Rheology of complex macromolecules: Relating their composition to their viscoelastic properties

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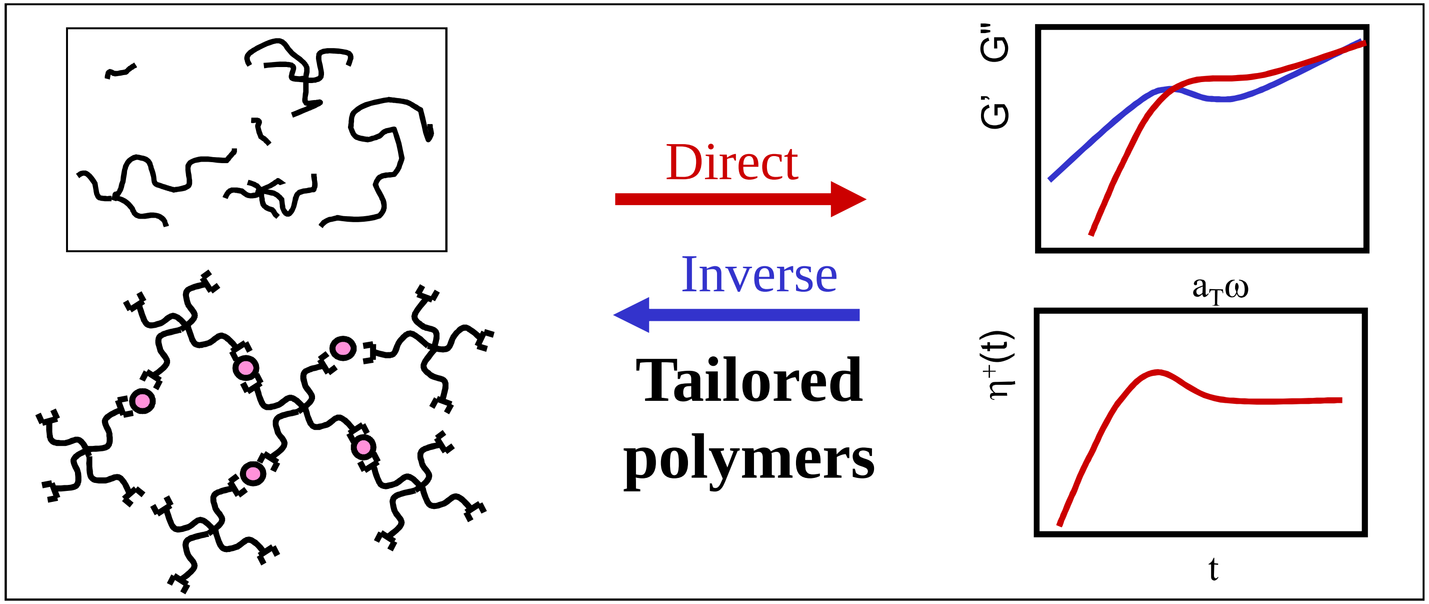
May 18, Gent

Structure - LVE relationship for complex polymers:



Molecular structure

Flow properties

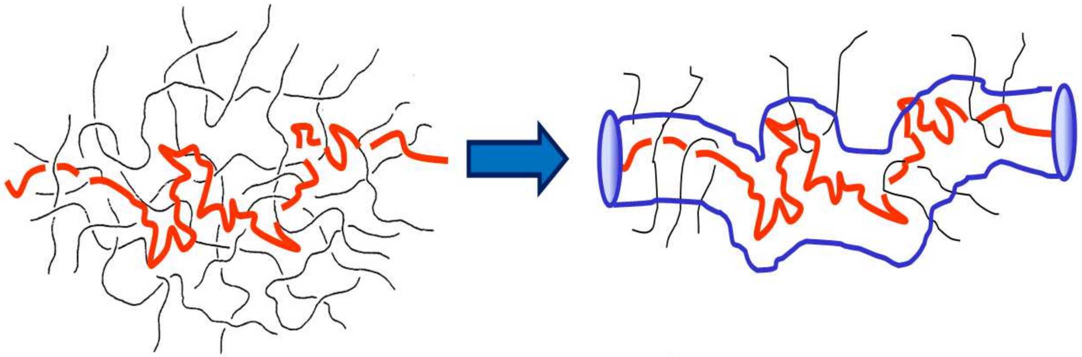
Linear regime

Modeling: Working on model polymers

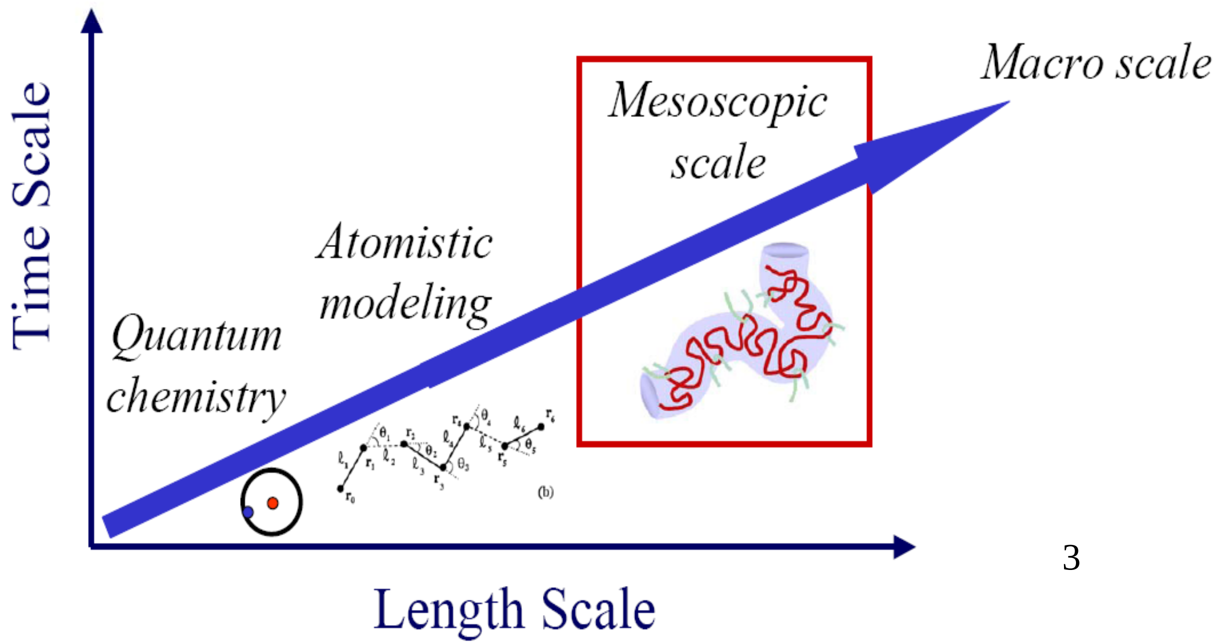
- polydisperse polymers
- Sample characterization
- Supramolecular polymers

Tube model – At the mesoscopic scale

Tube-based model for predicting the LVE of complex polymer melts

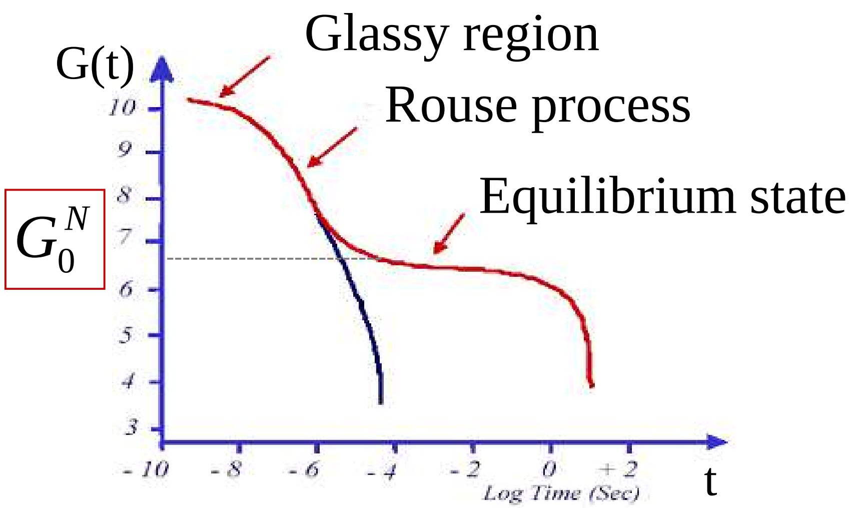


de Gennes, Doi and Edwards

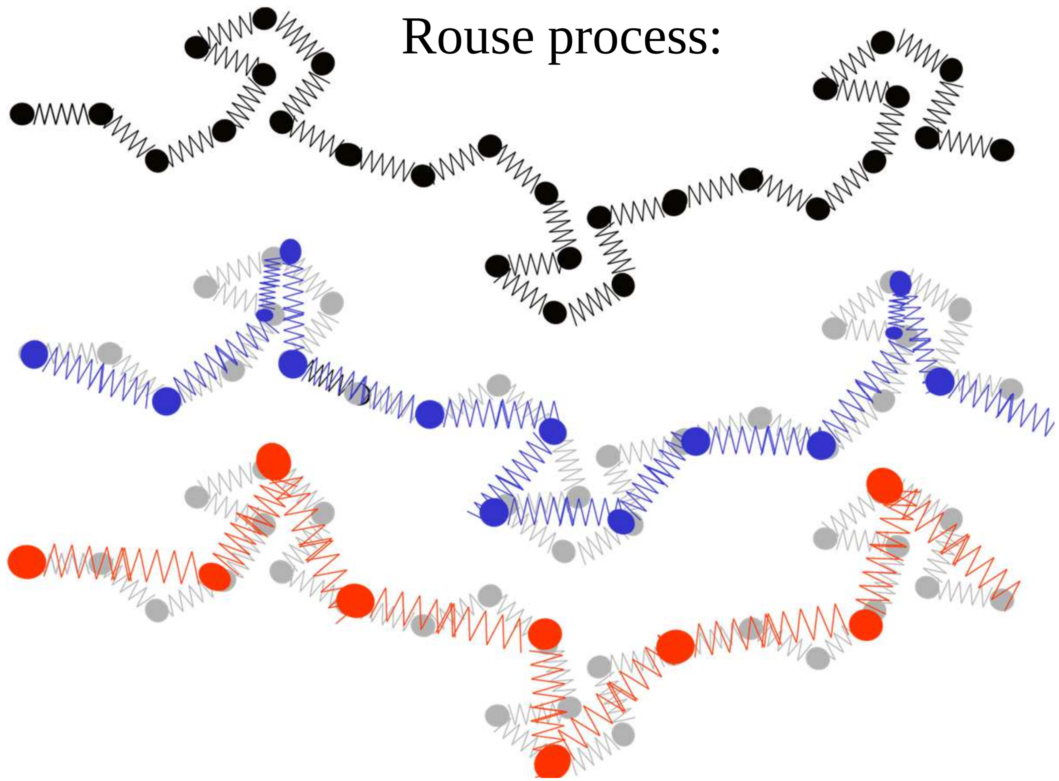


Relaxation modulus of a polymer

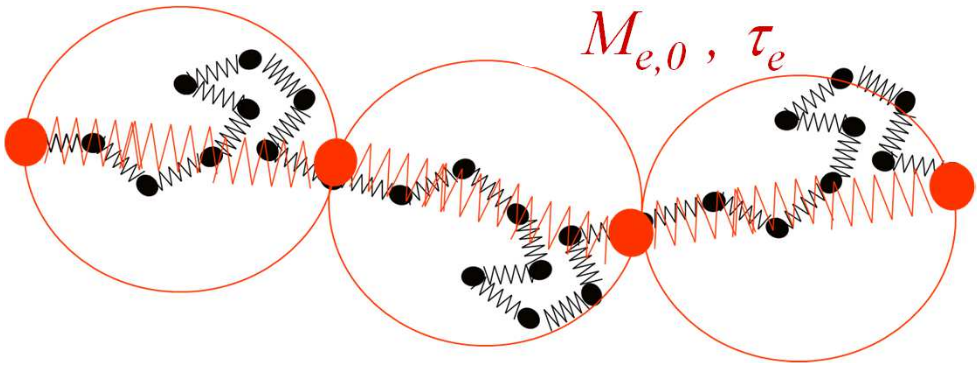
Relaxation modulus:



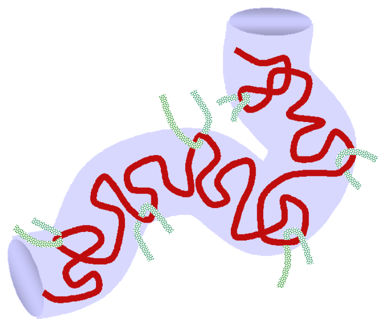
Rouse process:



Equilibrium state:



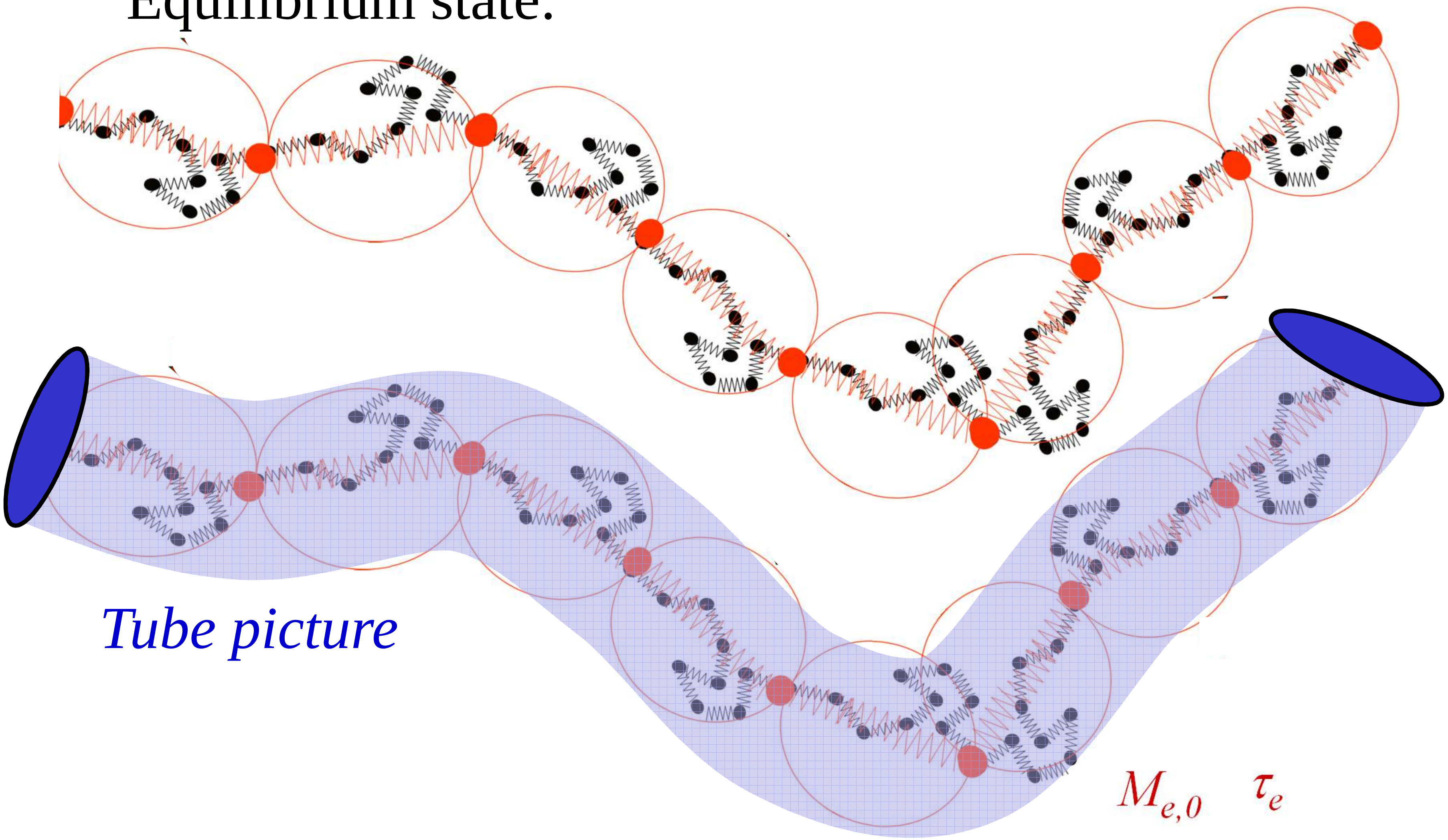
$$G_0^N = \frac{4}{5}\frac{\rho RT}{M_e}$$



Doi & Edwards (1967), de Gennes (1971)

