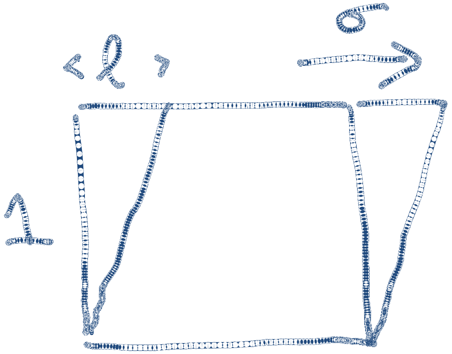
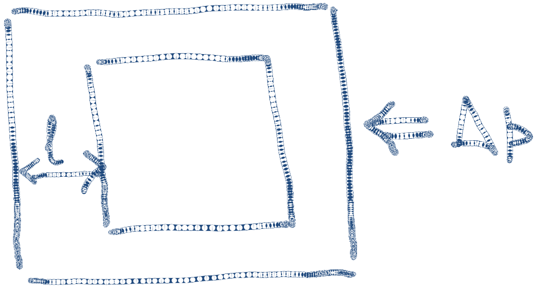
Soft Glassy Rheology : The SGR Model

Soft Matter





Shear

Shear strain ℓ

$\sigma = G\ell$

compression

comp. strain ℓ

$\Delta p \sim K\ell$

Hard C.M.: $G \approx K \simeq 10^{12}$ Pa

Soft C.M.: $G \ll K$

Shear deformation matters, volume changes don't

Soft Glasses

Soft nonergodic matter : dense emulsions (mayo)
(shaving) foam
dense colloids (paints)
etc.

System does not reach Boltzmann Eqm
(even at rest) ⇒ GLASS PHYSICS

Highly deformable, viscoelastic
⇒ PHYSICS OF FLOW
(rheology)

Approaches

First principles via $S(q,t)$: MCT

Empirical continuum models : "fluidity"

Approaches

First principles via $S(q,t)$: MCT

Mesoscopic model building : SGR , STZ

Empirical continuum models : "fluidity"

A compromise between tractability + empiricism

Goal of (theoretical) Rheology

The constitutive equation

velocity gradient tensor

$\kappa_{ij}(t) = \nabla_j v_i$

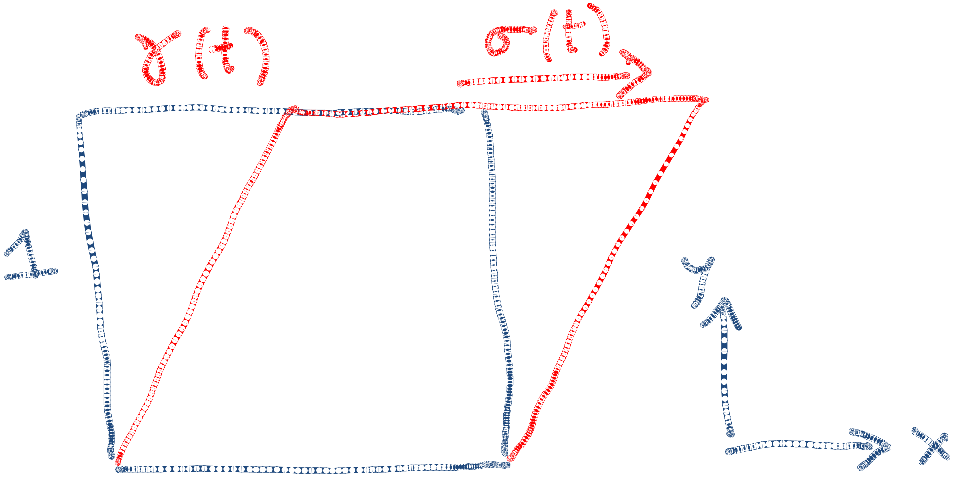
stress tensor $\sigma_{ij}(t)$

CE :

$$\sigma_{ij}(t) = \mathcal{F}[\kappa_{ij}(t'<t)]$$

functional relation between present stress and past deformation history

Today : Restrict to simple shear flows



$$K_{ij}(t) = \begin{pmatrix} 0 & \dot{\gamma}(t) & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

"Scalarized" C.E. :

$$\sigma(t) = \mathcal{F}[\dot{\gamma}(t'<t)]$$

For tensorial SGR :

MEC + P. Sollich, J. Rheol 48 (2004) 193

Bouchaud's Trap Model

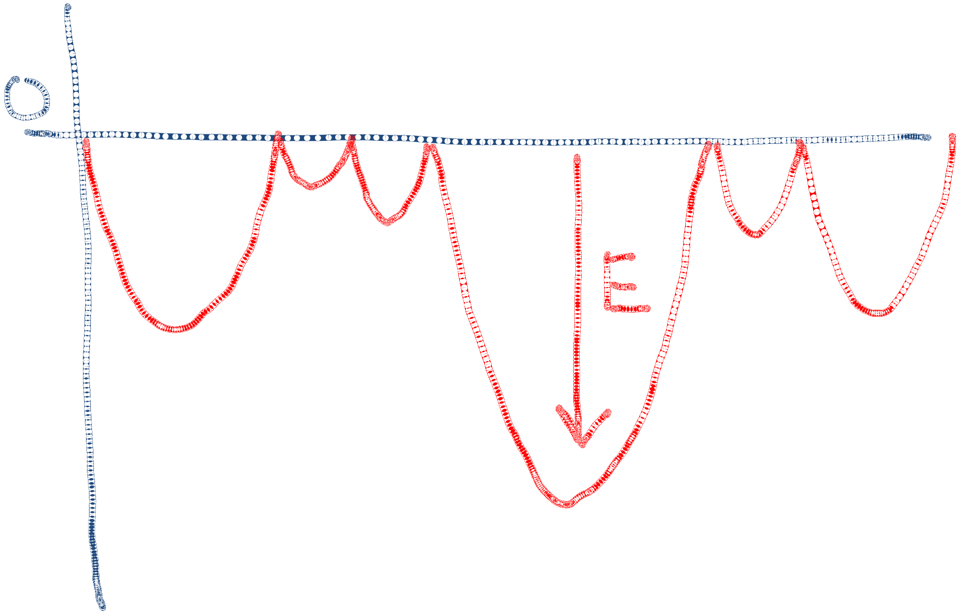
J-P Bouchaud J. Physique I 2 (1992) 1705

Glass : interacting many-body system

TM : ensemble of non-interacting particles hopping across well-chosen E-landscape

$\rho(E) =$ trap depth distribution

hop rate $\Gamma_0 e^{-E/x}$



Cunning Choice : $\rho(E) \propto \exp[-E/\langle E\rangle]$

units $\langle E\rangle = 1 \Rightarrow x = \frac{kT}{\langle E\rangle}$

Boltzmann S.S. : $P(E) \propto \rho(E)\, e^{+E/x}$

$= e^{-\left(1-\frac{1}{x}\right)E}$

Steady State exists only for $x > 1$: ERGODIC

Boltzmann not normalizable $x < 1$: weak E.B.

$x < 1$: particles move to ever-deeper traps

residence time $\sim \tau(t) \propto t$

"SIMPLE AGING"

From Trap Model to SGR

① Foams, emulsions etc

$\langle E \rangle \sim \gamma_{ow} R^2$ $\quad x = \frac{kT}{\langle E \rangle} \lesssim 10^{-3}$

rearrangement barrier

NEGLIBLE MOTION ☹

REMEDY (ad-hoc)

assume $x = \frac{kT_{eff}}{\langle E \rangle}$ is $O(1)$

$x \longleftrightarrow$ Effective (noise) temperature

Noise Sources

Coarsening / coalescence (foams/emulsions only)

Mechanical noise in rheometers etc.

or perhaps

$x \leftrightarrow$ Actual but nonequilibrium temperature of mesoscopic degrees of freedom

This view not necessary but consistent

PS + MEC arXiv : 1201.3275

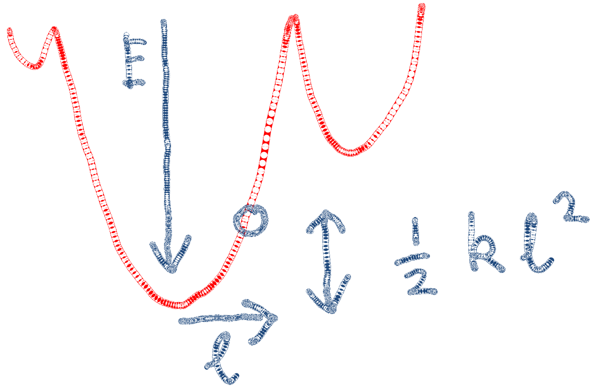
cf Langer + Bouchbinder on STZ (PRE 2010)

