Glassy rheology: Combining microscopic theory and macroscopic fluid mechanics

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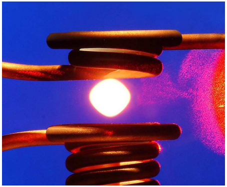
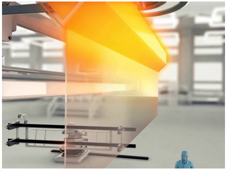
Process-Dependent Material Properties

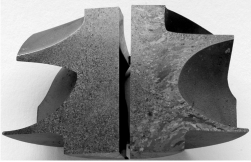


metallic melt (courtesy DLR Cologne)

fusion glass process (Corning Inc.)

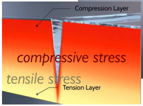


processing
solidification



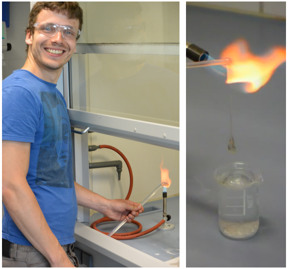
turbo charger gears
(courtesy ACCESS e.V. Aachen)

Xensation™ glass © Schott

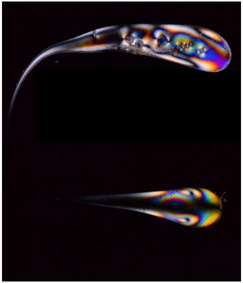


“materials design from the melt”

Residual Stresses: Prince Rupert's Drops



process

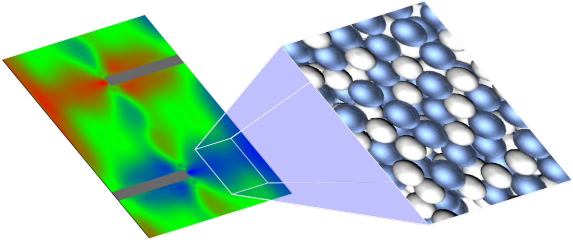


- residual stresses frozen in during production process
- spatial stress patterns determine material toughness
- other applications: spider silk, railway rails, …

Residual Stresses: Prince Rupert's Drops

[video: Smarter Every Day, http://www.youtube.com/user/destinws2]

Multiscale Theory/Simulation

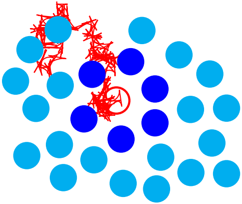


(basis for empirical) material laws $\Leftarrow$ nonlinear-response theory

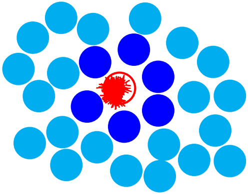
time-dependent, history-dependent material properties

… of *soft matter*, *viscous melts*, *active materials* etc.

Glasses: Liquid-Structured Solids



fluid: finite *viscosity*



glass: finite *elasticity*

slow dynamics ($\tau \to \infty$) $\Rightarrow$ generic behavior

empirical: *Maxwell model*

$$\sigma(t) = \int_{-\infty}^{t} \dot{\gamma}(t')\, G_\infty e^{-(t-t')/\tau}\, dt'$$

[U Queensland, Australia (1927–now); `http://smp.uq.edu.au/content/pitch-drop-experiment`]

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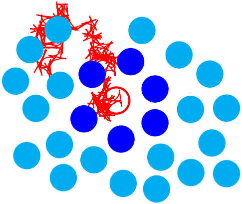

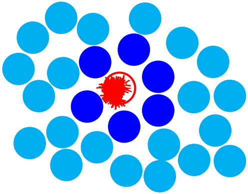

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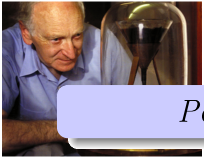
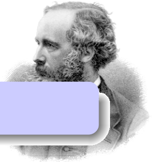




$Pe = \dot{\gamma}\tau \gg 1$: nonlinear response phenomena

[U Queensland, Australia (1927–now); `http://smp.uq.edu.au/content/pitch-drop-experiment`]

Outline

- **Microscopic Dynamics**
  - Mode-Coupling Theory (Rheology)
- **Continuum Description**
  - Hybrid Simulations
  - Empirical Models

Microscopic Dynamics

Mode-Coupling Theory (Rheology)

