Soft Matter Studies with X-rays

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Structure from Diffraction Methods, Eds. D.W. Bruce, D. O'Hare & R.I. Walton, (Wiley, 2014)

Soft-Matter Characterization, Eds. R. Borsali & R. Pecora (Springer, 2008)

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,"[1] 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

Soft Matter: Encounter in everyday life

Sustainable development and supply of consumer products

What is Soft Matter?

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

A significant fraction of consumer products fall in this category.

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 disappear.

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

Soft Matter Characteristics

Dominance of entropy

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

Characteristic size scale or microstructure ~ 100 – 1000 nm

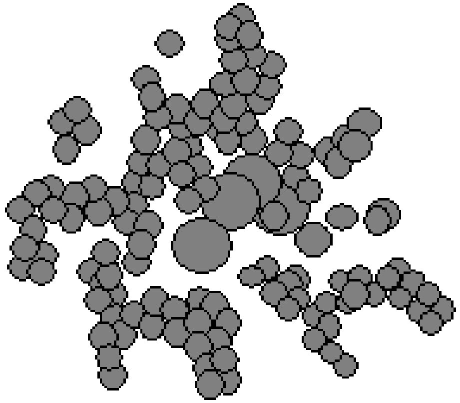
Shear modulus, G ~ Energy/Free volume » 10^9 – 10^{12} smaller

Low shear modulus (G) » soft and viscoelastic

Soft implies: (1) high degree of tailorability

(2) lack of robustness

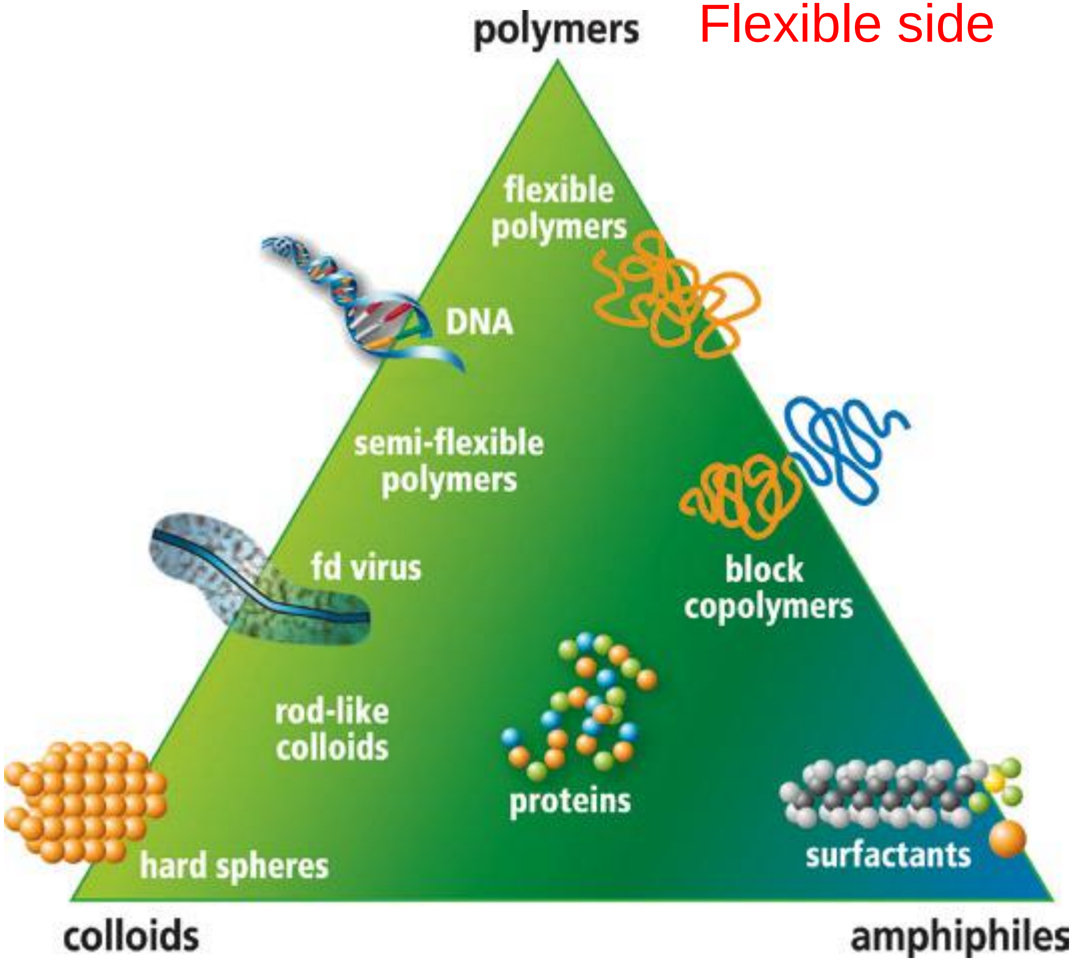
Multi-scale out-of-equilibrium systems



Soft Matter Triangle

3 main ingredients of soft matter

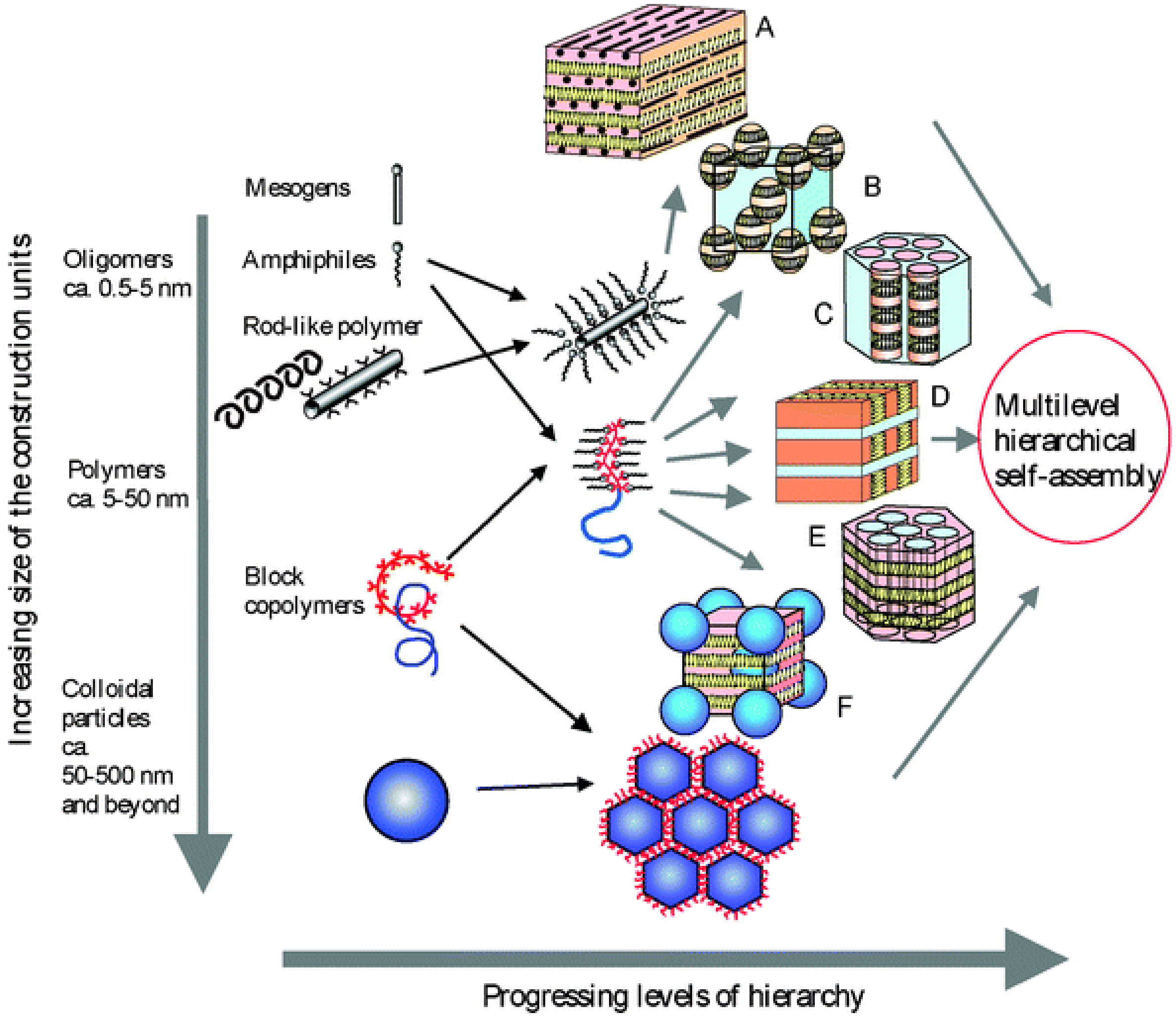
Flexible side

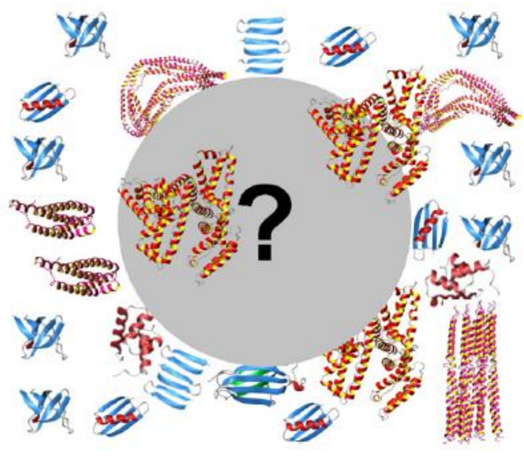


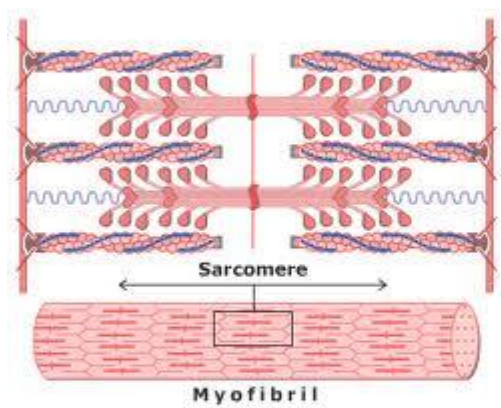
Harder side

Selective side

Soft Matter: Increasing levels of complexity







Elucidating the pathways of self-assembly

O. Ikkala and G. Brinke, Chem. Commun., (2004)

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***

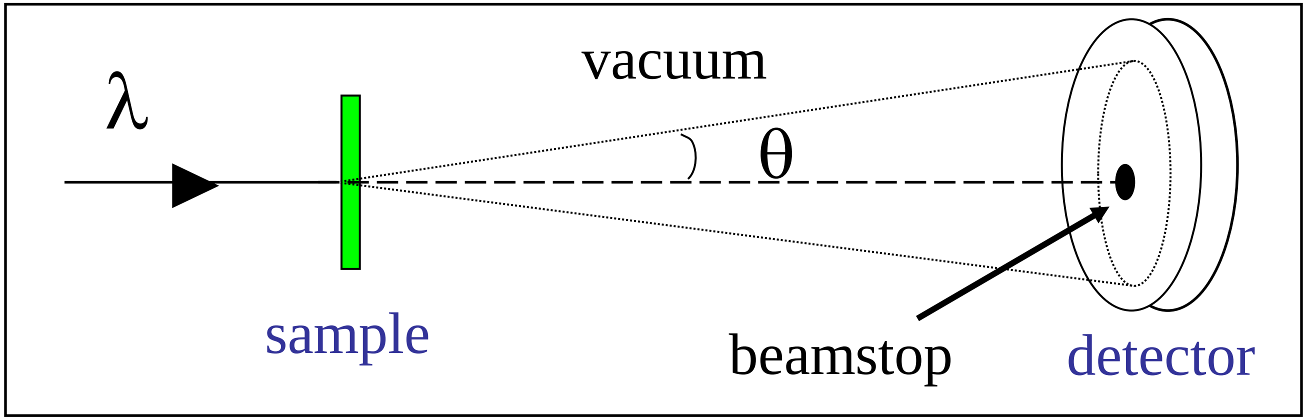
Contrast variation of certain heavier elements, e.g. Fe, Cu, Se, Br, Rb, Sr, etc.

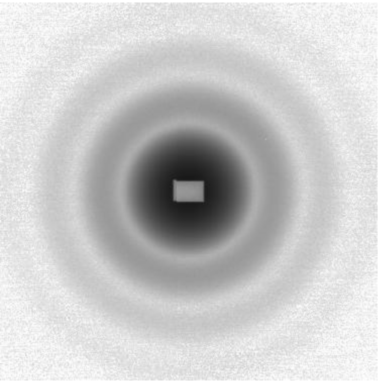
Anomalous SAXS

- ***Complementary imaging techniques***

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

Small-Angle X-ray Scattering (SAXS)





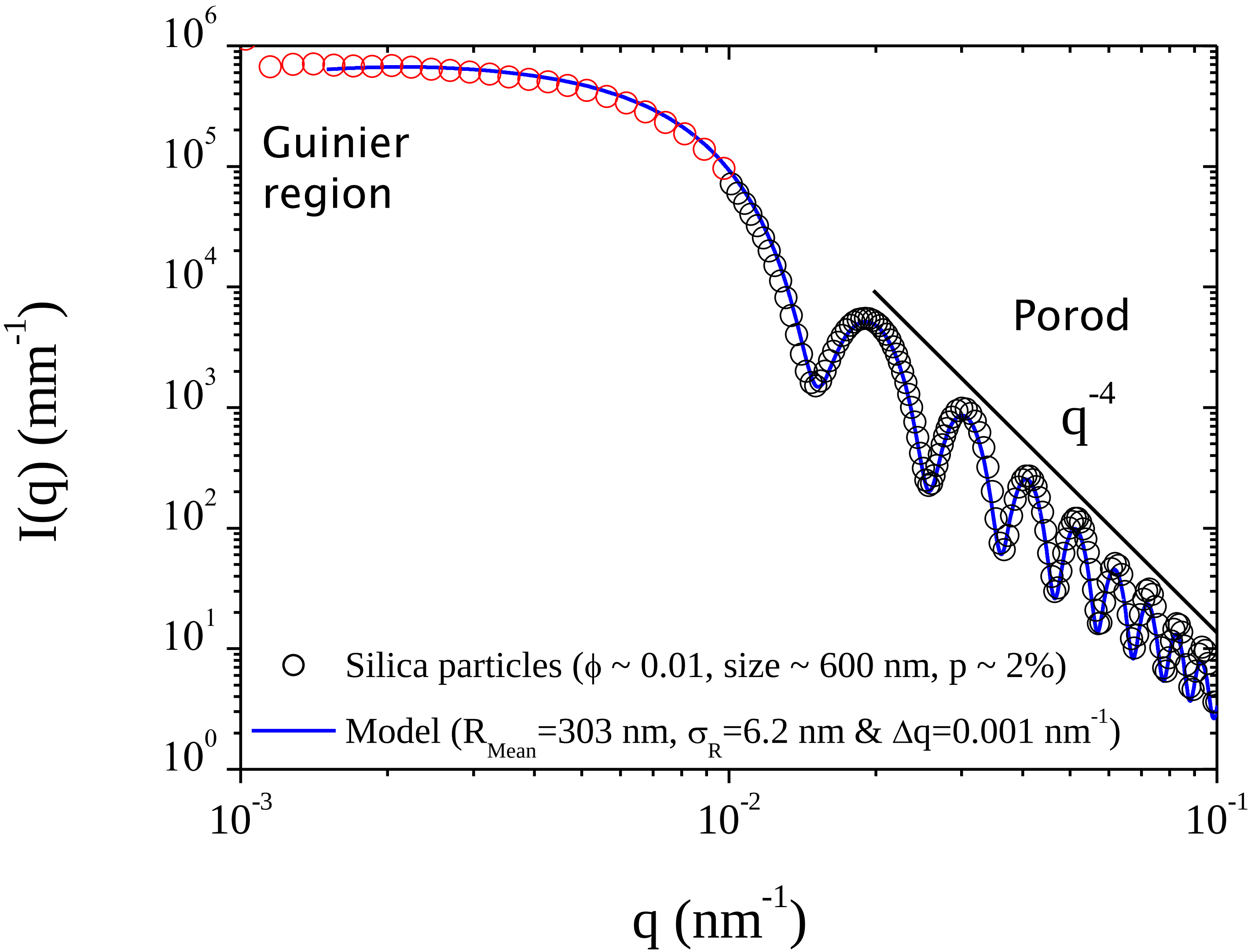
$$q = \frac{4\pi}{\lambda} \sin(\theta / 2)$$

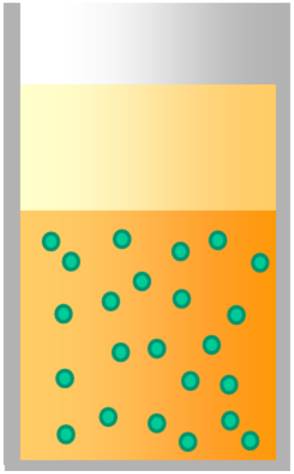
Measured Intensity: $I_S = i_0 \, T_r \, \varepsilon \, \Delta\Omega \frac{d\sigma}{d\Omega}$ Differential scattering cross-section

