Probing particle dynamics in dense colloidal suspensions with coherent radiation

Frank Scheffold
Soft Condensed Matter Group
Physics Department
University of Fribourg - Switzerland

http://www.unifr.ch/physics/mm

Thanks !

Dr. Luis Rojas
Colloids, Optics

Ronny Vavrin
Nanogels, SANS and Light Scattering

Frederic Cardinaux
Microrhelogy, Soft Gels

Nasser Ben Braham
Nanoparticles

Peter Schurtenberger
SANS, Micelles

Dr. Anna Stradner
SANS

SCM

Scattering Probes of Dense Media

Wet processing of ceramics

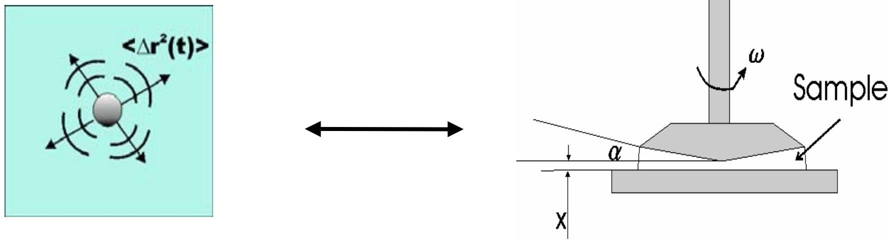
(*with H.Wyss and L.Gauckler, ETHZ*)

Materials

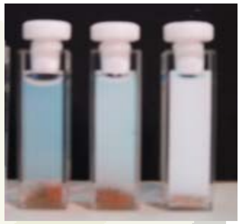
Micorheology

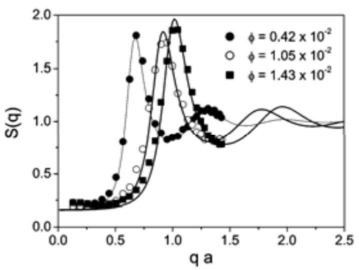
Mikro

Makro



Correlated Systems





Photonic Liquids

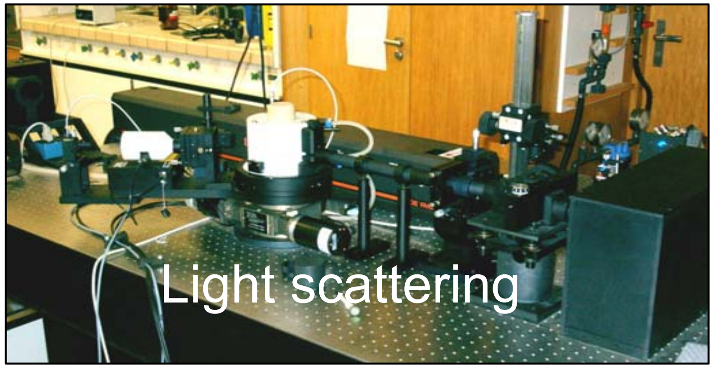
Food science

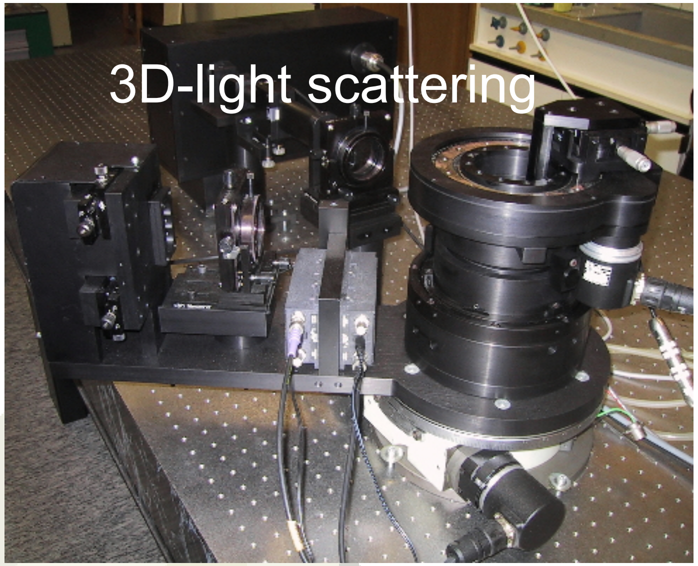
- Yoghurt and Cheese formation
- Biopolymer Gelation – Complexation induced gelation of starch/aroma systems (*w. B. Conde-Petit and F. Escher, Food Science ETHZ*)
- Critical Gelation of Gelatine (*with M.Lechtenfeld, Gelita Europe and A.Parker,V.Normand, Firmenich*)

Process Monitoring

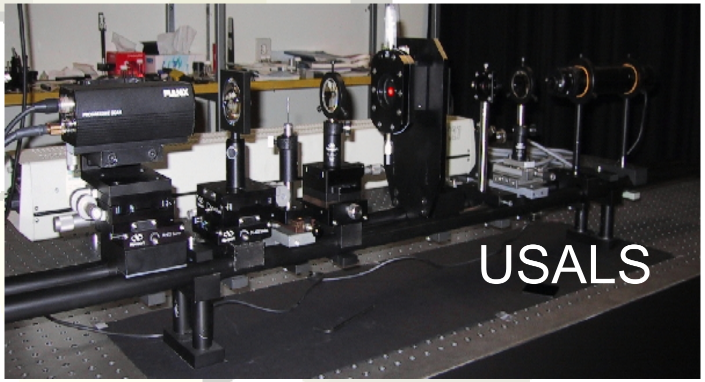
- L. F. Rojas, R. Vavrin, C. Urban, J. Kohlbrecher, A. Stradner, F. Scheffold and P. Schurtenberger, Faraday Discussions 123 (2003)
- F. Cardinaux, L. Cipelletti, Frank Scheffold and Peter Schurtenberger, Europhys. Lett. , **57**, 738 (2002)
- *C. Heinemann, F. Cardinaux, F. Scheffold, P. Schurtenberger, F. Escher and B. Conde-Petit, Carbohydrate Polymers 55 (2004) 155–161*
- H. Wyss, S.Romer, F. Scheffold, P. Schurtenberger, and L. J. Gauckler, J. Coll. Int. Sci., **241**, 89-97 (2001)

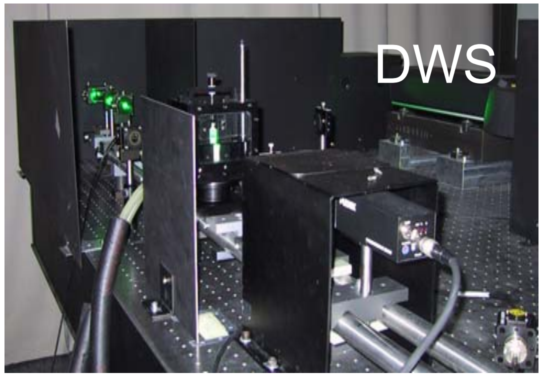
Experimental approach: Scattering, microscopy and Rheology





Challenge to the experimentalist
1-1000 nm
10^{-8}-10^{5} sec.





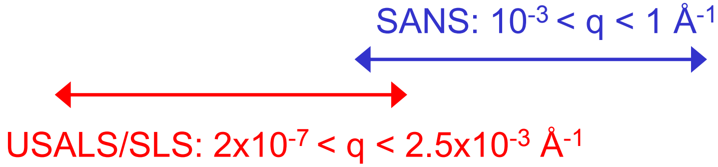
SCM

Nano-and mesoparticle assemblies - an experimentalists challenge

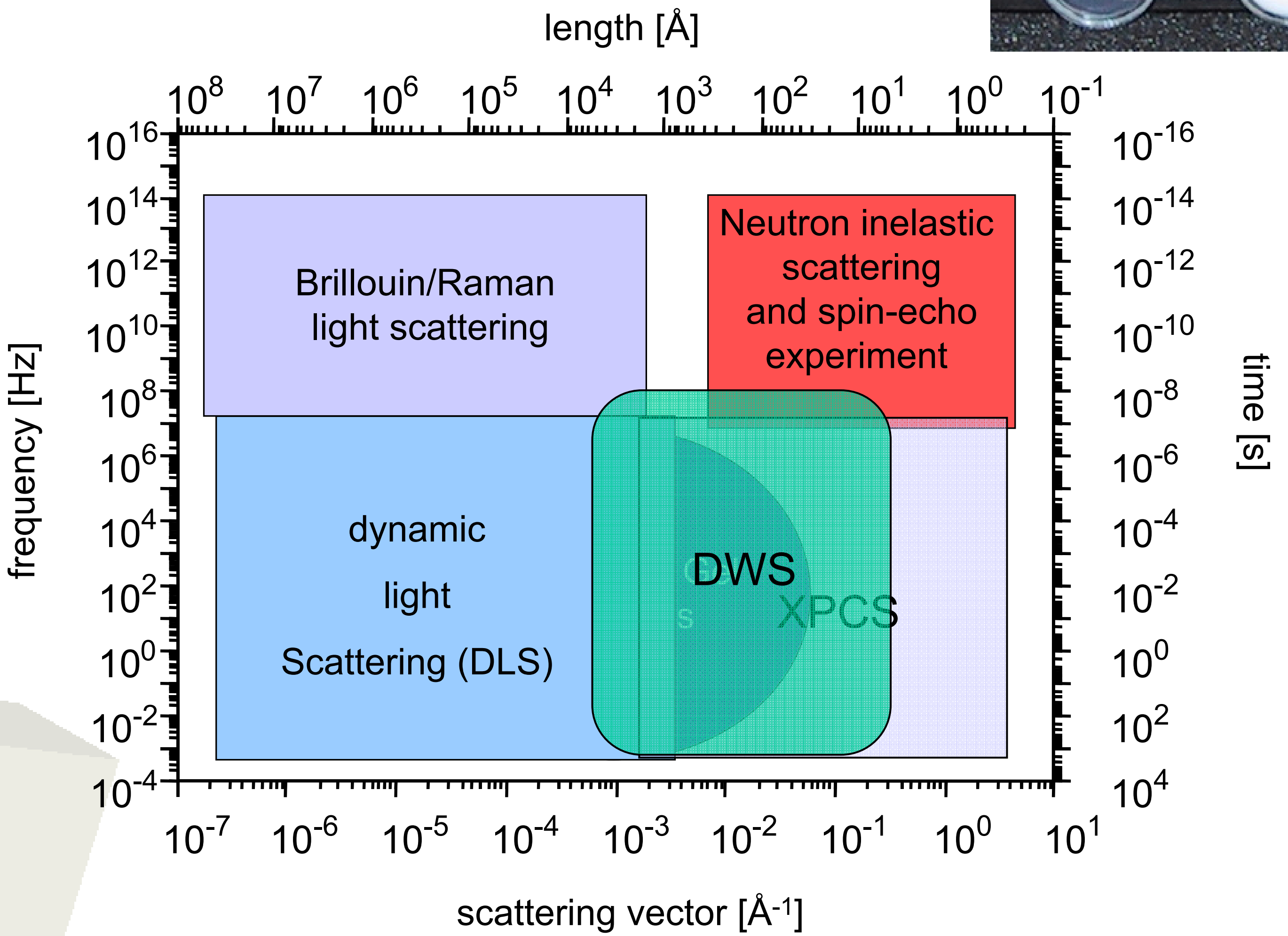
Structure

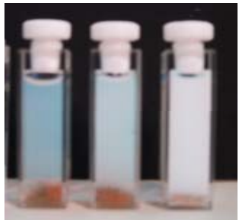
SANS: $10^{-3} < q < 1$ Å^{-1}

ideal technique for very dense and highly turbid samples



Dynamics

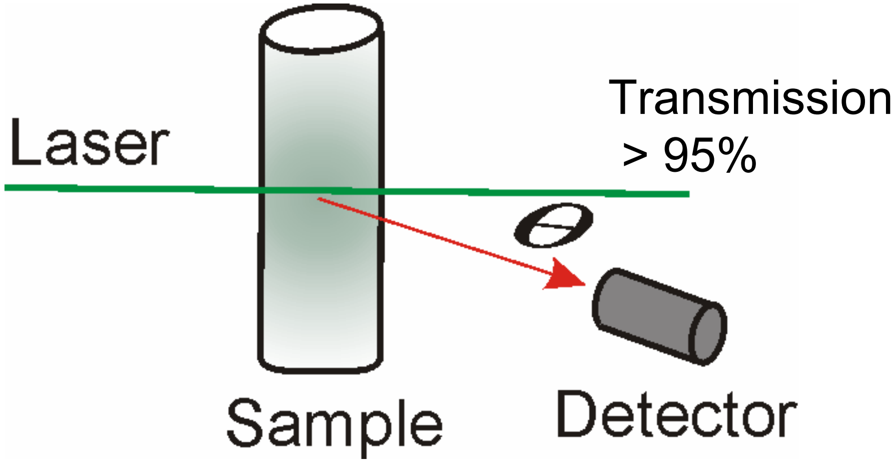




Dense Systems –
Slow Relaxations

- Light scattering from dense and turbid media
  - Multiple scattering suppression
  - Diffusing Wave Spectroscopy
- New developments in photon correlation spectroscopy
  - Multi-Speckle approaches
  - Echo-PCS
  - (XPCS)

Static Light Scattering (SLS)

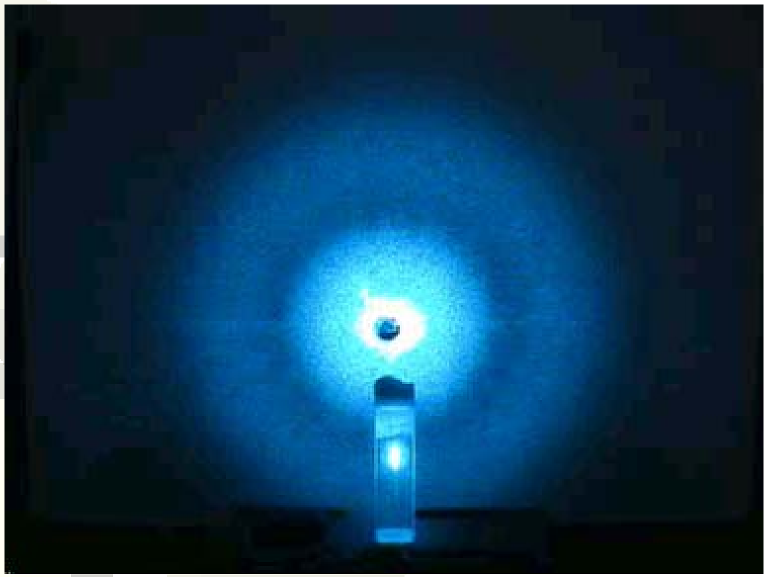


$$q = \frac{4\pi}{\lambda / n}\sin(\Theta / 2)$$

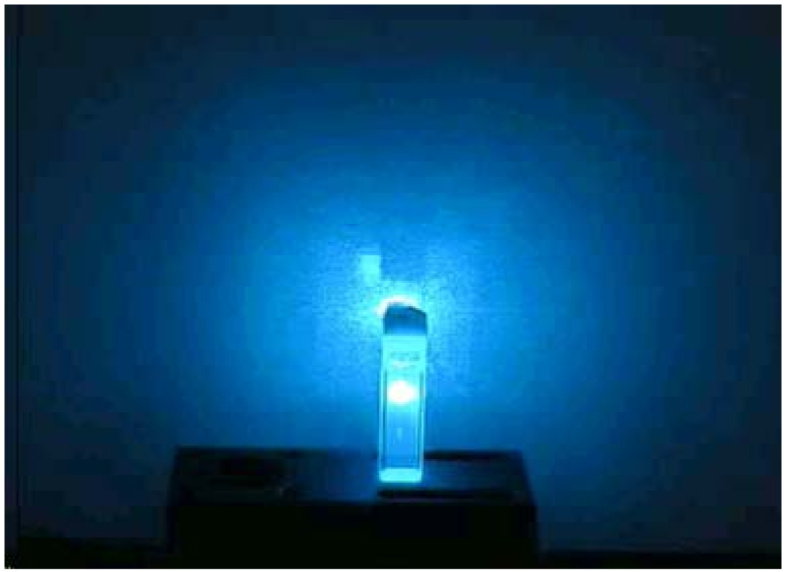
$$I_{sc} \propto \underbrace{F(q)}_{form\ factor} \times \underbrace{S(q)}_{structure\ factor}$$

