Direct Measurement of Molecular Mobility in Actively Deformed Polymer Glasses

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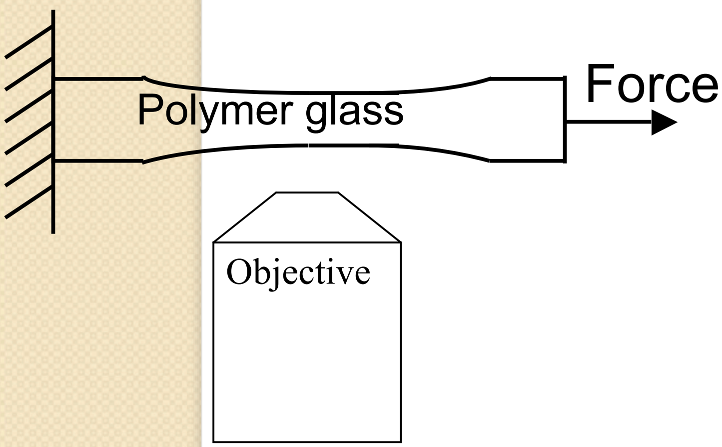


In collaboration with:

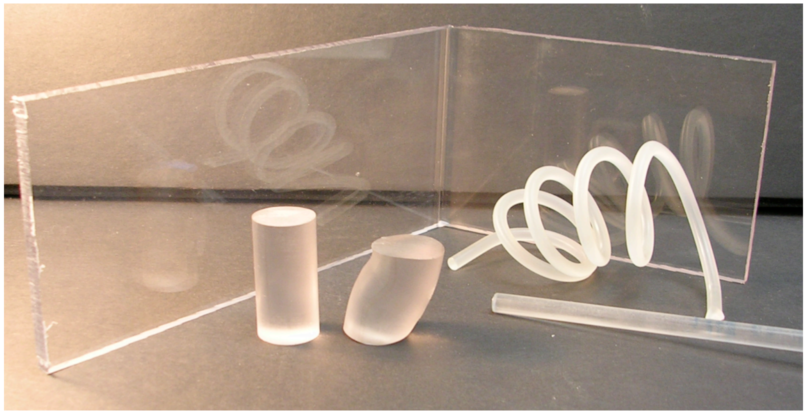
Juan de Pablo, Rob Riggleman (UW)

Jim Caruthers, Grisha Medvedev (Purdue)

Ken Schweizer, Kang Chen (Illinois)

Funding: NSF NIRT, DMR

What allows polymer glasses to flow?



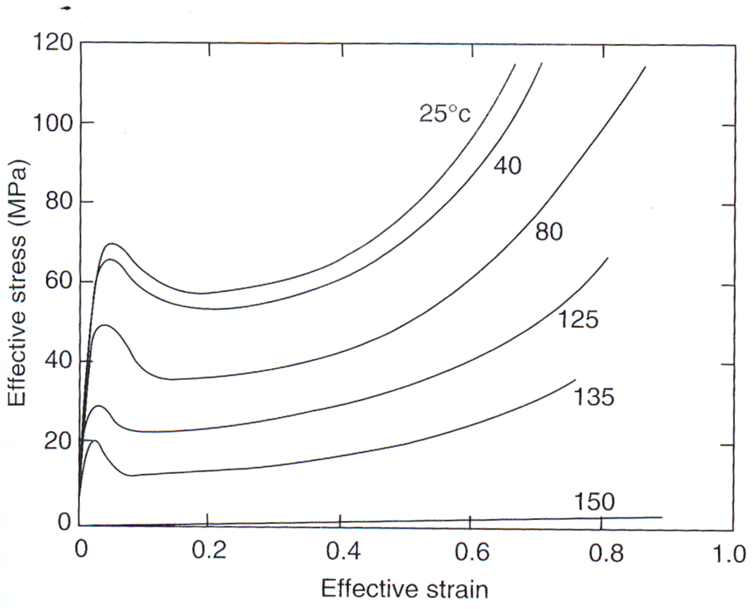


Figure 12.23 Stress–strain behavior of polycarbonate in uniaxial extension at various temperatures. (Reproduced from G'Sell, C., Hiver, J.M., Dahoun, A., and Souahi, A., *J. Mater. Sci.*, 27, 5031, 1992. With permission.)

Remarkable! Glasses (that by definition lack mobility) flow like a liquid!

From Polymer Chemistry, Hiemenz and Lodge

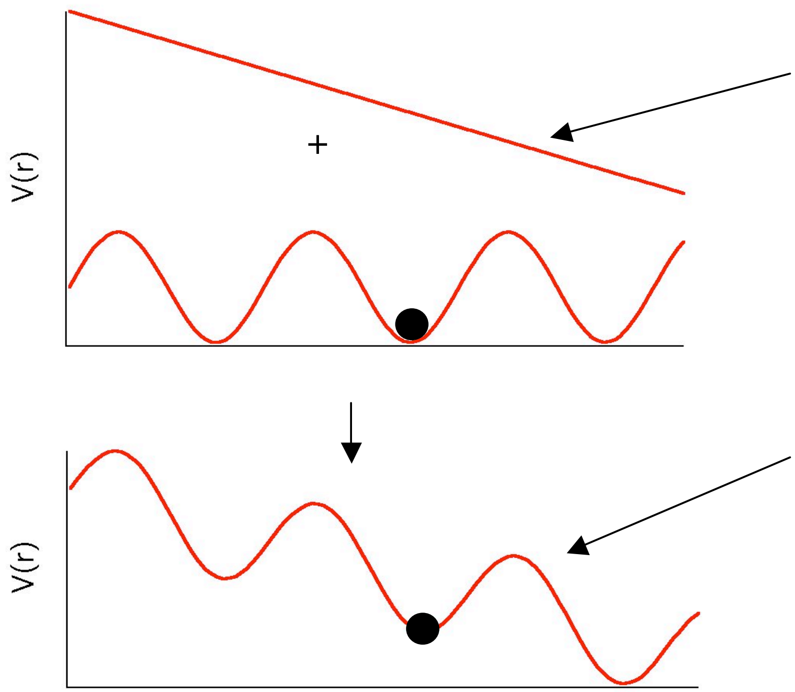
One viewpoint: Deformation induces mobility and transforms the glass into a very viscous liquid

APRIL, 1936 JOURNAL OF CHEMICAL PHYSICS VOLUME 4

Viscosity, Plasticity, and Diffusion as Examples of Absolute Reaction Rates

HENRY EYRING, *Princeton University*

(Received February 3, 1936)



Constant stress implies this potential

This barrier is lowered by stress

Han Meijer: "…yielding is mechanically passing T_g by applying stress…"

Recent efforts to model polymer glass deformation

Mobility is enhanced by:

- Stress (Meijer, Govaert, Tervoort, Buckley, Schweizer)
- Free volume (Knauss, Liechti)
- Configurational entropy (Caruthers)
- Configurational internal energy (Caruthers/Adolf)

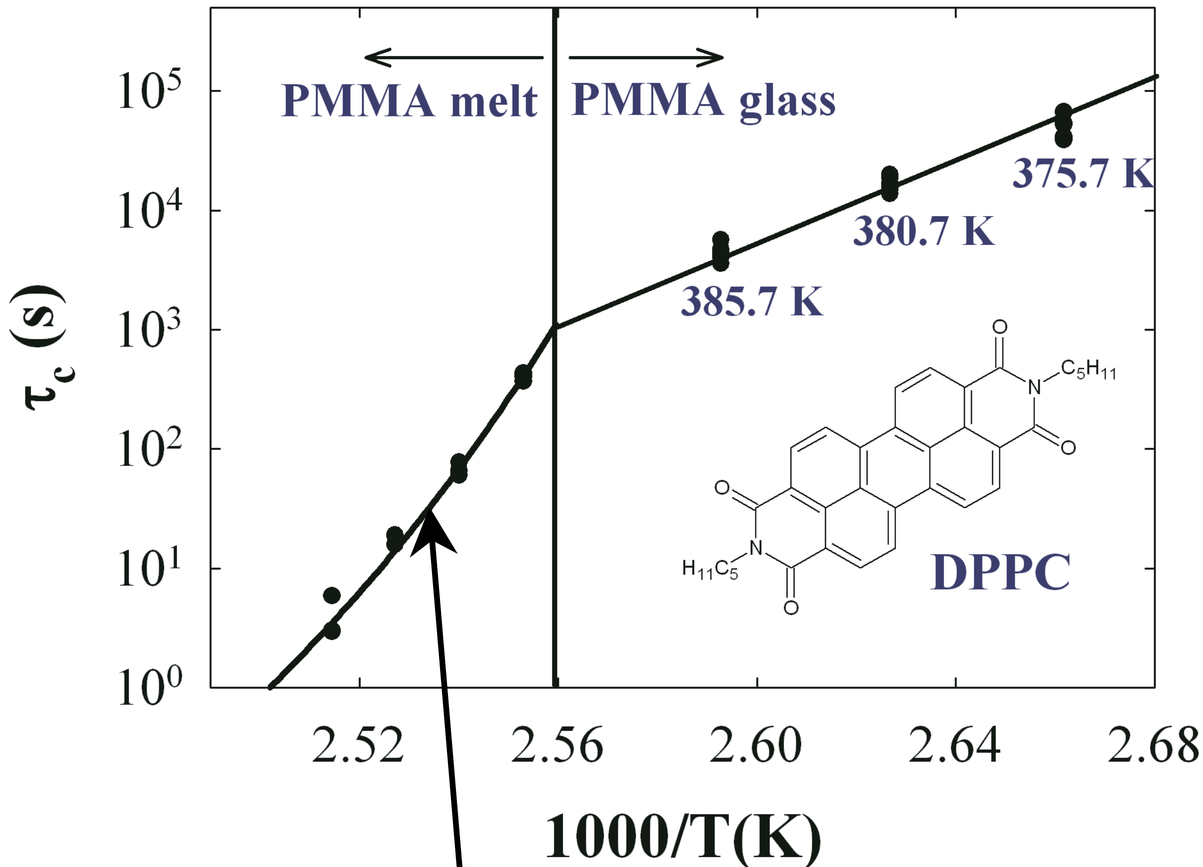
Alternate explanations do not invoke mobility changes (Boyce, Argon)

Almost no discussion in terms of shear transformation zones. Why? T/T_g is too high??