Nonlinear Response Theory

nonequilibrium phase-space density $\rho(\Gamma,t)$:

$$\partial_t\rho(\Gamma,t) = \left(\Omega_{\mathrm{eq}}(\Gamma) + \delta\Omega(\Gamma,t)\right)\rho(\Gamma,t)$$

formal solution for nonequilibrium averages

$$\rho(t) = \rho_{\mathrm{eq}} + \int_{-\infty}^{t} dt' \exp_+\left[\int_{t'}^{t}\Omega(\tau)\,d\tau\right]\Omega(t')\rho_{\mathrm{eq}}$$

$$\langle f\rangle(t) = \langle f\rangle_{\mathrm{eq}} + \int_{-\infty}^{t} dt' \left\langle \left[\frac{\delta\Omega(t')\rho_{\mathrm{eq}}}{\rho_{\mathrm{eq}}}\right] \exp_-\left[\int_{t'}^{t}\Omega^\dagger(\tau)\,d\tau\right] f \right\rangle_{\mathrm{eq}}$$

for example: stresses

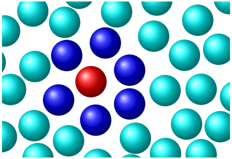
$$\boldsymbol{\sigma}(t) \sim \int_{-\infty}^{t} dt' \cdots \underbrace{\left[-\partial_{t'}\boldsymbol{B}(t,t')\right]}_{\text{deformation measure (Finger tensor)}} \cdots G(t,t',[\vec{\nabla}\vec{v}])$$

[Brader, ThV, Cates, Fuchs, Phys Rev Lett (2007); Brader *et al.*, Phys Rev Lett (2008)]

Mode Coupling Theory: Microscopic Approach

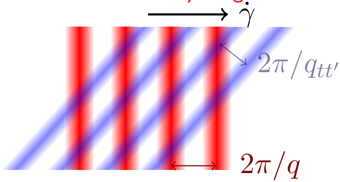
cage effect: $\tau \to \infty$

slow dynamics of density fluctuations



fluctuation advection: $\tau \sim 1/\dot{\gamma}$

shear destroys cages



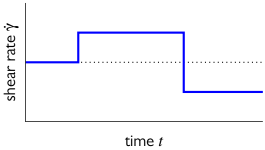
$$\boldsymbol{\sigma}(t) \sim \int_{-\infty}^{t} dt' \cdots \vec{\nabla}\vec{v}(t') \cdots G(t,t',[\vec{\nabla}\vec{v}])$$

$$G(t,t') \overset{\text{MCT}}{=} \int d\vec{k} \cdots \phi_{\vec{k}}^2(t,t')$$

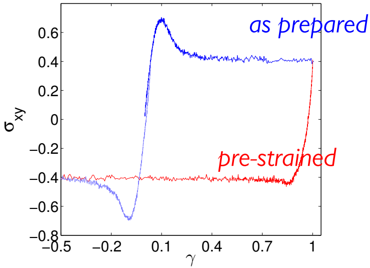
$$\tau_0 \partial_t \phi_{\vec{k}}(t,t') + \phi_{\vec{k}}(t,t') + \int_{t'}^{t} m_{\vec{k}}([\phi],[\vec{\nabla}\vec{v}],t,t'',t')\partial_{t''}\phi_{\vec{q}}(t'',t')\,dt' = 0$$

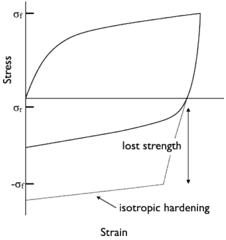
[Fuchs/Cates, PRL (2002); Brader *et al.*, PRL (2007); PRL (2008)]
[Brader, ThV, Fuchs, Larson, Cates, PNAS (2009)]

Limits of Elasticity – Bauschinger Effect



measure shear stress $\sigma(t)$
under *deformation reversal*
$\Rightarrow$ history-dependent elastic modulus G_{eff}