$$S(q) = 1 + \rho \int_V d^3r\ g(r) e^{iqr}$$

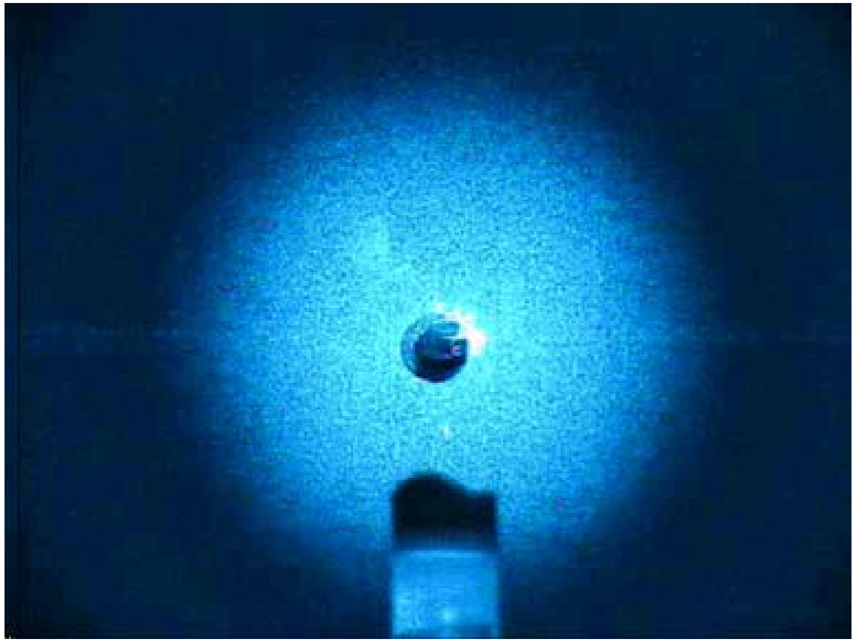
1.6 μm

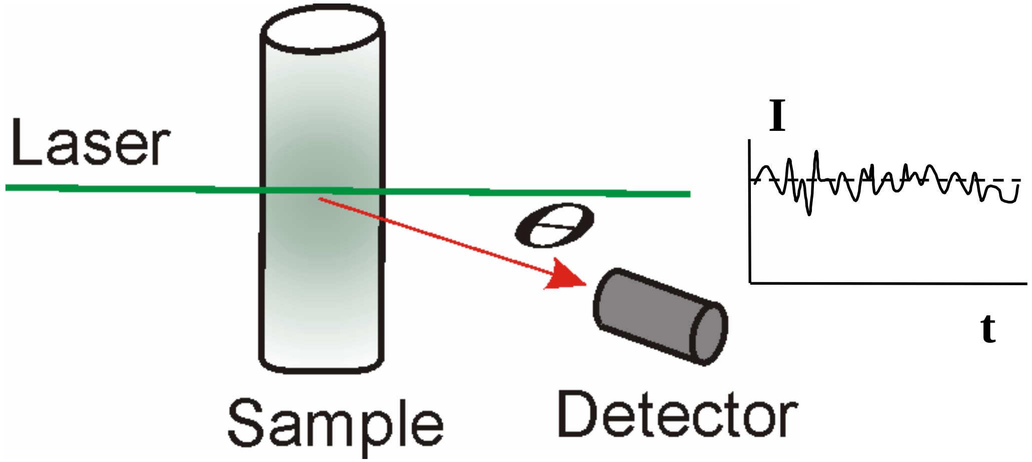


0.12 μm



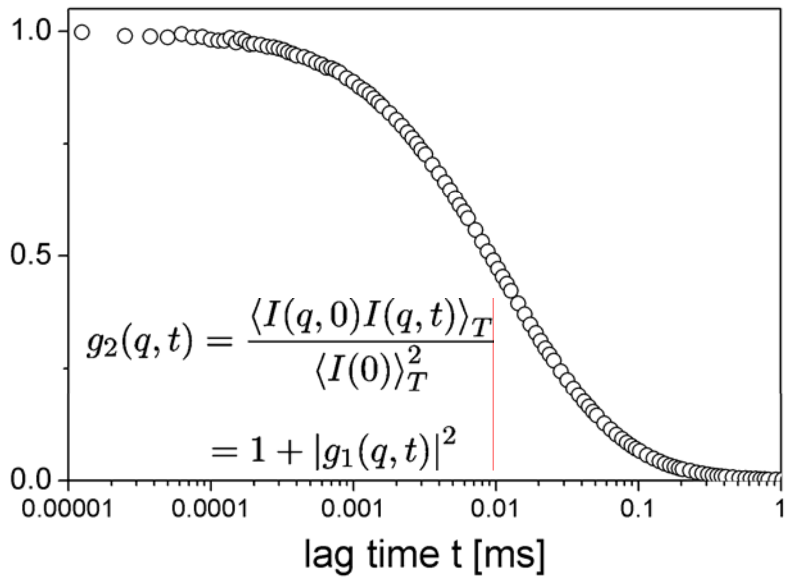
Dynamic Light Scattering (SLS)





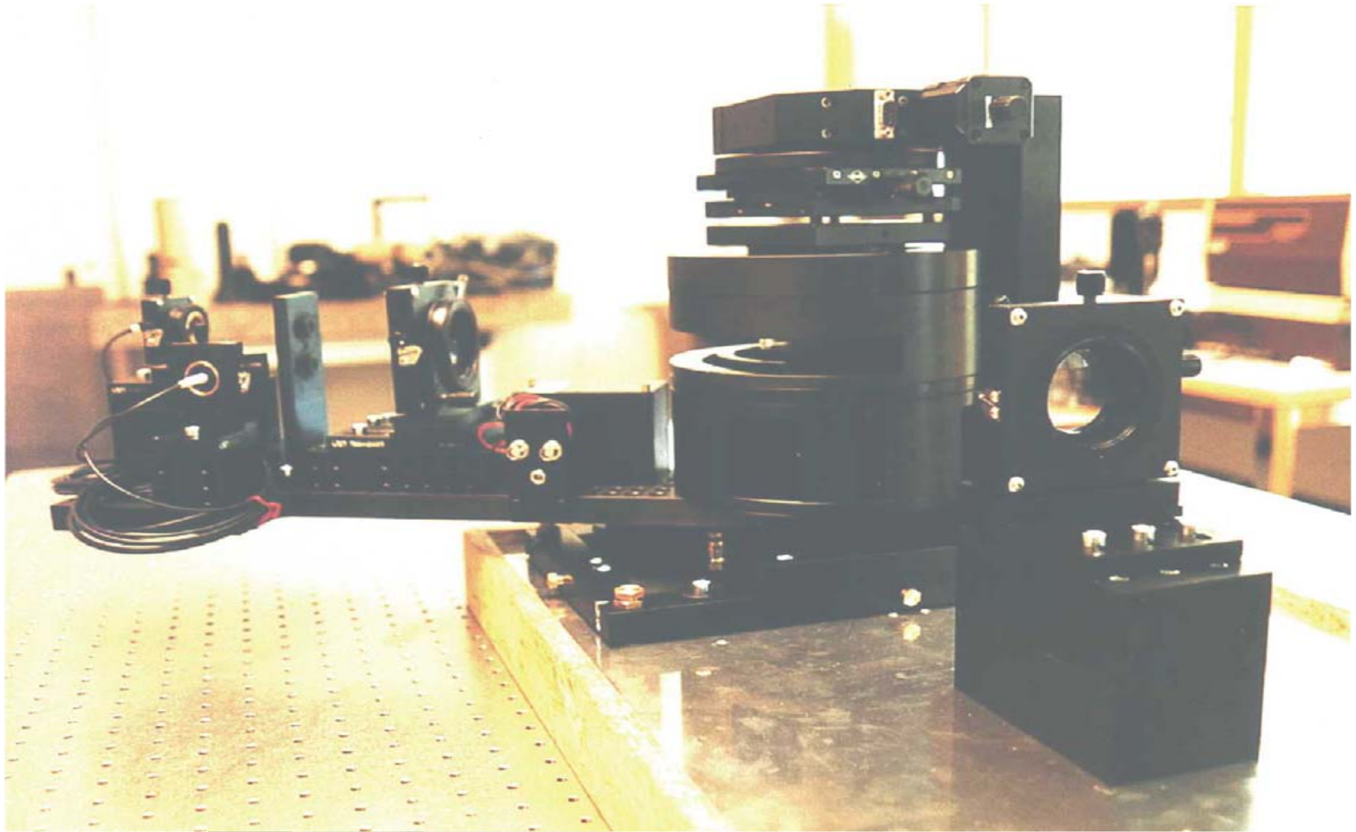
Dynamic Light Scattering (DLS)

Intensity Autocorrelation function (ICF)



Multiple Scattering Suppression

K. Schätzel. *J. Mod. Opt.*, 38:1849-1865, 1991
C. Urban. *J. Colloid Int. Sci.*, 207:150-158, 1998



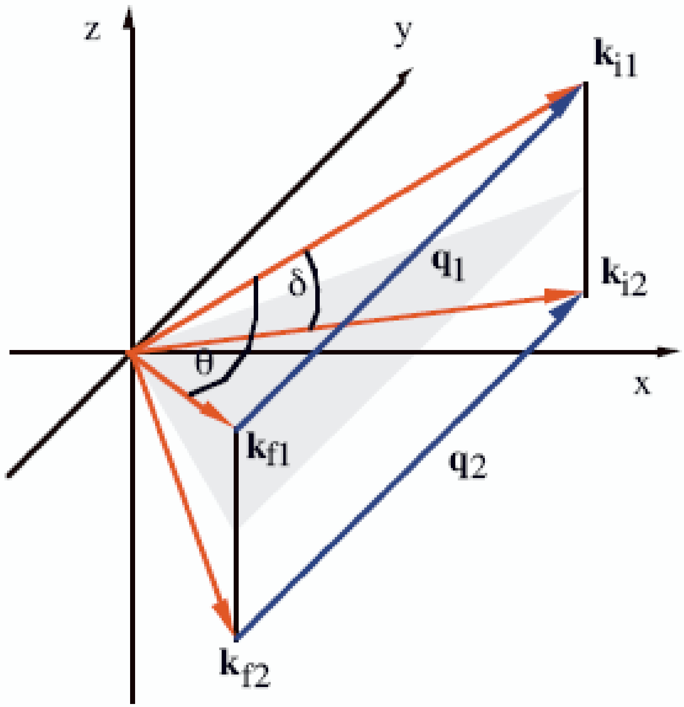
- Selective detection of singly scattered light

- Cross-correlation setup

www.lsinstruments.ch

LSInstruments

Principle of 3D-DLS



- For single scattering the intermediate scattering vector is the same for both experiments $\mathbf{q_1}=\mathbf{q_2}$

- For multiple scattering of order n the total scattering vector is still the same for both experiments $\mathbf{q_1}=\mathbf{q_2}$

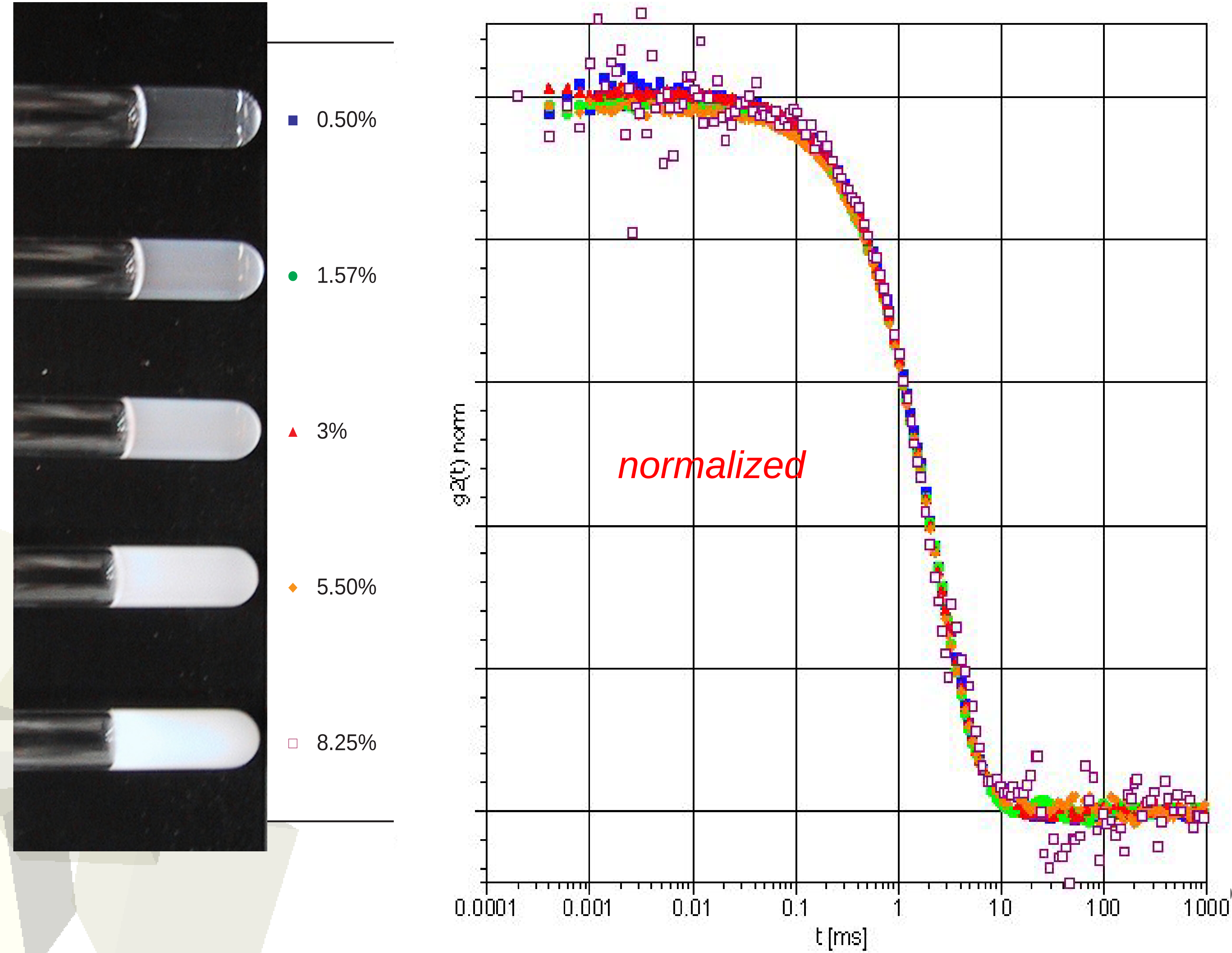
$$\vec{q}_1 = \sum_{l=1}^{n} \vec{q}_l = \vec{q}_2 = \sum_{j=1}^{n} \vec{q}_j = \vec{k}_f - \vec{k}_i$$

Perform two scattering experiments at slightly tilted angle (out of the scattering plane)

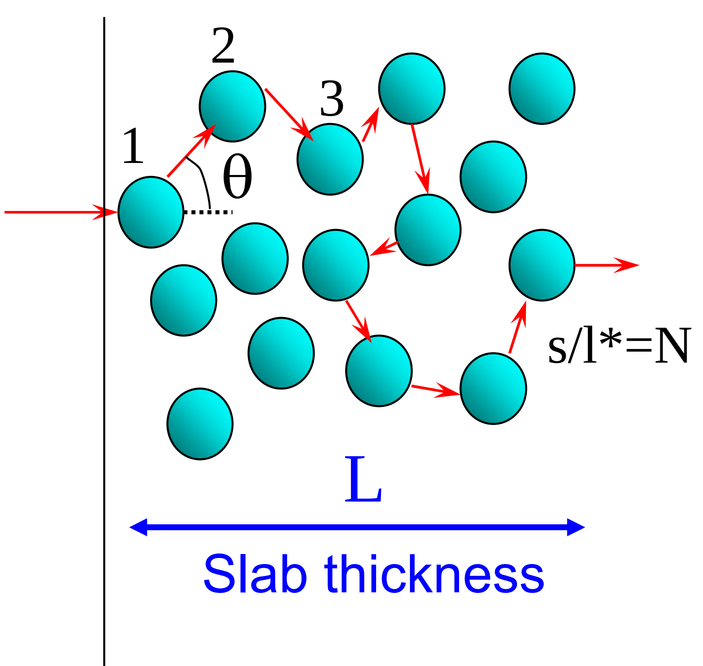
- **BUT:** $\{\vec{q}_l\} \neq \{\vec{q}_j\}$

Thus for multiple scattering different (uncorrelated) spatial Fourier components of the sample are probed by each detector

3D-DLS: Single Scattering in Turbid Suspensions !



