Methoden moderner Röntgenphysik I

Coherence based techniques III

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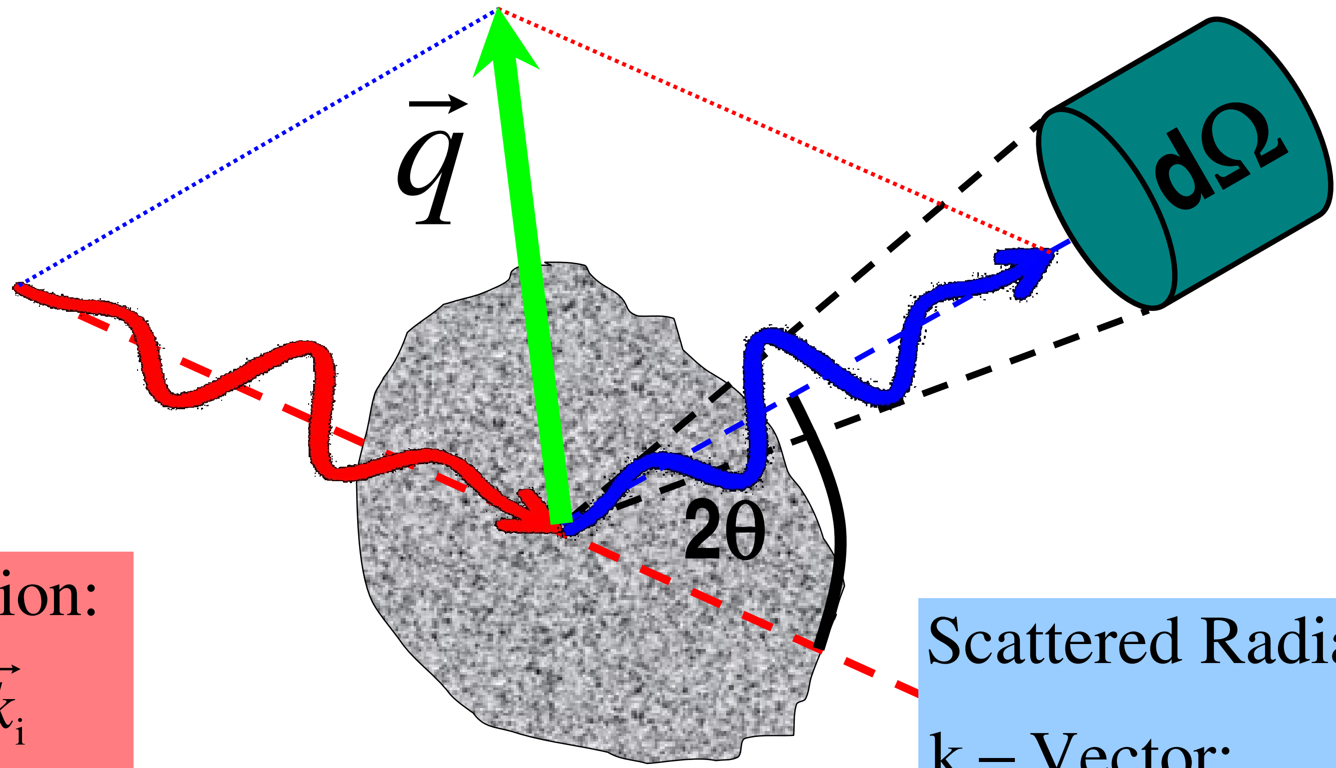
Outline

18.12. 2008
Introduction to Coherence

8.01. 2009
Structure determination techniques

15.01.2009
Correlation Spectroscopy

Scattering Geometry



Incident Radiation:

k – Vector: $\vec{k}_{\rm i}$

$|\vec{k}_{\rm i}| = 2\pi/\lambda$

Energy: $E_{\rm i}$

Polarization: $\vec{p}_{\rm i}$

Scattered Radiation:

k – Vector: $\vec{k}_{\rm f}$

Energy: $E_{\rm f}$

Polarization: $\vec{p}_{\rm f}$

Wavevector Transfer:

$\vec{q} = \vec{k}_{\rm f} - \vec{k}_{\rm i}$

Energy Transfer:

$\Delta E = E_{\rm f} - E_{\rm i} = \hbar\omega$

Polarization:

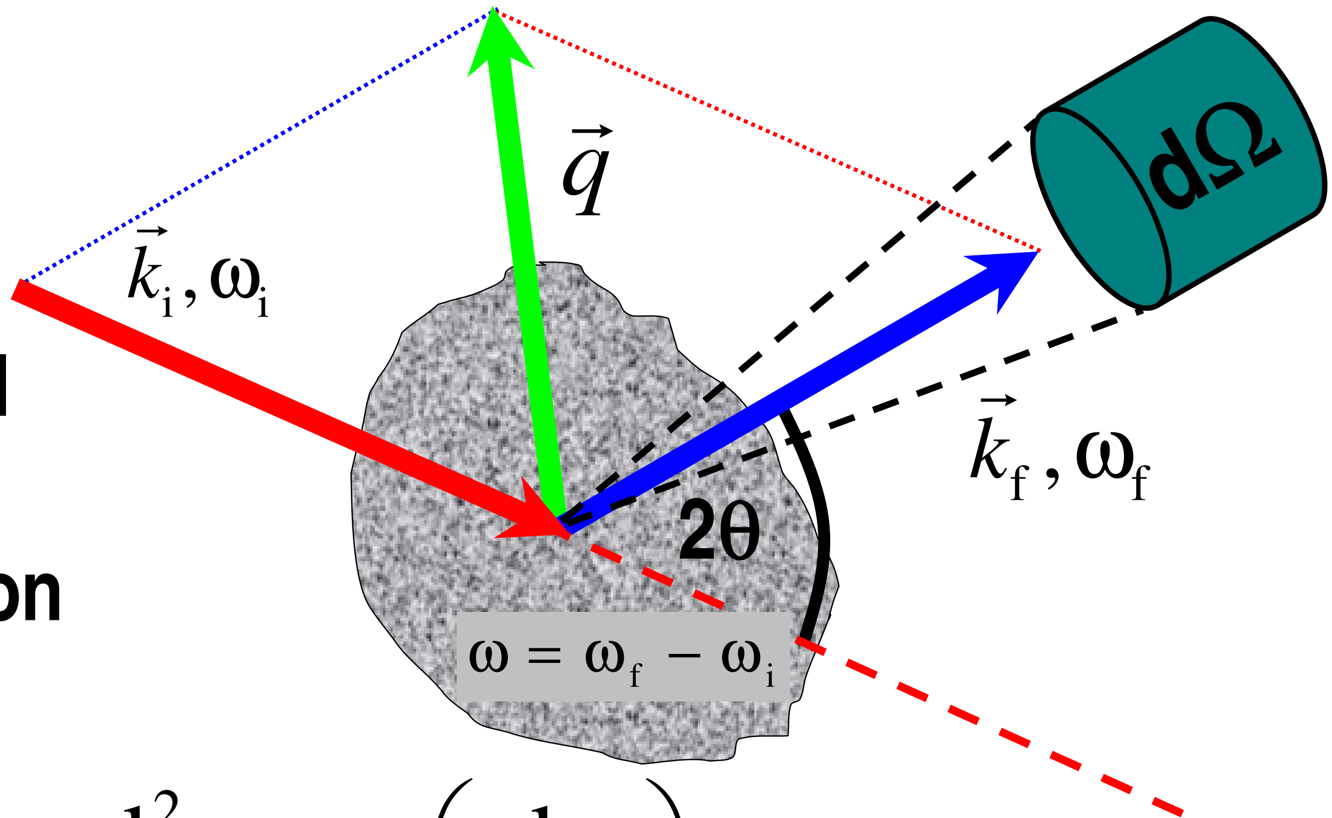
$\vec{p}_{\rm i} \rightarrow \vec{p}_{\rm f}$

For X-Rays:

$\Delta E << E_{\rm f}, E_{\rm i}$

$\Rightarrow \quad |\vec{q}| = 2k_{\rm i}\sin(2\theta/2)$

Double-Differential Scattering Cross Section



$$\frac{d^2\sigma}{d\Omega\, d\omega_f} = \left(\frac{d\sigma}{d\Omega}\right)_0 S(\vec{q}, \omega)$$

Intrinsic Cross Section
Coupling Beam ⇔ Sample

Properties of the Sample without Beam

$$\frac{d\sigma}{d\Omega} = \int d\omega \frac{d^2\sigma}{d\Omega\, d\omega} = \left(\frac{d\sigma}{d\Omega}\right)_0 S(\vec{q})$$

Intrinsic Cross Section
Coupling Beam ⇔ Sample

Properties of the Sample without Beam

Time and frequency dependent correlation functions

$$\rho(r,t) = e^{iHt/\hbar}\rho(r,0)e^{-iHt/\hbar}$$

Time dependence in the Heisenberg represantion
H - Hamilton operator of the system

$$\rho(r,t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega t}\rho(r,\omega)$$

time and frequency dependent electron densities are conjugate quantities connected via Fourier Transform

$$\rho(r,\omega) = \int_{-\infty}^{\infty} e^{i\omega t}\rho(r,t)$$

$$C(r,t,r',t') = \langle \rho(r,t)\rho(r',t') \rangle$$

time dependent correlation function

Time and frequency dependent correlation functions

system spatially homogenous and temporal stationary

$$C(r_1,t_1,r_2,t_2) = \langle \rho(r_1,t_1)\rho(r_2,t_2)\rangle = \langle \rho(r_1-r_2,t_1-t_2)\rho(0,0)\rangle = C(r,t)$$

$$r = r_1 - r_2, \text{ and } t = t_1 - t_2$$

Intermediate scattering function

$$S(q,t) = \iint dr_1 dr_2 \langle \rho(r_1,0)\rho(r_2,t)\rangle e^{iq(r_1-r_2)} = \langle \rho(-q,0)\rho(q,t)\rangle = \tilde{C}(q,t)$$

Dyanmic scattering function

$$S(q,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega e^{-i\omega t} S(q,t) = \tilde{C}(q,\omega)$$

Static scattering function

$$S(q,t=0) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega S(q,\omega)$$

How to calculate the dynamic correlation functions?
1. Linear response theory

$$H = \int dr\, F(r,t)\rho(r,t)$$

H interaction Hamiltonian
F Force

$$\rho(r,t) = \iint dr'\,dt'\ \chi(r,r',t-t')F(r',t')$$

$$\rho(r,\omega) = \int dr'\chi(r,r',\omega)F(r',\omega)$$

response function χ

Fluctuation Dissipation Theorem

$$S(q,\omega) = \frac{2k_B T}{\omega}\operatorname{Im}\chi(q,\omega)$$

valid for thermal equilibrium

Fluctuation Dissipation Theorem

Example : the driven, damped harmonic oscillator

equation of motion $$\ddot{x} + \omega_0^2 x + \gamma \dot{x} = f/m$$

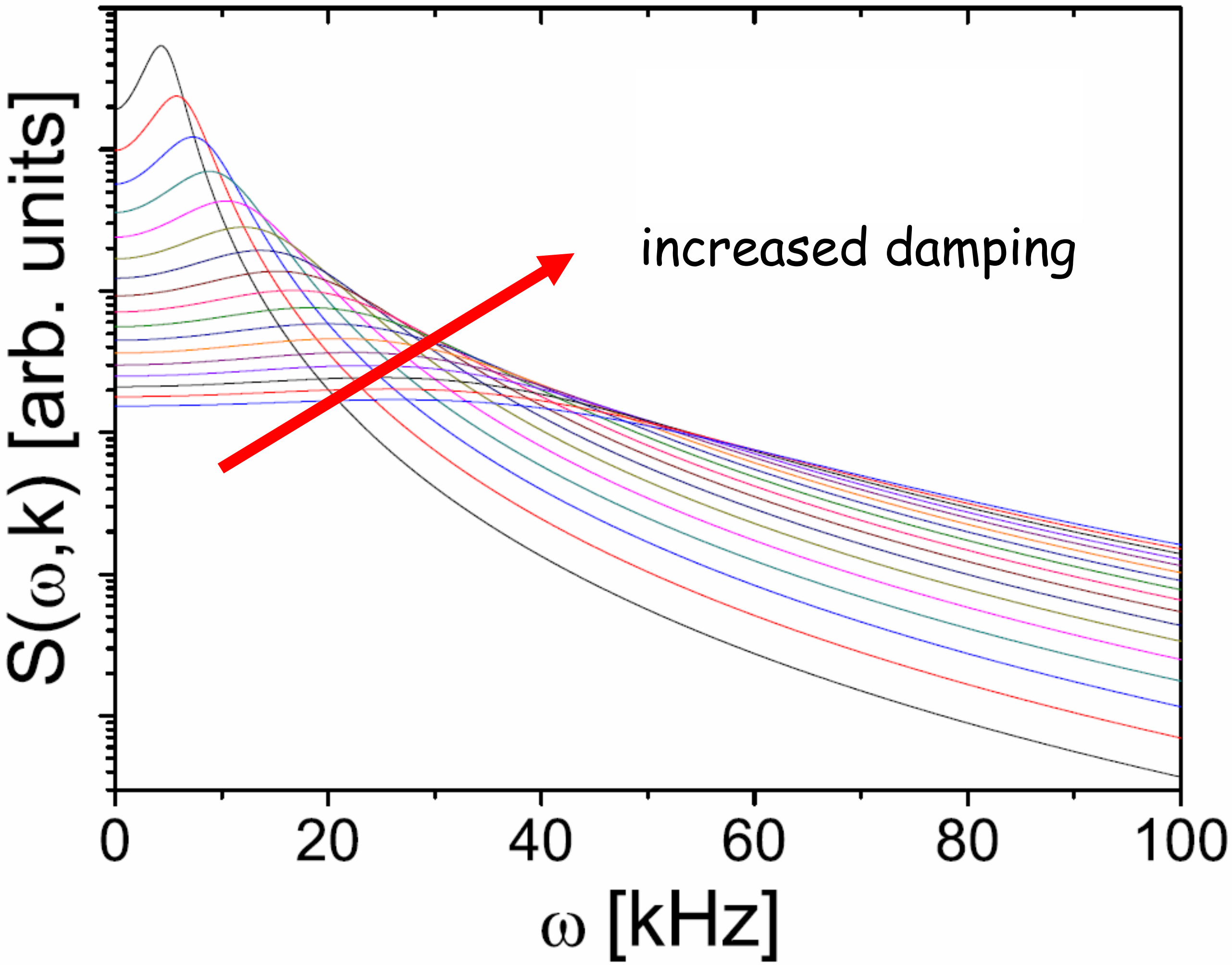
frequency dependent response $$\chi(\omega) = \frac{x(\omega)}{f(\omega)} = \frac{1}{m} \frac{1}{-\omega^2 + \omega_0^2 - i\omega\gamma}$$

$$\mathrm{Im}\,\chi(\omega) = \frac{1}{2m\omega_1}\left[\frac{\gamma/2}{(\omega-\omega_1)^2 + (\gamma/2)^2} - \frac{\gamma/2}{(\omega+\omega_1)^2 + (\gamma/2)^2}\right]$$

$$\omega_1 = \sqrt{\omega_0^2 - \gamma^2/4}, \quad \tau^{-1} = \tfrac{1}{2}\gamma\left[1 - (1 - 4\omega_0^2\gamma^{-2})^{1/2}\right]$$

(a) ω_1 is real -> Lorentzian lines, centered at ω_1 with HWHM $\gamma/2$
(b) ω_1 is imag -> Lorentzian line, centered at 0 with HWHM τ

