Transport Processes in
Melts under External Fields

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Nonlinear Rheology of Colloidal Suspensions

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Bangalore, February 2012

Outline

- Introduction: Kinetic Arrest
- Nonlinear Response Theory
- Yielding and Flowing

Introduction: Kinetic Arrest

"I have no data yet. It is a capital mistake to theorize before one has data. Insensibly one begins to twist facts to suit theories, instead of theories to suit facts."

[Sir Arthur Conan Doyle: The Adventures of Sherlock Holmes; A Scandal in Bohemia]

Viscous Liquids – Universal Aspects

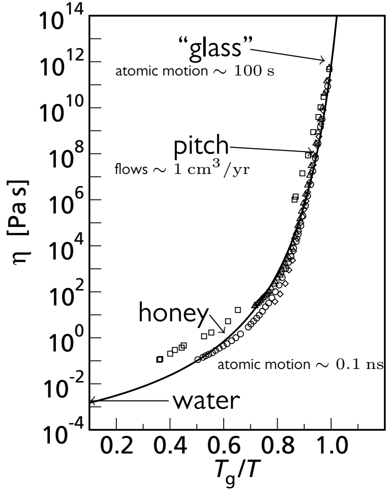
metallic glass © liquidmetal.com
SiO_2 melt © Schott Glas

the pitch drop experiment
U Queensland, Australia (1927–present)
`mms://drop.physics.uq.edu.au/PitchDropLive`

a colloidal suspension

- viscosity ≫ "normal-liquid" viscosity, ⇒ eventual arrest
- universal behavior ⇒ study model systems
- dense liquids ⇒ essentially hard spheres (Widom's argument)

To Flow or Not To Flow?



- $\eta(T)$ seems to diverge?
- transition from liquid to solid?
- visco-elastic behavior
  - slowness *vs.* observation time

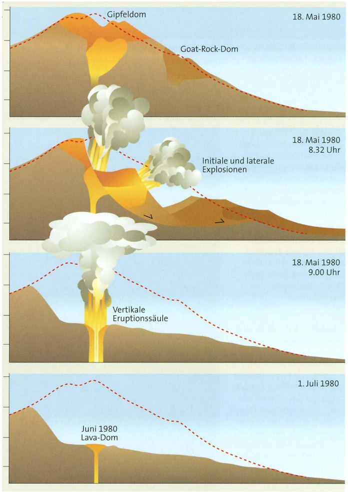
    “mountains melted from before the Lord”,
    [Song of Deborah]

$\Rightarrow$ slow relaxation time τ

- “Angell plot”
- suggested by Oldekop (1950’s)

(Stigler’s law of eponymy)?

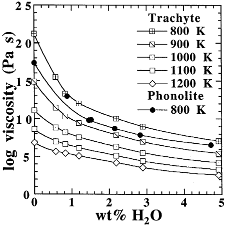
Flow or Blow?



volcanic dilemma: flow or blow

[Dingwell, Science (1996)]

- explosive volcanism: magma undergoes glass transition
  - magma: many-component mixture of SiO_2, GeO_2, …
  - very sensitive to H_2O content
- $\eta(T)$ to understand volcanism



[Whittington, Chem Geol (2001)]

protein ice nucleators

⇒ freeze-resistant animals

induced extra-cellular nucleation

preserves cells as sugary glass

rana sylvatica

[animaldiversity.org]

anti-freeze proteins

⇒ freeze-avoiding animals

proteins block growth of ice nuclei

zoarces americanus

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applied to ice cream: tastes better…

zoarces americanus

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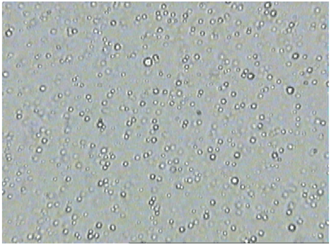
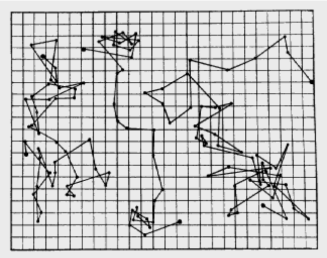
Colloidal Suspensions – Soft Matter Models

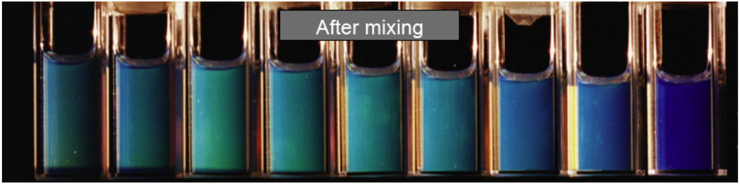




- $d \sim 1\ \mu\mathrm{m}$ particles in suspension
  $\Rightarrow$ Brownian motion
  mean-squared displacement
  $\langle \delta r^2 \rangle \sim 2D\Delta t$ (diffusion)
- many biological/biophysical systems
- scales: $k_\mathrm{B}T_\mathrm{r} \sim 4\,\mathrm{pN\,nm},\ \mu\mathrm{m},\ \mathrm{msec}$
  $\Rightarrow$ microscopy, direct imaging
- shear modulus $G \sim k_\mathrm{B}T/d^3 \sim \mathrm{Pa}$
  $\Rightarrow$ soft matter
- application-taylored tunable interations

movie: www.microscopy-uk.org.uk
image: Perrin [Ann Chim Phys VIII (1909)]

Hard Spheres / Hard-Sphere Colloids



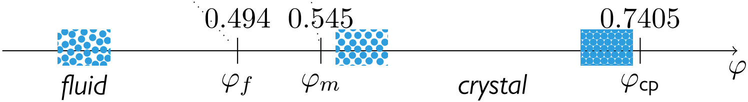
[Pusey and van Megen, Nature (1986)]

φ

- only parameter: *packing fraction* $\varphi = \mathrm{Vol}(\text{Spheres}) / \mathrm{Vol}(\text{Box})$
- purely entropic freezing/melting
- metastable liquid $\Rightarrow$ kinetic arrest: "glass transition"

Hard Spheres / Hard-Sphere Colloids

[Pusey and van Megen, Nature (1986)]



