Dispersion Rheology

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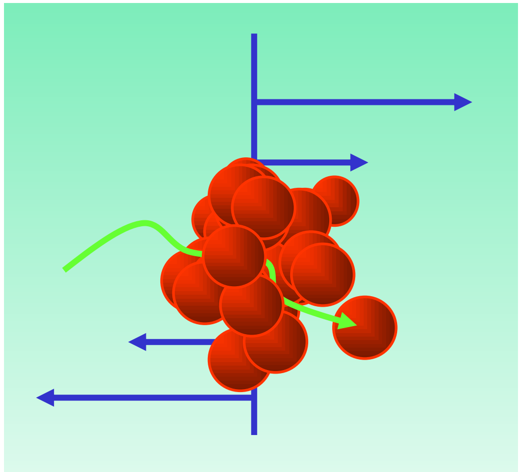


Outline

Dispersions of non-interacting hard spheres

- Volume fraction dependence
- Brownian particles and Péclet number
- Shear induced diffusion

Soft particle dispersions

Weakly aggregating dispersions

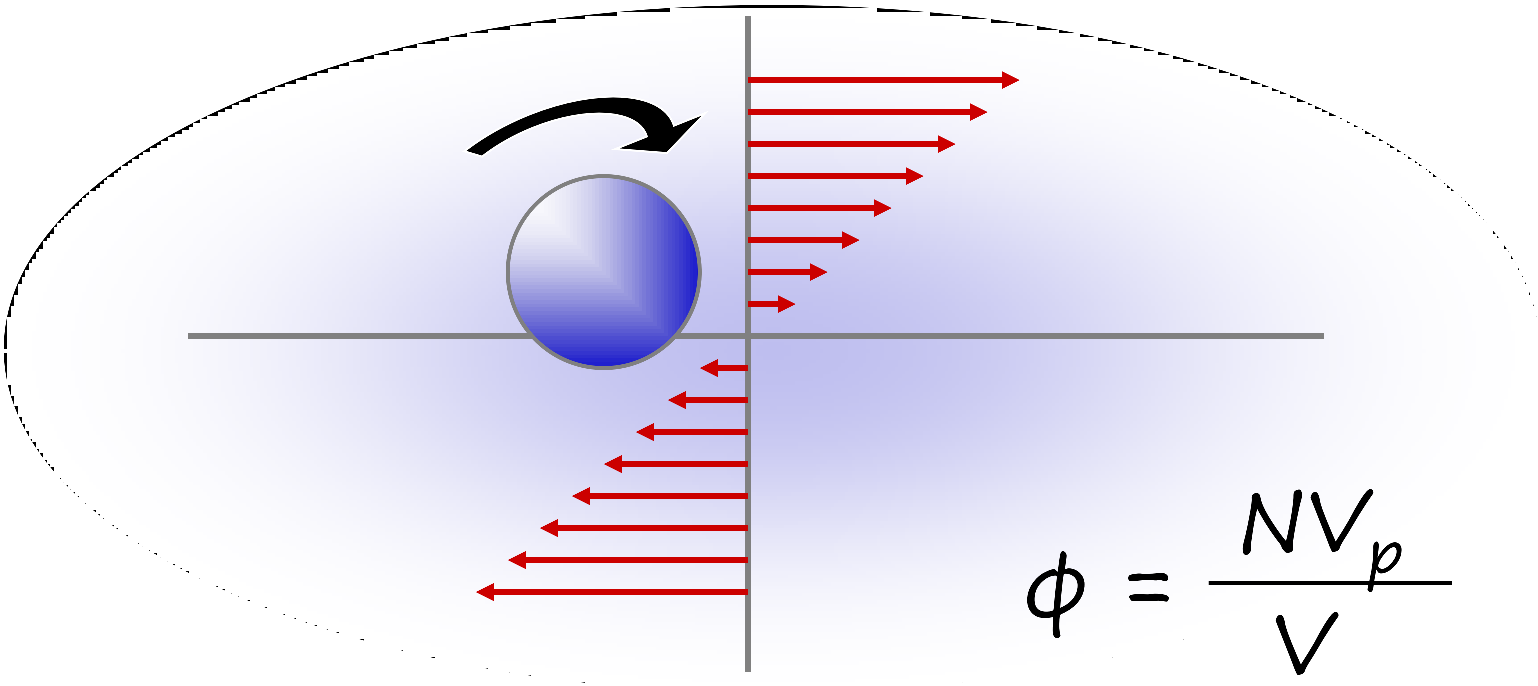
microstructure in relation to

- flowcurve
- linear viscoelasticity

Dispersions out of thermodynamic equilibrium

Sphere in liquid

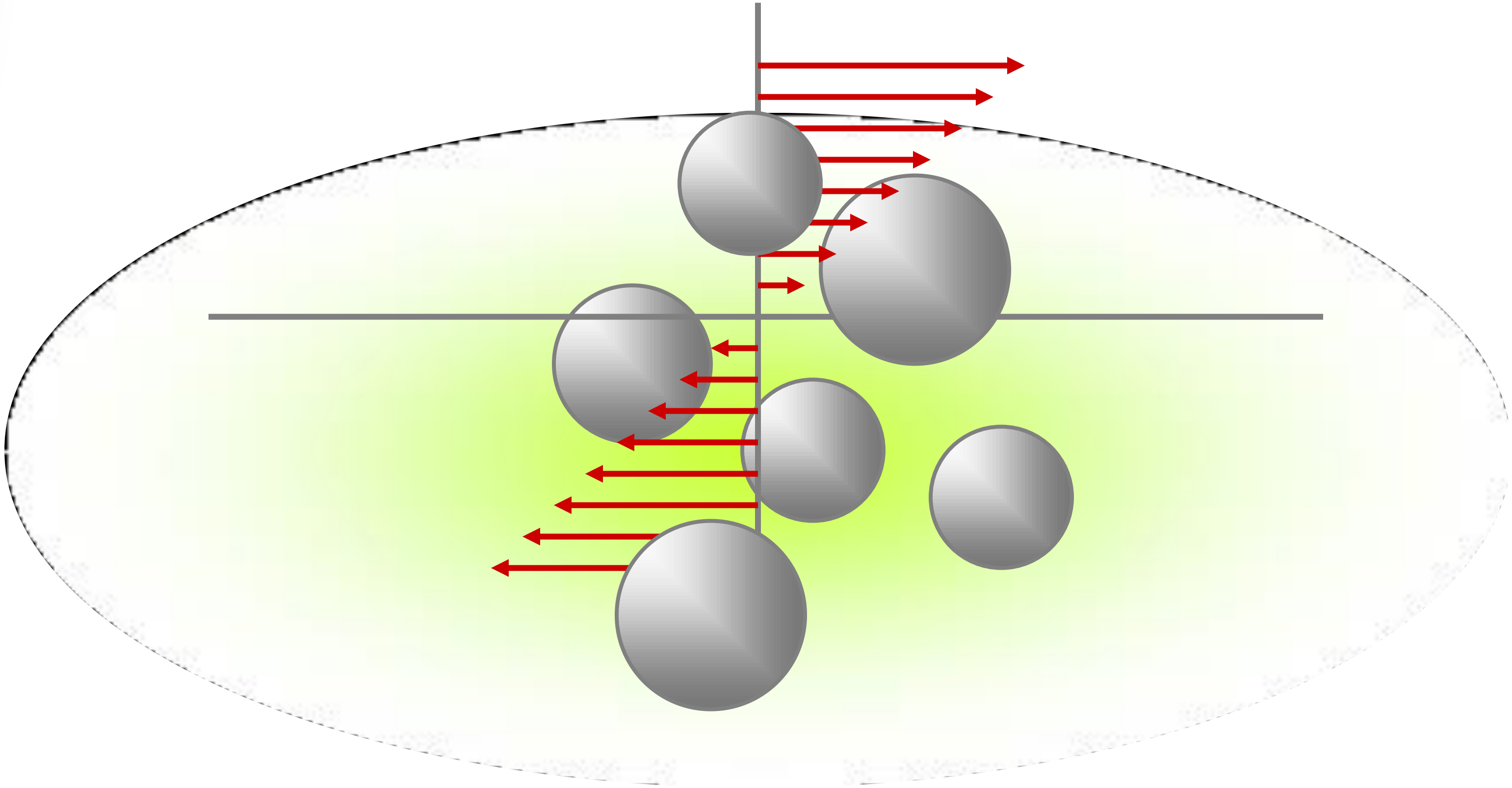
- goes with the flow
- has to rotate, additional friction



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

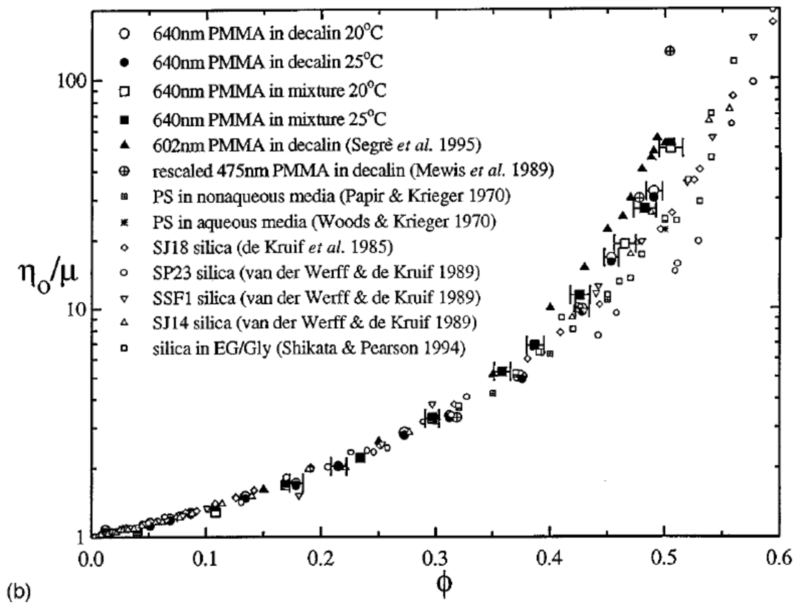
Einstein calculated:

$$\eta = \eta_0 (1 + 2.5\phi)$$

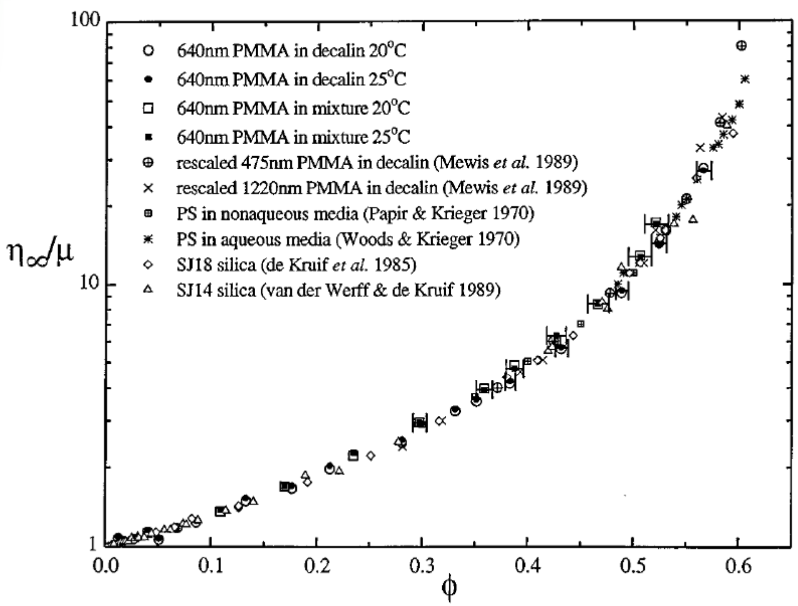


At higher concentrations

- particles collide with each other
- excluded volume effects

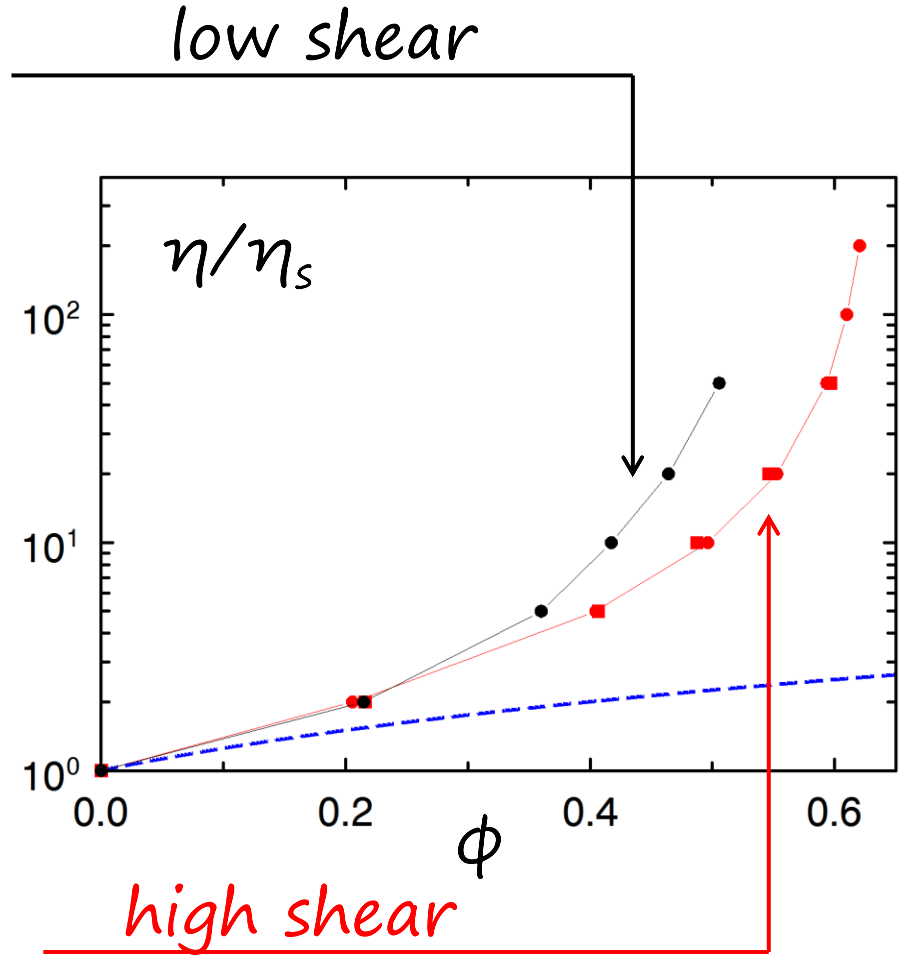


(b)



(a)

Phan and Russel; 1996



$\eta(\phi)/\eta_s$

Einstein's result

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

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

In terms of number of added particles, ΔN:

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

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

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

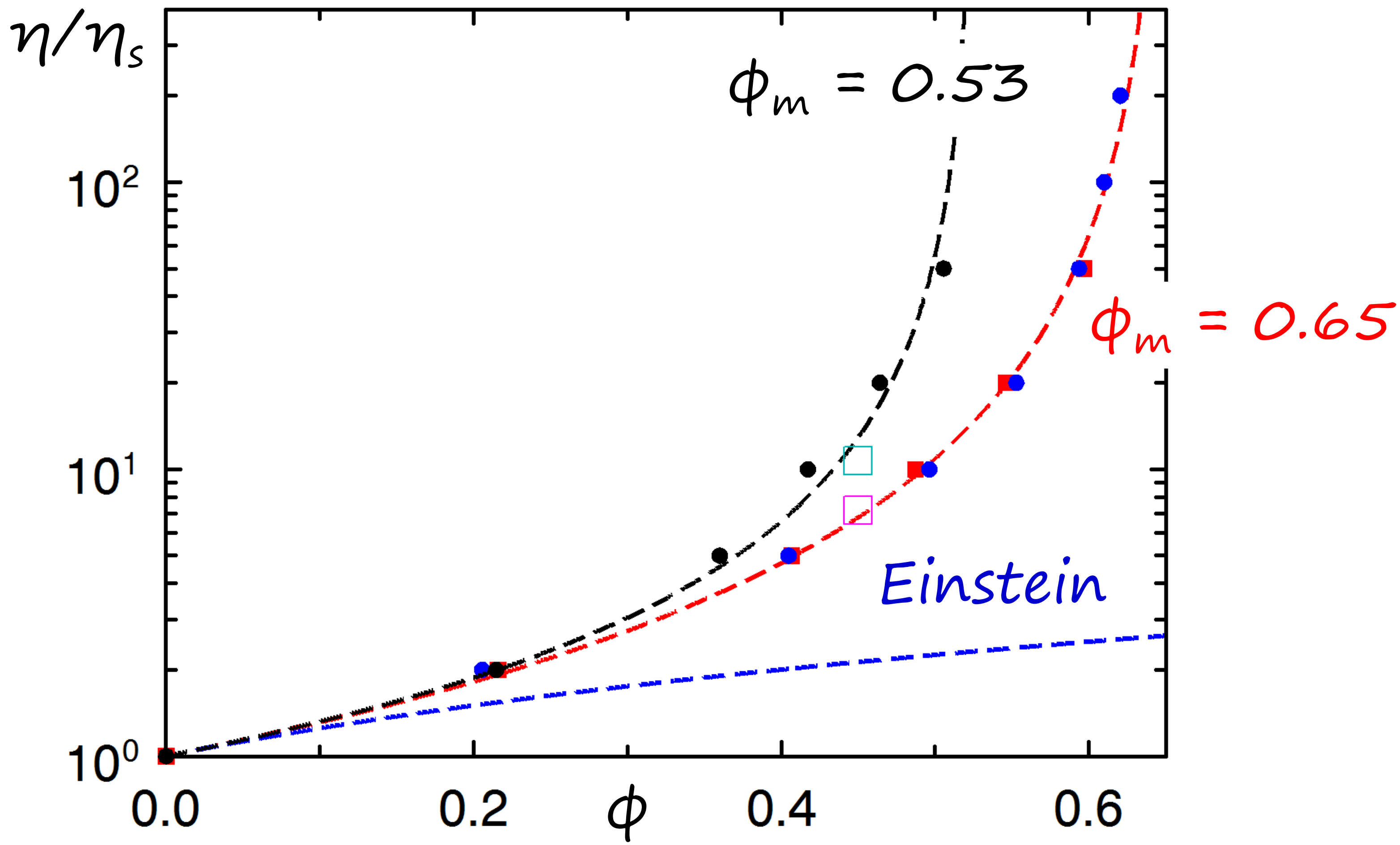
or

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

$\alpha = 1/\phi_m$

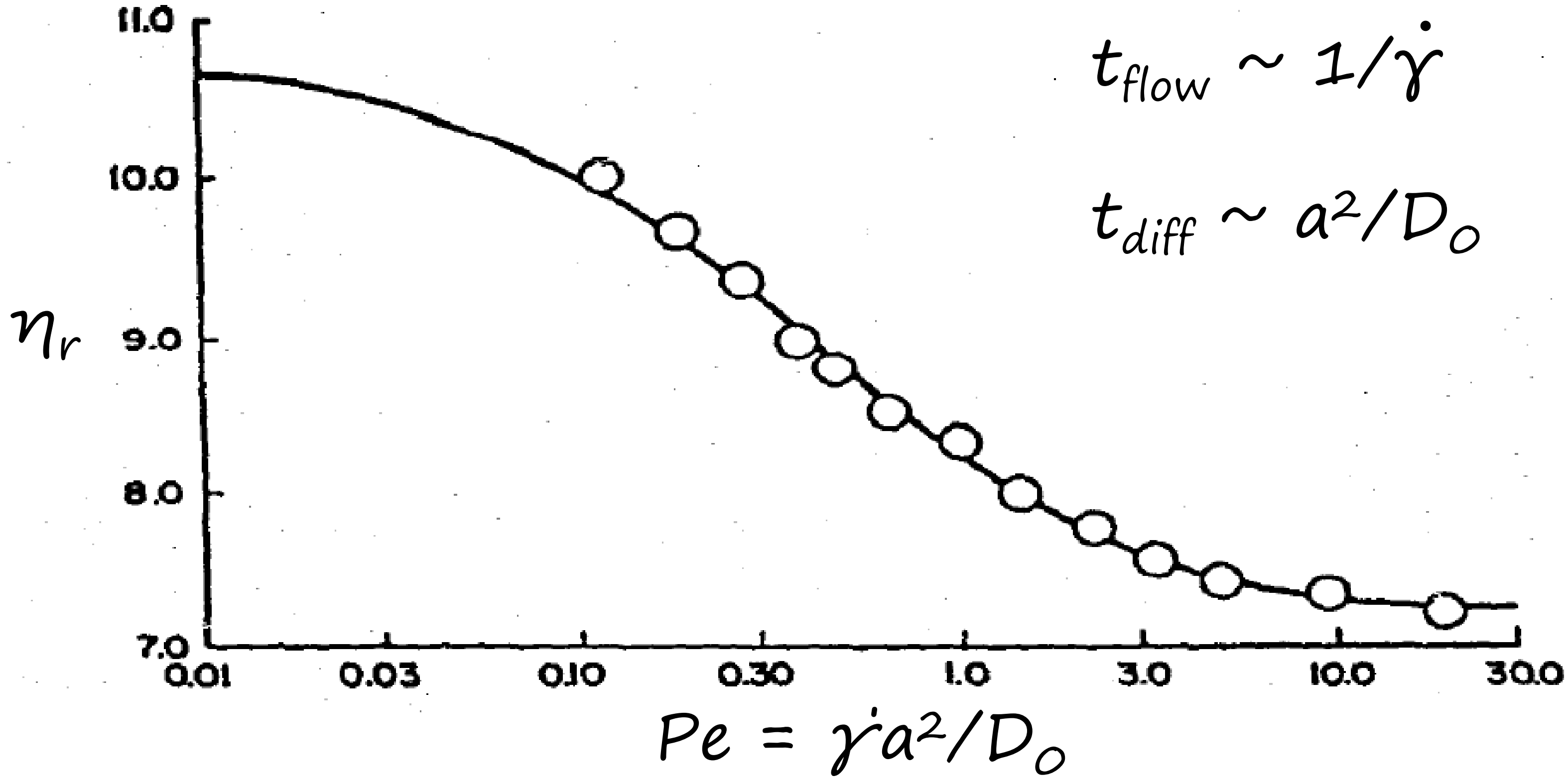
Krieger Dougerhty equation:

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


η/η_s
10^2
10^1
10^0
0.0
0.2
ϕ
0.4
0.6
ϕ_m = 0.53
ϕ_m = 0.65
Einstein

colloidal particles

competition between diffusion and convection



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

$t_{diff} \sim a^2/D_o$

polystyrene particles
a = 400 nm

Krieger, 1972

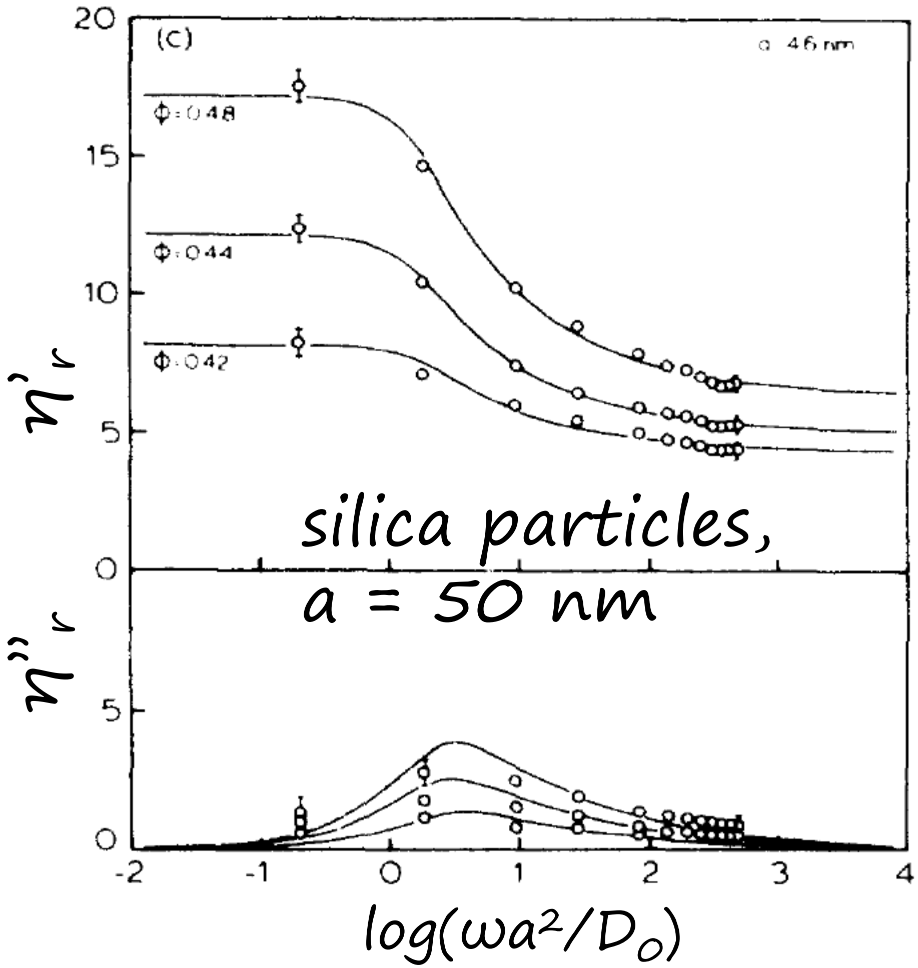
Viscoelastic effects:

HS dispersions show visco-elasticity.

What is the origine of the elasticity?

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

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



J. van de Werf et al.; 1989

Non colloidal particles

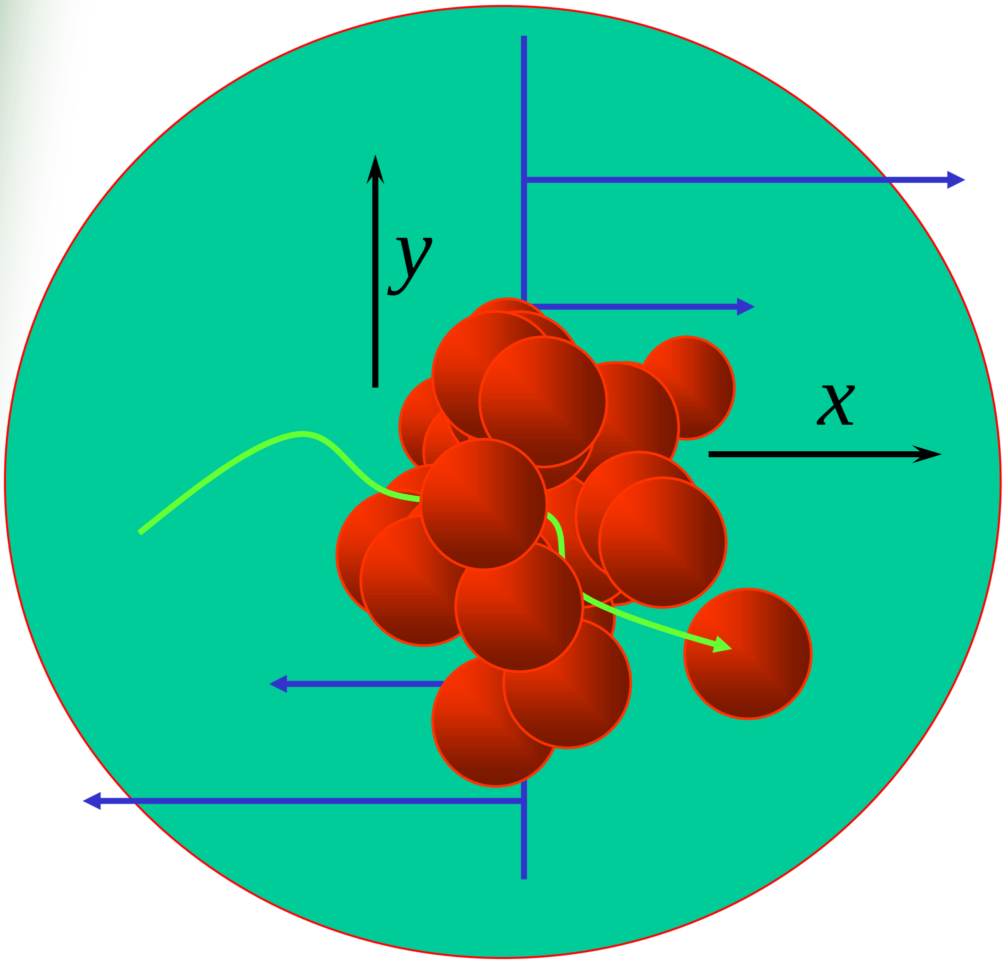
shear-induced self-diffusion in simple shear flow

$$D_{\alpha\beta} = a^2 \dot{\gamma}\, D_{\alpha\beta}(\phi)$$

a particle radius

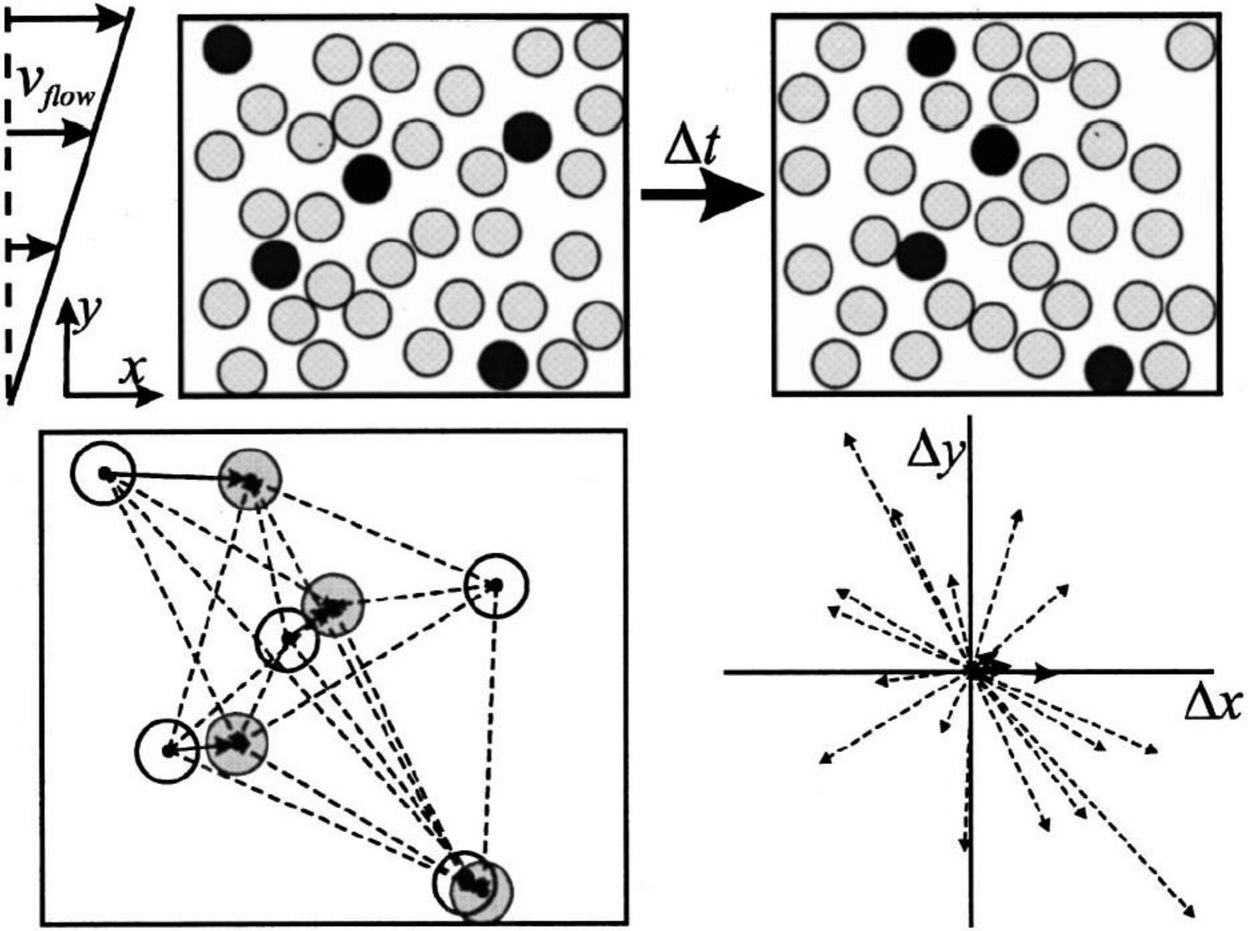
$\dot{\gamma}$ rate of shear

ϕ volume fraction

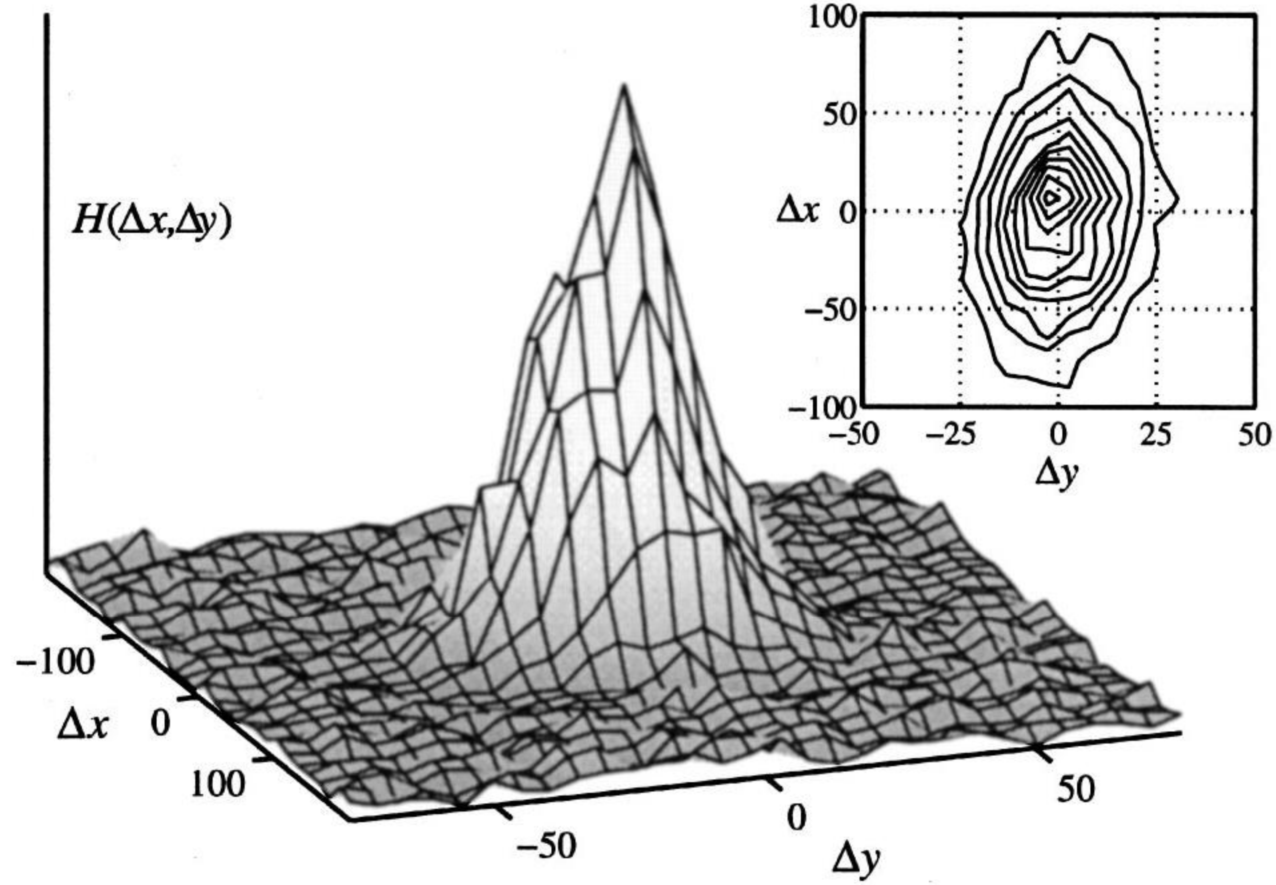


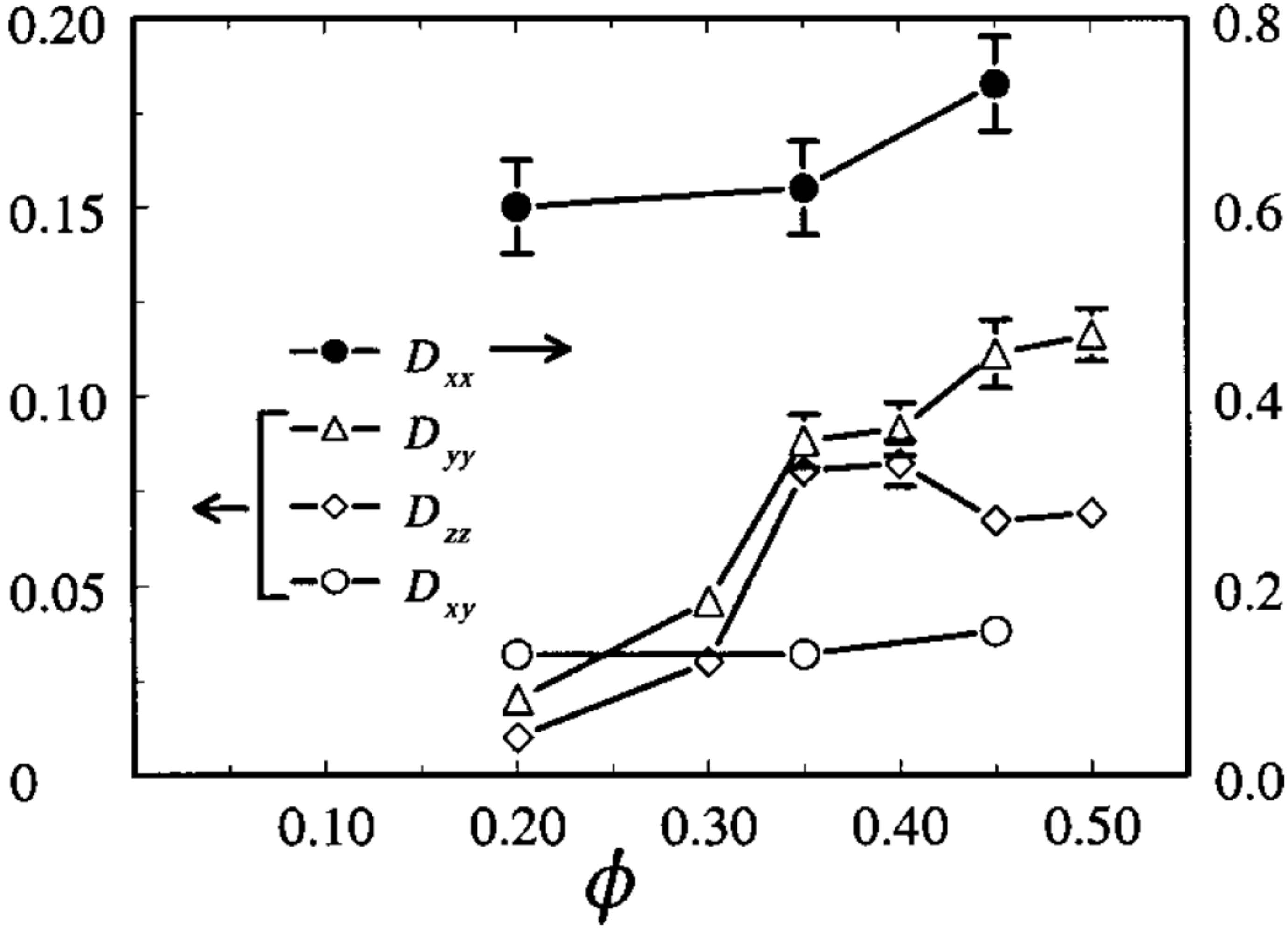
Tensor character:

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



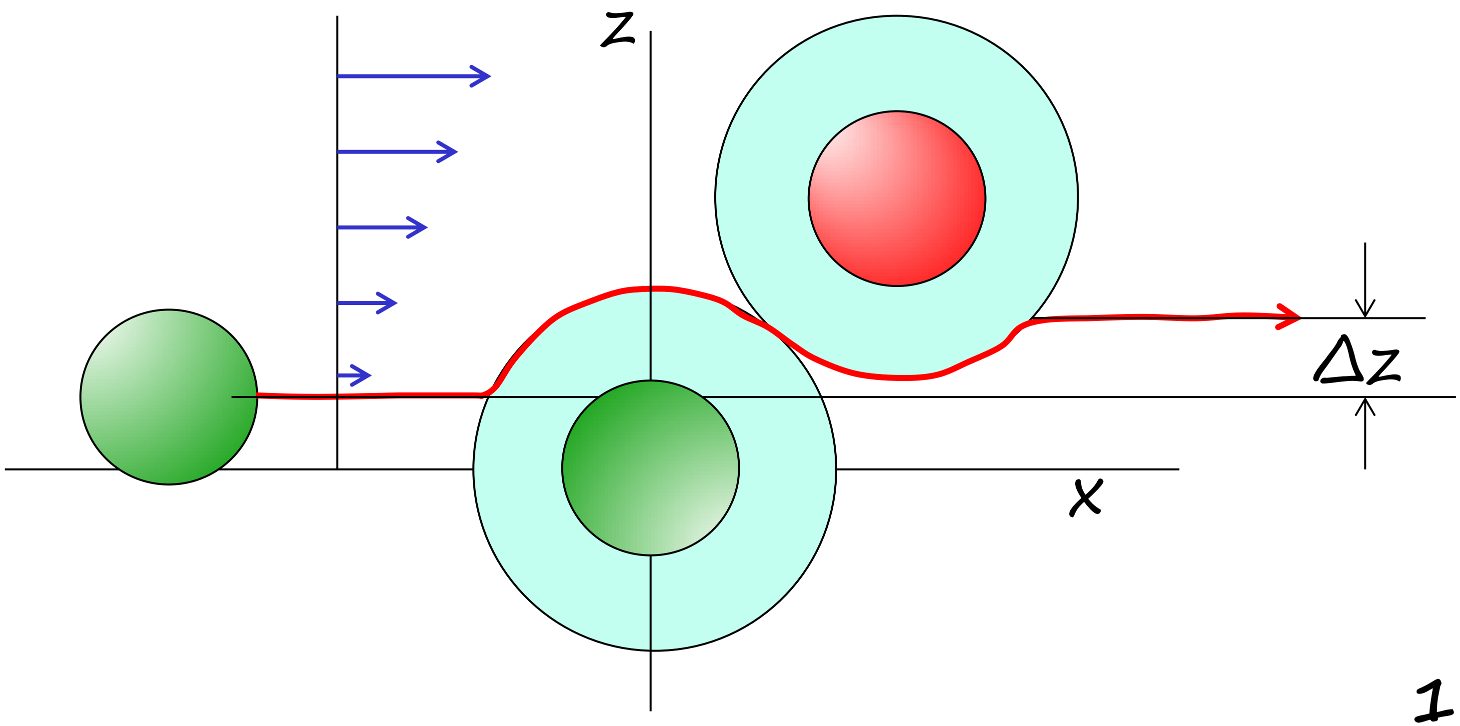
V. Breedveld et al. ; 2002

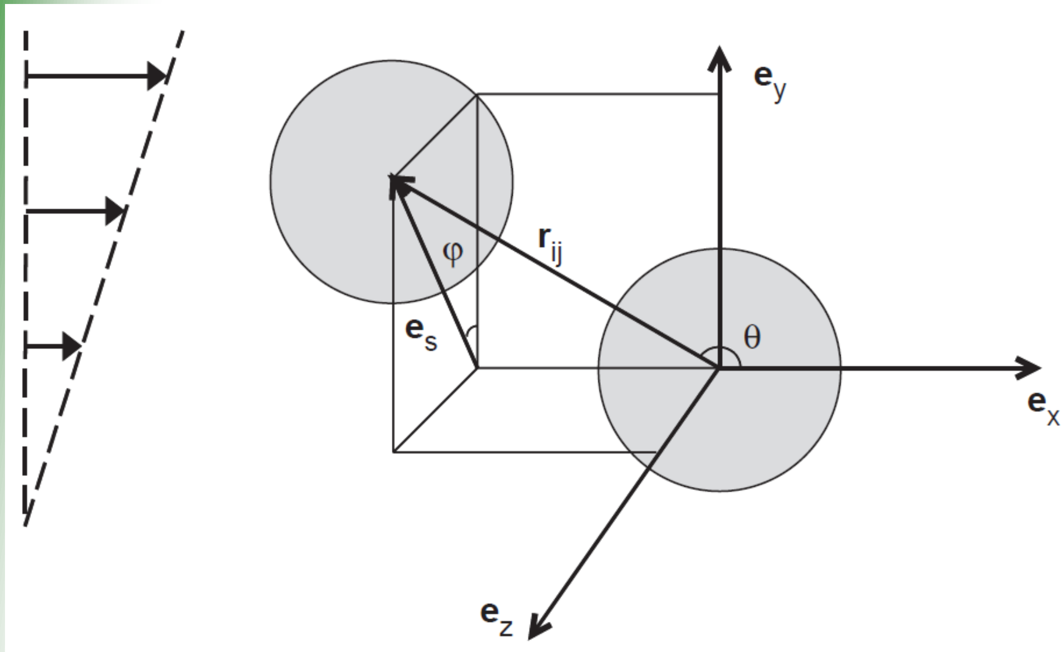

H(Δx,Δy)
−100
Δx
0
100
−50
0
50
Δy
100
50
Δx
0
−50
−100
−50
−25
0
25
50
Δy


0.20
0.15
0.10
0.05
0
0.8
0.6
0.4
0.2
0.0
0.10
0.20
0.30
0.40
0.50
ϕ
D_{xx}
D_{yy}
D_{zz}
D_{xy}

