X-Ray Photon Correlation Spectroscopy

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Outline

I. **Introduction**

II. **Coherence Properties of undulator radiation**
   - Coherence lengths
   - Experimental Details

III. **Disordered Systems under Coherent Illumination**
   - Speckle
   - Speckle Statistics
   - X-Ray Photon Correlation Spectroscopy (XPCS)

IV. **Structure and Dynamics of Complex Systems**
   - Colloidal Fluids
   - (Surface Dynamics)
   - Magnetic Speckle

V. **Perspectives with a FEL source**

VI. **Summary**

Introduction

If coherent light is scattered by a disordered system it gives rise to a random diffraction or **“speckle”** pattern.

“Speckle” patterns are interference patterns and they are related to the **exact spatial arrangement** of the disorder.

If the spatial arrangement of the disorder changes as a function of time the “speckle” pattern will also change. A measurement of the **temporal intensity fluctuations** of a single or equivalent speckles is thus a **measure of the underlying dynamics.**

The temporal intensity fluctuations can be characterized by:

Correlation Spectroscopy Techniques

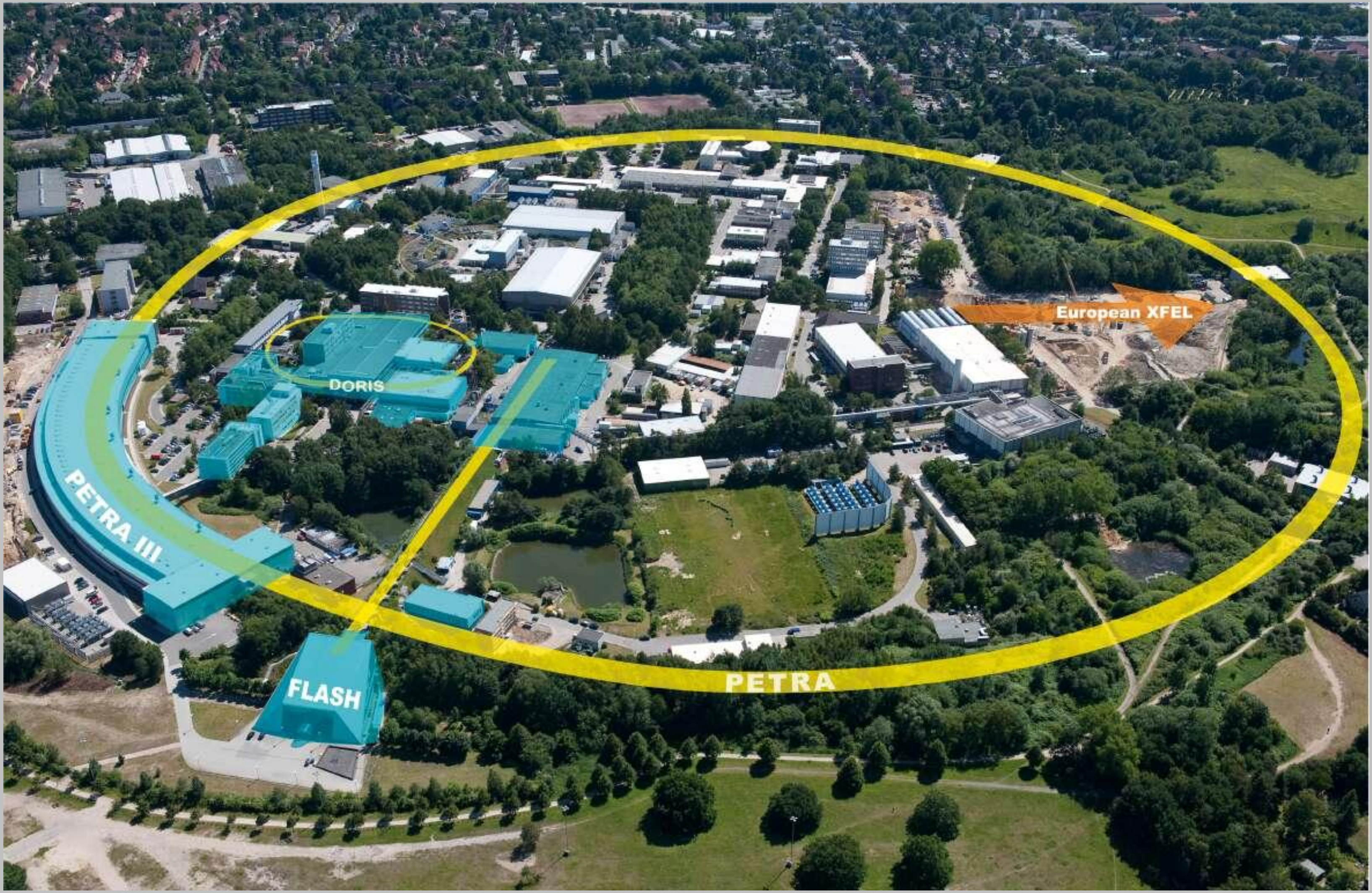
Coherent visible light from a laser source ($\lambda \approx 5300$Å):

Photon Correlation Spectroscopy (PCS) or **Dynamic Light Scattering (DLS)** ←

Coherent light from a synchrotron source ($\lambda \approx 1$Å):

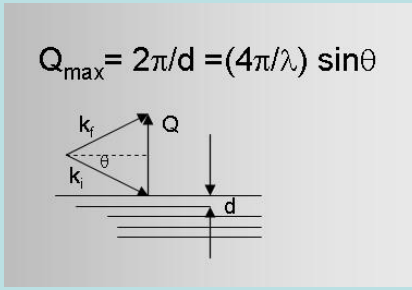
X-Ray Photon Correlation Spectroscopy (XPCS)

Third generation synchrotron radiation sources

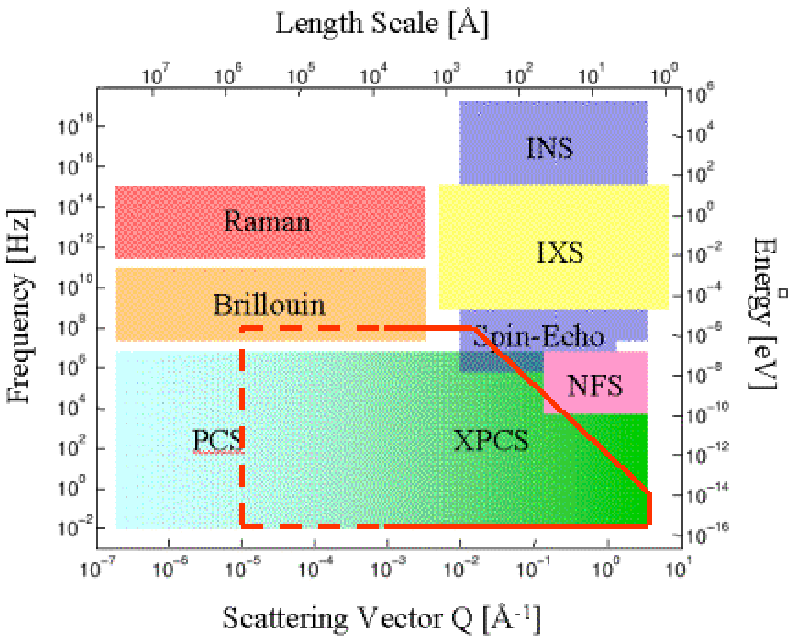


XPCS: Dynamic Light Sattering with X-Rays

- **Dynamics on short lengthscales**



- **No multiple scattering**
- **Opaque materials**



Dynamics of complex fluids
- colloidal suspensions (high ϕ, large Q,..)
- polymer systems (internal modes, …)

Slow dynamics: disordered systems
- domain formation phase separating …systems (glasses, alloys,…)
- glass transition(3-D, 2-D)
- time dependence of critical fluctuations

Domain wall dynamics in IC systems
- ferroelectrics, cdw systems, magnetic ...materials