S(q,ω) of the damped harmonic oscillator



How to calculate the dynamic correlation functions?
2. Differential equations of correlation functions

Example : Fick's law of diffusion

$$\frac{\partial}{\partial t} C(R,t) = D\nabla^2 C(R,t) \quad (1)$$

Spatial Fourier transform of Eq. (1)

$$\frac{\partial}{\partial t} S(q,t) = -Dq^2 S(q,t) \quad (2)$$

Intermediate Scattering function for free diffusion

$$S(q,t) = \exp(-Dq^2 t) \quad (3)$$

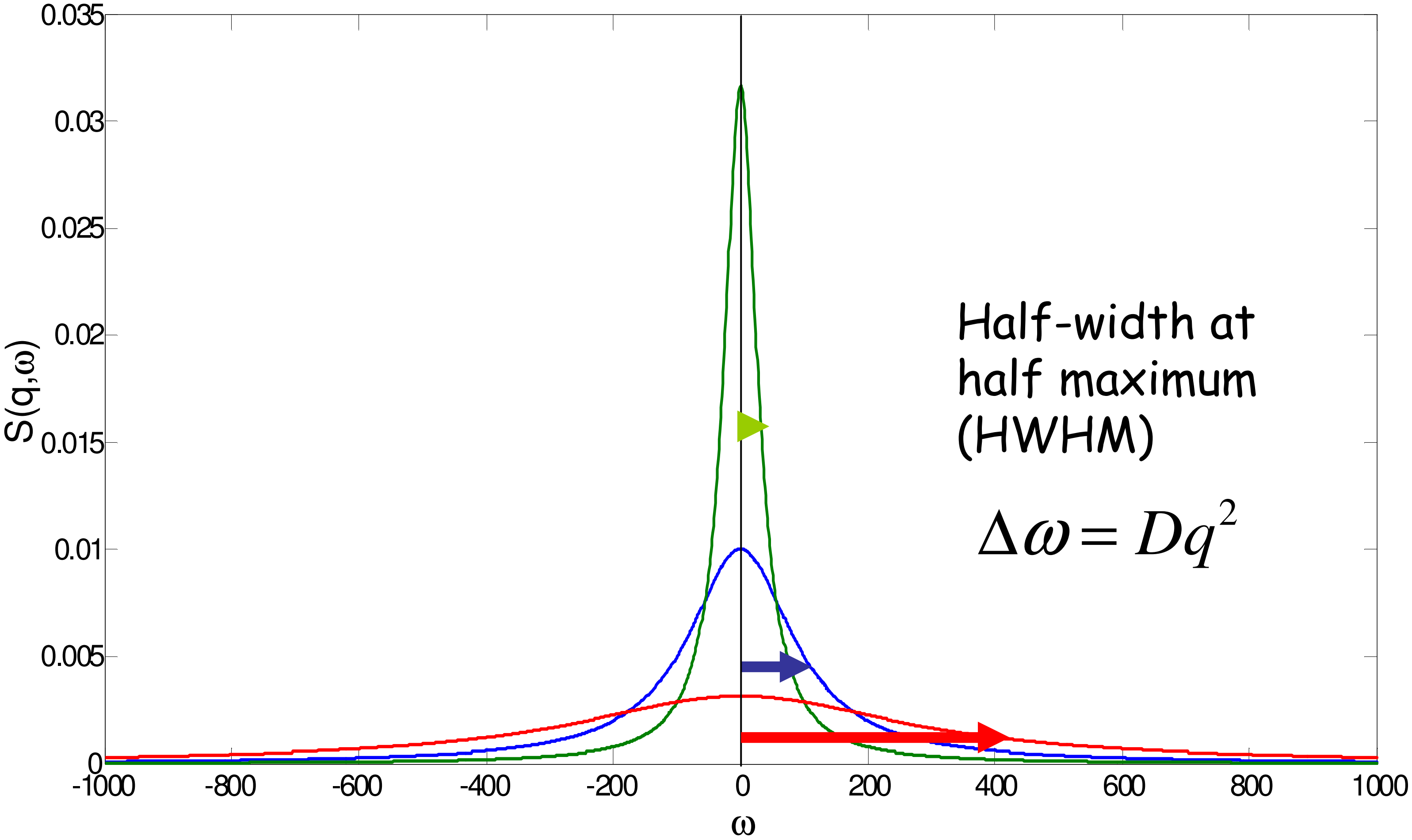
Dynamic Scattering function for free diffusion

$$D = \frac{k_B T}{6\pi\eta R}$$

$$S(q,\omega) = \frac{Dq^2}{\omega^2 + (Dq^2)^2} \quad (4)$$

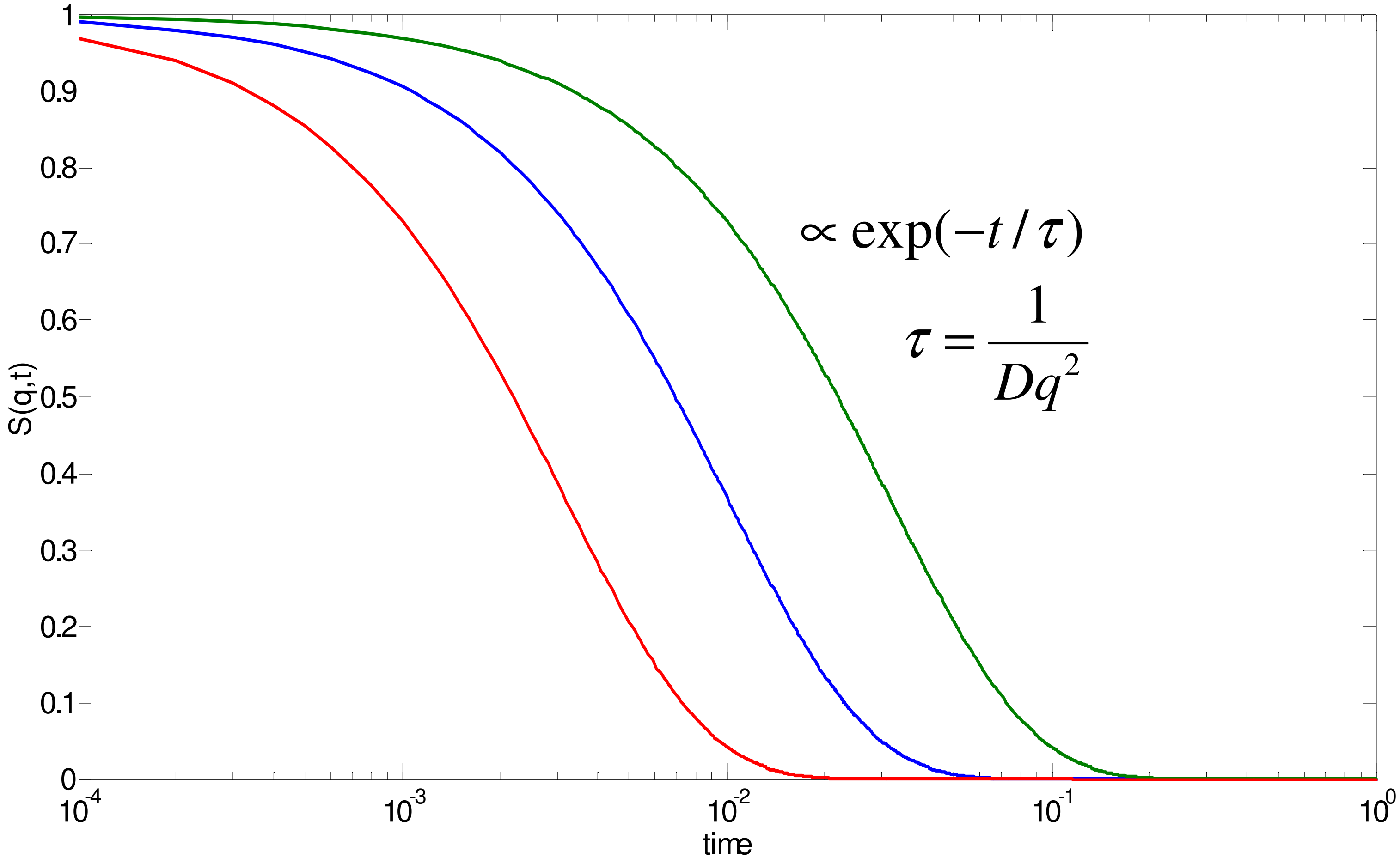
Einstein relation

Dynamic Scattering function for free diffusion



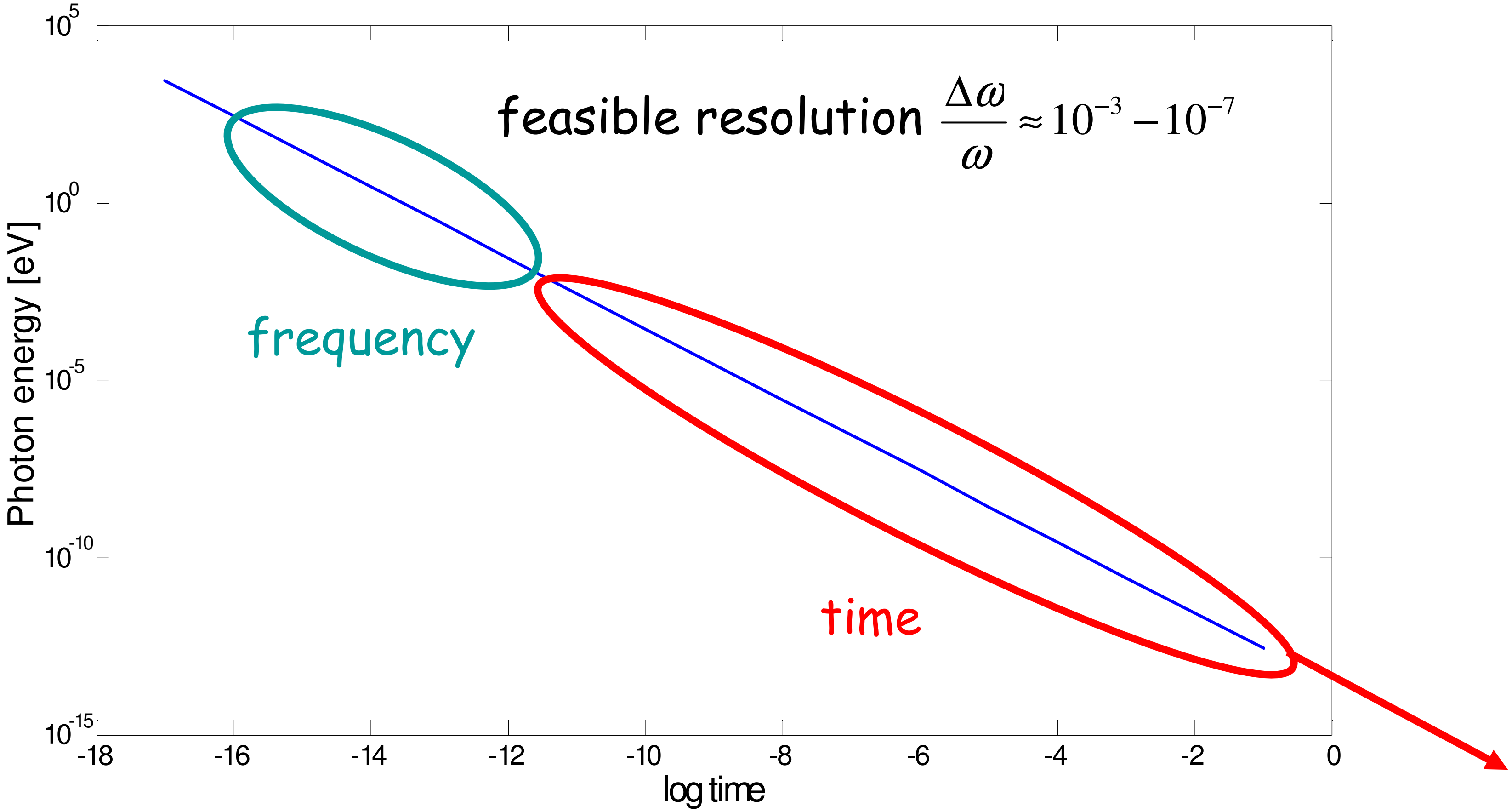
$$\Delta\omega = Dq^2$$

Intermediate Scattering function for free diffusion

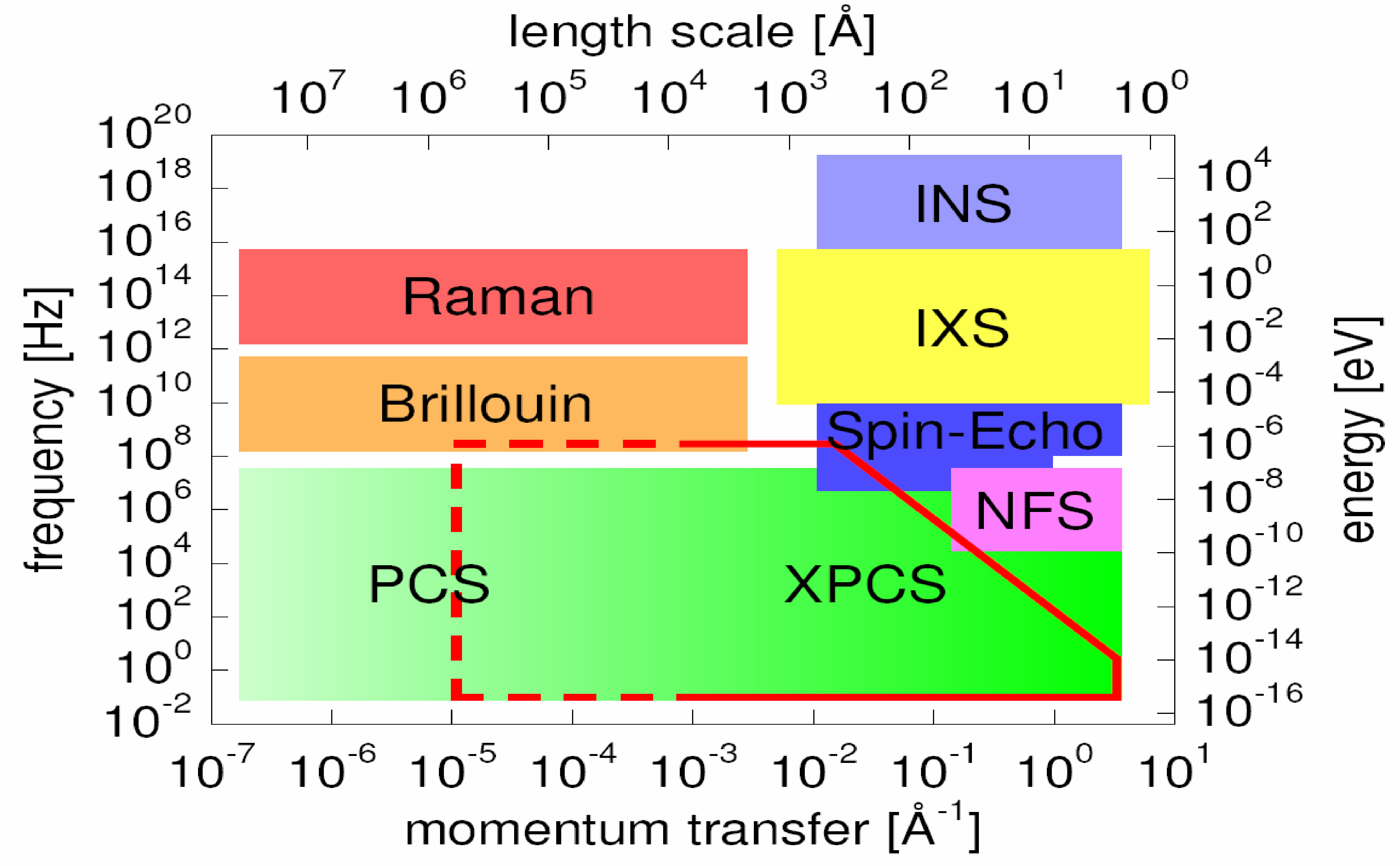


Measuring in frequency or time domain ?
equilibrium processes

typical frequency of X-rays $h\nu = 8\,\mathrm{keV}$ $h = 4.14 \cdot 10^{-15}\, eVs$



Measuring in frequency or time domain ?



