Colloidal Particles : Crystals, Glasses, and Gels

Annual Review of Condensed Matter Physics **4**, 217-233 (2013)

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Supplemental reading:

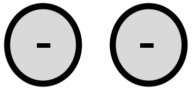
1. P.N. Pusey & W van Megen, *Phase behaviour of concentrated suspensions of nearly hard colloidal spheres*, Nature **320**, 340-342 (1986)
2. Trappe V, Prasad V, Cipelletti L, Segre PN, Weitz DA Jamming phase diagram for attractive particles. Nature **411,** 772–775 DA (2001)
3. Semwogerere D, Weeks ER, Confocal microscopy, CRC Press, 705–714 (2008)
4. Francesco Sciortino, Nature material **1**, 1-3 (2002)
5. Weeks, book chapter in *Statistical Physics of Complex Fluid*s, pp. 2-87, (Tohoku University Press, Sendai, Japan, 2007).

Colloids as big atoms

Particles suspended in a liquid phase

- **Driven by Brownian motion**
  Typical size R ≤ 10*μ*m
  Exquisite precision: 3% poly-dispersity

- **Interactions at stake**
  - Electrostatic interactions
  - Van der Waals interactions

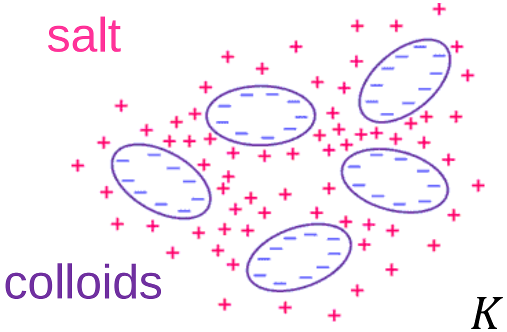


Milk

Mayonnaise

http://www.cuisineactuelle.fr/recettes/mayonnaise-maison-279999
http://www.ohmyfood.fr/wp-content/uploads/2013/08/lait-bon-ou-mauvais-pour-les-os.jpg

Screening of electrostatic interactions



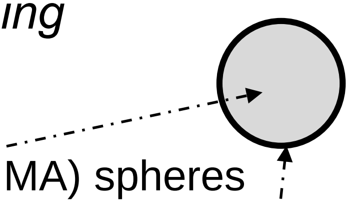
$$V(r) \propto \frac{e^{-Kr}}{r}$$

Debye length:

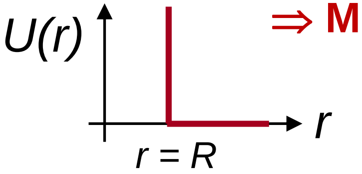
$$K^{-1} \propto 1/\sqrt{[salt]}$$

Suppress Van der Waals interactions

→ *refractive index matching*



Example:
Poly-methylmetacrylate (PMMA) spheres coated with poly-hydroxystearic acid (PHSA)



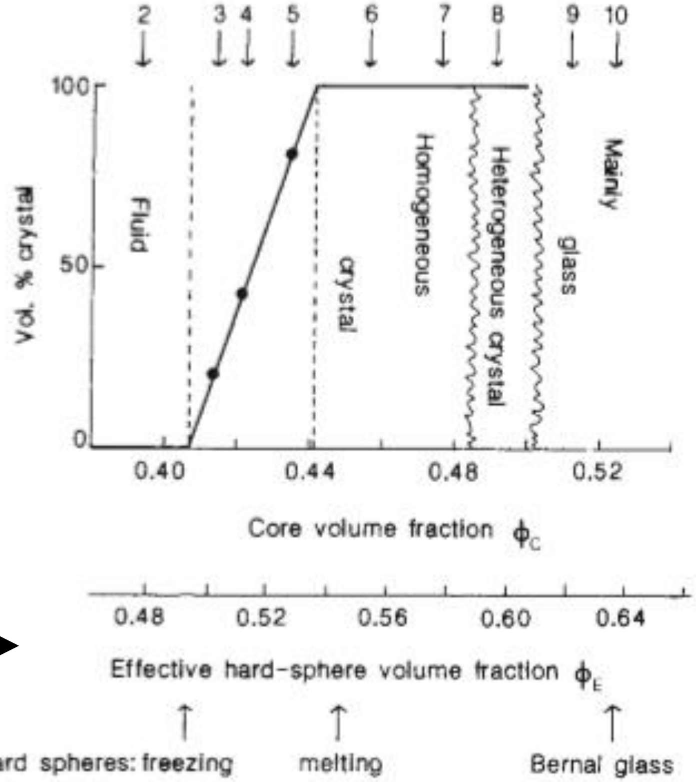
⇒ **Model Hard Spheres**

Hard Spheres: Phase diagram

Control parameter: volume fraction ϕ

0,48 0,51 0,52 0,53 0,56 0,57 0,58 0,62 0,64

Increasing ϕ



Main results:

- $\phi < 0.49$ – fluid behavior
- $0.49 < \phi < 0.54$ – fluid crystal coexistence
- $0.54 < \phi < 0.58$ – crystal
- $\phi > 0.58$ – glass

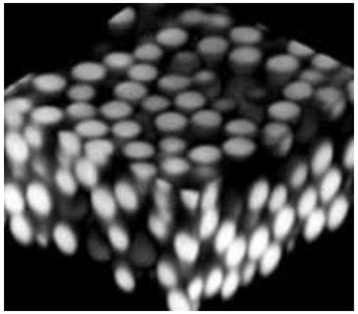
What about charged colloids?
"The range of ϕ over which crystallization is observed is much greater than that for hard shperes"

Pusey & van Megen, Nature **320**, 340-342 (1986)
Weeks, book chapter in *Statistical Physics of Complex Fluids*, pp. 2-87, (Tohoku University Press, Sendai, Japan, 2007).

