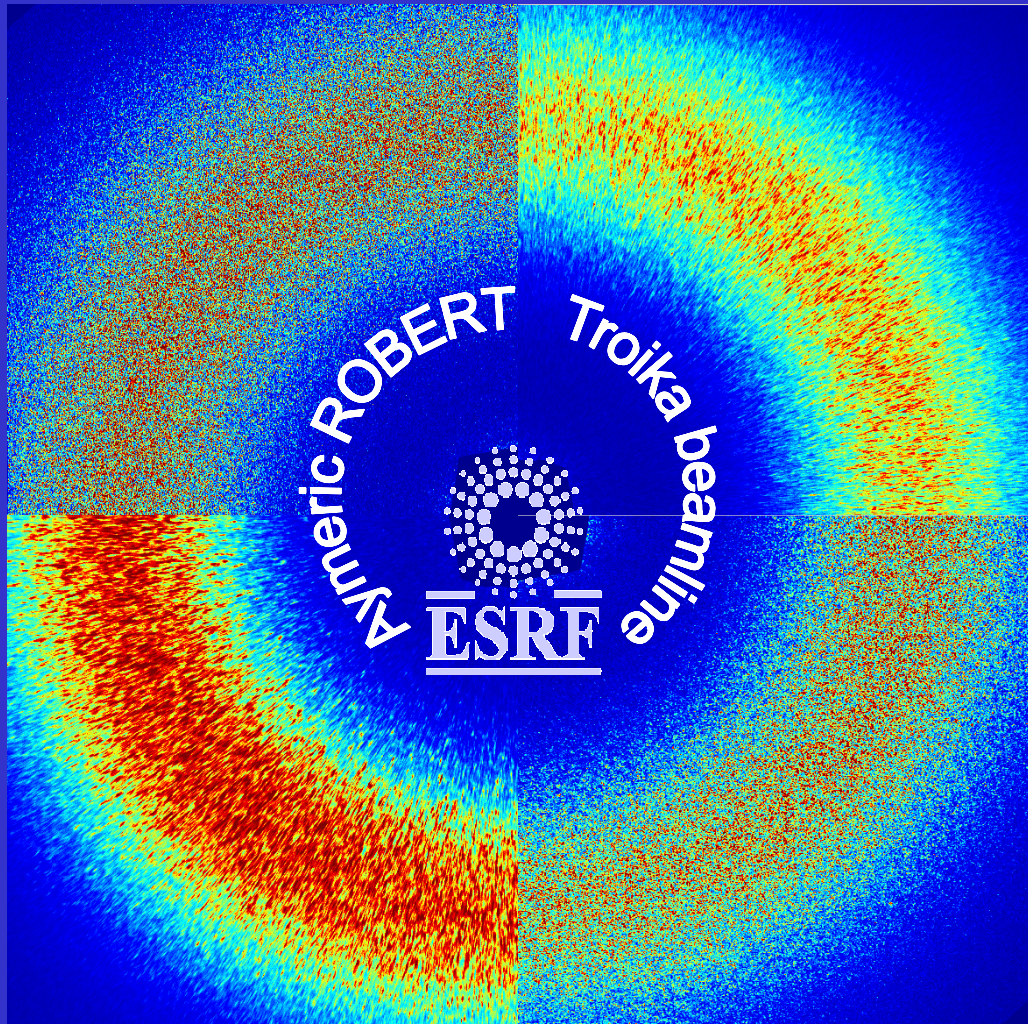
Probing Slow Dynamics in Complex Systems with 2D-XPCS



Probing slow dynamics in complex systems with 2D-XPCS

OUTLINE

- dynamics of complex systems (colloidal dispersions)
- XPCS
- Self-diffusive properties of colloidal dispersions
- probing α-relaxation of glassy materials (ferrofluids)
- conclusion and perspectives

Investigations on colloidal systems

STATICS | **DYNAMICS**

techniques : SAXS, SANS, SALS | DLS, NSE

measured : S(Q), F(Q) | **D(Q)** effective diffusion coefficient

F(Q) : characteristic sizes
shape
polydispersity
internal structure …

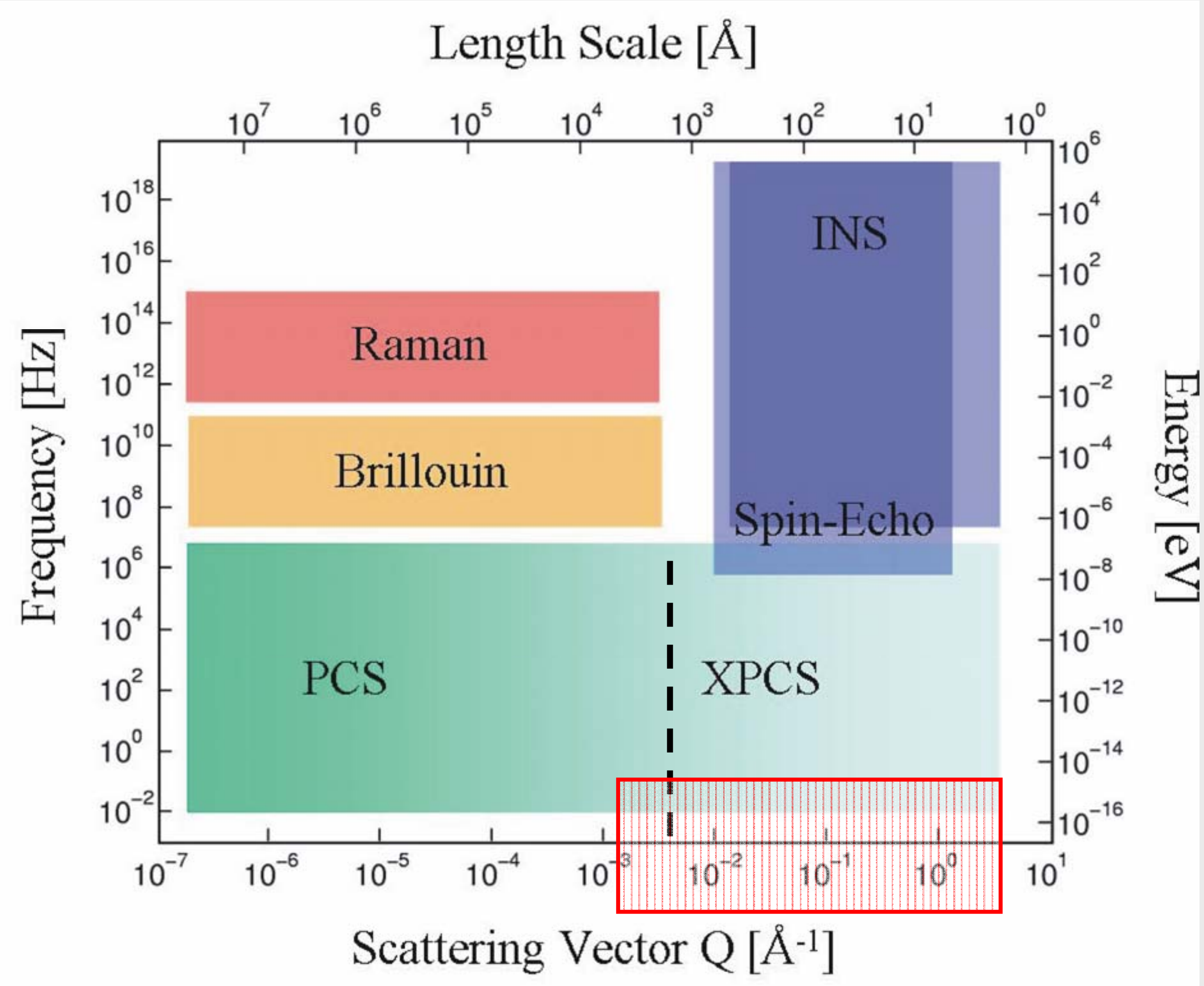
S(Q) : "interparticle" distances
interparticle interactions

