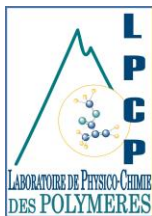


Development of a nanorheometer to study rheological behaviour of confined polymers

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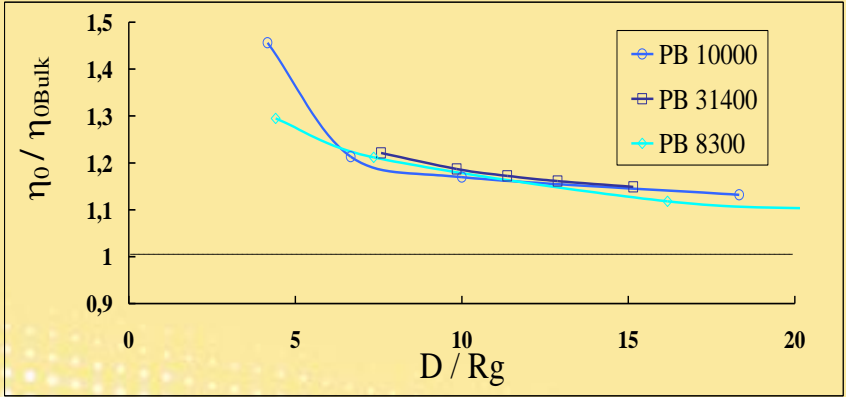
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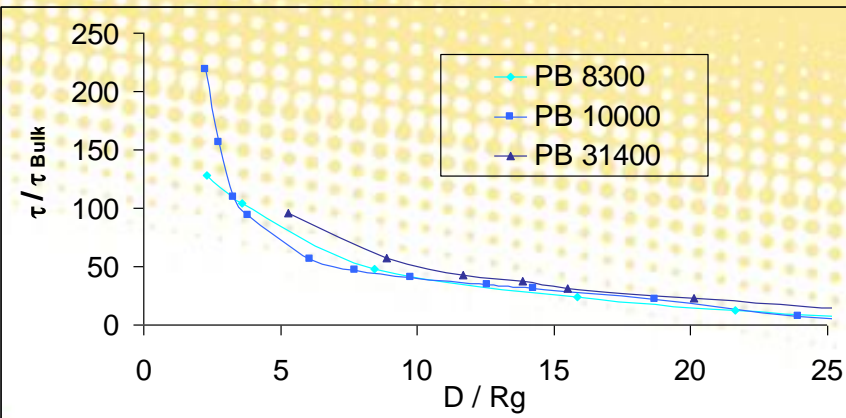
Development of a nanorheometer to study rheological behaviour of confined polymers

Previous works in the lab obtained on another surface force apparatus (ECL – Lyon):

For Polybutadiene in the terminal domain:



Viscosity is not affected by confinement



Elasticity particularly affected



**Increase of relaxation time
with a factor 200**

Development of a nanorheometer to study behaviour of confined polymers

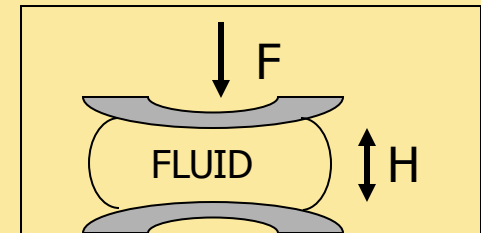
- ➔ • **Principle of dynamic surface force apparatus**
- ➔ • **Experimental technique**
- ➔ • **Validation of the experimental technique with Polydimethylsiloxane (PDMS)**
- ➔ • **Conclusions**

Principle of dynamic surface force apparatus

Principle:

Measure of F and H of a viscoelastic fluid between two surfaces

- Thickness between surfaces from nm to μm
- Force range of μN

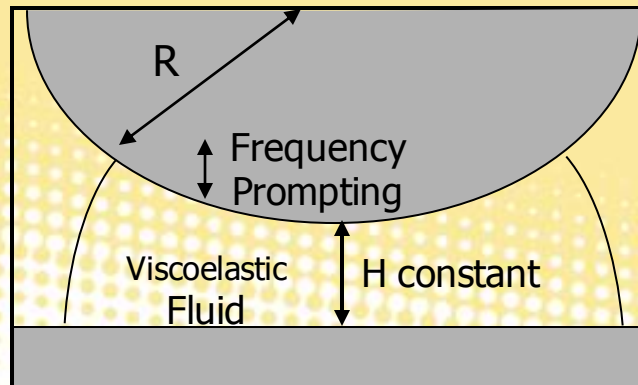


Different measurements:

- Steady tests → Interfacial energy measurement
- Dynamic tests
 - Drainage force measurement ($dH.dt^{-1}$ constant)
 - ↳ η_0
 - Oscillatory force measurement (H constant)
 - ↳ $G^*(\omega)$

Dynamic measurements with the nanorheometer

- ➔ Sphere/Plate geometry
Inorganic Surfaces: SiO₂
Radius of the sphere: **0.1 to 1mm**
Roughness negligible: about 1nm.μm⁻¹
(measured with a confocal rugosimeter)
- ➔ Frequency prompting with amplitude $a \ll H$



