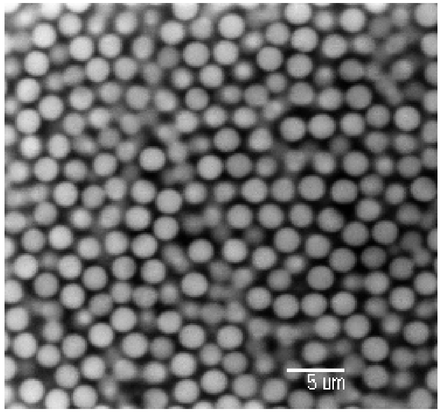
Dynamical heterogeneity in the glass and jamming transitions of soft systems

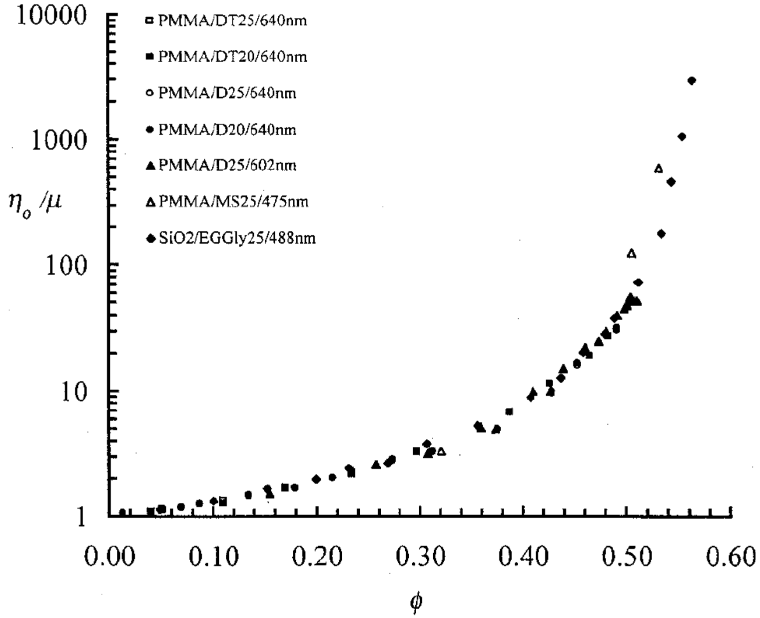
L. Cipelletti

LCVN, Université Montpellier 2 and CNRS

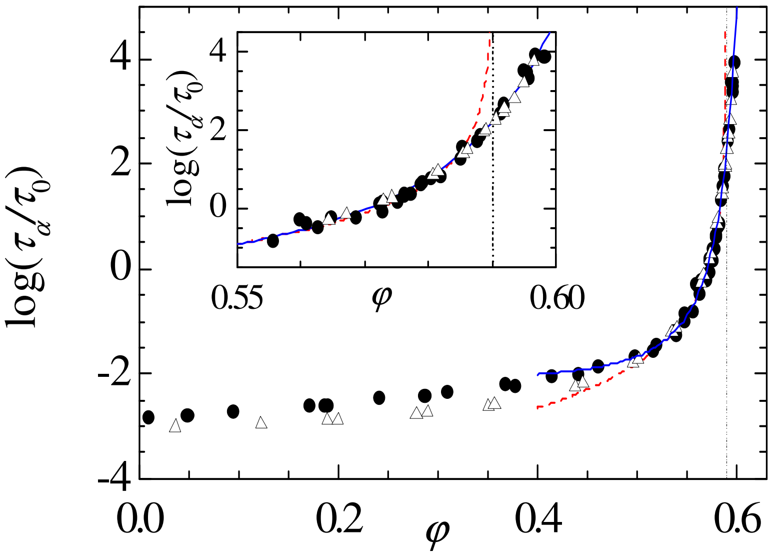
Soft glassy/jammed materials



E. Weeks

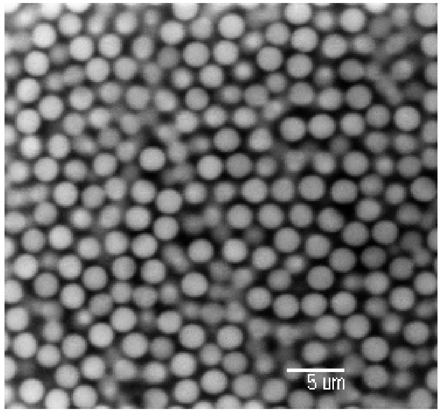


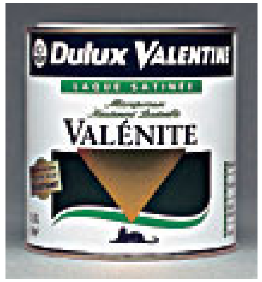
Cheng et al., Phys. Rev. E 2002



Brambilla et al., PRL 2009

Soft glassy/jammed materials





Outline

- **Probing average dynamics**
  - Dynamic light scattering
  - Multispeckle methods
- **Dynamical heterogeneity**
  - Motivation
  - Temporal fluctuations of the dynamics
  - Spatial correlation of the dynamics

Outline

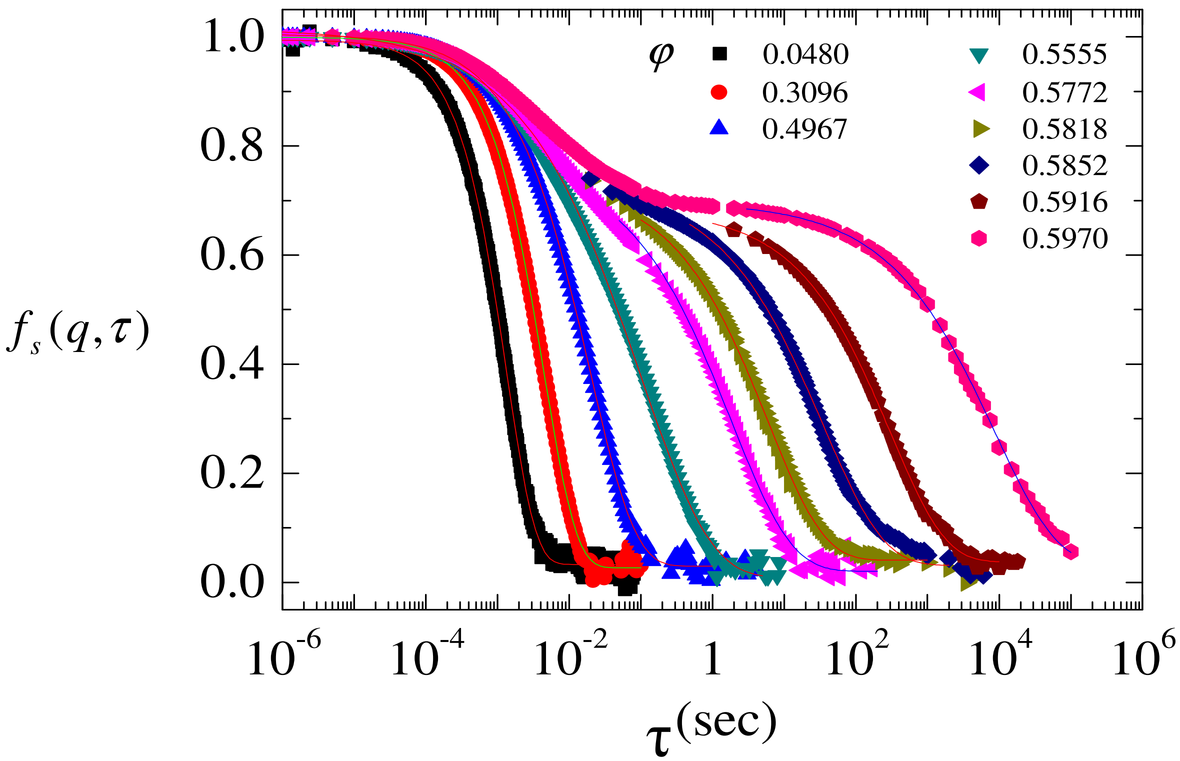
- **Probing average dynamics**
  - Dynamic light scattering
  - Multispeckle methods

- **Dynamical heterogeneity**
  - Motivation
  - Temporal fluctuations of the dynamics
  - Spatial correlation of the dynamics

Average Dynamics

Dynamic structure factor (intermediate scattering function):

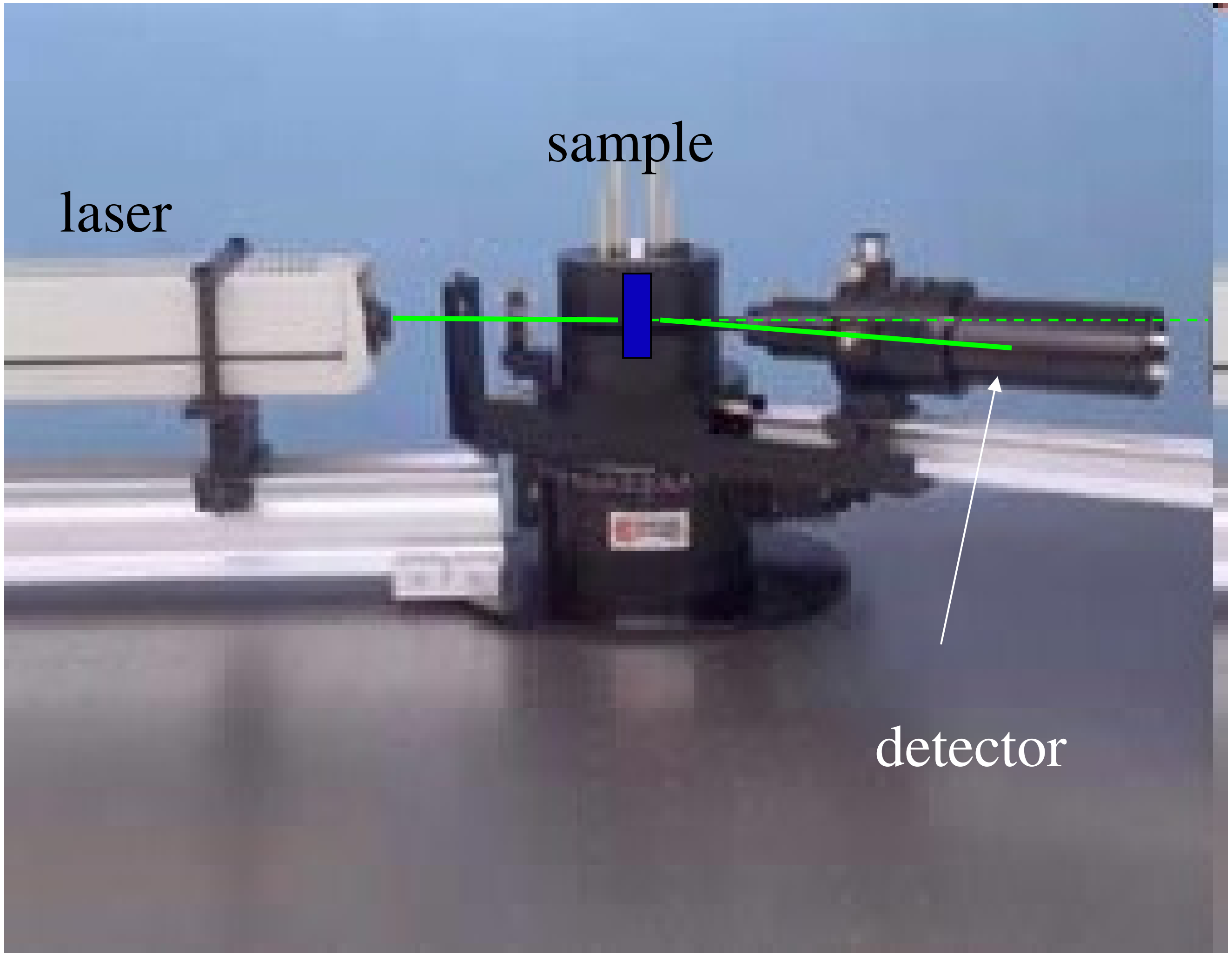
$$f(q,\tau) = \left\langle \frac{1}{N} \sum_{j,k=1}^{N} \exp\left[-i\mathbf{q}\cdot\left(\mathbf{r}_j(0) - \mathbf{r}_k(\tau)\right)\right] \right\rangle$$



