Coherence of light and matter: from basic concepts to modern applications

Part III: G. Grübel   Script 3

Coherence based X-ray techniques

Overview, Introduction to X-ray Scattering, Sources of Coherent X-rays, Speckle pattern and their analysis

Imaging techniques

Phase Retrieval, Sampling Theory, Reconstruction of Oversampled Data, Fourier Transform Holography, Applications

X-ray Photon Correlation Spectroscopy (XPCS)

Introduction, Equilibrium Dynamics (Brownian Motion), Surface Dynamics, Non-Equilibrium Dynamics

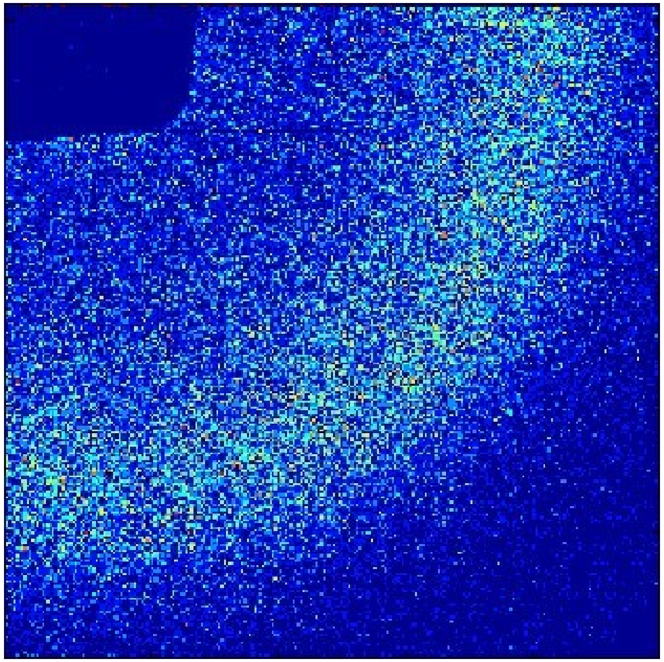
Imaging and XPCS at FEL Sources

▪

(Lensless) Imaging

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.

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



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

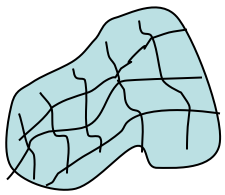
phase information

is lost

Phase Retrieval and Oversampling

without a priori information eq. ($) cannot be solved uniquely

== > decrease number of unknown variables:



i) use objects with some known scattering density

σ = total number of elements/number of unknown-valued pixels > 2

ii) increase number of known quantities in eq. ($) by “oversampling”

sample the magnitude of a Fourier transform finely enough to get a finite support for the object such that the element values outside the finite support is zero

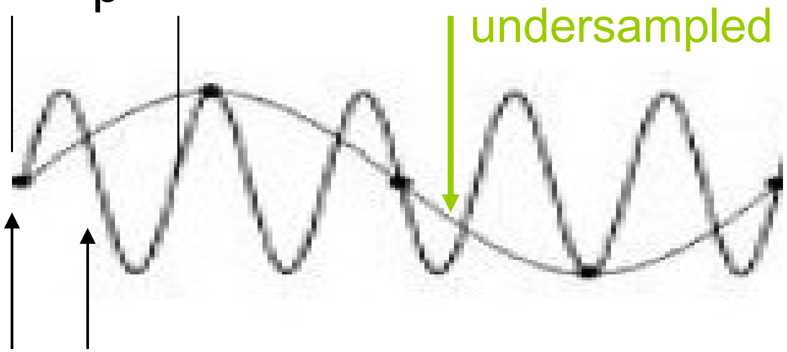
need: $\sigma > 2$ in 1D; $\sigma > 2^{1/2}$ in 2D; $\sigma > 2^{1/3}$ in 3D

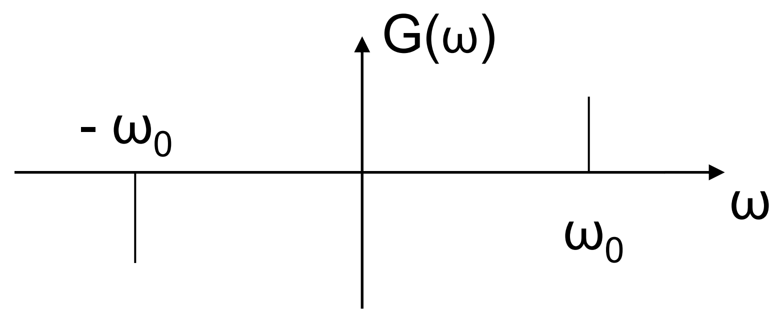
iii) apply iterative algorithms to retrieve phase

iv) resolution determined by maximum momentum transfer Q

Sampling Theory (1)

<u>Sampling Theorem:</u> A signal f(t) that is
i) bandwidth limited
ii) sampled above the Nyquist frequency
is completely determined by its samples.





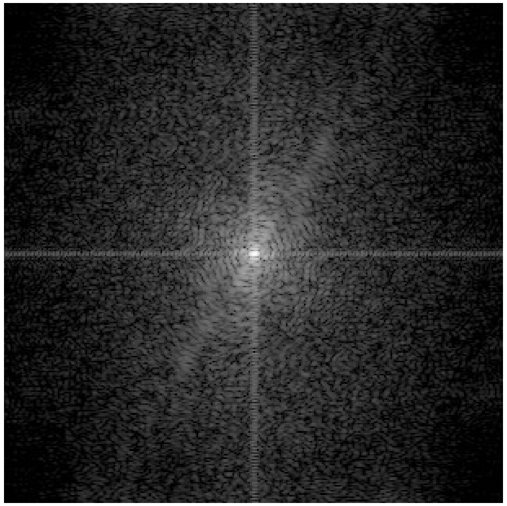
$$f(t) = \sin \omega_0 t \quad ===> \quad \text{FT} \quad <=== \quad G(\omega) = \int f(t)\, e(-i2\pi\omega t)\, dt$$

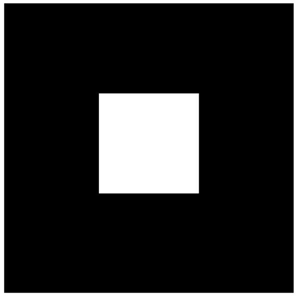
A signal is called bandwidth limited if it contains no frequencies outside the interval: $[-f_{max}, f_{max}]$. Here f_{max} ($=\omega_0$) is called the bandwidth of the function. The Nyquist frequency is usually given by $f_{NY} = 2\, f_{max}$ ($=2\omega_0$).

<u>Note:</u> period $p = 2\pi/\omega_0$ and (Nyquist) sampling period $p_{NY} = 2\pi/2\omega_0 = p/2$.
(undersampling: $p>p_{NY}$; oversampling: $p<p_{NY}$)

Reconstructing the real space structure – the main principle

Gerchberg&Saxton(1972); Fienup (1982)

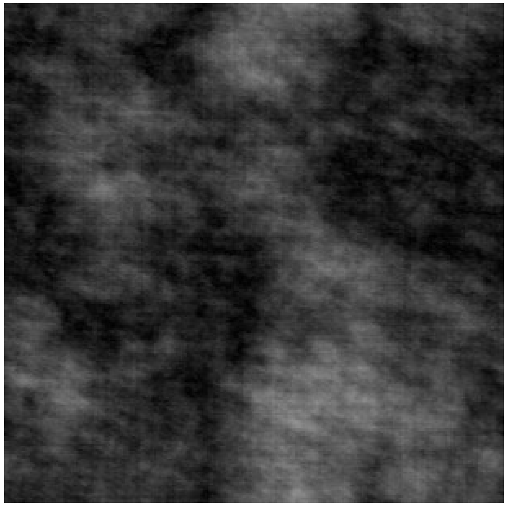




-1. Guess
support in real space

0. Add random phases to measured amplitudes
1. FT into real space
2. Set pixels outside support to zero and use positivity
3. FT into fourier space
4. Substitute amplitudes with measured values

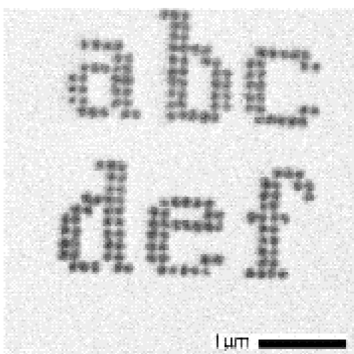
Loop over steps 1-4



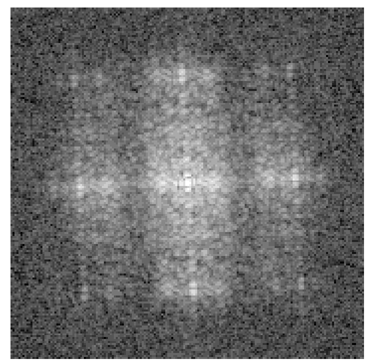
courtesy L. Stadler

Reconstruction of „oversampled“ data (1)

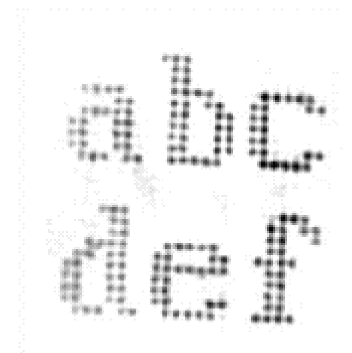
<u>Reconstruction (phasing) of a speckle pattern:</u> **“oversampling” technique**



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



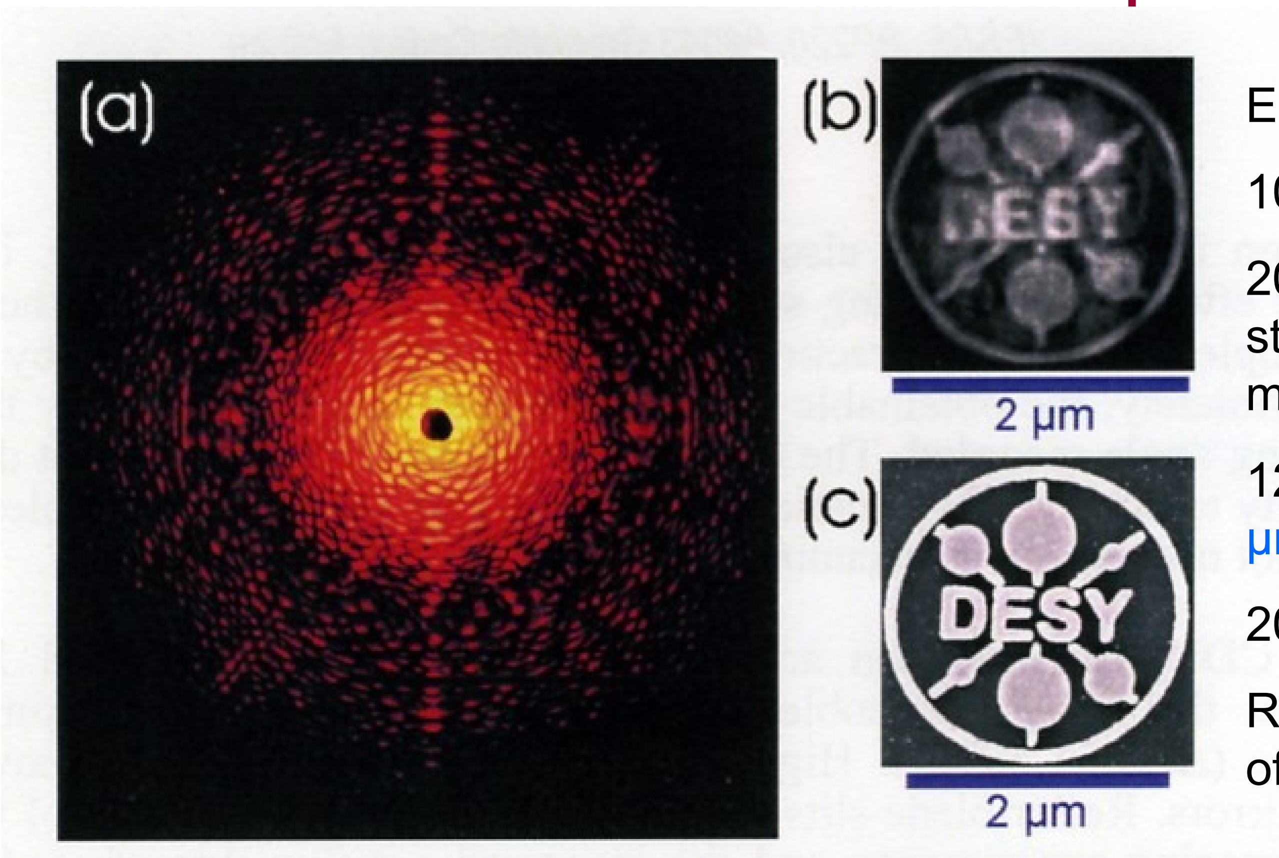
λ=17Å coherent beam at X1A (NSLS), $1.3 \cdot 10^9$ ph/s 10μm pinhole 24 μm x 24 μm pixel CCD



reconstruction “oversampling” technique

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

Reconstruction of “oversampled” data (3)



