Dispersion Rheology

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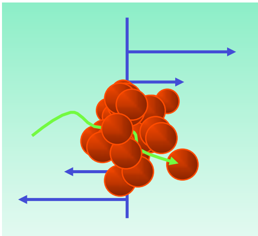

Outline

Dispersions of non-interacting hard spheres
- Volume fraction dependence
- Brownian particles and Péclet number
- Shear induced diffusion

Soft particle dispersions

Weakly aggregating dispersions
  microstructure in relation to
  - flowcurve
  - linear viscoelasticity

Dispersions out of thermodynamic equilibrium

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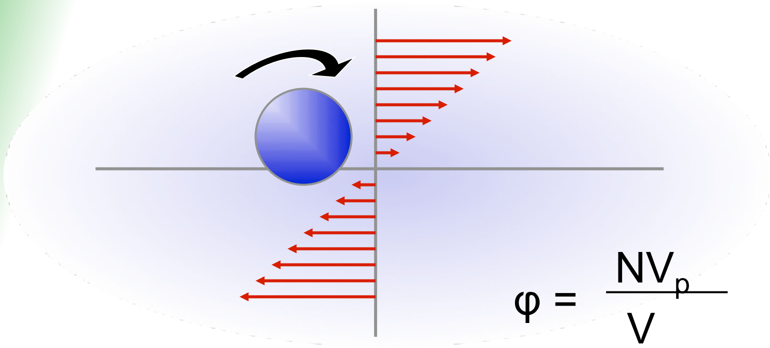
Sphere in liquid

- goes with the flow
- has to rotate, additional friction



$$\varphi = \frac{NV_p}{V}$$

Einstein calculated:

$\eta = \eta_o\,(1+2.5\varphi\,)$

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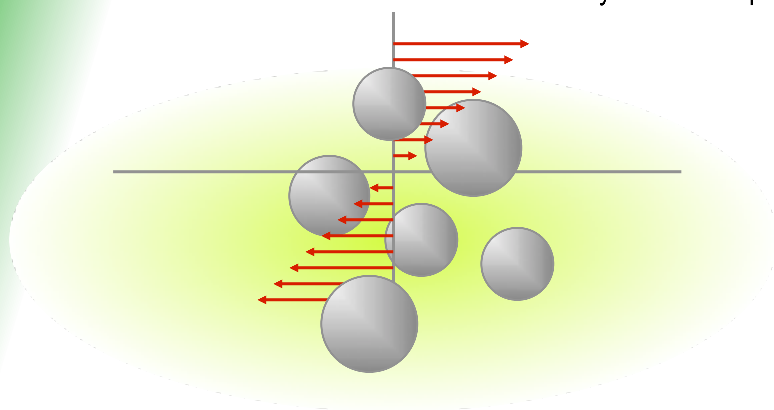
Dispersions



At higher concentrations

- *particles collide with each other*
- *excluded volume effects*

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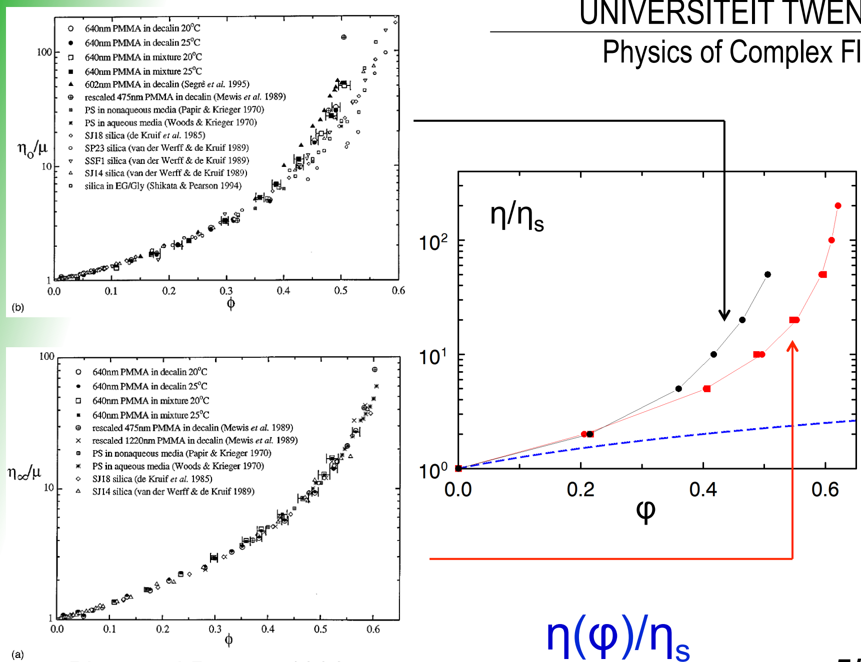

Phan and Russel; 1996

$\eta(\varphi)/\eta_s$

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Einstein's result

$$\eta = \eta_s(1 + [\eta]\phi), \qquad \phi \ll 1$$

$[\eta]=2.5$, $\varphi = NV_p/V$

In terms of number of added particles, ΔN:

$$\eta(\Delta N) = \eta_s \left(1 + [\eta]\frac{V_p}{V_{\text{free}}}\Delta N\right)$$

V_{free}: volume available to the added particles

Mean field approach: starting with N particles, call that your "solvent" and add again ΔN particles:

$$\eta(N + \Delta N) = \eta(N) \left(1 + [\eta]\frac{V_p}{V - \alpha N V_p}\Delta N\right)$$

α slightly larger than 1 due to interstitial solvent.

$$\eta(N+\Delta N) = \eta(N)\left(1 + [\eta]\frac{V_p}{V-\alpha N V_p}\Delta N\right)$$

rewriting this equation

$$\frac{\eta(N+\Delta N)-\eta(N)}{\eta(N)} = [\eta]\frac{V_p}{V-\alpha N V_p}\Delta N = [\eta]\frac{\Delta N V_p/V}{1-\alpha N V_p/V}$$

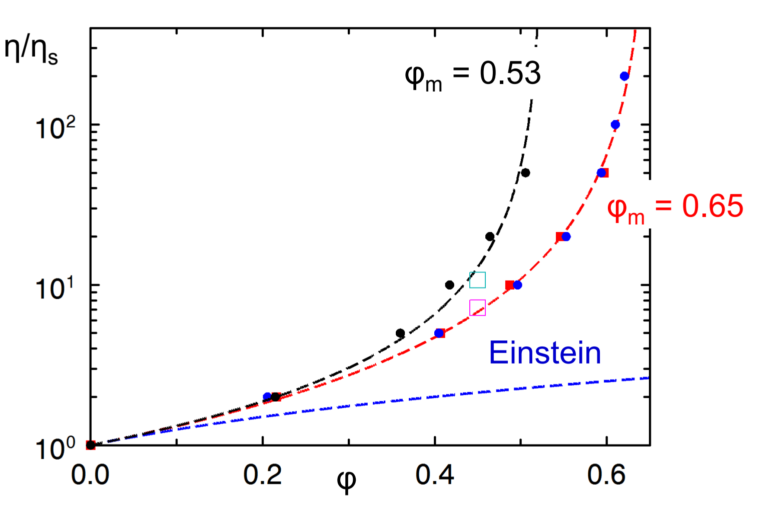
or

$$\frac{d\eta}{\eta} = [\eta]\frac{d\phi}{1-\alpha\phi}$$

$\alpha = 1/\varphi_m$

Krieger Dougerhty equation:

$$\eta = \eta_s\left(1-\phi/\phi_m\right)^{-[\eta]\phi_m}$$



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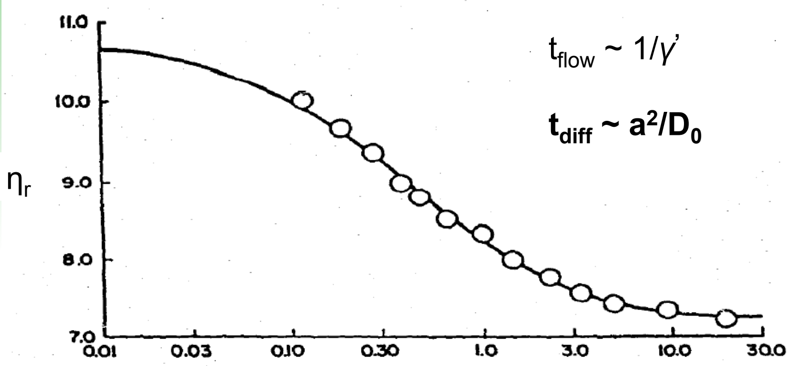
colloidal particles
competition between diffusion and convection