Tube picture

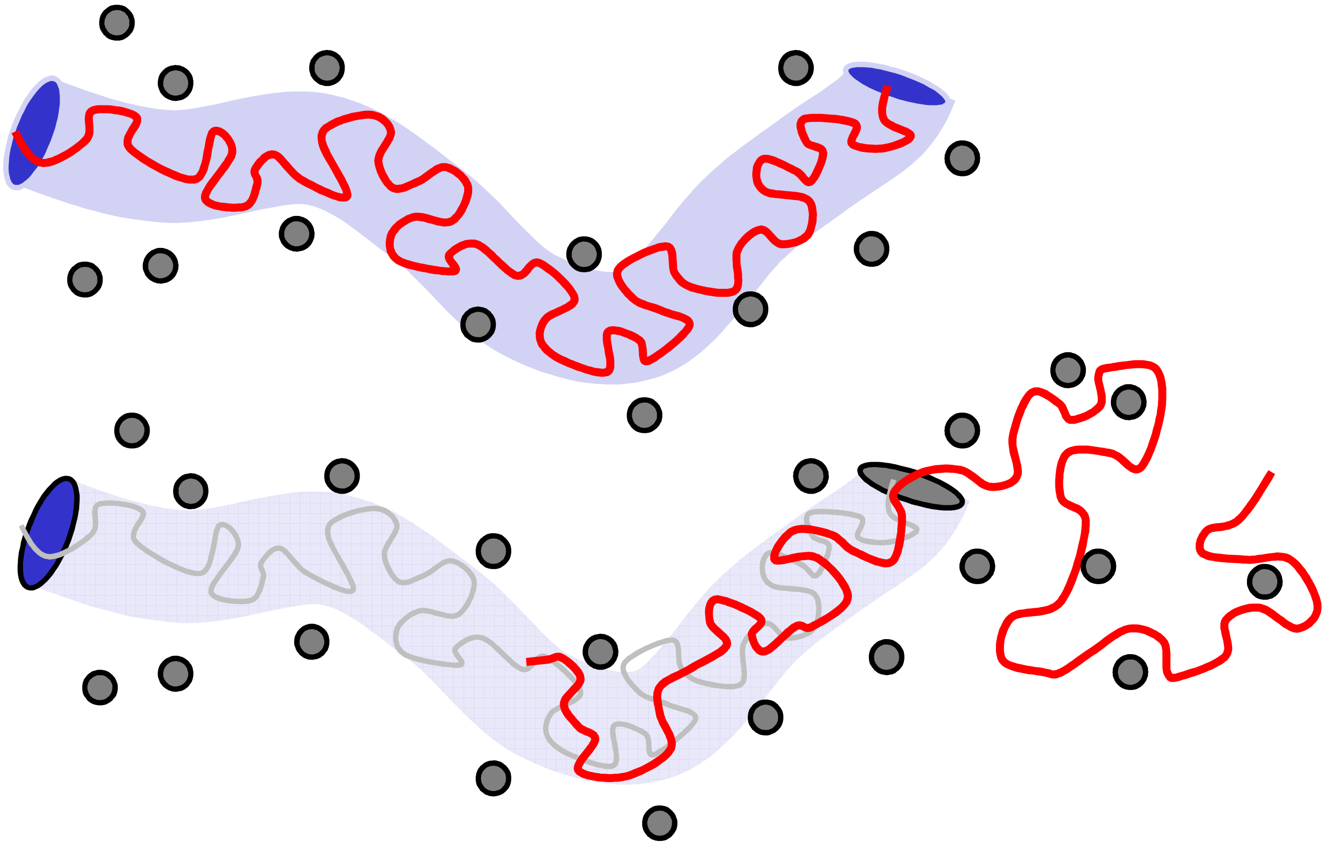
Equilibrium state:



Doi & Edwards (1967), de Gennes (1971)

Relaxation modulus of a polymer

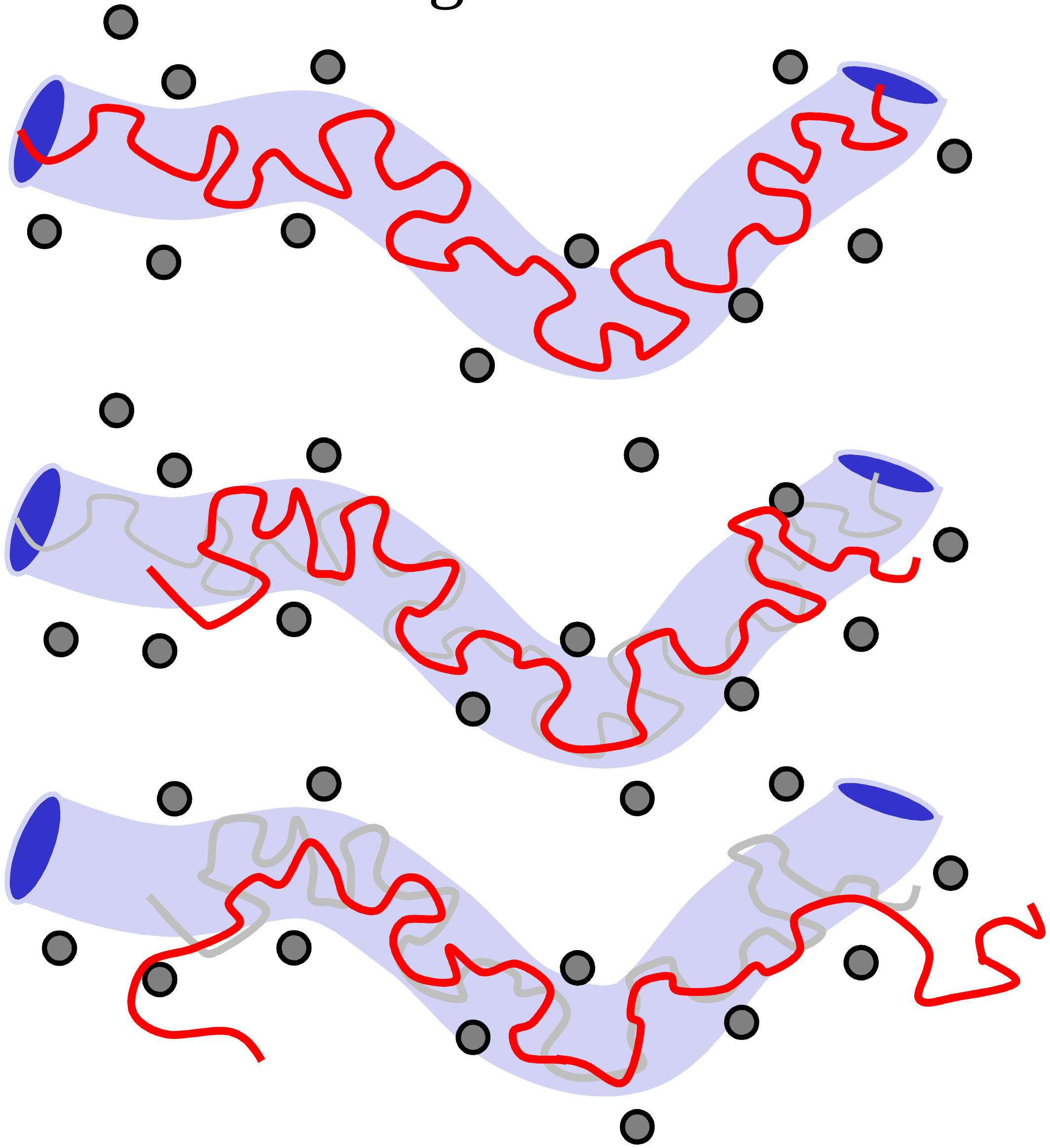
Reptation process



Diffusion process along the curvilinear axis of the tube

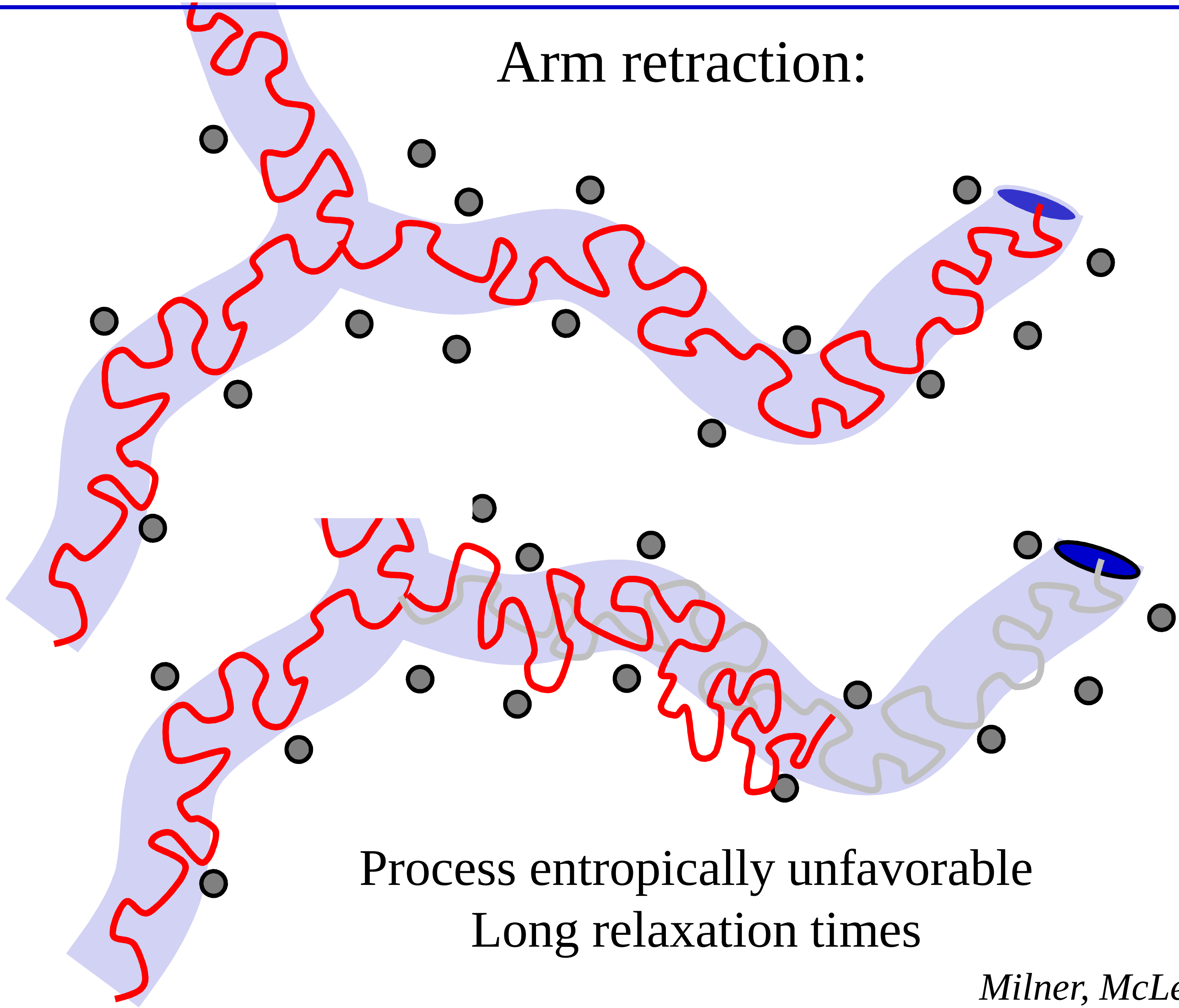
Relaxation modulus of a polymer

Contour length Fluctuations:



Relaxation modulus of a polymer

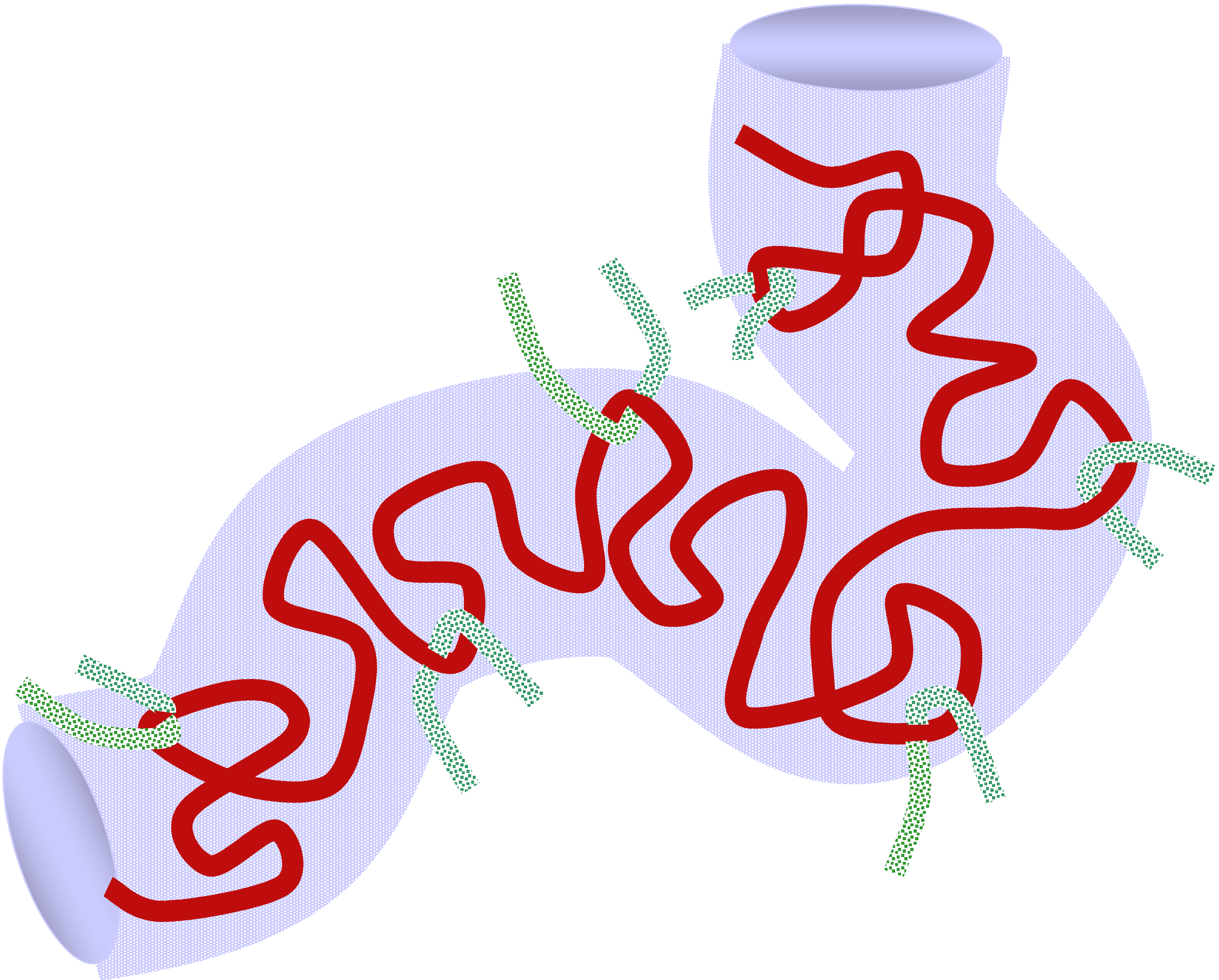
Arm retraction:



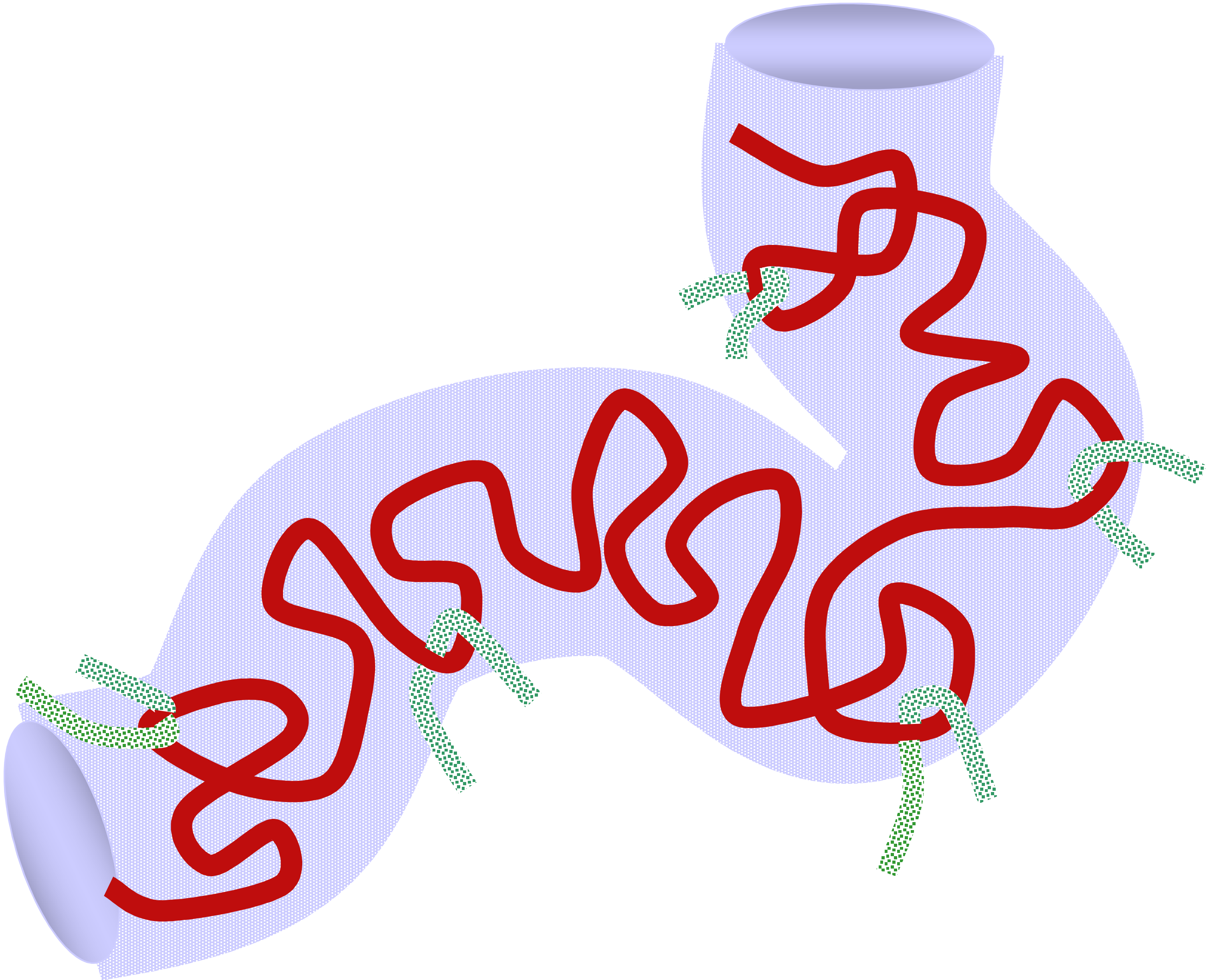
Process entropically unfavorable
Long relaxation times

