X-Ray Photon Correlation Spectroscopy

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Layout

I. Introduction

- Why use X-Rays?
- Coherence parameters of Undulator Sources

II. Scattering with Coherent X-Rays

- X-Ray Speckle
- X-Ray Photon Correlation Spectroscopy (XPCS)

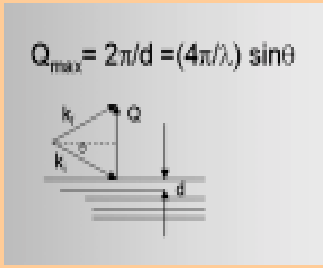
III. Scientific Applications

- Complex Fluids (Colloidal Suspension, Micellar Systems)
- Membrane Fluctuations and Capillary Wave Dynamics
- Non-Equilibrium Dynamics and Magnetic Speckle

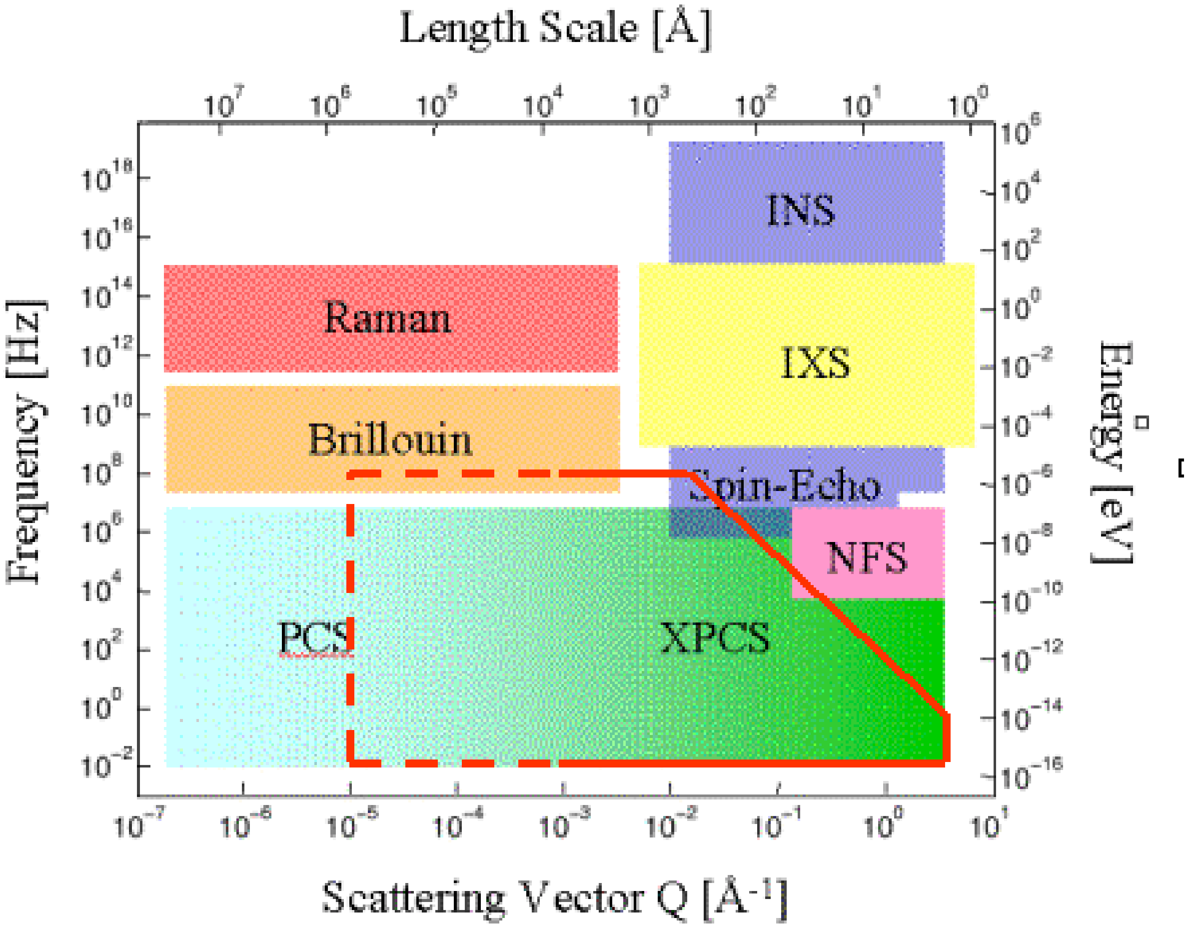
IV. Future Coherent Light Sources (FEL‘s)

V. Conclusions

- Dynamics on short lengthscales



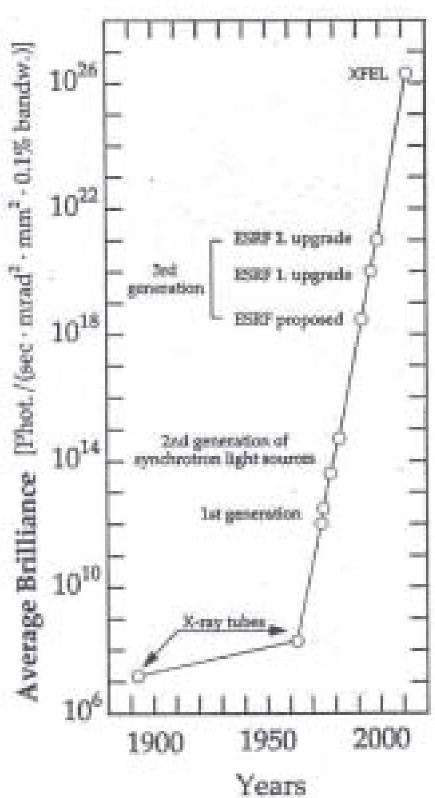
- No multiple scattering
- Opaque materials



Coherent light from a partially coherent source

Coherence is one of the most prominent features of third and future fourth generation light sources.

$$F_c = (\lambda/2)^2 \cdot B(\text{rilliance})$$



Fc

10^{16}

10^{10}

10^{5}

1

Coherence Parameters: λ=1 Å

Transverse coherence length: $\xi_t = \lambda R_s / 2d_s \approx 10\ \mu m$

Longitudinal coherence length: $\xi_l = \lambda(\lambda/\Delta\lambda) \approx 1\ \mu m$

Contrast (degree of coherence): $\beta = \beta(\Delta\lambda/\lambda, \ldots)$

Applications:

Scattering with coherent X-rays

Structure: speckle reconstruction
Dynamics: **X-ray photon correlation spectroscopy (XPCS)**

(Phase Contrast) Imaging

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Scattering with Coherent X-Rays

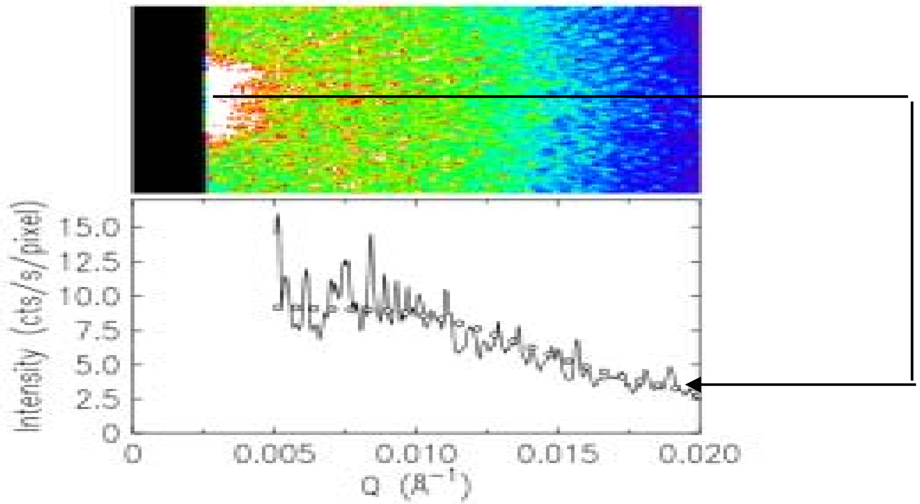
If coherent light is scattered from a disordered system it gives rise to a random (grainy) diffraction pattern, known as "speckle". A speckle pattern is an interference pattern and related to the exact spatial arrangement of the scatterers in the disordered system.

