Molecular plasticity; the crossover from perfect-plastic flow to polymeric strain hardening

The Big Question

In amorphous glasses, what is the effect of chain connectivity on mechanical response?

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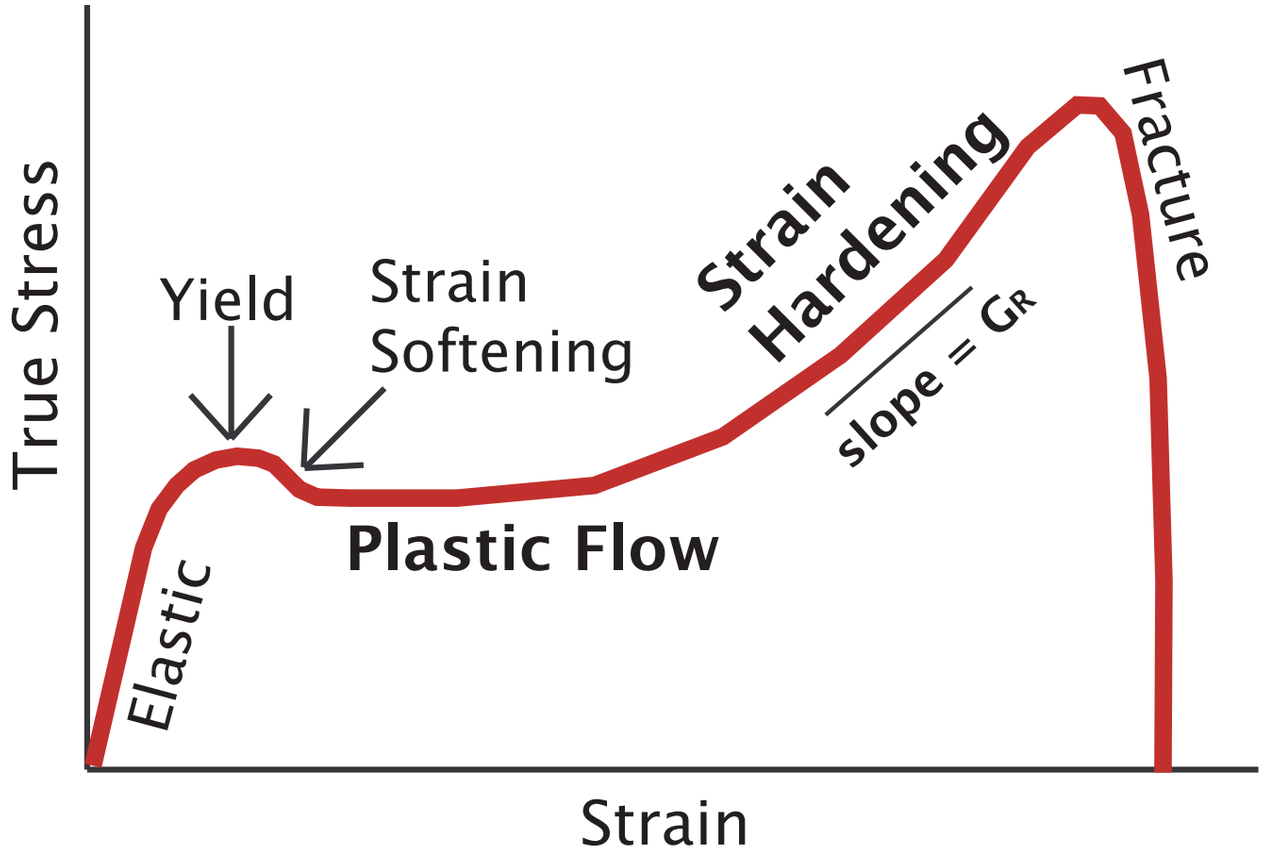
Stress-Strain Response in Ductile Glasses

Elastic response at small strains (few %)

Yield as barriers to local rearrangements overcome

Strain softening as material "rejuvenates"

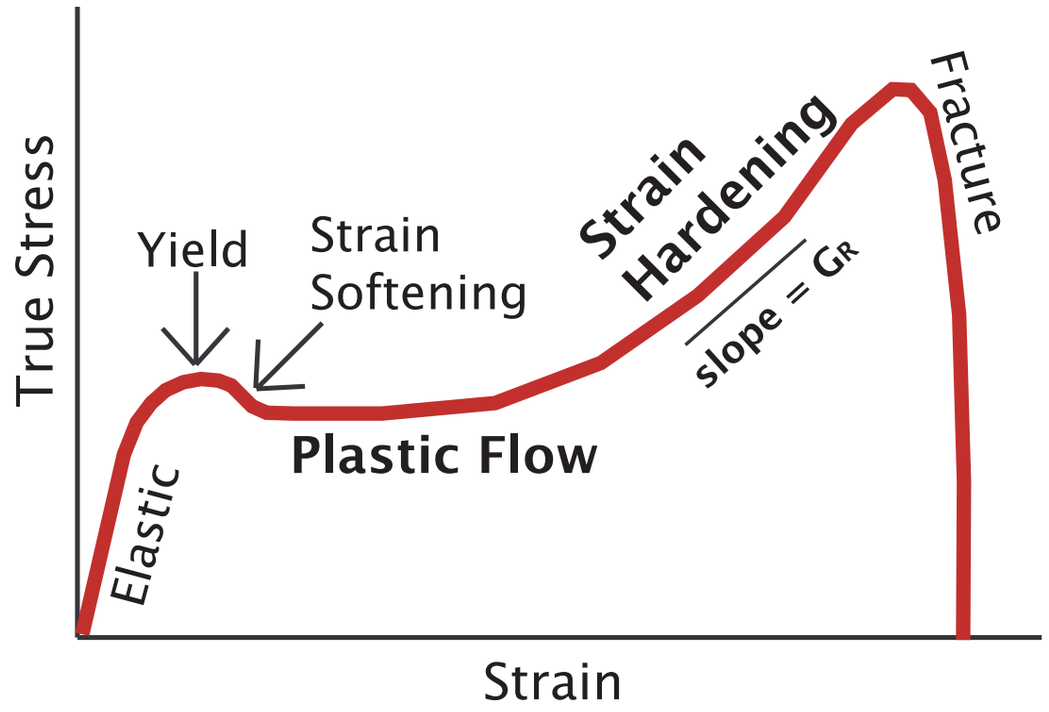


Plastic Flow

Polymers: chains orient -- strain hardening

Fracture

Similarities/differences between polymeric and ‘monomeric’ response



Similar

- elastic, yield, flow

Different

- hardening, fracture

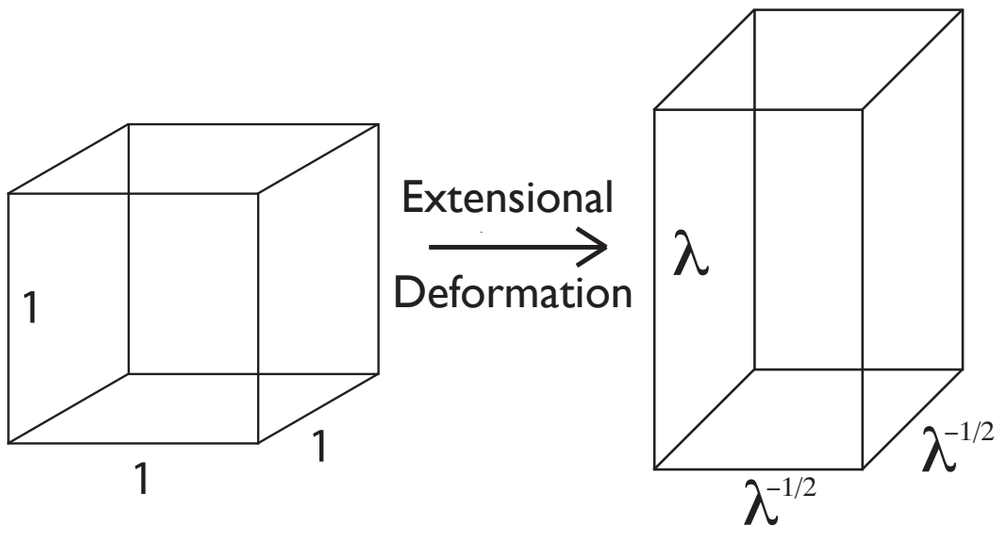
Broad-brush reason: covalently bonded chains can orient on large scales: increases material anisotropy, changes long- range order

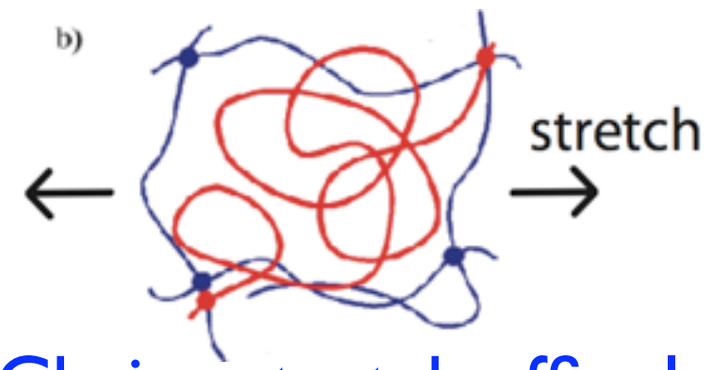
Traditional Interpretation of Polymeric Hardening

(Haward, Argon, Boyce et. al.)

- Hardening has same "shape" as in rubber -- model using entropic (rubber) elasticity, s*eparately from plastic flow*

Hardening stress arises from entropy of crosslinked network





Chains stretch affinely between entanglements

Equilibrium theory

$$F = E - TS \;:\; dE_{rubber} = 0$$

Entropic Elasticity

$$\sigma(\lambda) = \left(\frac{\partial f}{\partial \lambda}\right) = -\lambda T \left(\frac{\partial s}{\partial \lambda}\right)$$

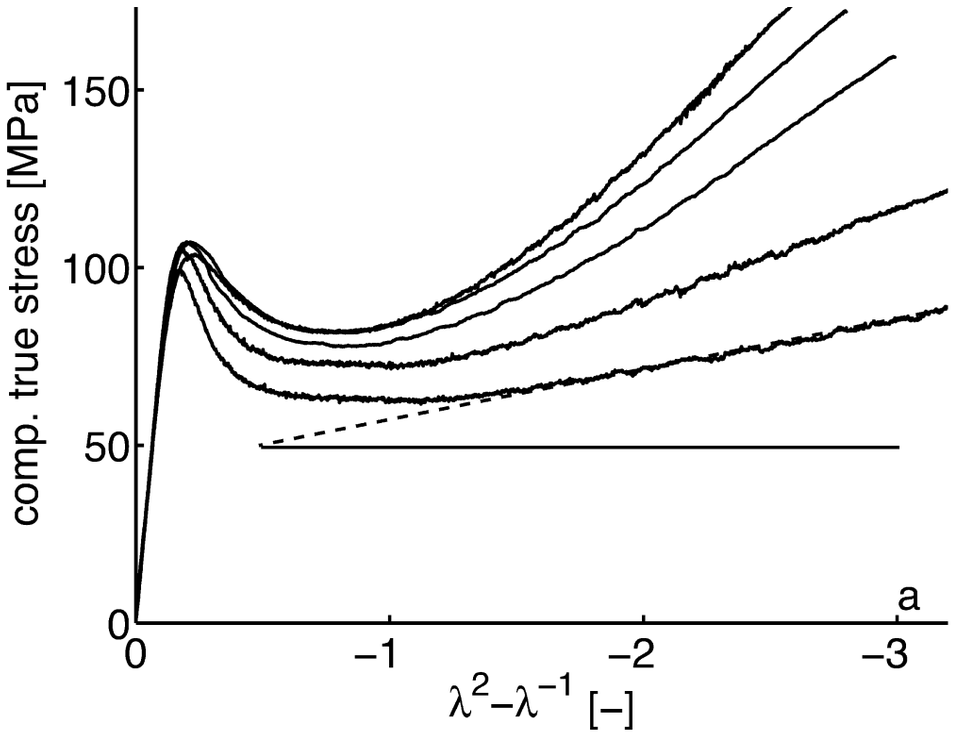
Assumes chain segments can move freely between crosslinks

