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An introduction to Atomic Force Microscopy

Olivier Arnould

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$$I_\varepsilon(\varphi) = \int \dots$$

$$\nabla \varphi(x)$$

$$\lim_{\det F \rightarrow 0^+}$$

$$W(\cdot, F) = \infty$$



Chemical imaging of plant cell walls, PhD-course
June 4-8 2018, University of Copenhagen

An introduction to Atomic Force Microscopy

Olivier ARNOULD

WOOD TEAM

Laboratory of Mechanics and Civil Engineering (LMGC)

CNRS/Université de Montpellier

France



LABORATOIRE DE MÉCANIQUE ET GÉNIE CIVIL - UM/CNRS

$$I_\varepsilon(\varphi) = \int \varphi(u) |du|$$

$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

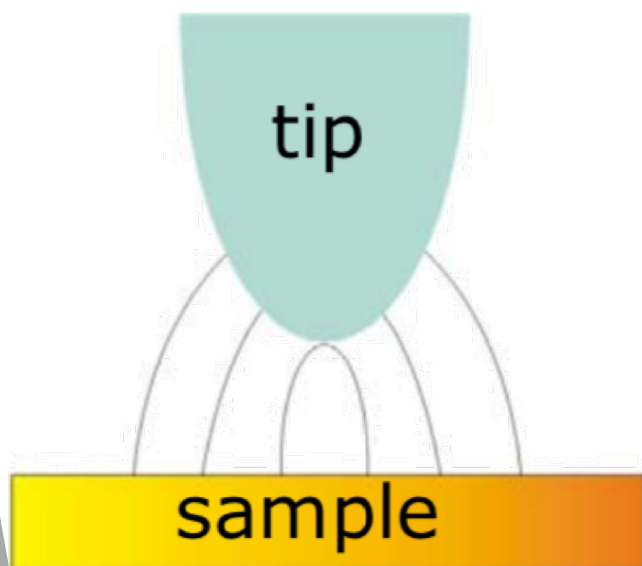
Outline

- Brief history and basic principles of scanning probe microscopy
- AFM principle and typical set-up
 - Tip probe-sample surface interactions
 - Tip and cantilever
 - Deflection sensor and scanner
 - Whole set-up
- Contact mechanics
- Operating modes
 - Contact
 - Intermittent
 - Force-distance curve and mechanical characterisation modes
- Image analysis and artefacts
- Sample preparation

$$I_\varepsilon(\varphi) =$$

Scanning Probe Microscopy

IDEA: To measure (and use) the local (near field) probe (sharp tip)-sample interactions to map the surface morphology (topography) and physical properties



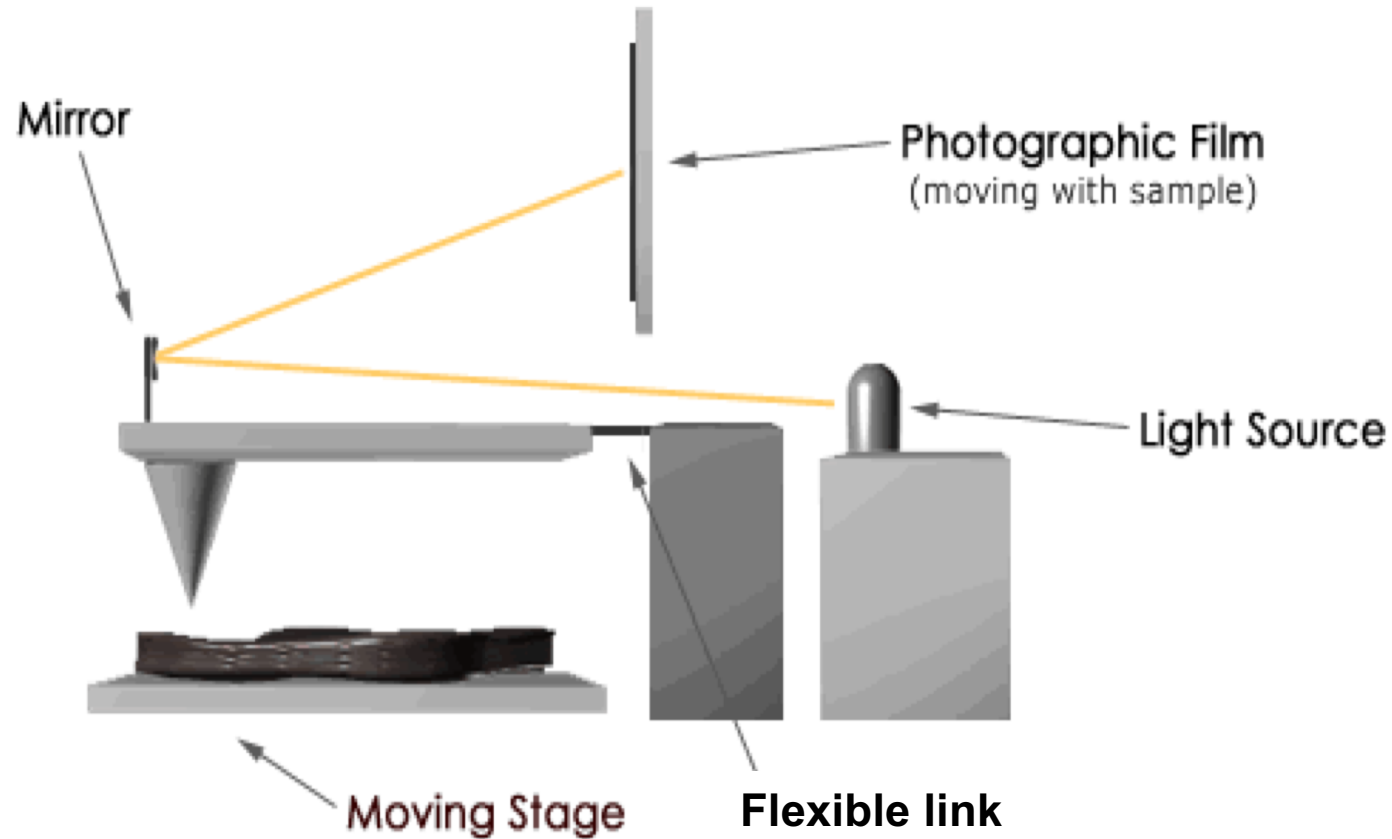
- ✓ Image resolution limited by probe-sample interaction volume, not by diffraction!
- ✓ Interaction can modify surface
→ nanolithography possible
- ✗ Scanning technique (quite) slow
- ✗ Limited maximum image size



All data in SPM are subjected to interpretation

$$I_\varepsilon(\varphi) = \int |\varphi(u)| du$$

History - Forerunners



Optical stylus (optical/light lever) profilometer by Schmalz in 1929
 ≈ 25 nm vertical resolution! (magnification $> 1000x$)

$$I_\varepsilon(\varphi) =$$

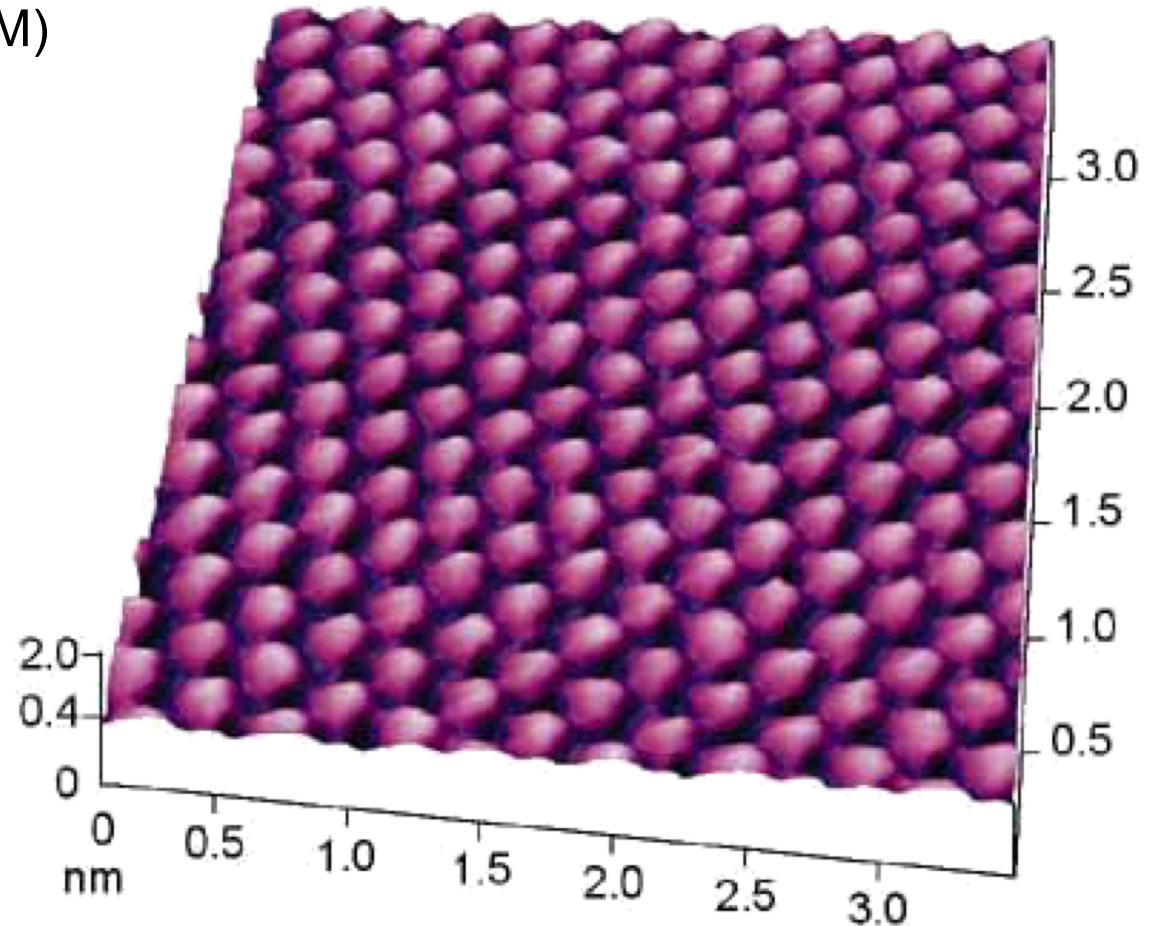
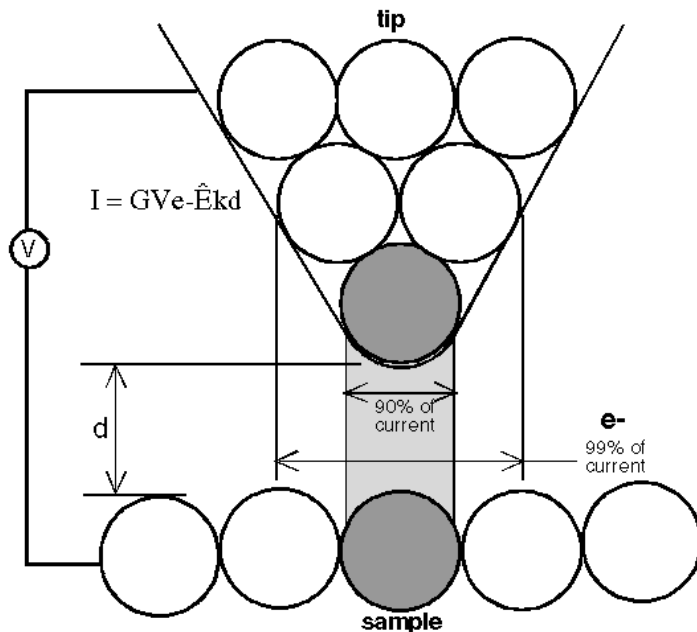
$$\int \varphi(x) dx$$

$$\lim$$

$$W(\cdot, F) = \infty$$

History - Forerunners

Scanning Tunnelling Microscopy (STM)
by Binnig and Rohrer in 1981
(Nobel Prize in 1986)



HOPG atoms view by STM

[www.ntmdt.com]

Drawback
need conductive material
and high vacuum!

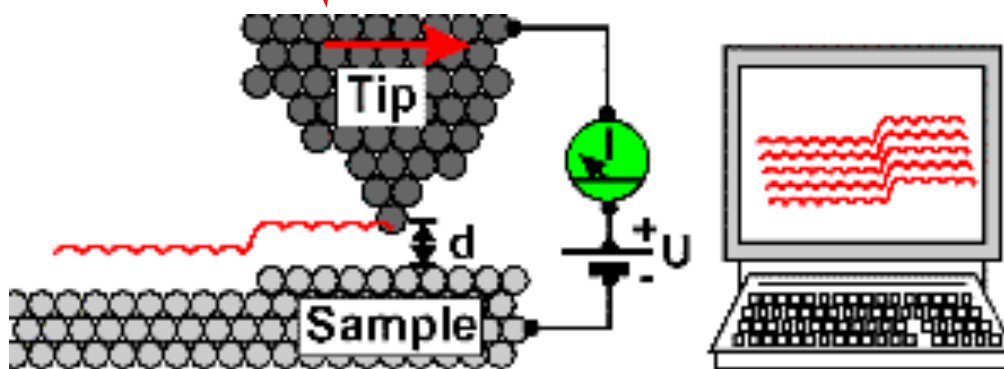
$$I_{\varepsilon}(\varphi) = \int_{\varphi} |\nabla \varphi(u)| du$$

$$\lim_{\varepsilon \rightarrow 0} \int_{\varepsilon} \varphi(u) du$$

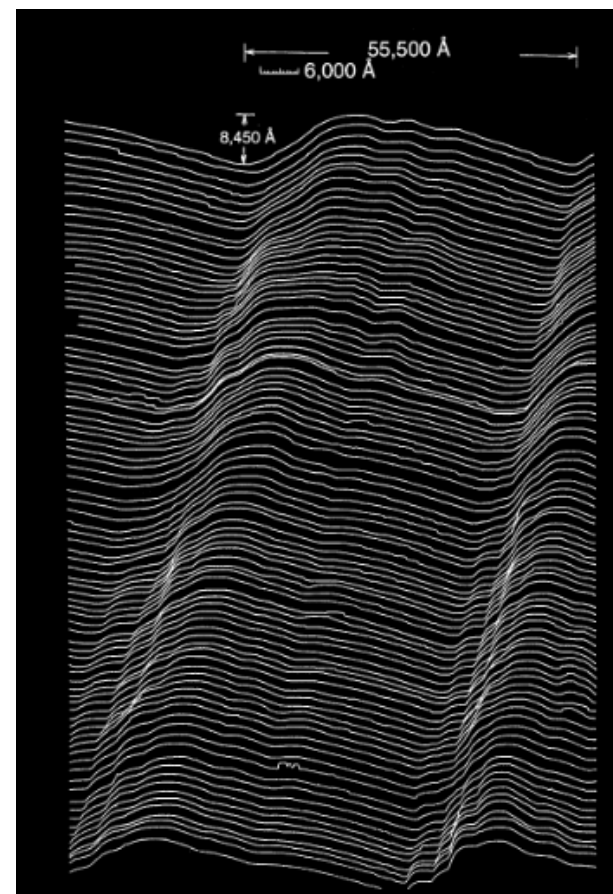
$$W(\cdot, F) = \infty$$

History - SPM timeline

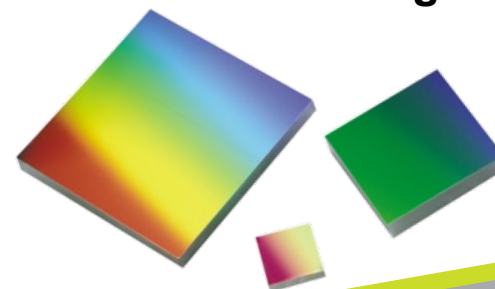
- 1972 Russel Young's topografiner →
- 1981 First STM results in the lab by Binnig, Rohrer and Gerber
- 1982 First publication - PRL
- 1984 Near field Optical Microscope
- 1985 Invention of AFM at Stanford by Binnig, Gerber and Quate
- 1986 Nobel Prize to Ruska, Binnig and Rohrer
- 1987 Dynamic AFM by Wickramasinghe
- 1987 First commercial instruments – spin-off from Quate Group in Stanford (Park Scientific) and Hansma Group in UCSB (Digital Instruments)
- 1989 IBM in atoms, by Don Eigler
- 1990 First microfabrication of AFM tips by Albrecht et al.



Constant current or constant height imaging



Topographic map of ruled diffraction grating



Rev. Sci. Instr. 43(7), 1972

$$I_{\varepsilon}(\varphi) = \int_{\varphi} |\nabla \varphi(u)|^2 du$$

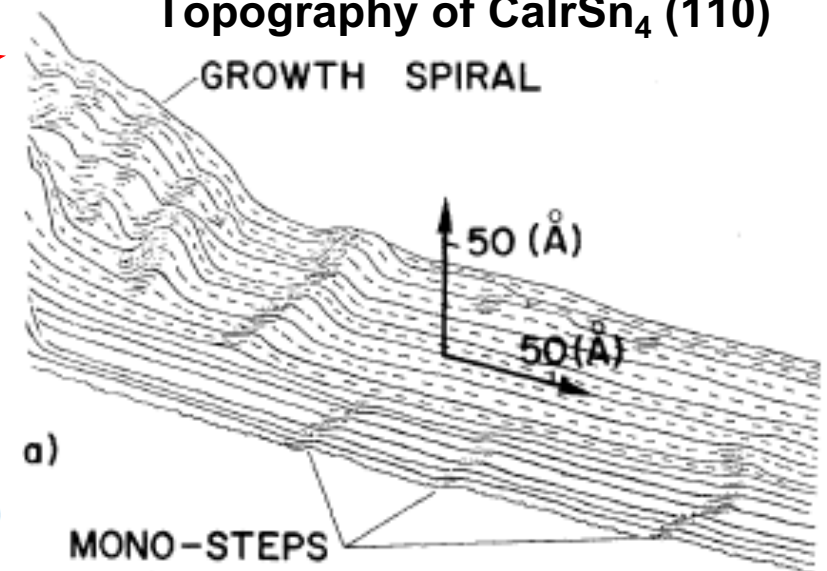
$$\lim_{\varepsilon \rightarrow 0} \int_{\varphi} |\nabla \varphi(u)|^2 du = \infty$$

$$W(\cdot, F) = \infty$$

History - SPM timeline

- 1972 Russel Young's topografiner
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Topography of CalrSn₄ (110)



Phys. Rev. Lett., 49(1), 1982

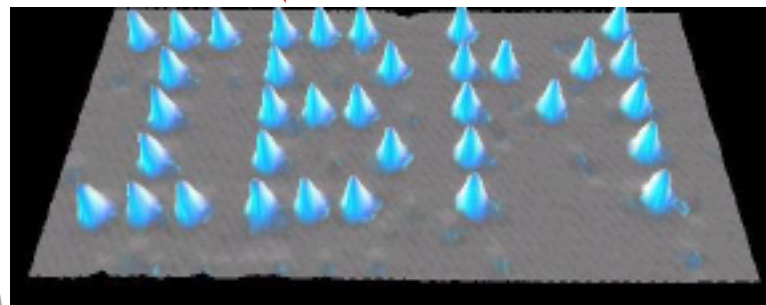
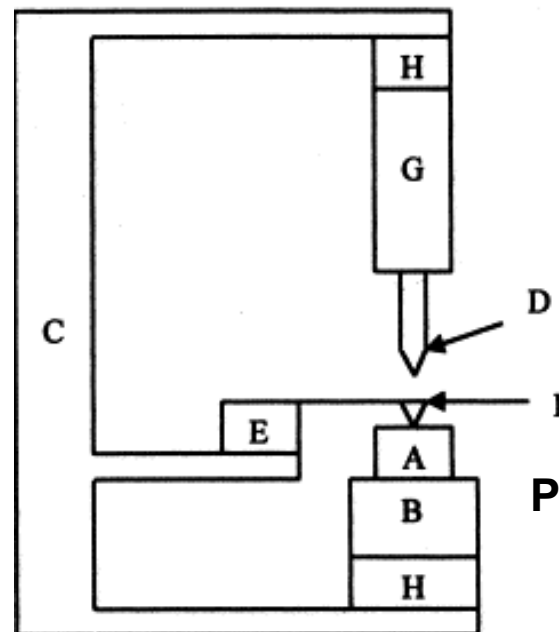


Image of Xenon atoms moved on Nickel (110) surface using an STM tip



- A: Sample
- B: AFM feedback and scanners
- C: Aluminium block
- D: STM tip (Au)
- E: Modulating piezo
- F: AFM tip = STM sample
- G: STM feedback
- H: Viton to damp mechanical vibrations

**Original AFM design
Phys. Rev. Lett., 56 (9) (1986)**

$$I_{\varepsilon}(\varphi) =$$

Scanning Probe Microscopy

SPM

STM

Scanning Tunneling
Microscopy

Tunneling current

AFM

Atomic Force
Microscopy

Local interaction forces
(Van der Waals, elastic,
electrostatic, friction,
adhesion...)

SNOM

Scanning Near-field
Optical Microscopy

Evanescent optical
waves

Nanoindentation
Mechanical
modes

Electrostatic
Force Microscopy
(EFM)

Conductive
AFM (C-AFM)

Scanning Thermal
Microscopy (SThM)

Chemical force
microscopy

A question of probe tip (apex)!

$$I_\varepsilon(\varphi) = \int \sqrt{\varphi'(x)} dx$$

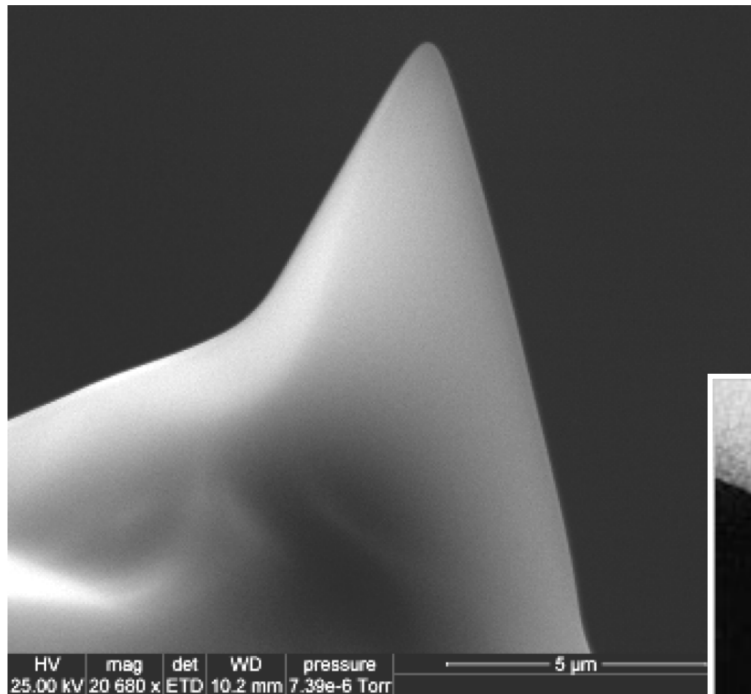
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Probe tip-sample interactions

- Tip (feels the surface)

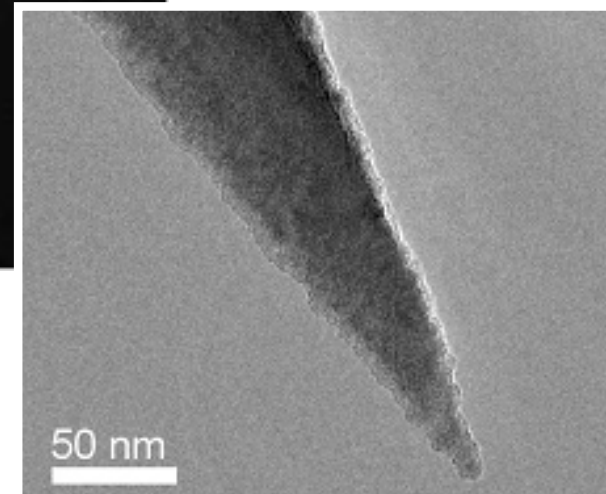
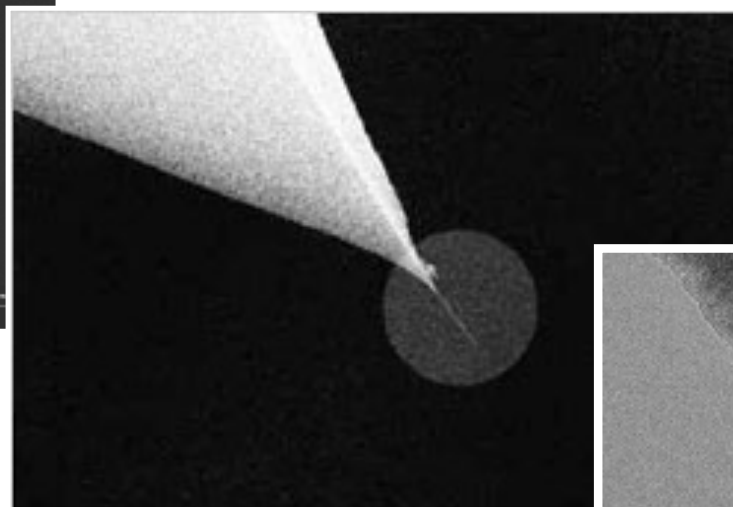
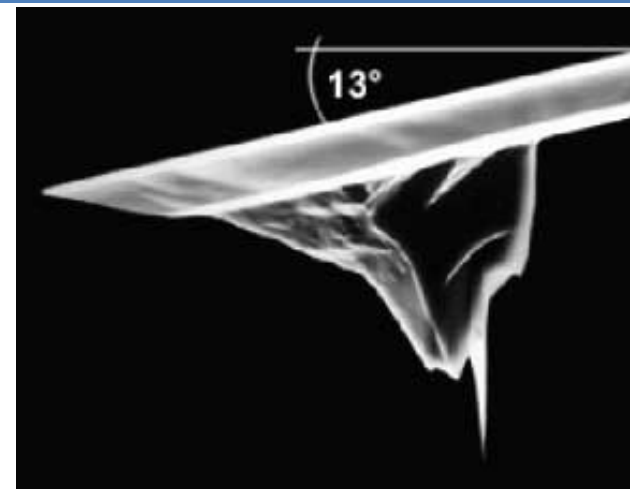


Apex radius $R \approx 2\text{-}200\text{nm}$

Height $H \approx 10\mu\text{m}$

Coating (Pt, CoCr, W_2C , diamond, etc),
functionalization, ...

Calibration!



[NanoAndMore, NT-MDT, BudgetSensor, ...]

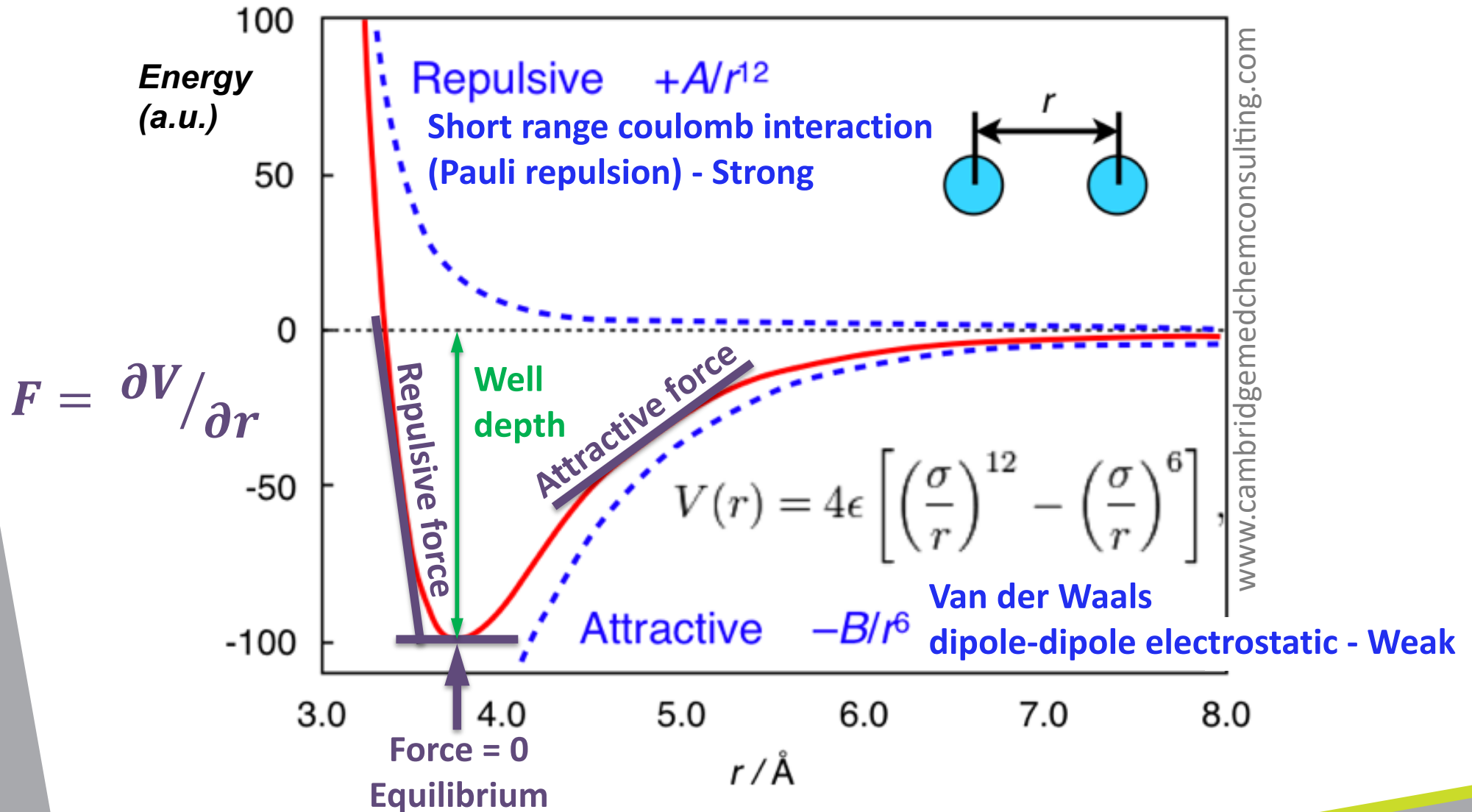
→ www.nanoandmore.com/afm-probes

$$I_{\epsilon}(\varphi) = \int \nabla \varphi(\mathbf{r}) \cdot d\mathbf{r}$$

$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

Probe tip-sample interactions

The Lennard-Jones potential



$$I_\varepsilon(\varphi) = \int_{\varphi} \nabla \cdot (\epsilon \nabla \varphi) \, dV$$

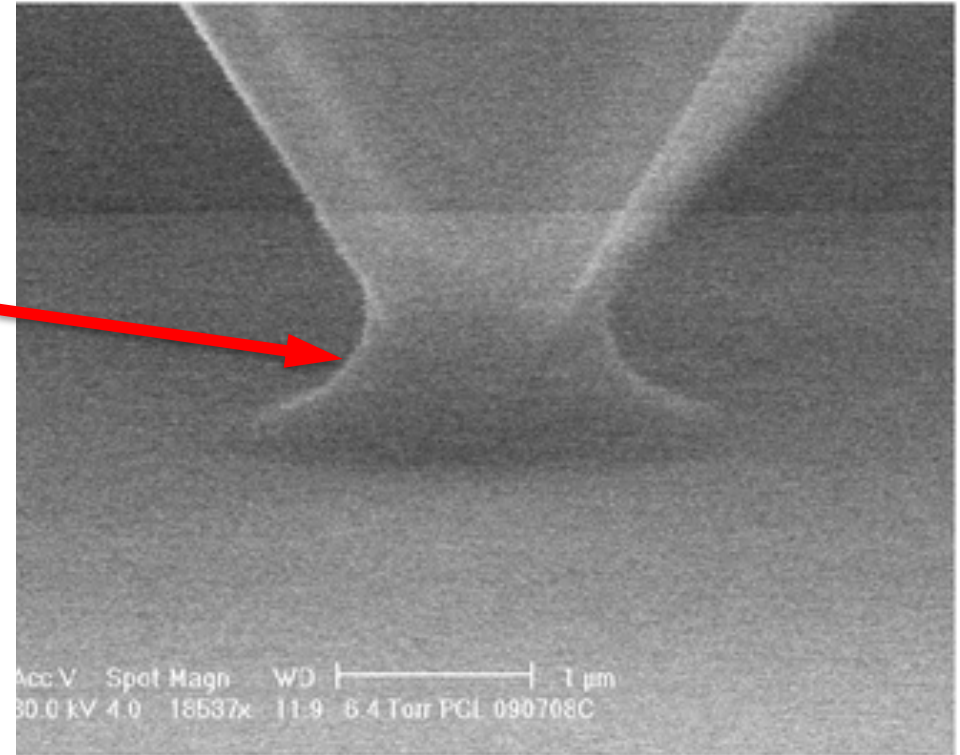
lim

$$W(\cdot, F) = \infty$$

Probe tip-sample interactions

Capillary force

Köber et al, Small 2010, 6, 2725



van Honschoten et al, Chem. Soc. Rev., 2010, 39, 1096-1114

$$F_{cap} \approx \frac{4\pi R \gamma \cos \theta}{(1 + d/h)} \quad \blacktriangleright \quad \cos \theta = \frac{\cos \theta_1 + \cos \theta_2}{2}$$

Surface tension of water: $\gamma = 72 \text{ mJ} / \text{m}^2$

Max at snap (pull) out

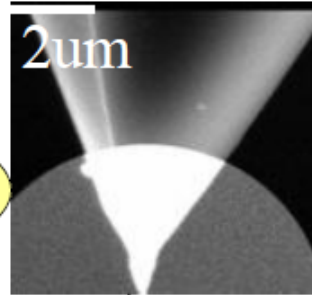
$$F_{cap} = 4\pi R \gamma$$

$$I_{\varepsilon}(\varphi) = \int \nabla \varphi(\mathbf{r}) \cdot d\mathbf{r}$$

$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

Probe tip-sample interactions

$$\vec{F}_{t/s} = \vec{F}_{E/M} + \vec{F}_{cap} + \vec{F}_{VdW} + \vec{F}_{rep}$$



Tip-surface Gap (z)

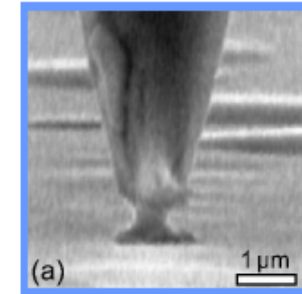
$$F_{elect} = \frac{1}{2} \frac{\partial C}{\partial z} V^2 \sim \frac{1}{2} \frac{\varepsilon_0 \varepsilon_r S}{z^n} V^2$$

$z > 20\text{nm}$

Electrostatic force ($1/z^n$; $1 < n < 2$) : Long range interaction => electric modes

$$F_{cap} = f(\gamma, R, \theta_{p/eau}, \theta_{eau/surf}, z)$$

Capillary Force



$z > 5\text{nm}$

$$F_{vaw}(z) = \frac{HR}{6z^2}$$

Van der Waals Force

$$F_{repulsion}(z) = \frac{A}{z^m}$$

$z < 0.5\text{nm}$

Repulsive Force ($m > 3$)

$$I_\varepsilon(\varphi) = \int \varphi(u) |du|$$

$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

AFM principle and typical set-up

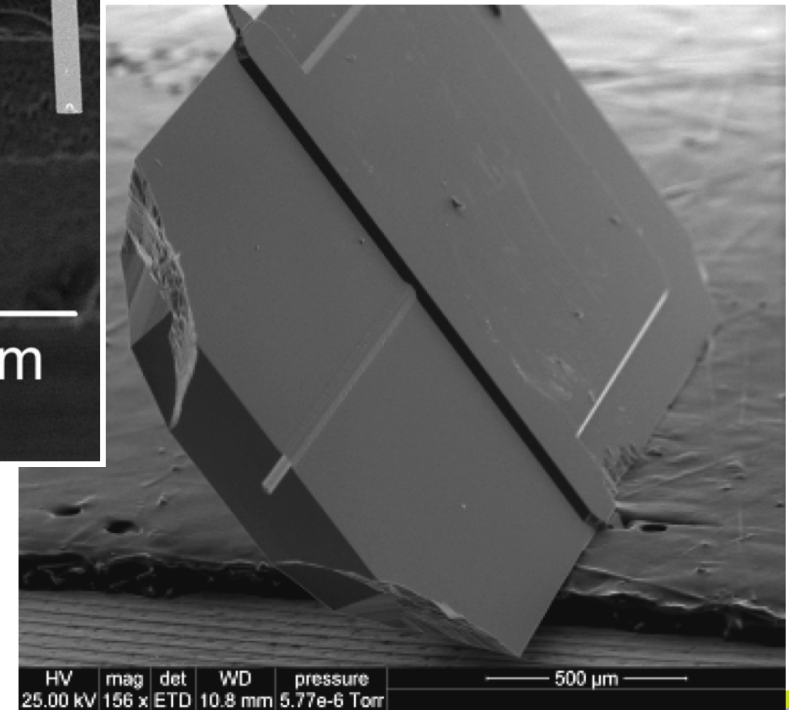
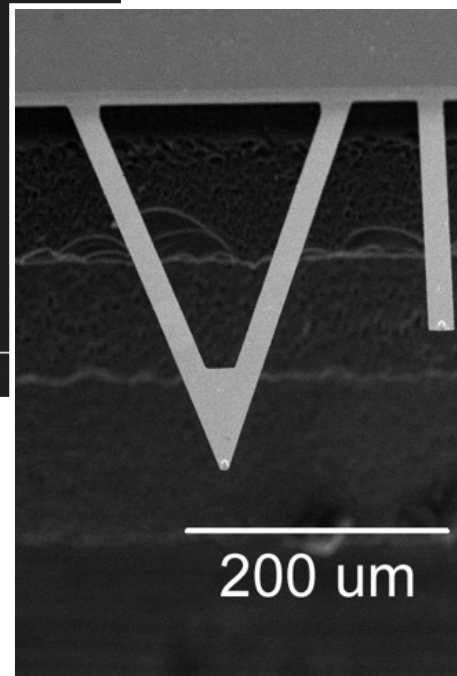
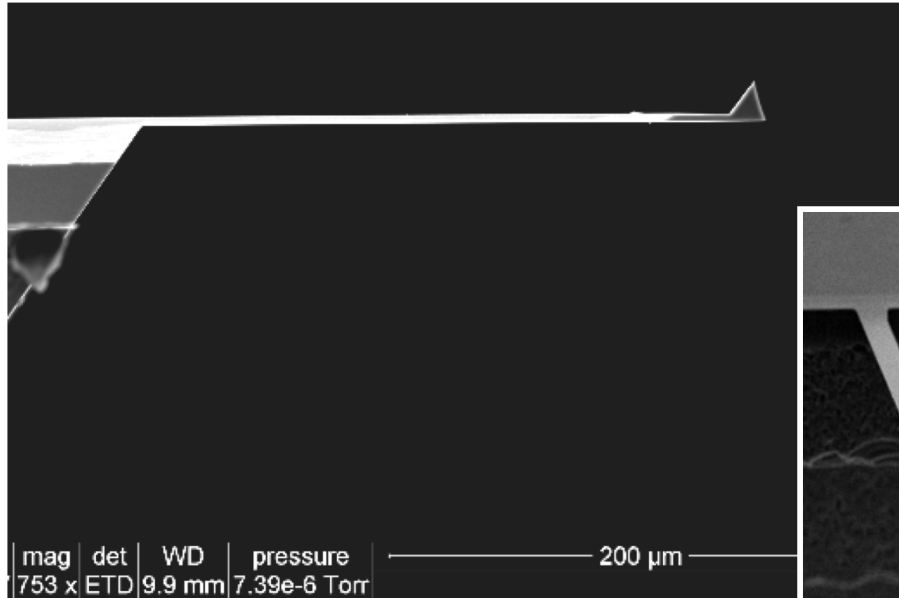
- Cantilever (spring, load sensor) Stiffness k_C : 0.01 – 100 N/m

Length L : 100-300 μm

Width w : 10-50 μm

Thickness e : 0.3-4 μm

Coating



→ www.nanoandmore.com



+ mounting on the holder 🤯

Calibration!

