Velocity dependence of adhesion in a sliding nanometer-sized contact

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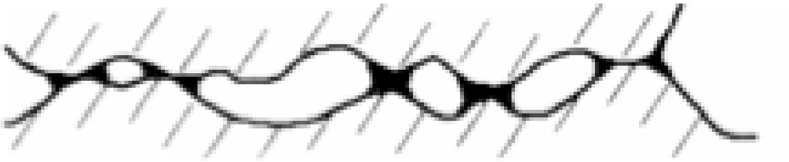
Motivations

- Capillary adhesion is involved in a high number of natural and industrial phenomena (granular media, friction in devices…)



L. Bocquet et al., Nature ***396****, 735 (1998).*

- Little is known about the evolution of the capillary forces in a sliding contact

→ **No direct experimental investigation**

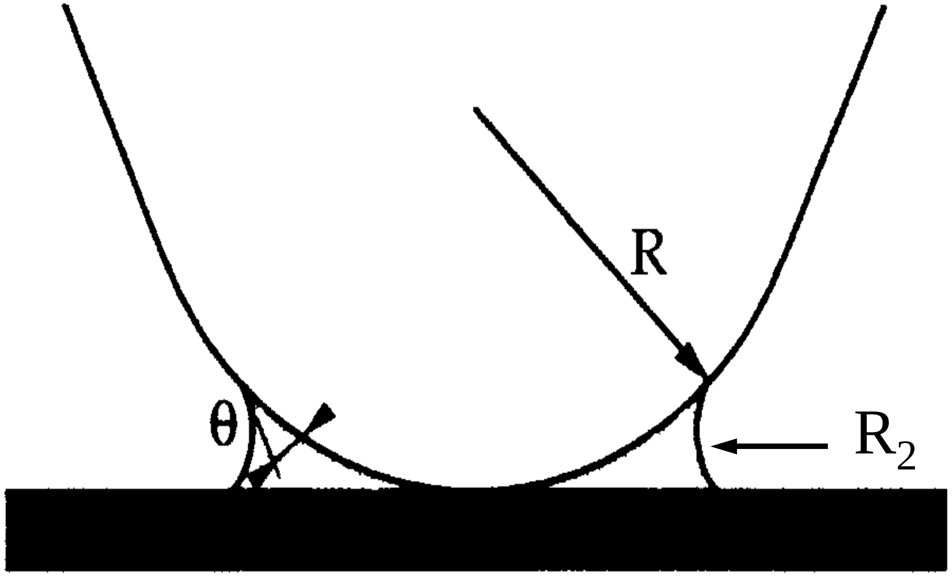
- What about existing models ?

Capillary adhesion

- Water condensation on hydrophilic surfaces

$$R_2 \approx R_K \approx 1-2\,nm$$

$$\frac{1}{R_K} \approx \left[\frac{k_B T}{\gamma_{LV} v_M}\right] \ln\left(\frac{P}{P_S}\right)$$



The volume of the capillary meniscus is dependent on the static contact angle with water of the surfaces in contact, on the relative humidity and on the tip radius

H.-J. Butt, Langmuir 24, 4715 (2008).

Capillary adhesion

- The Laplace pressure in the meniscus generates an adhesive force $F_{capillary} = \Delta P \times WetContactArea$

- For AFM experiments and hydrophilic surfaces,

$$\mathrm{F}_{\mathrm{capillary}} = 2\pi \mathrm{R}_{probe} \gamma_{\mathrm{LV}} \times (\cos\,\theta_{\mathrm{sample}} + \cos\,\theta_{probe}) = 10\text{-}100\ \mathrm{nN}$$

