Liquid nanodispensing

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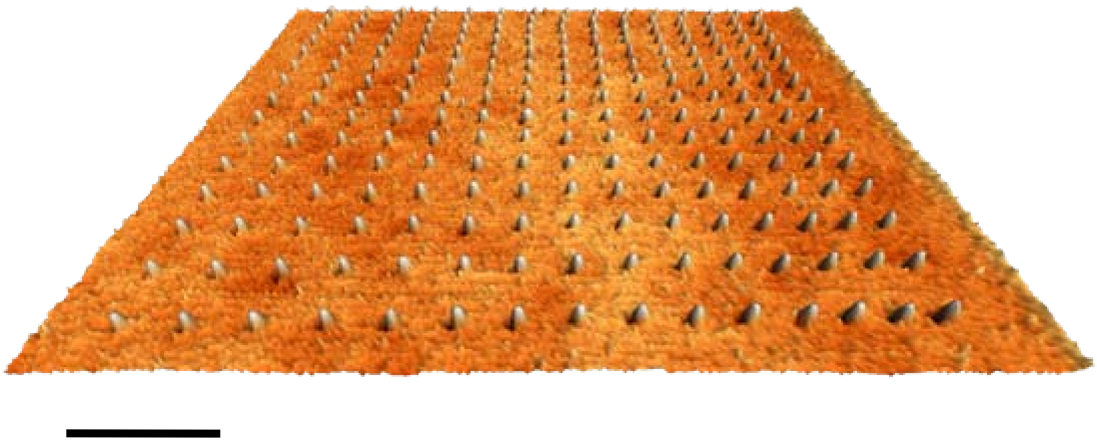
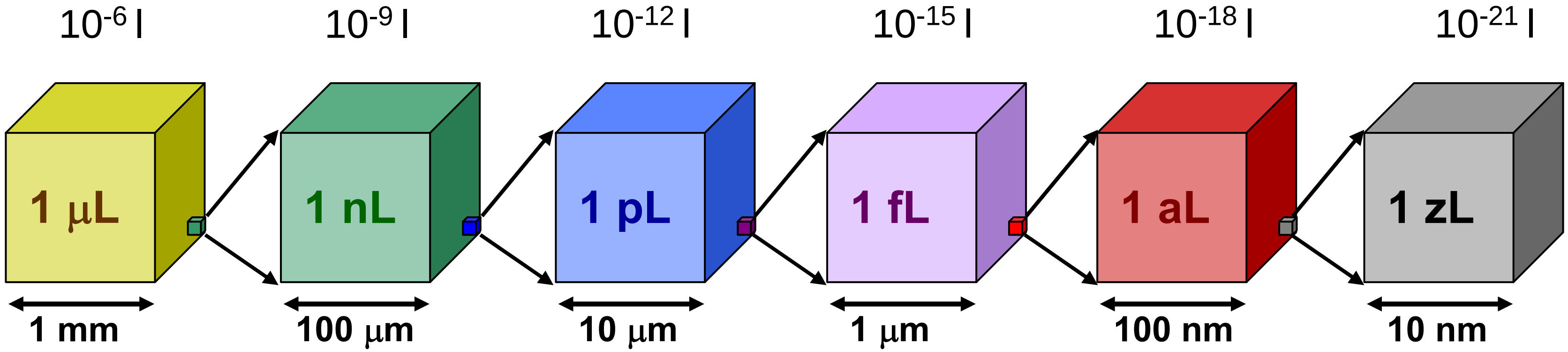
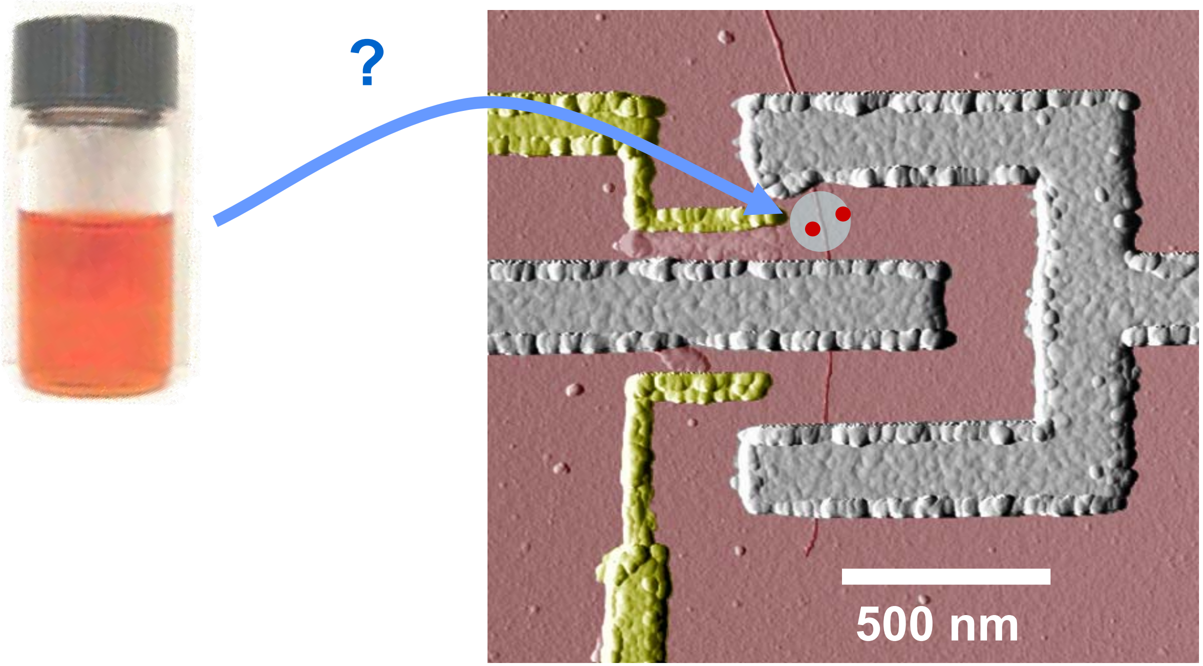


- **Nanopatterning, molecule deposition**
- **Dynamics of liquids at sub-micron scale**

Liquid volumes



Molecules deposition



JP Cleuziou, W. Wernsdorfer, V. Bouchiat, T.O., M. Monthioux, *Nature Nanotech* 2007

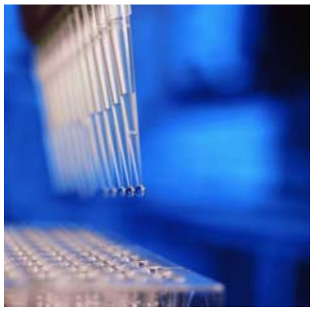
- **Deposited volume : towards single molecule**

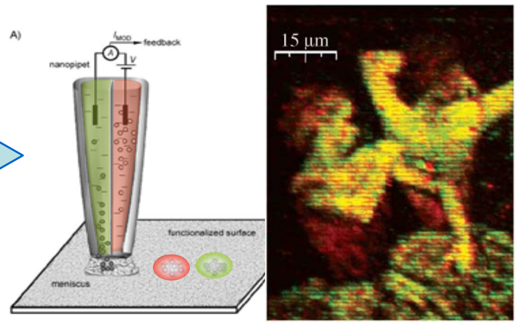
$(100\ \text{nm})^3$ = 1 attoliter (10^{-18}l) of 1µM solution ~ 1 solute molecule

- **Positioning on nanostructures**

Direct patterning : liquid lithography

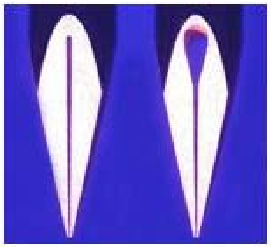
✓ Pipettes



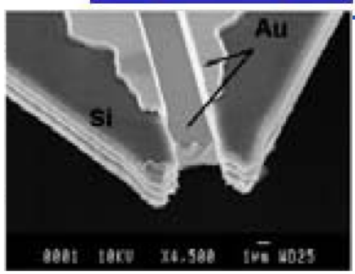


D. Klenermann et al., *Angew. Chem. Int. Ed.* 2005
Ionscope Ltd

✓ Pins

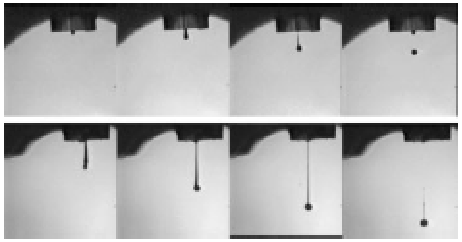


ArrayIt®



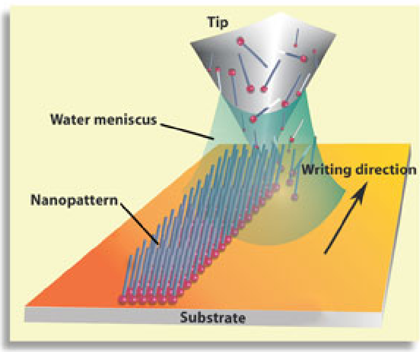
BioPlume (LAAS, Toulouse)
BioForce Nanosciences, Inc

