Soft Matter Studies with X-rays

Theyencheri Narayanan

ESRF – The European Synchrotron

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

R. Piazza, *Soft Matter: The Stuff that Dreams are Made of* (Springer, 2011)

M. Doi, *Soft Matter Physics* (OUP Oxford, 2013)

L.S. Hirst, *Fundamentals of soft matter science* (CRC press, 2020)

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

I.W. Hamley, *Small-angle Scattering (*Wiley 2021)

T. Narayanan and O. Konovalov, Materials, **13**, 752 (2020); https://doi.org/10.3390/ma13030752

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 physics (CMP) 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.

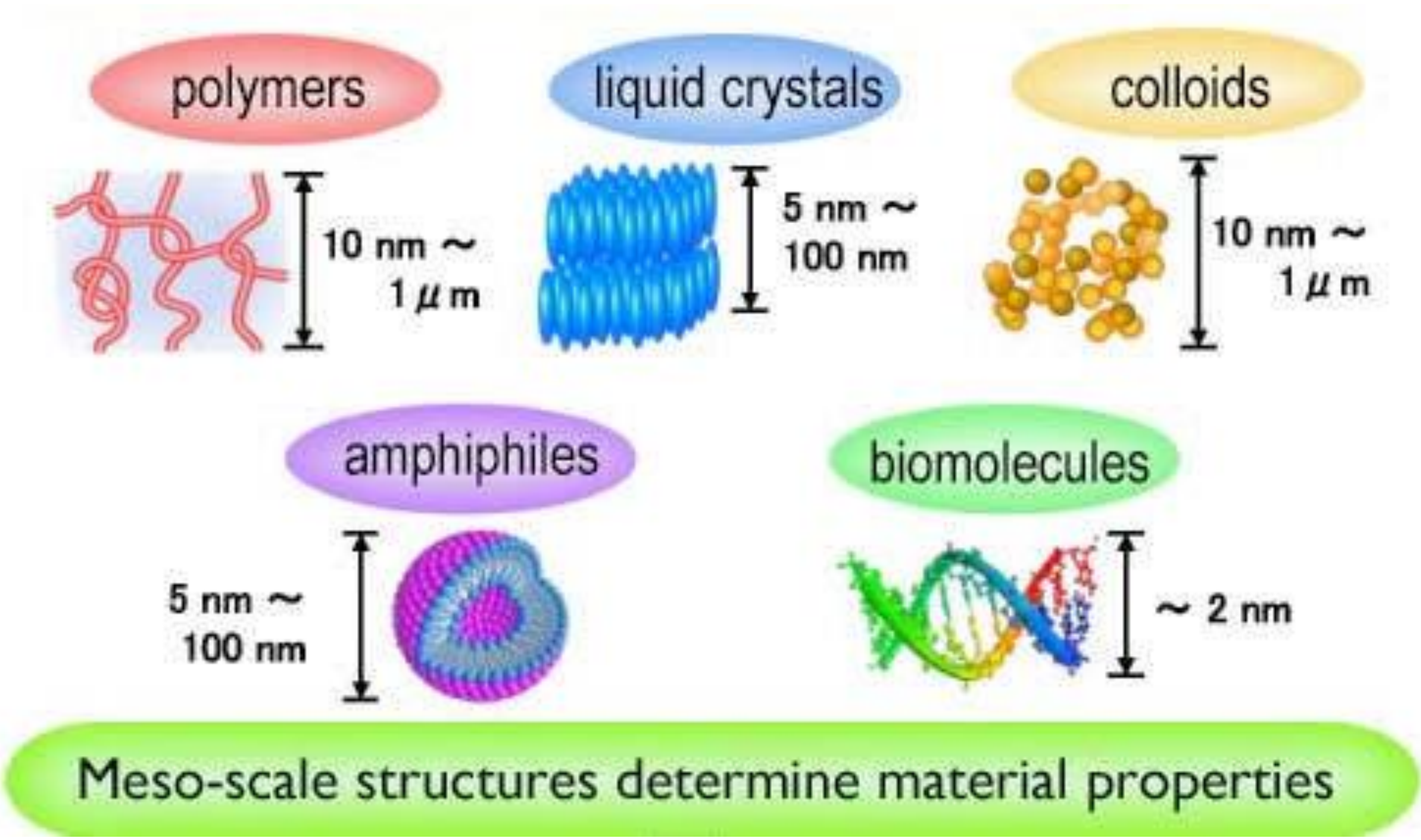
Matière molle » Madeleine Veyssié

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. It is one of the frontiers of CMP and forms part of broader complex systems.

Soft Matter: Encounter in everyday life

Sustainable development through more rational design of consumer products

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/dynamics and macroscopic properties.

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

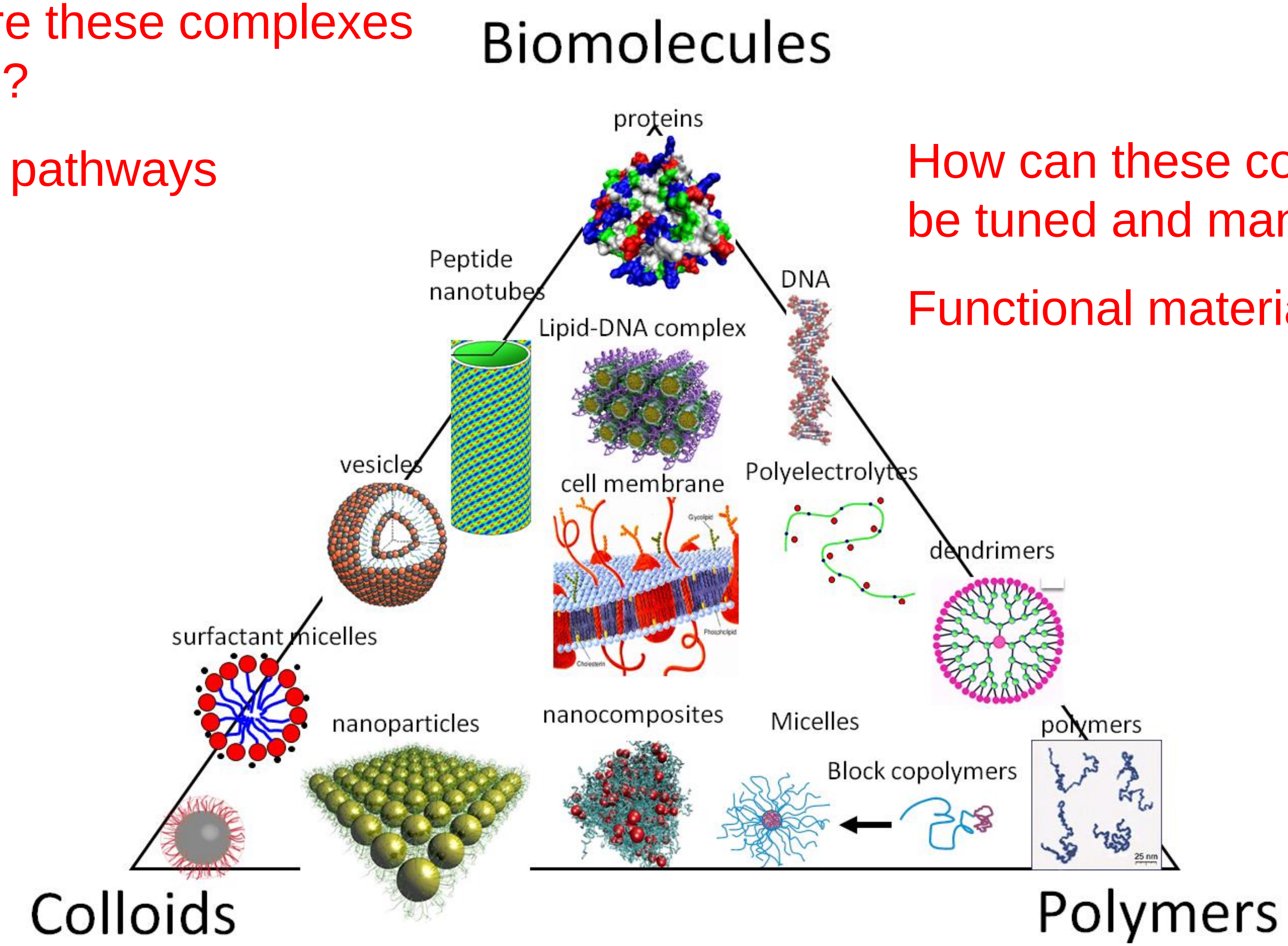
Self-Assembled Soft Matter Systems

How are these complexes formed?

Kinetic pathways

How can these complexes be tuned and manipulated?

Functional materials



T. Narayanan et al., Crystallogr. Rev. (2017)

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.

