How Different are Polymer Glasses from Glassy Simple Liquids?

Polymer Glasses:

Malleable solids (near Tg)

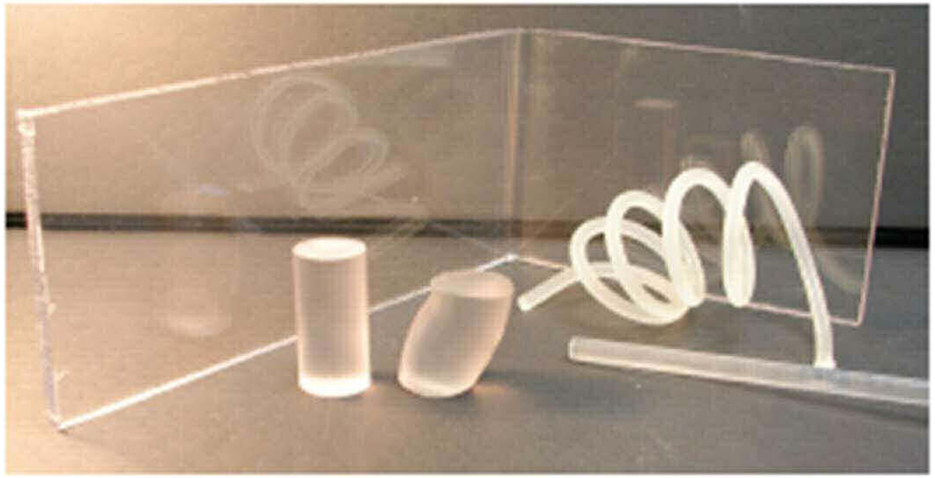
Hold shape after deformation

High dissipation

Structural plastics

Optical materials

CD's laptop screens etc.



Data on polycarbonates: C. G Sell et al, J. Mat. Sci 27 (1992) 5031

How Different are Polymer Glasses from Glassy Simple Liquids?

Mike Cates, Suzanne Fielding[1] and Ron Larson[2]

Simple glasses under flow: shear startup and creep

Fluidity model: A minimal theory of aging and rejuvenation

New features of polymer glasses: Strain hardening and $\tau(t)$

A minimal theory of polymer glasses under flow

S M Fielding, R G Larson and M E Cates, PRL in press (2012)

1. Durham University
2. University of Michigan

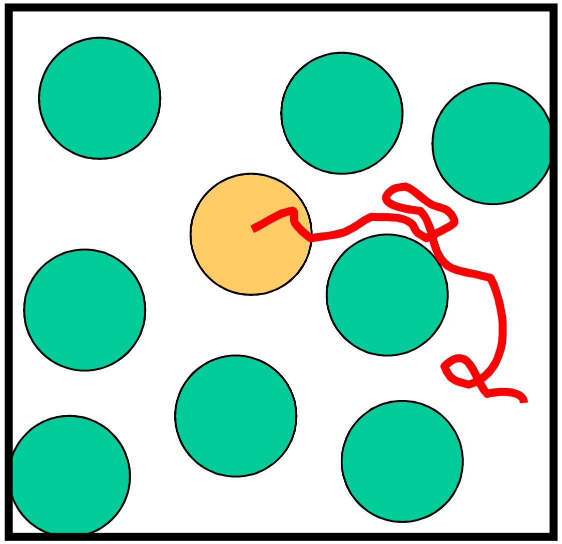
THE UNIVERSITY OF EDINBURGH

EPSRC

THE ROYAL SOCIETY

SUPA
Scottish Universities Physics Alliance

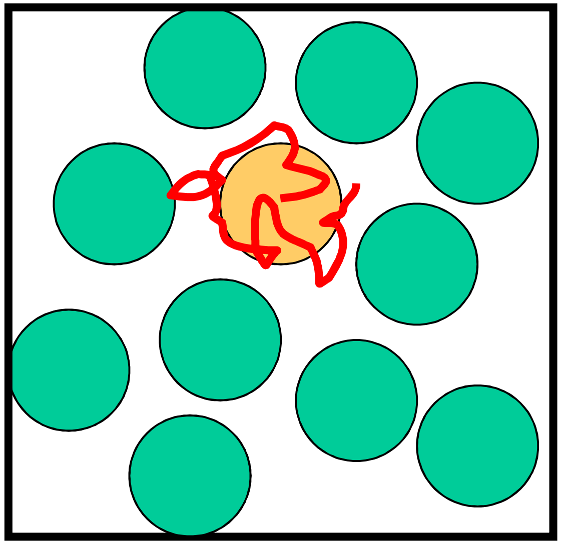
Simple Glasses



$T > T_g$: finite diffusivity

$\tau \approx$ cage lifetime

Viscoelastic liquid



$T < T_g$: zero diffusivity

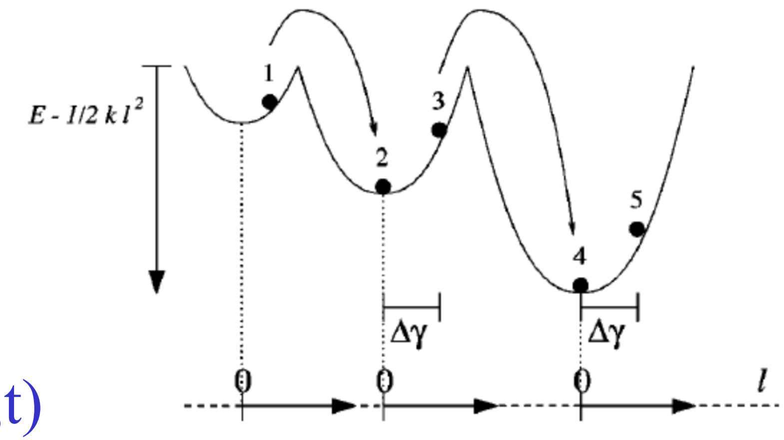
$\tau \approx \infty$

Elastoplastic solid

Theories: Mode Coupling (first principles; aging difficult)
Soft Glassy Rheology Model (SGR)

SGR Model

- Particles jump among traps; temperature parameter $x = T/T_g$
- l = local strain; $\sigma = k\langle l \rangle$
- $dl/dt = \dot{\gamma}(t)$ between hops
- Jump rate $\Gamma_0 \exp[-(E-k\, l^2/2)/x]$
- Time evolution equation for $P(E,l,t)$



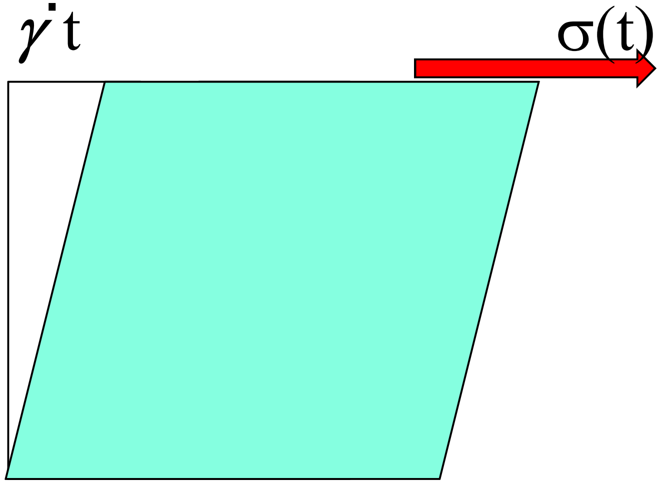
$$\frac{\partial}{\partial t}P = -\dot{\gamma}\frac{\partial}{\partial l}P - \Gamma_0 e^{-(E-\frac{1}{2}kl^2)/x}P + \Gamma(t)\rho(E)\delta(l)$$

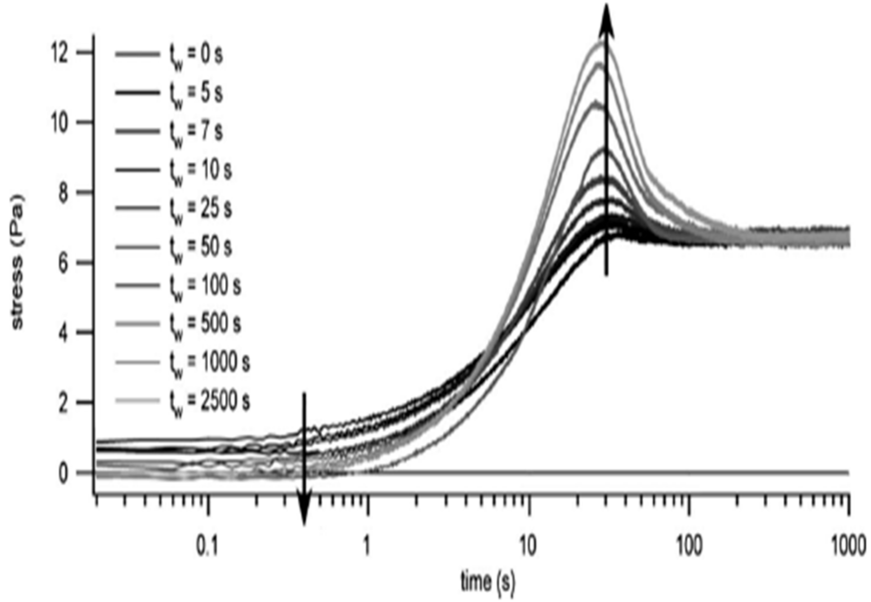
- Prior distribution for well depths $P_0(E) \sim \exp[-E]$
- Glass transition at $x = 1$, "simple aging" for $x < 1$

P. Sollich et al, PRL 78 (1997) 2020; S. Fielding et al J. Rheol 44 (2000) 323

Simple Glasses

Shear startup: switch on $\dot{\gamma}$, measure stress $\sigma(t)$



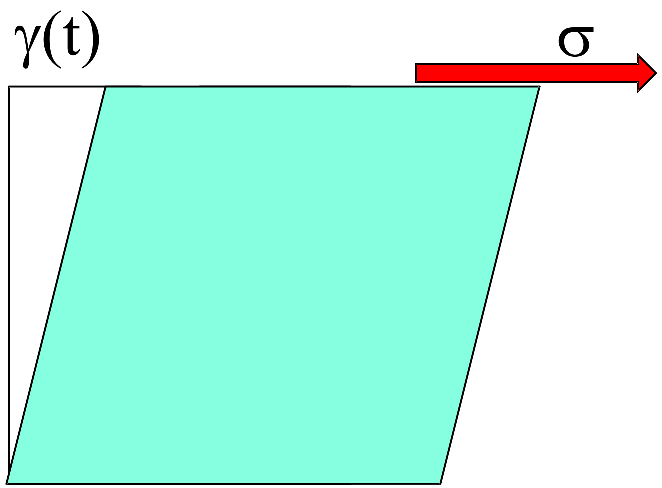


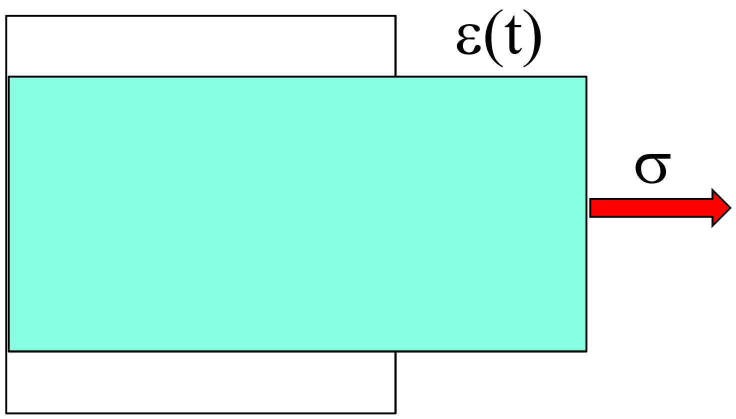
Age-dependent stress overshoot in soft spheres (stars)