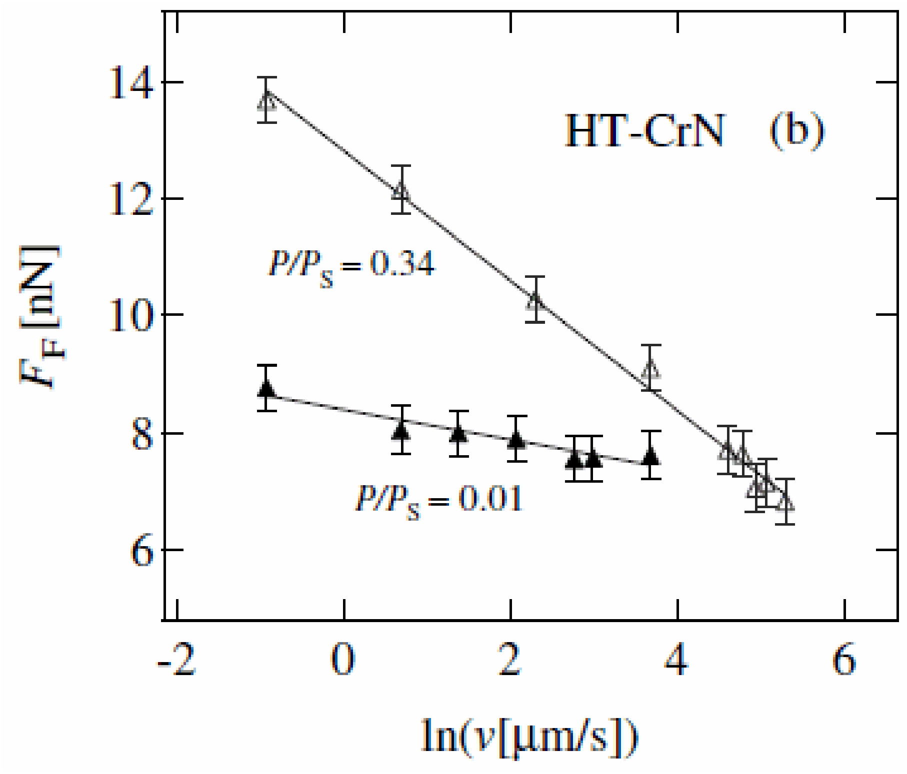
θ : Meniscus static contact angle with water

J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic Press, San Diego, 1997).

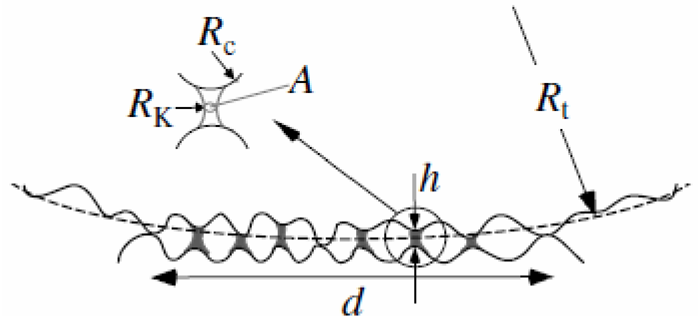
- Capillary forces are comparable to the acting normal load in friction at the nanoscale
- Capillary force adds to the external applied load (F_N) and plays an indirect role in friction mechanisms.

$$F_F = \mu\left(F_{adhesion \approx capillary} + F_N\right)$$

Capillary adhesion in a sliding contact



Riedo et al. PRL 88 (2002) 185505



- Multi-asperity contact
- Meniscus nucleation needs time (1 ms)
- Thus, capillary force is sliding velocity dependent
- The linear decrease of the friction force is related to the vanishing of the capillary forces

AFM experimental limitations

- AFM back and forth scanning :

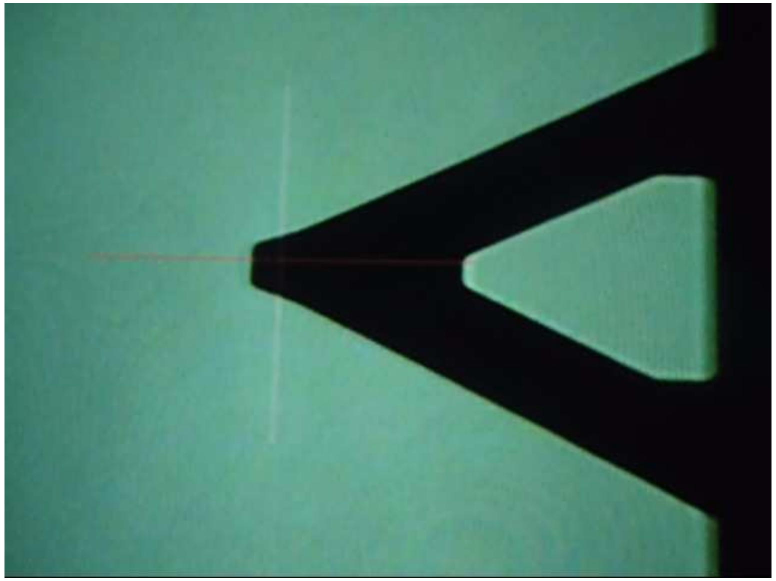
  Meniscus nucleates and grows during stop periods but vanishes during sliding