Mobility plays a central role in current efforts to describe polymer glass deformation

- Previous microscopic experiments lend qualitative support (Loo/Cohen/Gleason, Zhou/Cohen/Argon…)
- Our measurements provide quantitative microscopic mobility measurements during active deformation
- Better modeling needed to predict long-term performance, e.g., for composite materials in next-generation aircraft

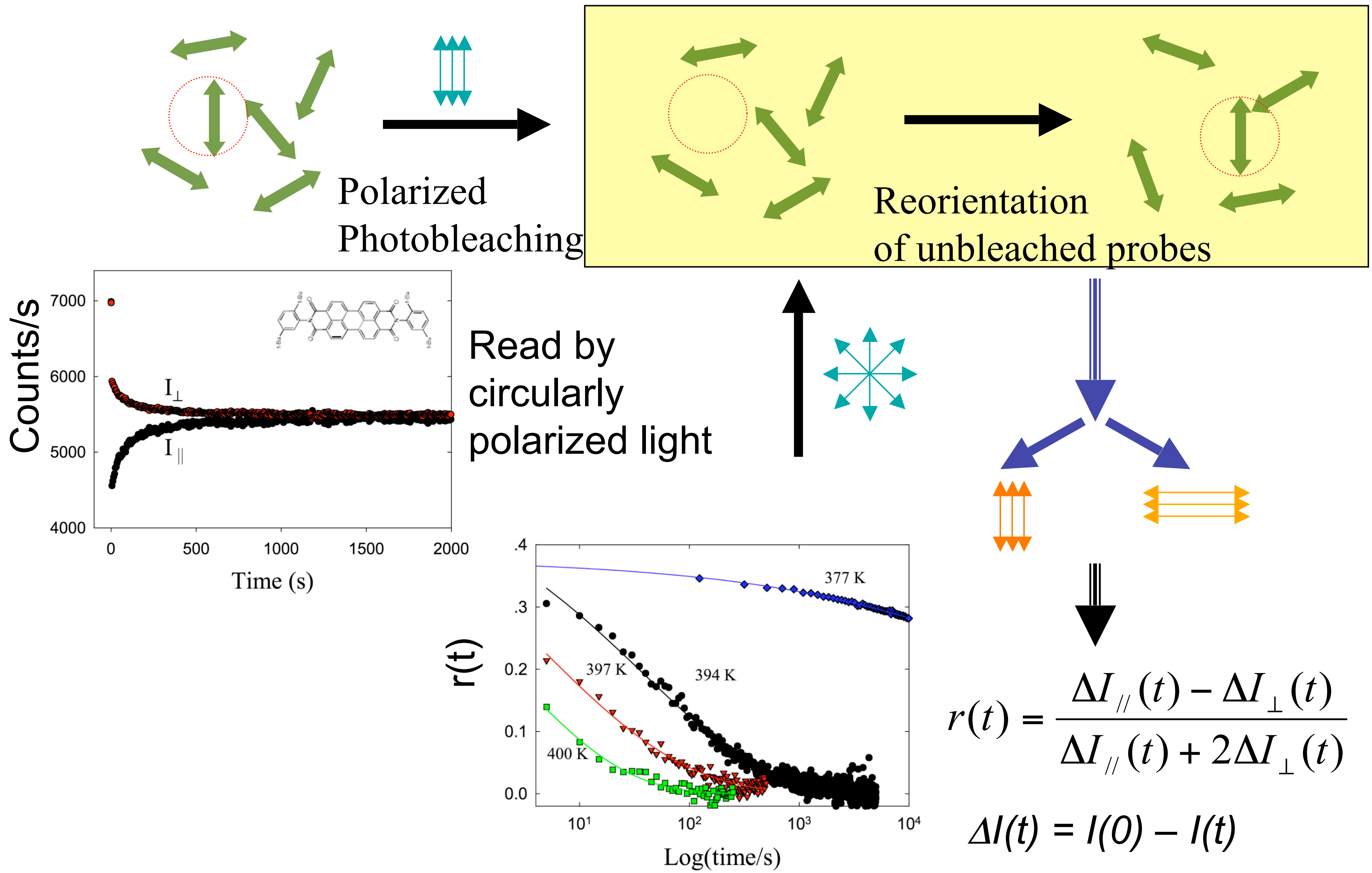
Key concept for our experiments--
Probe reorientation reports on polymer dynamics



The rotational correlation times τ_c follow the temperature dependence of the dielectric relaxation time τ_α

Rotational correlation times of probe molecule are strongly correlated with segmental dynamics of polymer

Dye reorientation measured with photobleaching technique



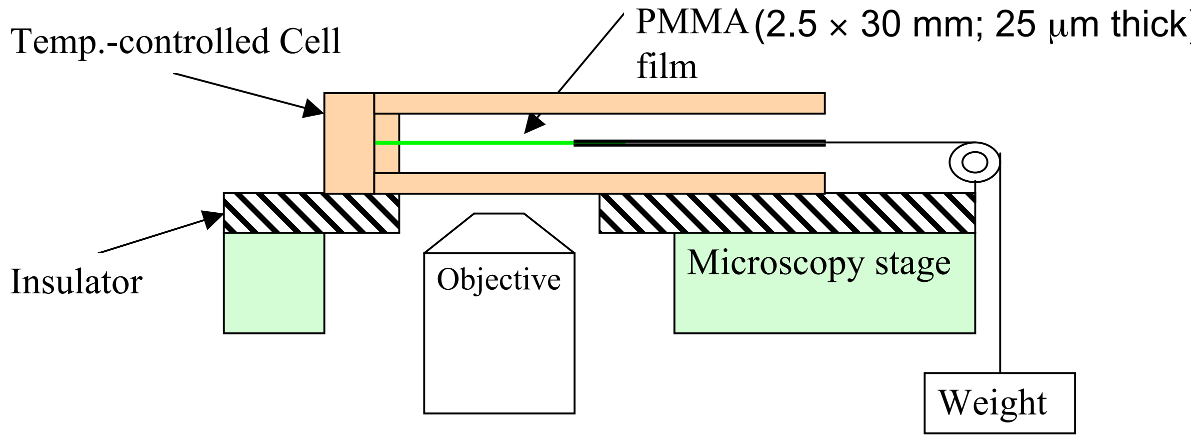
$$r(t) = \frac{\Delta I_{//}(t) - \Delta I_{\perp}(t)}{\Delta I_{//}(t) + 2\Delta I_{\perp}(t)}$$

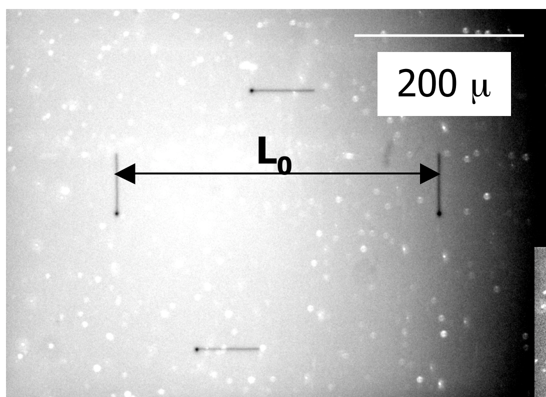
$$\Delta I(t) = I(0) - I(t)$$

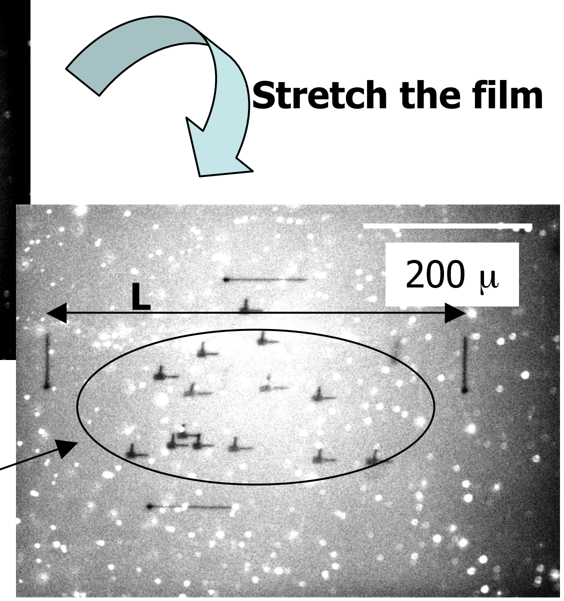
Strain and mobility are measured locally