Milner, McLeish 1997

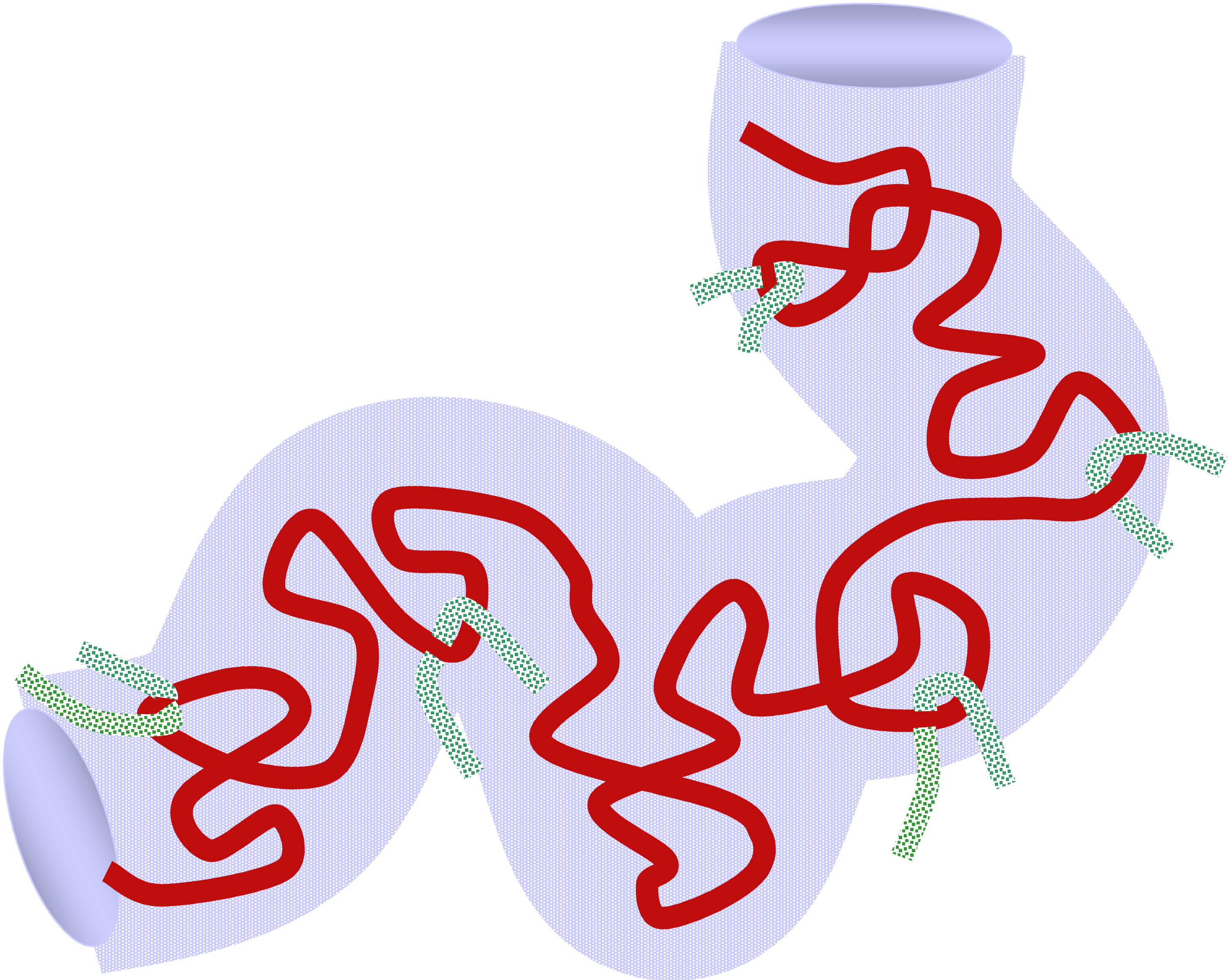
Constraint Release processes (CR)



Constraint Release processes (CR)

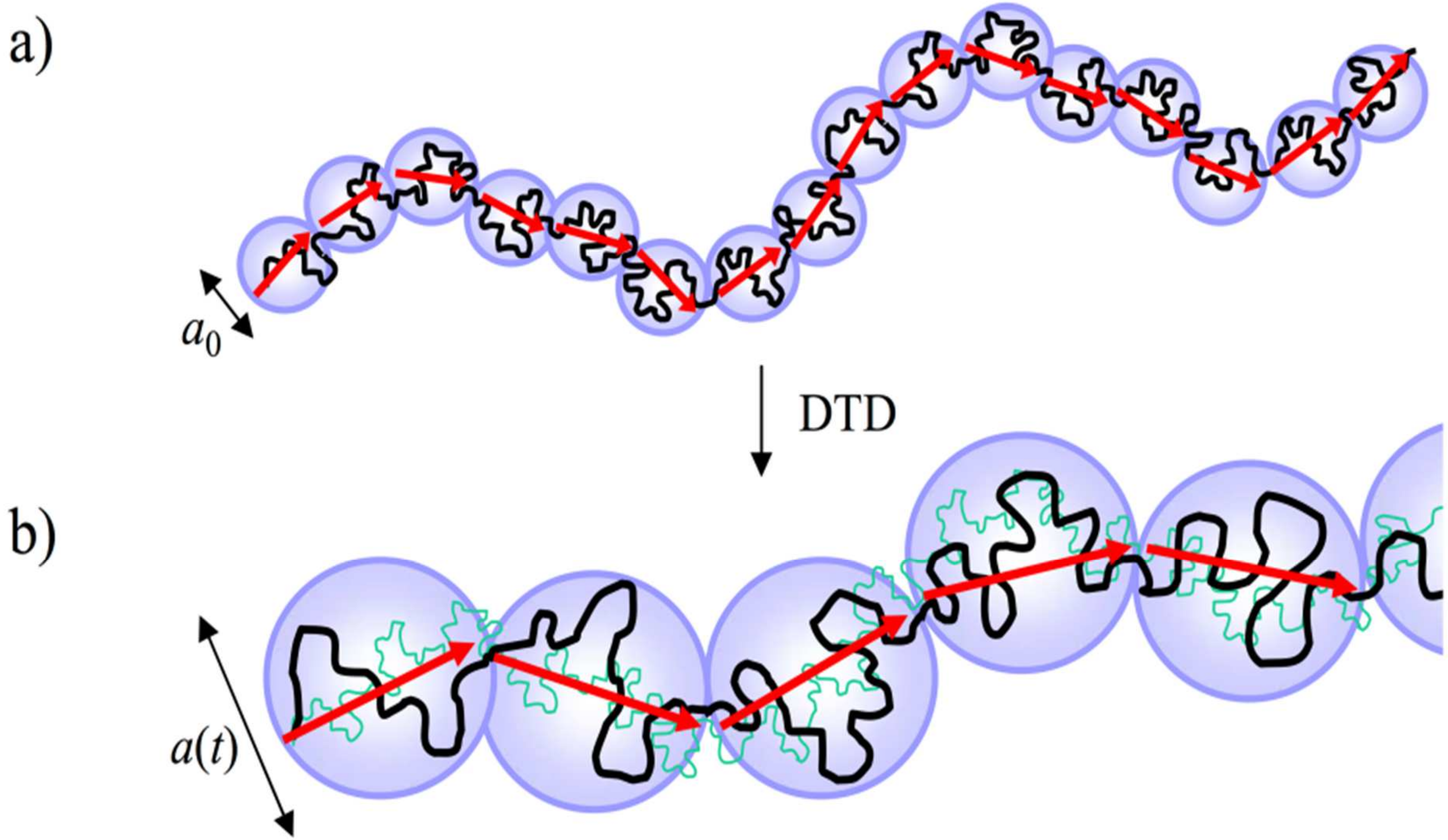


Constraint Release processes (CR)



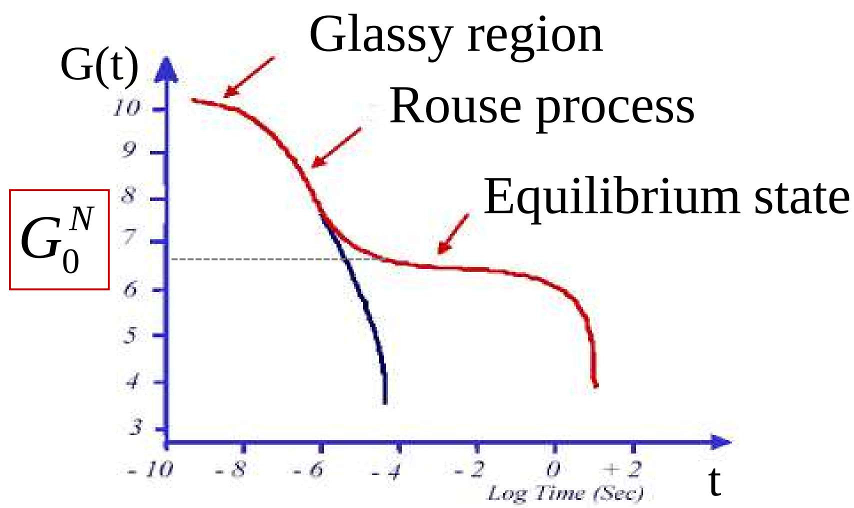
Constraint Release processes (CR)

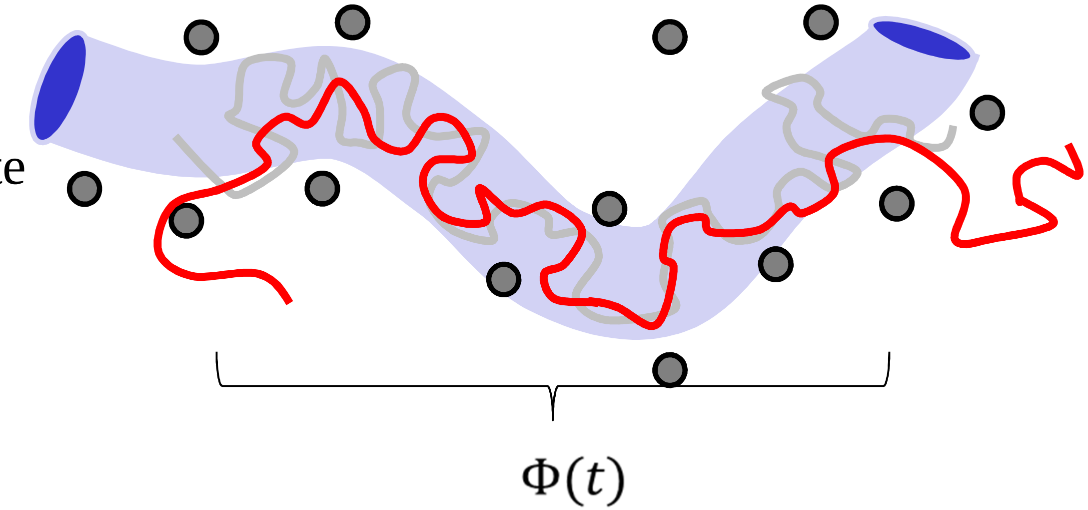
Dynamic tube dilation:



The polymer fraction already relaxed = solvent

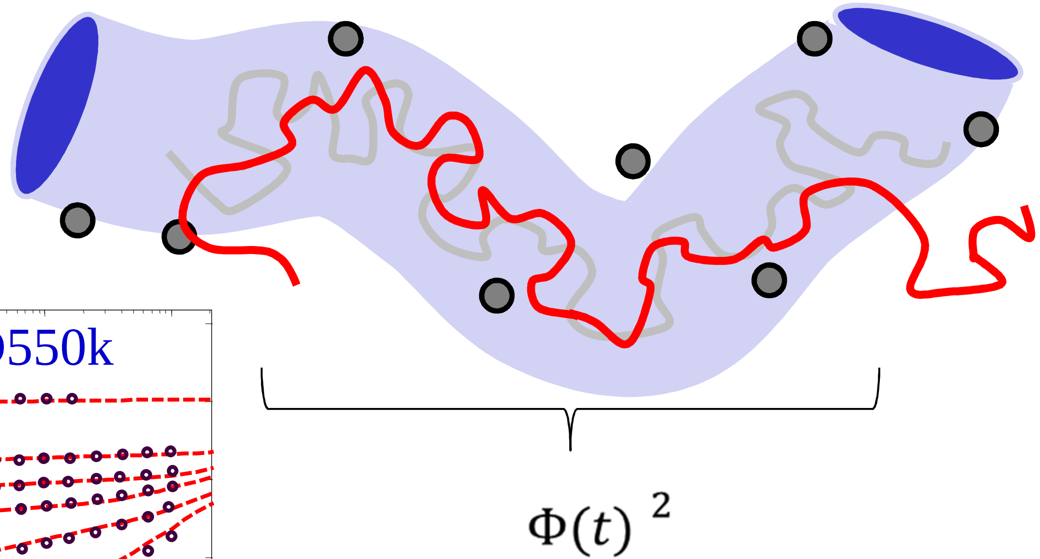
Relaxation modulus of a polymer

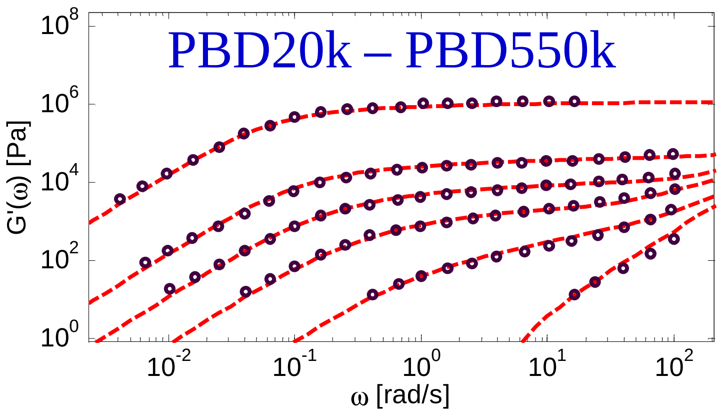




$$G(t) = G_{Rouse}(t) + \frac{\rho RT}{M_e(t)}\Phi(t)$$

$$G(t) = G_{Rouse}(t) + \frac{\rho RT}{M_{e,0}}\Phi(t)^{2}$$





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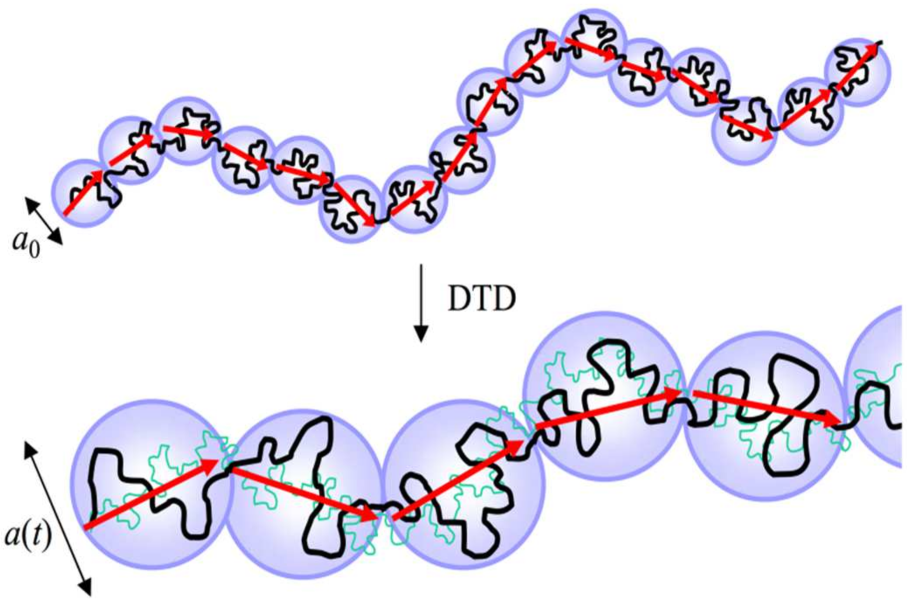
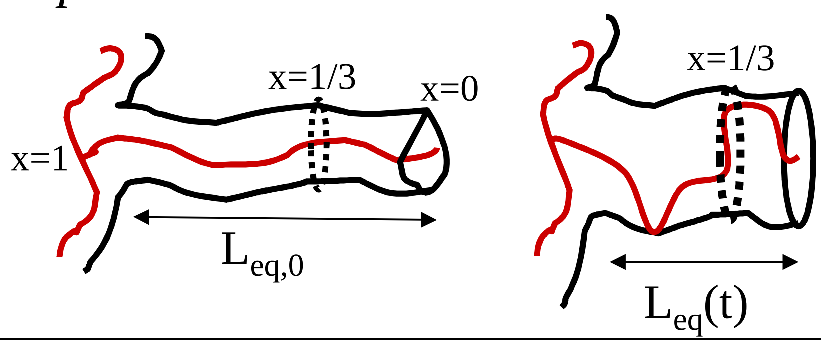