Lubrication Test

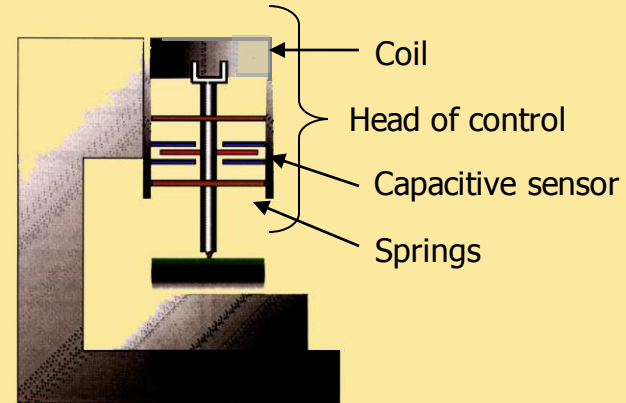
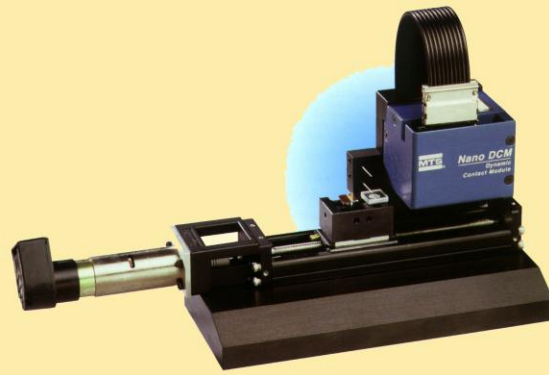
$$G^* = -\frac{H}{6\pi R^2} \left(\frac{F}{a} \right)^*$$

Typical Modulus range from 1 to 10⁶ Pa

Development of a nanorheometer to study behaviour of confined polymers

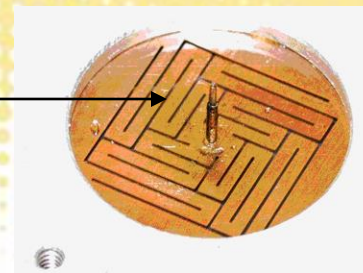
- Principle of dynamic surface force apparatus
- ➔ • Experimental technique
- Validation of the experimental technique with Polydimethylsiloxane (PDMS)
- Conclusions

General features of MTS nanoindenter with DCM head



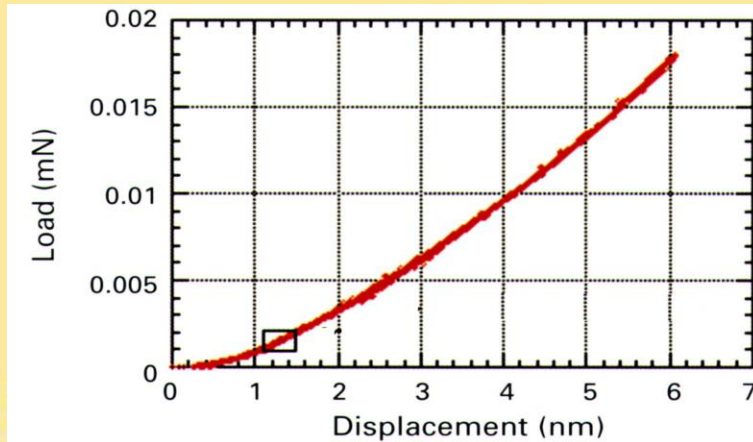
- ➡ STRESS CONTROLLED APPARATUS: Force created by a coil
- ➡ DISTANCE ENSLAVEMENT: Position measured by capacitive sensor

Springs of the apparatus



General features of MTS nanoindenter with DCM head

In the case of our nanorheometer

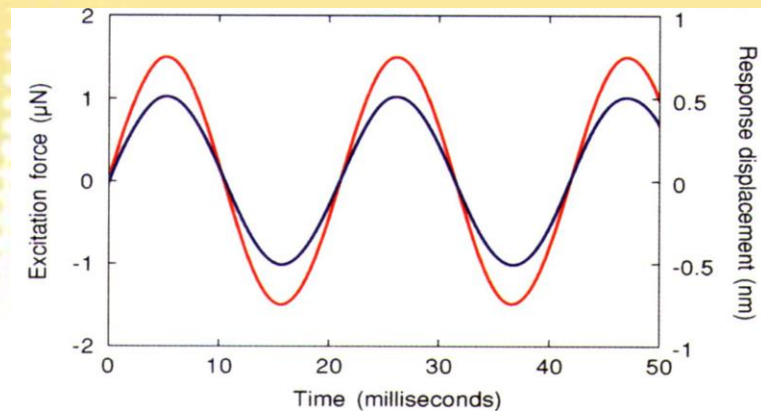


Static and hydrodynamic measurements:

- Displacement resolution: **1 nm**
- Static measurement from **10 nm to 10 μm**
- Force resolution: **100 nN**
- Maximum force allowed: **10 mN**
- Speed drainage from **1 to 100 nm.s⁻¹**

Dynamic measurements:

- Frequency range: **$10^{-2} <$ to 10^2 Hz**
- Amplitude of about **1 nm**
- Displacement resolution: **0.2 nm**
- Force resolution: **100 nN**



Parameter to be controlled: temperature

Dilatation between sphere and plate:

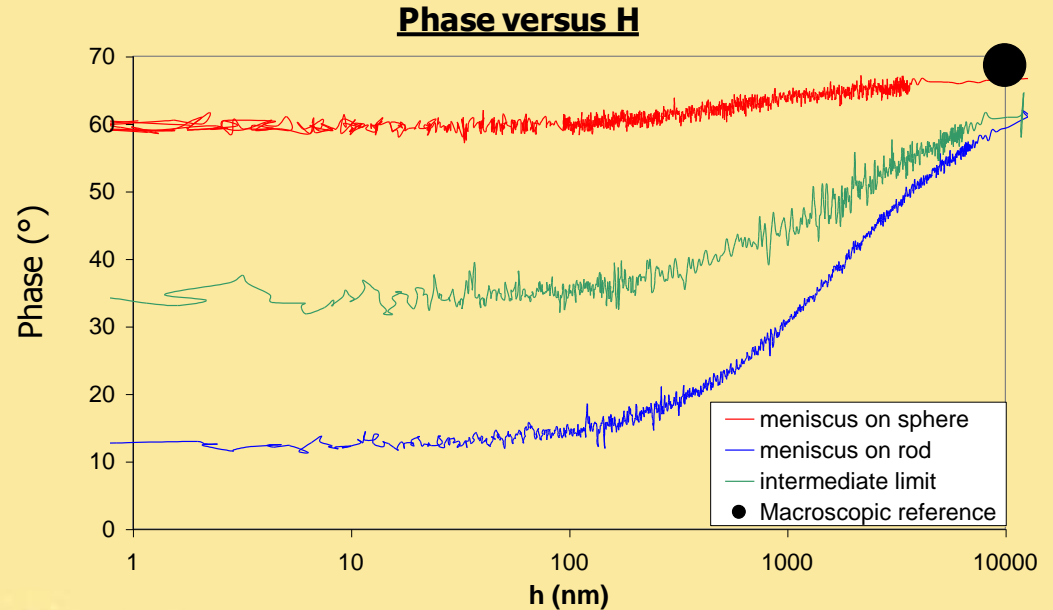
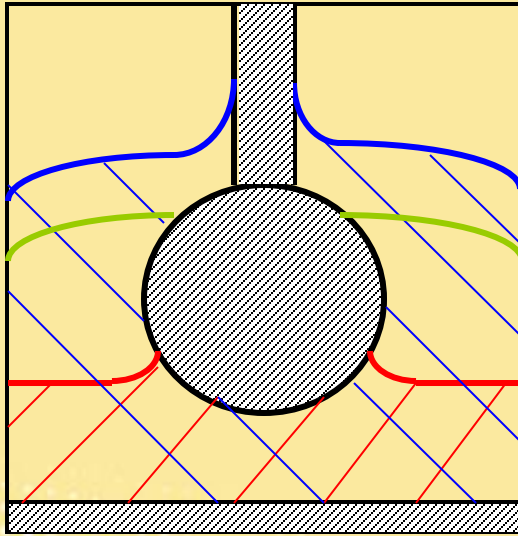
500nm.°C⁻¹