NSE : very fast dynamics (10^{-9}s)
on molecular lengthscales

DLS : dynamics in transparent systems
on micron's lengthscale
for intermediate timescales
(10^{-7}s to 10^{4}s)

SAXS with coherent x-rays (XPCS) can be used as a new probe of the dynamics

XPCS experiment



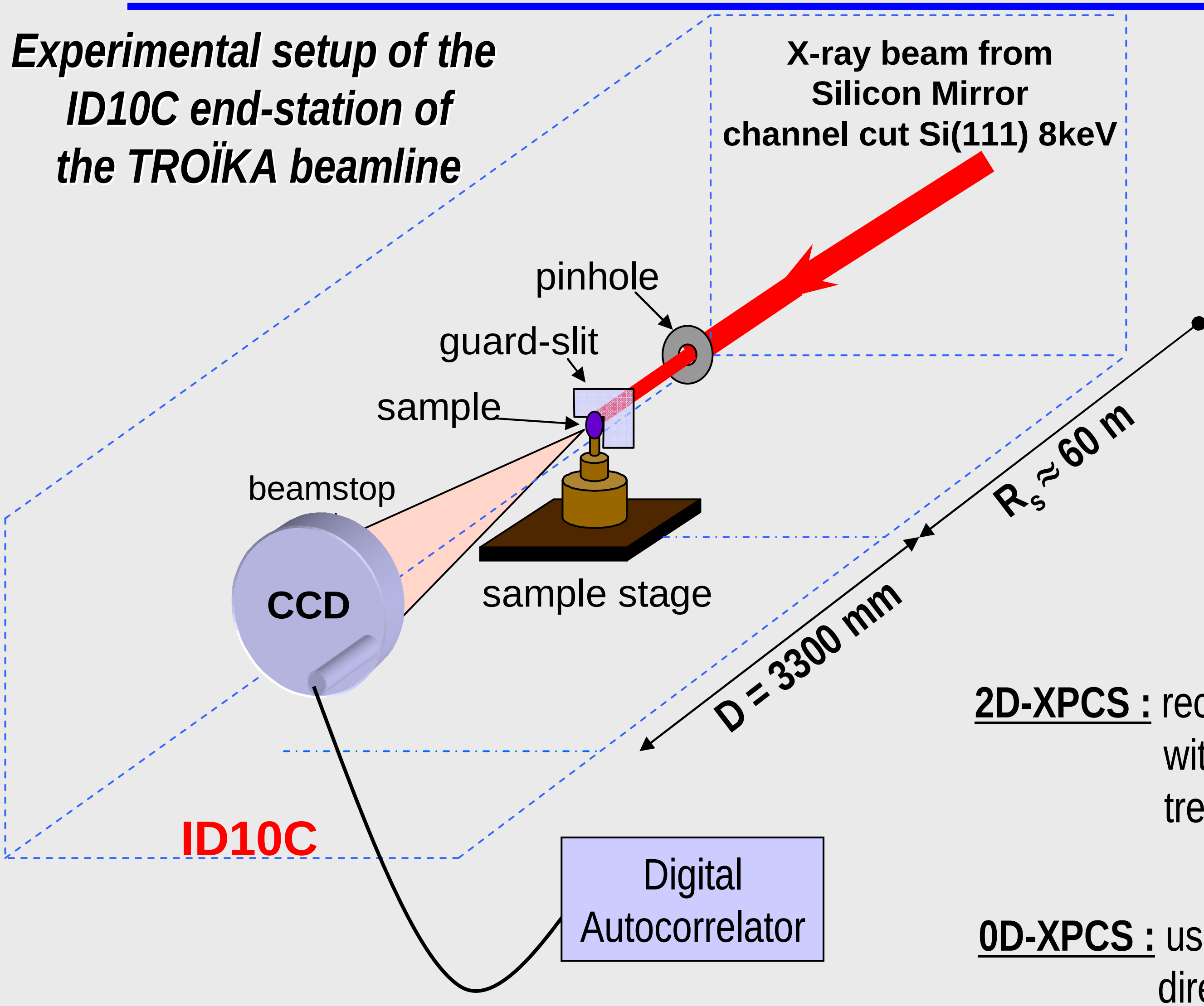
→ No limitation in accessible Q-range

→ Not subject to multiple scattering

Ref : G. Grübel et al., J. Appl. Cryst. 33, 424 (2000)