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

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

SAXS from dilute spherical particles





SAXS from spherical colloidal particles

$$I(q) = N\ F(q)\ S(q)$$

N – particle number density,
F(q) – single particle scattering function,
S(q) – structure factor of interactions

Thomson scattering

$$F(q) = A(q)A^*(q)$$

$\rho(r)$ – radial electron density

$$A(q) = 4\pi\ r_e \int_0^\infty [\rho(r) - \rho_m] \frac{\sin qr}{qr} r^2 dr$$

r_e – classical electron radius =2.82x10^{-15} m

$$\rho^* = r_e \rho_S$$

scattering length density for homogeneous particles

$$\Delta\rho^* = \rho^*_S - \rho^*_m$$

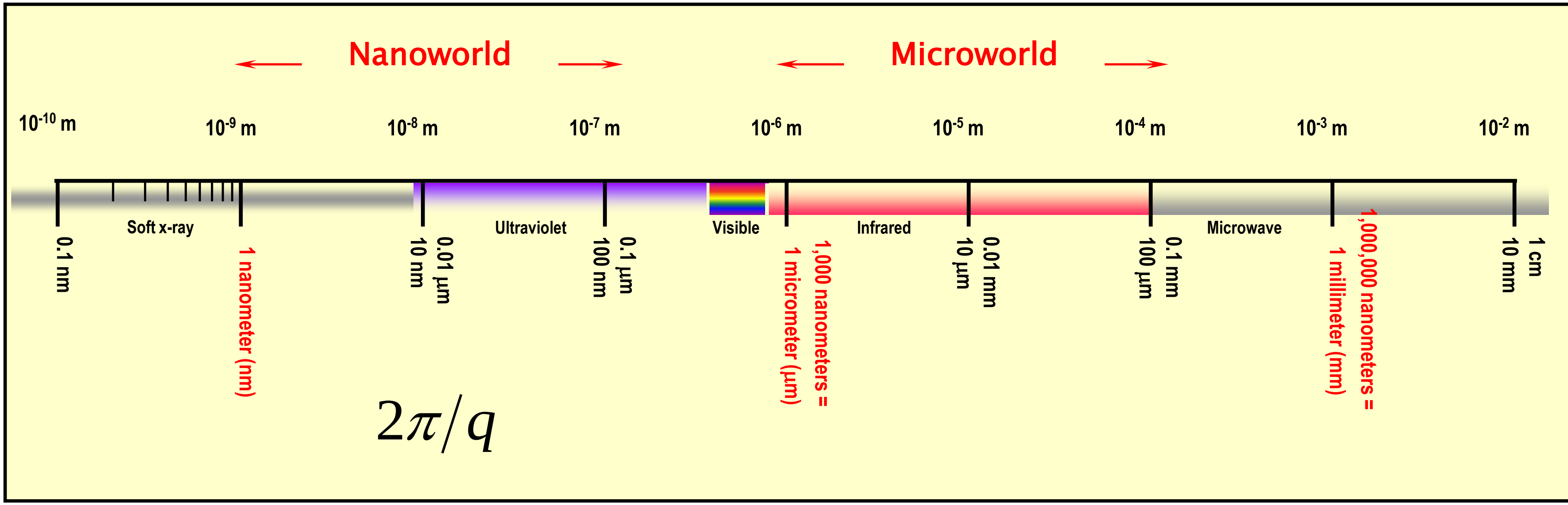
contrast

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

V – volume of the particle
P(q) – form factor

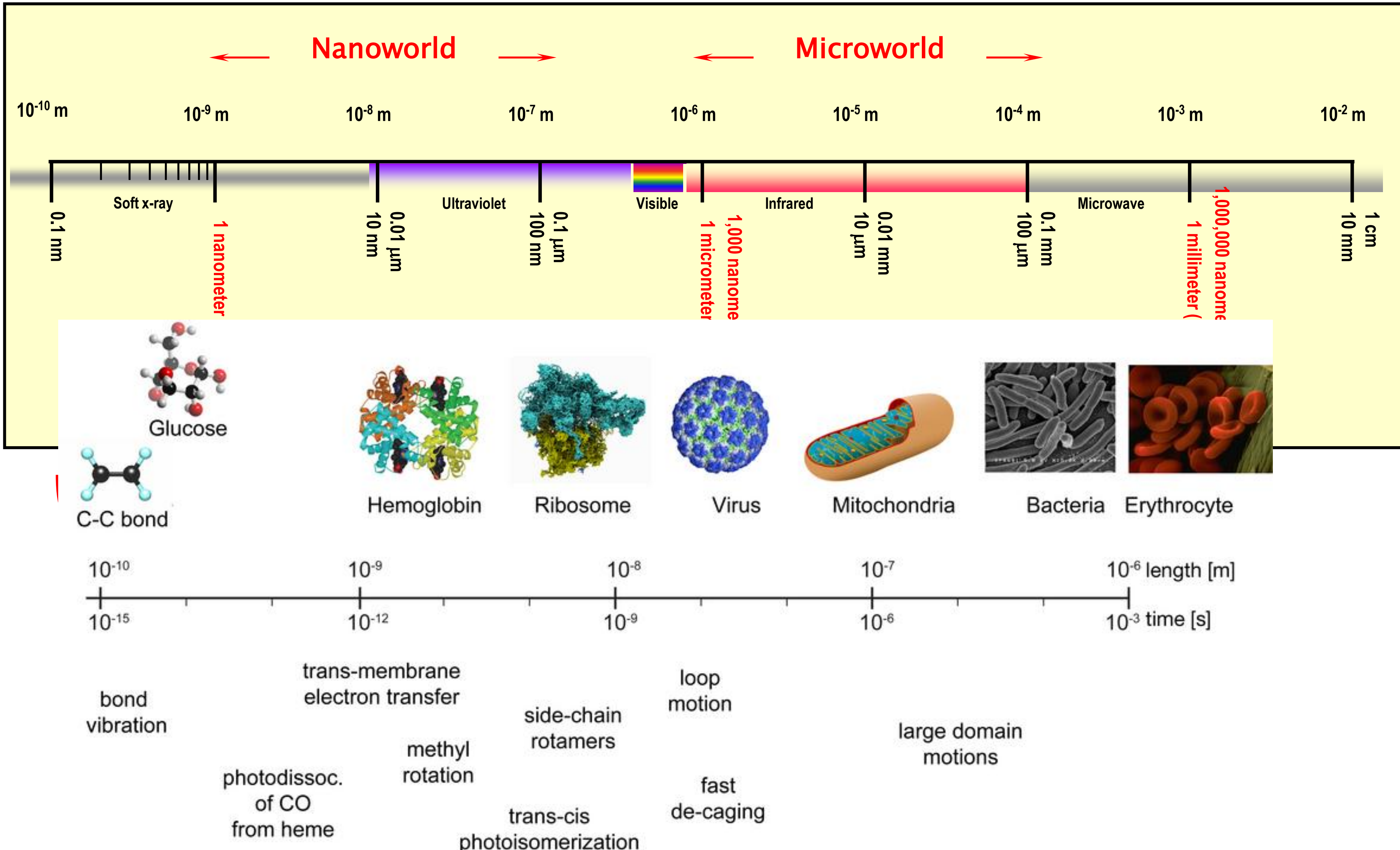
Calculation of S(q) involves approximations (e.g. Percus-Yevick closure)

Size scales probed by SAXS & related techniques



Colloids
Polymers
Surfactants
Liquid crystals
Etc.

Size scales probed by SAXS & related techniques

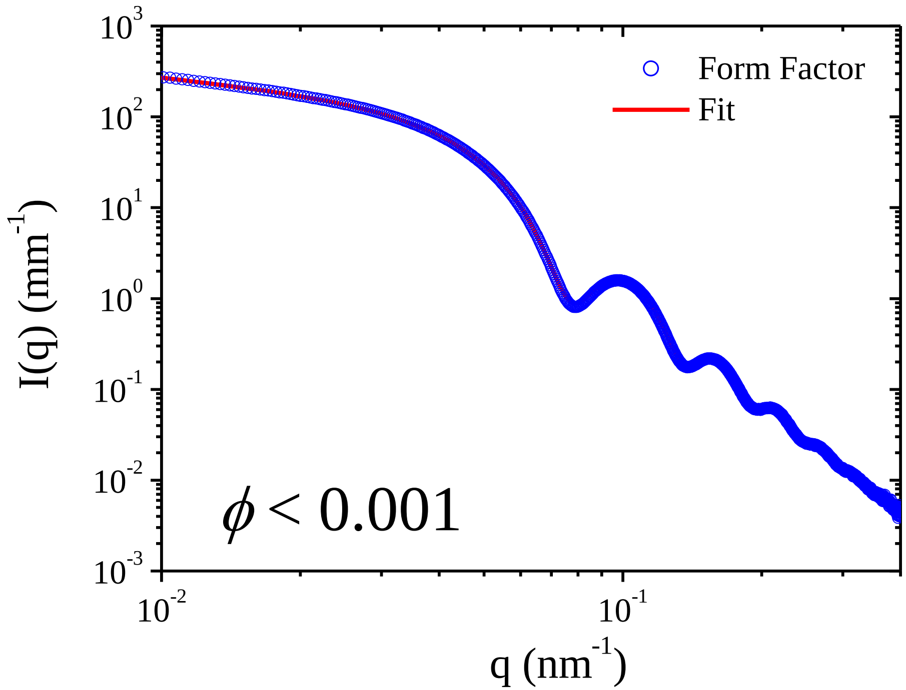


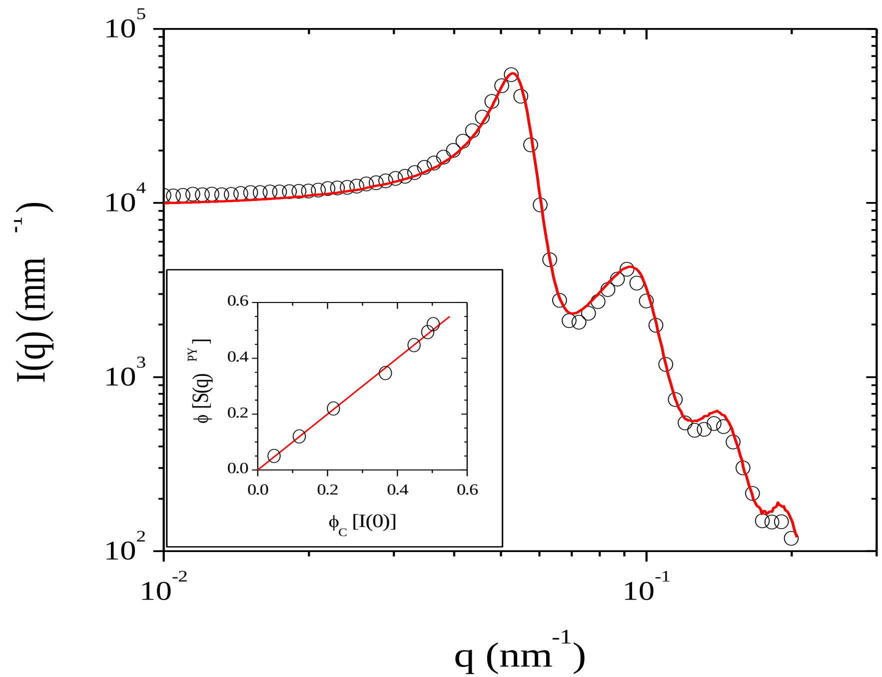
Form & Structure Factors

Differential scattering cross-section per unit volume

$$I(q) = N(\Delta\rho^{*} V)^{2} P(q)\ S_{M}(q)$$

Experimental *P(q)*, polydisperse & *S (q)* within Percus-Yevick (PY) approximation





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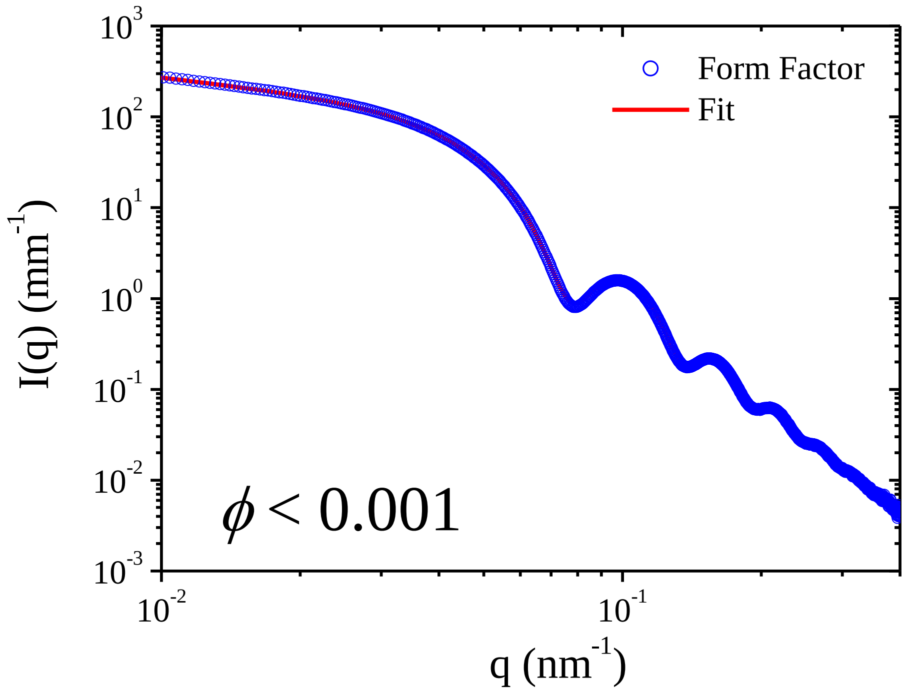
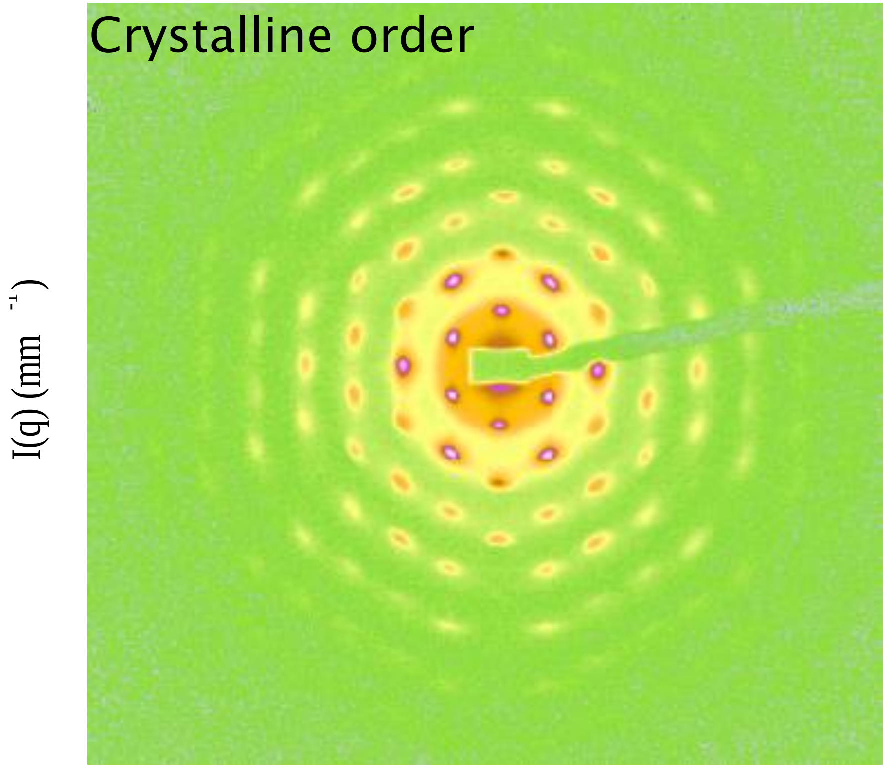
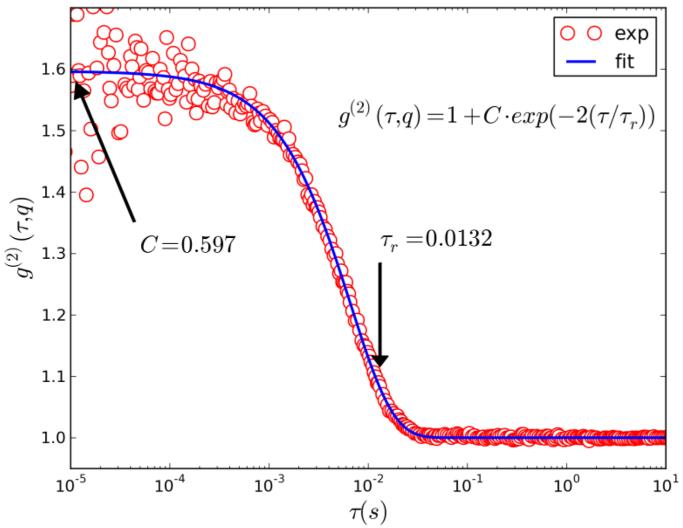




X-ray Photon Correlation Spectroscopy (XPCS)

