Michael Cates KITP Glasses, Apr 13, 2010

(Soft) Glass Rheology

Phenomenology of Colloidal/Soft Glasses

Experiments: Viscosity Bifurcation, Bulk Shear Banding

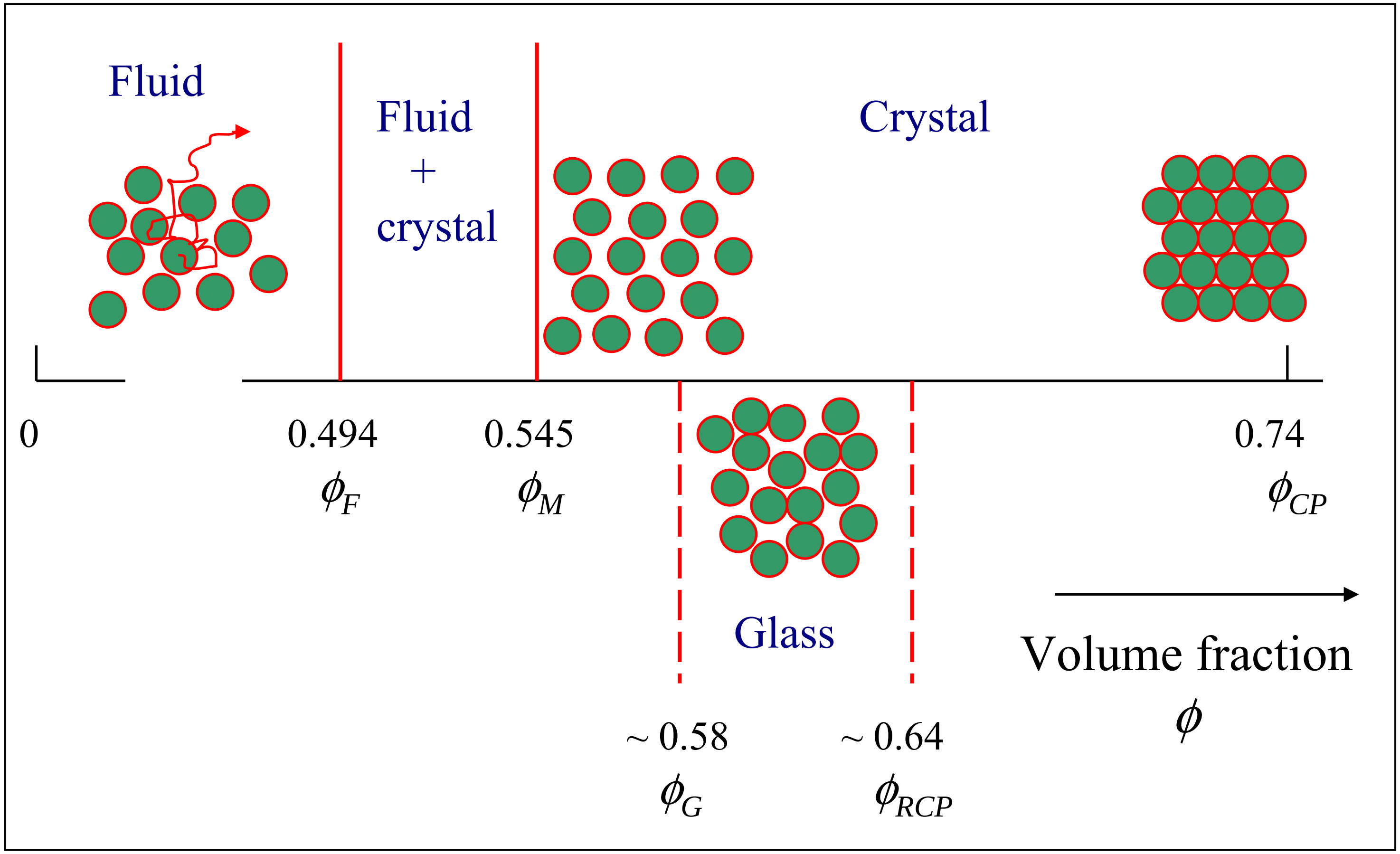
Yet: Monotonic Flow Curves in Standard Models (SGR, MCT)

Various Models for Viscosity Bifurcation

1. SGR with ‘noise diffusion’
S. M. Fielding, P. Sollich, MEC, Soft Matter 5, 2378 (2009)
2. MCT: dynamic vs static yield stress
J. Brader, T. Voigtmann, M. Fuchs, R. Larson, MEC, PNAS 106,15186 (2009)
3. Concentration coupling
V. Schmitt, C. Marques, F. Lequeux, PRE, 52, 4009 (1995),
R. Besseling et al, in preparation
4. Discontinuum model (wall effects)
L. Isa, R. Besseling, W.C.K. Poon, PRL 98, 198305 (2007)

FUNDING: SUPA EPSRC THE ROYAL SOCIETY

Equilibrium and Metastable States of Hard Sphere Colloids



crystallization suppressed: fluid/glass transition observable

Hard-sphere colloidal crystals and glasses (P. Pusey)

Fluid	Fluid + Crystal	Crystal	Glass
$\phi < 0.494$		$\phi > 0.545$	$\phi > 0.58$

<u>Hard Sphere Glasses: A Paradigm for Arrested Soft Matter</u>

HS colloids at $\phi \approx 0.58$ closely approximate an <u>ideal glass transition</u> at which:

Terminal time τ smoothly diverges [hence also $\eta = G_o\tau$]

$\Rightarrow$ $G'(\omega \rightarrow 0)$ jumps from zero to G_o

A nonzero yield stress σ_y develops

$G_o \approx k_B T$ per particle: 10-1000 Pa

Rheological studies practical (cf. molecular glasses)

First-principles statistical mechanics viable (MCT)

Clean model for generic soft glasses

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Terminal time τ smoothly diverges [hence also $\eta = G_o\tau$]

$\Rightarrow$ $G'(\omega\to 0)$ jumps from zero to G_o

A nonzero yield stress σ_y develops [discontinuously]

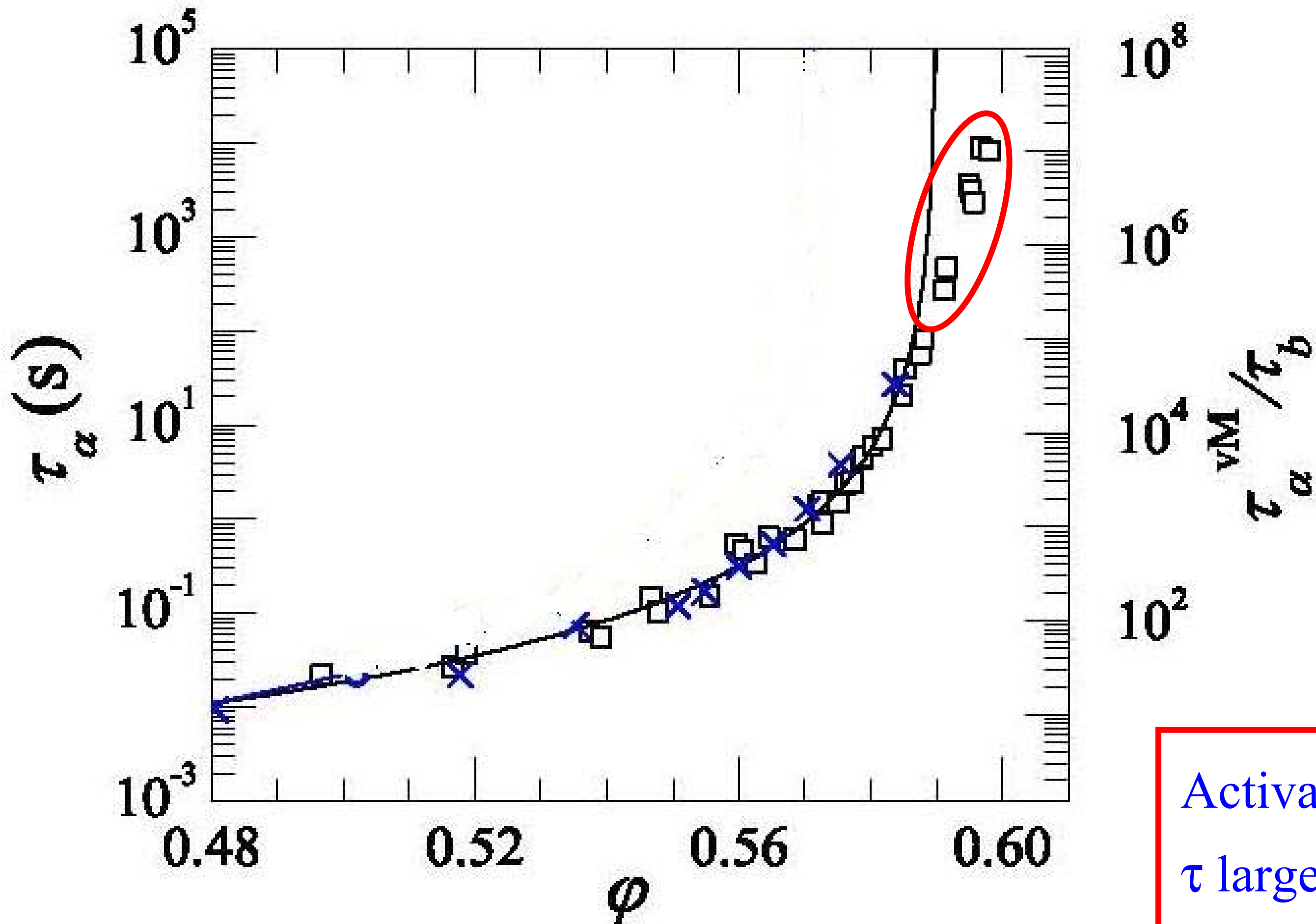
$G_o \approx k_BT$ per particle: 10-1000 Pa

