Exploring soft glassy rheology: Mesoscopic analysis of simulation data and effective temperature dynamics

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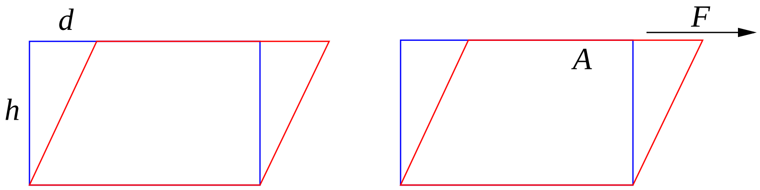
Soft glasses

- Emulsions, dense colloidal suspensions, foams, microgels
- Structural similarities: made up of squishy "particles"
- Oil droplets [ignore coalescence], colloidal particles, air bubbles [ignore coarsening]
- Typical particle scale μm, larger for foams, smaller for colloids
- Particles have different shapes and sizes (polydisperse)
- Particle packing is amorphous (disordered)
- Metastable: $k_B T$ too small to make system ergodic & reach optimal packing (crystalline, if polydispersity not too strong)
- So glassy (repulsive glass) – but soft, can easily be made to flow

Outline

Outline

Shear stress and strain



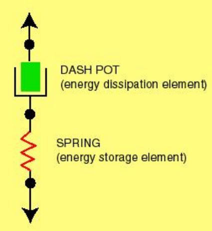
- Shear strain: $\gamma = d/h$, shear stress $\sigma = F/A$ (really tensors)
- Elastic solid: $\sigma = G\gamma$, elastic (shear) modulus G
- Newtonian fluid: $\sigma = \eta\dot{\gamma}$, viscosity η

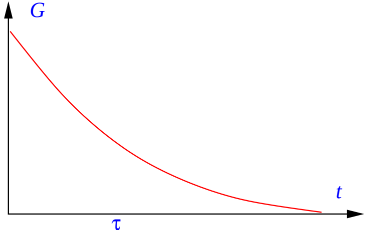
Linear rheology & viscoelasticity

- Small strain increment (step) $\Delta\gamma$ at $t = 0$ causes stress $\sigma(t) = G(t)\Delta\gamma$
- $G(t)$ = stress relaxation function
  Constant for solid, spike $\eta\delta(t)$ for fluid
- Most materials are in between: viscoelastic
- For short t, $G(t)$ nearly constant (solid), but eventually $\to 0$ (fluid)
- Linear superposition of many small strain steps $\Delta\gamma = \dot{\gamma}\Delta t$:

$$\sigma(t) = \int_0^t G(t - t')\dot{\gamma}(t')\, dt'$$

Maxwell model





- Elastic solid and viscous fluid "in series" (spring & damper)
- Common stress σ, elastic strain obeys $\sigma = G_0\gamma_{\rm el}$, viscous strain $\sigma = \eta\dot\gamma_{\rm visc}$
- Total strain rate $\dot\gamma = \dot\gamma_{\rm el} + \dot\gamma_{\rm visc} = \dot\sigma/G_0 + \sigma/\eta$
- Solve for small strain step ($\dot\gamma(t) = \Delta\gamma\,\delta(t)$):

$$G(t) = G_0 \exp(-t/\tau), \qquad \tau = \eta/G_0$$

- Note $\eta = \int_0^\infty G(t)\,dt$, generally true if(!) flow with constant strain rate is a linear perturbation

Another Maxwell model

Complex modulus

- Experimentally, oscillatory measurements often easier
- If $\gamma(t) = \gamma_0 \cos(\omega t) = \gamma_0 \,\mathrm{Re}\, e^{i\omega t}$, then

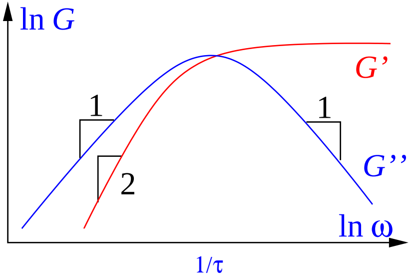
$$\begin{aligned} \sigma(t) &= \mathrm{Re} \int_0^t G(t-t') i\omega\gamma_0 e^{i\omega t'} dt' = \mathrm{Re}\, G^*(\omega)\gamma(t) \\ G^*(\omega) &= i\omega \int_0^\infty G(t'') e^{-i\omega t''} dt'' \qquad \text{for large } t \end{aligned}$$

- Write complex modulus $G^*(\omega) = G'(\omega) + iG''(\omega)$, then

$$\sigma(t) = G'(\omega)\gamma_0 \cos(\omega t) - G''(\omega)\gamma_0 \sin(\omega t)$$

- Elastic modulus $G'(\omega)$: in-phase part of stress
- Viscous or loss modulus $G''(\omega)$: out-of-phase (ahead by $\pi/2$)

Complex modulus of Maxwell model



- $G^*(\omega) = i\omega \times$ Fourier transform of $G_0 \exp(-t/\tau) = G_0 \frac{i\omega\tau}{1+i\omega\tau}$

$$G'(\omega) = G_0 \frac{\omega^2\tau^2}{1+\omega^2\tau^2}, \qquad G''(\omega) = G_0 \frac{\omega\tau}{1+\omega^2\tau^2}$$

- Single relaxation time gives peak in $G''(\omega)$ at $\omega = 1/\tau$

Nonlinear rheology

- For most complex fluids, steady flow (rate $\dot{\gamma}$) is not a small perturbation, don't get $\sigma = \eta\dot{\gamma}$
- Flow curve $\sigma(\dot{\gamma})$: stress in steady state
- Often shear-thinning: downward curvature
- Many other nonlinear perturbations:
  - large step stress or strain
  - large amplitude oscillatory stress or strain
  - startup/cessation of steady shear etc
- Most general description: constitutive equation

$$\sigma(t) = \text{some function(al) of strain history } [\gamma(t'), t' = 0 \ldots t]$$

Outline

Soft glasses: Linear rheology

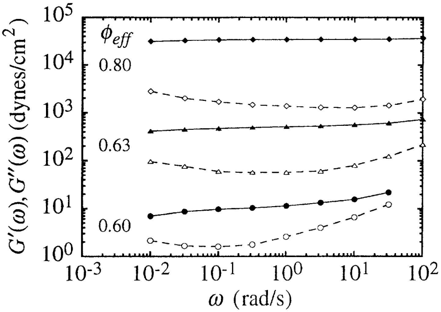
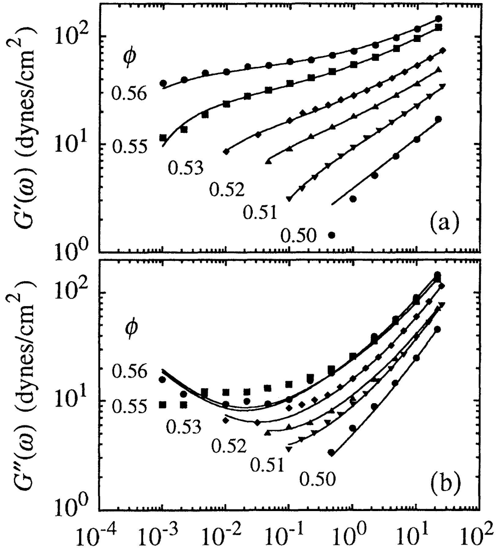


