Soft Matter Studies with X-rays

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ESRF – The European Synchrotron

M. Mitov, *Sensitive Matter - Foams, Gels, Liquid Crystals, and Other Miracles* (Harvard University Press, 2012)

T. Narayanan, *in Structure from Diffraction Methods*, Eds. D.W. Bruce, D. O'Hare & R.I. Walton, (Wiley, 2014)

W. de Jeu, *Basic X-ray Scattering for Soft Matter*, (Oxford University Press, 2016)

Outline

- What is Soft Matter?
- Some general features
- Different X-ray techniques employed
- Self-assembly & complexity
- Out-of-equilibrium phenomena
- Summary and outlook

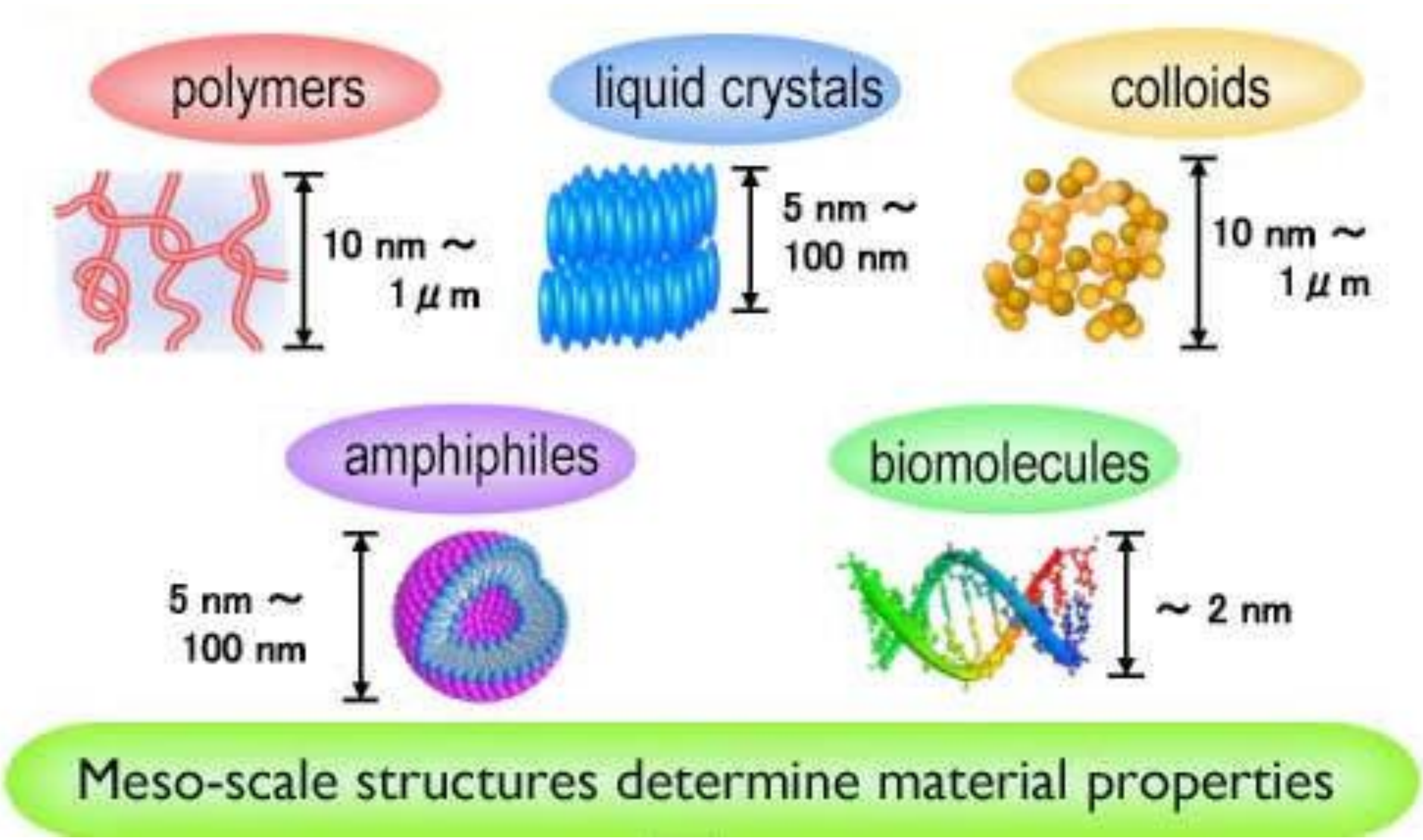
What is Soft Matter?

Soft matter is a subfield of condensed matter comprising a variety of physical states that are easily deformed by thermal stresses or thermal fluctuations. They include liquids, colloids, polymers, foams, gels, granular materials, and a number of biological materials. These materials share an important common feature in that predominant physical behaviors occur at an energy scale comparable with room temperature thermal energy. At these temperatures, quantum aspects are generally unimportant. Pierre-Gilles de Gennes, who has been called the "founding father of soft matter,“ received the Nobel Prize in physics in 1991 for discovering that the order parameter from simple thermodynamic systems can be applied to the more complex cases found in soft matter, in particular, to the behaviors of liquid crystals and polymers.

Matière molle » Madeleine Veyssié

Today soft matter science is an interdisciplinary field of research where traditional borders between physics and its neighboring sciences such as chemistry, biology, chemical engineering and materials science have disappeared.

Soft Matter Systems



SAXS, WAXS, USAXS, GISAXS
(SANS, USANS, GISANS, etc.)

Soft Matter Features

Materials which are soft to touch – characterized by a small elastic modulus (energy/characteristic volume), typically 10^9 – 10^{12} times lower than an atomic solid like aluminum.

Dominance of entropy

Strong influence of thermal fluctuations (~ $k_B T$)

Characteristic size scale or microstructure ~ 100 – 1000 nm

Shear modulus, G ~ Energy/Free volume » 10^9 – 10^{12} smaller

Low shear modulus (G) » soft and viscoelastic

Soft Matter studies seek to address the link between microscopic structure/interactions and macroscopic properties.

A significant fraction of consumer products fall in this category.

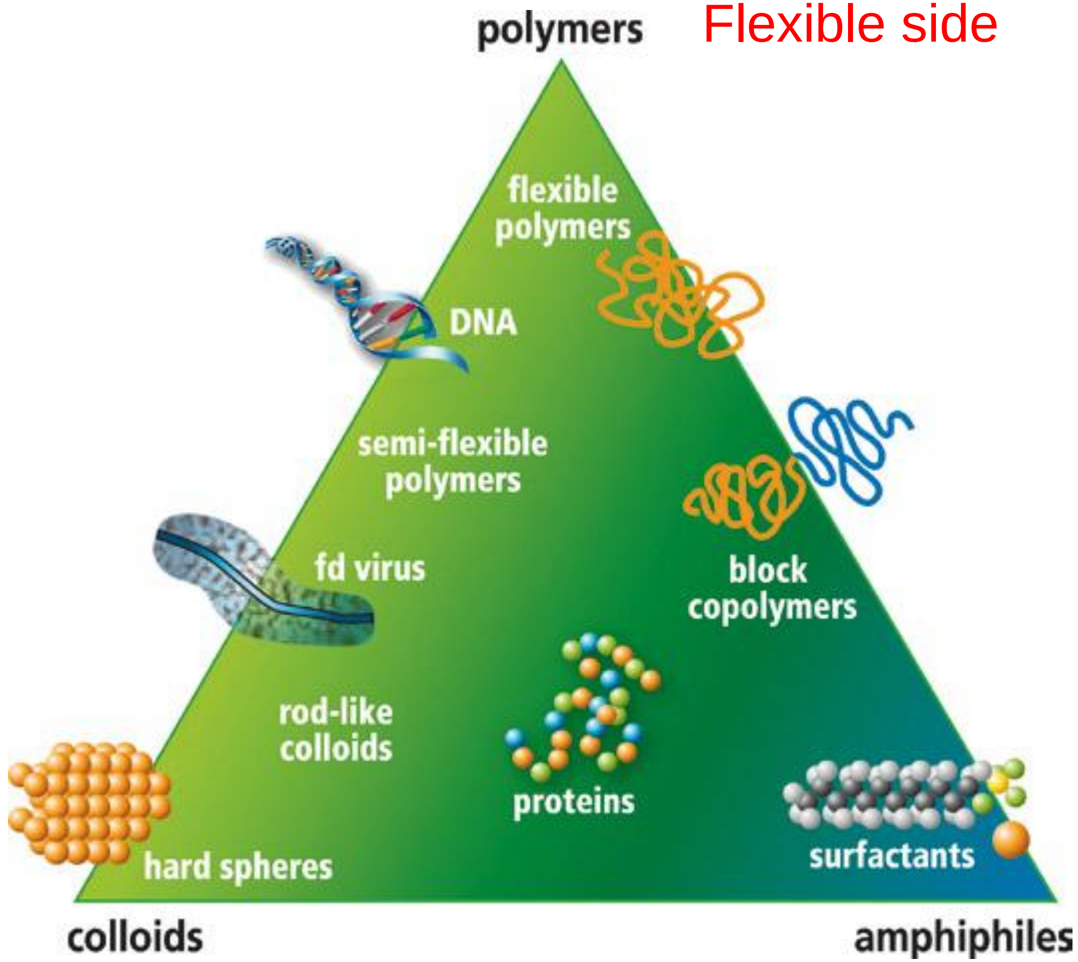
Soft Matter: Encounter in everyday life

Sustainable development and supply of consumer products

Soft Matter Triangle

3 main ingredients of soft matter

Flexible side



Harder side

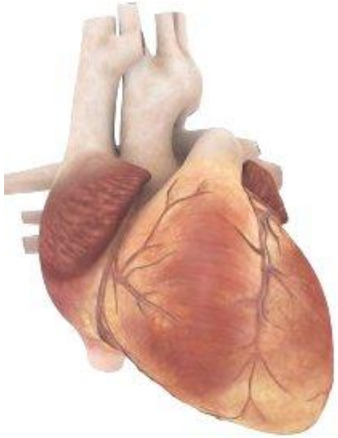
Selective side

Soft Matter Characteristics

Soft implies: (1) high degree of tailorability

Multi-scale out-of-equilibrium systems

(2) lack of robustness



Learning from biology

Impact of Soft Matter in Condensed Matter Physics

Over the last 40 years

- Critical Phenomena (static and dynamic)
- Freezing, glass transitions, etc.
- Fractal growth (e.g. colloid aggregation)
- Self-organized criticality (granular matter)

Soft Matter constitutes a significant fraction of modern day Nanoscience/Nanotechnology.

Synchrotron Techniques used in Soft Matter

Synchrotron Radiation Studies of Soft Matter

- ***High spectral brilliance or brightness***

Real time studies in the millisecond range, micro/nano focusing and high *q* resolution

Time-resolved SAXS, WAXS, micro-SAXS, USAXS, etc.

High detectivity for studying extremely dilute systems ($\phi < 10^{-6}$)

- ***Partial coherence***

Equilibrium dynamics using the coherent photon flux (for concentrated systems)

Photon correlation spectroscopy (XPCS)

- ***Continuous variation of incident energy***

Contrast variation of certain heavier elements, e.g. Fe, Cu, Se, Br, Rb, Sr, etc.

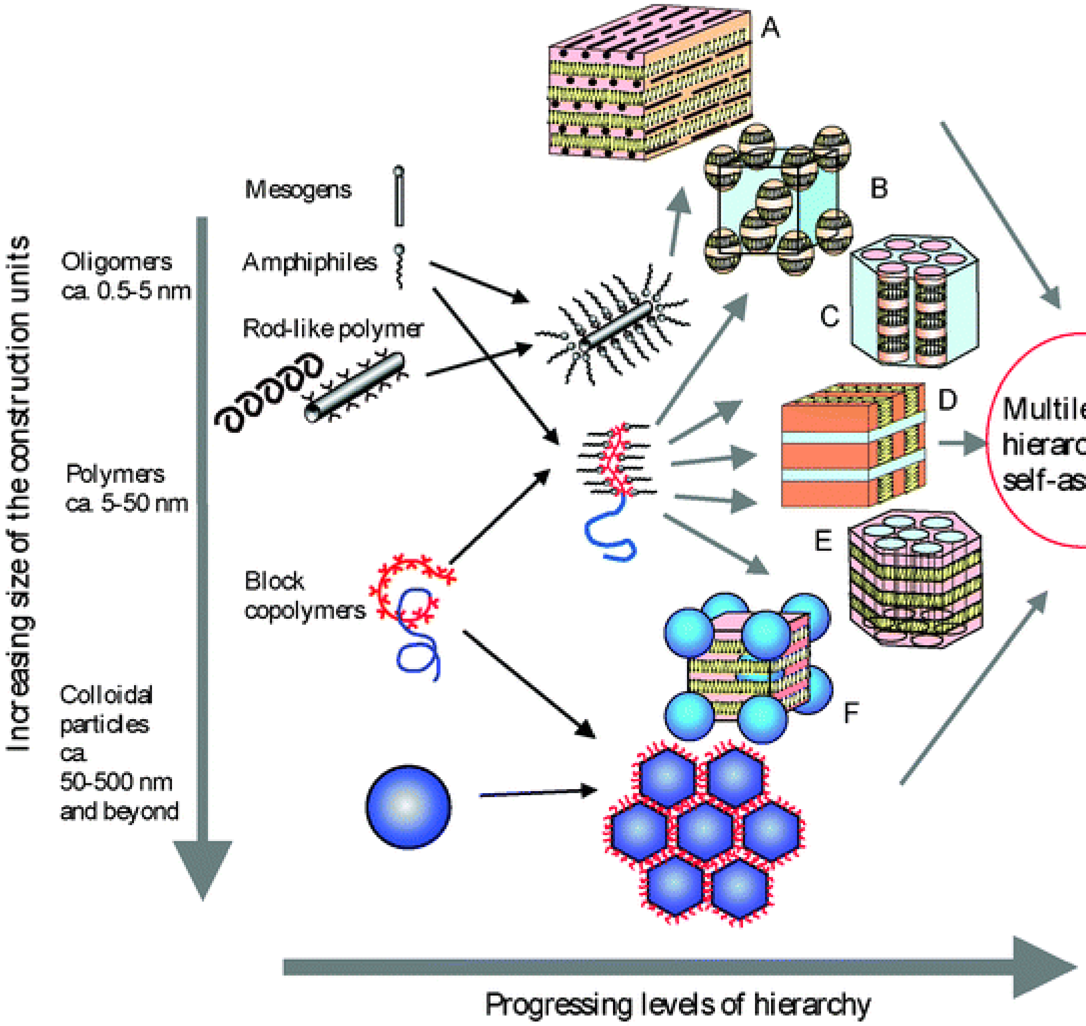
Anomalous Scattering – contrast variation

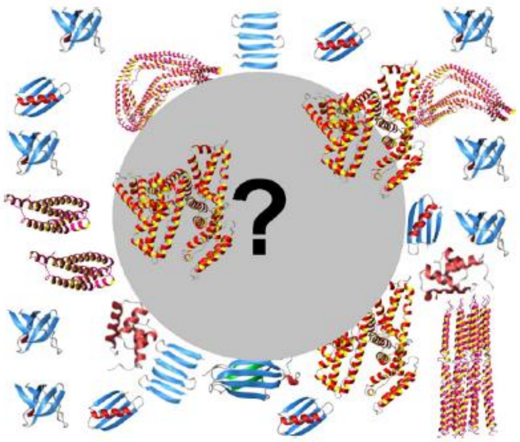
- ***Complementary imaging techniques***

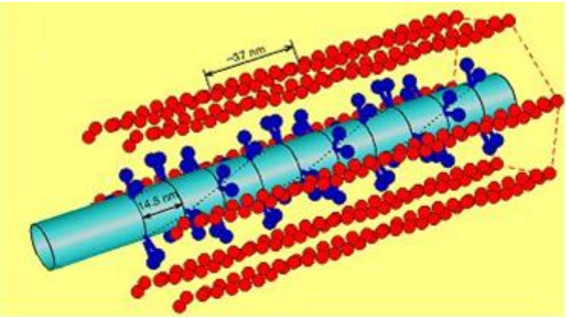
X-ray microscopy, micro and nano tomography, etc.