Rheological studies practical (cf. molecular glasses)

First-principles statistical mechanics viable (MCT)

Clean model for generic soft glasses [although not typical]

Glass Transition: Close to Ideal... but not Ideal

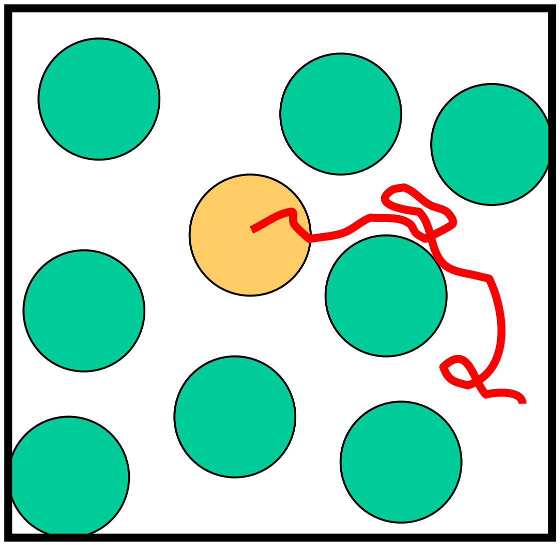


x: van Megen et al (1998)
□: Cipelletti 2009
—: MCT fit

Activated cage hopping:
τ large but not infinite
Yield stress → "apparent"
"Glass" = $\tau \gg t_{exp}$

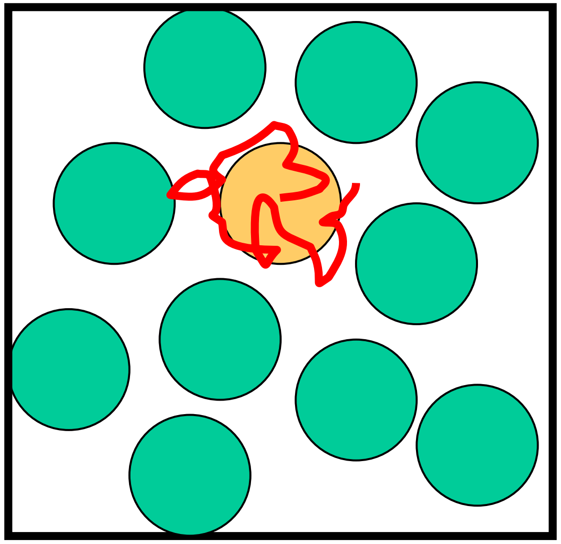
Linear Rheology at Ideal Glass Transition

Caging:



$\phi < \phi_g$: finite diffusivity

$\boxed{\tau \approx \text{cage lifetime}}$

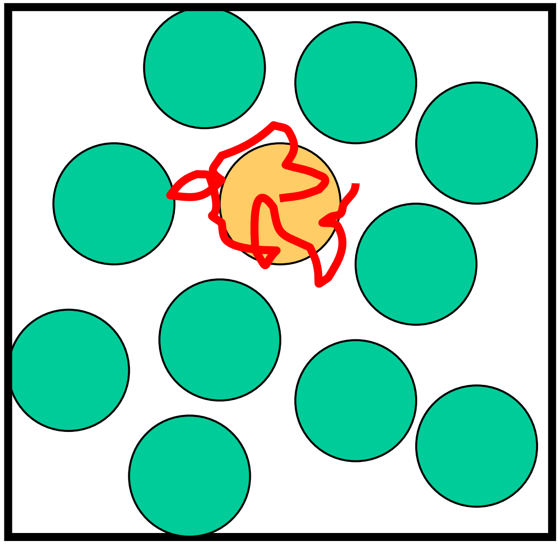


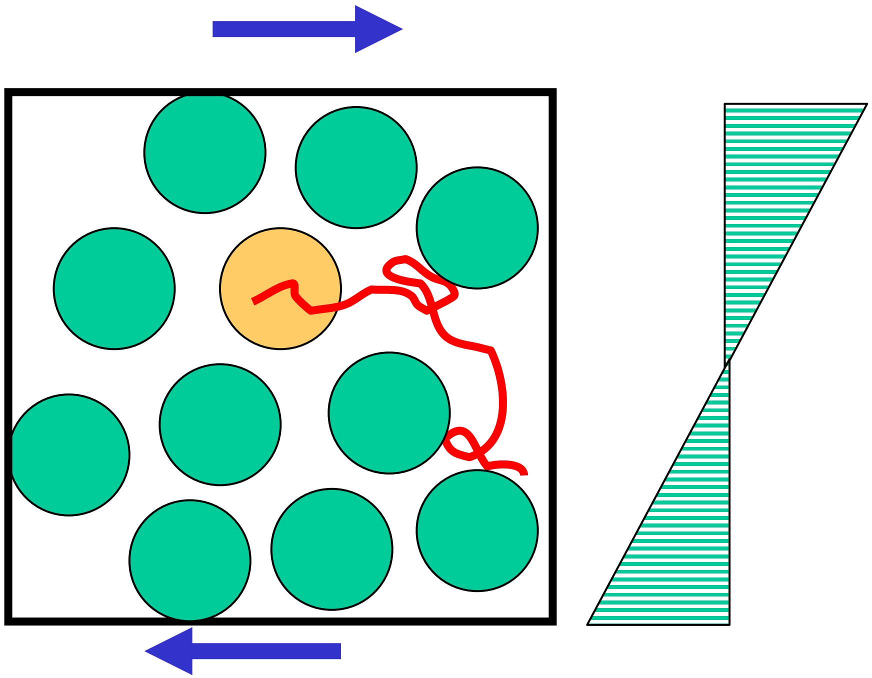
$\phi > \phi_g$: zero diffusivity

$\boxed{\tau = \infty}$

Yield and Shear Thinning

Shear stress σ can break cages





$\sigma < \sigma_y$: elastic solid, strain γ

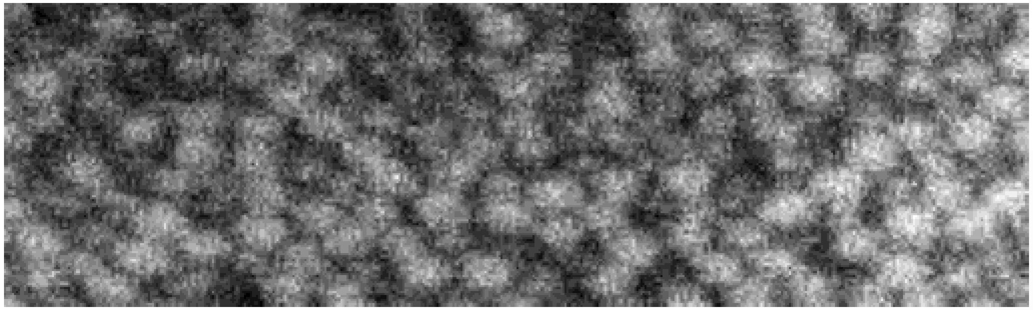
$\sigma > \sigma_y$ flowing liquid, strain rate $\dot{\gamma}$

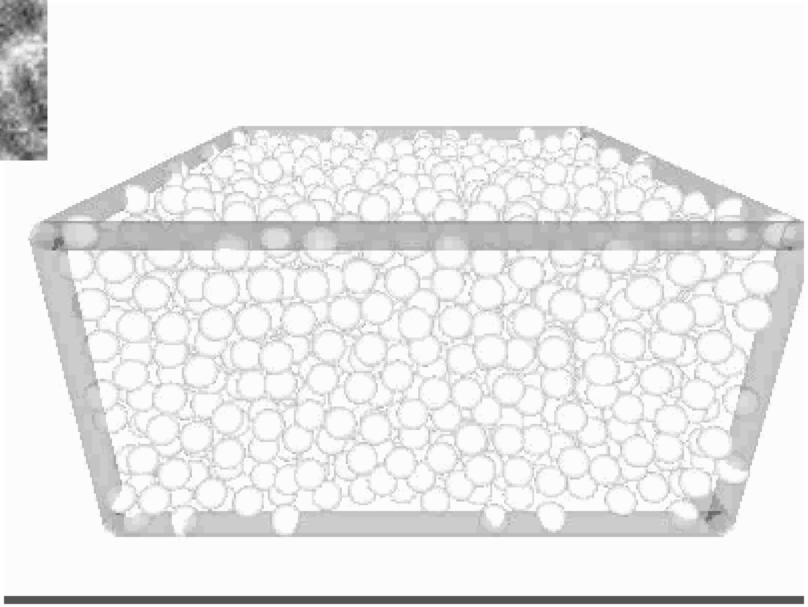
Dynamic yield stress in simple shear: $\sigma(\dot{\gamma} \rightarrow 0) = \sigma_y$

Yield of Colloidal Glasses: Experiments

Confocal microscopy: can probe structural correlations under flow

$\phi = 0.62$; 850nm radius particles, shear rate 10^{-3}/s, Pe = 0.03





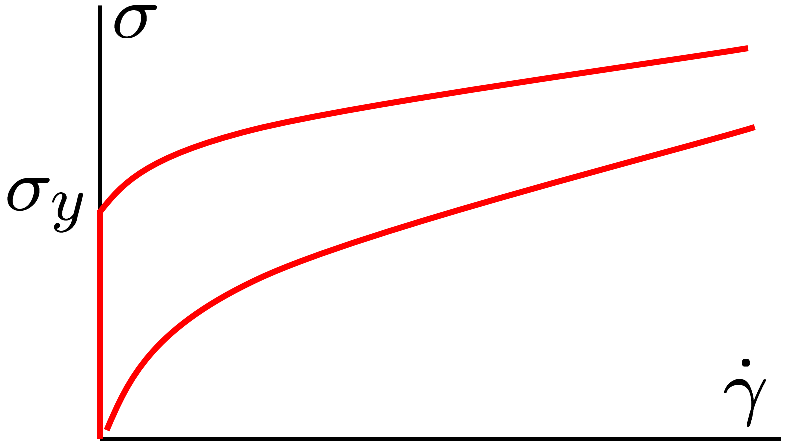
Movies: x100 speedup, from Rut Besseling, Edinburgh