E= 8 keV ID10C (ESRF}

10x10 μm^2 beam

200 nm height gold structures on 50nm Si_3N_4 membrane (c: SEM)

1242x1152 pixel, 22.5 μm^2 pixel CCD in 3.29 m

200 x 3 s exposure (a)

Reconstruction (average of 4 best runs) (b)

oversampling ratio σ = object image / pixelsize = (λ•L/d)/pixel ≈ 10

speckle size = (λ•L/aperture=object) = 240 µm ≡ 10 pixels

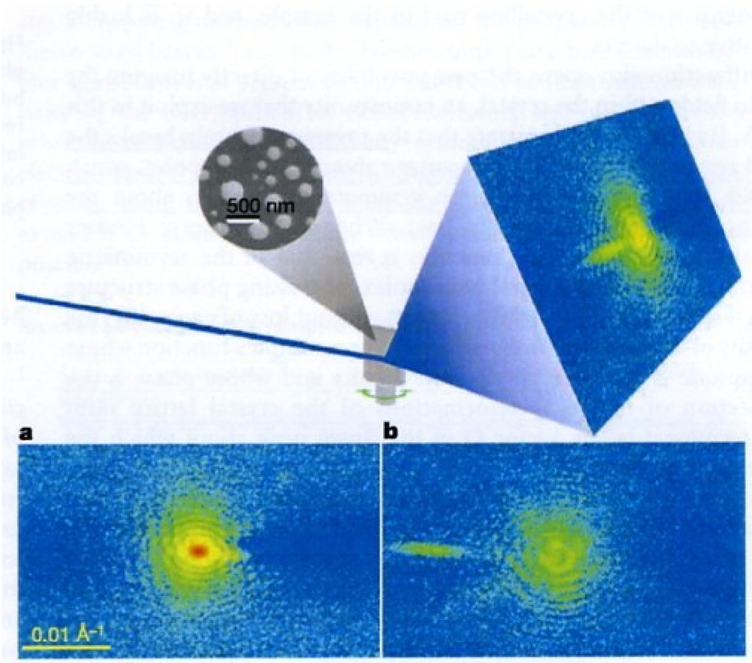
➔ Extrapolate content of a missing pixel by content of neighbouring pixels!

Deformation fields inside nanocrystals

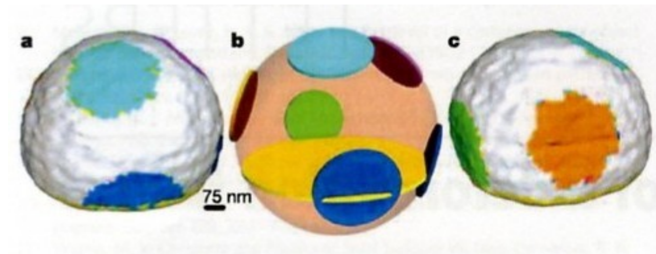
I.K. Robinson, I.A. Vartaniants, G.J. Williams, M.A. Pfeifer, J.A. Pitney, Phys. Rev. Lett. 87, 195505 (2001)
M.A. Pfeifer, G.J. Williams, I.K. Vartaniants, R. Harder and I.K. Robinson, Nature 442, 63 (2006)

CDI of (about 750 nm) Pb nanocrystals on Si substrate illuminated with 1.38Å coherent x-rays and CCD tuned to the Pb (111) reflection (with 2 images separated by a 0.01 deg. rotation of the sample shown below).

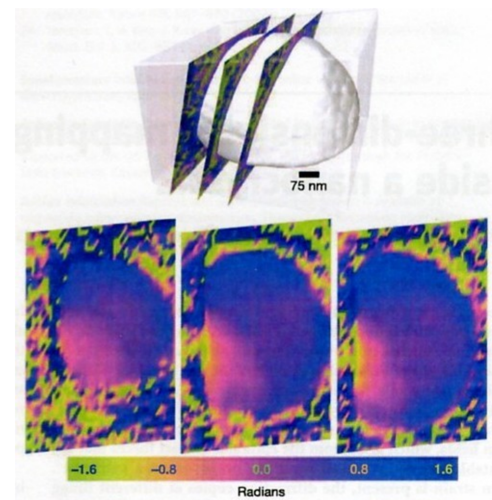
Density of crystals is regarded as a complex function with the real part being the electron density and the imaginary part representing the projection of the local deformation of the crystal onto the Q vector of the Bragg peak being measured.



Reconstructed electron density revealing (111) facets.



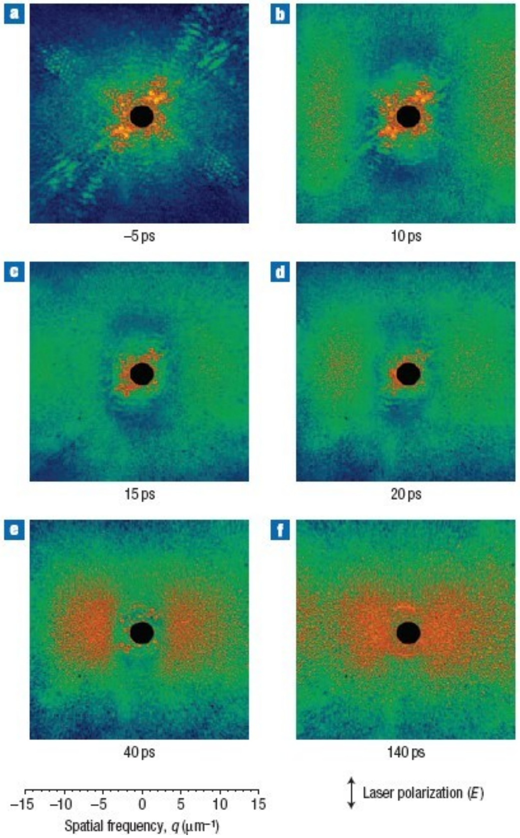
Reconstructed imaginary part revealing (in the center) a phase-shift corresponding to about 1.1/2π (111) lattice spacings or about 0.5Å

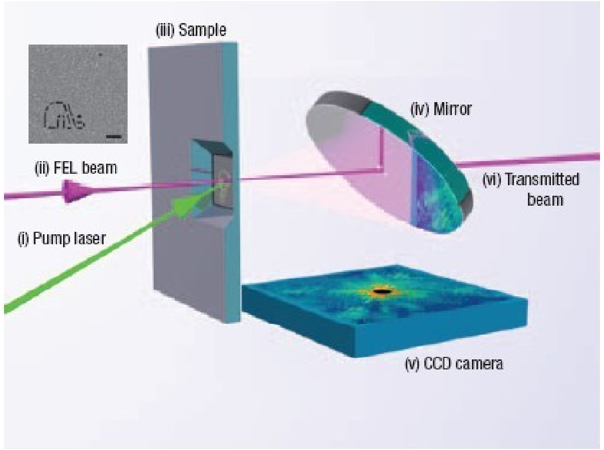


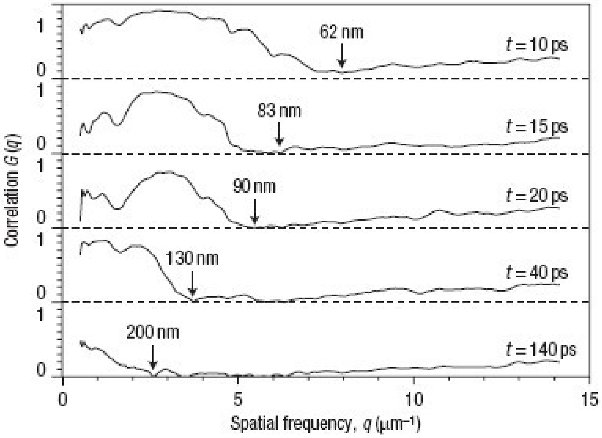
Ultrafast single-shot diffraction imaging of nanoscale dynamics

A. Barty et al., nature photonics 2, 415 (2008)

Pump-probe experiment on nano-patterned (FIP-etched) Si_3N_4 membrane (Ir-coated) pumped with Nd:YLF 523 nm, 12.5 ps long 25 µJ pulses and probed with 10 fs 13.5 nm 20 µm FLASH pulses.

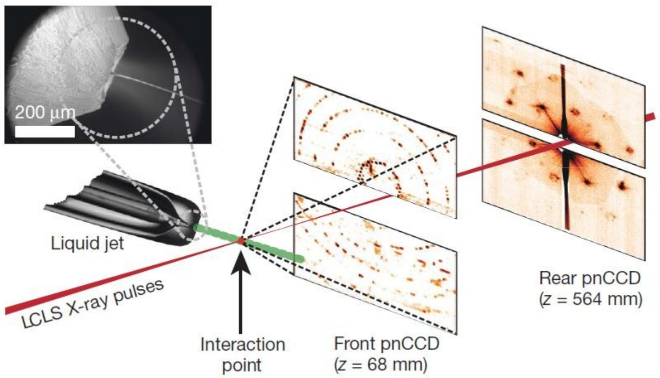






Correlation functions indicate sample disintegration with a speed of about 5000-6000 m/s

Femtosecomd X-ray protein nanocrystallography

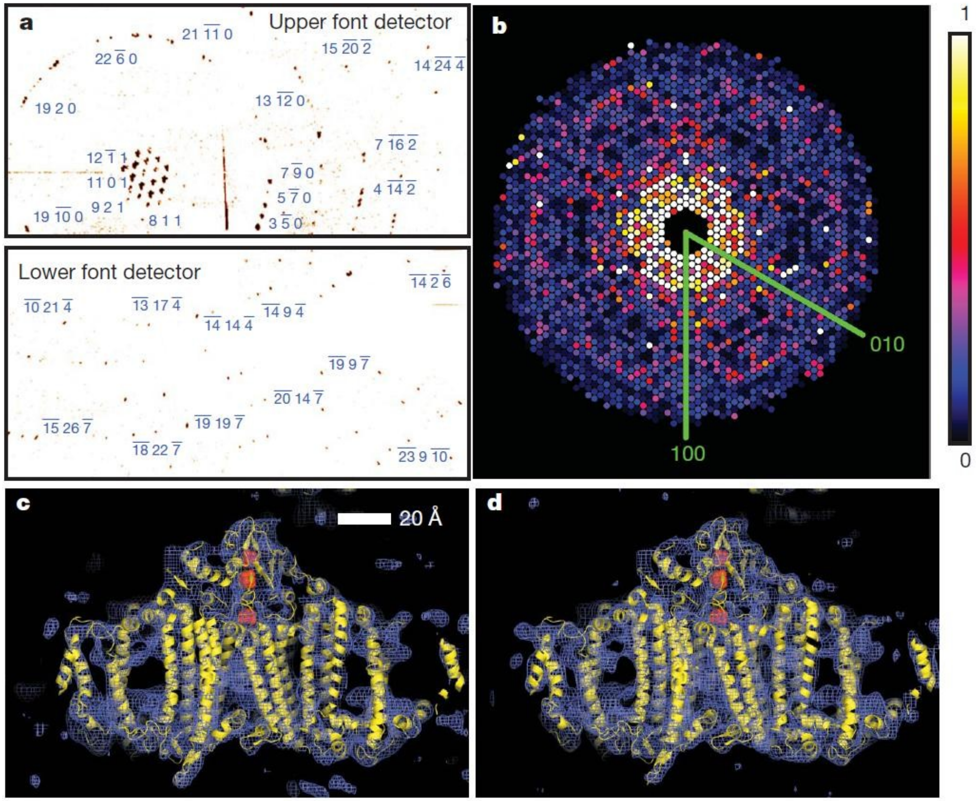


Nanocrystals (200 nm to 4 microns) of photosystem I flow in their buffer solution in a gas-focused, 4-mm-diameter jet at a velocity of 10ms/s perpendicular to the pulsed 1.8 keV X-ray FEL beam that is focused on the jet.

(a) Diffraction pattern recorded on the front pnCCDs with a single 70-fs pulse after background subtraction and correction of saturated pixels. The resolution in the lower detector corner is 8.5A˚.