✓ Ink-jet

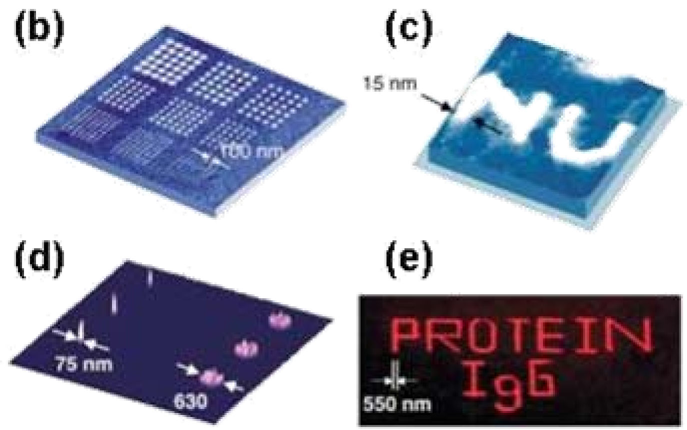


Park et al., Nature Mat. 2008

Dip pen nanolithography



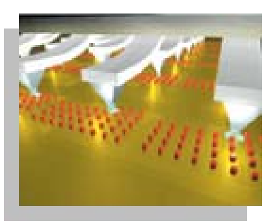
Piner, R. D. *Science* **1999**,
NanoInk, Inc

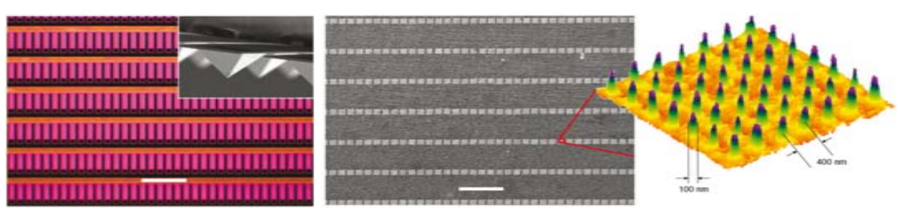


Review :

Salaita et al. *Nature Nanotechn.* **2007**

✓ Massive parallelisation

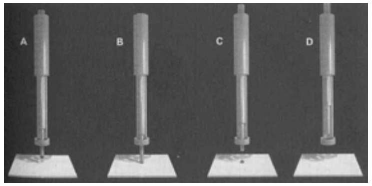




Methods

✓ Liquid lithography

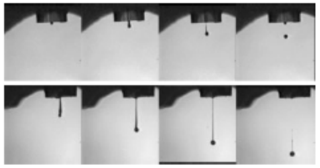
Pin and Ring method (DNA chips)



~ 200 µm

Ink jet

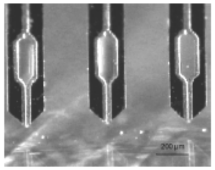
De Gan et al., *Adv Mat* 2004



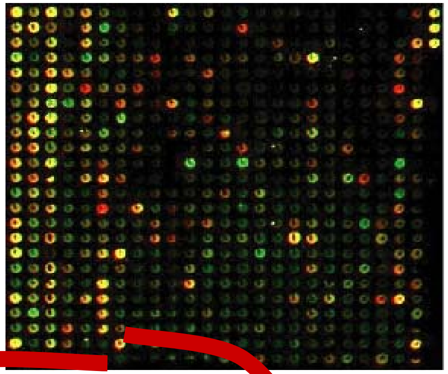
1 µm

Microlever plotters

Belaubre et al., *APL* 2003



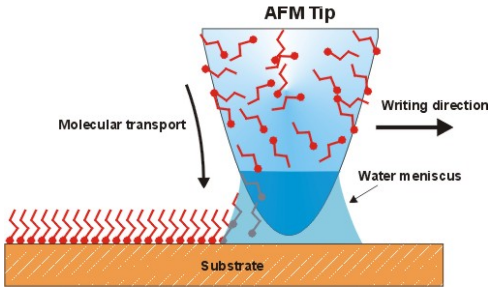
Few µm



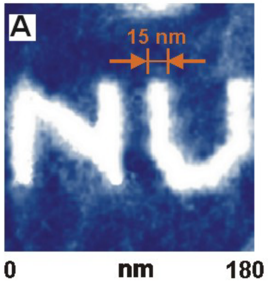
+ Versatile

-- Ø ~ 1 to 200 µm

✓ Dip pen lithography



Piner et al., *Science* 1999
Hong, Mirkin, *Science* 2000



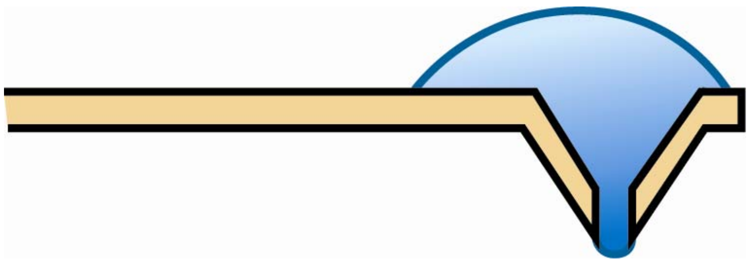
+ Ø ~ 10 nm

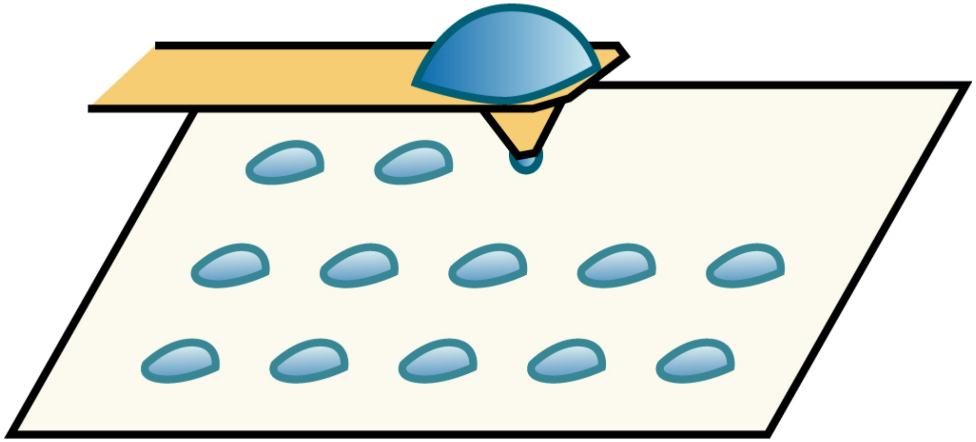
-- Limits in terms of transferrable molecules

-- No reservoir

NADIS : liquid NAno DISpensing

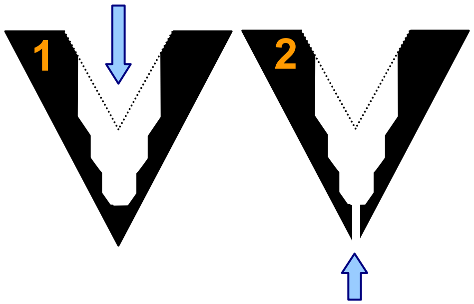
Meister et al, *Appl. Phys. Lett*. 2004
A. Fang, E. Dujardin, T.O., *NanoLett* 2006

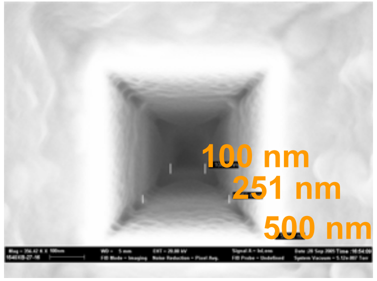


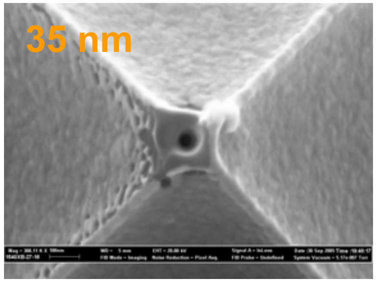


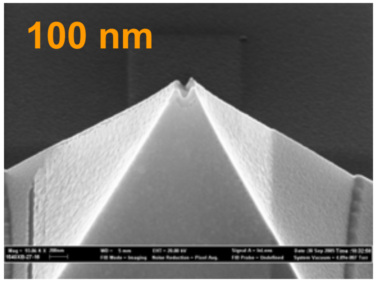
Fabrication of NADIS tips by focused ions beam (FIB)

✓ **2 steps : (i)** *Thinning of tip wall from the top* **(ii)** *milling at tip apex from tip side (record : **35 nm**)*

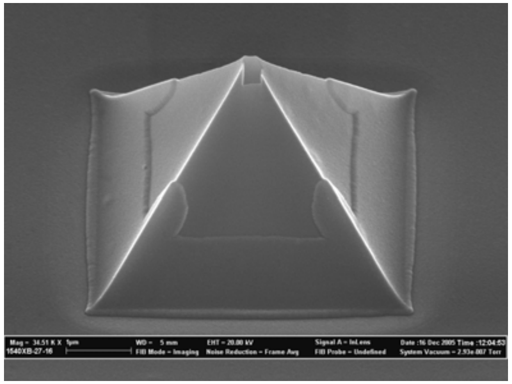




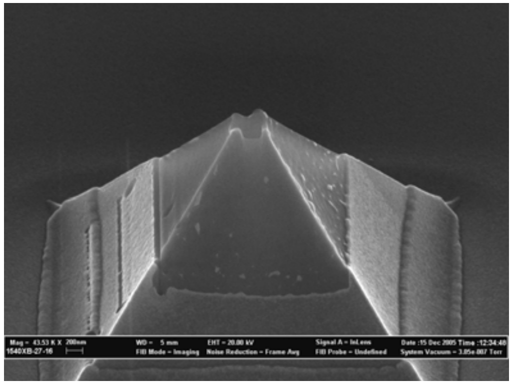




✓ **Surface functionalization**



Intact smooth gold surface (for thiolate chemistry)



