Transport Processes in Melts under External Fields

HELMHOLTZ GEMEINSCHAFT

Deutsches Zentrum für Luft- und Raumfahrt e.V. in der Helmholtz-Gemeinschaft

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On the Yielding of Colloidal (and Other) Glass Formers

Thomas Voigtmann

Institute of Materials Physics in Space, German Aerospace Center, Cologne
& Zukunftskolleg, Universität Konstanz, Germany

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- S. Egelhaaf (D'dorf), M. Ballauff, M. Siebenbürger (HZ Berlin)

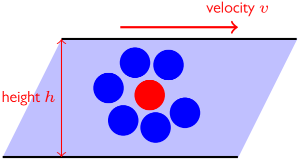
Outline

- Dynamical Yield Stress
- Startup: Creep and Micro-Rheology
- Residual Stresses

Introduction

Rheology of Dense Fluids

shear flow of dense fluids:



- external flow rate $\dot\gamma \sim v/h$ $[1/\mathrm{s}]$
- large structural relaxation time τ $[\mathrm{s}]$

$\Rightarrow$ large effect when $\dot\gamma\tau \gg 1$

- (glassy) kinetic arrest: $\tau \to \infty$

- apply perturbation (shear $\dot\gamma$) $\Rightarrow$ measure response (stress σ)

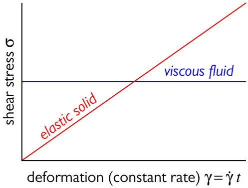
$$\mathcal{F}\,[\,\dot\gamma\,] = \sigma$$

constitutive equation

- $\mathcal{F}$ is a *model* of the material
- *linear response, steady state*: Newtonian liquid $\sigma = \dot\gamma \times \eta$

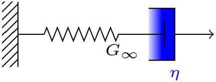
Visco-Elasticity: Maxwell's Model

- Newtonian fluid: $\eta =$ const. $\Rightarrow \sigma \propto \dot{\gamma}$
- Hookian elastic solid: $\sigma \propto \gamma$
- dense fluids: ??
- Maxwell: combine $\sigma \sim \gamma$ and $\sigma \sim \dot{\gamma}$



$$\dot{\gamma} = \dot{\sigma}/G_\infty + \sigma/\eta$$

- "spring-and-dashpot" model:
  Hookian spring constant G_∞



- differential equation solved by

$$\underset{\text{output}}{\sigma(t)} = \int_{-\infty}^{t} \underset{\text{input}}{\dot{\gamma}(t')}\, G_\infty \underset{\text{model}}{e^{-(t-t')/\tau}}\, dt' \qquad \eta = G_\infty \tau$$

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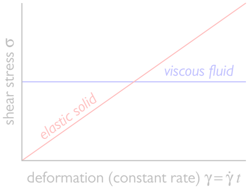

$$\dot\gamma = \dot\sigma / G_\infty + \sigma/\eta$$

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- Maxwell's constitutive equation

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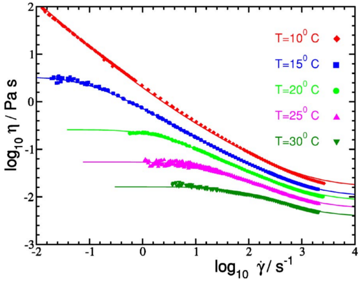
Nonlinear Rheology: Shear Thinning

apply (steady) shear $\Rightarrow$ dramatic decrease in apparent viscosity



thermosensitive colloids

[Fuchs and Ballauff, J Chem Phys (2005)]

- non-linear response
  - linear response: $\eta \sim$ const.
  - $\eta \to \infty$: glass
- $\eta \sim 1/\dot{\gamma}$
- applications: painting, coating, lubrication, …
- "universal": metallic melts, geophysics, soft matter, …

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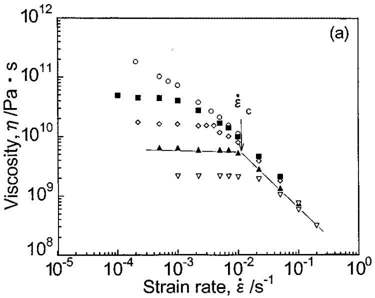

$Pd_{40}Ni_{10}Cu_{30}P_{20}$, various temperatures

[Kato *et al.*, JAP (1998)]