$$I(Q,t) \propto S_c(Q,t) \propto \left| \sum_{j} e^{iQR_j(t)} \right|^2$$

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

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

Photon Correlation Spectroscopy

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

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

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

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

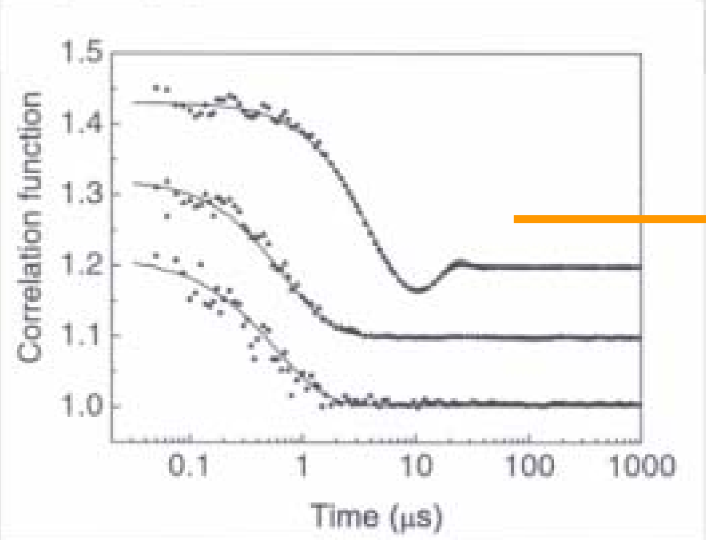
Diffusive Processes:

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:

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



Livet
Gutt

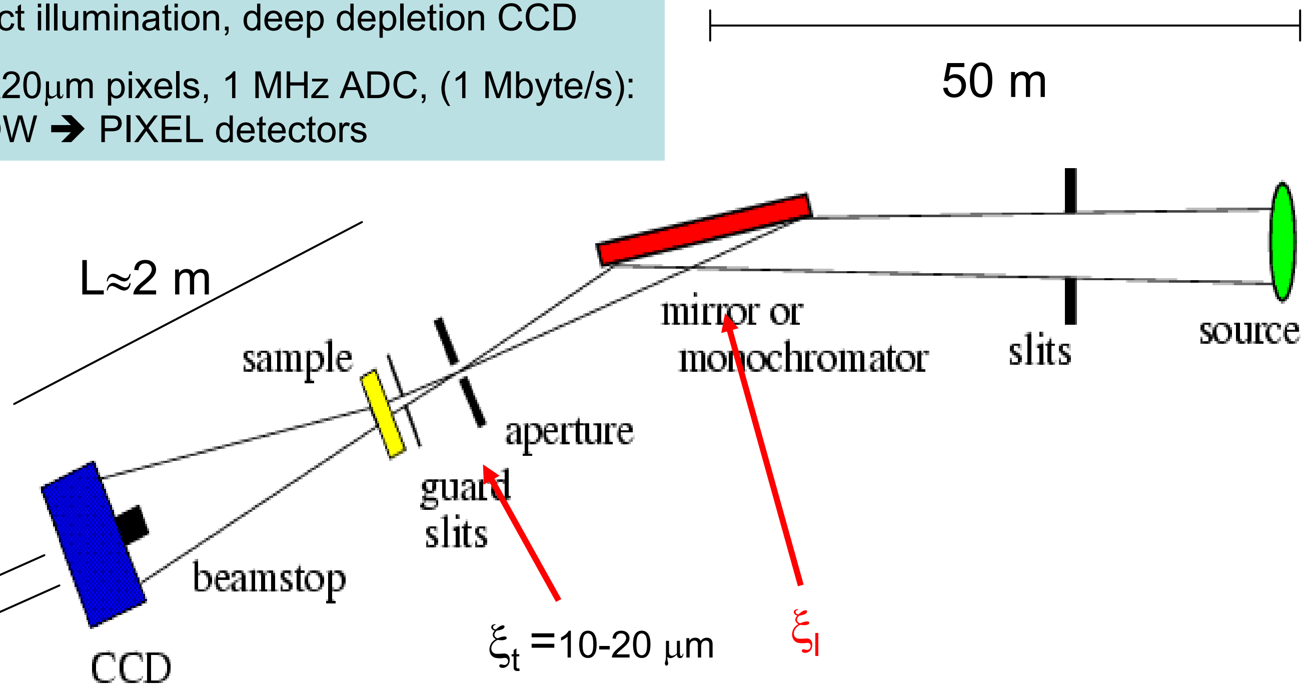
Beamline for coherent scattering

→ **Falus**

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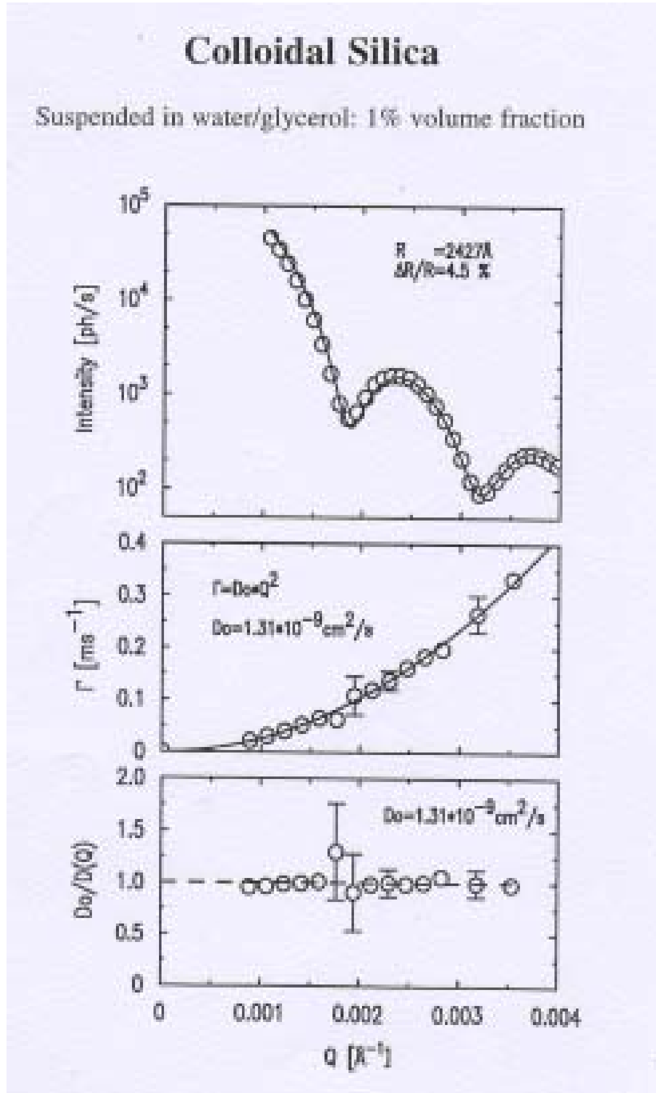
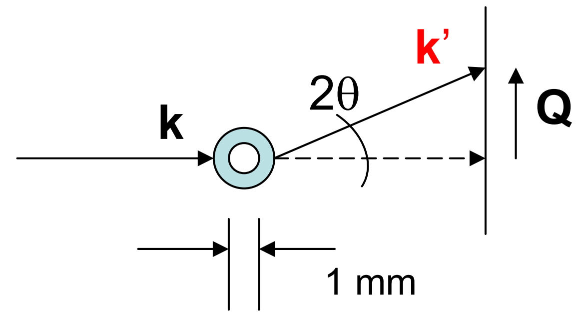
$I \sim |F(Q)|^2 S(Q)$

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

$\Gamma = D_o Q^2$





$Q = k' - k$

$Q = 2k \sin\theta$

$k = 2\pi/\lambda$

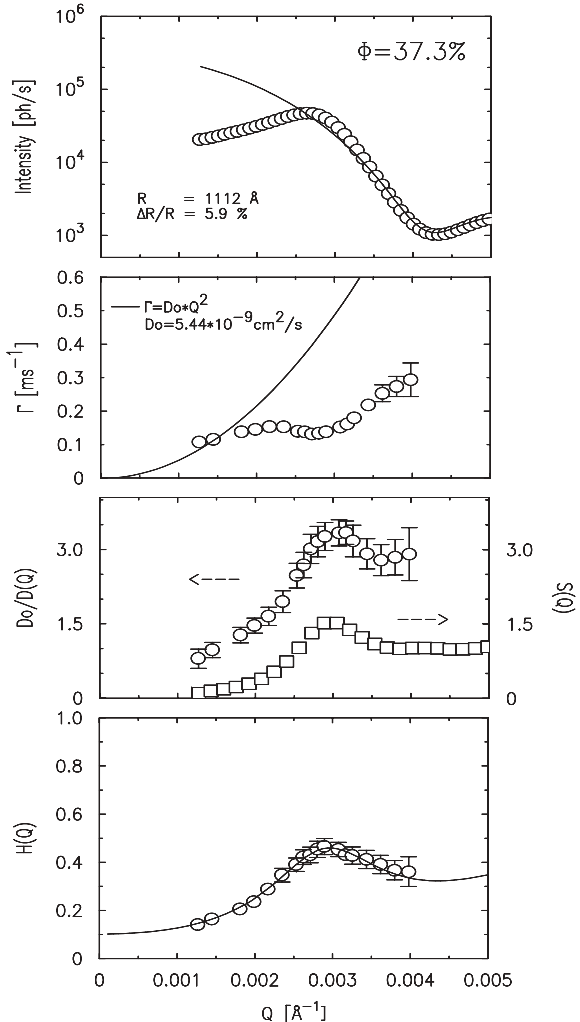
G. Grübel, A. Robert, D. Abernathy
8th Tohwa University International Symposium on "Slow Dynamics in Complex Systems", 1998, Fukuoka, Japan