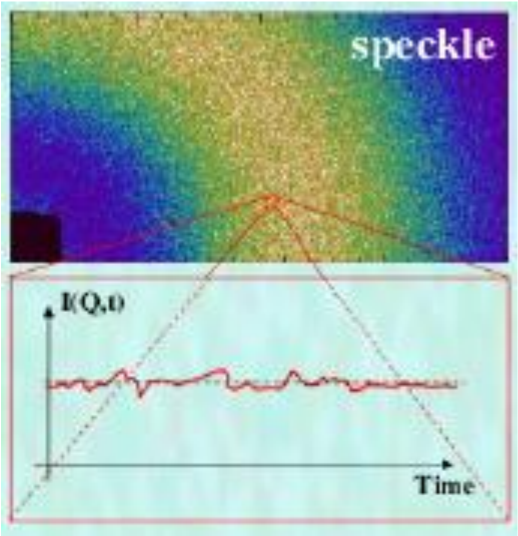
$$g^{(2)}(\tau) = \frac{\langle I(t) I(t+\tau) \rangle}{\langle I(t) \rangle^2}$$

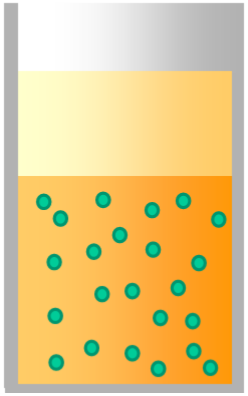


Silica microspheres in water
d=0.49±0.02µm, q=0.09 nm^{-1}

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

Beamline – ID10





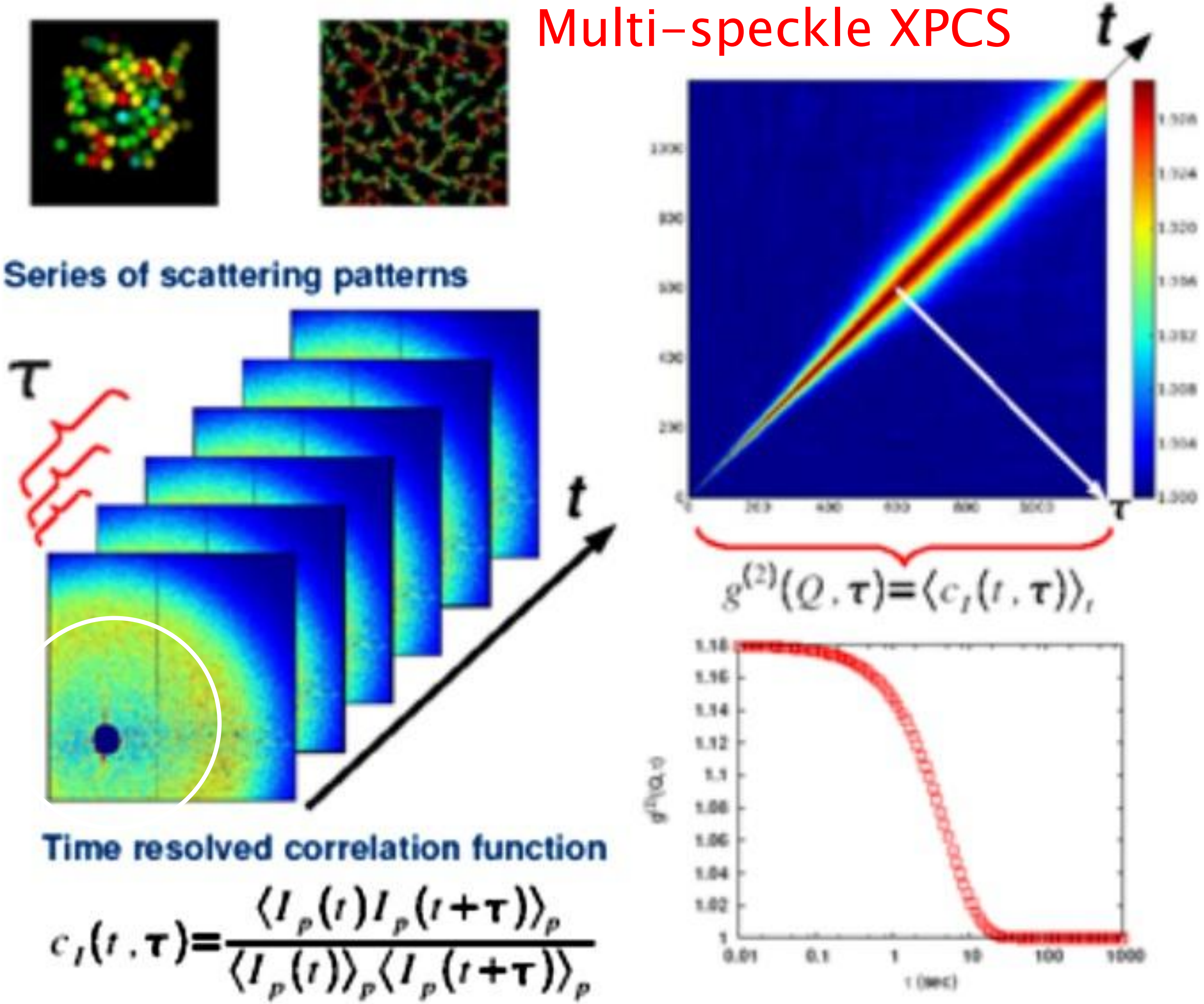
$$\langle \Delta r^2(\tau) \rangle = 6 D_0 \tau$$

mean-square displacement

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

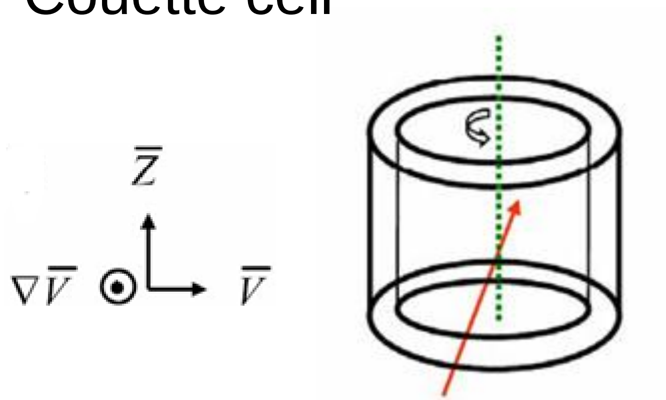
diffusion constant
(Stokes-Einstein)

Multi-speckle XPCS

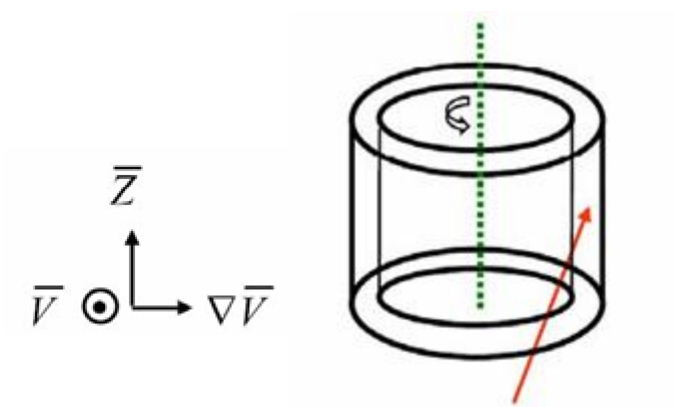


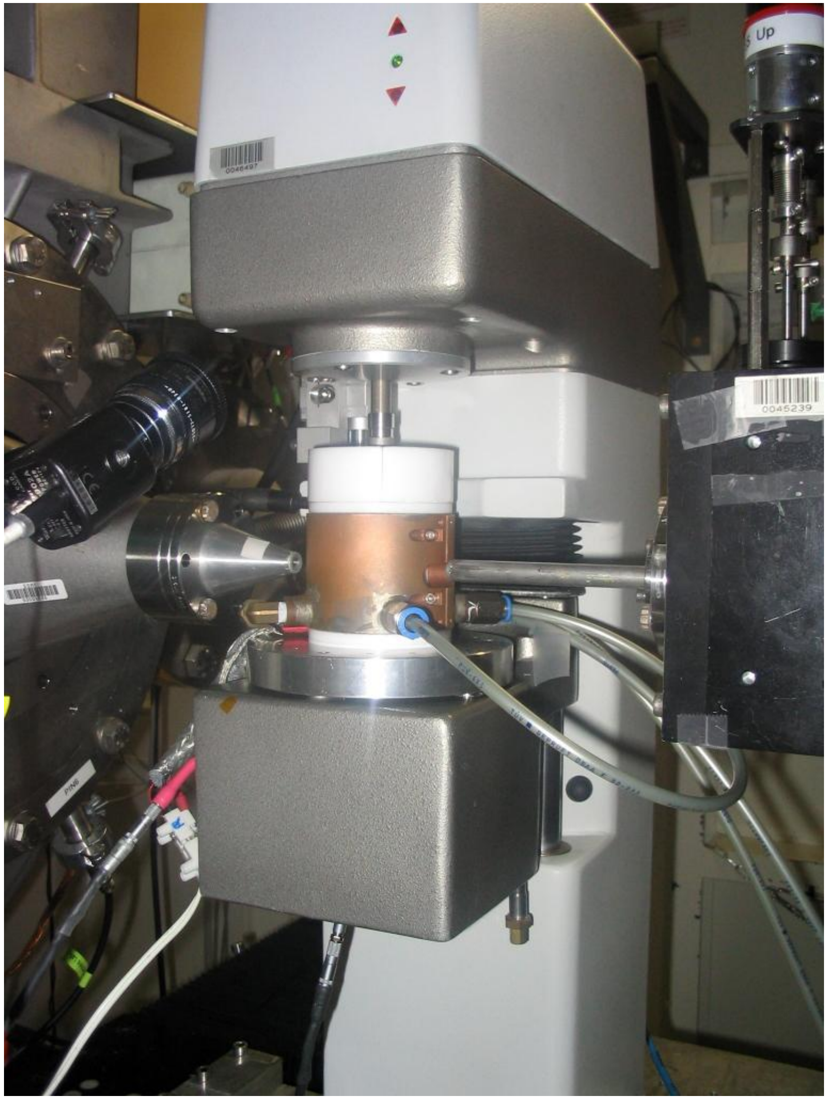
Combination with shear flow

Couette cell



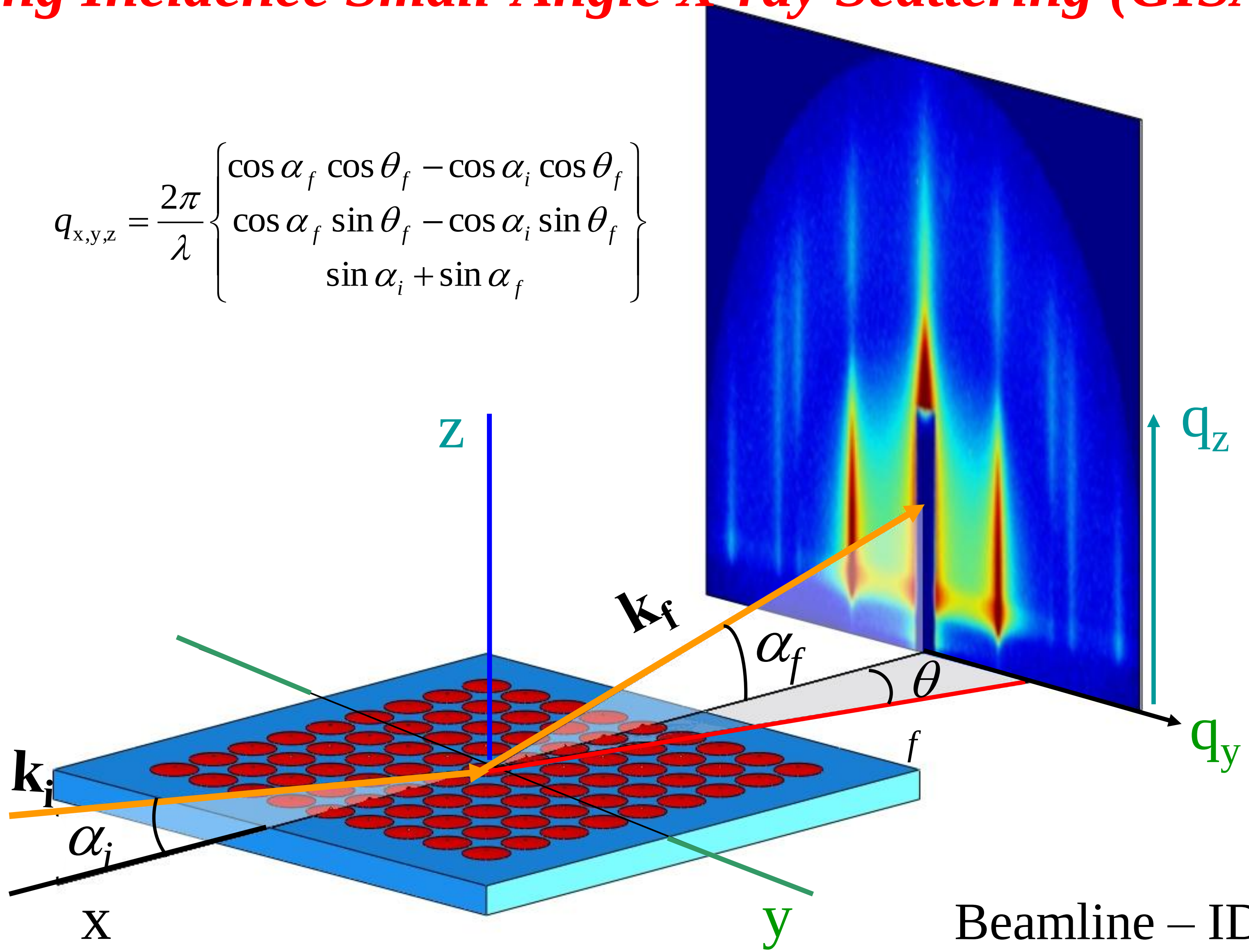
X-ray beam





Grazing Incidence Small-Angle X-ray Scattering (GISAXS)

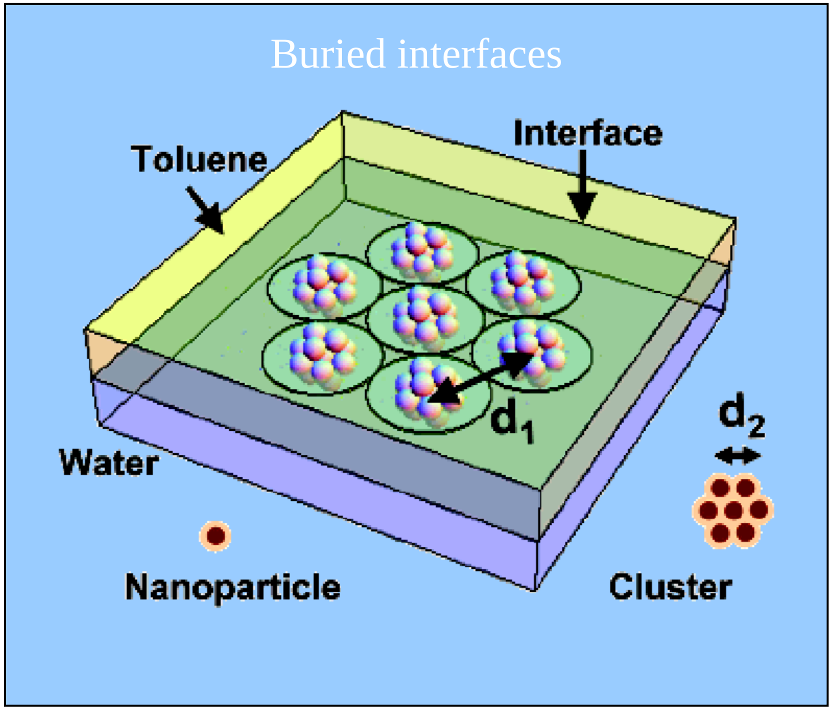
$$q_{x,y,z} = \frac{2\pi}{\lambda}\begin{Bmatrix} \cos\alpha_f \cos\theta_f - \cos\alpha_i \cos\theta_f \\ \cos\alpha_f \sin\theta_f - \cos\alpha_i \sin\theta_f \\ \sin\alpha_i + \sin\alpha_f \end{Bmatrix}$$

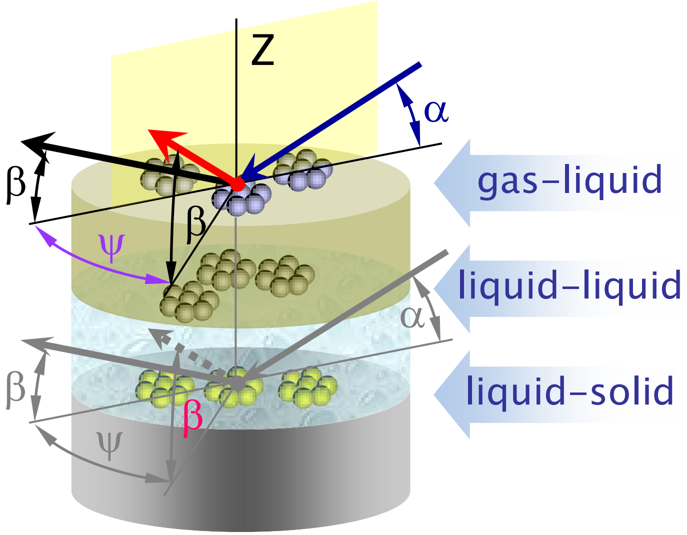


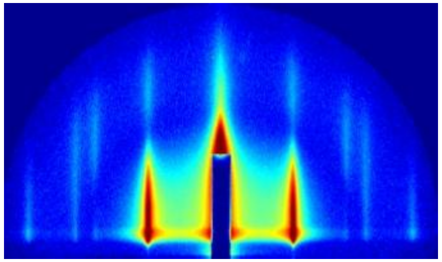
Beamline – ID10

Soft Interfaces Scattering

- Surface structure of simple and complex fluids (colloid, gel, sol,…)
- Morphology and crystalline structure of thin organic and inorganic films
- 2D organization of molecules, macromolecules and nanoparticles
- Bio-mimetic systems & Bio-mineralization