Sample: lightly cross-linked PMMA glass; T_g = 395 K

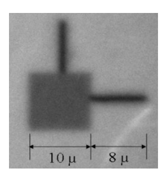
Tensile creep experiment





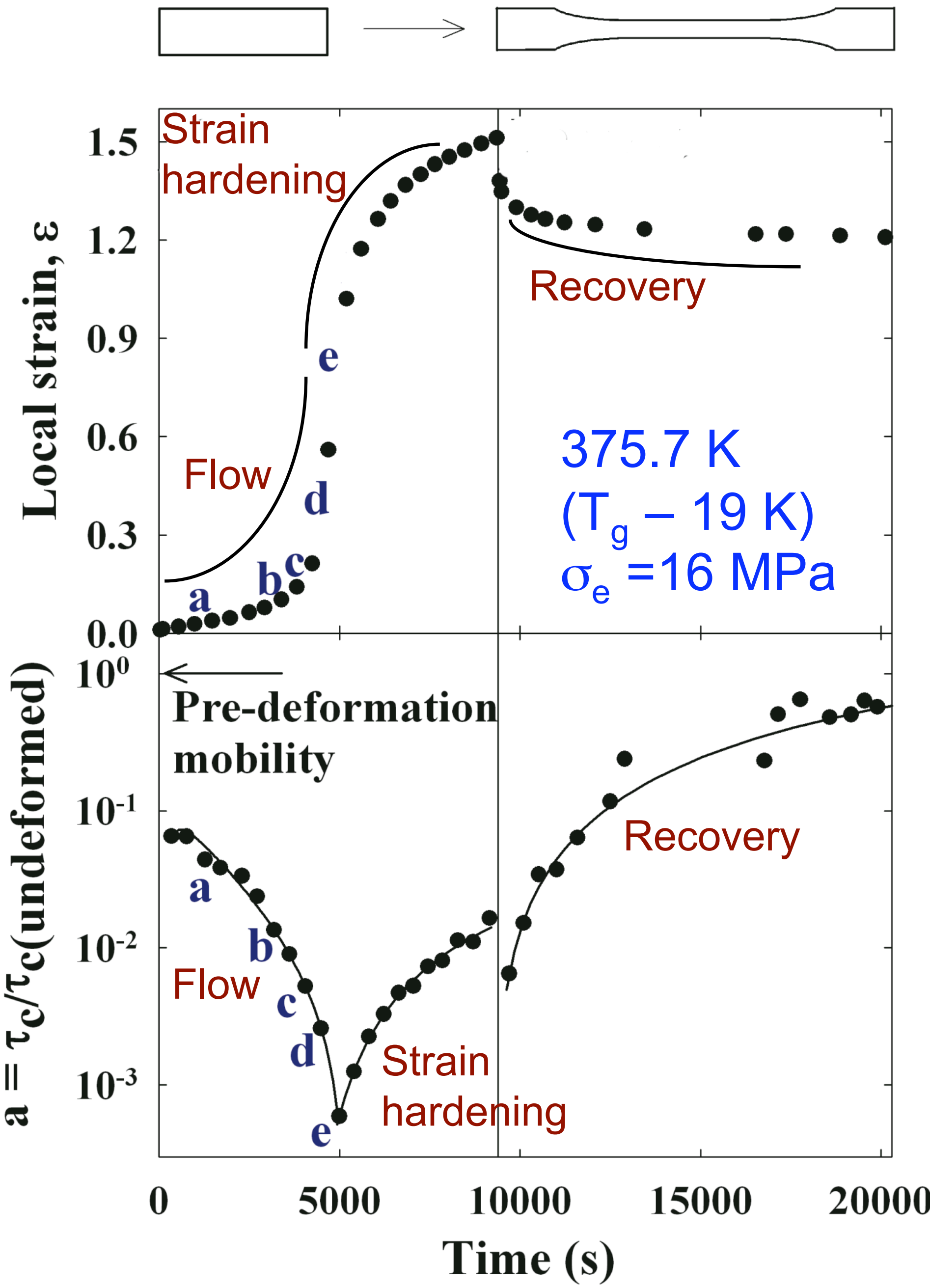


Strain = $(L(t) - L_0)/L_0$

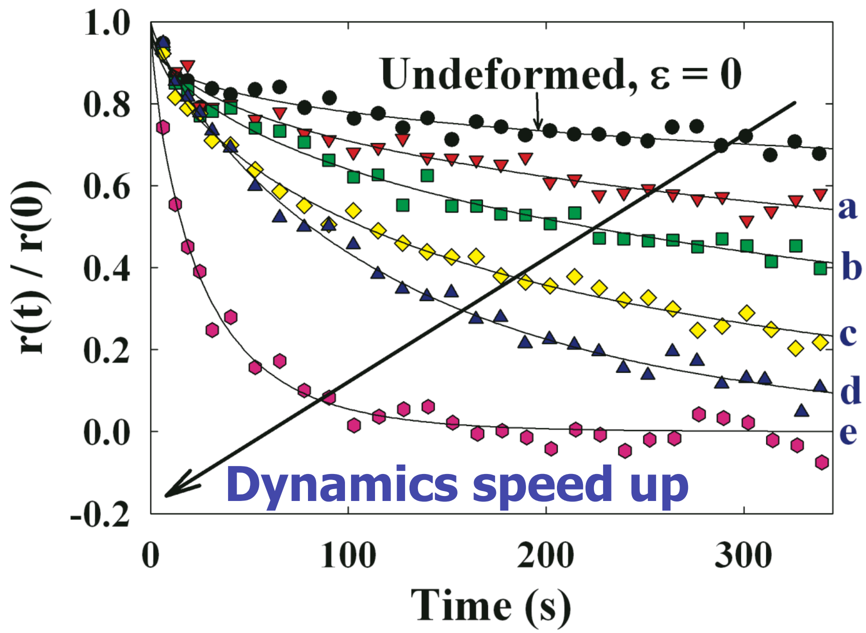


Measure mobility of polymer in these small regions using polarized photobleaching

Evolution of mobility during deformation



Lee, Paeng, Swallen and Ediger, Science, 2009, 323, 231



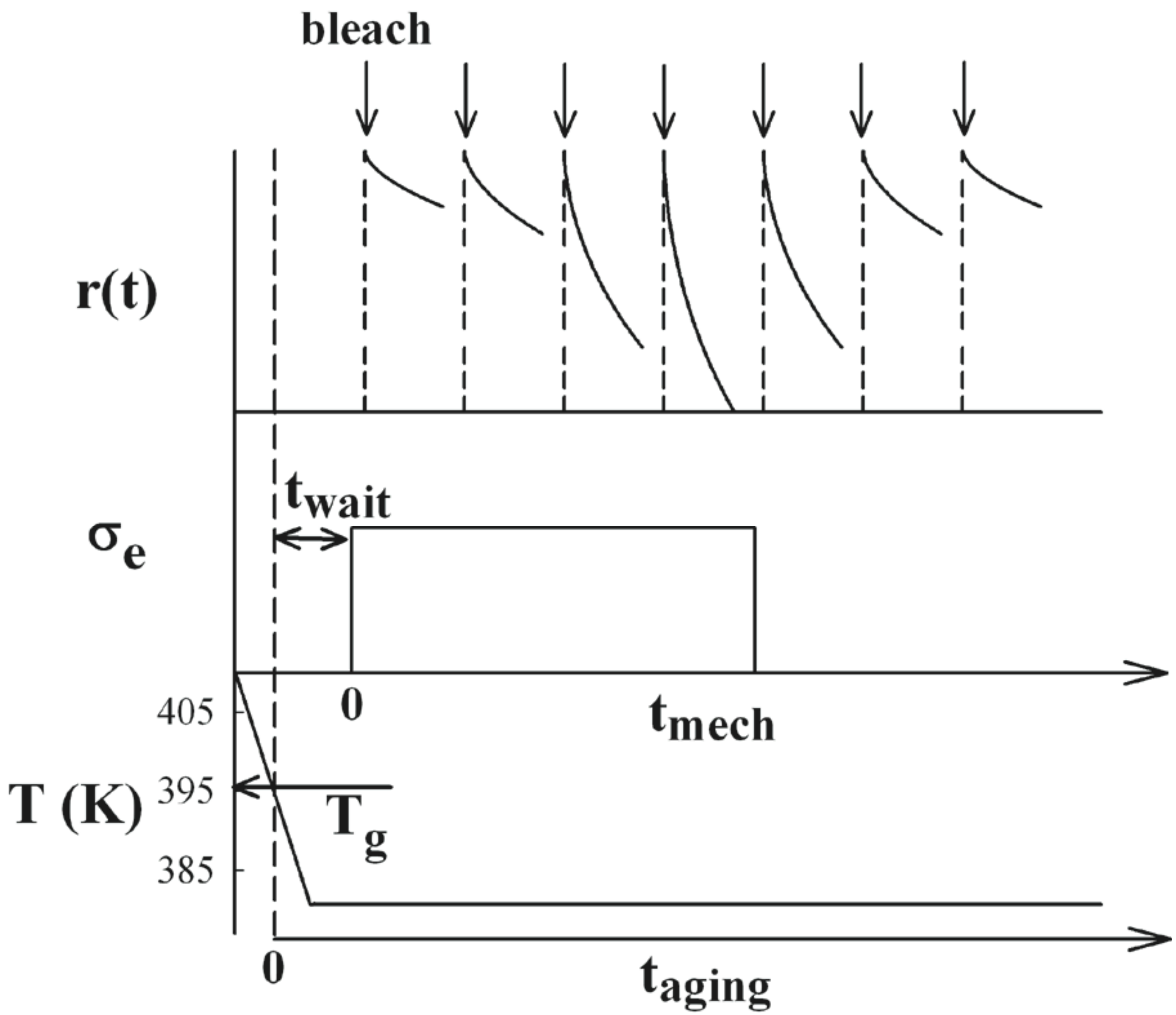
r(t): anisotropy function

$$r(t) = r(0)\exp[-(t/\tau)^{\beta}]$$

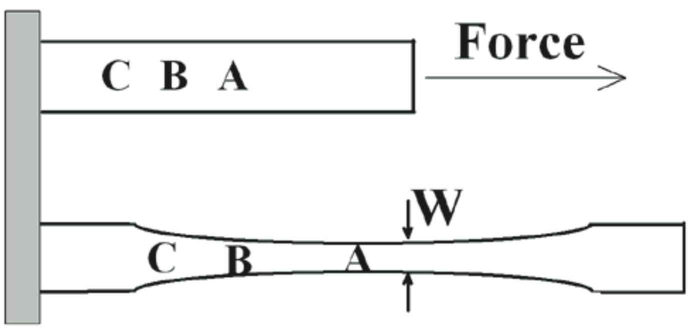
KWW function

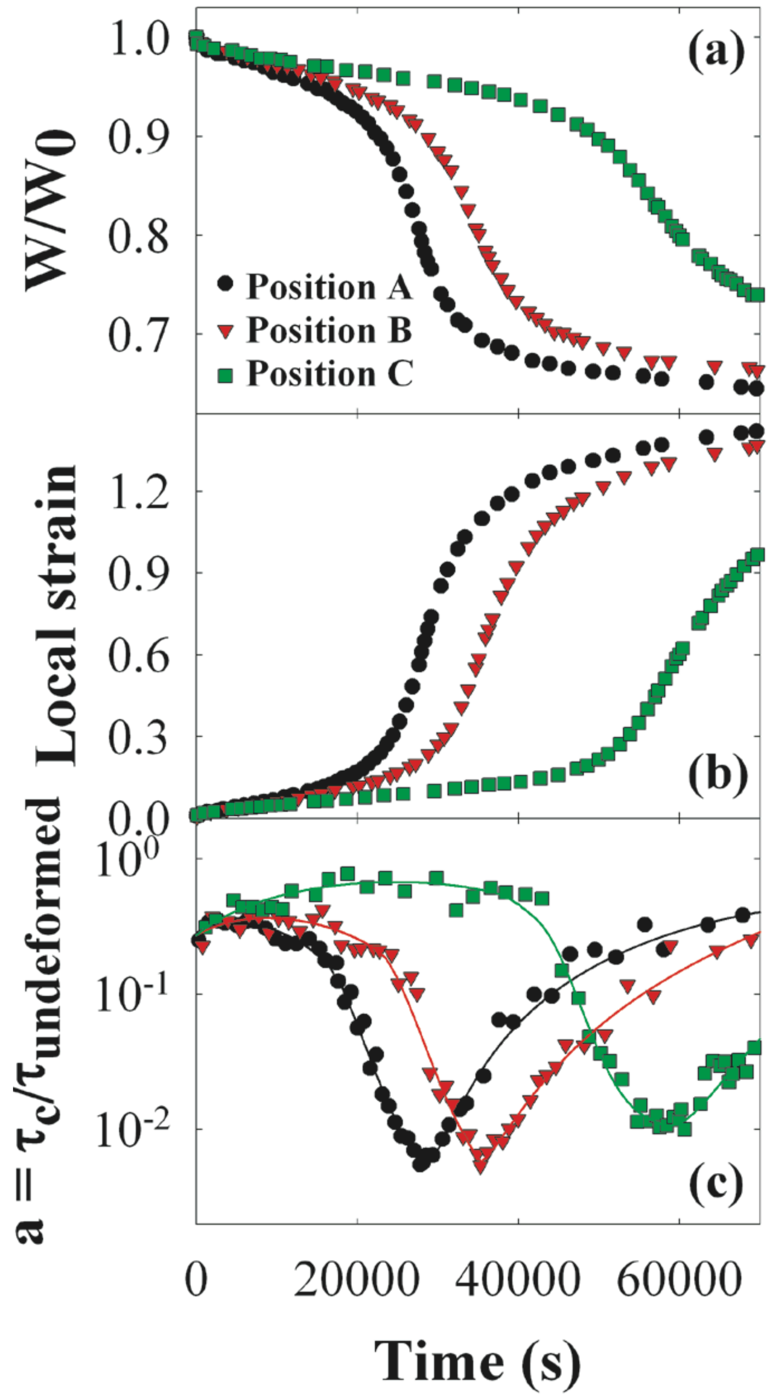
Segmental dynamics speed up by a factor of 2000 during deformation

