Dynamics of Polymer Glasses Under Active Deformation

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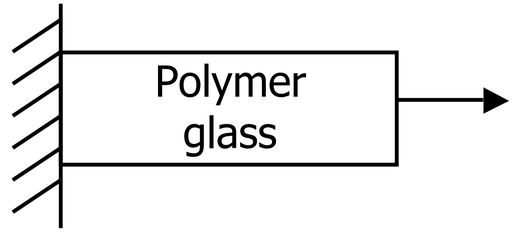
NSF NIRT

Why are polymer glasses tough?

Polycarbonate = bullet-proof glass



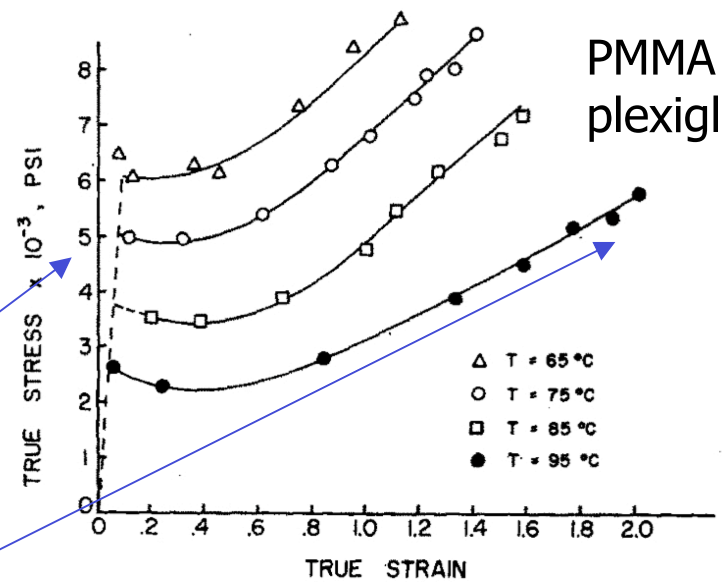


FIG. 6. True stress–strain curves at different temperatures (extension rate=0.5 in./min in all cases).

PMMA = plexiglass

High modulus +
Large strain prior to fracture +
Low energy input in molding

Allison,… J.Appl. Phys.38, 4164 (1967)

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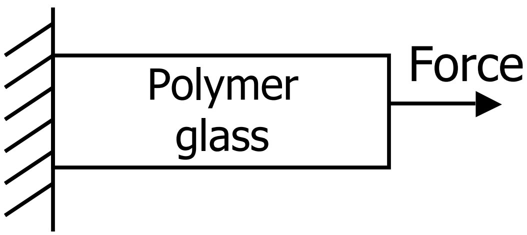
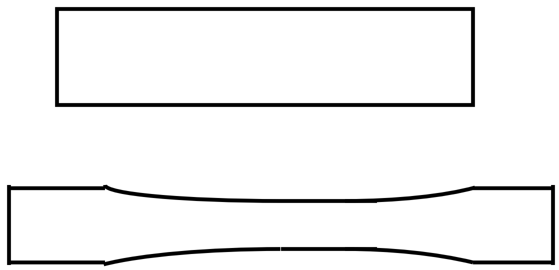
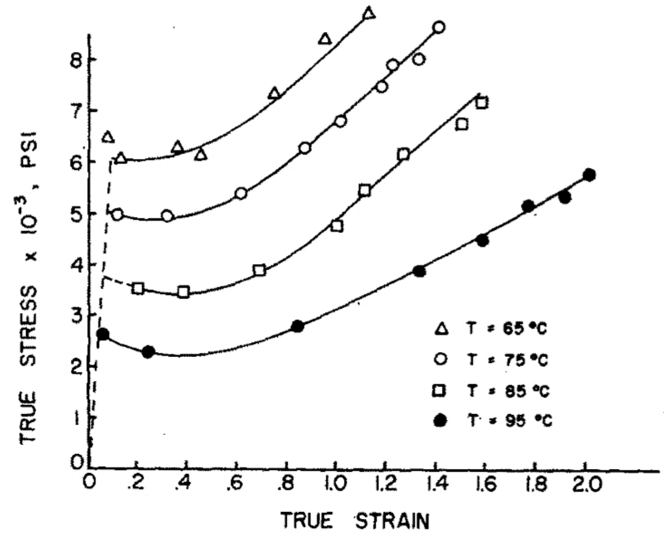
d) The real answer ≈ 20 J

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







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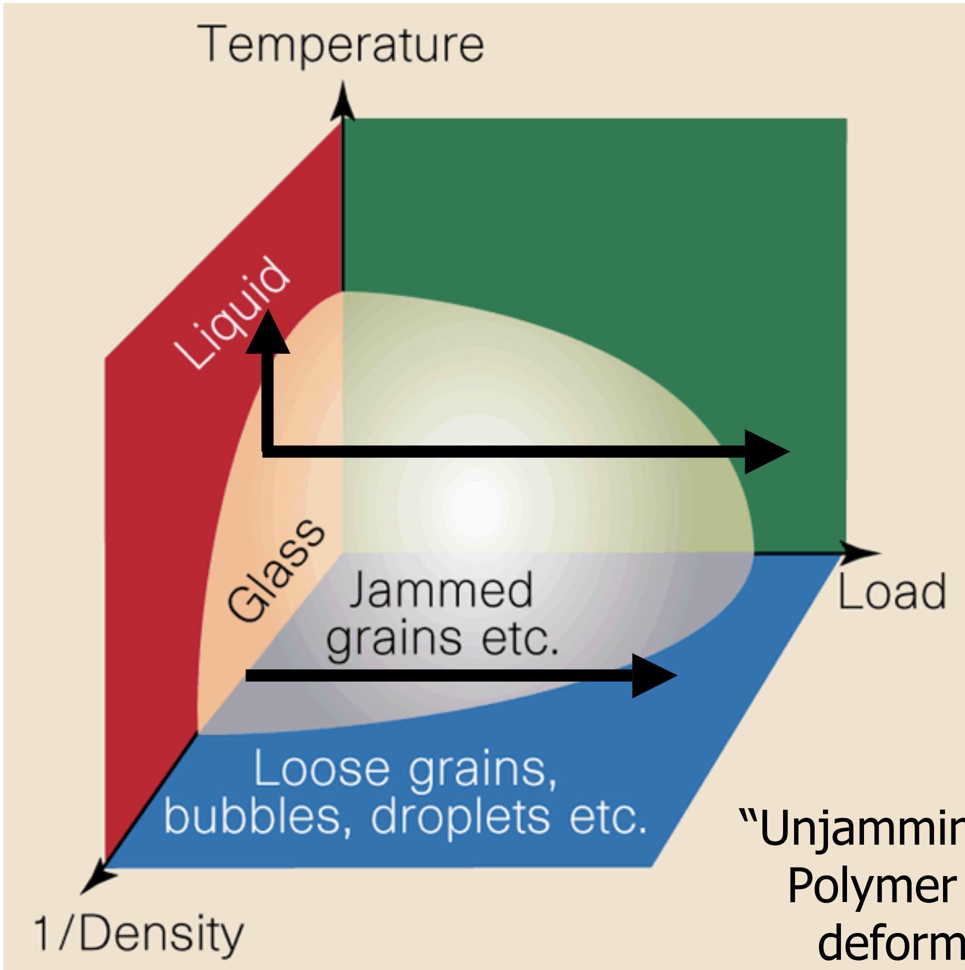
Above T_g, small force, mobility allows flow, have molecular theories

