Ústav fyzikální chemie Jaroslava Heyrovského, AVČR v.v.i.
Dolejškova 3, 182 23 Praha 8

Nanobubliny na grafenu

Odd. elektrochemických materiálů
Laboratoř mikroskopie rastrovací sondou

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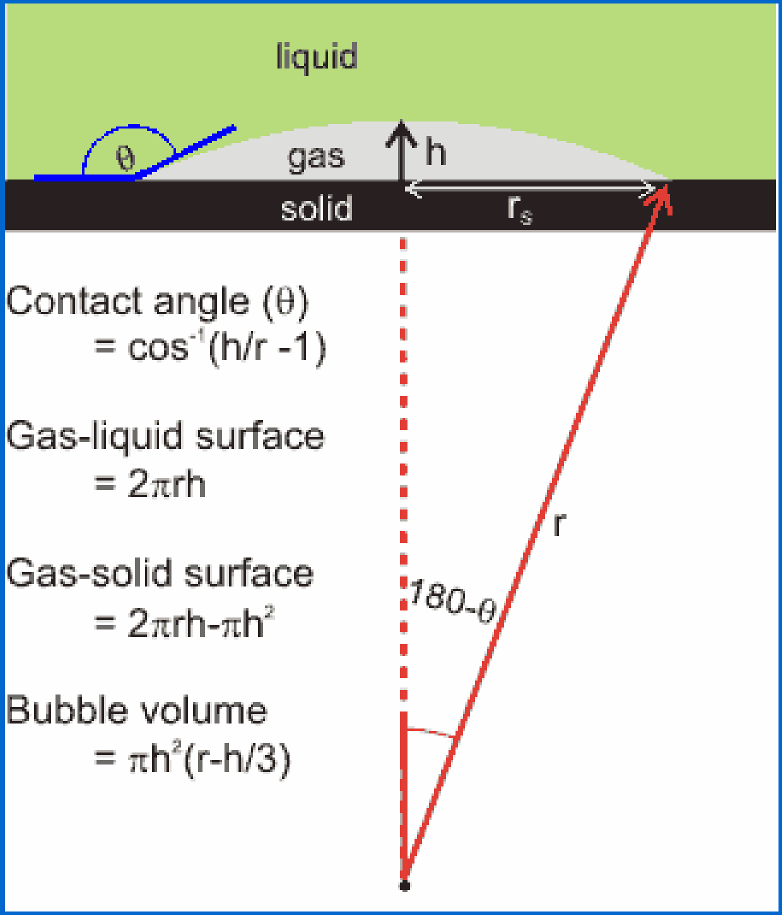
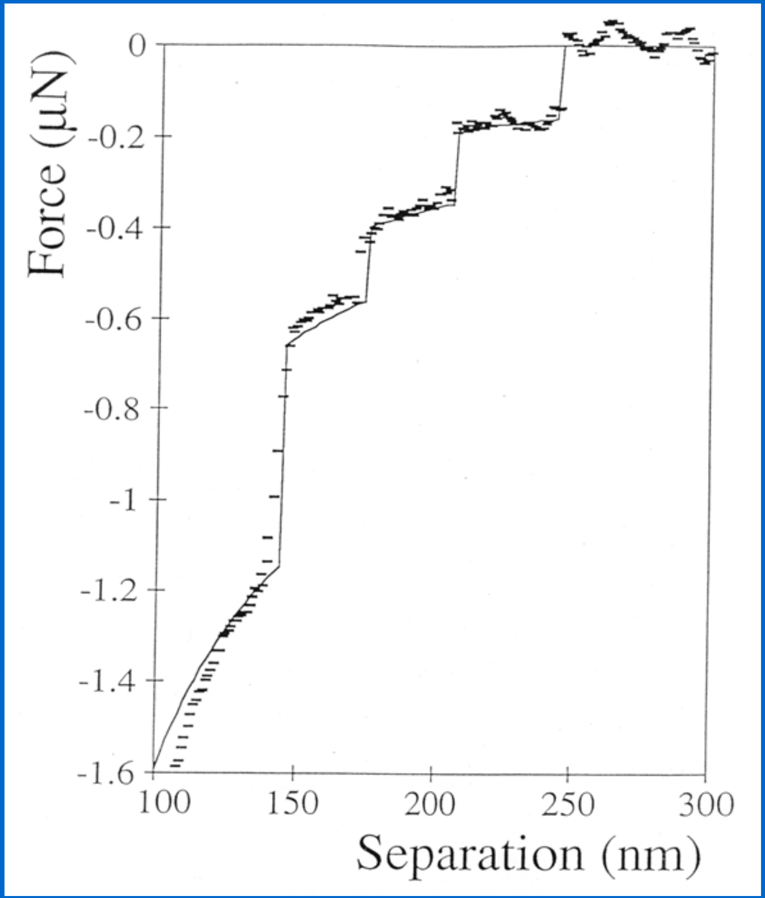
Nanobubbles

Dimensions:
***r*(curvature) = 50 nm - 6 µm,**
r_{surf} = 10 - 1000 nm
***h* = 2 - 20 nm**
Contact angle ***θ* = 135° - 175°**
>> than expected from macroscopic studies



Nanobubble history

Long range (>10^2 nm) attractive forces between macroscopic hydrophobic surfaces in water



Discontinuities in the force at separations ~10^2 nm: bridging of bubbles between surfaces (P. Attard)

J. L. Parker, P. M. Claesson, P. Attard, J. Phys. Chem. 98, 8468 (1994)

Nanobubble formation/existence

Incomplete wetting of hydrophobic surfaces

(degassing does not prevent NB formation)

A.C. Simonsen et al. Journal of Colloid and Interface Science 273 (2004) 291–299

Gas dissolved in aqueous phase forms NB on surface nanostructures

H. Xue et al, Langmuir, 2006, 22 (19), 8109-8113

EC generation

L. Zhang et al, *Langmuir*, 2006, 22 (19), 8109-8113

Charged gas/liquid interface (counterbalancing surface tension)

(charge repulsion x surface tension)<= NB self organization as colloids

N. F. Bunkin et al., *Small-angle scattering of laser radiation by stable micron particles in twice-distilled water Quantum Electron.* 35 (2005) 180-184

High density of inner NB gas

Z. LiJuan et al.: Sci China G-Phys Mech Astron (2008) 51, 219-224

Balancing outflux gas by influx at NB contact line

M. P. Brenner, Mezger et al., J. Chem. Phys. 128, 244705 (2008)

Nanobubble properties

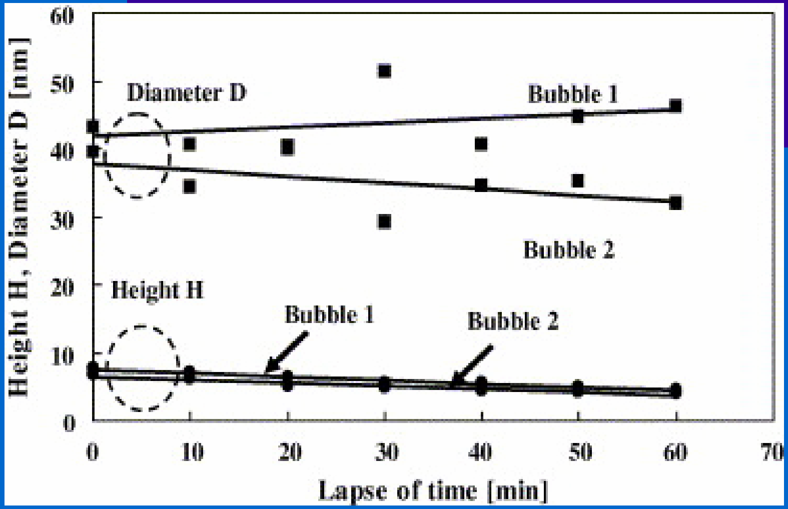
Formed on hydrophobic/hydrophilic interface
May contain highly soluble/reactive gasses: ozone, CO_2
Lifetime ~ hours/days
Rapidly reformed when disturbed
Nanoindents formed on soft hydrophobic surfaces (PS)
NB length ~ mean-free-path of gas molecules inside the bubble.
(=> validity?? Young-Laplace eq. for Δp)