$t_{flow} \sim 1/\dot{\gamma}$

$\mathbf{t_{diff} \sim a^2/D_0}$

Pe = $\dot{\gamma} a^2/D_0$

polystyrene particles
a = 400 nm

Krieger, 1972

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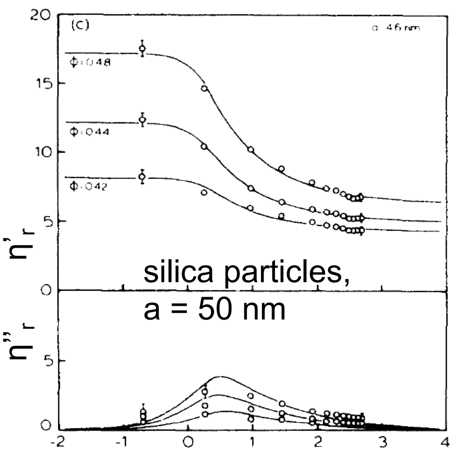
Viscoelastic effects:

HS dispersions show visco-elasticity.

What is the origine of the elasticity?

Entropy and distorsion of the pair distribution fuction g($\underline{r}$)

$$\underline{T}^{[\mathrm{str}]} = n \int p(\underline{r}) \, [\underline{r}\,\underline{F}] \, d^3 r$$



J. van de Werf et al.; 1989

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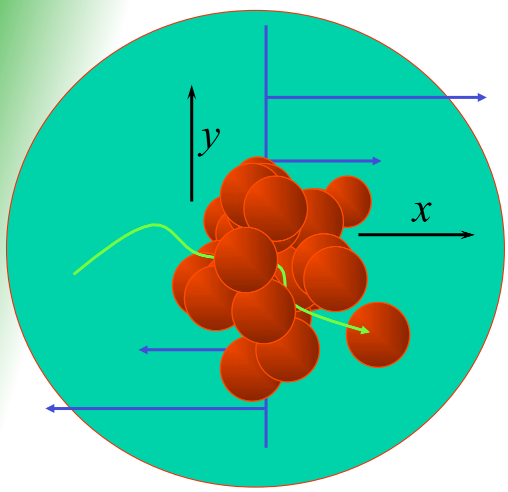
Non colloidal particles

shear-induced self-diffusion in simple shear flow



$D_{□□} = a^2 □ \, D_{□□}(□)$

- a particle radius
- □ rate of shear
- □ volume fraction

Tensor character:

$$\begin{Bmatrix} D_{xx} & D_{xy} & 0 \\ D_{yx} & D_{yy} & 0 \\ 0 & 0 & D_{zz} \end{Bmatrix}$$

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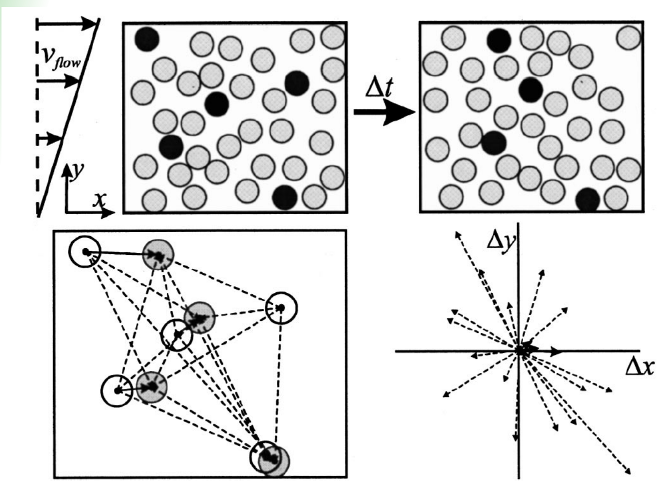
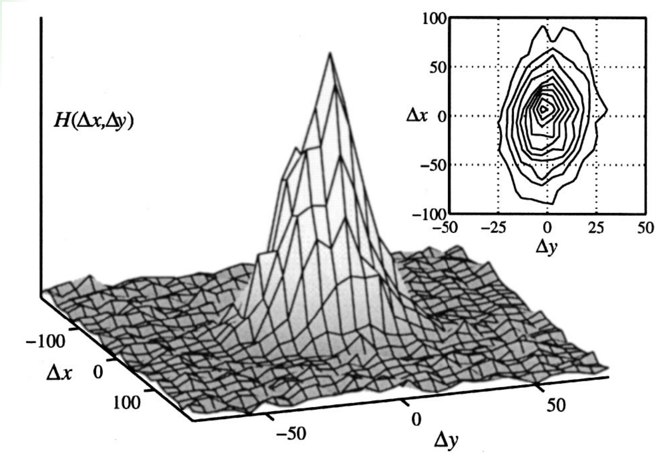


V. Breedveld et al. ; 2002



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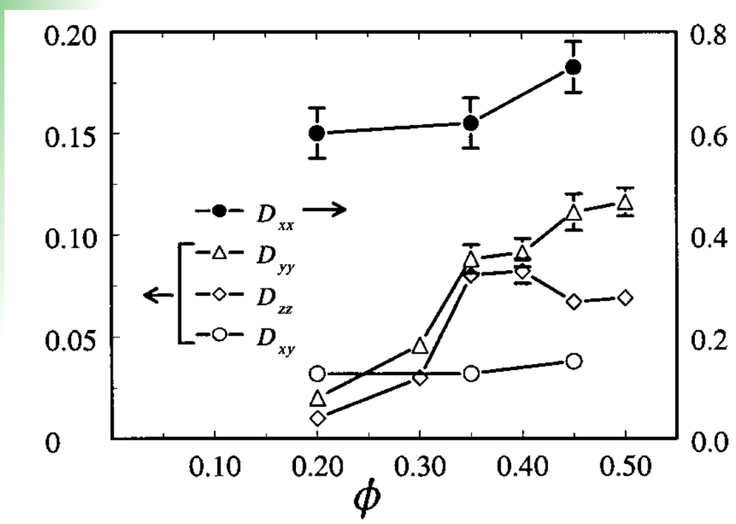

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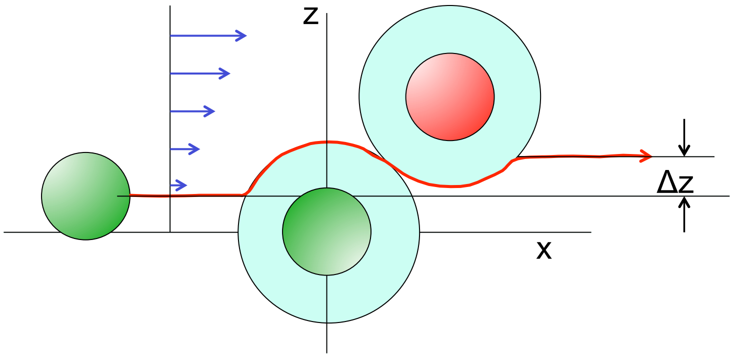
Simple model

- Particles follow flow lines
  if not prohibited by excluded volume
- While colliding they role over each other
- Collisions are not completed due
  to interaction with a third particle



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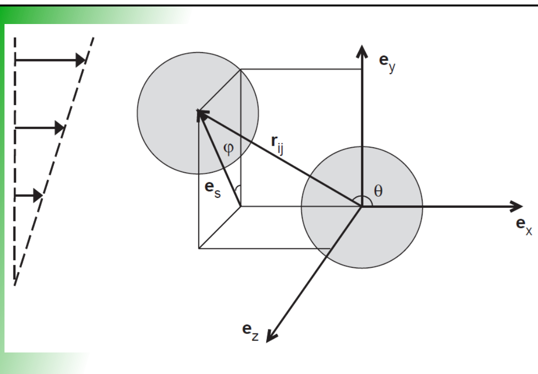

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Taking an average collision time $t_c(\varphi)$, we calculate the displacement vector $\underline{s}(\theta,\varphi)$ per collision.