Below T_g, large force, mobility allows flow?, no molecular theory

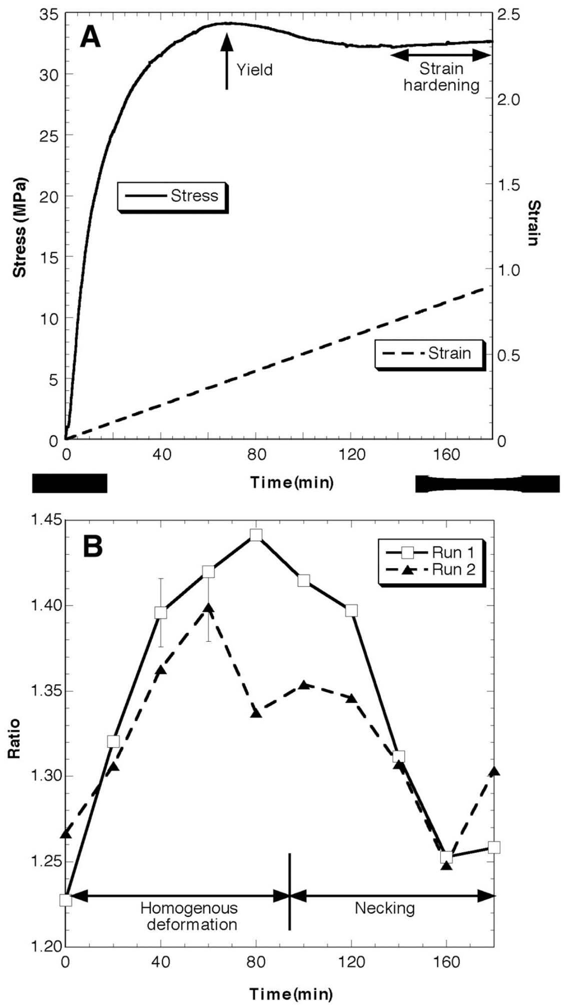
Broader context: Jamming



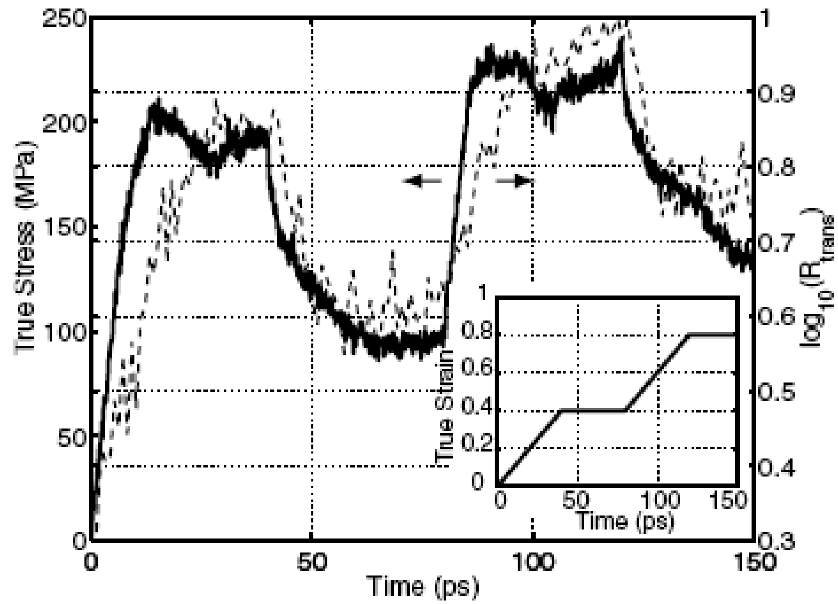
Liu and Nagel, Nature 1998

"Unjamming" is seen in many systems.
Polymer glasses are unique - large deformation without failure due to long chains

Observations of deformation-induced mobility in polymer glasses



NMR experiments on nylon
(Loo, Gleason, Cohen: Science 2000)



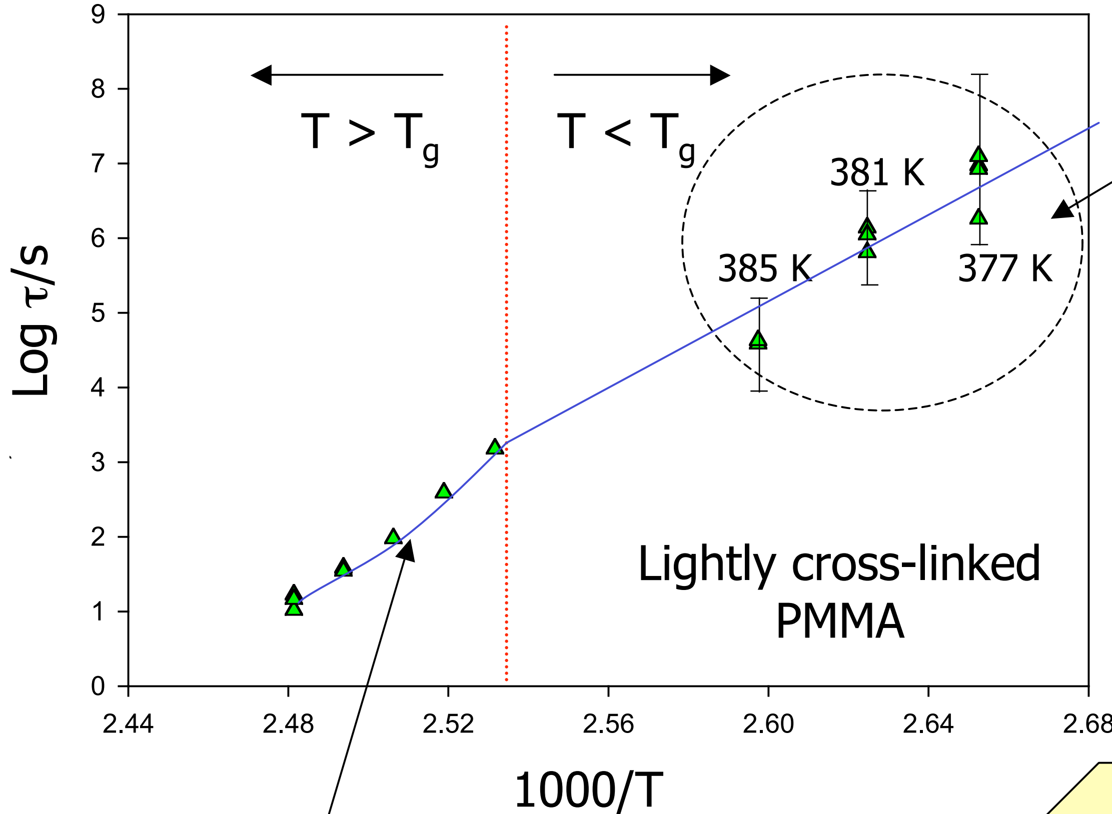
MD simulation on polyethylene
(Capaldi, Boyce, Rutledge: PRL 2002)

Mechanical "tickle" measurements are controversial
(Yee, Gacougnolle, McKenna, Zapas)

Goals

- Quantify deformation-induced mobility
- Fundamental understanding of mechanism
- Better predictions of non-linear mechanical properties
- Extend to composite systems