AFM principle and typical set-up

- Photodetector (deflection sensor)

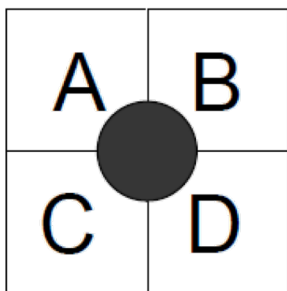


Photodiode + geometry + laser position sensitivity $\approx \times 10$ nm/V

\rightarrow minimum measurable deflection < 0.1 nm!

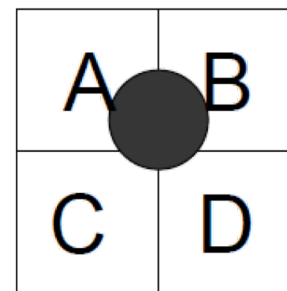


Calibration!



$$(A+B) - (C+D) = 0$$

no deflection



$$(A+B) - (C+D) > 0$$

deflected up

$$I_\varepsilon(\varphi) = \int \nabla \varphi(x) \cdot dx$$

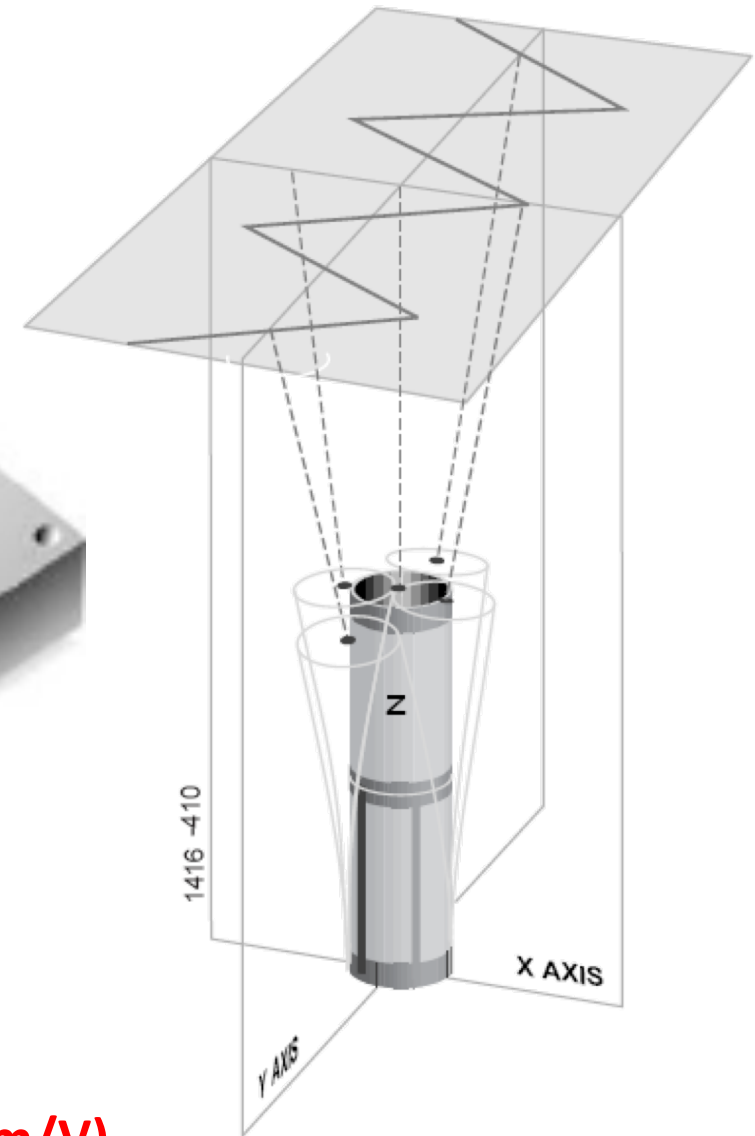
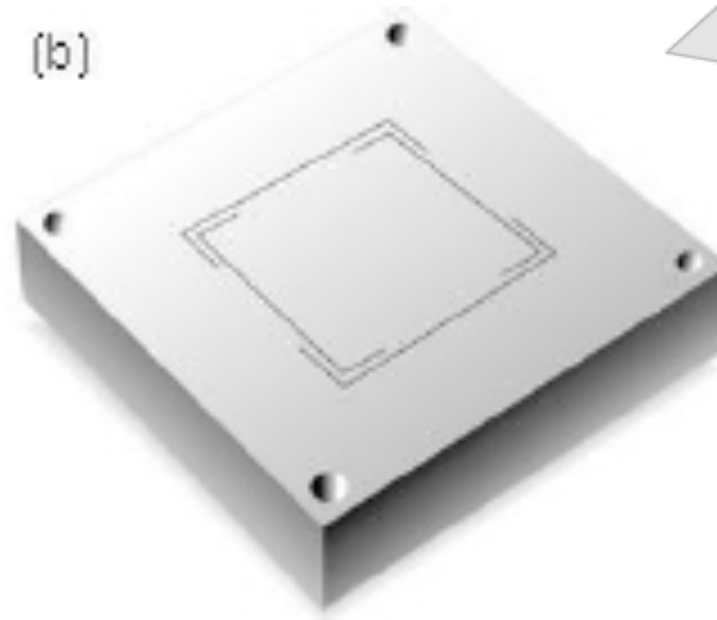
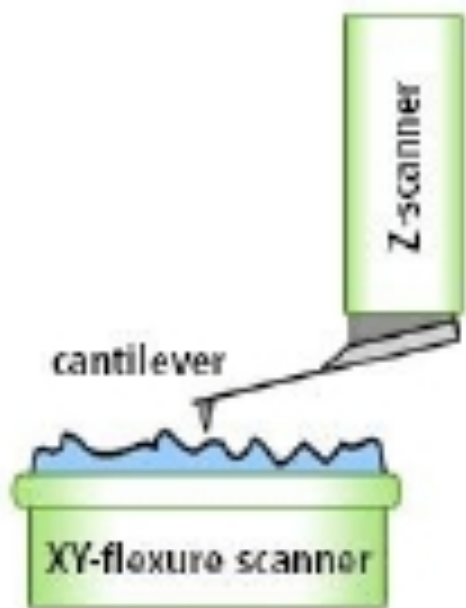
$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

$$W(\cdot, F) = \infty$$

AFM principle and typical set-up

- Scanner

Calibration!

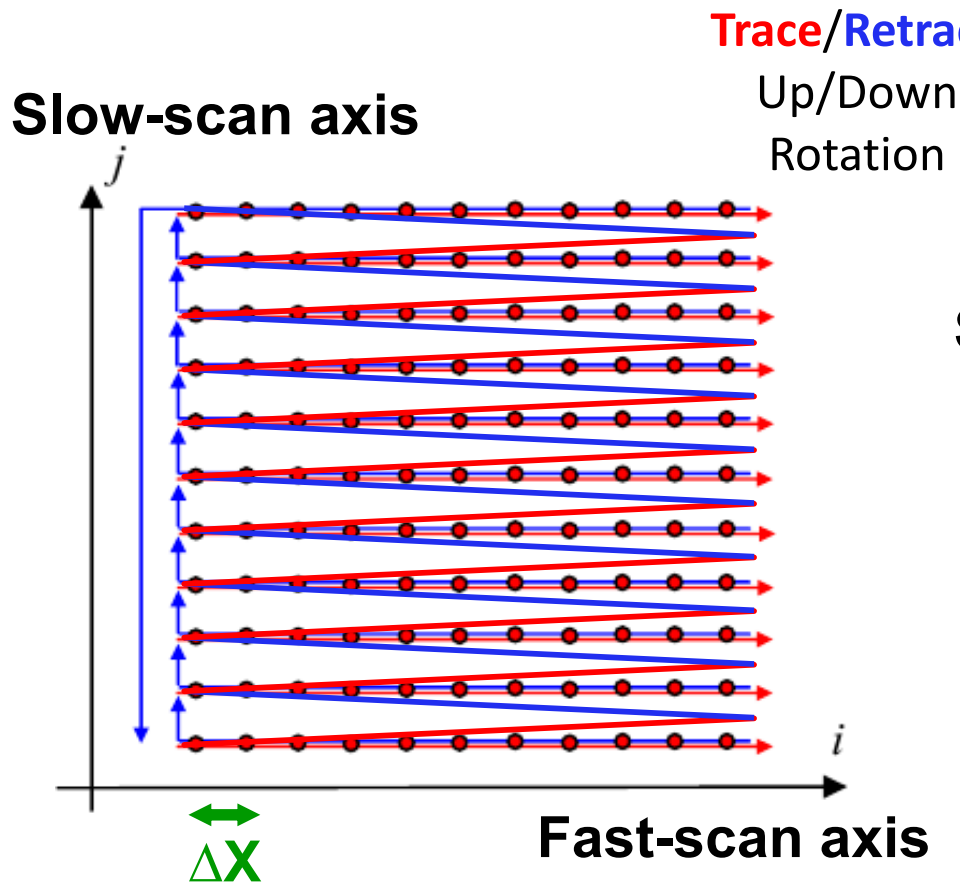


[www.parkafm.com]

**Typical piezo-response $\approx 0.1 \text{ nm/V}$ ($0.01\text{-}10 \text{ nm/V}$)
mV control \rightarrow displacement step $< 0.1 \text{ nm}$!**

[www.veeco.com]

AFM principle and typical set-up



The information collected by the SPM is stored as a two-dimensional file of integer numbers a_{ij} (square matrix in general)

Commonly
 256×256 or 512×512
elements

The image spatial resolution is conditioned by the digitalisation

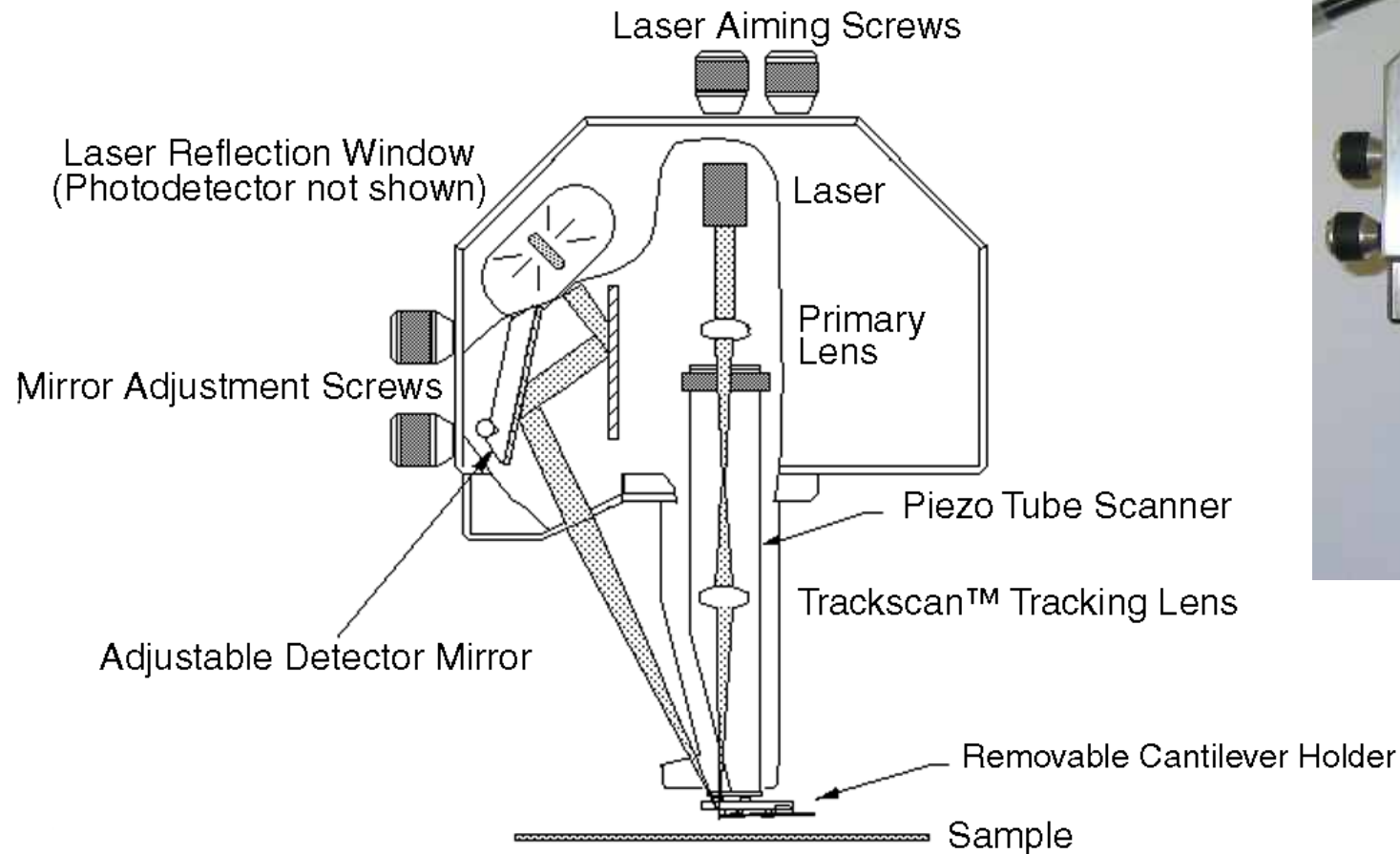
Example: Image size $10 \mu m$ $\Delta X = \frac{10 \mu m}{511} = 0.02 \mu m = 20 nm$
 512×512 elements

$$I_{\varepsilon}(\varphi) = \int_{\varphi} |\nabla \varphi(u)| du$$

$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

AFM principle and typical set-up

- Whole set-up



[www.veeco.com]

$$I_\varepsilon(\varphi) = \int \sqrt{\varphi'(x)} dx$$

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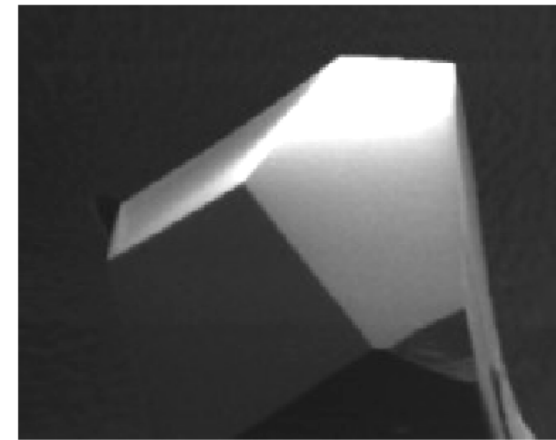
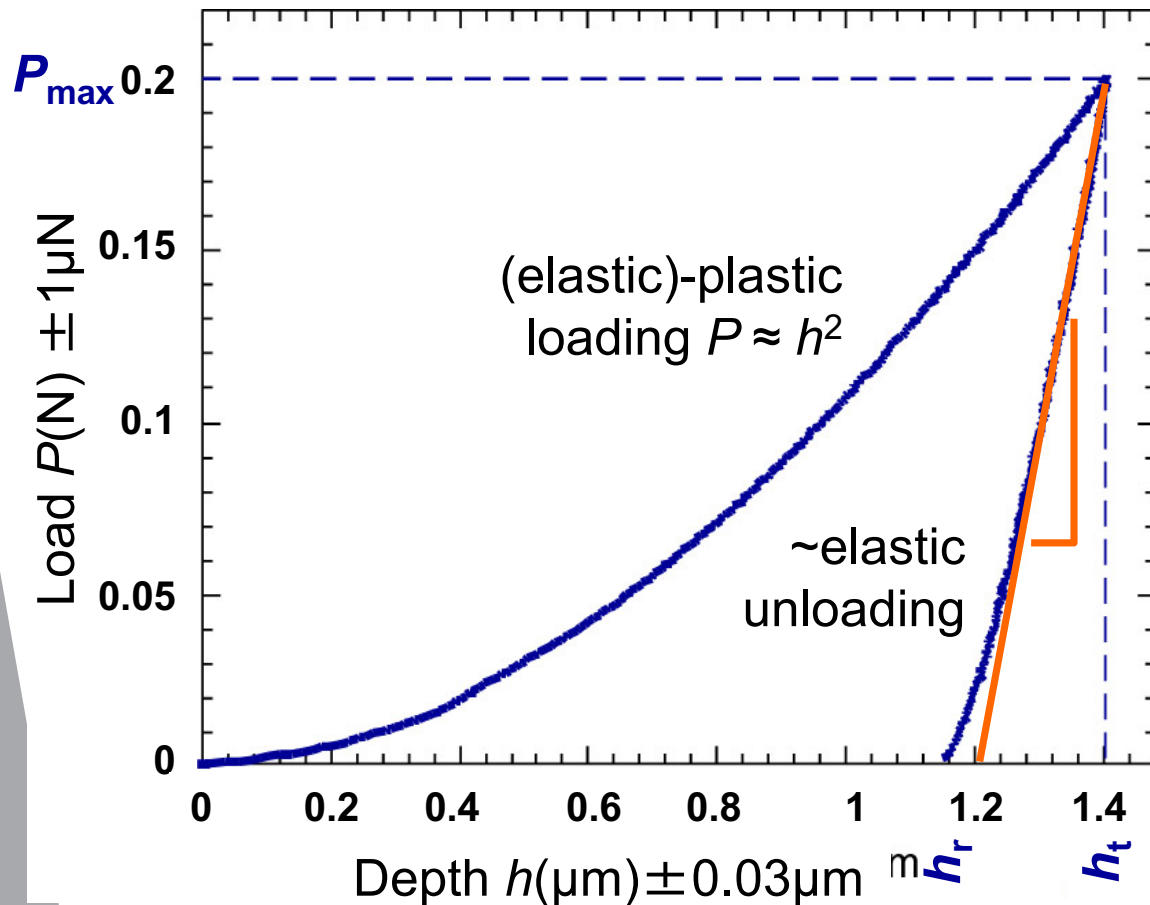
lim

$$W(\cdot, F) = \infty$$

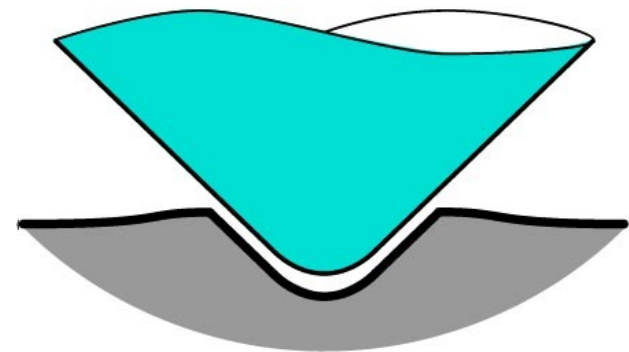
Contact mechanics

• (Depth-sensing) Nanoindentation

- ➔ The depth of penetration h (δ !) is measured during load application mainly with a Berkovich indenter (3-sided pyramid)



[www.microstartech.com]



Nanoindentation curve on electrodeposited Ni

Contact mechanics

- (Depth-sensing) Nanoindentation

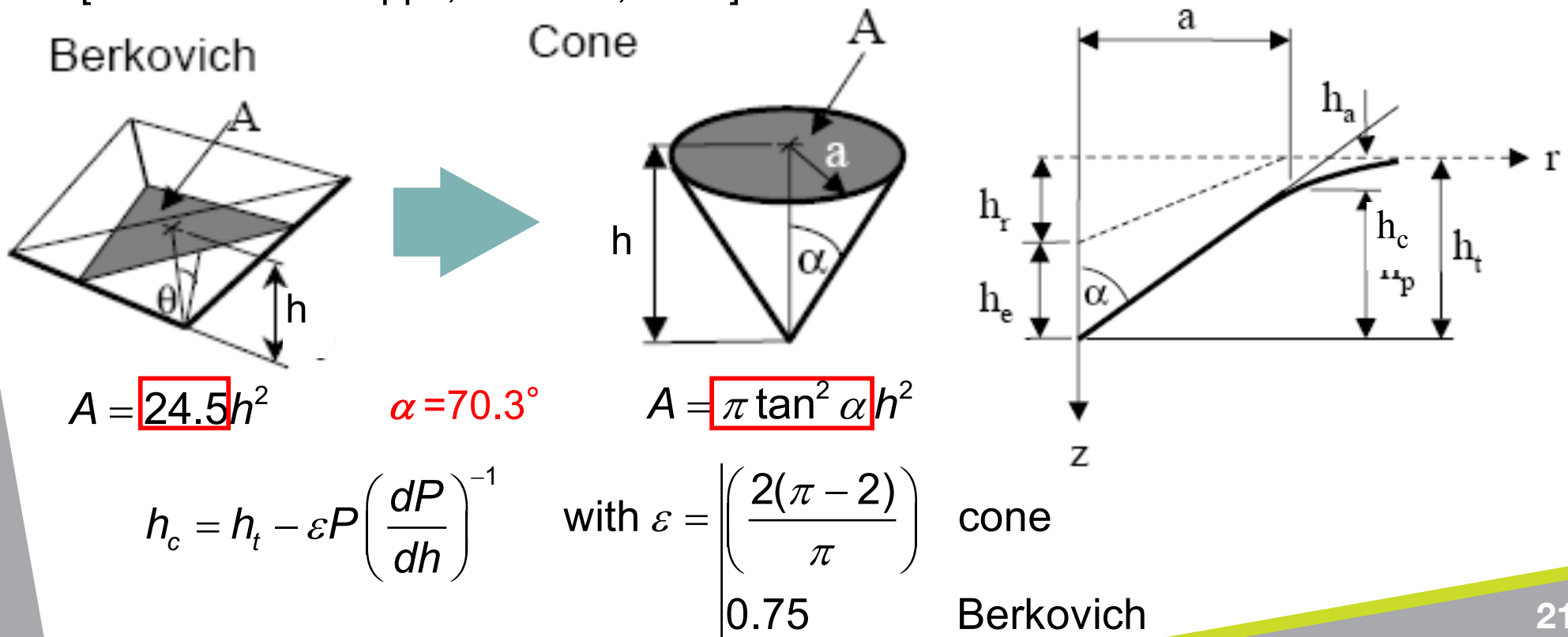
$$E^* = \frac{\sqrt{\pi}}{2} \frac{dP}{dh} \frac{1}{\sqrt{A_c}}$$

With E^* or M reduced/contact/indentation modulus

$$\frac{1}{E^*} = \frac{1-\nu_i^2}{E_i} + \frac{1-\nu^2}{E} \text{ for linear } \textit{ISOTROPIC} \text{ material}$$

- Case of the Berkovich indenter

[A.C. Fischer-Cripps, *Vacuum*, 2000]



$$I_\varepsilon(\varphi) = \int \nabla \varphi(\mathbf{r}) \cdot d\mathbf{s}$$

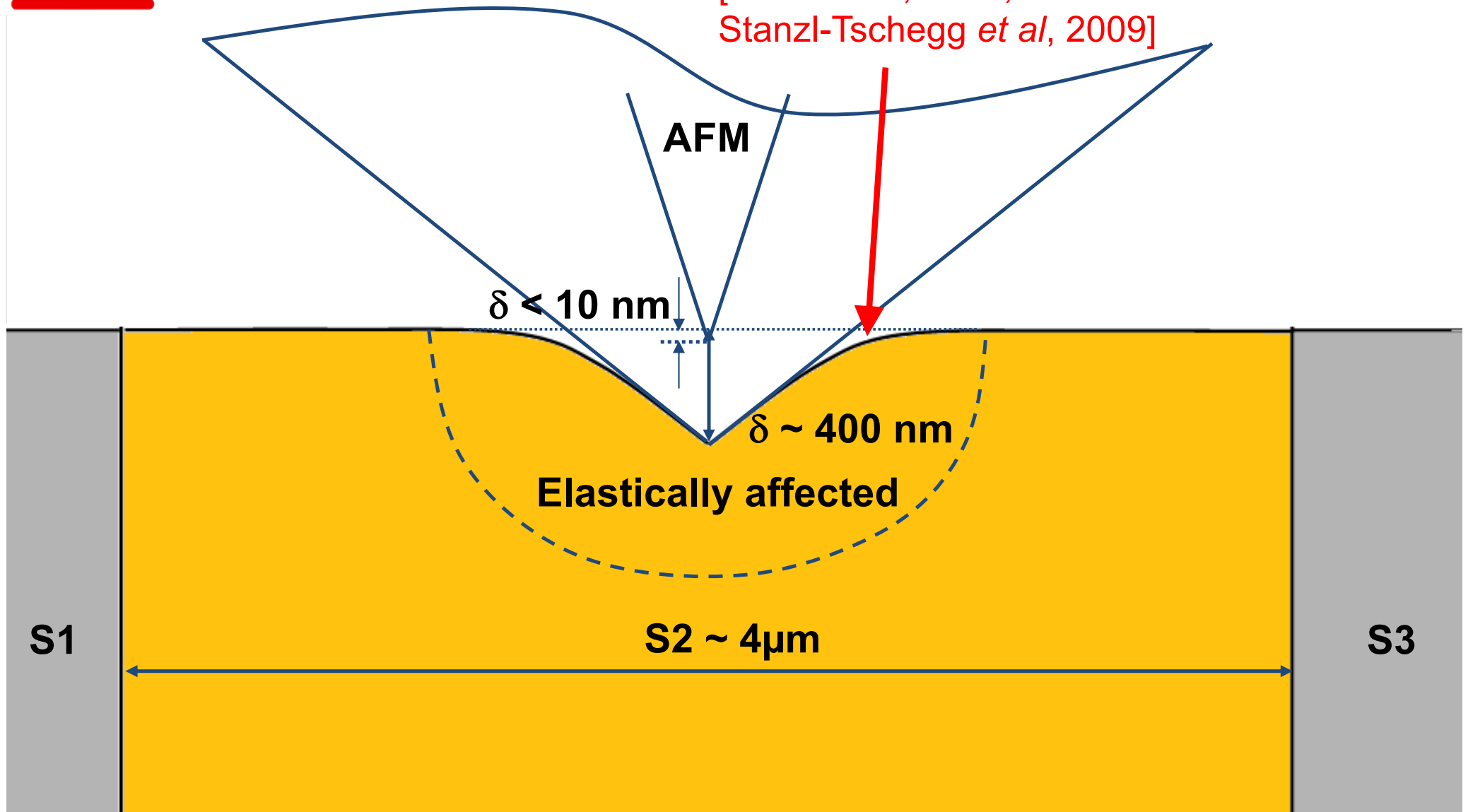
$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

Contact mechanics – NI vs AFM

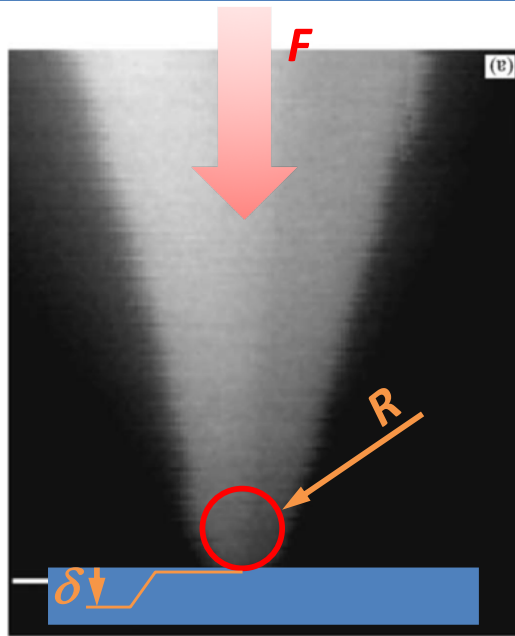


NEAR SURFACE measurements
→ **sample surface preparation!!!**

Sink-in
[Jakes *et al*, 2009;
Stanzl-Tschegg *et al*, 2009]



Contact mechanics without adhesion



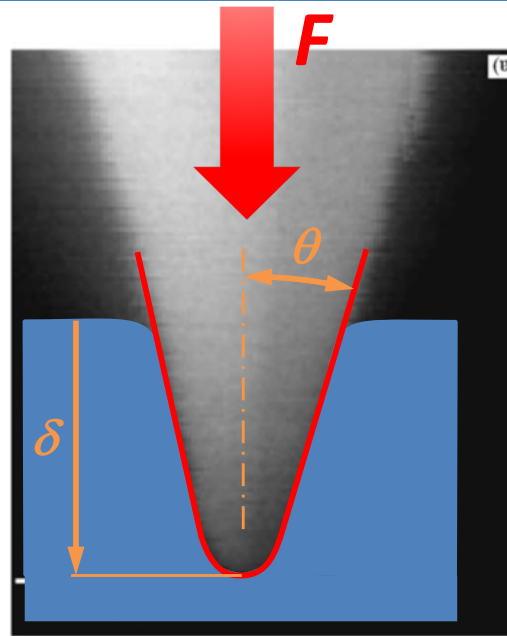
✓ Hertz (1885)

$$F = \frac{4}{3} M R_{eq}^{1/2} \delta^{3/2}$$

$$k_N = (6 M^2 R_{eq} F)^{1/3}$$

$$\delta \ll R$$

Non conforming



✓ Sneddon (1965)

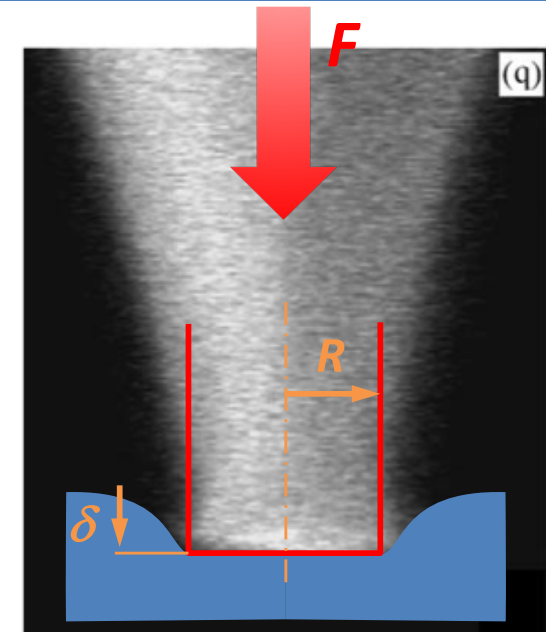
$$F = \frac{2}{\pi} M \tan \theta \delta^2$$

$$k_N = \left(\frac{32}{\pi^3} M \tan \theta F \right)^{1/2}$$

$$\delta \approx R???!$$

$$\delta \gg R$$

$$E^*_{sample} \ll E^*_{tip}$$



✓ Flat punch (??)

$$F = 2MR \delta$$

$$k_N = 2MR$$

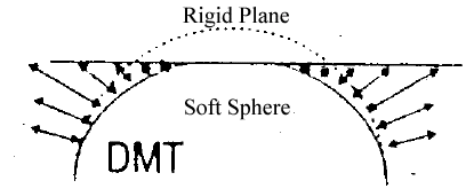
M: Reduced/contact modulus

$$\frac{1}{M} = \frac{1 - \nu_{Tip}^2}{E_{Tip}} + \frac{1 - \nu_{Sample}^2}{E_{Sample}}$$

LINEAR ELASTIC HOMOGENEOUS and ISOTROPIC materials

Contact mechanics + adhesion (capillary, Van der Waals, ...)

