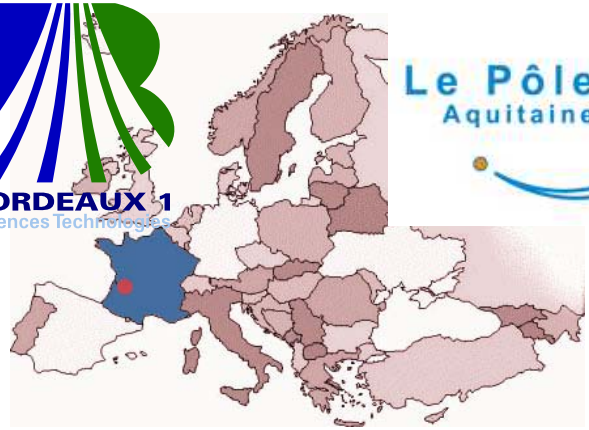


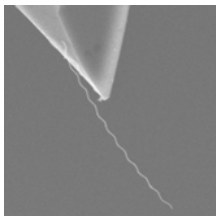
Carbon Nanotube NanoNeedle Nanomeniscus

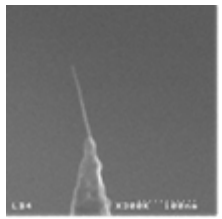
Jean-Pierre Aimé
jp.aime@cpmoh.u-bordeaux1.fr

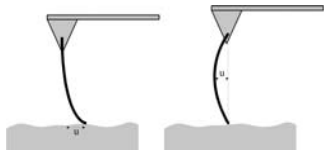
Frontier in Scanning Probe Microscopy
PURDUE October 2006

I- Carbon Nanotubes as AFM probes: competition between adhesion and elasticity
C. Bernard et al

Carbon Nanotube: C.V. Nguyen (NASA), A. M. Bonnot (LEPES)

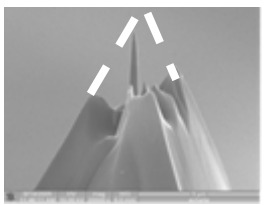


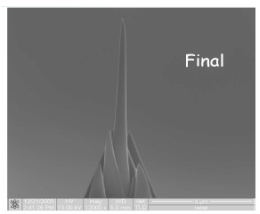


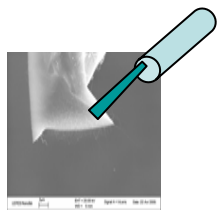


II- Oscillating NanoNeedle at Air liquid Interface: Dynamical behavior of NanoMeniscus
C. Jai et al

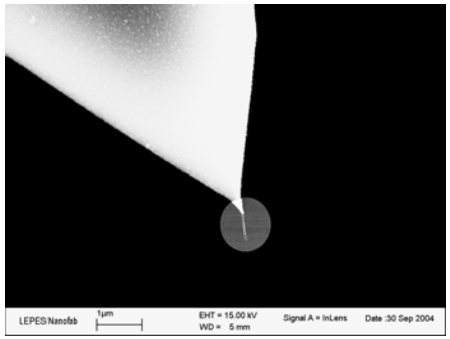
Nano-Needle / FIB: D. Mariolle, F. Bertin, A. Chabli LETI-Minatec

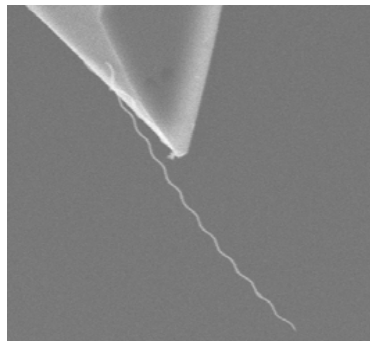


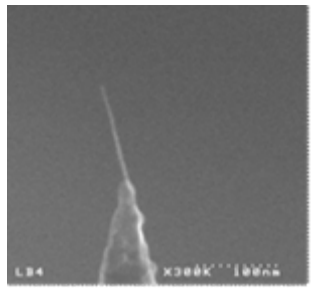




CNT Possible Tip-Sample Interactions

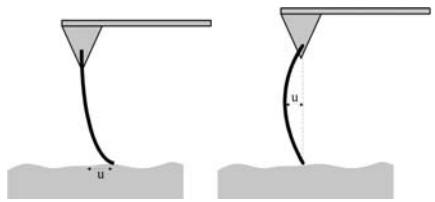






Interaction

- **Attractive interaction: van der Waals**
- **Repulsive interaction: (compression) / bending**
- **Boundary conditions : sticked (clamped) / non sticked (sliding)**

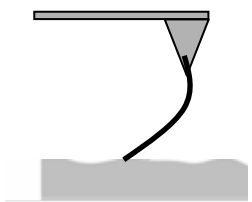


Geometry effects:

- $k_{bending}$ $k \sim r^4 L^{-3}$
- $k_{compression} \sim 10^3 k_{bending}$

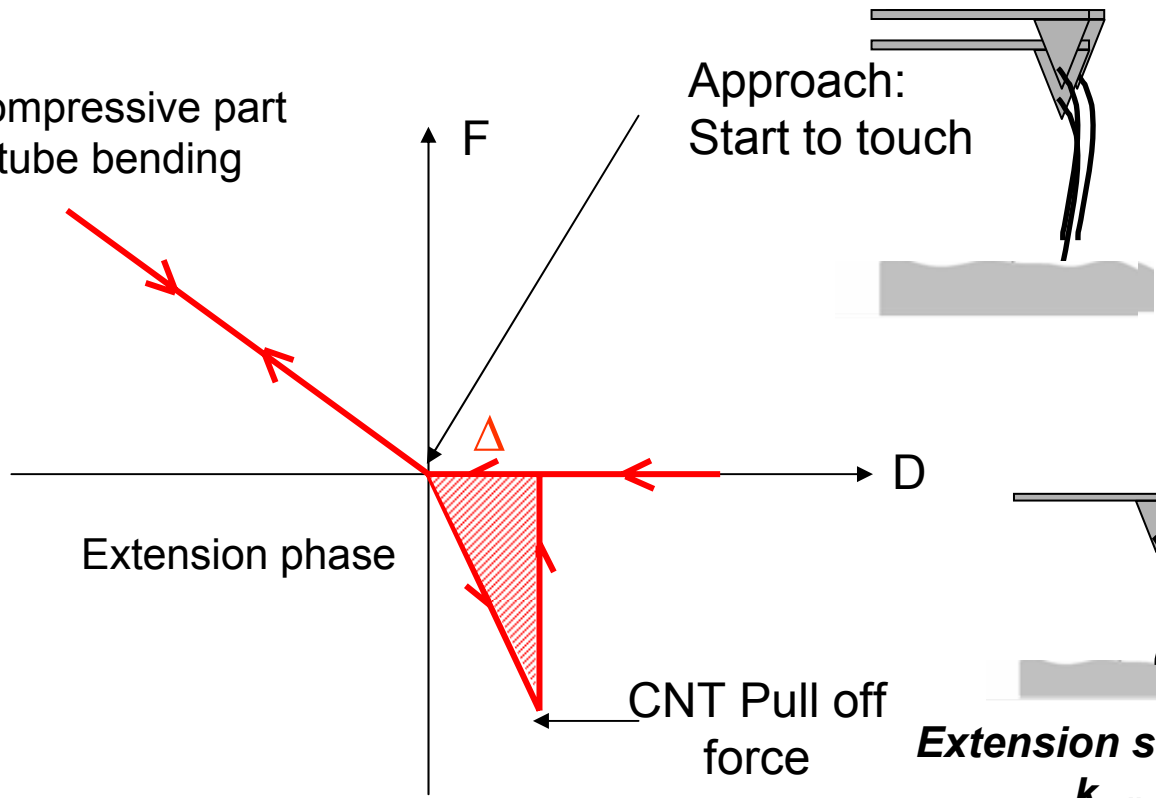
D. Dietzel, et al *Physical Review B* 72, 035445 (2005), *Nanotechnology* (2005) 16, p.S73-S78, *JSPM* (2006)