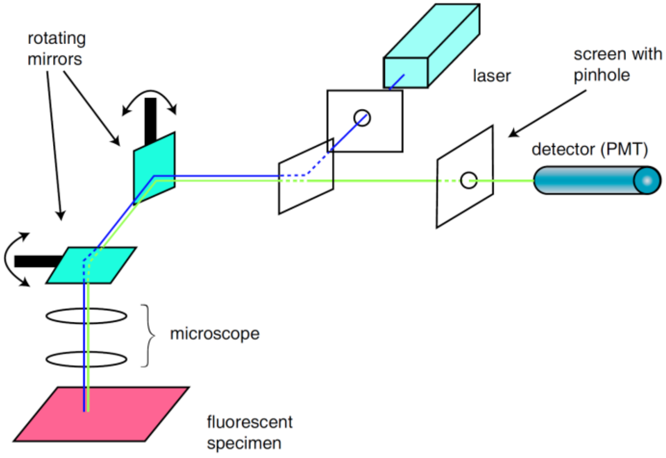
Confocal & diffraction microscopy

Confocal microscopy

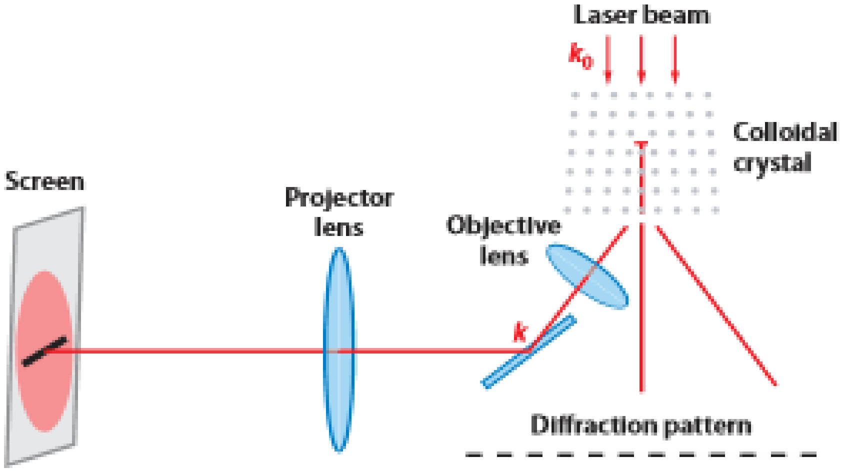
- *Microscope with shallow depth of field*
- *Allow to follow individual particles*
- *Rebuild a 3D picture of the sample*



Three-dimensional reconstruction of a series of 2D images of PMMA spheres suspended in a cyclohexyl-bromide and decalin solution



Semwogerere & Weeks, Encyclopedia of Biomaterials and Biomedical Engineering (2005)

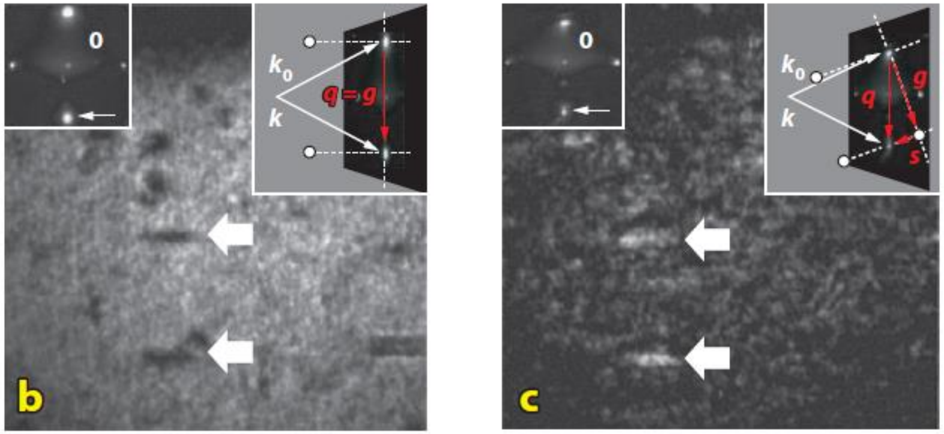


Laser Diffraction Microscopy

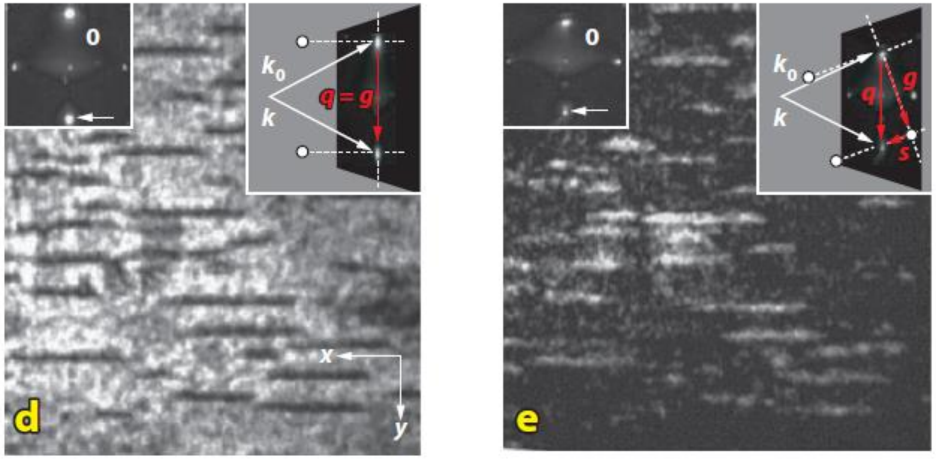
- *Characterize crystalline zone*
- *Determine the structure and dimension of the crystalline zone*
- *Detect structural defaults (=**dislocations**)*

