

Aging and rheology in soft materials

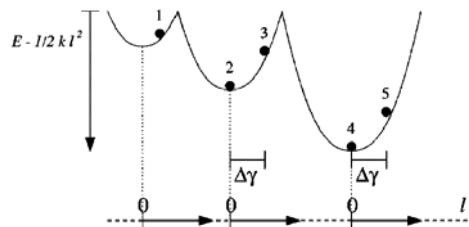
Fielding, Sollich, and Cates
J. Rheol. 2000

Presented by

Randy H. Ewoldt

Summer Reading Group Presentation

June 27, 2006



Context



• Prior work

- Struik, 1978 (book): Aging in polymer glasses
 - Introduced “effective” relaxation time $\tau(t_w)$ to collapse data
 - SGR model is more general
- Bouchaud, 1992 (272 cites)
 - Introduced hopping (trap) model for disordered (complex) systems (glassy systems)
 - 80% of SGR model is Bouchaud’s model (in my humble opinion)
- Sollich et al., 1997 (165 cites)
 - PRL article, introduced basics of SGR model
- Sollich, 1998 (136 cites)
 - Phys. Rev. E; describe SGR model in detail

Context



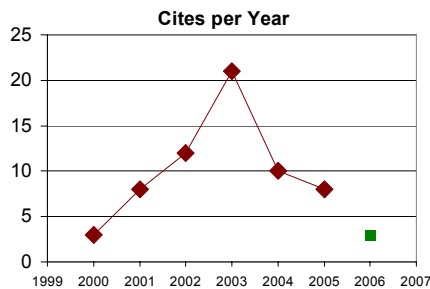
- **This work:** details of aging in SGR model

- **Later work**
 - ❑ Trap models applied to other areas: fragile glasses, granular materials, pinning of extended defects such as domain walls, etc. (Bertin & Bouchaud, Phys. Rev. E, 2003)
 - ❑ Cates & Sollich, JoR, 2004, "...generalizations of the SGR model that combine its nontrivial aging and yield properties with a tensorial structure..."
 - ❑ Some results confirmed by experiments (Abou, Bonn, and Meunier, JoR, 2003)

Citation History



65 total cites (Web of Science, June 26, 2006)



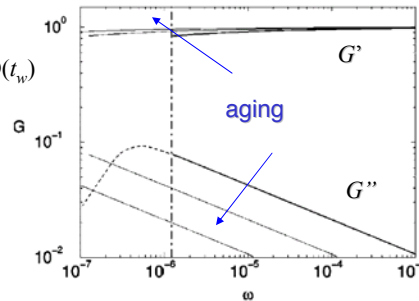
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RHEOLOGICA ACTA	2	3.1 %	■

(12 Source Title value(s) outside display options.)

Soft Glassy Materials (SGMs)



- SGM Definition
 - Material with structural disorder and metastability
 - e.g. wet foams, emulsions, pastes, and slurries
 - metastable: a state of pseudo-equilibrium having higher free energy than the true equilibrium state
- Typical behavior
 - Extremely long relaxation time
 - Aging
 - Relaxation time grows
 - Peak not accessible if $\tau \sim O(t_w)$



Aging



- Time translation invariance (TTI)
 - Same properties (or results) if test is performed at a different time
 - Violated by [aging](#) or [transients](#)
 - Article develops formal framework of rheology without TTI
- [Aging](#) definition
 - Sample ages if the long time response does not converge for $t_w \rightarrow \infty$
 - Formally: ages if at least one response function violates Eq. 18

$$\lim_{t \rightarrow \infty} G(t - t_w, t_w) = \lim_{\Delta t \rightarrow \infty} \lim_{t_w \rightarrow \infty} G(\Delta t, t_w)$$

- [Transients](#)
 - Any violation of TTI that is not aging
- Thixotropy - the word is never mentioned!
 - I believe article's definition of [aging](#) is a subset of Barnes' definition of thixotropy
 - Thixotropy may include the [transients](#) as they are defined here
 - e.g. viscosity overshoot