For NOW : x = some constant

From Trap Model to SGR

② Couple TM to deformation (scalar)

(2a)



Barrier height $E - \frac{1}{2}k\ell^2$

ℓ = local strain

k = elastic constant

JUMP RATE $\Gamma(E,\ell) = \Gamma_0 \exp\left[-\left(E - \frac{k\ell^2}{2}\right)/x\right]$

TOTAL " " $\Gamma(t) = \int P(E,\ell,t)\,\Gamma(E,\ell)\,dl\,dt$

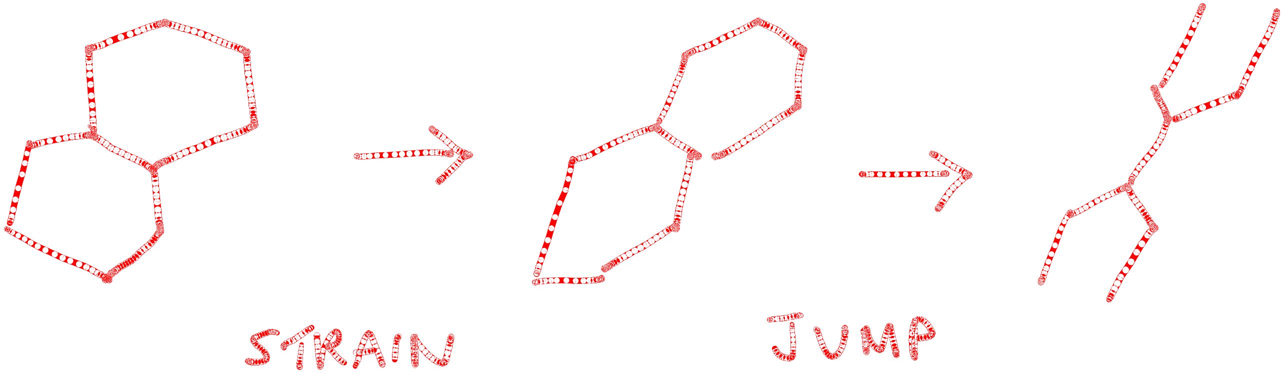
Post-jump: new well drawn from $\rho(E)$

$\ell = 0$ (unstrained)

(2b) BETWEEN JUMPS : Affine deformation

$\dot{\ell} = \dot{\gamma}(t)$ macroscopic strain rate

e.g. foam



Affine Model :

Parallel Mechanical Circuit

All elements share common $\dot{\gamma}$

Contrast : series circuit in STZ model

Langer + Bouchbinder PRL 106 (2011) 148301

2c Macroscopic Stress

$$\sigma(t) = k\langle l\rangle = k\int l\, P(E,l,t)\, dE\, dl$$

2d Equation of motion for P

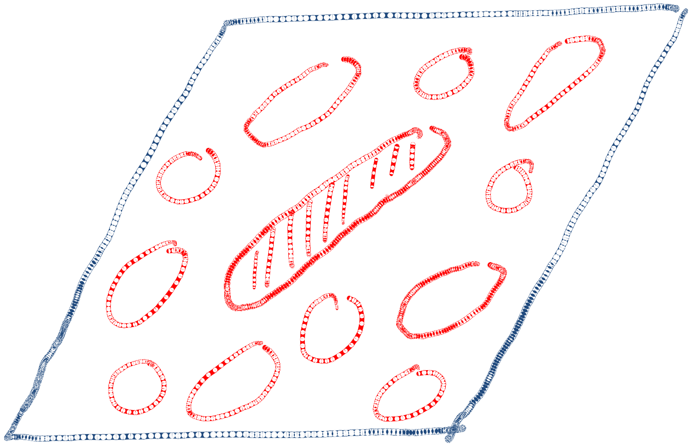
$$\frac{\partial}{\partial t} P(E,l,t) = \underbrace{-\dot{\gamma}\frac{\partial}{\partial l} P}_{\substack{\text{strain rate}\\ \dot{\gamma}\ \text{betw. jumps}}} \underbrace{- \Gamma_0 e^{-(E-\frac{1}{2}kl^2)/x} P}_{\substack{\text{strain-assisted}\\ \text{hopping}}} + \underbrace{\Gamma(t)\,\rho(E)\,\delta(l)}_{\substack{\text{new}\\ \text{wells}\\ \text{from } \rho(E)}}$$

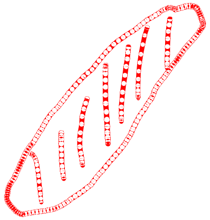
$$\boxed{\text{THATS IT!}}$$

PS et al PRL 78 (1997) 2020

P Sollich PRE 58 (1998) 738

SNAPSHOT





E large:
slow to yield

$\downarrow \quad \Gamma(E, \ell)$

E is reset,
drawn at random
from $\rho(E)$

FEATURES OF SGR MODEL

Physics controlled by deep traps

Large mesoscopic strains arise

Flow interrupts aging:

$$\dot{l} = \dot{\gamma} \quad \Rightarrow \quad E' = E - \tfrac{1}{2} k l^2$$

$\rightarrow 0$ in time $\sim \sqrt{E}/\dot{\gamma}$

$\ll$ quiescent $\tau \sim e^{E/x}$

In Glass Phase $(x < 1)$

$$P(E) \sim \underbrace{\rho(E)\; e^{E/x}}_{\text{Boltzmann}} \;\; \underbrace{f\left(E/E_{max} \right)}_{\text{cut-off}}$$

Bouchaud $(\dot{\gamma} = 0)$: $E_{max} = E_{max}(t)$

Steady flow : $E_{max} \sim x \ln\left[\sqrt{x} / \dot{\gamma} \right]$

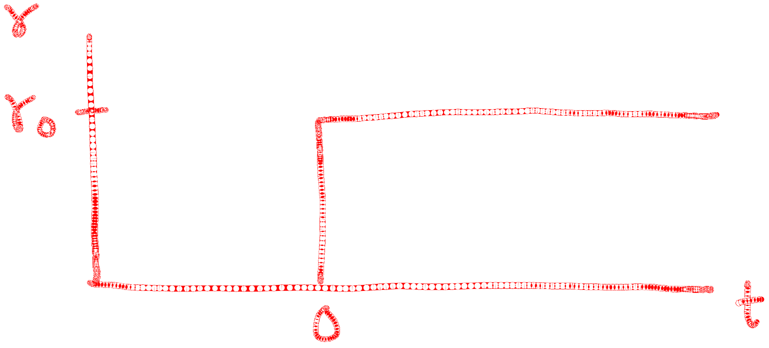
Time-dependent flow : complicated but aging persists in general

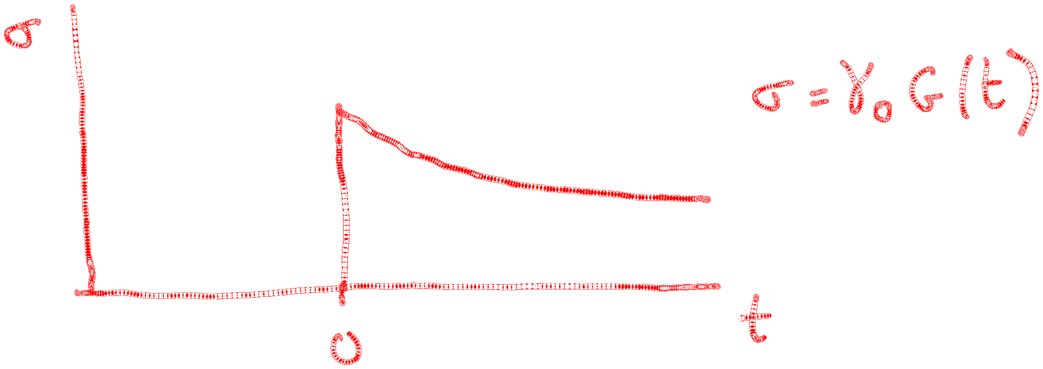
S Fielding, PS + MEC, J. Rheol. 44 (2000) 323

