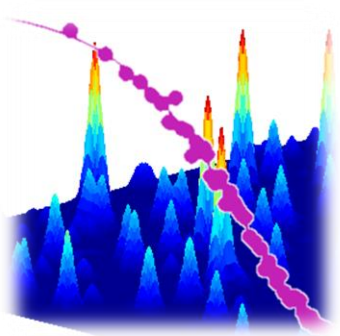
Using coherent X-rays to probe dynamical properties of materials at ESRF-EBS

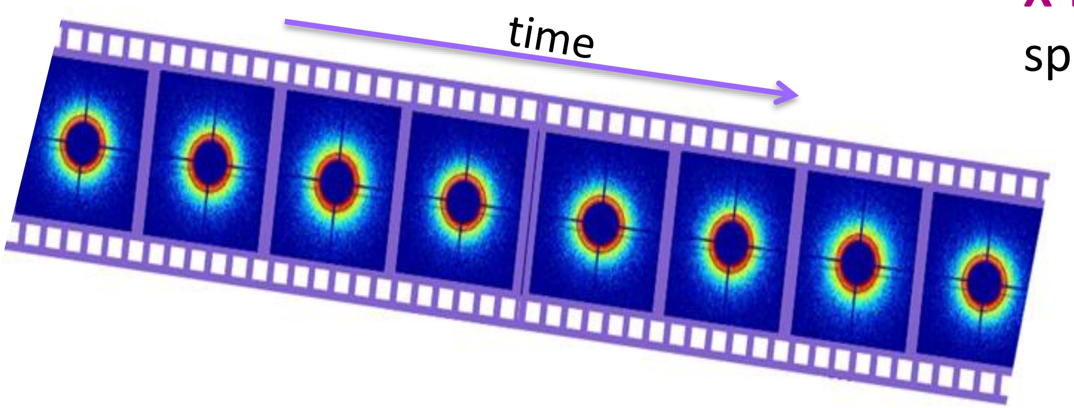


Beatrice Ruta

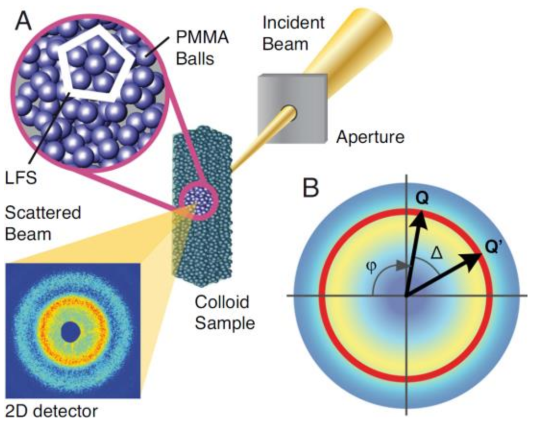
Coherence applications at ID10

Measurements of speckles correlations in complex systems …

X-ray Photon Correlation Spectroscopy (XPCS):
temporal correlations → **Dynamics**



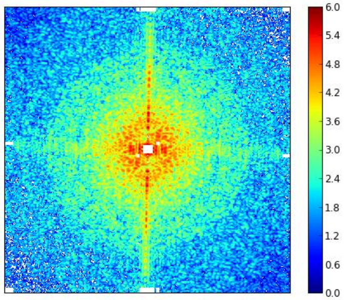
X-ray Cross Correlation Analysis (XCCA):
spatial correlations → **Structure**



Wochner et al. PNAS (2009)

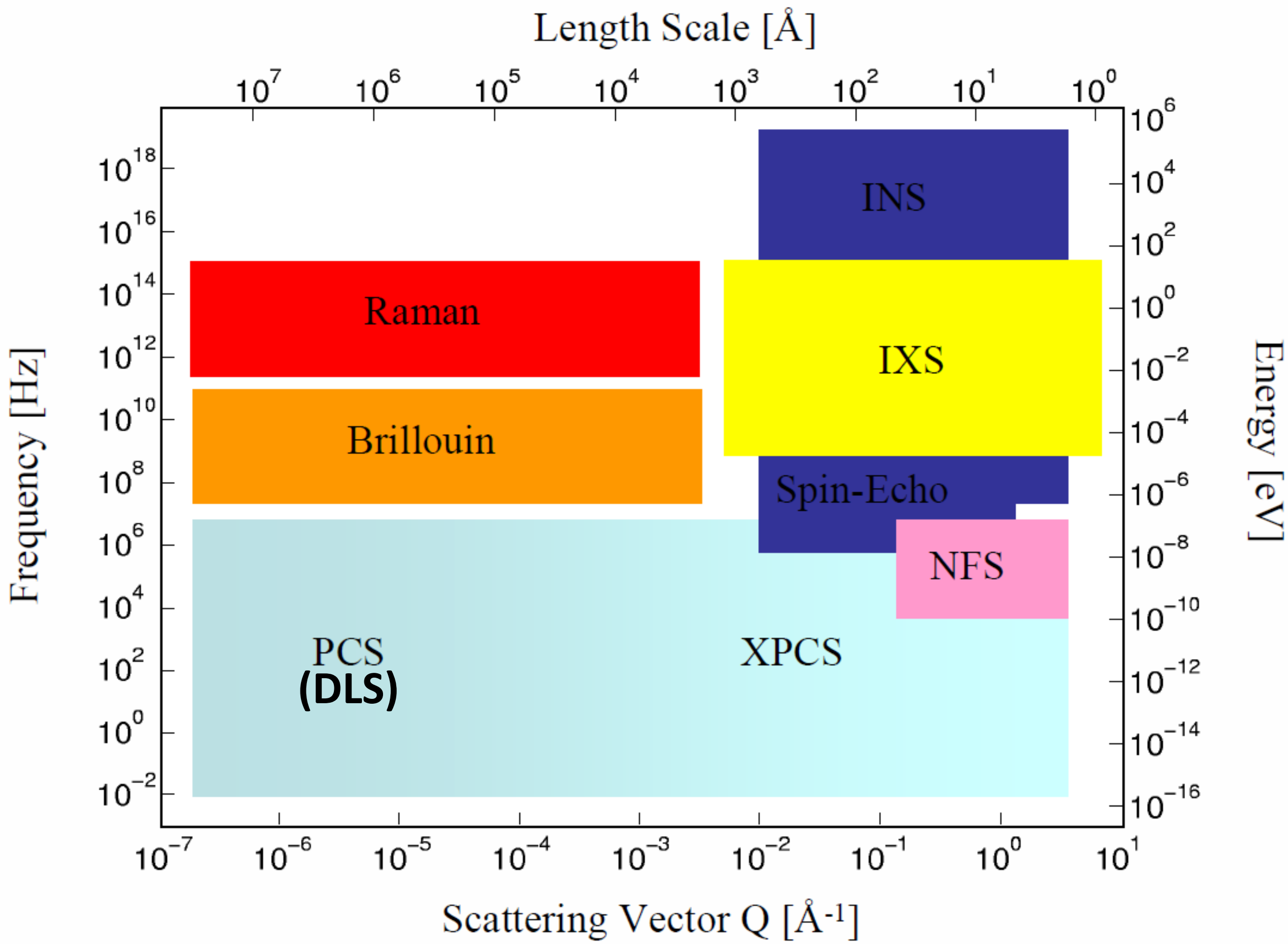
… and imaging of biological systems

Coherent X-ray Diffraction Imaging (CXDI): 2D & 3D reconstructions



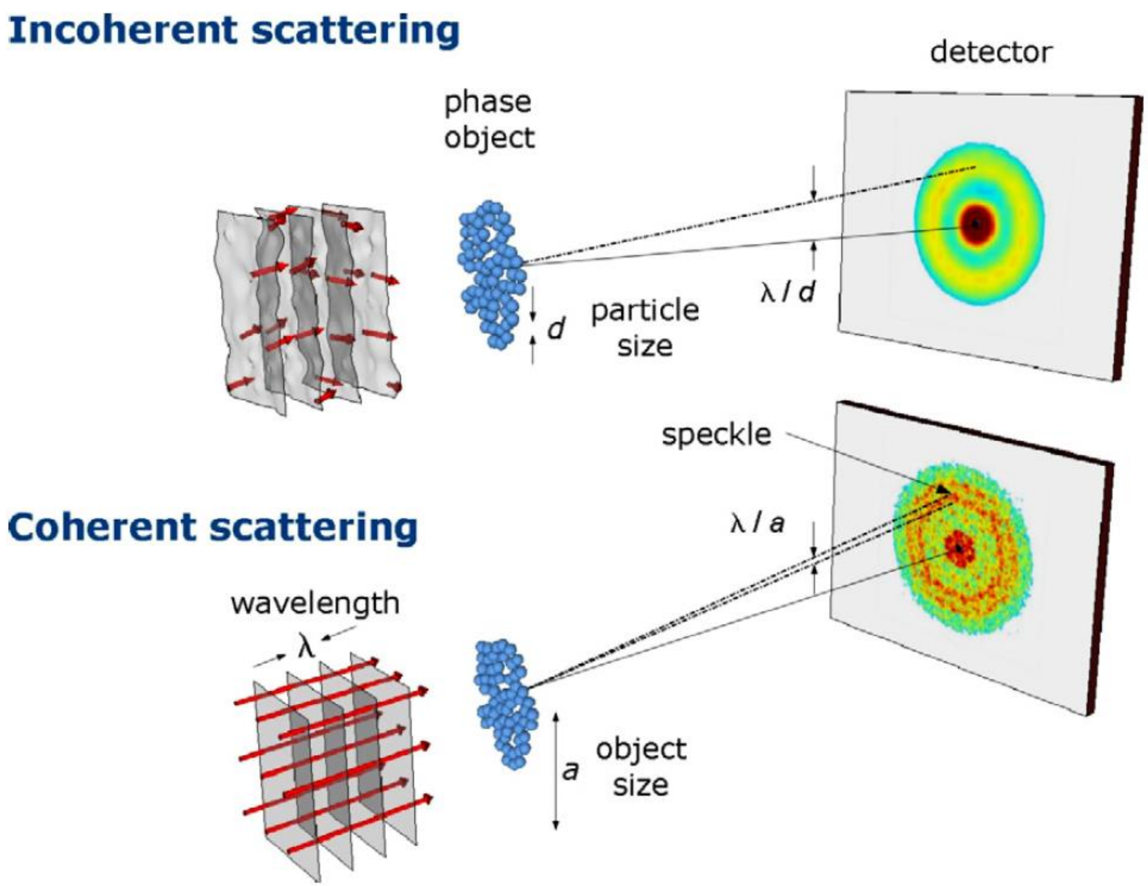
X-ray Photon Correlation Spectroscopy (XPCS)

