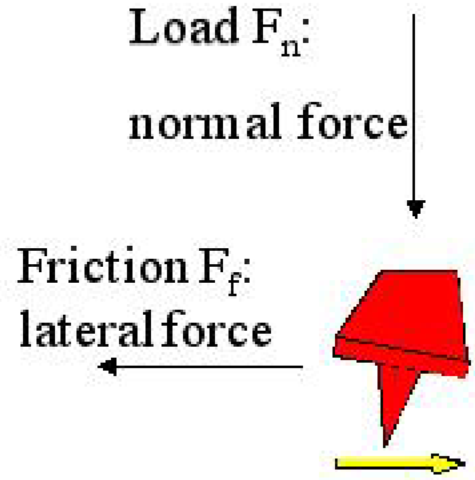
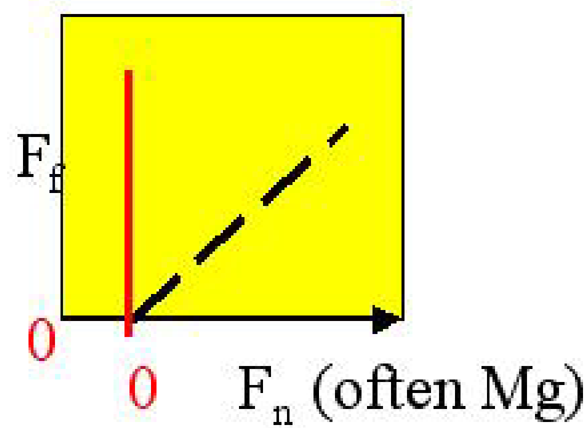



Fig. 3. Plots of friction force versus applied load for graphite (■), CN$_x$ (★) and amorphous carbon (●) surfaces.




$F_n > 0$ [0,20nN] the cantilever pushes on the surface

$F_n < 0$ [-10,0nN] the cantilever pulls: adhesive regime



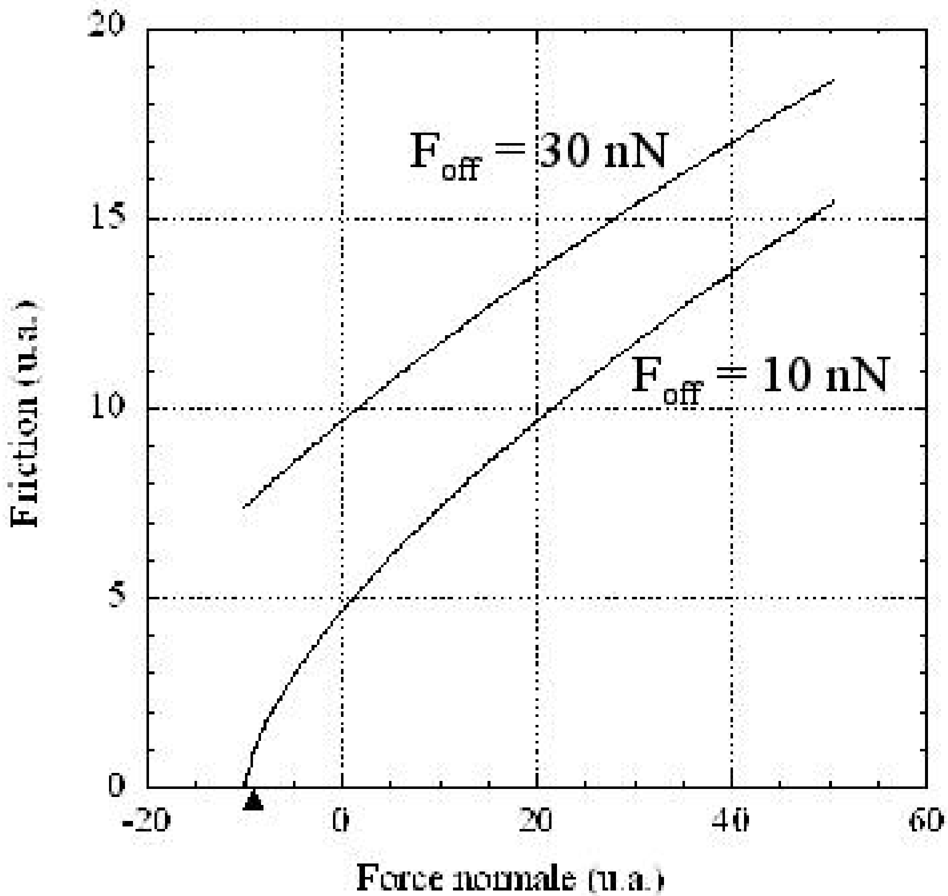
# Friction and adhesion …

Derjaguin Muller Toporov (DMT) model:

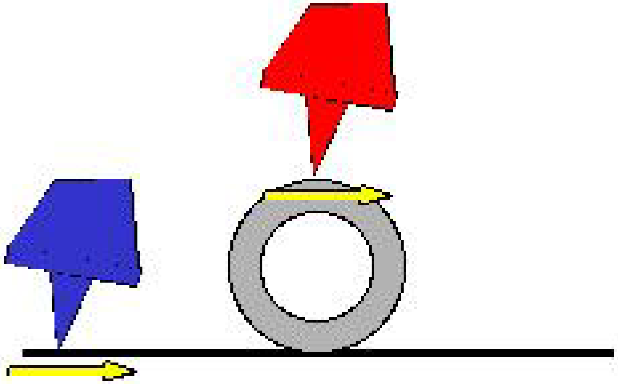
$$F_{friction} \propto C(\tau) \,.\, (F_{normale} - F_{offset})^{2/3}$$

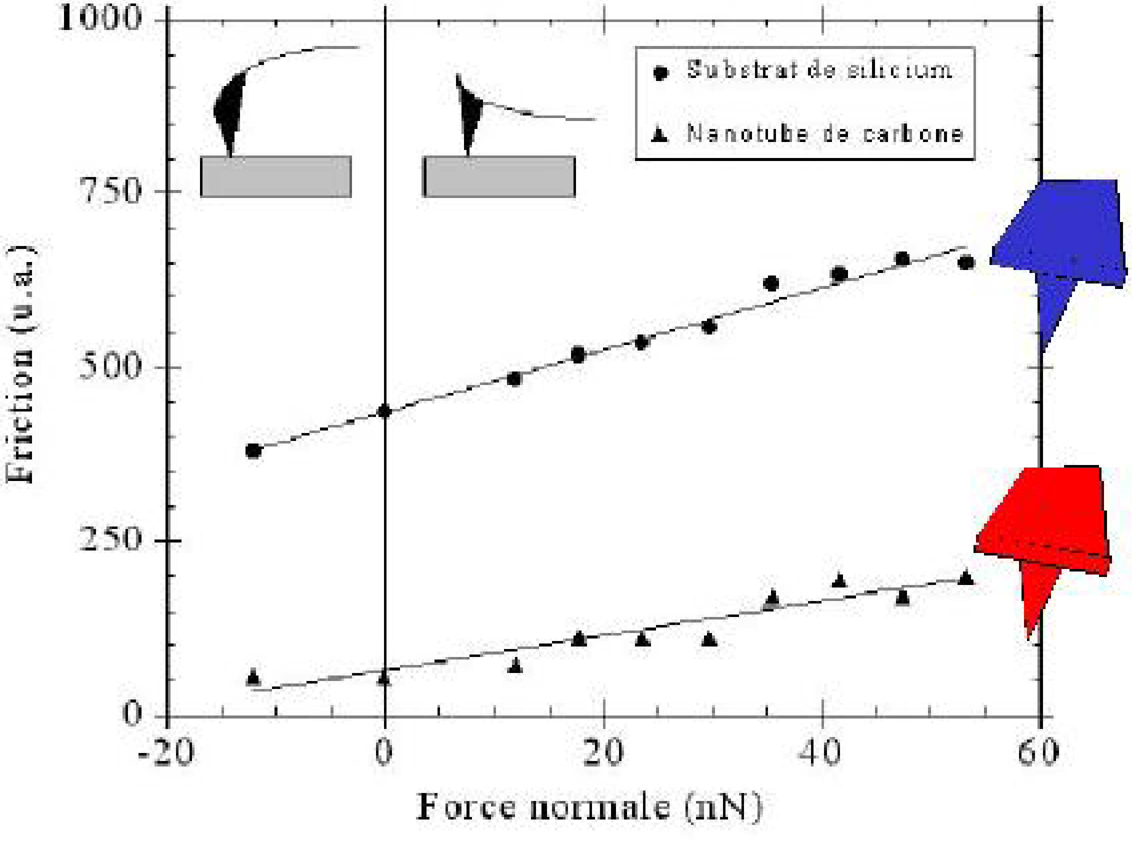
lateral force

adhesion is there



# Friction on a carbon nanotube versus friction on silicon surface



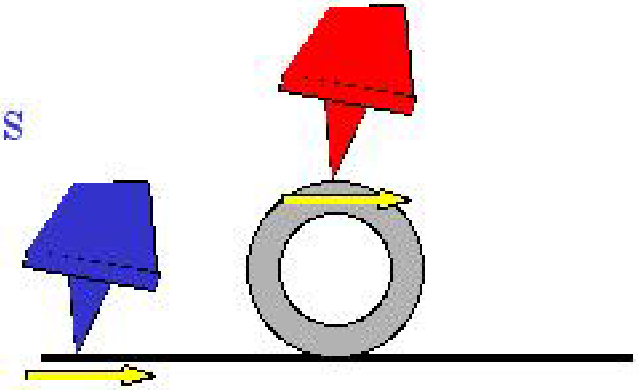


## *Low adhesion and low fiction on carbon nanotubes compared to silicon, mica, germanium*

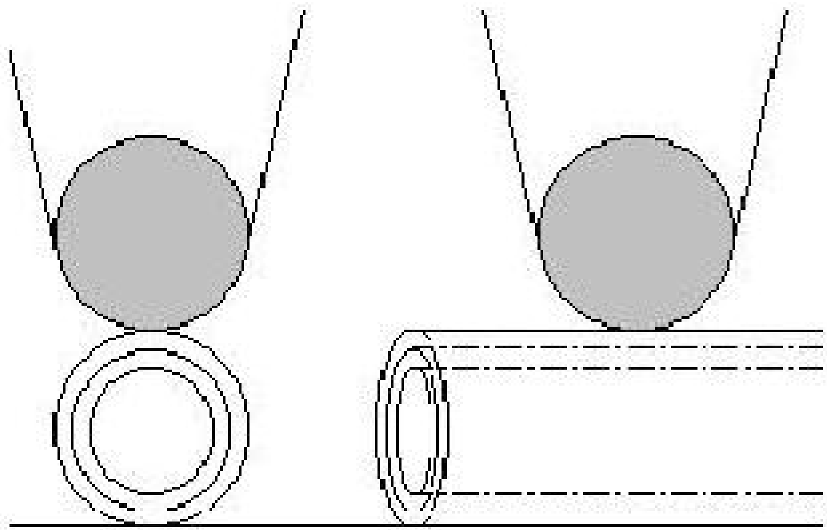
- Basic mechanism ?
  - No clear chemical effect
  - Not capillarity (dry atmosphere)
  - Van der Waals interaction (always present….)
- *Empirically* nanotube acts as a spacer:
  - Tip/surface distance increases:

    vdw interaction decreases

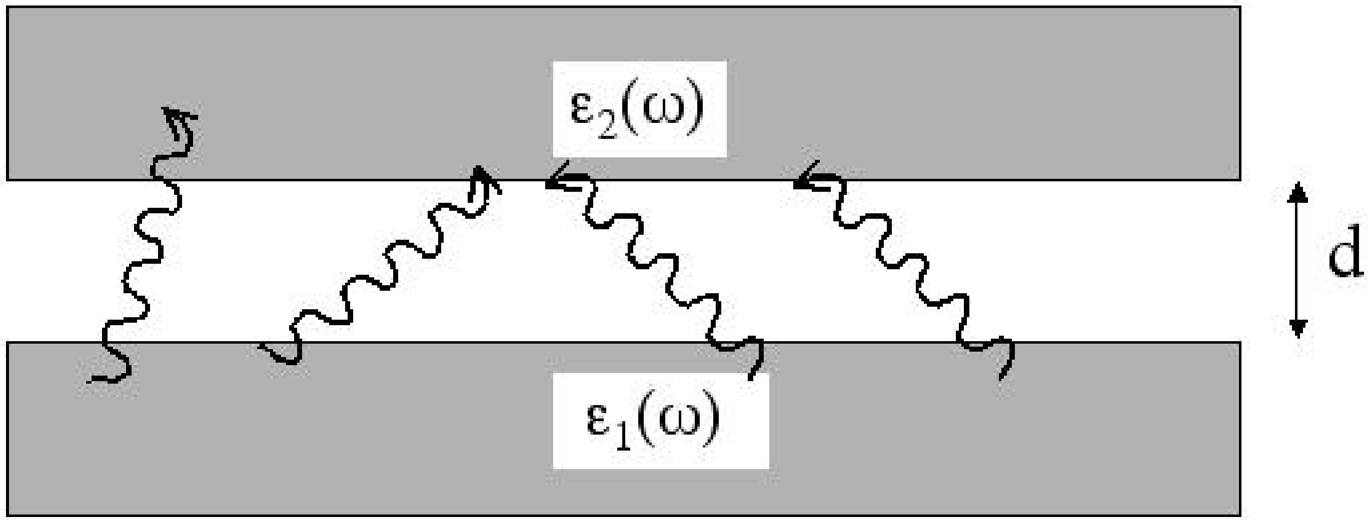
Adhesion decreases/ Friction decreases



# Carbon nanotubes as spacer: decrease of the van der Waals interaction



# Van der Waals interaction: dispersion forces




## Exchange of virtual phonons between two slabs

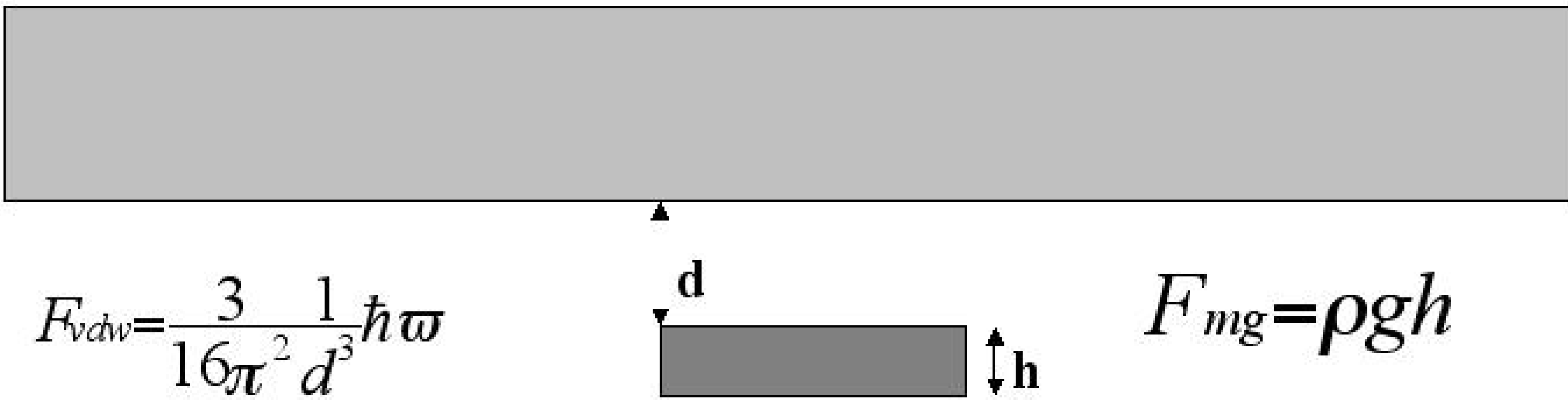
$$F_{vdw} = \frac{3\hbar}{16\pi^2}\frac{1}{d^3}\int_0^\infty du \left[\frac{\varepsilon_1(iu)-1}{\varepsilon_1(iu)+1}\,\frac{\varepsilon_2(iu)-1}{\varepsilon_2(iu)+1}\right]$$