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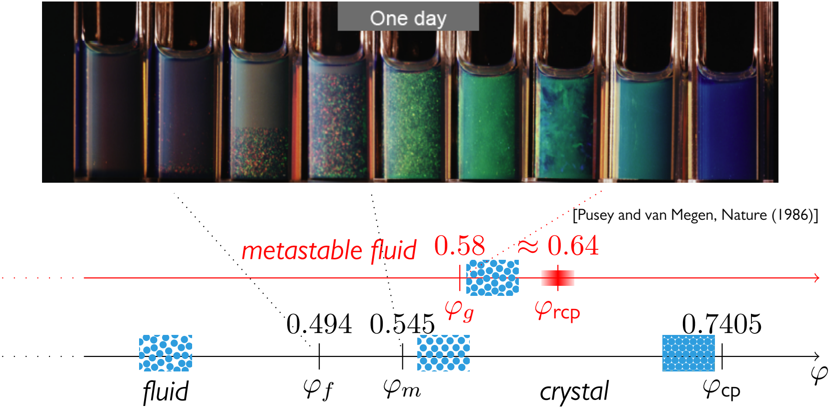

- only parameter: *packing fraction* $\varphi = \mathrm{Vol(Spheres)} / \mathrm{Vol(Box)}$
- purely entropic freezing/melting
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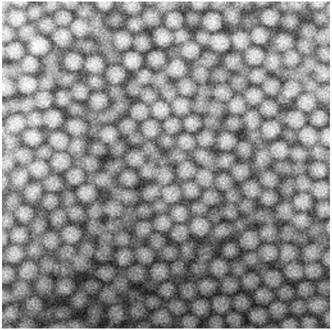
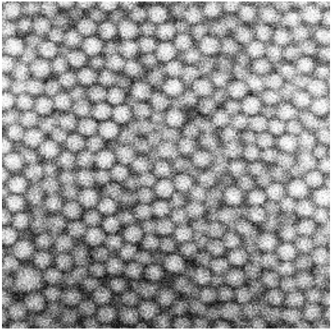
How (Not) To Be Seen



52% packing fraction



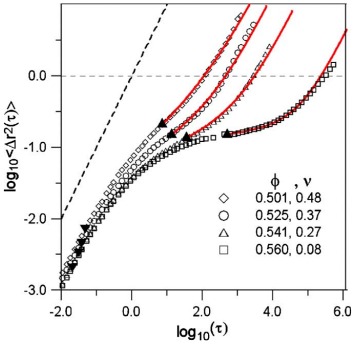
58% packing fraction

- small structural difference $\Rightarrow$ huge effect on dynamics
- nearest neighbor cage effect – no visible order parameter
- slow structural relaxation, time scale $\tau \gg \tau_0 \sim a^2/D_0$

[confocal microscopy movies: Rut Besseling, U Edinburgh]

Glassy Dynamics: Mean-Squared Displacement

characterize dynamics by tagged-particle mean-squared displacement (MSD), $\delta r^2(t) = \langle|\vec{r}(t) - \vec{r}(0)|^2\rangle \sim 6Dt$ as $t \to \infty$



mean-squared displacement $\delta r^2(t)$
[van Megen *et al.*, PRE (1998; 2007)]

- slow dynamics:
  long-time diffusion coefficient
  $D_L \ll D_{\text{short}}$
- subdiffusive regime
  - 'plateau' ⇔ "cage effect"
- dynamical arrest at high densities $\varphi \geq \varphi^c$
  - $D_L(\varphi \to \varphi^c) \to 0$
- collective slowing down

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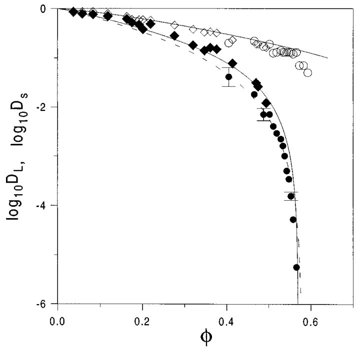

long-time diffusion coefficient D_L
[van Megen *et al.*, PRE (1998)]

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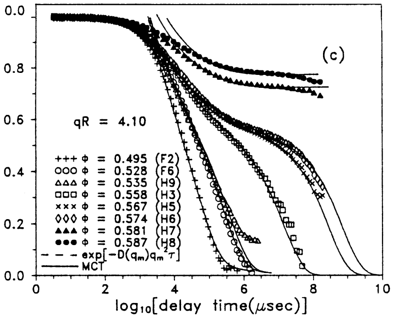
Glassy Dynamics

characterization of collective dynamics: density correlation function $\phi(q,t)$ – measured in light scattering *etc.*



dynamic light scattering signal $\sim \phi(q,t)$ [van Megen *et al.*, PRL (1993)]

- dense suspensions: slow relaxation time τ

  $\Rightarrow$ dynamical arrest
- intermediate plateau
- *two-step relaxation process*
- non-exponential final decay

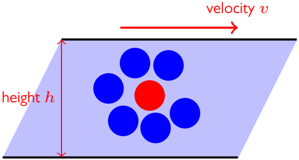
Introduction: Rheology

"I do not know – I only guess. But I can examine my guess critically, and if it withstands criticism, then this fact may be taken as a good reason in favour of it."

[Sir Karl Popper: Conjectures and Refutations]

Rheology of Dense Fluids

shear flow of dense fluids:



- external flow rate $\dot{\gamma} \sim v/h$ $[1/\mathrm{s}]$
- large structural relaxation time τ $[\mathrm{s}]$

$\Rightarrow$ large effect when $\dot{\gamma}\tau \gg 1$

- (idealized) kinetic arrest: $\tau \to \infty$

$\Rightarrow$ even if $Pe = \dot{\gamma}\tau_0 \ll 1$

- apply perturbation (shear $\dot{\gamma}$) $\Rightarrow$ measure response (stress σ)

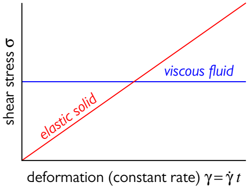
$$\mathcal{F}\,[\,\dot{\gamma}\,] = \sigma$$

constitutive equation

- $\mathcal{F}$ is a *model* of the material
- linear response: Newtonian liquid $\sigma = \dot{\gamma} \times$ const.
  - perturbation-independent material constant: viscosity $\eta = \sigma/\dot{\gamma}$
- how to derive $\mathcal{F}$ microscopically? (from particle interactions)