Soft Matter: Increasing levels of complexity

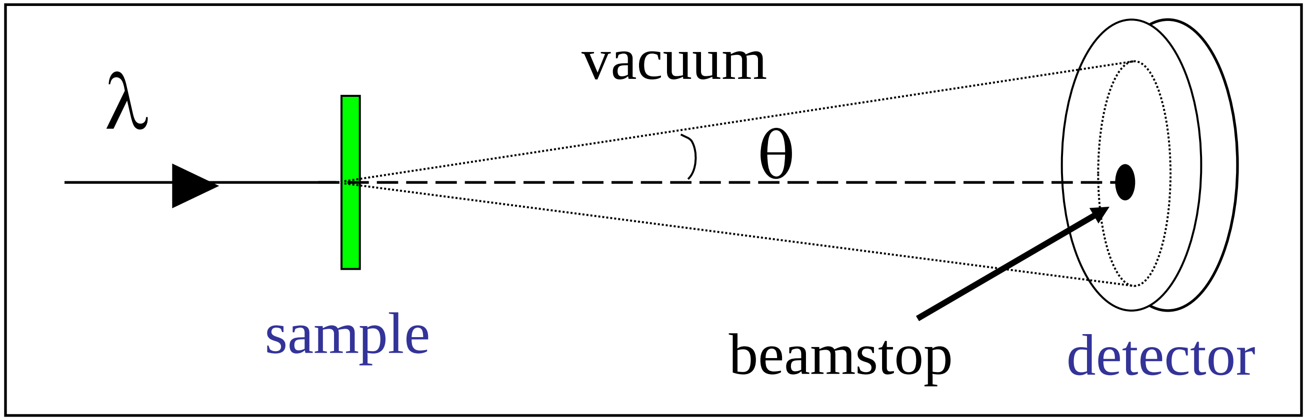
Elucidating the pathways of self-assembly

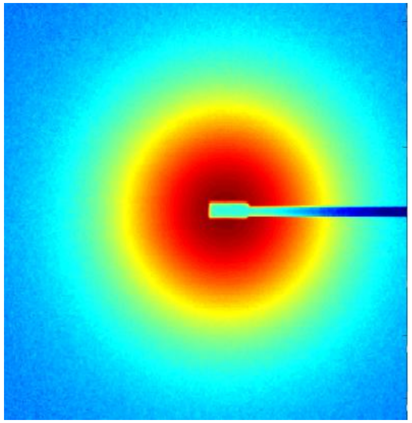






Small-Angle X-ray Scattering (SAXS)





$$q = \frac{4\pi}{\lambda}\sin(\theta/2)$$

Measured Intensity: $I_S = i_0\, T_r\, \varepsilon\, \Delta\Omega \frac{d\sigma}{d\Omega}$ Differential scattering cross-section

i_0 - incident flux
T_r - transmission
ε - efficiency
$\Delta\Omega$ - solid angle

$$I(q) = \frac{d\Sigma}{d\Omega} = \frac{1}{V_{Scat}} \frac{d\sigma}{d\Omega}$$

Beamline – ID02

Ultra SAXS/SAXS/WAXS

Beamline ID02

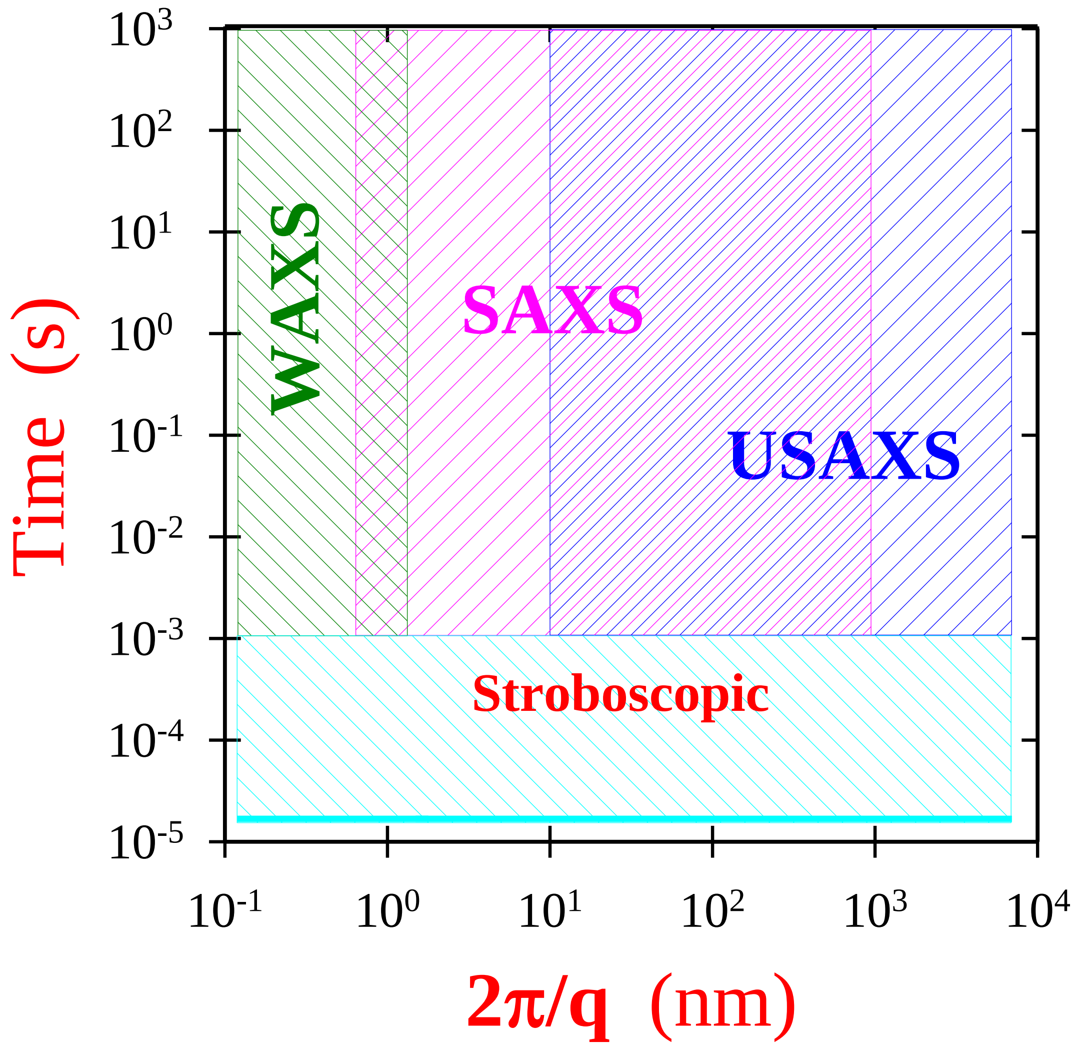
Sample-detector distance: 1 - 31 m

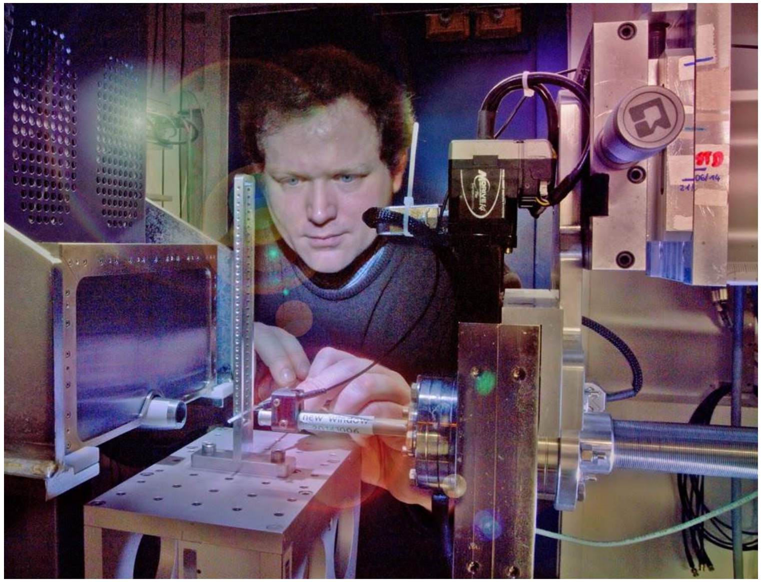
WAXS Setup

Energy range: 8–20 keV
q – range: 10^{-3} – 50 nm^{-1}
Δq: 5×10^{-4} nm^{-1} (FWHM)
Time resolution: < 100 µs

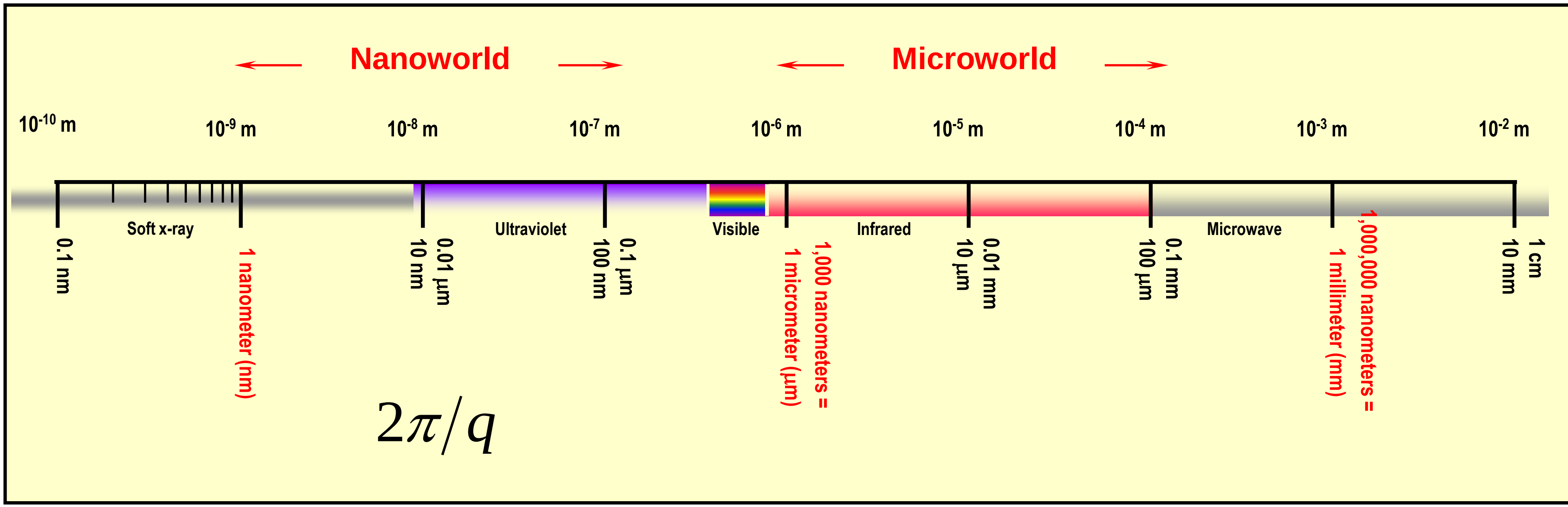
Ultra SAXS/SAXS/WAXS

Beamline ID02

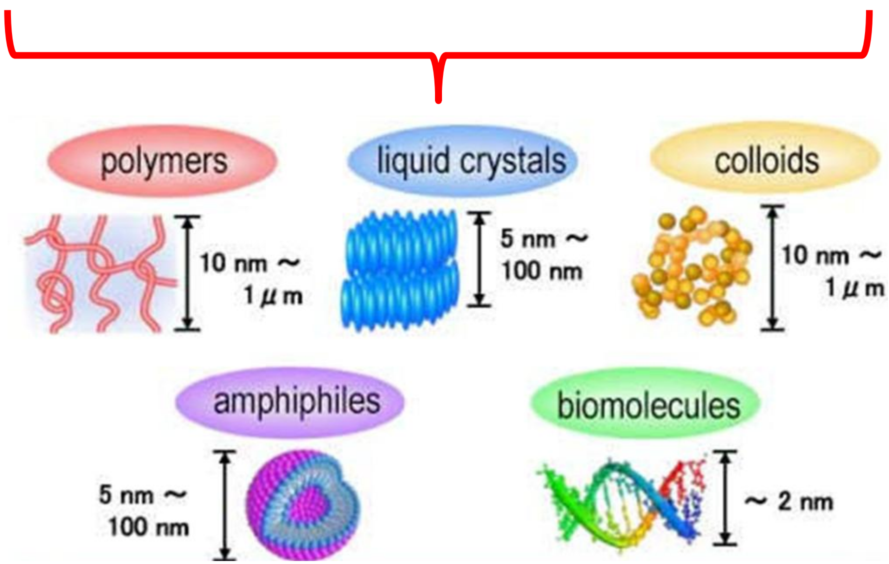




Size scales probed by SAXS & related techniques

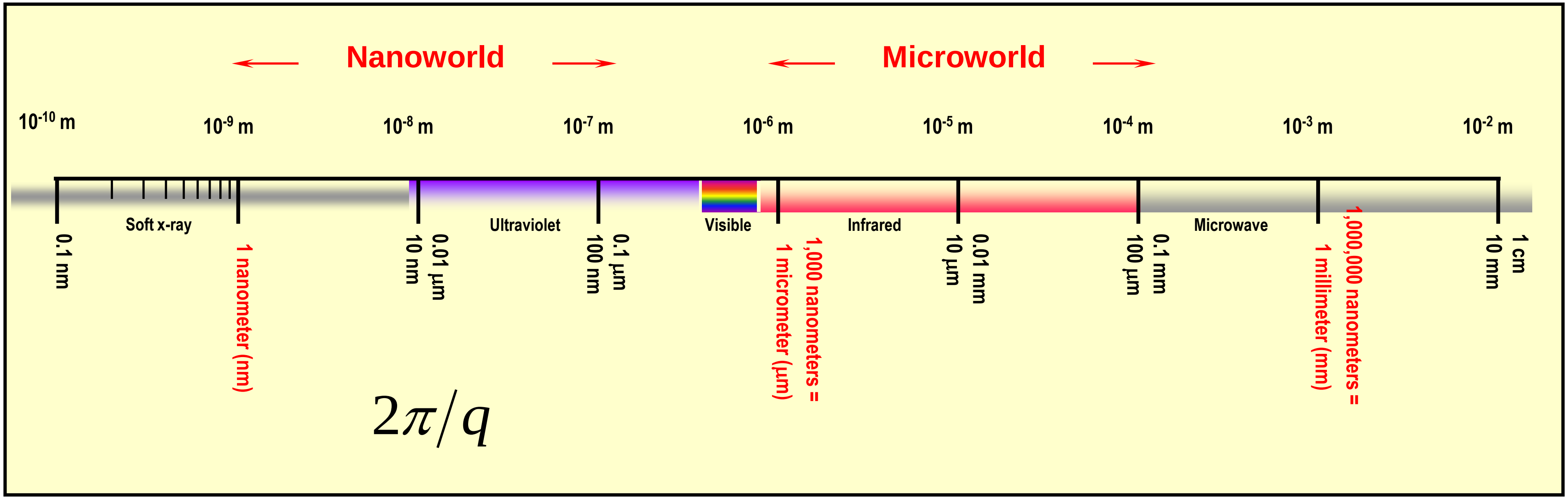


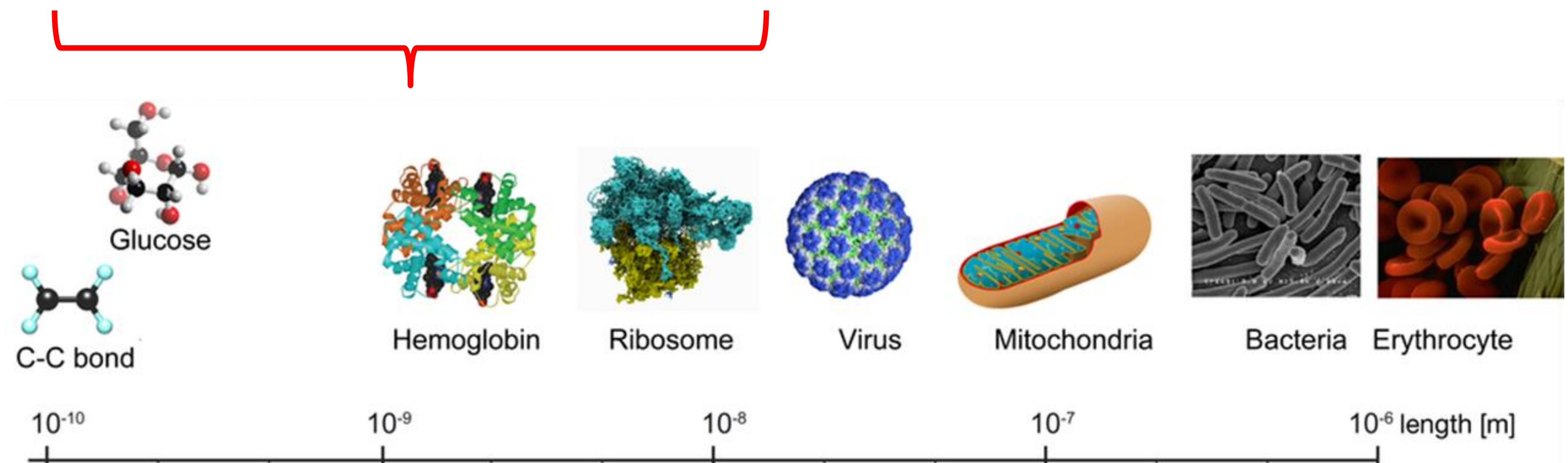
$$2\pi/q$$



Colloids
Polymers
Surfactants
Liquid crystals
Etc.