Experimental setup

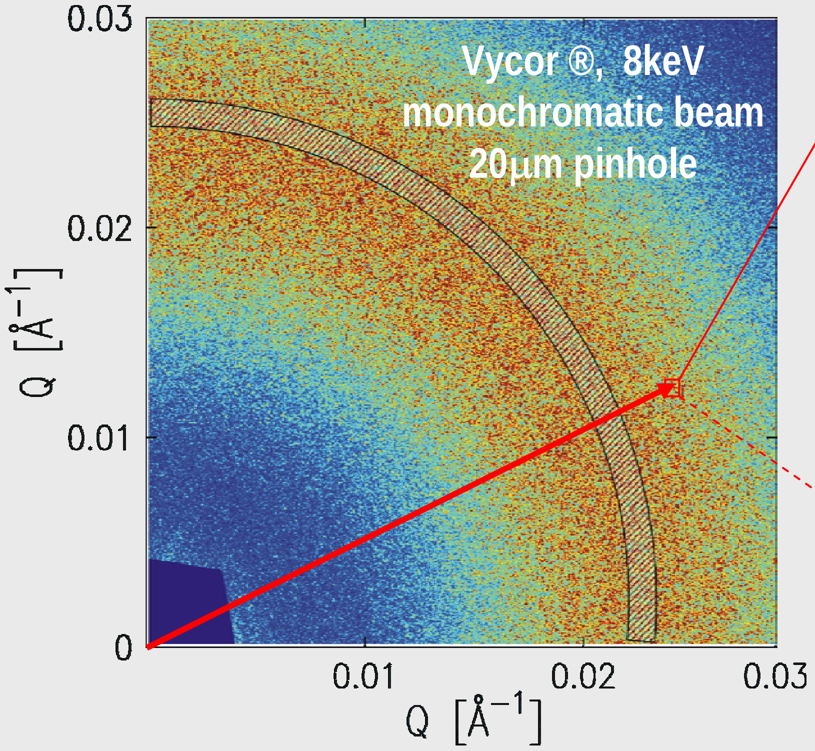
Experimental setup of the ID10C end-station of the TROÏKA beamline



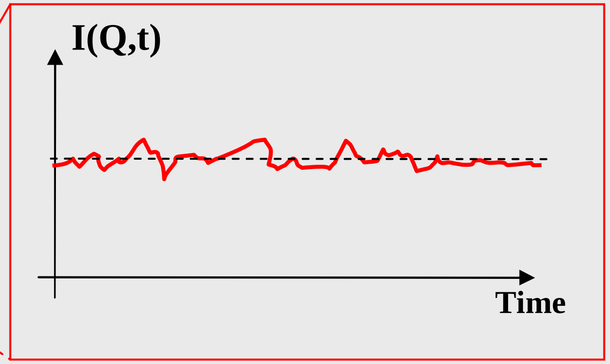
<u>2D-XPCS :</u> recording speckle patterns with a CCD and computer treatment afterwards

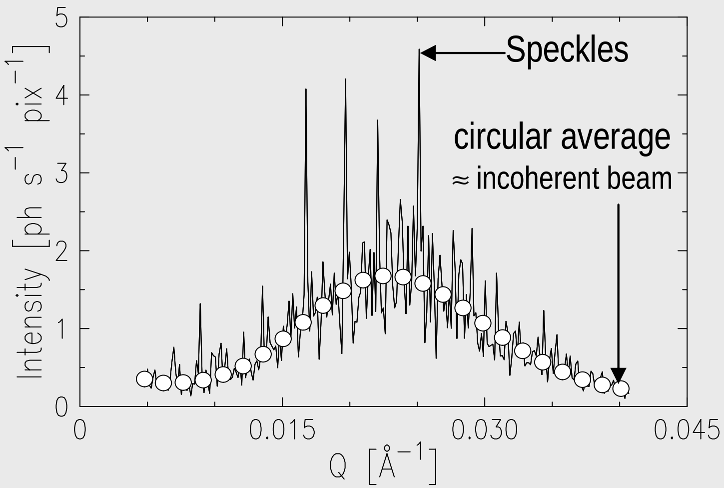
<u>0D-XPCS :</u> use a point detector, directly connected to digital autocorrelator (⇔ DLS)

Speckle patterns



If scatterers move ⇒ evolution of speckle pattern





quantifying intensity time-fluctuations

Information on the underlying dynamics of the system

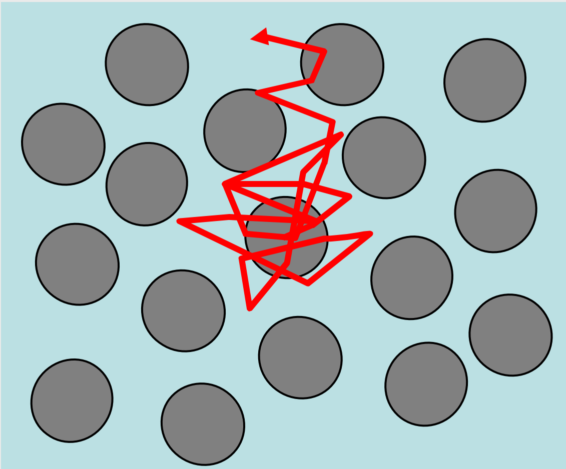
Intensity autocorrelation function

$$g_2(Q,\tau) = \frac{\langle I(Q,t) \cdot I(Q,t+\tau) \rangle}{\langle I(Q) \rangle^2}$$

$$g_2(Q,\tau) = 1 + C \cdot |f(Q,\tau)|^2$$

2D-XPCS : Silica spheres in cooled glycerol

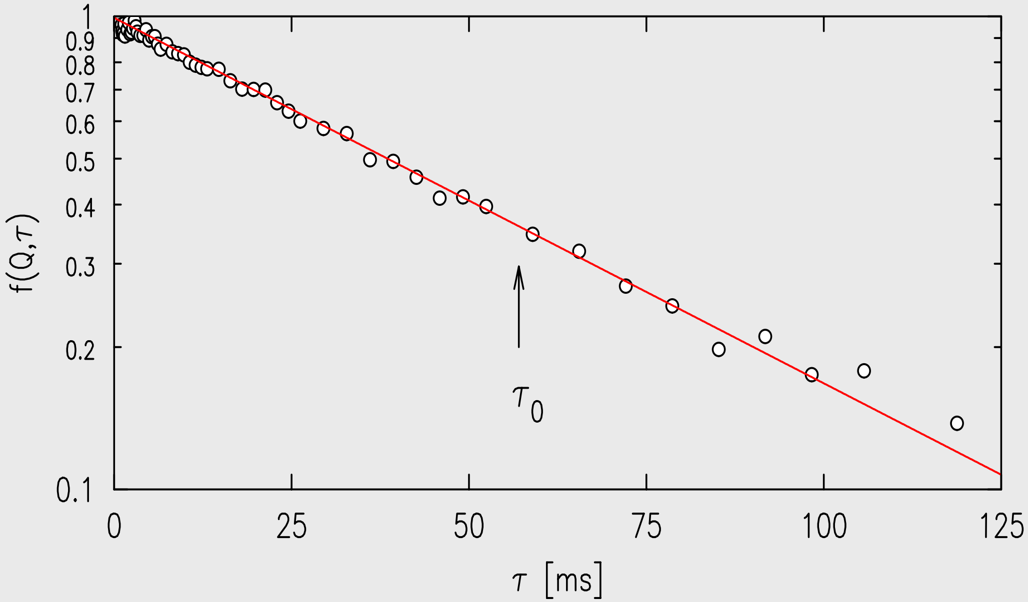
V. Trappe (University of Fribourg) & L. Cipelletti (Universite Montpellier)