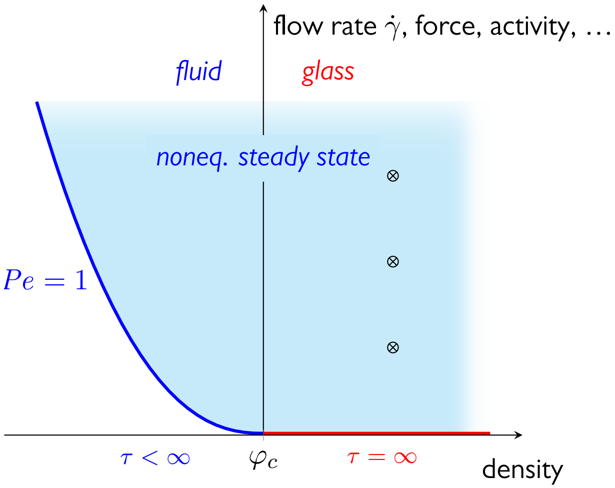


[Kassner, International Journal of Plasticity (2013)]

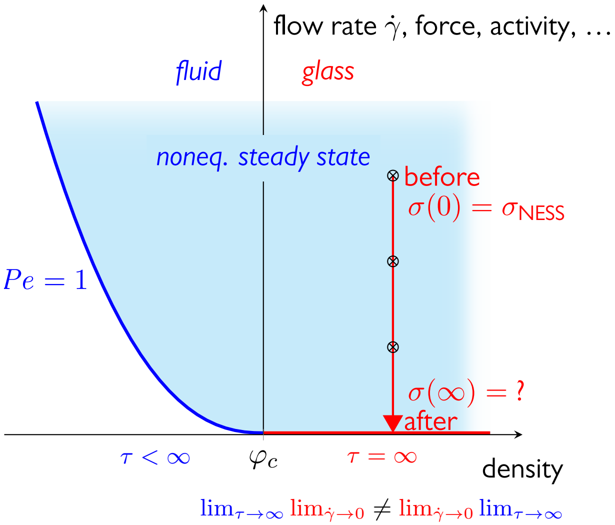
- microscopic explanation for empirical *"Bauschinger effect"*

[Frahsa, Bhattacharjee, Horbach, Fuchs, Voigtmann , J Chem Phys **138**, 12A513 (2013)]
[Bhattacharjee, Soft Matter (2015)]

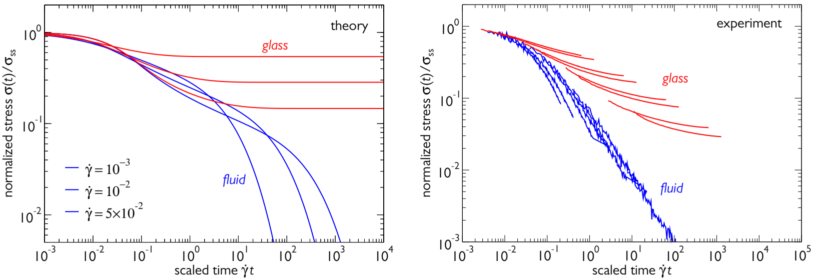
Stopping Flow



Stopping Flow



Residual Stresses: Microscopic Theory



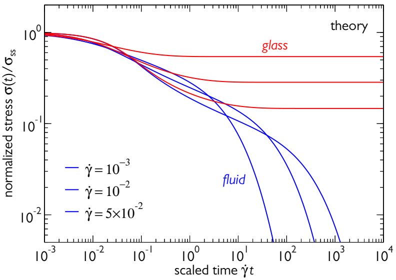
- residual stress: *true nonlinear-response effect*

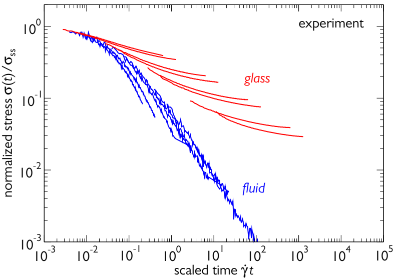
non-stationary flow: $$\sigma(\dot\gamma,t) \sim \int^t \dot\gamma(t')\,G(t,t';[\dot\gamma])\,dt'$$

- theory: *homogeneous shear*, instantaneously stopped

[Ballauff *et al.*, Phys Rev Lett **110**, 215701 (2013)]
[Physics (Focus article) **6**, 60 (2013)]

Residual Stresses: Microscopic Theory





- residual stress: *true nonlinear-response effect*

non-stationary flow: $$\sigma(\dot\gamma,t) \sim \int^t \dot\gamma(t')\, G(t,t';[\dot\gamma])\, dt'$$

- theory: *homogeneous shear*, instantaneously stopped

this makes a huge difference!

