Dynamics of glassy and jammed colloidal systems

L. Cipelletti

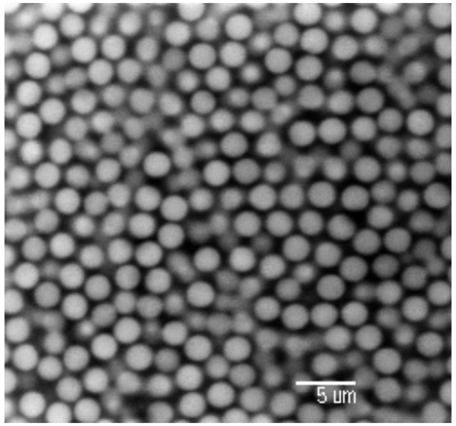
L2C, Université Montpellier 2 and CNRS

Collaborators: L. Berthier (LCVN), V. Trappe (Fribourg)

Students: P. Ballesta, G. Brambilla, A. Duri, D. El Masri

Postdocs: S. Maccarrone, M. Pierno

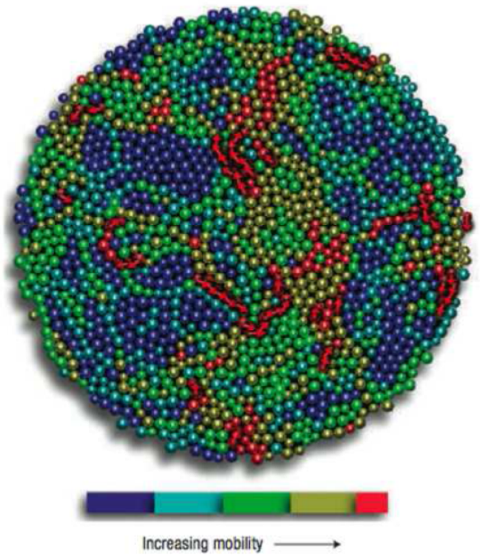
Soft glassy/jammed materials



E. Weeks

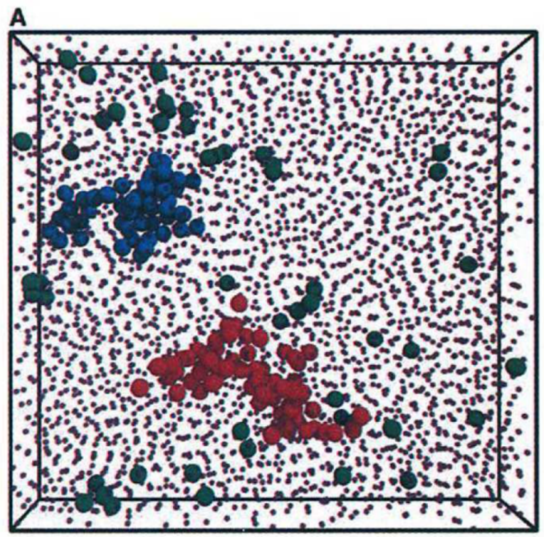
Dynamical heterogeneity is ubiquitous!

Granular matter



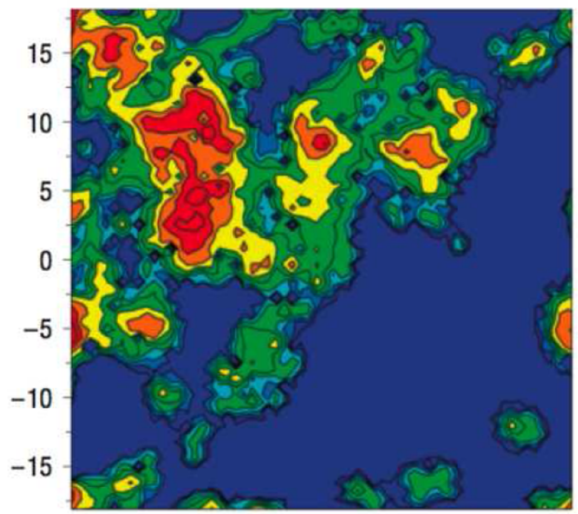
Keys et al. Nat. Phys. 2007

Colloidal Hard Spheres



Weeks et al. Science 2000

Repulsive disks



A. Widmer-Cooper Nat. Phys. 2008

Outline

- Average dynamics and dynamical hetrogeneity of supercooled colloidal HS

- Temporal fluctuations of the dynamics in jammed/glassy materials

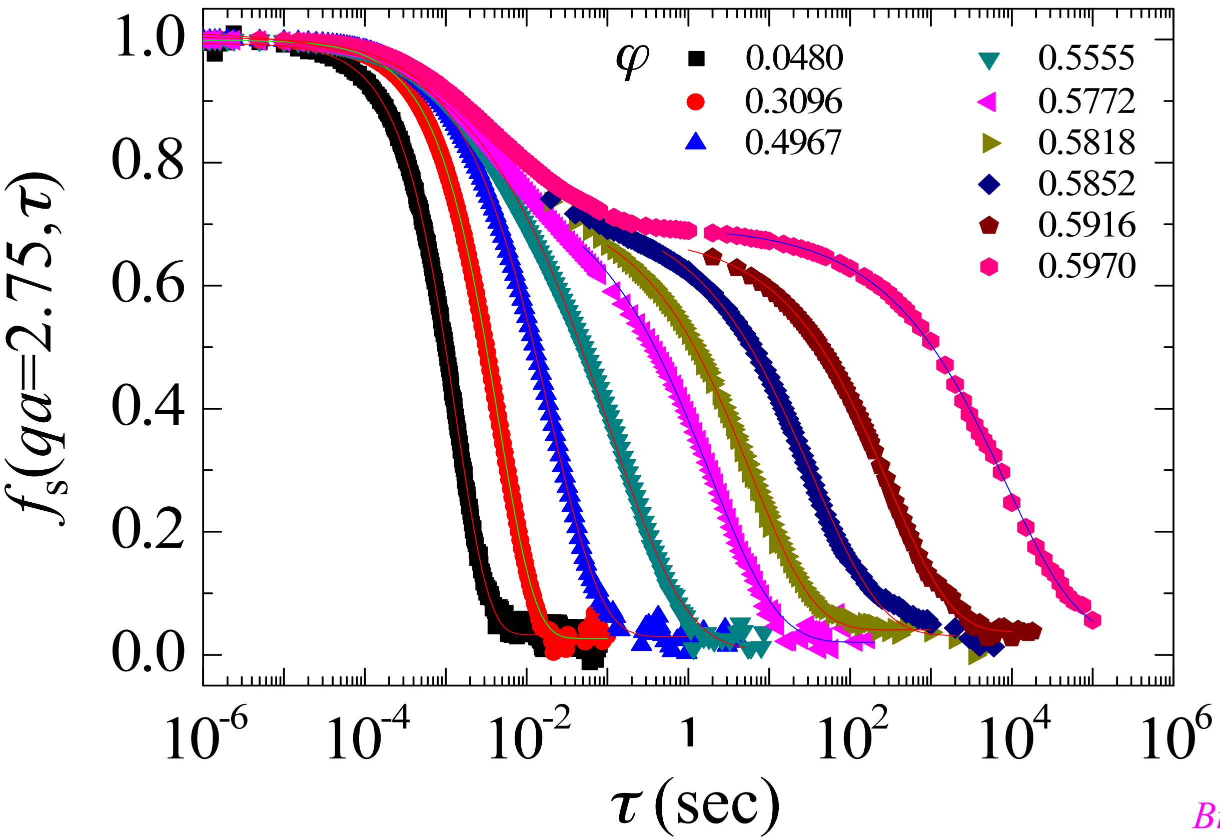
- Real-space measurements of correlations: ultra-long range spatial correlations and elasticity

Equilibrium dynamics of supercooled HS

Multispeckle DLS

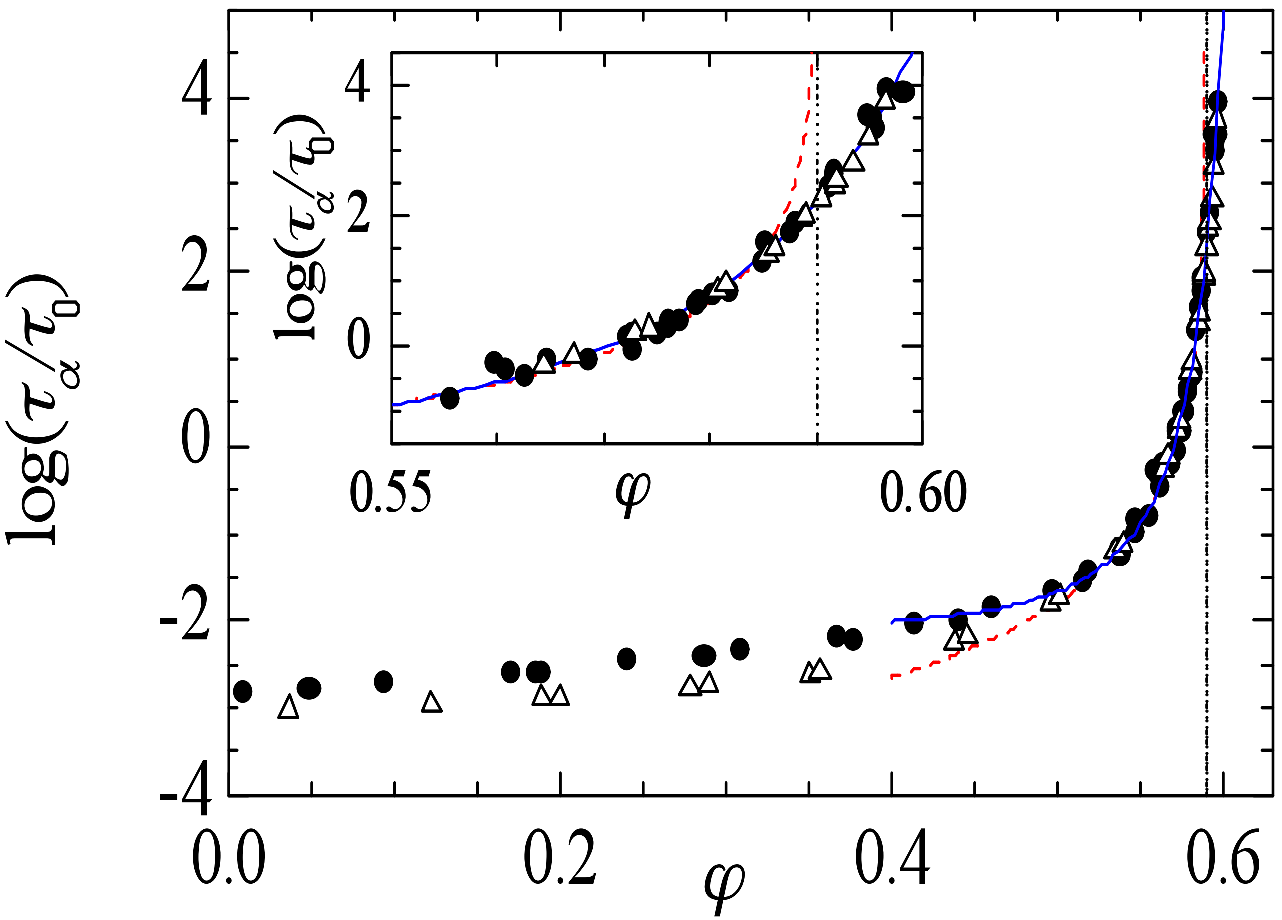
$$f_s(q,\tau) = \left\langle \frac{1}{N} \sum_{j=1}^{N} \exp\left[-i\mathbf{q} \cdot \left(\mathbf{r}_j(0) - \mathbf{r}_j(\tau) \right) \right] \right\rangle$$

- PMMA in decalin/tetralin
- $a \sim 110$ nm
- polidispertsity 12.2% (TEM)



Brambilla et al., PRL 2009

φ dependence of the relaxation time



MCT : $\tau_\alpha \sim (\varphi_c - \varphi)^{-\gamma}$

$\varphi_c = 0.59$, $\gamma = 2.6$

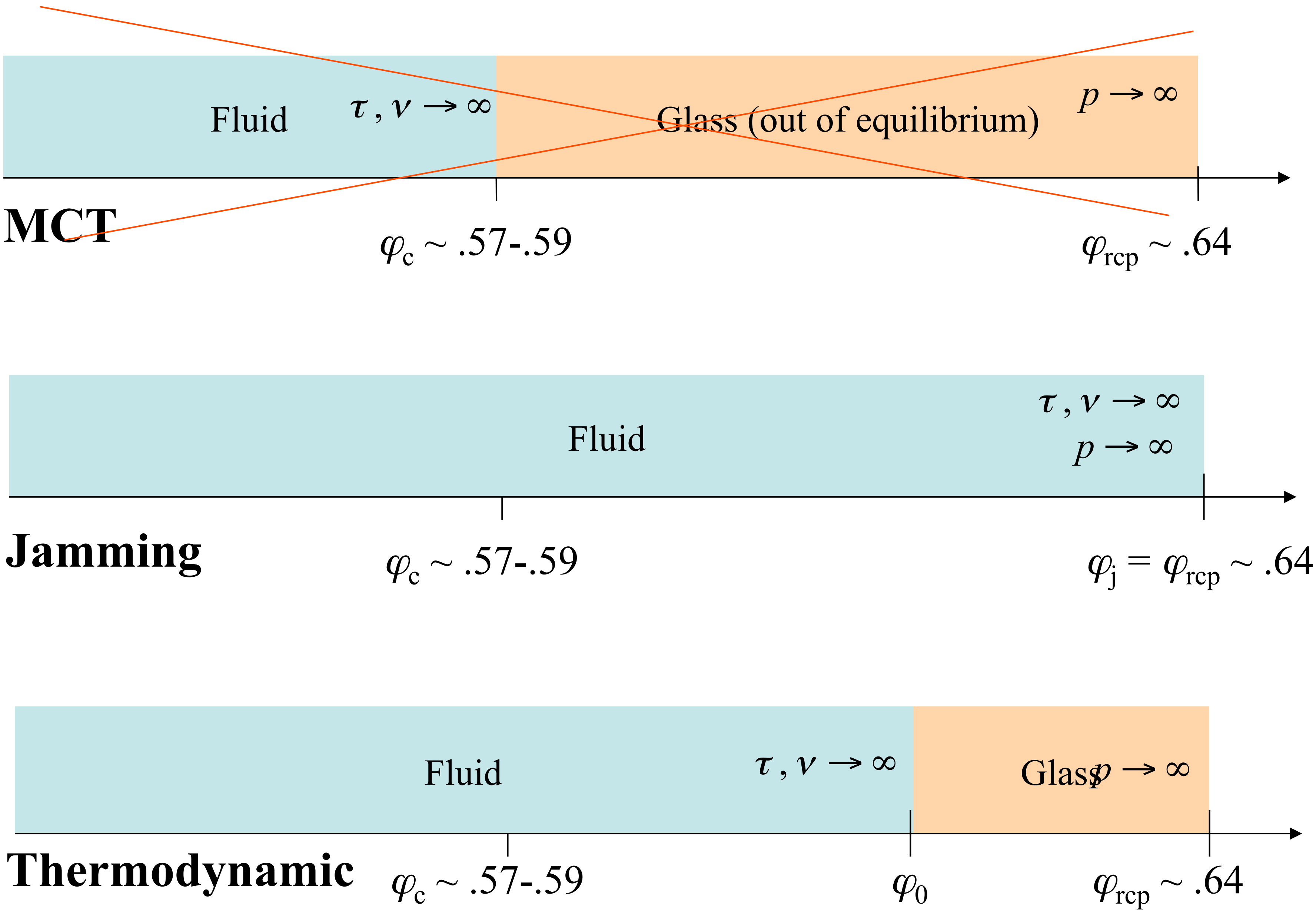
VFT: $\tau_\alpha \sim \exp[(\varphi_0 - \varphi)^{-\delta}]$