Defects in crystalline structures

Visualization with Laser Diffraction Microscopy



b,c : lattice constant d_0 = 1.61µm



d,e: lattice constant d_0 = 1,63µm

$\vec{k}_0$ incident wave vector

$\vec{\vec{k}}$ watching directions vector

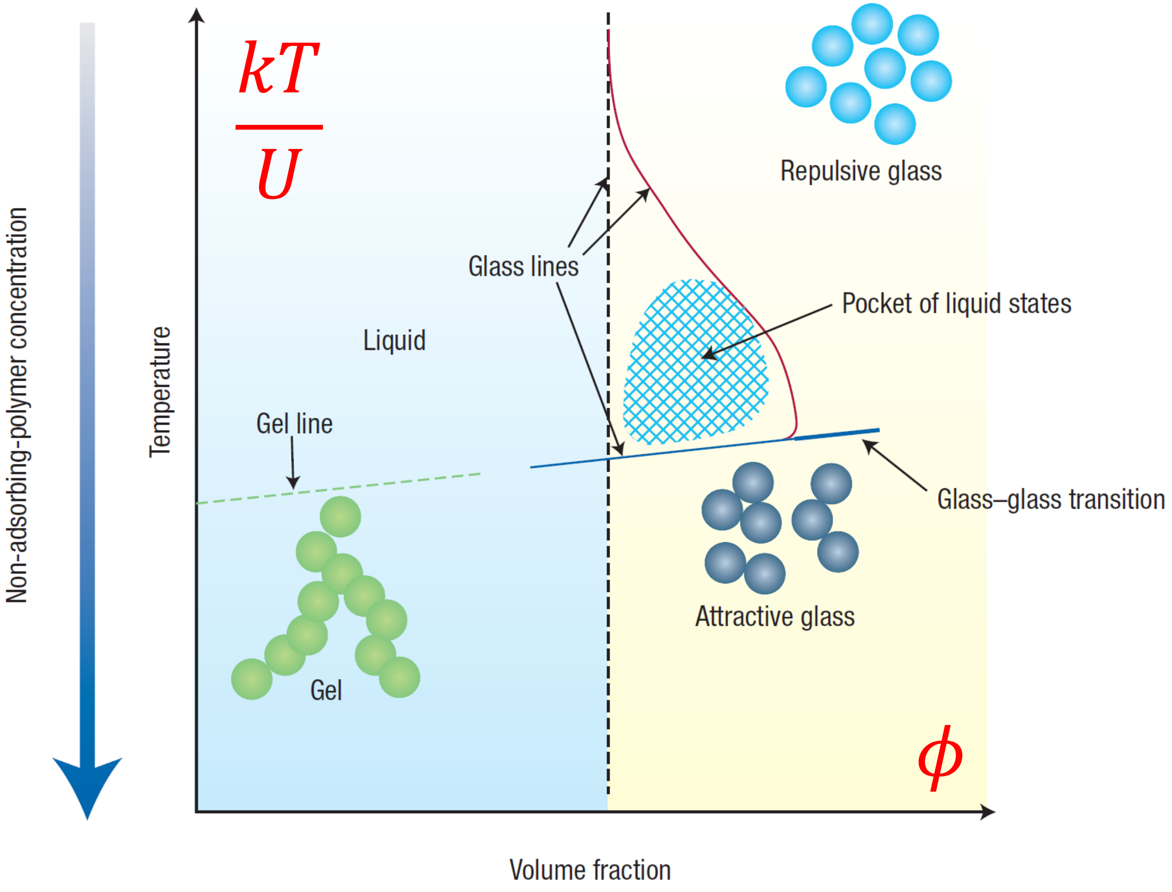
$\vec{q} = \vec{\vec{k}} - \vec{k}_0$

Glasses and Gels

Role of attractive interactions on the phase diagram

U : *interaction strength*

ξ : *range interaction*

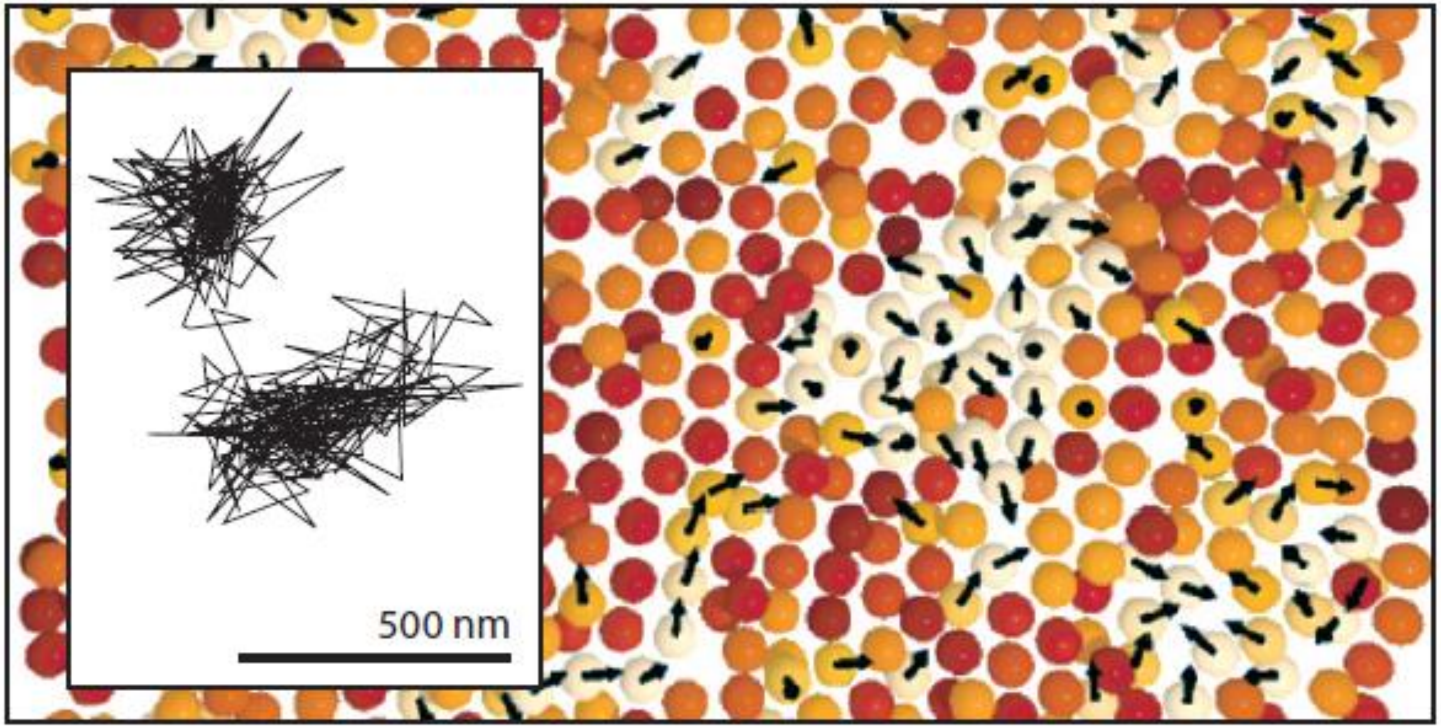


Sciortino *Nature Materials* 1, 1-3 (2002)