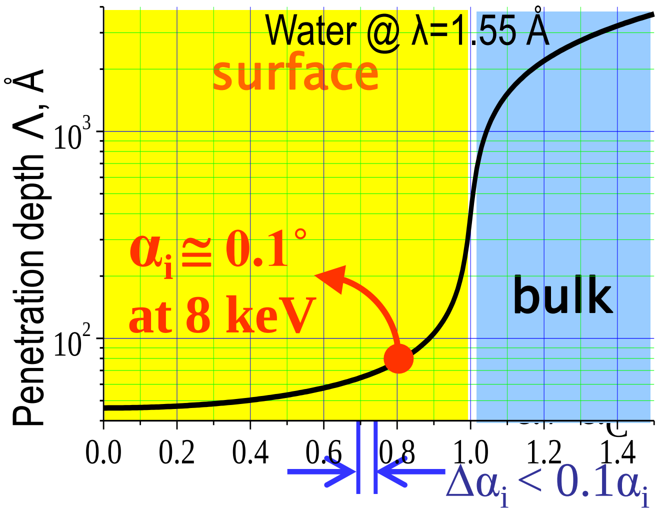


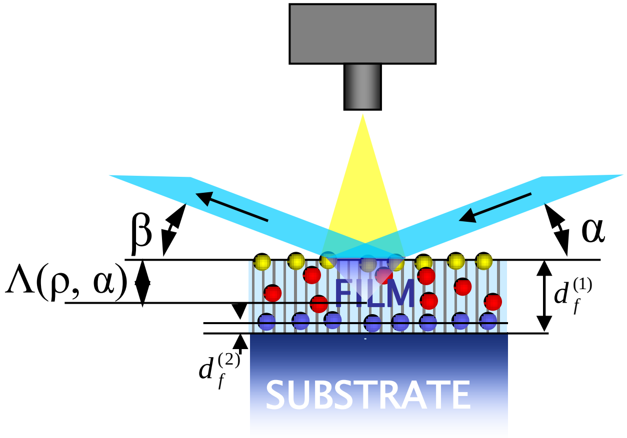




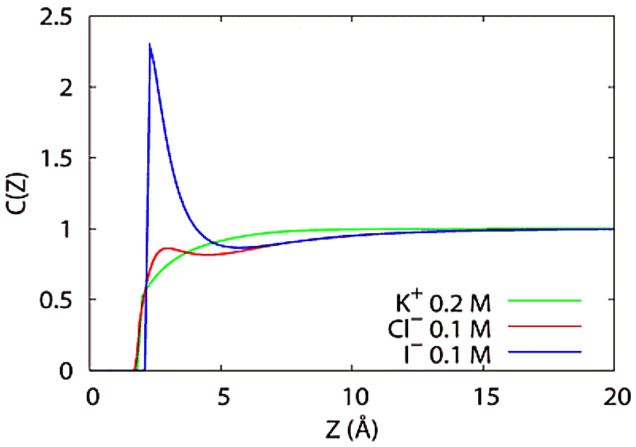
Soft Interfaces Scattering

Varying the penetration depth

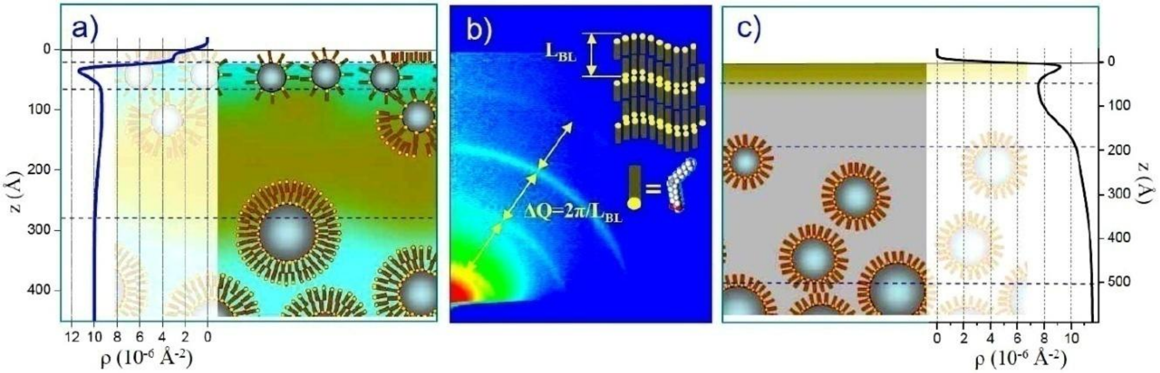




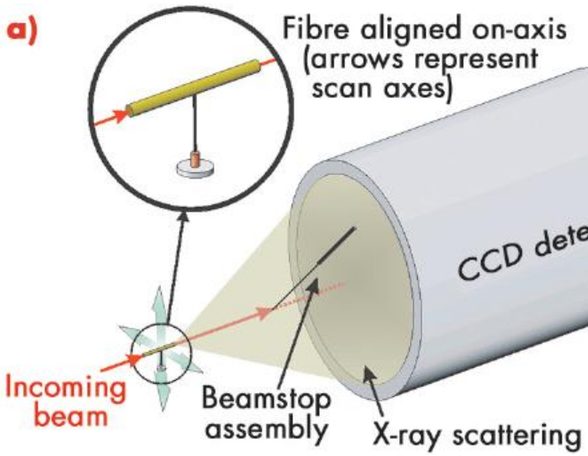
Elements distribution



Complex fluids



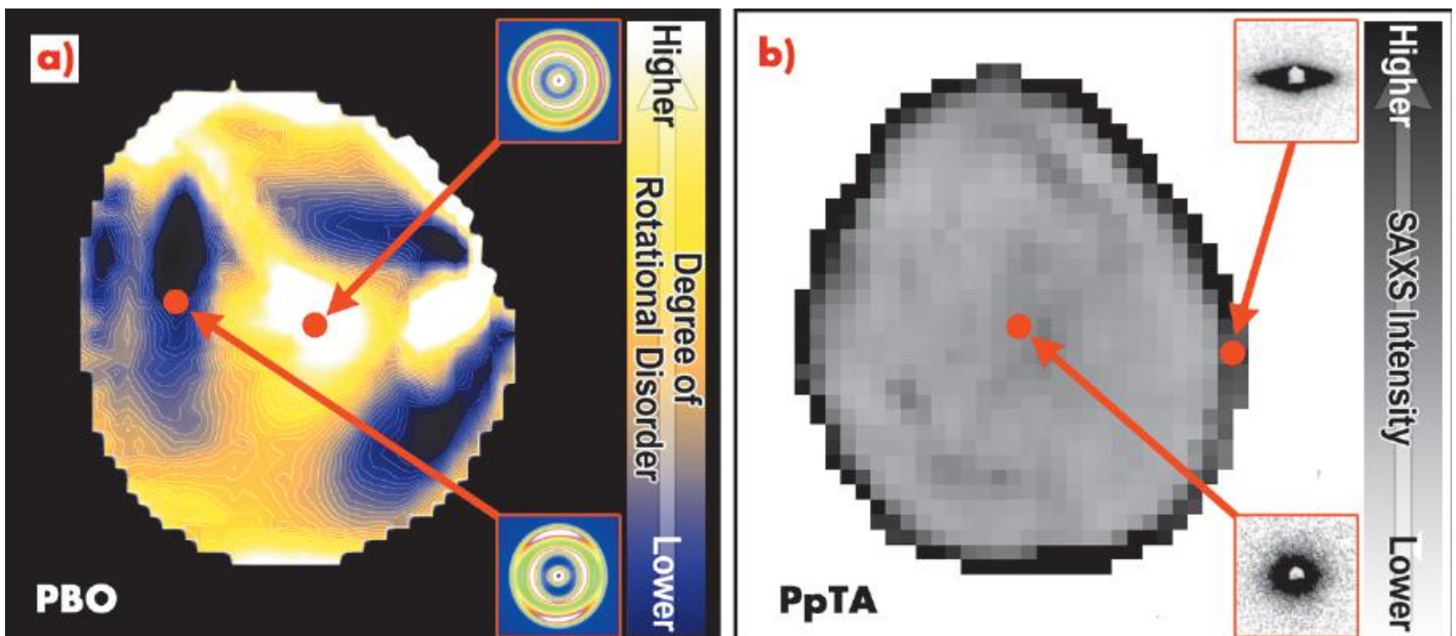
Micro-diffraction (ID13)



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

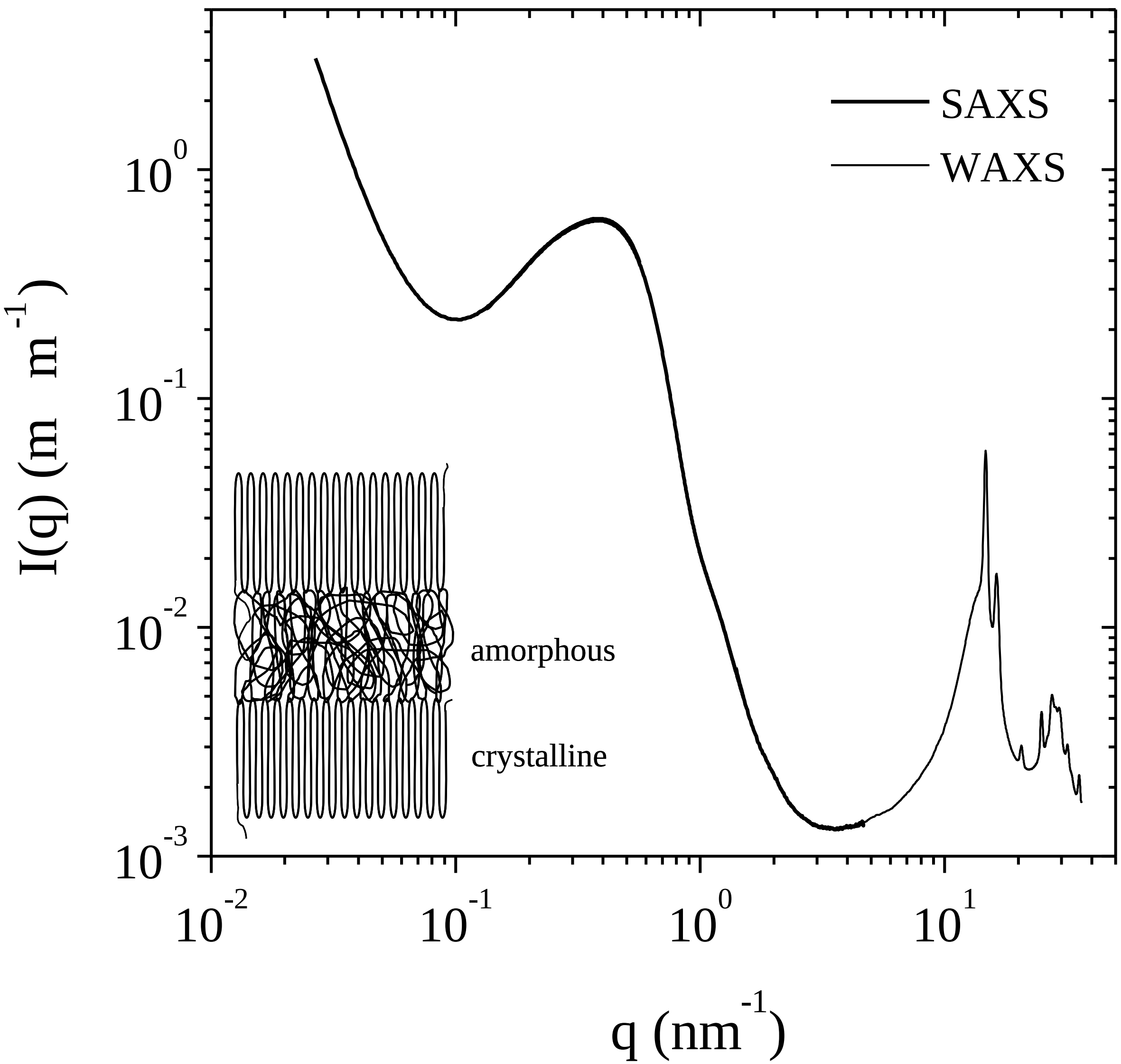
Correlate the local nanostructure to the fiber mechanical properties.

Elucidating the local nanostructure

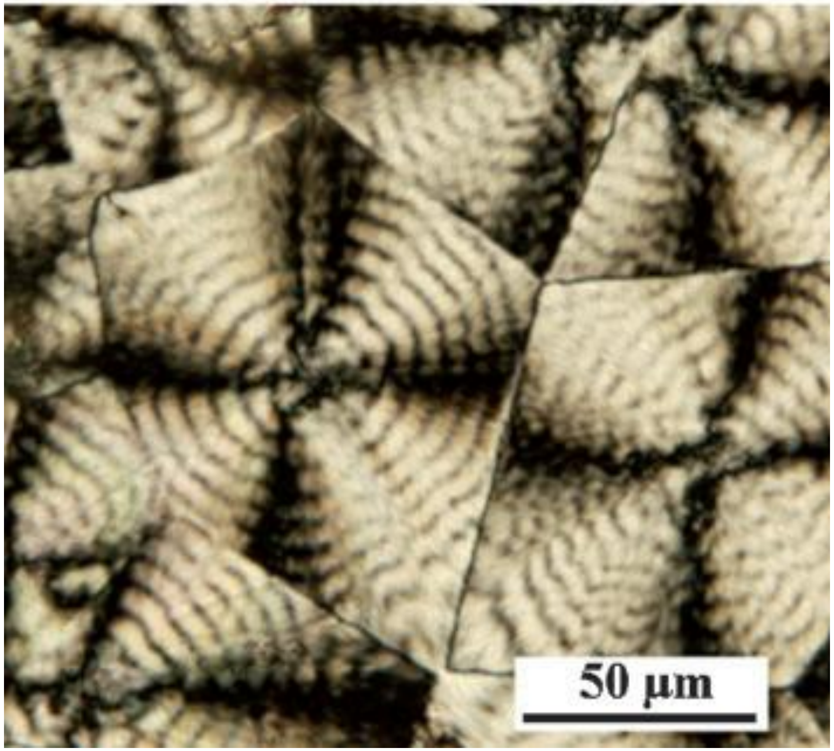


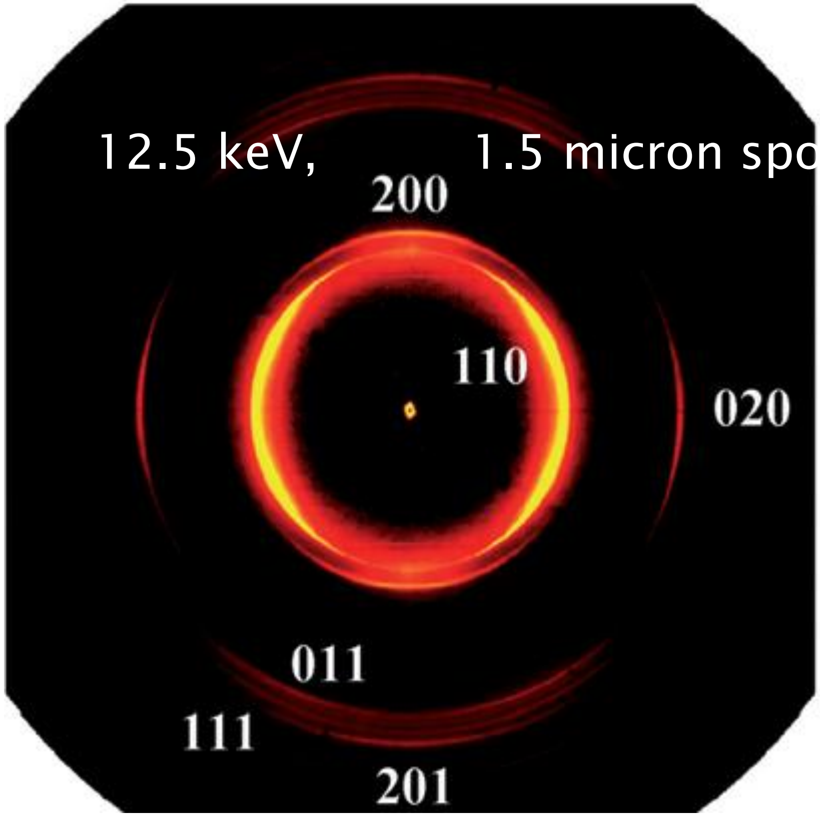
R. Davies *et al.*, *APL (2008)*

SAXS/WAXS from Semi-crystalline polymers



Scanning Micro-diffraction on HDPE spherulites



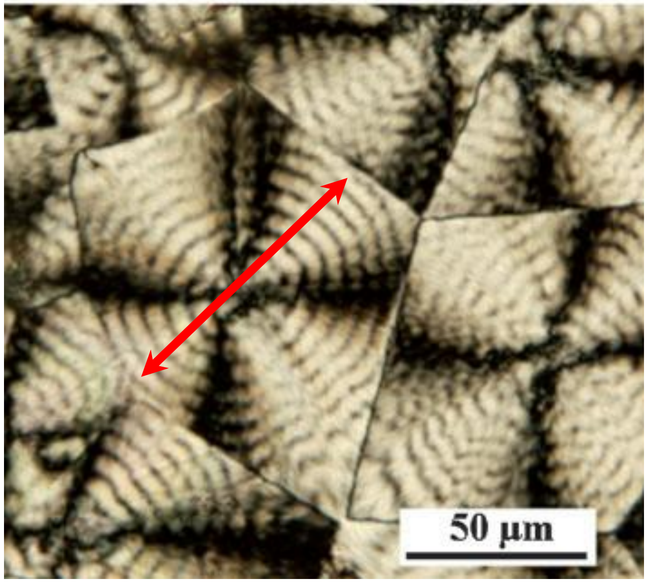


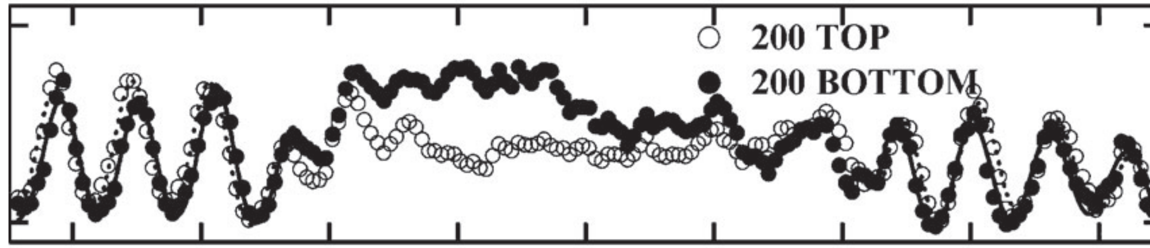
- high density poly-ethylene
- spherulites under polarized light banded structures indicating long range order