L. Isa et al, PRL 98, 198305 (2007), P. Ballesta et al, PRL 101, 258301 (2008)

Standard Models of Yield-Stress Fluid

Herschel Bulkley equation

$$\sigma(\dot{\gamma}) = \sigma_y + c\dot{\gamma}^p$$



$\sigma_y = 0$: power-law fluid

$\sigma_y > 0$: amorphous solid (glass)

Viscosity $\eta(\dot{\gamma})$ diverges at small shear rates ($\sigma \to \sigma_y^+$)

$$\eta(\dot{\gamma}) \equiv \sigma(\dot{\gamma})/\dot{\gamma} = \sigma_y \dot{\gamma}^{-1} + c\dot{\gamma}^{p-1}$$

This scenario predicted by both SGR and MCT

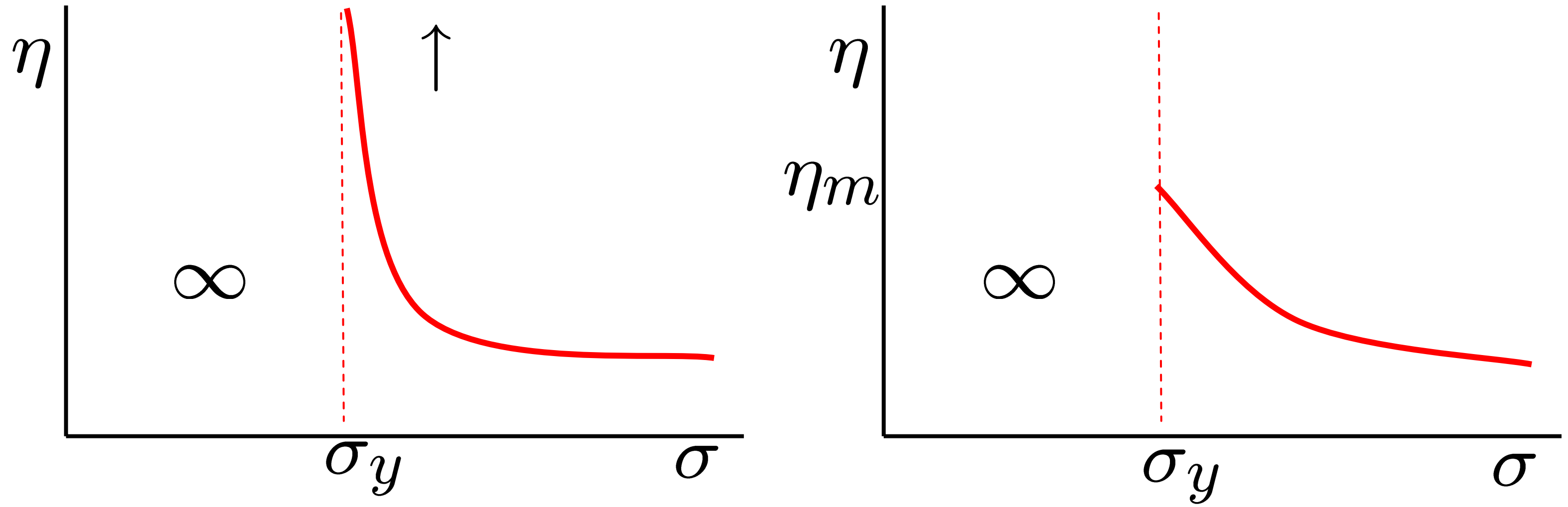
Viscosity Bifurcation

Scenario widespread in complex fluids

P. Coussot, D. Bonn et al, PRL (2002), J. Rheol. 46, 573 (2002) et seq.

Steady state viscosity jumps to infinity at σ_y

Maximum non-infinite viscosity η_m



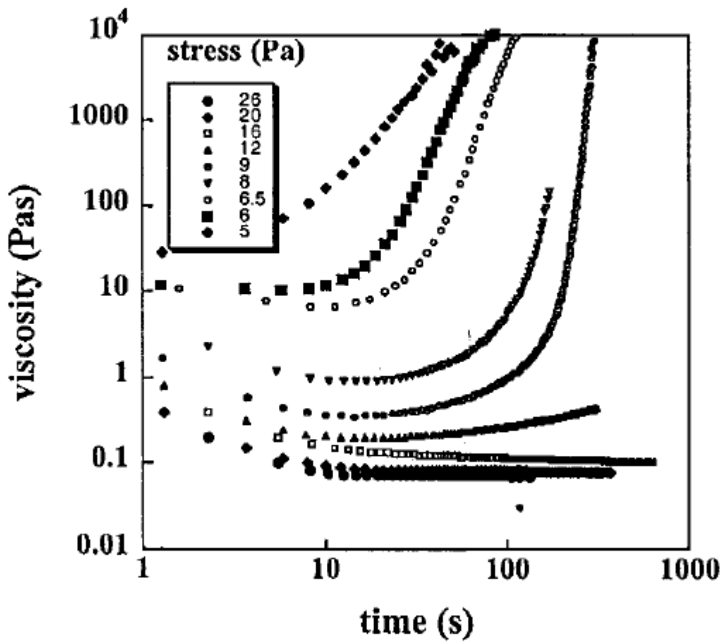
HB VB

Viscosity Bifurcation

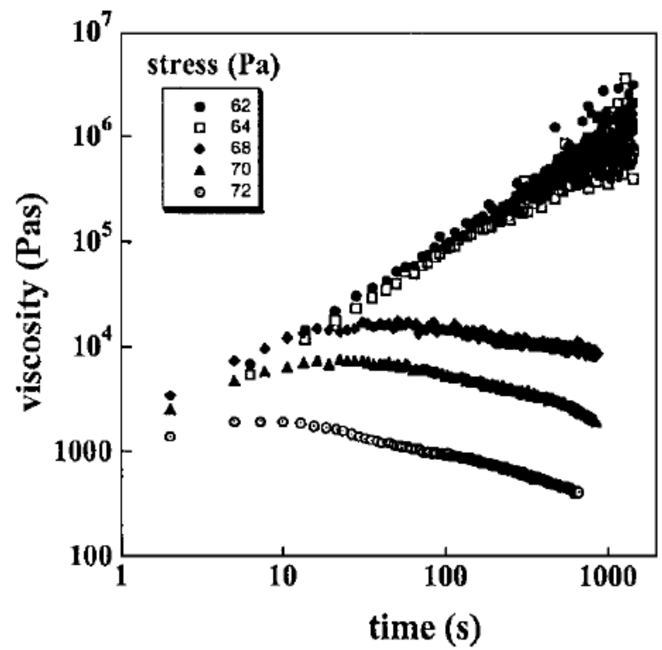
Scenario widespread in complex fluids

P. Coussot, D. Bonn et al, PRL (2002), J. Rheol. 46, 573 (2002) et seq.

Characteristic $\eta(t) = \sigma/\dot{\gamma}(t)$ in creep: $\eta(\infty)$ finite for $\sigma = \sigma_y^+$