Colloidal hard spheres

Brambilla et al., PRL 2009

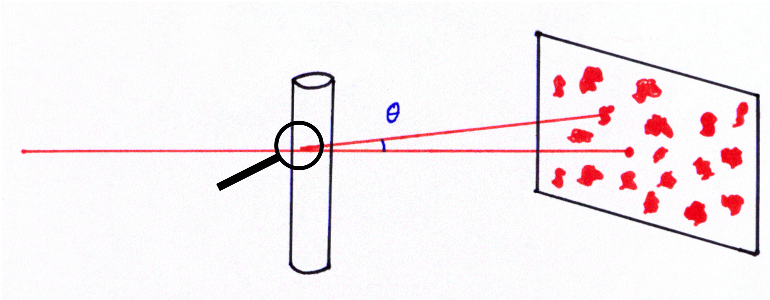
The DLS experiment

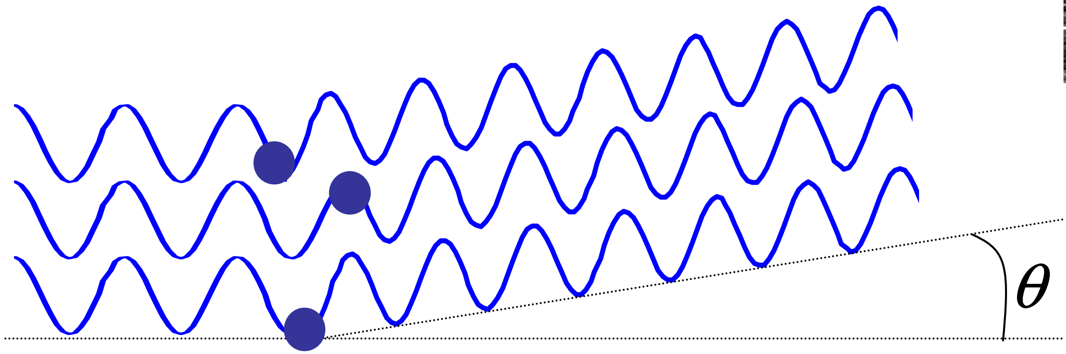


Brookheven

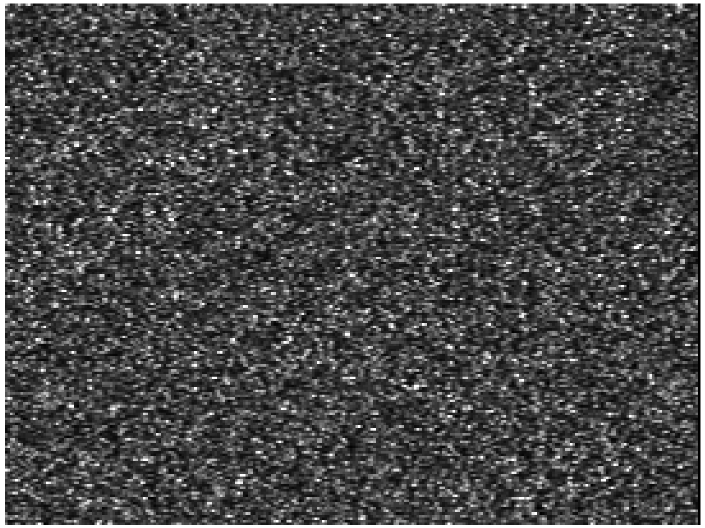
Light scattering: the concept

A light scattering experiment

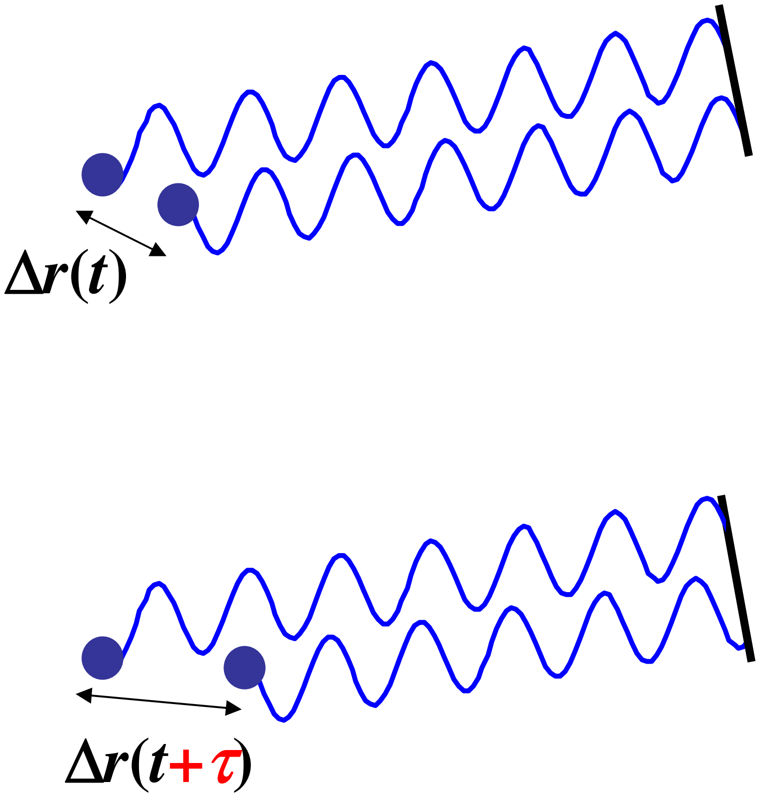


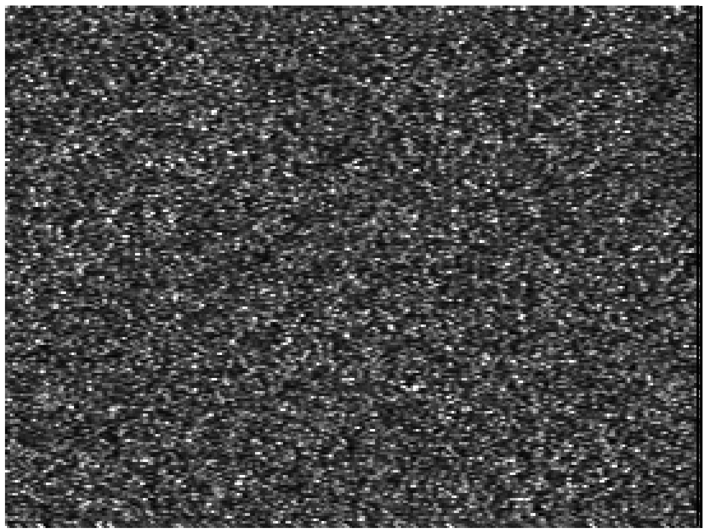


Speckle image

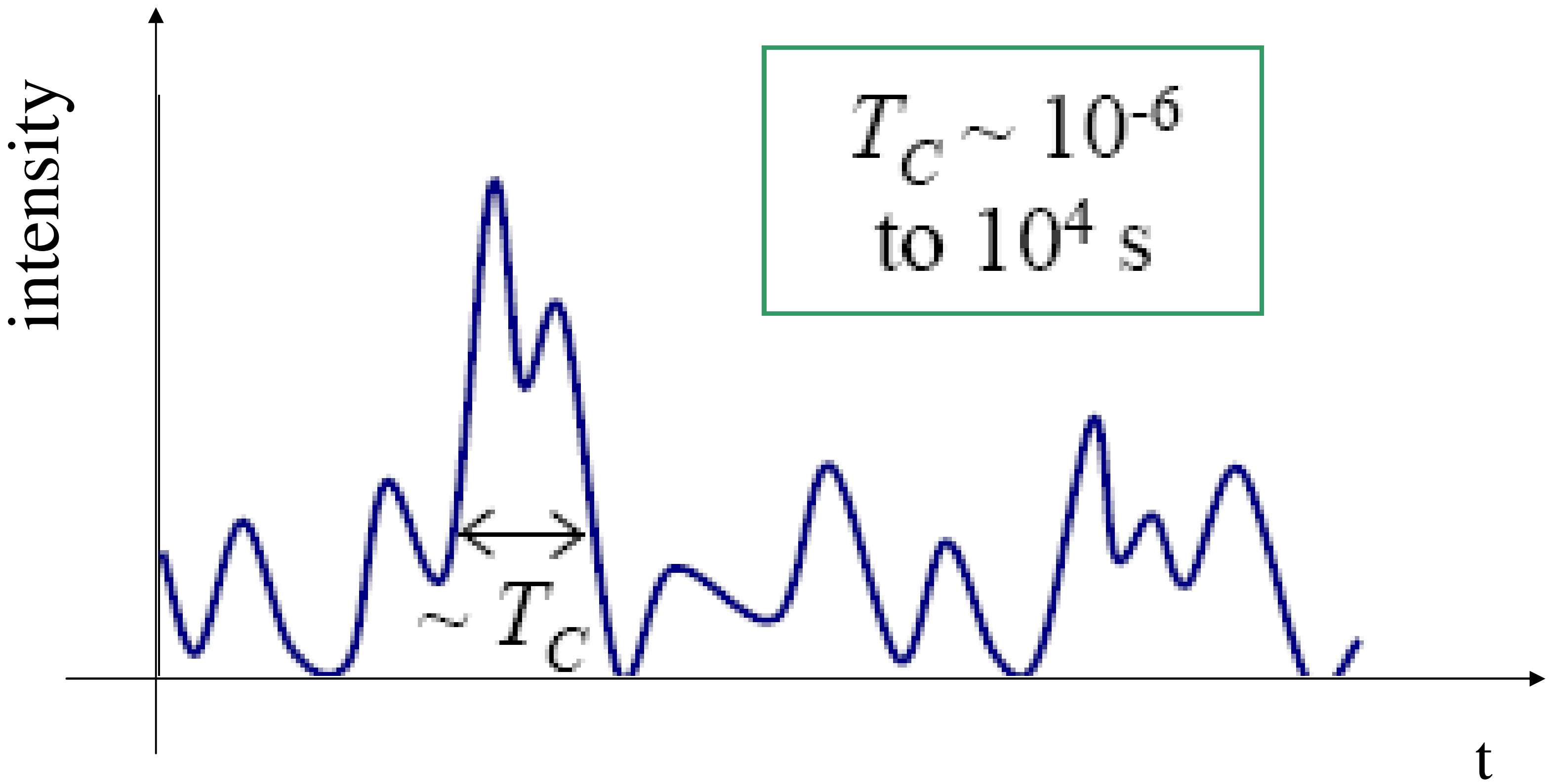


From particle motion to speckle fluctuations



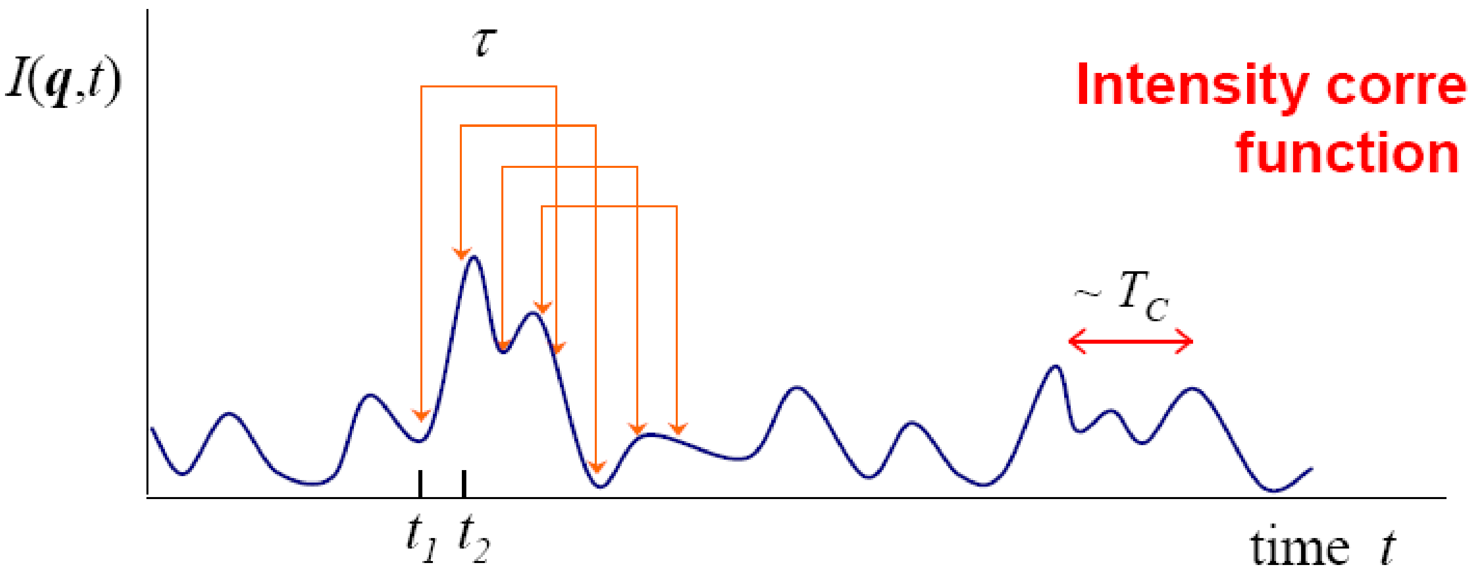


How to characterize intensity fluctuations?



from P. Pusey

Intensity correlation function

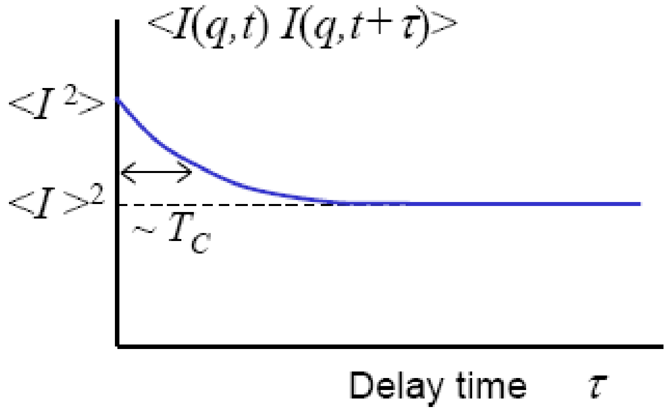


$$\langle I(q,0)I(q,\tau)\rangle = \frac{1}{T}\int_0^T \mathrm{d}t\, I(t)I(t+\tau) \qquad T >> T_C$$

Repeat for many different τ

$$\tau = 0, \quad \langle I(q,0)I(q,0)\rangle = \langle I^2(q)\rangle$$

$$\tau \to \infty, \quad \langle I(q,0)I(q,\tau)\rangle \to \langle I(q)\rangle^2$$



For 'ergodic' medium, time average (measure)
≡ ensemble average (calculate)

from P. Pusey

Intensity autocorrelation function and dynamic structure factor

Intensity a.f.

$$g_2(\tau)-1=\frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle\langle I(t+\tau)\rangle}-1=\frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle^2}-1$$

Field a.f.

$$g_1(\tau)=\ f(q,\tau)=\sqrt{\frac{g_2(\tau)-1}{\beta}}$$

Siegert relation

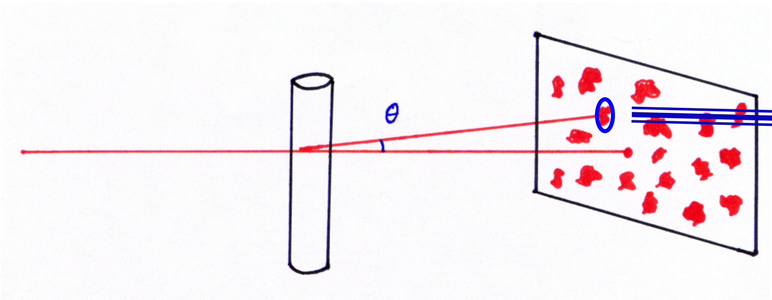
Speckle contrast (speckle/detector size ratio) → β

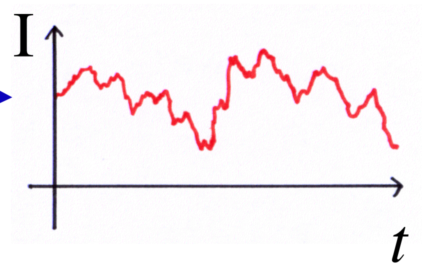
Outline

- **Probing average dynamics**
  - Dynamic light scattering
  - Multispeckle methods
- **Dynamical heterogeneity**
  - Motivation
  - Temporal fluctuations of the dynamics
  - Spatial correlation of the dynamics

Multispeckle method

Traditional technique:





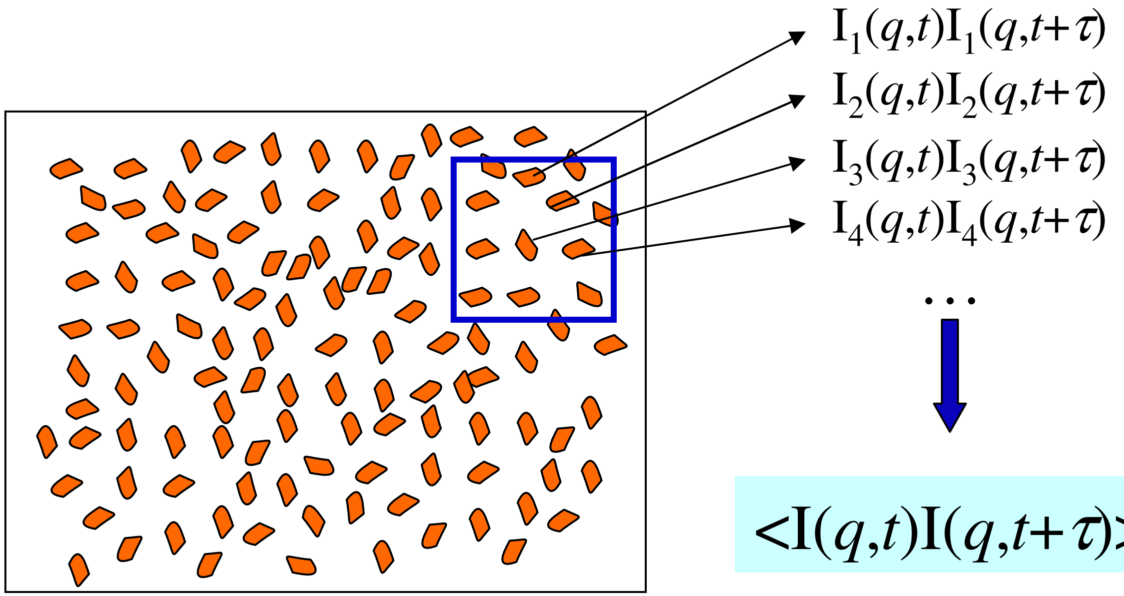
- we *measure* : $\langle I(t)I(t+\tau) \rangle_{\text{Time}}$
- we *want*: $\langle I(t)I(t+\tau) \rangle_{\text{Ensemble}}$

- **non-ergodic** samples
- **“slow”** samples
- **non-stationary** samples

?