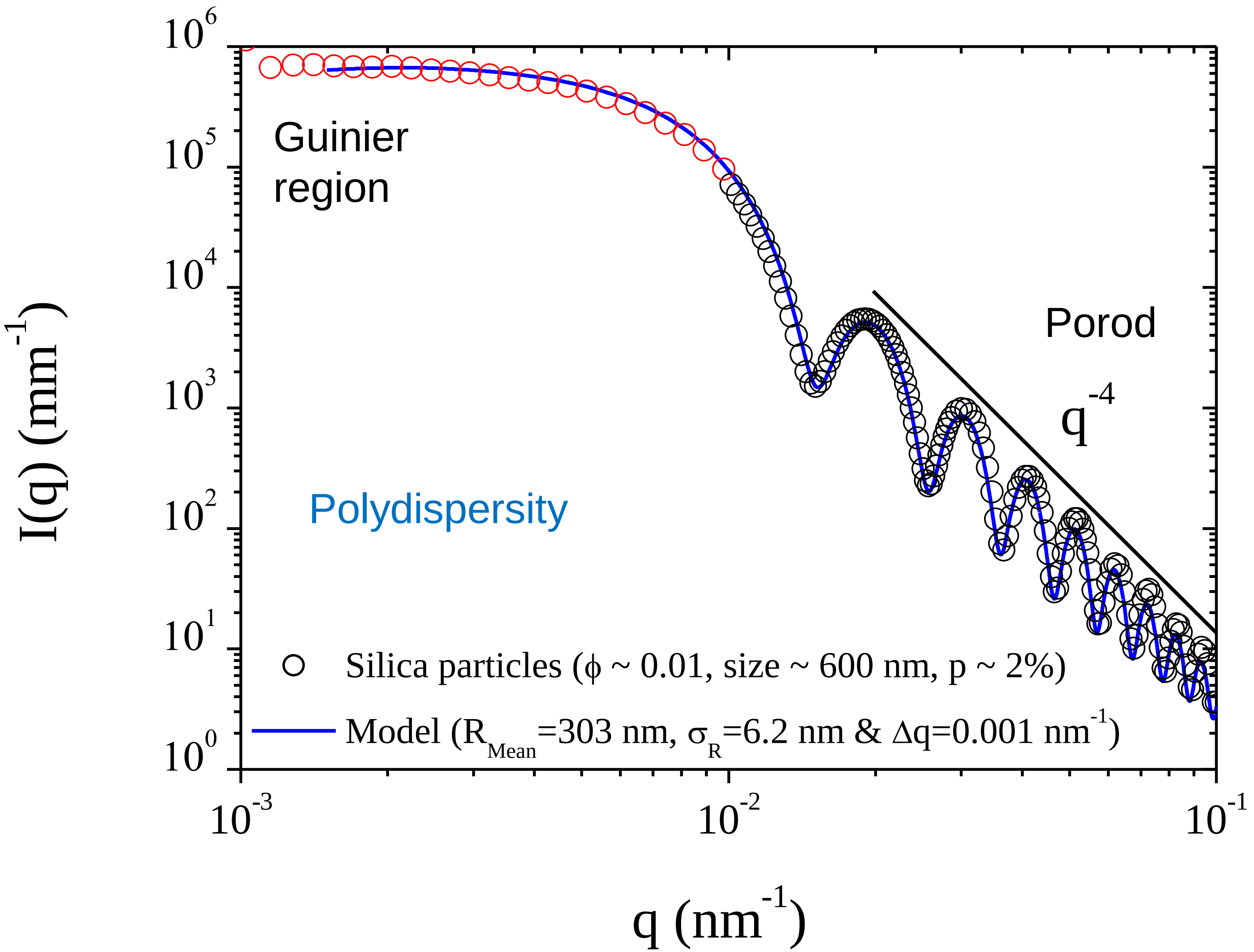
Size scales probed by SAXS & related techniques

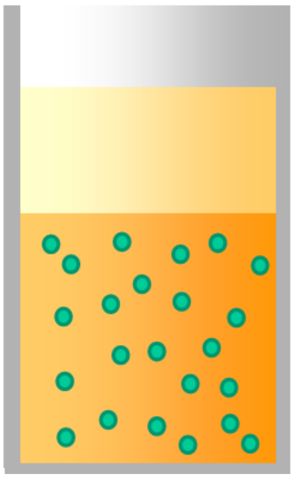




SAXS from dilute spherical particles

Modeling or simulation required to extract quantitative information



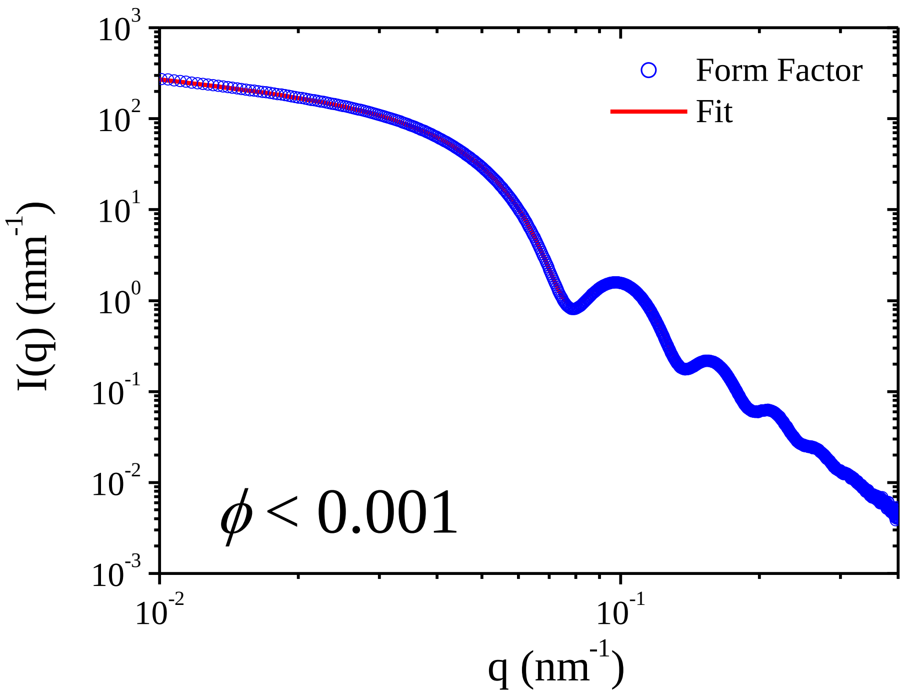


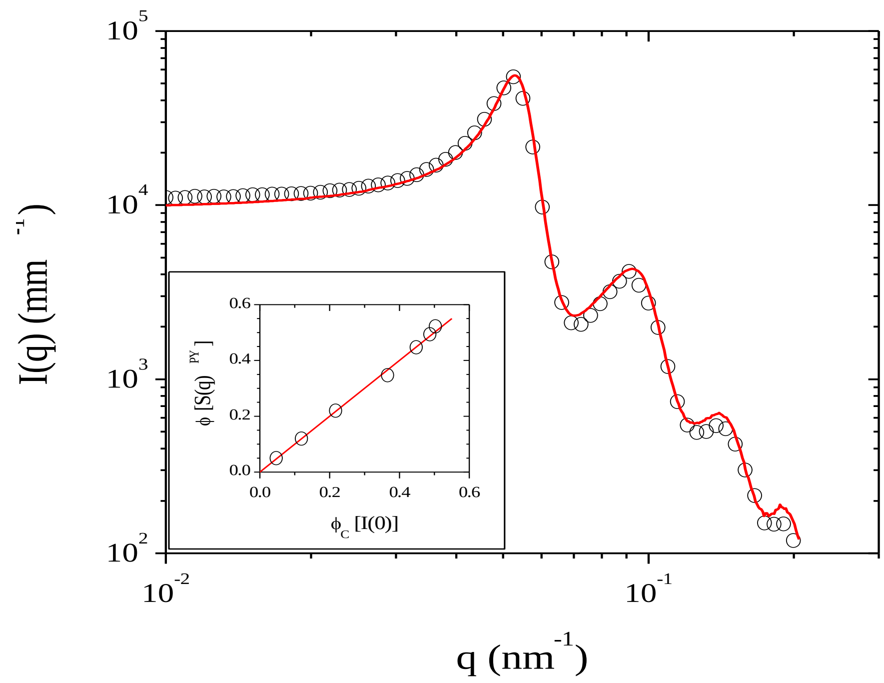
Form & Structure Factors

Differential scattering cross-section per unit volume

$$I(q) = N(\Delta\rho^* V)^2 P(q)\ S_M(q)$$

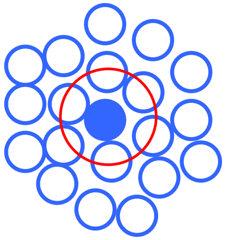
Experimental *P(q)* & *S (q)* from liquid state theories [e.g. Percus-Yevick (PY)]