➡ Controlled temperature enclosure made with peltier moduli

{ Temperature range: 13°C to 35°C
Precision after stabilisation: ±0.01 °C

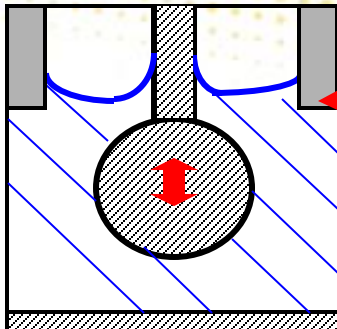
➡ Thermal drift below 10 nm/h

Parameter to be controlled: geometry of the sample



➔ Influence of the meniscus forces on the phase

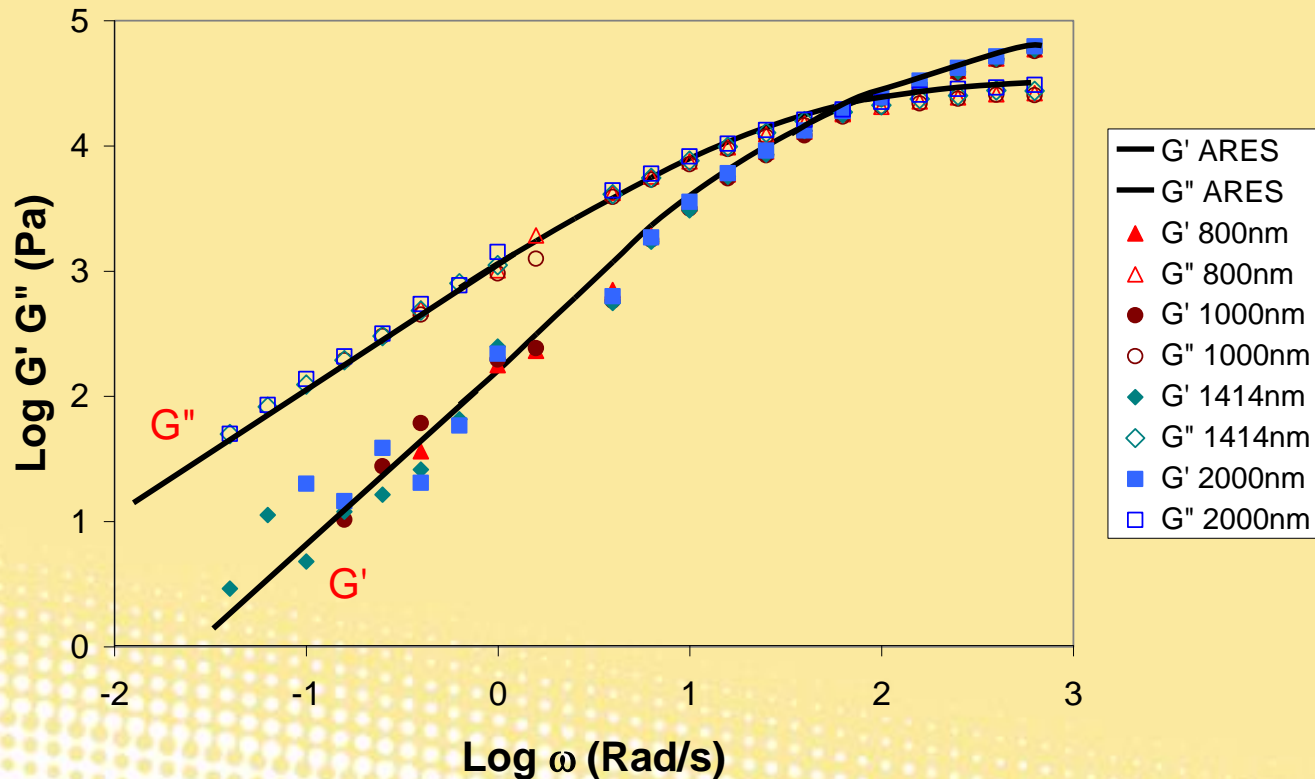
➔ Solution: use of a drop
in contact with
this fixed circle



Development of a nanorheometer to study behaviour of confined polymers

- Principle of dynamic surface force apparatus
- Experimental technique
- ➔ • Validation of the experimental technique with Polydimethylsiloxane (PDMS)
- Conclusions

Validation of the technique with PDMS Comparison with bulk measurements



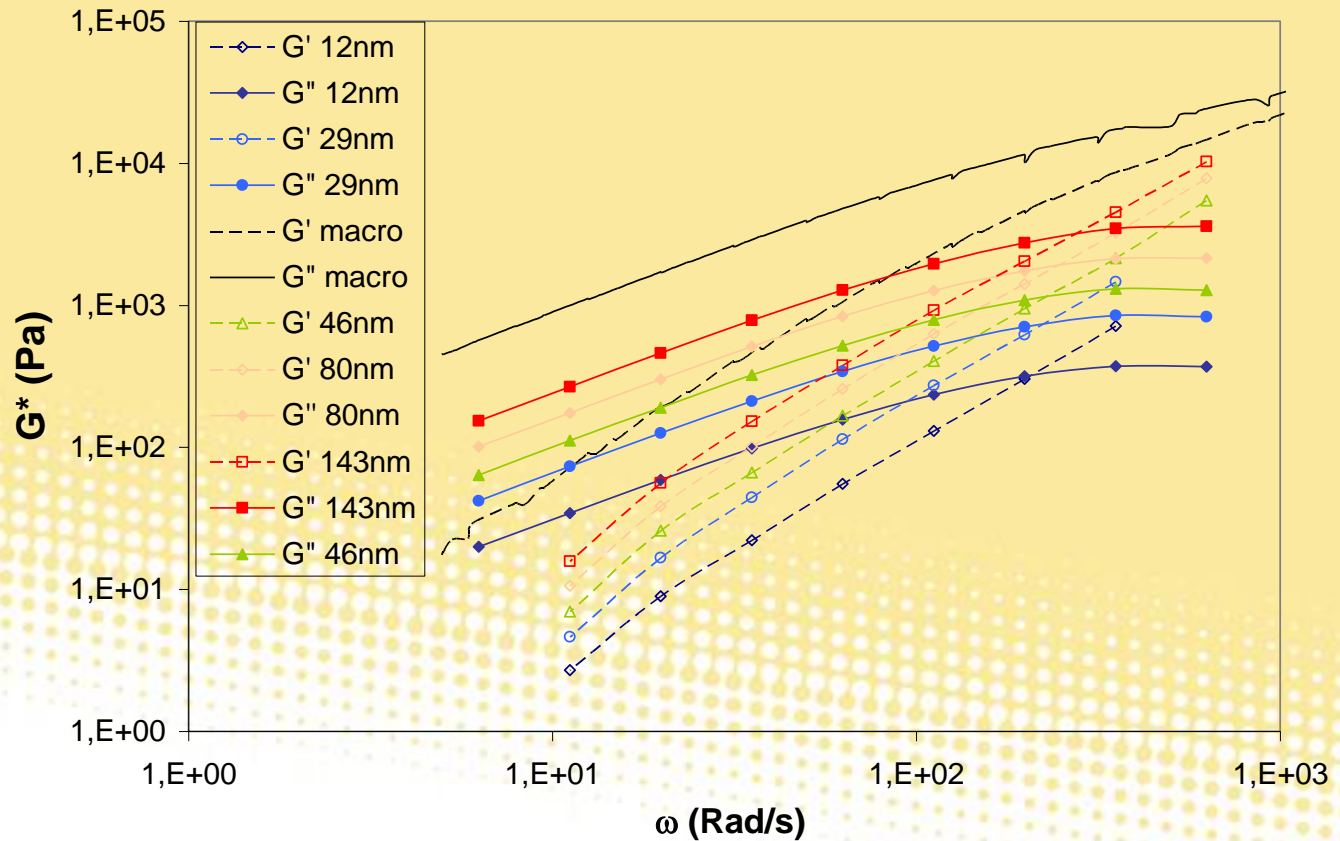
PDMS: $M_w = 249\,000 \text{ g}\cdot\text{mol}^{-1}$ / $\eta_0 = 10^3 \text{ Pa}\cdot\text{s}$
 $T = 20^\circ\text{C}$

