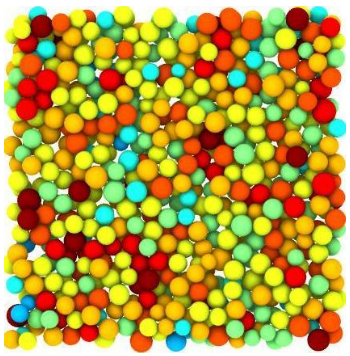
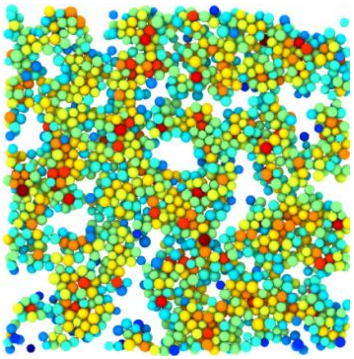
Non-linear mechanics of colloidal gels and attractive glasses

George Petekidis

IESL-FORTH & Department of Materials Science and Technology - University of Crete,

Heraklion, Crete, Greece





work with Alan Jacob (now in NC State) and Esmaeel Moghimi

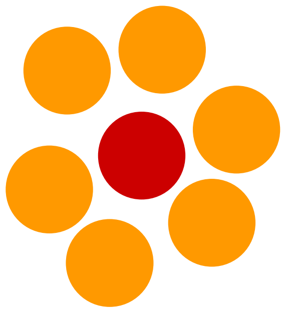
Following work with
Nick Koumakis (now Edinburgh)
John Brady (Caltech), BD simulations
Wilson Poon, Rut Besseling (Edinburgh), rheo-confocal

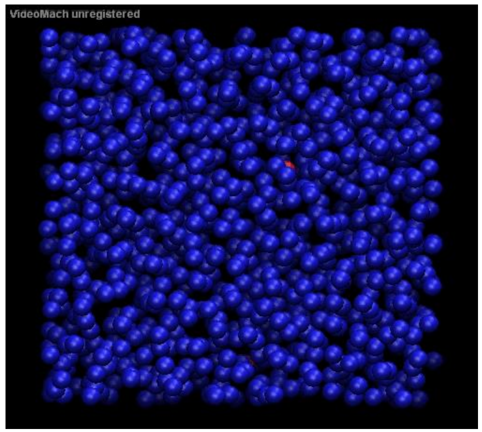
KITP, January 2018

HS Colloids: Liquid-solid transition increasing volume fraction

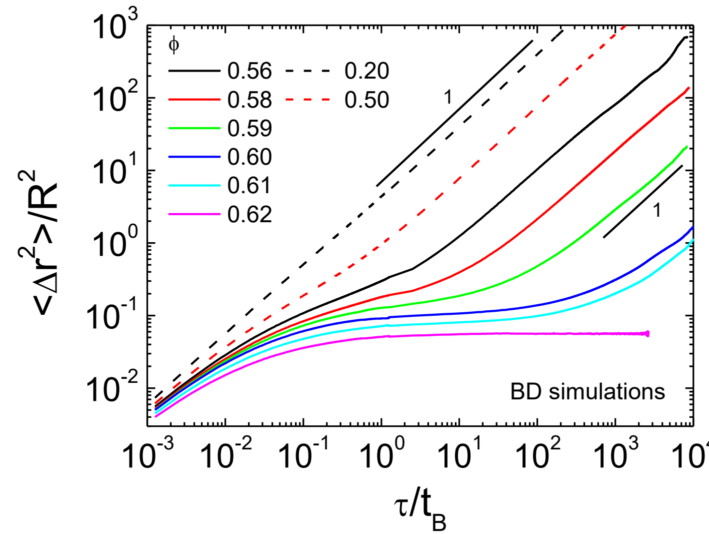
Hard spheres approaching glass transition

At high φ particles are caged => glass (φ>0.58)

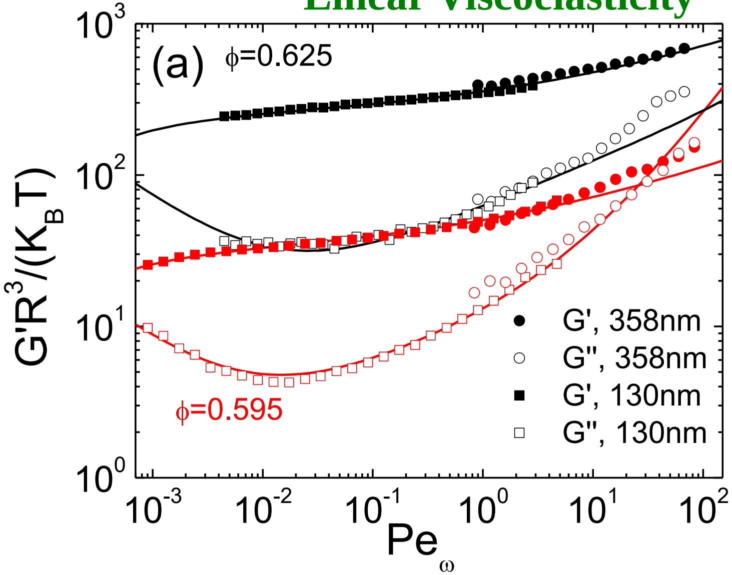




Dynamics

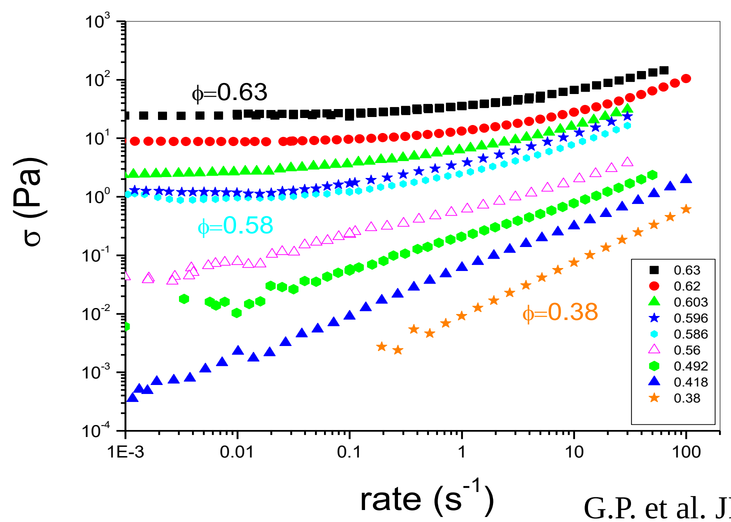


Linear Viscoelasticity



Koumakis et al, Soft Matter, 2012

Steady shear: Flow curve

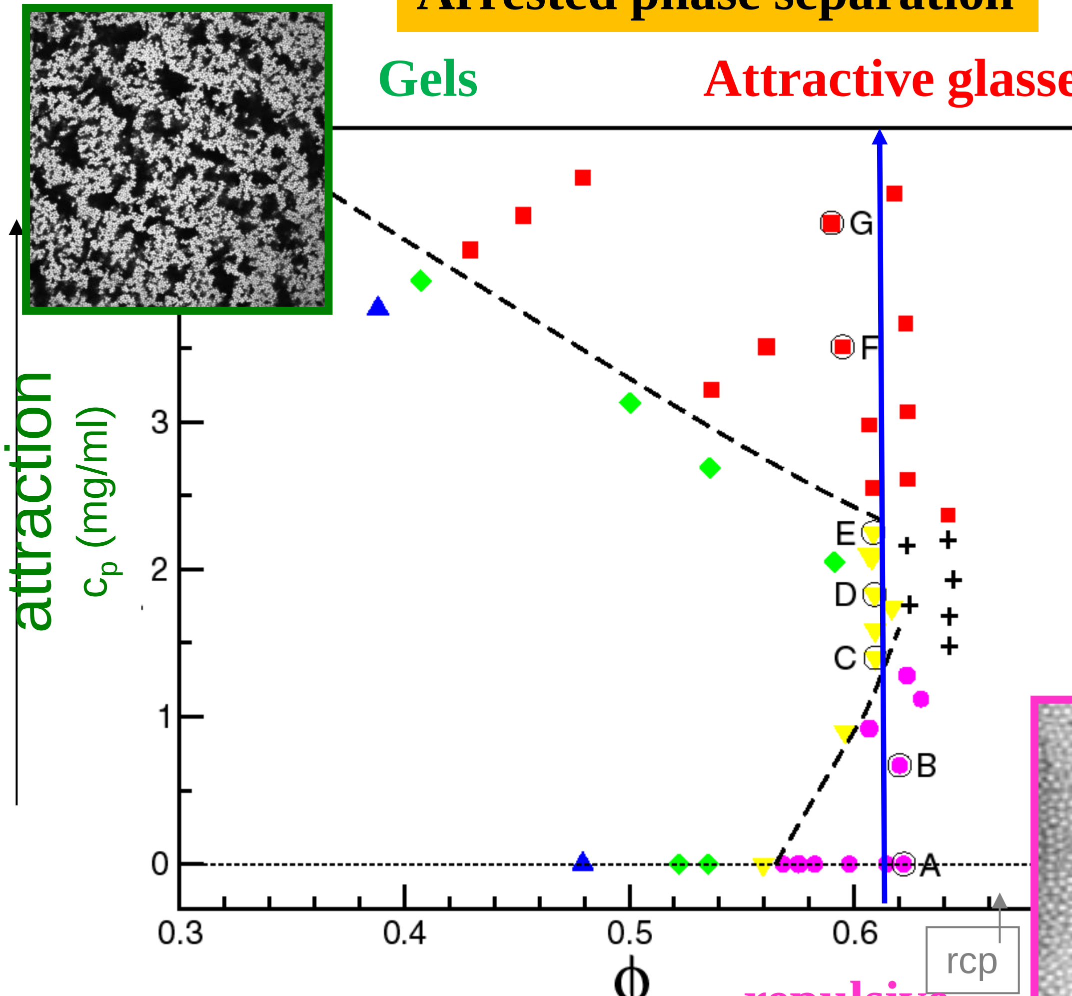


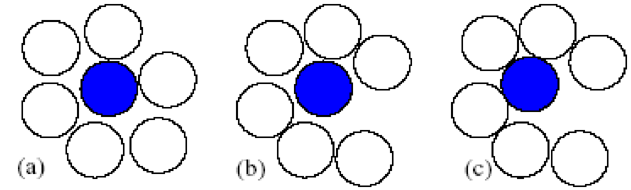
G.P. et al. JPCM, 2004

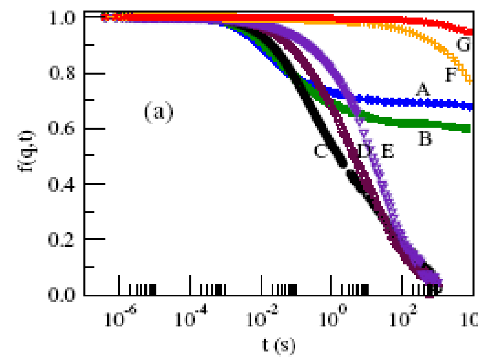
Colloidal non-ergodic states: Glasses- Gels