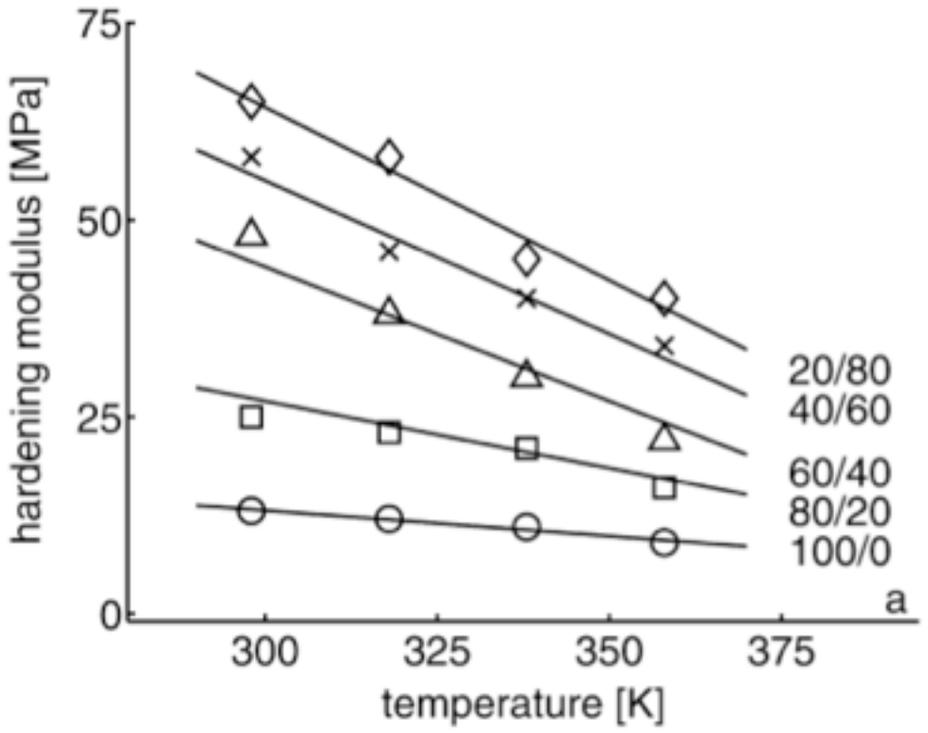
This is wrong for glasses!

Problems w/traditional approach

(Van Melick et. al., E. J. Kramer)

- qualitatively predicts shape of stress-strain curves, but:
- prediction; $G_R = \rho_e k_B T \sim 100$ times too high; inconsistent with rheolog. measurements of ρ_e
- wrong trend with T

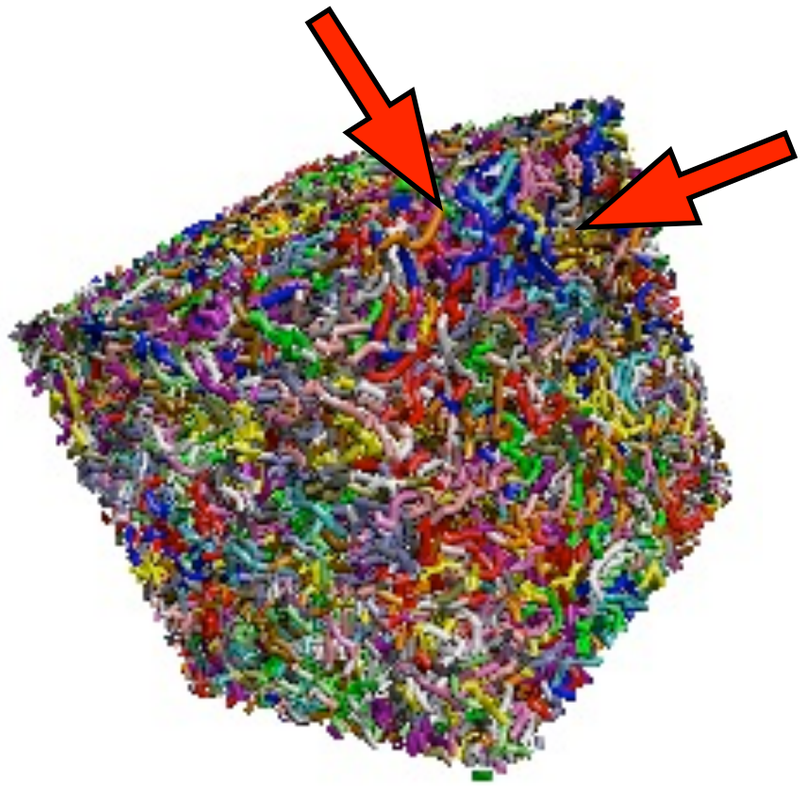




Molecular dynamics simulations

Kremer-Grest bead-spring model: natural polymeric analogue of LJ, Kob/Anderson 'monomeric' glasses

Compress using strain control



LAMMPS MD code
(S. J. Plimpton, Sandia NL)

Maintain isothermal conditions using Langevin thermostat

Maintain zero pressure along one or both transverse directions using Nose-Hoover barostat

Strain rates ~ 10^5-10^8/s
but in experiment-like regime where thermal activation makes stresses logarithmic in strain rate

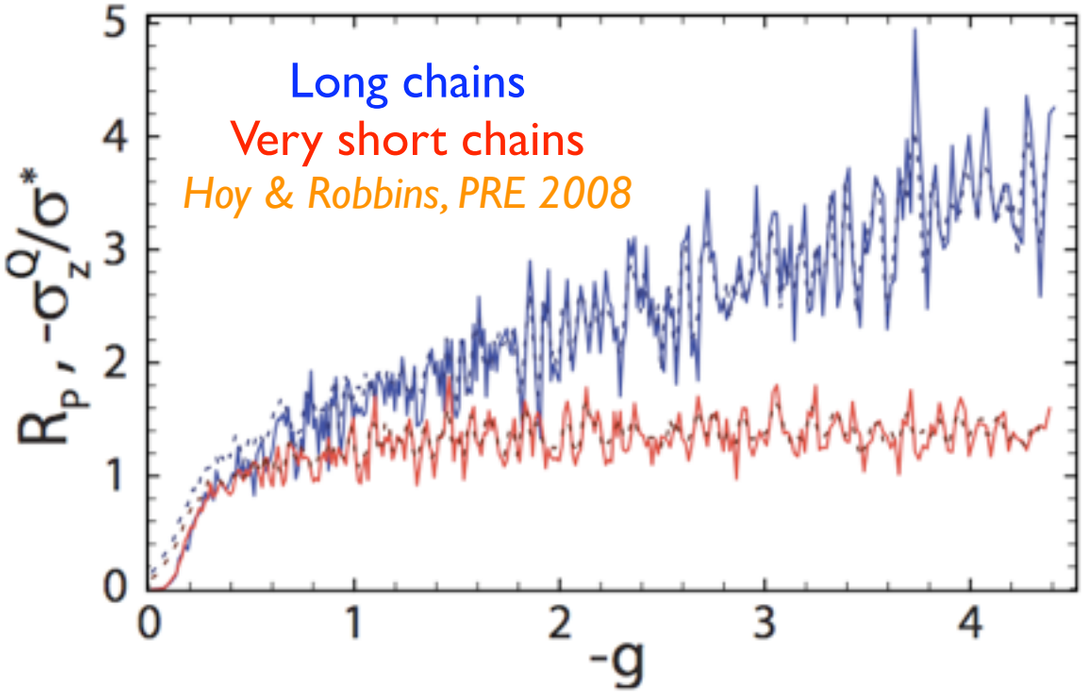
Progress over the past several years

Experiments: Govaert+Wendlandt, van Melick+Meijer, Dupaix+Boyce, Lee+Ediger, Hine/Duckett

Sims/Theory: Hoy+Robbins, Riggleman+de Pablo, Lyulin+Vorselaars, Chen+Schweizer

and many others

- most evidence shows entanglements secondary under most conditions
- instead hardening ~ flow stress, chain orientation
- hardening can occur for unentangled chains (if no brittle fracture)
- dissipative stress σ^Q dominates: related to to local plastic rearrangements
- rearrangements similar in flow, hardening but rate R_p increases



Chain Orientation vs. Entanglement

Entropic models predict $G_R \sim \rho_e$, no hardening for $N < N_e$

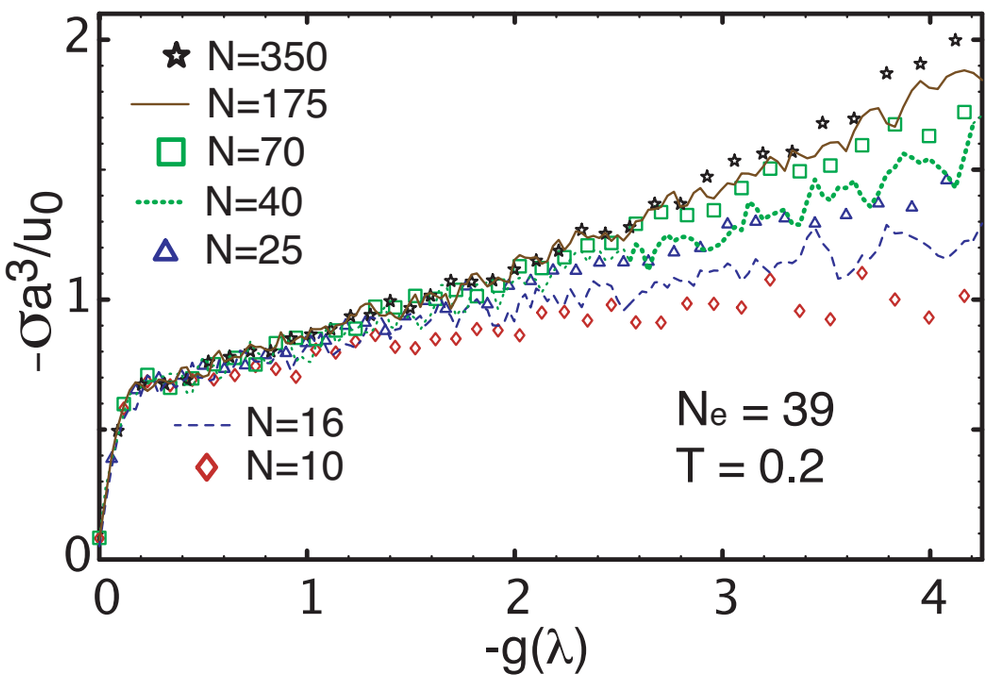
Simulations: hardening can occur *independent of entanglement* as long as some order parameter keeps evolving with increasing strain