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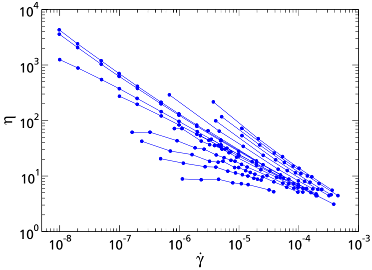


granular simulation

[Olsson/Teitel, PRL (2007)]

- non-linear response
  - linear response: $\eta \sim$ const.
  - $\eta \to \infty$: glass
- $\eta \sim 1/\dot{\gamma}$
- applications: painting, coating, lubrication, …
- "universal": metallic melts, geophysics, soft matter, … (?!?)

Rheo-Mode-Coupling Theory, Schematically

nonlinear schematic model – strain history $\gamma_{tt'} = \int_{t'}^{t} \dot\gamma(\tau)\,d\tau$

$$\sigma(t) \sim \int_{-\infty}^{t} dt'\,\dot\gamma(t')G(t,t',[\dot\gamma]) \overset{\text{MCT}}{\approx} \int_{-\infty}^{t} dt'\,v_\sigma\,\dot\gamma(t')\,\phi^2(t,t',[\gamma])$$

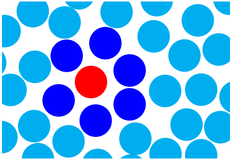
output

model input

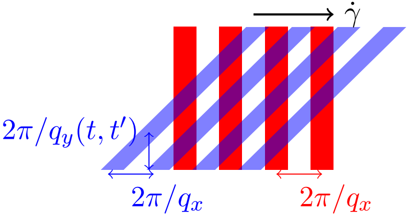
$$\partial_t\phi(t,t') + \phi(t,t') + \int_{t'}^{t} m(t,t'',t')\partial_{t''}\phi(t'',t')\,dt' = 0$$

$$m(t,t'',t') = h[\gamma_{tt'}]h[\gamma_{tt''}]\left(v_1\phi(t,t'') + v_2\phi(t,t'')^2\right)$$

cage effect

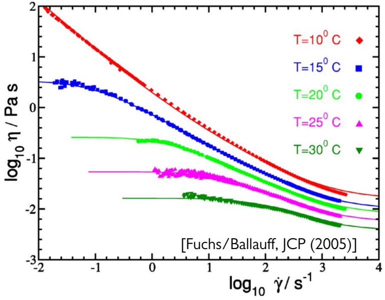


wave-vector advection

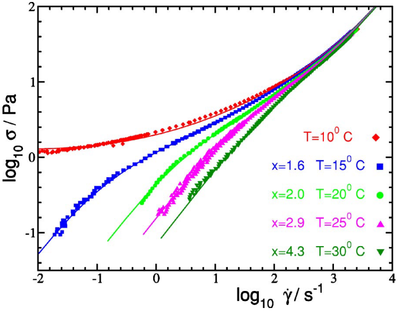


[Fuchs/Cates, PRL (2002); Brader *et al.*, PRL (2007); PRL (2008)]
[Brader, ThV, Fuchs, Larson, Cates, PNAS (2009)]

Dynamical Yield Stress



thermosens. colloids: $\eta(\varrho, \dot\gamma)$



flow curves in steady state

- $\sigma(\dot\gamma \to 0) = \sigma_y > 0$ in the (idealized) glass: dynamic yield stress
- $\dot\gamma \to 0$ is singular; $\sigma = \dot\gamma \int_{-\infty}^{t} G(t-t', \dot\gamma)\, dt'$

A Nonlinear Maxwell Model

- *shear accelerates dynamics:* relaxation time $\sim 1/\dot{\gamma}$

$$\tau^{-1} \mapsto \tau^{-1} + \dot{\gamma}$$

- nonlinear Maxwell model

$$G_\infty \dot{\gamma} = \dot{\sigma} + \sigma/\tau + \sigma\dot{\gamma}/\gamma_c$$

(plus a high-shear Newtonian viscosity…)

$$\sigma = G_\infty \tau_0 \dot{\gamma} + G_\infty \tau \frac{\dot{\gamma}}{1 + \dot{\gamma}\tau/\gamma_c}$$