R = 2610Å , ΔR/R ≈ 3% , Φ=10vol%

ISF for brownian dynamics

$$f(Q,\tau) = \exp[-\Gamma(Q)\cdot\tau] \quad , \quad \text{with} \quad \Gamma(Q) = D(Q)\cdot Q^2$$



For dilute non-interacting suspensions : $D(Q) = D_0 = kT/(6\pi\eta R)$

For interacting suspensions : $D(Q) = \dfrac{D_0}{S(Q)} H(Q)$

2D-XPCS : Silica spheres in cooled glycerol

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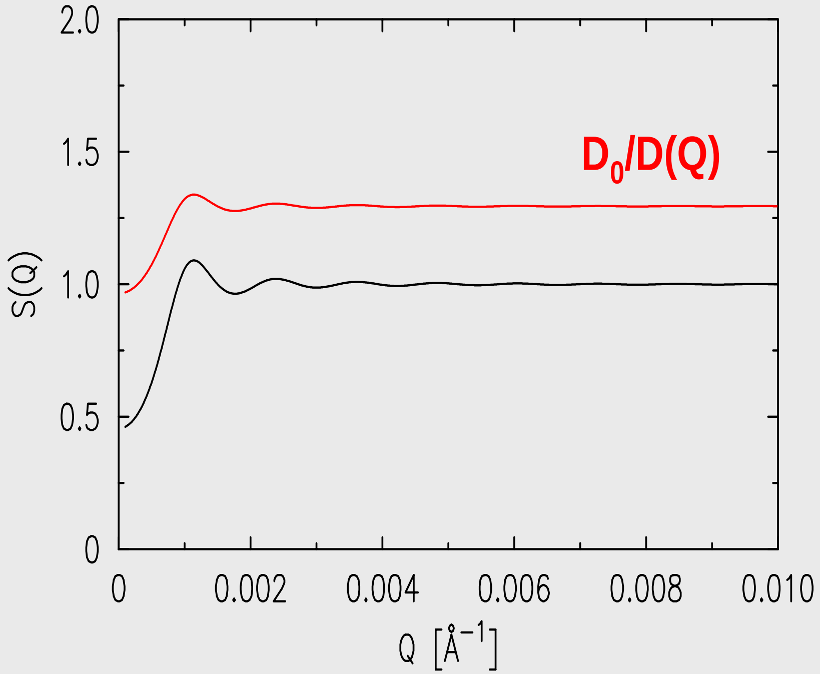
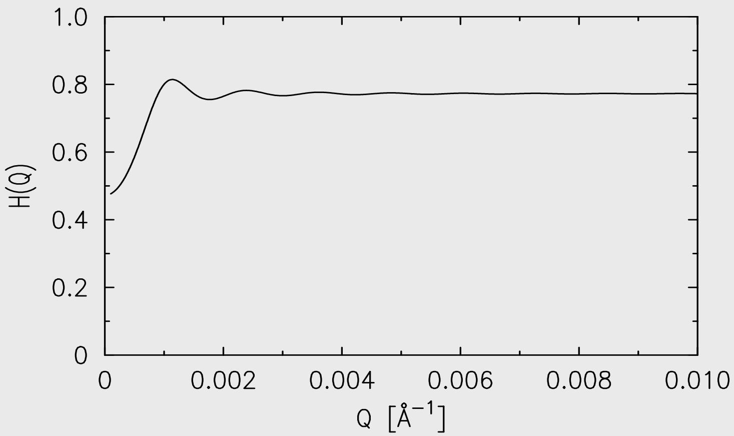




For interacting suspensions :