➡ Measurement of the macroscopic shear modulus
 at long distance with only one drop of liquid

Validation of the technique with PDMS Comparison with bulk measurements

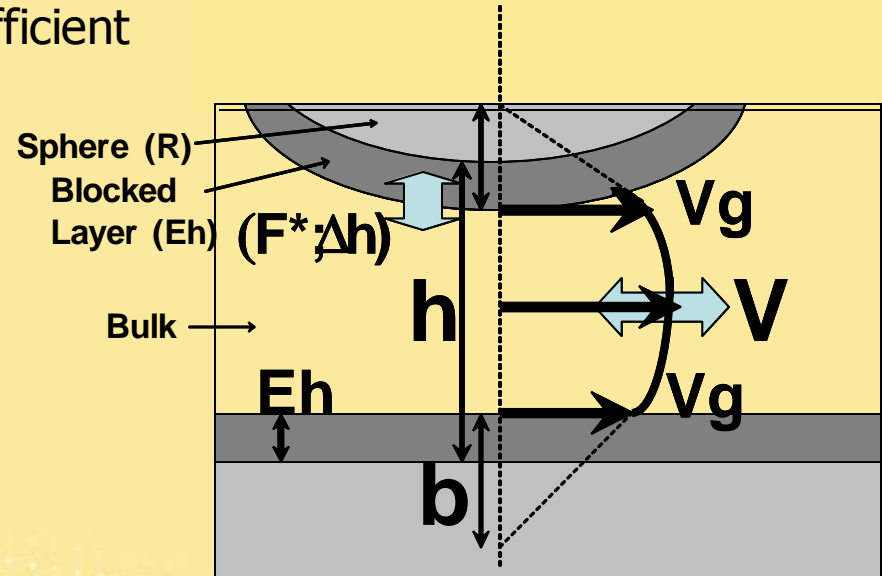
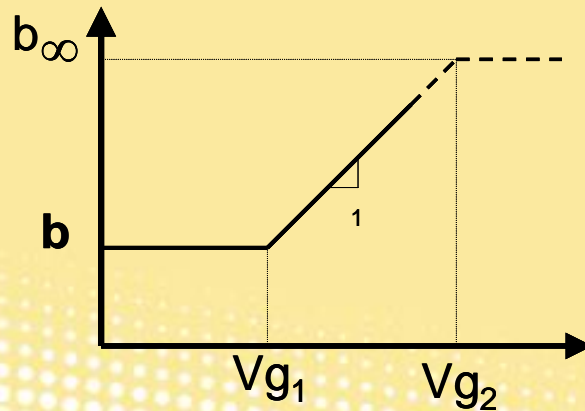
For PDMS 60 Pa.s