Properties of glasses at rest

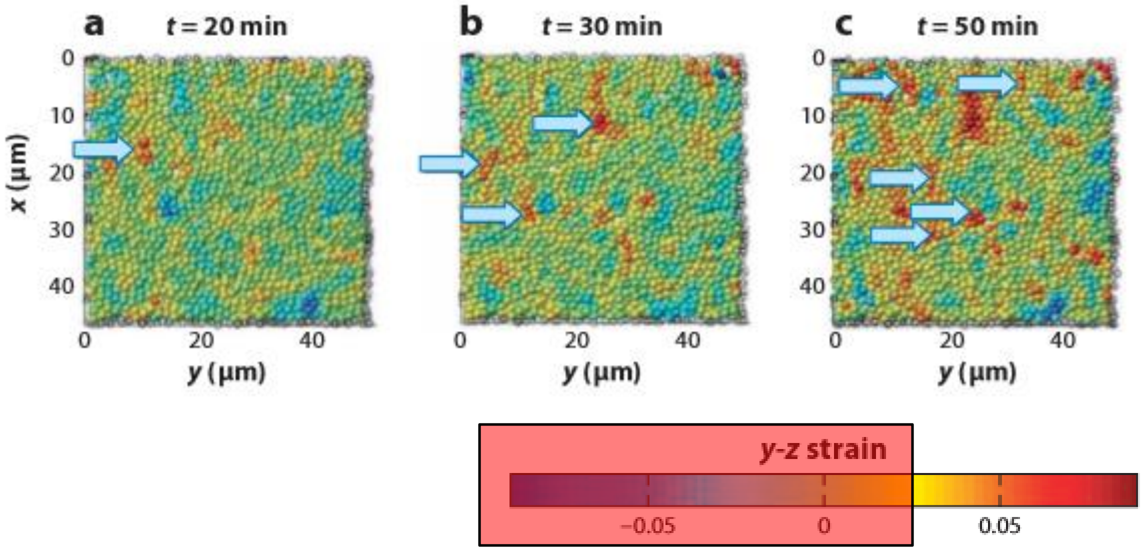
- Similarities with liquid : viscous behavior, disorder
- Main difference with liquids: **long relaxation times & <u>dynamical heterogeneities</u>**

Observation of one slice of a bulk colloidal glass using confocal miscroscopy



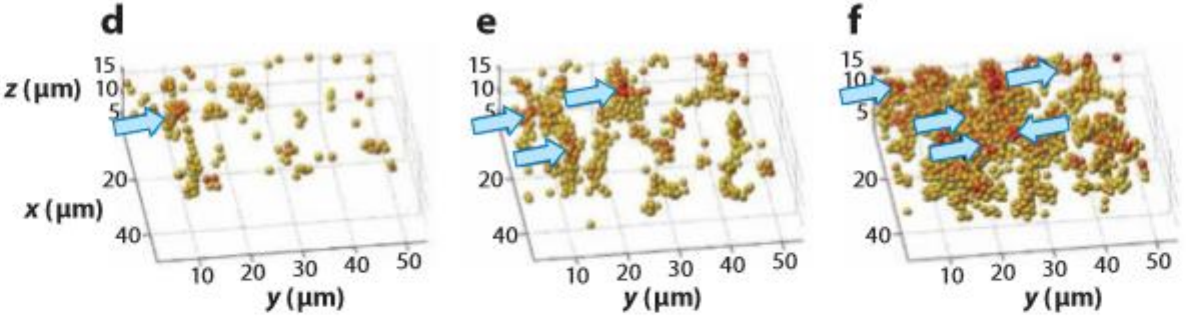
- Volume fraction: $\boldsymbol{\phi = 0.5}$
- Thickness of the slice: 2.5 µm (~1 layer of particles)
- Black arrows = direction of motion for particles with displacement > 0.2 mm during 600s