bentonite 4%



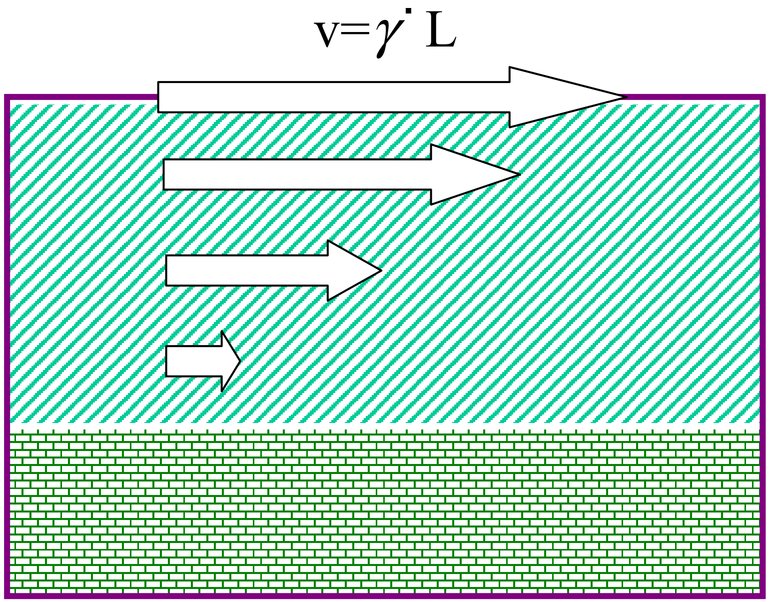
unspecified polymer gel

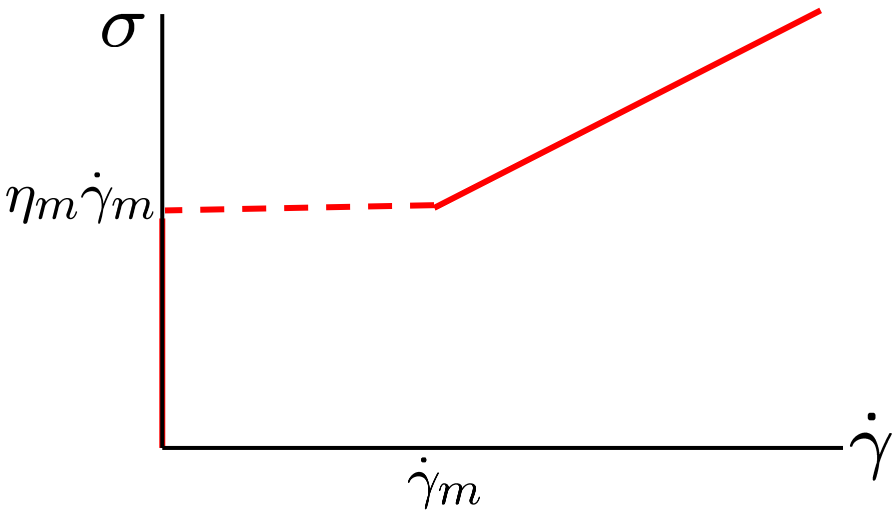
Viscosity Bifurcation

Scenario widespread in complex fluids

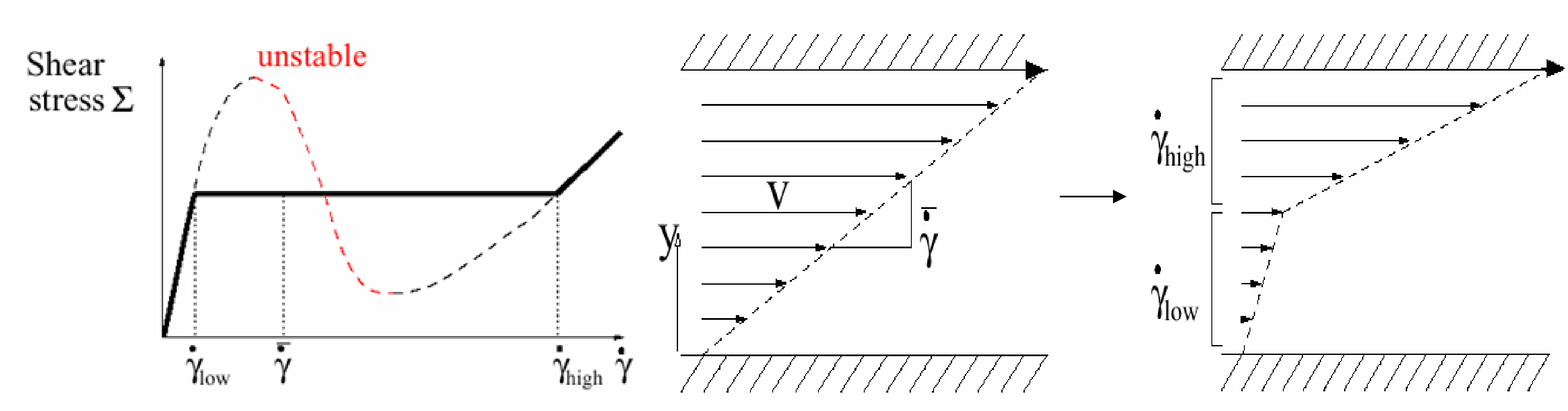
P. Coussot, D. Bonn et al, PRL (2002), J. Rheol. 46, 573 (2002) et seq.

Banded flow at <u>small</u> imposed strain rates: one static band, one fast flowing

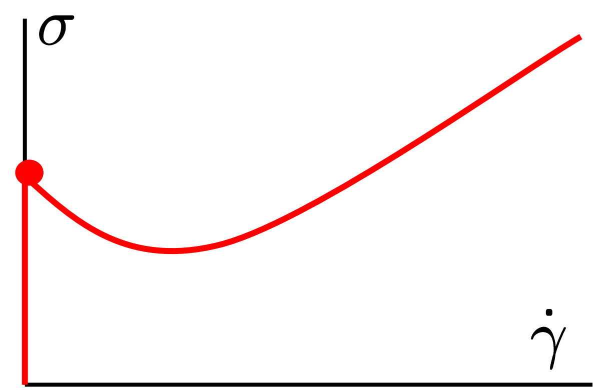




Compare Classical Shear Banding



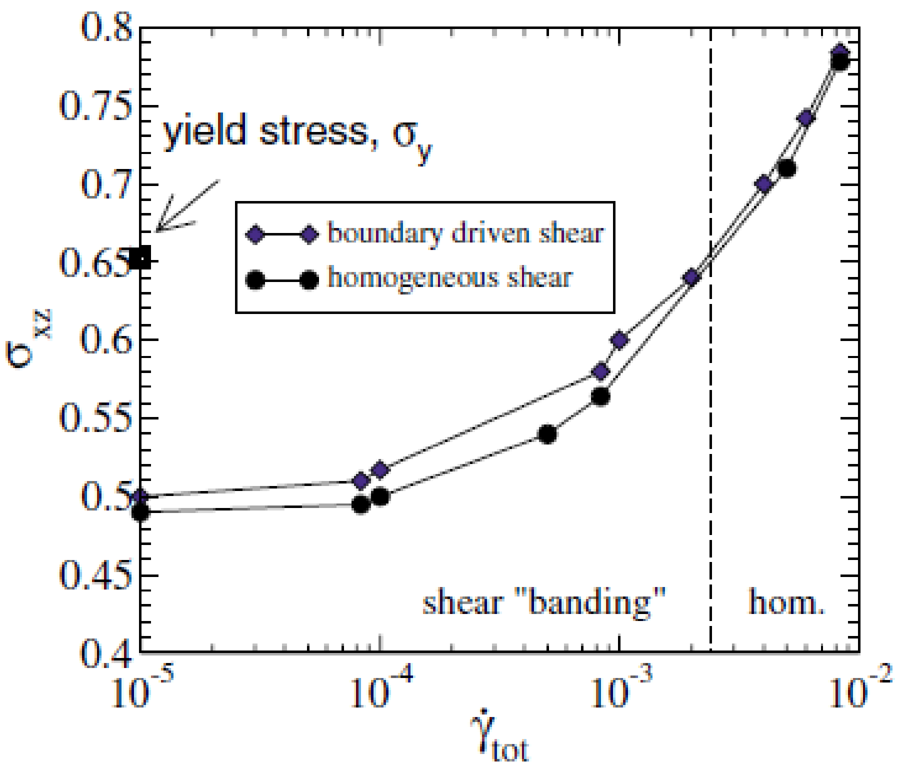
- Flow unstable on decreasing branch
- Steady bands or unsteady flow
- $\dot\gamma_{low} = 0$ in VB: how different?
- simplest scenario:

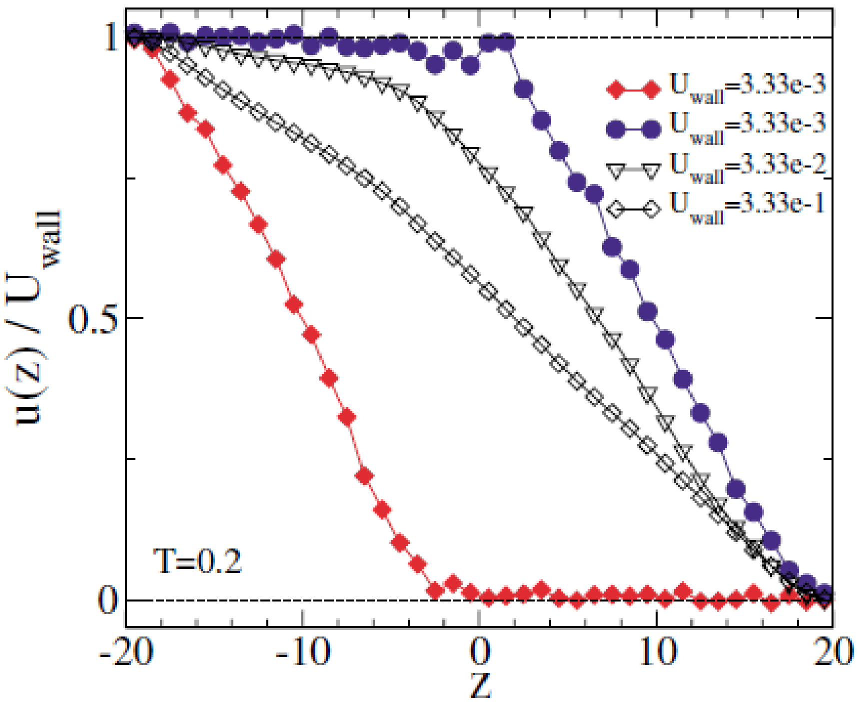


flow curve from fluidity models

Compare MD Simulations

F. Varnik et al, PRL 90, 095702 (2003)





Static yield stress measured from creep (step stress)

Flow curve has separate static branch

SGR model

• Particles jump independently among traps at noise temperature x

• l = local strain

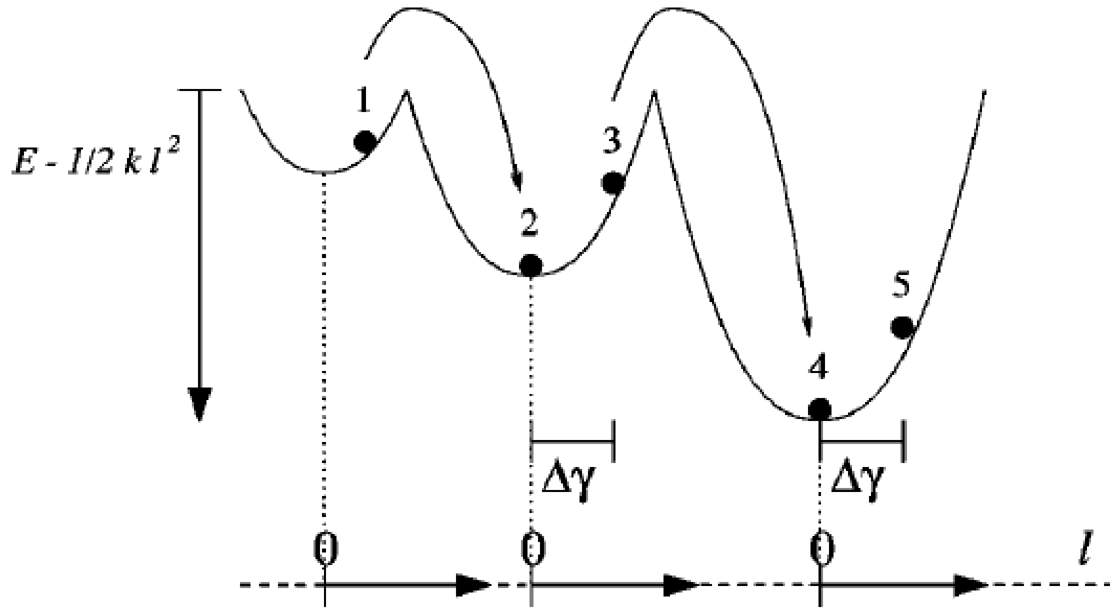
•dl/dt = $\dot{\gamma}$ (t) between hops