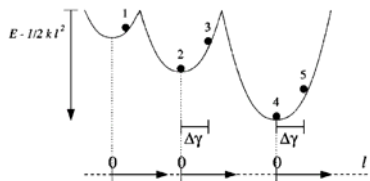
SGR Model



Assumptions

- Scalar model relating shear stress to shear strain
- Mesoscopic, heterogeneous elements
- Continuous variables of stress and strain apply
- Locally affine deformation

$$l = \gamma$$



Causality

- Stress response is linear elastic for each element
- Elements have a probability of “yielding” (function of strain l and effective temp x)
- Yielding resets element to *local* strain equilibrium ($l=0$), at new trap depth E
- New depth probability determined from previous distribution

Q: Under continuous macroscopic straining, what is shape of local stress with time?

A: sawtooth

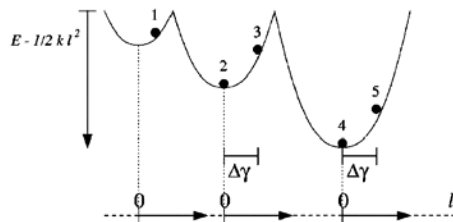
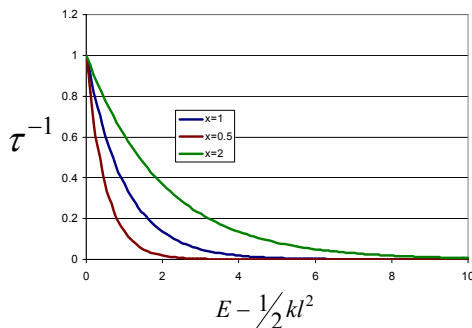
SGR Model



- From Bouchaud, with two modifications
 1. Thermal temp replaced with “effective temp” x
 2. Introduce strain into trap model
- Exponential distribution of relaxation times
 - Strain lowers energy barrier

$$\tau = \tau_0 \exp\left[\left(E - \frac{1}{2}kl^2\right)/x\right]$$

Rate of yielding probability



SGR Model – constitutive equations



stress ↔ strain $\sigma(t) = \gamma(t)G_0(Z(t,0)) + \int_0^t [\gamma(t) - \gamma(t')] Y(t') G_\rho(Z(t,t')) dt'$
~ strain rate

conservation of probability units? $1 = G_0(Z(t,0)) + \int_0^t Y(t') G_\rho(Z(t,t')) dt'$

Effective time interval
 (reduces to $t-t'$ in limit
 of small strains)

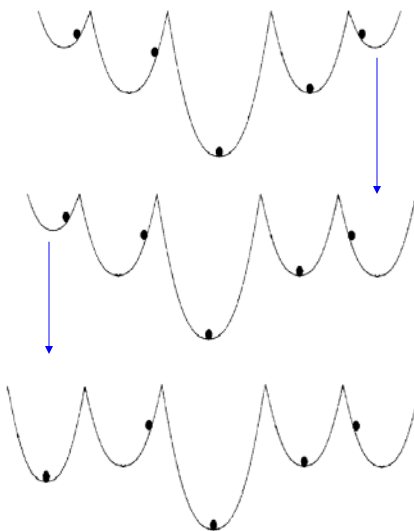
$$Z(t,t') = \int_{t'}^t \exp([\gamma(t'') - \gamma(t')]^2 / 2x) dt''$$

$$G_\rho(Z) = \int_0^\infty \rho(E) \exp(-Ze^{-E/x}) dE$$

distribution of trap depths Proportion which survive until t
 (which yielded at t')

$G_0(Z) =$ Same as above, but with initial distribution

Cause of Aging for $x < 1$



Q: Which trap(s) most likely to yield first?

A: Shallow traps

Q: How is new trap depth determined?

A: New depth assigned by probability distribution, based on previous distribution of depths

Q: What is most probable new depth?