Glasses undear shear



- Map of ***cumulative strain*** *under external shear*
- *Blue arrows indicate* ***Shear Transformation Zones*** *that have been formed in the time interval before the frame shown*

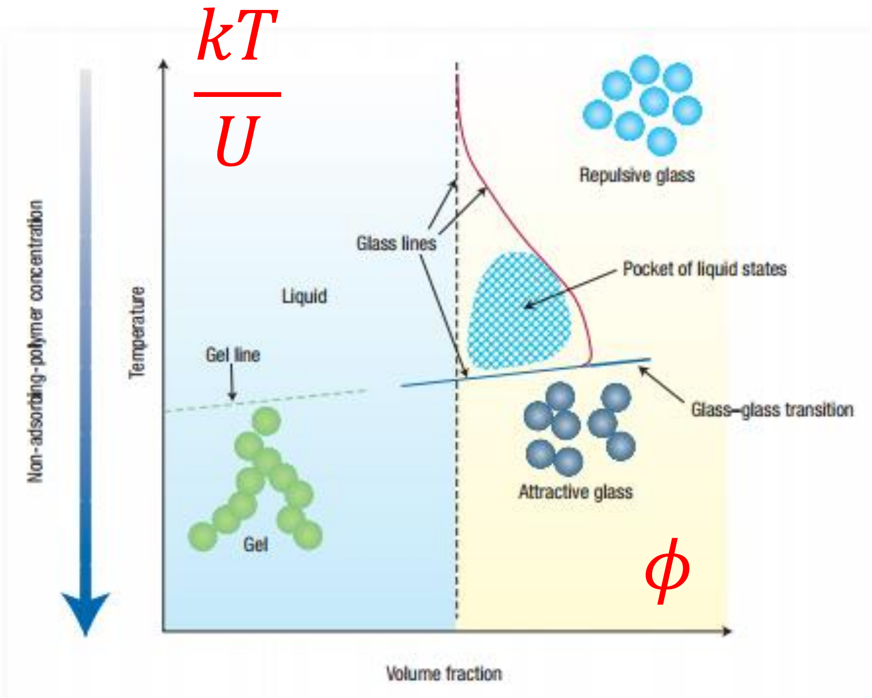
Strain threshold 0.025

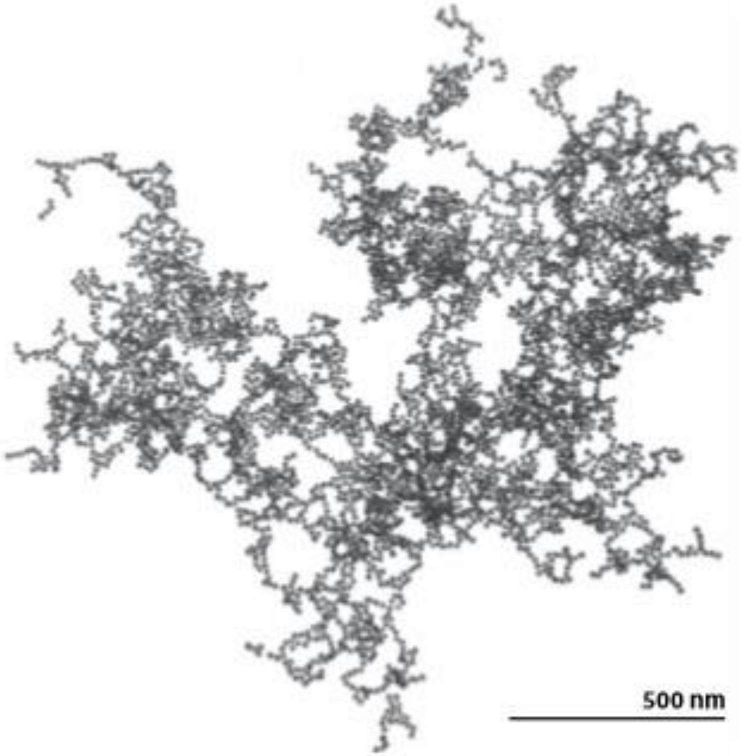


- *Image showing only the particles which have experienced a strain larger than a threshold of 0.025 .*

Gels

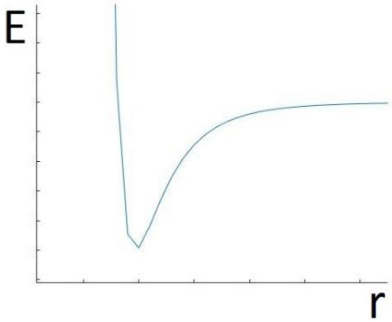
- **Conditions to form a Gel**
  Low volume fractions
  Attractive interactions