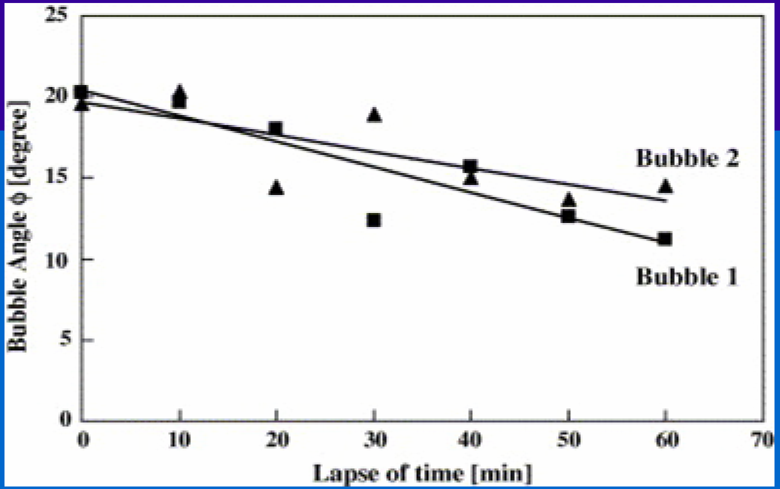
Young-Laplace (nm-scale validity?)
$\Delta p = 2\gamma / r_s$

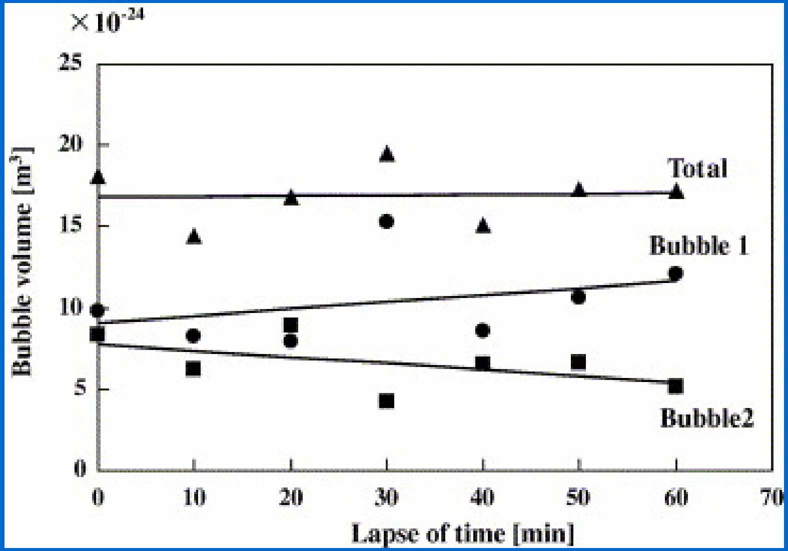
r_s ...NB radius
γ...surface tension
Δp... inside-outside pressure difference
=> high internal pressure => **dissolution**

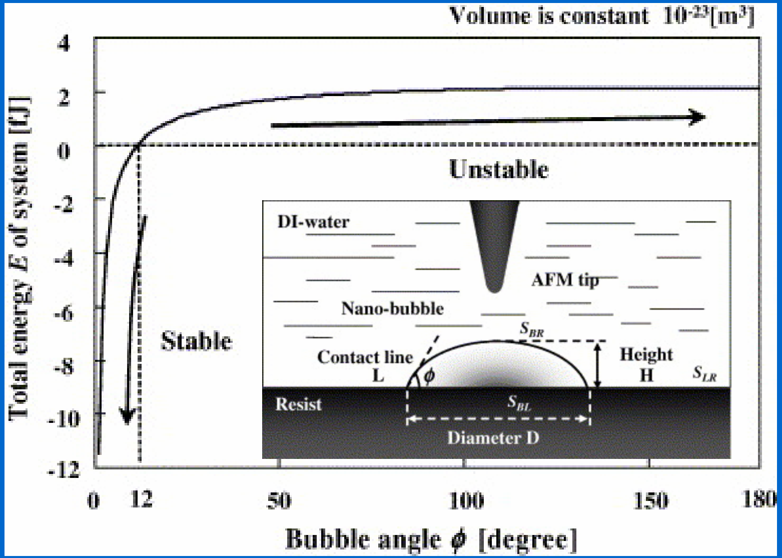
Contact angle
θ_{NB} (liq) >> θ_{MB}
for V = const $r_{NB} > r_{MB}$

Nanobubble properties



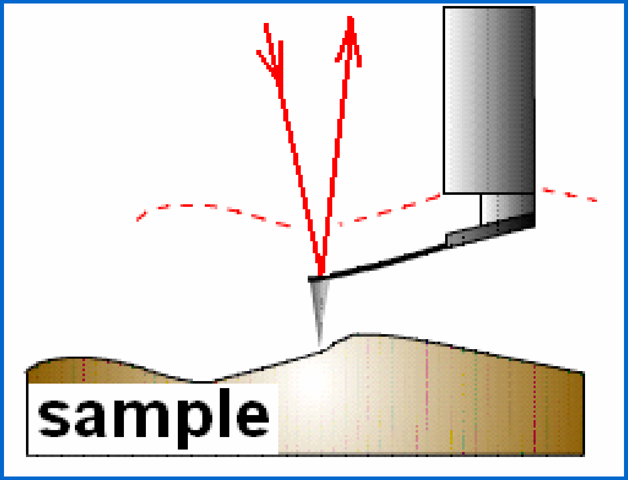


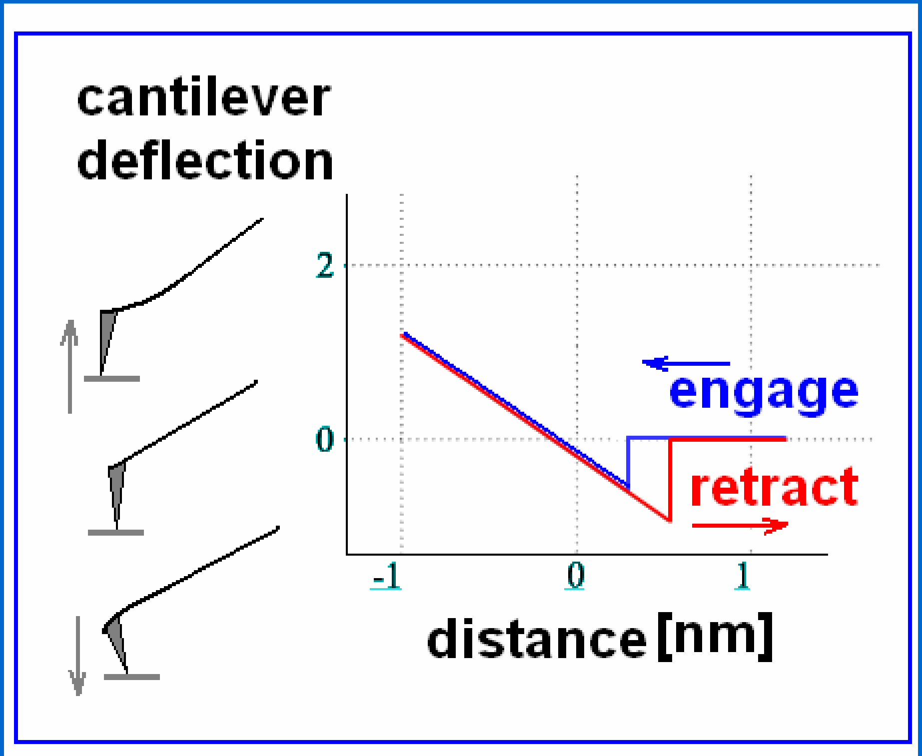




Akira Kawai, Kenta Suzuki: ***Removal mechanism of nano-bubble with AFM for immersion lithography*****,** **Microelectronic Engineering 83 (2006), 655-658**

