Filled elastomer mechanics and polymer dynamics modification near surfaces

Soft Matter Science and Engineering

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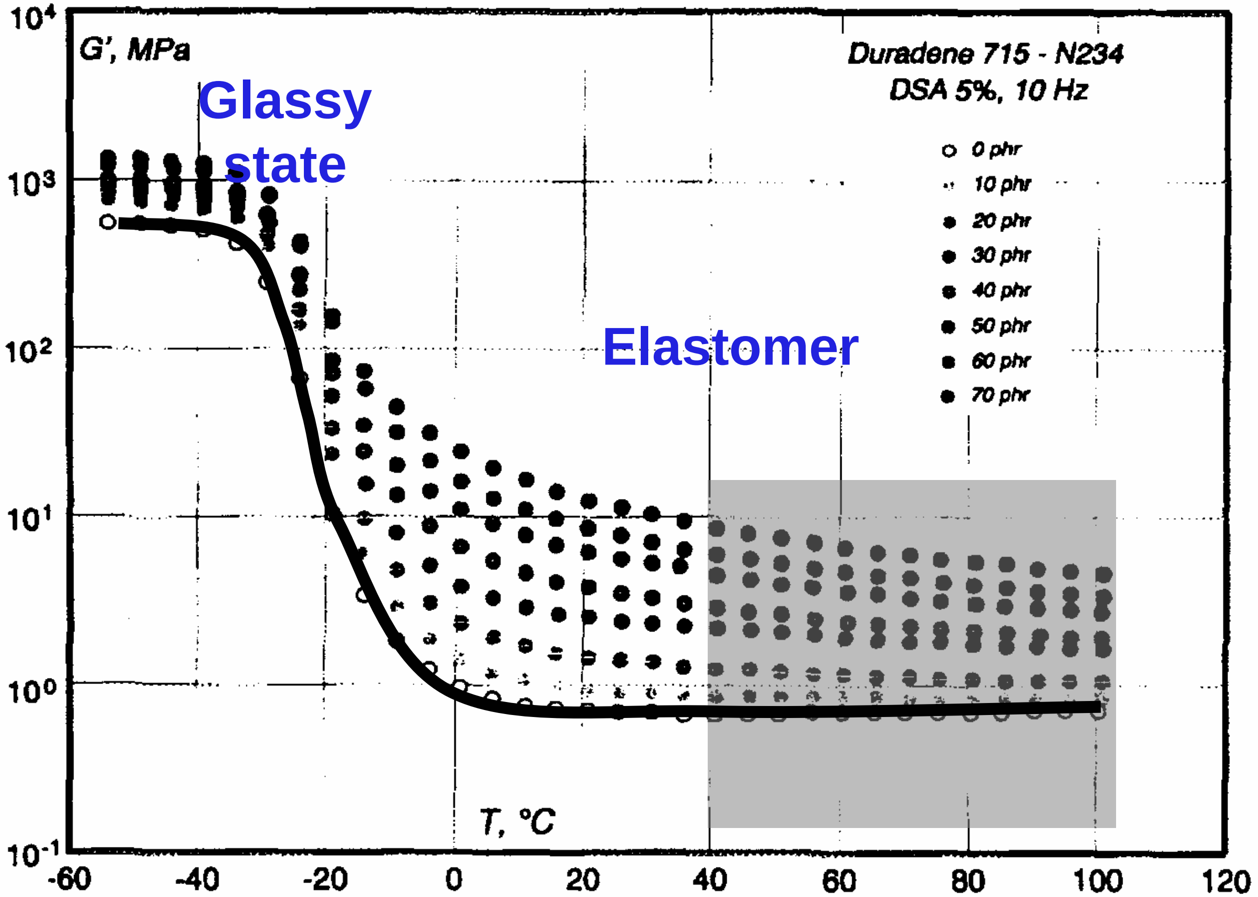
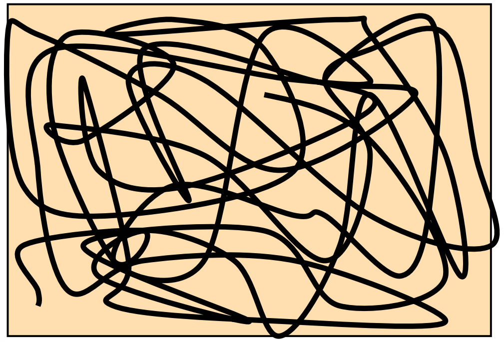
Usually here

This afternoon

Pure elastomer matrix

- Linear regime: low strain amplitudes

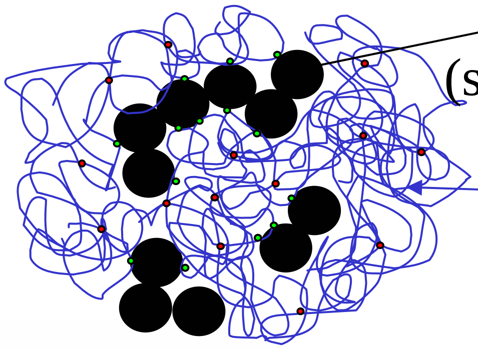


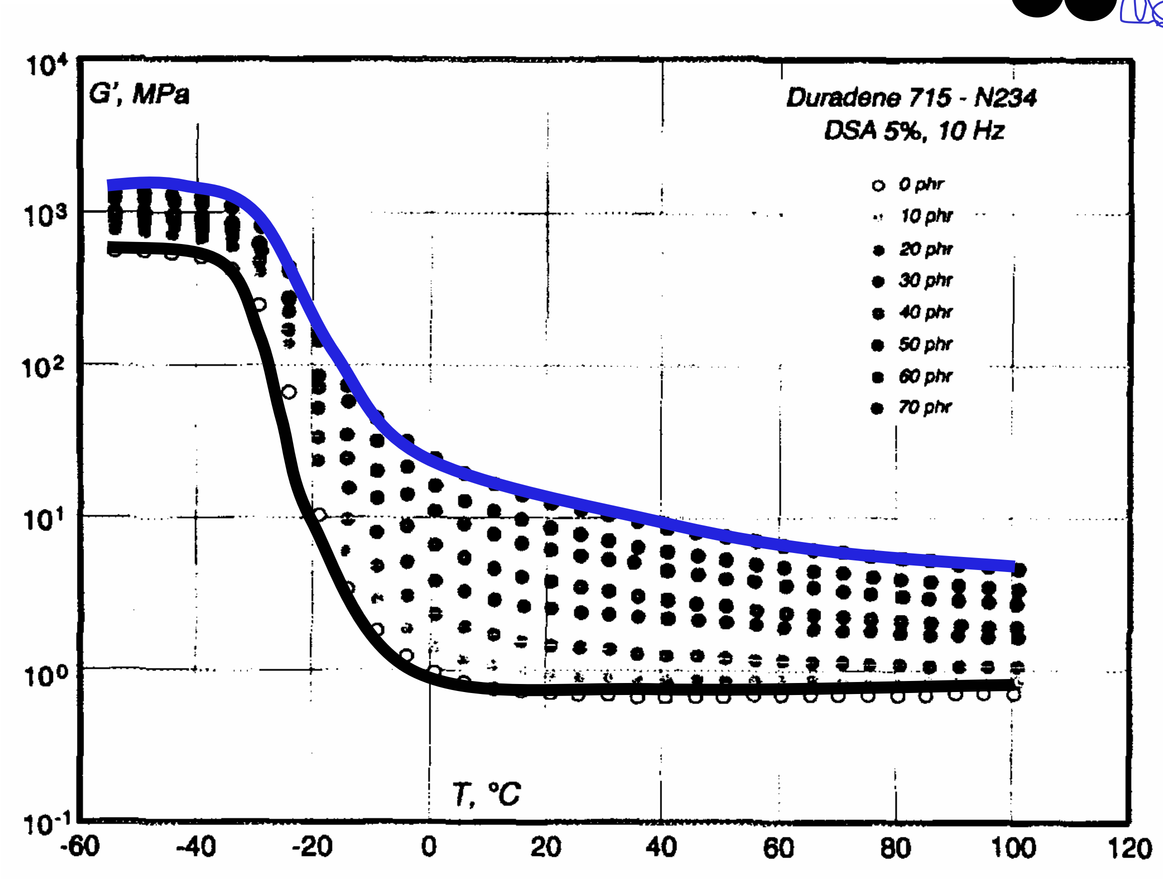


Polymer chains

From Wang, Rubb. Chem. Technol. 1998

Elastomer + solid fillers



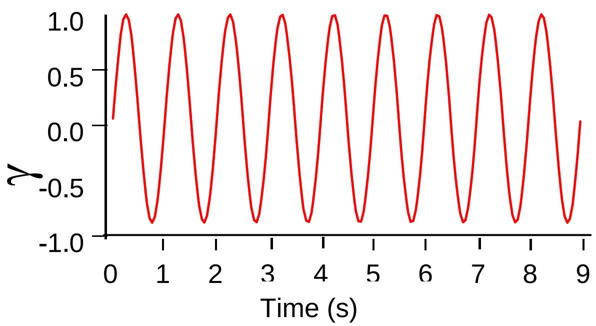


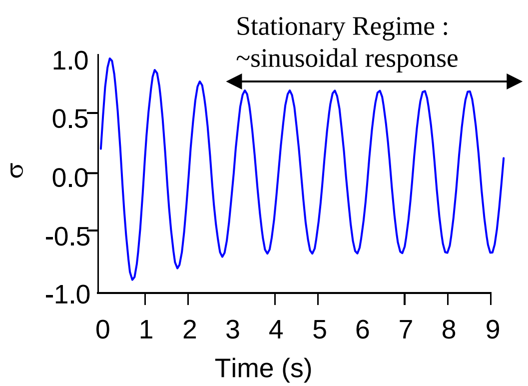
Reinforcement is not only an geometrical effect

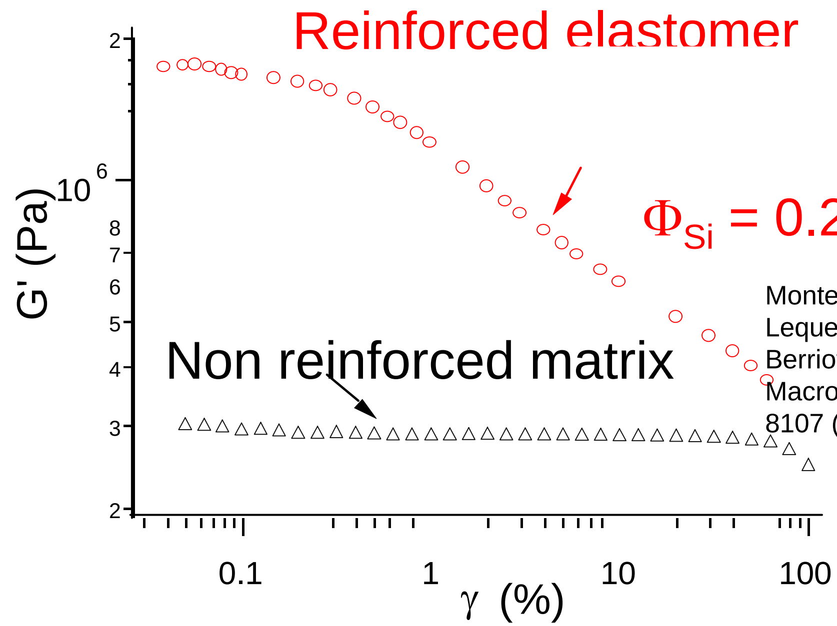
It reveals a deep modification of the polymer dynamics modification, in the vicinity of solid surfaces

From Wang, Rubb. Chem. Technol. 1998

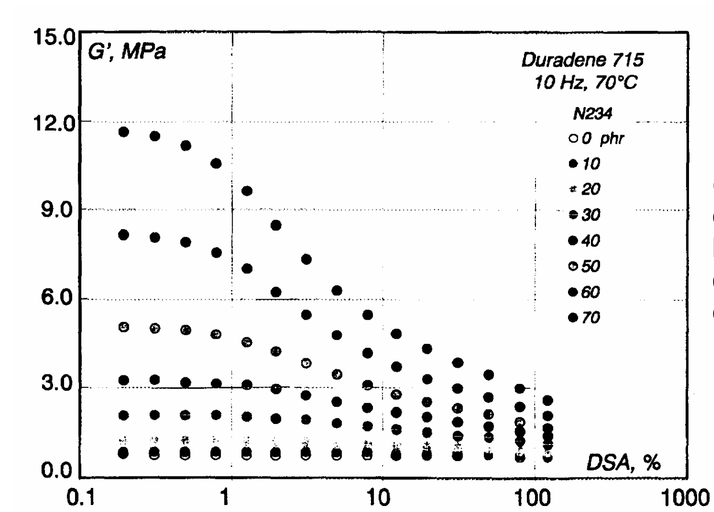
Payne effects







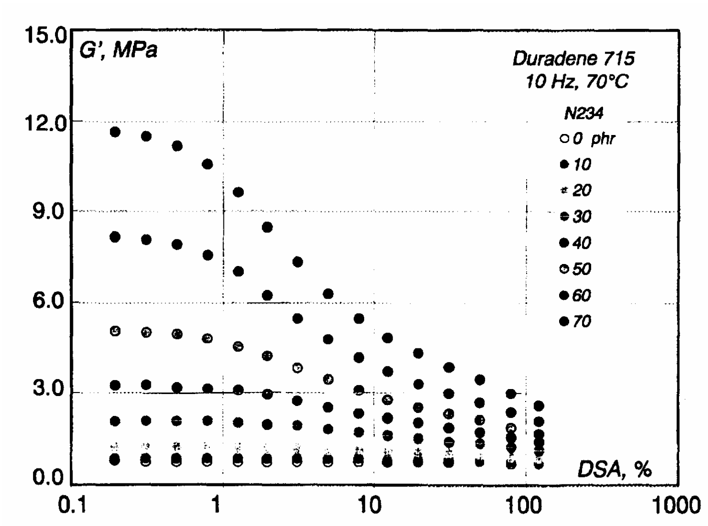
Montes H, Lequeux F, Berriot J Macromol.**36** 8107 (2003)



(Data measured on SBR/Carbon black systems of different filler concentrations, *Wang, Rubb. Chem. Technol. 1998*)

Non linearities – at small amplitudes – are induced

Payne effects



(Data measured on SBR/Carbon black systems of different filler concentrations,
Wang, Rubb. Chem. Technol. 1998)

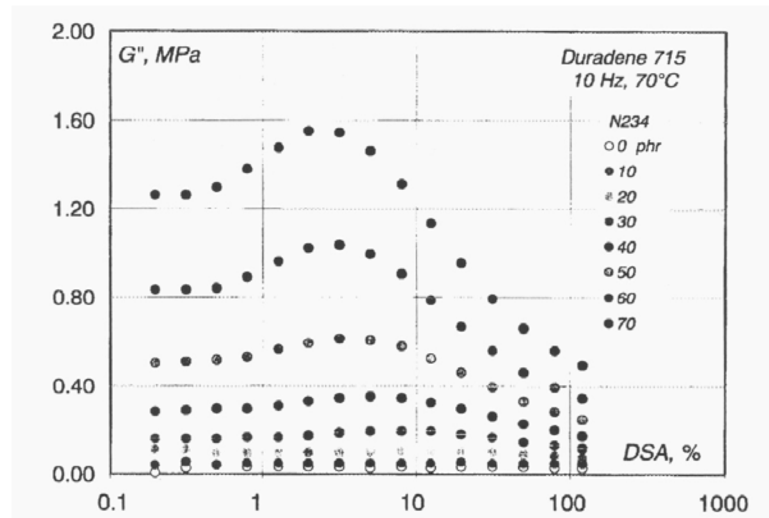


FIG. 10.—Strain dependence of G'' at 70 °C and 10 Hz for SSBR compounds with different loadings of carbon black N234.[14] Same compounds as Figure 4.