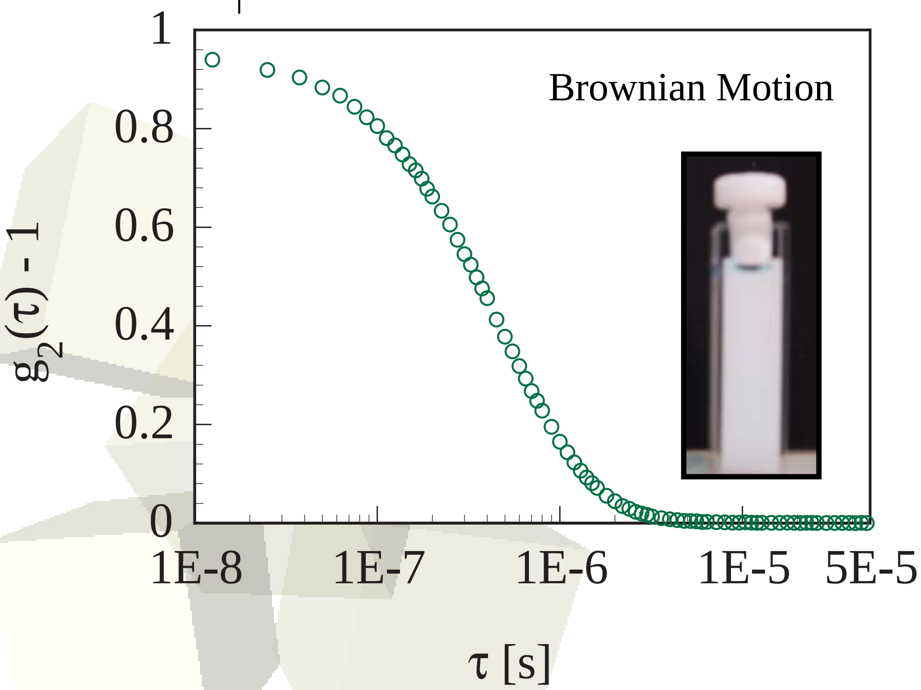
Diffusing Wave Spectroscopy

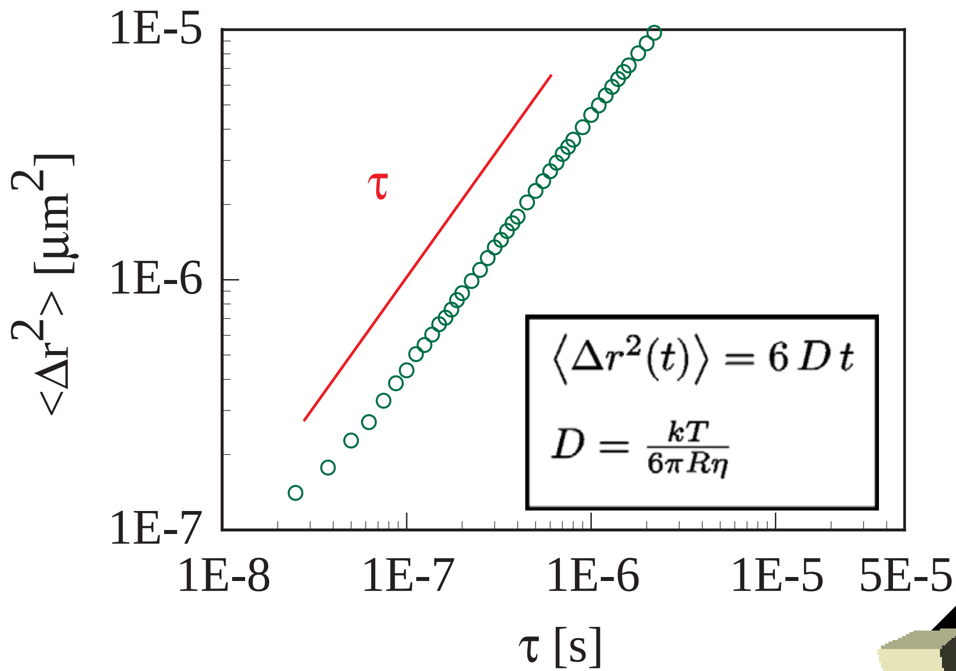


$$g_2(\tau)-1=\int_0^\infty P(s)\ \exp\left(-\frac{1}{3}k_0^2\left\langle\Delta r(\tau)^2\right\rangle\frac{s}{l^*}\right)ds$$

Photon diffusion (transmission)

Length scale ~ 1 nm to 50nm

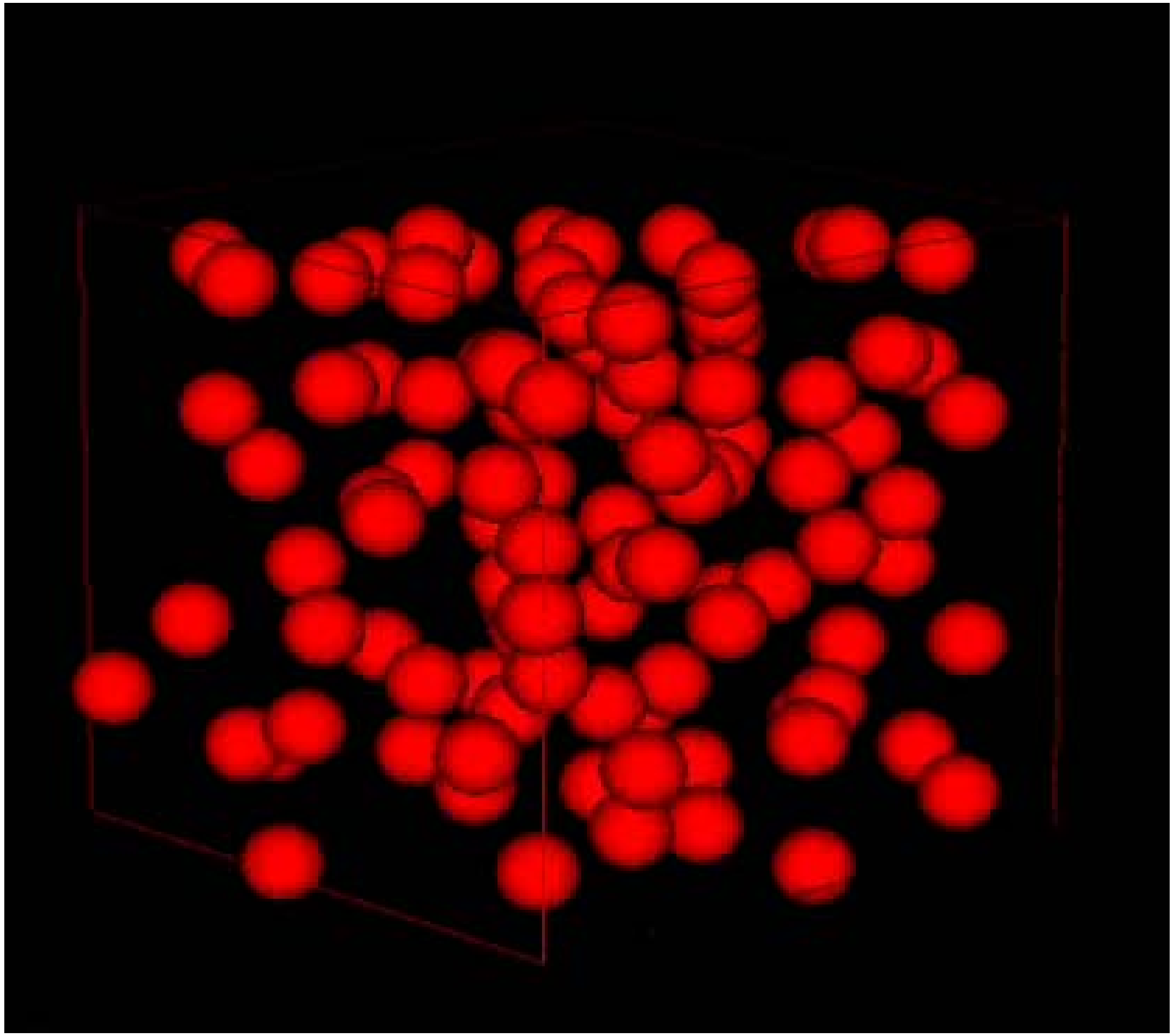




Application 1

Nanoparticle Gels

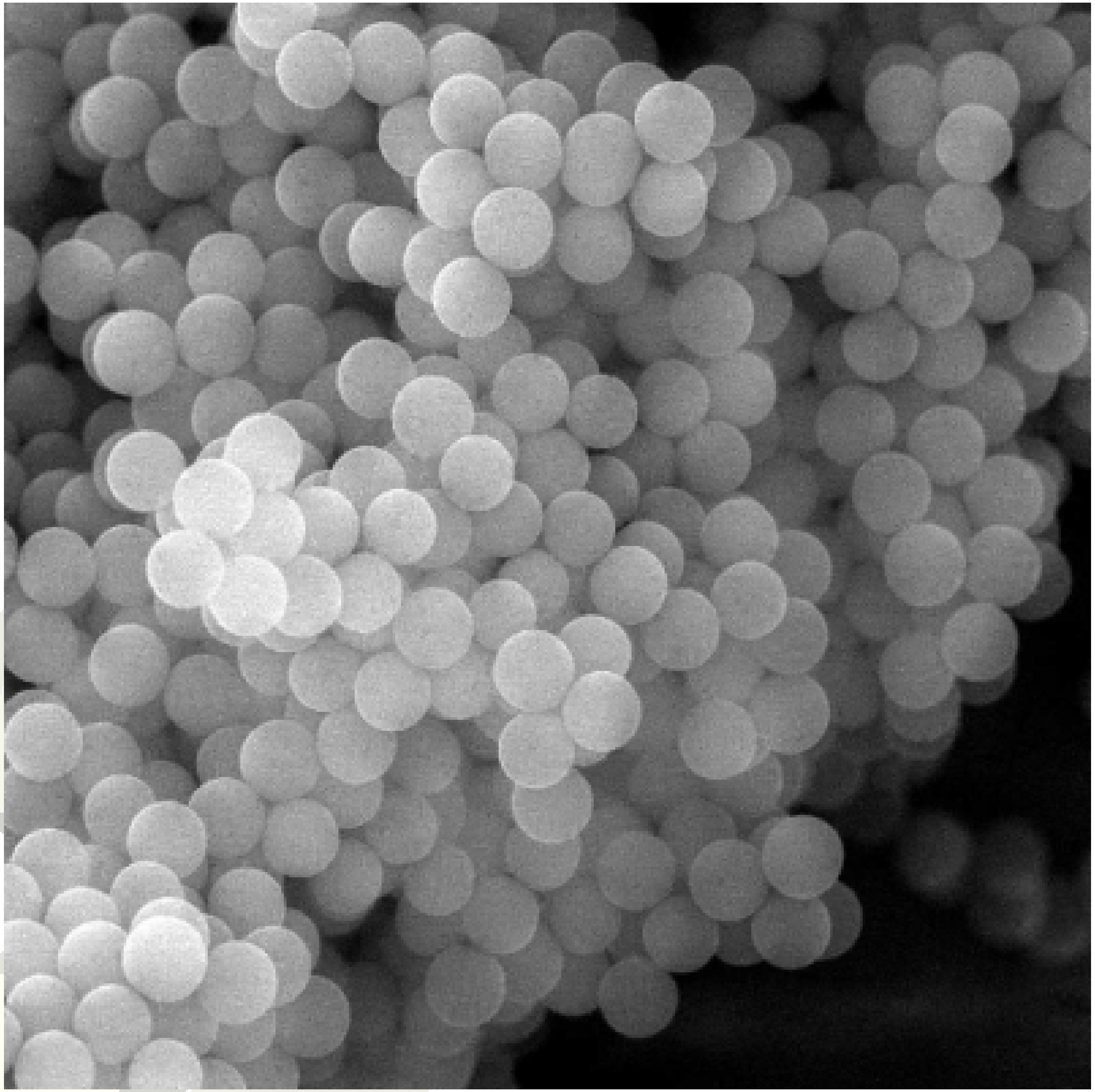
From strong repulsions to attractions



Simulations: V. Lobaskin, now MPI Mainz

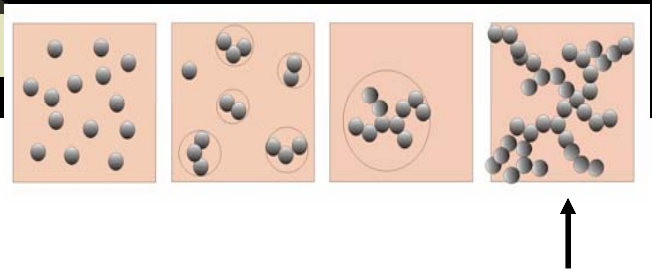
Sol-gel transition of concentrated colloidal suspensions

Addition of salt : (Van der Waals) attraction of particles by screening the Coulomb repulsion.

