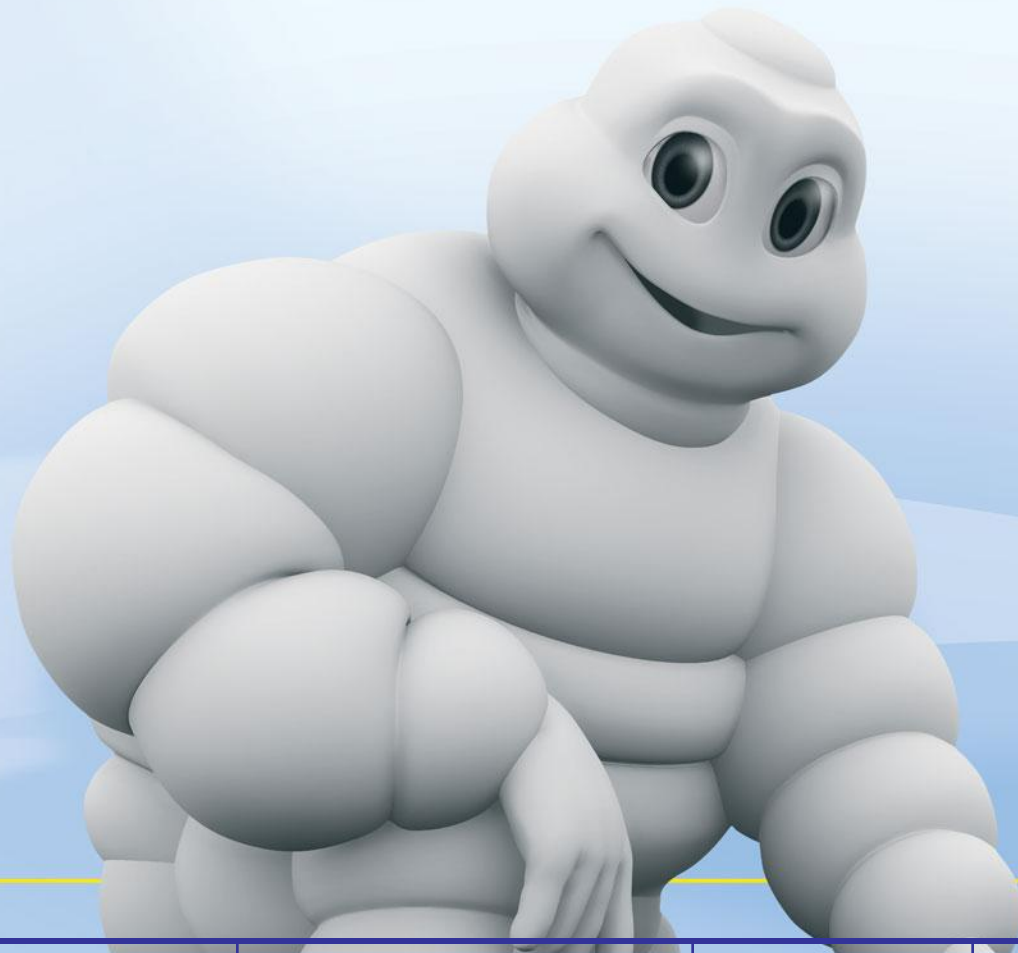


Multi-scale studies of elastomer materials *(in a tire tread)*

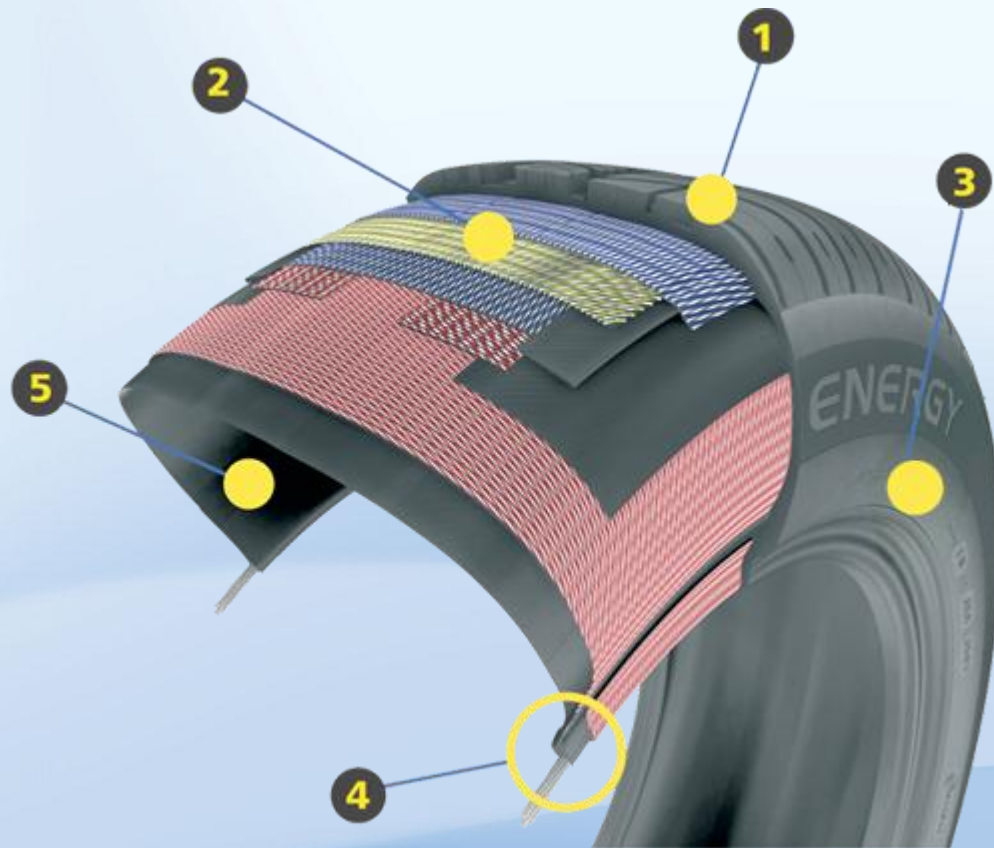


TERATEC 2013
Materials Science Session
B. Schnell



Tire description

A tire : a highly functional structure composed of specific successive layers



- 5 Inner liner**
Makes the tire almost totally impermeable and maintains the correct inflation pressure
- 4 Bead area for attachment to the wheel rim**
- 3 Sidewalls**
Cover and protect the textile casing whose role is to attach the tire tread to the wheel rim
- 2 Crown plies**
Reinforced belt with both vertical flexibility and high lateral rigidity providing the steering capacity
- 1 Tread**
Thick layer of rubber providing contact with the ground and thus transmitting the efforts (acceleration, braking, ...)



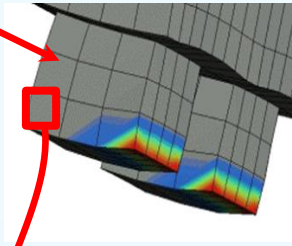
Tire : a multi-scale approach



Complex process



Tire = multi-component product (~200)

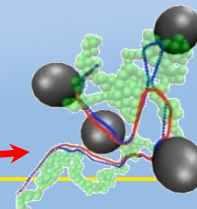
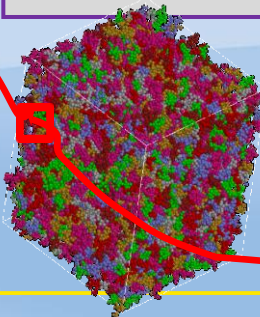


Prediction of tire performances through FE calculations (given material \rightarrow behaviour law)
 \Rightarrow **3 main performances governed by the tire tread : grip, wear, RR**

Complete characterization to get the new material \Leftrightarrow behaviour law is costful
 \rightarrow Use of **descriptors** relating **materials properties and tire performances**

Two main goals for multi-scale simulations

- Improvement of structure-properties relationships at each length scales
- \rightarrow Design of new structures \nearrow descriptors
- Behavior laws by a bottom-up approach



Multi-scale materials

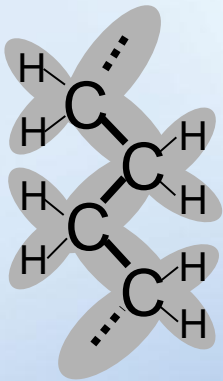


Multi-scale simulations

Bottom-up approach

Ab initio

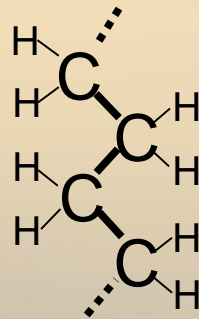
Explicit electrons



1-20 Å

All-atom

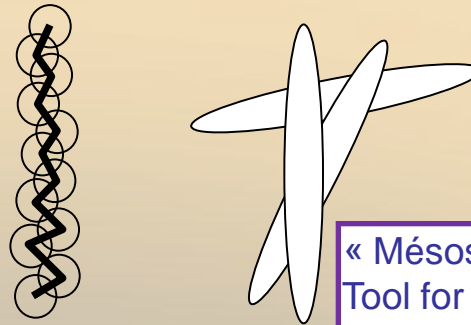
Atomistic Force Field



1-10 nm

Mesososcopic

Coarse-grained,
particle- or molecule-based



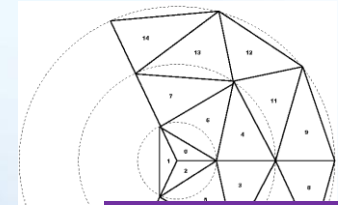
5-50 nm

10-100 nm

« Mésoscope »
Tool for studying
nanocomposites

Macroscopic

Materials modeling



FE method
most used by
Michelin

>100 nm

**Tire
performances**

Molecular simulations (**MD** (*DPD*, ...) / **MC**)

- Elastomer rigidity → *wear*
- Dissipation H_f / H_T → *grip*

- Network structures
(*chains*, *fillers*)
→ *wear*, *RR*



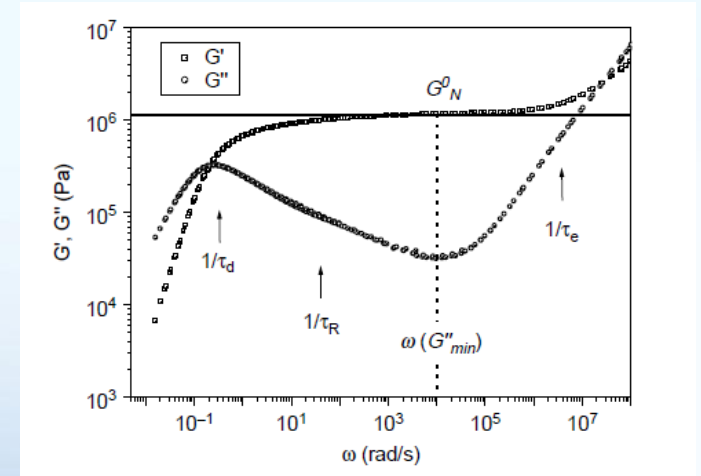
Elastomer rigidity (*rubbery plateau*)

Goal : predicting the intrinsic rigidity of an elastomer (microstructure related)

Best approach in theory

- ⇒ Reproducing the shear modulus evolution $G(t)$ (or $G(\omega)$) → huge systems ($M/M_e > 20$) and long relaxation times (\sim ms)
- not realistic at all-atom scale
- ⇒ Mesoscopic scale (*works ongoing*)