Non linearities – at small amplitudes – are induced.
At Large amplitude the modulus tends towards the one of the matrix (remember Roberto lecture Monday evening)

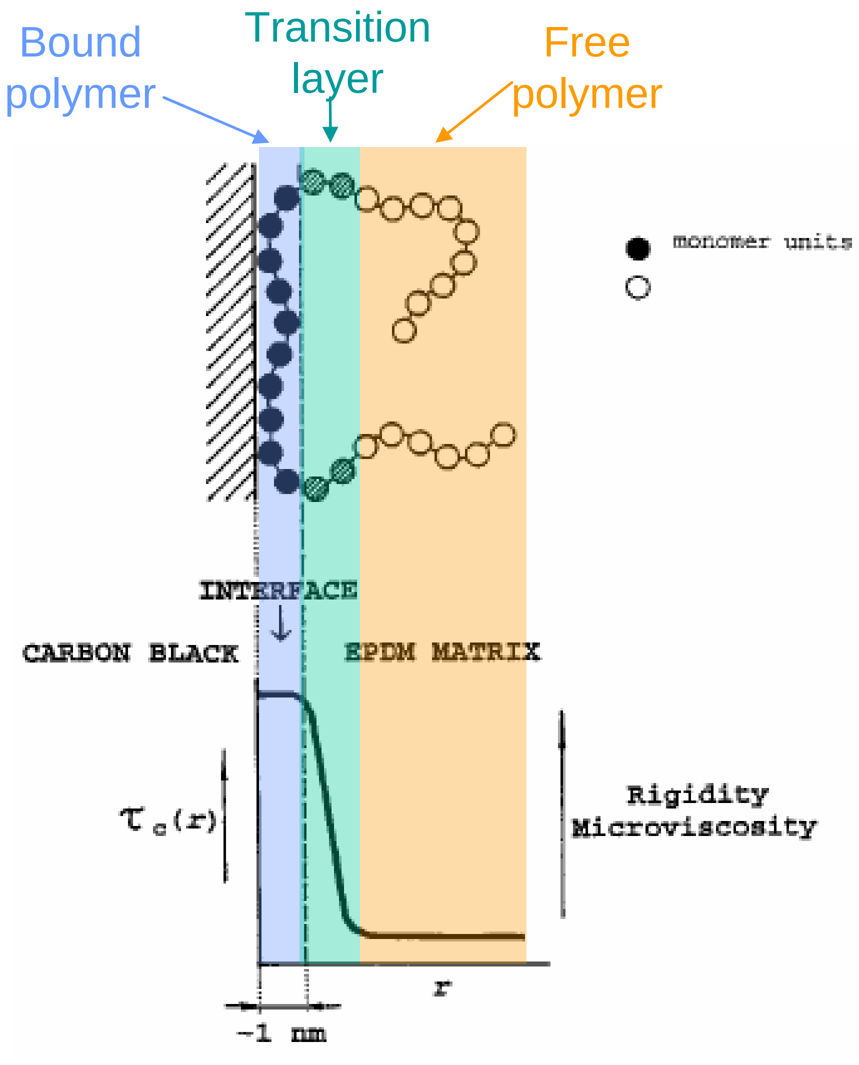
Mechanical data indicate that the polymer dynamics is modified by the embedding of particles.

This well know results is at the origin of numerous papers.

Polymer dynamics near surfaces

- Previous NMR studies have shown that polymer dynamics is slowed down near solid surfaces.

Kaufman. *J. Polym. Sci. Part A-2* **1971**, 9, 829
Kenny et al *Macromolecules* **1991,** 24, 436
Litvinov et al. *Macromolecules* **1999,** 32, 167



There some indications that the “immobilized” ou “bound” polymer may be glassy, indeed by Struik (1976) in his book :

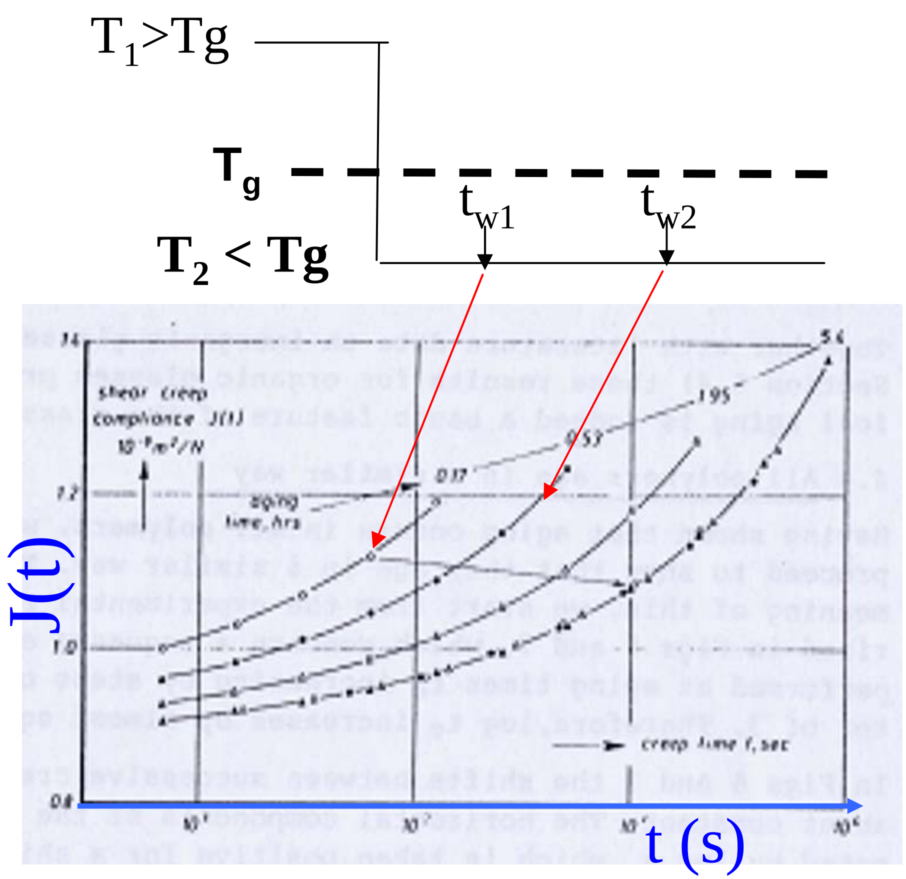
The clearest evidence is that filled rubbers age like glasses, above their glass transition.

However this observations was completely forgotten (or rejected) by the whole community for decades,

Until ~2000

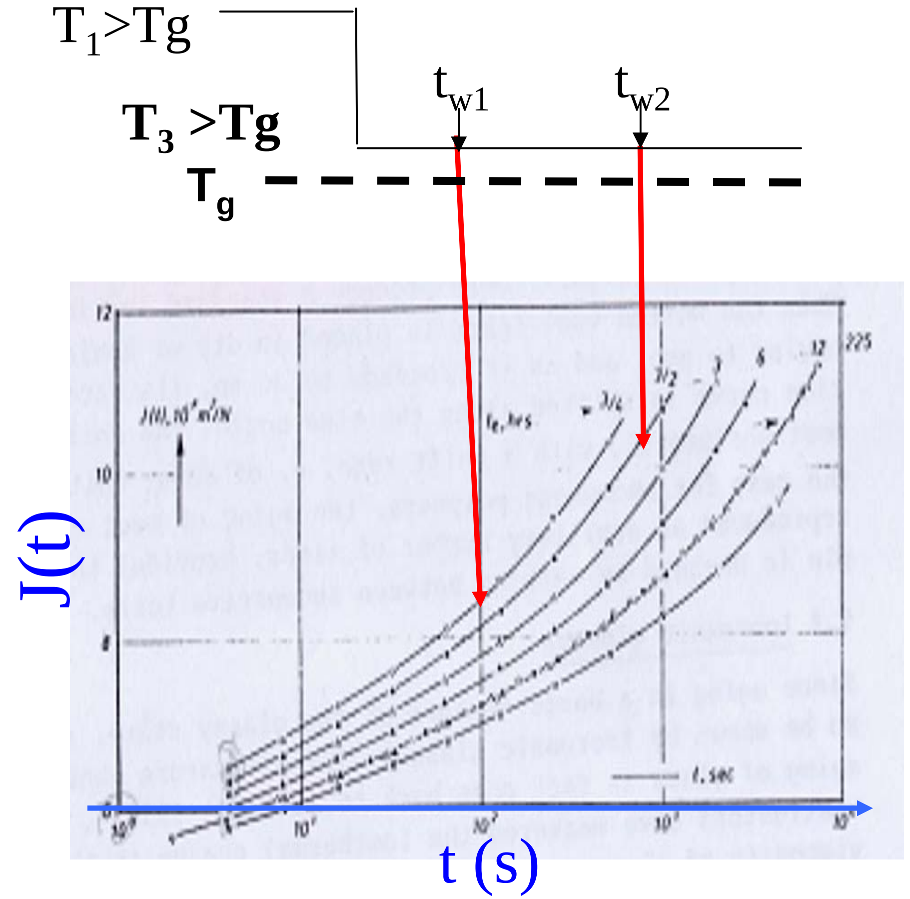
Physical aging in filled elastomers (Struik, Elsevier, 1978)

Glassy polymers at T<Tg



PS at T=Tg-20K

Reinforced elastomers at T>Tg



SBR / Carbon black at T = Tg + 20 K, Φ_{NC}=0.4

=> At T>Tg existence of glassy domains in a reinforced elastomer

There some indications that the “immobilized” ou “bound” polymer may be glassy, indeed by Struik (1976) in his book :

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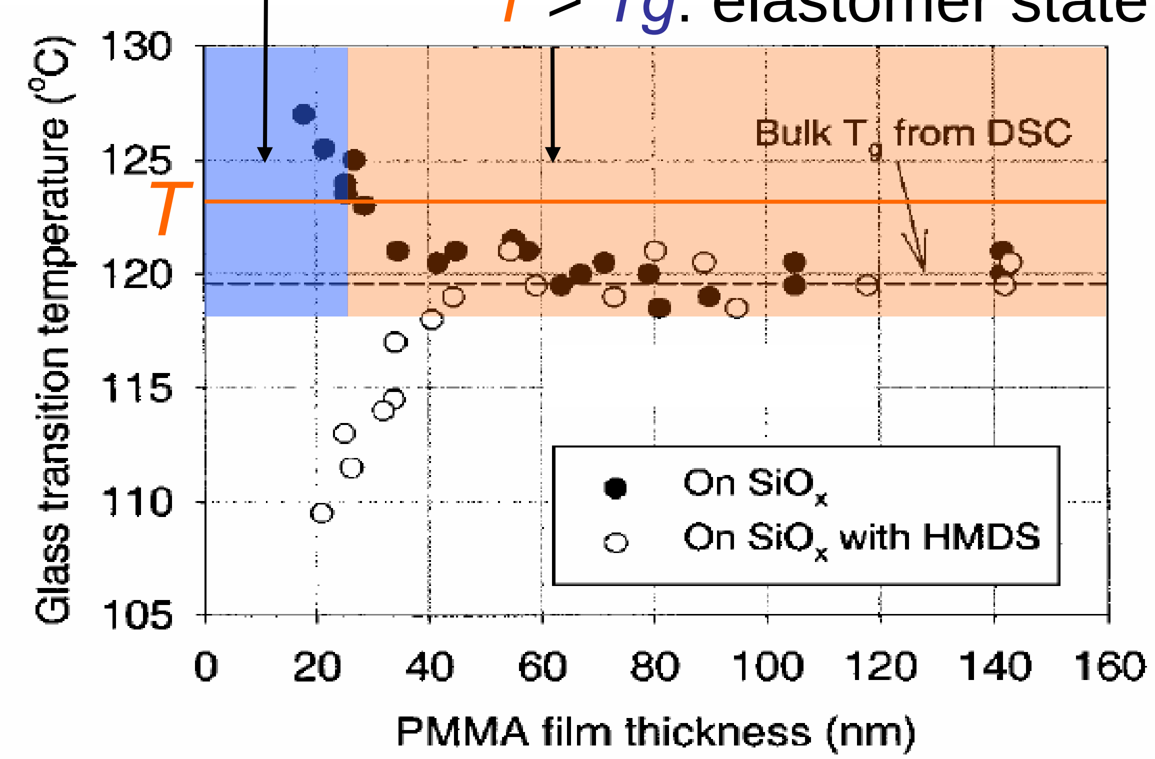
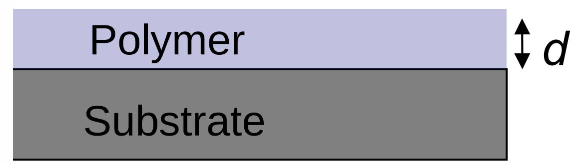
Since 1995 ➔
Polymer dynamics is modified in thin films

T < *Tg*: glassy state

T > *Tg*: elastomer state





*D.S. Fryer, P.F. Nealey, J.J. de Pablo, Macromolecules, **2000**, 33*

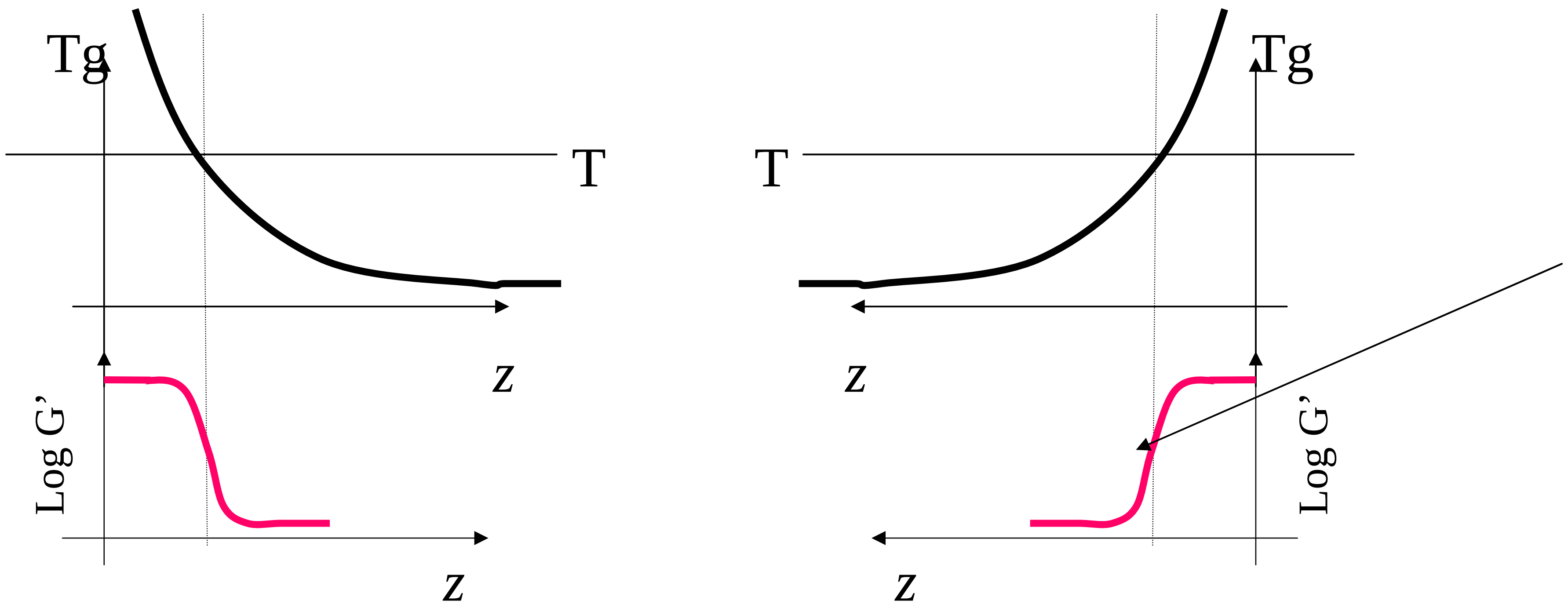
$$T_g(z) = T_g^{\infty}\left(1+\frac{\delta}{z}\right)$$

T_g at a distance *z* from a solid surface

Tg in the bulk

In agreement with
Most of the numerous data on thin films,

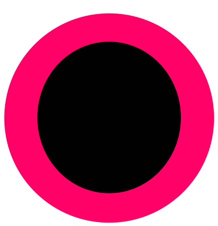
∇ Tg and linear mechanical response

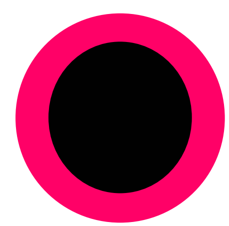


$$T_g(z) = T_g^{\infty}\left(1 + \frac{\delta}{z}\right)$$

Tg at a distance *z* from a solid surface

Tg in the bulk





-There is a huge modification of the polymer dynamics near a solid surface, of great importance in filled elastomer:

We suggested that it is related to Tg Gradient observed on thin films

J. Berriot, H. Montes, F. Lequeux, D. Long, and P. Sotta *"Evidence for the shift of glass transition near the particles in silica-filled elastomers*" Macromolecules 35 p 9756-9762 (2002)

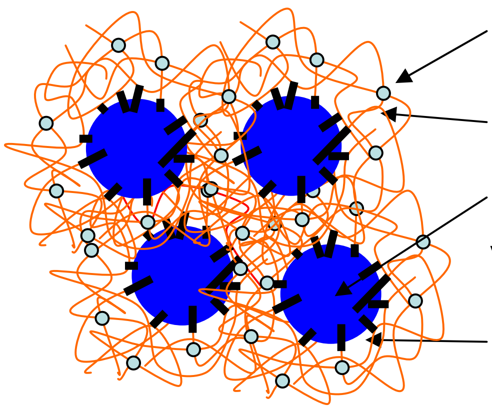
Montes H, Lequeux F, Berriot J «Influence of the glass transition temperature gradient on the nonlinear viscoelastic behavior in reinforced elastomers» Macromol.36 8107 (2003)

➔use a well controlled system with a huge confinement…

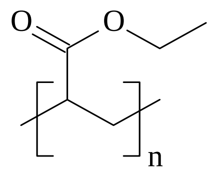
Prepare model filled rubbers

➔ well controlled structure, especially particles dispersion

➔ various fillers-polymer interactions possible depending on the grafters



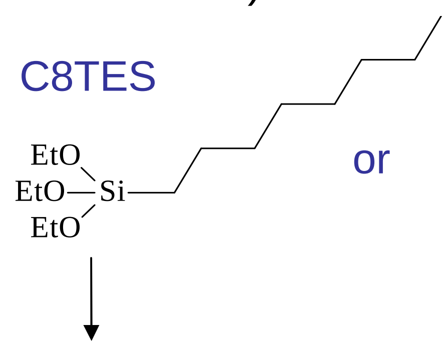
Polymer — Poly(ethyle acrylate) - PEA

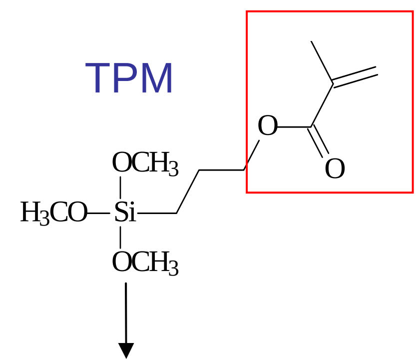


Cross-links — 1,4-butanedioldiacrylate

Silica (Ø =30, 50 or 100 nm, volume fraction = 10-30%)

Grafters — C8TES or TPM





Non-covalent link between the silica and the polymer

(H bonds between residual Si-OH and the polymer)

Covalent link between the silica and the polymer

BERRIOT J. *et al.*, *Polymer*, **44** (2003) 4909.
BERRIOT J. *et al.*, *Polymer*, **44** (2003) 1437.
BERRIOT J. *et al.*, *Polymer*, **43** (2002) 6131.

➔Make series of samples with various volume fraction of silica (up to 25%, various diameter of silica (30 nm to 100 nm), various grafters, various stabilities)

➔Measure the structure factor of the silica particles by small angle neutrons scattering

➔Reconstruct by Inverse Monte Carlo the pair distribution of the silica particles (with J. Oberdisse)

➔For each samples

➔ about 10 years of work *(initial idea of Lucien Monnerie in 1995)*

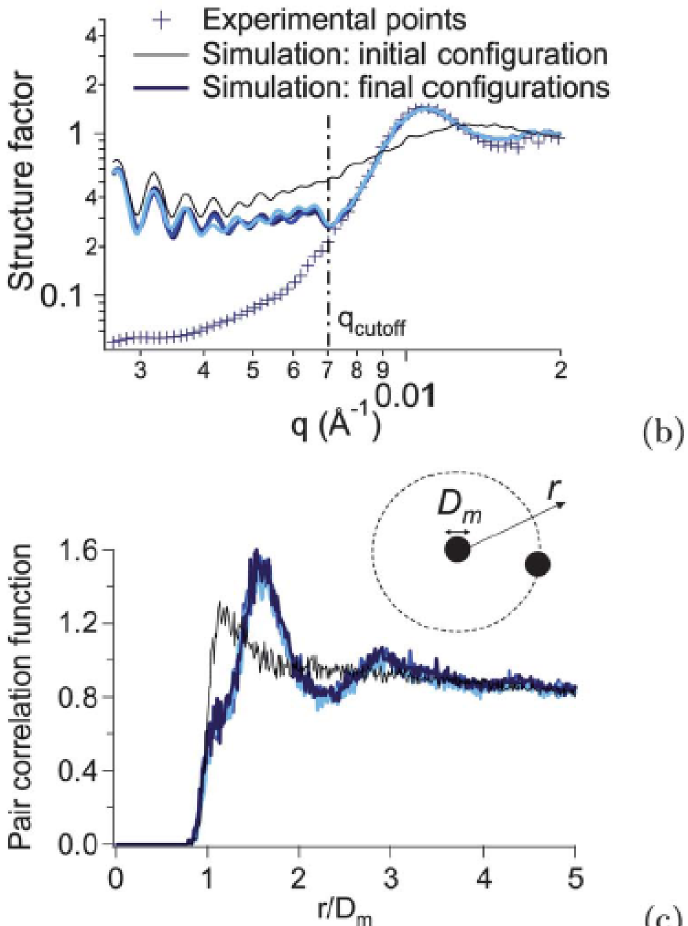
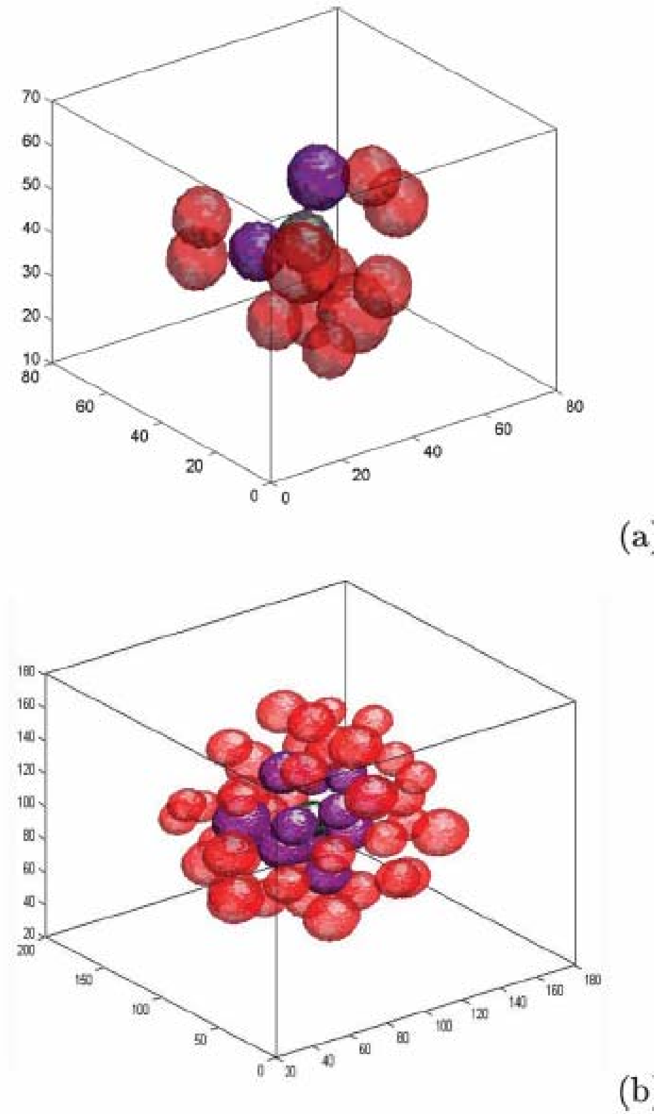


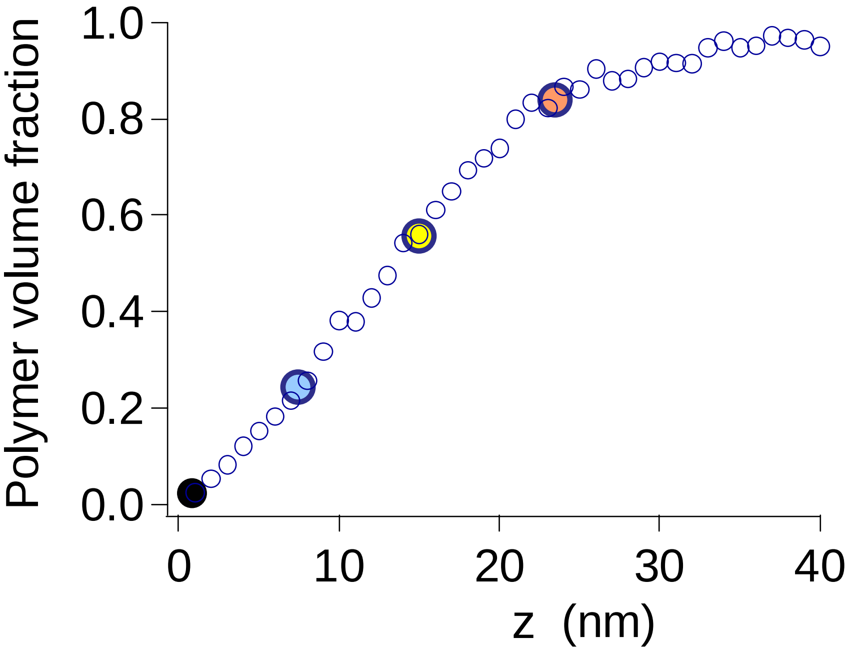
Fig. 2 RMC simulation results for different initial configurations, either crystaline (light blue) or random (dark blue). Number of particles = 8000, total number of steps = 1.6×10^7. (a) χ^2 as a function of the number of steps in the simulepsation normalized by the number of particles N_{tot}. (b) Experimental (crosses) and simulated (lines) structure factors. The structure factor corresponding to the initial random configuration is shown with the thin line. (c) Pair correlation function in the initial (thin line) and final configurations (thick lines), as a function of r/D_m, the distance normalized by the mean diameter of the particles. We observe that the final configurations are equivalent, and thus independent of the initial configuration chosen.

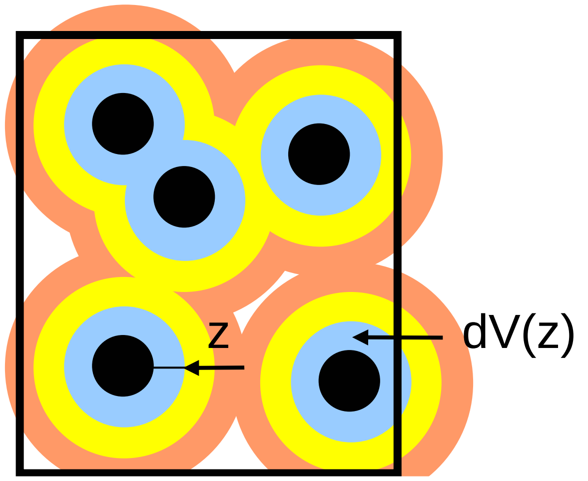


3D representation of the silica particles arrangement in the ...es MIST TPM 30 (a) and T50 TPM 30 (b) (at different scales). A ...le is chosen—in green—and its first neighbors are represented in ...nd the second ones in red.

Characterize precisely the geometry from SANS

- Polymer volume fraction at a distance *z* from solid surfaces:





By inverse Monte Carlo Method /(col; J. Oberdisse)
Papon et al *Soft Matter 2012*

Measure precisely the dynamics by NMR

1H solid NMR
Magic Sandwich
Echo sequence

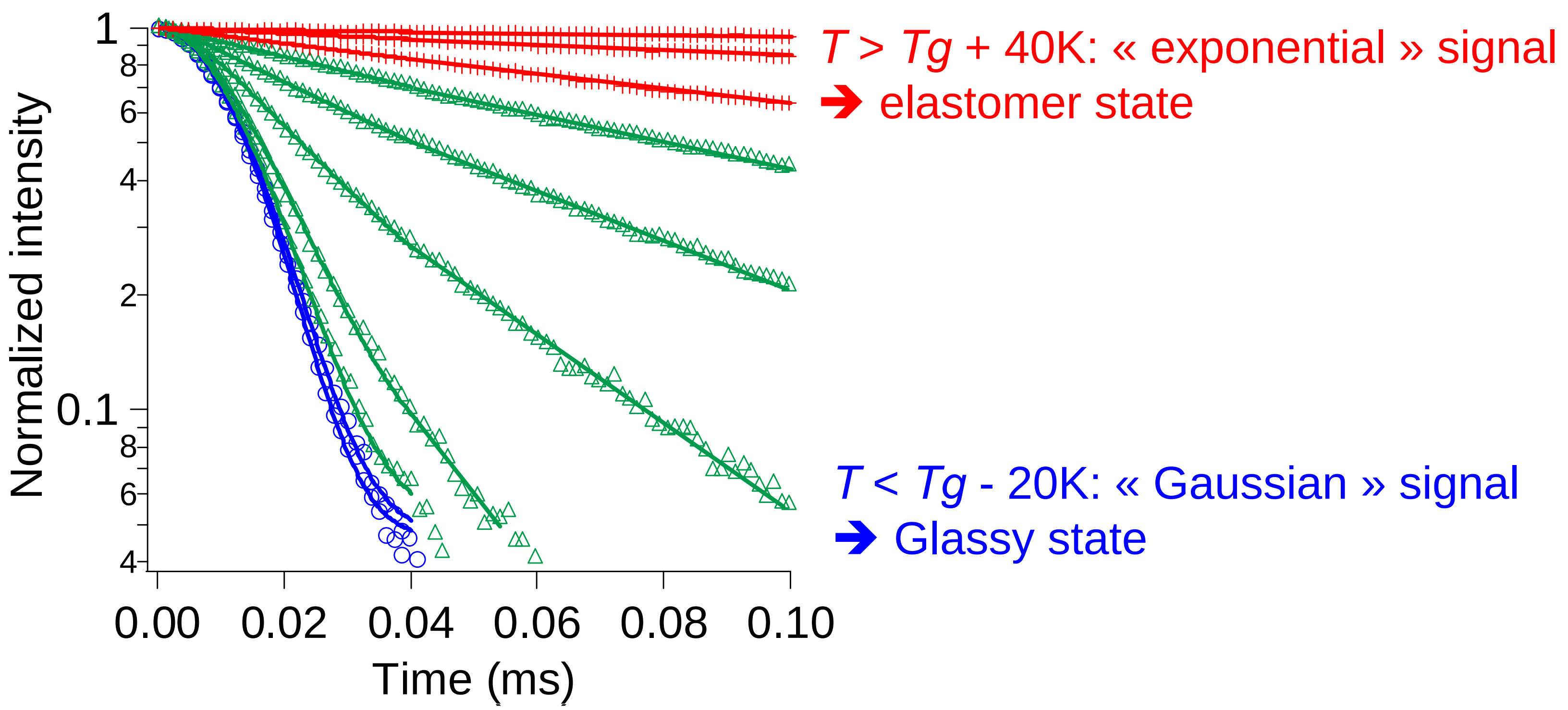
Free Induction Decay of protons: sensitive to elastomer/glassy dynamics