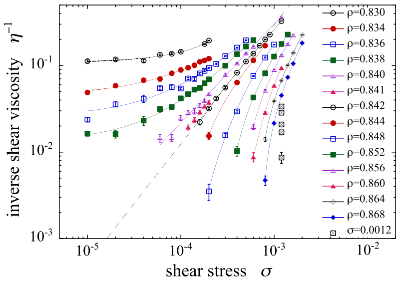
$\Rightarrow$ as $\tau \to \infty$: *critical dynamical yield stress*

$$\sigma_y = G_\infty \gamma_c > 0$$

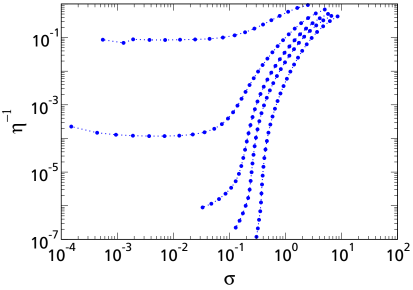
[Fuchs/Cates, Faraday Discuss. (2003)]
[ThV, EPJE (2011)]

Flow Curves

granular material



colloidal suspension

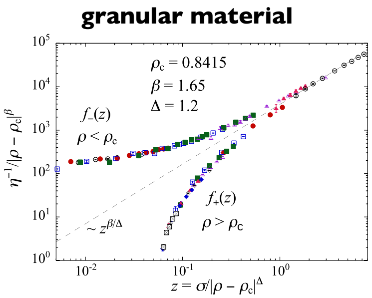


[Olsson/Teitel, PRL (2007)]

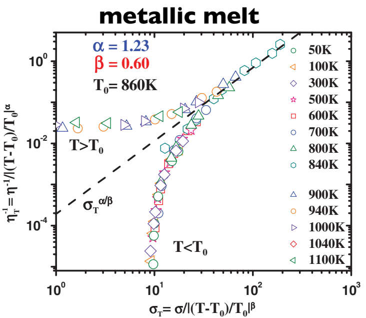
[data: M. Siebenbürger]

- scenarios for dynamical yielding: colloidal *vs.* granular
- remember: different protocols, $k_B T$ finite *vs.* zero

Flow Curves: Scaling Proposal



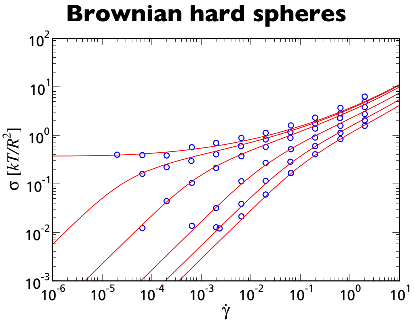
[Olsson/Teitel, PRL (2007)]



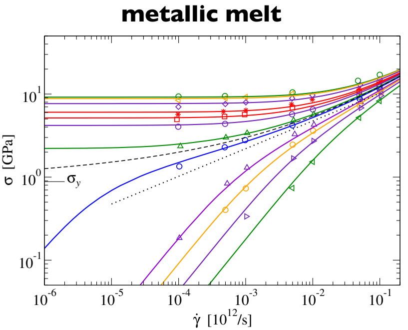
[Guan/Chen/Egami, PRL (2010)]

- (granular) point J as a critical point
- scaling: suggests $\sigma(T \to T_c) \sim \dot{\gamma}^x \Rightarrow$ hence: $\sigma_y^c = 0$

Flow Curves: Finite Yield Stress



[data: Henrich *et al.*, Phil Trans Roy Soc (2009)]

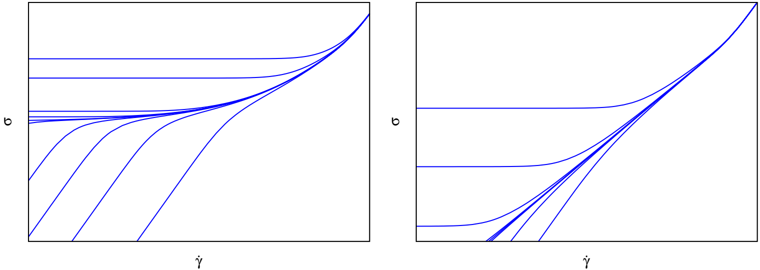


[Guan/Chen/Egami, PRL (2010)]

- fits using schematic model of mode-coupling theory (MCT)
- prediction $\sigma_y^c = \mathcal{O}(0.1\,k_BT/R^3)$ – *apparent* power laws