Time domain

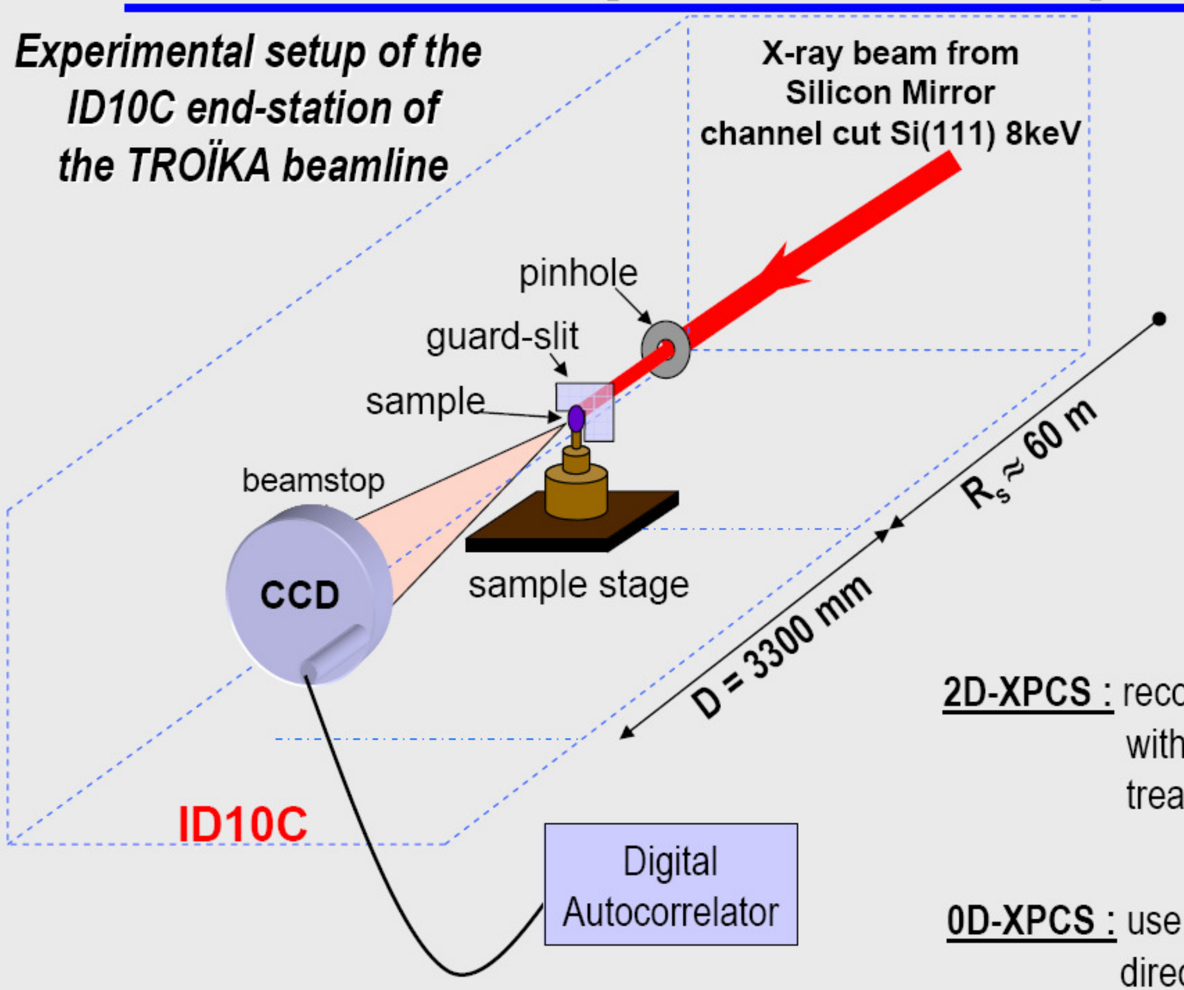
+ cover a very large time window 1000 seconds -> 1e-12 seconds (XFEL)
+ sensitive to non-equilibrium processes
-photon hungry

XPCS is a „Photon-Hungry“ Method ....

X-ray Photon Correlation Spectroscopy

Experimental setup

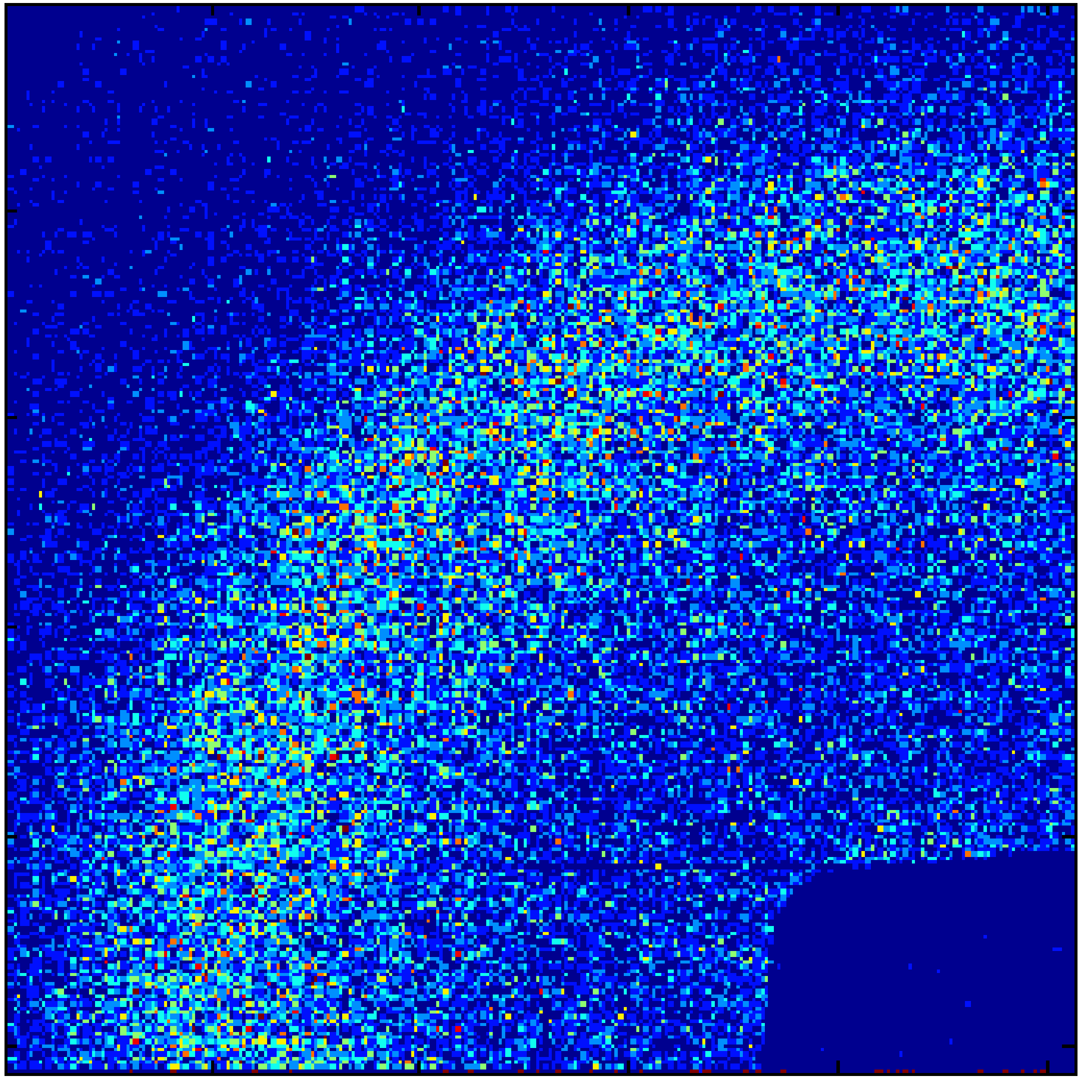
Experimental setup of the ID10C end-station of the TROÏKA beamline



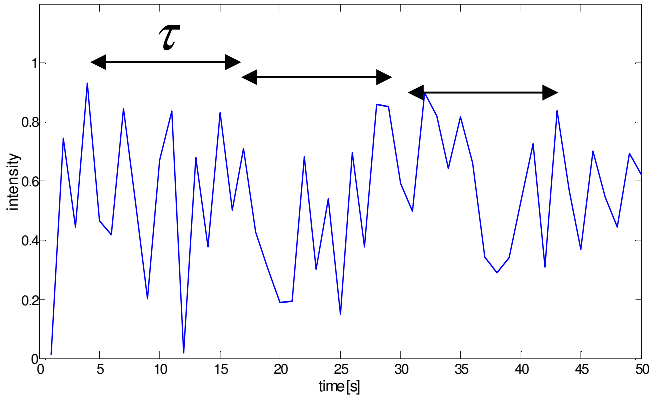
2D-XPCS : recording speckle patterns with a CCD and computer treatment afterwards

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

Fluctuating Speckle Pattern



Intensity Autocorrelation Function



$$< I(q,0)I(q,\tau) >= \frac{1}{T}\int_0^T I(q,t)I(q,t+\tau)$$

remember $$I(q,t) = \langle \rho(q,t)\rho(-q,t) \rangle$$

$$\langle I(q,t_1)I(q,t_2) \rangle = \langle \rho(q,t_1)\rho(-q,t_1)\rho(q,t_2)\rho(-q,t_2) \rangle$$

Gaussian momentum theorem and Siegert relation

$$\langle \rho(q,t_1)\rho(-q,t_1)\rho(q,t_2)\rho(-q,t_2)\rangle = \langle \rho(q,t_1)\rho(-q,t_1)\rangle\langle \rho(q,t_2)\rho(-q,t_2)\rangle$$
$$+\underbrace{\langle \rho(q,t_1)\rho(q,t_2)\rangle}_{=0}\langle \rho(-q,t_1)\rho(-q,t_2)\rangle + \langle \rho(q,t_1)\rho(-q,t_2)\rangle\langle \rho(q,t_1)\rho(-q,t_2)\rangle$$

$$\langle \rho(q,t_1)\rho(-q,t_1)\rho(q,t_2)\rho(-q,t_2)\rangle = \langle \rho(q,t_1)\rho(-q,t_1)\rangle\langle \rho(q,t_2)\rho(-q,t_2)\rangle$$
$$+\langle \rho(q,t_1)\rho(-q,t_2)\rangle\langle \rho(q,t_1)\rho(-q,t_2)\rangle$$

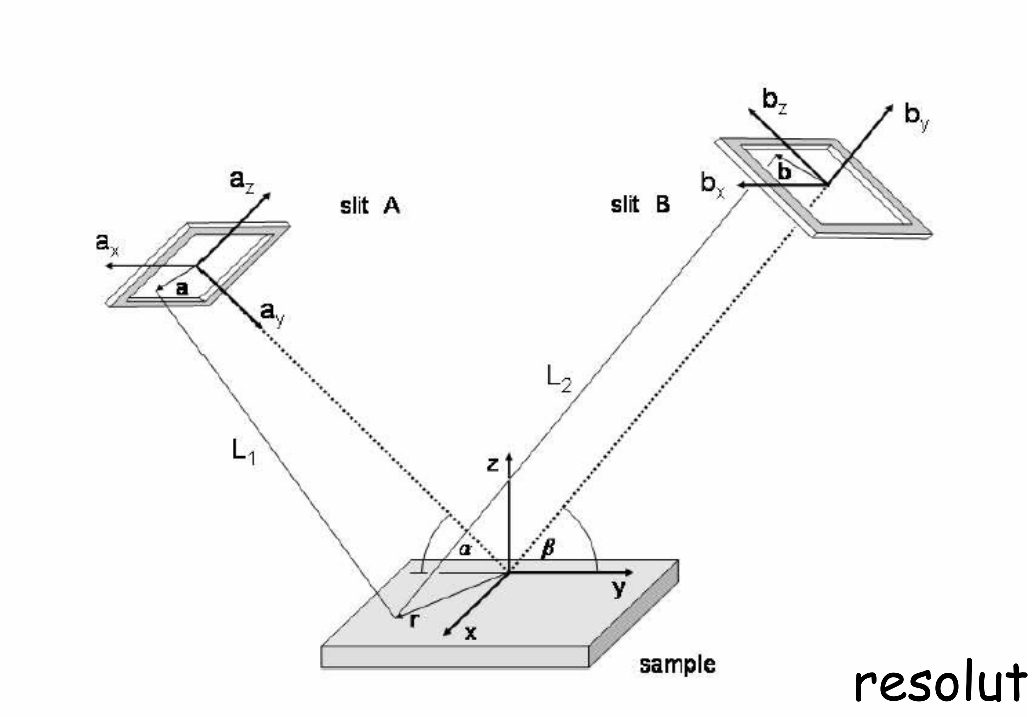
$$= \langle \rho(q,0)\rho(-q,0)\rangle\langle \rho(q,0)\rho(-q,0)\rangle + \langle \rho(q,0)\rho(-q,\tau)\rangle\langle \rho(q,0)\rho(-q,\tau)\rangle$$

$$\downarrow$$

$$\langle I(q,0)I(q,\tau)\rangle = \langle S(q,0)\rangle^2 + \left|\langle S(q,\tau)\rangle\right|^2$$

phase information lost, if S is complex (QM) $k_B T << \hbar\omega$

Effects of partial coherence



resolution functions F,H

$$g_2(q,\tau) = \frac{\langle I(q,0)I(q,\tau)\rangle}{\langle I(q,0)\rangle^2} = 1 + \frac{\iint dq'\,dq''\,\tilde{C}(q',\tau)\tilde{C}(q'',\tau)F(q,q',q'')}{\left(\int dq'\,\tilde{C}(q',0)H(q,q')\right)^2}$$

approximation

$$g_2(q,\tau) = \frac{\langle I(q,0)I(q,\tau)\rangle}{\langle I(q,0)\rangle^2} \approx 1 + \beta^2 \frac{|I(q,\tau)|^2}{\langle I(q,0)\rangle^2}$$

comprising effects of partial coherence

Heterodyne mixing in XPCS

analogue to Holography – built in a reference source

$$\rho(q,t) = \rho_0 + \rho(q,t)$$

$$\langle I(q,0)I(q,\tau)\rangle \sim 2I_s I_r \langle S(q,\tau)\rangle + I_s{}^2 \left|\langle S(q,\tau)\rangle\right|^2$$

field correlation function

$$I_s = \langle \rho(q,t)\rho(-q,t)\rangle, \; I_r = \langle \rho_0 \rho_o^* \rangle$$

By choosing a strong reference signal the intensity autocorrelation function is dominated by S(q,t) - on the expense of signal to noise ratio.