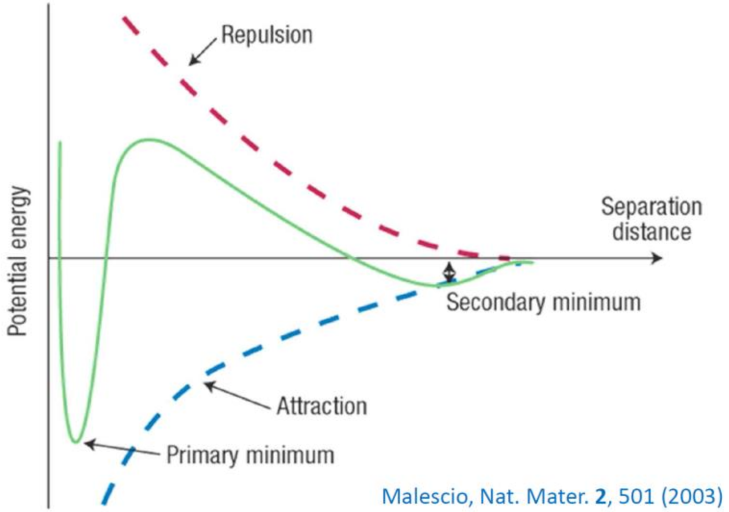




Kinetics of gels formation

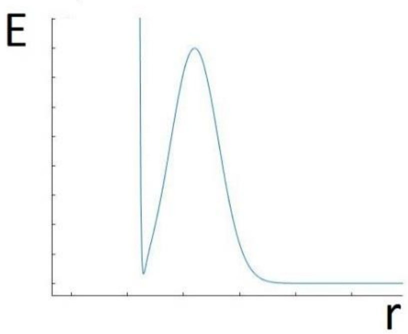
Diffusion-Limited Cluster Aggregation (DLCA)

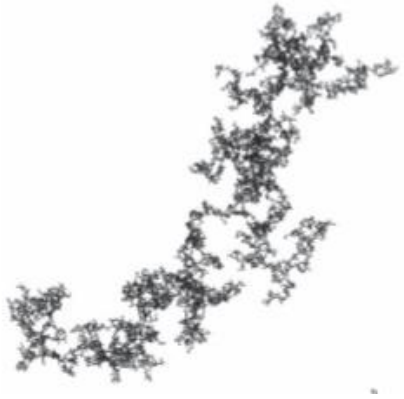




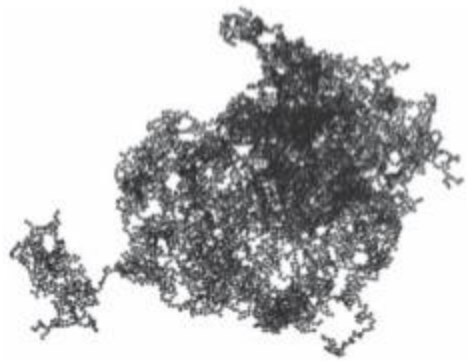
Malescio, Nat. Mater. **2**, 501 (2003)

Reaction-limited cluster aggregation (RLCA)