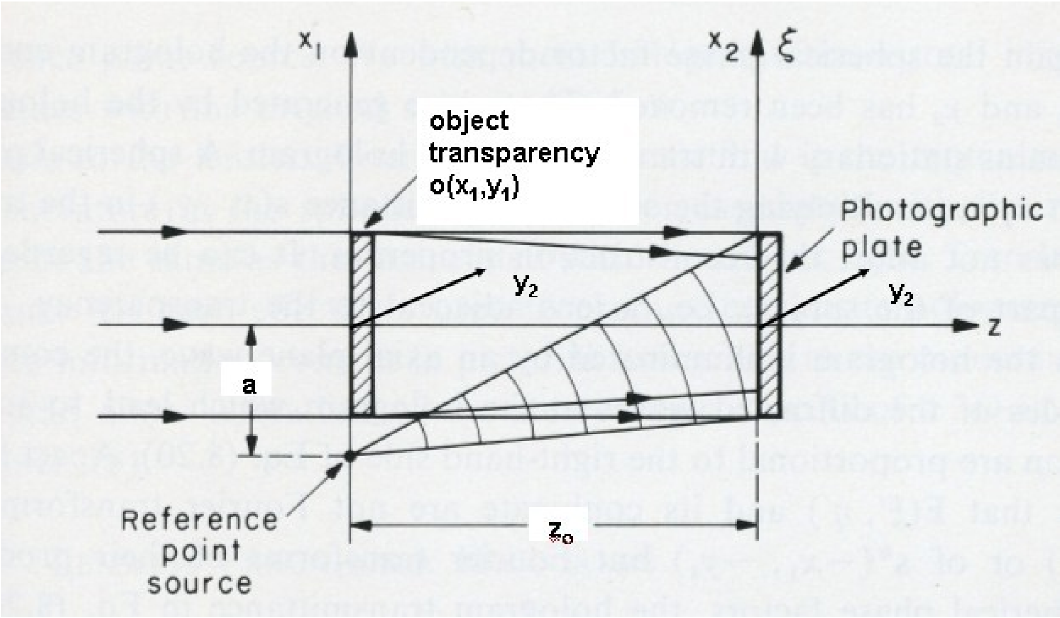
(b) Precession-style pattern of the [001] zone for photosystem I, obtained from merging femto-second nanocrystal data from over 15,000 nanocrystal patterns.

(c, d) Region of the electron density map calculated from the 70-fs data (c) and from conventional synchrotron data truncated at a resolution of 8.5A˚ and collected at a tempera-ture of 100K (d)



Henry N Chapman et al., Nature 470. 73 (2011)

Fourier Transform Holography – FTH (1)



$o(x_1,y_1)$: amplitude of the wave transmitted through object o

$r(x_1,y_1)$: reference wave

R.J. Collier, C.B. Burckhardt, L.H. Lin "Optical Holography", Academic Press (1971)

Fresnel Kirchhoff Theory

$$o(x_2,y_2) = (i/\lambda z_o)\exp\{i\pi/\lambda z_o)(x_2^2+y_2^2)\}\ \bar{O}(\xi,\eta)$$

$$r(x_2,y_2) = (i/\lambda z_o)\exp\{i\pi/\lambda z_o)(x_2^2+y_2^2)\}\ \check{R}(\xi,\eta)\ \exp\{-2i\pi\xi a\}$$

with $\bar{O}(\xi,\eta) = FT\{o(x_1,x_2)\}$, $\check{R}(\xi,\eta) = FT\{r(x_1,y_1)\}$, $\xi = x_2/\lambda z_o$, $\eta = y_2/\lambda z_o$

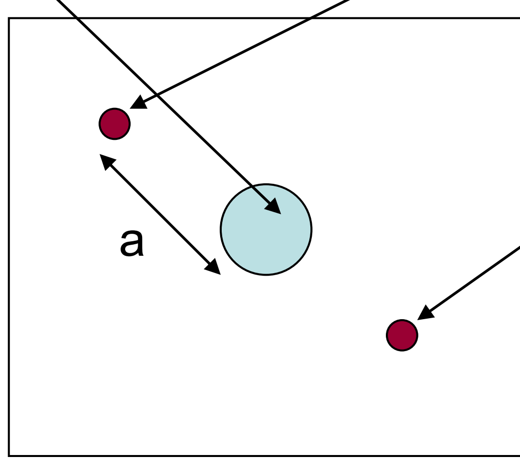
Fourier Transform Holography (2)

$$I(x_2,y_2) = |\, r(x_2,y_2) + o(x_2,y_2)\, |^2$$

$$I(x_2,y_2) = |r(x_2,y_2)|^2 + |o(x_2,y_2)|^2 + r^*(x_2,y_2)\, o(x_2,y_2) + r(x_2,y_2)\, o^*(x_2,y_2)$$

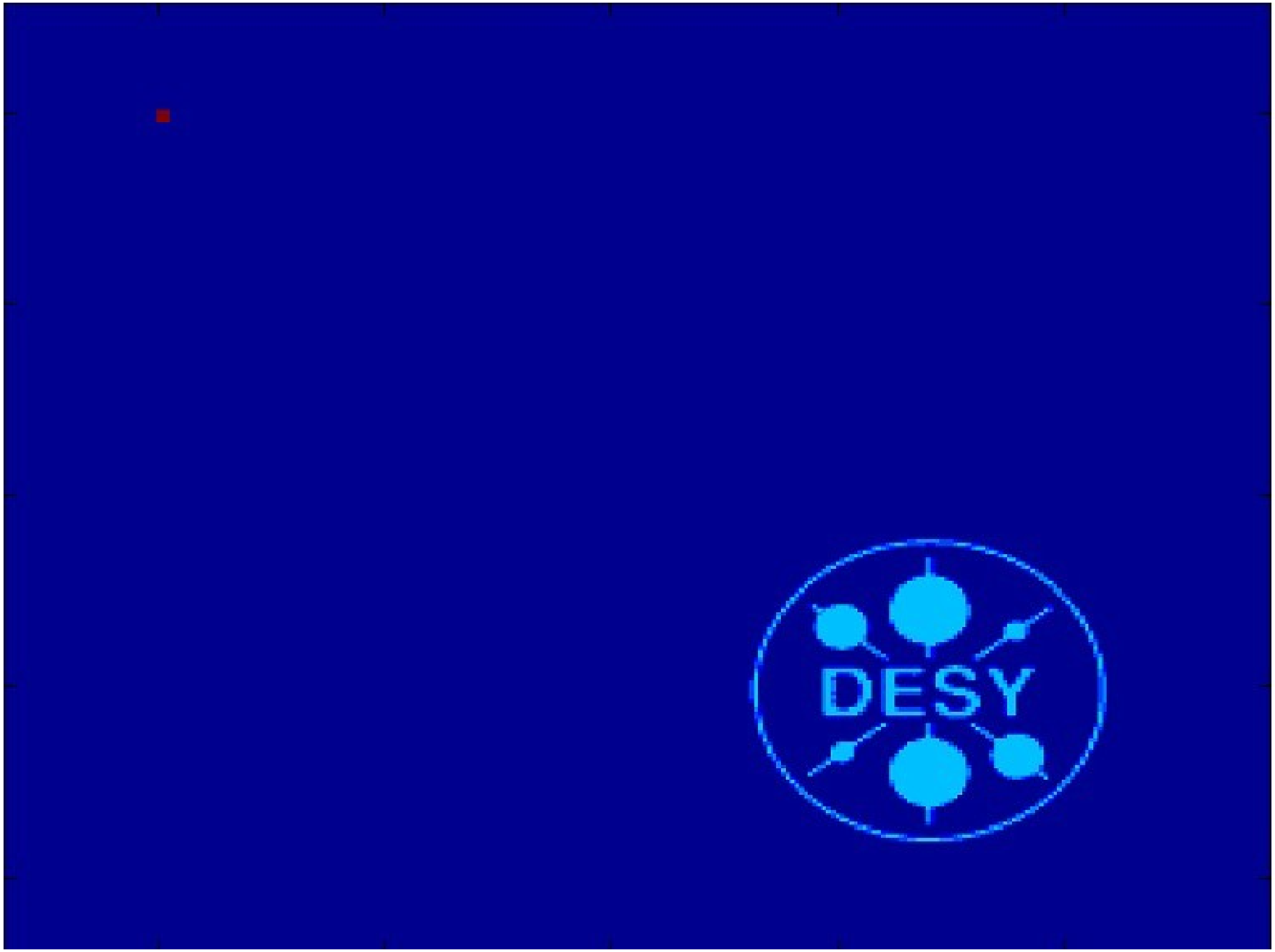
$$I(x_2,y_2) \approx |\check{R}(\xi,\eta)|^2 + |\bar{O}(\xi,\eta)|^2 + \check{R}^*(\xi,\eta)\, \bar{O}(\xi,\eta)\, e^{\,i\pi a\xi} + \check{R}(\xi,\eta)\, \bar{O}^*(\xi,\eta)\, e^{\,-i\pi a\xi}$$