XPCS allows to measure slow relaxation processes in complex systems

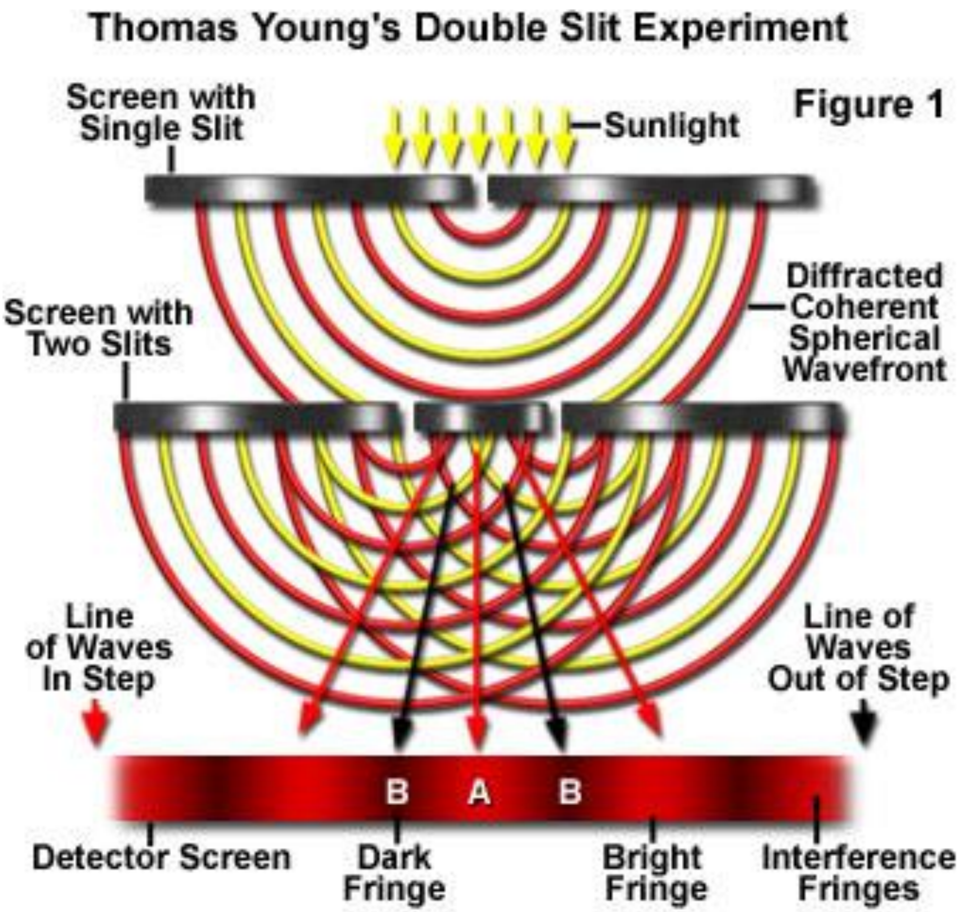


X-ray Photon Correlation Spectroscopy (XPCS)

XPCS uses the partial **coherent properties** of X-rays in 3rd generation synchrotrons



F. van der Veen & F. Pfeiffer, J. Phys. Cond. Mat. 1998



The intensity fluctuations are related to the constructive and destructive interference between the two waves

http://micro.magnet.fsu.edu/primer/java/interference/doubleslit/

X-Ray Photon Correlation Spectroscopy

The intensity of the speckles is related to the **exact spatial arrangement** of the scatters inside the system

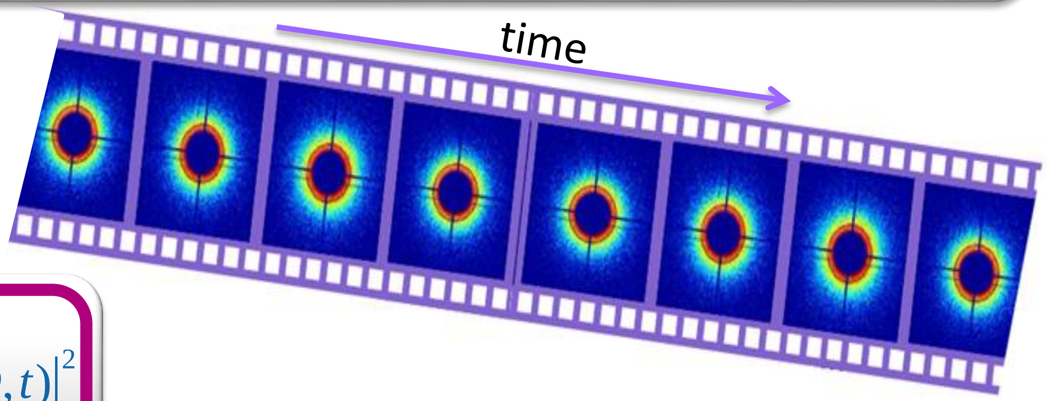
$$I(Q,t) \propto \left| \sum_n f_n(Q) \cdot e^{iQ \cdot r_n(t)} \right|^2$$

X-Ray Photon Correlation Spectroscopy

The intensity of the speckles is related to the **exact spatial arrangement** of the scatters inside the system

$$I(Q,t) \propto \left| \sum_n f_n(Q) \cdot e^{iQ \cdot r_n(t)} \right|^2$$

Information on the dynamics can be obtained by measuring a series of speckles patterns and quantifying **temporal correlations of intensity fluctuations** at a given wave-vector q

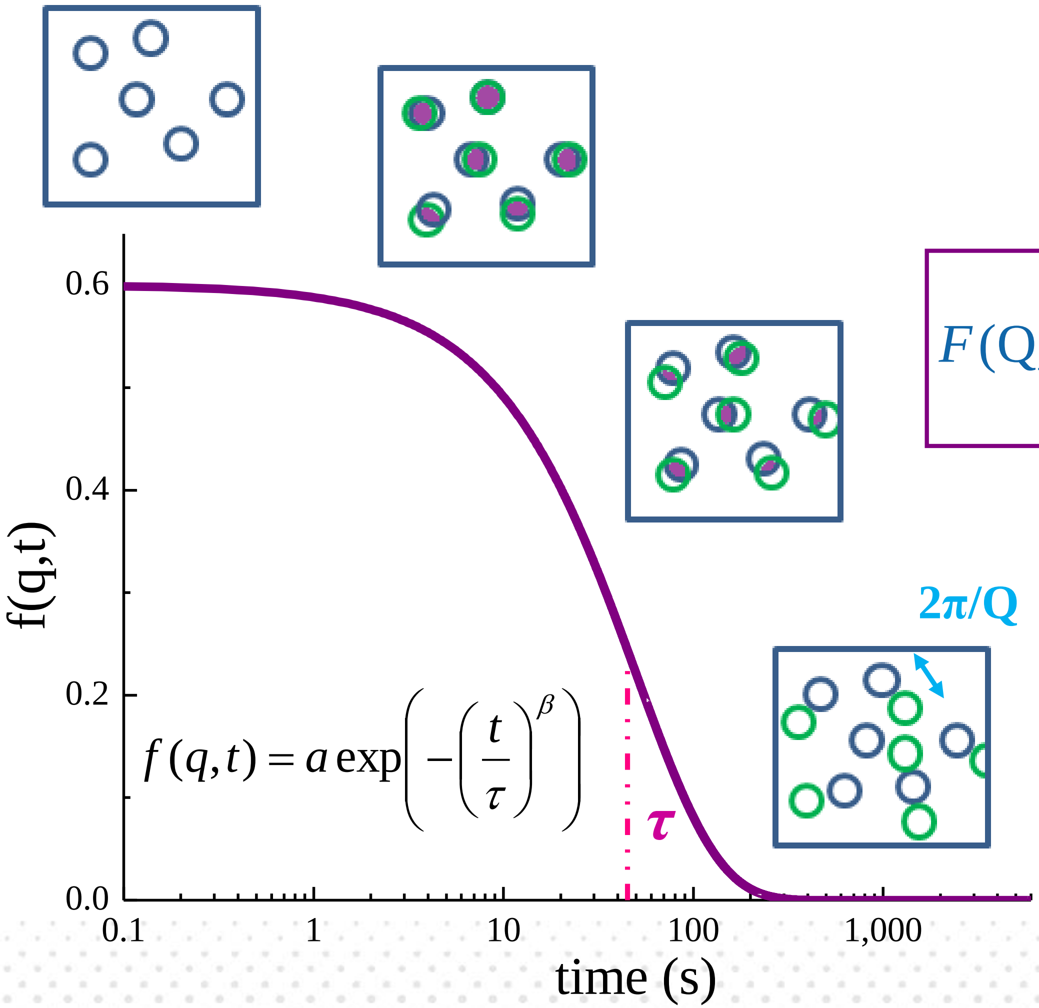


$$g_2(Q,t) = \frac{\langle I(Q,0) I(Q,t) \rangle}{\langle I(Q) \rangle^2} = 1 + A(Q) |F(Q,t)|^2$$

A. Madsen, A. Fluerasu and B. Ruta, Springer, 2015

The intermediate scattering function

Information on the relaxation dynamics can be obtained from the decay of the **intermediate scattering function** on a scale 2π/Q



$$F(\mathrm{Q,t}) = \frac{S(Q,t)}{S(Q)} = \frac{\left\langle \delta\rho_{\mathrm{Q}}^{*}(0)\delta\rho_{\mathrm{Q}}(t)\right\rangle}{\left\langle \delta\rho_{\mathrm{Q}}^{*}(0)\delta\rho_{\mathrm{Q}}(0)\right\rangle}$$