- ✓ **DMT Model:**
 - Adhesive model
 - Hertz model + offset of applied load



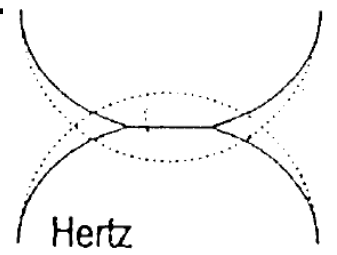
$$k_{N_{DMT}} = \left(6M^2R(F + F_{ad_{DMT}}) \right)^{1/3}$$

Adhesion force $F_{ad_{DMT}} = 2\pi R w_{ad}$

➔ Used for hard samples, low adhesion force and low tip radius R

- ✓ **JKR Method:**
 - Adhesive model
 - Evaluation of the energy of adhesion between two solids

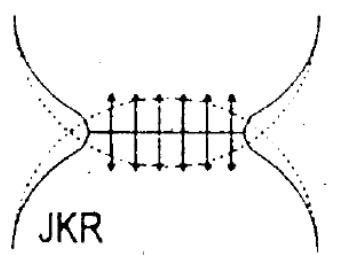
Hertz's theory is no longer valid: no direct relation between F and δ



$$k_{N_{JKR}} = 2Ma_{JKR} \frac{1 - \frac{1}{2} \left(\frac{a_{0_{JKR}}}{a_{JKR}} \right)^{3/2}}{1 - \frac{1}{6} \left(\frac{a_{0_{JKR}}}{a_{JKR}} \right)^{3/2}}$$

with

$$\left\{ \begin{aligned} a_{JKR} &= \left[\frac{3R}{4M} \left(\sqrt{F_{ad_{JKR}}} + \sqrt{F_{ad_{JKR}} + F} \right)^2 \right]^{1/3} \\ a_{0_{JKR}} &= \left[\frac{3RF_{ad_{JKR}}}{M} \right]^{1/3} \\ F_{ad_{JKR}} &= \frac{3}{2} \pi R w_{ad} \end{aligned} \right.$$



At pull-off $a \neq 0$ and $F = -F_{ad}$

[R.M. Overney]

➔ Adapted to soft samples, high adhesion force and high tip radius R

Contact mechanics

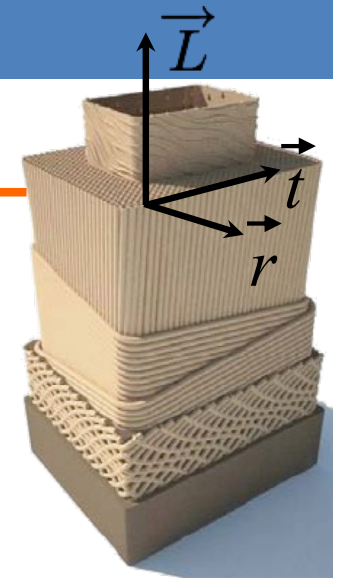
• Elastic anisotropy

For a typical S2-layer with MFA $\sim 0^\circ$ [Jäger et al, 2011]

$$M_L \approx 19 \text{ GPa} \text{ whereas } E_L \approx 45 \text{ GPa}$$

$$(E_t \approx E_r \approx 12 \text{ GPa}, \nu_{tL} \approx \nu_{rL} \approx 0.028, \nu_{rt} \approx 0.28)$$

$$G_{tL} \approx G_{rL} \approx 2.5 \text{ GPa}, G_{rt} \approx 2 \text{ GPa}$$



Kevlar fibre: $M// \approx 15\text{-}20 / E// \approx 80 \text{ GPa}$ [Arnould et al, 2017]

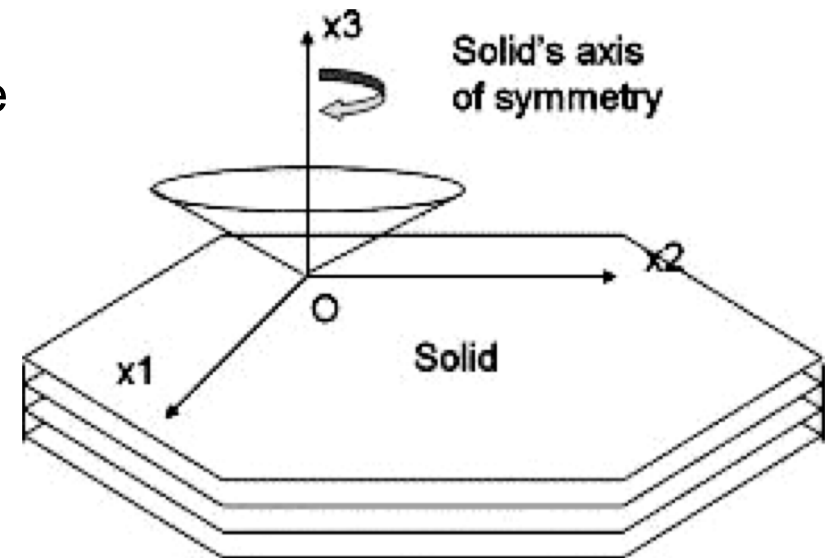
in particular case...

→ transversely isotropic // contact surface

[Hanson, J. Appl. Mech., 1992]

$$M_3 = 2 \sqrt{\frac{C_{11}C_{33} - C_{13}^2}{C_{11}}} \left(\frac{1}{C_{44}} + \frac{2}{\sqrt{C_{11}C_{33} + C_{13}}} \right)^{-1}$$

1=2: C_{22} C_{23} $G_{13} = G_{23}$

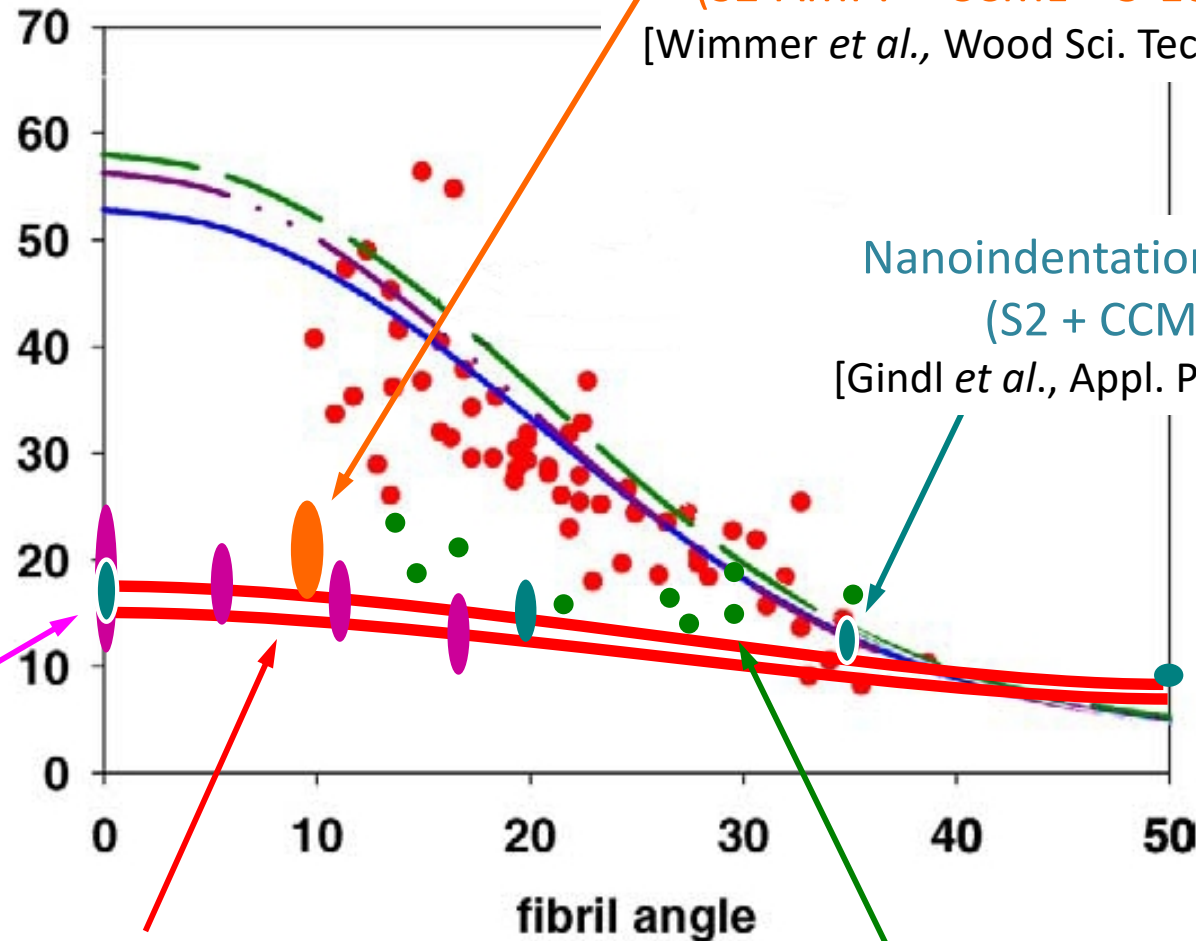


[Delafargue et al., Int. J. Sol. Struct., 2004]

Contact mechanics – Fibre cell wall anisotropy



longitudinal fiber wall elastic modulus, GPa



Nanoindentation on Spruce (S2-AMF? + CCML ~ 5-10GPa)

[Wimmer *et al.*, Wood Sci. Tech., 1997]

Nanoindentation on Spruce (S2 + CCML ~ 7-12GPa)

[Gindl *et al.*, Appl. Phys. A, 2004]

Nanoindentation on Spruce

[Konnerth *et al.*, J. Mater. Sci., 2009]

Anisotropic indentation model (7,5-15%)

[Vlassak *et al.*, J. Mech. Phys. Sol., 2003]

[Jäger *et al.*, Comp. A, 2011]

Nanoindentation on Pine (S2)

[Tze *et al.*, Comp. A, 2007]

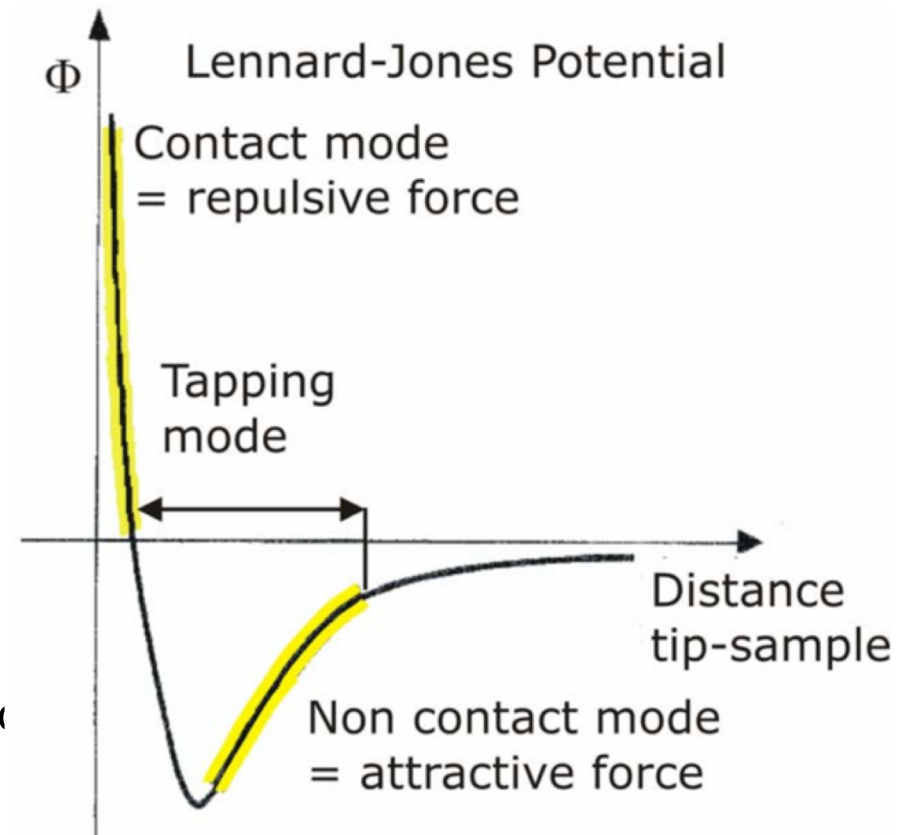
[Eder, Arnould *et al.*, Wood Sci. Technol., 2013]

$$I_\varepsilon(\varphi) = \int \sqrt{\varphi'(x)} dx$$

$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

Outline

- Brief history and basic principles of scanning probe microscopy
- AFM principle and typical set-up
 - Tip probe-sample surface interactions
 - Tip and cantilever
 - Deflection sensor and scanner
 - Whole set-up
- Contact mechanics
- Operating modes (some)
 - Contact
 - Intermittent
 - Force-distance curve and mechanical properties
- Image analysis and artefacts
- Sample preparation

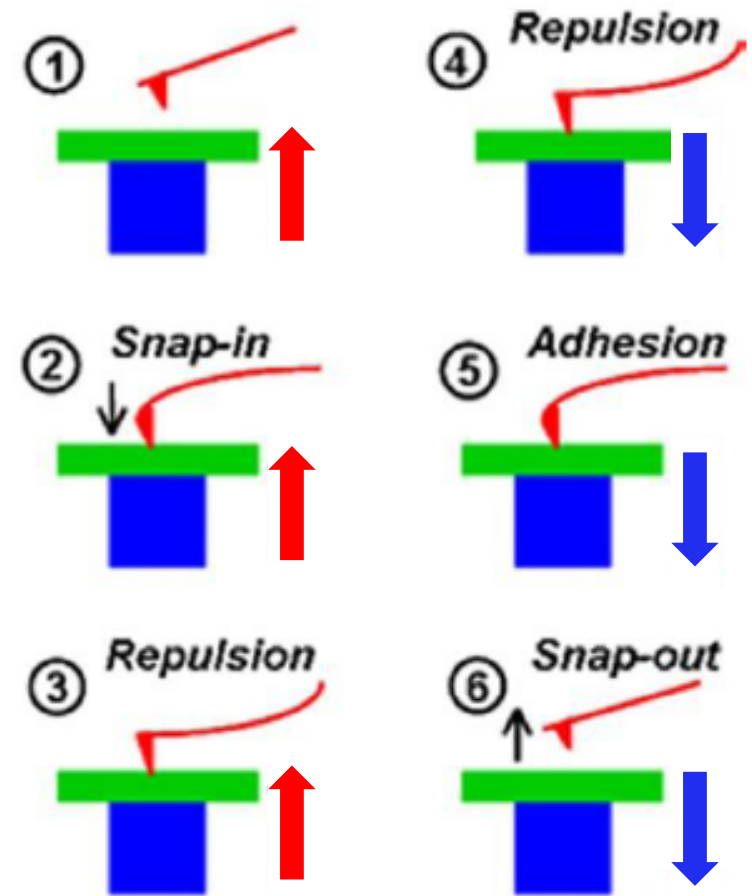
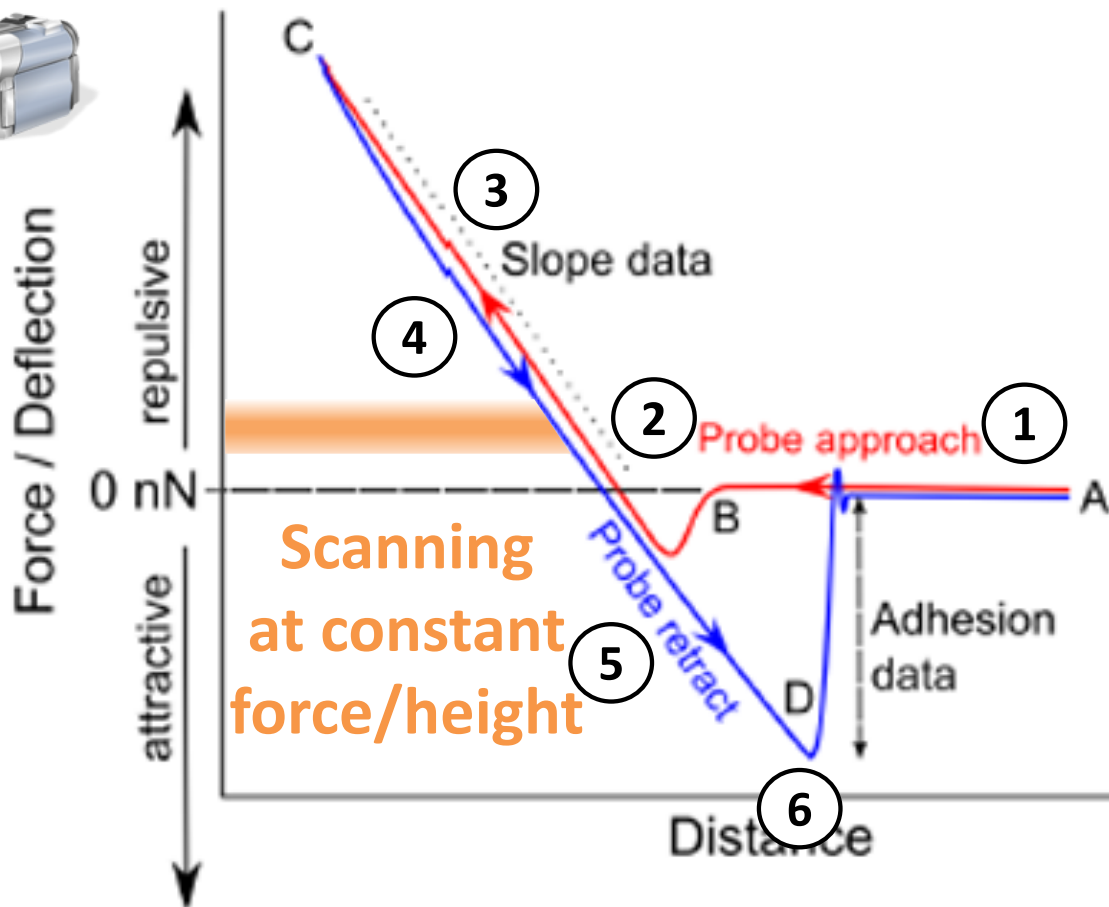


$$I_\varepsilon(\varphi) = \int \nabla \varphi(\mathbf{r}) \cdot d\mathbf{r}$$

$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

Force-distance curve

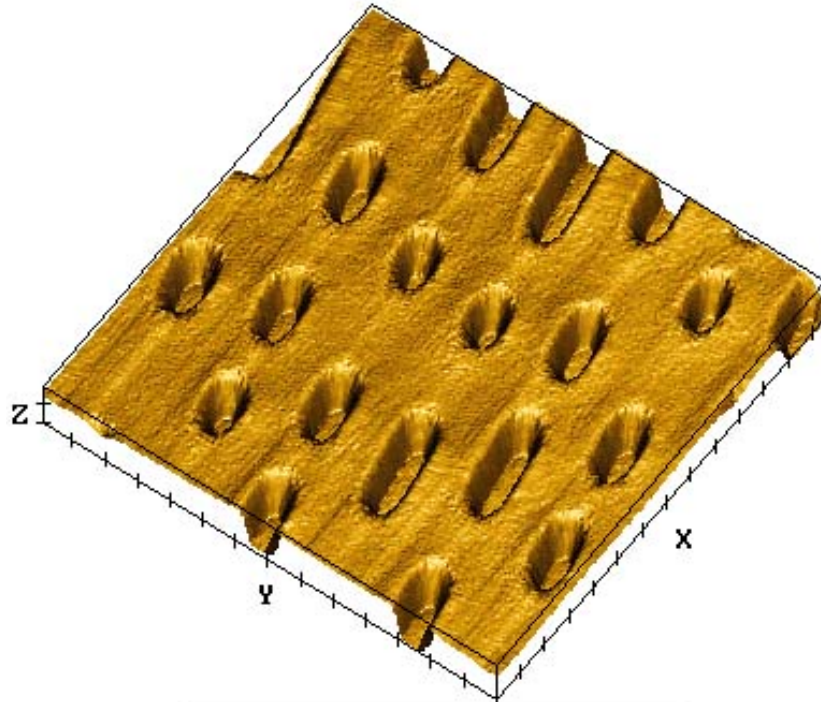
- Van der Waals force, electrostatic force, contact stiffness, adhesion force, ...



[B. Nysten, 2007]

Contact mode

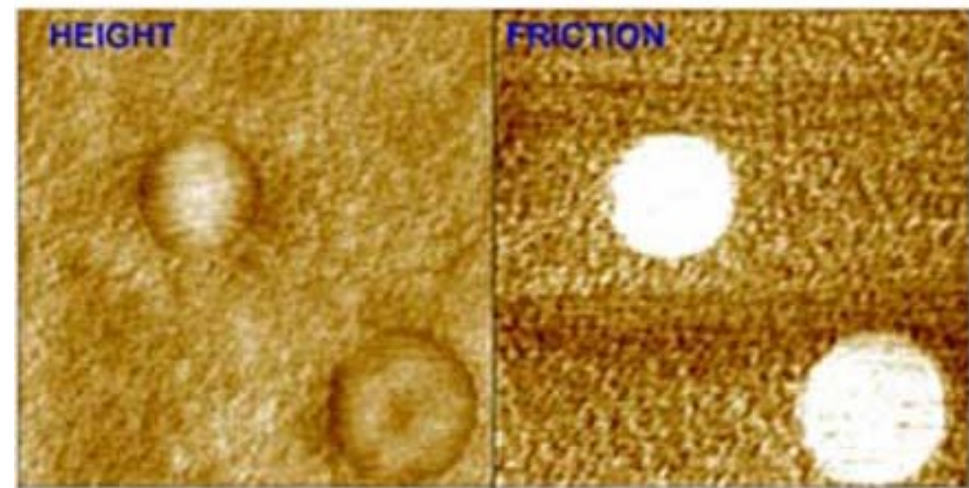
- Constant height or force and friction



SCALE X:1 μM Y:1 μM Z:0.1 μM

CD disk surface
[www.ntmdt.com]

\pm Fast scan speed in constant force mode (topography/closed-loop feedback)
Limited topography in height force mode
Tip wear, **effect of sample elasticity**
~Poor resolution (surface deformation, large tip surface contact area)



Cantilever with low stiffness (0.01-1 N/m)

PS-PMMA polymer blend
[Feldman et al., *Langmuir*, 1998]



$$I_\varepsilon(\varphi) = \int_0^{2\pi} |\nabla \varphi(u)|^2 du$$

$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

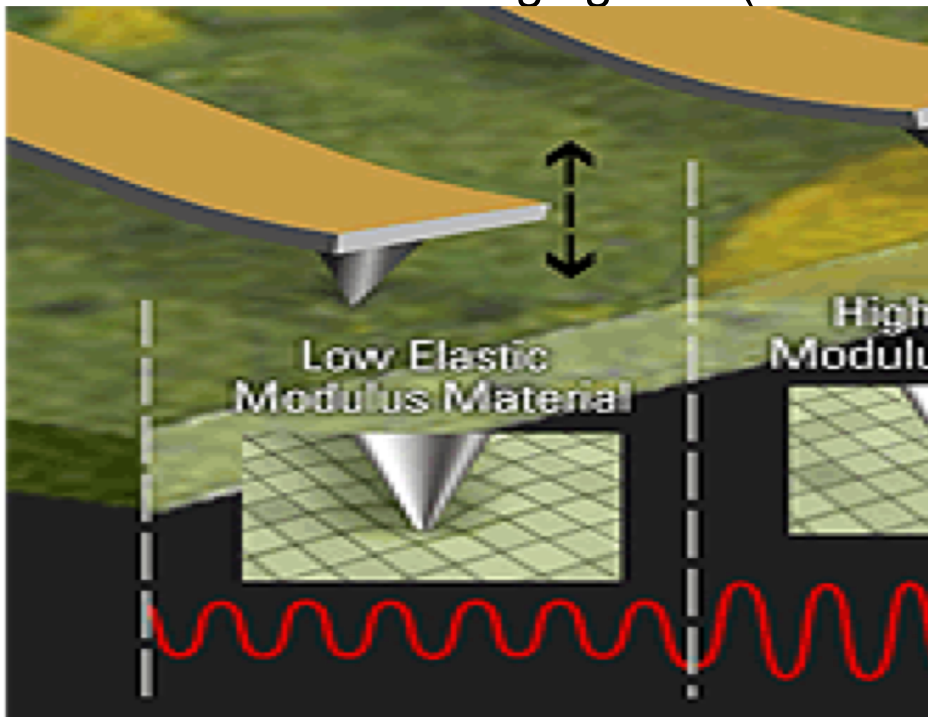
$$W(\cdot, F) = \infty$$

Contact mode

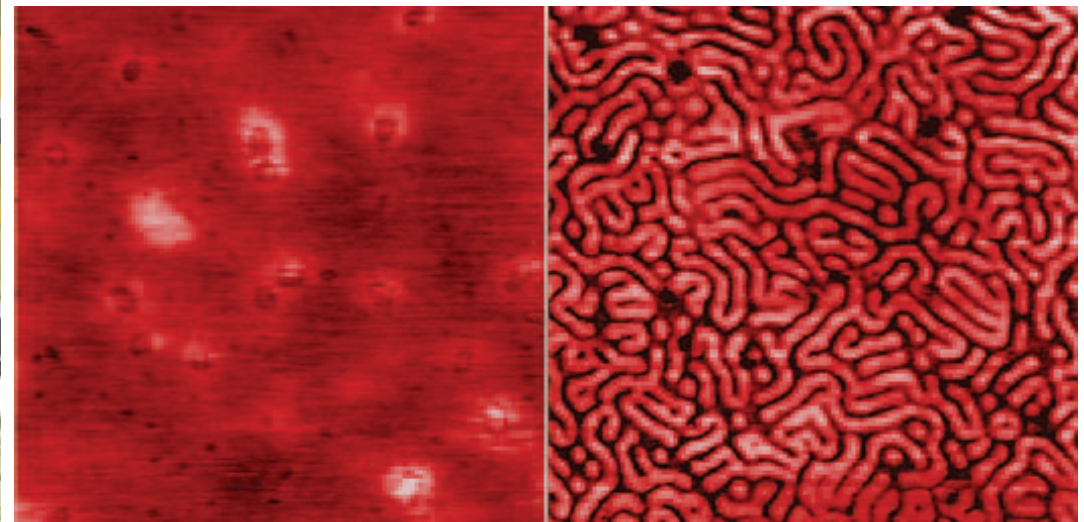
● Force Modulation (FMM) ~ DMA



- ➔ Few nm oscillations @ few kHz, longitudinal or transversal!
- ➔ Cantilever vibration **amplitude** and **phase-shift** related to surface **elastic** and **viscoelastic** properties
- ➔ Same limitations as F-d curves but better resolution (≈ 100 nm on polymer) and lower imaging time (scan rate < 0.5 line/s)



[www.afmuniversity.org]



Topography and force modulation images (900 nm scans) of a two-phase block copolymer (softer = black)

[www.veeco.com]

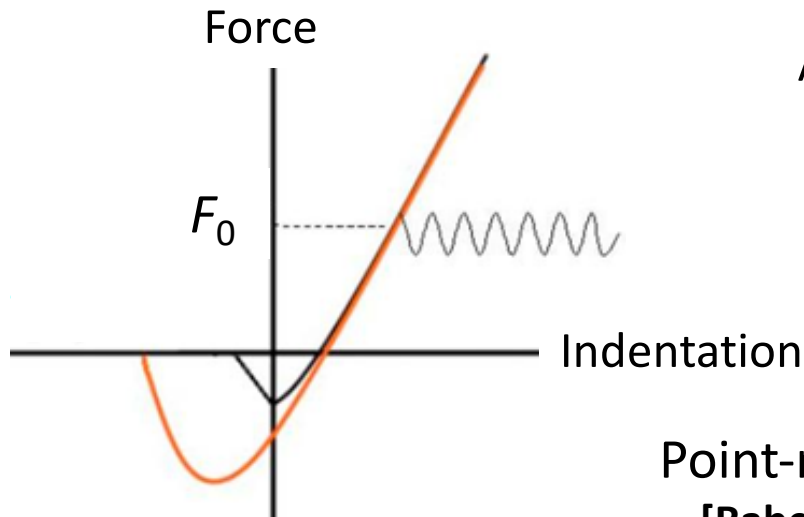
$$I_\varepsilon(\varphi) = \int_{-\infty}^{\infty} \varphi(x) dx$$

lim

$$W(\cdot, F) = \infty$$

Contact Resonance-AFM (CR-AFM)

IDEA: To probe the local elastic stiffness of the tip-sample system by means of cantilever's resonance frequency in contact mode **at reduce applied force**

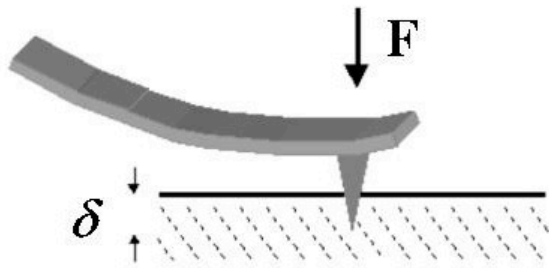


Applied force is modulated $F = F_0 + F_{excitation} \times \sin \omega t$

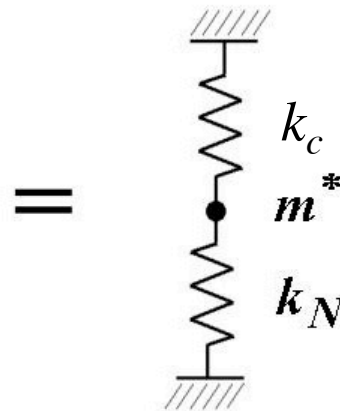
if $F_{excitation}$ is small \rightarrow LINEAR contact stiffness

if F_0 is small \rightarrow Good spatial resolution + Hertz theory validity

Cantilever-tip-sample system



Point-mass model [Rabe et al, 1996]



$$f_0 = \frac{1}{2\pi} \sqrt{\frac{k_c + k_N}{m^*}} \quad \text{with} \quad m^* = \frac{1}{4} m + m_{tip}$$

Amplitude of vibration and resonance frequency depend on the contact stiffness k_N ... but how?

$$I_\varepsilon(\varphi) = \int_{\varphi_0}^{\varphi} \frac{1}{\varepsilon} d\varphi$$

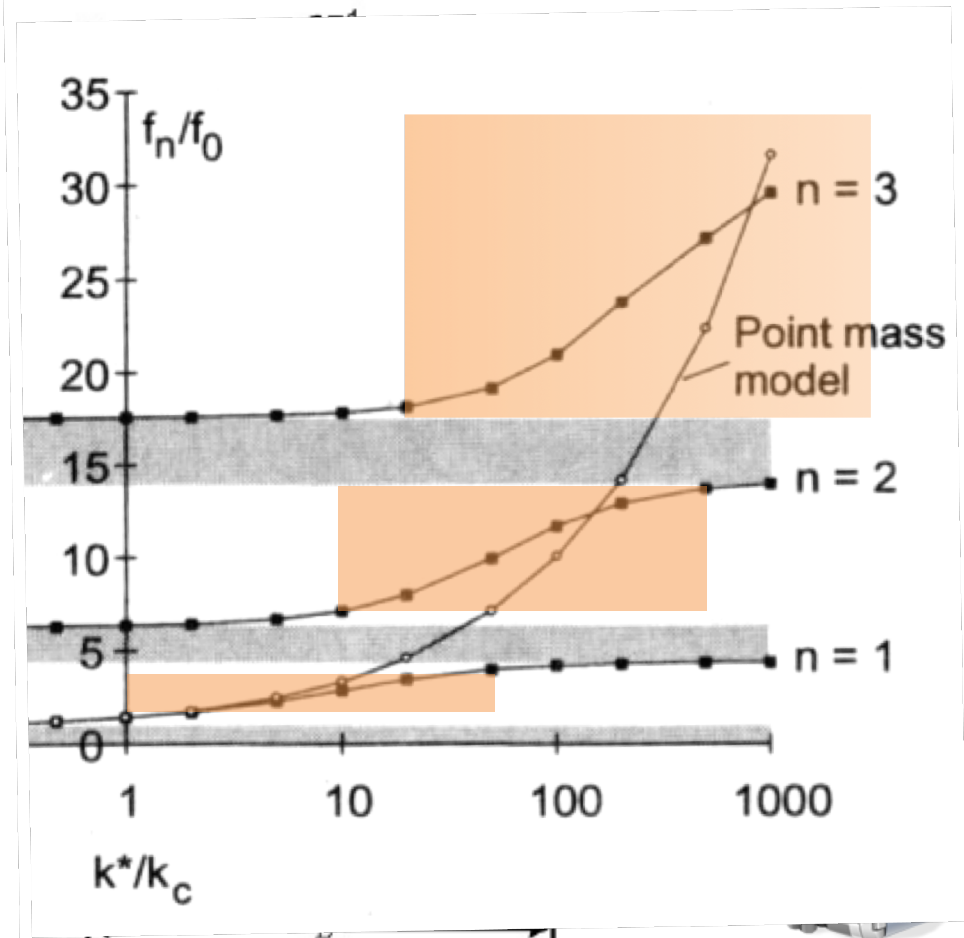
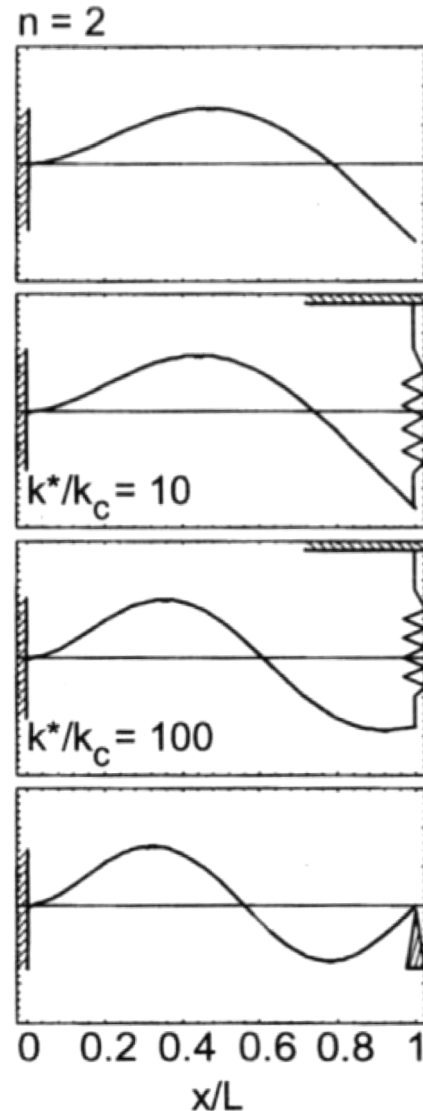
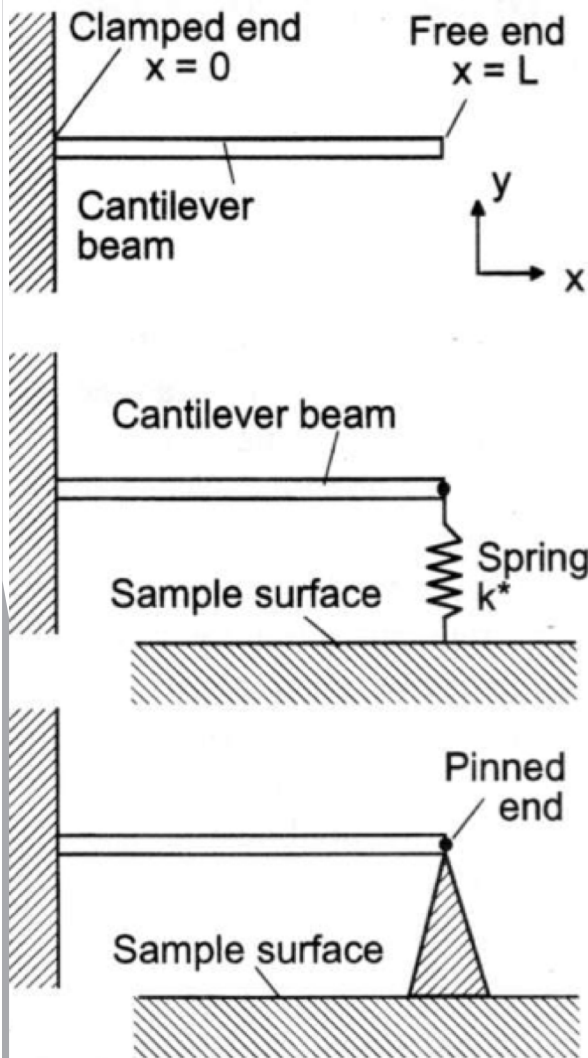
lim

$$W(\cdot, F) = \infty$$

Contact Resonance-AFM (CR-AFM)

Cantilever dynamic and response

[Rabe *et al*, 1996]



$$I_\varepsilon(\varphi) = \int \rho(\varphi) |d\varphi|$$

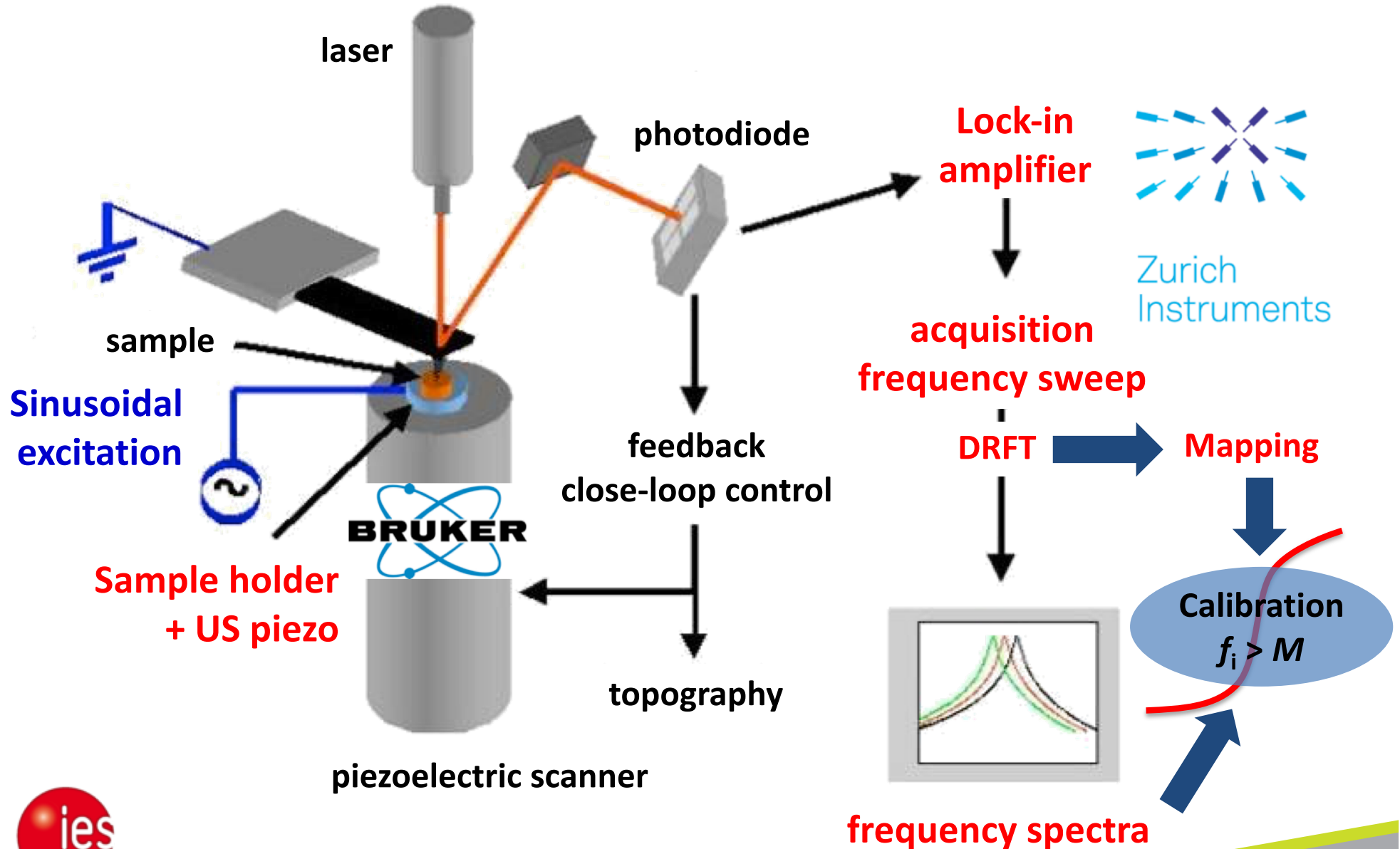
$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

$$W(\cdot, F) = \infty$$

Contact Resonance-AFM principle with Dual Resonance Frequency Tracking

[Arinero and L ev eque, Rev. Phys. Instr., 2003]