[ThV, EPJE **34**, 106 (2011)]

Different Scenarios for Flow Curves



- “discontinuous” *vs.* “continuous” yield-stress scenario
- different yielding mechanisms: local cages *vs.* avalanches
- energy densities $k_B T/R^3$ *vs.* overlap energies

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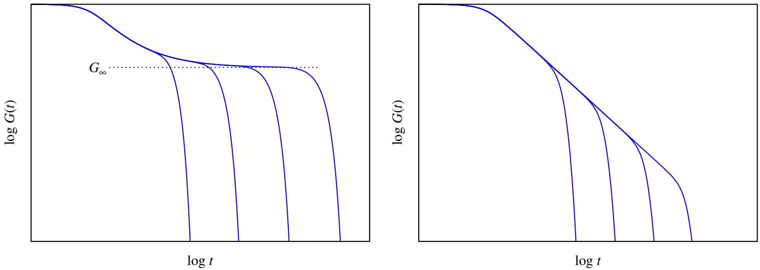

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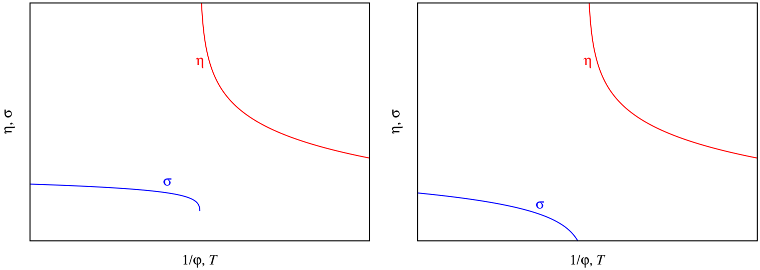

- "discontinuous" *vs.* "continuous" yield-stress scenario
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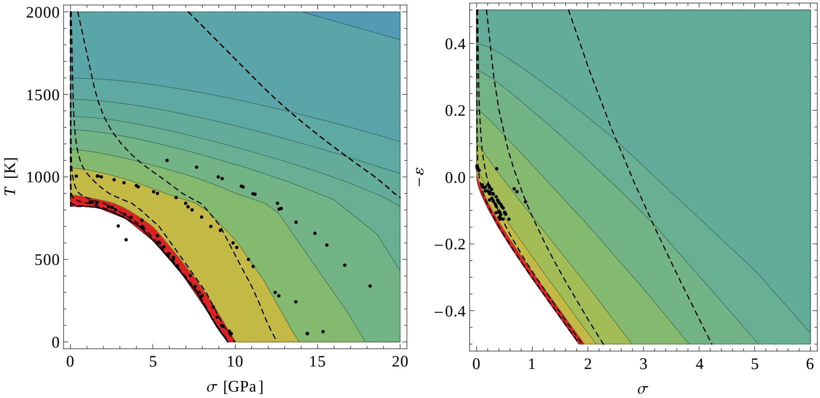
Jamming Diagram

iso-viscosity lines in the (T, σ) and $(1/\varrho, \sigma)$ plane:



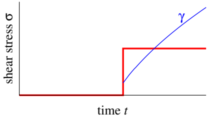
(white: "jammed")

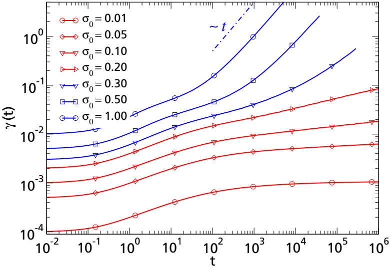
[ThV, EPJE **34**, 106 (2011)]

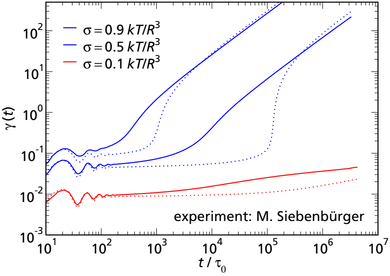
Startup: Creep and Micro-Rheology

Creep

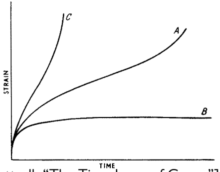
- deformation $\gamma(t)$ after sudden step stress