*Vdw force per unit area*

*No retardation effect*

# Persson calculation:
# van der Waals versus gravity

*(see sliding friction 1998)*




$$F_{vdw}=\frac{3}{16\pi^2}\frac{1}{d^3}\hbar\varpi$$

with

$$\hbar\omega \sim 1eV - 10eV$$

$$F_{mg}=\rho g h$$

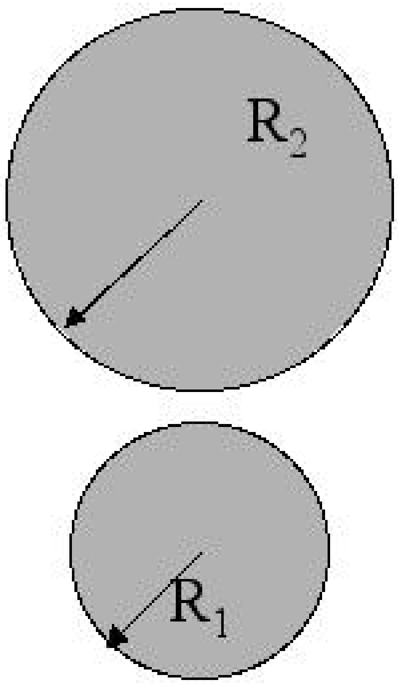
$$d=\left(\frac{3\hbar\varpi}{16\pi^2}\frac{1}{\rho g h}\right)^{1/3}$$

h=1μm

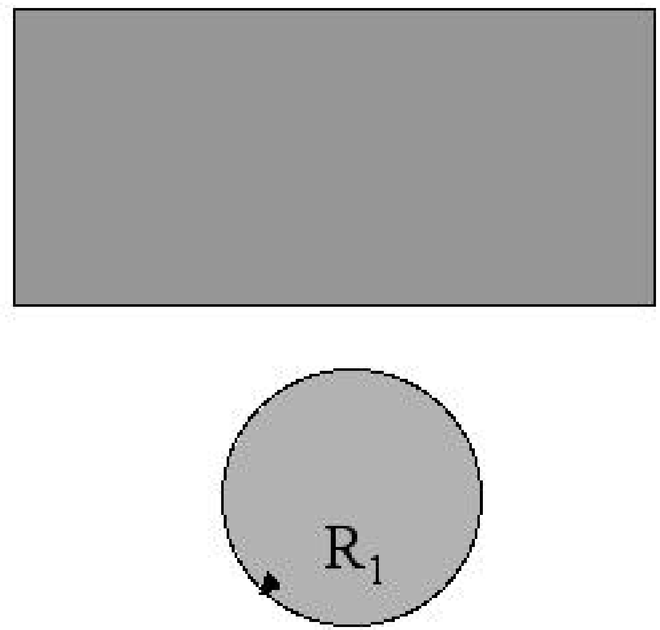
d<1μm

# Tip surface interaction in van der waals scheme (London dispersive force)

Simple geometry: sphere/ sphere and sphere/plan



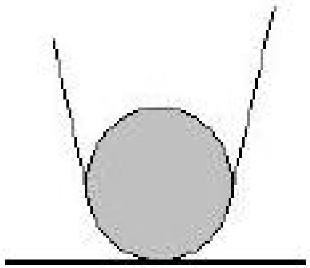





$$V_{vdw}(D) = -\frac{H R^*}{6D}$$

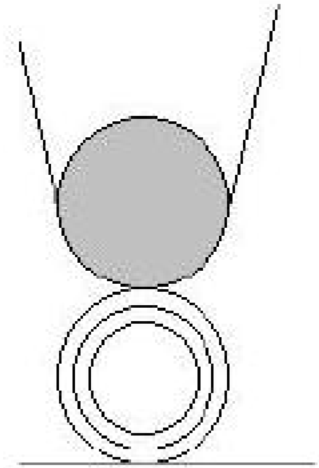
$$R^* = \frac{R_1 R_2}{R_1 + R_2}$$

$R_2, R_1 >> D$



$$Vsp(D) = -\frac{HR^*}{6D}$$

$$R^* = R_1$$

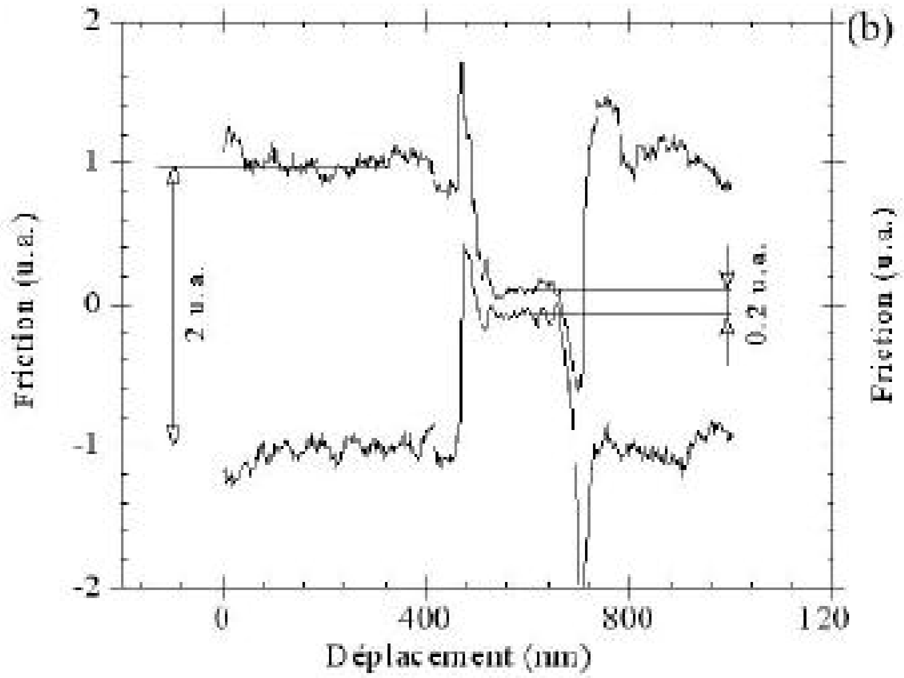


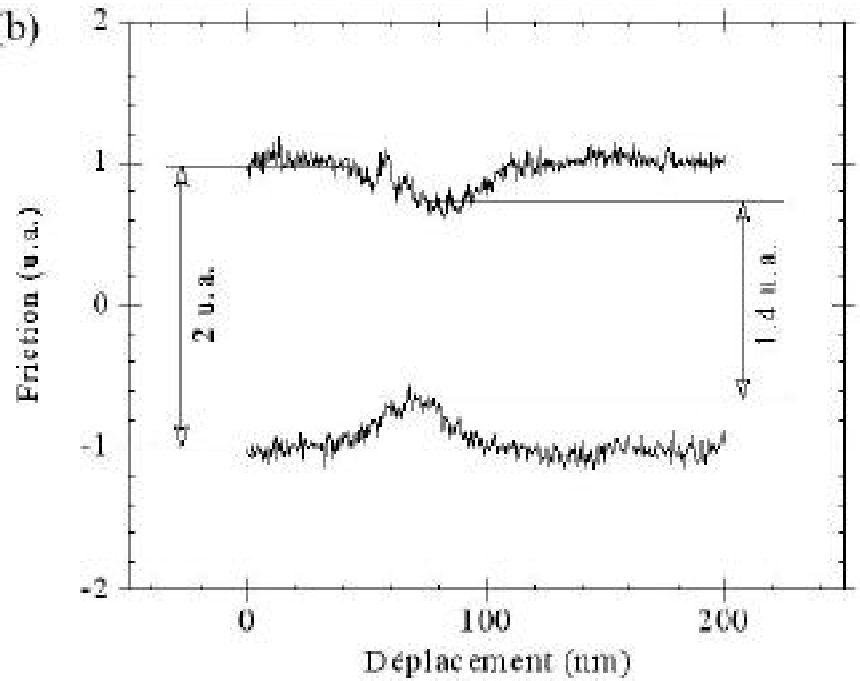
$$Vss(D) = -\frac{HR^*}{6D}$$

$$R^* = \frac{R_1}{2}$$

$$Vsp(D) = 2Vss(D)$$

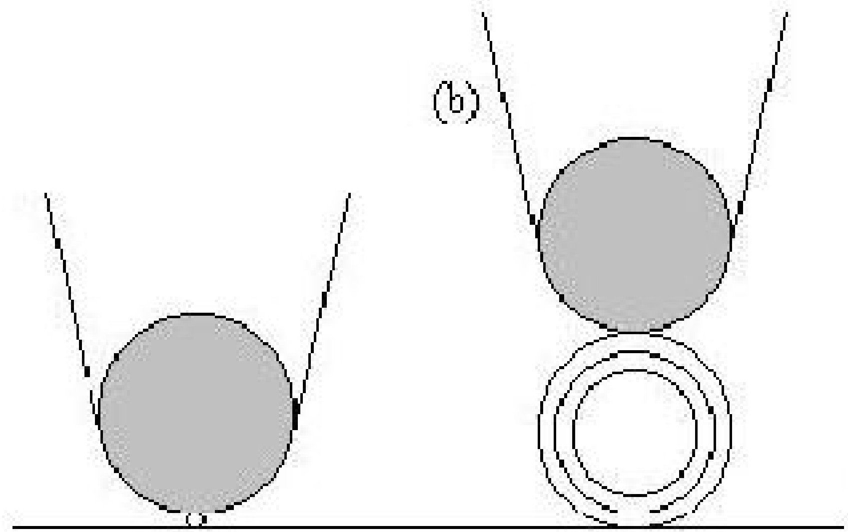
# *However*…….Friction on nanotubes of different sizes




Carbon nanotubes
Diameter: 15nm

Carbon nanotubes
Diameter: 1nm


(b)

# Carbon nanotubes and van der Waals interaction:

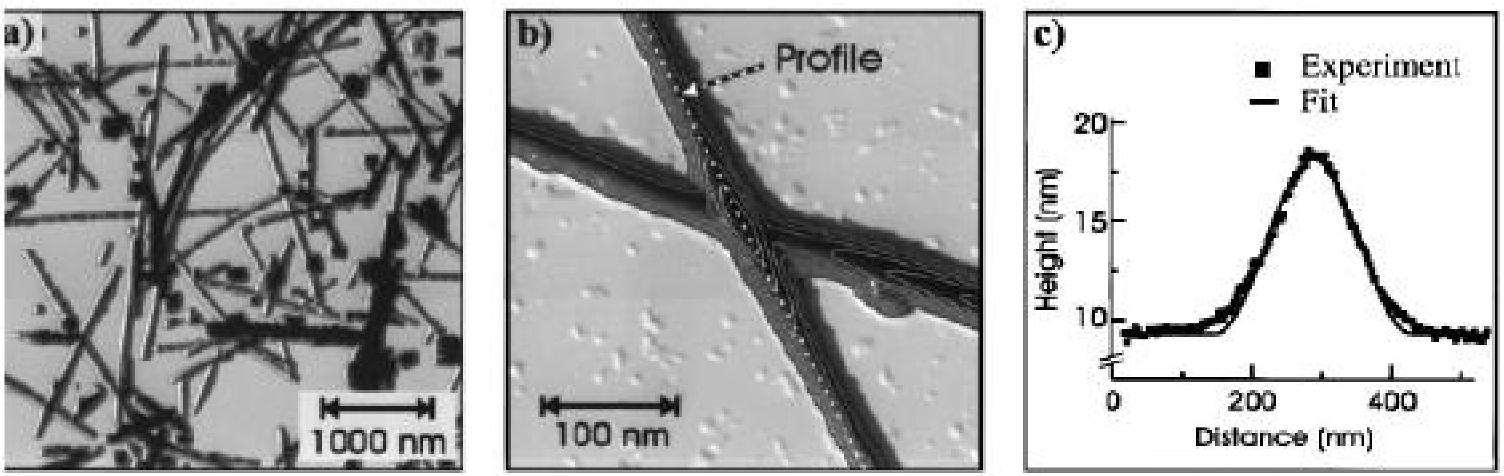
## Nanotube/surface: see Ruoff and Yakobson talks

PHYSICAL REVIEW B VOLUME 58, NUMBER 20 15 NOVEMBER 1998-II

**Deformation of carbon nanotubes by surface van der Waals forces**

Tobias Hertel, Robert E. Walkup, and Phaedon Avouris*
*IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, New York 10598*
(Received 12 February 1998; revised manuscript received 7 May 1998)

The strength and effect of surface van der Waals forces on the shape of multiwalled and single-walled carbon nanotubes is investigated using atomic-force microscopy, continuum mechanics, and molecular-mechanics simulations. Our calculations show that depending on the tube diameter and number of shells, the van der Waals interaction between nanotubes and a substrate results in high binding energies, which has also been determined experimentally. Nanotubes on a substrate may consequently experience radial and axial deformations, which significantly modify the idealized geometry of free nanotubes. These findings have implications for electronic transport and the tribological properties of adsorbed nanotubes.
[S0163-1829(98)05744-0]



From Hertel et al, the energy of the deformed nanotube interacting with a passivated silicon surface (H terminated):

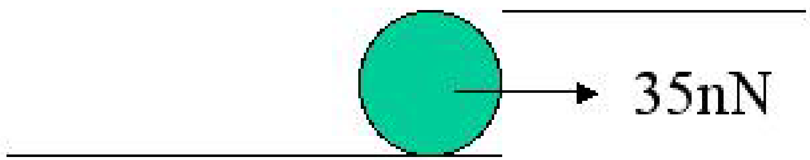
$$E=\int\left[u(c)+V(z)\right]dx$$

- u(c) is the elastic energy due to curvature
- V(z) is the van der Waals interaction between the nanotube and the surface

*(binding energy to the surface)*

Estimation of this binding energy (same reference): 1eV/A

Nanotube diameter: 9nm



At this scale, with « no chemistry » present, vdw is a strong interaction!!!