The Multispeckle technique

Average $g_2(\tau)$-1 measured **in parallel** for many “statiscally equivalent” **speckles**

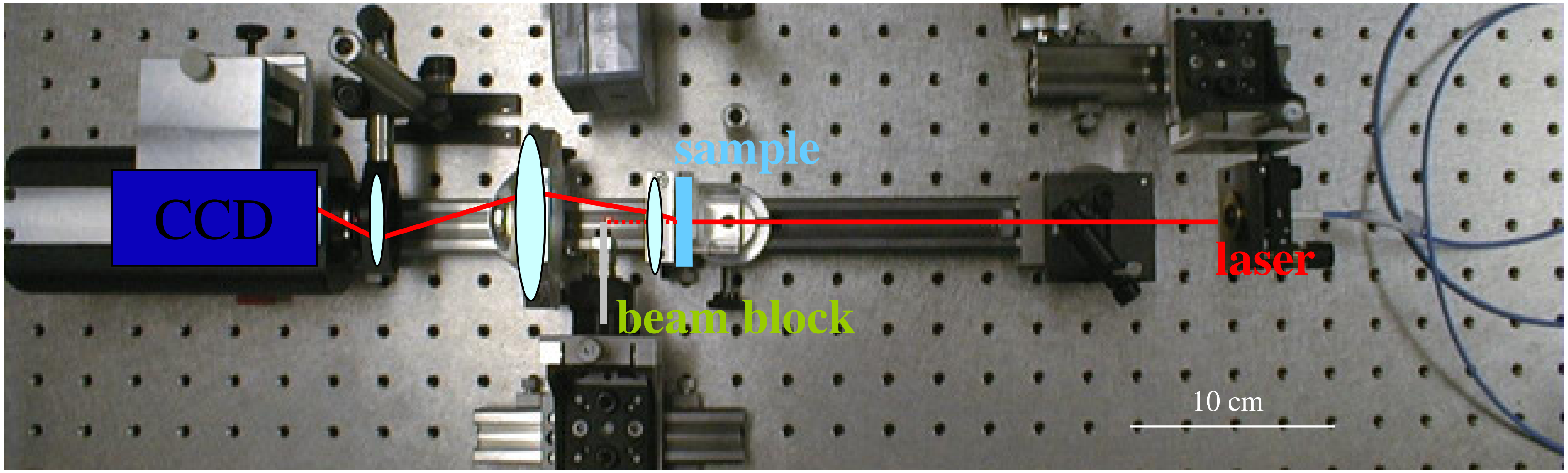


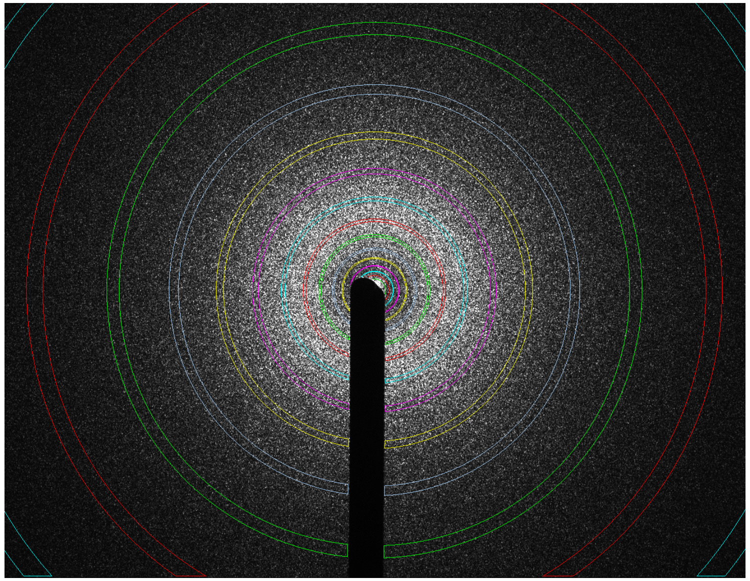
$\langle I(q,t)I(q,t+\tau)\rangle_{\text{speckle}}$

Multi-element detector (CCD),
software correlator

- **slow** relaxations, **non-stationary** dynamics
- **non-ergodic** samples
- **dynamical heterogeneity**

Small angle multispeckle setup





"Statiscally equivalent" speckles belong to the **same ring of pixels** ($|\mathbf{q}|$ = const.)

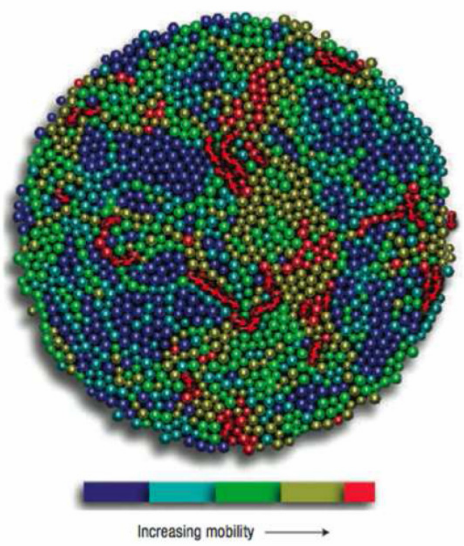
Outline

- **Probing average dynamics**
  - Dynamic light scattering
  - Multispeckle methods

- **Dynamical heterogeneity**
  - Motivation
  - Temporal fluctuations of the dynamics
  - Spatial correlation of the dynamics

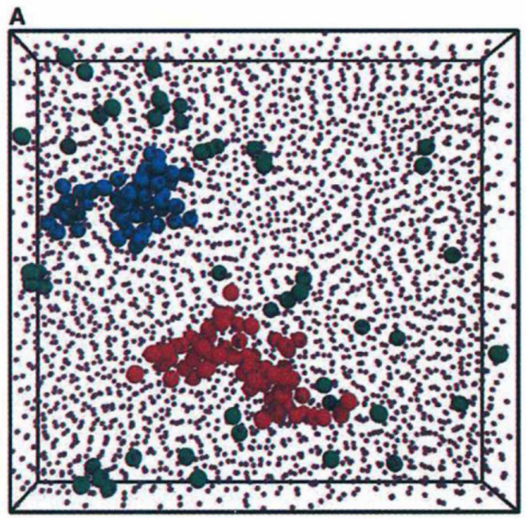
Dynamical heterogeneity is ubiquitous!

Granular matter



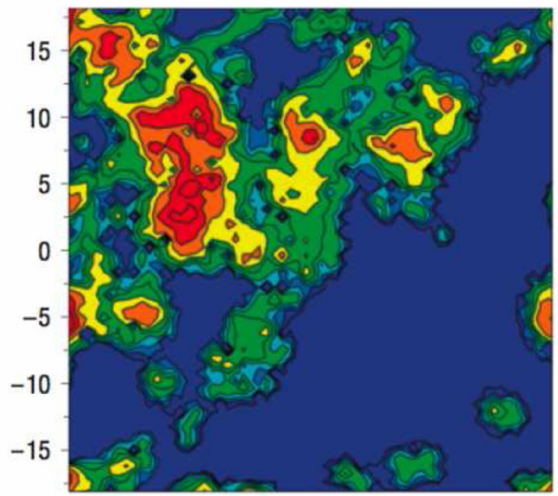
Keys et al. Nat. Phys. 2007

Colloidal Hard Spheres



Weeks et al. Science 2000

Repulsive disks

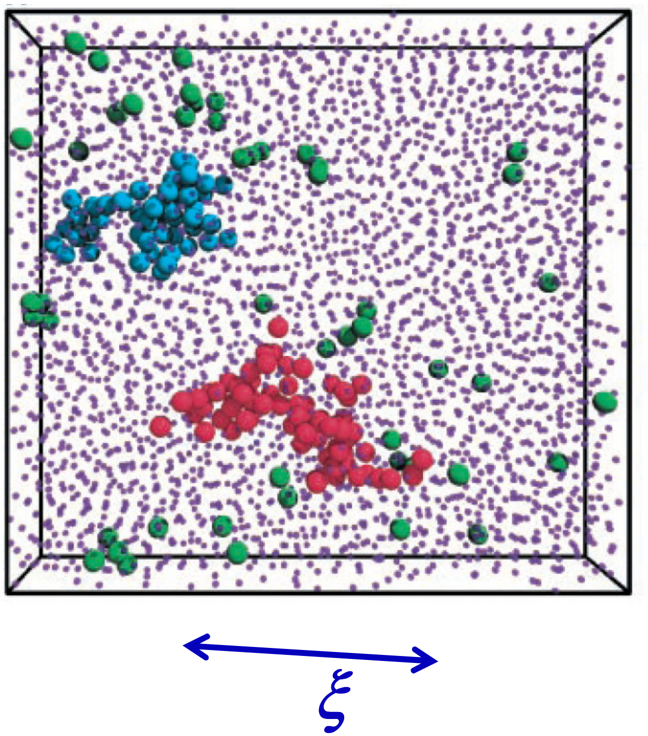


A. Widmer-Cooper Nat. Phys. 2008

Why are DHs important?

Crucial role in the slowing down of the dynamics close to the glass transition

- Adam-Gibbs: relaxation through **cooperatively rearranging regions.** Their size **increases** approaching the glass transition.
- Glass transition as a (dynamical) **critical phenomenon** ?
- DHs may allow one to **discriminate between competing theories**



Weeks et al. Science 2000

What quantities should we measure?

Space- and time-resolved correlation functions $f(t,t+\tau,\mathbf{r})$ or particle displacement

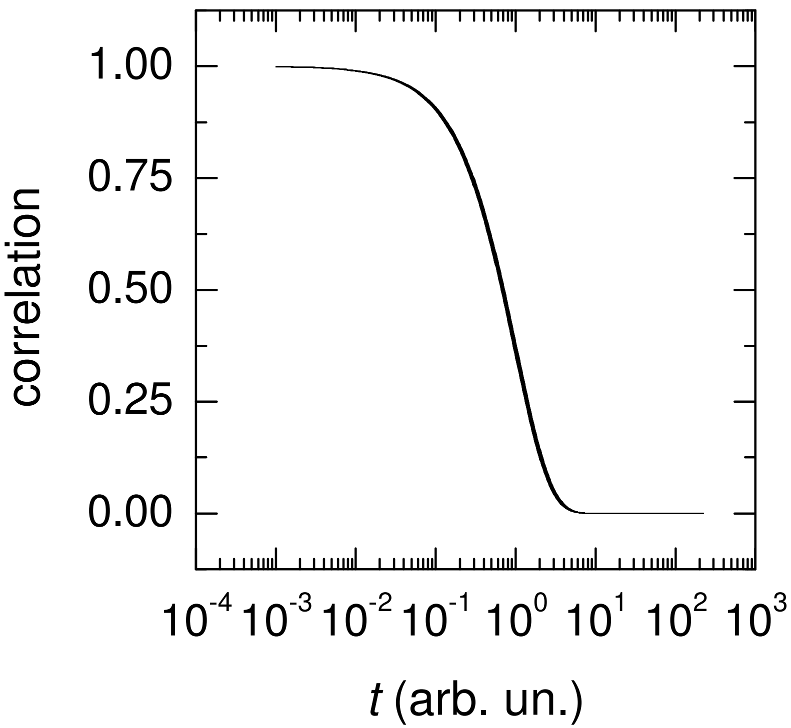
- **Simulations** (far from T_g!)
- (Confocal) **microscopy** on colloidal systems (limited statistics, stringent requirements on particles (size, optical mismatch…), can not go very close to φ_g…)

Outline

- **Probing average dynamics**
    - Dynamic light scattering
    - Multispeckle methods

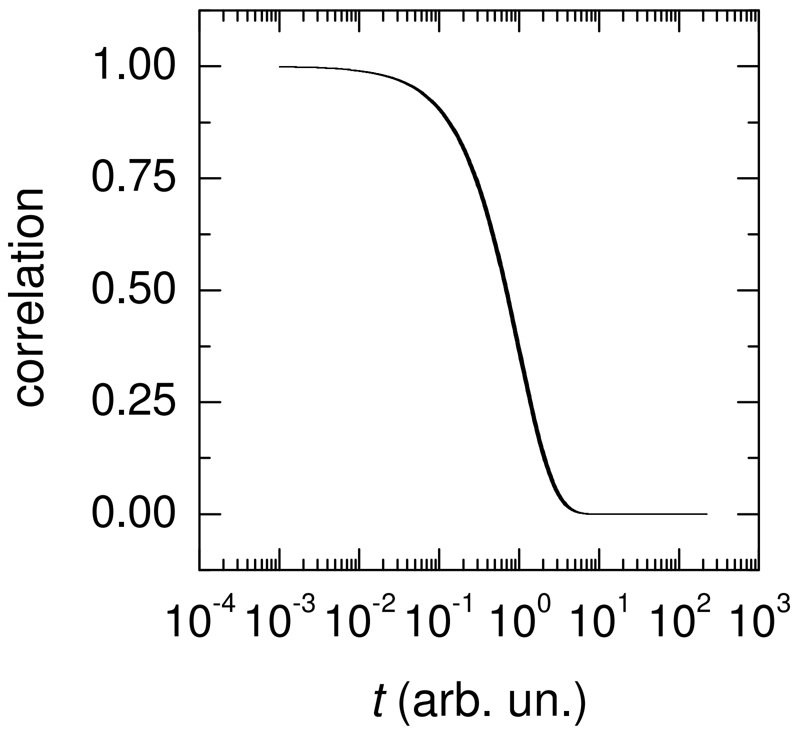
- **Dynamical heterogeneity**
    - Motivation
    - Temporal fluctuations of the dynamics
    - Spatial correlation of the dynamics