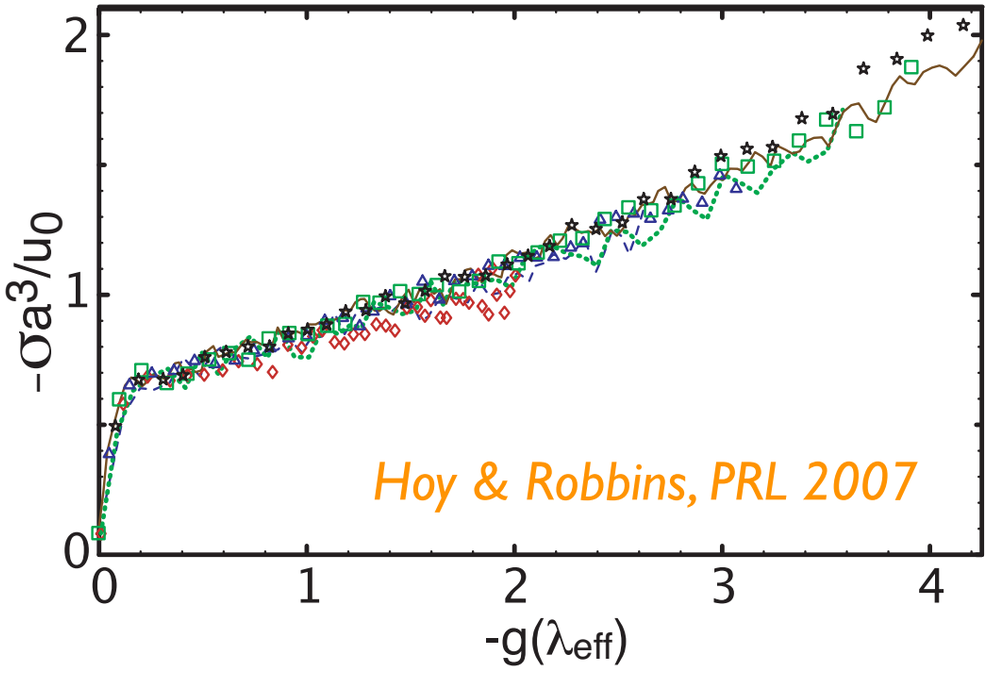
(Fracture of low-N systems suppr. by PBCs)

Strain hardening controlled by microscopic chain orientation

$$\lambda_{eff} = \frac{R_z}{R_z^0}$$

rather than macroscopic stretch λ, if energetic stress small



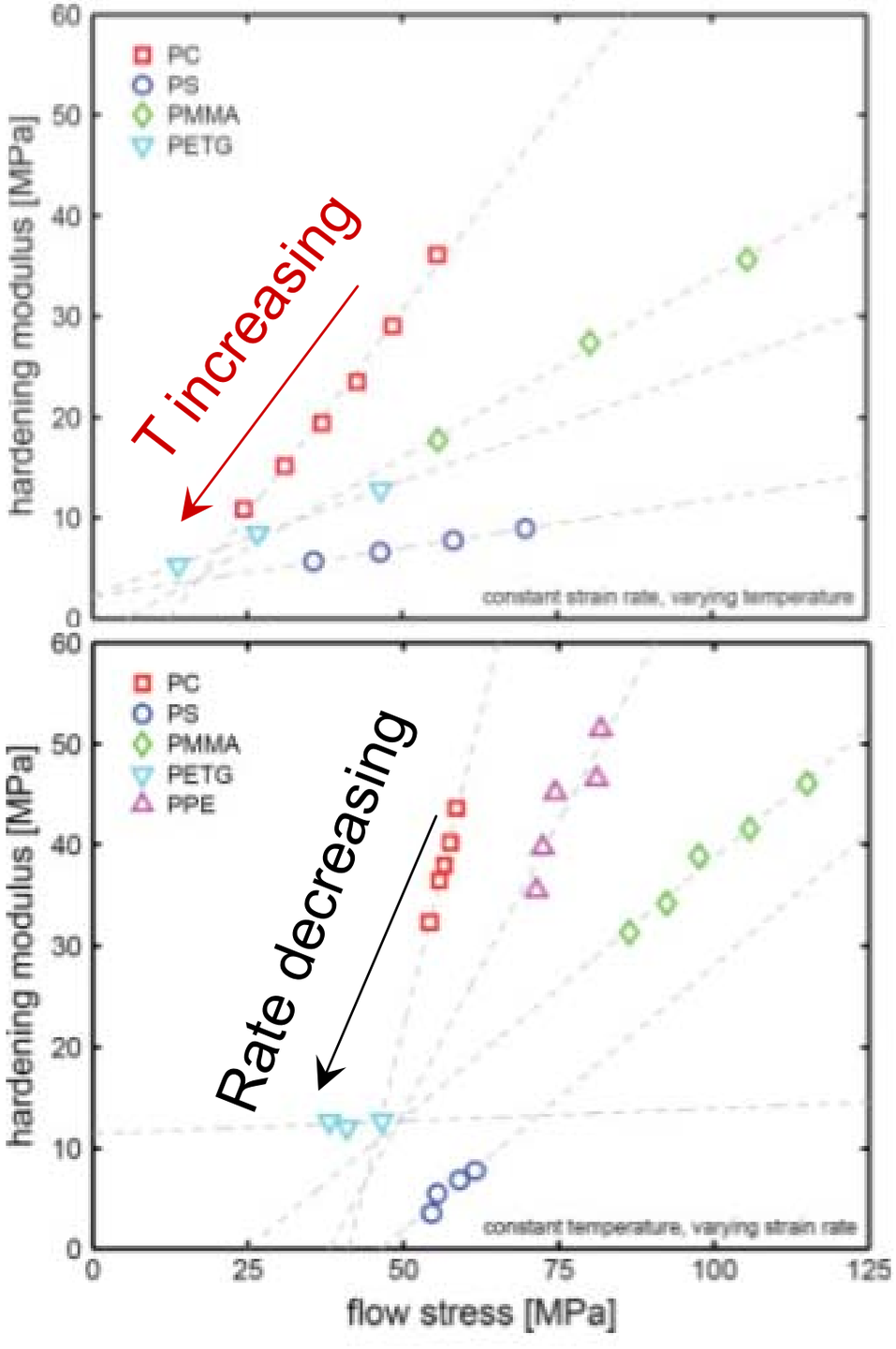


$$\sigma(\bar{\lambda}) = \sigma_0 + G_R^0 g(\bar{\lambda}_{eff})$$

$$g(\lambda) \equiv \frac{1}{\lambda} - \lambda^2$$

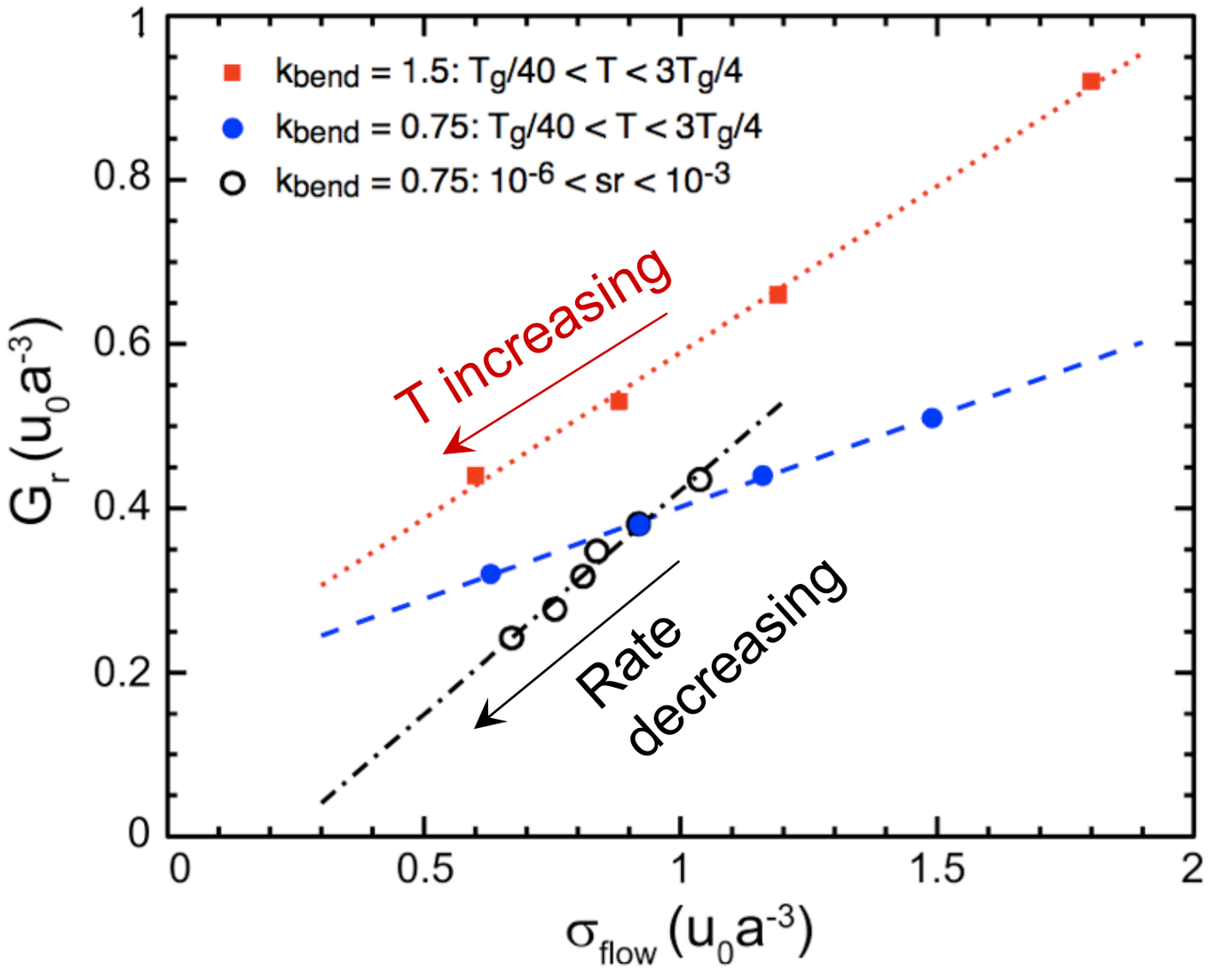
Glassy Hardening Modulus Rises Linearly with the Flow Stress