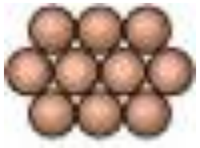


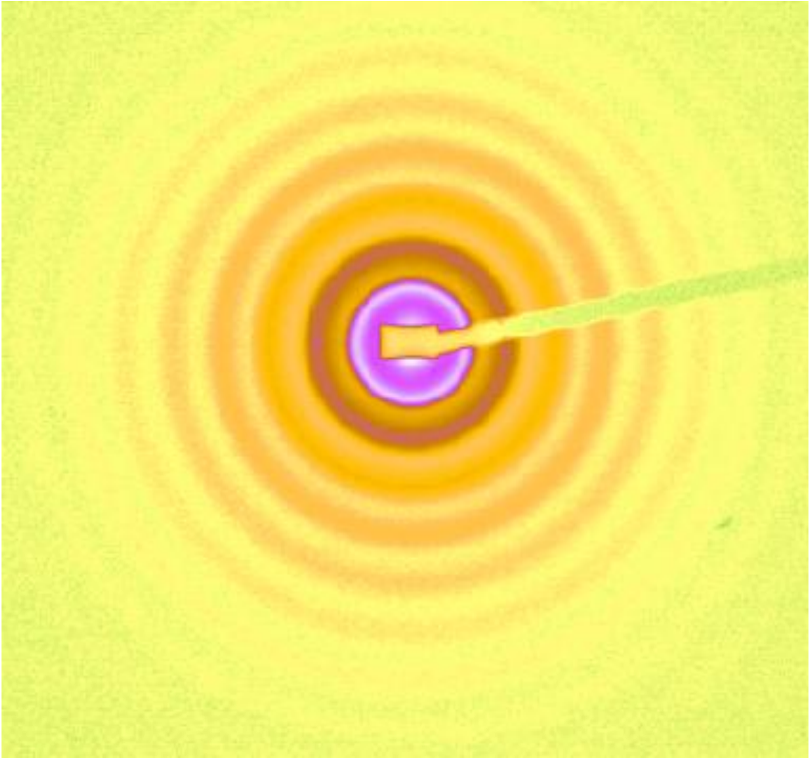


Structure Factors at high packing fractions

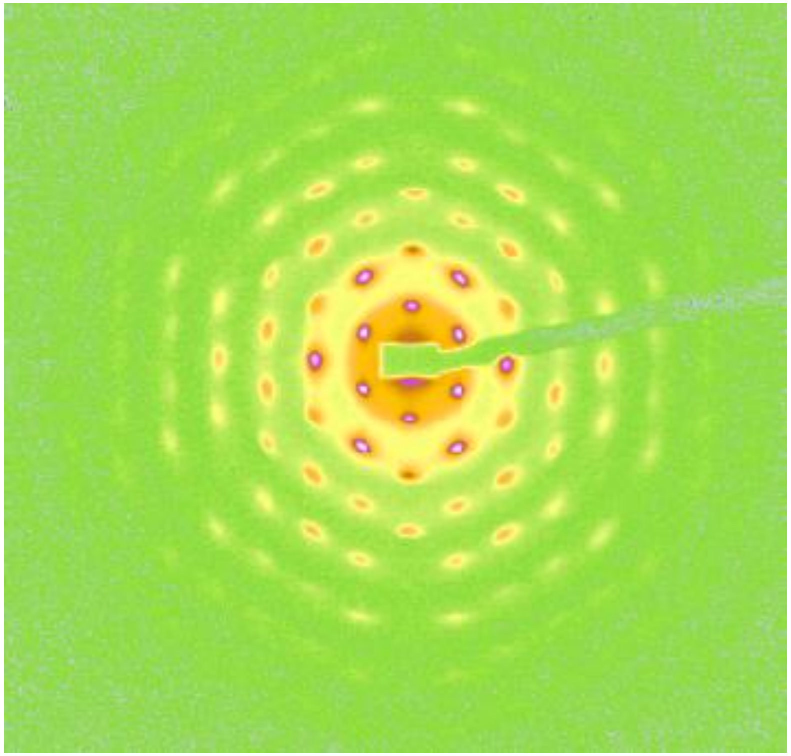
E.g. 60%





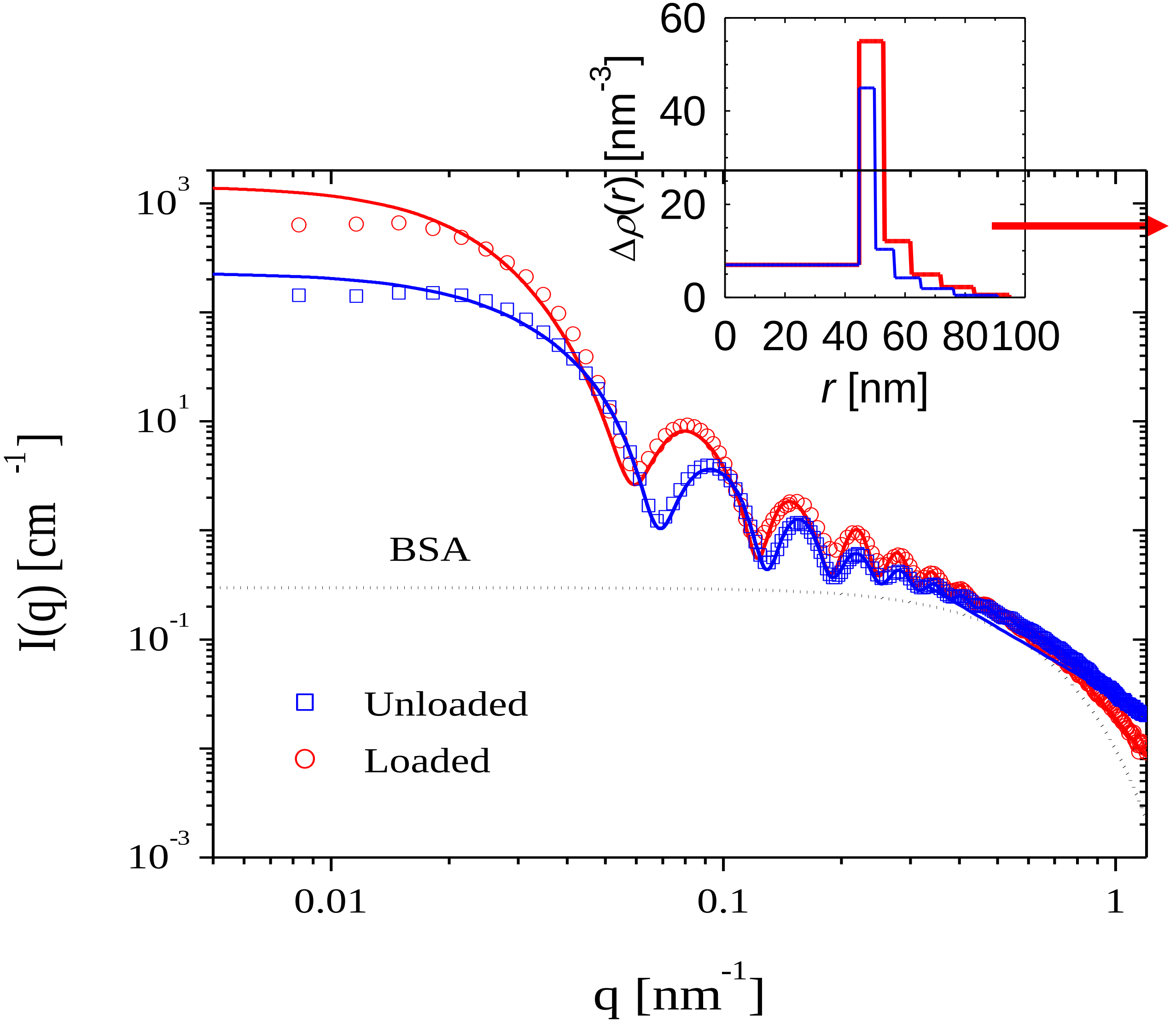


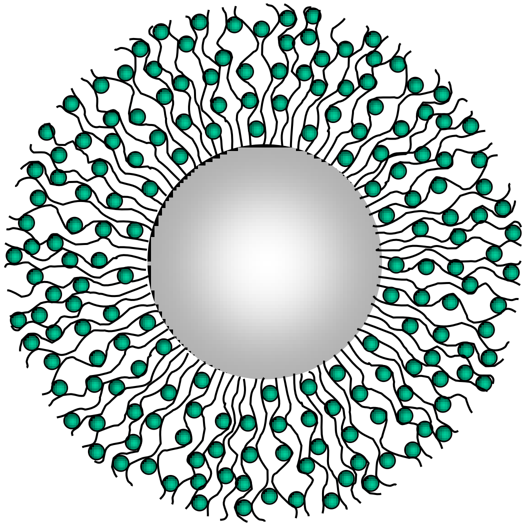
Glass



Crystal

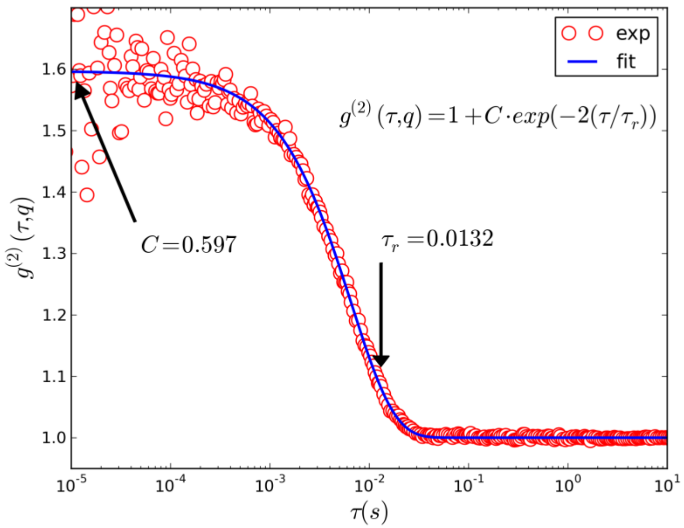
Core Shell Structures





X-ray Photon Correlation Spectroscopy (XPCS)

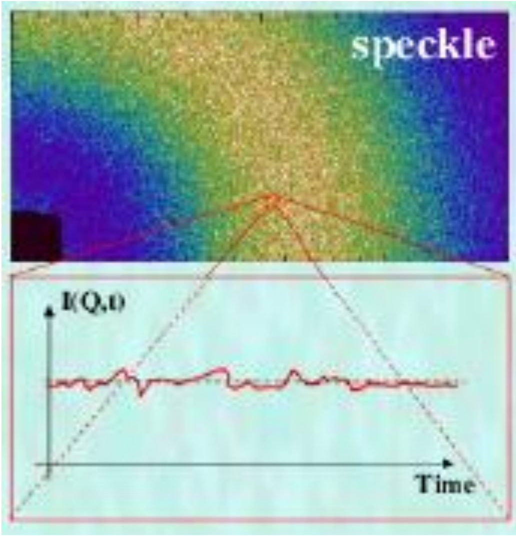
$$g^{(2)}(\tau) = \frac{\langle I(t) I(t+\tau)\rangle}{\langle I(t)\rangle^2}$$

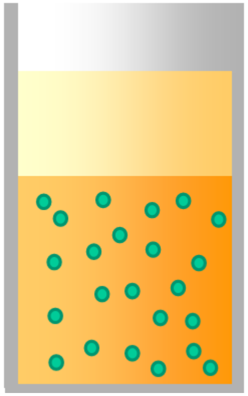


Silica microspheres in water
d=0.49±0.02μm, q=0.09 nm^{-1}

$$1/\tau_C = D_0\, q^2$$

Beamline – ID10





$$\langle \Delta r^2(\tau)\rangle = 6 D_0 \tau$$

mean-square displacement

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

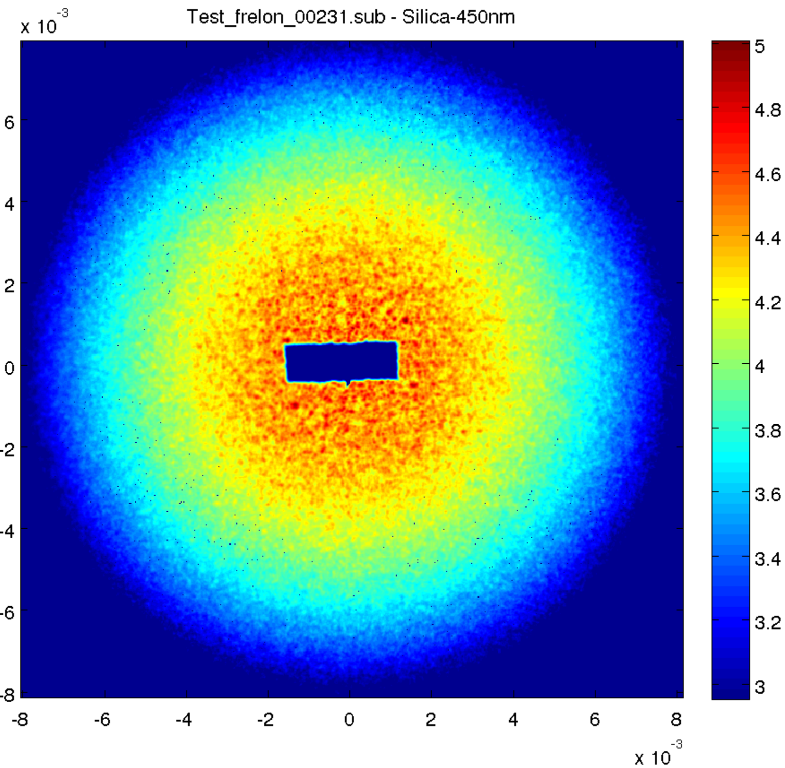
diffusion constant
(Stokes-Einstein)

Multi speckle XPCS

Multi speckle XPCS at low angles, $10^{-3} \leq q \leq 10^{-2}$ nm^{-1}

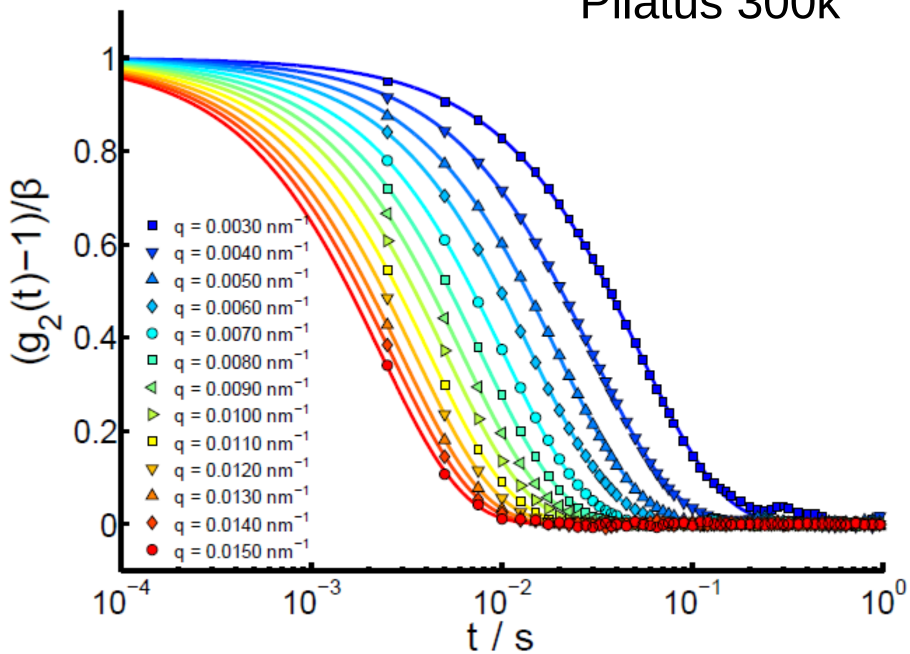
Simultaneous static & dynamic scattering

Dilute silica colloids of 450 nm in size



Intensity autocorrelation function

Pilatus 300k



J. Moeller, *et al.* (2016)

Multi speckle XPCS

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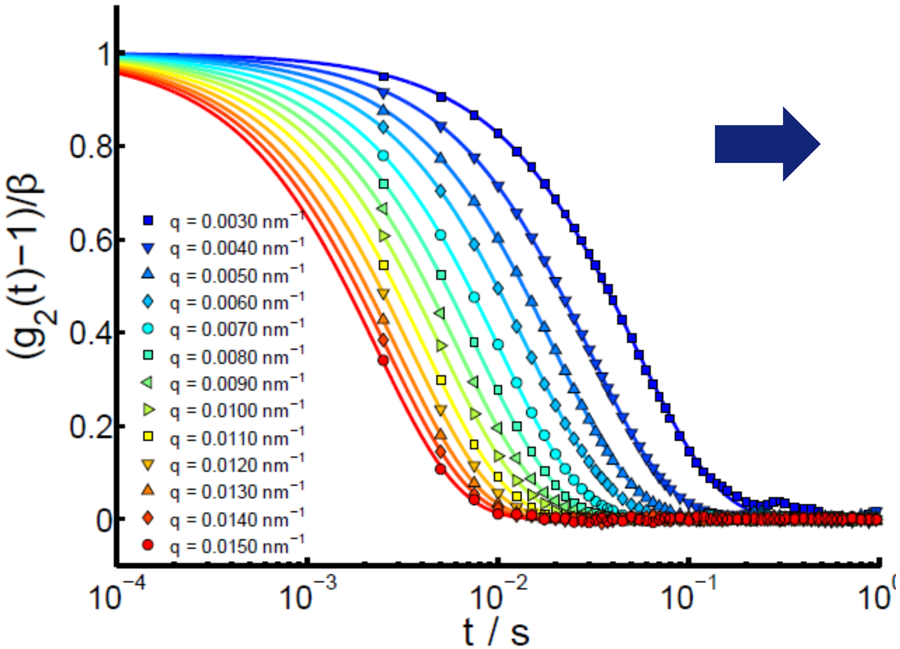
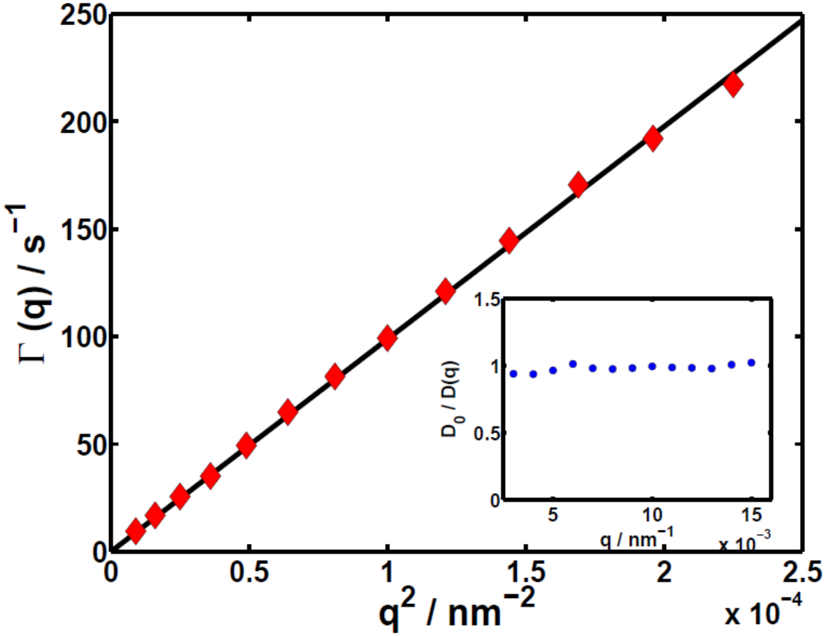


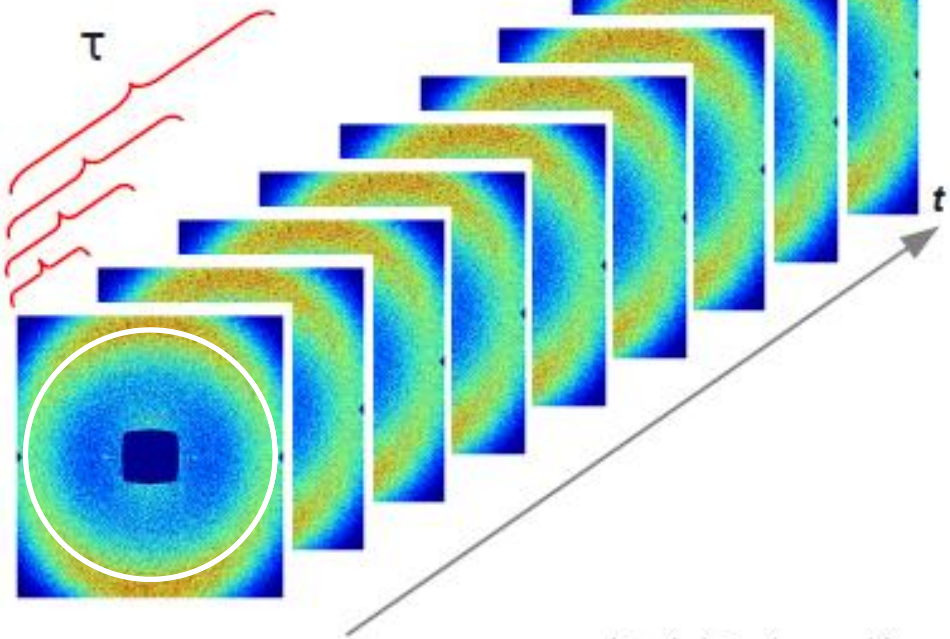
Diffusive dynamics



J. Moeller, *et al.* (2016)

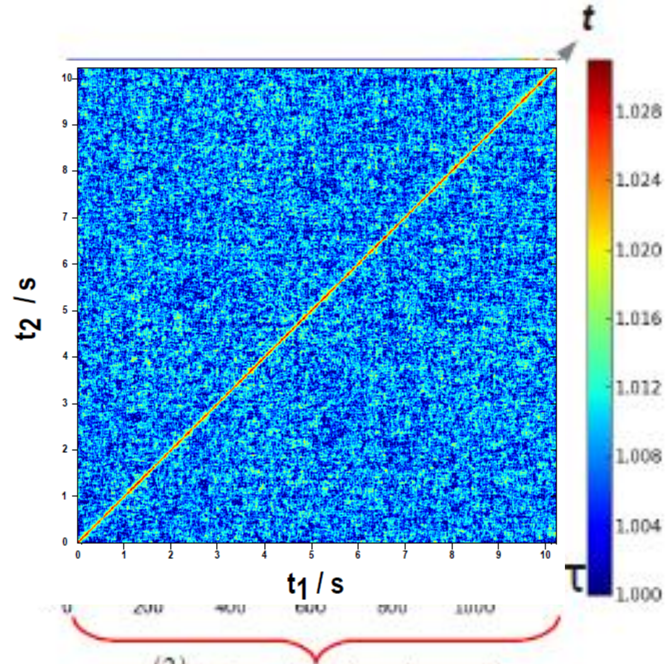
Multi-speckle XPCS

Series of scattering patterns

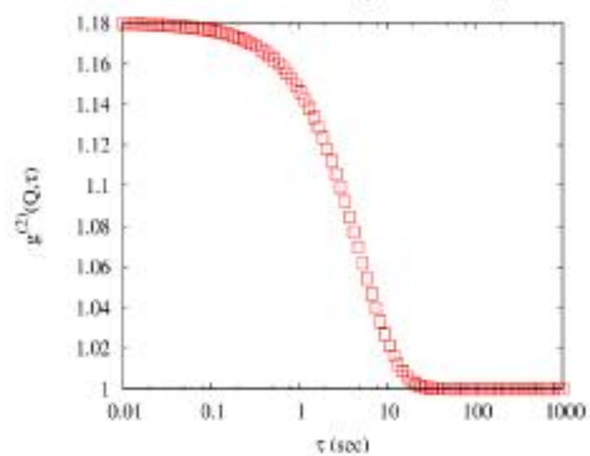


$$c_I(t,\tau) = \frac{\langle I_p(t) I_p(t+\tau) \rangle_p}{\langle I_p(t) \rangle_p \langle I_p(t+\tau) \rangle_p}$$

