GT NanoMécanique – 16/10/2018 Montpellier

Mesure par AFM de la raideur de contact sur matériaux élastiques rigides :

De quoi parle-t-on ?

Quelles sont les domaines de validité et les limites (actuelles) ?

Olivier ARNOULD

EQUIPE BOIS

Laboratoire de Mécanique et Génie Civil (**LMGC**)

CNRS/Université de Montpellier

France

olivier.arnould@umontpellier.fr

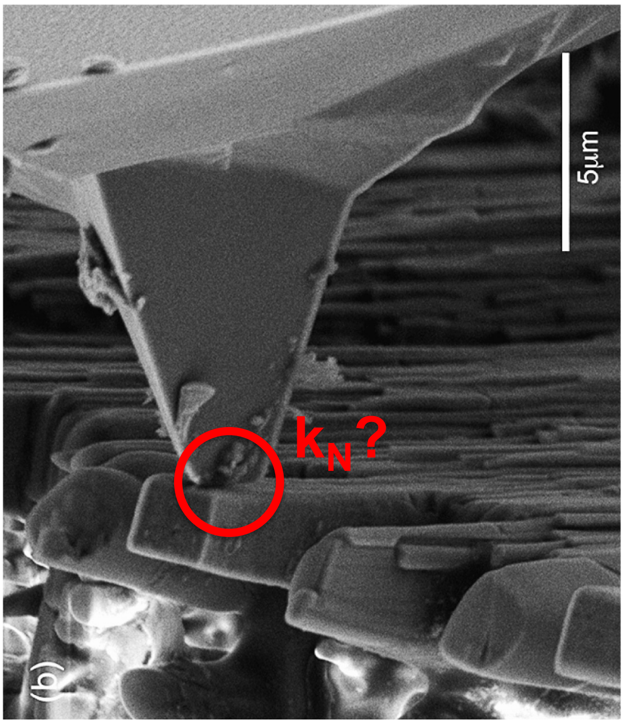
LABORATOIRE DE MÉCANIQUE ET GÉNIE CIVIL - UM/CNRS

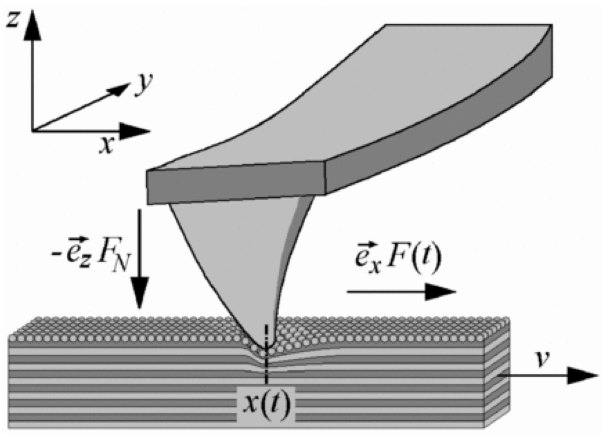
Sommaire

- Mécanique du contact et indentation
  - Contact élastique – Hertz
  - Nano-indentation – Oliver and Pharr
  - Domaines de validité, adhésion, anisotropie
- Courbe force-distance
  - Principe et prérequis
  - Traitement des courbes
- Contact résonant
  - Principe
  - Dynamique du levier et effet de la raideur latérale
- Préparation de la surface et calibrations

Contact mechanics

Bone micromechanics using in situ AFM in SEM

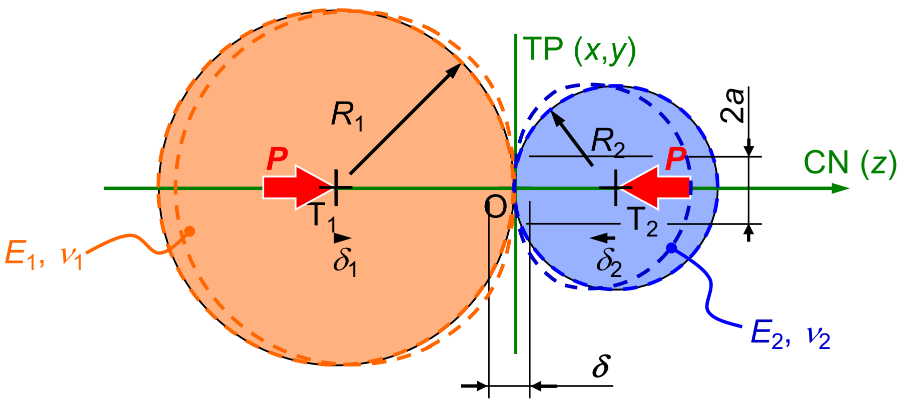




[http://www.physik.uni-bielefeld.de]

[Jimenez-Palomar *et al.*, J. Mech. Beh. Bio. Mat., 2011]

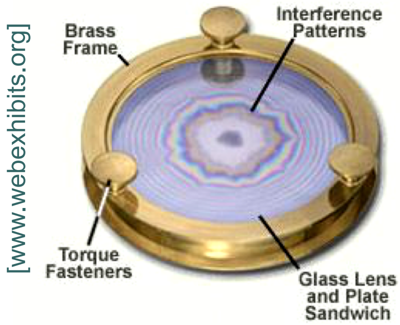
Contact mechanics



- Aims at finding the relationship between:
  - the load P and the relative displacement δ of the two bodies (far away from the contact)
  - the load P and the shape and size a of the contact area
  - the load P and the stress fields in each bodies

Contact mechanics

- Hertz's theory (1882 Ger. → 1896 Eng.)
  - Elastic deformation of two glass lenses in contact



  - Assumptions:
    - Surfaces are continuous and **non-conforming** (i.e., $R_1 \neq -R_2$) → $a << R$
    - Strains are small: $a << R$
    - Linear elastic isotropic and homogeneous materials
    - Friction is neglected
  - Each solid is considered as an elastic half-space (plane) loaded over a small *elliptical* region of its plane surface

[K.L. Johnson, Contact Mechanics, Cambridge University Press, 2001]

Contact mechanics

- Hertz's theory (1882)
  - Results: macroscopic relationship

$$a = \left(\frac{3RP}{4E^*}\right)^{1/3} \qquad p_0 = \left(\frac{6PE^{*2}}{\pi^3 R^2}\right)^{1/3}$$

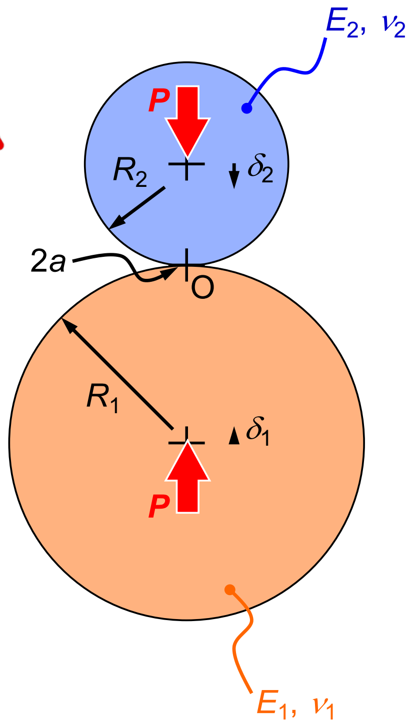
$$\delta = \delta_1 + \delta_2 = \left(\frac{9P^2}{16RE^{*2}}\right)^{1/3} = \frac{a^2}{R} \quad \Big| \quad P = \frac{4}{3}E^*\sqrt{R}\delta^{3/2} \qquad P = \frac{4}{3}E^*\frac{a^3}{R}$$

$$k_N = \frac{\partial P}{\partial \delta} = \left(6E^{*2}RP\right)^{1/3} = 2E^*\sqrt{R\delta} = 2E^*a$$

$$\mathbf{0 \leq k_t \leq \frac{2-\nu}{2(1-\nu)}}$$

$$\frac{1}{E^*} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2} \qquad \frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2}$$

Contact modulus — Plane-stress modulus



Visco-elasticity…

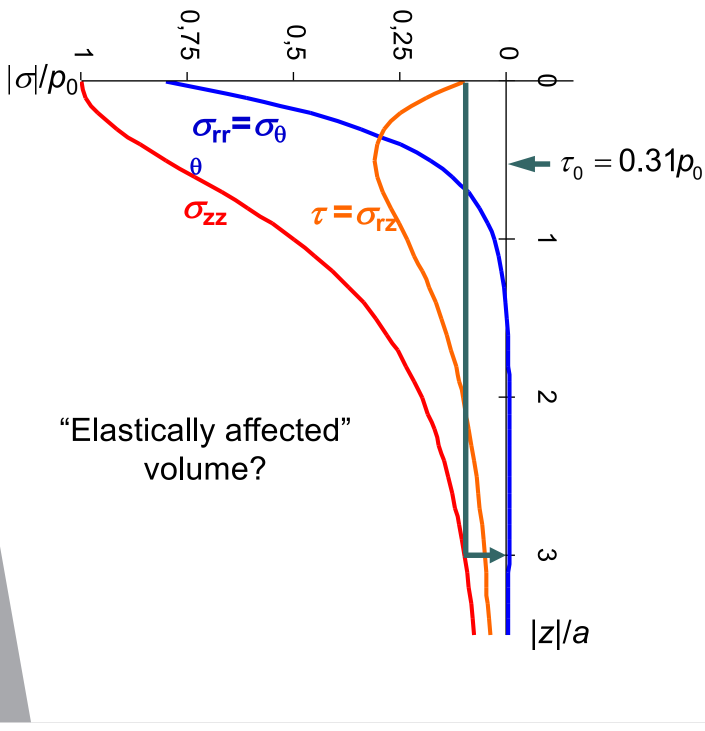
Contact mechanics

- Hertz's theory (1882)
  - Examples in the case of Si-AFM probe (R_2=10nm, E_2≈150GPa) in contact with the planar surface ($R_1 \rightarrow \infty$) of different materials [www.ntmdt.com]