Nanobubble imaging: AFM contact mode

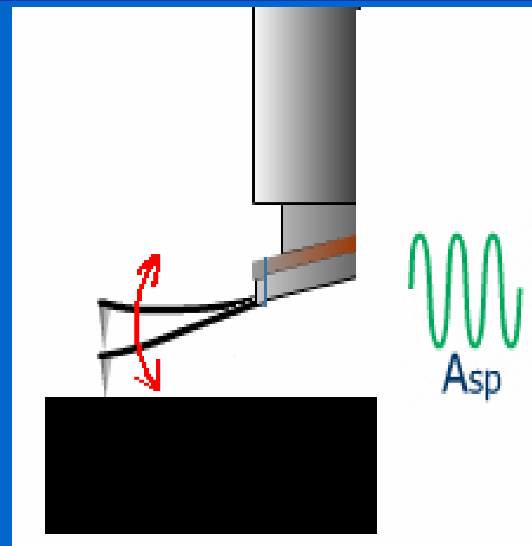


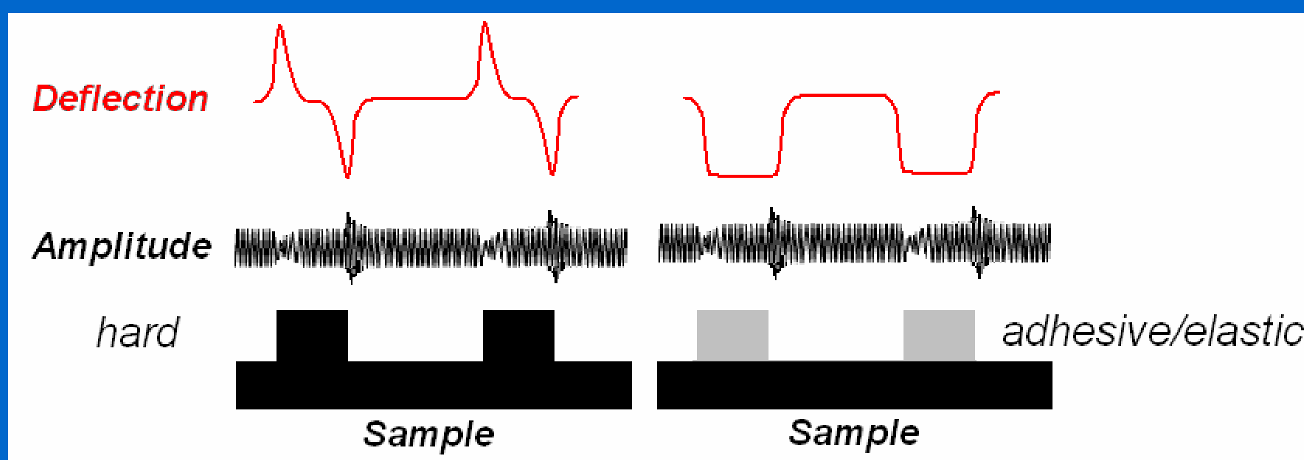


Hooke: $F = -k\,x$

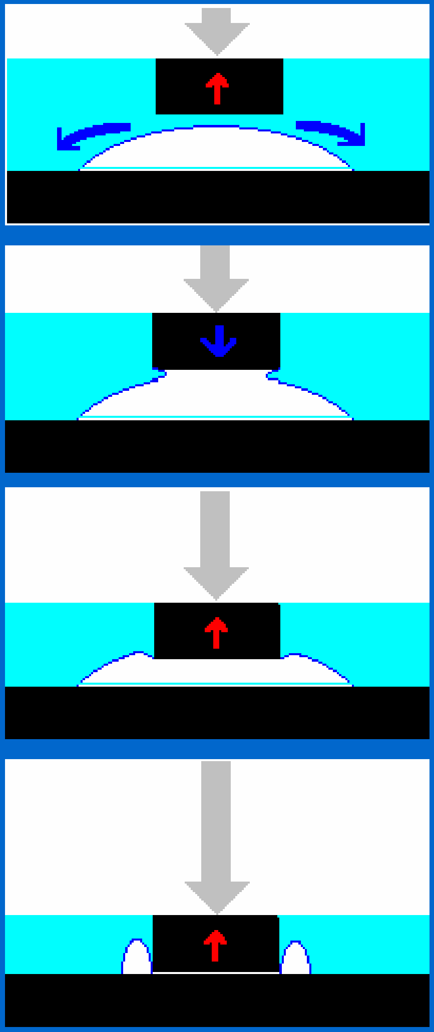
k…spring const. 0.01-1 N/m

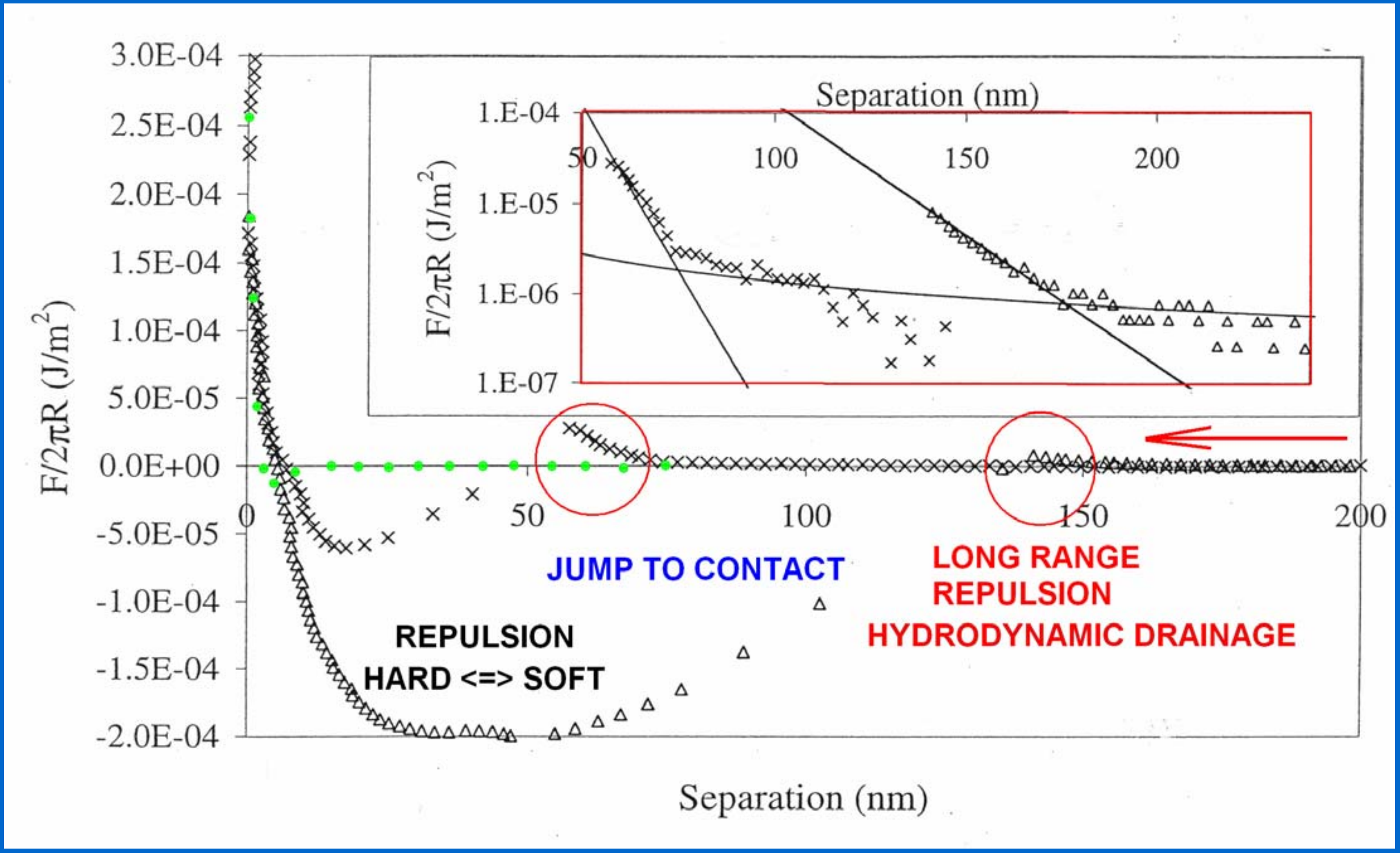
Nanobubble imaging: AFM semicontact mode (tapping)