Time resolved correlation function



$$g^{(2)}(Q,\tau) = \langle c_I(t,\tau) \rangle_t$$



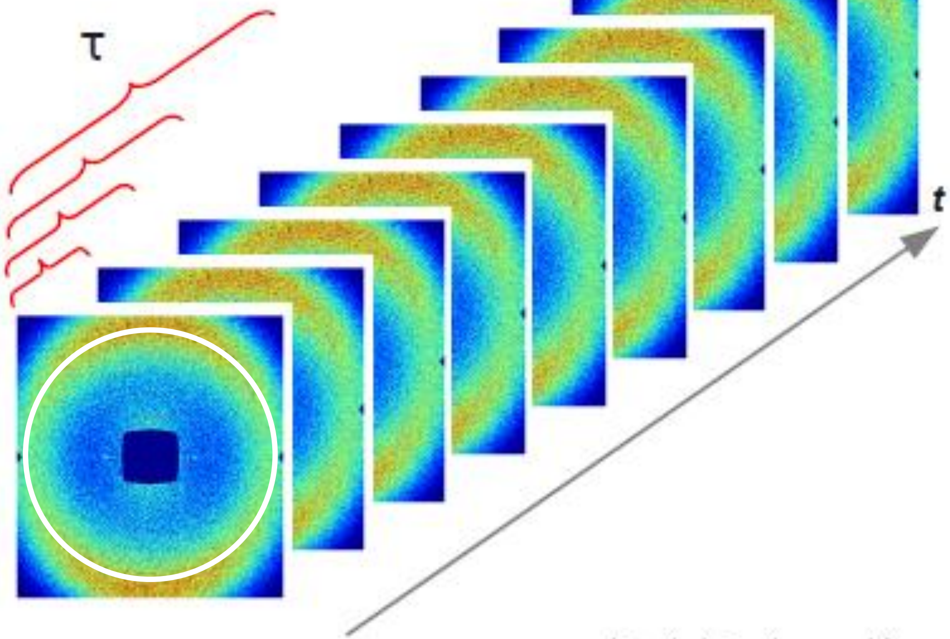
ESRF

Soft Matter: out-of-equilibrium dynamics

Out-of-equilibrium dynamics of systems far away from equilibrium

Multi-speckle XPCS

Series of scattering patterns



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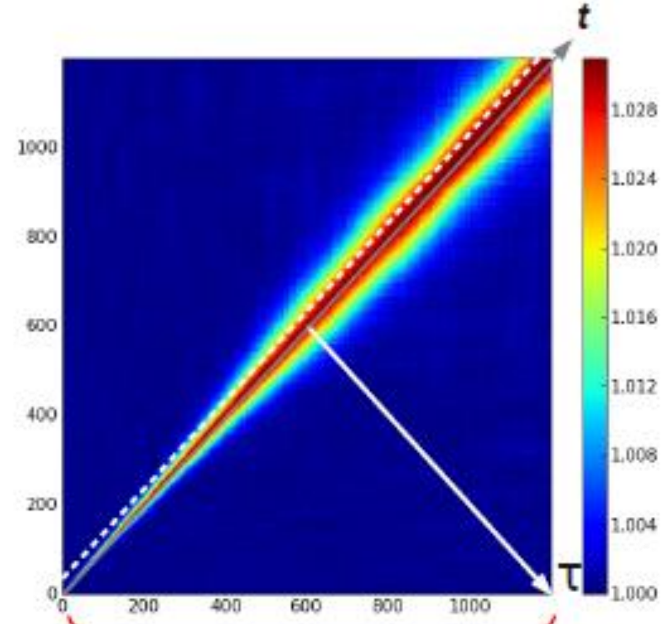
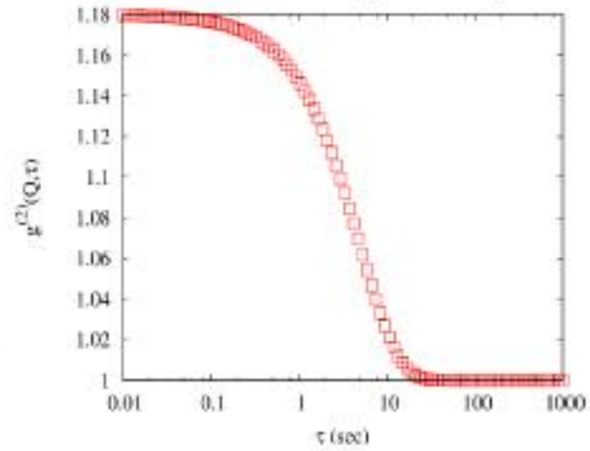
Time resolved correlation function



$$g^{(2)}(Q,\tau)=\langle c_I(t,\tau)\rangle_t$$



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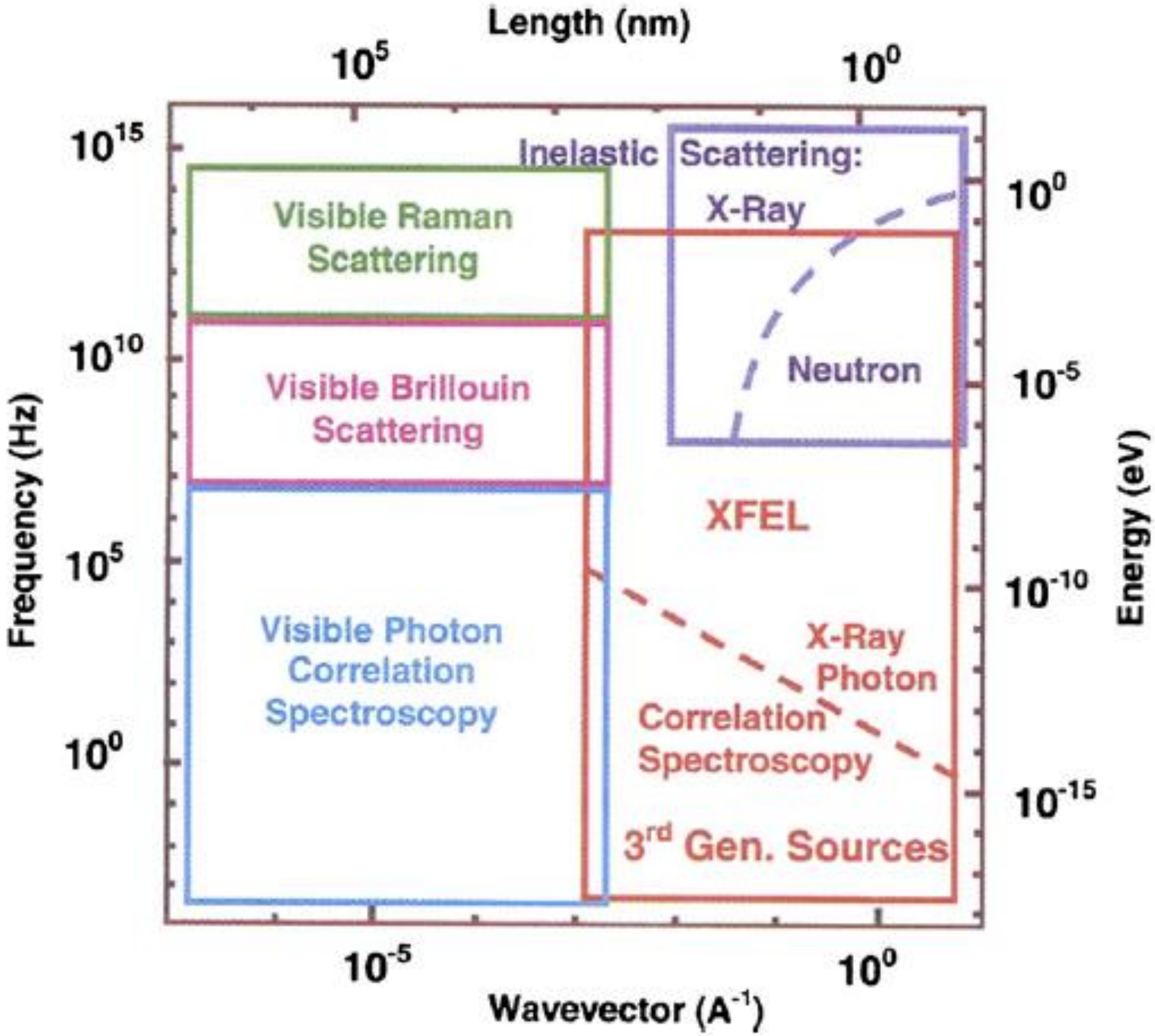
X-ray Photon Correlation Spectroscopy (XPCS)

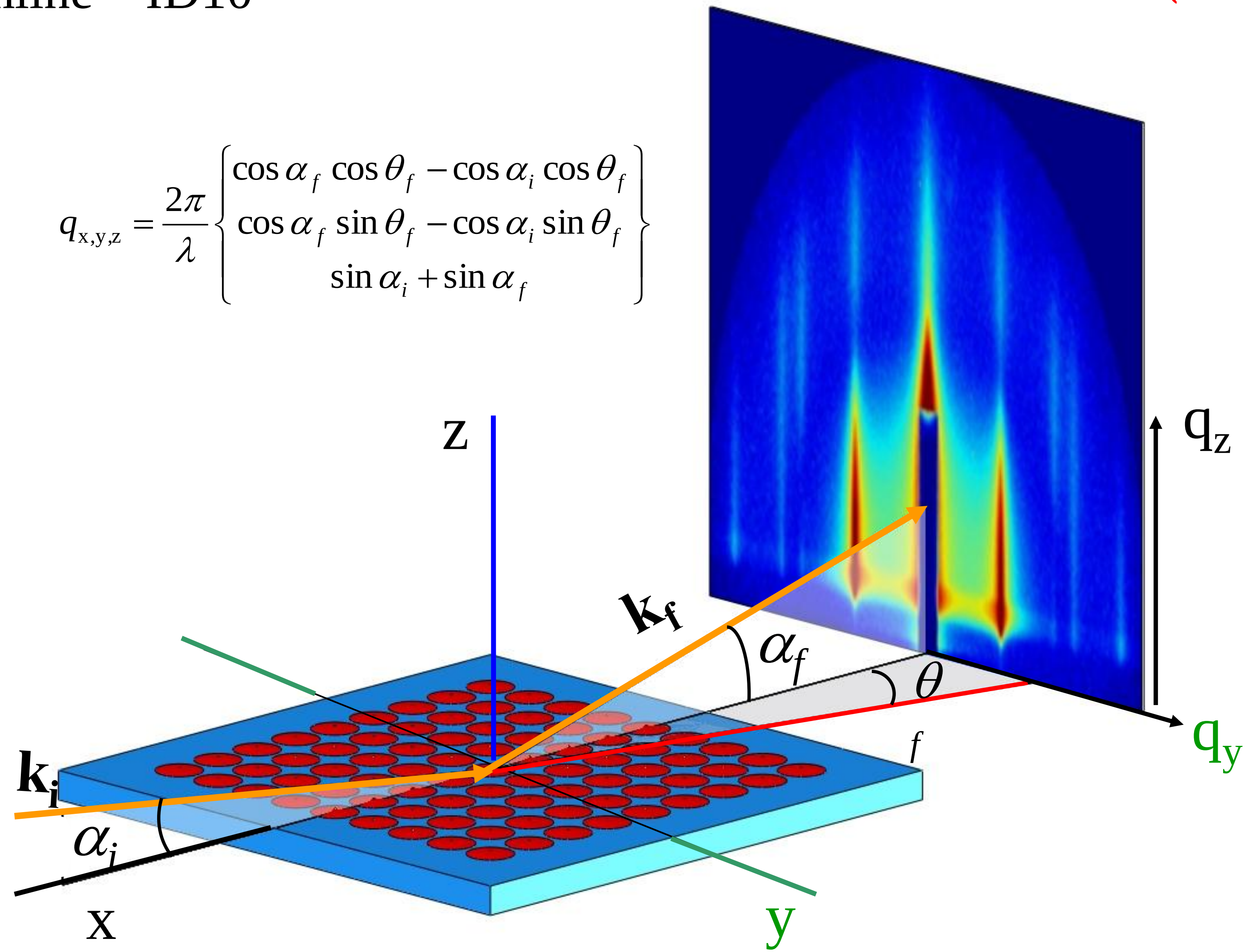


Grazing Incidence Small-Angle X-ray Scattering

Beamline – ID10

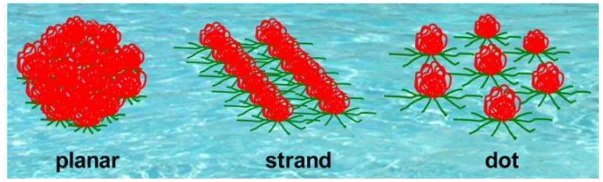
(GISAXS)

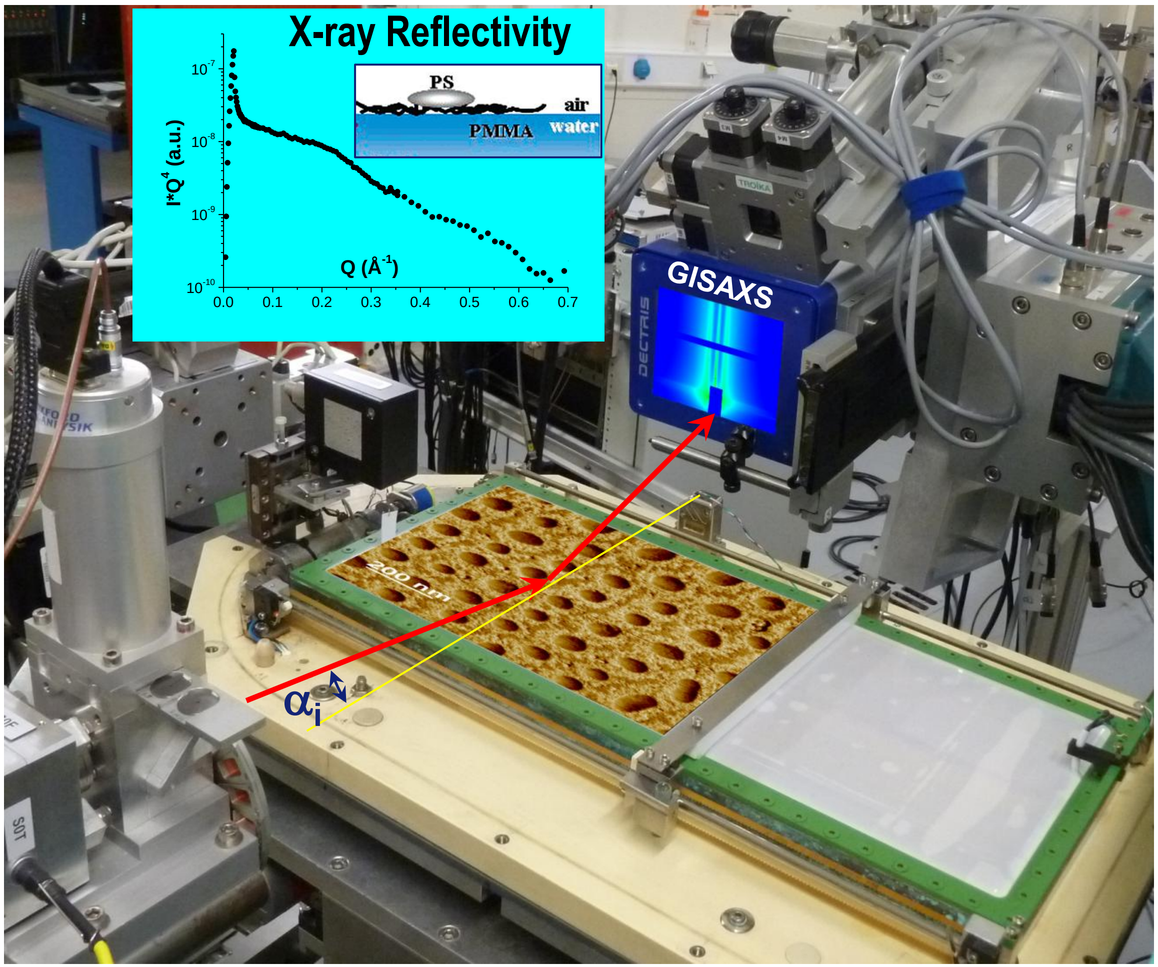
$$q_{x,y,z} = \frac{2\pi}{\lambda}\begin{Bmatrix} \cos\alpha_f \cos\theta_f - \cos\alpha_i \cos\theta_f \\ \cos\alpha_f \sin\theta_f - \cos\alpha_i \sin\theta_f \\ \sin\alpha_i + \sin\alpha_f \end{Bmatrix}$$