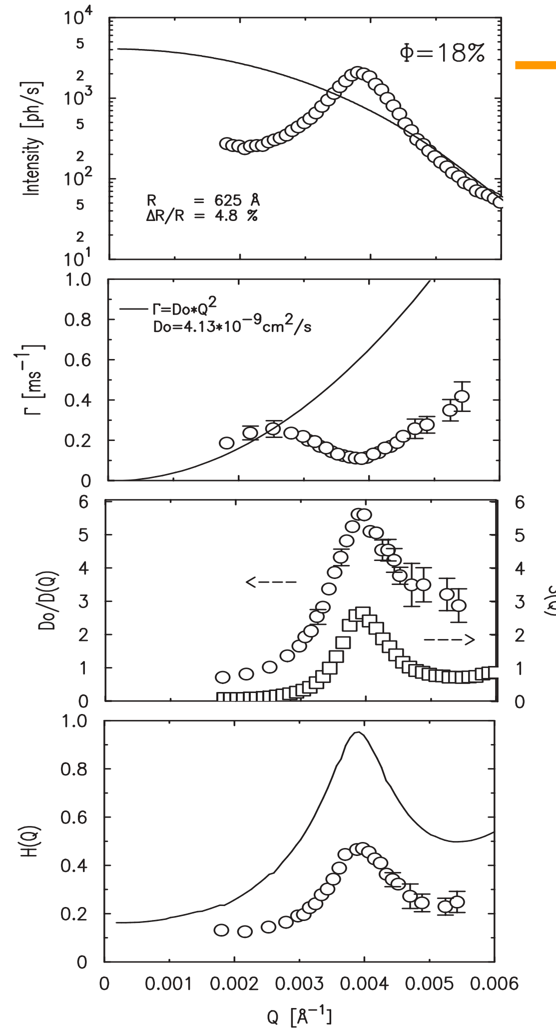
Poly-methylmetacrylate

37% volume fraction in cis-decaline
sterically stabilized (**hard-spheres**)

Poly-octafluoropentylcrylate

18% volume fraction in H_2O/glycerol
charge-stabilized (**soft-spheres**)





Robert Scheffold

$|F(Q)|^2$

$\Gamma = DoQ^2$

"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

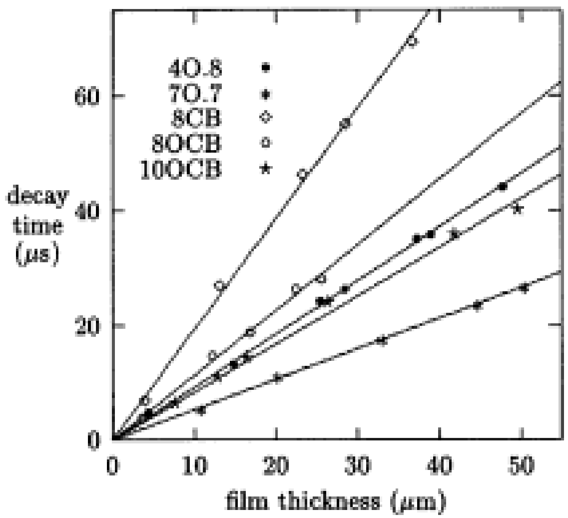
Zontone, Moussaid, Robert, Grübel

Robert, Härtl, Wagner, Grübel

Membrane Fluctuations

Motivation: **Study thermally driven layer fluctuations in freely suspended films of smectic liquid crystals**

Price, Sorensen, Kevan, Toner, Poniewierki & Holyst, PRL 82,755(1999)



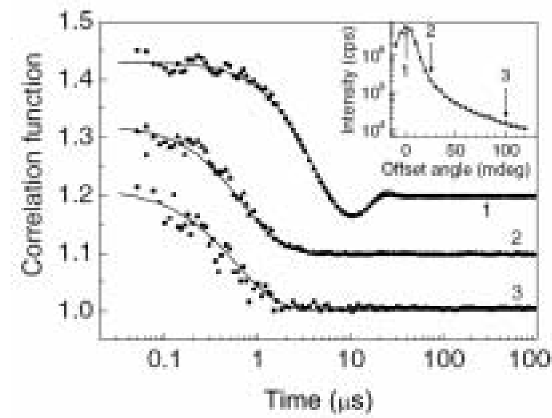
λ = 44 Å
ALS

$$\tau = \left(\frac{\eta}{2\gamma}\right) L$$

η layer sliding viscosity
γ surface tension
L layer thickness

Fera et al. PRL 85,2316 (2000)
Sikharulidze et al. PRL 88,115503 (2002)

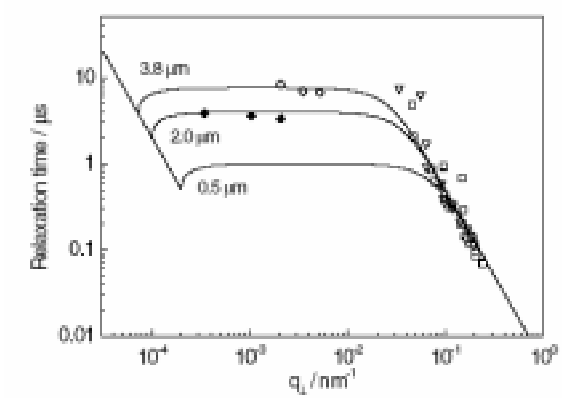
→ **Sikharudlidze**



λ = 1.54 Å, ESRF
2.83 μm
FPP
q_z = 2.18 mm^{-1}

(1) $q_x = 0$
(2) $q_x = 0.95\ 10^{-3}\ nm^{-1}$
(3) $q_x = 3.8 \cdot 10^{-3}\ nm^{-1}$

Sikharulidze et al. PRL 91,165504(2003)



8CB

□ NSE (λ=9 Å)
▽ NSE (λ=15Å)
◆ XPCS (λ=0.9 Å)

NOTE: heterodyning, sub-μs, overlap NSE

Capillary Wave Dynamics (1)

Synopsis:

Every liquid is subject to thermally excited capillary (surface) waves. Harmonic waves with $f = \omega_p + i\Gamma$ depending on wavevector q, surface tension γ, the dynamic viscosity η, and the density ρ of the liquid. The dispersion relation is given by:

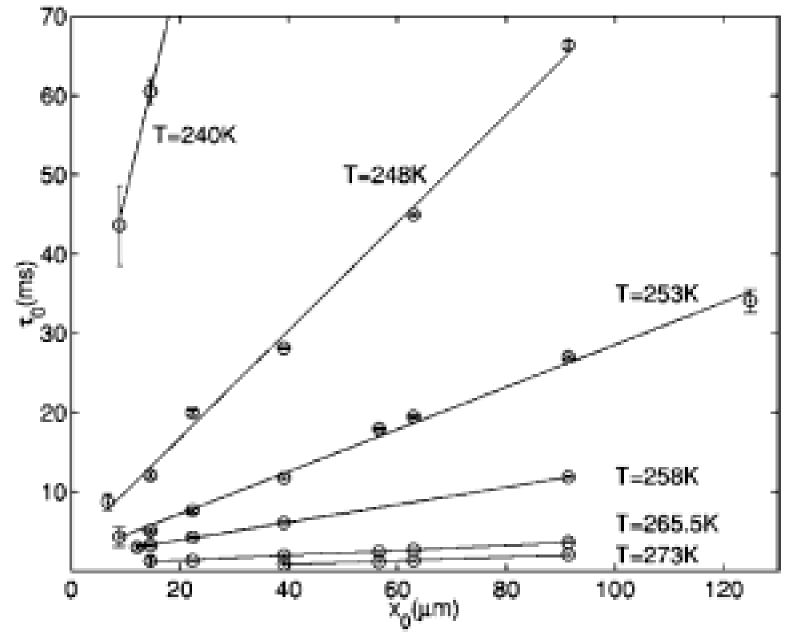
$$D(q,\omega) = gq + \gamma\, q^3/\rho - (\omega+2i\nu q^2)^2 - 4\nu^2 q^4 (1 - i\omega/(\nu q^2))^{1/2}$$