SGR : Rheological Predictions

Linear response : $x > 1$ only

step strain





Oscillatory :

$$\gamma(t) = \gamma_0 e^{i\omega t}$$

$$\sigma(t) = \gamma_0 e^{i\omega t} G^*(\omega)$$

$$G^*(\omega) = i\omega \int G(t) e^{i\omega t} dt$$

SGR: Power law spectrum of relaxation times

$$\tau^{-1}(E) = \Gamma_0 e^{E/x}$$

$$P_{ss}(E) = \rho(E) e^{E/x} = e^{-(1-\frac{1}{x})E}$$

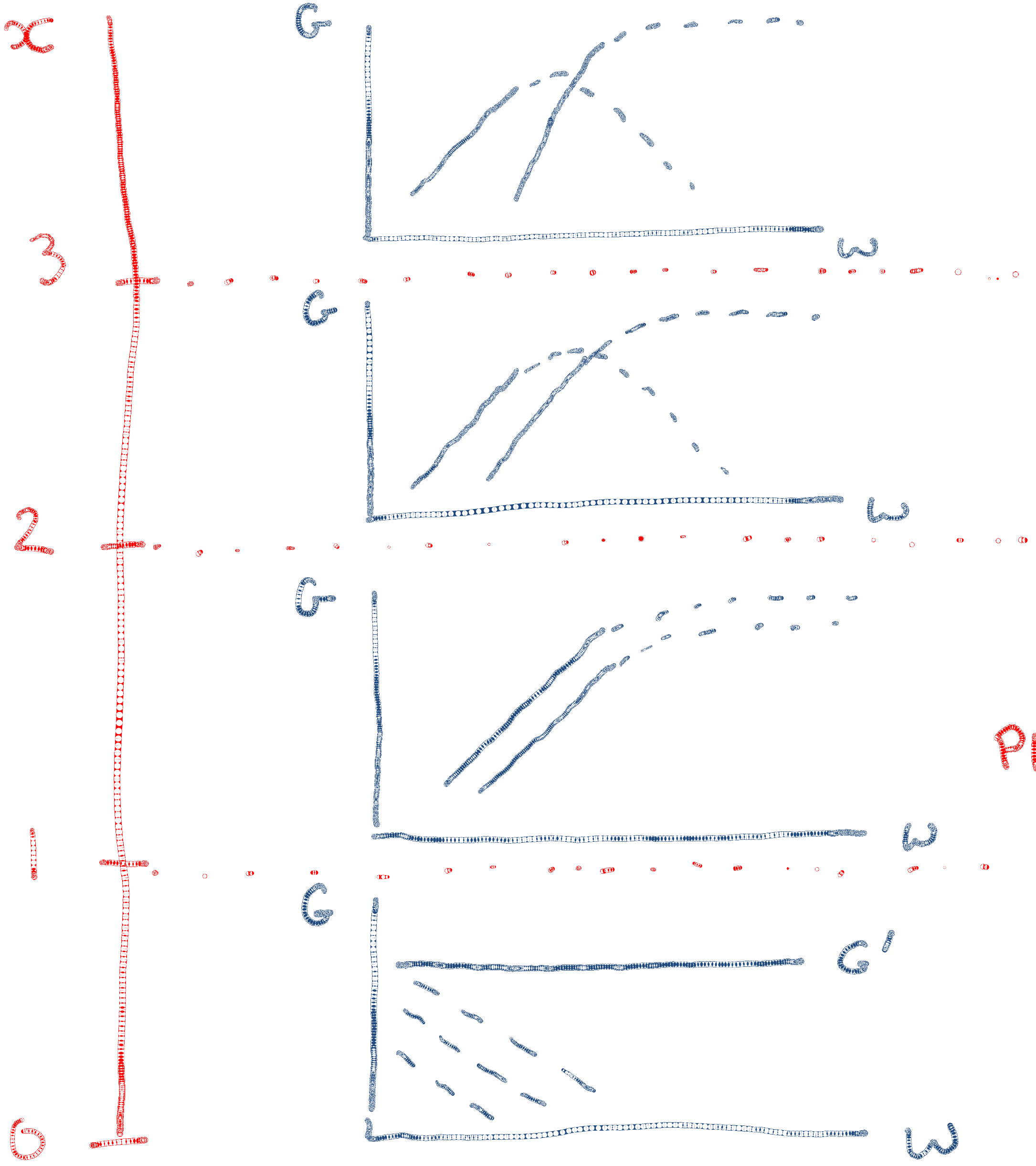
$$\Rightarrow \quad P(\tau) \propto \tau^{-x}$$

$$G(t) = \int P(\tau) e^{-t/\tau} dt$$

$$G^*(\omega) = \int P(\tau) \frac{i\omega\tau}{1+i\omega\tau} dt = G'(\omega) + i G''(\omega)$$

(Recall: no s.s. for $x<1$)

Low-frequency behaviour of G', G'':



$G' \sim \omega^2$

$G'' \sim \omega$

"Normal"
(maxwell)