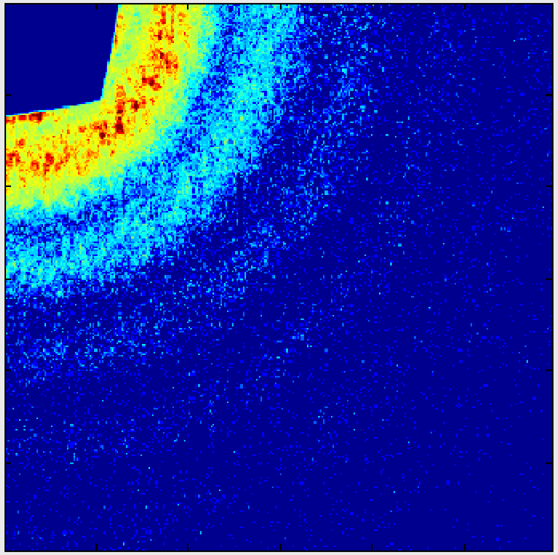
$$D(Q) = \frac{D_0}{S(Q)} H(Q)$$

Self-diffusive properties

$$D_S = D(Q \to \infty) = D_0 \cdot H(\infty)$$

$$\Gamma(Q) = D_S \cdot Q^2$$

2D-XPCS : Silica sphere in cooled glycerol

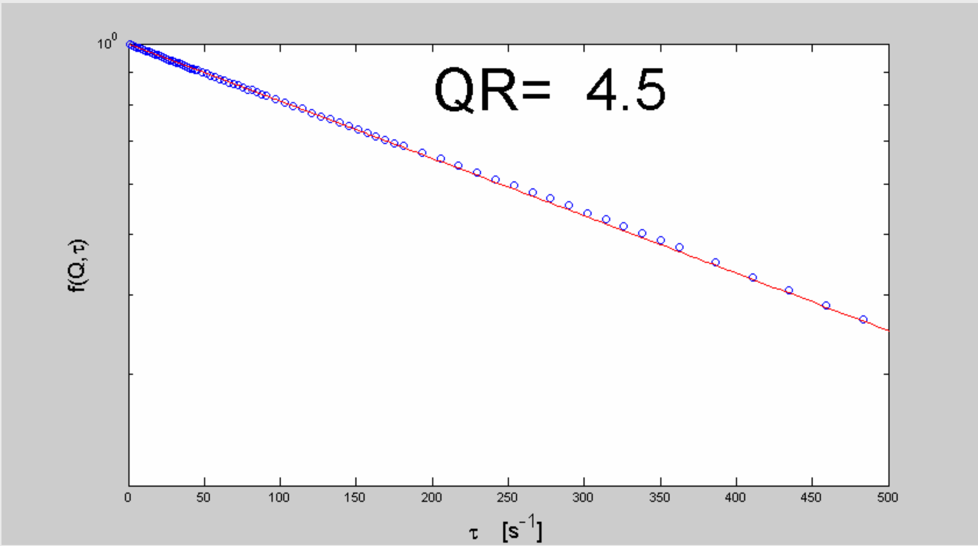


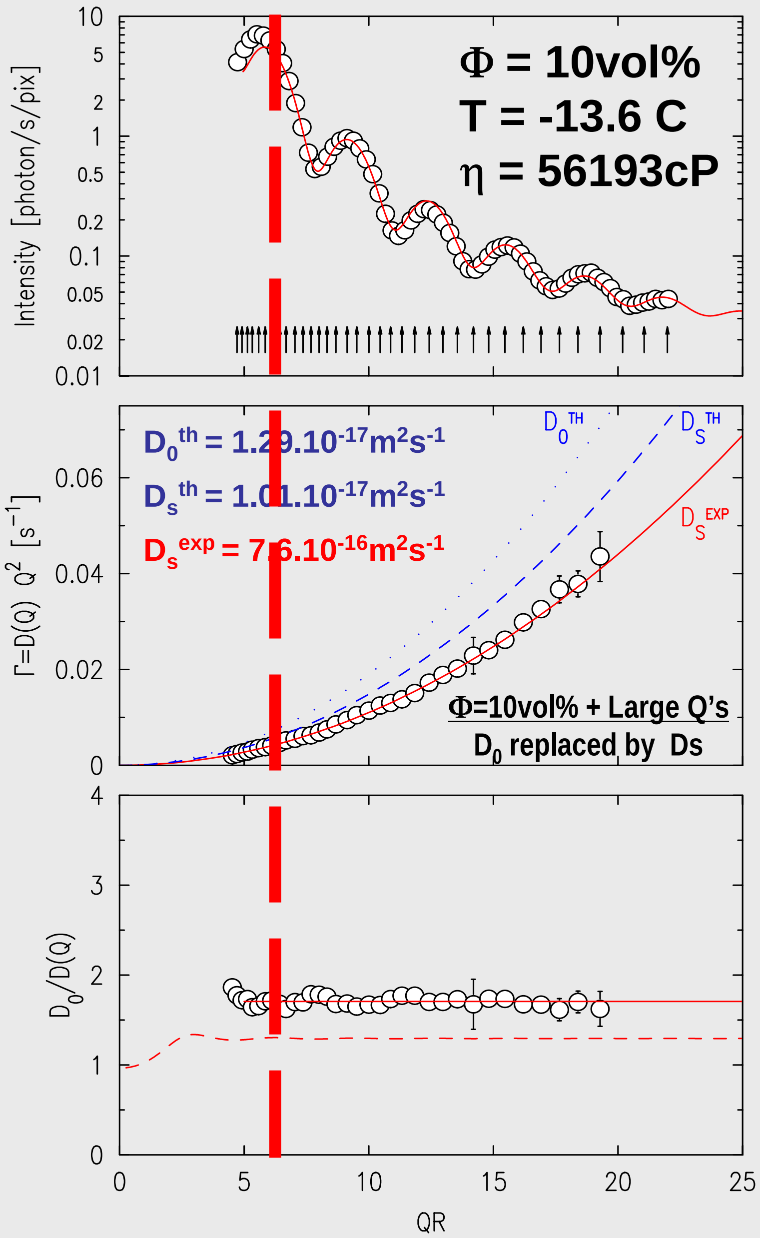
R = 2610Å

ΔR/R ≈ 3%

⇒extension of the Q-range (vs DLS)

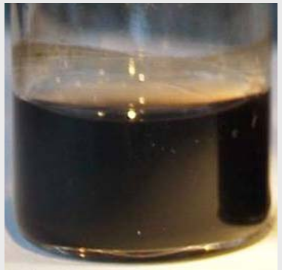
⇒opaque system





Ferrofluids : magnetic colloidal dispersions

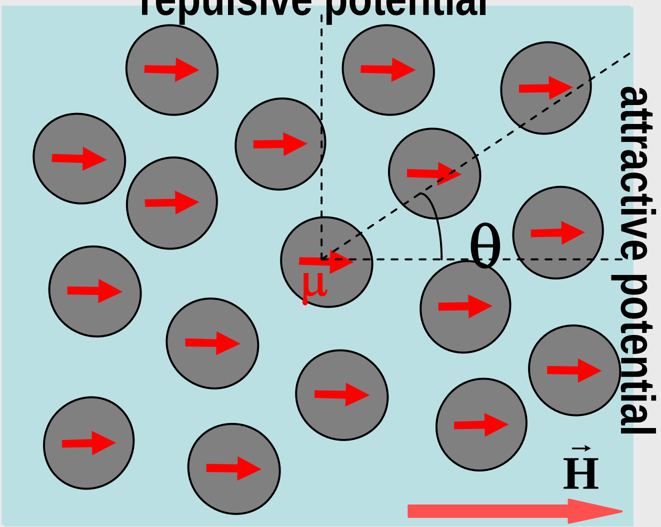
R. Perzynski, E. Dubois, E. Wandersman, V. Dupuis, G. Meriguet, LI2C , Universite Pierre et Marie Curie, Jussieu