Nanotube mechanical cycle



Elastic bending

$$k_{NT} \approx E\pi r^4 / L^3$$

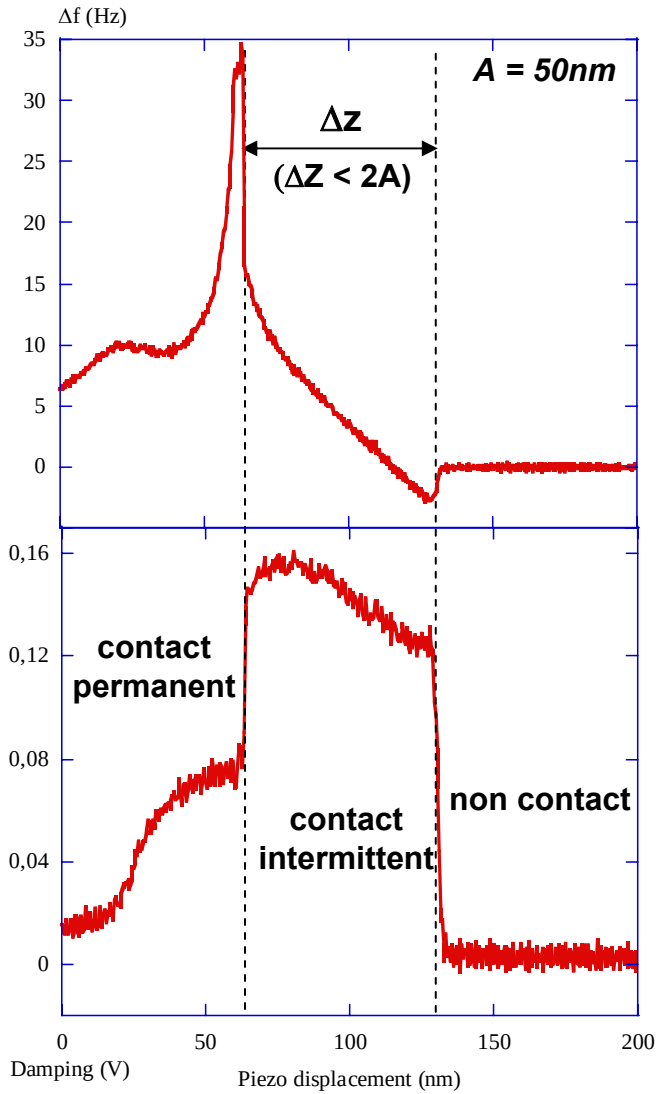


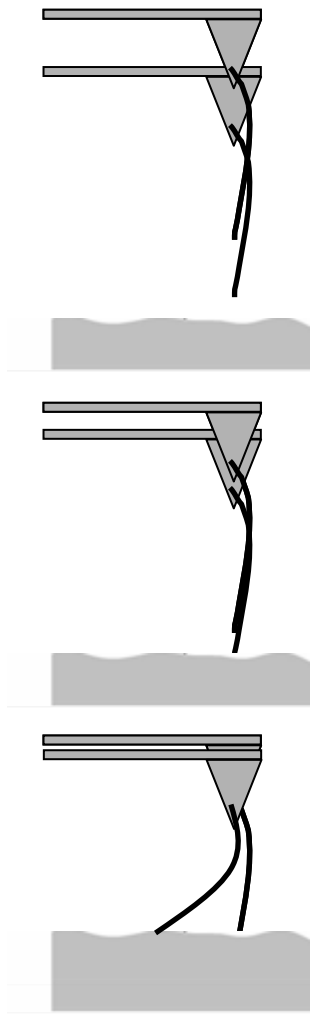
Extension stiffness
k_{adh}

Cycle area: $\langle E_{diss} \rangle_T \approx \frac{1}{2} k_{adh} \Delta^2 = cste$

U. Dürig, New J. of Physics **2** , 5.1 (2000).

SWNT's FM AFM frequency and damping curves



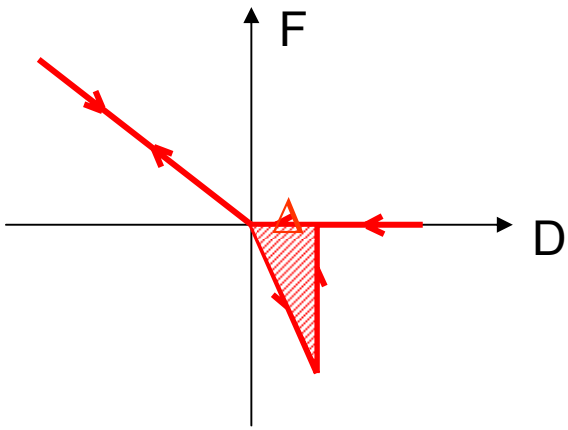


1. Non contact

2. Intermittent Contact

3. Permanent Contact

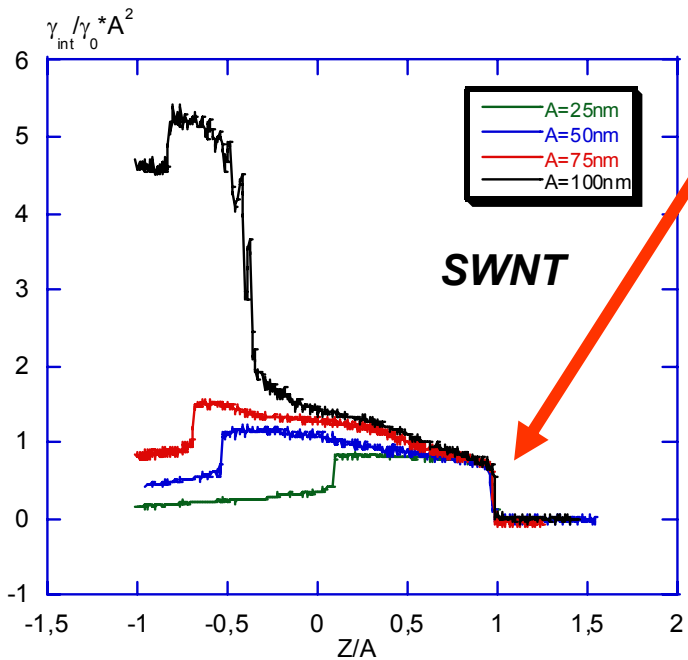
Nanotube mechanical cycle

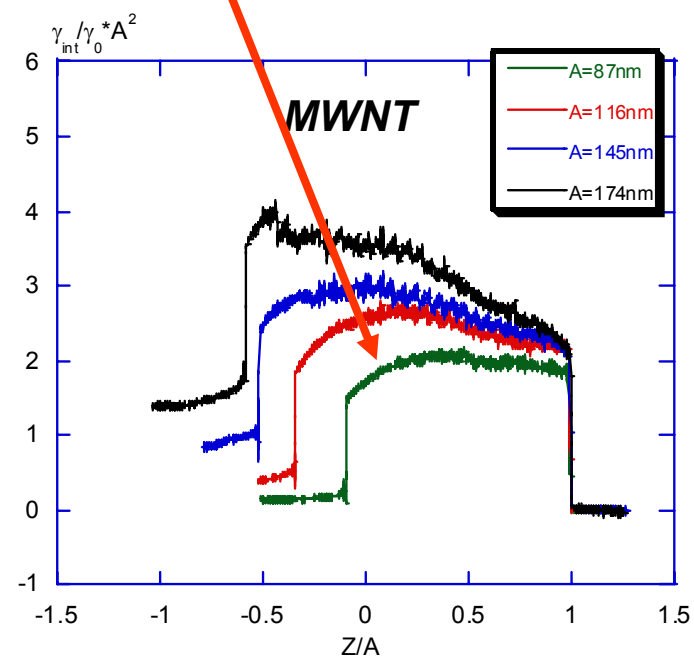


Adhesion force gives constant area

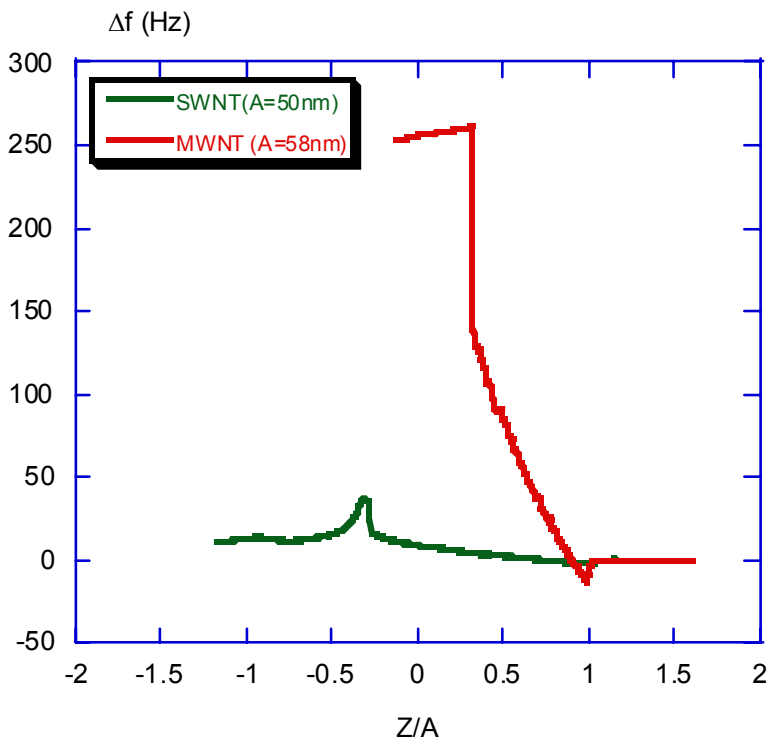
$$\langle E_{diss}^{\text{int}} \rangle_T \approx \frac{1}{2} k_{adh} \Delta^2 = cste$$