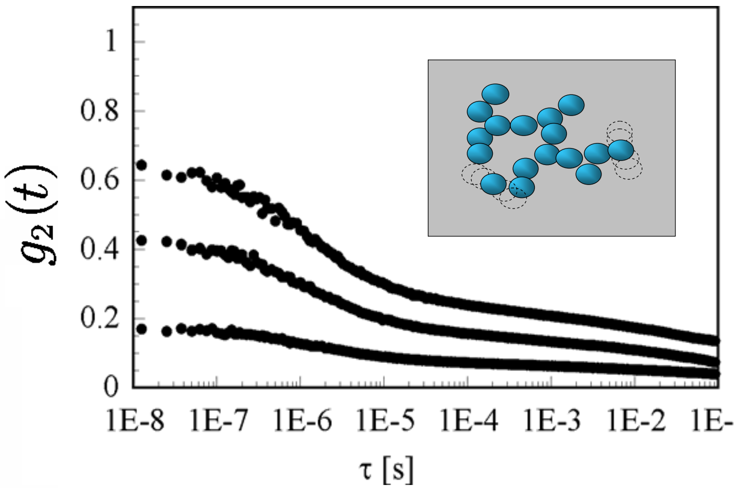


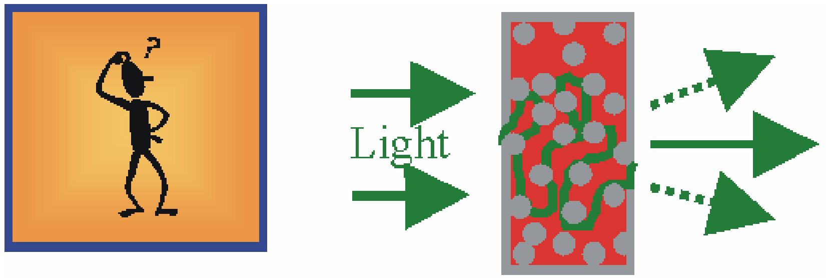
Picture: Gel of 30% ca. 500nm SiO_2 particles, courtesy Hans Wyss, ETHZ

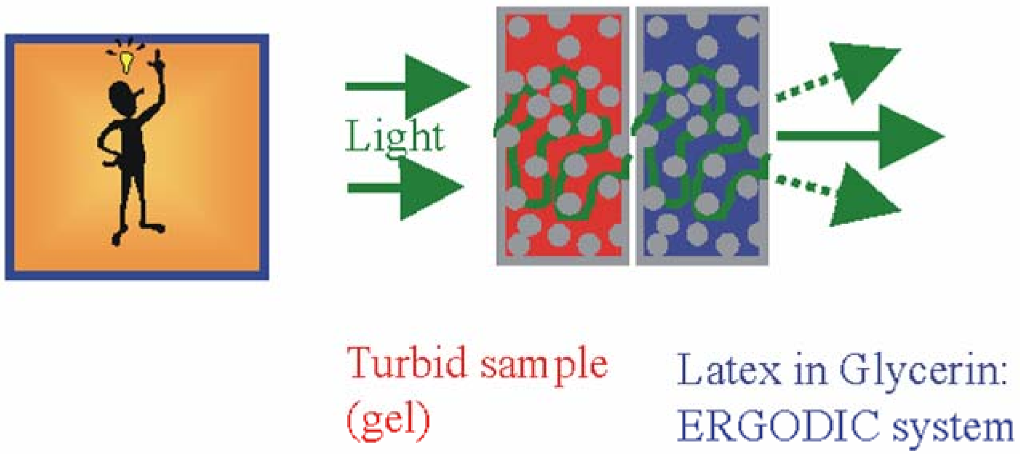
- ? Particle dynamics in a concentrated suspension from sol to gel
- ? System preparation-reproducibility
- ? Methods of investigation
- ? Link to viscoelastic properties
- ? From fractal to dense gels

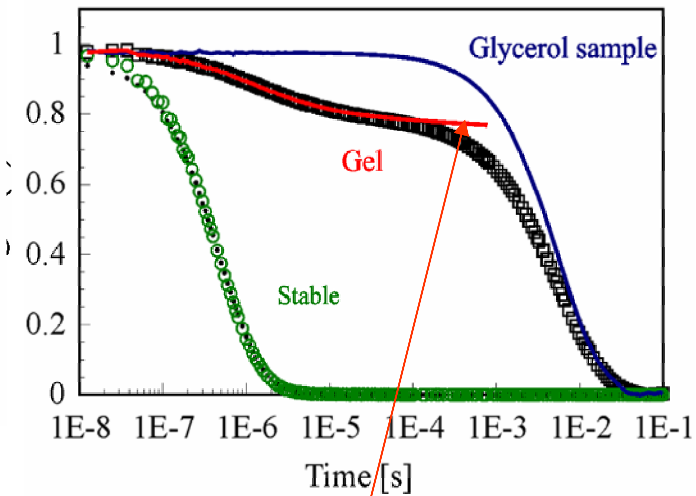


Gel: System is solid-like and particles execute only limited excursions







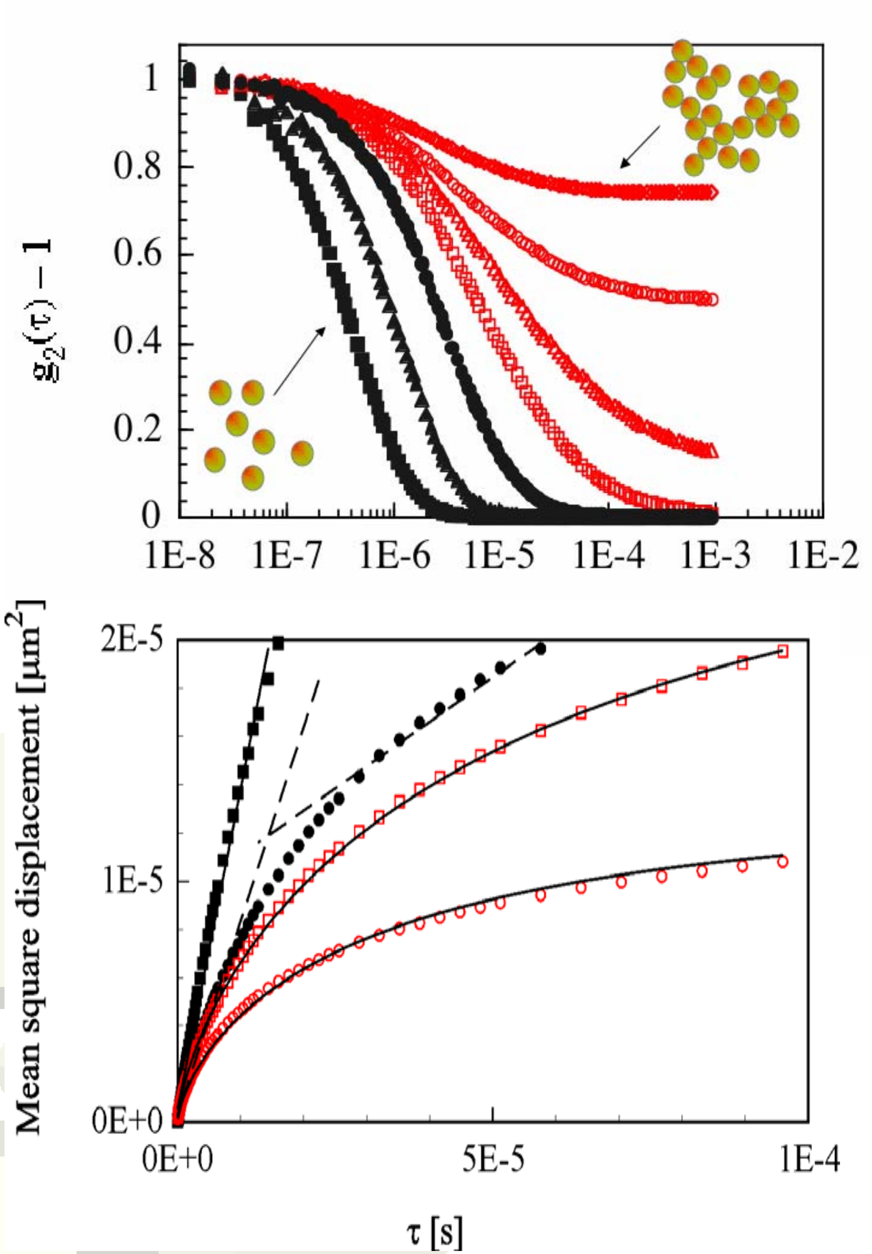


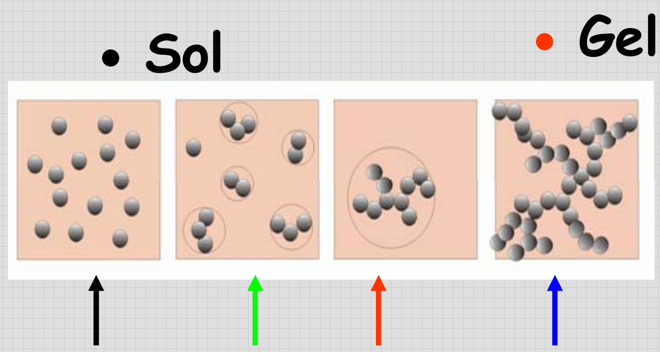
The Two-Cell Technique (TCDWS)

F. Scheffold, S.E. Skipetrov, S. Romer and P. Schurtenberger , Phys. Rev. E **63**, 61404 (2001)

$$g_2(\tau, L_1) - 1 = \frac{g_2(\tau, L) - 1}{g_2(\tau, L_2) - 1}$$

DWS: Sol-gel transition of a destabilized colloidal suspensions





Time evolution:

t = 0, 18, 108, 256, 734, 4683, 14400 min (10 days)

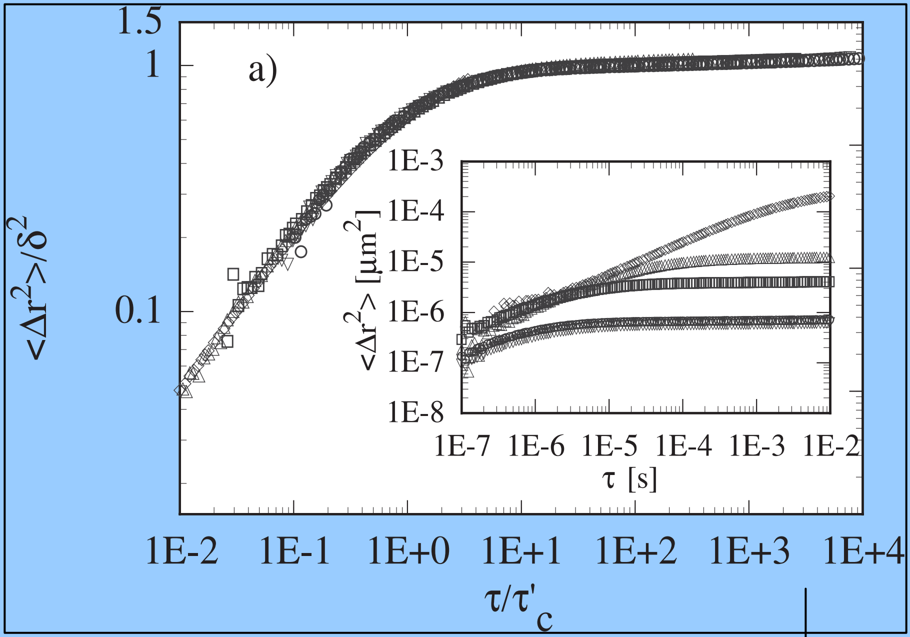
t_{gel}= 87 min

(a=150nm, Φ = 0.2)

S. Romer, F. Scheffold and P. Schurtenberger, Phys. Rev. Lett. **85**, 4980 (2000)

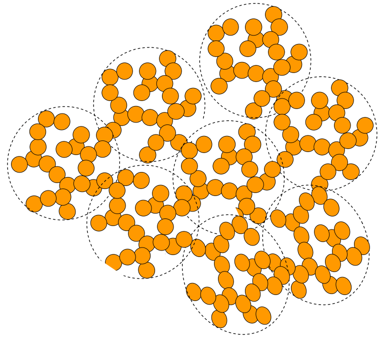
Dynamics of fractal gels from DWS

Experiments (high concentrations, t ca. 24h)



Overdamped thermal motion of gel segments on all length scales within a cluster

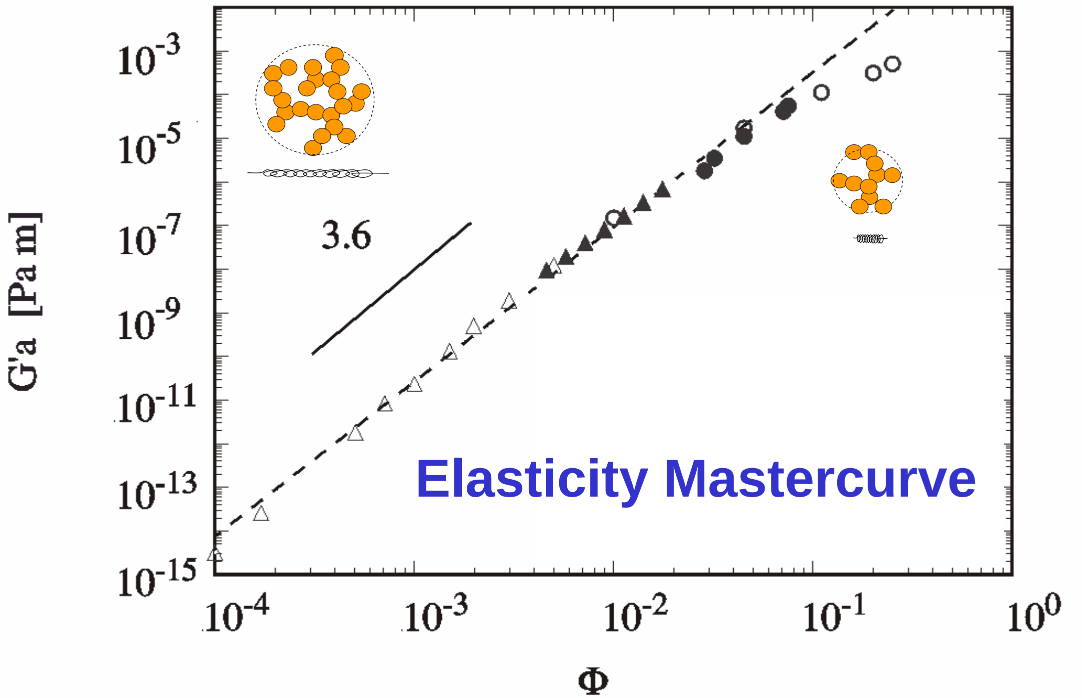
[Krall and Weitz, PRL 80, 778 (1998)]



$$G_0' = kT/(\delta^2 \cdot R_c)$$
$$= 6\pi\eta / \tau_c$$

- **Open circles: <u>DWS</u>, a=85nm**
- **Open diamonds: <u>DLS</u>, a= 9.8nm**

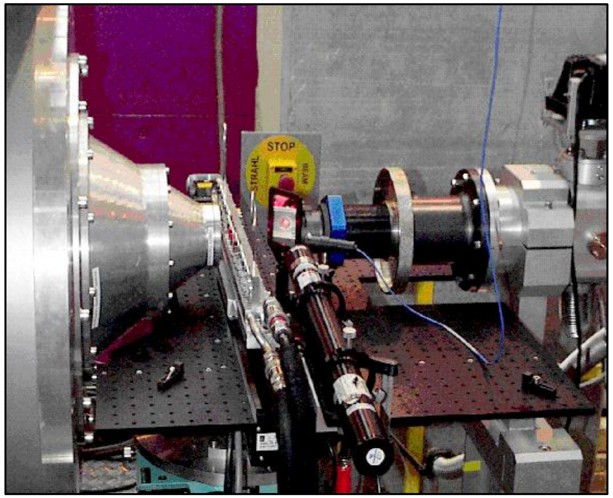
- **Full circles: a=85nm**
- **Full triangles/squares:a=7-10nm**

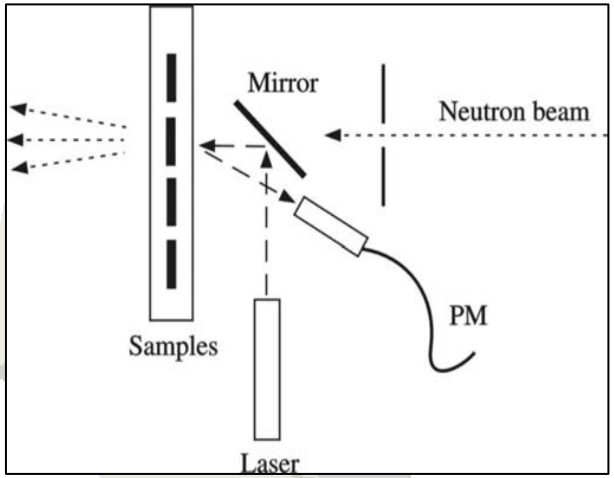


DLS-Data for a=7-10 nm published by Krall, Weitz, Gisler, B... and Weitz & Cipelletti)

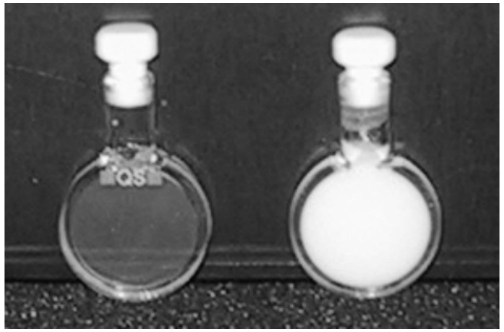
DWS: Hugo Bissig, Sara Romer, Veronique Trappe, Frank Scheffold and Peter Schurtenberger, in preparation

Structure: Simultaneous light and small angle neutron scattering (SANS)