2-D systems
- surfaces (liquid, solid), thin films, …membranes,…

Ultra-slow Dynamics
- jammed systems

Non-equilibrium Dynamics

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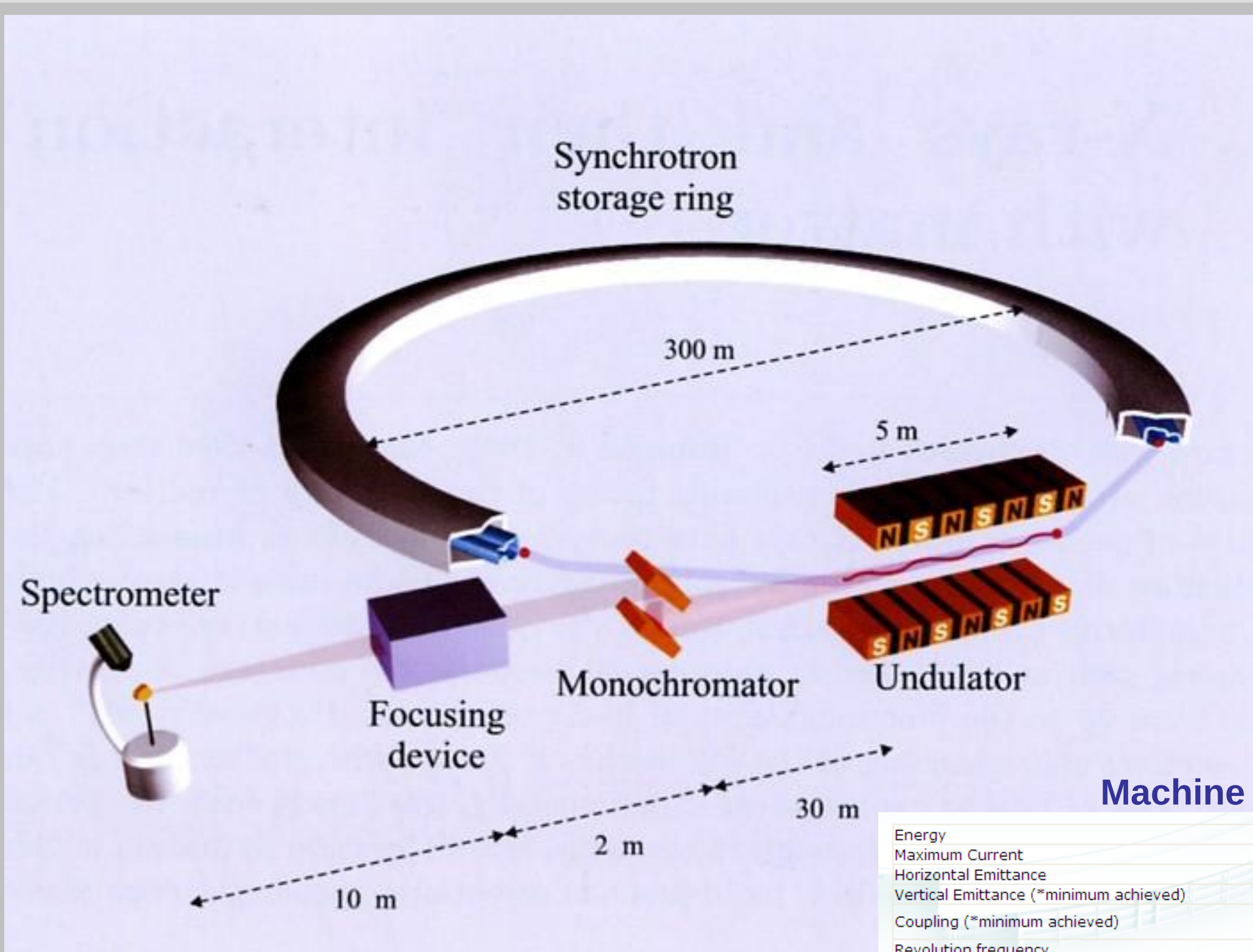
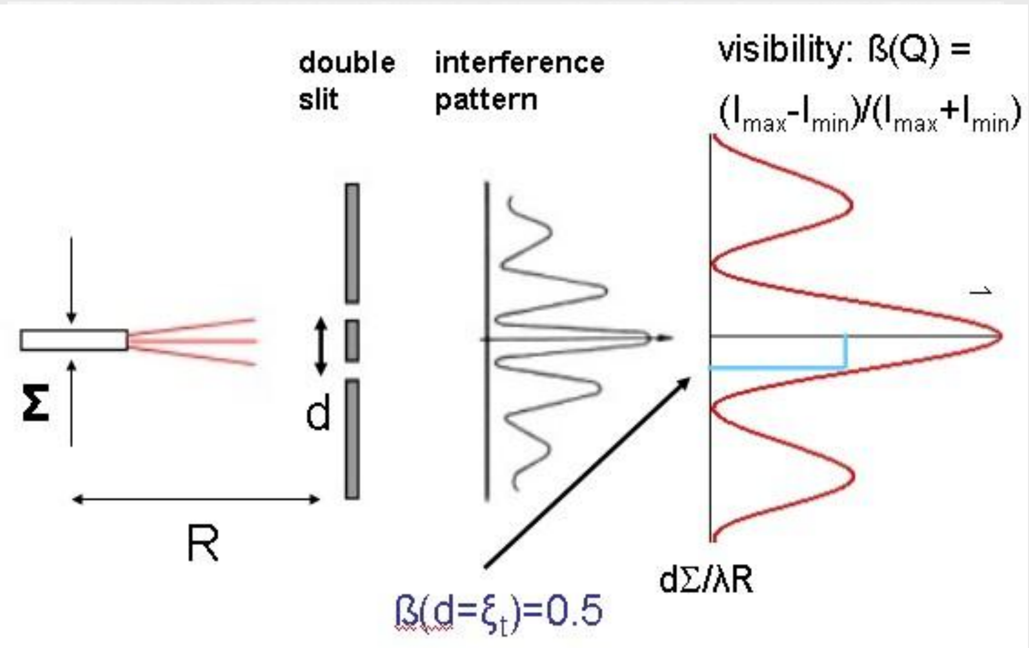
Coherence Properties of Undulator Radiation



Machine parameters ESRF

Energy	GeV	6.03
Maximum Current	mA	200
Horizontal Emittance	nm	4
Vertical Emittance (*minimum achieved)	nm	0.025 (0.010*)
Coupling (*minimum achieved)	%	0.6 (0.25*)
Revolution frequency	kHz	355
Number of bunches		1 to 992
Time between bunches	ns	2816 to 2.82

Coherence properties of undulator radiation



Coherent Flux:

Fc = $(\lambda/2)^2 \cdot$ B = $3.5 \cdot 10^{10}$ ph/s ♠

B=10^{20} ph/s/mm²/mrad²/0.1%bw

$\Delta\lambda/\lambda=10^{-4}$; λ=1Å

Temporal Coherence:

longitudinal coherence length:

$\xi_l = \lambda(\lambda/\Delta\lambda)$ = 1 μm

$\Delta\lambda/\lambda = 10^{-4}$; λ=1Å

Transverse coherence length:

$\xi_t = (\lambda/2)\ (R/\Sigma)$ = 2.5μm(h), Σ_x=1mm

= 25 μm(v); Σ_z= 0.1mm

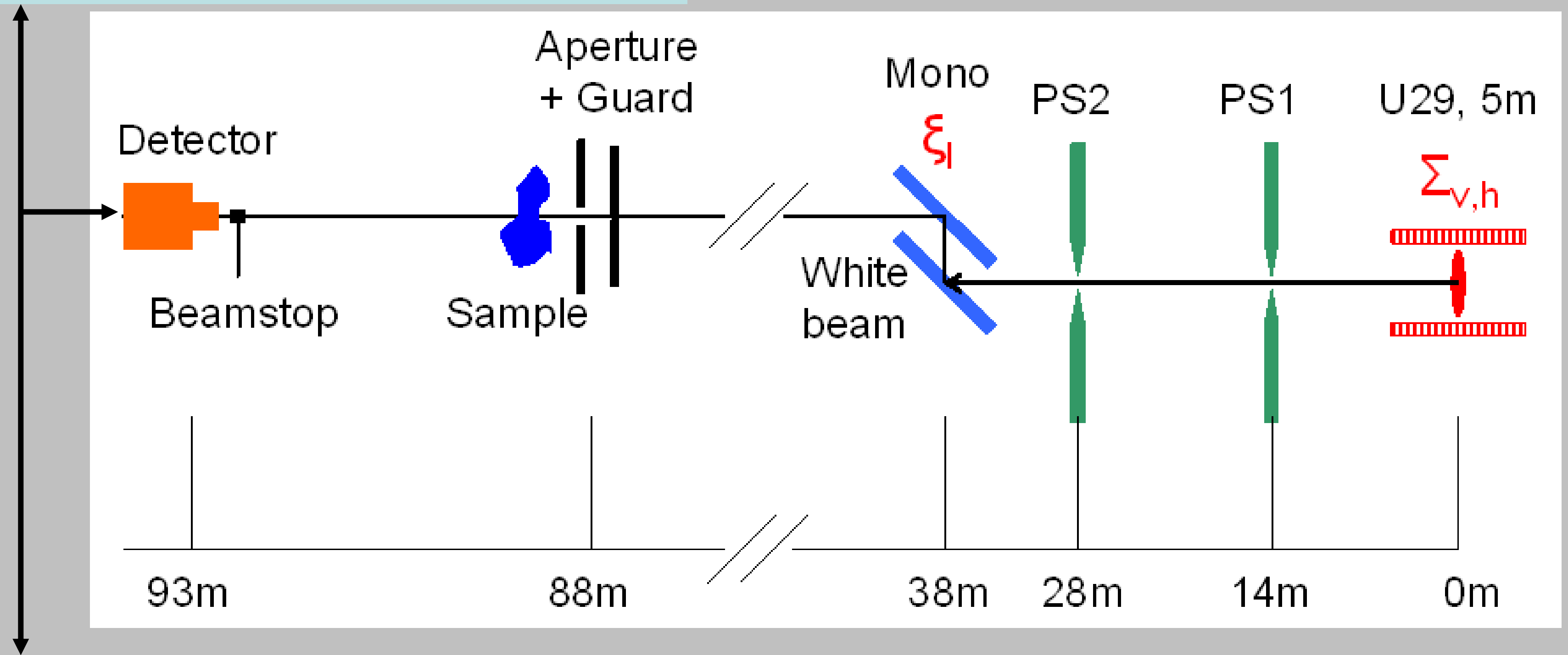
(λ=1 Å, R=50m)