$\varphi_0 = 0.614$, $\delta = 1$

$\varphi_0 = 0.637$, $\delta = 2$

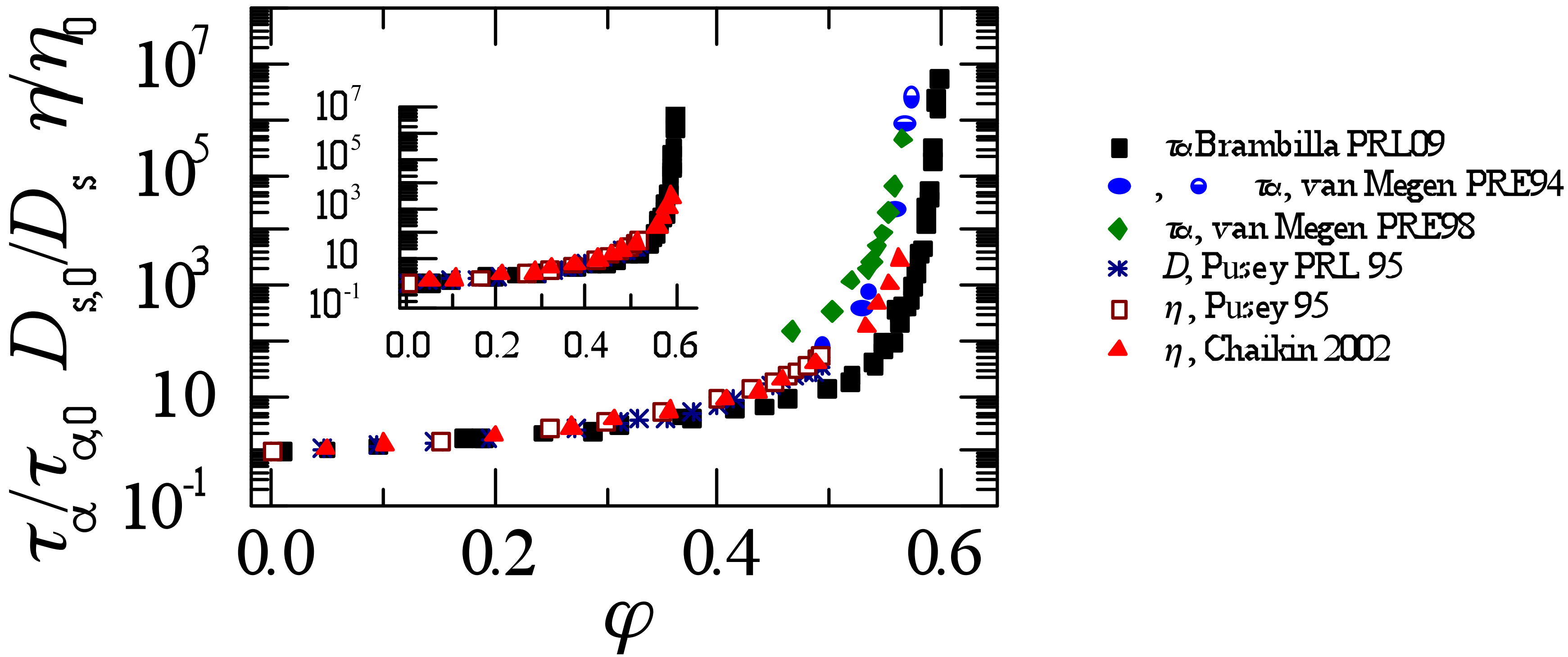
Brambilla et al., PRL 2009

Glass/jamming transition in colloidal HS



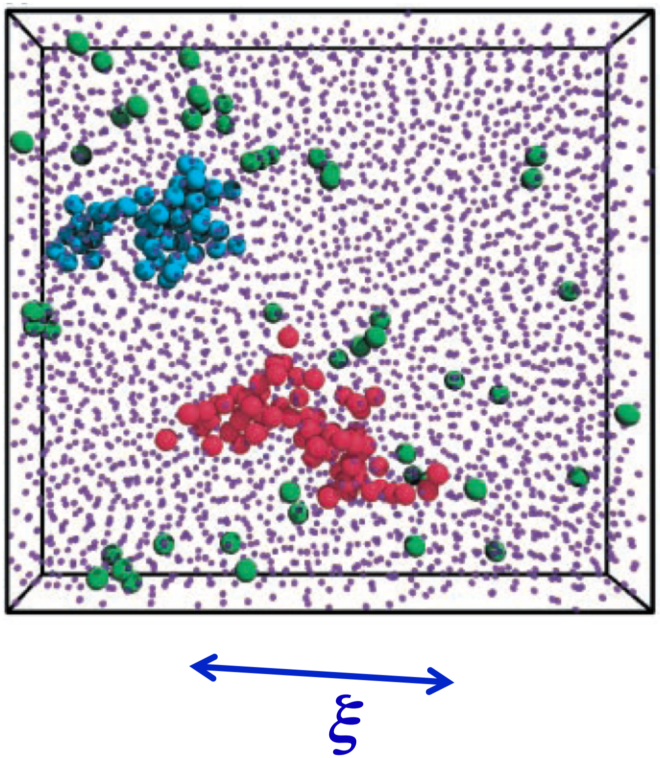
Something experimentalists in colloids know well (but seldom tell you)...

Absolute determination of φ **very difficult!**

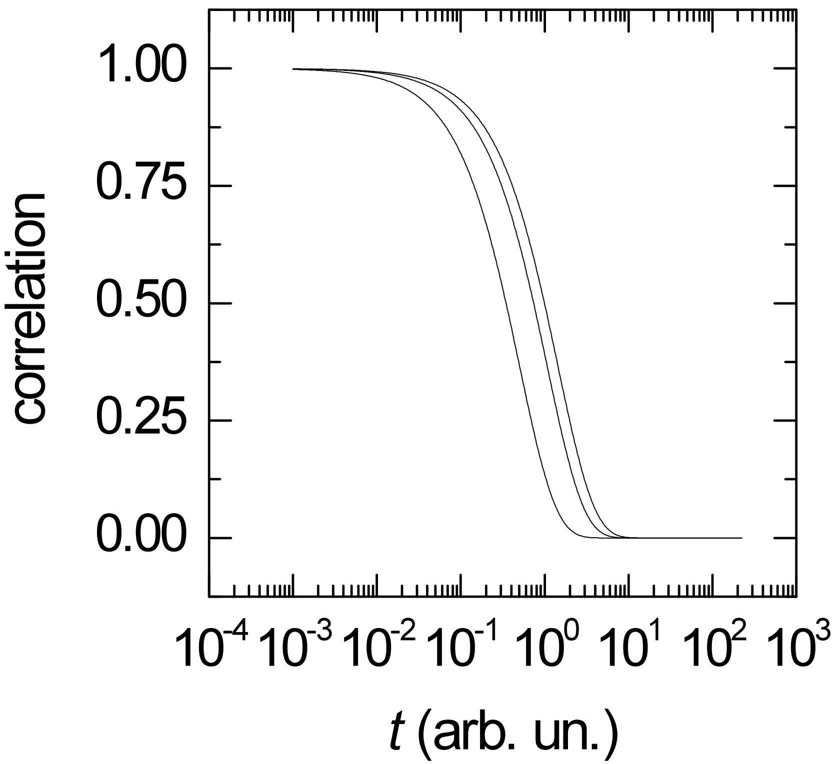


Cipelletti & Weeks, in OUP DH book (2011)