Material and its Young's modulus	Contact area radius a, nm		Penetration due to deformation h, nm		Contact pressure P, GPa	
Elastomer, $E = 0.65$ GPa	3.74	8.04	1.04	6.46	0.11	0.25
PS, $E = 1$ GPa	3.24	6.98	1.05	4.87	0.15	0.33
Copper, $E = 120$ GPa	0.79	1.7	0.062	0.29	2.55	5.51
Tungsten, $E = 400$ GPa	0.68	1.46	0.046	0.21	3.44	7.47
Diamond, $E = 1000$ GPa	0.64	1.38	0.041	0.19	3.88	8.36
	at loading force F, nN					
	5	50	5	50	5	50

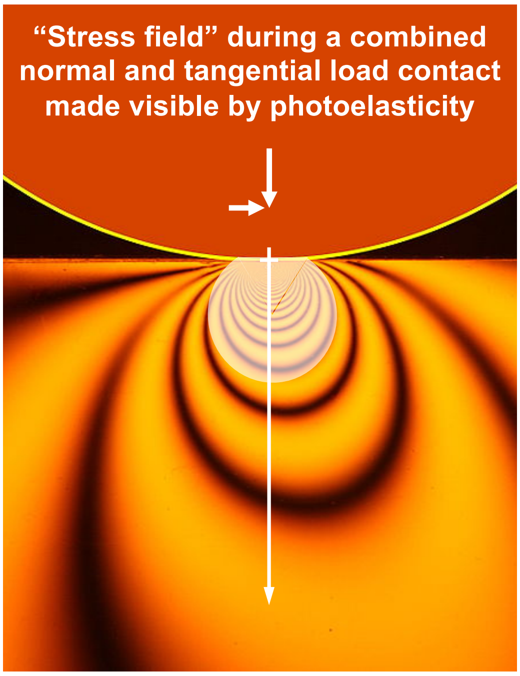
Contact mechanics

- Hertz's theory (1882)
  - Results: stress field



"Elastically affected" volume?

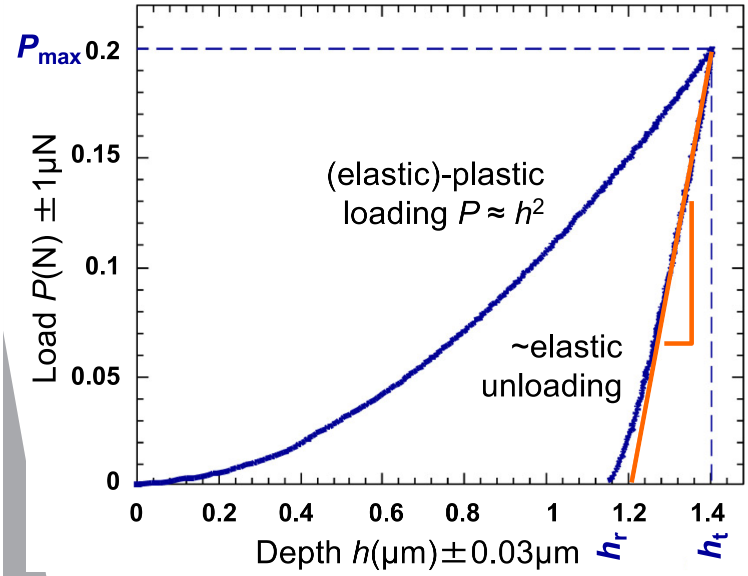
"Stress field" during a combined normal and tangential load contact made visible by photoelasticity



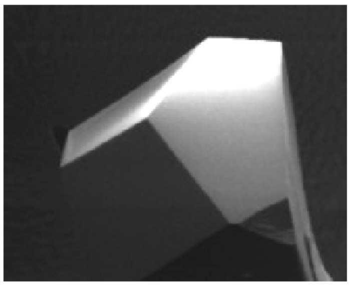
[www.wikimedia.org]

Contact mechanics

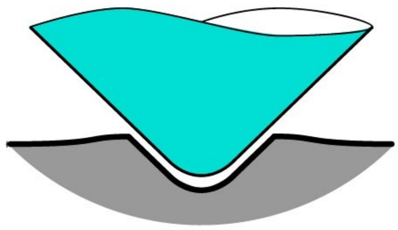
- (Depth-sensing) Nanoindentation
  - ➲ The depth of penetration h (δ!) is measured during load application mainly with a Berkovich indenter (3-sided pyramid)



Nanoindentation curve on electrodeposited Ni



[www.microstartech.com]



Contact mechanics

- (Depth-sensing) Nanoindentation

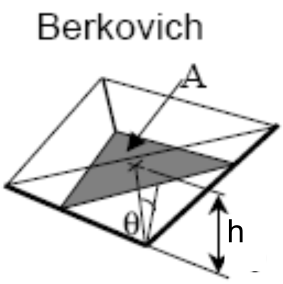
$$E^* = \frac{\sqrt{\pi}}{2}\frac{dP}{dh}\frac{1}{\sqrt{A_c}}$$

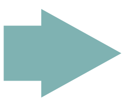
With E* or M reduced/contact/indentation modulus

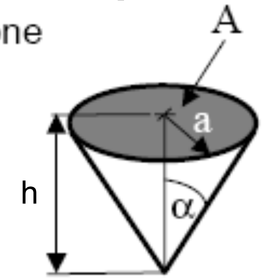
$$\frac{1}{E^*} = \frac{1-\nu_i^2}{E_i} + \frac{1-\nu^2}{E}$$ for linear ***ISOTROPIC*** material

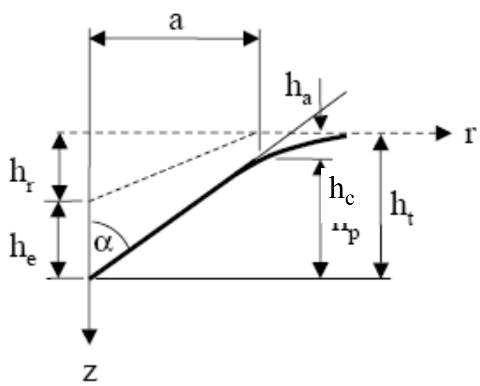
- Case of the Berkovich indenter

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









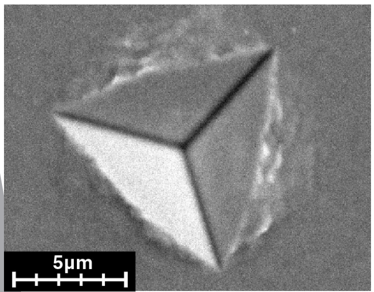
$A = 24.5 h^2$ $\quad$ $\alpha = 70.3°$ $\quad$ $A = \pi \tan^2 \alpha \, h^2$

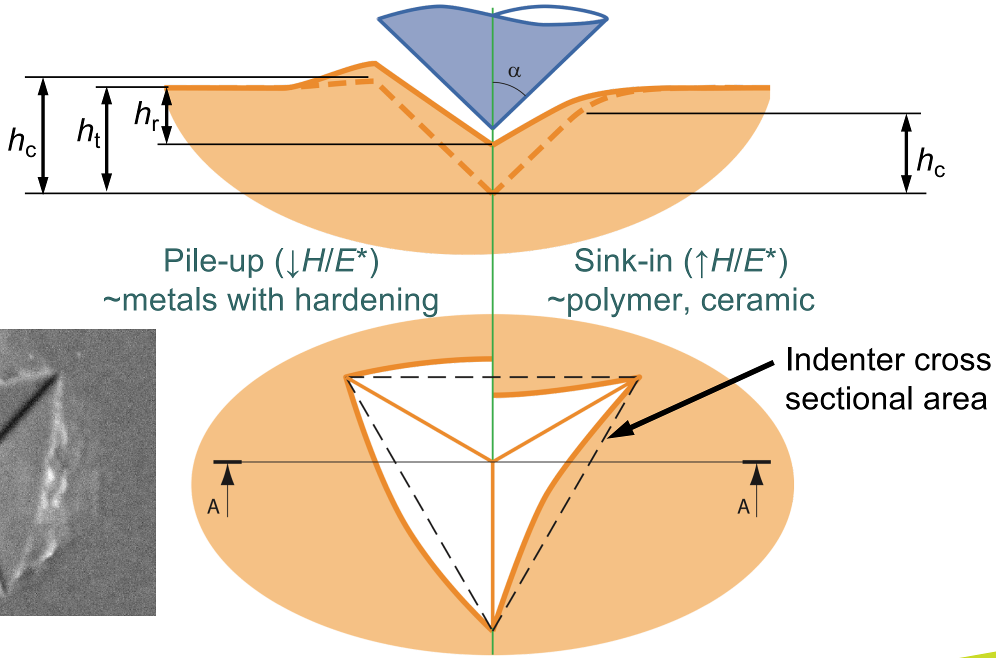
$$h_c = h_t - \varepsilon P \left(\frac{dP}{dh}\right)^{-1}$$

with $\varepsilon = \begin{cases} \left(\dfrac{2(\pi-2)}{\pi}\right) & \text{cone} \\ 0.75 & \text{Berkovich} \end{cases}$