Temporally heterogeneous dynamics

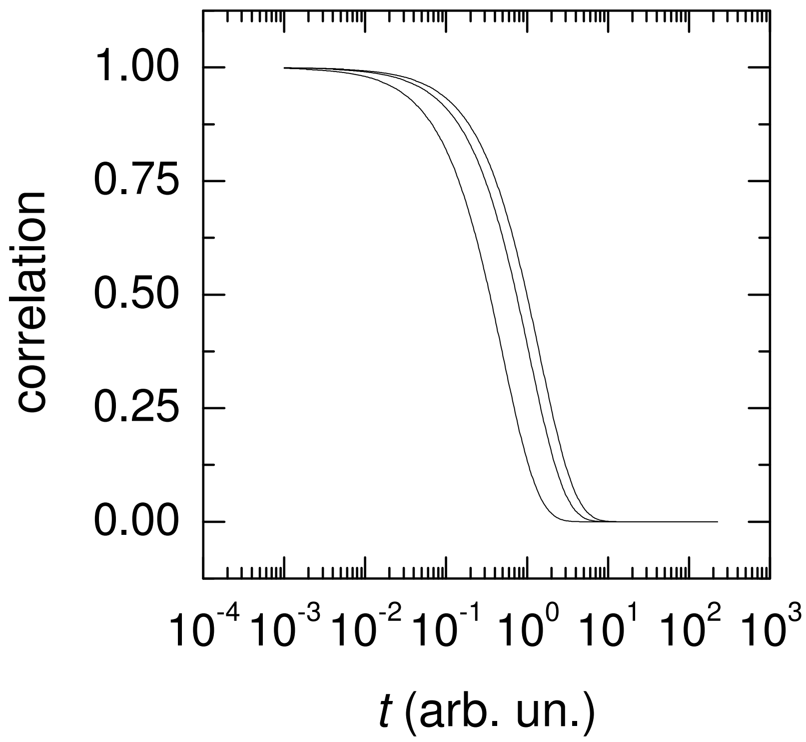


homogeneous

Temporally heterogeneous dynamics

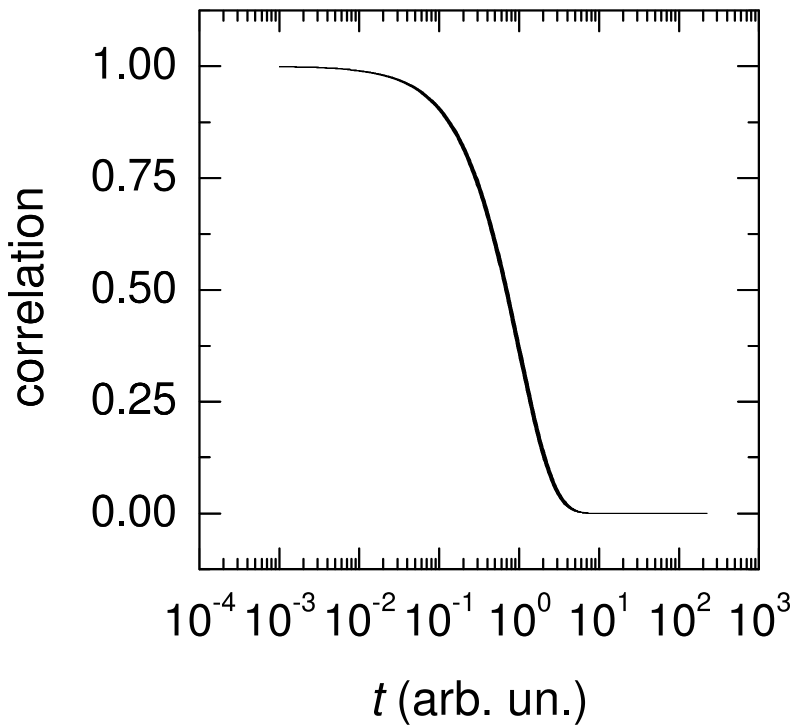


homogeneous

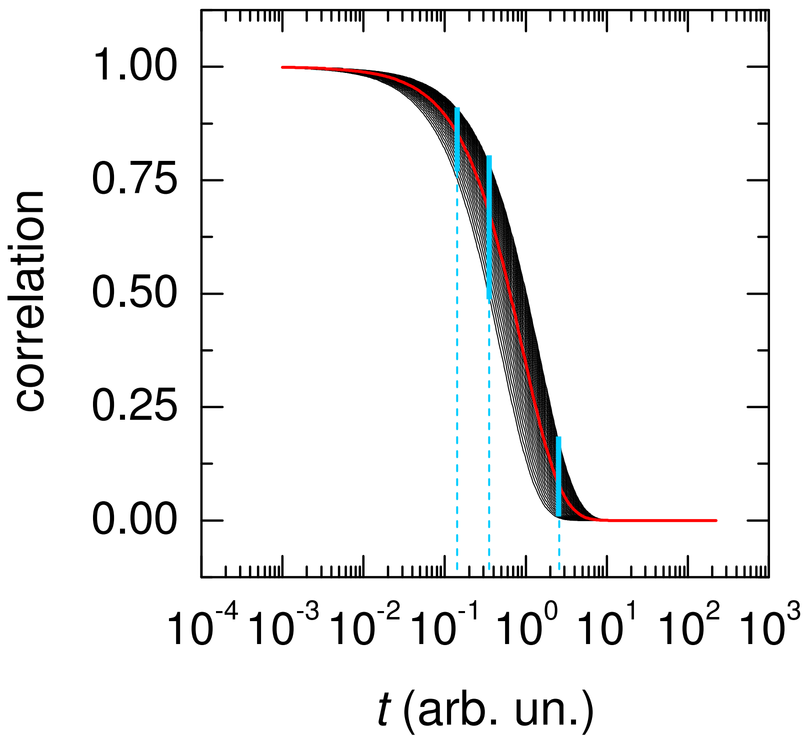


heterogeneous

Temporally heterogeneous dynamics



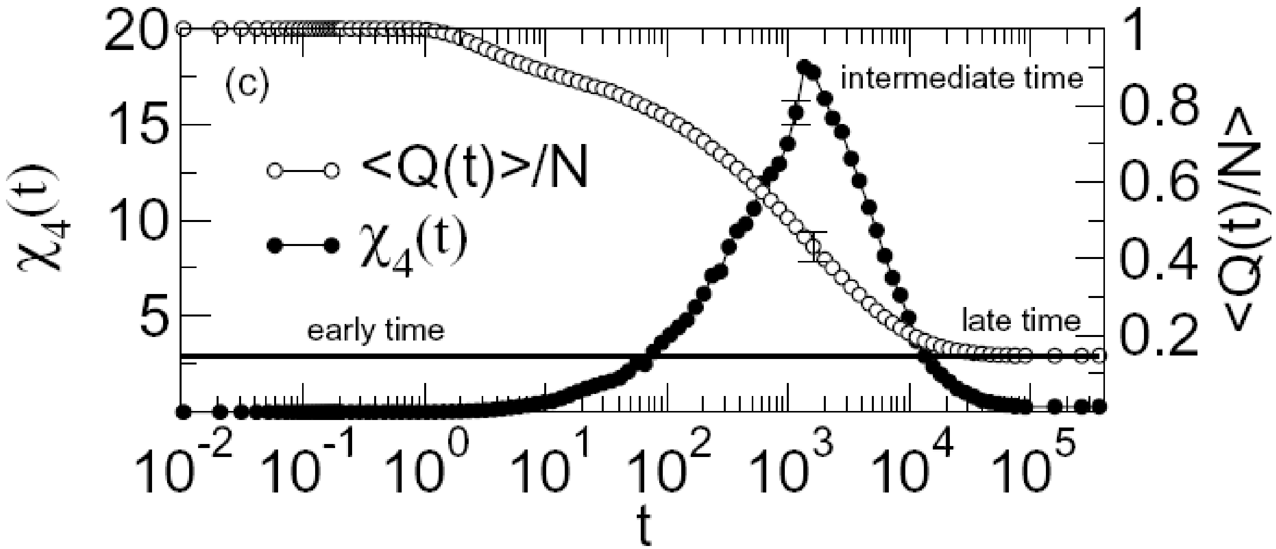
homogeneous



heterogeneous

Dynamical susceptibility in glassy systems

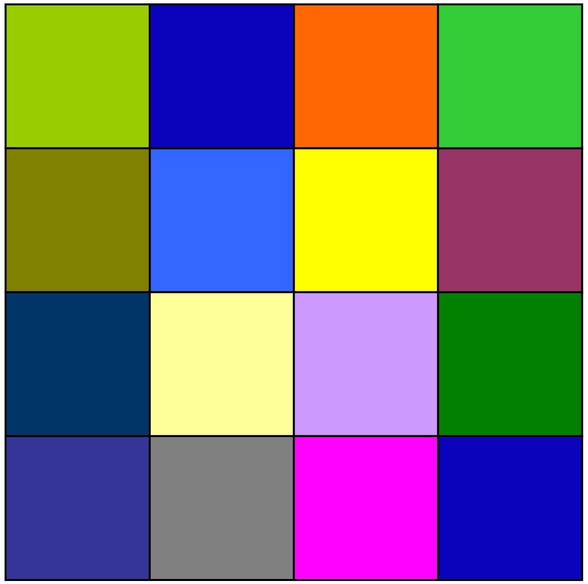
Supercooled liquid (Lennard-Jones)



Lacevic et al., Phys. Rev. E 2002

$$\chi_4 = N \, \mathrm{var}[Q(t)]$$

Dynamical susceptibility in glassy systems



N regions

$\chi_4 = N \,\mathrm{var}[Q(t)]$

$\chi_4 \Longleftrightarrow$ dynamics spatially correlated

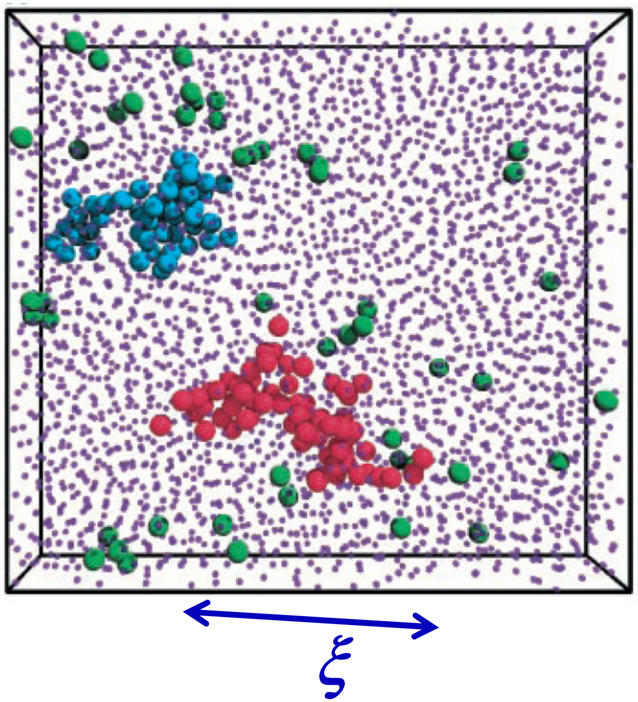
Dynamical susceptibility in glassy systems

$$G_4(r;t) = \langle c(r;t,0)c(0;t,0)\rangle - \langle c(0;t,0)\rangle^2$$

Spatial correlation of the dynamics

$$G_4(r;0,t) \sim \frac{A(t)}{r^p} e^{-r/\xi_4(t)}$$

$$\chi_4(t) = \int \mathrm{d}r\, G_4(r;t)$$



Weeks et al. Science 2000

How can we measure χ_4?

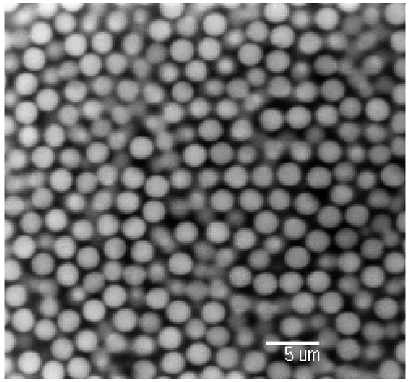
- « Smart » trick: **estimate χ_4 from average dynamics**
- **Time-resolved light scattering** experiments (TRC)

How can we measure χ_4?

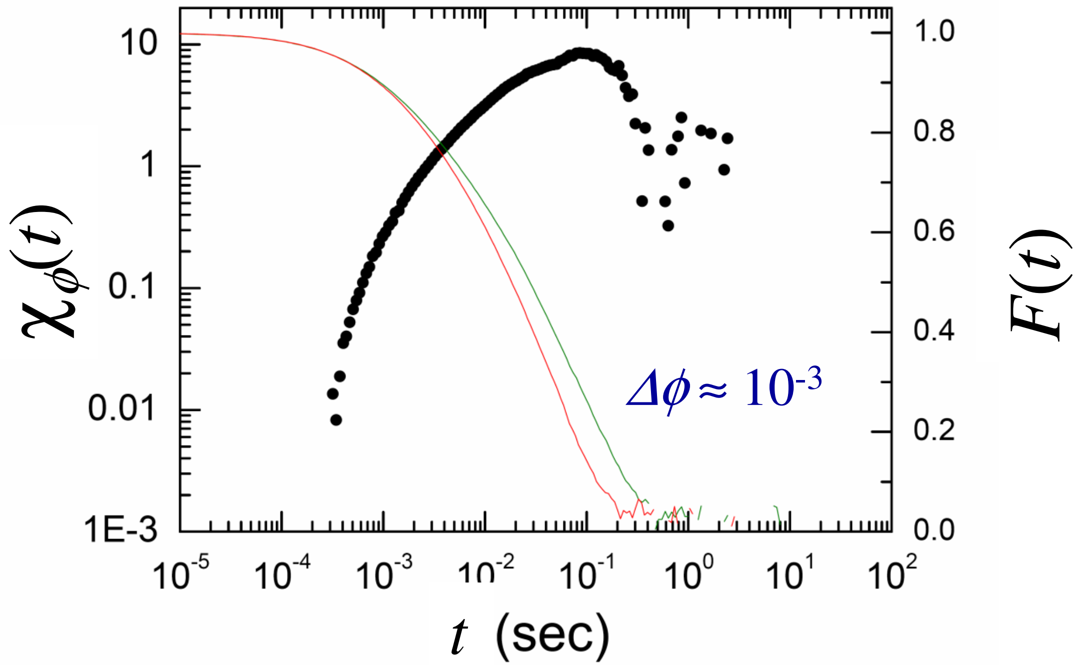
- « Smart » trick: **estimate χ_4 from average dynamics**

- **Time-resolved light scattering** experiments (TRC)

The smart trick applied to colloidal HS



Define $\chi_\phi(t) = \frac{\partial F(t)}{\partial \phi}$



Dynamical heterogeneity: the theoreticians' trick

Goal: calculate 4-point dynamical susceptibility χ_4 ~ size of rearranged region

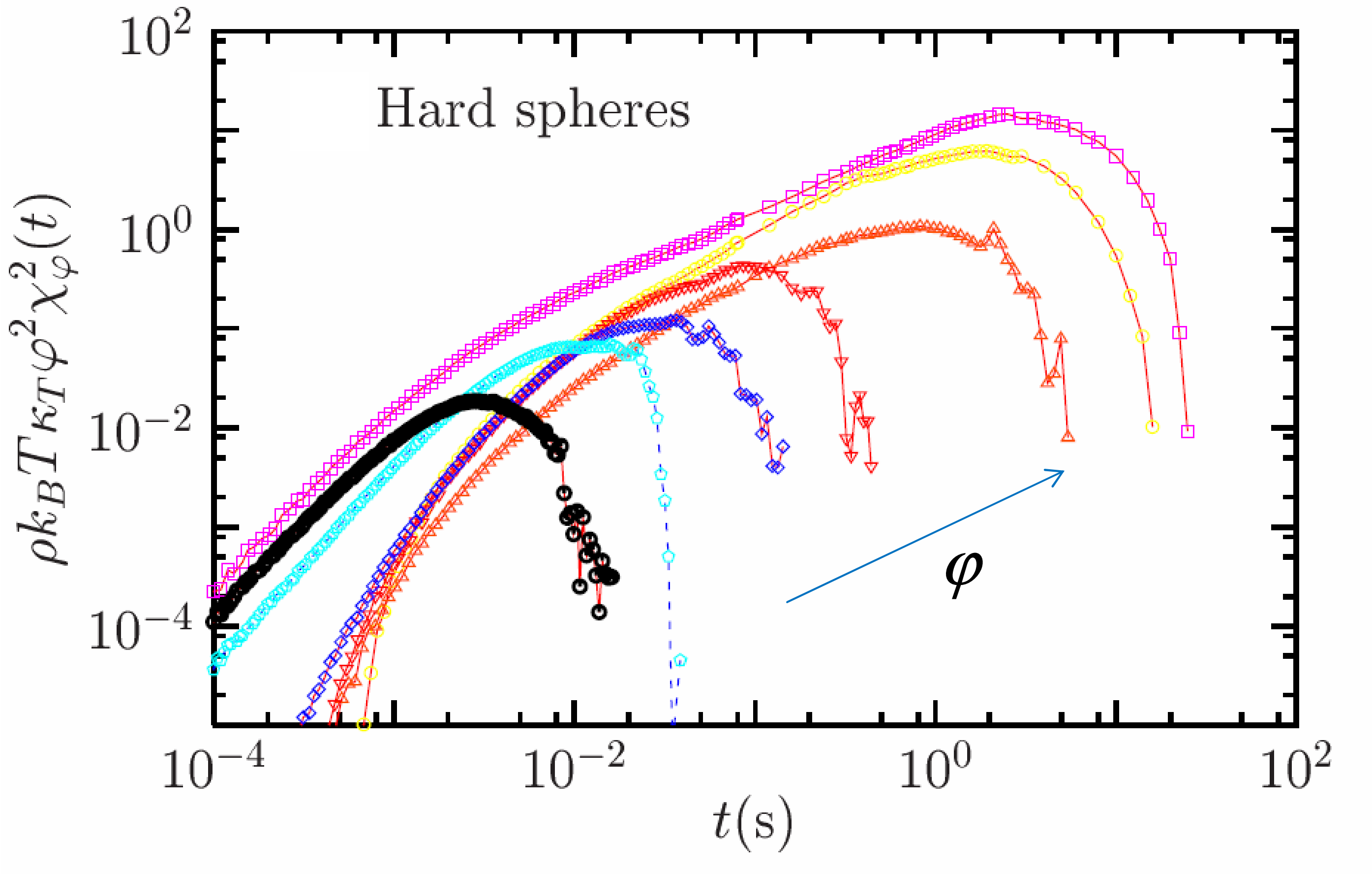
For colloidal HS at high φ

$$\chi_T(t) = \frac{\partial f(t)}{\partial T} \qquad \chi_\varphi(t) = \frac{\partial f(t)}{\partial \varphi}$$

$$\chi_4^{NPT}(t) = \chi_4^{NVE}(t) + \frac{k_B}{c_V} T^2 \chi_T^2(t) + S(0)\varphi^2 \chi_\varphi^2$$