MSE sequence: better refocus than classical solid-echo

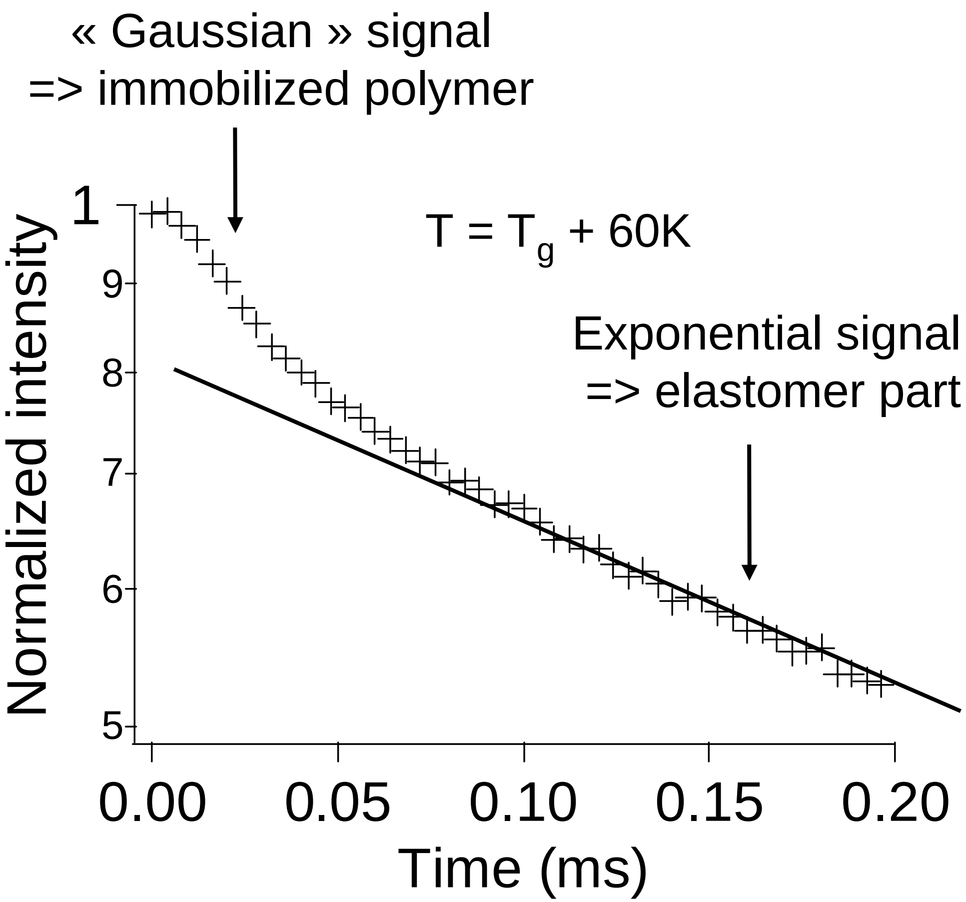
Col; K Saalwaechter

Magic Sandwich Echo sequence: measurement of the Free Induction Decay (FID)

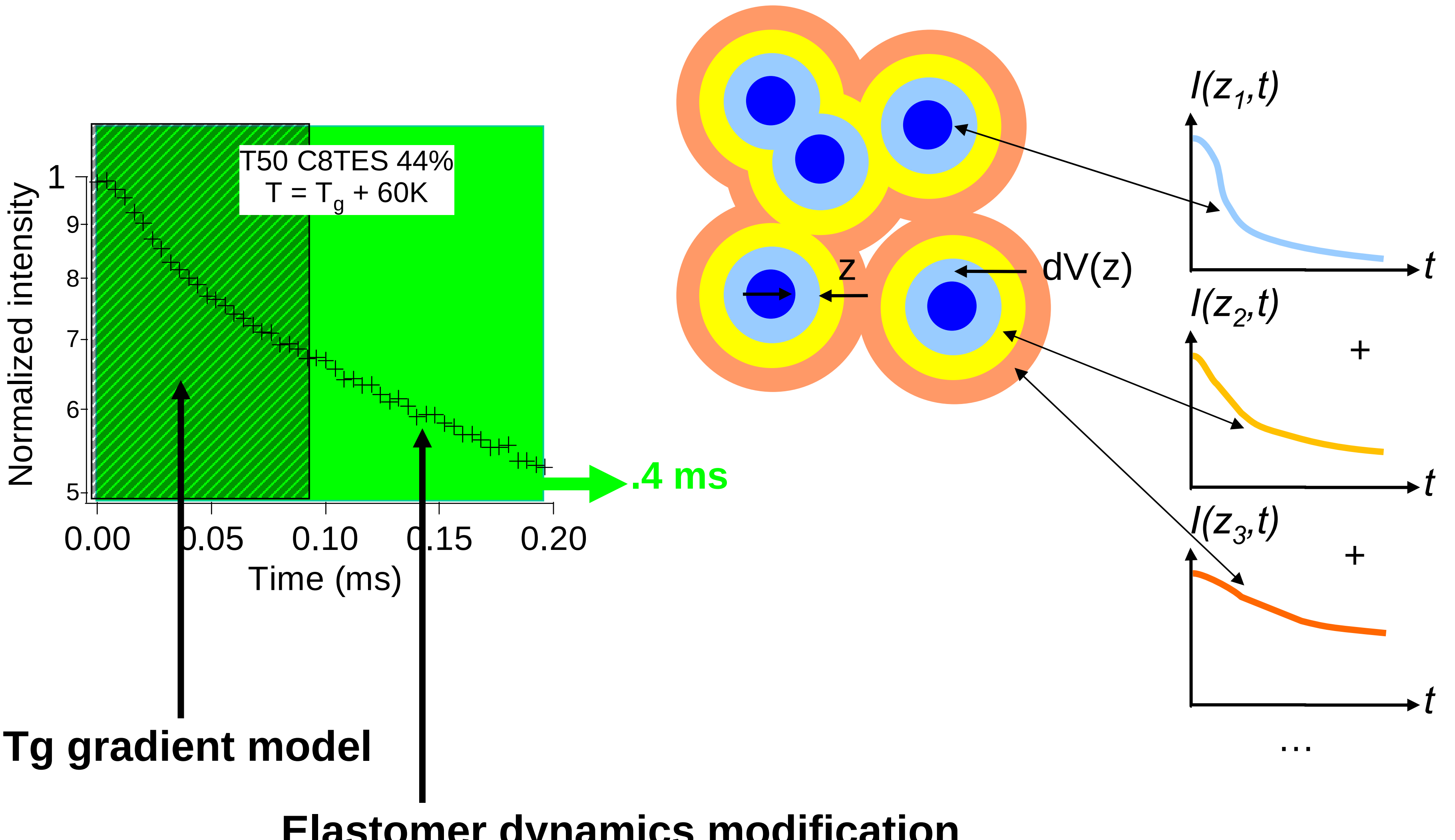
Elastomer classical behavior:



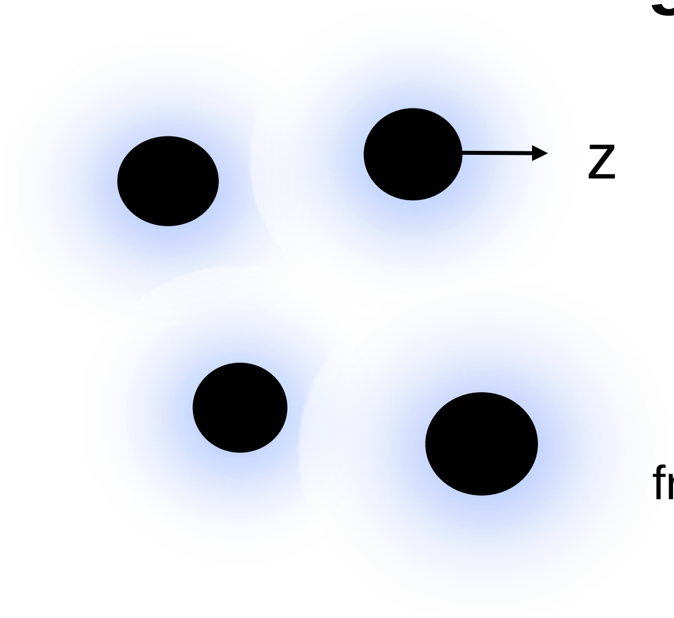
Filled elastomer NMR response



I(t) = superposition of signals *I(z,t)*



Tg gradient model analysis



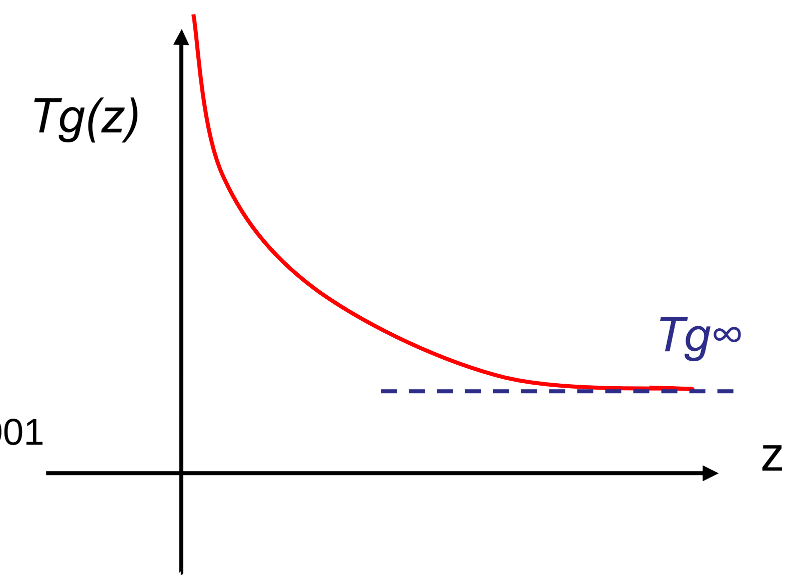
$$T_g(z) = T_g^{\infty}\left(1 + \frac{\delta}{z}\right)$$

Tg at a distance *z* from a solid surface

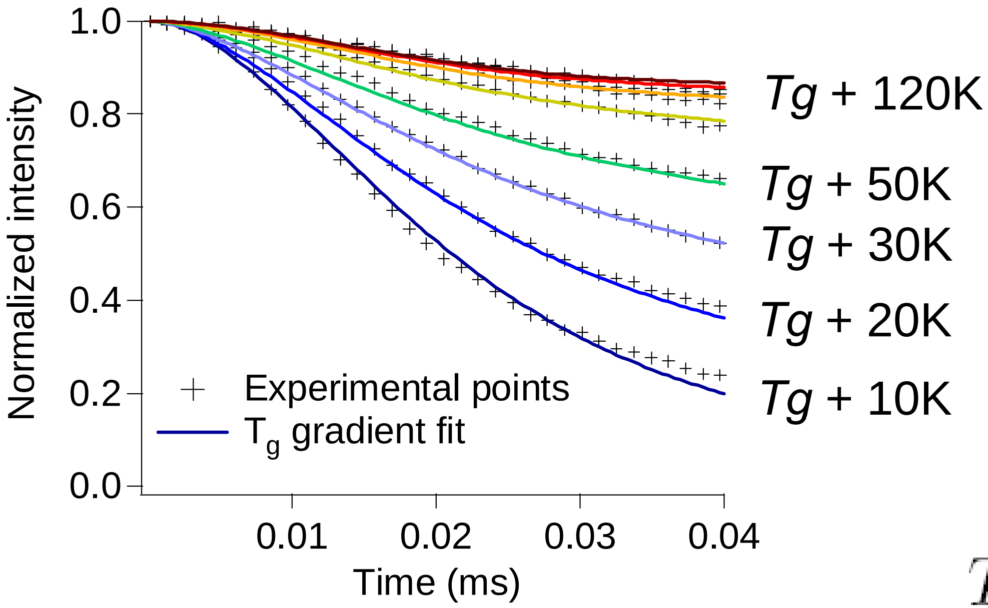
Tg in the bulk

- ***Tg gradient model :***
  (Long D., Lequeux F.
  EPJE 2001)

In agreement with
Most of the numerous data on thin films,
Tg gradient model Long D., Lequeux F. *EPJE* 2001



Tg gradient model analysis



$$T_g(z) = T_g^{\infty}\left(1 + \frac{\delta}{z}\right)$$

Tg at a distance *z* from a solid surface

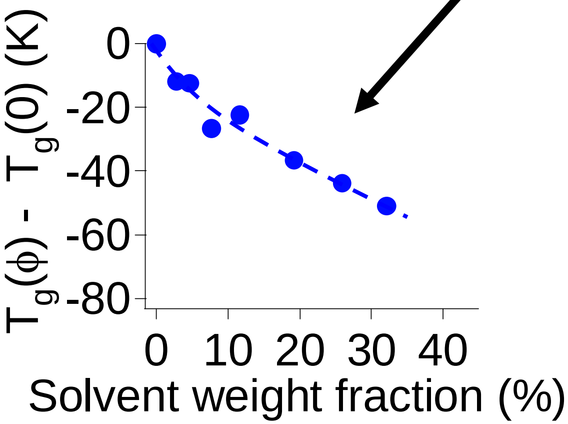
Fit of NMR curves between *Tg* + 10K and *Tg* + 120K with a single parameter δ