Clarification of measurement scheme



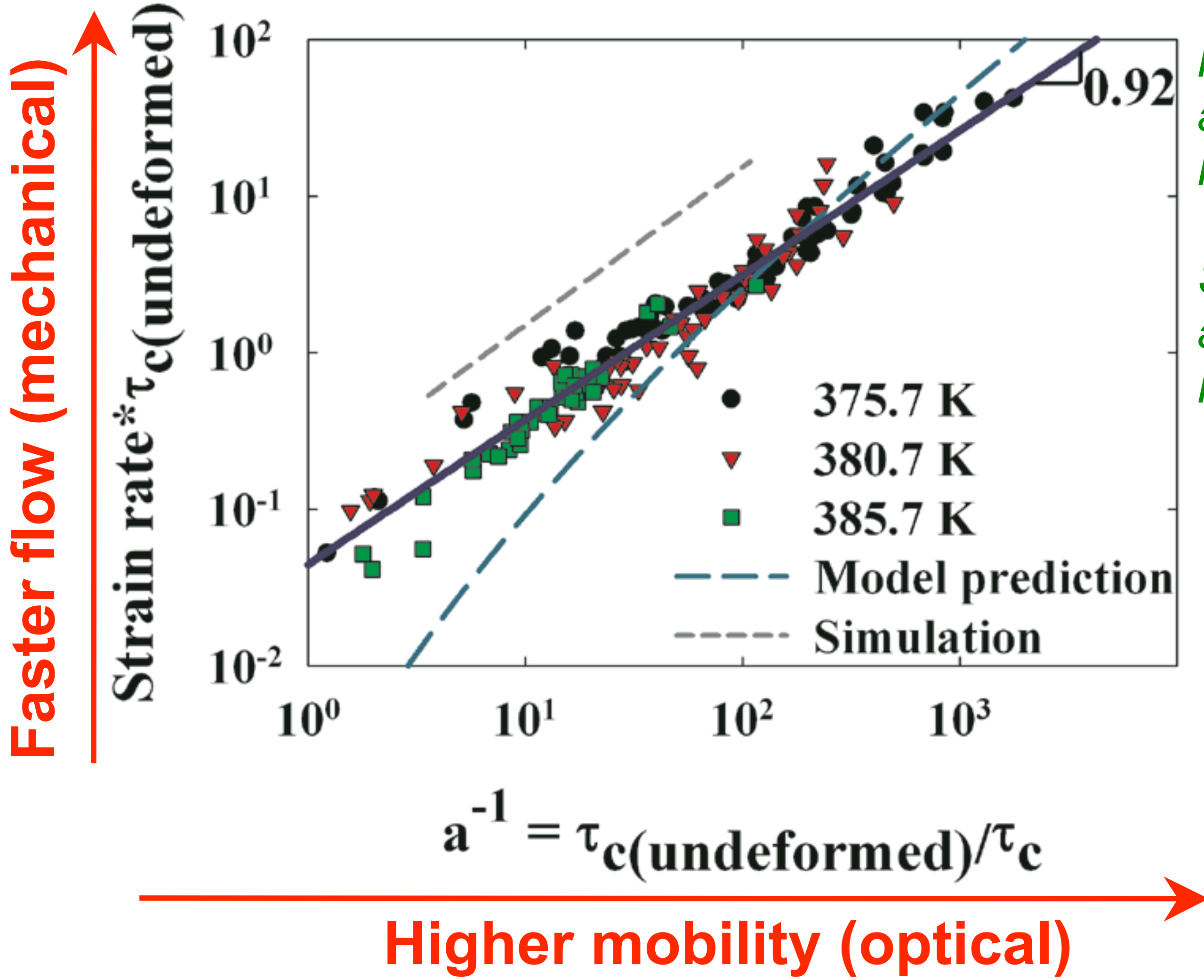
Simultaneous measurements in different parts (neck, shoulder…) of an inhomogeneously deformed sample





Molecular mobility is highest in the shoulder, rather than the neck

1) Does deformation induce mobility that allows flow?

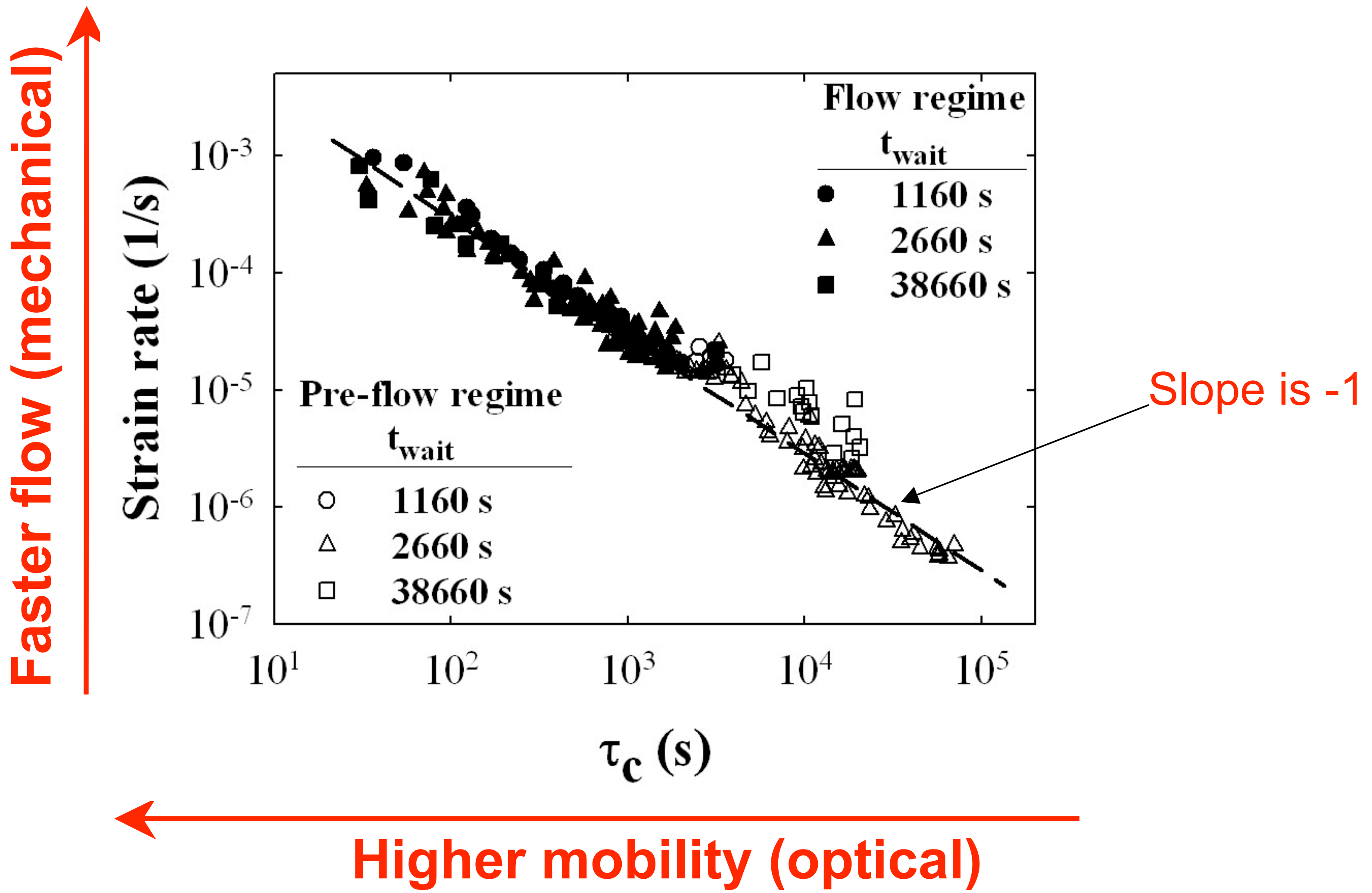


Model prediction by Chen and Schweizer, Macromolecules, 2008

Simulation by Riggleman and de Pablo, Macromolecules, 2008

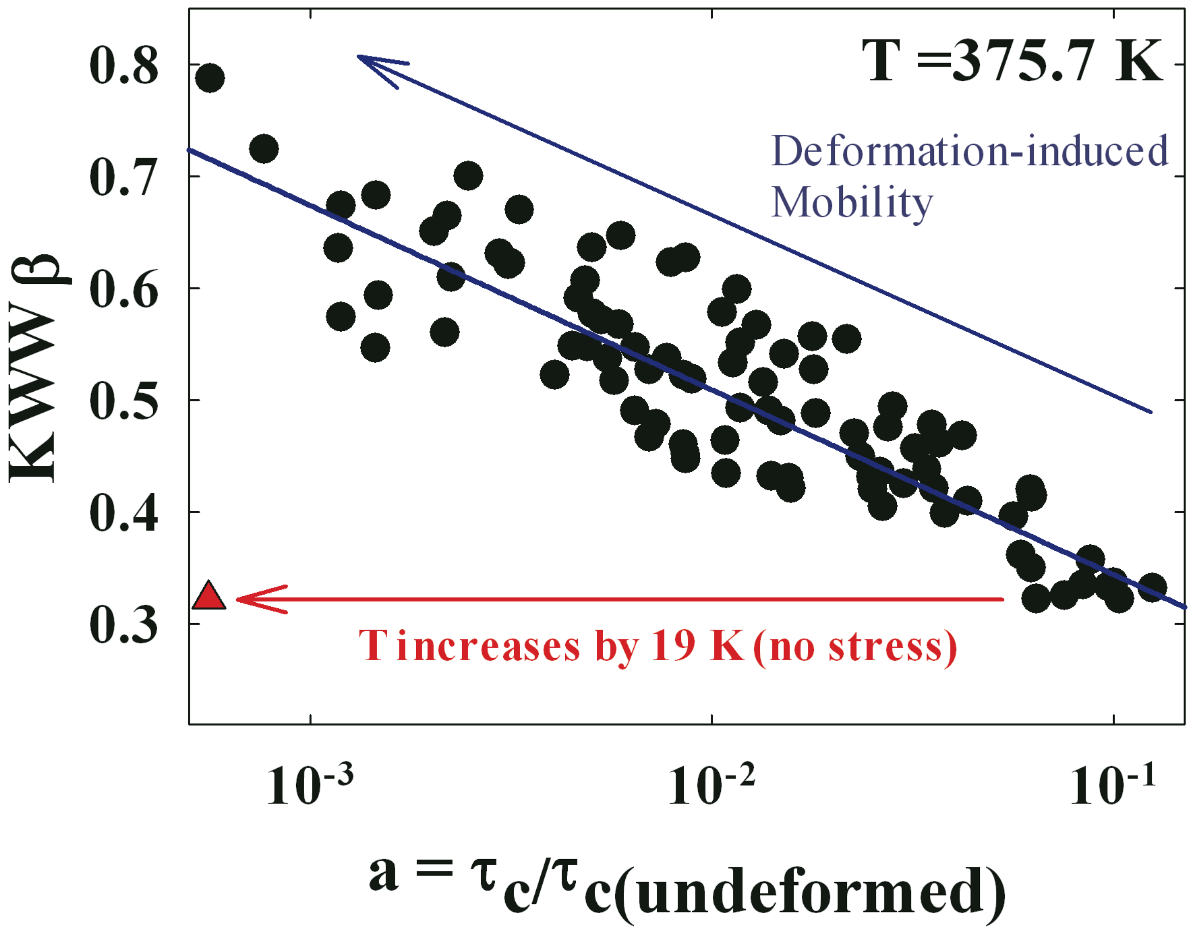
Answer: Data is consistent with this hypothesis