[Gannepalli *et al.*, Nanotechnol. 2011]



$$I_\varepsilon(\varphi) = \int_{\varphi} \dots$$

lim

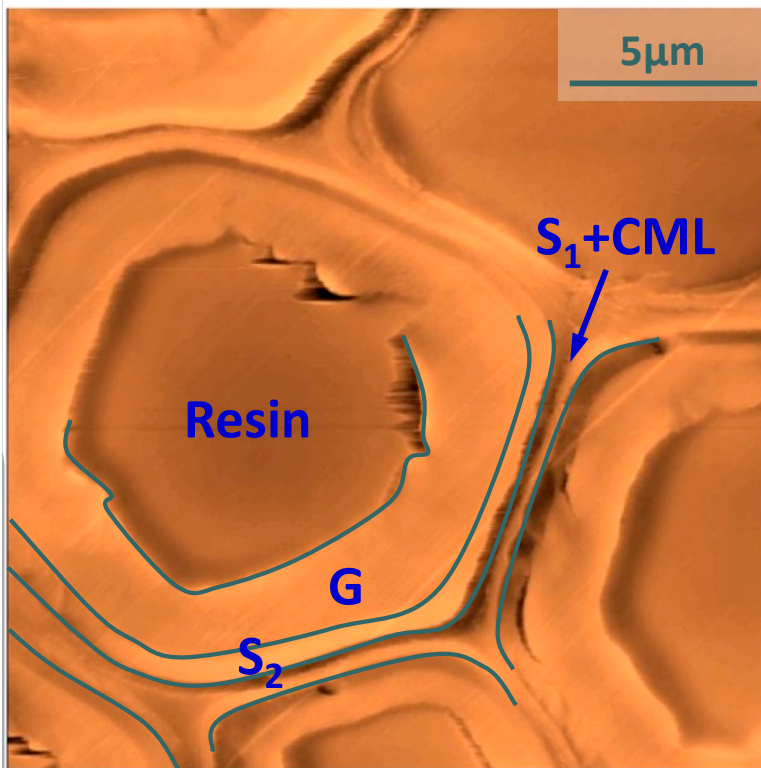
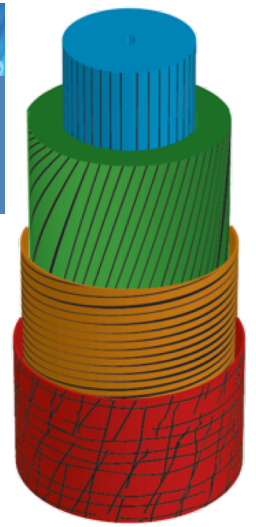
W(·)

Chestnut tension wood

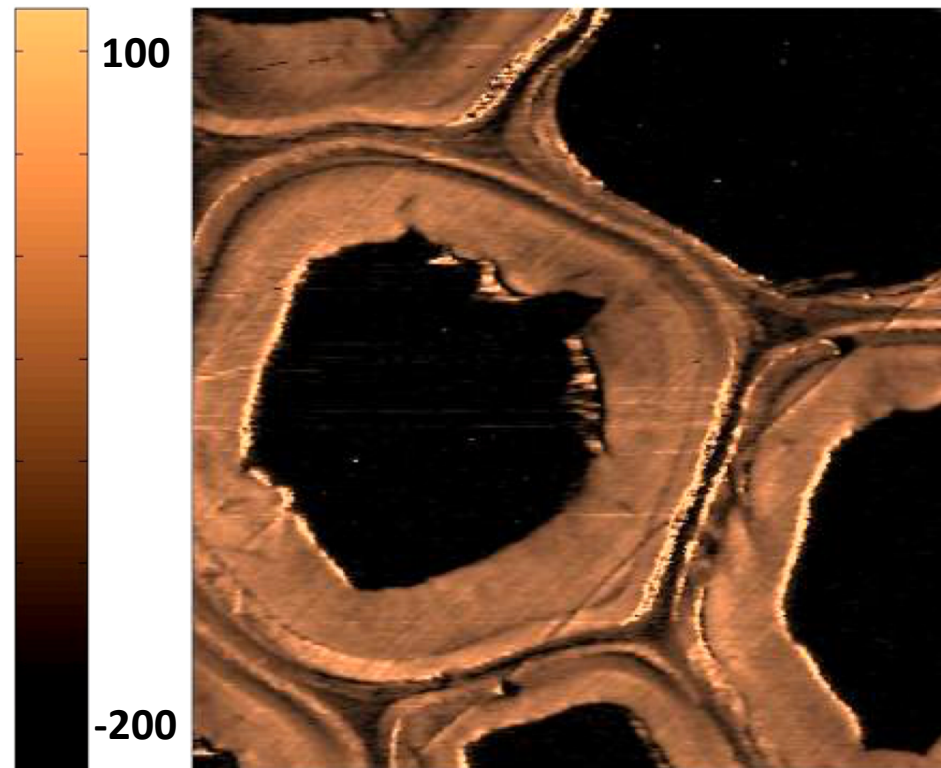
[Arnould and Arinero, *Comp. A*, 2015, 74: 79-76]

Effect of the topography and sample orientation

[Konnerth et al, *J. Mater. Sci.*, 2009]



Topography (nm)



Contact modulus (GPa)

$$I_\varepsilon(\varphi) = \int_{\varphi} \sigma(\varphi) d\varphi$$

lim

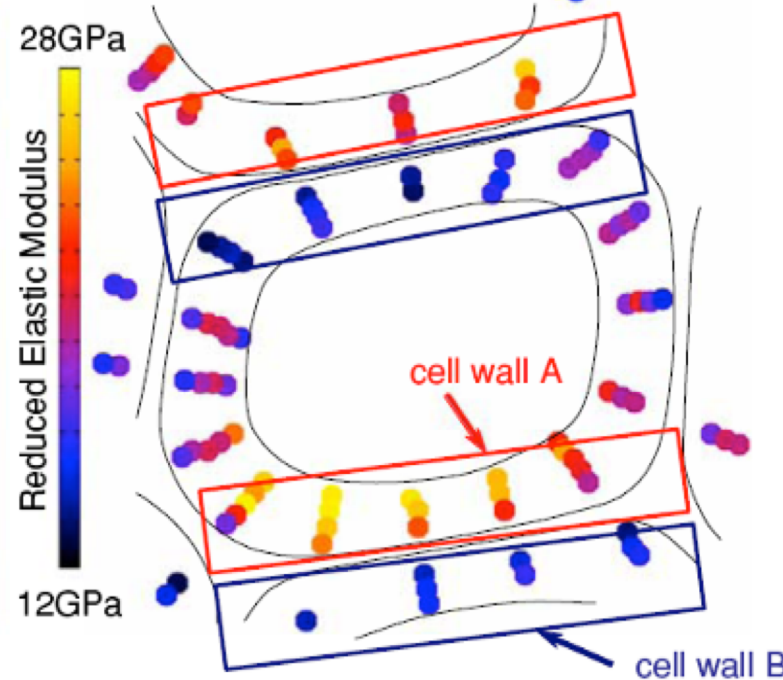
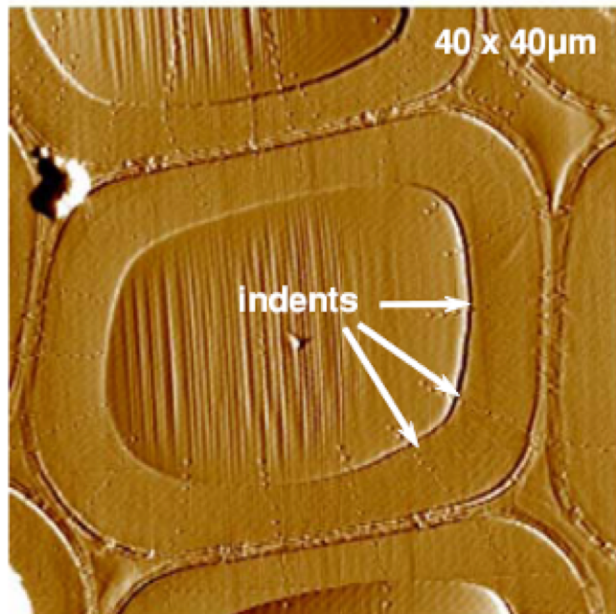
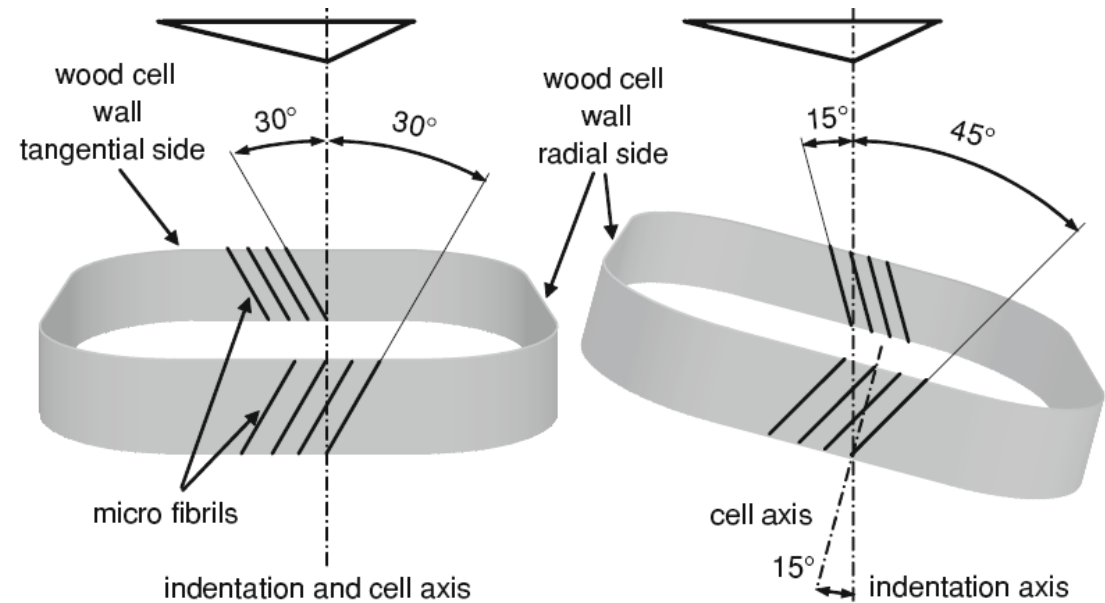
$$W(\cdot, F) = \infty$$

Chestnut tension wood

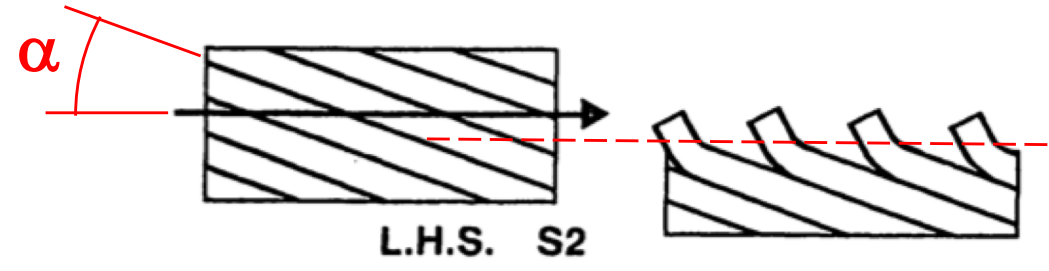
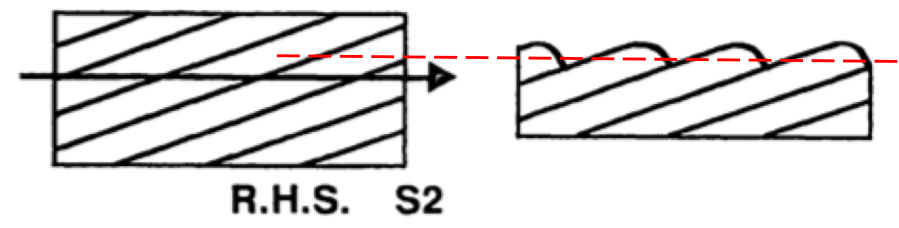
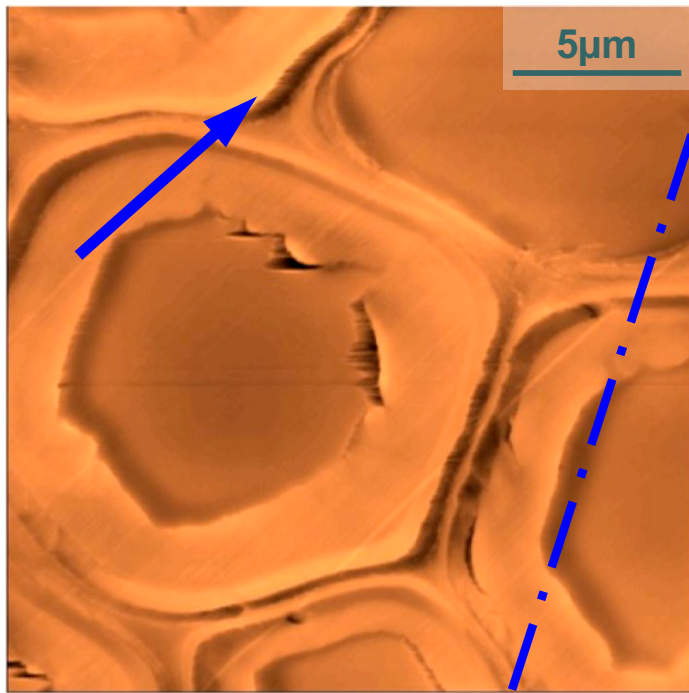
[Arnould and Arinero, Comp. A, 2015]

Effect of sample orientation

[Konnerth et al, J. Mater. Sci., 2009]

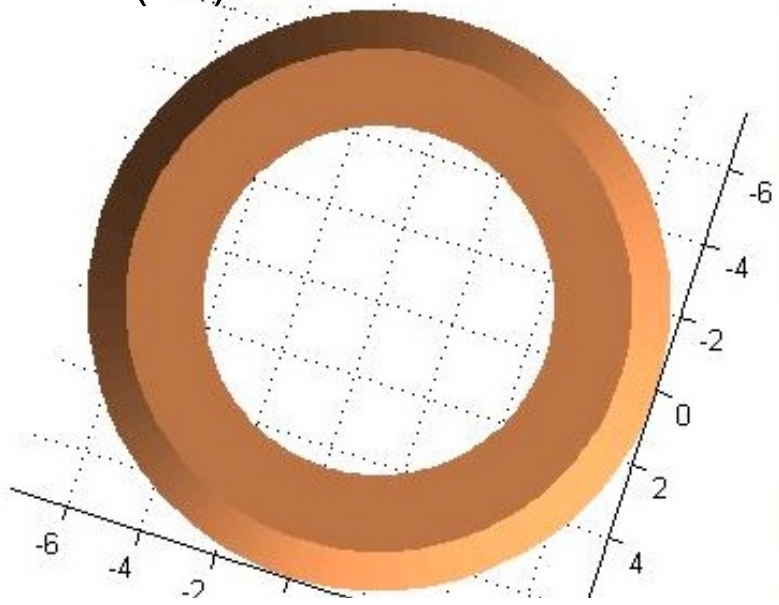


Topography (nm)

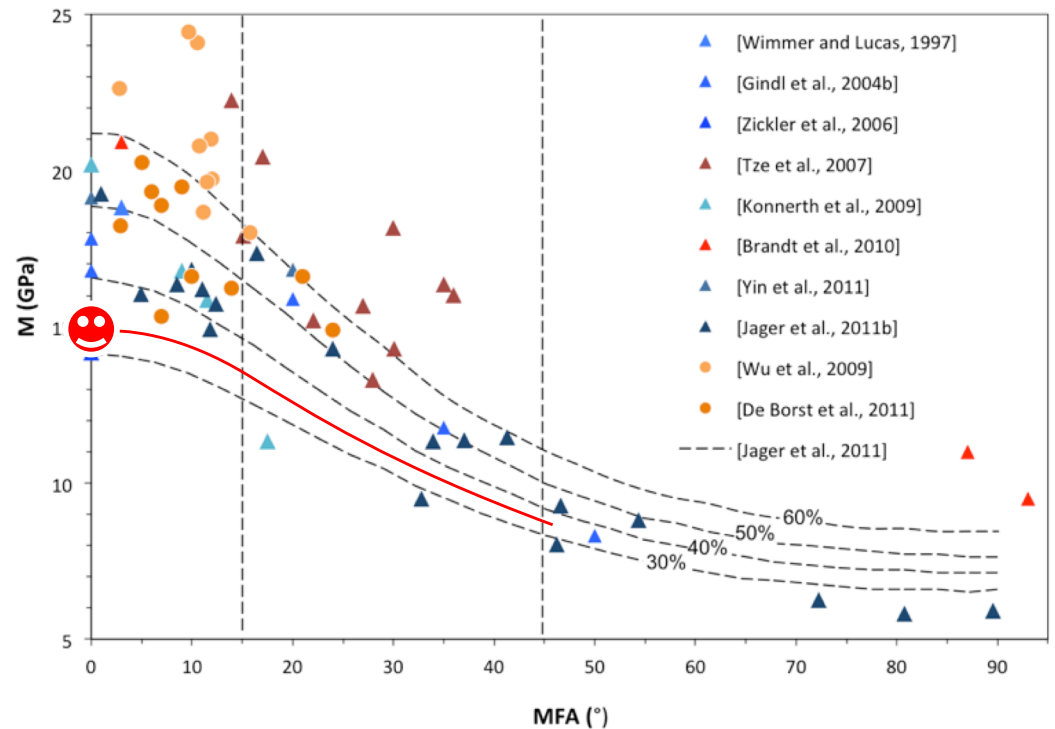


[Shaune et al, Holzforschung, 1994]

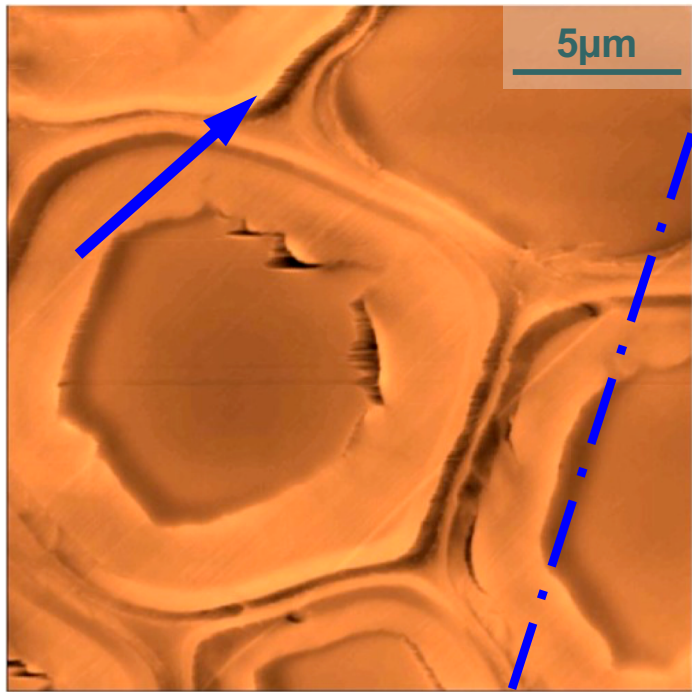
Simplified model
AMF(S2) $\sim 20^\circ$ et tilt $\sim -20^\circ$



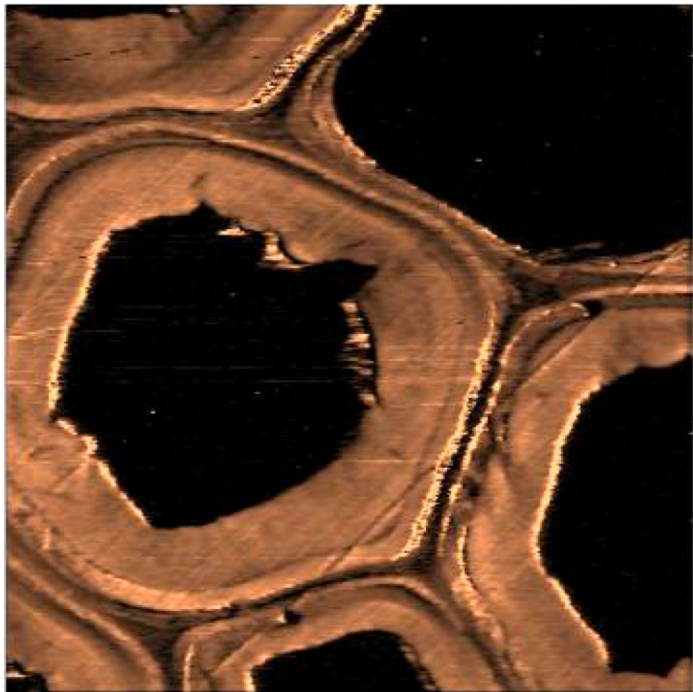
Cutting angle / MFA α ($^\circ$)



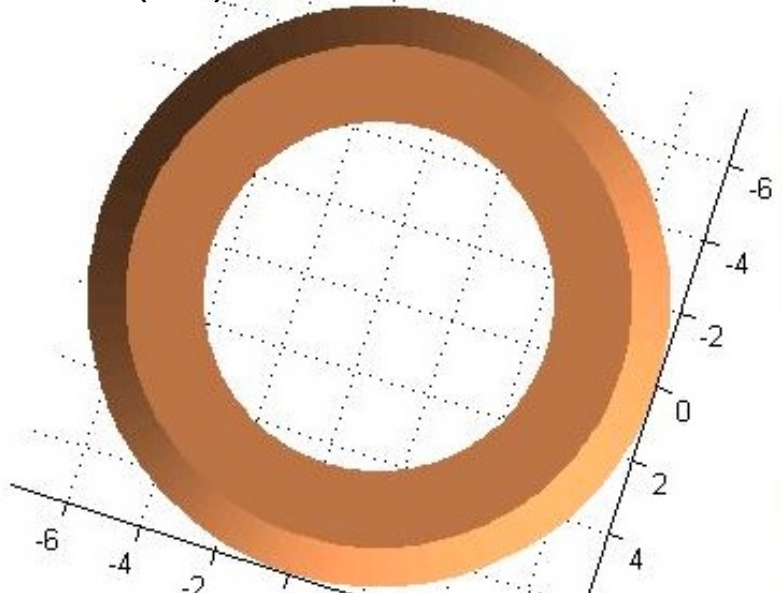
Topography (nm)



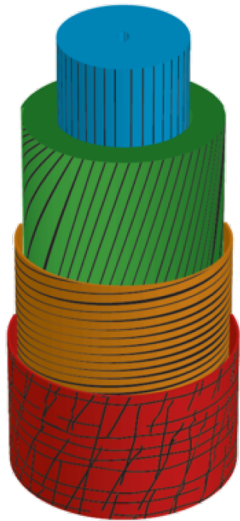
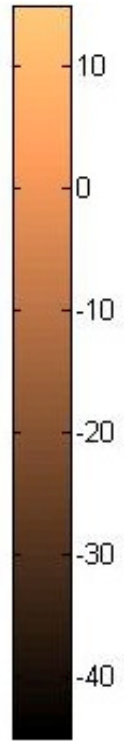
Contact modulus (GPa)



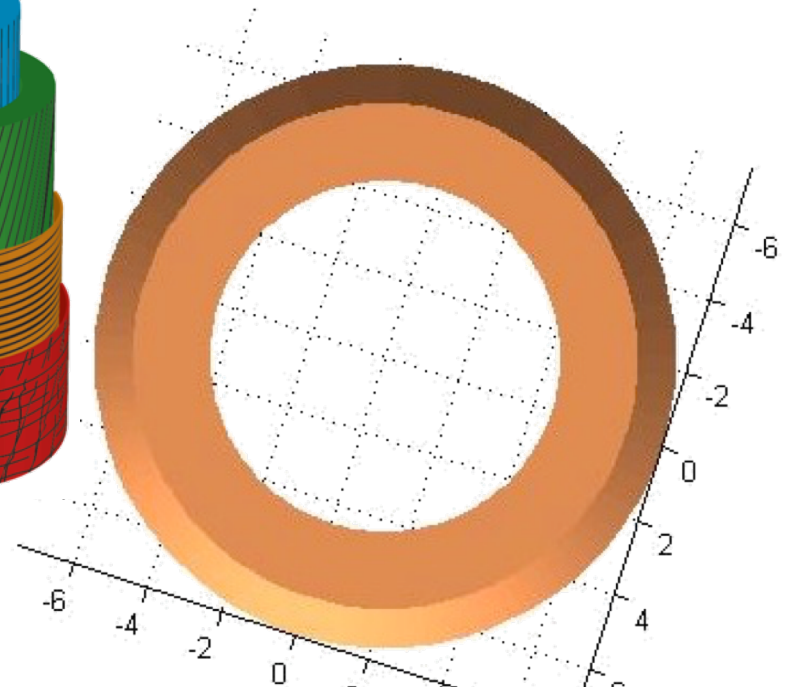
Simplified model
AMF(S2) $\sim 20^\circ$ et tilt $\sim -20^\circ$



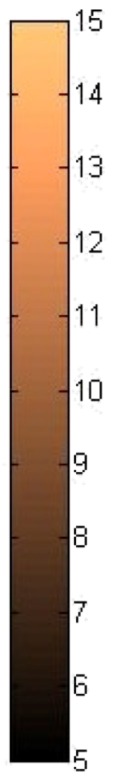
Cutting angle / MFA α ($^\circ$)



37



Contact modulus (GPa)



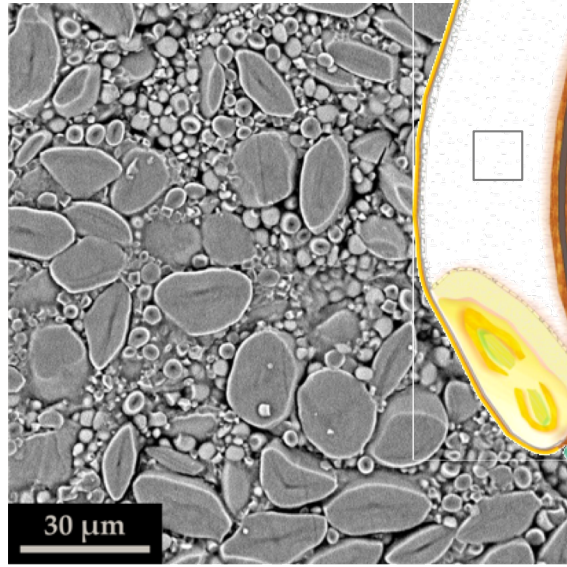
$$I_\varepsilon(\varphi) = \int \rho(\varphi) |d\varphi|$$

$$\lim_{\varepsilon \rightarrow 0} \int \rho(\varphi) |d\varphi|$$

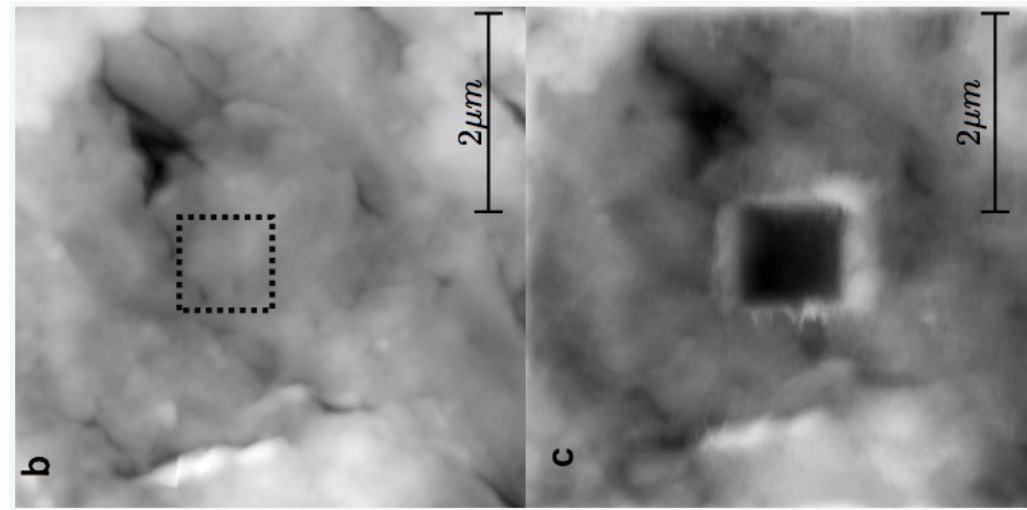
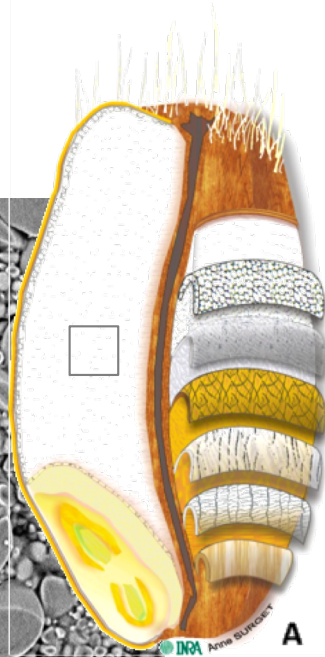
$$W(\cdot, F) = \infty$$

Contact mode

- Abrasion

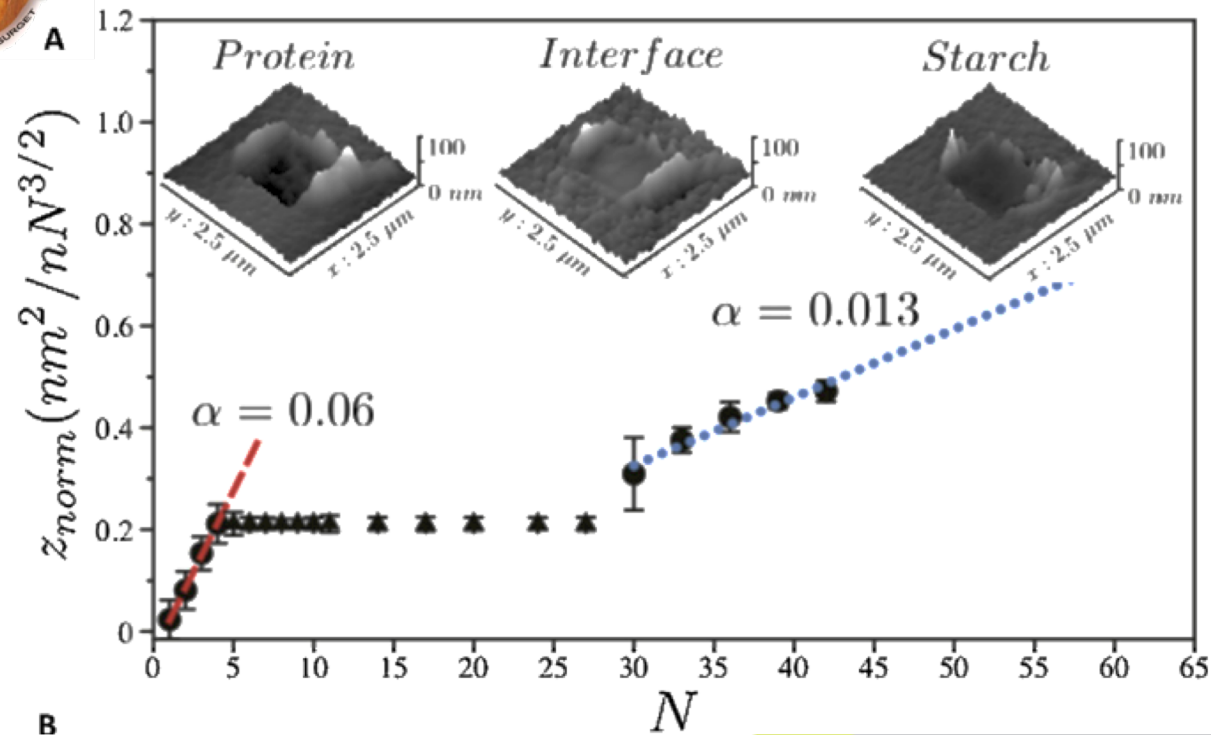


Starch granules inside a wheat endosperm (SEM)



Tablet of pure gluten before/after abrasion (SEM)

Occurrence of “lubricated” interface in soft wheat



$$I_{\varepsilon}(\varphi) = \int_{\varphi} \rho(\varphi) d\varphi$$

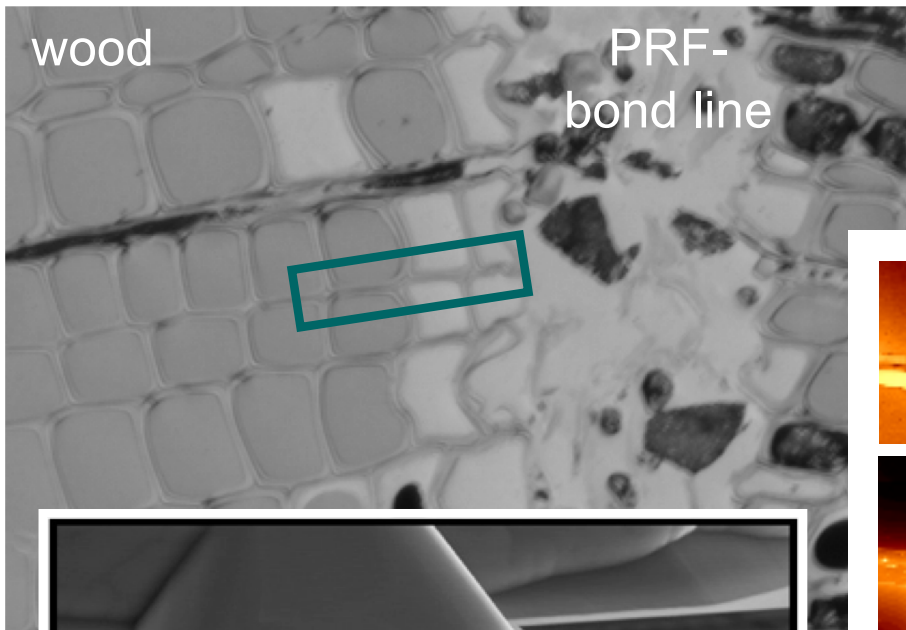
$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