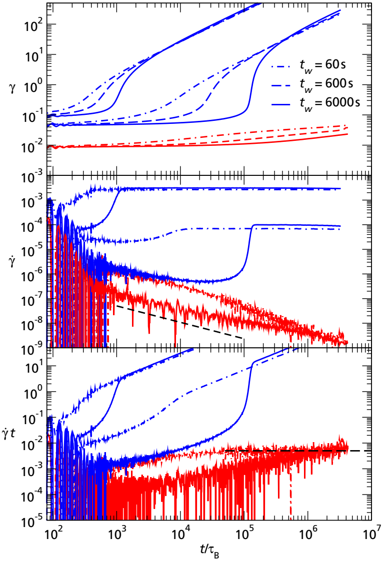
- nonequilibrium transition:
  plastic deformation / flow
- static yield stress σ_c
- anomalous flow behavior (creep)?



[Cottrell, "The Time Laws of Creep"]

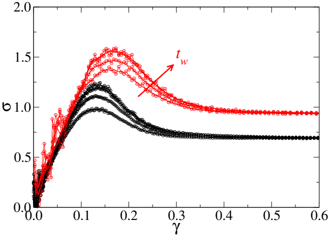
[Siebenbürger, Ballauff, ThV (in preparation)]

Creep Continued



[Siebenbürger, Ballauff, ThV (in preparation)]

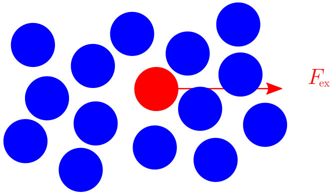
- creep laws (hard matter):
  - logarithmic, $\dot\gamma(t)t \sim$ const.
  - Andrade, $\dot\gamma(t) \sim t^{-\alpha}$, $\alpha \approx 2/3$
  - secondary, $\dot\gamma(t) \sim$ const.
- "viscosity thinning", $\dot\gamma(t) \sim t^{1+x}$
  - related to stress overshoot?
  - aging-time dependent!

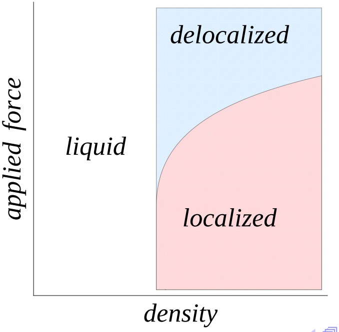


Static Yielding: A Force Threshold

- steady external shear $\Rightarrow$ glass molten (always)
- steady external force $\Rightarrow$ yielding transition σ_c
- microscopic analog?
  - yielding of individual "cages" by local external force

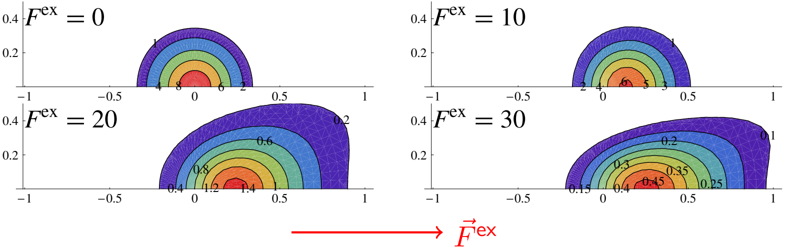
$\Rightarrow$ microrheology





[Gazuz, Puertas, ThV, Fuchs, PRL (2009)]

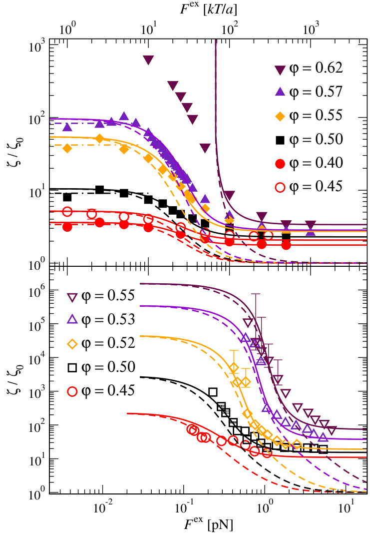
- $F^{\text{ex}} < F_c^{\text{ex}}$: localized probe
- distorted probe probability density $\phi^s(\vec{r}, t \to \infty)$