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

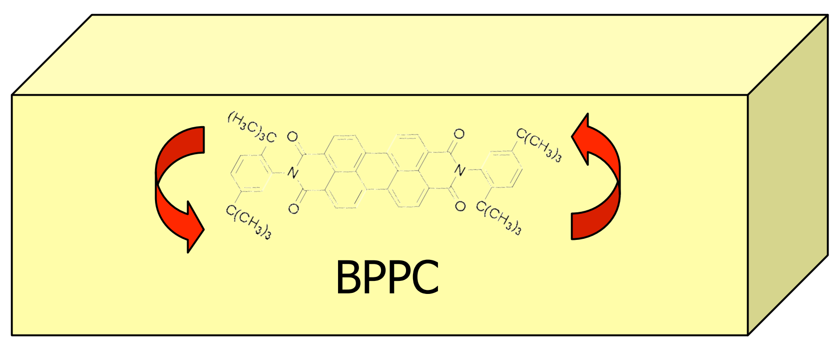


Experiments are done at this temperature range

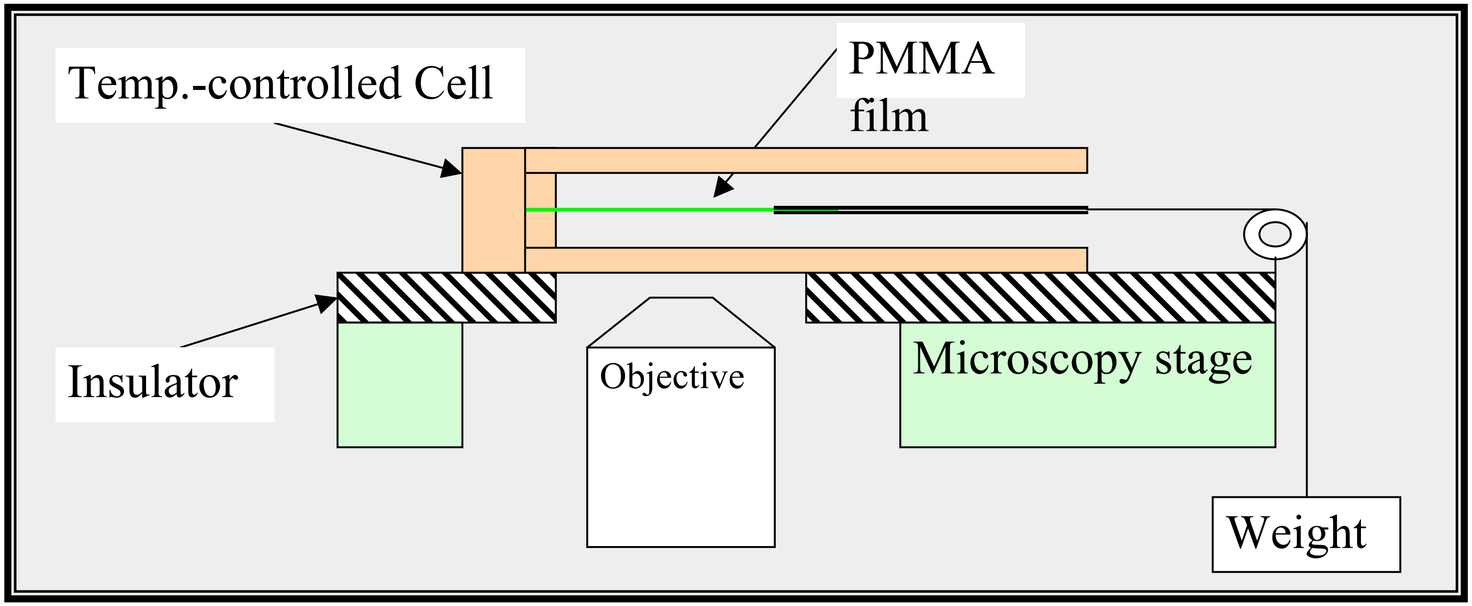
$T_g = 395.3$ K

T dependence matches dielectric relaxation τ_α

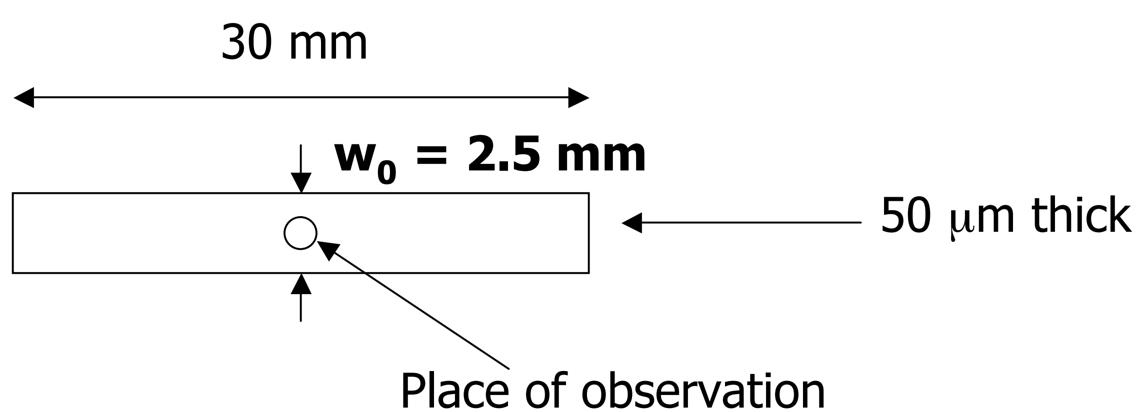
Rotational correlation times of probe molecule are strongly correlated with segmental dynamics of polymer



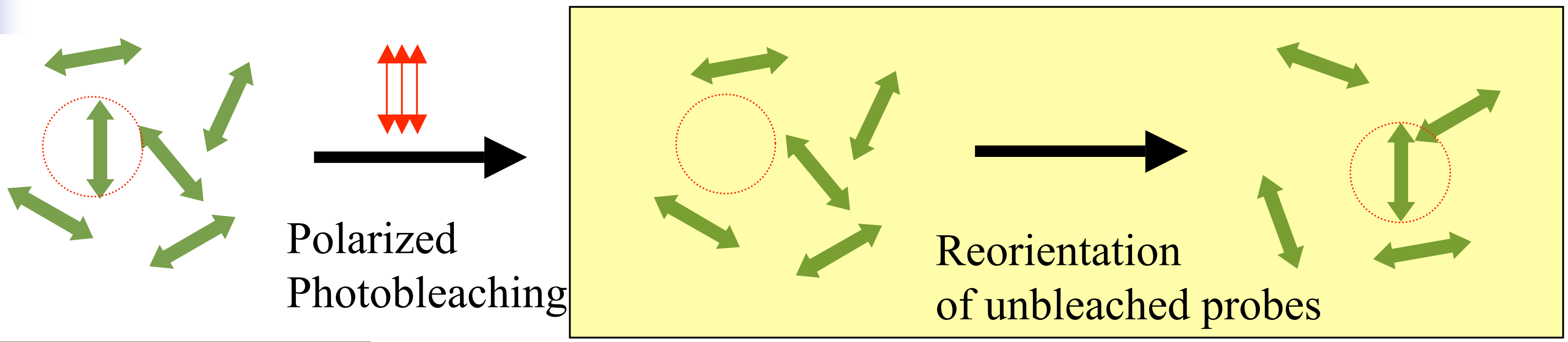
Deformation Cell (Creep Experiment)

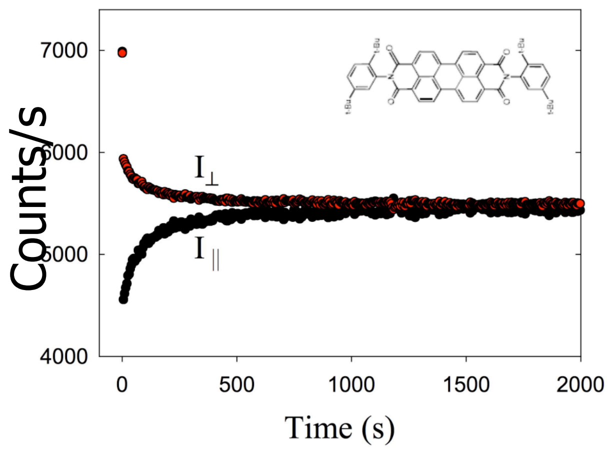


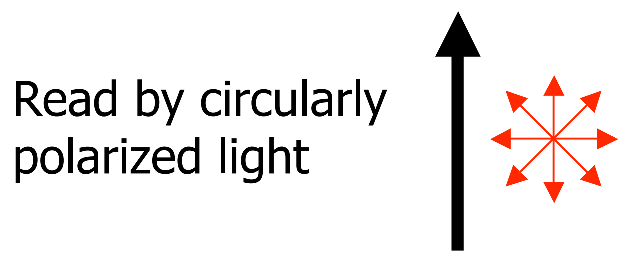
Top view of sample

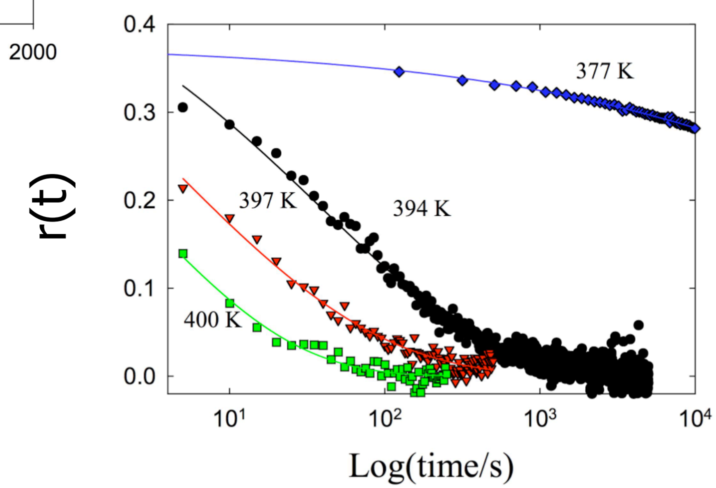


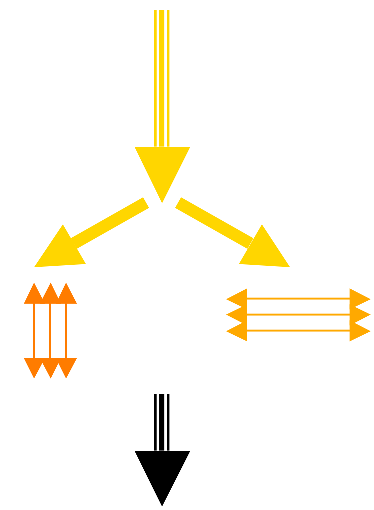
Dye reorientation measured with photobleaching technique