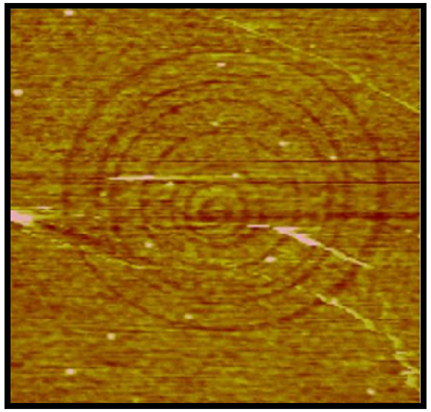
- Is that possible to achieve a stationary state ?

- Is that possible to measure directly the capillary adhesion force as a function of the sliding velocity ?

AFM experimental limitations

AFM circular mode





Circular tracks on a GaAs sample obtained with the circular mode

- Probe is submitted to a circular displacement in the plane of the surface:

  Circular frequency : 100 Hz

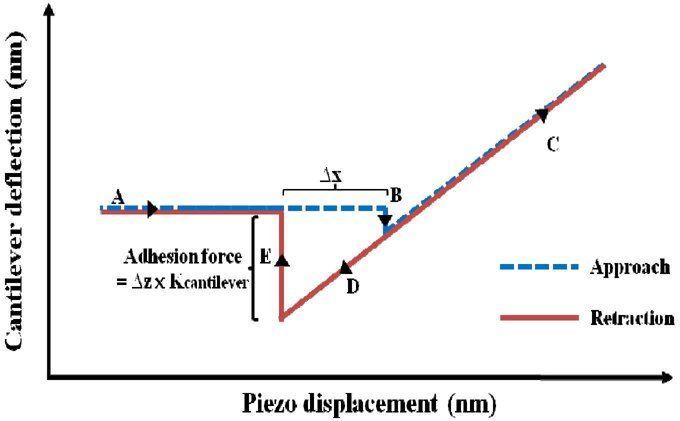
  Circular radii : 0 nm to 1500 nm

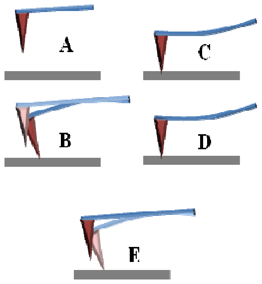
  Sliding velocities : 0 to 1 mm.s^{-1}
- Relative displacement at constant and continuous velocity: Stationary state
- Combination of the circular mode with the force spectrum mode:

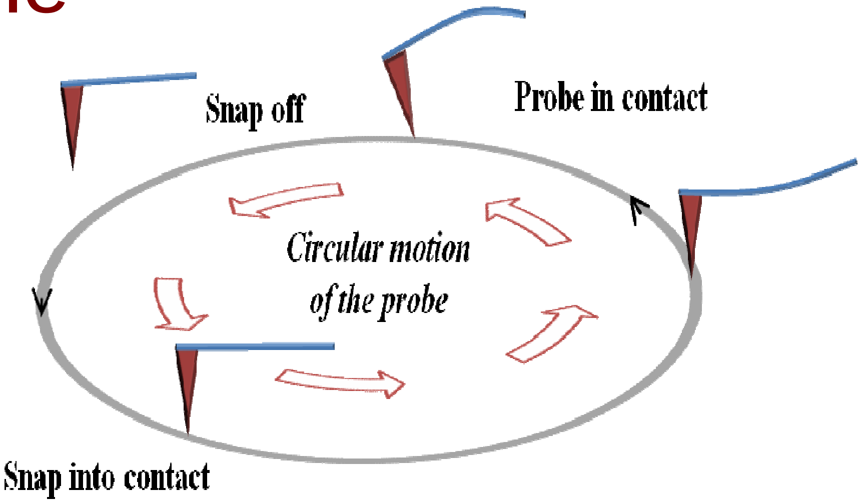
Measurement of adhesion forces as a function of the sliding velocity

Experimental set-up

Principle







- Si_3N_4 probes R = 15-40 nm, θ =70°
- Retracting velocity is set at a constant value of 0.1μm.s