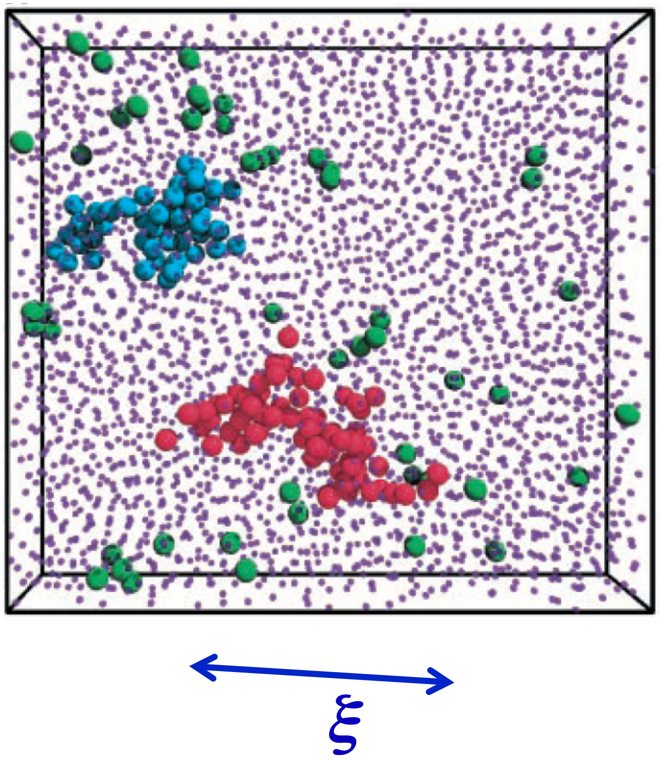
Dynamical heterogeneity



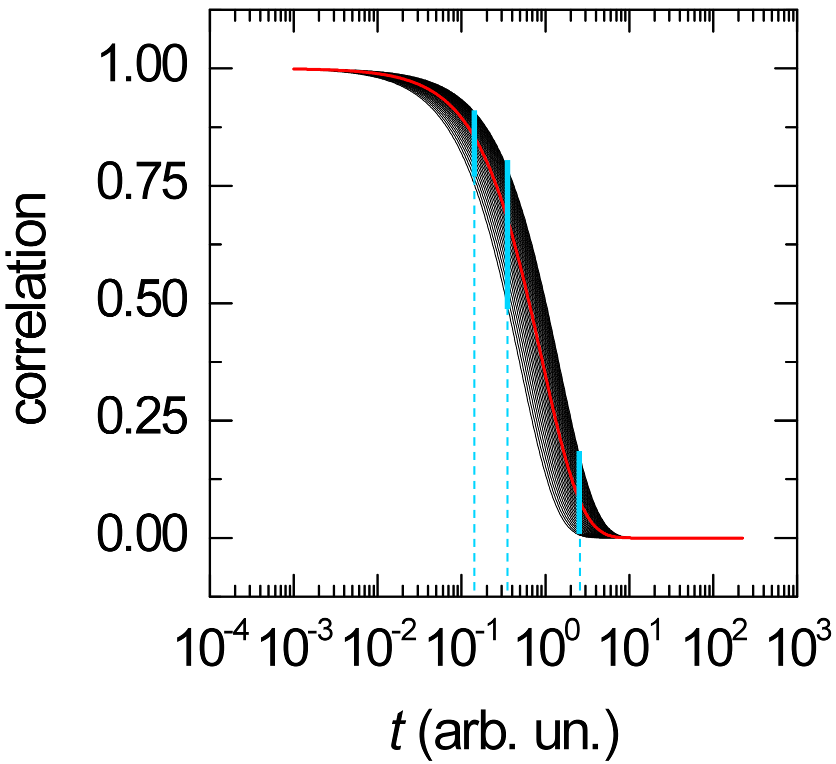
Weeks et al. Science 2000



Dynamical heterogeneity



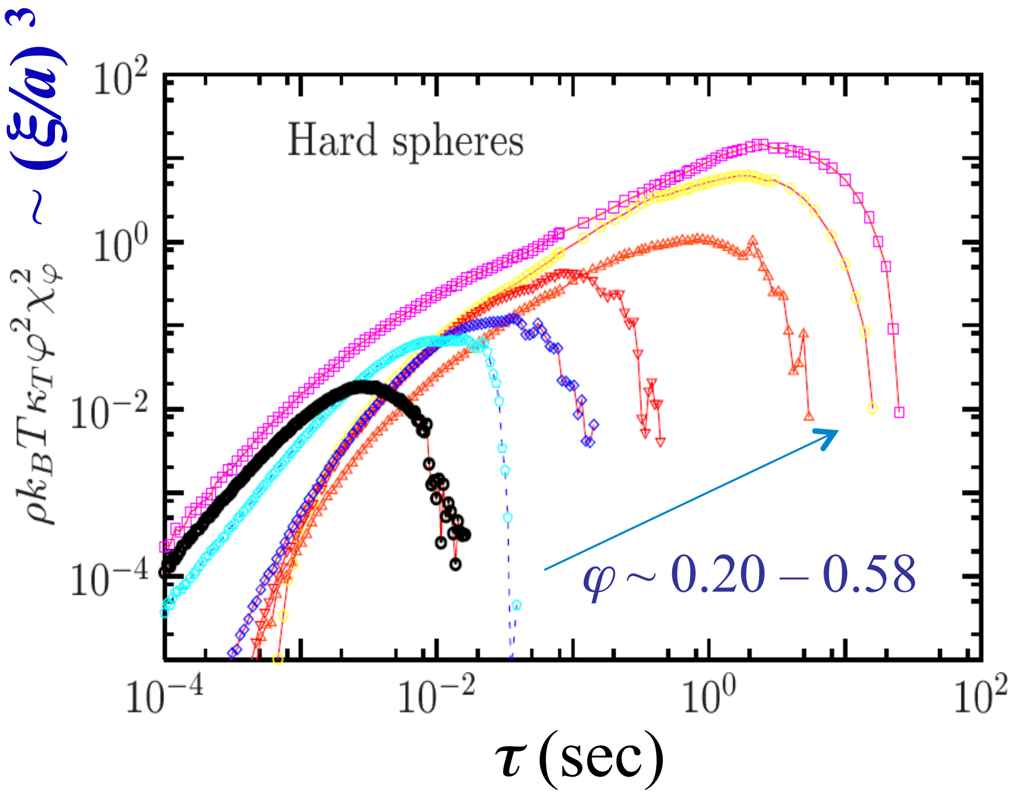
Weeks et al. Science 2000



$\mathrm{var}[f(\tau)] \longrightarrow \chi_4(\tau)$

dynamical susceptibility

DH in colloidal HS



dynamical susceptibility $\chi_4(\tau)$

Berthier et al., Science 2005

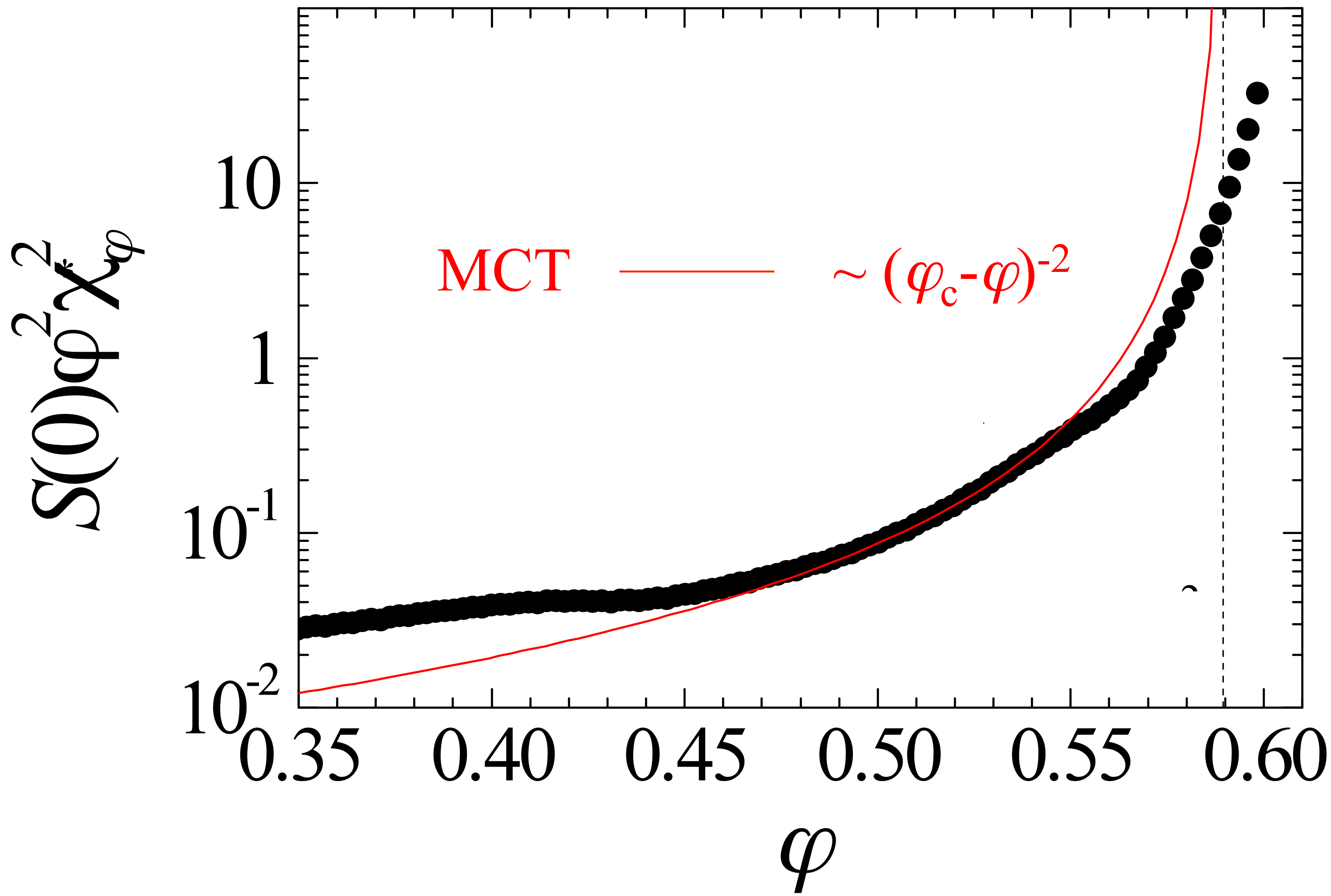
A useful relationship

$$\chi_4(\tau) \geq S(0)\varphi^2 \chi_\varphi^2(\tau)$$

- $\chi_\varphi(\tau) = \dfrac{\partial f(\tau)}{\partial \varphi}$
- equilibrium
- OK at high φ

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

φ dependence of the max of χ_4



High φ :
deviation from MCT

Brambilla et al., PRL 2009

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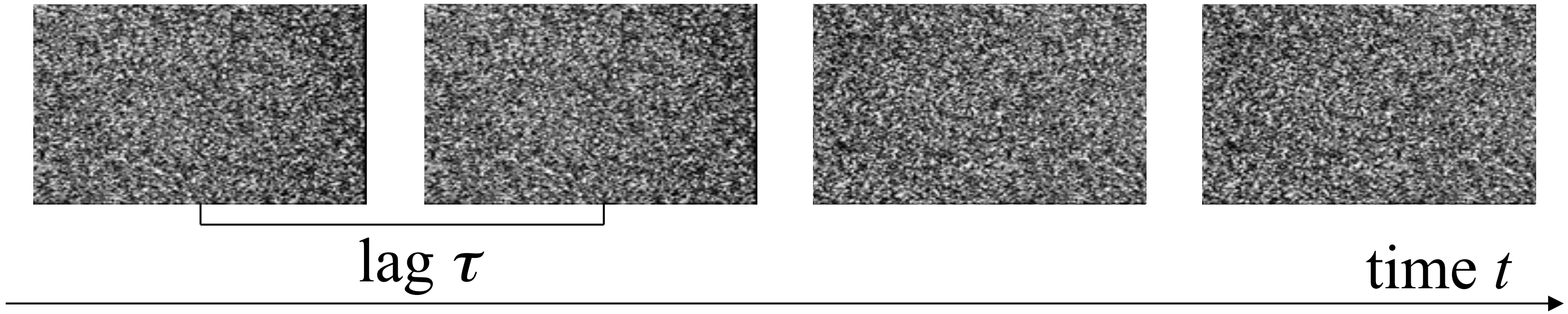
- **Temporal fluctuations of the dynamics in jammed/glassy materials**

- Real-space measurements of correlations: ultra-long range spatial correlations and elasticity

Time Resolved Correlation (TRC)



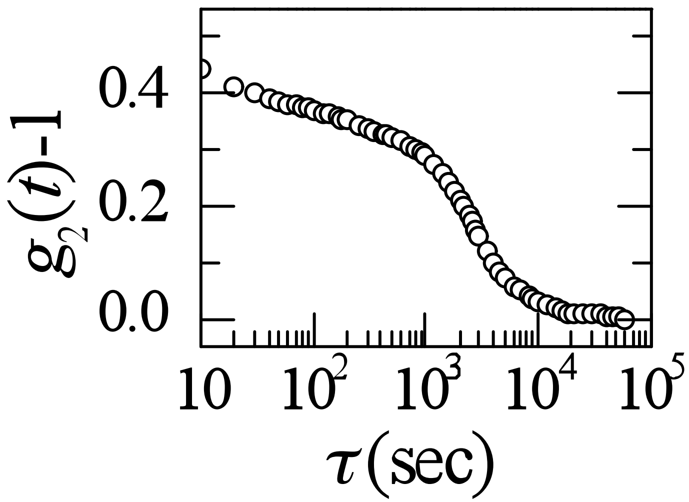
degree of correlation $c_I(t,\tau) = \dfrac{< I_p(t)\, I_p(t+\tau) >_p}{< I_p(t) >_p < I_p(t+\tau) >_p} - 1$

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 **$g_2(\tau) - 1$**



$g_2(\tau) - 1 \sim f(\tau)^2$ → Average dynamics

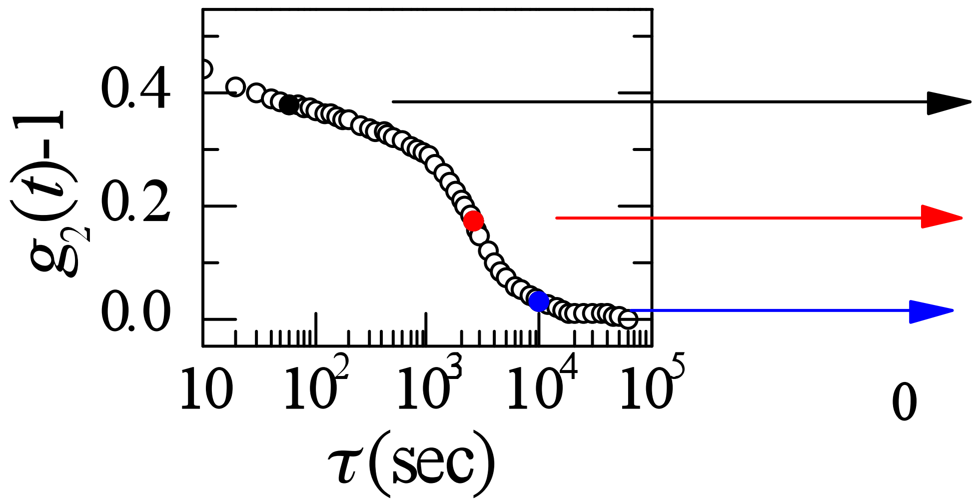
degree of correlation $c_I(t,\tau) = \dfrac{< I_p(t)\, I_p(t+\tau)>_p}{< I_p(t)>_p < I_p(t+\tau)>_p} - 1$

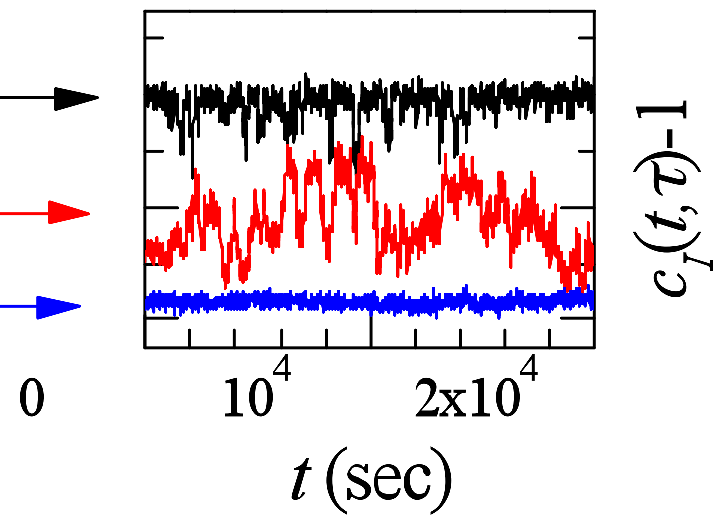
Average over t

fixed τ, *vs.* t

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

fluctuations of the dynamics

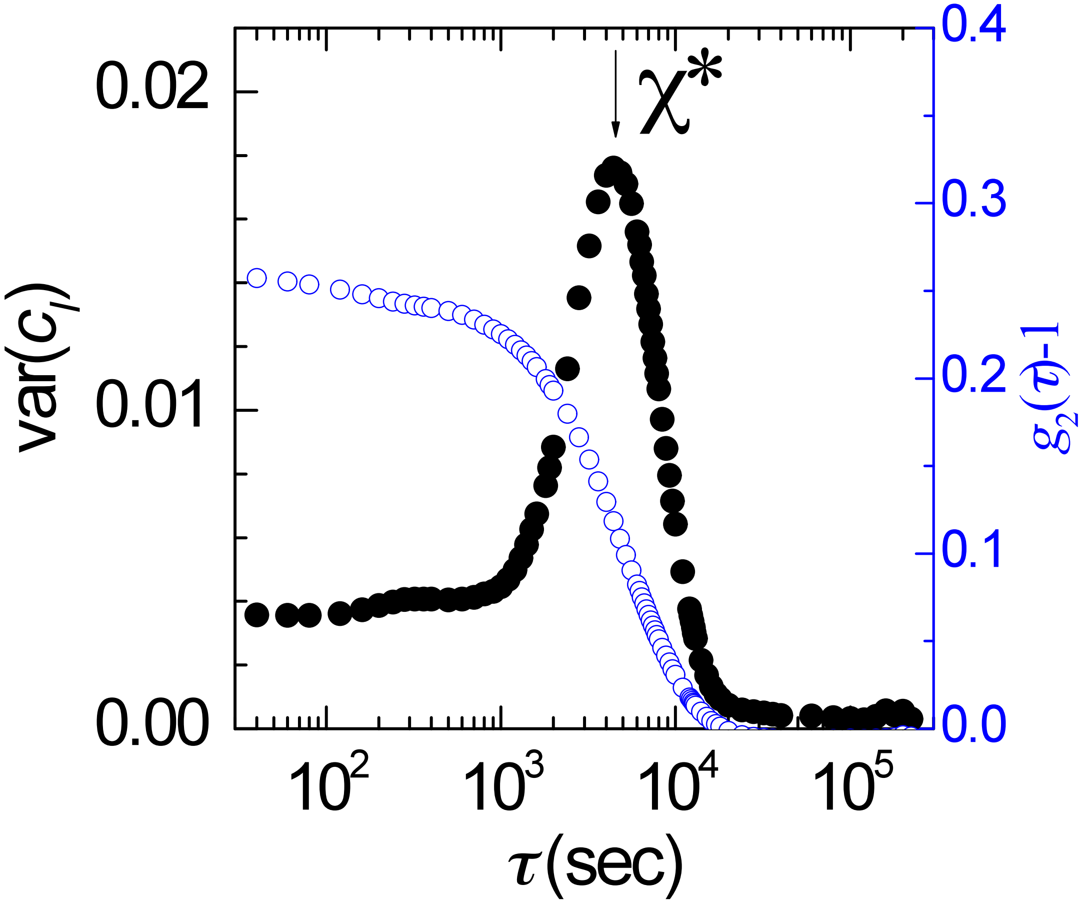




$g_2(\tau) - 1 \sim f(\tau)^2$ → Average dynamics

$\mathrm{var}[c_I(\tau)] \sim \chi(\tau)$

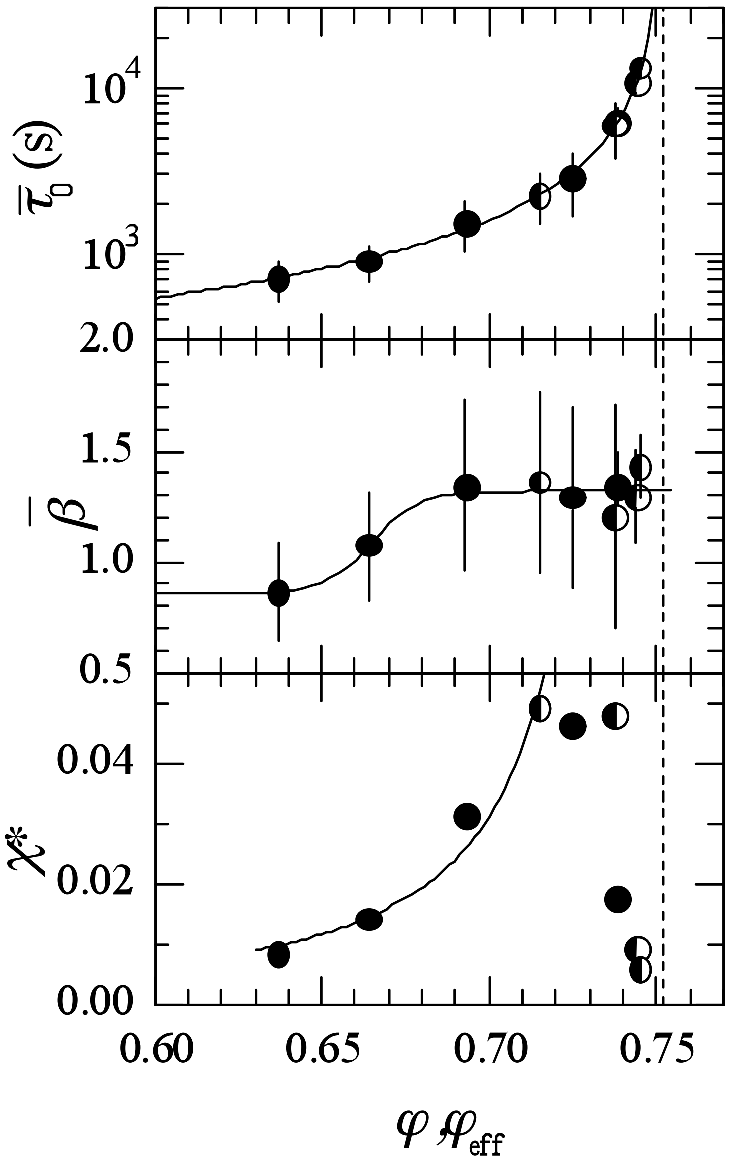
(Polydisperse) colloids near rcp



- PVC in DOP
- a ~ 5 µm
- polidispertsity ~33%
- slightly soft
- φ close to rcp
- multiple scattering (DWS)
  Λ ~ 10 nm << a