The intermediate scattering function

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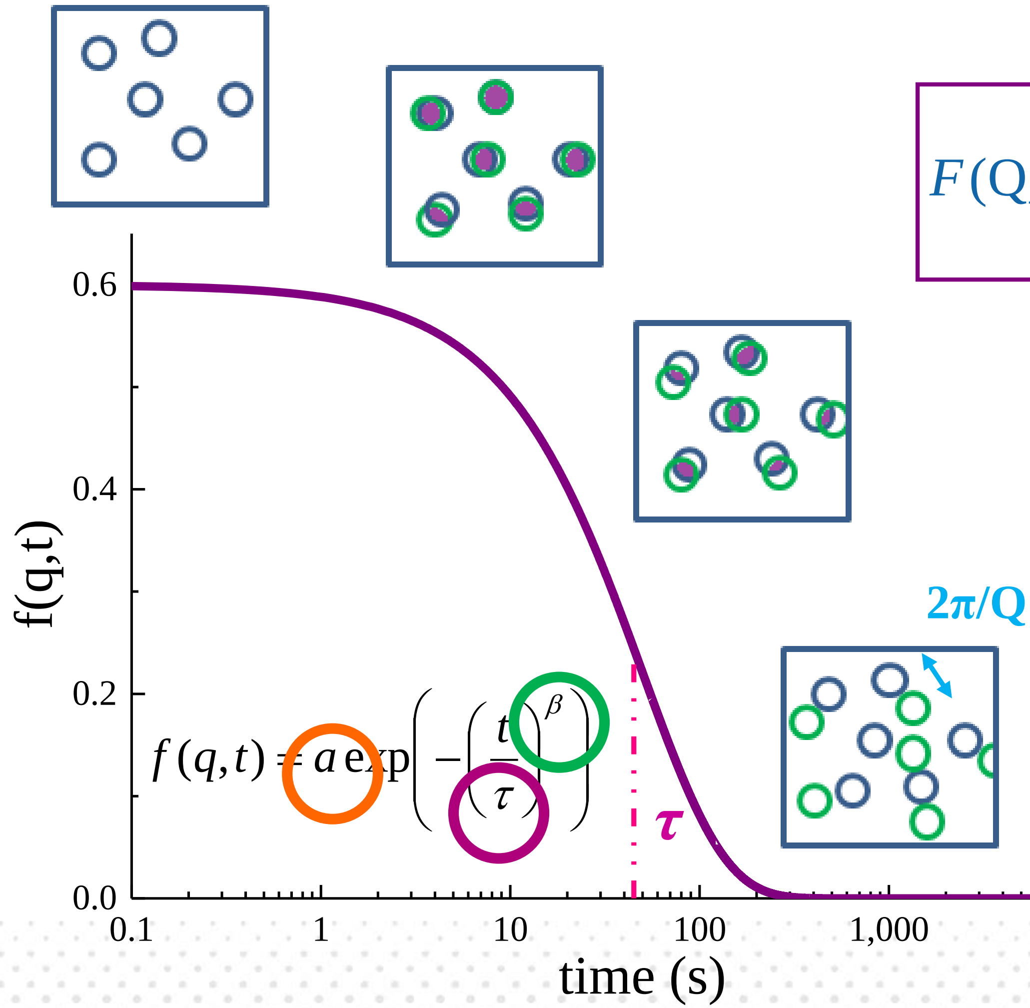
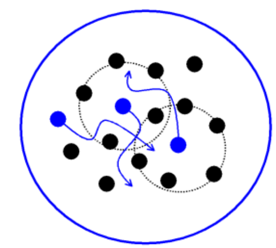


$$F(\mathrm{Q,t}) = \frac{S(Q,t)}{S(Q)} = \frac{\left\langle \delta\rho_Q^*(0)\delta\rho_Q(t)\right\rangle}{\left\langle \delta\rho_Q^*(0)\delta\rho_Q(0)\right\rangle}$$



τ: time necessary for structural rearrangement of the particles.

Scientific activity with XPCS at ID10

XPCS: (saxs, waxs, gi-xpcs)

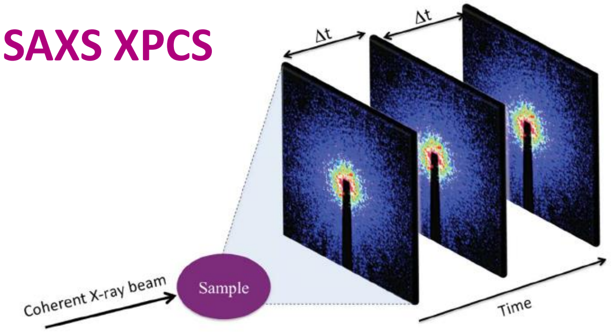
- Supercooled liquids and glasses
- Soft materials (gels, colloids, …)
- Fluctuations at ordering phase transitions
- Driven dynamics by external fields T, E, B
- Interface dynamics in soft matter systems
- Atomic diffusion in alloys
- …

Energy range: 7,8,10 & 21 keV

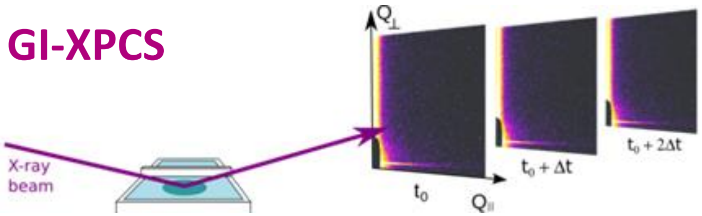
Time resolution [2D det.]: ≈ ms - 10^4 s

Probed length scales: $8\cdot10^{-4}$ - 3 Å^{-1}

SAXS XPCS



GI-XPCS

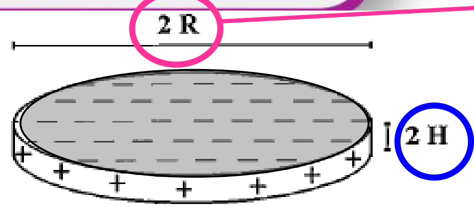


Y. Chushkin

F. Zontone

Relaxation processes in colloidal suspensions

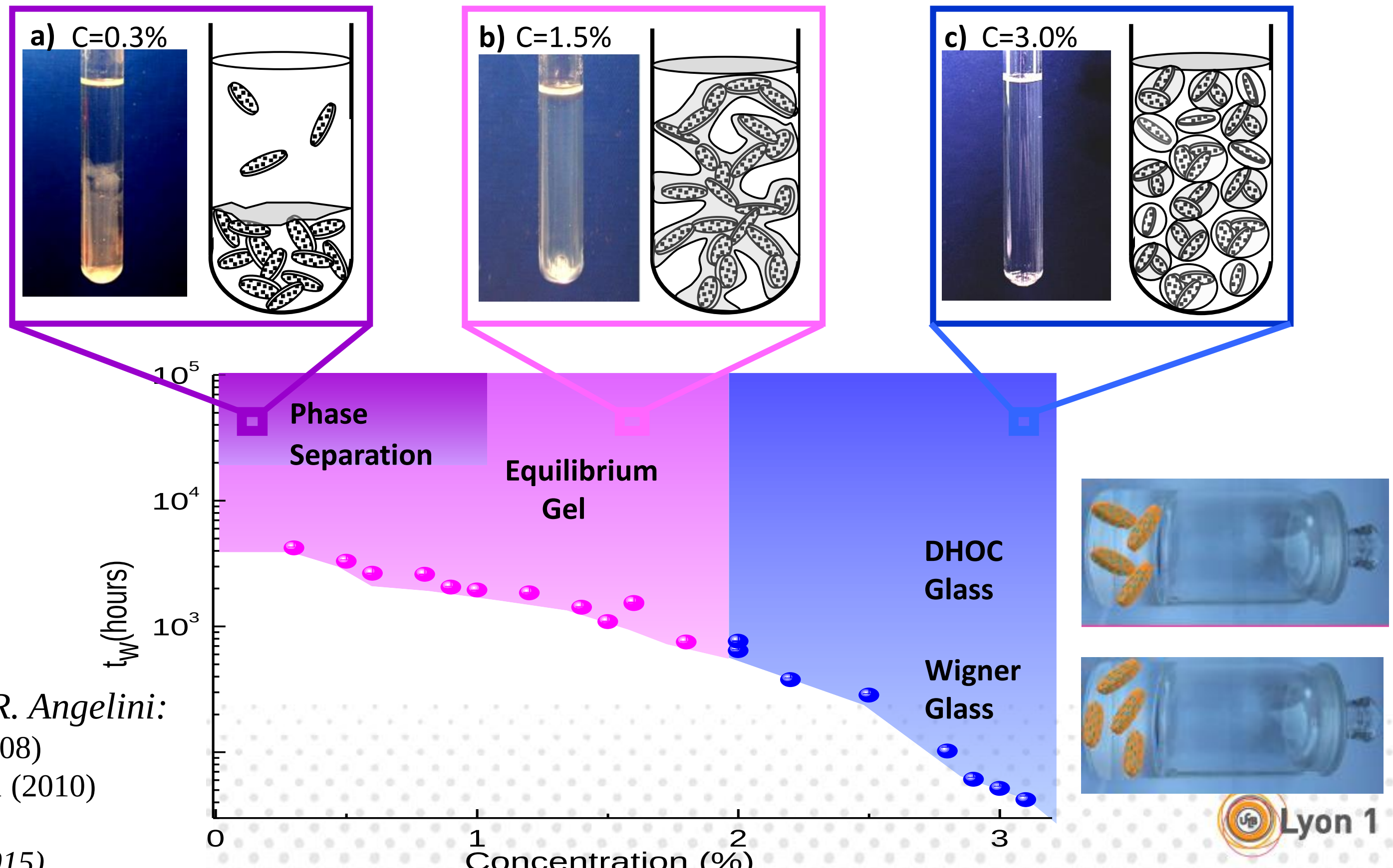
Colloidal suspensions of Laponite



2R = (25 ± 2) nm

2H = (0.9 ± 0.1) nm

Dispersed in water Laponite originates a charged colloidal suspension of disks of nanometric size with inhomogeneous charge distribution



Group of B. Ruzicka & R. Angelini:

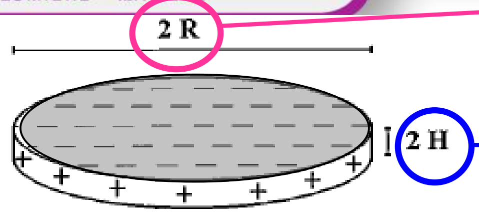
Phys. Rev. E **77**, 020402 (2008)

Phys. Rev. Lett. **104**, 085701 (2010)

Nature Mat. **10**, 56 (2011)

Nature Commun. **5**, *4049(2015)*

Colloidal suspensions of Laponite



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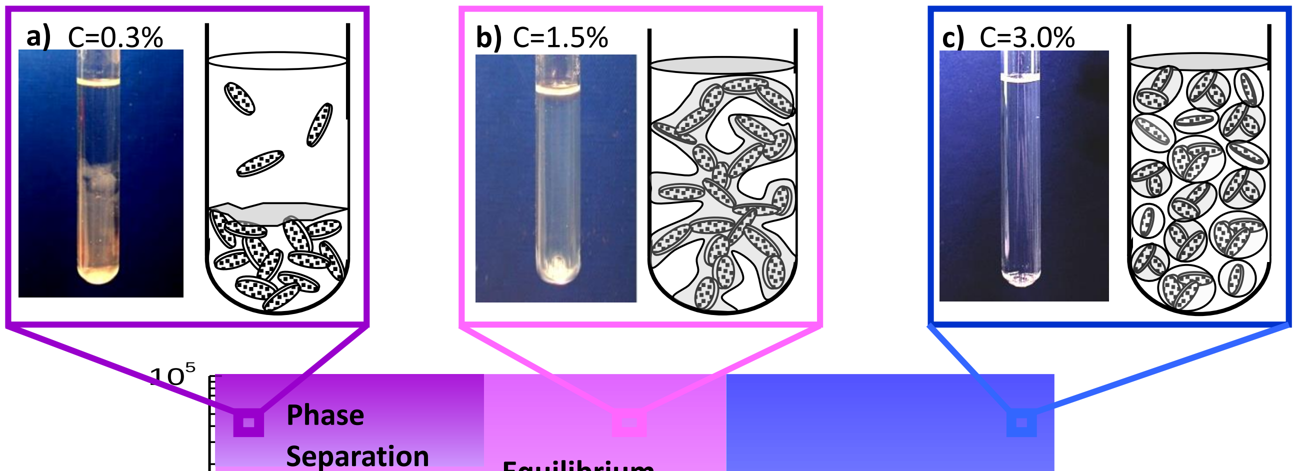