Contact mechanics

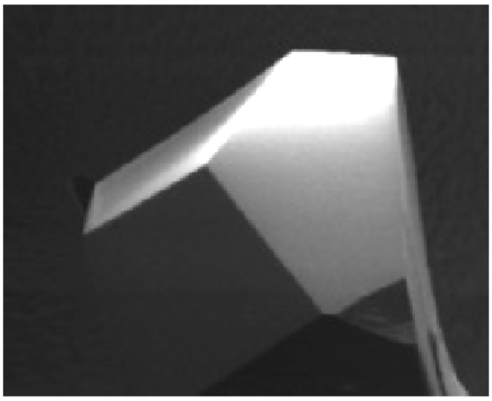
- (Depth-sensing) Nanoindentation



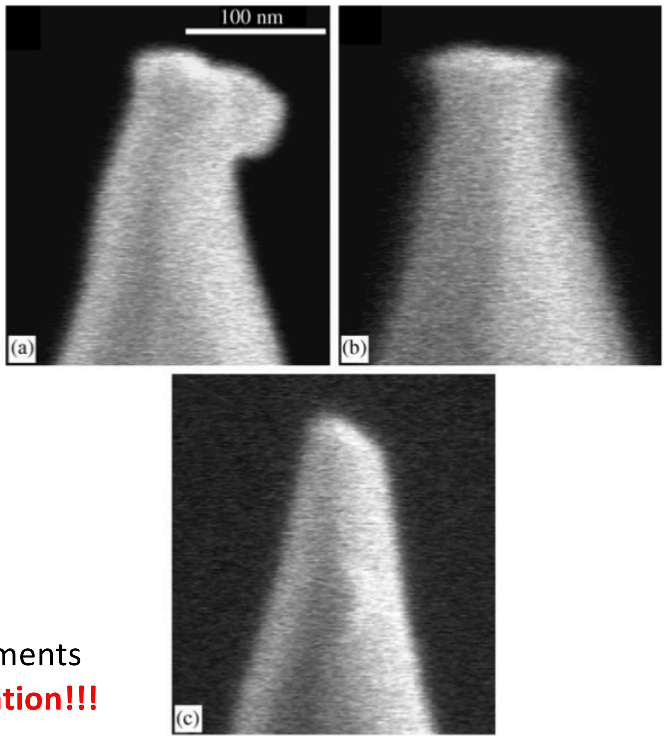


Contact mechanics – NI vs AFM

Tip deformation on (very) stiff material and high load (set-point) !



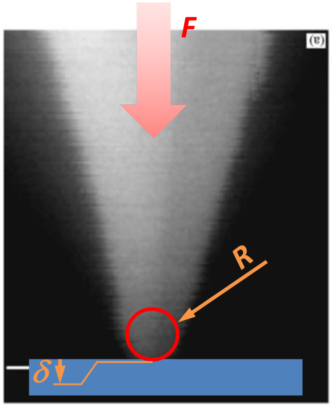
[www.microstartech.com]

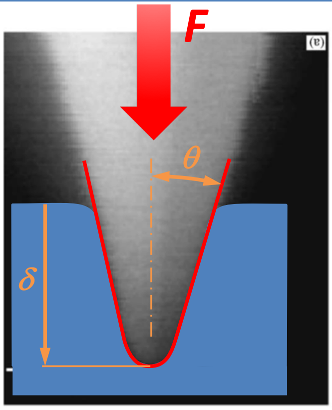


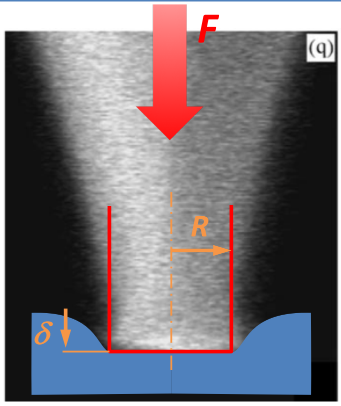
NEAR SURFACE measurements
⇢ **sample surface preparation!!!**

[Kopycinska-Müller et al, Ultramicroscopy, 2006; Nanotechnology, 2016]

Contact mechanics – NI vs AFM







✓ Hertz (1885)

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

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

✓ Sneddon (1965)

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

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

✓ Flat punch (??)

$$F = 2MR\,\delta$$

$$k_N = 2MR$$

M: Reduced/contact modulus

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

δ << R

Non conforming

δ ≈ R??!!

[Lin et al 2007]

δ >> R

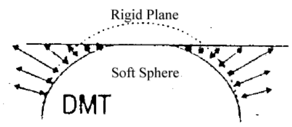
E^*_{sample} << E^*_{tip}

LINEAR ELASTIC HOMOGENEOUS and *ISOTROPIC* materials

[Kopycinska-Müller et al, Ultramicroscopy, 2006]

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

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

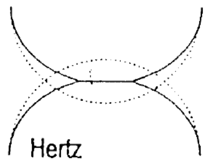


$$k_{N_{DMT}} = \left(6M^2 R\left(F + F_{ad_{DMT}}\right)\right)^{1/3}$$

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

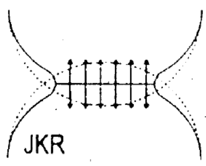
$$k_{N_{JKR}} = 2Ma_{JKR} \frac{1 - \frac{1}{2}\left(\frac{a_{0_{JKR}}}{a_{JKR}}\right)^{3/2}}{1 - \frac{1}{6}\left(\frac{a_{0_{JKR}}}{a_{JKR}}\right)^{3/2}}$$

with

$$a_{JKR} = \left[\frac{3R}{4M}\left(\sqrt{F_{ad_{JKR}}} + \sqrt{F_{ad_{JKR}} + F}\right)^2\right]^{1/3}$$

$$a_{0_{JKR}} = \left[\frac{3RF_{ad_{JKR}}}{M}\right]^{1/3}$$

$$F_{ad_{JKR}} = \frac{3}{2}\pi R w_{ad}$$



[R.M. Overney]

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

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

Contact mechanics - Anisotropy

- Extension of the theory to the case of anisotropic solids → Green's function? [Willis, J. Mech. Phys. Solids, 1966; Vlassak *et a*l., J. Mech. Phys. Solids, 1994/2003; Swadener *et al., Philos. Mag. A*, 2002…]

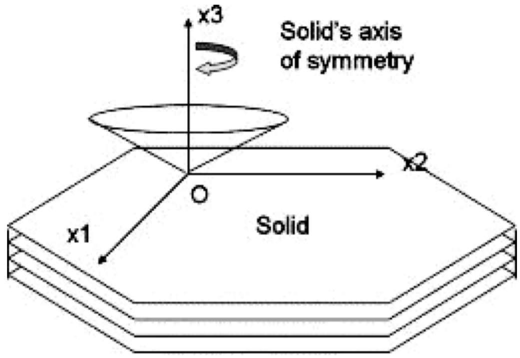
$$\frac{E}{1-\nu^2} = \frac{C_{11}^2 - C_{12}^2}{C_{11}} \rightarrow M$$

1=2=3

- Closed form solution of M only available 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} $G_{13}=G_{23}$



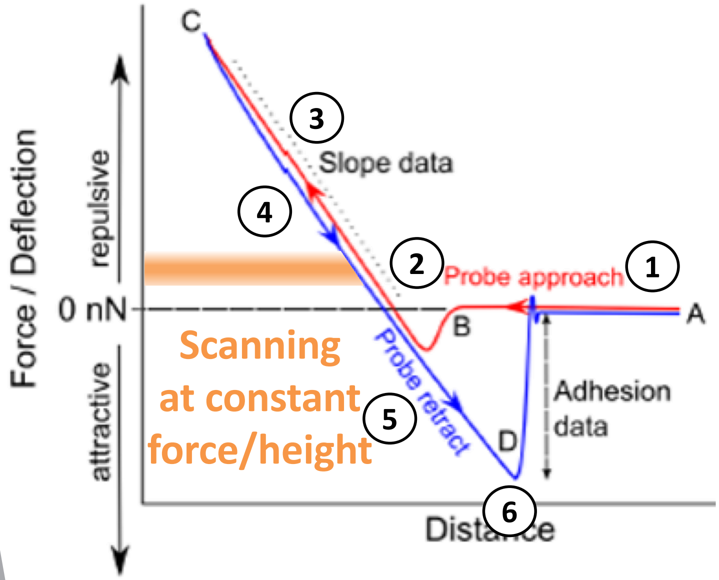
[Delafargue *et al*., Int. J. Sol. Struct., 2004]

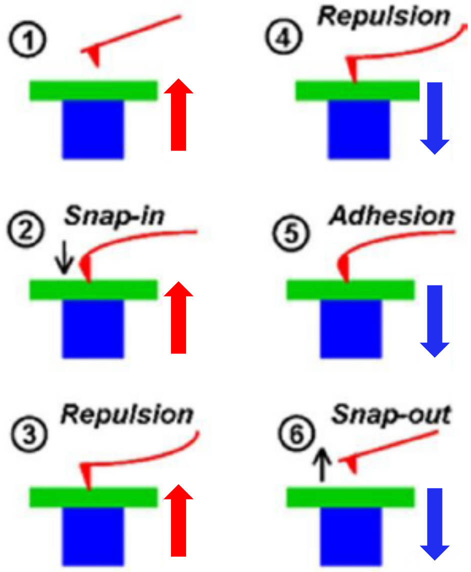
k_t = ?