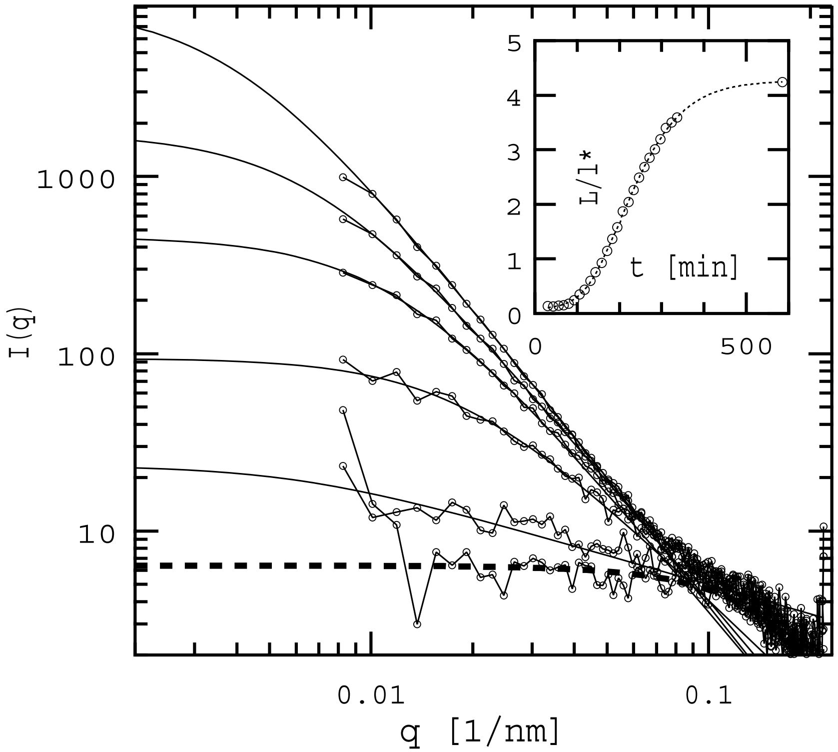




PSI-Villingen



Nanoparticle suspension
(Φ=3.8% , a=12nm)



$$l^*_{susp}/l^*_{gel} = 4k_0^4 \Big/ \int_0^{2k_0} \left[I_{gel}(q)/I_{susp}(q) \right] q^3 dq$$

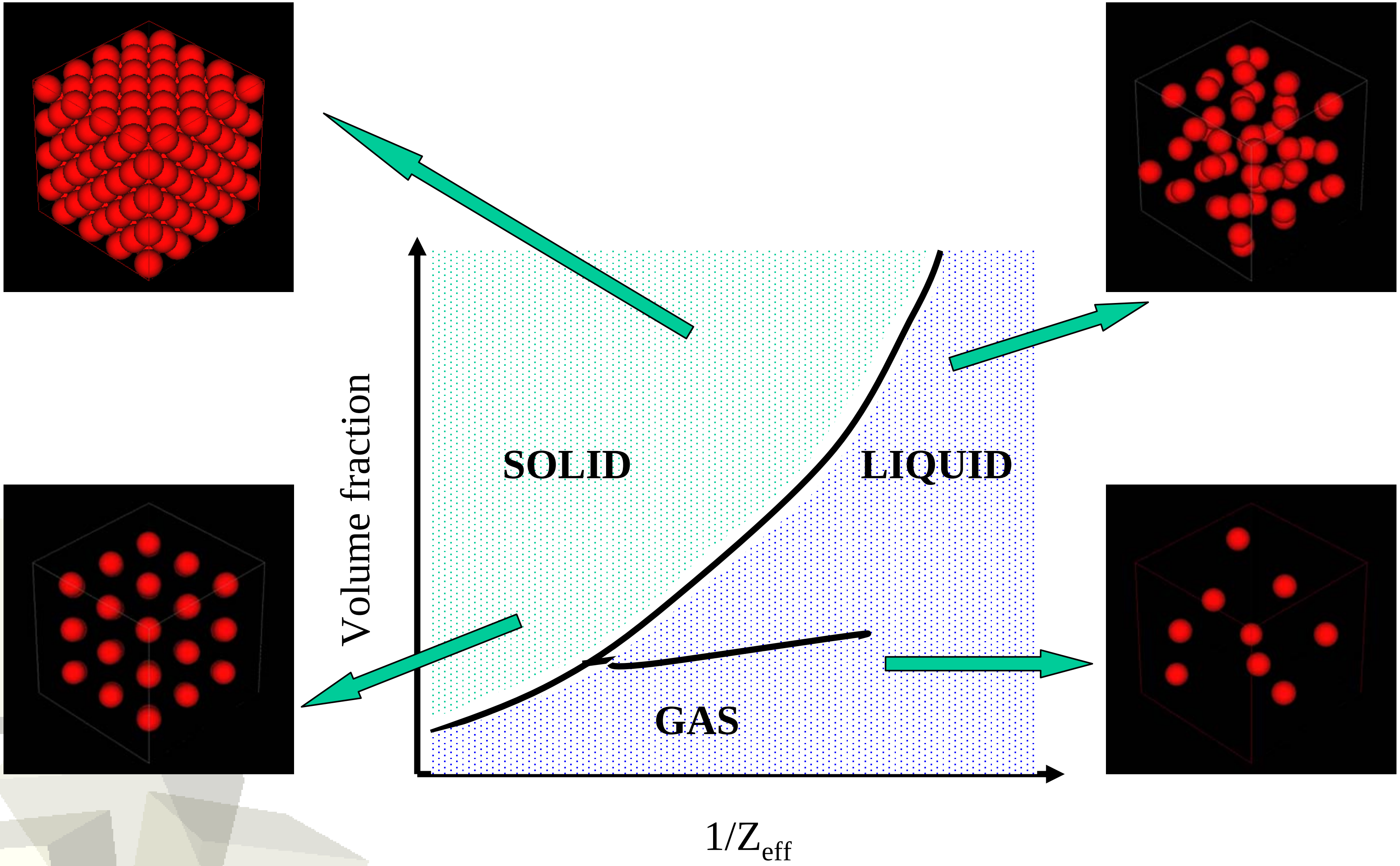
Optical density

S. Romer, C. Urban, V. Lobaskin, A. Stradner, F. Scheffold, J. Kohlbrecher and P. Schurtenberger, J.Appl. Cryst.,36,1-6 (2003)

Topic 2

Dense colloidal suspensions

Long- and short-range order in charged colloidal suspension

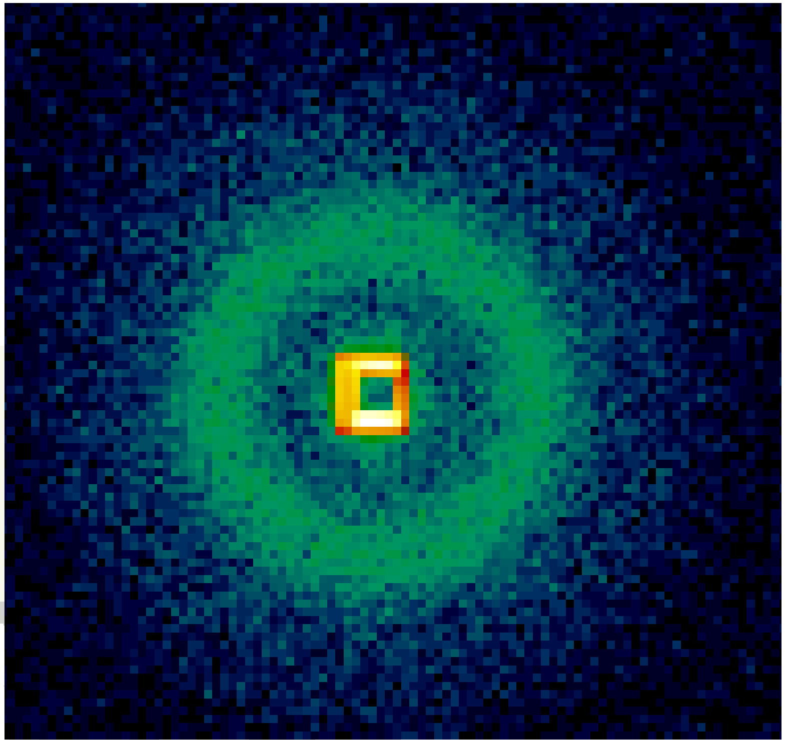


Z_{eff}= effective charge

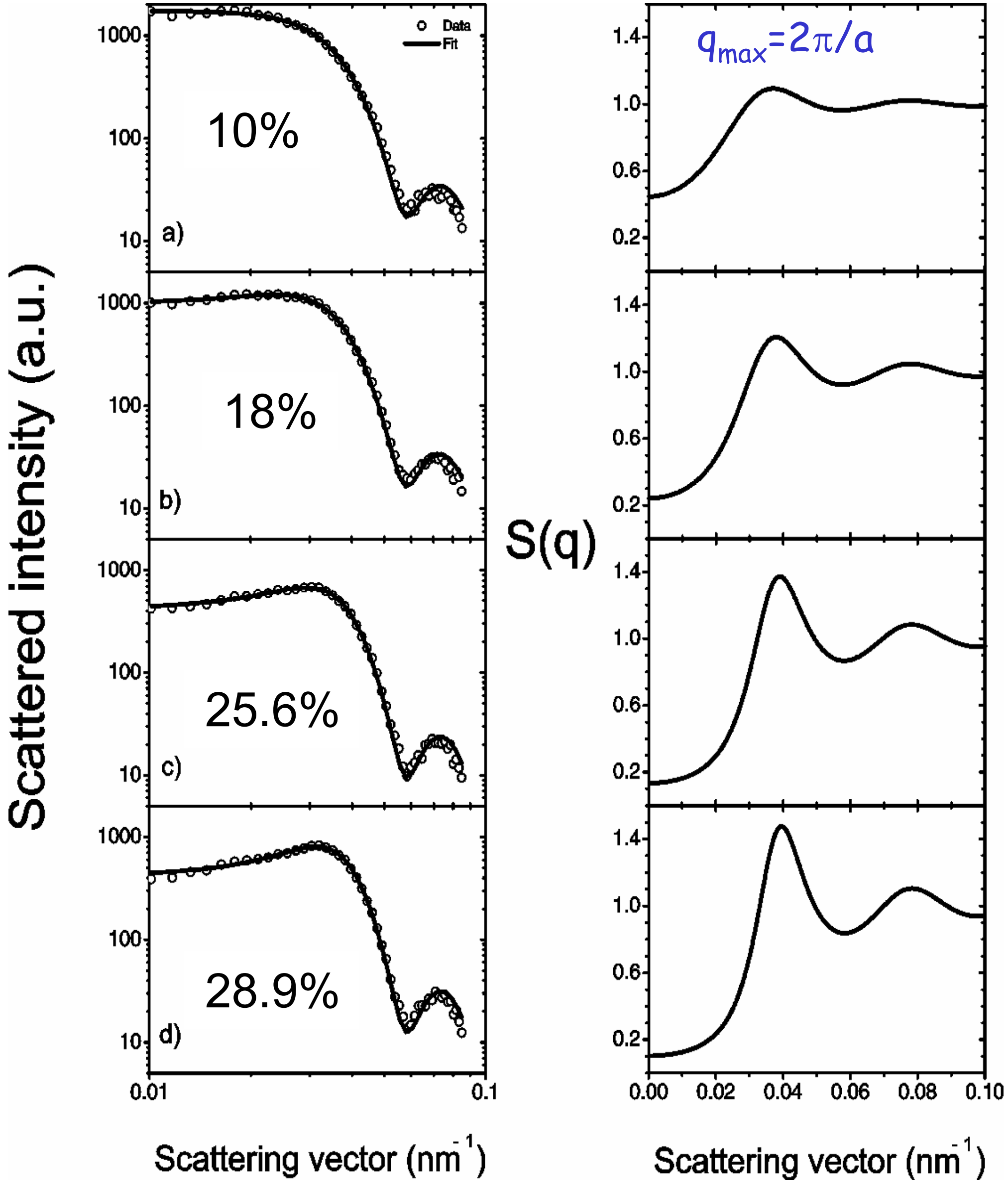
Courtesy V. Lobaskin, now MPI Mainz

Structural Analysis: Suspensions of hard spheres

SANS from **hard-sphere-like** concentrated colloidal suspensions (a=85nm Polystyrene spheres in water/deuterium, 5mM KCl)

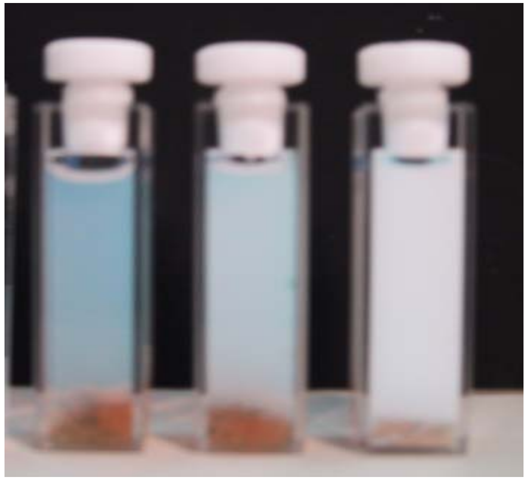


SINQ- PSI, Villingen(CH)

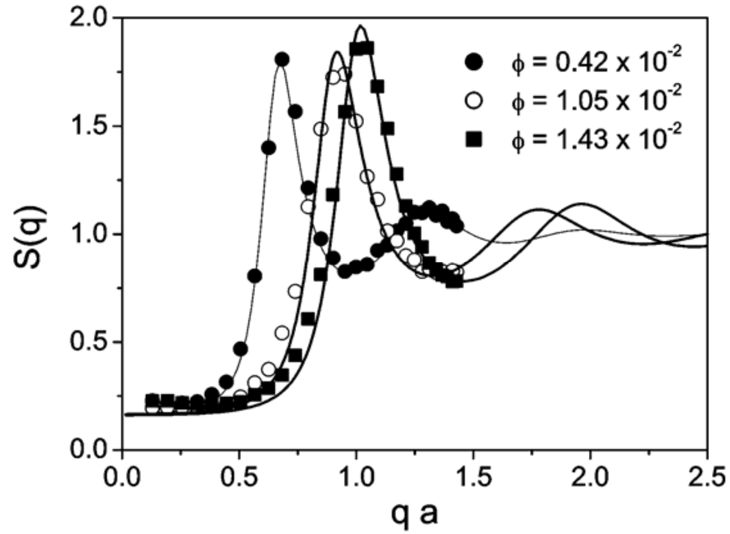


L. Rojas, S. Romer, F. Scheffold and P. Schurtenberger, Phys. Rev.E, **65**, 051403 (2002)

Highly charged spheres
Structure and Dynamics from 3D-DLS and SANS

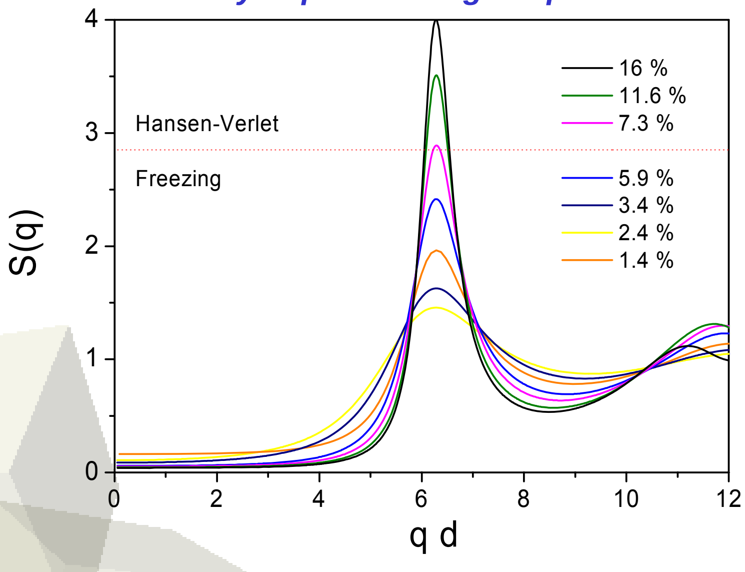


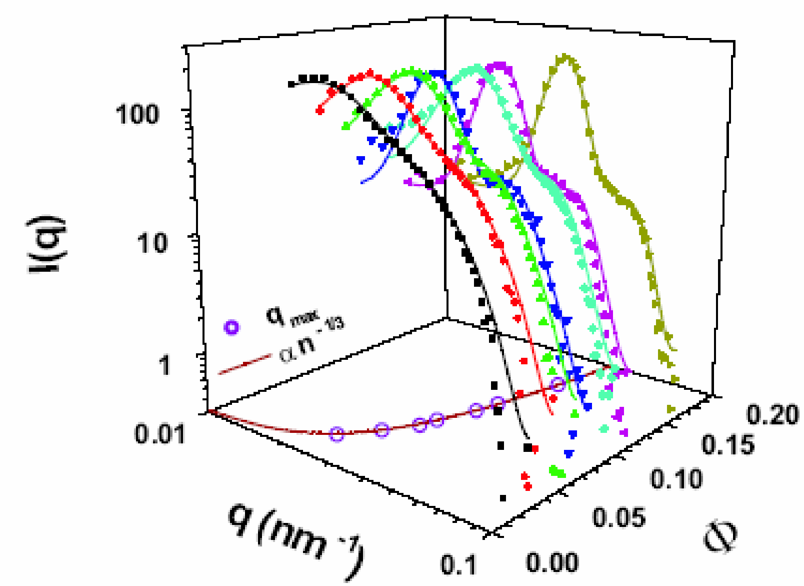
Highly charged polystyrene latex spheres (radius a=59 nm), in a fully deionized mixture of water and ethanol (30:70) to prevent crystallization



Klein & D'Aguanno, Physical Review A, 1992. 46: p. 7652-7656.