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

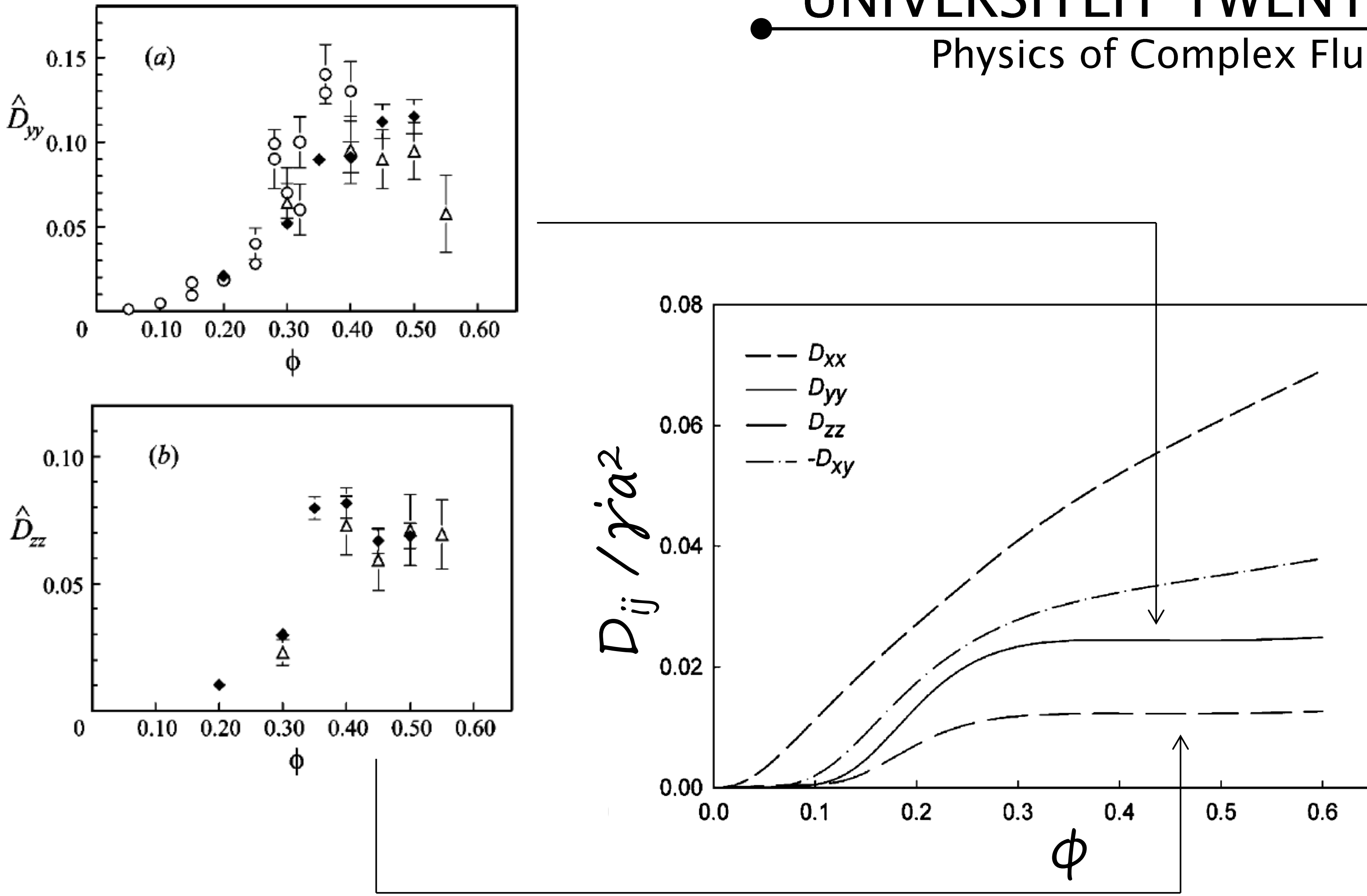




Taking an average collision time $t_c(\phi)$, we calculate the displacement vector $\underline{s}(\theta,\phi)$ per collision.

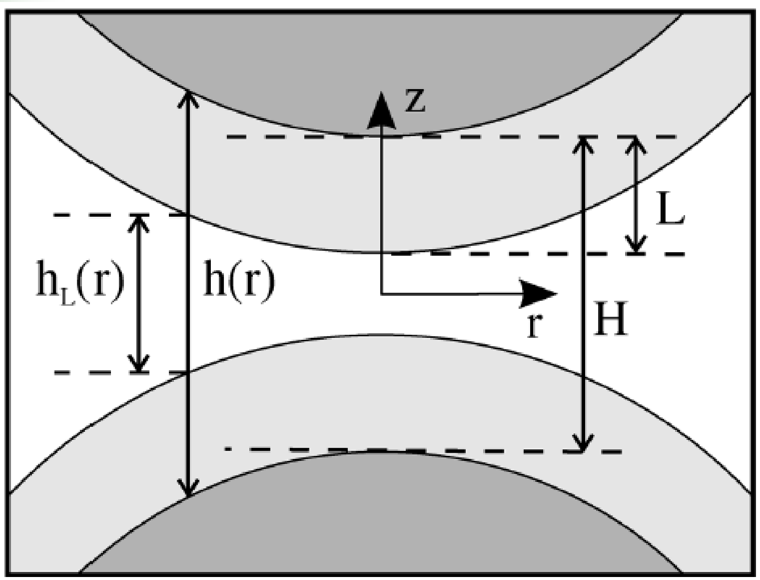
Diffusion tensor:

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



V. Breedveld, thesis UT ; 2000
J. Kromkamp et al. ; 2006

Soft particle rheology



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

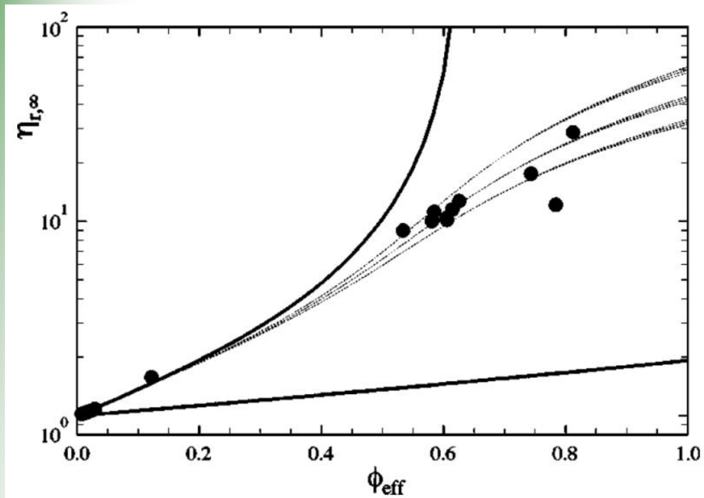
$$\eta_{r,\infty} = 1 + \tfrac{5}{2}\phi_{\text{eff}} + \frac{\mu_{\text{lub}}}{\mu}$$

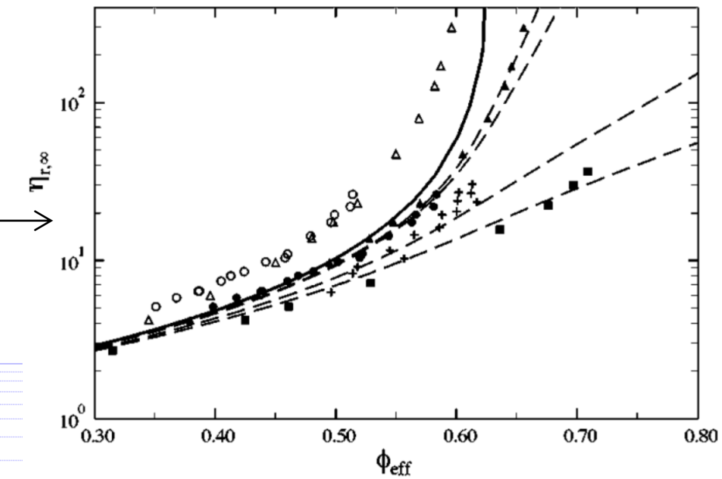
$$\frac{\mu_{\text{lub}}}{\mu} = 9\frac{2R_c}{2R_c + H_{\text{av}}}\overline{F}(H_{\text{av}})$$

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

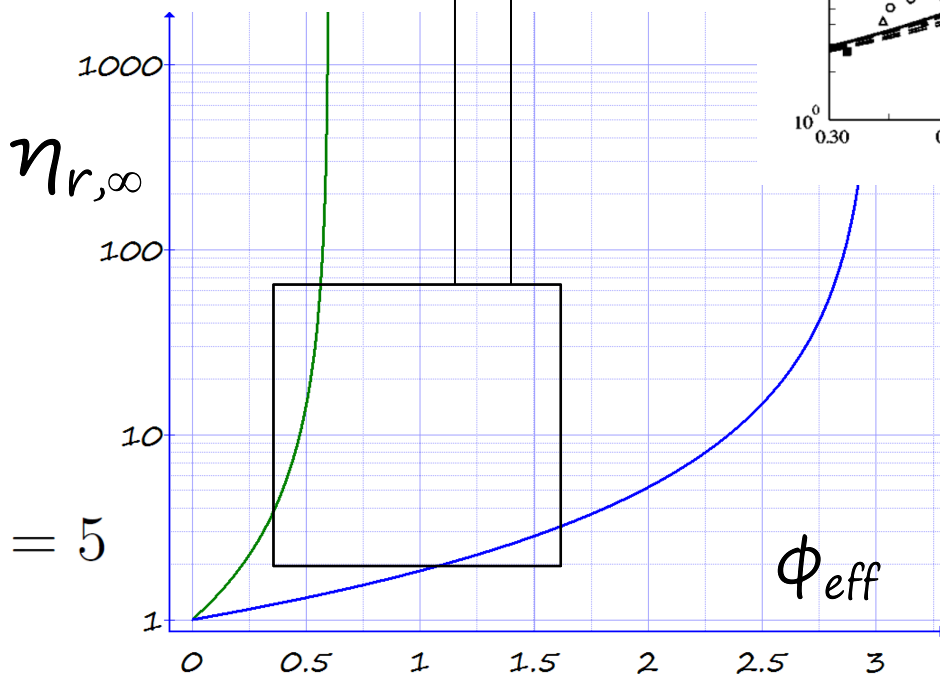
$$H_{\text{av}} = 2R_c\left[\left(\frac{\phi_{\max}^{\text{core}}}{\phi_{\text{core}}}\right)^{1/3} - 1\right]$$