Contact mode

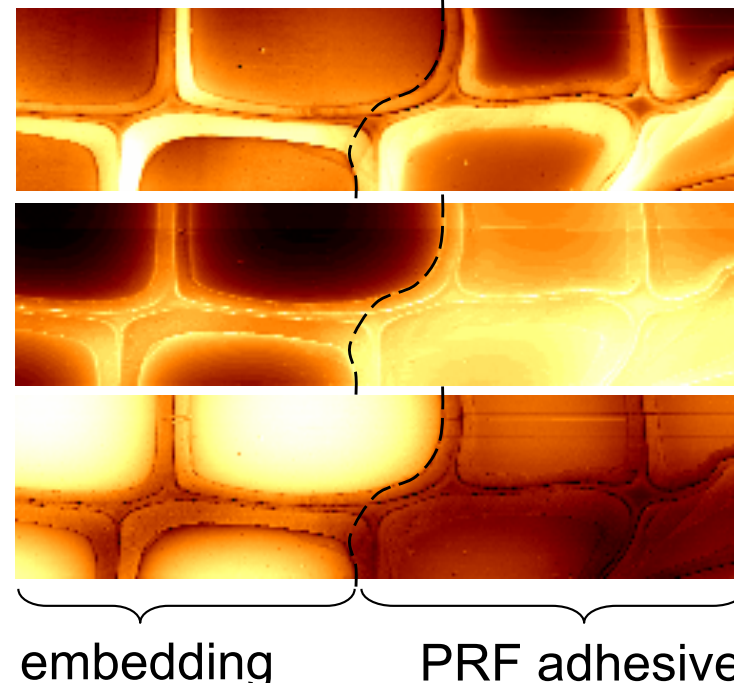
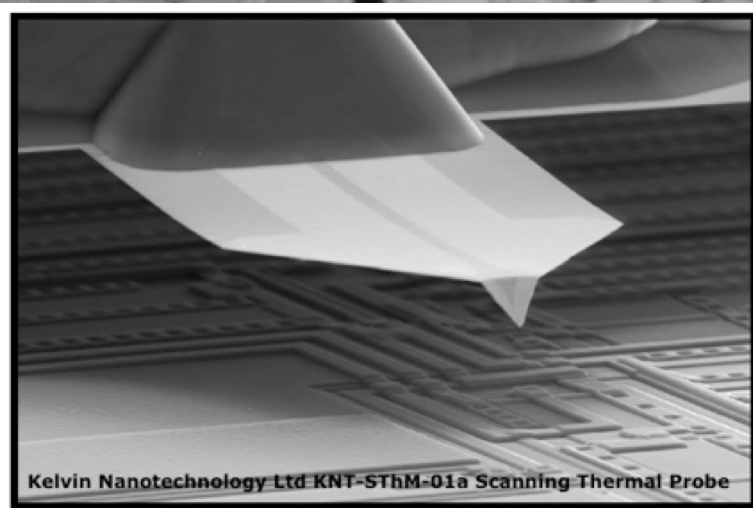
- Scanning Thermal Microscopy (SThM)

[Konnerth *et al.*, Holzforschung, 2008]

$R \approx 100 \text{ nm}$
Scan rate 0.1-0.5 Hz
Spruce wood

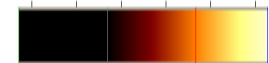


20 μm



Probe Current
CCM-mode

SThM Error
TCM-mode
Low high



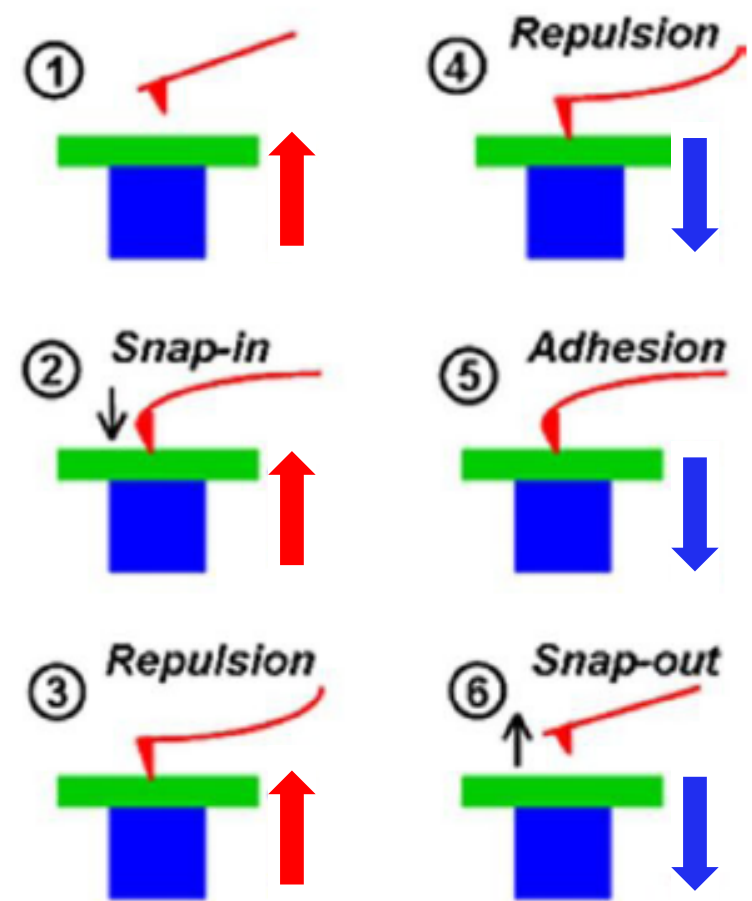
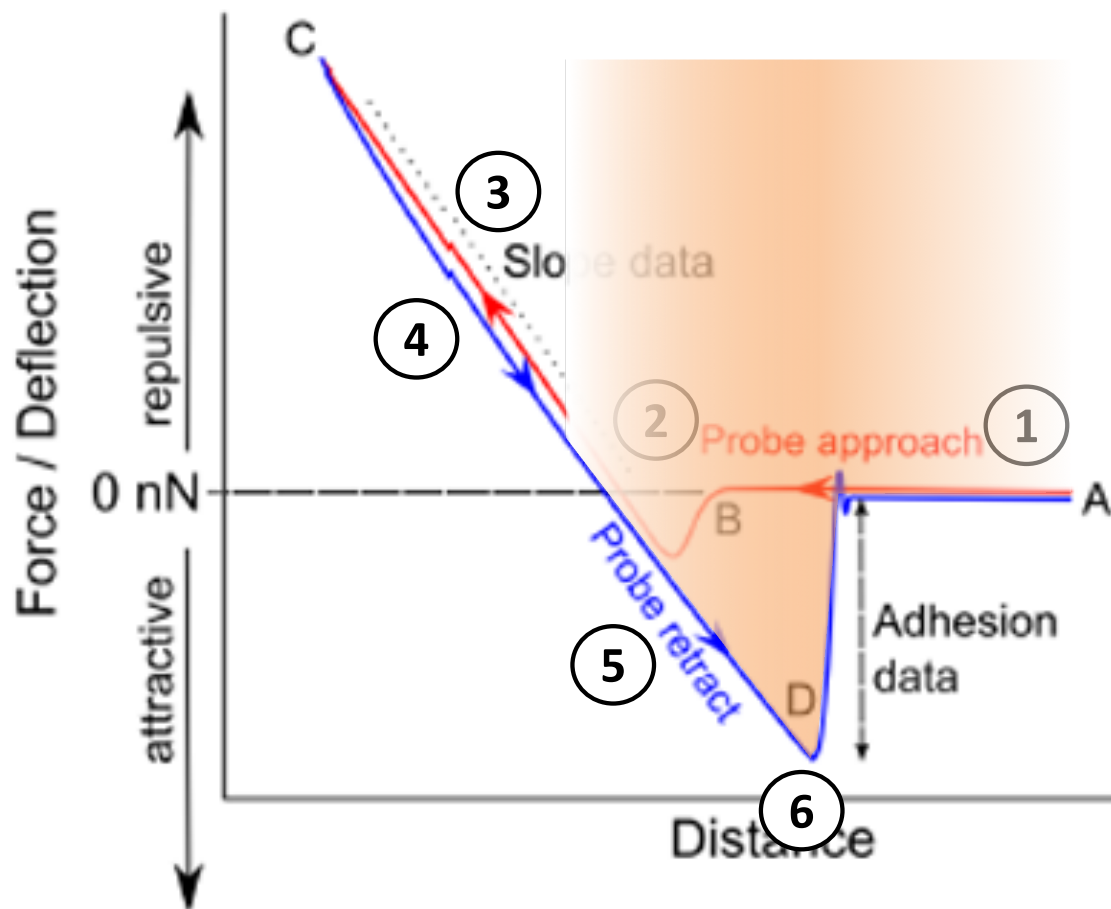
$$I_\varepsilon(\varphi) = \int \varphi(x) dx$$

$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

$$W(\cdot, F) = \infty$$

Force-distance curve

- Van der Waals force, electrostatic force, contact stiffness, adhesion force, ...



[B. Nysten, 2007]

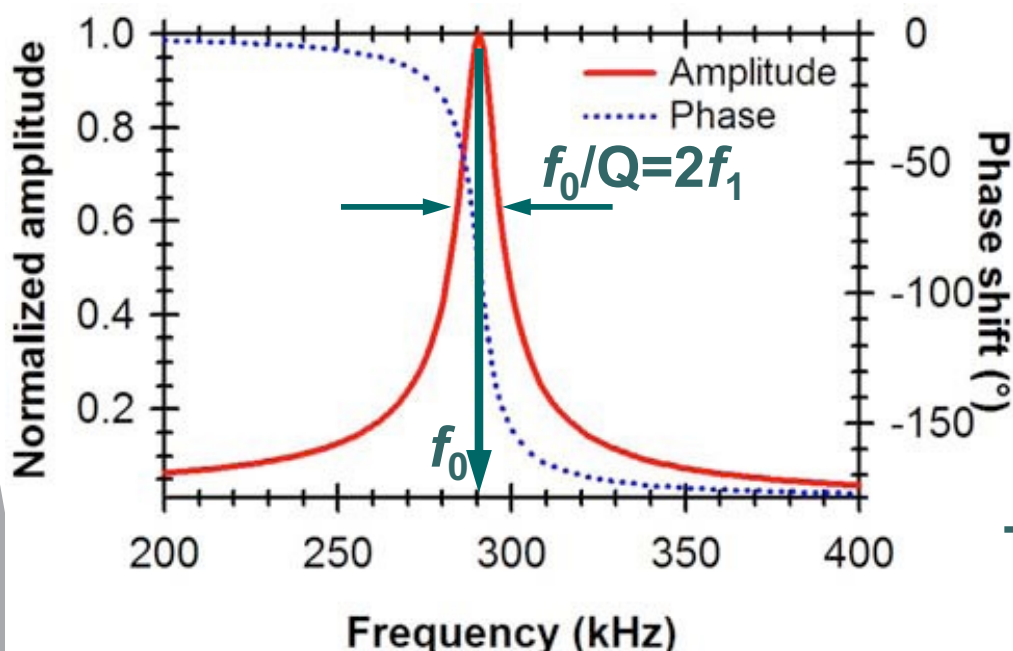
$$I_\varepsilon(\varphi) = \int \nabla \varphi(\mathbf{r}) \cdot d\mathbf{r}$$

lim

$$W(\cdot, F) = \infty$$

Intermittent contact/tapping™/...

- Knocking on the surface!
 - ⇒ Linear harmonic oscillator approximation (free)



$$\omega_0 = \sqrt{\frac{k_C}{m_{\text{eff}}}}$$

$$k_C > 10\text{N/m}$$

$$f_0 > 100\text{kHz}$$



Media	Liquid	Air	High vacuum
Q	10	400	10^4

$$I_\varepsilon(\varphi) = \int \sqrt{\varphi'(z)} dz$$

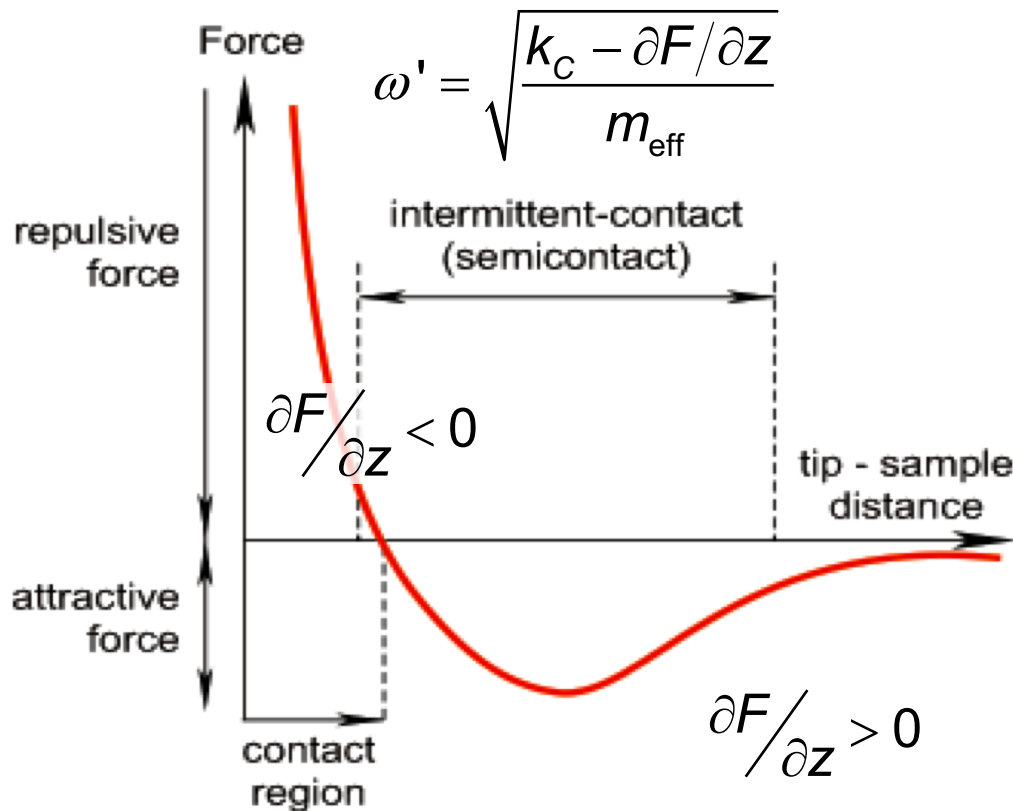
$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

$$W(\cdot, F) = \infty$$

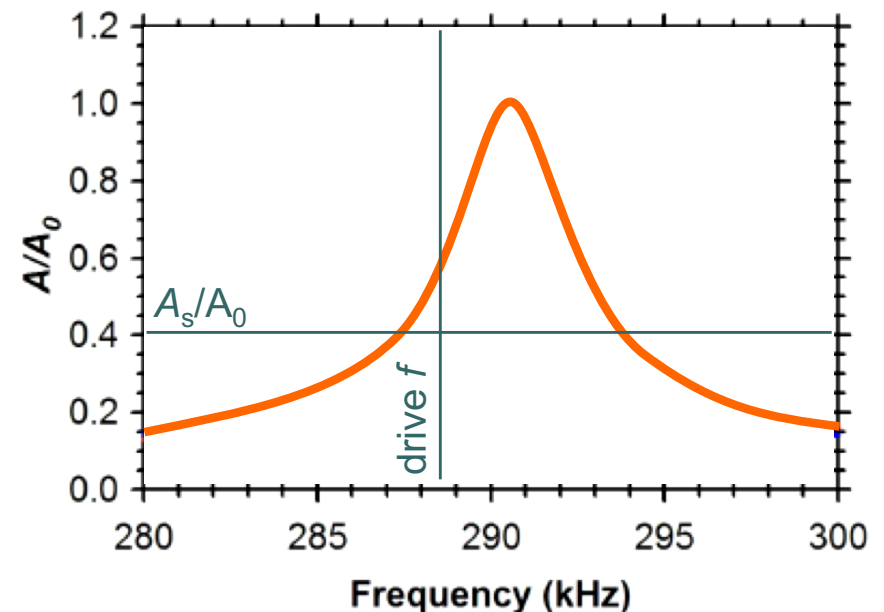
Intermittent contact/tapping™/...



- ➔ Scan at constant vibration amplitude = topography + stiffness contrast
- soft (topography) $A_s/A_0 > 0.8 + A_0 \downarrow$ / hard (elasticity) $A_s/A_0 < 0.4 + A_s \uparrow$ tapping
- ➔ **Linear** harmonic oscillator approximation in a force gradient
[Magonov et al., *Surf. Sci. Lett.*, 1997; Nysten, 2007]



$$\frac{\Delta \omega}{\omega_0} \approx \frac{1}{2k_c} \frac{\partial F}{\partial z}$$



Intermittent contact/tapping™/...

- What are we measuring?

- ➔ **Linear** harmonic oscillator approximation in a force gradient
 [Magonov et al., Surf. Sci. Lett., 1997; Nysten, 2007]

$$\Delta\varphi \approx \frac{Q}{k_C} \frac{\partial F}{\partial z} \text{ if } \omega \sim \omega' \sim \omega_0 \text{ and } \frac{\partial F}{\partial z} \ll \frac{k_C}{Q}$$

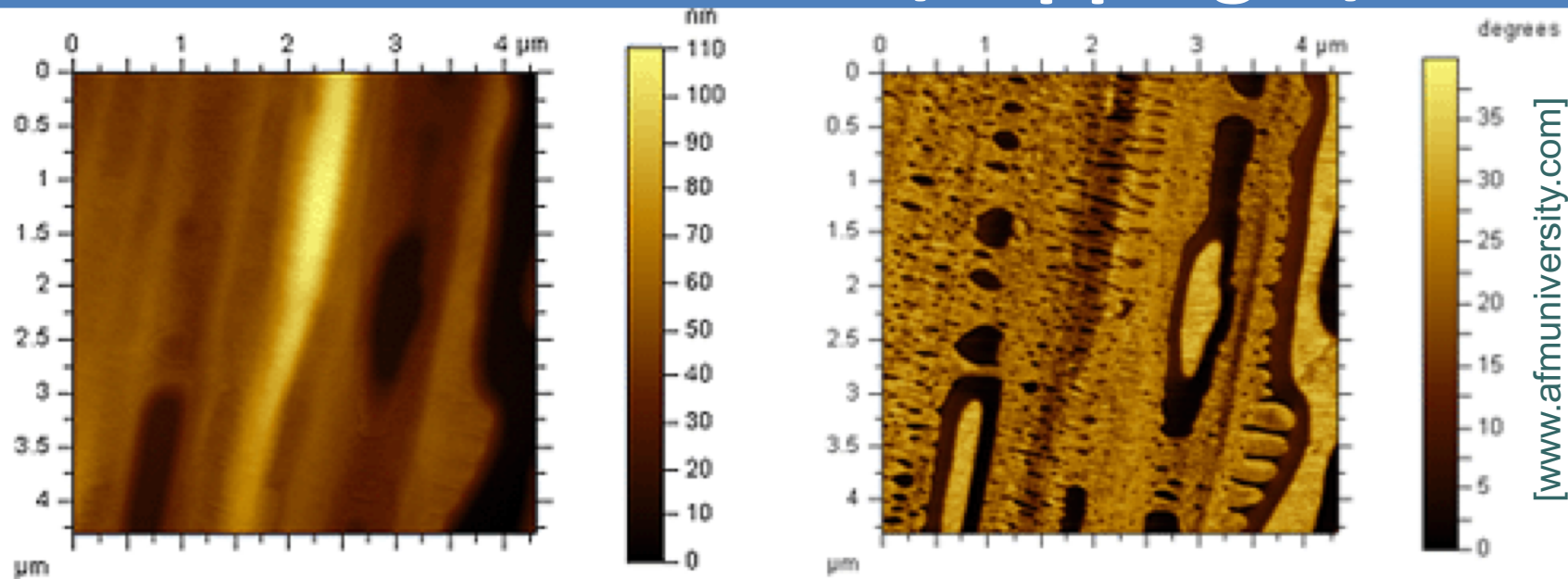
Pure elastic material with Hertz: $F = \frac{4}{3} E^* \sqrt{Rz}^{3/2} \rightarrow \frac{\partial F}{\partial z} \approx 2E^* a$ ➔ $\Delta\varphi \approx \frac{Q}{k_C} 2E^* a$

- ➔ Phase-lag proportional to the contact stiffness in certain condition
 ($k_N \ll k_C/Q + A_0 \uparrow$ and $A_s \downarrow$) → phase images...
 but more generally “proportional” to any dissipation (capillarity, viscoelasticity, adhesion, ...) ➔ difficult to interpret quantitatively!
- ➔ High resolution (<10nm) and **±slow** imaging (cantilever with high frequency)
- ➔ Less tip and sample damages, ~no friction, ...

$$I_\varepsilon(\varphi) = \int_{\varphi} |\nabla \varphi(x)| dx$$

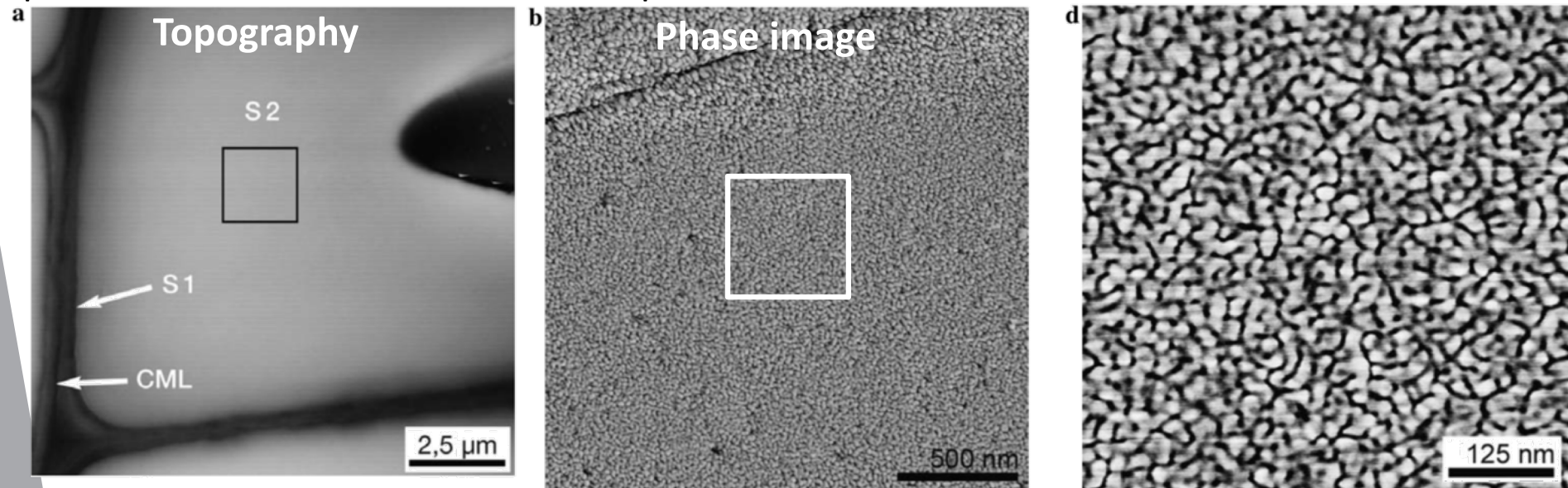
$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

Intermittent contact/tapping™/...



(Figure 8a & b) Topographic (Left) and phase image (Right) of polydiethylsiloxane polymer

Spruce tracheid wood cell wall, AFM probe and condition?



$$I_\varepsilon(\varphi) = \int \varphi(u) |d\mu|$$

$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

Intermittent contact/tapping™/...

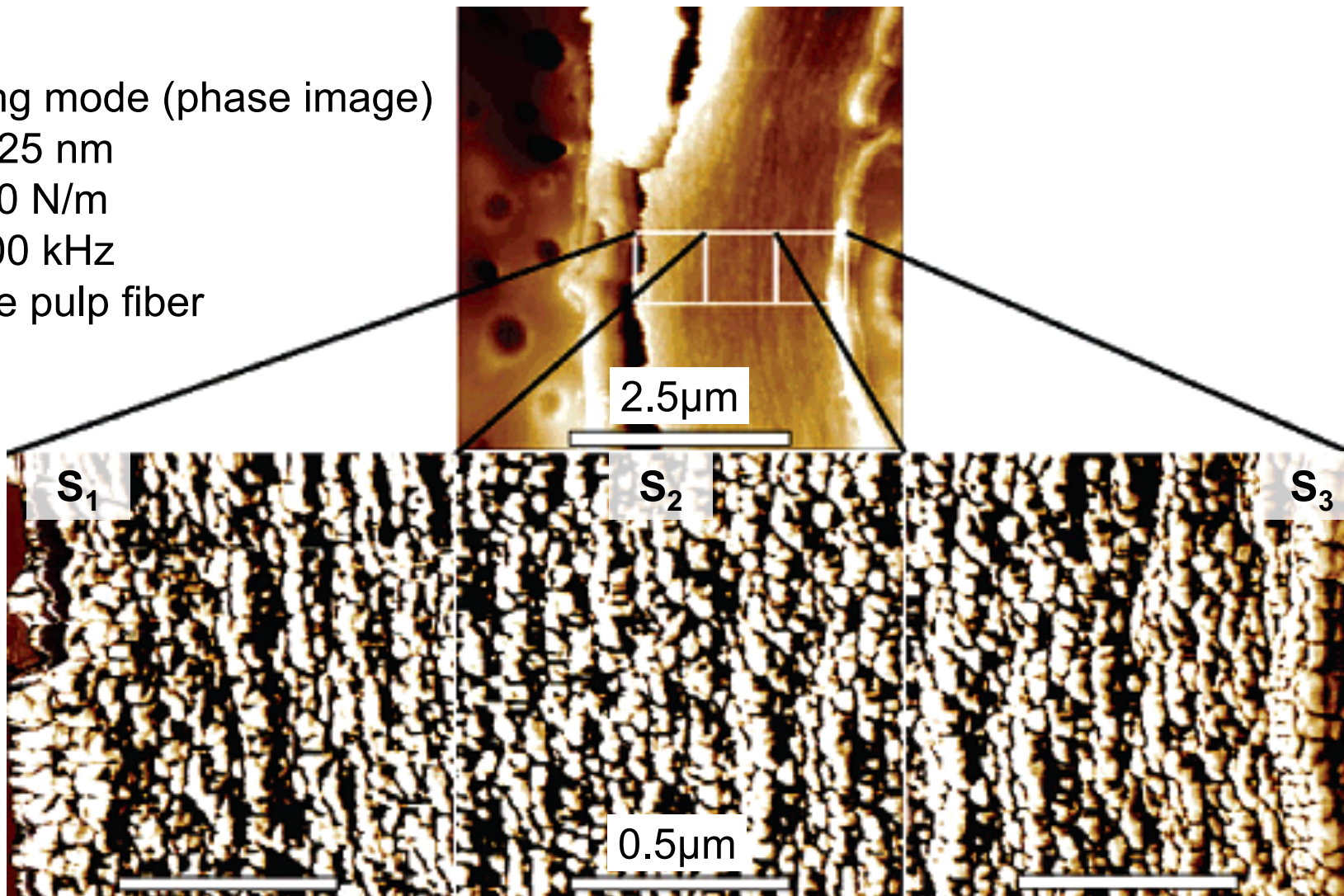
Tapping mode (phase image)

$R \approx 4.25 \text{ nm}$

$k_C \approx 40 \text{ N/m}$

$f_0 = 300 \text{ kHz}$

Spruce pulp fiber



[Fahlén and Salmén, Biomacromolecules, 2005]

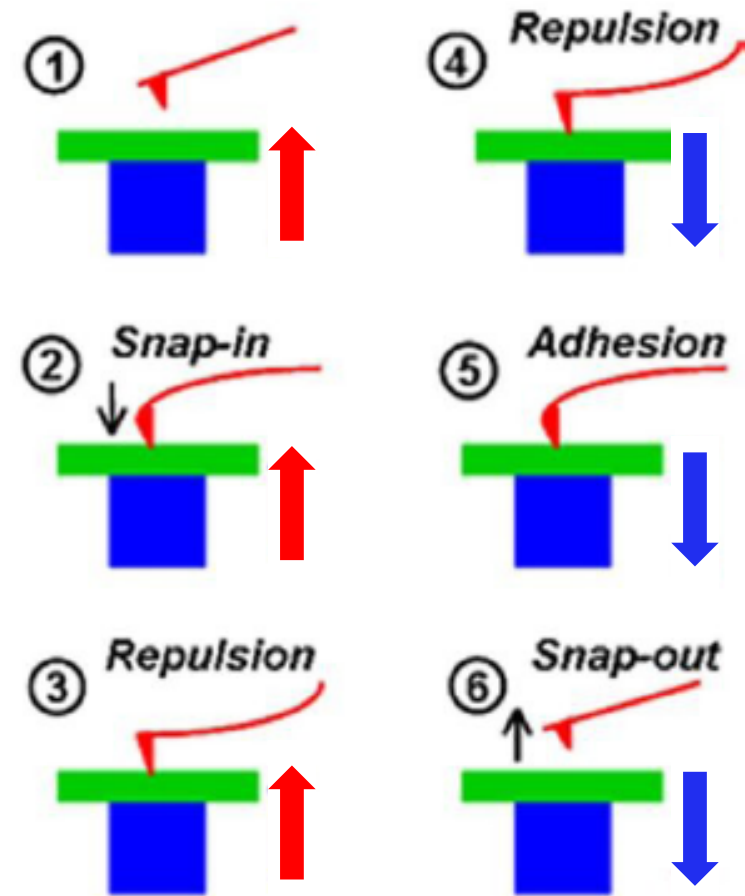
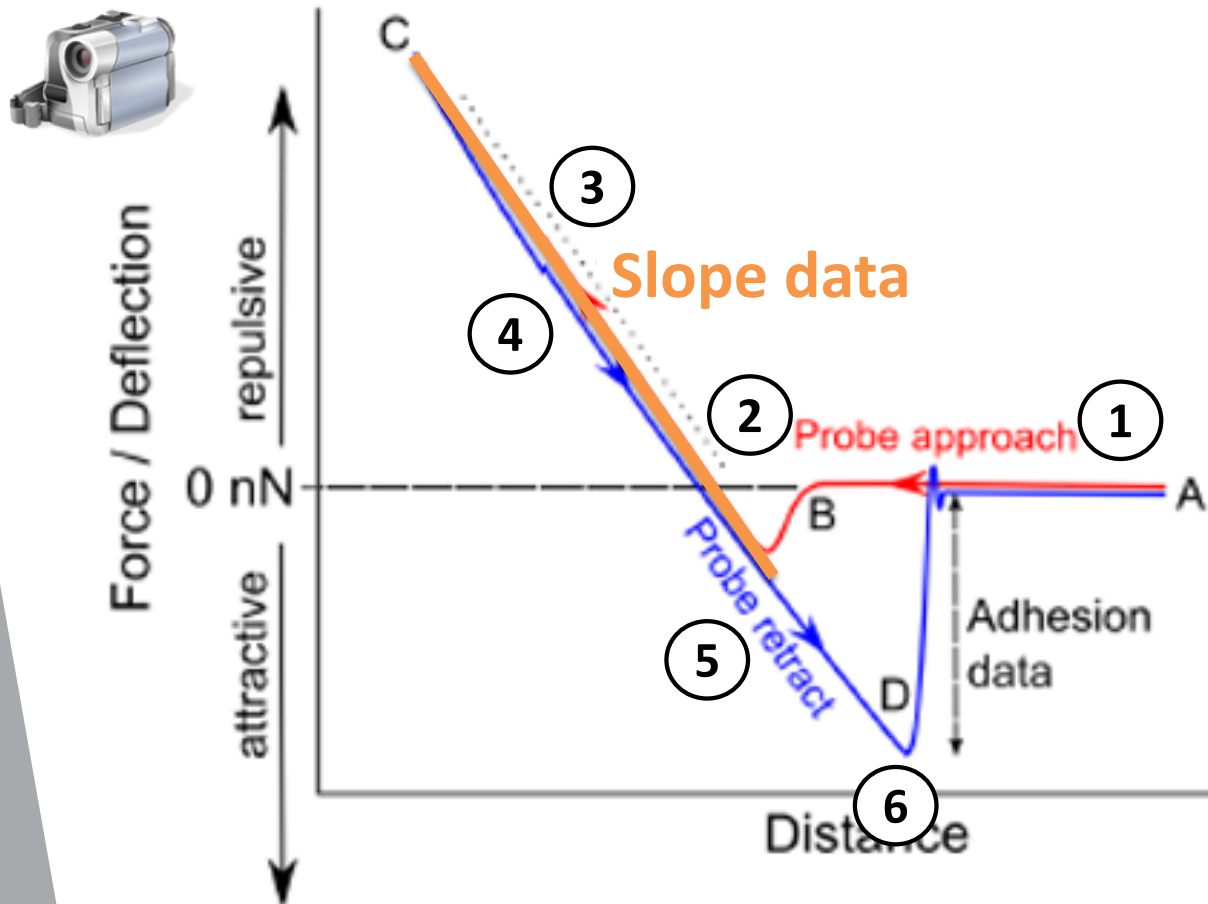
$$I_\varepsilon(\varphi) = \int \nabla \varphi(u) \cdot du$$

$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

$$W(\cdot, F) = \infty$$

Force-distance curve

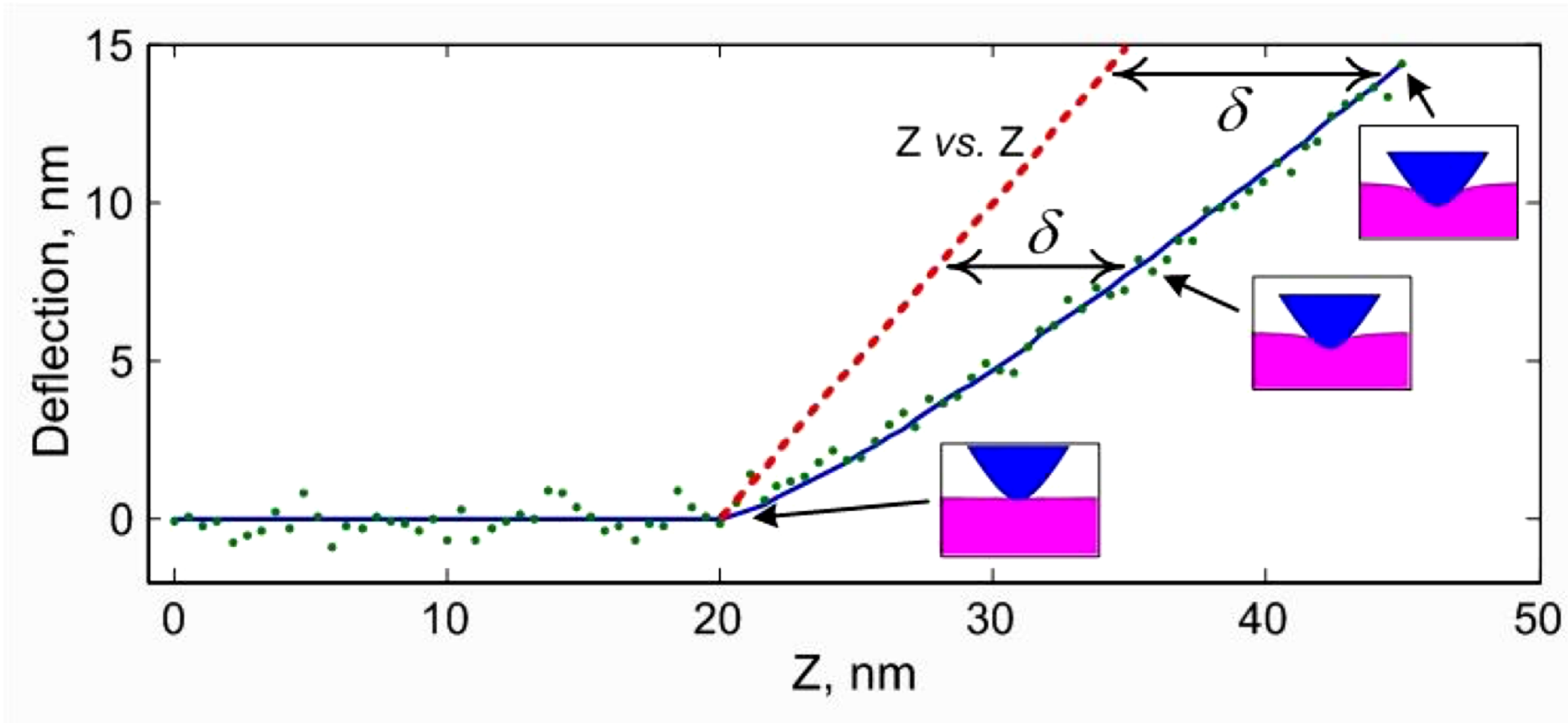
- Van der Waals force, electrostatic force, contact stiffness, adhesion force, ...