$$FT\{r^*(-x,-y) \otimes o(x+a,y)\} + FT\{r(x,y) \otimes o(-x-a,-y)\}$$

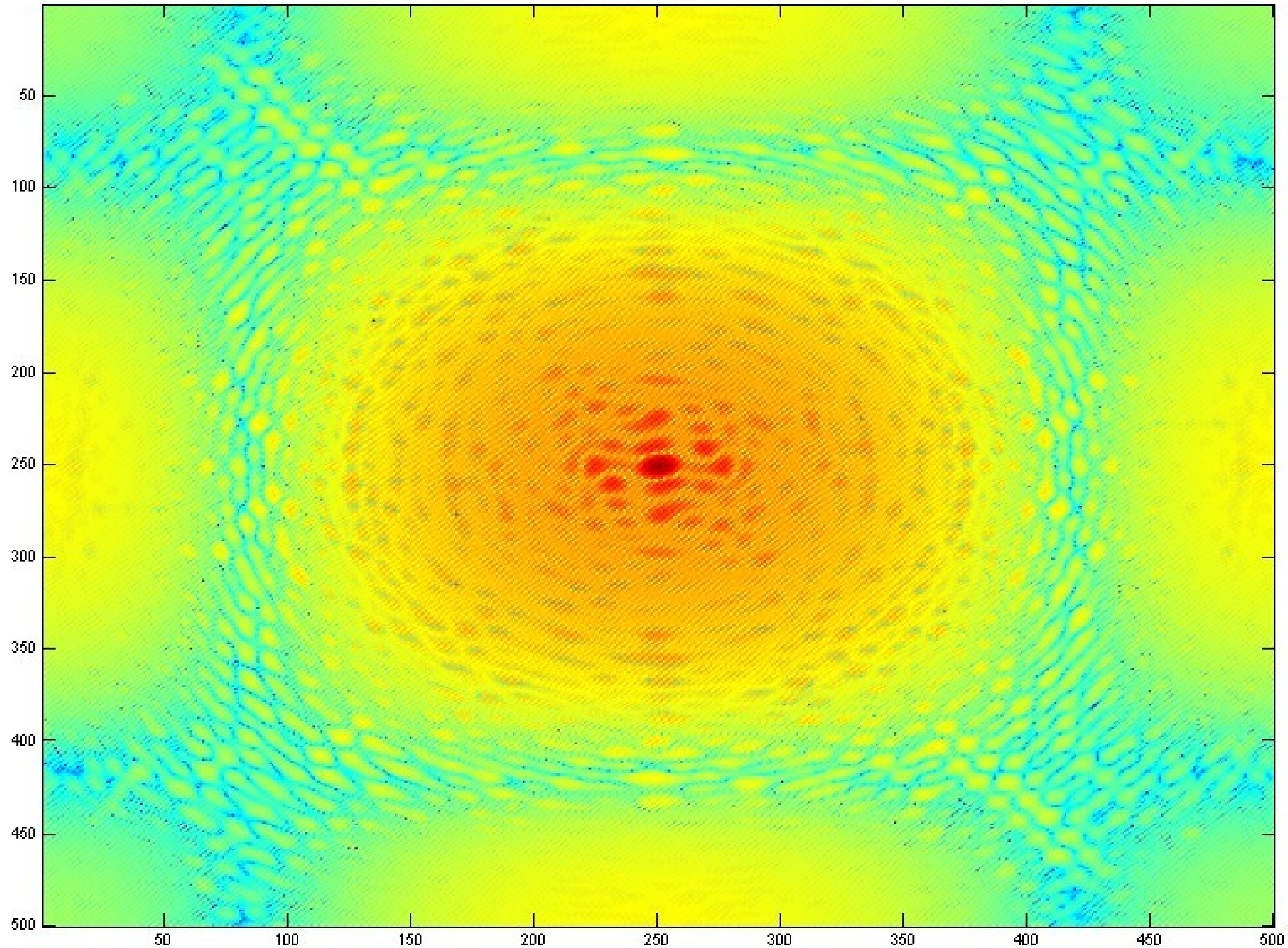


<u>note:</u> resolution determined by size of reference aperture

- FTH (3): small reference hole



FTH (4)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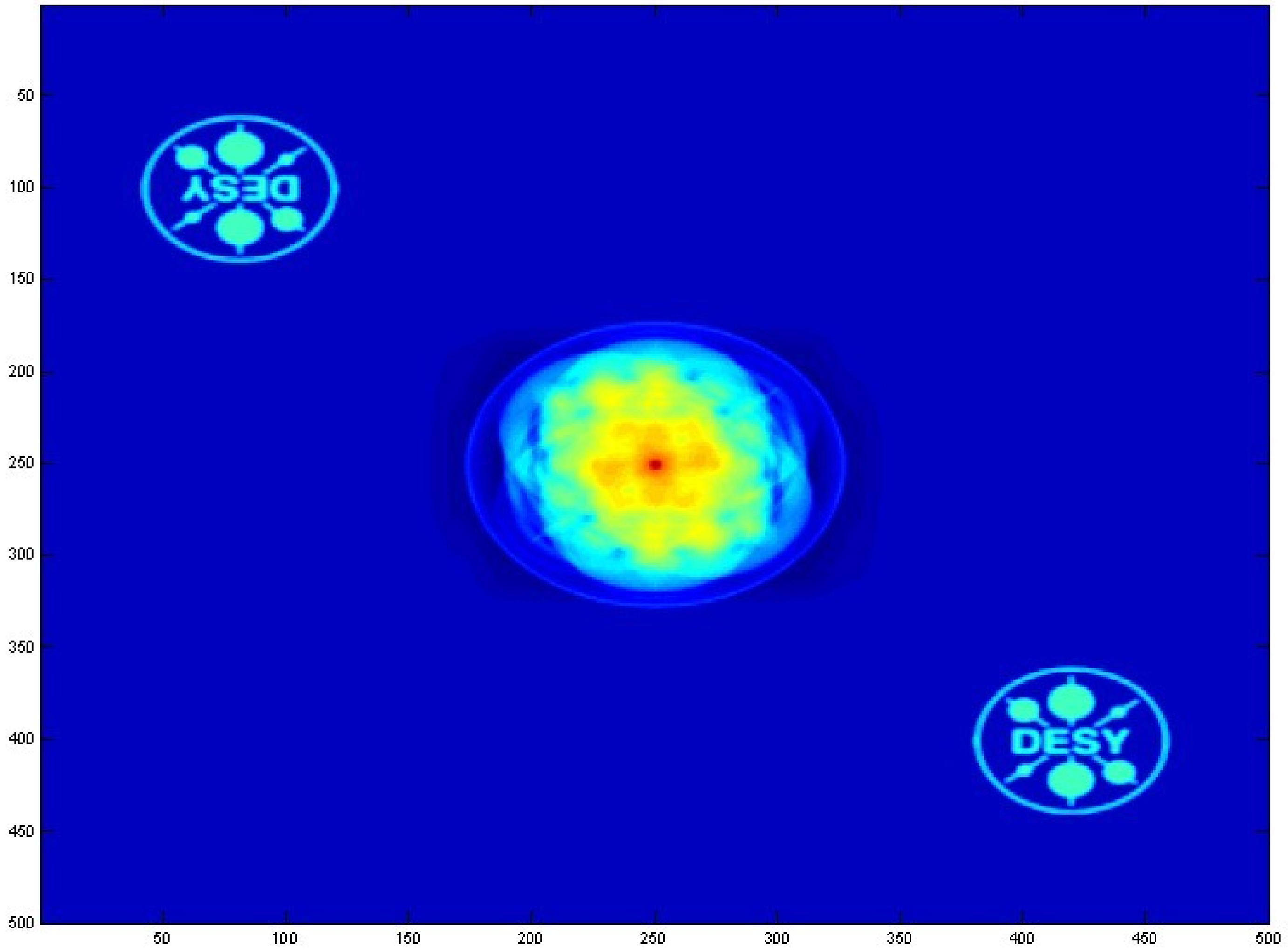
▪ FTH (5)



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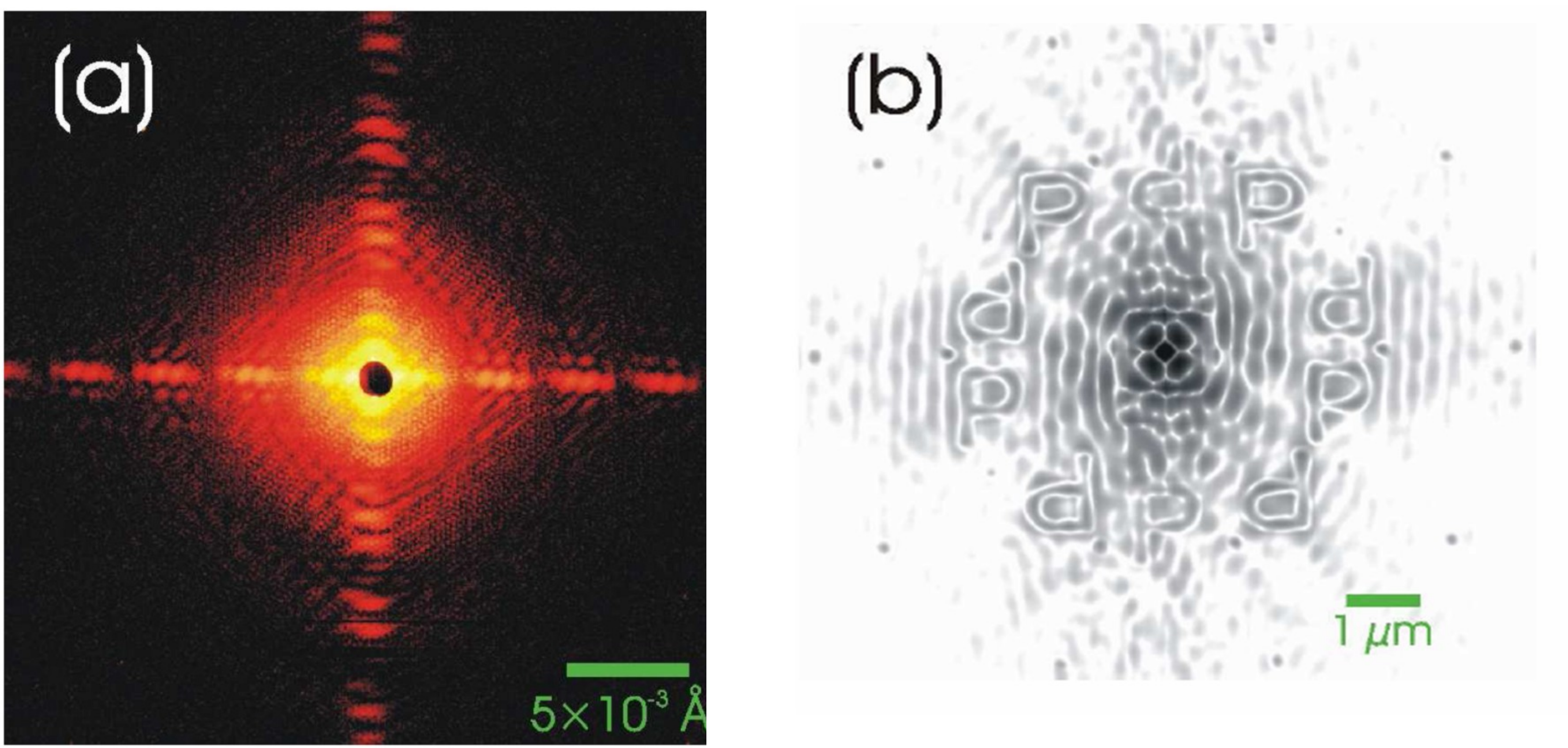
FTH (10)

Au reference structure (letter P): letter elements 200 nm in width and 220 nm heigh on 50 nm Si_3N_4-membrane. 5 Au reference dots of 175 nm diameter and 220 nm height on a circle of 2.5 μm around the sample. 200x 3s exposures (≈$1.4x10^8$ ph/s through $10x10μm^2$ at 8 keV.

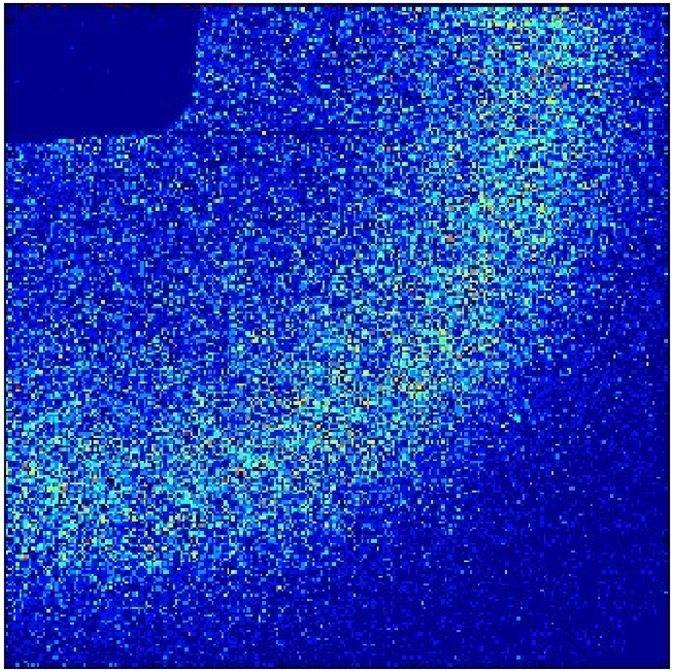


(Magnetic) Scattering with coherent X-rays

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 interference pattern and related to the exact spatial arrangement of the scatterers in the disordered system.

$$I(Q,t) \sim S_c(Q,t) \sim |\ \Sigma\ (f_j^{charge}+f_j^{magnetic})\ e^{iQRj(t)}\ |^2$$

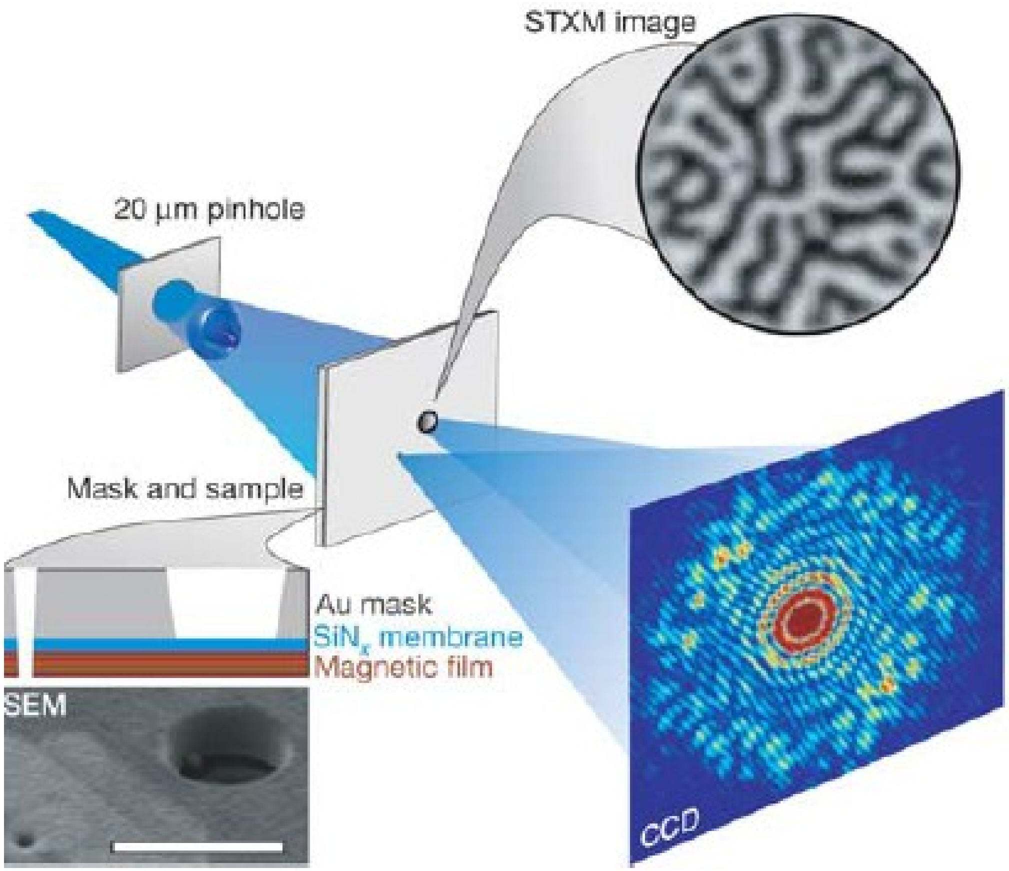
j in coherence volume $c= \xi_t^2 \xi_l$



<u>Incoherent Light:</u>

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

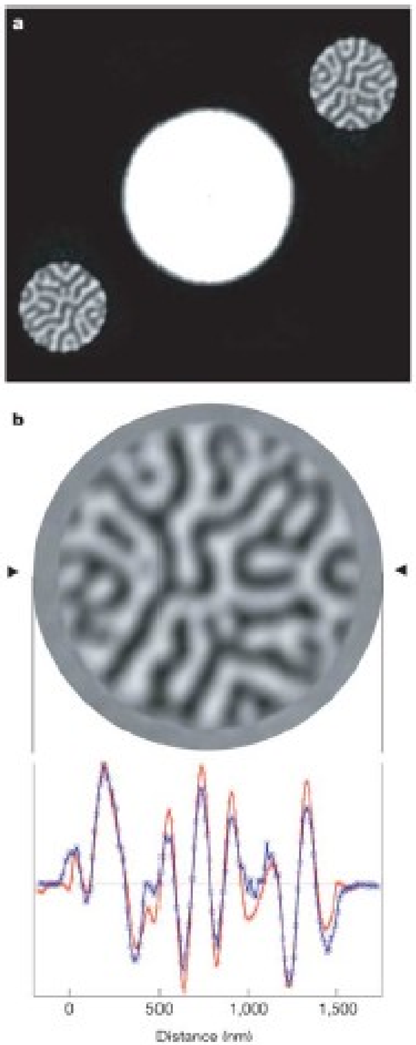
Fourier Transform Holography (1)



Random magnetic (stripe) domains in a [Co(4)Pt(7)]50 ML sample, illuminated together with a reference aperature (1.5 µm) at the Co LIII edge absorption edge with a 778 eV (1.59 nm) 20 µm coherent soft x-ray beam.