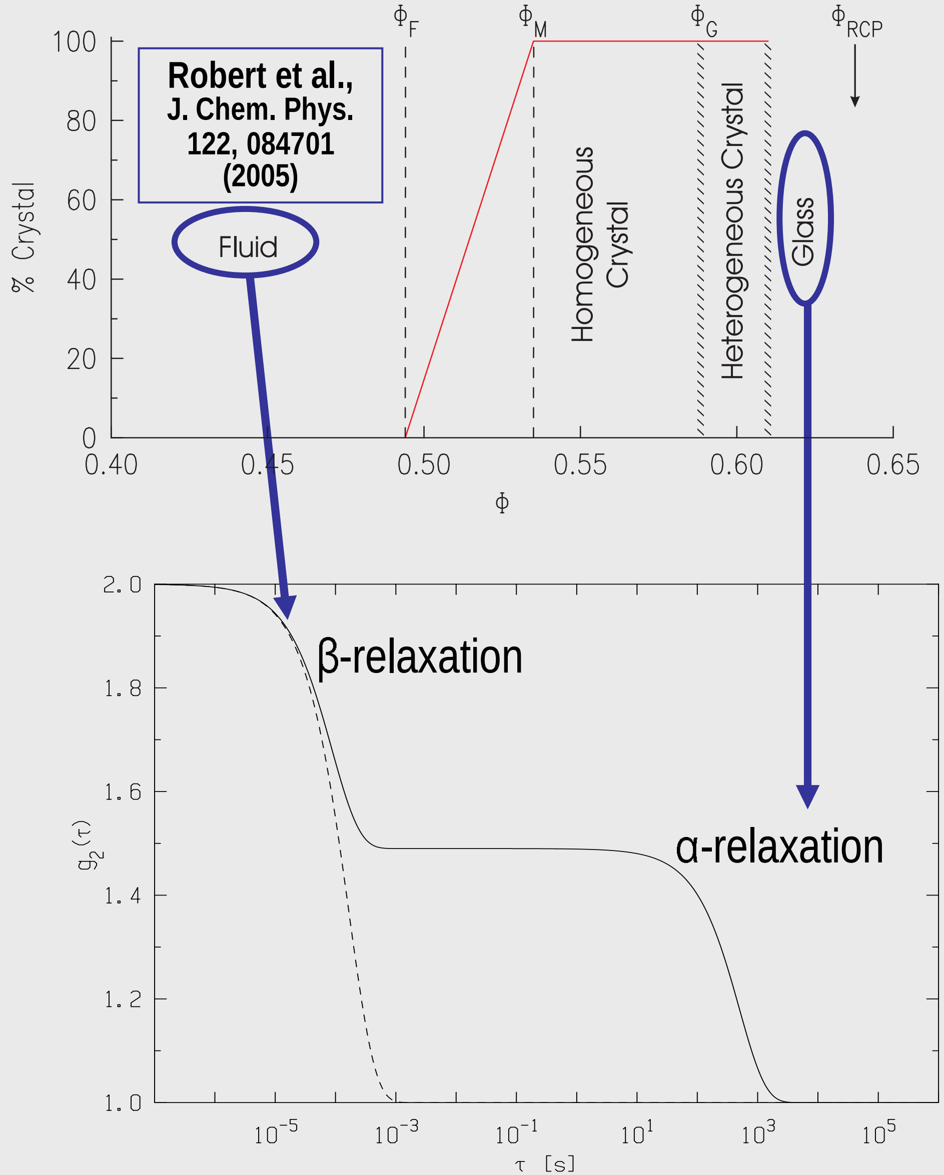
magnetic particles (ferrofluid)

γ-Fe_2O_3 particles in water

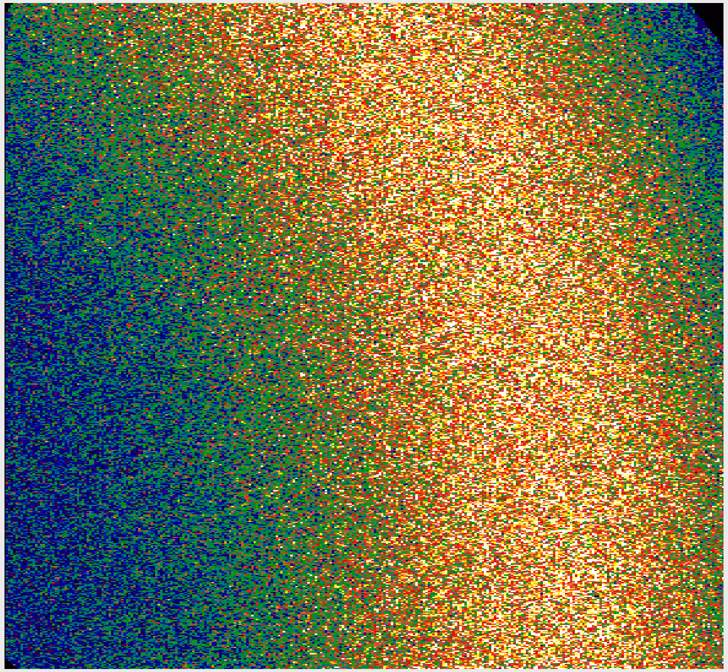
⇒ **opaque suspension that can not be studied by DLS**



External magnetic field
isotropic phase
H = 0T
H > 0T

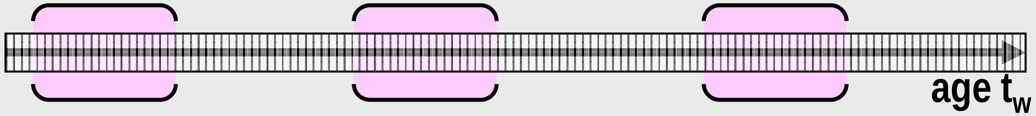


Glassy Ferrofluids : Evidence of Aging



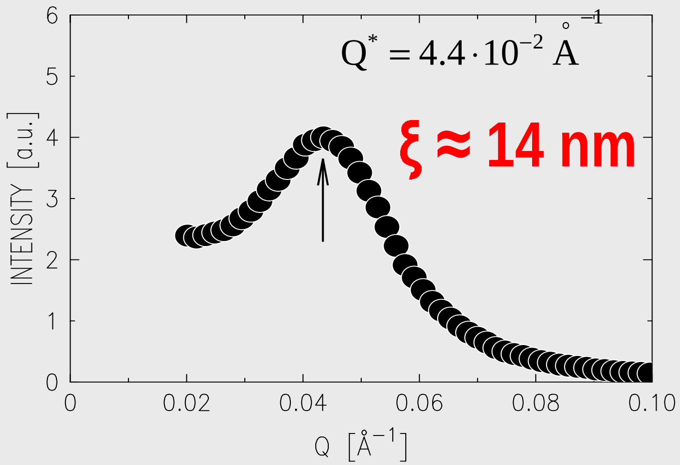
D=2R ≈ 11nm , Φ ≈ 35vol%
without magnetic field