Sommaire

- Mécanique du contact et indentation
  - Contact élastique – Hertz
  - Nano-indentation – Oliver and Pharr
  - Domaines de validité, adhésion, anisotropie
- Courbe force-distance
  - Principe et prérequis
  - Traitement des courbes
- Contact résonant
  - Principe
  - Dynamique du levier et effet de la raideur latérale
- Préparation de la surface et calibrations

Force-distance curve

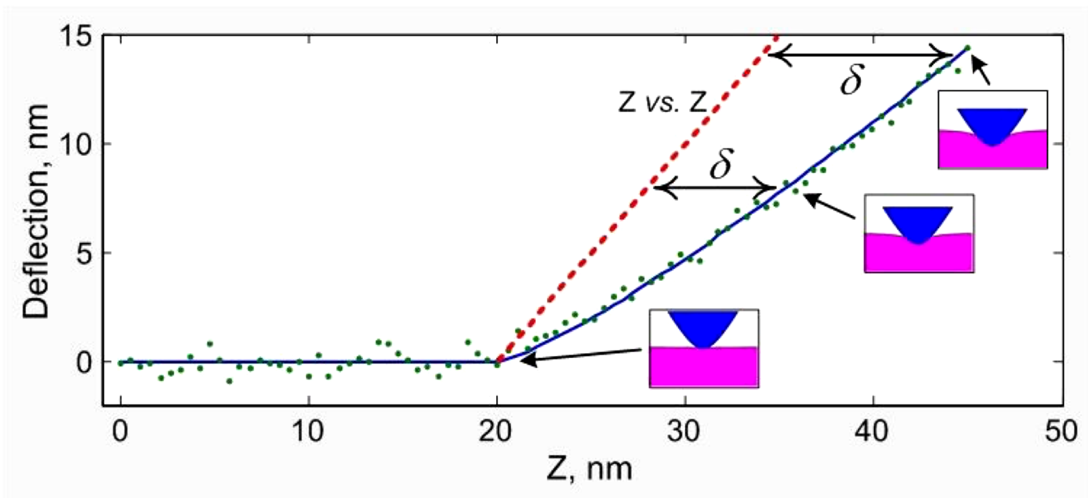




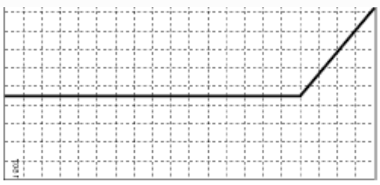
[B. Nysten, 2007]

Fd - Indentation

- Decoupling load/displacement

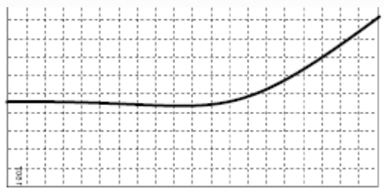


[www.chem.duke.edu/~boris/research/elasticity/]



Hard sample

[www.veeco.com]



Soft sample

Fd - Indentation

- Requirements:
  - Cantilever stiffness

$$\frac{d}{z} = \frac{1}{1+\frac{k_C}{k_N}} \quad \begin{array}{l} k_N \gg k_C \rightarrow d = z \\ k_N \ll k_C \rightarrow d = 0 \end{array} \quad k_N \sim k_C$$

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

with

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

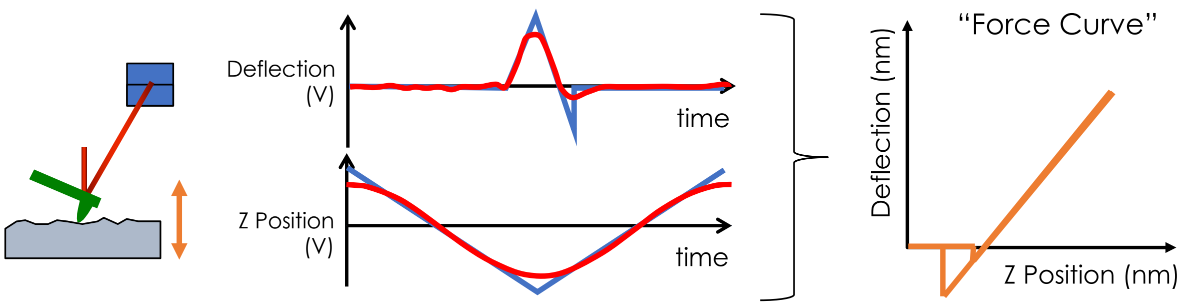
  - Calibration of the laser/photodetector
  - Calibration of the cantilever stiffness
  - Measurements of the real tip apex shape + ***suitable*** contact model…
  - Non-normal load (shear) due to cantilever tilt + tip sliding?
  - Limited resolution (>100 nm on polymer) due to large tip surface contact area

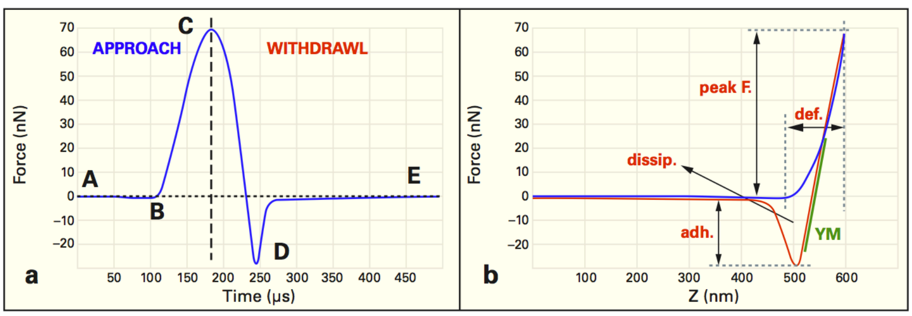
  - Mapping (Force-Volume mode) of the elastic properties is very time consuming (256 x 256 points = 18h)

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

Fd - Indentation

- Peak Force Quantitative NanoMechanical (QNM) [www.bruker-axs.com]
  - force curve recording at some kHz with sinusoidal displacement





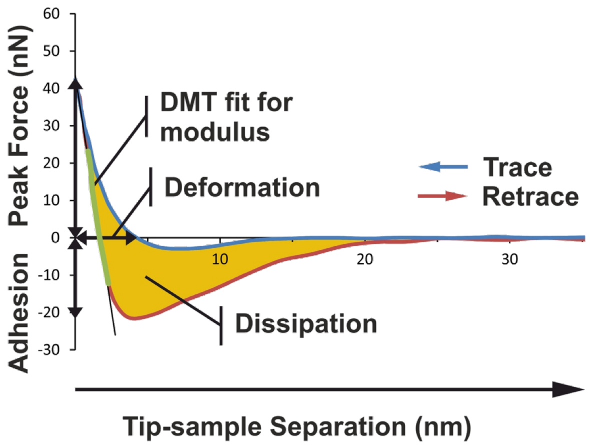
Calibration!

DMT modulus
Dissipation (hysteresis loop)
Adhesion force

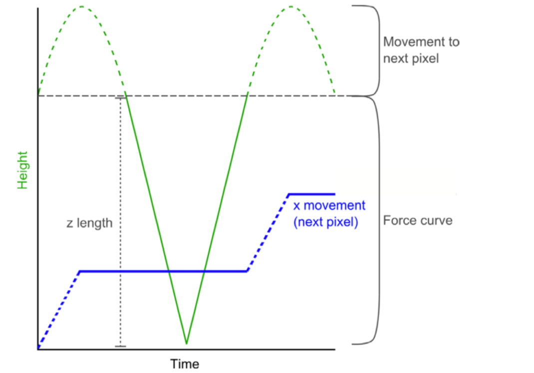
Fd - Indentation

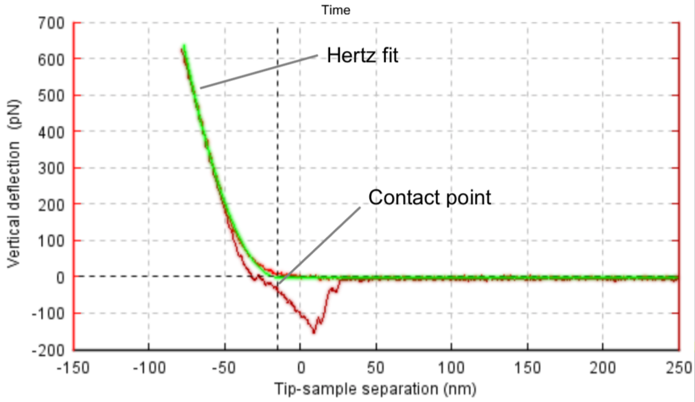
- Peak Force QNM (Bruker) vs. QI (JPK)

[JPK Appl Note]