$$\langle E_{diss}^{\text{int}} \rangle_T = \pi \gamma_{\text{int}} \omega A^2$$





SWNT vs MWNT



Δf

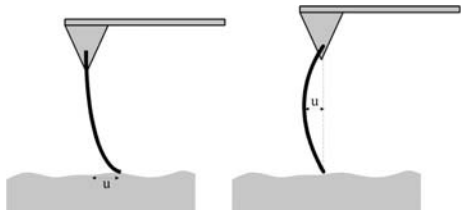
MWNT : typ. **200 Hz**

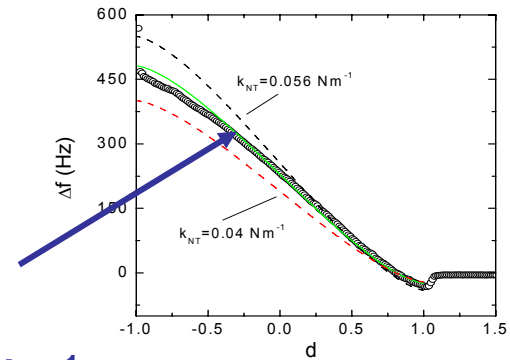
SWNT : typ. **20 Hz**

Elastic contribution

$$\frac{\left(\omega^2-\omega_0^2\right)}{\omega_0^2}=\frac{k_{NT}}{\pi k_c}\left(d\sqrt{1-d^2}-\cos^{-1}(d)\right)$$

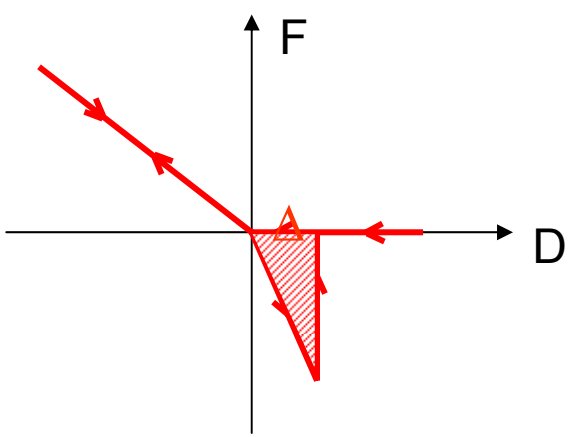
d=Z/A





k_{NT} = 0.048 Nm^{-1}

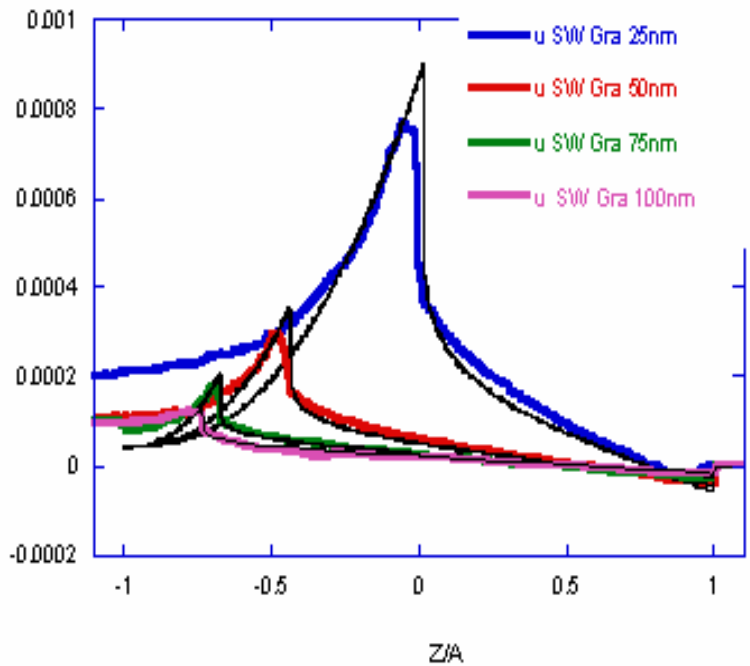
Adhesion Contribution



$$\frac{\Delta\omega}{\omega_0}=-\frac{1}{k_cT}\left[\int_{\tau_{res}}^{\tau_{res}+\tau_\Delta} k_{adh}\left(\frac{z}{A}-\cos(\omega t)\right)\cos(\omega t)dt\right]$$

. D. Dietzel, et al *Physical Review B* 72, 035445 (2005), C. Bernard et al (submitted)

