Models for tensorial rheology of soft glassy materials

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Outline

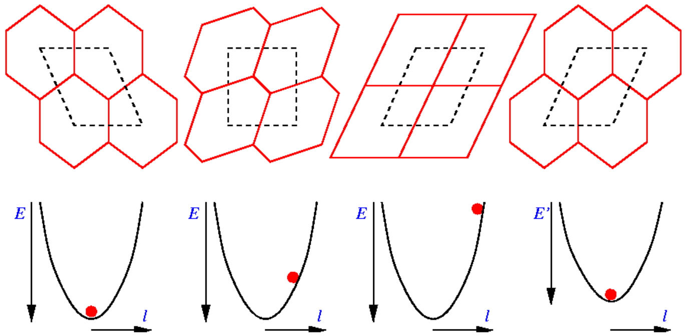
- Soft glassy materials
- The scalar SGR model
- Doing it right: SGR with tensors
- Some choices for mesoscale rheology
- Example predictions
- Discussion

Soft glassy materials

- Foams, dense emulsions, onion phases, colloidal glasses, clays, pastes, ...
- Common rheological features:
  - flow curves $\sigma(\dot\gamma) - \sigma_Y \sim \dot\gamma^p$ $(0 < p < 1)$ Herschel-Bulkley (if yield stress $\sigma_Y \neq 0$) or power-law
  - Nearly 'flat' viscoelastic spectra $G'(\omega)$, $G''(\omega)$ for low frequencies ω
  - Rheological aging
- Suggests common underlying features: arrangements of particles/droplets etc are disordered and metastable
- Analogy with glasses
- Soft glassy rheology approach exploits this; minimal model (based on Bouchaud's trap model)

SGR model (scalar version)

- Divide sample into mesoscopic elements
- Each has local shear strain l, which increments with macroscopic shear γ
- But when strain energy $\frac{1}{2}kl^2$ gets close to yield energy E, element can yield
- Yielding resets $l = 0$, and element acquires new E from some distribution $\rho(E) \sim e^{-E}$
- Yielding is activated by an effective temperature x; models interactions between elements



Equation of motion

- In dimensionless units (for time, energy)

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

$\Gamma(t) = \langle e^{-(E-kl^2/2)/x}\rangle$ = aver. yielding rate

- Macroscopic stress $\sigma(t) = k\langle l\rangle$
- Without shear, $P(E,t)$ approaches equilibrium $P_{\rm eq}(E) \propto \exp(E/x)\rho(E)$ for long t
- Get glass transition if $\rho(E)$ has exponential tail; happens at $x = 1$ if $\rho(E) = e^{-E}$ (possible justification from extreme value statistics)
- For $x < 1$, system is in glass phase; never equilibrates $\Rightarrow$ aging

SGR predictions

- Find Herschel-Bulkley $(x < 1)$ and power-law flow curves $(1 < x < 2)$
- Viscoelastic spectra G', $G'' \sim \omega^{x-1}$ are flat near $x = 1$
- In glass phase $(x < 1)$ find rheological aging, loss modulus $G'' \sim (\omega t)^{x-1}$ decreases with age t
- Steady shear always 'interrupts' aging, restores stationary state
- Stress overshoots in shear startup, nonlinear G' and G'', linear and nonlinear creep, ...

Constitutive equation

- Solve equation of motion; get 'birth-death' relation between stress and strain:

$$\sigma(t) = G_0(z_{t0})k\gamma(t) + \int_0^t dt'\, \Gamma(t')G_1(z_{tt'})k\left[\gamma(t)-\gamma(t')\right]$$

- Survival probabilities from $t = 0$ & after yield:

$$G_0(z) = \langle e^{-z\exp(-E/x)}\rangle_{P_0}$$
$$G_1(z) = \langle e^{-z\exp(-E/x)}\rangle_{\rho}$$