Arrested phase separation

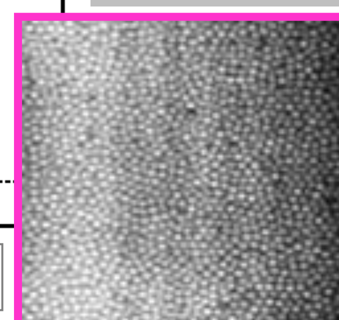
Gels | **Attractive glasses**







Re-entrant melting



repulsive glasses

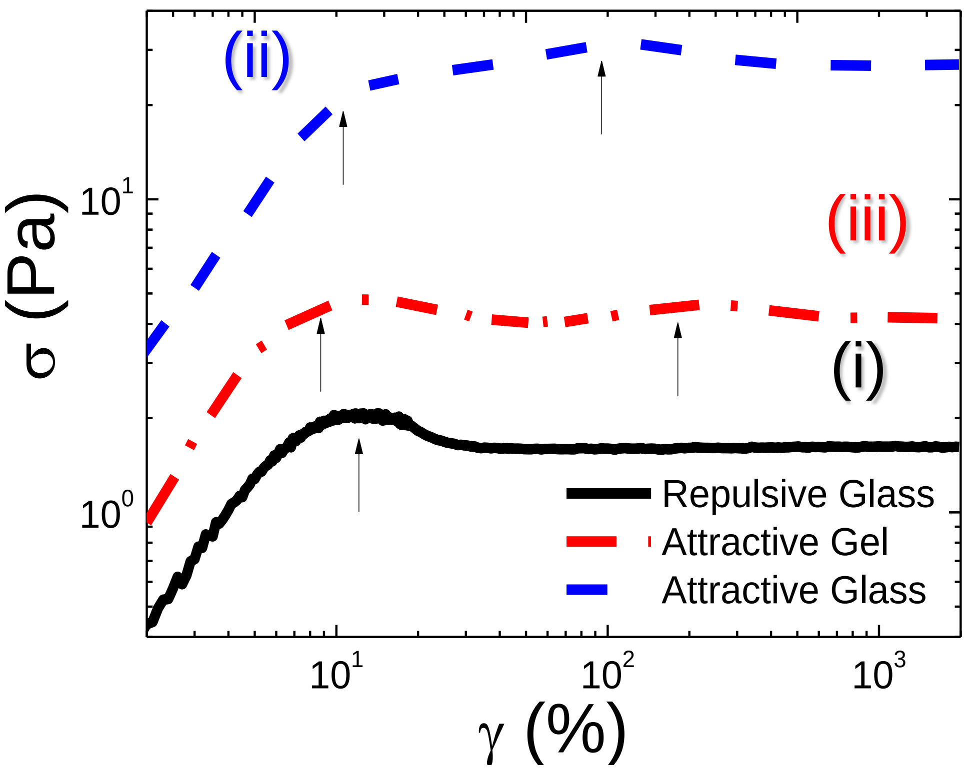
Pham et al., Science, 2002

Poon, Pusey, Bartsch, …; Bergenholtz, Cates, Fuchs, Sciortino, Zaccarelli, …

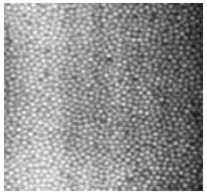
Yielding during start-up shear

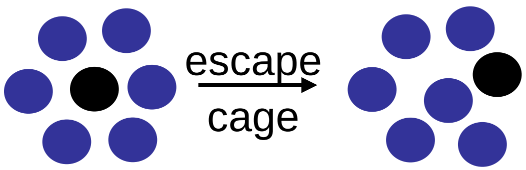
(i) One yielding for repulsive (HS) glasses

(ii) Two step in attractive glasses
& (iii) lower φ gels



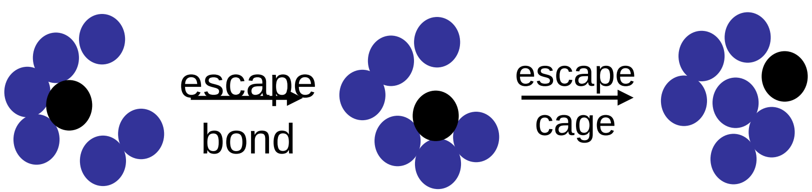
(i) HS glass at φ=0.6



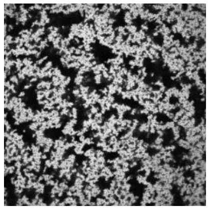


Koumakis et al., PRL 2012, PRL 2013, JoR 2016

(ii) attractive glass at φ=0.6
(Pham et al. EPL, 2006; JoR, 2008)



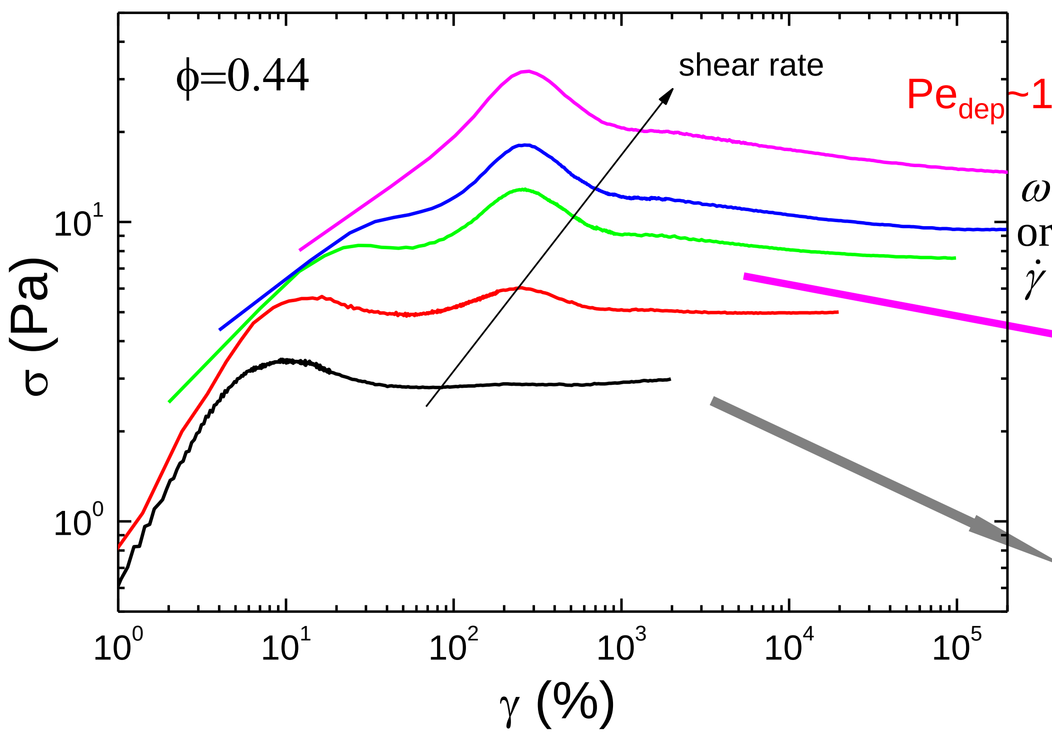
(iii) attractive gel at φ=0.44
(Koumakis et al. Soft Matter 2011 & 2015;
Laurati et al., JCP, 2009 & JoR 2011, 2014;
Ballesta et al, Soft Matter 2013;
Moghimi et al Soft Matter 2017)



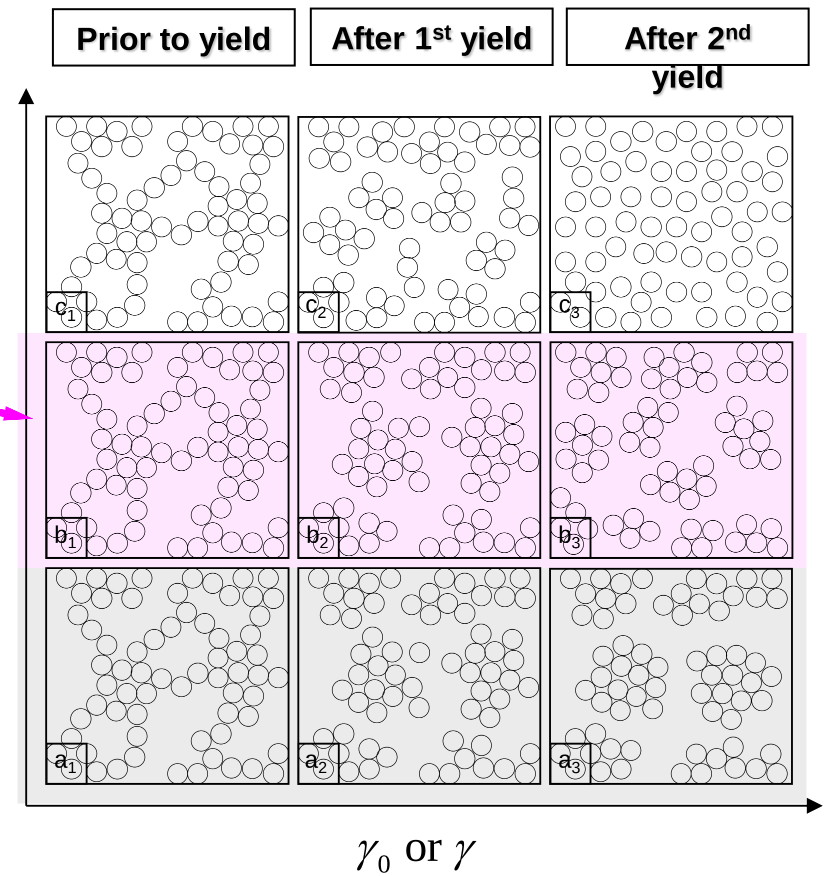
Similar response in oscillatory shear (LAOS)

Rate dependence of gel yielding

N. Koumakis and GP, Soft Matter (2011)



A simplified picture



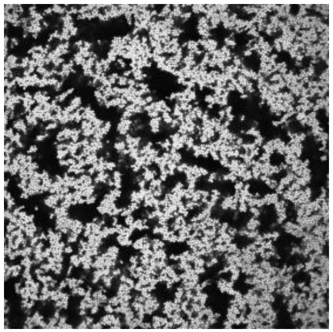
For $F_{visc} = 6\pi\eta R\upsilon > F_{dep}$ bonds will rupture

$$Pe_{dep} = \frac{F_{visc}}{F_{dep}} = \frac{12\pi\eta\xi R^3\dot{\gamma}}{U_{dep}(2R)} \rightarrow$$ ratio of viscous to depletion forces >1 => clusters break

with $\xi = \delta / R$ (attraction range/particle size)

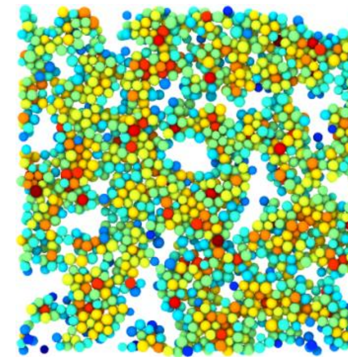
$\mathrm{Pe}_{dep} \equiv M_n$ (Mason # for magnetorheological fluids)