[Ballauff *et al.*, Phys Rev Lett **110**, 215701 (2013)]
[Physics (Focus article) **6**, 60 (2013)]

Continuum Description

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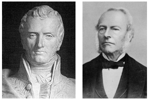
Hybrid Simulations

Macroscopic Modeling

Navier Stokes equations



$$\underbrace{\rho \left[\partial_t \vec{v} + (\vec{v} \cdot \vec{\nabla}) \vec{v} \right] = \rho \vec{f}^{\text{ext}} - \vec{\nabla} p}_{\text{balance law of momentum}} + \underbrace{\vec{\nabla} \cdot \boldsymbol{\sigma}}_{\text{friction}}$$

need constitutive equation for $\boldsymbol{\sigma}$ (closure relation)

$$\boldsymbol{\sigma}(t) \;=\; \mathcal{F}\,[\;(\vec{\nabla}\vec{v})_{t' \leq t}, \ldots\;]$$

historically,
"educated guesses"

$\dot{\gamma} = dv_x/dy$

Newton (1687)
$\sigma = \eta \dot{\gamma}$
resistentiam … proportionalem esse velocitati

$\gamma = \Delta x / \Delta y$

Hooke (1676)
$\sigma = G_\infty \gamma$
ut tensio, sic vis

how to *derive* constitutive equations from *microscopic principles?*

Multi-Scale Computational Fluid Dynamics

Navier Stokes

$\rho[\partial_t \vec{v} + (\vec{v}\cdot\vec{\nabla})\vec{v}] = \rho\vec{f} - \vec{\nabla}p + \vec{\nabla}\cdot\boldsymbol{\sigma}$

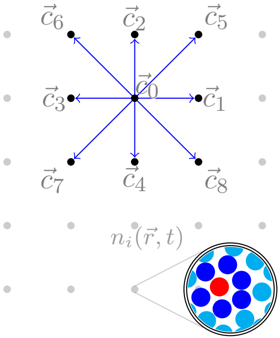
macro

constitutive equation

microscopic dynamics

$\boldsymbol{\sigma}(t) = \int^t dt'\,[-\partial_{t'}\boldsymbol{B}(t,t')]G(t,t',[\boldsymbol{B}])$

micro



$$n_i(\vec{r}+\vec{c}_i\delta t, t+\delta t) = n_i(\vec{r},t) - \frac{1}{\tau_{\text{LB}}}\left[n_i(\vec{r},t) - n_i^{\text{eq}}(\vec{r},t)\right] + F_i$$

physical fields $\rho = \sum_i n_i^{\text{eq}}$, $\vec{v} = \sum_i \vec{c}_i n_i^{\text{eq}}$

$$F_i = \frac{-a^{c_i}}{2c_s^4\tau_{\text{LB}}}\bar{\boldsymbol{\sigma}}^{\text{non-Newt}}[(\vec{\nabla}\vec{v})] : (\vec{c}_i\vec{c}_i - c_s^2\mathbf{1})$$

[Papenkort and ThV, J Chem Phys 140, 164507 (2014)]

Integral Constitutive Equations

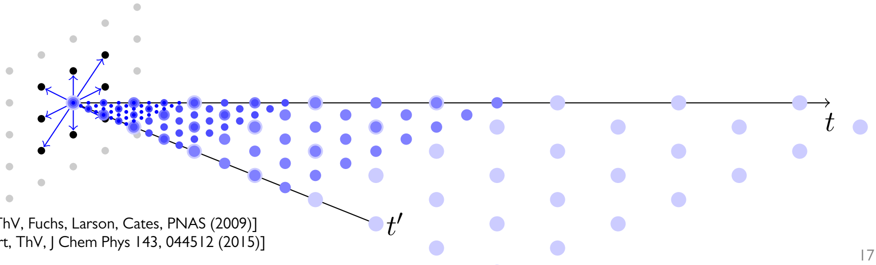
nasty task: need to solve Navier Stokes + *integral equations*

$$\boldsymbol{\sigma}(t) = \int^t dt'[-\partial_{t'}\boldsymbol{B}_{tt'}]\phi^2(t,t',[\boldsymbol{B}])$$

history effects $\Rightarrow$ generalized Langevin equation

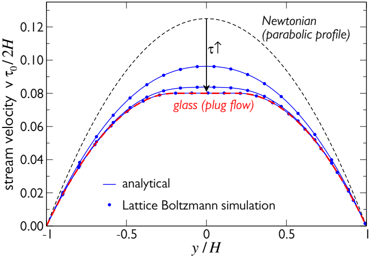
$$0 = \tau_0\partial_t\phi(t,t') + \phi(t,t') + \int_{t'}^{t} dt''\, m(t,t'',t')\partial_{t''}\phi(t'',t')$$

