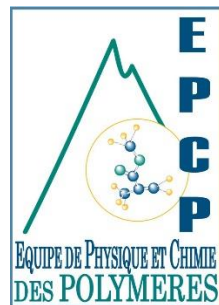


# VISCOELASTIC ANALYSIS BY A DYNAMIC SURFACE FORCE APPARATUS OF ADSORBED AND GRAFTED POLYMERS ON INORGANIC SUBSTRATES

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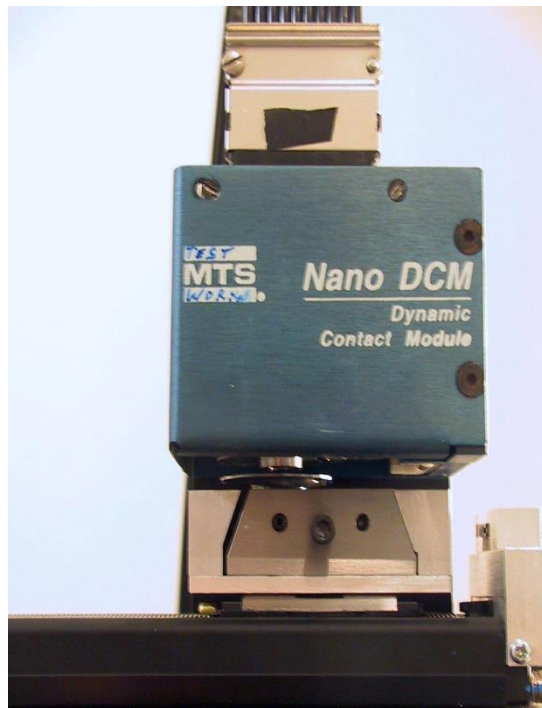


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l'Environnement et les Matériaux  
UMR-CNRS-5254

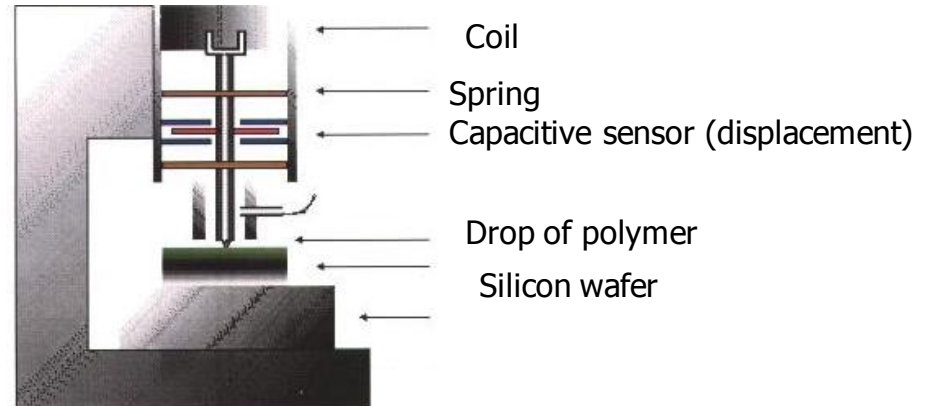


# Description of the apparatus

## *The Surface Force Apparatus*



*the displacement of the indenter is "given" by a coil and measured with a capacitive sensor. Springs measure the stiffness and damping....*



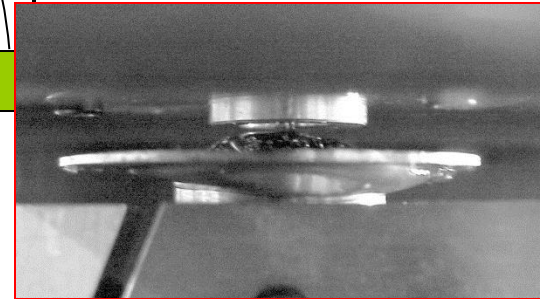
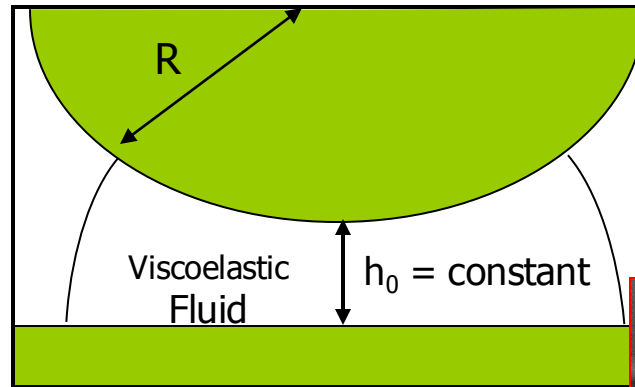
# Description of the apparatus

## *Lubrication between a sphere and a plate*

The Surface Force Apparatus is used as a **Nanorheometer**

*the sphere oscillates at a constant strain around the  $h_0$  position. The magnitude of the oscillation is around 2 nm.*

$$F^* = \frac{6\pi R^2 U^*}{h_0} G^*$$



The polymer is confined between the sphere which is made of glass. The radius is equal to about 1 mm. The plate is a Silicon Wafer.