S. Eisebitt, J. Lüning,W.F. Schlotter, M. Lörgen, O. Hellwig, W.Eberhardt and J. Stöhr,
NATURE, 432, 885 (2004)

Fourier Transform Holography (2)

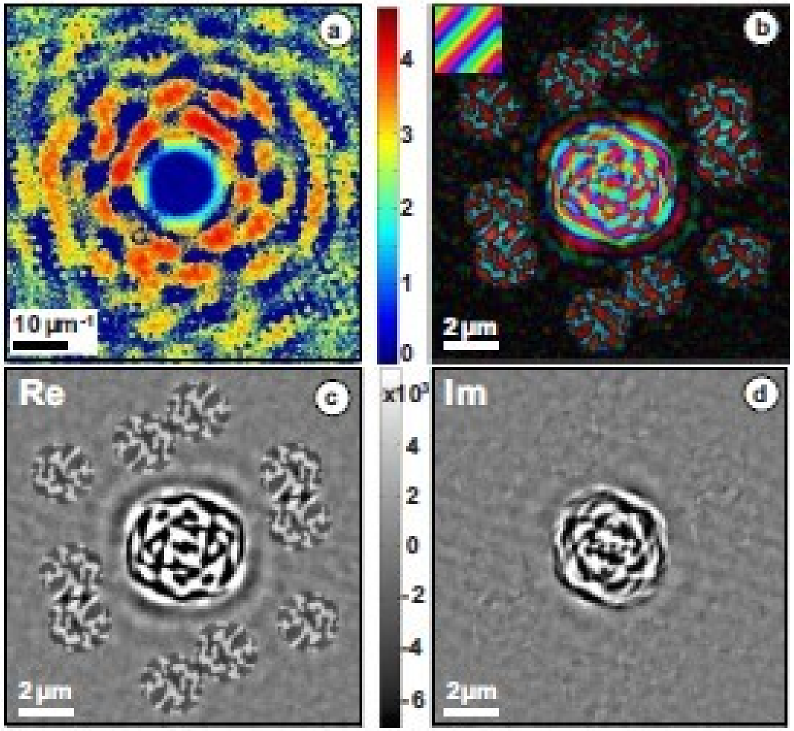


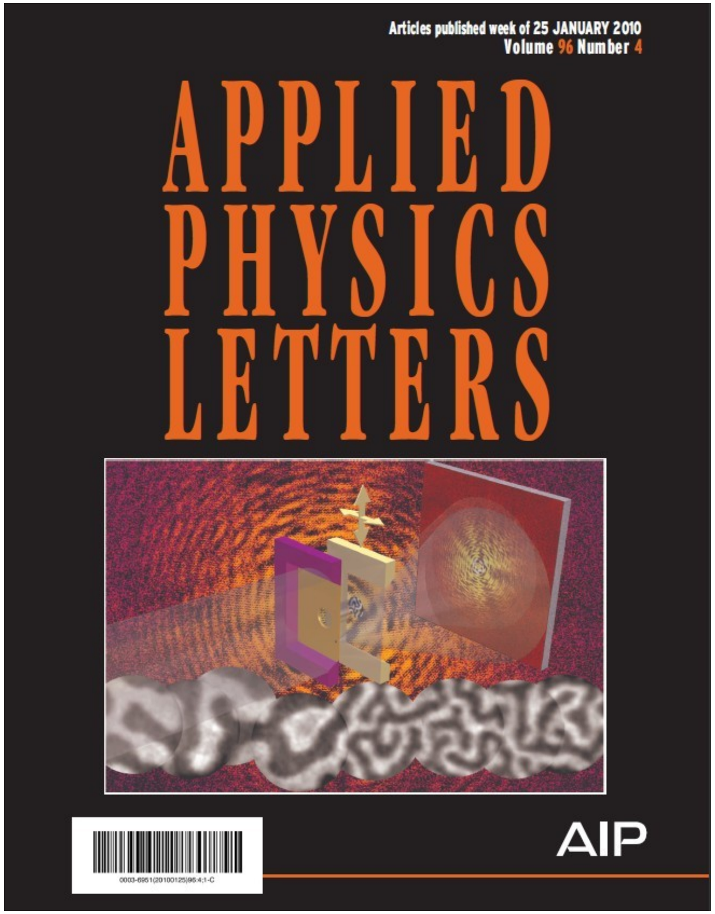
Reconstruction via direct 2-D Fourier transform of the [Co(4)Pt(7)]50 speckle pattern (top). Difference pattern obtained form two reconstructed images recorded with different helicity (bottom) compared to line profiles through the difference pattern (red) and an STXM image (blue) revealing 50 nm resolution.

S. Eisebitt, J. Lüning,W.F. Schlotter, M. Lörgen, O. Hellwig, W.Eberhardt and J. Stöhr, NATURE, 432, 885 (2004)

FTH at ESRF

use 5 reference apertures

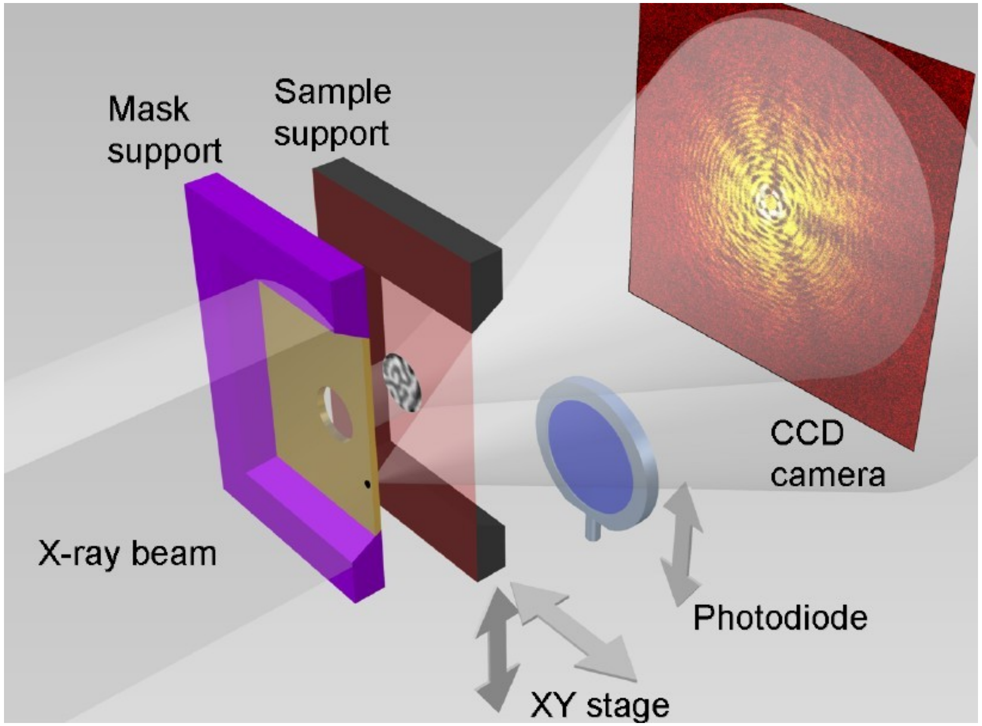


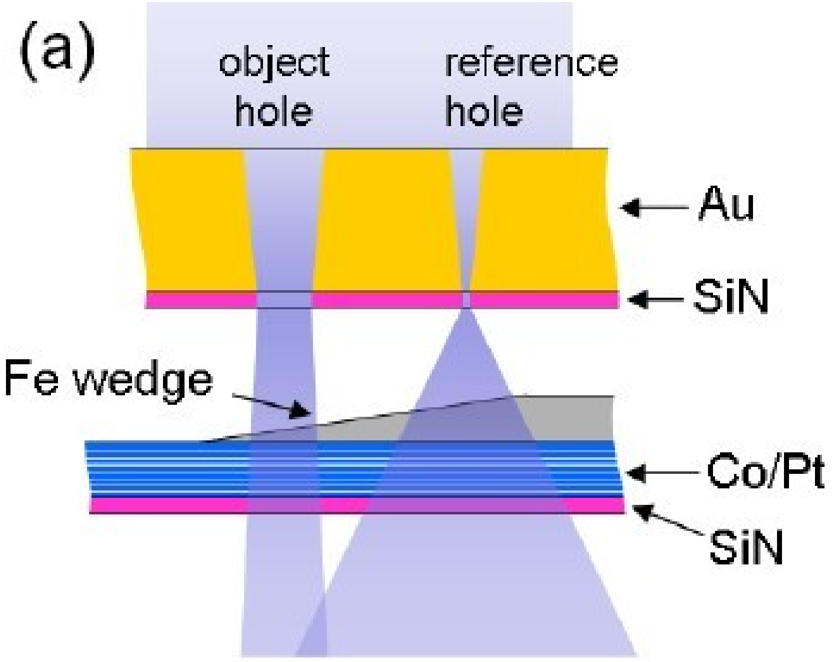


S. Streit-Nierobisch, D. Stickler, C. Gutt, L.-M. Stadler, H. Stillrich, C. Menk, R. Frömter, C. Tieg, O. Leupold, H. P. Oepen, and Grübel
JOURNAL OF APPLIED PHYSICS **106**, 1 (2009)

D. Stickler, R. Frömter, H. Stillrich, C. Menk, C. Tieg, S. Streit-Nierobisch, M. Sprung, C. Gutt, Lorenz-M. Stadler, O.Leupold, G. Grübel, and H. P. Oepen
APPLIED PHYSICS LETTERS **96**, 042501 (2010)

Soft X-ray holographic microscopy (I)

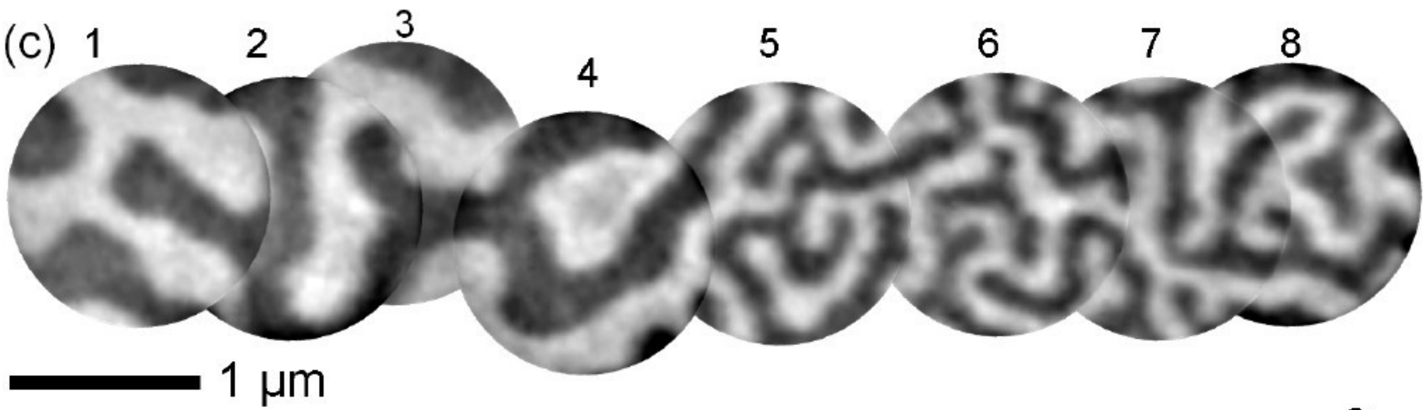


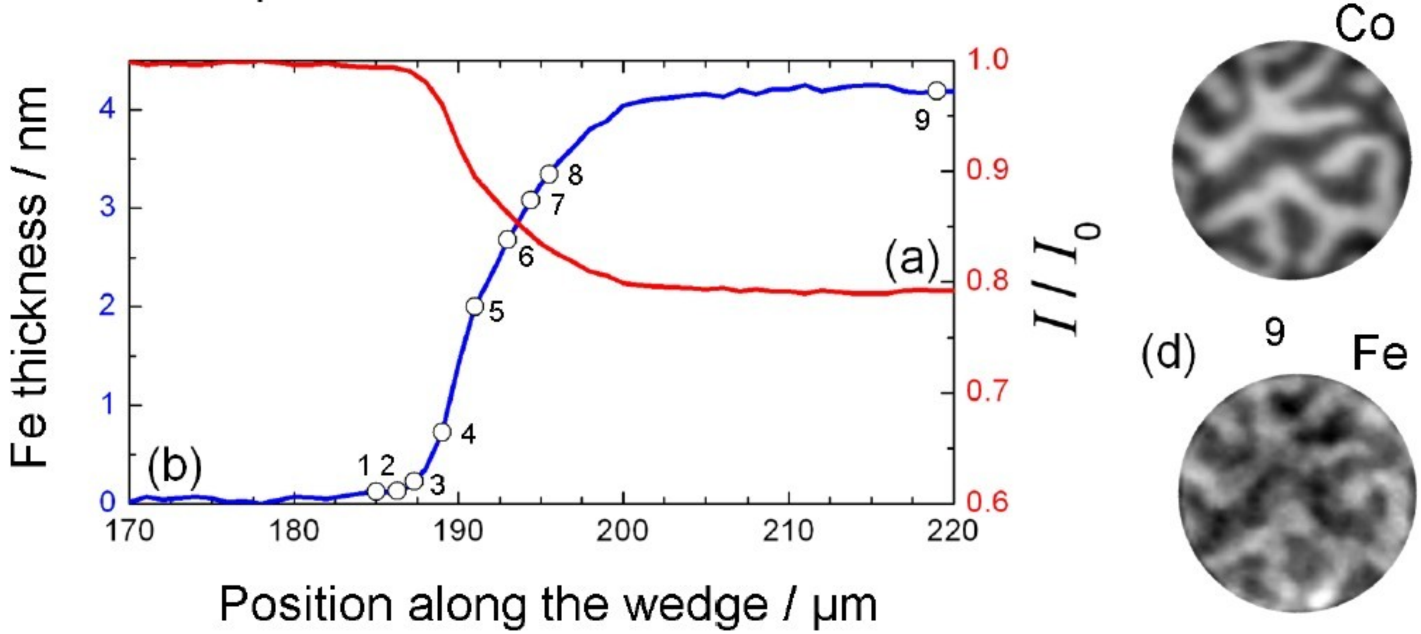


D. Stickler et al., APL **96**, 042501 (2010)

Soft X-ray holographic microscopy (II)

shift towards smaller domains with increasing thickness of Fe layer





Identical domain pattern indicates parallel orientation of the probed out-of-plane magnetization components