$\nu = \eta/\rho$: **kinematic viscosity**

$$S(q,\omega) = -2k_B T\ (q/\rho\omega) \cdot \mathit{Im}\, D(Q,\omega) / |D(q,\omega)|^2$$

Glycerol (λ=1.548Å) @ID10A

Seydel, Madsen, Tolan, Grübel, Press, PRB61,73409(2001)



Small damping limit ($\gamma\rho/4\eta^2 q_{||} > 0.145$):

$\Gamma = \Gamma_0 = (2\eta/\gamma) q_{||}^2 \qquad \omega = \omega_0 = \sqrt{(\gamma/\rho)}\, q_{||}^{3/2}$

"propagating waves"

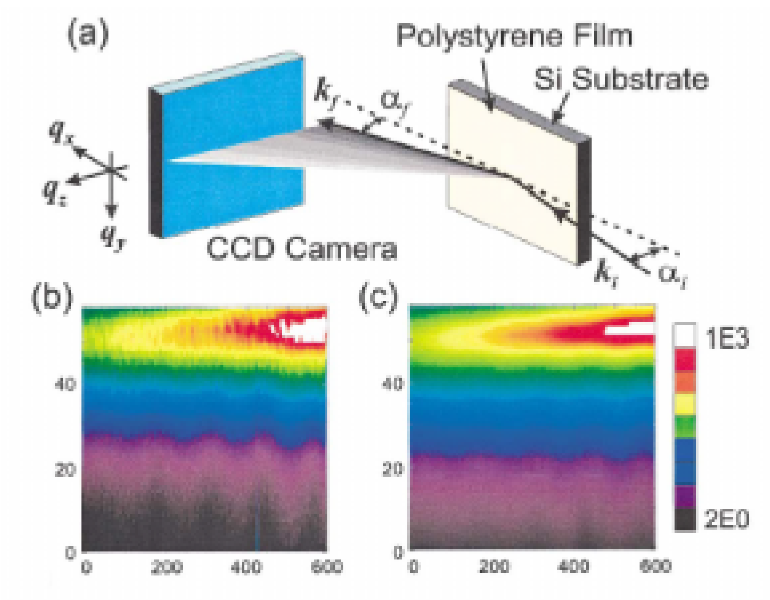
Large damping limit ($\gamma\rho/4\eta^2 q_{||} < 0.145$):

$\Gamma = (\gamma/2\eta) q_{||} \qquad \omega = 0 \quad \longrightarrow \quad \tau_0 = (1/\pi)(\eta/\gamma)\, x_0$

"overdamped waves"

Surface Dynamics of Polymer Films

Test the validity of models for film thicknesses h approaching the typical length scales of polymer chains (h→Rg)

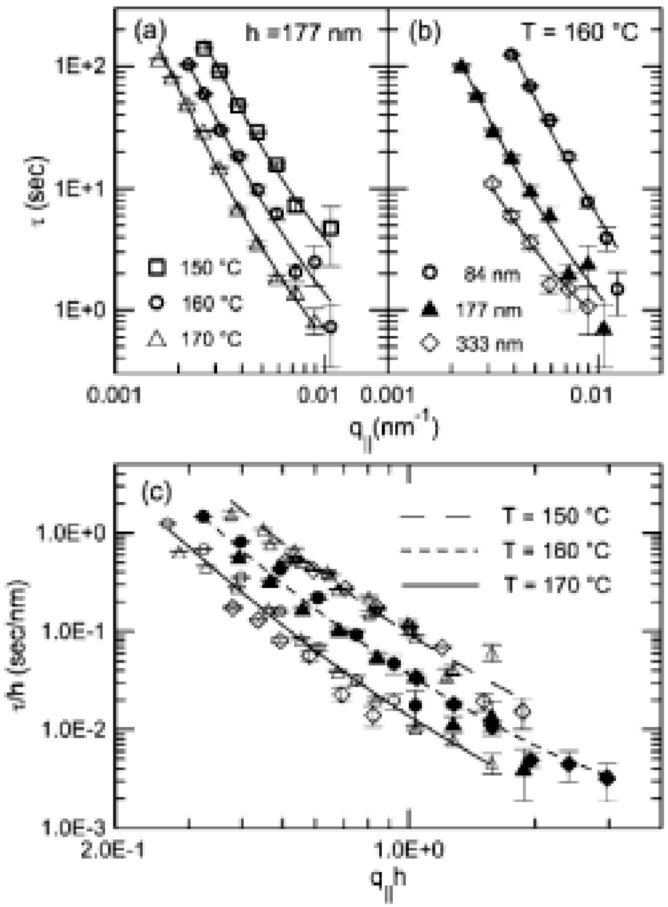


Kim, Rühm, Lurio, Basu, Lal, Lumma, Mochrie, Sinha, PRL 90,68302 (2003) @ APS 8-ID

→ **Lurio**

$$\tau \approx (2\eta/\gamma q_{||})\ (H/F)$$

$H=\cosh^2(q_{||}h)+q_{||}^2h^2$, $F=\sinh(q_{||}h)\cosh(q_{||}h)-q_{||}h$



Goal:

Study capillary waves at the transition from propagating to overdamped behaviour.

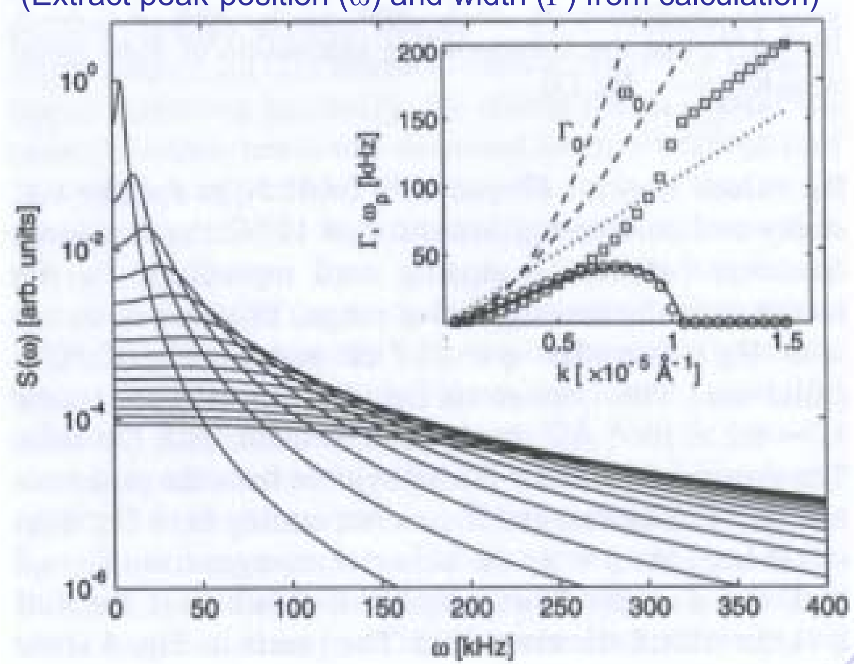
Model Calculation: Glycerol/Water

(linear response theory; Jäckle et al;. J. Phys.C.M. 7(1995)4351)

$\rho = 1156 kg/m^3; \eta = 18.8 cp; \sigma = 0.039 N/m;$
$q = 1,2,3,4......10^{-6}$ Å^{-1};

ω_p (o); Γ (□) ,

(Extract peak-position (ω) and width (Γ) from calculation)



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"propagating waves"

Large damping limit ($\gamma\rho/4\eta^2 q_{||} < 0.145$):

$\Gamma = (\gamma/2\eta) q_{||}$ $\omega = 0$

"overdamped waves"

Experiment:
65wt% Glycerol/Water

T=12 C

$q_c = 4\sigma\rho/5\eta^2$;