Berthier et al., J. Phys. Chem. 2007

Evidence of a growing dynamic length scale



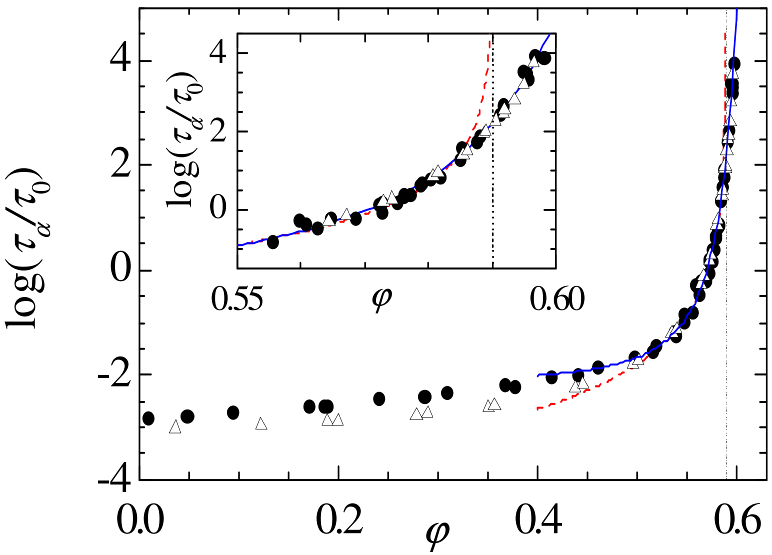
ϕ ~ 0.20 – 0.58

Berthier et al., Science 2005

Supercooled colloidal HS: beyond mode coupling theory

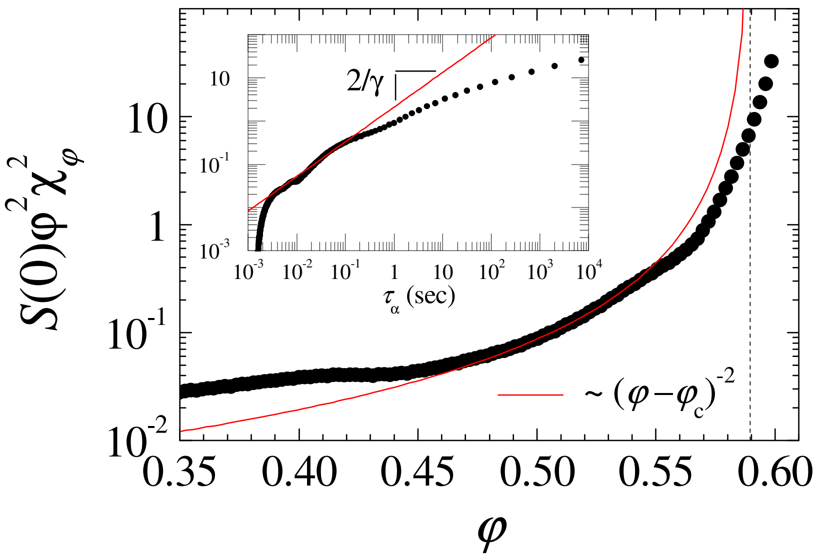
Average dynamics

Glass transition of Hard Spheres:
A new equilibrium regime beyond MCT



Dynamical heterogenity

« Dynamical susceptibility »:
Experimental evidence of a growing ξ on approaching the glass transition



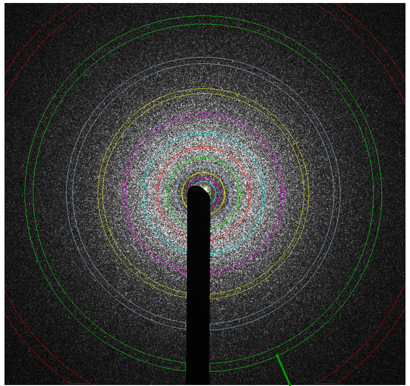
Brambilla et al., PRL 2009

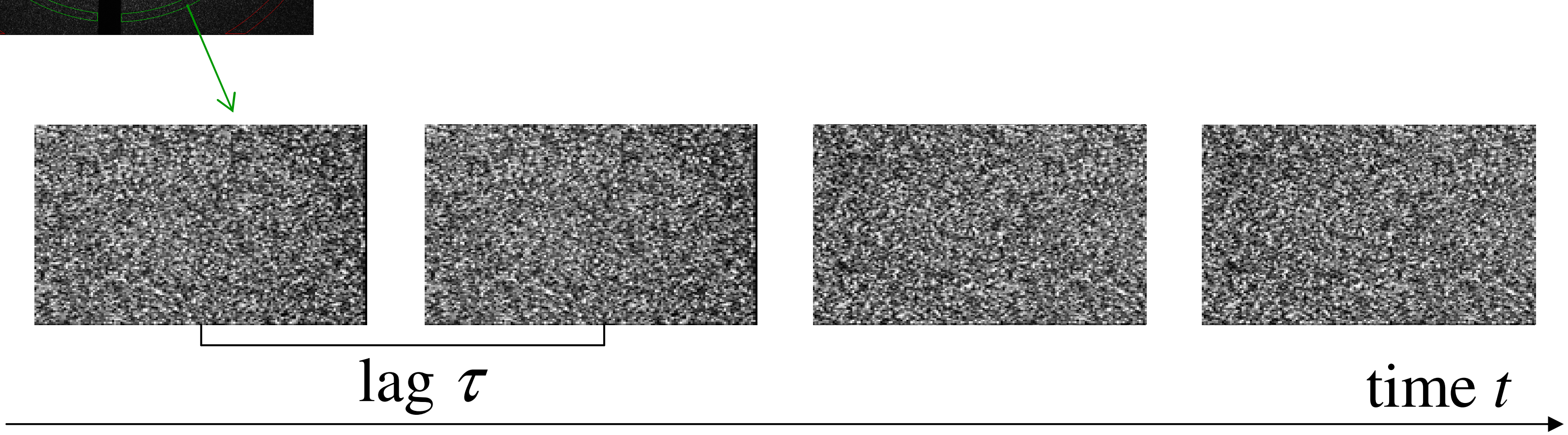
How can we measure χ_4?

- « Smart » trick: **estimate χ_4 from average dynamics**

- **Time-resolved light scattering** experiments (TRC)

Time Resolved Correlation





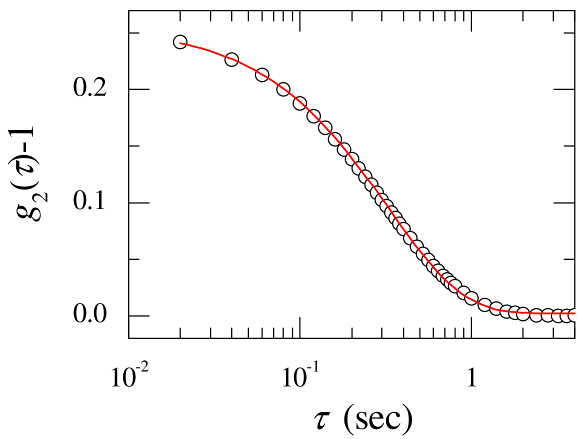
degree of correlation $c_I(t,\tau) = \dfrac{< I_p(t)\, I_p(t+\tau) >_p}{< I_p(t) >_p < I_p(t+\tau) >_p} - 1$

Cipelletti et al. J. Phys:Condens. Matter 2003,
Duri et al. Phys. Rev. E 2006

degree of correlation $c_I(t,\tau) = \dfrac{< I_p(t)\, I_p(t+\tau)>_p}{< I_p(t)>_p <I_p(t+\tau)>_p} - 1$

Average over t

intensity correlation function $g_2(\tau) - 1$



$g_2(\tau) - 1$ → Average dynamics

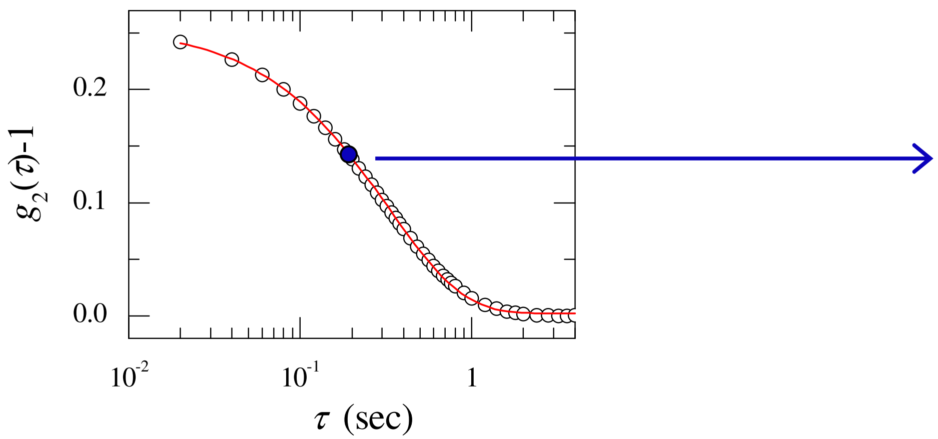
degree of correlation $c_I(t,\tau) = \dfrac{< I_p(t)\, I_p(t+\tau)>_p}{< I_p(t)>_p < I_p(t+\tau)>_p} - 1$

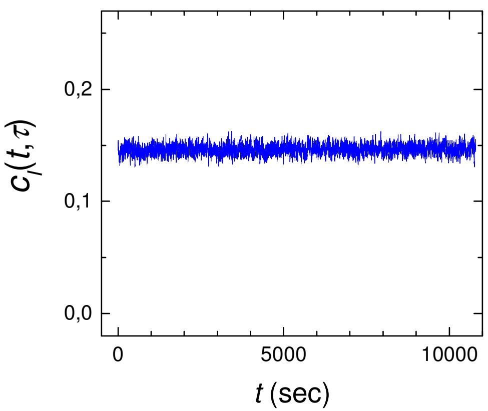
Average over t

intensity correlation function $g_2(\tau) - 1$

fixed τ, *vs.* t

fluctuations of the dynamics





$g_2(\tau) - 1$ → Average dynamics

Brownian particles

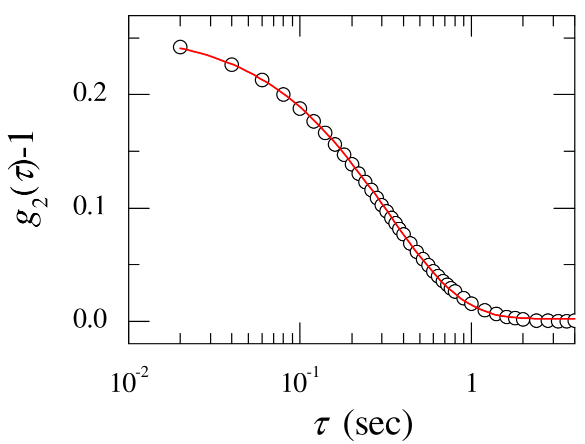
$$\textbf{degree of correlation } c_I(t_w,\tau) = \frac{< I_p(t_w)\, I_p(t_w+\tau)>_p}{< I_p(t_w)>_p < I_p(t_w+\tau)>_p} - 1$$

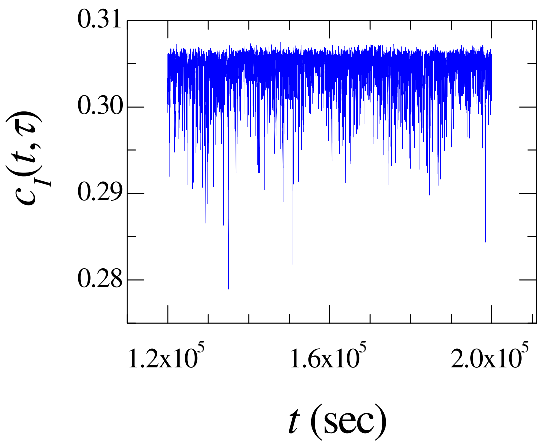
Average over t_w ↓

intensity correlation function $g_2(\tau) - 1$

↓ fixed τ, *vs.* t_w

fluctuations of the dynamics

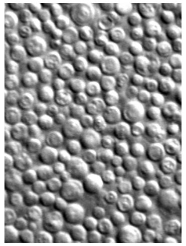




$g_2(\tau) - 1$ → Average dynamics

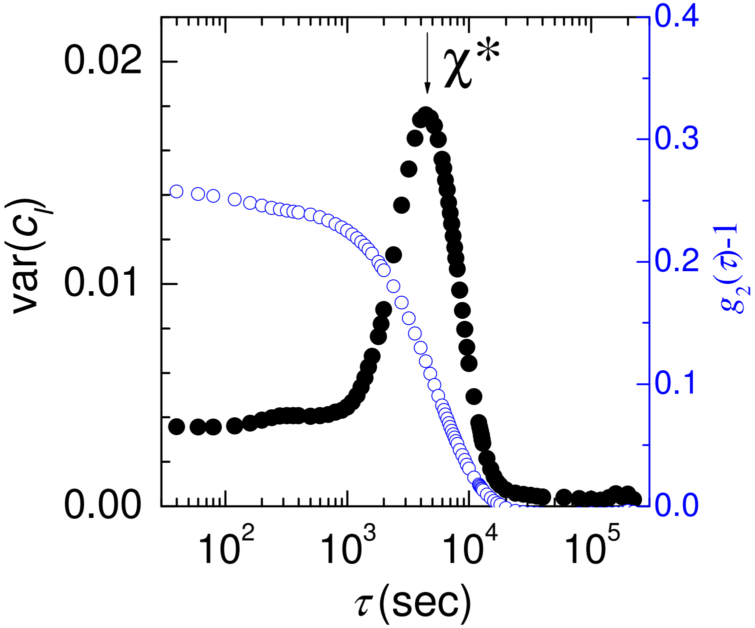
Soft spheres

« onion gel »



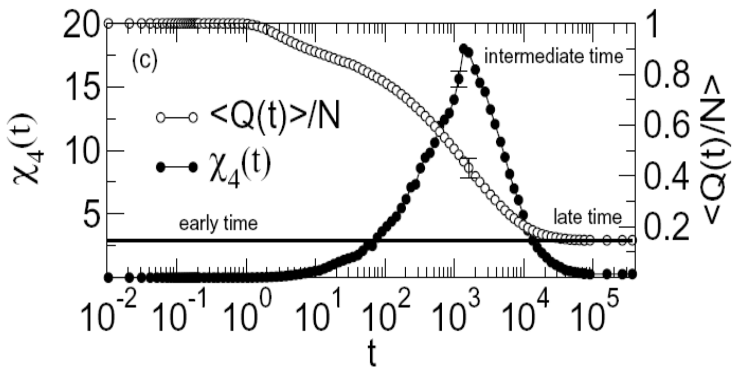
Variance of c_I: dynamical susceptibility

Polydisperse colloids close to maximum packing



Ballesta et al., Nat. Phys. 2008

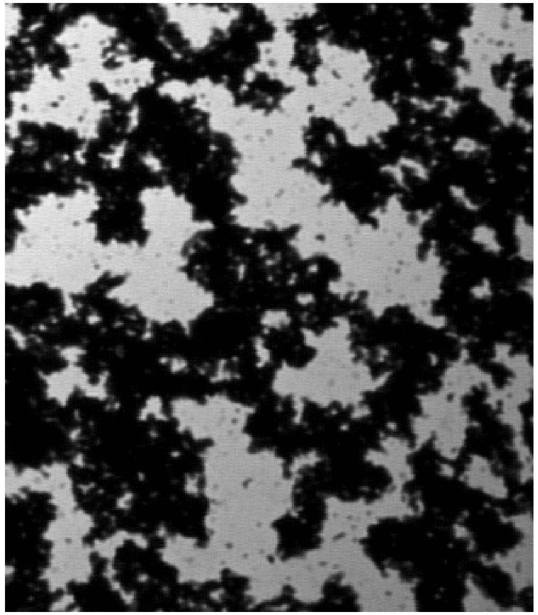
Supercooled Lennard Jones fluid



Lacevic et al., Phys. Rev. E 2002

XPCS measurements of the dynamics of a Carbon Black gel

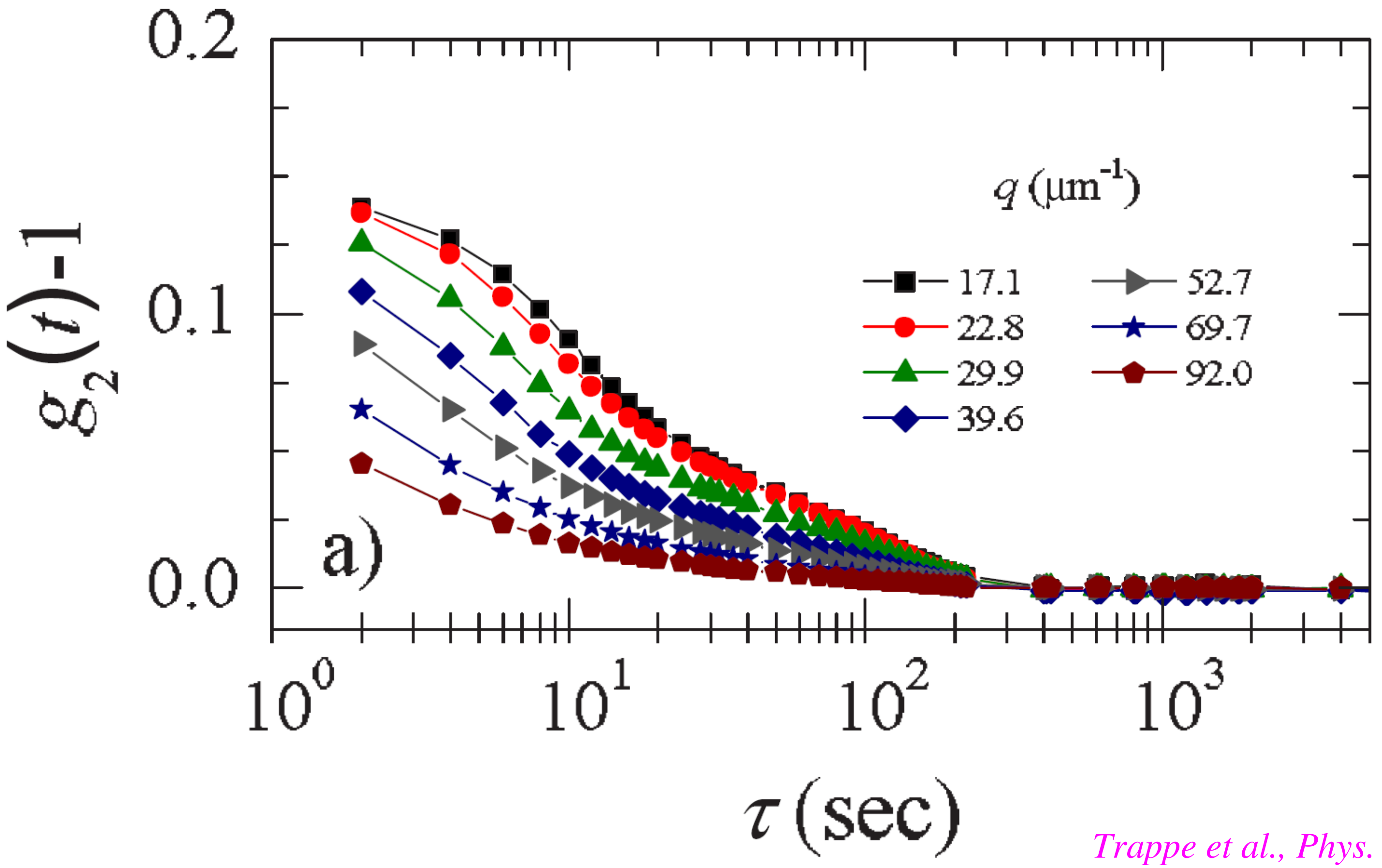
- Particle size R= 180 nm
- Suspended in mineral oil at $\varphi = 6\%$
- Attractive interactions controlled by adding a dispersant: $U \sim 12\ k_B T$ and $U \sim 30\ k_B T$
- XPCS @ ID10 Troika beamline (ESRF)