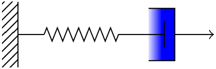
Visco-Elasticity: Maxwell's Model

- Newtonian fluid: $\eta \propto$ const. $\Rightarrow \sigma \propto \dot\gamma$
- Hookian elastic solid: $\sigma \propto \gamma$
- dense fluids: ??
- Maxwell: combine $\sigma \sim \gamma$ and $\sigma \sim \dot\gamma$



$$\dot\gamma = \dot\sigma / G_\infty + \sigma/\eta$$

- "spring-and-dashpot" model: Hookian spring constant G_∞



- differential equation solved by

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

output input model

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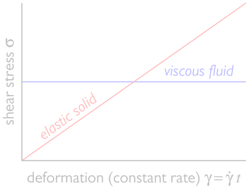


$$\dot{\gamma} = \dot{\sigma}/G_\infty + \sigma/\eta$$

- "spring-and-dashpot" model:
  Hookian spring constant G_∞

- Maxwell's constitutive equation

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

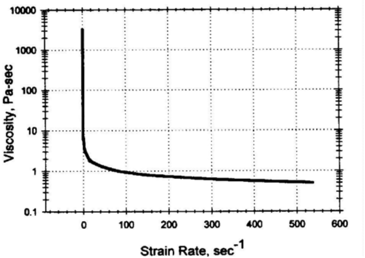
output — input — model

typical flow rates in industrial processes and applications

process	$\dot{\gamma}$ [s^{-1}]	**examples**
aging, creep	$10^{-8} \ldots 10^{-5}$	polymers
sedimentation	$\lesssim 10^{-2}$	emulsion paints, fruit juices
surface leveling, sagging	$10^{-2} \ldots 10^{0}$	paints, chocolate coatings
chewing, swallowing	$10^{1} \ldots 10^{2}$	cheese, yogurt
spreading	$10^{1} \ldots 10^{3}$	butter, toothpaste
coating, painting	$10^{2} \ldots 10^{4}$	paints, plasters, adhesives
rubbing	$10^{3} \ldots 10^{5}$	skin creams, lotions
blade coating	$10^{3} \ldots 10^{7}$	paper coatings
engine lubrication	$10^{3} \ldots 10^{7}$	mineral oils, greases

Nonlinear Rheology: Shear Thinning

apply (steady) shear $\Rightarrow$ dramatic decrease in apparent viscosity



white latex paint

[K. Weiss, cited after Settles, ILASS (1997)]

- non-linear response
  - linear response: $\eta \sim$ const.
  - huge variation in $\eta(\dot{\gamma})$
  - $\eta \to \infty$: glass
- "visco-plastic" behavior
- applications: squeezing of toothpaste, painting, coating, …
- "universal"
  - metallic melts, geophysics, soft matter, …

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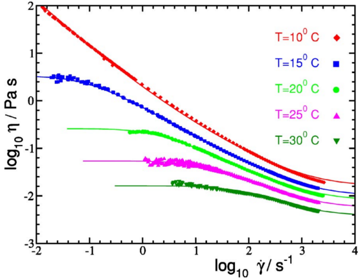

thermosensitive colloids

[Fuchs and Ballauff, J Chem Phys (2005)]

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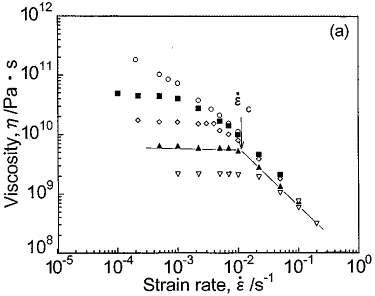

$Pd_{40}Ni_{10}Cu_{30}P_{20}$, various temperatures

[Kato *et al.*, JAP (1998)]

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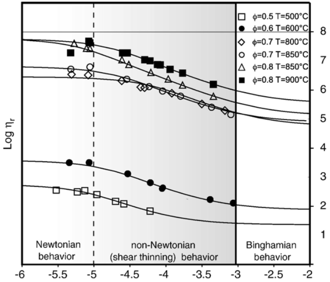

magma, various compositions

[Caricchi *et al.*, Earth Pl Sci Lett (2007)]

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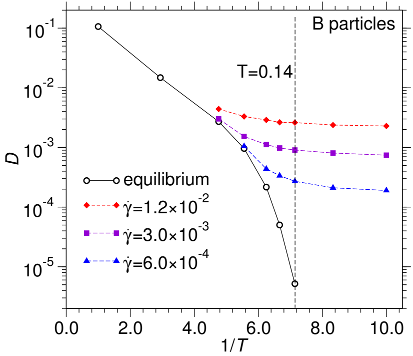
Diffusion under Shear

- *transverse* diffusion induced by shear

⇒ steady shear melts the glass



[Zausch *et al.*, J Phys Condens Matt (2008)]

Nonlinear Response Theory

"I've always been astonished by the absurd turns rivers have to take to flow under every bridge."
[Beppe Grillo]

Shear Flow

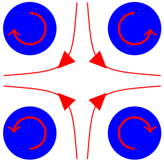
- shear stress: σ = force $\parallel$ flow/area; viscosity: $\eta = \sigma/\dot{\gamma}$
- typical shear rate $\dot{\gamma} \sim |dv/dx|$
- characterize any flow by velocity gradient tensor

$$\mathbf{\Gamma} = (\vec{\nabla} \otimes \vec{v})^T = \begin{pmatrix} \partial v_1/\partial r_1 & \partial v_2/\partial r_1 & \partial v_3/\partial r_1 \\ \partial v_1/\partial r_2 & \partial v_2/\partial r_2 & \partial v_3/\partial r_2 \\ \partial v_1/\partial r_3 & \partial v_2/\partial r_3 & \partial v_3/\partial r_3 \end{pmatrix}$$

simple shear

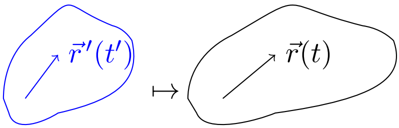
$$\mathbf{\Gamma} = \begin{pmatrix} 0 & \dot{\gamma} & \\ & 0 & \\ & & 0 \end{pmatrix}; \ \dot{\gamma} = v/h$$

planar extensional flow



$$\mathbf{\Gamma} = \begin{pmatrix} \dot{\gamma} & & \\ & -\dot{\gamma} & \\ & & 0 \end{pmatrix}$$

deformation: $(\vec{r}', t') \mapsto (\vec{r}, t)$



$$\boldsymbol{E} = \frac{d\vec{r}}{d\vec{r}'} = \begin{pmatrix} \partial r_1/\partial r_1' & \partial r_2/\partial r_1' \\ \partial r_1/\partial r_2' & \ddots \end{pmatrix}$$