L. E. Govaert et. al, JPSPP 2008



$$G_R = C_0 + C_1 \times \sigma_{flow}$$

Robbins and Hoy, JPSPP 2009



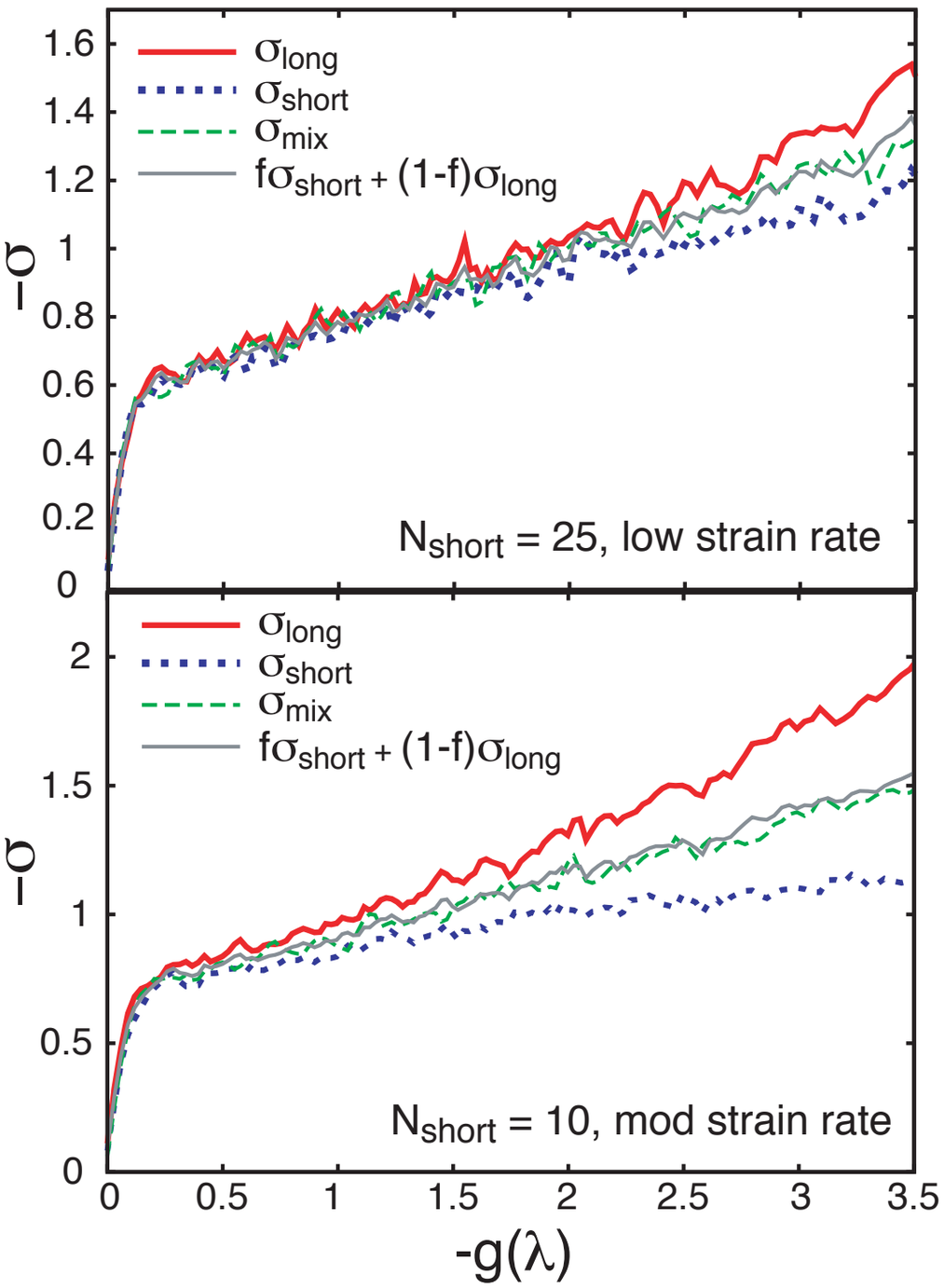
Are Polymer Glasses "Slow Melts"?

"Yes and no"; some illustrative examples

Consider bidisperse mixtures
of "short" and "long" chains

	Large scale relax. time $\tau \sim N^{\gamma}$	Chains relax indepdntly under strain?
Melts	$\gamma = 2, 3.4$	No
Glasses	*New results*	*Often*

Hardening in bidisperse mixtures



Weight fracs: (f) short unentangled chains, (1-f) well-entangled chains

Stress = weight avg. of stresses in pure systems:

$$\sigma = f\sigma_{short} + (1-f)\sigma_{long}$$

Hardening stress ~ work to orient chains in a glassy medium

arises from plastic activity necessary to maintain chain connectivity

Mixtures where short chains don't harden:

$G_R \sim (1\text{-}f)$ not $G_R \sim \rho_e \sim (1\text{-}f)^2$

Would be $G_R \sim \rho_e \sim (1\text{-}f)^2$ *if controlled by entanglements*

Independent orientation -- "mean field" picture?

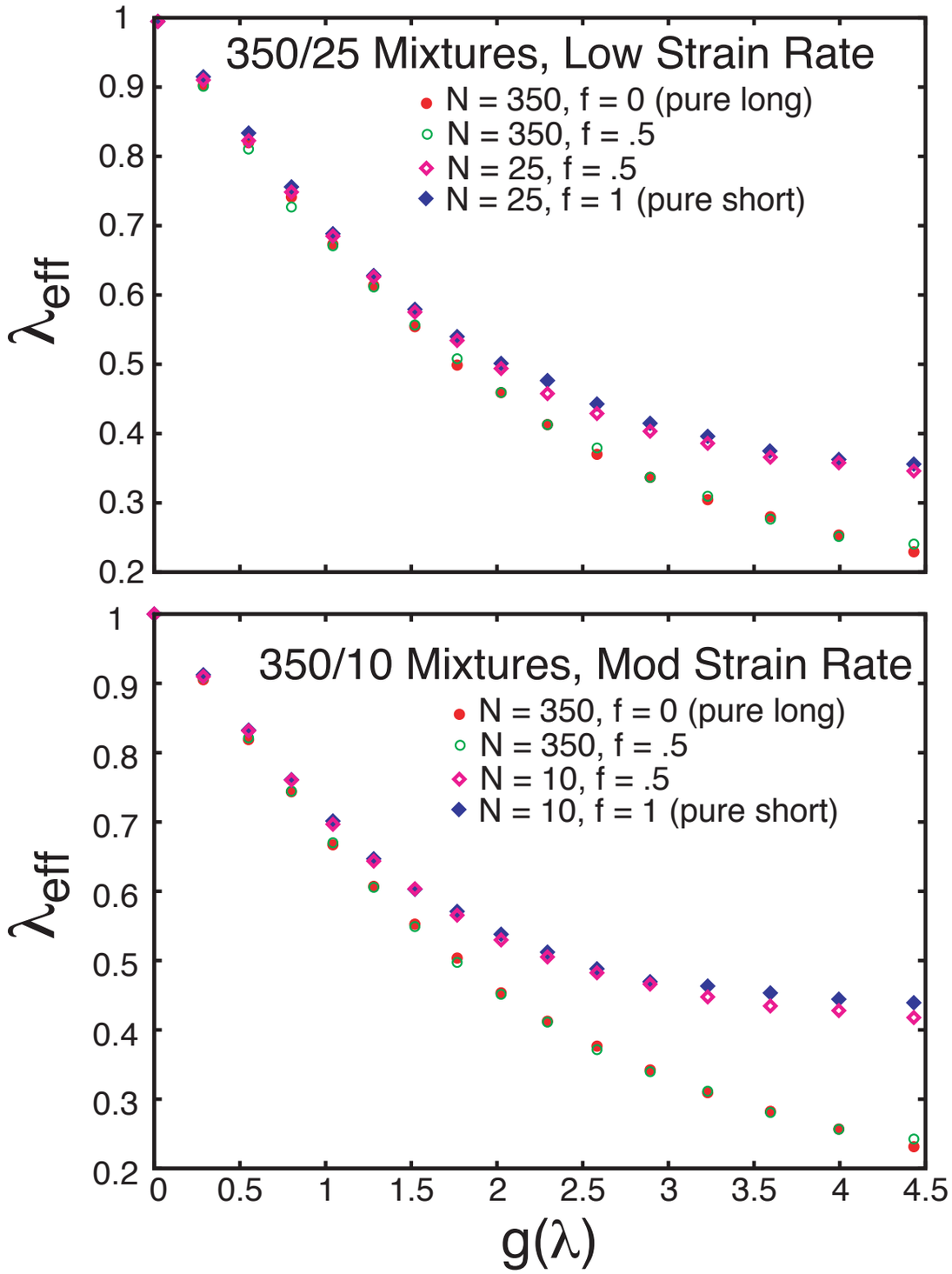
Same systems

$$\lambda_{eff} = \frac{R_z}{R_z^0}$$

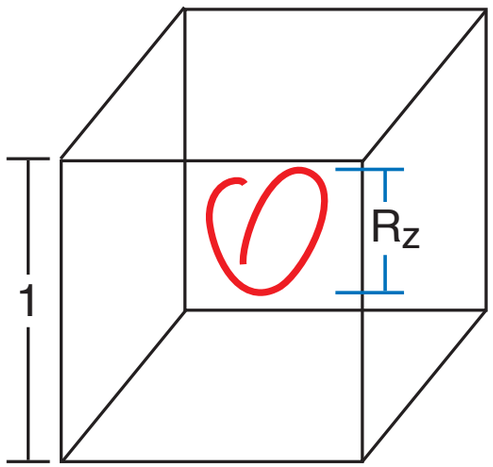
Well below T_g, λ_{eff} is independent of f!
(very different from melts)

Verified this holds for other f, chain lengths, T up to ~ .8T_g

Chains orient independently: suggests can understand in terms of single chain in glassy "medium"

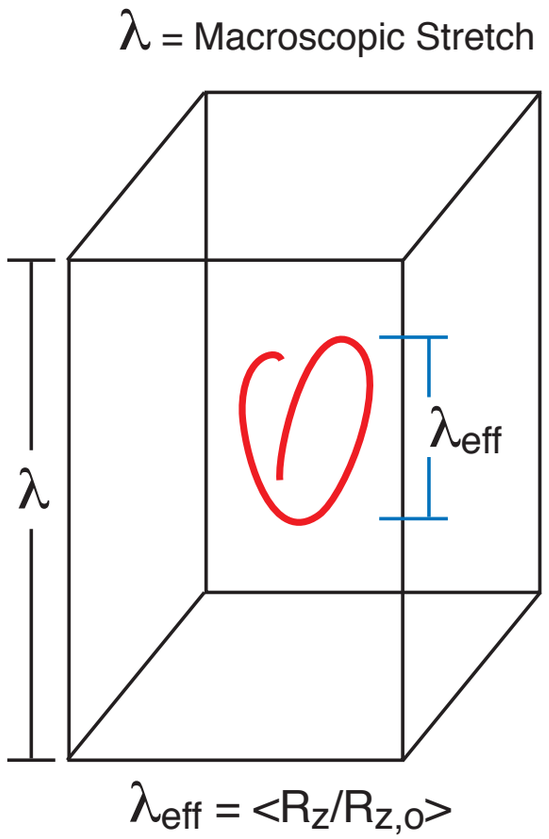


Maxwell-like Model



λ_{eff} = Chain-level Stretch

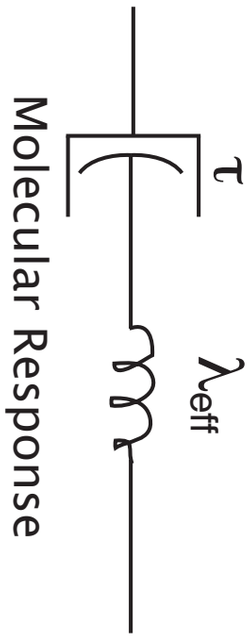
Nonaffine deformation:
$\lambda_{eff} \neq \lambda$