The magnitude of the oscillation corresponds to the linear domain.

We performed frequency sweep.

## Systems studied

### ***Adsorbed polymers***

We have studied series of homopolymers (as Polybutadiene, PolybutylAcrylate, PDMS...)

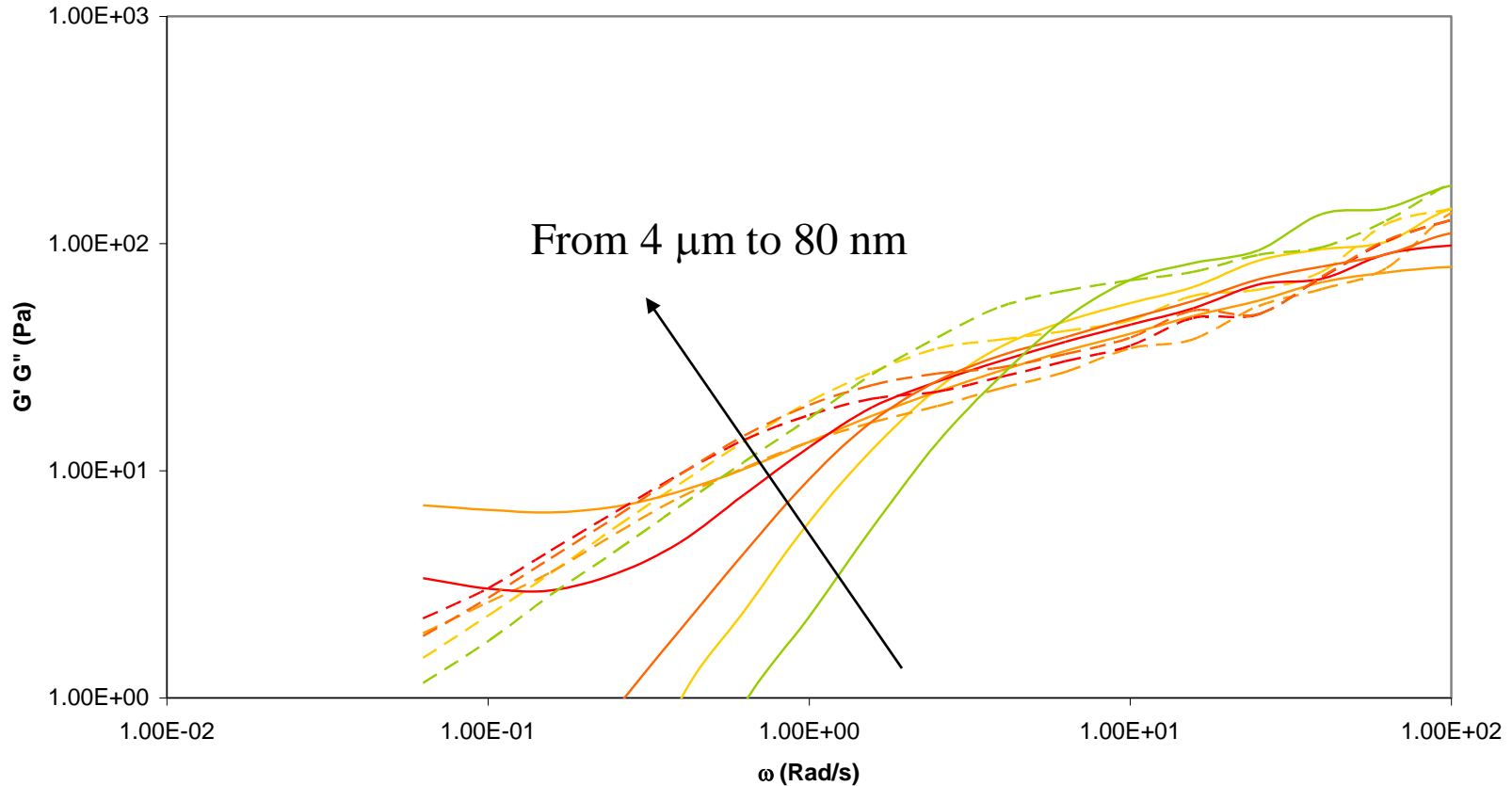
Frequency range:  $3 \cdot 10^{-2} \text{ s}^{-1} < \omega < 3 \cdot 10^3 \text{ s}^{-1}$