$G' \sim \omega^{x-1}$ anomaly

$G'' \sim \omega$

$G' \sim \omega^{x-1}$

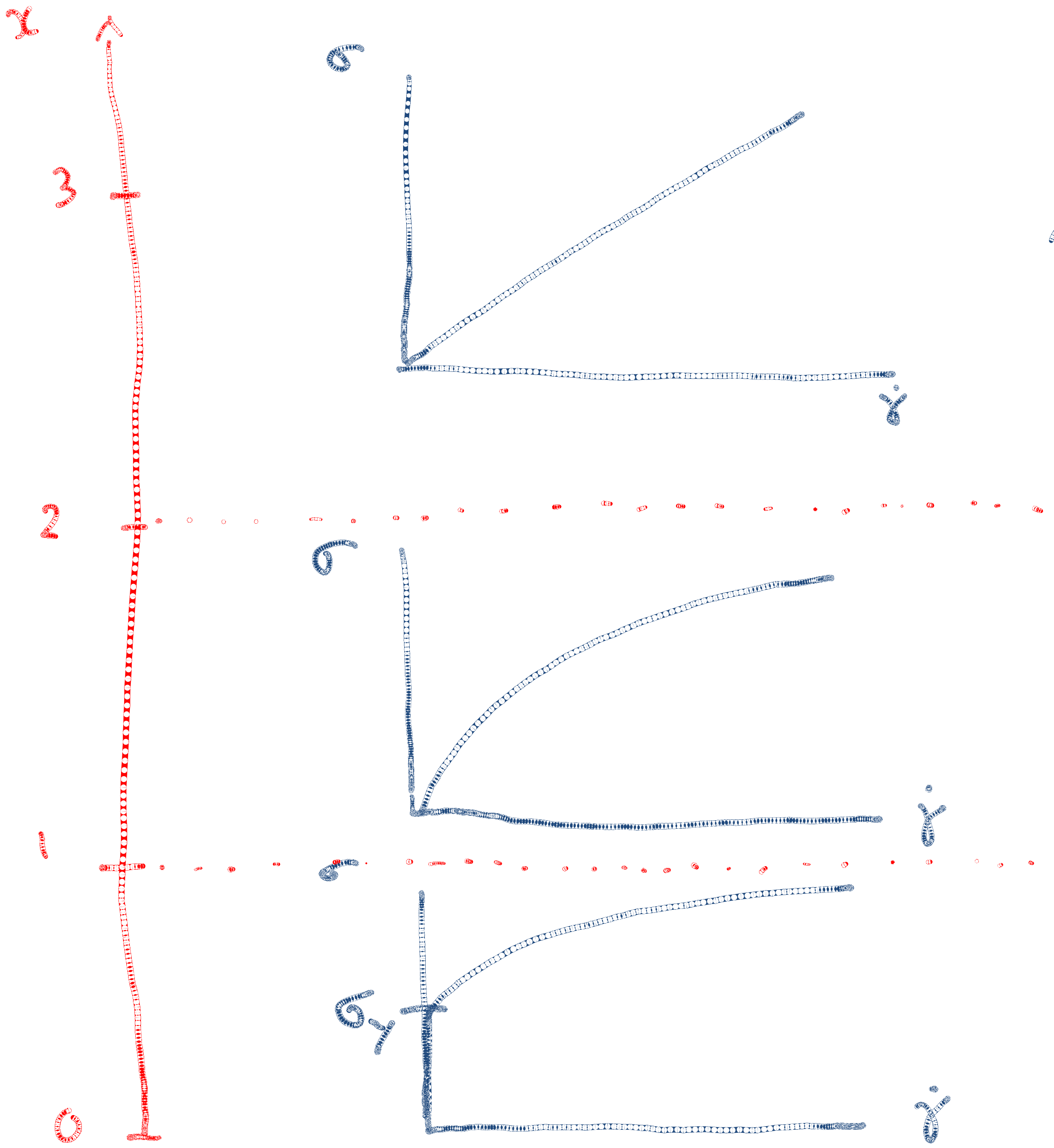
$G'' \sim \omega^{x-1}$

PLF = POWER LAW FLUID

$G' \sim \omega^0$ solid

G'' ↓ with age

NONLINEAR RHEOLOGY : steady flow, $\dot{\gamma} \ll \Gamma_0$



$\sigma = \eta \dot{\gamma}$

Newtonian

$\eta \sim \langle \tau \rangle \sim \frac{x}{2-x}$

$\sigma \sim \dot{\gamma}^{x-1}$

PLF

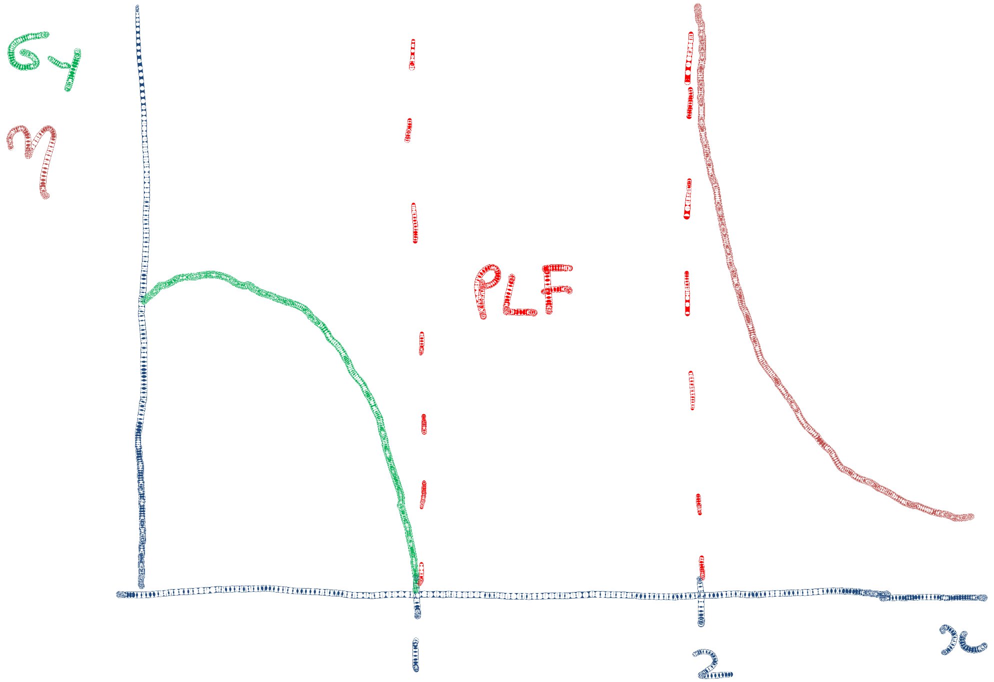
$\sigma \sim \sigma_y + \dot{\gamma}^{1-x}$

"Herschel-Bulkley"

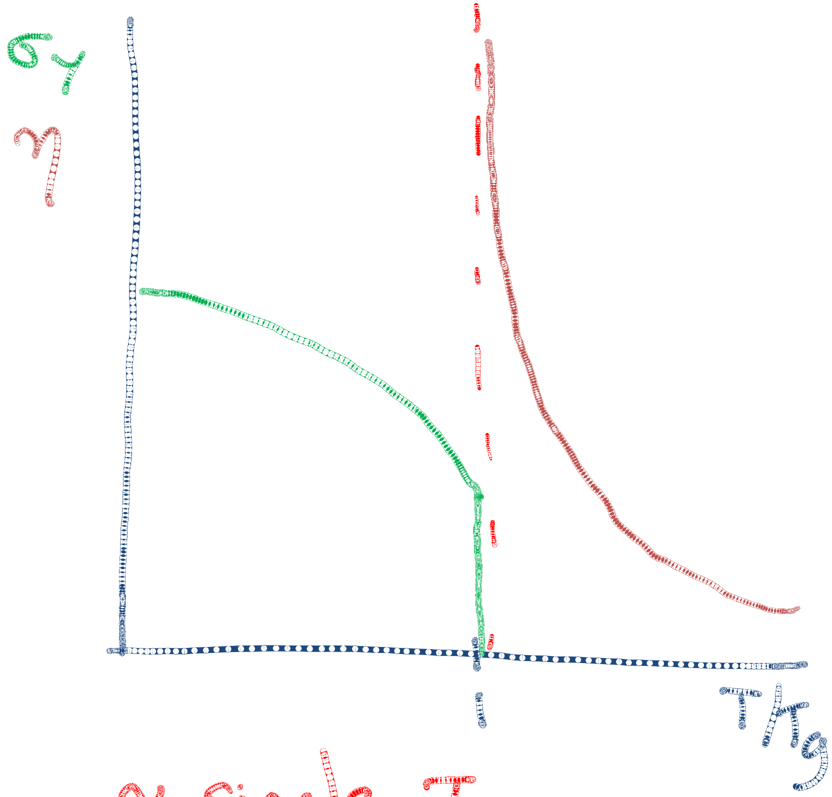
Comments: ① PLF & Herschel-Bulkley widely reported in soft matter

e.g. S. Holdsworth, Trans Inst ChE 71 (1983) 139

② SGR vs MCT



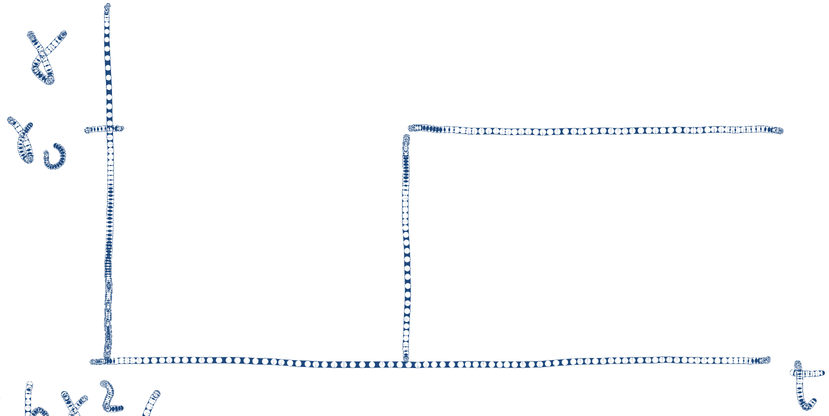
~ power law P(τ)



~ single τ diverges at T_g

STRAIN SOFTENING

Nonlinear step strain



All jump rates:

$$\Gamma_0 e^{-E/x} \to \Gamma_0 e^{-E/x} e^{\frac{1}{2}k\gamma_0^2/x}$$

linear response $\sigma = \gamma_0 G(t)$ $\gamma_0 \to 0$

nonlinear response

$$\sigma(t) = \gamma_0 G\left(e^{\frac{1}{2}k\gamma_0^2/x} t\right)$$

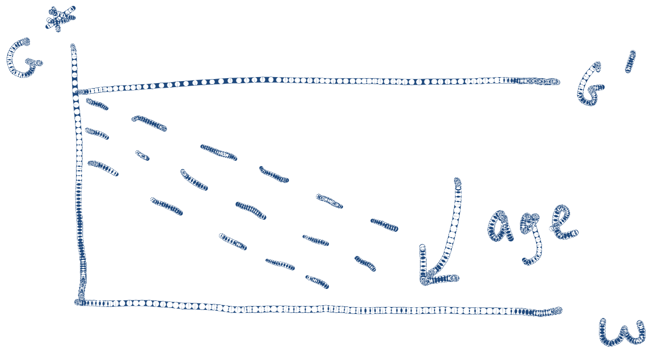
$\Uparrow$

strain-induced speed-up

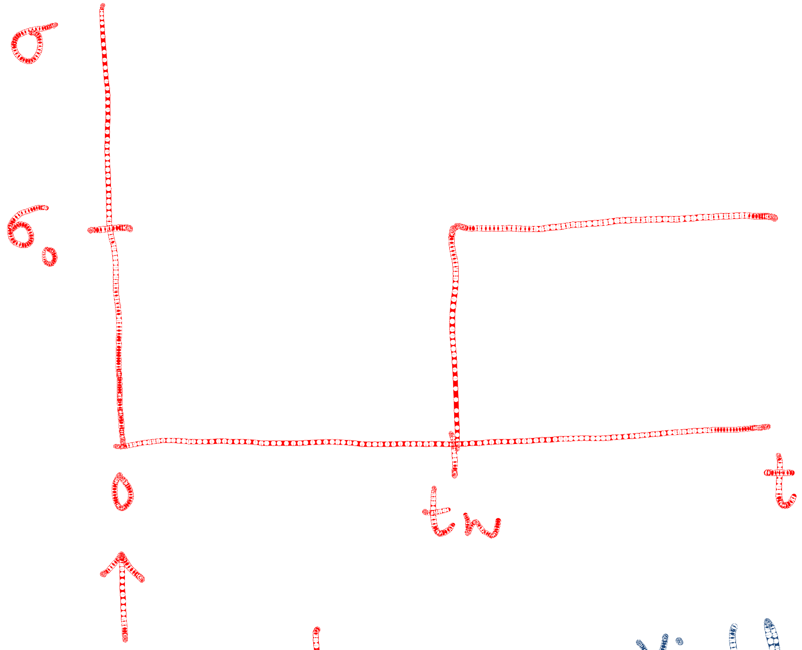
WIDELY SEEN:
Holdsworth op. cit.