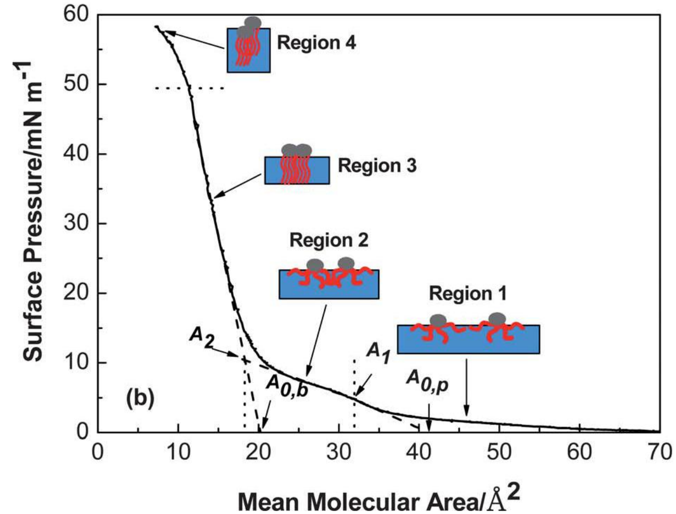


Soft Interfaces Scattering Beamline (ID10)

PS-PMMA: blocks length ratio →







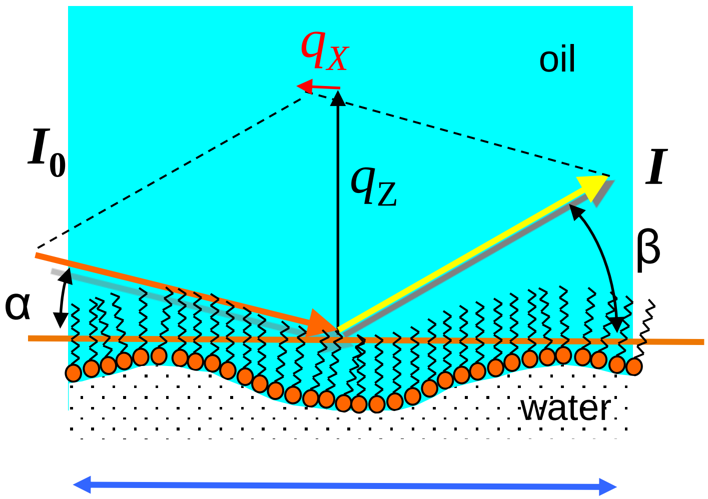
E.g.:
PS-PMMA (1:1) & (2:1)

The beat 2D order at:
PS-PMMA (1:1)
π=12 mN/m

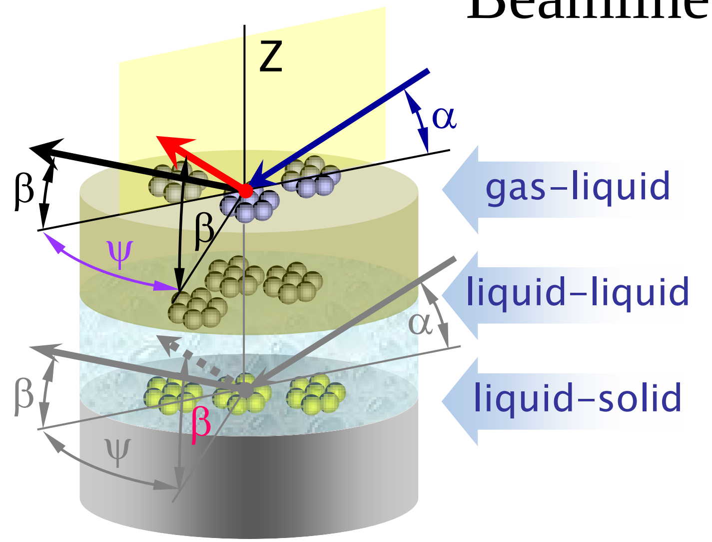
G. Li Destri , O.Konovalov, (ID10)

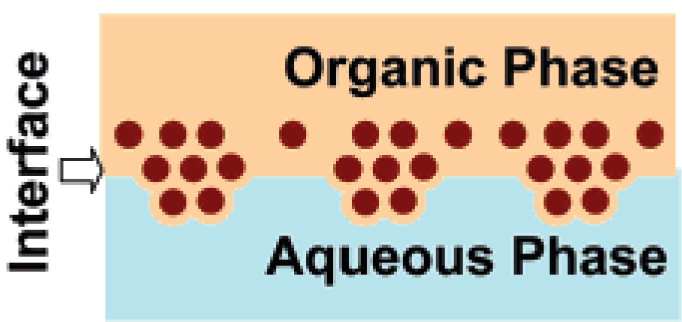
Soft Interfaces Scattering

Beamline ID10

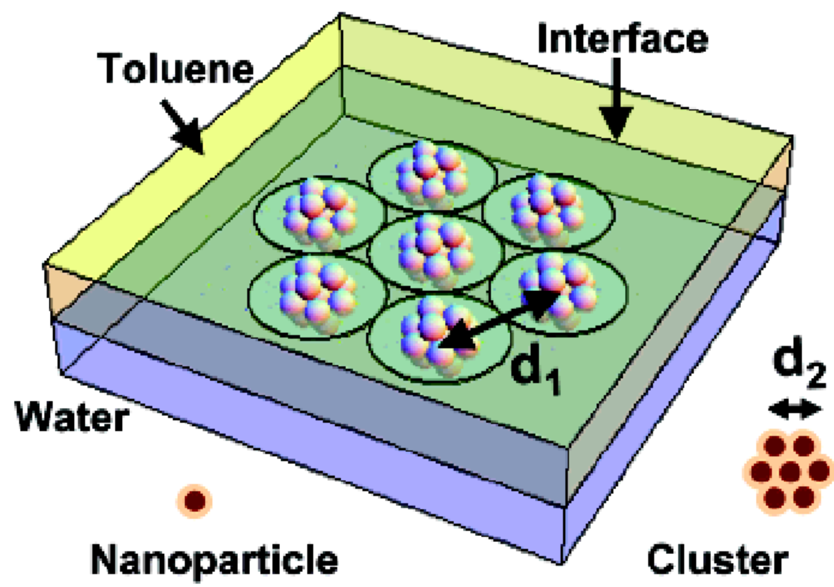


Beam travel path 70 mm



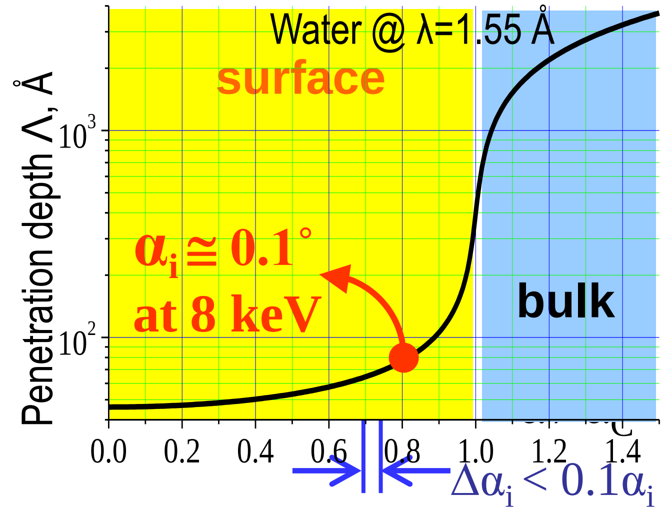


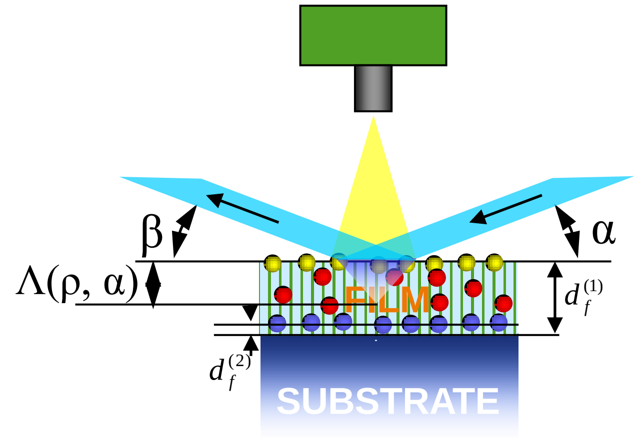
Interfacial cavities for reaction

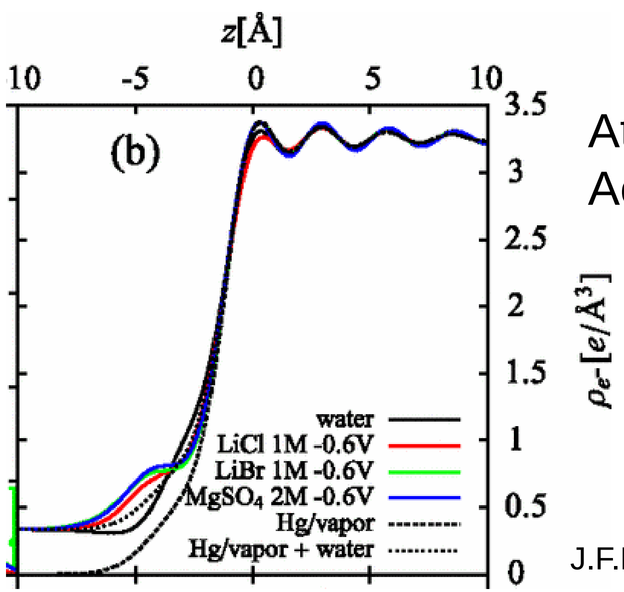


Soft Interfaces Scattering (ID10)

Varying the penetration depth



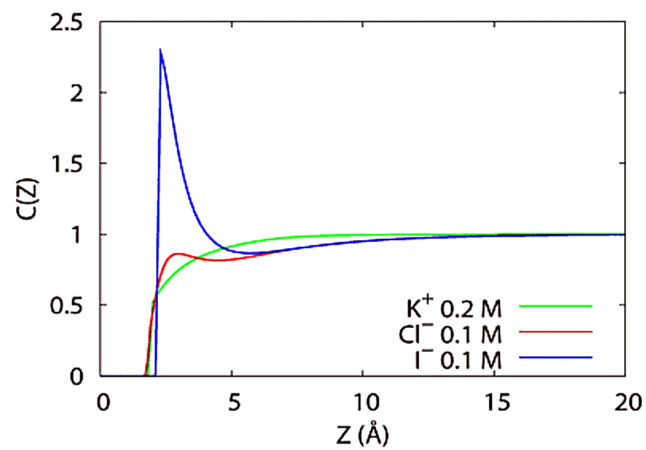




Atomic layering

Accumulation of ions

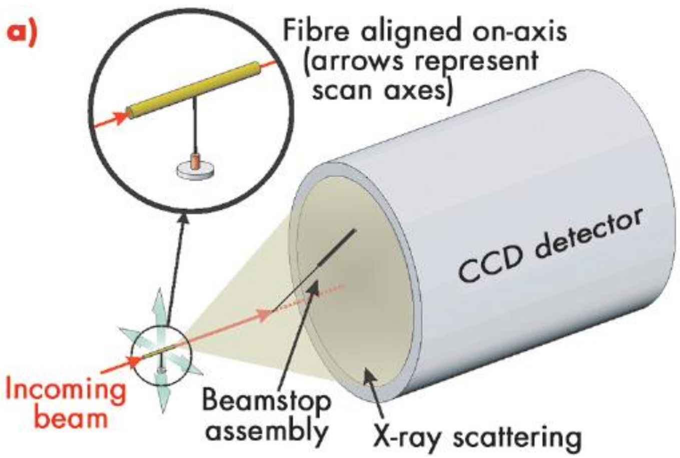
Elements distribution



J.F.L. Dual, *et al.* Phys.Rev.Lett. (2012)

Scanning Micro-diffraction

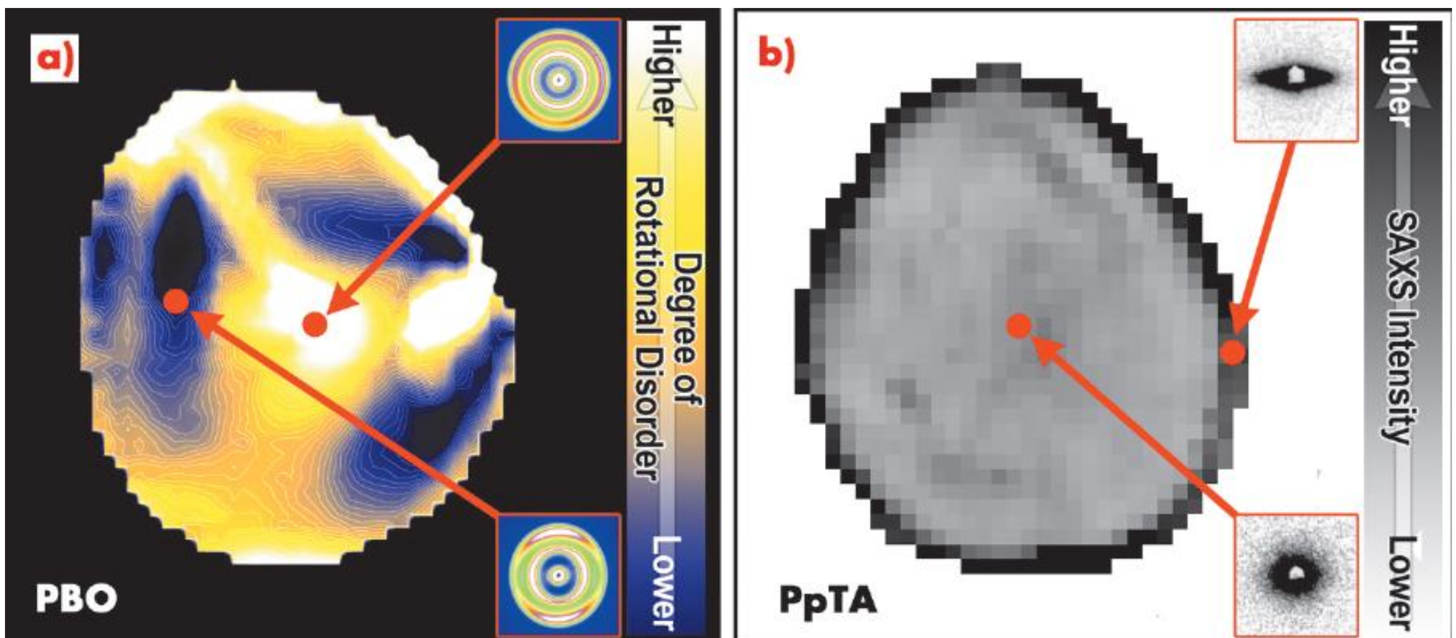
Beamline (ID13)