Single Wall NT Mechanical properties

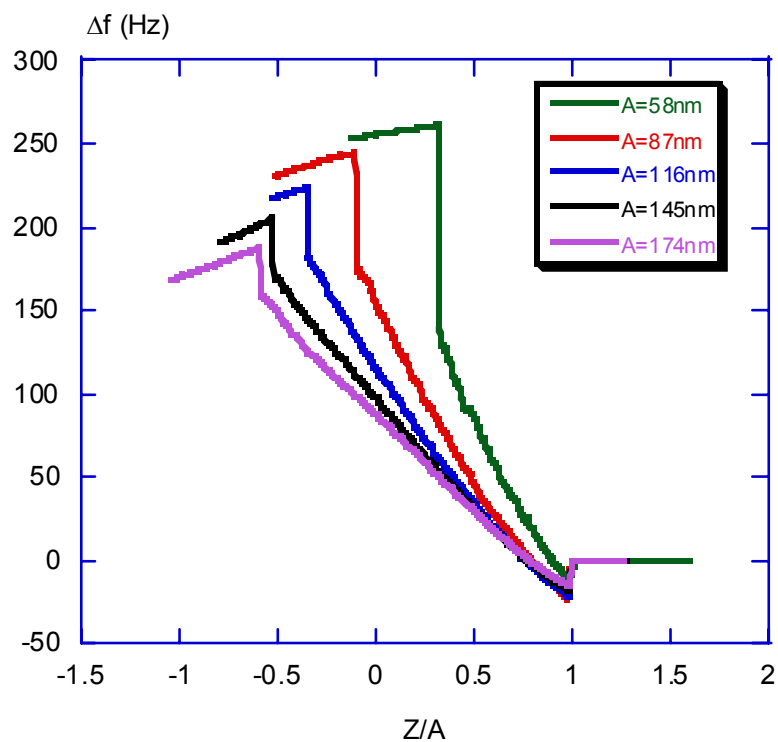


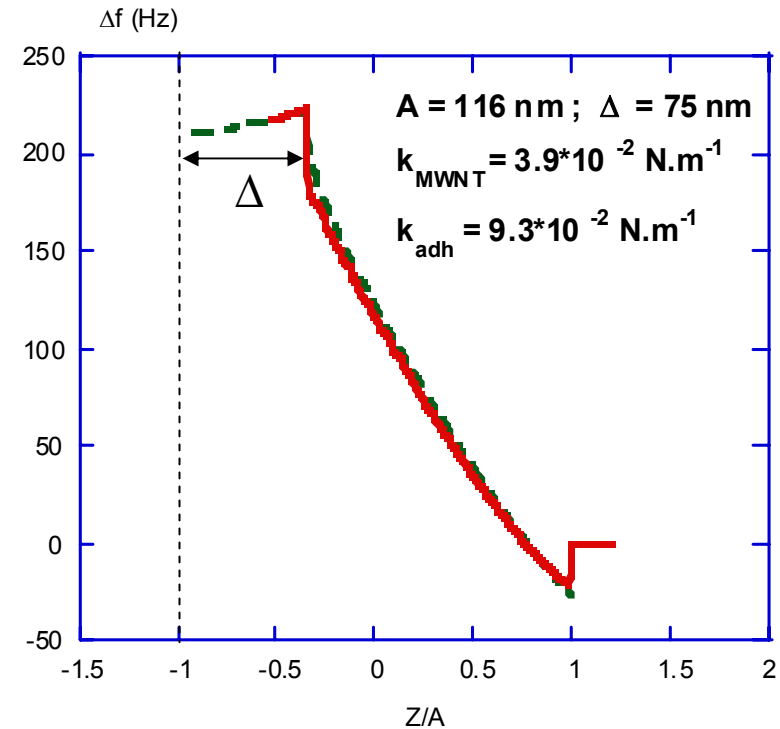
$k_{SWNT} = 1*10^{-3}\ N.m^{-1}$

$E_{dis} = 1.5\ 10^{-17}\ J$

Adhesion mostly governs SWNT behavior

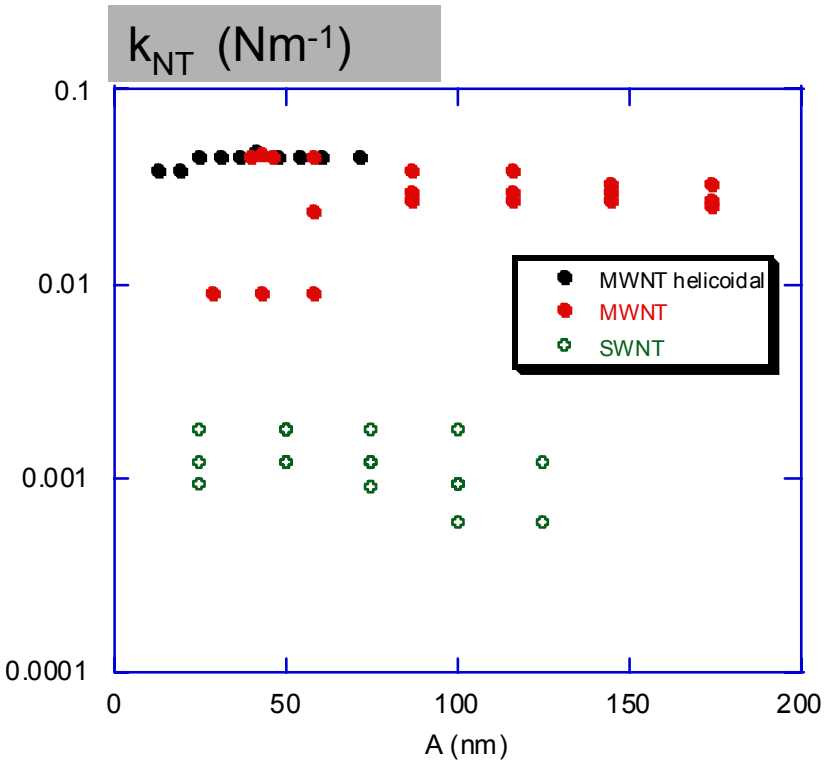
Multi Wall NT mechanical properties

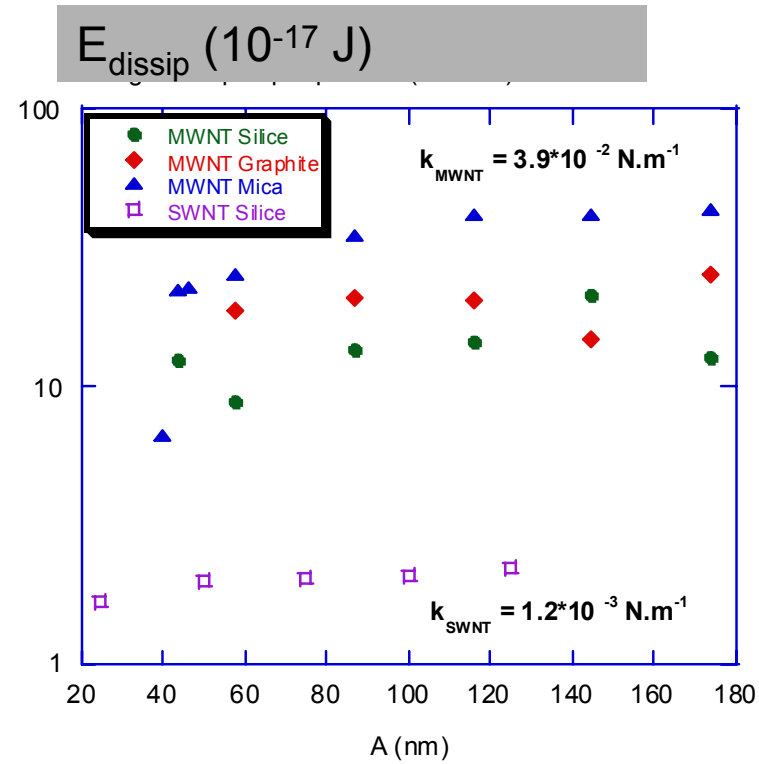




MWNT with diameters 15-30 nm mixing of elastic and adhesion contribution

SWNT vs MWNT





$k_{MWNT} \approx 30\ k_{SWNT}$

Energy loss

MWNT : $1.5*10^{-16}$J

SWNT : $1.5*10^{-17}$J

Summary
CNT Adhesion / elasticity

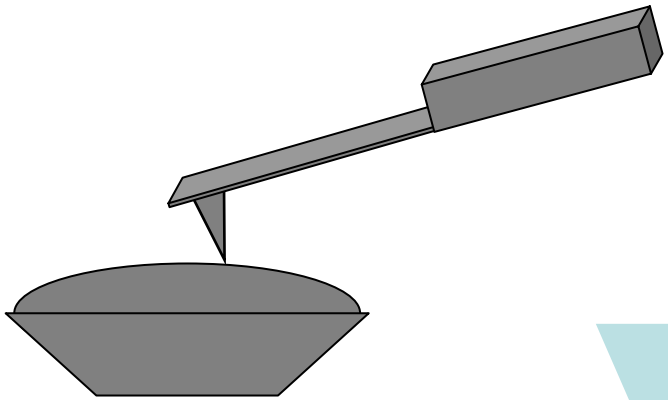
SWNT:
- adhesion governs CNT-Surface interaction,
- strong modification may occur due to change of contact area between SWNT and surface

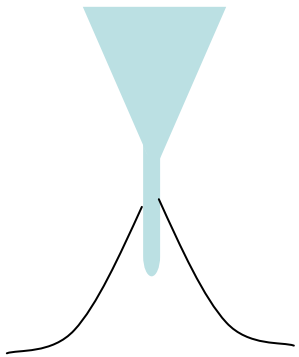
MWNT:
-Mixing of the rwo (adhesion and elasticity) strongly dependant on tube diameter.

FM-AFM: tool to make accurate analysis for nanomaterials contact mechanics.

Oscillating NanoNeedle at Air liquid Interface Dynamical behavior of NanoMeniscus

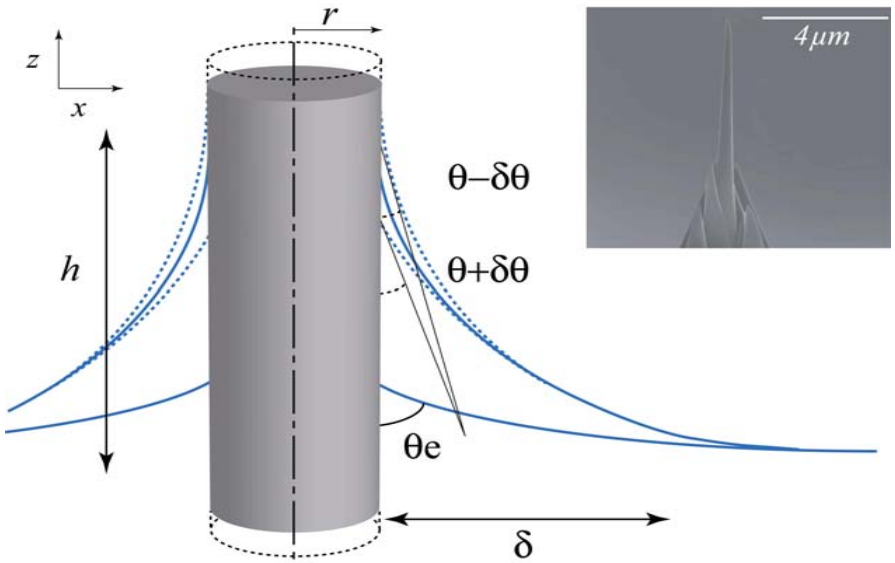
C. Jai, J.P. Aimé, R. Boisgard (University Bordeaux I)
D. Mariolle, F. Bertin (LETI-MINATEC)
*(**Nanoletter** Vol 6 issue 11, 2006)*