Smooth Si_3N_4 surface for silane chemistry

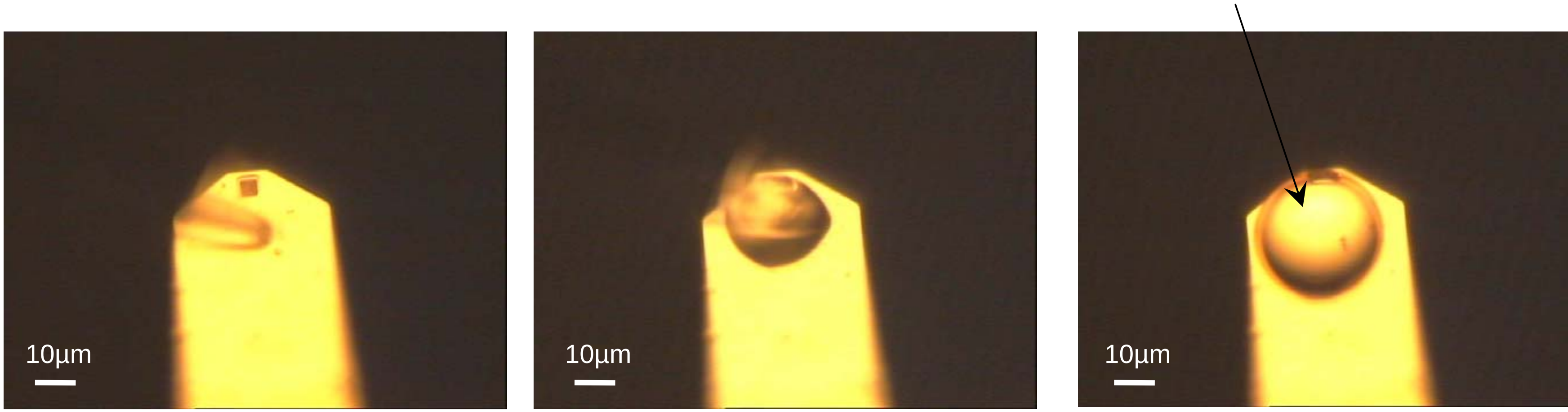
Deposition procedure

- **Liquid**

  Glycerol ou glycerol-water mixtures (dilution max 6:4)

  Solutions of molecules, dendrimers, proteines, nanoparticules…

- **Loading of reservoir**

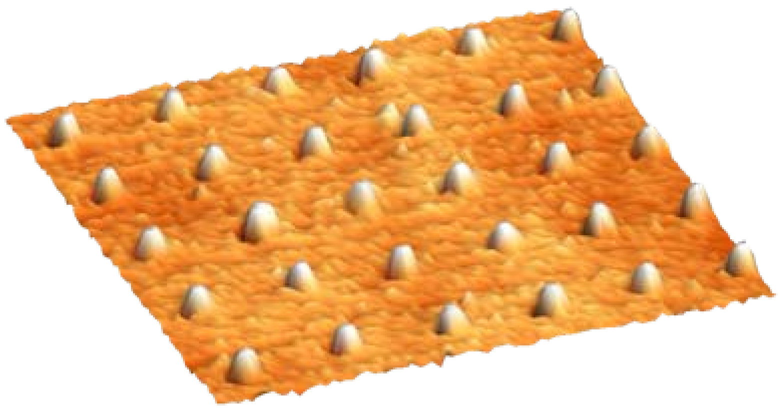


Droplet deposited with a micropipette and micromanipulator

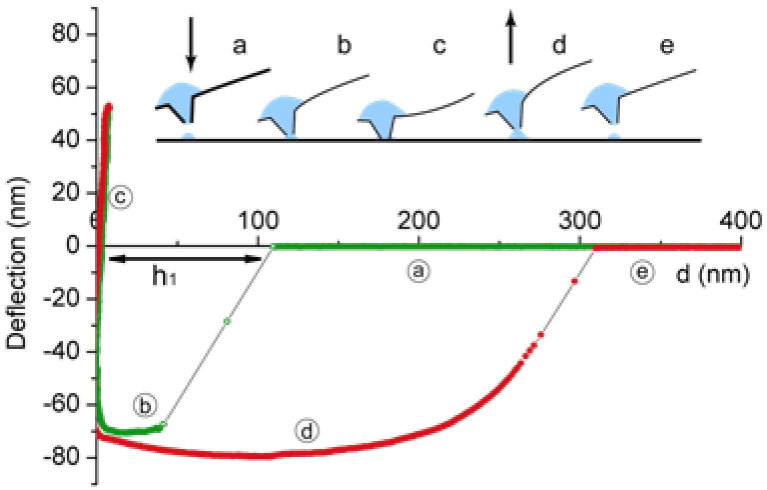
Deposition procedure

- **AFM Multimode Picoforce in force curve mode**

  - ✓ Imaging of molecules spots

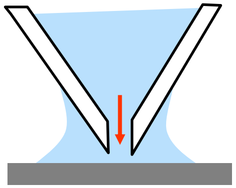
    

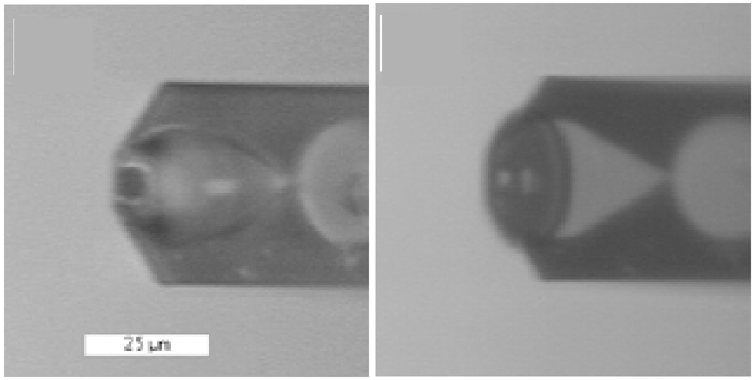
  - ✓ Force curve

Influence of substrate properties

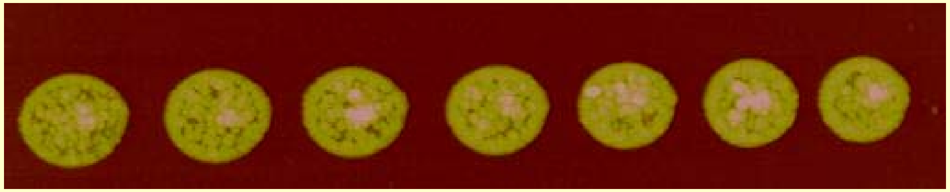
- Hydrophilic tip with 400 nm aperture





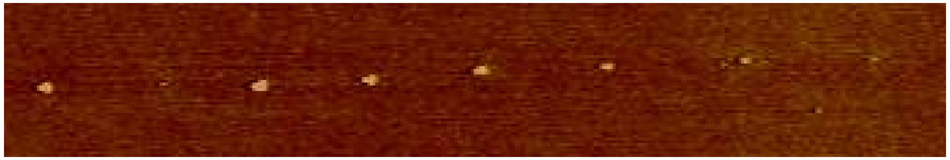
- On hydrophilic SiO_2

- On NH_2-treated SiO_2
  (θ_{av} = 53 °)



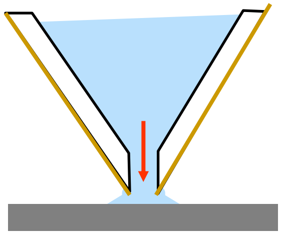
1 µm

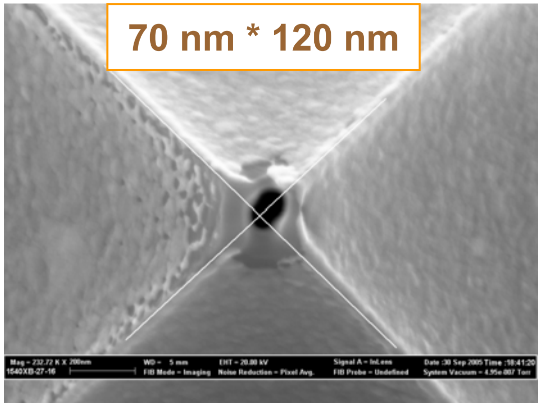
- On CF_3-treated SiO_2
  (θ_{av} = 105 °)

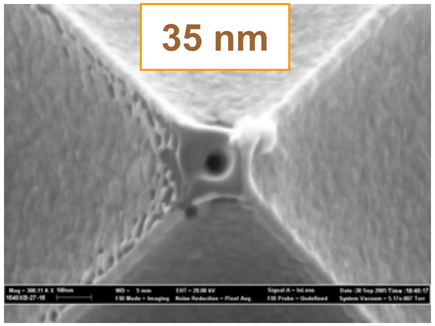


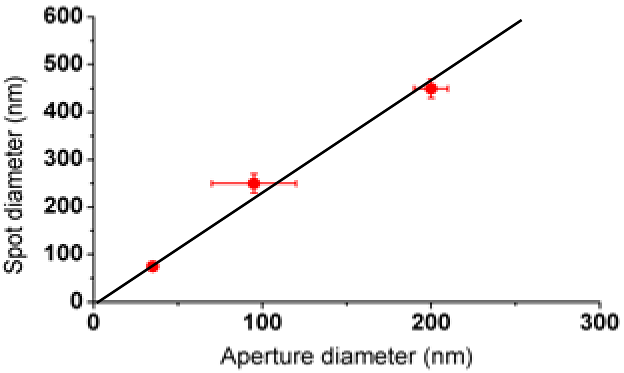
Ultimate dimensions : hydrophobic tips

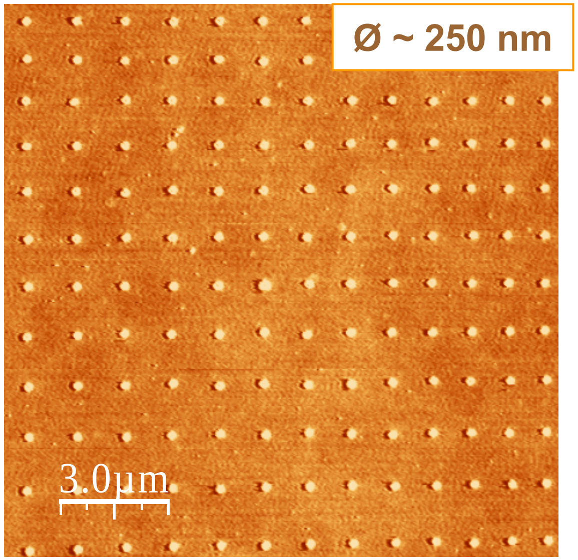
- Hydrophobic tips (functionalized by dodecanethiol)