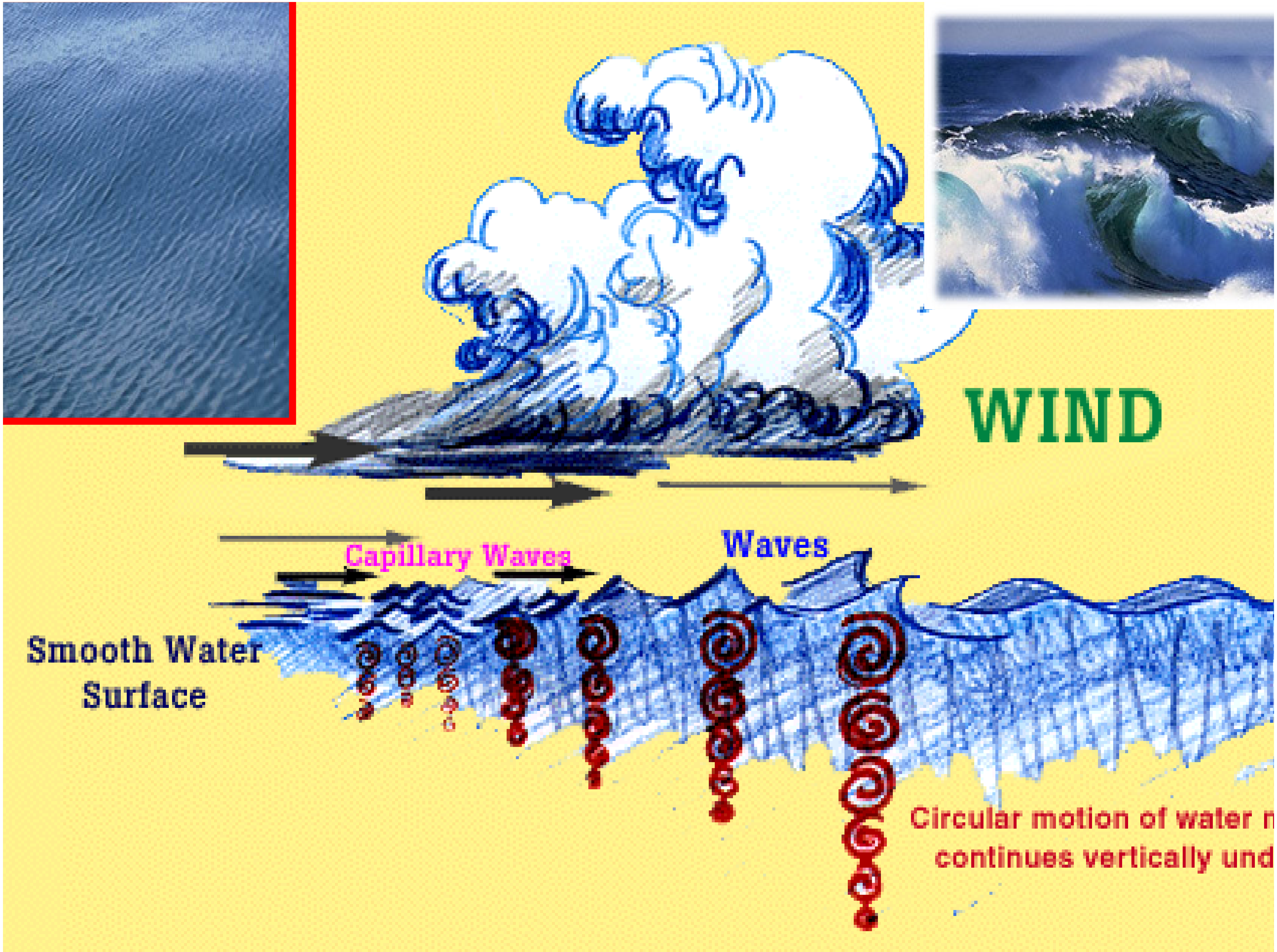
Examples

Surface fluctuations

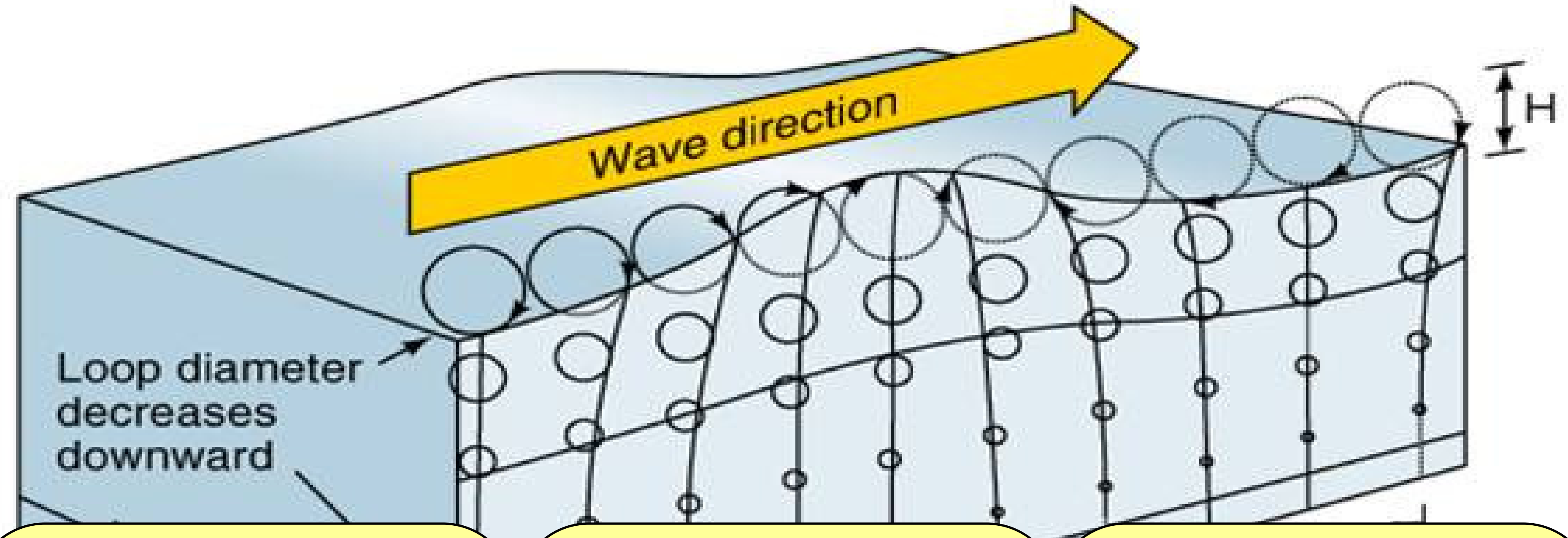
Heterodyne mixing
Transition propagating – overdamped behavior

Bulk fluctuations

Colloidal diffusion
Domain dynamics in Chromium


WIND
Capillary Waves
Waves
Smooth Water
Surface
Circular motion of water m
continues vertically und

Fluctuating Interfaces: Capillary Waves

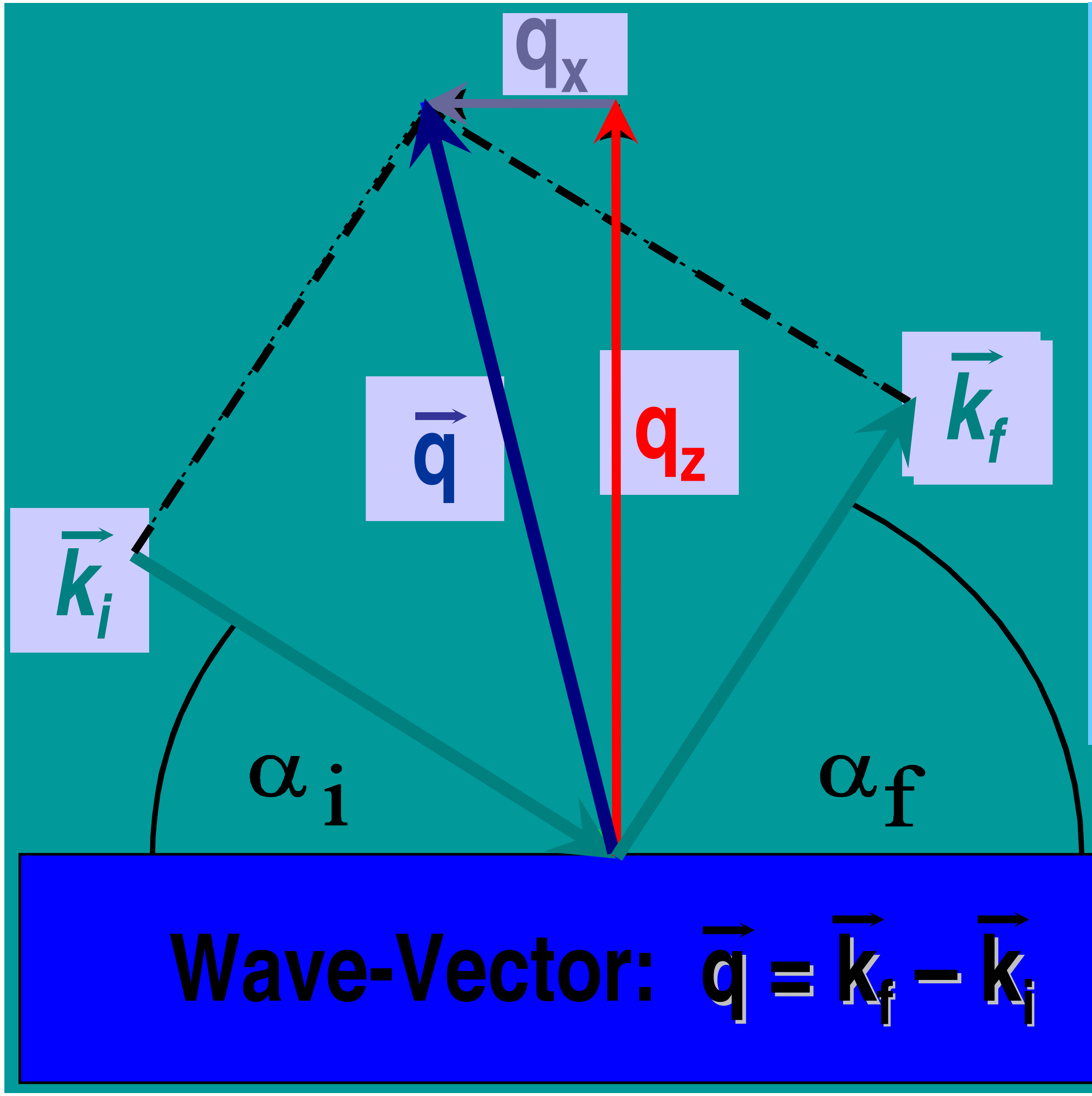


Thermal energy

Surface tension

Viscosity

Scattering Geometry & Notation



Reflectivity:

$q_x = q_y = 0$

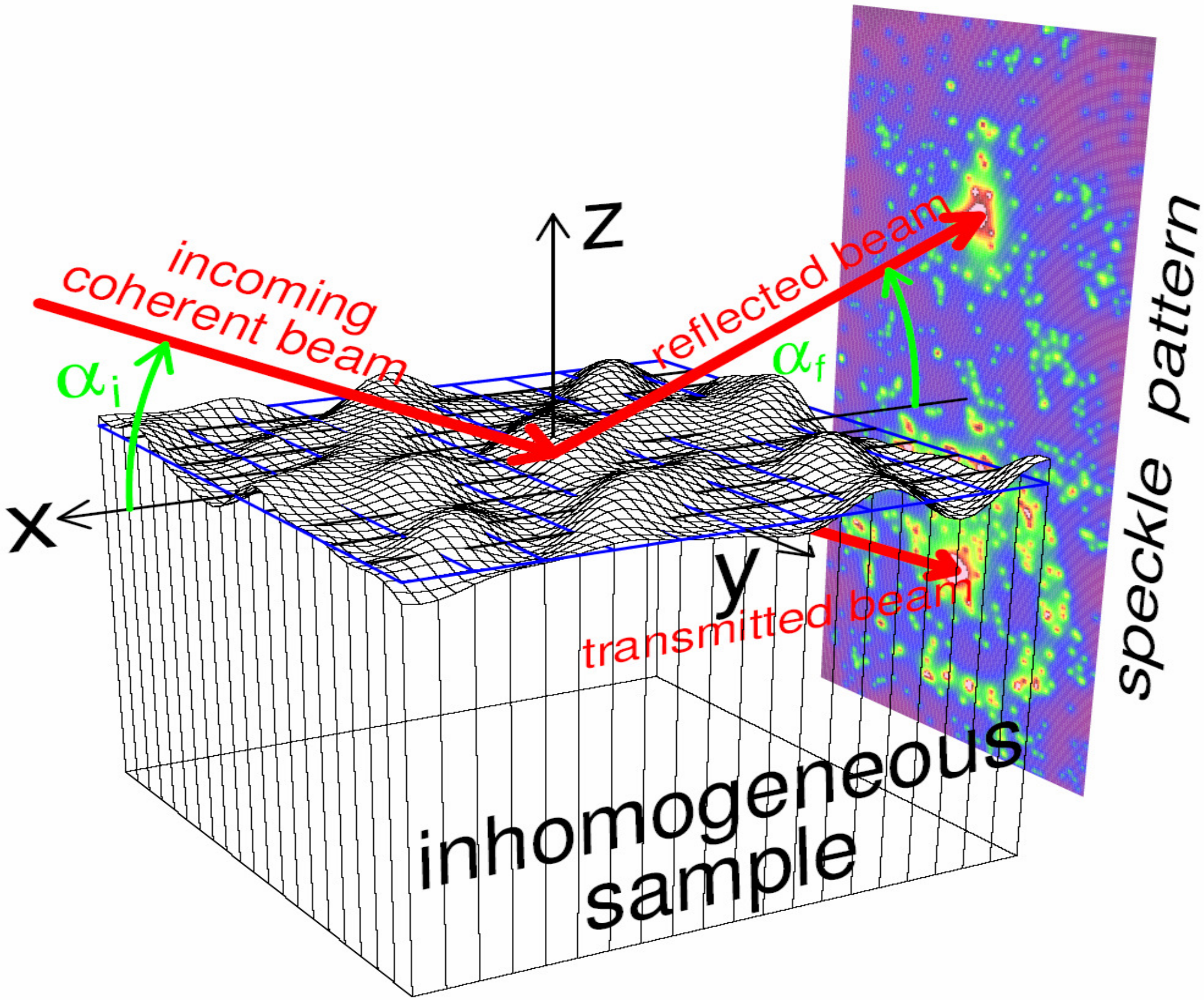
$q_z = (4\pi/\lambda)\sin\alpha_i$

Diffuse Scattering:

$q_x, q_y \neq 0$

$q_z = (4\pi/\lambda)\sin(\alpha_i+\alpha_f)/2$

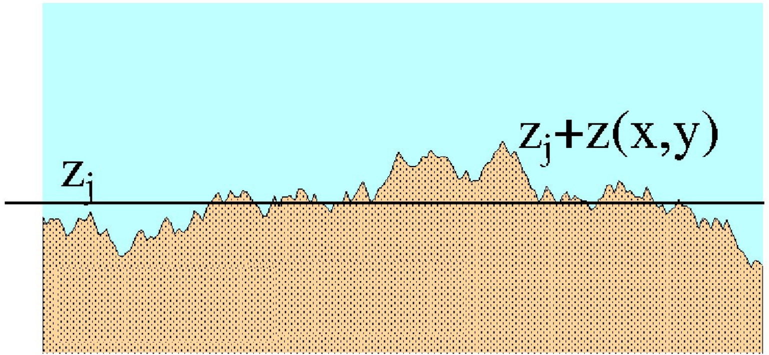
$\alpha_i, \alpha_f < 5°$


z
incoming
coherent beam
reflected beam
α_i
α_f
x
y
transmitted beam
speckle pattern
inhomogeneous
sample