*Fit: Polydisperse charged spheres**

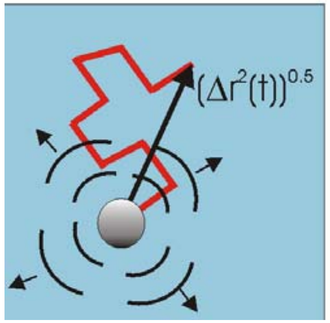




L.F. Rojas-Ochoa, J.M. Mendez-Alcaraz, J.J. Sáenz, P. Schurtenberger and F. Scheffol, PRL, Phys. Rev. Lett. 93, 073903 (2004)

L. F. Rojas, R. Vavrin, C. Urban, J. Kohlbrecher, A. Stradner, F. Scheffold and P. Schurtenberger, Faraday Discussions 123 (2003)

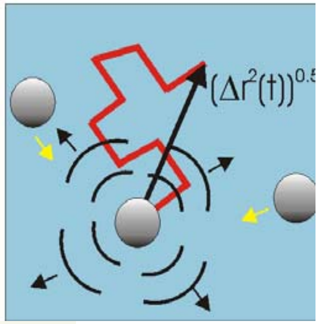
Φ



Free diffusion

$$g_1(q,t) = e^{-Dq^2 t}$$

$$D_{eff}(q) = D_0$$



Hindered Diffusing

short times

long times

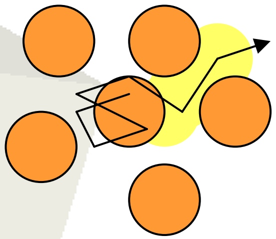
Hydrodyn. Interactions

$$D_{eff}(q) = D_0 \frac{H(q)}{S(q)}$$

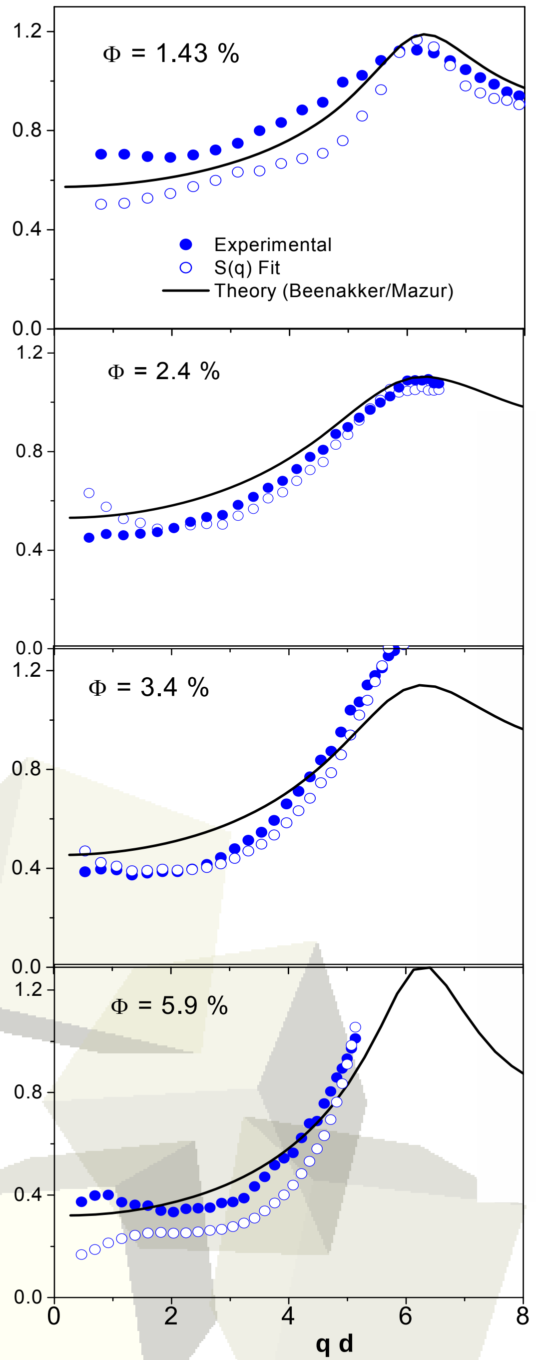
Structural Relaxation

$$D_L(q)$$

Repulsive Interactions



Caging and Release in Glassy Systems



$$g_1(q, t \to 0) = \exp\left(-D(q) \cdot q^2 \cdot t\right) \qquad H(q) = D(q)S(q)/D_0$$

H(0) = Sedimentation velocity u/u(Φ=0)

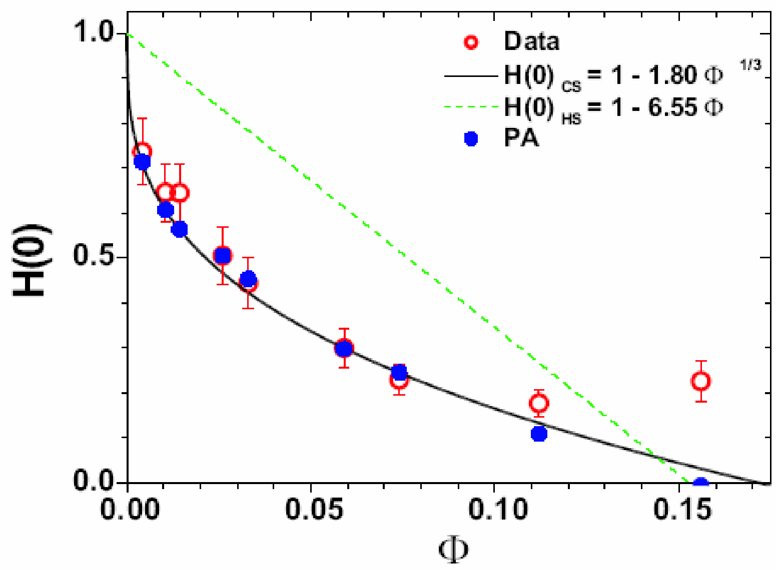


Figure 6.4: $q = 0$ limit of the measured $H(q)$ for charged sphere suspensions. Solid black line: parametric relation Eqn. 6.9 with $p = 1.8$. Dashed blue line: Batchelor's lowest-order result for hard-spheres [123]. Blue symbols: PA calculations.

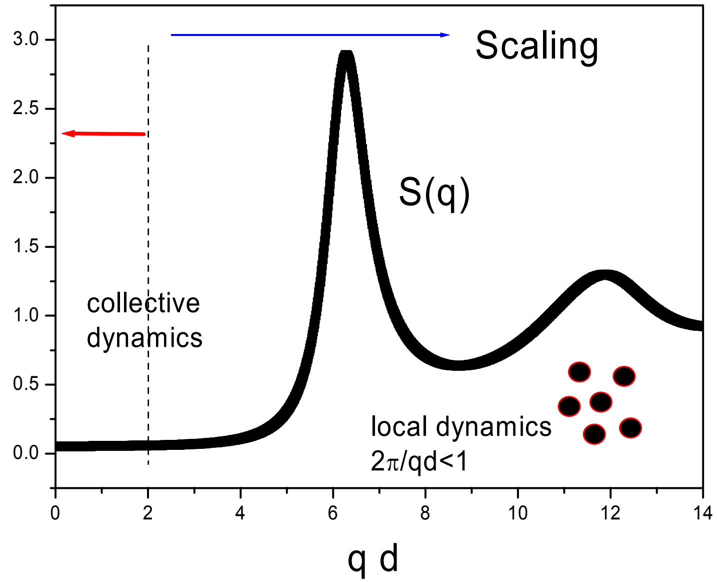
PA Theory: Watzlawek & Nägele, JCIS 214 (1999)

Scaling properties of $g_1(q,t)$ for long time scales.

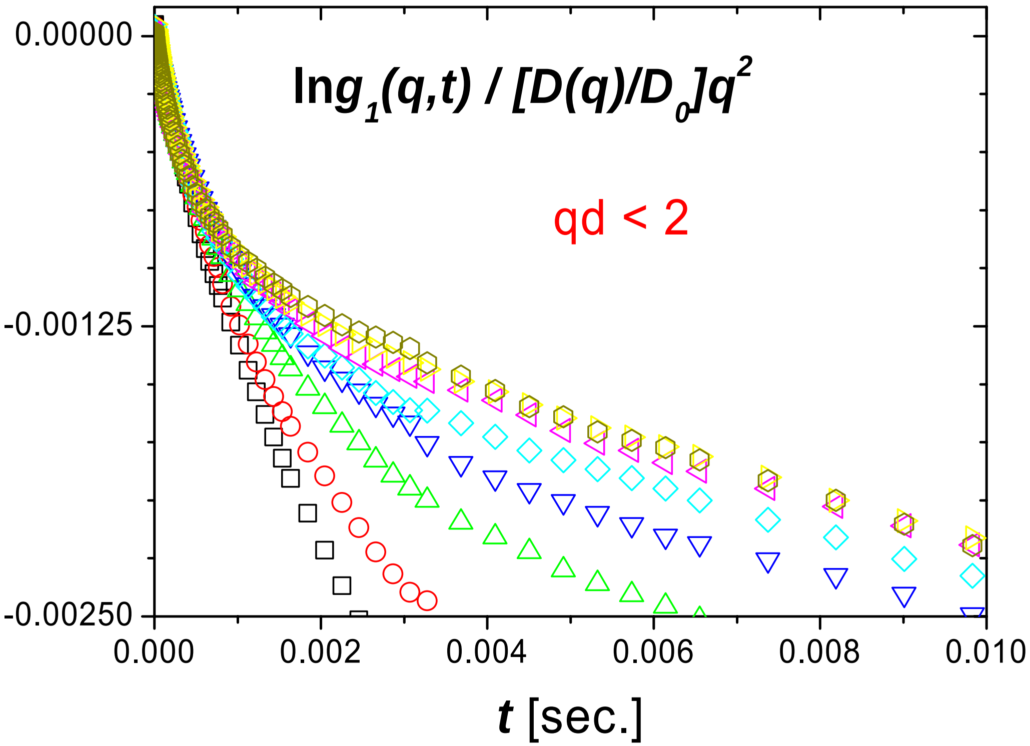
Short and long time dynamics

$$g_1(q,t \to 0) = \exp\left(-D(q)\cdot q^2 \cdot t\right)$$

$$g_1(q) \propto \exp\left(-D_L(q)\cdot q^2 \cdot t\right), t > \tau_c$$



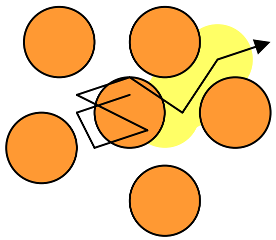
Scaling → $D(q)/D_L(q)$=const



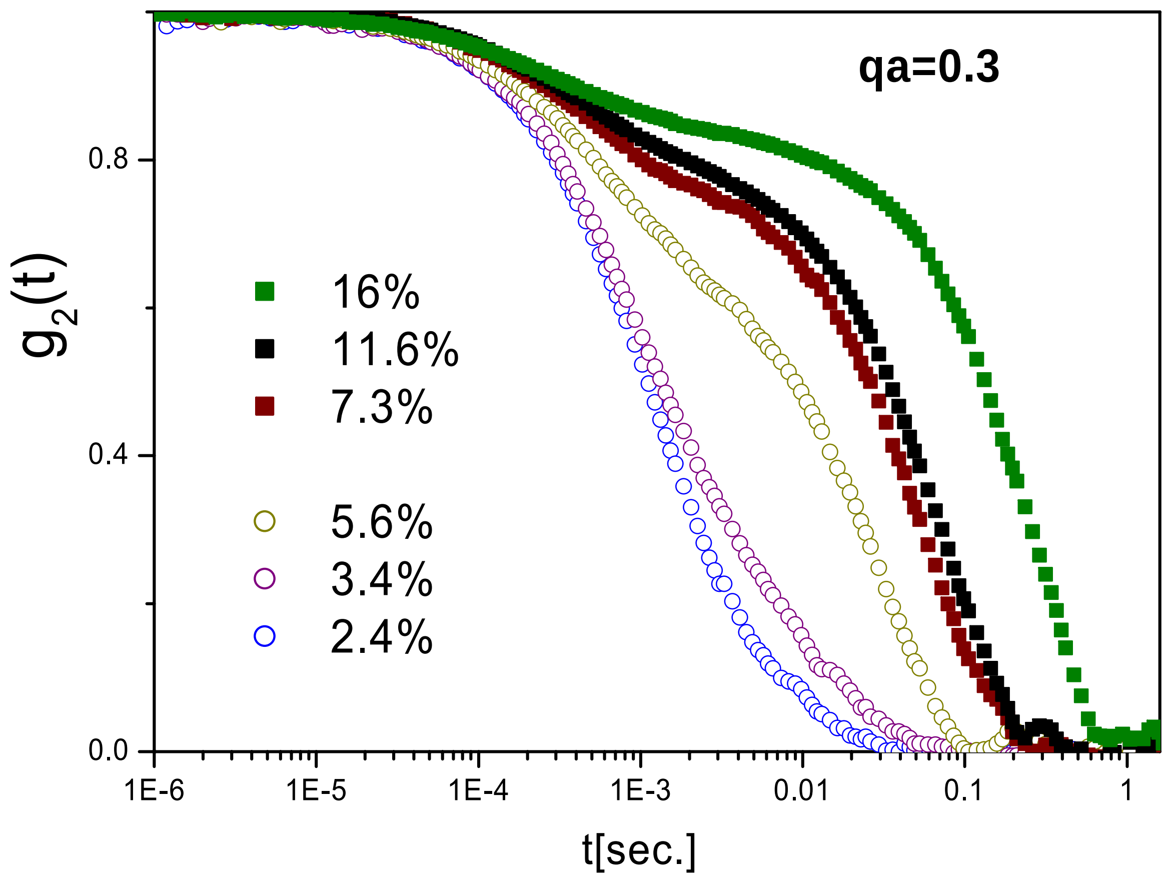
Φ=5.9%

Hard-Spheres: P. N. Segrè and P. N. Pusey; Phys. Rev. Lett. 77, 771-774 (1996)

Approaching the glass transition



Caging and Release close to the glassy transition



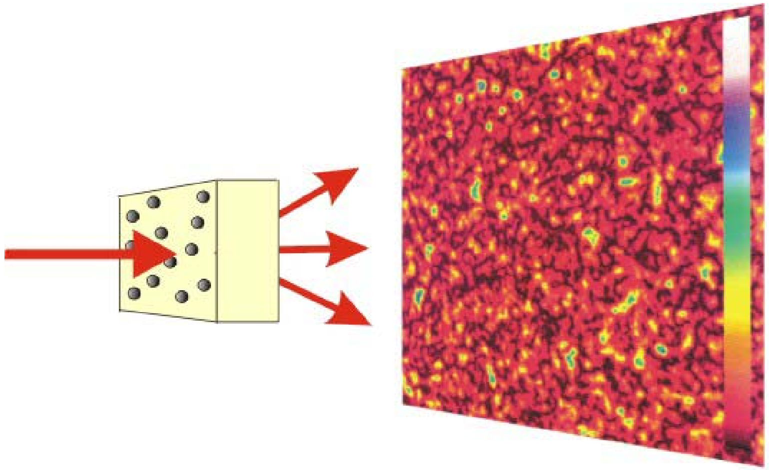
Luis F. Rojas, PhD thesis 2004; pdf at www.unifr.ch/physics/mm