A beamline for coherent scattering: P10 at PETRA-III

2-D detector

Direct illumination, deep depletion CCD

10^6x20μm pixels, 1 MHz ADC, (1 Mbyte/s):
SLOW ➔ PIXEL detectors



0-D detector

+ digital autocorrelator: FAST

speckle size: $(\lambda/\xi_t)\cdot L \approx$ 20-40 μm ♠

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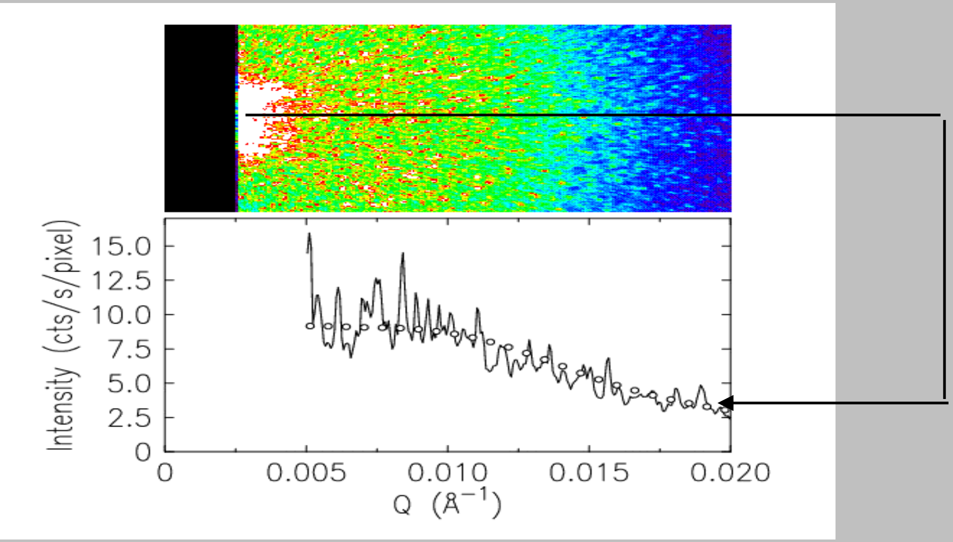
If coherent light is scattered from a disordered system it gives rise to a random (grainy) diffraction pattern, known as "speckle". A speckle pattern is an interference pattern and related to the exact spatial arrangement of the scatterers in the disordered system.

$$I(Q,t) \propto S_c(Q,t) \propto | \sum e^{iQR_j(t)} |^2$$

j in coherence volume $c=\xi_t^2\xi_l$ ♠

Incoherent Light: $S(Q,t) = < S_c(Q,t)>_{V>>c}$ **ensemble average**

Aerogel
λ=1Å
CCD (22 μm)



Abernathy, Grübel, et al.

J. Synchroton Rad. 5, 37, 1998

Speckle Statistics

fully coherent illumination:

If the amplitude $f_n(Q)$ and phases $Q \cdot r_n$ are statistically independent and statistically distibuted over 2π:

$$P(I) = (1/\langle I\rangle) \exp(-I/\langle I\rangle)$$

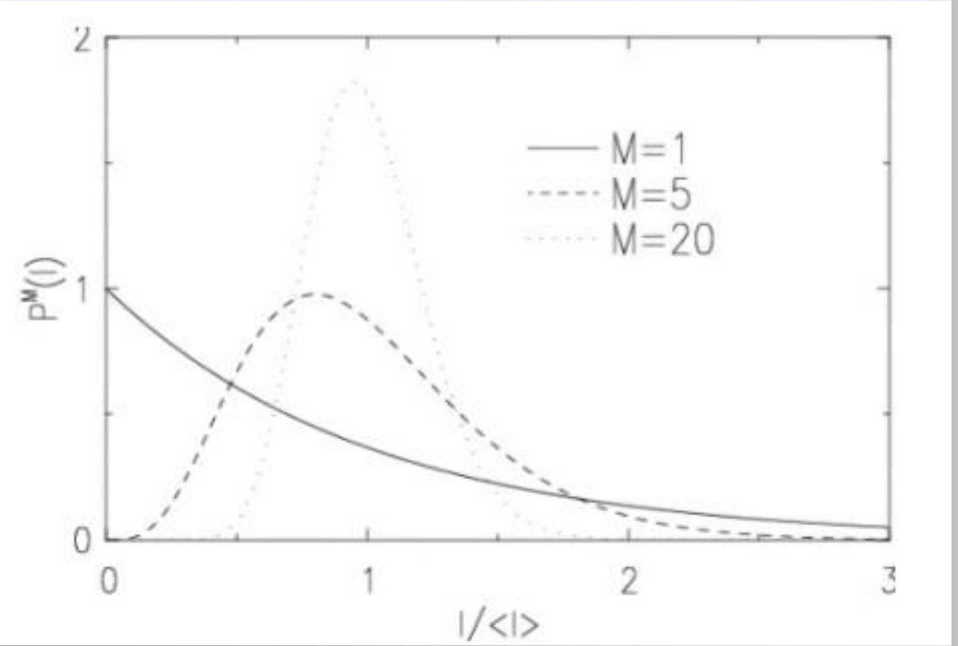
Mean:	$\langle I\rangle$
StdDev:	$\sigma = \sqrt{(\langle I^2\rangle - \langle I\rangle^2)} = \langle I\rangle$
Contrast:	$\beta = \sigma^2/\langle I\rangle^2 = 1$

partially coherent illumination:

The speckle pattern is the sum of M independent speckle patterns:

$$P_M(I) = (M^M I^{M-1})/(\Gamma(M)\langle I\rangle^M)\exp(-MI/\langle I\rangle)$$

Mean:	$\langle I\rangle$
	$\sigma = \langle I\rangle/M^{1/2}$
Contrast:	$\beta = 1/M$



No information on:

Size and shape of individual speckles

Contrast: $\beta = \beta(\Delta\lambda/\lambda, Q, \ldots.)$

Abernathy et al., J. Synchrotron Rad. 5,37 (1998)

Scattering with Coherent X-Rays

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j in coherence volume $c=\xi_t^2\xi_l$