Ballesta et al., Nature Physics 2008

Non-monotonic behavior of $\chi^*(\varphi)$



Fit: $g_2(\tau)$-1 ~ $\exp[-(\tau/\tau_0)^\beta]$

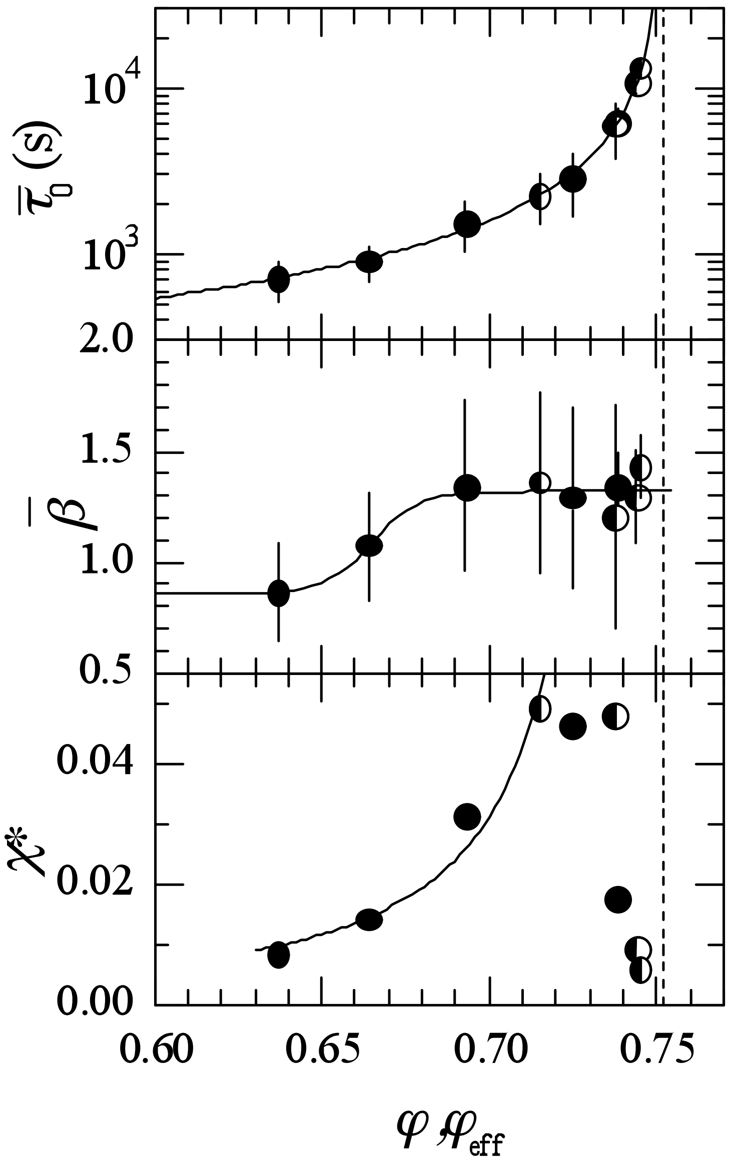
relaxation time

stretching exponent

peak of dynamical susceptibility

non monotonic!

Non-monotonic behavior of $\chi^*(\varphi)$



Competition between:

increasing ξ ($\chi^*\nearrow$ as $\varphi\nearrow$)

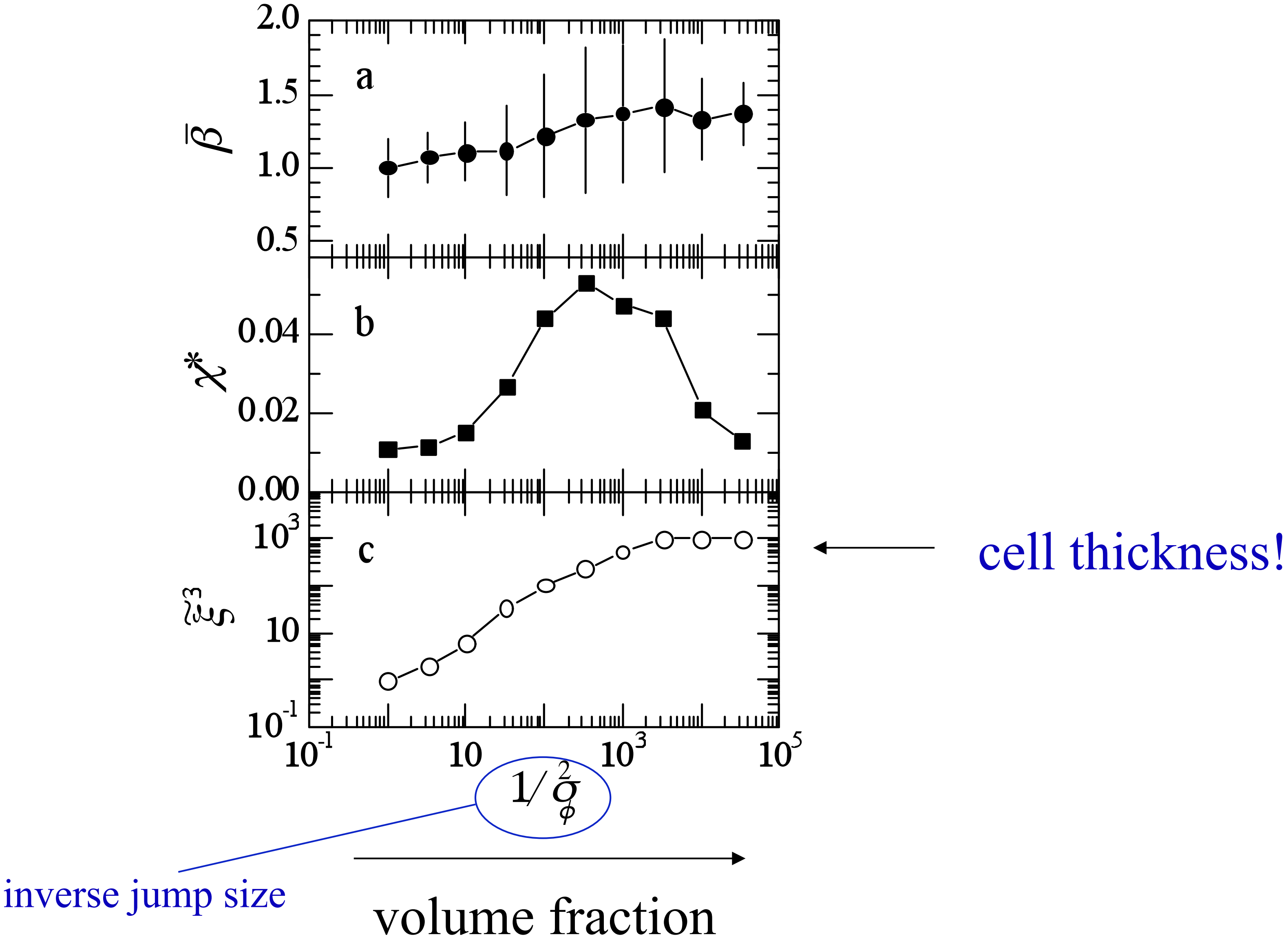
increasingly restrained displacement
(many events over τ_0, $\chi^*\searrow$ as $\varphi\nearrow$)

Model:

- random events of size ξ
- Poissonian statistics
- Quasi-ballistic motion

($\langle\delta r^2\rangle \sim n^p$, $p = 1.65$)

Simulating the model



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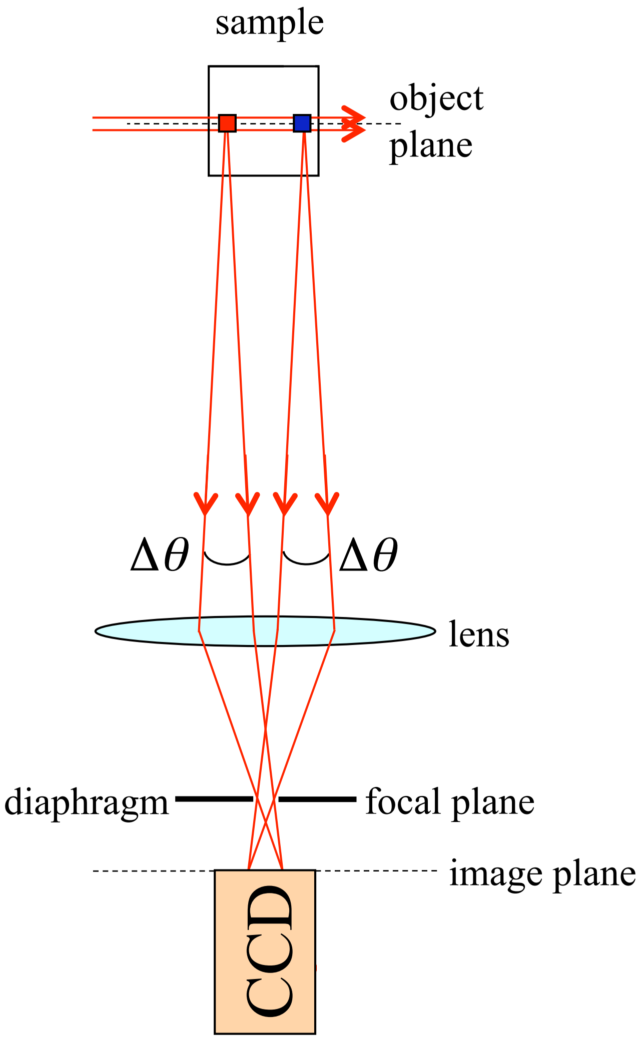
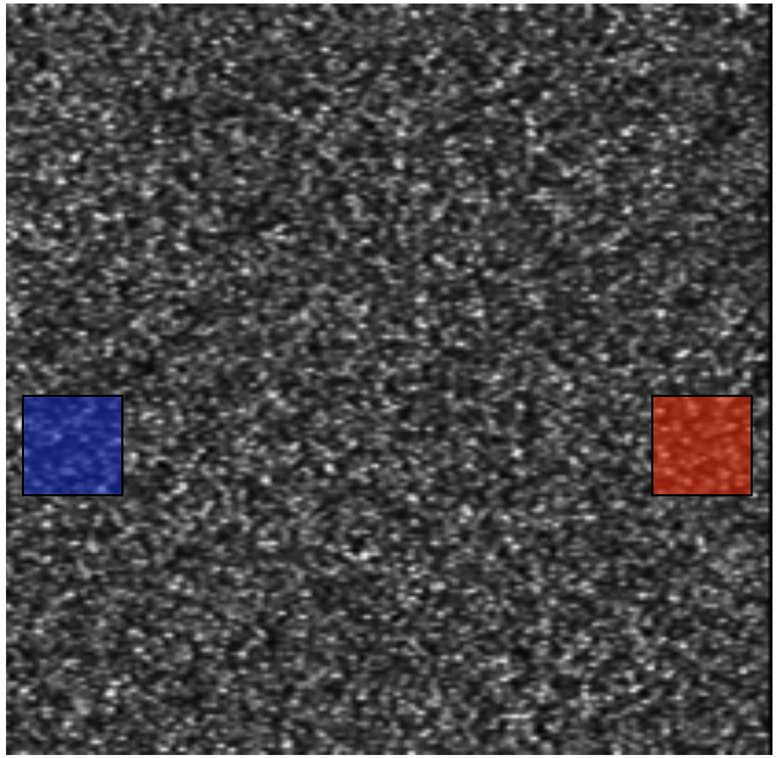
Measuring ξ by Photon Correlation Imaging