RHEO-AGING

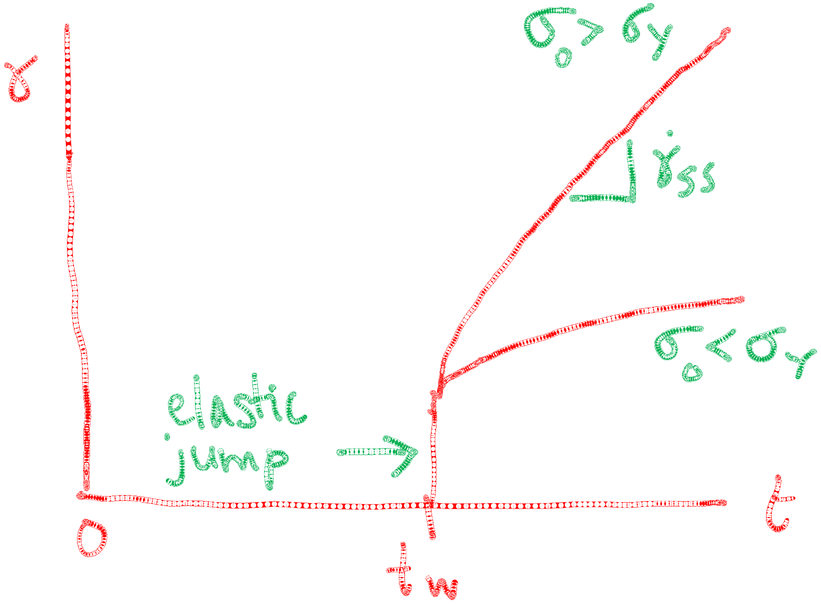
A: $G^*(\omega)$



B: Creep test

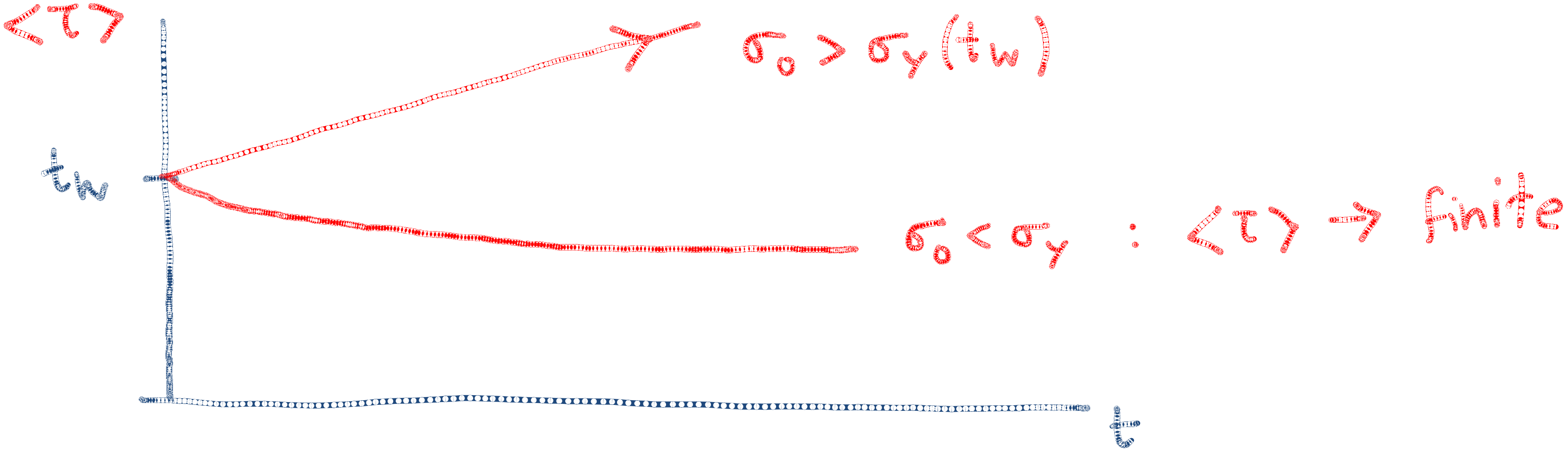


prepare sample

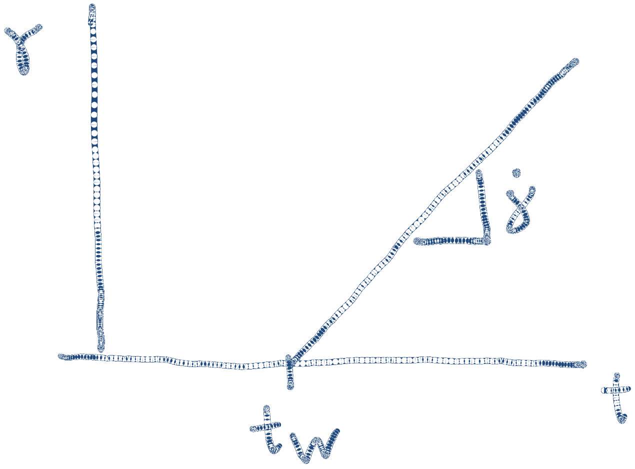


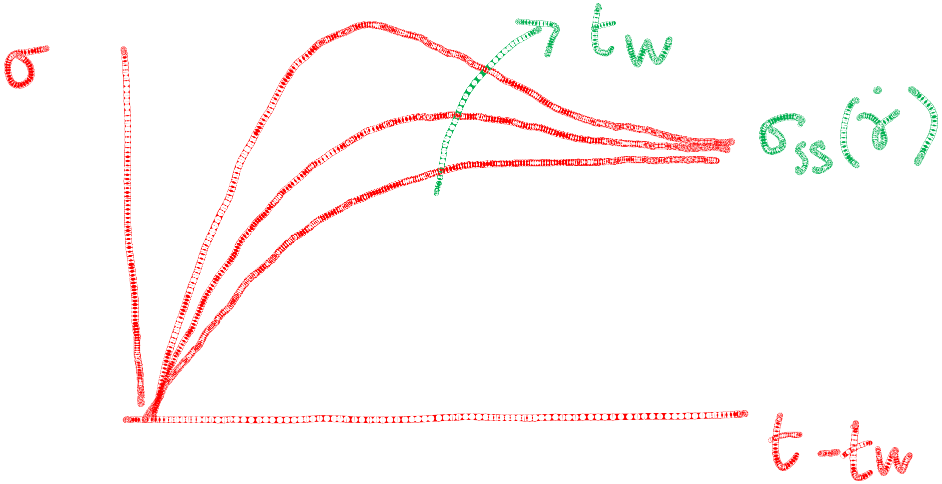
Yield stress $\sigma_y(t_w)$

Bifurcation in aging dynamics



C. Stress overshoot : startup of steady shear





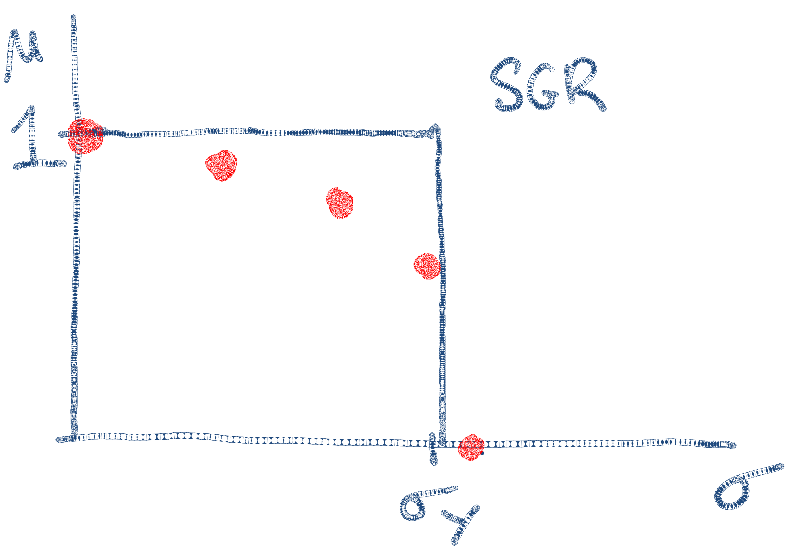
RHEO-AGING : widely reported in experiment

CAVEAT : SGR has simple aging only $\tau \propto t_w$

Reality is more complicated !

Sub-aging $\tau \sim t_w^{\mu}$

$\mu < 1$



- Data on microgel suspensions

M. Cloitre PRL 85 (2000) 4819

Super-aging $\mu > 1$

[mostly chemistry ?]

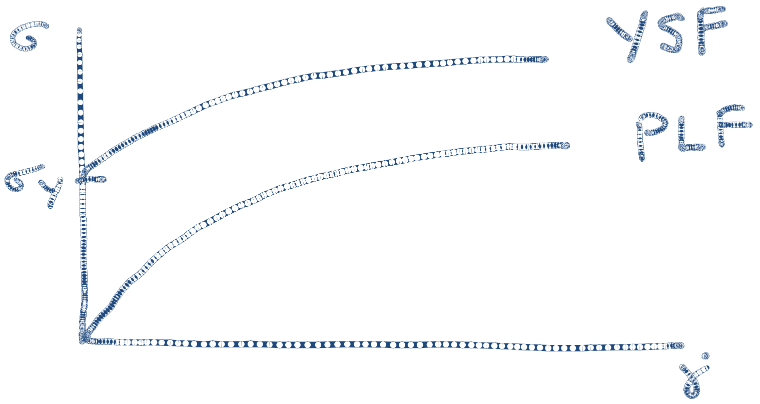
Over-aging

strain-assisted finding of deep traps

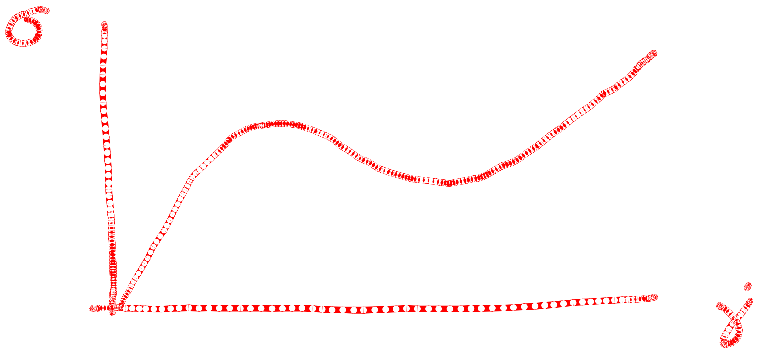
SHEAR-BANDING IN SGR

Flow curves $\sigma_{ss}(\dot{\gamma})$

"shear thinning"



Extreme shear thinning
(micelles etc.)
mechanical instability $\frac{d\sigma}{d\dot{\gamma}} < 0$



SHEAR-BANDING IN SGR

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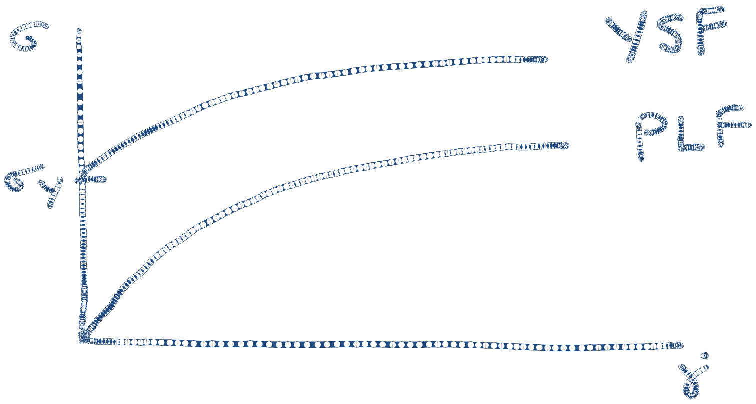

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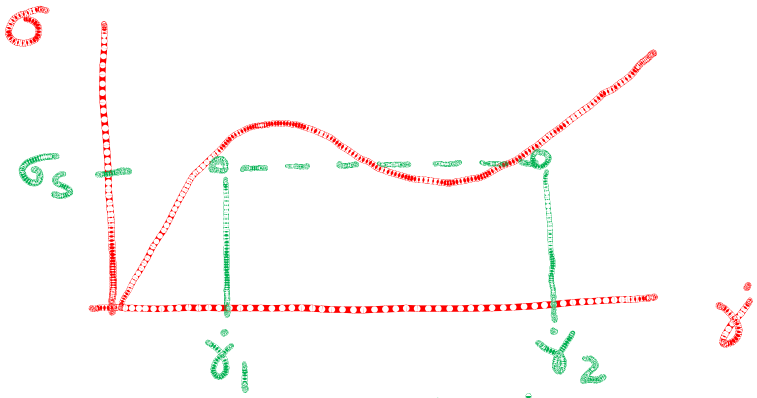


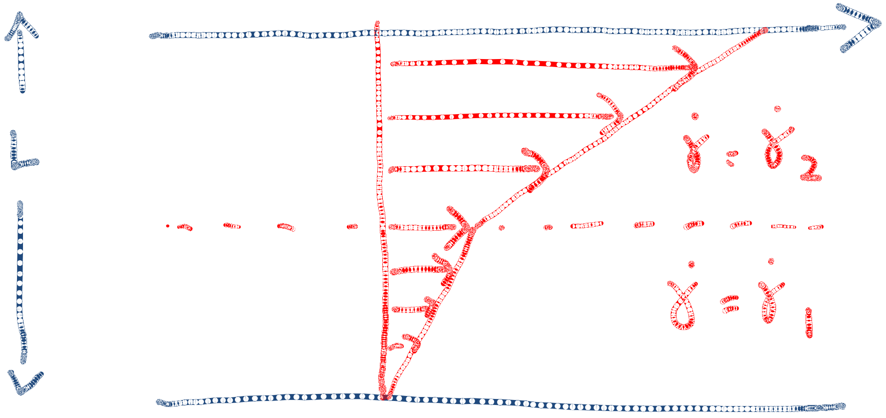
coexisting $\dot\gamma$ at common σ

stress selection:

σ_s fixed by nonlocal physics

(interfacial tension between bands)

Outcome :