X-Ray Photon Correlation Spectroscopy (XPCS)

analogous to Dynamic Light Scattering (DLS) or Photon Correlation Spectroscopy (PCS) with visible light

- gives access to larger momentum transfers ($Q_{max}=2\pi\bullet\sin\theta/\lambda$) or shorter lengthscales
- not subject to multiple scattering
- can be combined with the surface sensitivity of X-rays

▪

Introduction: Scattering with coherent X-rays

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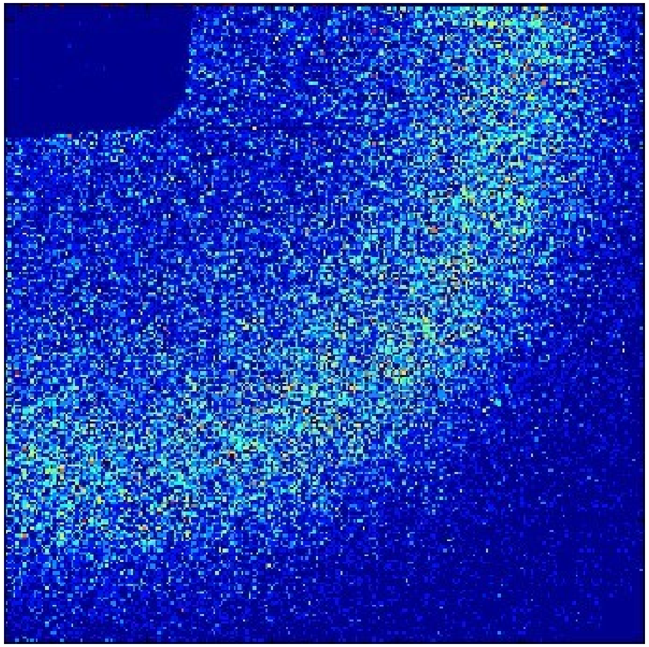
$$I(Q,t) \sim S_c(Q,t) \sim | \sum e^{iQRj(t)} |^2$$



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

<u>Incoherent Light:</u>

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

- quantify dynamics in terms of the intensity correlation function $g_2(Q,t)$:

$$I(\mathbf{Q},t) = |\mathbf{E}(\mathbf{Q},t)|^2 = |\sum b_n(\mathbf{Q}) \exp[i\mathbf{Q}\bullet\mathbf{r}_n(t)|^2$$

Note: $\mathbf{E}(\mathbf{Q},t) = \int d\mathbf{r}' \rho(\mathbf{r}') \exp[i\mathbf{Q}\bullet\mathbf{r}'(t)]$ $\rho(\mathbf{r}')$: *charge density*

$$g_2(\mathbf{Q},t) = \langle I(\mathbf{Q},0) \bullet I(\mathbf{Q},t)\rangle / \langle I(\mathbf{Q})\rangle^2$$

if $\mathbf{E}(\mathbf{Q},t)$ is a zero mean, complex gaussian variable:

$$g_2(\mathbf{Q},t) = 1 + ß(\mathbf{Q}) \langle\mathbf{E}(\mathbf{Q},0)\mathbf{E}^*(\mathbf{Q},t)\rangle^2 / \langle I(\mathbf{Q})\rangle^2$$

$\langle\rangle$ ensemble av.;$ß(\mathbf{Q})$ contrast

$$g_2(\mathbf{Q},t) = 1 + ß(\mathbf{Q}) |f(\mathbf{Q},t)|^2$$

with $f(\mathbf{Q},t) = F(\mathbf{Q},t) / F(\mathbf{Q},0)$

$F(Q,0)$: static structure factor

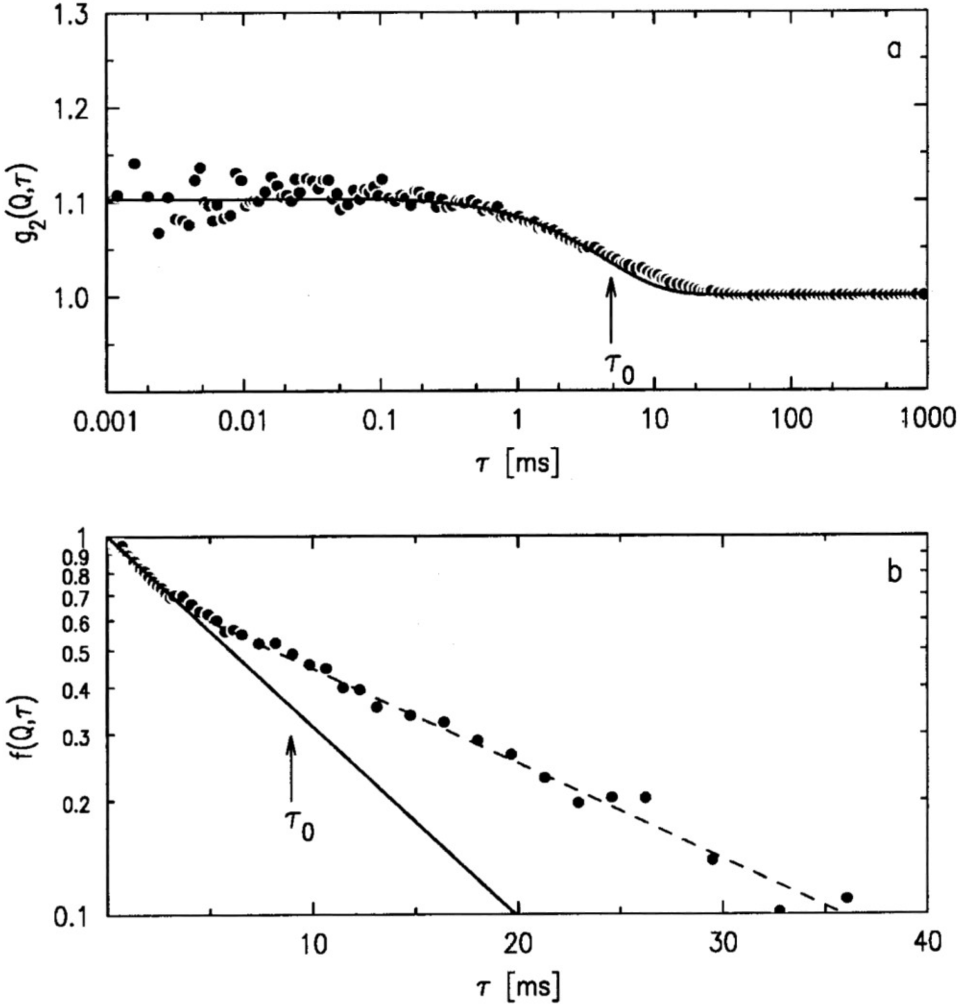
N: number of scatterers

$$F(\mathbf{Q},t) = [1/N\{b^2(\mathbf{Q})\} |\sum^N_{m=1}\sum^N_{n=1} \langle b_n(\mathbf{Q})b_m(\mathbf{Q})\bullet\exp\{i\mathbf{Q}[\mathbf{r}_n(0)-\mathbf{r}_m(t)]\}\rangle$$

A time correlation function $g_2(Q,\tau)$

$g_2(\mathbf{Q},t) = 1 + \beta(\mathbf{Q})\,|f(\mathbf{Q},t)|^2$ and $f(Q,t) = \exp(-\Gamma\, t) = \exp(-t/\tau)$

$\beta(Q)$ ↕



▪

Examples:

Dynamics of interacting colloidal particles

Dynamics in heterodyne mode detection

Dynamics at surfaces/interfaces

Dynamics (of a liquid crystalline system) near a phase transition

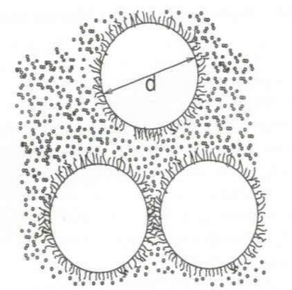
Non-equilibrium dynamics

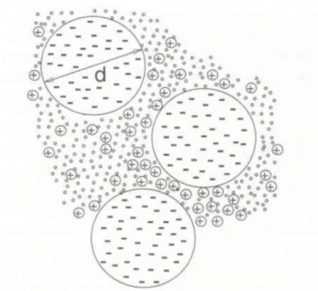
…

Dynamics of interacting Colloidal Particles

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

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

$\Phi > 1\%$:

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

$S=S(Q,\Phi)$ (Percus-Yevick)

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

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

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

Smoluchowski (many particle) diffusion equation:

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

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

(Time averaged) Structure

Correlation lengths ≈ particle size ➔

Small Angle X-ray Scattering (SAXS)

$(d\sigma/d\Omega)/V = r_o^2\, n\, (\rho_p - \rho_s)^2\, v^2\, P(Q)\, S(Q)$ monodisperse, spherical particles

n: volume fraction, ρ: electron densities, v: particle volume

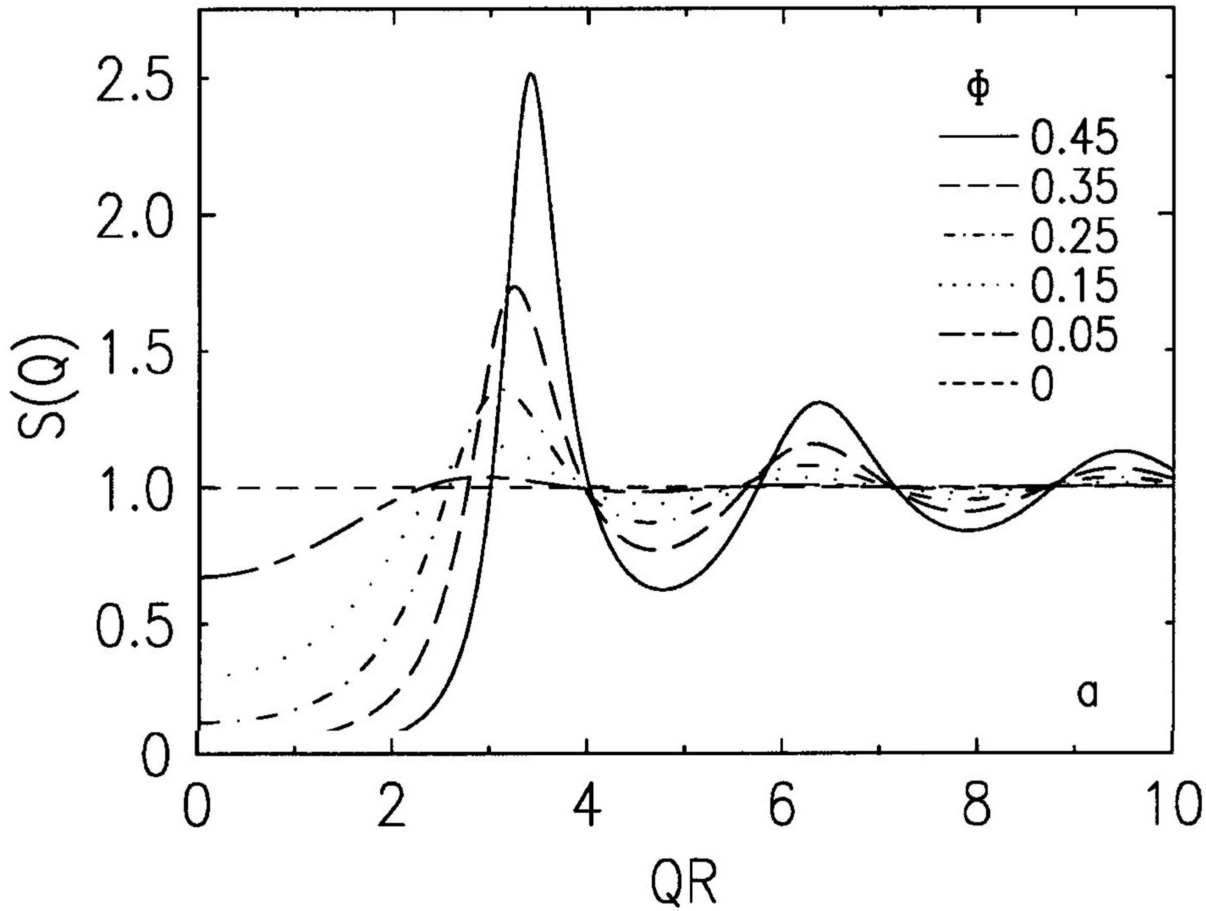
$P(Q) = [3/(QR)^3]^2\, [\sin(QR) - (Qr)\cos(QR)]^2$ sphere form factor