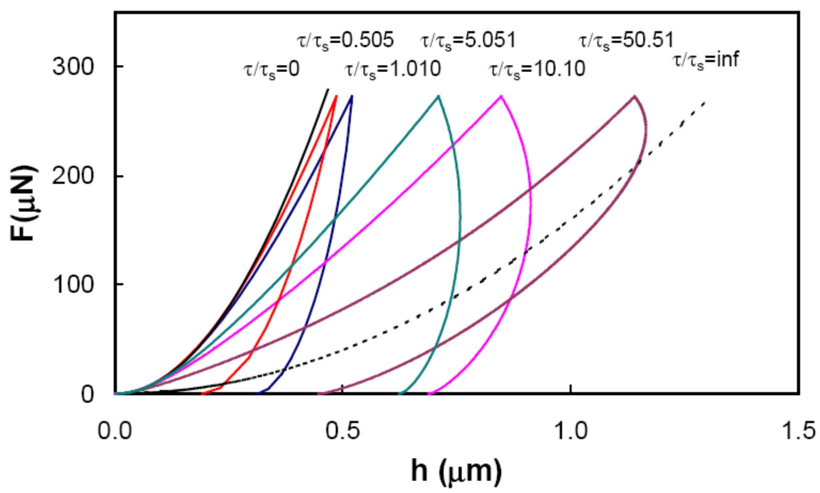
[Bruker Appl Note]

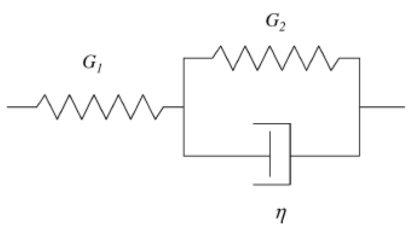




Fd - Indentation

- Viscoelastic properties?
  - Unloading curve of a viscoelastic material [Cheng and Cheng, *Mat. Sci. Eng. R*, 2004]



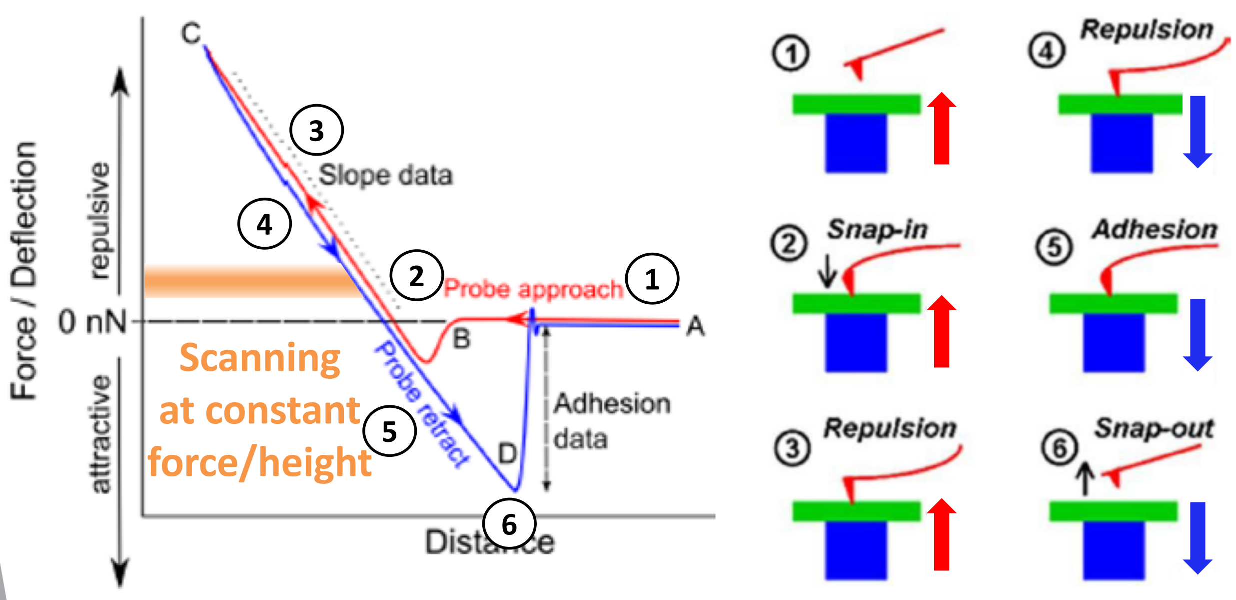


G_1 = 234MPa G_2 = 26MPa t_s = 1s
K =688MPa

Sommaire

- Mécanique du contact et indentation
  - Contact élastique – Hertz
  - Nano-indentation – Oliver and Pharr
  - Domaines de validité, adhésion, anisotropie
- Courbe force-distance
  - Principe et prérequis
  - Traitement des courbes
- Contact résonant
  - Principe
  - Dynamique du levier et effet de la raideur latérale
- Préparation de la surface et calibrations

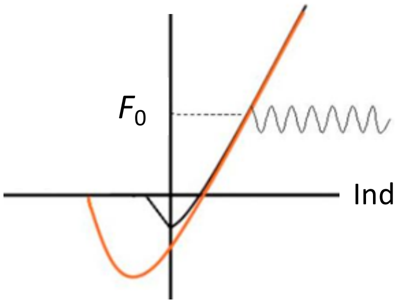
Contact Resonance-AFM (CR-AFM)



[B. Nysten, 2007]

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 $F = F_0 + F_{excitation} \times \sin\omega t$

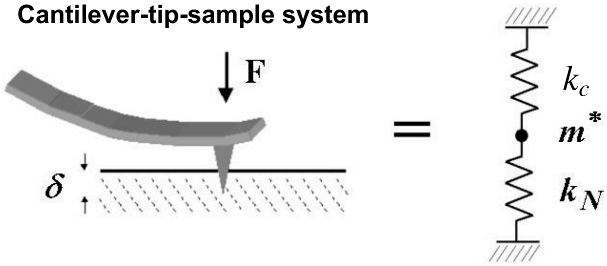
if $F_{excitation}$ is small → ≈LINEAR contact stiffness

if F_0 is small → Good spatial resolution + Hertz theory validity

Point-mass model **[Rabe et al, 1996]**

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

Cantilever-tip-sample system

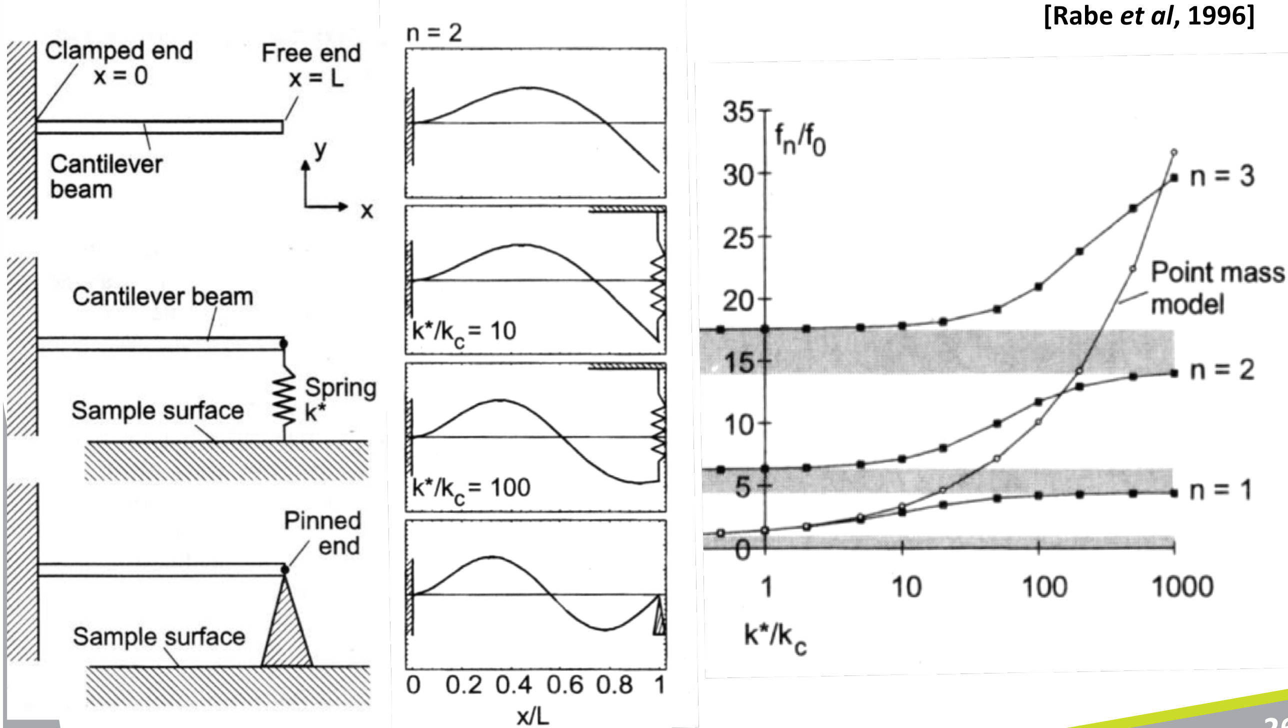


Amplitude of vibration and resonance frequency depend on the contact stiffness k_N… but how?