A: Mean of previous depth distribution

	$x < 1$	$x = 1$	$1 < x$
$Y =$	$\frac{t^{x-1}}{x\Gamma(x)\Gamma(1-x)}$	$\frac{1}{\ln(t)}$	$\frac{x-1}{x}$

Linearity with SGR model



- Linearity requirement
 - ❑ Local strains remain small
 - ❑ Effects of strain on the effective time interval $Z(t, t')$ are small
- Consequences of linearity
 - ❑ Effective time interval $Z(t, t') \rightarrow t - t'$
 - ❑ Noise induced yielding

$$\frac{1}{2}kl^2 \ll E$$

- ❑ Internal dynamics independent of imposed deformation
- ❑ Lifetimes are independent of γ

$$\tau = \tau_0 \exp\left[\left(E - \frac{1}{2}kl^2\right)/x\right] \rightarrow \tau = \tau_0 \exp[E/x]$$

Step Strain

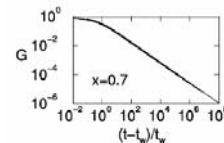
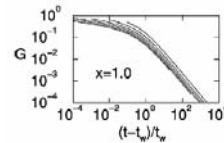
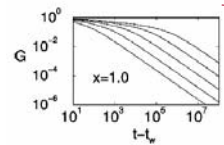
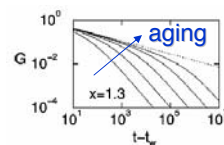
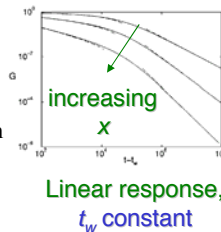


- In general, from Eq. 34

$$G(t - t_w, t_w) = 1 - \int_{t_w}^t Y(t') G_p(Z(t, t')) dt'$$

$Z \rightarrow t - t'$ in linear regime

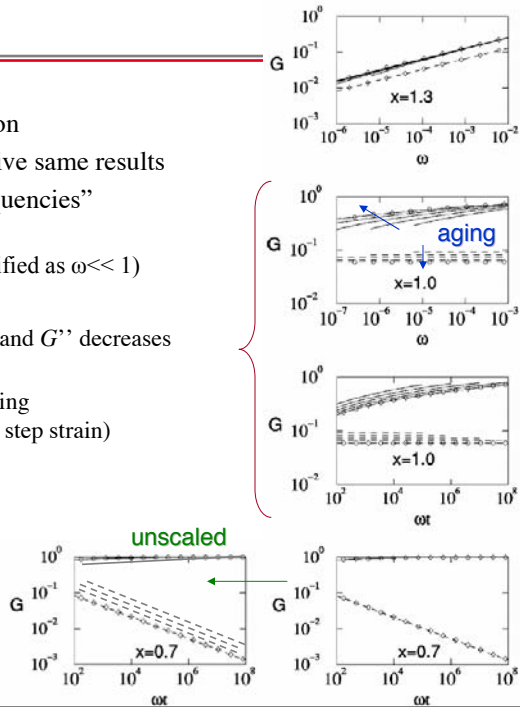
- Linear
 - ❑ Increased x hastens relaxation
 - ❑ Aging slows relaxation
 - ❑ For $x < 1$, data collapses with $t - t'/t_w$ scaling "major part of decay occurs on timescale of order t_w itself"
- Nonlinear G v. time
 - ❑ Same G_0
 - ❑ Faster relaxation (strain hastens yield events through Z)



Oscillatory Shear

- Only consider linear oscillation
- Controlled strain and stress give same results
- Applicable only for “low frequencies”
 - $\omega\tau_0 \ll 1$
(they set $\tau_0=1$, so often specified as $\omega \ll 1$)
- For $x < 1$
 - Ages such that G' increases and G'' decreases with time
 - data collapses with ωt_w scaling
(scaling in with t_w similar to step strain)

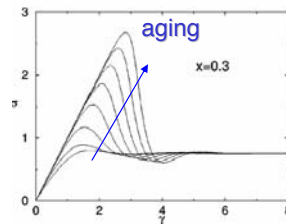
	$1 < x < 2$	$2 < x < 3$	$3 < x$
$G' \sim$	ω^{x-1}		ω^2
$G'' \sim$	ω^{x-1}	ω	