λ_{eff} ~ "elastic" (reversible) chain-level deformation

τ ~ quiescent chain relaxation time ~ N^{γ}

stiff covalent bonds --- strain activated coherent chain relaxation



$$\lambda = \lambda_{eff} + (\lambda - \lambda_{eff})$$

$$\epsilon_{eff} = ln(\lambda_{eff})$$

$$\dot{\epsilon}_{eff} = \dot{\epsilon} - \epsilon_{eff}/\tau$$

Contour length L preserved

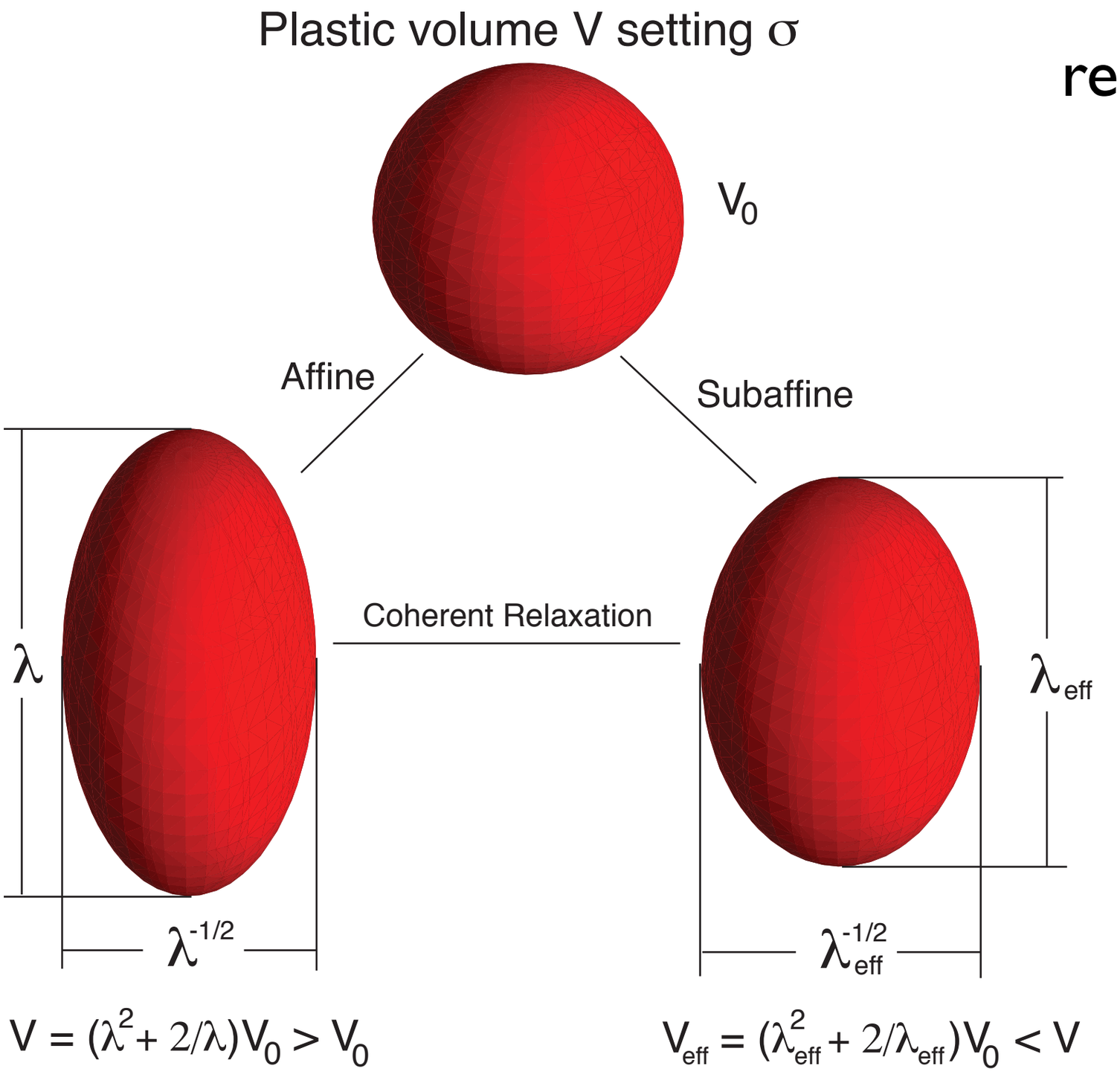
$$\frac{dL}{dt} = \frac{\partial L}{\partial \epsilon}\frac{\partial \epsilon}{\partial t} + \frac{\partial L}{\partial t}$$

$$\frac{\partial L}{\partial t} = -\frac{\partial L}{\partial \epsilon}\frac{\partial \epsilon}{\partial t}$$

$$\tau \sim \tau_0 \dot{\epsilon}^{-1} N^{\gamma-1}$$

Piece of puzzle for faster relaxation under active deformation!

Coherently relaxing chain contours control scaling of hardening relative to flow?



"Few models account for relaxation *during* deformation"

(Grassia et al, JPSPP,2009)

Assume plastic events correlated over volume V set by chain dimensions

V increases during deformation, but less if chains relax: mechanism for both hardening and relaxation

Stress from anisotropic plasticity

- dissipative stress related to local plastic rearrangements events in both flow and hardening regimes

- assume stress is set by density of coherently relaxing contours

$$R_c = \text{extent of polymer } \sqrt{l_0 l_K N}$$

$$R_c^3 = \text{size of plastic events - varies with stretch}$$

$$\sigma^*(\lambda_{eff}) \sim \rho_{cr} R_c^3(\lambda_{eff})$$

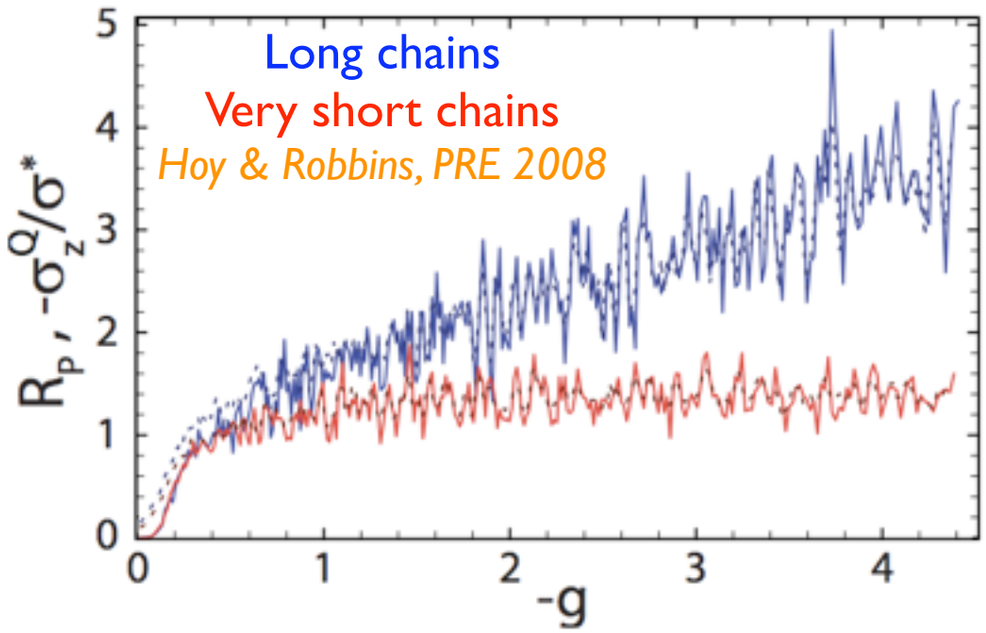
$$\sigma^*(\lambda_{eff}) \sim \rho N^{-1} l_0 R_c^2(\lambda_{eff})$$

$$\sigma^*(\lambda_{eff}) \sim \rho l_0^2 l_K \tilde{g}(\lambda_{eff})$$

$$\sigma^* = \sigma/\sigma_{flow} = \tilde{g}(\lambda_{eff})$$

$$\tilde{g}(\lambda) = (1/3)(\lambda_x^2 + \lambda_y^2 + \lambda_z^2)$$

ρ = monomer number density
l_0 = backbone bond length
l_K = Kuhn length



With theory of relaxation of λ_{eff}, have full model

$$\dot{\epsilon}_{eff} = \dot{\epsilon} - \epsilon_{eff}/\tau$$

$$\epsilon_{eff} \equiv ln(\lambda_{eff})$$

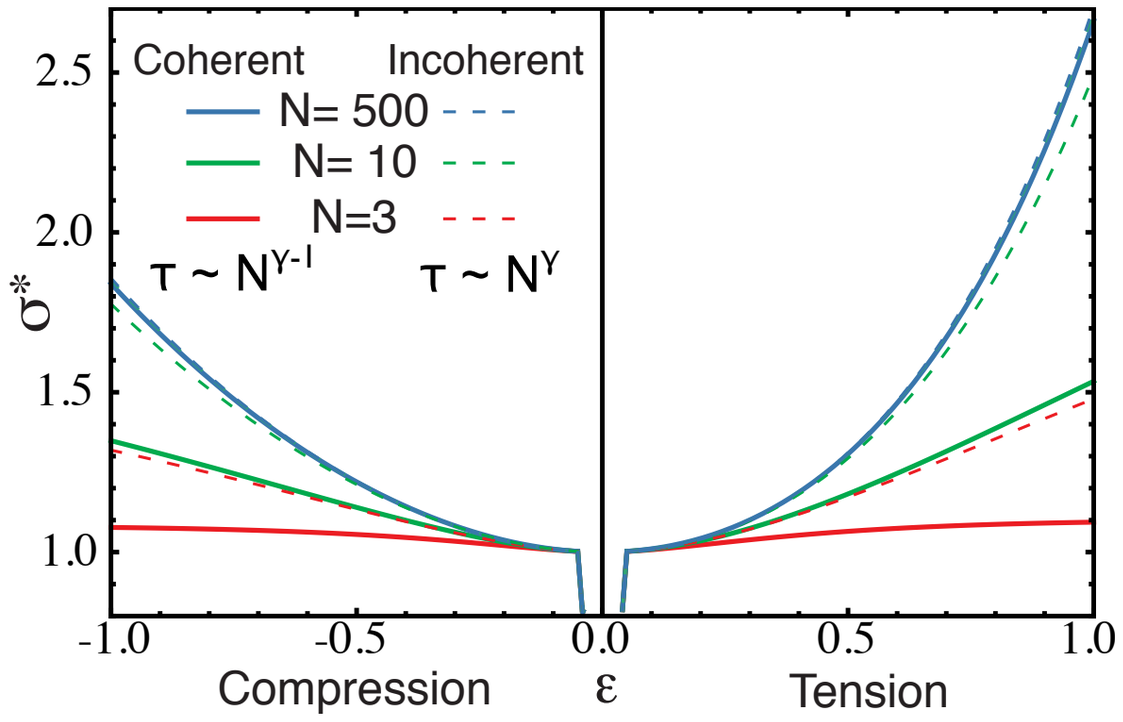
$\tau \sim \tau_0 \dot{\epsilon}^{-1} N^{\gamma-1}$ under active deformation
$\tau \sim \tau_0 N^{\gamma}$ otherwise