Diffusion tensor:

$$\underline{D} = \frac{\langle \underline{s}\,\underline{s} \rangle}{2t_c} = \frac{4\phi\dot{\gamma}}{\pi}\langle \underline{s}\,\underline{s} \rangle$$

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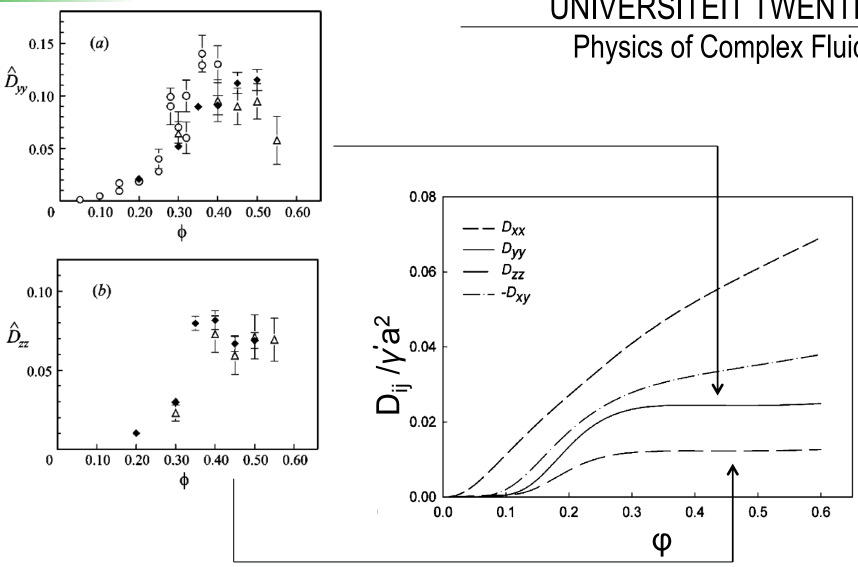

V. Breedveld, thesis UT ; 2000

J. Kromkamp et al. ; 2006

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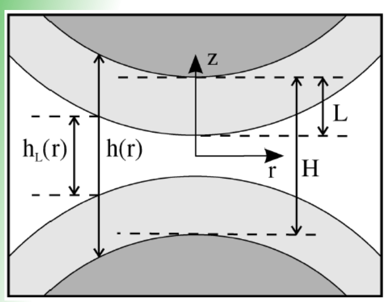
Soft particle rheology



$$\left(\frac{R+L}{R}\right)^3 = 5$$

$$\phi_{\text{eff}} = \left(\frac{R_c + L}{R_c}\right)^3 \phi_{\text{core}}$$

$$\eta_{r,\infty} = 1 + \tfrac{5}{2}\phi_{\text{eff}} + \frac{\mu_{\text{lub}}}{\mu}$$

$$\frac{\mu_{\text{lub}}}{\mu} = 9\frac{2R_c}{2R_c + H_{\text{av}}}\overline{F}(H_{\text{av}})$$

$$H_{\text{av}} = 2R_c\left[\left(\frac{\phi_{\max}^{\text{core}}}{\phi_{\text{core}}}\right)^{1/3} - 1\right]$$

P.A. Nommensen; 1999

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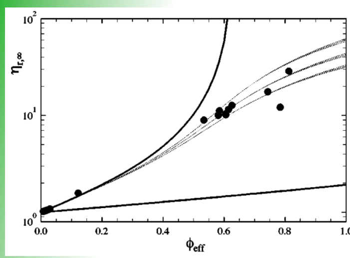

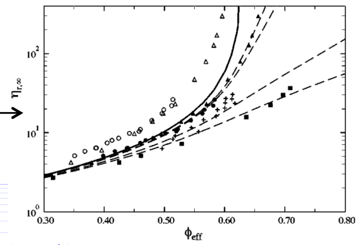

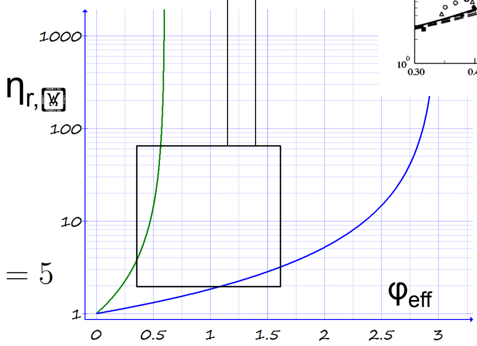

$$\left(\frac{R+L}{R}\right)^3 = 5$$

D'Haene,
thesis Leuven; 1992

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The mystery of the missing factor 3

$$\langle \Delta x^2(t)\rangle = \frac{k_B T}{3\pi R} J(t)$$

$$\langle \Delta r^2(t)\rangle = \langle \Delta x^2(t)\rangle + \langle \Delta y^2(t)\rangle + \langle \Delta z^2(t)\rangle = 3\,\langle \Delta x^2(t)\rangle$$

$$\langle \Delta r^2(t)\rangle = 3\,\frac{k_B T}{3\pi R} J(t) = \frac{k_B T}{\pi R} J(t)$$

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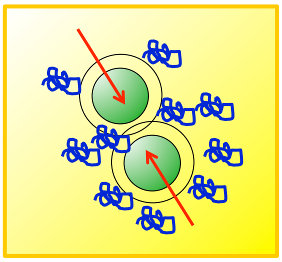
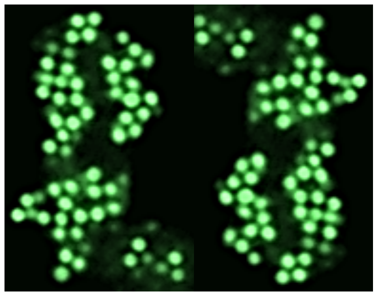
Weakly aggregating colloidal dispersions





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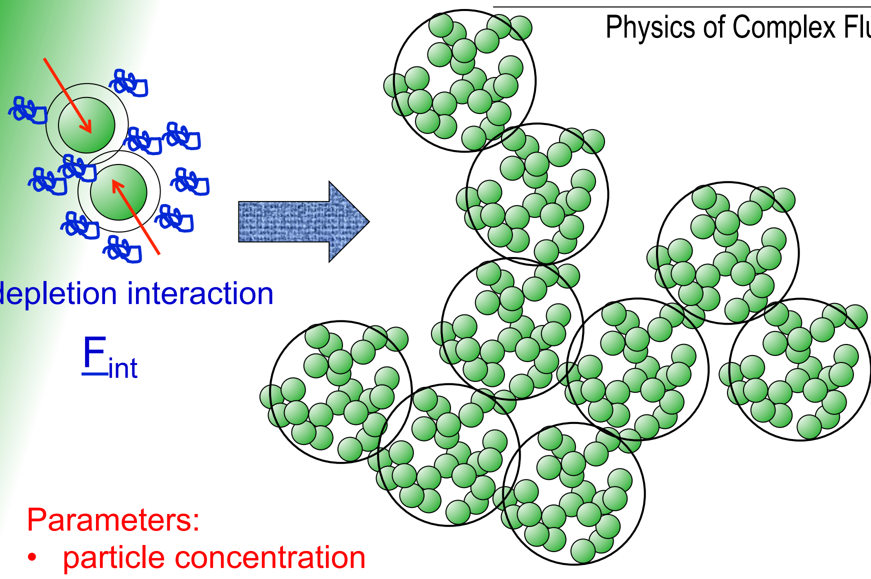