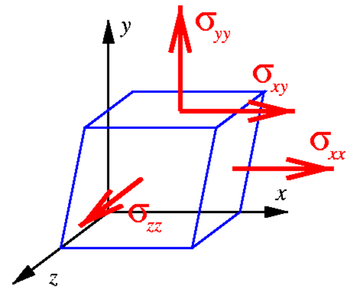
- Get nonlinearities only via effective time interval: strain 'speeds up the clock'

$$z_{tt'} = \int_{t'}^{t} dt''\, \exp\left(k\left[\gamma(t'')-\gamma(t')\right]^2/2x\right)$$

- Yielding rate $\Gamma(t)$ determined from similar relation as for $\sigma(t)$ (from normalization of P)

Drawbacks of scalar SGR model

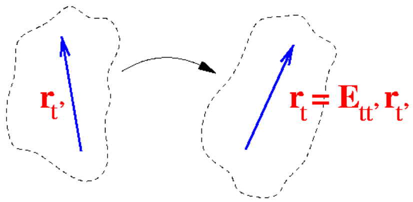
- Interpretation of effective temperature x; also so far constant but should have own dynamics
- Scalar description: only shear strain and stress considered
- Want a proper tensorial model to study e.g. normal stresses N_1, N_2, uniaxial deformations, . . .



- Also linear elasticity (stress $= kl$) at mesoscale (element level) very naive
- Want more flexible modelling of mesoscale rheology

Doing it right: SGR with tensors

- Idea: deformation tensor $\mathbf{E}_{tt'}$ replaces strain difference



- Changes constitutive equation to

$$\boldsymbol{\sigma}(t) = G_0(z_{t0})\mathbf{Q}(\mathbf{E}_{t0}) + \int_0^t dt'\, \Gamma(t') G_1(z_{tt'})\mathbf{Q}(\mathbf{E}_{tt'})$$

with effective time interval

$$z_{tt'} = \int_{t'}^t \exp\left[R(\mathbf{E}_{t''t'})/x\right] dt''$$

- $\mathbf{Q}(\mathbf{E})$: local stress tensor for deformation $\mathbf{E}$
- $R(\mathbf{E})$: lowering of energy barrier for yielding

Choices for mesoscale rheology

- By analogy with scalar SGR, assume energy barrier is lowered by stored elastic (free) energy (density):

$$R(\mathbf{E}) = \lambda \frac{\mathcal{F}(\mathbf{E}) - \mathcal{F}_0}{\mathcal{F}_0}$$

- $\lambda = O(1)$ determines which fraction of $\Delta\mathcal{F}$ can be converted into work to overcome yield barrier
- For small shear strains, $R(\gamma) = \lambda\chi\gamma^2/2$; $\chi = G/\mathcal{F}_0$ is dimensionless ratio of shear modulus G and $\mathcal{F}_0$
- $\mathbf{Q}(\mathbf{E})$ determines instantaneous stress response, in particular ratio $\varphi = N_1/N_2$ of normal stress differences

Dense emulsions & foams

- Model 1: Assume affine deformation of isotropic ensemble of fluid interfaces; Doi & Ohta showed

$$Q_{\mu\nu}(\mathbf{E}) = \frac{15}{4}\int \frac{d^2\mathbf{u}}{4\pi}\,\frac{\frac{1}{3}\delta_{\mu\nu} - u_\mu u_\nu}{|\mathbf{E}^\top\!\cdot\mathbf{u}|^4}$$

  with $R(\mathbf{E})/\lambda = -1 + \int \frac{d^2\mathbf{u}}{4\pi}\,|\mathbf{E}^\top\!\cdot\mathbf{u}|^{-4}$