$S(Q) = 1 + 4\pi n \int [g(r)-1]\, \sin(QR)/QR\, r^2\, dr$ structure factor

$g(r) = \exp[\, V(r) / kT\,]$

Structure (the Hard Sphere case)

$V(r) = 0$ for $r \geq d$; $V(r) = \infty$ for $r < d$

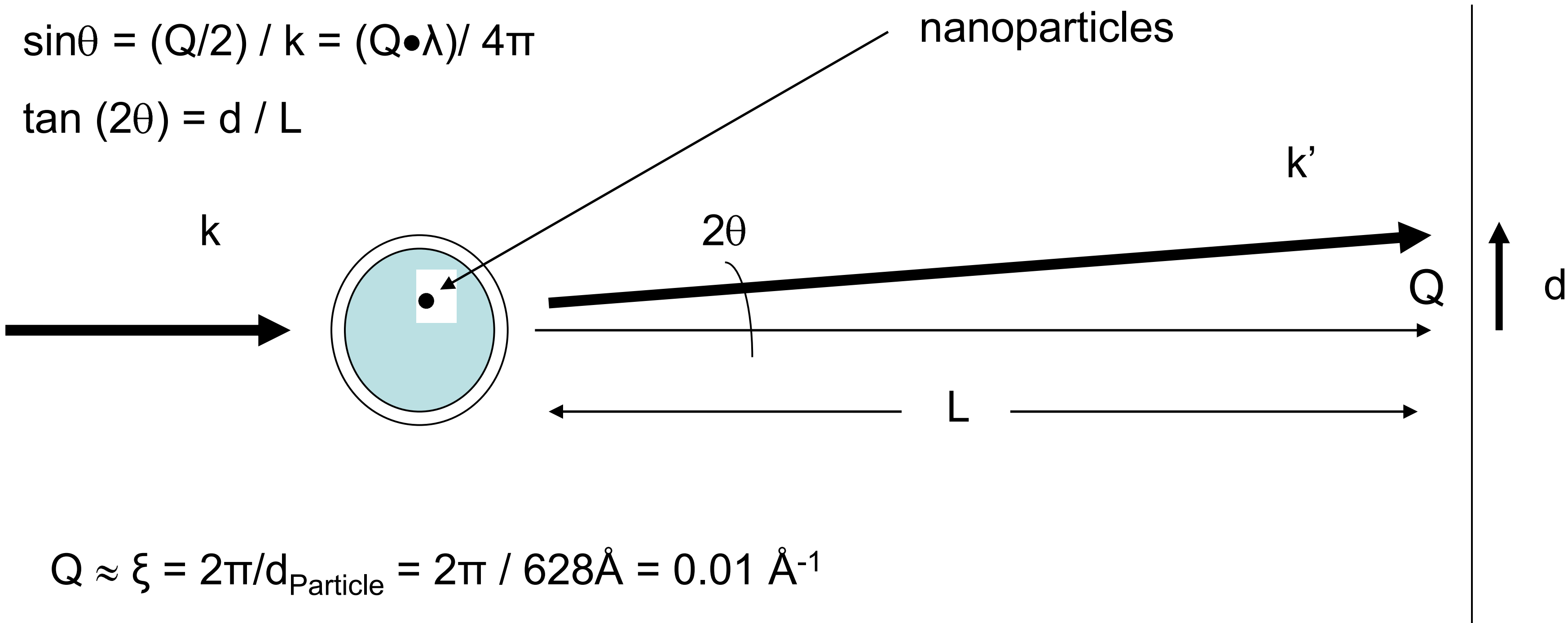


Percus-Yevick S(Q)

Small Angle X-ray Scattering (SAXS)

$\sin\theta = (Q/2) / k = (Q \bullet \lambda) / 4\pi$

$\tan(2\theta) = d / L$



$Q \approx \xi = 2\pi / d_{Particle} = 2\pi / 628Å = 0.01\ Å^{-1}$

$\theta = \sin^{-1}(Q \bullet \lambda / 4\pi) = \sin^{-1}(0.01Å^{-1} \bullet 1Å / 4\pi) \approx 0.0456$ deg

$d = L \bullet \tan(2\theta) = 2\text{ m} \bullet 1.58 \cdot 10^{-3} = 3.183$ mm

screen

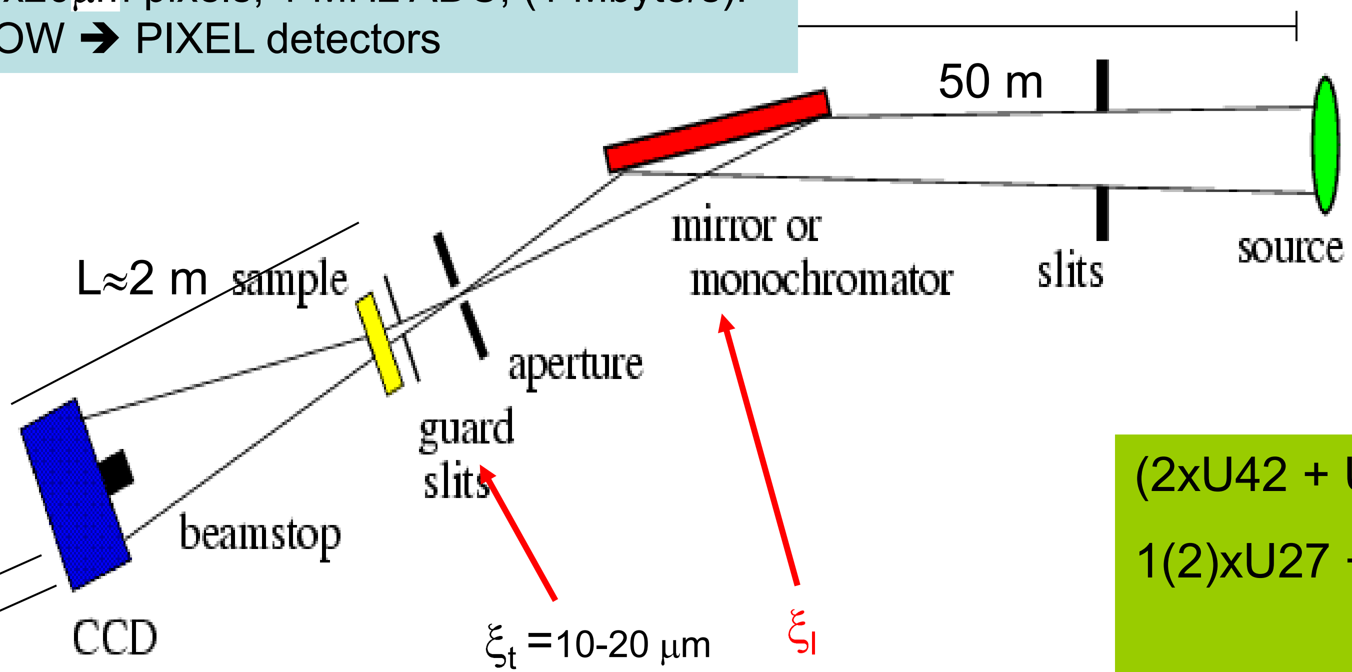
2-D detector

Beamline for coherent scattering: ID10A @ ESRF

2-D detector

Direct illumination, deep depletion CCD

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



(2xU42 + U26)

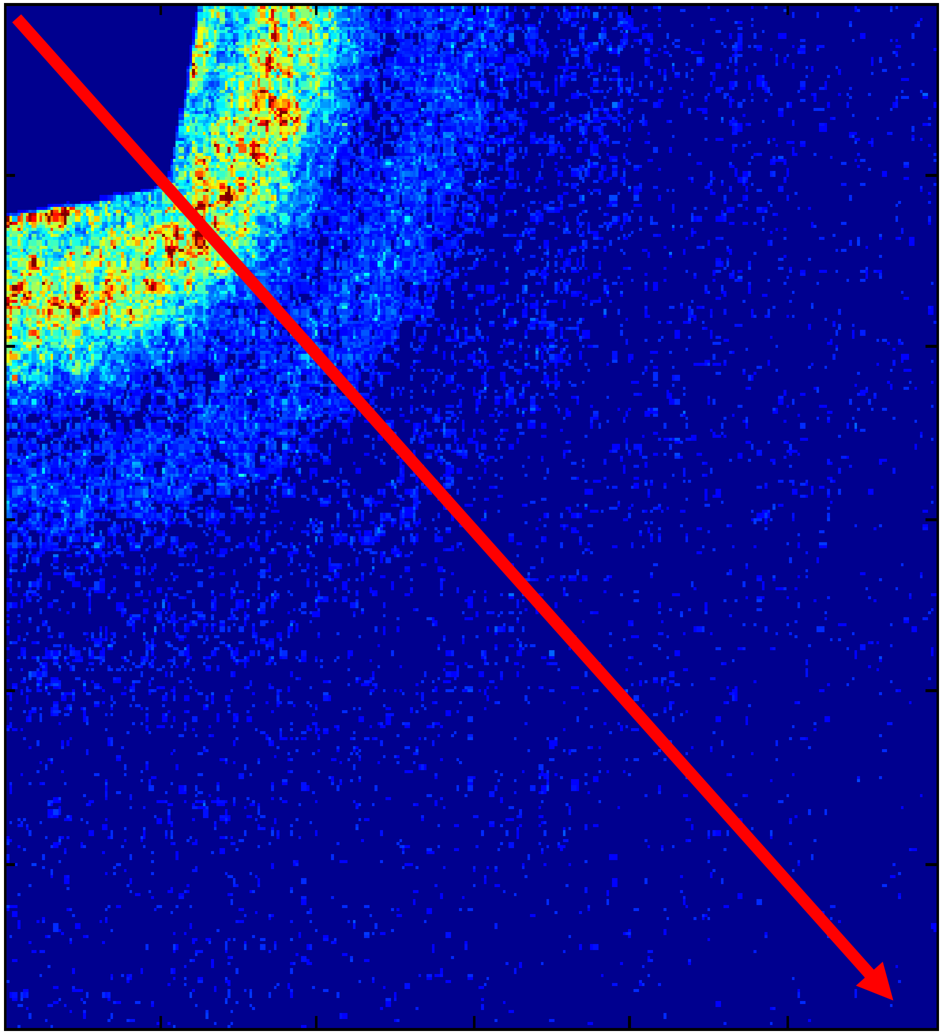
1(2)xU27 +2(1)xU35

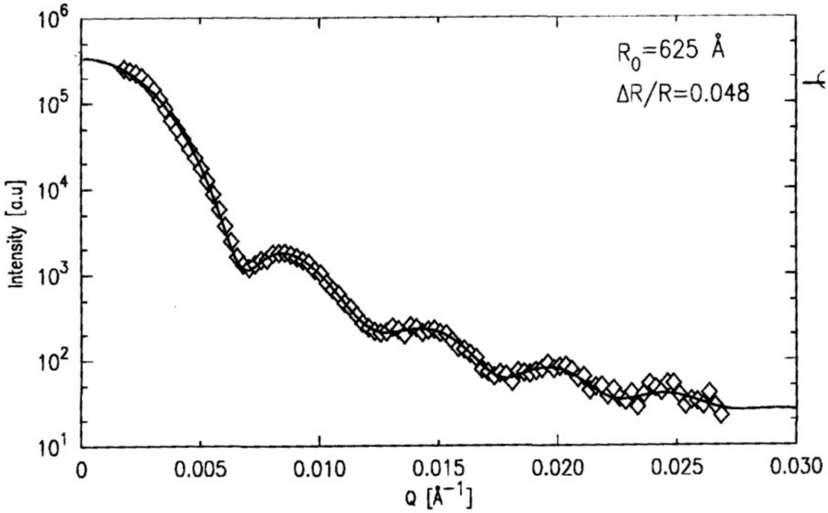
0-D detector

\+ digital autocorrelator: FAST

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

- **colloidal silica particles undergoing Brownian motion in high viscosity glycerol** (R = 2610 Å, ΔR/R=0.03, 10 vol% in glycerol,T=-13.6C, η ≈ 56000 cp)