Classical experimental curves : cis-PB ($M/M_e = 260$)
Wang et al. *Polymer* 47 (2006), p4461



Proposed approach at atomistic scale

- ⇒ Using known polymer melt properties

$$G_N^0 = \frac{4}{5} \frac{\rho k_B N_A T}{M_e} \quad (\text{analogy to elastomeric network})$$

M_e can be related to R_e^2

$$\Rightarrow G_N^0 = K(T) \left(\rho \frac{R_e^2}{M} \right)^3$$

↓
Simulation

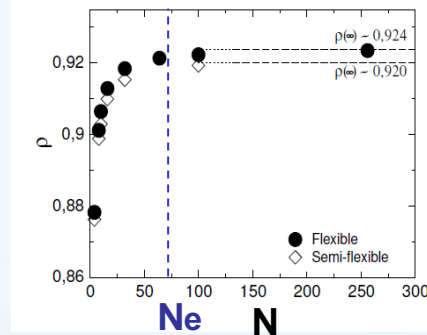
Absolute or relative prediction ?
“Universal” $K(T)$ proposed by Fetters et al.
Macromolecules 1994, vol 27, p4639



Elastomer rigidity (*rubbery plateau*)

Chosen system size $M_{ch} \sim M_e$
(adequate N_{ch})

→ Compromise between a good description of the packing effect and calculation optimization



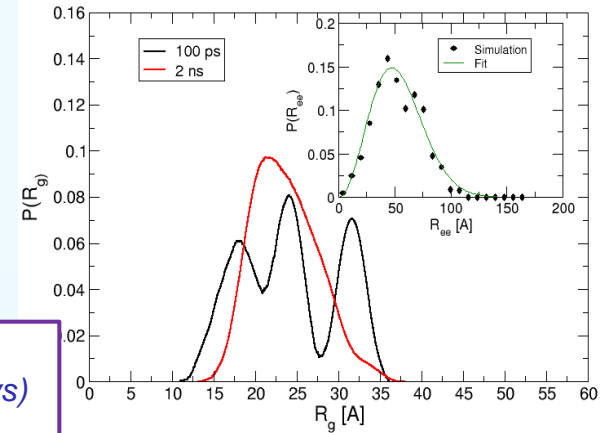
Ex: SBR $M_{ch} \sim M_e$ (600K)
(Equilibration time 2ns ~ 5 days)

Properties

$$\langle R_e^2/M \rangle = 0.690 \text{ \AA}^2 \cdot \text{mol} \cdot \text{g}^{-1}$$

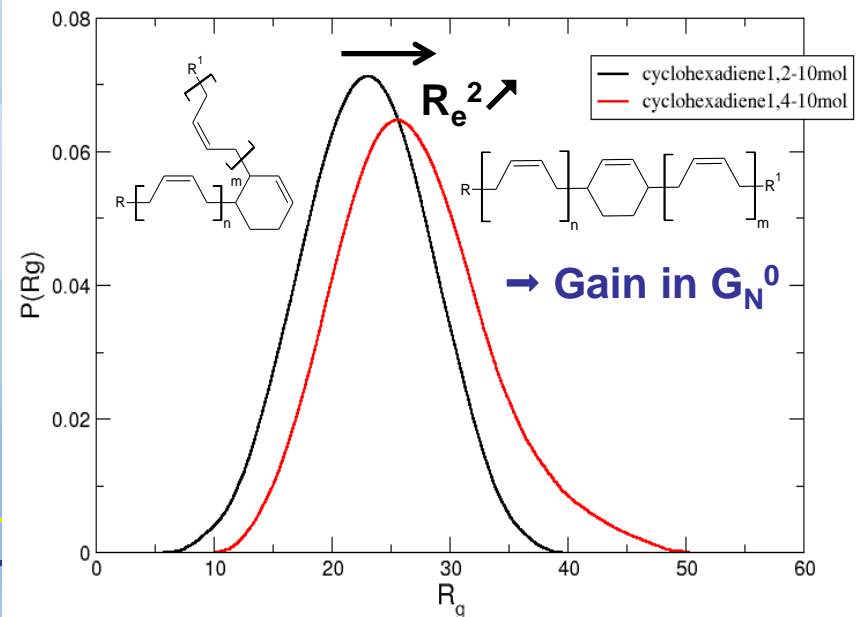
$$\langle R_g^2/M \rangle = 0.113 \text{ \AA}^2 \cdot \text{mol} \cdot \text{g}^{-1}$$

$$\rightarrow \langle R_e^2 \rangle / \langle R_g^2 \rangle \sim 6,1$$

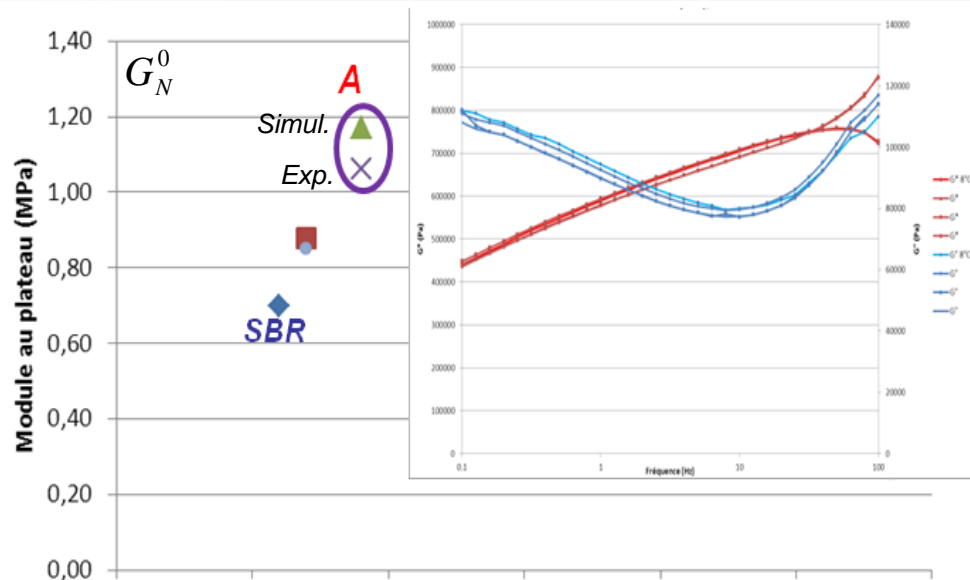
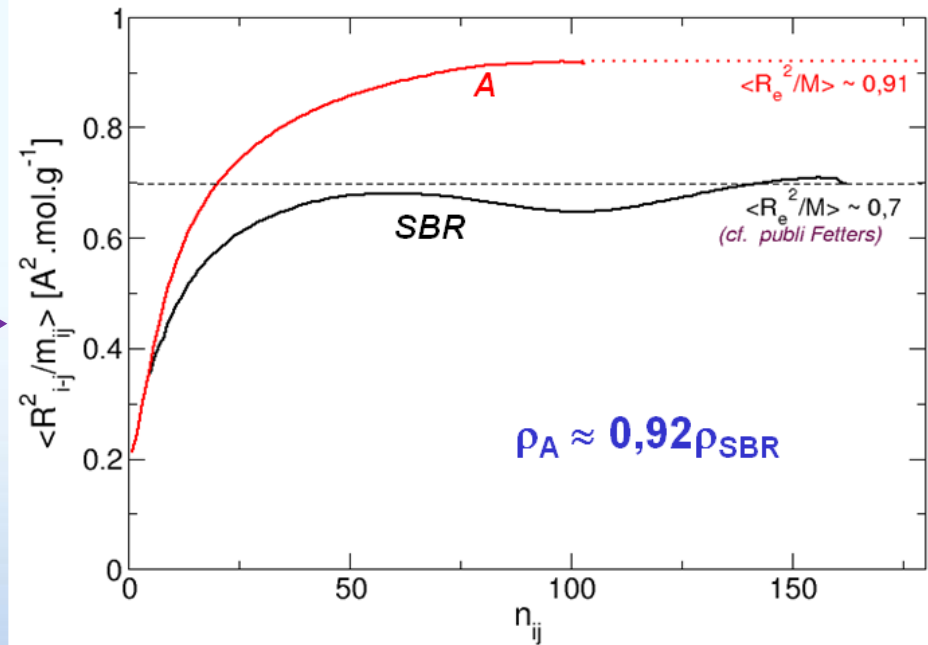
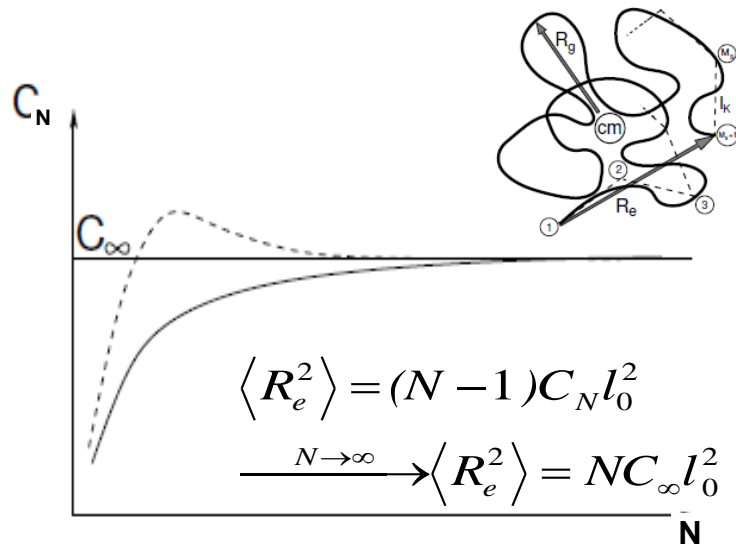


Example of investigation

→ "backbone" cycles vs "pending" cycles



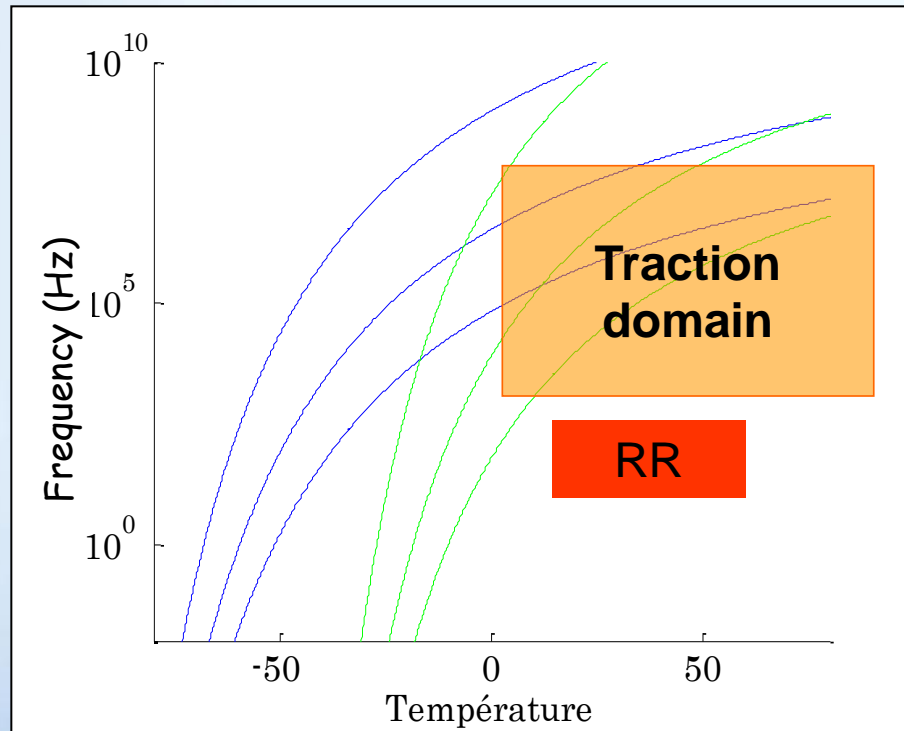
Elastomer rigidity (*rubbery plateau*)