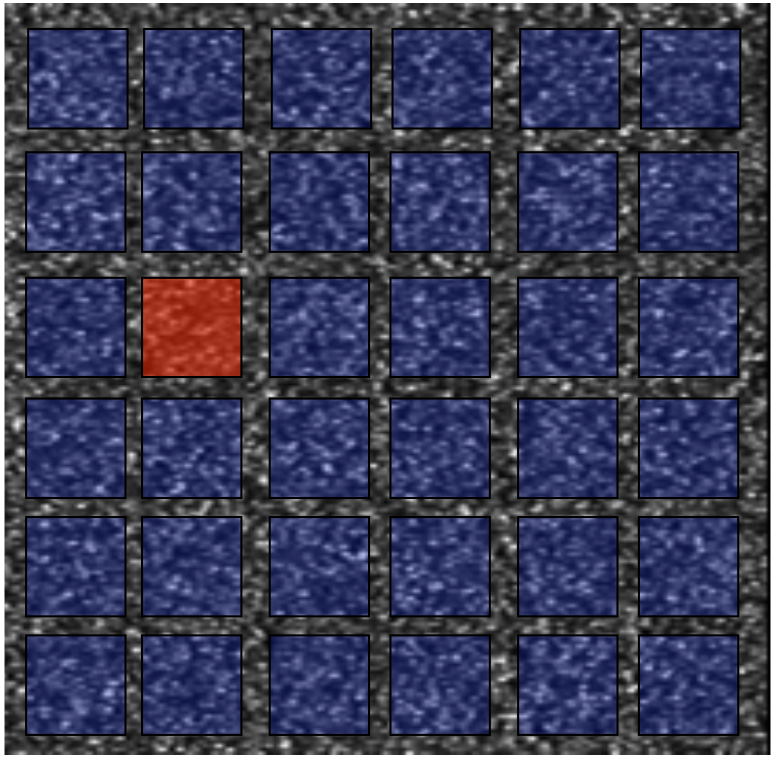
2.3 mm

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

$\theta = 90°$ ⟶ $1/q \sim 45$ nm

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

$[g_2(\tau)-1] \sim f(\tau)^2$

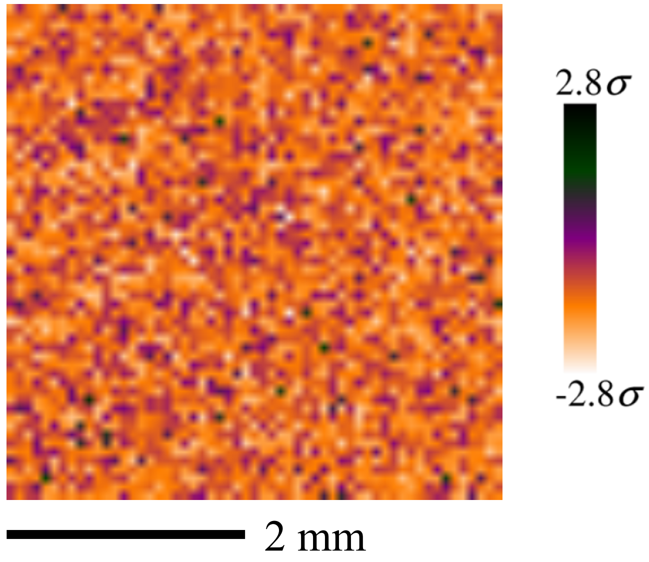
Dynamic Activity Maps

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

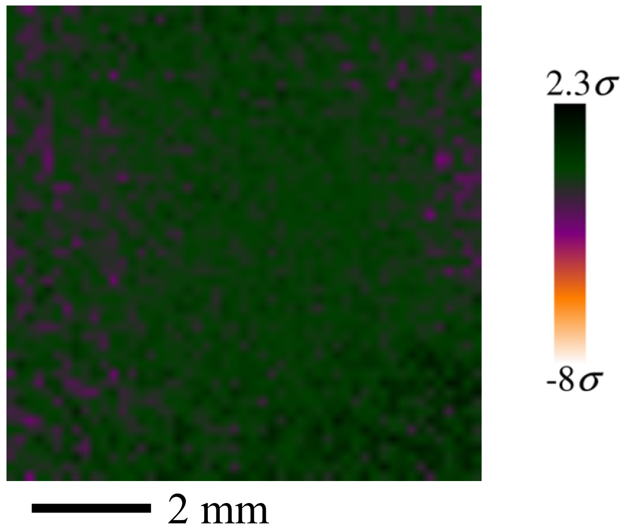


Colloidal gel

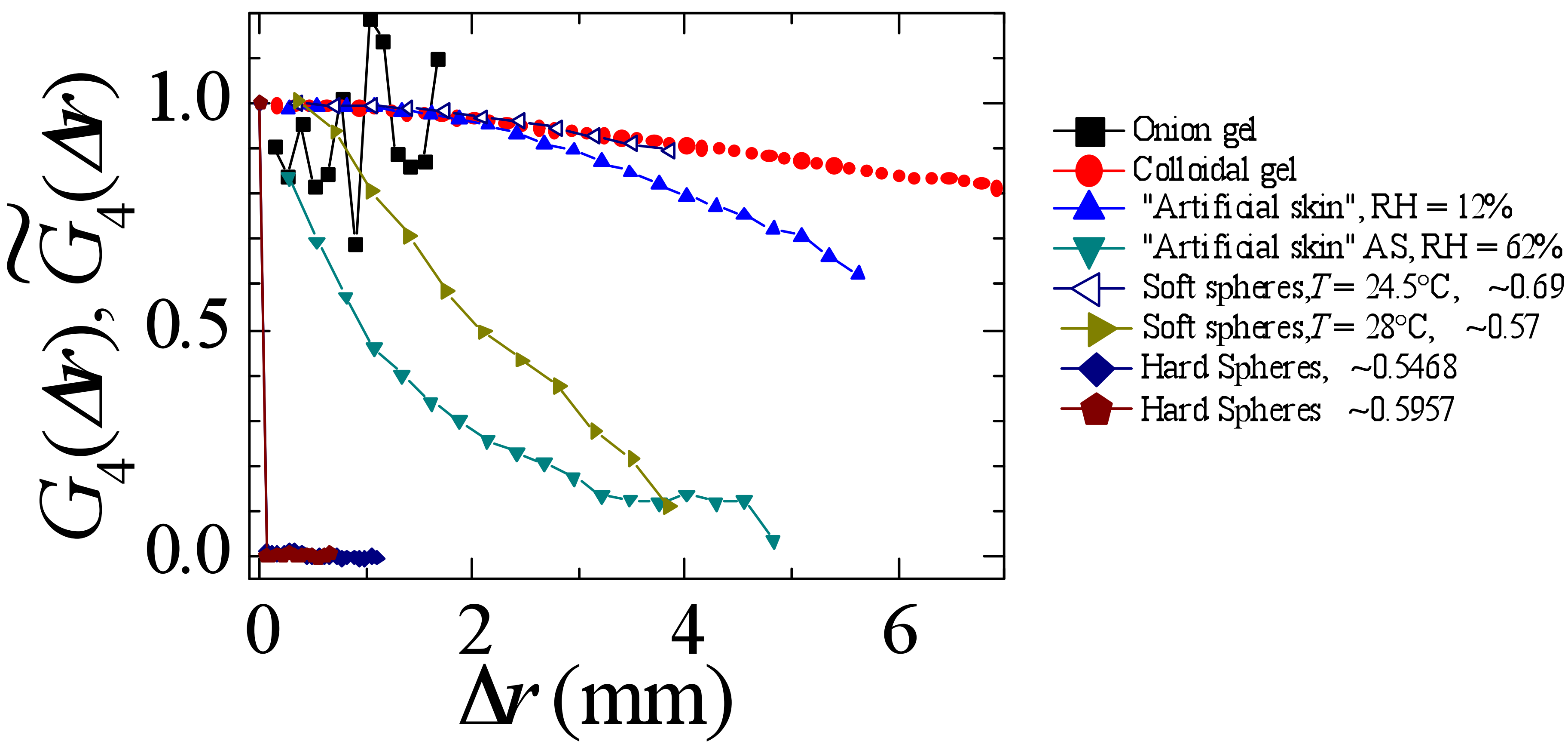
$g_2(\tau)\text{-}1\sim \exp[-(\tau/\tau_r)^{1.5}],\ \tau_r = 5000$ s

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

Movie accelerated 500x



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



Maccarrone et al., Soft Matter 2010

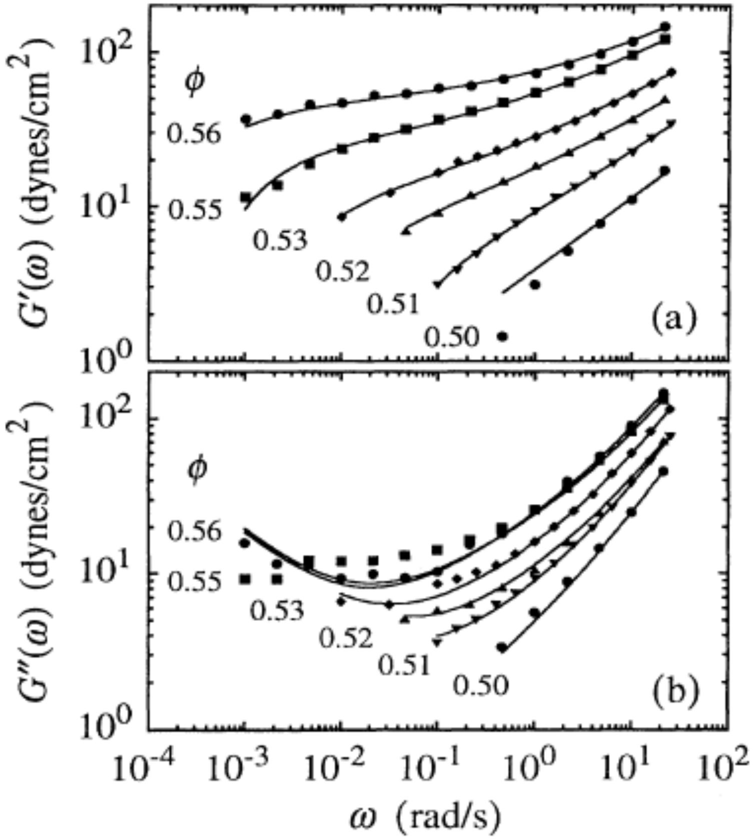
When does $\xi \longrightarrow$ infinity?

- $G' > G''$: **strain propagation** in a predominantly **solid-like** material

- **Magnitude** of G' **unimportant** ($G'_{\mathrm{onions}}/G'_{\mathrm{colloidal\ gel}} \sim 6 \times 10^4$!!)

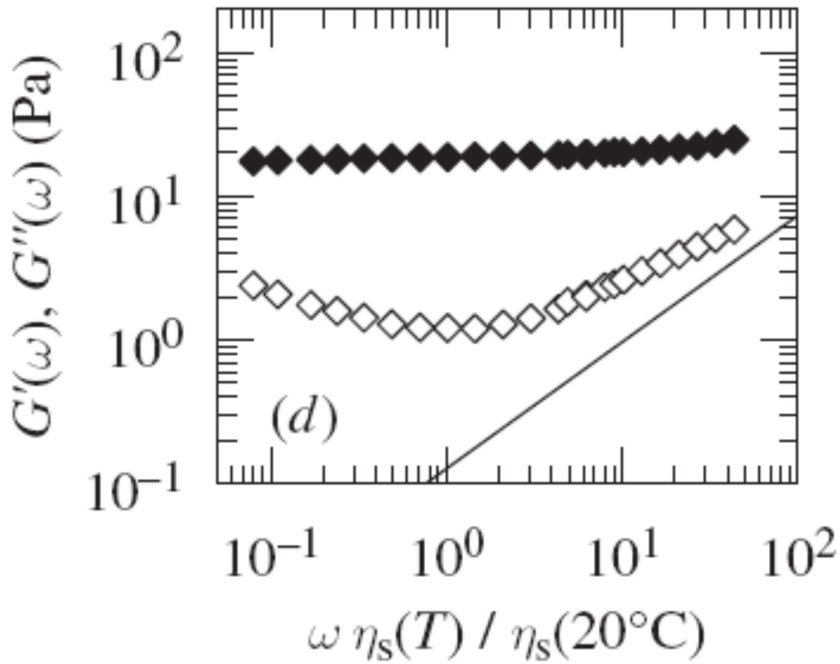
Rheology of hard and soft spheres

Hard spheres



Mason & Weitz., Phys. Rev. Lett. 1995

Soft spheres, $\varphi_{nom} = 0.69$



Sessoms et al.., Phil. Mag. A 2009

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- **Magnitude** of G' **unimportant** ($G'_{\text{onions}}/G'_{\text{colloidal gel}} \sim 6\text{x}10^4$!!)

- **Origin of elasticity**:
  - ***entropic*** (e.g. hard spheres) ξ very **small**
  - ***enthalpic*** (attractive gels, squeezed particles...) ξ **system-size**

Conclusions

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

- Supercooled hard spheres:
  - **equilibrium dynamics** above the (apparent) MCT divergence
  - ξ **limited** to 5-10a

- Jammed materials:
  - ξ and χ **may decouple!**
  - $\xi \sim$ **system size**
  - role of the **origin of elasticity**

Some open questions...

- Structural signature of Dynamical Heterogenity?
- Dynamical Heterogeneity and aging
- Origin of the dynamics and its long range correlation in (undriven) jammed soft materials. Internal stress ?
- DH in the spontaneous dynamics and plasticity/shear banding/fracture in driven systems

Thanks to...

L. Berthier (LCVN), V. Trappe (Fribourg)

Hard spheres
G. Brambilla, M. Pierno, D. El Masri (LCVN), A. Schofield (Edinburgh), G. Petekidis (FORTH)

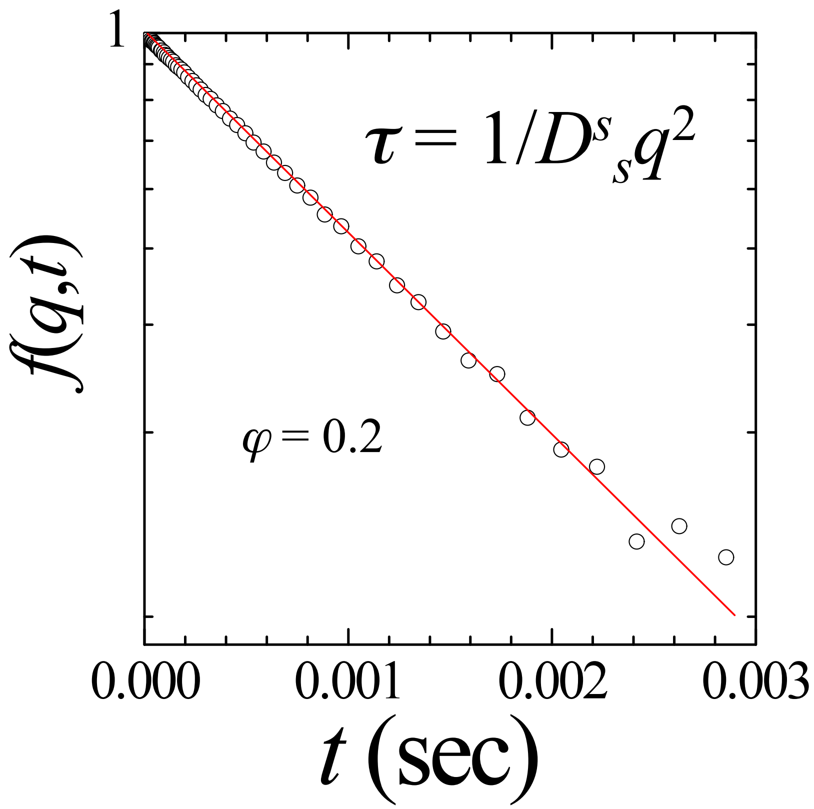
TRC
A. Duri, P. Ballesta (LCVN), D. Sessoms, H. Bissig (Firbourg)

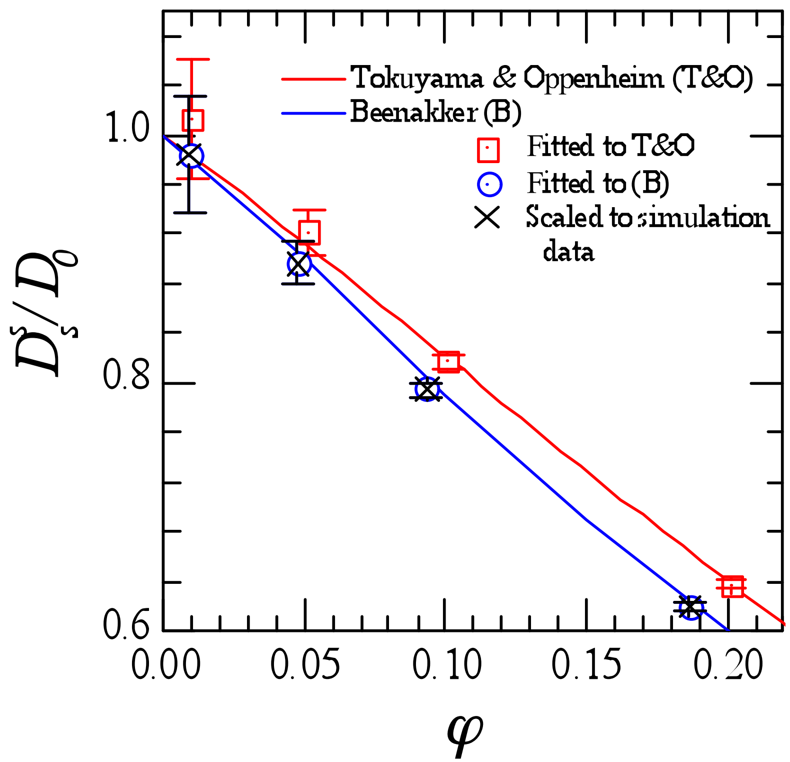
PCI
A. Duri, S. Maccarrone (LCVN), D. Sessoms (Fribourg), E. Pashkowski (Unilever)

Funding
CNES, ACI, ANR, PICS, Unilever

Determining the volume fraction

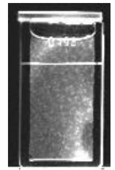
φ dependence of the short-time diffusing coefficient