S. Rogers et al, J. Rheology 54 (2010) 133

Simple Glasses

Creep measurement: step stress, measure strain $\gamma(t)$ or $\varepsilon(t)$





standard for colloids

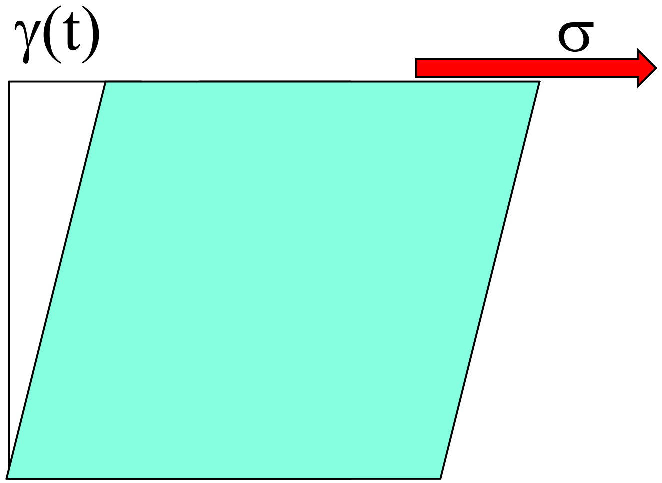
standard for polymer glasses

$J(t,t_w,\sigma) \equiv \gamma(t)/\sigma$

$J(t,t_w,\sigma) \equiv \varepsilon(t)/\sigma$

Simple Glasses

Creep measurement: step stress, measure strain $\gamma(t)$

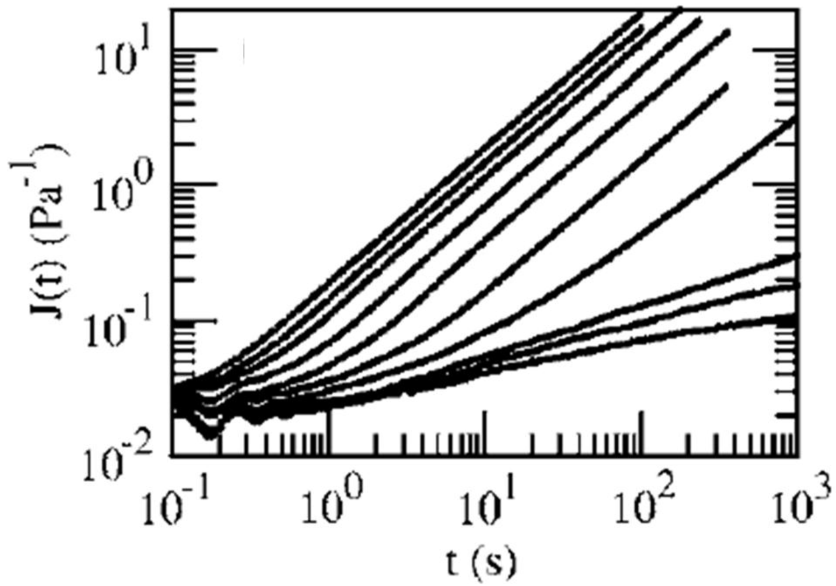


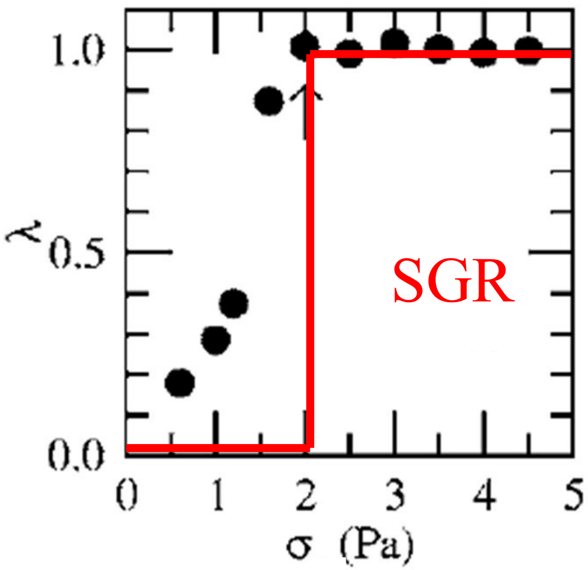
standard for colloids

$J(t,t_w,\sigma) \equiv \gamma(t)/\sigma$

Simple Glasses

Creep measurement: step stress, measure strain $\gamma(t)$



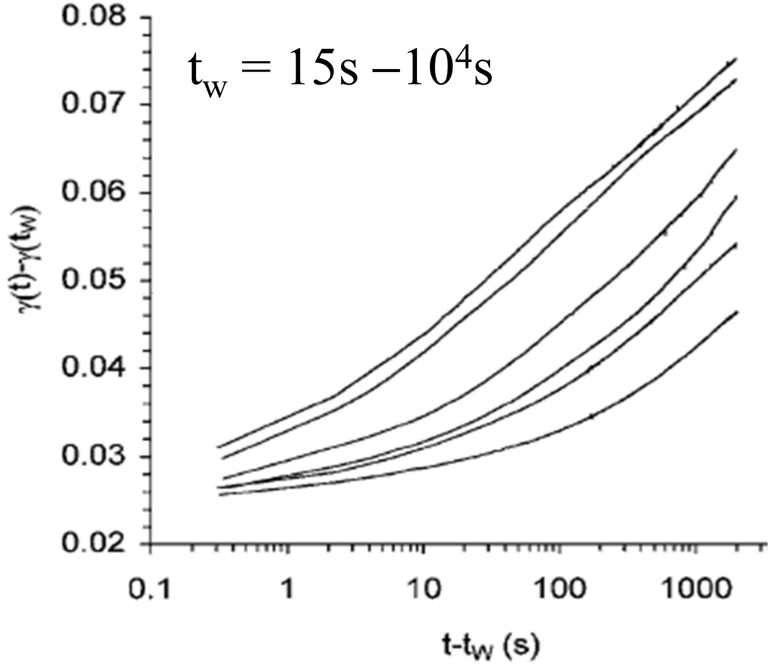


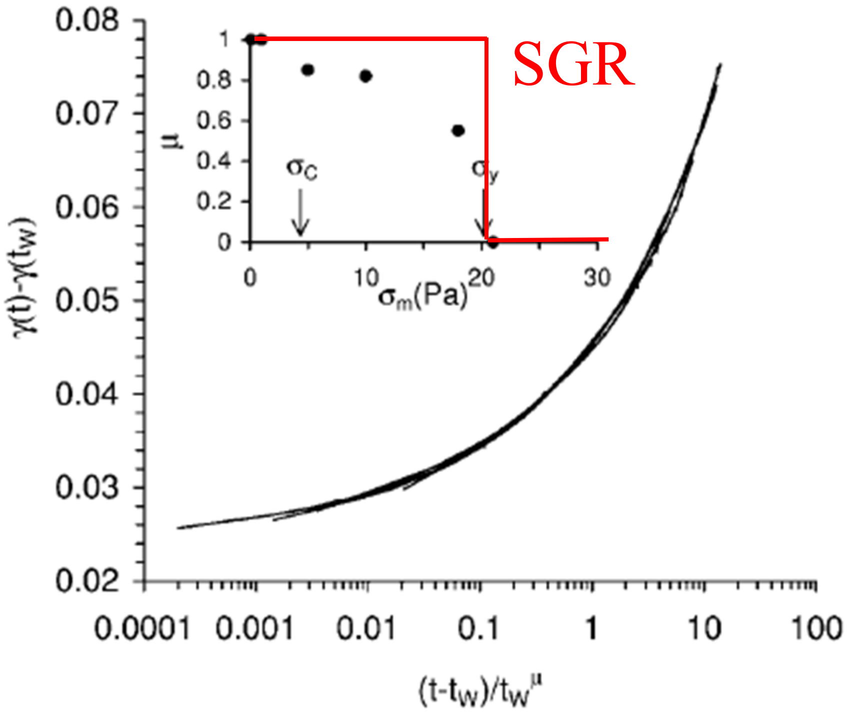
$J(t,t_w,\sigma) \equiv \gamma(t)/\sigma$

asymptotic exponent:
$\lambda = 1$ for $\sigma > \sigma_Y$

Data on hard-sphere colloids:
K. Pham et al, J. Rheol. 52 (2008) 469

Role of Aging





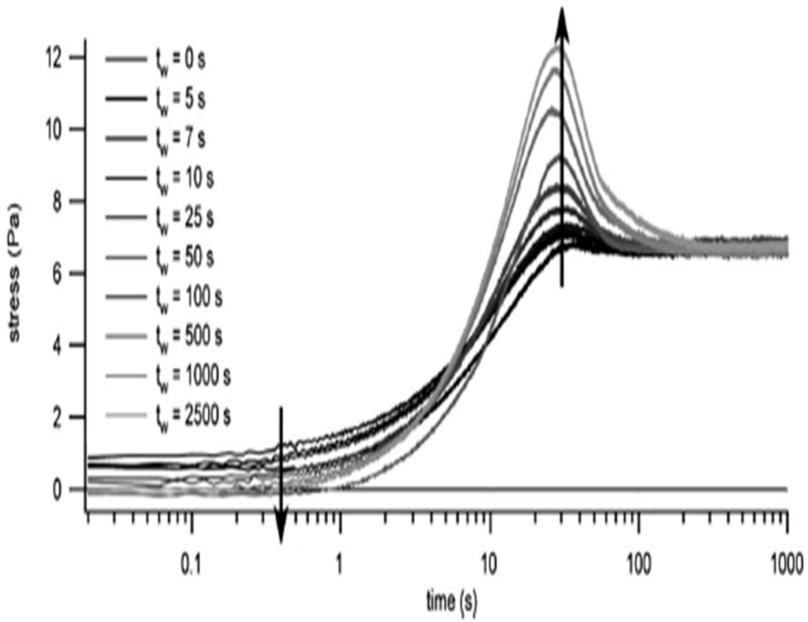
"Simple aging": longest relaxation time $\tau \propto$ system age t_w

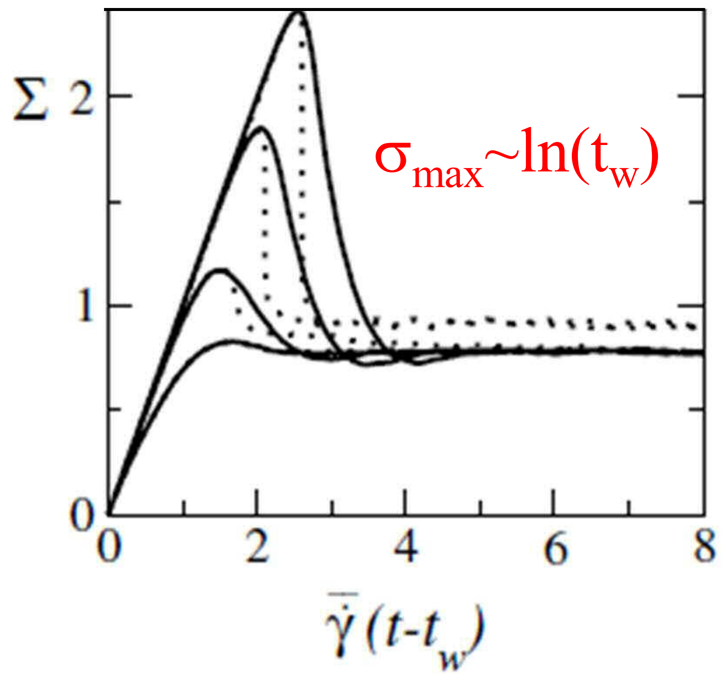
SGR shows simple aging scenario
Data on (some) simple glasses broadly agrees