- ***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

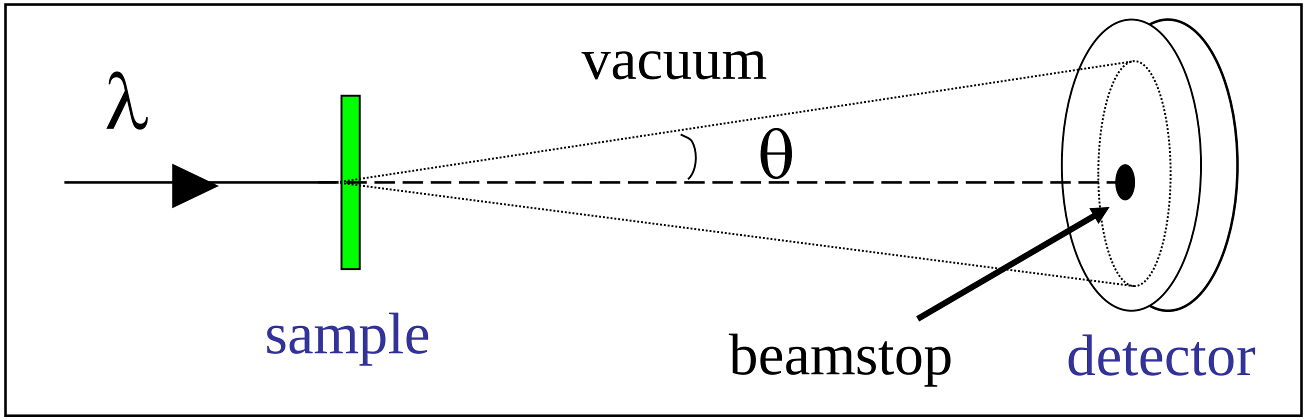
- ***Complementary imaging techniques***

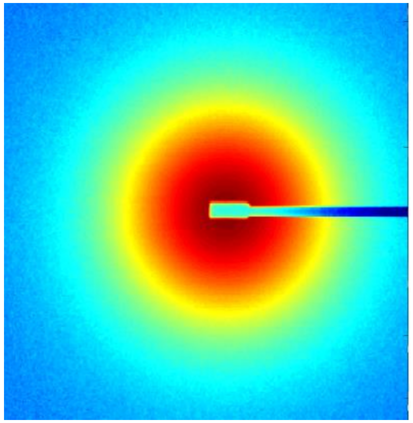
X-ray microscopy, micro and nano tomography, etc.

Radiation damage

Small-Angle X-ray Scattering (SAXS)

Scattering originates from the spatial fluctuations of electron density





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

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

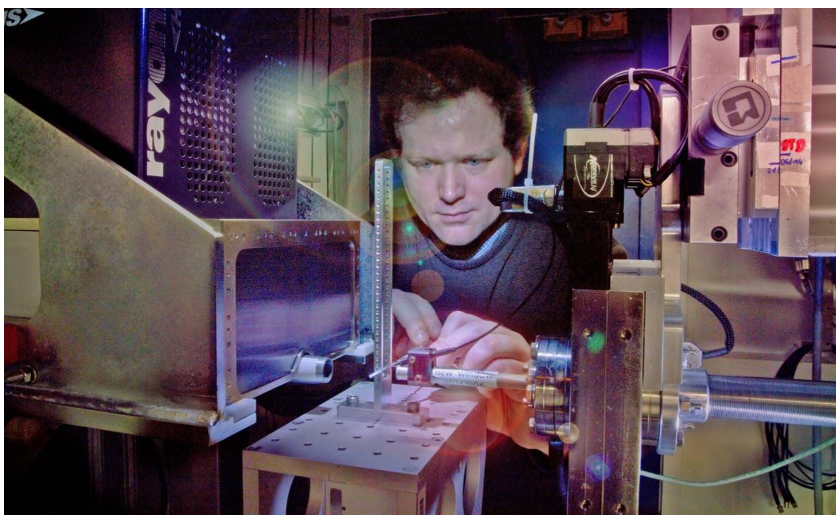
$\Delta\Omega$ - solid angle

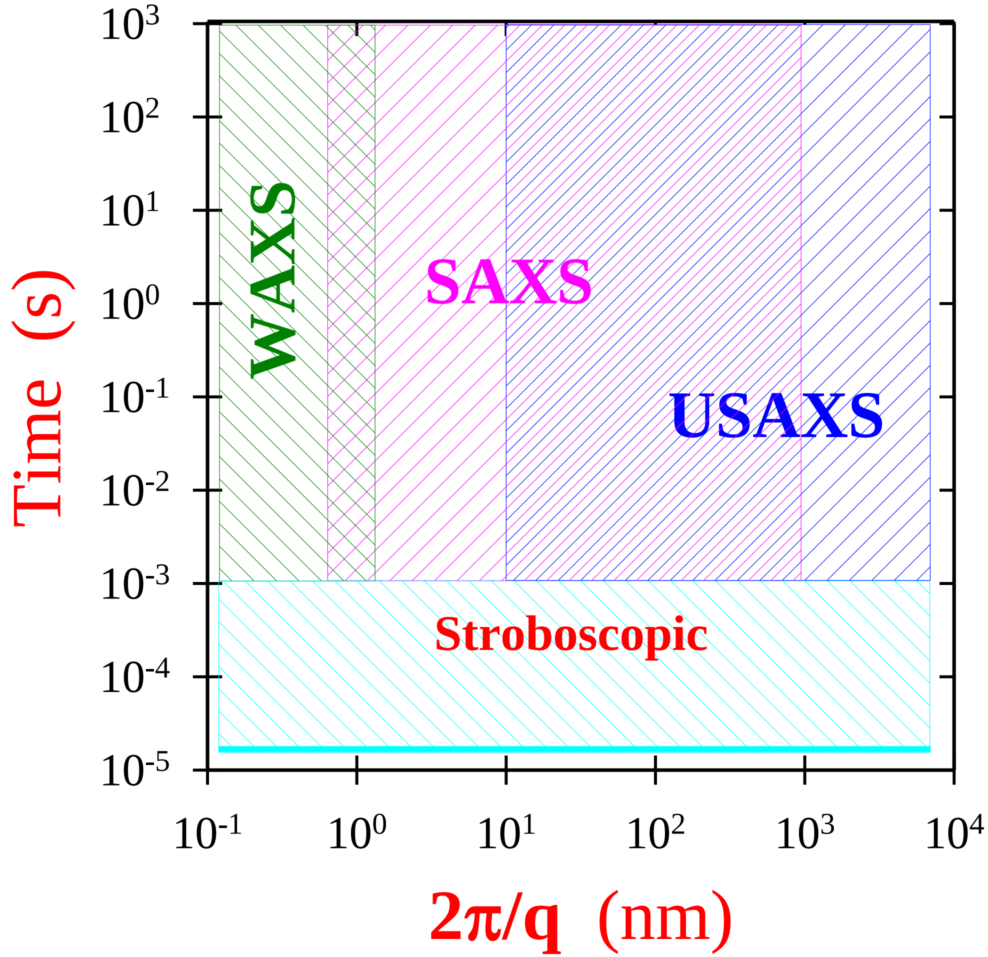
$$I(q) = \frac{d\Sigma}{d\Omega} = \frac{1}{V_{Scat}} \frac{d\sigma}{d\Omega}$$