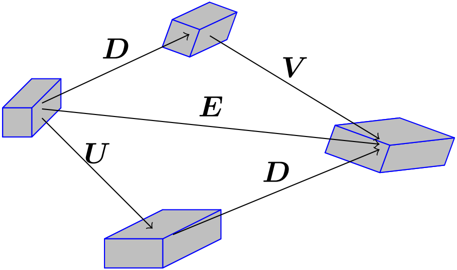
$$\partial_t \boldsymbol{E}(t,t') = \boldsymbol{\Gamma}(t)\boldsymbol{E}(t,t')$$

$$\Rightarrow \boldsymbol{E}(t,t') = \exp_+ \left[\int_{t'}^{t} \boldsymbol{\Gamma}(\tau)\, d\tau \right]$$

- examples:
  - simple shear, $\boldsymbol{E}(t,t') = \begin{pmatrix} 1 & \gamma_{tt'} & \\ & 1 & \\ & & 1 \end{pmatrix}$; $\gamma_{tt'} = \int_{t'}^{t} \dot{\gamma}(\tau)\, d\tau$
  - elongational, $\boldsymbol{E}(t,t') = \begin{pmatrix} e^{2\gamma} & & \\ & e^{-2\gamma} & \\ & & 1 \end{pmatrix}$
  - general elongational, uniaxial, $\boldsymbol{E}(t,t') = \begin{pmatrix} e^{2\gamma} & & \\ & e^{-(1+\alpha)\gamma} & \\ & & e^{-(1-\alpha)\gamma} \end{pmatrix}$

Elasticity Theory (Cont'd)

- principle of *material objectivity*: rotation = irrelevant



- polar decomposition theorem: $\boldsymbol{E} = \boldsymbol{D}\boldsymbol{U} = \boldsymbol{V}\boldsymbol{D}$ $(\boldsymbol{D}^T = \boldsymbol{D}^{-1})$
- rotational invariant: Finger tensor

$$\boldsymbol{B}(t, t') = \boldsymbol{E}(t, t')\boldsymbol{E}^T(t, t')$$

Brownian Particle in Shear Flow

stochastic differential equation

$$d\vec{r} = \boldsymbol{\Gamma}(t)\vec{r}\,dt + \sqrt{2D}d\vec{W}$$

solved with $\boldsymbol{E}(t,t') = \exp_+\left[\int_{t'}^{t}\boldsymbol{\Gamma}(\tau)d\tau\right] - \mathbf{1}$

$$\vec{r}(t) = \boldsymbol{E}(t,0)\vec{r}(0) + \sqrt{2D}\int_0^t \boldsymbol{E}(t,t')\,d\vec{W}(t')$$

$$\langle\delta\vec{r}\otimes\delta\vec{r}\rangle = [(\boldsymbol{E}(t,0)-\mathbf{1})\vec{r}_0]\otimes[(\boldsymbol{E}(t,0)-\mathbf{1})\vec{r}_0] + 2D\int_0^t \boldsymbol{E}(t,t')\boldsymbol{E}^T(t,t')\,dt'$$

Brownian Particle in Shear: Taylor Dispersion

example: simple shear, $\Gamma_{ij} = \dot{\gamma}\delta_{ix}\delta_{jy}$

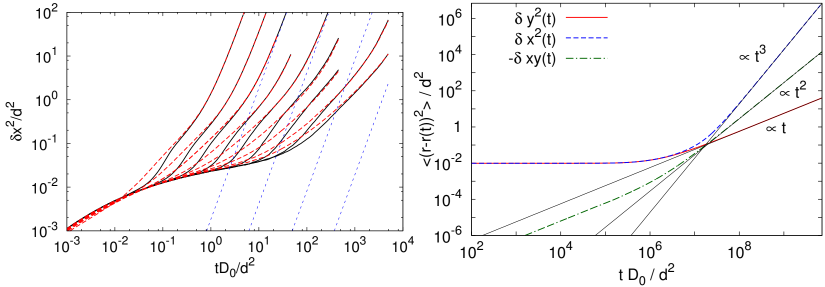
$$\boldsymbol{E}(t,t') = \begin{pmatrix} 1 & \gamma_{tt'} & \\ & 1 & \\ & & 1 \end{pmatrix} \quad \boldsymbol{B}(t,t') = \begin{pmatrix} 1+\dot{\gamma}^2(t-t')^2 & \dot{\gamma}(t-t') & \\ \dot{\gamma}(t-t') & 1 & \\ & & 1 \end{pmatrix}$$

mean-squared displacement:

$$\begin{pmatrix} \langle\delta x^2\rangle & \langle\delta x\delta y\rangle & \langle\delta x\delta z\rangle \\ \langle\delta y\delta x\rangle & \langle\delta y^2\rangle & \langle\delta y\delta z\rangle \\ \langle\delta z\delta x\rangle & \langle\delta z\delta y\rangle & \langle\delta z^2\rangle \end{pmatrix} \sim \begin{pmatrix} \dot{\gamma}^2 y_0^2 t^2 & & \\ & 0 & \\ & & 0 \end{pmatrix}$$

$$+ \begin{pmatrix} 2t & & \\ & 2t & \\ & & 2t \end{pmatrix} + \begin{pmatrix} 0 & \dot{\gamma}t^2 & \\ \dot{\gamma}t^2 & 0 & \\ & & 0 \end{pmatrix} + \frac{2}{3}\begin{pmatrix} \dot{\gamma}^2 t^3 & & \\ & 0 & \\ & & 0 \end{pmatrix}$$

Taylor Dispersion



[Krüger, Weysser, Fuchs, EPJE (2011)]

- neutral/gradient direction: $\delta z^2 \sim \delta y^2 \sim t$ (diffusion)
- flow direction: $\delta x^2 \sim t^3$ (Taylor dispersion)
- shear-induced cross-correlation $\delta xy \sim \pm t^2$
- holds even for structural relaxation!