➡ **Shear modulus decreases with the confinement !**



A parasitic effect that is corrected: the slippage

→ Variation of the slippage coefficient with the excitation



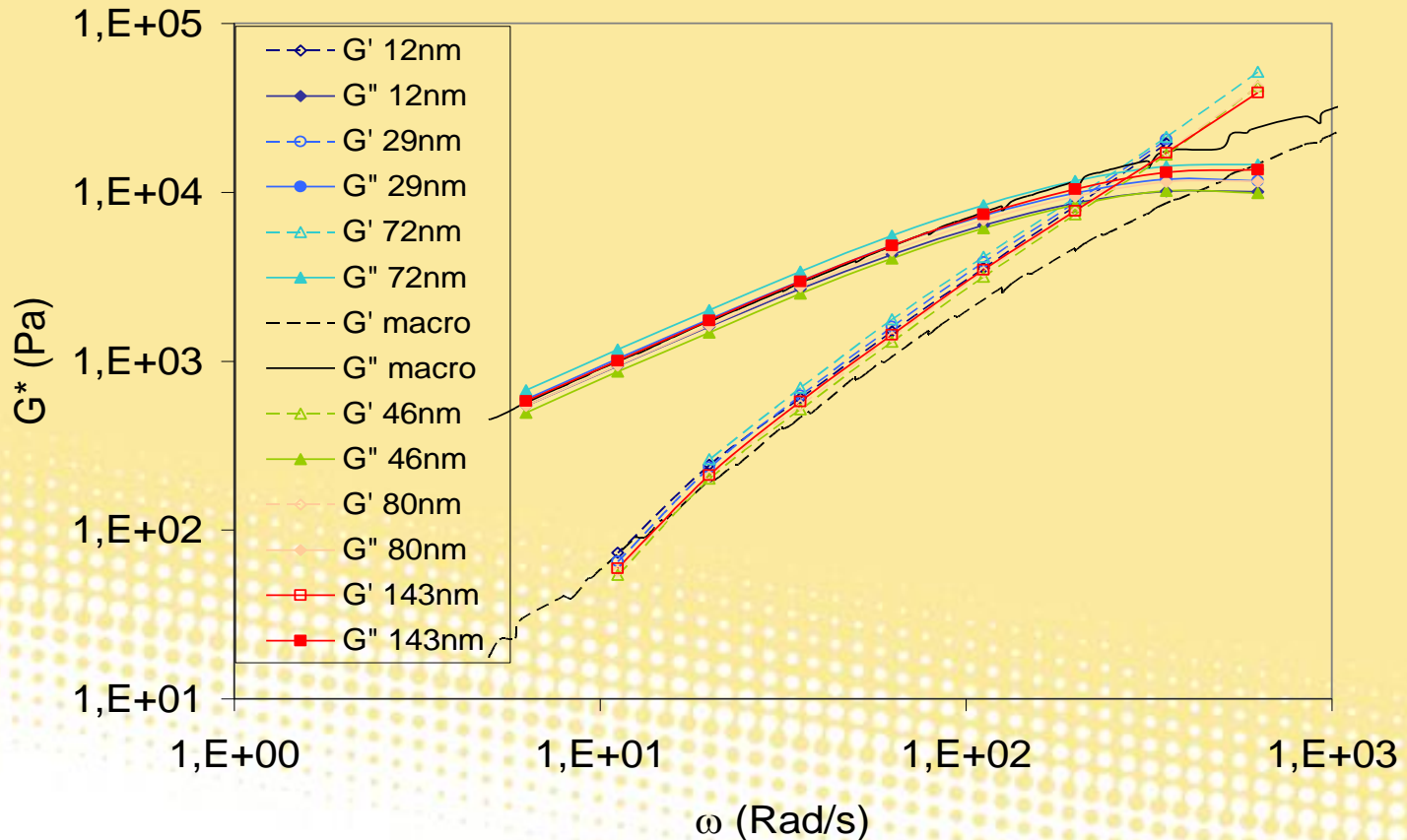
Lubrication test

→
$$G^* = -\frac{H}{6\pi R^2} \left(\frac{F}{a} \right)^*$$

$$X f(\underbrace{b, b_\infty, V_{g1}, V_{g2}}_{\text{Polymer}}, \underbrace{H, R, \omega, a}_{\text{Conditions}})$$