Trappe et al., Phys. Rev. E 2007

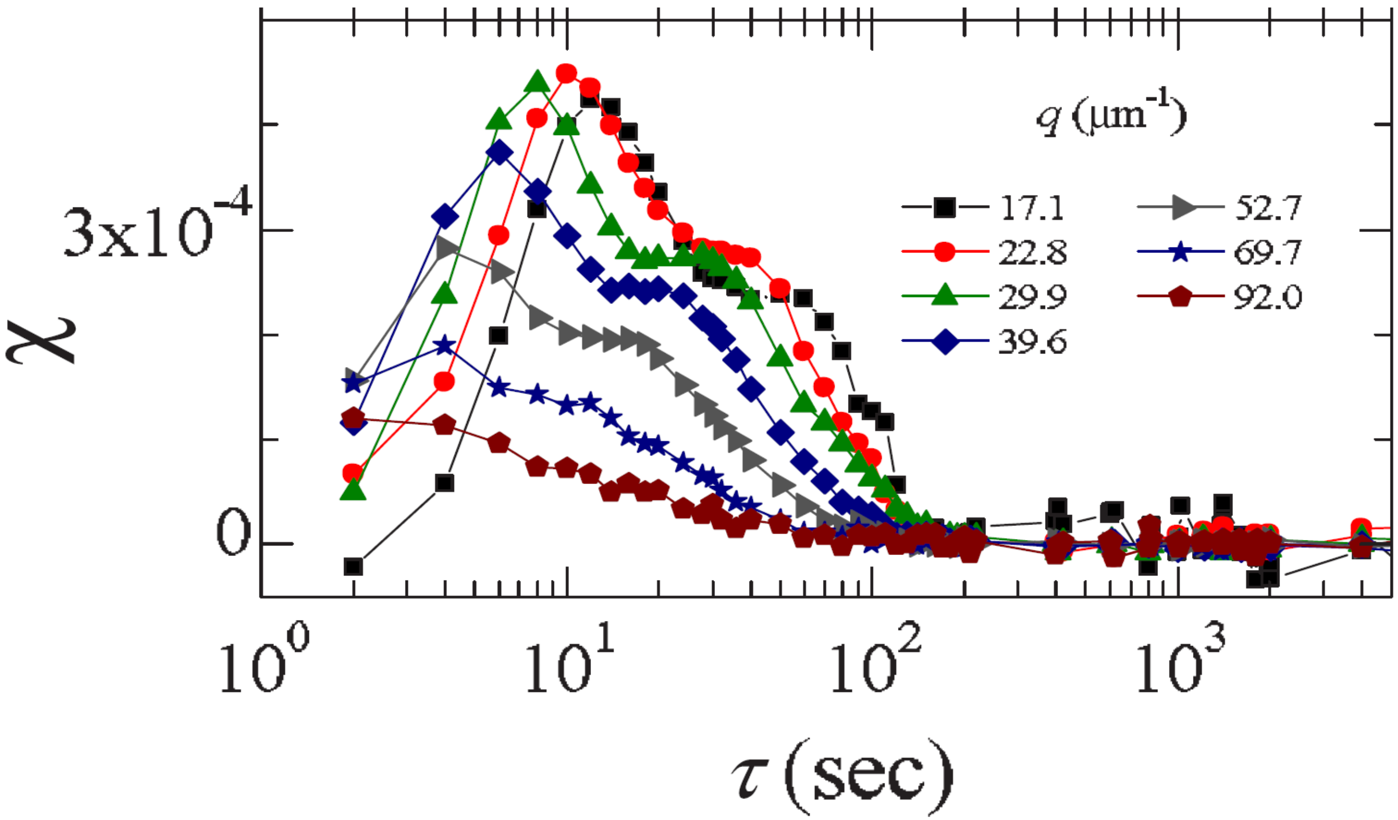
Average dynamics

***U* ~ 12 $k_B T$**



Trappe et al., Phys. Rev. E 2007

Fluctuations of the dynamics: dynamical susceptibility $\chi = \mathrm{var}[c_I]$

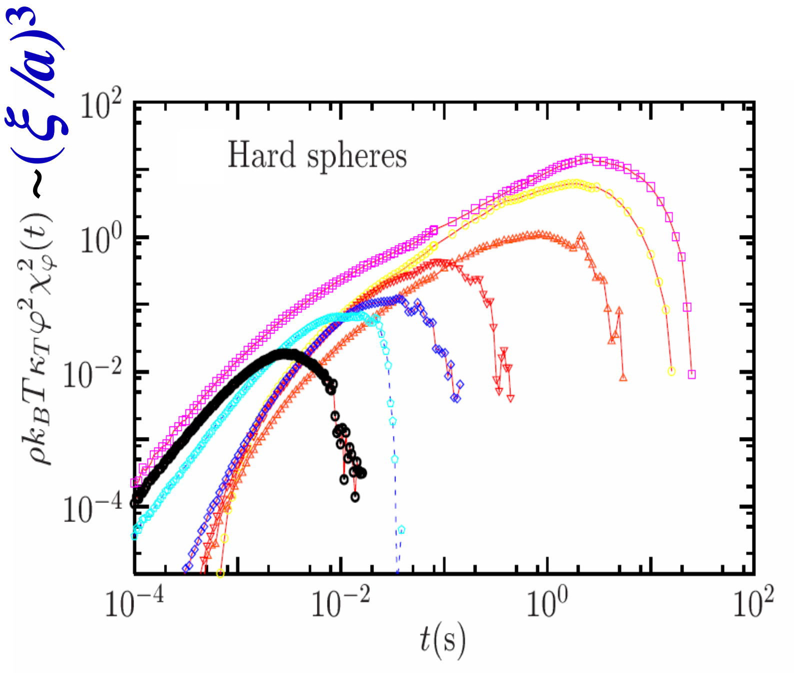


Trappe et al., Phys. Rev. E 2007

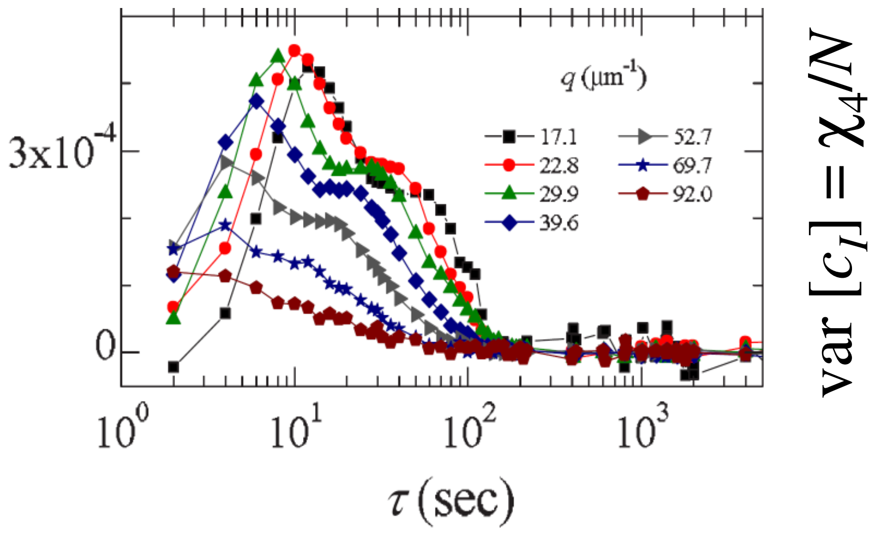
Are DH different at the glass and jamming transitions?

Supercooled HS approaching GT
- Equilibrium dynamics
- viscous fluid
- ξ ~ a few particle sizes

Jammed gels (+ foams, onions, …)
- Non-equilibrium dynamics (aging…)
- Elasticity dominates over viscosity
- ξ ~ thousands of particle sizes ?



Berthier et al., Science 2005



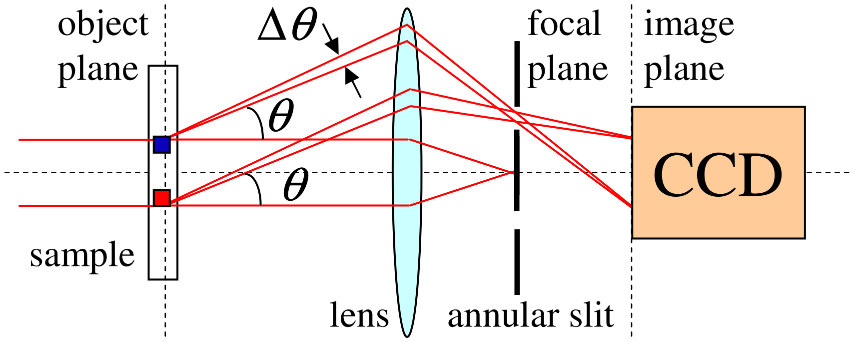
Trappe et al., Phys. Rev. E 2007

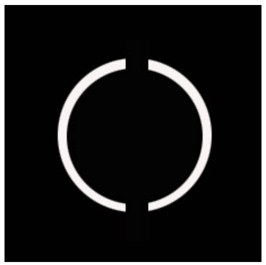
Outline

- **Probing average dynamics**
  - Dynamic light scattering
  - Multispeckle methods

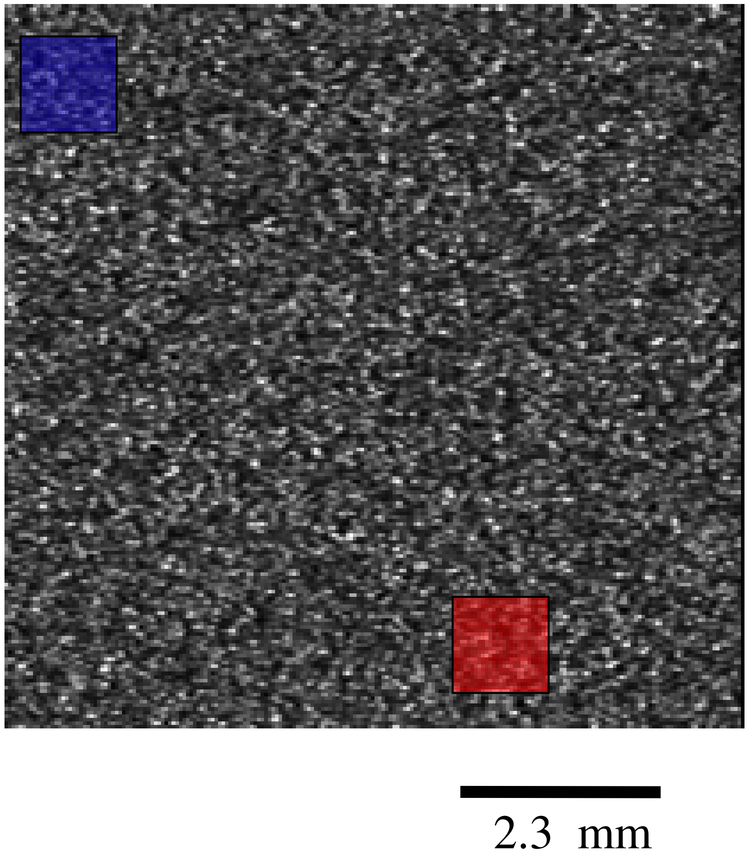
- **Dynamical heterogeneity**
  - Motivation
  - Temporal fluctuations of the dynamics
  - Spatial correlation of the dynamics

Photon Correlation Imaging (PCIm)





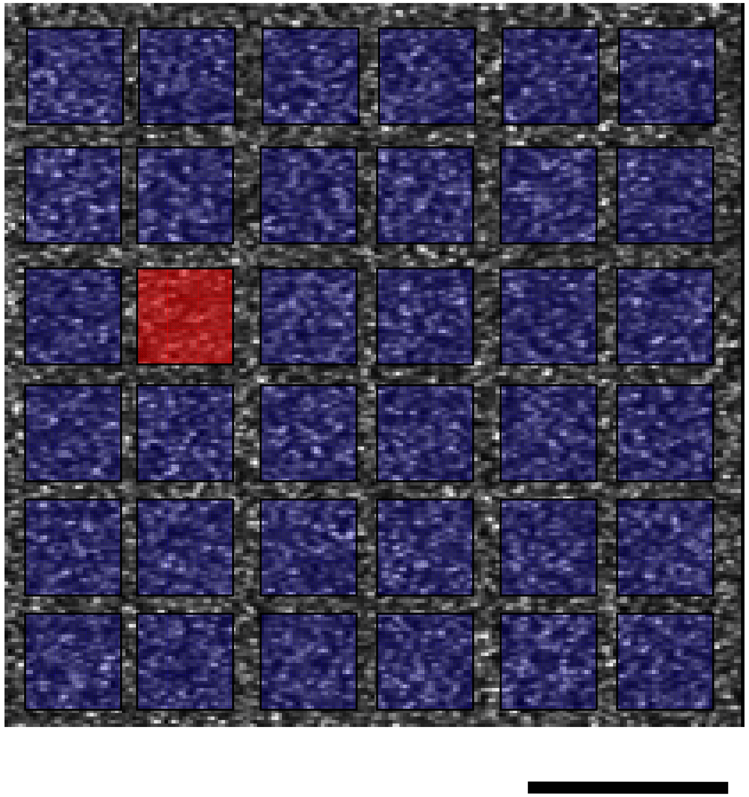
$\theta = 6.4°$ ⟶ $q = 1\ \mu m^{-1}$.