• Stress s = k<l>

• Jump rate $\Gamma_0 \exp[-(E-k\, l^2/2)/x]$

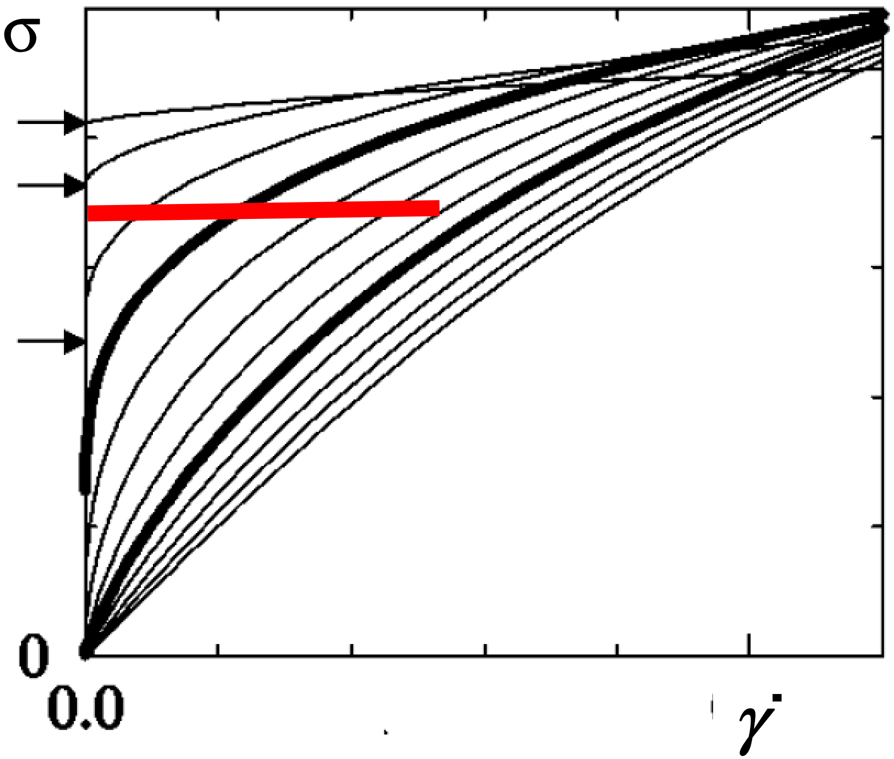
• Trap depth distribution exp[-E]
$\Rightarrow$ glass transition at x=1

• Yield stress rises smoothly for x < 1
[contrast MCT]

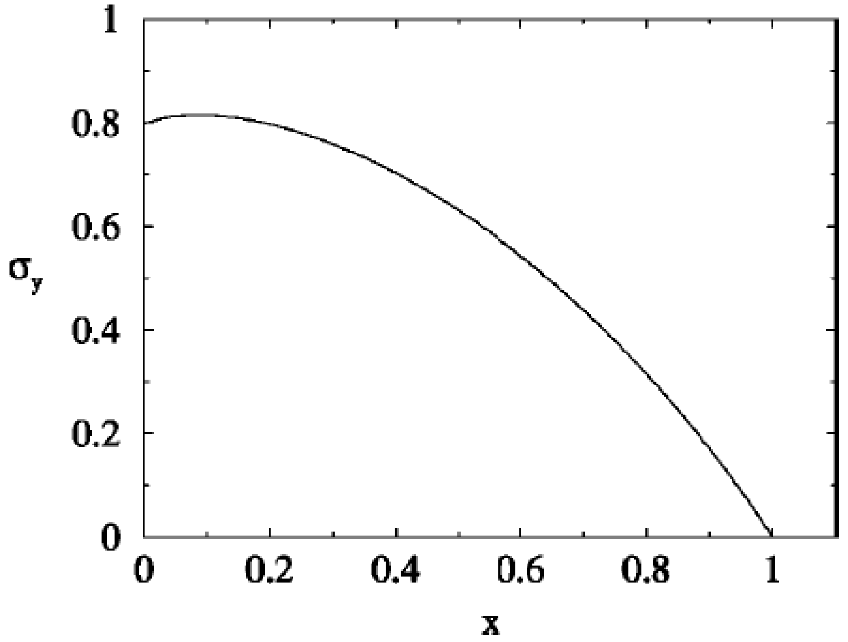


P. Sollich et al, PRL 78, 2020 (1997), S. Fielding et al J. Rheol. 44, 323 (2000)

SGR Flow Curves



Yield Stress vs Noise Temp



Coexistence of static and flowing band at equal σ:

Requires unequal x

1. Noise Diffusion SGR model

- Introduce dynamics for spatially varying noise temperature x(**r**,t)

$$\tau\dot{x} = x_0 - x + S + \lambda\nabla^2 x$$

$$S = a\langle \ell^2 \exp[-(E - k\ell^2)/x]\rangle_{P(E,\ell)}$$

- x decays locally to ‘quiescent’ x_0 at rate τ^{-1}
- Diffuses (diffusivity λ)
- Pumped by dissipation of elastic energy
- All other rules: per vanilla SGR

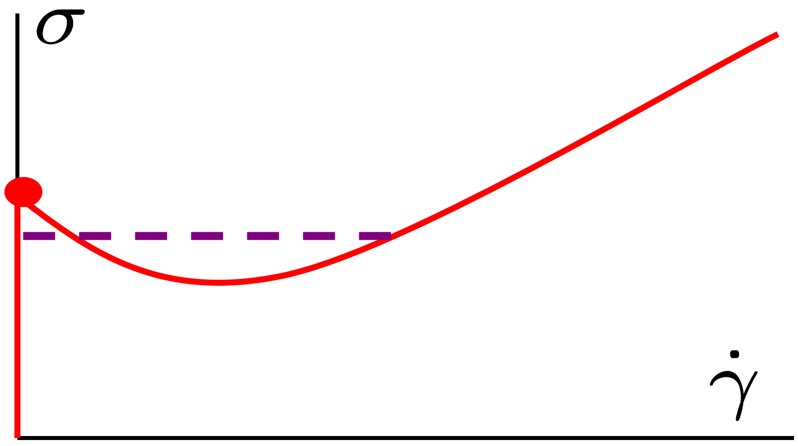
S M Fielding, P Sollich and MEC, Soft Matter 5, 2378 (2009)

Compare, contrast and discuss: STZ theory with slow-mode temperature

E Bouchbinder & J S Langer, PRE 80, 033121,033132,033133 (2009)

1. Noise Diffusion SGR model

• For suitable a, x_0:



• Coexistence of 'cold' solid band and 'hot' flowing band

• Flow curves resemble that of simplest 'fluidity' model of VB

$$\eta = \eta_0(1 + \zeta^n) \qquad \dot{\zeta} = 1/\tau - \alpha\zeta\dot{\gamma}$$

P Coussot et al, PRL 88, 175501 (2002)

• Full aging dynamics, frequency dependent rheology (as per SGR)

• Strong age dependence of viscosity bifurcation point

S M Fielding, P Sollich and MEC, Soft Matter 5, 2378 (2009)

1. Noise Diffusion SGR model

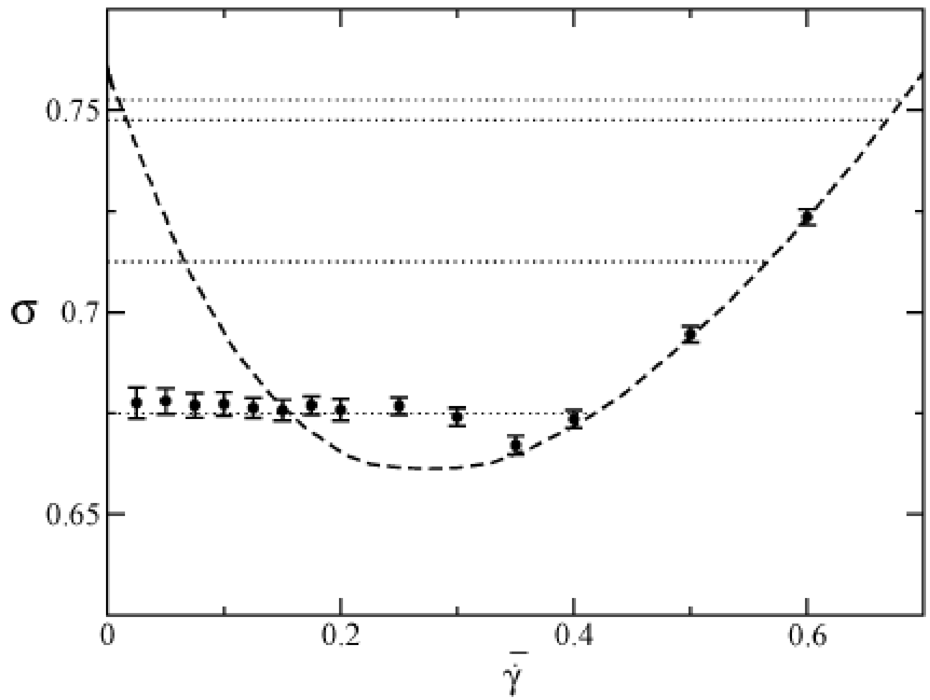


Fig. 1 Dashed line: constitutive curve $\sigma(\dot{\gamma})$ for $x_0 = 0.3$, $a = 2.0$. Symbols: WTMC results for quasi-stationary stress σ at various imposed mean strain rates $\bar{\dot{\gamma}}$ found after start up of steady shear. Shear banding is present whenever the WTMC data deviates significantly from the dashed curve. Dotted lines: viscosity bifurcation points (± 0.05) in step stress for $\log_{10} t_w = 1.0, 1.5, 2.0, 2.5$ (bottom to top); cf. Fig. 3.