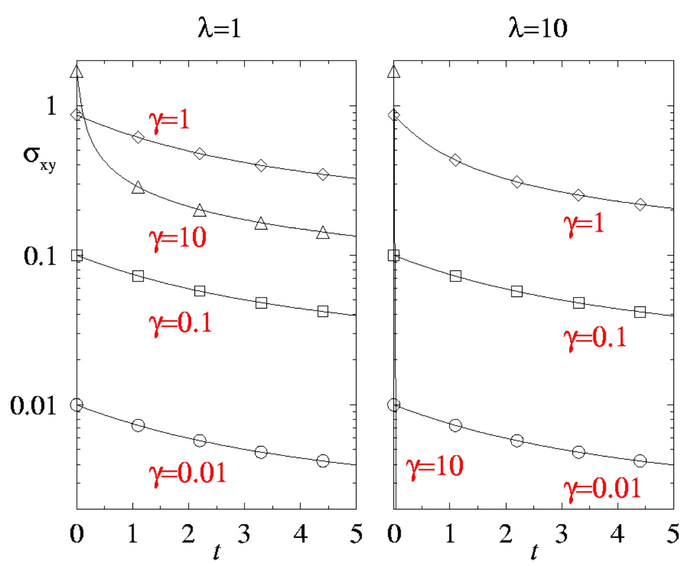
- Has $\chi = G/\mathcal{F}_0 = 4/15$, and for shear strains $\varphi = N_1/N_2 = -7/6\ldots -1$ as γ increases
- Model 2: Analytic approximation for shear strains; has $\chi = 1/3$, and $\varphi = -1$ for all γ
- Model 3: Due to Larson, $R/\lambda = -1 + \frac{1}{3}\mathrm{tr}\,(\mathbf{E}^\top\mathbf{E})^{-1/2}$
- Designed to allow for constant contact angles (120°) between films; gives $\chi = 1/6$ and $\varphi = -3/4\ldots -1$, closer to numerical results for dry foams
- Focus mainly on models 1 & 2 in the following

Predictions: Step strain

- In equilibrium (requires $x > 1$) find after step deformation $\mathbf{E}$, with $G_{\rm eq}(z) \propto \int_z^\infty dz'\,G_1(z')$:

$$\boldsymbol{\sigma}(t) = \mathbf{Q}(\mathbf{E})\,G_{\rm eq}(t\exp[R(\mathbf{E})/x])$$

- Nonlinearities in t-dependence only via factor $\exp[R(\mathbf{E})/x]$, as in scalar model
- Extra nonlinearities via instantaneous $\mathbf{Q}(\mathbf{E})$; but ratios of σ_{xy}, N_1 and N_2 constant in time

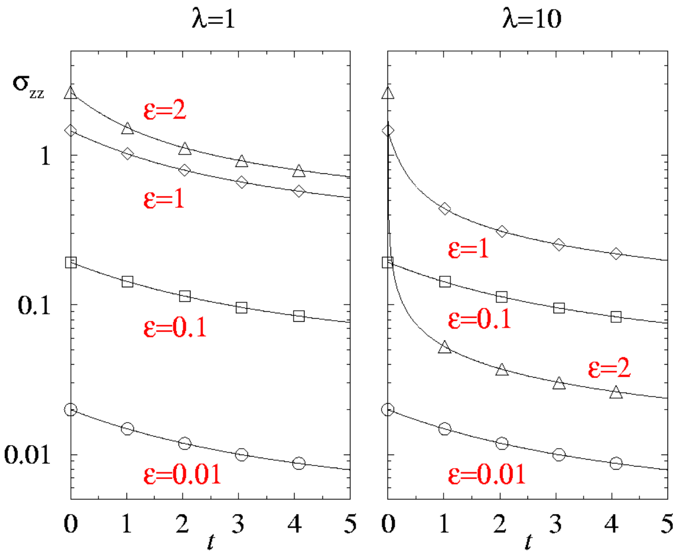


Uniaxial step strain

- Step deformation with

$$\mathbf{E} = \begin{pmatrix} e^{-\epsilon/2} & 0 & 0 \\ 0 & e^{-\epsilon/2} & 0 \\ 0 & 0 & e^{\epsilon} \end{pmatrix}$$

- Can use unapproximated model 1
- As before, all stress tensor components have t-independent ratios