Step Strain Rate



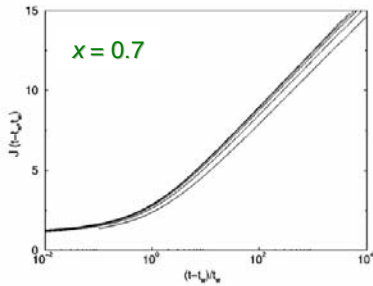
- All results applicable only at “low rates”
 - $\dot{\gamma}\tau_0 \ll 1$
(they set $\tau_0=1$, so often specified as $\dot{\gamma} \ll 1$)
- Linear – uninteresting (limited to small strains)
 - An explicit dependence on t_w resides only in subdominant corrections
 - “Thus, linear shear startup is not a good experimental test of aging or slow transient effects”
 - Purely elastic, anomalous power law, Newtonian (with increasing x)
- Nonlinear
 - Forced rate immobilizes aging
 - even deepest traps eventually yield
 - yield times obey power-law distribution (rather than exponential in E)
 - Overshoot stress *why?*
 - $\Delta\sigma \sim \ln(t_w)$
 - is undershoot physical?



	$x < 1$	$1 < x < 2$	$2 < x$
$\sigma_{ss} \sim$		$\dot{\gamma}^{x-1}$	$\dot{\gamma}$
$\sigma_{ss} - \sigma_y \sim$	$\dot{\gamma}^{1-x}$	aging interrupted by flow	

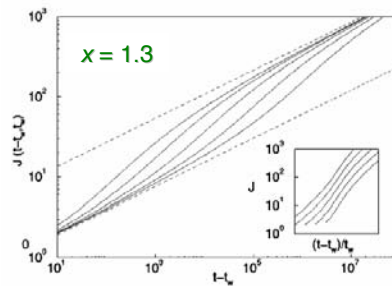
Step Stress - linear

- For $x < 1$
 - Aging (weak)
 - $\sim \ln((t-t_w)/t_w)$
 - $\sim \ln(t-t_w) - \ln(t_w)$
 - Strain must increase with time, but at a rate that could tend to zero at long times \rightarrow yield



weak correction
for $t \gg t_w$

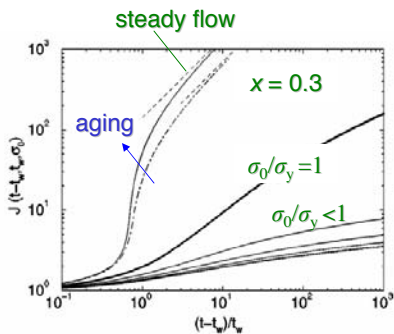
- For $x > 1$
 - No "aging"
 - Long time response not affected by t_w
 - Transient affected by t_w
 - So I would say the transient experiences aging



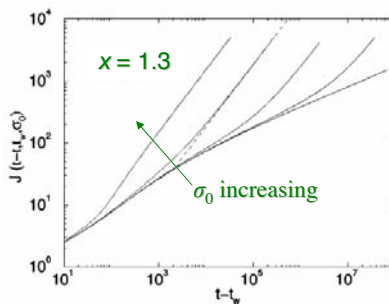
transient affected by t_w

Step Stress - nonlinear

- For $x < 1$
 - Yield stress:
 - Below yield stress the strain rate tends to zero at long times
 - Aging decreases transient?
 - I find this very weird
 - Viscosity v. time would be interesting



- For $x > 1$
 - Would be interesting to see viscosity v. time
 - Then we could see more general "thixotropy"?



Discussion



- Does it actually match experimental data?
- Applicability
 - ❑ Predicting behavior for engineering applications?
 - ❑ Better understanding of the physics?
 - Hans Wyss (Harvard) may be interested in nonlinear oscillatory response, to see if it's consistent with his model for SGMs (though this paper didn't discuss it)
 - ❑ If you cite it people may think you're smart
- **SGM** may refer to: (from Wikipedia)
 - ❑ Standard Gross Margin used for classification of agricultural businesses
 - ❑ SG-43 Gorunov machine gun, modified
 - ❑ Second Generation Multiplex DNA profiling system - also see SGM+
 - ❑ Sleepytime Gorilla Museum, an avant-prog band based in Oakland, CA
 - ❑ **Soft Glassy Material**, a material with structural disorder and metastability (e.g. wet foam, emulsion, paste, or slurry)
 - ❑ Sergeant-Major, a military rank