Beamline – ID02

Ultra SAXS/SAXS/WAXS

Beamline ID02

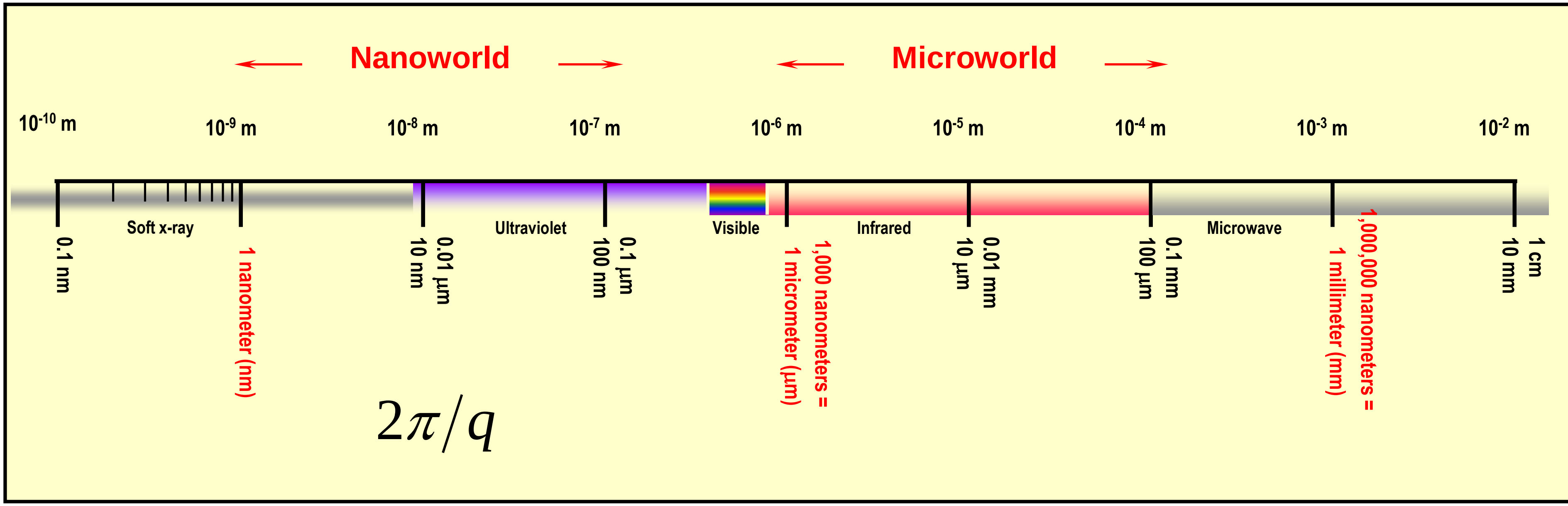


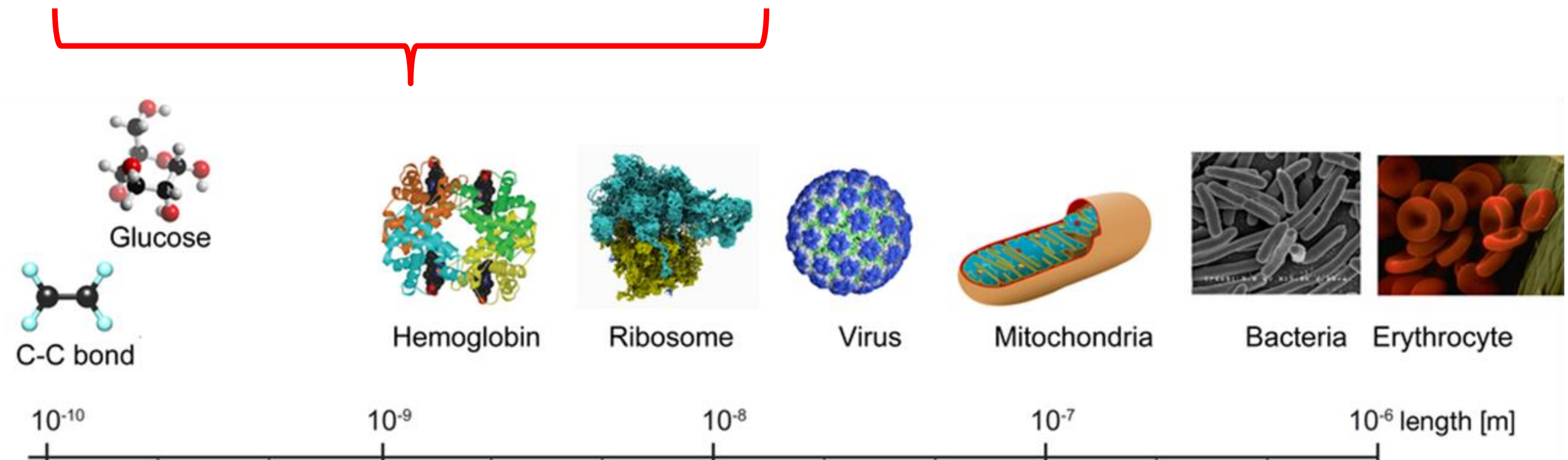


Δq: 3x10 nm (FWHM)