FIG. 2. The frequency dependence of the storage G' (solid points) and loss G'' (open points) moduli of a monodisperse emulsion with $r \approx 0.53$ μm for $\phi_{\text{eff}} = 0.80$ (diamonds), 0.63 (triangles), and 0.60 (circles). The results for the two larger

- Complex modulus for dense emulsions (Mason Bibette Weitz 1995)
- Almost flat $G''(\omega)$: broad relaxation time spectrum, glassy

Colloidal hard sphere glasses

Mason Weitz 1995



Onion phase
Panizza et al 1996

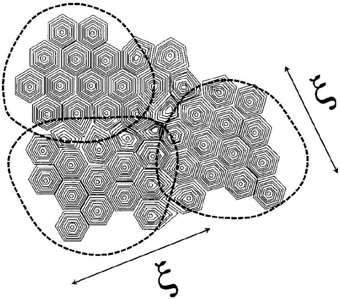
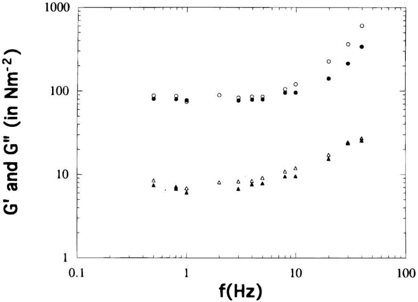


Figure 3. Schematic representation of an onion phase. ξ is the characteristic length of monodomains. Each monodomain is



- Vesicles formed out of lamellar surfactant phase
- Again nearly flat moduli

Microgel particles

Purnomo van den Ende Vanapalli Mugele 2008

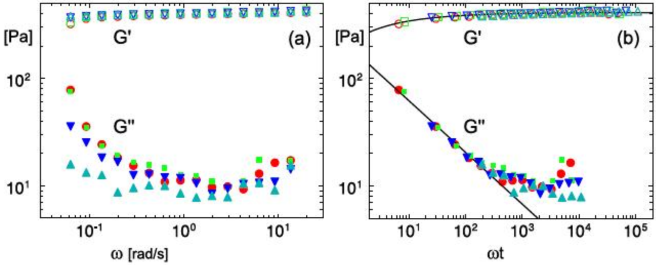
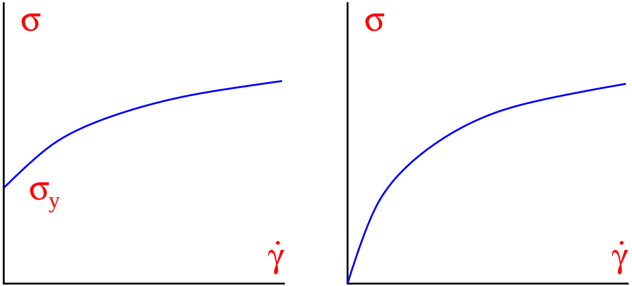


FIG. 1 (color online). G' (open symbols) and G'' (solid symbols) of a 7% w/w suspension at 25 °C plotted versus ω (a) or ωt (b) for t_w = 3 (○), 30 (□), 300 (▽), and 3000 s (△). Lines represent the SGR model ($x = 0.55$, $G_p = 410$ Pa).

- $G''(\omega)$ flat but with upturn at low frequencies
- Aging: Results depend on time elapsed since preparation, typical of glasses

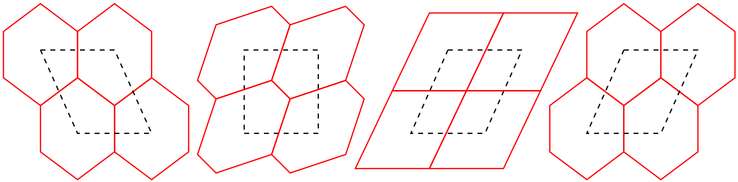
Nonlinear rheology: Flow curves



- Flow curves typically well fitted by $\sigma(\dot\gamma) - \sigma_y \sim \dot\gamma^p$ $(0 < p < 1)$
- Herschel-Bulkley if yield stress $\sigma_y \neq 0$,
  unsheared state = "glass"
- Otherwise power law flow curve,
  unsheared state = "fluid" (but $\eta = \sigma/\dot\gamma \to \infty$ for $\dot\gamma \to 0$)
- Shear thinning: $\sigma/\dot\gamma$ decreases with $\dot\gamma$

A non-glassy model for foam rheology
Princen 1968

- Ideal 2d foam (identical hexagonal cells), $T = 0$
- Apply shear: initially perfectly reversible response, stress increases
- Eventually interfaces rearrange, bubbles "slide": global yield
- Process repeats under steady shear
- We get: yield stress
- We don't get: broad relaxation time spectrum (Buzza Lu Cates 1995), aging



SGR model

PS Lequeux Hébraud Cates 1997, PS 1998

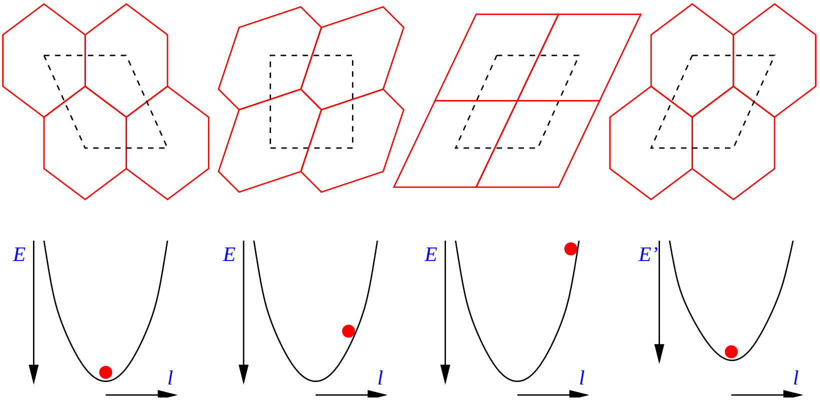
- How do we incorporate structural disorder?
- Divide sample conceptually into mesoscopic elements
- Each has local shear strain l, which increments with macroscopic shear γ
- Assumes strain rate $\dot{\gamma}$ uniform throughout system, but allows for variation in local strain and stress (compare STZ)
- When strain energy $\frac{1}{2}kl^2$ reaches yield energy E, element can yield and so reset to $l = 0$
- k = local shear modulus
- If all elements have same E and k, this would essentially give back the Princen model

SGR model

PS Lequeux Hébraud Cates 1997, PS 1998

- New ingredient 1: disorder $\Rightarrow$ every element has its own E
- Initial distribution of E across elements depends on preparation
- When an element yields, it rearranges into new local equilibrium structure $\Rightarrow$ acquires new E from some distribution $\rho(E) \propto e^{-E/\bar{E}}$ (assume no memory of previous E)
- New ingredient 2: Yielding is activated by an effective temperature x, to model interactions between elements
- x should be of order $\bar{E}$, $\gg k_B T$ (negligible)
- Model implicitly assumes low frequency/slow shear: yields are assumed instantaneous, no solvent dissipation