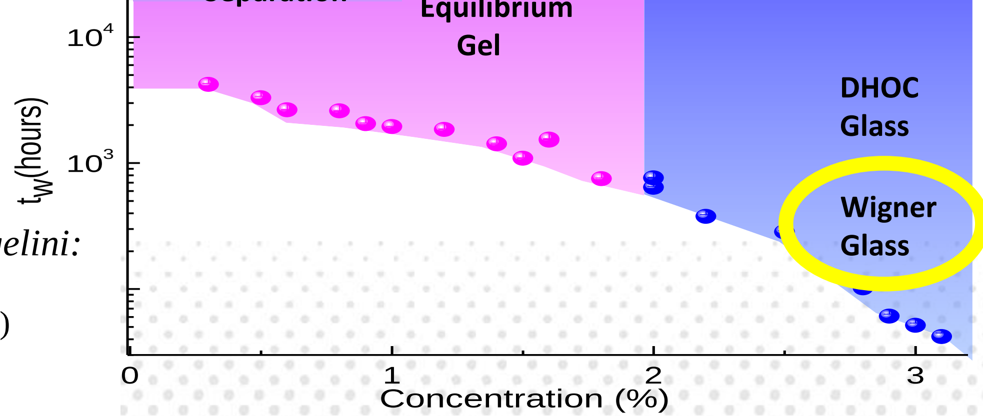

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Phys. Rev. E **77**, 020402 (2008)

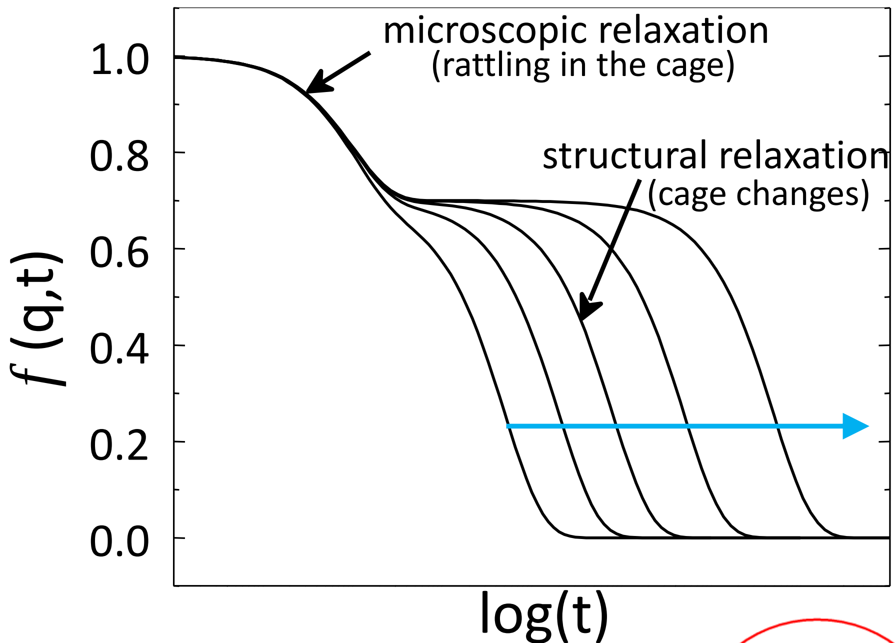
Phys. Rev. Lett. **104**, 085701 (2010)

Nature Mat. **10**, 56 (2011)

Nature Commun. **5**, *4049(2015)*

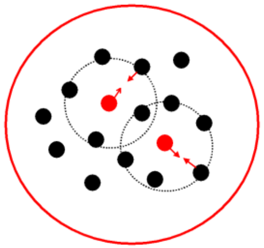
Relaxation dynamics

The slow down of the dynamics toward an arrested state corresponds to a continuous shift of the decay time toward longer time scales and the emerging of different relaxation processes.



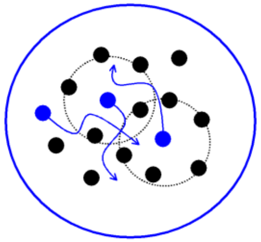
t_w waiting time

τ_1 microscopic relaxation time related to the interactions between a particle and the cage of its nearest neighbors.



fast relaxation

τ_2 structural relaxation time related to a structural rearrangement of the particles.



slow relaxation

Colloidal suspensions of Laponite in D_2O

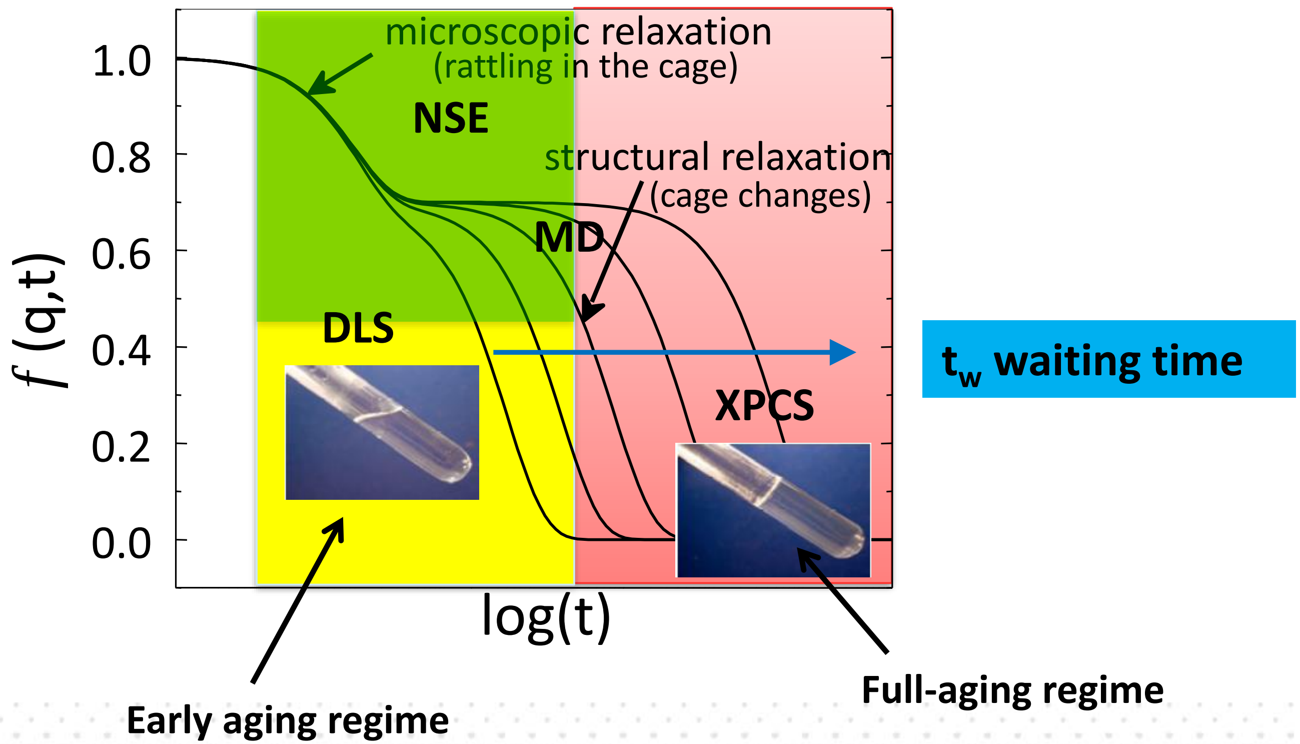
Multi-scales and techniques approach:

Dynamic Light Scattering→ early aging regime τ_1& τ_2 (Q [6.2×10^{-4} - 2.1×10^{-3}] $Å^{-1}$)

Neutron Spin Echo→ early & full aging regime τ_1 (Q [1.3×10^{-2} - 1.3×10^{-1}] $Å^{-1}$)

X-ray Photon Correlation Spectroscopy → full aging regime τ_2 (Q [3.1×10^{-3}- 2.2×10^{-1}] $Å^{-1}$)

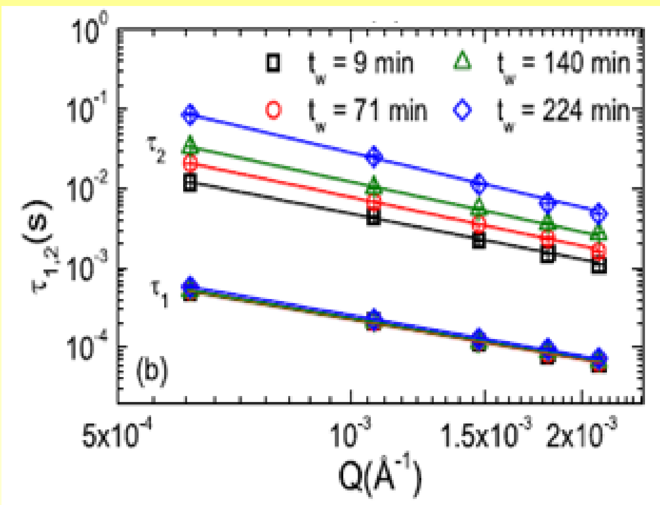
Molecular Dynamics → early & full aging regime τ_1& τ_2 (around the structure factor peak)



Colloidal suspensions of Laponite in D_2O

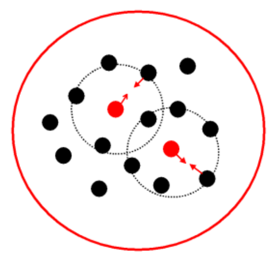
Cw=3.0 % in D_2O at different waiting time and for Q [6.2×10^{-4} -2.1×10^{-3}] $Å^{-1}$