Time resolution: < 100 μs

Size scales probed by SAXS & related techniques

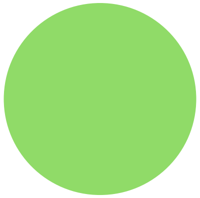


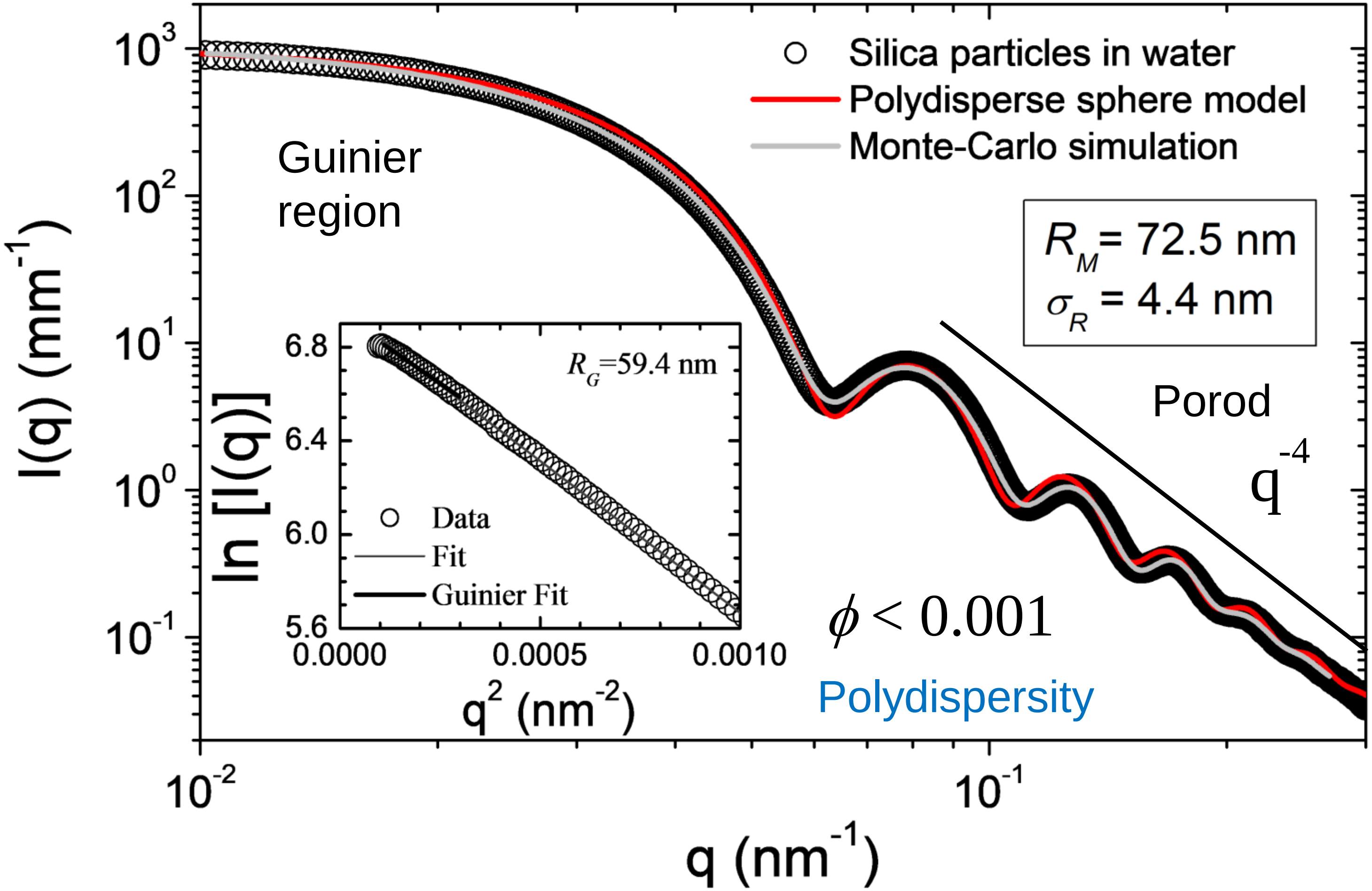


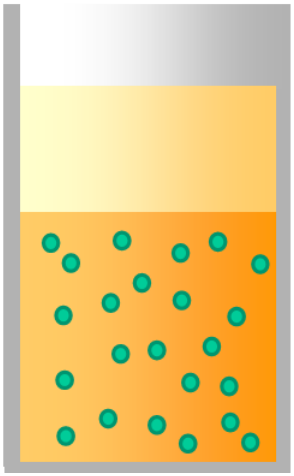
SAXS from dilute spherical particles

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

Fourier transform of the radial electron density >> spherical Bessel function





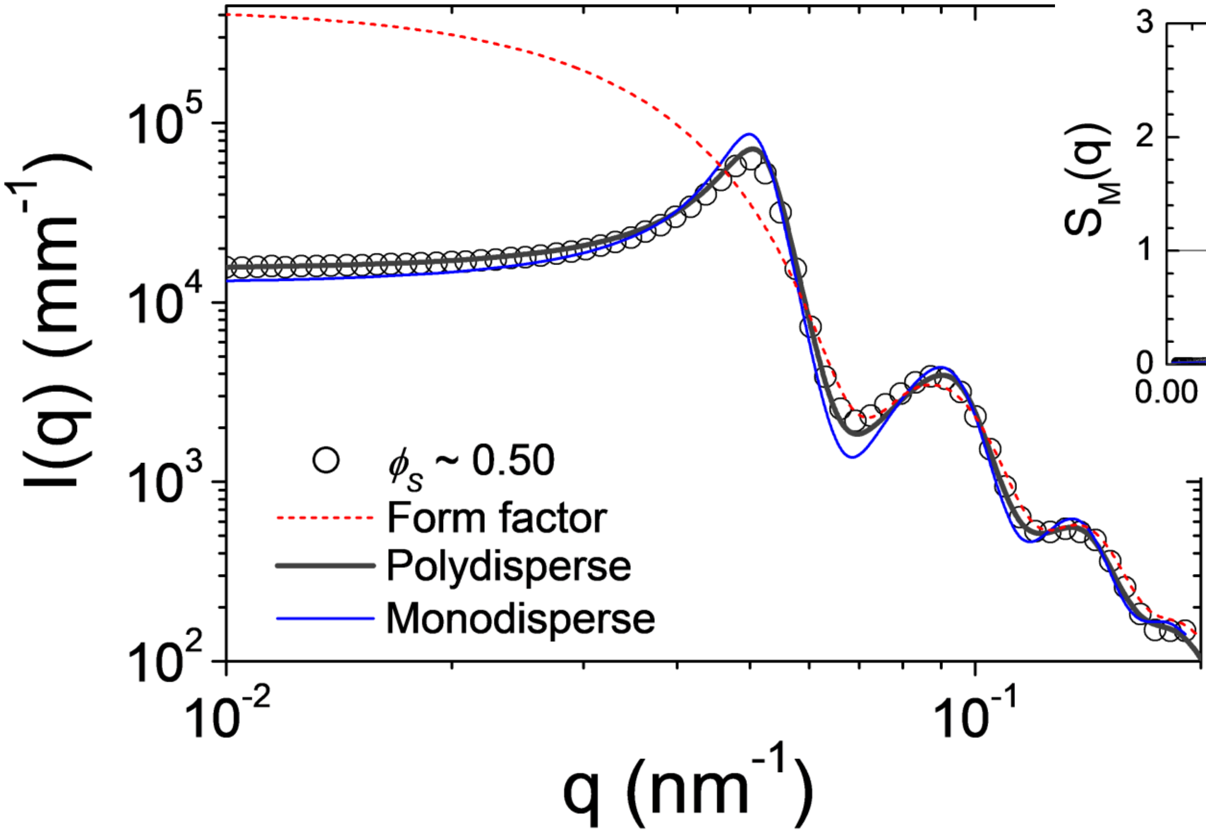


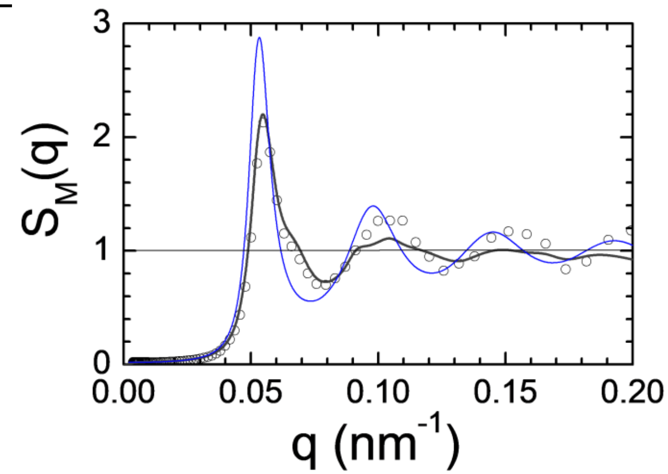
Modeling or simulation required to extract quantitative information

Structure Factor

Differential scattering cross-section per unit volume

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



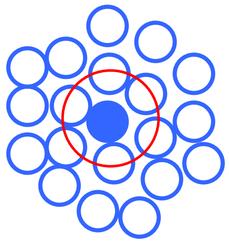


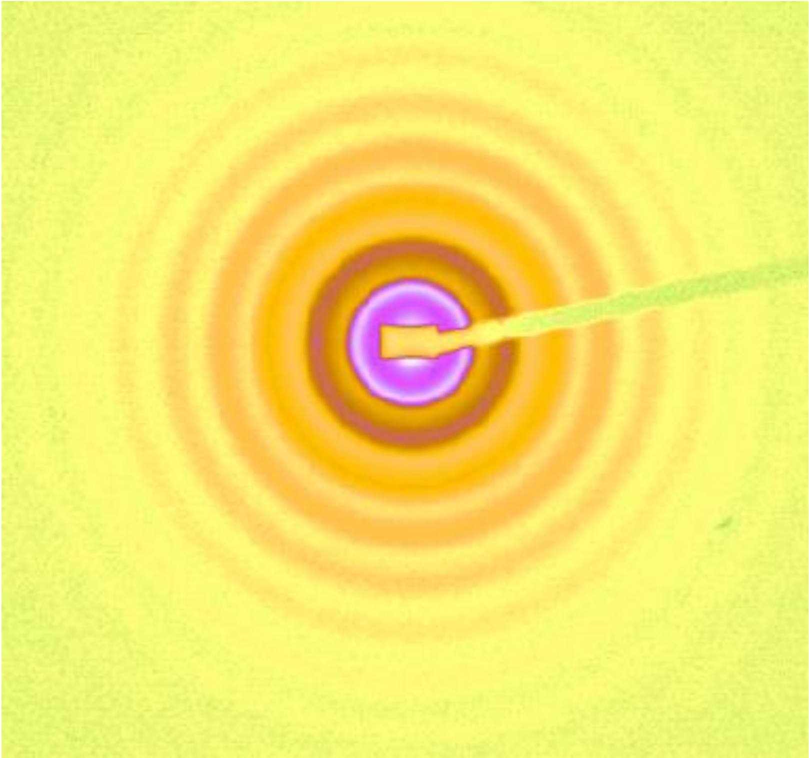
FT of pair correlation function

S (q) from liquid state theories (e.g. Percus-Yevick (PY)) or simulations or reverse engineering

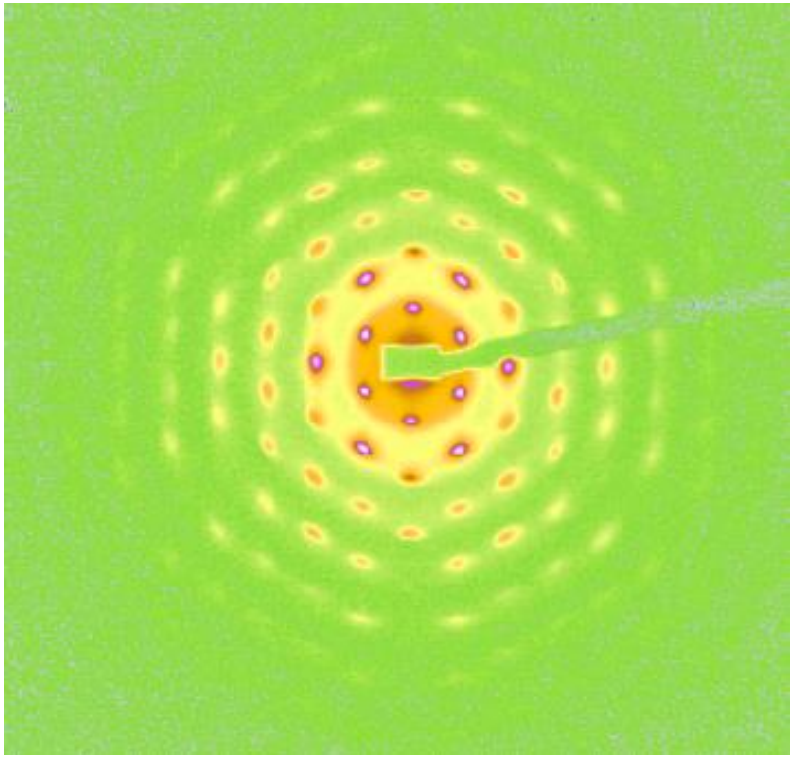
Structure Factors at high packing fractions