Topic 3

Slow Relaxations

CCD-camera based multi-speckle DWS

Access to slow relaxation times



Advantages:

Fast data acquisition time

Access to nonergodic media

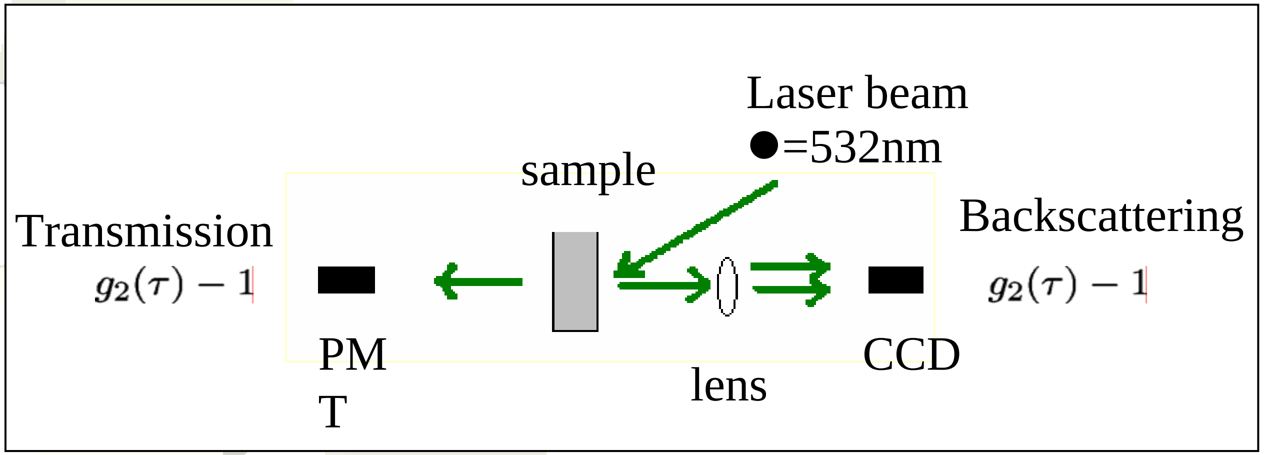
Problem :

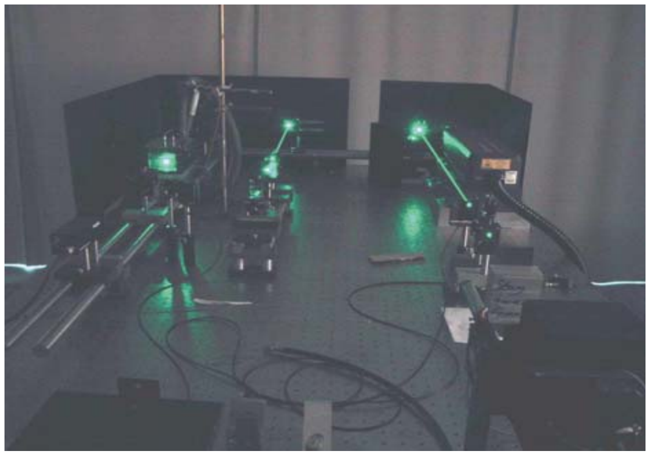
Limited time resolution (100 frames per second) τ > 10 ms

•Kirsch, S.; Frenz, V.; Schartl, W.; Bartsch, E.; Sillescu, H. Multispeckle autocorrelation spectroscopy and its application to the investigation of ultraslowdynamical processes. J. Chem. Phys. 1996, 104, 1758.

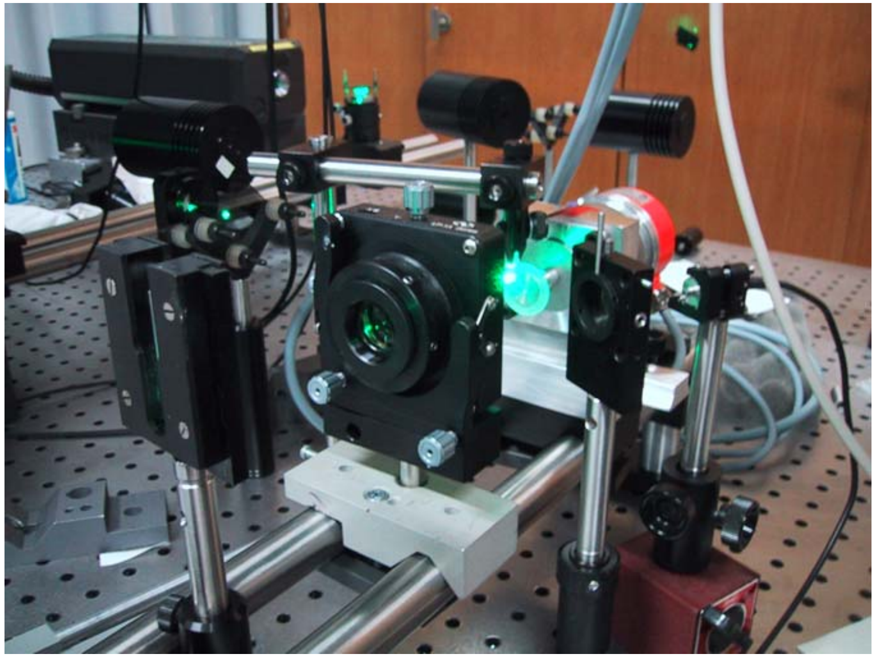
•Knaebel, A.; Bellour, M.; Munch, J.-P.; Viasnoff, V.; Lequeux, F.; Harden, J.L, Europhys. Lett. 2000, 52, 73.

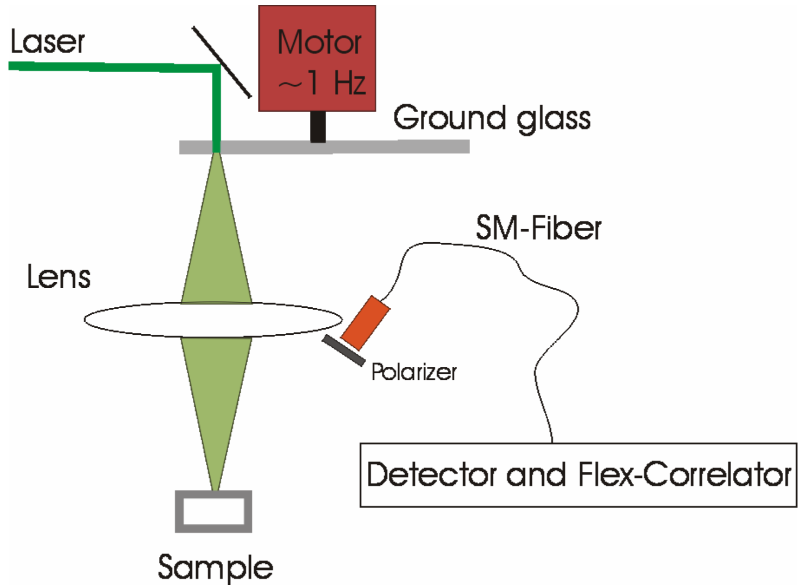
→ **Simultaneous Fiber and Camera based DWS**

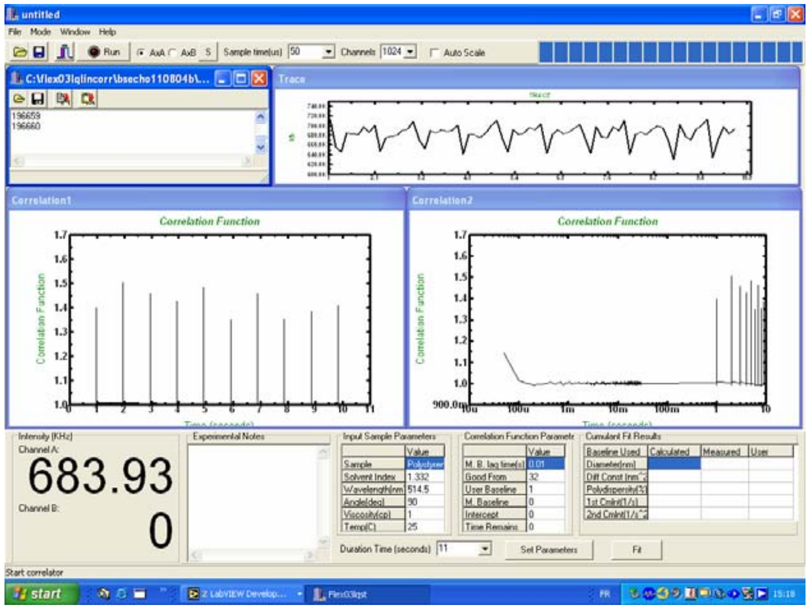




Multispeckle dynamic light scattering



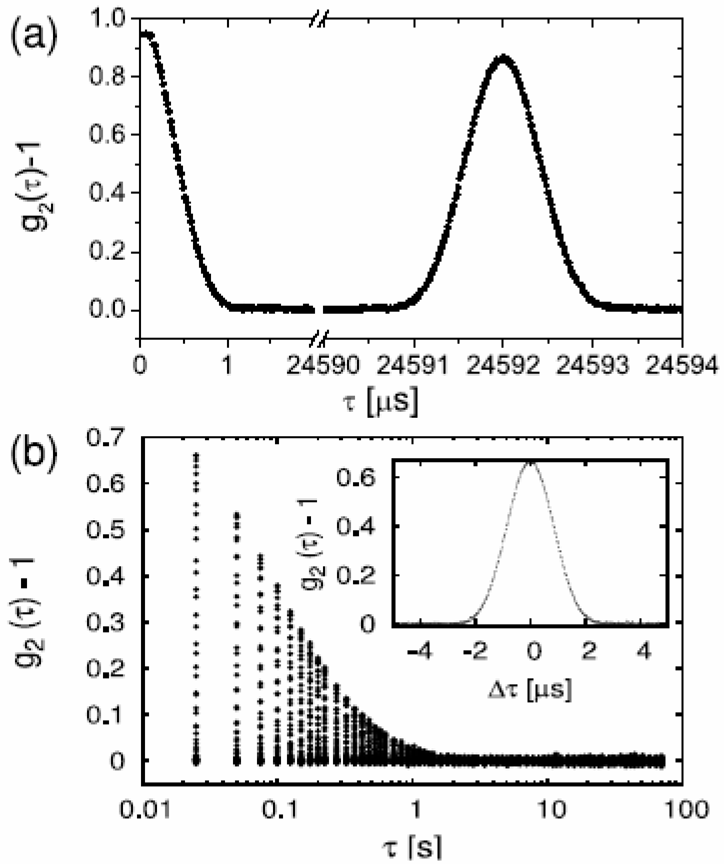




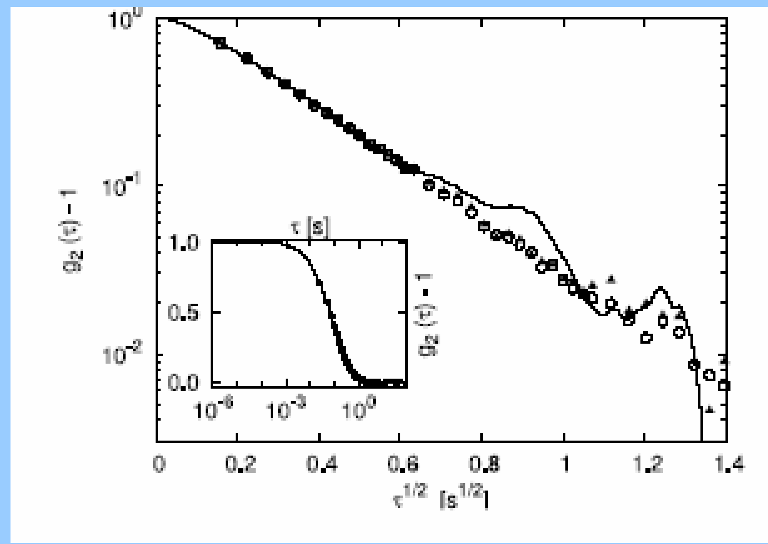
New: Multi-Speckle DWS with a Single-Mode Fiber !

Echo two-cell DWS

10 sec measurement Flex02LQ-3 – *www.correlator.com*



- At each cycle (multi-speckle) correlation echoes appear
- The peak of the echoes decays as the correlation function of the sample

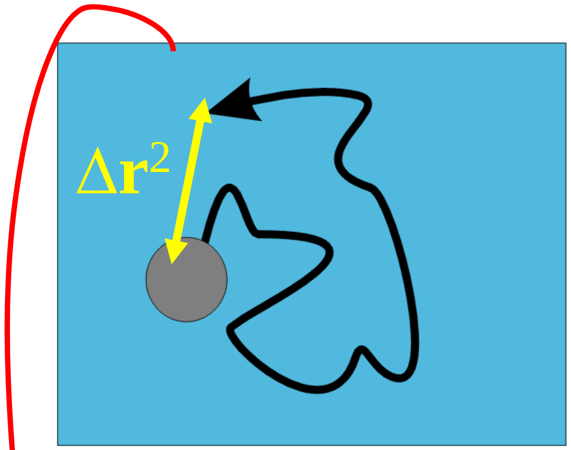


Comparison of
- Duration 12 second Echo experiment (symbols)
- Duration 20 minute time average (solid line)

DWS of TiO_2 (0.5 wt. %) in glycerol at 5.7°C

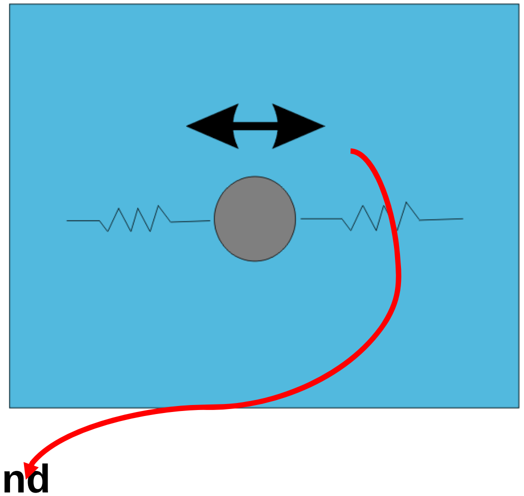
Two-cell Echo DWS: P. Zakharov, F. Cardinaux and F. Scheffold, submitted to PRE (2005)
Echo DLS: K. Pham, S. Egelhaaf, A. Moussaid, and P. Pusey, Rev. Sci. Instrum. 75, 2419 (2004).