(we have used also the SFA from Ecole Centrale de Lyon for this study)

Distance range  $10 \text{ nm} < h_0 < 1 \text{ mm}$

## Results for adsorbed polymers

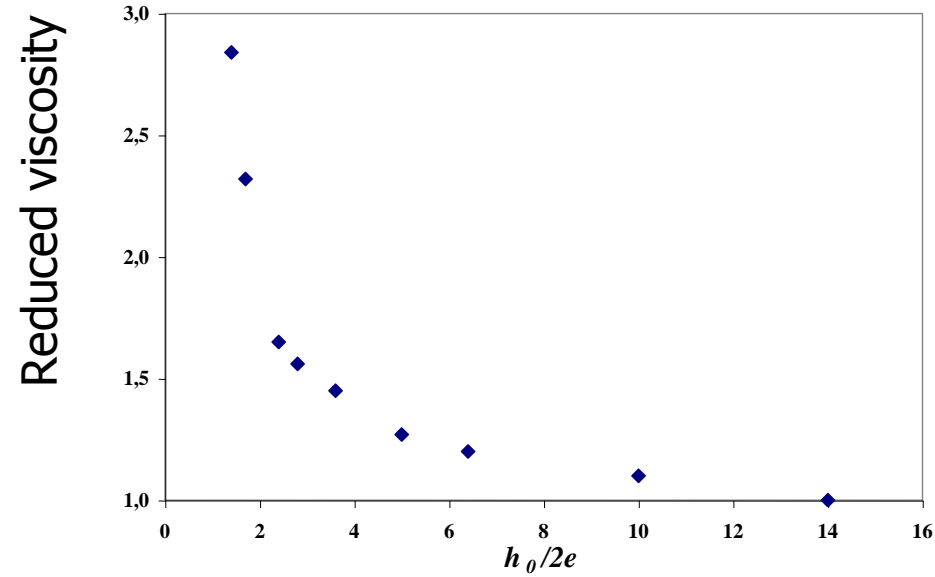
Polybutadiene,  $M_w=10000 \text{ g}\cdot\text{mol}^{-1}$



One can evaluate easily the passage from nonoverlapping (liquid like) to overlapping (solid like) layers.

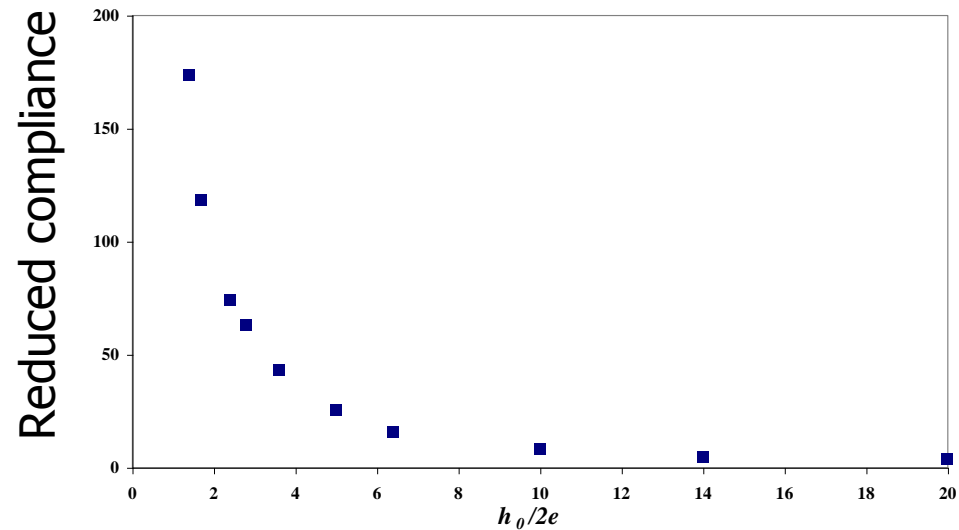
For the nonoverlapping situation we have measured the zero-shear viscosity and the steady-state compliance for each distance...