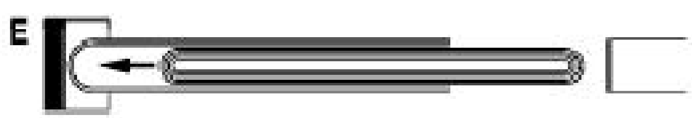
Another example on vdw relevance:

REPORTS

**Low-Friction Nanoscale Linear Bearing Realized from Multiwall Carbon Nanotubes**

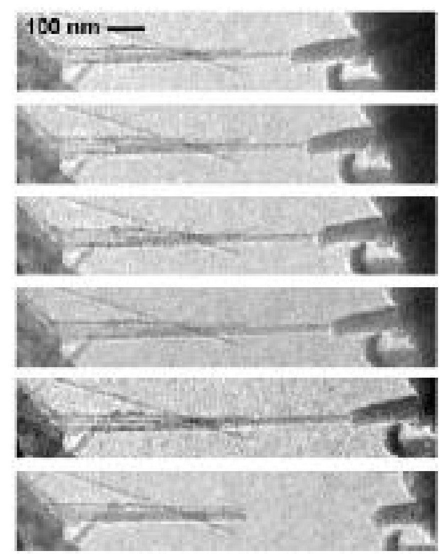
John Cumings and A. Zettl*

SCIENCE VOL 289 28 JULY 2000




$$F_{vdw} = -\frac{dU(x)}{dx} \quad \text{with} \quad U(x) = -0.16Cx$$

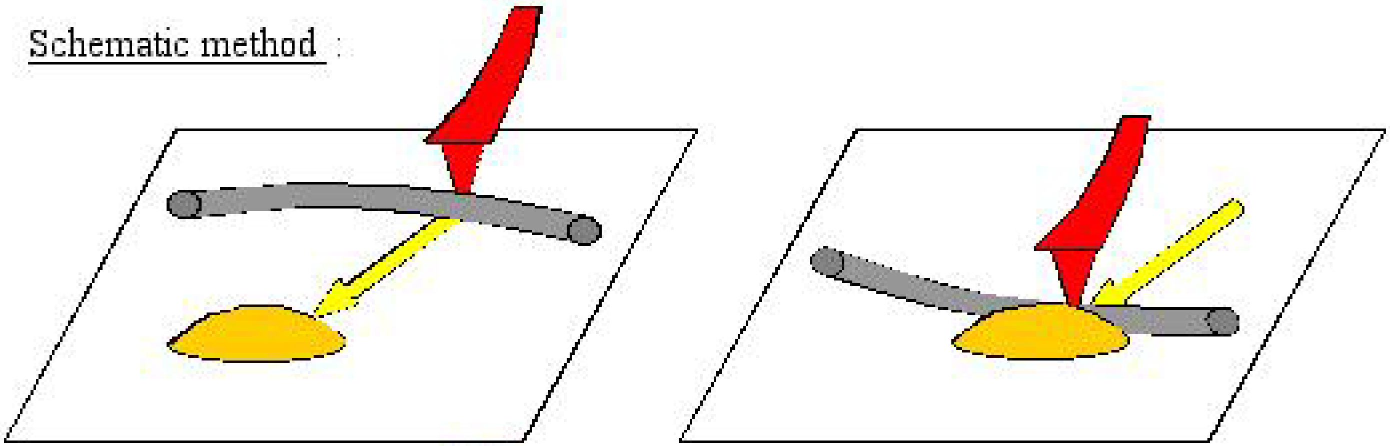
From L.X. Benedict et al, Chem. Phys. Lett., 286,490, (1998)

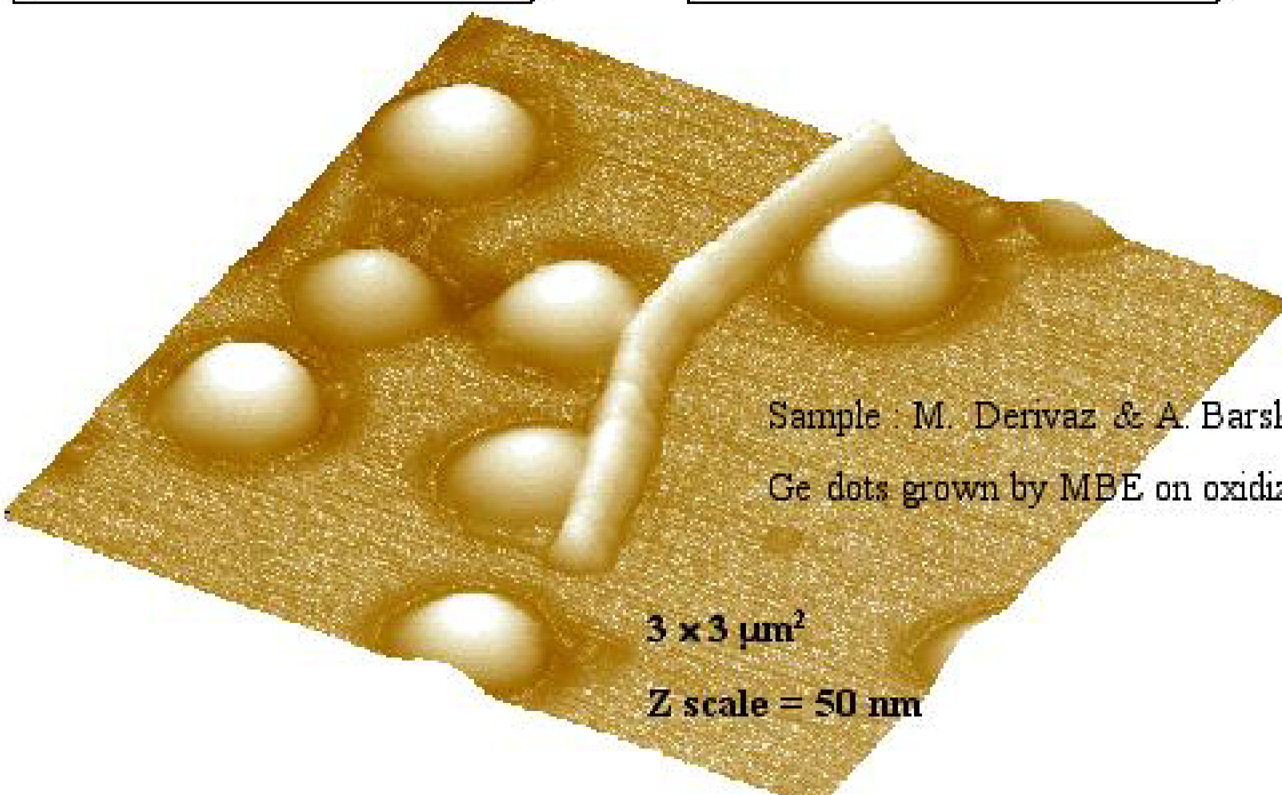



$F_{vdw} = 9nN$

# Manipulation of nanotube on nanostructured Silicon

Schematic method :

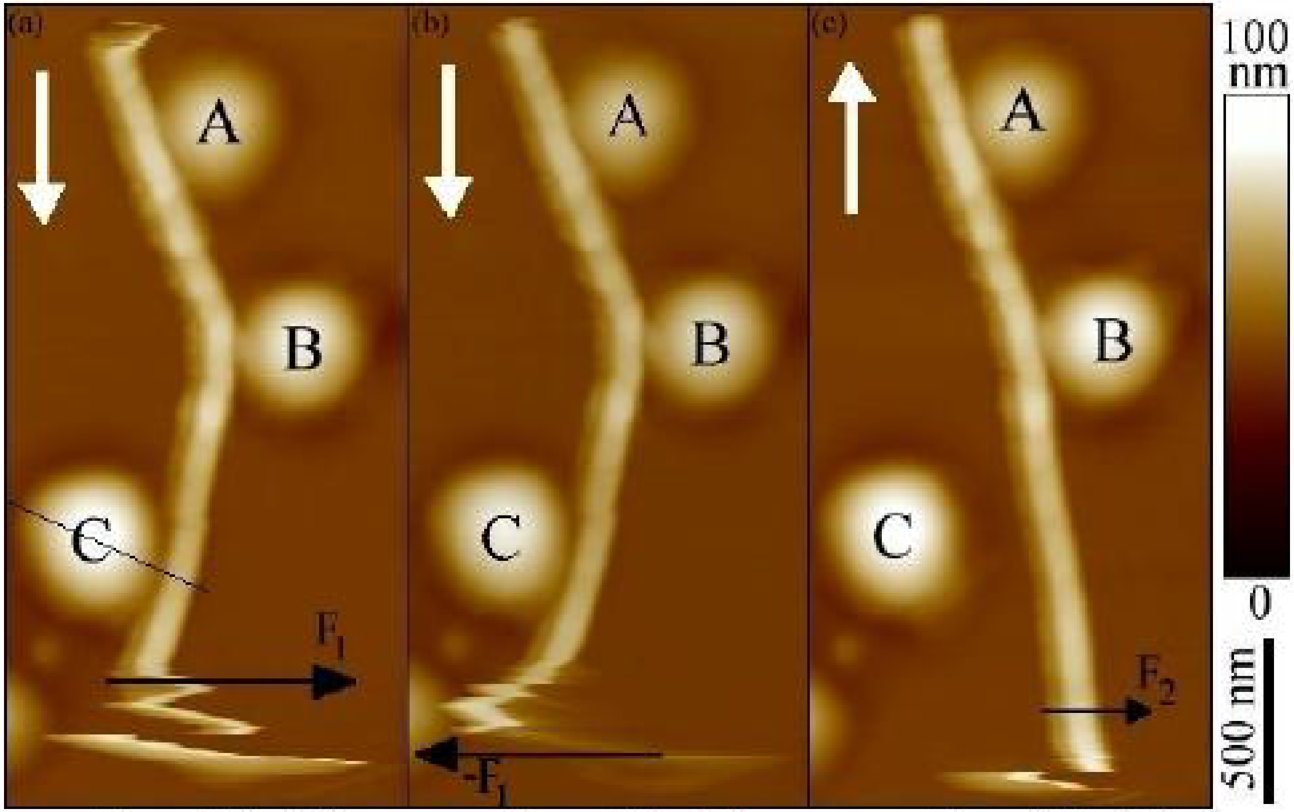





Sample : M. Derivaz & A. Barski (DRFMC/CEA)

Ge dots grown by MBE on oxidized Silicon

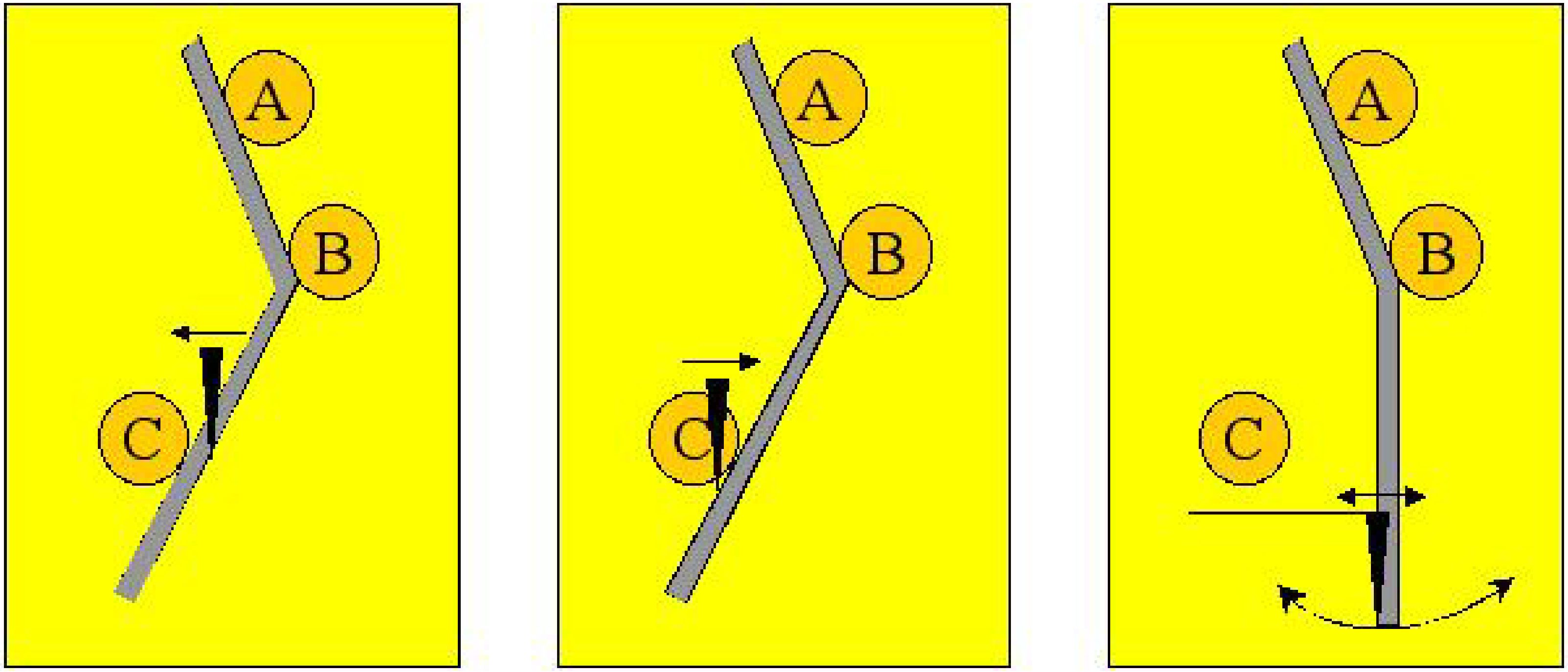
# Interaction between Ge dots and nanotubes