Sketch



Dynamical equation for SGR

- $P(E,l,t)$: probability of an element having yield energy E and local strain l at time t
- Master equation (Γ_0 = attempt rate for yields)

$$\begin{aligned}\dot{P}(E,l,t) &= -\dot{\gamma}\frac{\partial P}{\partial l} && \text{convection of } l \\ &\quad - \Gamma_0 e^{-(E-kl^2/2)/x} P && \text{elements yield} \\ &\quad + \Gamma(t)\rho(E)\delta(l) && \text{elements reborn after yield}\end{aligned}$$

where $\Gamma(t) = \Gamma_0 \langle e^{-(E-kl^2/2)/x} \rangle$ = average yielding rate

- Macroscopic stress $\sigma(t) = k\,\langle l \rangle$
- Given initial condition $P(E,l,0)$ and strain history (input) can in principle calculate stress (output)
- We'll rescale E, t, l so that $\bar{E} = \Gamma_0 = k = 1$; this means also typical yield strains are 1

Equilibrium & glass transition in the trap model

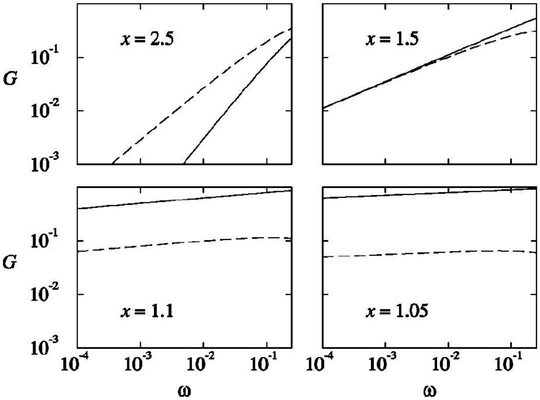
- Master equation for $P(E,t)$ in absence of flow ($l = 0$)

$$\dot{P}(E,t) = -e^{-E/x}P + \Gamma(t)\rho(E)$$

- $P(E,t)$ approaches equilibrium $P_{\text{eq}}(E) \propto \exp(E/x)\rho(E)$ for long t (Boltzmann distribution; E is measured downwards)
- Get glass transition if $\rho(E)$ has exponential tail (possible justification from extreme value statistics)
- Reason: for low enough x, $P_{\text{eq}}(E)$ cannot be normalized
- For $\rho(E) = e^{-E}$ this transition happens at $x = 1$
- For $x < 1$, system is in glass phase; never equilibrates
- Aging: evolution into ever deeper traps

Outline

Linear response in the fluid phase

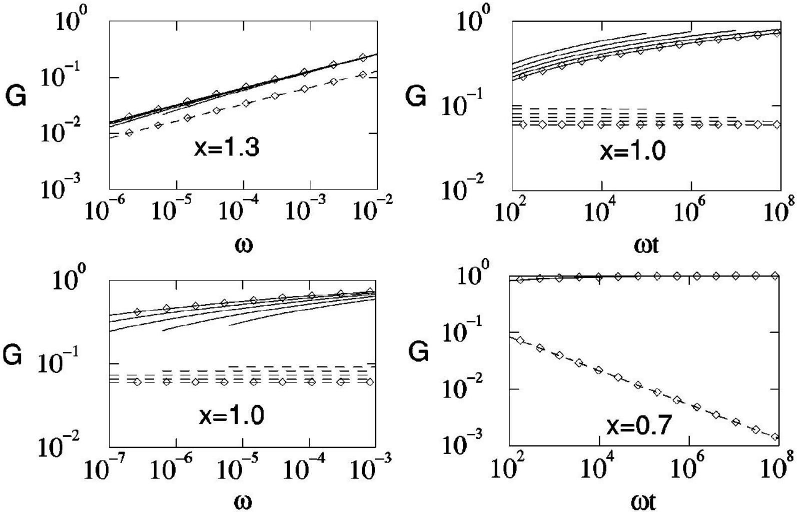


- Calculation yields average of Maxwell models: $G^*(\omega) = \left\langle \frac{i\omega\tau}{1+i\omega\tau} \right\rangle$, average is over $P_{\rm eq}(\tau)$, $\tau = \exp(E/x)$
- For large x, get usual power-law dependences for small ω
- But near $x = 1$ get $G' \sim G'' \sim \omega^{x-1}$: both become flat

Linear response: Aging
Sollich PS Cates 2000

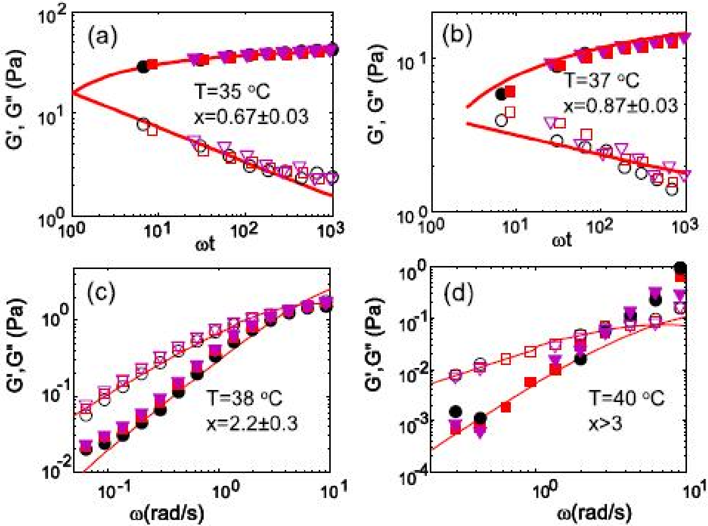
- Conceptual issue: with aging, $G^*(\omega) \to G^*(\omega, t, t_\mathrm{w})$
- $G^*(\omega, t, t_\mathrm{w})$ could depend on final time t and start time t_w of shear
- Luckily, dependence on t_w is weak: $G^*(\omega, t)$
- Find simple aging $1/\omega \sim t$: $G^*(\omega, t) \sim 1 - (i\omega t)^{x-1}$

Linear response: Aging

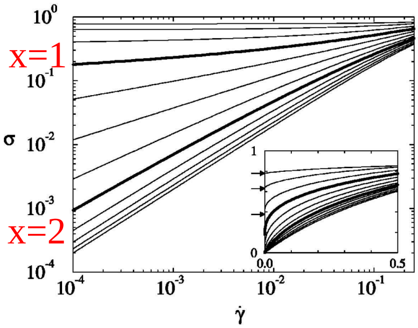


Comparison with experiments on microgel particles

Purnomo van den Ende Vanapalli Mugele 2008



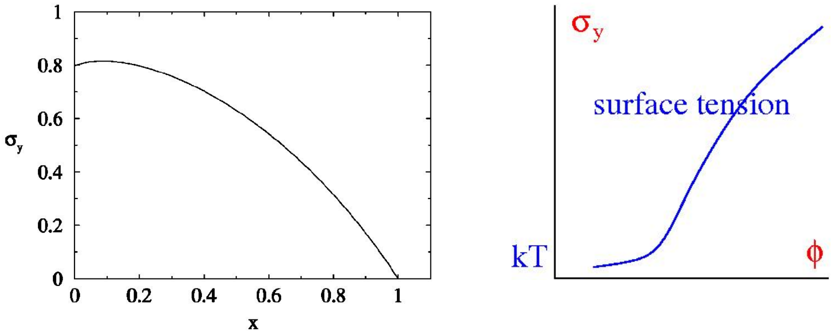
Flow curve



- Calculation: steady state, so set $\dot{P} = 0$ in master equation, integrate differential eq[n] for l; Γ from normalization
- Three regimes for small $\dot{\gamma}$:

$$\sigma \sim \begin{cases} \dot{\gamma} & \text{for} \quad 2 < x: \quad \text{Newtonian} \\ \dot{\gamma}^{x-1} & \text{for} \quad 1 < x < 2: \quad \text{power law} \\ \sigma_y(x) + \dot{\gamma}^{1-x} & \text{for} \quad x < 1: \quad \text{Herschel-Bulkley} \end{cases}$$