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

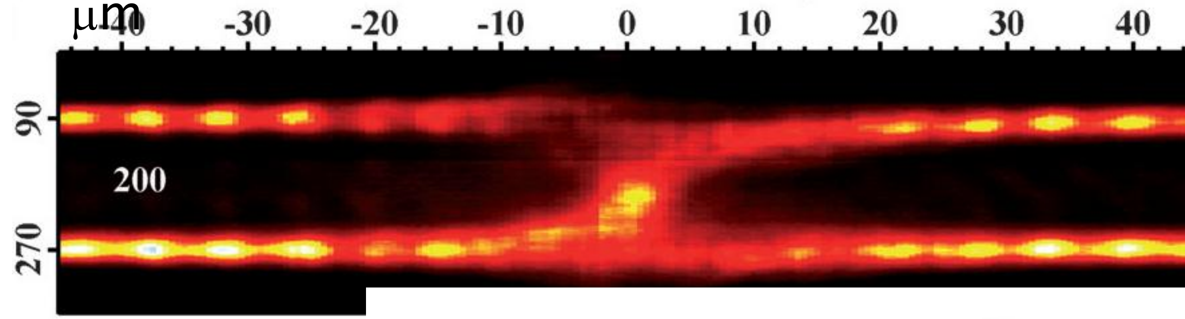
Rosenthal M. et al., Angewandte Chemie, (2011)

Micro-diffraction on HDPE spherulites

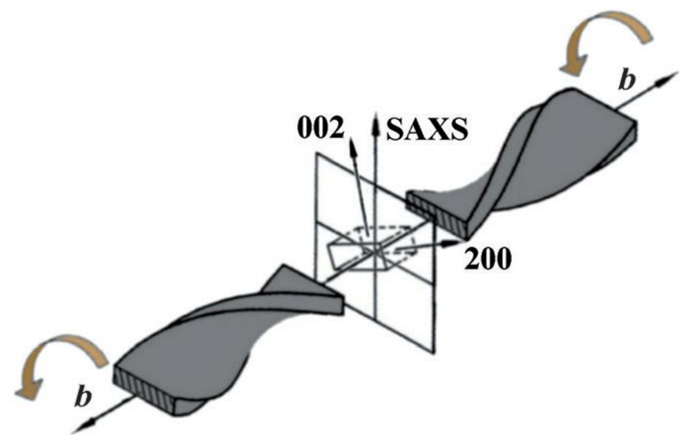




Azimuth/Intensity vs Distance from the center in µm



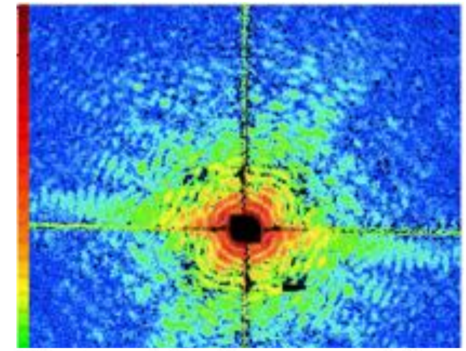
- 35° tilt between c-axis and the normal of the base plane of crystalline lamellas
- orientation of b-axis aligned with growth direction
- chirality can be determined



Coherent X-ray Diffractive Imaging (CDI)

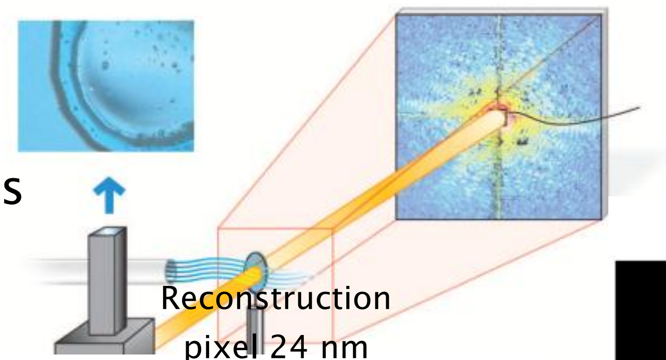
2D and 3D imaging of non-crystalline objects, biological samples with nanometers resolution

Lensless imaging technique



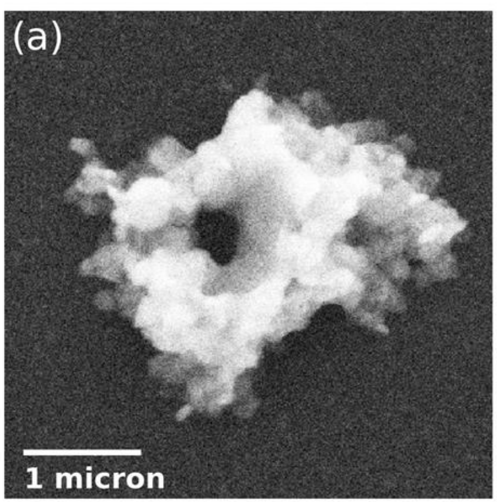
Cluster of Fe_2P nanoparticles

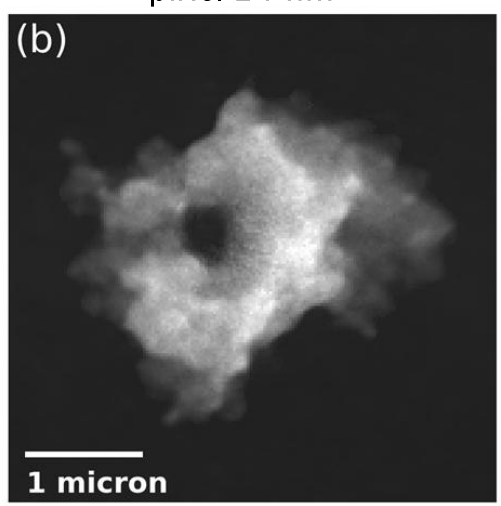
Thick or small samples (single molecules)

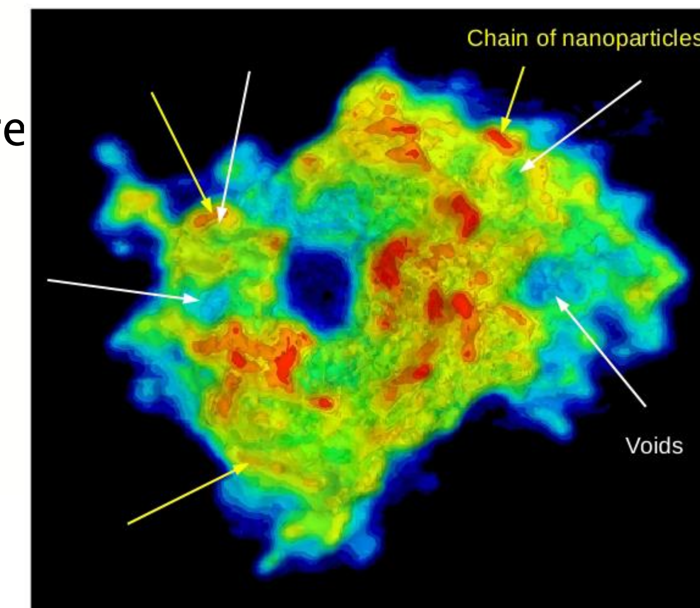


Reconstruction pixel 24 nm

SEM image

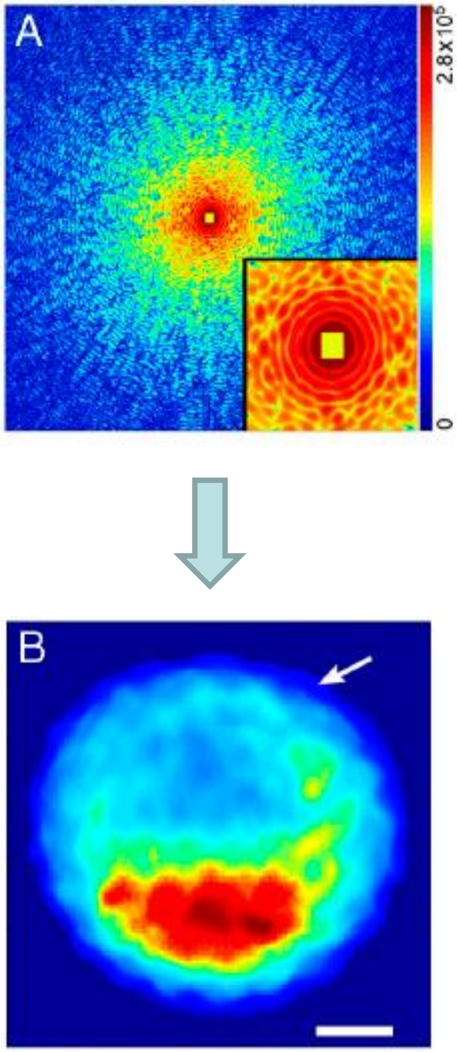




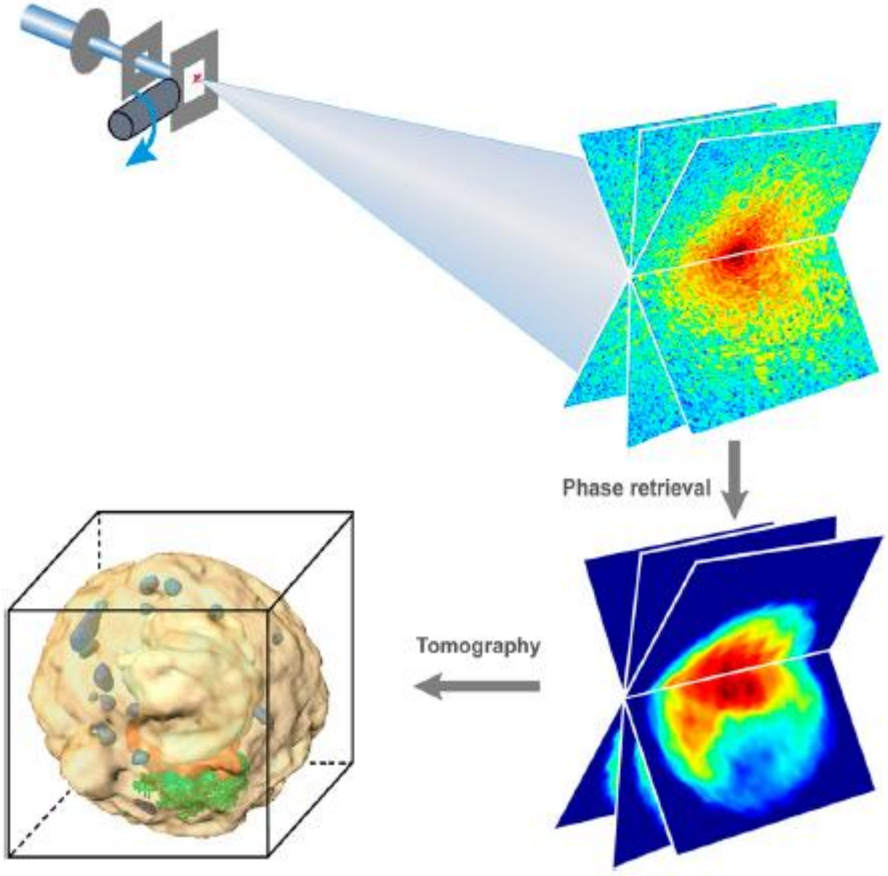


CDI of Biological Specimen

Phases encoded by over sampling of the diffraction pattern



3D reconstruction



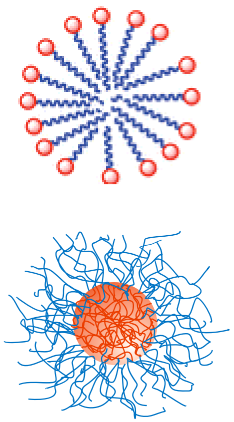
H. Jiang *et al.*, PNAS *(2010)*

Spontaneous self-assembly

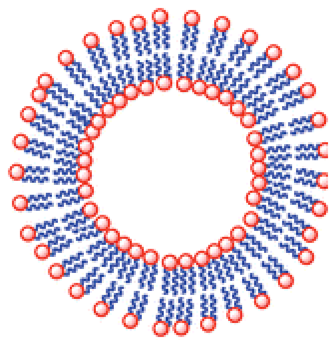
Motivation: understanding self-assembly in nature

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

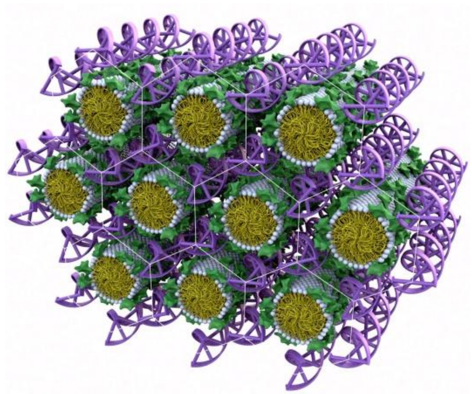
Complexity →



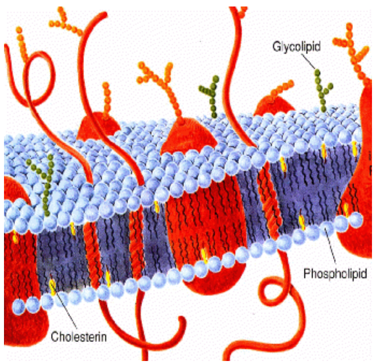
Micelles



Vesicles



Lipid-DNA complex



Cell

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

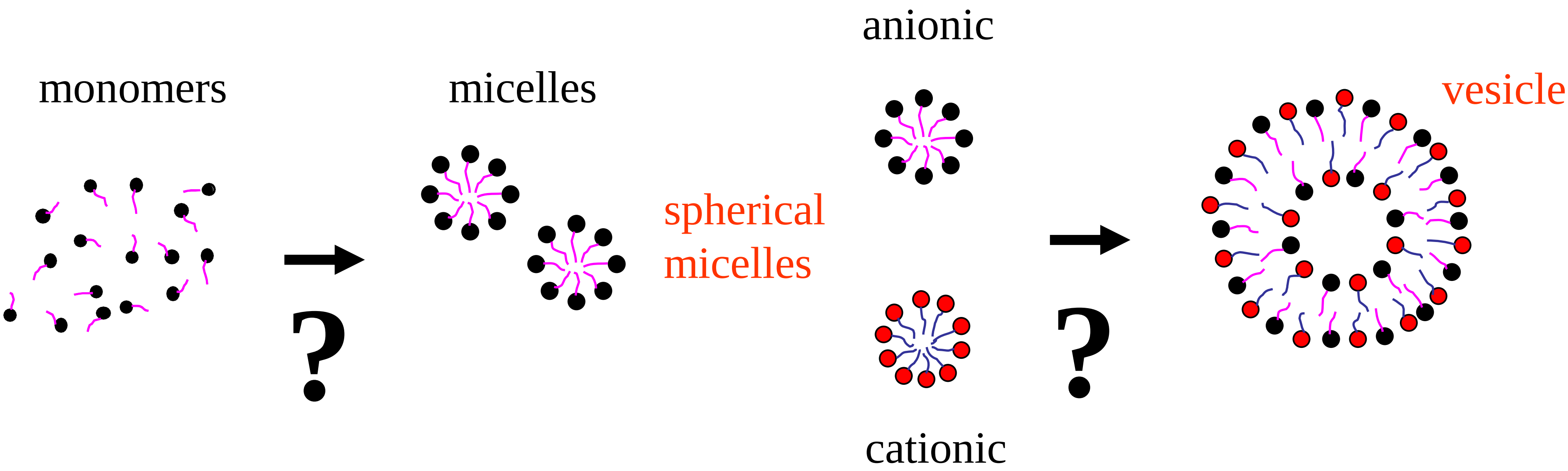
→ How can these complexes be tuned and manipulated to new materials (e.g. biomedical/pharmaceutical applications) ?