Nonequilibrium Smoluchowski Equation

stochastic differential equation

$$d\vec{r}_i = \mathbf{\Gamma}(t)\vec{r}_i\,dt + \frac{1}{\zeta}\vec{F}_i\,dt + \sqrt{2D}d\vec{W}_i$$

Fokker-Planck equation

$$\partial_t p(\{\vec{r}\},t) = \left[\sum_{i=1}^{N} D\vec{\partial}_i\cdot\left(\vec{\partial}_i - \vec{F}_i/k_BT\right) - \sum_{i=1}^{N}\vec{\partial}_i\cdot\mathbf{\Gamma}(t)\cdot\vec{r}_i\right]p(\{\vec{r}\},t)$$

$$\partial_t p(\{\vec{r}\},t) = \Omega_{\text{eq}}p(\{\vec{r}\},t) + \delta\Omega(t)p(\{\vec{r}\},t)$$

solved by time-ordered exponential,

$$p(t) \propto p_{\text{eq}} + \int_{-\infty}^{t}\exp_{+}\left[\int_{t'}^{t}\Omega(\tau)\,d\tau\right]\Omega(t')p_{\text{eq}}\,dt'$$

Nonlinear Response Theory

- nonequilibrium probability distribution $p(\{\vec{r}_i\}, t)$
- time-evolution operator $\Omega(t) = \Omega_{\text{eq}} + \delta\Omega(t)$

$$\partial_t p(t) = \Omega(t) p(t) \qquad \text{e.g. } \delta\Omega(t) = -\sum_{i=1}^{N} \vec{\partial}_i \cdot \underbrace{\boldsymbol{\Gamma}(t)}_{\partial \otimes v} \cdot \vec{r}_i$$

$\Rightarrow$ calculation of non-equilibrium averages (ITT)

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

- schematically: *cf.* Maxwell, microscopic definition for $G(t, t')$
- extension to nonlinear response: $G(t, t') \equiv G(t, t', [\dot{\gamma}])$

$$\boldsymbol{\sigma}(t) \sim \int_{-\infty}^{t} \left[-\partial_{t'} \boldsymbol{B}(t, t') \right] G(t, t', [\dot{\gamma}])\, dt' \sim \int_{-\infty}^{t} \dot{\gamma}(t') G(t, t', [\dot{\gamma}])\, dt'$$

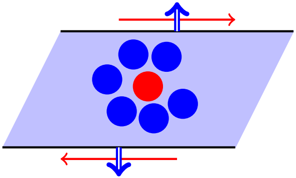
Excursion: Normal Stress Differences

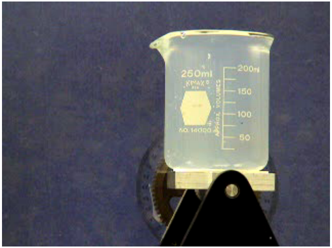
nonequil. $\Rightarrow$ normal-stress differences

anisotropic pressure

$N_1 = \sigma_{xx} - \sigma_{yy} = \mathcal{O}(\dot{\gamma}^2) \neq 0$

- push plates together/pull plates apart





polymeric liquid

- such fluids can 'climb' a stirring rod (Weissenberg's rod climbing)
- "ductless syphon"

Excursion: Normal Stress Differences

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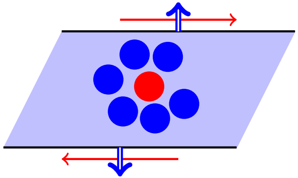
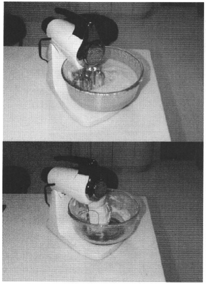




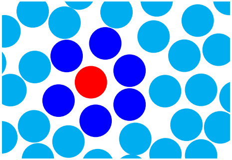
- such fluids can 'climb' a stirring rod (Weissenberg's rod climbing)
- "ductless syphon"

Mode-Coupling Theory

"There is something fascinating about science.
One gets such a wholesale returns of conjecture
out of such a trifling investment of fact."
[Mark Twain]

Rheo-MCT: The Idea

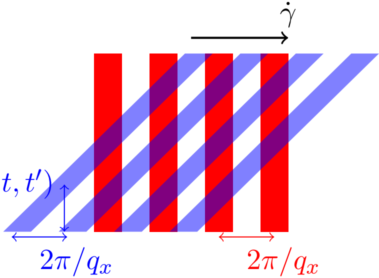
- mode-coupling theory: slow dynamics by density fluctuations $e^{i\vec{q}\cdot\vec{r}_i}$
  - transient density correlators $\phi(\vec{q}, t, t')$
  - retarded friction: memory kernel
  - cage effect $\Rightarrow$ glass transition



- advected wave vector
  - shear destroys cages

$$\vec{q}(t,t') = \vec{q}\cdot \boldsymbol{E}^{-1}(t,t')$$

$$\boldsymbol{E}(t,t') = \exp_+ \left[\int_{t'}^{t} \boldsymbol{\Gamma}(\tau)\, d\tau\right]$$



[Brader *et al.*, Phys Rev Lett (2008)]

[Brader, ThV, Cates, Fuchs, Phys Rev Lett (2007)]
[Brader, ThV, Fuchs, Larson, Cates, PNAS (2009)]

A First-Principles Approach

mode-coupling theory, integration through transients (MCT+ITT):

$$\boldsymbol{\sigma}(t) \overset{\text{MCT}}{\approx} \int_{-\infty}^{t} dt' \int \frac{d^3k}{(2\pi)^3} \left[-\frac{\partial}{\partial t'} \left(\vec{k} \cdot \boldsymbol{B}(t,t') \cdot \vec{k} \right) \vec{k} \otimes \vec{k} \right] \left[\frac{S'_k S'_{k(t,t')} \phi_{\vec{k}(t,t')}(t,t')^2}{4kk(t,t') S_k^2} \right]$$

- microscopic potential stress element $\hat{\sigma}_{ab} = \sum_{i=1}^{N} r_{i,a} F_{i,b}$
- rotational invariant Finger tensor $\boldsymbol{B}(t,t') = \boldsymbol{E}(t,t') \boldsymbol{E}^T(t,t')$
- nonequilibrium time evolution Ω (e.g., Smoluchowski operator)
- transient density correlations:

$$\Gamma_{\vec{q}}(t,t')^{-1} \partial_t \phi_{\vec{q}}(t,t') + \phi_{\vec{q}}(t,t') + \int_{t'}^{t} m_{\vec{q}}(t,t'',t') \partial_{t''} \phi_{\vec{q}}(t'',t')\, dt' = 0$$

$$m_{\vec{q}}(t,t'',t') = \int \frac{\varrho\, d^3k}{16\pi^3} \frac{S(q_{tt'}) S(k_{t''t'}) S(p_{t''t'})}{q_{t''t'}^2 q_{tt'}^2} \times$$