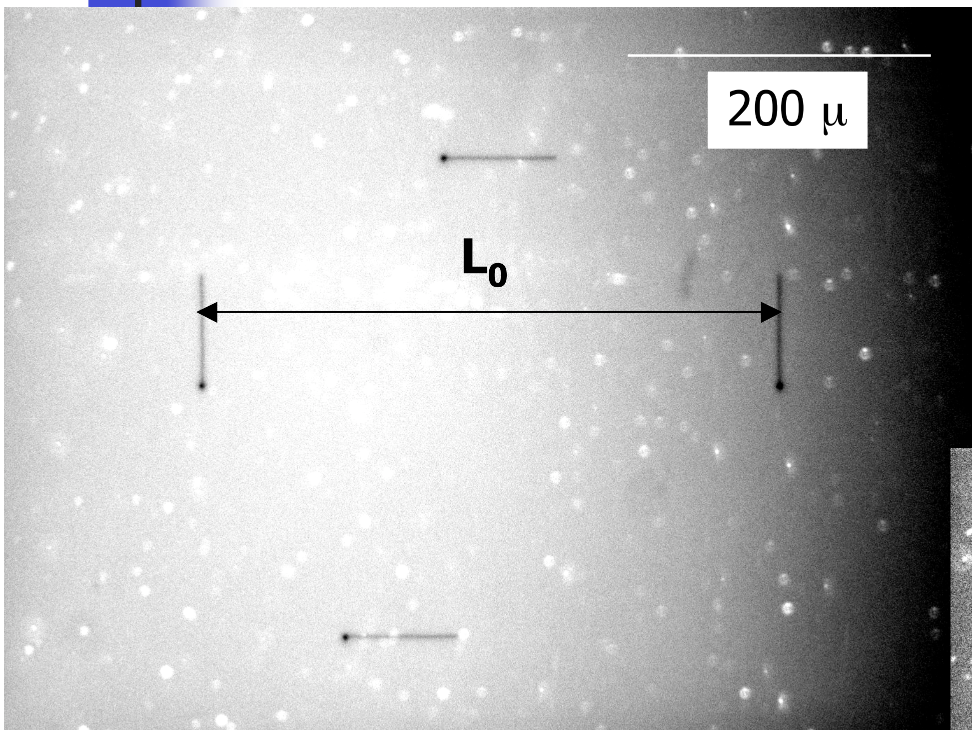




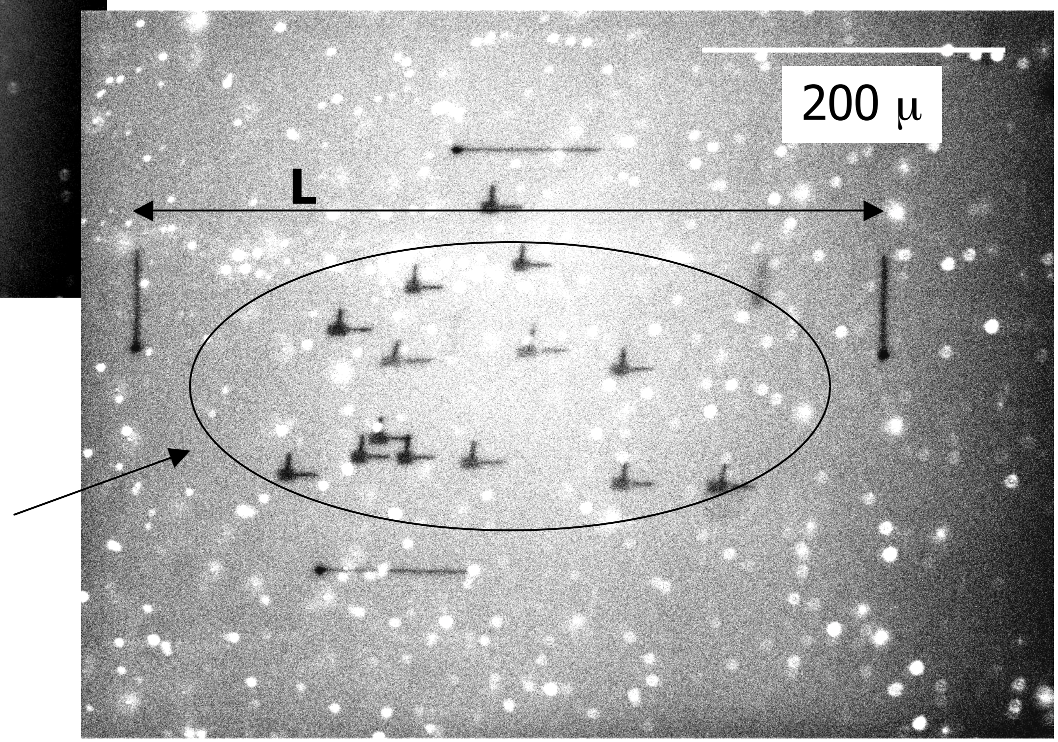
$$r(t) = \frac{\Delta I_{//}(t) - \Delta I_{\perp}(t)}{\Delta I_{//}(t) + 2\Delta I_{\perp}(t)}$$

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

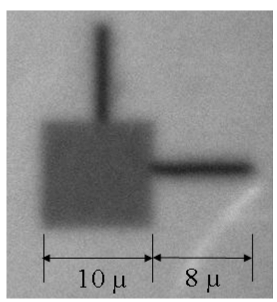
Strain and mobility are measured locally



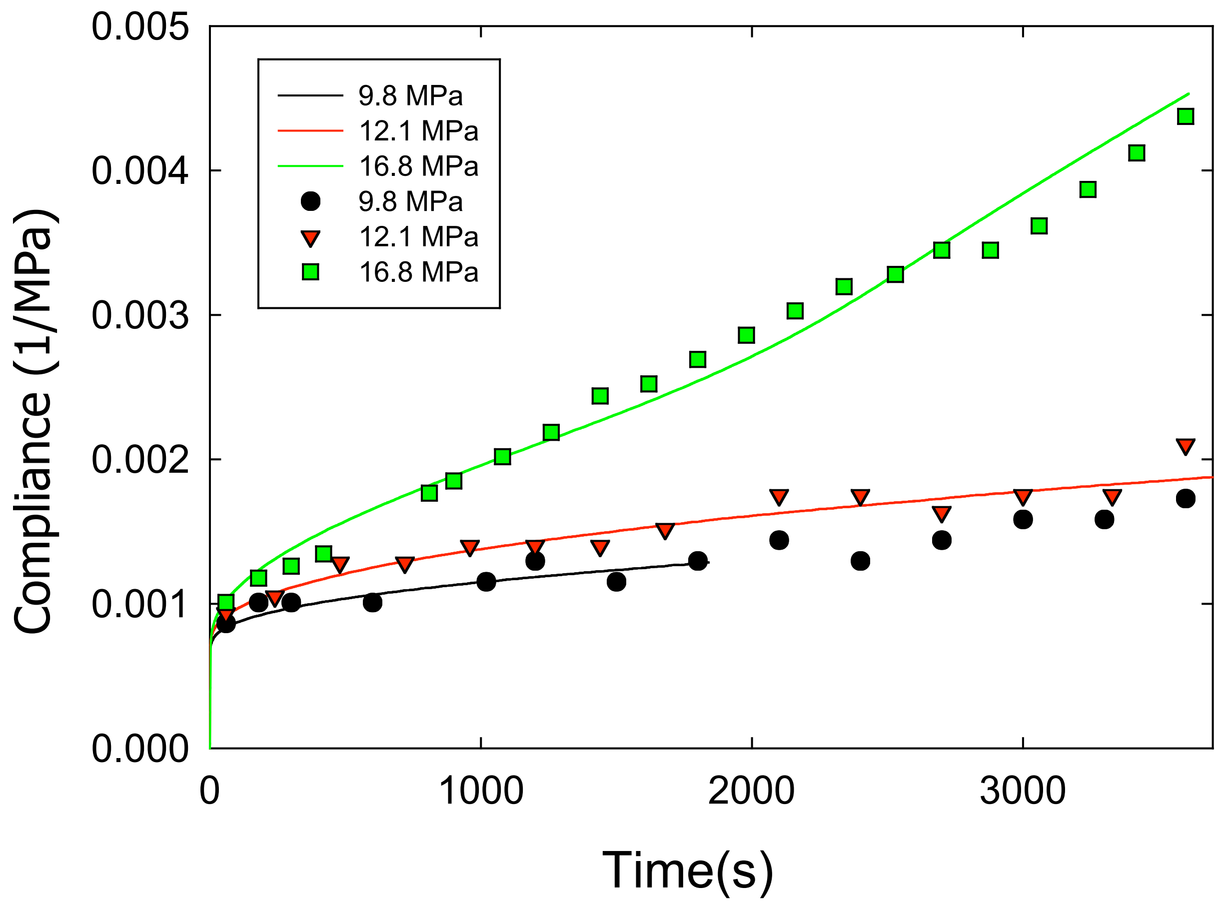
Stretch the film



Measure mobility of polymer in these small regions



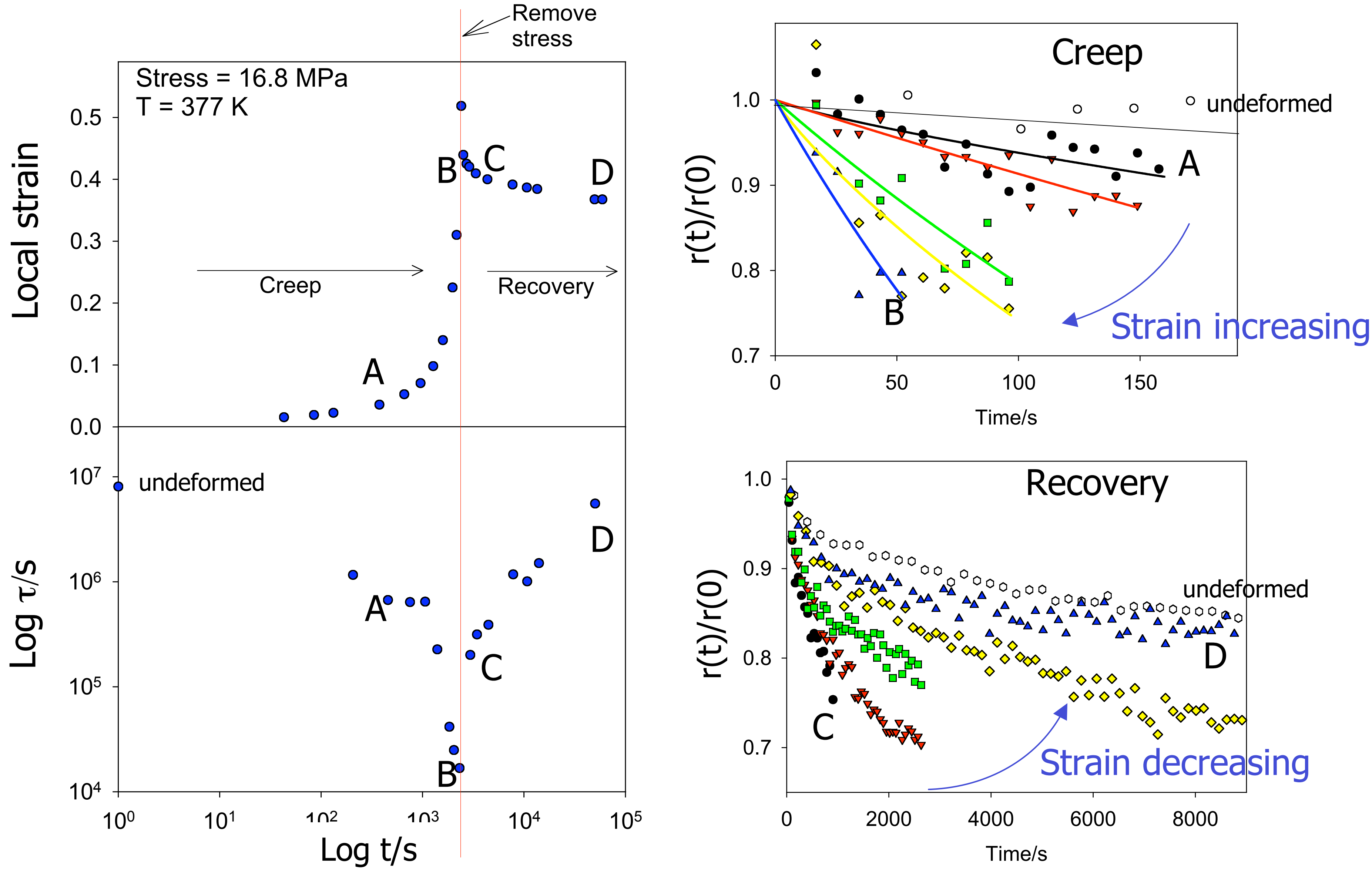
Local creep measurements agree well with standard creep measurements during homogeneous deformation