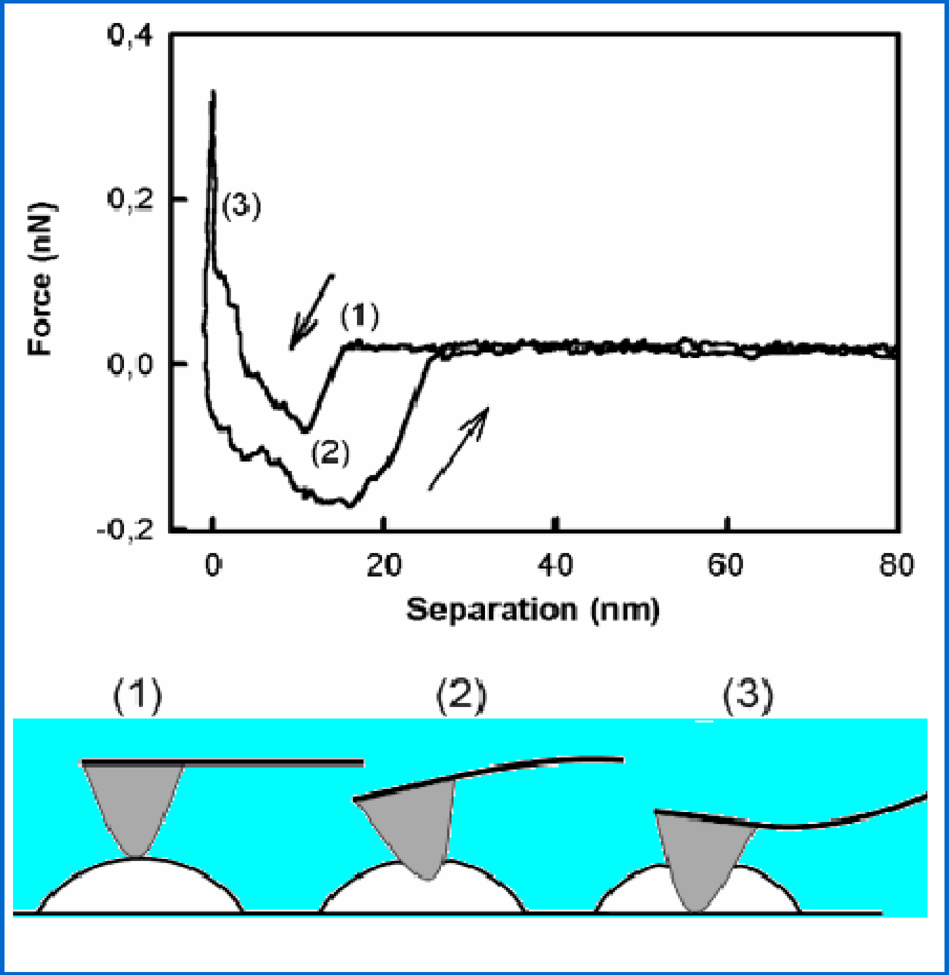
Nanobubble imaging: AFM force curve





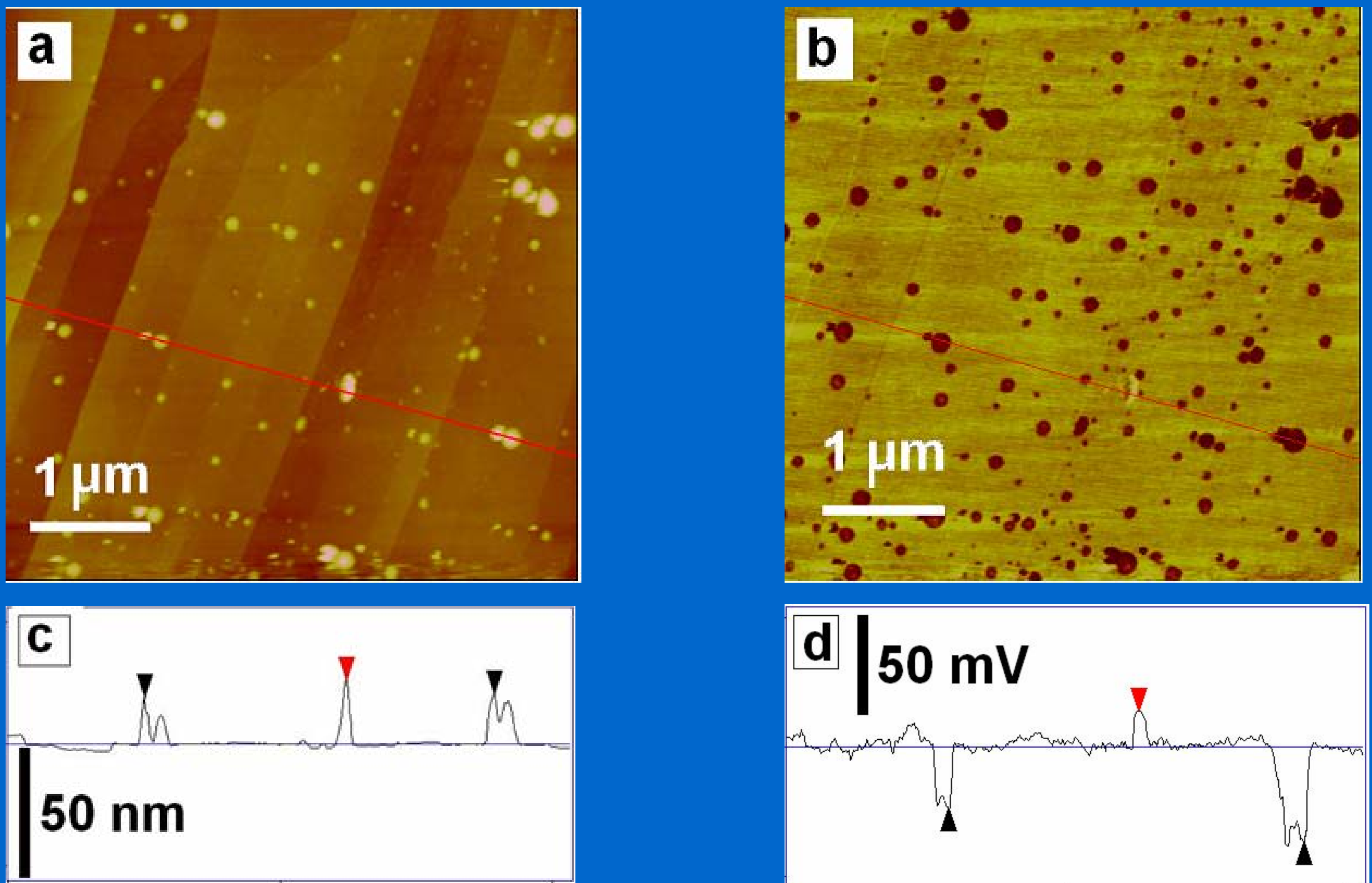
A. Carambassis, L. C. Jonker, P. Attard, and M. W. Rutland, Phys. Rev. Lett. 80, 5357-5360 (1998)