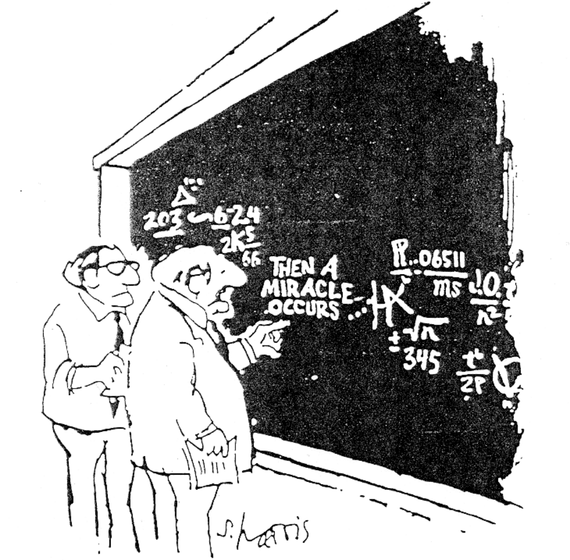
$$\times V_{\vec{q}\vec{k}\vec{p}}(t'',t') V_{\vec{q}\vec{k}\vec{p}}(t,t') \phi_{\vec{k}_{t''t'}}(t,t'') \phi_{\vec{p}_{t''t'}}(t,t'')$$

[Brader, ThV, Fuchs, Larson, Cates, PNAS (2009)]

A First-Pr

mode-coup … +ITT):

$$\boldsymbol{\sigma}(t) \overset{\text{MCT}}{\approx} \int_{-\infty}^{t} \cdots \frac{\phi_{\vec{k}(t,t')}(t,t')^2}{\cdots(t,t')S_k^2}\Big]$$



"I think you should be more explicit here in step two."
(Scientific American)

- microsc…
- rotationa… …, t')
- nonequili… …or)
- transient

$$\Gamma_{\vec{q}}(t,t \cdots dt' = 0$$

…ates, PNAS (2009)]

Rheo-Mode-Coupling Theory, Schematically

schematic model:

$$\sigma(t) \sim \int_{-\infty}^{t} dt' \, \dot\gamma(t') G(t,t',[\dot\gamma]) \overset{\text{MCT}}{\approx} \int_{-\infty}^{t} dt' \, v_\sigma \, \dot\gamma(t') \, \phi^2(t,t',[\gamma])$$

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

$$m(t,t''t,') = h[\gamma_{tt'}] h[\gamma_{tt''}] \left(v_1 \phi(t,t'') + v_2 \phi(t,t'')^2 \right)$$

- nonlinear: accumulated strain history $\gamma_{tt'} = \int_{t'}^{t} \dot\gamma \, d\tau$
- steady state qualitatively: nonlinear Maxwell model

$$\eta(\dot\gamma) \sim \eta_\infty + G_\infty \tau / [1 + \dot\gamma \tau / \gamma_c]$$

- invert constitutive equation?

[Brader, ThV, Fuchs, Larson, Cates, PNAS (2009)]

Rheo-Mode-Coupling Theory, Schematically

schematic model:

output, input, model

$$\sigma(t) \sim \int_{-\infty}^{t} dt'\,\dot\gamma(t')G(t,t',[\dot\gamma]) \overset{\text{MCT}}{\approx} \int_{-\infty}^{t} dt'\,v_\sigma\,\dot\gamma(t')\,\phi^2(t,t',[\dot\gamma])$$

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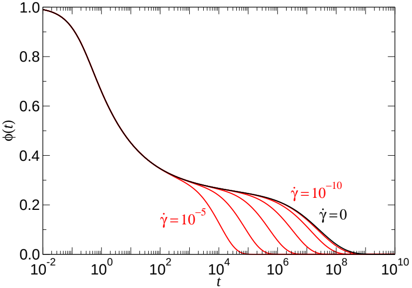
[Brader, ThV, Fuchs, Larson, Cates, PNAS (2009)]

Advection and Cageing: Shear Thinning

- MCT combines cage effect with shear advection
- approach to glass transition: $\tau(\varphi) \sim (\varphi_c - \varphi)^{-\gamma}$
- vertex $V(\vec{q}, \vec{k}\vec{p}, \dot{\gamma}, t)$ decays with $\dot{\gamma}t \Rightarrow$ loss of memory
- steady-state dynamics speeded up: $\tau(\dot{\gamma}) \sim 1/\dot{\gamma}$



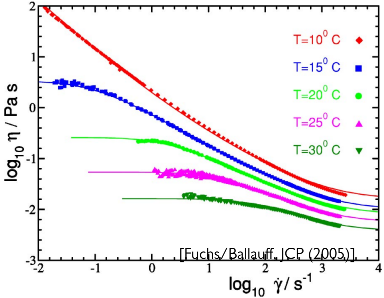
$\Rightarrow$ shear thinning: $\eta(\dot{\gamma}) = \sigma/\dot{\gamma} \sim \int \phi^2(t')\,dt'$

$\Rightarrow$ relaxation time decreases with $\dot{\gamma}$, diverges as $\dot{\gamma} \to 0$, $\varphi \to \varphi^c$ (shear melting of glasses by any small shear rate)

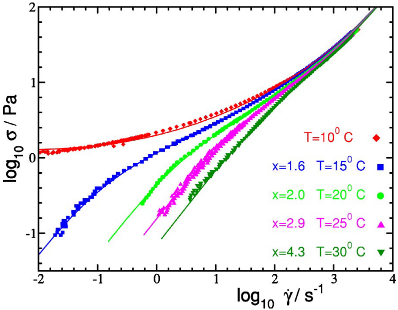
Yielding and Flowing

"Science is true. Don't be misled by facts."
[Finagle's Creed]