Electron Density: Surface Scattering

$$\tilde{\varrho}(q,t) \;=\; \frac{\mathrm{i}\,\varrho_0}{q_z}\iint \exp\left\{-\mathrm{i}[q_x x + q_y y + q_z\, z(x,y,t)]\right\}\mathrm{d}x\mathrm{d}y$$

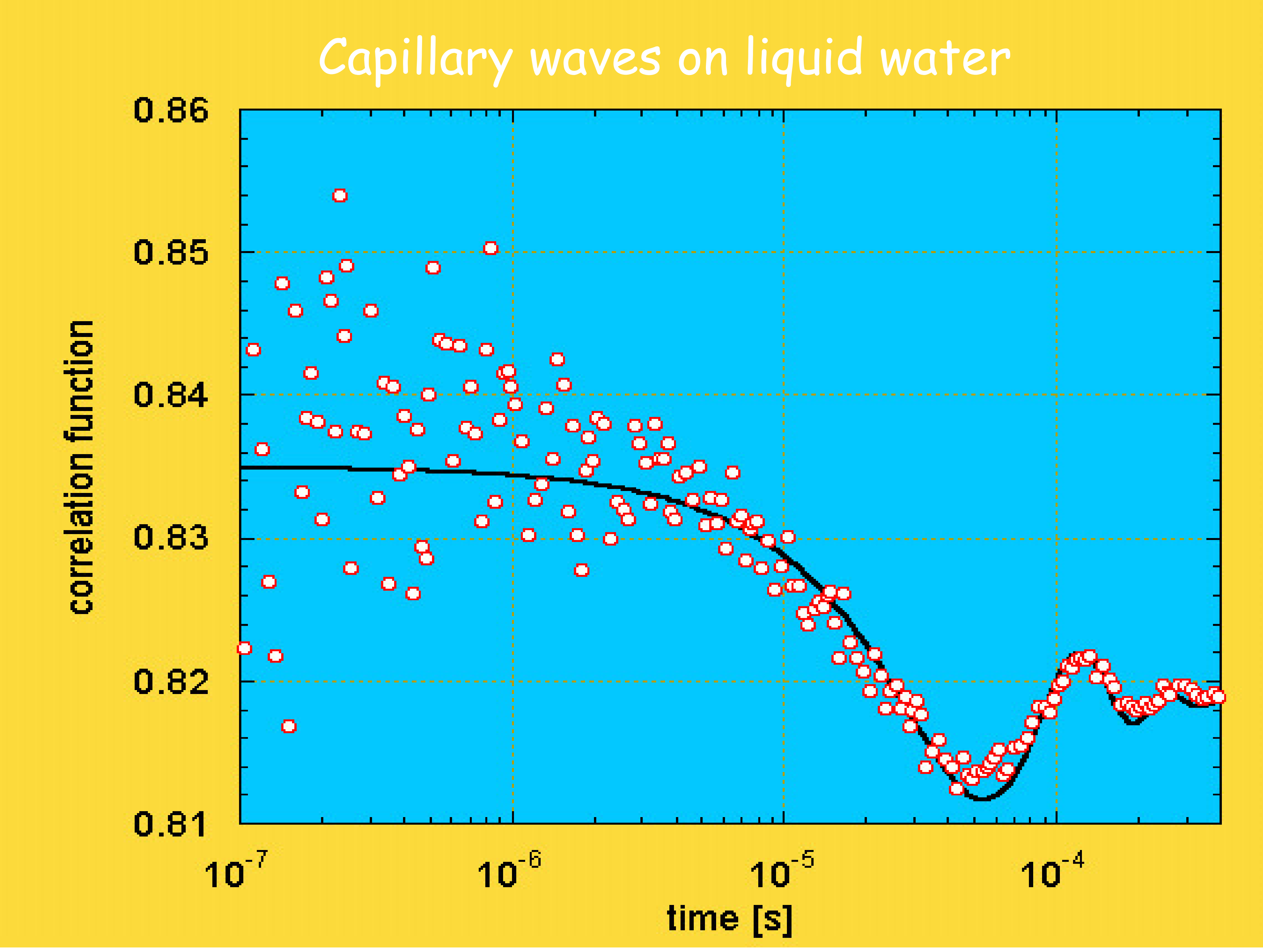
$$|q_z\, z(x,y,t)| \ll 1$$



$$\tilde{\varrho}(q,t) \;\approx\; \delta(q_x)\delta(q_y) + \varrho_0\,\tilde{z}(q_x,q_y,t)$$

reference source for heterodyning

fluctuating signal

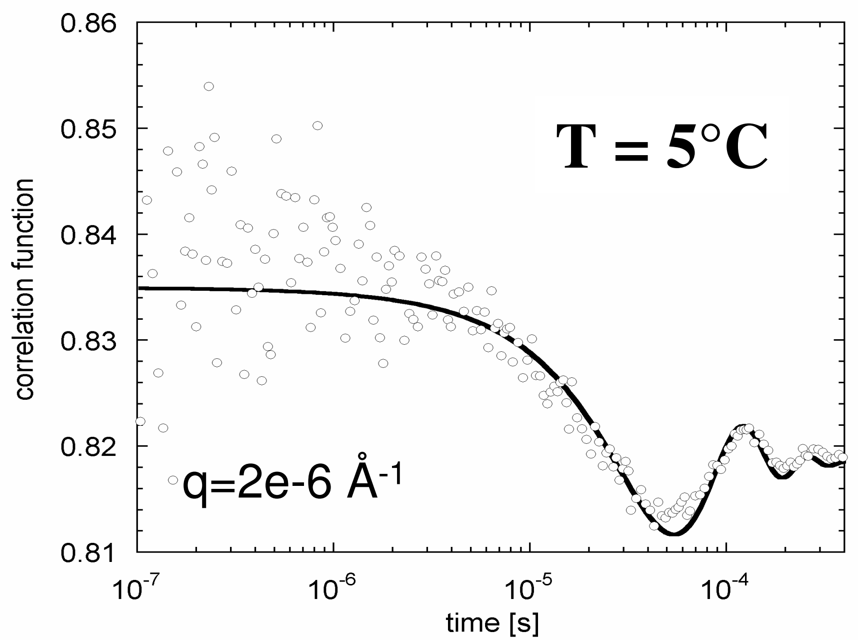

Capillary waves on liquid water
0.86
0.85
0.84
0.83
0.82
0.81
correlation function
10^{-7}
10^{-6}
10^{-5}
10^{-4}
time [s]

Correlation functions of surface fluctuations

$$\omega_s = \sqrt{\gamma/\rho\, q^3}$$

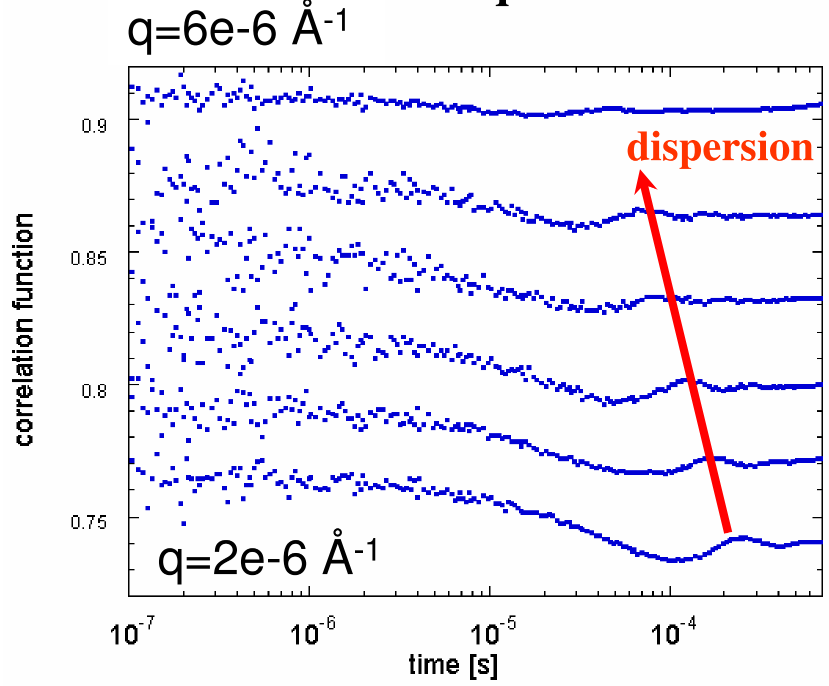
$$\langle I(q,0)I(q,\tau)\rangle \sim 2I_s I_r \langle S(q,\tau)\rangle + I_s{}^2 |\langle S(q,\tau)\rangle|^2$$

$$\cos(\omega\tau)e^{-\Gamma\tau} \qquad \cos^2(\omega\tau)e^{-2\Gamma\tau}$$



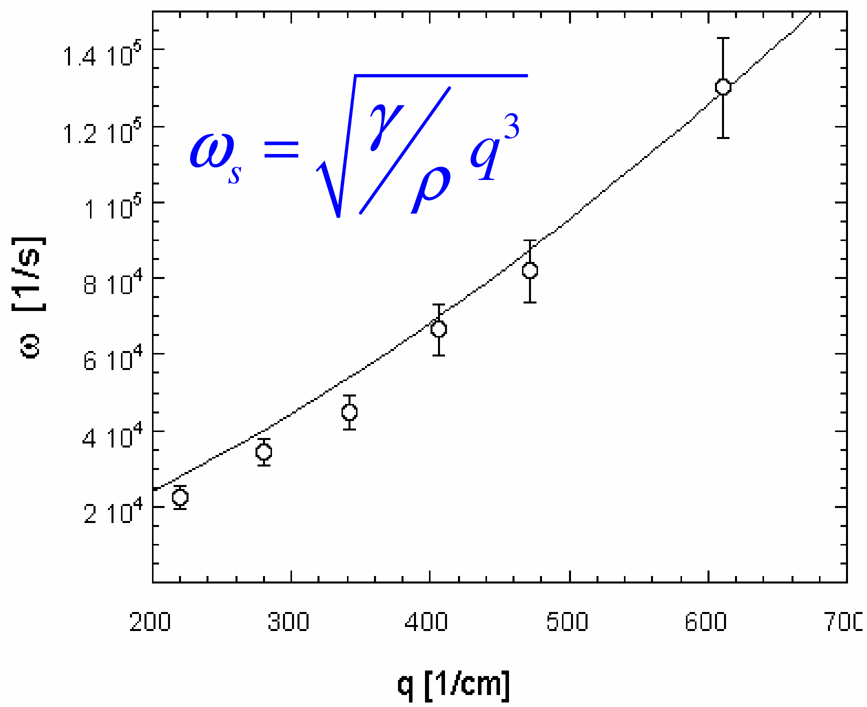
damped cosine behavior
→ heterodyne mixing