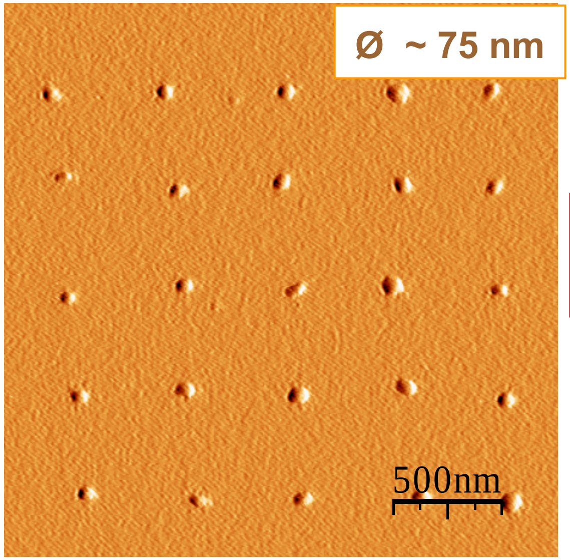










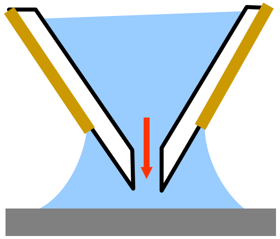


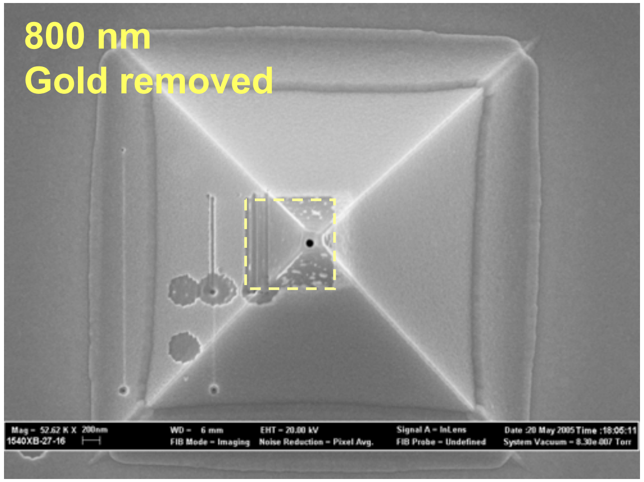
Spot diameter ~ 2x aperture diameter

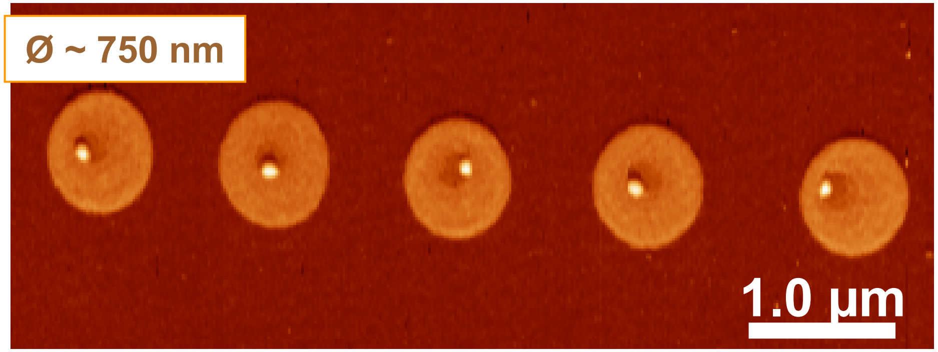
A. Fang, E. Dujardin, T.O., *NanoLett* (2006)

Intermediate sizes

- Mixed tips



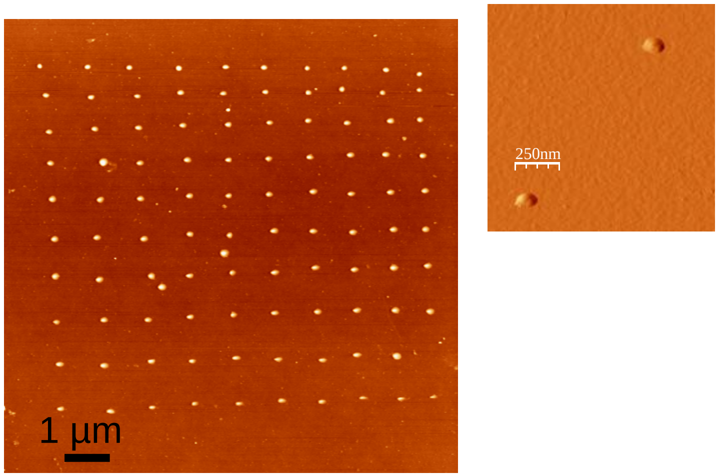




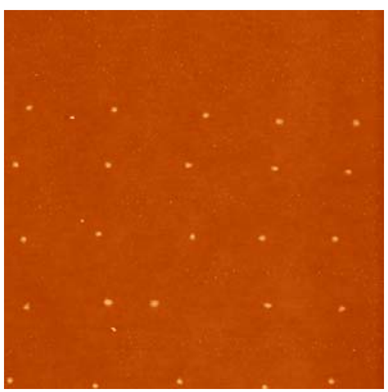
Spot diameter ~ size of hydrophilic region