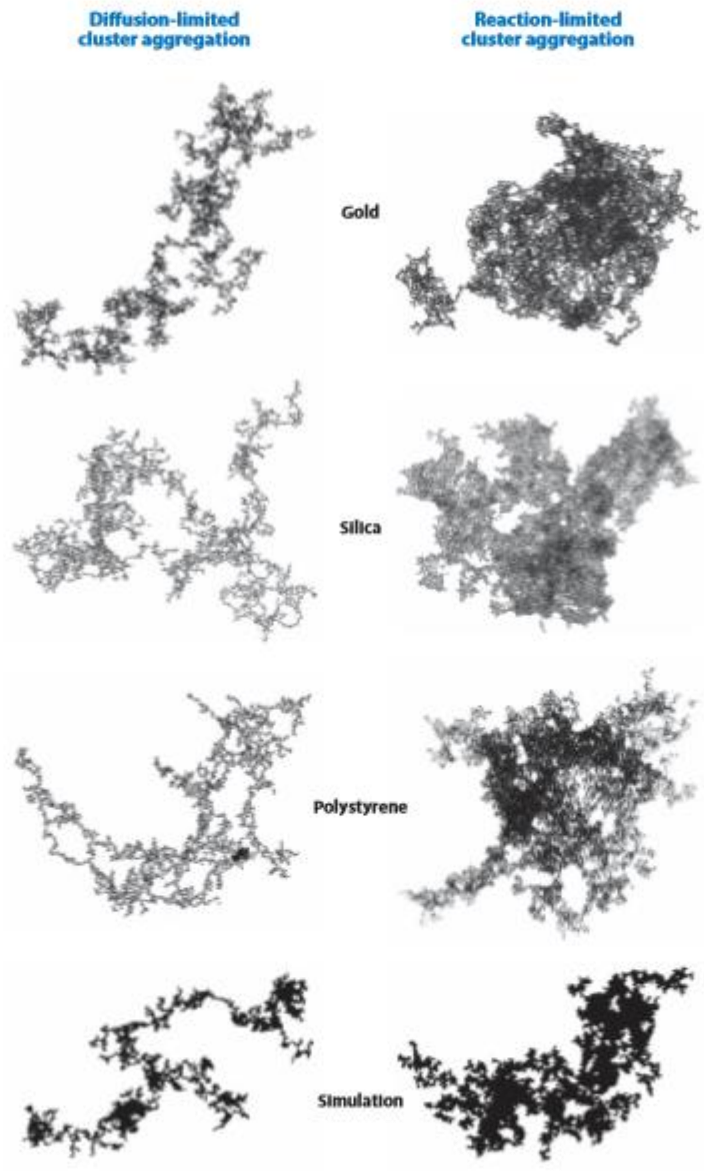


Fractal dimension : 1.8



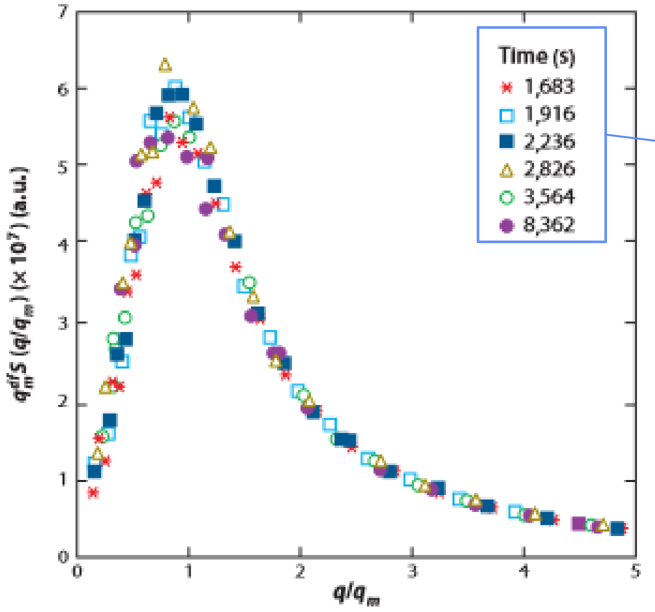
Fractal dimension : 2.3

Robust scenario – exp. & simulations



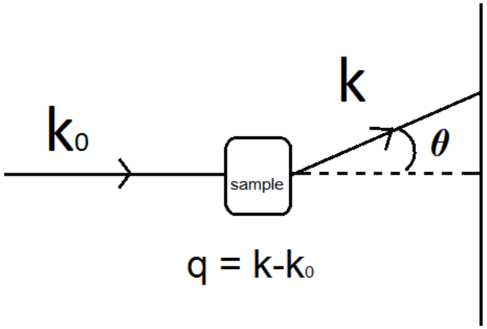
Analogy with spinodal decomposition

- Gelation = purely kinetic process
- Surprising connection with **thermodynamic phase separation**, i.e. the spinodal decomposition, which is observed in a wide range of liquid/gas system (split into two phases to minimize free energy)



Different data series correspond to measurements at different times during the formation of the gels (DLCA)

$$q = 2k\left|\sin\left(\frac{\theta}{2}\right)\right|$$

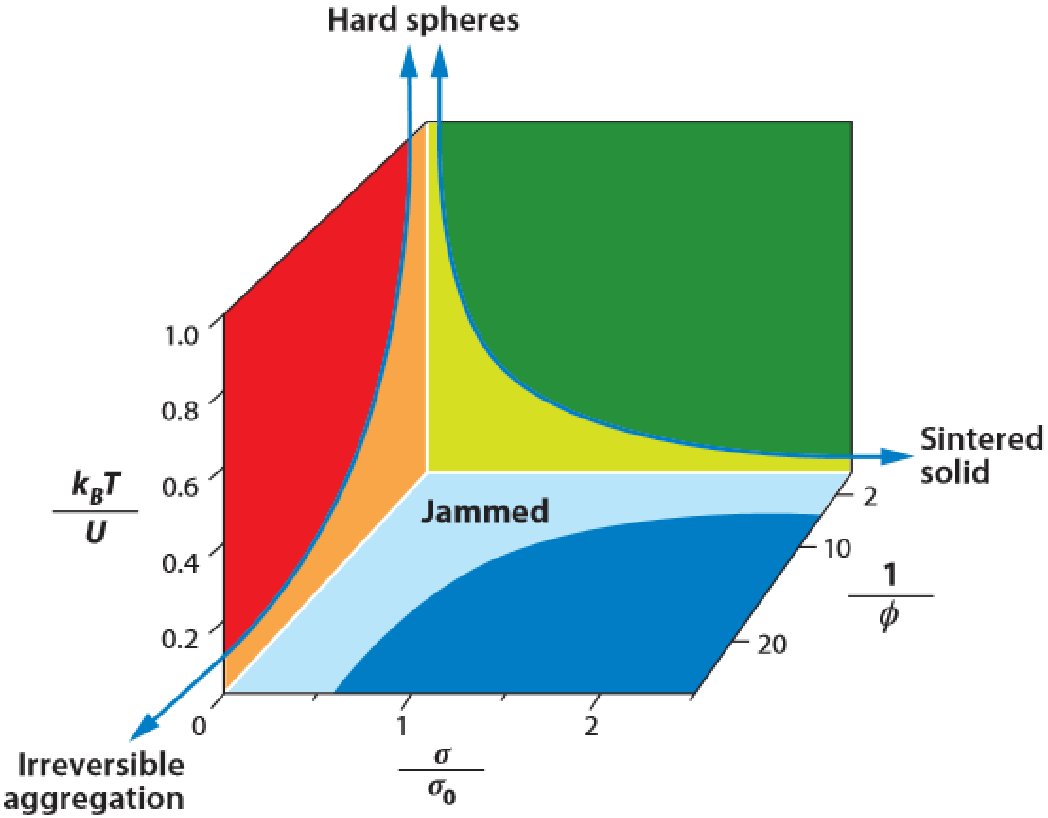


q = k-k₀

Normalized scaled function from light scattering data, $q_m^{d_f} S(q/q_m)$,

Jamming phase transition

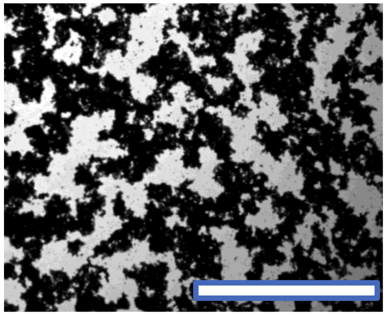
- Reversible non equilibrium solid/liquid transition under external shear
- Set of parameters $\frac{kT}{U}, \frac{\sigma}{\sigma_0}\ and\ \frac{1}{\phi}$