correlation functions of a water surface at T=5ºC as a function of q

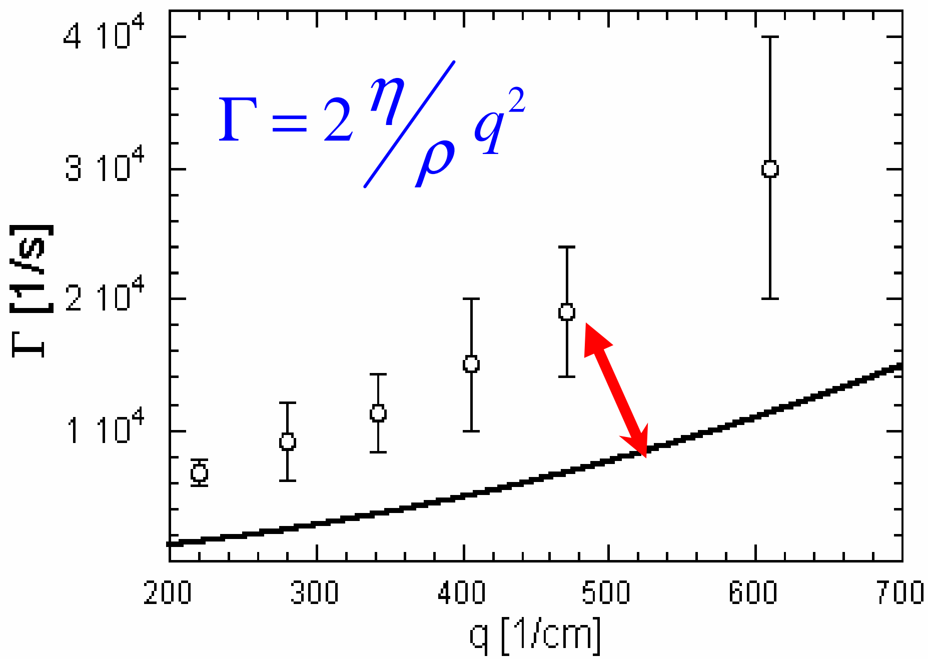


Correlation functions of surface fluctuations

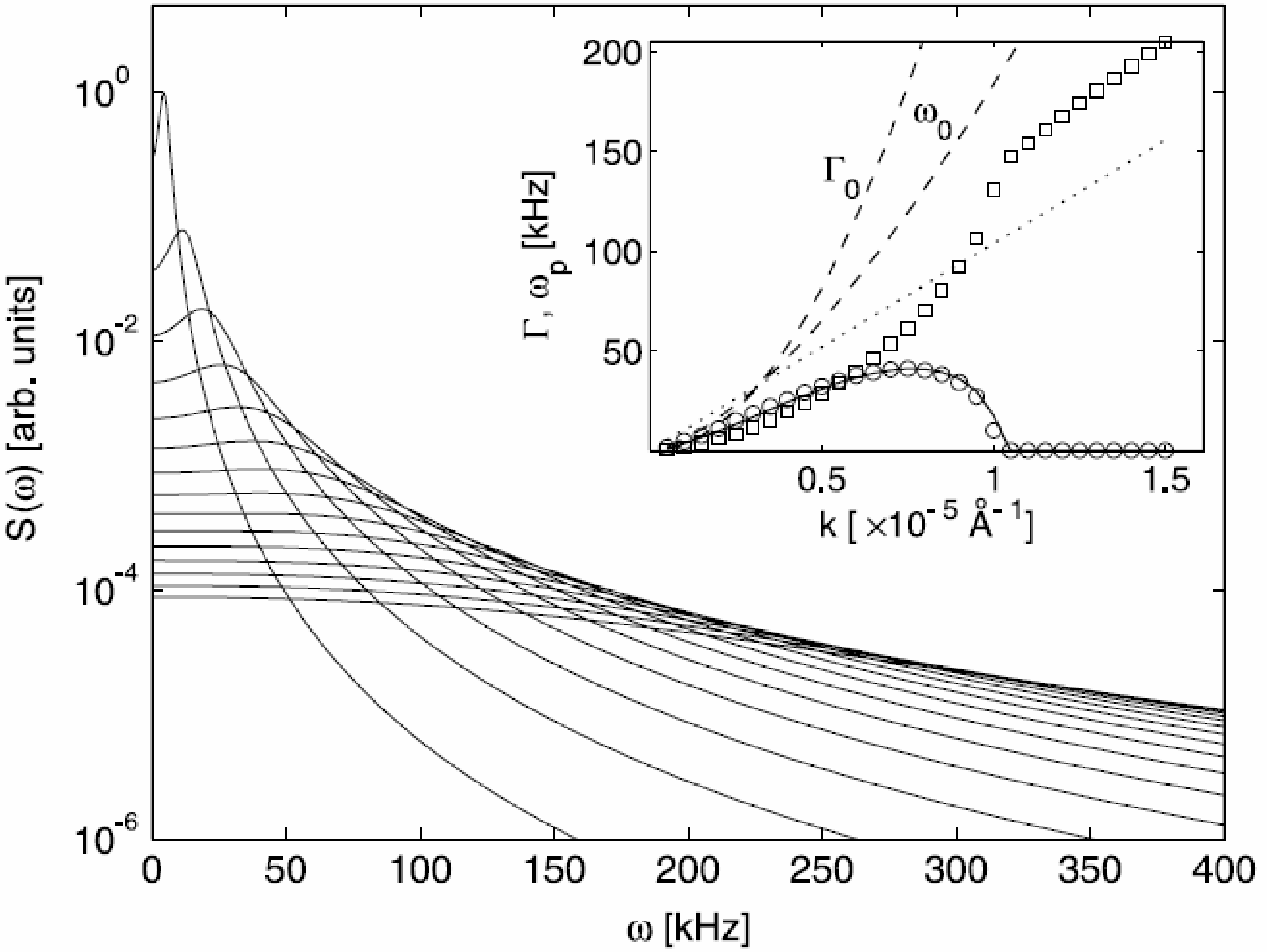
Dispersion



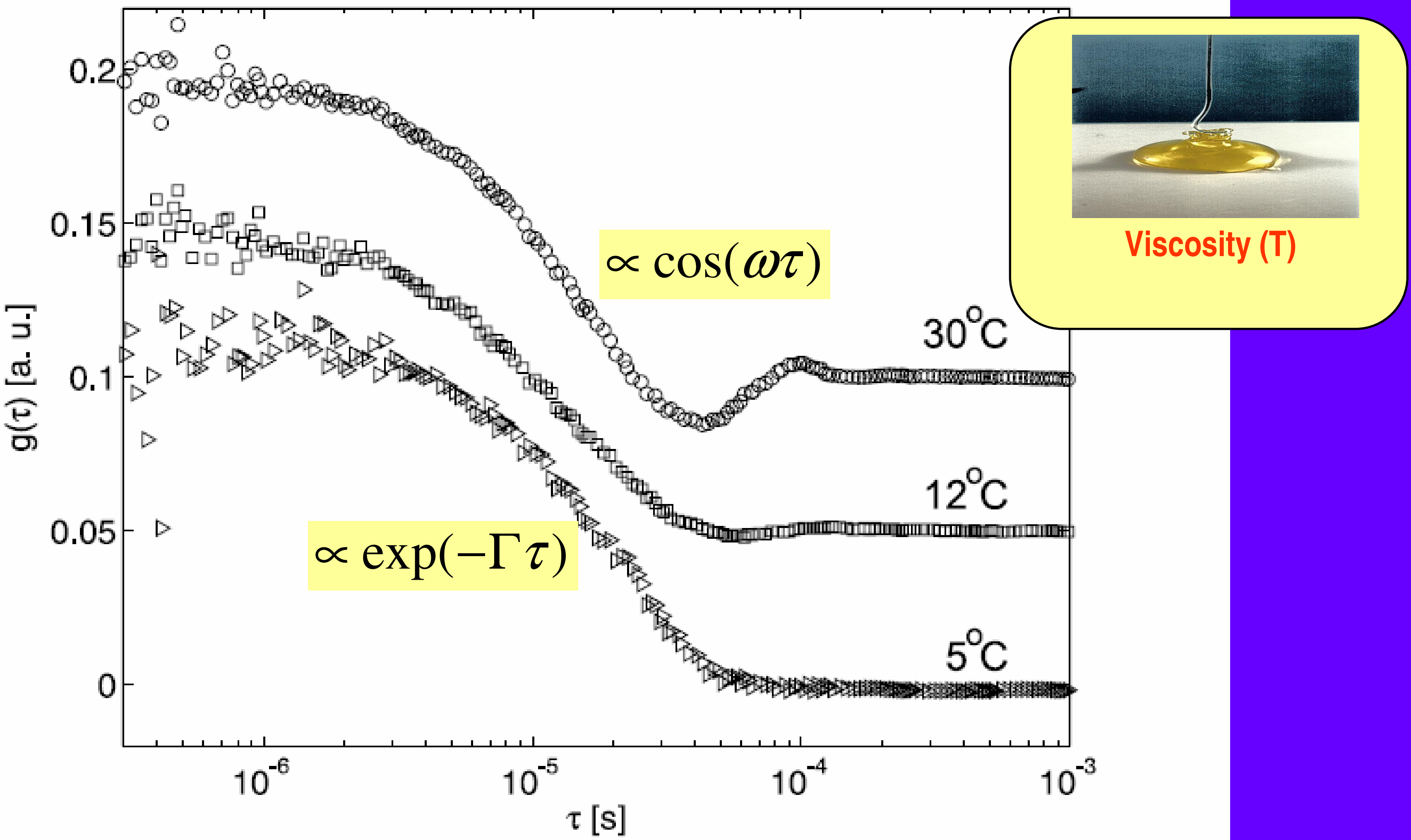
Damping



Spectral features of damped capillary waves



Mixtures of liquid water and glycerol
tuning the viscosity (damping) as a function of temperature



Measurement

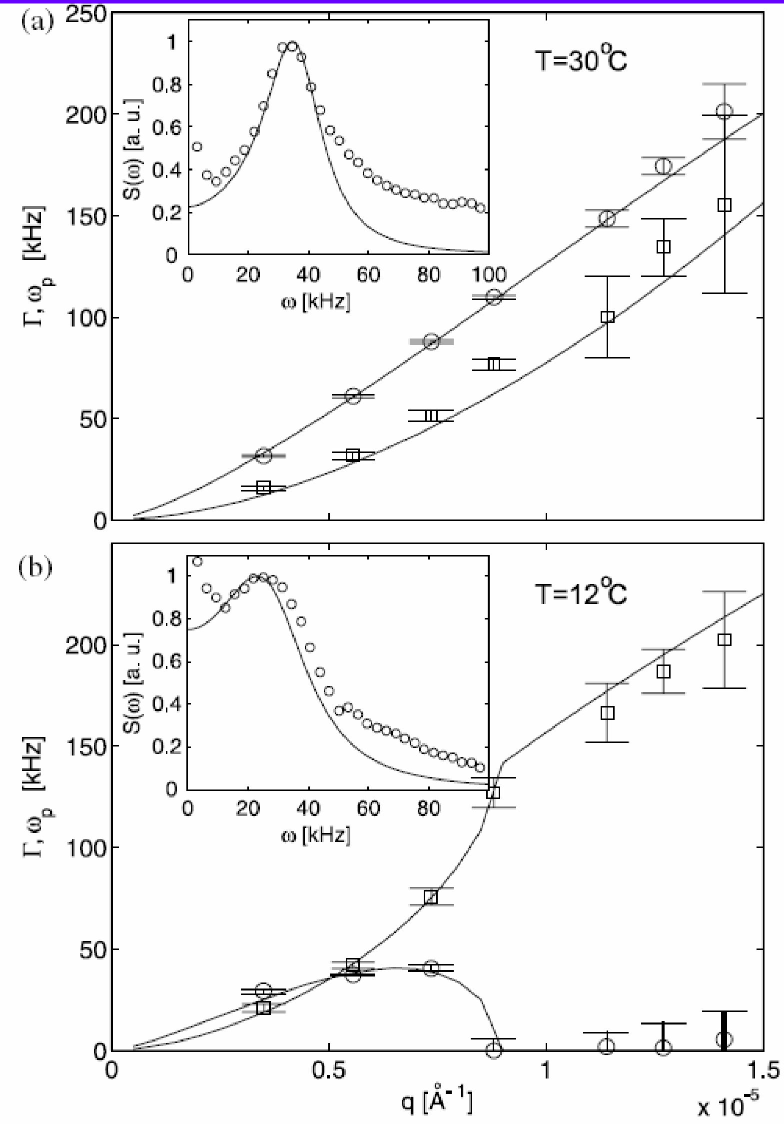
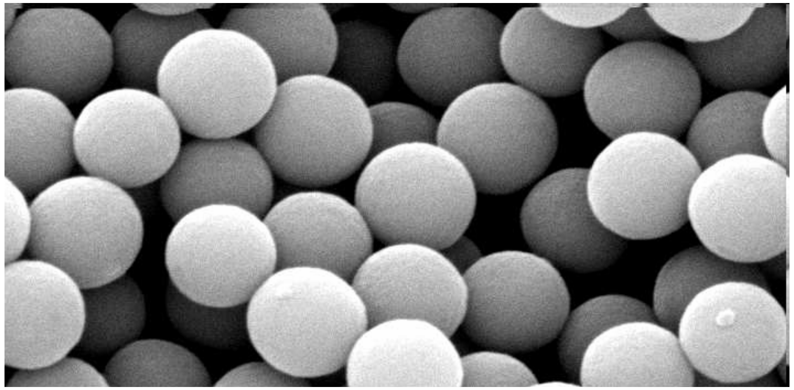
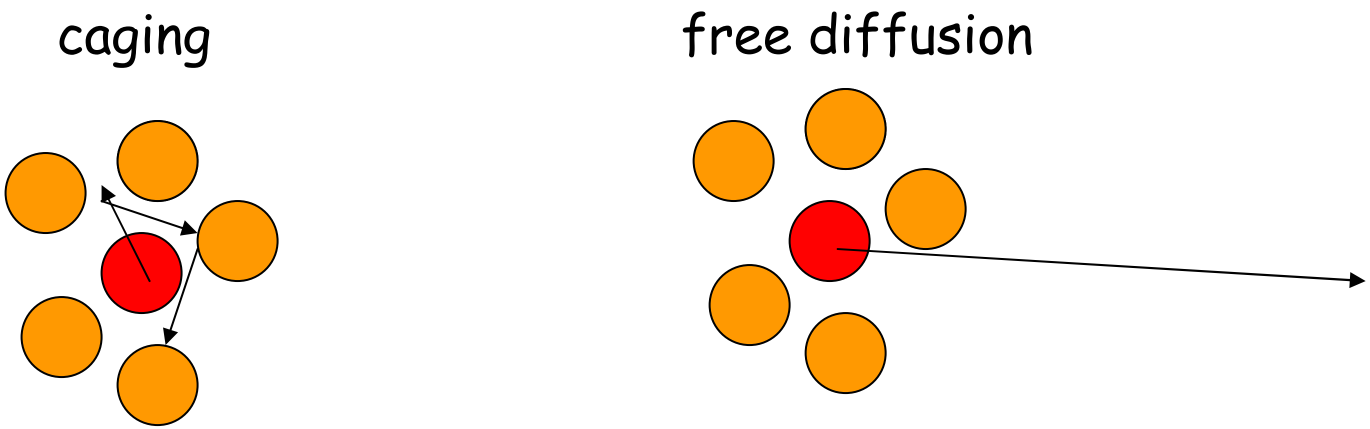


FIG. 4. Experimental data (from Fig. 2) that are well de-

Diffusion in Colloidal Suspensions



Free diffusion is valid for large length scales. What is happening when the probed length scales becomes comparable to particle size ?