## Results for adsorbed polymers (nonoverlapping layers)

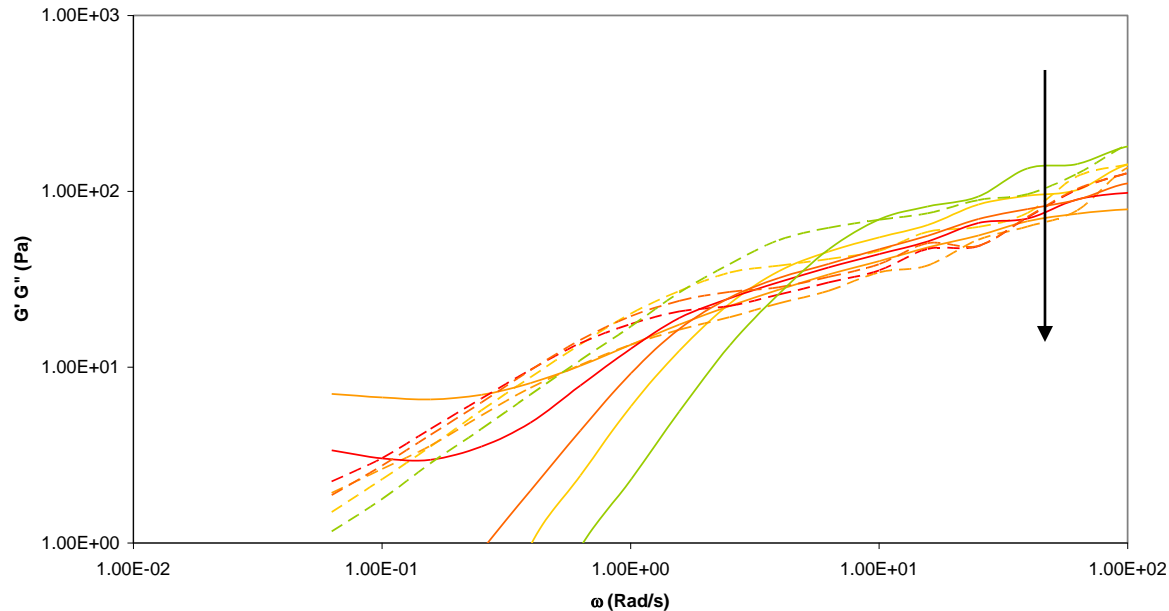


- The reduced distance is equal to the distance between the sphere and the plate over  $2e$ .  $e$  is defined as the compression threshold of the adsorbed layer (adsorbed layer are overlapped for  $h < e$ ). For this polymer we have measured  $e = 4 \text{ nm} = 1.3 R_g$ .

- The reduced value is equal to the ratio between the parameter at high distance (no confinement) over the parameter at small distance.



## Results for adsorbed polymers



- at higher frequencies, near the rubbery plateau domain, the modulus is lower than the plateau modulus of the homopolymer

***which can be explained by slipping effects....***

## Systems studied

### ***Grafted polymers***

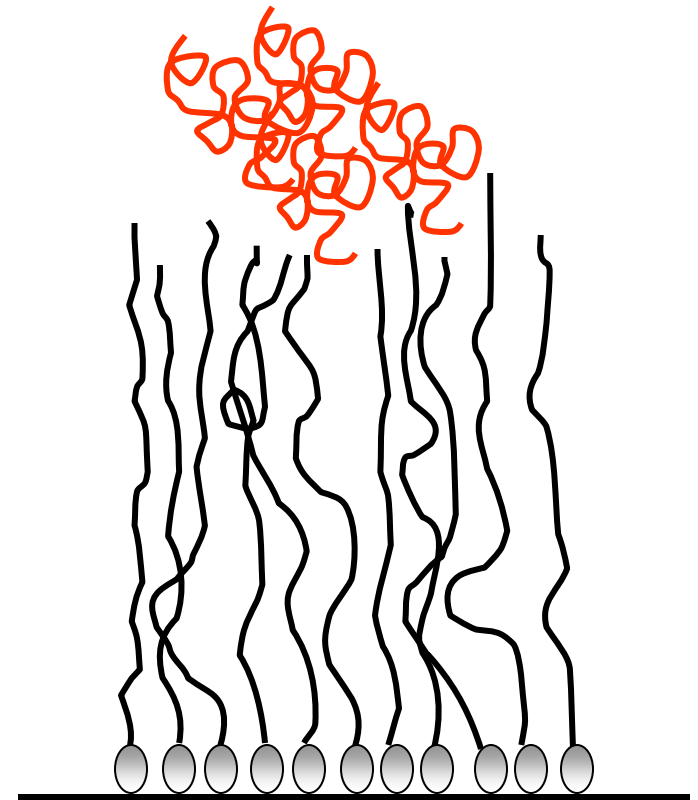
To control the surfaces, we have synthesized brushes by using «Grafting from» process which allows to control brushes.