Nanobubble AFM imaging: Narrow parameter range

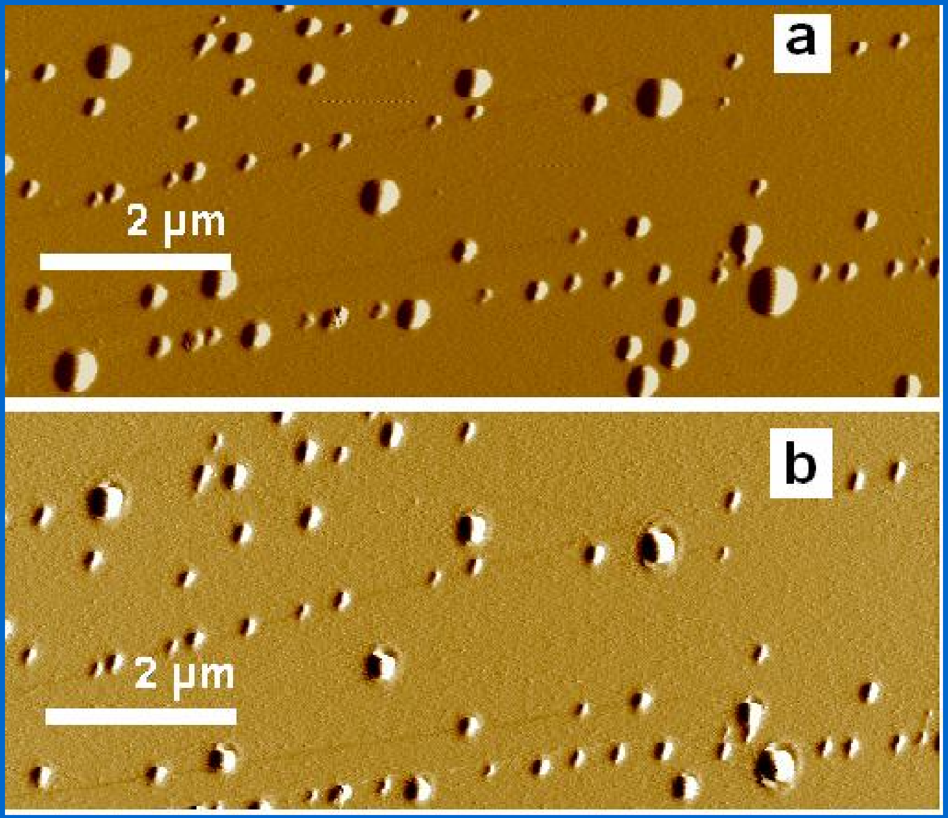


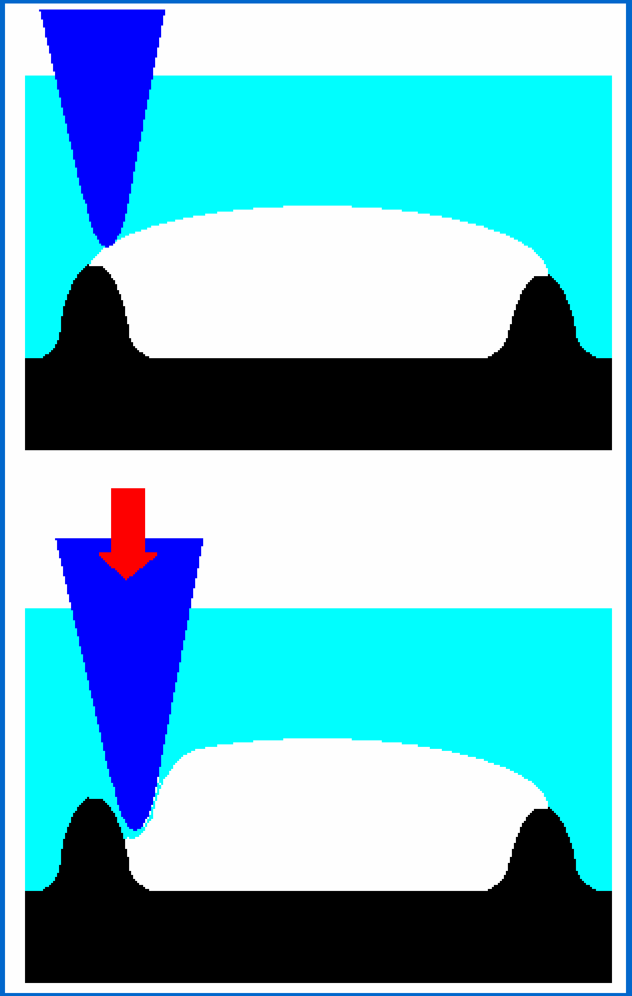
Holmberg et al.: *Langmuir,* Vol. 19, No. 25, 2003

Nanobubble imaging: AFM tapping/deflection



Nanobubbles on HOPG, compression: graphene erosion

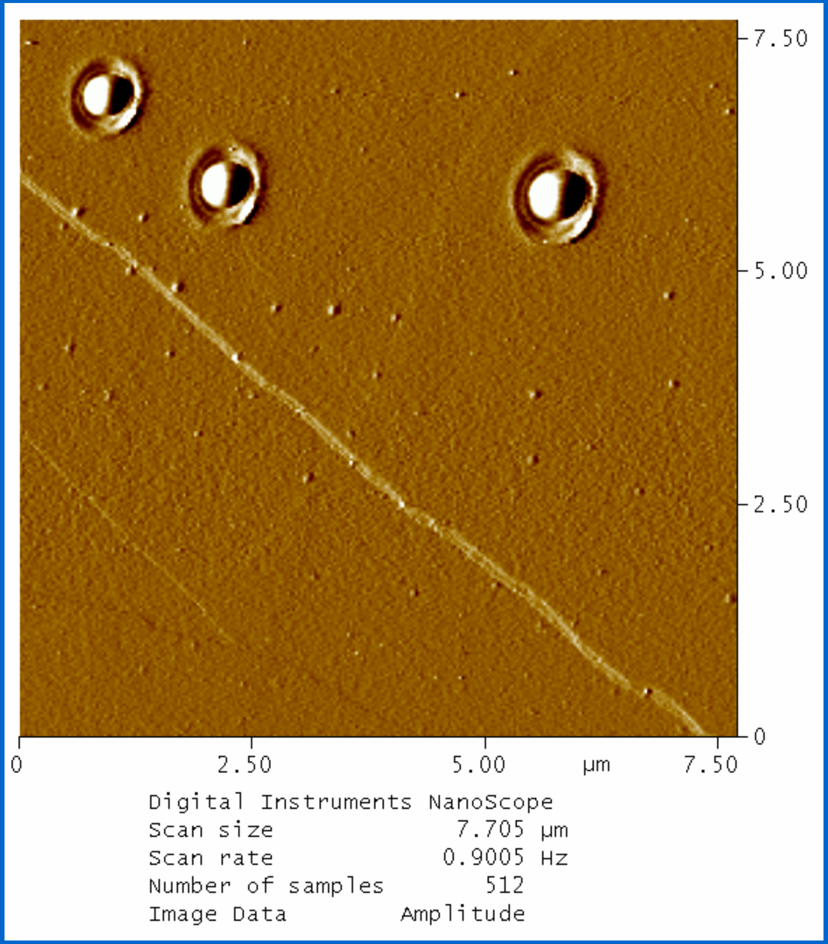


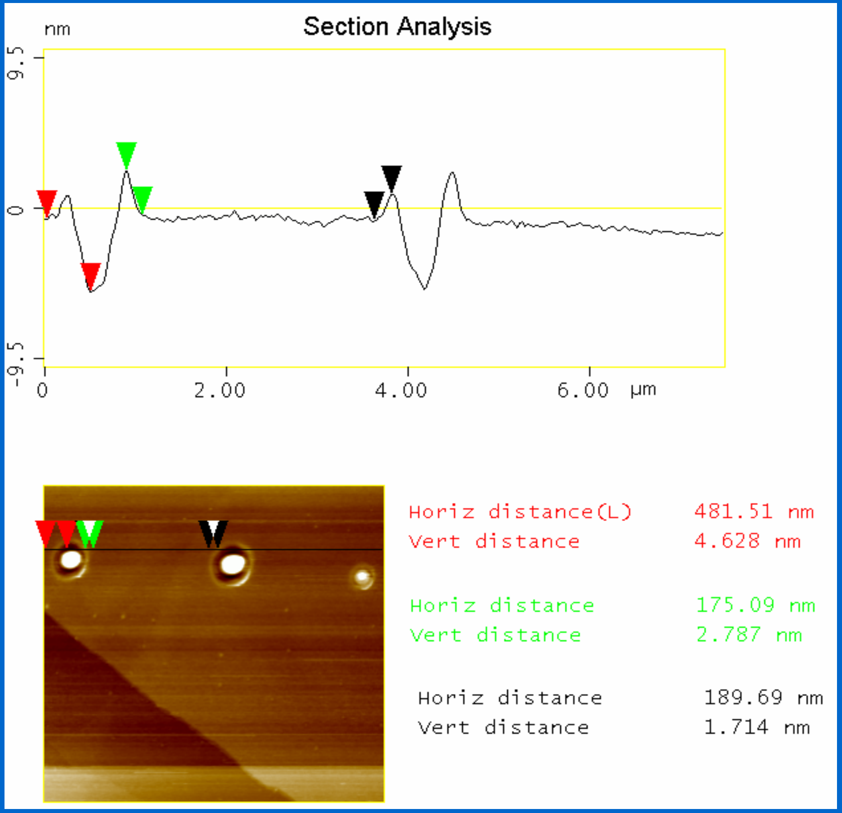


P. Janda, O. Frank, Z. Bast, M. Klementová, H. Tarábková, L. Kavan,
Nanotechnology 21 (2010) 095707

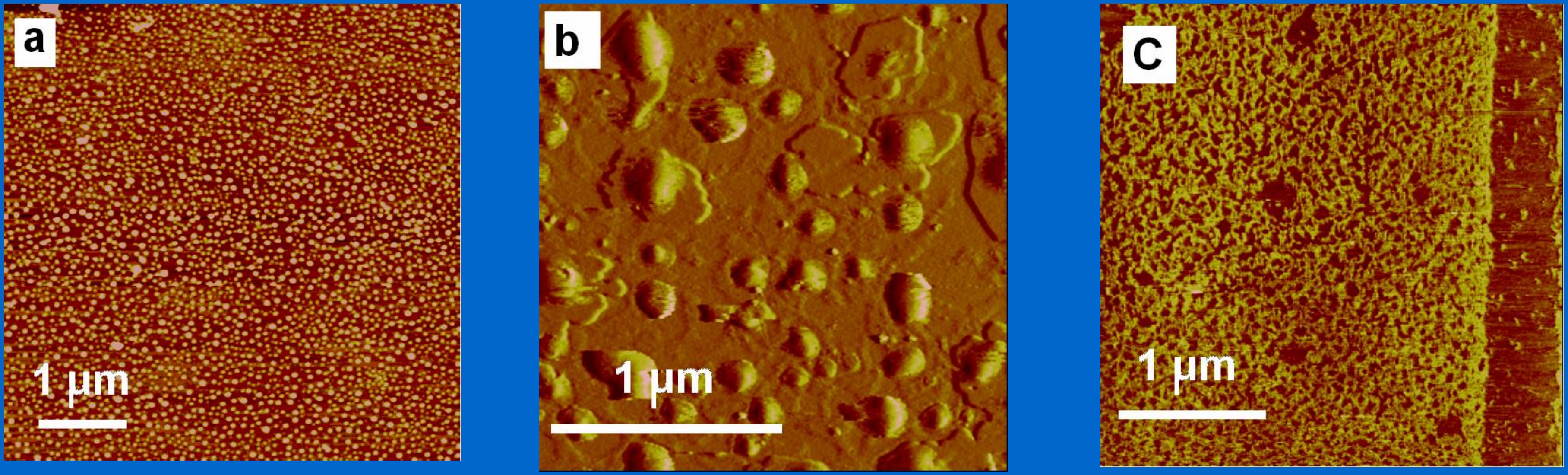
Nanobubble-assisted HOPG basal plane erosion