Local effect

On the reptation and the fluctuations process:



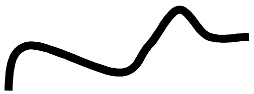
Speeds up the polymer relaxation

Inter-relationship between all the relaxation mechanisms

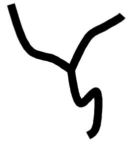
Marrucci, 1985

Structure - LVE relationship for complex polymers:

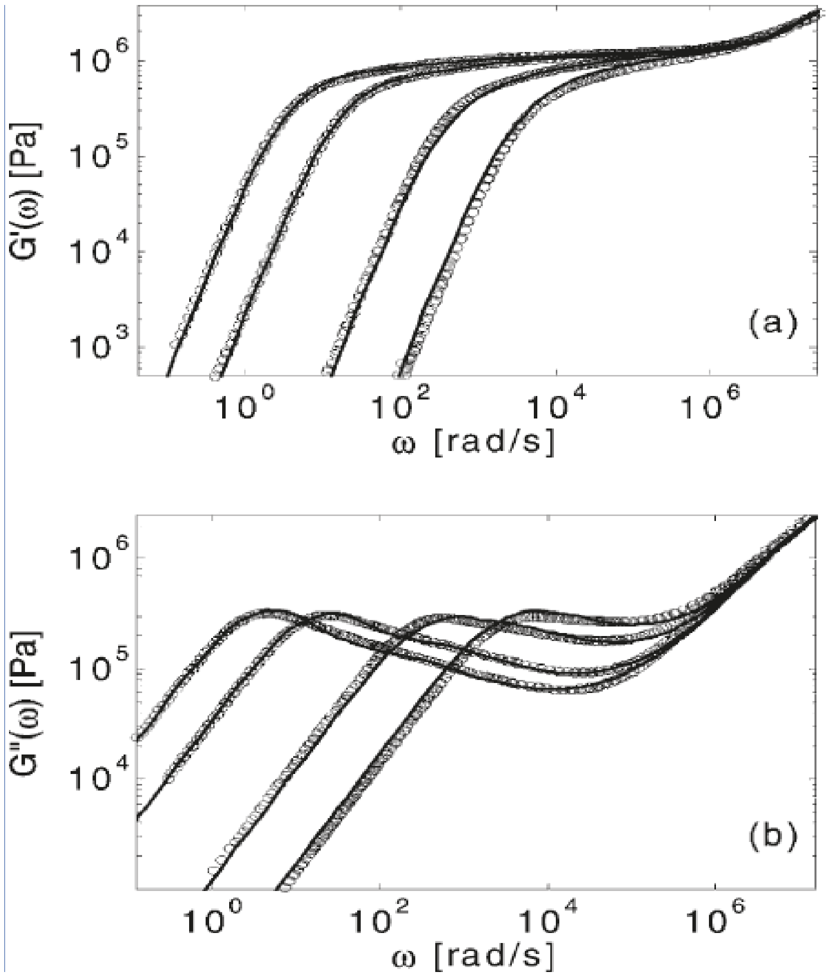
Model architectures:

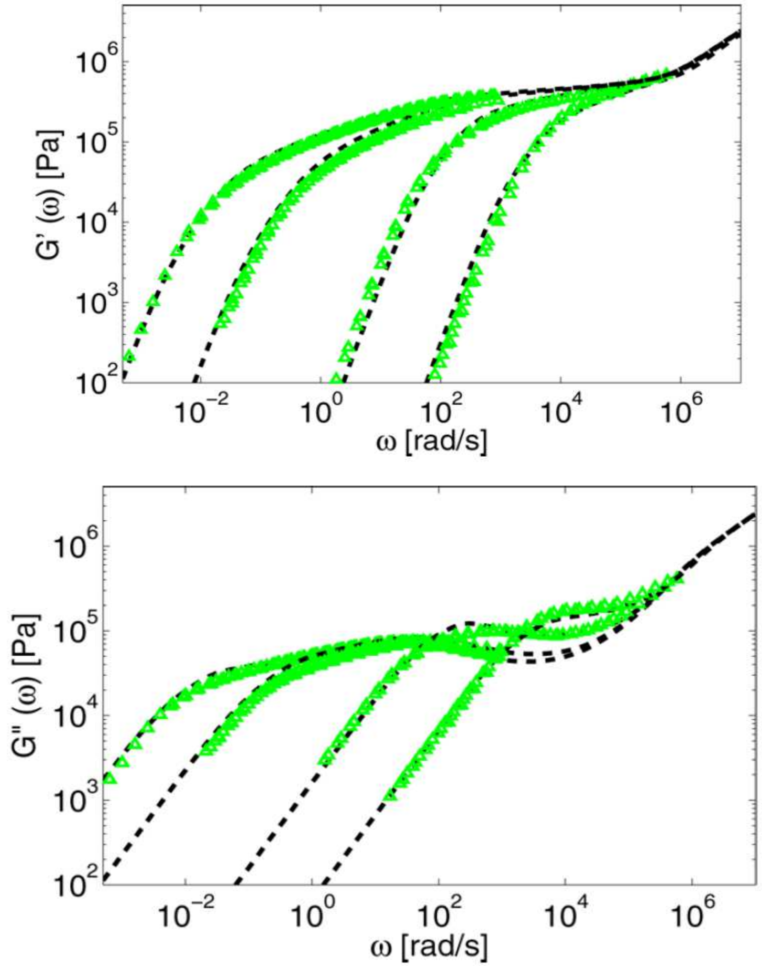


Linear chains

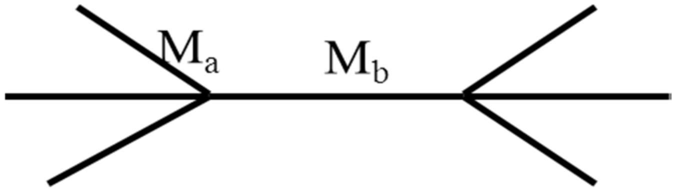


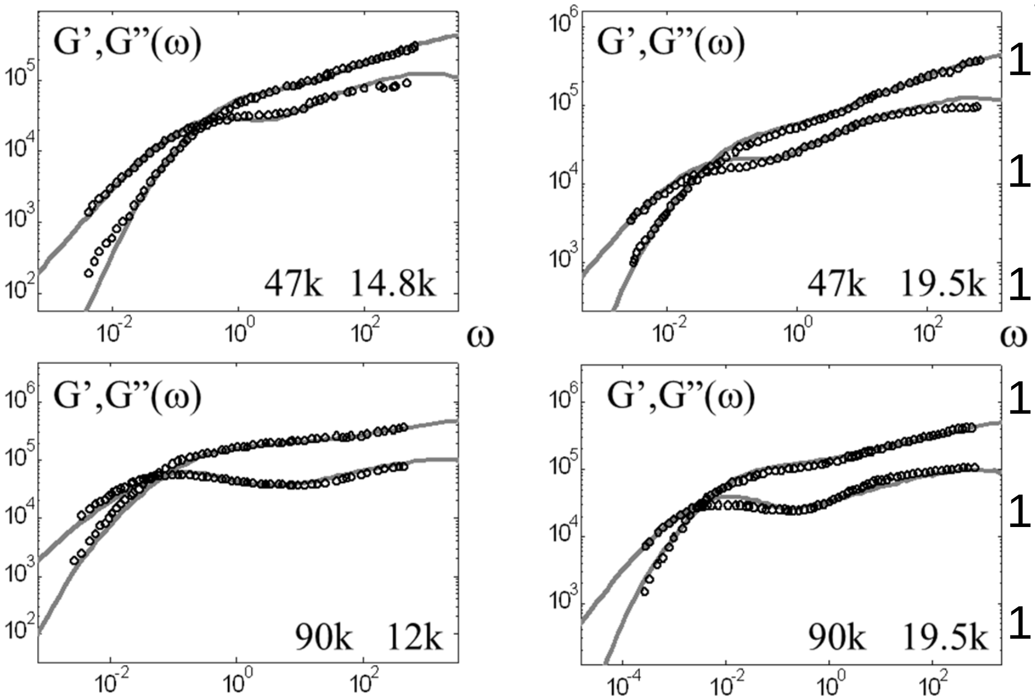
symmetric star

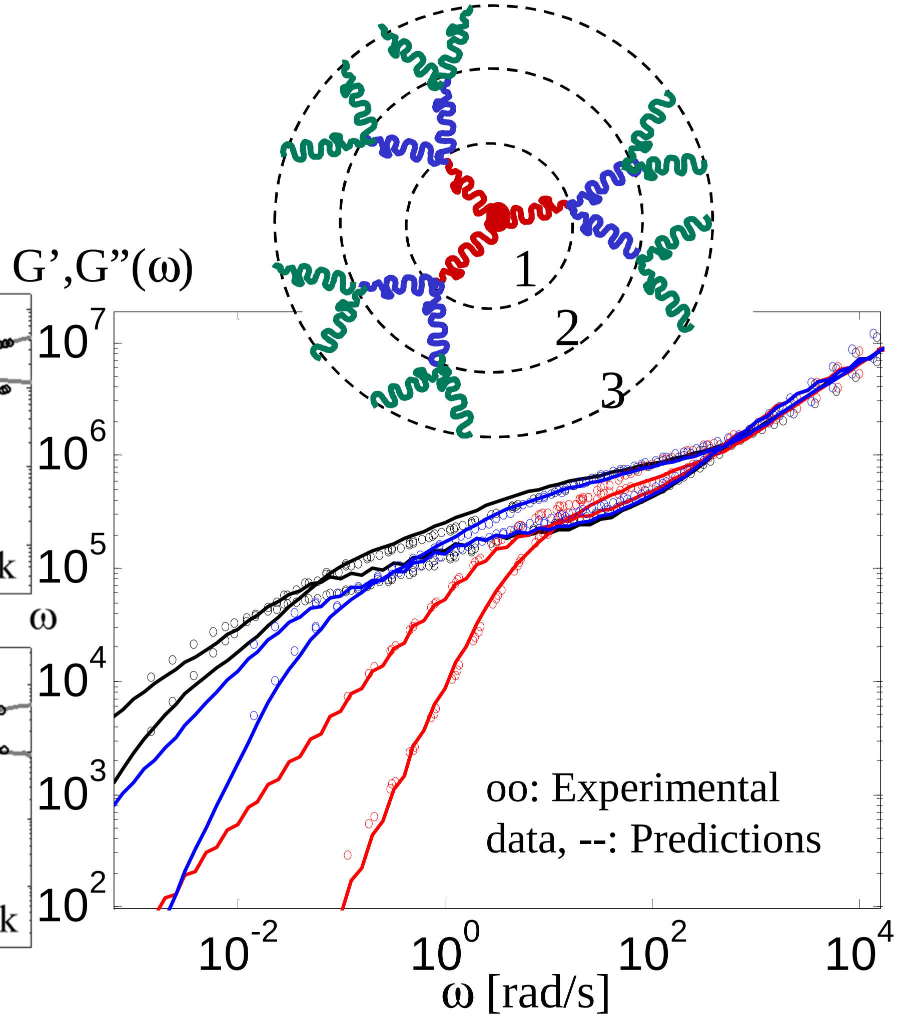




Structure - LVE relationship for complex polymers:







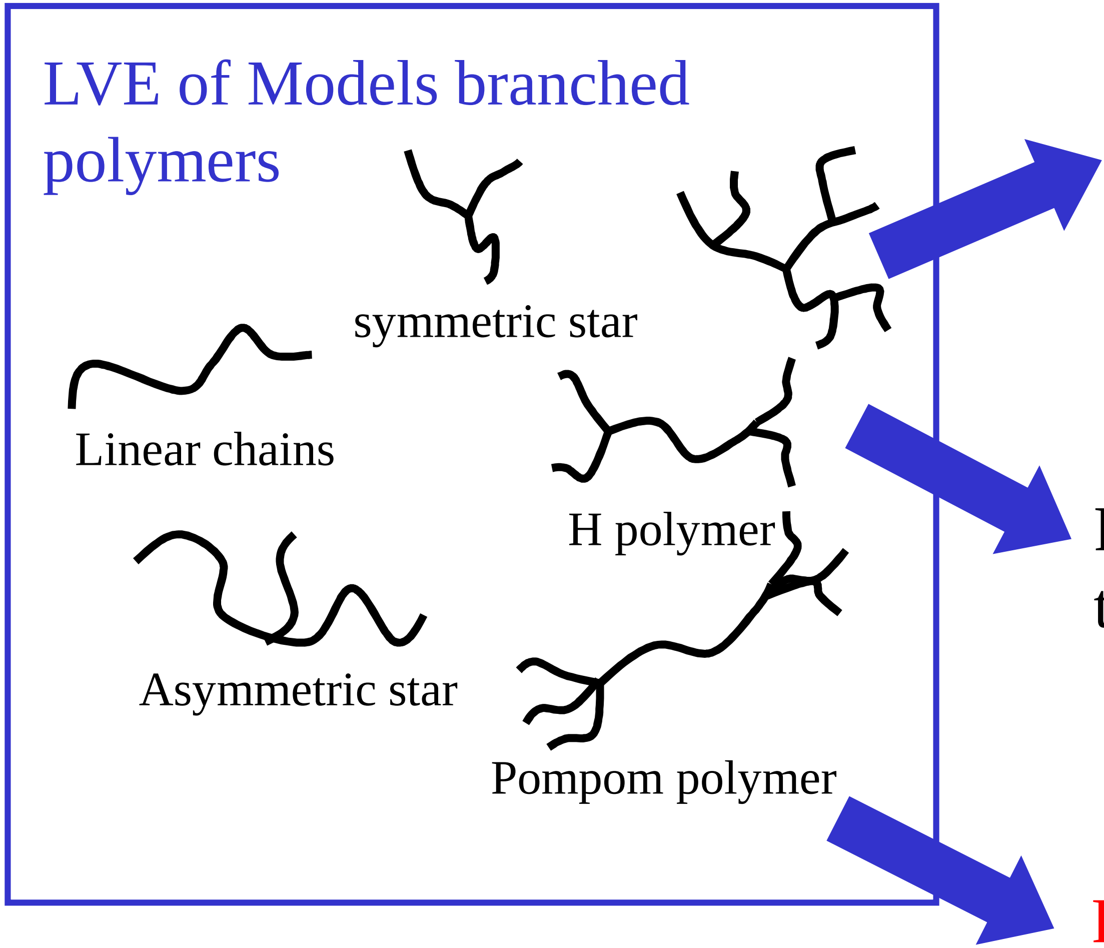
Hierarchy of relaxation processes

E. van Ruymbeke, R. Keunings, C. Bailly, J.N.N.F.M., 2005

E. van Ruymbeke, C. Bailly, R. Keunings, D. Vlassopoulos, Macromolecules, 2006.

M. Ahmadi, C. Bailly, R. Keunings, M. Nekoomanesh, E. van Ruymbeke, Macromolecules, 2011

Objectives

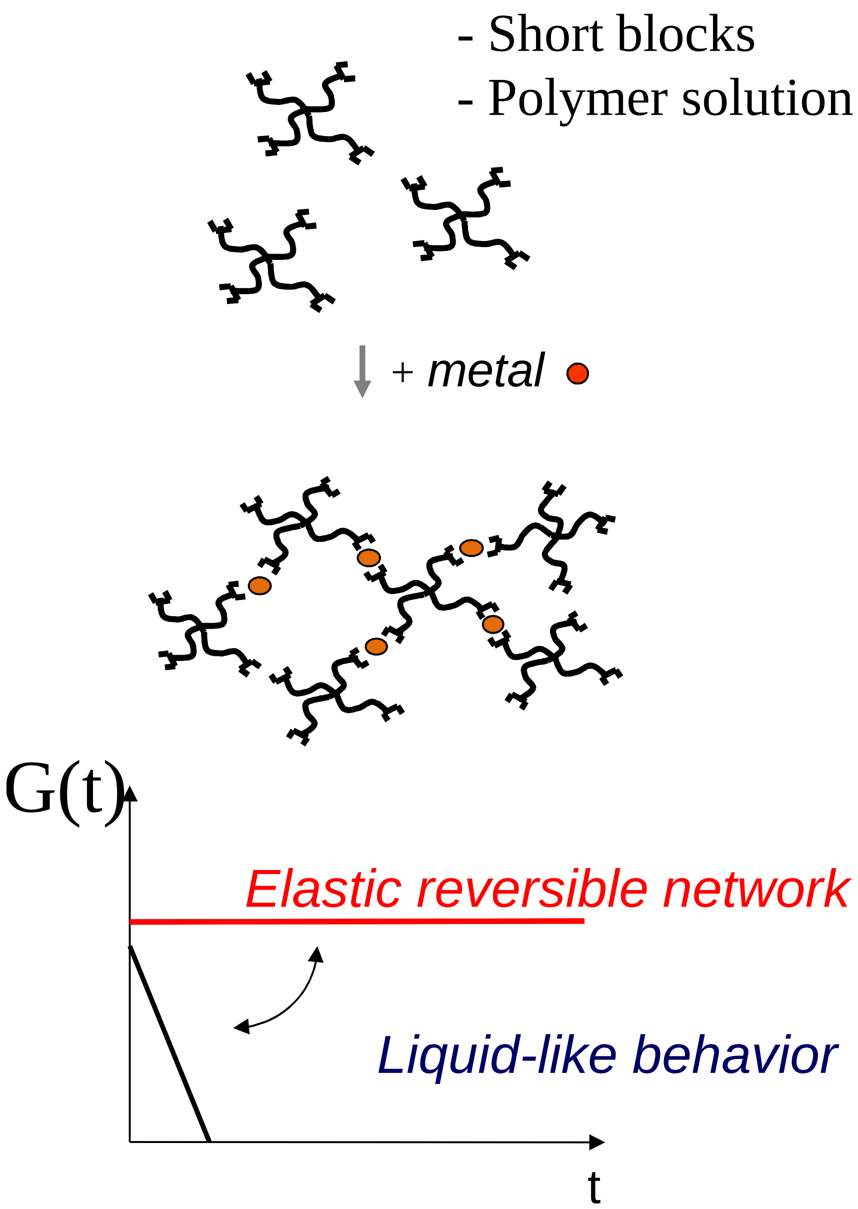


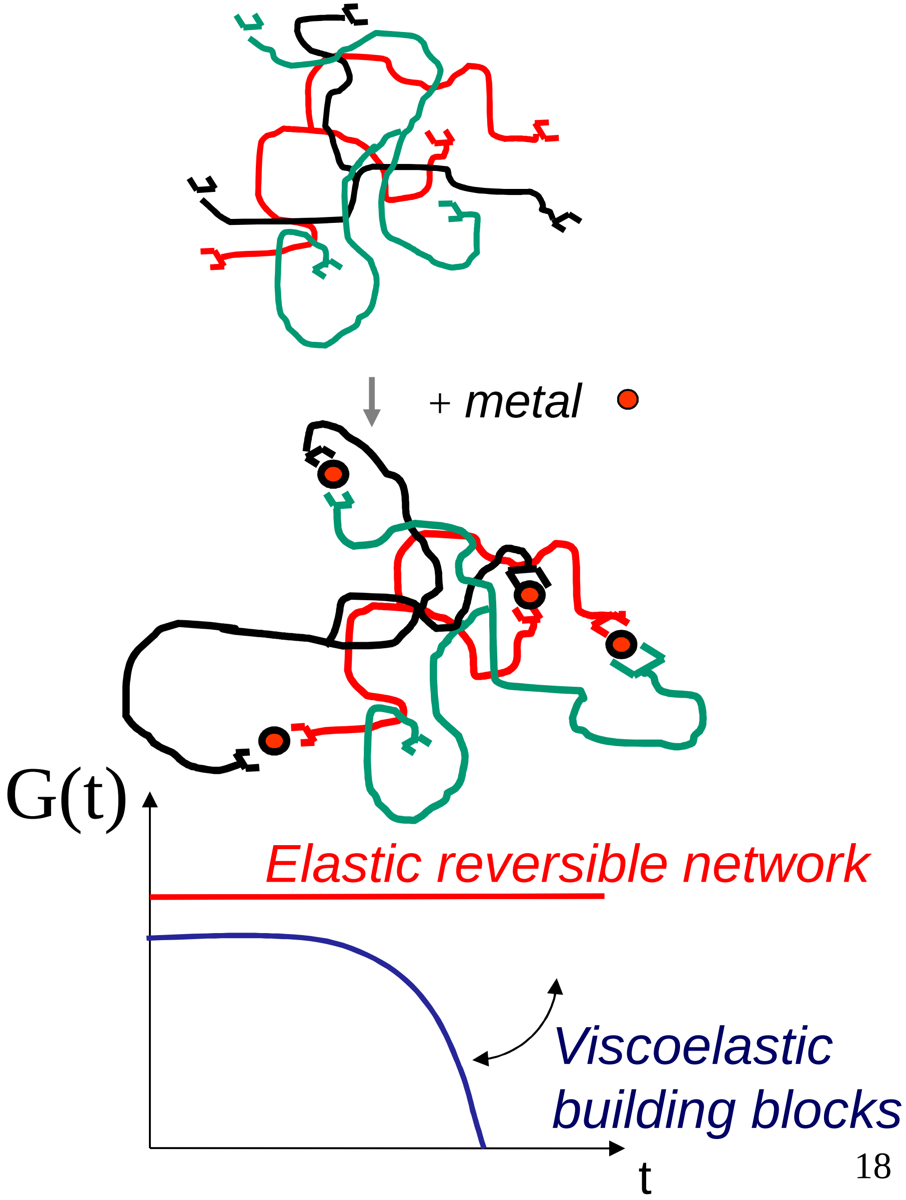
Rheology polydisperse samples

Rheology as characterization tool for industrial samples

Rheology of entangled associating polymers

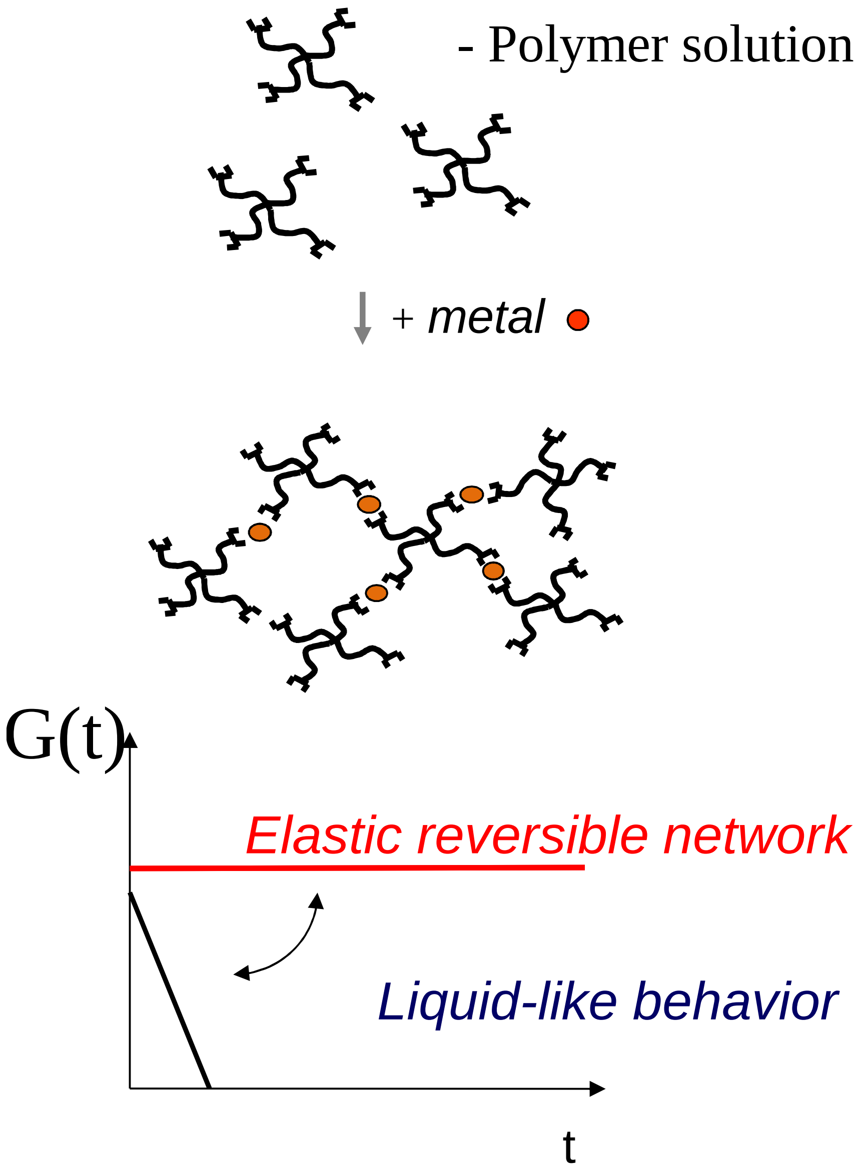
Unentangled versus entangled supramolecular building bocks

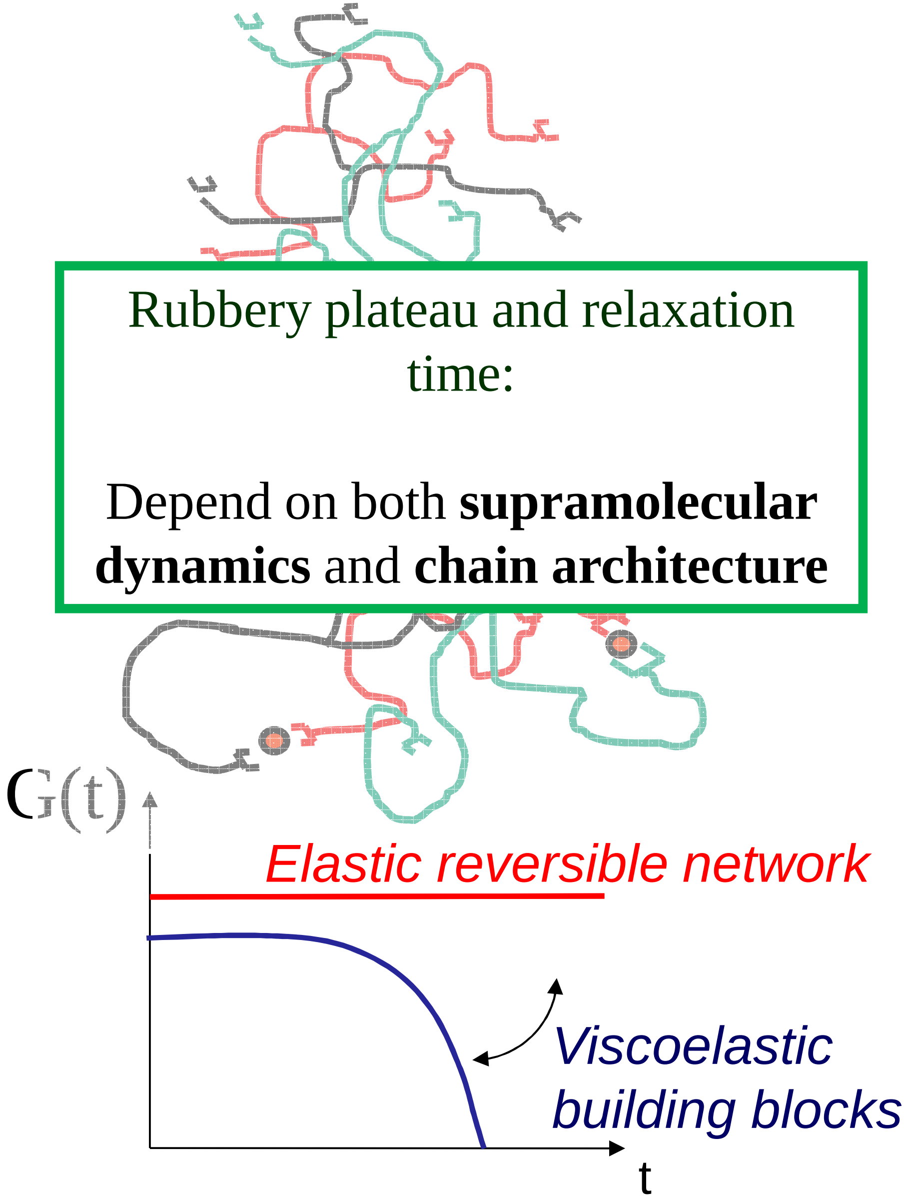




Unentangled versus entangled supramolecular building bocks

- Short blocks
- Polymer solution

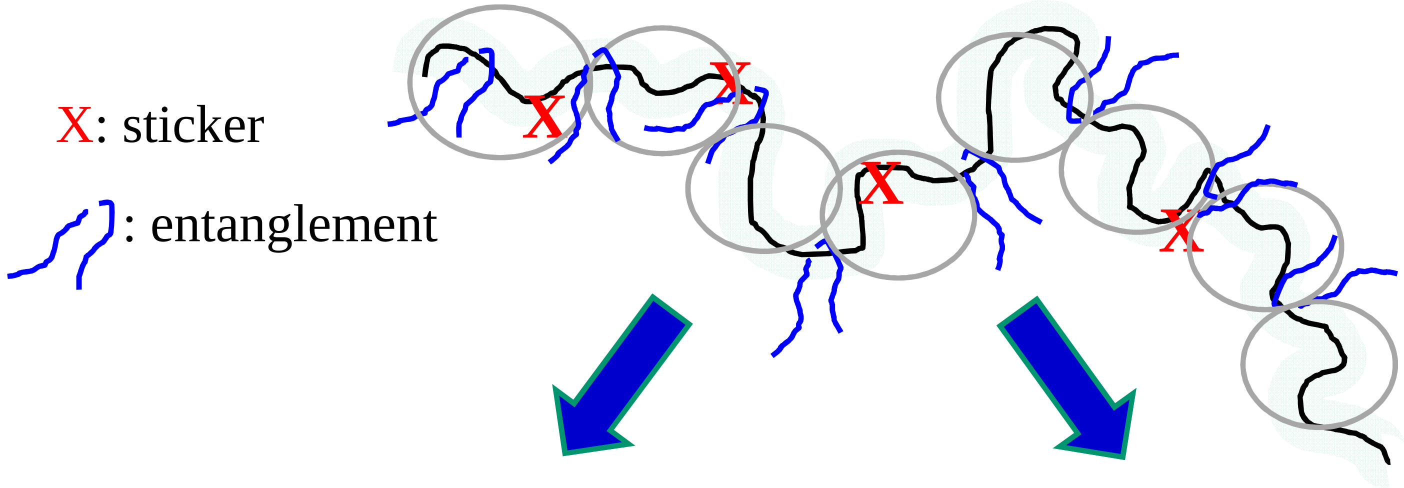




Rubbery plateau and relaxation time:

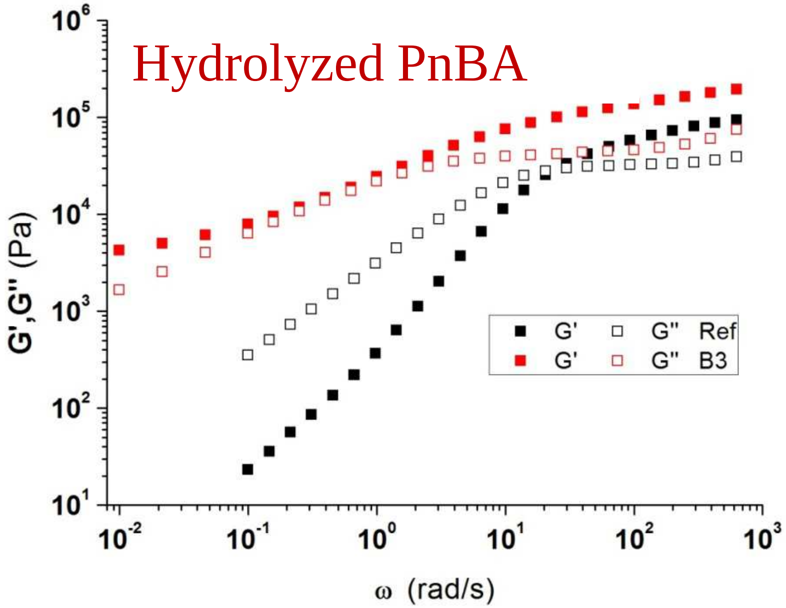
Depend on both **supramolecular dynamics** and **chain architecture**

