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Mechanical rejuvenation and ageing of glassy polymers: effect of plastic deformation

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Mechanical rejuvenation and ageing of glassy polymers : effect of plastic deformation

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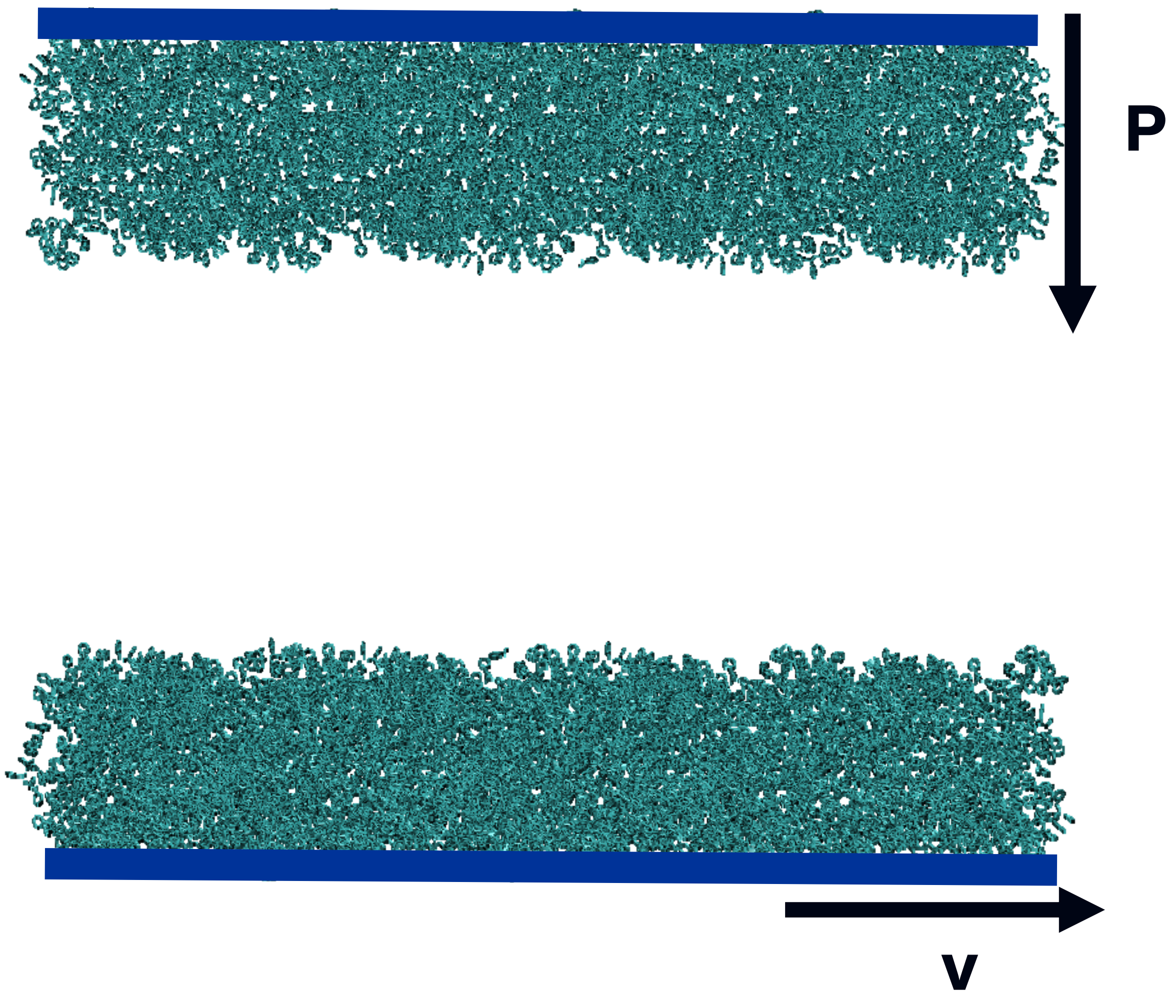
CONFINEMENT EFFECTS ON GLASS TRANSITION IN THIN ATACTIC POLYSTYRENE FILMS: MOLECULAR MODELLING APPROACH

D. V. Hudzinskyy, A. V. Lyulin, M. A. J. Michels



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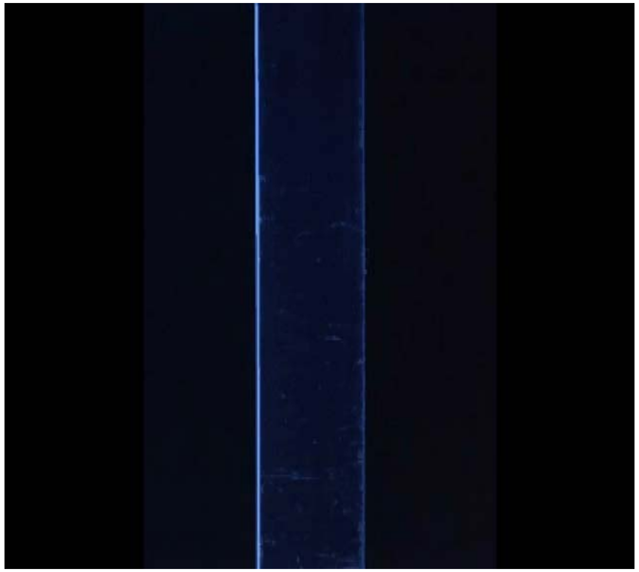
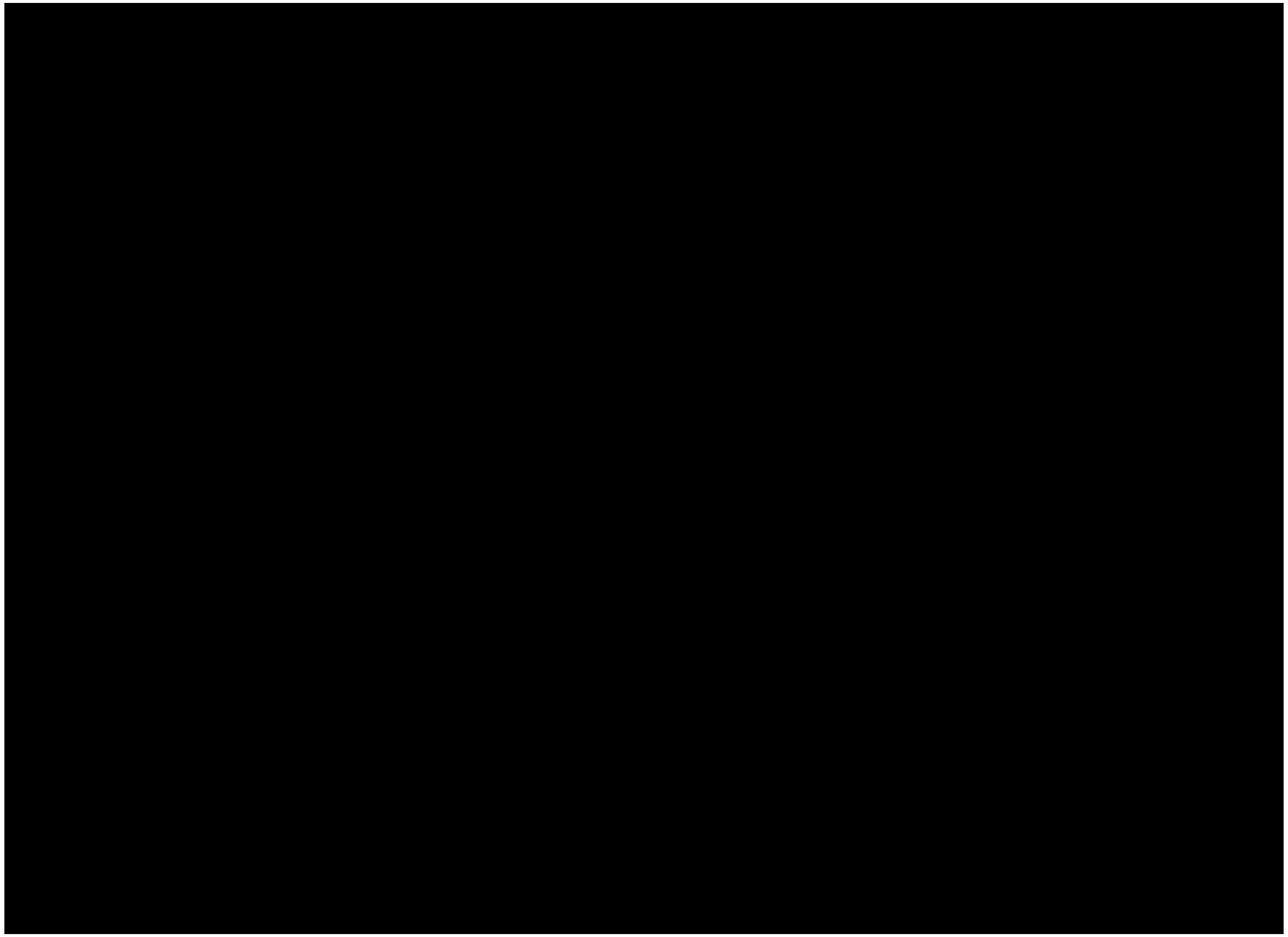
Goal

- How to make old polymer materials younger?
- What are the (atomistic) mechanisms of such a rejuvenation?