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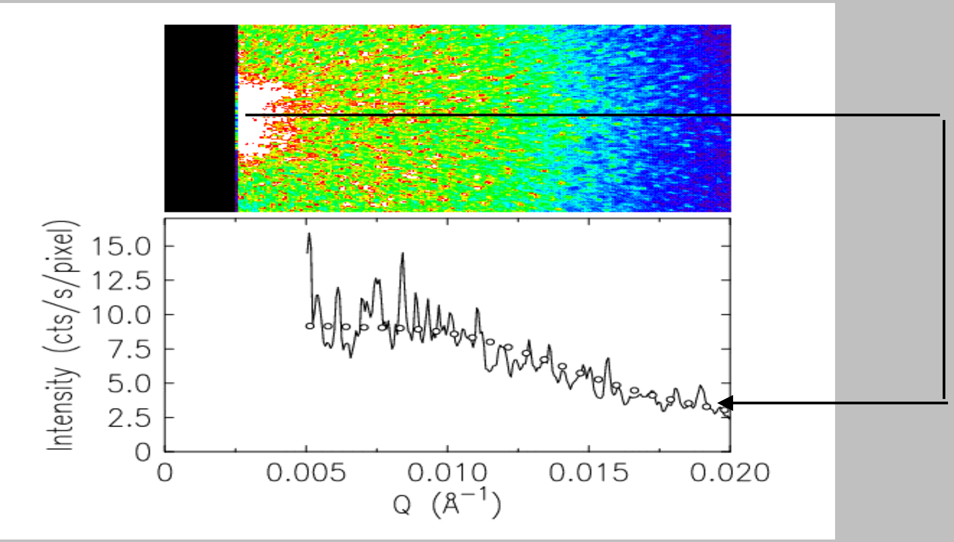
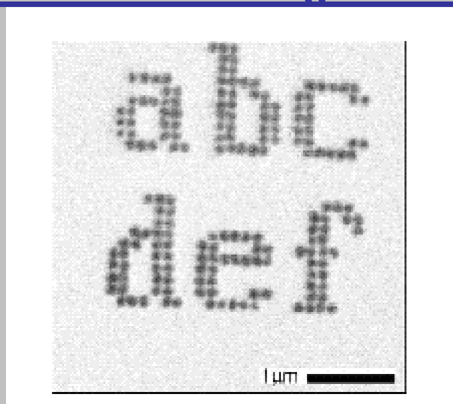


Abernathy, Grübel, et al.

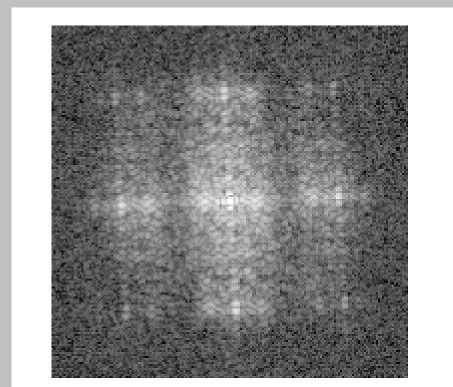
J. Synchroton Rad. 5, 37, 1998

Speckle Reconstruction

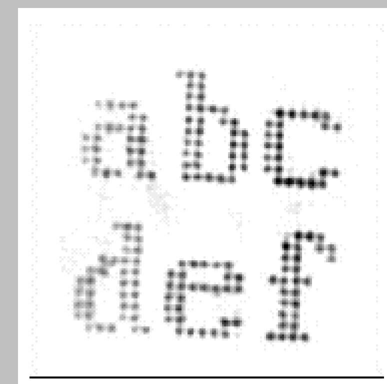
<u>Reconstruction (phasing) of a speckle pattern:</u> “oversampling” technique



gold dots on SiN membrane
(0.1 μm diameter, 80 nm thick)



λ=17Å coherent beam at X1A
(NSLS), 1.3·10^9 ph/s 10μm pinhole
24 μm x 24 μm pixel CCD



reconstruction
“oversampling” technique

Miao, Charalambous, Kirz, Sayre, Nature, 400, July 1999

<u>other examples:</u> nanocrystalline materials (Williams et al., PRL90,175501,2003; He et al.,PRB67,174114,2003
Robinson et al., PRL87,195505-1)

Scattering with Coherent X-Rays

If coherent light is scattered from a disordered system it gives rise to a random (grainy) diffraction pattern, known as "speckle". A speckle pattern is an inter-ference pattern and related to the exact spatial arrangement of the scatterers in the disordered system.

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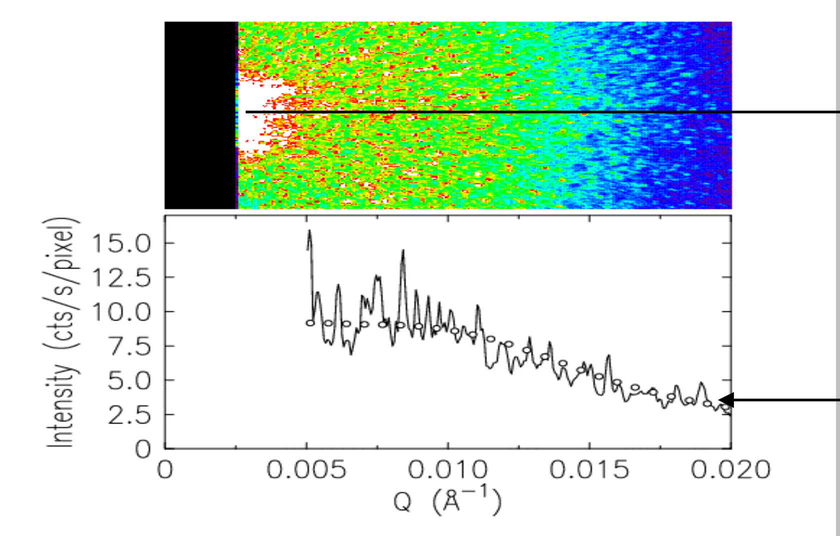

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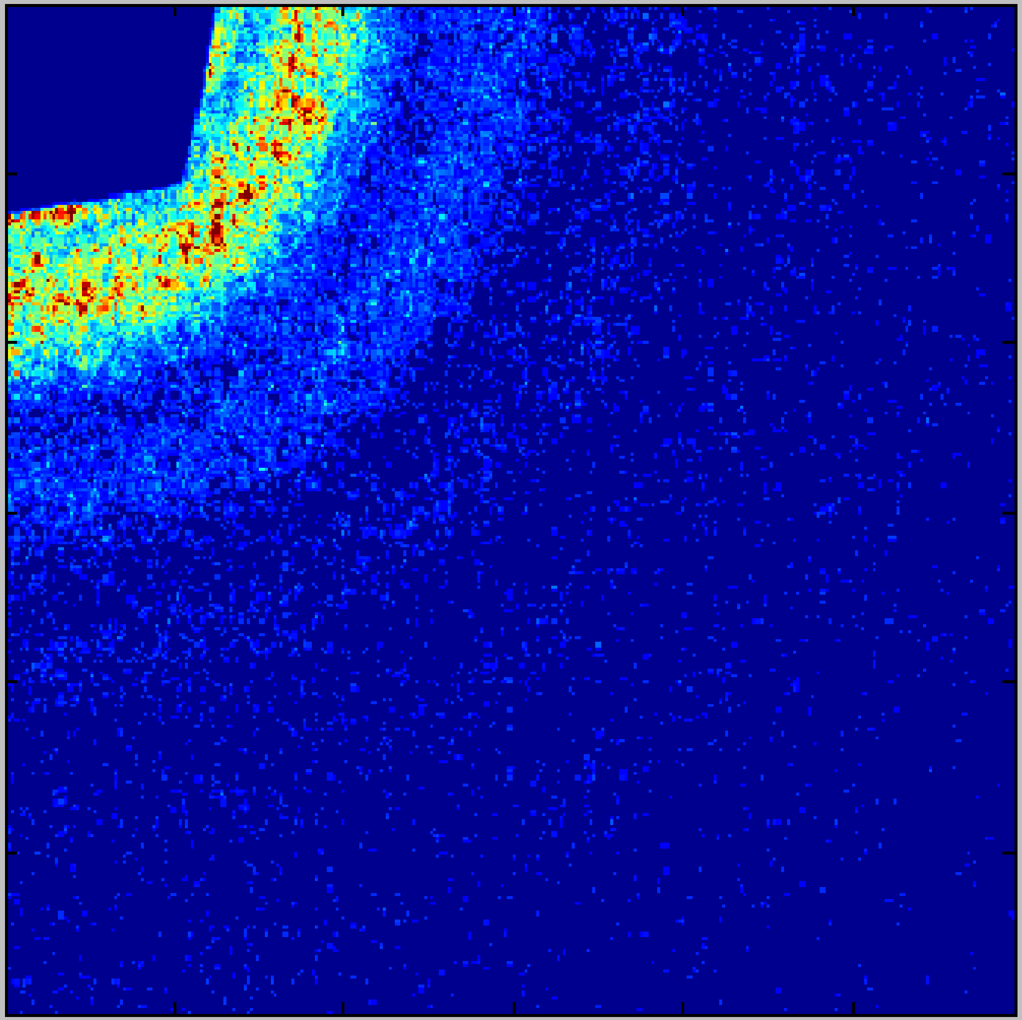
Abernathy, Grübel, et al.