$F_N = 50$ nN   $F_N = 50$ nN   $F_N = 35$ nN

- **Ge dots = Pinning centers**(due to adhesion)
- **Nanotube Blocking by Ge dots** (due to nanotube elastic deformation)
- **Nanotube displacement while imaging**(due to lateral force applied by the tip)

S. Decossas et al., to appear



A
B
C
A
B
C
A
B
C

# Forces involved in pinning center phenomenon

All our surfaces are chemically inert in air condition

**Chemical ?**

Friction and Adhesion measurement under air and dry $N_2$ atmosphere

**Capillary ?**

**Electrostatic ?**

Contact
In air

**Van der Waals ?**

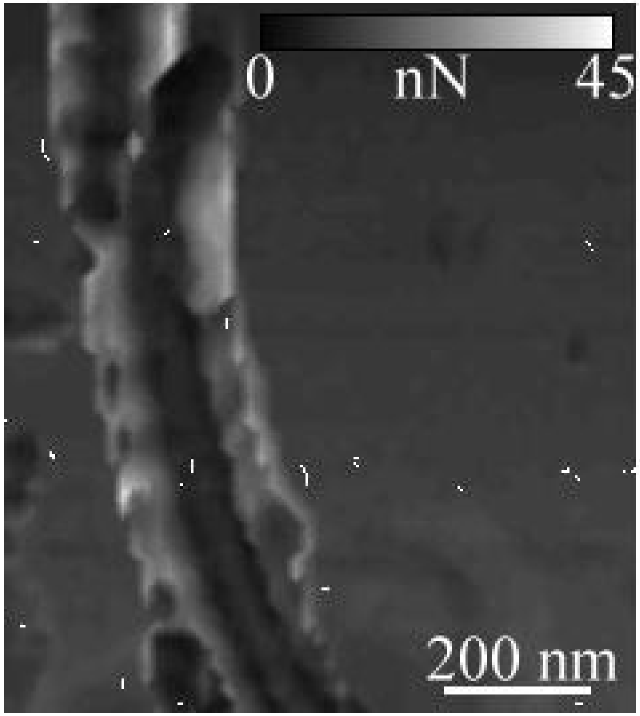
Force curve mapping

In air

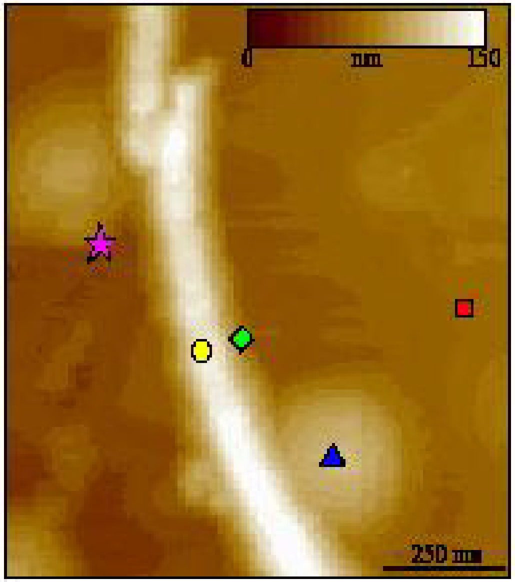
In dry atmosphere

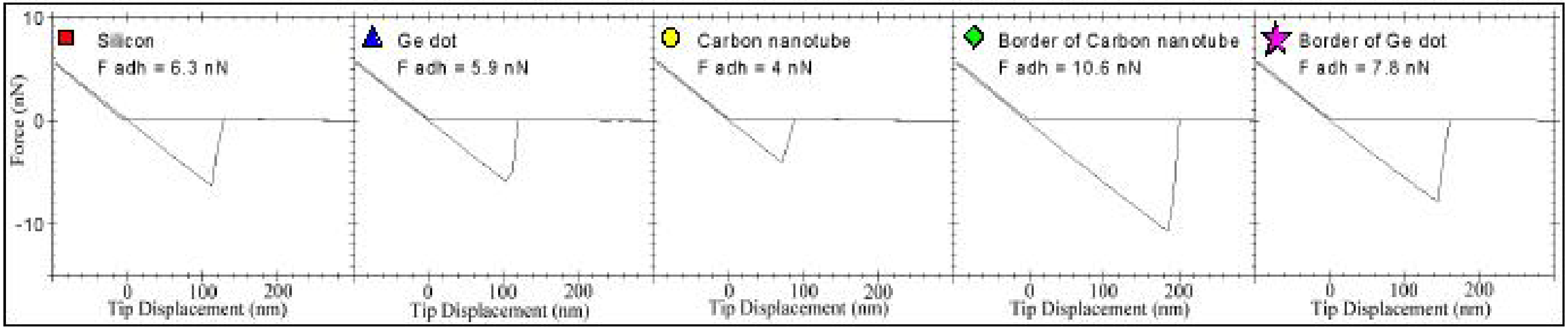
# Force curve mapping

**Adhesion force:**



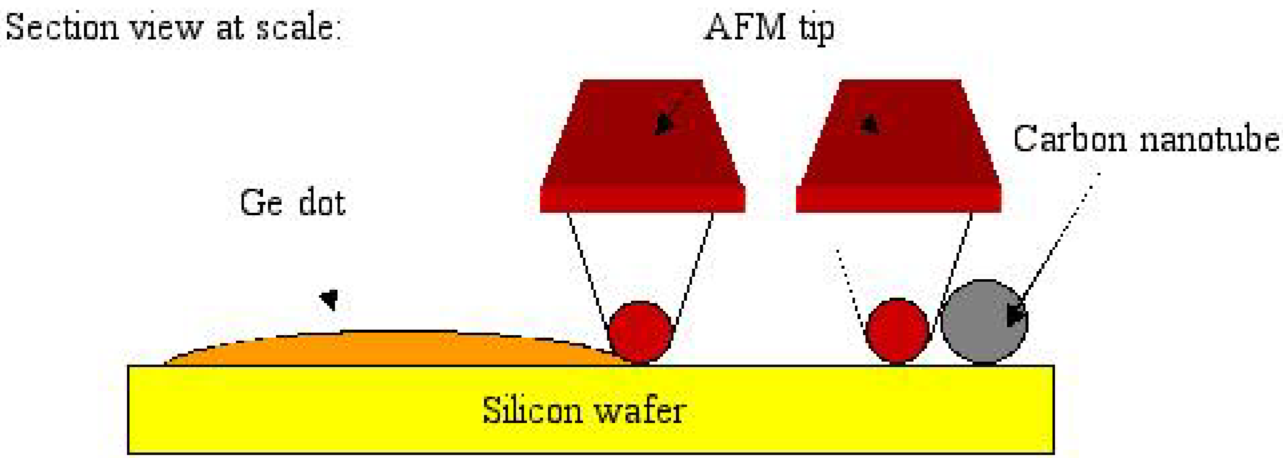

**Height :**



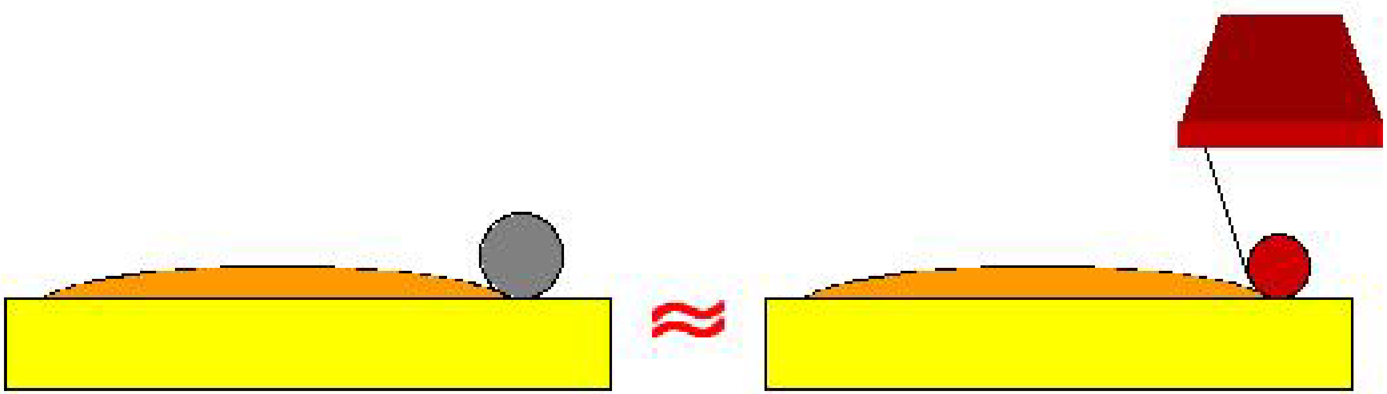

Same behavior whatever the atmosphere is (air or dry $N_2$)

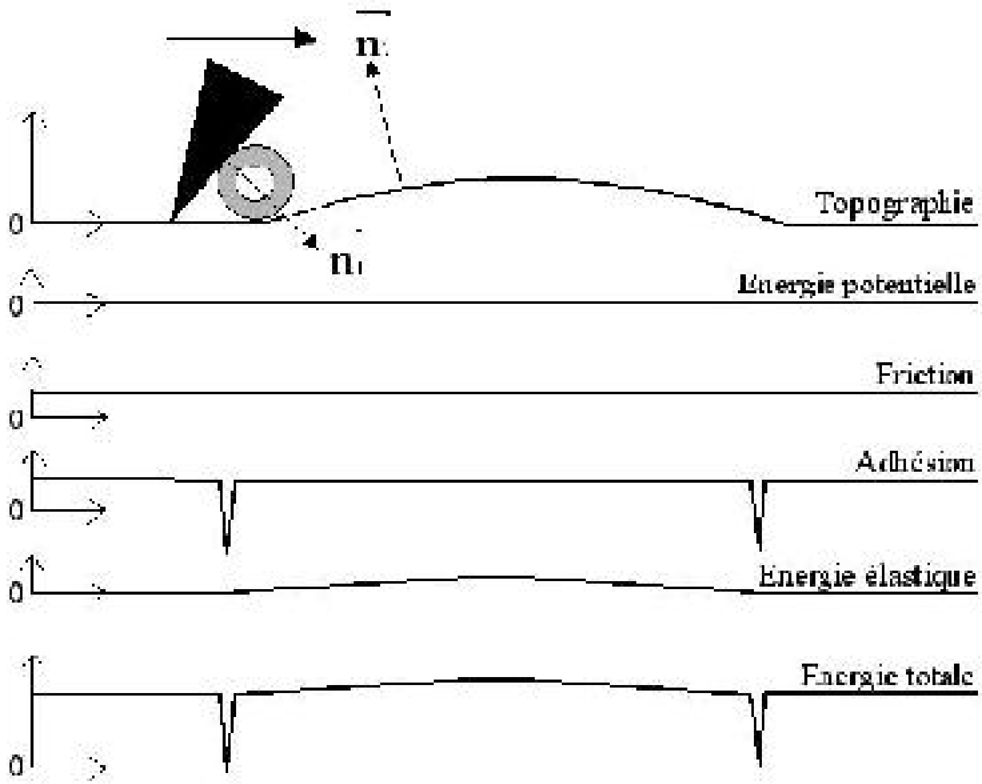
# Geometrical effect on adhesion measurement




In a Van der Waals scheme:

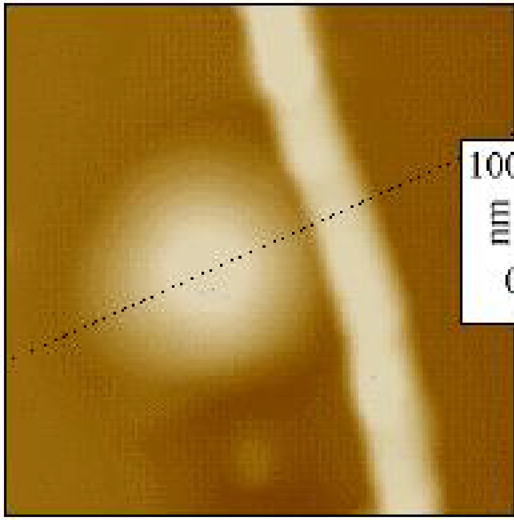
a key parameter is the amount of matter involved



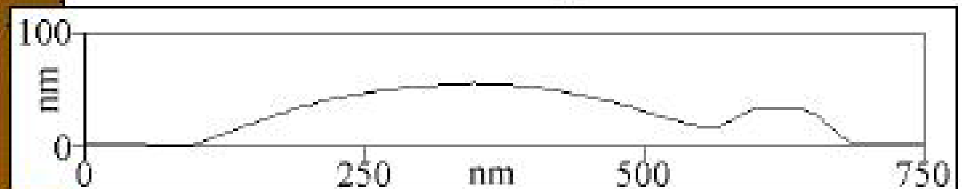


n
n
0
Topographie
0
Energie potentielle
Friction
0
Adhésion
0
0
Energie élastique
Energie totale
0

# Nanotube blocking by Ge dots



**Continuous nanotube displacement over Ge dot impossible**

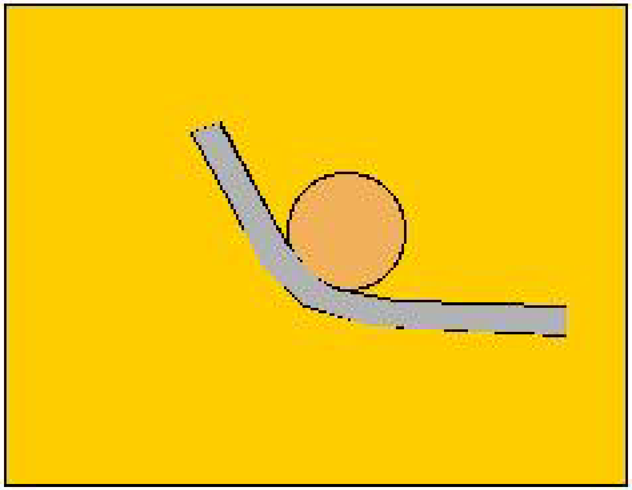



Friction on Ge dot = Friction on Silicon
Adhesion on Ge dot = Adhesion on silicon
Weight is negligible