P.A. Nommensen; 1999



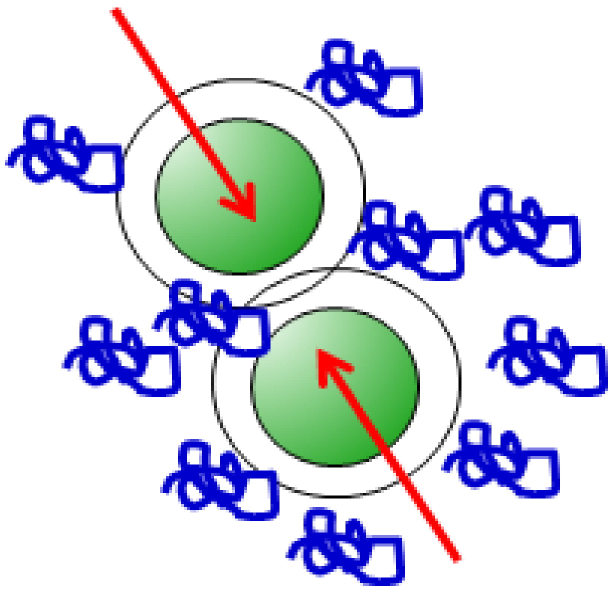


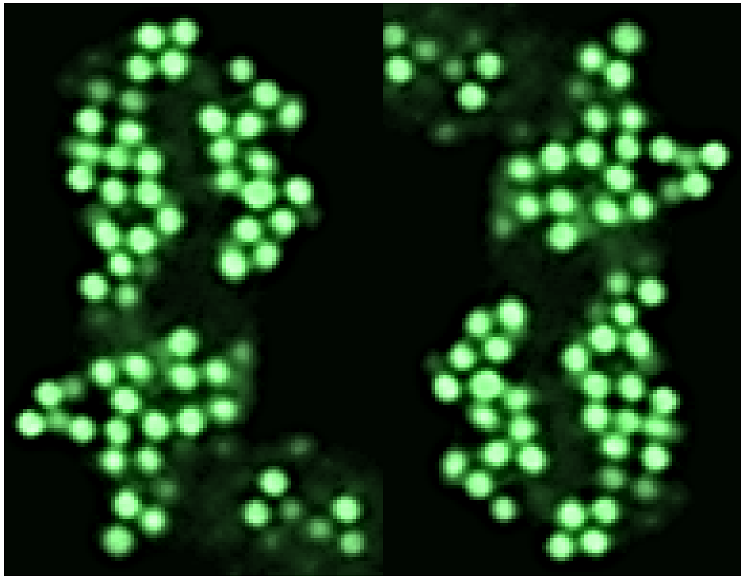
D'Haene,
thesis Leuven; 1992

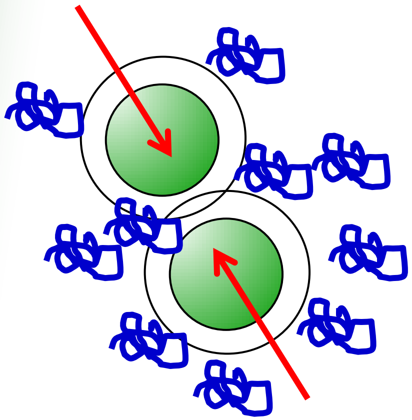


$$\left(\frac{R+L}{R}\right)^3 = 5$$

Weakly aggregating colloidal dispersions

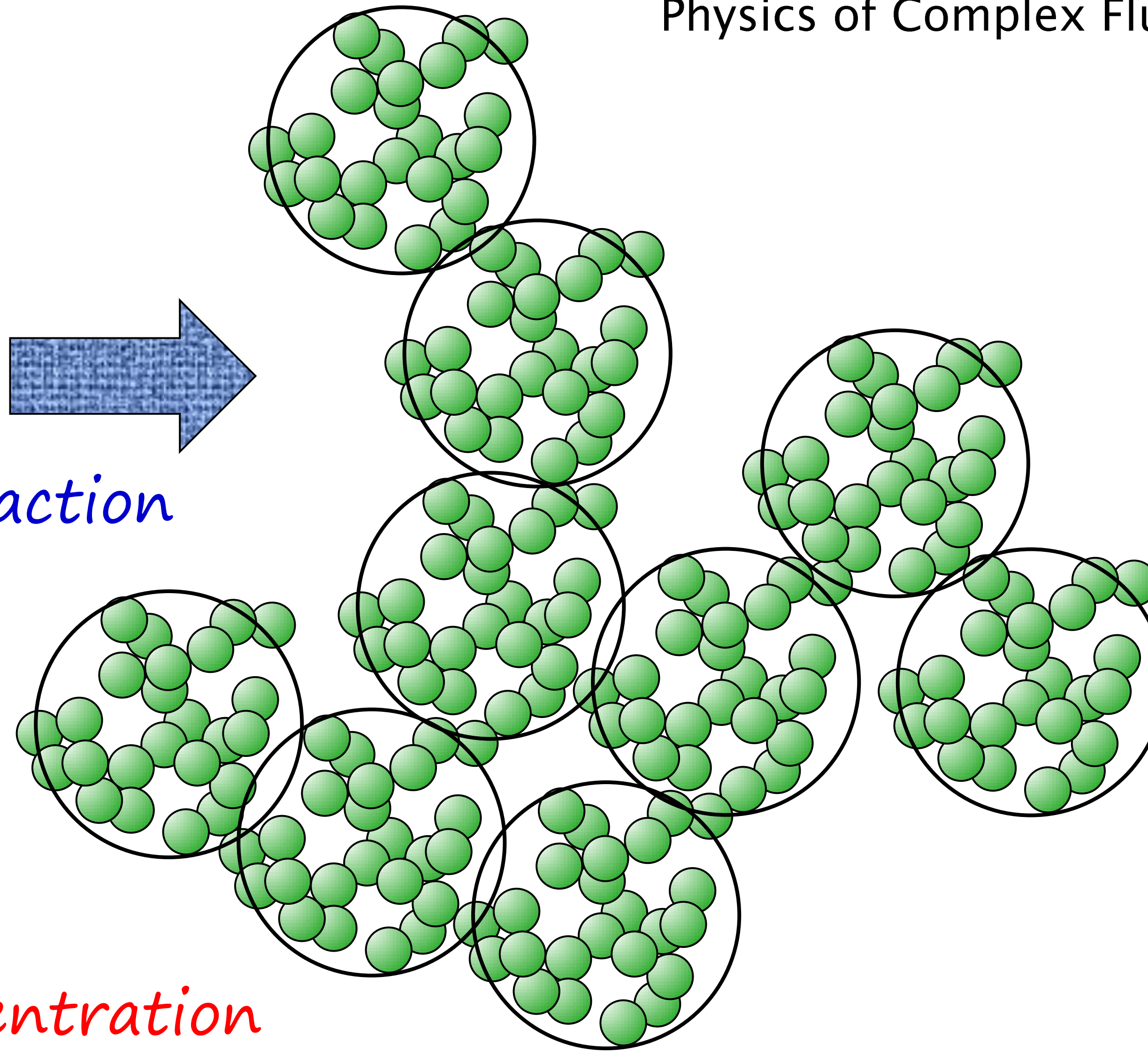






depletion interaction

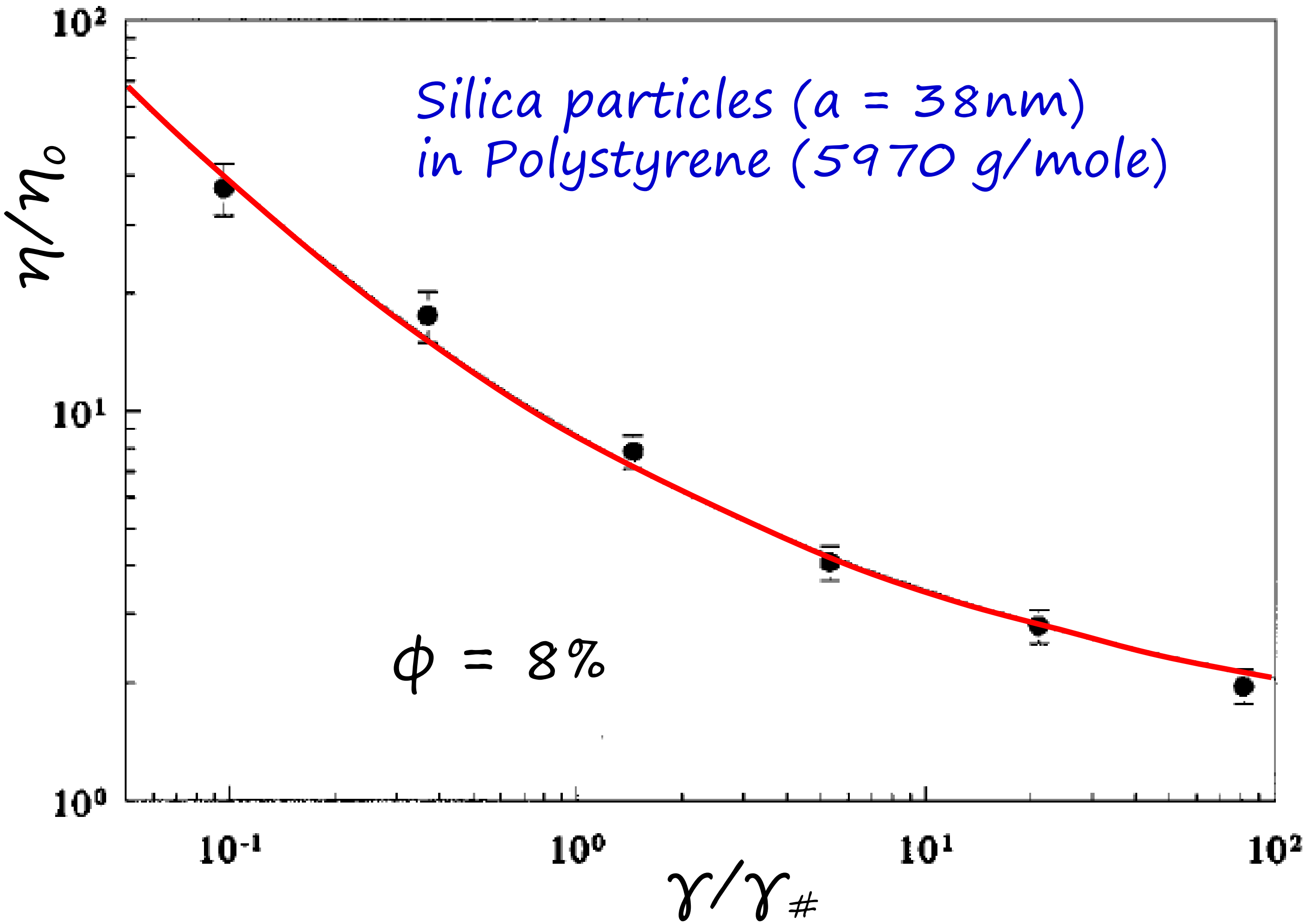
F_{int}



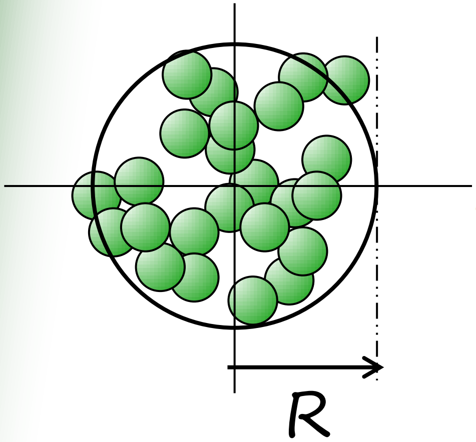
Parameters:

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

Flow curve



Wolters et al. 1996



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

fractal aggregate

volume fraction of aggregates:

$$\phi_a = \frac{\phi_p}{N_0} \left(\frac{R}{a}\right)^{3-d_f}$$

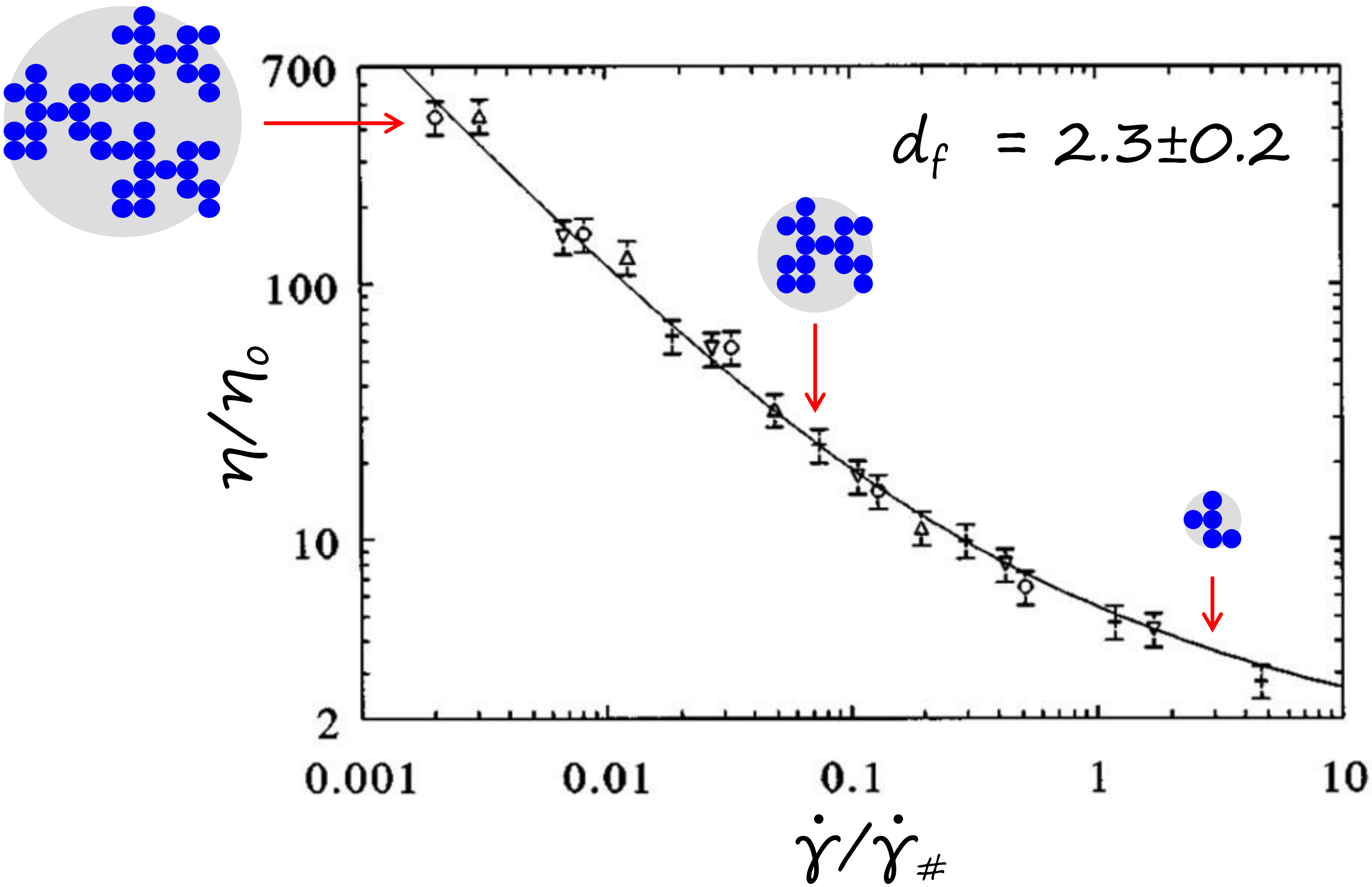
$F_{int} \geq F_{hyd}$:

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

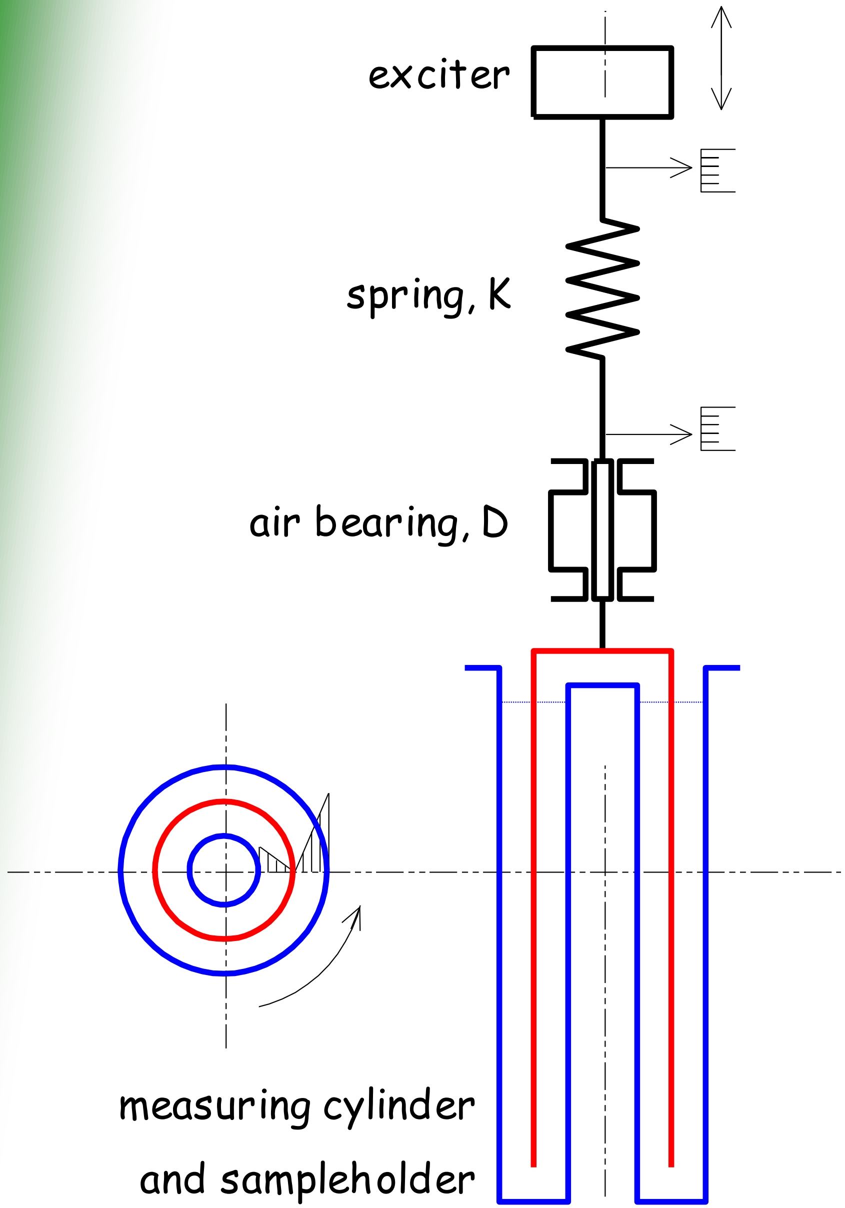
mean field approximation

viscosity curve:

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



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



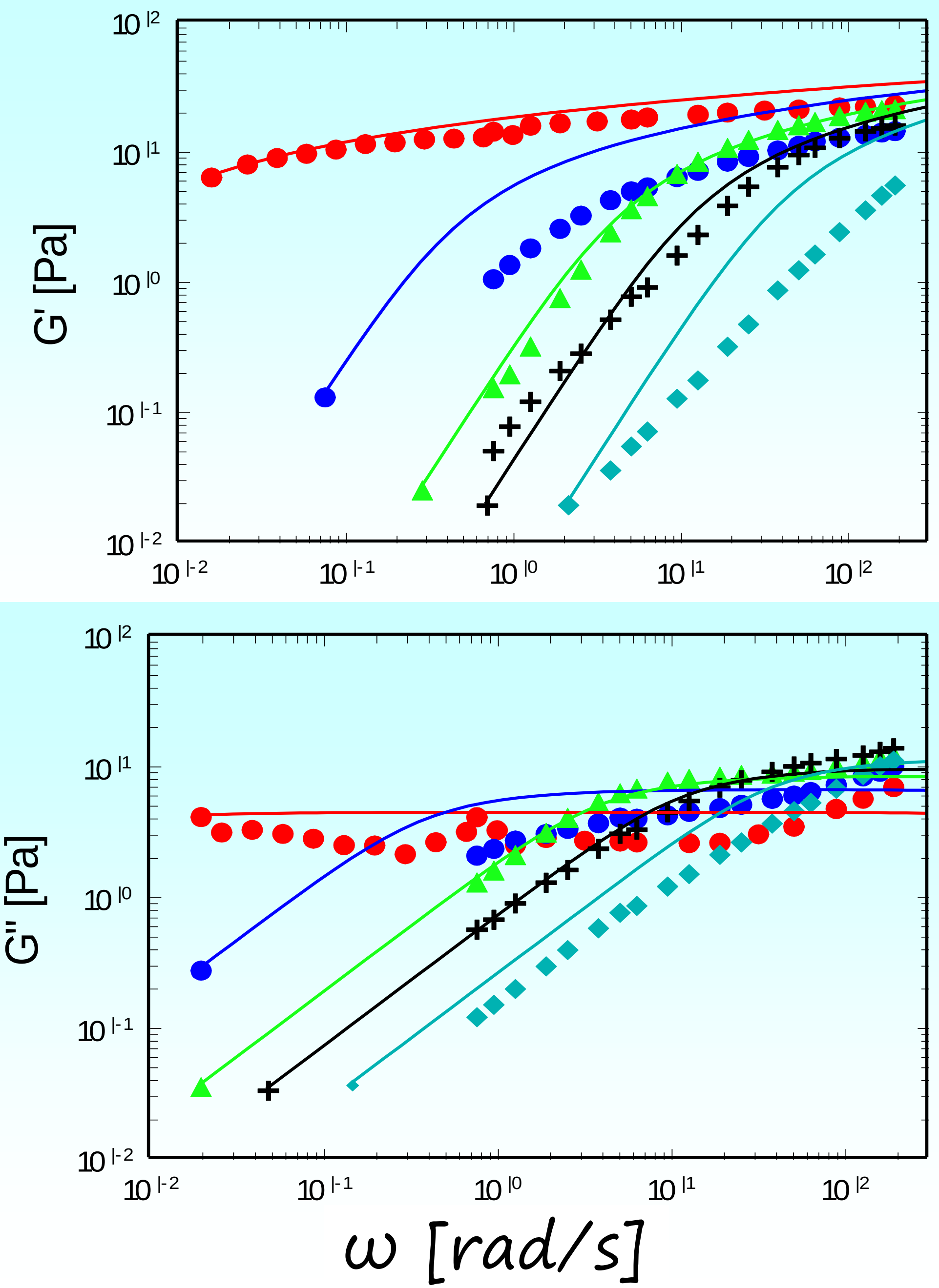
measuring elasticity in a shear flow:

$G'(\dot{\gamma},\omega)$

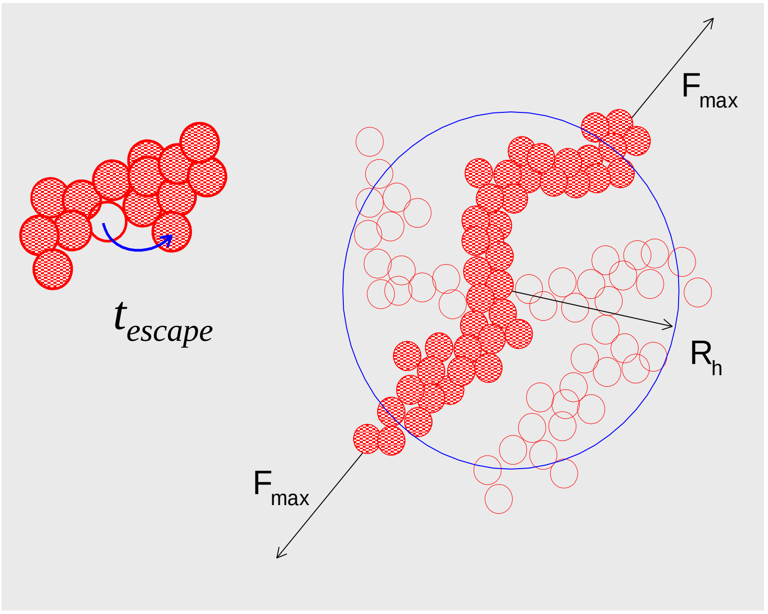
$G''(\dot{\gamma},\omega)$

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

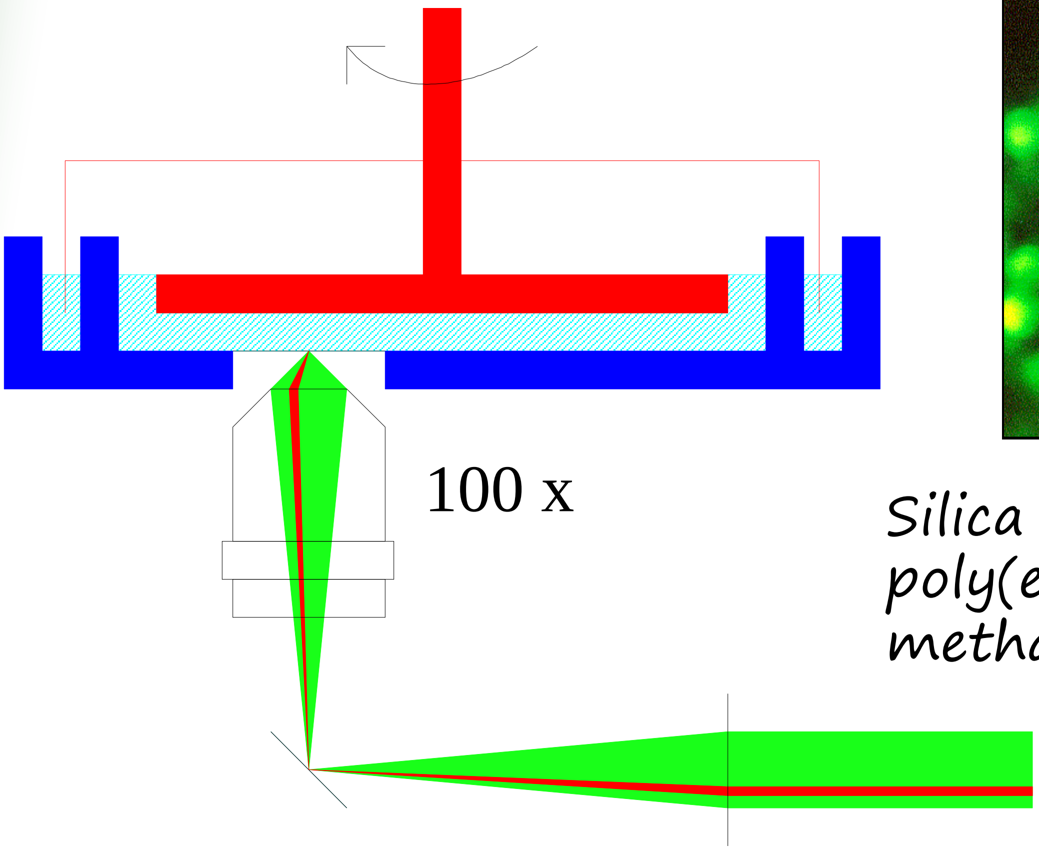
Zeegers et al. ; 1995

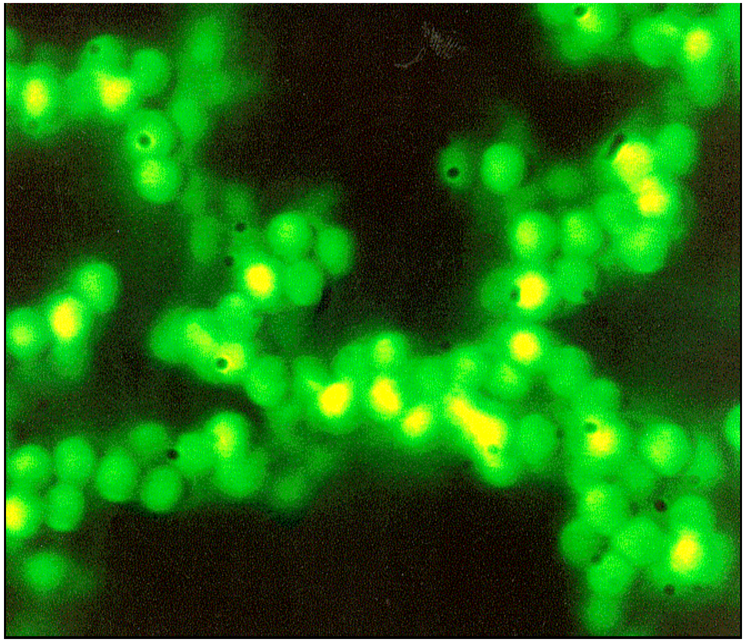


increasing $\dot{\gamma}$

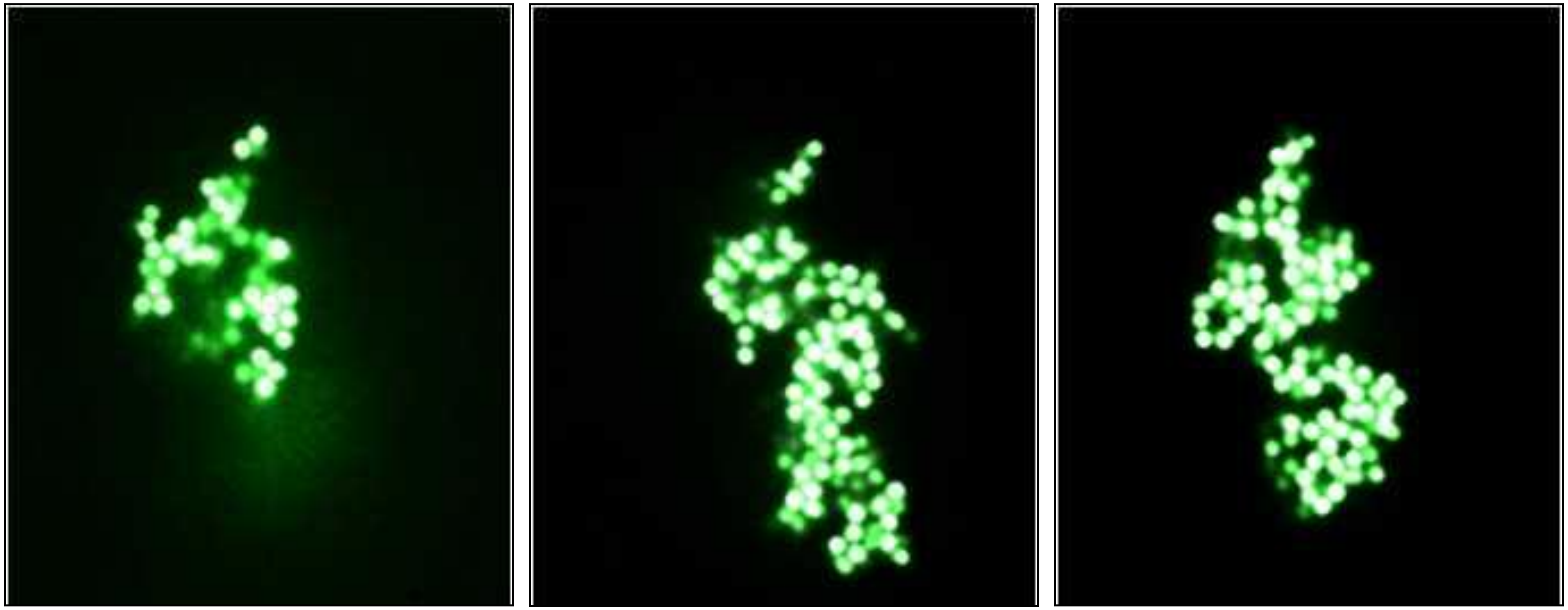


Shear cell on Confocal Scanning Laser Microscope



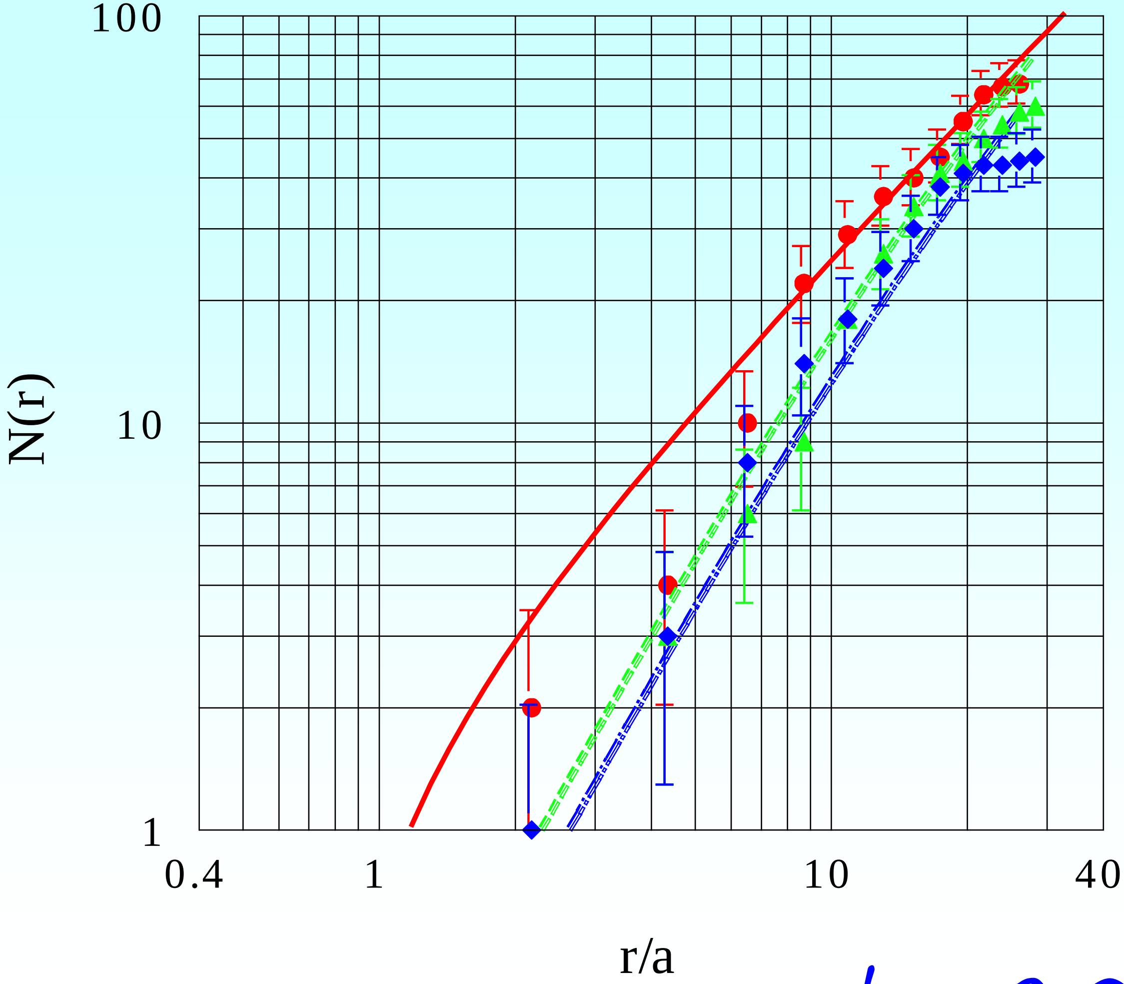


Silica particles (1 μm) and poly(ethylene glycol) in a methanol-bromoform mixture



Different cross sections through an aggregate

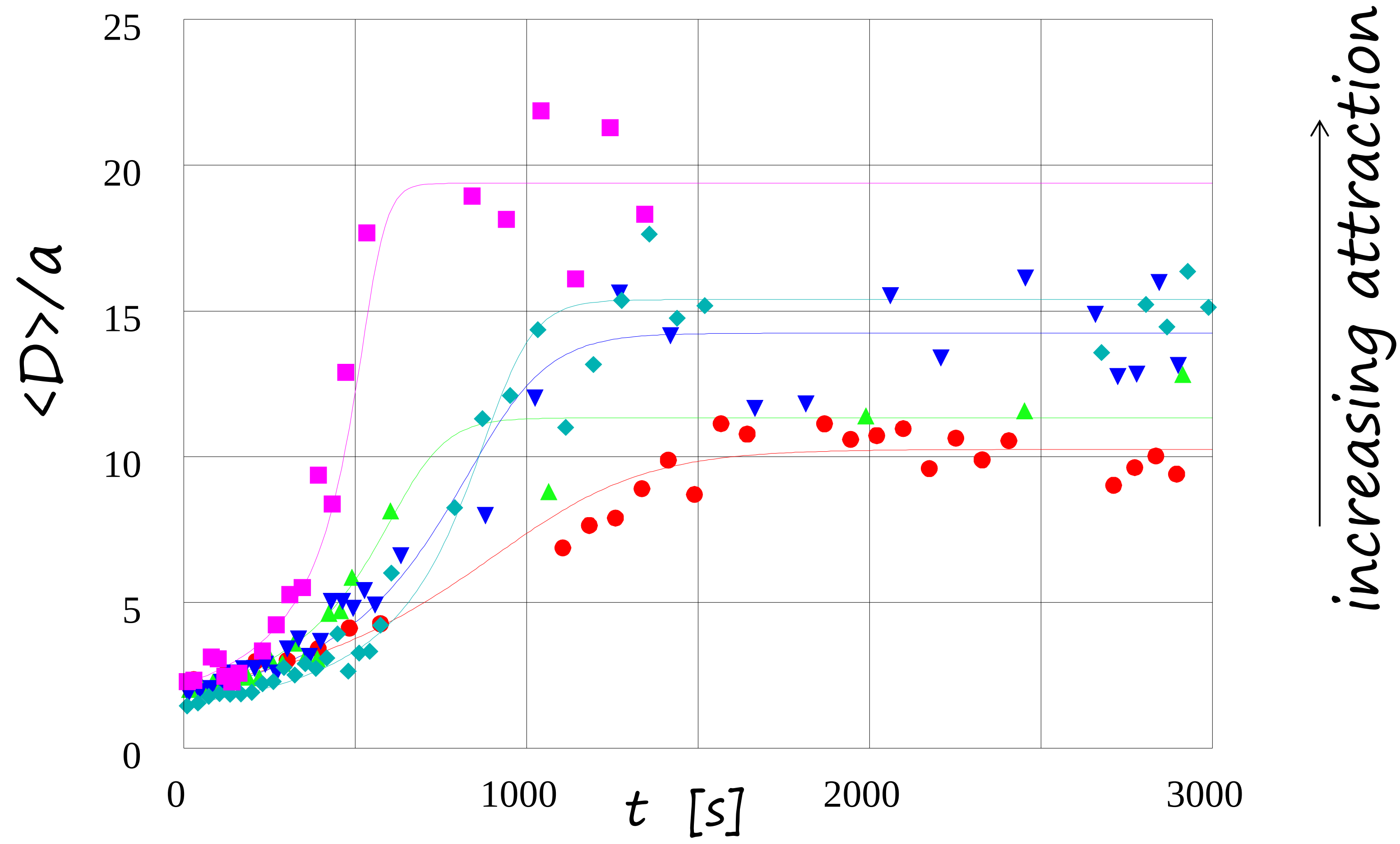
V. Tolpekin, thesis UT; 2004



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

$d_f = 2.0 \pm 0.1$

Aggregate growth



Modeling the aggregate growth

$$dn_i/dt = \tfrac{1}{2}\sum A_{i-j,j}\, n_{i-j}\, n_j - \sum A_{ij}\, n_i\, n_j + \sum B_j\, p_{ji}\, n_j - B_i\, n_i$$

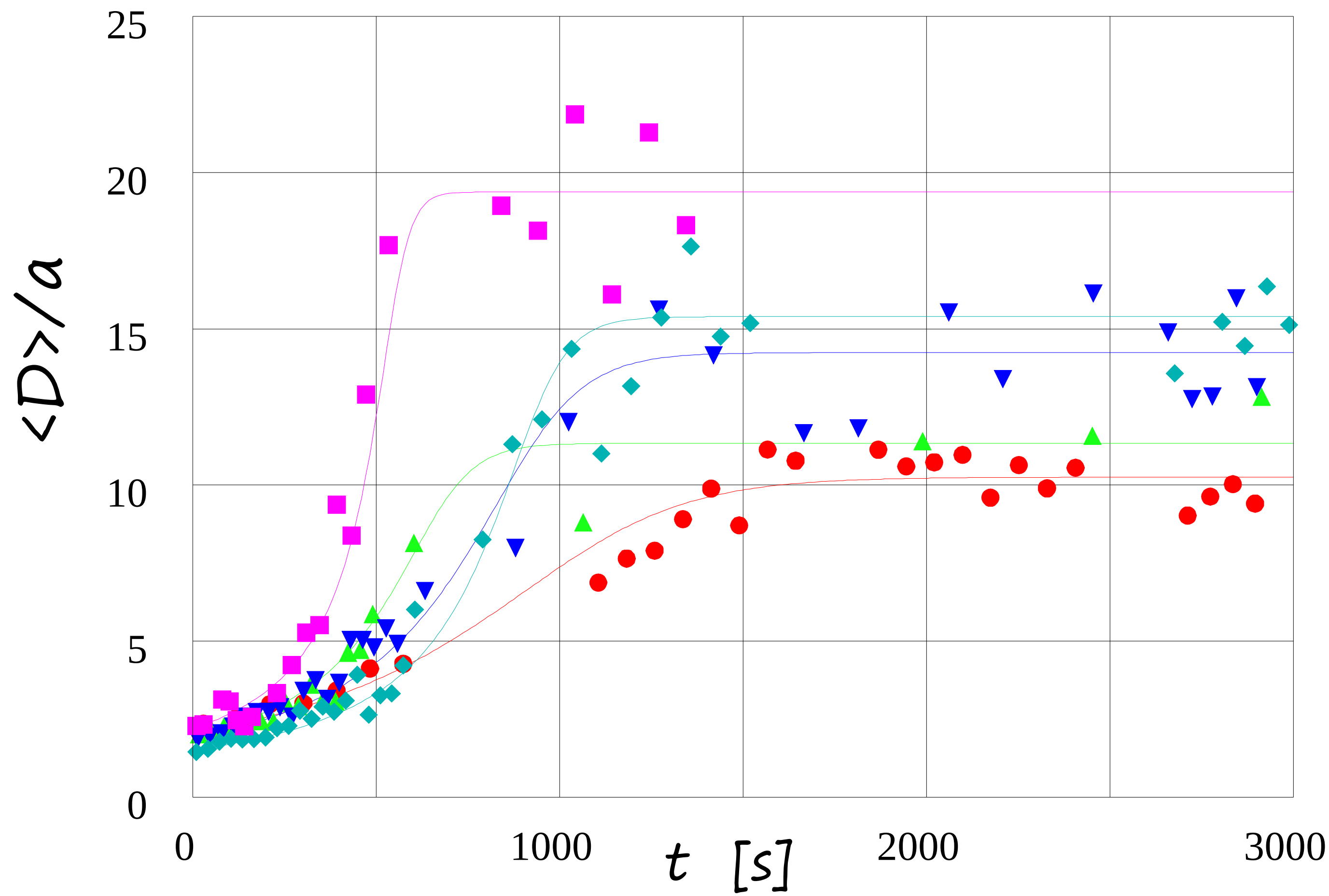
Aggregation: $A_{ij} = 4/3\, \dot{\gamma}\, (R_i + R_j)^3$

Break-up: $B_i = K_o(\dot{\gamma})\, (R_i/a)^Q$

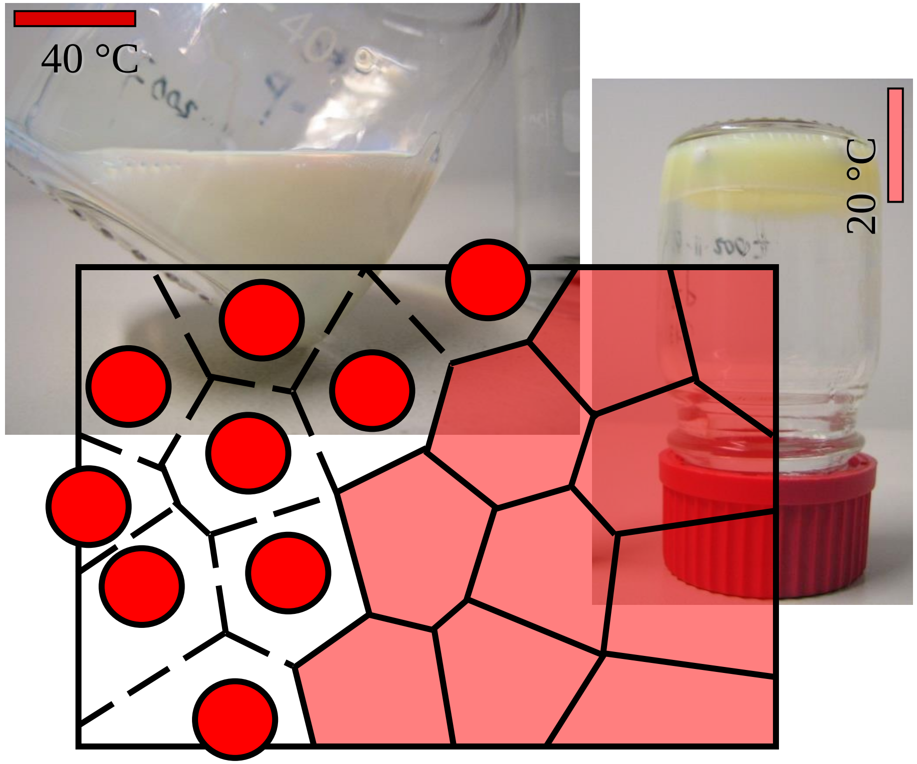
$$d\langle R^{df}\rangle/dt = C\,[\langle R^3\rangle + 3\langle R^2\rangle\langle R\rangle] - K_o(\dot{\gamma})\,\langle R^Q\rangle\langle R^{df}\rangle$$

adjustable: $K_o(\dot{\gamma})$, Q

Results of the modeling



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



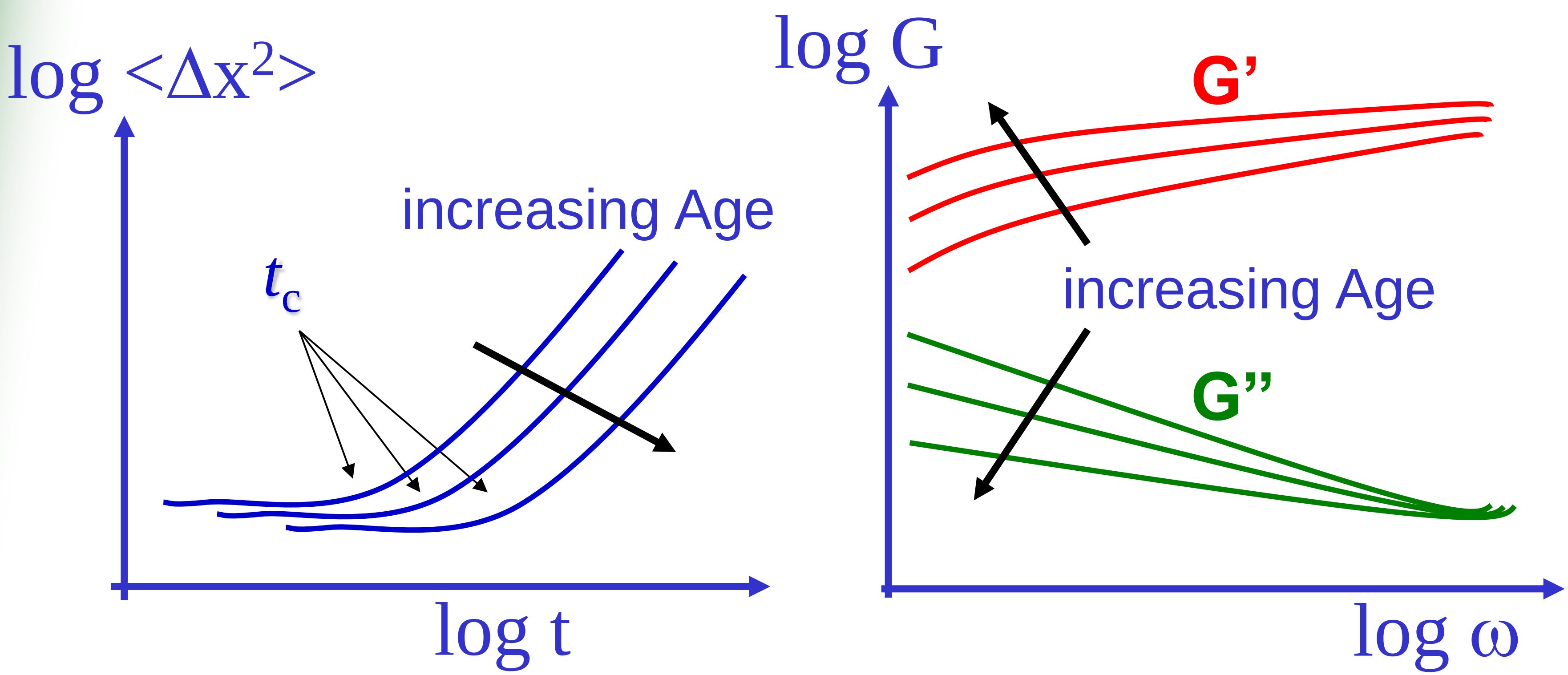
Aging of soft colloidal suspensions studied by macro- and micro-rheology

E.H. Purnomo et al.; 2008

Aging in soft glassy materials

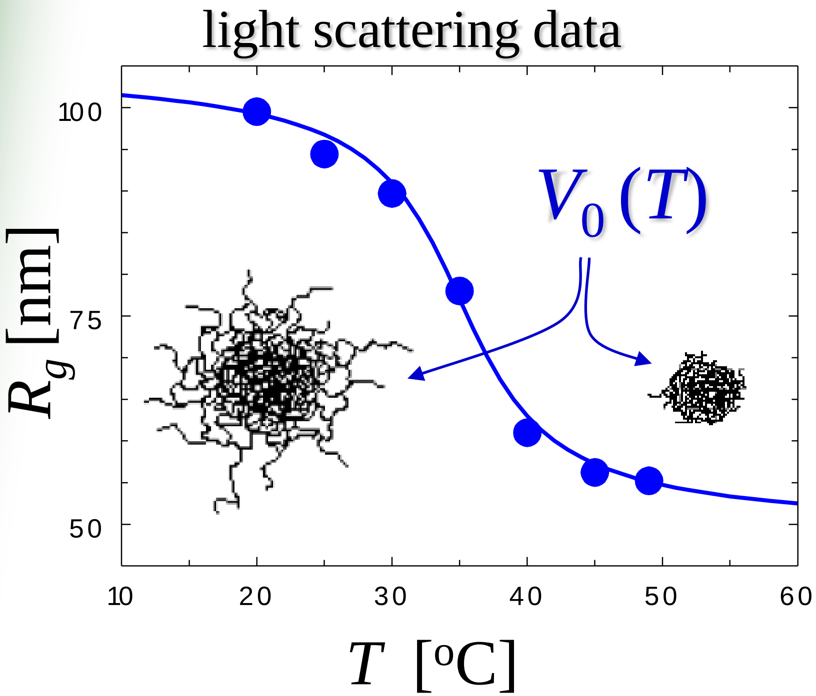
* relaxation processes slow down with age of the sample...
* equilibrium is never reached...