E.g. 60%





Glass

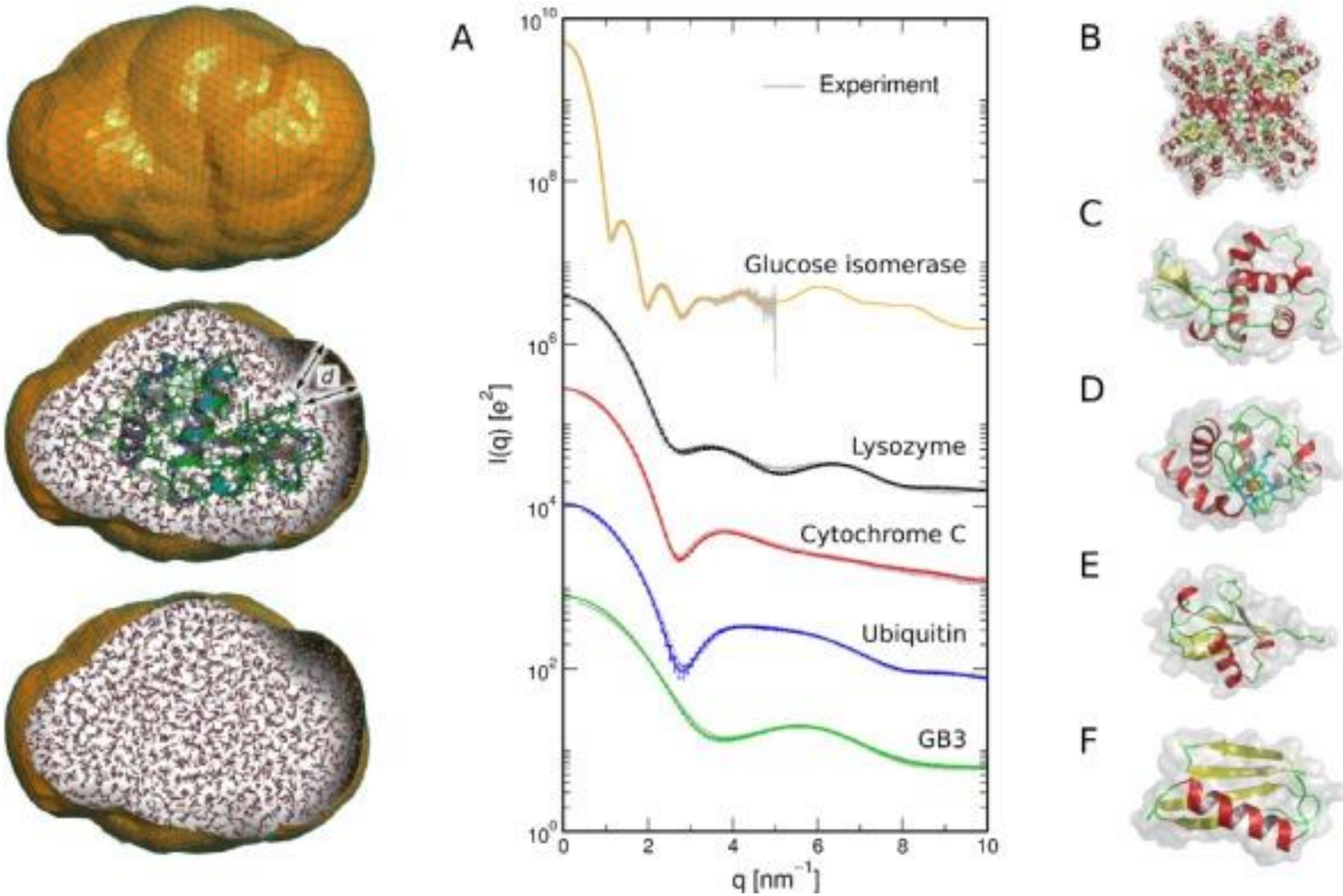


Crystal

Protein Solution Scattering

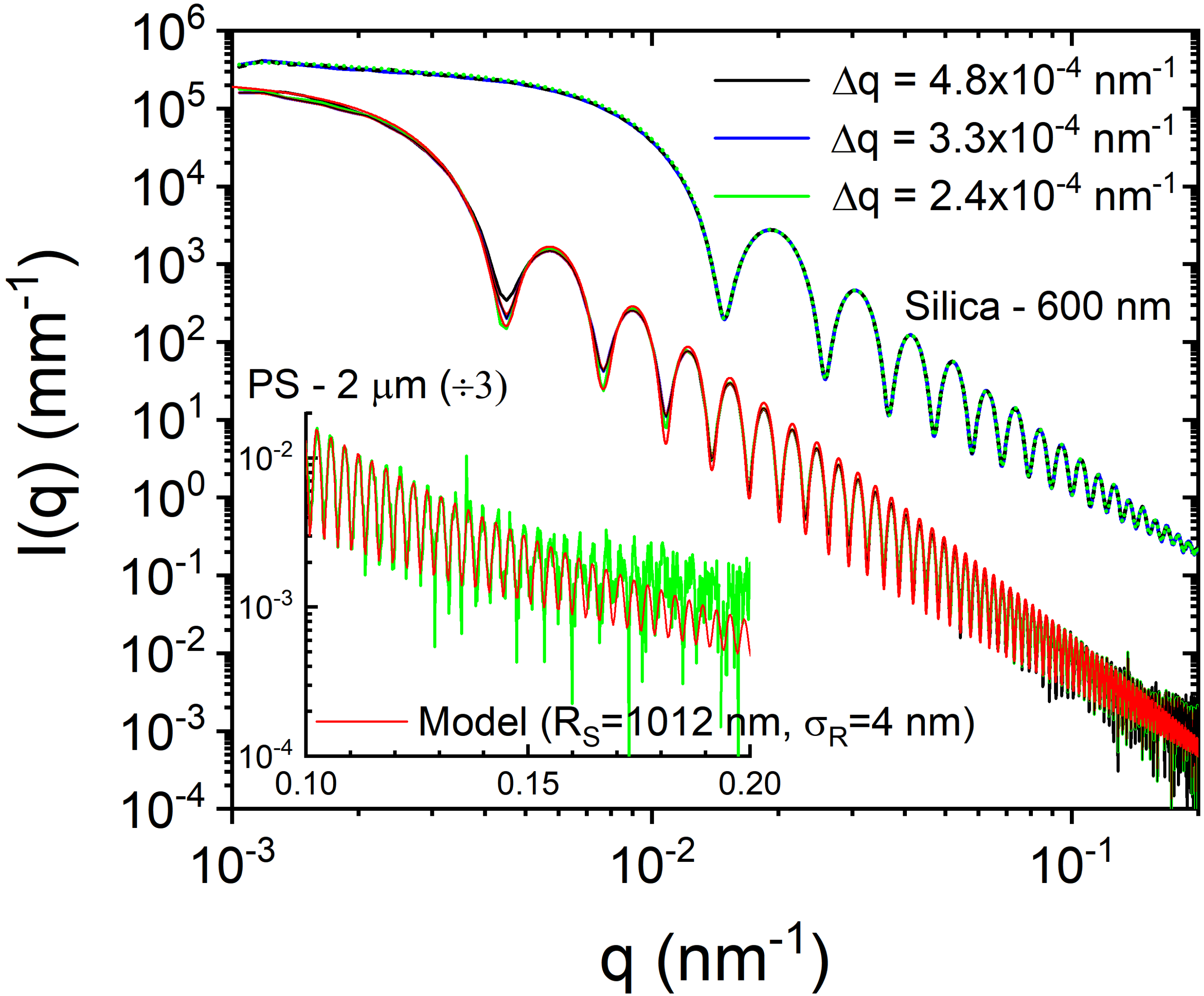
Traditionally a few structural features: size, shape, size or density distribution

Beamline - BM29



J. Hub - Universität Göttingen

High Resolution USAXS

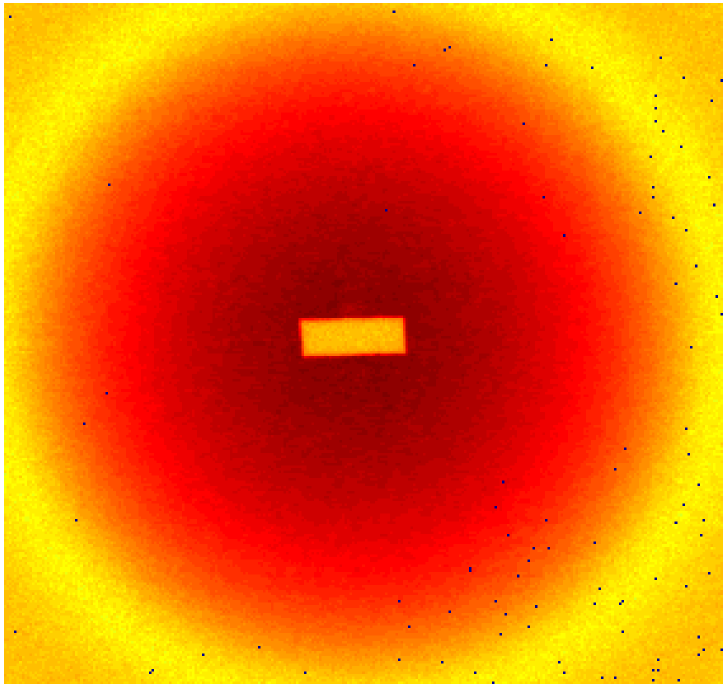


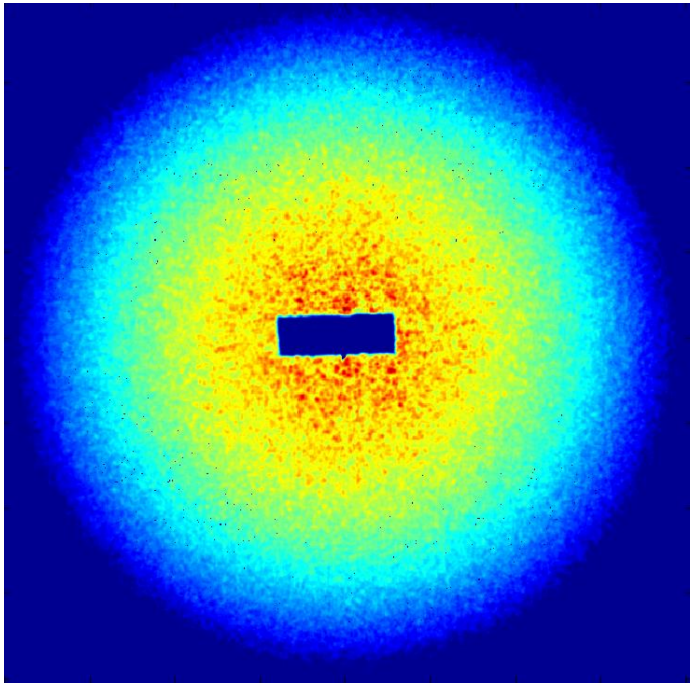
T. Narayanan *et al.* JAC (2022)