$J(t) = \varepsilon(t)/\sigma$

Symbols: Optical creep measurement : T = 375.8 K (T_g-24.3 K)
Solid lines: Standard creep measurement (Caruthers) : T = 368.1 K (T_g-25 K)

Evolution of mobility during creep and recovery



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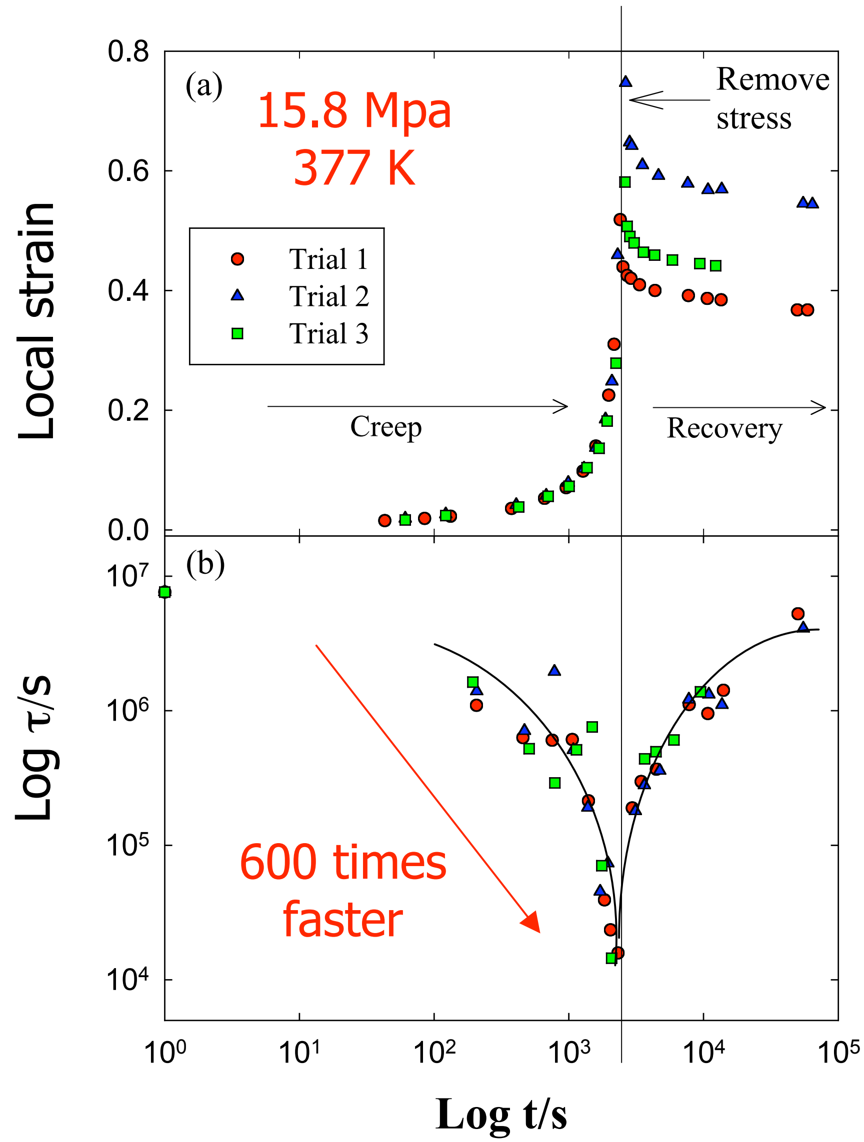

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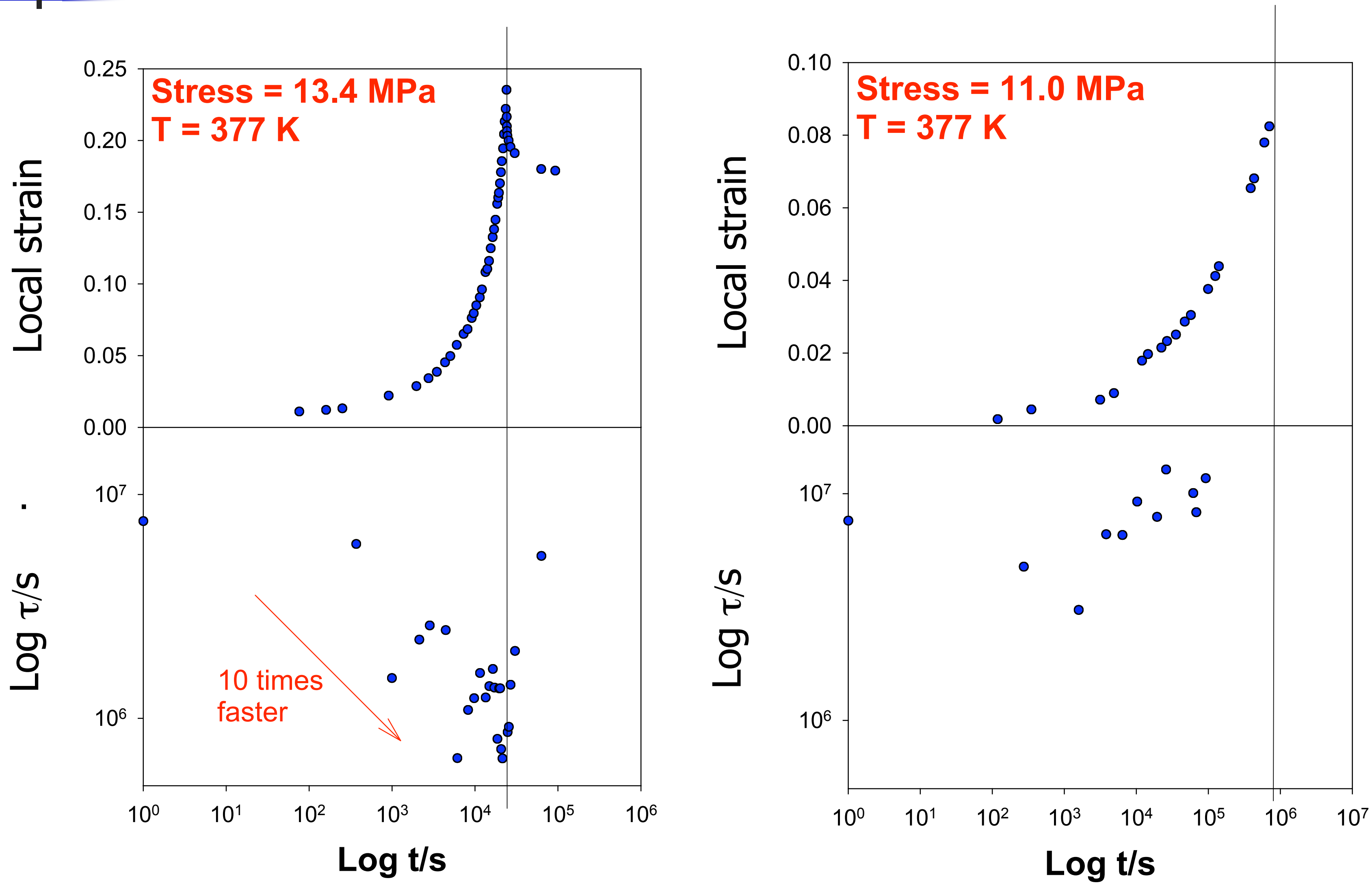

Goals

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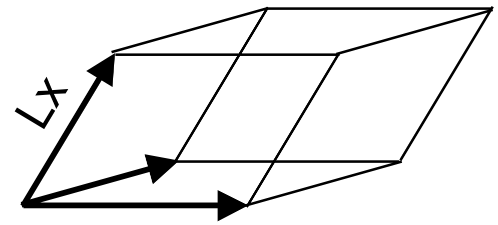
- Fundamental understanding of mechanism
- Better predictions of non-linear mechanical properties
- Extend to composite systems

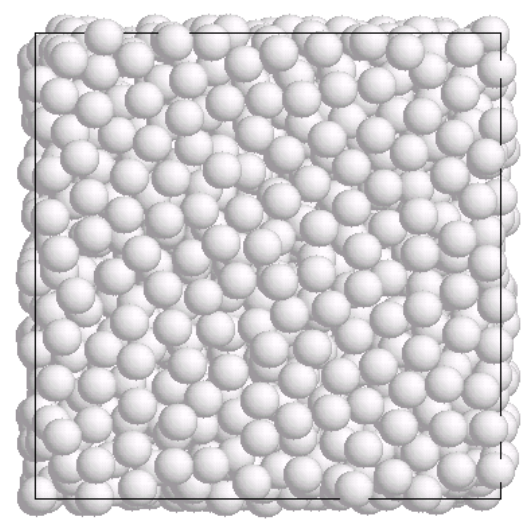
Can free volume explain these results?