Correlation between mobility and strain rate is quite robust in single step creep measurements.



Correlation works for different aging times and different deformation temperatures

2) Is deformation equivalent to increasing temperature?



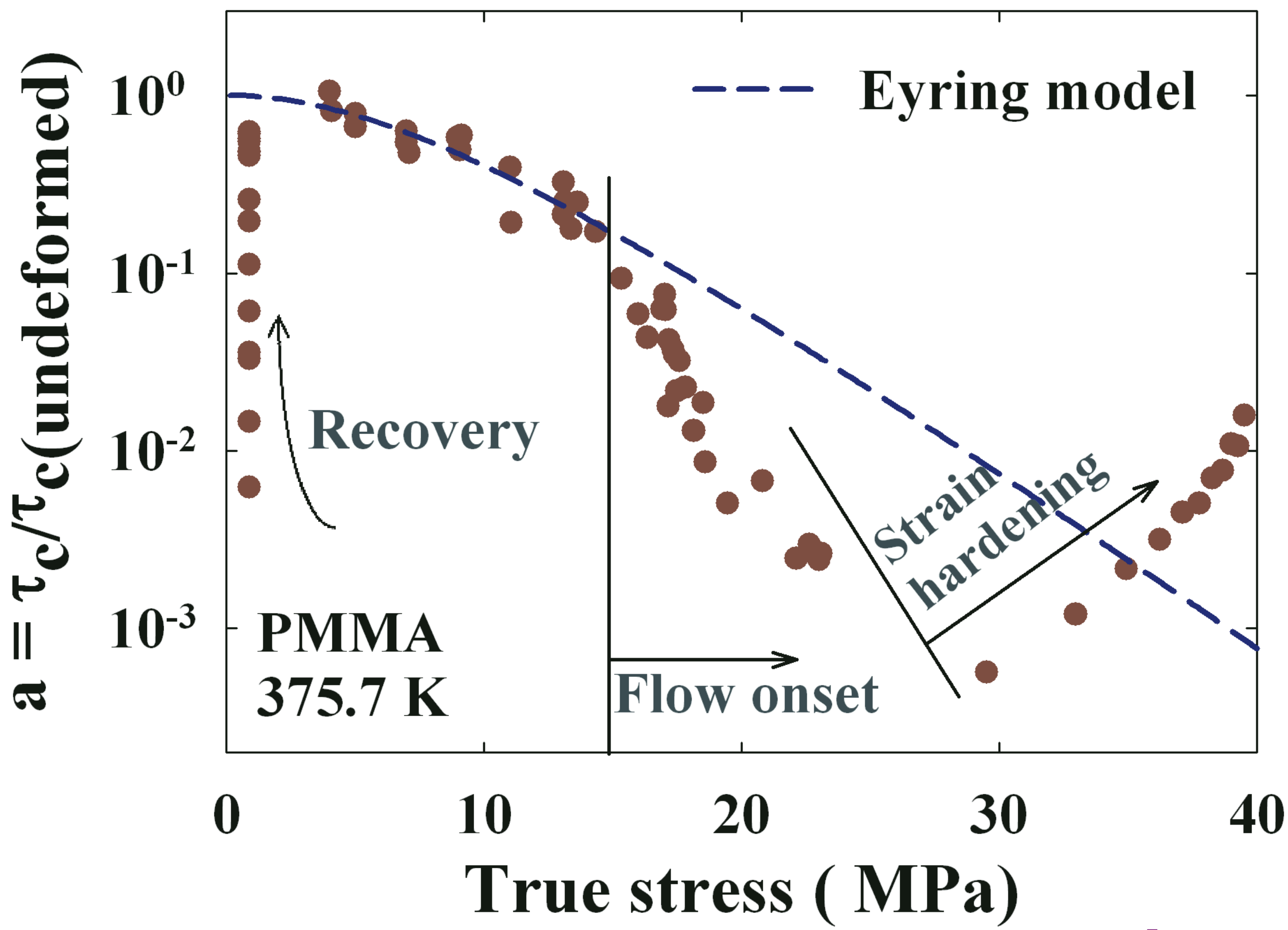
- ❖ KWW β is an indication of the width of the relaxation time spectrum
- ❖ A small β implies a broad spectrum
- ❖ A small β indicates dynamic heterogeneity

Temperature and stress have a qualitatively different effect on molecular mobility. Stress induces dynamic *homogeneity*.

Answer: No

3) Can the Eyring model describe the results?

Eyring model: stress lowers the energy barriers for molecular motion and thus effectively transforms a glass into a viscous liquid



$$\tau \propto \sigma / \sinh\left(\frac{\sigma \cdot V}{2 \cdot k_b T}\right)$$

The Eyring model works only in the pre-flow regime

Answer: No, but…

4) Is "enhanced mobility" a legitimate description?

Alternative view: Of course molecules move! The sample dimensions have been altered! New types of processes occur during deformation (STZs??). These processes are unlike those that occur in the equilibrium melt at higher temperatures.

Best answer comes from MD simulations of polymer glass deformation (with Riggleman and de Pablo).

Coarse-grained model, 81 chains, 500 beads per chain, NσT ensemble, both tensile and compressive deformation. The simulations directly analyze segmental mobility (no probes). 7 different measures of segmental mobility were utilized (bond reorientation, decay of $S(q_i,t)$, reorientation of longer chain units (up to 16 units).

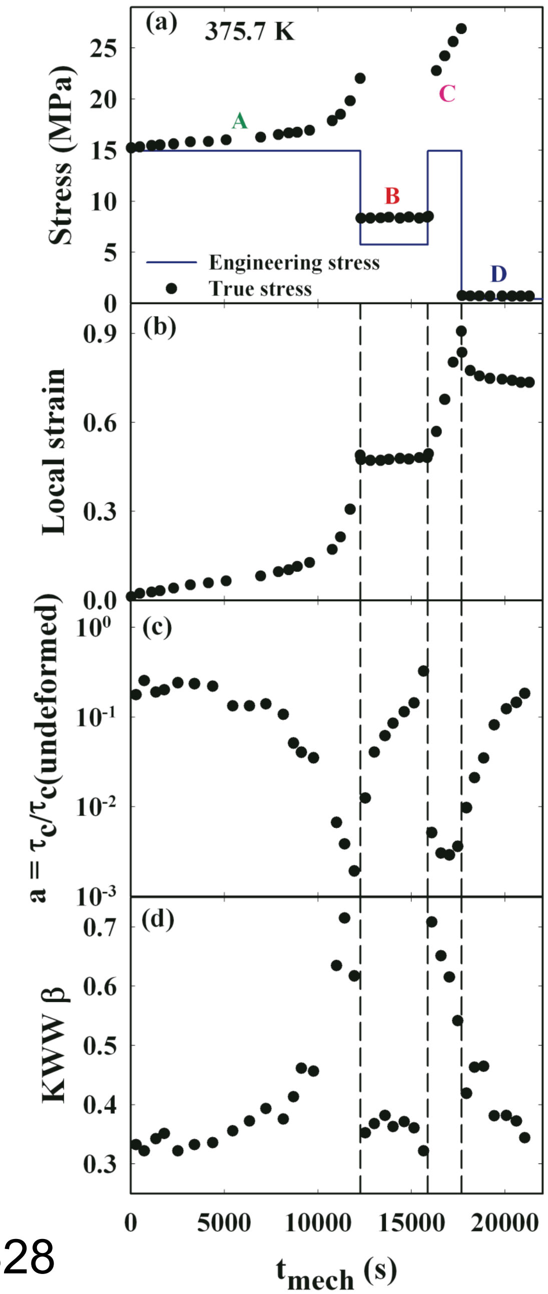
Answer: Yes

Comparison between optical experiments and MD simulations shows good agreement for all major trends.