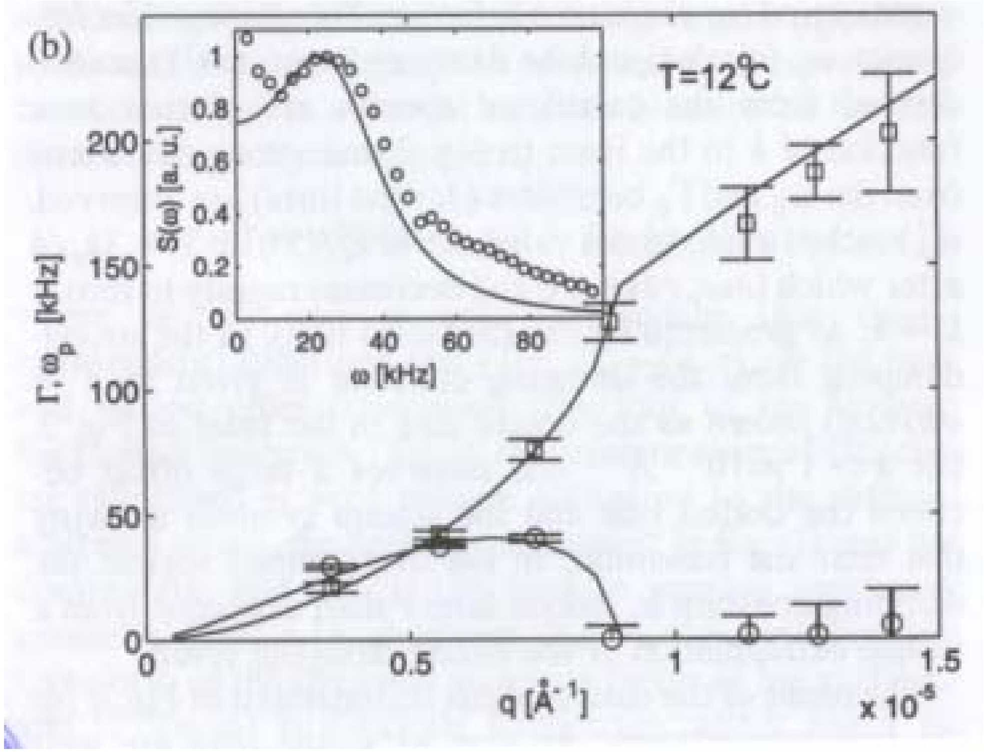
Measure capillary wave spectrum with a coherent x-ray beam (XPCS) in grazing incidence geometry (surface sensitivity).

The measured correlation function is a combination of homo- and heterodyne terms:

$g_2(q,\tau) = \alpha Re\{g_1(q,\tau)\} + \beta g_2(q,\tau) + \gamma$;

$g_1(q,\tau) = \exp(-\Gamma_0\tau)\cos(\omega_0\tau)$ (in the small damping limit).

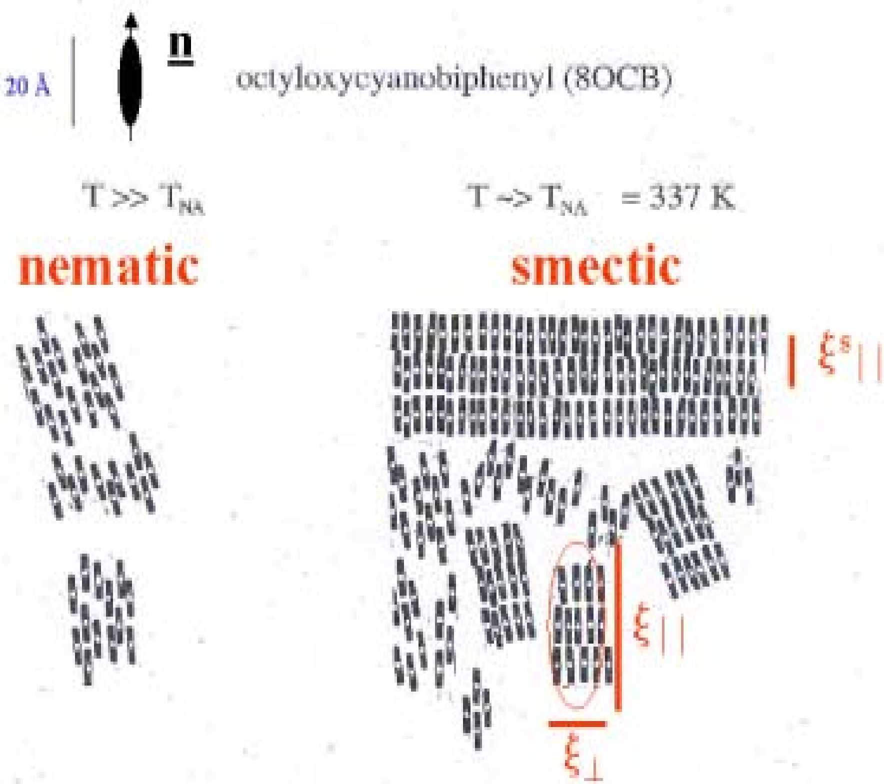
The reference signal for the heterodyne case is the specular reflectivity



Madsen, Seydel, Sprung, Gutt, Tolan, Grübel, PRL 92, 96104 (2004)

Viscosity of a Liquid Crystal near the Nematic-SmecticA Transition

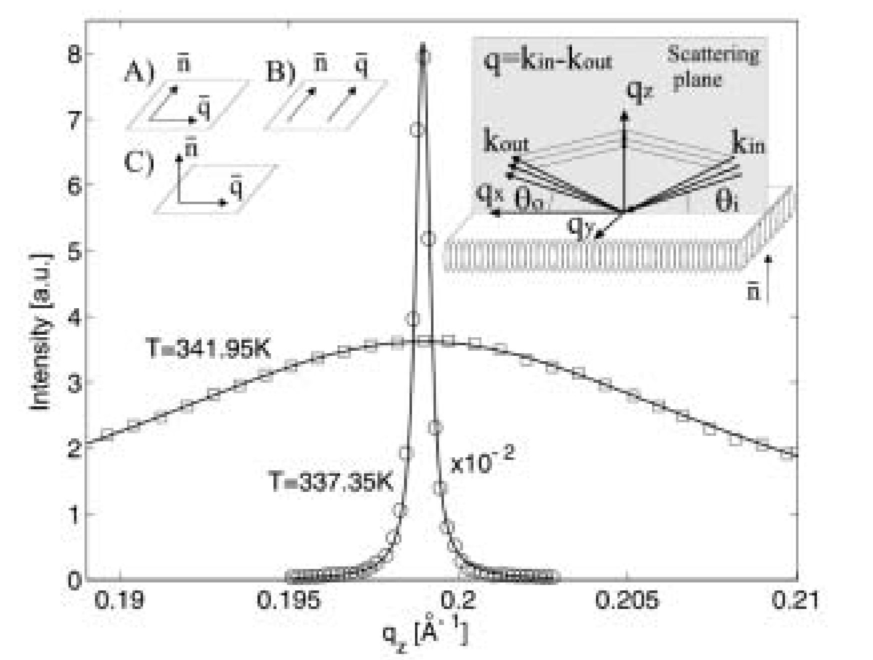
A. Madsen, J. Als-Nielsen and G. Grübel, PRL,90,85701(2003)



$\xi_{\parallel} \sim \{(T - T_{NA})/T_{NA}\}^{\nu_{\parallel}} = \xi^{s}_{\parallel}$

$\xi_{\perp} \sim \{(T - T_{NA})/T_{NA}\}^{\nu_{\perp}}$

$\nu_{\parallel} = 0.71;\ \nu_{\perp} = 0.58$



References: *Pershan and Als-Nielsen, PRL52,759(1984)*

Pershan, Braslau,Weiss, Als-Nielsen, PRA35,4800(1987)

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Dynamics:

viscosity is anisotropic: η_1, η_2, η_3

depending on the relative orientations: $\mathbf{n}, \mathbf{v}, \nabla \bullet \mathbf{v}$

described by Leslie coefficients $\alpha_1 \ldots \alpha_5$,
or parameters $\nu_1 \ldots \nu_5$ (Harvard notation)
($\nu_4 = \nu_5 = 0$ for incompressible fluids)

Theory: (N-SmA transition)

$$\eta_1 \sim \exp(E_A/kT)$$

$$\eta_2 \sim \exp(E'_A/kT)$$

$$\eta_3 = c(T-T_{NA}/T_{NA})^{-\beta} + \text{non.div.}$$

Predictions:

$\beta = 3\nu_{||} - 2\nu_{\perp}$ [1]

$\beta = 1/3$ [2]

$\beta = 1/2$ [3]

[1] Hossein, Swift, Chen, Lubensky, PRB19,432(1979)

[2] Jähnig,Brochard, J.Phys.,35,301(1974); deGennes, Sol. State Comm., 10,753(1972)

[3] Langevin, J.Phys.37,101(1975)