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



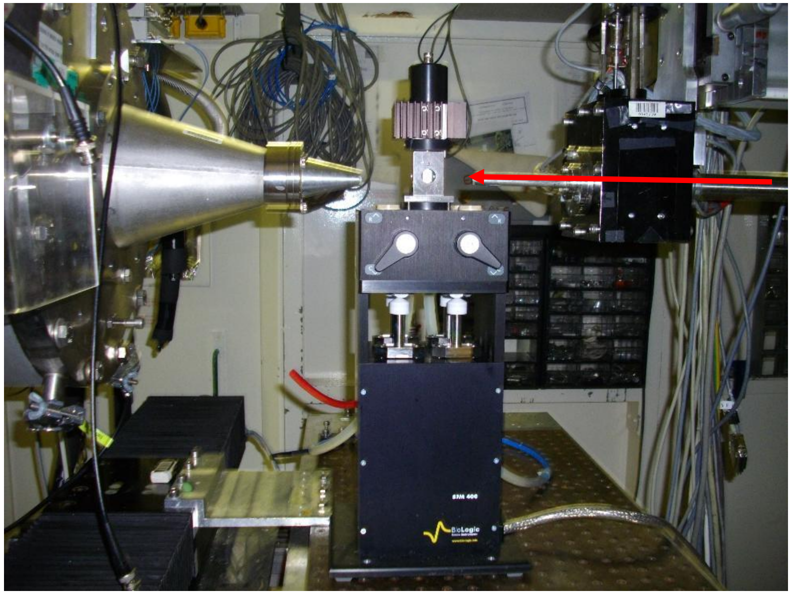
Rate-limiting steps » predictive capability

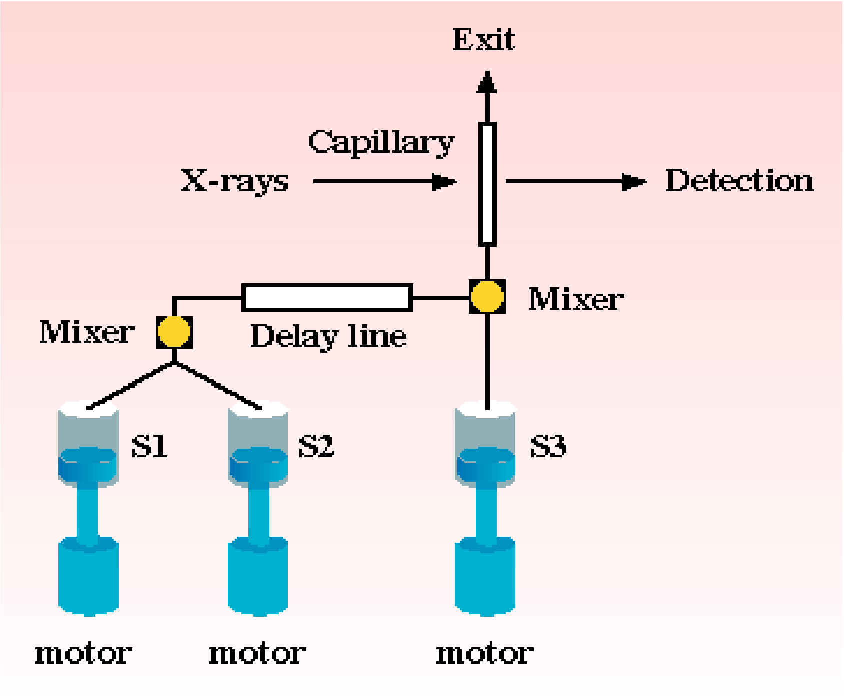
Kinetic pathway: stopped-flow rapid mixing & time-resolved SAXS

Stopped-Flow Mixing Device

- Rapid mixing of reactants in turbulent flow through a mixer
- Solenoid valve at the exit to stop the flow of the mixture
- Deadtime ~ a few millisecond

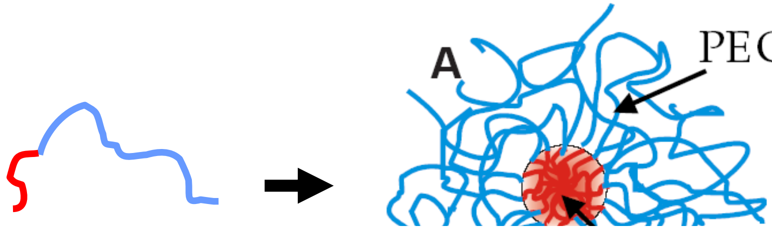
Beamline ID02@ESRF

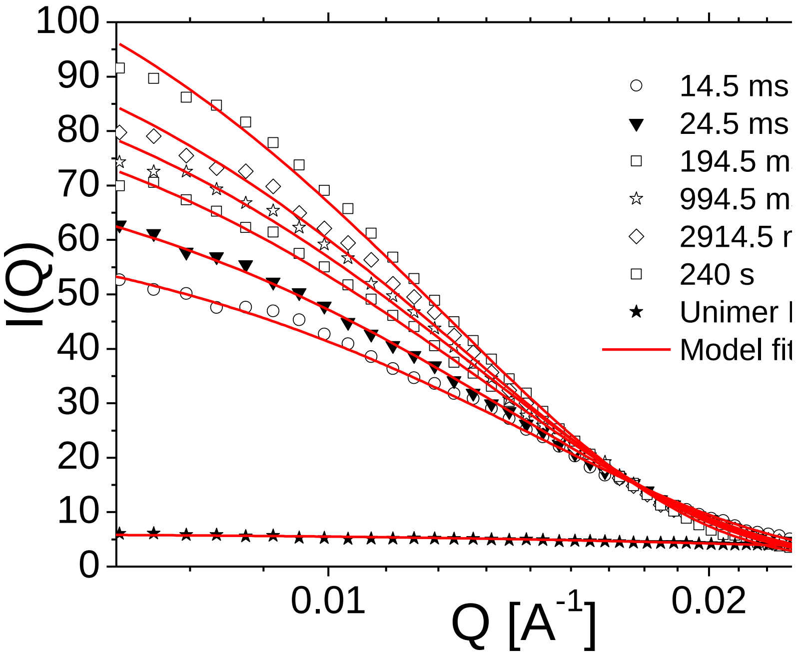


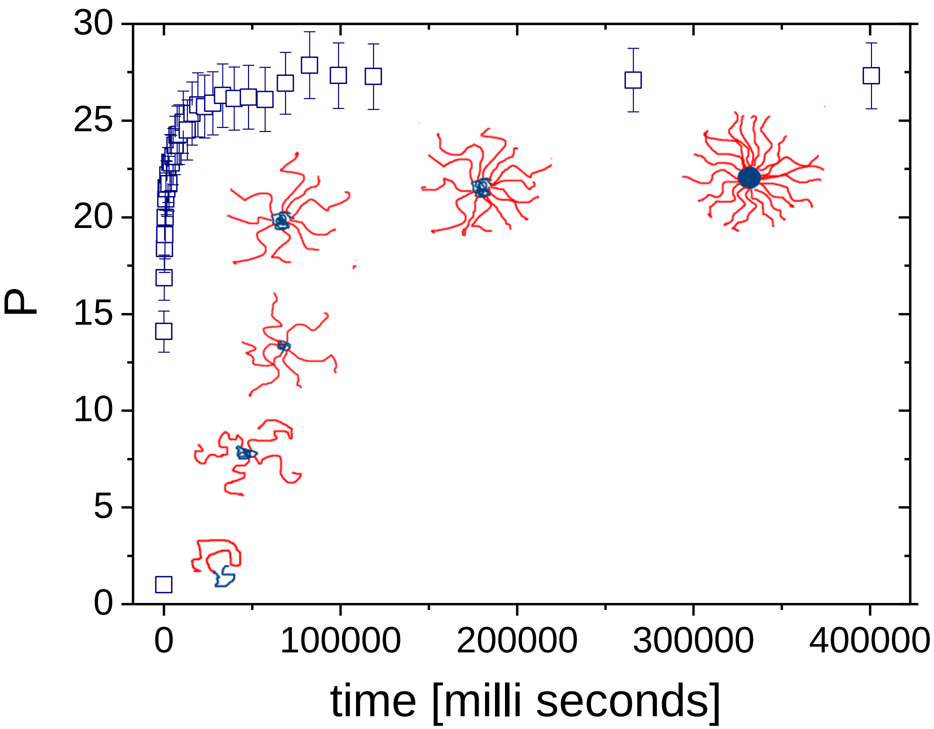


Spontaneous self-assembly of block copolymer micelles

Rapid jump in solvent selectivity / Interfacial tension



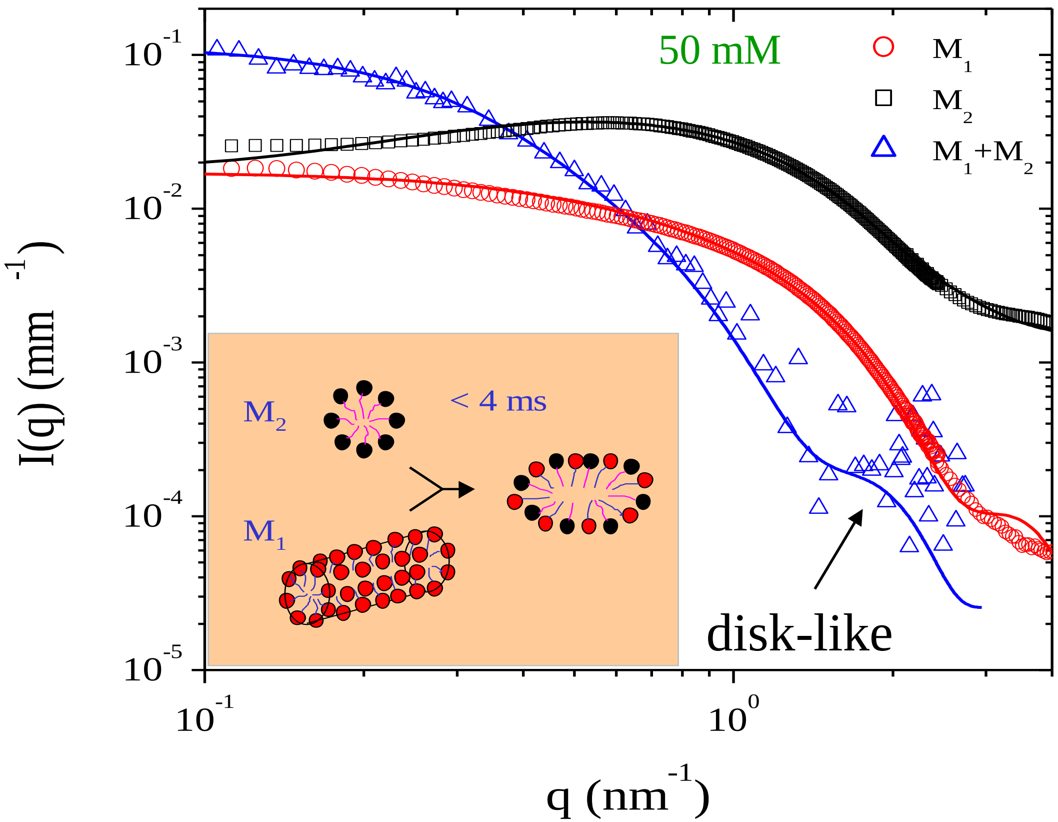


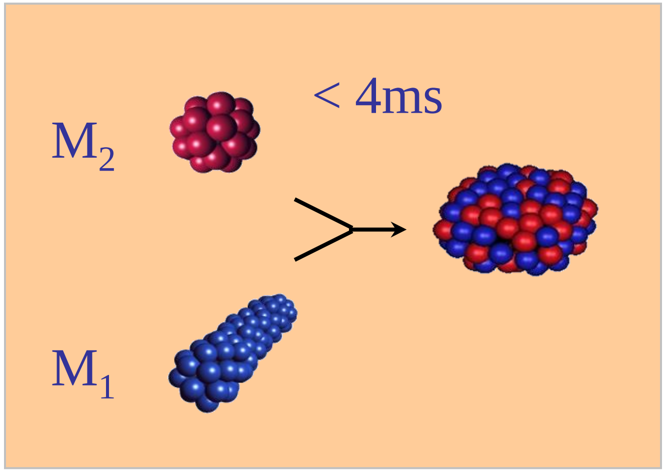


» mean aggregation number

R. Lund, *et al.*, PRL, 102, 188301 (2009)

Self-assembly of unilamellar vesicles





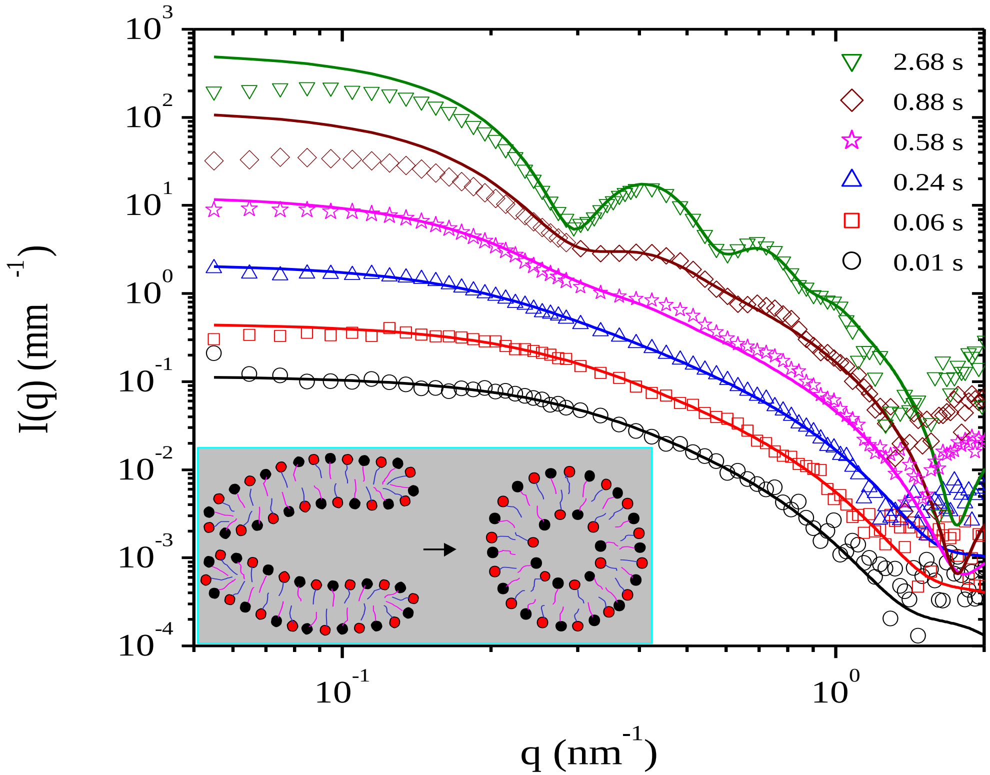
- disk-like objects with:
  R = 7.5nm; H = 4.8nm
- size of initial disks:
  670 ~ 2 x size rod-like micelle

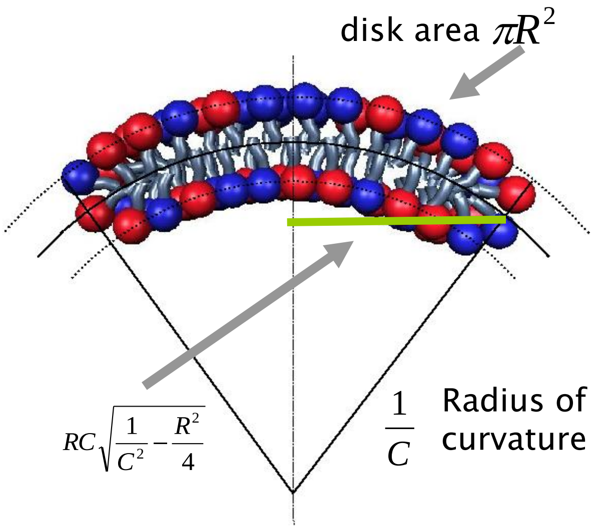
T.M. Weiss *et al.*, PRL (2005)

Langmuir (2008)