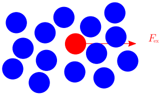
- $F^{\text{ex}} > F_c^{\text{ex}}$: delocalized probe
- $F_c^{\text{ex}} \gg k_B T/\sigma$: cages, not thermal forces

Microscopic Yielding

sim.: A M Puertas / exp.: Habdas *et al.* [Europhys Lett (2004)]



- depinning signature at $F \approx F_c$: measures typical cage strength
- fits: schematic model (MCT)
  - modes $\parallel \vec{F}^{\text{ex}}$, $\perp \vec{F}^{\text{ex}}$
  - high-force plateau: fluctuations $\perp$ force
  - strong influence of hydrodynamic interactions
- MCT power laws $\curvearrowright$ $\langle v \rangle_\infty \sim (F - F_c)^{1/a-1}$



[Gnann, Gazuz, Puertas, Fuchs, ThV, Soft Matter (2011)]

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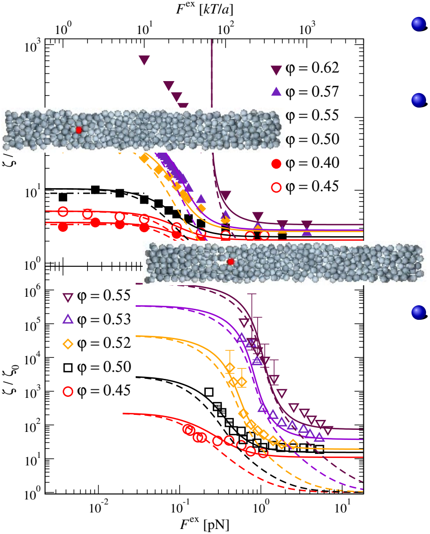

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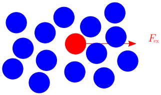


[Gnann, Gazuz, Puertas, Fuchs, ThV, Soft Matter (2011)]

Residual Stresses

Constitutive Equations

common Ansatz: nonlinear *Boltzmann superposition principle*

$$\sigma(t) = \int_{-\infty}^{t} \gamma_{tt'}\, \psi(t-t', \gamma_{tt'})\, dt' \qquad \text{(BKZ)}$$

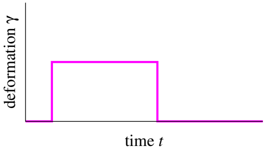
$\Rightarrow$ prediction: single-step-strain response contains it all

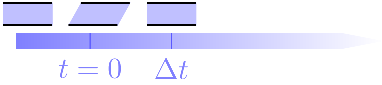
$\Rightarrow$ $\sigma(\infty) = 0$ whenever $\sum_i \gamma_i = 0$ in n-step-strain

- test: double step strain
  - note: MCT does *not* reduce to BKZ form

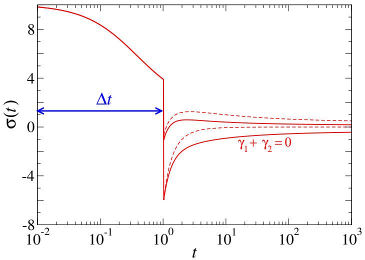
  $\Rightarrow$ prediction of *residual stresses*

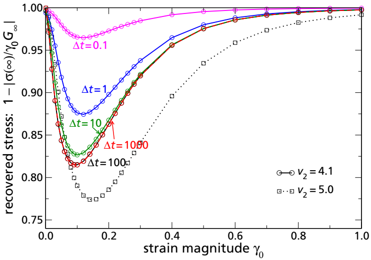
Stress Recovery After Reversing Strain





measure stress relaxation $\sigma(t)$

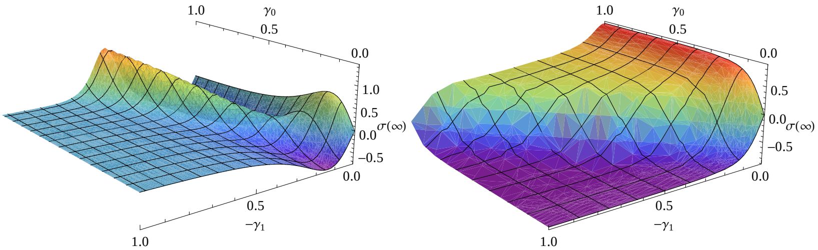




- glass: finite $\sigma(\infty)$ even for reversed strain
- recovered stress: $< 100\%$ due to memory effects