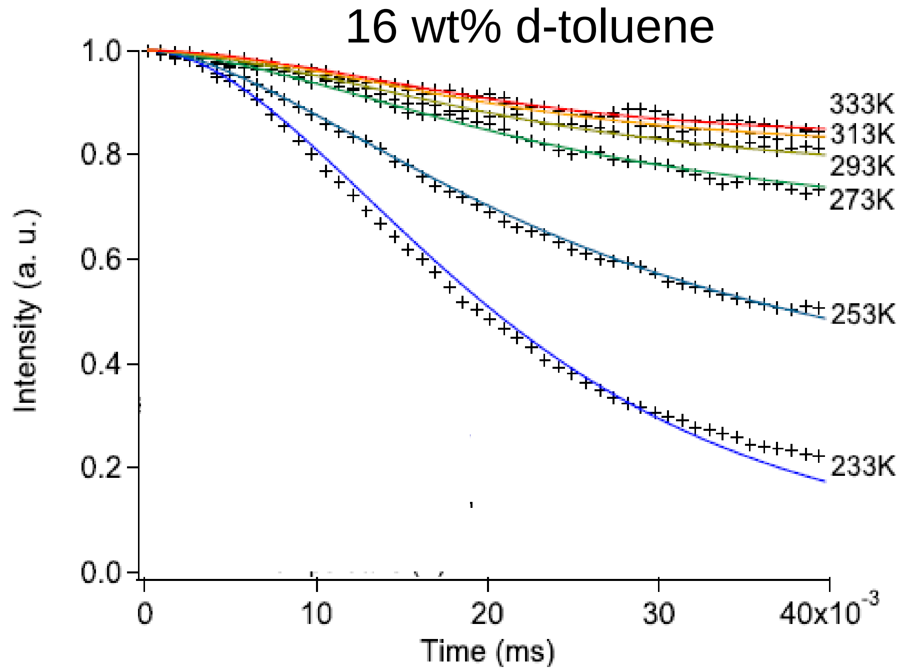
δ = 0,15 nm

Tg gradient model analysis

- This law remains valid in presence of solvent

$$T_g(z) = T_g^{\infty}(\phi)\left(1+\frac{\delta}{z}\right)$$





The gradient of T_g is also valid with the same value of δ

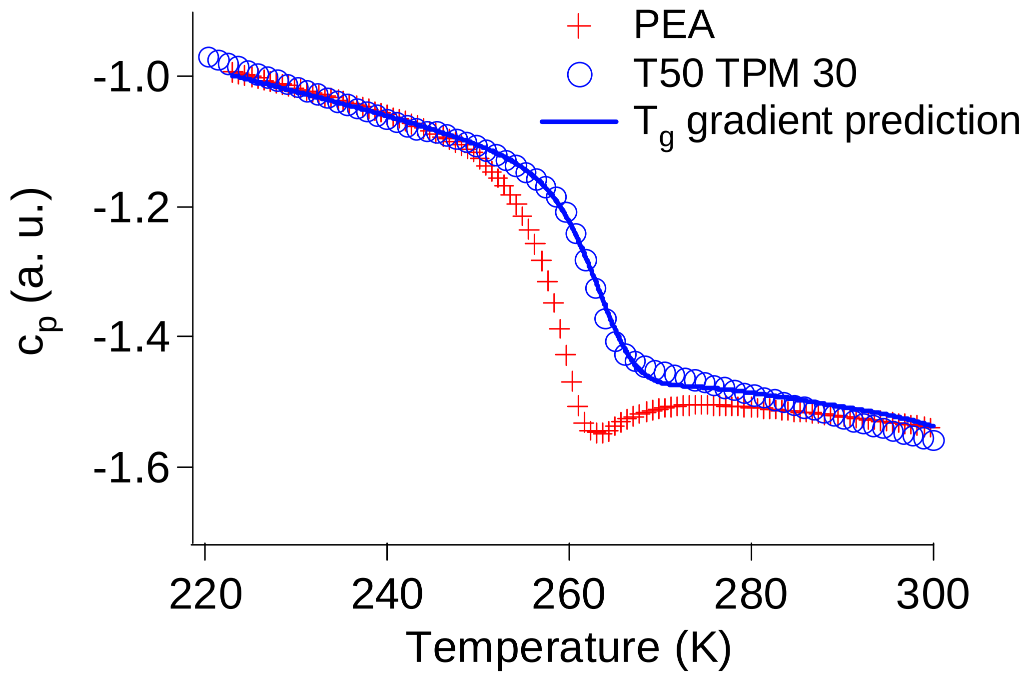
δ = 0,15 nm

Tg gradient model analysis

➔ Differential Scanning Calorimetry

dH/dT signal on pure PEA

⊗ shift thanks to the *Tg* gradient model, using the NMR parameter



Quantitative prediction of the

Calorimetric response

Papon at al PRL 2012

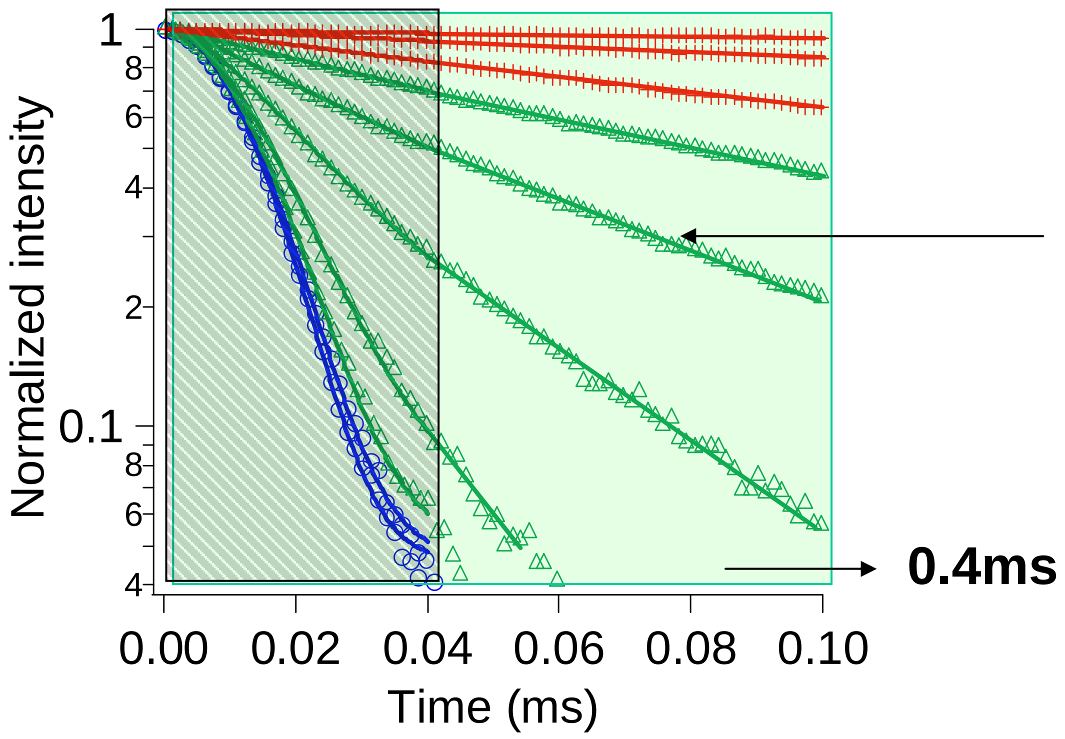
Tg gradient model analysis

- One parameter description fast glassy relaxation near surfaces from Tg to Tg +100K (as measured by NMR)

-With the same parameter : quantitative prediction of the solvent effect on confinement

-With the same parameter : prediction of the DSC (calorimetric) response

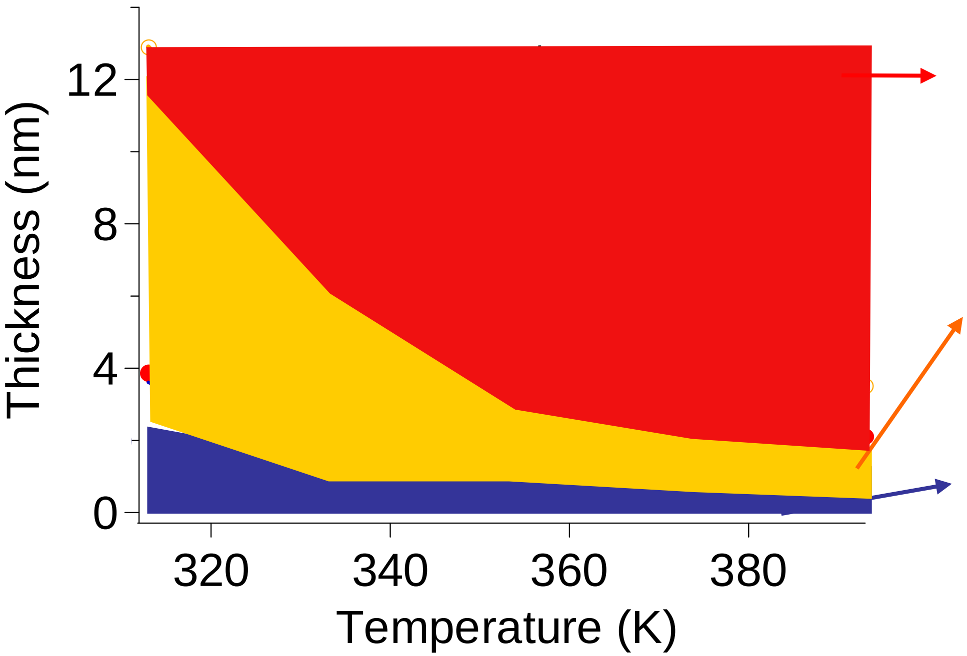
Elastomer dynamics modification analysis



In this domain there is a non exponential decay for filled elastomer

Elastomer dynamics modification analysis

➔Use a 3 components model: glassy, elastomer and intermediate



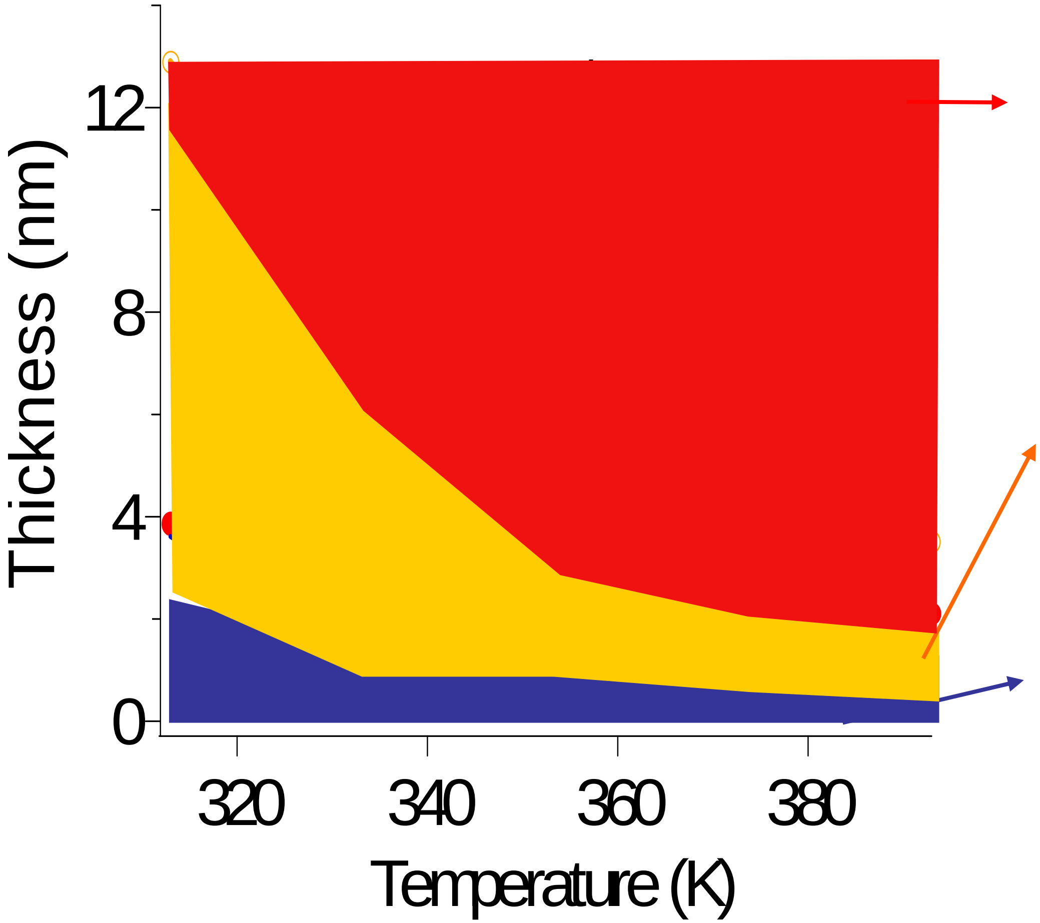
Elastomer dynamics (exponential signal)

Intermediate dynamics (stretched exponential)

Glassy dynamics (Gaussian signal)

A. Papon et al Macromolecules, 2011, 44, 913.

Elastomer dynamics modification analysis



Elastomer dynamics (exponential signal)

Intermediate dynamics (stretched exponential***)=***

Not seen by DSC

Glassy dynamics (Gaussian signal)

=similar to gradient of Tg analysis, seen by DSC

A. Papon et al Macromolecules, 2011, 44, 913.

There is a gradient of glass transition

AND

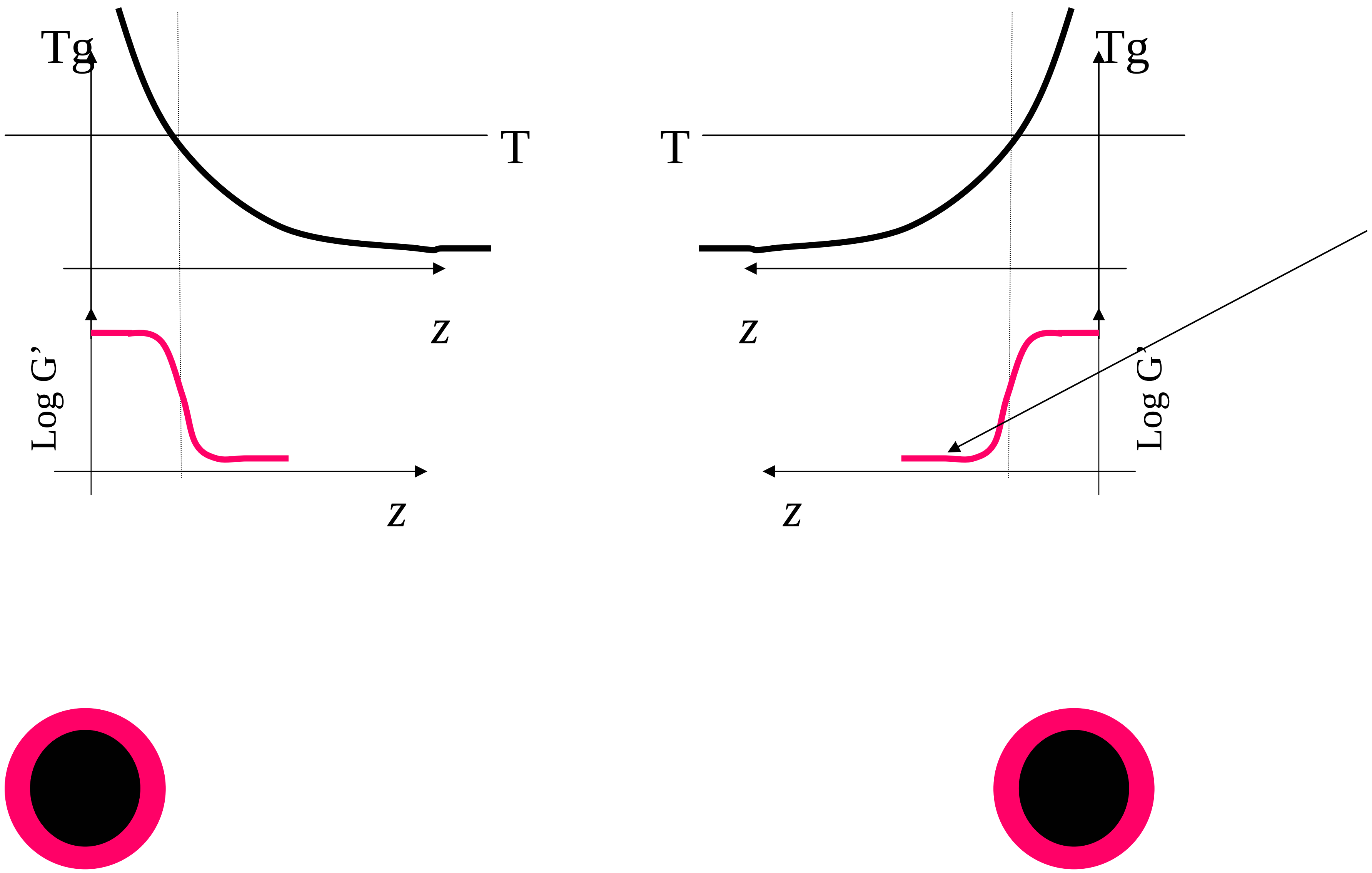
A broadening of the glass transition (on the low frequency side)

Back to mechanics :

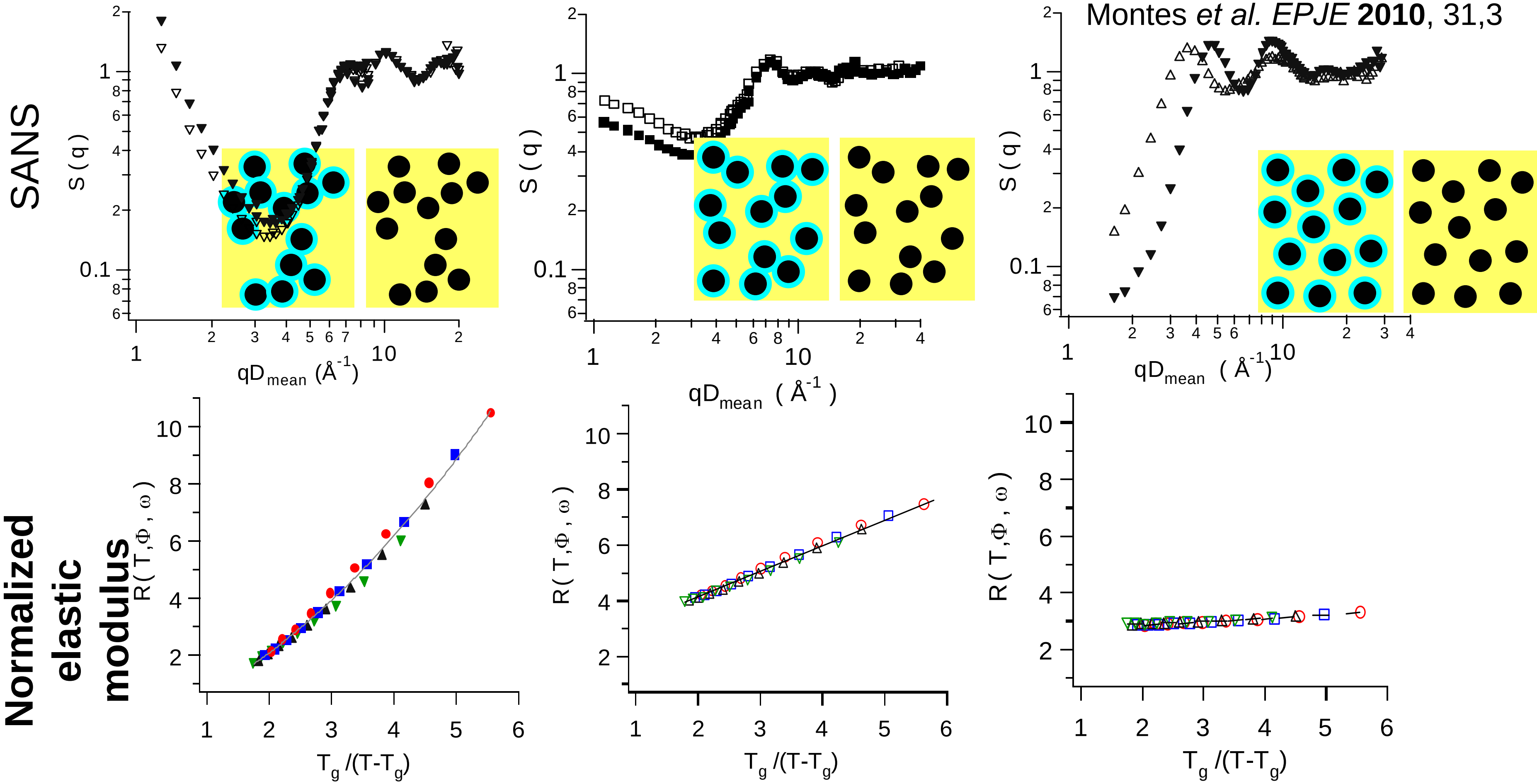
Confined polymer exhibit a different dynamics (~glassy)

Consequences on mechanics ?