Data on microgels:
M. Cloitre et al, PRL 85 (2000) 4819

S. Fielding et al,
J. Rheol. 44 (2000) 323

Role of Aging





"Simple aging": longest relaxation time $\tau \propto$ system age t_w

SGR shows simple aging scenario
Data on (some) simple glasses broadly agrees

Data on soft spheres:
S. Rogers et al, J. Rheol. 54 (2010) 133

S. Fielding et al
J. Rheol. 44 (2000) 323

Fluidity Model: Simple Shear

Elastic modulus G, conformation tensor σ

Stress $\Sigma = G(\sigma - I)$

Simple shear $\sigma \to \sigma_{xy} = \sigma$

$\dot{\sigma} = \dot{\gamma} - \sigma/\tau$

$\dot{\tau} = 1 - (\tau - \tau_0)\lambda$

$\lambda = |\dot{\gamma}|$

$\sigma \approx$ local elastic strain

Maxwell fluid, stress relaxation time τ

simple aging, but flow rejuvenates

steady state: $\sigma_{ss} = \dot{\gamma}\,\tau_{ss}(\dot{\gamma})$

$\tau_{ss} = \tau_0 + 1/\lambda$

Antecedents:

G. Picard et al, PRE 66 (2002) 051501

P. Coussot et al, PRL 88 (2002) 175501

R. Moorcroft, MEC and S. Fielding, PRL 106 (2011) 055502

Fluidity Model: General Flows

Elastic modulus G, conformation tensor σ

Stress $\Sigma = G(\sigma - I)$

General flow velocity $v(r)$

$$\dot{\sigma} + v\cdot\nabla\sigma = \sigma\cdot\nabla v + (\nabla v)^T\cdot\sigma - (\sigma - I)/\tau$$

$$\dot{\tau} = 1 - (\tau - \tau_0)\lambda$$

$$\lambda = \nu\sqrt{2\mathrm{Tr}(D:D)} \quad ; \quad 2D \equiv \nabla v + (\nabla v)^T$$

Tensorial version:

nonuniformity, elongational flow now allowed

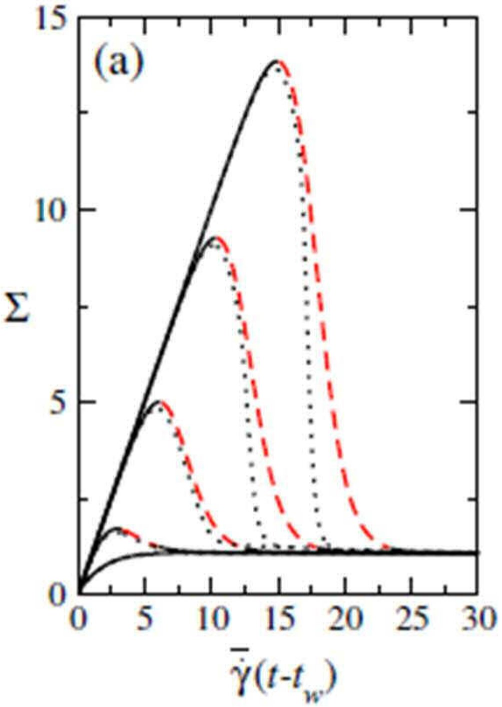
Antecedents:

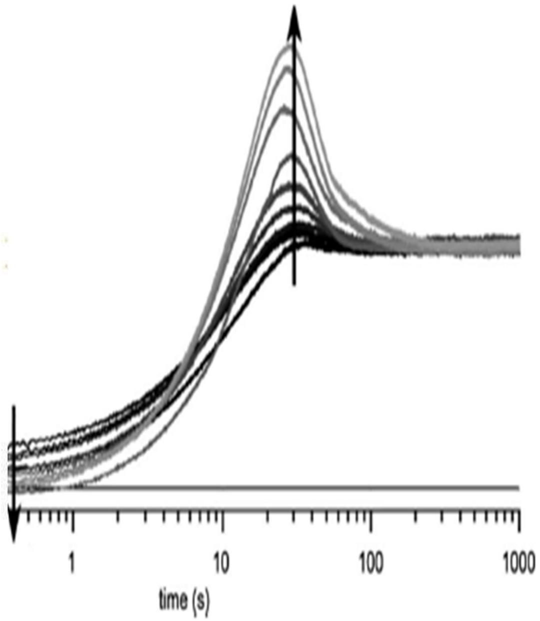
G. Picard et al, PRE 66 (2002) 051501

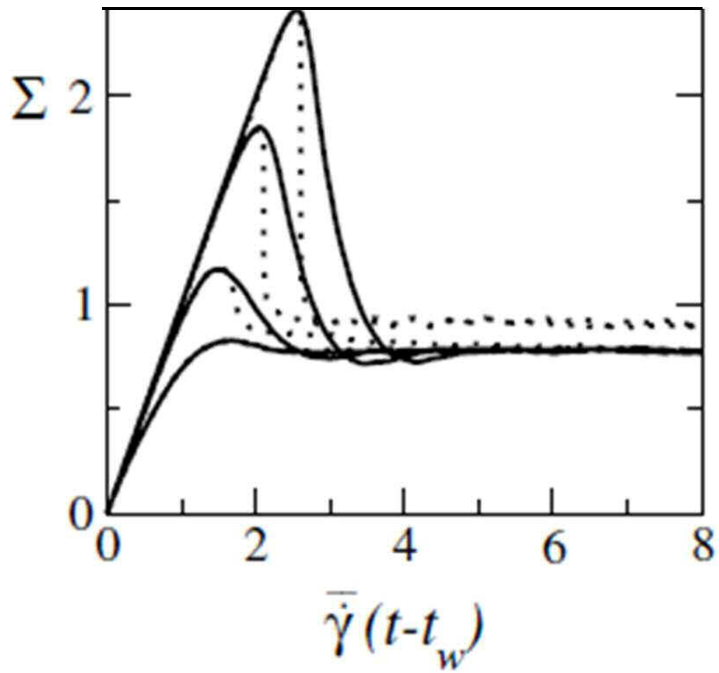
P. Coussot et al, PRL 88 (2002) 175501

R. Moorcroft, MEC and S. Fielding, PRL 106 (2011) 055502

Aging + Flow Rejuvenation: Shear Startup







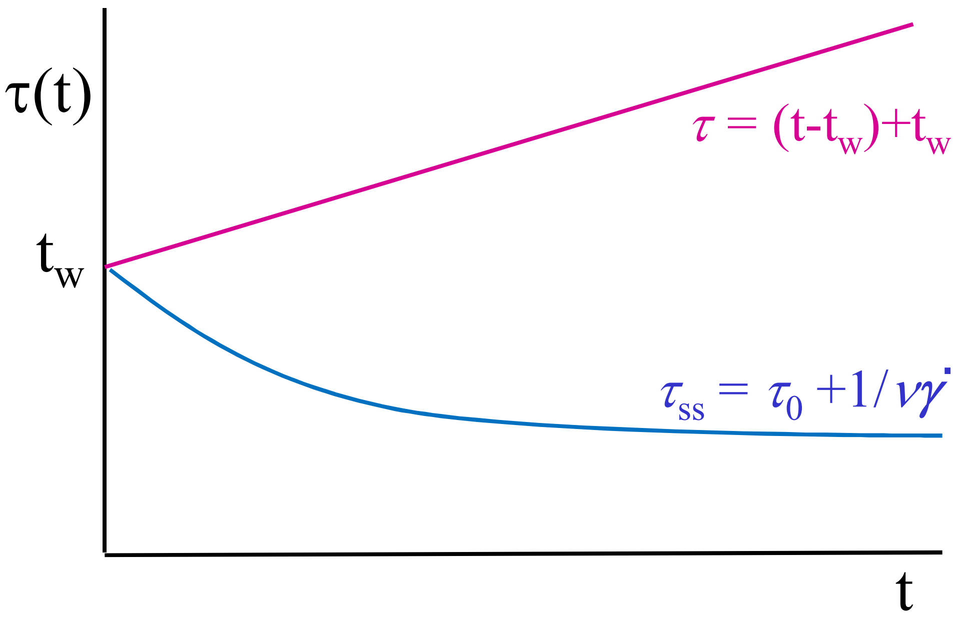
$$\sigma_{max} \approx G \log(\dot{\gamma}\, t_w)$$