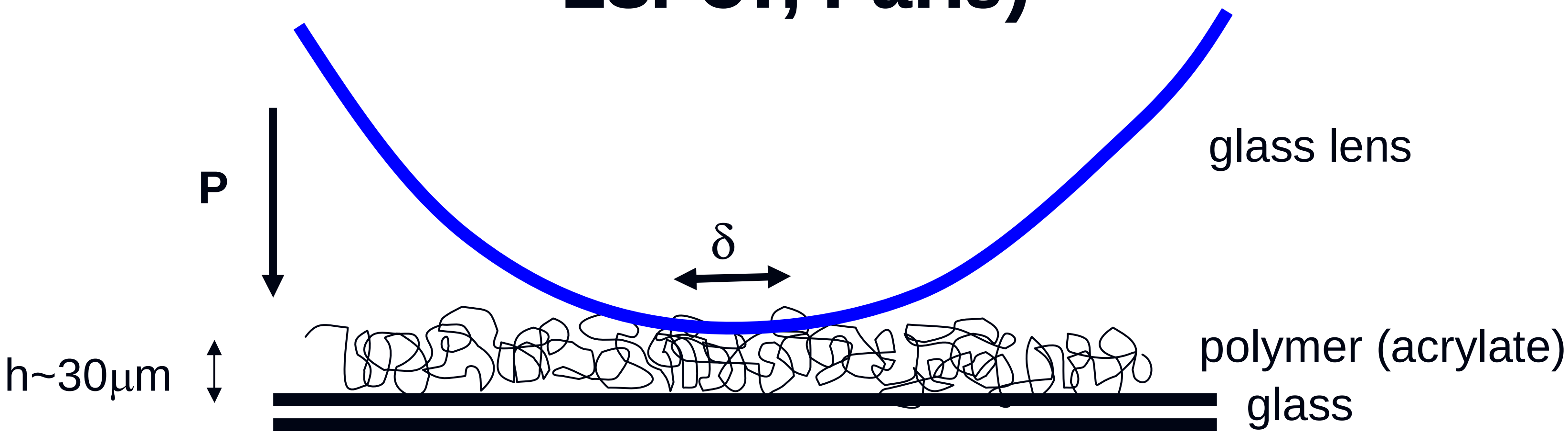
Uniaxial stretching experiment (H.E.H. Meijer, Eindhoven)

brittle (old) vs **tough (young)**

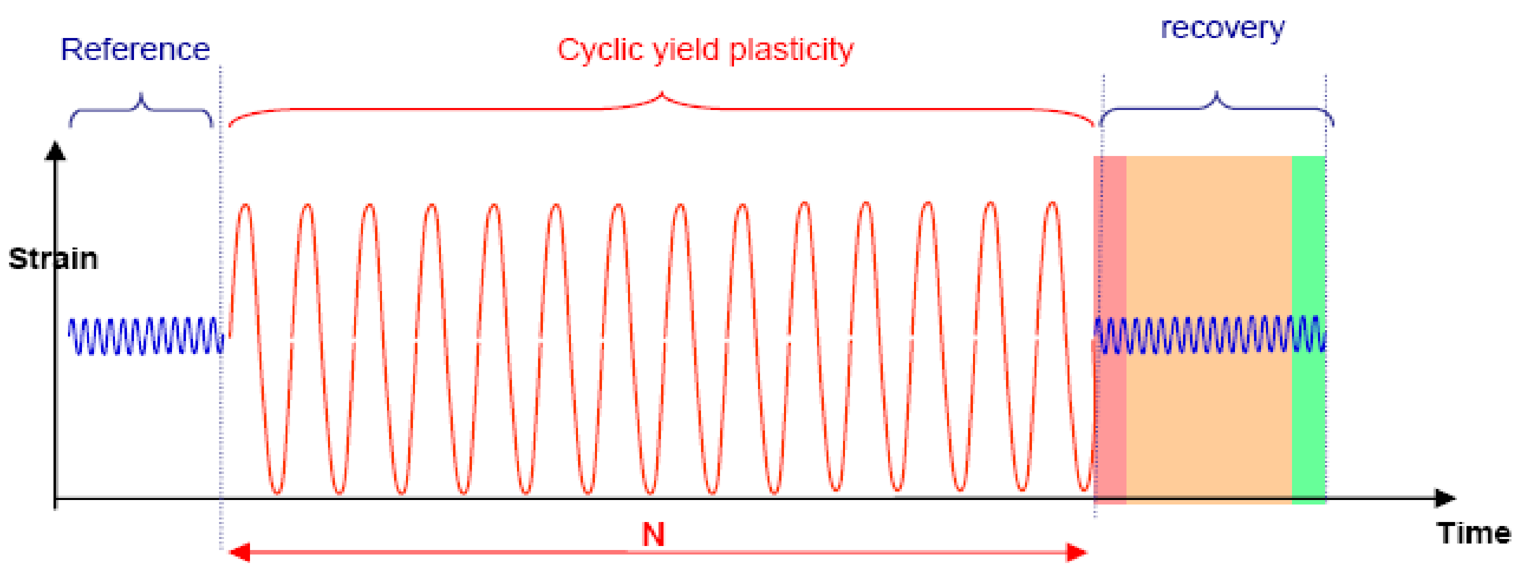




Cyclic experiment (A. Chateauminois, E. Janiaud, ESPCI, Paris)



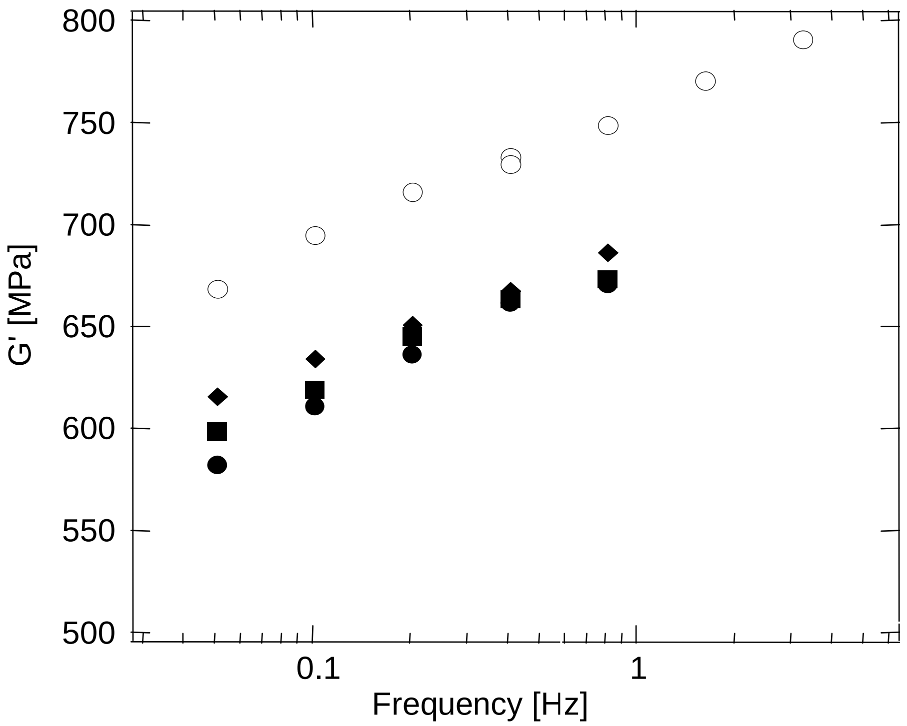
strain= $\gamma=\delta/\mathbf{h}$



strain<1% strain ~8% strain<1%

Rejuvenation after cyclic yield (2000 cycles, $\gamma=7.4$ %, 1 Hz)