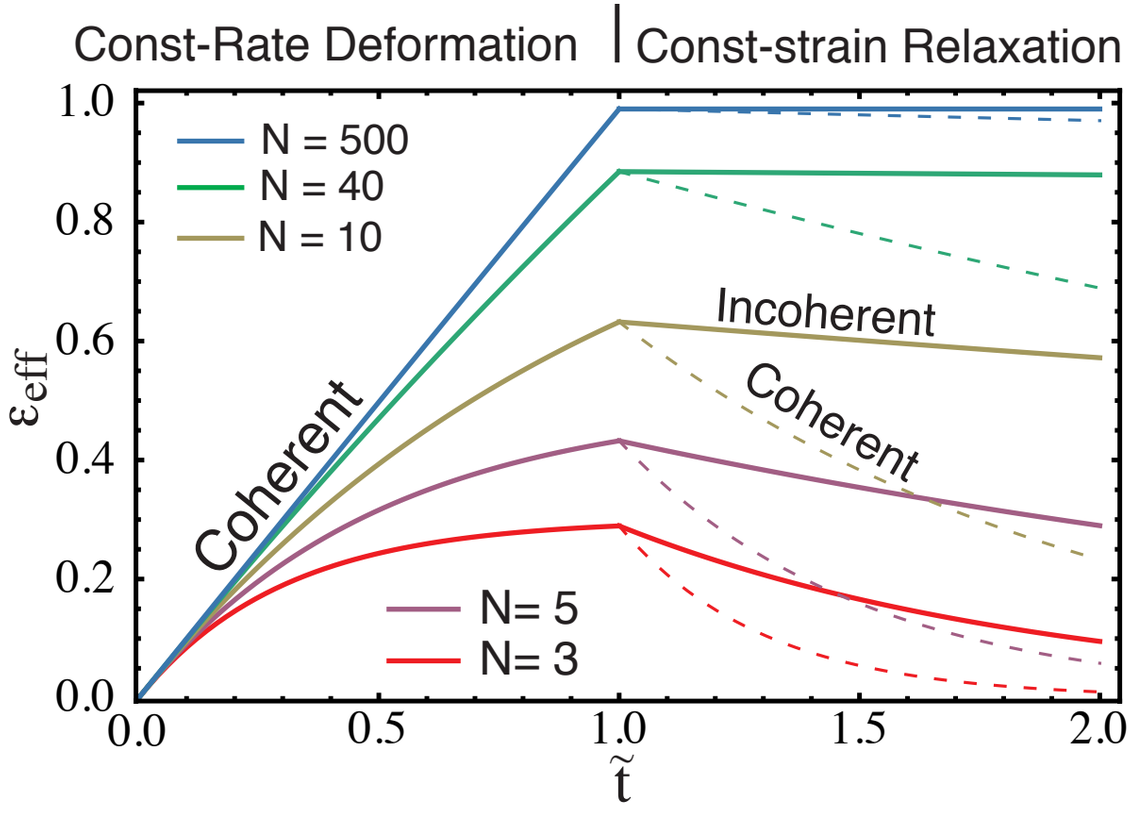
Hardening ~ plastic flow stress in increasingly anisotropic medium!

Some key results

- nonlinear viscoplastic "fading memory" eqn for $\sigma^* = \sigma/\sigma_{flow}$
- continuous crossover from perfect-plastic flow to Gaussian-like hardening as N increases, *without invoking entanglements*
- coherent $\tau \sim N^{\gamma-1}$ matches experimental trends much better than incoherent $\tau \sim N^{\gamma}$

very consistent with speedup in local relaxation observed in experiments (Lee, Ediger, etc.)!



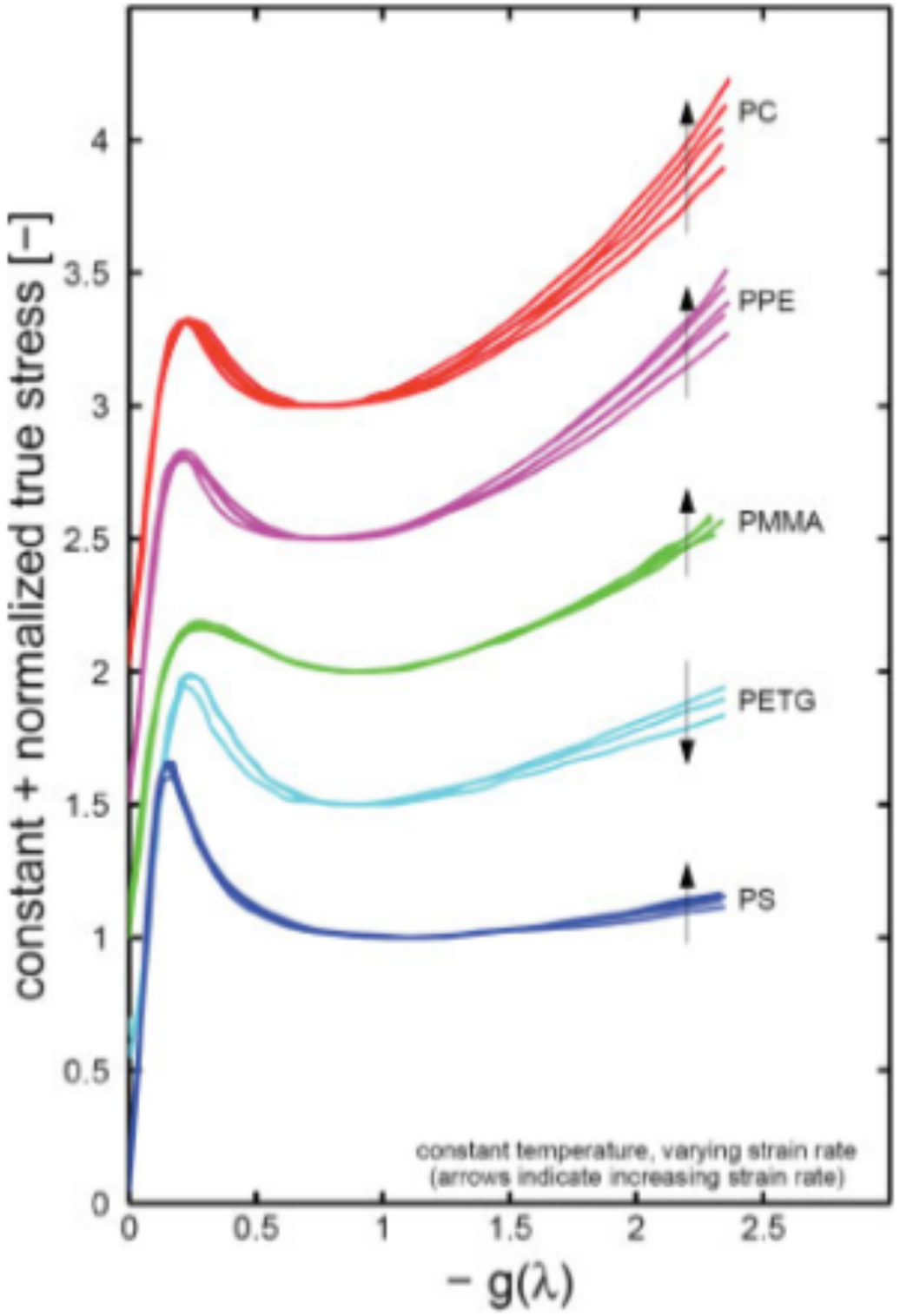


Comparison to Experiment

- $\tilde{g}$ better than g for long chains; captures plastic flow "plateau"

- can predict stress only qualitatively; theory neglects softening, thermal relaxation, etc.

- *but very consistent* with observed scaling of hardening with flow (both rate- and T- dependent)

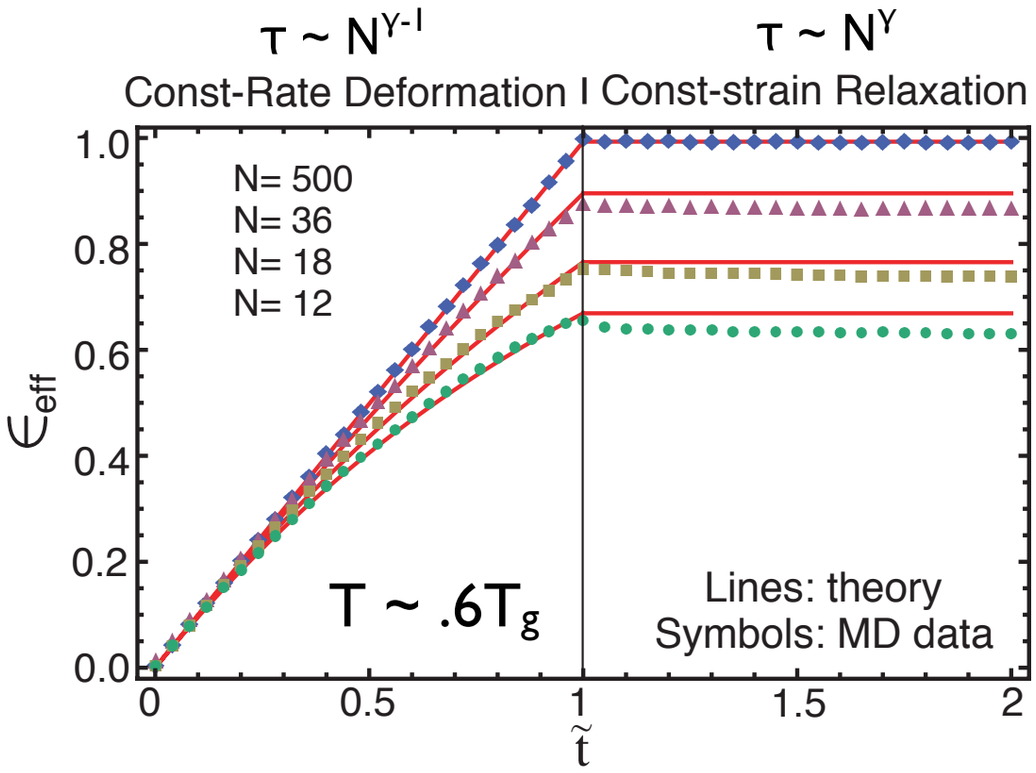


Govaert et. al., JPSPP 2008

Testing model with MD simulations

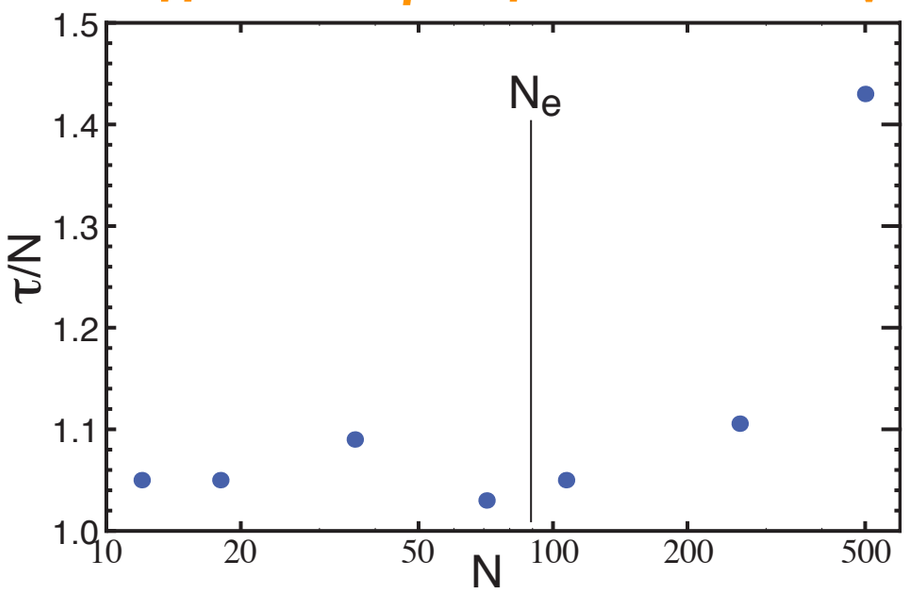
relxn. slows upon cessation of deformation