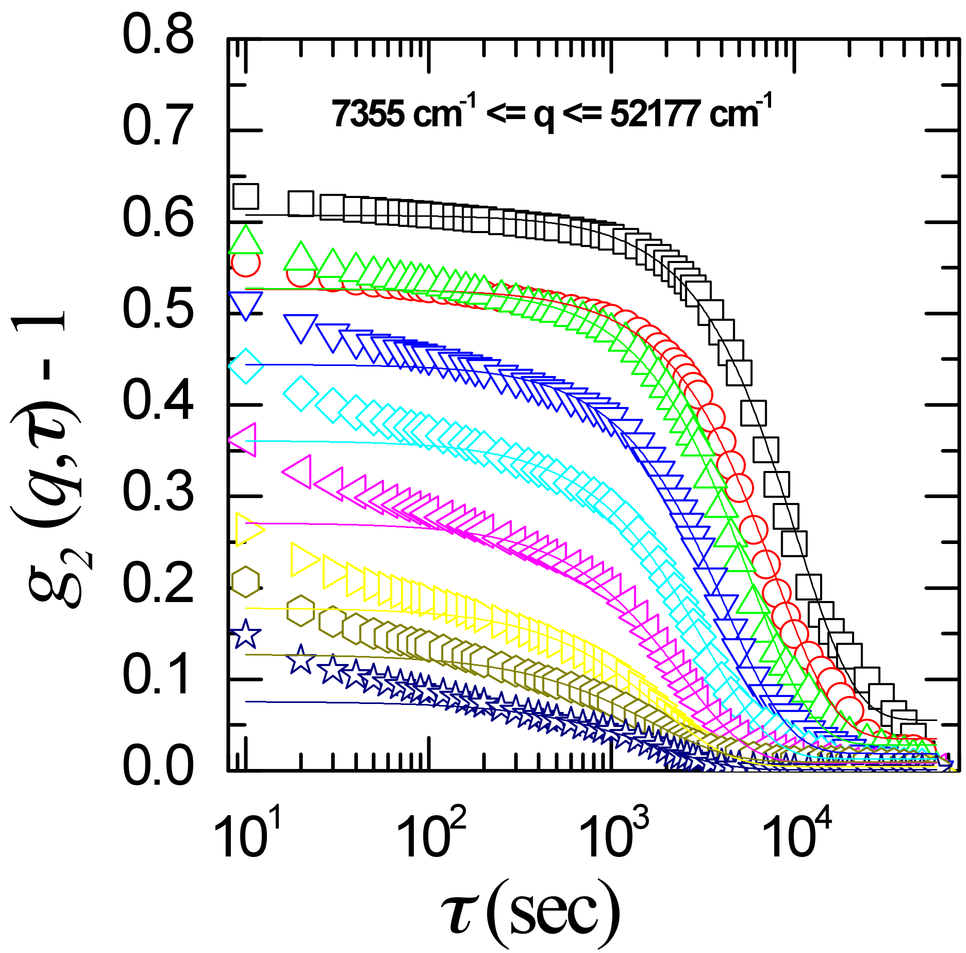


Absolute **uncertainty: ~4%** ***Relative*** **uncertainty: ~ 10^{-4}**

PS gel: time-averaged dynamics



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

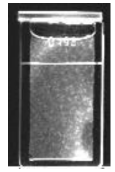


- **Fast dynamics**: overdamped vibrations (~ 500 nm) *Krall & Weitz PRL 1998*

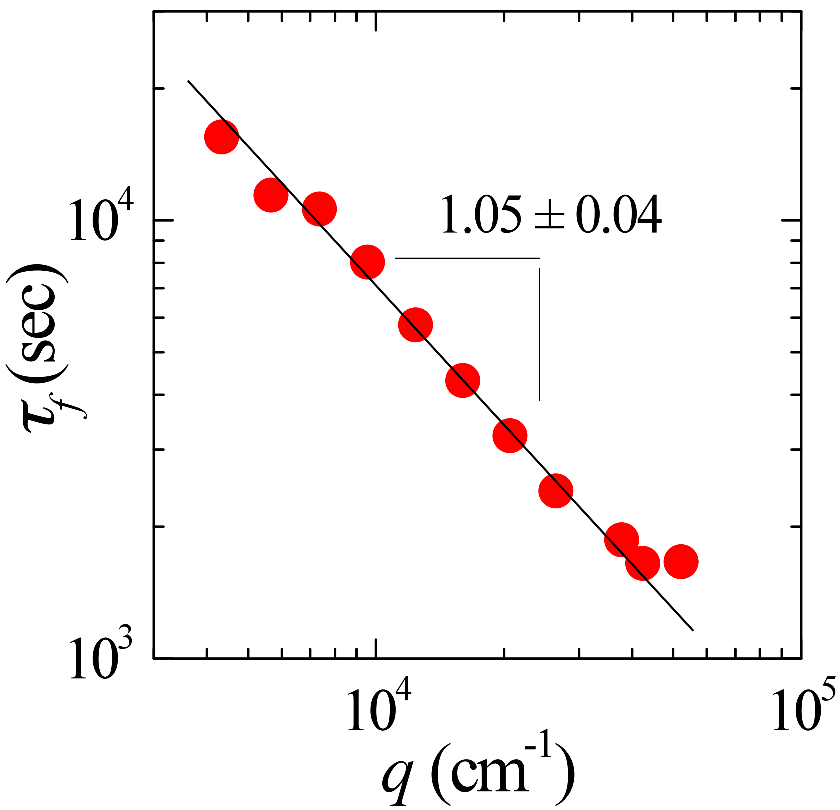
- **Slow dynamics**: rearrangements

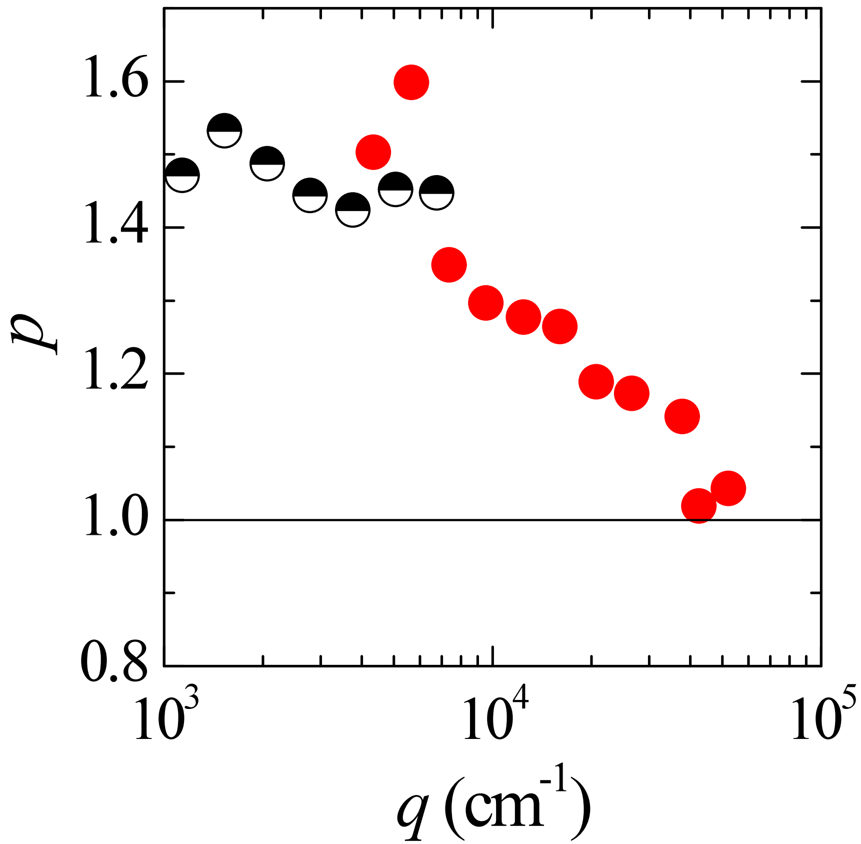
$$g_2(q,\tau) - 1 \sim \exp\left[-\left(\tau/\tau_f\right)^p\right]$$

PS gels: q dependence of τ_f and p



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

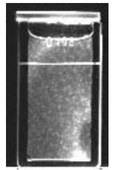


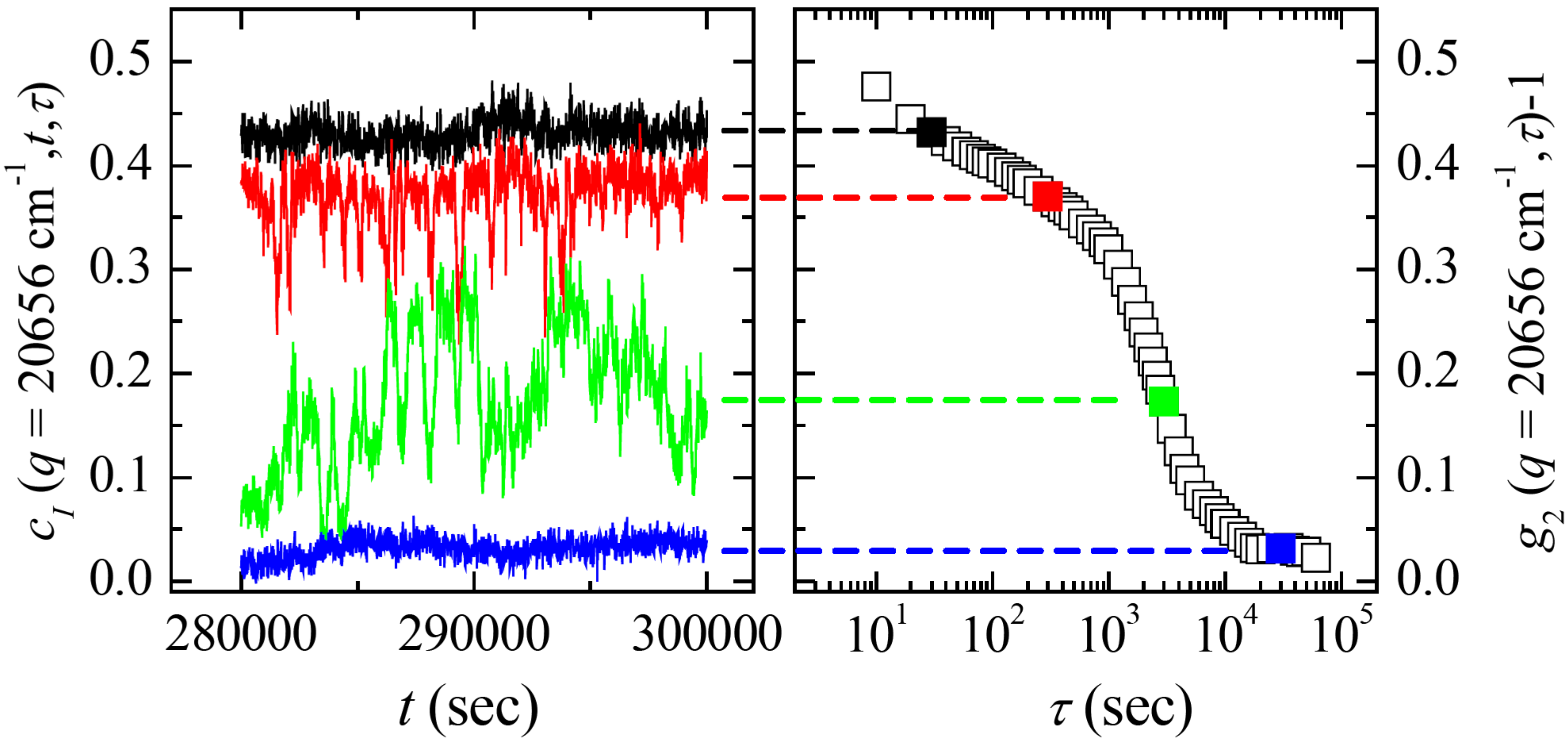


« ballistic » motion

« compressed » exponential

PS gel: temporally heterogeneous dynamics

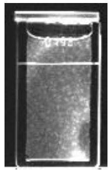




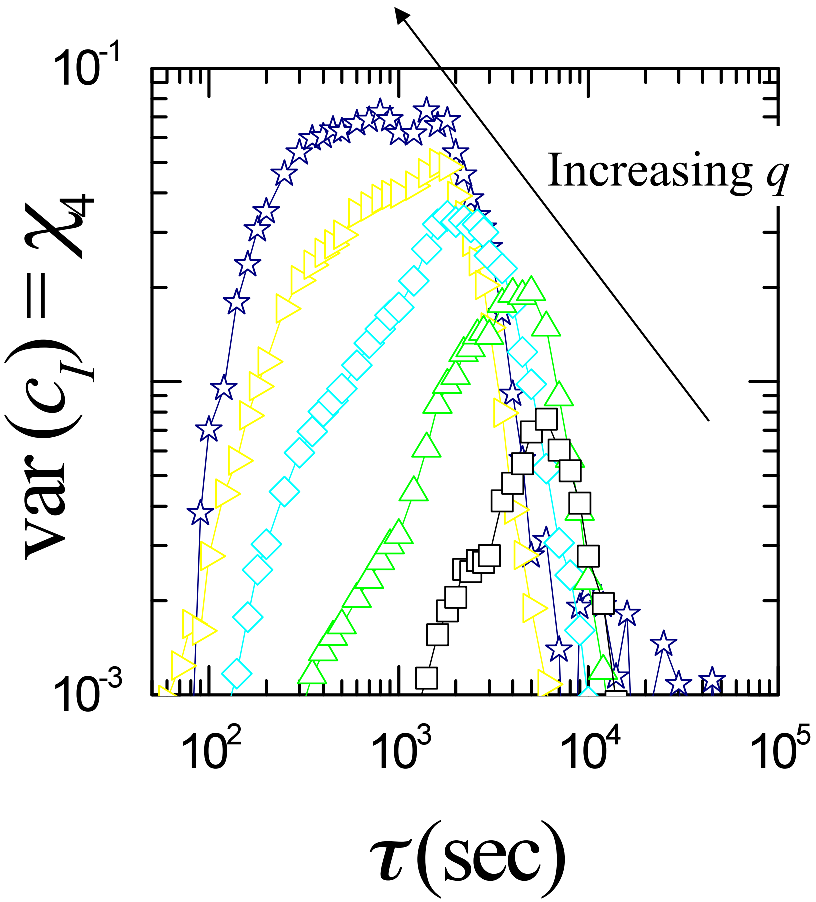
$c_I(t_w,\tau)$ @ fixed τ : temporal **fluctuations**

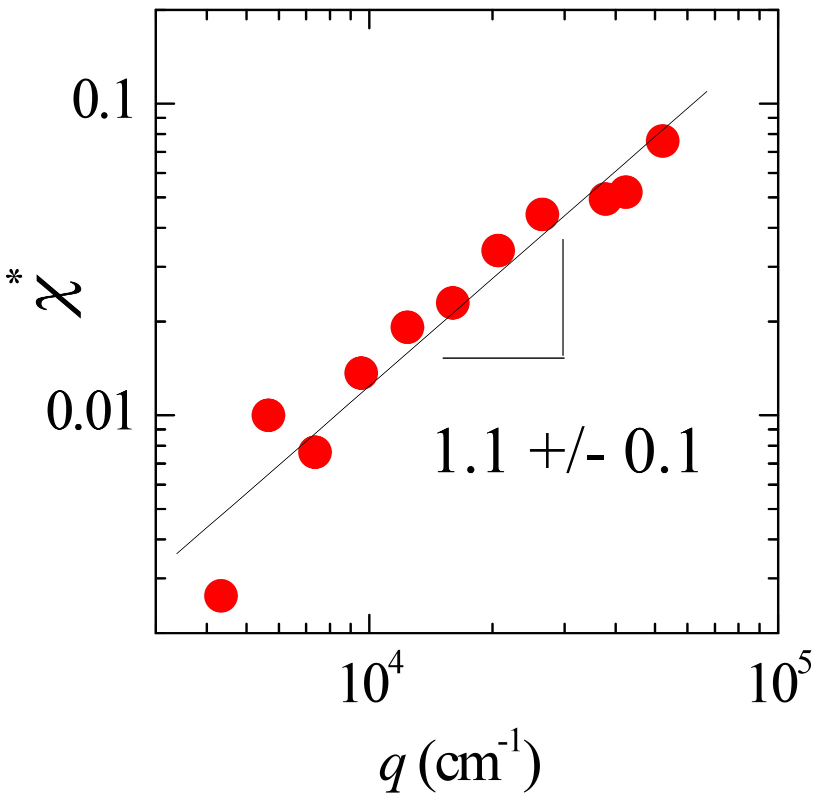
$<c_I(t_w,\tau)>_{tw}$: **average** dynamics