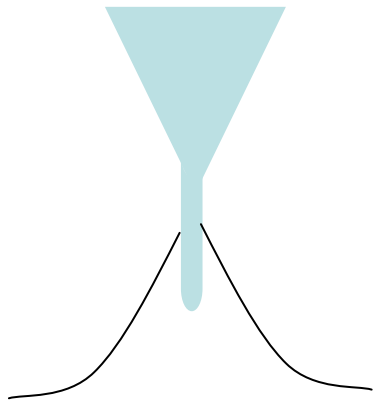




- Q>>Qwater
- Φ interface
- Nanometer scale Wetting deWetting processes
- Dynamical stability attoliter
- No- substrat
- Weak perturbation for Membranes and proteins

Dynamical behavior of NanoMeniscus



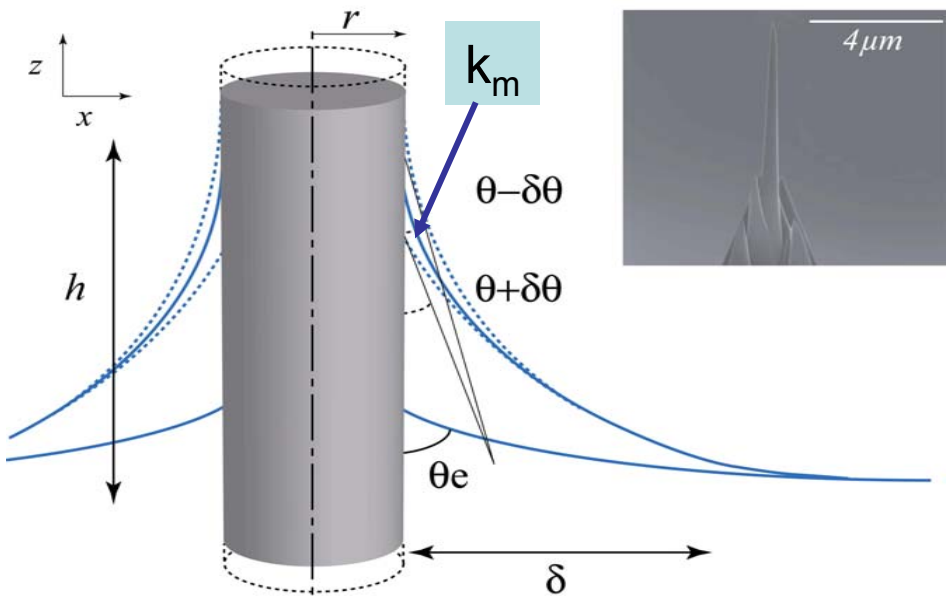


$$f_{cap} = \gamma\phi\cos(\theta) = 1-5nN$$

$$h \approx r\ln\frac{\delta}{a} \approx 100nm$$

$$f_{dis} \approx \eta\frac{v}{e}\phi^2 = 10-100\,pN$$

Frontier Elasticity : Triple line Air-Liquid-Solid

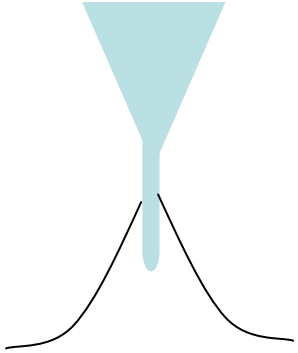


$$k_m \approx \pi \frac{\gamma}{\log(\delta/R)} \sin^2\theta \cos\theta \approx \pi \frac{\gamma}{\log(\delta/R)} \theta^2$$

$= 10^{-2}\ \mathrm{Nm}^{-1}$

$$\Delta\nu \approx \frac{\pi}{2}\nu_0 \frac{\gamma}{k\ln(\delta/R)} \sin^2\theta \cos\theta - \frac{1}{2}\nu_0 \frac{m_{added}}{m^*}$$

$$\frac{\Delta\nu}{\nu_0} \approx \frac{\gamma}{k}\theta_d^2$$



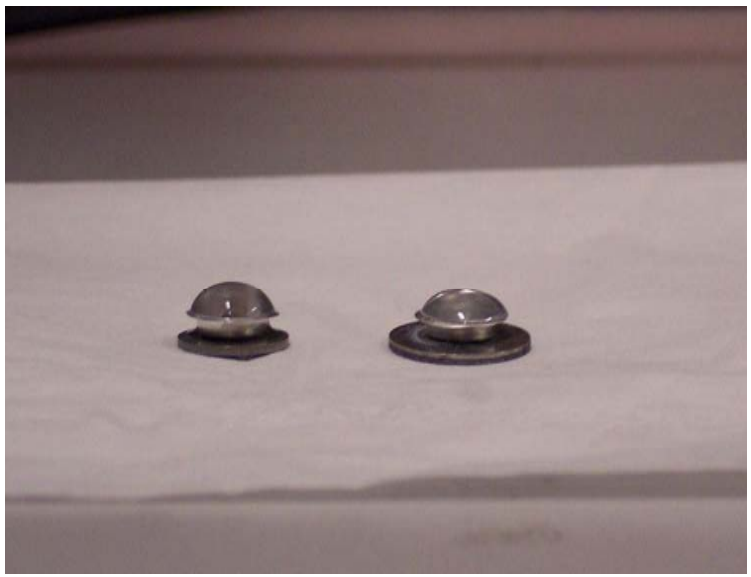
$$f_{dis} \approx \eta \frac{v}{\theta_d}$$

Meniscus Shape ⟷ Frequency shift

Thinning effect ⟷ Viscous Damping

Water

- η=1.10−3 Pa.s
- γ=72.8mN/m²
- ρ=1000g/L

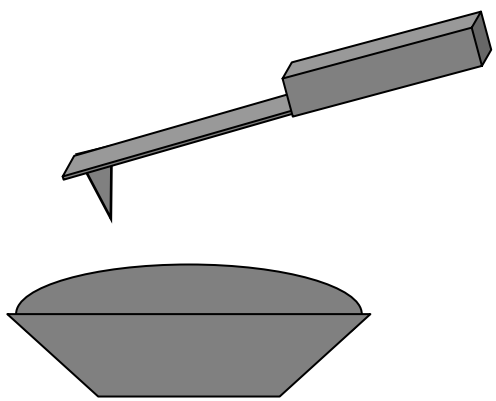


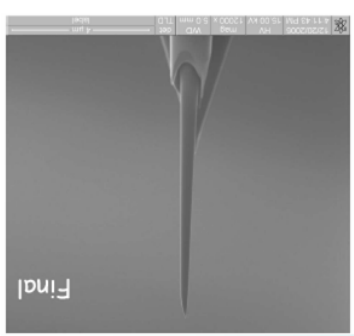
Glycerol

- η=1.485 Pa.s
- γ=63.4mN/m²
- ρ=1260g/Lm

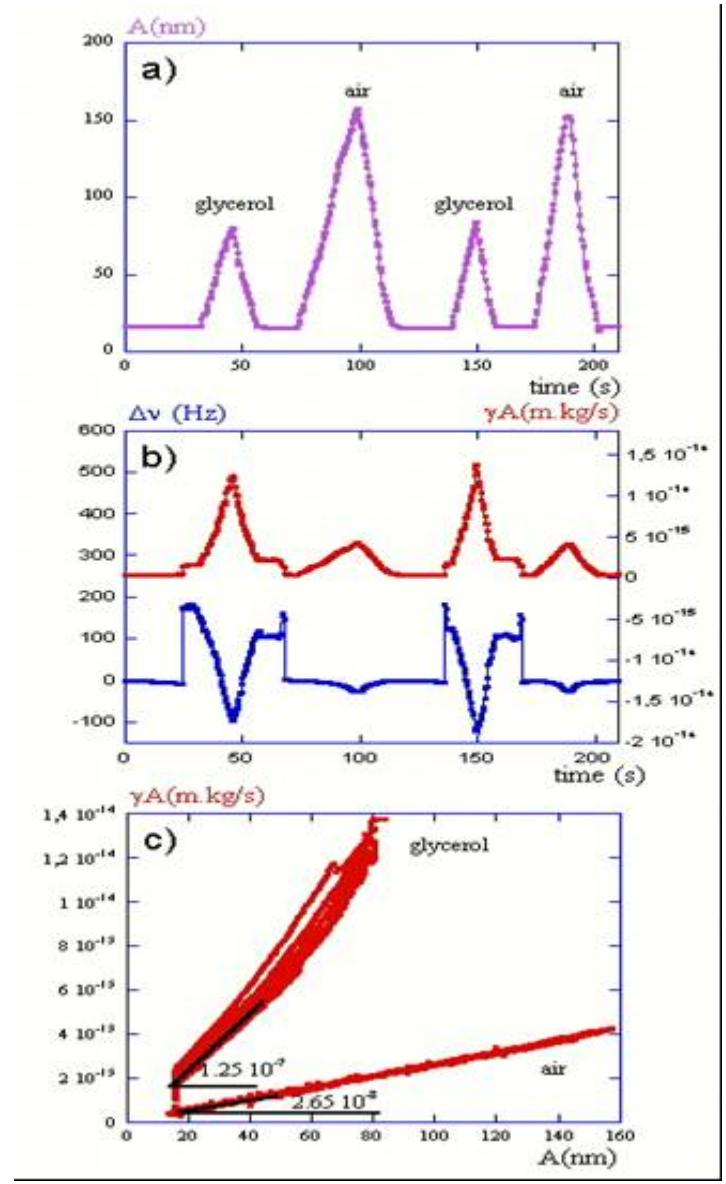
Oscillating at the air-liquid interface
Nano-Meniscus
C. Jai et al