- Gain in G_N^0 for microstructure A is nicely predicted
- Semi-quantitative approach ($K(T)$) but approach seems to be able saying whether or not an important gain can be expected



Grip performance

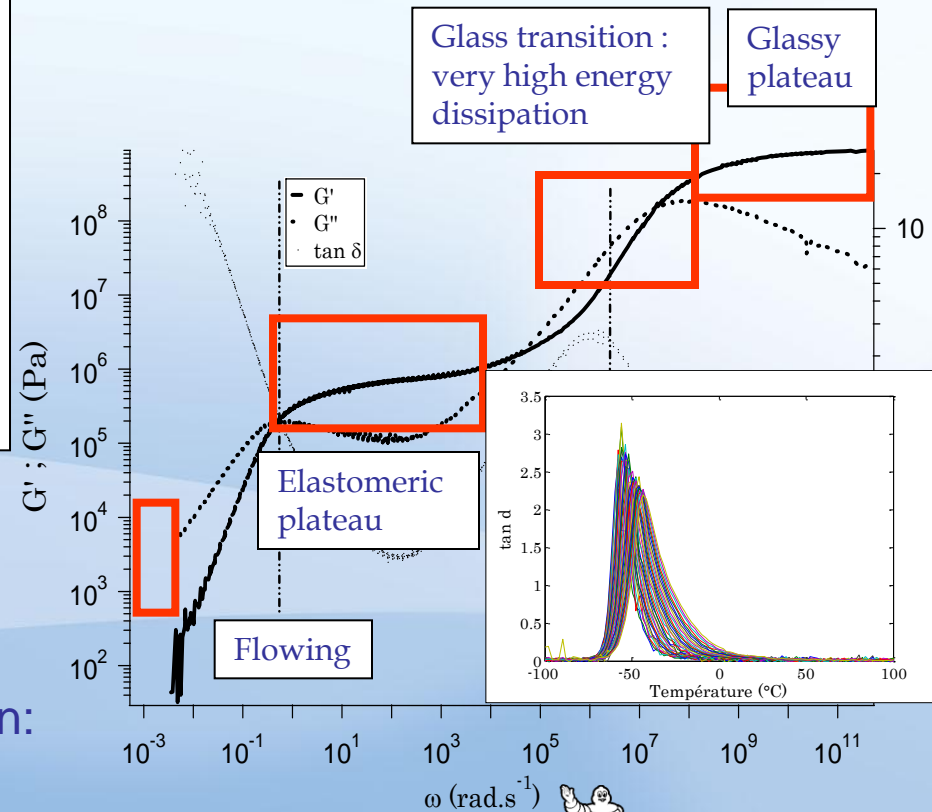


Grip is highly related to the dynamic glass transition. Improvements can be expected through

- a better understanding of polymer melts dynamics (better control of the dissipation: TTS, height, width, ...)
- calculation of $G(t)$ via simulations and the FT

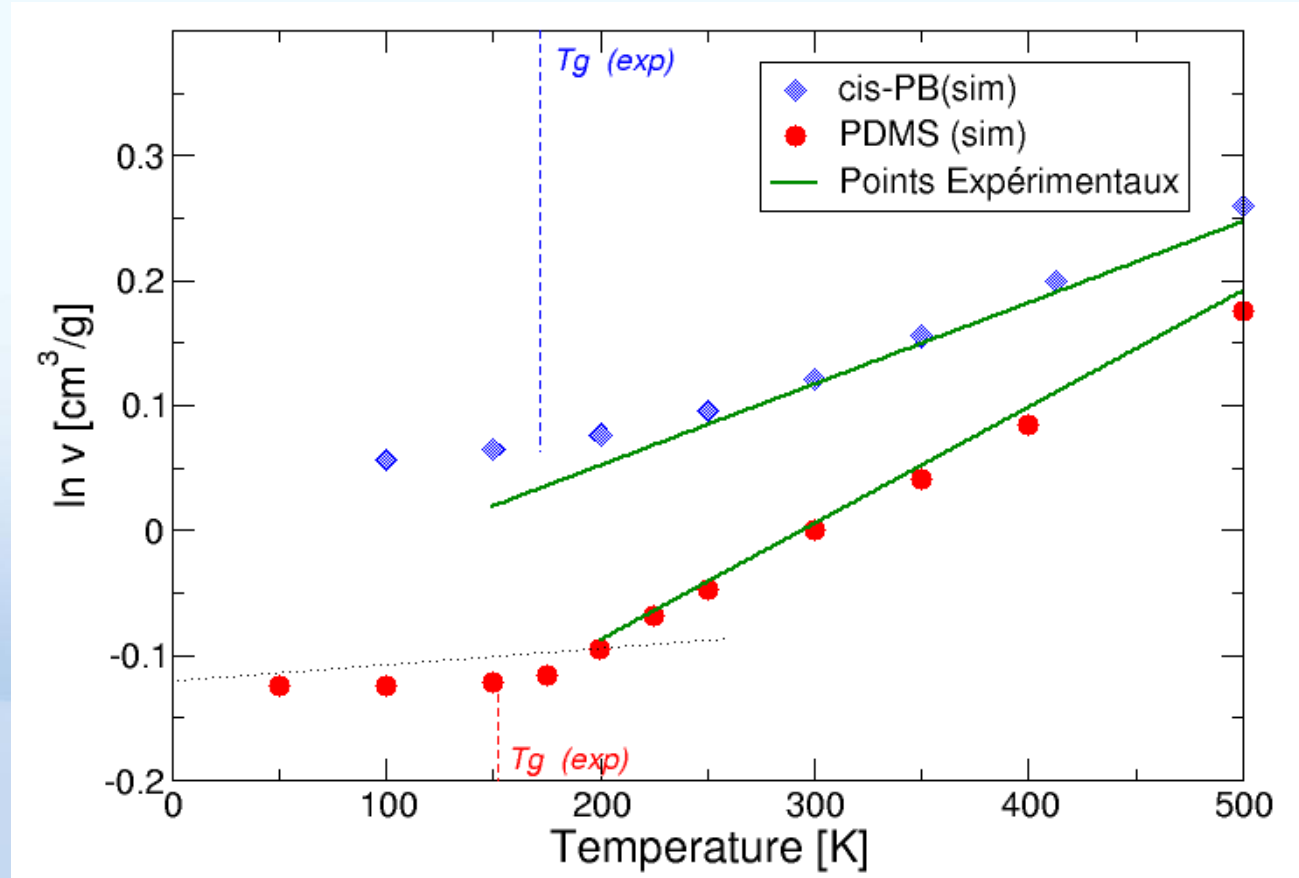


In terms of mechanical properties ($T > T_g$)



Grip performance

"Reproduction" of a dilatometry experiment



- Liquid branch very nicely reproduced and good estimation of T_g
- *Validation for studying local dynamics hf - HT*



Grip performance

Study of the local dynamics hf - hT

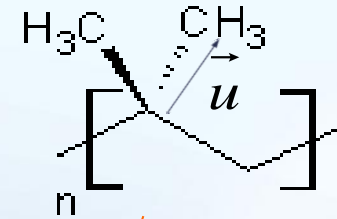
Unavailability of Dynamic Mechanical Analysis (DMA) in the frequency domain of use
 ⇒ other experiments (dielectric spectroscopy, neutron scattering, NMR, ...) and atomistic simulations (specific mechanism ?)

The method of choice ? NMR

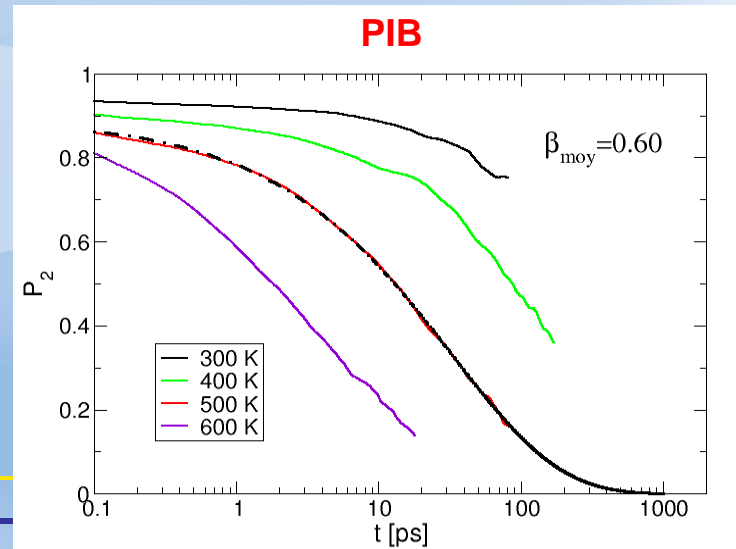
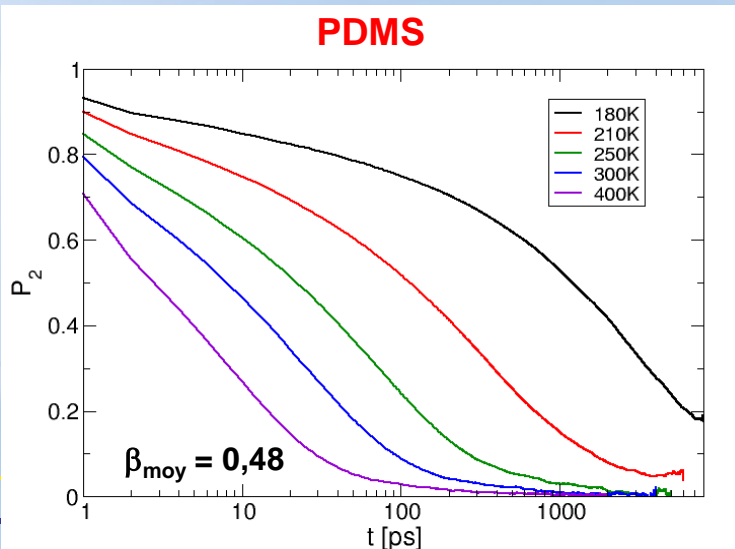
→ The orientational order parameter P_2 intervening in the NMR dipole – dipole interaction is easily calculated by simulations

$$\tau_c = \tau \frac{\Gamma(\frac{1}{\beta})}{\beta} = \int_0^\infty P_2(t) dt$$