Patterning of nanoparticles and proteins

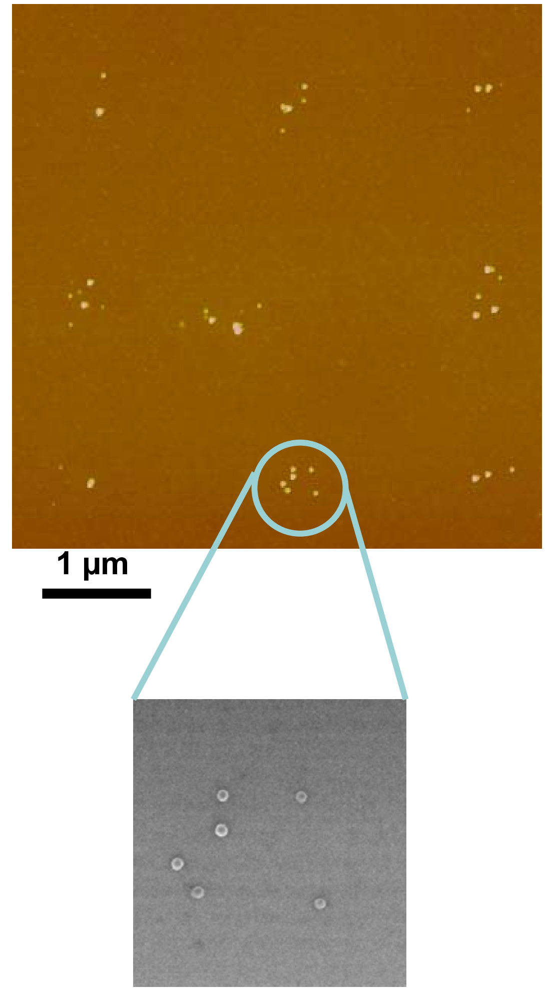
➢ DsRed proteins



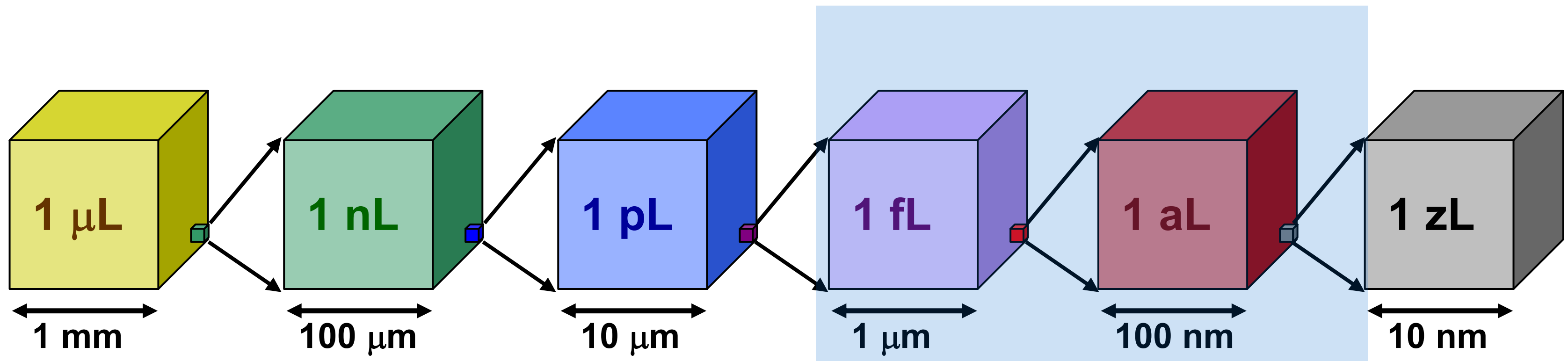
➢ EGFP proteins

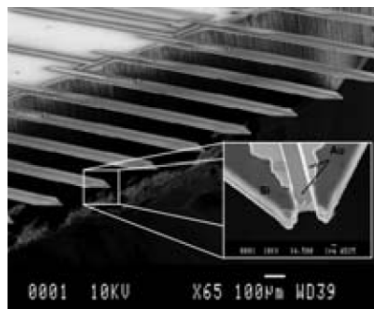


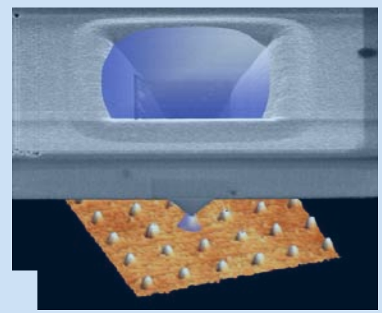
➢ 25 nm PS NPs

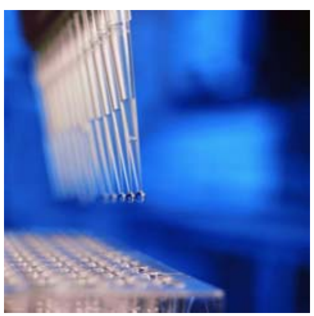


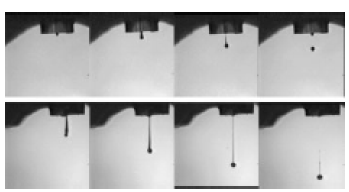
Comparison with other liquid dispensing methods

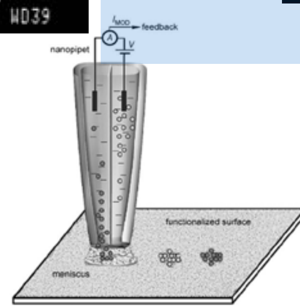


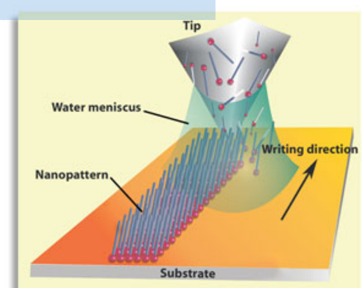








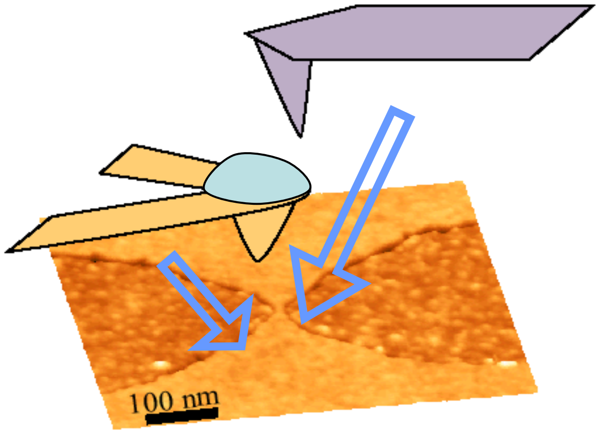


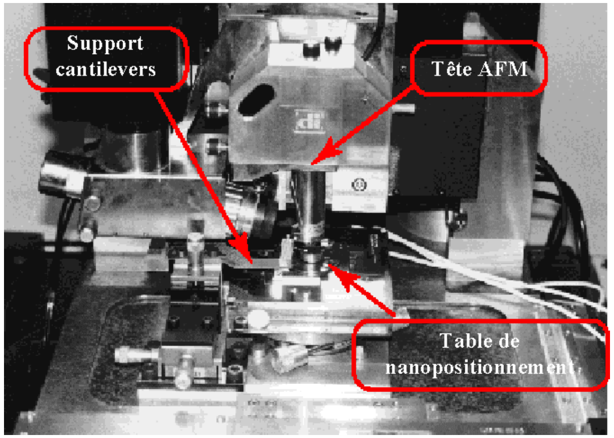


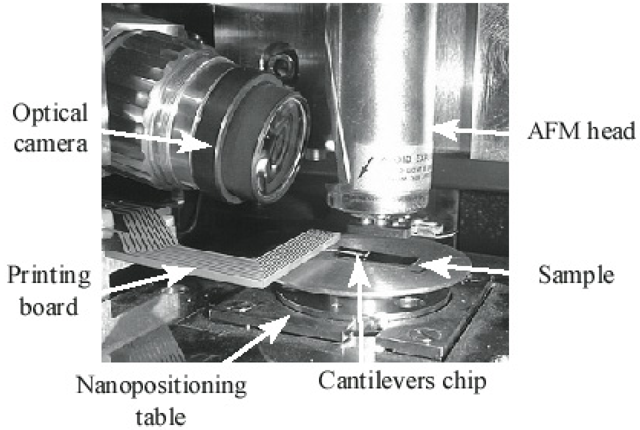
Deposition set-up

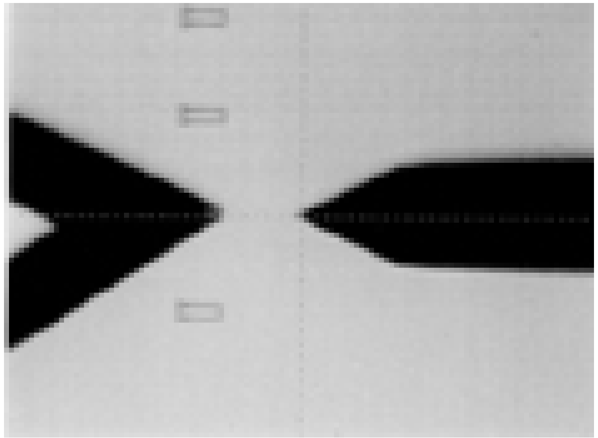
Ondarçuhu et al., *Rev. Sci. Instr.* 2000