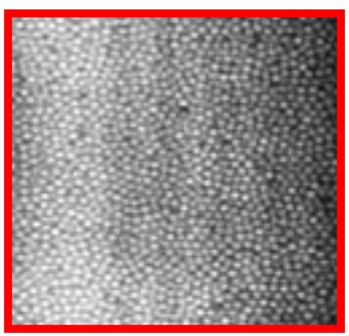
Attractive colloids at different states - Outline



a) **Tuning colloidal gels by steady and oscillatory shear**

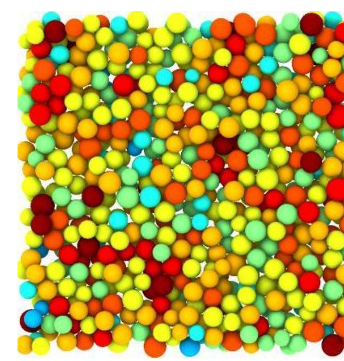
Koumakis et al. Soft Matter 2015,
Moghimi et. al. Soft Matter 2017





b) Yielding of attractive glasses

(*Moghimi et al. in preparation, 2018*)



Techniques:

Experimental rheometry - BD simulations

Experiments

Use model colloidal systems:
PMMA HSs + depletion attractions

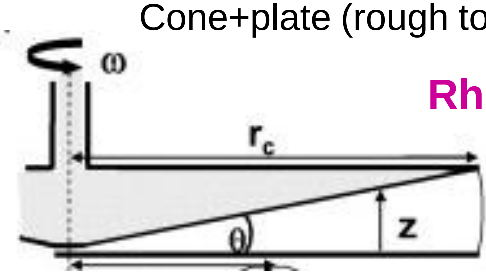
PMMA particles + PB (or PS) linear chains in octadecene (non volatile solvent)
or cis-decalin/CHB for imaging …
Strength of attraction: $U(2R)/k_BT \approx 0$ to -20,
Range: size ratio, $\xi \approx 0.1$

Rheometry:

MCR -501, 302, Anton-Paar
Stress controlled rheometers

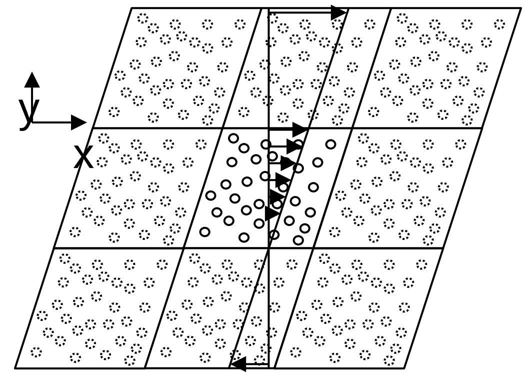
ARES , Strain controlled

Cone+plate (rough to avoid slip)



Rheo-Confocal

Brownian Dynamics simulations
(Foss & Brady, J. Rheology, 2000)



BD: **No HI, Periodic boundary conditions,**
Here: Typically ~30000 particles, polydispersity ~10%

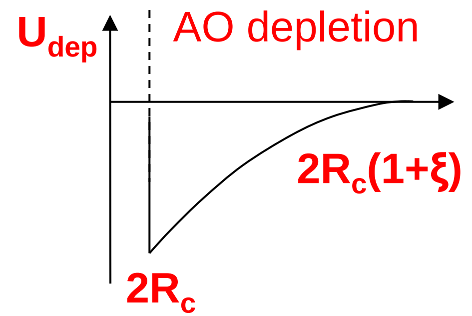
$$\mathbf{F}^{\mathbf{P}} = \mathbf{F}^{HS} + \mathbf{F}^{dep}$$

HS part: "Potential free" algorithm

$$\mathbf{F}^{HS} = 6\pi\eta R \frac{\Delta x^{HS}}{\Delta t}$$

$$F_{dep} = -\frac{dU}{dr}$$

Attractive part :
AO depletion



N. Koumakis et al. Soft Matter (2015)

Tuning colloidal gels by steady and oscillatory shear

Shear history effects - Thixotropy

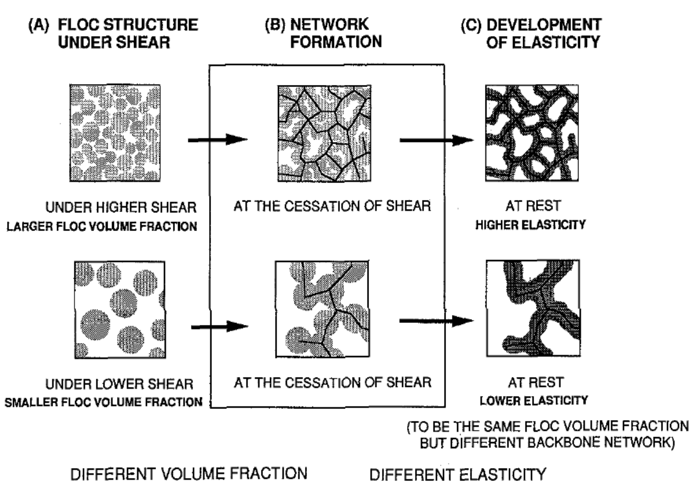
Wide range of systems: flocculated suspensions, particle networks, gels, pastes, glasses

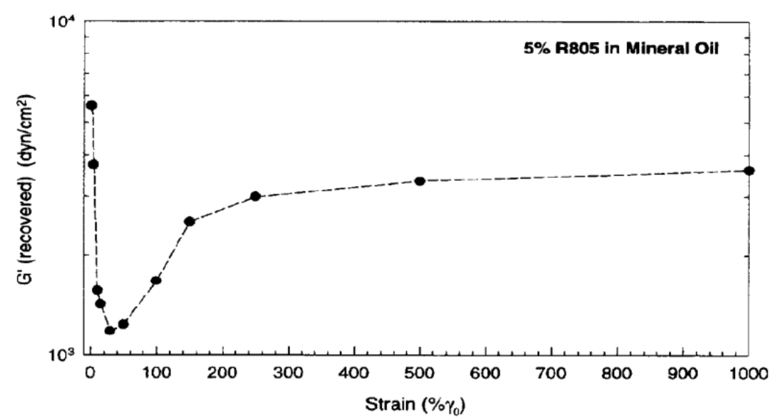
Crude oils, waxes, paints, food products, clay minerals (cement, drilling muds), biological systems…

Thixotropic systems: J. Mewis, J. Coll. Int. Sci. 1972, JNNFM. 1979 … Rheo Acta 2005, Soft Matter 2006 …etc