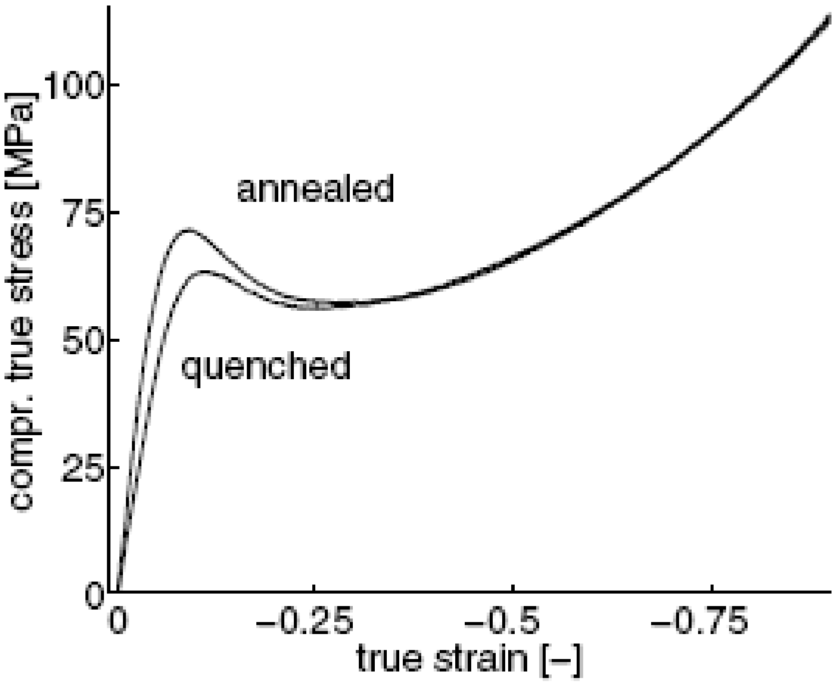
P=70MPa, f=1 Hz, $T_{exp}=T_g-33^0$, $T_g=53^0C$



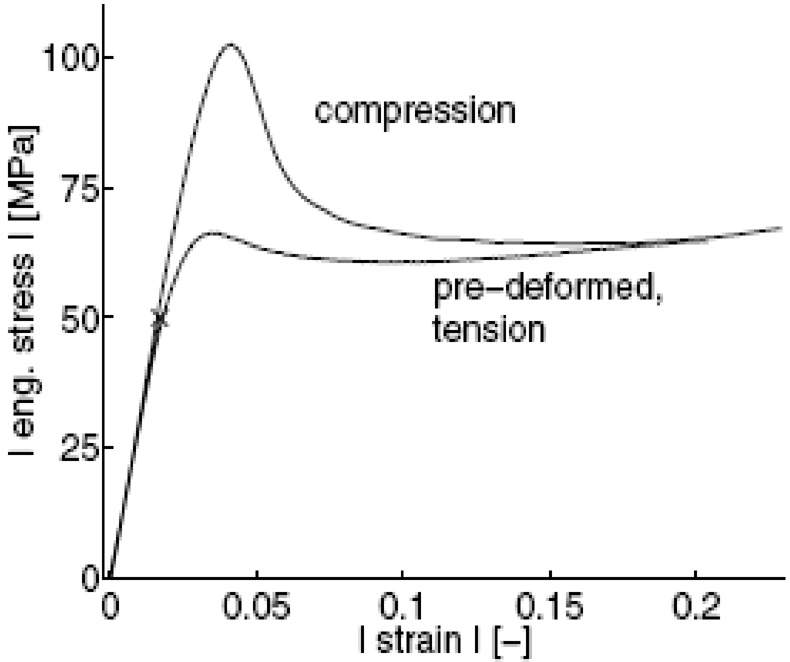
○ **Before cyclic yield**
◆ **30 s after cessation of cyclic yield**
● **210 s**
■ **1990 s**

Thermal vs. mechanical rejuvenation

heating up above T_g, then quenching



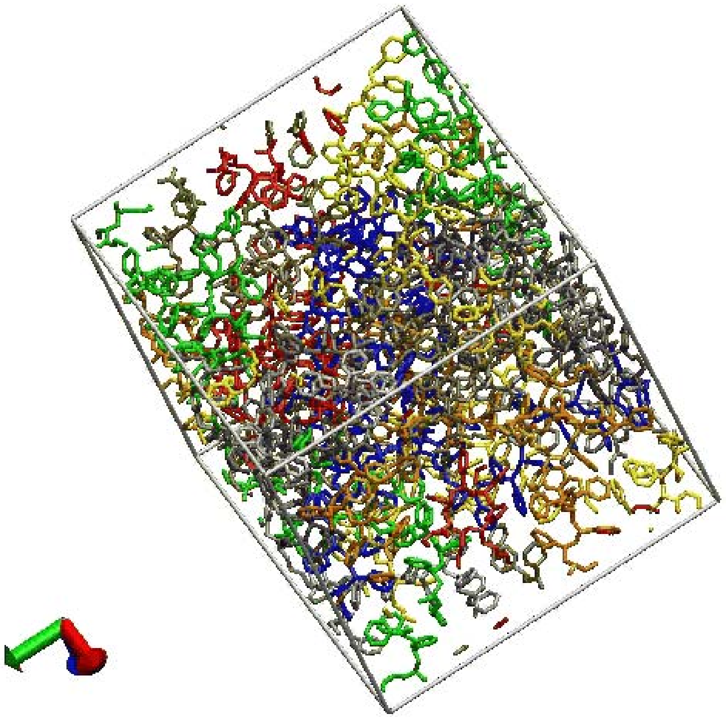
deformation above the yield point, then compression



H.G.H. van Melick, PhD thesis, Eindhoven, 2002

Simulations

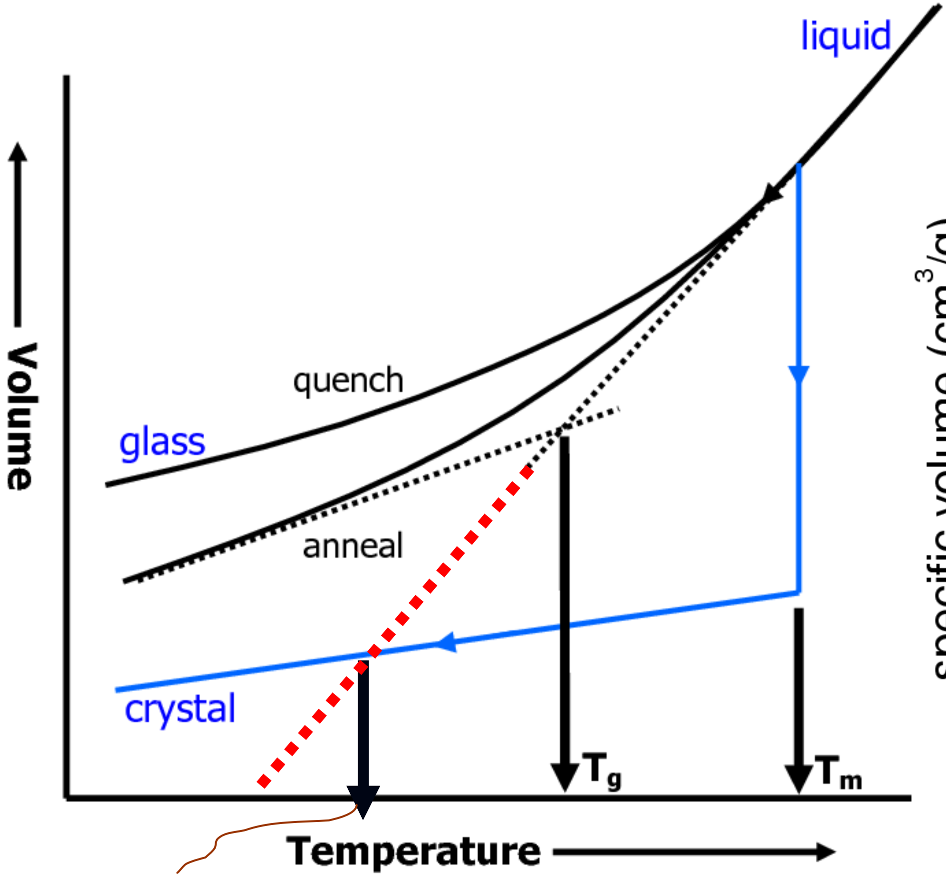
PS: T_g~373 K, PC: T_g~425 K, T_{exp}=300 K