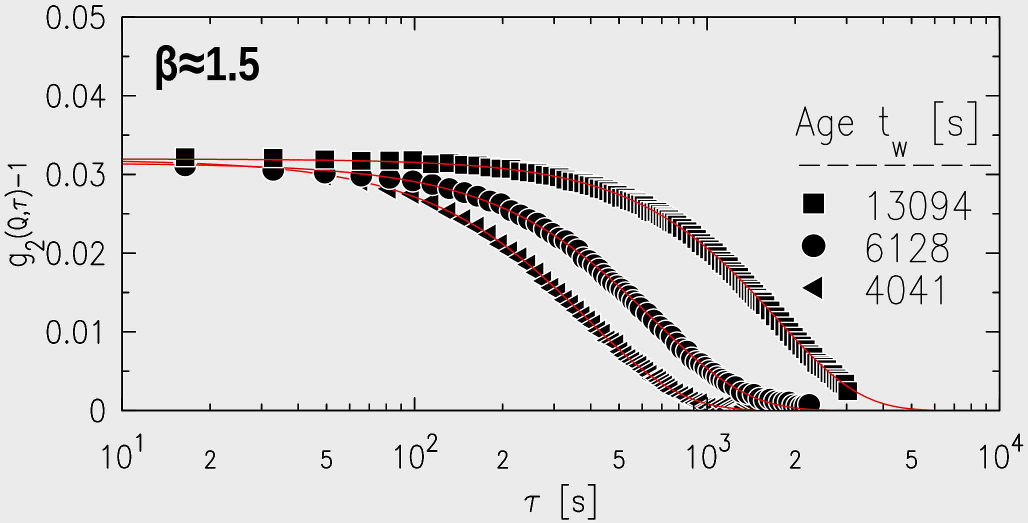
out-of-equilibirum dynamics
(strong non-ergodicity)



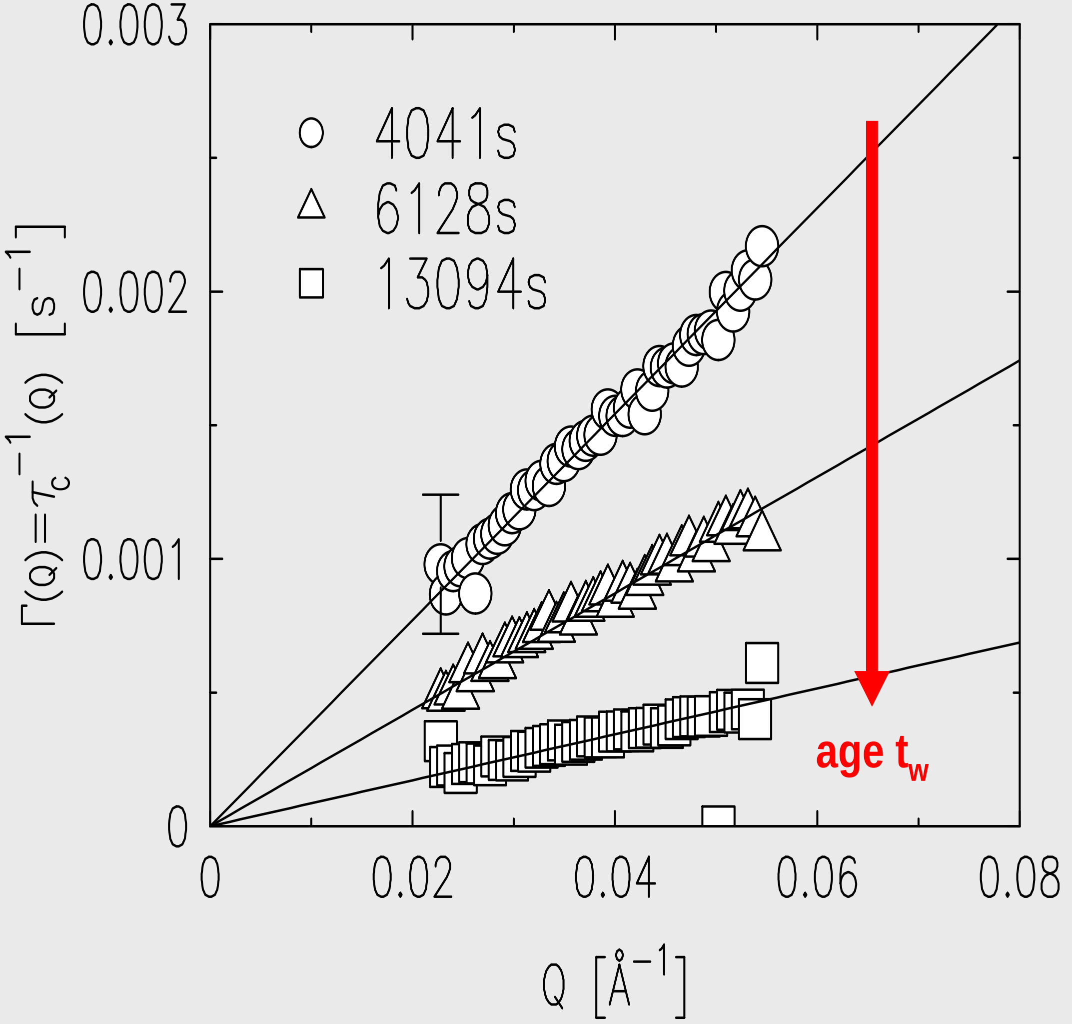
$$g_2(Q,\tau) = 1 + A\exp\left\{-2(\tau/\tau_C)^\beta\right\}$$

stretched exponential decay





Glassy Ferrofluids : Q-dependence of the α-relaxation



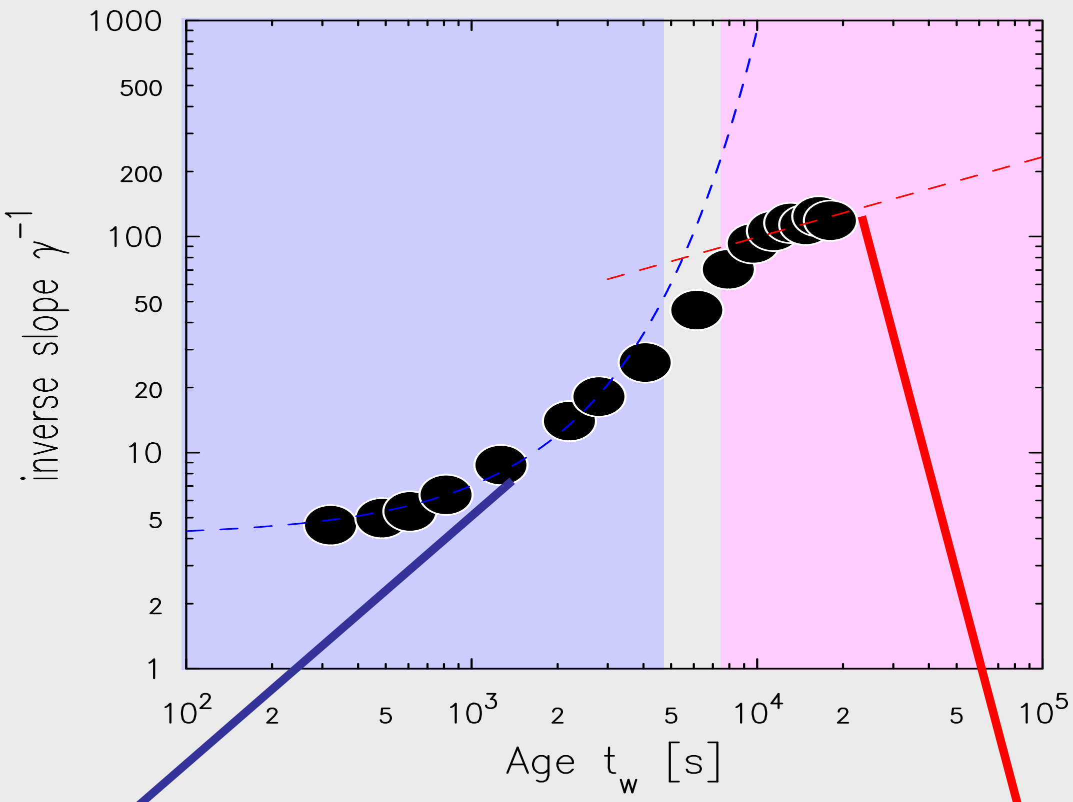
$$\Gamma(Q) = 1/\tau_C = \gamma \cdot Q$$