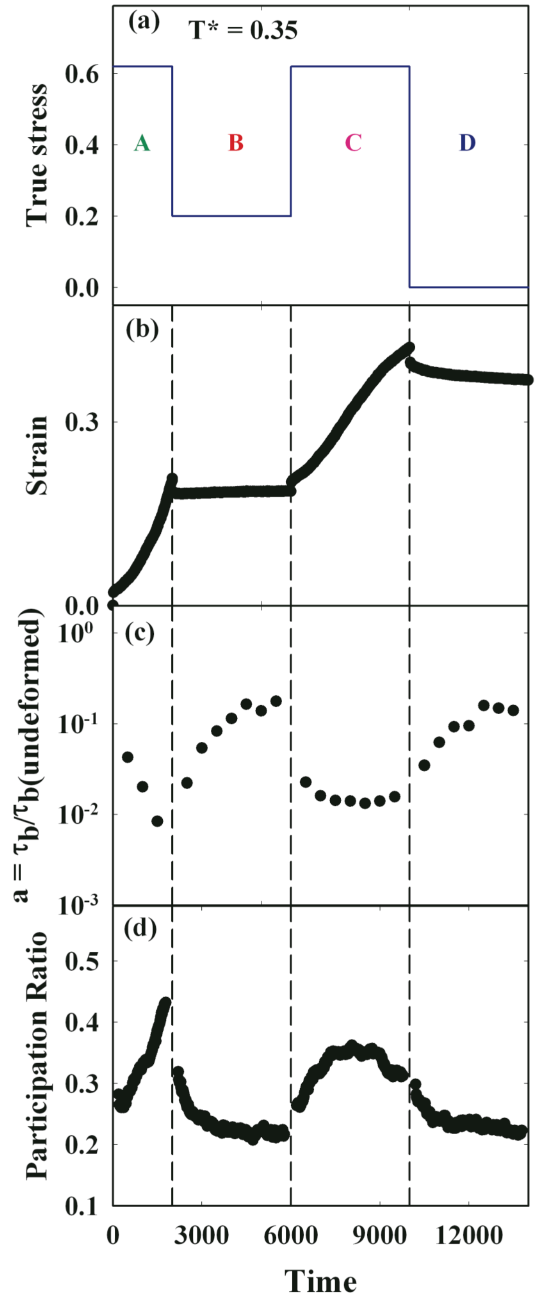
- dye is a good reporter
- simulations are big and slow enough to capture most major trends (!)
- all 7 local observables show the same mobility enhancement.
- mobility enhancement is isotropic
- "enhanced mobility" is a legitimate description of the effect of deformation

Macromolecules 2009, 4328

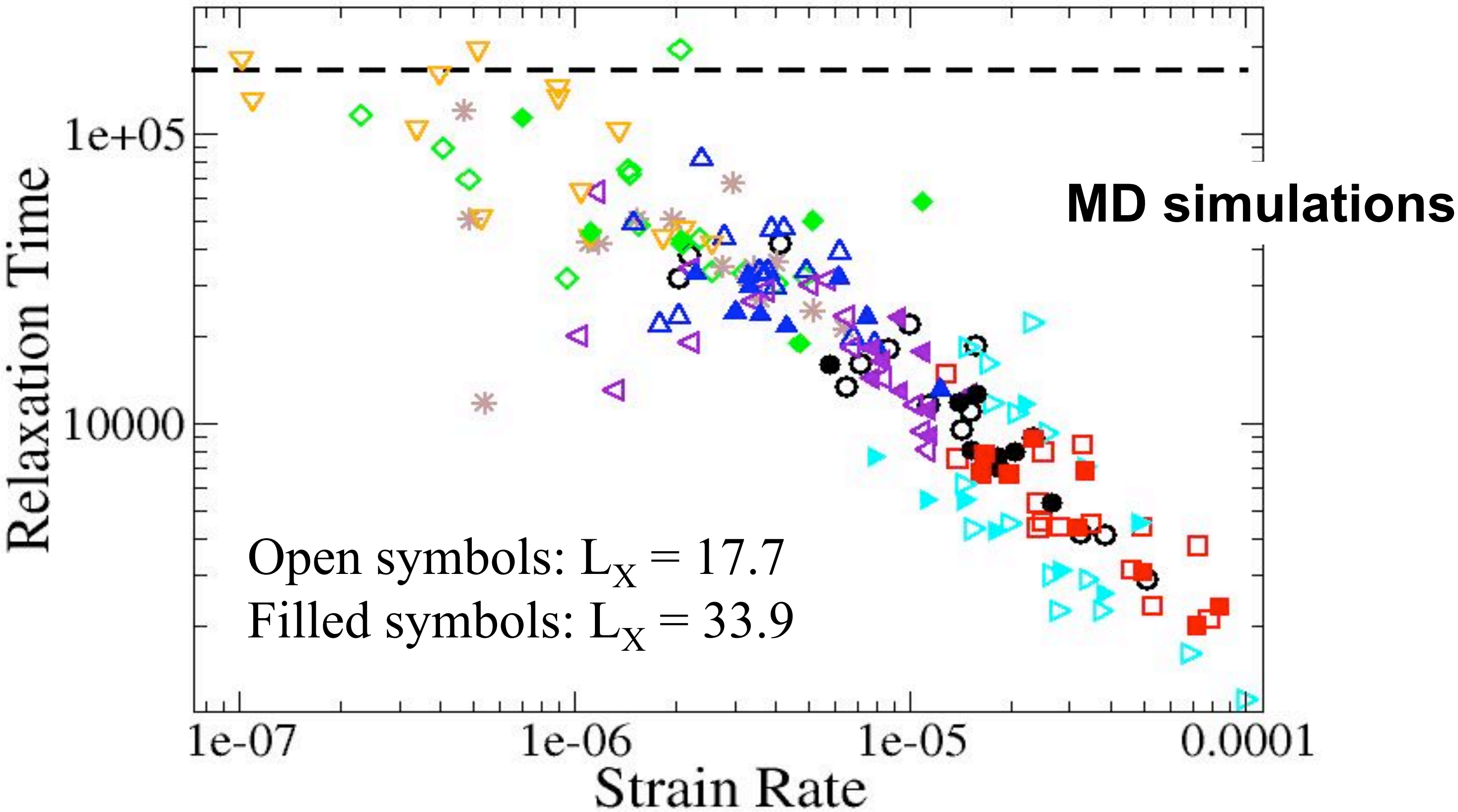
Experiment



Simulation



5) Can volume changes explain enhanced mobility?



= Compressive stress, σ_{zz} = -{0.27, 0.54, 0.62, 0.75}

= Tensile stress, σ_{zz} = {0.27, 0.425, 0.54, 0.62}

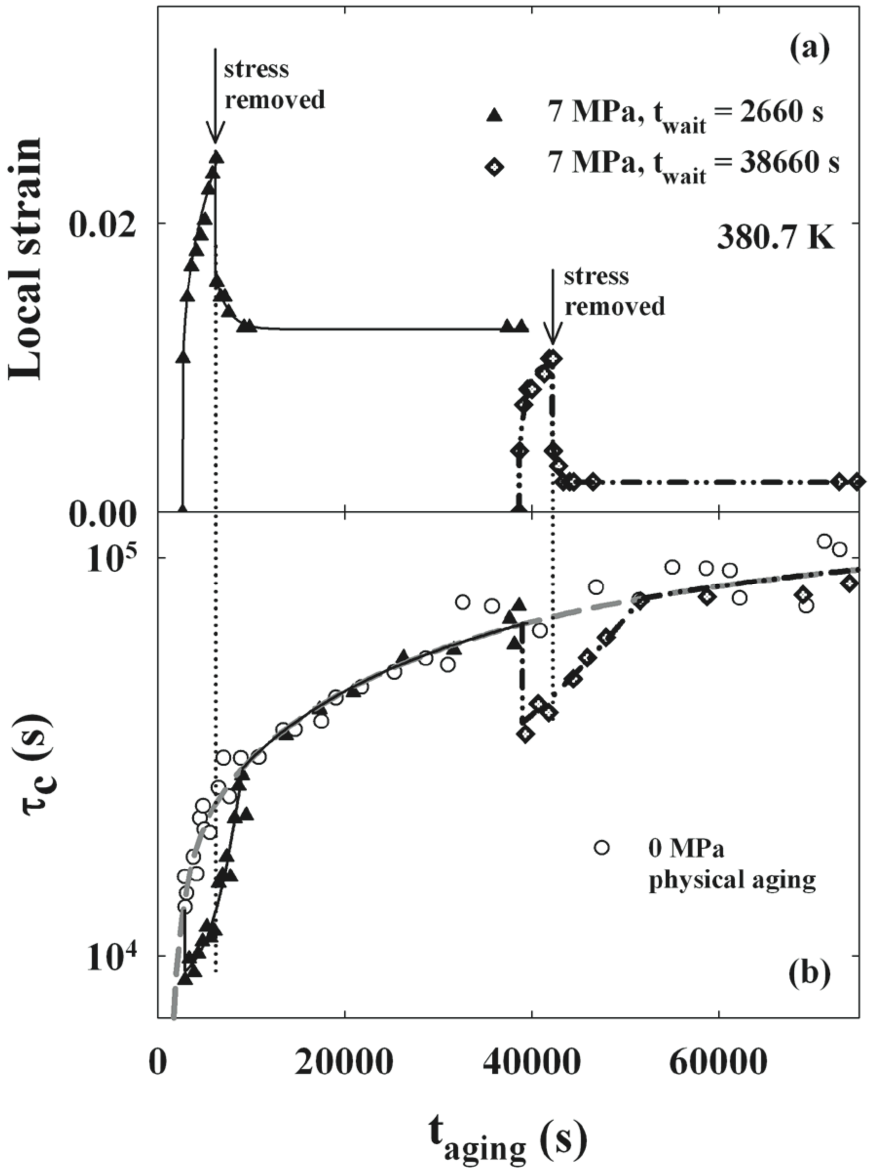
Riggleman et al., Macromolecules 2008

Answer: No

A central challenge: How to disentangle effects of deformation and changes in position on energy landscape?