An anchoring group is attached to the surface and the polymer grafting from in situ by using Controlled Radical Polymerization (CRP)

We add free chains (non entangled chains) to swell the network of tethered chains and confined this system

Self-Assembled Mono-layer of the agent

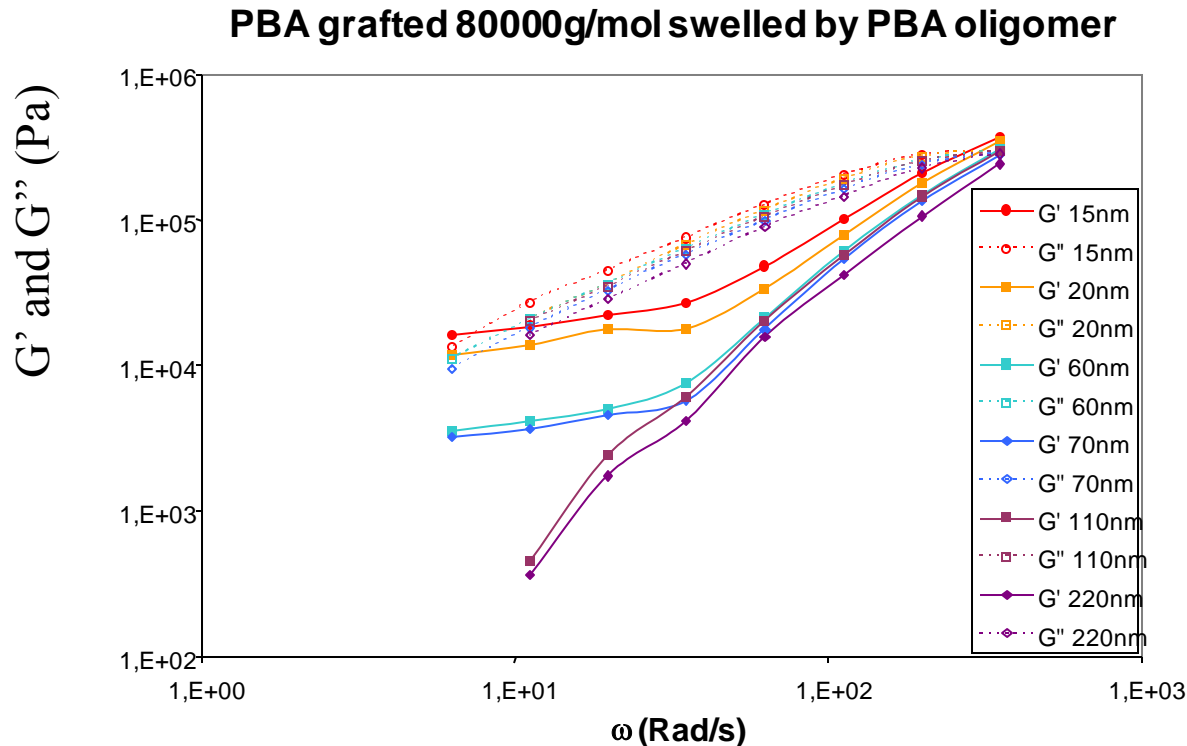
In-situ generation of the polymer





## Preliminary Results for grafted polymers

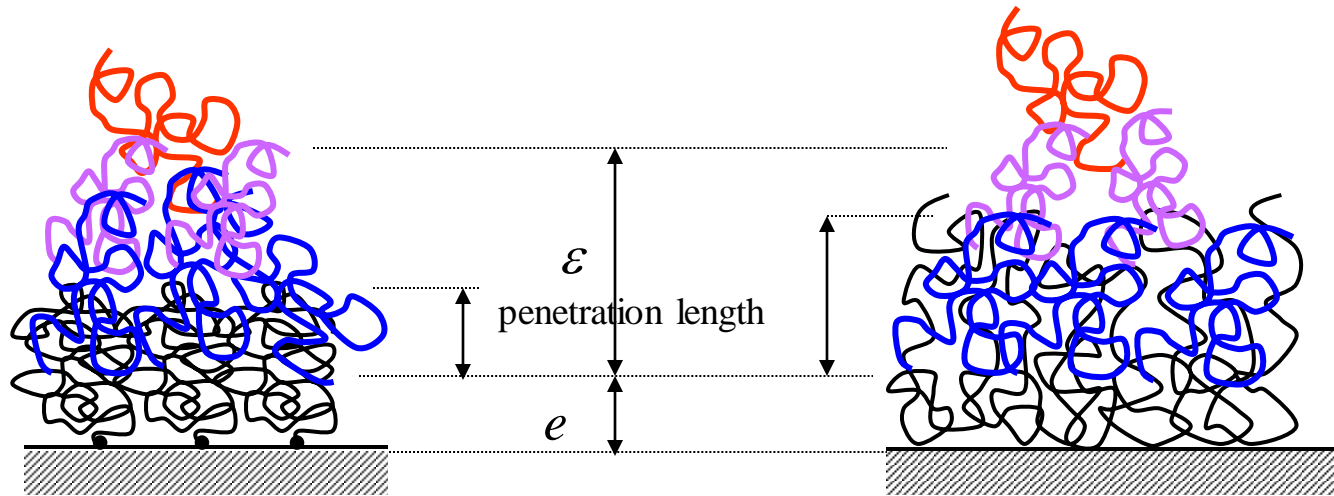
We have added free chains on the brushes and explore the behavior according to the confinement. Results show that it is easier to obtain the transition between liquid like and solid like



We will explore different molecular weight and grafted density... and analyzed slipping effect on the system developed by *L. Léger et al.* We also prepared symmetrical system (sphere and plate grafted).