Yield stress

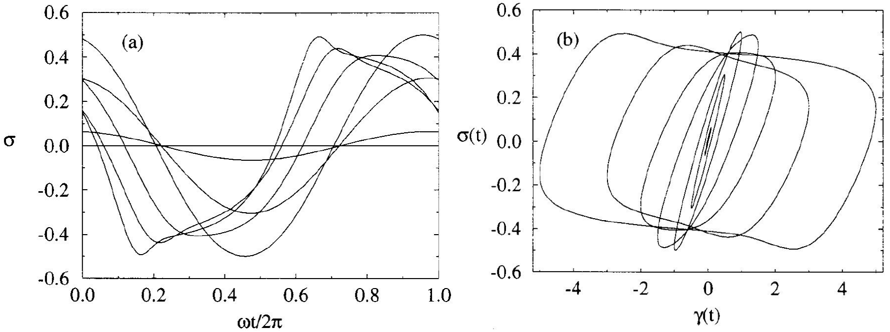


- Yield stress increases continuously at glass transition
- Compare MCT prediction: discontinuous onset of yield stress
- Physics?

  Elastic networks/stress chains vs caging?
  Jamming transition vs glass transition?
- Could e.g. emulsions exhibit both transitions?

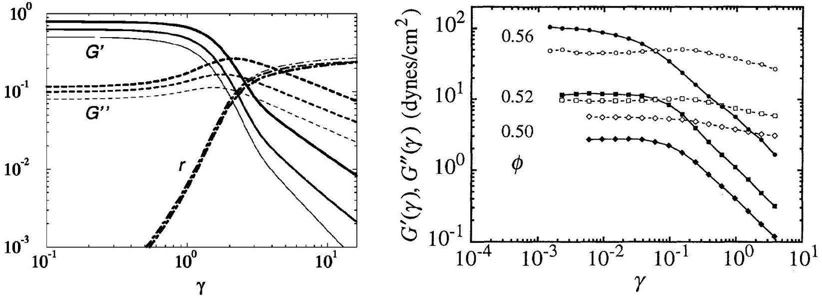
General nonlinear rheology

Example: Large amplitude oscillatory strain



- Close to but above glass transition ($x = 1.1$, $\omega = 0.01$)
- Increasing strain amplitude gives stronger nonlinearities
- Hysteresis-like loops

Large oscillatory strain: Complex modulus



- G'' first increases with amplitude, becomes larger than G'
- Large strain fluidizes an initially predominantly elastic system
- Compare experiments on colloidal hard spheres (right)
- Quantitative comparison for foam
  (Rouyer Cohen-Addad Höhler PS Fielding 2008)

SGR predictions: Summary

- Flow curves: Find both Herschel-Bulkley ($x < 1$) and power-law ($1 < x < 2$)
- 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
- Large amplitude G' and G'' show fluidization behaviour similar to experiments
- Stress overshoots in shear startup, linear and nonlinear creep, rejuvenation and overaging (Lequeux, Viasnoff, McKenna, Cloître, Roettler . . .)

Limitations of SGR model

- Scalar model with ideal local elasticity up to yield – both can be fixed (Cates PS 2004)
- No spatial information: geometry of stress redistribution might be important, also non-affine flow
- Length scale of elements: needs to be large enough to allow local strain and stress to be defined, but otherwise unspecified
- Interpretation of effective temperature x?
  Link to material parameters?
  Should have own dynamics? (see later)
- What sets fundamental time scale (attempt rate for yielding)?

Thermodynamic interpretation of SGR model

- Can interpret SGR within Bouchbinder & Langer non-equilibrium thermodynamics framework
- Slow degrees of freedom Λ used to characterize non-equilibrium state: $P(E,l)$ (finite but large nr. of bins)
- Internal energy and entropy associated with these:

$$
\begin{aligned}
U_\Lambda(\Lambda) &= (V/v_e)\int dE\,dl\,P(E,l)(\tfrac{1}{2}kv_e l^2 - E) \\
S_\Lambda(\Lambda) &= -(V/v_e)\int dE\,dl\,P(E,l)\,(\ln[P(E)/\rho(E)] - 1)
\end{aligned}
$$

- Note: no entropy for l-distribution as l-dynamics is “slaved” to E-dynamics (times of yields)
- Thermodynamic consistency (2nd law) requires that x must be identical to thermodynamic temperature χ of slow d.o.f.
- Most plausible choices of yield rates $\Gamma(E,l)$ are allowed

Comparison to Jim Langer's "simple" SGR model

- What would we get only with effective temperature dynamics and a Maxwell model with temperature-dependent relaxation time?

$$\dot{\chi} = \ldots e^{-1/\chi} + \ldots (T - \chi), \qquad \dot{\sigma} = k\dot{\gamma} - \ldots e^{-1/\chi}\sigma$$

- $G''(\omega)$ in steady state always Maxwell, not broad
- Broadening of spectra can arise only from aging effects
- Also no nonlinearities in strain amplitude, so no solid-liquid crossover in oscillatory strain
- Interesting flow curves only from additional flow-dependent driving terms for χ

Outline

Simulations to the rescue?

- Can we use simulation data to:
- See how far the SGR model represents physical reality?
- Get better understanding of model parameters?
- Tell us where we should improve the model?
- Need to develop method for explicit coarse-graining of simulation data

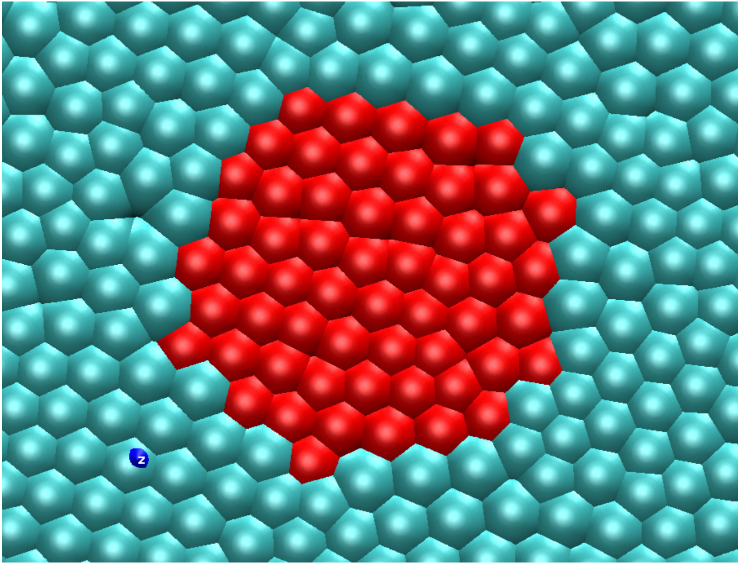
Defining elements

- Focus on $d = 2$ ($d = 3$ can be done but more complicated)
- Make elements circular to minimize boundary effects
- Position circle centres on square lattice to cover all of the sample (with some overlap)
- Once defined, element is co-moving with strain: always contains same particles
- Avoids sudden change of element properties when particles leave/enter, but makes sense only up to moderate $\Delta\gamma$
- Measuring average stress in an element is easy but how do we assign strain l, yield energy etc for a *given* snapshot?