$v = \dot{\gamma}_T L$

$\dot{\gamma}_1 < \dot{\gamma}_T < \dot{\gamma}_2$

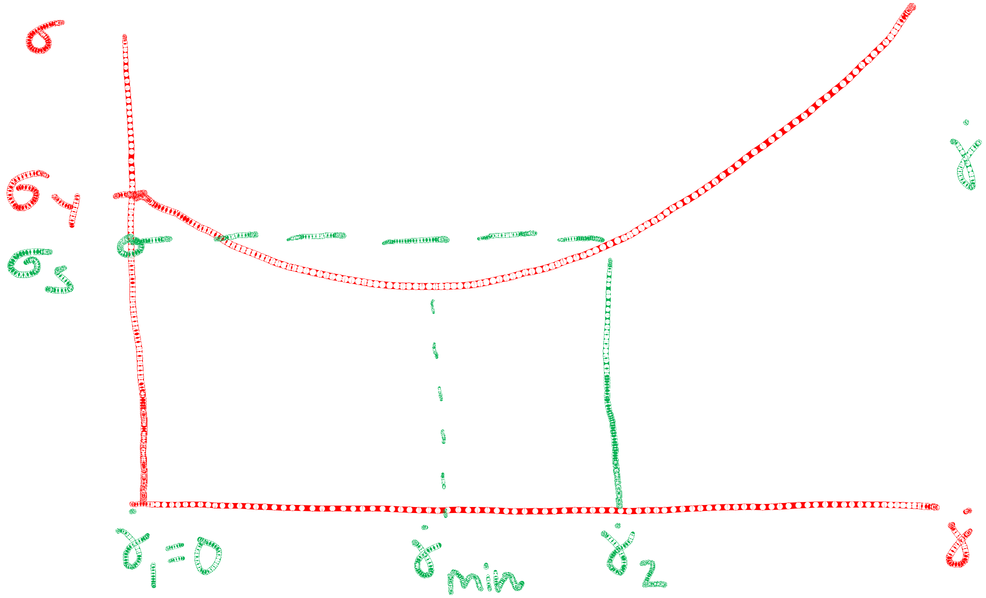
= shear banding

"Viscosity Bifurcation"

Shear banding with $\dot{\gamma}_1 = 0$

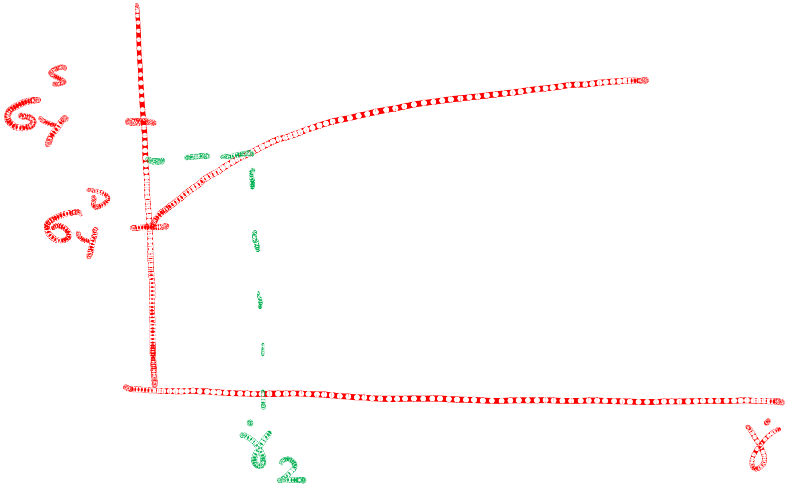
Scenario 1

P Coussot et al PRL 88 (2002) 218301



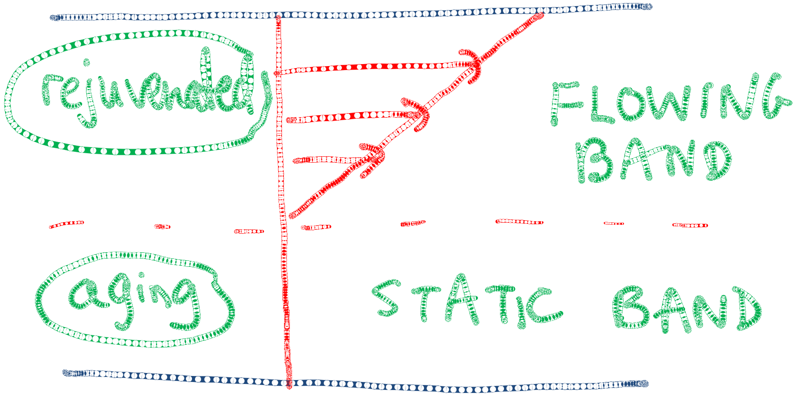
$\dot{\gamma}_{min}$ = lowest possible SS $\dot{\gamma}$

Scenario 2 (MCT)



static yield stress > dynamic

Both Scenarios :



CAN SHOW

SGR with x = constant exhibits neither scenario

YET

Shear banding (static + flowing) widespread in soft glasses!

P. Coussot Soft Matter 3 (2007) 528

SGR WITH $x \neq$ CONSTANT

Idea : shear in flowing band maintains "hot" x

arrested band has $x < 1$: aging

makes sense if x = noise caused by rearrangements

perhaps also if x = true temperature of mesoscopic modes

S Fielding et al Soft Matter 5 (2009) 2378

SUPPOSE

$$\dot{x}(r,t) = \underset{\substack{\uparrow \\ \text{local relax}^n \\ \text{to } x_0}}{\frac{-(x-x_0)}{\tau_x}} + \underset{\substack{\uparrow \\ \text{"heat" source} \\ \text{from jumps}}}{\zeta} + \underset{\substack{\uparrow \\ \text{"heat"} \\ \text{diffusion}}}{\lambda^2 \nabla^2 x}$$

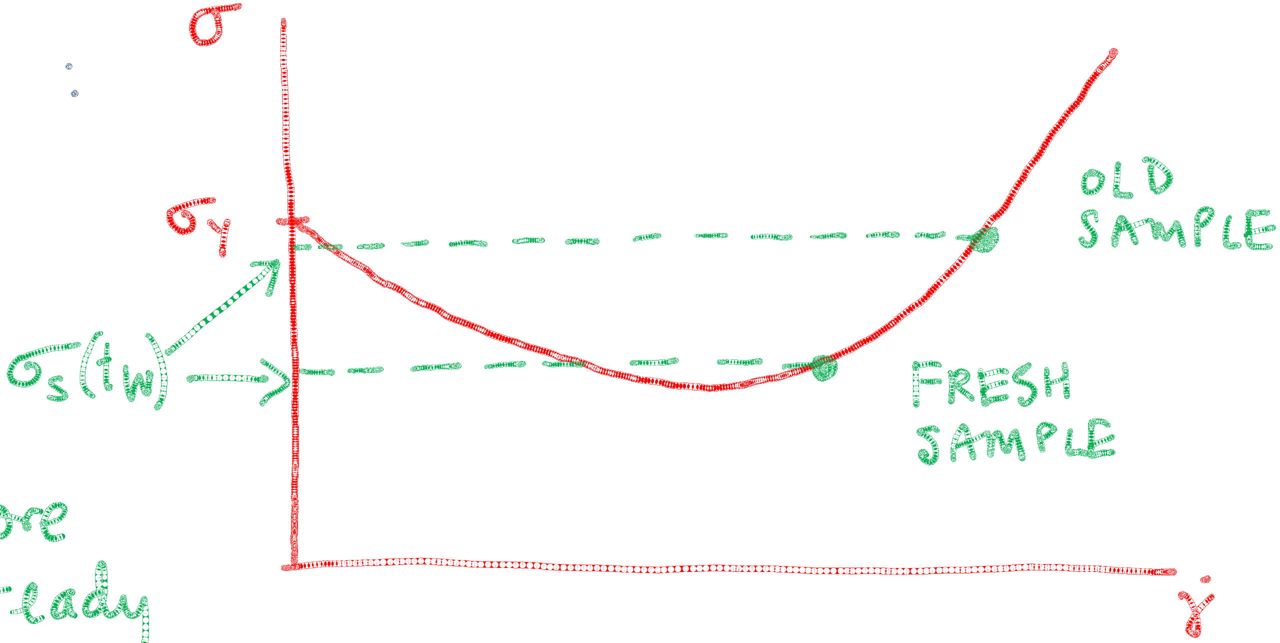
$$\zeta = \alpha \left\langle \ell^2/\tau \right\rangle_{P(E,\ell,t)} \qquad \Gamma_0 \tau(E,\ell) = e^{(E - \frac{1}{2} k \ell^2)/x}$$