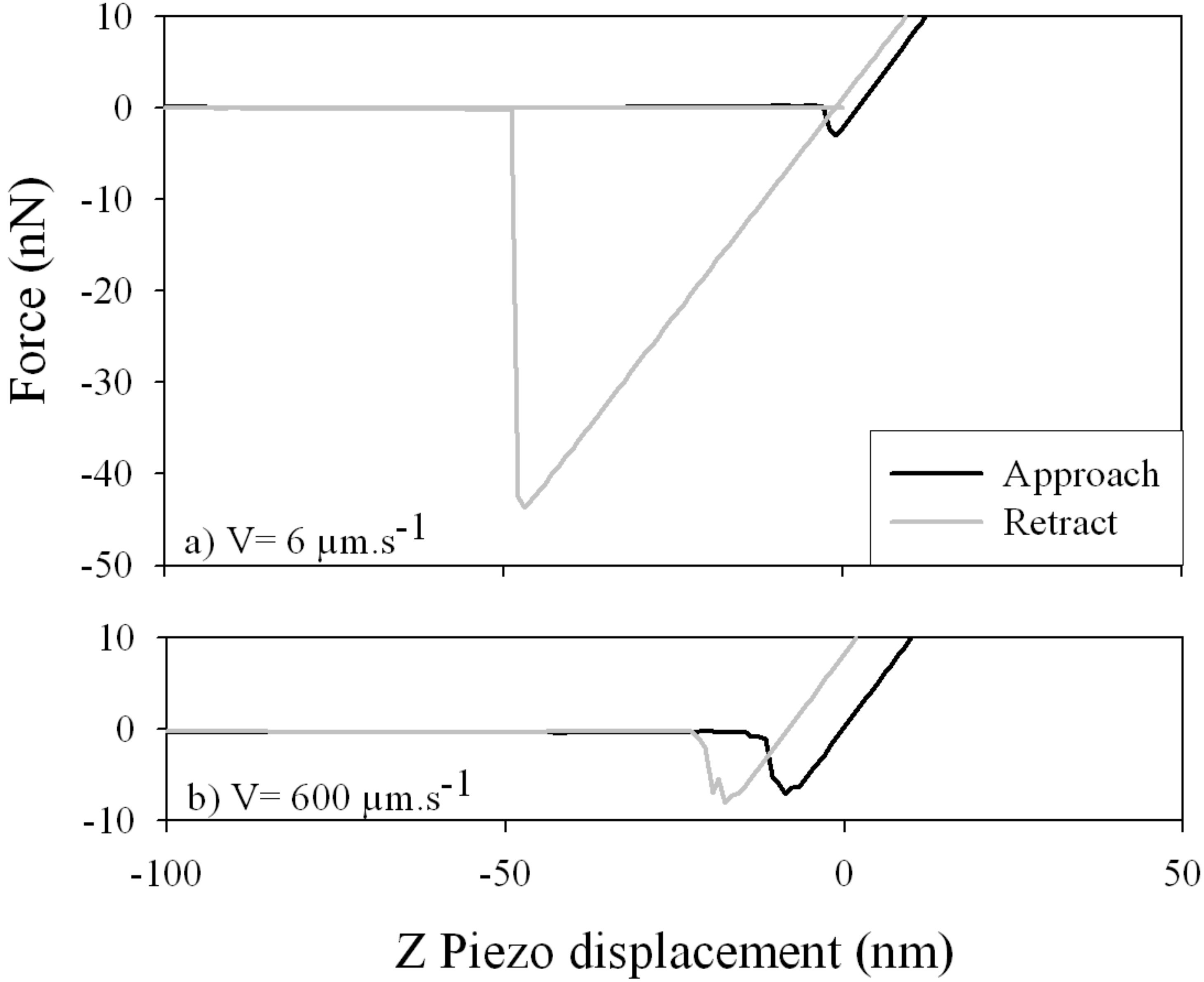
Hydrophobic Surfaces

	Rq (nm)	θ (°)
HOPG	0.05	105
Si_{CH3}	0.20	100

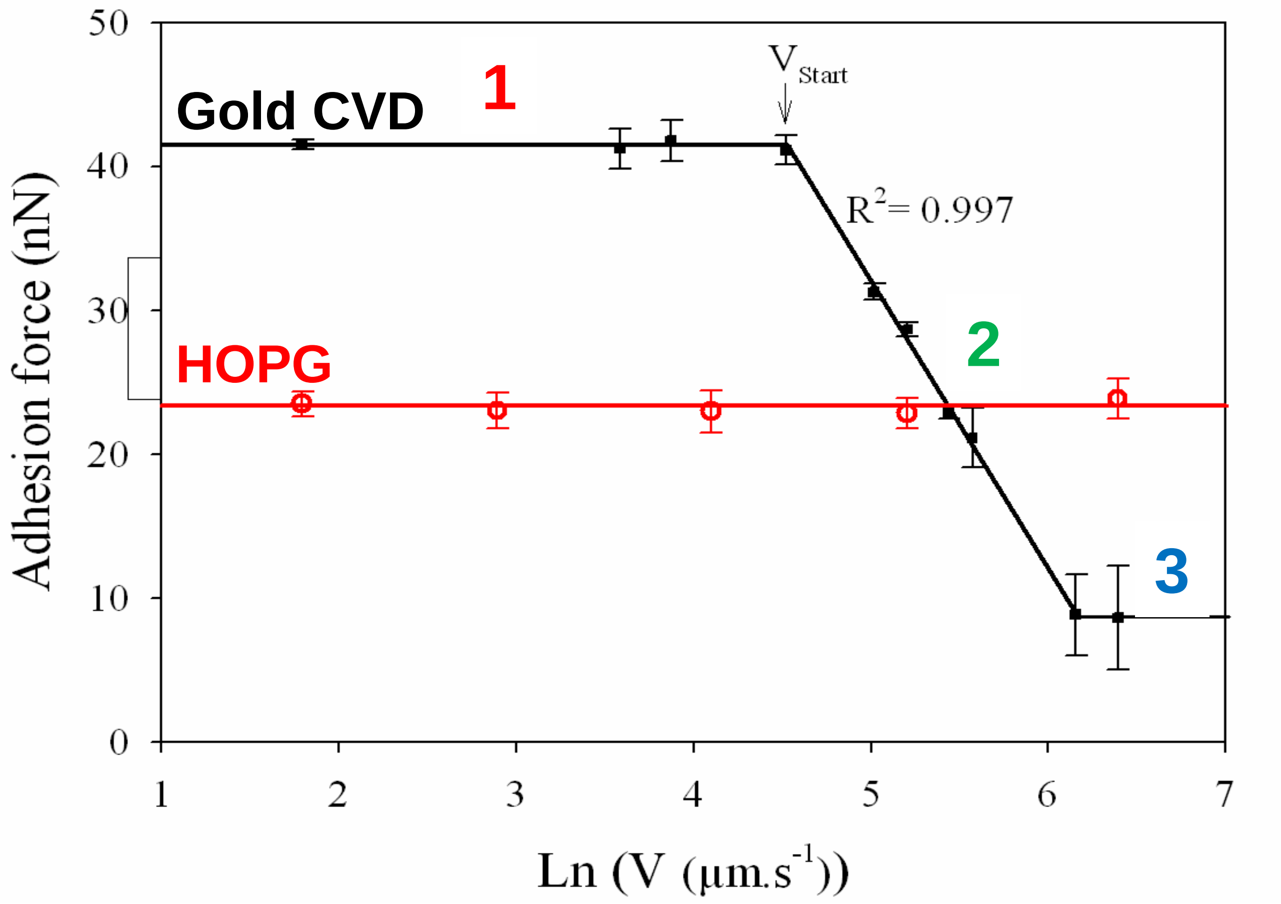
Hydrophilic Surfaces

	Rq (nm)	θ (°)
Mica	0.03	5
Si	0.16	60
Si_3N_4	0.34	70
Gold	0.23	75

Hydrophilic surface – Gold CVD



Hydrophilic-hydrophobic surfaces
Adhesion vs Sliding velocity



3 Regimes :

1 : Meniscus at the equilibrium state

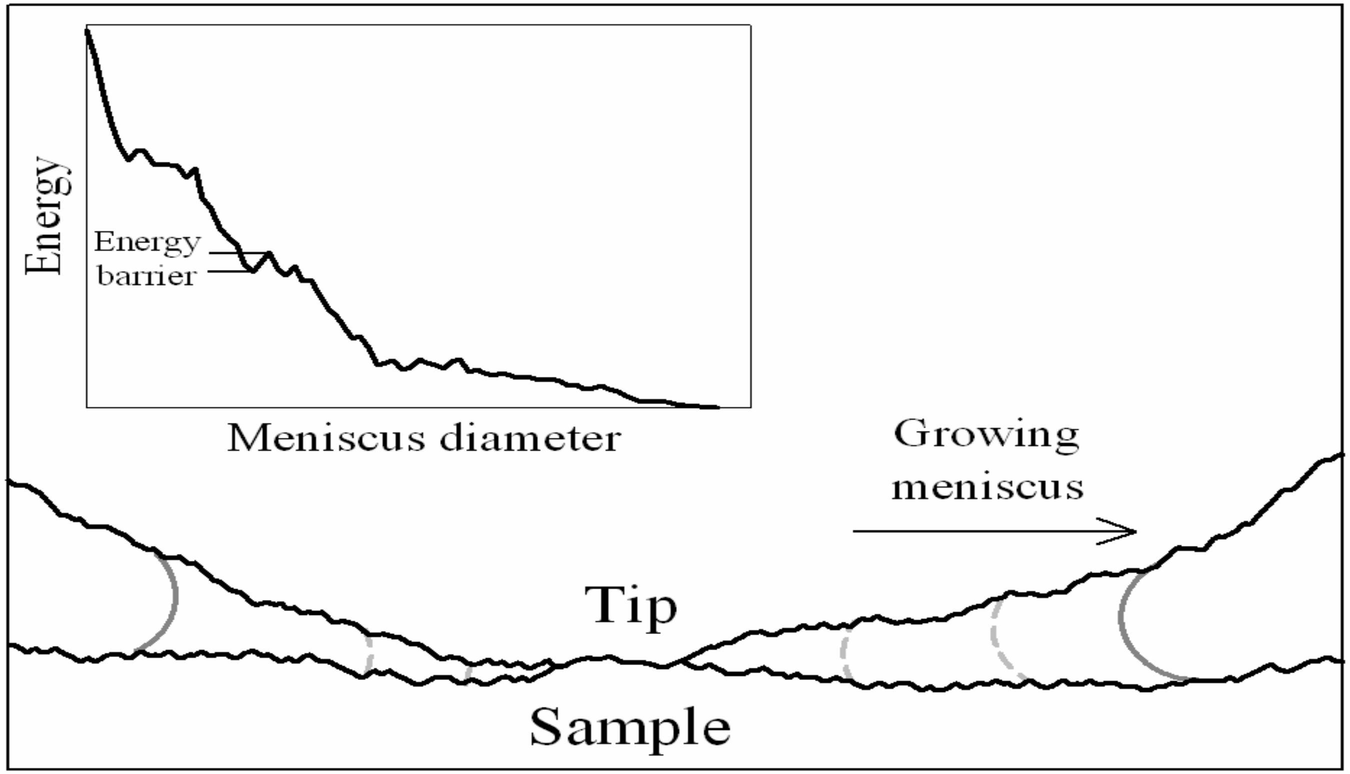
2 : Meniscus not at the equilibrium state

3 : No more capillary meniscus

V_{start} defines a threshold sliding velocity from which the capillary meniscus cannot reach its equilibrium state anymore.

Model

In regime 2, the adhesive force decreases linearly with a logarithmic increase of the sliding velocity. This suggests a thermally activated process, like a growth process of a capillary meniscus, in which water molecules have to overcome energy barriers due to surface defects.



Model based on the growth process of a capillary meniscus

The sliding velocity, *V*, is related to the time, t, needed to overcome the total distribution of energy barriers due to surface defects

$$t = t_0 . \exp\left[\frac{\Delta E}{k_B T}\right]$$

then

$$V \propto t^{-1} \propto \exp\left[-\frac{\Delta E}{k_B T}\right]$$

In a first approximation, ΔE is proportional to the perimeter of the wet contact areas