A parasitic effect that is corrected: the slippage

PDMS 60 Pa.s **with correction:** $b=300\text{nm}$



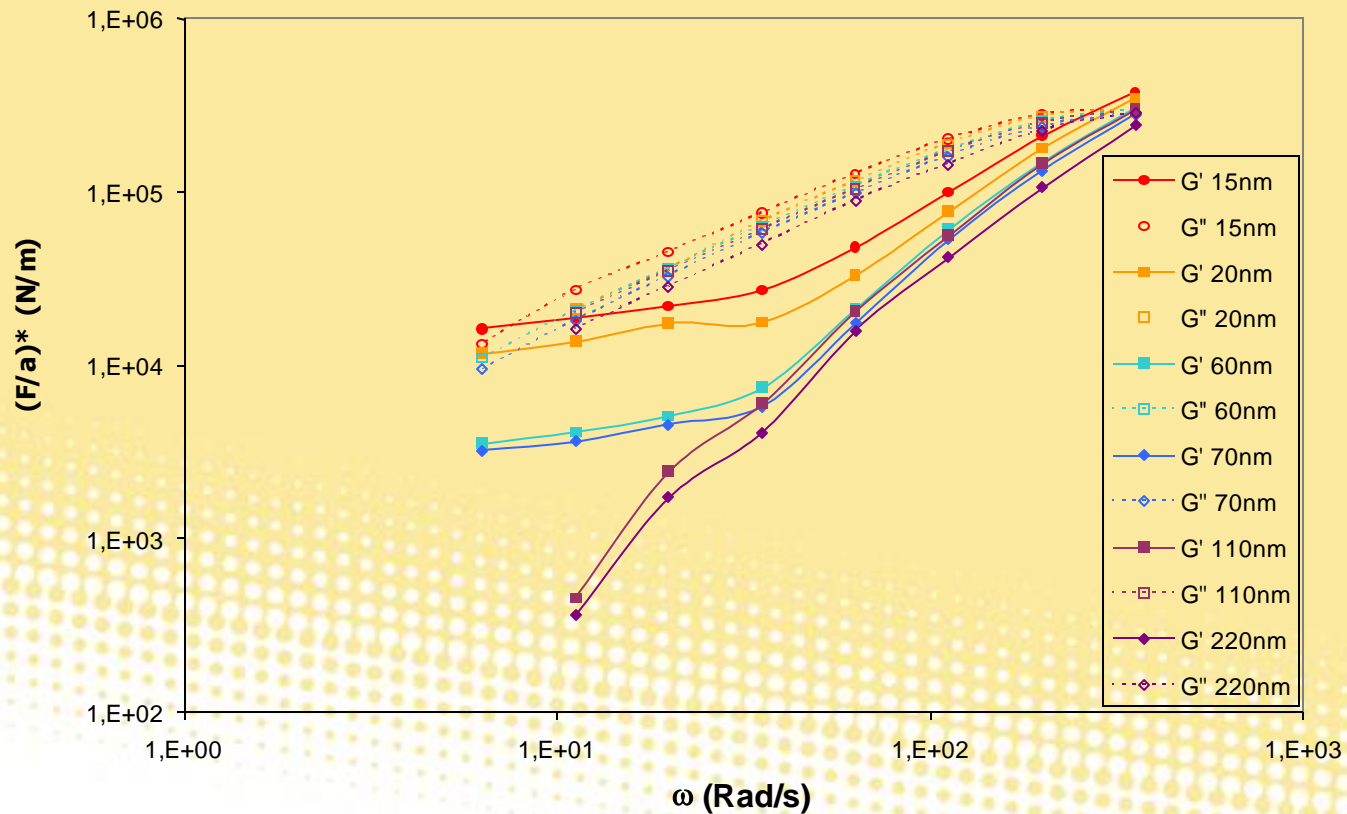
➔ **Correction of the slippage effects**

Conclusions

- ➡ • **Modification of a commercial nanoindenter to use as a nanorheometer**
- ➡ • **Validation of the experimental technique to use as a microrheometer with different polymers and different viscosities**
- ➡ • **Possibility to measure and correct slippage**
- ➡ • **Validation of the experimental technique to study interfacial rheology**

Study of interfacial rheology of Poly-n-Butylacrylate

PBA grafted 80000g/mol swelled by PBA oligomer- $(F^*/a^*)=f(\omega)$



➔ Visualisation of the h-dependence of G' at low frequency

Perspectives

- ➡ • **Analysis and synthesis of the results with PDMS, PBA, Polybutadiène PB**
- ➡ • **Functionalisation of surfaces to control slippage**
- ➡ • **Study of nanorheology of grafted surfaces**
- ➡ • **Others applications: nanotack (tests validated), study of thin films...**

Different polymers tested

Samples	Mw (g.mol ⁻¹)	η_0 (Pa.s)	Rg (nm)
PB 8300	8300	4,15	3,4
PB 10000	10000	9,8	3,8
PB 22600	22600	70	5,5
PB 31400	31400	393	6,6
PB 61700	61700	5000	9
PDMS 90000	90000	60	8,2
PDMS 170000	170000	290	11,3
PDMS 200000	200000	500	12,2
PDMS 249000	249000	1000	14
PBA 6000	6000	33	3,1
PBA 13500	13500	200	4,6
PBA 29000	29000	1250	7,5
PBA 56000	56000	6500	9,9
PBA 92000 grafted	92000	18500	