and many others: Coussot, Buscall, Vermant, Bonn, Denn, Metzner, Beris, …

Ferric-oxide suspensions, Kanai & Amari, Rheo. Acta, 1993

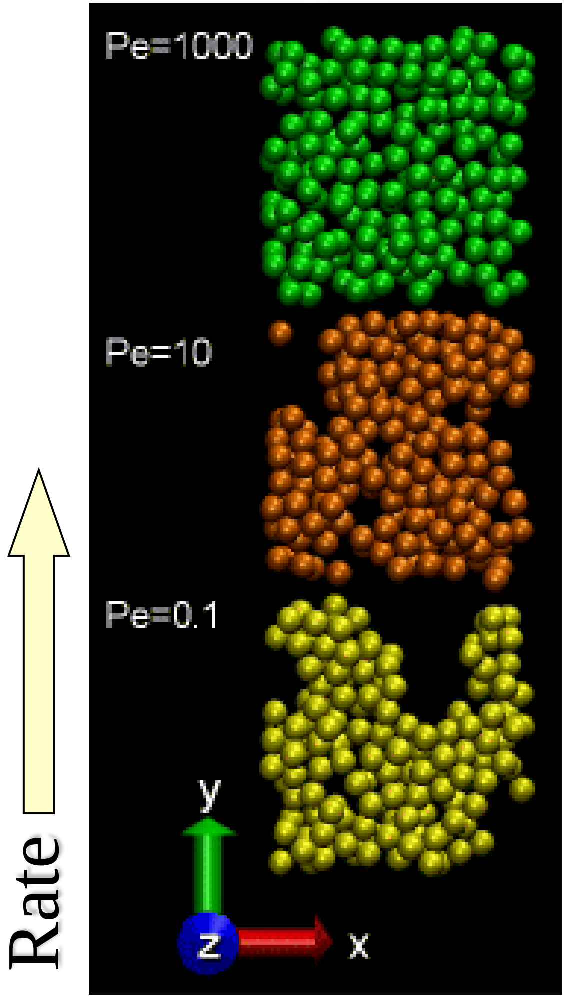




Flocculated suspensions of fumed silica,

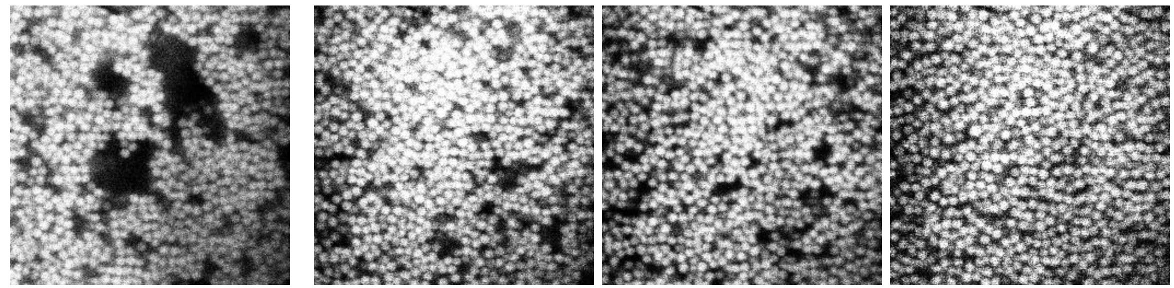
Raghavan & Khan, JoR, 1995

Tuning gel heterogeneity by steady shear

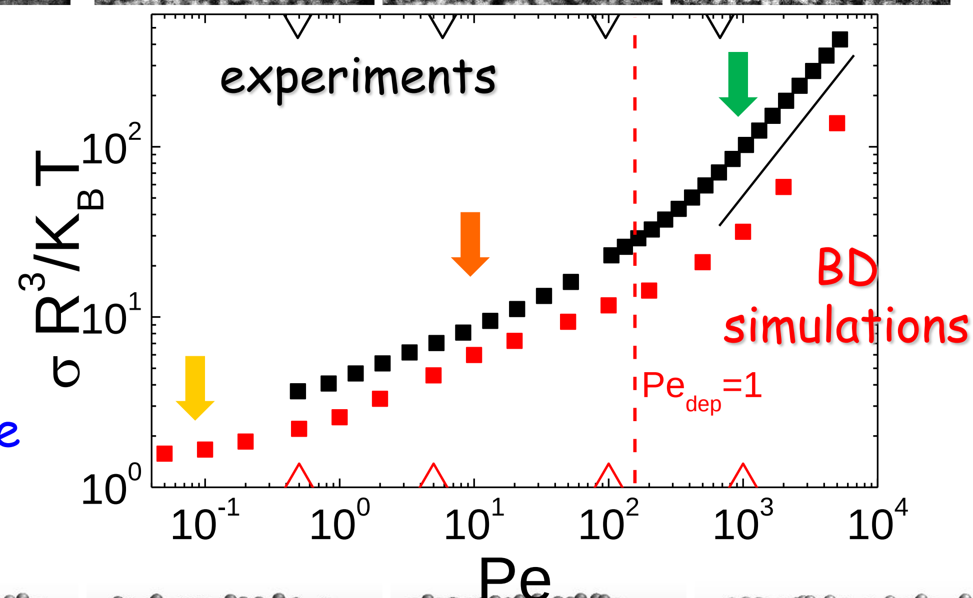


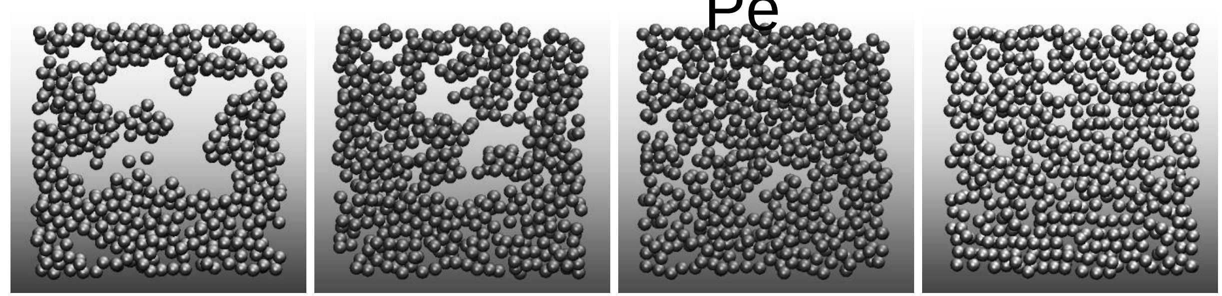
ξ=0.1, φ=0.44
$U_{Dep}(2R)=-20k_BT$
$Pe/Pe_{dep}\approx 100$

Rheo-Confocal: φ=0.44, $U/k_BT\approx-20$, R=800nm and $\xi\approx0.1$



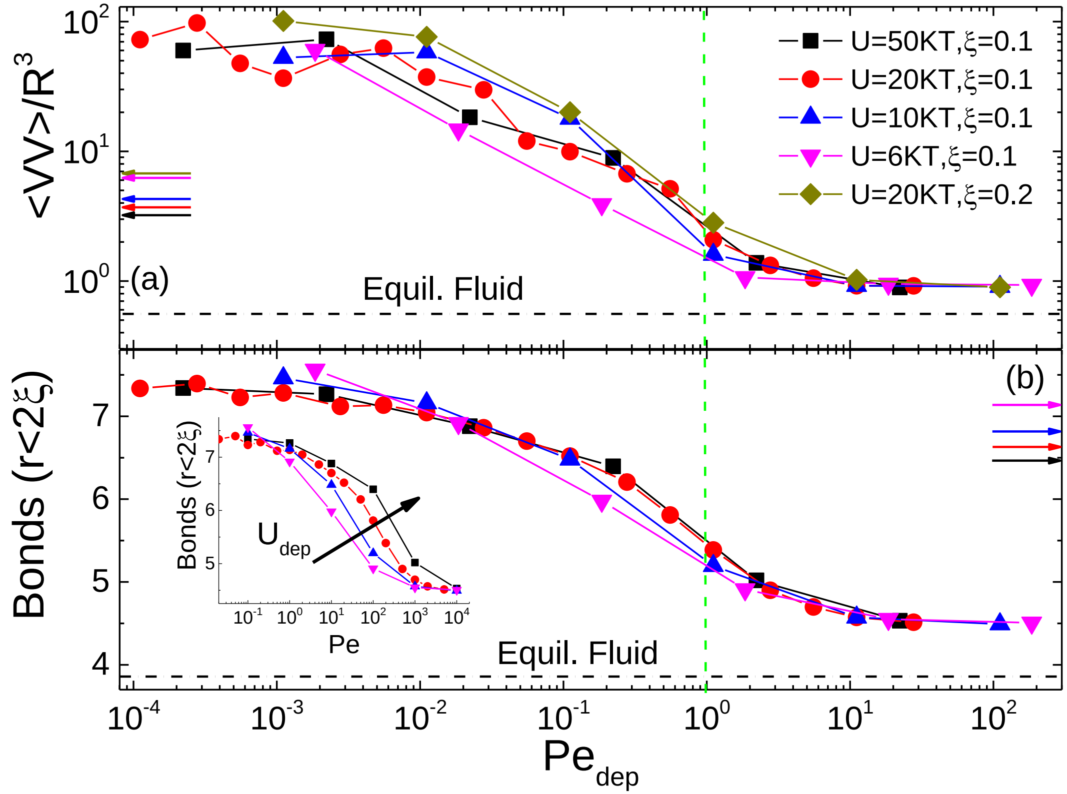
steady state





Tuning gels by steady shear

Ratio of viscous to depletion forces: $Pe_{dep} = \frac{F_{visc}}{F_{dep}} = \frac{12\pi\eta\xi R^3\dot{\gamma}}{U_{dep}(2R)}$

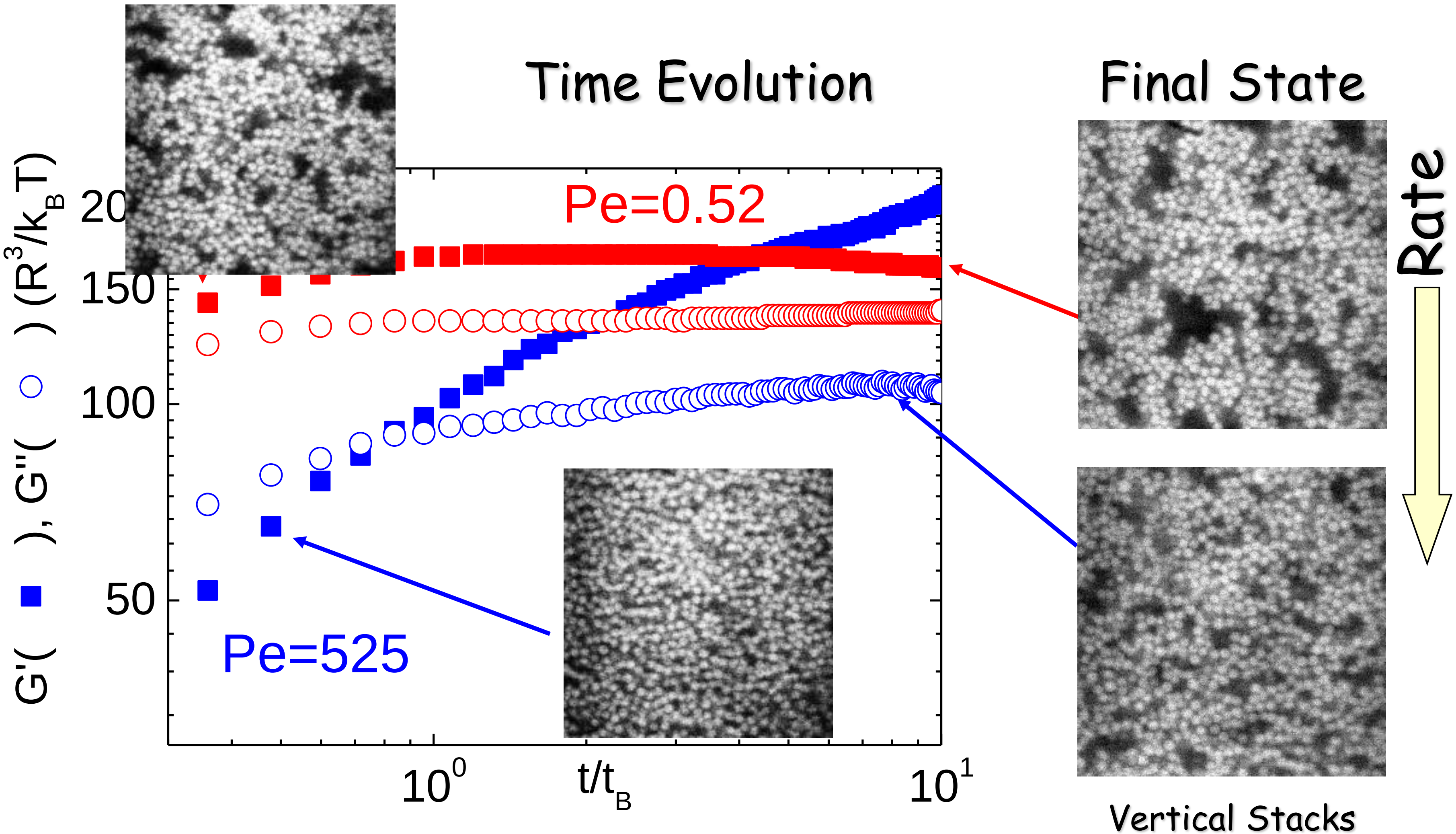


Structural characteristics: void volume, # bonds scale with Pe_{dep} for different ranges and strengths of attraction

Good agreement between experiments and BD simulations

N. Koumakis et al. Soft Matter 11, 4640, (2015)

Tuning gels by steady shear:
Structure and rheology after shear cessation

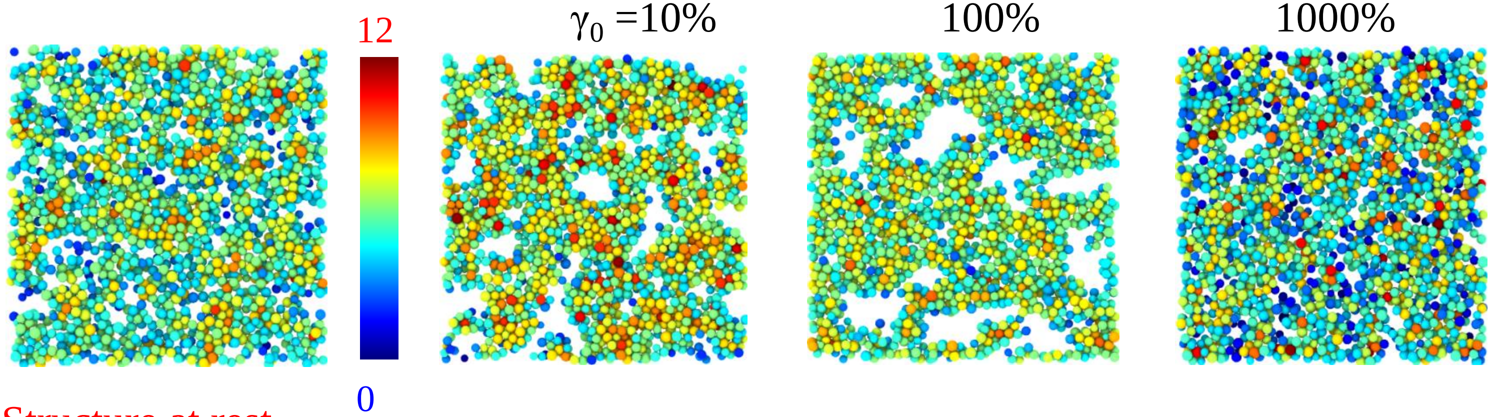


Higher rates are followed by longer restructuring
But eventually create a stronger solid