Contact Resonance-AFM (CR-AFM)

Cantilever dynamic and response

[Rabe *et al*, 1996]



CR-AFM - Cantilever dynamic

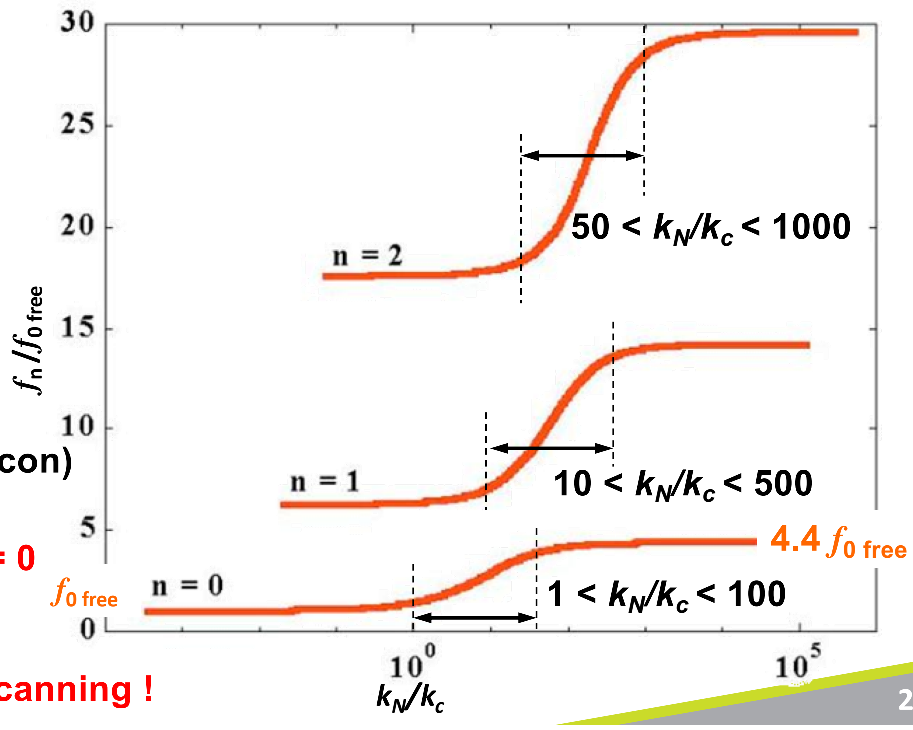
Sensitivity of the cantilever contact stiffness and considered mode

Example:

Probe: $k_c \approx 3$ N/m,
$R \approx 50$ nm
$F_0 \approx 200$ nN

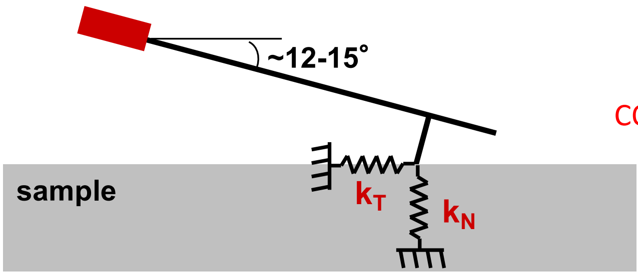
"Soft" sample
(Low T_g polymer)
$k_N \approx 10$ N/m
OK using n = 0

"Hard" sample (Silicon)
$k_N \approx 1000$ N/m
Not OK using n = 0
OK using n > 0
with low applied
static force for scanning !



Cantilever dynamic: analytical model

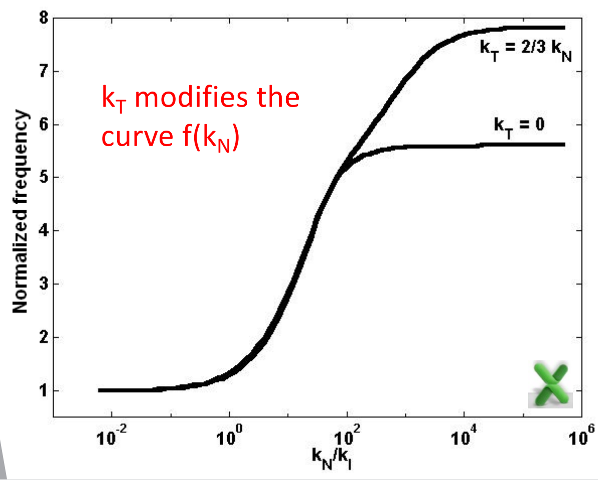
More realistic modelling: cantilever tilt



Normal and tangential components
of the tip displacement

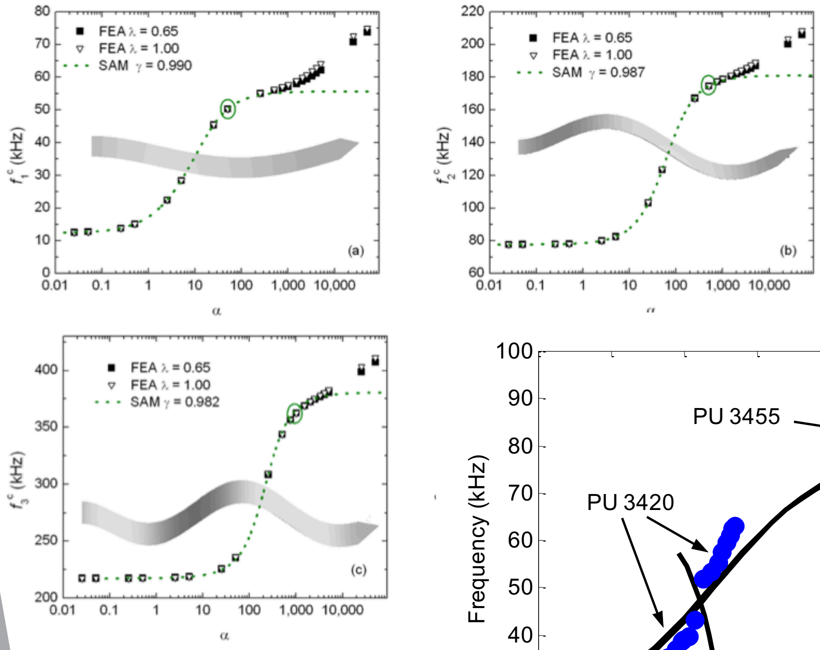
CONTACT = normal spring k_N + tangential spring k_T

2 cases
- $k_T \neq 0$ + adhesion → Pinned contact
- $k_T = 0$ or no adh. → Sliding contact



Problem: Analytical model do not allow to take into account the exact geometry of the cantilever (defaults, V-shaped…) and the specificities of the real excitation

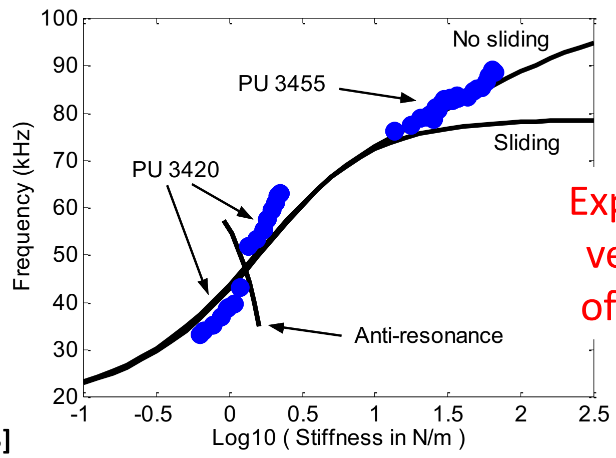
Cantilever dynamic: FE model…



[Arinero and Levêque, 2003]

[Killgore and Hurley,2012]

Cantilever and tip calibration…!

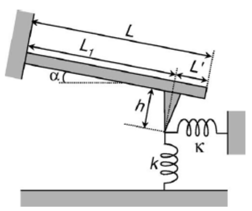


Experimental verification of FE model

Cantilever dynamic: flexural and torsional resonance

Measurement of Poisson's ratio with Contact-resonance atomic force microscopy

[Hurley and Turner, 2007]



k and K provided by flexural and torsional resonance respectively

Young's modulus | **Shear modulus**

$$k = 2aE^*$$ $$\kappa = 8G^*a$$

Contact area

$$M = E/(1-\nu^2)$$ $$N = G/(2-\nu)$$

$$E_s^* = E_{\text{ref}}^*\left(\frac{k_s}{k_{\text{ref}}}\right)^m$$ $$G_s^* = G_{\text{ref}}^*\left(\frac{\kappa_s}{\kappa_{\text{ref}}}\right)\left(\frac{k_s}{k_{\text{ref}}}\right)^{m-1}$$

Hertzian Contact m=3/2

Flat punch m=1

$$\frac{1}{E_s^*} = \frac{1}{M_{\text{tip}}} + \frac{1}{M_s}$$ $$\frac{1}{G_s^*} = \frac{1}{N_{\text{tip}}} + \frac{1}{N_s}$$

Reference sample

Material	Source	M	N	$\nu = \frac{M-4N}{M-2N}$	$G = N(2-\nu)$	$E = M(1-\nu^2)$
SiO_2	Literature	74.9	17.0	0.171	31.1	72.7
Glass	Literature	84.7	18.7	0.206	33.6	81.1
	Expt. $m=1$	81±5	18±2	0.21±0.11	32±5	76±6
	Expt. $m=3/2$	85±8	19±3	0.17±0.16	35±8	79±10

"Unknown" material

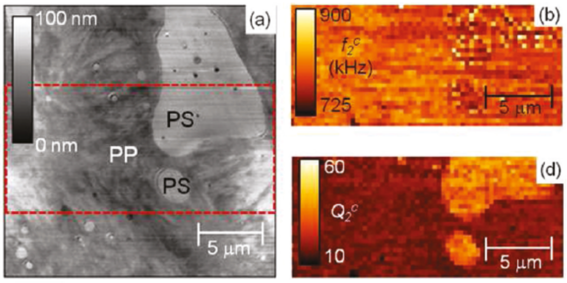
$$\nu = \frac{M-4N}{M-2N}$$

Cantilever dynamic: effect of scanning velocity

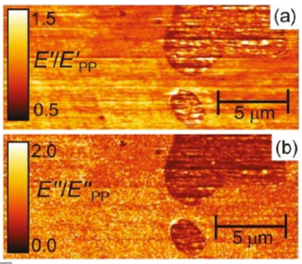
Polystyrene polypropylene blend

[Killgore et al, langmuir, 27, 13983, 2011]

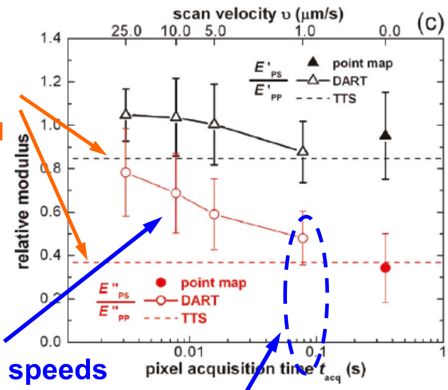
PS regions: f_2=792.1 ±31.7 kHz, Q_2=37.3 ±5
PP regions: f_2=801.7 ±17.4 kHz, Q_2=18.4 ±2.7



Tracking images



Cantilever modelling
+contact mechanics model



Expected at 1MHz (DMA low freq and low T + time temp superposition)

Higher scan speeds NO! (contact mechanics or instruments effects)

V = 1 µm/s OK!