- High Viscosity: 10^3 water viscosity
- Stable Interface



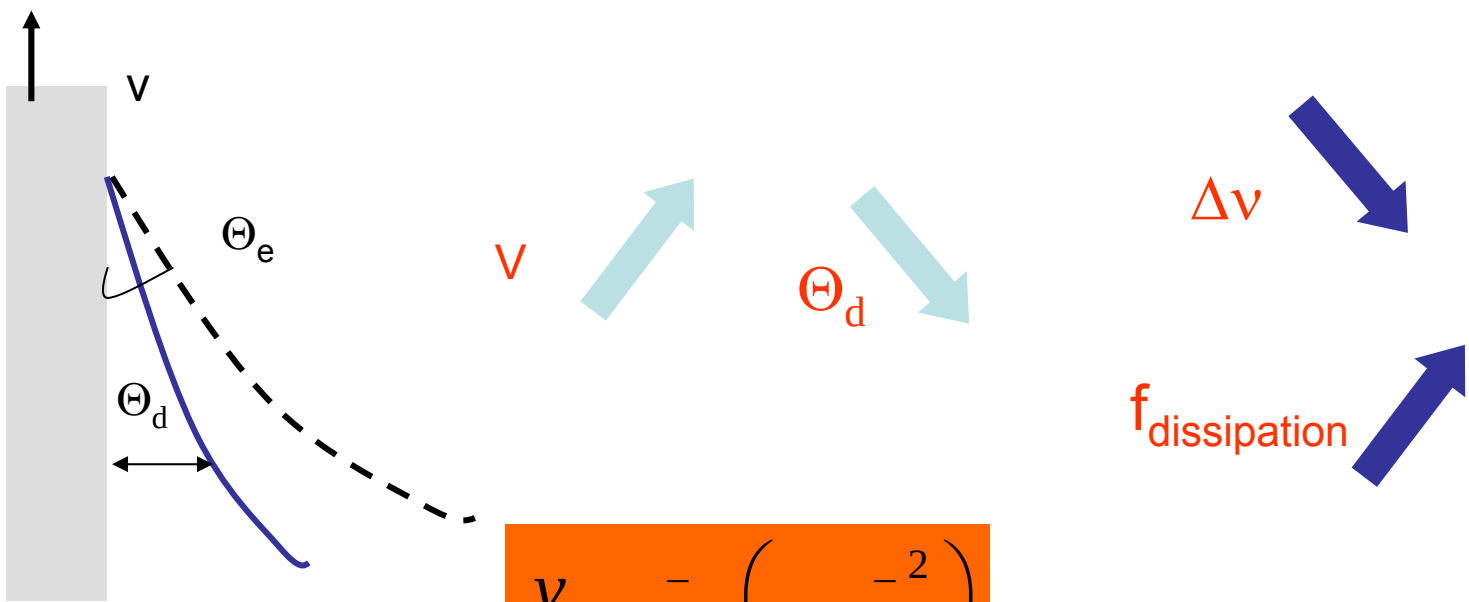


Glycerol



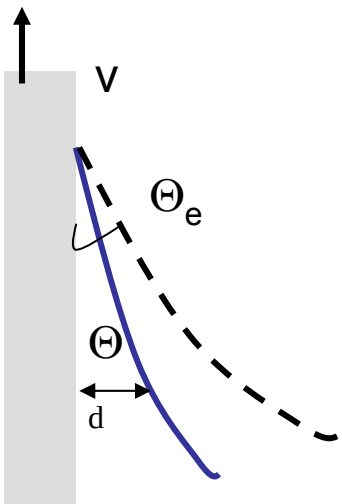
Meniscus Dynamical Shape

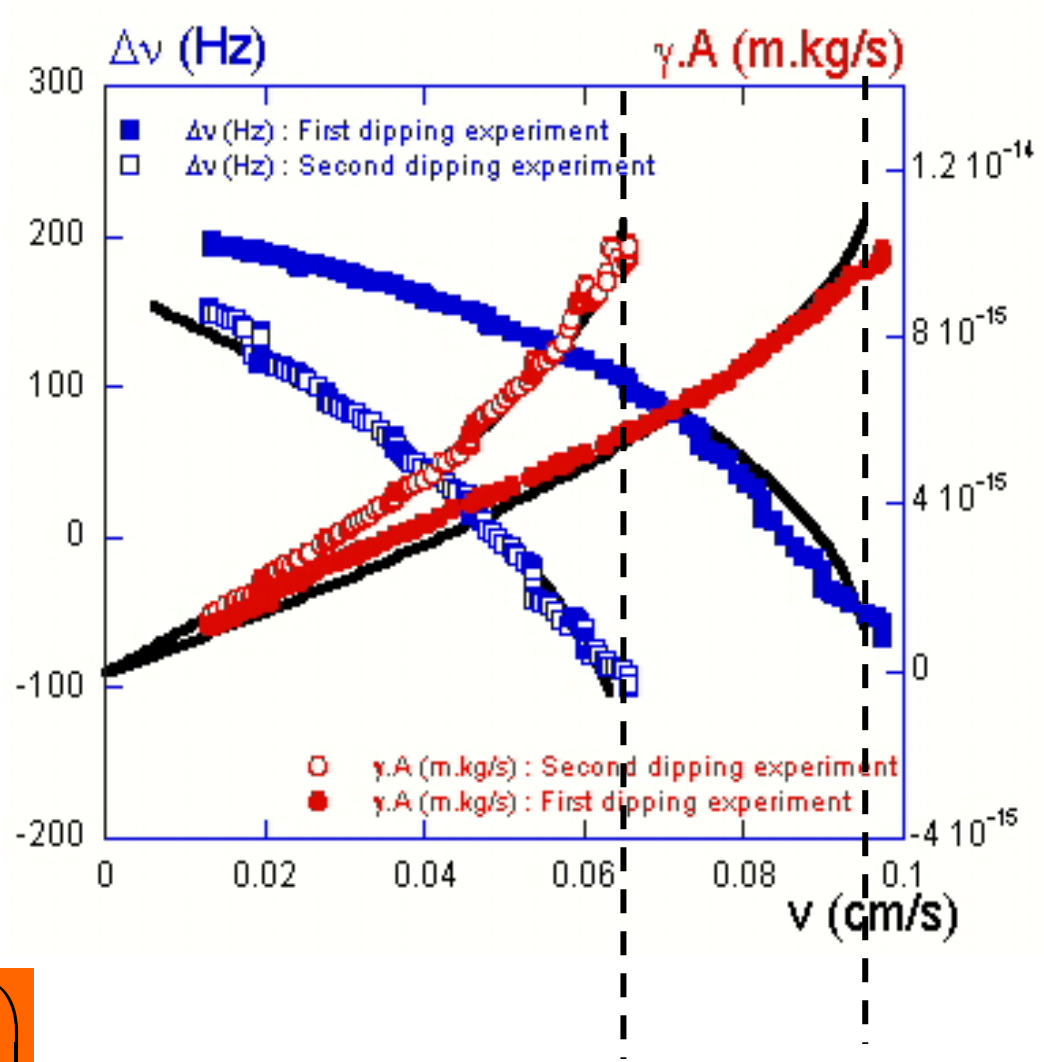
$$f_{el} = \gamma\phi\left(\cos\theta_e - \cos\theta_d\right) \approx \frac{\gamma\phi}{2}\left(\theta_d^2 - \theta_e^2\right) = \eta\frac{v}{\theta_d} \approx f_{dis}$$