MD simulations of creep (Riggleman/de Pablo)

- MD Simulations of a coarse-grained polymer melt at Tg ($T_g^* = 0.37$)
- Polymer: 32 Lennard-Jones sites connected by harmonic springs
- Creep simulations in NσT ensemble under compression and tension
- Four system sizes studied:
  - Lx = {8.8; 11.7; 17.7; 39.9}
  - Lx / ξ = {1.1; 1.46; 2.21; 4.24}

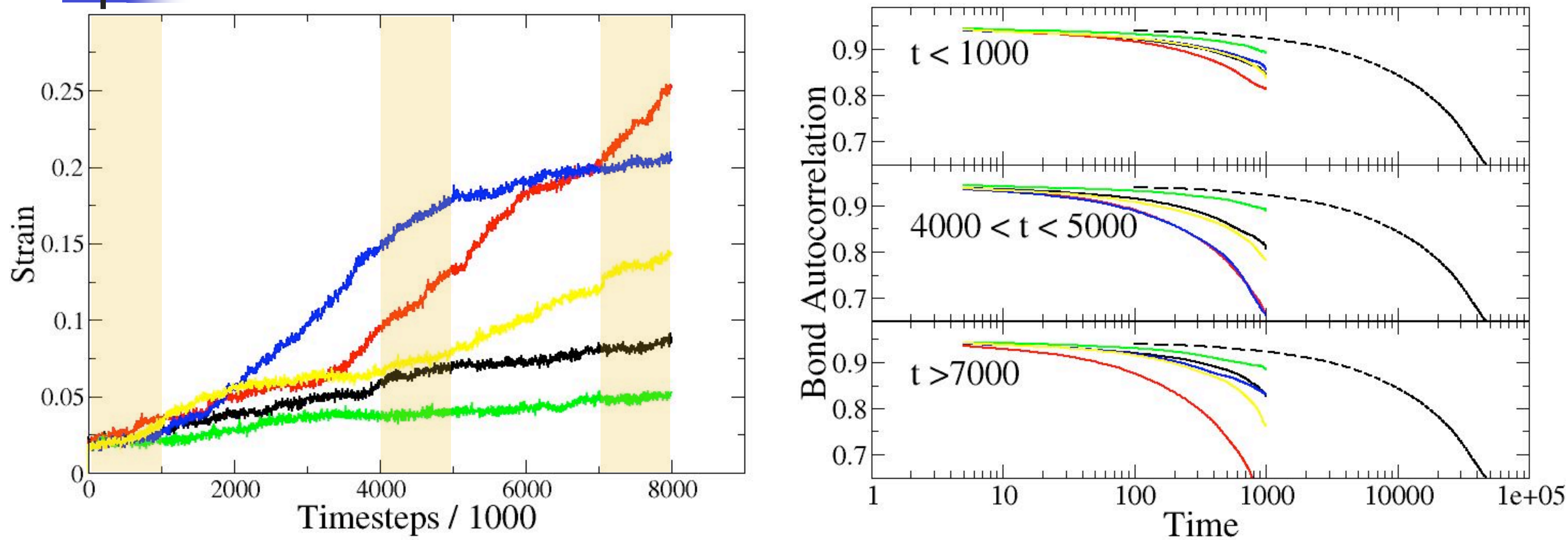


NσT ensemble



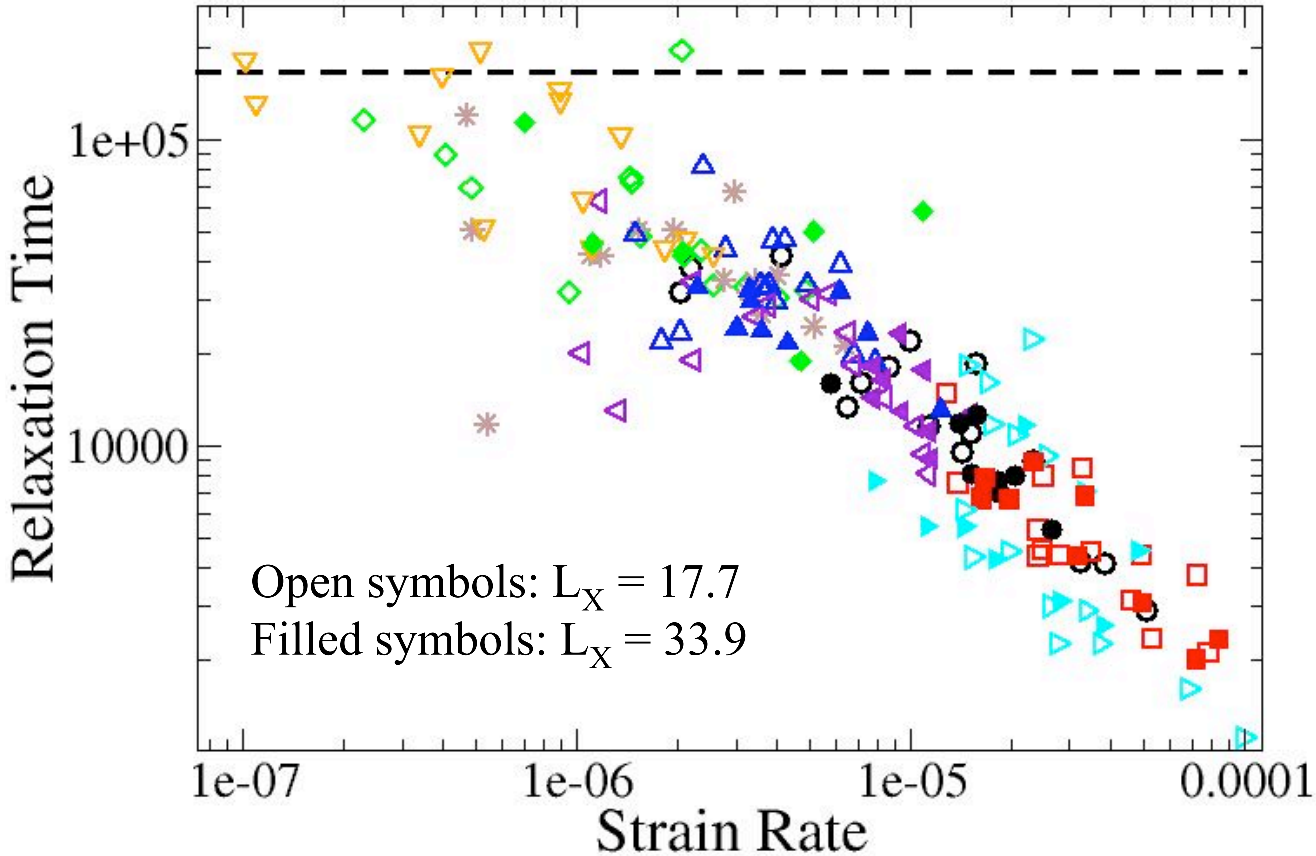
Pure polymer glass before deformation

Dynamics are enhanced during creep ($\sigma_{zz} = 0.54$)



- Strain and dynamic response of LJ polymer melt under tensile stress
- Dynamics measured separately for individual configurations
- All configurations show significant enhancement