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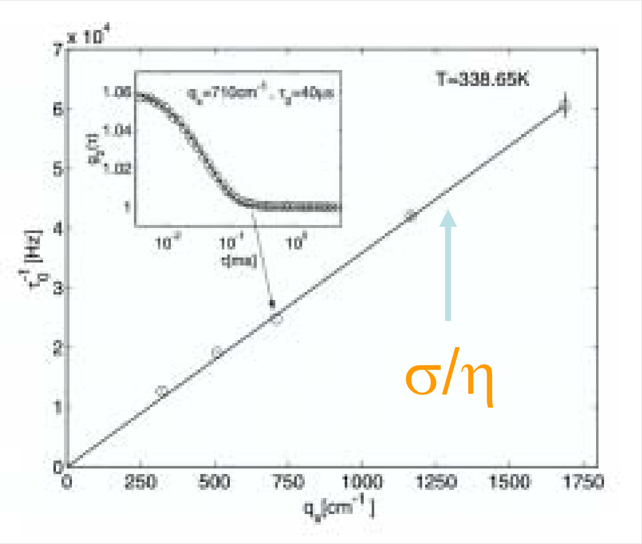
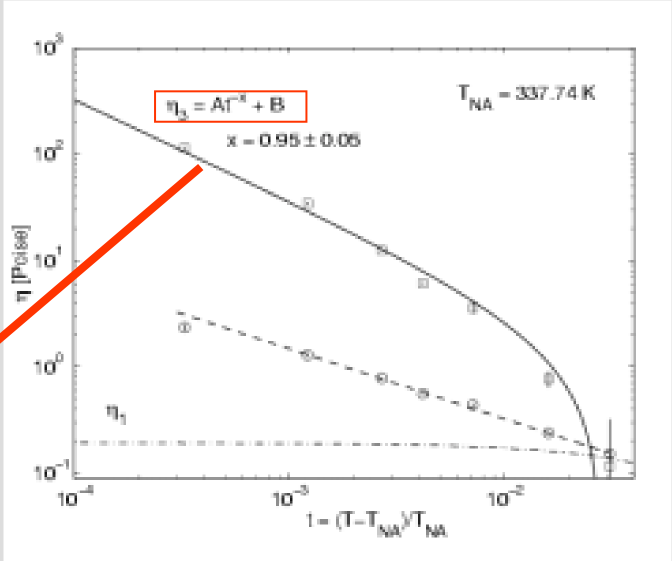


XPCS: overdamped modes



η / σ diverging
σ constant [1]; data reflect temperature dependence of viscosity

$\eta_3 \sim (T\text{-}T_{NA}/T_{NA})^{-\beta}$

$\beta = 0.95(2)$

<u>in agreement with theory [1]:</u>

$\beta = 3\nu_{||} - 2\nu_{\perp} = 0.94$

$\nu_{||} = 0.70$; $\nu_{\perp} = 0.58$ (static data)

- Out-plane movements (ζ || n) within the smectic layers are strongly damped (η_3 critical).
- The smectic layers remain viscous in-plane (η_2 non-critical)

Non-Equilibrium Dynamics (1)

Non-equilibrium Dynamics

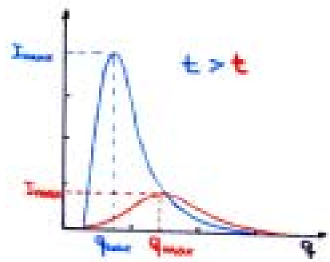
Domain coarsening in phase separating systems (glasses, alloys,…) e.g. after quenching, aging…

A B

quench

A-rich B-rich

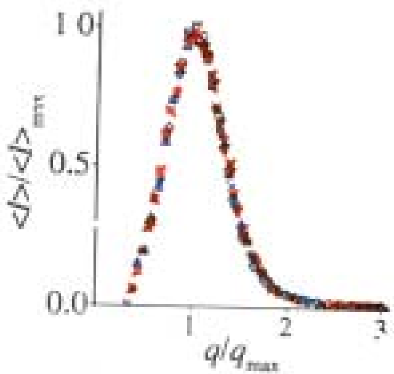
< R(t) >



Mullins J. Appl. Phys. 59, 1341, 1986
Guston, San Miguel, Sahni: „Phase Transitions and Critical Phenomena“

Dynamic Scaling: $< R(t) > \propto t^{n}$

n=1/3 conserved order parameter (model B)
n=1/2 non-cons. order parameter (model A)



$<I> (q,t)/<I>_{max} = F (q/q_{max})$

XPCS: investigate fluctuations around the average scaling behaviour: $\tau = \tau (q,t)$

Al Li: Livet et al. (ID10) PRE(2001),63,36108

Cu_3Au: Fluerasu et al. PRL(2005),94,55501

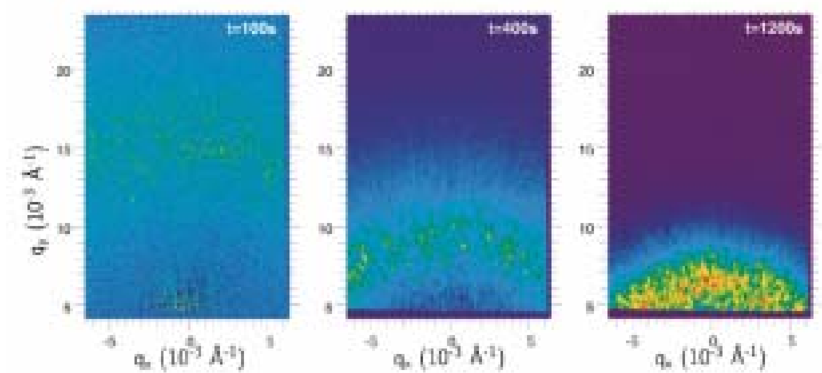
Phase – separating Glass

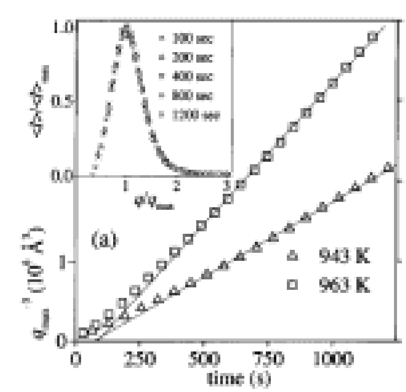
Malik et al., PRL 81, 5832, 1998

$(Na_2O)_{0.07}(B_2O_3)_{0.22}(SiO_2)_{0.71}$ T=1033K

quench

(B_2O_3)-rich (SiO_2)-rich 943K<T<963K





$< R(t) > \sim t^{n}$ →

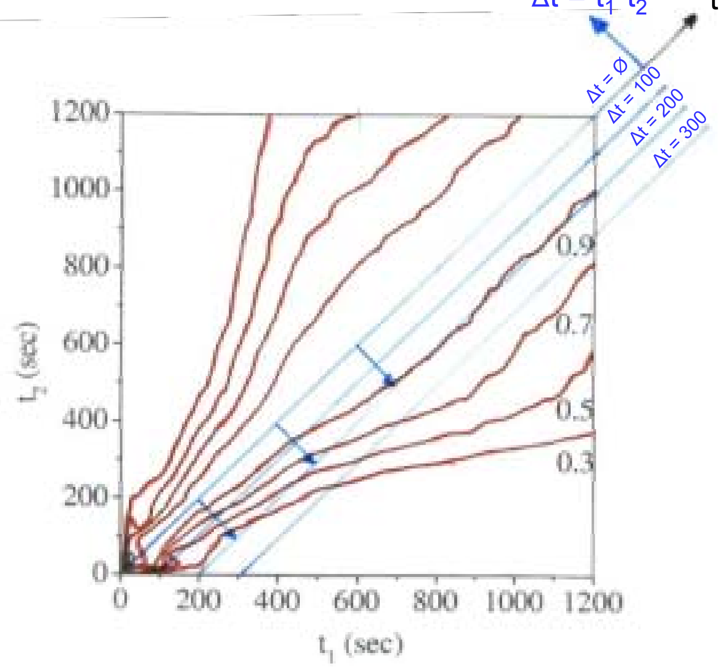
$q_{max} = [A(t-t_o)]^{-n}$

n=1/3

Two time correlation function:

$$C(q,t_1,t_2) = \frac{\langle I(t_1)\, I(t_2)\rangle - \langle I(t_1)\rangle \langle I(t_1)\rangle}{[\langle I^2(t_1)\rangle - \langle I(t_1)\rangle^2]^{1/2}\, [\langle I^2(t_2)\rangle - \langle I(t_1)\rangle^2]^{1/2}}$$