Characteristic relaxation time τ_C varies in Q^{-1}

➡ **typical α-relaxation**

(≠ brownian motion in Q^{-2})

Glassy Ferrofluids : aging behavior



Exponential behavior

$$\propto \exp(bt_w)$$

rarely observed

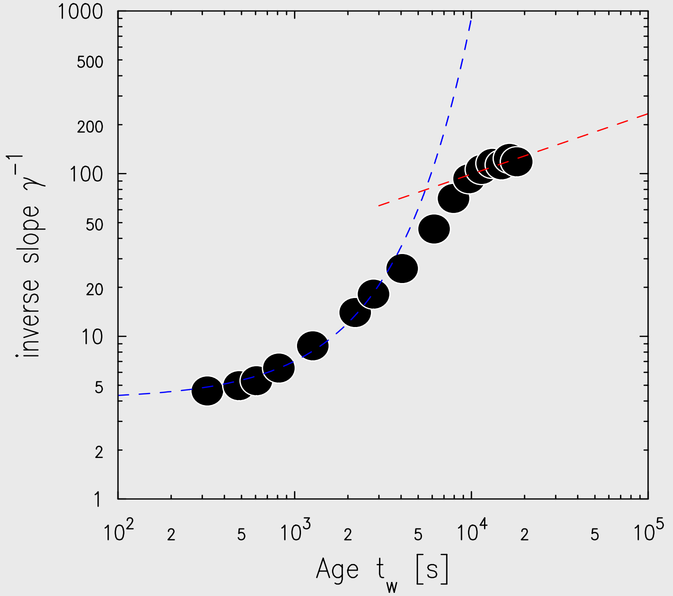
Bellour et al., Phys. Rev. E 89 (2002)
Cipelletti et al, Phys. Rev. Lett. 84 (2000)

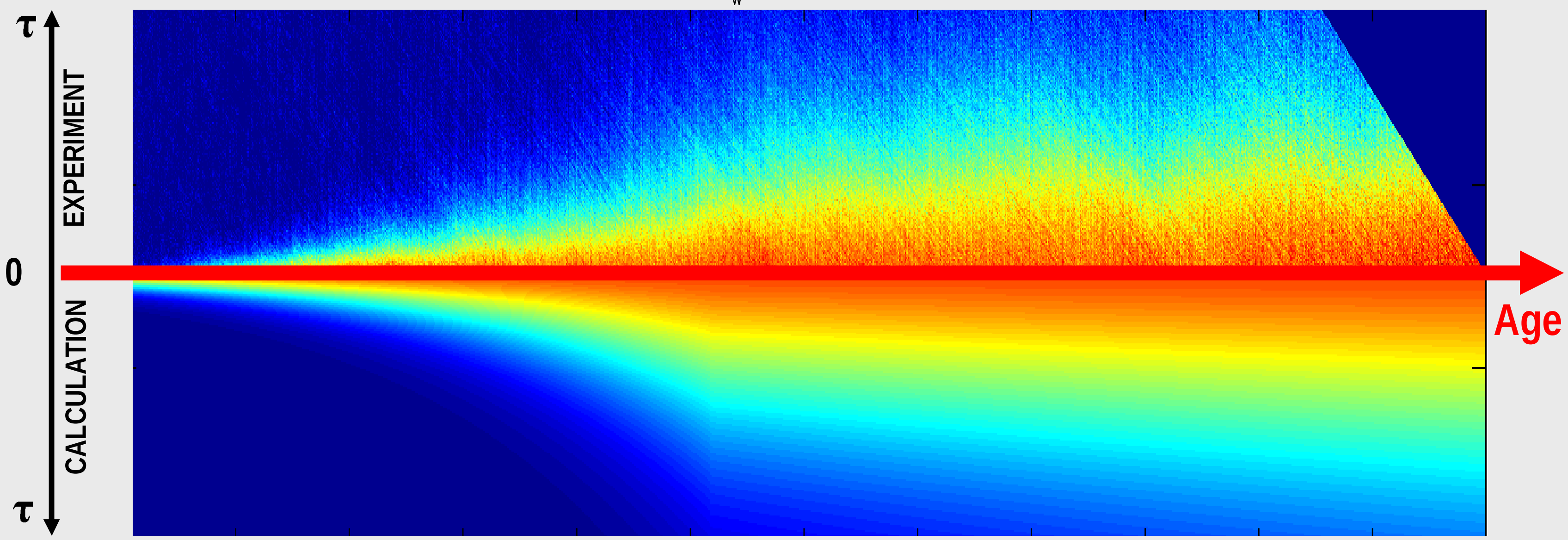
Power-law behavior

$$\propto t_W^{\,y} \;,\; y \approx 0.4$$

(observed in the range [0,1.8])

Aging behavior : Time Resolved XPCS





“Time-resolved correlation: a new tool for studying temporally heterogeneous dynamics” *Cipelletti et al., J. Phys : Condens. Matt 15 (2003)*

Conclusion & Perspectives

- slow dynamics in complex systems especially in opaque systems
- can probe dynamics up to nanometer lengthscales
- new probe for probing both equilibrium and non-equilibrium dynamics

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- development of 2D-detectors, extension of the timescales that can be probed
- follow-up of anistropic dynamics (under applied field for magnetic systems)
- …

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