Early aging regime
Dynamic Light Scattering

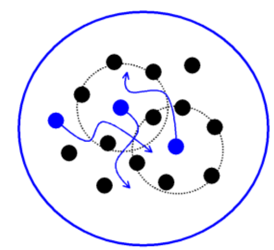


$$g^{(2)}(Q,\tau)-1 = a\,exp\left(-\frac{t}{\tau_1}\right)+(1-a)\,exp\left(-\left(\frac{t}{\tau_2}\right)^{\beta}\right)$$

Diffusive dynamics of both the microscopic and the structural relaxation time



$\tau_1 \approx Q^{-2}$
stationary

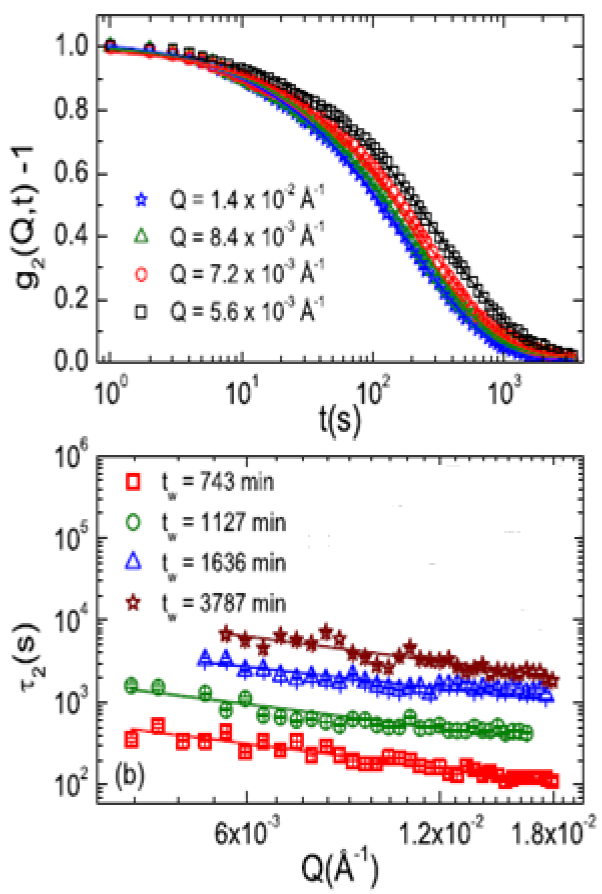


$\tau_2 \approx Q^{-2}$ & $\beta<1$
aging

F. A. Melo Marques/B. Ruta et al. Soft Matter, 2015

Colloidal suspensions of Laponite in D_2O

Full-aging regime
XPCS



Cw=3.0 % in D_2O at different waiting time and for Q [3.1 x 10^{-3}-2.2 x 10^{-1}] Å^{-1} (glass transition at t_w≈600 min)

Kohlrausch-Williams-Watts (KWW)

$$g^{(2)}(\vec{Q},t)-1=b\left[\exp\left(-\left(\frac{t}{\tau_2}\right)^{\beta}\right)\right]^2$$

$\tau_2 \approx Q^{-1}$
$\beta<1$

Discontinuous hopping of caged particles

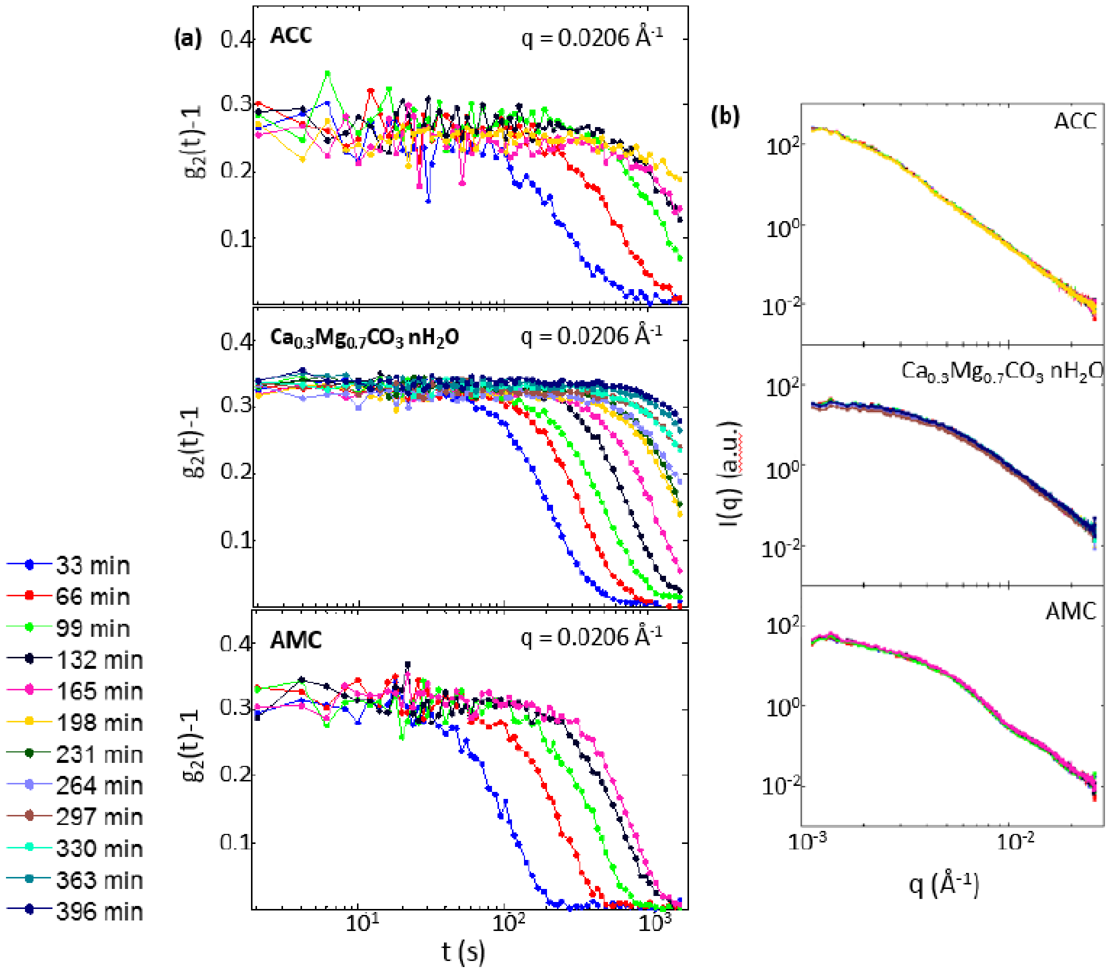
Agreement with MD simulations

F. A. Melo Marques/B. Ruta et al. Soft Matter, 2015

Nanoscopic dynamics in biominerals

Nanoscopic dynamics of amorphous calcium carbonate (ACC)

Ca1-xMgxCO3·nH2O (*x*=0 - ACC, *x*=1 - AMC)



Study of the effect of different additives on the control of the crystallization kinetics

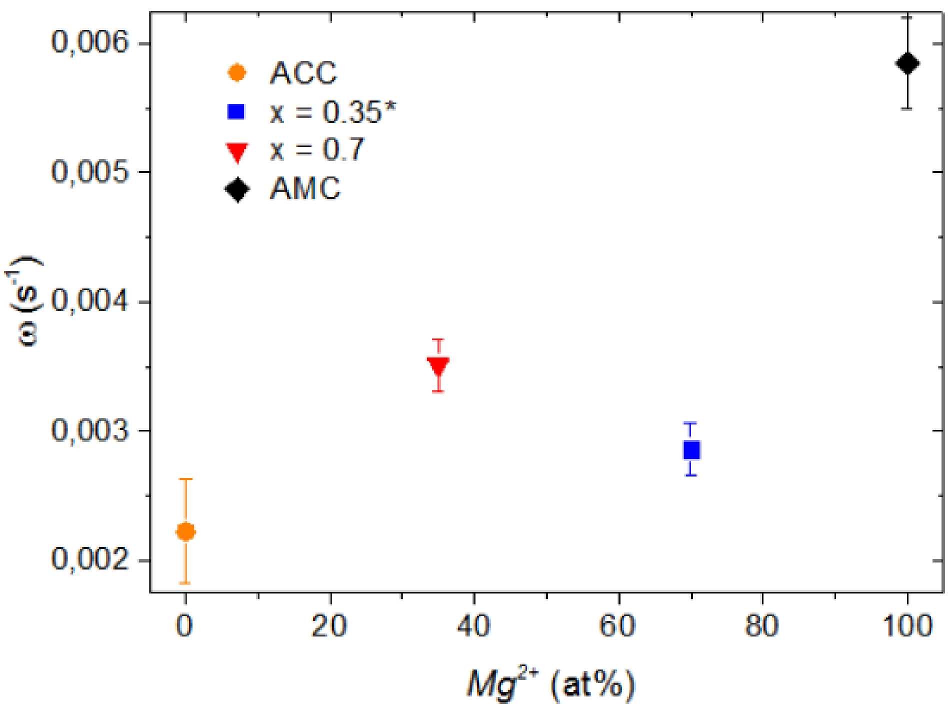
Mg-doped ACC reveal aging phenomena concomitant to dehydration of the structure

A. Koishi/B. Ruta/A. Fernandez Martinez (in preparation)

Lyon 1

Nanoscopic dynamics of amorphous calcium carbonate (ACC)

Ca1-xMgxCO3·nH2O (*x*=0 - ACC, *x*=1 - AMC)



The presence of Mg^{2+}

→ Increases the frequency for structural rearrangements)

XPCS + neutrons (IINS)