- Set-up with two AFM tips



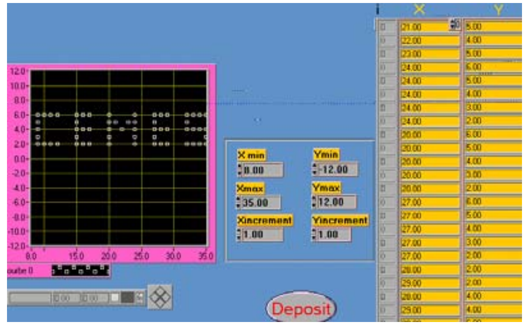


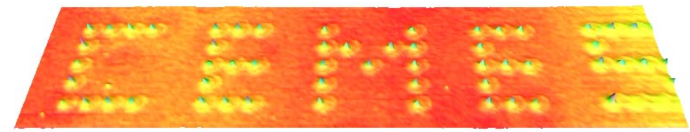




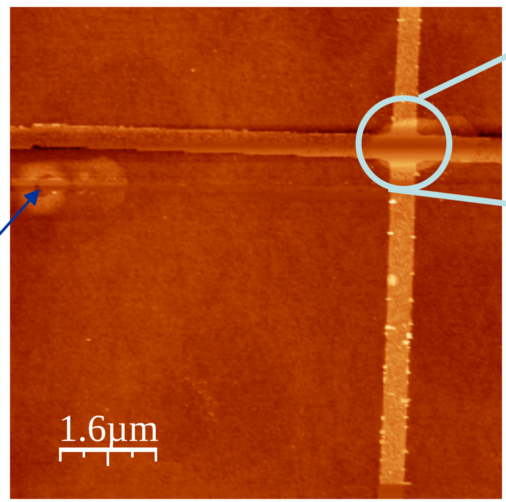
Deposition set-up

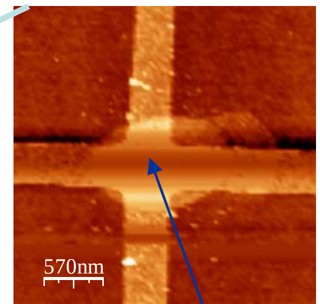
- **Automated deposition**





- **Nanopositioning at a predefined place**

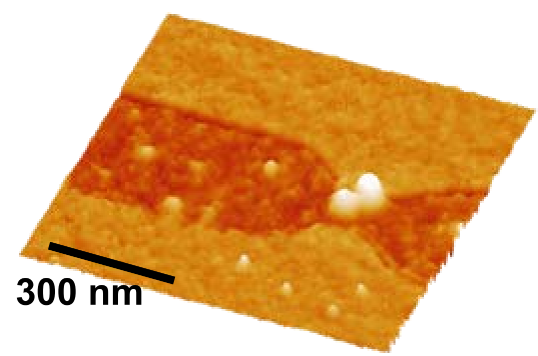




2- Droplet deposited on electrodes

1- Reference droplets

Position accuracy : Δx, Δy ~ 100 nm



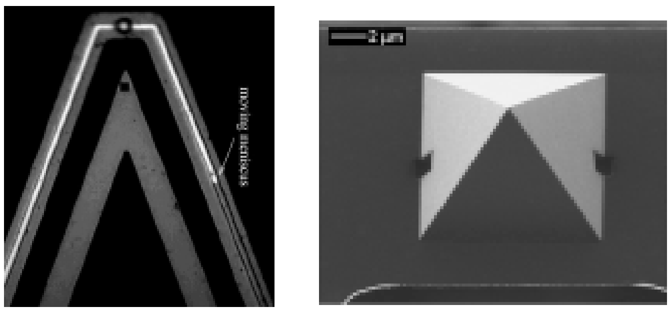
M. Ben Ali. T.O., *Langmuir.* 2002

Limitation

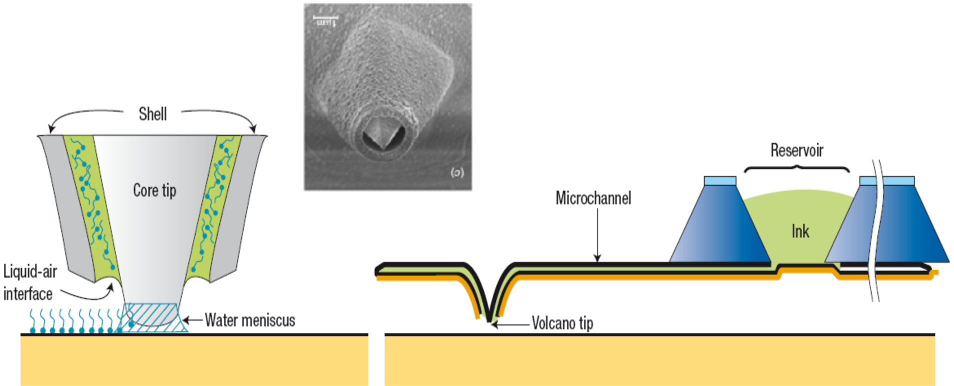
➤ Evaporation of the open reservoir

Cantilevers with integrated microfluidic channel

Ex : NanoFountain pen

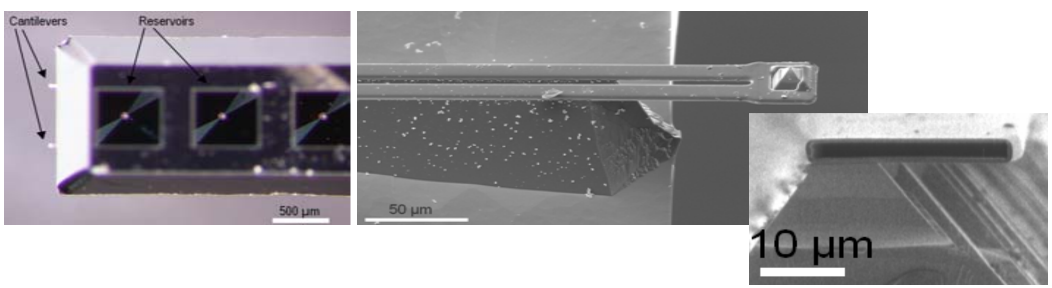


Deladi et al., *J. Micromech. Microengin. 2005*

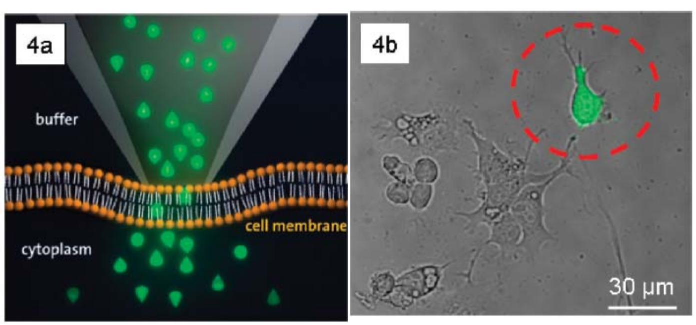


Kim et al., *Small 2005*

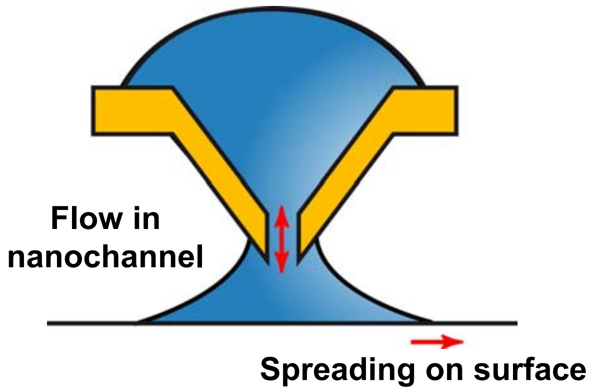
FluidFM



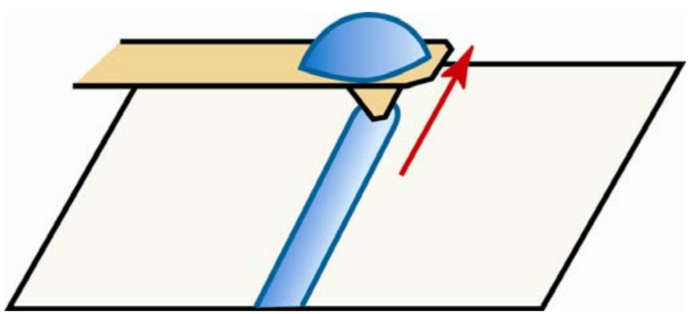
Meister et al., *NanoLett 2009*

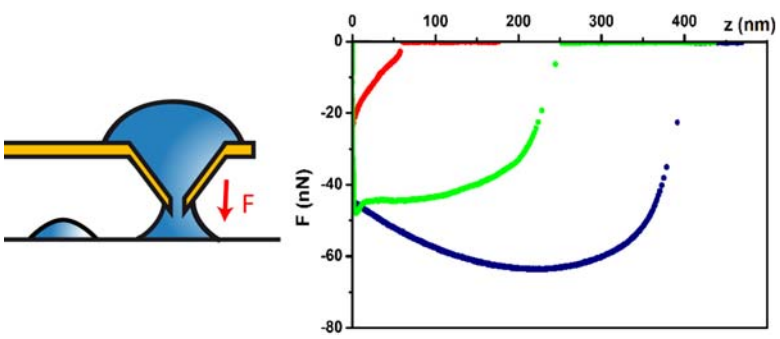


Liquid transfer mechanism

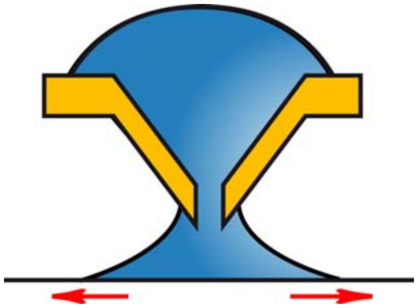


- **Spreading dynamics**
- **Capillary force**

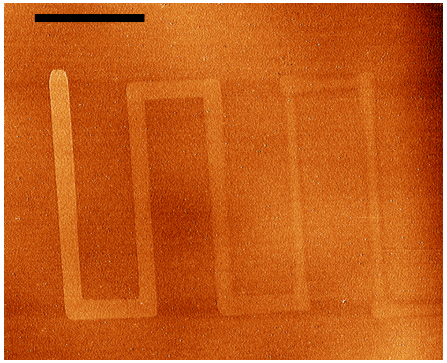


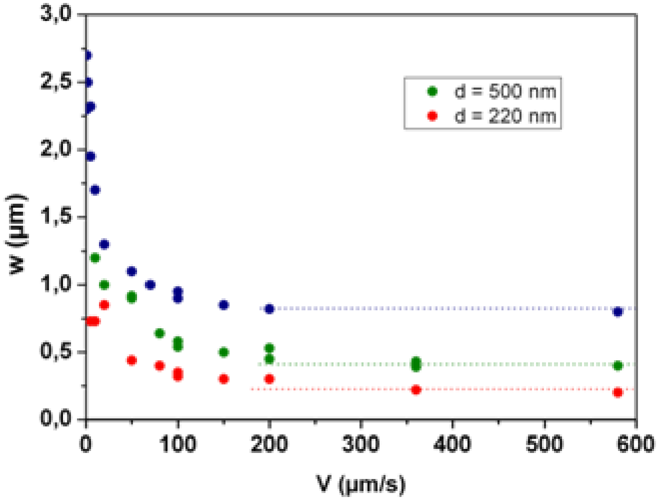


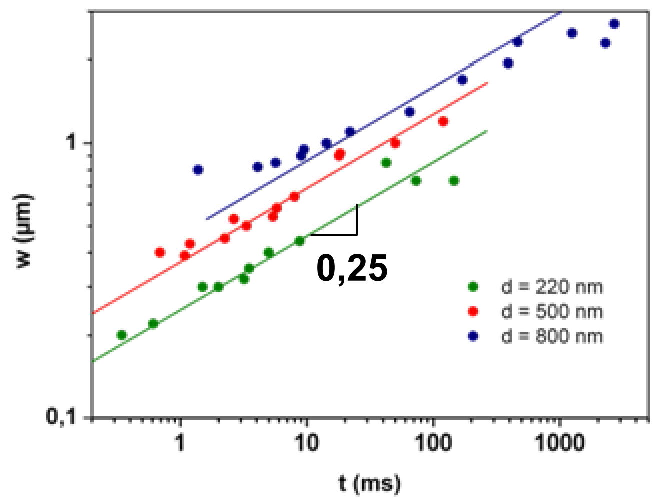
Writing lines



5 µm







t = w/V

➢ **Dynamics of spreading at sub-micron and millisecond scales**

Interpretation

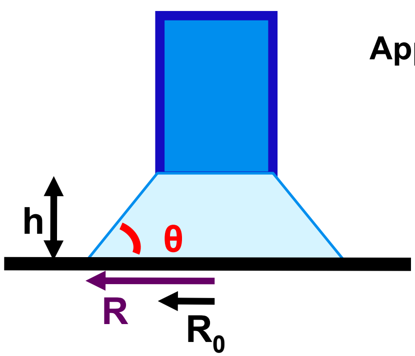
- **Dynamics of spreading : Cox-Voinov equation**

$$\boxed{\theta^3 = \theta_m^3 + 9.V\eta/\gamma.\ln\left(L/s\right)}$$

- **Spreading at constant volume (θ_m=0) : Tanner's law**

$$\theta \propto 1/R^3 \longrightarrow 1/R^9 \propto \frac{dR}{dt} \longrightarrow \boxed{R \propto t^{1/10}}$$