Viscous fluid



Elastic solid

Particle of Radius R



Harmonically bound
Brownian particle

$$\langle \Delta r^2(t) \rangle = 6\,D\,t$$

$$D = \frac{kT}{6\pi R \eta}$$

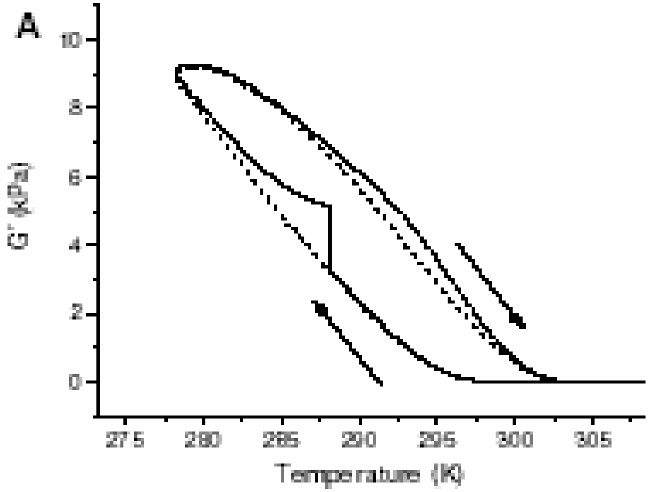
$$\langle \Delta r^2(t) \rangle = \delta^2 \left(1 - e^{-t/\tau_B}\right)$$

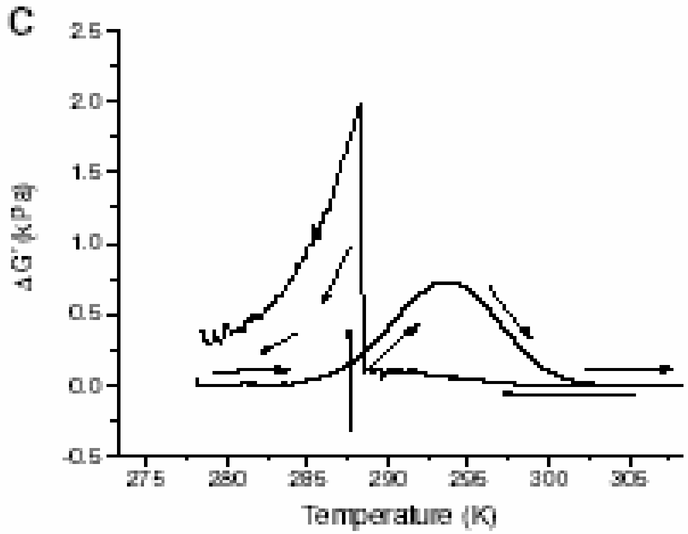
$$\tau_B = \frac{6\pi\eta R}{\kappa}; \quad \kappa = \frac{3kT}{\delta^2} = \pi R\, G'(\omega = 0)$$

PCS → $< \Delta r^2(\tau) >$ → **Viscosity η, spring constant κ, G'(ω), G''(ω)**

Microrheology

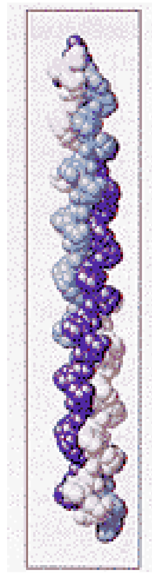
Example: Elasticity,memory and ageing in biopolymer gels





Temperature ramp (0.2 $Kmin^{-1}$) with and without stop

Gelatin is degraded collagen. When its solutions are cooled below about 40°C, the separate chains start to combine and re-form portions of collagen triple helix, which cross link the system, eventually forming an elastic gel.



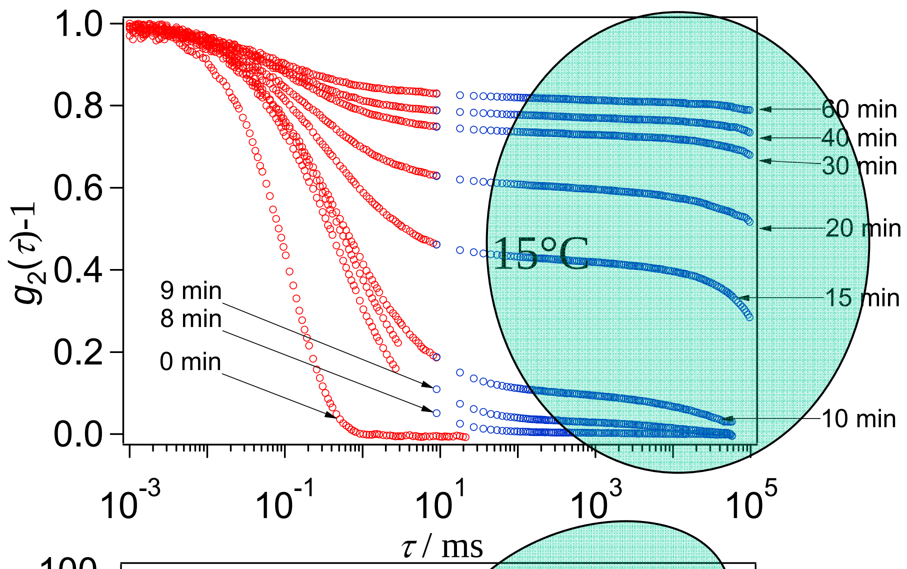
→ (Spin) glass like dynamics !

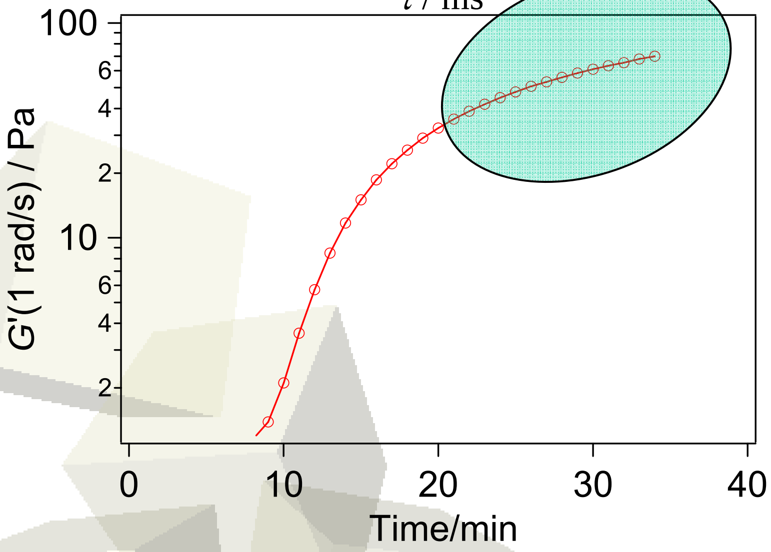
→ Memory and Ageing ?

Ageing is a physical property of systems trapped far from equilibrium → usually they get harder

A. Parker and V. Normand, cond-mat/0306056

Slow Relaxation





Gelatine/Collagen 2%w/w Tracer Latex 2%w/w (d=720nm)

Collaboration with Alan Parker, Valery Normand (Firmenich, Geneva) and M. Lechtenfeld (Gelita Europe, Eberbach, D)

heated to 25°C

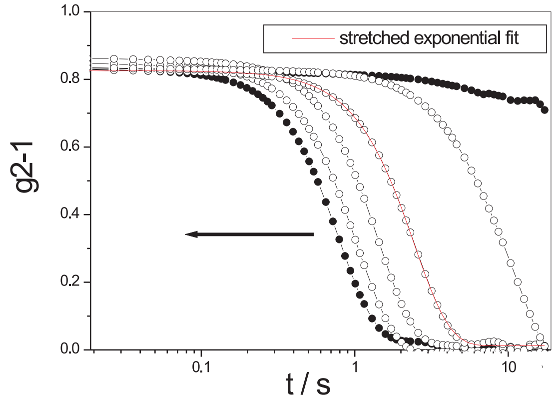
at 1°C/min

Three stage melting

I) Rejuvenation

old (well aged) structures disappear

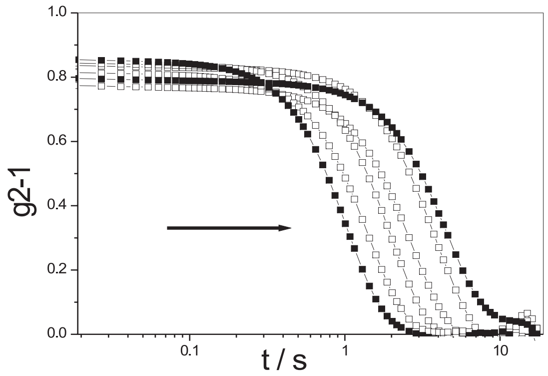
(start T ramp) 0min< time < 2min



II) New structures

New structures are formed and start to age

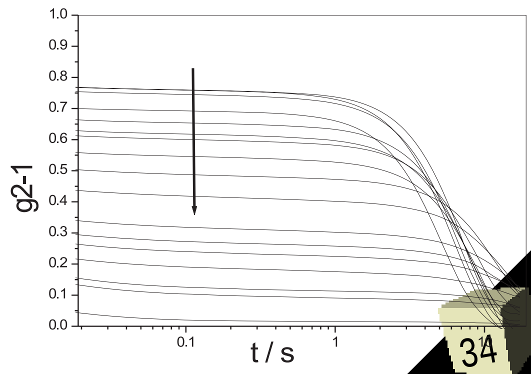
2min< time < 4min



III) Melting

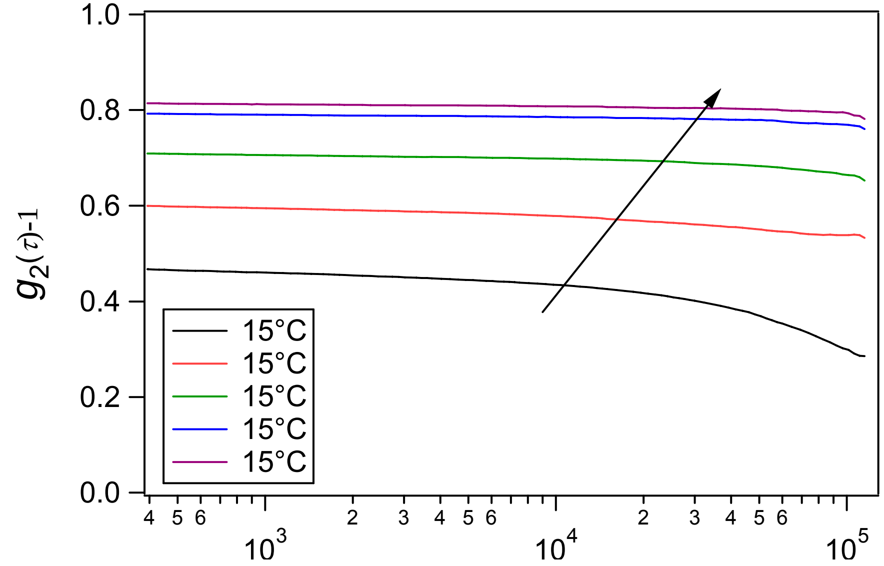
Gel melts partially and new structures age

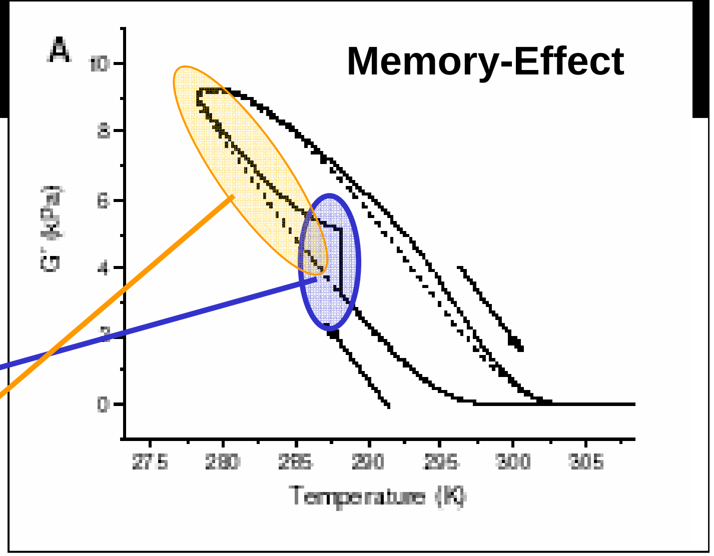
4min< time < 14min

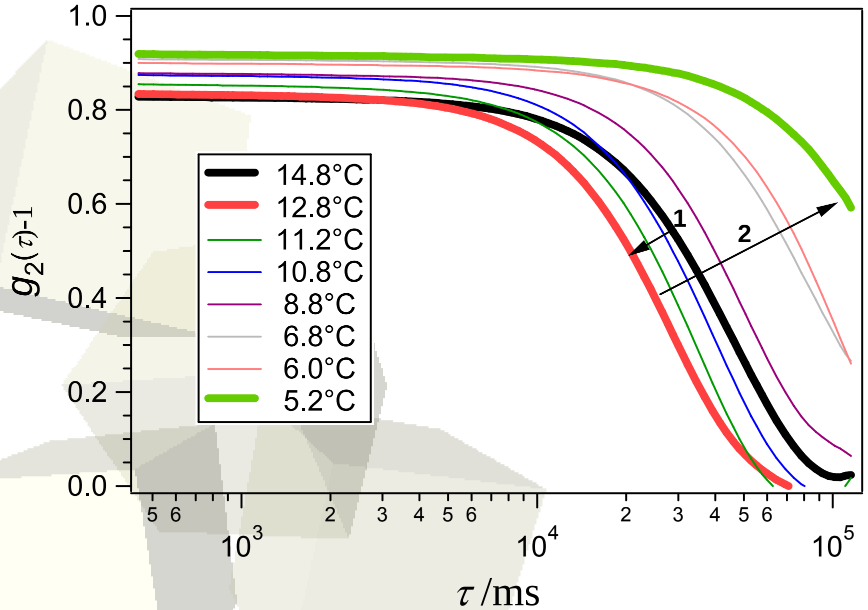


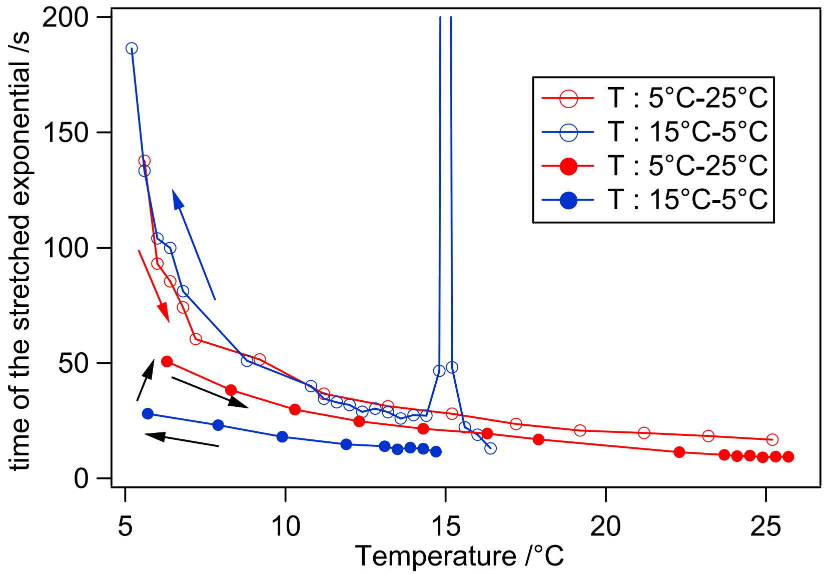
The same happens when temperature is <u>decreased</u>:

Rejuvention but Hardening









Goal: Microscopic insight into ageing and memory

Summary and Conclusions

- Modern scattering techniques allow characterisation of dense particle assemblies.

  - Combined light and neutron scattering (SANS)
  - 3D-Dynamic light scattering
  - Diffusing Wave Spectroscopy (DWS)
  - slow relaxation processes and solid media

- Structure and Dynamics in Turbid Suspensions

- Elastic properties around the sol-gel transition

- Optical Microrheology: Links the microscopic dynamic to the macroscopic mechanic (visco-elastic) properties.

FN SNF
Fonds national suisse
Schweizerischer Nationalfonds
Fondo nazionale svizzero
Swiss National Science Foundation

KTI/CTI

Finally: my point of view + some ideas and suggestions about

Applications of XPCS !?

Why XPCS ?

Unique advantages of XPCS

- o extended q-range, self-motion on nanoscales
- o Structure and dynamics in a single shot
- o unlimited access to dense and turbid media, full q-resolution (unlike DWS)
- o fast (multi-speckle) data acquisition

Problems

- o (Often) Limited temporal resolution, in particular since $\tau = 1/Dq^2$ (both D and q increase for many nanoscale systems)
- o beam damage

Immediate applications of high interest

- o Slow Relaxations in nanoscale systems (nanoparticles, proteins, polymers)
- o Glasses, Nanocomposites, Arraying nanoparticles/Phase behaviour

Thank you for your attention !