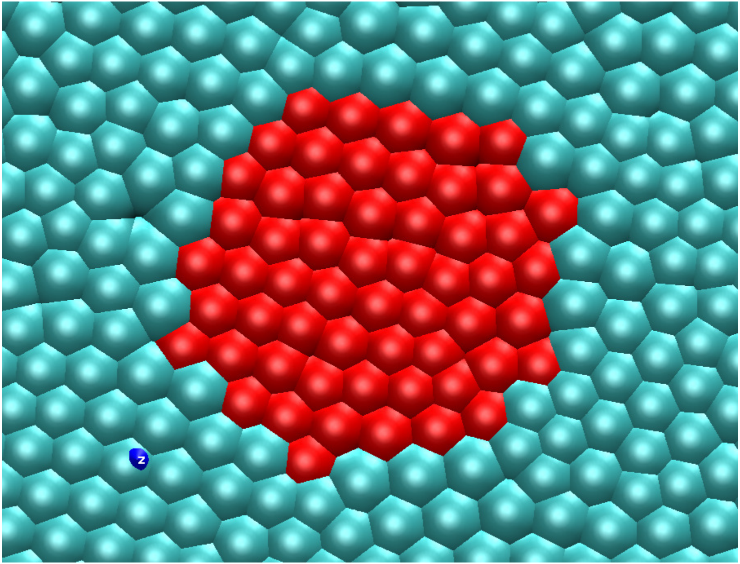
Virtual strain analysis

- Deliberately want local yield points etc: interaction between elements is accounted for separately within model
- Cannot "cut" an element out of sample and then strain until yield – unrealistic boundary condition
- Idea: Use rest of sample as a frame
- Deform the frame affinely to impose a virtual strain $\tilde{\gamma}$
- Particles inside element relax non-affinely to minimize energy
- Gives energy landscape $\epsilon(\tilde{\gamma})$ of element
- Yield points are determined (for $\tilde{\gamma} > 0$ and < 0) by checking for reversibility for each small $\Delta\tilde{\gamma}$ (adaptive steps)