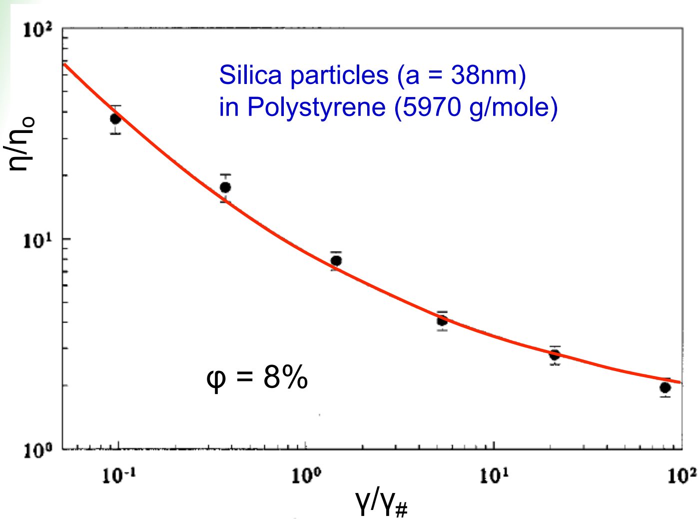
depletion interaction

$\underline{F}_{int}$

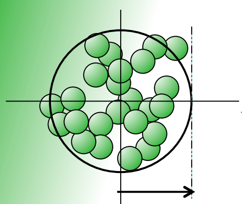
Parameters:

- particle concentration
- polymer concentration and size
- structure of the aggregates

Flow curve



Wolters et al. 1996



R

$$N(R) = N_0 \left(\frac{R}{a}\right)^{d_f}$$

fractal aggregate

volume fraction of aggregates: $$\phi_a = \frac{\phi_p}{N_0}\left(\frac{R}{a}\right)^{3-d_f}$$

$F_{int} \geq F_{hyd}$: $$F_{\rm int} = F_{\rm hyd} = \frac{5}{2}\pi R^2 \eta \dot{\gamma}$$

mean field approximation

viscosity curve:

$$\eta = \eta_0 \left(1 + \frac{\phi_p}{\phi_m}\left(\frac{\tau_{\rm int}}{\eta\dot{\gamma}}\right)^{(3-d_f)/2}\right)^{-2.5\phi_m} \qquad \tau_{\rm int} = \frac{2F_{\rm int}}{5\pi a^2}$$

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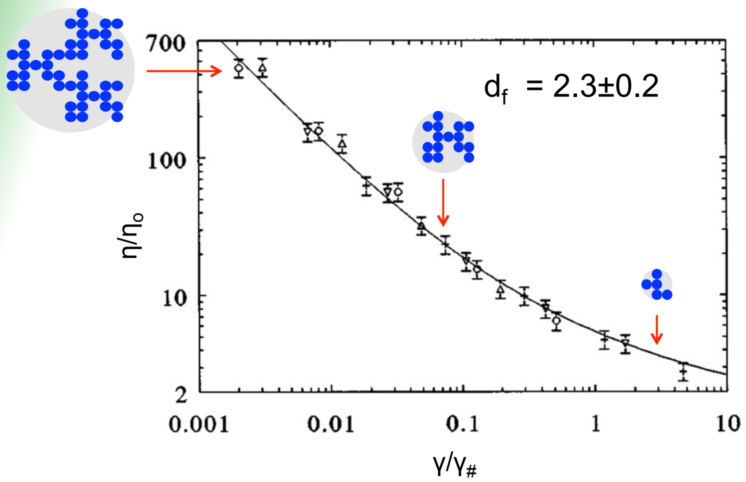

$$\dot{\gamma}_{\#} = \left(\frac{\phi}{\phi_m}\right)^{2/(3-d_f)} \frac{\tau_{\text{int}}}{\eta_0}$$

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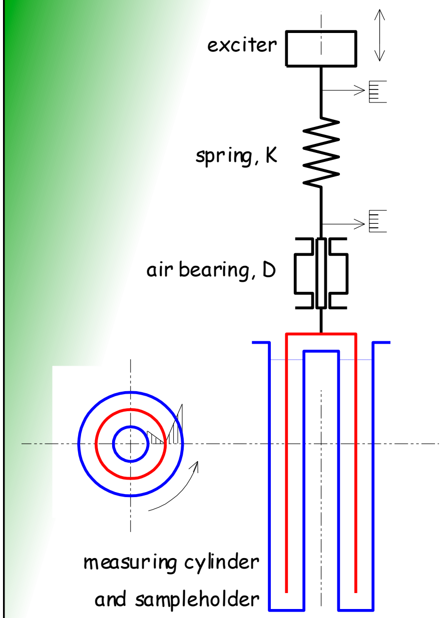

measuring
elasticity
in a shear flow:
G' ([illegible],[illegible])
G" ([illegible],[illegible])

Steady rotation in
the r,φ plane,
Oscillation in the r,z plane

Zeegers et al. ; 1995

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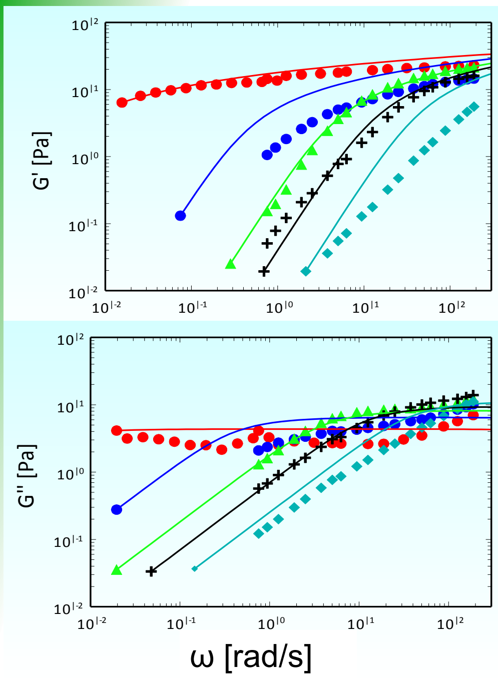
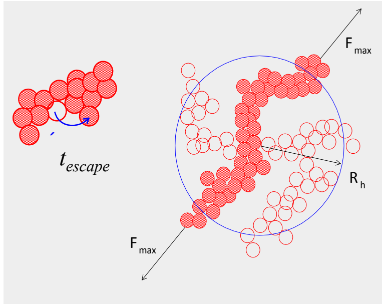


increasing $\dot{\gamma}$



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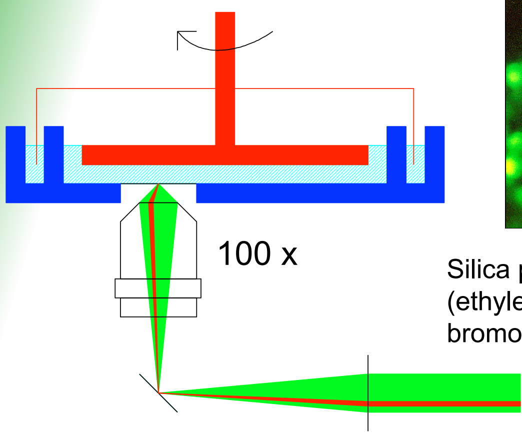
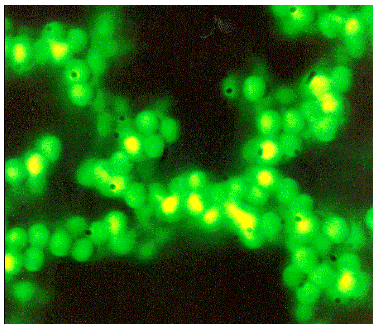
Shear cell on Confocal Scanning Laser Microscope





Silica particles (1 μm) and poly (ethylene glycol) in a methanol-bromoform mixture