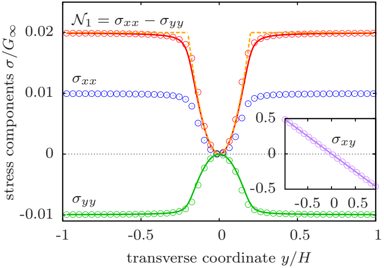
$$m(t,t'',t') = h(\boldsymbol{B}_{tt''})h(\boldsymbol{B}_{tt'})\mathcal{F}[\phi(t,t'')]$$



[Brader, ThV, Fuchs, Larson, Cates, PNAS (2009)]
[Papenkort, ThV, J Chem Phys 143, 044512 (2015)]

Plug Flow

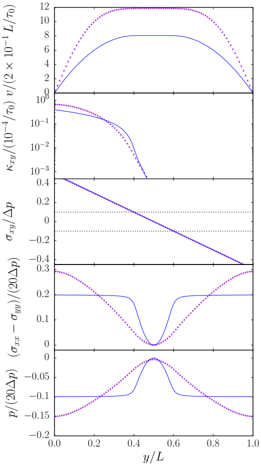




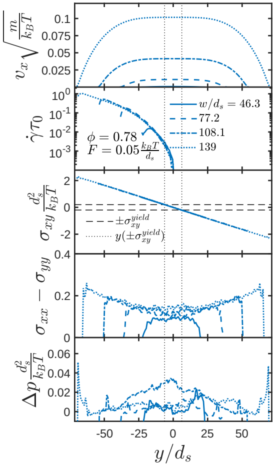
- yield stress ⇒ plug flow
- LB resolves analytical solution
- large normal stress coefficient
  $\mathcal{N}_1 = (\sigma_{xx} - \sigma_{yy})/\dot{\gamma}^2$

[Papenkort, ThV, JCP (2014)]

Theory and Brownian Dynamics (BD) Simulations



LB/MCT



BD, fluid

- glass: non-local rheology develops

[Cárdenas *et al.*, EPJ ST (2017)]

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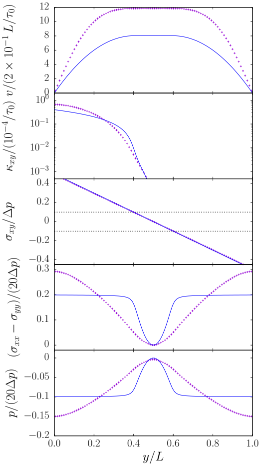

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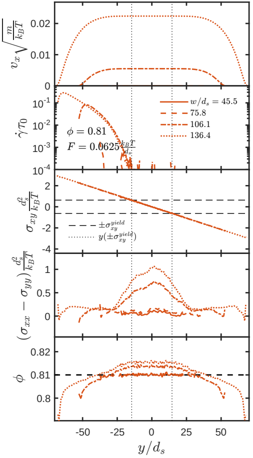


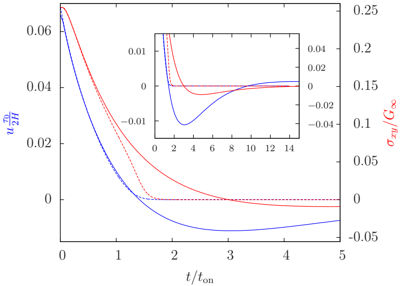
BD, *glass*

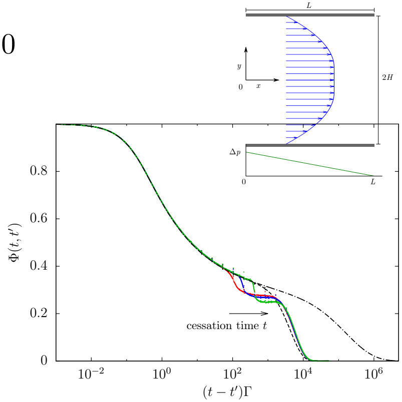
- glass: non-local rheology develops

[Cárdenas *et al.*, EPJ ST (2017)]