J. Synchroton Rad. 5, 37, 1998

Dynamics

Silica: 2610 Å, ΔR/R=0.03, 10 vol% in glycerol, T=-13.6C, η ≈ 56000 cp



V. Trappe and A. Robert

Photon Correlation Spectroscopy

$$G(Q,t)=\langle I(Q,0)\cdot I(Q,t)\rangle/\langle I(Q)\rangle^2=\alpha\, Re\,\{g_1(Q,t)\}+\beta\, g_2(Q,t)+(1-\beta)$$

$g_1(Q,t) = \langle\rho(Q,0)\cdot\rho^*(Q,t)\rangle$

$g_2(Q,t) = \langle\rho(Q,0)\cdot\rho^*(Q,0)\cdot\rho(Q,t)\cdot\rho^*(Q,t)\rangle$

$\rho(Q,t)$: FT (electron density)

Gaussian fluctuations ($g_2=1+|g_1|^2$), no optical mixing ($\alpha = 0$) :

$$G(Q,t) = 1+\beta(Q)\,|g_1(Q,t)|^2$$

$g_1(Q,t) \equiv f(Q,t) = F(Q,t) / F(Q,0)$:
normalized intermediate scattering function

$$F(Q,t)=(1/(Nf^2(Q))\,\Sigma_n\Sigma_m\langle f_n(Q)\, f_m(Q)\exp(iQ\,[r_n(0)-r_m(t)]\rangle$$

$F(Q,0) = S(Q)$ static structure factor

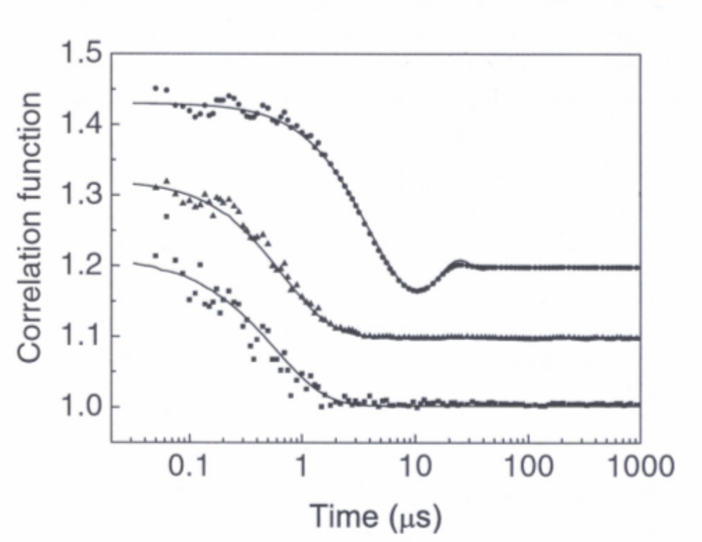
Diffusive Processes:

Monodisperse, non-interacting scatterers:
$F(Q,0)=1$, $\langle[r(0)-r(t)]^2\rangle = 6\,Do\,t$

$f(Q,t) = \exp(-\Gamma t)$, $\Gamma = Do\,Q^2$

interacting scatterers:

$f(Q,t) = \exp(-\Gamma t)$, $\Gamma = D(Q)\,Q^2$



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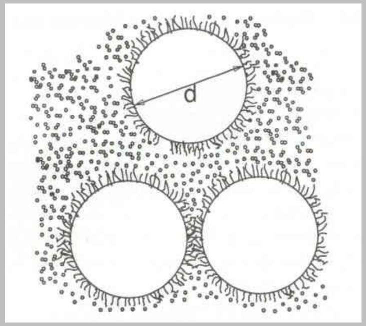
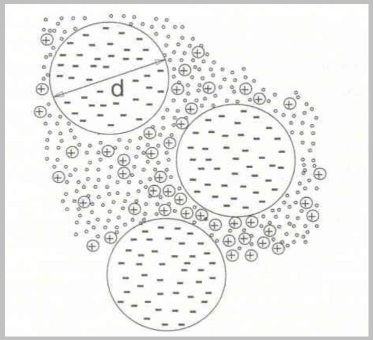
Structure and Dynamics of Colloidal Fluids

Colloidal particles (paints, ink, clays, ……silica,…..) suspended in a solvent (molecular fluid, …).
Stabilised against „van der Waals“ attraction.

„Hard Spheres“





„Soft Spheres“

Structure: $S(Q)=1+4\pi\rho \int [g\{r\}-1] (\sin(Qr)/Qr) r^2 dr$; $g\{r\}=\exp[-V(r)/kT]$ ρ: number density N/V

$\Phi \ll 1\%$: $S(Q)=1$ $D(Q) = D_o\ (=kT/6\pi\eta R_H)$

$\Phi > 1\%$:

$$V(r)=\begin{cases} 0 & r \geq d \\ \infty & r < d \end{cases}$$

weak interaction: DLVO

$V(r) \propto (eZ_{eff})^2/r \exp(-\kappa r)$

$S=S(Q,\Phi)$ (Percus-Yevick) $S=S(Q,\Phi,Z_{eff},\kappa)$ (MSA, RMSA)

Dynamics: Interaction: colloid-solvent, colloid-colloid, hydrodynamics

Smoluchowski (many particle) diffusion equation:

$$D_{short}(Q) = D_o/S(Q) * H(Q) \qquad t \ll R^2/D_o$$

H(Q) (Beenakker and Mazur) H(Q) (via Do, S(Q), D(Q))

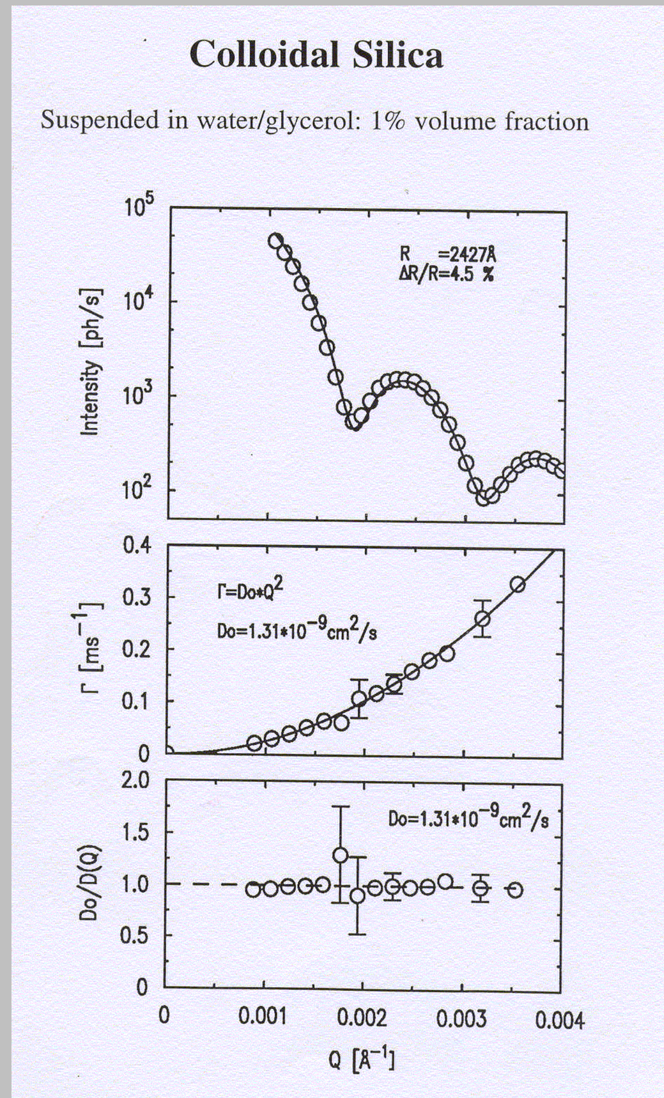
Dilute, non-interacting system

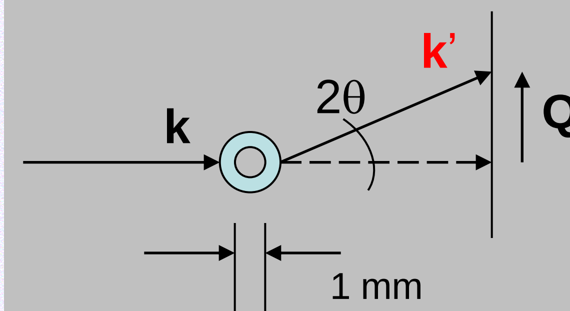
$I \sim |F(Q)|^2 \, S(Q)$

$\sim [(\sin QR - QR\cos QR)/(QR)^3]^2$

$\Gamma \;= Do\, Q^2$

$Do = k_B T/6\pi\eta R$ ♠





$Q = k' - k$

$Q = 2k \sin\theta$

$k = 2\pi/\lambda$

G. Grübel, A. Robert, D. Abernathy
8th Tohwa University International Symposium on "Slow Dynamics in Complex Systems", 1998, Fukuoka, Japan