SAXS with a Partially Coherent Beam

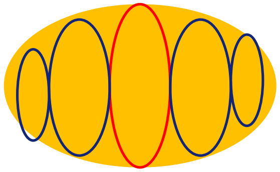
Standard beam and area detector

Highly collimated beam and high resolution detector





Speckle size ~ $\frac{\lambda\, d_{SD}}{\sigma}$



$\xi_T \sim \frac{\lambda R_S}{d}$ ~ (10 – 100 μm)

$\xi_L = \frac{c}{\Delta\nu} = \lambda\left(\frac{\lambda}{\Delta\lambda}\right)$ ~ 1 μm

The European Synchrotron | ESRF

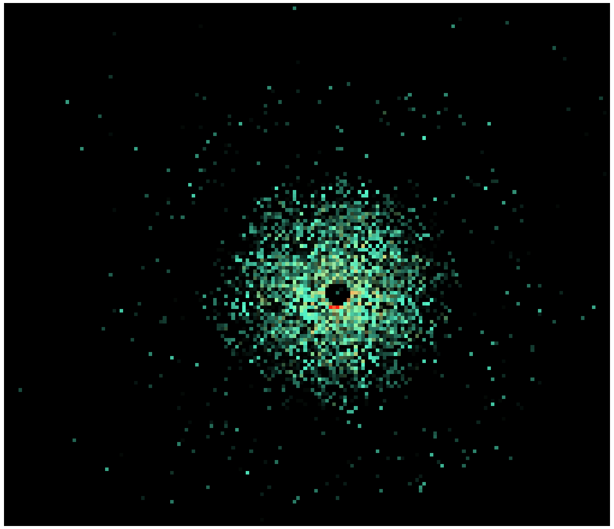
X-ray Photon Correlation Spectroscopy (XPCS)

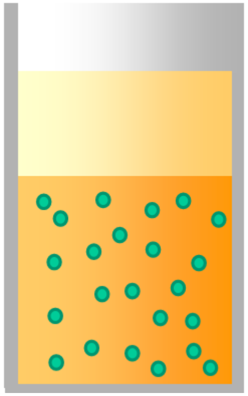
XPCS at small and wide angles: ID10 beamline (M. Cammarata/Y. Chushkin)

At ultra low angles, $10^{-3} \leq q \leq 10^{-1}$ nm^{-1} : ID02 beamline

Analogous to dynamic light scattering

Dilute silica colloids of 600 nm in size





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

mean-square displacement

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

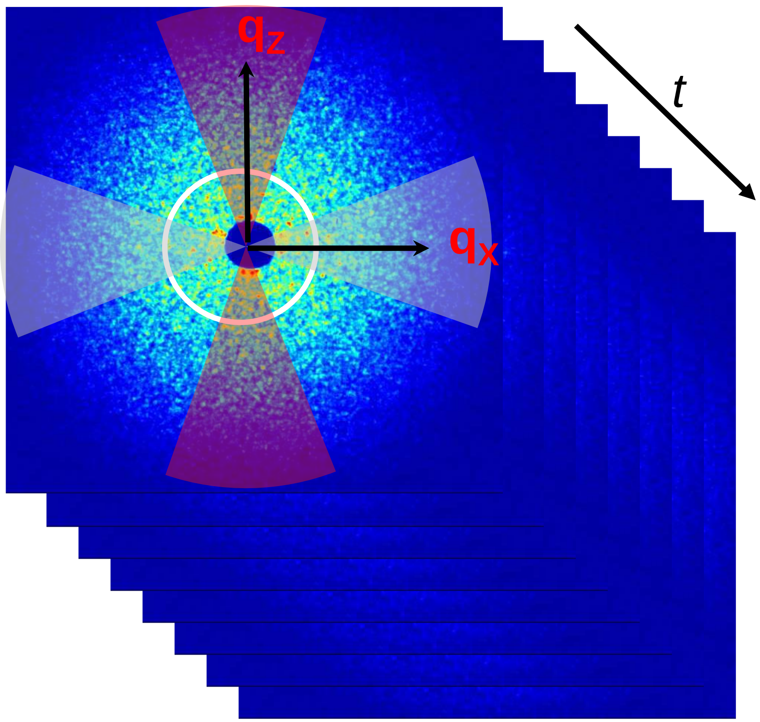
diffusion constant
(Stokes-Einstein)

Multi-speckle XPCS

Suitable for optically opaque systems

Multi-Speckle XPCS

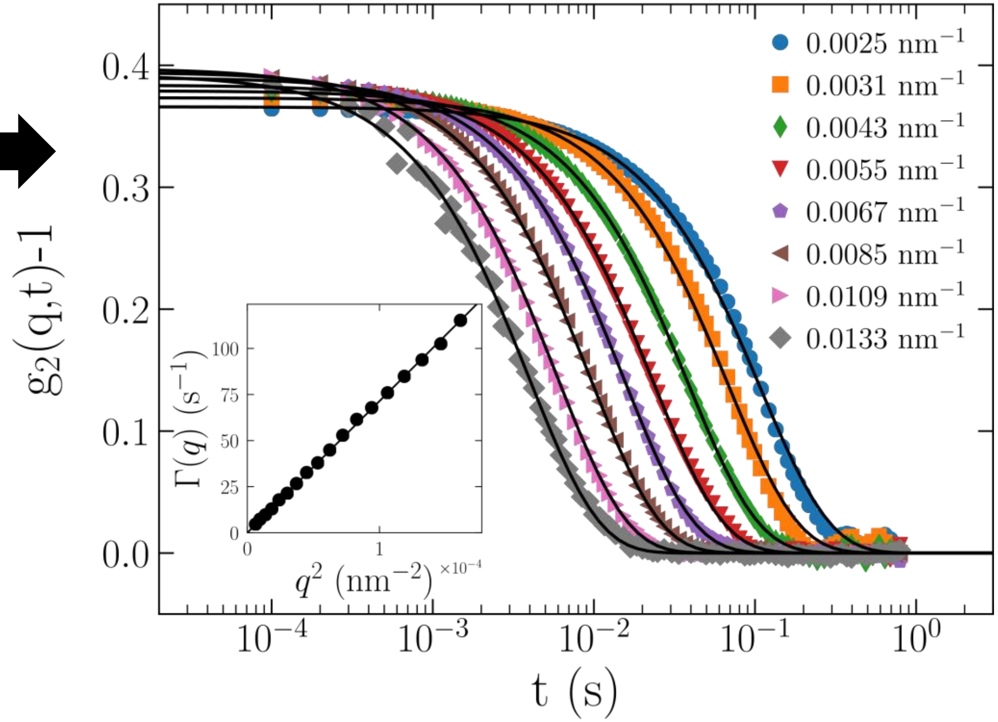
Dilute silica colloids of 600 nm in size



Ensemble averaged
Intensity autocorrelation function

$$g_2(\boldsymbol{q},t) = \frac{\langle I(\boldsymbol{q},\tau) I(\boldsymbol{q},\tau+t)\rangle}{\langle I(q)\rangle^2} = 1 + \beta\, g_1(\boldsymbol{q},t)^2$$