Skin-core morphology of high performance fibers
E.g. Kevlar

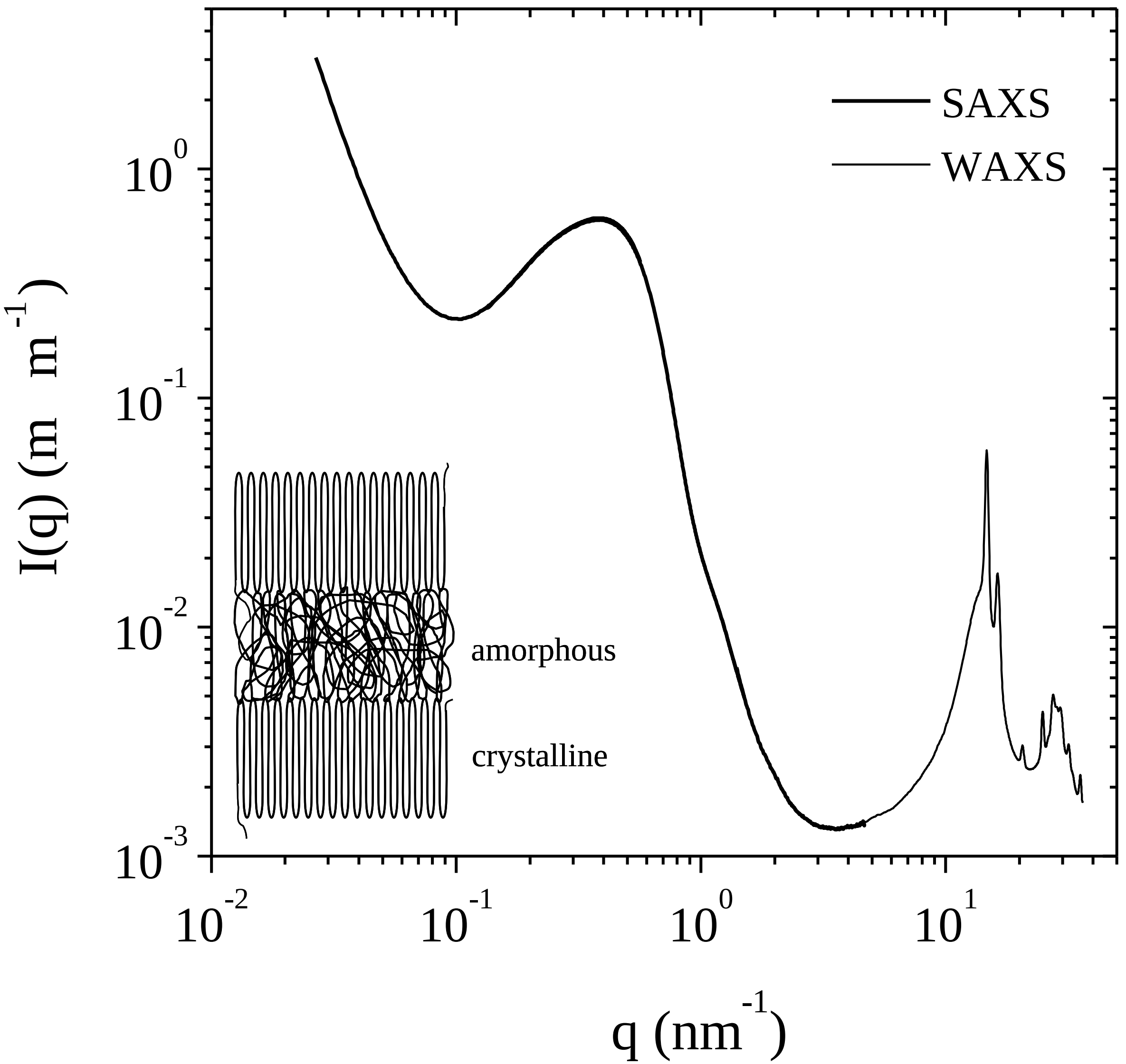
Correlate the local nanostructure to the fiber mechanical properties.

Elucidating the local nanostructure

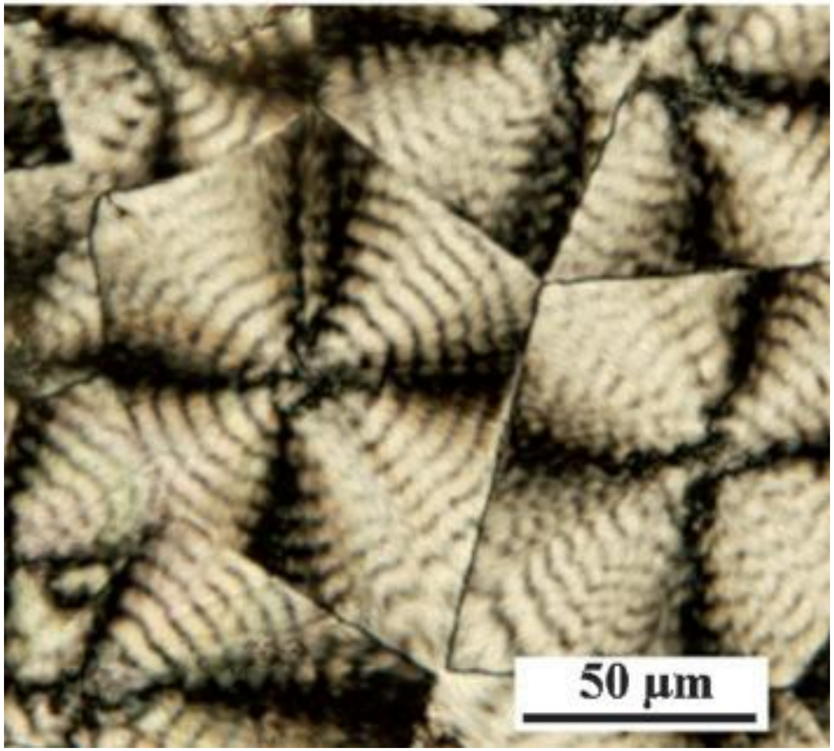


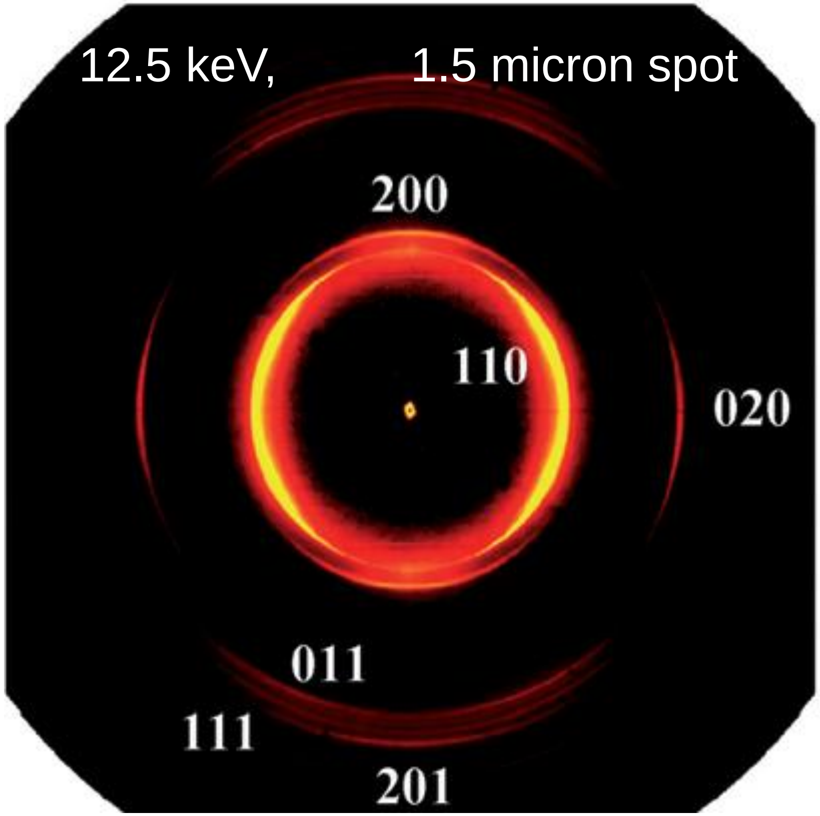
R. Davies *et al.*, *APL (2008)*

SAXS/WAXS from Semi-crystalline polymers



Scanning Micro-diffraction on HDPE spherulites



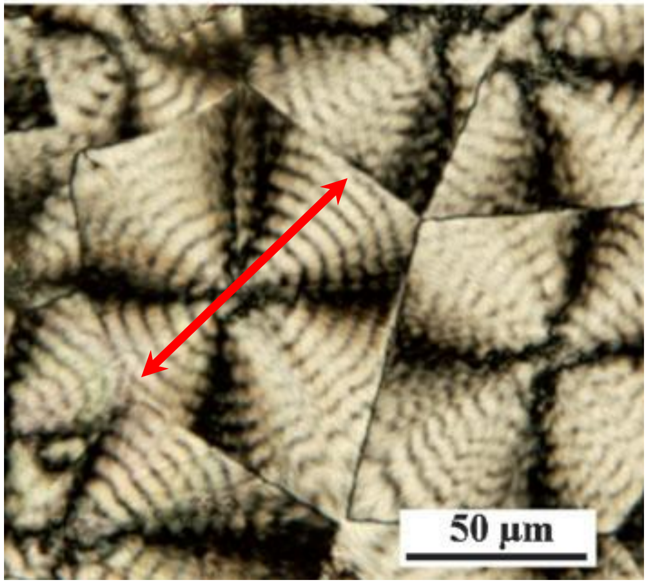


- **high density poly-ethylene**
- spherulites under polarized light banded structures indicating long range order

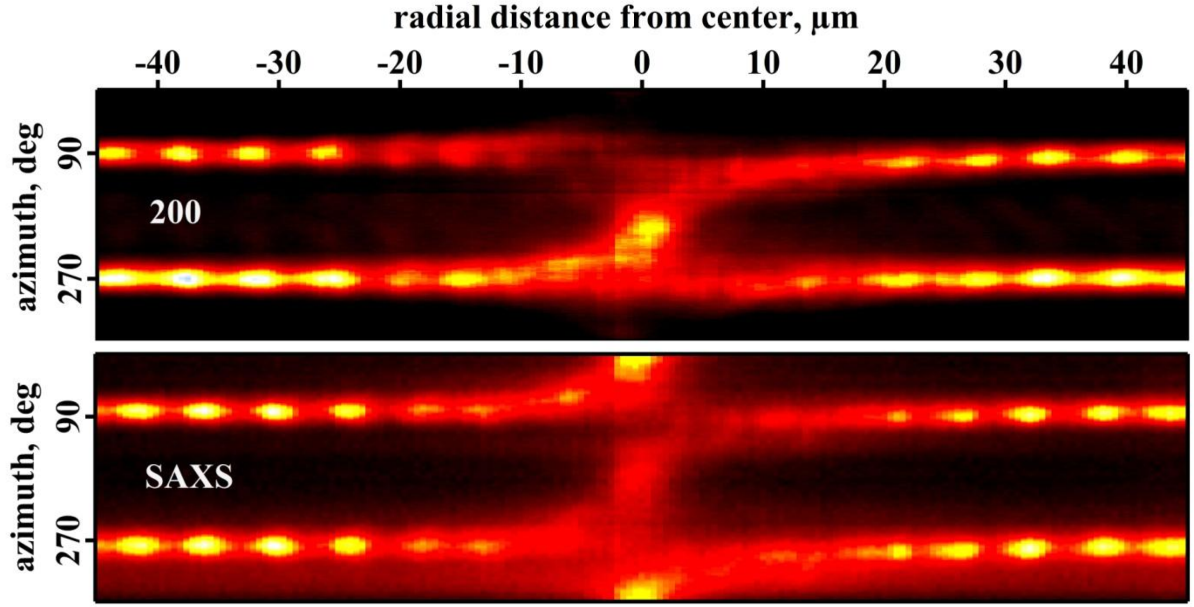
- **SAXS/WAXS** patterns
- line scans across the center reveal information on crystallite orientation

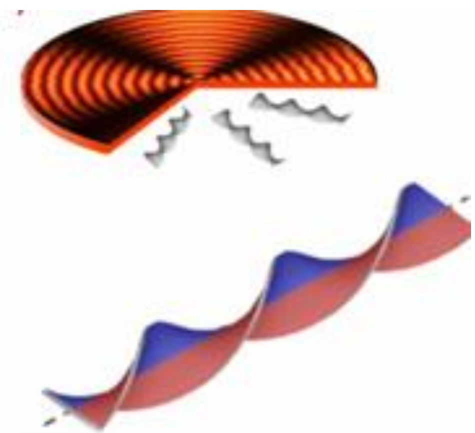
*M. Rosenthal et al., Angewandte Chemie, **123**, 9043-9047 (2011)*

Chirality of twisted polymer crystals



Azimuth/Intensity vs Distance from the center in µm





- 35° tilt between c-axis and the normal of the base plane of crystalline lamellas
- orientation of b-axis aligned with growth direction
- chirality can be determined

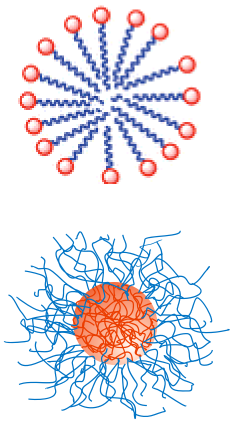
*M. Rosenthal et al., Angewandte Chemie, **123**, 9043-9047 (2011)*

Soft Matter Self-Assembly

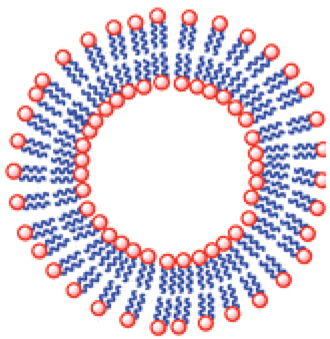
Motivation: understanding self-assembly in nature

Kinetics of self-assembling systems → understanding of properties and functionalities – material stability, cell trafficking (drug delivery), detergency, etc.

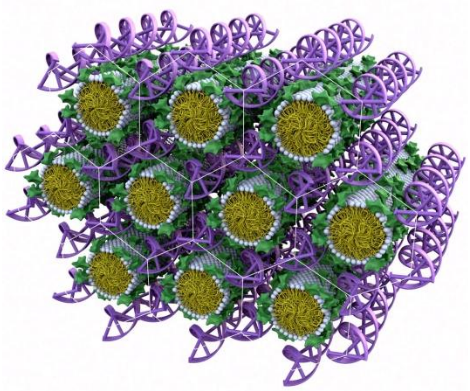
Complexity →



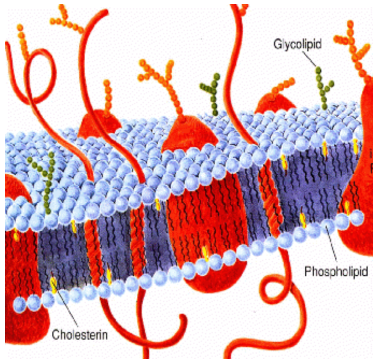
Micelles



Vesicles



Lipid-DNA complex



Cell

→ How are these complexes formed: kinetic pathways to (non-)equilibrium?

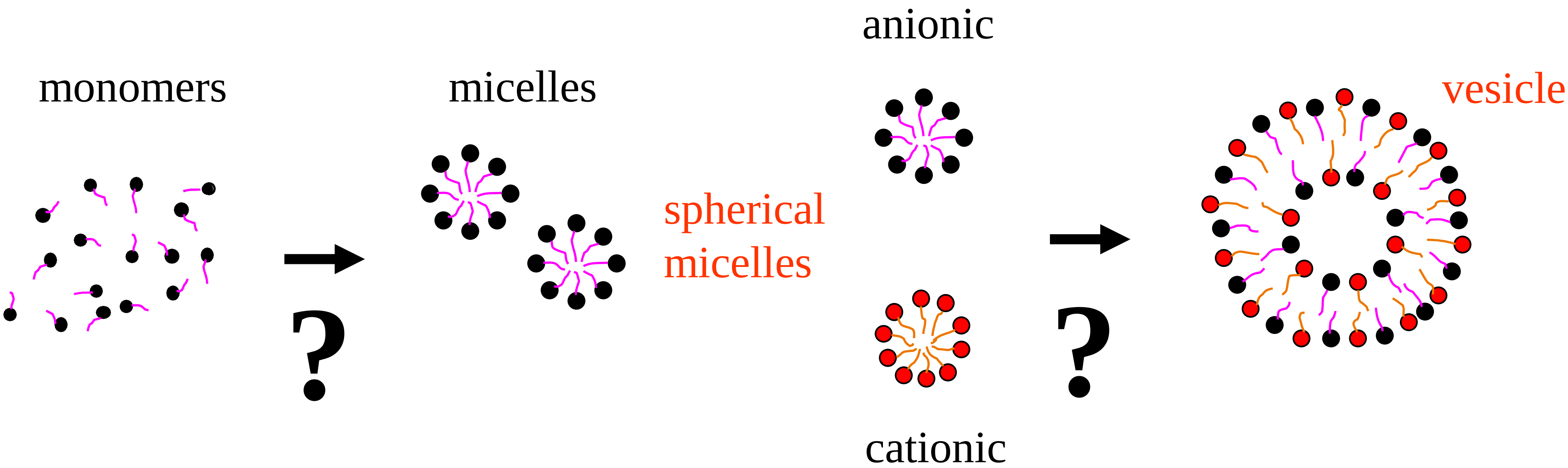
→ How can these complexes be tuned and manipulated to new materials (e.g. biomedical/pharmaceutical applications) ?