$$\frac{v}{v_c} = \bar{\theta}_d\left(1 - \bar{\theta}_d^2\right)$$

Meniscus Dynamical Shape





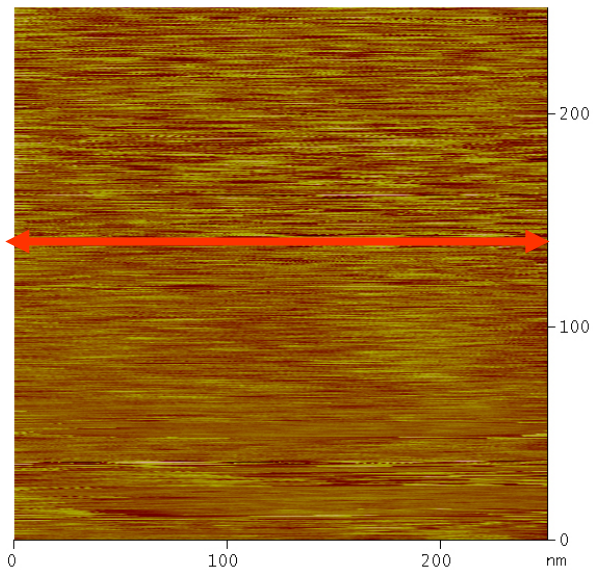
$f_{dissipation}$

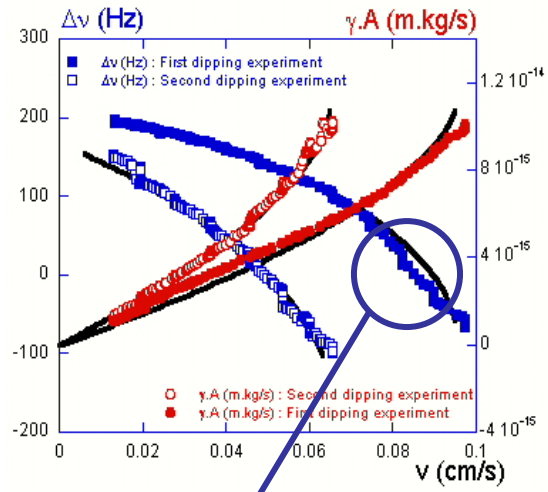
$\Delta\nu$

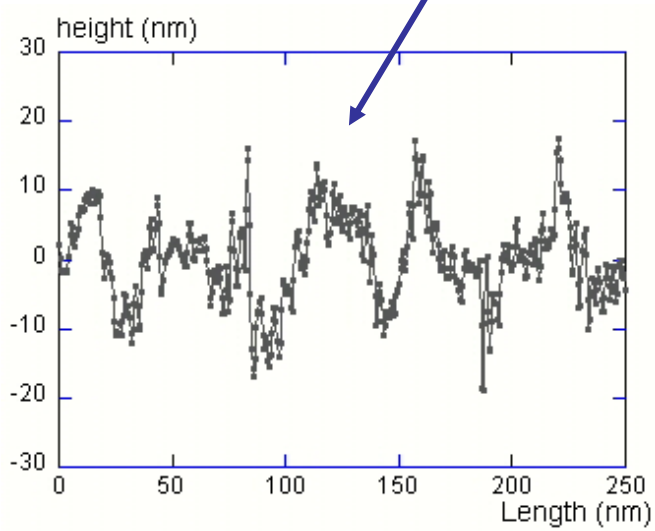
$$\frac{v}{v_c} = \bar{\theta}_d \left(1 - \bar{\theta}_d^{\,2}\right)$$