- λ_{eff} very well predicted; fits show $\tau \sim N^{\gamma-1}$ during deform.
- $\gamma = 2$ --- Rouselike relxn!
- stress prediction qualitatively captures trends & quantitatively within ~20% ***(will show at end!)***

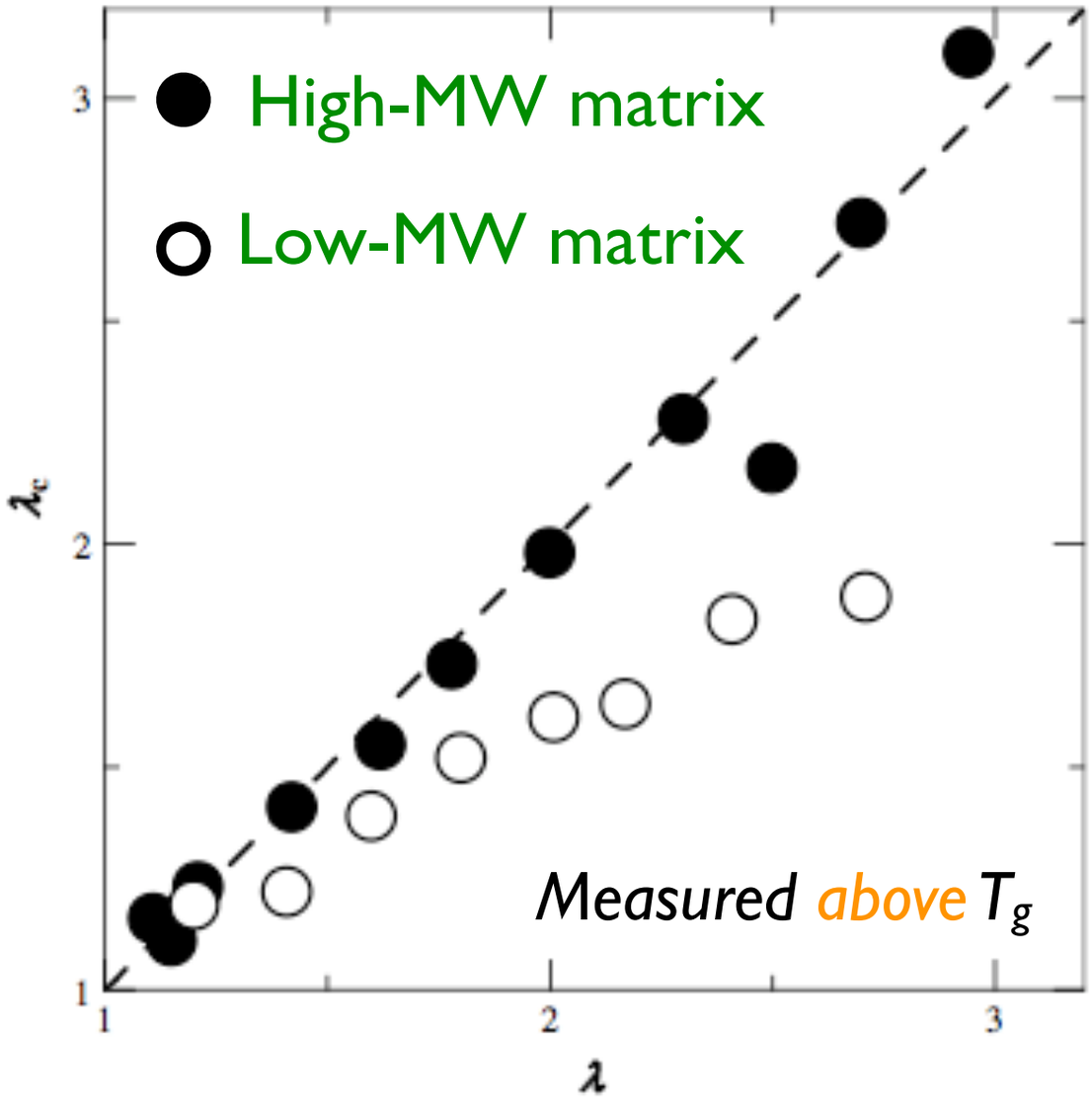


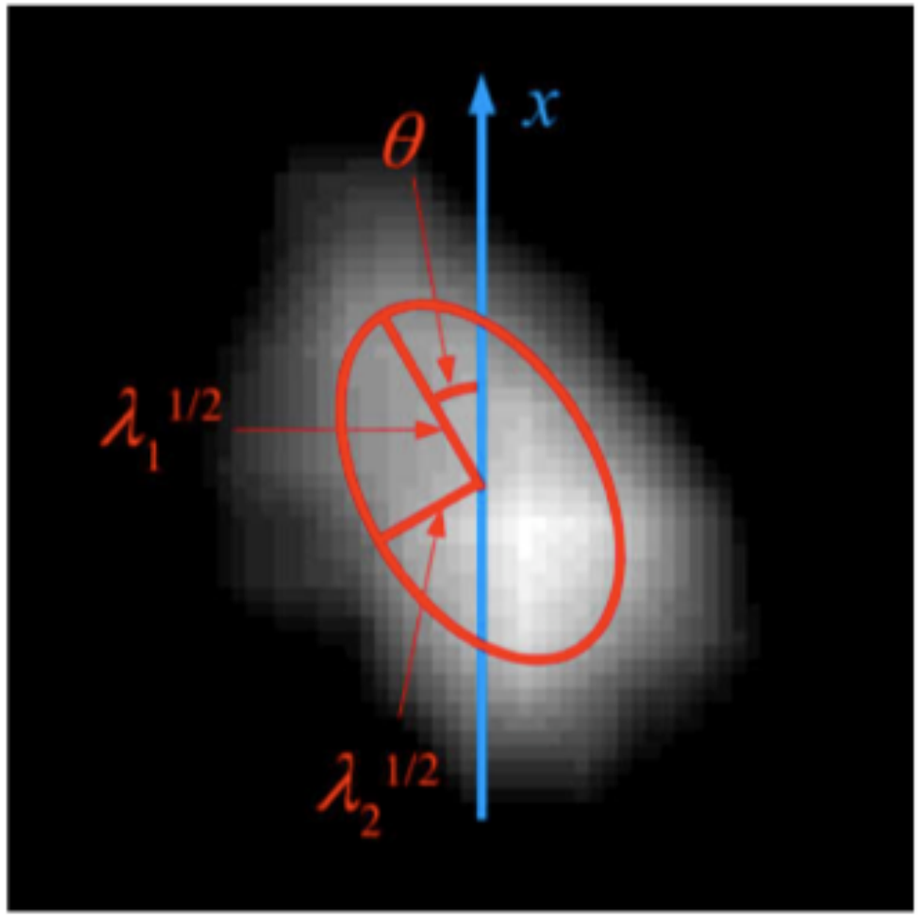
- expected to break down along with MFT as $T \longrightarrow T_g$ or in densely entangled systems with large energetic "chain stretching" contributions to stress

effect in prefactor, not γ



Experimental Testability?





- λ_{eff} experimentally measurable! *(Ube et al, Polymer, 2007, 2009)*
- used scanning near-field optical microscopy
- extensible to $T < T_g$?

Compared to other recent non-entropic models

- Chen/Schweizer *(PRL 2009)*: similar analytic form for constitutive law, accounts for thermal relaxation but not $\lambda \neq \lambda_{eff}$

- Wendlandt *(Polymer 2005)*: also associates rate dependence with a plastic volume V, but Eyring-like model, V *decreases* with increasing strain

- Constitutive *(very many)*: sophisticated and fit data for real polymers, but not "microscopic", and only *(Miehe et al, 2004, 2009)* accounts for $\lambda \neq \lambda_{eff}$

Summary

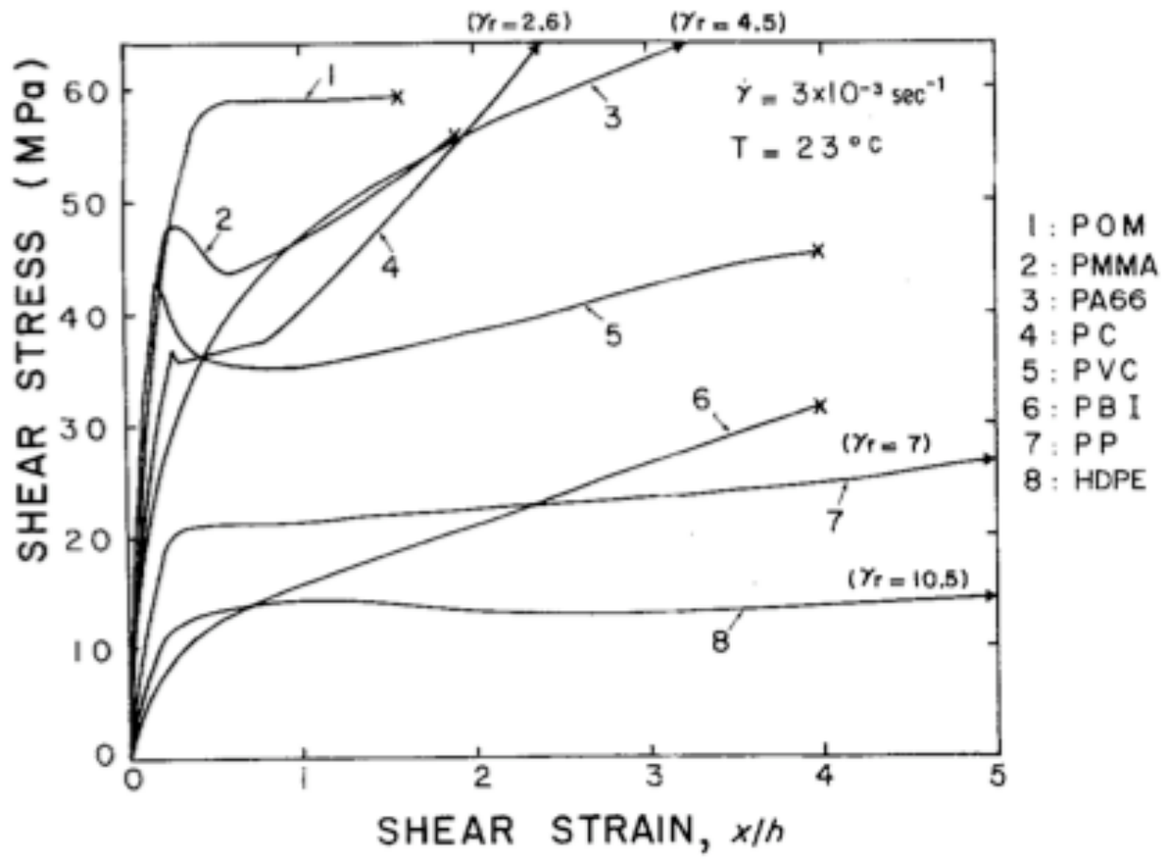
- mech. behavior of short chain polymer glasses ~ "atomic" glasses; differences arise from *covalent connectivity*
- glassy polymeric strain hardening arises from the stress necessary to orient individual chains *as long as bond/entanglement stretching not important;* this is the usual case in experiment
- Large scale chain orientation controls the dissipative part of polymer plasticity (well past yield strain)
- rising stress post-yield can be viewed as flow stress in increasingly anisotropic medium of coherently relaxing chain contours
- coherent relaxation concept explains N dependence of relaxation times under active deformation
- effect of entanglements may be primarily *slowing* relaxation?