Spontaneous self-assembly of micelles and vesicles

E.g. surfactants, lipids or block copolymers

Large variety of equilibrium structures
Dynamics of formation is very little explored

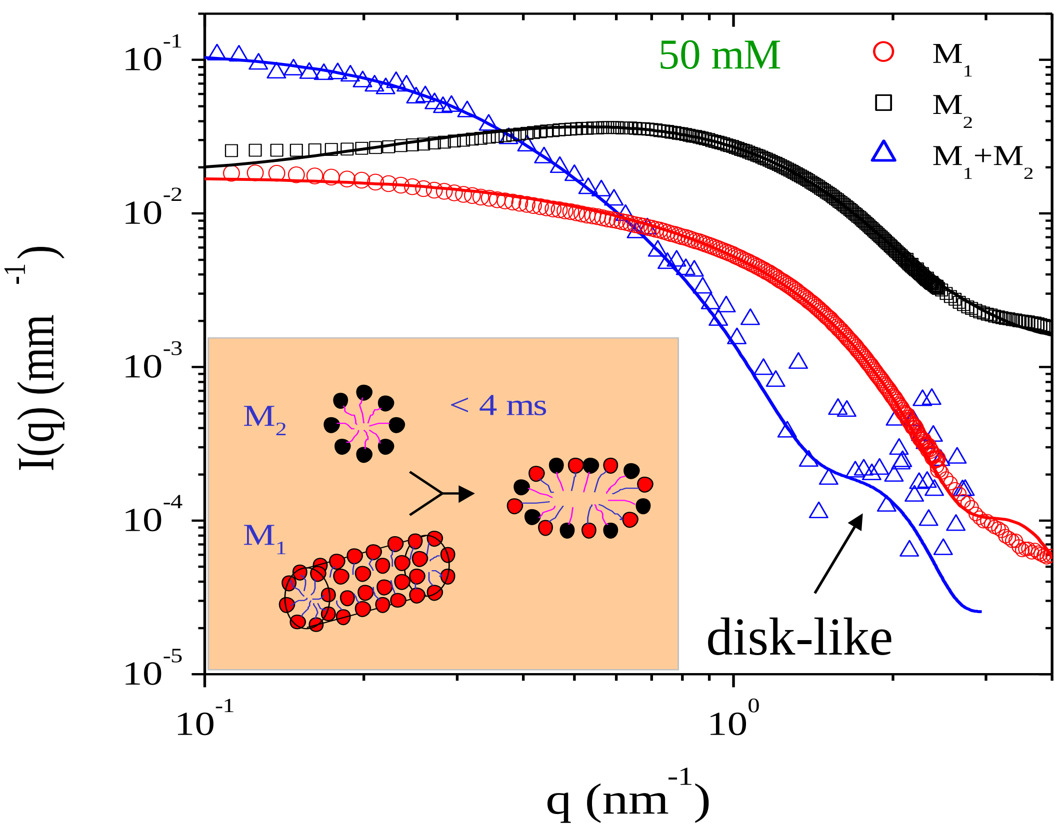
Self-assembly of micelles and vesicles

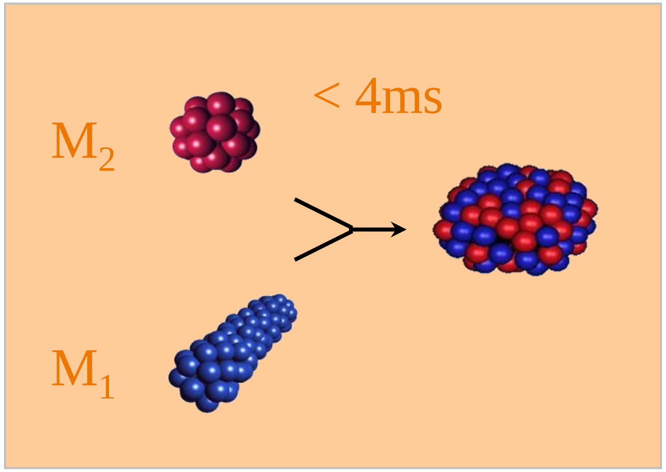


Rate-limiting steps » predictive capability

Kinetic pathway: stopped-flow rapid mixing & time-resolved SAXS

Self-assembly of unilamellar vesicles





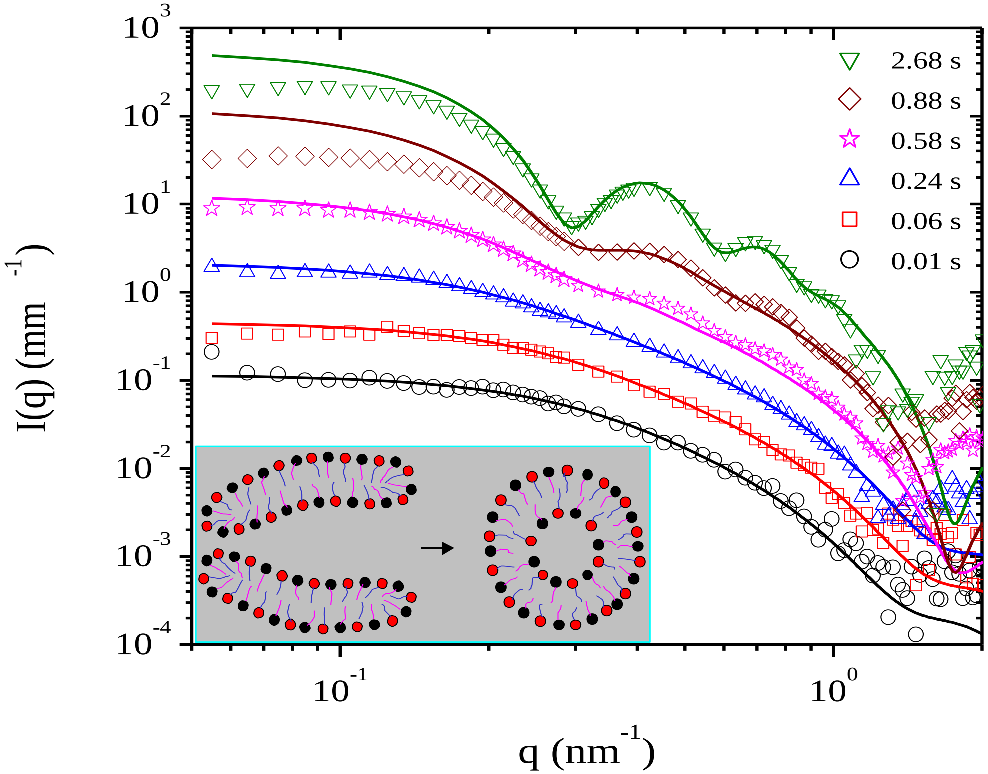
- disk-like objects with: R = 7.5nm; H = 4.8nm
- size of initial disks: 670 ~ 2 x size rod-like micelle

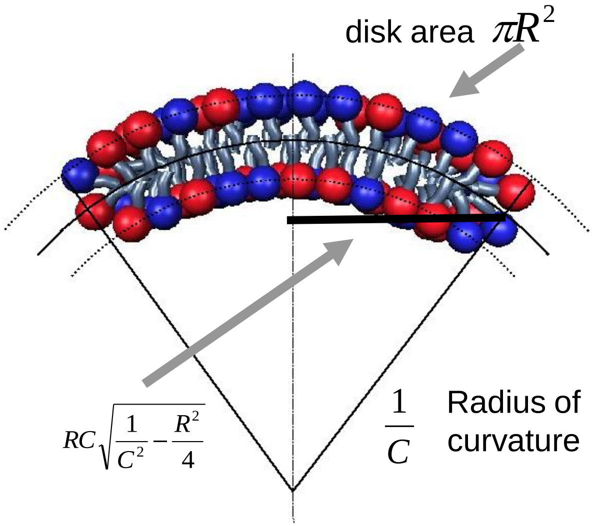
T.M. Weiss *et al.*, PRL (2005)

Langmuir (2008)

Transient disk-like micelles are formed within the mixing time (< 4 ms)

Growth of disk-like micelles





Bending energy vs Edge energy

$$E_{bend} = 4\pi(2\kappa + \bar{\kappa})RC$$

$$E_{edge} = 2\pi\Lambda RC\sqrt{\frac{1}{C^2} - \frac{R^2}{4}}$$

At the closing state: $$R_{\max} \approx \frac{4(2\kappa + \bar{\kappa})}{\Lambda}$$

κ & $\bar{\kappa}$ - bending moduli

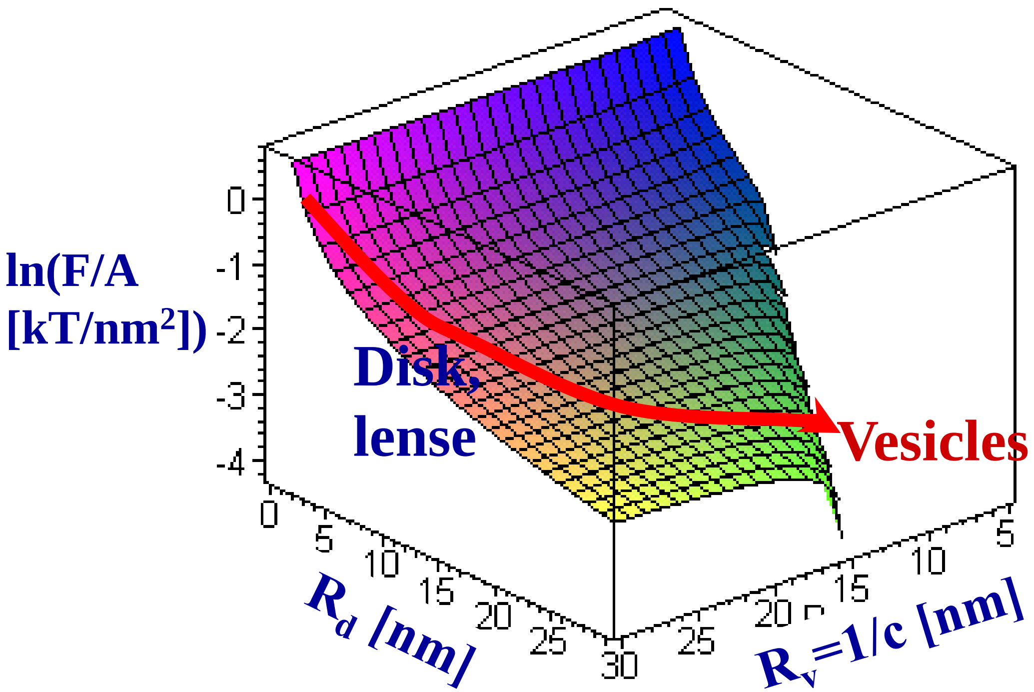
Λ - line tension

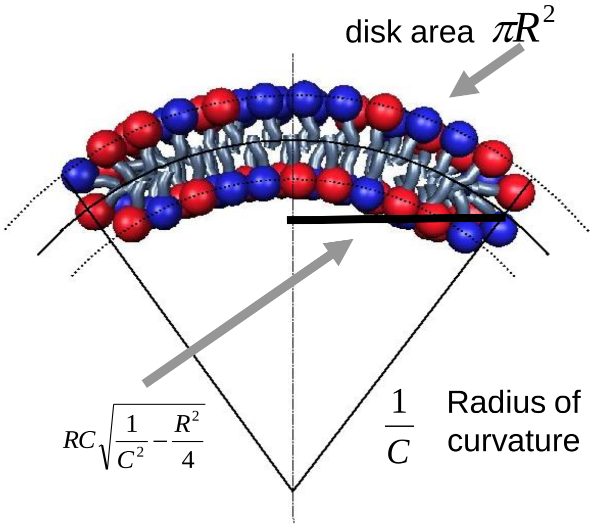
T.M. Weiss *et al.*, PRL (2005)

Langmuir (2008)

Growth of disk-like micelles

Free energy of a bend bilayer





κ & $\bar{\kappa}$ - bending moduli

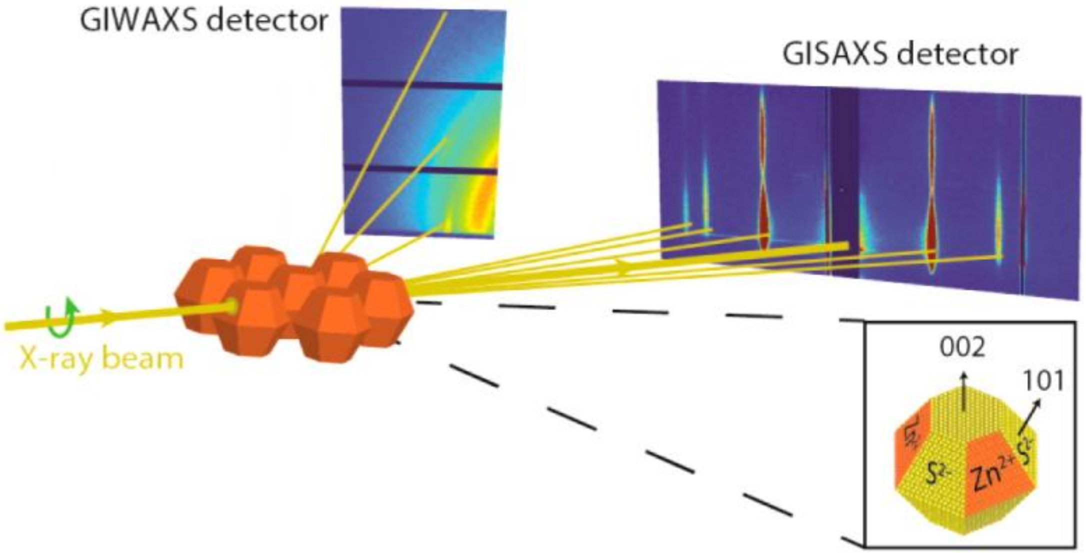
Λ - line tension

T.M. Weiss *et al.*, PRL (2005)

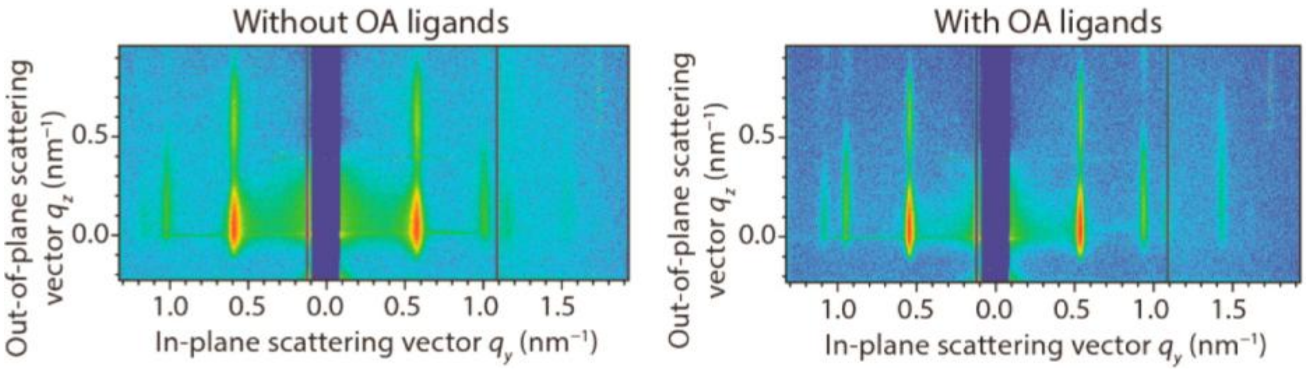
Langmuir (2008)

Soft matter self-assembly at interfaces

2D ZnS nanocrystal superlattice structure development at the vapour-liquid interface



W. van der Stam, Nano Lett. 16, 2608 (2016)



Oleic Acid (OA) ligands which induce atomic scale alignment of nanocrystals and promote superlattice formation

Summary & Outlook

• High brilliance X-ray scattering is a powerful method to elucidate the non-equilibrium structure & dynamics of soft matter.

• Time-resolved scattering experiments in the millisecond range can be performed even with dilute samples.

• Combination of nanoscale spatial and millisecond time resolution makes synchrotron techniques unique in these studies.

• Experiments can be performed in the functional state of the system.

• Challenges lie in the ability to investigate complex polydisperse systems with competing interactions.

• The emphasis will be on quantitative studies made possible by the high detection capability and reduced radiation damage, and complemented by advanced data analysis.