Image duration ~1h
15 µm15 µm
256*256 pixels

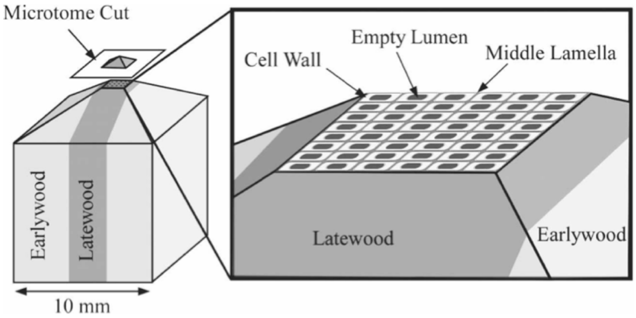
+ Stick to sliding transition…

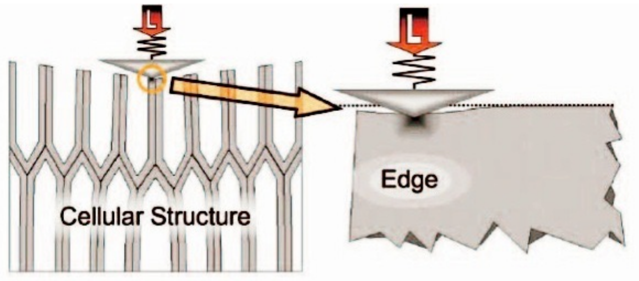
Sommaire

- Mécanique du contact et indentation
  - Contact élastique – Hertz
  - Nano-indentation – Oliver and Pharr
  - Domaines de validité, adhésion, anisotropie
- Courbe force-distance
  - Principe et prérequis
  - Traitement des courbes
- Contact résonant
  - Principe
  - Dynamique du levier et effet de la raideur latérale
- Préparation de la surface et calibrations

Sample preparation…

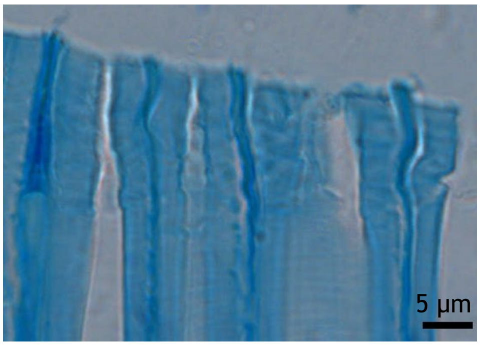
Without embbeding in a resin: no sample modifications but ±measurement articfacts





[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

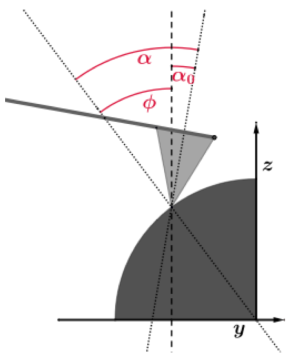
±no thermo-chemical modification of the cell wall (extractives…)?
Resin penetration / inclusion time?
Cell wall water content?

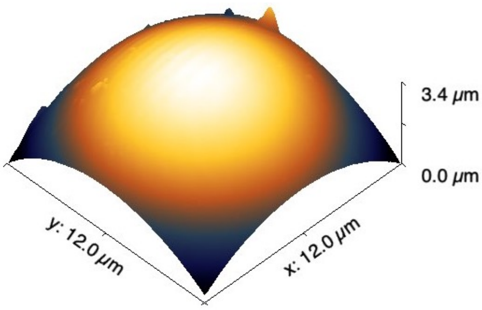
Microtome/Grinding/FIB…??!!

Sample surface effect

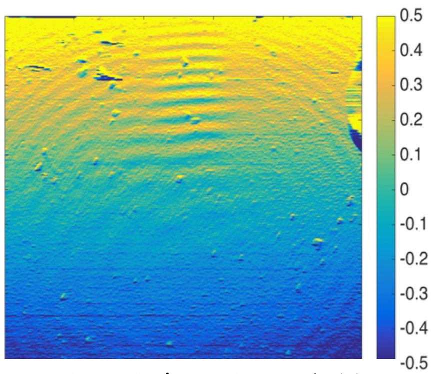
- Effect of sample local slope

[Heinze et al, Ultramicroscopy, 2018]

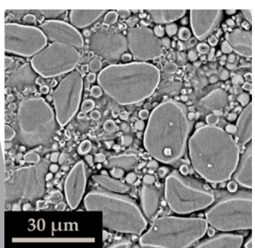




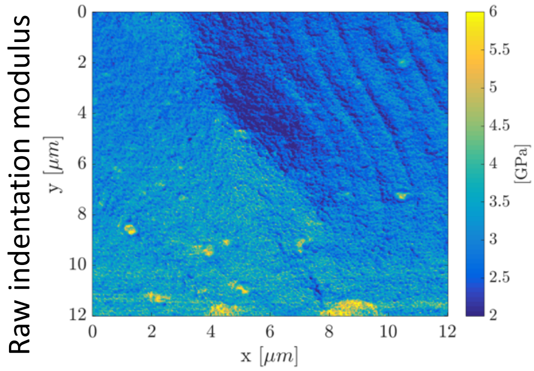
Topography

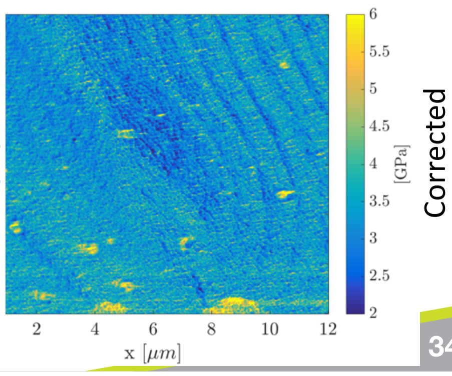


Local angle/cantilever ϕ (°)



Starch granules

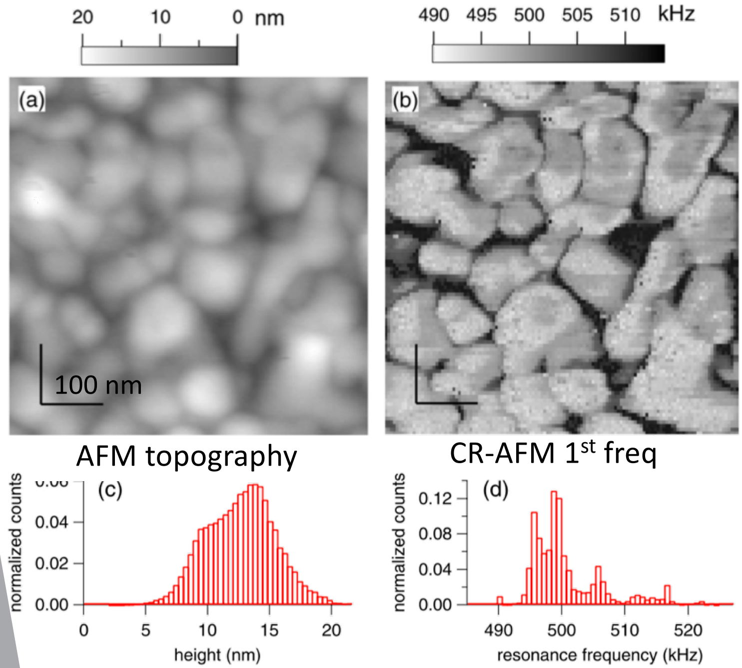


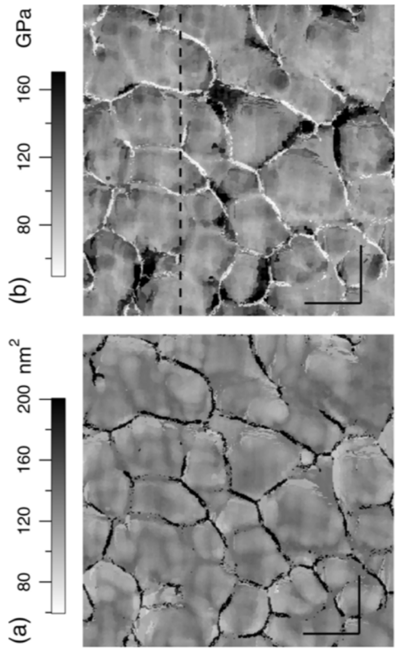


Sample surface effect

- Effect of sample roughness

Stan and Cook, Nanotechnology, 2008, 19, 235701



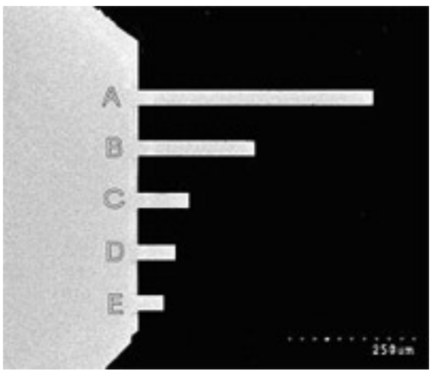


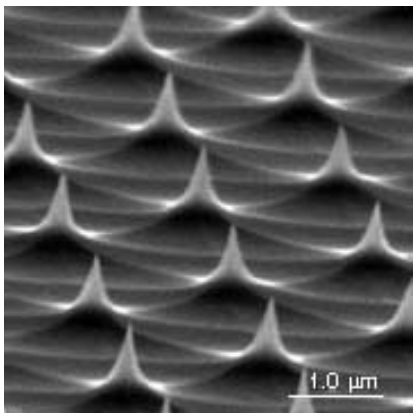
Au film ≈ <110>, k_C = 14.8±0.5 N/m, 350 nN