∇ Tg and linear mechanical response



Influence of the fillers dispersion

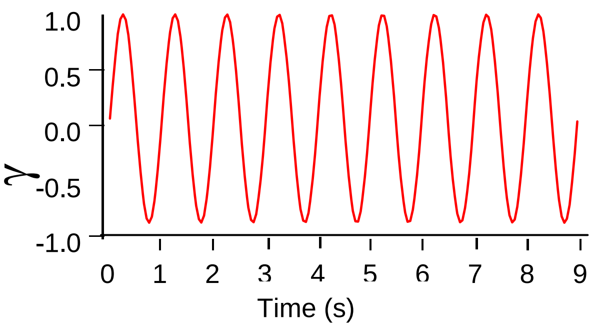


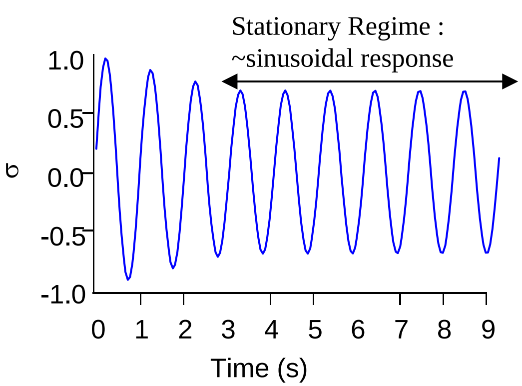
Montes *et al.* *EPJE* **2010**, 31,3

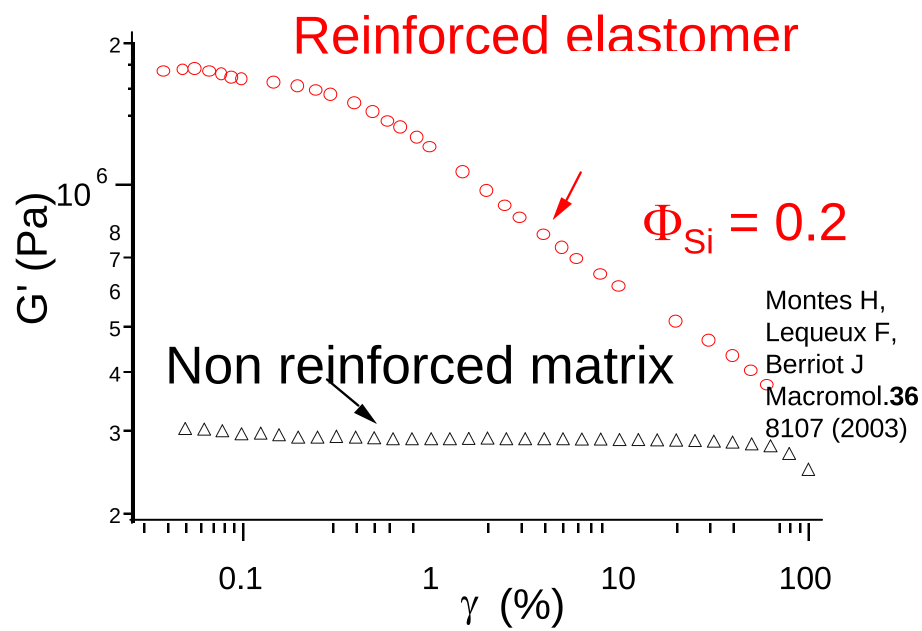
Tg/(T-Tg) is proportionnal to the glassy layer thickness

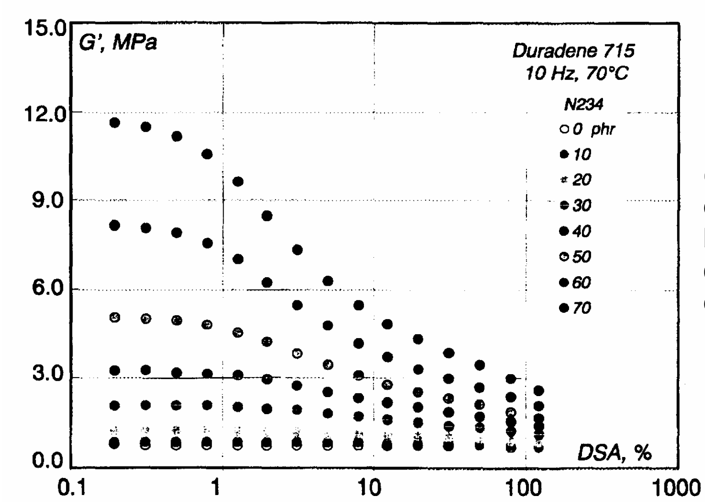
- **Distance between particles controls the elastic modulus T-dependance**

Payne effects





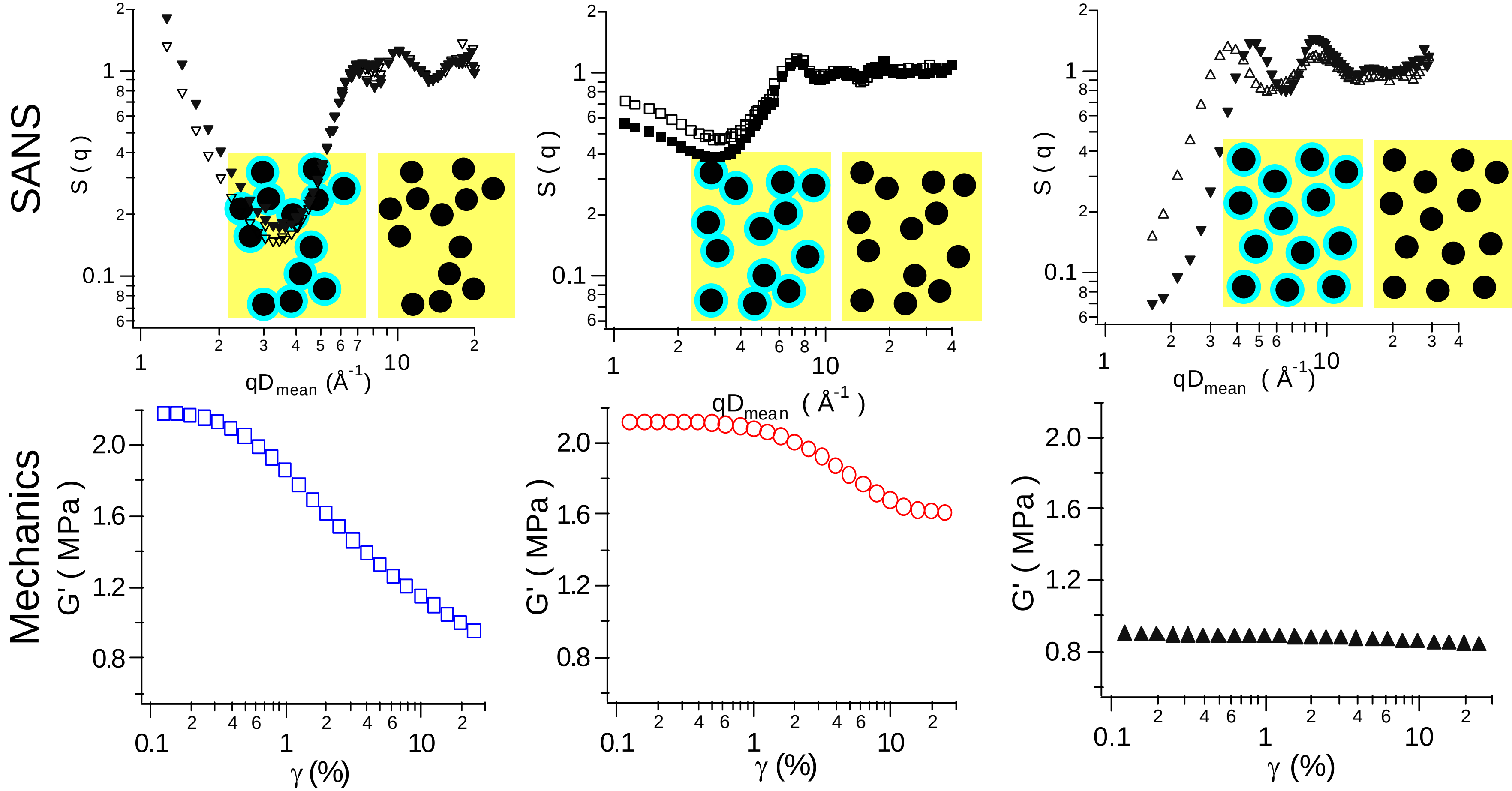




(Data measured on SBR/Carbon black systems of different filler concentrations, *Wang, Rubb. Chem. Technol. 1998*)

Non linearities – at small amplitudes – are induced

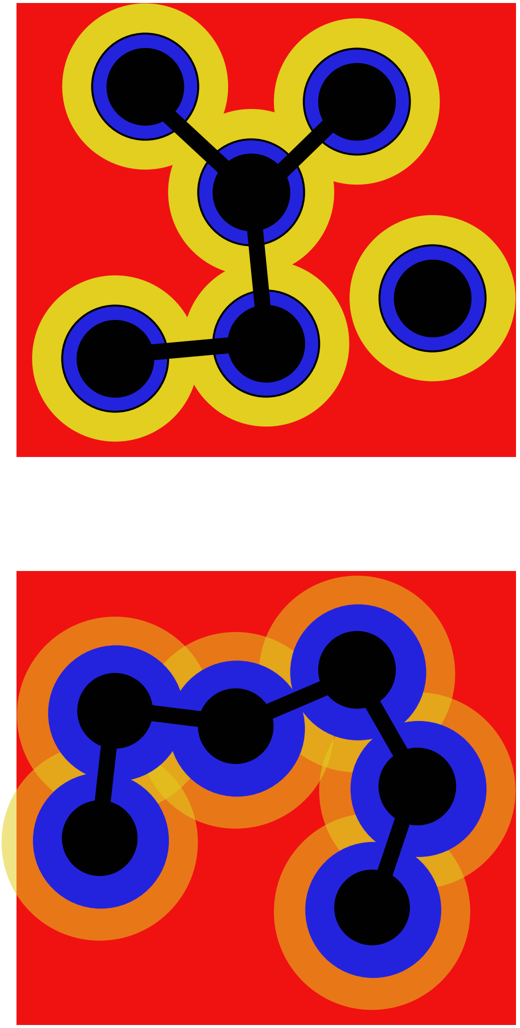
PAYNE EFFECT: Influence of the fillers dispersion



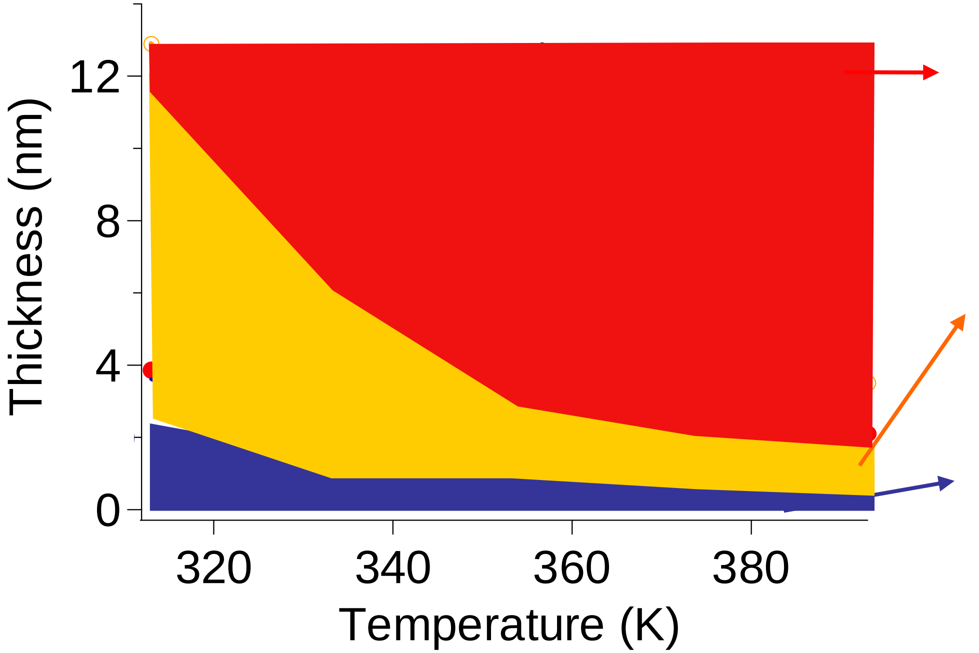
Tg/(T-Tg) is proportionnal to the glassy layer thickness

What is the range of mechanical interaction ?

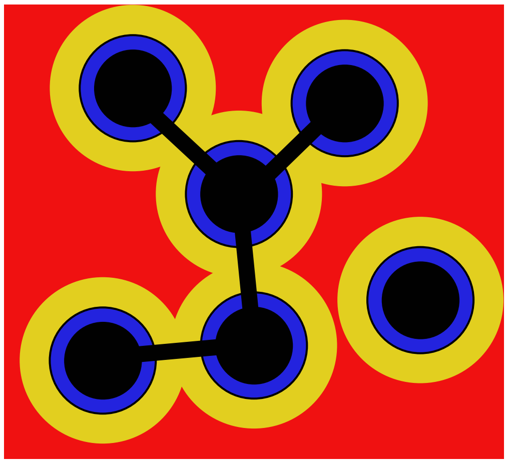
Payne effect and immobilized polymer ?

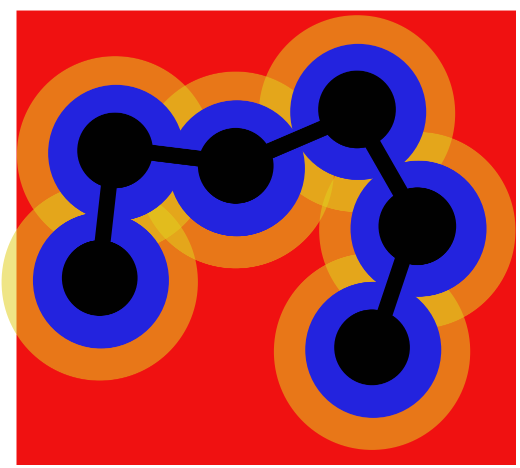


Network of particles connected by slow (and thus non-linear) polymer ?