Dynamical Yield Stress



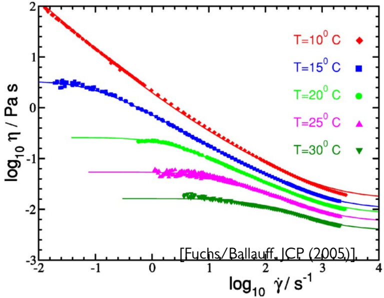
thermosensitive colloids: $\eta(\varrho, \dot{\gamma})$

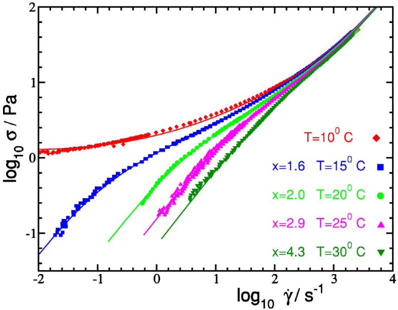


flow curves in *steady state*

- $\eta_{\text{steady state}} \ll \eta_{\text{equil.}} \Rightarrow$ transient dynamics!
- finite stress $\sigma(\dot{\gamma} \to 0) = \sigma_y$ in the glass: dynamic yield stress
- $\dot{\gamma} \to 0$ is singular; $\sigma = \dot{\gamma} \int_{-\infty}^{t} G(t - t', \dot{\gamma})\, dt'$

Dynamical Yield Stress





thermosensitive colloids: $\eta(\varrho, \dot\gamma)$

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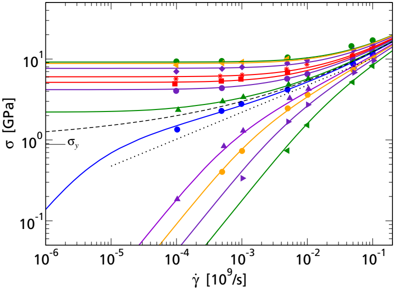
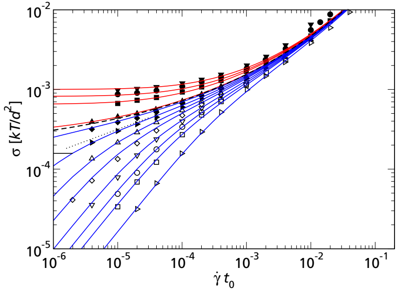
Discontinuous Yield-Stress Transition



metallic glass [Egami group, PRL (2010)]



agitated granular system [Haxton/Liu, PRL (2007)]

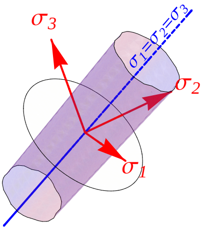
- glass transition: $\sigma_y^c(T \to T_c) > 0$ – discontinuous transition
- power-law-like crossover – but no critical-point scaling
- true granular matter, $T \to 0$: different?

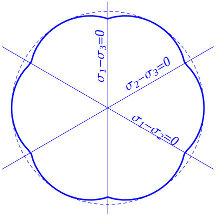
[ThV, Eur Phys J E (2011)]

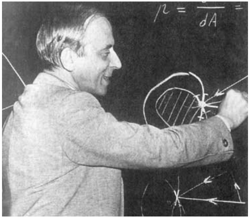
von Mises' Criterion

when does a material yield under arbitrary deformation?

- von Mises (1913): when distortion energy > critical value
  $\Rightarrow$ yield surface $\left((\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_1 - \sigma_3)^2\right)/6 = \sigma_y^2$
- MCT: "first-principles" derivation for dynamical yield surface
  - normal stress differences $\Rightarrow$ non-circular yield surface







[Brader, ThV *et al.* PNAS (2009)]

Rheo-Mode-Coupling Theory, Schematically

schematic model:

output, input, model

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[Brader, ThV, Fuchs, Larson, Cates, PNAS (2009)]

Rheo-Mode-Coupling Theory, Schematically

schematic model:

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$$\eta(\dot\gamma) \sim \eta_\infty + G_\infty\tau/[1+\dot\gamma\tau/\gamma_c]$$

- invert constitutive equation?

Creep: Maxwell Model

$$\sigma = G_\infty \tau_0 \dot\gamma + G_\infty \frac{\dot\gamma}{1/\tau + \dot\gamma/\gamma_c}$$

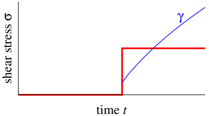
solution for constant σ

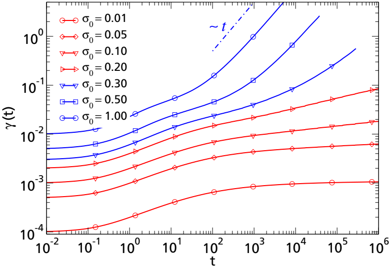
$$\dot\gamma = \begin{cases} \frac{\sigma}{\sigma_y - \sigma}\frac{\gamma_c}{\tau} + \mathcal{O}(1/\tau^2) & \text{for } \sigma < \sigma_y \\ \frac{\sigma - \sigma_y}{G_\infty \tau_0} + \frac{\sigma_y}{\sigma - \sigma_y}\frac{\gamma_c}{\tau} + \mathcal{O}(1/\tau^2) & \text{for } \sigma > \sigma_y \end{cases}$$

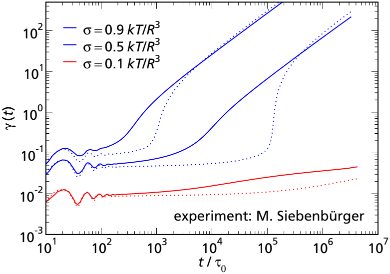
yield stress $\sigma_y = G_\infty \gamma_c$

Creep

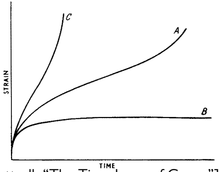
- deformation $\gamma(t)$ following sudden step stress







- nonequilibrium transition:
  plastic deformation / flow
- static yield stress σ_c
- anomalous flow behavior (creep)?