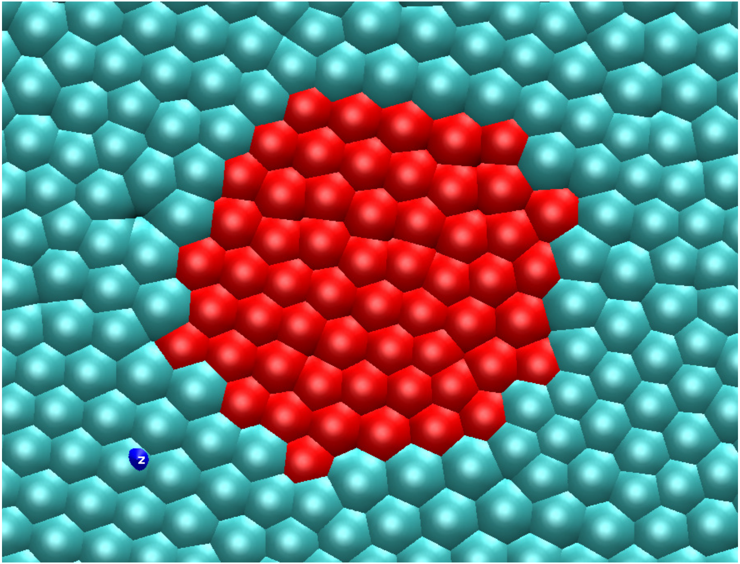
Example: Virtual strain sequence 1



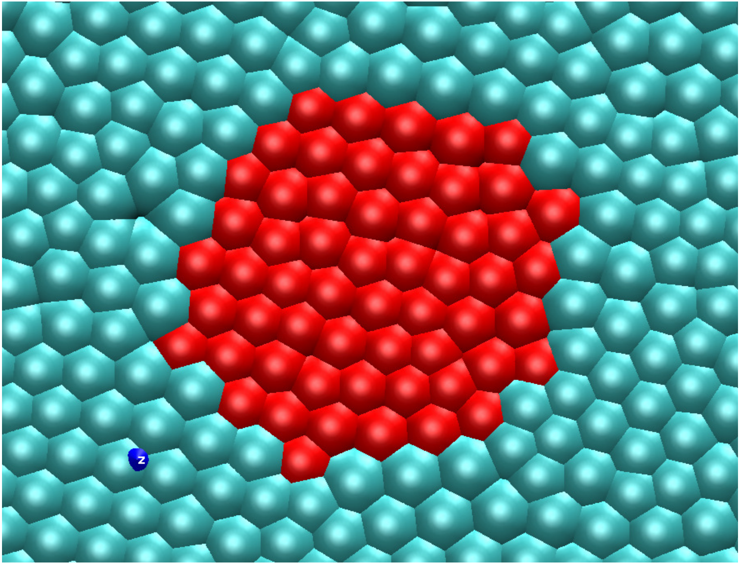
Example: Virtual strain sequence 2



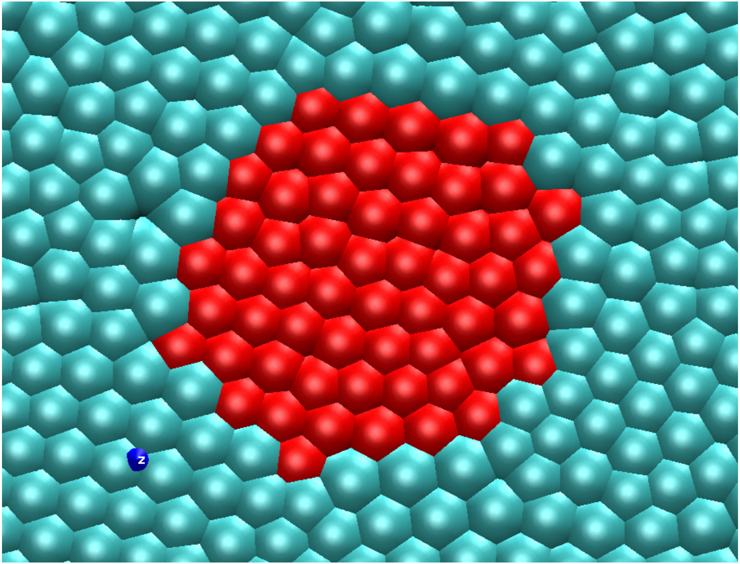
Example: Virtual strain sequence 3



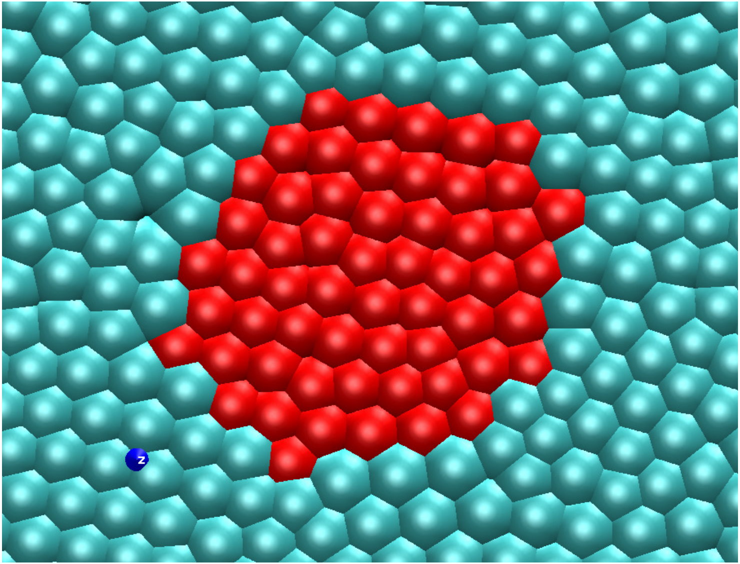
Example: Virtual strain sequence 4



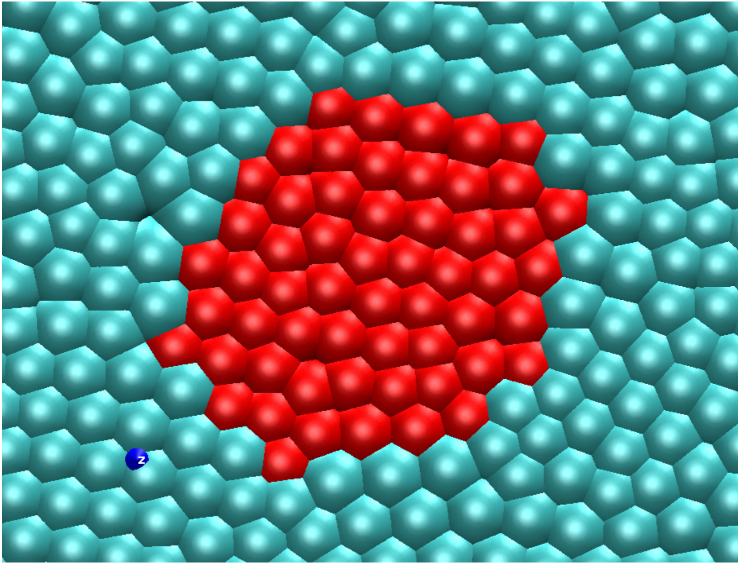
Example: Virtual strain sequence 5



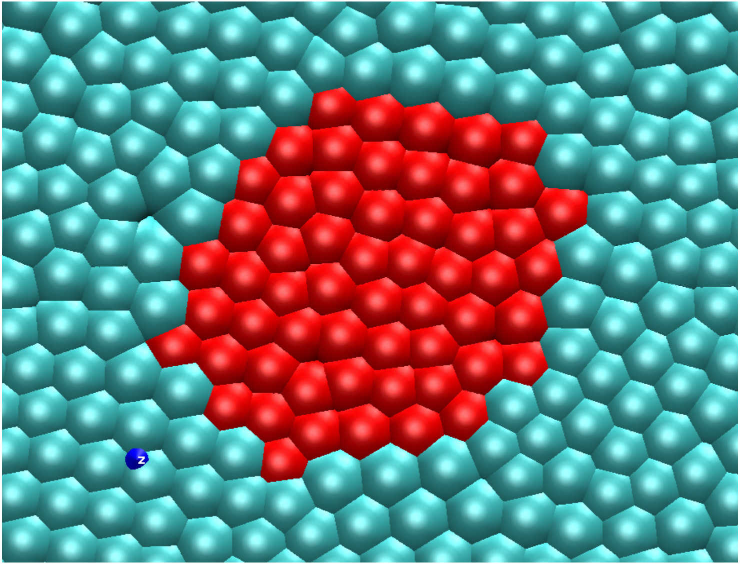
Example: Virtual strain sequence 6



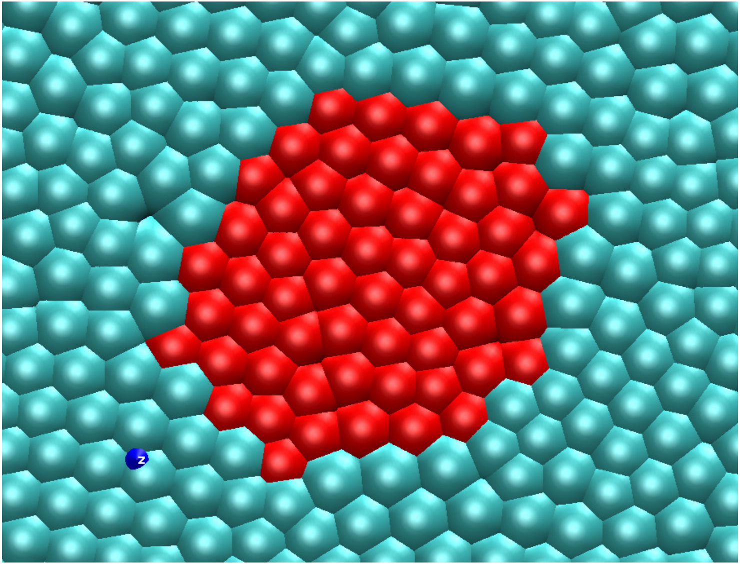
Example: Virtual strain sequence 7



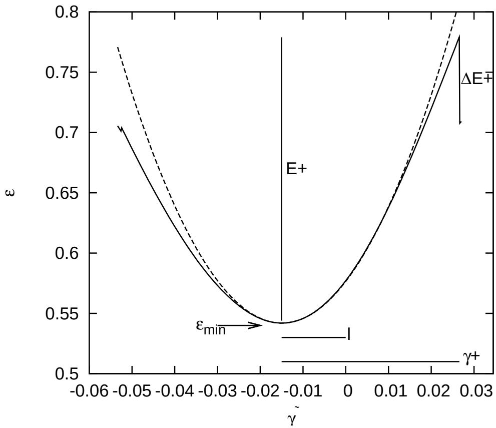
Example: Virtual strain sequence 8



Example: Virtual strain sequence 9



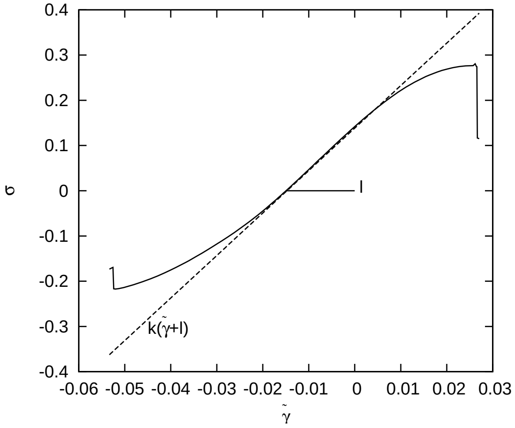
Element energy landscape



Extract: minimum energy $\epsilon_{\rm min}$, strain away from local minimum $l = -\tilde{\gamma}_{\rm min}$, yield strains $\gamma_{\pm}$, yield barriers $E_{\pm}$