τ_c is the segmental time given by NMR



$$P_2(t) = \frac{3\langle (\vec{u}(t) \cdot \vec{u}(0))^2 \rangle - 1}{2}$$

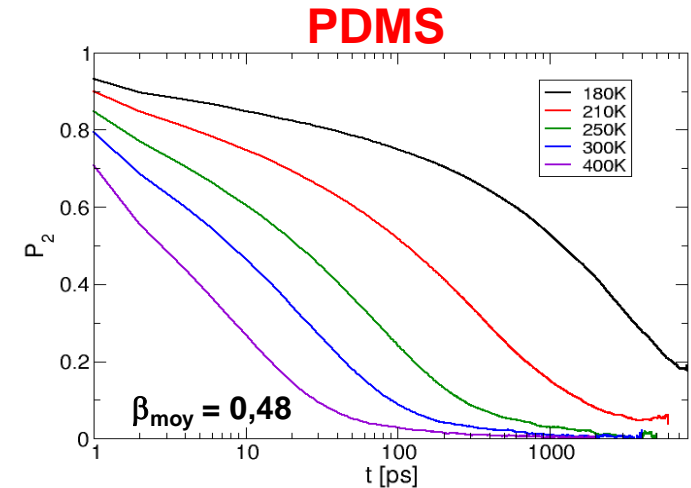
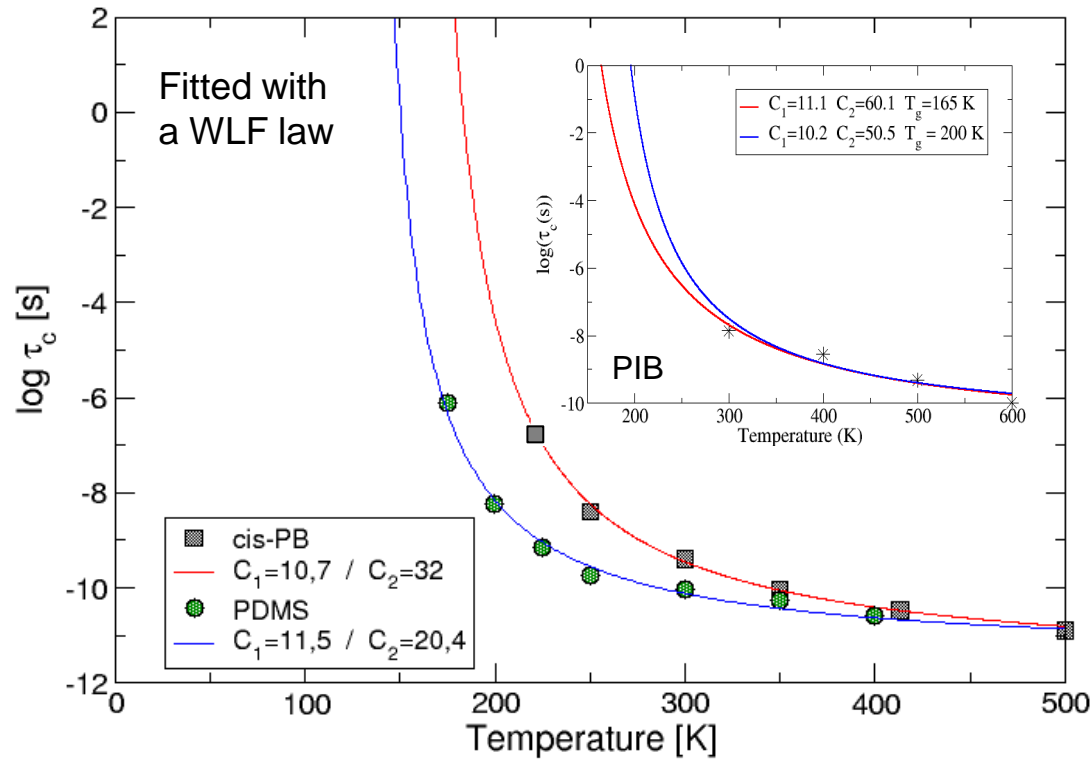


→ TTS

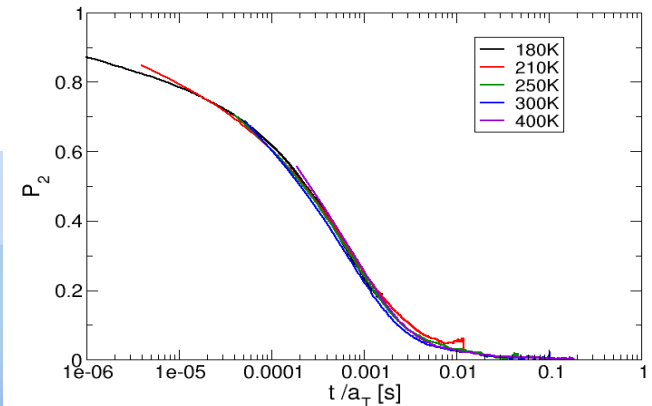
→ $\beta(\text{PDMS}) < \beta(\text{PIB})$
 Good agreement with exp.



Grip performance



↓ a_T



Study of local dynamics Hf – HT

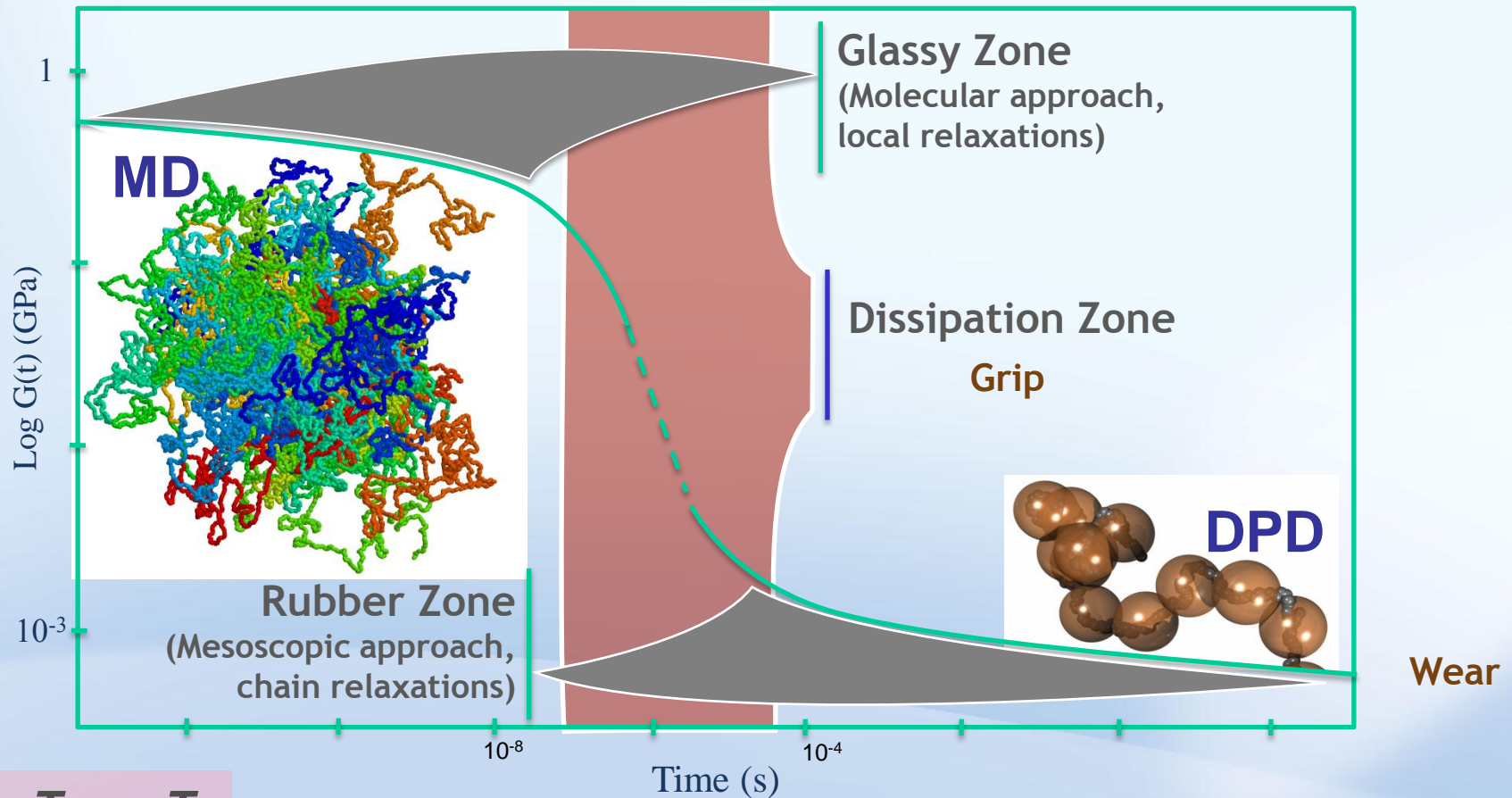
→ Exp. data well reproduced

C_2 (PDMS) $\sim 20 < C_2$ (cis-PB) $\sim 30-35 < C_2$ (PIB) ~ 60

→ New microstructures or mechanisms leading to particular behaviours ?



Multi-scale calculation of $G(t)$



$$T \sim T_{tire} > T_g$$

$(G(t) \text{ obtained from the stress tensor fluctuations})$

- Static properties of the glass-to-rubber transition

(G. Maurel's PhD work – supervision of P. Malfreyt, ICCF Clermont-Ferrand)

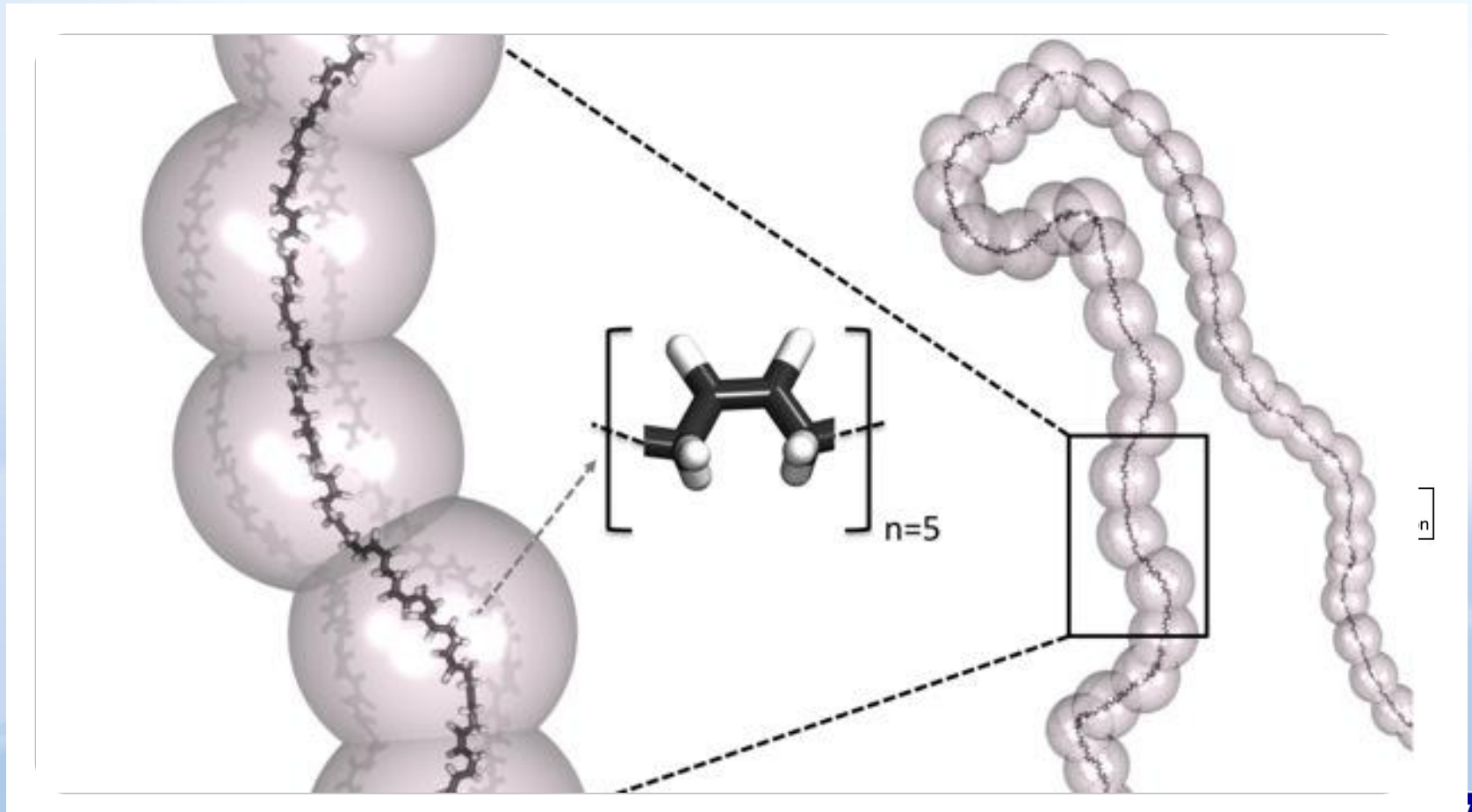
- Friction term in DPD

(S. Trément's PhD work – supervision of B. Rousseau, LCP Orsay)