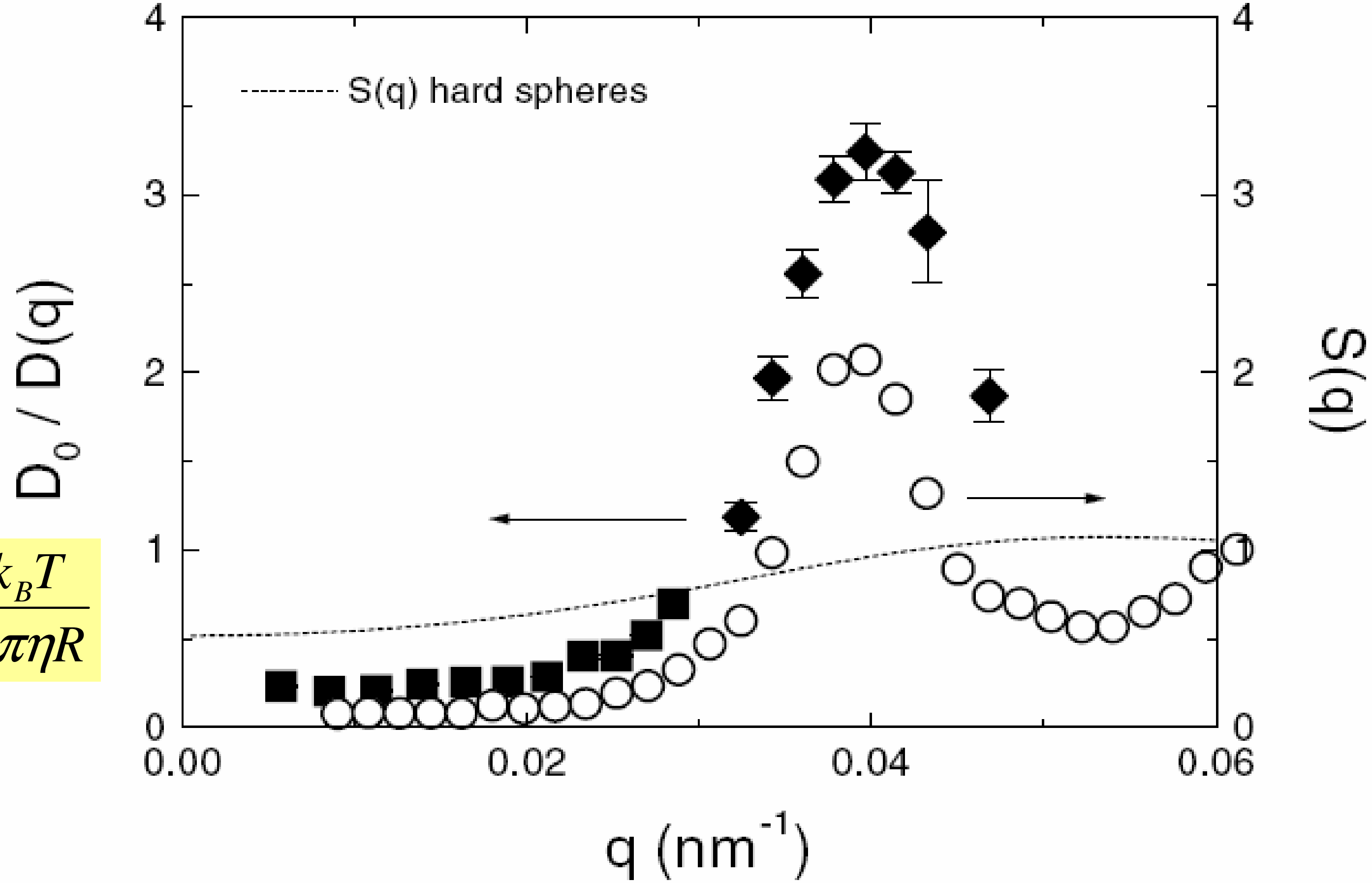


Diffusion in Colloidal Suspensions

$$D(q) = \frac{\Gamma(q)}{q^2}$$

de Gennes narrowing
microscopic structure of the liquid becomes visible

$$D_0 = \frac{k_B T}{6\pi\eta R}$$



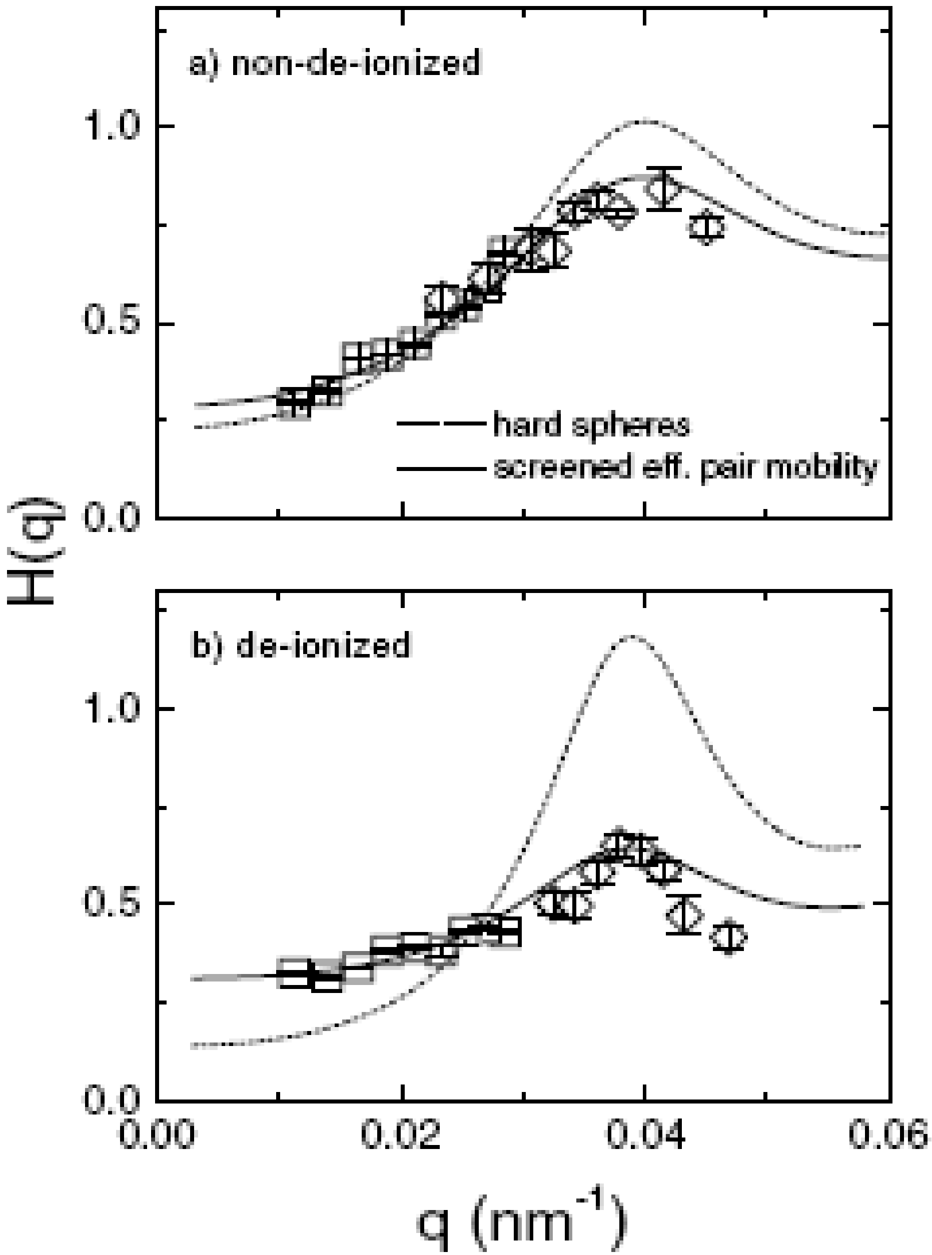
Hydrodynamic function H(q)

indirect hydrodynamic interactions mediated by the solvent medium

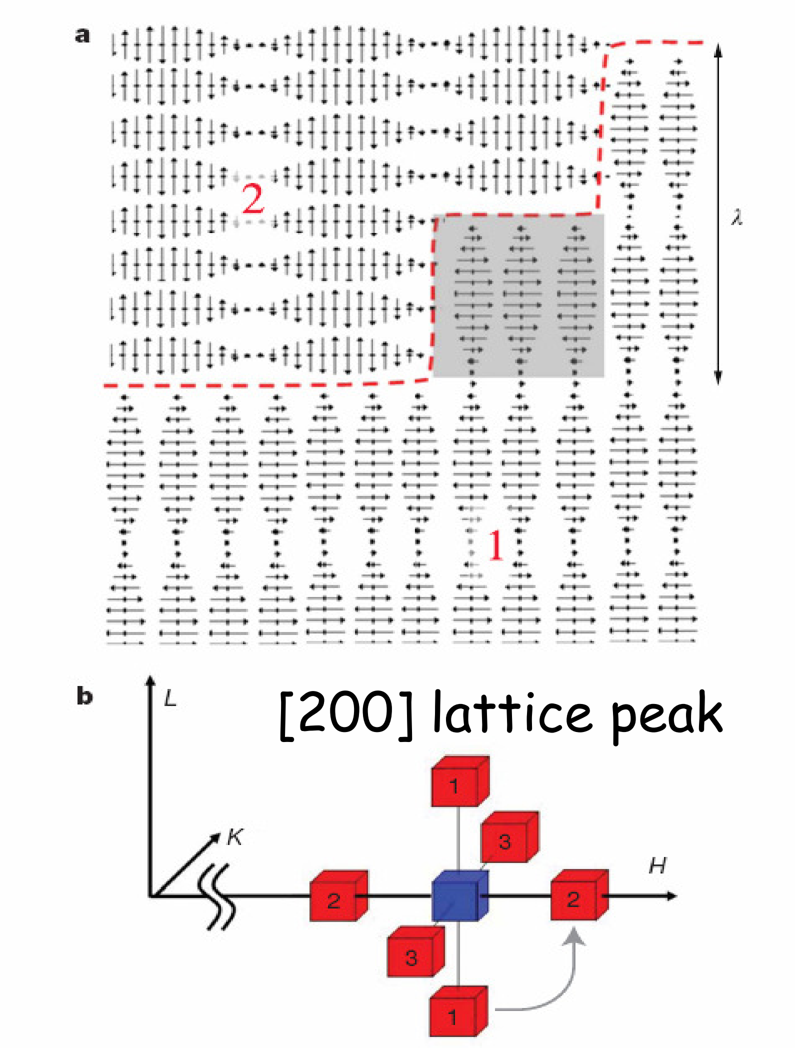
$$H(q) = \frac{D(q)}{D_0} S(q)$$

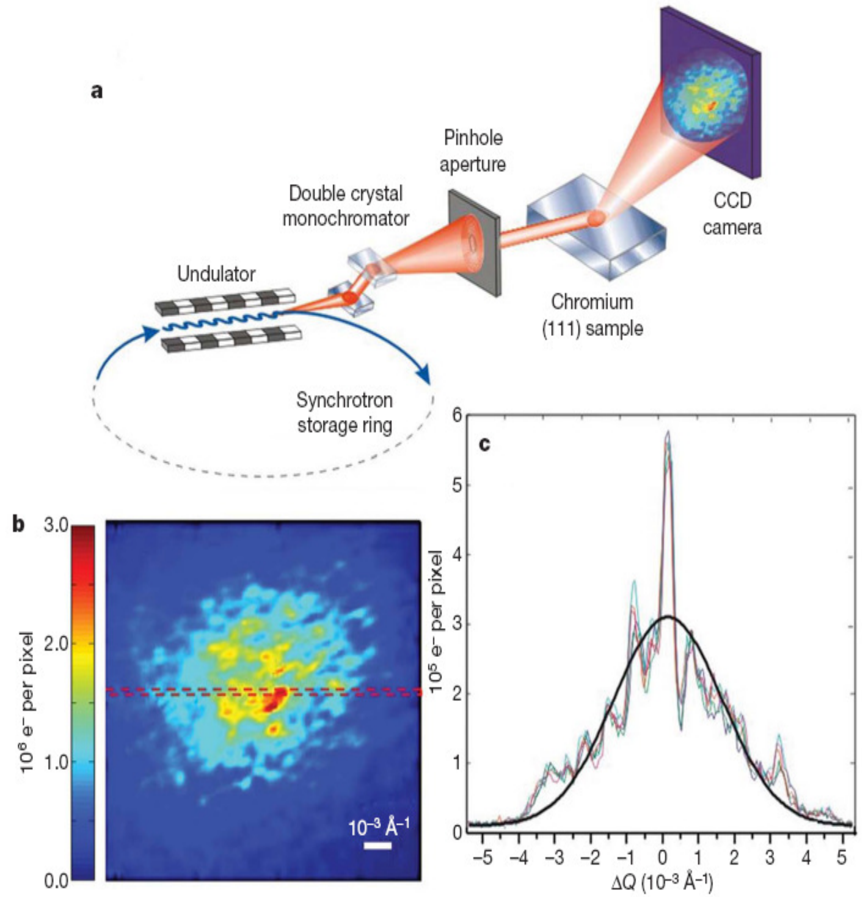
$$H(q) < 1$$

indirect hydrodynamic interactions slow down the dynamics



Antiferromagnetic Domain fluctuations in Chromium



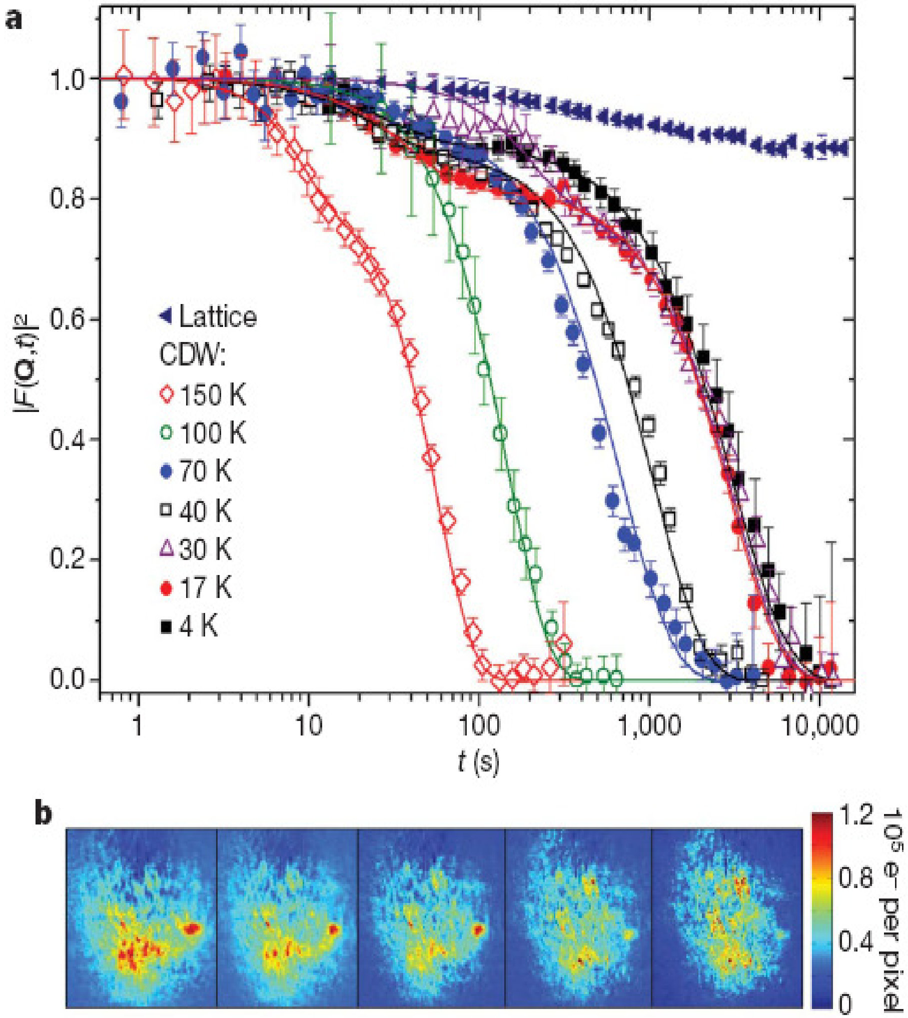


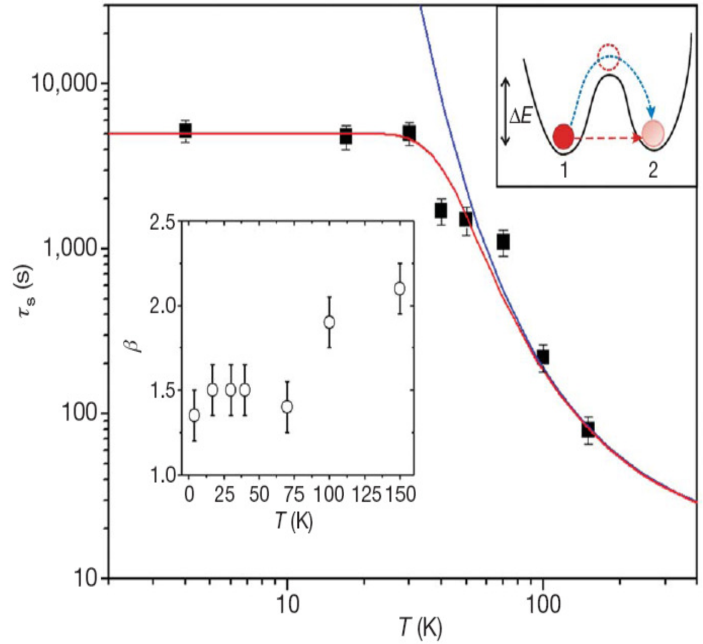
[200] lattice peak

Charge density wave satellite peaks (CDW)

O.G. Sphyrko et al. Nature 447, 68 (2007)