Local modulus

Quadratic fit of energy near minimum, or linear fit of stress, gives local modulus k



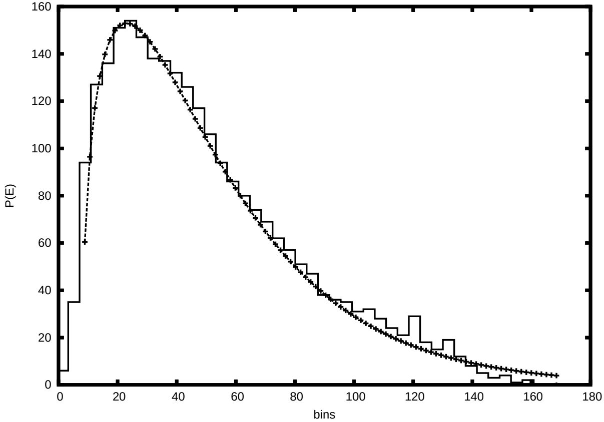
Systems studied

- Polydisperse Lennard-Jones mixtures (Tanguy et al), quenched to low temperatures ($T = 0.005 \ll T_{\rm g}$)
- Low shear rates $\dot{\gamma} \sim 10^{-3}$; $N = 10^4$ particles at $\rho = 0.95$
- Steady shear driven from the walls (created by "freezing" particles in top/bottom 5% some time after quench)
- Check for stationarity & affine shape of velocity profile before taking data
- Each element contains ≈ 40 particles (diameter $= 7$): large enough to have near-parabolic energy landscape, small enough to avoid multiple local yield events inside one element

Simulation demo

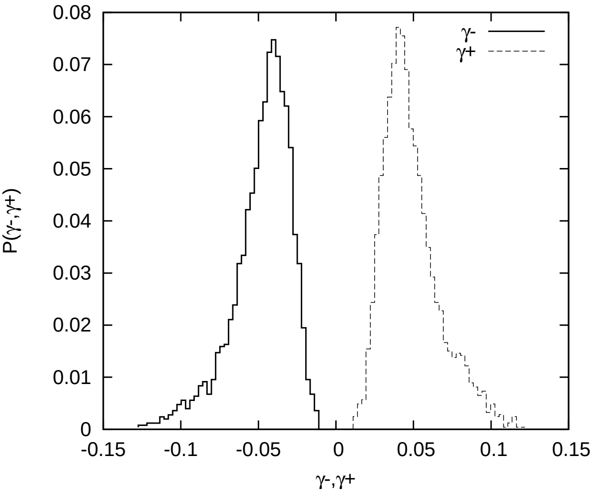
Close-up

Results: Yield energy distribution



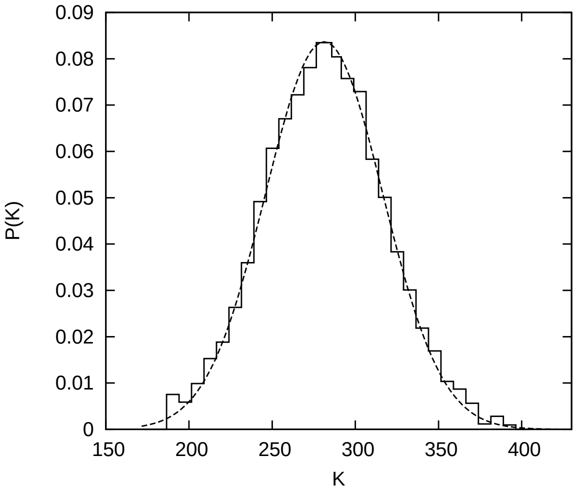
Exponential tail; detailed form can be fitted by SGR model

Yield strain distributions



Symmetric as assumed in SGR; gap around 0 or maybe power-law approach (exponent ≈ 4)

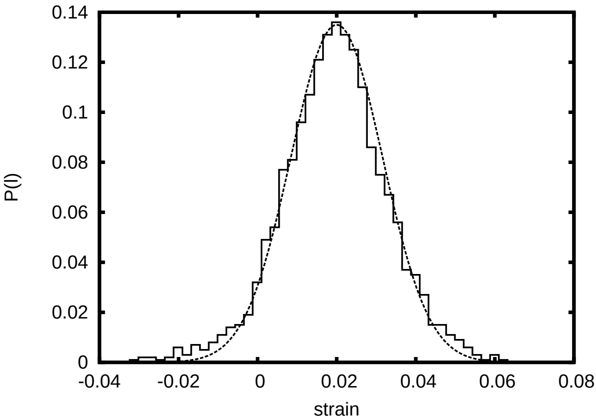
Modulus distribution



Clear spread; not constant as assumed in model.

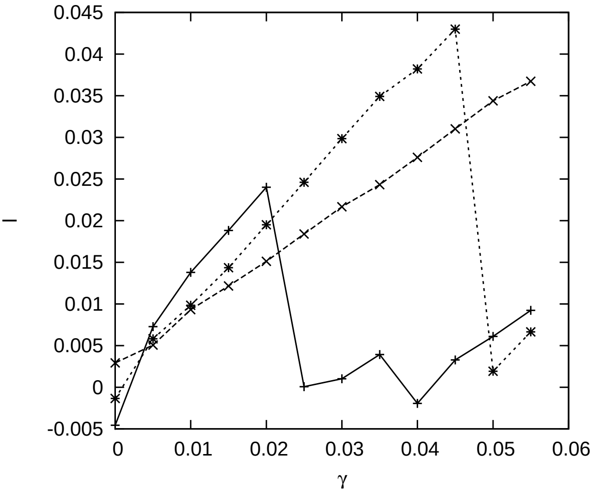
But yield strains $\gamma_{\pm}$ still controlled by $E_{\pm}$; no correlation with k

Local strain distribution



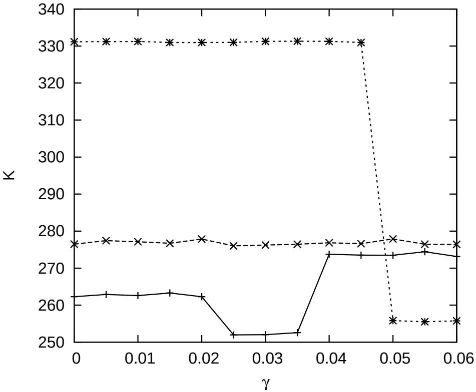
Negative l, need to extend SGR to allow frustration: $l \neq 0$ after yield ($\delta(l) \rightarrow \rho(l|E) \propto (1 - kl^2/2E)^b$ – but thermodynamics then broken?)