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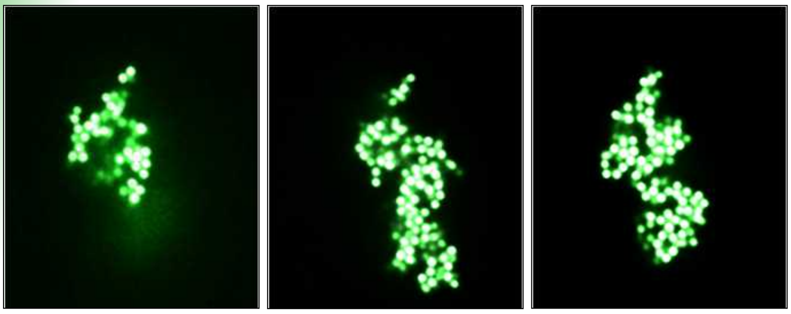

Different cross sections through an aggregate

V. Tolpekin, thesis UT; 2004

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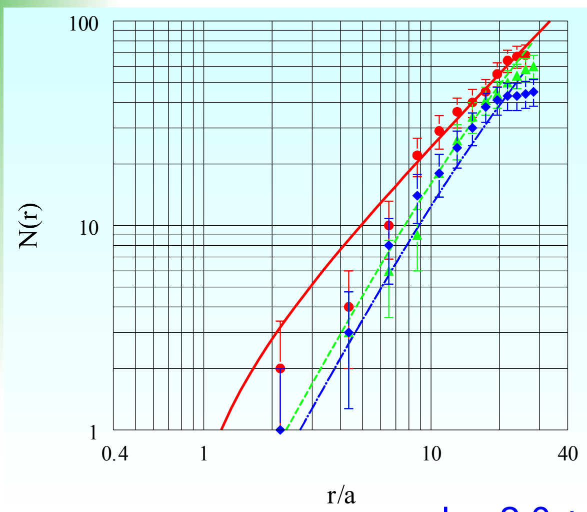

z = +5 um
z = 0 um
z =-5 um

$d_f = 2.0 \pm 0.1$

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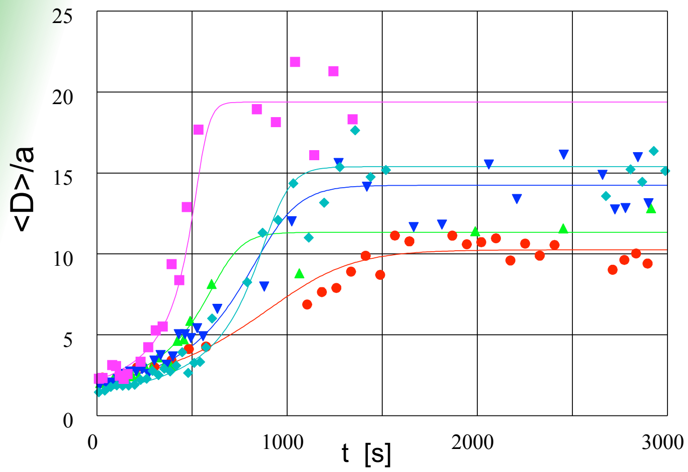
Aggregate growth



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Modeling the aggregate growth

$dn_i/dt = ½ □ A_{i\text{-}j,j}\, n_{i\text{-}j}\, n_j - □ A_{ij}\, n_i\, n_j + □ B_j\, p_{ji}\, n_j - B_i$ ...

Aggregation: $A_{ij} = 4/3\ □\ (R_i + R_j)^3$

Break-up: $B_i = K_o(□)\ (R_i/a)^Q$

$d\, □ R^{df}\, □ /dt = C\ [□ R^3\, □ + 3\, □ R^2\, □\ □ R\, □] - K_o($ ...

adjustable: $K_o(□),\ Q$

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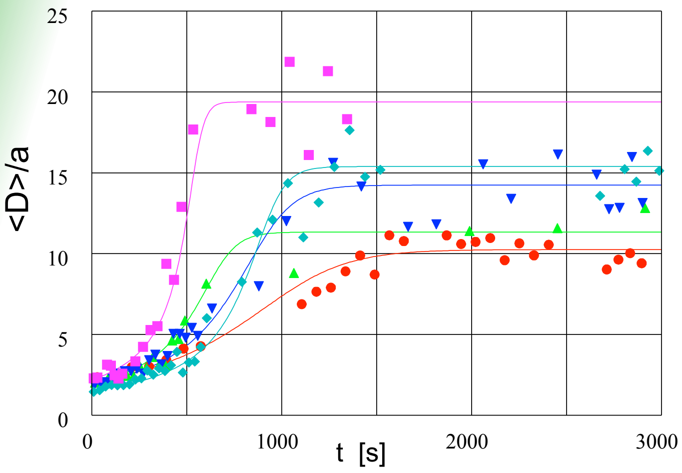
Results of the modeling



(input: $d_f = 2.0$, $t_{agg} = 460$ s)

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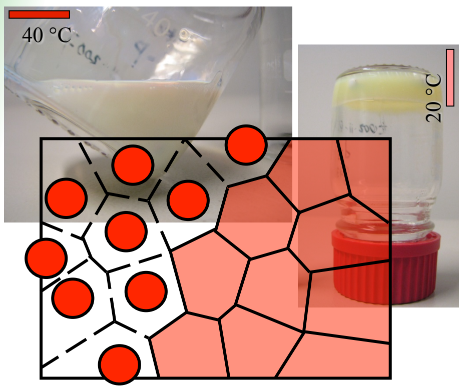


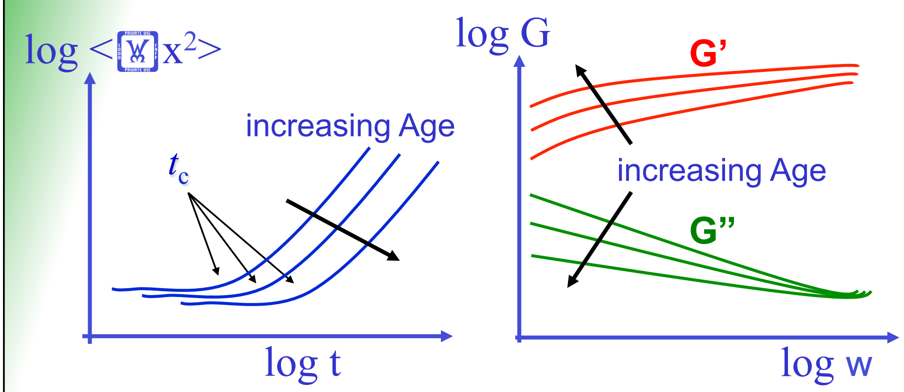
Aging of soft colloidal suspensions studied by macro- and micro-Rheology

E.H. Purnomo et al.; 2008

Aging in soft glassy materials

* relaxation processes slow down with age of the sample…
* equilibrium is never reached…

(micro-) rheology probes the aging



Structural relaxation time: $t_s \sim t_c$

Thermosensitive polyNipam-polyNipmam particles

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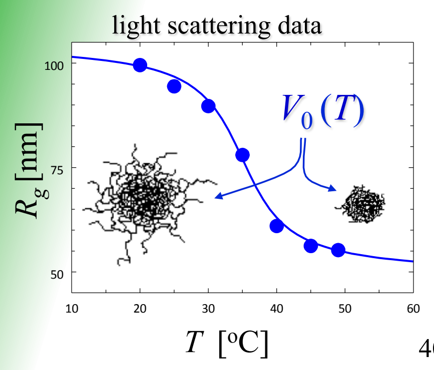
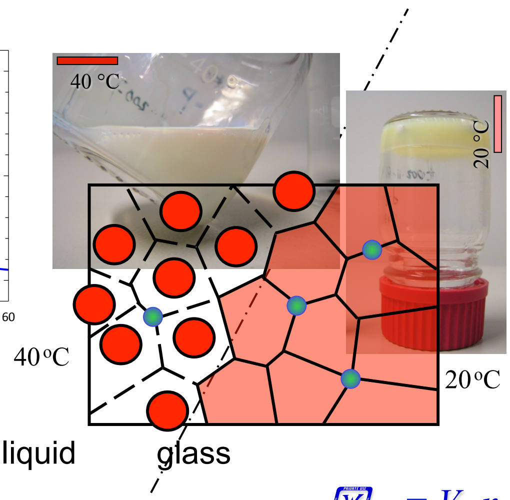