▸ **Blocking mechanism = CNT elastic deformation**

# Pinning of carbon NANOTUBES

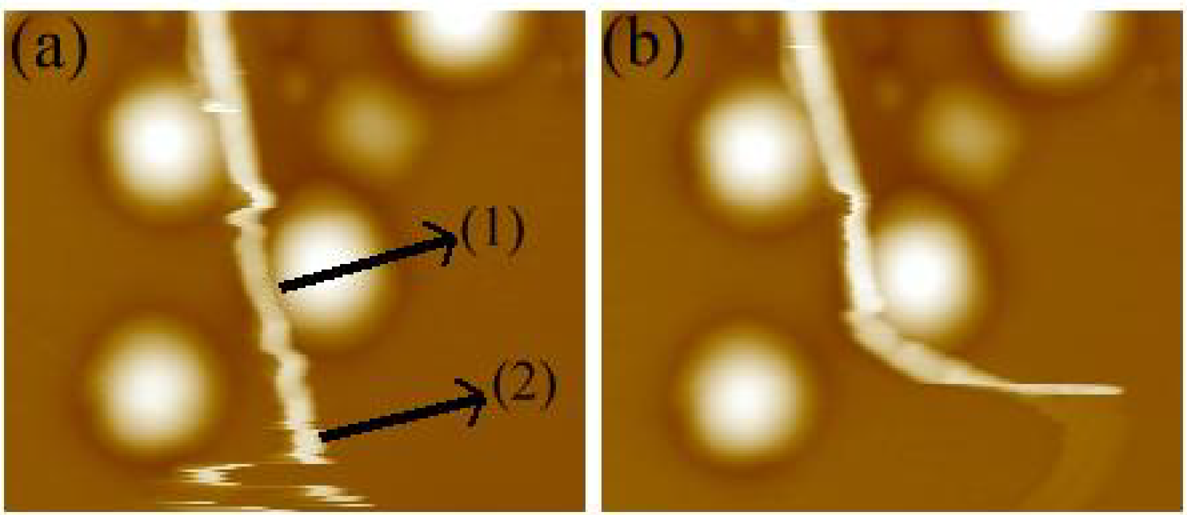
$$\frac{E.I}{2}\int\left(\frac{1}{R}-\frac{1}{R_0}\right)^2 dz = F_{Lateral} \leftrightarrow d_{Tip}$$



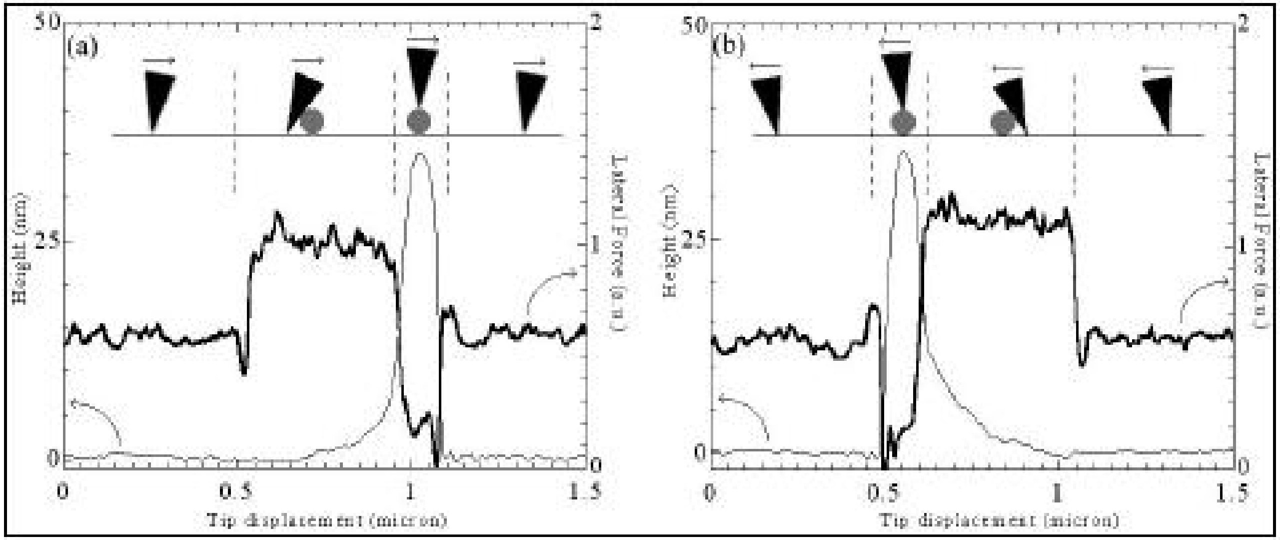
$$\Rightarrow F_{lateral} \gg 40\ nN$$

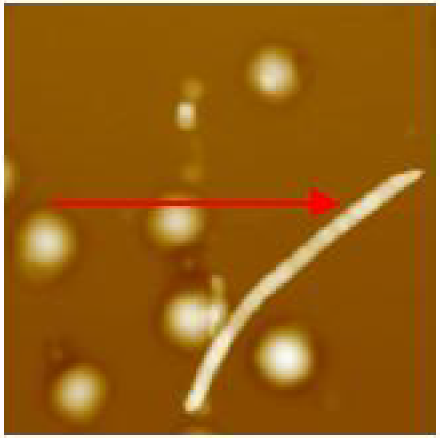
$\Rightarrow$ $E_{elastique} \approx 2\ 10^{-13}$ J

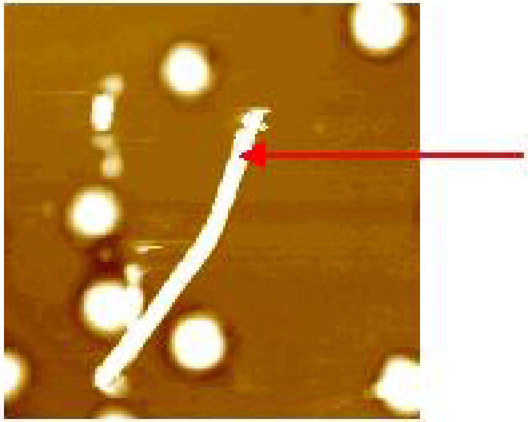
Vdw adhesive energy on dot
close to
Deformation energy



# Displacement of nanotube while imaging

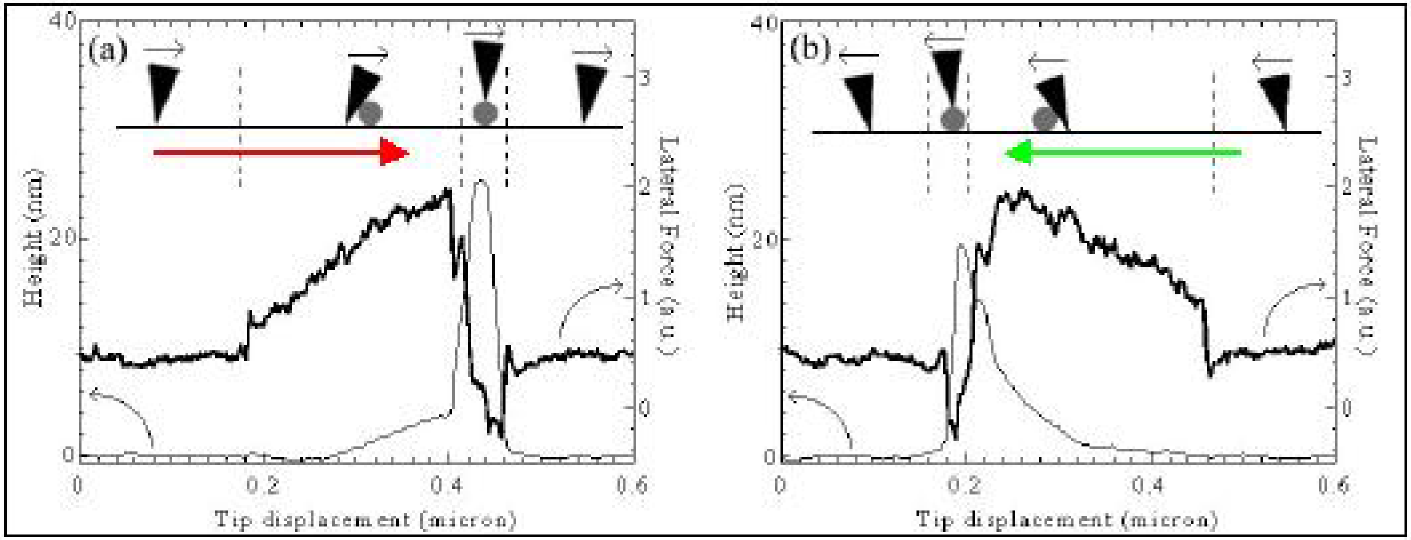


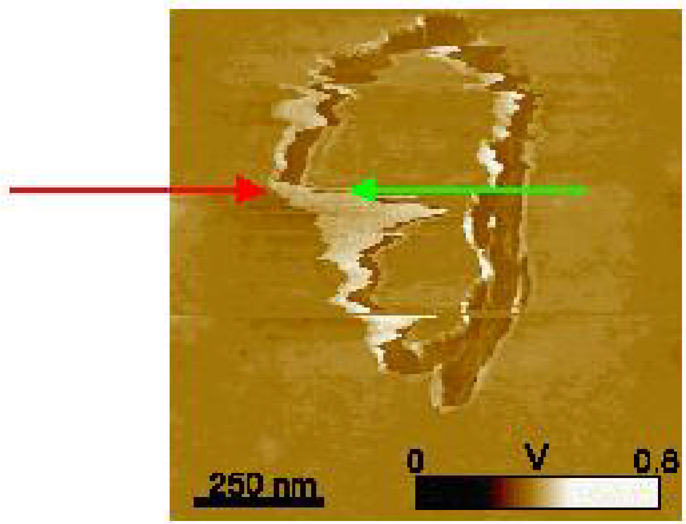





=> Lateral force contrast =nanotube Friction work

# Displacement of nanotube while imaging



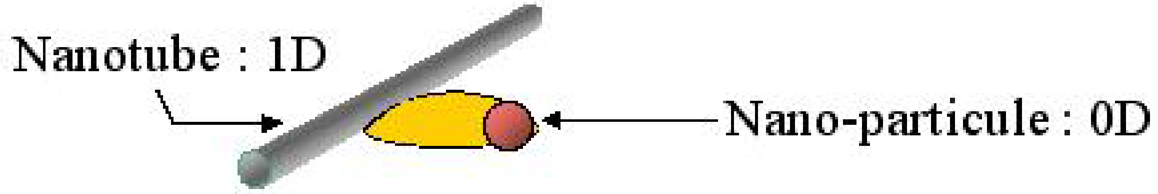




=> Lateral force contrast =nanotube elastic bending & friction work

- Absolute positioning: we can deposit nanotubes with a precision of 500nm on any kind of surface
- Tip / nanotube Adhesion << Tip / Silicon Adhesion (air or dry $N_2$)
- Tip / nanotube Friction << Tip / Silicon Friction (air or dry $N_2$)
- Ge dots are pinning centers for nanotubes
- Controlled deformation of nanotubes: mechanical properties (reversible large deformations)

# Perspectives

- Pinning mechanisms study by changing nanostructure characteristics (height, diameter, …)
- Adhesion and friction mechanisms study by changing CNT characteristics (length, diameter, …) or the nature of thenano-objects.



# Friction:

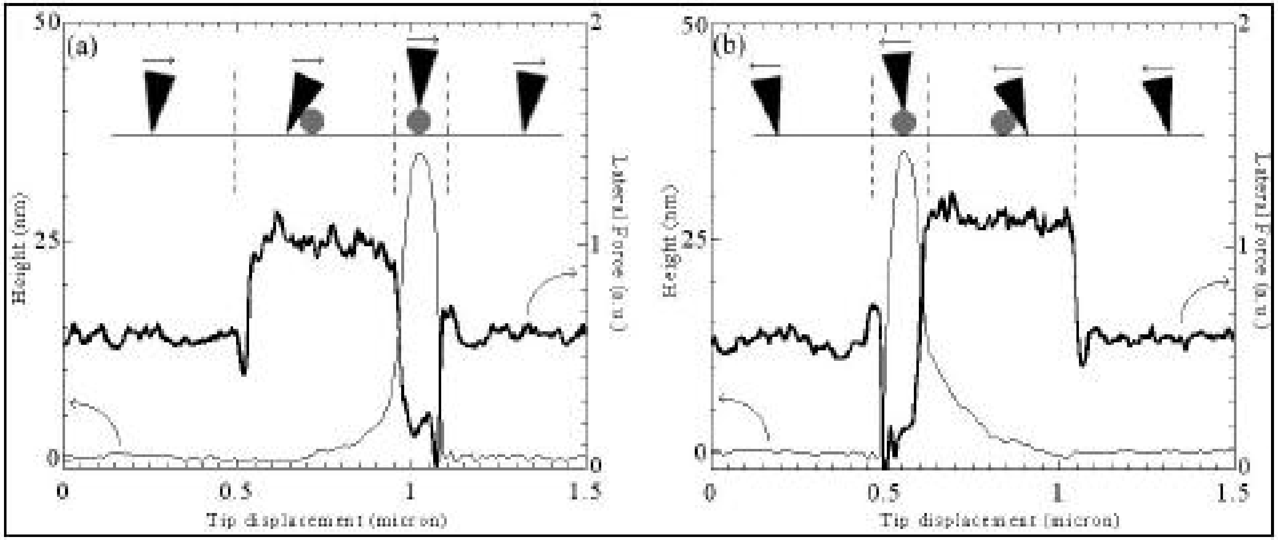
## nanoscale:

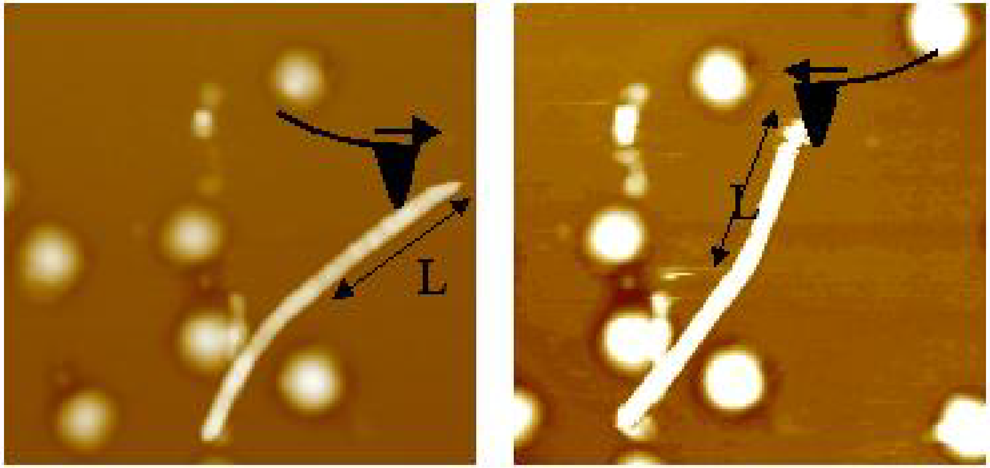
-continuous surface and nanoobject:
rolling and sliding

-atomic periodicity: mica

-commensurability/superlubricity

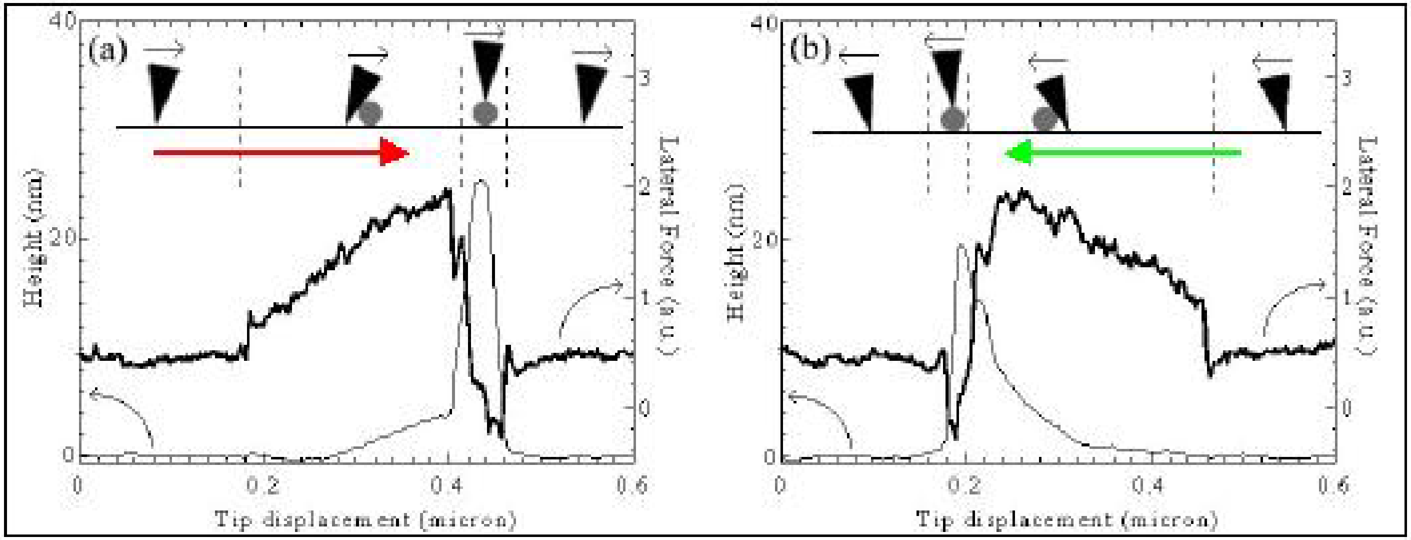
# Displacement of nanotube while imaging

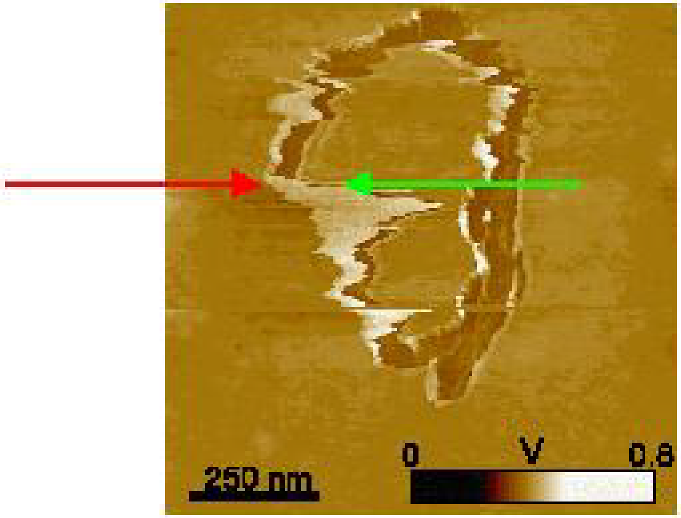


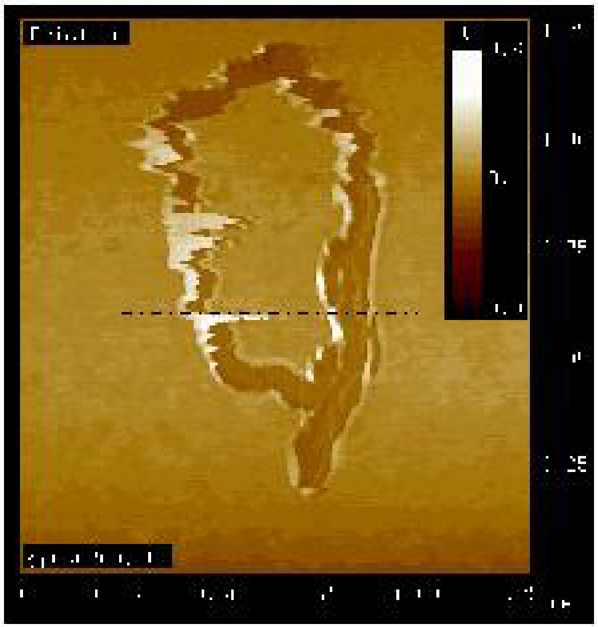

=> Lateral force contrast = nanotube Friction work

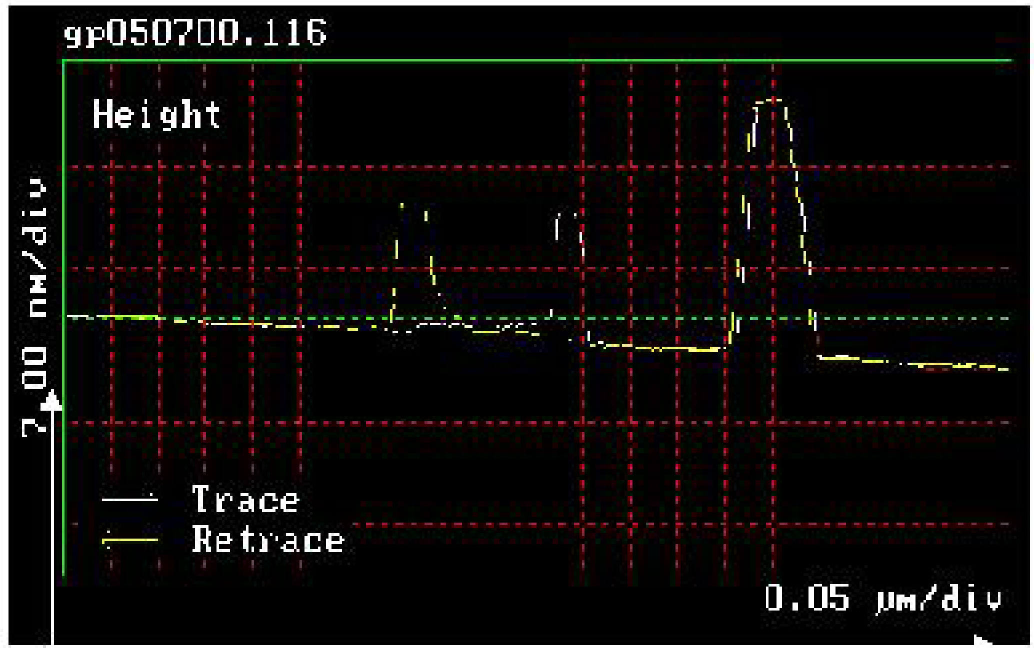
# Displacement of nanotube while imaging




=> Lateral force contrast =nanotube elastic bending & friction work





gp050700.116
Height
7.00 nm/div
Trace
Retrace
0.05 µm/div


(b)

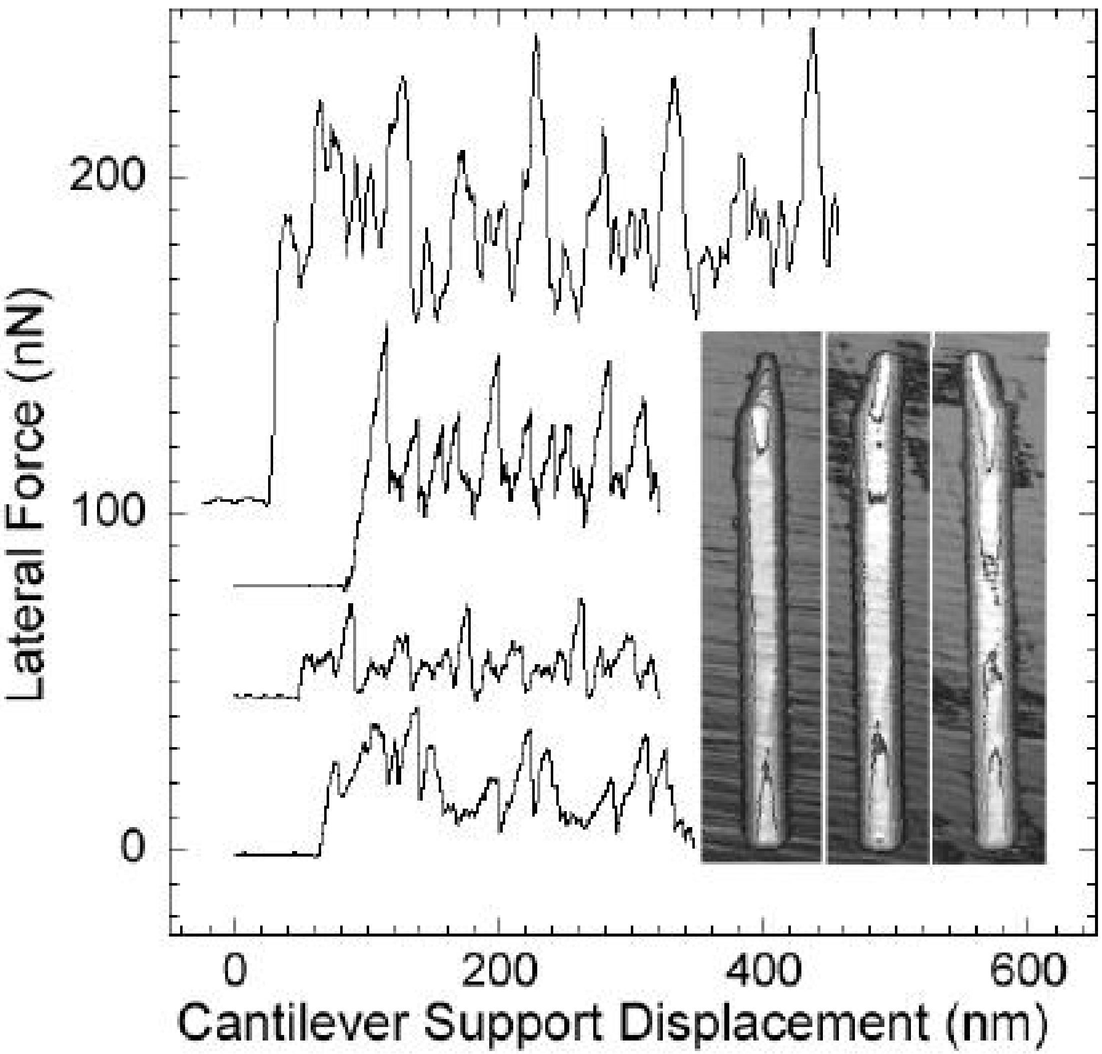



**Figure 5.** Periodic lateral force traces indicating rolling motion. The four traces are for four different CNT. In each case, the periodicity in the traces matches the circumference of the nanotube, indicating rolling without slipping motion. The dimensions of the CNT for the four traces going from top to bottom are :D (diameter)=35nm, L(length) = 500nm ; D=26nm, L = 450nm; D=27nm, L=590 nm; D=29nm L= 550 nm. The inset illustrates the topographical evidence for rolling. The top end of the nanotube has an asymmetry that changes in a way that is consistent with rolling motion. The second trace from the top corresponds to the nanotube in the inset sequence.