Flow Cessation in a Channel

removal of pressure gradient at $t = 0$





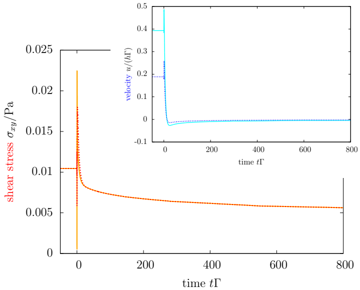
- flow stops at *finite time*; stresses set fluid in motion again
- competition of time scales:

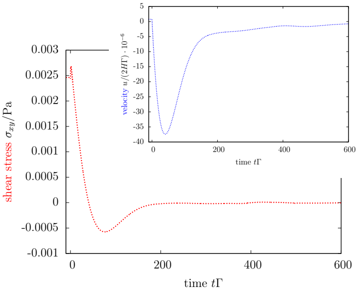
structural relaxation $\tau \propto \eta$ $\Leftrightarrow$ fluid mechanics $\tau \propto \eta^{-1}$

microscopic *macroscopic*

[Papenkort and ThV, J Chem Phys (2015)]

Residual Stresses: The Role of Geometry





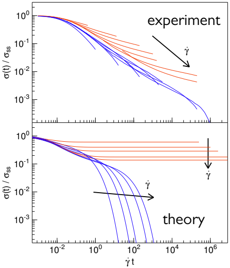
- channel geometry prevents residual stresses

$$0 = \vec{\nabla} \cdot \boldsymbol{\sigma}$$

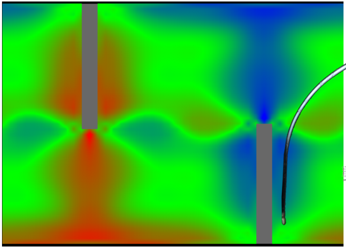
- *unless* translational invariance is broken!

[Papenkort, ThV (to be published)]

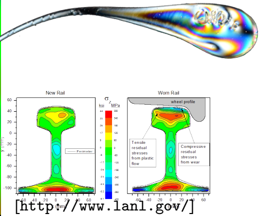
Processing Dependence of Materials: Residual Stresses



microscopic



multi-scale CFD



macroscopic

residual stresses: fingerprint of previous flow

$$\tau \to \infty$$

coupling of microscopic and macroscopic time scales

$$\vec{\nabla} \cdot \boldsymbol{\sigma} = 0$$

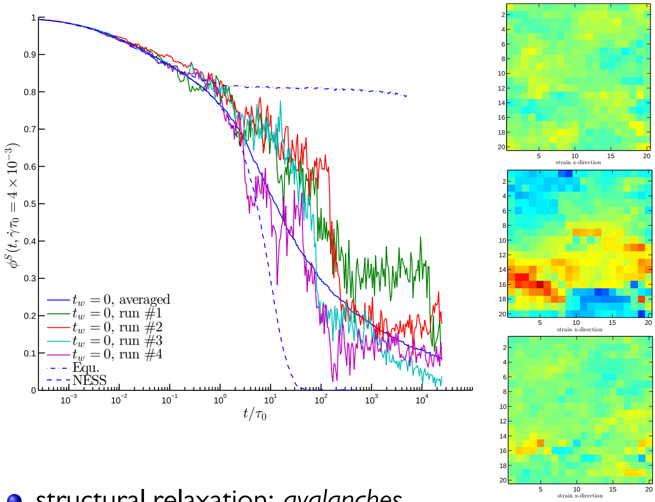
hydrodynamic boundaries change microscopic dynamics

[Ballauff *et al.*, Phys Rev Lett **110**, 215701 (2013)]
[Papenkort, Cárdenas, Voigtmann, to be published]