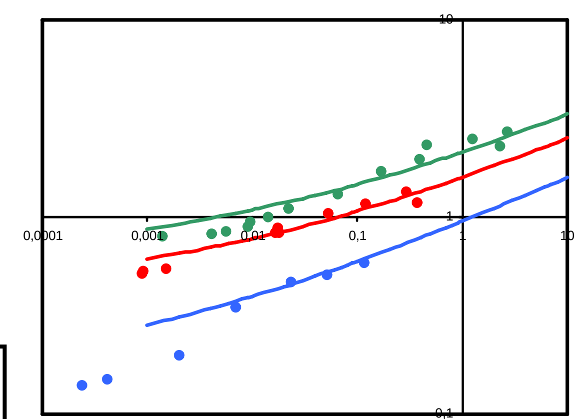
- **Spreading at constant pressure**



Approximations :

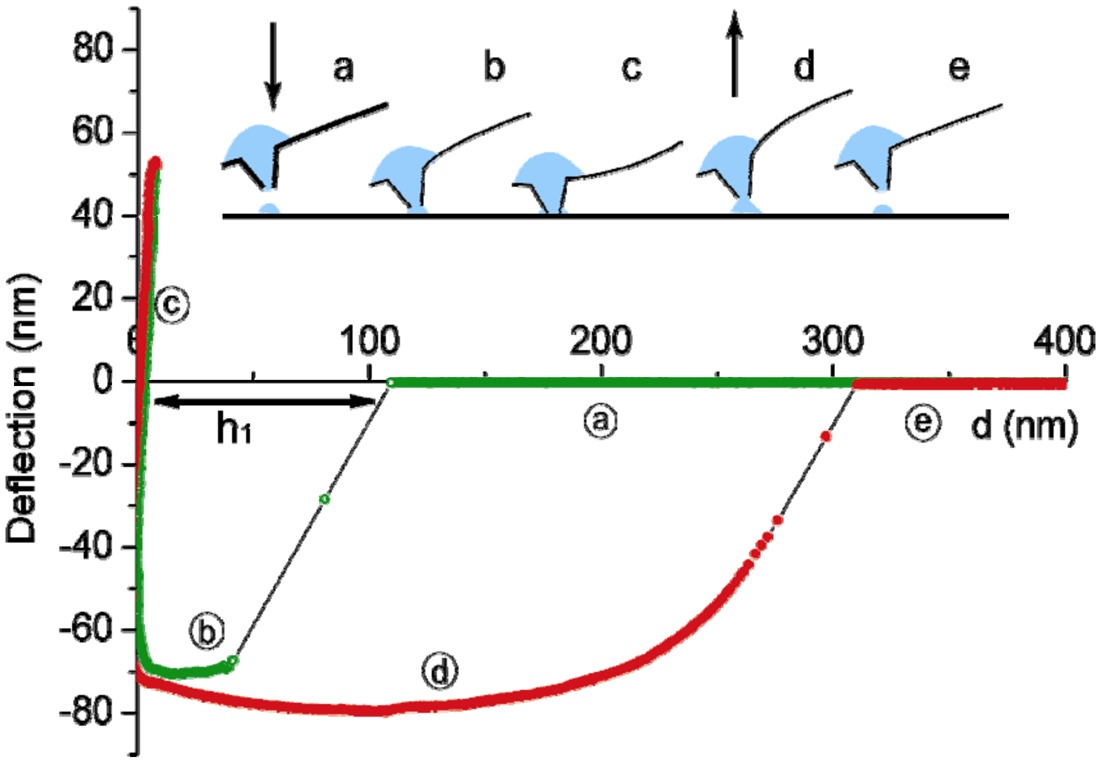
- **2 D**
- **Pressure = 0 → straight interfaces**
- **θm=0**
- **Small angles** $\qquad \theta \approx \dfrac{h}{R-R_0}$

$$1/(R-R_0)^3 \propto \frac{dR}{dt} \longrightarrow \boxed{R-R_0 \propto t^{1/4}}$$

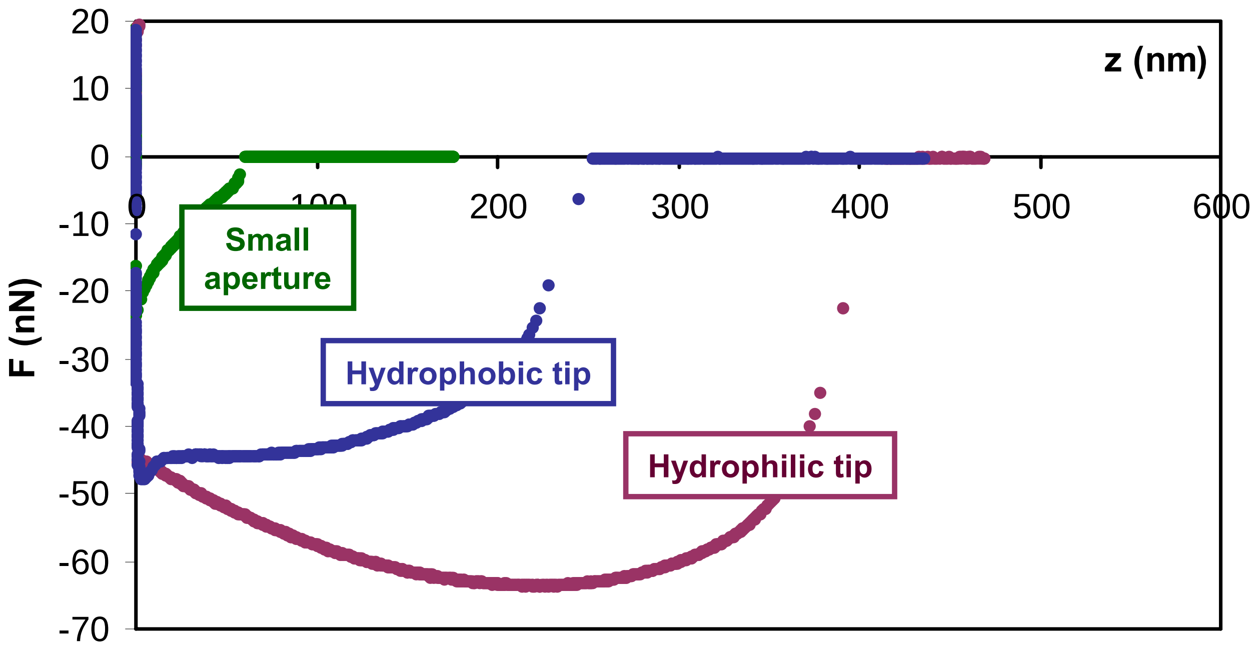


Capillary force during nanodispensing

- Real-time information



Interpretation of retraction force curves



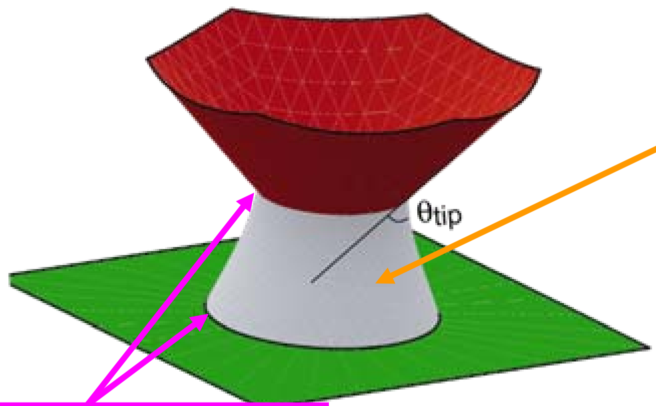
Profile of retraction force curves → ***Liquid transfer mechanism***

Correlation force curve shape - drop size → ***Realtime monitoring of deposit***

Modelization with “surface evolver”

http://www.susqu.edu/brakke/evolver/evolver.html

- **Energy minimization for différent boundary conditions and constraints**



Pressure or volume

Radius or contact angle

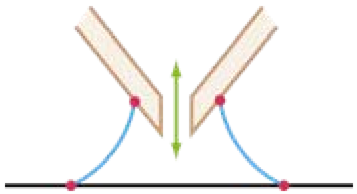
- **Surface shape**
- Energy
- Pressure
- Volume
- **Force**