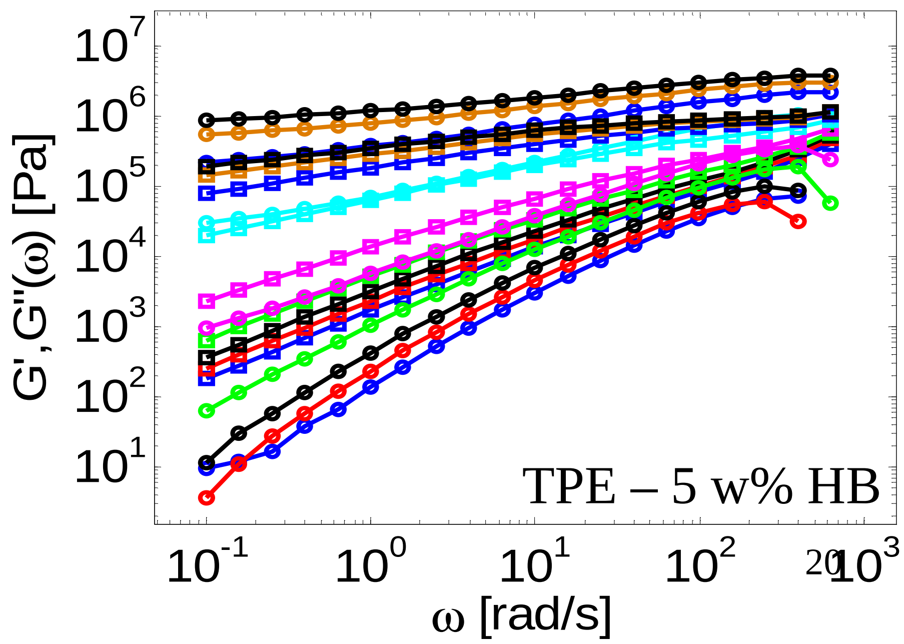
Dynamics of sticky entangled polymer melts



Two elastic plateaus

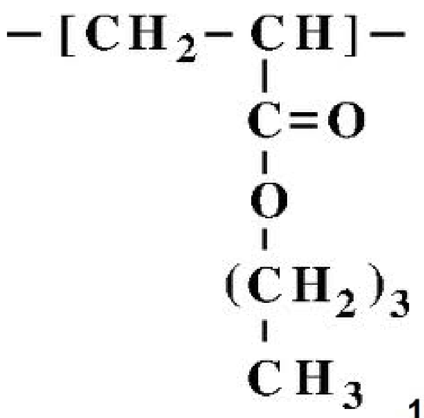
Slow decrease of G’





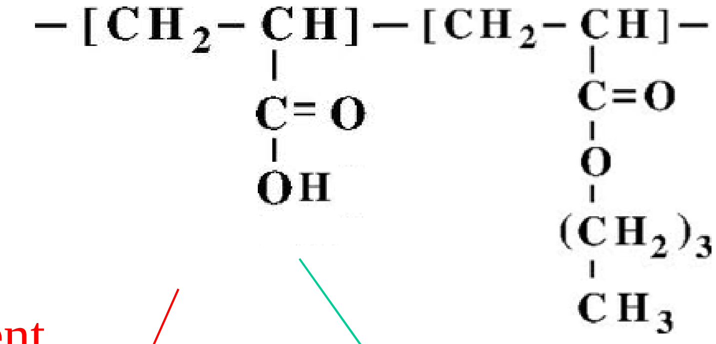
Hydrolyzed PnBA polymers

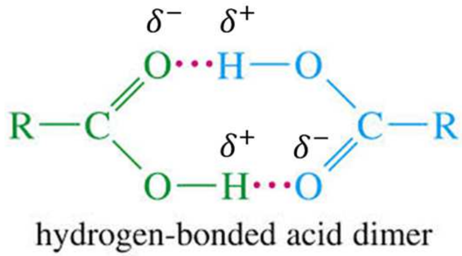
PnBA: Poly (n-butyl acrylate)



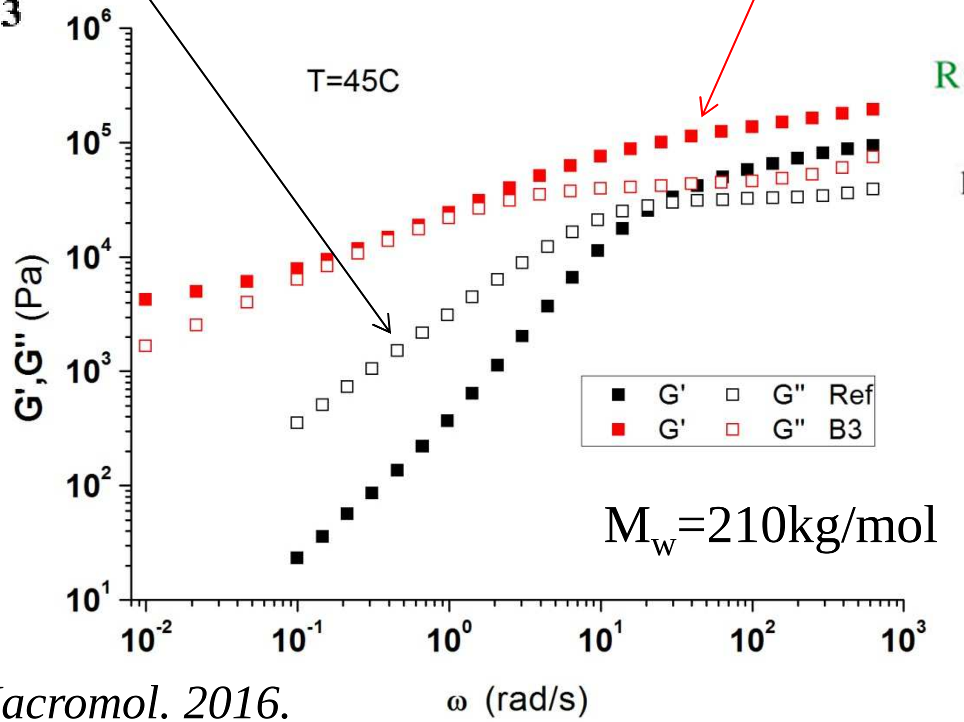
Hydrolysis

Basic environment





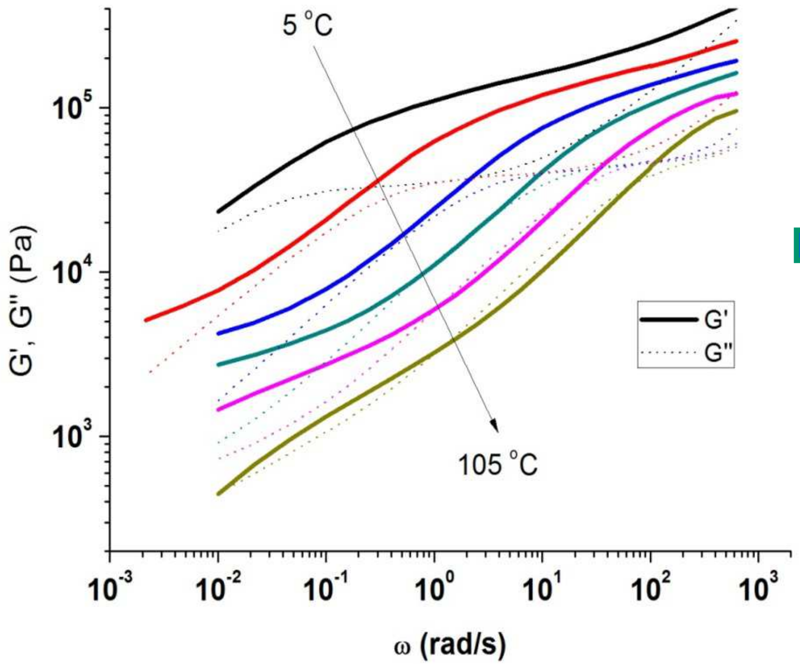
Two elastic plateaus

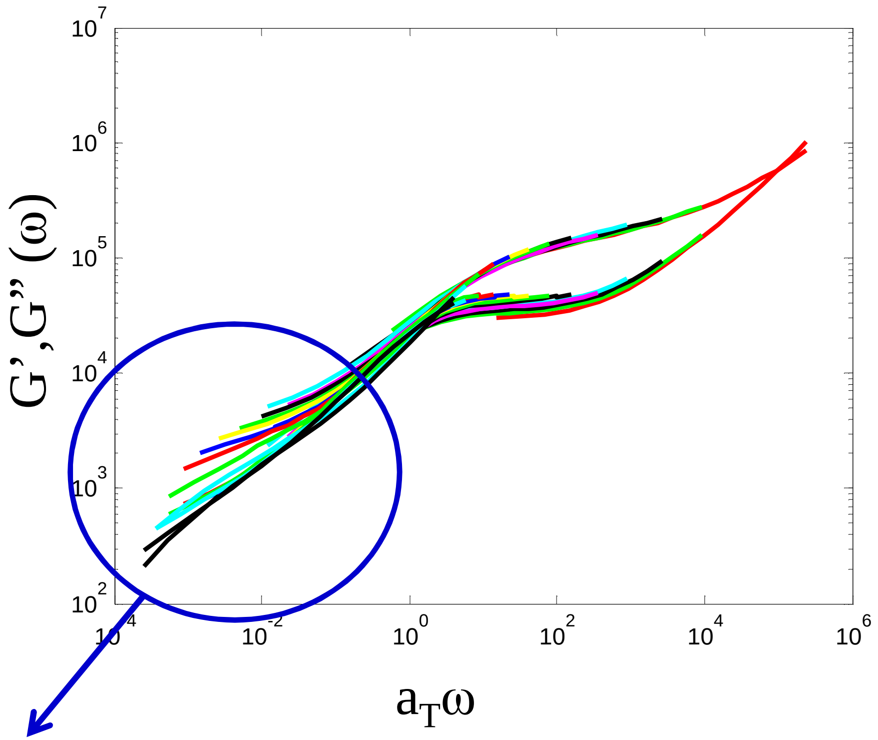


Goldansaz et al., Macromol. 2016.

Hydrolyzed PnBA polymers

Temperature effect:

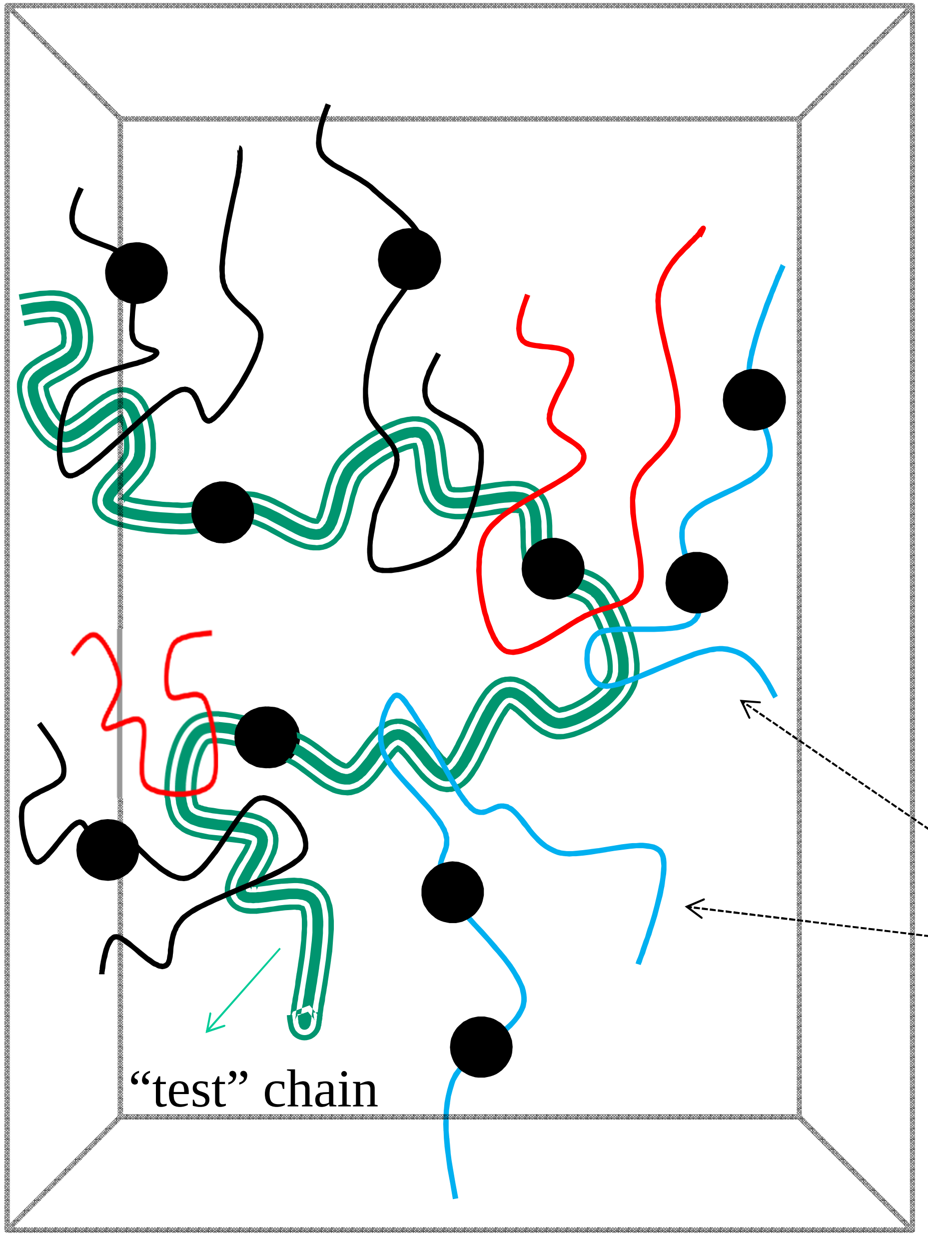




- The second plateau disappears with increasing T
- Thermo-rheological complexity $\longrightarrow$ governed by the association dynamics

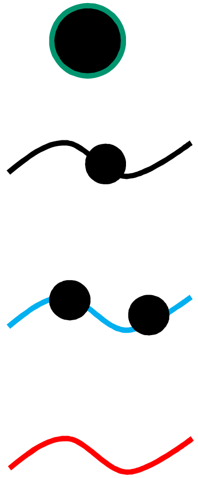
➡ Lifetime (sticker) > Lifetime (entanglement)

Trapped segments versus dangling ends:



p_{st}, the probability to find an associated sticker

↓

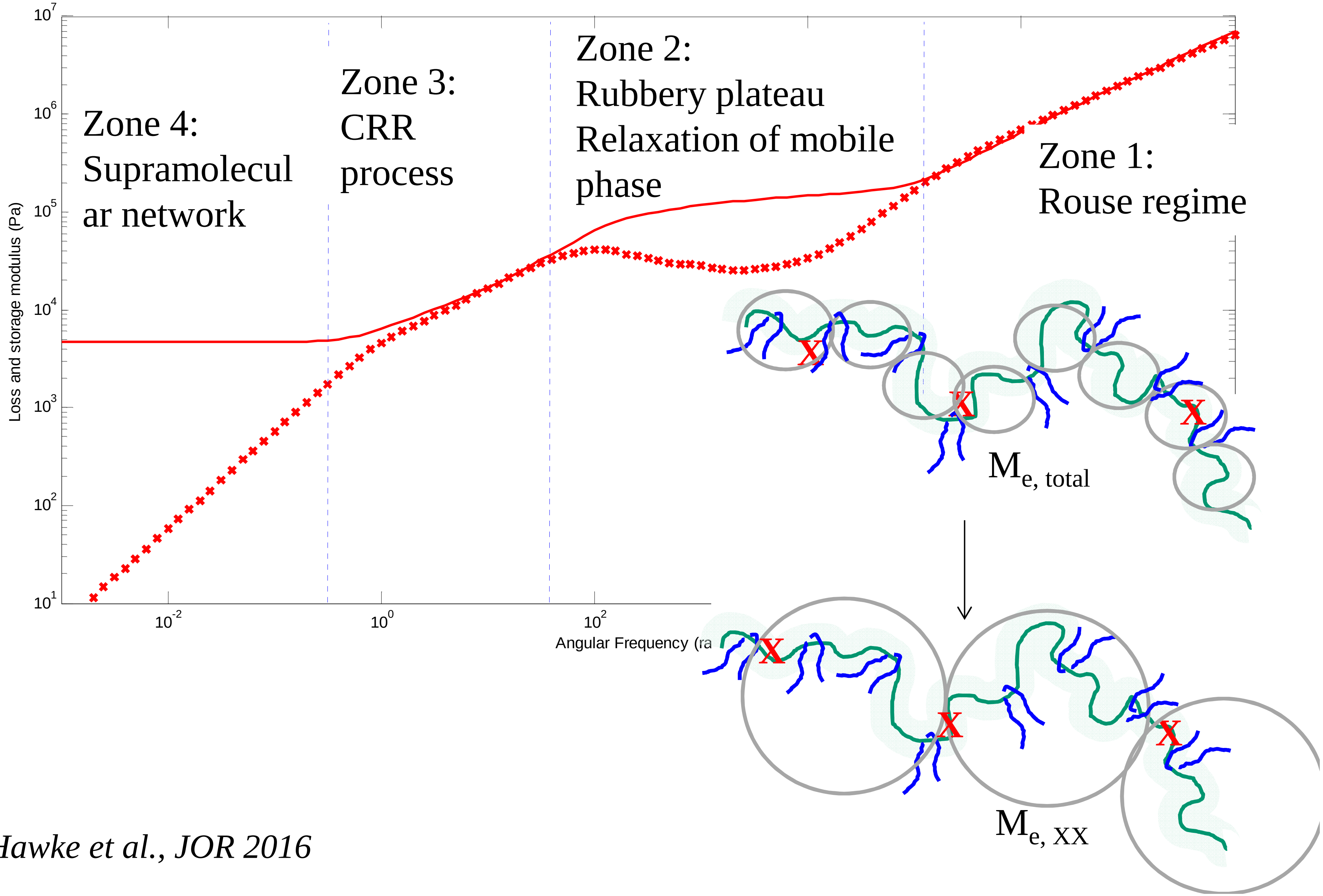


dangling ends of trapped chains

Only the trapped chains cannot relax

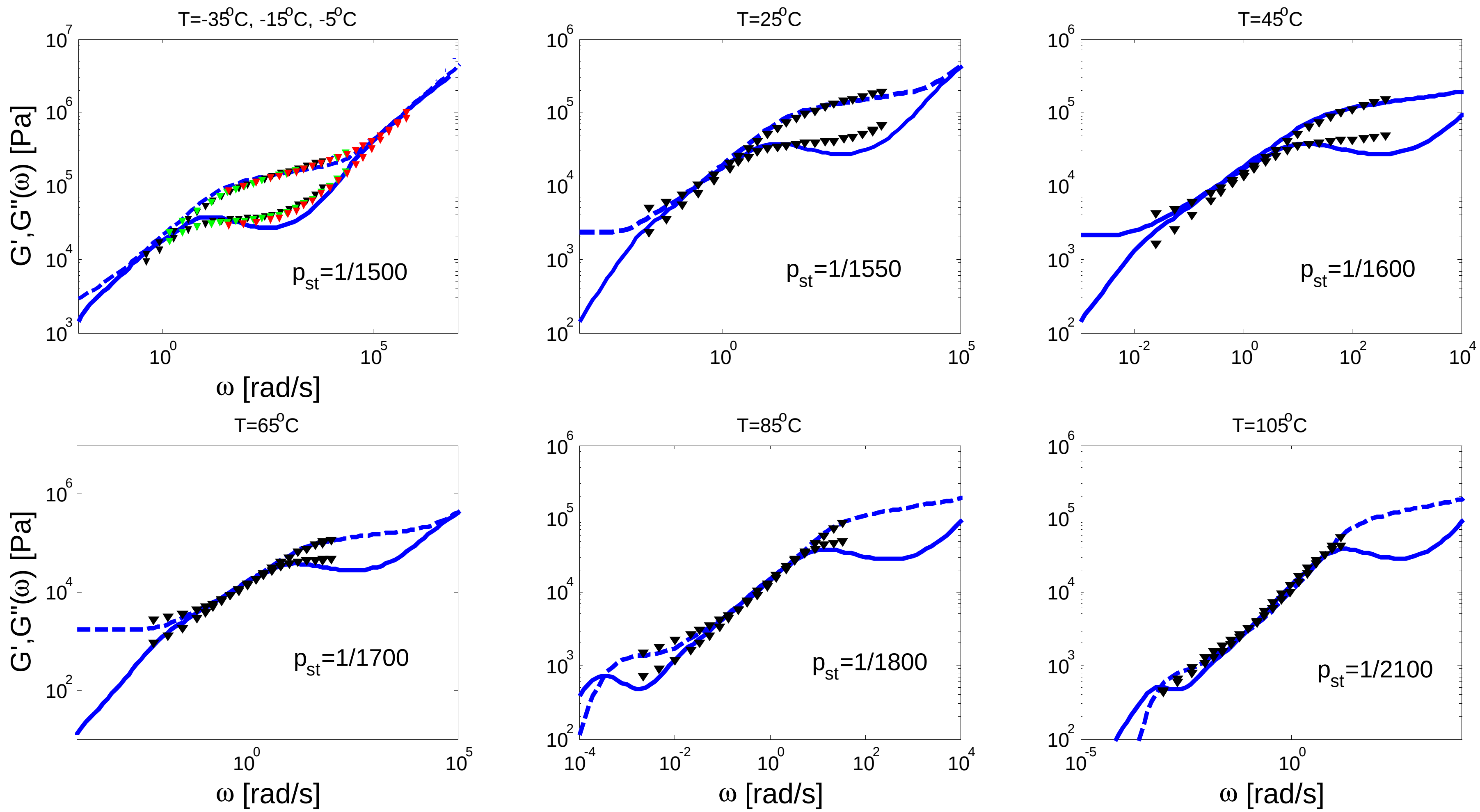
Hawke et al., JOR 2016

Molecular picture: related rheology



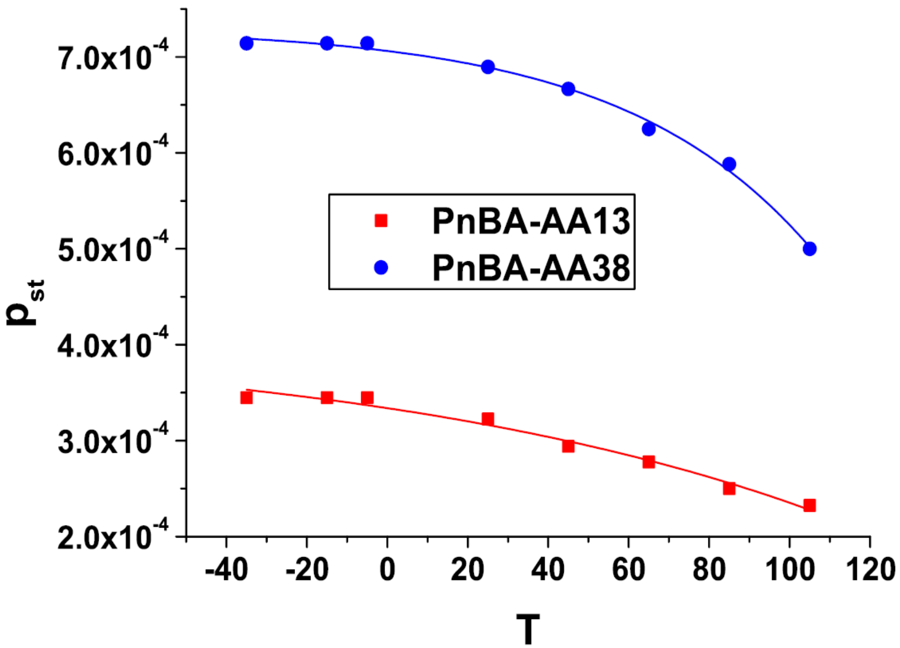
Hawke et al., JOR 2016

Comparison to experimental data

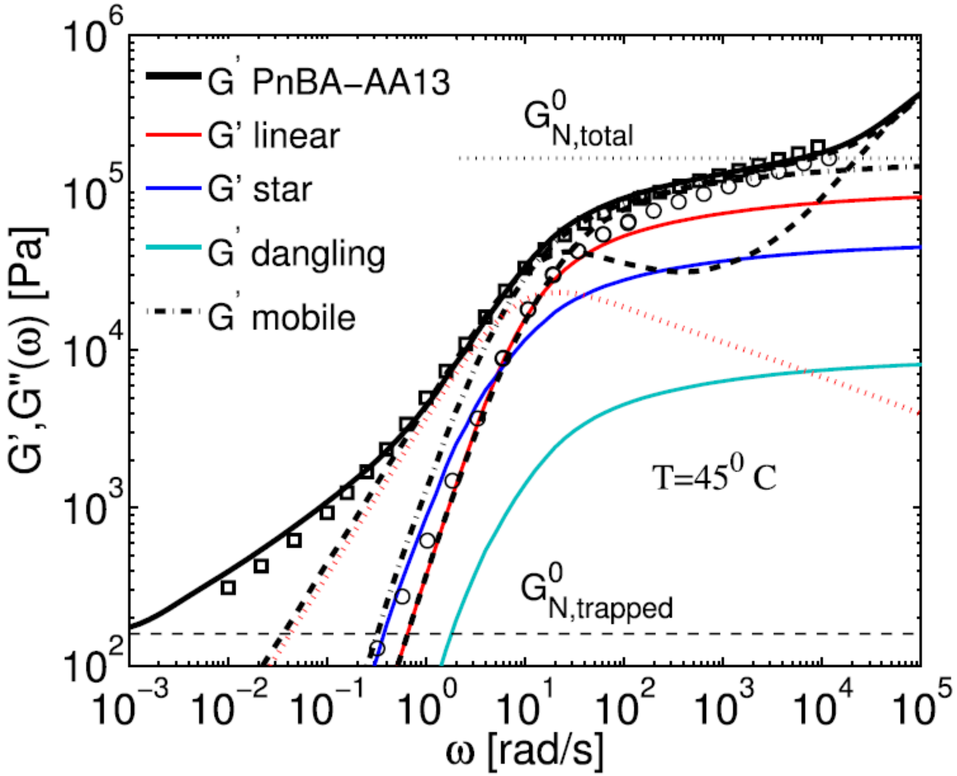


Comparison to experimental data

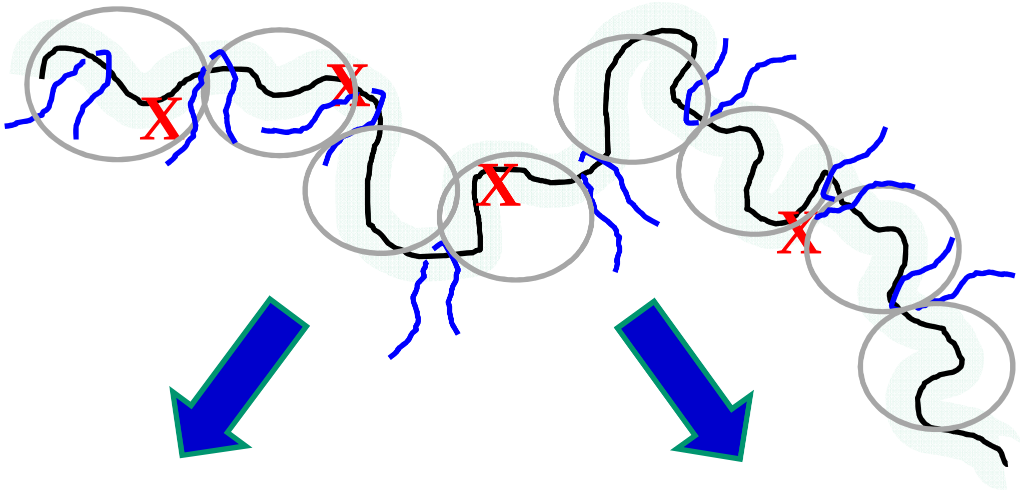
Exponential decay of p_{st}:



Delay in the first transition:

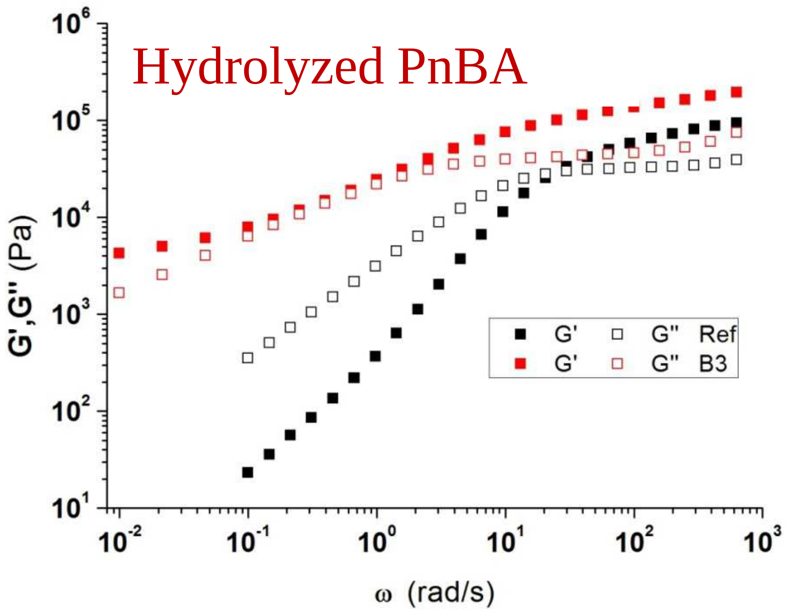


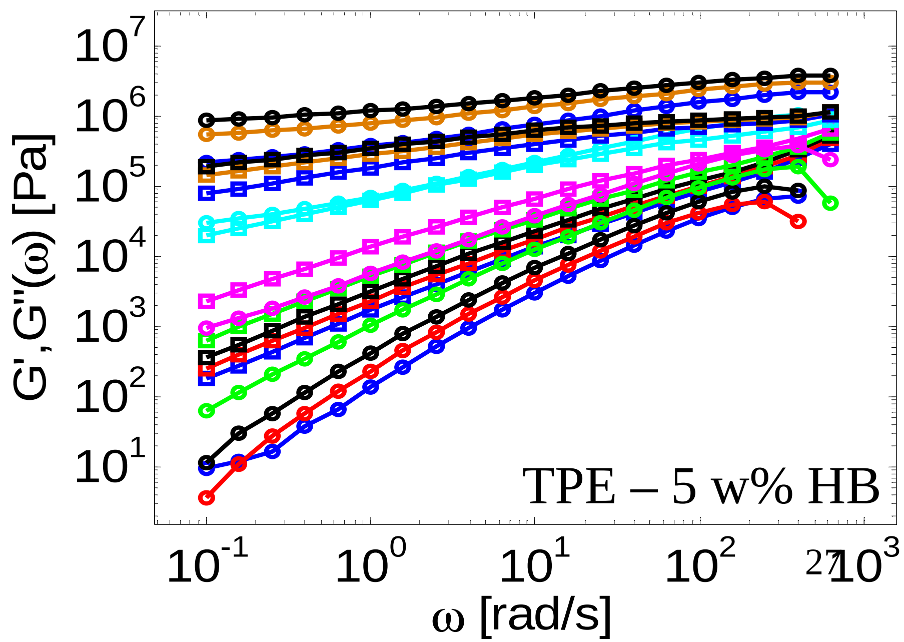
Dynamics of sticky entangled polymer melts



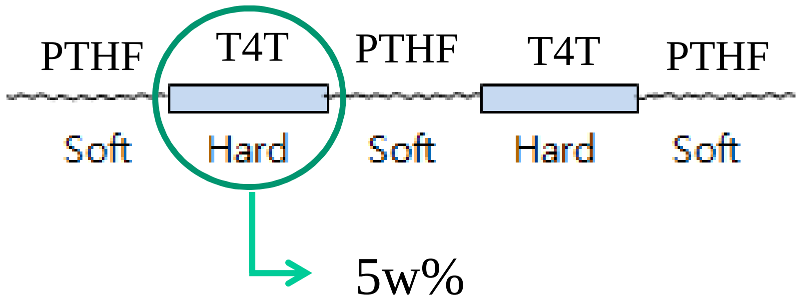
Two elastic plateaus

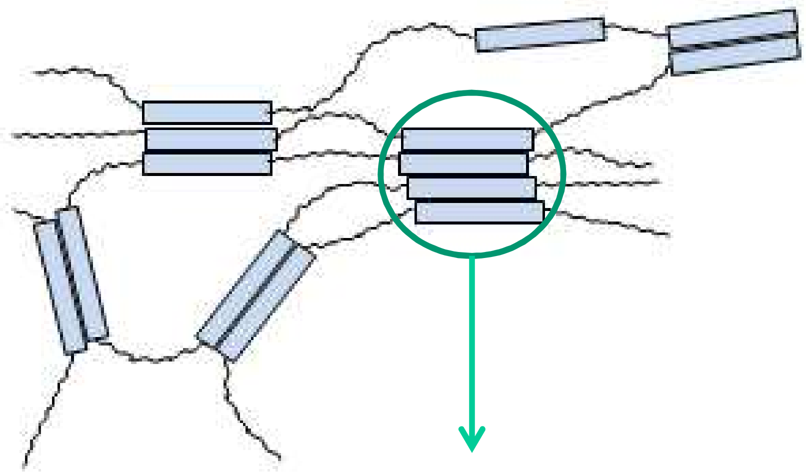
Slow decrease of G’

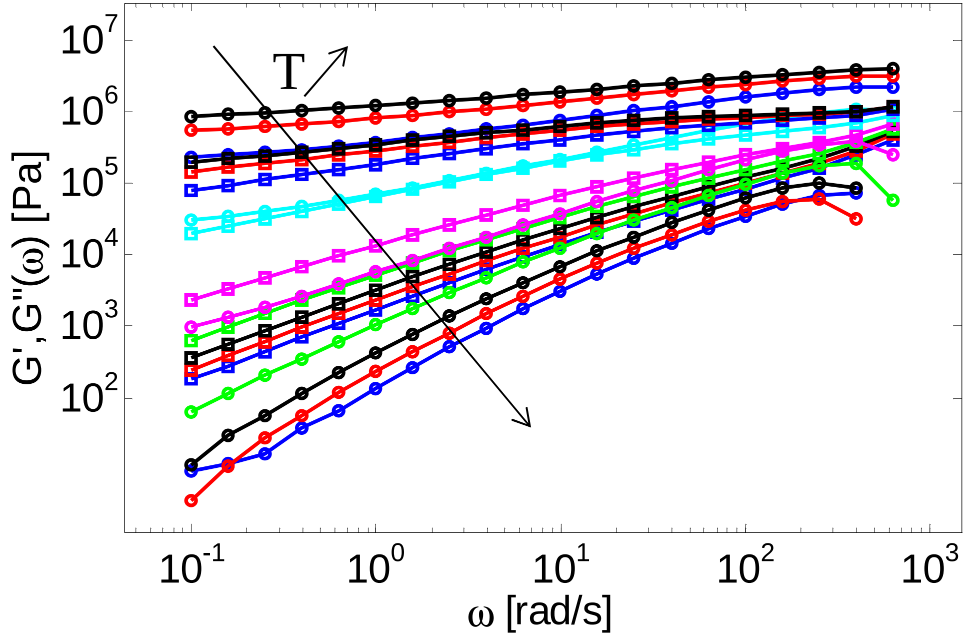




Thermoplastic elastomers: TPEs

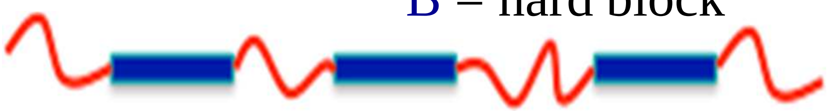






Connected with supramolecular bonds (H bond type) and by crystallization

A = soft block
B = hard block



The stickers can dissociate and associate again

Samples: A. Sharma, W. Appel, DSM (Geleen, The Netherlands)