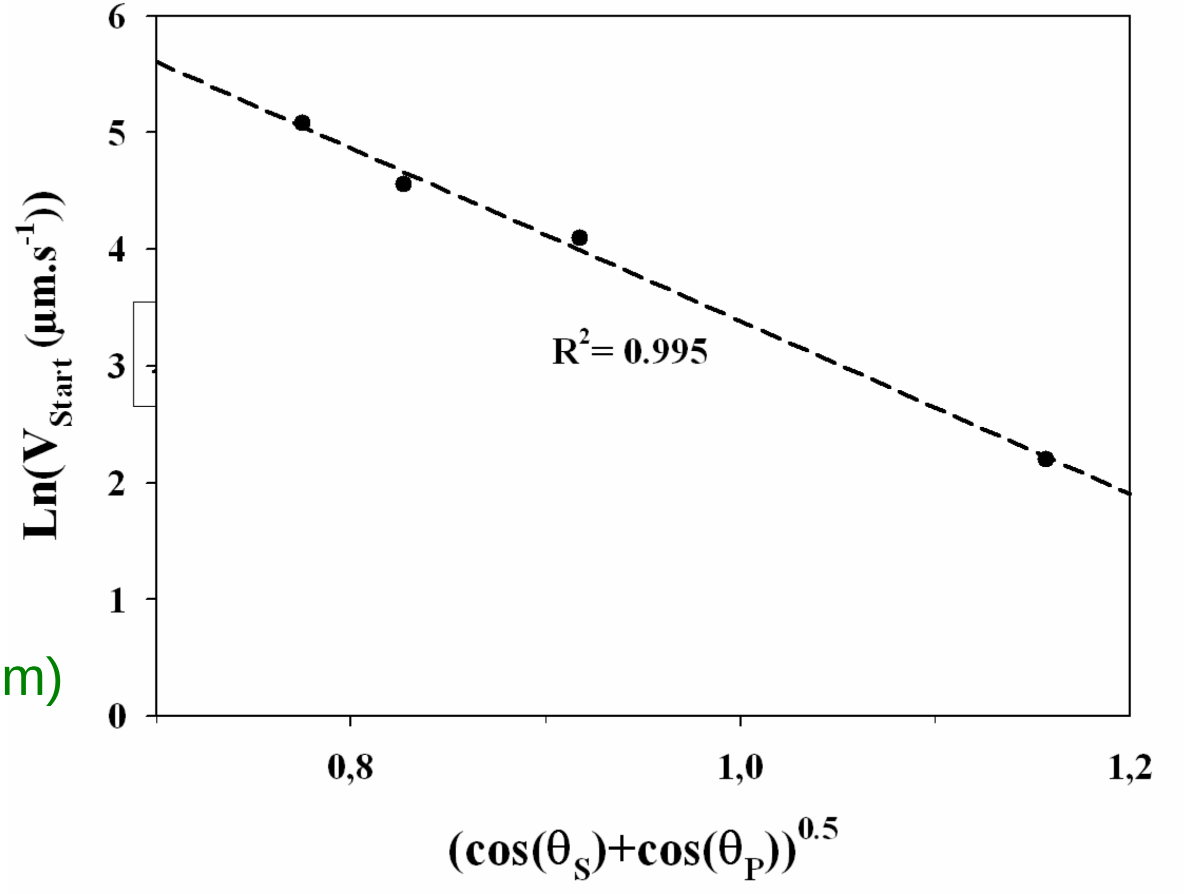
$$\Delta E \propto \sqrt{R_{probe} R_K} \sqrt{\cos\theta_{probe} + \cos\theta_{sample}}$$

and at $V = V_{start}$

$$\ln(V_{start}) \propto \sqrt{R_{probe} R_K} \sqrt{\cos\theta_{probe} + \cos\theta_{sample}}$$

Experimental dependence of $\mathrm{Ln}(V_{start})$ on contact angle

$$\ln\left(V_{start}\right) \propto \sqrt{R_{probe} R_K} \sqrt{\cos\theta_{probe} + \cos\theta_{sample}}$$



Experimental conditions:

- Different surfaces
- Humidity 40%
- Same probe (R_{probe}= 30 nm)
- *$R_{probe}.R_K$= Constant*
- *Temperature = constant*

Conclusions

- Innovative experimental set-up :

AFM circular mode

- Direct experimental evidence of a linear decrease of the capillary forces with a logarithmic increase of the sliding velocity, for hydrophilic surfaces.
- This dependence could be related to a thermally activated growth process of the capillary meniscus.
- The energy barrier is linked to the meniscus perimeter (humidity, probe radius and contact angles)

Acknowledgements / References of our work

- Agence Nationale de la Recherche: Pénélope par Médée - ANR 08 JCJC 0051 01
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