N. Koumakis et al. Soft Matter, (2015)

Tuning gels by oscillatory shear

BD Simulations: Structure after oscillatory pre-shear



Structure at rest

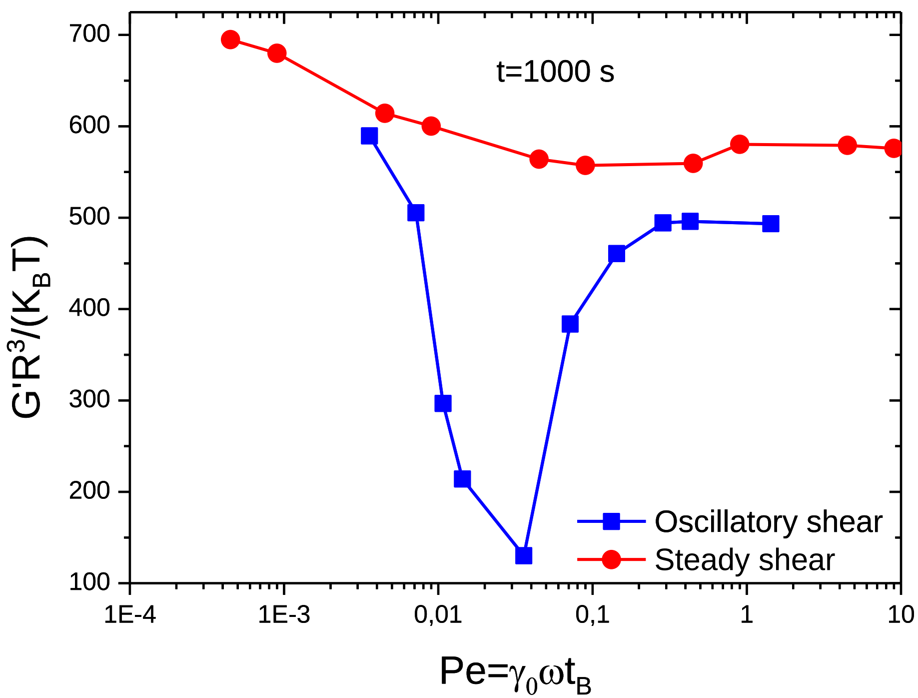
BD simulations, 30k particles

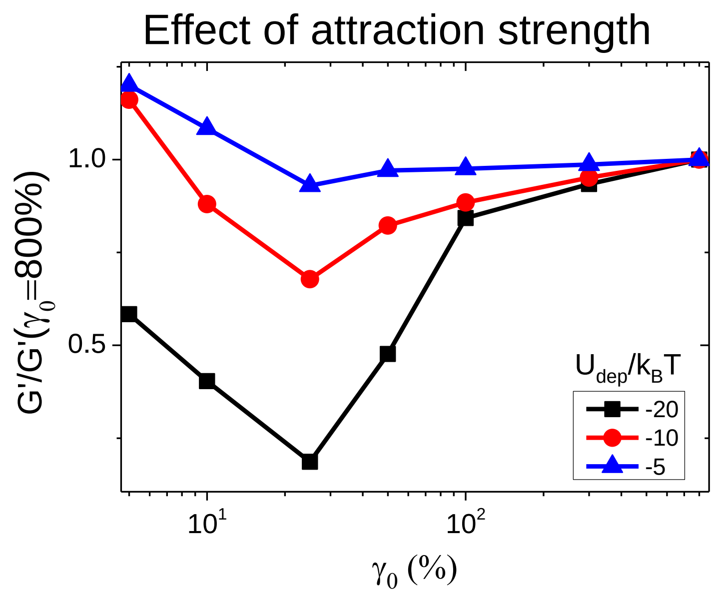
Larger heterogeneity at intermediate strain amplitudes

Moghimi et al. Soft Matter (2017)

Steady vs. oscillatory preshear

Experiments





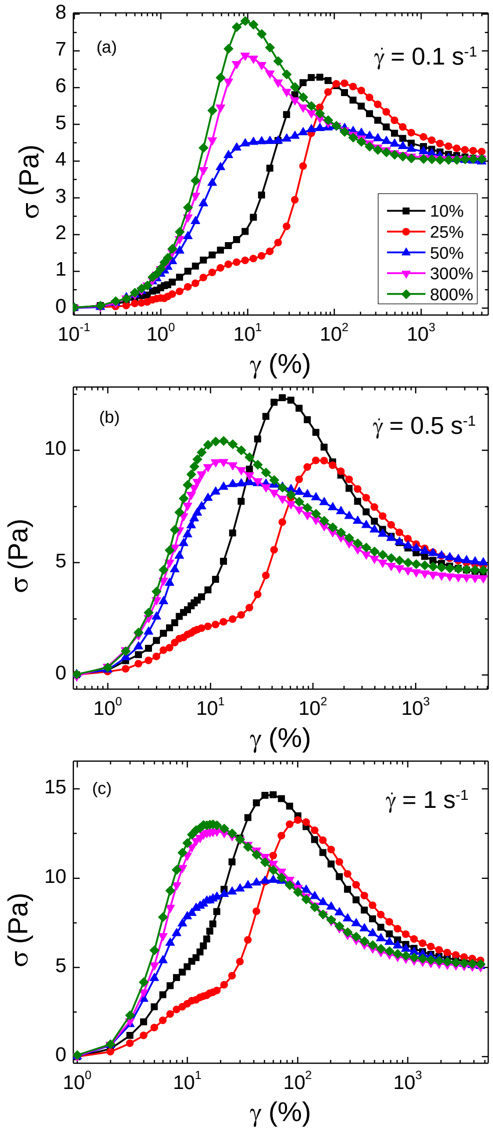
Oscillatory shear creates weaker gels at intermediate Pe
<=> more heterogeneous structure?

Higher attraction strengths affected more by preshear

=>*Indication of arrested phase separation*

Tuning colloidal gels by oscillatory shear

experiments



Nonlinear response:

Experiments:

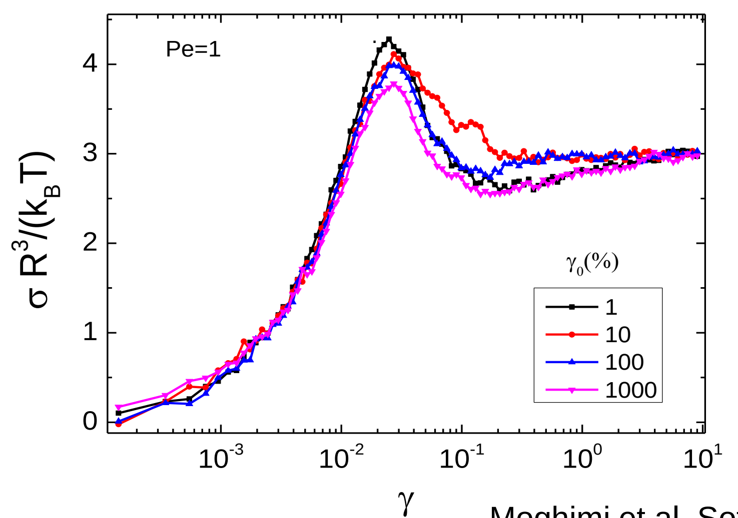
-two step yielding affected by preshear

-promoted by intermediate strain amplitude preshear, creating larger heterogeneity

BD Simulations:

weaker effects of preshear due to absence of HI

BD simulations



Moghimi et al. Soft Matter (2017)

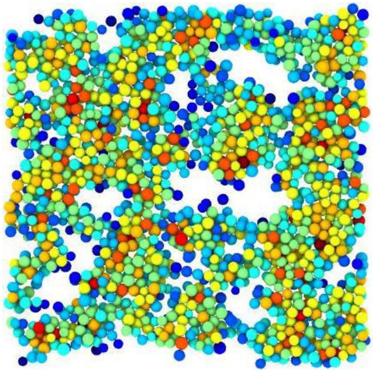
Tuning colloidal gels by shear
Conclusions

External deformation fields => induce "memory" in metastable states

-Oscillatory pre-shear more efficient in tuning structure and mechanical properties of colloidal gels

Low rates/strain amplitude
=> large heterogeneities/weak gels

High rates/strain amplitudes
$\Rightarrow$ More homogeneous/stronger gels



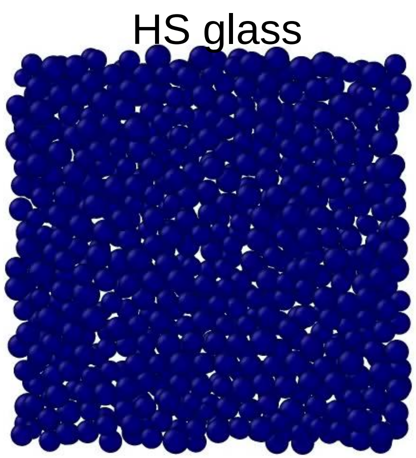
-Nonlinear response affected by shear history:
Two step yielding promoted by heterogeneity
Two step yielding not evident in gels without HI

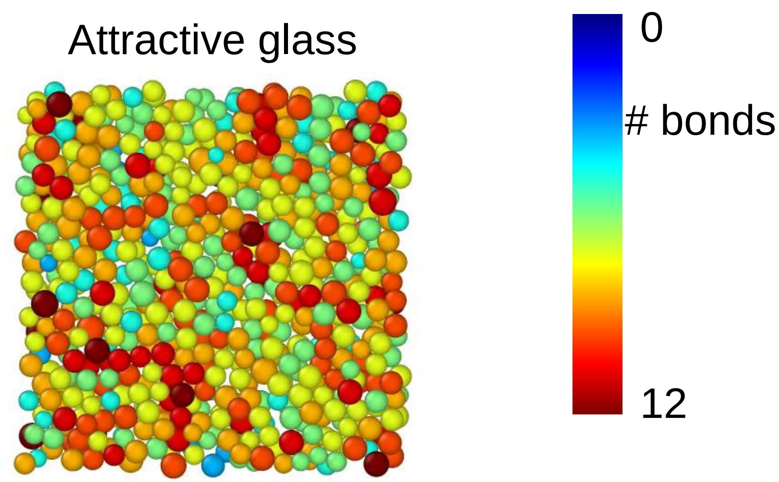
Attractive vs. repulsive glasses

- Probe the microscopic structural changes during yielding in attractive glasses

- Relate the two step process with specific mechanisms at particle level
  => Probe current hypothesis of bond and cage braking

- Follow structure - dynamics and link it with stress during yielding

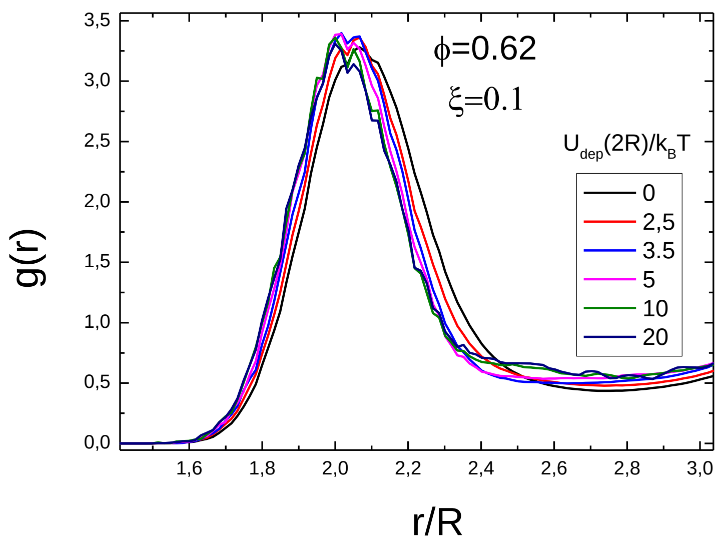




Repulsive vs. Attractive glass (BD simulations)