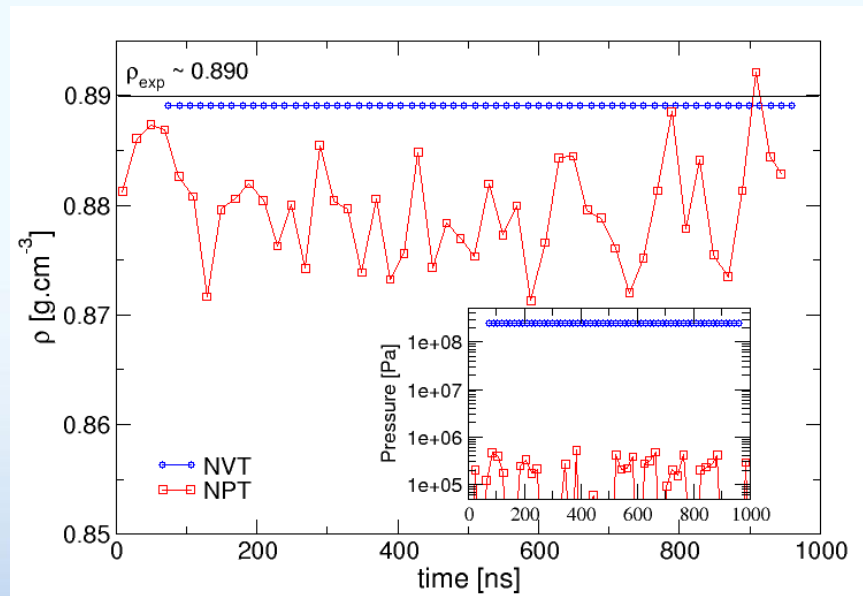
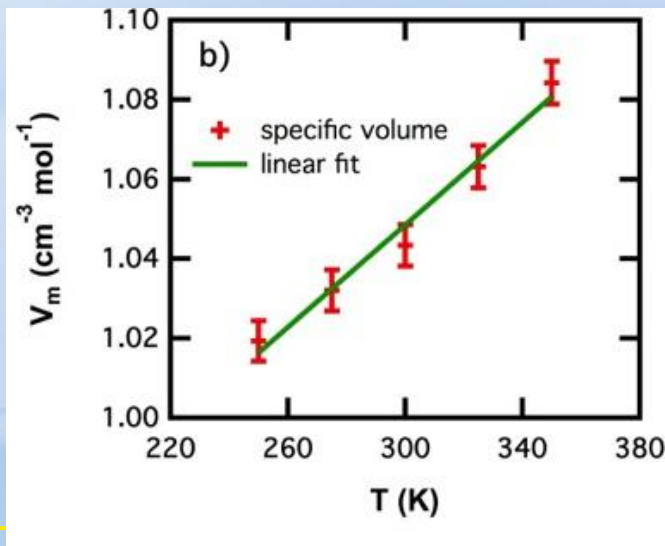
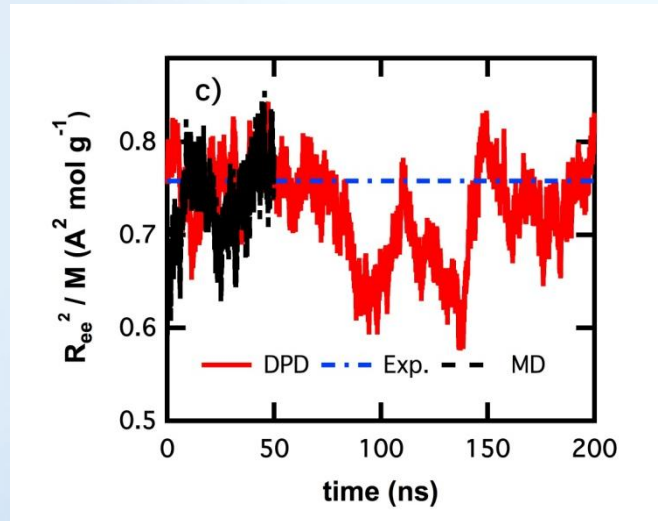
Determination of realistic CG models

- cis-polybutadiene (*CG level $\lambda = 5$*)



Realistic CG models

Static properties



⇒ ρ and R_e^2/M in good agreement with experiment for the potentials developed in both ensemble
(the same $g(r)$ are reproduced during this development)

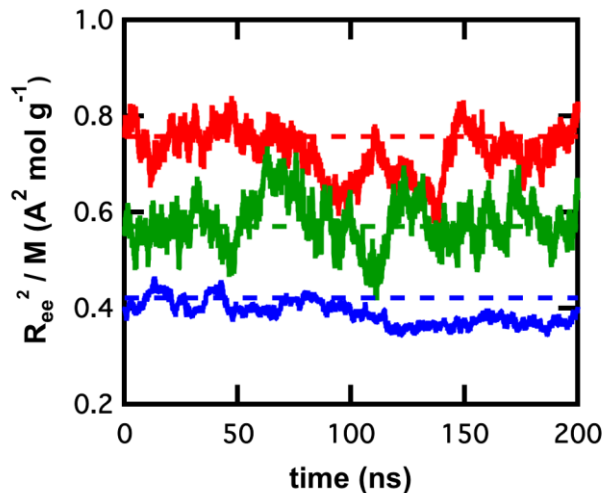
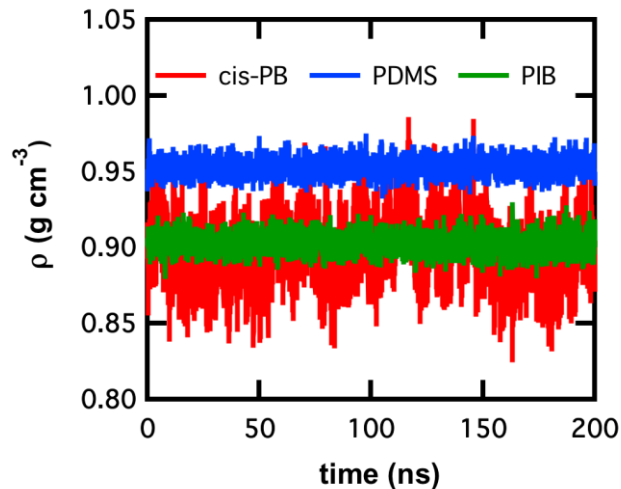
⇒ Huge pressure needed for "NVT" potentials
→ Cannot model real systems

⇒ Transferability in temperature : $\alpha_p (\sim 6.10^{-4} \text{K}^{-1})$



Realistic CG models

- cis-polybutadiene (cis-PB)
- polydimethylsiloxane (PDMS)
- polyisobutylene (PIB)



G_N^0 estimation

$$G_N^0 \propto \left(\frac{\rho R_{ee}^2}{M} \right)^3$$

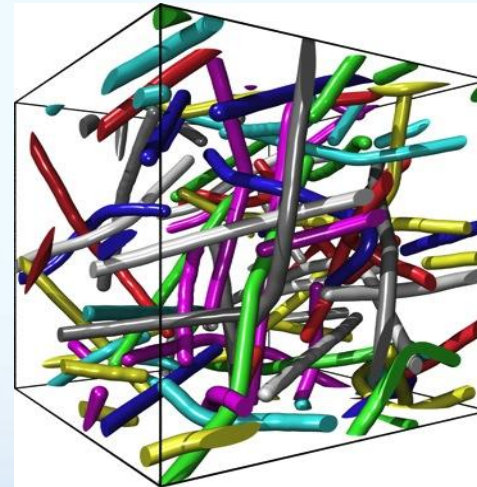
⇒ Possible to distinguish between different microstructures
at the mesoscale !!!



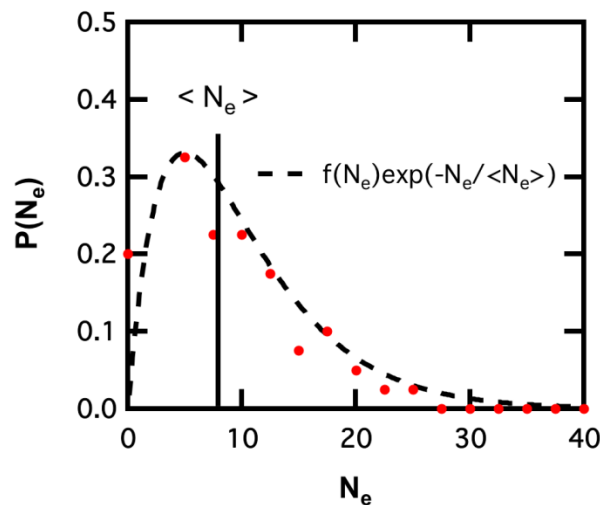
Realistic CG models

Entanglements

- Primitive Path Analysis



- Entanglement length



$$M_e = \frac{R_e^2}{L_{pp}^2} M$$

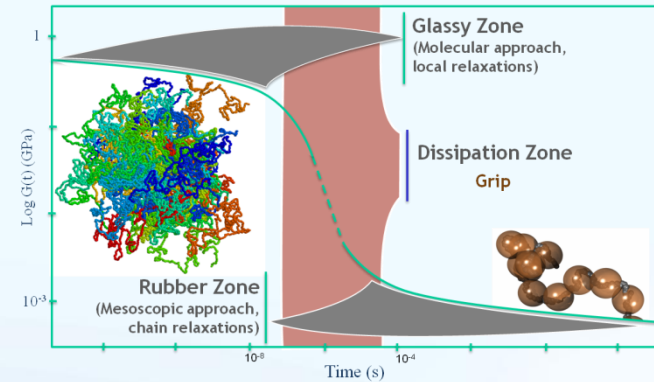
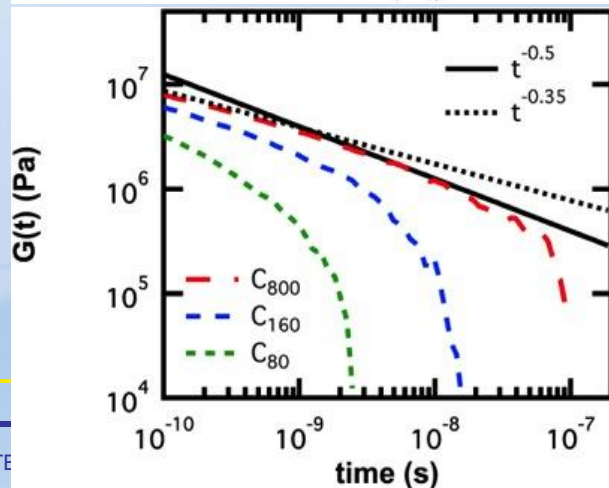
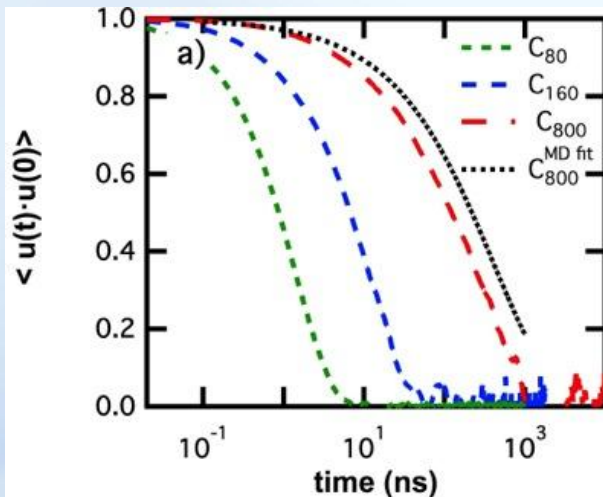
- $M_e = 2749$ g/mol
(2363 g/mol à partir de G_N^0)
- $N_e = 10$ (9)
- Poisson-like distribution