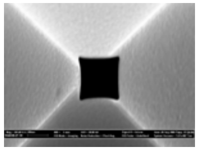
Hydrophilic NADIS tips

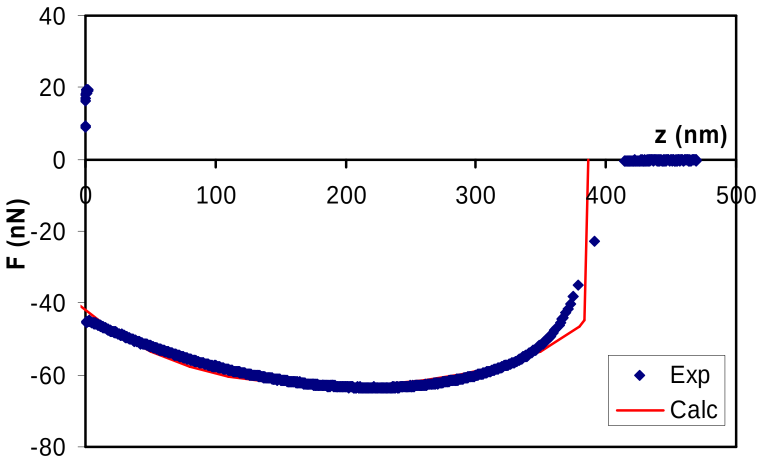
- **Large apertures (400 nm)**

  Constant P

  defined by réservoir







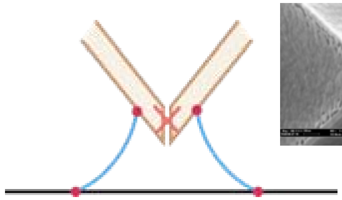
Rsurf = 400 nm, **Rtip** = 300 nm
P = 1.4 10^4 Pa

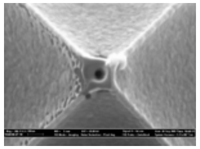
$$\frac{Q_{Poiseuille}}{Q_{Nadis}} \approx 10$$

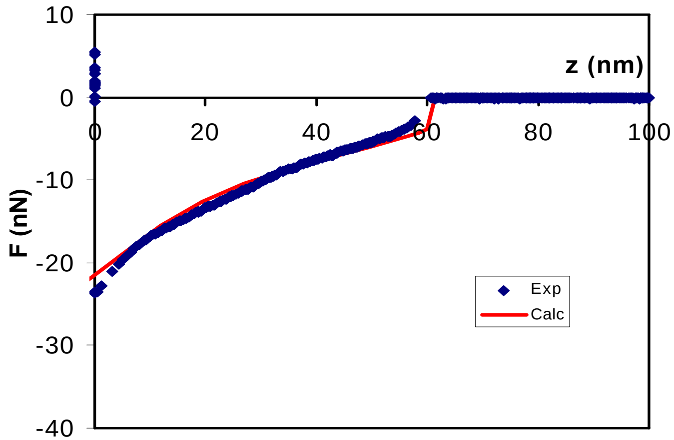
- **Small apertures (35 nm)**

  Constant V

  No liquid flow during retraction







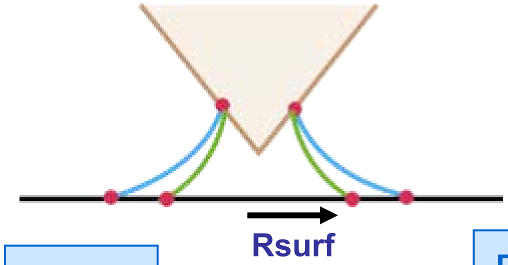
Rsurf = **Rtip** = 37.5 nm
V = 0.4 aL

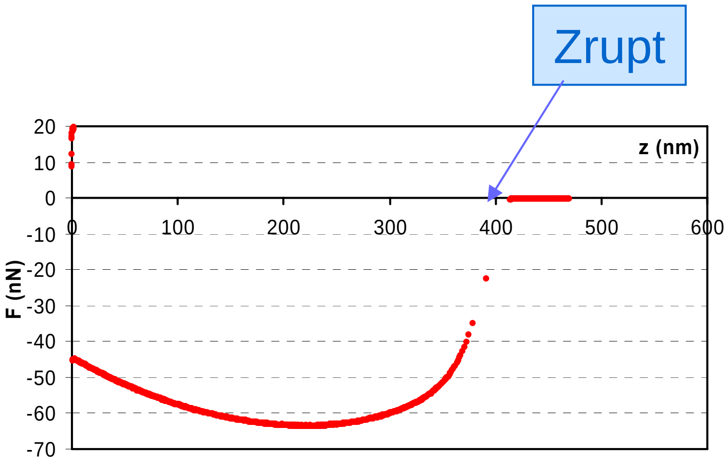
$$\frac{Q_{Poiseuille}}{Q_{Nadis}} \approx 0{,}12$$

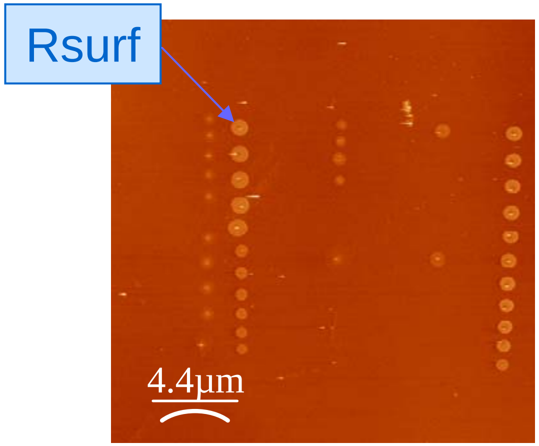
L. Fabié, H. Durou, T.O., *Langmuir*, 2010

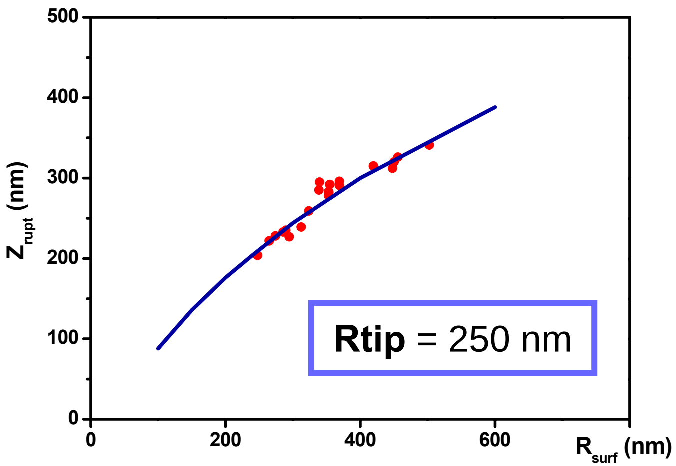
Correlation between droplet size and force curve

- **Hydrophilic tip**









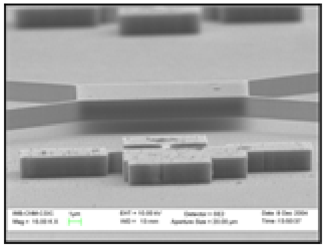
Direct correlation between force curve and deposit size

Evaporation of femto-droplets

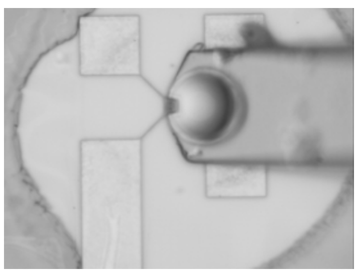
J. Arcamone, et al., *J.Phys.Chem B* (2007)

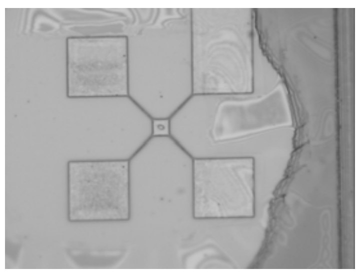
- **Mass sensing device (picogramme)**

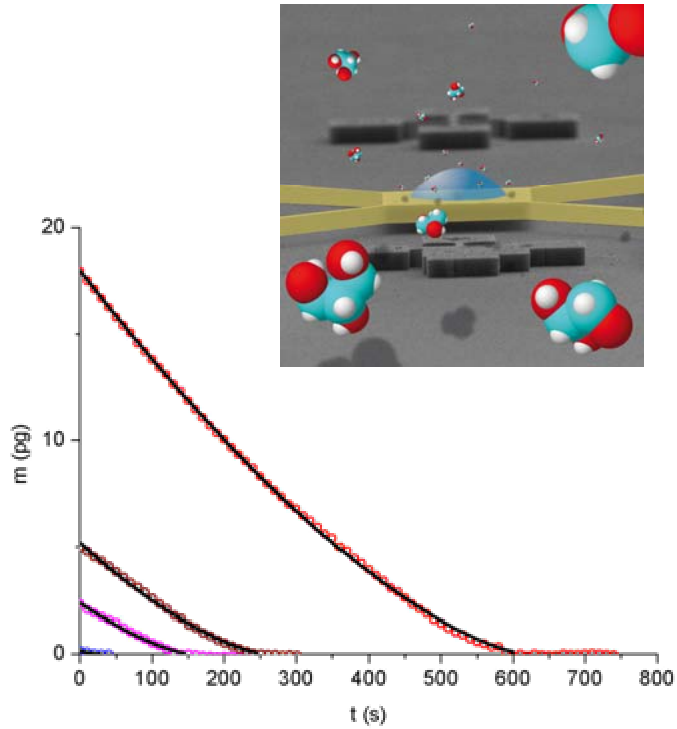
CENTRO NACIONAL DE MICROELECTRÓNICA



- **Droplet dispensing by NADIS**







- Litterature : « microdroplets » in volume (1µl = 1 mm^3)
- This study : « femtodroplets » (1µm^3 = 1 fl)

$\div 10^9$

Conclusion

- **NADIS : manipulation of liquid at sub-micron scale**

  - ✓ Patterning method

    Towards single molecule deposition

    Nanopositioning on predefined structures

  - ✓ Tool for studying liquid dynamics at sub-micron scale

    Spreading dynamics

    Nanomechanics of meniscus

    Evaporation of femtodroplets