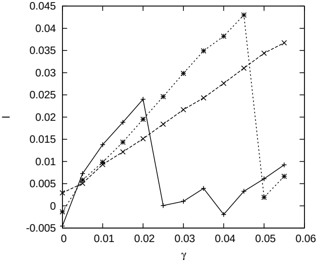
Dynamics: Evolution of local strain with time



Typical sawtooth shape assumed by SGR

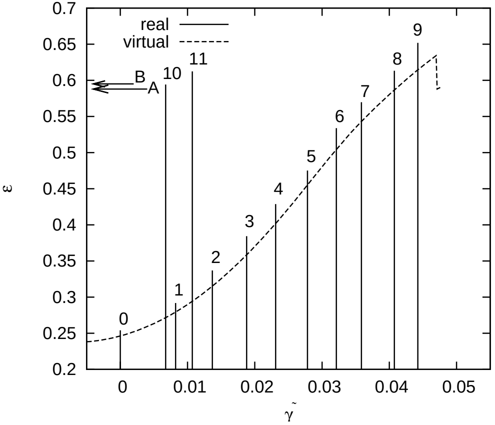
Change in other landscape properties
Example of modulus





Stays largely constant between yields as expected; same for yield barriers etc

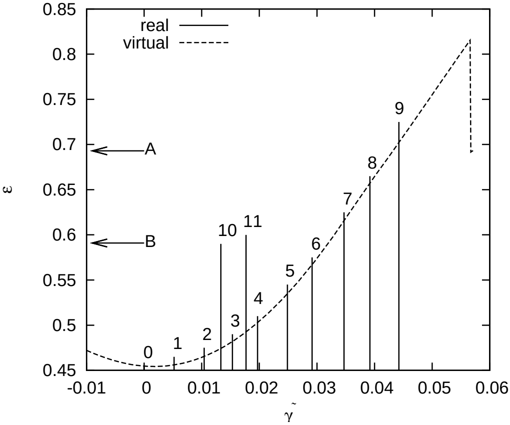
Comparing real and virtual deformations
Primary yield



Curve: virtual energy landscape.
Vertical lines: Real ϵ versus $l - l_0$ for uniform steps $\Delta\gamma$
Good match, even for energy drop after yield

Comparing real and virtual deformations (cont)

Induced yield



Curve: virtual energy landscape.

Vertical lines: Real ϵ versus $l - l_0$ for uniform steps $\Delta\gamma$

Summary for virtual strain analysis

- Virtual strain method for assigning local strains, yield energies
- Generic: can be used on configurations produced by any (low-T) simulation
- Steady state distributions in shear flow seem in line with SGR (detailed fits in progress), though e.g. local modulus $\neq$ const
- Dynamics of local strain has typical sawtooth shape; local strain rate is of same order as global one but not identical
- Energy landscapes for real and virtual deformations match (but not purely quadratic)
- To do: analysis of induced yield events – well modelled by effective temperature?

Outline

Effective temperature dynamics

Fielding Cates PS 2008

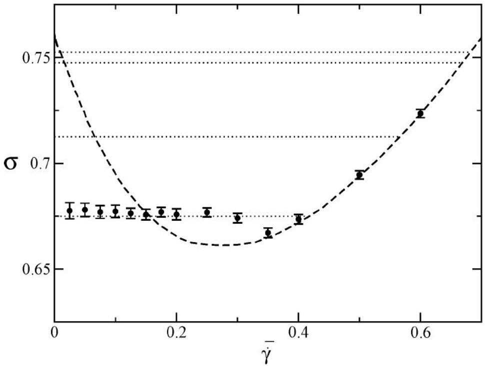
- Shouldn't effective temperature x be determined self-consistently by dynamics?
- To allow for potential shear banding, split sample in y (shear gradient)-direction
- Separate SGR model for each y, with $x(y)$
- Relaxation-diffusion dynamics:

$$\tau_x \dot{x}(y) = -x(y) + x_0 + S(y) + \lambda^2 \frac{\partial^2 x}{\partial y^2}$$

- x is "driven" by energy dissipation rate: $S = a\langle l^2 \exp(-[(E - l^2/2)/x])\rangle$
- Assume that x equilibrates (locally) quickly: $\tau_x \to 0$

Flow curve

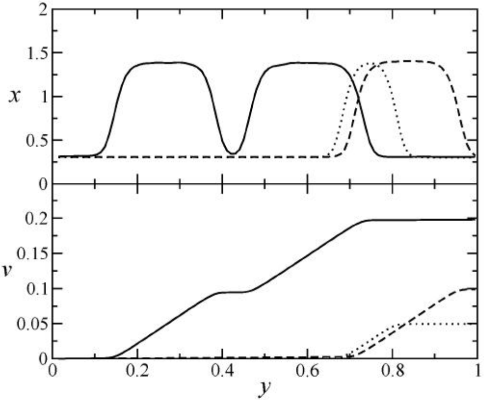
$a = 2,\ x_0 = 0.3$



- Steady state: $x = x_0 + 2a\sigma(x, \dot{\gamma})\dot{\gamma}$
- Shear startup with imposed mean $\dot{\gamma}$ across sample: shear banding

Nature of banded state

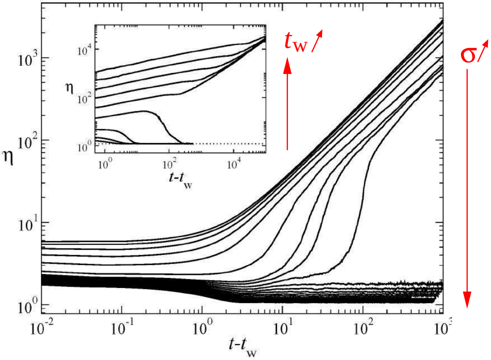
$a = 2$, $x_0 = 0.3$, $\dot{\gamma} = 0.05, 0.1, 0.2$



- "Hot" band: $\dot{\gamma} > 0$, ergodic
- "Cold" band: $\dot{\gamma} = 0$, aging

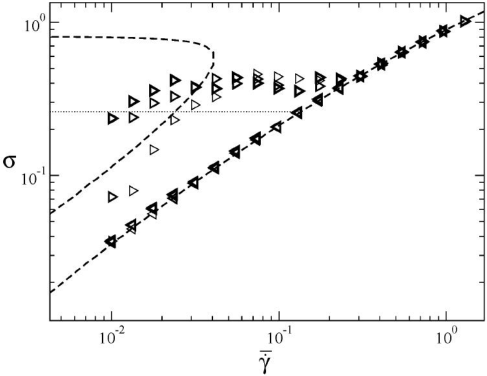
Viscosity bifurcation at imposed stress

Coussot, Bonn, . . .



- Plot instantaneous viscosity $\eta = \sigma/\dot{\gamma}$
- Sample only reaches steady flow when σ is large enough
- Depends on age $t_{\rm w}$ when stress is applied

Variation of driving term for x



- x now driven by yield rate, $S \propto \langle \exp(-[(E - l^2/2)/x]) \rangle$
- Hysteresis in shear rate sweep: banding on way up, stay on fluid branch on way down
- Resembles data for multi-arm polymers (Holmes Callaghan Vlassopoulos Roovers 2004)

Outline

Summary & Outlook

- Trap models for aging dynamics in glasses, focus on activation
- SGR model adds strain to this & re-interprets trap depths as yield energies
- Reproduces much (not all) of rheological behaviour of soft glasses
- . . . and some cytoskeletal rheology(?)
- Virtual strain method allows detailed comparison with simulations: some encouraging agreement, but also suggests modifications
- Dynamics of x: phenomenological models useful, but too much choice? Thermodynamic approach could fix driving term
- To do: linking to other approaches (STZ, Picard et al); coarse-graining from "microscopic" models?