Structure at rest

(pair correlation function)

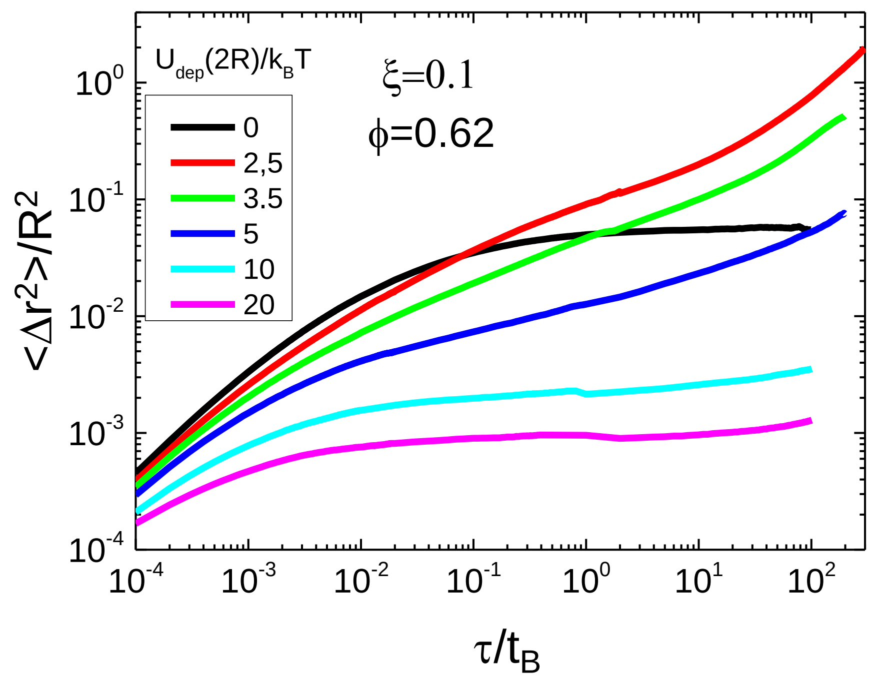


HS glass, φ=0.62, vs.
attractive glass, attraction range ξ =0.1,
various attraction strengths.

Dynamics at rest

Mean Square Displacements (MSD)

$$\langle \Delta r^2(\tau)\rangle = \langle \frac{1}{N}\sum_{i=1}^{N}[r_i(t+\tau)-r_i(t)]^2\rangle_t$$



Particle localization distance for a HS glass (φ=0.62)

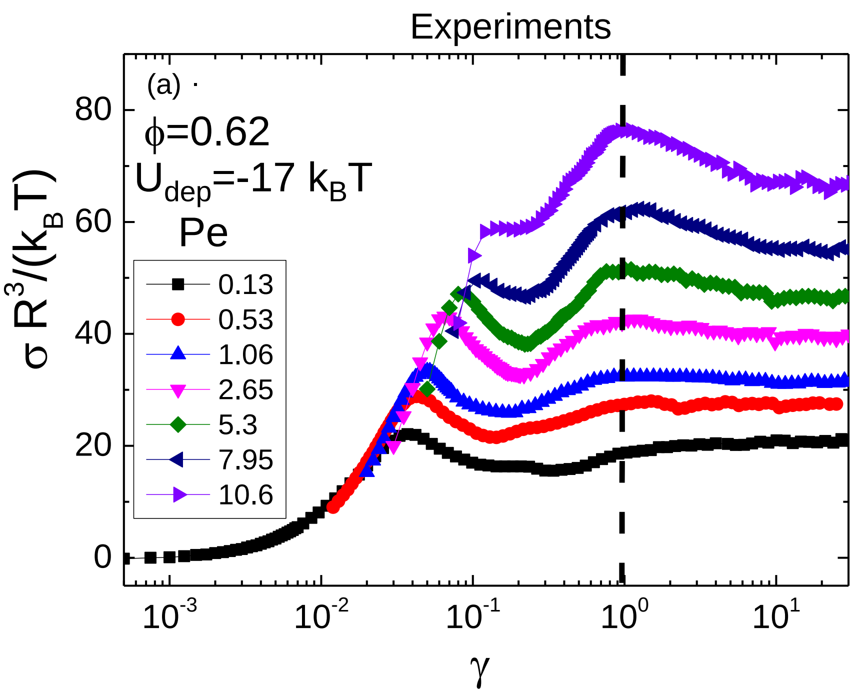
Structure: (peak of g(r): δ/R=0.07

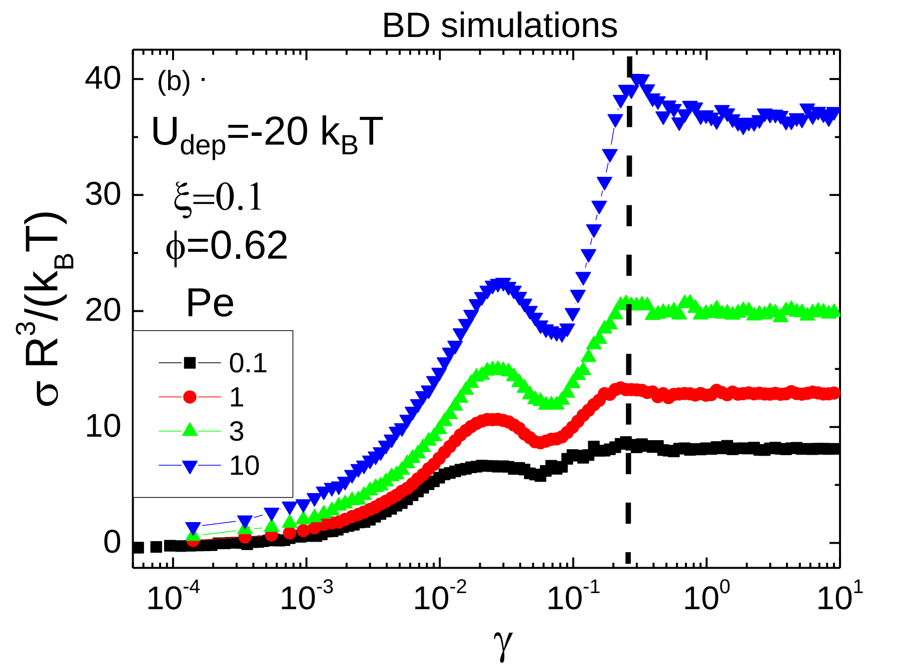
Dynamics: plateau of MSD: δ/R=0.24

For attractive glass localization is much less ~ bond range

Repulsive vs Attractive glass

Start-up shear – Different shear rates (Pe)





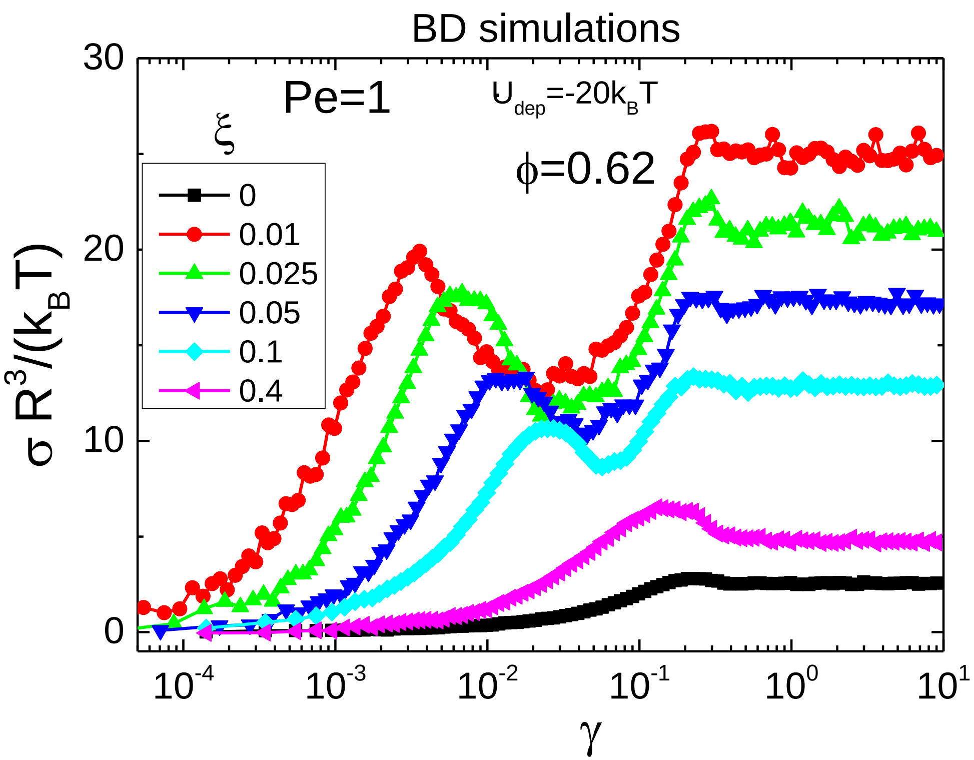
<u>Similar qualitative findings in BD simulations and experiments:</u>

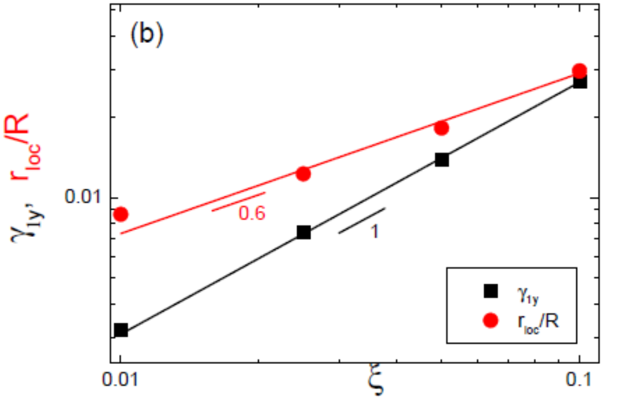
- Two step yielding seen in BD, contrary to lower φ gels

- *Both peaks in attractive glass increase with Pe*
- *1st peak at around 5% in both experiments and BD*
- *2nd peak at same characteristic strain (~100% in experiments, ~30% in BD)*