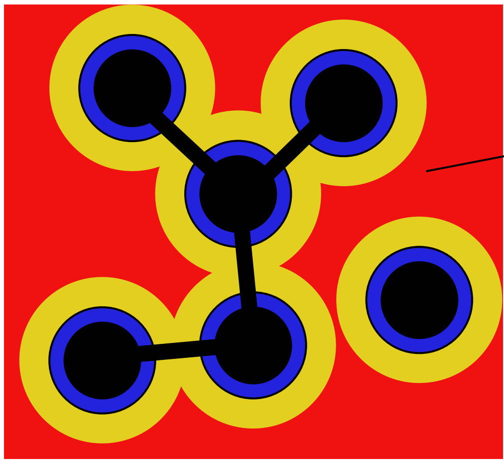
Payne effect and immobilized polymer ?





From Structure and NMR ➔ compute the network connectivity for various :

- Temperature
- Silica diameter
- Silica volume fraction



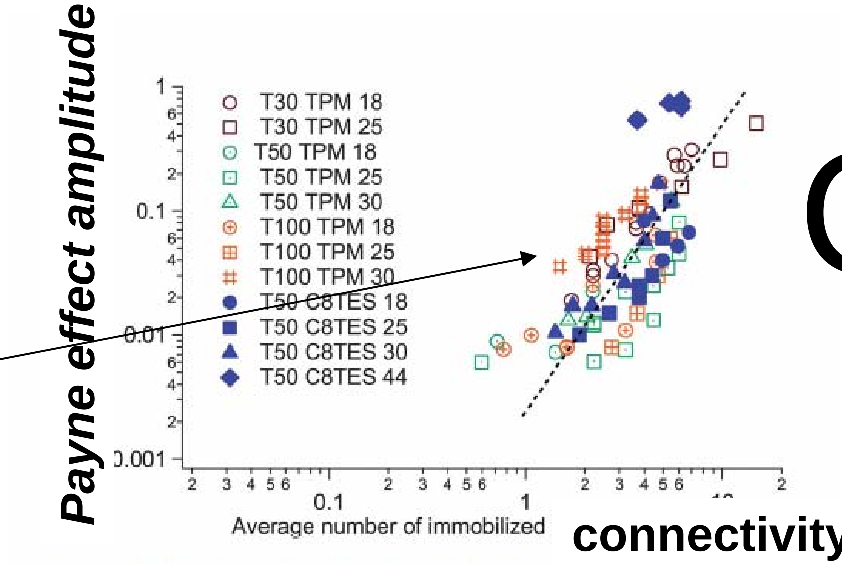
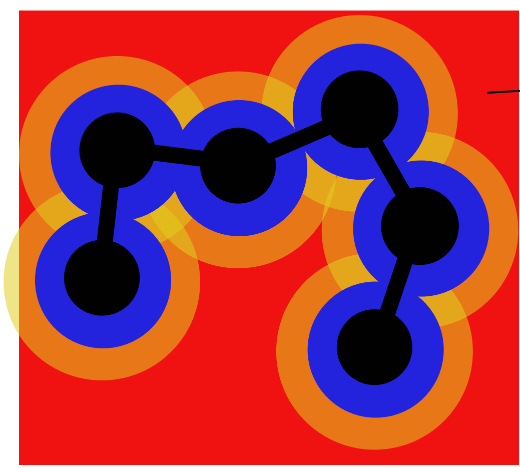
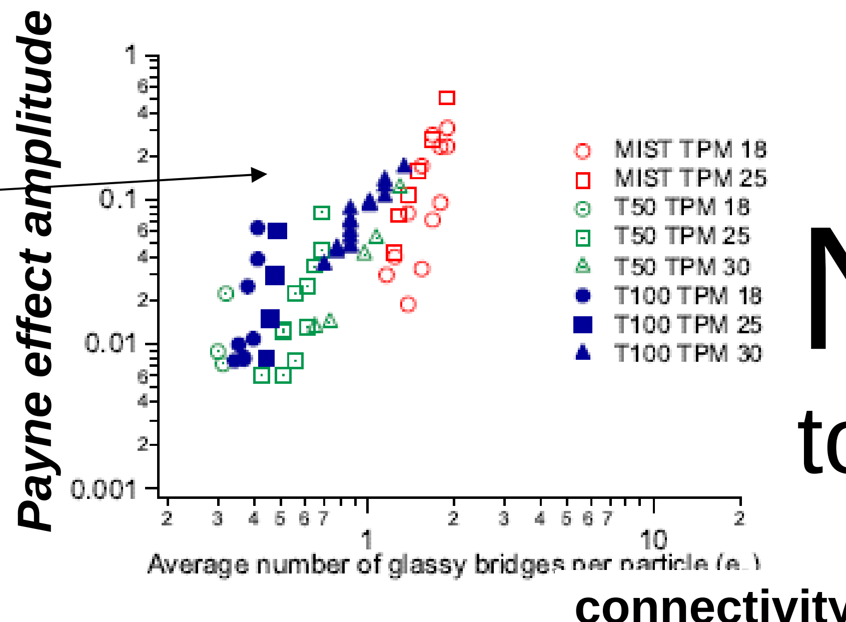


Fig. 6 Amplitude of the Payne effect as a function of the average number of immobilized bridges in various samples and several temperatures between 6 °C to 70 °C. The line is a guide for the eyes.

OK

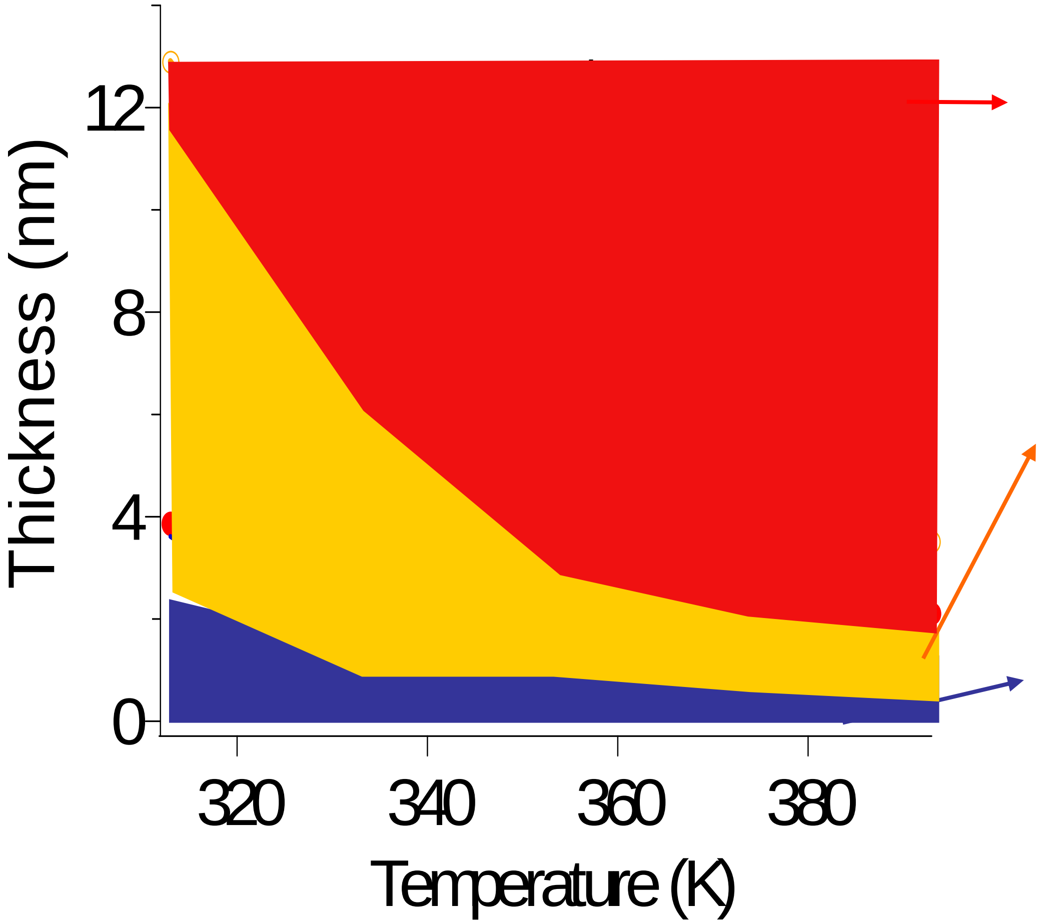




No

too low

Elastomer dynamics modification analysis



Elastomer dynamics
(exponential signal)

Intermediate dynamics
Not seen by DSC, but relevant for mechanics

Glassy dynamics Similar to gradient of Tg analysis, seen by DSC

A. Papon et al Macromolecules, 2011, 44, 913.

Conclusion

In nanocomposite , confinements leads to :

- A shift of the glass transition temperature

- A broadening of the glassy dynamics (for the low frequency)

➔ calorimetry is moslty sensible to the shift of Tg

➔ mechanics is sensible to the broadening

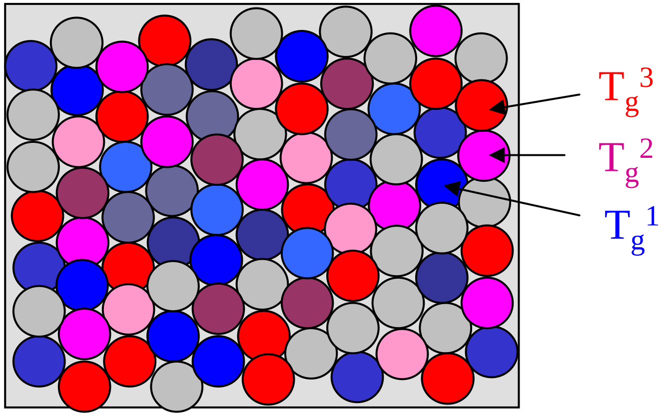
Papon et al *Soft Matter 2012*

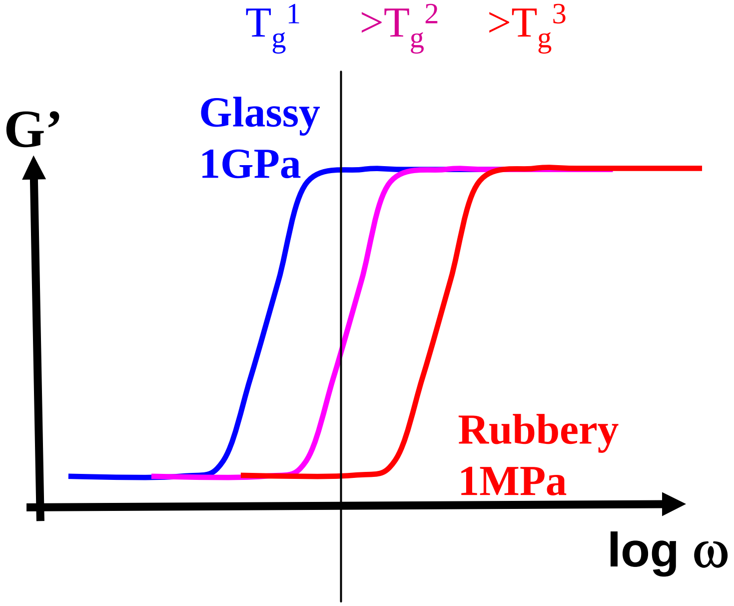
Understanding the dynamics near the particles

Slide from Peiluo Shi lecture:

Rheology prediction

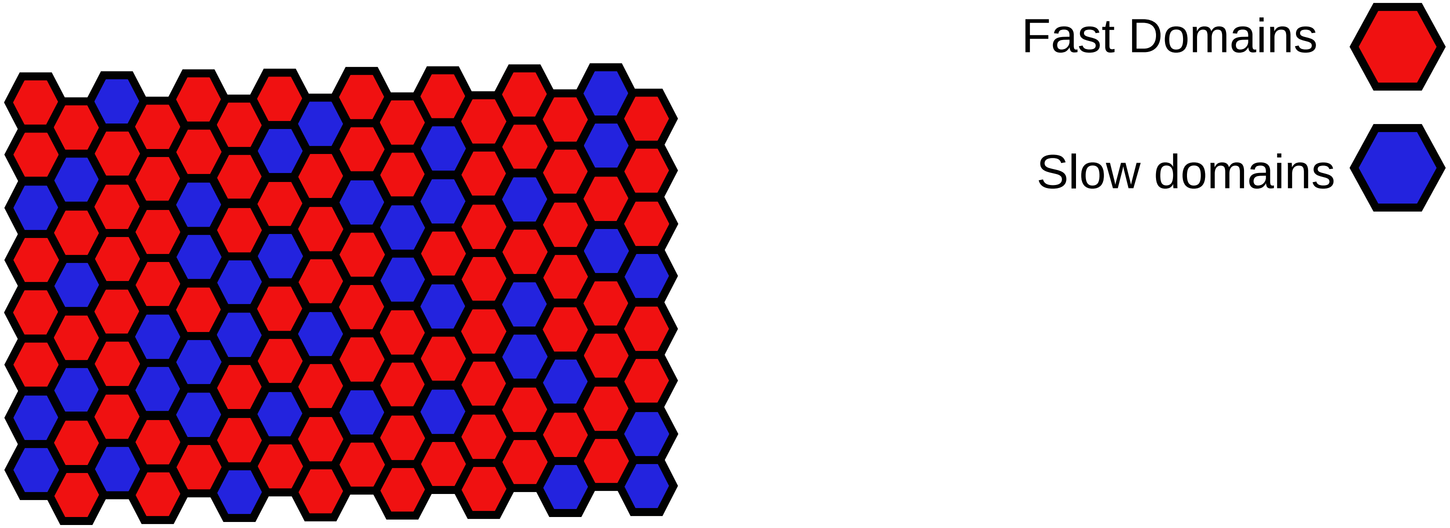
P(log τ) or *P(Tg)*



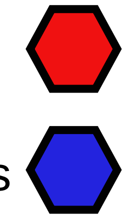


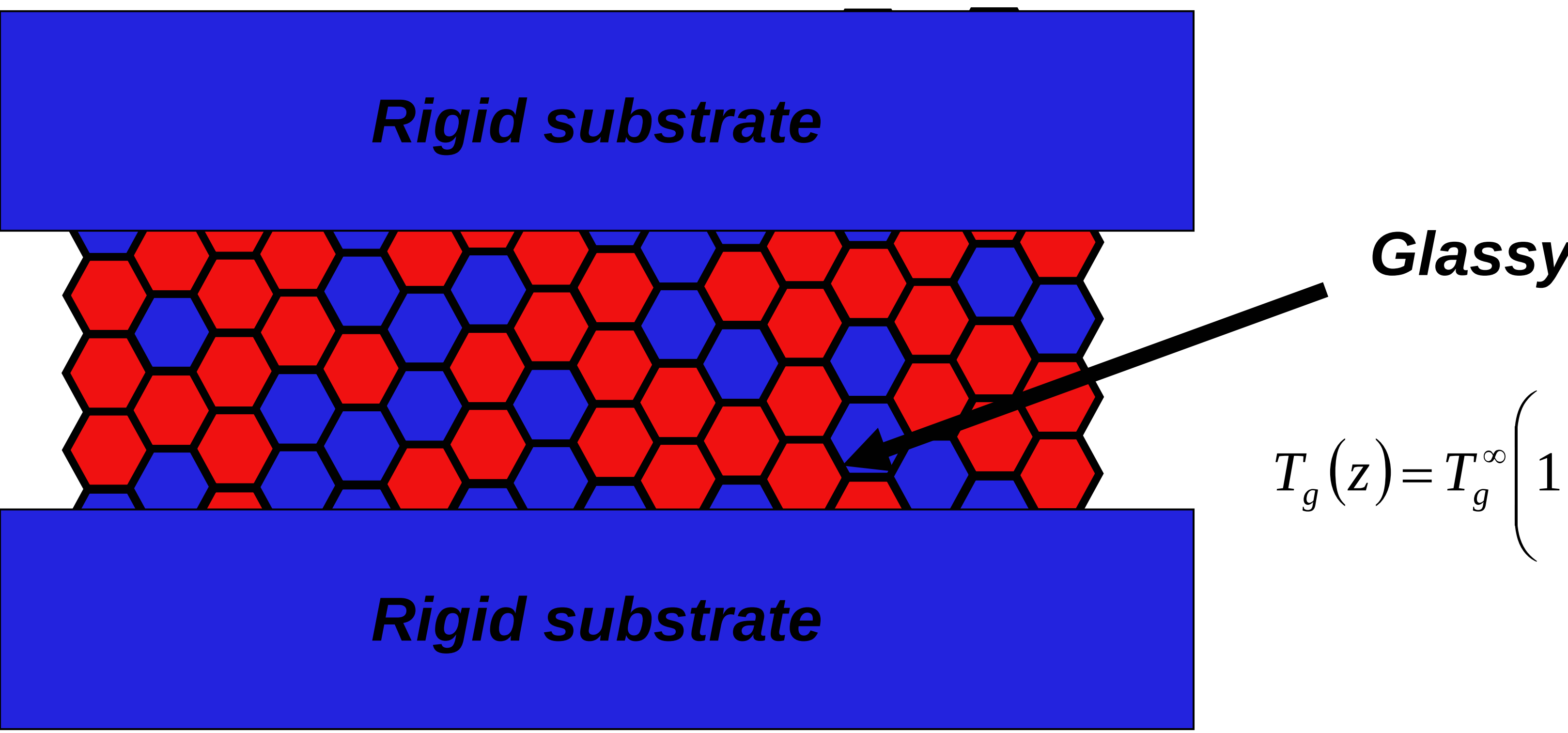
Tg gradient model Long D., Lequeux F. *EPJE* 2001