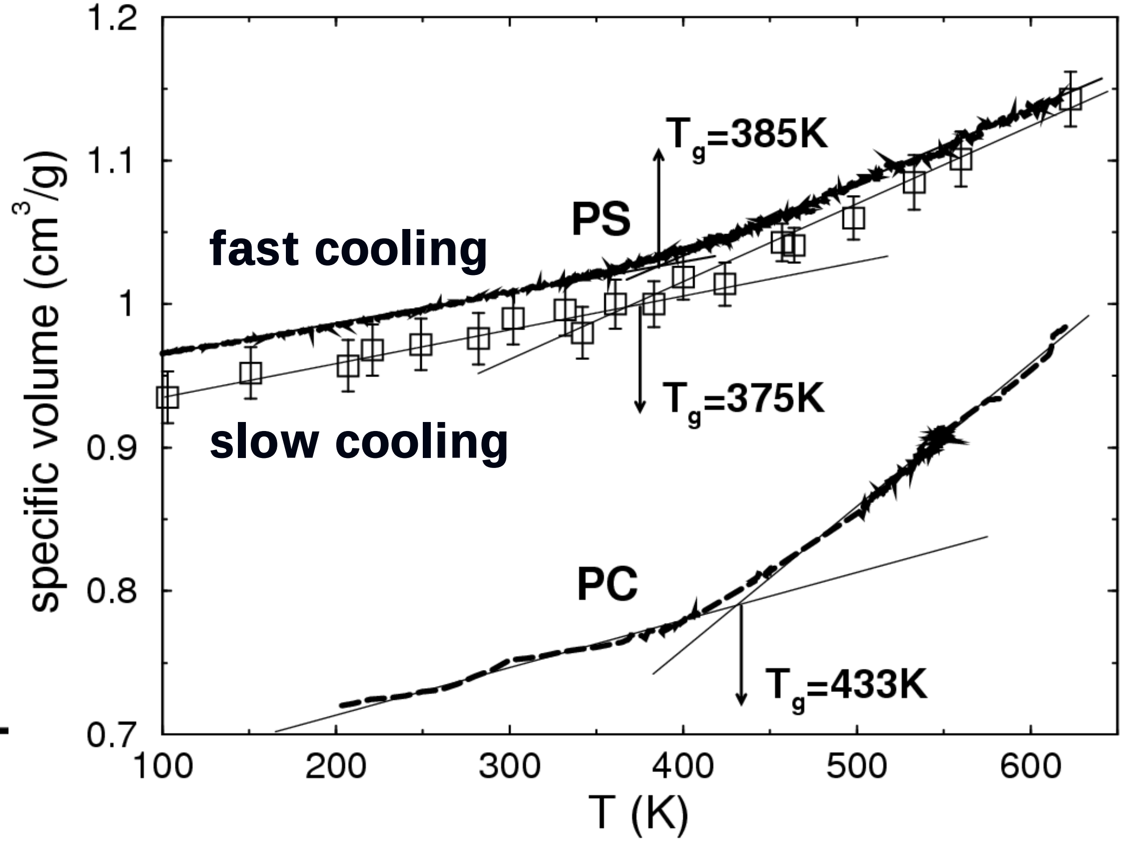


<u>Preparation</u>

The samples were equilibrated for ~25 ns at T=540 K, and cooled down with 0.01 K/ps cooling rate for 24 ns to T=300 K.

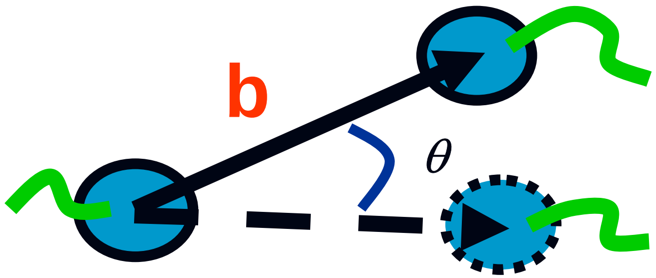
Glasses





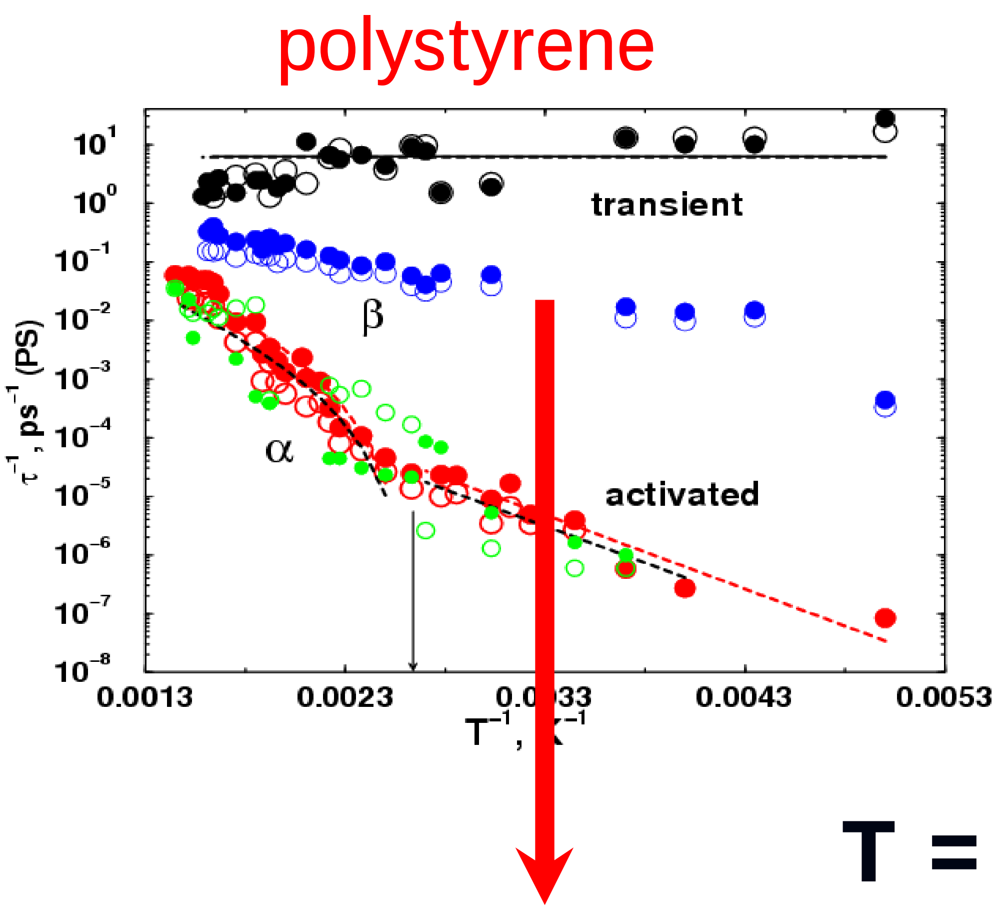
AVL, B. Vorselaars, M. Mazo, N. Balabaev, M.A.J. Michels, *Europhys. Lett.* **2005**