Poly-methylmetacrylate

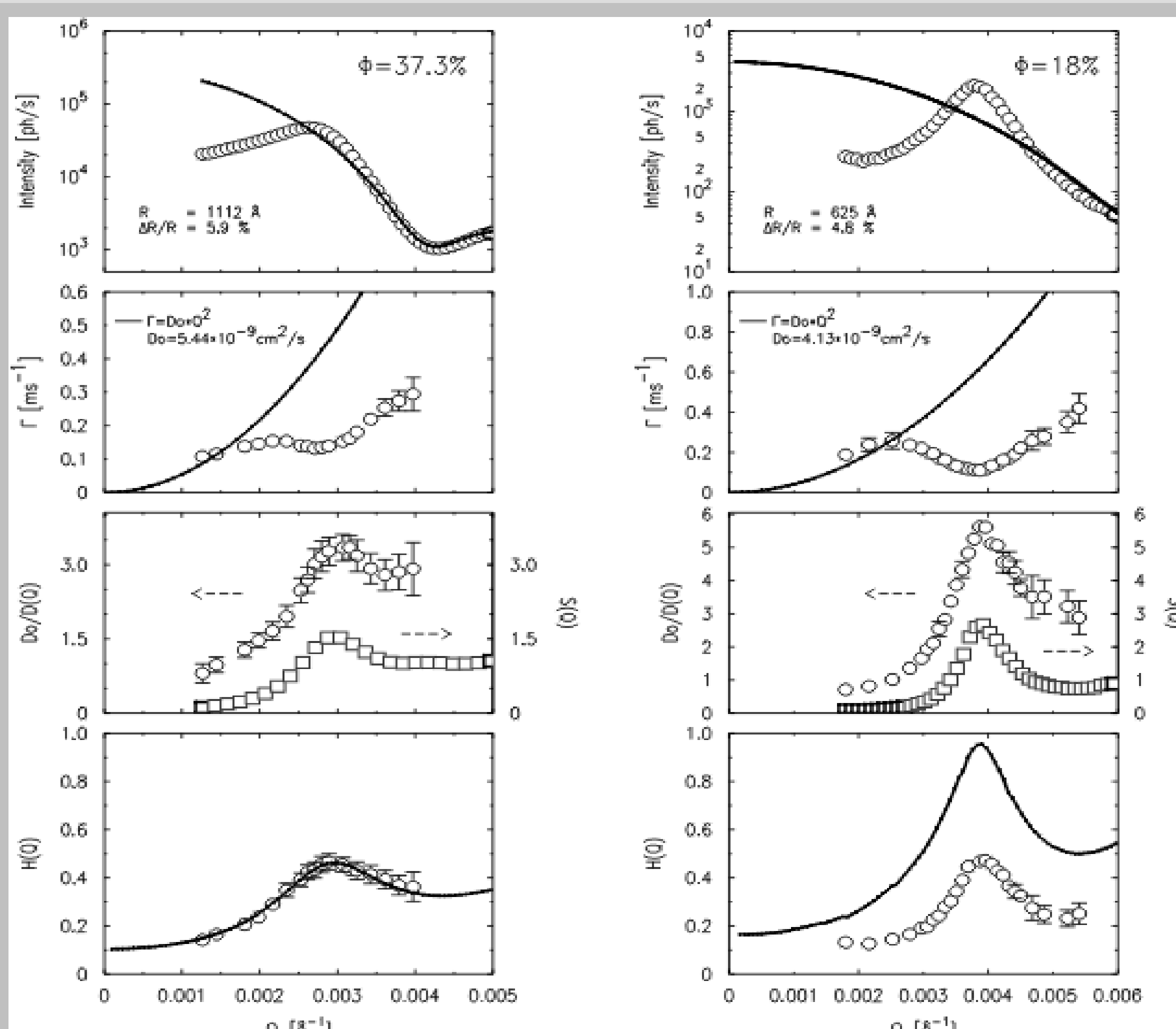
37% volume fraction in cis-decaline

sterically stabilized (**hard-spheres**)

Poly-octafluoropentylcrylate

18% volume fraction in H_2O/glycerol

charge-stabilized (**soft-spheres**)



“caging“ (deGennes narrowing)

δ-γ expansion

$|F(Q)|^2$

$\Gamma = DoQ^2$

$S(Q)=I(Q)/|F(Q)|^2$

δ-γ expansion

$H(Q)=S(Q)/[Do/D(Q)]$

no model

QR=5.6

Zontone, Moussaid, Robert, Grübel

Robert, Härtl, Wagner, Grübel

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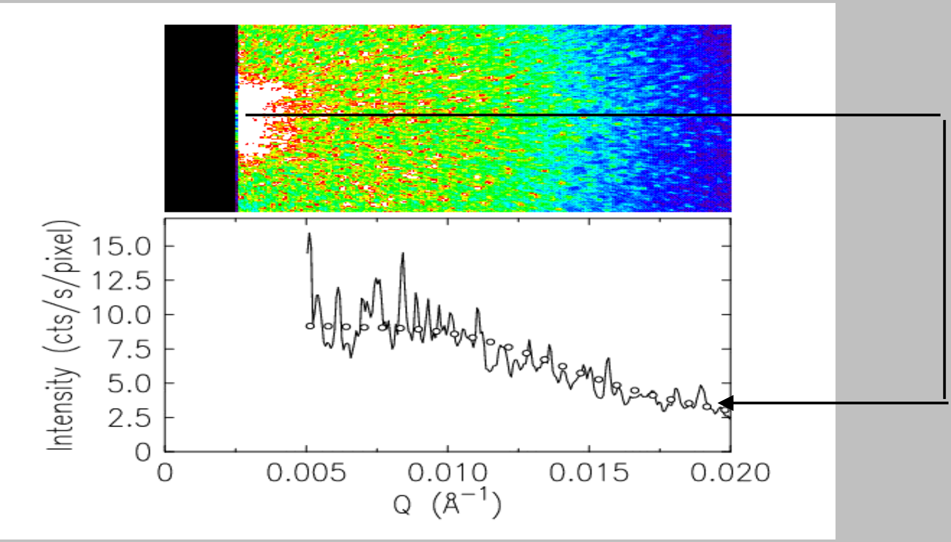
$$I(Q,t) \propto S_c(Q,t) \propto \Big| \sum_{j \text{ in coherence volume } c=\xi_t^2\xi_l} (f_n^{\text{charge}} + f_n^{\text{magnetic}})\, e^{iQR_j(t)} \Big|^2$$

Incoherent Light: $S(Q,t) = \langle S_c(Q,t) \rangle_{V>>c}$ **ensemble average**