Realistic CG models

Dynamic properties

Goal : explicit quantitative determination of the rubbery plateau and more generally to be able studying chains relaxation more quickly



Chain relaxation

	Micro	Meso
Simulated Time	200 ns	200 ns
Calculation Time	≈ 100 days	≈ 1 day

(~10⁴ particles, 16 CPUs – 2.67 GHz / 2 GB memory per CPU)

- Slowing-down of the relaxation but no plateau
- Plateau observation seems to need $N / N_e > 20^{[1]}$
($N / N_e \approx 4-5$ in our case)

^[1] Likhtman, A. E., & Sukumaran, S. K. (2010), *Macromolecules*, 43(8), 3980–3983
→ Slip-link model : a plateau can be distinguished but in a qualitative way ...

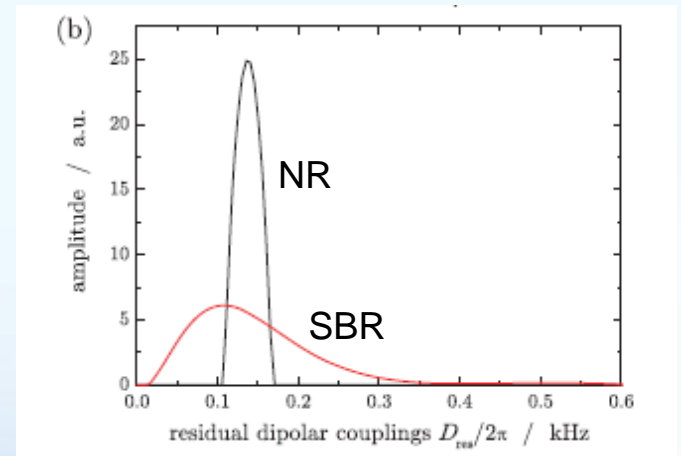


Study of polymer networks

Why studying polymer networks ?

⇒ Structure obtained by classical vulcanization is not really controlled → **random network** (*a priori*)

DQ NMR measurements



⇒ Develop a method able to give an accurate description of a network (*heterogeneity of cross-linking / chain length distribution between cross-links, quantity and nature of defects, trapped entanglements, ...*)

→ Method coupling NMR “double quanta (DQ)” and Simulation

Able to capture an heterogeneity of cross-linking and to quantify defects (Macromolecules 2010, 43, p4210)

Can identify accurately the structure responsible of NMR signals

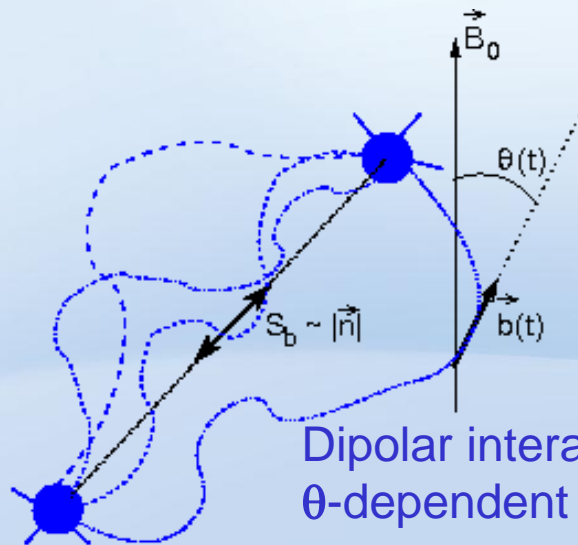


Study of polymer networks

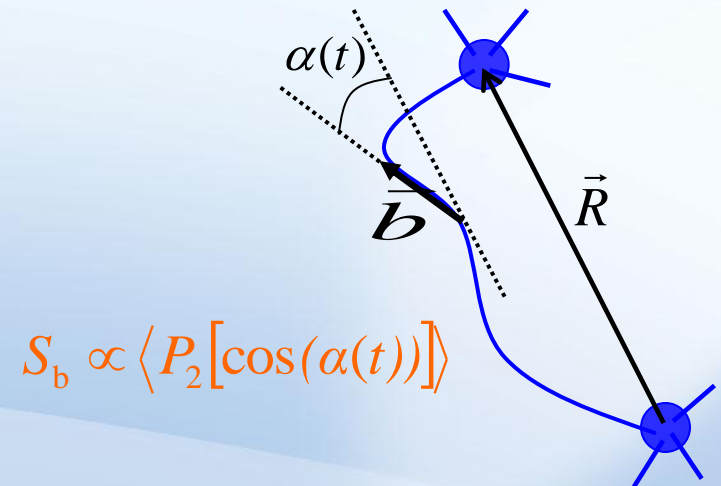
NMR/Simulation coupled method

Principle: Kuhn segments of a cross-linked chain fluctuate anisotropically around their mean direction due to topological constraints (cross-linking + entanglements) \Rightarrow *local nematic order described by the order parameter S_b*

➤ **measurable in NMR**



➤ **calculable by simulation**



$$M_c = \frac{K_G D_{stat} / 2\pi k}{D_{res} / 2\pi} \frac{C_\infty l_0^2}{n_0 l_p^2} M_0$$

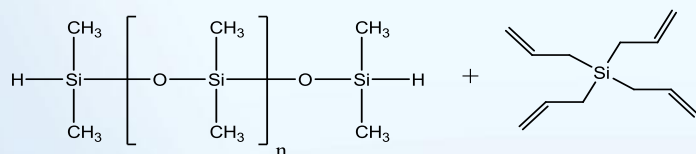


Study of polymer networks

PDMS model network

Purpose: check the capability of the coupled method NMR/Simulation

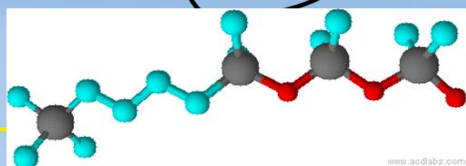
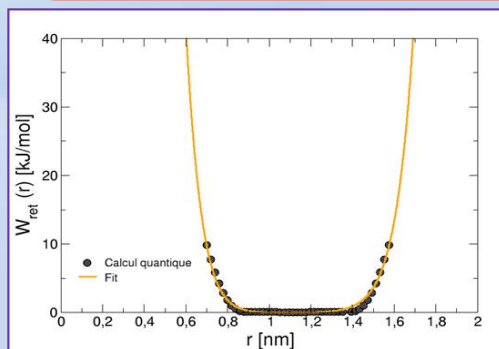
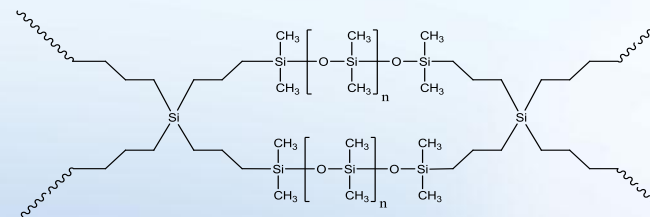
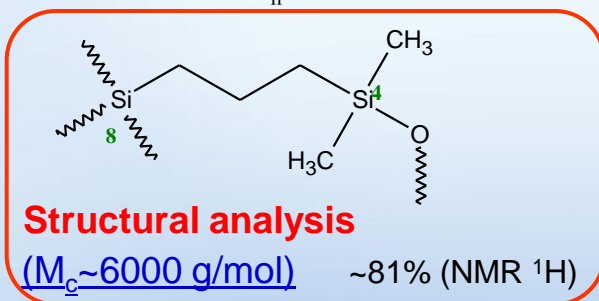
⇒ **PDMS model network** (based on Genesky et al., Macromolecules 2008)



Pt^0

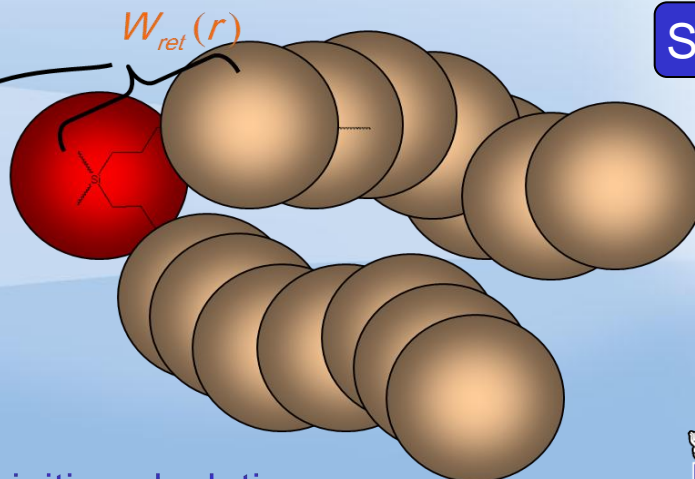
xylene

Experimental part



- Ab initio calculation
 for the new bonding (at CG level)
 potential $W_{ret}(r)$