Speckle contrast: $\beta > \mathbf{0.4}$



Brownian dynamics: $\Gamma(q) = D_0 q^2$

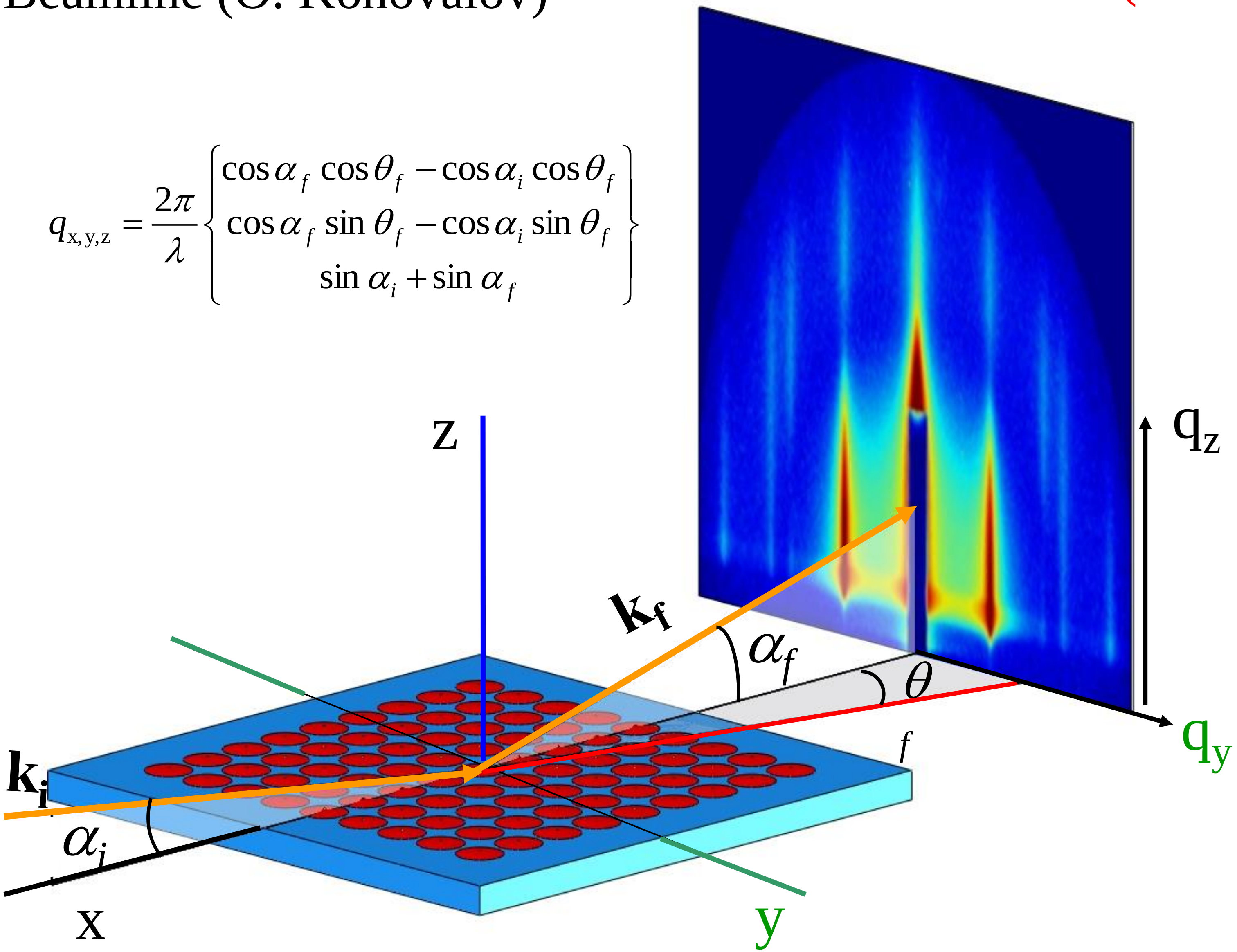
Direction dependent analysis

Grazing Incidence Small-Angle X-ray Scattering

ID10 Beamline (O. Konovalov)

(GISAXS)

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



ID10 Surface & Interface Scattering Beamline

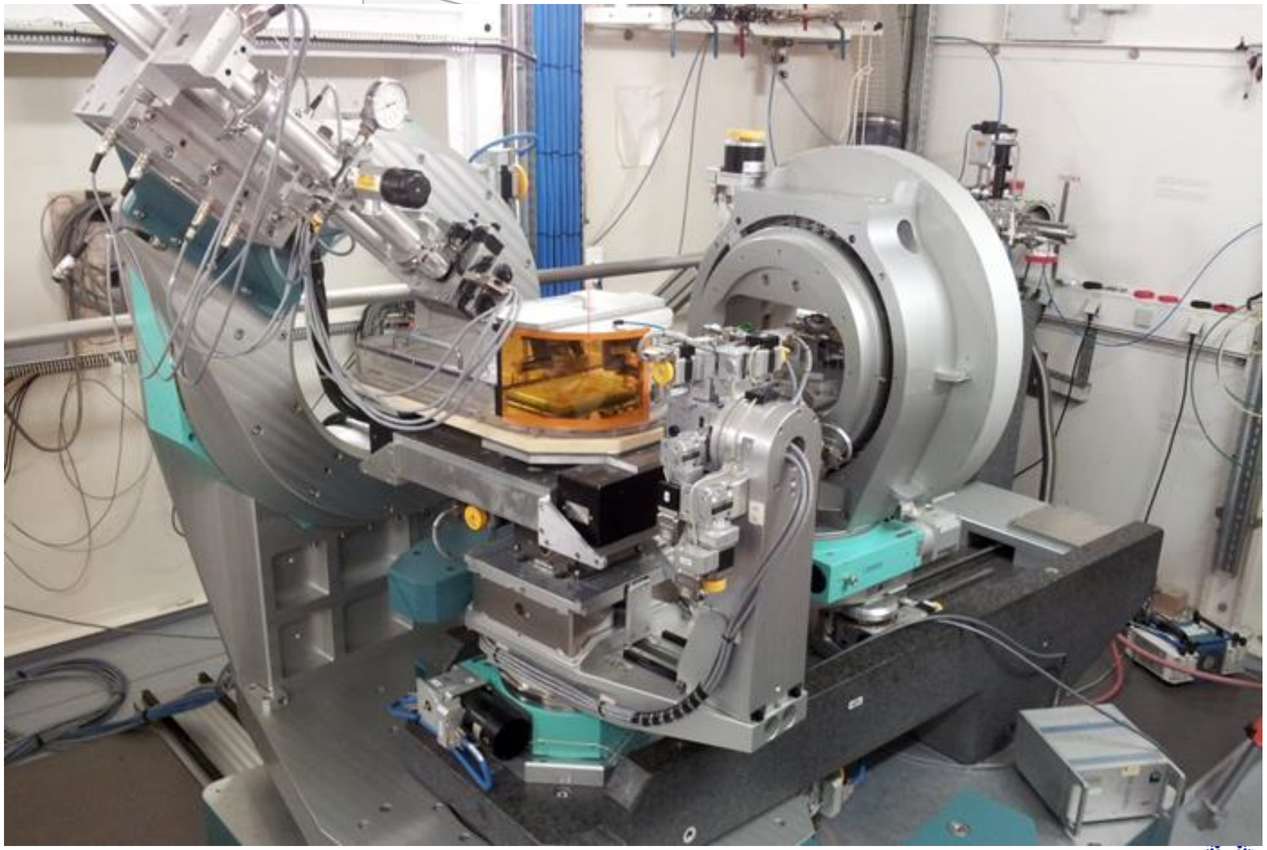
GISAXS, GID, XRR, GIXF

(O. Konovalov)

Multipurpose instrument for surface/interface studies
4 circle diffractometer
Beam deflector stage for liquid surfaces

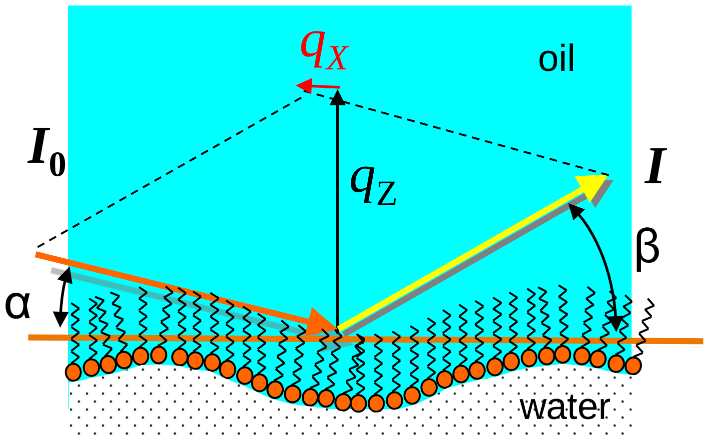
The two-crystal deflector stage rotates the X-ray beam around a fixed point on the liquid surface