Duri et al., Phys. Rev. Lett. 2009

Local, instantaneous dynamics: $c_I(t, \tau, \mathbf{r})$

$$c_I(t, \tau, \mathbf{r}) = \frac{< I_p(t)\, I_p(t+\tau) >_{p(\mathbf{r})}}{< I_p(t) >_p < I_p(t+\tau) >_{p(\mathbf{r})}} - 1$$



2.3 mm

Note: $<< c_I(t, \tau, \mathbf{r}) >_t >_\mathbf{r} = g_2(\tau) - 1$

$[g_2(\tau)-1]^{1/2}$ ~ dynamic structure factor

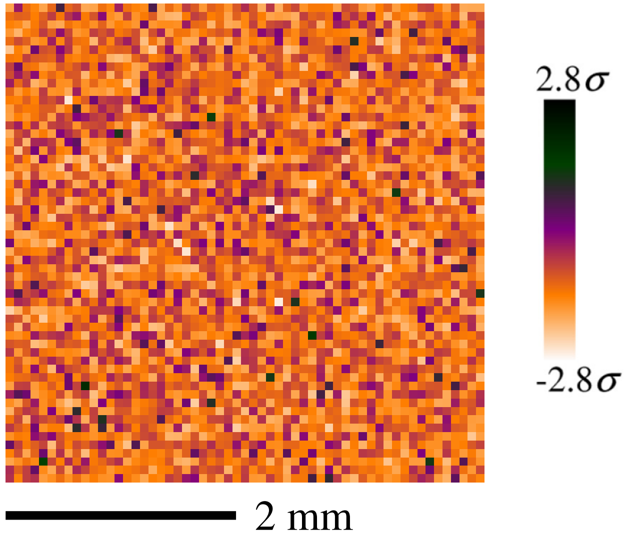
Dynamic Activity Maps

Brownian particles

$g_2(\tau)\text{-}1 \sim \exp[-\tau/\tau_r]$, $\tau_r = 40$ s

$c_I(t_0, \tau_r/200, \mathbf{r})$

Movie accelerated 10x

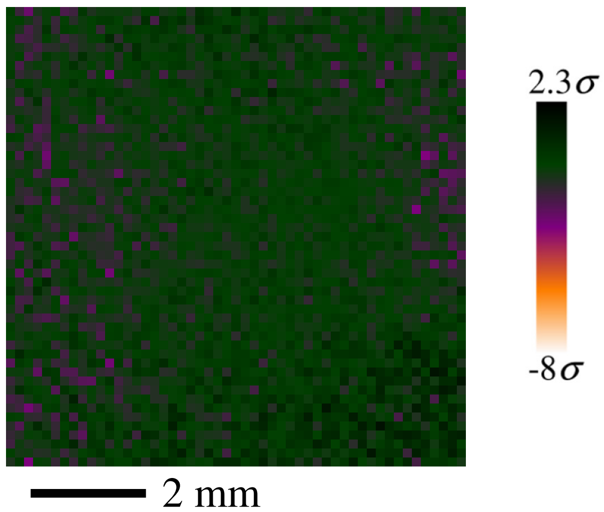


Colloidal gel

$g_2(\tau)\text{-}1 \sim \exp[-(\tau/\tau_r)^{1.5}]$, $\tau_r = 5000$ s

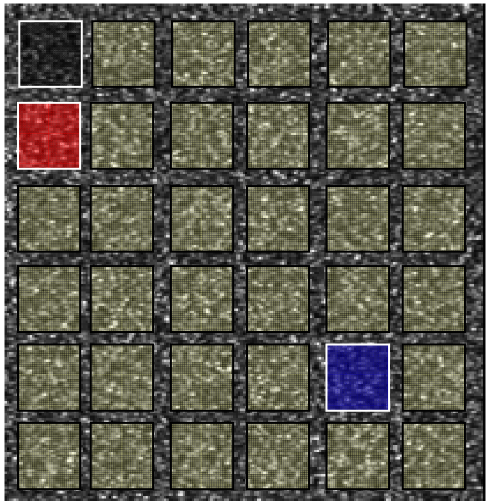
$c_I(t_0, \tau_r/10, \mathbf{r})$

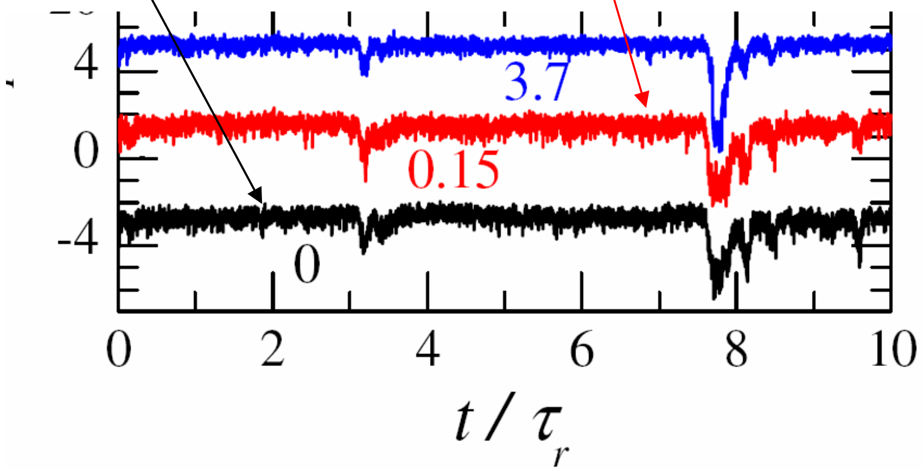
Movie accelerated 500x



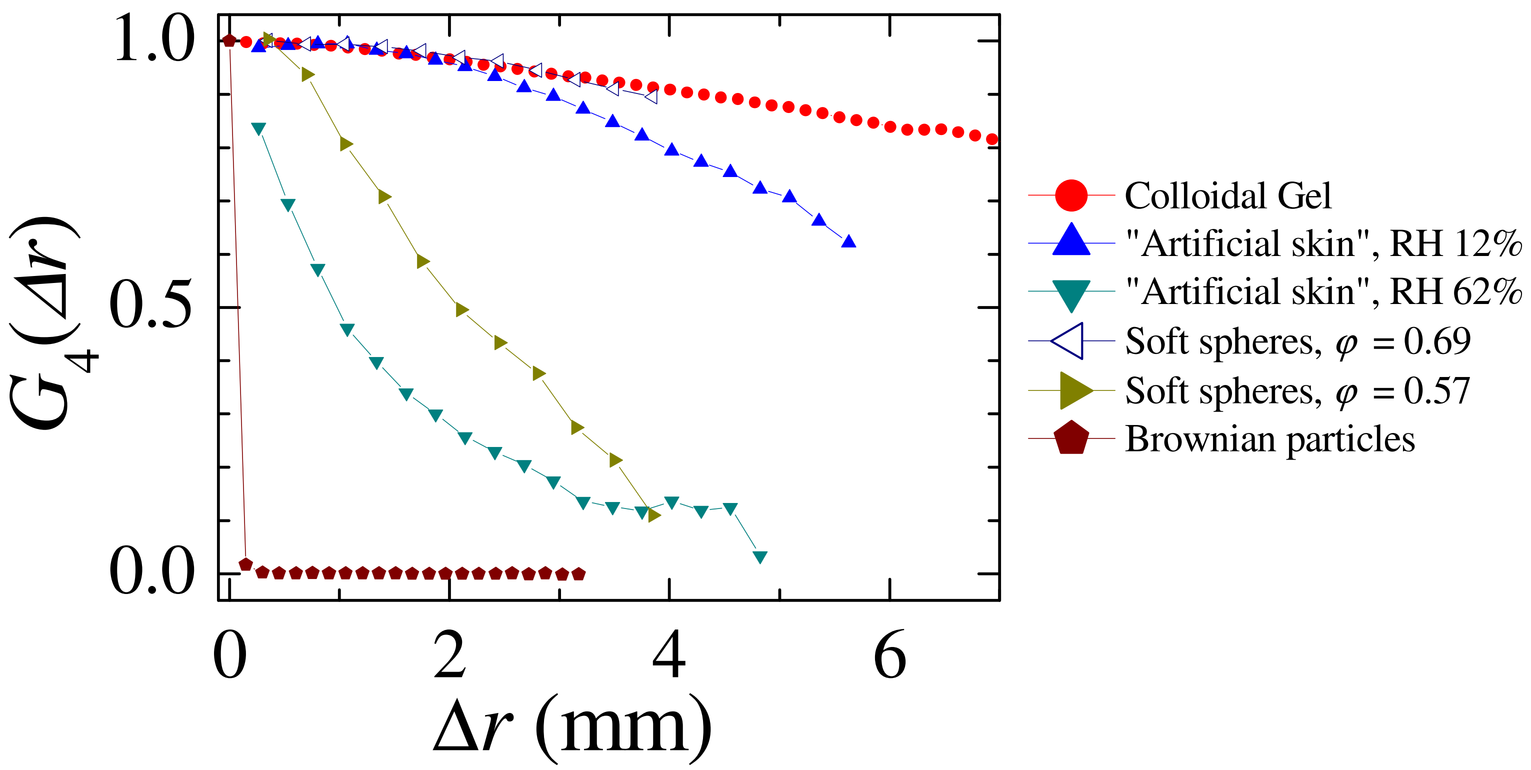
Spatial correlation of the dynamics

$$\tilde{G}_4(\Delta r, \tau) = \left\langle \frac{\langle \delta c_I(t, \tau; \mathbf{r}_1)\delta c_I(t, \tau; \mathbf{r}_2)\rangle_t}{\sigma(\tau, \mathbf{r}_1)\sigma(\tau, \mathbf{r}_2)} \right\rangle_{|\mathbf{r}_1 - \mathbf{r}_2| = \Delta r}$$





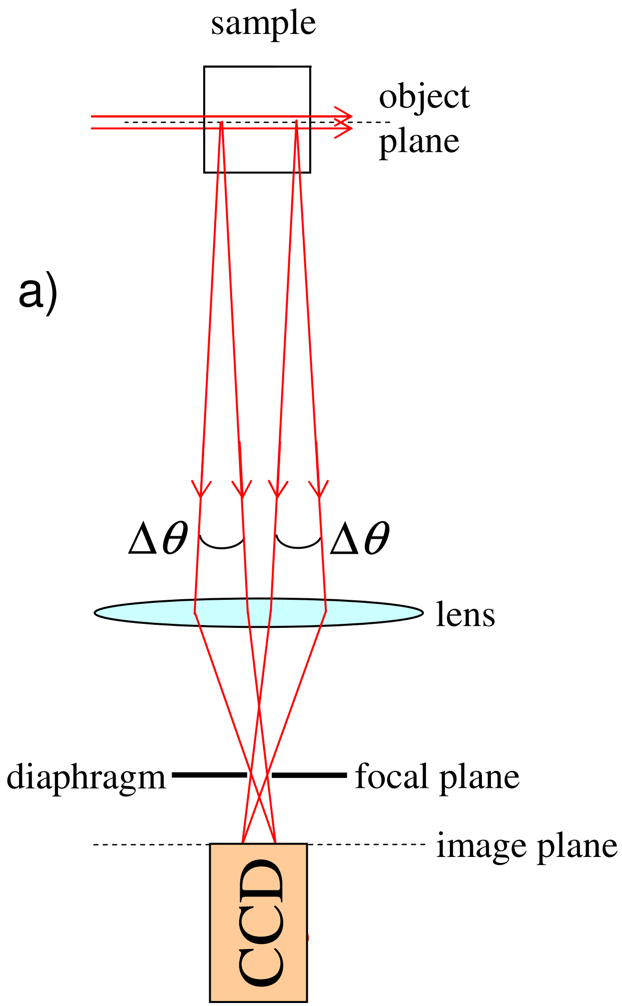
Spatial correlation of the dynamics: $\xi \sim$ system size in jammed soft matter!



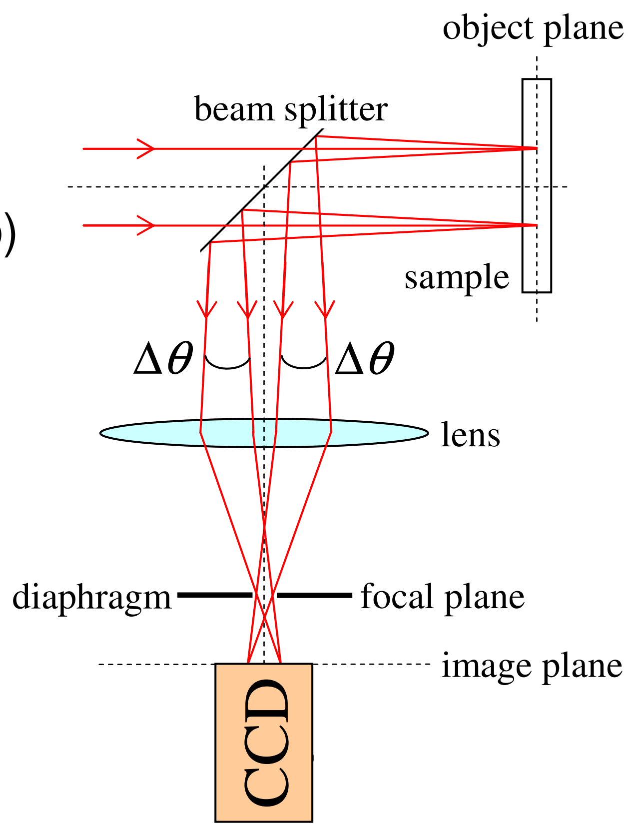
S. Maccarrone et al., submitted

Other PCIm geometries

a)



b)



Conclusions

- DH a **general feature** of glassy dynamics

- **Average dynamics: « 2-point »** correlation functions

  $<I(t)I(t+\tau)>$

- **Dynamical fluctuations: « 4-point » correlation functions**

  $< <I(t)I(t+\tau)> <I(t')I(t'+\tau)> >$ with $t = t'$: χ_4 (TRC)

  $< <I(\mathbf{r},t)I(\mathbf{r},t+\tau)> <I(\mathbf{r}',t)I(\mathbf{r}',t+\tau)> >$ G_4 (PCI)

  $< E(\mathbf{q},t)E^*(\mathbf{q},t)E(\mathbf{q}',t)E^*(\mathbf{q}',t)>$ see Wochner's talk

- **Equilibrium dynamics** in supercooled glass formers: ξ **~10*a***

- **Out-of-equilibrium dynamics** in jammed soft matter:
  ξ **~ system size**

Useful references

• B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976).

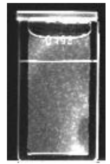
• P. N. Pusey, *Colloidal suspensions* (1991), pp. 763-943, Les Houches session LI.

Chapters 2 and 3 of an upcoming book on Dynamical Heterogenity in glasses, colloids and granular matter :

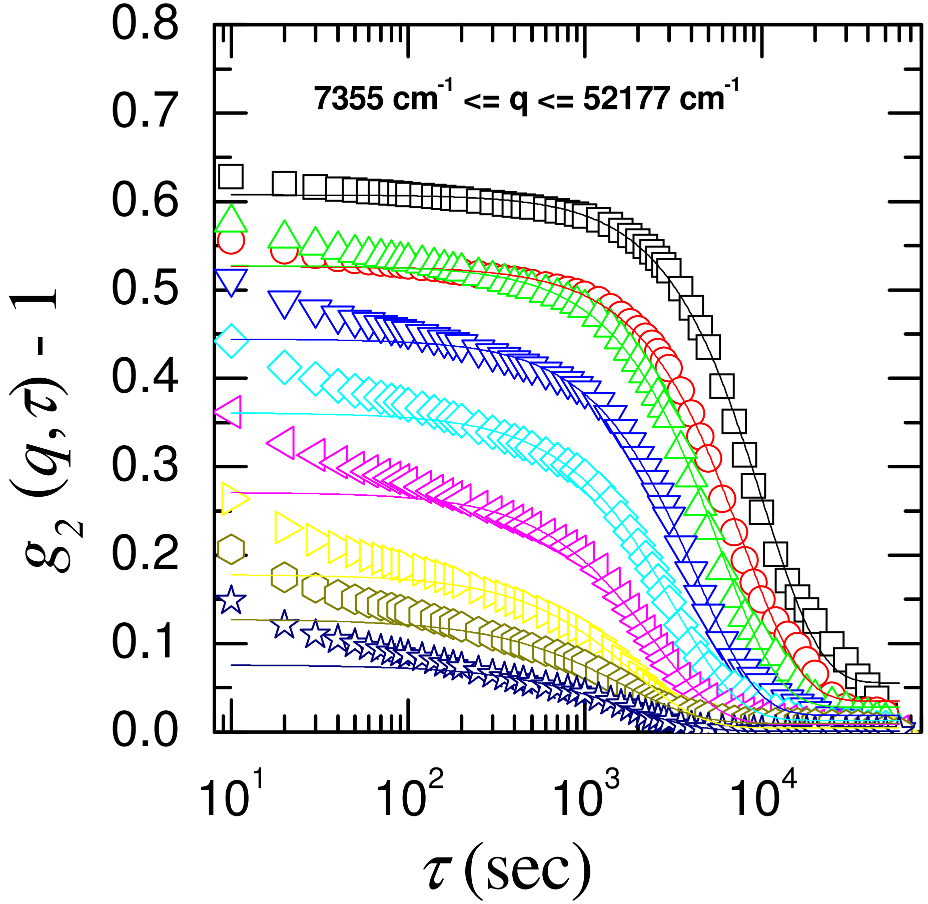
• L. Berthier, G. Biroli, J.-P. Bouchaud, and R. L. Jack,
Overview of different characterizations of dynamic heterogeneity
http://w3.lcvn.univ-montp2.fr/~berthier/chapterfinal.pdf