S. M. Fielding, P. Sollich, MEC, Soft Matter 5, 2378 (2009)

1. Noise Diffusion SGR model

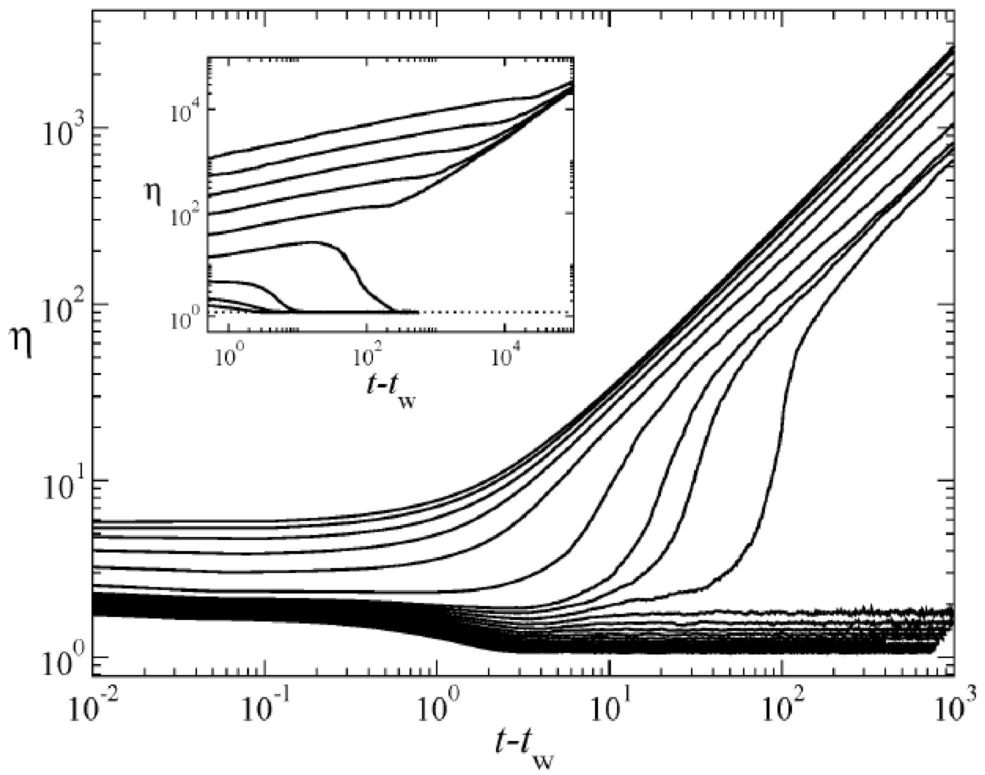
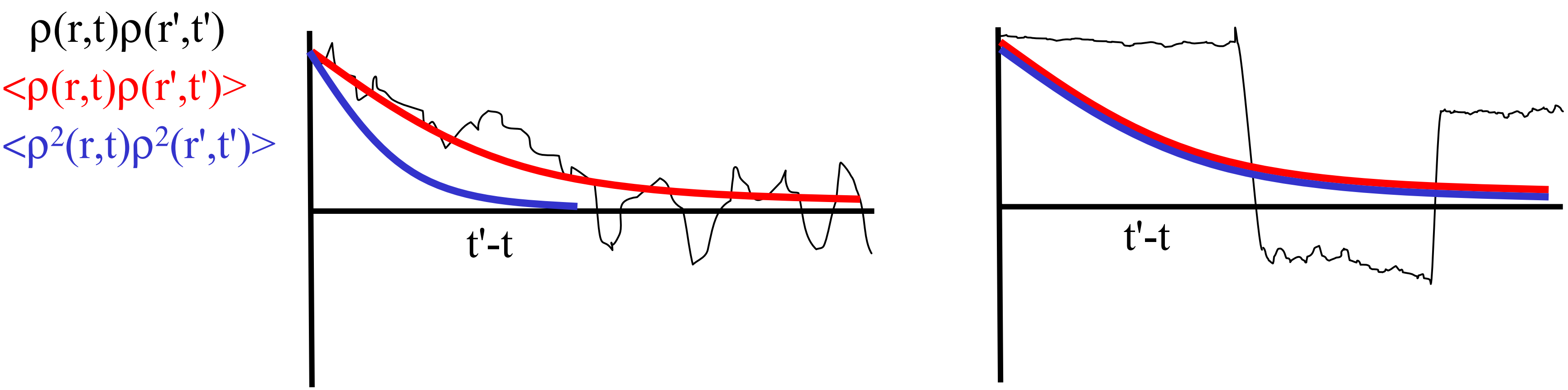


Fig. 3 Viscosity bifurcation for $x_0 = 0.3$, $a = 2.0$, $n = 100$, $m = 1000$. Main figure: age before shear $t_w = 1$; stress values (top to bottom at right) $\sigma = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.64, 0.65, 0.66, 0{,}67, 0.68, 0.69, 0.70, 0.71, 0.72, 0.73, 0.74, 0.75, 0.76, 0.77, 0.8$. Inset: stress $\sigma = 0.72$, age before shear $\log_{10} t_w = 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4$. Dotted line shows the asymptote calculated semi-analytically.

S. M. Fielding, P. Sollich, MEC, Soft Matter 5, 2378 (2009)

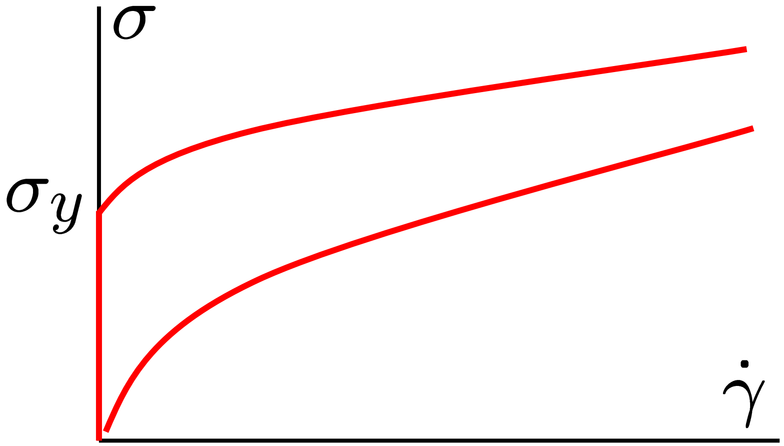
2. MCT for Dense Colloidal Suspensions

- Fully microscopic starting point
- Central assumption for density fluctuations: $\langle\rho^2(r,t)\rho^2(r',t')\rangle \approx \langle\rho(r,t)\rho(r',t')\rangle^2$
- Good when local relaxation caused by cumulative small shuffles
- Bad when local relaxation caused by rare large moves (hopping regime)
- Complementary (even opposite!) viewpoint to SGR



2. MCT Predictions: Steady Shear

M. Fuchs + MEC, PRL 89, 248304 (2002)



- Flow curves: very like SGR
- Yield stress curve: different (discontinuous jump at glass point)
- Everything monotonic: no sign of shear-banding

2. Physical Content of MCT Results

Viscoelastic liquid $\rightarrow$ elastoplastic solid (glass transition)

- Current relaxation time depends on flow history
- Prolonged steady strain fluidizes glass by erasing memory
- Time lag to rebuild solidity after cessation of flow
- Step strains also erase memory... but never completely

These features captured by a schematic constitutive model

J. Brader, T. Voigtmann, M. Fuchs, R. Larson, MEC, PNAS 106,15186 (2009)

2. Schematic CE for Colloid Rheology

Stress Equation

$$\sigma_{\alpha\beta}(t) = v_\sigma \int_{-\infty}^{t} dt' \left(-\frac{\partial \mathrm{B}(t,t')}{\partial t'}\right) \Phi^2(t,t')$$

v_σ sets stress scale

B = **E**.**E**^{T} Finger Tensor describing deformation between t and t' [**r**(t) = **E.r**(t')]

Φ = schematic correlator

Memory Equation

$$\frac{\partial}{\partial t}\Phi(t,t_0)+\Gamma(t,t_0)\left(\Phi(t,t_0)+\int_{t_0}^{t} dt'\, m(t,t',t_0)\frac{\partial}{\partial t'}\Phi(t',t_0)\right)=0$$