➔ ***Percolation approximation (rigid/soft domains approximation)***



Melt in the bulk at the time scale considered





$$T_g(z) = T_g^{\infty}\left(1+\left(\frac{\delta}{z}\right)^{1/\nu}\right)$$

The rigidity is ensured by the percolation of slow domains, propagates near a rigid wall

Percolation like propagation near a solid surface

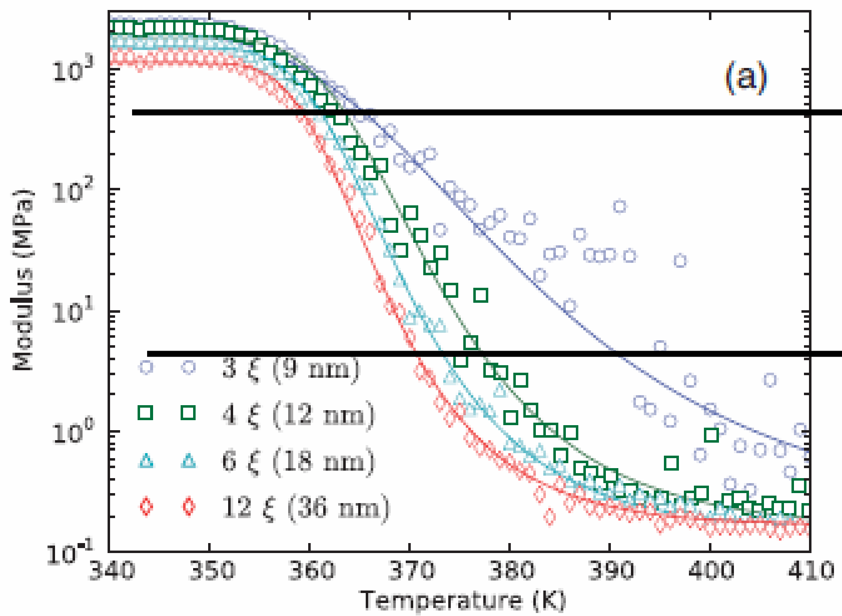
ν=0.88 (3d percolation exponent for spatial correlation)

Beyond the rigid/soft domains approximation:

A. Dequidt lecture

Simulation paper by A. Dequidt et al (see Friday, presentation of Alain Dequidt)

Eur. Phys. J. E (2012) **35**: 61

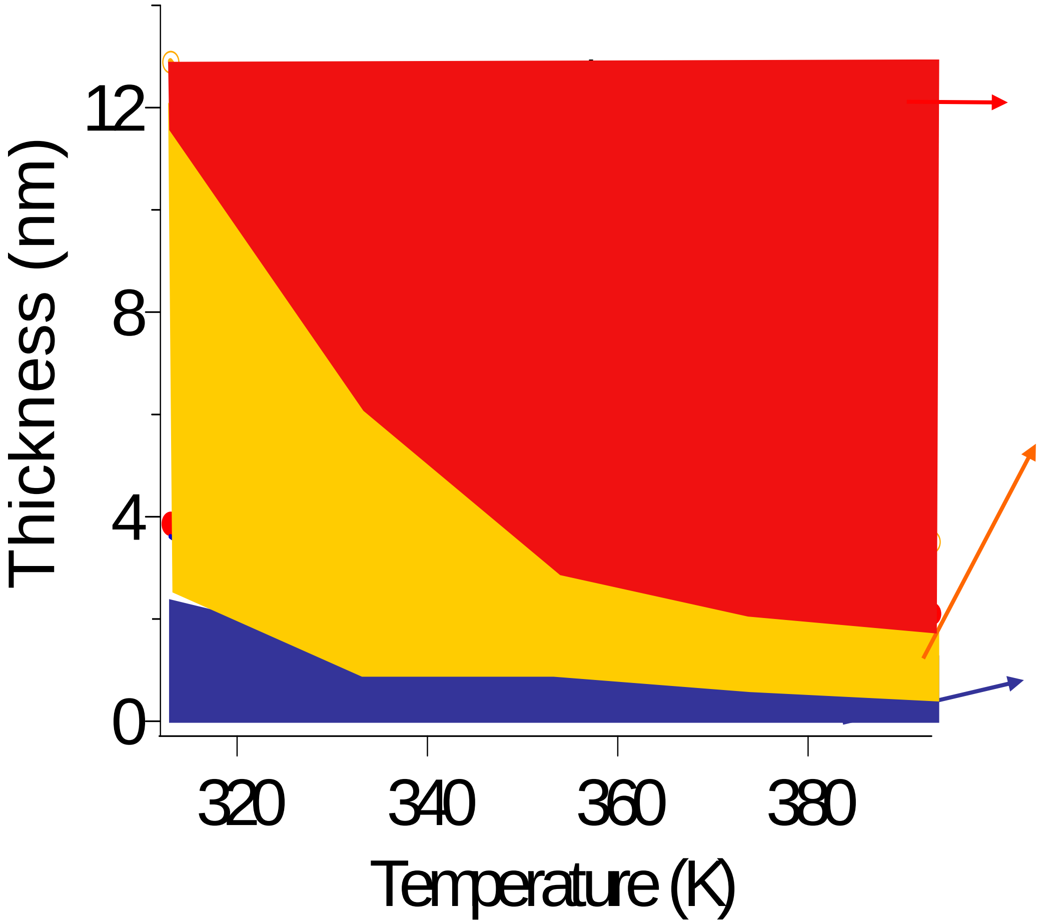


fast modes : short range, DSC

Slow modes : long range, mechanics

→ The range of the confinement effect depends on the measured parameter !!

Elastomer dynamics modification analysis



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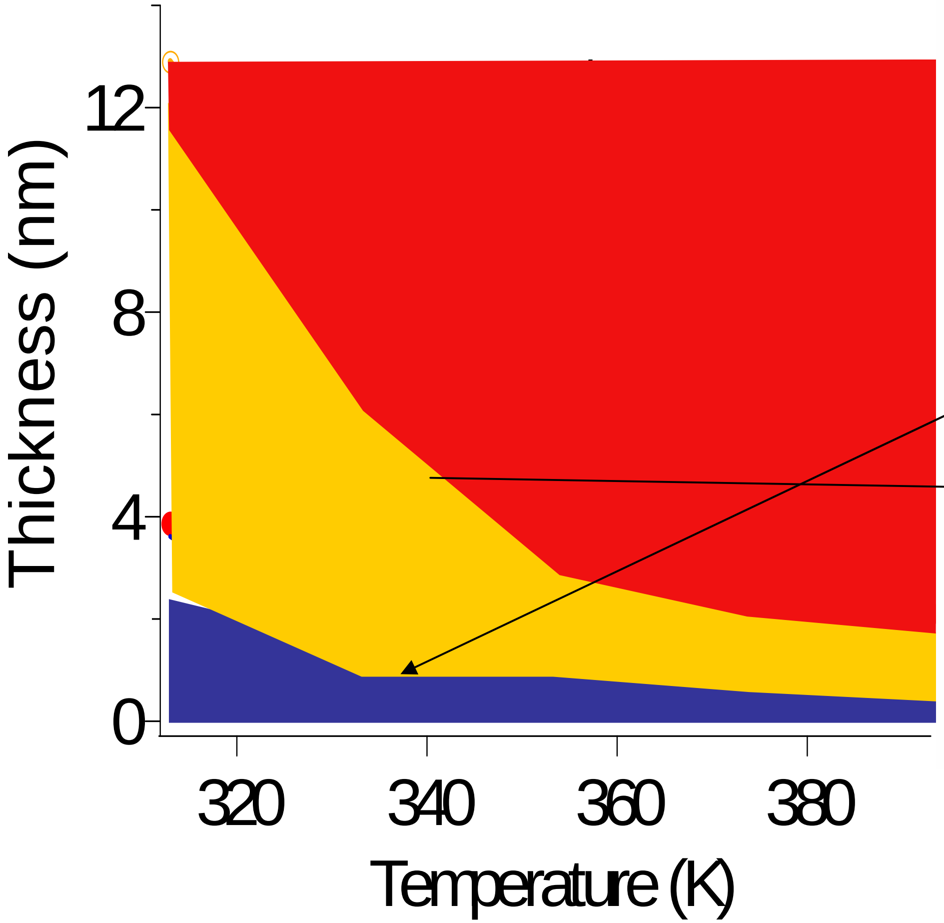
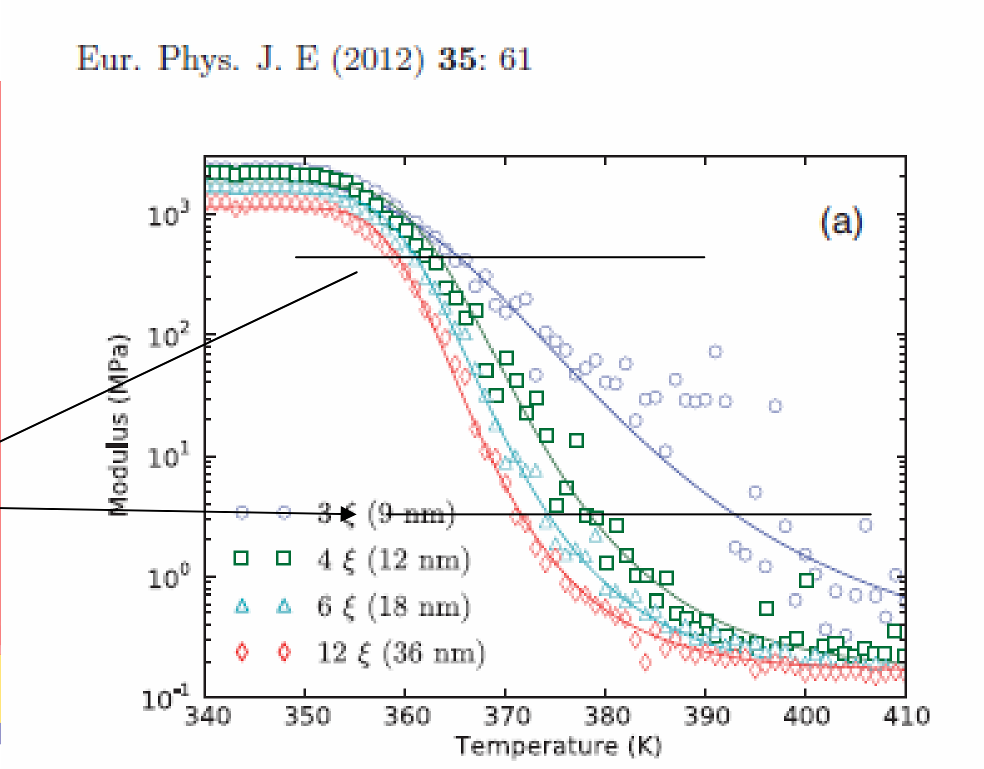
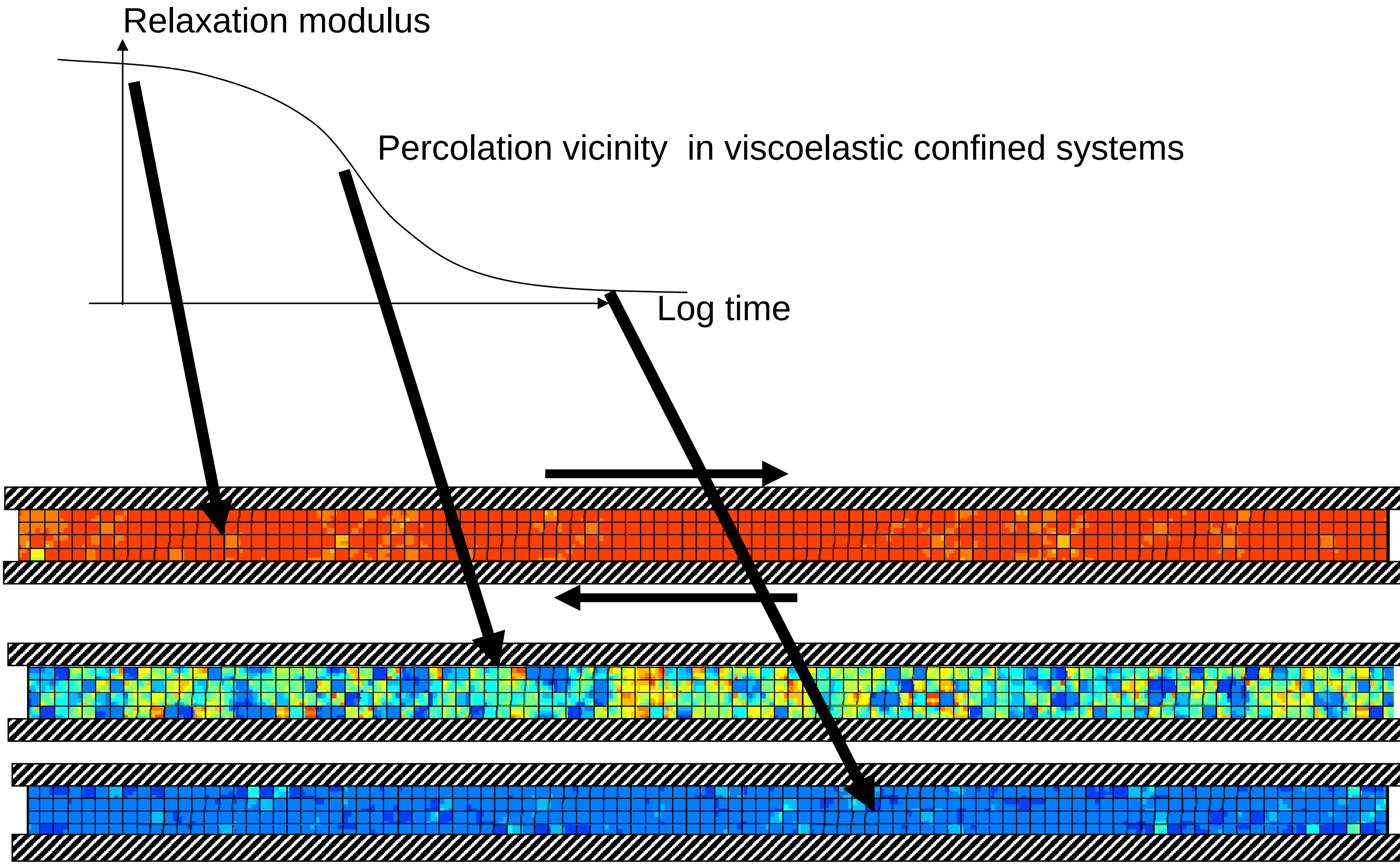
Elastomer dynamics modification analysis





Finite elements simulations similar to Peiluo SHI, but for confined system (in progress).



Take home message

1)In nanocomposite , polymer confinements leads to a modification of the mechanics near the fillers

2) It can be approximated by a gradient of glass transition, but the range depends on the measured quantity

3) It originates mainly in the dynamical heterogeneities of glasses

➔ Need to develop approaches that do not approximate mechanics by simple stress (or strain) average.