$\Delta t = t_1 - t_2$ $\qquad \bar{t} = \frac{t_1 + t_2}{2}$



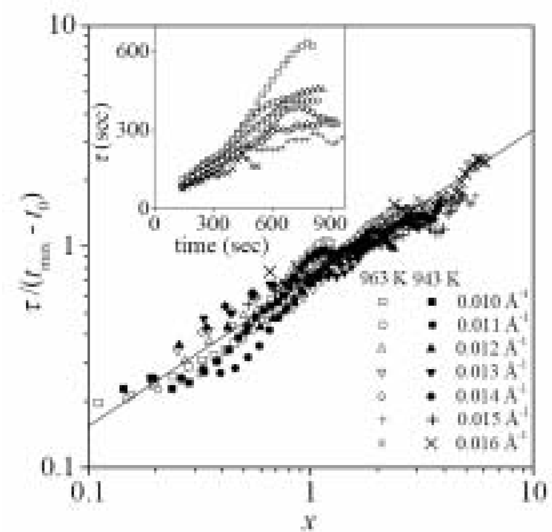
$\tau = \tau\,(\,t\,)$

Fluctuations $\tau = \tau\,(\,q,t\,)$

Prediction: Brown et al. PRE 56,6601,1997

$$\tau(q,t) = [t_{max}(q)-t_o]\,\{\underbrace{a\,[t-t_o]\,/\,[t_{max}(q)-t_o]}_{x}\}^{(1-n)} \sim \frac{1}{q}\; t^{2/3}$$

$$B\,[t_{max}(q)-t_o] = q^{-1/n}$$



a = 0.72(2) **(1-n) = 0.65(4)** $\hat{=}\ 1 - ⅓$

Malik et. al., PRL 81,5832,1998

→ **Ludwig, Sutton**

Magnetic Colloidal Particles

→ **Eisebitt**
Chesnel

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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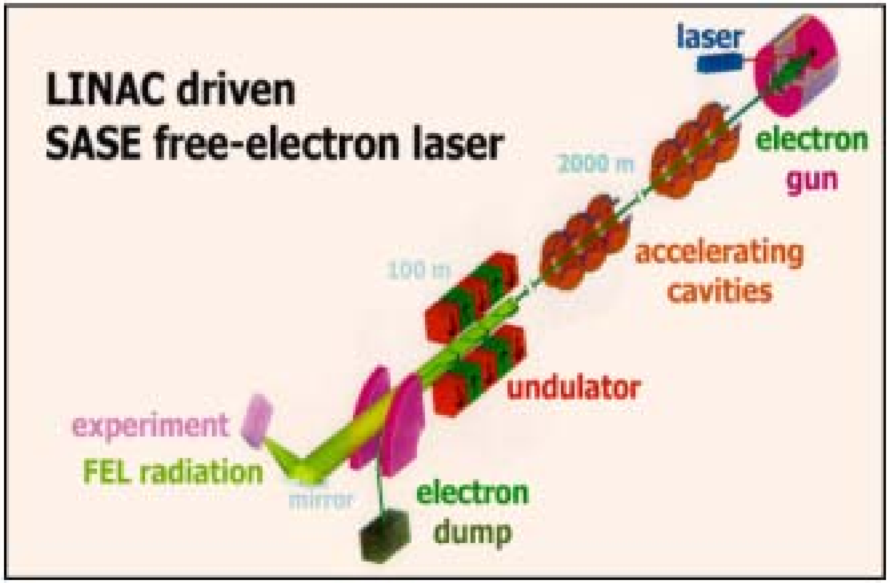
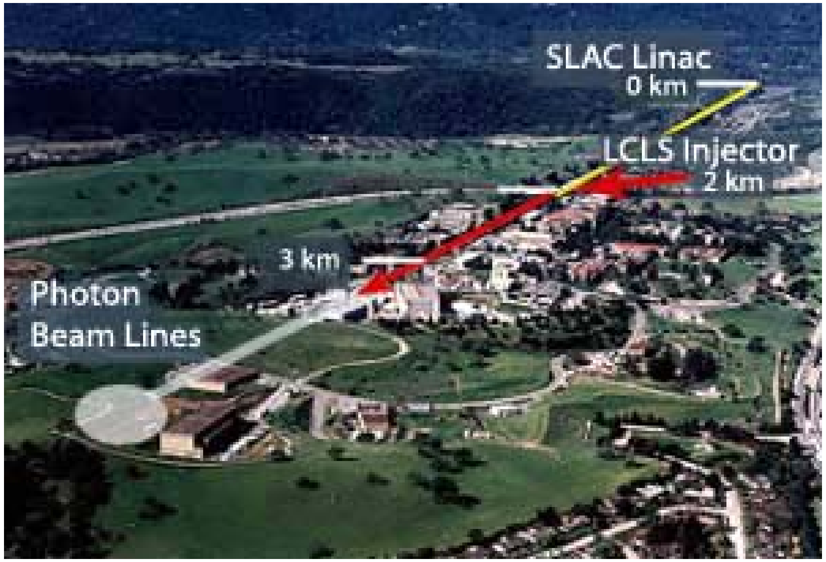
X-Ray Free Electron Laser(s)



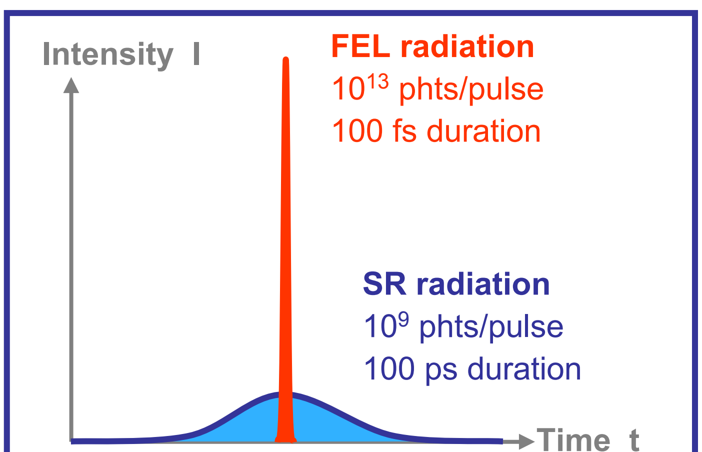


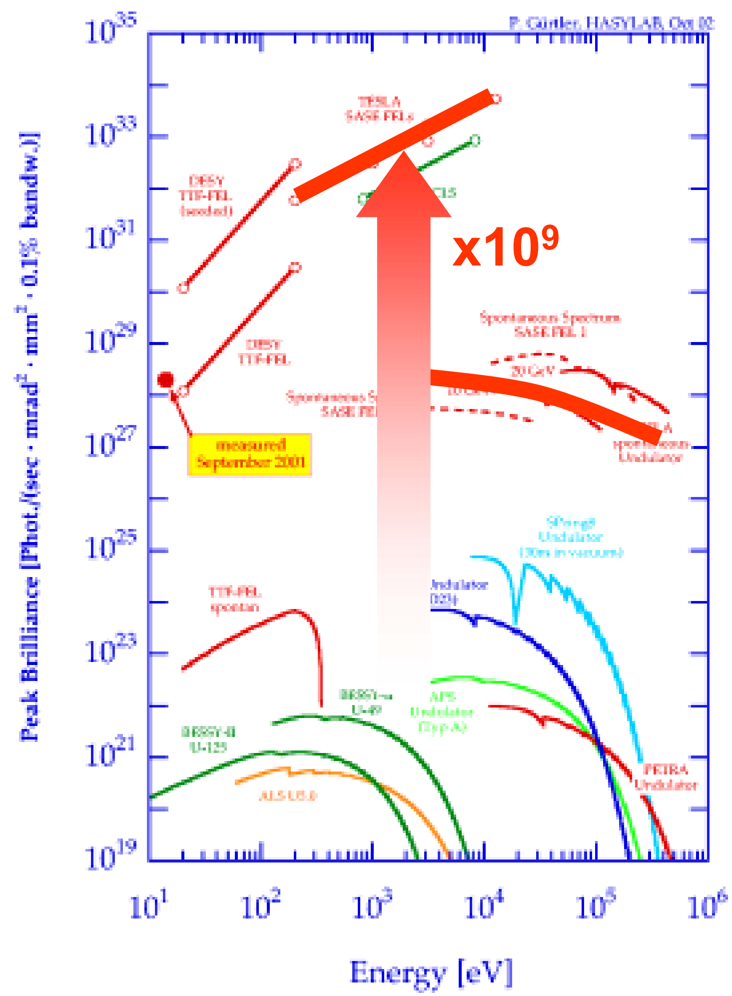
X-ray FEL radiation (0.2 - 14.4 keV)