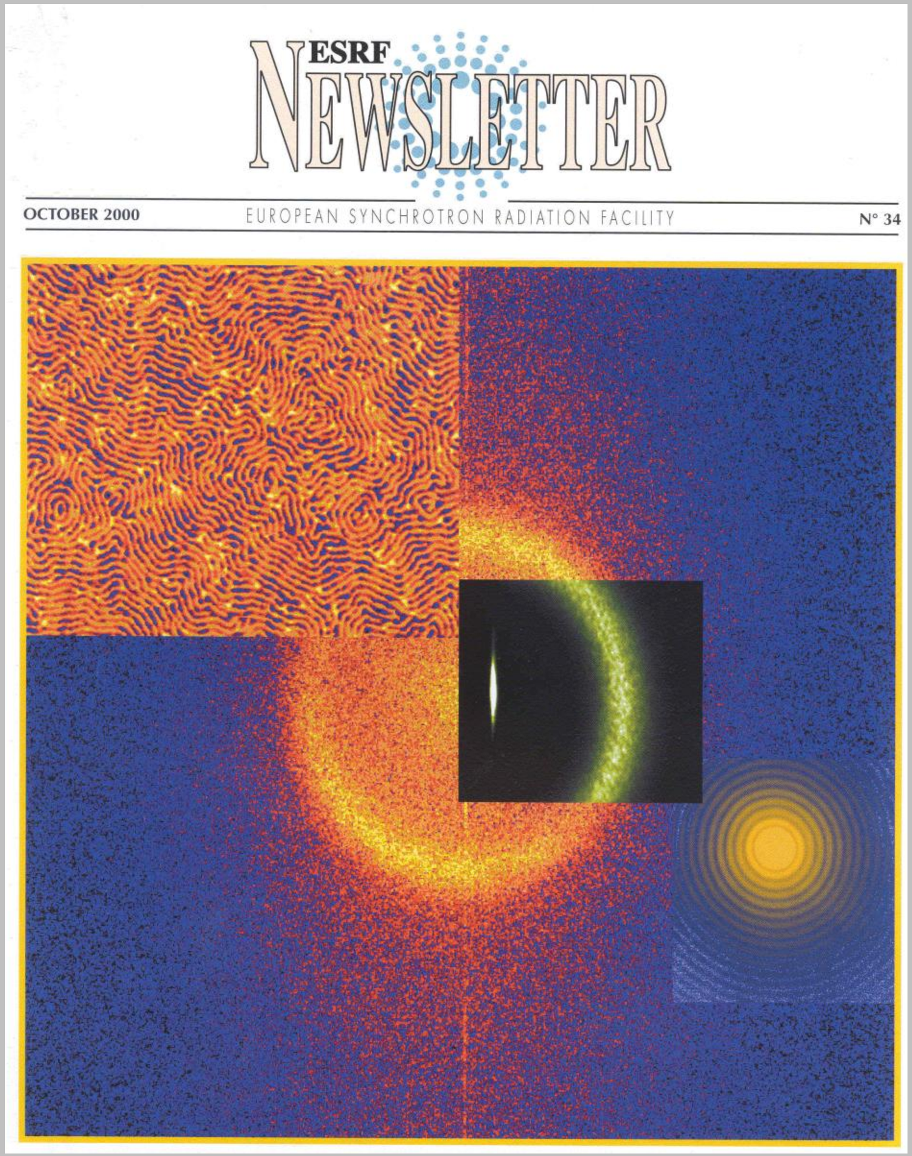
Aerogel
λ=1Å
CCD (22 μm)



Abernathy, Grübel, et al.

J. Synchroton Rad. 5, 37, 1998

Magnetic Speckle



Magnetic Force Microscopy image and magnetic x-ray speckle from (meandering) magnetic stripe domains in a 350Å thick film of $GdFe_2$. Data from ID12B (ESRF) with λ=11Å (Gd-M_v).

J.F. Peters, M.A. deVries, J. Miguel, O. Toulemonde and J.Goedkoop, ESRF Newslett. 34, 15 (2000)

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Perspectives with a coherent XFEL source

XFEL
X-Ray Free-Electron Laser

The European X-Ray Laser Project XFEL

XFEL Homepage | Organization | Technical Information | Project Group

XFEL > XFEL Homepage

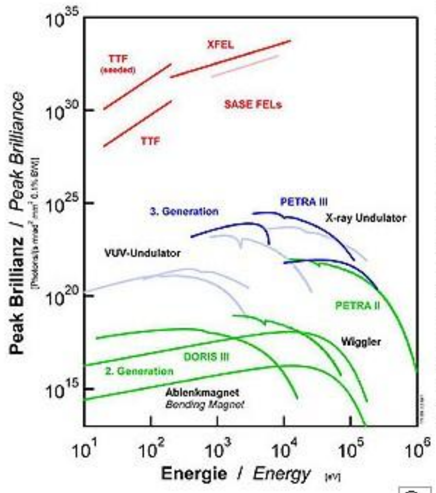
- XFEL Homepage
- Facts & Figures

Website Hosted by DESY

The European X-Ray Laser Project XFEL

The X-Ray Free-Electron Laser—A Light Source of Superlatives

In February 2003, the German Federal Ministry of Education and Research gave the green light for the X-ray laser. Together with European partners, the project is to be further developed in such a way that a decision to begin construction can be made at the end of 2004. After a construction period lasting about six years, the commissioning of the facility could start in 2012. An international research team—the TESLA collaboration—is currently trying out the facility's pioneering technology at a test facility in Hamburg—and it has already achieved the key milestones it has been aiming for. The free-electron X-ray laser will make it possible to do leading-edge research in Europe and will guarantee a major role for Germany as a location for research and industry.



Brilliance in comparison
This comparison of the peak brilliance of synchrotron radiation sources with free-electron lasers (FELs, red lines) shows the great leap in brilliance offered by the FELs. (Source: DESY Hamburg)

Brilliance x 10^{10}

$\cong 10^{12}$ ph/pulse

Ultrashort pulses (< 100 fs)

Scientific applications using x–ray FELs

Atoms, ions, molecules, and clusters →	• Multiple ionization and multiphoton events • Creation and spectroscopy of excited states (hollow atoms, Rydberg states, Laser states, ...) • Dynamics, electronic & geom. cluster properties
Plasma physics →	• Generation of solid-density plasmas • Plasma diagnostics
Condensed-matter physics →	• Ultrafast (magnetic) dynamics • Electronic structure • Disordered materials & soft matter
Materials sciences →	• Dynamics of hard materials • Structure and dynamics of nanomaterials
Chemistry →	• Reaction dynamics in solid, liquid systems • Analytical solid-state chemistry • Heterogenous catalysis
Structural biology →	• Single molecule/particle imaging • Dynamics of biomolecules
Optics and nonlin. Phen. →	• Nonlinear effects in atoms and solids • High field science

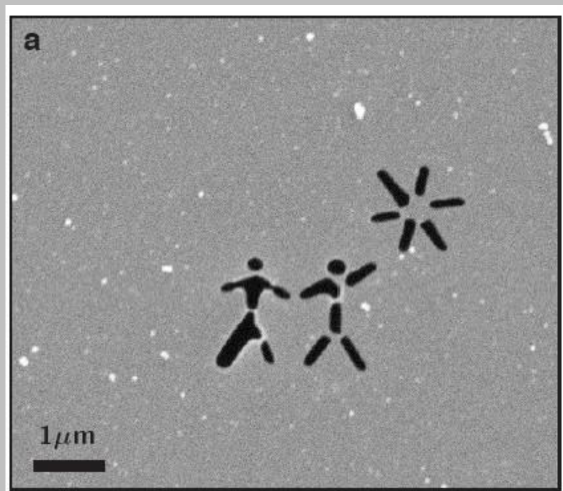
The VUV-FEL at DESY

$\lambda \geq 4.5$ nm

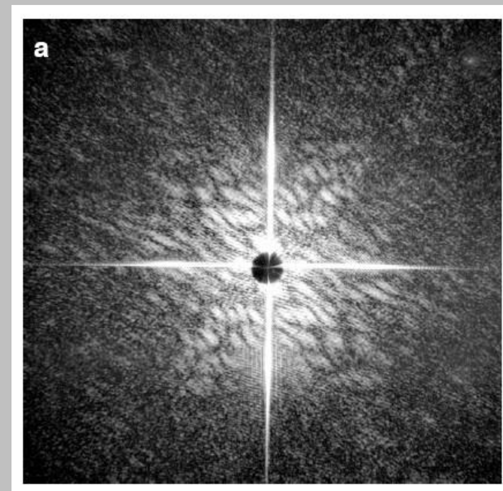
Commissioning: 2004/5

User experiments: 2005

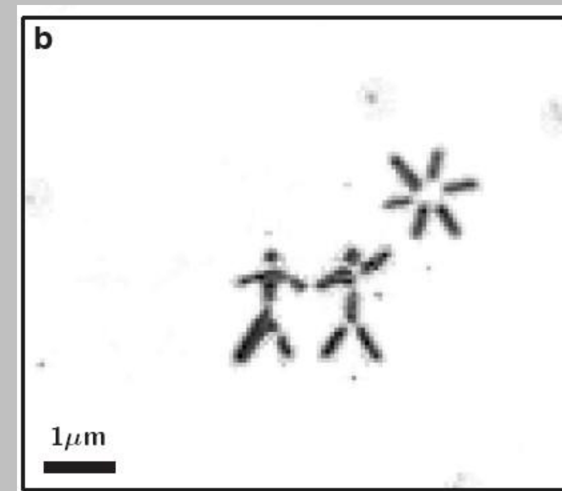
Femtosecond diffractive Imaging



Model structure in 20 nm SiN membrane

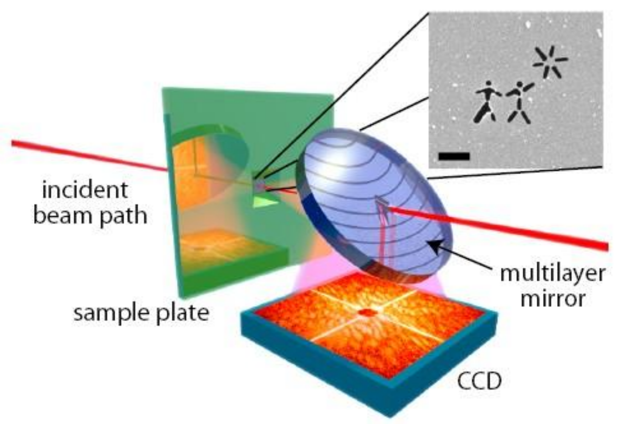


Speckle pattern recorded with a single (25 fs) pulse



Reconstructed image

Incident FEL pulse:
25 fs, 32 nm,
4 x 10^{14} W cm^{-2} (10^{12} ph/pulse)