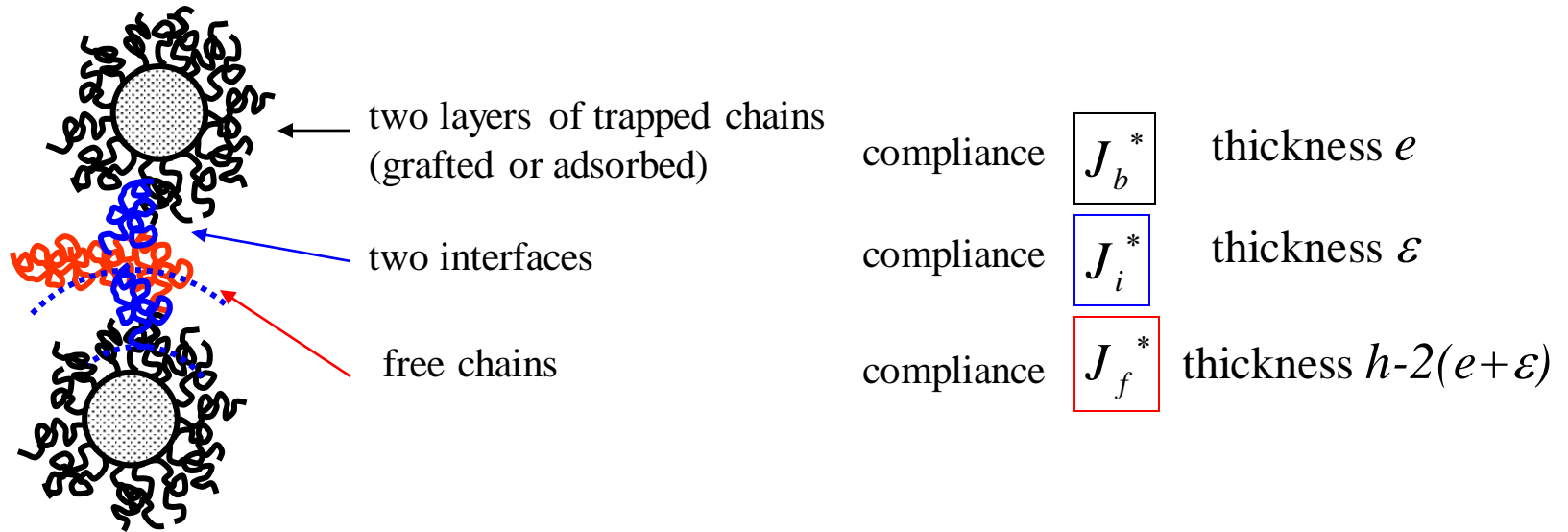
# Chain dynamics

Pr. Montfort has recently proposed a five layer representation of the experimental system :



- the interpenetration between tethered and free chains creates a transition zone or interface
- the penetration length depends on the grafting density and on the chains length
- its dynamics is that of free chains modified by the change of environment: loss of entanglements, variation of the lifetime of entanglements (therefore, of the tube renewal time)
- its extension  $\epsilon$  is higher than the penetration length