# Mechanics and friction at the nanometer scale

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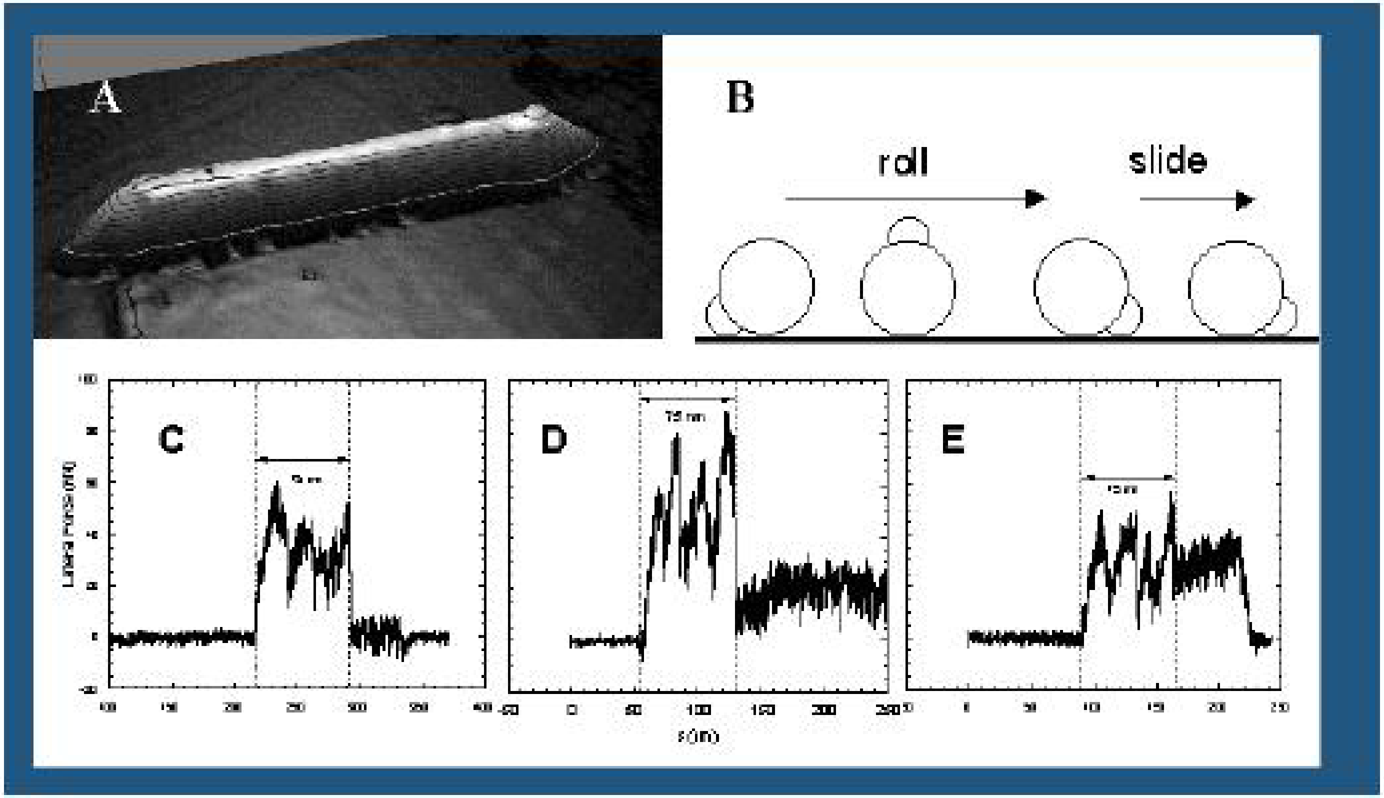
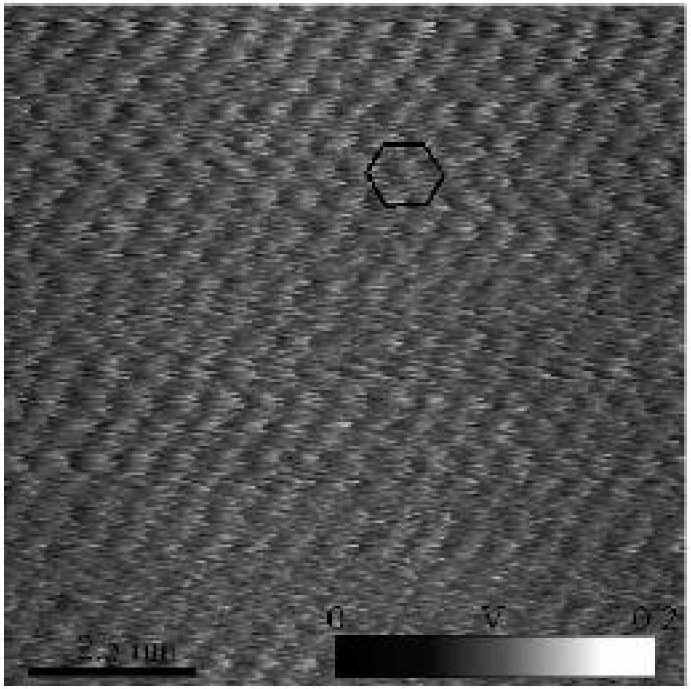
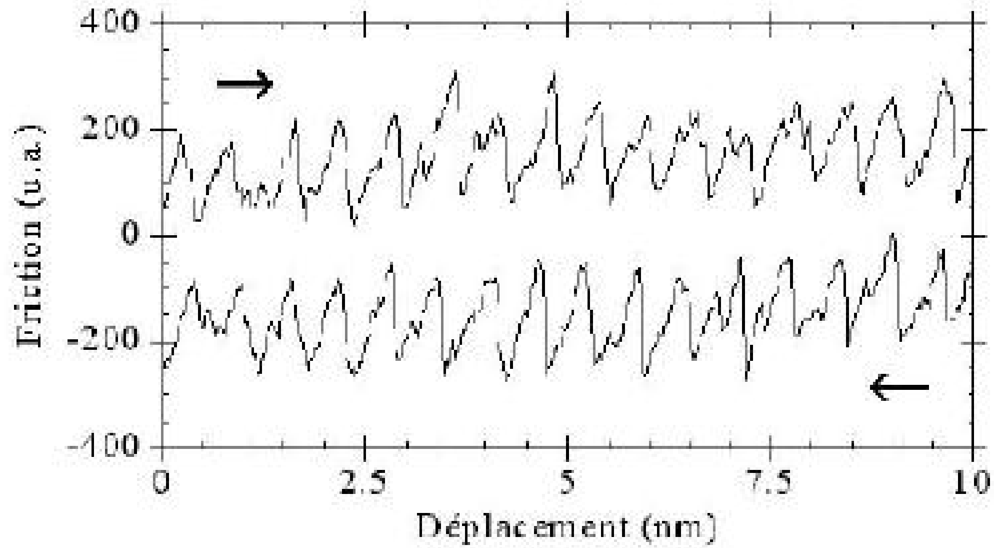
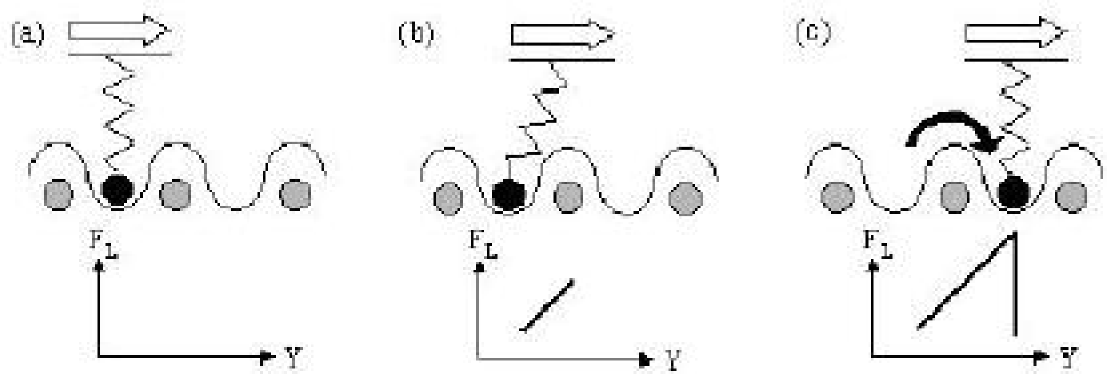



Falvo, M. R., R. M. Taylor II, A. Helser, V. Chi, F. P. Brooks Jr. , S. Washburn and R. Superfine (1999). "Nanometre-scale rolling and sliding of carbon nanotubes." Nature 397, 236-238.

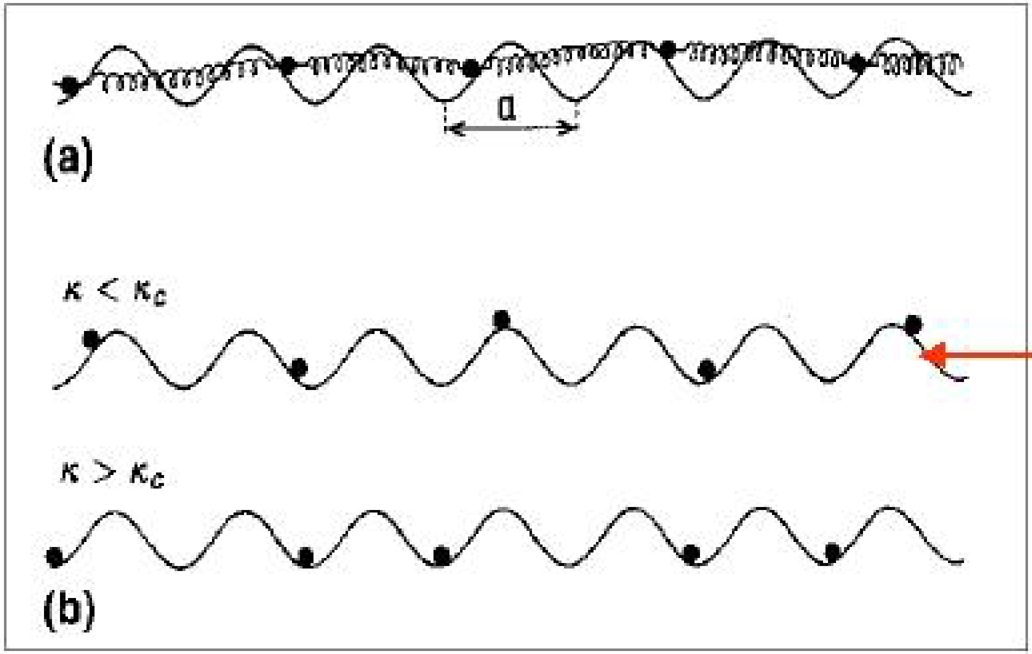



400
200
0
-200
-400
Friction (u.a.)
0
2.5
5
7.5
10
Déplacement (nm)


(a)
(b)
(c)
$F_L$
Y

# Commensurability, friction and nanotubes

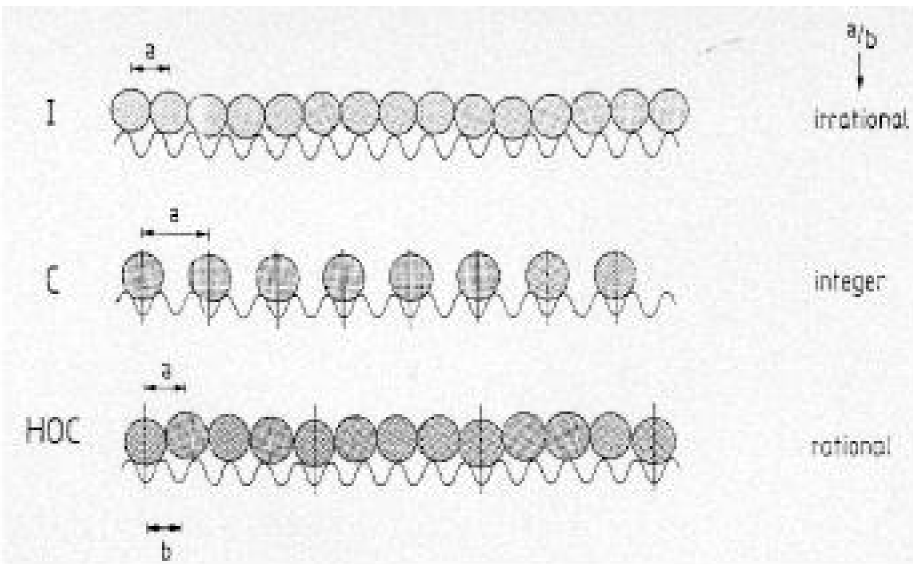
Friction and commensurability:
Frenkel Kontorova




*See BNJ Persson Sliding friction*

Low coupling:
no static friction

Old story in surface physics….
One example from G. Comsa et al, (1992) Xe/Pt




Incommensurate
Structure …
Free translation

Commensurate
Structure:
Pinned

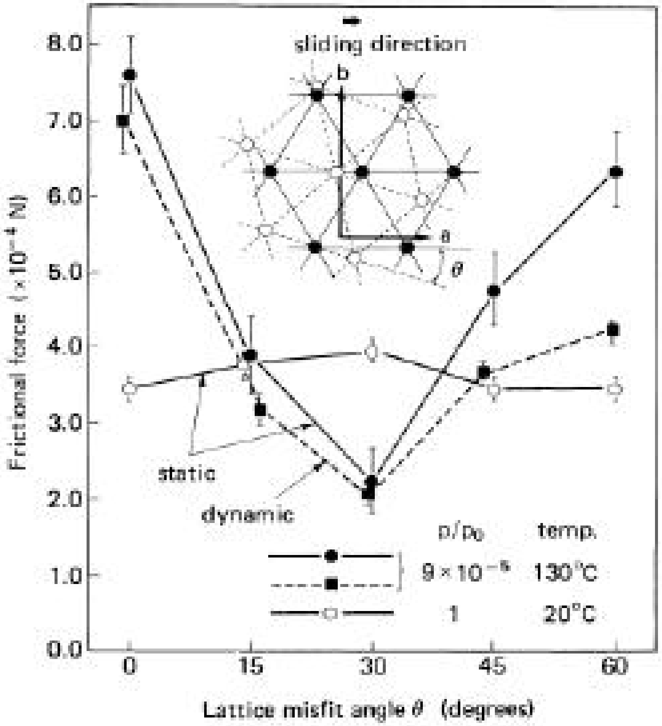



FIG. 3. The change in the measured static and dynamic frictional forces as a function of the lattice misfit angle $\theta$ between two contacting mica lattices. The misfit angle is approximately 0° when the two specimens are brought into commensurate contact without rotation of the lower specimen.

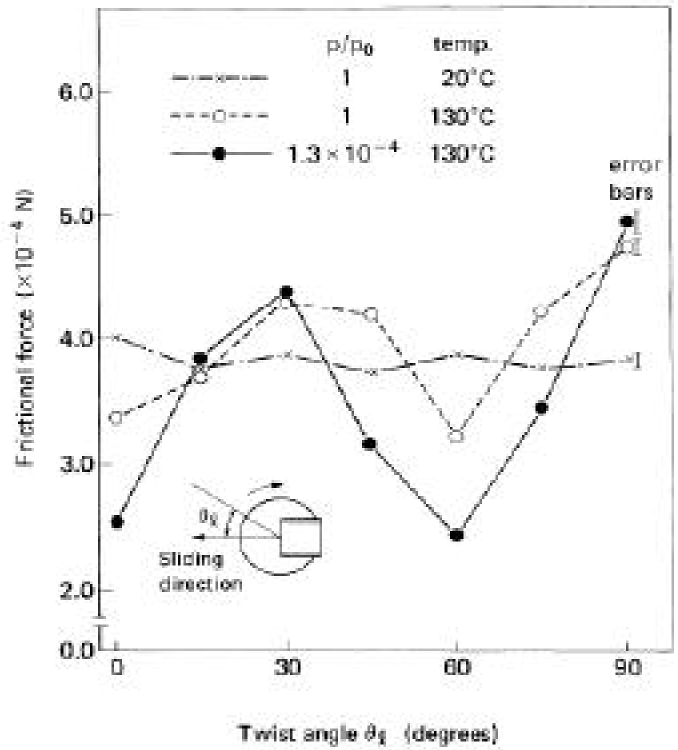



FIG. 4. The change in the measured static frictional force as a function of twist angle $\theta_t$ between the two contacting specimens.