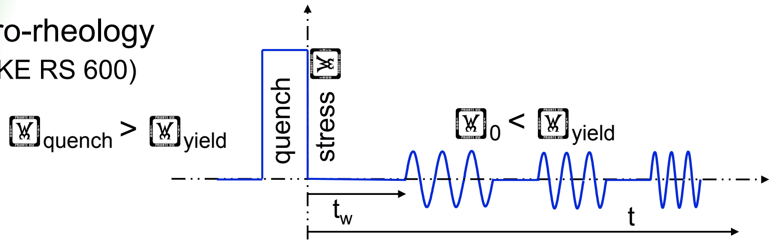
$_{\mathrm{eff}} = V_0\, n$

with fluorescent (●) tracer particles

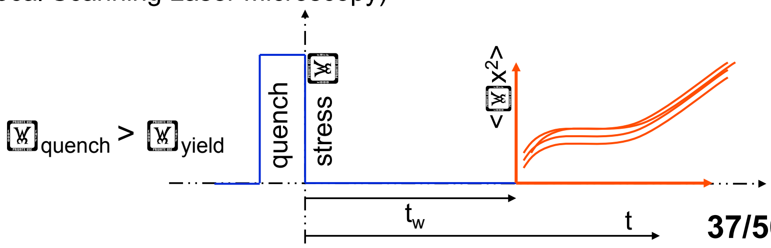
Experiment

To obtain reproducible results…
…rejuvenate the sample

1: macro-rheology
(HAAKE RS 600)

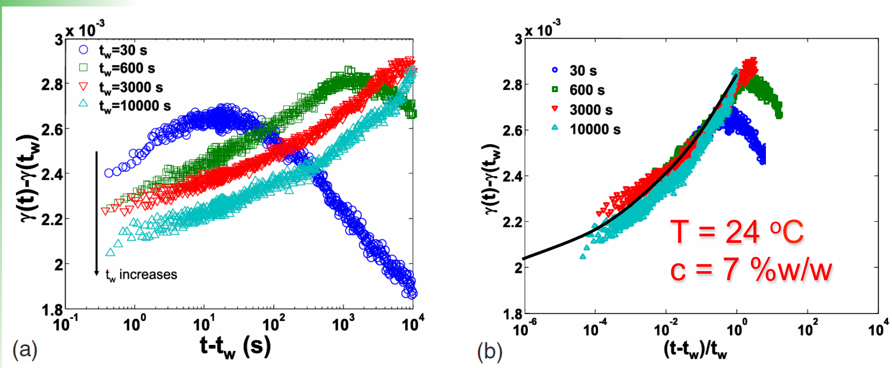


2: particle tracking
(Confocal Scanning Laser Microscopy)



Creep measurements

$J(t-t_w,t_w) = (\gamma(t)-\gamma(t_w))/\sigma_0$



$$J(t-t_w,t_w) = \frac{1+c[(t-t_w)/t_w]^{1-x}}{G_p}$$

Linear rheology, age dependence

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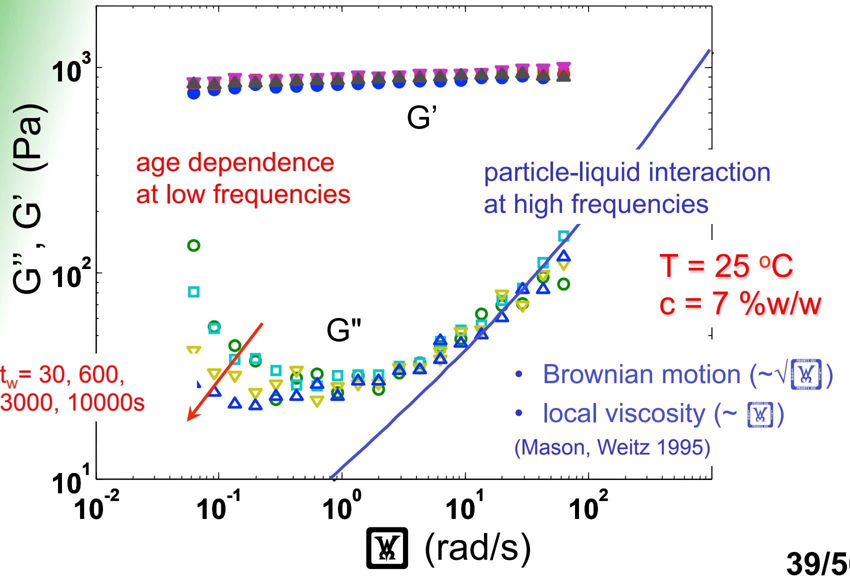

T = 25 °C
c = 7 %w/w

- Brownian motion (~√ω)
- local viscosity (~ ω)

(Mason, Weitz 1995)

Soft Glassy Rheology model

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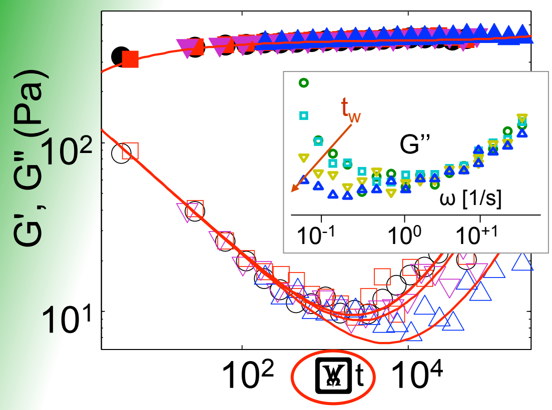
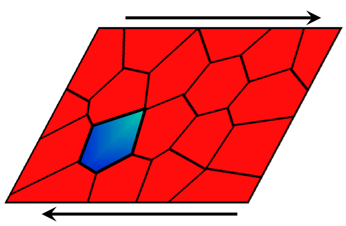


Microscopic picture



Elastic response

- Dissipation due to internal yielding of the particles
- Activated rate process with effective noise temperature *x*
  - *x* > 1: liquid, *G** = *fnc* (ω), *J* = *fnc* ($t-t_w$)
  - *x* < 1: glass, *G** = *fnc* (ω*t*), *J* = *fnc* ($(t-t_w)/t_w$)

P. Sollich *et al.*, Phys. Rev. Lett. 78, 2020 (1997);
S.M. Fielding *et al.*, J. Rheol. 44, 323 (2000)

Macro-rheology (curves: SGR model)

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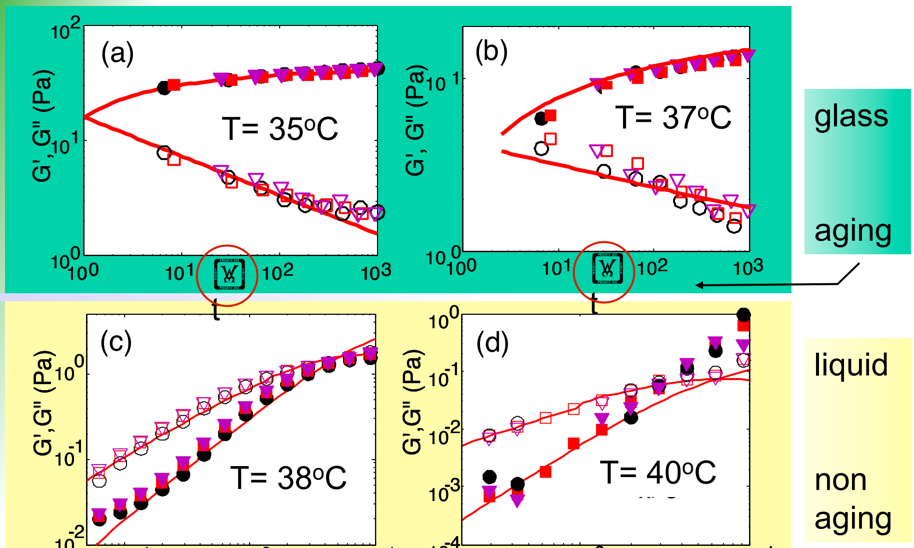
mass concentr. *c*: 7 %w/w t_w: 3, 30, 300 s