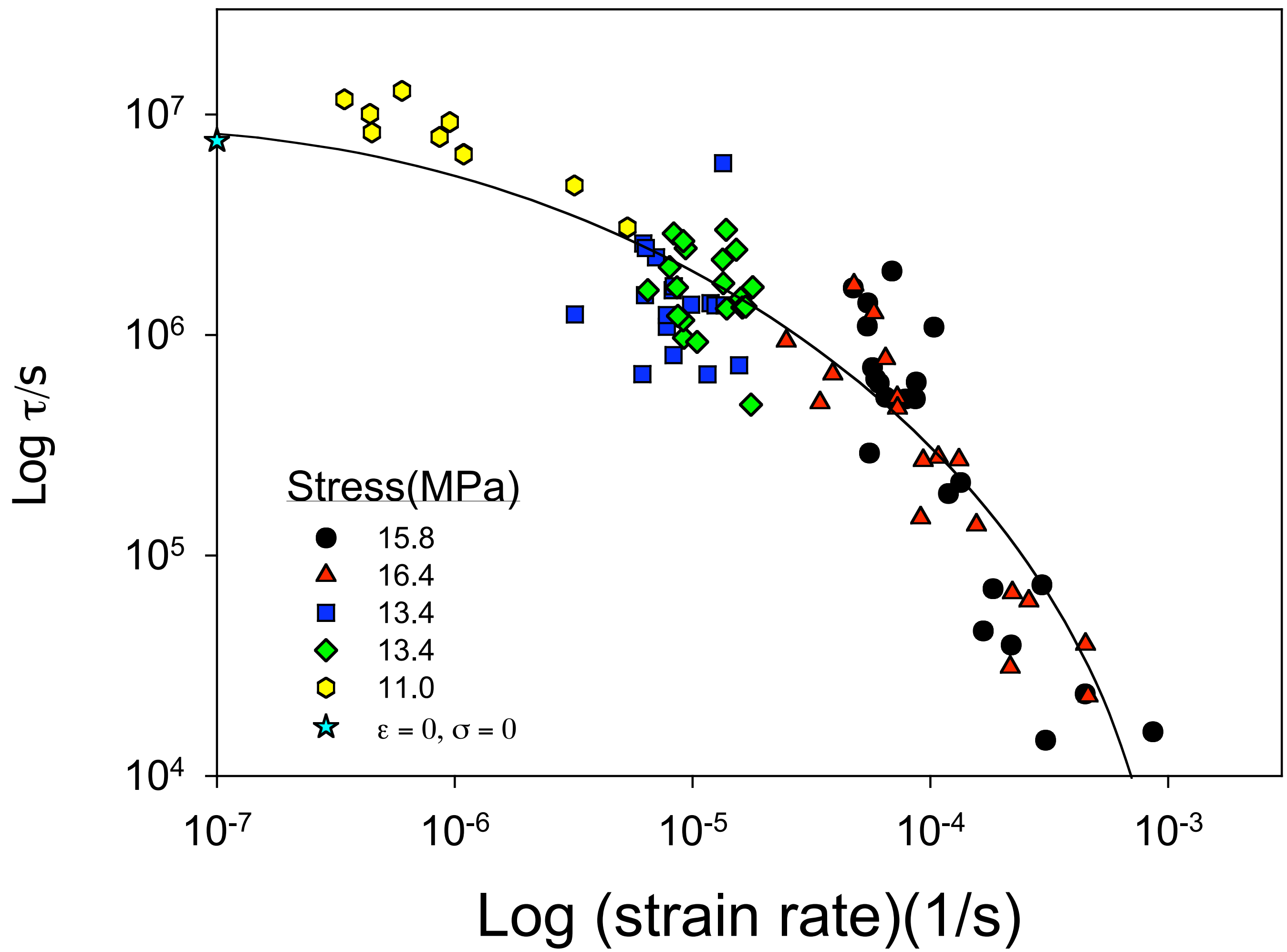
Evolution of τ_c with the strain rate (MD)



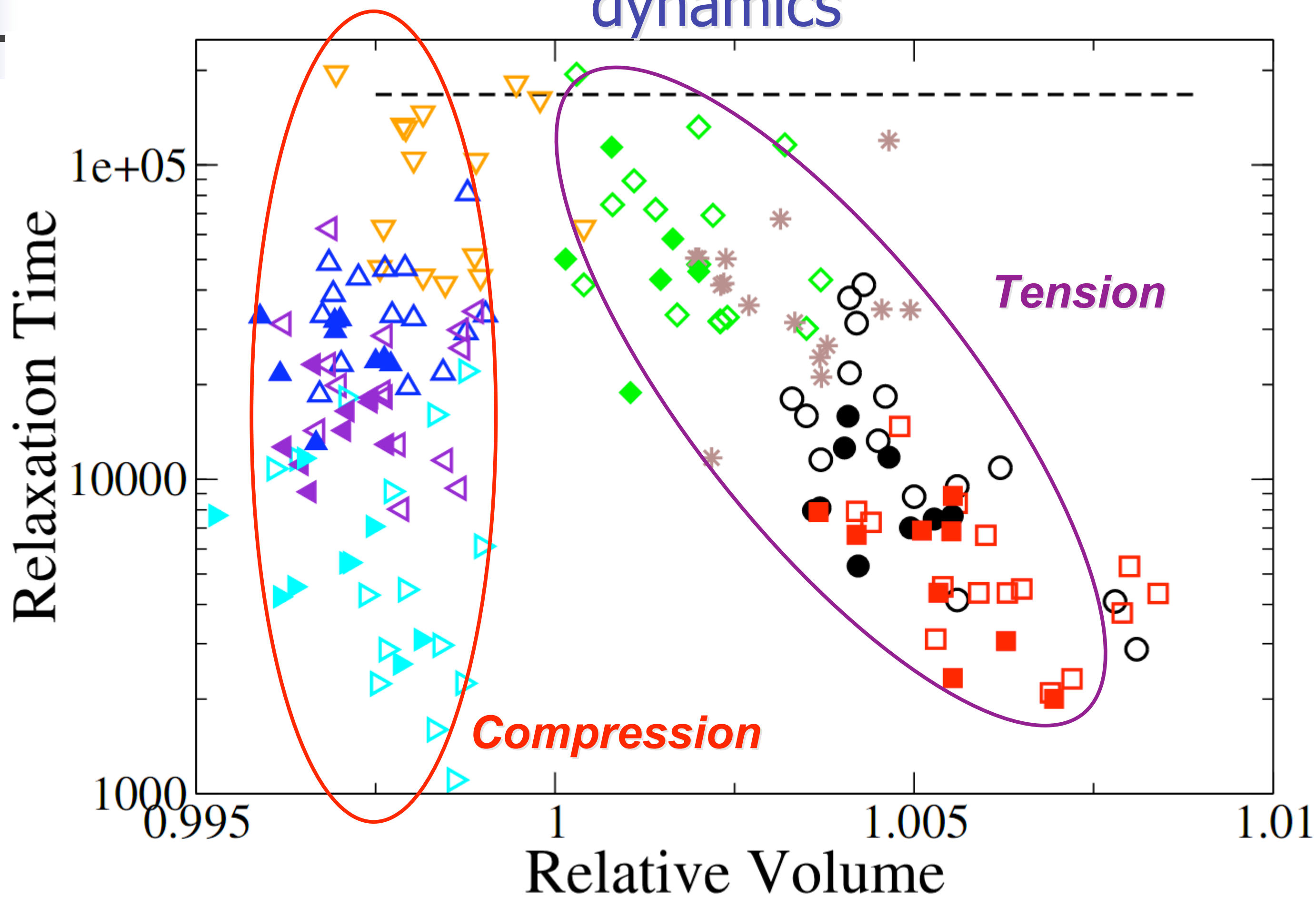
▽ △ ◁ ▷ = Compressive stress, σ_{zz} = -{0.27, 0.54, 0.62, 0.75}

◇ * ○ □ = Tensile stress, σ_{zz} = {0.27, 0.425, 0.54, 0.62}

Evolution of τ_c with the strain rate at 377 K (expt)