# Anisotropy of Frictional Forces in Muscovite Mica

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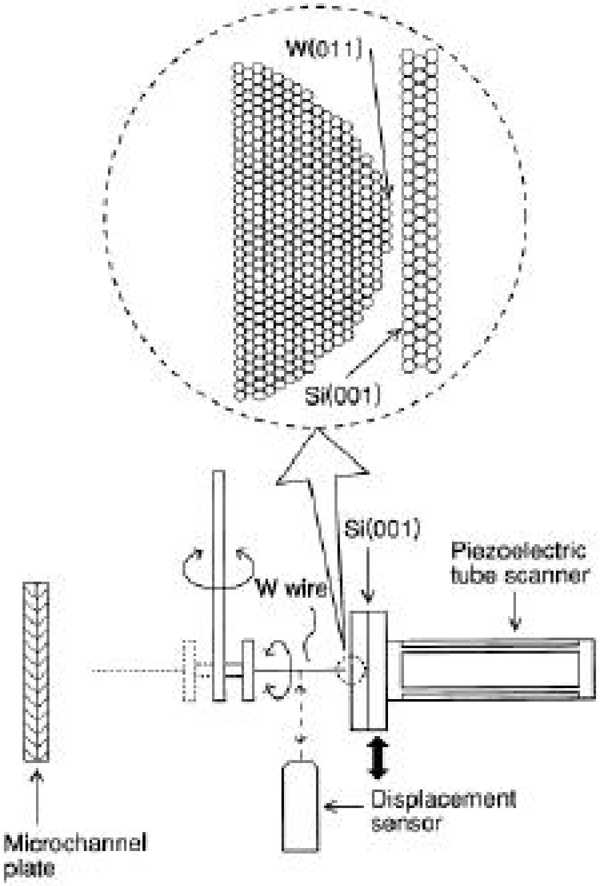
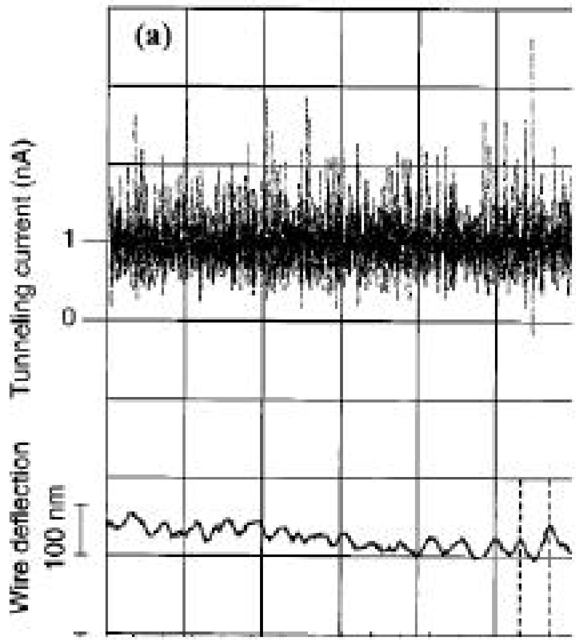
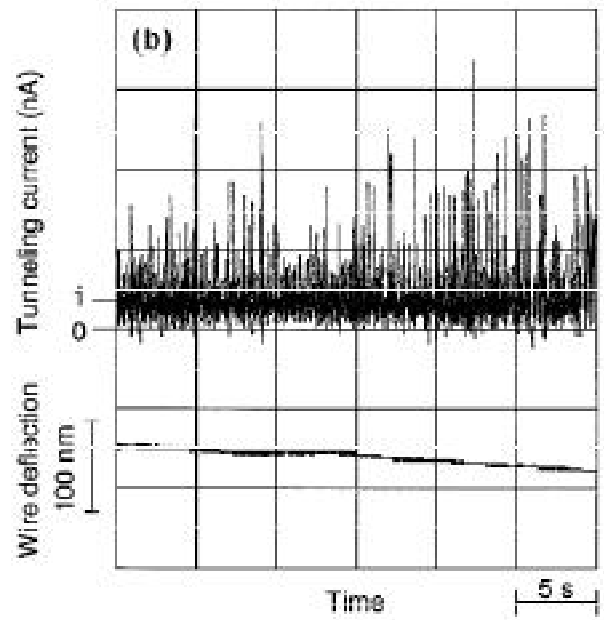
(Received 6 February 1991; revised manuscript received 27 June 1991)




VOLUME 78, NUMBER 8 PHYSICAL REVIEW LETTERS 24 FEBRUARY 1997

# Observation of Superlubricity by Scanning Tunneling Microscopy

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# Commensurability , friction and nanotubes

## Mechanics and friction at the nanometer scale

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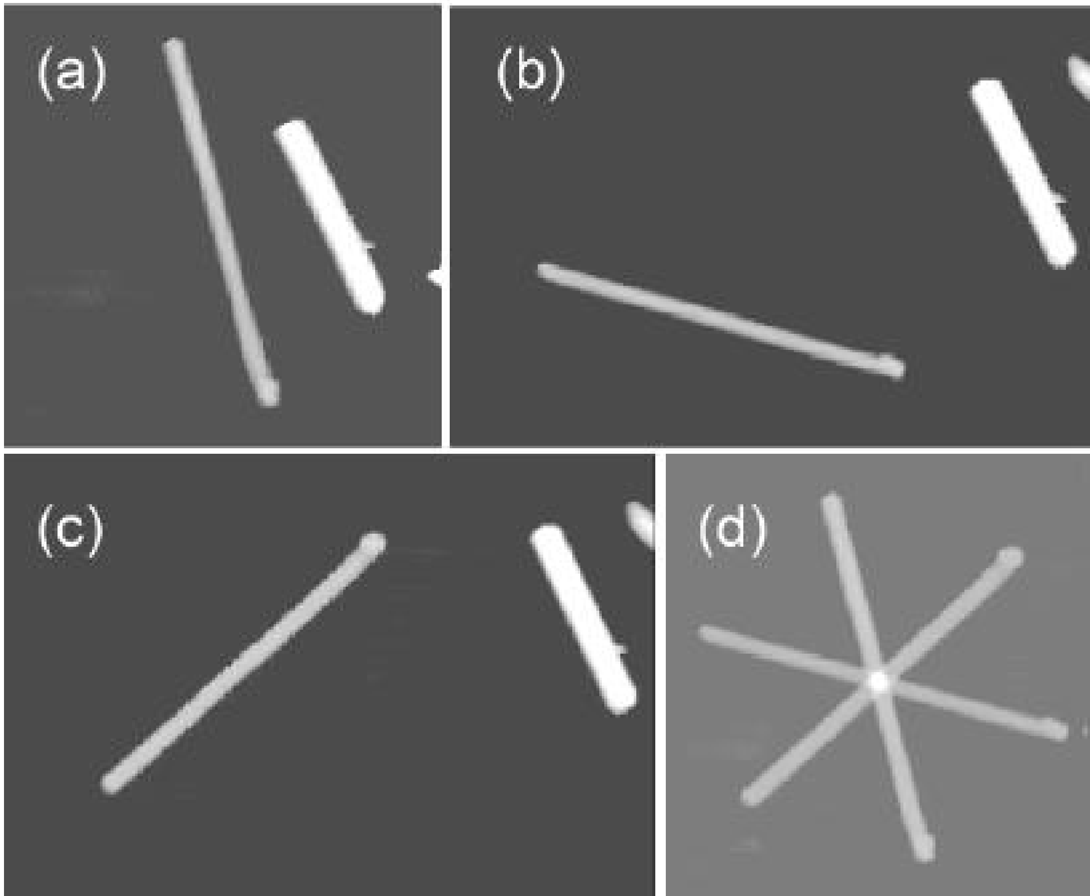
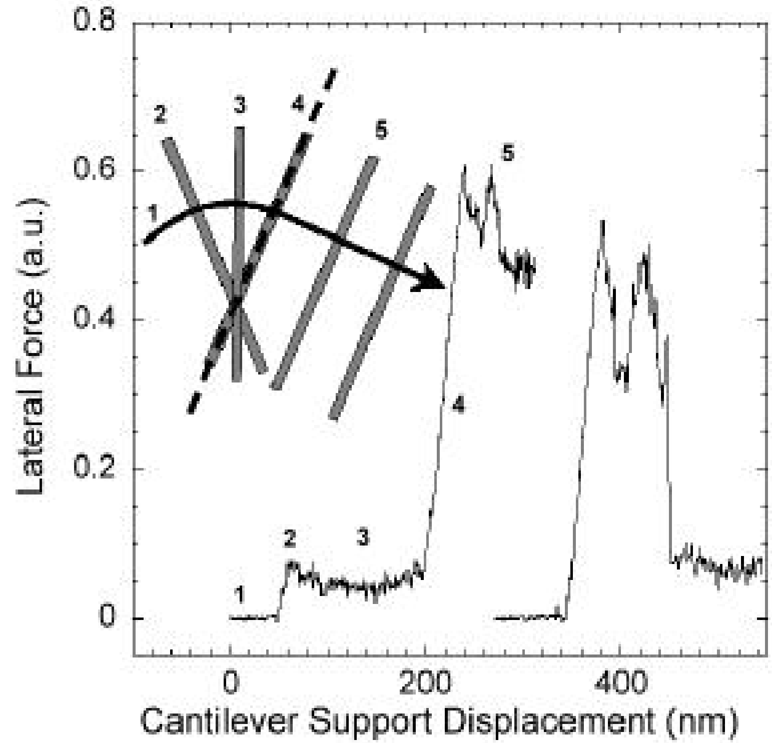



**Figure 4**. Commensurate orientations of a CNT on graphite. Left CNT- 950nm long, 20nm diameter, right CNT - 500nm long, 34nm diameter. The nanotube on the left of (a), (b), and (c) is rotated in-plane into three commensurate orientations indicated by pronounced increase in lateral force as shown in Fig. 1. In (d), the three images were overlain to emphasize the 3-fold symmetry of the commensurate orientations. Note that the nanotube was not rotated about its center as (d) implies. The images were translated in order to emphasize the 60 degree intervals. The second nanotube on the right of (a), (b), and (c) is also lying in commensurate contact. This nanotube was also rotated to reveal its set of 3-fold symmetric orientations. However its set of commensurate orientations differ by 11 degrees relative to the left hand CNT. This is due to the differing wrapping chiralities of the outer graphene sheet of the two CNTs.

**Figure 3.** Lateral force trace as a CNT is rotated into (left trace) and out of (right trace) commensurate contact. The inset shows a top-view schematic the process for the left trace. (1) The AFM tip is moving along in contact with the graphite substrate. (2) The CNT is contacted and begins rotating in-plane (3). (4) The commensurate state is reached (indicated by the dashed line) and the lateral force rises dramatically before rolling motion begins (5). The right trace begins with the tip on the substrate, the tip then contacts the CNT in the commensurate state, begins rolling and then pops out of commensurate contact and begins rotating in plane with a corresponding drop in lateral force.



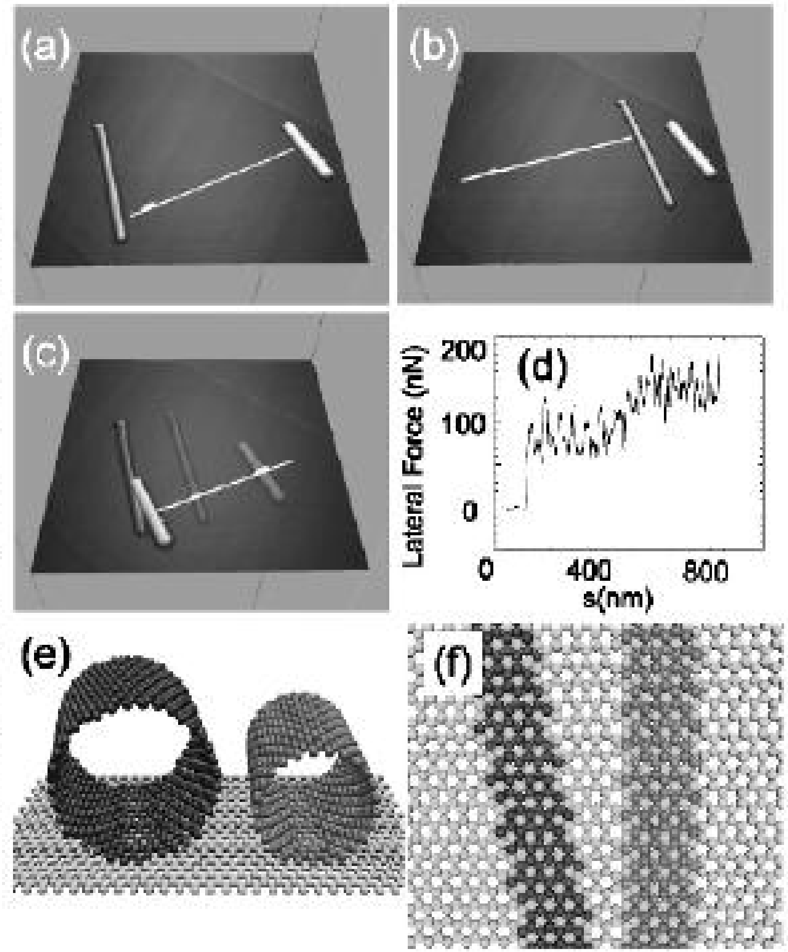



FIG. 2. Manipulation of CNT on HOPG. The threefold locking axes for the tubes are off by 11 degrees relative to each other. (a) The white streak indicates the trajectory of the AFM tip during the manipulation, from lower left toward upper right. Both CNT are pushed from lower left to upper right (a)–(b). After (b), both CNT's are individually pushed back across the same area and as (c) indicates, the shorter CNT has been pushed into contact with the longer CNT such that both tubes translate further (the fainter CNT's show the original position and the bold CNT's show the final position). Figure (d) shows the lateral force during this manipulation. (e) Model of two nanotubes resting in commensurate contact on a HOPG surface. Lying on the left is a (25, 5) CNT and on the right, a (25, 0) CNT. (f) Shows the contact zone of the commensurate lattices. The tube axes of the two CNT's are 11 degrees relative to each other when in commensurate contact. This model of the two tubes is shown to stress the point that tubes of differing chiralities will have differing orientations of the tube axis when in commensurate contact.

# Mica and atomic structure