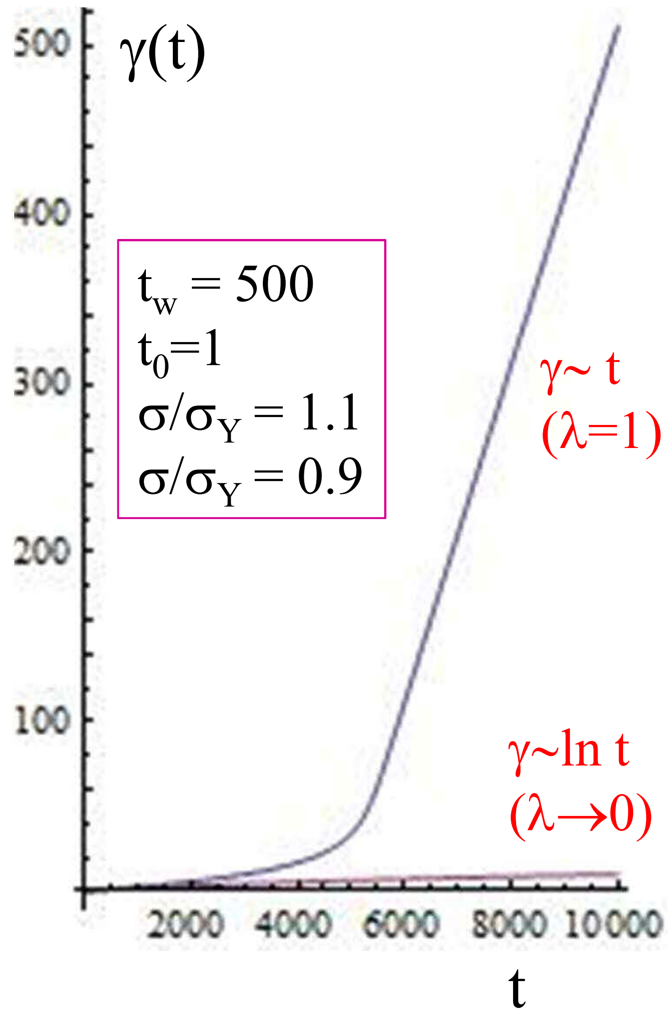
Fluidity | Soft Spheres | SGR

R. Moorcroft, MEC and S. Fielding, PRL 106 (2011) 055502

Data on soft spheres: S. Rogers et al, J. Rheol. 54 (2010) 133

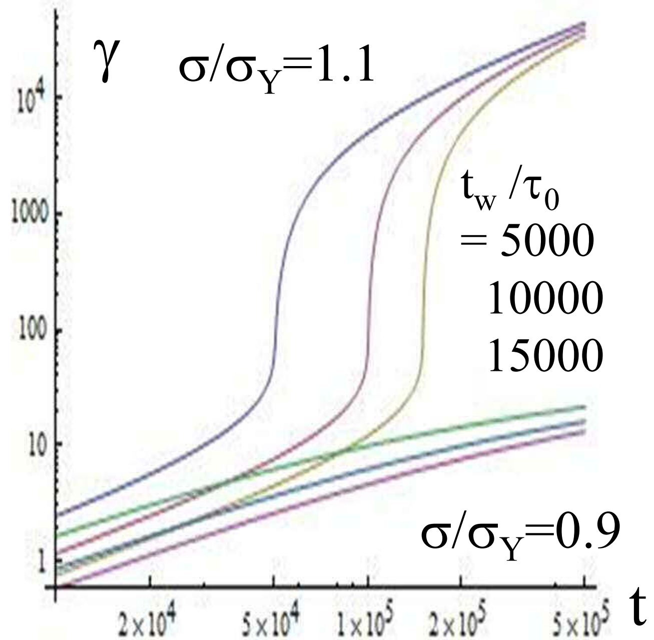
Aging + Flow Rejuvenation: Creep

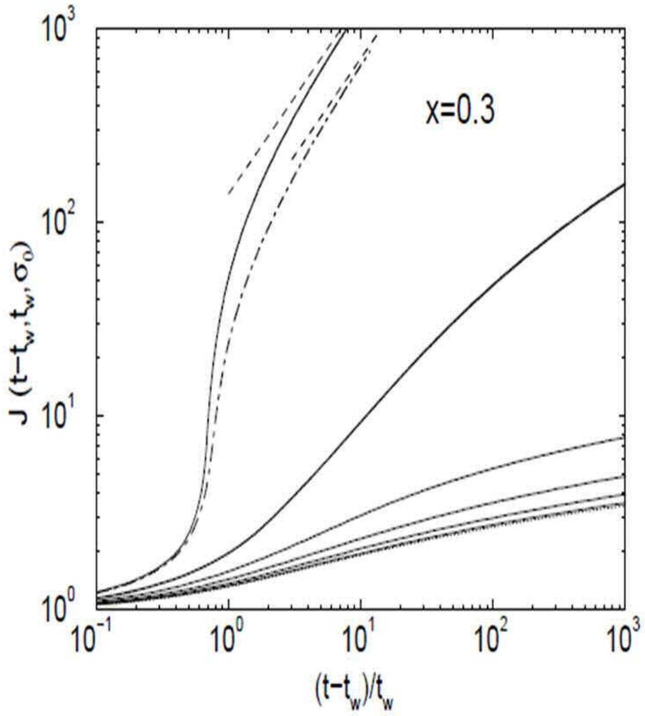




Fluidity model:
Bifurcation in τ(t) at yield stress

Aging + Flow Rejuvenation: Creep





Fluidity

SGR

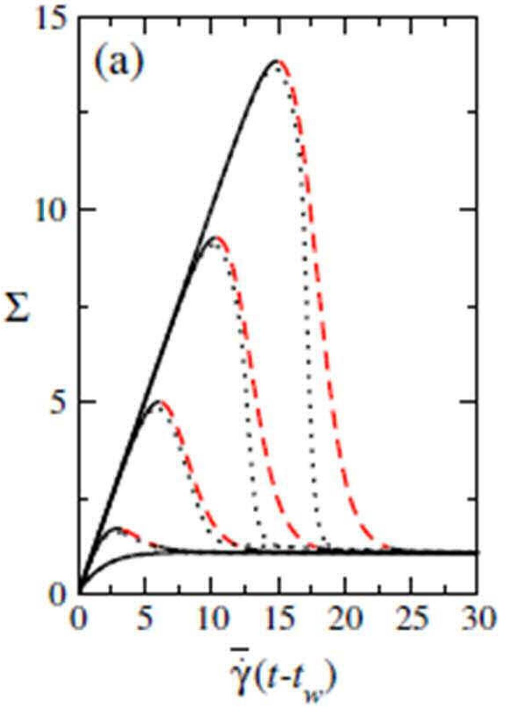
The Story So Far:

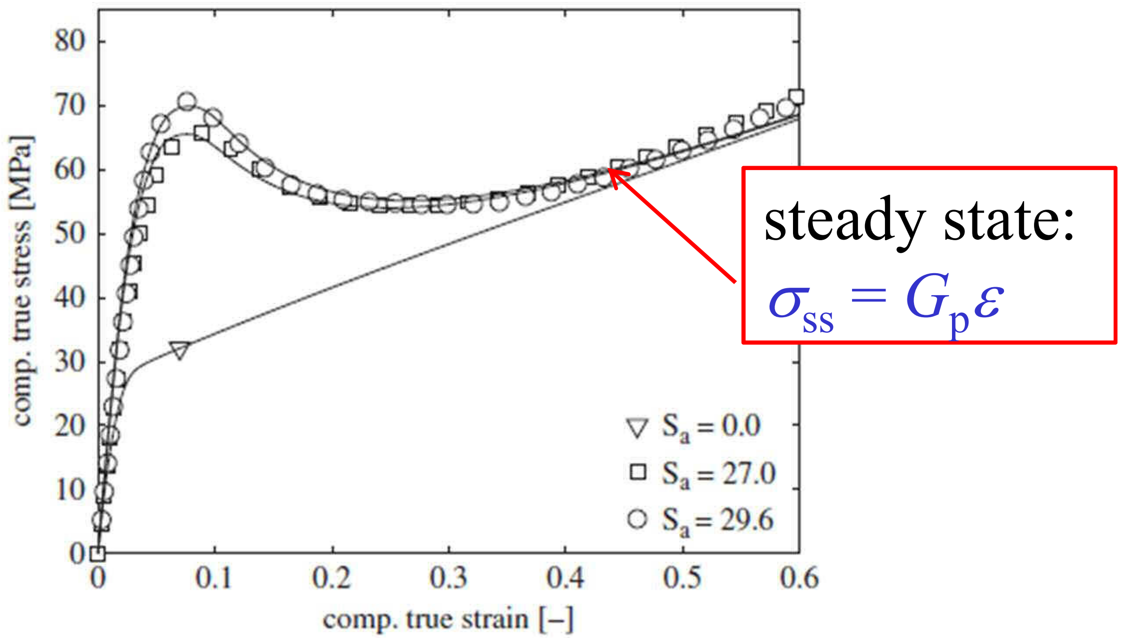
Fluidity model gives reasonable account of aging and flow in simple glasses

The Rest of the Talk:

What s different about polymer glasses? Is there a similarly minimal theory?

Polymer Glasses: Strain Hardening in Startup





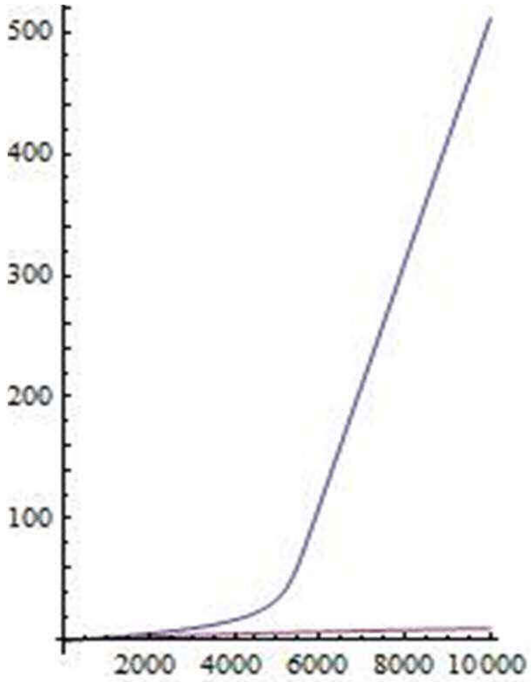
Simple glass

Polymer glass (compression)

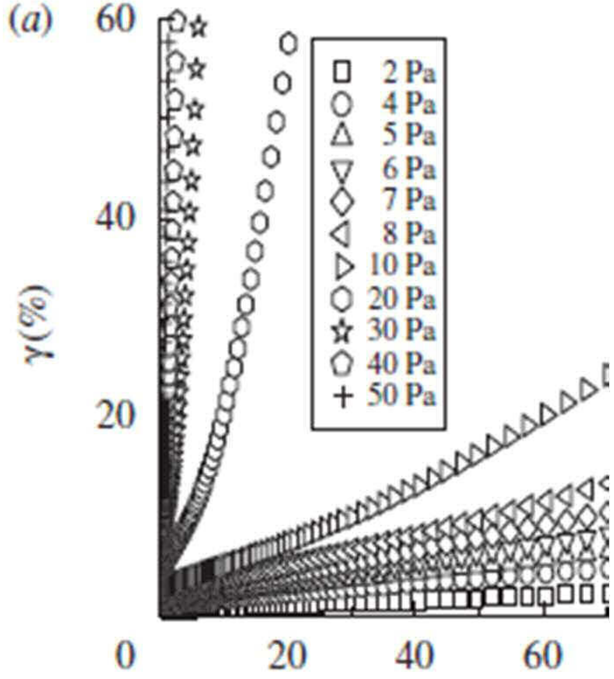
symbols: polycarbonate data

L. van Breemen et al, J. Mech. Phys. Solids 59 (2011) 2191

Polymer Glasses: Strain Hardening in Creep



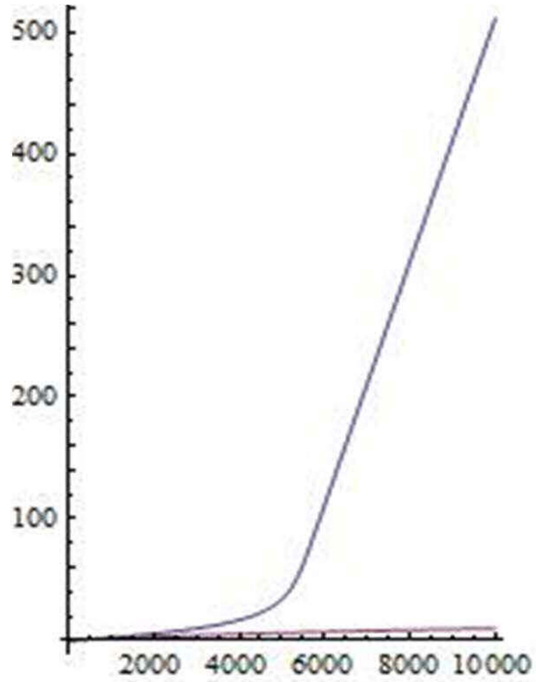
Simple glass
(fluidity model)



Simple glass

Soft spheres in shear:
C. Christopoulou et al, Phil. Trans. RS A 367 (2009) 5051

Polymer Glasses: Strain Hardening in Creep



Simple glass
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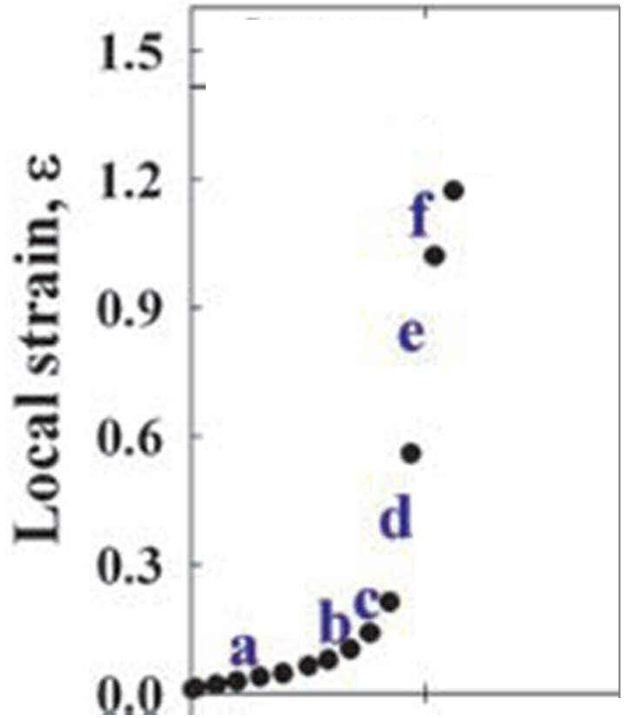
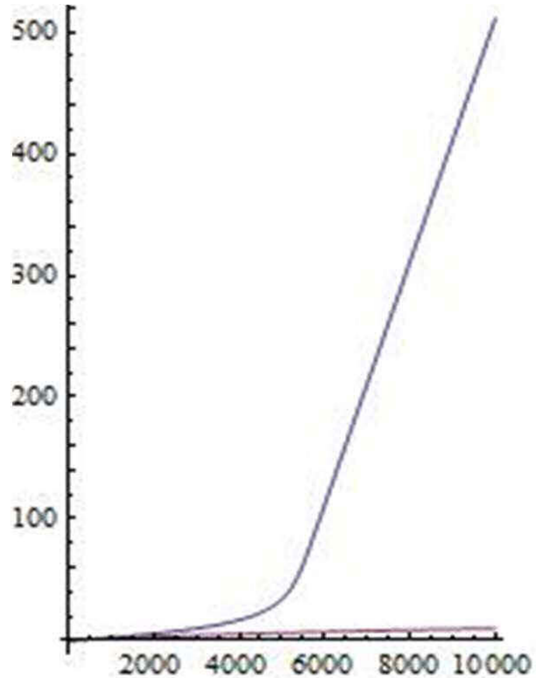