in situ AFM imaging



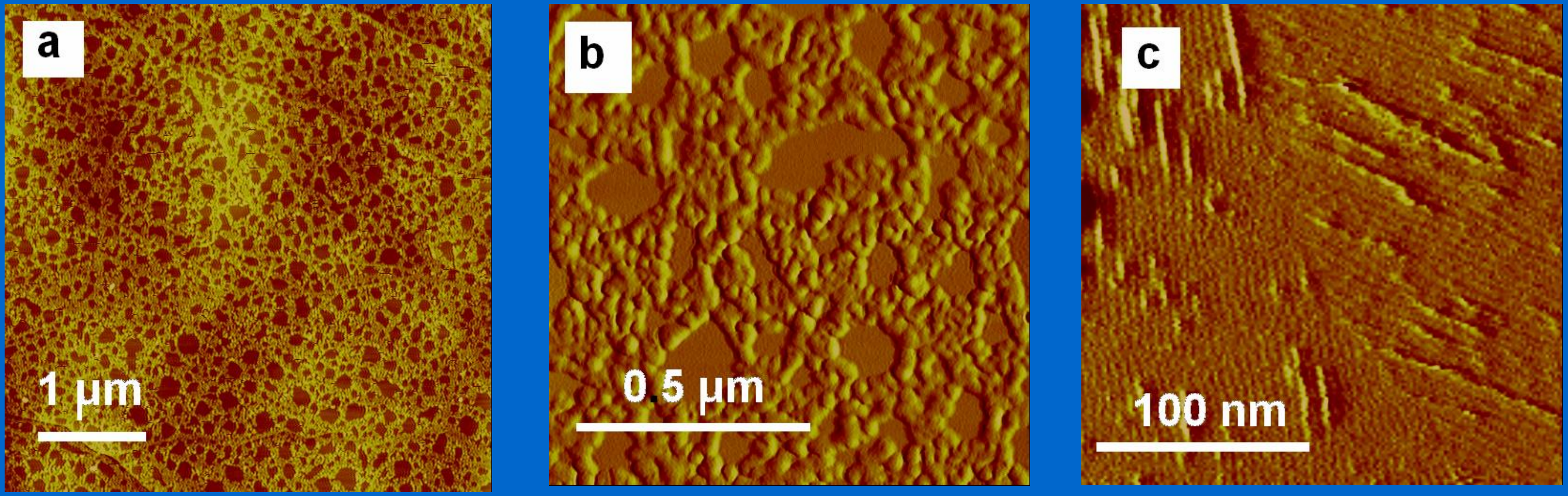


HOPG basal plane erosion in water: *in situ* AFM



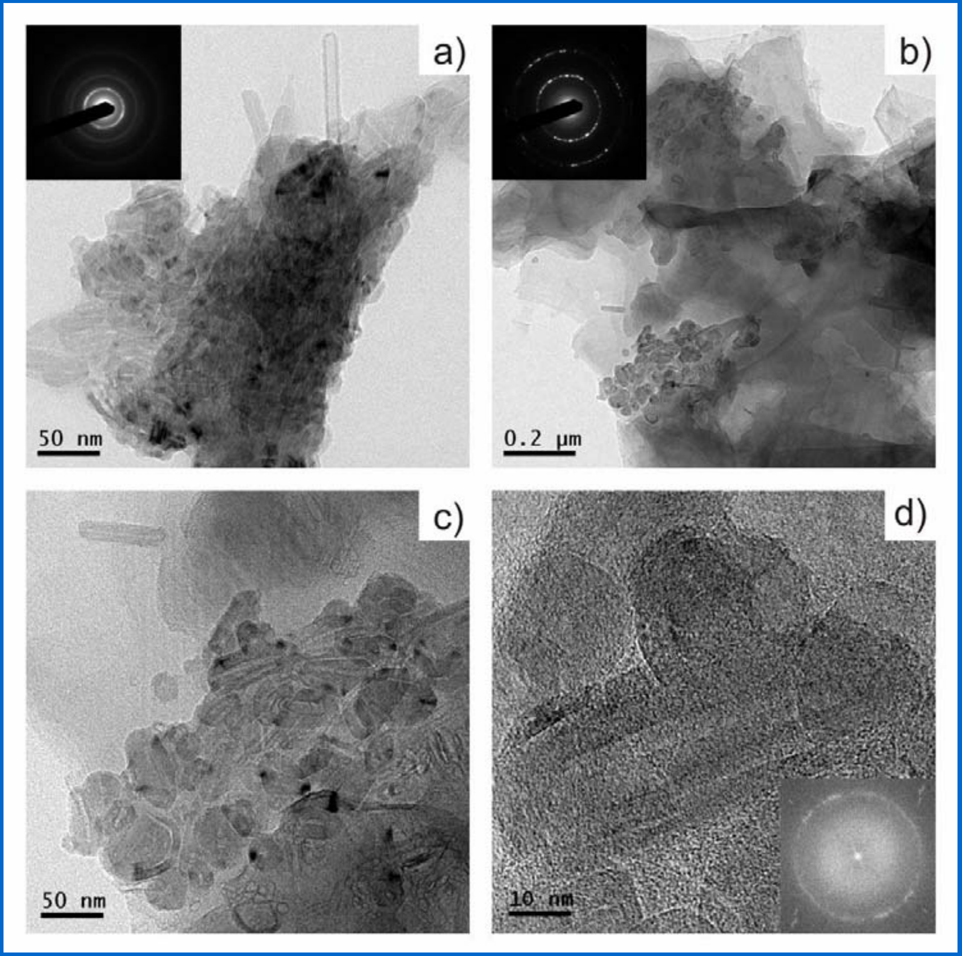
P. Janda, O. Frank, Z. Bast, M. Klementová, H. Tarábková, L. Kavan, *Nanotechnology* 21 (2010) 095707