Simulation part



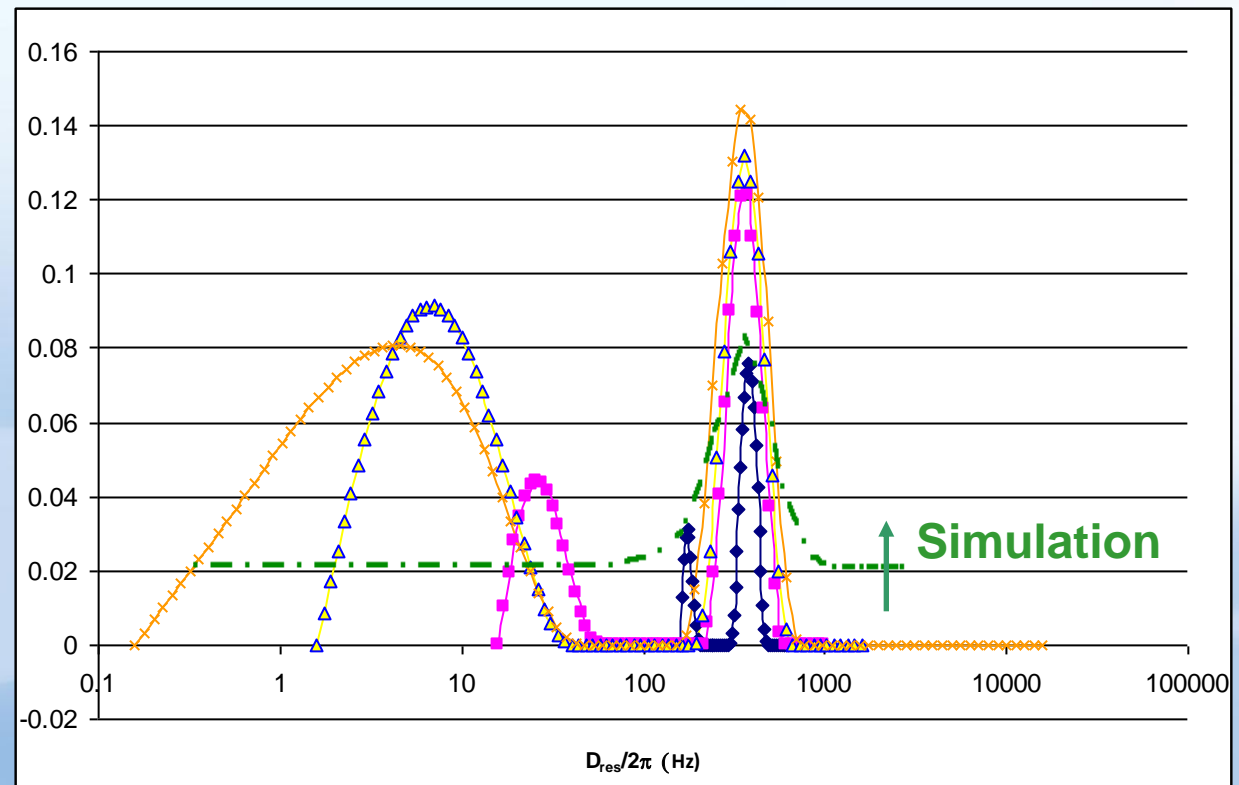
Study of polymer networks

PDMS model network

NMR DQ : *analysis vs simulation*

Order parameter distribution $P(D_{\text{res}} \propto S_b)$

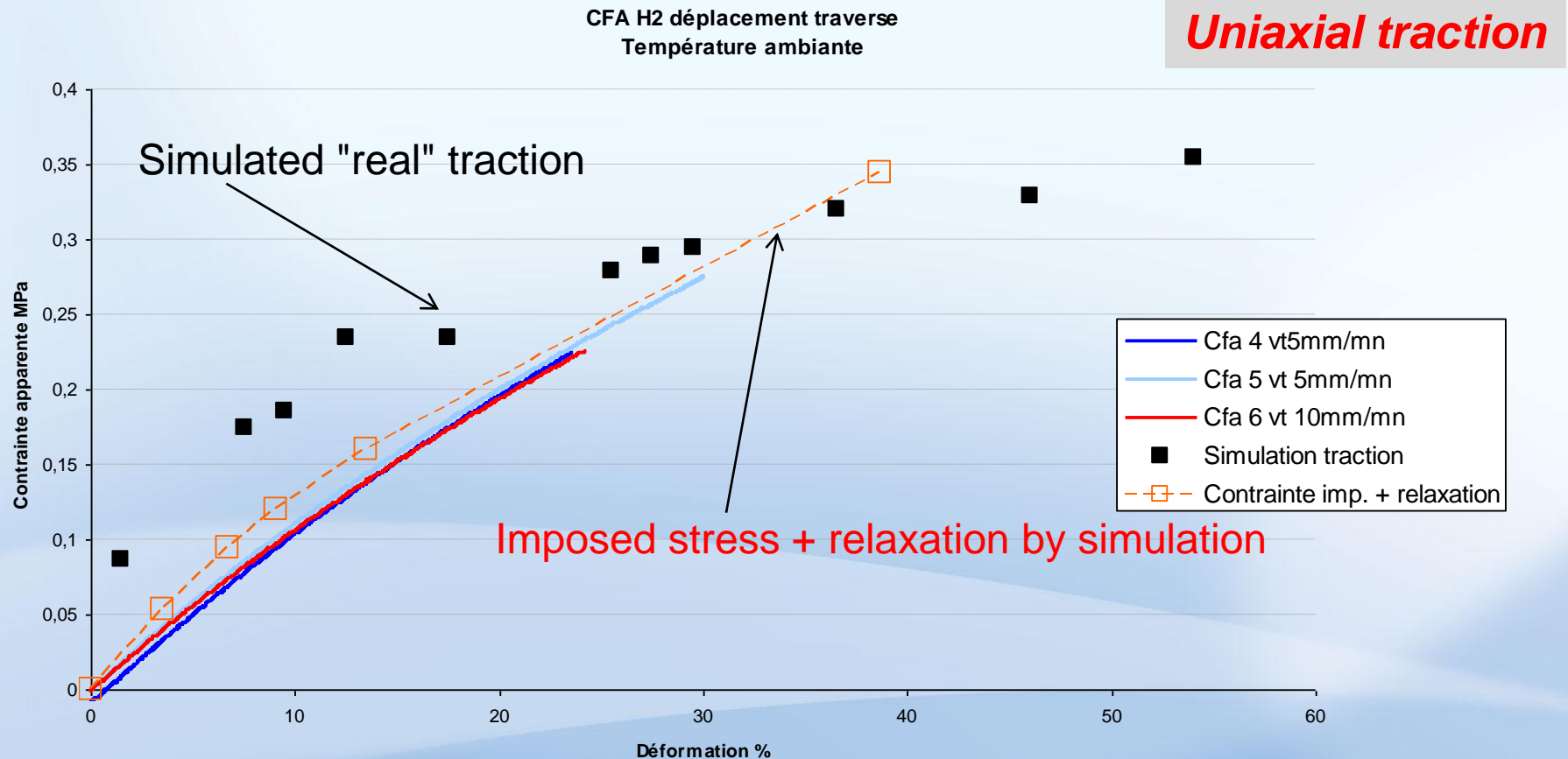
$$(D_{\text{res}}/2\pi)_m = 343\text{Hz}$$



Study of polymer networks

PDMS model network

Mechanical properties : *analysis vs simulation*



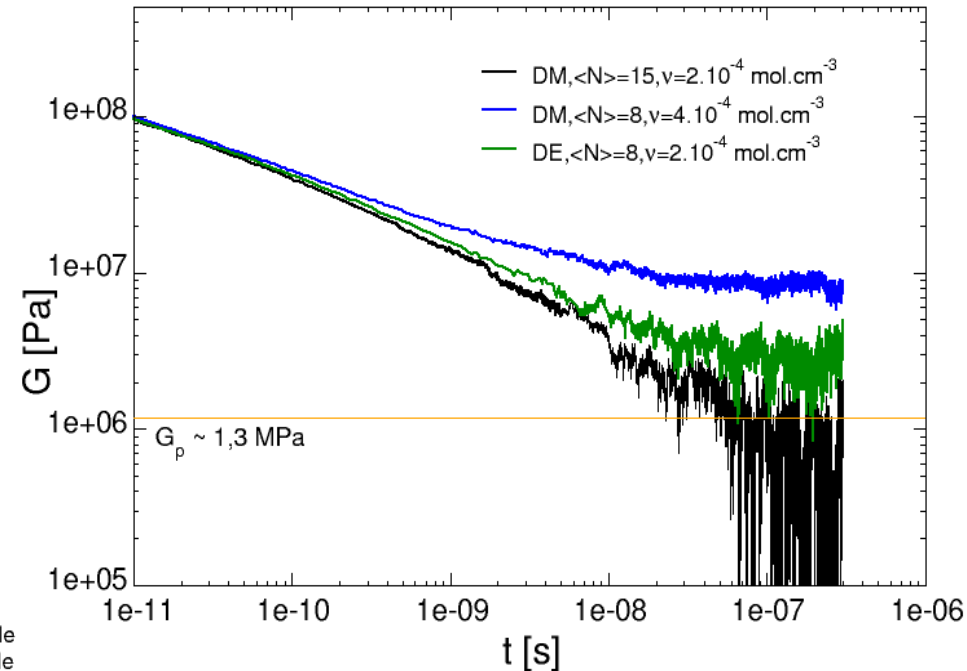
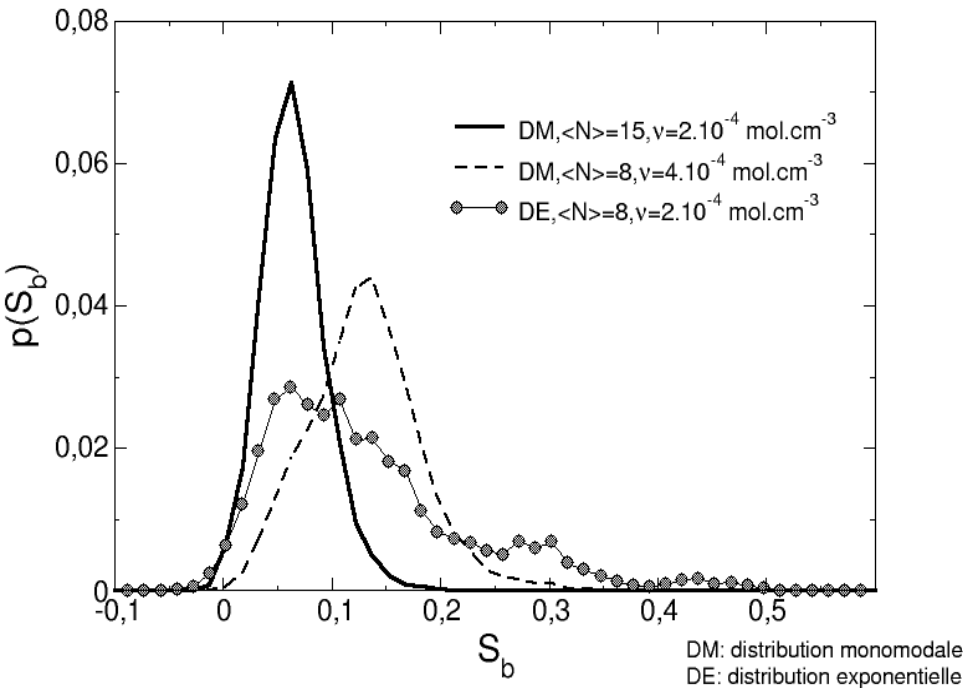
➤ Coupling NMR DQ/simulation seems to be a powerful method to predict network behaviours



Study of polymer networks

Study of network structures

Example shown for cross-linked cis-PB (300K)



⇒ The order parameter distribution and the mechanical response are specific for each network

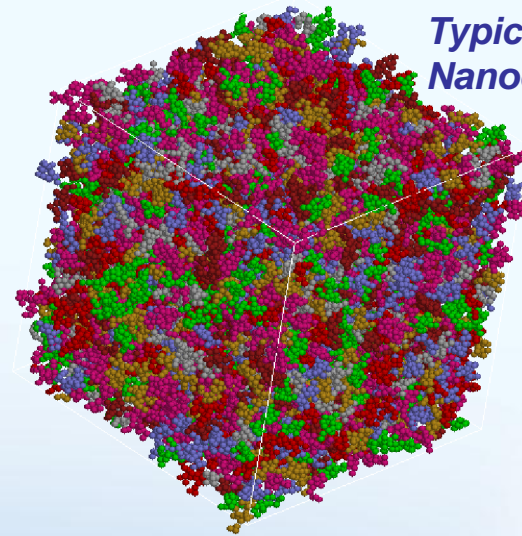
⇒ Associating the two analysis leads to an improved characterization of a polymer network (*structure-properties relationships*)