[B. Nysten, 2007]

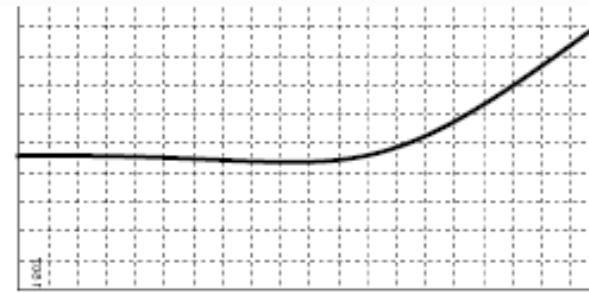
Fd - Indentation

- Decoupling load/displacement



Hard sample

[www.veeco.com]



Soft sample

Fd - Indentation

● Requirements:

- ➔ Cantilever stiffness



$$\frac{d}{z} = \frac{1}{1 + \frac{k_C}{k_N}}$$

$$k_N \gg k_C \rightarrow d = z$$

$$k_N \ll k_C \rightarrow d = 0$$



$$k_N \sim k_C$$

$$k_{N_{DMT}} = \left(6M^2R(F + F_{ad_{DMT}}) \right)^{1/3}$$

with

$$F = k_c d = k_c \chi V_{A-B}$$

- ➔ Calibration of the laser/photodetector
 - ➔ Calibration of the cantilever stiffness
 - ➔ Measurements of the real tip apex shape + **suitable** contact model...
 - ➔ Non-normal load (shear) due to cantilever tilt + tip sliding?
 - ➔ Limited resolution (>100nm on polymer) due to large tip surface contact area
-
- ➔ Mapping (Force-Volume mode) of the elastic properties is very time consuming (256 x 256 points = 18h)

→ Force Modulation Mode... PeakForce QNM, QI, etc

$$I_\varepsilon(\varphi) = \int \nabla \varphi(x) \cdot dx$$

$$\lim$$

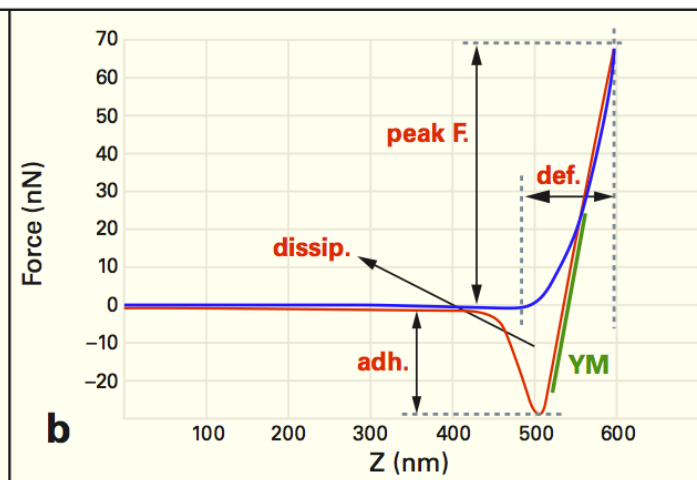
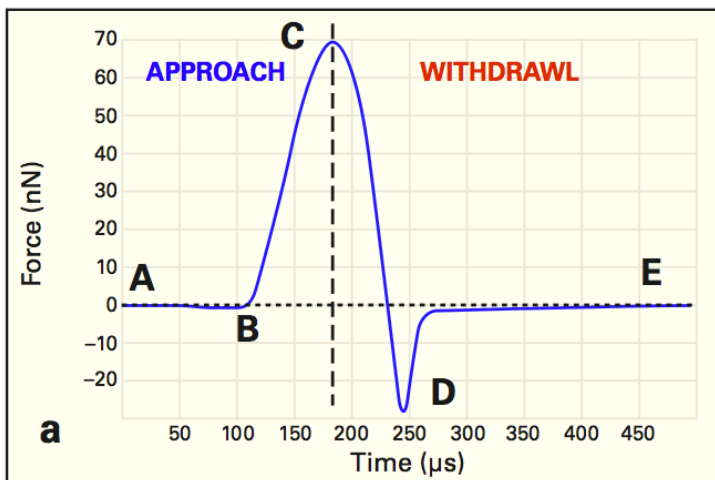
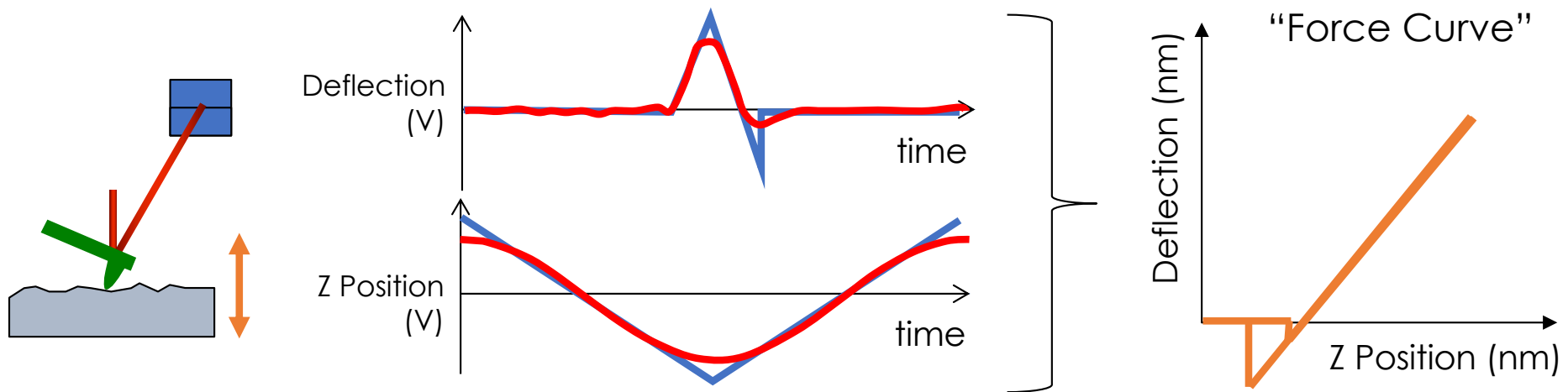
$$W(\cdot, F) = \infty$$

Fd - Indentation

- Peak Force Quantitative NanoMechanical (QNM)

[www.bruker-axs.com]

➔ force curve recording at some kHz with sinusoidal displacement



Calibration!

DMT modulus
Dissipation (hysteresis loop)
Adhesion force

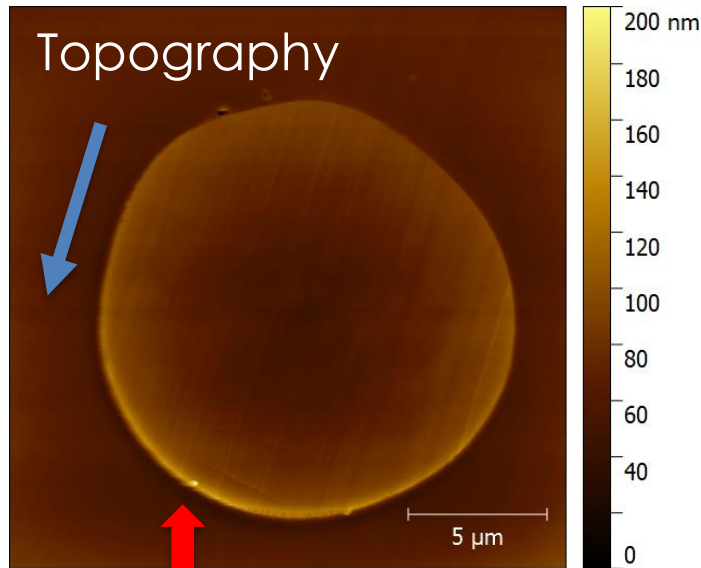
$$I_\varepsilon(\varphi) = \int_{\varphi} \rho(\varphi) d\varphi$$

lim

$$W(\cdot, F) = \infty$$

Kevlar® Dupont™ K48 fibres

[Arnould et al, Ind. Crops Prod, 2017]



[Wollbrett-Blitz et al, J. Polym. Sci., 2016]

Core:

$$E_l = 84 \text{ GPa} / E_t = 3 \text{ GPa}$$

Skin:

$$E_l = 85 \text{ GPa} / E_t = 0,2 \text{ GPa}$$

$$G_{lt} = 1,8 \text{ GPa} / G_{tt} = 1,2 \text{ GPa}$$

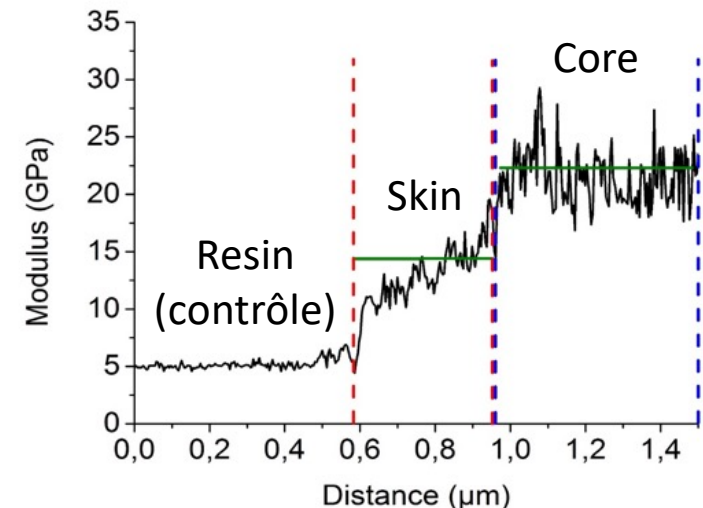
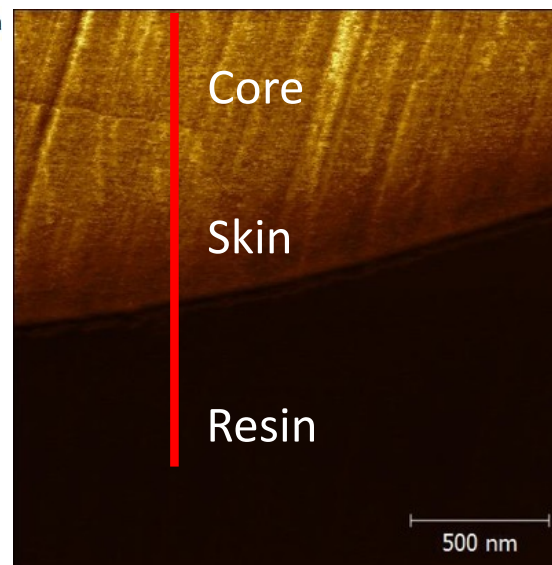
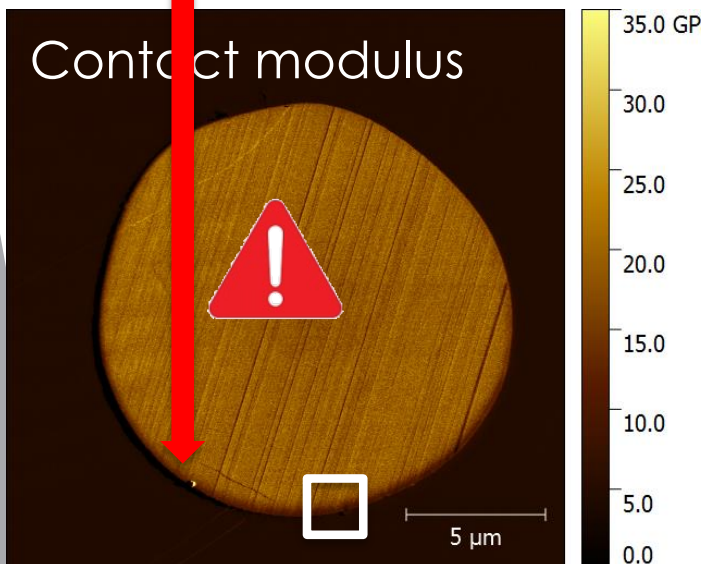
$$\nu_{lt} = 0,6 / \nu_{tt} = 0,25$$

$$M_{\text{core NI}} = 22,8 \pm 1,7 \text{ GPa}$$

(150 nm @ 1 µN/s + 20 s + 10 µN/s)

$$M_{\text{core calc}} \approx 21 \text{ GPa}$$

$$M_{\text{skin calc}} \approx 17 \text{ GPa}$$



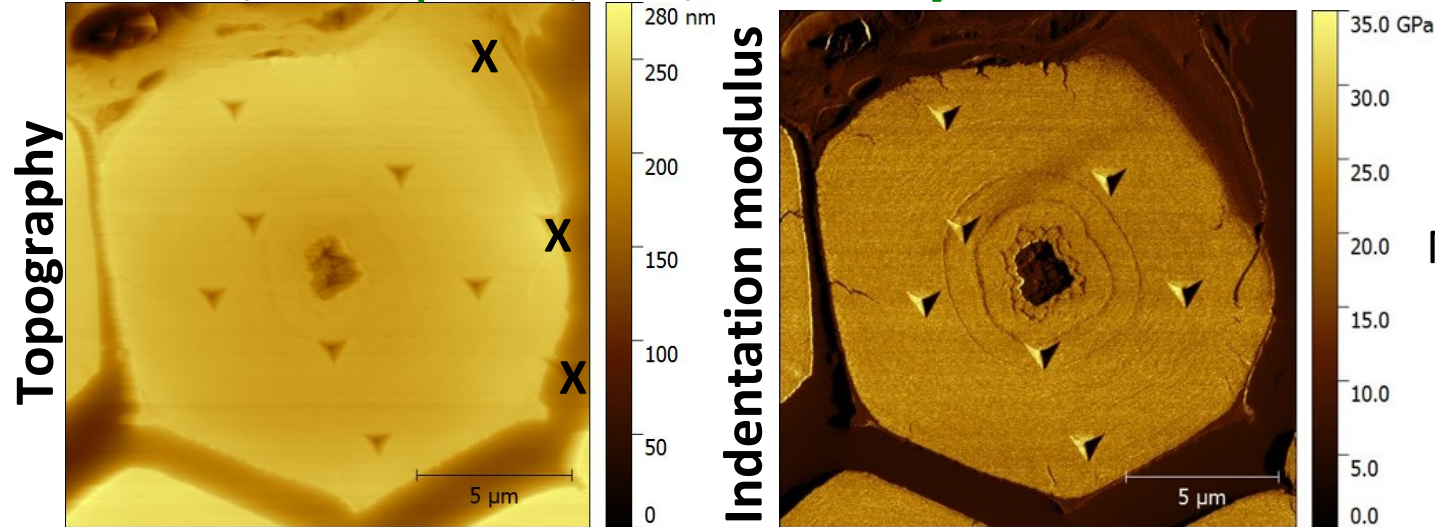
$$I_\varepsilon(\varphi) = \int_{\varphi} \rho(\varphi) d\varphi$$

lim

$$W(\cdot, F) = \infty$$

Flax fibres for bio-composites

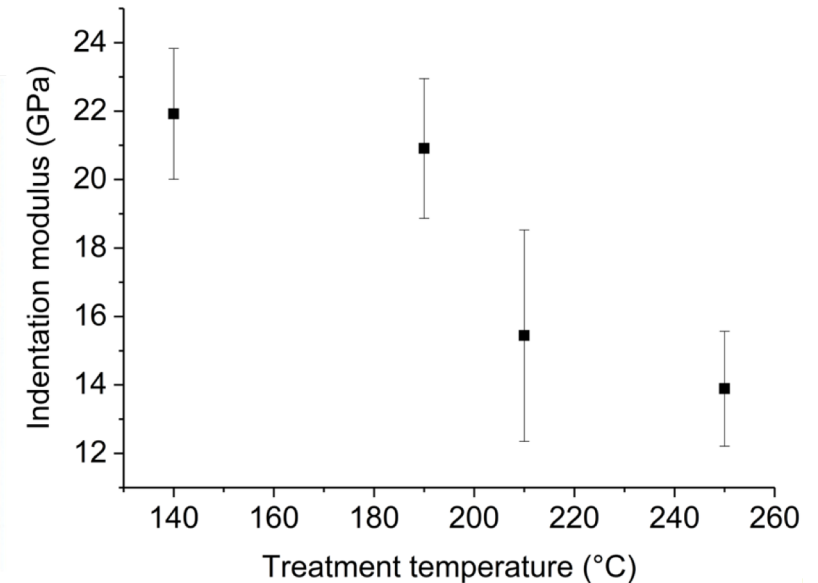
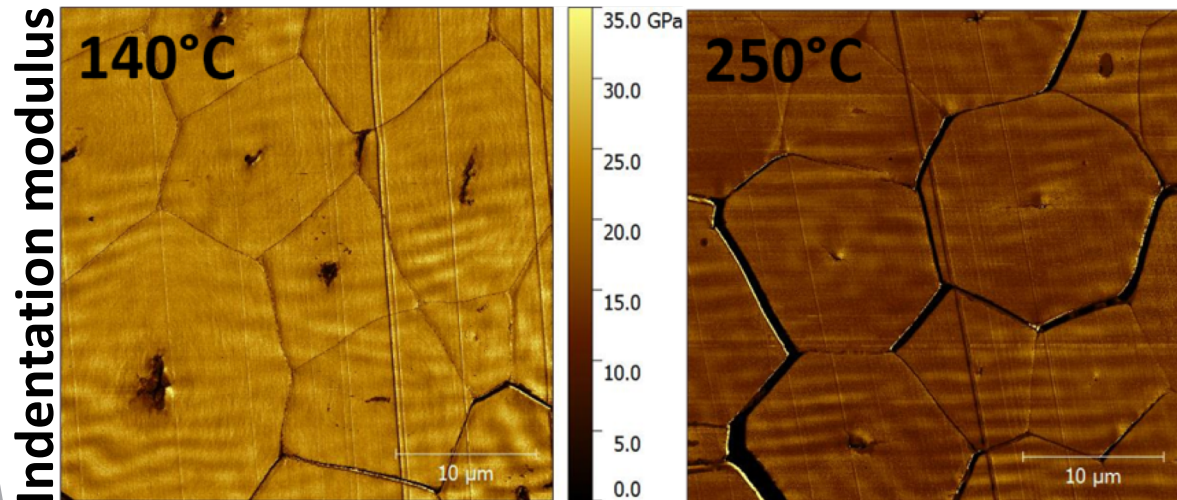
[Arnould et al, Ind. Crops Prod., 2017, 97: 224-228]



E_l fibre \approx 50-60 GPa !
 M_{NI} fibre = 21.3 ± 2.2 GPa
 (150 nm @ 1 μ N/s
 + 20 s - 10 μ N/s)

Effect of processing temperature and fibres confinement in the composite matrix

[Sinsicalco et al, Polym. Test., 2018, 69:91-99]



$$I_\epsilon(\varphi) = \int_{\varphi} \rho(x) dx$$

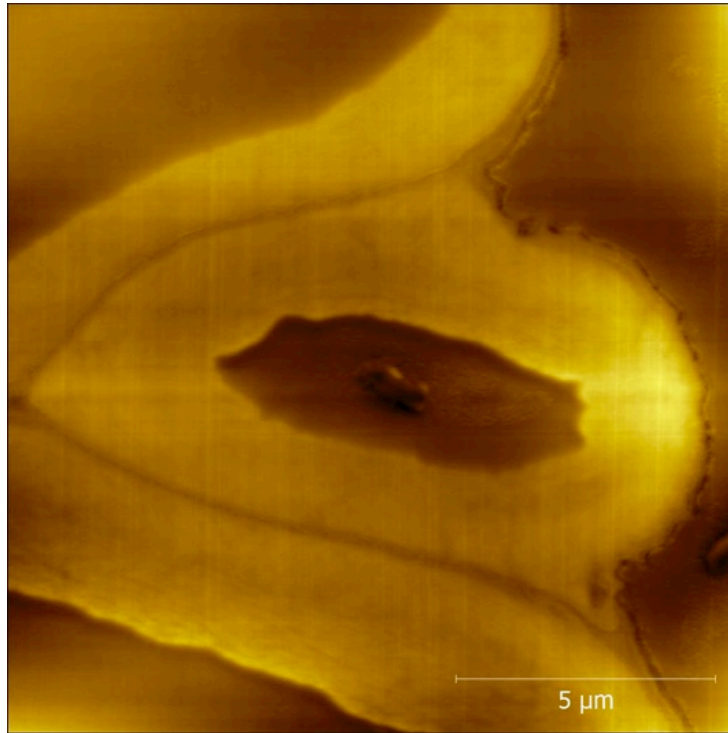
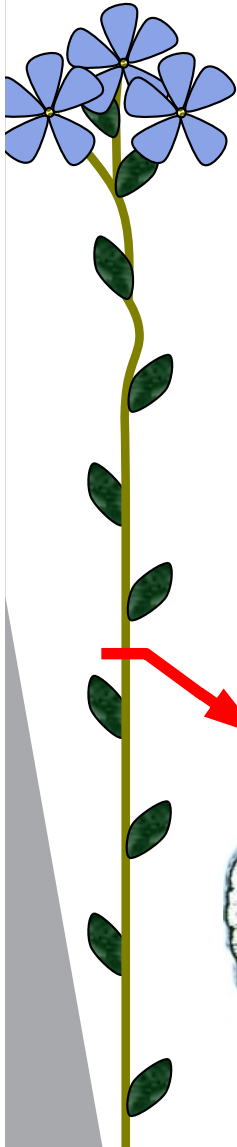
lim

$$W(\cdot, F) = \infty$$

Developping flax fibres

[Arnould et al, Ind. Crops Prod., 2017, 97: 224-228]

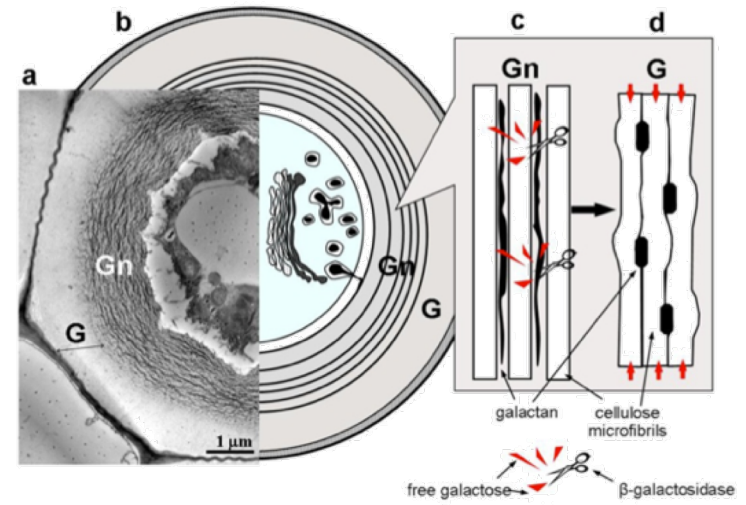
IRDL



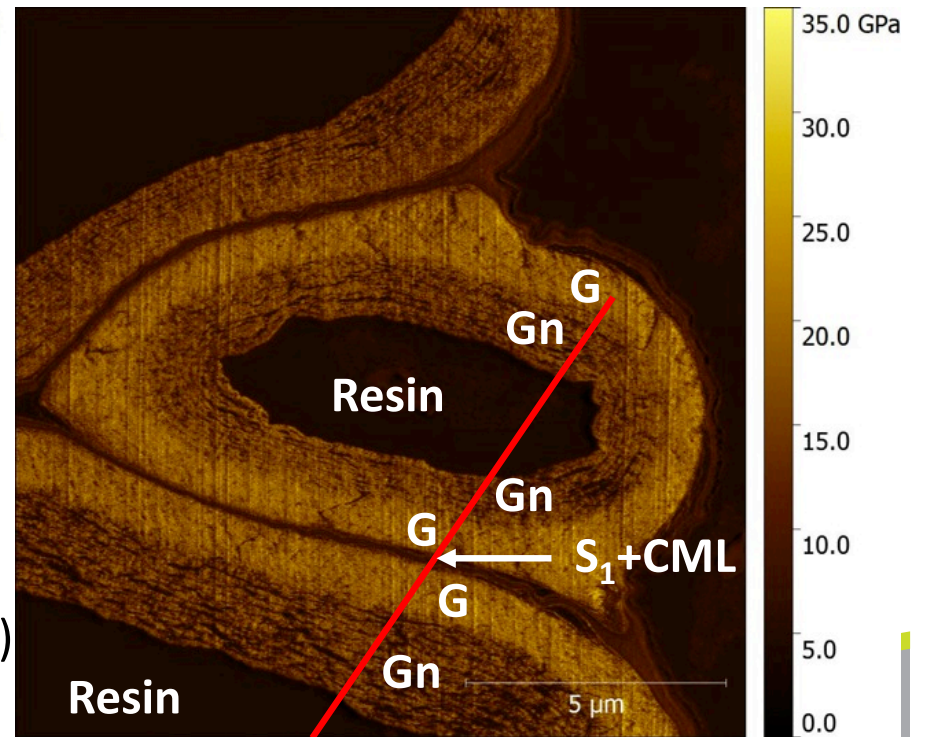
Topography (nm)



MultiMode 8, PF-QNM
 Bruker RTESPA-525
 139 N/m, 32 nm (HOPG)
 200 nN



Indentation modulus (GPa)



[Mikshina et al, InTech, 2013]

$$I_\varepsilon(\varphi) = \int_{\varphi} \rho(\varphi) d\varphi$$

 \lim

$$W(\cdot, F) = \infty$$

Developping flax fibres

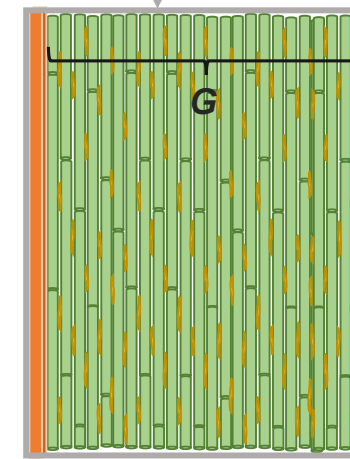
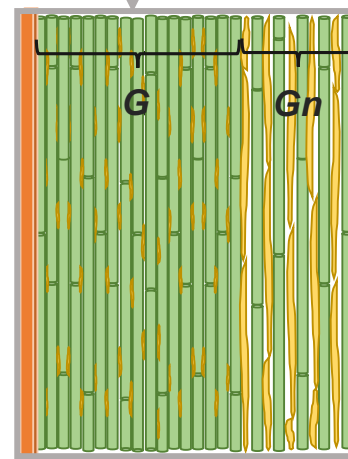
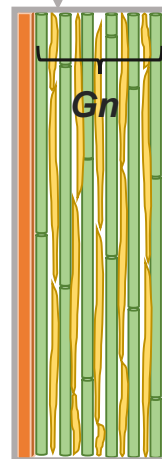
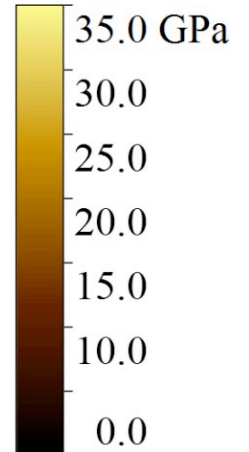
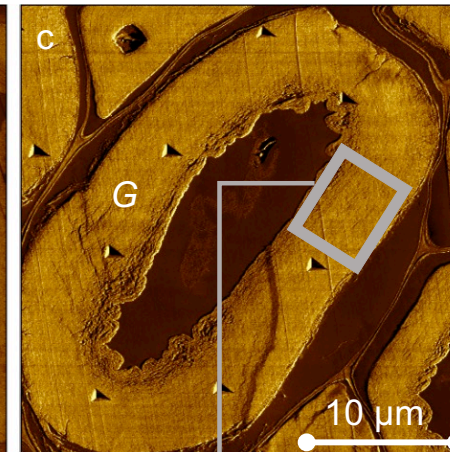
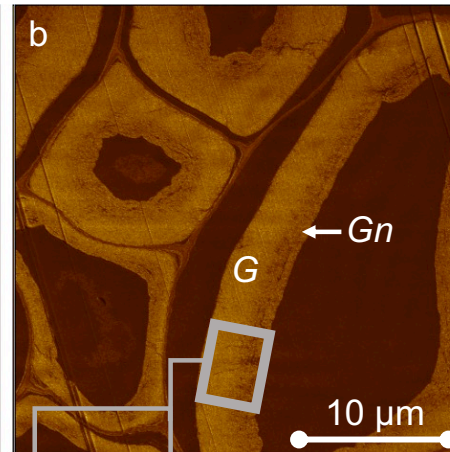
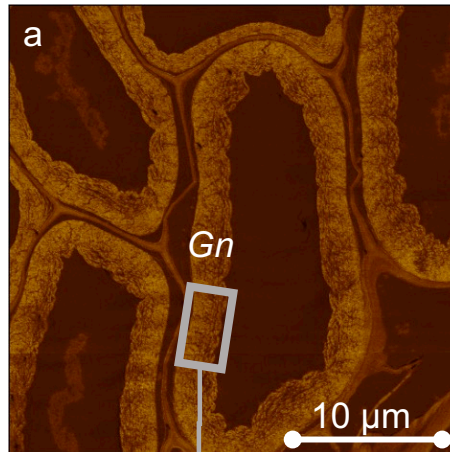
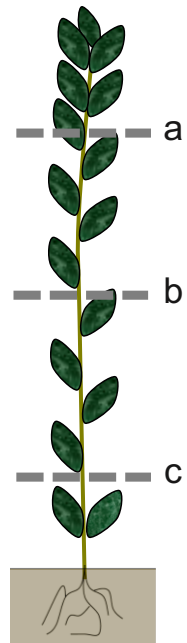
[Goudenhooff et al, *Fibers*, 2018, 6(6): 9p]



Average thickness
 Gn : $2.0 \pm 0.5 \mu\text{m}$
Average modulus
 Gn : $13.0 \pm 2.5 \text{ GPa}$

Average thickness
 Gn+G : $3.2 \pm 1.3 \mu\text{m}$
Average modulus
 G : $18.0 \pm 1.9 \text{ GPa}$
 Gn : $14.0 \pm 1.8 \text{ GPa}$

Average thickness
 G : $5.0 \pm 1.5 \mu\text{m}$
Average modulus
 G : $19.5 \pm 2.9 \text{ GPa}$



Scheme legend:

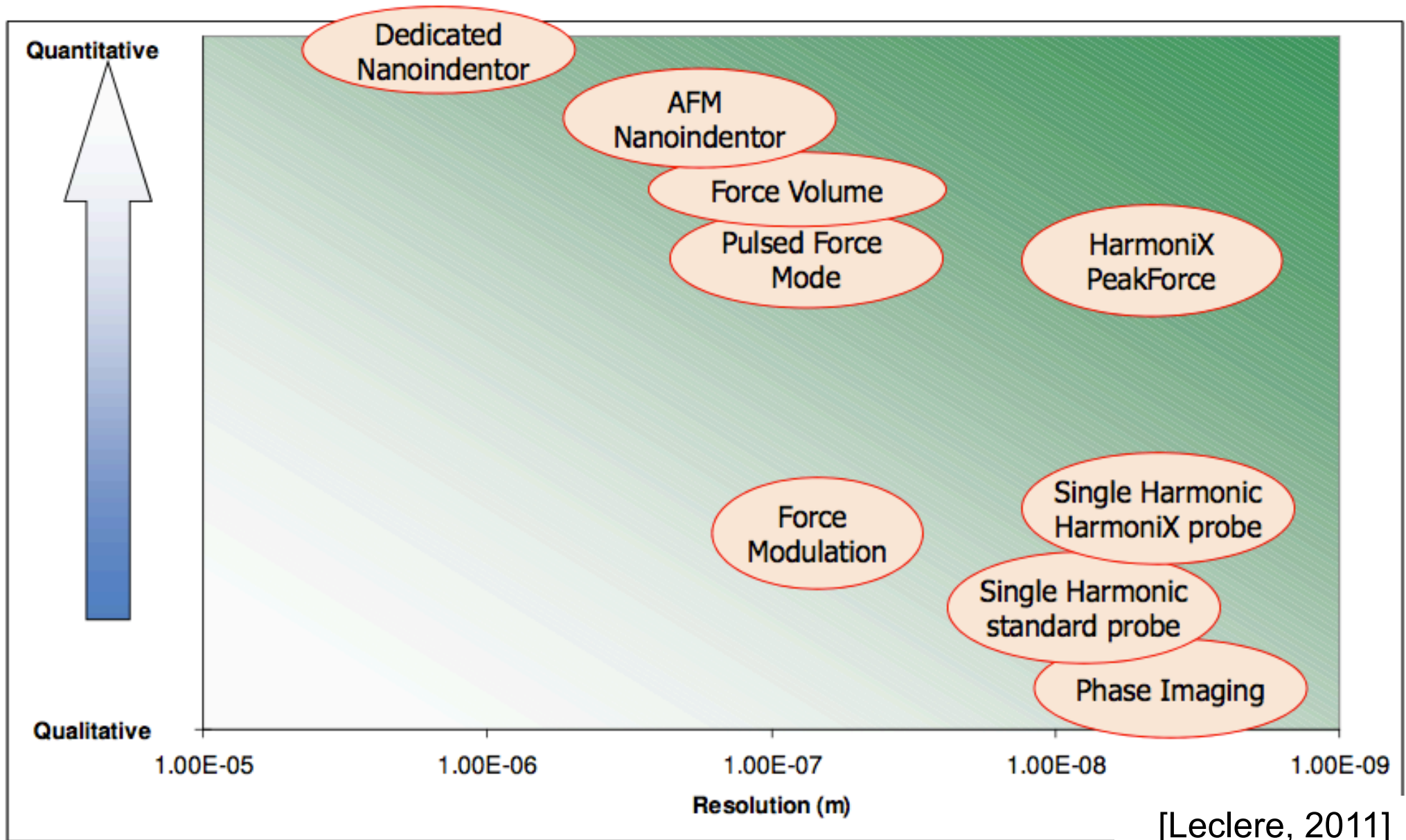
- Primary cell wall and S₁ layer
- Cellulose microfibril
- Untight galactan
- Entrapped galactan

$$I_\varepsilon(\varphi) = \int \varphi(u) |du|$$

lim

$$W(\cdot, F) = \infty$$

Quality of data vs. Resolution



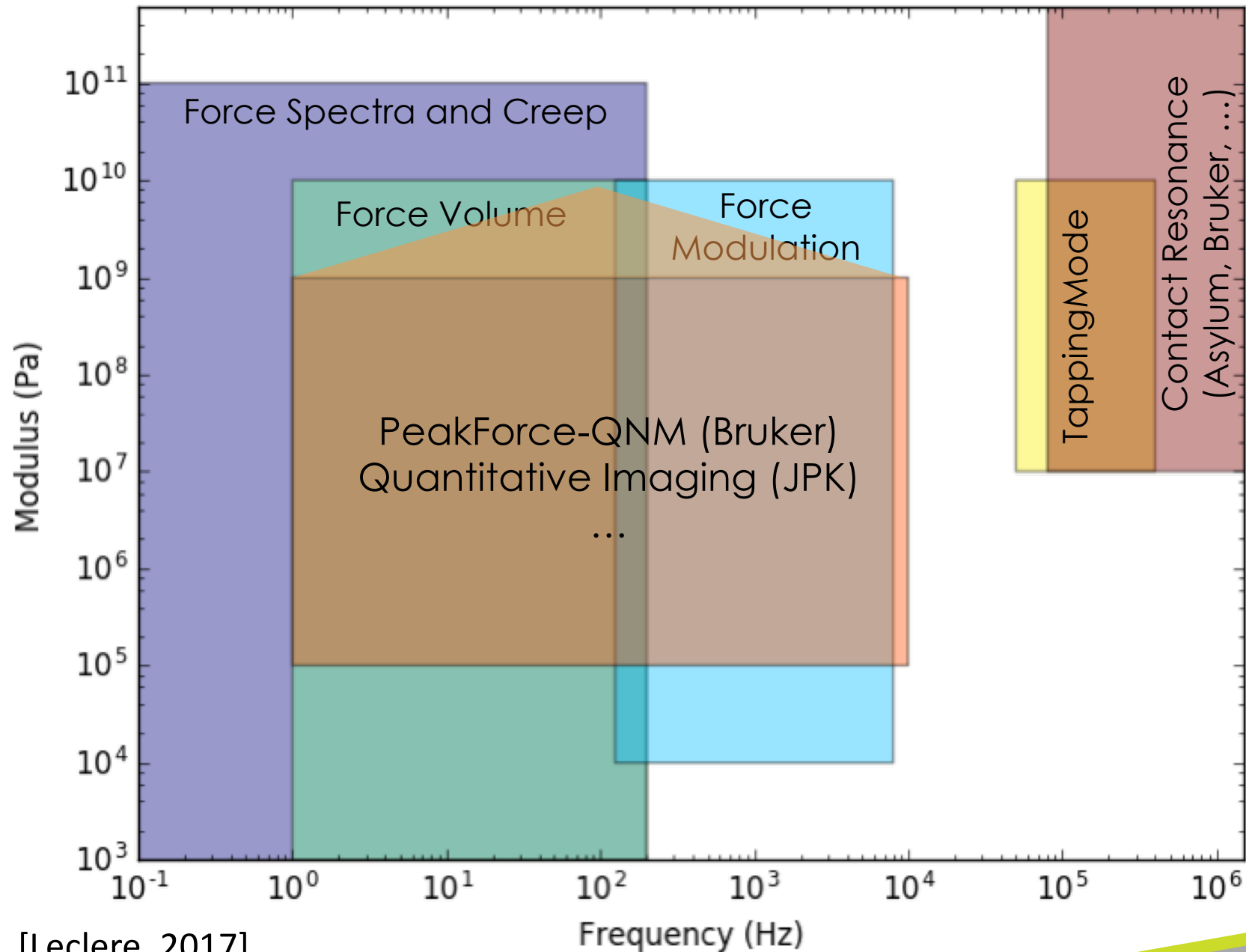
$$I_\varepsilon(\varphi) =$$

$$\int \rho(\mathbf{r}) d\mathbf{r}$$

lim

$$W(\cdot, F) = \infty$$

AFM frequency and elastic modulus range...