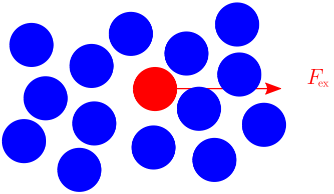
[Cottrell, "The Time Laws of Creep"]

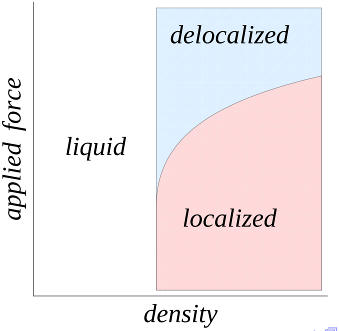
[Siebenbürger, Ballauff, ThV (in preparation)]

Static Yielding: A Force Threshold

- steady external shear $\Rightarrow$ glass molten (always)
- steady external force $\Rightarrow$ yielding transition σ_c
- microscopic analog?
  - yielding of individual "cages" by local external force

$\Rightarrow$ microrheology

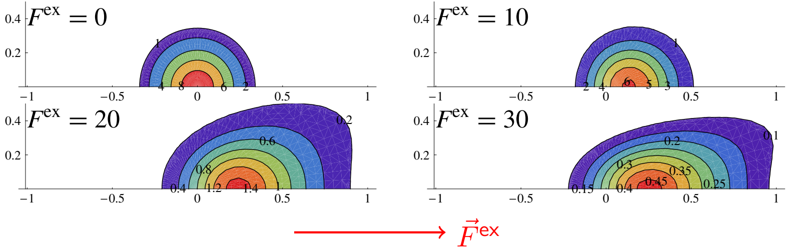




[Gazuz, Puertas, ThV, Fuchs, PRL (2009)]

Local Melting of the Glass

- $F^{\text{ex}} < F_c^{\text{ex}}$: localized probe
- distorted probe probability density $\phi^s(\vec{r}, t \to \infty)$

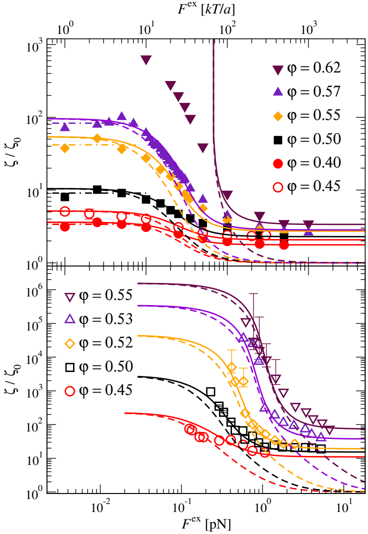


- $F^{\text{ex}} > F_c^{\text{ex}}$: delocalized probe
- $F_c^{\text{ex}} \gg k_B T/\sigma$: cages, not thermal forces

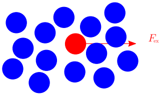
[Gazuz, Puertas, ThV, Fuchs, PRL (2009)]

Microscopic Yielding

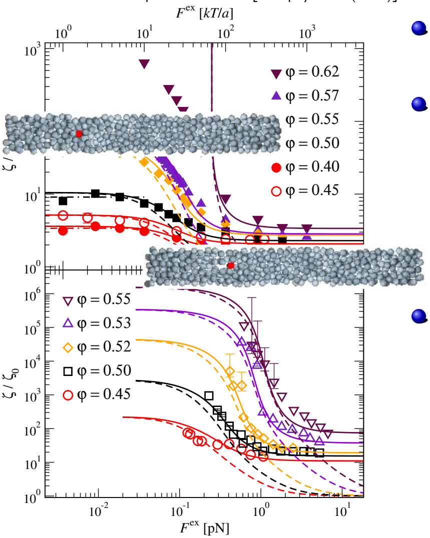
sim.: A M Puertas / exp.: Habdas *et al.* [Europhys Lett (2004)]



- depinning signature at $F \approx F_c$: measures typical cage strength
- fits: schematic model (MCT)
  - modes $\parallel \vec{F}^{\text{ex}}$, $\perp \vec{F}^{\text{ex}}$
  - high-force plateau: fluctuations $\perp$ force
  - strong influence of hydrodynamic interactions
- MCT power laws $\curvearrowright$ $\langle v\rangle_\infty \sim (F - F_c)^{1/a-1}$



[Gnann, Gazuz, Puertas, Fuchs, ThV, Soft Matter (2011)] sim.: A M Puertas / exp.: Habdas *et al.* [Europhys Lett (2004)]



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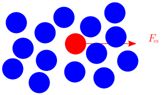


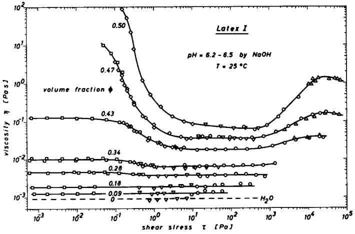
[Gnann, Gazuz, Puertas, Fuchs, ThV, Soft Matter (2011)]

Beyond...

*"I have yet to see any problem, however complicated,
which when you looked at it in the right way,
did not become still more complicated."*
[Paul Anderson, New Scientist (1969)]

Shear Thickening and Jamming

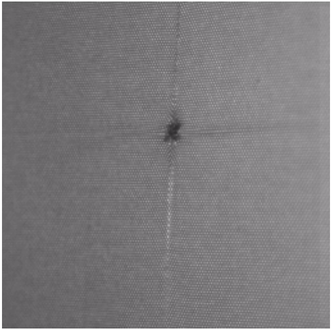
for some complex liquids, viscosity can increase again at high $\dot{\gamma}$



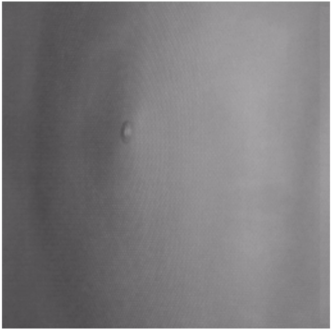
[Laun, Ang Makromol Chem (1984)]

- here, similarly, at high imposed external shear
- most famous example: mixture of cornstarch and water
- extreme case: "jamming"
  - the limit of *granular materials*

Example: Shear Thickening



3 layers nylon



2 layers, colloid-impregnated

N. J. Wagner and coworkers (U Delaware)

[http://www.ccm.udel.edu/STF/images1.html]

Shear Thickening Fluids: Fun With Cornstarch

Spanish Television Show ‘El Hormiguero’

thank you
for your attention!

my thanks for support to:
M Ballauff/R Besseling/
J M Brader/M E Cates/
S Egelhaaf/M Fuchs/W Götze/
J Horbach/M Laurati/A Meyer/
A M Puertas/M Siebenbürger
and thanks to
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Ch Harrer/S Papenkort/
S Schnyder

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