Nanocomposites simulation

Approach description :

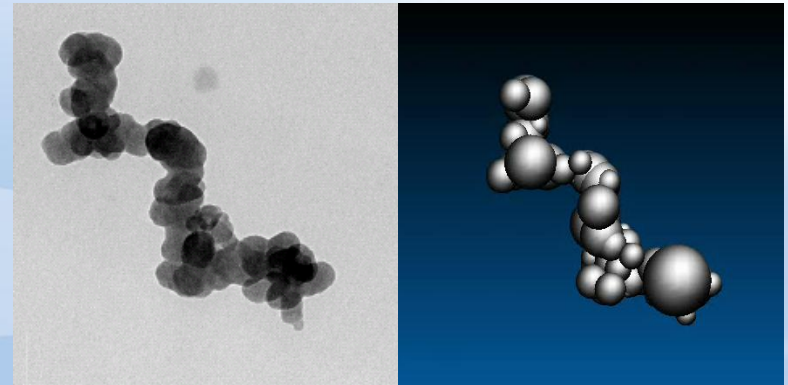
- Only fillers are considered
- Polymer is implicitly taken into account through the filler-filler interaction
- A polymer-mediated POMF for fillers



*Typical box for
Nanocomposites simulation*

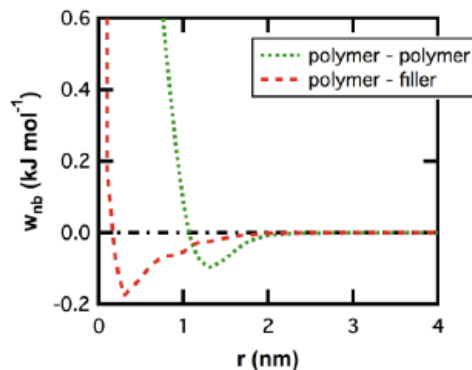
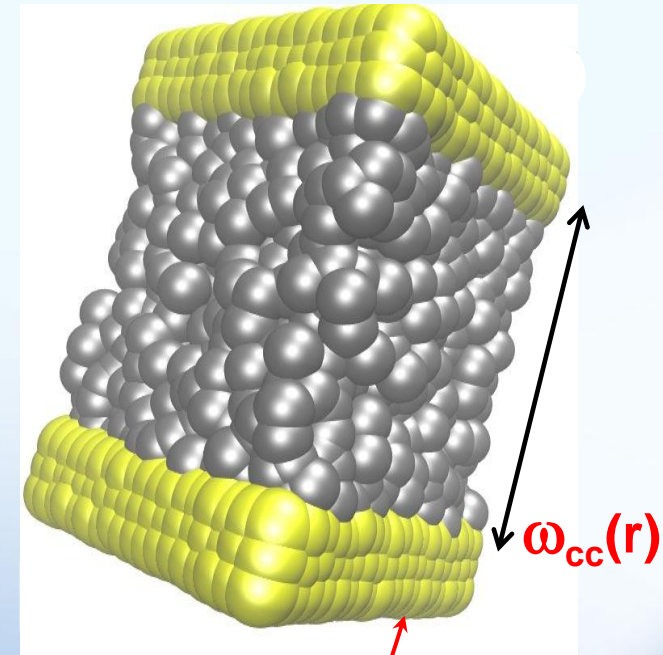
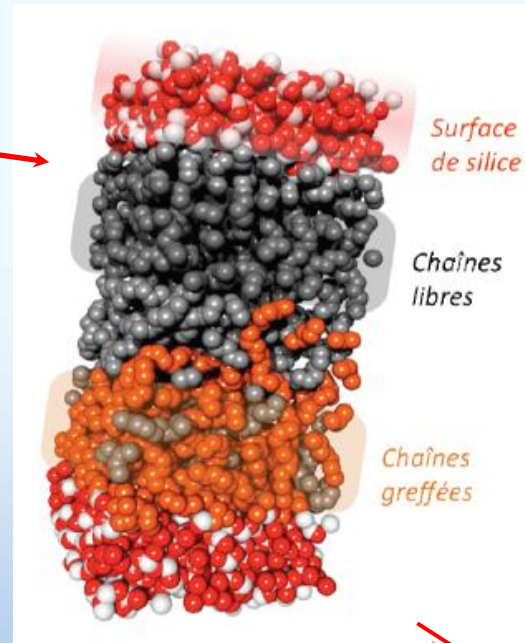
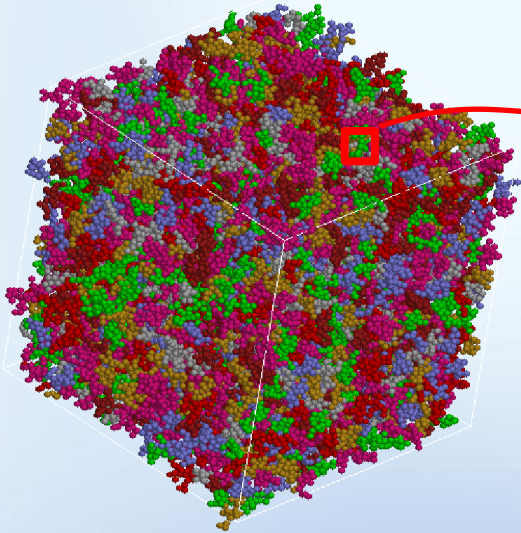
How to get the POMF ?

- Analytically
(K. Schweizer – Urbana Champaign)
- From the bottom by simulation



Aggregates are reconstructed from TEM

Nanocomposites simulation

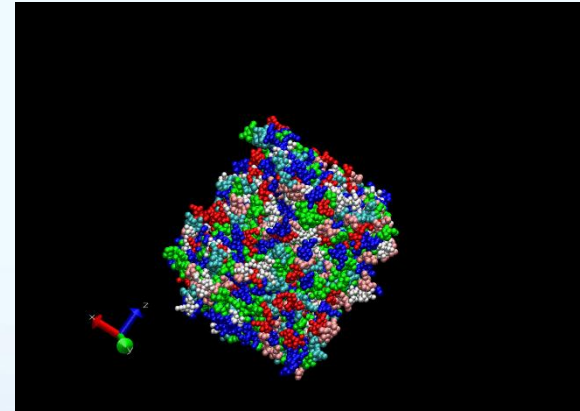
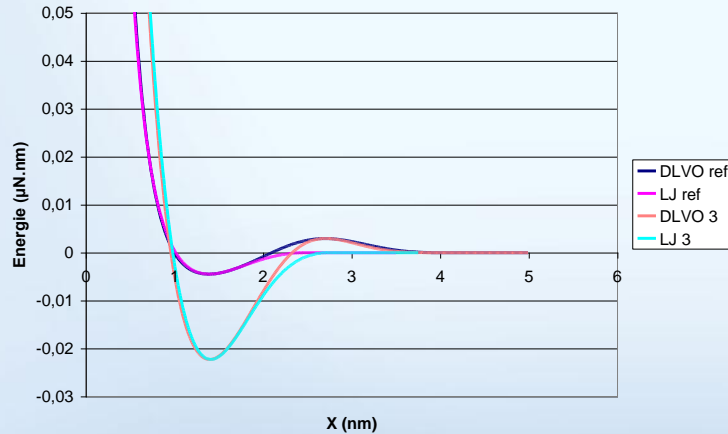


Model composites at atomistic scale to obtain realistic CG polymer-filler potentials of interaction (grafted/non-grafted, density of grafting, ...)

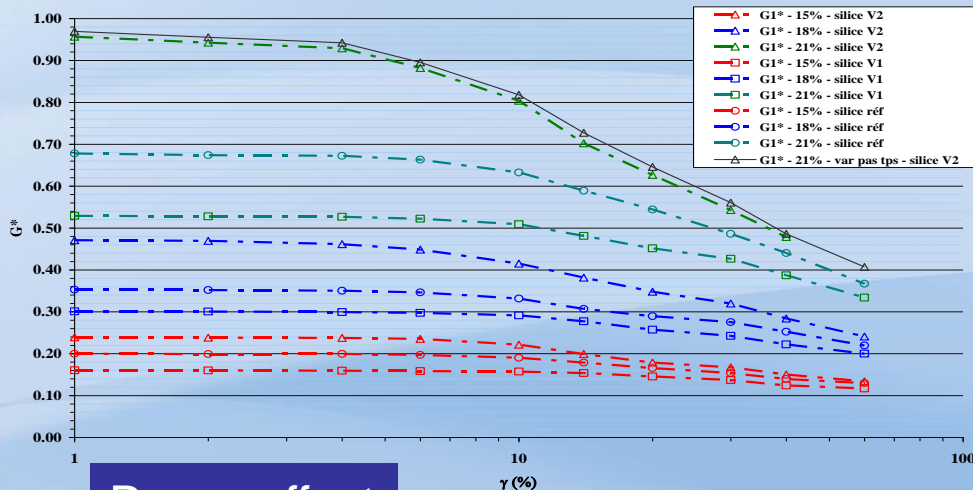
Simulation of open systems at the mesoscale to get $\omega_{cc}(r)$

Nanocomposites simulation

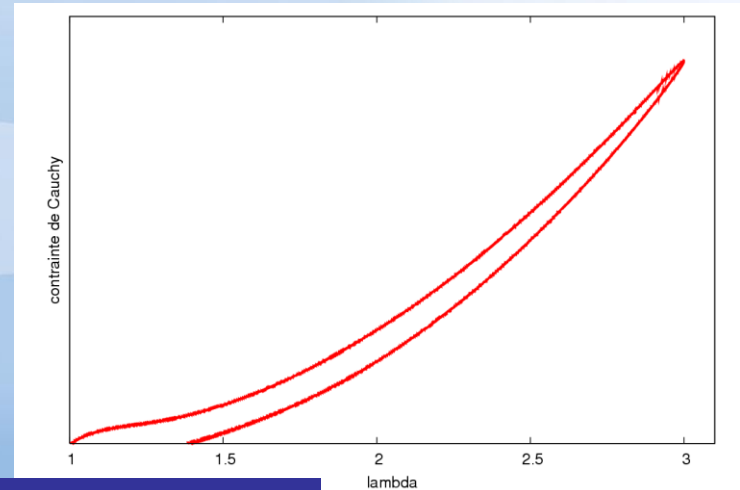
Example with a colloidal type of POMF



⇒ The well-known phenomena for nanocomposites can be reproduced



Payne effect



Mullins effect



Conclusion & Outlook

- Multi-scale materials constitutive of tire (tread) are particularly well suited for multi-scale simulations → *possible to improve the structure-properties relationships at each length scale*
- Obtention of a complete quantitative $G(t)$ should be possible through a multi-scale approach (*HPC could be helpful*)
- Use the method coupling NMR / simulation to design a polymer network with optimized mechanical properties (*expansion of the coupling analysis/simulation*)
- Determination of realistic CG filler-polymer interaction in different cases (*nature of the grafting, grafting density, ...*) → *achieve the establishment of POMF and check whether or not the approach is able to reproduce the behaviour of nanocomposites*