- ultrashort pulse duration 100 fs
- extreme pulse intensities 10^{12}-10^{14} ph
- coherent radiation $x10^9$
- average brilliance $x10^4$

Spontaneous radiation (20-200 keV)

- ultrashort pulse duration <200 fs
- high brilliance





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 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 nonlinear phenomena →

- Nonlinear effects in atoms and solids
- High field science

Coherence   Ultrashort pulses   Pulse intensities   Average brilliance

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 fully (spatially) coherent beams with a time averaged coherent flux: $\langle F_c \rangle \cong 10^{16}$ 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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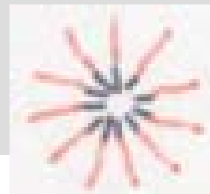
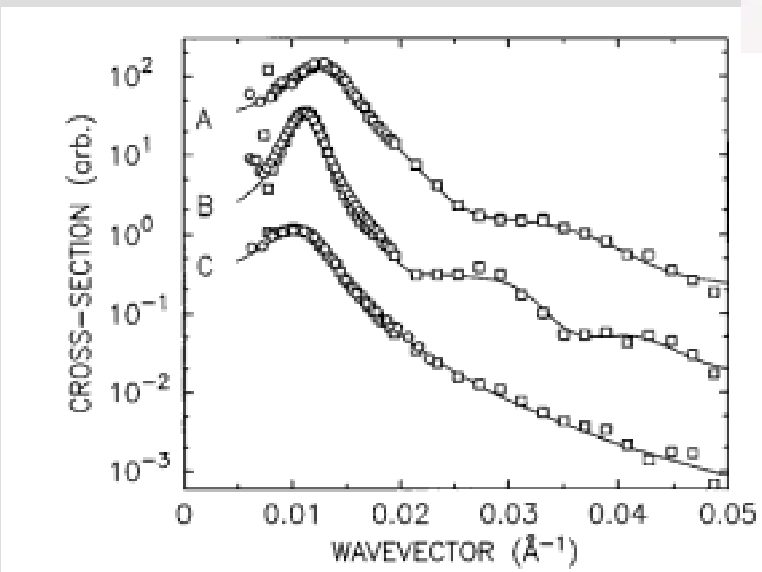
The End

Complex Fluids (2): Copolymer Micelles

Dynamics of Block Copolymer Micelles

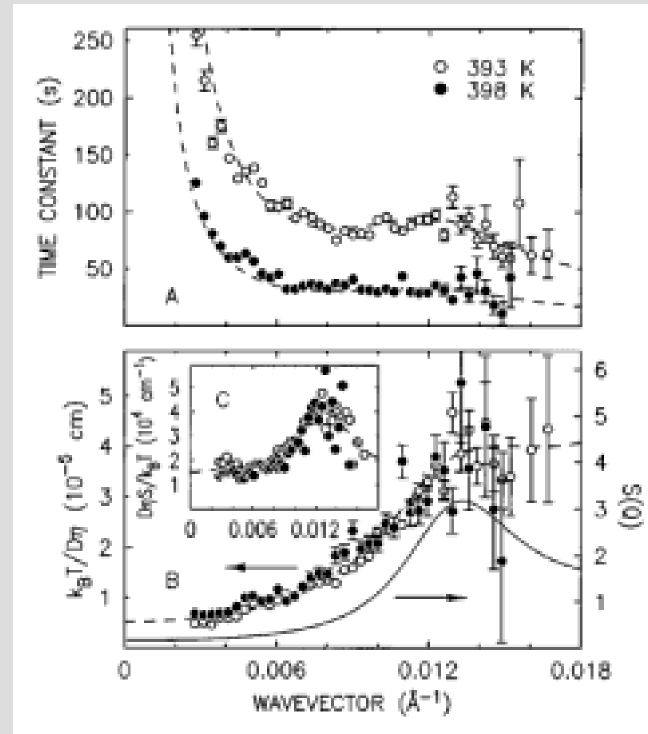
- ▪ Study of molecular scale dynamics of block copolymer melts.
- ▪ Samples: Polystyrene polyisoprene block copolymers in a polystyrene monopolymer matrix (Tg ~ 360K)
  - Spherical micelles (radius ~240 Å, PI core ~ 180 Å
  - Cylindrical (worm-like) micelles





S. Mochrie, A. Mayes, A. Sandy, S. Brauer, B. Stephenson, G. Grübel, D. Abernathy, M. Sutton PRL 78, 1275 (1997)

Spherical Micelles

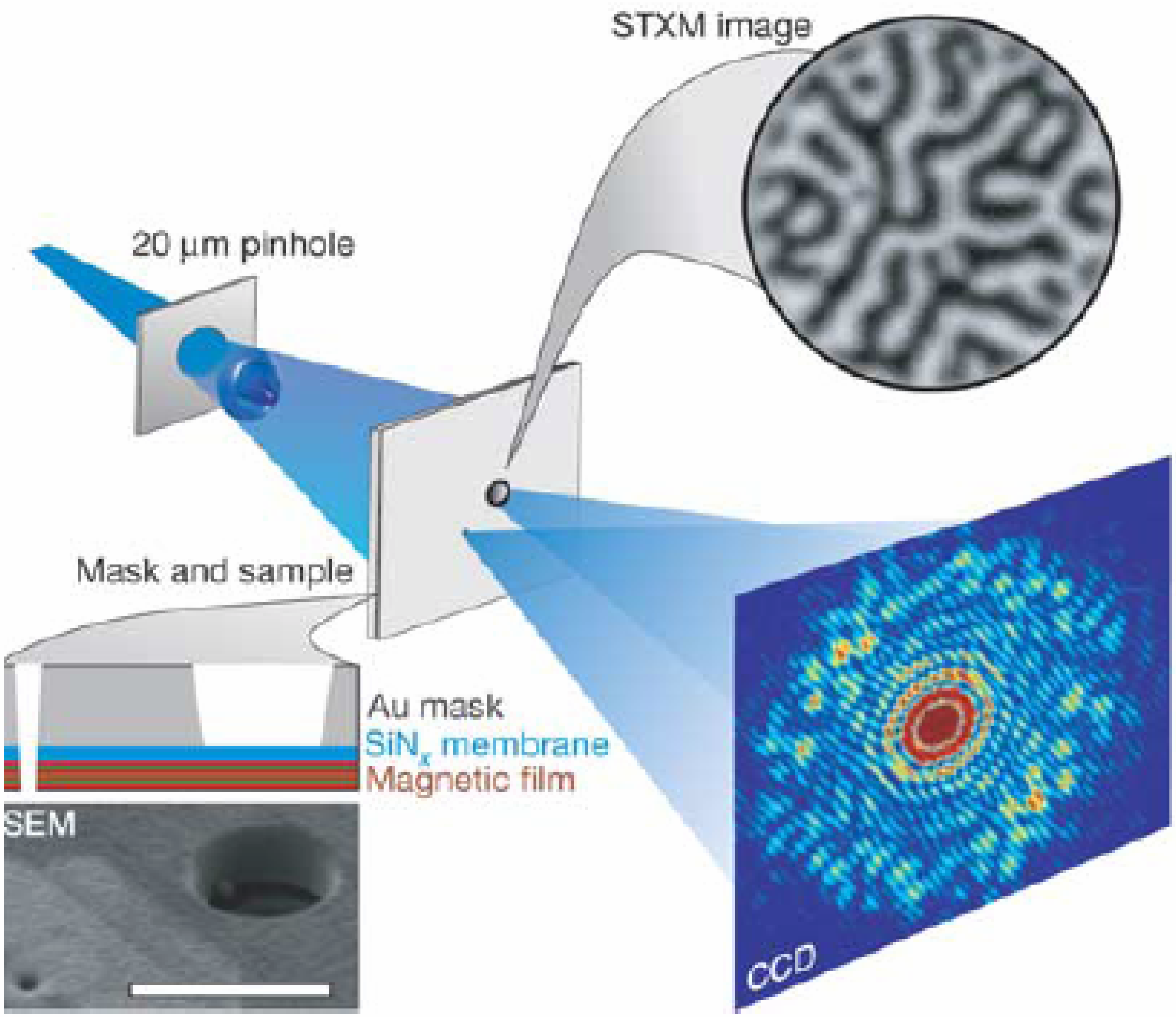


- ▪ The spherical micelles show Q-dependent diffusion, which is expected for densely packed spheres.

- ▪ The data taken at different temperatures collapse on a single curve when scaled by the viscosity of the homopolymer matrix and the temperature.

D(q) ▪ S(q) not constant
(hydrodynamic interactions between particles, mediated by suspending medium are important)

Lensless Imaging of magnetic Nanostructures



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 L_{III} 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)