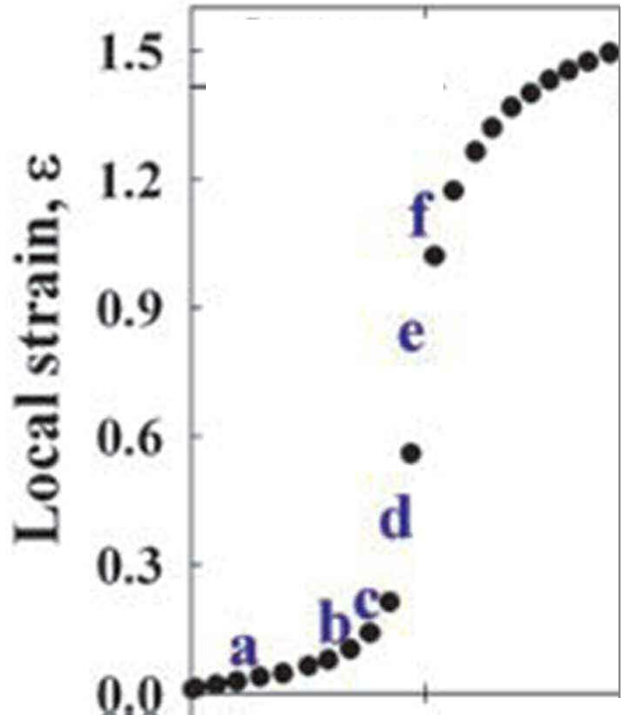
PMMA glass
(tensile load)

Key paper:
H-N. Lee, K. Paeng S. Swallen
and M. Ediger, Science 323 (2008) 232

Polymer Glasses: Strain Hardening in Creep



Simple glass
(fluidity model)



PMMA glass
(tensile load)

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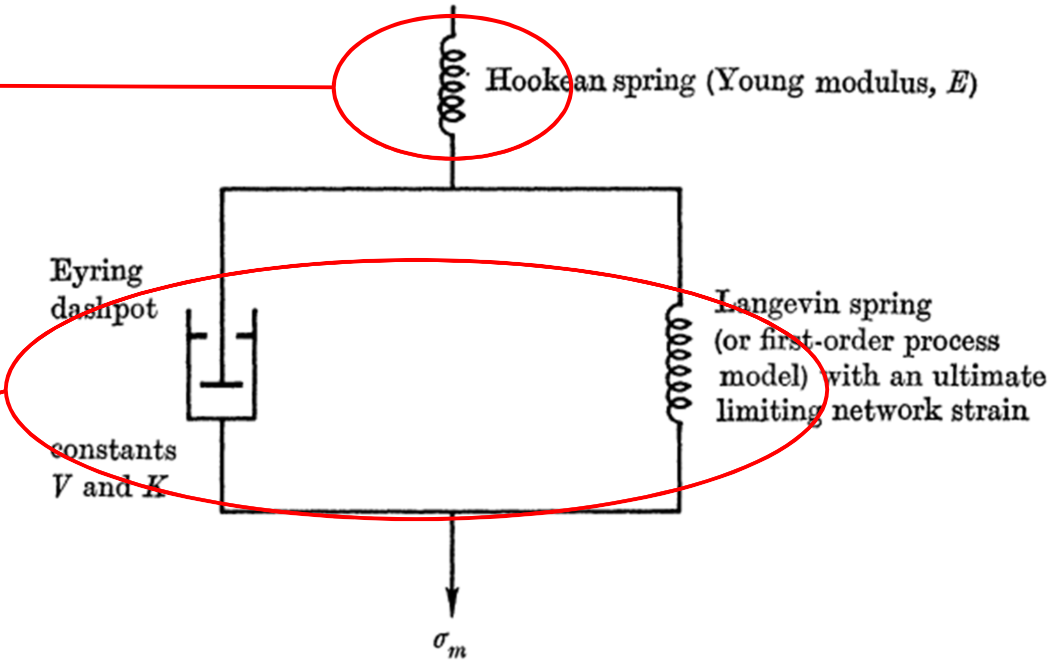
and M. Ediger, Science 323 (2008) 232

Polymer Glasses: Strain Hardening

Polymers restore elastic response at large strains

H-T model (1968):

polymer
in
(series with)
viscoelastic
solvent :
$\tau = \tau(\sigma)$



minimal...
but no aging

Haward and Thackaray Proc Roy Soc A 302 (1968) 453

Polymer Glasses: Strain Hardening

Starting from H-T model (1968):

omitting

25 years work by many people

ignoring

recent efforts at first principles theory e.g. polymers + MCT

(K. Chen, K. Schweitzer, Macromolecules 41 (2008) 5908; PRL 98 (2007) 167802, et seq.)

recent MD and other simulation-based models

(R. A. Riggleman et al, PRL 99 (2007) 215501; M. Warren and J. Rottler PRL 104 (2010) 205501; R. S. Hoy and M. O. Robbins, PRL 99 (2007) 117801; R. S. Hoy and C. S. O Hern, PRE 82 (2010) 041803; K. Nayak et al J. Pol. Sci B 49 (2011) 920)

Polymer Glasses: Strain Hardening

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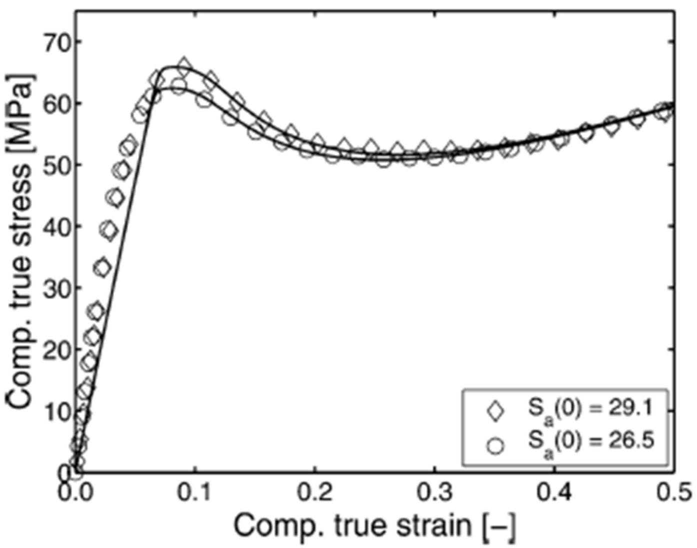
.... we arrive at:

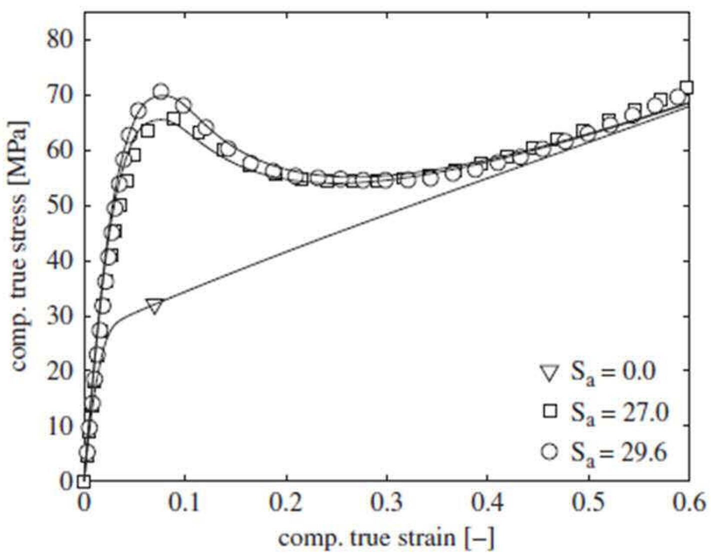
Eindhoven Glassy Polymer (EGP) model

Hookean polymer in "solvent" with

$$¿ = f_1(t;T)\,f_2(¾)\,f_3(\tilde{º})$$

Relaxation time rises with age, falls with stress and (plastic) strain





EGP 2005

EGP 2011 + 30 parameters

J. Klompen, T. Engels, L. Govaert, H. Meier, Macromolecules 38 (2005) 6997

L. van Breemen et al, J. Mech. Phys. Solids 59 (2011) 2191

Eindhoven Glassy Polymer (EGP) model

Hookean polymer in "solvent" with

$$\tau = f_1(t;T)\, f_2(\sigma)\, f_3(\gamma)$$

Relaxation time rises with age, falls with stress and (plastic) strain

$\tau \approx$ simple aging $\times$ function of strain, stress

This is not what SGR or fluidity models suggest

J. Klompen, T. Engels, L. Govaert, H. Meier, Macromolecules 38 (2005) 6997

L. van Breemen et al, J. Mech. Phys. Solids 59 (2011) 2191

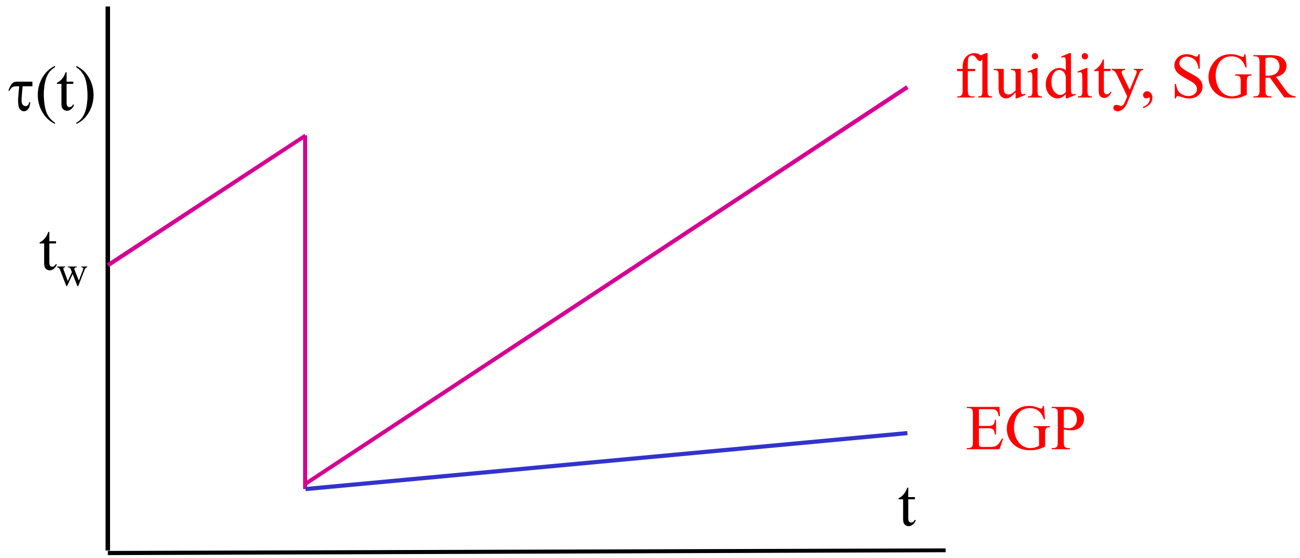
Eindhoven Glassy Polymer (EGP) model

Hookean polymer in "solvent" with

$$\tau = f_1(t;T)\, f_2(\sigma)\, f_3(\tilde{\gamma})$$

Relaxation time rises with age, falls with stress and (plastic) strain

e.g. step strain:



J. Klompen, T. Engels, L. Govaert, H. Meier, Macromolecules 38 (2005) 6997

L. van Breemen et al, J. Mech. Phys. Solids 59 (2011) 2191

Key Experiment

Direct measurement of segmental relaxation time $\tau(t)$

Lightly crosslinked PMMA at T just below T_g

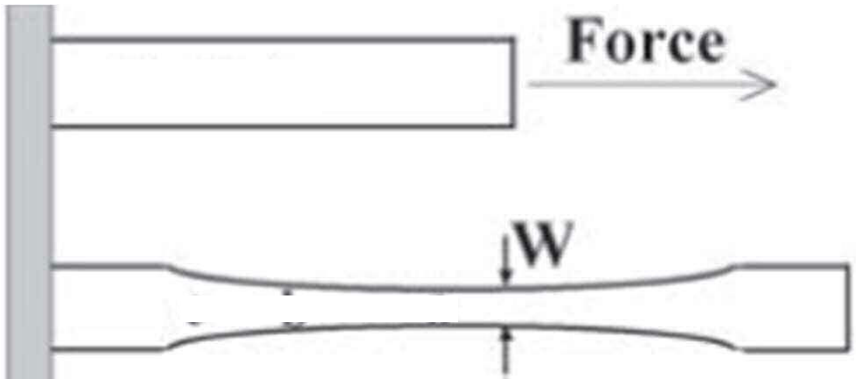
Tensile creep test

Reporter molecules probed via optical photobleaching

Direct Measurement of Molecular Mobility in Actively Deformed Polymer Glasses

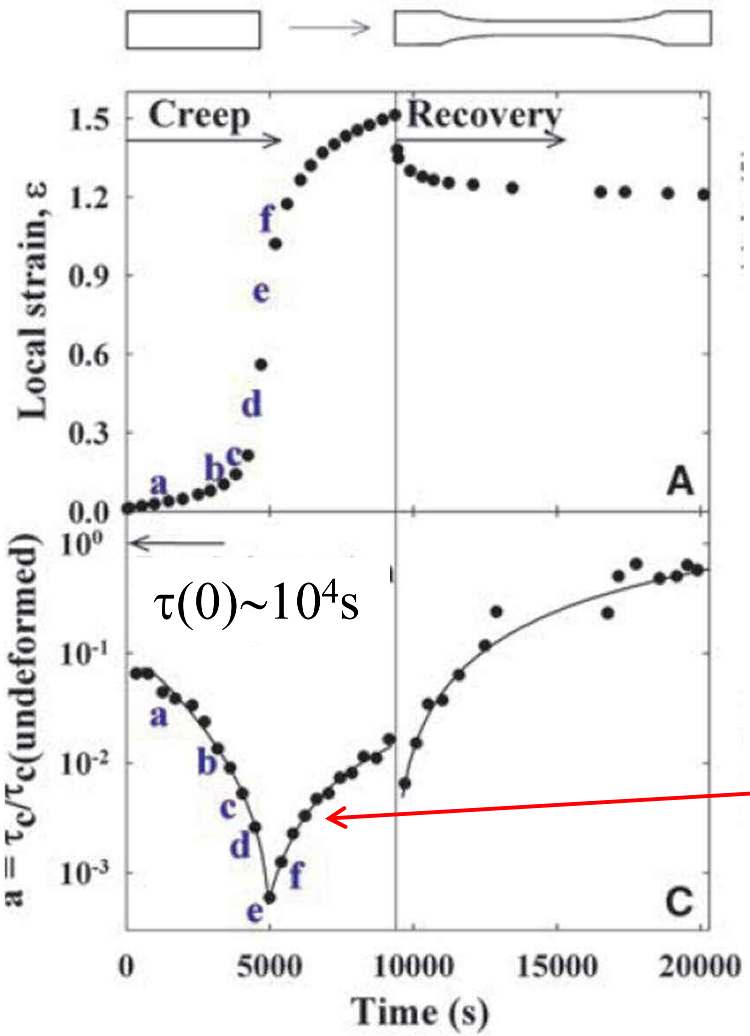
Hau-Nan Lee, Keewook Paeng, Stephen F. Swallen, M. D. Ediger

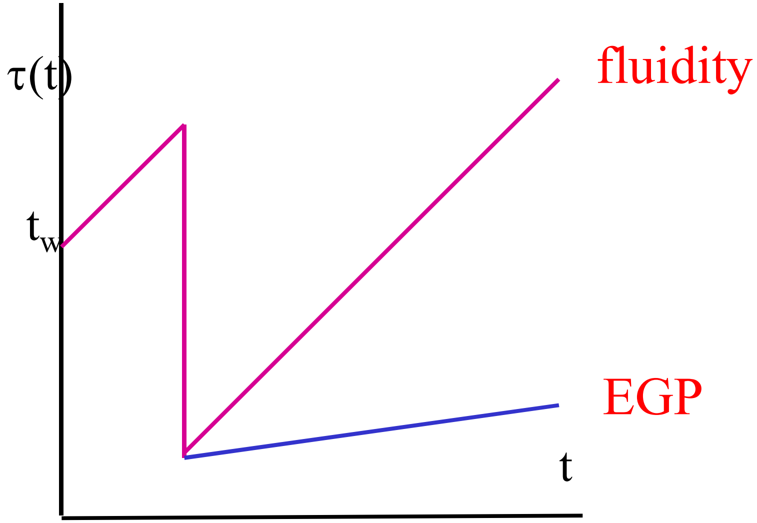
SCIENCE VOL 323 9 JANUARY 2009 231



Experiments (PMMA glass)

Lee, Paeng, Swallen, Ediger,
*Science **323**, 231 (2009)*





1000-fold drop,
then rapid recovery

Fluidity Model + Hookean Polymer

Elastic moduli $G_s; G_p$, conformation tensors $\sigma_s; \sigma_p$

Stress $\Sigma = G_s(\sigma_s - I) + G_p(\sigma_p - I)$

General flow velocity $v(r)$

$$\dot{\sigma}_s + v.\nabla\sigma_s = \sigma_s.\nabla v + (\nabla v)^T.\sigma_s - (\sigma_s - I)/\tau$$

$$\dot{\sigma}_p + v.\nabla\sigma_p = \sigma_p.\nabla v + (\nabla v)^T.\sigma_p - (\sigma_p - I)/N^{\alpha}\tau$$

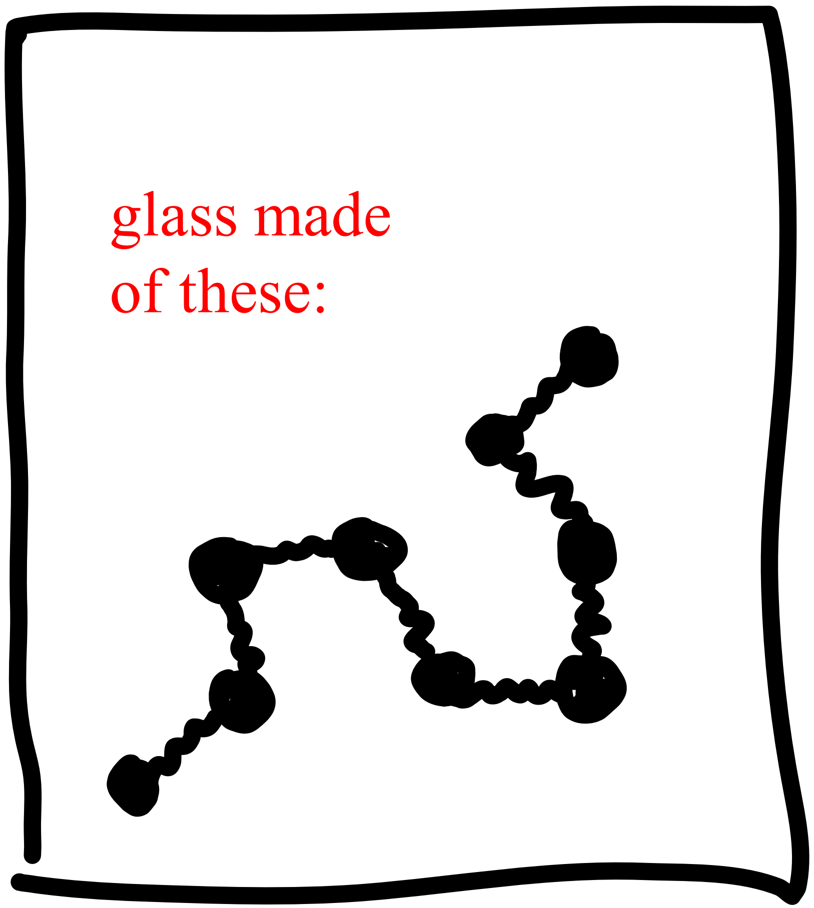
new bits

$$\dot{\tau} = 1 - (\tau - \tau_0)\lambda$$

$$\lambda = \gamma\sqrt{2\mathrm{Tr}(D.D)} \quad ; \quad 2D \equiv \nabla v + (\nabla v)^T$$

Fluidity Model + Hookean Polymer

Physical picture:



Fluidity Model + Hookean Polymer

Loading phase:

t_w = initial relaxation rate $\tau(0)$

G_p = strain-hardened "plateau" modulus

G_s from initial drop $\tau(0) \rightarrow \tau(0+)$ on loading

rejuvenation rate ν from strain rate vs $1/\tau$

τ_0 is fit to all remaining features (dip etc.)

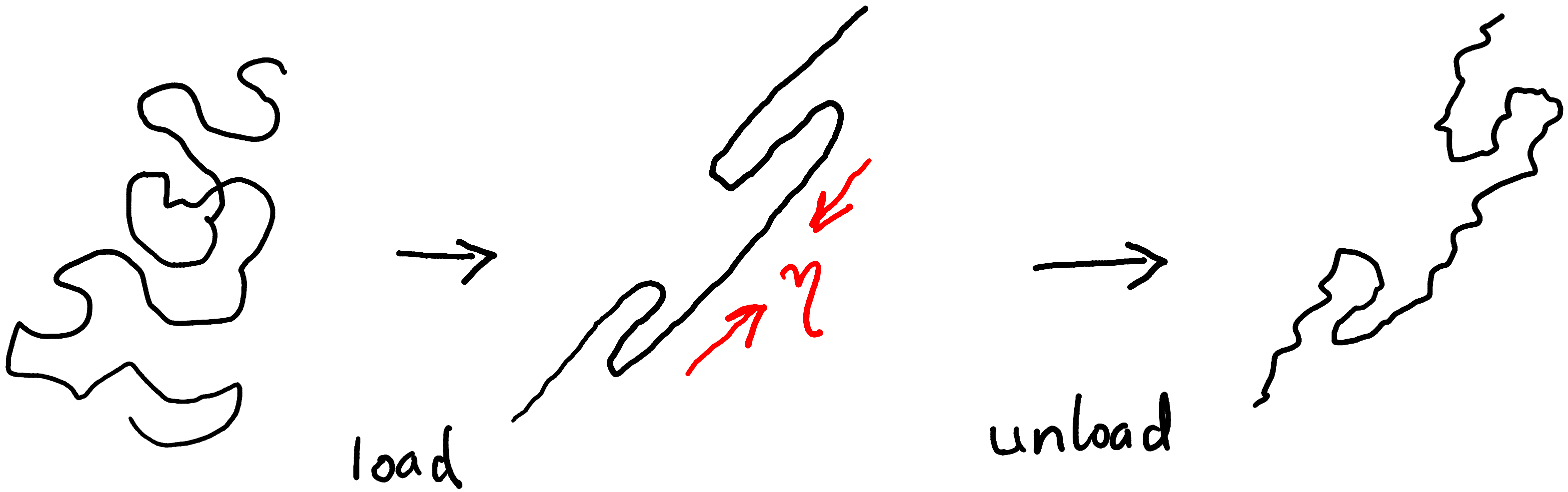
Unloading:

Allow for chain conformation hysteresis (CCH)

R. Larson, Rheol. Acta 29 (1990) 371

Chain Conformation Hysteresis

Polymer stress in strong elongation is mainly viscous



Viscous drag on fully stretched sections falls rapidly on unload

R. Larson, Rheol. Acta 29 (1990) 371

Simple Model for Unloading:

$G_p \rightarrow \theta\, G_p$ with "crinkle factor" $\theta = 0.1$ via CCH

Consistent with fitted $G_p \sim 10$ times rubbery modulus in melt

in other words:

Primary stress in polymer glass is not entropic-elastic

Schweitzer ops cit, Hoy and Robbins op cit + many others

Our elastic polymer dumb-bell proxies the CCH viscous stress

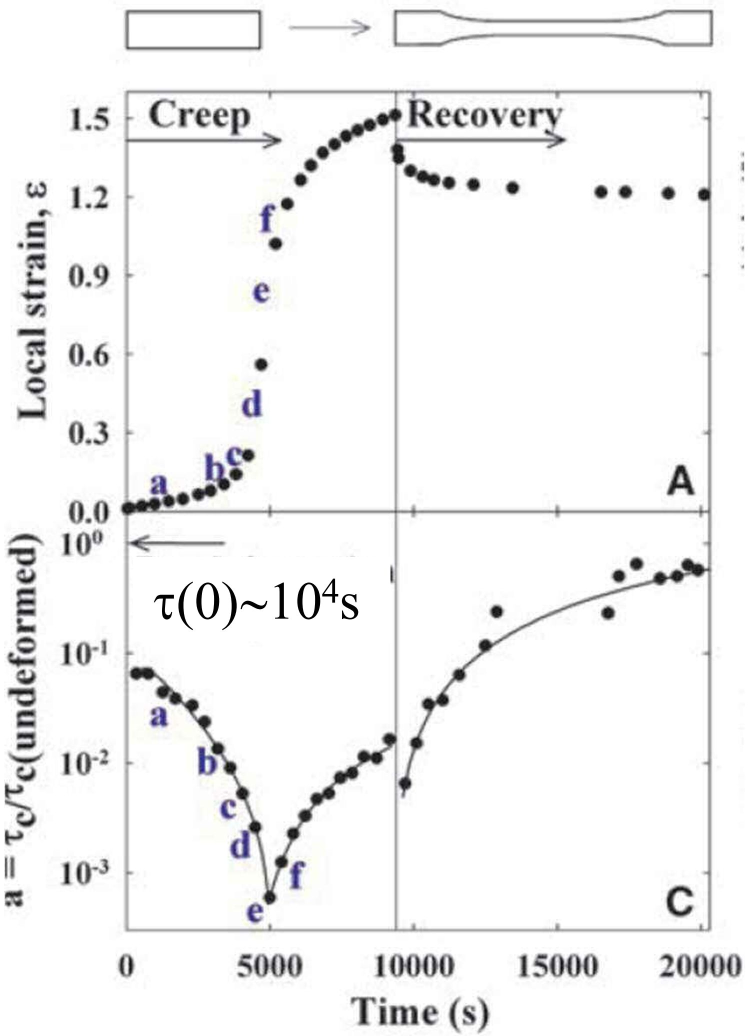
This becomes elastic "solvent" stress on freezing

in other words:

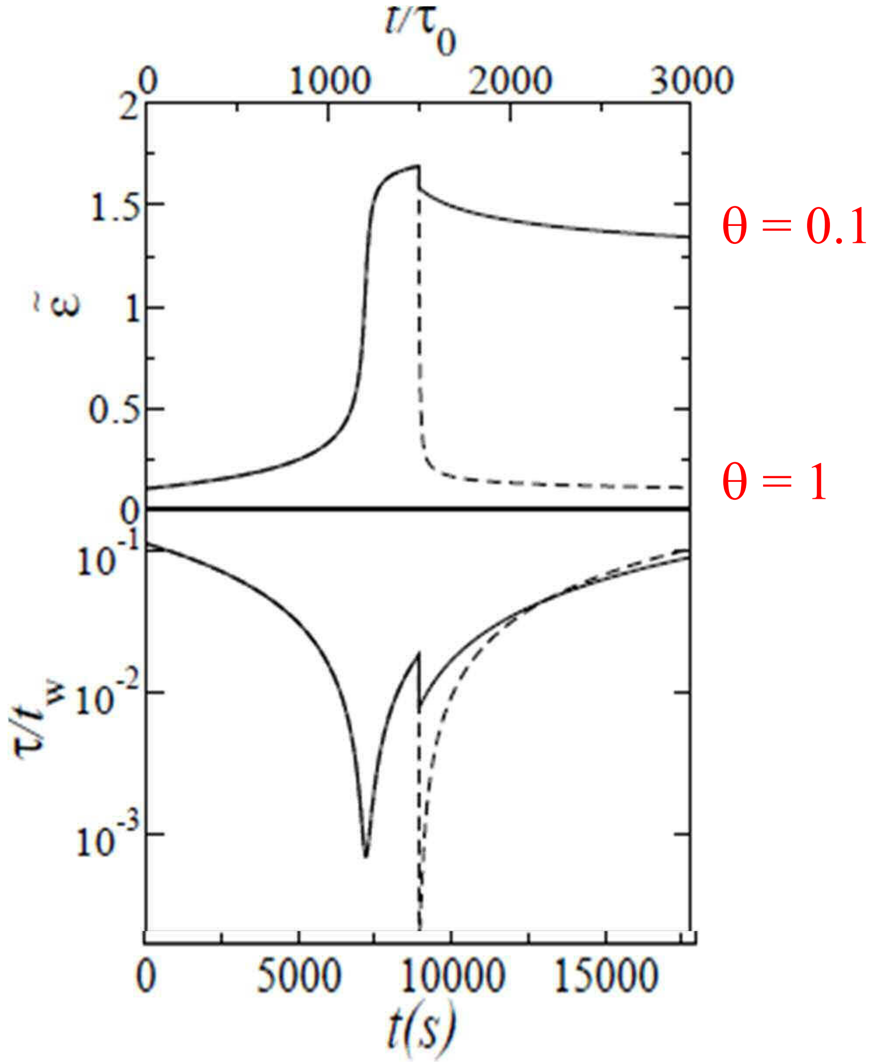
Static int<u>er</u>-chain monomeric interactions dominate

Experiments (PMMA glass)

Lee, Paeng, Swallen, Ediger,
*Science **323**, 231 (2009)*

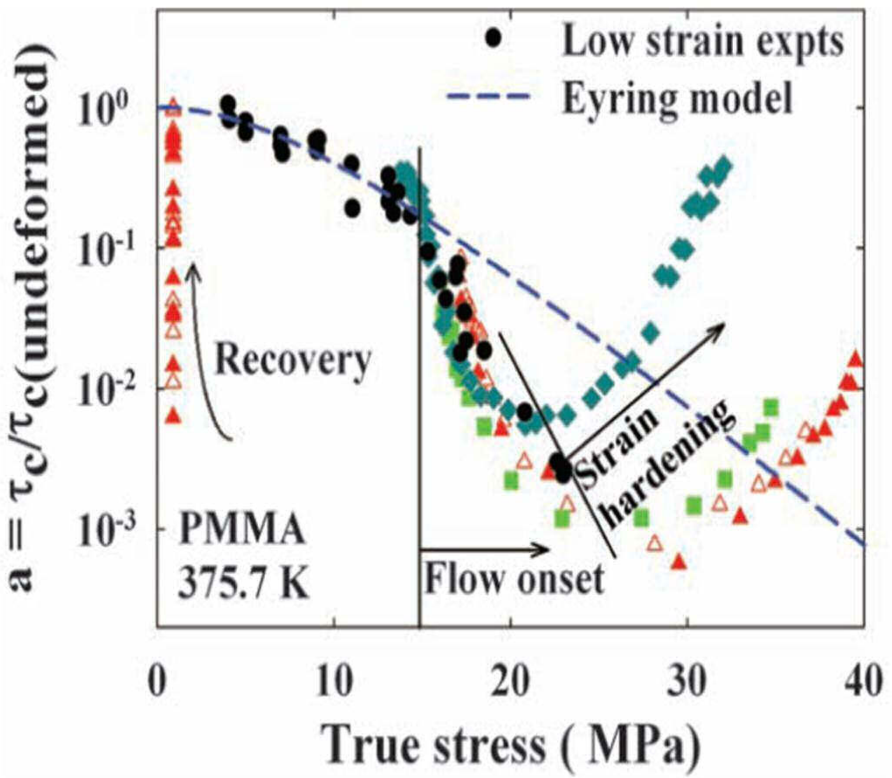


Our Model

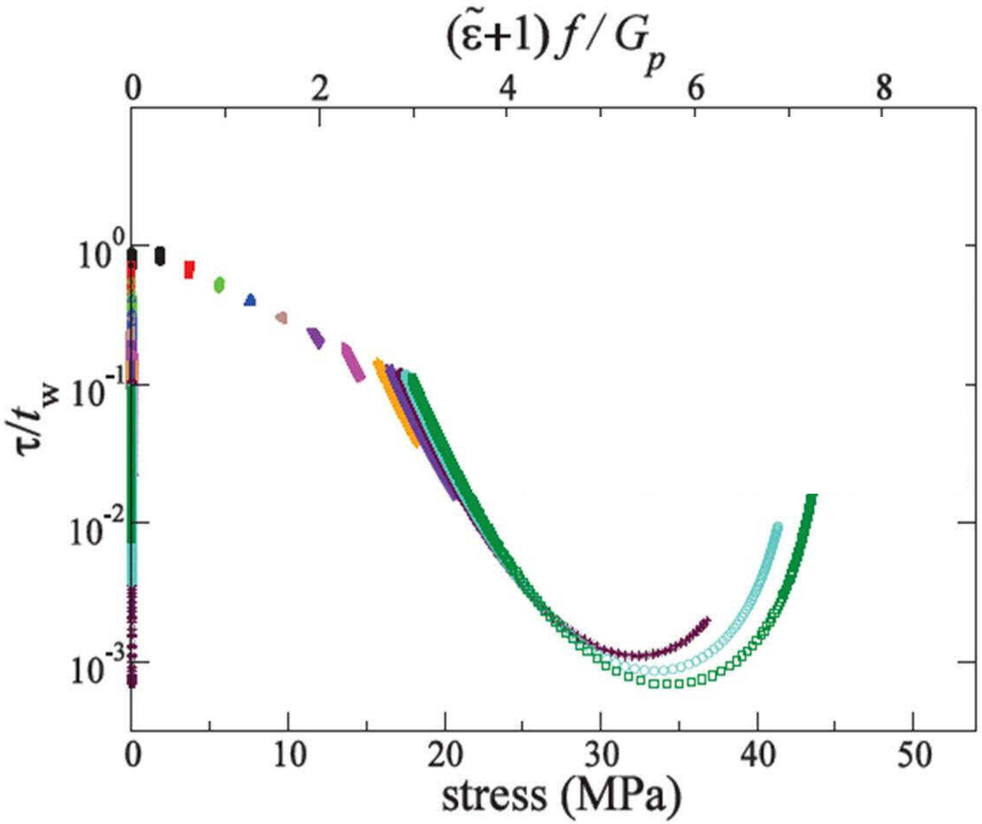


Experiments (PMMA glass)