= dissipation rate of stored elastic energy

For $x < 1$: Scenario 1

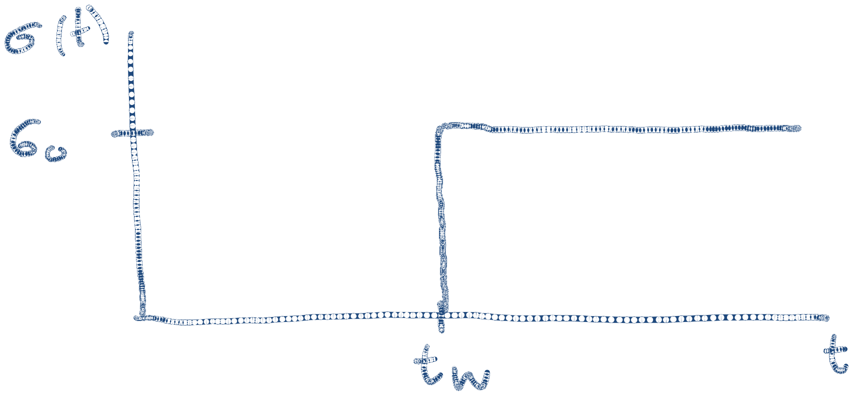
new feature : σ_s is history/age dependent

Flow curve :

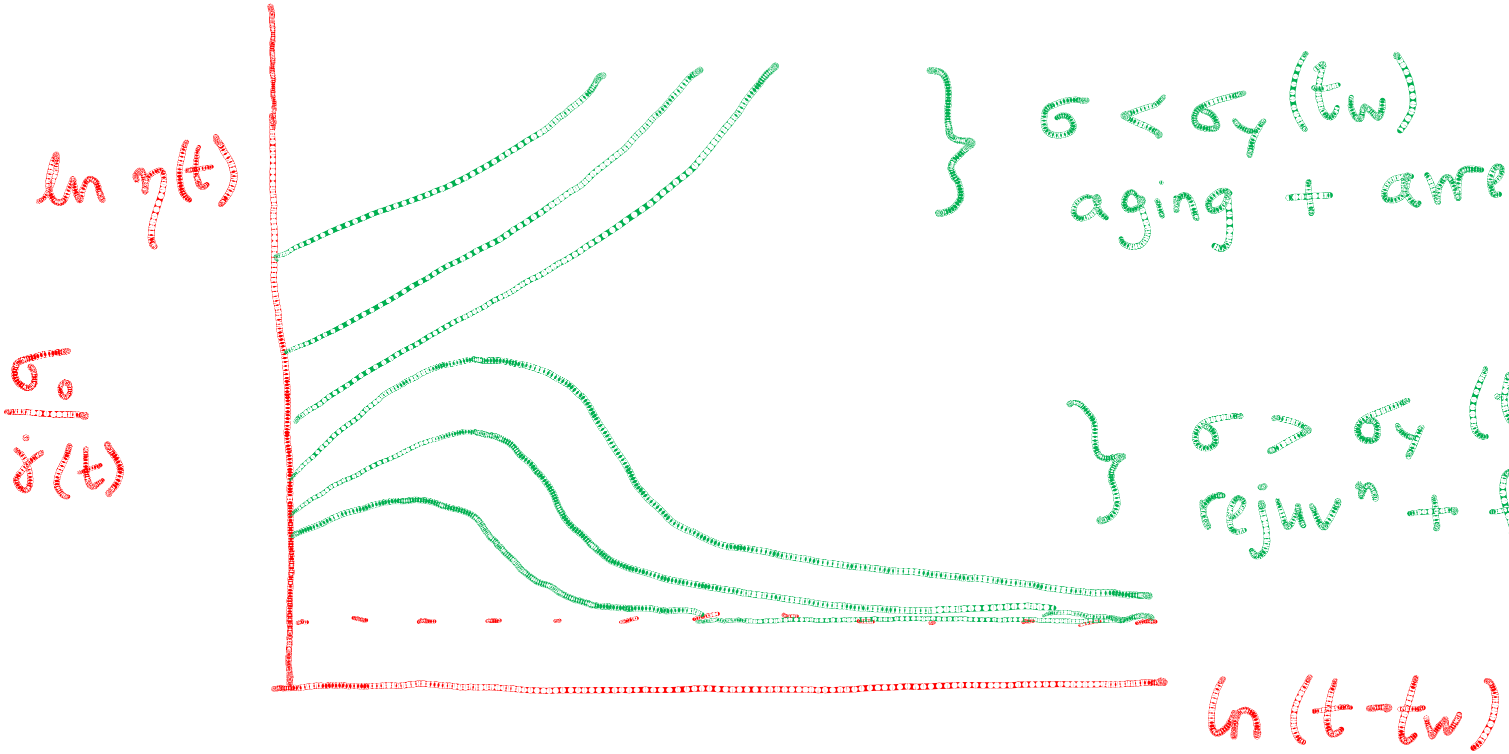


t_w = time before startup of steady flow

Viscosity Bifurcation in Creep Test



unless $\sigma_0 = \sigma_s(t_w)$
flow homogeneous
once steady



$$\eta = \frac{\sigma_0}{\dot{\gamma}(t)}$$

$\sigma < \sigma_y(t_w)$
aging + arrest

$\sigma > \sigma_y(t_w)$
rejuv^n + flow

THERMODYNAMIC VIEW ON SGR

Let χ = actual temp of mesoscopic modes

$\chi \neq$ room temp : slow equilibration

Follow Langer + Bouchbinder PRE 80 (2009) 031131, 2, 3

FIRST LAW

$$\underset{\substack{\uparrow\\ \text{config/}\\ \text{meso}}}{\dot{U}_c} + \underset{\substack{\uparrow\\ \text{kinetic/}\\ \text{vibr}^{n}}}{\dot{U}_K} + \underset{\substack{\uparrow\\ \text{reservoir}}}{\dot{U}_R} = \underset{\substack{\uparrow\\ \text{energy}\\ \text{from flow}}}{V\sigma\dot{\gamma}}$$

$$\chi = \frac{\partial U_c}{\partial S_c}, \quad \Theta = \frac{\partial U_K}{\partial S_K}, \quad T = \frac{\partial U_R}{\partial S_R}$$

First law becomes

$$\chi \dot{S}_c + \theta \dot{S}_K + \dot{U}_R - \underbrace{V\sigma\dot{\gamma}}_{\text{ext. work}} + \underbrace{\dot{\Lambda}\cdot\left.\frac{\partial U_\Lambda}{\partial \Lambda}\right|_{S_c}}_{\text{work done on meso modes }\Lambda} = 0$$

Second law

$$\dot{S}_c + \dot{S}_K + \dot{S}_R \geq 0$$

$\Big\downarrow$ plausible steps

$$W = V\sigma\dot{\gamma} - \dot{\Lambda}\cdot\frac{\partial F_\Lambda}{\partial \Lambda} \geq 0$$

$$F_\Lambda = U_\Lambda - \chi S_\Lambda$$ free energy of meso modes

For SGR :

$$\Lambda \quad \leftrightarrow \quad P(E,\ell)$$

$$U_\Lambda \quad \leftrightarrow \quad \int dE\, d\ell \;\; P(E,\ell)\left[\tfrac{1}{2}k\ell^2 - E\right]$$

$$S_\Lambda \quad \leftrightarrow \quad \int dE \;\; P(E)\, \ln(P(E) - 1)$$

with $P(E) = \int P(E,\ell)\, d\ell$

[ℓ is $\underline{\text{not}}$ independent dynamically].

Can confirm $\quad w \geq \quad$ at fixed x

$$x = \chi = T_{meso}$$

$w = 0$ iff $P =$ Boltzmann

P.S: MEC arXiv 1201.3275

Constraints on x-dynamics

Recall $$\dot{x} = -\frac{(x-x_0)}{\tau_x} + \zeta + \lambda^2 \nabla^2 x$$

$$\zeta = \alpha \left\langle \ell^2/\tau \right\rangle_{P(E,\ell,t)}$$

$\propto W$ in steady state

Consistent with Thermodynamic view

Alternative choice

$$\zeta = \alpha \left\langle 1/\tau \right\rangle \propto \Gamma(t)$$

total yield rate

Plausible if x = "just noise"

Ruled out if $x = T_{meso}$

CONCLUSIONS

SGR : Appealing but ad-hoc model for mesoscopic dynamics in soft glasses

Yield stress fluids

Power law fluids

(Simple) rheo-aging

Interpretation of x remains elusive

SGR with x dynamics

plausible extension describes

viscosity bifurcation

shear banding – static + flowing

Thermodynamic View

$x = T_{meso}$

consistent, not necessary

if adopted, constrains x dynamics

Experiments

$\gtrsim$ qualitative agreement widespread

a lot still missing (eg. sub-aging)

Thank you for your attention !