H. Chapman et al., Nature Physics, 2,839 (2006)

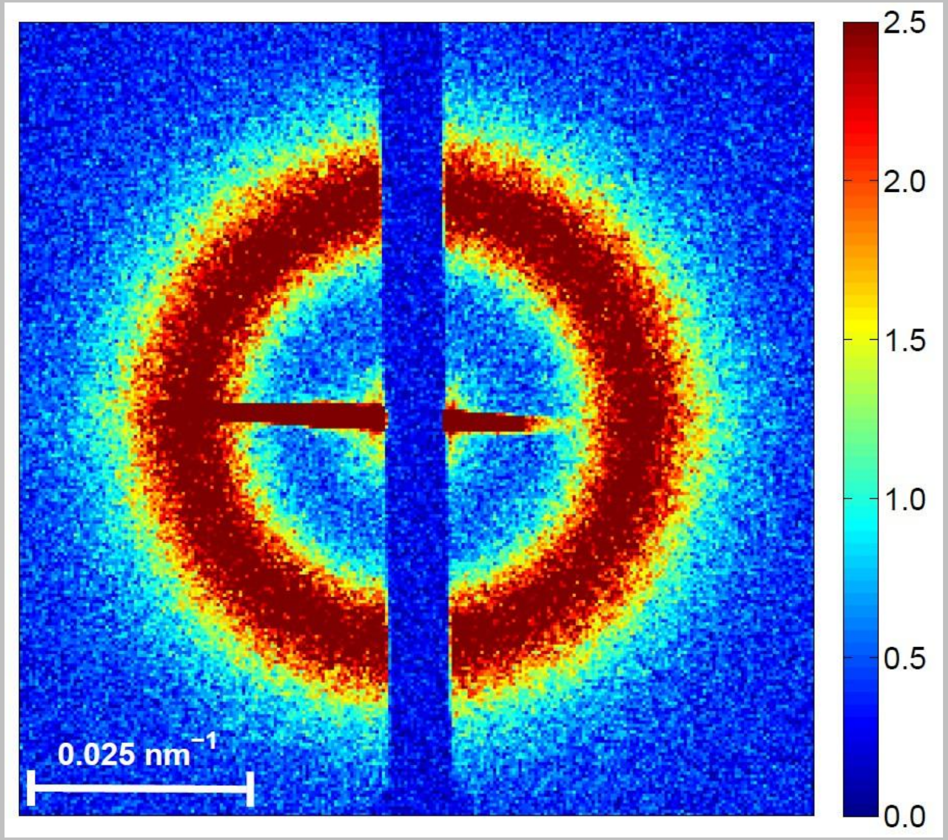
Magnetic SAXS of CoPt multilayer at Co $M_{II/III}$

λ=20.8 nm (59 eV): Co $M_{2,3}$

30 femtosecond pulse length
(4 µJ/pulse $4x10^{11}$ ph/pulse)
ΔE/E ≈ 0.5–1 %
250 µm beamsize
(5 Hz, single pulse)

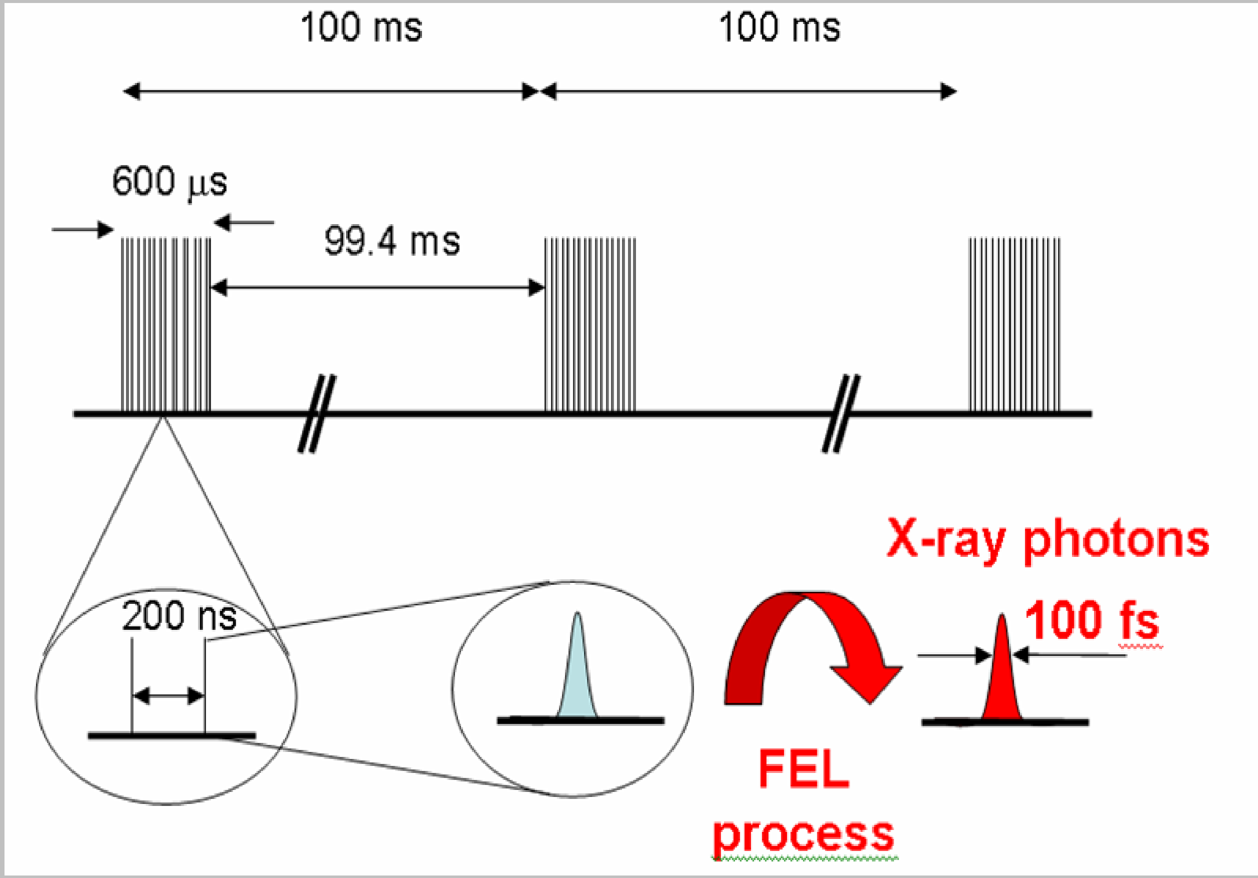
Single-shot (30 fs) magnetic SAXS pattern.

CoPt multilayer sample is not destroyed!



$[Co(0.8nm)/Pt(1.4nm)]_{16}$ on 50nm Si_3N_4 substrate
2048x2048 13.5µm pixel CCD (40 mm from sample)

C. Gutt et al., PRB(Rapid), 2010



t > 0.1 s
200ns < t < 600 µs:

” movie” mode

.

1ps < t< 10 ns: “delay-line” mode

for “all” times: “pump-probe” mode

Conclusion

Third generation, storage ring based, sources permit novel scattering and imaging techniques based on coherent X-rays. Among them is:

X-Ray Photon Correlation Spectroscopy (XPCS).

XPCS today covers timescales down to about 100 ns up to moderately large momentum transfers.

Fields of activity:	Dynamics of complex fluids
	Critical Dynamics
	2-D systems
	Non-equilibrium dynamics
Exploit:	Anomalous scattering, polarization
Develop:	2-D detector technologies to reach atomic resolution and time scales down to 1 ns.

Future XFEL sources will provide (spatially) coherent beams with a time averaged coherent flux: $<F_c> \cong 10^{16}$ ph/s and 10^{12} photons/bunch:

The high flux of photons/100 fs bunch will allow **single "shot" experiments**.
XPCS might be extended in the **ns - ps regime**.

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The End