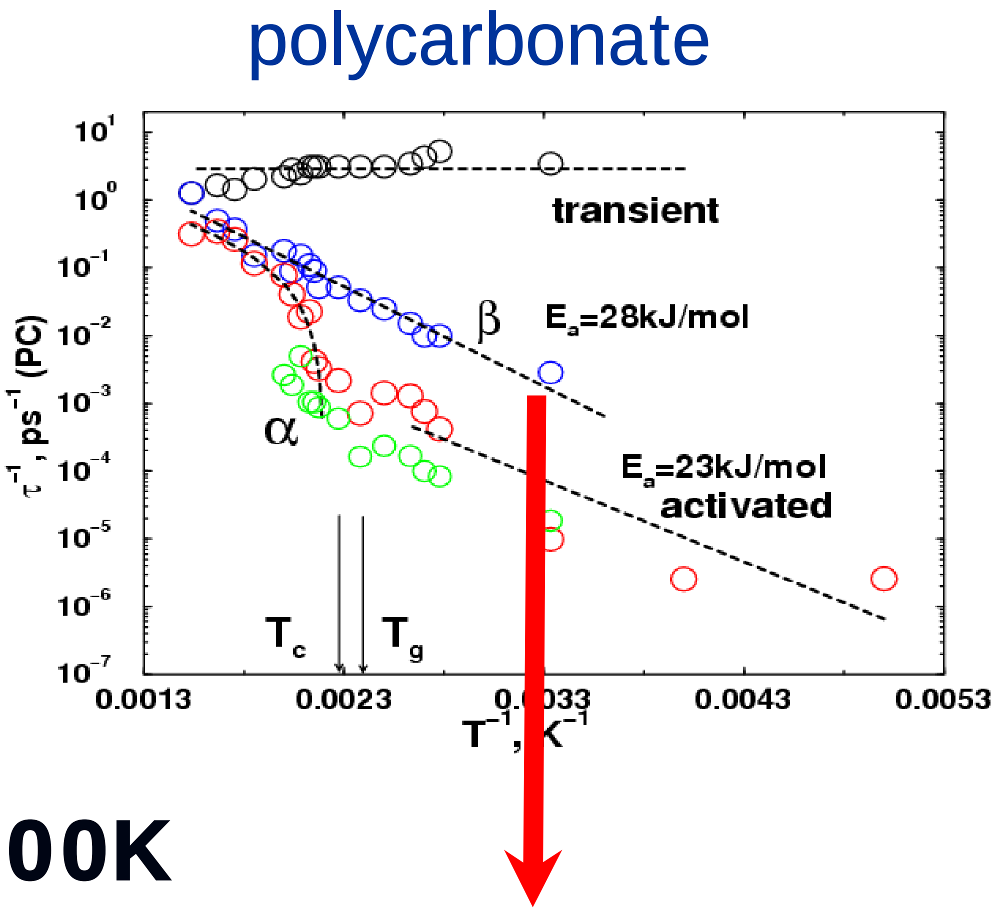
P_2 autocorrelation function



$$P_2(t) = \left\langle 3/2\cos^2\theta - 1/2 \right\rangle = \int_{-\infty}^{+\infty} F(\ln\tau)\exp(-t/\tau)\,d\ln\tau$$

Temperature dependence of P_2 relaxation times

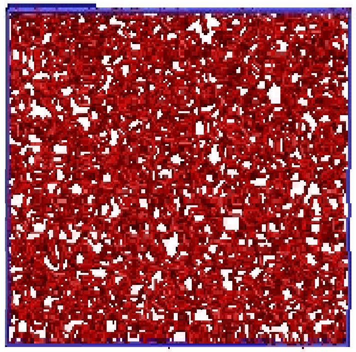


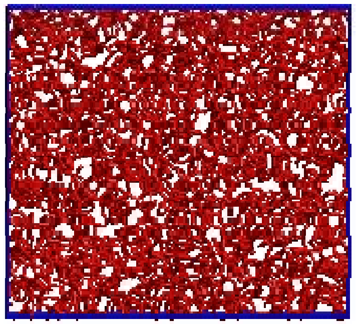


T = 300K

τ_β ~ **50-100 ps** **<** τ_β ~ **500 ps**

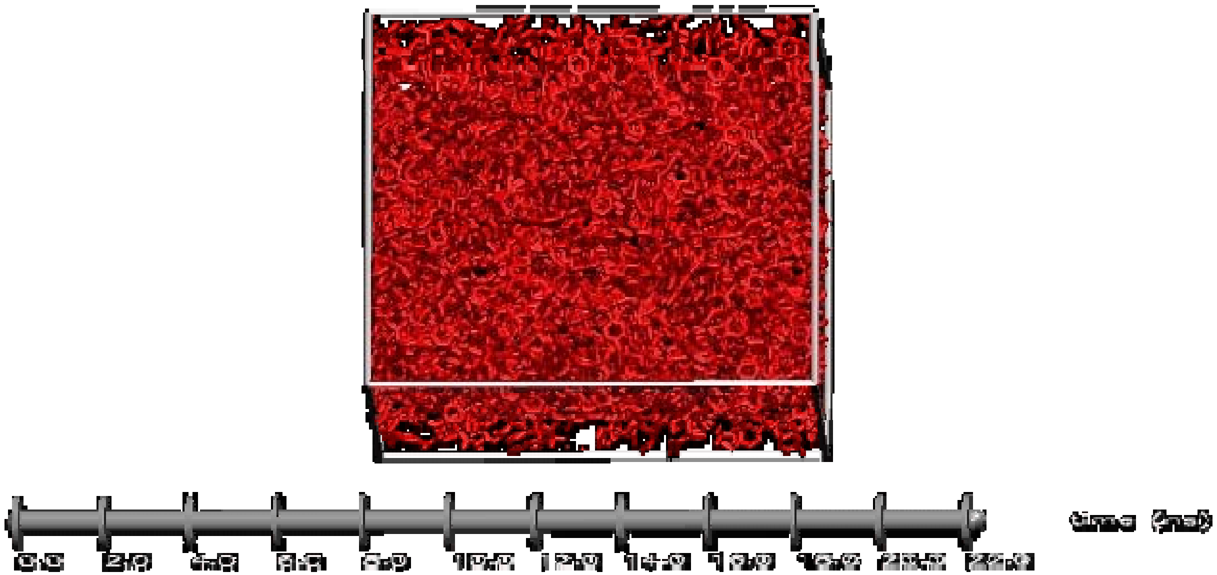
PS:



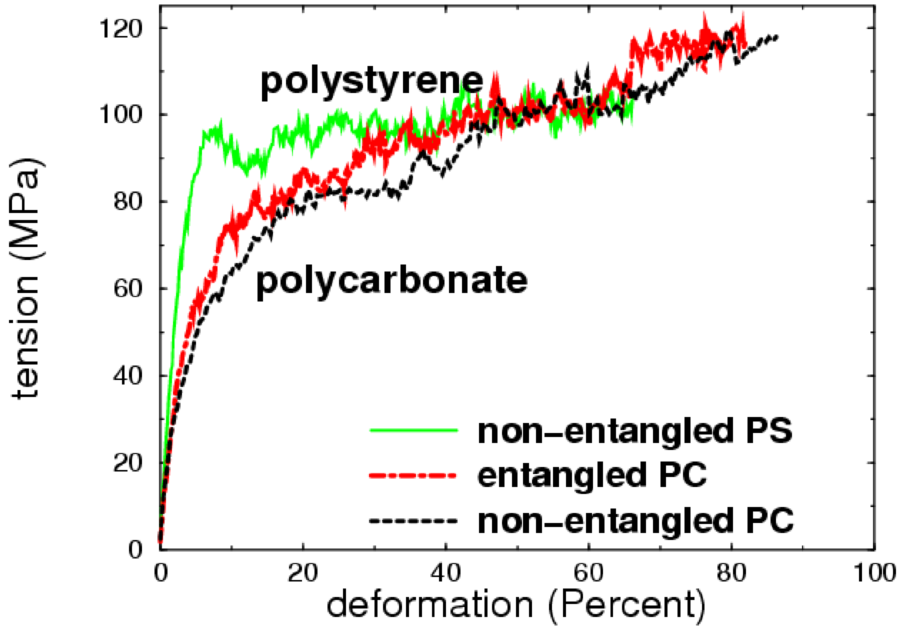


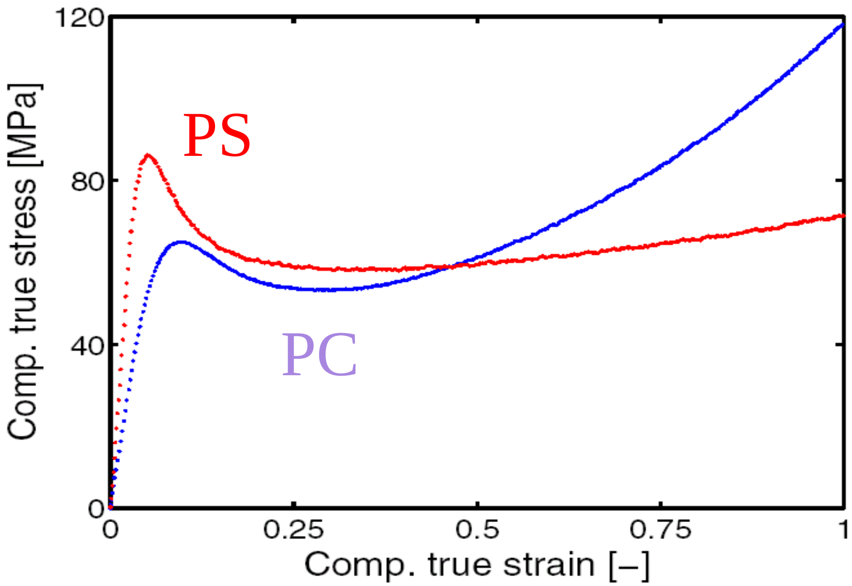
$T << T_g$

PC:



Simulation vs. experiment

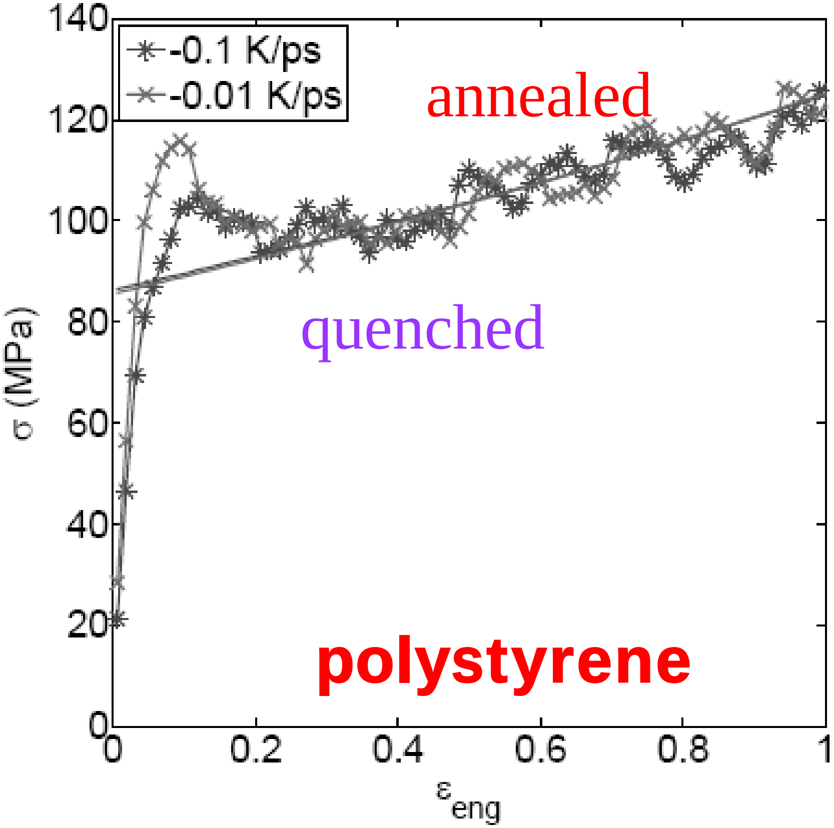


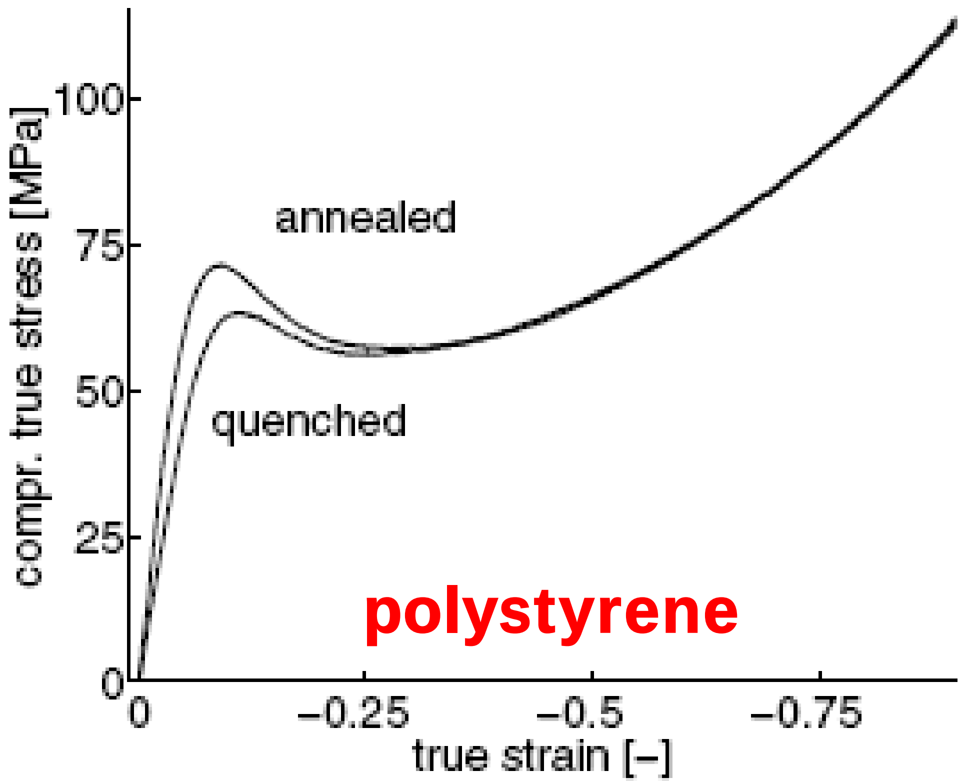


AVL, B. Vorselaars, M. Mazo,
N. Balabaev, M.A.J. Michels,
Europhys. Lett. **2005**