jamming phase diagram for attractive colloidal particles

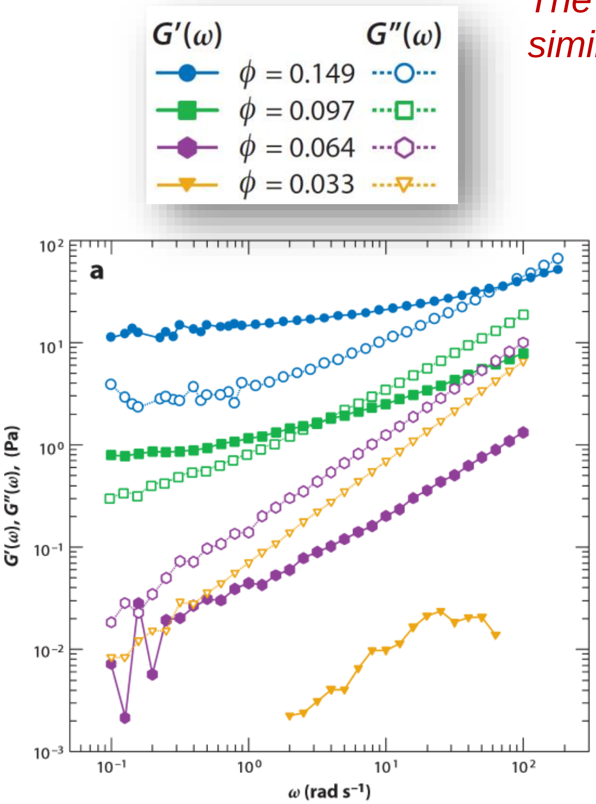
Gel linear rheology

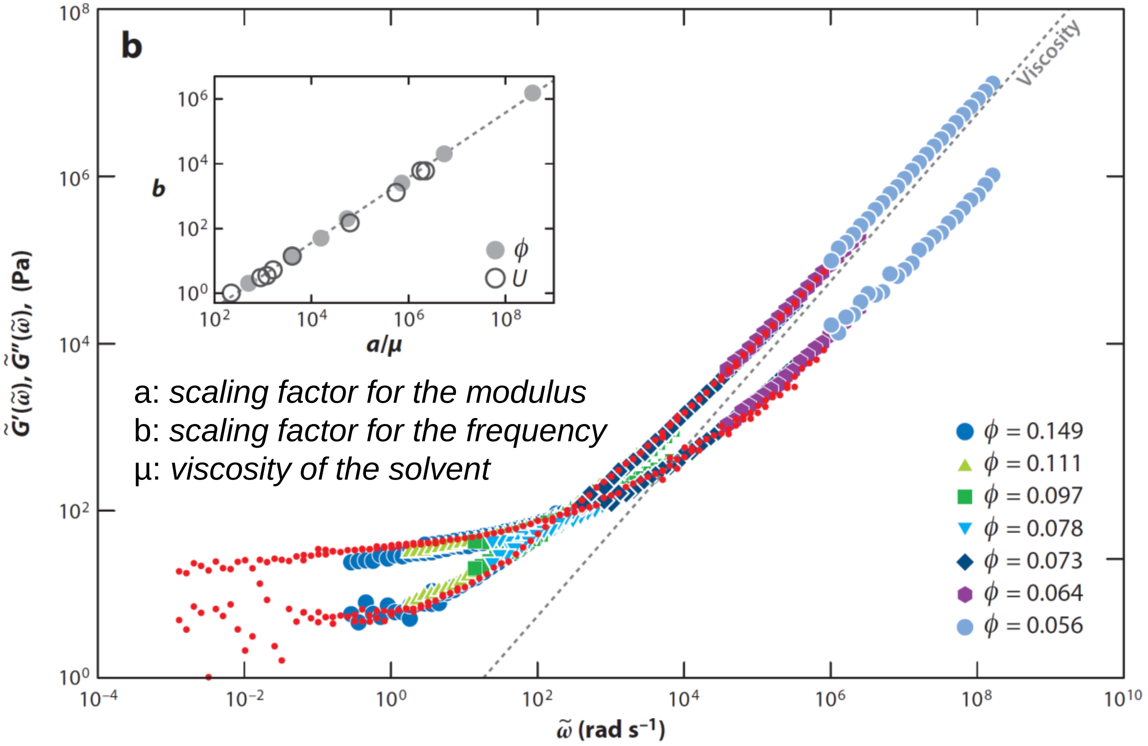
Attractive soot particles in a light mineral oil – reversible gelation



100 μm

The fact that data scale so well implies that there is a strong similarity in the structures of the networks that form at different ϕ.





a: *scaling factor for the modulus*
b: *scaling factor for the frequency*
μ: *viscosity of the solvent*

Take home messages

Conclusions

- Colloidal particles can interact in three different manners: as crystals, glasses and gels. Each case is characterized by specific properties such as defects, dynamic heterogeneities and a universal frequency-dependent linear viscoelasticity
- Colloids are a model system to study basic physics with direct microscopic visualization

Outlook

- Link between glass and gels:
  - Winter, *Glass Transition as the Inverse of Gelation ACS macromol 2013*
- Scaling properties of linear viscoelasticity in gels:
  - Shi et al. *Scaling Behavior of the Elastic Properties of Colloidal Gels,* Phys. Rev. A 1990
  - Bremer et al. On the fractal nature of the structure of acid casein gels, *Colloids & Surfaces A* 1990
- Non-linear rheology of gels:
  - Van Vliet, *Rheology and Fracture Mechanics of Foods, Chapter 13 - Gels*
  - Groot et al., *Molecular Theory of the Yield Behavior of a Polymer Gel*, J. Chem Phys. 1996
- Polymer Networks:
  - Leibler et al., *Dynamics of Reversible Networks* Macromolecules 1991
- Microrheology in polymer gels
  - Larsen & Furst, *Microrheology of the Liquid/Solid Transition during gelation,* PRL 2008
  - Lee et al. *Combined Passive & Active Rheology of Protein Layer…*, Langmuir 2009