- in sims, MF picture holds for $T \sim .8T_g$ and below: obviously breaks down at "high" T since chains in melts don't orient independently, but how high? "high" T may be rate dependent

- further work needed to describe energetic component of stress, thermal/rate effects *(e. g. Chen & Schweizer, 2007-09)*

- chemistry dependence certainly important, especially for non-compressive deformation, prob. have gone as far as possible with CG simulations

Behavior of different polymers in shear
(G'Sell et. al., J. Mat. Sci. '83)



A question to ponder

How do polymeric glasses compare to other "atomic" glasses in which some units much more strongly connected than others?

Thanks: Ken Schweizer, Ed Kramer, Grisha Medvedev, Daniel Read, LAMMPS MD software, NSF-DMR grants, Yale Anderson fellowship

Bead-spring polymer model

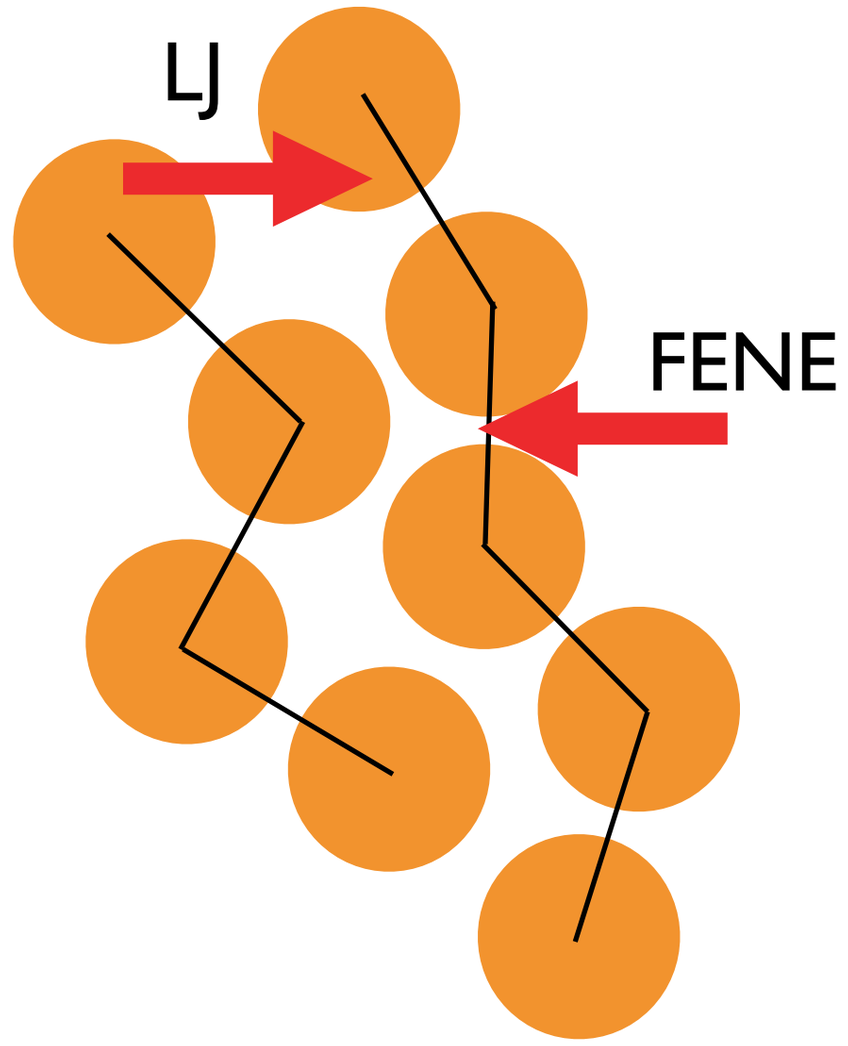
$$U_{LJ}(r) = 4u_0\left(\left(\left(\frac{a}{r}\right)^{12} - \left(\frac{a}{r_c}\right)^{12}\right) - \left(\left(\frac{a}{r}\right)^{6} - \left(\frac{a}{r_c}\right)^{6}\right)\right)$$

$$U_{FENE}(r) = -\frac{1}{2}kR_0^2\log(1-(r/R_0)^2)$$

$$U_{bend} = k_{bend}\left(1 - cos(\theta)\right)$$

Kremer & Grest, 1980s-present

captures RW structure, chain stiffness and uncrossability, excluded volume & adhesion, but no chemical detail



strength of adhesive interactions ~ r_c

N spherical monomers per chain, measurable entanglement length N_e, density ρ_e *(Everaers et. al.)*

increasing k_{bend} raises ρ_e,
diluting w/ short chains lowers ρ_e

very good at predicting "universal" features of real melts and glasses *(800 citations)*

Details of nonlinear viscoplastic "constitutive law"

Math easier if use true strain ε rather than λ_{eff}

$$\sigma^*(\epsilon_{eff}) = \sigma(\epsilon_{eff})/\sigma_{flow} = \tilde{g}(\epsilon_{eff})$$

"Modulus" k(ε)

$$k(\epsilon) \equiv d\epsilon_{eff}/d\epsilon$$

$$\frac{\partial \sigma^*}{\partial \epsilon} = h(\epsilon_{eff})k(\epsilon),$$

where

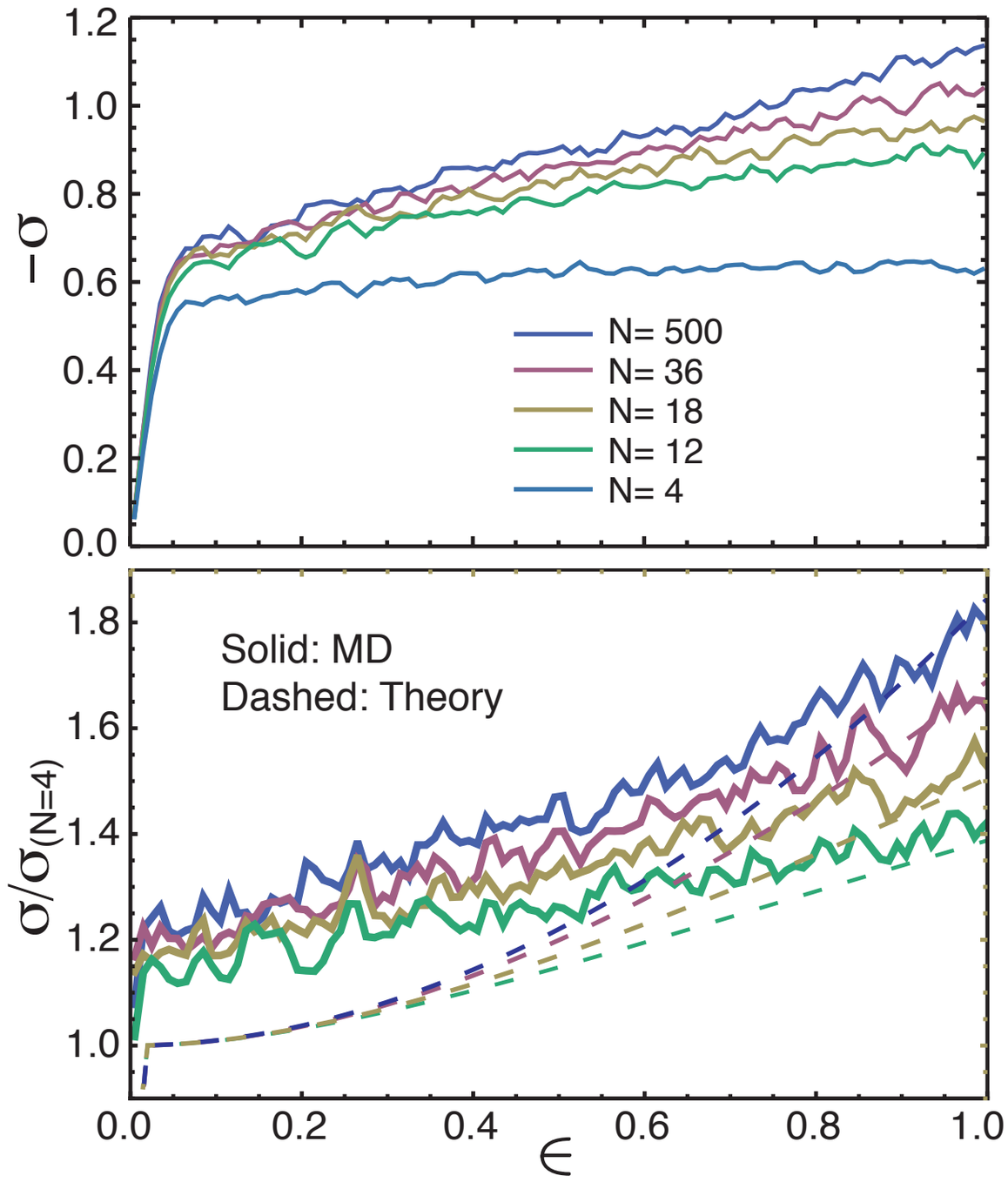
$$h(\epsilon_{eff}) \equiv \left.\frac{\partial \tilde{g}(\epsilon)}{\partial \epsilon}\right|_{\epsilon_{eff}(\epsilon)}.$$

Stress depends only on k-history; used simple model for yield

$$\sigma^*(\epsilon) = \min\left(\frac{\epsilon}{\epsilon_y}, 1\right) + \int_0^{\epsilon} h\left(\int_0^{\epsilon'} k(\epsilon'')d\epsilon''\right) k(\epsilon')d\epsilon'$$

Analytic solution for const strain rate uniaxial def.

$$\sigma^*(\epsilon) = \frac{1}{3}\exp\left[2\dot{\epsilon}\tau(1-\exp(-\frac{\epsilon}{\dot{\epsilon}\tau}))\right] + \frac{2}{3}\exp\left[-\dot{\epsilon}\tau(1-\exp(-\frac{\epsilon}{\dot{\epsilon}\tau}))\right] - \max\left(1-\frac{\epsilon}{\epsilon_y}, 0\right)$$

Theory vs MD: predictions for σ^*

- stress predictions qualitatively captures trends & quantitatively within ~20%
- better agreement not expected because theory leaves much out; thermal effects, energetic terms, local relaxation & its variation with stress, etc.
- shape of theoretical curves seemingly agree better with experiment!