H.G.H. van Melick et al., Polymer **2003**

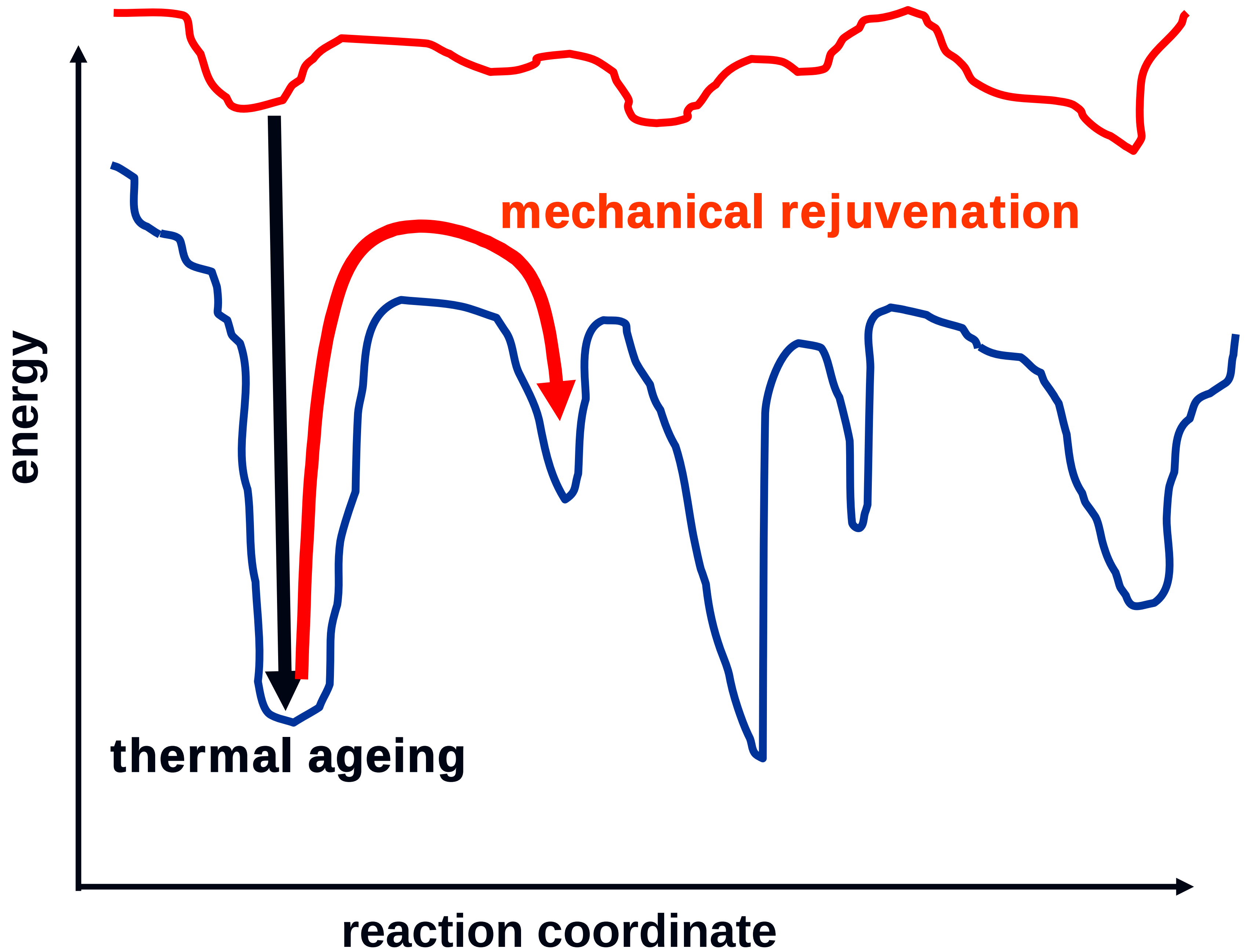
Simulation vs. experiment





AVL, M.A.J. Michels, *Phys. Rev. Lett.*, **2007**
B. Vorselaars, PhD, **2008**

H.G.H. van Melick, PhD thesis, Eindhoven, **2002**



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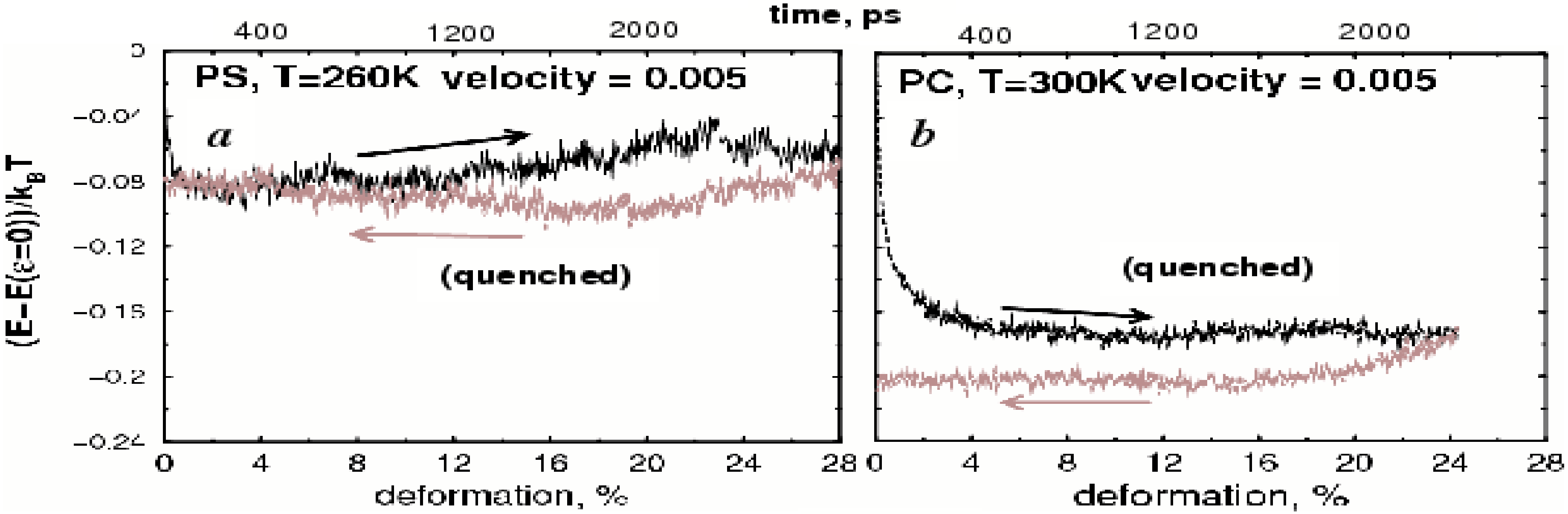
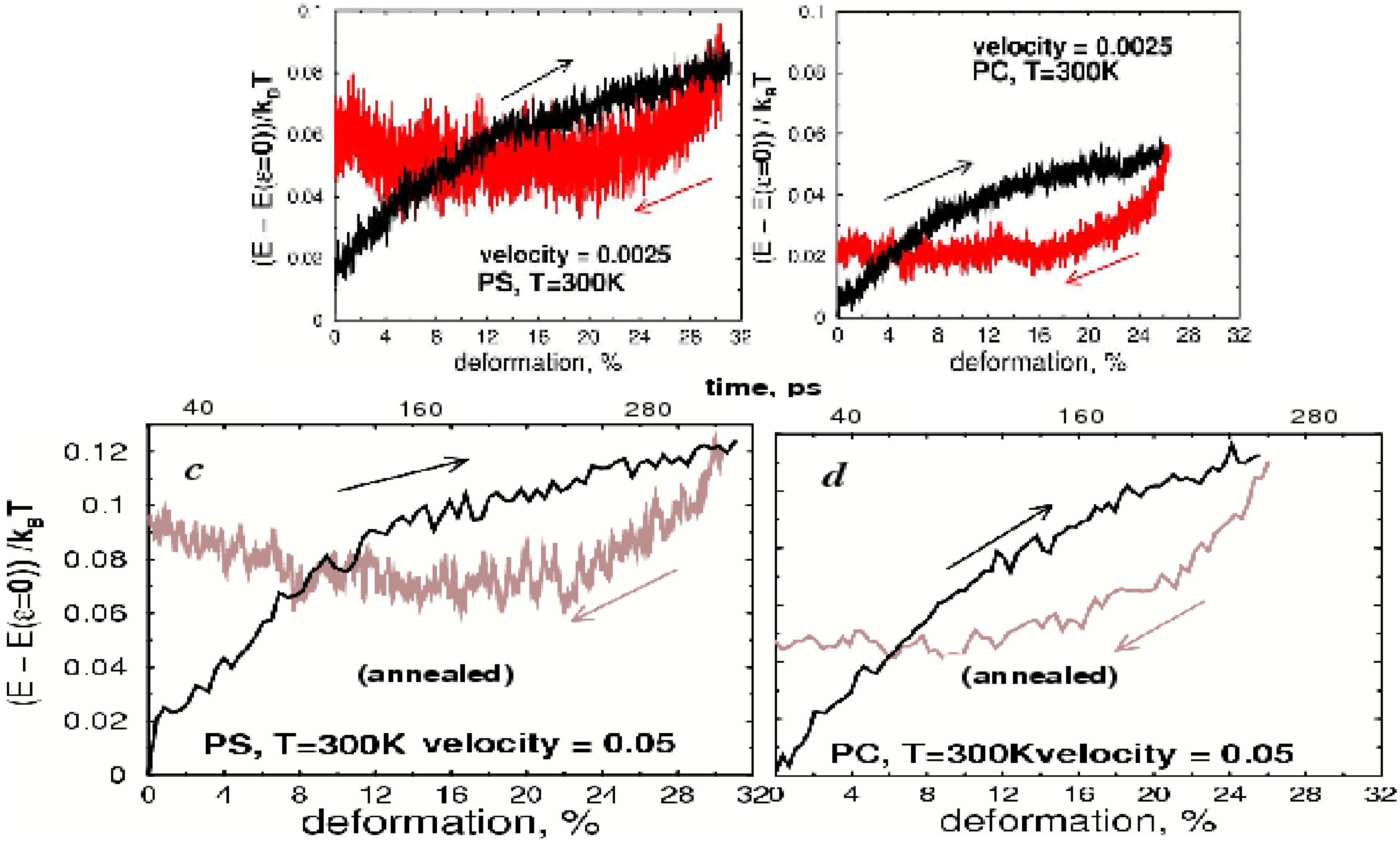
Stretching - compression loop: quenched samples



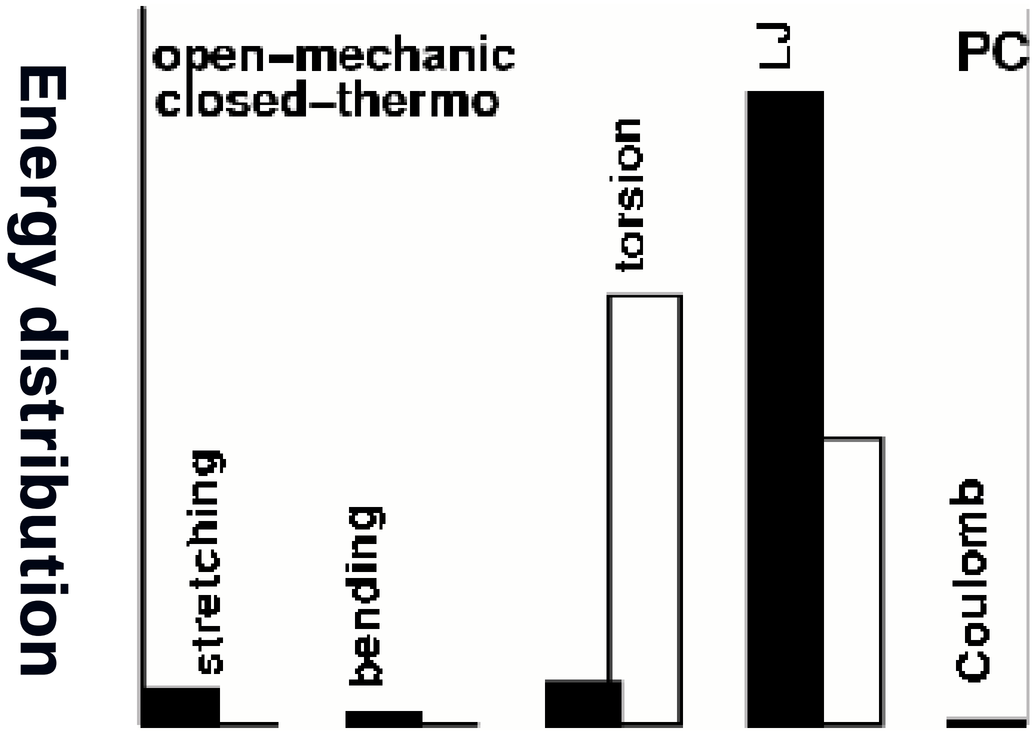
mechanical overaging because of the β process