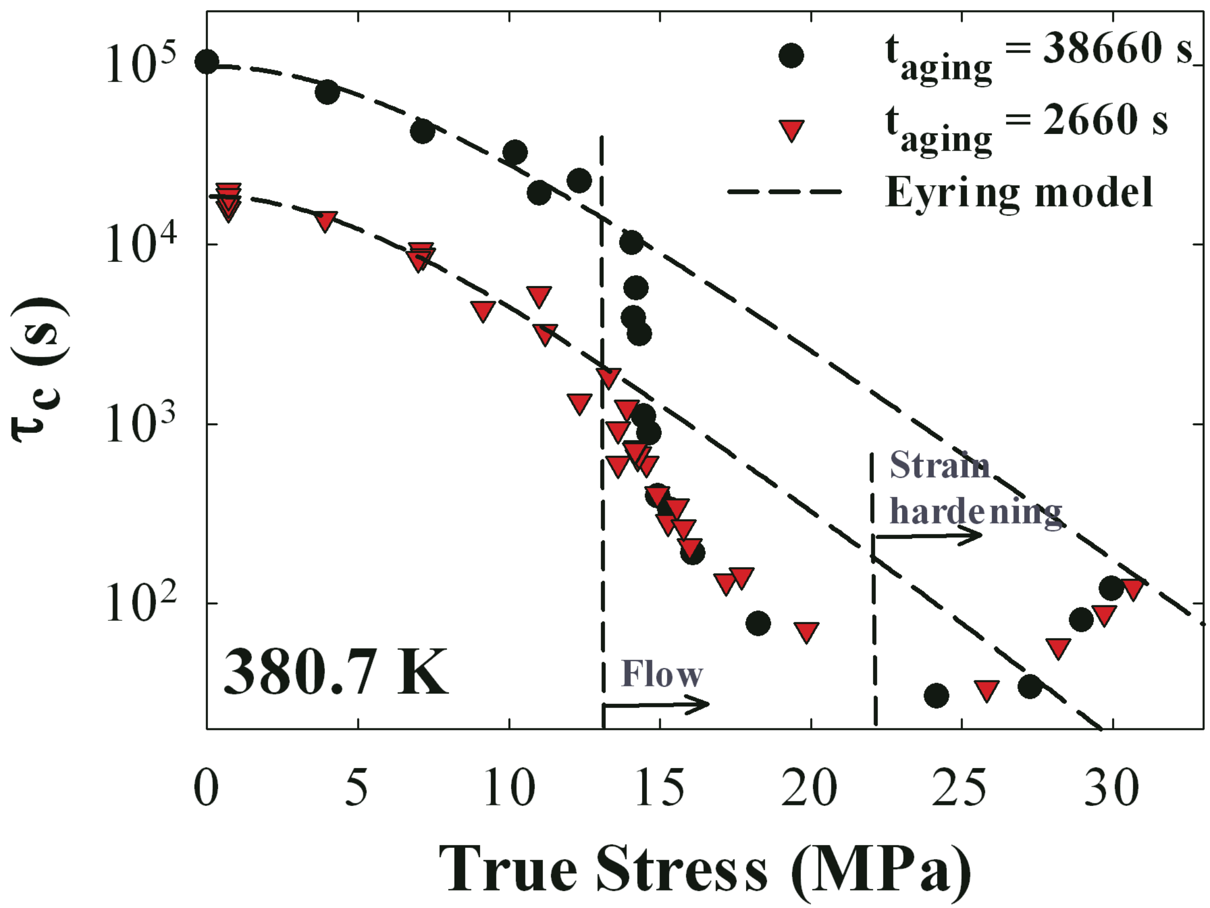
- Aging (structural recovery) slows dynamics and lowers position on the landscape
- Deformation enhances dynamics - so does deformation raise position on the landscape?
- Previous experiments: Struik, McKenna, Govaert, Meijer, Boyce
- Simulations: Warren/Rottler, Lacks, Lyulin, Debenedetti/Stillinger, Riggleman/de Pablo
- A CENTRAL CHALLENGE for modeling the deformation of polymer glasses

6) Does transient deformation affect position on the energy landscape?



Answer: Not for short, pre-yield deformation.

7) Deformation into the flow regime does affect position on the energy landscape



- At low stress, the effects of aging and stress on mobility are independent
- At higher stress, plastic flow apparently erases the influence of aging

8) Can existing models reproduce observed mobility?

Microscopic model of segmental barrier hopping

Combined:

- **Eyring-like Barrier Reduction**
- **Aging**
- **Rejuvenation (erasure of aging)**
- **Strain Hardening**

5 Regimes :

--> Elastic

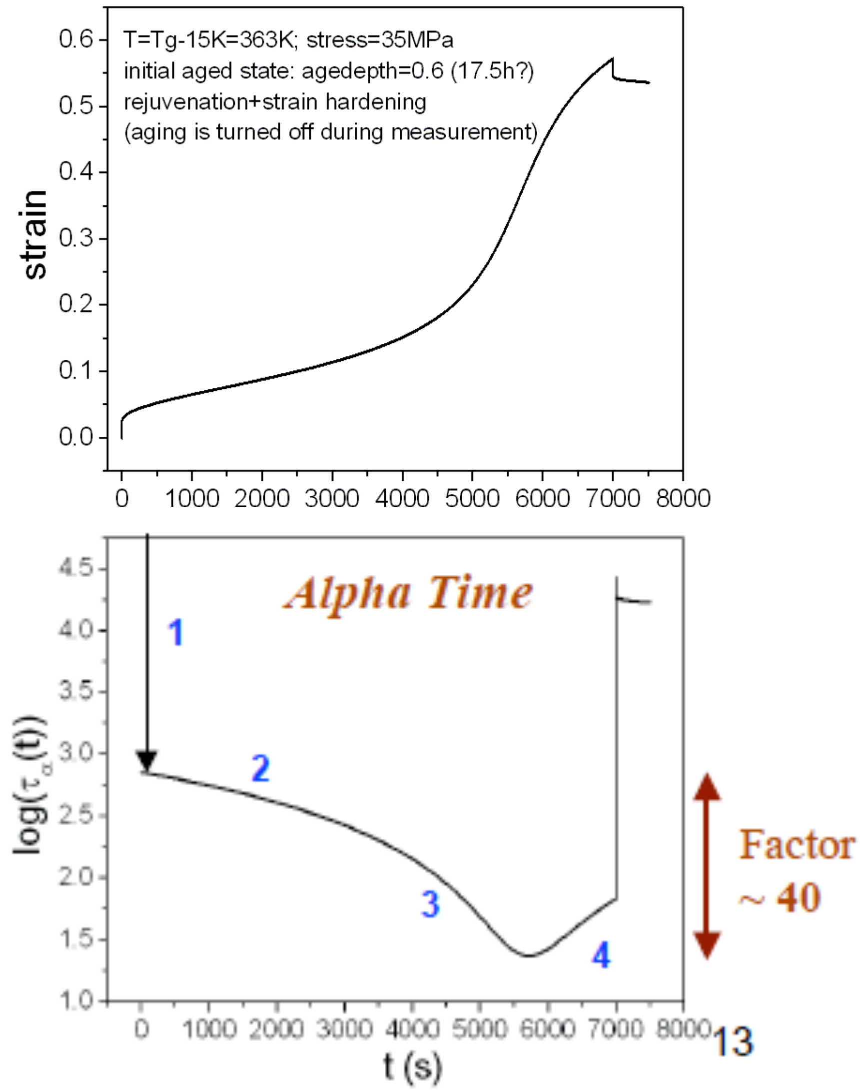
--> “Normal” Creep

--> Large strains driven by rejuvenation

--> Hardening

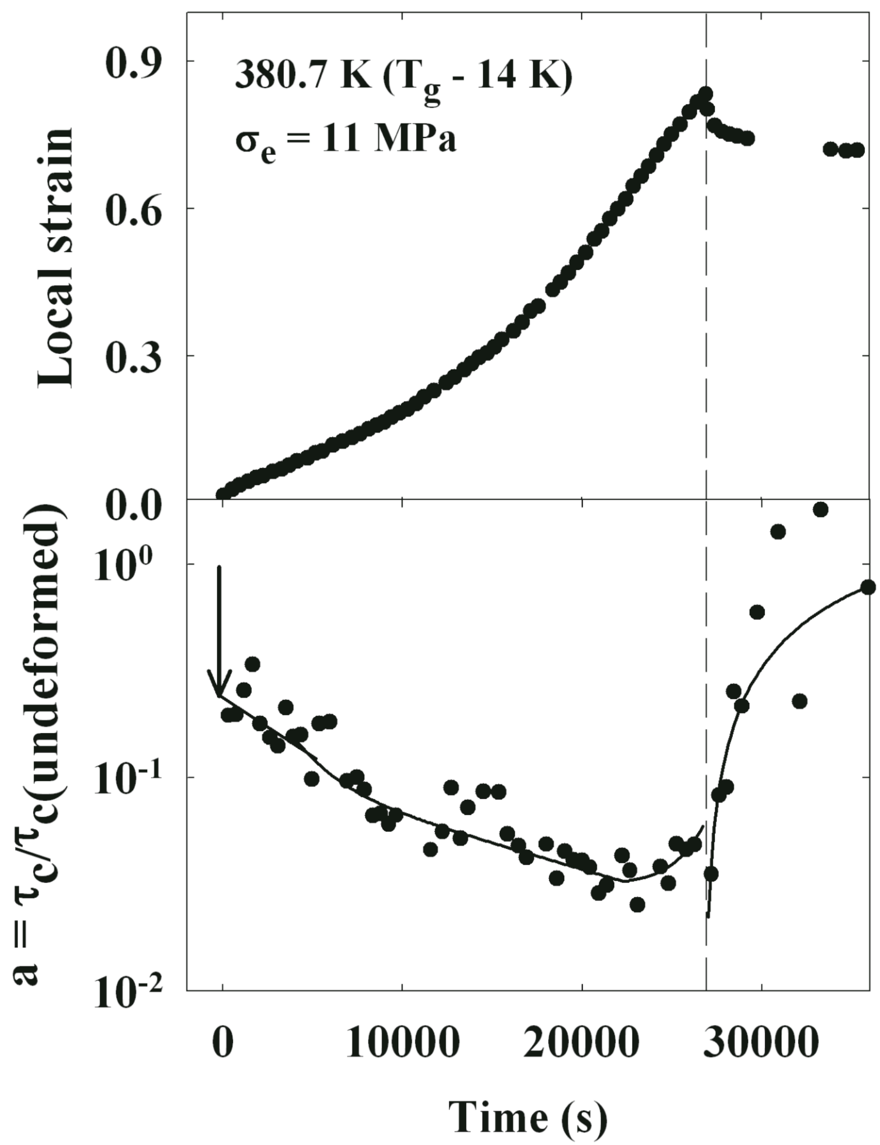
--> Recovery (no stress)