Calibrations

- Probe calibrations

  - Cantilever stiffness calibration methods: added mass, SEM imaging and mechanical beam model, Sader method, Thermal noise method, Reference cantilever array, …



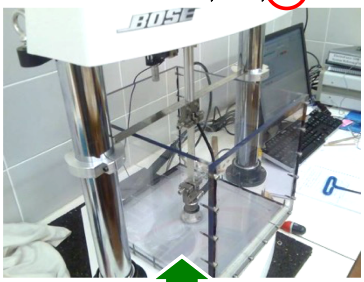


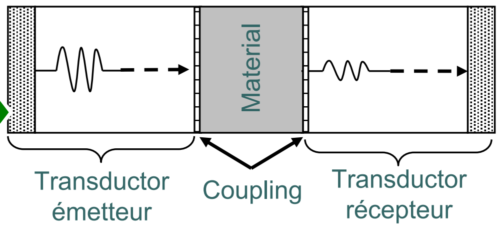
  - Tip shape: SEM imaging, gratings (TipCheck, TGT), reference material(s)
  - Tip position: SEM imaging, reference material(s)

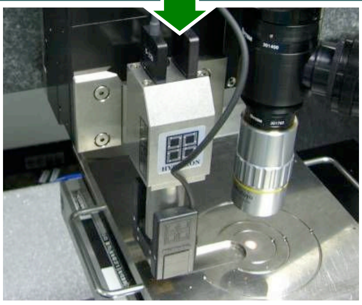
Reference material samples

- Calibration?

	~ Hz	~ 100 kHz
Macro	DMTA: *E'*, *E"*, *ν*	US : *E'*, *E"*
µ-nano + Contact	Creep + nanoDMA: rheology, *M'*, *M"*	**AFM:** ***M'*, *M"* ? TTSP ?**



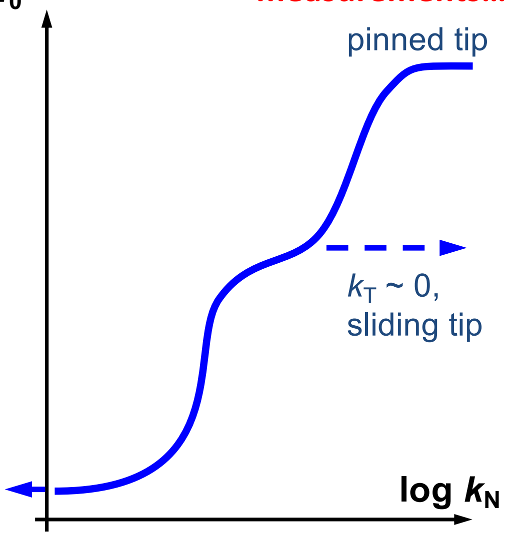




Cantilever and tip calibration / reference samples

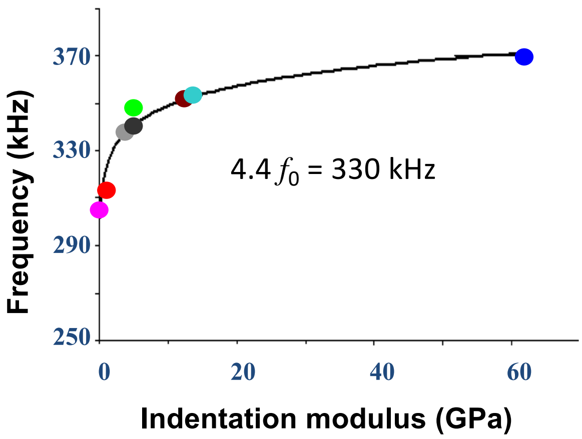
- CR-AFM

Static point or during a scan measurements...



Nanoworld ARROW FMR:
$k_C \approx 2.8$ N/m, $f_0 = 75$ kHz, $R \approx 55$ nm
Veeco Enviroscope: $F_0 \approx 180$ nN

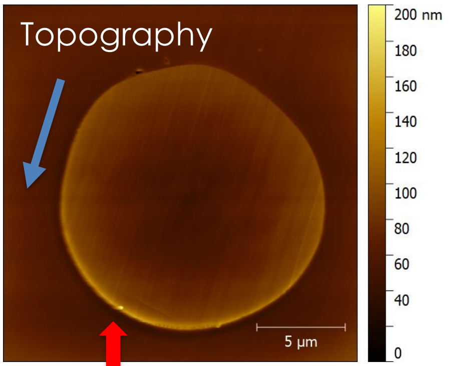
Single reference method??



Material	M_N (GPa)	f_0 (kHz)
PU	0,14	305
PE	1,2	313
PMMA	4,9	350
glass	62	370
LR-White	5	338
S1/LM	5,5	341
S2	13	352
G	15	354

Kevlar® Dupont™ K48 fibres

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

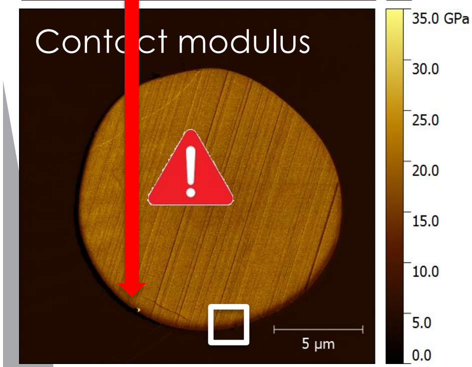


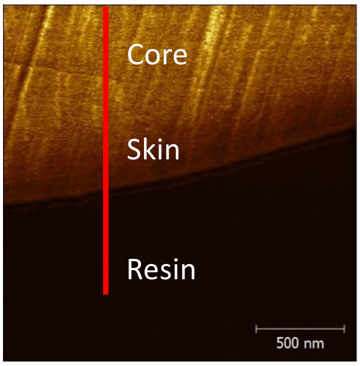
[Wollbrett-Blitz et al, J. Polym. Sci., 2016]

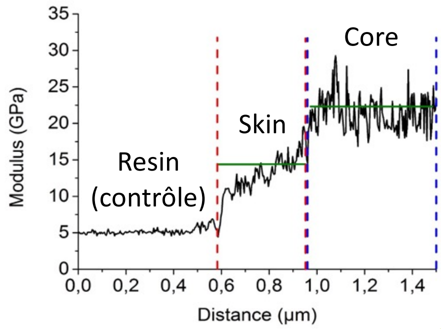
Core:
E_l = 84 GPa / E_t = 3 GPa
Skin:
E_l = 85 GPa / E_t = 0,2 GPa
G_{lt} = 1,8 GPa / G_{tt} = 1,2 GPa
ν_{lt} = 0,6 / ν_{tt} = 0,25

$M_{core\ NI}$ = 22,8 ± 1,7 GPa
(150 nm @ 1 µN/s + 20 s + 10 µN/s)

$M_{core\ calc}$ ≈ 21 GPa
$M_{skin\ calc}$ ≈ 17 GPa







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

Conclusions – Questions ouvertes

- Respecter/vérifier les domaines de validité des modèles d'indentation suivant les conditions expérimentales (transition entre modèles ?)
- Attention au comportement anisotrope (*E ≠ M*) surtout aux échelles nano
- Indentation non normale… raideur tangentiel en anisotrope ? Comment la mesurer ?
- Utilisation de la courbe d'approche ou de retrait ou … ? Et effet de la viscosité ?
- Choix de la forme optimale de la pointe / rugosité ou hétérogénéité de la surface (+ tenue à l'usure)
- Choix de la raideur (et facteur de qualité) du levier / matériau à tester
- Effet de la topographie et de la profondeur de mesure par rapport aux effets de surface (liés à la préparation des échantillons + comportement matériaux)
- Mesure « intégrant » plus en profondeur ?
- Calibration des échantillons de référence en terme d'échelle, de fréquence (TTSP ?) et de mode de sollicitation ? Idem pour le matériau mesuré…
- Problème de la vitesse de sollicitation / comportement viscoélastique
- Mesure en milieu liquide, problème de l'adhésion (CR-AFM), mesure visco (Q)…