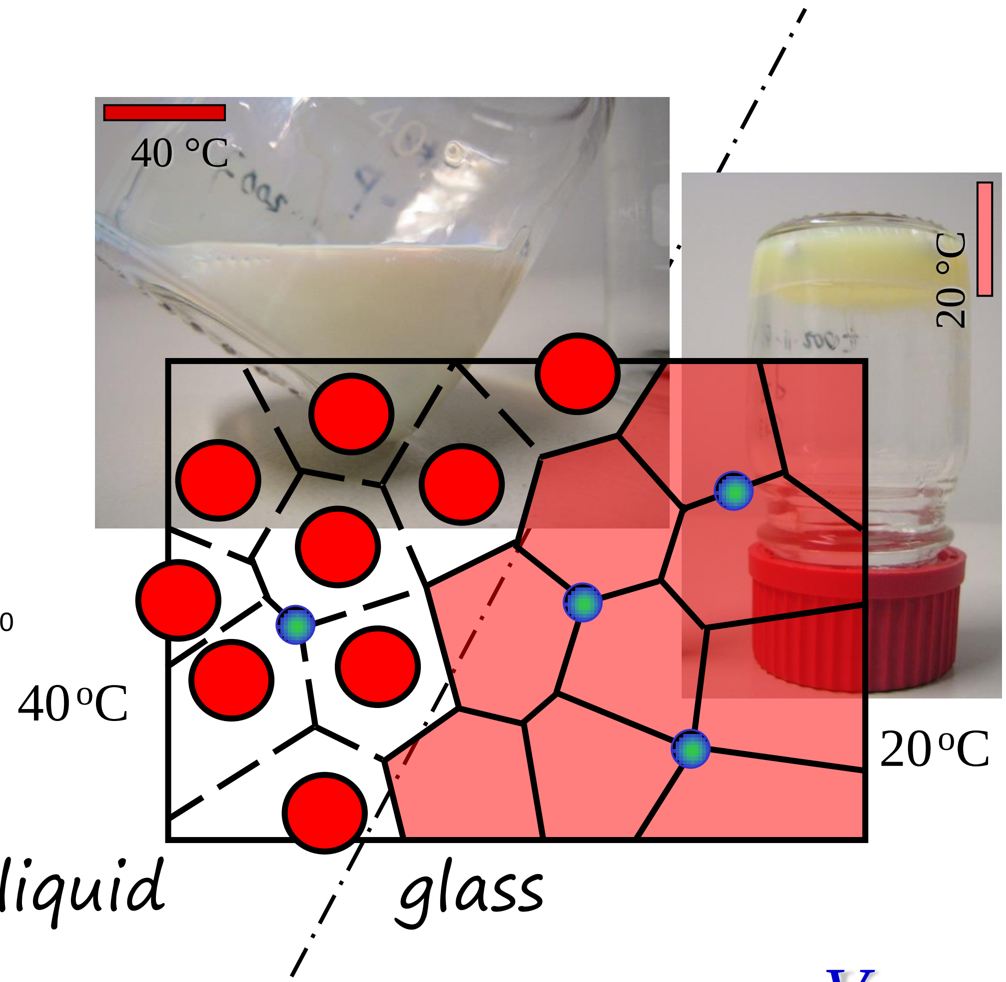
(micro-) rheology probes the aging



Structural relaxation time: $t_s \sim t_c$

Thermosensitive polyNipam particles





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

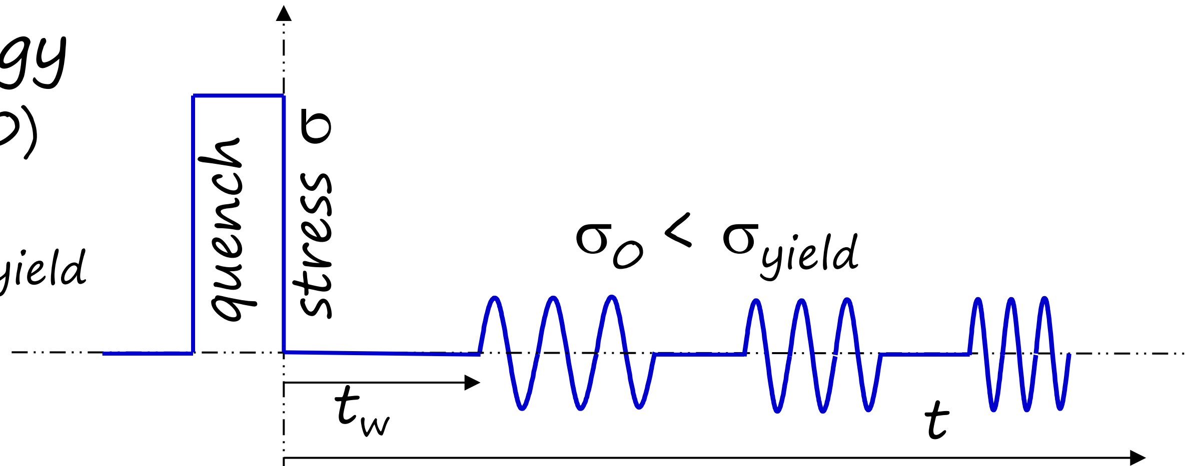
with fluorescent ( ) tracer particles

Experiment

To obtain reproducible results…
…rejuvenate the sample

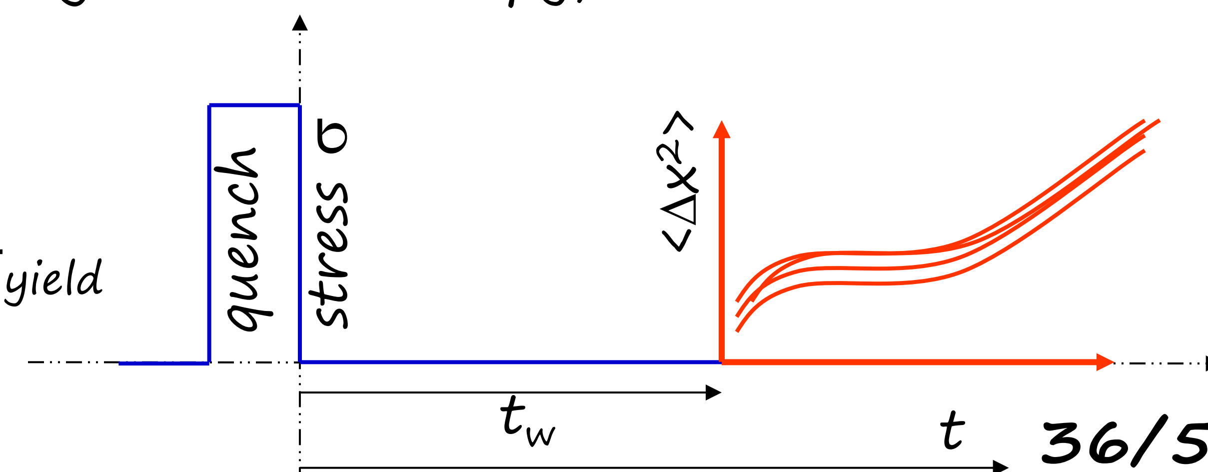
1: macro-rheology
(HAAKE RS 600)

$\sigma_{quench} > \sigma_{yield}$



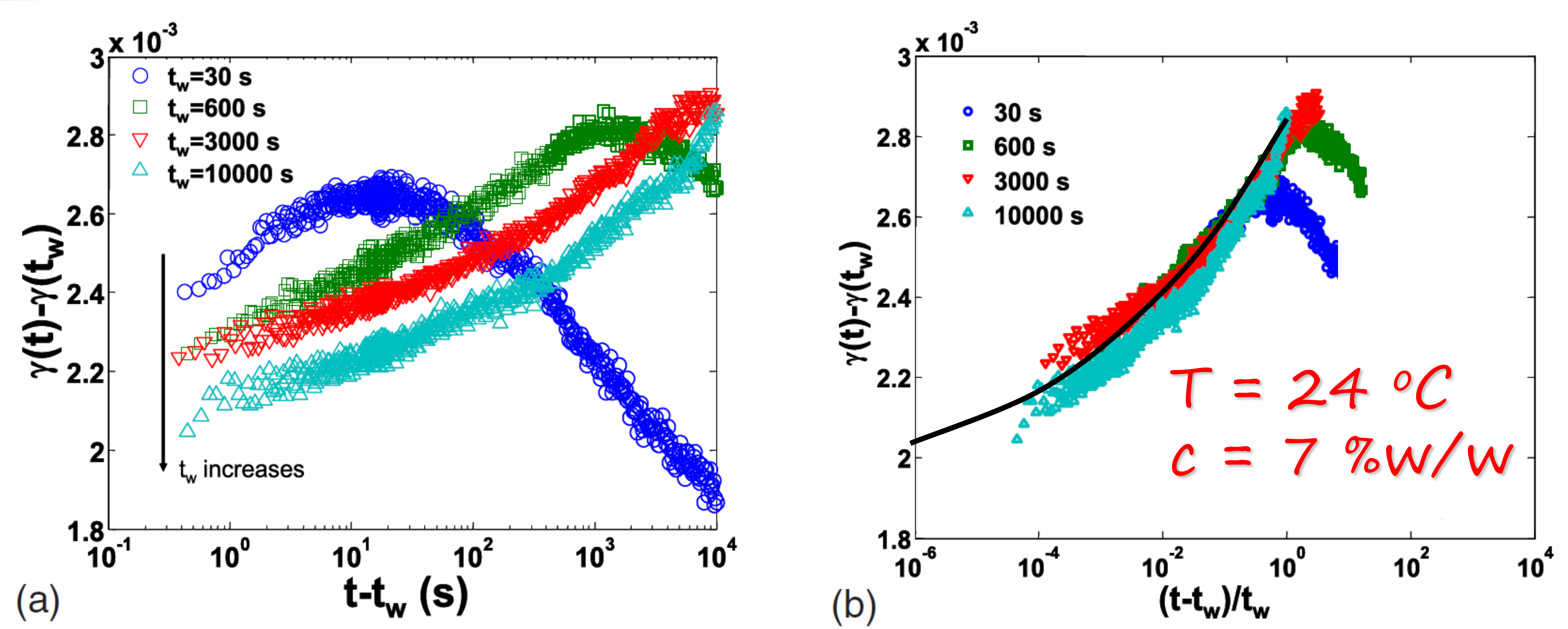
2: particle tracking
(Confocal Scanning Laser Microscopy)

$\sigma_{quench} > \sigma_{yield}$



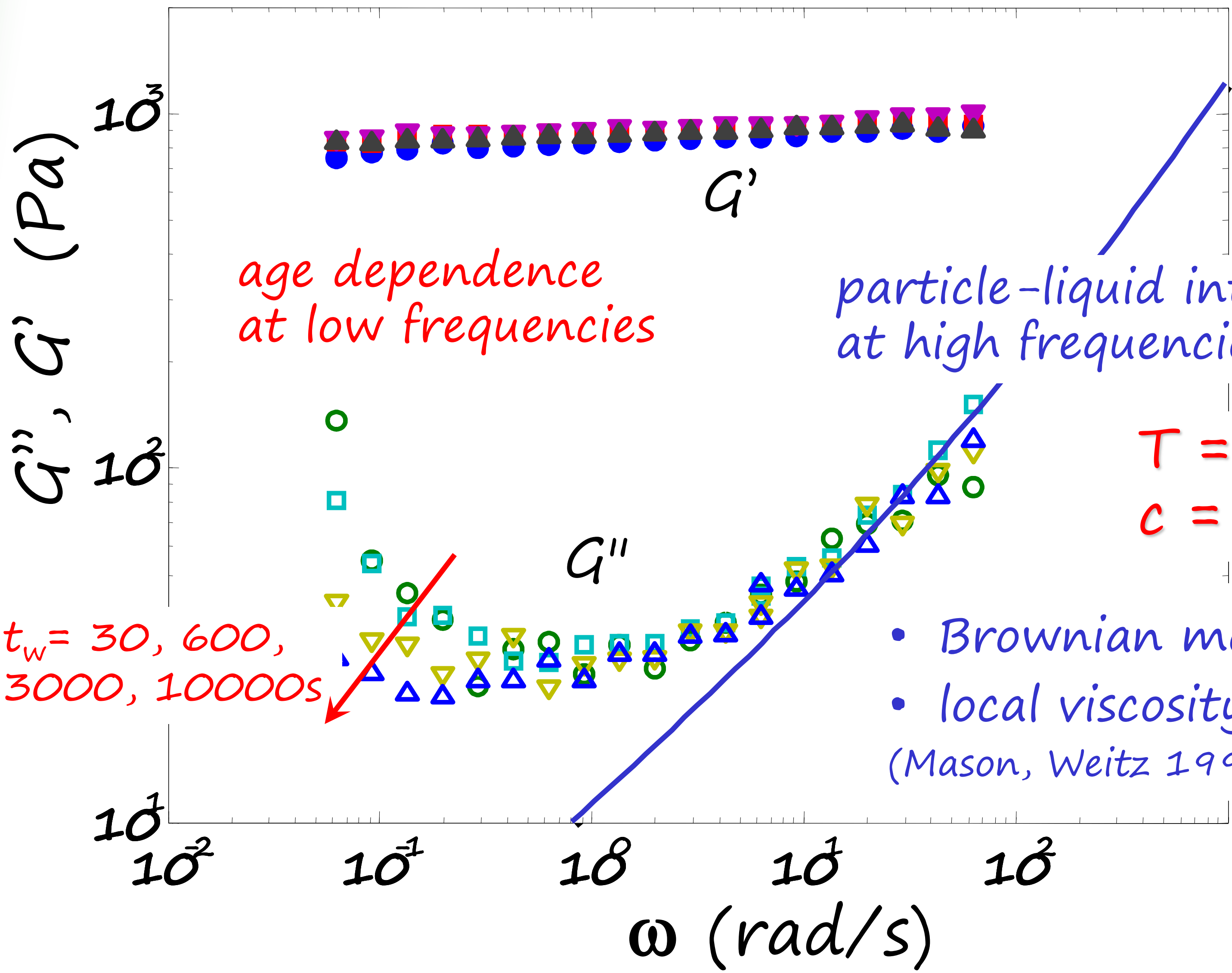
Creep measurements

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



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

Linear rheology, age dependence

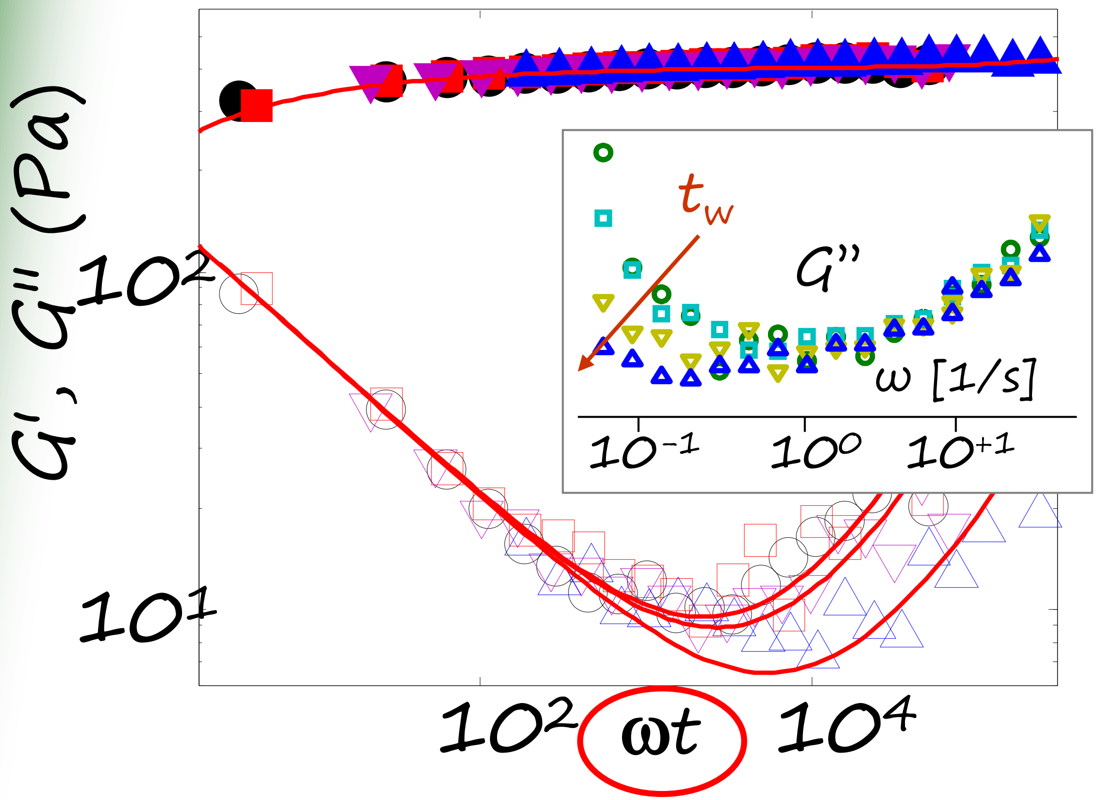


T = 25 °C
c = 7 %w/w

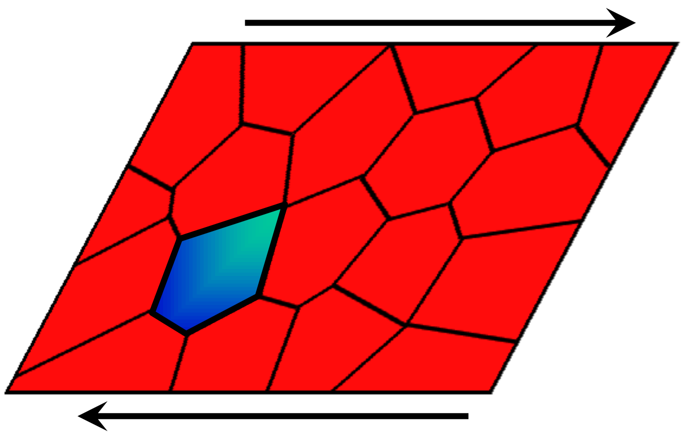
- Brownian motion (~√ω)
- local viscosity (~ ω)

(Mason, Weitz 1995)

Soft Glassy Rheology model



Microscopic picture



Elastic response

- Dissipation due to internal yielding of the particles
- Activated rate process with effective noise temperature x

$x > 1$: liquid, $G^* = fnc(\omega)$, $J = fnc(t-t_w)$

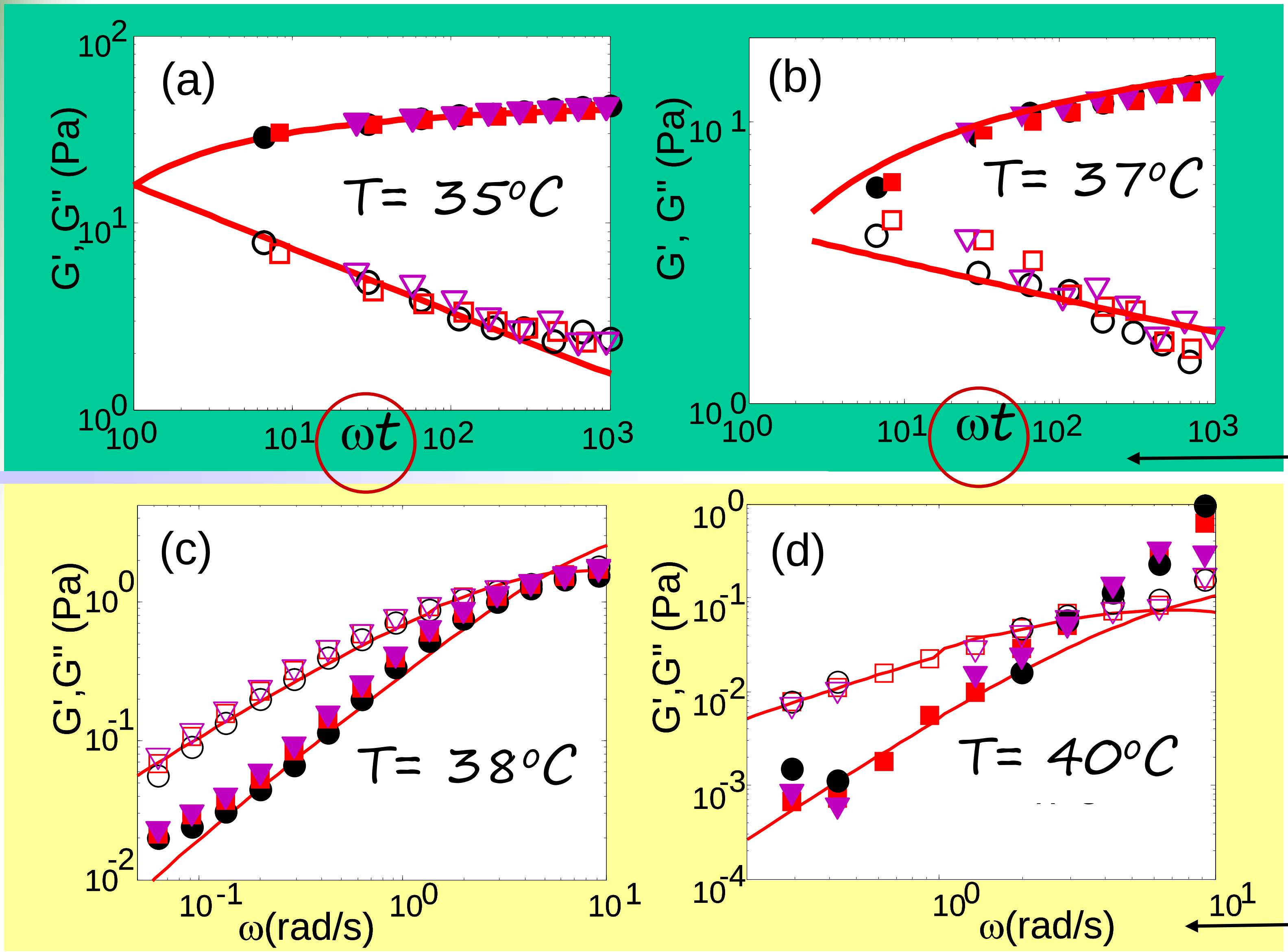
$x < 1$: glass, $G^* = fnc(\omega t)$, $J = fnc((t-t_w)/t_w)$