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



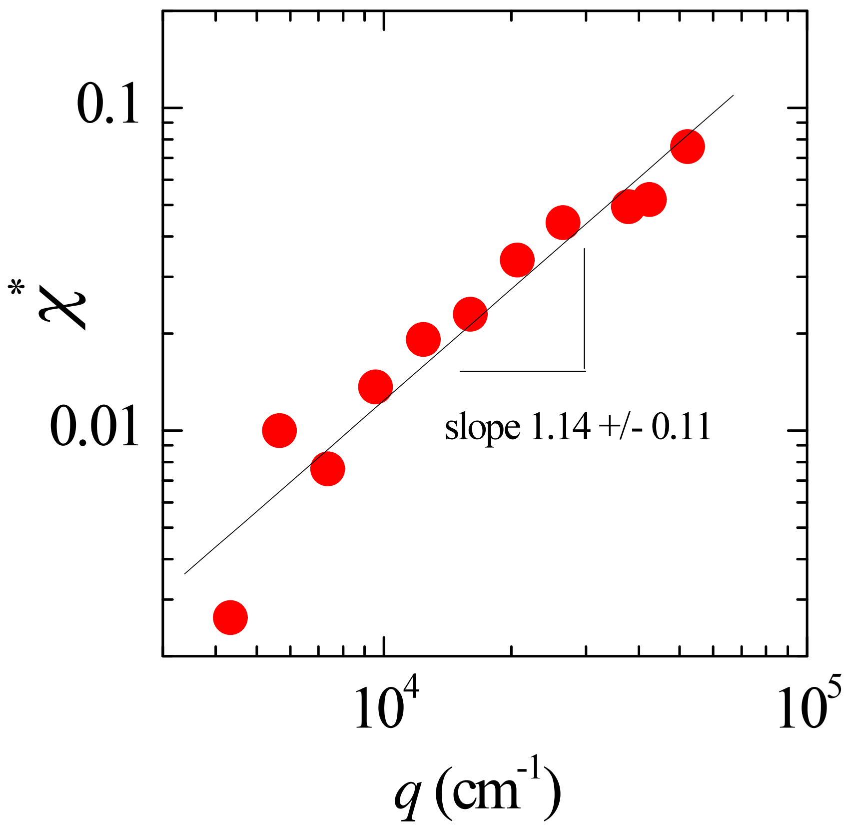
PS gel





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

Scaling of χ^*



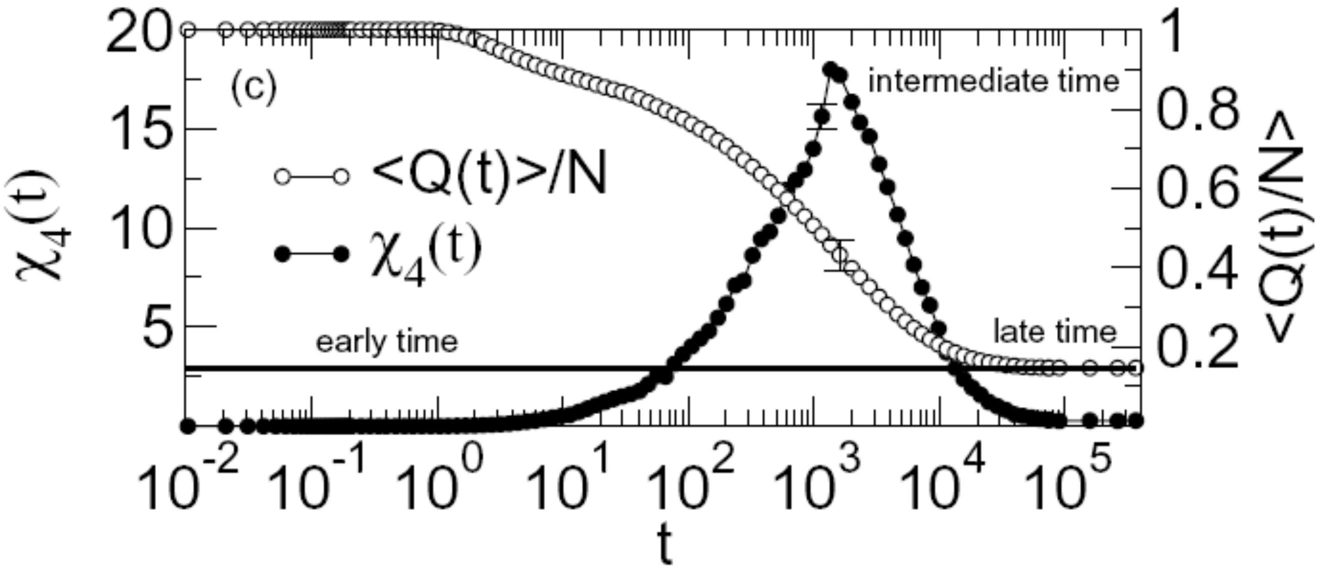
$$\chi^* \sim \mathrm{var}(n)/\langle n \rangle \sim 1/\langle n \rangle$$

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

$$\chi^* \sim q$$

Dynamical susceptibility in glassy systems

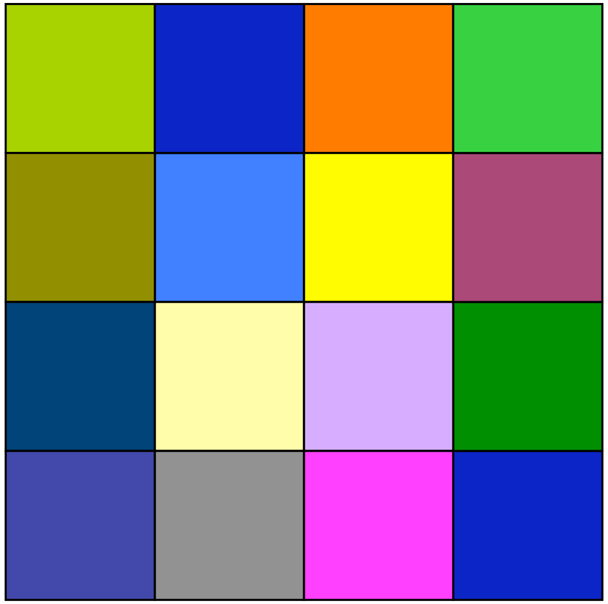
Supercooled liquid (Lennard-Jones)



Lacevic et al., Phys. Rev. E 2002

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

Dynamical susceptibility in glassy systems



N regions

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

$\chi_4 \Leftrightarrow$ dynamics spatially correlated

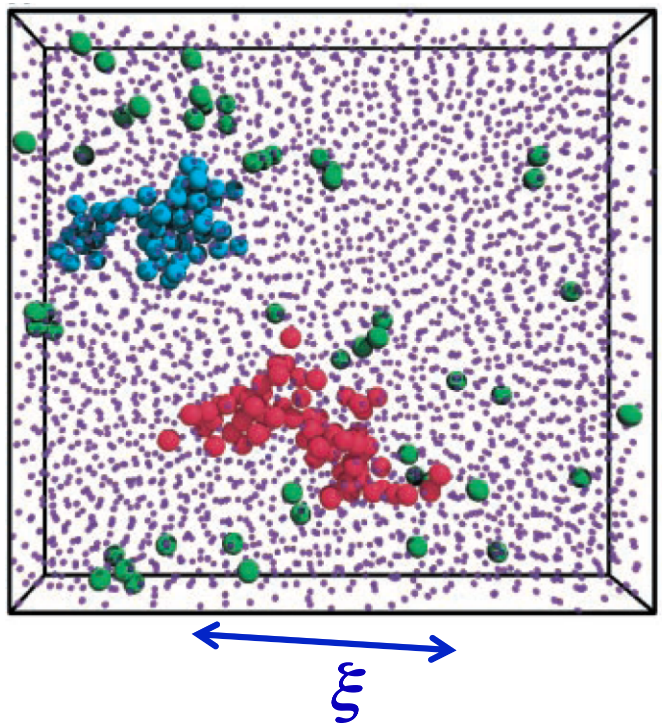
Dynamical susceptibility in glassy systems

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

Spatial correlation of the dynamics

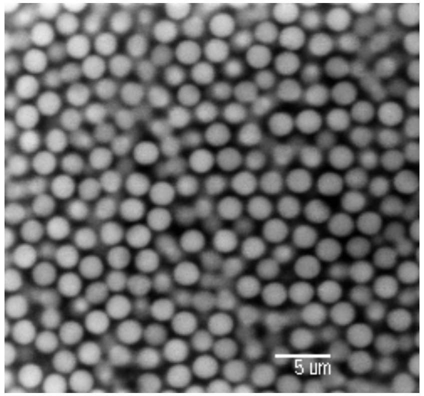
$$G_4(r;0,t) \sim \frac{A(t)}{r^p} e^{-r/\xi_4(t)}$$

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

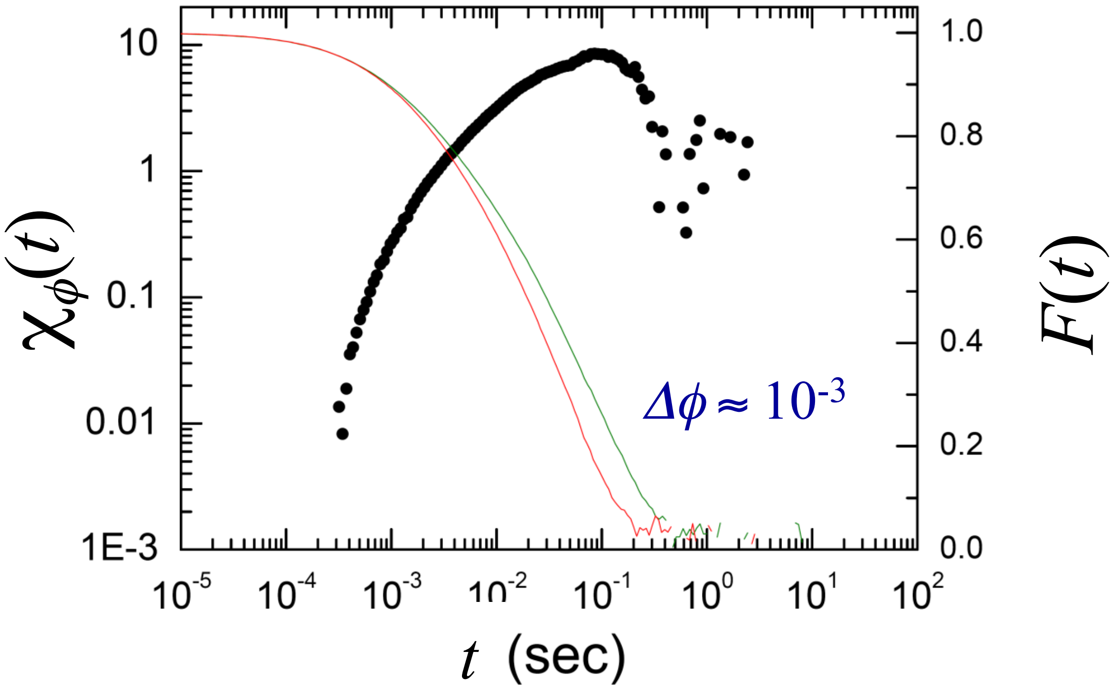


Weeks et al. Science 2000

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

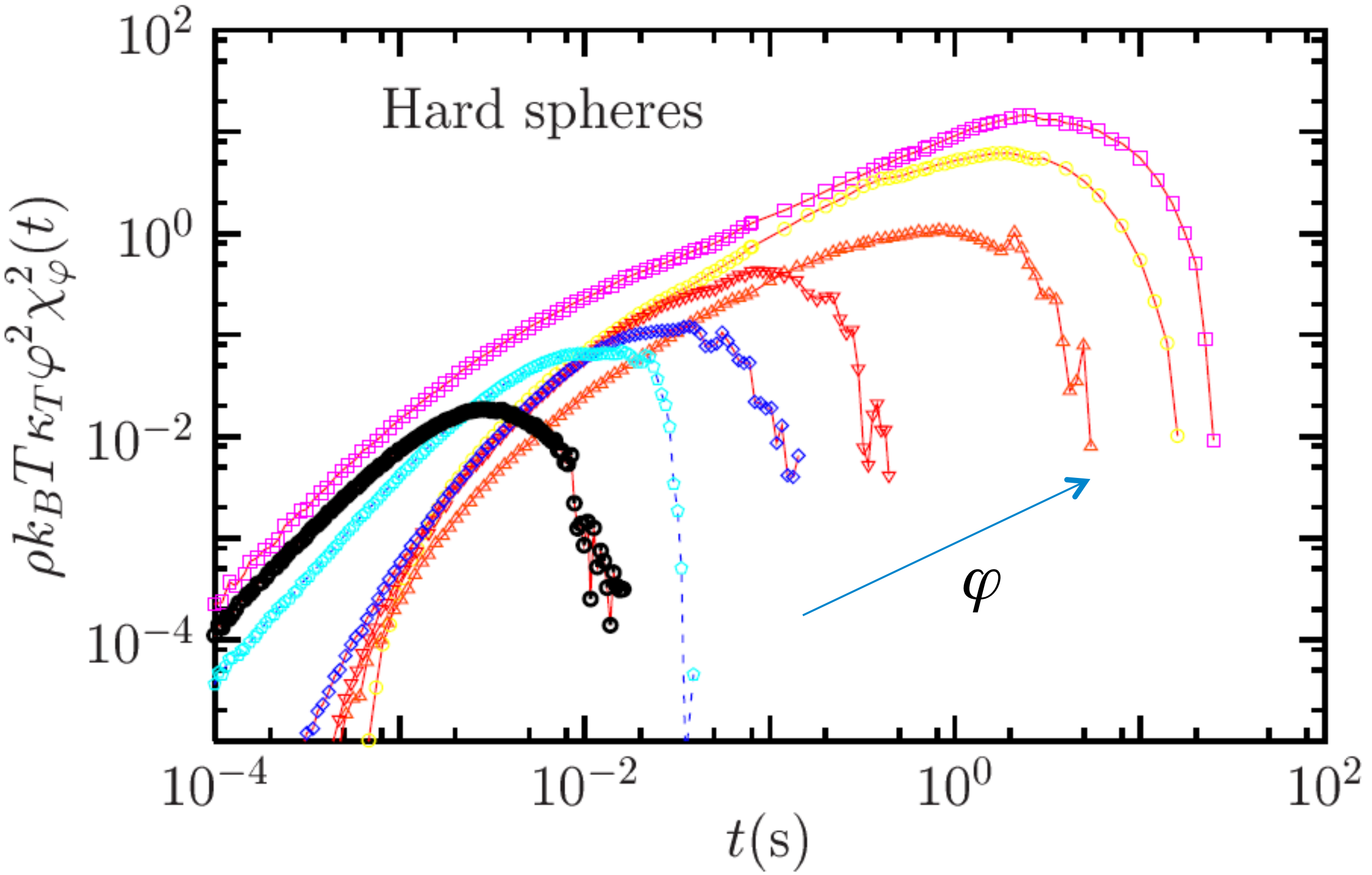
For colloidal HS at high φ

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

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

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

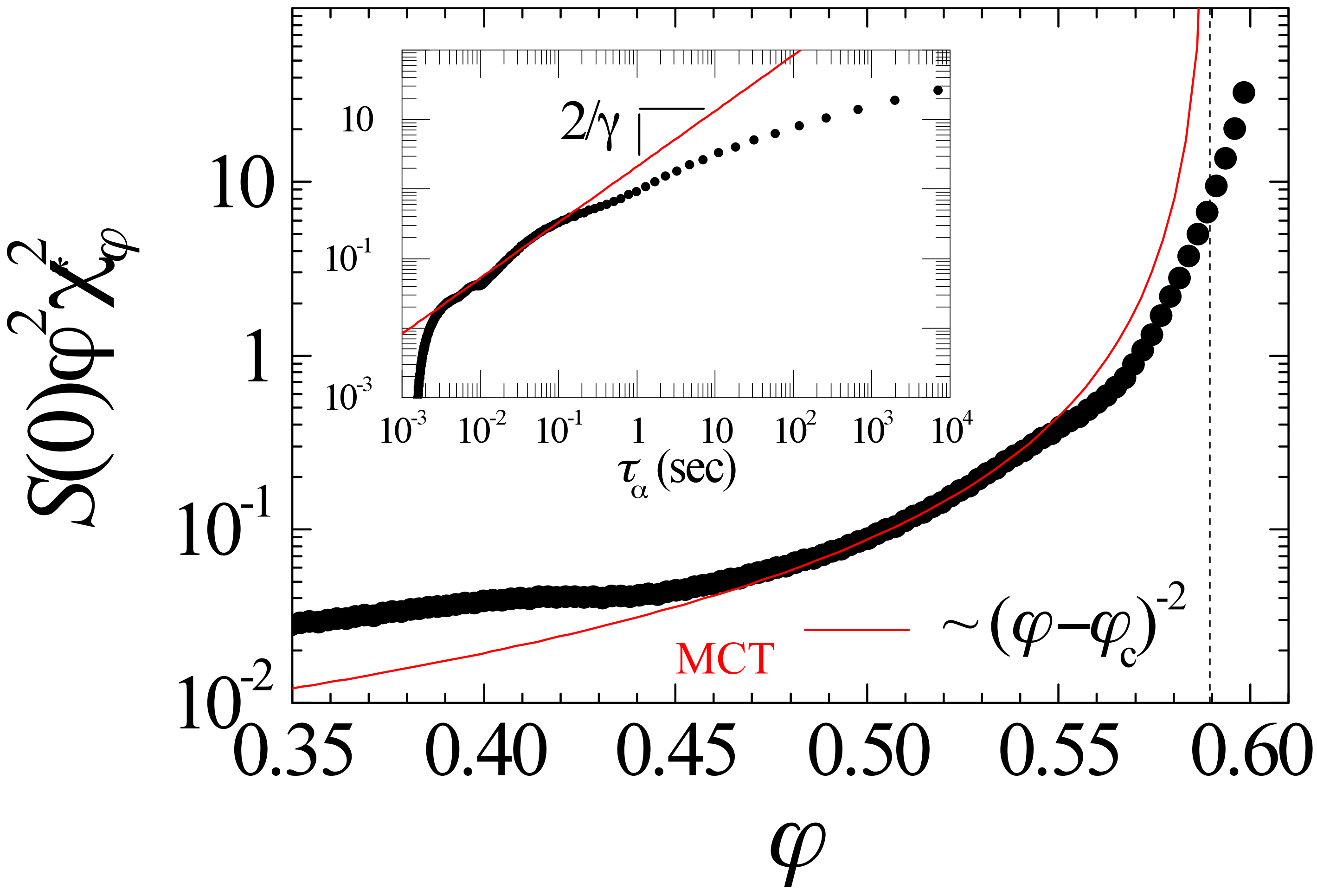
Evidence of a growing dynamic length scale