# Modelization



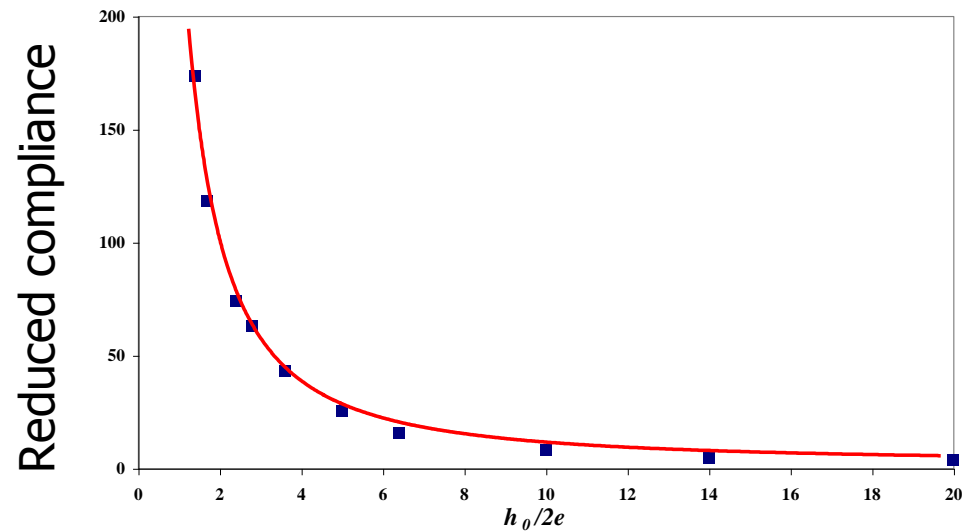
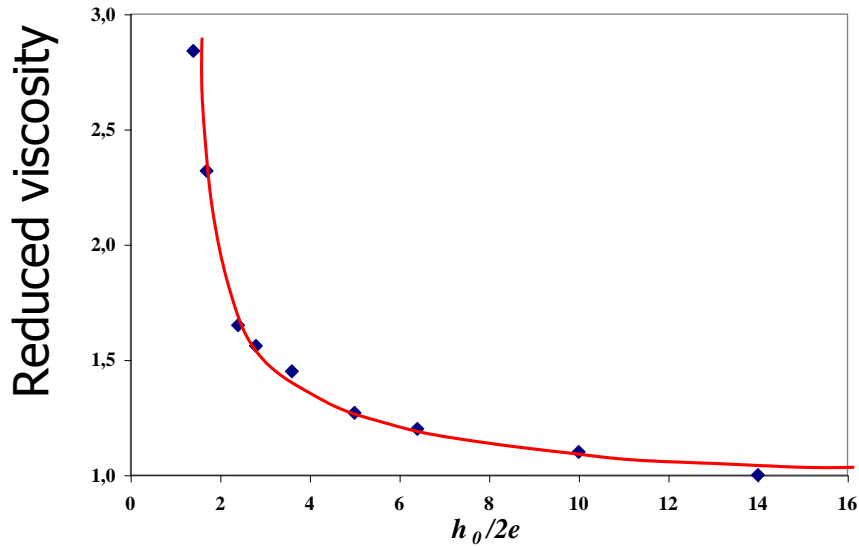
## Semi-local complex compliance:

$$J^*(\omega, h) = \frac{2}{h^3} [(J_b^* - J_i^*)(4e^2 - 6eh + 3h^2)e + (J_i^* - J_f^*)\{4(e + \varepsilon)^2 - 6h(e + \varepsilon) + 3h^2\}(e + \varepsilon) + \frac{1}{2}J_f^*h^3]$$

## Global complex elasticity:

$$G^*(\omega, h_0) = h_0 \int_{h_0}^{\infty} dh \int_h^{\infty} \frac{2dh}{h^3 J^*(\omega, h)}$$

# Confrontation model-experimental results for adsorbed polymers



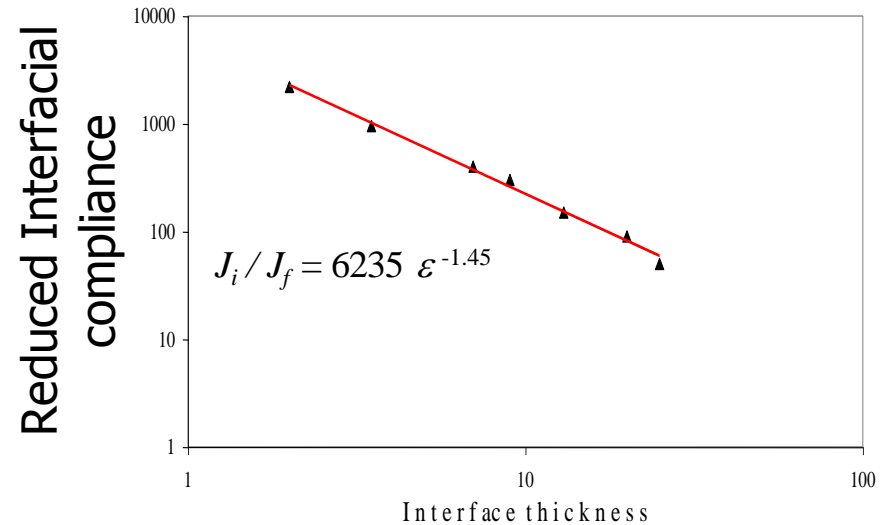
Fit:

$$e = 5 \text{ nm}$$

$$\varepsilon = 5e \text{ for } h_0 > 12e$$

$$\eta_b/\eta_f = 12, \quad J_b/J_f = 3$$

$$1 < \eta_i/\eta_f < 1.8 \quad 20 < J_i/J_f < 2200$$



# Conclusion

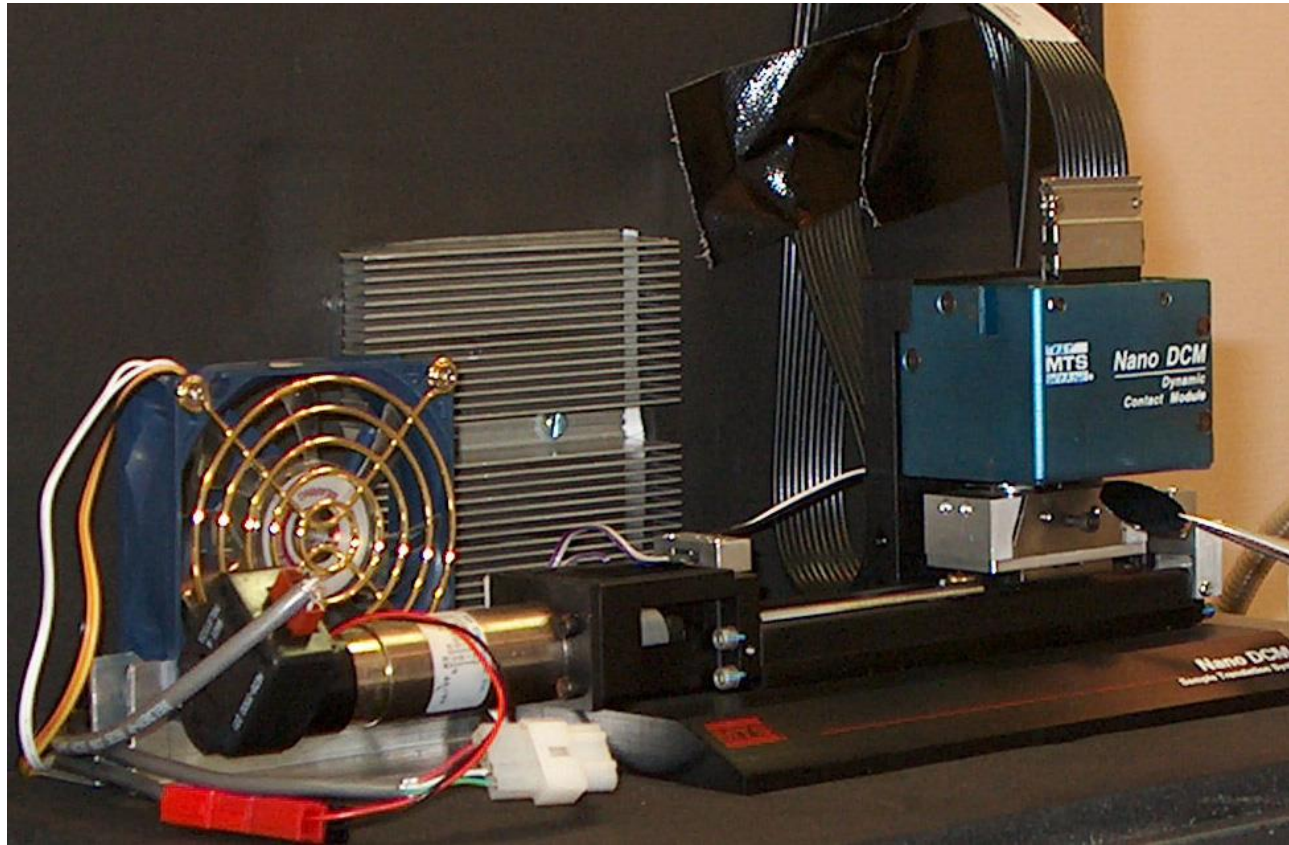
We have sketched out a picture of submicronic gaps of polymer melts, dividing it into homogeneous layers

*Prominent role of the interface between trapped and free chains*

**Compliance much more sensitive to the details of the local structure than viscosity**

To improve experimental measurement we propose a symmetrical systems with chains grafted from the sphere and the plate \*, and study the slipping effects.

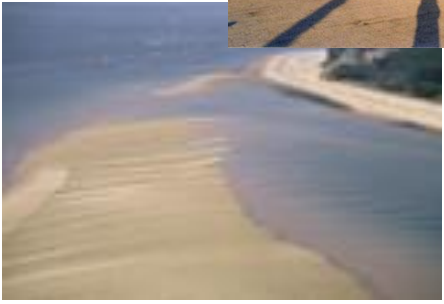
# ! Thank you !





# WCARP IV – September, 26-30<sup>th</sup>, 2010

## Arcachon, (France)



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