[ThV, Brader, Fuchs, Cates, Soft Matter (submitted)]

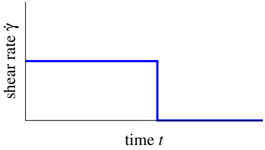
Double Step Strain: Protocol Dependence

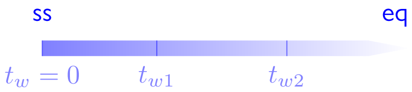


- protocol dependence: sudden “affine” deformation *vs.* strain-rate-ramp
- response: “echo” *vs.* “wipe-out”

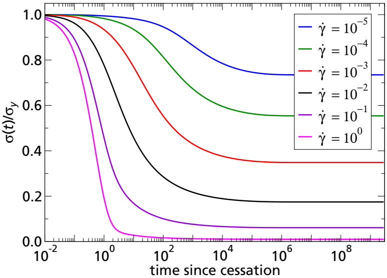
[ThV, Brader, Fuchs, Cates, Soft Matter (submitted)]

Residual Stresses: Switching off Steady Shear





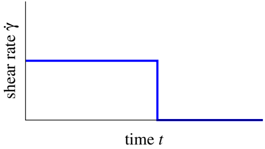
measure decay of shear stress $\sigma(t)$

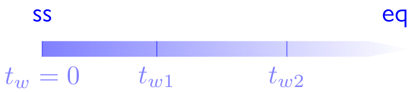


- glass can sustain finite residual stress $\sigma(\infty)$
- strong shear "forgotten" quicker

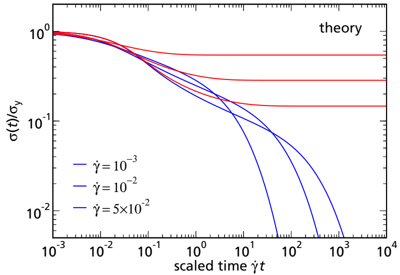
[Siebenbürger/Ballauff, ThV, SFB-TR6 A6/A7 collab. (unpublished results)]

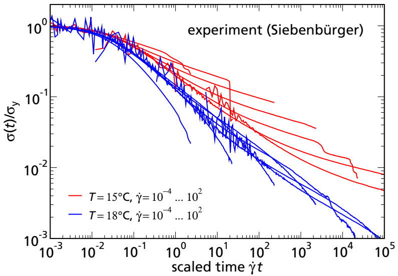
Residual Stresses: Switching off Steady Shear





measure decay of shear stress $\sigma(t)$





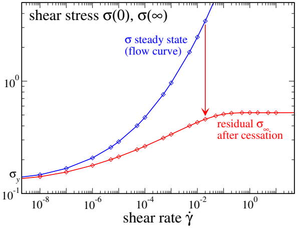
- glass can sustain finite residual stress $\sigma(\infty)$ – transition
- strong shear “forgotten” quicker

[Siebenbürger/Ballauff, ThV, SFB-TR6 A6/A7 collab. (unpublished results)]

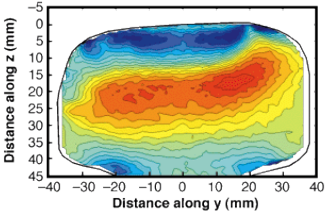
Frozen-In Stresses: History Dependence

- glass re-freezes after shear melting
  $\Rightarrow$ frozen in stresses: memory of flow history

$$\sigma(t) = \dot\gamma \int_{-\infty}^{0} dt'\, G(t>0, t'<0; \dot\gamma)$$



- relevant for applications



residual stress in a worn railway rail

[Webster *et al.*, MRS Forum (2002)]

stress birefringence

[image: wikipedia.org]

Summary

- dynamical yield stress σ_y
  - goes to zero continuously as liquid is approached? $\Rightarrow$ "granular case"
  - goes to constant? $\Rightarrow$ "Maxwell case" ($G_\infty \neq 0$ in liquid)
- creep
  - analogy colloidal systems – metallic systems
  - "failure time" – overshoot in startup flow
- residual stresses
  - signature of energy dissipation due to relaxation processes
  - not obtained in standard BKZ-type constitutive equations

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SFB TR6 Physics of Colloidal Dispersions in External Fields

FOR1394 DFG Research Unit Nonlinear Response to Probe Vitrification

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