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)

UNIVERSITEIT TWENTE.
Physics of Complex Fluids

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



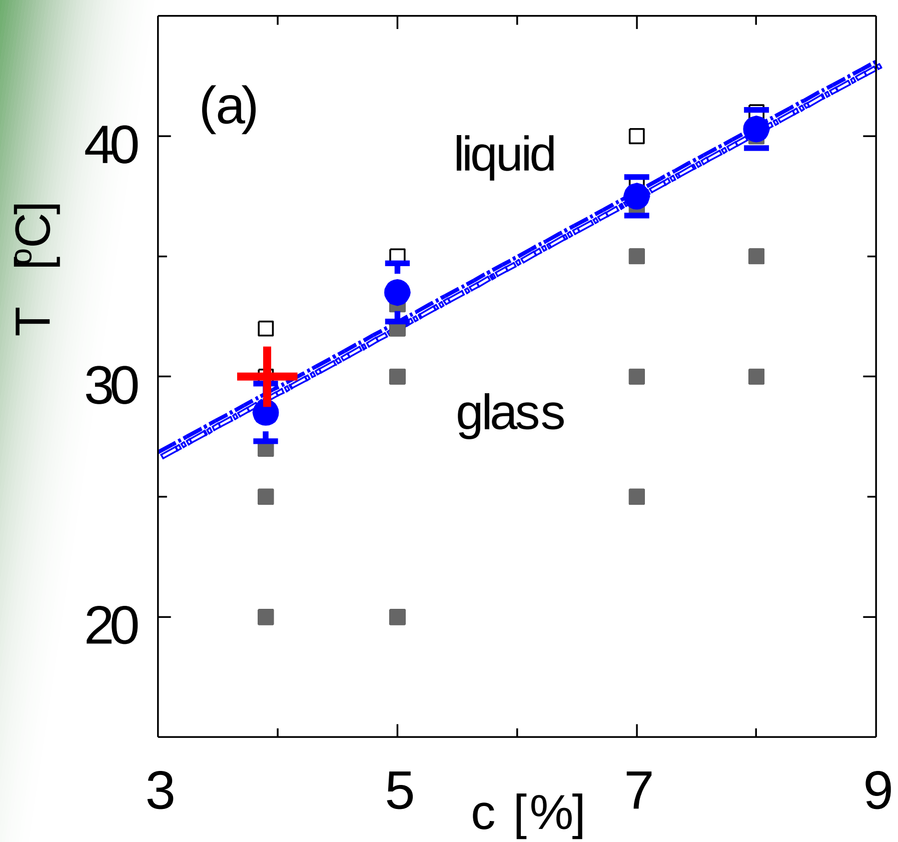
glass

aging

liquid

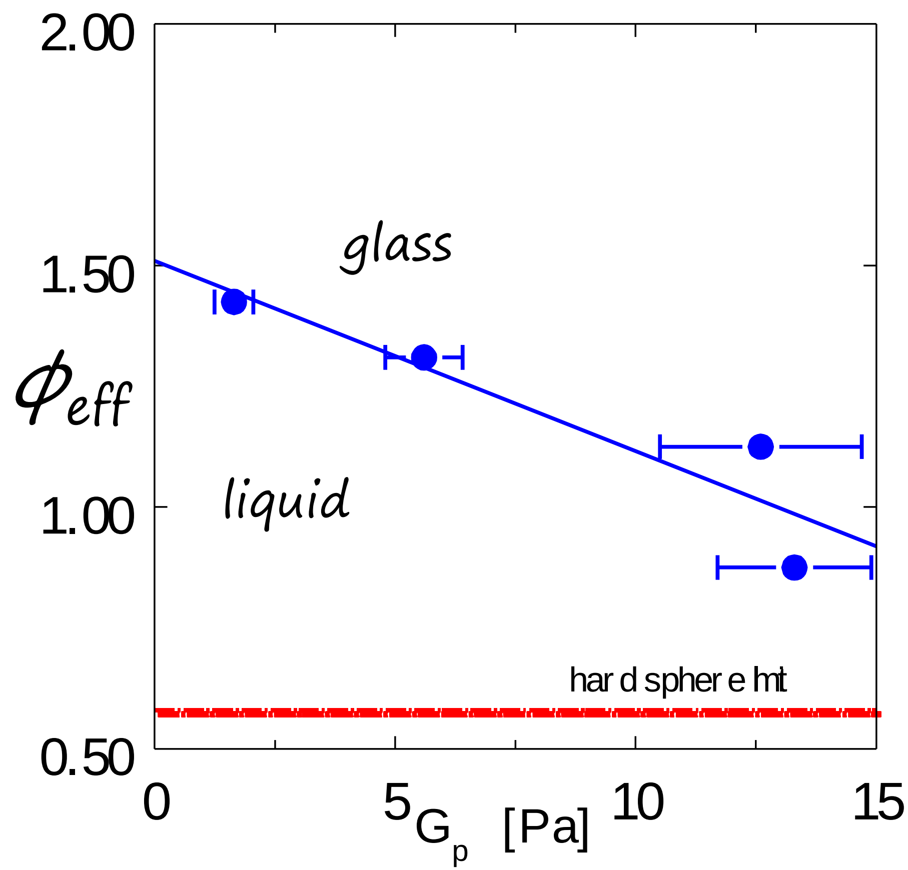
non aging

Phase diagrams



+: micro-rheology

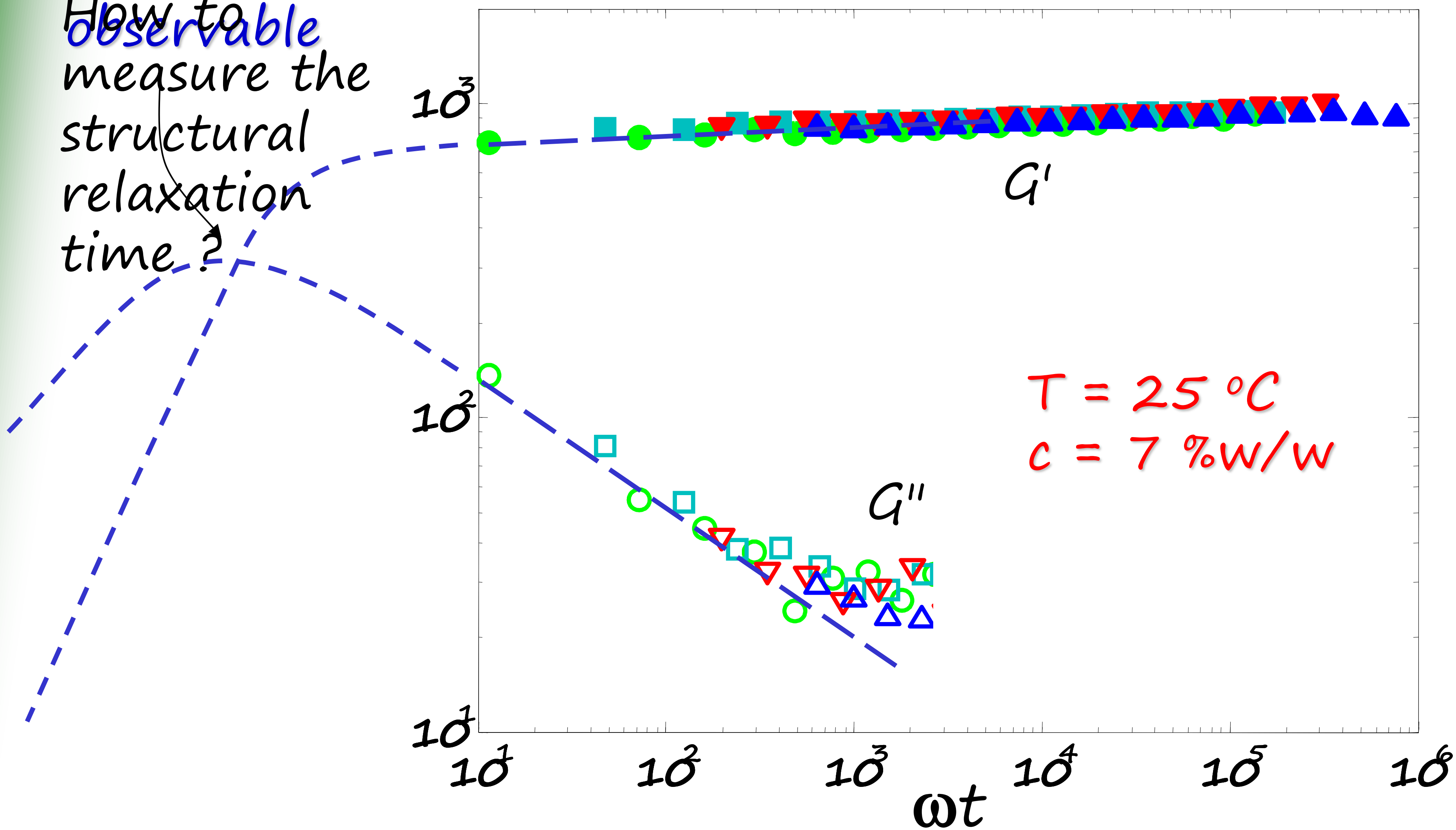
$\varphi_{eff} = V_0 n$

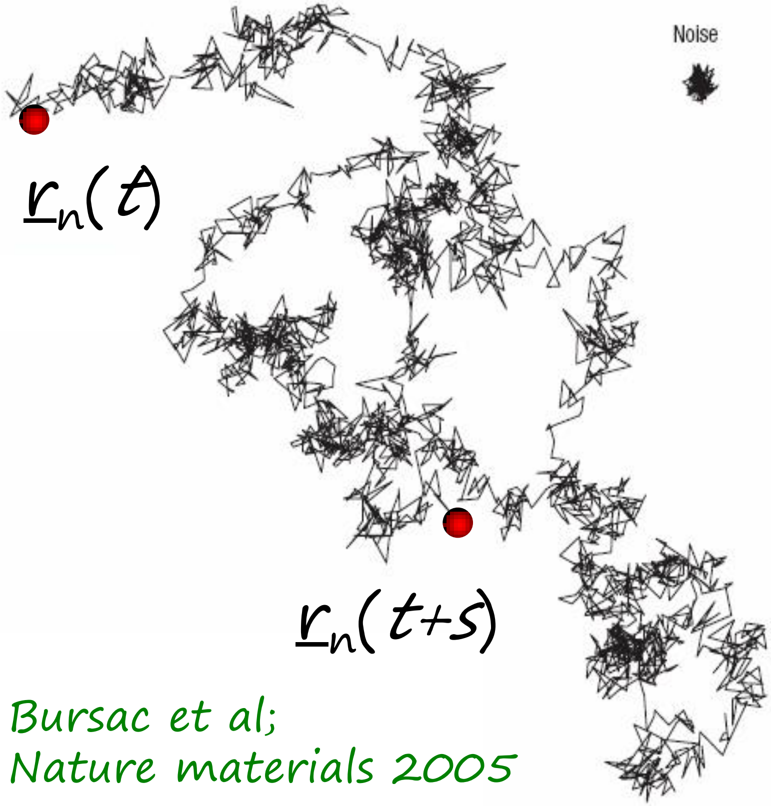


E.H. Purnomo *et al.*, 2008

The structural relaxation time is not observable

How to measure the structural relaxation time ?





Bursac et al;
Nature materials 2005

● : fluoresent tracer observed by CSLM
$\underline{r}_n = (x_n, y_n)$

Stokes Einstein Relation (Newtonian fluid):

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

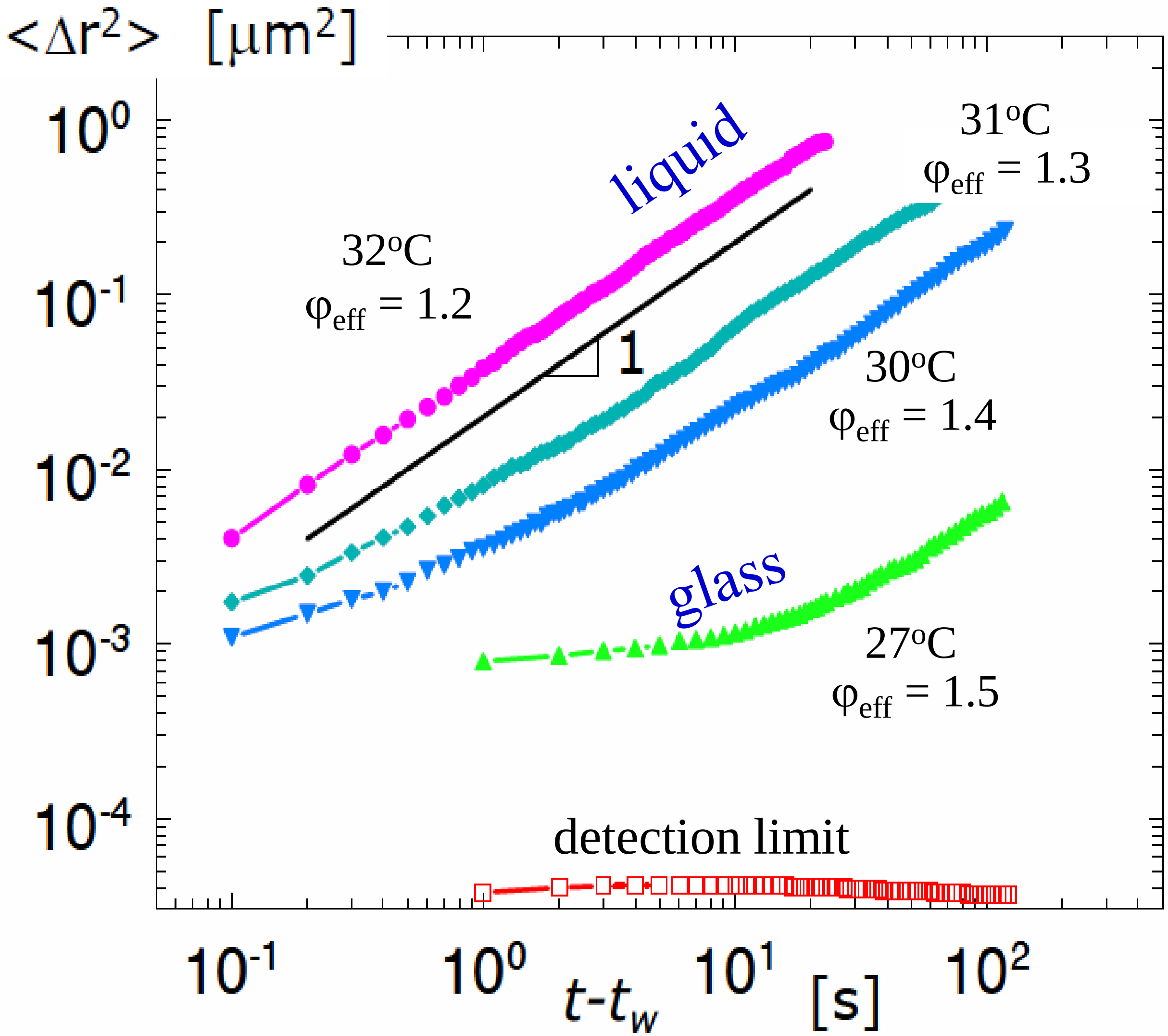
Generalized Stokes Einstein Relation:

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

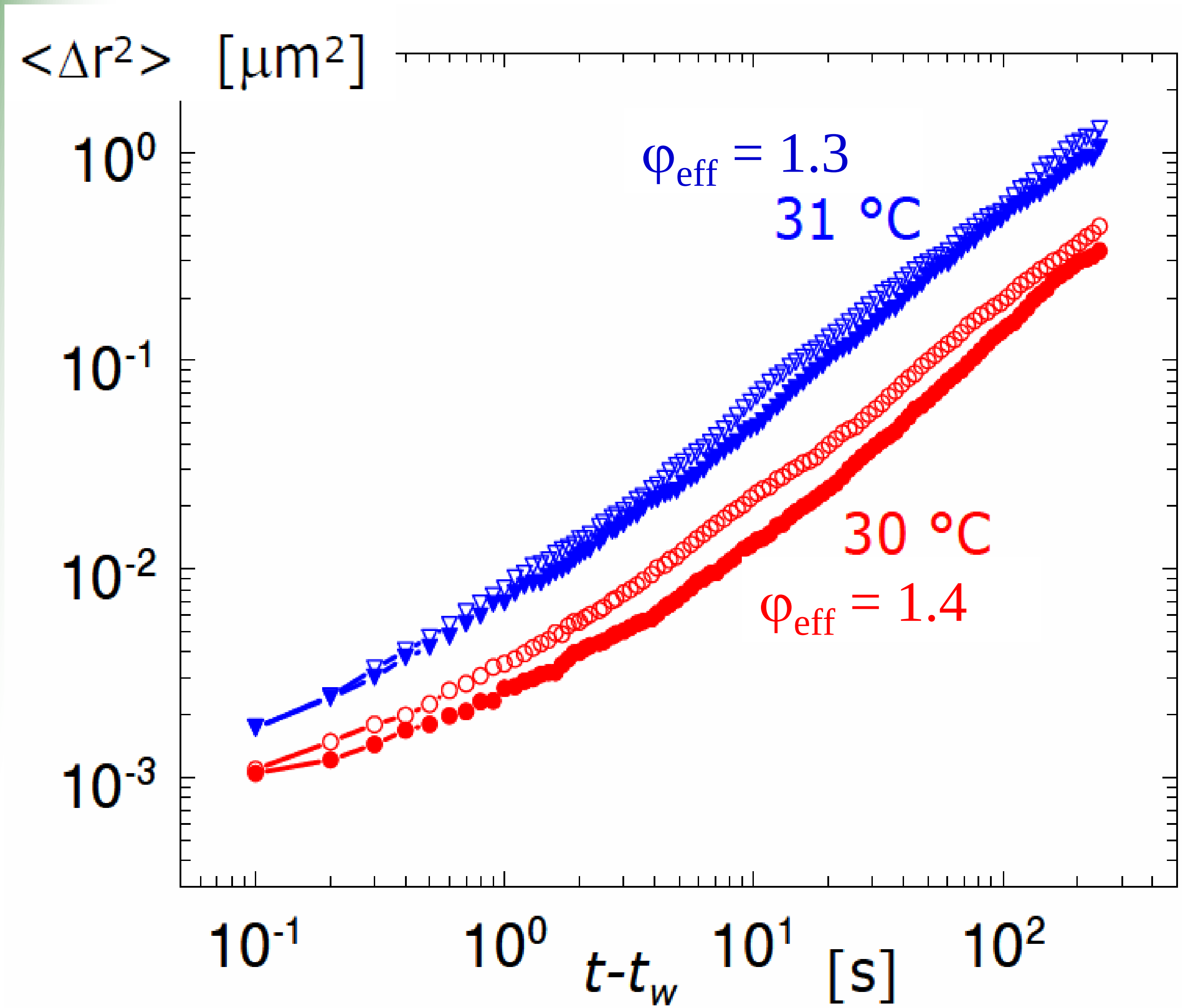
J(t): retardation function

<>: ensemble averaging

$\langle \Delta r^2 \rangle$ *polyNipam*, 4%



Glass transition at c = 4%



t_w

300 s (○)
3000 s (●)