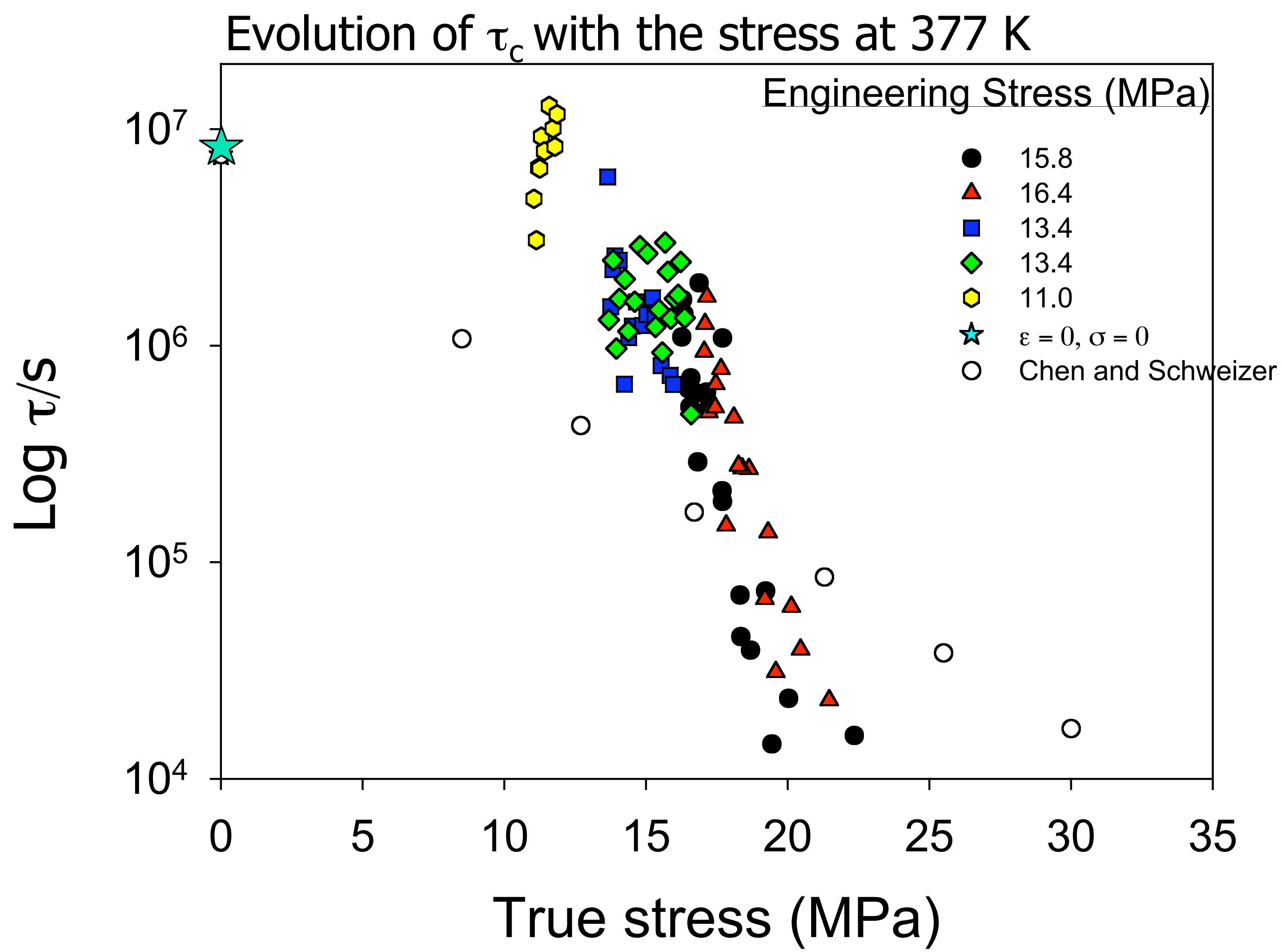


Simple free volume cannot explain enhanced dynamics



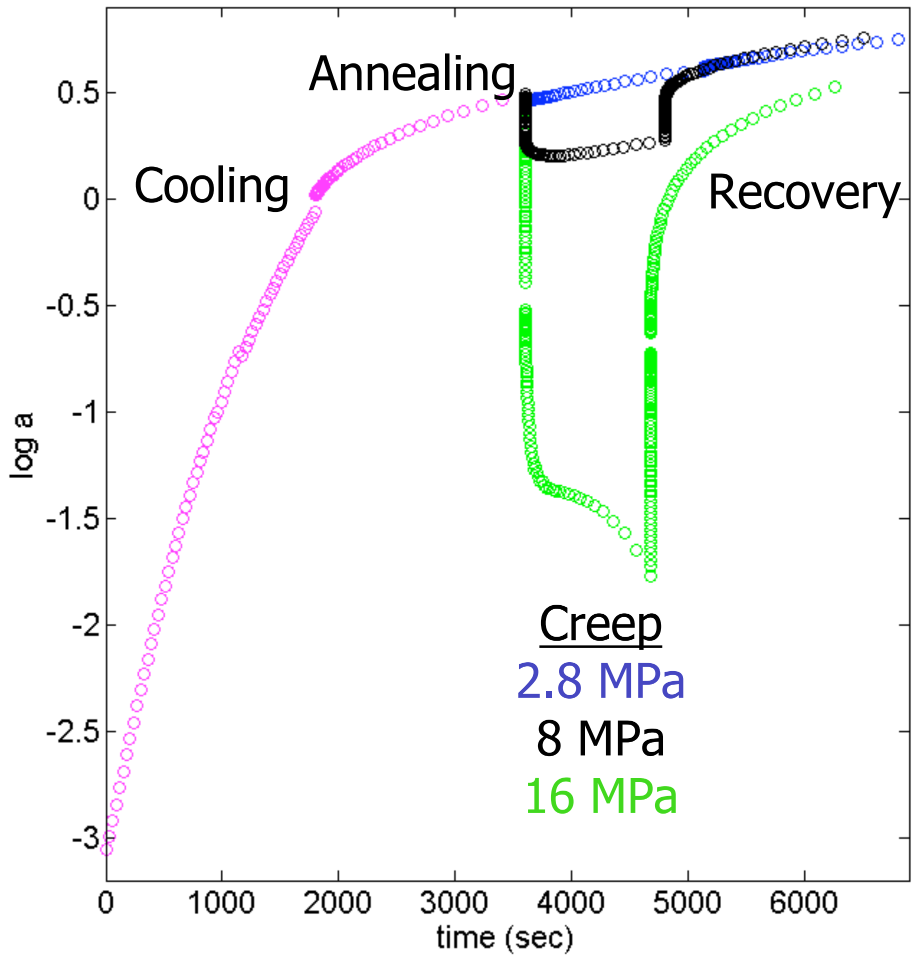
Plan to do experiments in compression also

Preliminary comparison with "molecular level Eyring theory" (Chen and Schweizer)



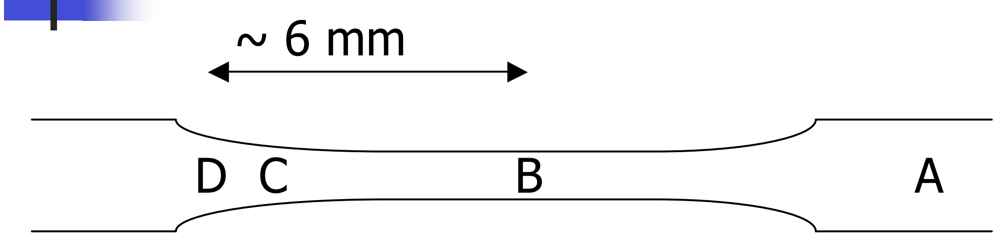
Modelling the evolution of τ_c during creep

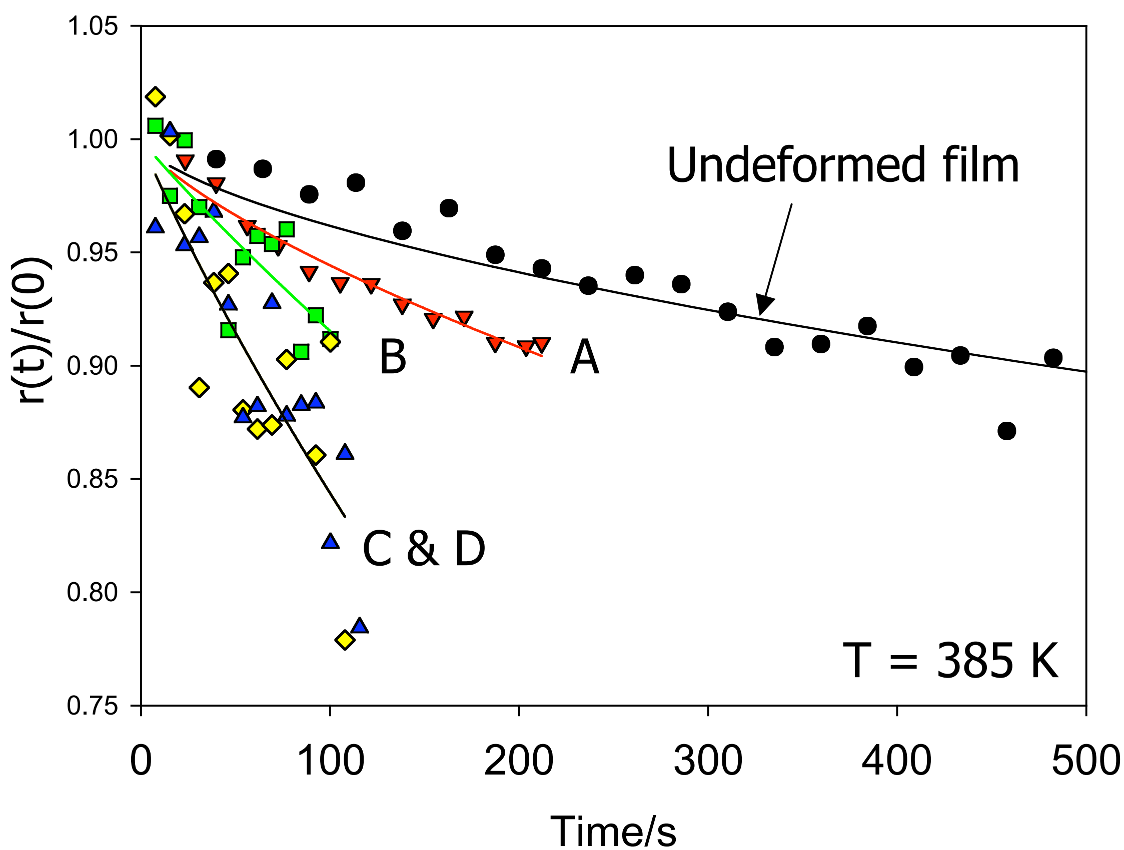
Medvedev and Caruthers, March 2007 APS Meeting



- Thermoviscoelastic model
- PMMA, 358 K
- Moderate stress has little effect
- Large stress has big effect

Mobility in different regions of necked film





➢Local strain in neck area (B) is ~1.70 and strain rate is ~ $5x10^{-5}$/s

➢Local strain in non-necked are (A) is ~0.30 and strain rate is ~ 10^{-5}/s

Largest mobility changes occur in regions with locally high strain rates

Summary

- Quantitative determination of mobility changes during deformation and recovery.
- Huge effect! A dominant contribution to non-linear deformation behavior.
- Simulations argue against free volume interpretation
- Critical for theory/modelling.
- Local measurement of mobility useful for understanding inhomogeneous deformation.