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

Growth of disk-like micelles





Bending energy vs Edge energy

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

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

κ & $\bar{\kappa}$ - bending moduli

Λ - line tension

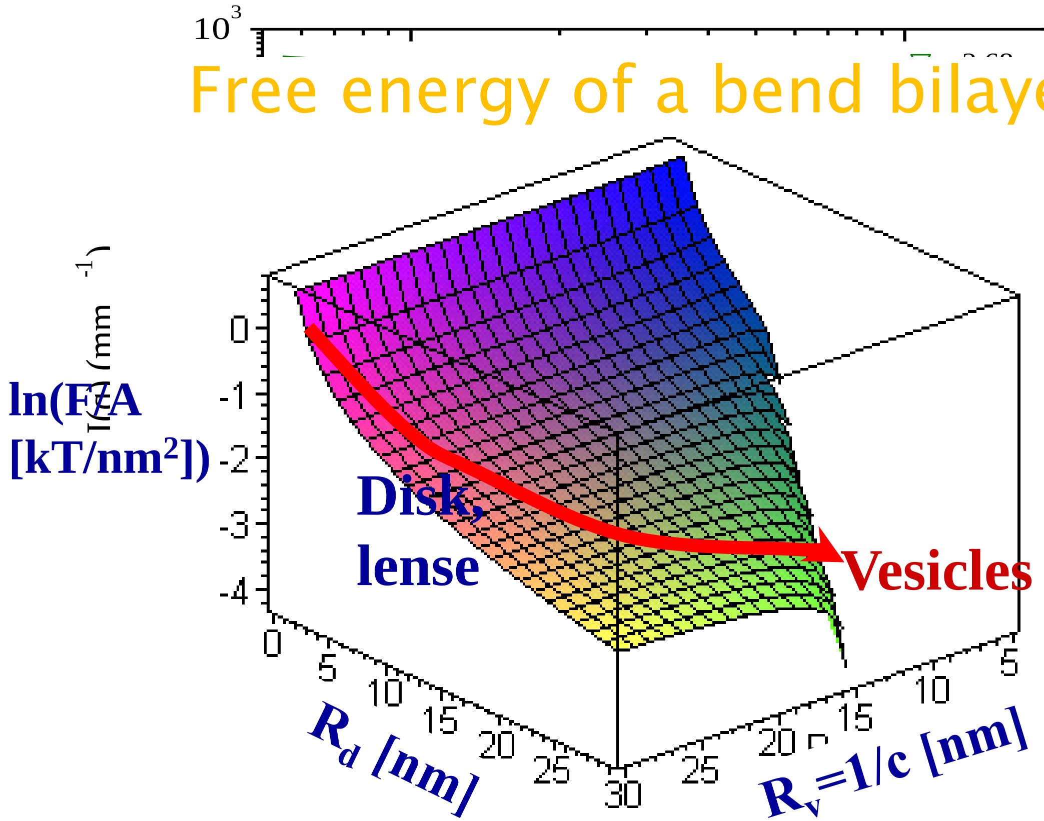
At the closing state: $R_{\max} \approx \dfrac{4(2\kappa + \bar{\kappa})}{\Lambda}$

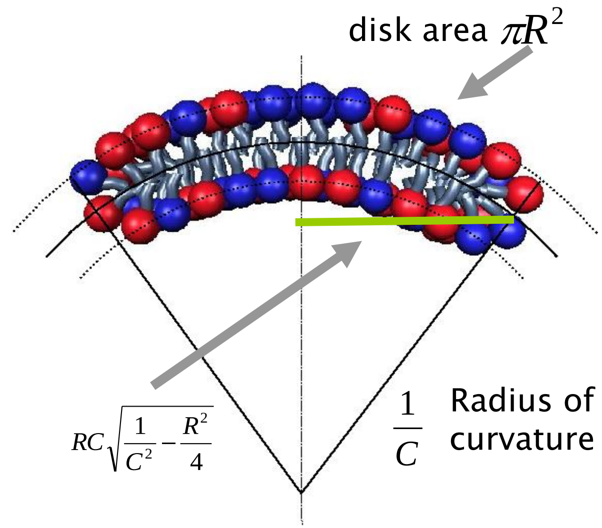
T.M. Weiss *et al.*, PRL (2005)

Langmuir (2008)

Growth of disk-like micelles

Free energy of a bend bilayer





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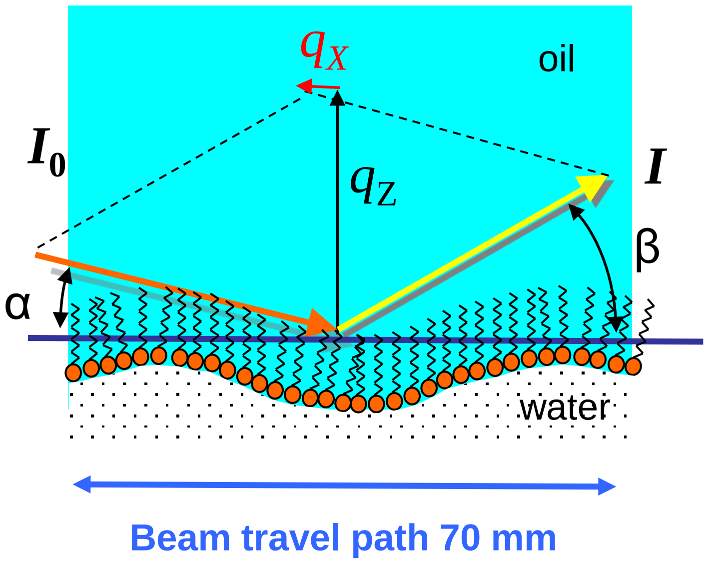
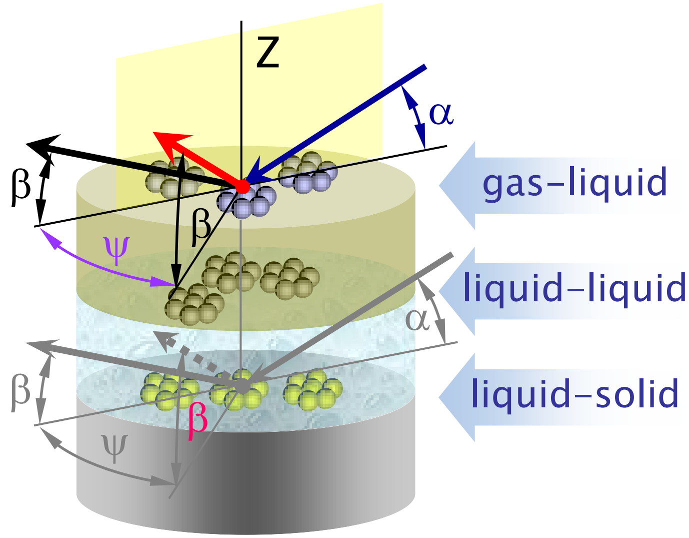
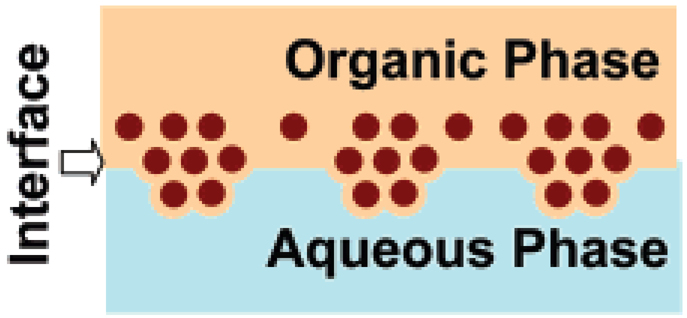
T.M. Weiss *et al.*, PRL (2005)

Langmuir (2008)

Soft matter self-assembly at interfaces

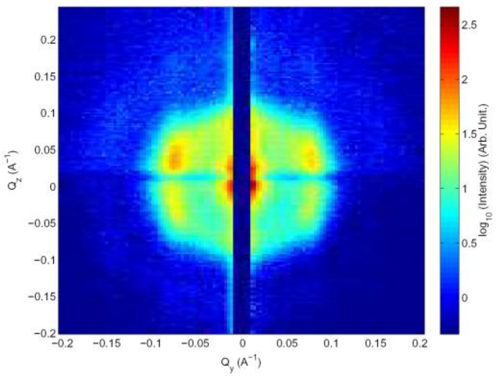


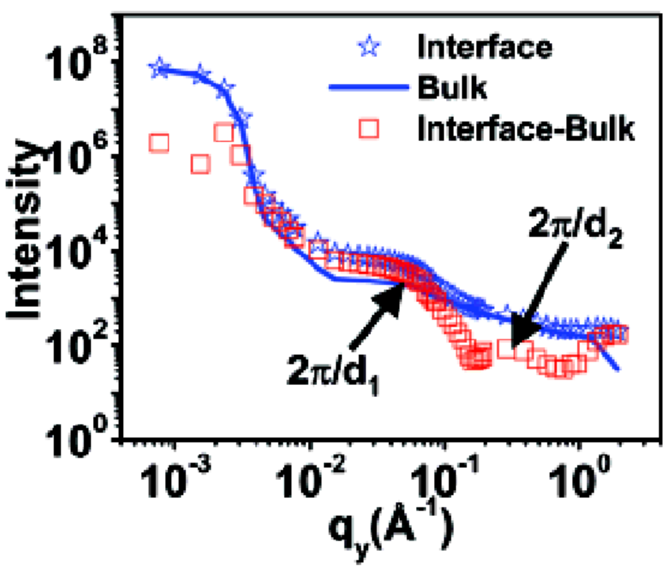


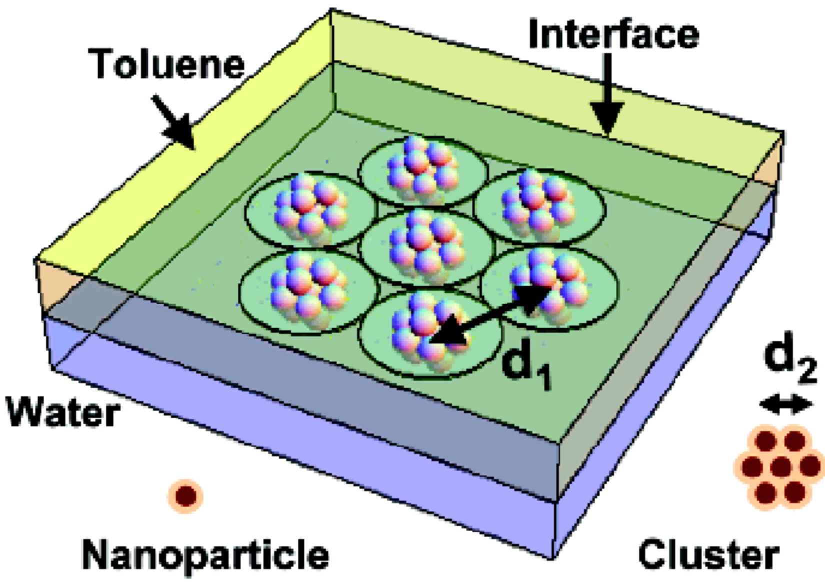


Interfacial cavities for reaction

Formation and Ordering of Gold Nanoparticles at the Toluene-Water Interface







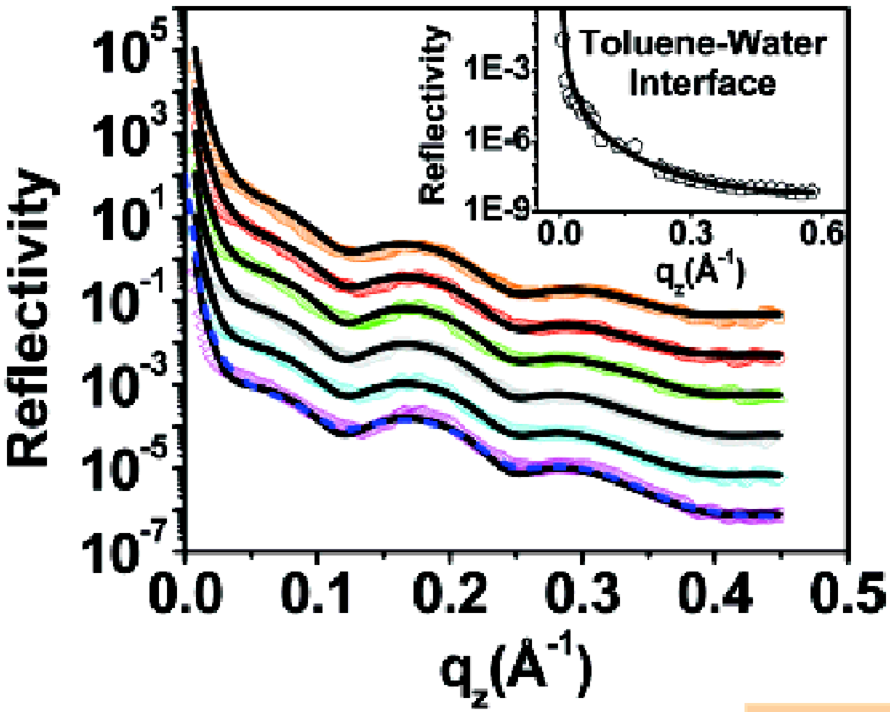
cluster–cluster separation, d_1=180 Å

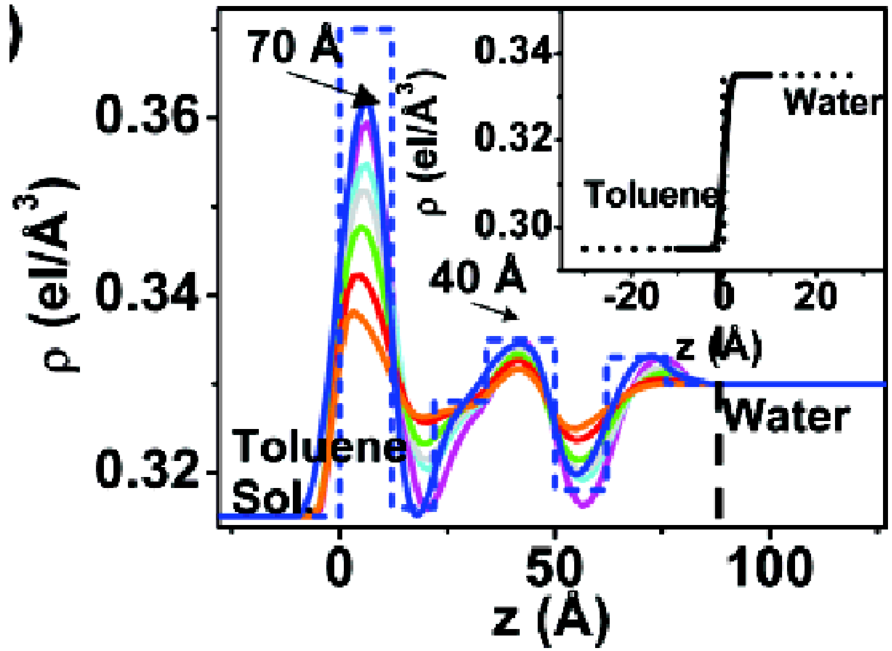
particle–particle separation, d_2 = 34 Å

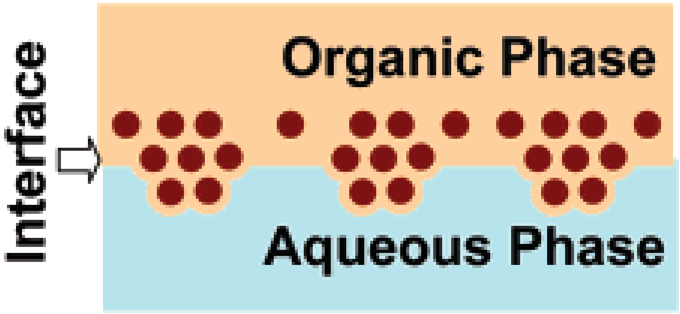
Each cluster consists of 13 NPs with Ø 12 Å & 11 Å thick organic layer

M.K. Sanyal et al., J. Phys. Chem. C, 112, 1739 (2008)

Formation and Ordering of Gold Nanoparticles at the Toluene-Water Interface







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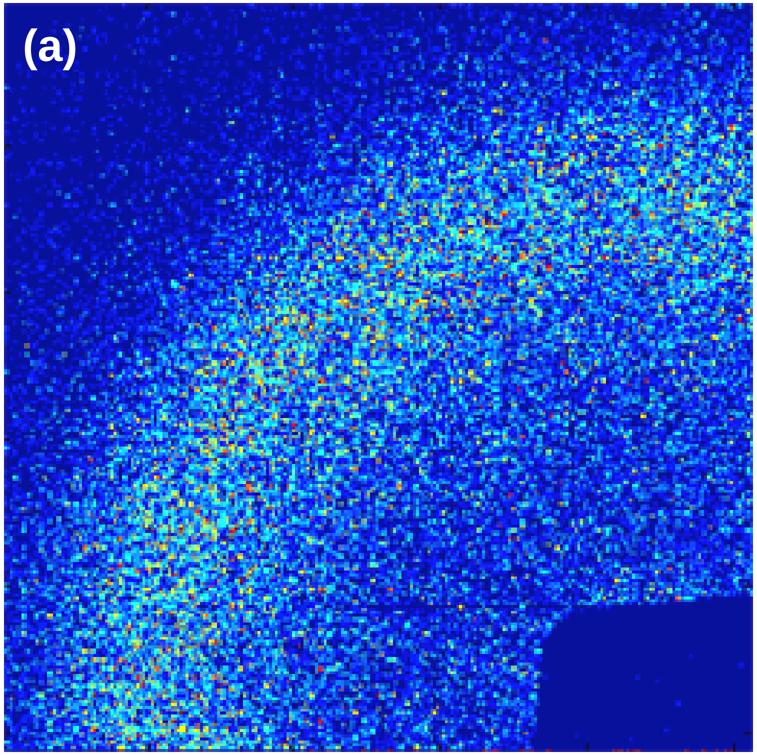
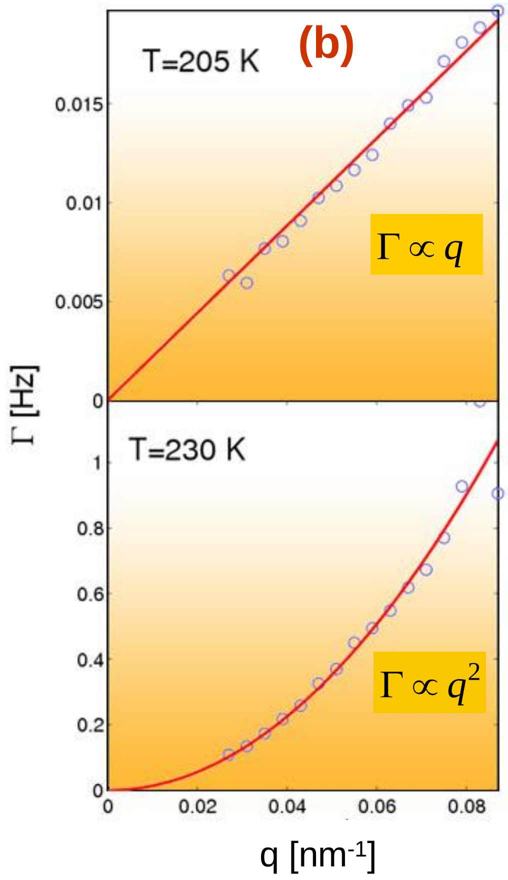
M.K. Sanyal et al., J. Phys. Chem. C, 112, 1739 (2008)