→ Mg^{2+} acts as stabilizer against crystallization

A. Koishi/B. Ruta/A. Fernandez Martinez (in preparation)

The Extremely Brilliant Source upgrade

Main parameters for XPCS

Coherent X-ray flux $$F_c = \frac{B\lambda^2}{2}$$

Fastest time scale $$\tau_{min} \propto \frac{1}{B^2}$$

XPCS at ESRF - EBS

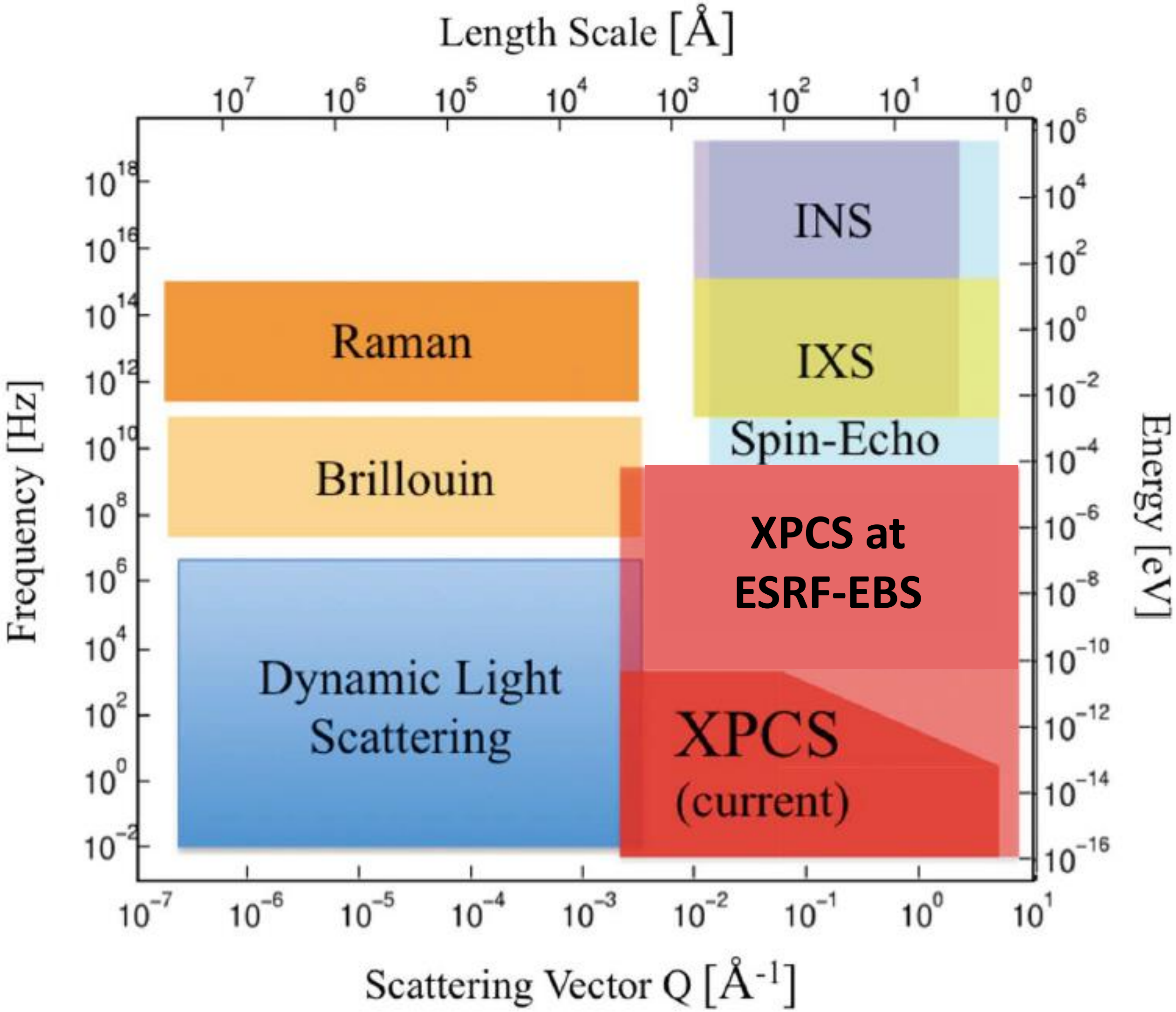
EBS will break new ground for XPCS

- **Up to 10.000 times faster time scales**
- Up to 100 times larger signal to noise ratio
- Extension into hard x-rays beyond 10 keV

XPCS at ESRF - EBS

$\tau_{min} \approx 100$ ns
(now only ≈ ms)

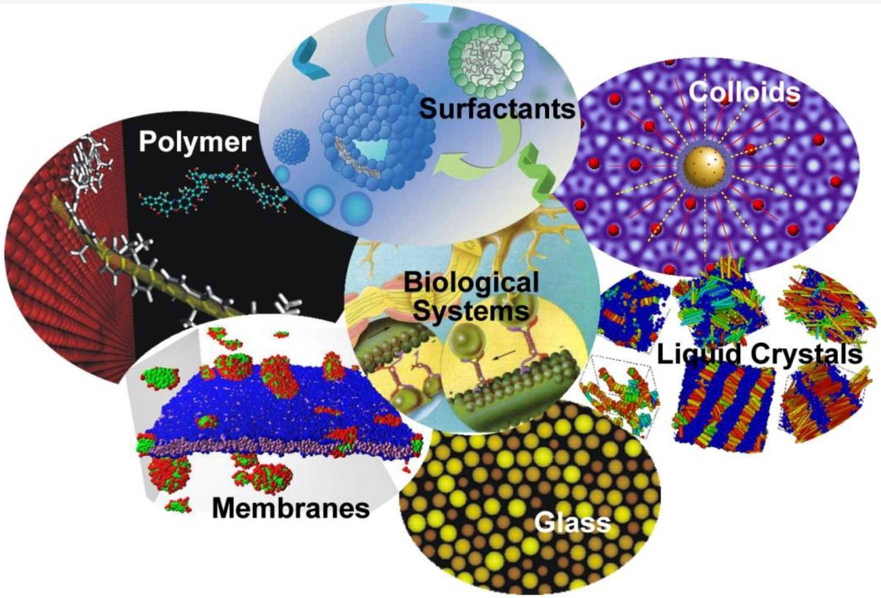
Energy: 6.5 - 35 keV
(now at 8 keV)



Adapted from O. Shpyrko J. Synch, Rad. 2014

Dynamics in biological & soft systems

Fast dynamics + High Energy (≈100ns-1s)



® Pierre Gilles De Gennes

Dynamics in biological & soft systems

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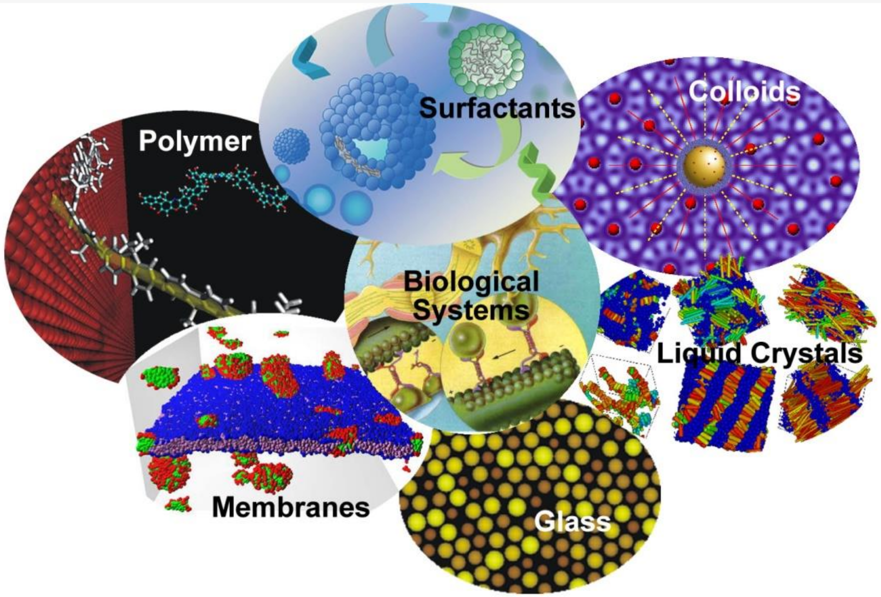
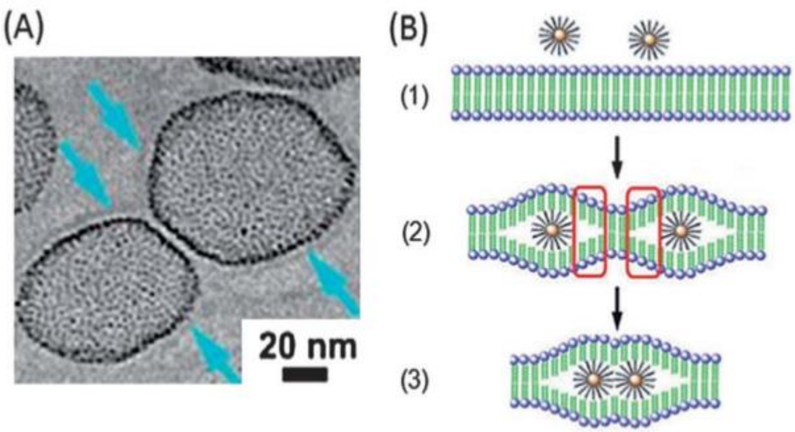


® Pierre Gilles De Gennes



[Nano Lett. 2010 10 3733]

Ex. Lipid bilayers in presence of nanoparticles (with different philicity): incorporation of hydrophobic nanoparticles, membrane deformations …

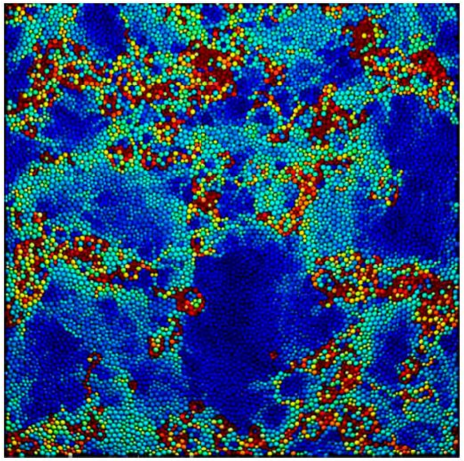
Intermittent correlations

- ***Dynamical & spatial heterogeneity*** are ubiquitous in nature
  - *Supercooled liquids and glasses*
  - *Domain fluctuations and avalanches in high-Tc superconductors and magnetic systems*
  - *Polymers and biomaterials*

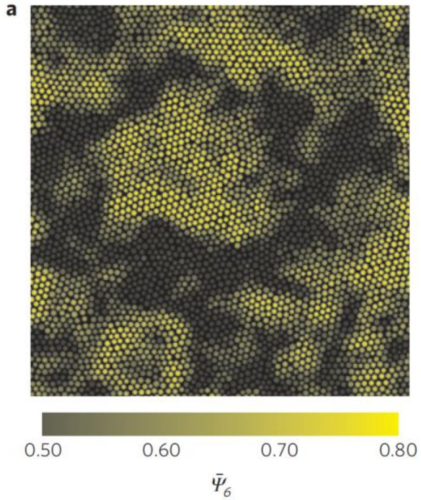
ESRF - EBS:

1. *Dynamics from (sub-)µs to s*
2. *Length scales: from single particles to particle clusters*
3. *Structure-dynamics correlations by combined XPCS and XCCA*

J.P. Garrahan, PNAS (2011)



H. Tanaka et al. Nat. Mat. 2010



Dynamical (left) and spatial (right) heterogeneity in simulations of 2D glass transitions