2. Schematic CE for Colloid Rheology

Memory Kernel

Frame indifferent, single-mode approximation to full MCT memory

$$m(t,t',t_0) = h(t,t_0)h(t,t')\left[v_1\Phi(t,t') + v_2\Phi^2(t,t')\right]$$

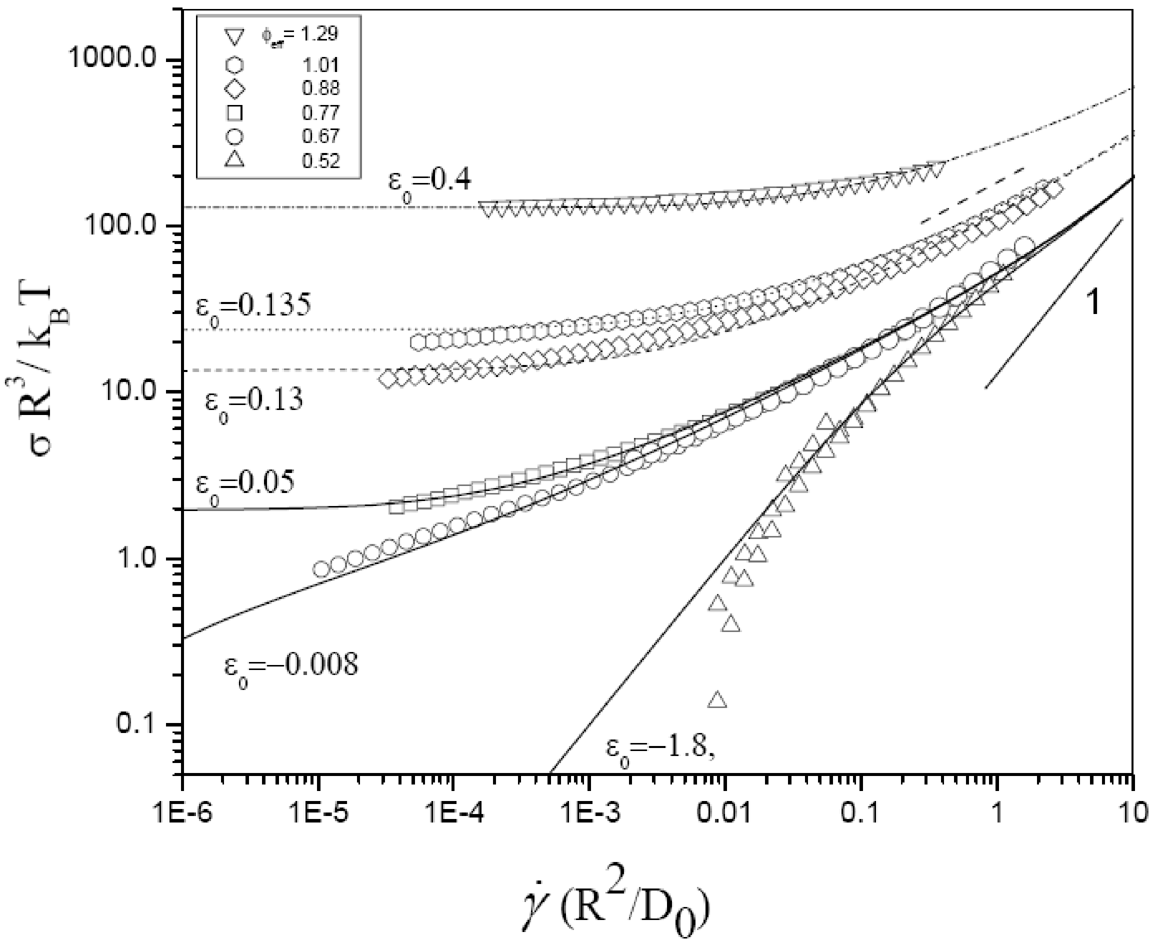
$I_1 = \mathrm{Tr}(\mathbf{B}(t,t'))$

$I_2 = \mathrm{Tr}(\mathbf{B}^{-1})$

$$h = \frac{\gamma_c^2}{\gamma_c^2 + \nu I_1 + (1-\nu)I_2 - 3}$$

Reasoned schematic impersonation of the full MCT equations

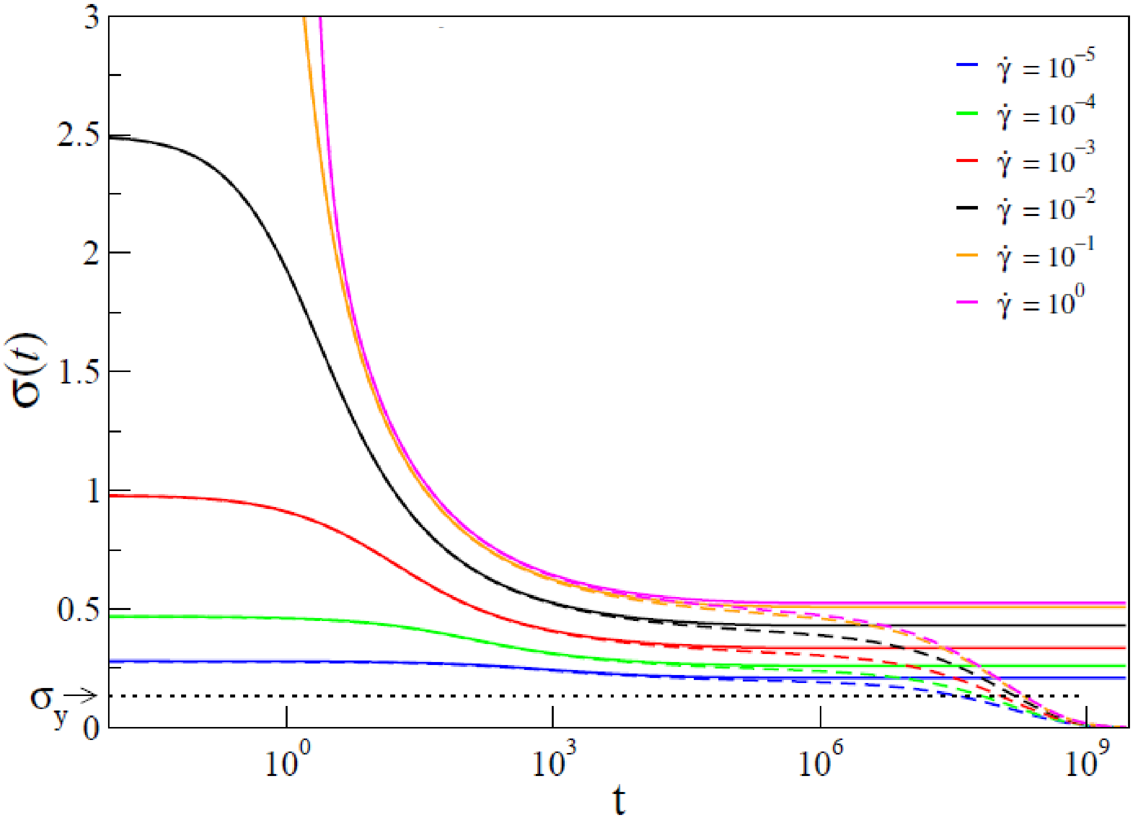
2. Schematic MCT Results: Steady Shear



Experiments and fit: V. Carrier and G. Petekidis, J. Rheol 2009

2. Cessation of Steady Shear

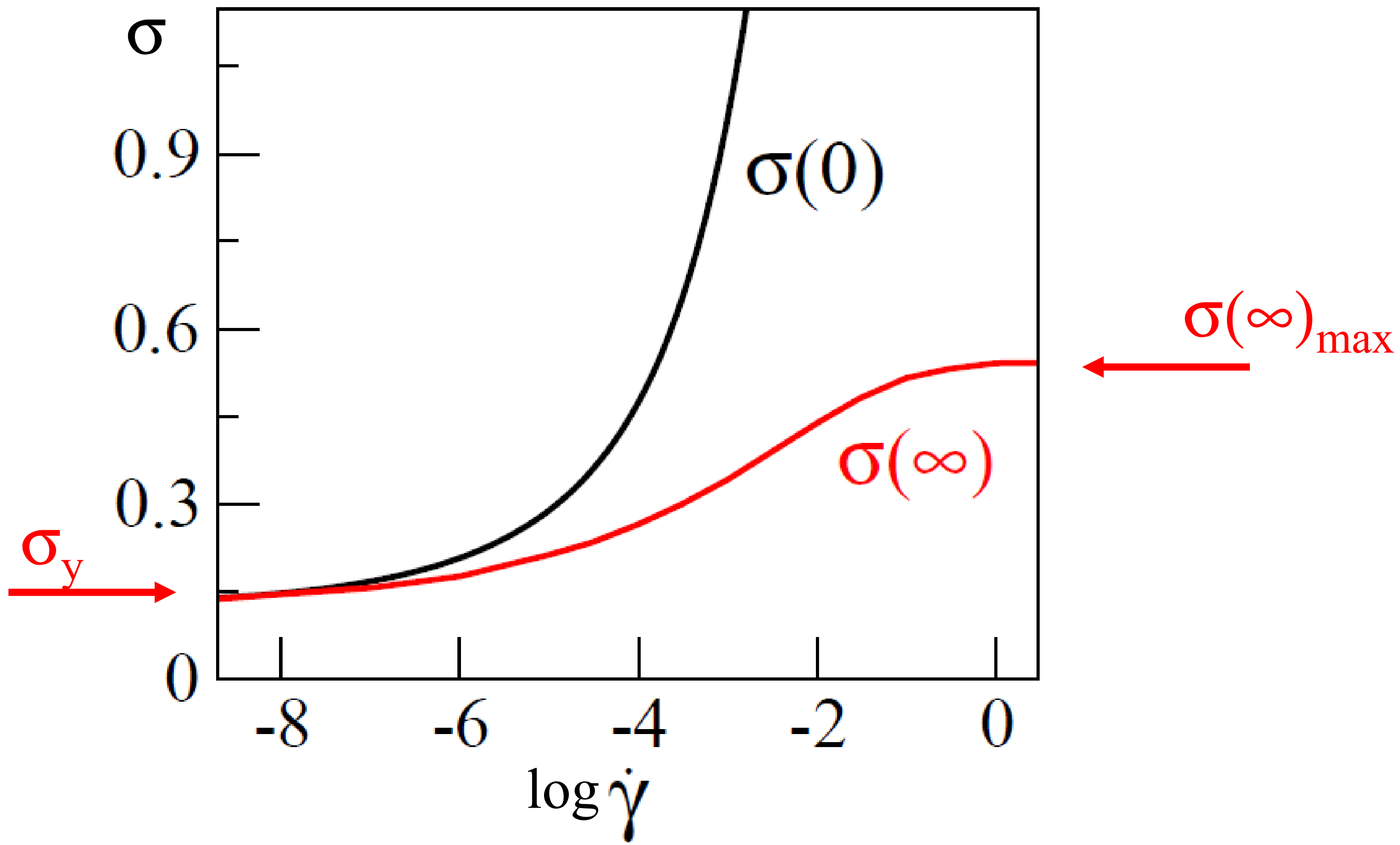
$\varepsilon = \pm 10^{-4}$



in glass: residual stress at long times

2. Residual Stress: Dependence on Prior Shear Rate

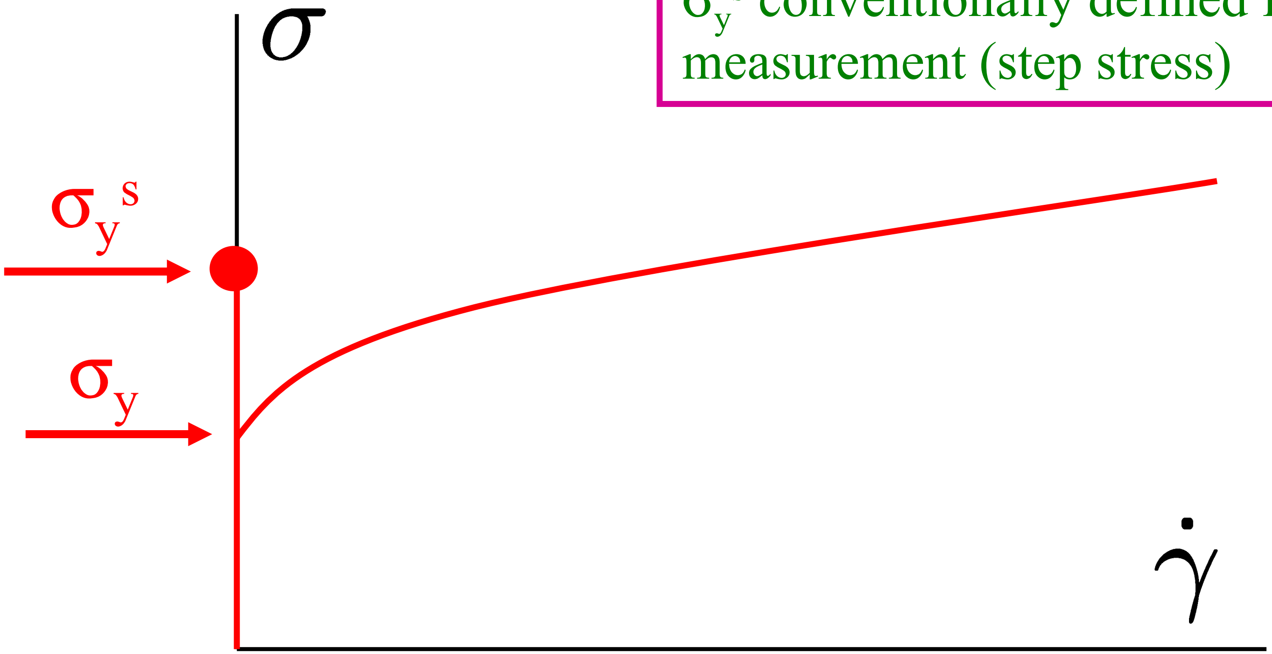
$\varepsilon = +10^{-4}$



in glass: $\sigma(\infty)_{max} > \sigma(\infty) > \sigma_y$

2. Proves existence of static states with $\sigma > \sigma_y$