[Leclere, 2017]

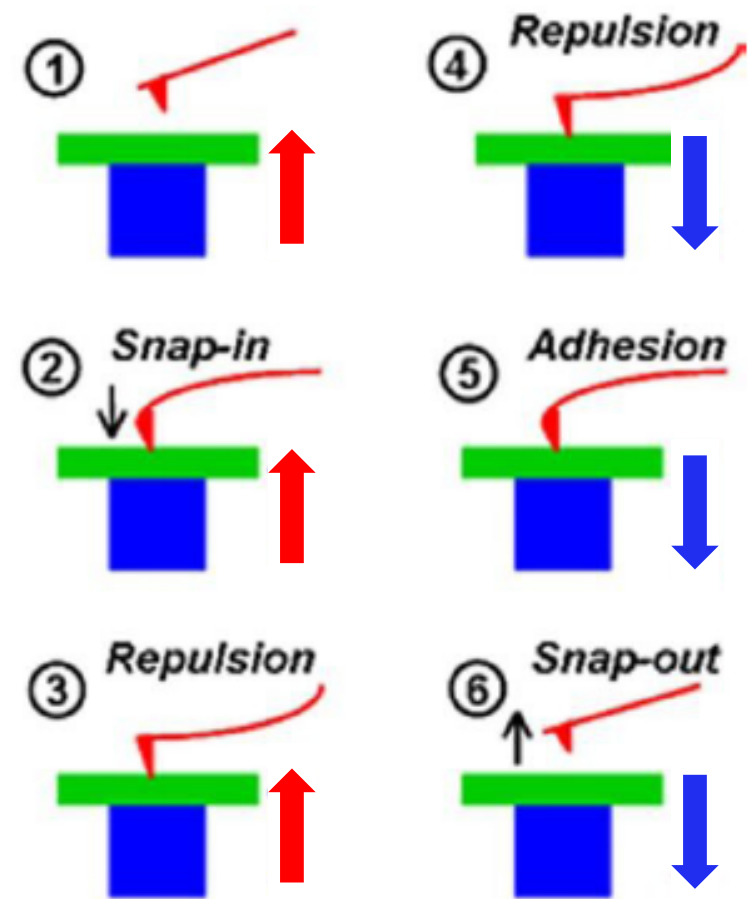
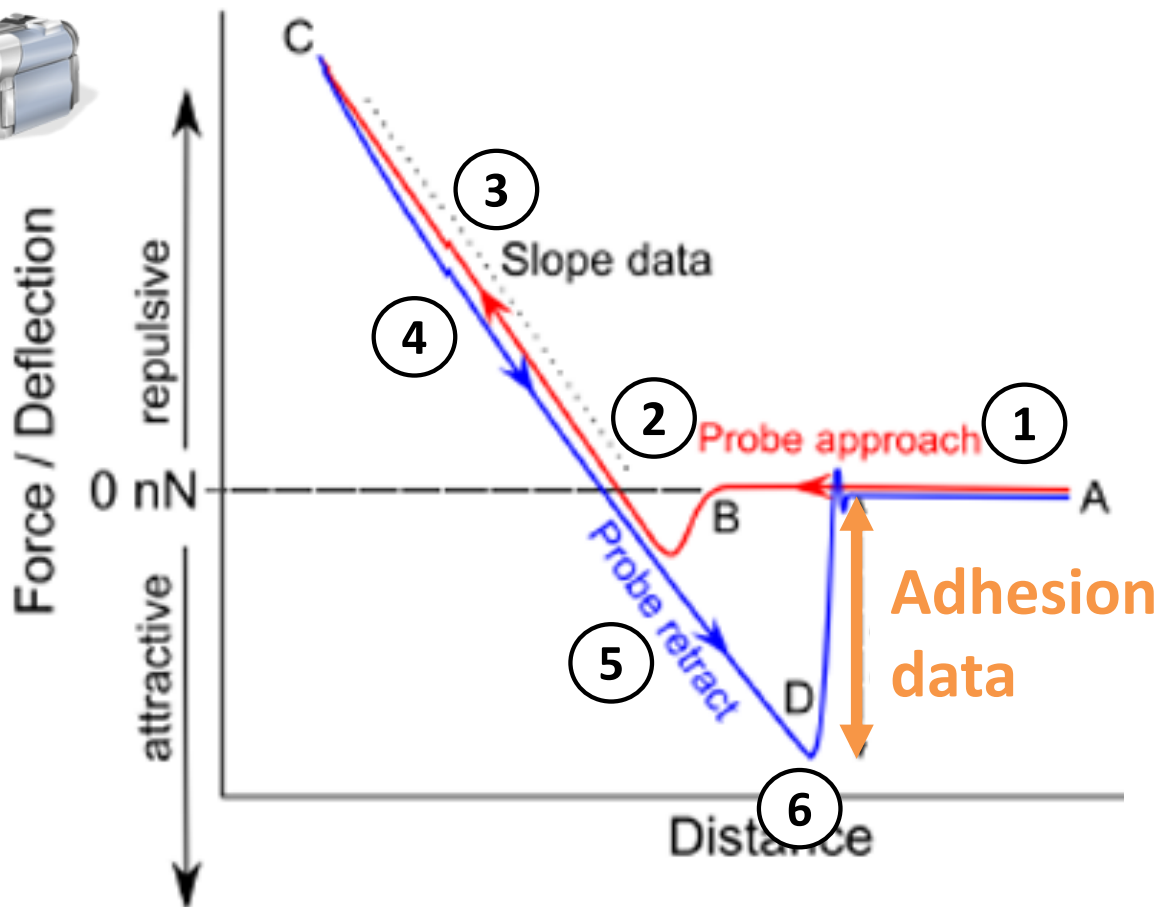
$$I_\varepsilon(\varphi) = \int \nabla \varphi(u) \cdot d\mathbf{u}$$

$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

$$W(\cdot, F) = \infty$$

Force-distance curve

- Van der Waals force, electrostatic force, contact stiffness, adhesion force, ...



[B. Nysten, 2007]

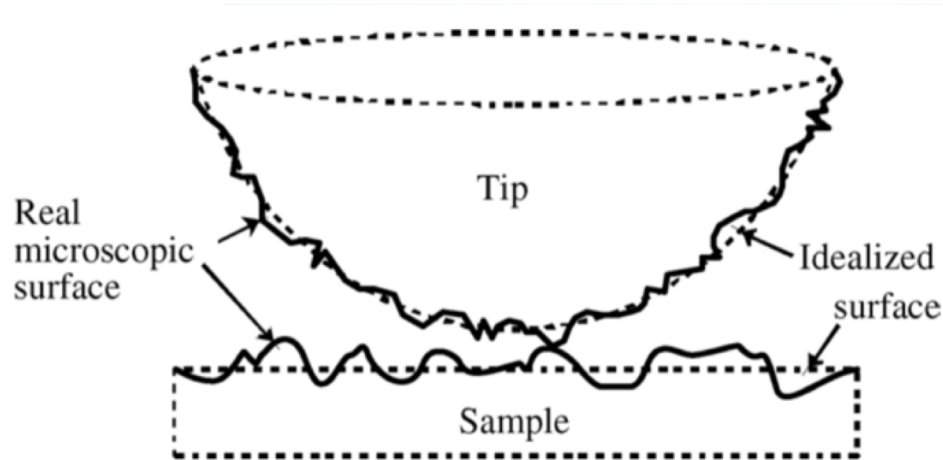
$$I_\varepsilon(\varphi) = \int \varphi(u) |du|$$

$$\lim_{\varepsilon \rightarrow 0} W(\cdot, F) = \infty$$

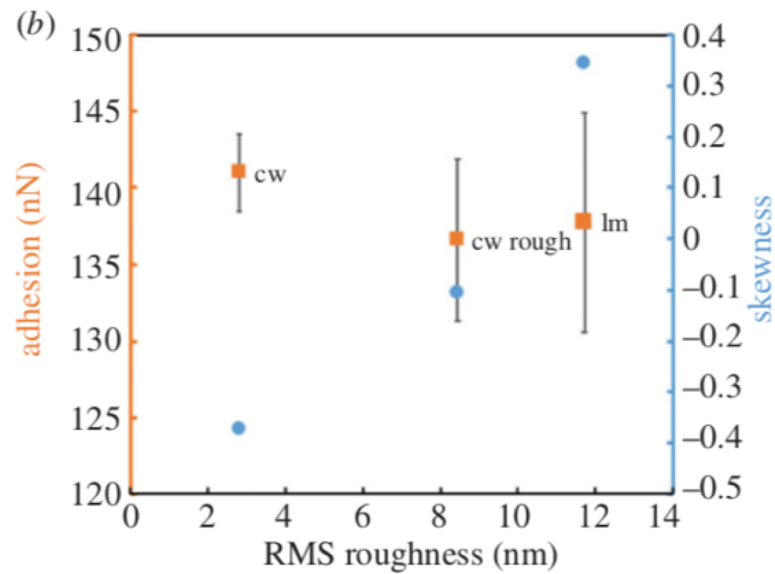
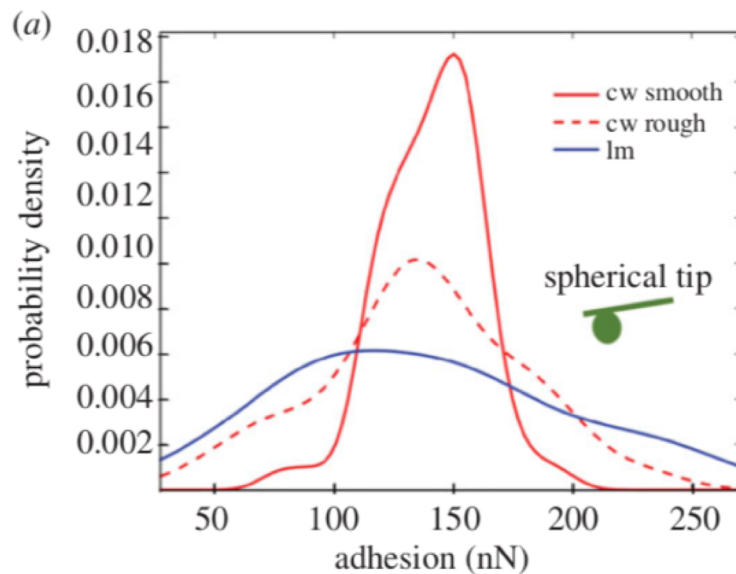
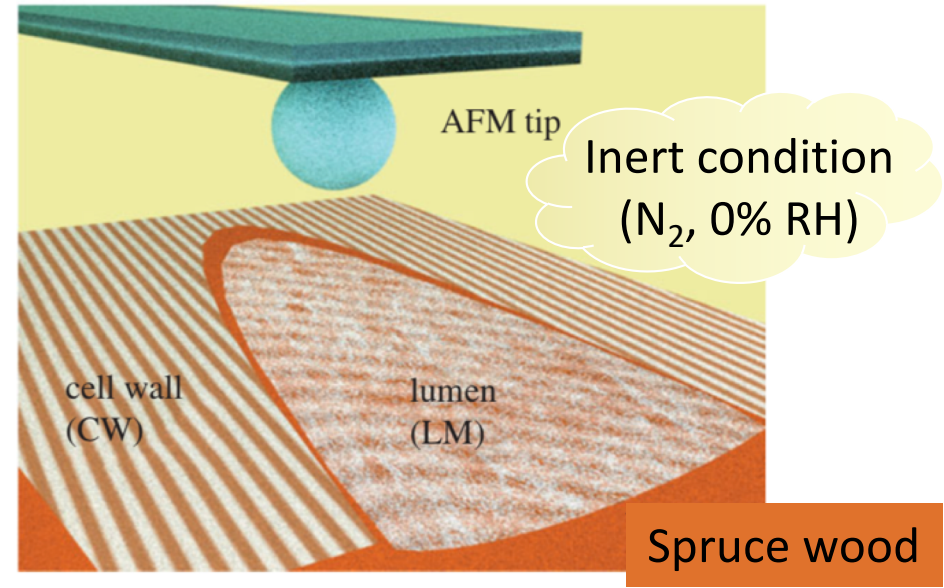
$$W(\cdot, F) = \infty$$

Adhesion force spectroscopy

- Influence of surface roughness and tip geometry



Butt et al, Surf. Sci. Rep. 2005, 59, 1–152



$$I_\varepsilon(\varphi) = \int \varphi(u) |du|$$

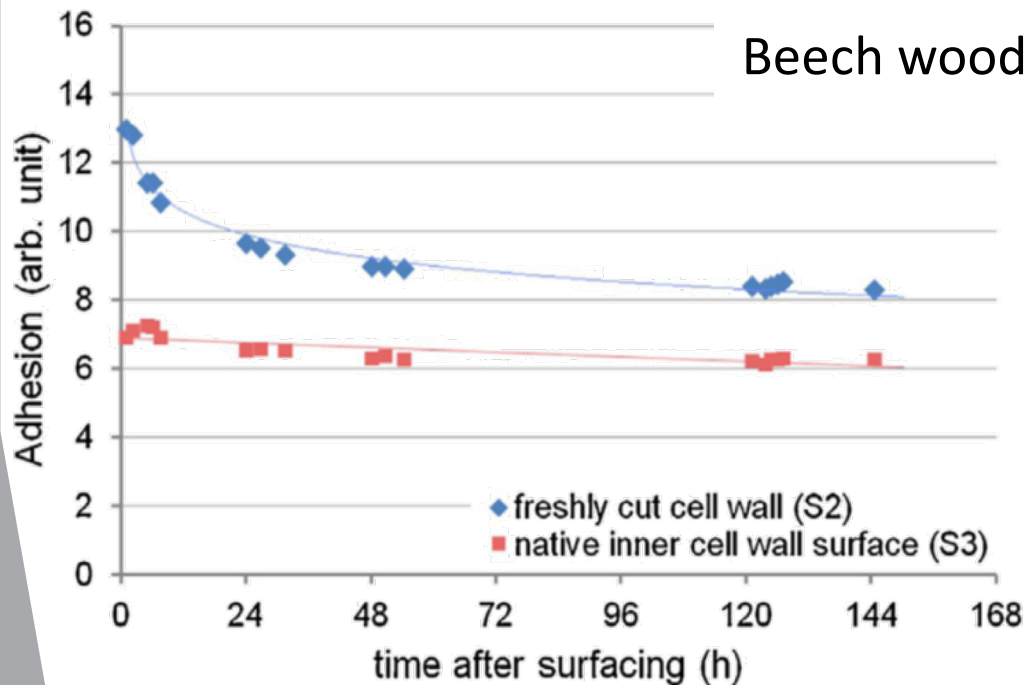
$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

$$W(\cdot, F) = \infty$$

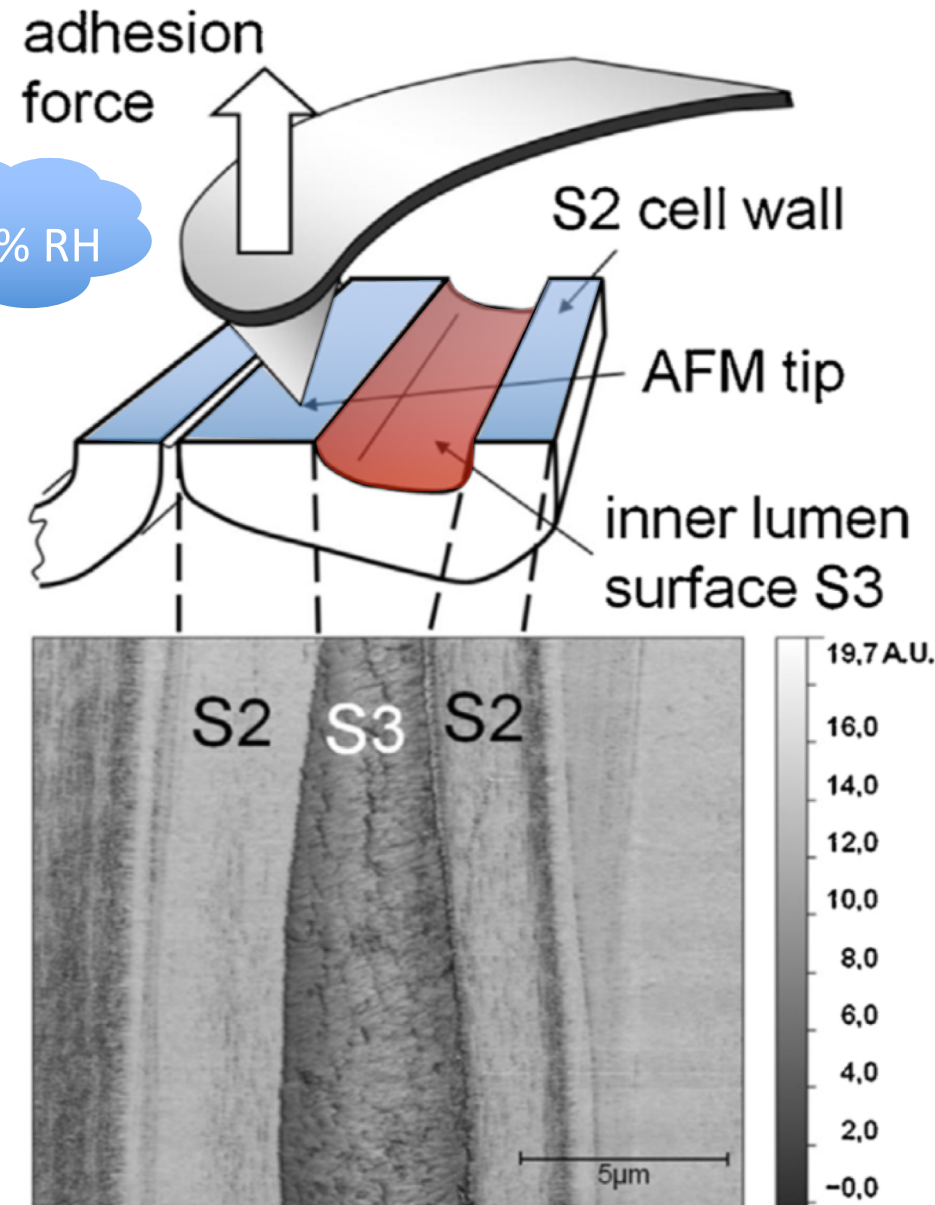
Adhesion force spectroscopy

- Variability in surface polarity and aging

23°C and 50% RH



Frybort et al, Colloids and Surfaces A, 457 (2014) 82–87



$$I_\varepsilon(\varphi) = \int \rho(\varphi) |d\varphi|$$

$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

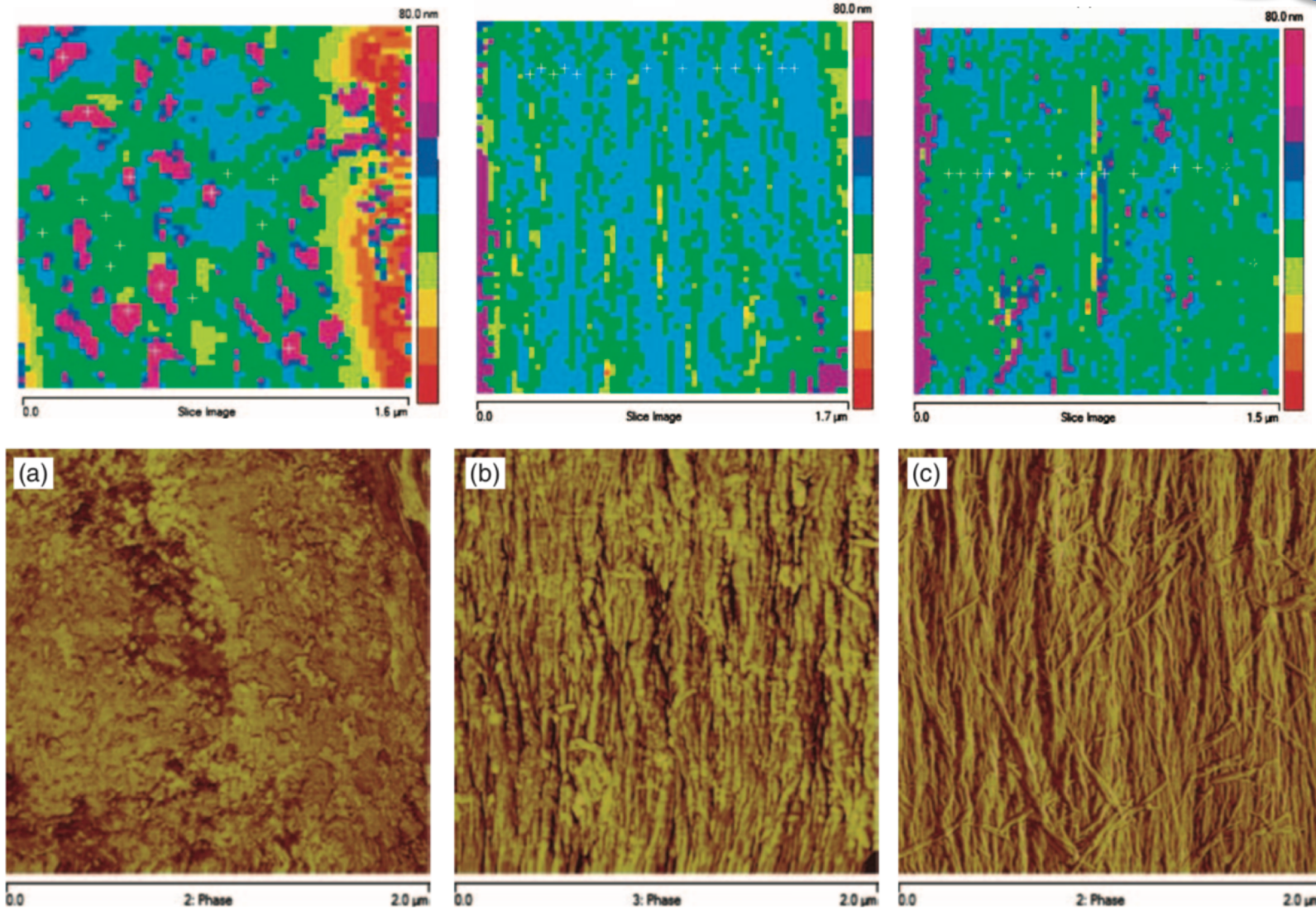
$$W(\cdot, F) = \infty$$

Adhesion force spectroscopy

Room conditions

- Effect of surface treatment

Flax fibres



TM-AFM phase image of (a) raw flax fibre, (b) NaOH (10%) treated flax fibre, (c) Enzyme treated (18 h) flax fibre.

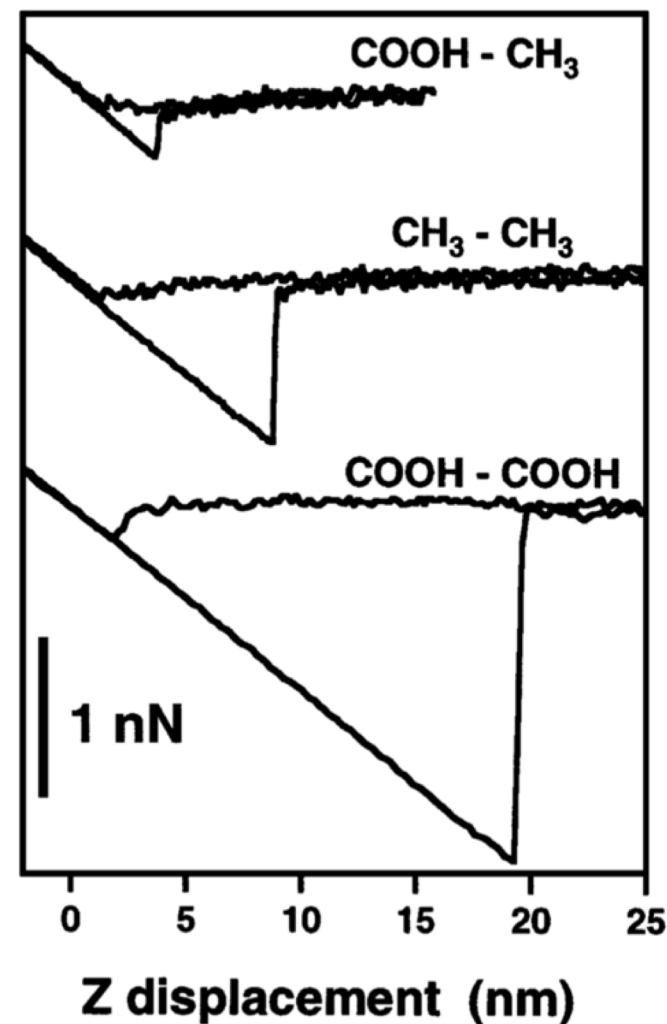
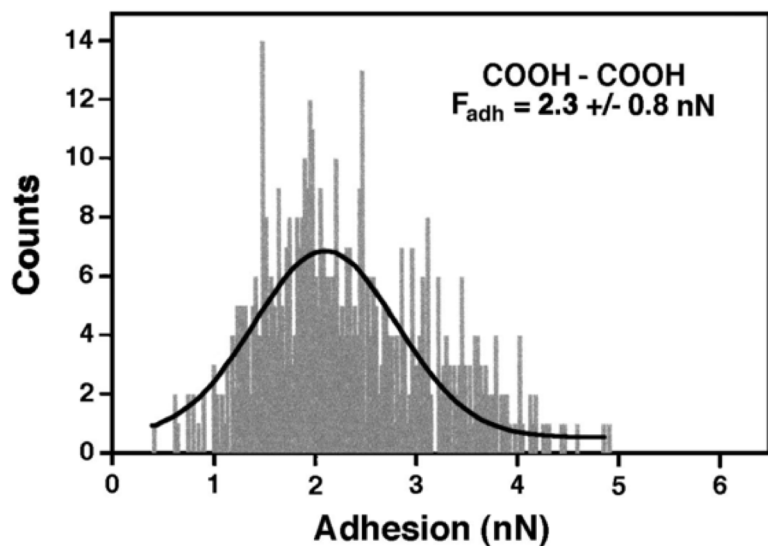
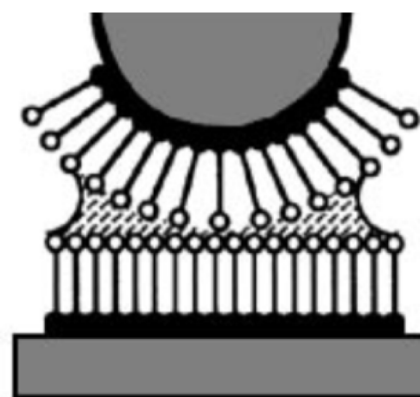
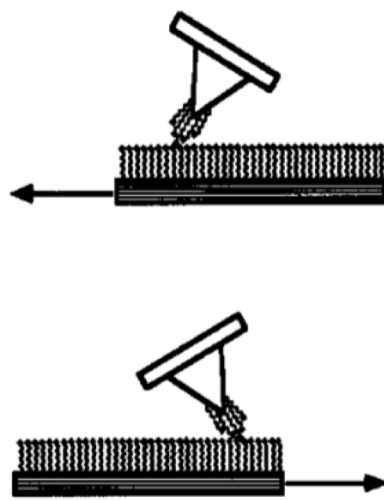
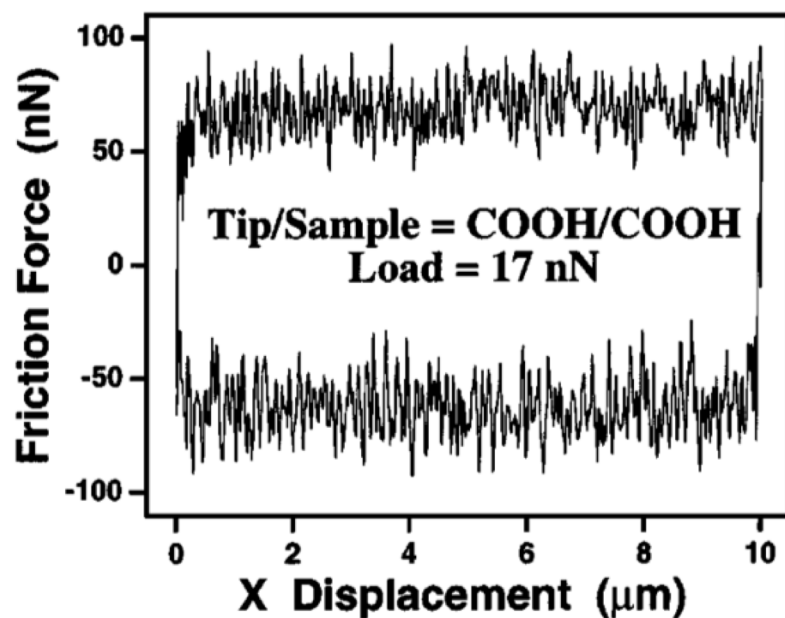
$$I_\varepsilon(\varphi) = \int_{\varphi}^{\infty} \rho(\theta) d\theta$$

$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

$$W(\cdot, F) = \infty$$

Adhesion force spectroscopy

- Tip functionalisation - Chemical force microscopy

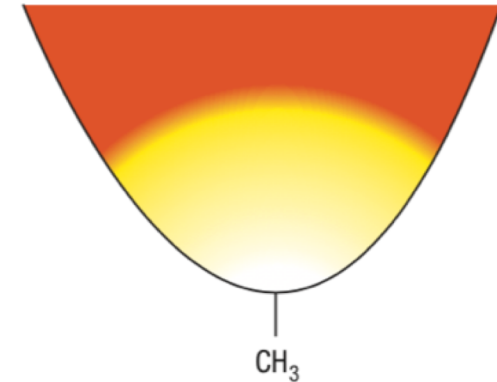
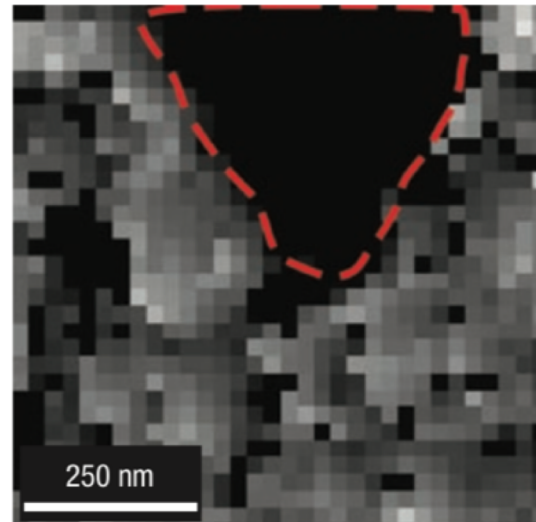
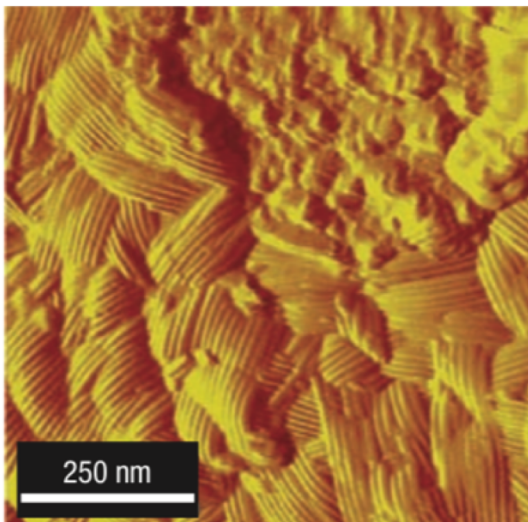
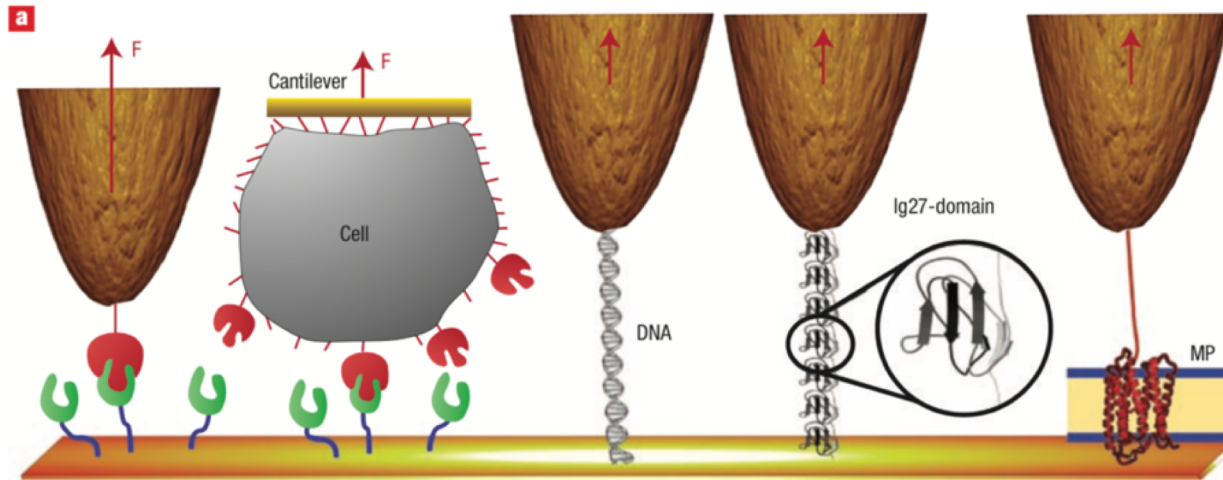


$$I_\varepsilon(\varphi) = \int \rho(\varphi) d\varphi$$

$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

Adhesion force spectroscopy

- Tip functionalisation - Molecular force microscopy



Fungus Aspergillus fumigatus

$$I_\varepsilon(\varphi) = \int \sqrt{\varphi'(x)} dx$$

$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

Outline

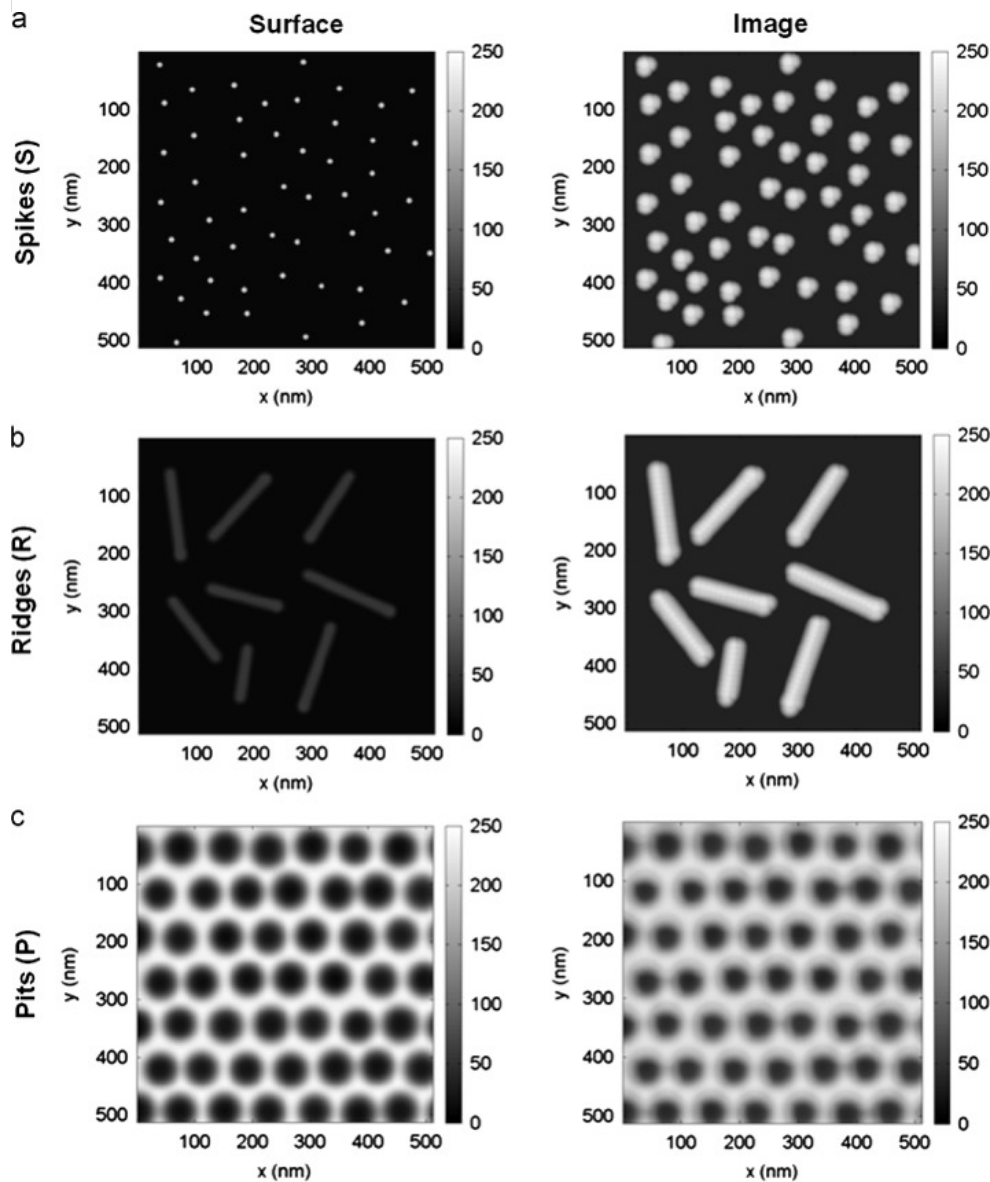
- Brief history and basic principles of scanning probe microscopy
- AFM principle and typical set-up
 - Tip probe-sample surface interactions
 - Tip and cantilever
 - Deflection sensor and scanner
 - Whole set-up
- Contact mechanics
- Operating modes
 - Contact
 - Intermittent
 - Force-distance curve and mechanical characterisation modes
- **Image analysis and artefacts**
- Sample preparation

$$I_\varepsilon(\varphi) = \int |\varphi(u)|^2 du$$

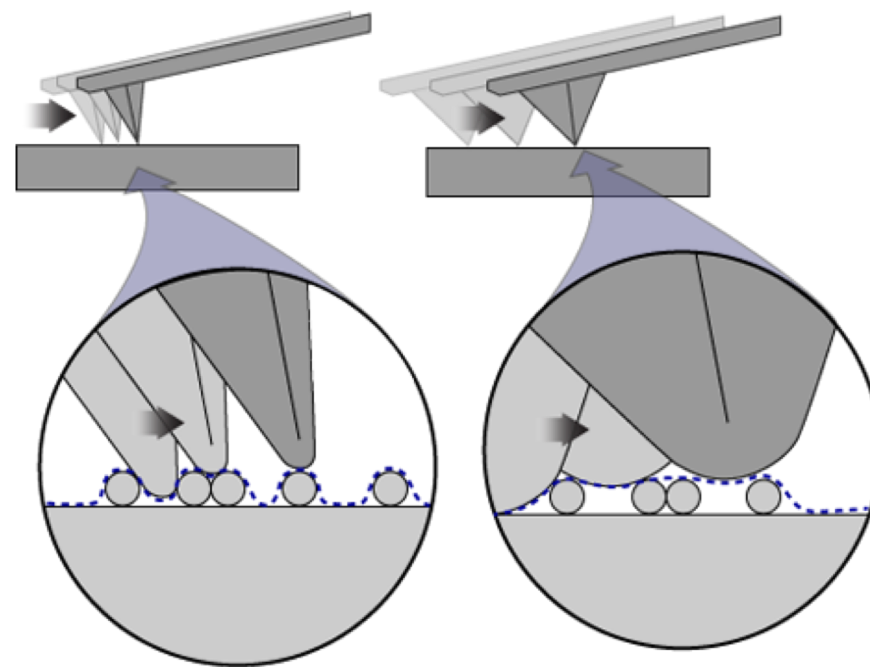
$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