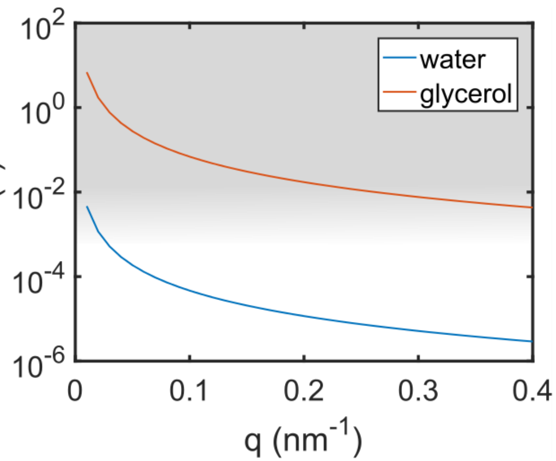
Courtesy of F. Lehmkühler, Desy, Hamburg, Germany

Soft matter in „natural“ environments

- Most soft materials are **water-based (**particles dispersed in water**)**:
  - *(bio-)macromolecules, polymers, gels, colloids, membranes, …*
- Typically nanometer dimensions → **(sub-)microseconds** time scales

Unaccessible by state-of-the-art XPCS – two approaches to overcome limitations

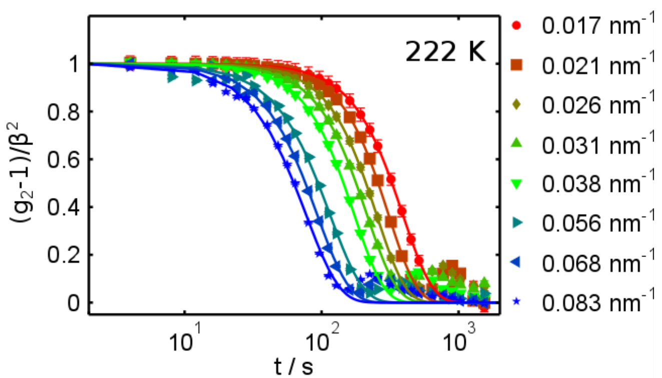
Solvent exchange: glycerol



Grey area: accessible time range in current XPCS

Changed sample systems: no access to solvent-particle interactions in the „real“ environment

Microrheology: use of tracer particles

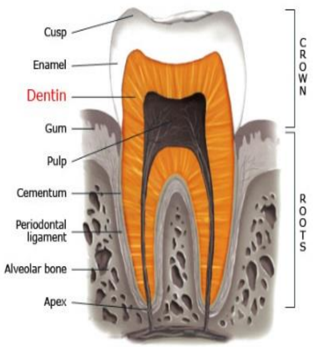


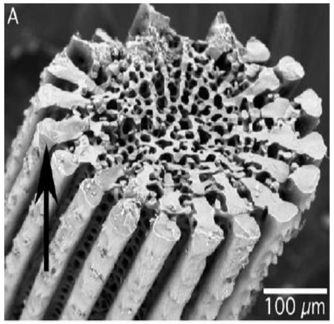
Indirect access to solvent properties only

Courtesy of F. Lehmkühler, Desy, Hamburg, Germany

Biomineralization processes

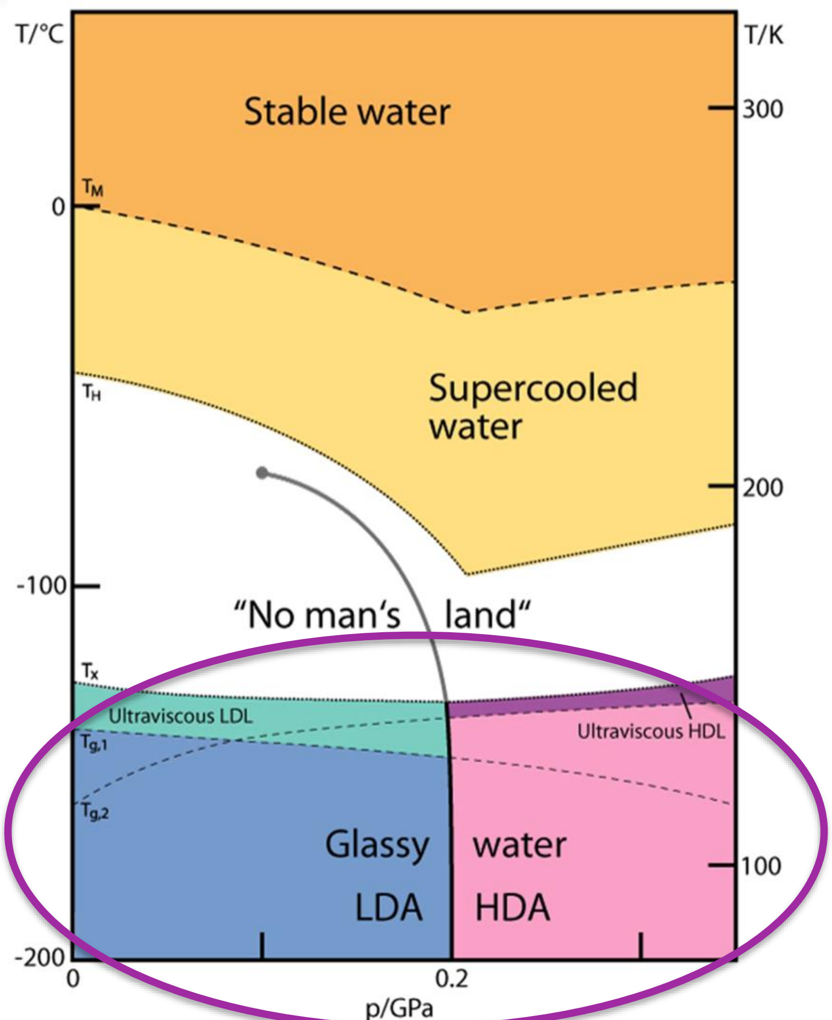
Multi-step, non-classical nucleation pathways involving amorphous precursors occurs in a wide variety of biological and engineered systems: phosphates, carbonates, sulphates, iron oxides…





XPCS at EBS can provide unique information on the '**frequency of structural re-organization**', which is directly involved in the kinetic pre-factor of the kinetic barrier to nucleation.

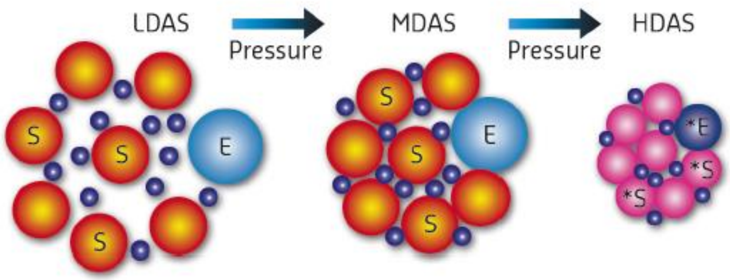
Courtesy of A. Fernandez Martinez, IST - Terre, Grenoble



P. Gallo et al. Chem. Rev. 2016
Mischima et al. Nature 1985

Dynamical evolutions during polyamorphic transitions

Hierarchical densifications in metallic glasses



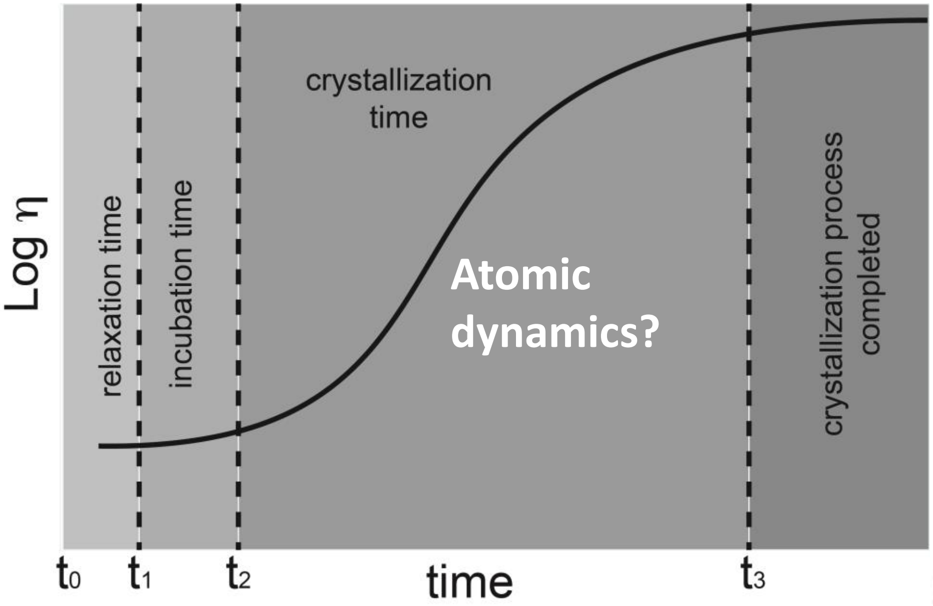
Q. Luo et al. Nat. Commun. 2015
H. W. Sheng et al. Nat. Materials 2007

Nucleation in magmas

Volcanos are among the most productive glassmakers on Earth.

Magmas are mainly silicate melts.

Crystallization in magmas strongly affects viscosity, and thus magma flow.



Determining the microscopic mechanism of crystallization can lead to an *a priori* assessment of the volcanic risk.

Courtesy of M. Zanatta, Padova University, Italy

Nucleation in magmas

XPCS can clarify the microscopic atomic dynamics in crystallizing magmas

High incident energy → Edge selective XPCS , sensitivity to impurities.

Improved brillance → High temperature studies (HT, about 1000°C).

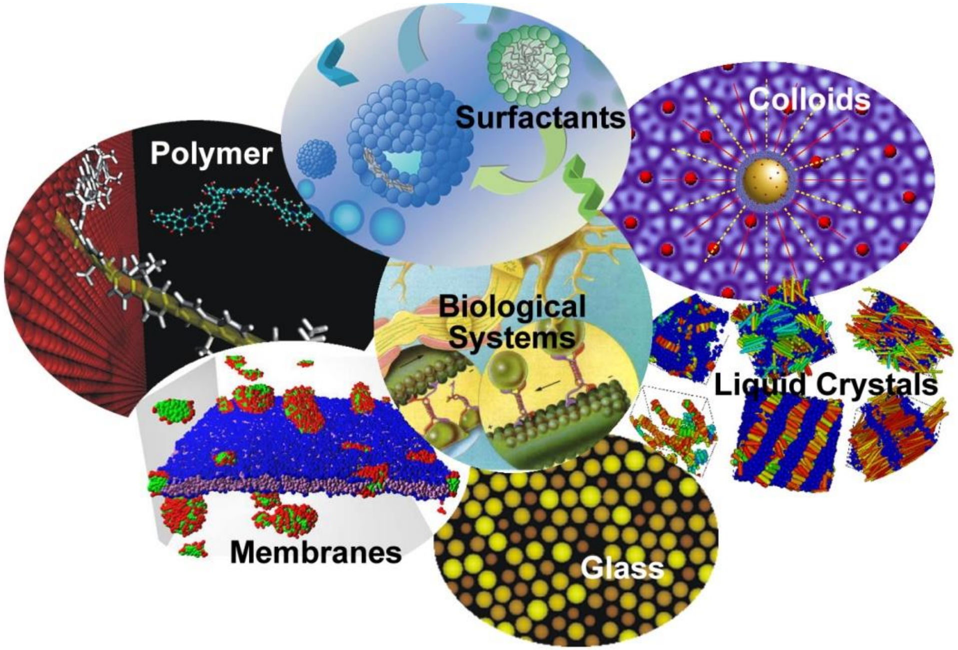
→ High pressure studies (HP, about 3-4 kbar).