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Phase diagrams

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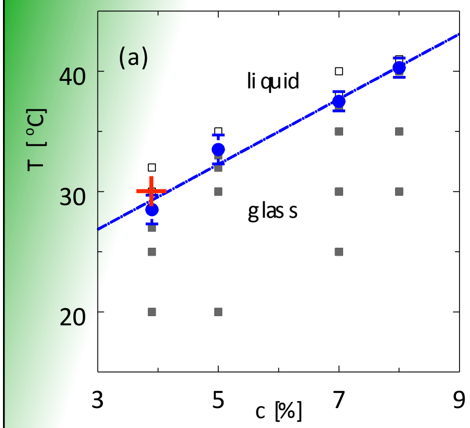
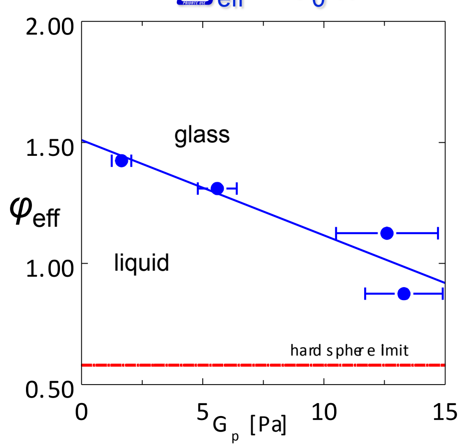


+: micro-rheology

$\varphi_{eff} = V_0\, n$



E.H. Purnomo *et al.*, 2008

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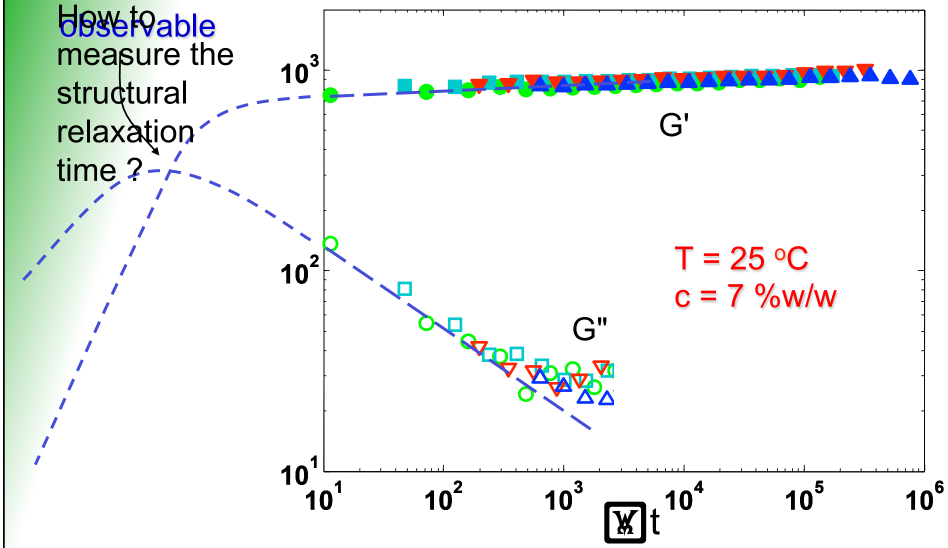
The structural relaxation time is not observable

How to measure the structural relaxation time ?



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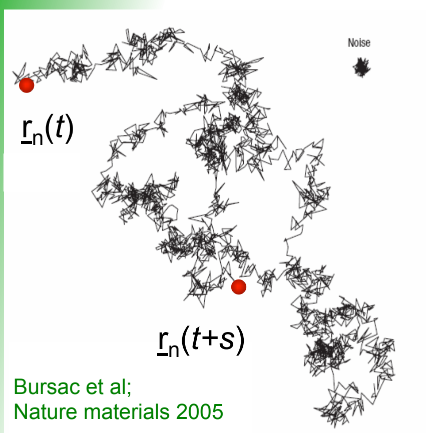
particle tracking μ-rheology



Bursac et al;
Nature materials 2005

● : fluoresent tracer observed by CSLM
$r_n = (x_n, y_n)$

Stokes Einstein Relation (Newtonian fluid):

$$\langle \Delta x^2(t) \rangle = \frac{k_B T}{3\pi a} \frac{t}{\eta}$$

Generalized Stokes Einstein Relation:

$$\langle \Delta x^2(t) \rangle = \frac{k_B T}{3\pi a} J(t)$$

J(*t*): retardation function

<>: ensemble averaging

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$<\Delta r^2>$ polyNipam, 4%

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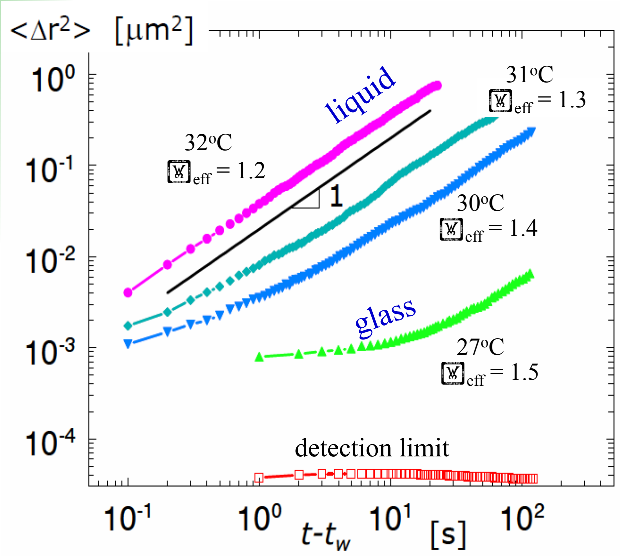

Glass transition at c = 4%

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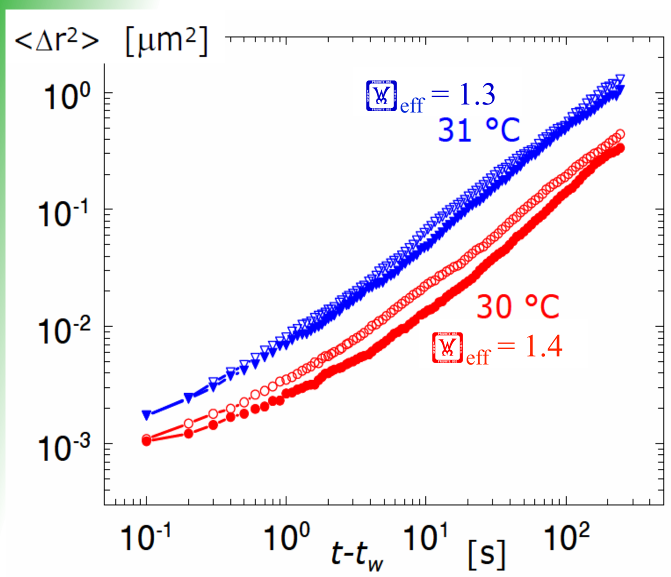

t_w

300 s (o)
3000 s (●)