AFM artifacts

- Images dilation due to the “finite” tip shape



Flater et al, Ultramicroscopy, 2014, 146: 130-143



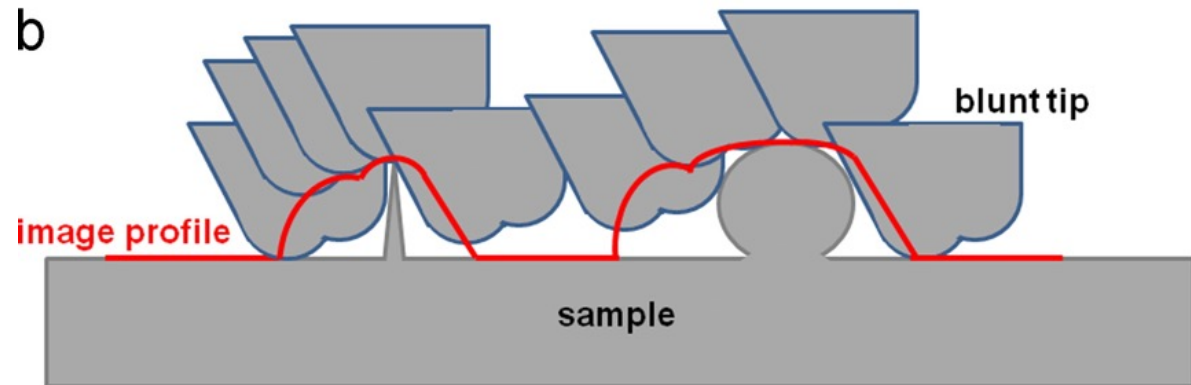
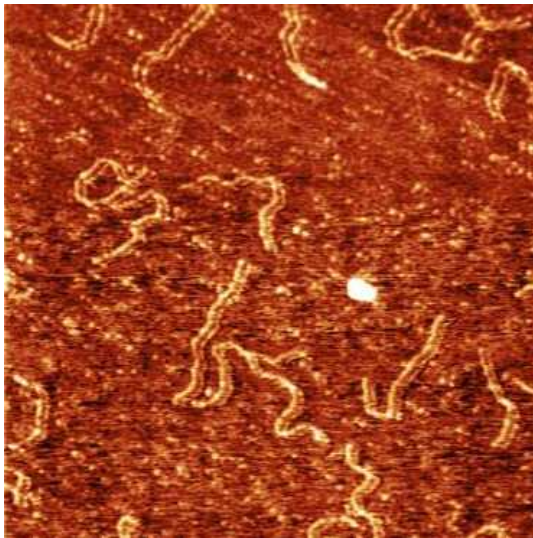
$$I_\varepsilon(\varphi) = \int |\nabla \varphi(x)| dx$$

$$\lim_{\varepsilon \rightarrow 0} I_\varepsilon(\varphi) = \int |\nabla \varphi(x)| dx$$

$$W(\cdot, F) = \infty$$

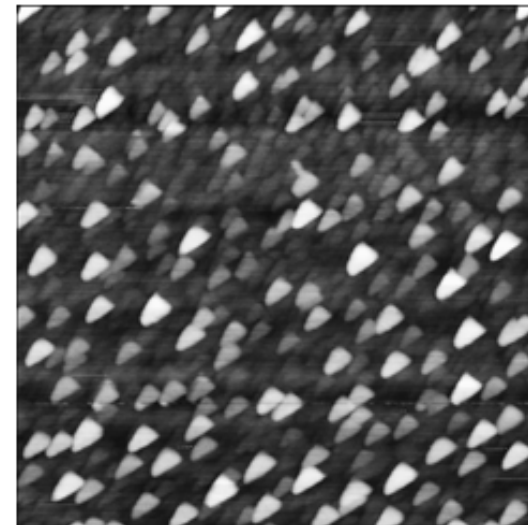
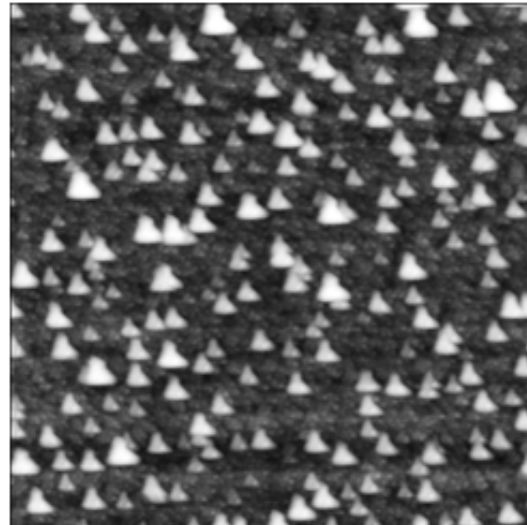
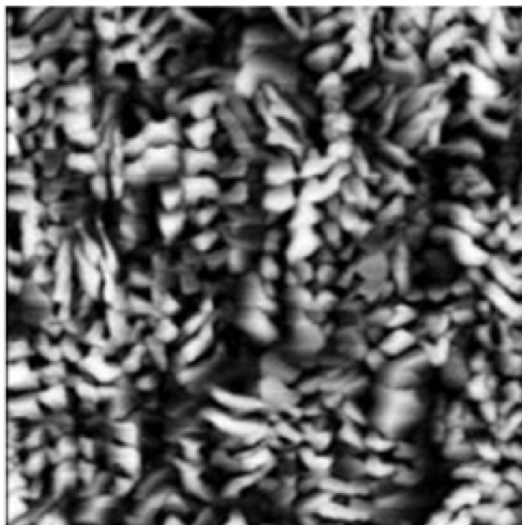
AFM artifacts

- Images dilation due to tip shape default, dirt or wear



Flater et al, Ultramicroscopy, 2014, 146: 130-143

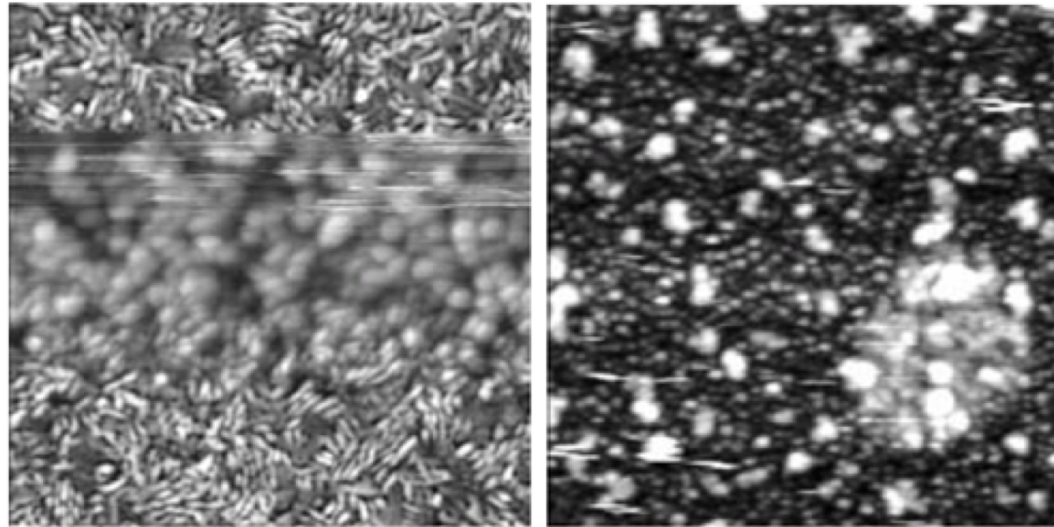
<http://www.fc.up.pt/pessoas/peter.eaton/artifacts/artifacts.html>



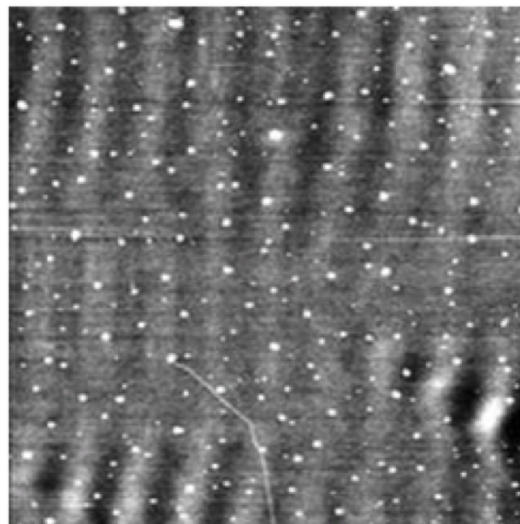
<http://www.nanophys.kth.se/nanophys/facilities/nfl/afm/>

AFM artifacts

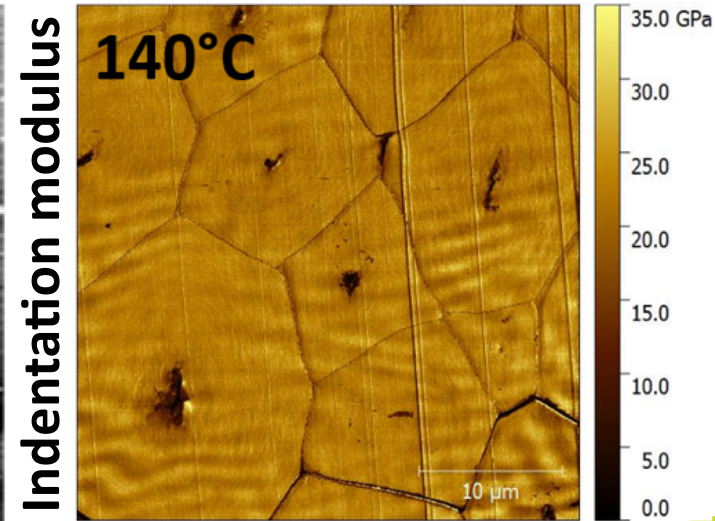
- Images dilation due to tip contamination



- Optical interference



[Sinsicalco et al, Polym. Test., 2018, 69:91-99]



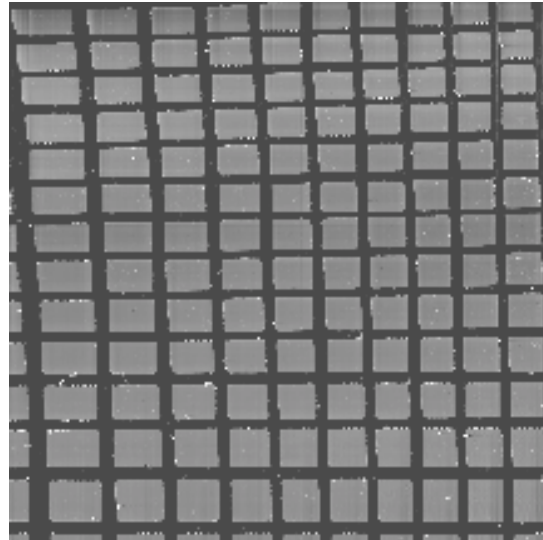
$$I_\varepsilon(\varphi) = \int \varphi(x) dx$$

$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

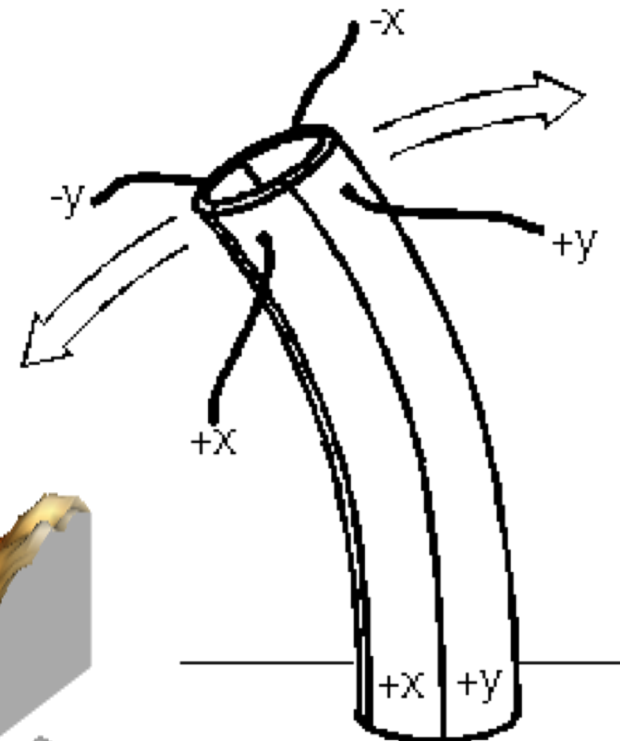
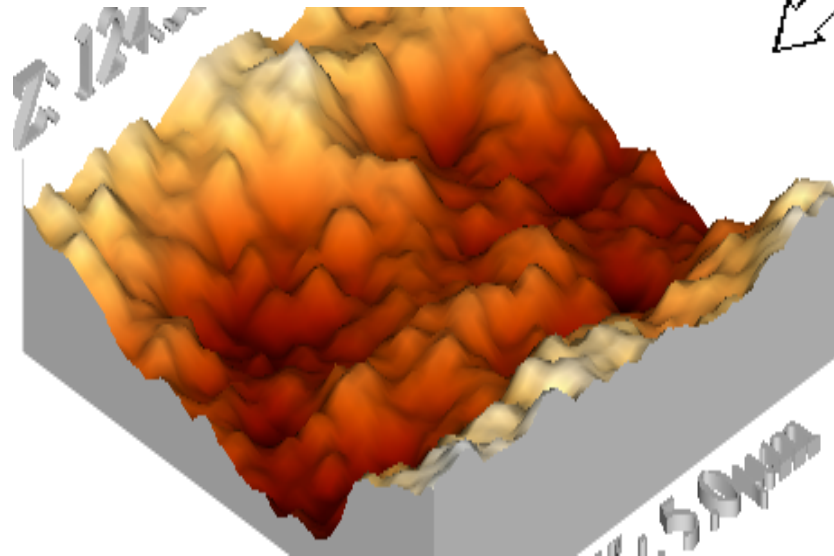
$$W(\cdot, F) = \infty$$

AFM artifacts

- Distortion due to non-linear piezo-scanner response + aging/creep



- Background bow/tilt



$$I_\varepsilon(\varphi) = \int \varphi(u) |du|$$

$$\lim_{F \rightarrow \infty} W(\cdot, F) = \infty$$

Outline

- Brief history and basic principles of scanning probe microscopy
- AFM principle and typical set-up
 - Tip probe-sample surface interactions
 - Tip and cantilever
 - Deflection sensor and scanner
 - Whole set-up
- Contact mechanics
- Operating modes
 - Contact
 - Intermittent
 - Force-distance curve and mechanical characterisation modes
- Image analysis and artefacts
- **Sample preparation**

$$I_\varepsilon(\varphi) = \int_{\varphi} \rho(\varphi) d\varphi$$

 \lim

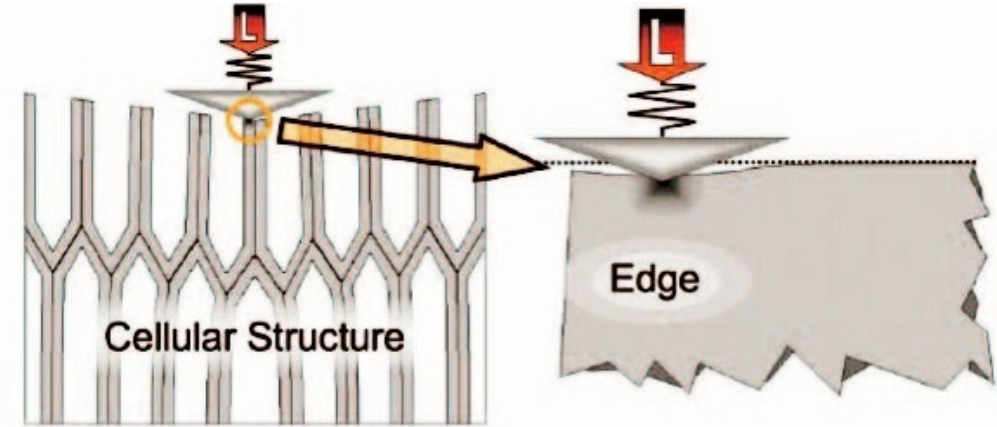
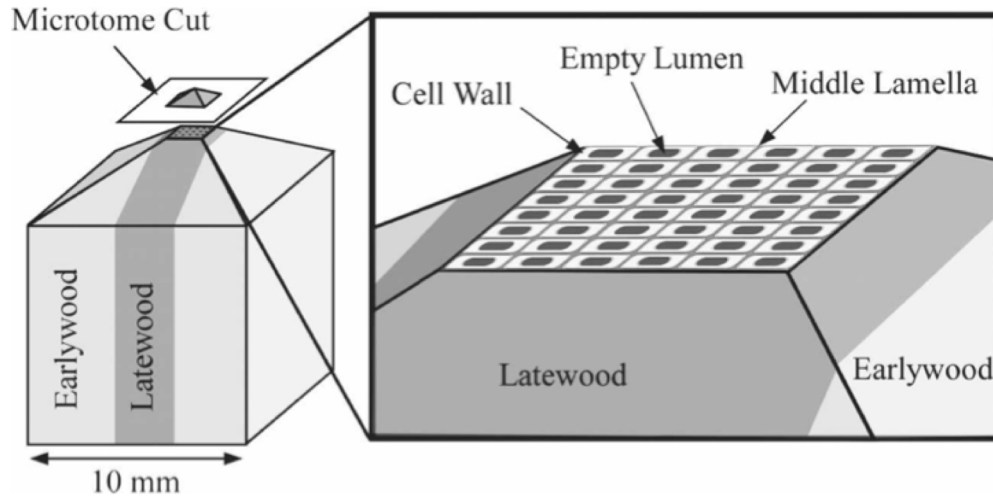
$$W(\cdot, F) = \infty$$



Sample preparation...

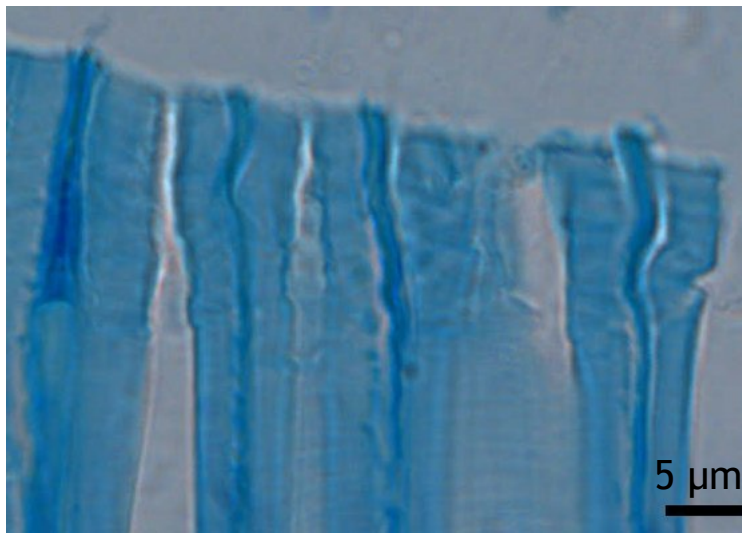


Without embedding in a resin: no sample modifications but \pm measurement artifacts



[Jakes et al, J. Mater. Res., 2008]

and topography...



[Clair, Gril et al, IAWA J., 2005]

Dehydration in ethanol and embedding in resin (LR-White, SPURR, ...) or PEG

- \pm no thermo-chemical modification of the cell wall (extractives...)?
- Resin penetration / inclusion time?
- Cell wall water content?

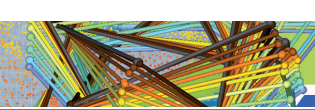


Microtome/Grinding/FIB...??!!

$$I_\varepsilon(\varphi) =$$



$$\int \rho(\mathbf{r}) |\mathbf{d}\mathbf{r}|$$



$$\lim$$

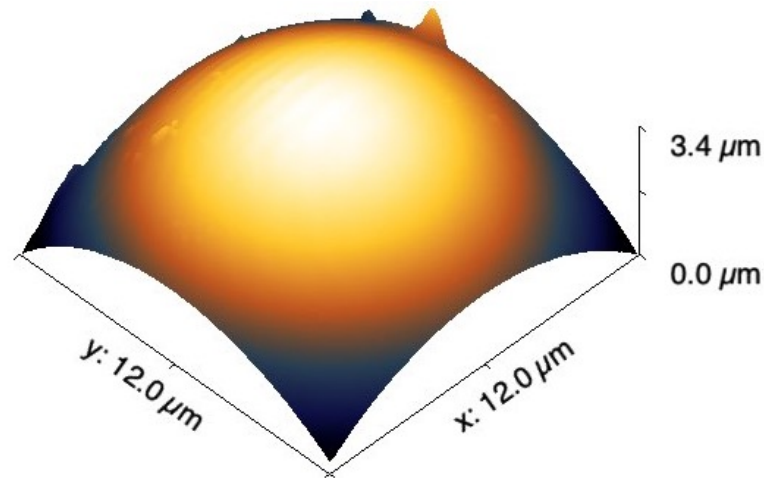
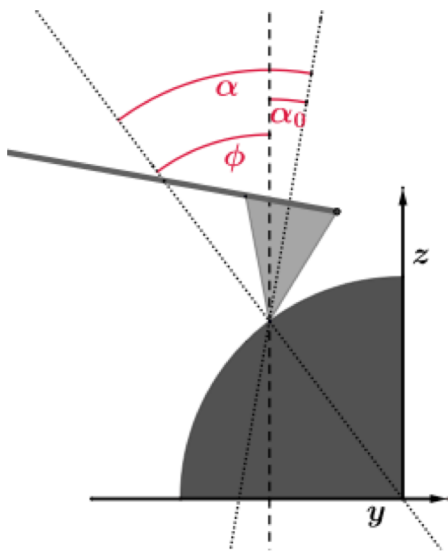


$$W(\cdot, F) = \infty$$

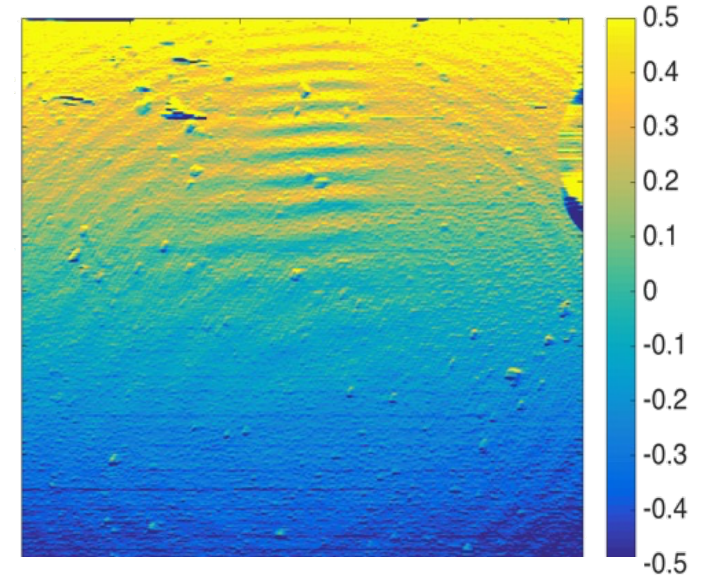
Sample surface effect

- Effect of sample local slope

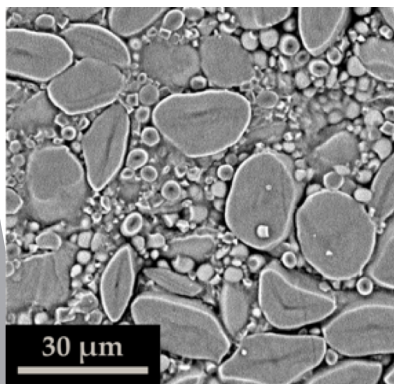
[Heinze et al, Ultramicroscopy, 2018, to appear...]



Topography

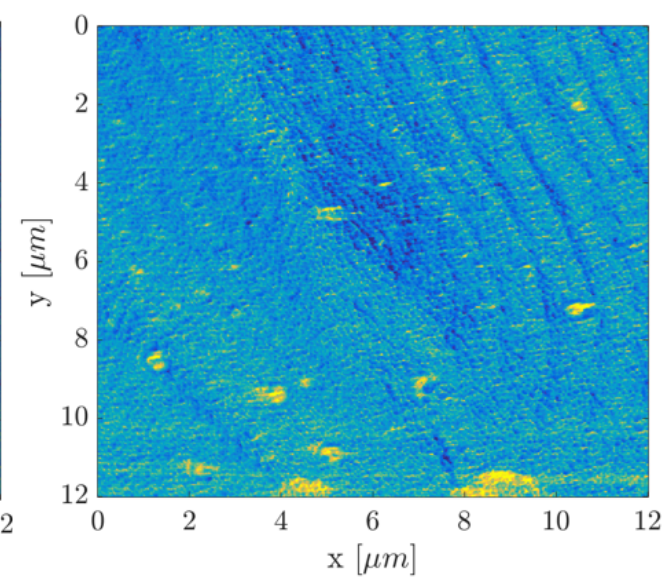
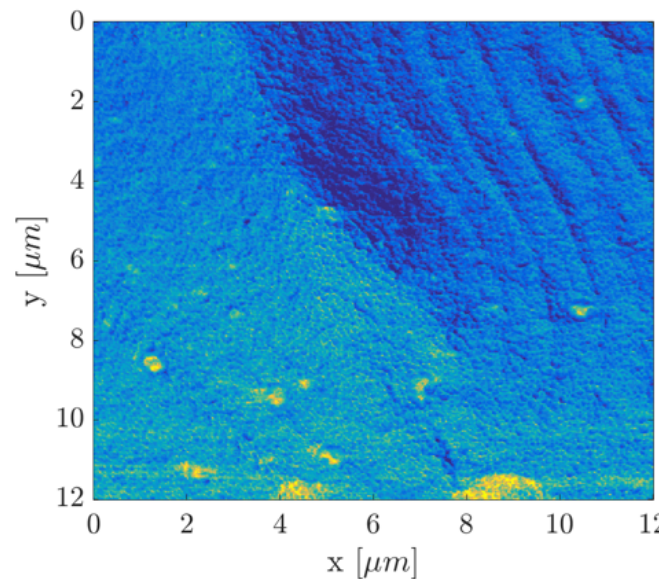


Local angle/cantilever ϕ ($^\circ$)



Starch granules

Raw indentation modulus



Corrected [GPa]

Corrected

$$I_\varepsilon(\varphi) = \int_{\varphi} |\nabla \varphi(x)| dx$$

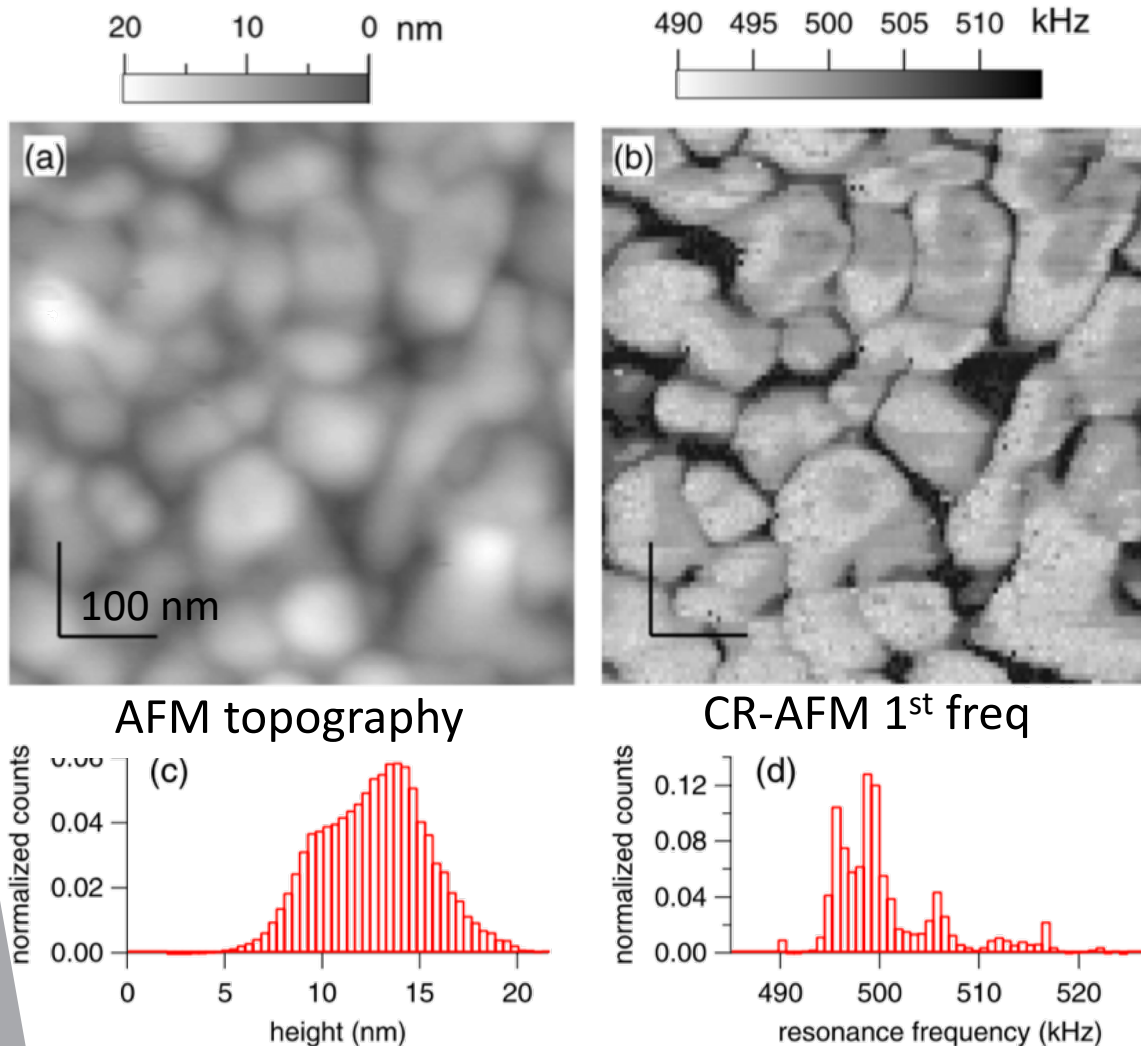
lim

$$W(\cdot, F) = \infty$$

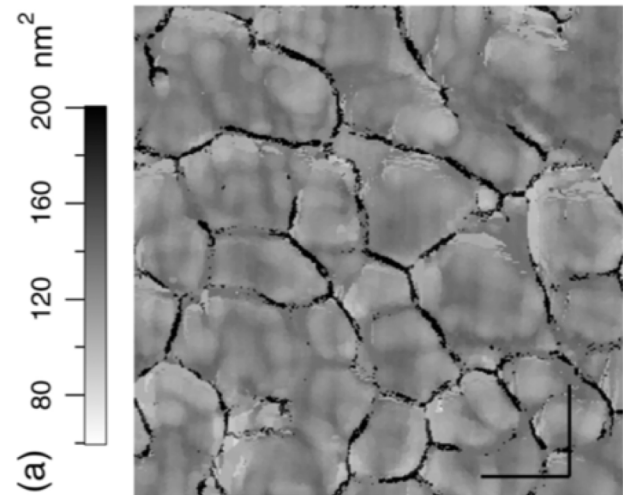
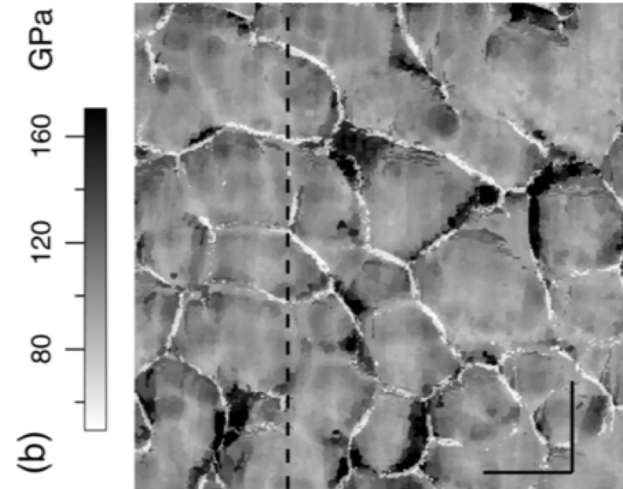
Sample surface effect

● Effect of sample roughness

Stan and Cook, Nanotechnology, 2008, 19, 235701



Corrected indentation modulus



Tip-sample contact area

Au film \approx <110>, $k_C = 14.8 \pm 0.5$ N/m, 350 nN