HOPG basal plane erosion: *ex situ* AFM



P. Janda, O. Frank, Z. Bast, M. Klementová, H. Tarábková, L. Kavan, *Nanotechnology* 21 (2010) 095707

HR TEM

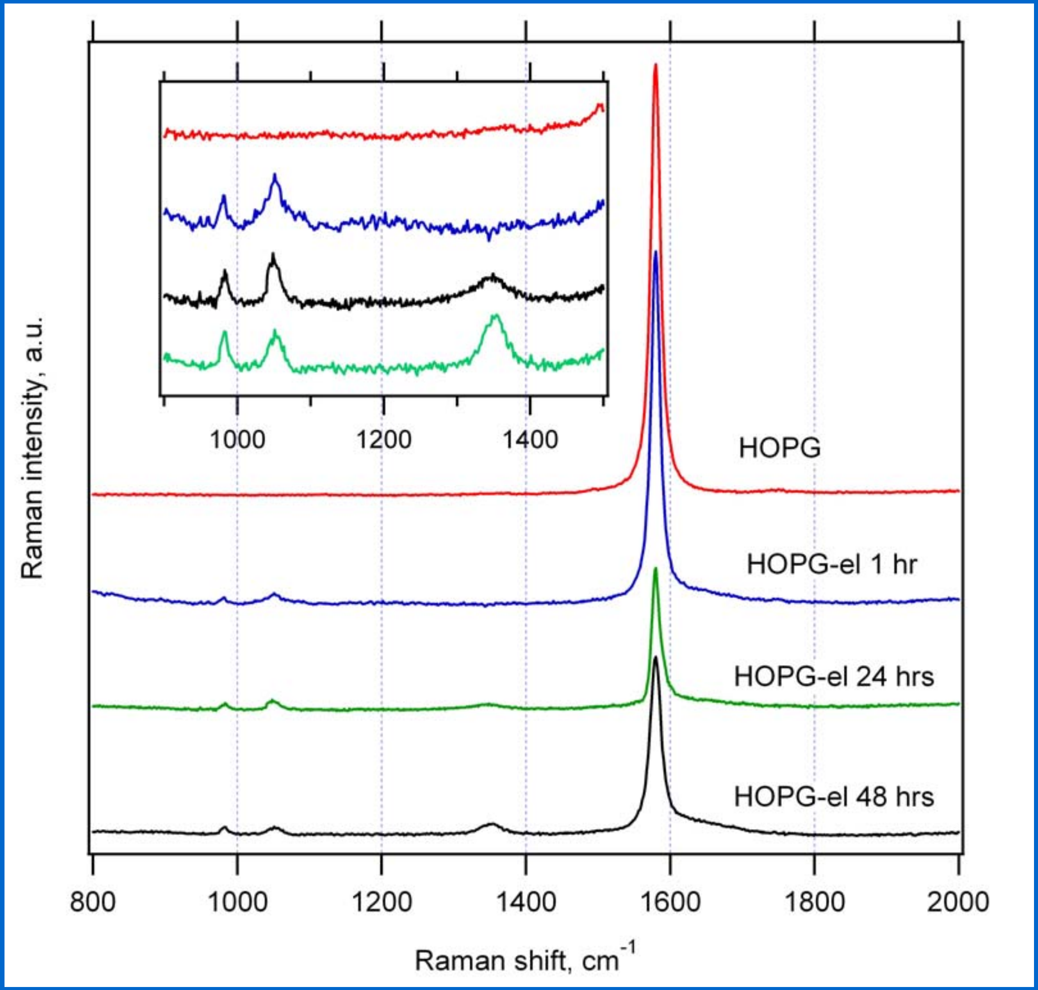


SAED (e-diffraction) patterns ⇔ CNT-like interlayer spacing

P. Janda, O. Frank, Z. Bast, M. Klementová, H. Tarábková, L. Kavan,
***Nanotechnology* 21 (2010) 095707**

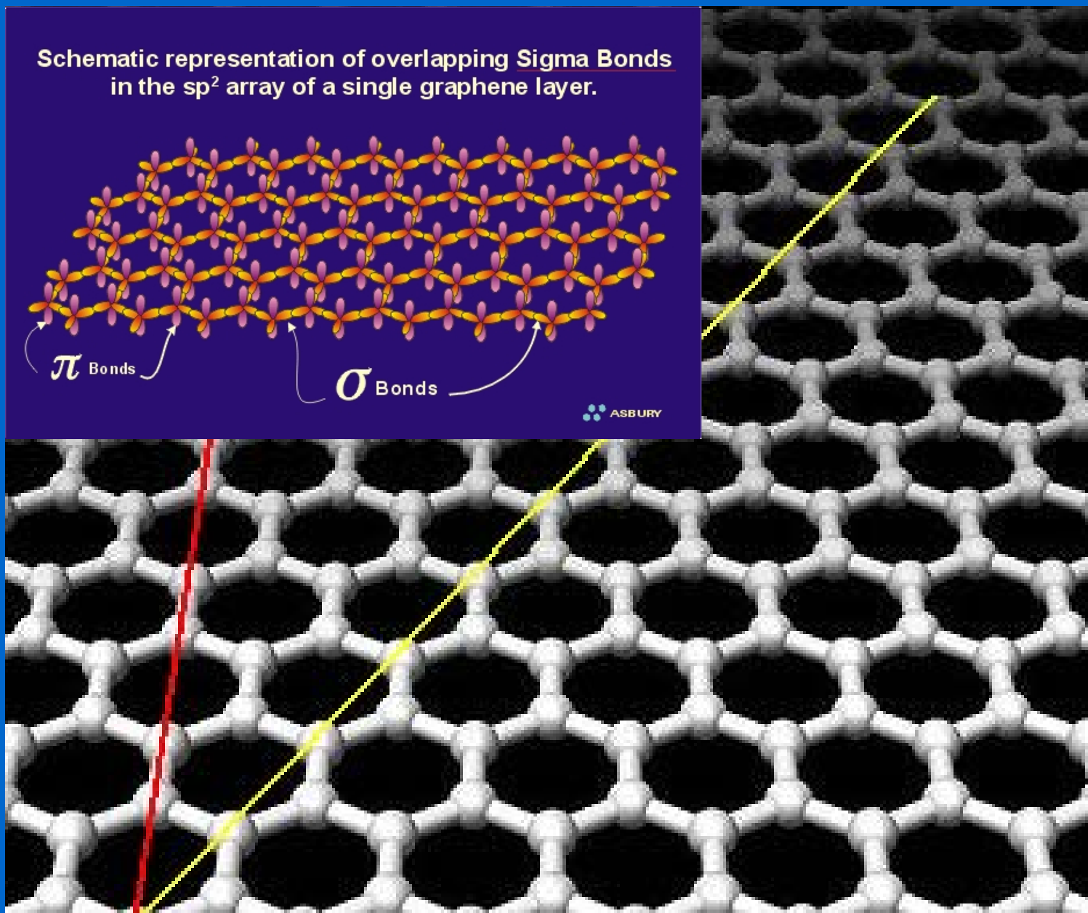
Raman spectroscopy *in situ*

HOPG basal plane
exposed to water
for 0 – 48 h
(defect D-band, G-band)

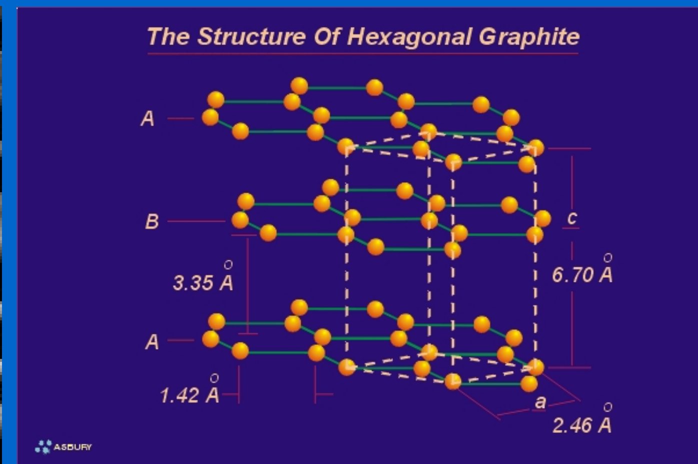


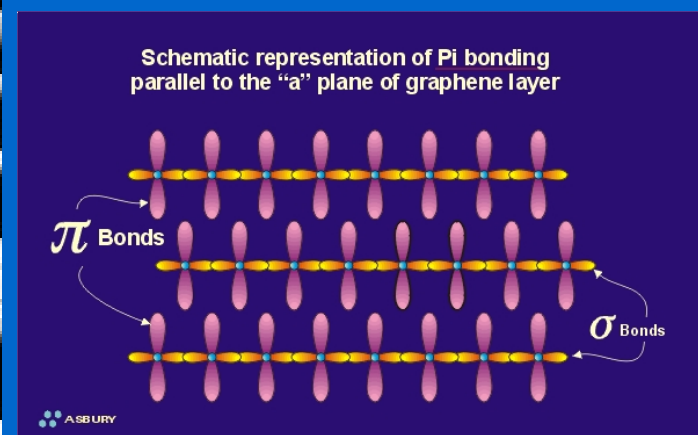
P. Janda, O. Frank, Z. Bast, M. Klementová, H. Tarábková, L. Kavan, ***Nanotechnology*** **21 (2010) 095707**

Graphene - the strongest 2D network structure known



zig-zag armchair





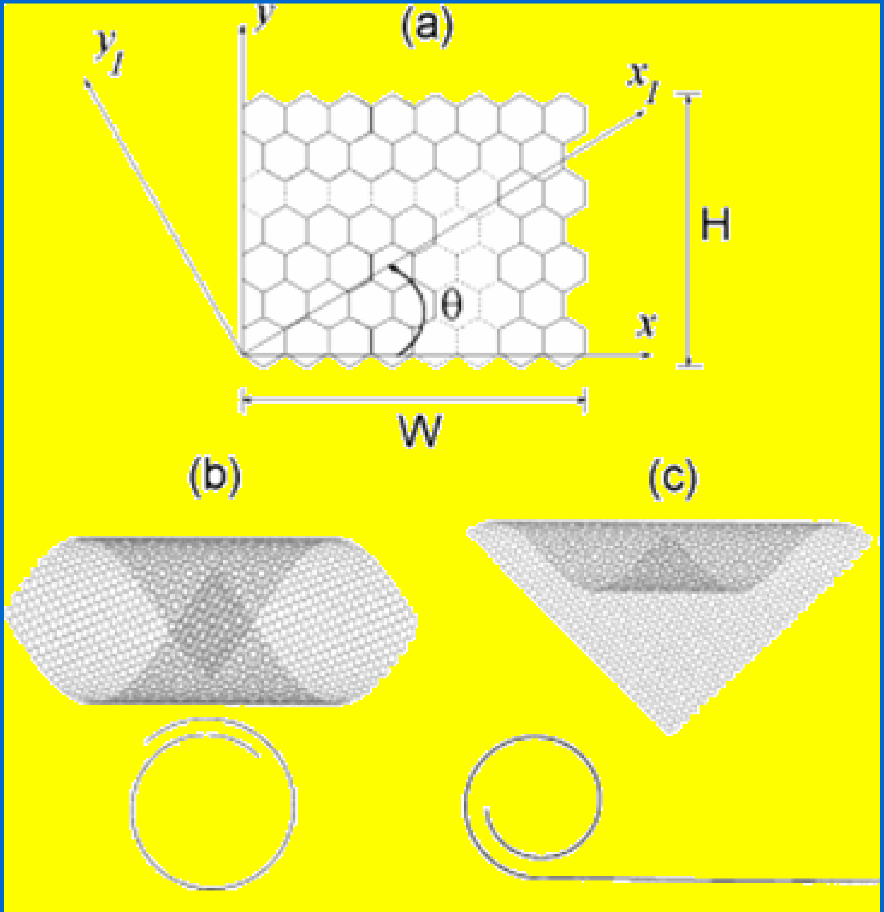
Young´s modulus (1-layer graphene defect free) ~ 1 TPa