σ_y^s conventionally defined for creep measurement (step stress)



Is $\sigma_y^s \equiv \sigma(\infty)_{max}$?

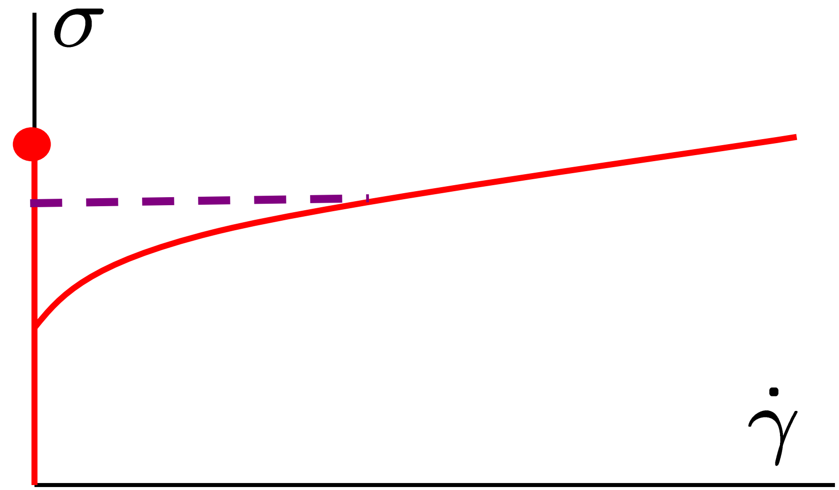
Yes, if maximum static stress is flow-history independent

If not, each protocol (creep, slow ramp, cessation...) defines new value

2. Implications

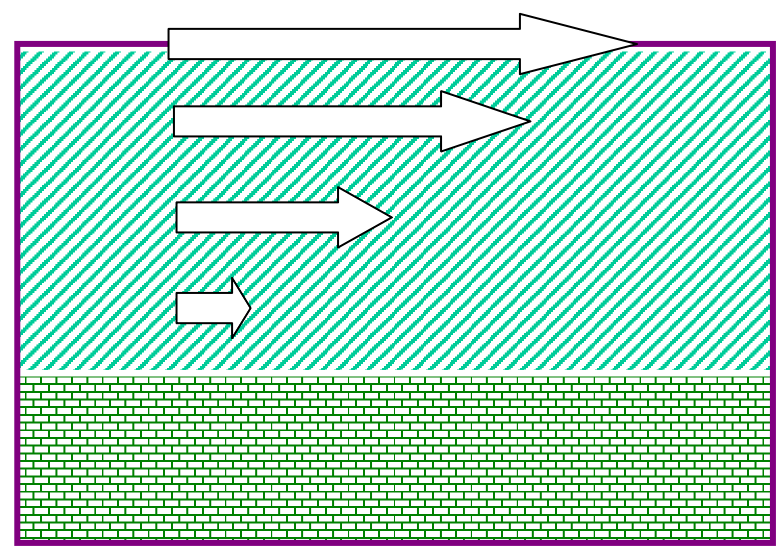
MCT admits shear bands of VB type

- Solid band for which $\sigma < \sigma_y^s$
- Fluid band for which $\sigma > \sigma_y$
- No region of negative slope



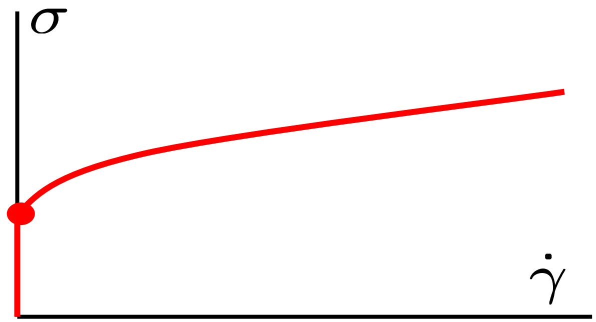
Kinetics, stability, onset?

- Nothing known yet
- Inhomogeneous MCT:
  hard problem!



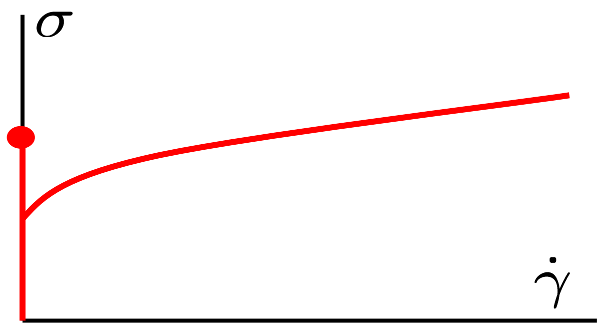
Viscosity Bifurcation: SGR vs MCT

VB



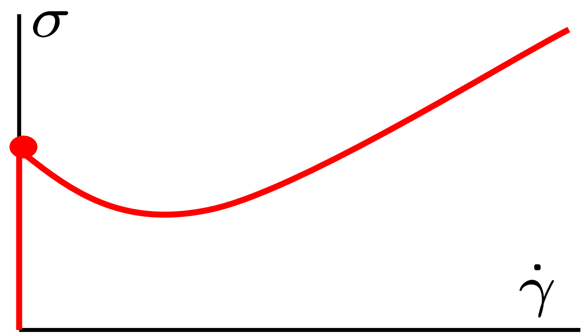
Vanilla SGR:
- monotonic curve
- $\sigma_y^{\ s} = \sigma_y$

No



MCT:
- monotonic flow curve
- now find $\sigma_y^{\ s} > \sigma_y$

?



Noise diffusion SGR:
- nonmonotonic flow curve

Yes