Flory distribution – TPE 5% HB

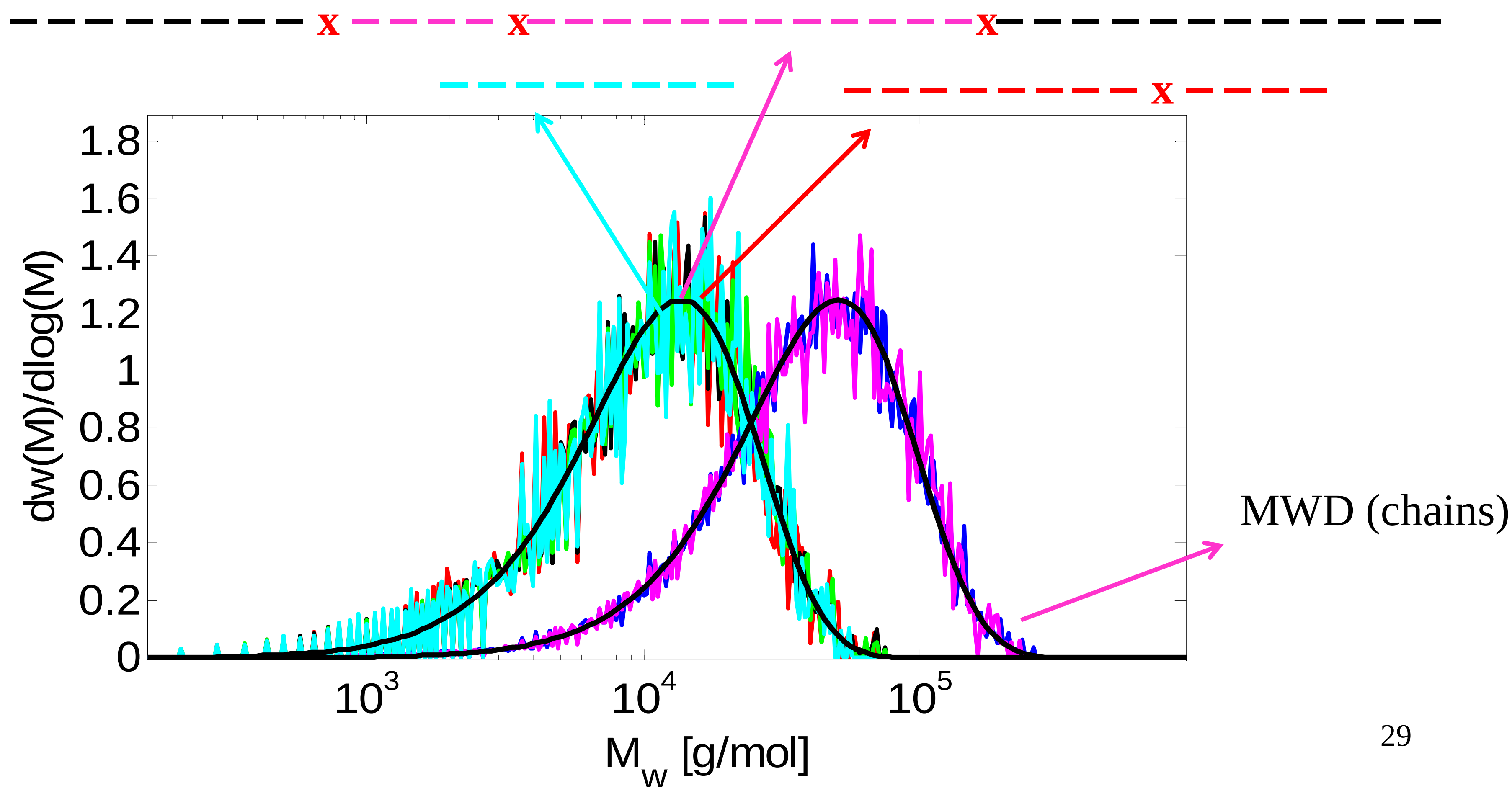
$M_{n,\ strand}$ = 6840 g/mol

$M_{n,\ chain}$ = 25200 g/mol

$\#_{monomers\ in\ the\ box} = 10^7$

p_{end} = 2.85/1000

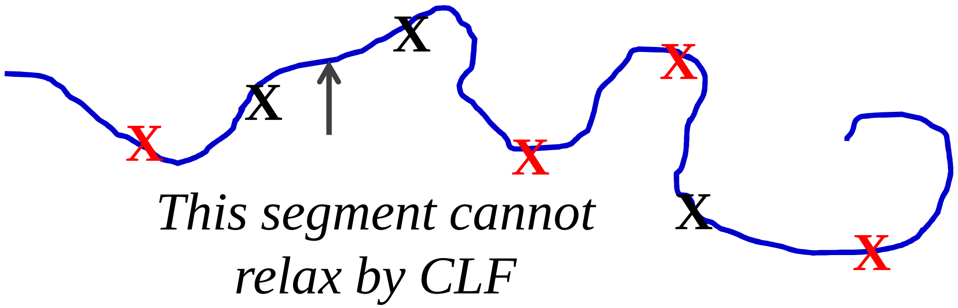
$p_{sticker}$ = 7.7/1000



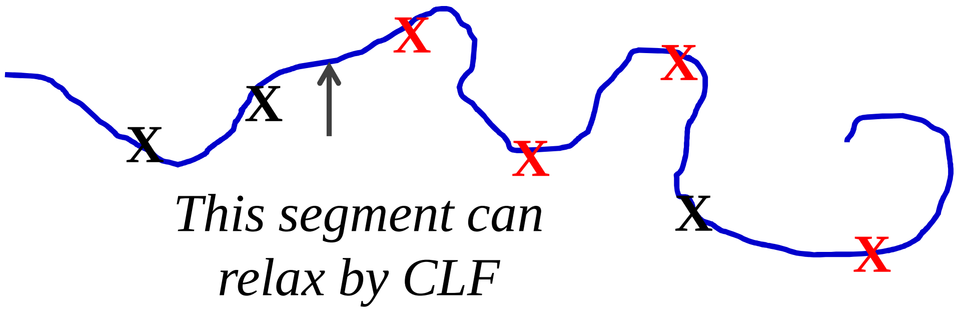
Accounting for sticky groups in tube model

Assumptions:

- Statistical distribution of the stickers
- A sticker can be associated, or not: p_{st}
- Fluctuations process of a segment x only takes place if there is no active sticker between the chain extremity and x



X: active sticker
X: unassociated sticker



X: active sticker
X: unassociated sticker

Penalty on the time during which a chain is relaxing

Accounting for sticky groups in tube model

Input data:

- *Flory distribution with Mn=25.2 kg/mol*
- $p_{sticker}$ *= 7.7/1000 (active or not)*
- ***p_{st} = prob (a sticker is active)***

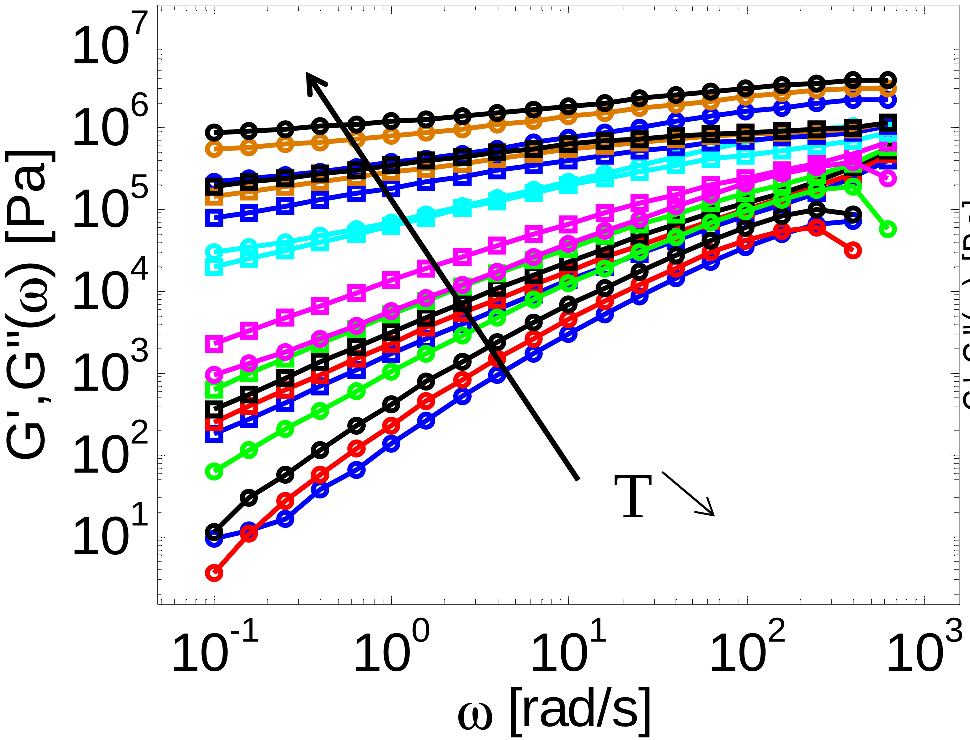
Tube model parameters:

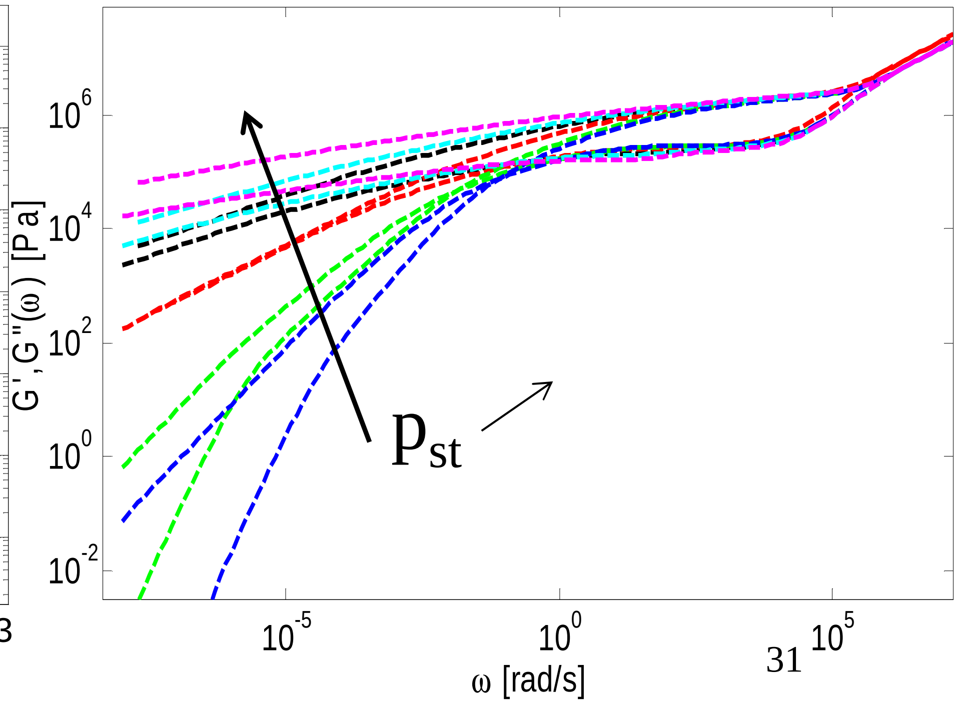
$G_{N,\,pure} = 2.5\ MPa$

$M_{e,\,pure} = 1750\ g/mol$

$\tau_{e,\,pure} = 10^{-5}\ s$

TPE – 5 w% HB





Conclusions

- By using **statistical tool**, we can often have a good representation of branched or sticky polymers.

- The rheological behavior of **sticky entangled polymers** strongly depends on the balance between association and entanglement dynamics.

- Based on tube models, one can rationalize their **relaxation process**.

- (Rheology + model) gives us a powerful **characterization tool**.

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UCL colleagues:
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Charles-André Fustin
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Christian Bailly

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Nikos Hadjichristidis (KAUST)
Hiroshi Watanabe (Univ. of Kyoto)
Salvatore Coppola (Polymeri Europa, Bologna)
Paul Steeman, Han Slot, W. Appel (DSM, Geleen)
Taihyun Chang (Corea)

INITIAL TRAINING NETWORK

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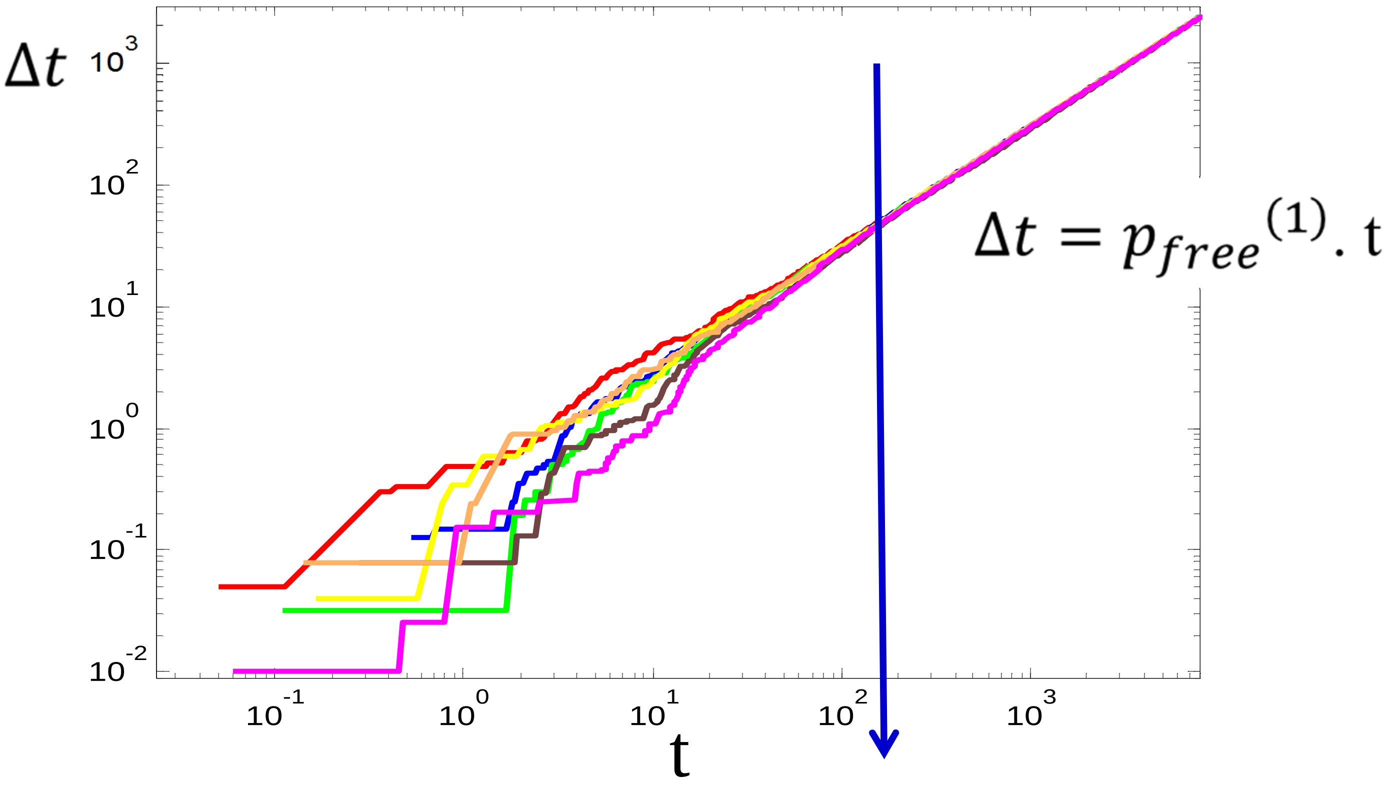
Thank you!

Association dynamics of the stickers:

Assumptions:

- p_{free} = prob (a sticker is not active)
- After a time t, a sticker was free during $\Delta t = {p_{free}}^{(1)}.\, t$



This assumption is valid only at long times