Model prediction by Chen and Schweizer

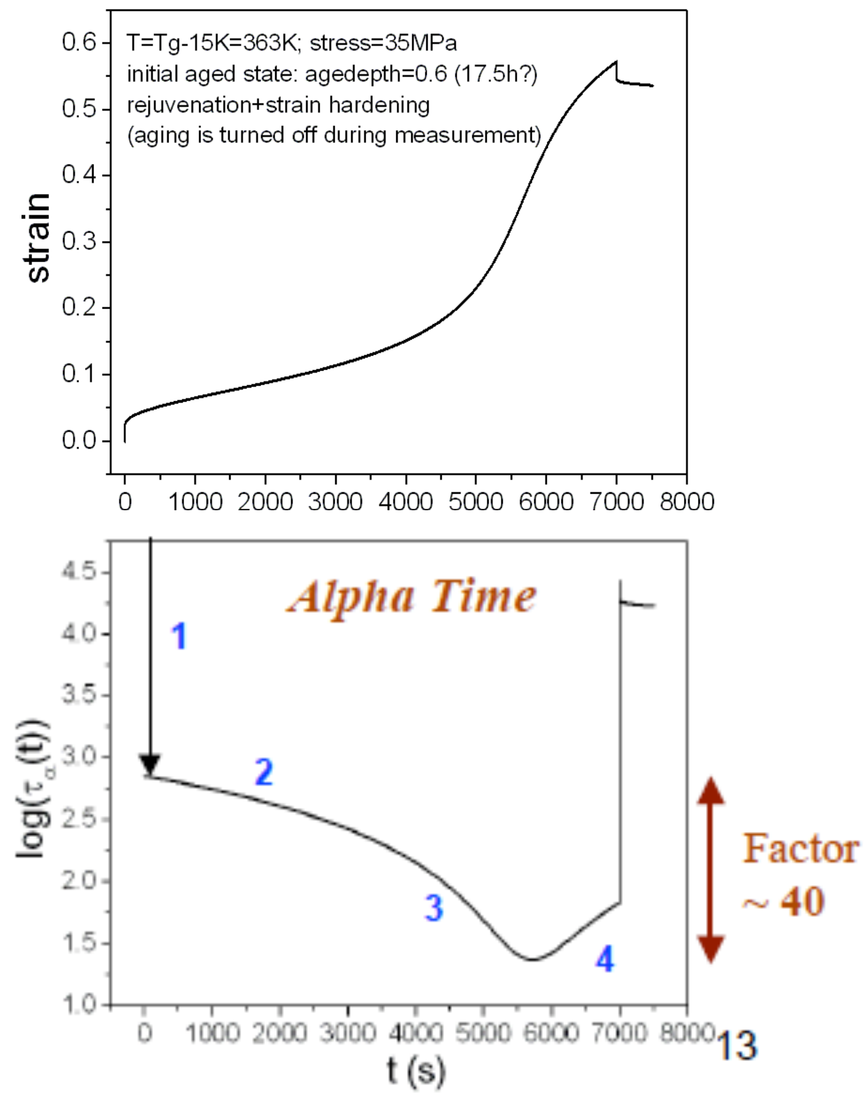


Modelling the evolution of τ_α during creep

Optical photobleaching experiment



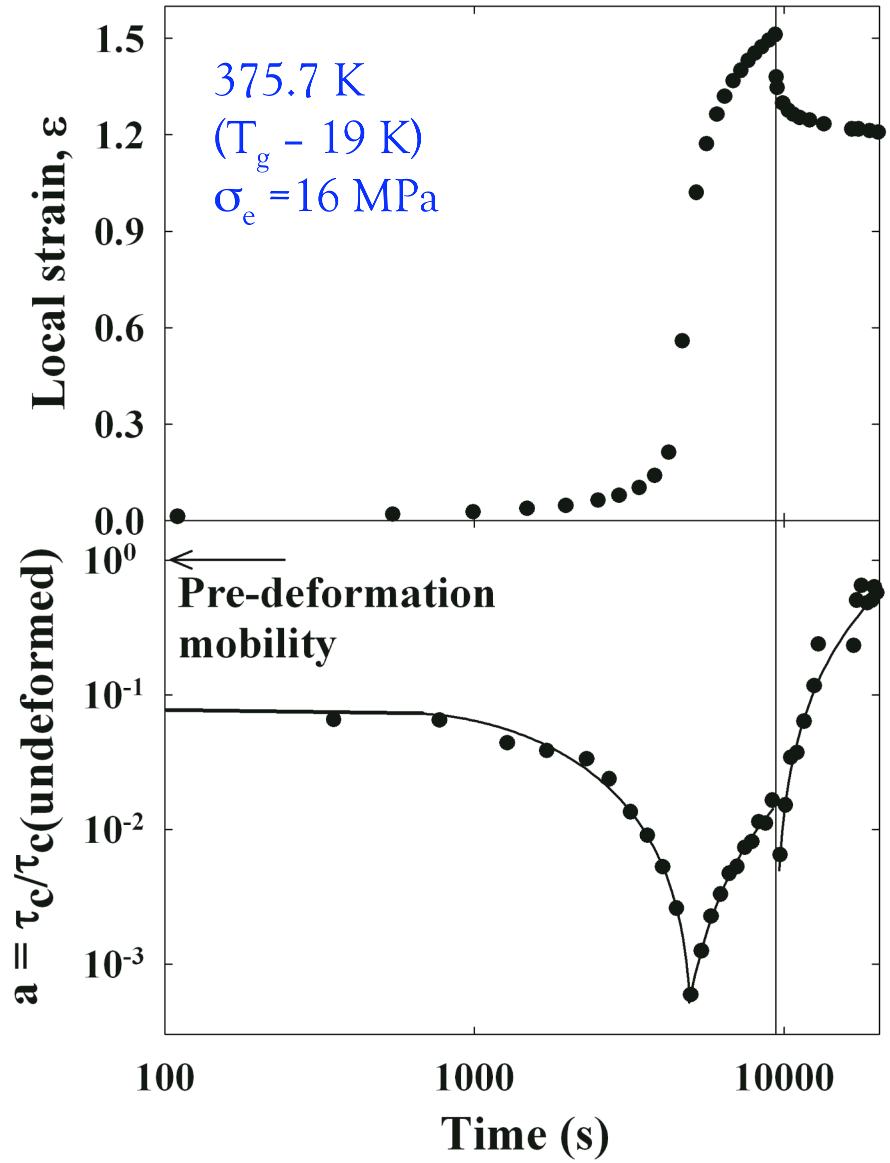
Model prediction by Chen and Schweizer



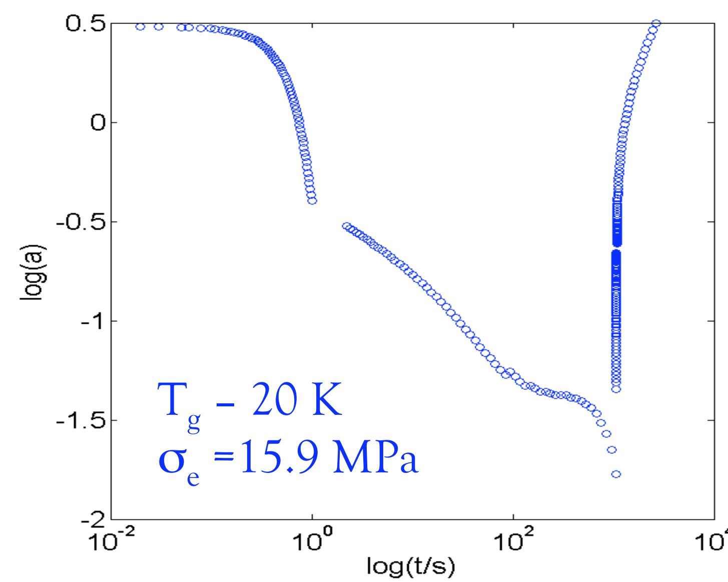
Non-linear viscoelastic model prediction

Medvedev and Caruthers, 2009 APS meeting

Optical photobleaching experiment



Preliminary NLVE prediction of log(a) is promising, but fails during recovery and cannot predict changes in the KWW β



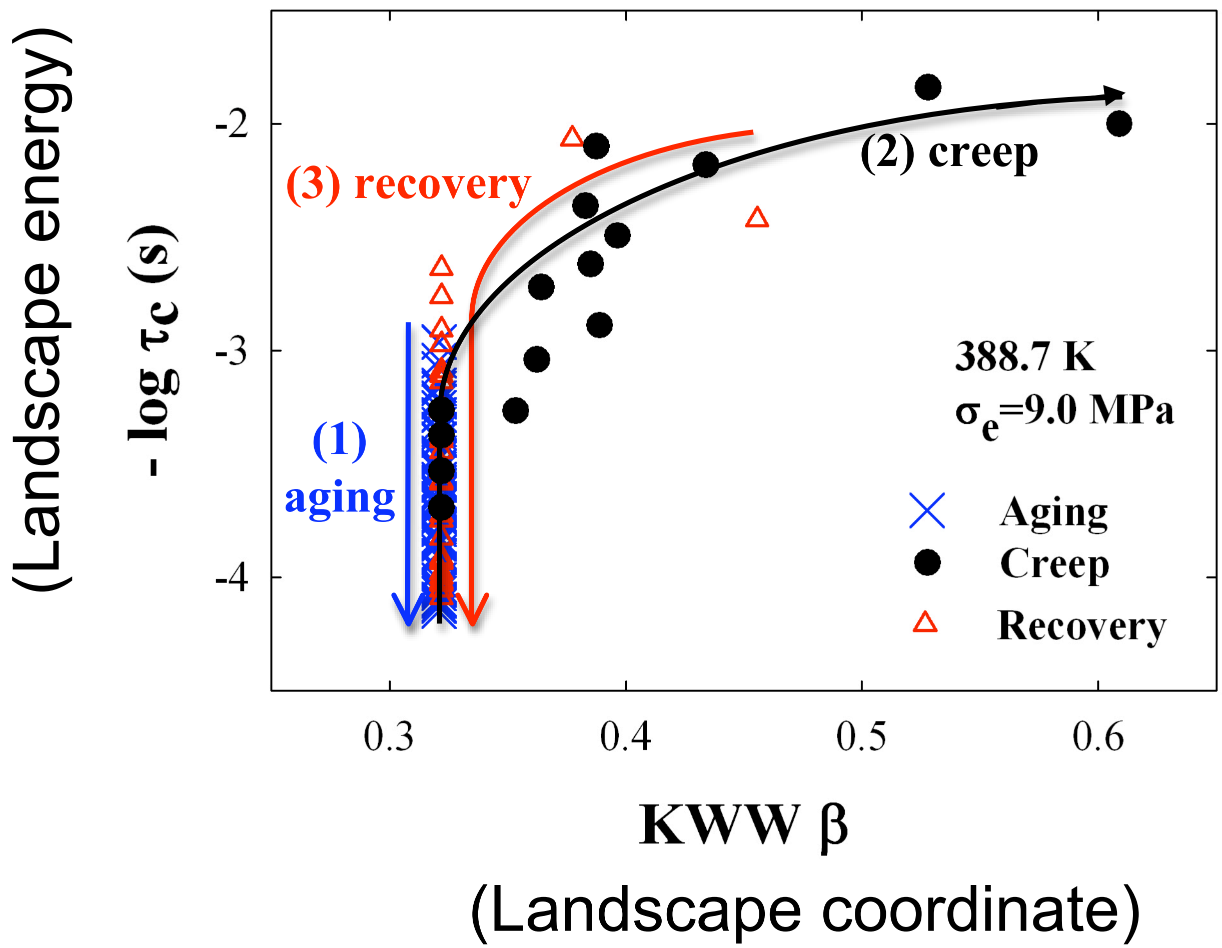
Summary

- Optical experiments provide access to segmental mobility during deformation; spatially resolve mobility during inhomogeneous deformation
- Deformation can accelerate segmental mobility by a factor of 1000 (and likely much more).
- New phenomena revealed: distribution of segmental relaxation times narrows significantly, mobility can initially increase during recovery, complex stress history decouples mobility and flow rate
- Major features of experiments also seen in computer simulations; some features not predicted by recent models.

Challenges

- Position on the energy landscape
- Enhanced mobility vs. shear transformation zones
- Interaction with simulation, theory will be required

Landscape changes during creep and recovery



Landscape changes during creep and recovery