$30 < T_g < 31$ °C
$1.3 < \varphi_g < 1.4$

polyNipam-polyNipam, 4%, 27°C
scaling with t_w

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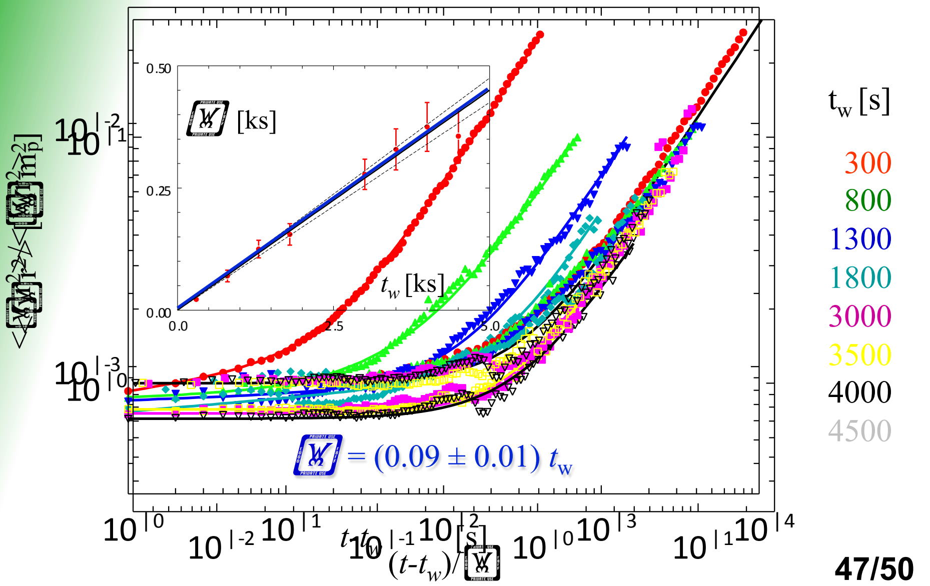

micro-rheology
viscoelastic moduli

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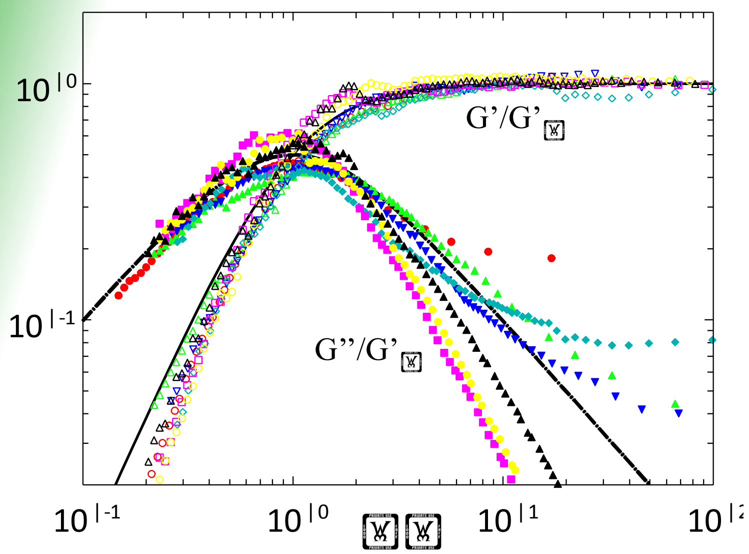
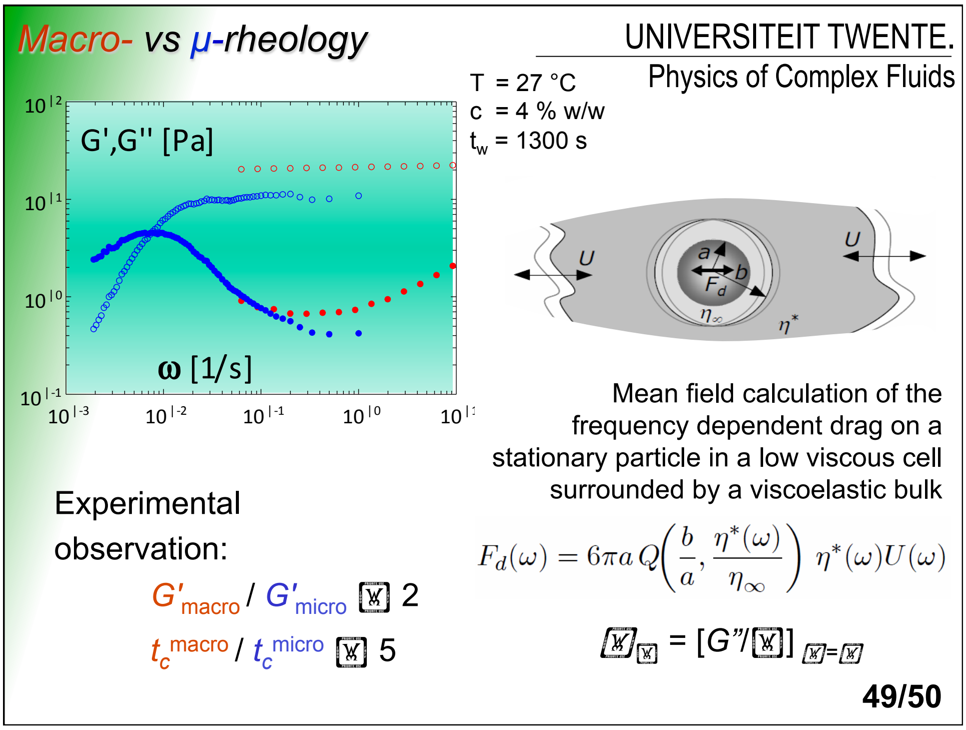


T.G. Mason, 2000


Macro- vs μ-rheology
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T = 27 °C
c = 4 % w/w
t_w = 1300 s
G',G'' [Pa]
ω [1/s]
U
U
a
b
F_d
η∞
η*
Mean field calculation of the frequency dependent drag on a stationary particle in a low viscous cell surrounded by a viscoelastic bulk
F_d(ω) = 6πa Q(b/a, η*(ω)/η∞) η*(ω)U(ω)
Experimental observation:
G'macro / G'micro 2
t_c^macro / t_c^micro 5
= [G"/]
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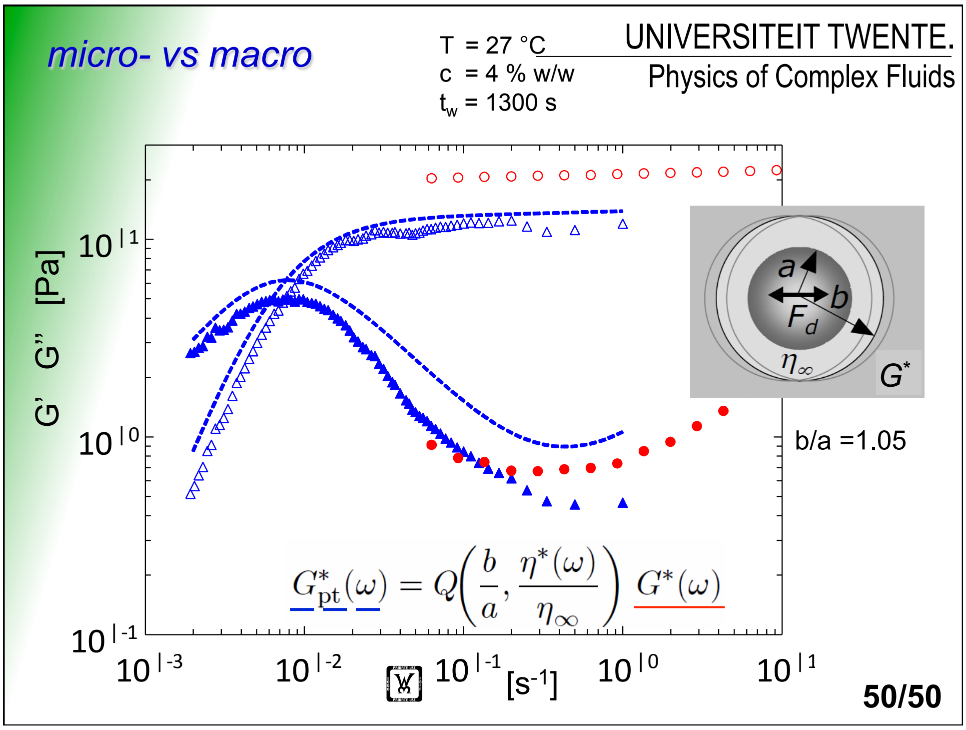
micro- vs macro
T = 27 °C
c = 4 % w/w
t_w = 1300 s
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G' G'' [Pa]
a
b
F_d
η∞
G*
b/a =1.05
G*_pt(ω) = Q(b/a, η*(ω)/η∞) G*(ω)
[s-1]
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Thank you for listening