→ Realistic conditions (HT-HP, chaotic mixing,…).

Courtesy of M. Zanatta, Padova University, Italy

It’s time to think…

• protein dynamics in living cells
• dynamics under confinement
• dynamics of polymers, macromolecules, membranes, foams, …
• dynamics at buried interfaces
• polyamorphism (LL/GG phase transitions)
• dynamics at extreme conditions



® *Pierre Gilles De Gennes*

XPCS at ESRF- EBS will have the world leading position with unique outstanding properties for many years!!!


A LIGHT FOR SCIENCE
ESRF news
Number 77 December 2017
Extremely Brilliant Source
Green light for new beamlines
Algae turn fat to fuel
Cryo-EM arrives
ESRF

EoI from the European User Community

ESRF Upgrade – XPCS at diffraction limited storage rings

Submitted on February 2016

C. Gutt[1], B. Ruta[2], Y. Chushkin[2], F. Zontone[2], K. Nygard[3], P. Schurtenberger[4], A. Fernandez-Martinez[5], L. Cristofolini[6], D. Orsi[6], J. Wagner[7], M. Zanatta[8], A. Ricci[9], G. Grübel[9], F. Lehmkühler[9], W. Roseker[9], A. Madsen[10], V.M. Giordano[11], R. Busch[12], I. Gallino[12], M. Stolpe[12], S. Hechler[12], Z. Evenson[13], S. De Panfilis[14], B. Ruzicka[15], R. Angelini[15], F. Pignon[16], G. Baldi[17], G. Monaco[18], A. Matic[19], G. Portale[20], D. Constantin[21], D. LeBolloc'h[21], J. Vincent[21], E. Pineda[22], D. Crespo[22], G. Beutier[23], M. de Boissieu[23], B. Rufflè[24], B. Fischer[25], P. Huber[26]

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14 Italian Institute of Technology, Rome, Italy
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18 Trento University, Italy
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20 Zernike Institute for Advanced Materials, Groningen, The Netherlands
21 Laboratoire de Physique des Solides, Universite Paris Sud, France
22 Universitat Politècnica Catalunya, Castelldefels, Spain
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40 authors:

- 26 different institutes
- 6 countries: Germany, France, Italy, Sweden, Netherlands, Spain

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ESRF-EBS
EBS Science Workshop
8 • 9 December 2016, ESRF, Grenoble

Program of the CDR1- Beamline for coherence applications
EBS Science Workshop - ESRF, 8th December 2016

Presentation of the CDR1 part I

09:00 h	Introduction	B. Ruta, ESRF/ILM – Lyon, France
09:20 h	Technical design of the new beamline	F. Zontone, ESRF
10:00 h	Experimental end-station and detectors	Y. Chushkin, ESRF

10:30 h *Coffee break*

Presentation of the CDR1 part II

11:00 h	Alternative scenarios	Y. Chushkin, ESRF
11:20 h	Comparison between the different projects	B. Ruta, ESRF/ILM – Lyon, France
11:40 h	Open discussion	

12:30 h *Lunch*

Future scientific possibilities

14:00 h Soft matter in motion - challenges and opportunities for XPCS at the ESRF-EBS
C. Gutt, University of Siegen, Germany - PI of the EOI
14:30 h Future scientific possibilities with XCCA at EBS
F. Lehmkühler, DESY, Hamburg, Gemany
14:45 h Dynamics of soft matter at interfaces
L. Cristofolini, Parma University, Italy
15:10 h Dynamics of complex fluids- investigating concentrated protein solutions
P. Holmqvist, Lund University, Sweden
15:35 h Nanoscale dynamics in high temperature superconductors
A. Ricci, DESY, Hamburg, Gemany

16:00 h *Coffee break*

Future scientific possibilities and closing discussions

16:30 h Structural fluctuations in hard condensed matter
G. Beutier, Simap, Grenoble, France
16:55 h Toward imaging of mesoscopic architecture of cell DNA. Modelling and X-ray imaging experiments - J. Uličný, Pavol Jozef Šafárik University in Košice , Slovakia
17:20 h Open Discussion

18:00 h *End of the session*

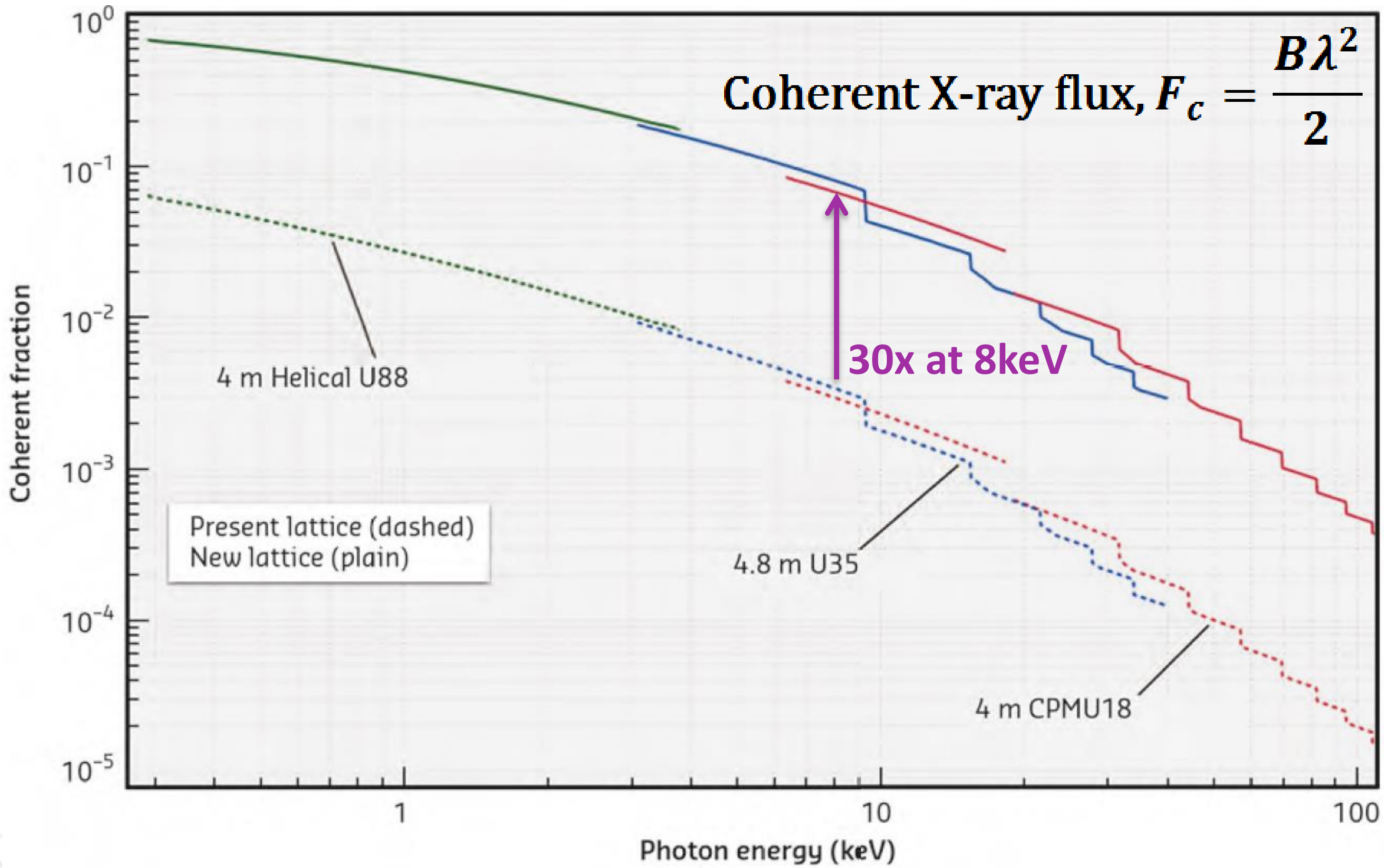
December 2016

48 participants:

- 30 different institutes
- 9 countries: Germany, France, Italy, England, Sweden, Slovakia, Russia, Japan, United States

Lyon 1 CNRS

Coherence: a key feature of the EBS upgrade



ESRF Orange Book

Dynamics in model membranes

Molecular dynamics simulations show intermittent dynamics at sub-micron scales in lipid membranes (time scale below 10 microseconds) depending on the «crowding» of the film

Protein Crowding in Lipid Bilayers Gives Rise to Non-Gaussian Anomalous Lateral Diffusion of Phospholipids and Proteins

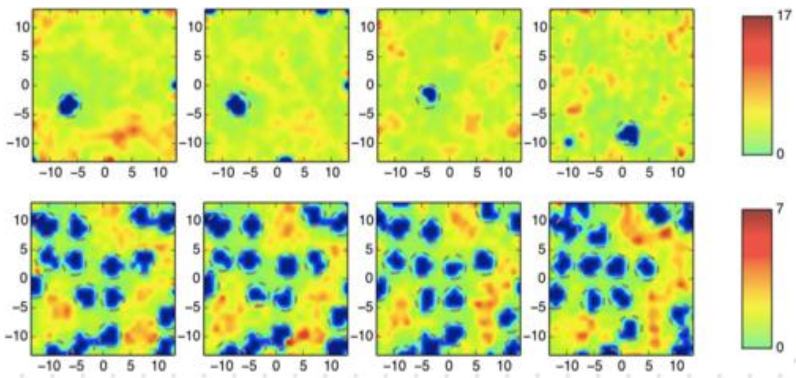
Jae-Hyung Jeon, Matti Javanainen, Hector Martinez-Seara, Ralf Metzler, and Ilpo Vattulainen
Phys. Rev. X **6**, 021006 – Published 12 April 2016

Top: protein poor membrane
Bottom: protein rich membrane

In the crowded environment, faster dynamics (red) is observed.

(scales in nm)

t=0ns 10ns 100ns 1000ns



Courtesy of L. Cristofolini, University of Parma - Italy