Intrinsic strength $\sigma_{graphite}$ ~ 130 GPa

graphene rolling

self-sustained curling after a critical overlap area is reached

CNS $^{min}d_{in}$ ~ 2 nm
(conical ⇔ metastable)
- initial sheet dimension
-orientation vs. rolling axis
-$\tau_{rolling}$ ~ psec



Scheila F. Braga, Vitor R. Coluci, Sergio B. Legoas, Ronaldo Giro, Douglas S. Galva˜o and Ray H. Baughman: Structure and Dynamics of Carbon Nanoscrolls, Nano Letters (2004), Vol. 4, No. 5, 881-884

graphene rolling

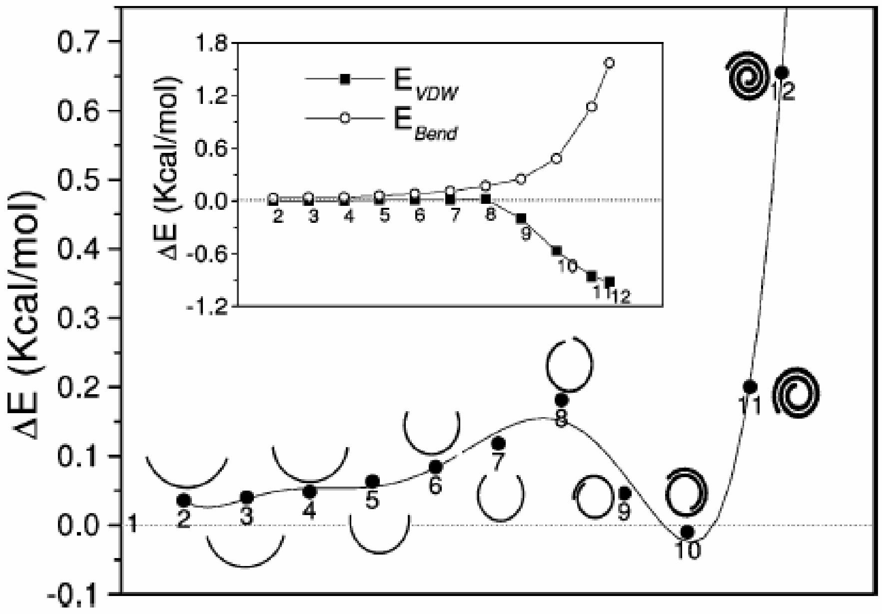
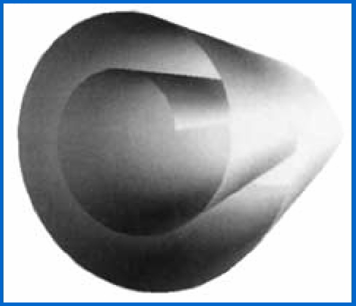
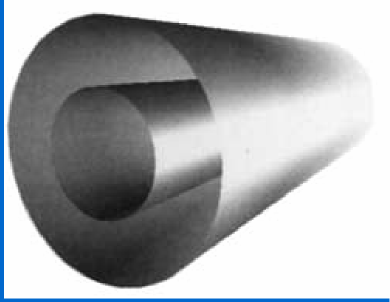


Figure 2. Change in total energy (relative to an undistorted graphene sheet) during the wrapping of a single graphite sheet to make a CNS. The torsion plus inversion (E_{Bend}) and van der Waals energies (E_{vdW}) are shown in the inset graph.

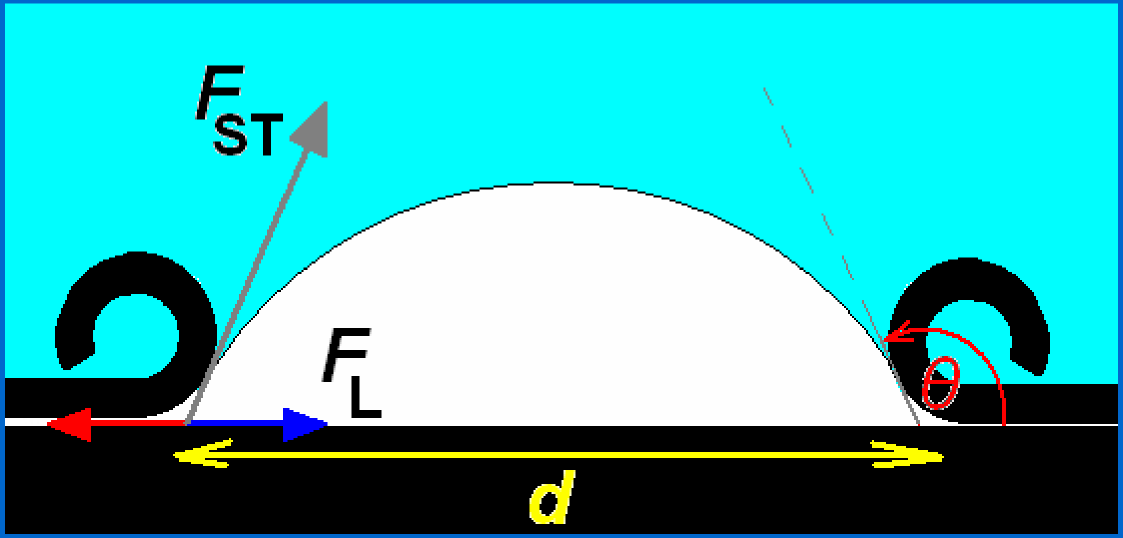




CNS precursor for MWCNT?

Scheila F. Braga, Vitor R. Coluci, Sergio B. Legoas, Ronaldo Giro, Douglas S. Galva˜o and Ray H. Baughman: Structure and Dynamics of Carbon Nanoscrolls, Nano Letters (2004), Vol. 4, No. 5, 881-884

Nanobubble-triggered (multi)layer graphene tearing/rolling



NB-perimeter induced tensile stress* $\boldsymbol{\sigma = F_L/\pi d_{NB} h_{layer}}$ ~ **10^1 MPa** (h = 3 nm)

****Young´s modulus** (1-layer graphene defect free) ~ **1 TPa**

**** Intrinsic strength $\sigma_{graphite}$ ~ 130 GPa**

***Y. Wang *et al:* Nanotechnology 20 (2009) 045301**
****J. Hone *et al*: *Science* 321 (2008) , 385**

Fields affected by nanobubbles

* Liquid Immersion Lithography using water as fluid
* Light Scattering
* Adsorption and wetting properties (surface blocking)
* Electrode blocking (electrolytic processes)
* Defects/Surface rearrangement: Erosion of hydrophobic surfaces in water
* Nanoparticle/nanobubble mismatch (AFM *in situ*)
* Increased friction forces between hydrophobic surfaces in water (increased adhesion)

Fields affected by nanobubbles

* Facilitation of liquid flow in hydrophobic capillaries – lowered hydrodynamic drag (liquid transport in pipes, water transport, medicine)
* Fast folding of proteins and assembly
* Drug delivery vesicle (nanomedicine)
* Long lasting disinfection vesicle (*ozone 2 mgL^{-1}: mB: =>0.1 mgL^{-1}/h, nB: >1$mgL^{-1}/10^3h$)
* Nanoparticle/colloid-nanobubble interaction (flotation processes)
* Challenges for established notions of macroscopic thermodynamics

*K. Chiba, M. Takahashi, University of Manchester

Hydrophobic surfaces are more like a fluid than a solid interface due to their covering by nanobubbles, - consequently they exhibit much less hydrodynamic drag. The flow in narrow hydrophobic capillaries greater than predicted (by stick boundary conditions) can now be explained as due to a covering of the nanobubbles.

Phil Attard

Acknowledgements

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Czech Ministry of Education,Youth and Sports (LC-510)
AS CR (IAA 400400804, KAN 200100801)