- faster for PS, slower for PC
- effect is larger for PC

Stretching - compression loop: annealed samples



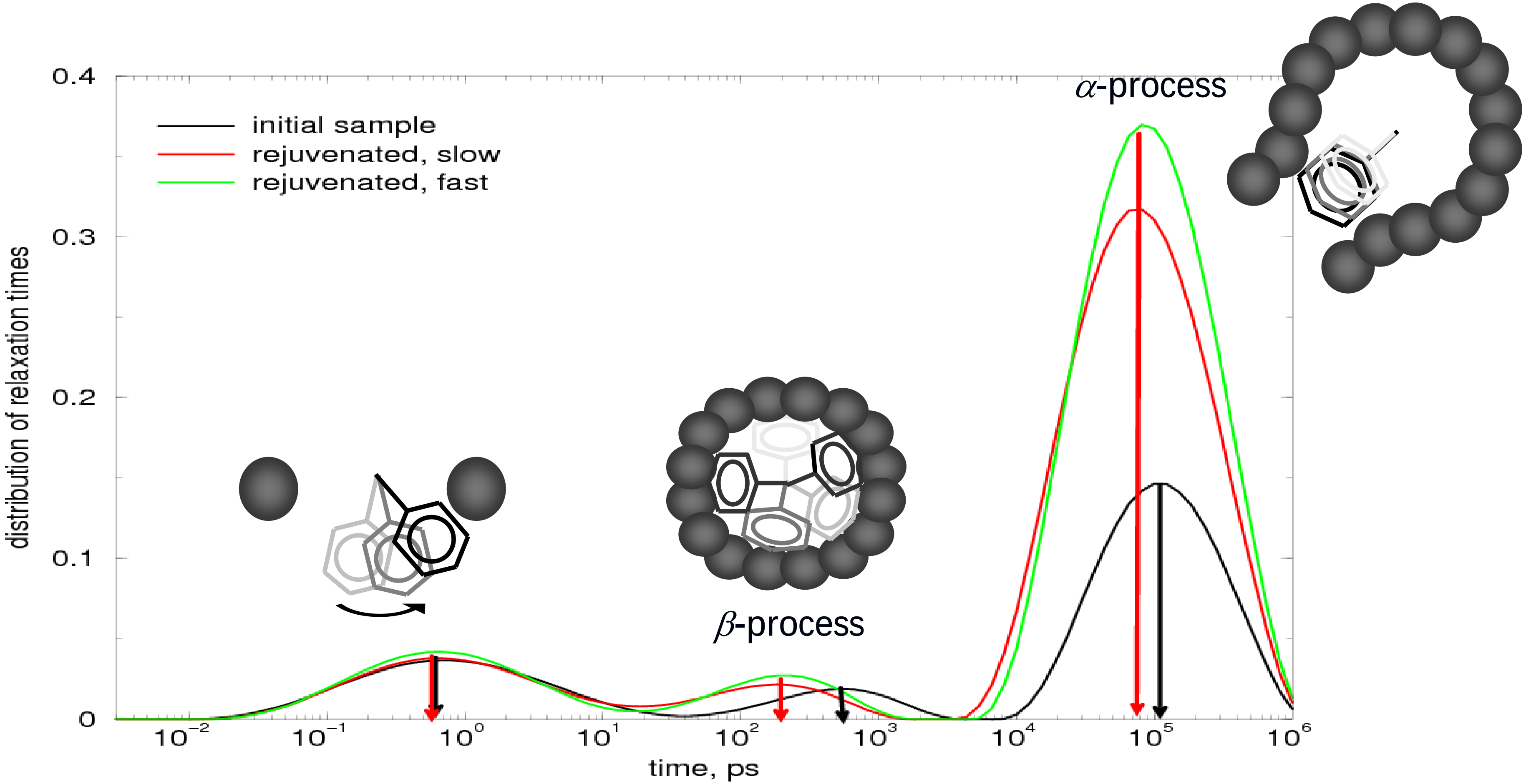
Energy partitioning



mechanically rejuvenated glass is different from thermally rejuvenated glass

AVL, M.A.J. Michels, *Phys. Rev. Lett.*, 2007

Distribution of relaxation times



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Summary

Asymptotic glass-transition T_g reproduced well for PS and PC;

Overaging and rejuvenation for typical polymer glasses have been simulated;

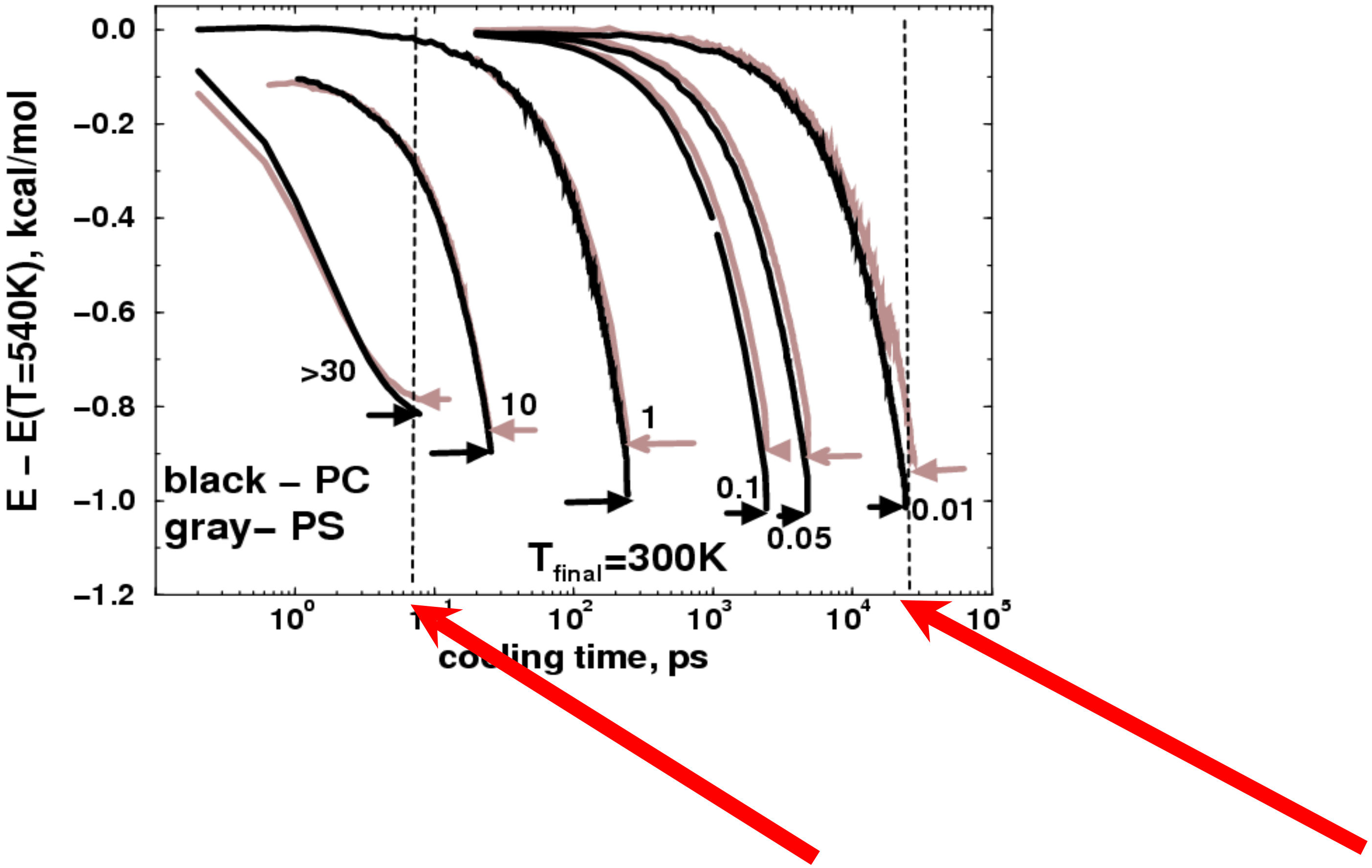
Key factors are ratios between three time scales:

- β relaxation;
- cooling time;
- deformation time;

Fast β relaxation for PS, slow for PC;

Ageing rate is increased after mechanical rejuvenation

Cooling down below T_g



Cooling time, τ_c

10 ps (quenched)

25 ns (annealed)