Continuum Description

Empirical Models

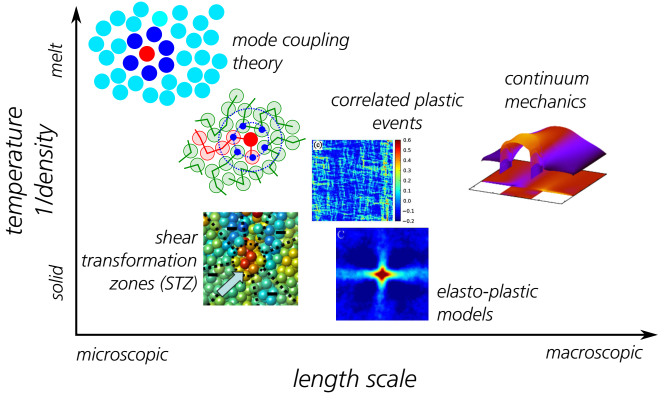
Cessation Dynamics: Avalanches



- structural relaxation: *avalanches*
- sudden stress drops

[Fritschi, Fuchs, ThV (to be published)]

Approaches to Glassy Rheology



[review: ThV, Curr Opin Colloid Interf Sci **19**, 549 (2014); DOI:10.1016/j.cocis.2014.11.001]

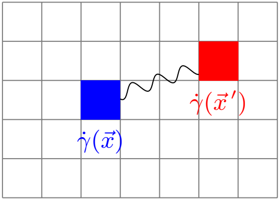
Spatial Cooperativity: Fluidity Model

$$\overset{\triangledown}{\boldsymbol{\sigma}}(t) + f(t)\boldsymbol{\sigma}(t) = G_\infty \boldsymbol{D}(t)$$

$$\tau_f \frac{D}{Dt} f(\vec{x},t) + f(\vec{x},t) = \left(\frac{1}{\tau} + \frac{\dot{\gamma}(\vec{x},t)}{\gamma_c}\right) + \xi^2 \nabla^2 f(\vec{x},t)$$

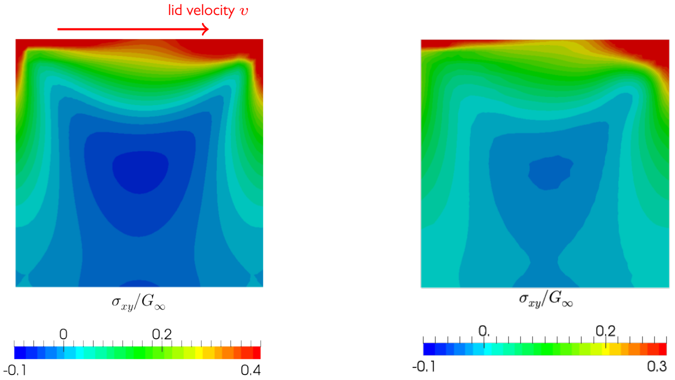
- drop integral equation – for computational ease
- ad-hoc spatial diffusion term – equivalent not yet in MCT

- ξ: spatial cooperativity length



Fluidity Model: Cessation

lid-driven cavity flow (low-Re), finite-volume method (FVM)



steady-state shear stress

residual stress

- fluidity diffusion breaks symmetry of low-Re residual stresses

[H. Cárdenas, unpublished results]

Summary

Summary

- **history-dependent nonlinear response**
  - material state *not uniquely fixed by thermodynamic control variables*

Siebenbürger, Ballauff, ThV, PRL **108**, 255701 (2012);
Ballauff *et al.*, Phys. Rev. Lett. **110**, 215701 (2013)

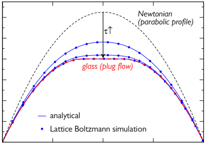
- **statistical-physics foundations of material laws**
  - *coupling between micro- & macroscopic time scales*
  - *multi-scale simulation* using microscopic theory

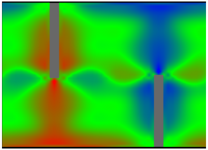
Papenkort and ThV, J. Chem. Phys. **143**, 204502 (2015)

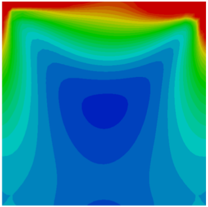
Cárdenas *et al.*, Eur. Phys. J. ST **226**, 3039 (2017)

- effects of **non-local rheology**
  - empirical *glassy fluidity model*

Cárdenas and ThV, to be published (2018)







Thank you

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