V. Trappe and A. Robert

Brownian Motion of Colloidal Particles

$f(\mathbf{Q},t) = F(\mathbf{Q},t) / F(\mathbf{Q},0)$

$F(\mathbf{Q},t) = [1/N\{b^2(\mathbf{Q})\} |\Sigma^N_{m=1}\Sigma^N_{n=1} \langle b_n(\mathbf{Q})b_m(\mathbf{Q})\bullet\exp\{i\mathbf{Q}[\mathbf{r}_n(0)-\mathbf{r}_m(t)]\}\rangle$

<u>mean square displacement:</u>

$\langle[\mathbf{r}(0)-\mathbf{r}(t)]^2\rangle = 6\, D_0\, t$ with $D_0 = k_BT/6\pi\eta R$

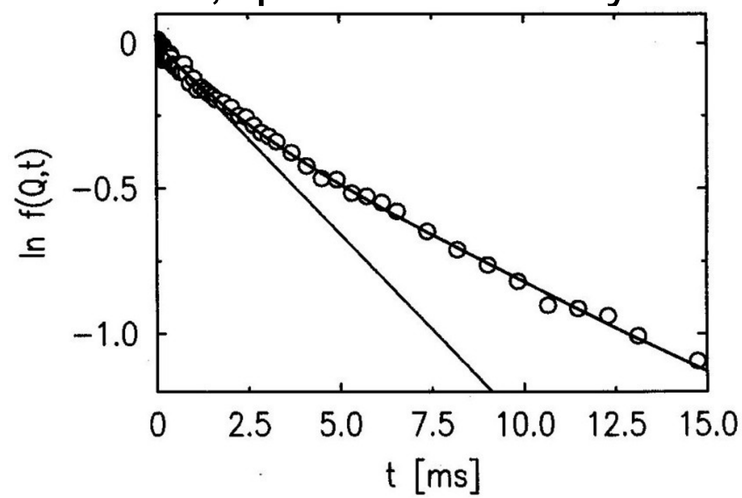
D_0 free particle (Stokes-Einstein) diffusion coefficient, η shear viscosity

$f(\mathbf{Q},t) = \exp(-\Gamma\bullet t) = \exp(-D_0\mathbf{Q}^2 t)$

<u>in general:</u>

$D=D(\mathbf{Q},t)$ with

$= \lim_{t\to 0} d/dt\, [\ln\{f^{measured}(\mathbf{Q},t)\}] = -D(\mathbf{Q})\bullet Q^2$

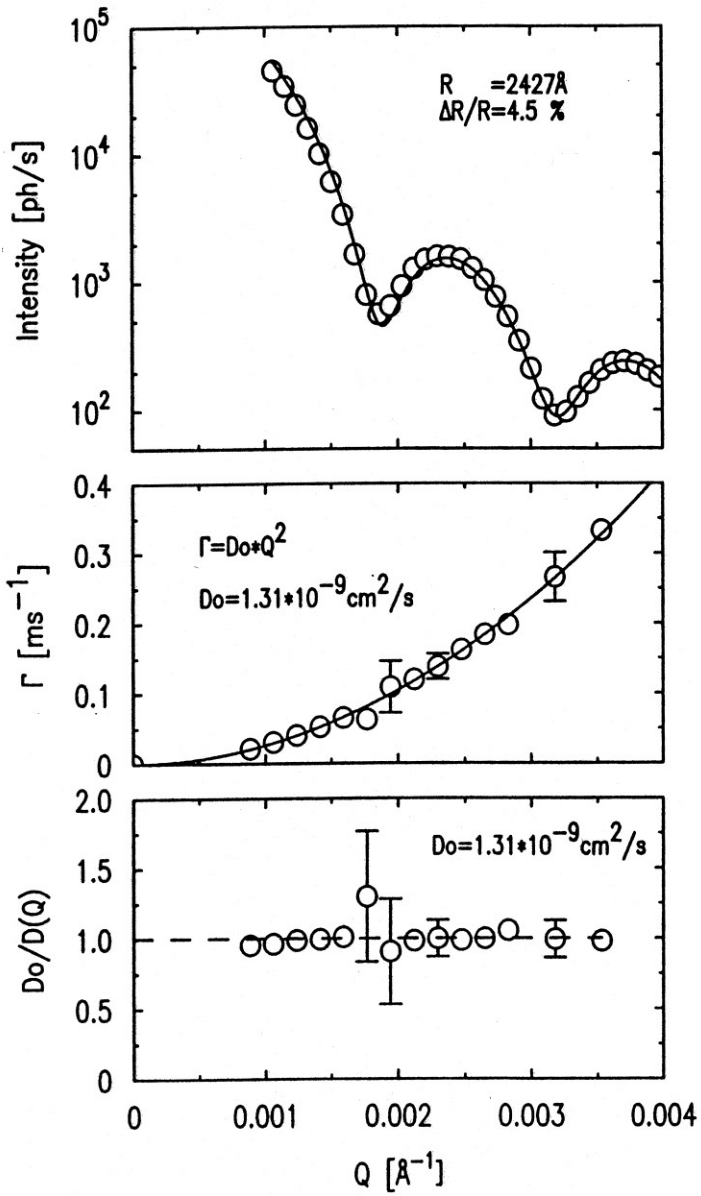


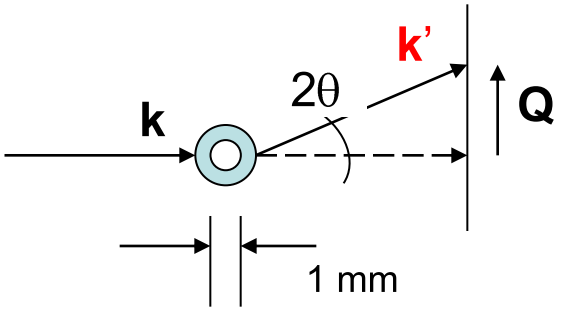
The dilute case

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

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

$\Gamma = D_o Q^2$





$Q = k' - k$

$Q = 2k \sin\theta$

$k = 2\pi/\lambda$

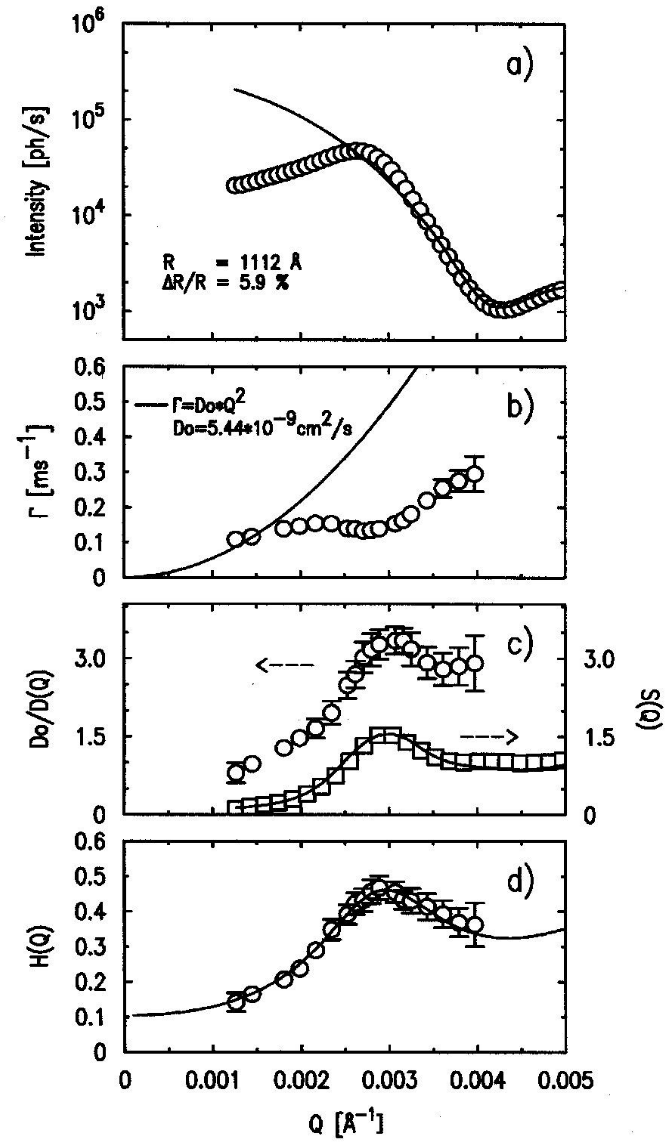
G. Grübel, A. Robert, D. Abernathy
8th Tohwa University International Symposium on "Slow Dynamics in Complex Systems", 1998, Fukuoka, Japan

The Hard Sphere Case

Poly-methylmetacrylate

37% volume fraction in cis-decaline

sterically stabilized (**hard-spheres**)



--- F(Q)

--- $\Gamma = D_0 Q^2$

$S(Q) = I(Q)/F(Q)$

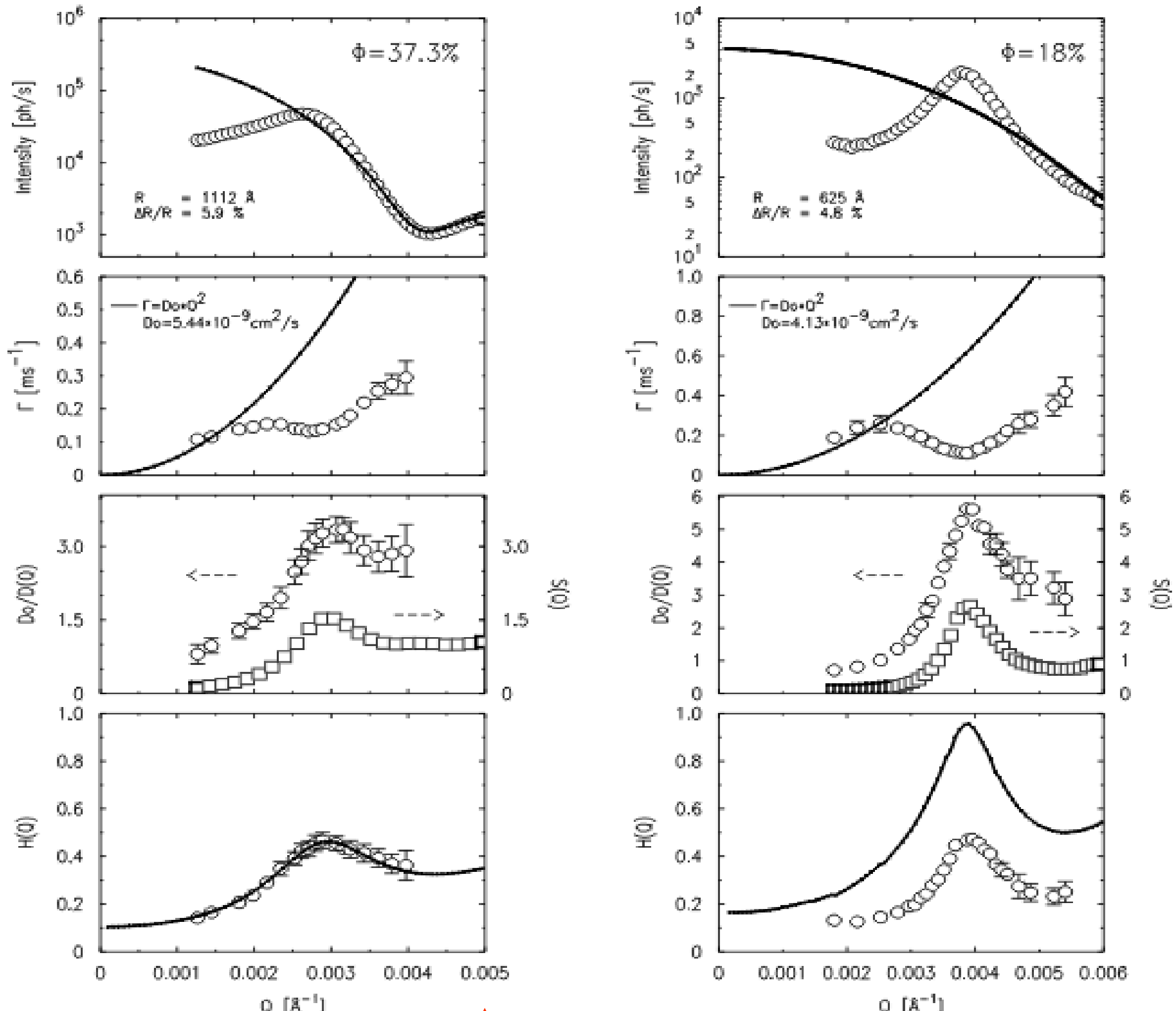
caging (deGennes narrowing)

$H(Q) = S(Q) / [D_0 / D(Q)]$

--- δ-γ expansion

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**)



$|F(Q)|^2$

$\Gamma = DoQ^2$

"caging" (deGennes narrowing)

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

δ-γ expansion

δ-γ expansion

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

no model

QR=5.6

Zontone, Moussaid, Robert, Grübel

Robert, Härtl, Wagner, Grübel

Surface Dynamics studied with XPCS