Critical velocity v_c : $v > v_c$ complete wetting of the nanoneedle

IMAGING air-LIQUID interface

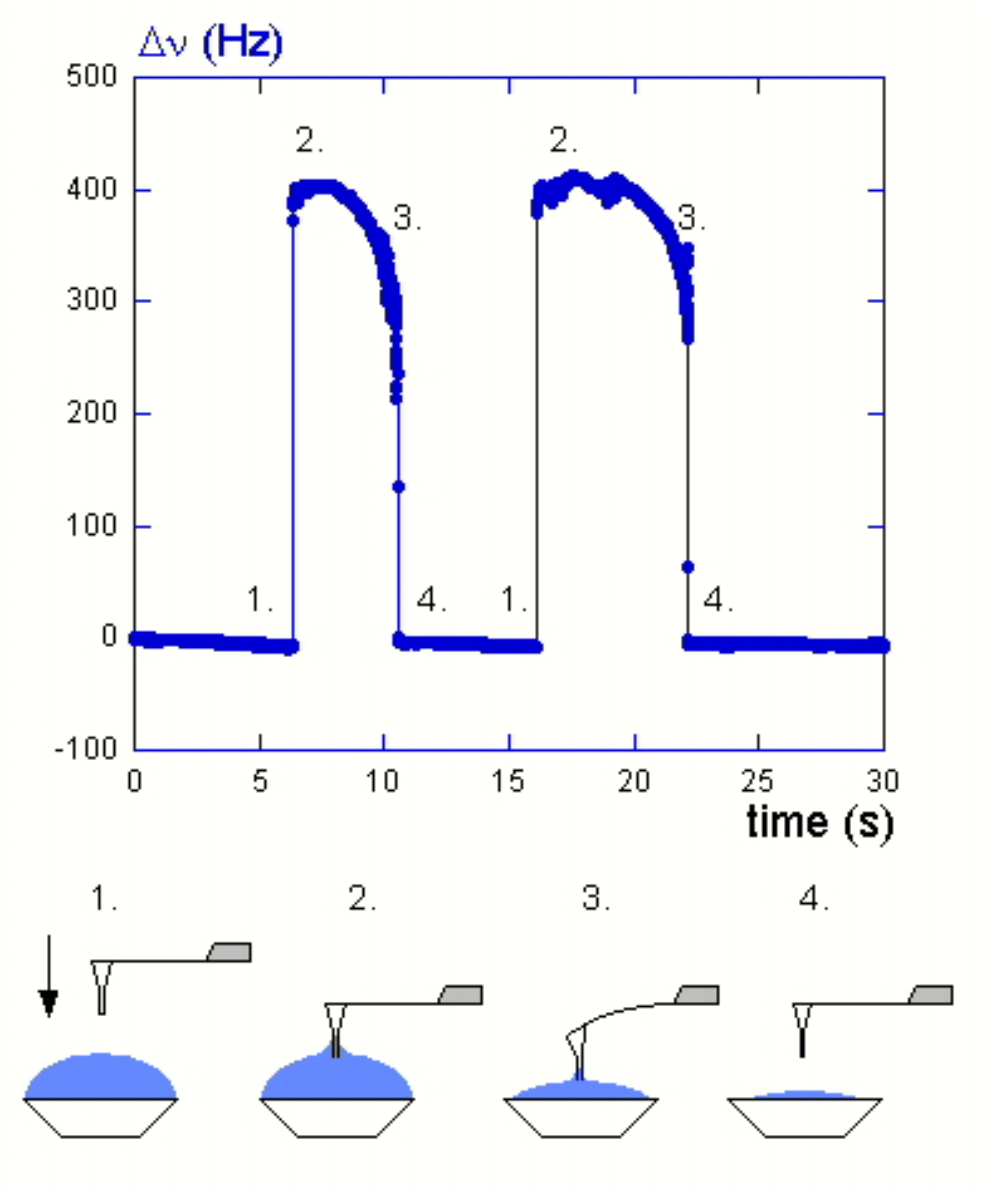






Evaporation and ultra thin meniscus

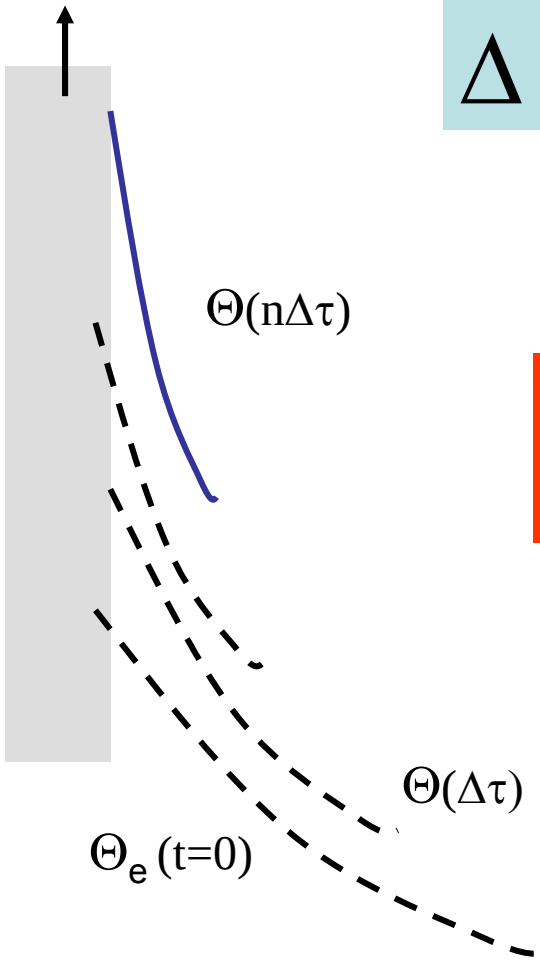
WATER



Water

Viscosity very low, dynamical effect small

Pinned triple line ⟷ Ultra thin meniscus



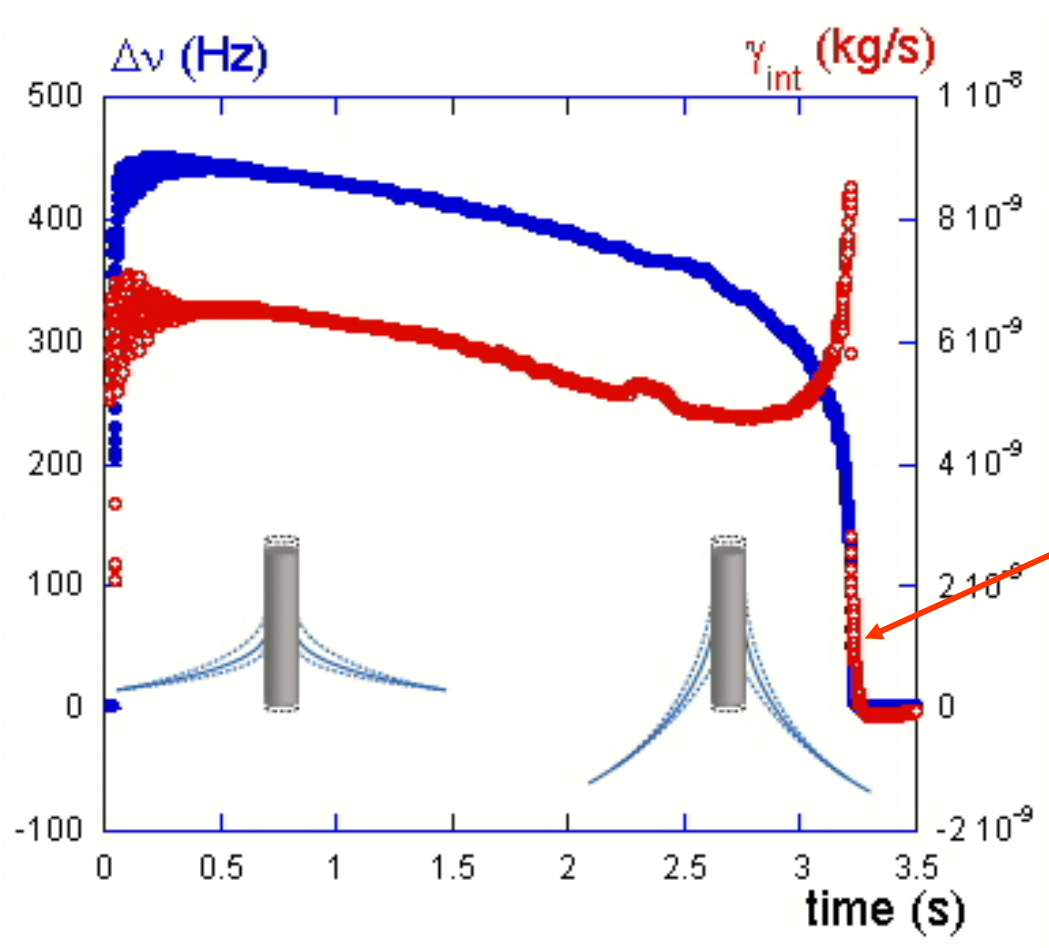
$$\Delta\nu \approx \theta^2$$

to zero

« Infinite »

$$f_{dis} \approx \frac{1}{\theta}$$

Ultra thin meniscus until it breaks



$f_{dissipation}$

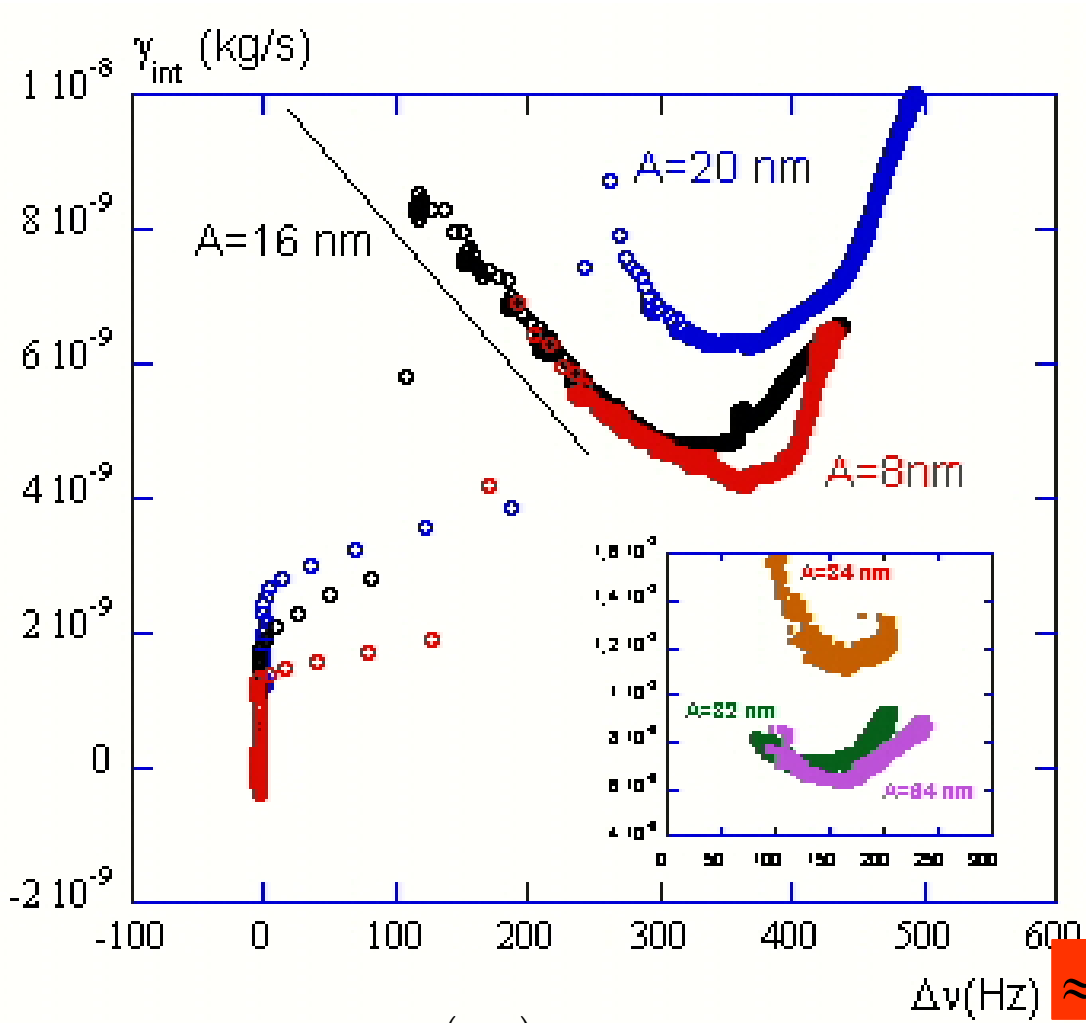
« Infinite »

until it breaks

$\Delta\nu$

to zero

Relationship between nanomeniscus shape and dissipation



$\approx \theta^2$

$$\gamma_{\text{int}} \approx -\frac{2k\ln\left(\delta/R\right)}{\omega^2}\frac{\phi}{A}\Delta\nu + \frac{1}{\sqrt{2}}\frac{\gamma\phi}{A\omega}\theta_e^2$$

air glycerol interface

Viscous fluid: Dynamical non linear thinning effect.
Θ_D behaves as the order parameter of a first order phase transition.
Critical tip velocity, above which complete wetting occurs : $\Theta_D=0$

air water interface

-Hot problems related to evaporation at nm scales.
-Diverging behavior of the Dissipation: viscous contribution dominant for very thin meniscus (!?).