$30 < T_g < 31$ °C

$1.3 < \varphi_g < 1.4$

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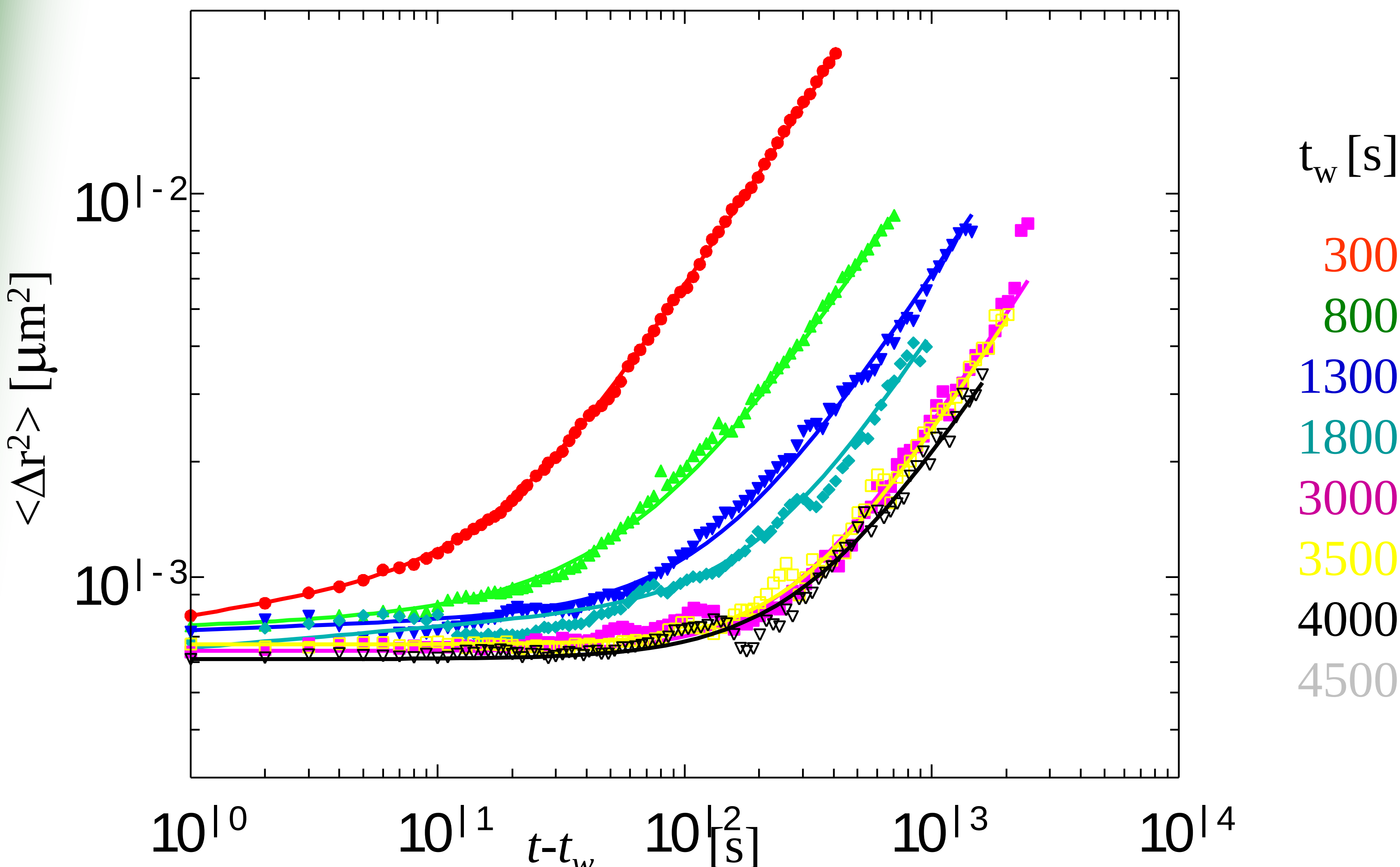
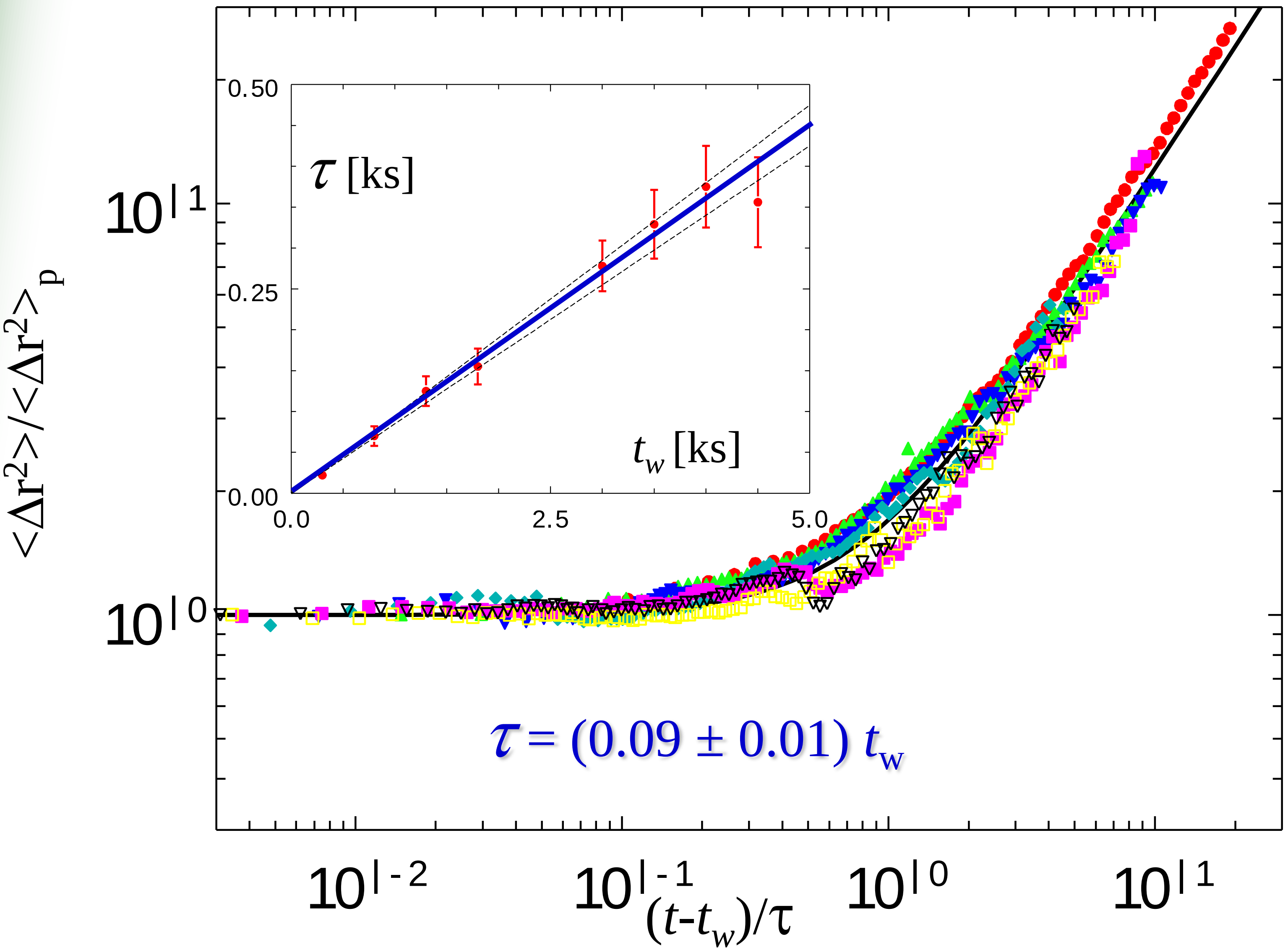
Physics of Complex Fluids

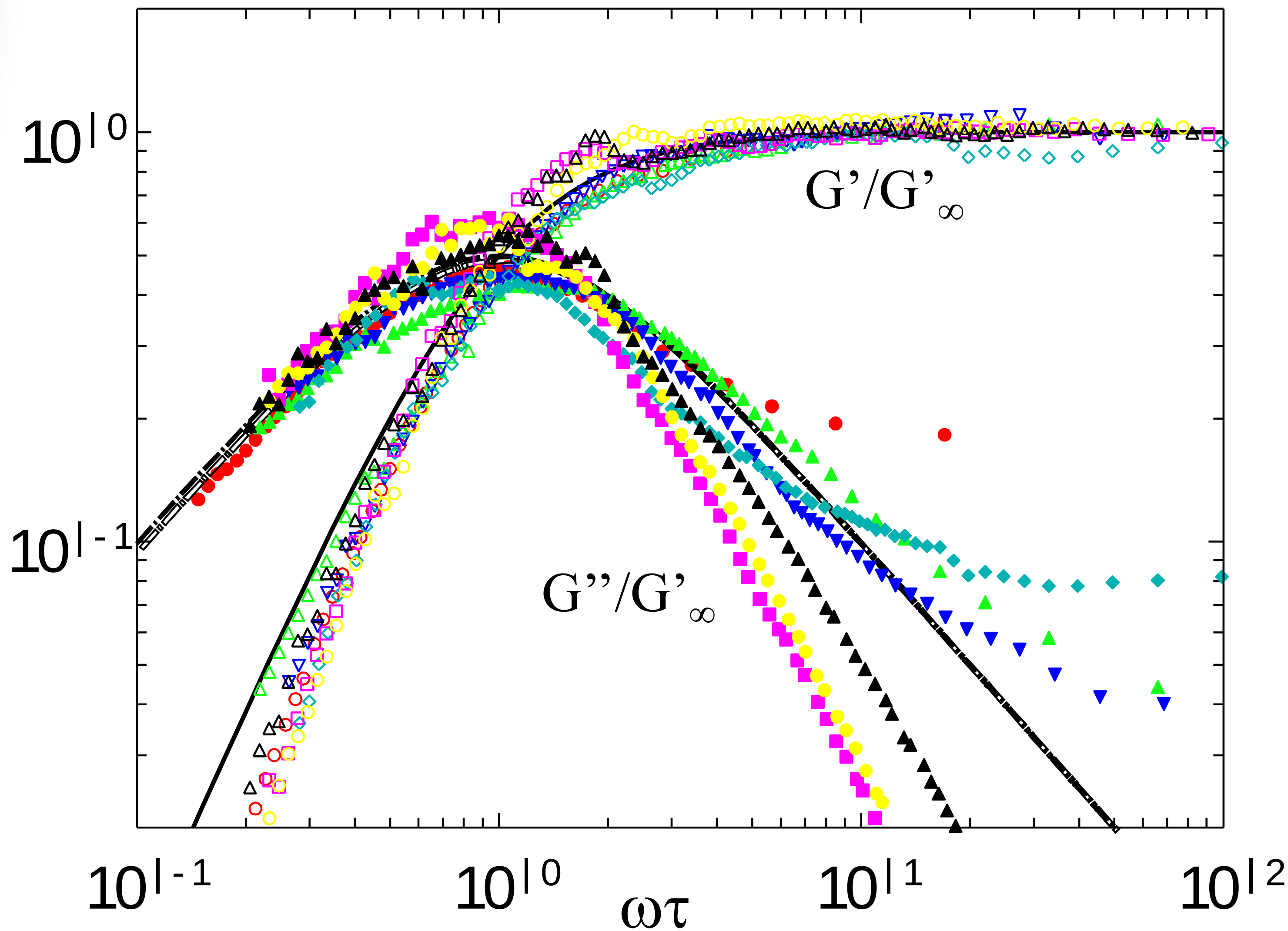
polyNipam
4%, 27 °C *Age dependence*



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



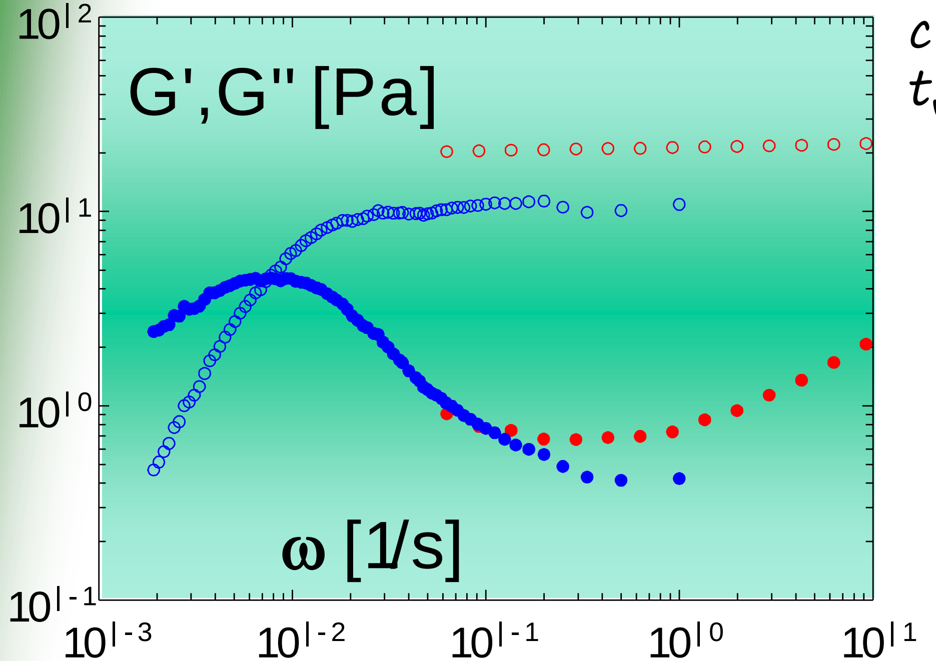
micro-rheology viscoelastic moduli

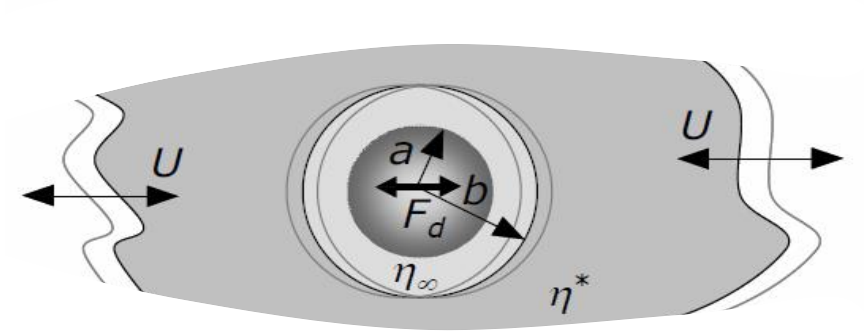


T.G. Mason, 2000

Macro- vs μ-rheology

T = 27 °C
c = 4 % w/w
t_w = 1300 s





Mean field calculation of the frequency dependent drag on a stationary particle in a low viscous cell surrounded by a viscoelastic bulk

$$F_d(\omega) = 6\pi a\, Q\left(\frac{b}{a}, \frac{\eta^*(\omega)}{\eta_\infty}\right)\, \eta^*(\omega) U(\omega)$$

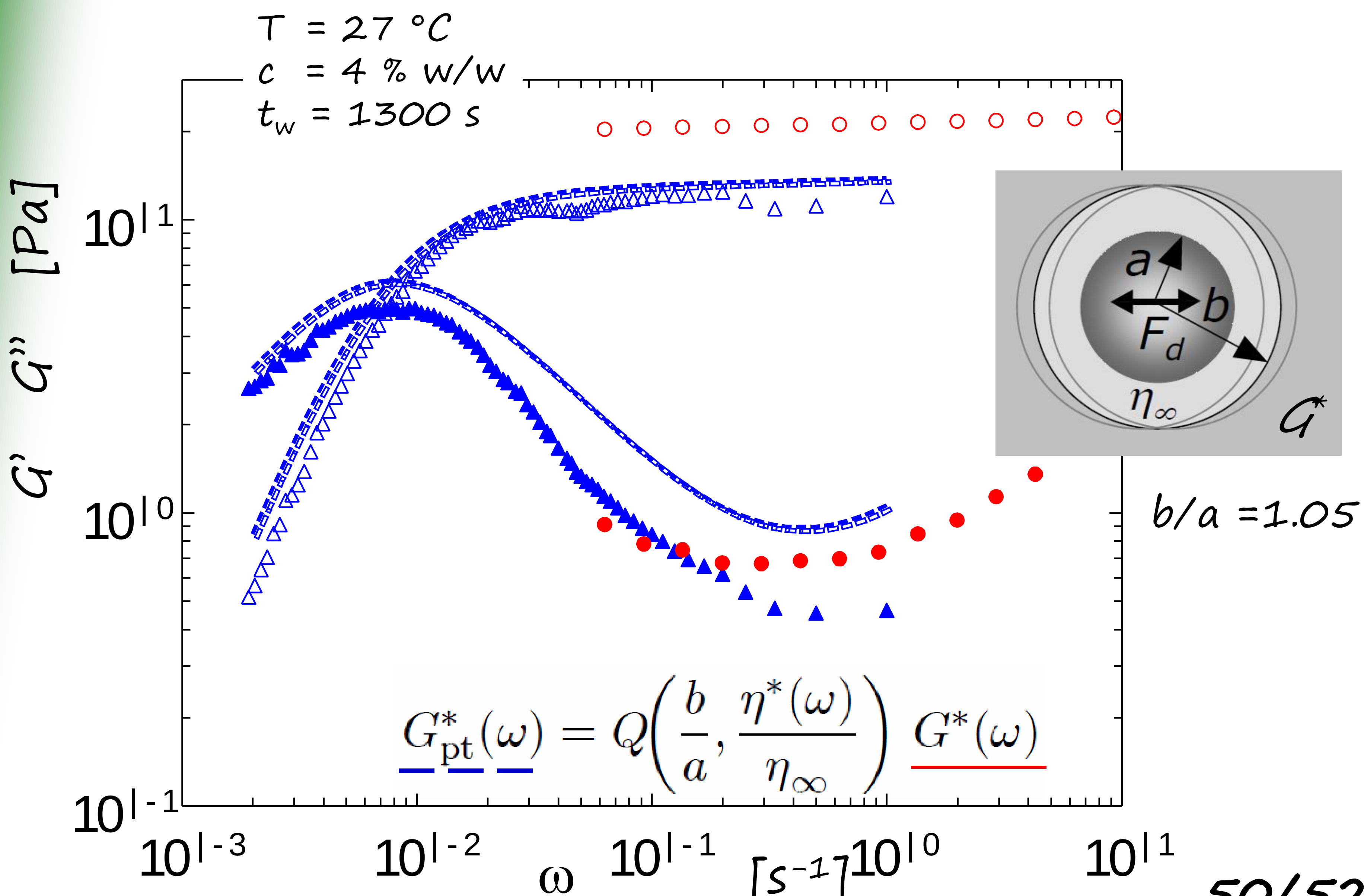
$$\eta_\infty = [G''/\omega]_{\omega=\infty}$$

Experimental observation:

$G'_{macro} / G'_{micro} \approx 2$

$t_c^{macro} / t_c^{micro} \approx 5$

micro vs macro



non-interacting colloids:

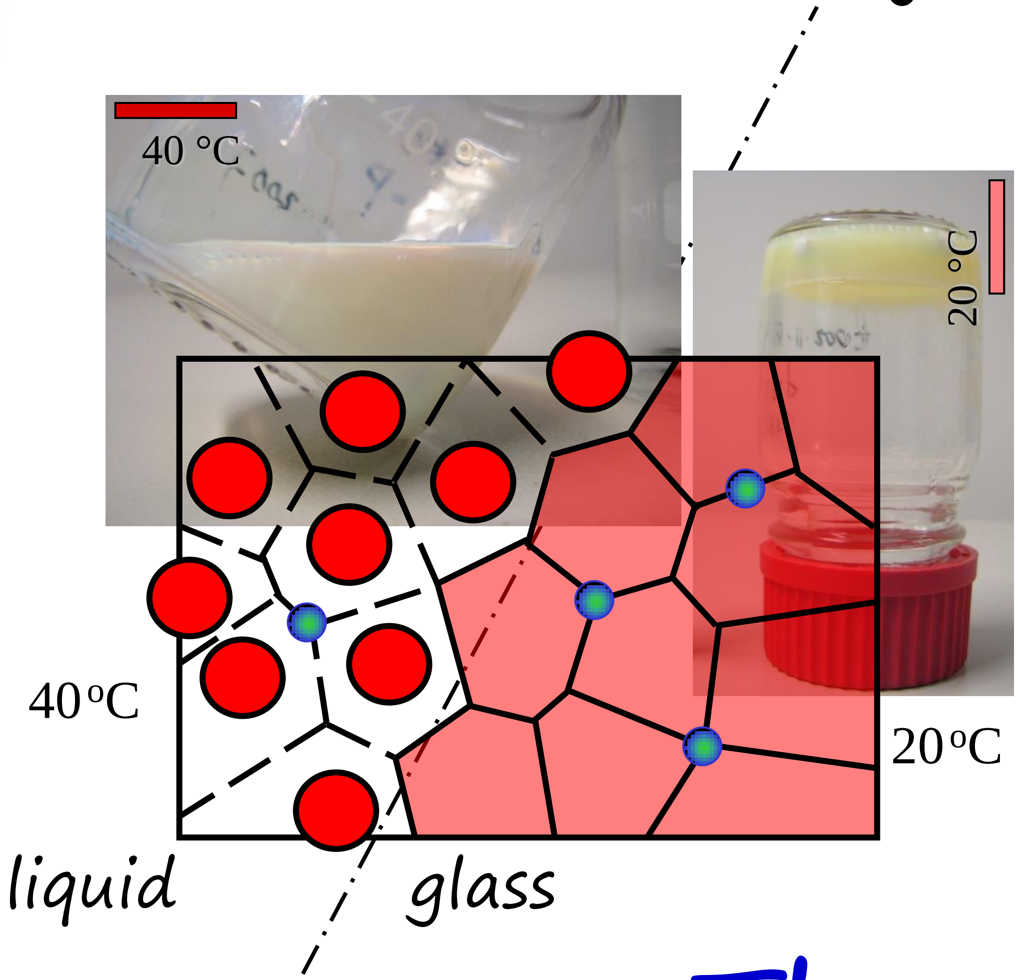
excluded volume effects
- Krieger-Dougherty viscosity
- Shear induced diffusion

aggregating colloids:

intricate balance
- flow determines structure
- structure determines flow

deformable colloids:

at high density
- dissipation due to structural relaxation
- non-equilibrium systems



Thank you for listening