$\phi \sim 0.20 - 0.58$

Berthier et al., Science 2005

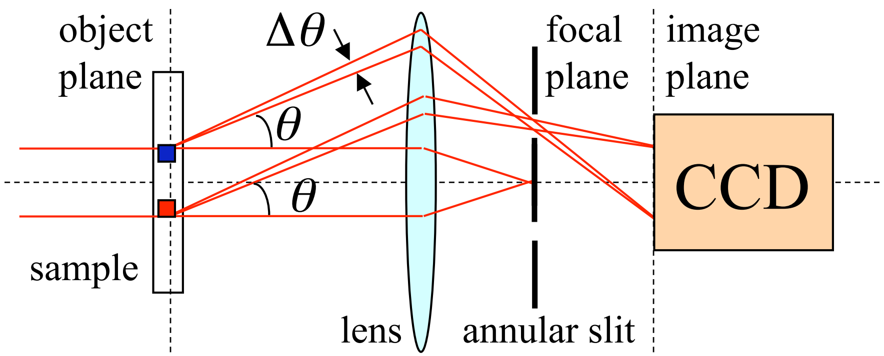
φ dependence of the max of χ_4



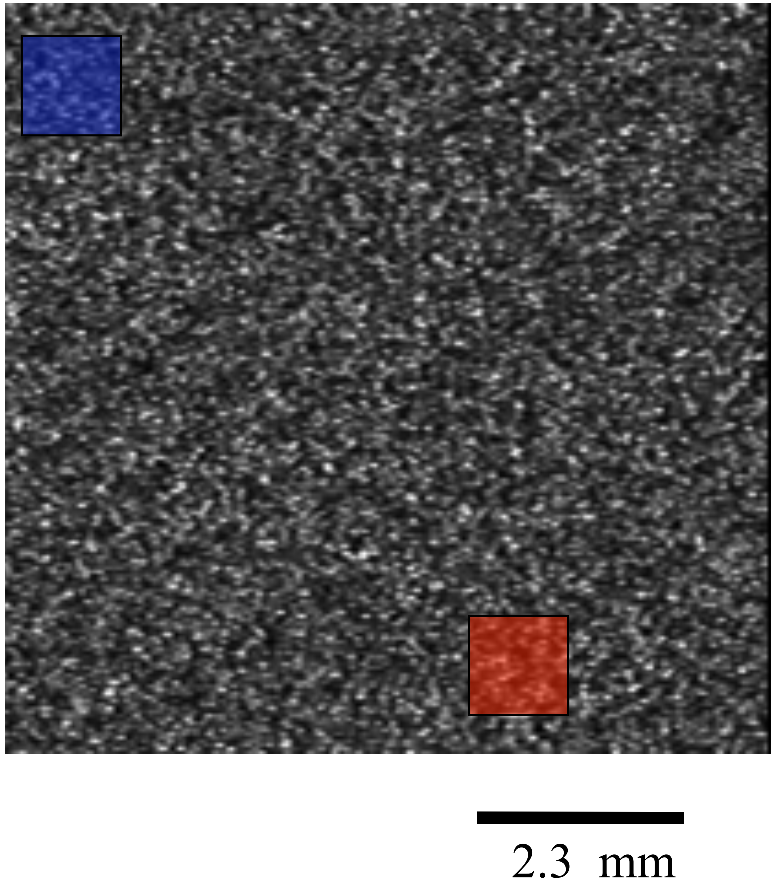
High φ :
deviation from MCT

Brambilla et al., PRL 2009

Photon Correlation Imaging (PCIm)



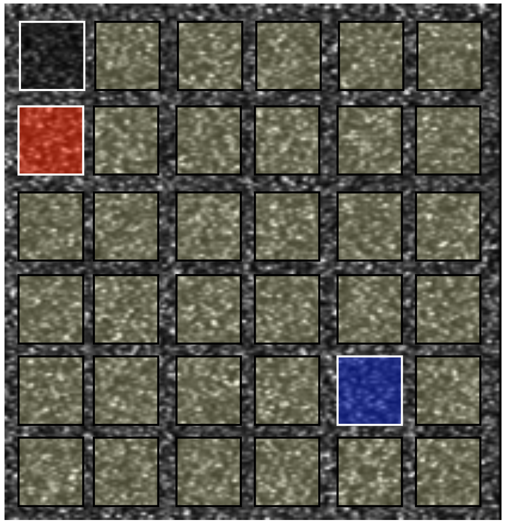
$\theta = 6.4°$ ⟶ $q = 1\ \mu m^{-1}$.

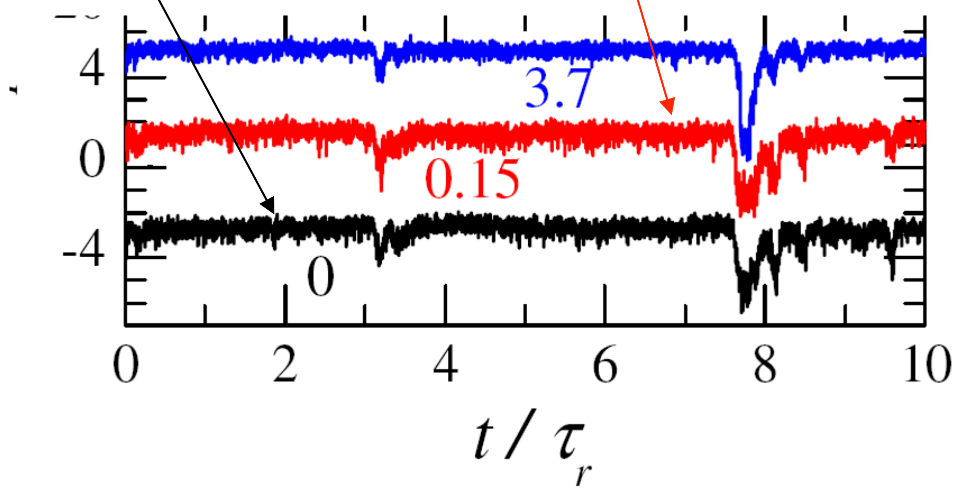


Duri et al., Phys. Rev. Lett. 2009

Spatial correlation of the dynamics

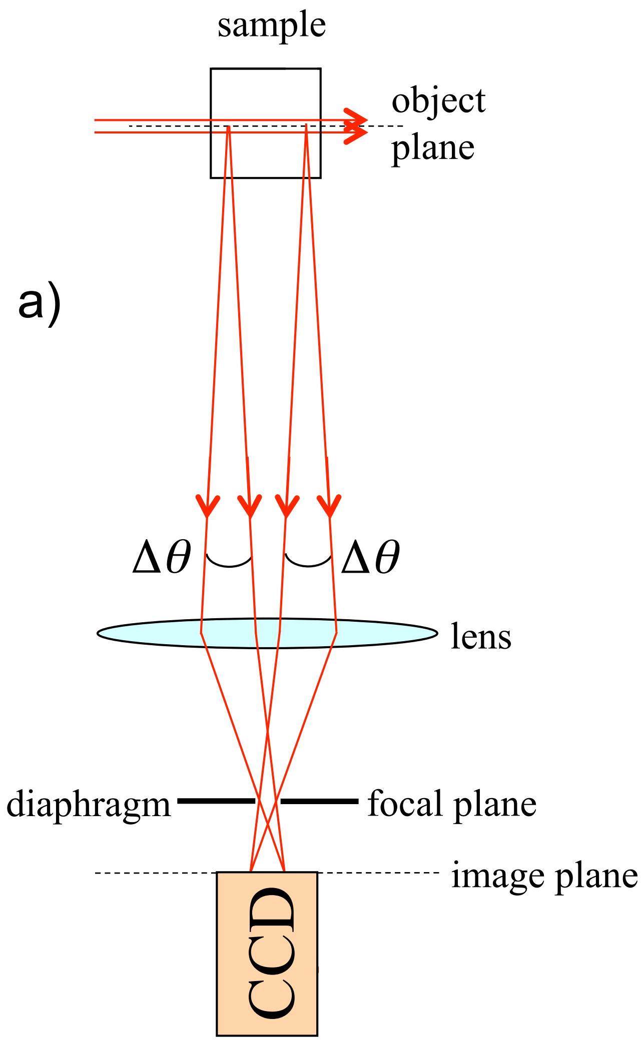
$$\tilde{G}_4(\Delta r, \tau) = \left\langle \frac{\langle \delta c_I(t, \tau; \mathbf{r}_1) \delta c_I(t, \tau; \mathbf{r}_2) \rangle_t}{\sigma(\tau, \mathbf{r}_1)\sigma(\tau, \mathbf{r}_2)} \right\rangle_{|\mathbf{r}_1 - \mathbf{r}_2| = \Delta r}$$



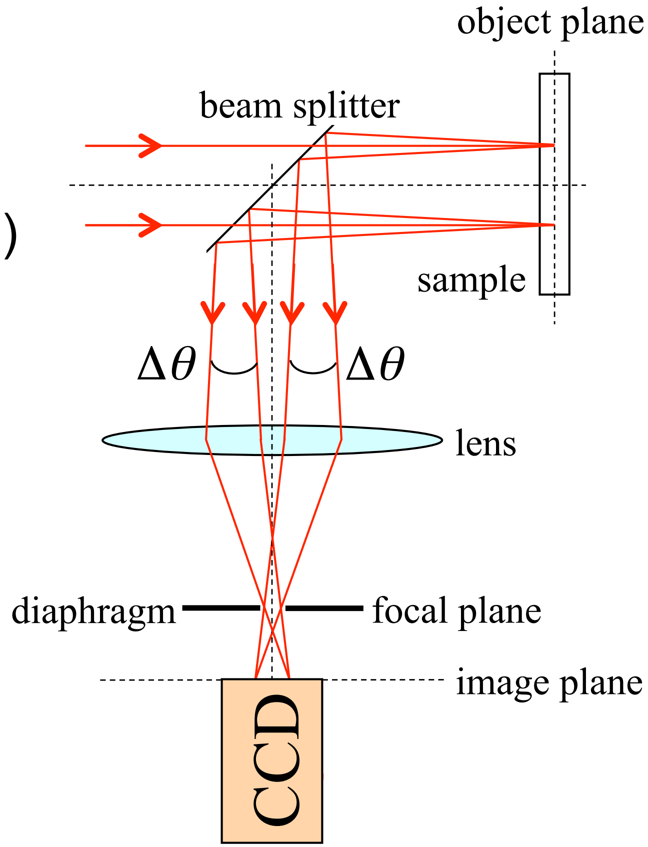


Other PCIm geometries

a)



b)



Additional stuff on diverging ξ

TABLE I: Rheological parameters of most of the system shown in Figs. 5 and 6. The sample names are as in the caption of Fig. 5.

	ν (Hz)	$G'(\nu)$ (Pa)	$G'(\nu)/G''(\nu)$	Ref.
On	1	600	15	[40]
CG	1	$\sim 0.9 \times 10^{-3}$	10	[52]
SoS, $\varphi = 0.57$	1.6	0.6	0.3	[27]
SoS, $\varphi = 0.69$	1.6	20	8	[27]
HS, $\varphi = 0.5468$	1	210	1.25	[53, 54]
HS, $\varphi = 0.5957$	1	> 400	> 1.4	[53, 54]
Laponite	0.7	$\gtrsim 300$	20	[48, 49]

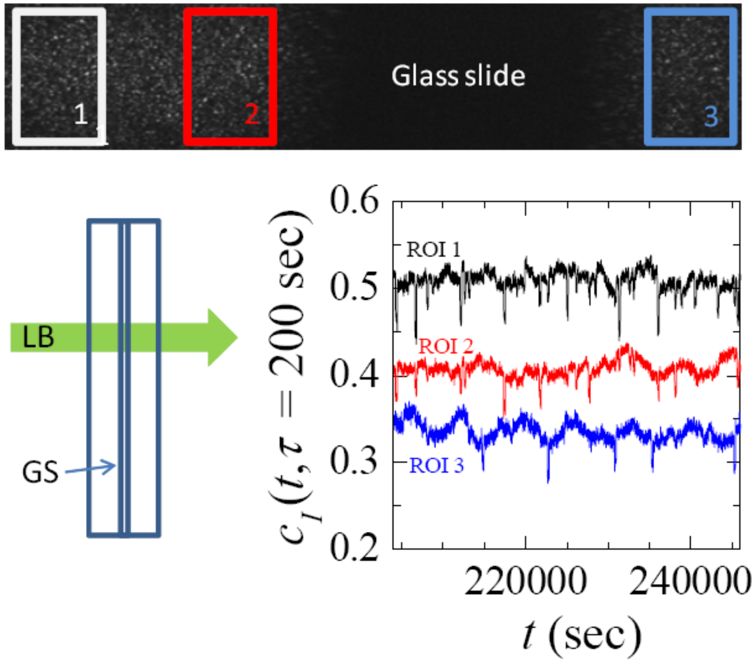


FIG. 6: Bottom left: schematic side view of the cell used for the experiment on Laponite. LB: laser beam, GS: glass slide. Top: typical CCD image of the scattering volume. The dark region corresponds to the thickness of the glass slide, view from the side. The three ROIs for which the degree of correlation is shown in the bottom right plot are highlighted. The size of the imaged region is $2.62 \times 0.52\text{mm}^2$. Bottom right: time dependence of c_I, for a delay time $\tau = 200$ sec, for the three ROIs shown above. For the sake of clarity, the curves of ROIs 1 and 2 have been offset vertically by 0.2 and 0.1, respectively. Note that the signals measured on the same side of the glass slide (ROIs 1 and 2) are correlated, while signals from opposite sides are uncorrelated.