*Lee, Paeng, Swallen, Ediger, Science **323**, 231 (2009)*

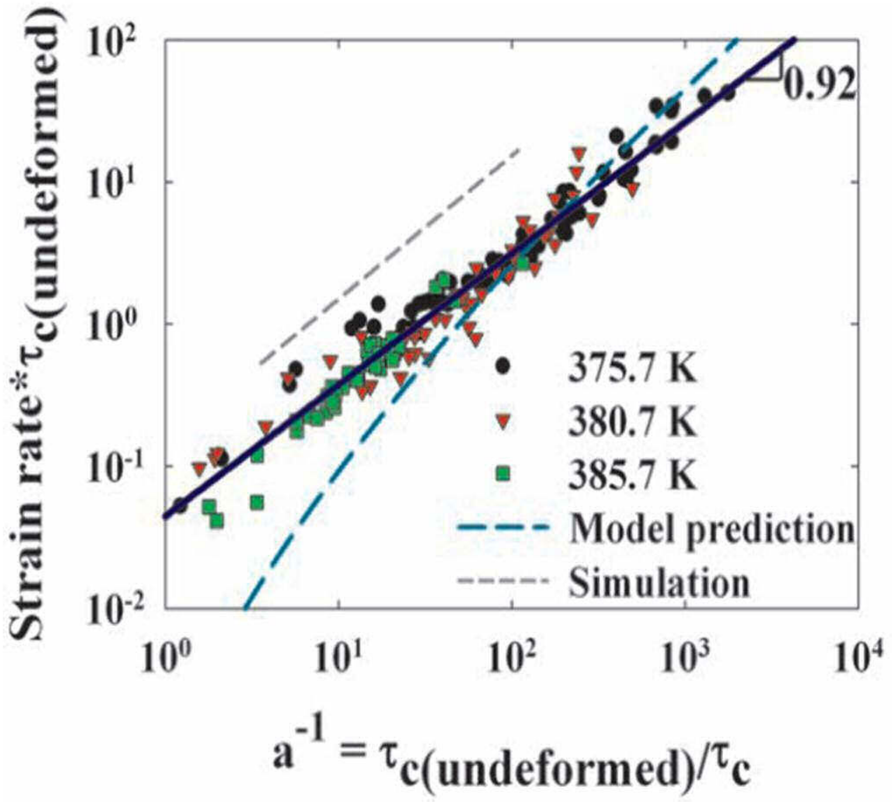


Our Model

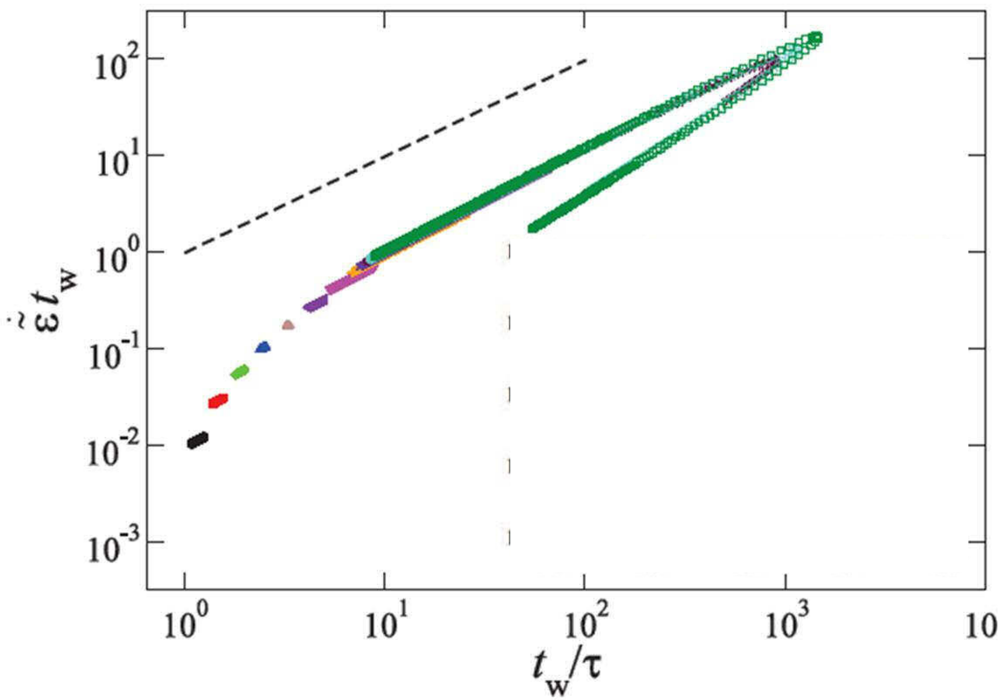


Experiments (PMMA glass)

Lee, Paeng, Swallen, Ediger, Science ***323****, 231 (2009)*



Our Model



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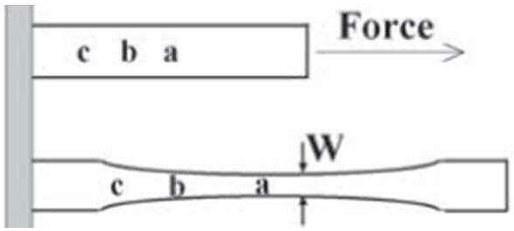
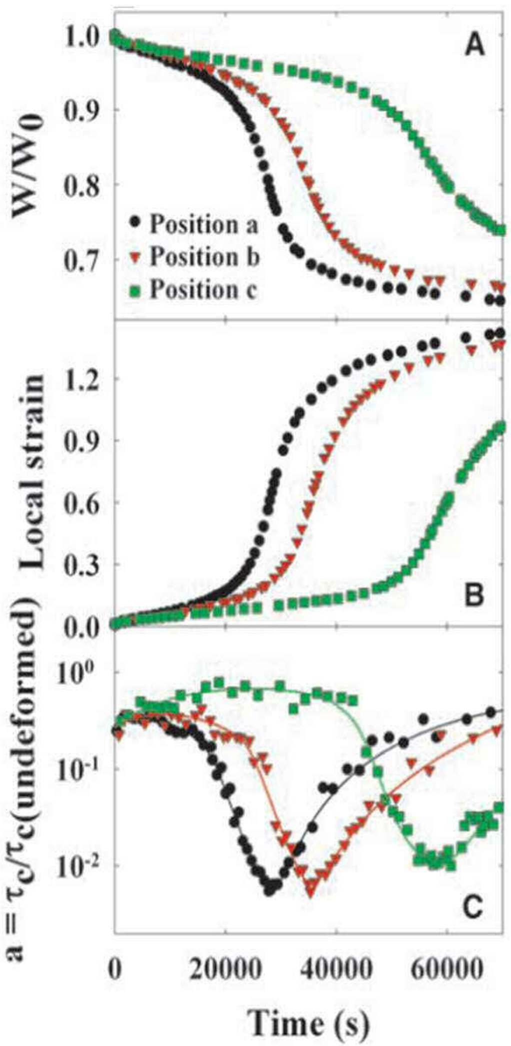
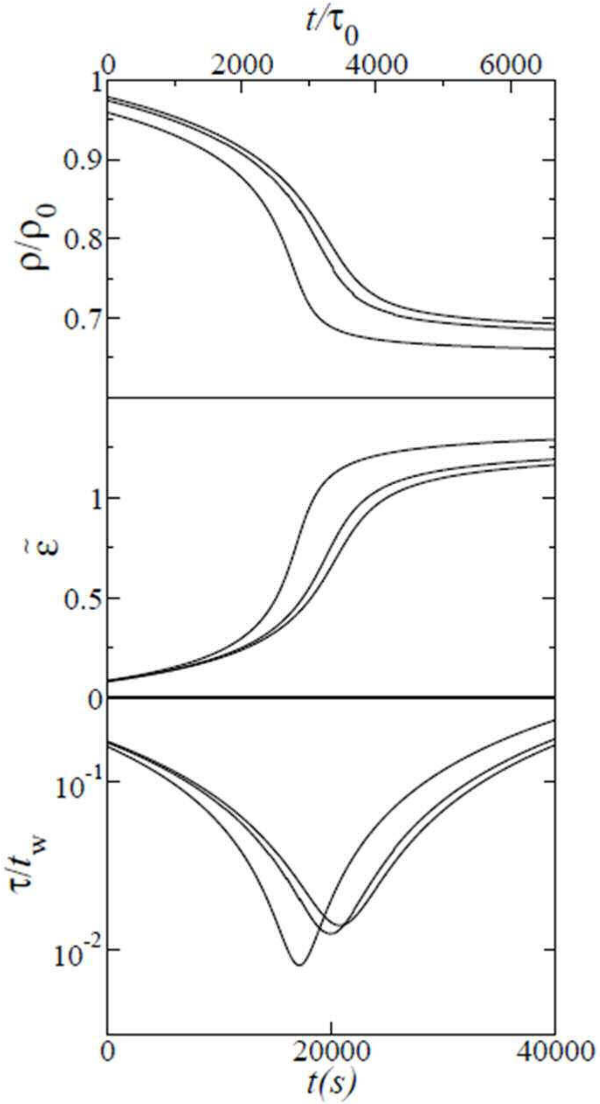
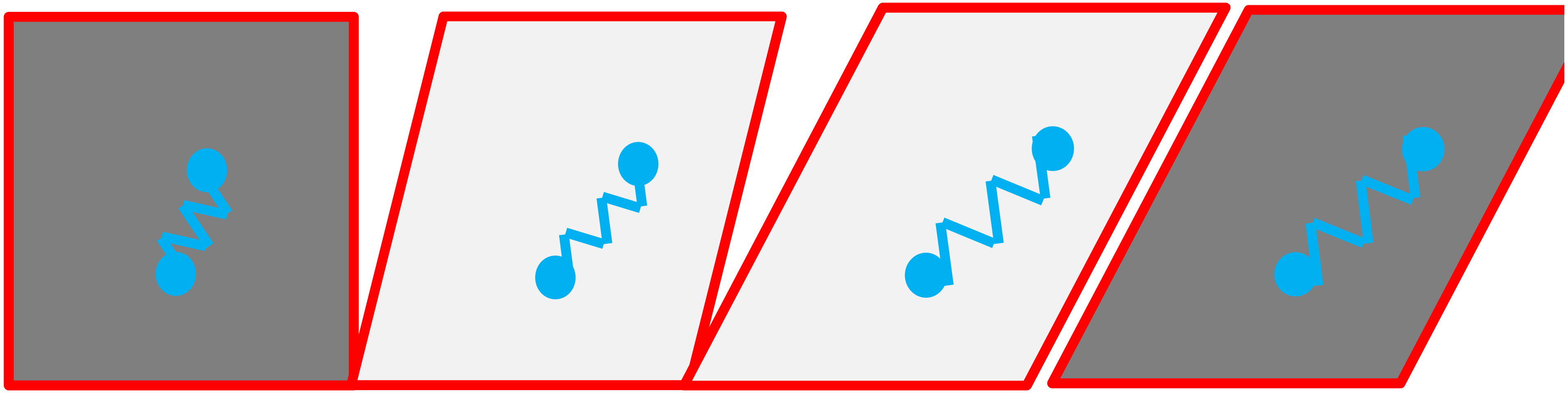






Fluidity Model + Hookean Polymer

Physical picture:



$\sigma = \sigma_s > \sigma_Y$: solvent melts

deformation: σ_p rises σ_s falls

$\sigma_s = \sigma - \sigma_p < \sigma_Y$: revitrification

Fluidity Model + Hookean Polymer

Physical picture:

On loading the sample, initial stress carried by solvent

Relaxation time drops due to fluidization

Polymers stretch and pick up increasing share of the stress

Deformation rate slows

Relaxation time rises rapidly again as solvent resolidifies

$\tau \neq f_1(t,T)f_2(\sigma)f_3(\gamma)$

$$\dot{\tau} = 1 - (\tau - \tau_0)\,\gamma\sqrt{2\mathrm{Tr}(D:D)}$$

More to do:

Multimode, careful treatment of CCH, other flows...

More polymer physics (entanglements etc.)

How Different are Polymer Glasses from Glassy Simple Liquids?

Fluidity model: A minimal theory of aging and rejuvenation

Polymer glasses:

New complications: strain hardening and $\tau(t)$

Direct measurement of $\tau(t)$ challenges current theories

Simple approach:

Fluidity model + Hookean polymers: explains $\tau(t)$ data

Creep: polymer coupled to aging solvent

Revitrification: aging is dominant physics

Unloading: CCH via θ as first approximation

How Different are Polymer Glasses from Glassy Simple Liquids?

Polymer glasses are more complicated

but

Simple models may (still) be the best starting point