Development of large frequency range method

Frequency range: $10^{-2} < f < 10^2$ Hz

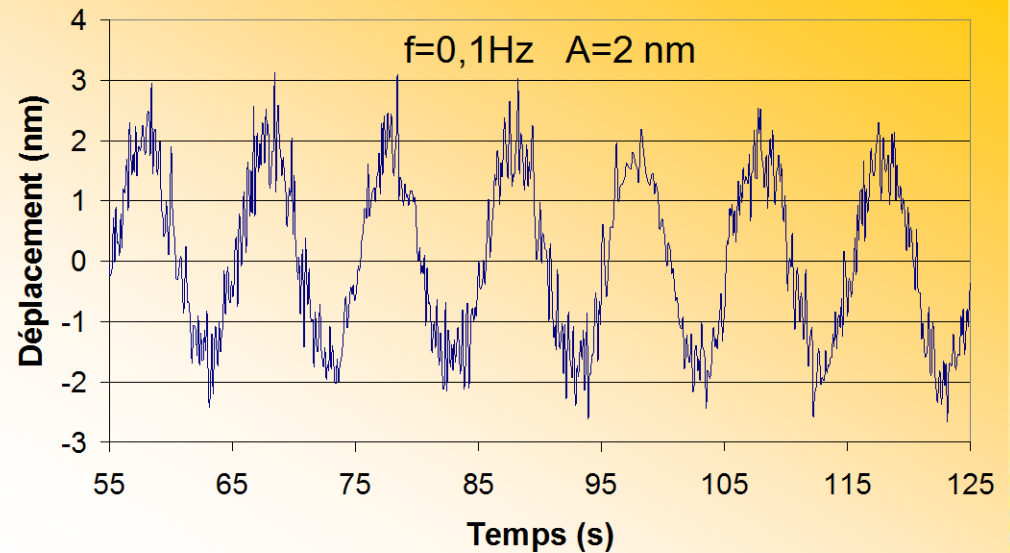
Lock-In limit

Auto-Level limit

f

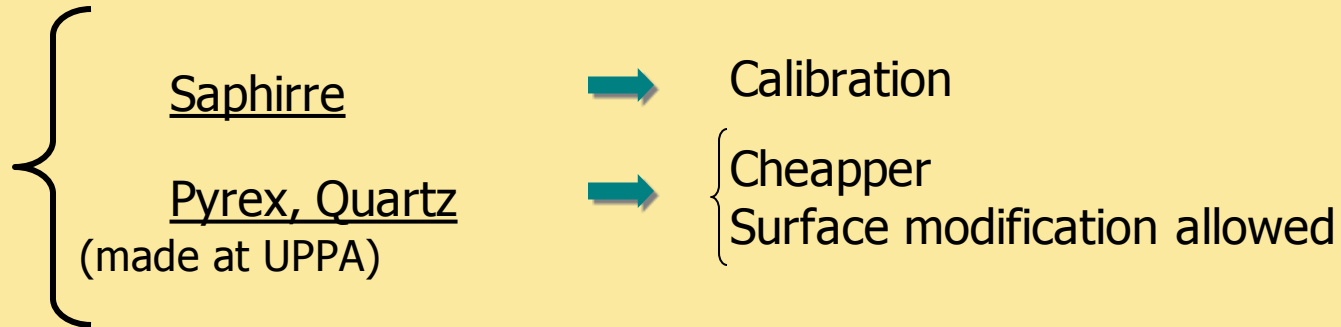
$f < 0.4$ Hz

Lock-In Off
Use of static displacement
function with
 $z = z_0 \sin(\omega(t-t_0))$
Analysis of the signal
by calculation of
Fourier series coefficients



General features of MTS nanoindenter with DCM head

Different spheres used:



Diameter from $\sim 100 \mu\text{m}$ to $\sim \text{mm}$



Typical G^* range: 1 to 10^6 Pa

**Roughness negligible: about $1\text{nm rms} \cdot \mu\text{m}^{-1}$
(measured with a confocal rugosimeter)**

Interest of viscoelastic measurements with this surface force apparatus

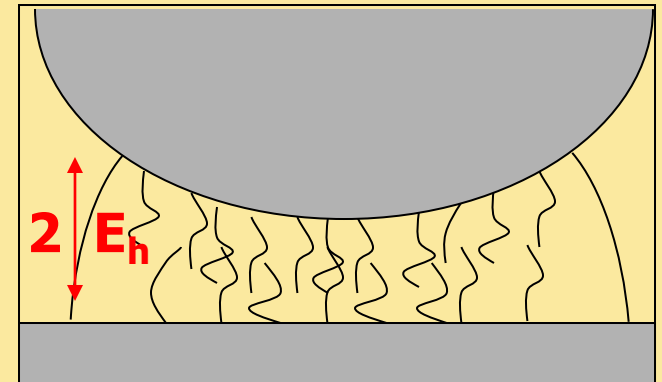
Field of study:

Polymer flow at room temperature

Typical Modulus range from 1 to 10^6 Pa

Rheological study:

- bulk
- adsorption
- grafting



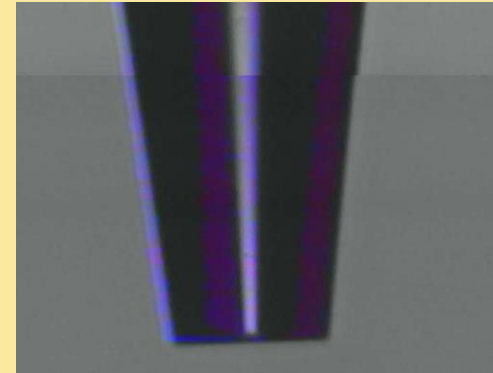
Important parameter



hydrodynamic thickness E_h

Other application: nanotack

Tests made with a flat punch of 100 μm diameter
with adhesive polymers
(Speed about 50 $\mu\text{m}\cdot\text{s}^{-1}$)



Begin of pulling out