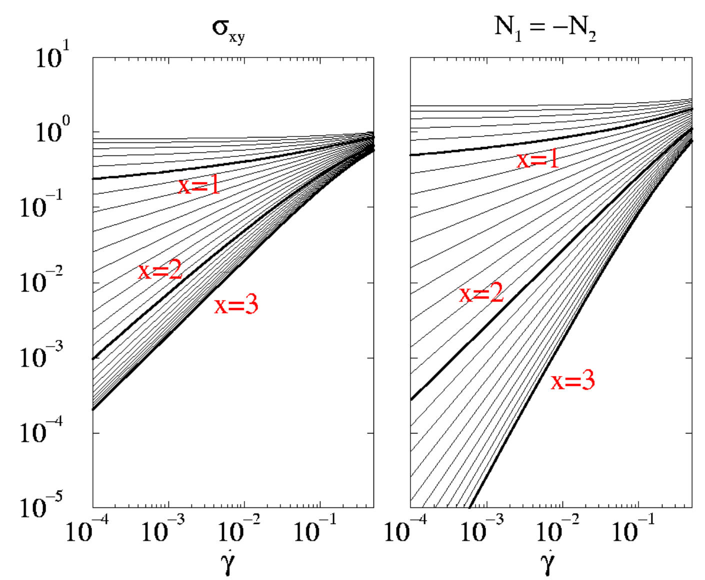


Steady shear flow

- For low shear rate $\dot\gamma$, Newtonian scalings are $\sigma_{xy} \sim \dot\gamma$, $N_{1,2} \sim \dot\gamma^2$
- Effects of glassiness (for any reasonable $\mathbf{Q}$, R)

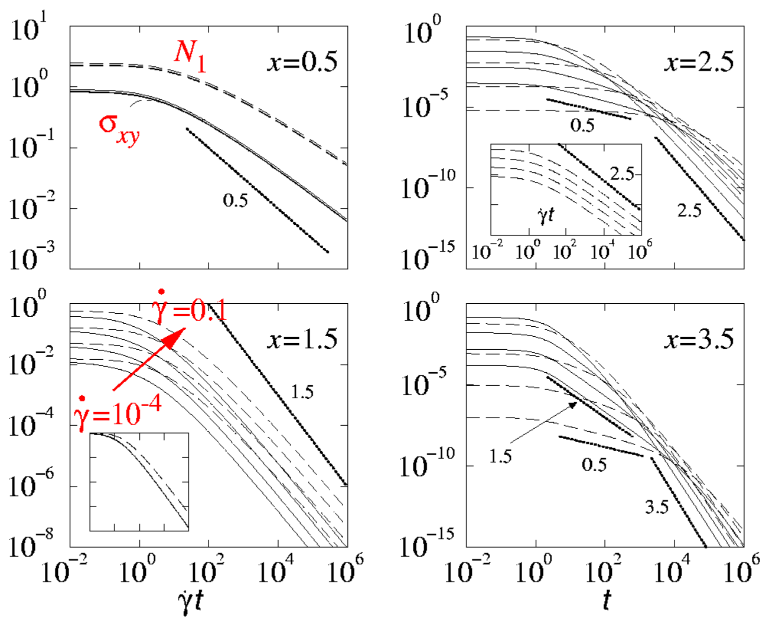
$$\sigma_{xy}, N_{1,2} \propto \begin{cases} \dot\gamma^{x-1}, & 1 < x < \begin{Bmatrix} 2 \\ 3 \end{Bmatrix} \text{ for } \begin{Bmatrix} \sigma_{xy} \\ N_{1,2} \end{Bmatrix} \\ \text{const.}, & x < 1 \end{cases}$$

- For model 2 with $\lambda = 1$:



Cessation of steady shear

- Steady shear $\dot{\gamma}$, stop at $t = 0$. Stress relaxation?
- In glassy regime, get scaling with $\dot{\gamma}t$: shear flow has 'imprinted' relaxation timescale $\sim 1/\dot{\gamma}$
- $N_{1,2}$ relax more slowly than shear stress
- For model 2 with $\lambda = 1$:



Conclusions

- Tensorial structure can be added to SGR model without 'damaging' appealing glassy phenomenology
- Flexible description of mesoscale rheology
- Examples for emulsions/foams but can be adapted to soft colloids etc
- Falsifiable predictions – experiments welcome
- Foams? Aging caused by coarsening seems to produce $\approx$ single relaxation time; different from SGR model
- Dense emulsions, microgel beads etc better to see 'glassy' aging experimentally