Repulsive vs Attractive glass

Start up shear for different range of attractions

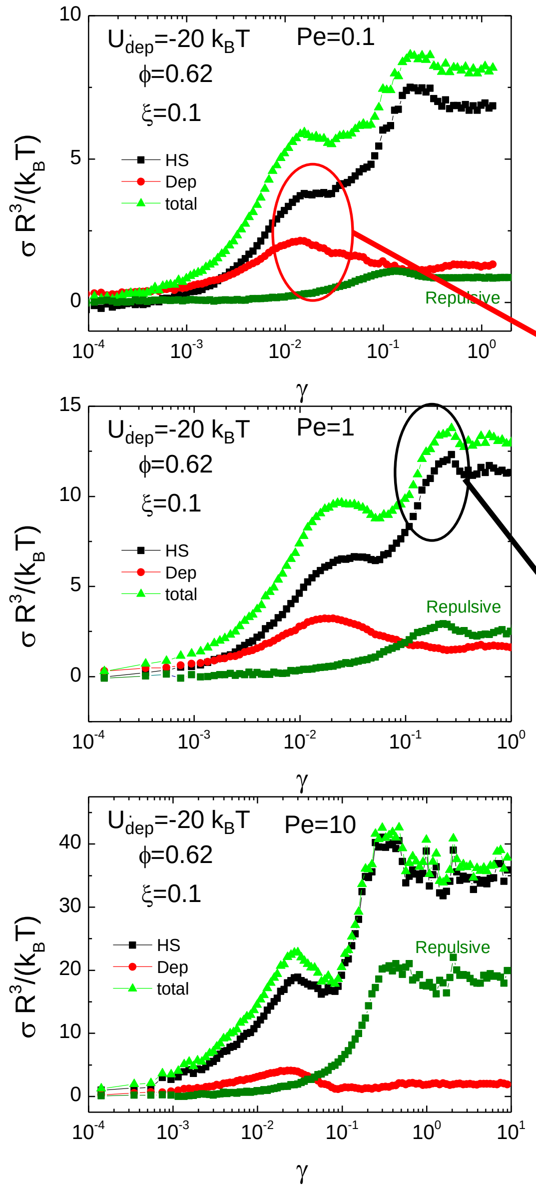




- *1^{st} peak increase in size and shifts to lower strains as range is decreased*

- *1^{st} yield strain (γ_1) follows attraction range => relates with bonds similar findings in experiments (Koumakis et al, Soft Matter 2011)*

Repulsive vs. Attractive glass
BD simulations



Stress decomposition to HS and depletion contributions

$$\mathbf{F}^{HS} = 6\pi\eta R \frac{\Delta x^{HS}}{\Delta t} \qquad F_{dep} = -\frac{dU}{dr}$$

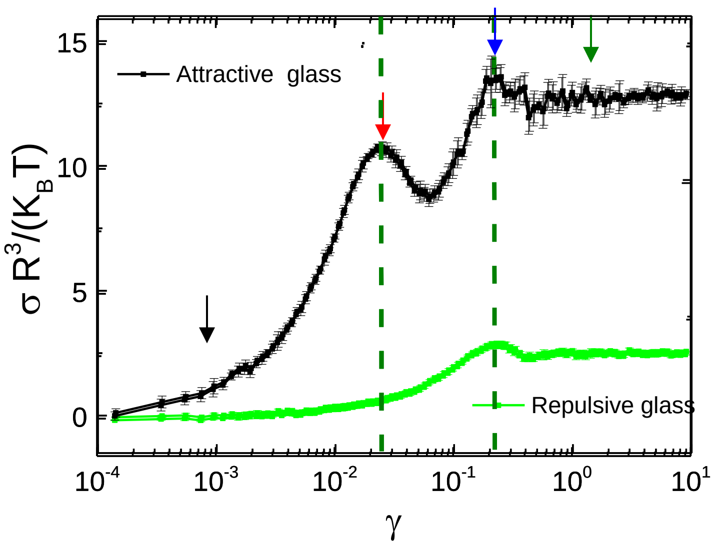
1st peak: <u>due attractive bonds + HS contributions</u>

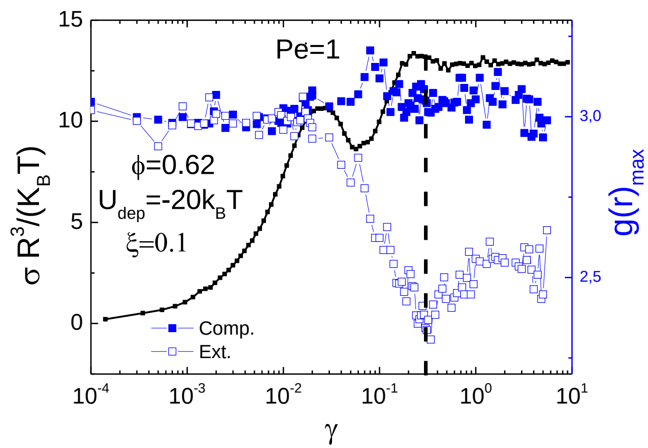
2nd peak: <u>due to HS contributions only</u>
=> cage breaking

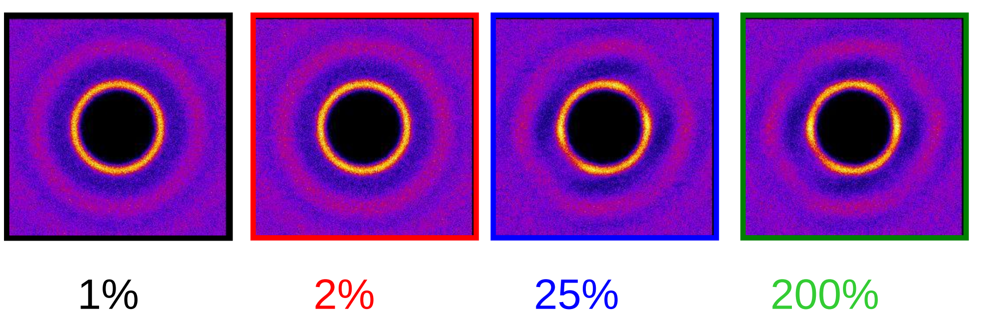
Also happens at similar strain with the HS glass yield strain

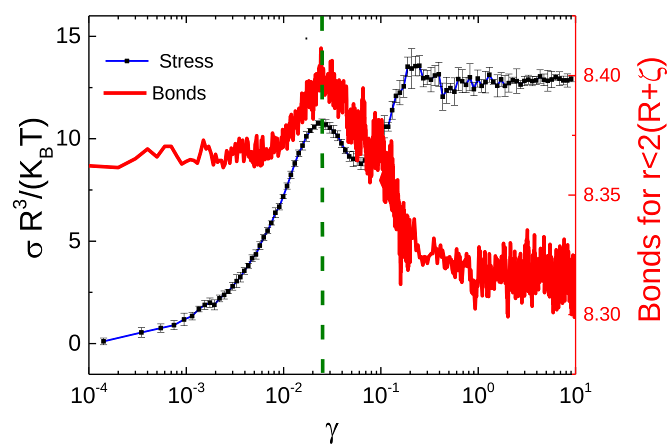
Attractive glass (BD simulations)

Follow as a function of strain during start-up shear: a) bond number and b) structural anisotropy (max. g(r) in compression and extension axis)









- *2^{nd} peak follows structural anisotropy as in HS glasses (cage deformation)*
- *1^{st} peak relates with bonds: increase (particles come closer due to shear) and then decrease (bond breaking) (however both weak ??)*

Repulsive vs. Attractive glass
BD simulations

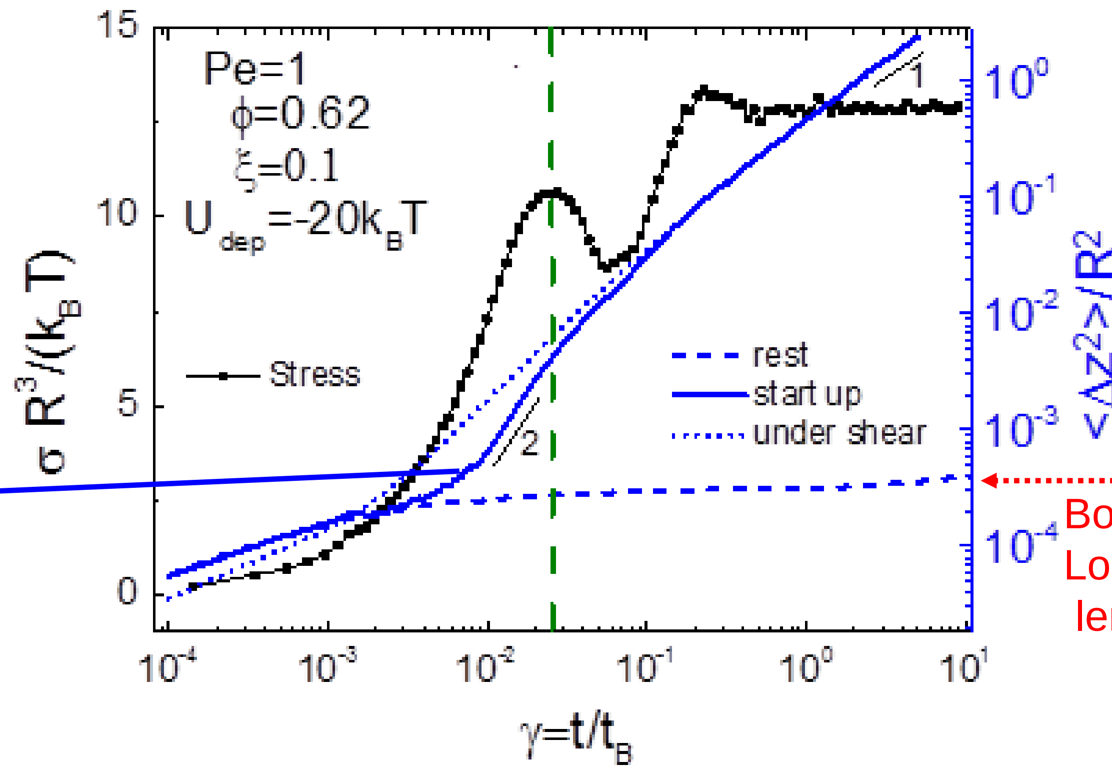
Follow Dynamics (MSD) during start-up shear

$$\langle \Delta r_i^{\,2}(\tau,t_w)\rangle_N = \frac{1}{N}\sum_{j=1}^{N}\left[r_j^i(t_w+\tau)-r_j^i(t_w)\right]^2 \;,\quad i=x,y,z$$