• L. Cipelletti and E. R. Weeks,
Glassy dynamics and dynamical heterogeneity in colloids.
http://w3.lcvn.univ-montp2.fr/~lucacip/chapter3v1.pdf

PS gel: time-averaged dynamics



$$g_2(q,\tau) - 1 \sim [f(q,\tau)]^2 \qquad f(q,\tau) = \sum_{j,k} \left\langle \exp\left[i\mathbf{q}\cdot\left(\mathbf{r}_j(\tau) - \mathbf{r}_k(0)\right)\right]\right\rangle$$

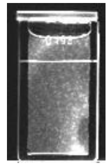


- **Fast dynamics**: overdamped vibrations (~ 500 nm) *Krall & Weitz PRL 1998*

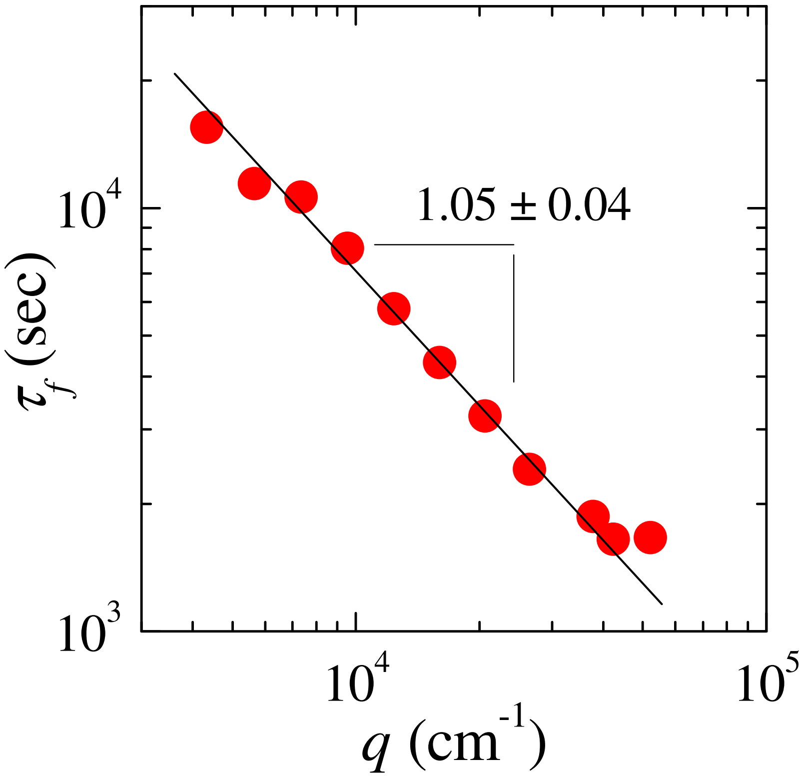
- **Slow dynamics**: rearrangements

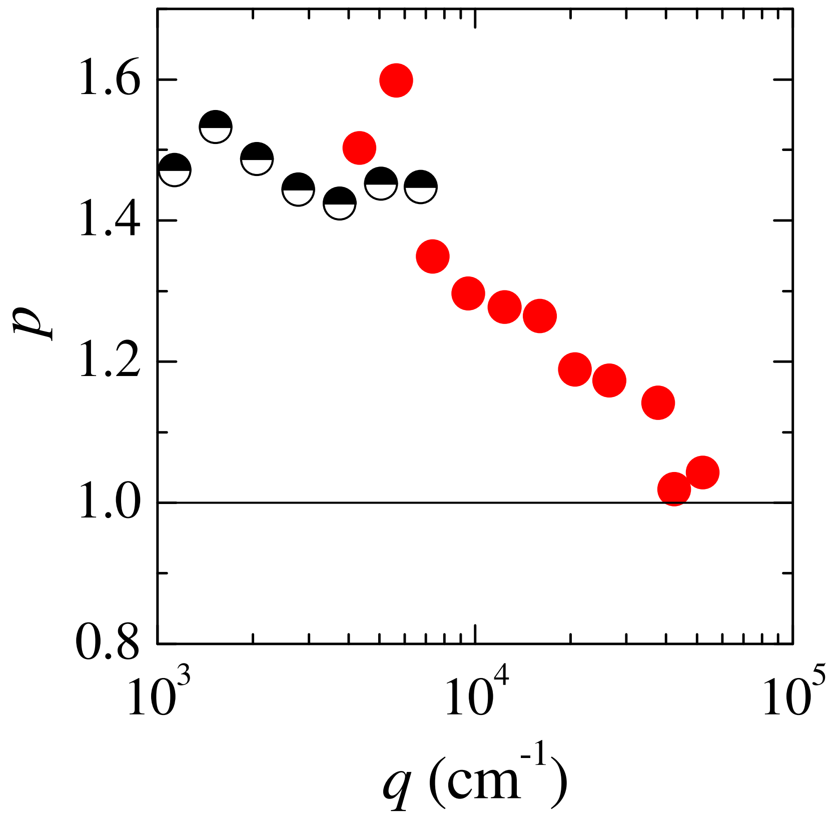
$$g_2(q,\tau) - 1 \sim \exp\left[-\left(\tau/\tau_f\right)^p\right]$$

PS gels: q dependence of τ_f and p



$$g_2(q,\tau)-1 \sim \exp\left[-\left(\tau/\tau_f\right)^p\right]$$

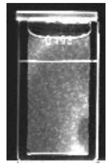


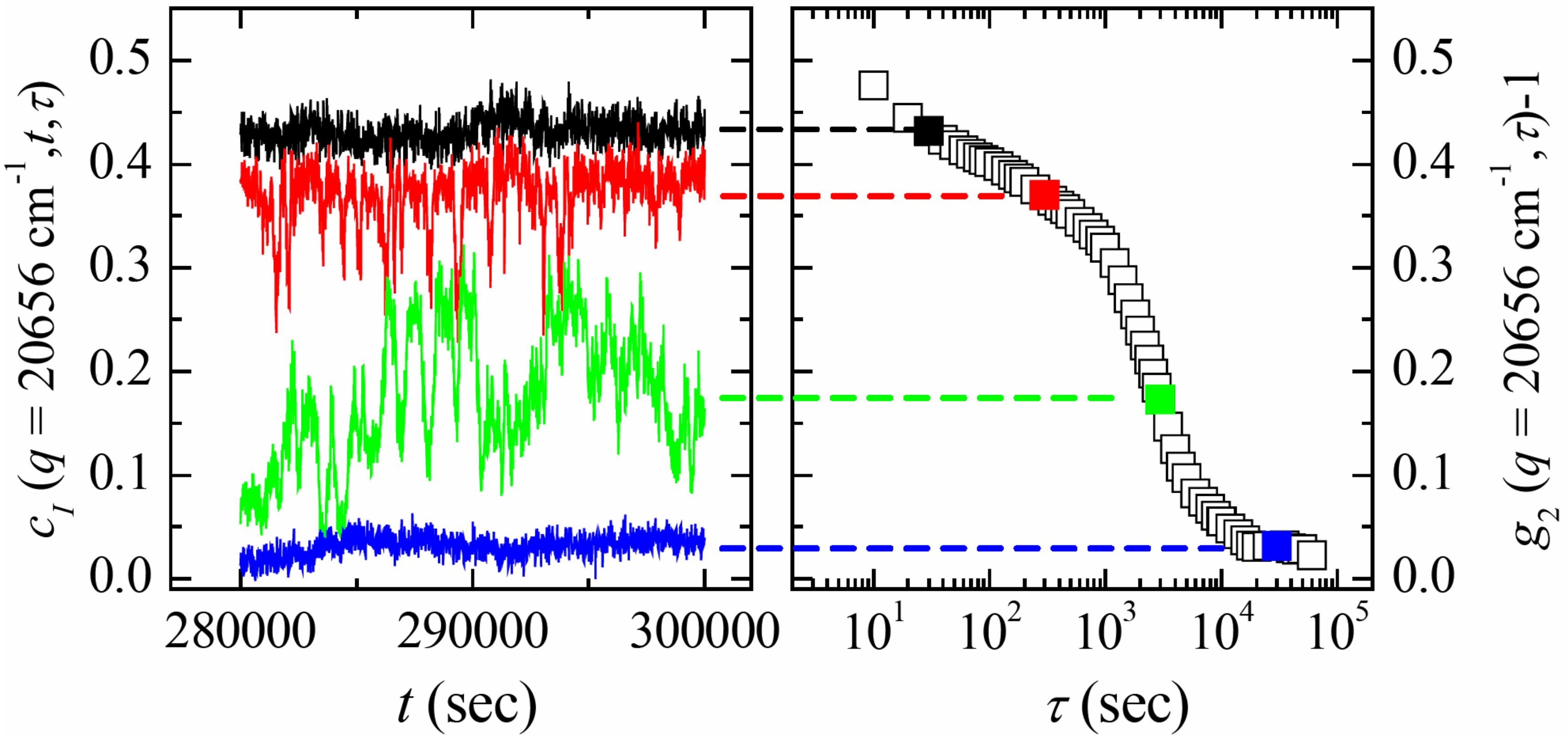


« ballistic » motion

« compressed » exponential

PS gel: temporally heterogeneous dynamics

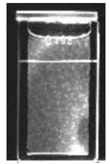




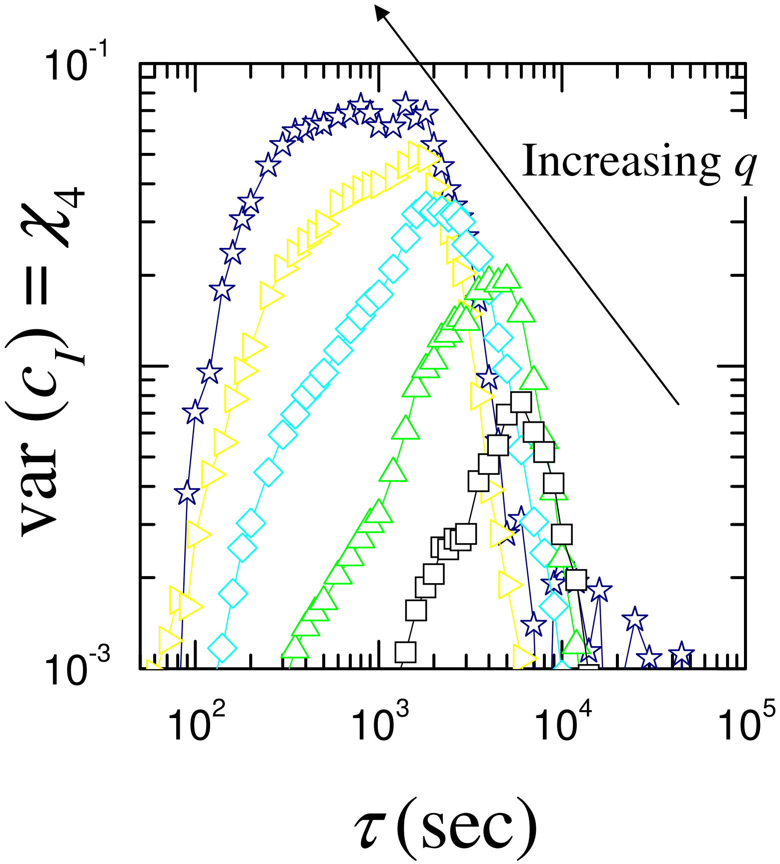
$c_I(t_w, \tau)$ @ fixed τ: temporal **fluctuations**

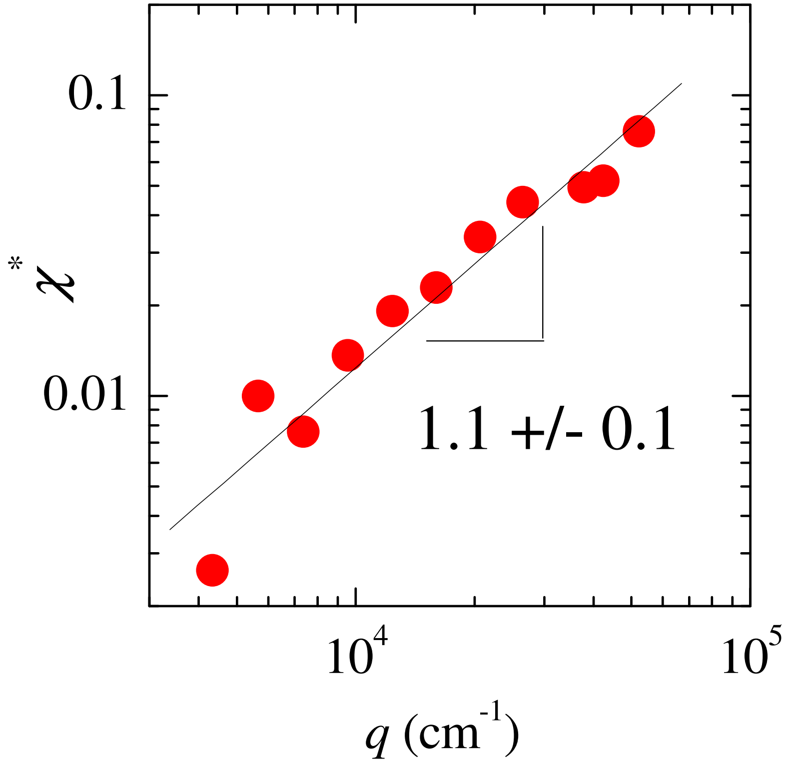
$<c_I(t_w, \tau)>_{tw}$: **average** dynamics

Length scale dependence of $\chi = \mathrm{var}(c_I)$



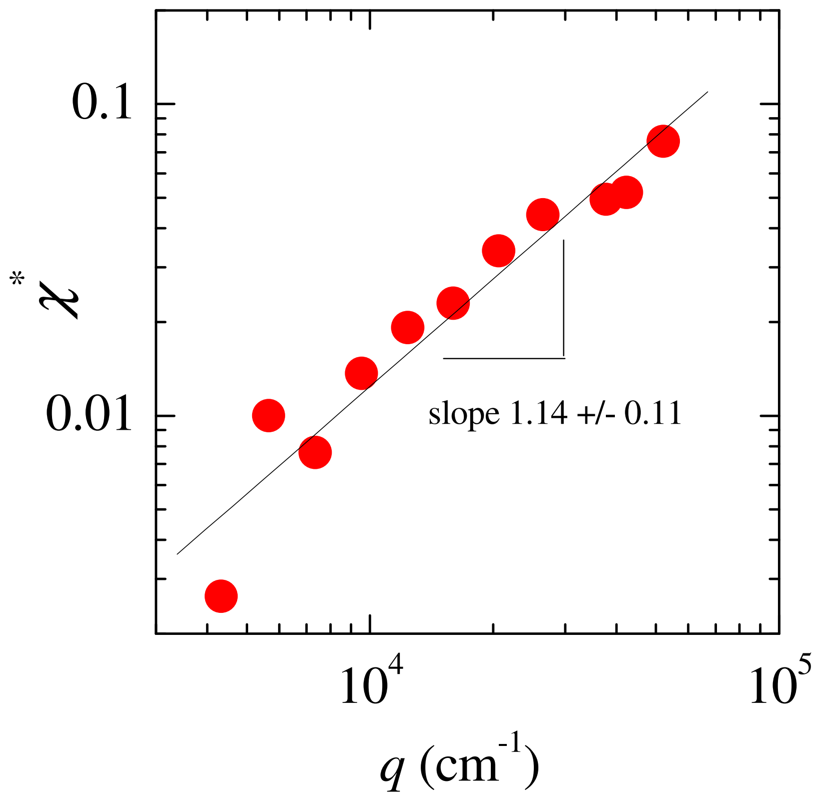
PS gel





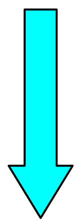
*Duri & LC, EPL **76**, 972 (2006)*

Scaling of χ^*



$$\chi^* \sim \mathrm{var}(n)/\langle n \rangle \sim 1/\langle n \rangle$$

$$\langle n \rangle \sim \tau_f \sim 1/q$$



$$\chi^* \sim q$$