Intensity Autocorrelation Function





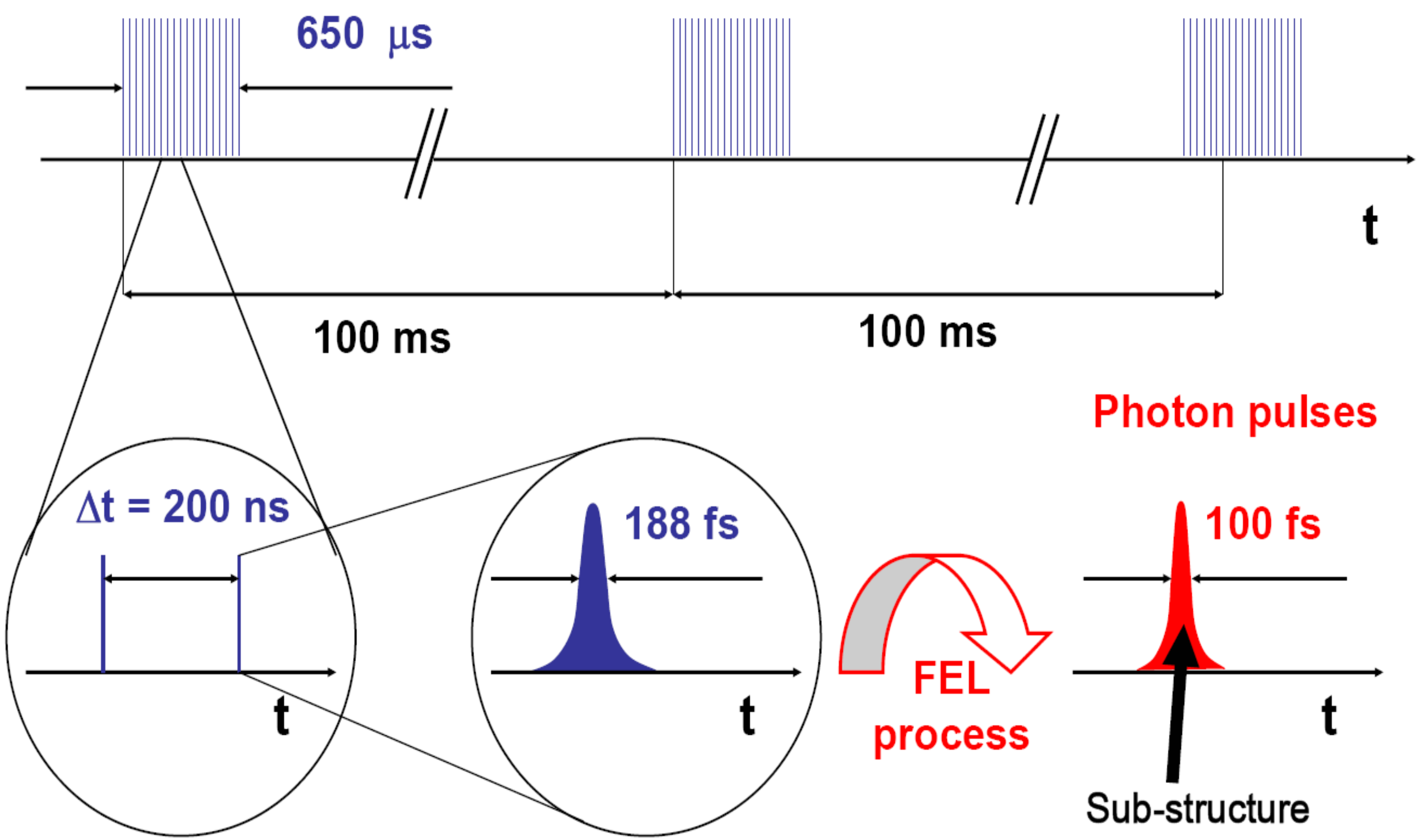
non Arrhenius behavior

CDW satellite peak

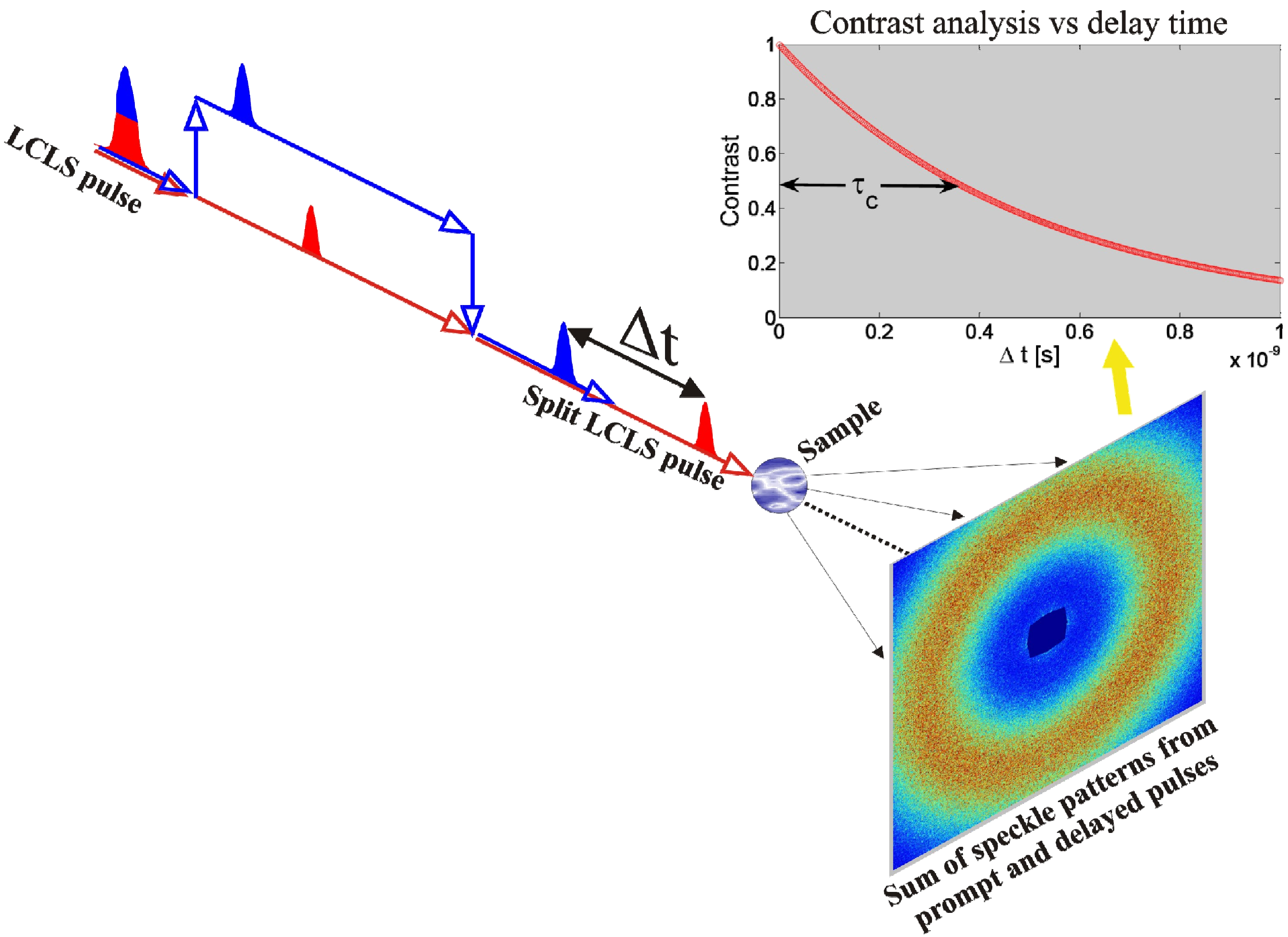
O.G. Sphyrko et al. Nature 447, 68 (2007)

The XFEL time structure

Electron bunch trains
(with up to 3250 bunches à 1 nC)



XPCS at XFEL



Contrast analysis vs delay time
Contrast
τc
Δ t [s]
x 10-9
LCLS pulse
Δt
Split LCLS pulse
Sample
Sum of speckle patterns from
prompt and delayed pulses

Sequential technique

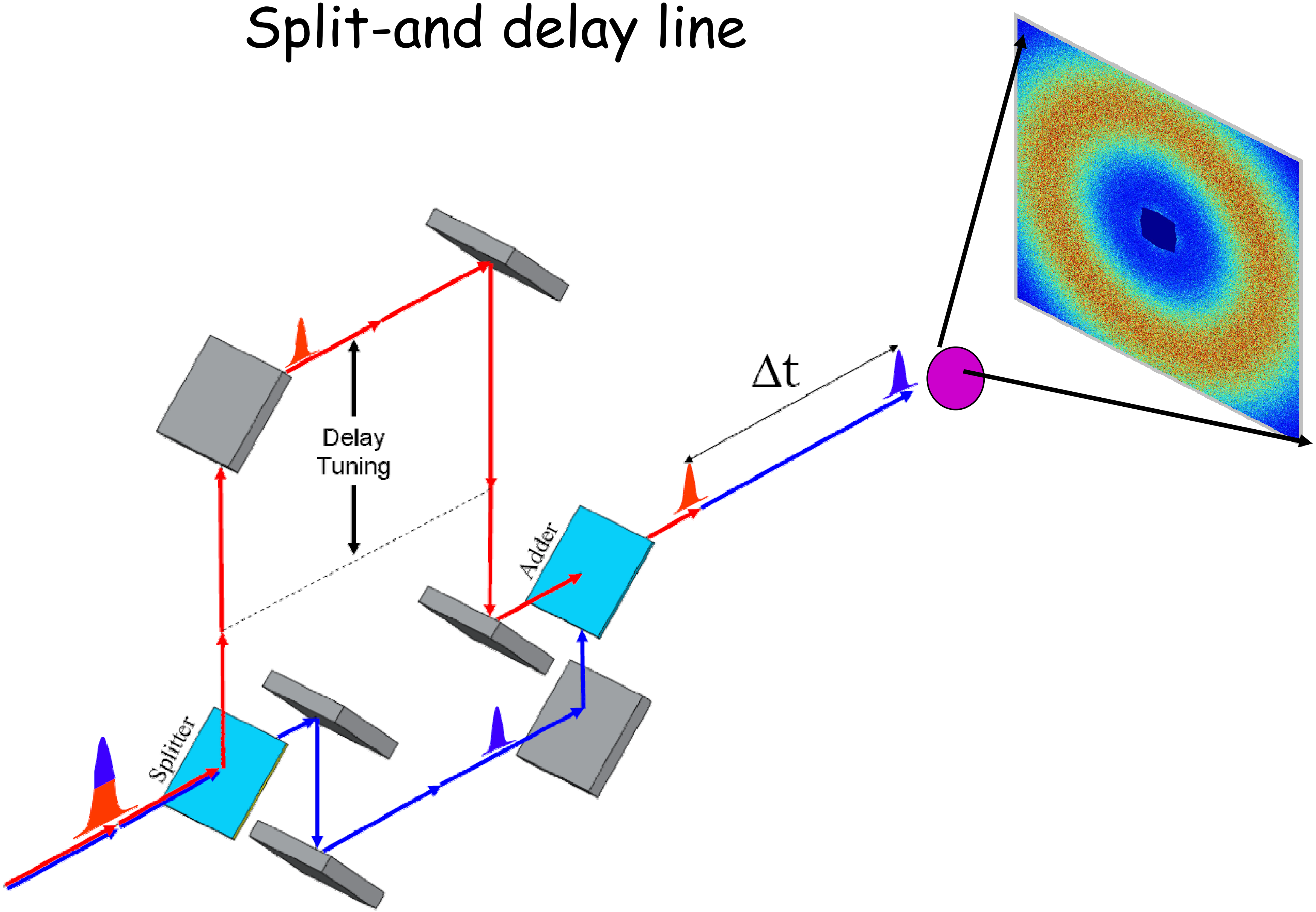
$$g_2(\tau) = \frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle^2} = 1 + \beta|f(\tau)|^2$$

Split-Pulse technique

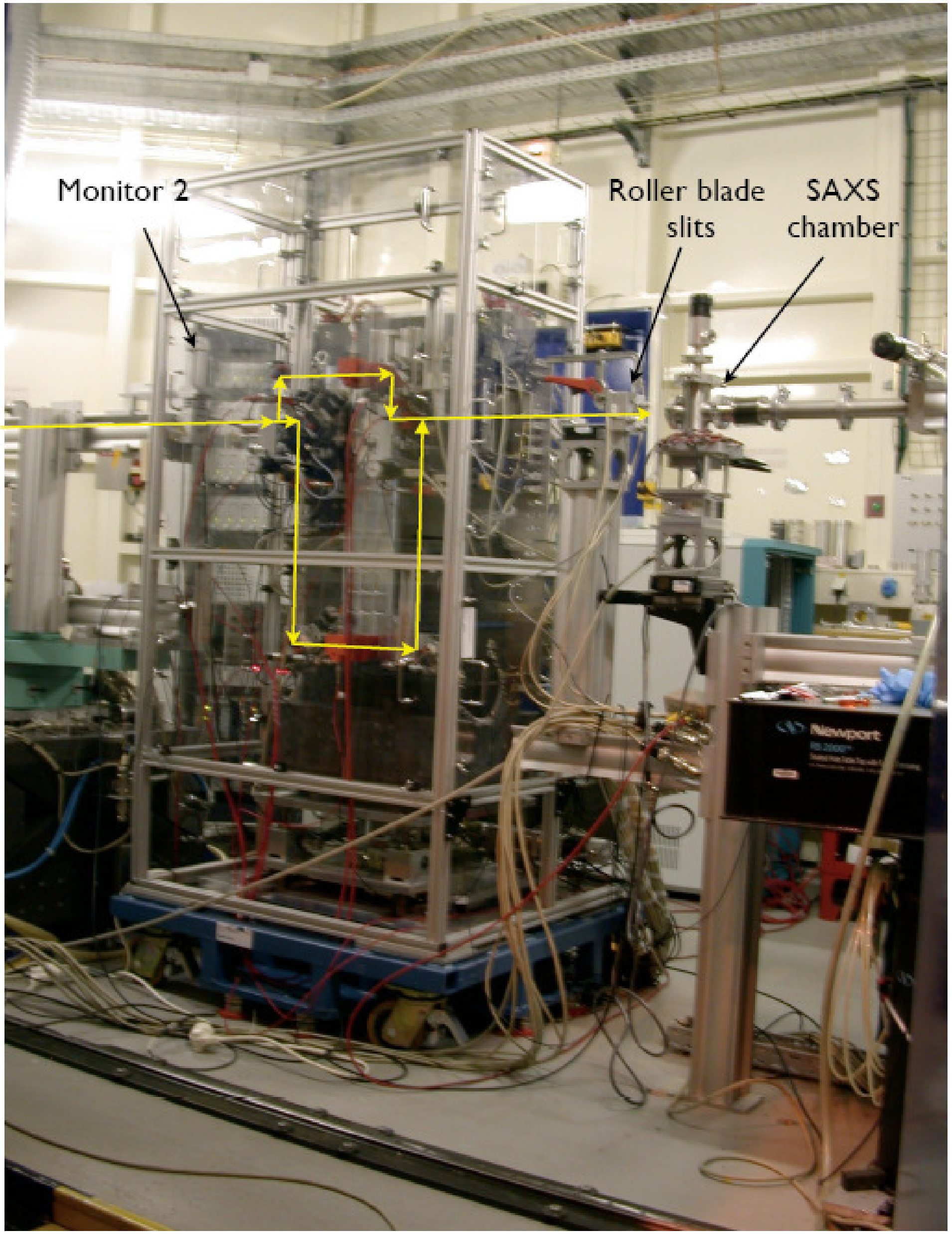
$$S(\tau) = I(t) + I(t+\tau)$$

$$c_2(\tau) = \frac{\langle S(\tau)^2\rangle - \langle S(\tau)\rangle^2}{\langle S(\tau)\rangle^2} = \frac{\beta}{2}\left(1 + |f(\tau)|^2\right)$$

Split-and delay line



X-ray Split and Delay Unit



Development of an X-ray delay unit for correlation spectroscopy and pump - probe experiments

Dissertation zur Erlangung des Doktorgrades des Fachbereichs Physik der Universität Hamburg

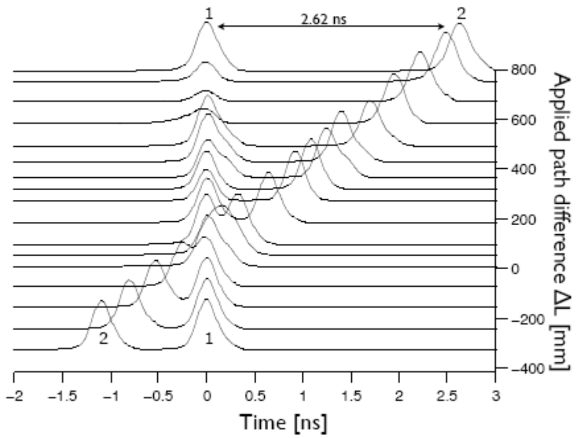
vorgelegt von

Wojciech Roseker

aus Bydgoszcz, Polen

Hamburg

2008



First XFEL light in Stanford 2009

to come   XFEL Japan, European XFEL DESY, PSI, Korea ?, China ?

The End