n=1, Diffusive motion

MSD
in vorticity direction

$$<\Delta z^2> \propto t^n$$



n>1,
Super diffusive motion

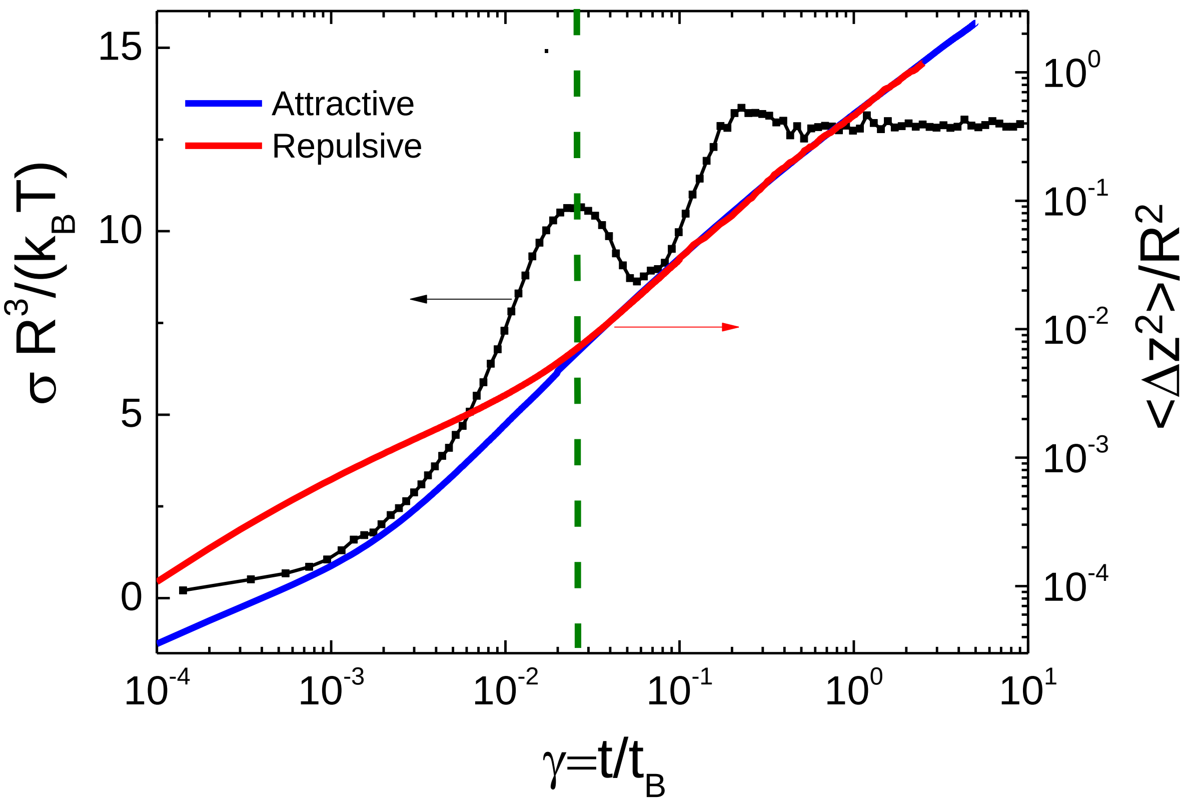
Bond
Localization
length

- **Super-diffusive behavior of particles near the first stress peak (1st yield): ballistic motion of particles during bond extension (mainly in extension axis)**

- **Shear induced diffusive motion beyond the 1st yield point**

Repulsive vs Attractive glass

Follow Dynamics (MSD) during start-up shear



For Pe>1

MSD at steady state in vorticity direction

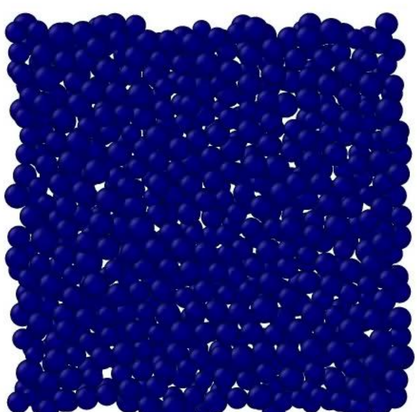
MSD the same for attractive and HS glass beyond corresponding to the length-scale of the 1st stress peak of attractive glass =>
Attractions are not important beyond this length-scale
Then 2nd yield strain => cage deformation & breaking

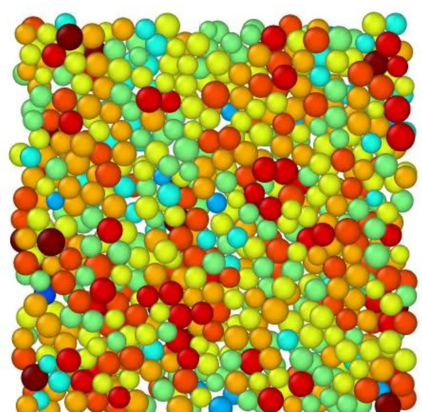
Attractive glasses: Conclusions

- Experiments + BD simulations: qualitative agreement on two step yielding (HI are not crucial at such high φ)

- Attractive glasses yield in two steps, first related with bond stretching & breaking (+HS contribution) and second cage breaking (similar to HS glass)

- Particles escape from the bonds through super-diffusive motions (around 1st yield) and exhibit diffusive behavior after the 1st stress overshoot





E. Moghimi and G.P. in preparation (2017)

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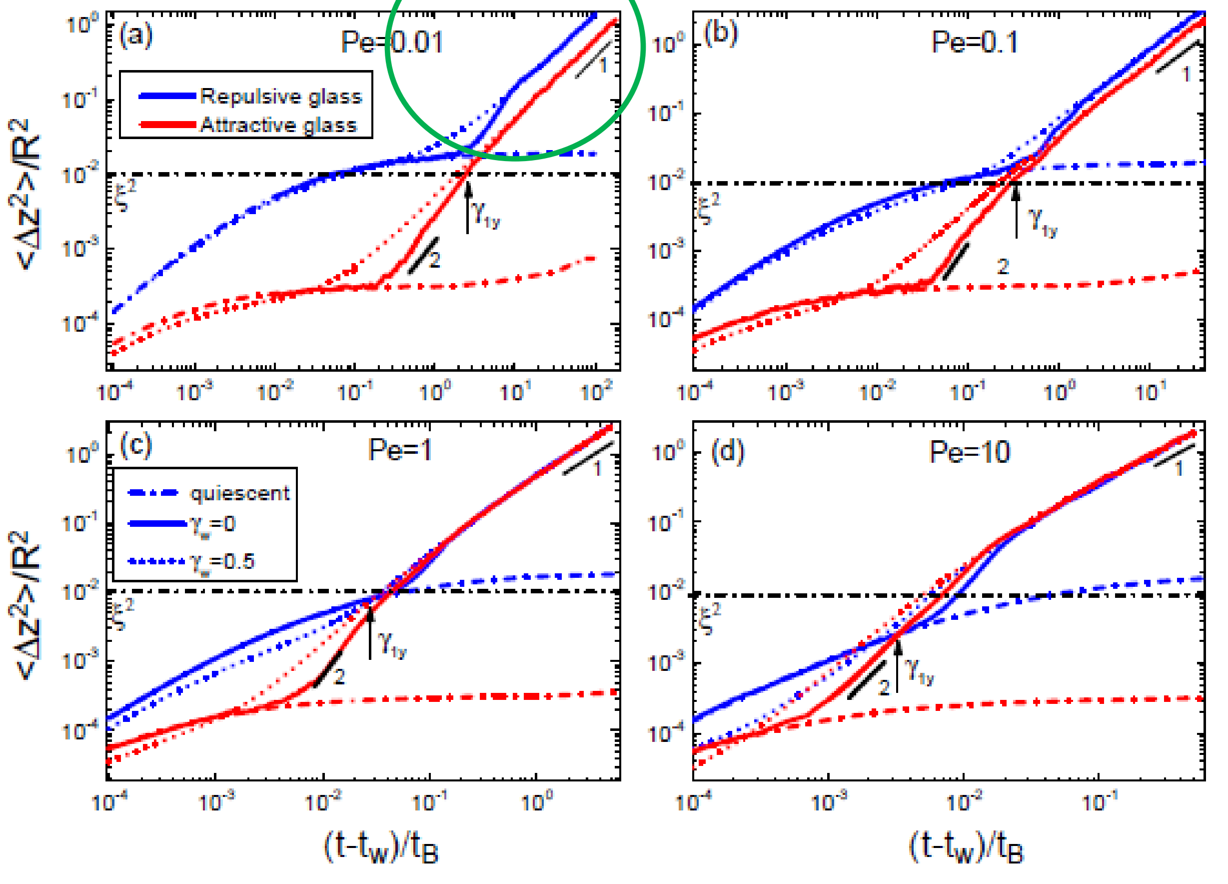
Repulsive vs Attractive glass

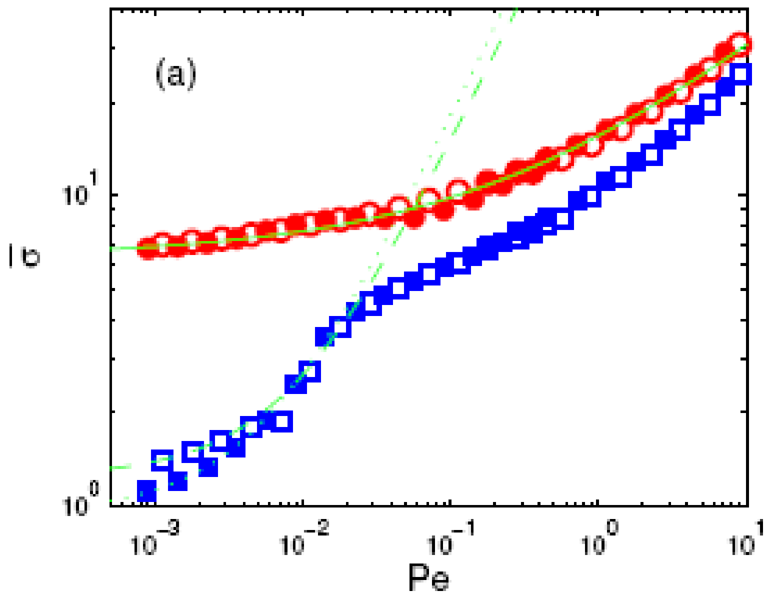
Dynamics (MSD) during different start-up shear rates



Long time shear induced diffusion different in attractive and HS glass at low Pe (<1) => probably due to different structural changes

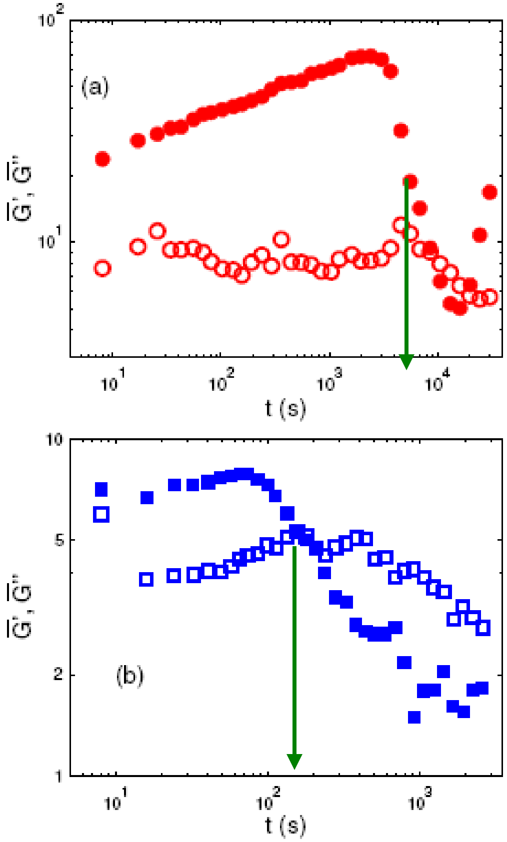
Slip of colloidal gels

Flow curve: with serrated plates=> no slip
Normal or coated plates => slip at low rate



φ=0.45, and c_p=0.5c* (contact potential U_0= -24 k_BT)

U_0=-18 k_BT (a) φ=0.35, (b) φ=0.25



Ballesta et al., Soft Matter, 2013

Transient slip:

Gels restructuring/ sedimentation =>
Slip due to detachment from the wall