Out-of-equilibrium Dynamics

Multi-speckle XPCS analysis

Dynamics of tracer particles in a glass-forming liquid





Silica particles in propylene glycol

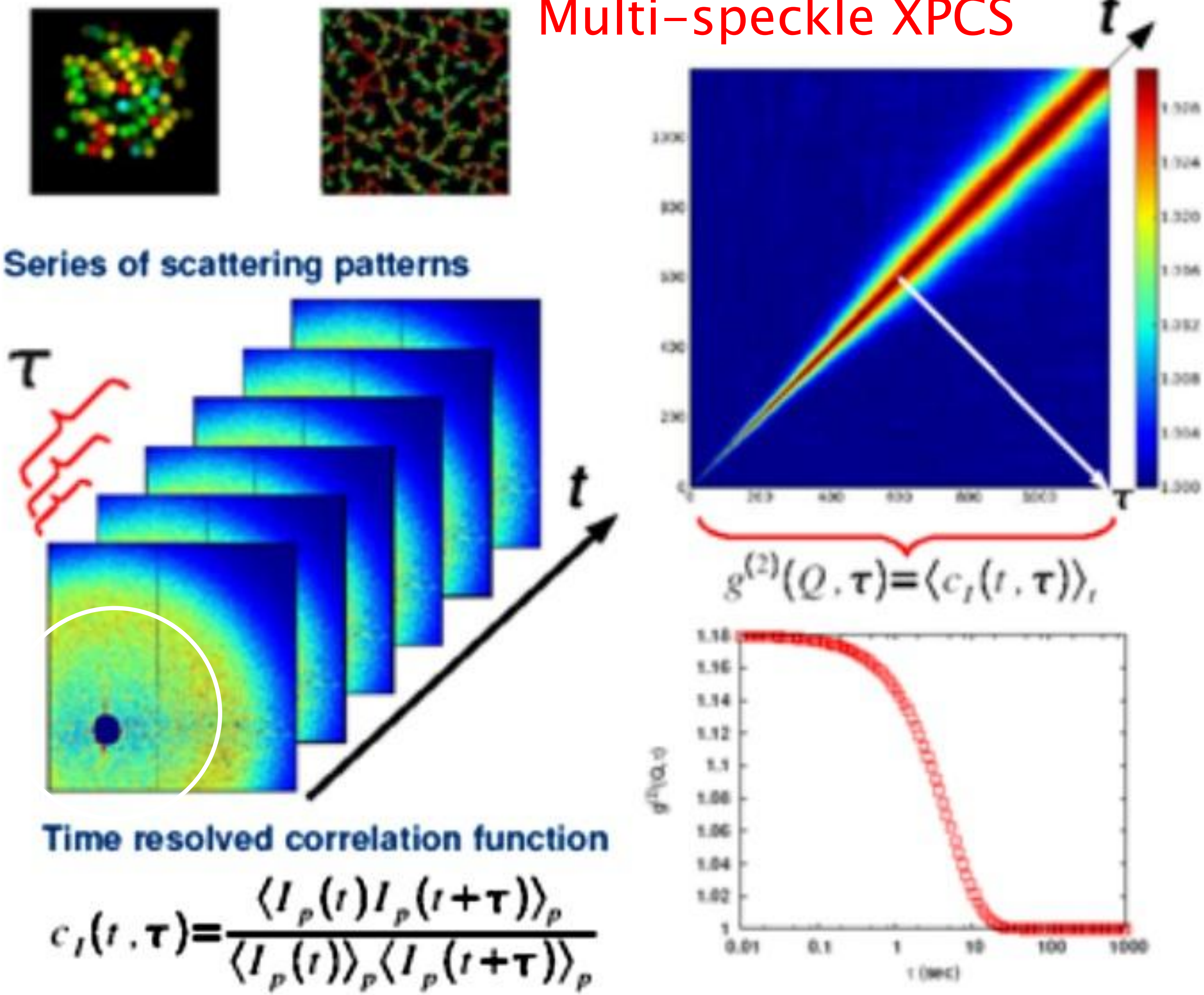
C. Coronna et al., PRL (2008)

This type of dynamics studies can be performed in the sub-millisecond range

Diffusive to ballistic dynamics near glass transition

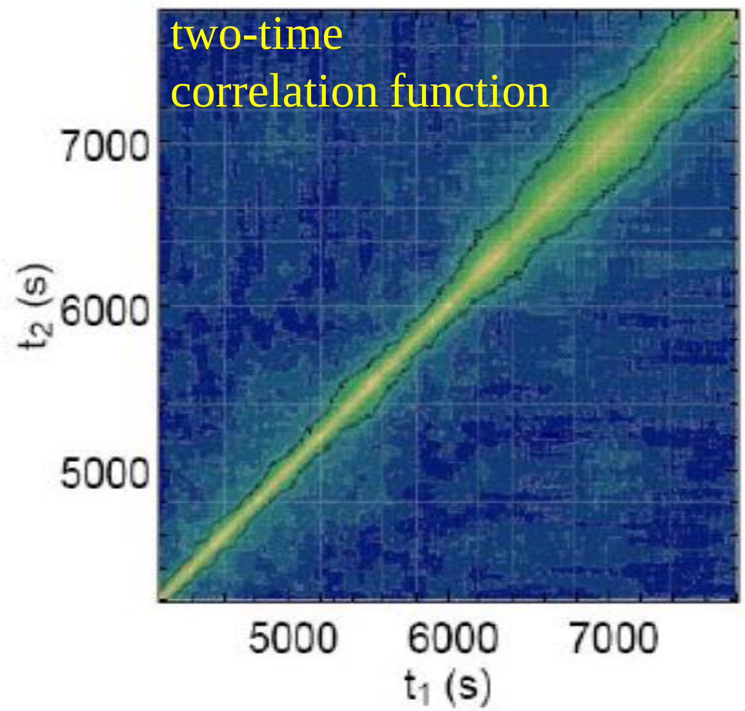
Soft Matter: out-of-equilibrium dynamics

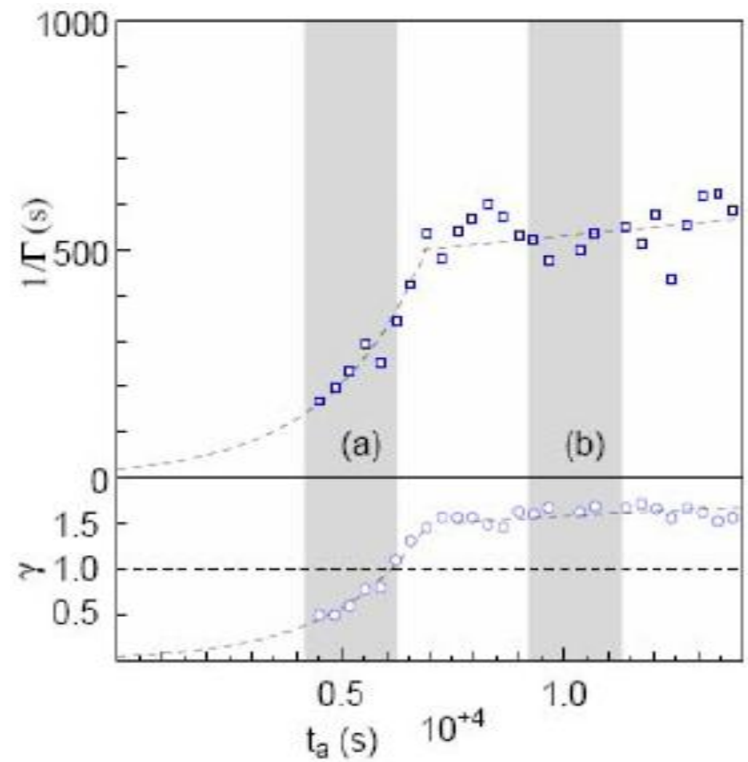
Multi-speckle XPCS



Soft Matter: out-of-equilibrium dynamics

Probing the dynamics of ageing: related to shelf-life of products





Crossover of dynamic behavior – large scale reorganization

A. Fluerasu, A. Moussaid, *et al.*, *PRE(R) (2007)*

UPBL9a: TRUSAXS Beamline

SAXS/WAXS/USAXS

Multiple detectors

Energy range: 7–20 keV

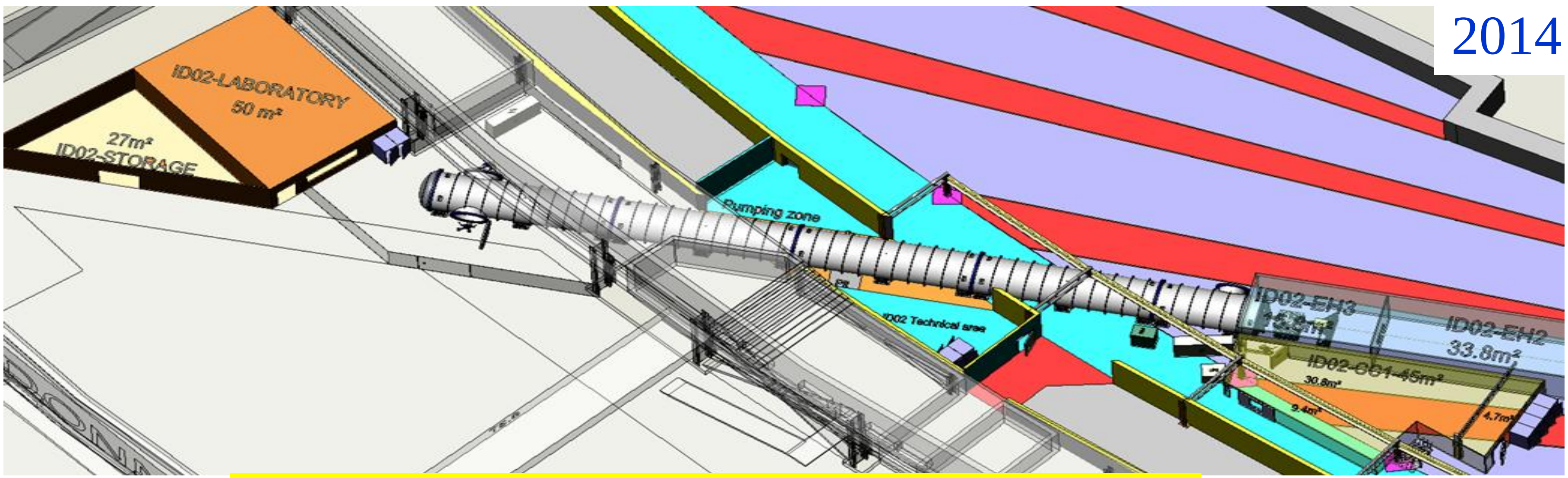
Δq: 5x10^{-4} nm^{-1} (FWHM)

q – range: 10^{-3} – 50 nm^{-1}

Time res. – 10 µs

32 m long and 2 m diameter

2014



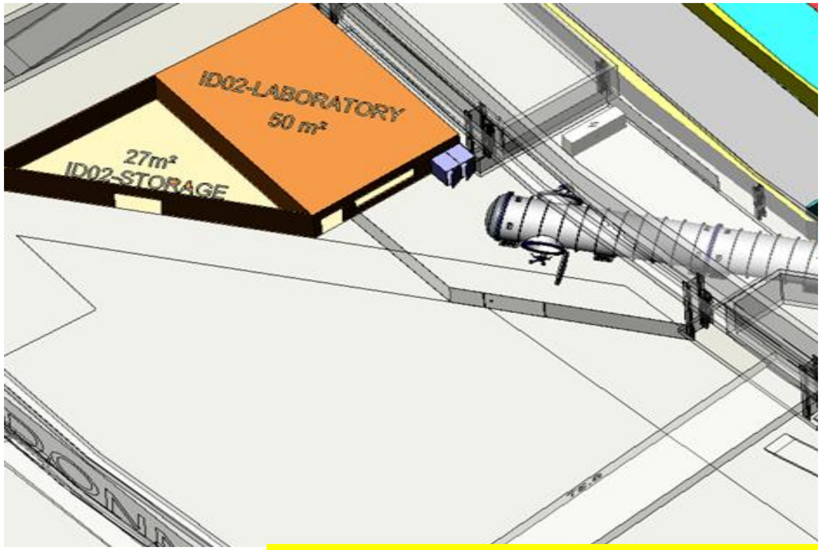
Sample-detector distance: 0.6 – 30 m

UPBL9a: TRUSAXS Beamline

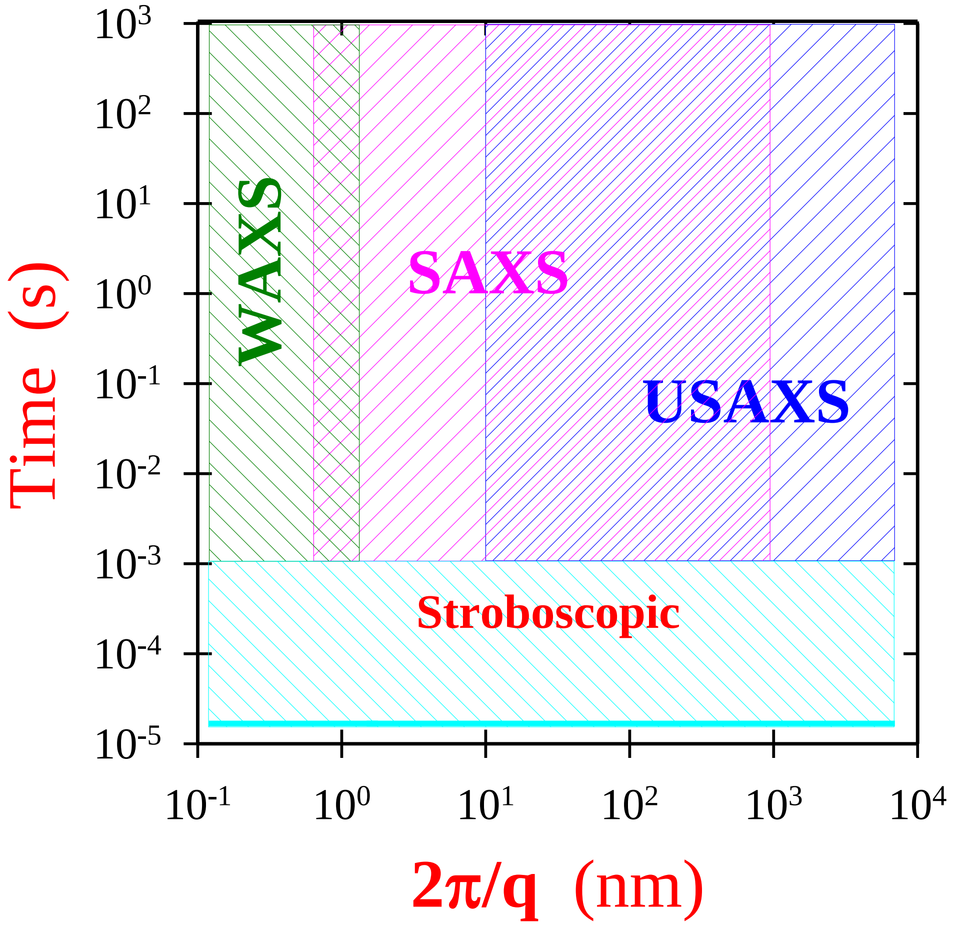
SAXS/WAXS/USAXS

Multiple detectors

32 m long and 2 m diameter



Sample-detector distar



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.
- Challenges lie in the ability to investigate complex polydisperse systems with competing interactions.
- Experiments can be performed in the functional state of the system.
- The emphasis will be on quantitative studies made possible by the high detection capability and reduced radiation damage, and complemented by advanced data analysis.