$$\left\{ \begin{array}{l} q_X \\ q_Y \\ q_Z \end{array} \right.$$



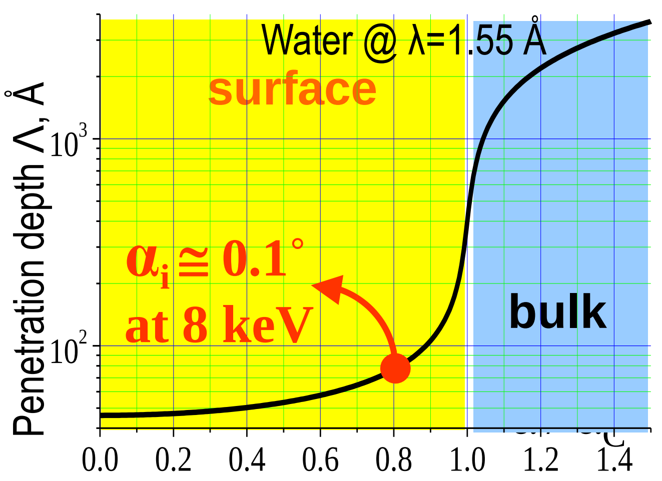
Soft Interfaces Scattering

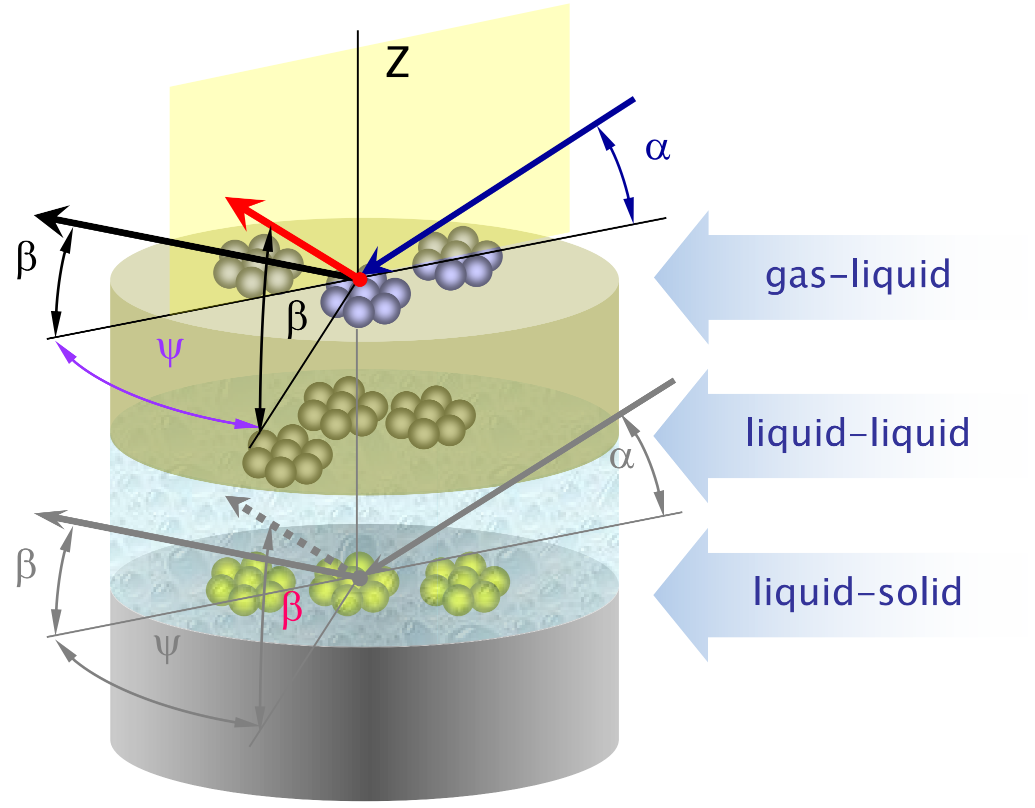
Beamline ID10



Using higher energy X-rays (> 30 keV)

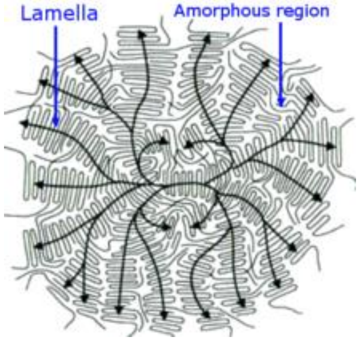
Varying the penetration depth

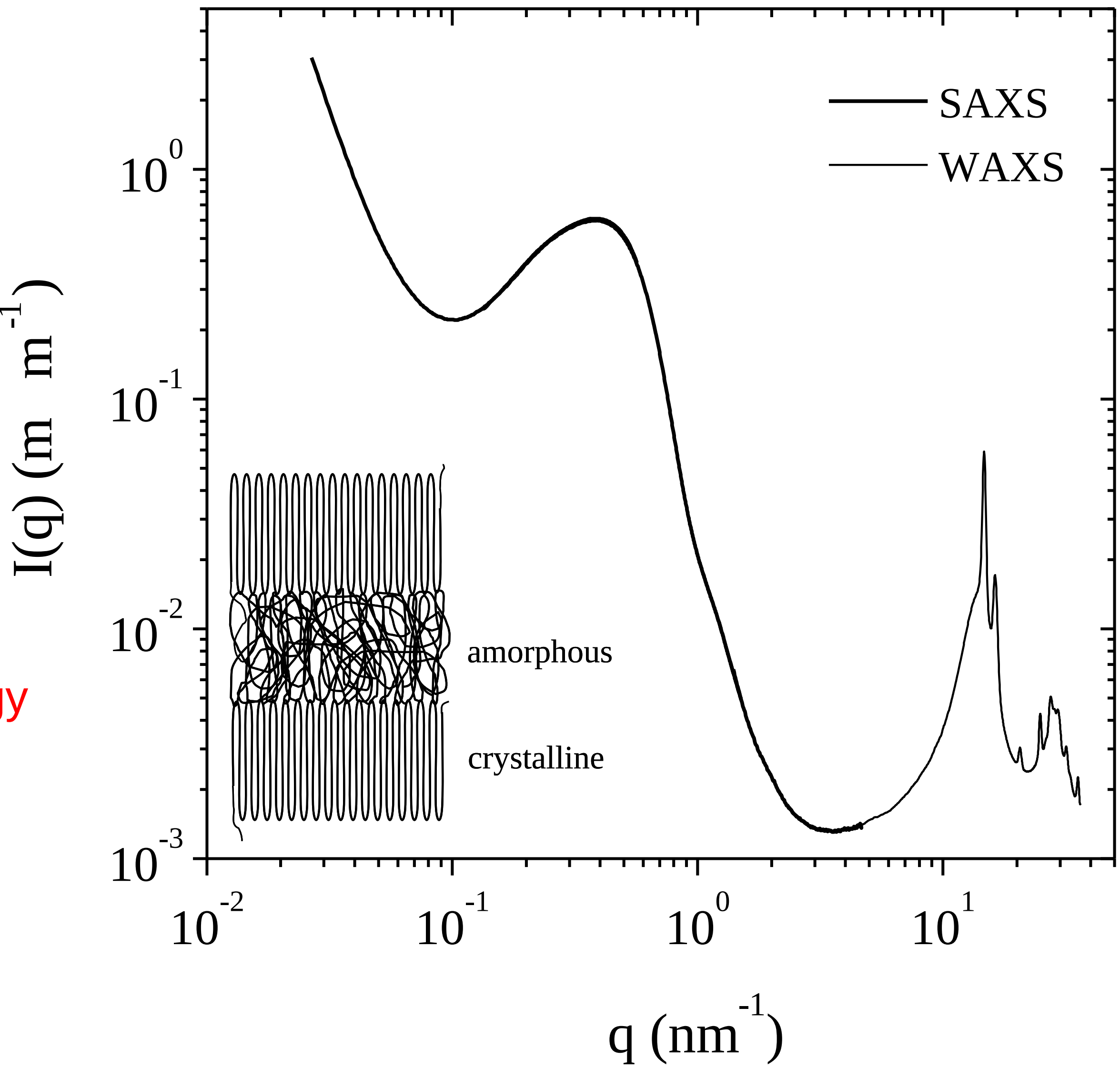




SAXS/WAXS from Semi-crystalline Polymers

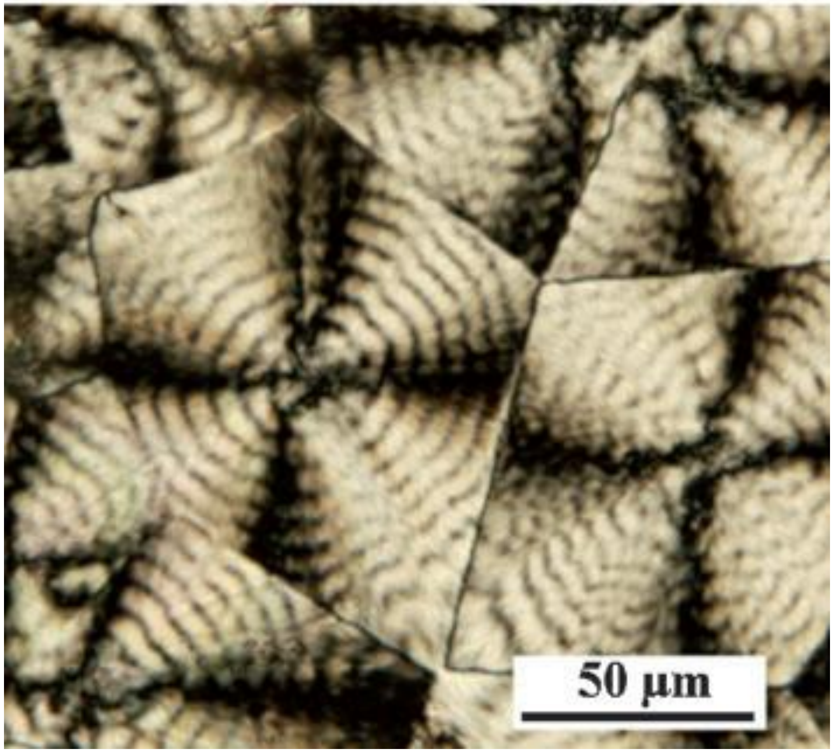
Spherulite morphology

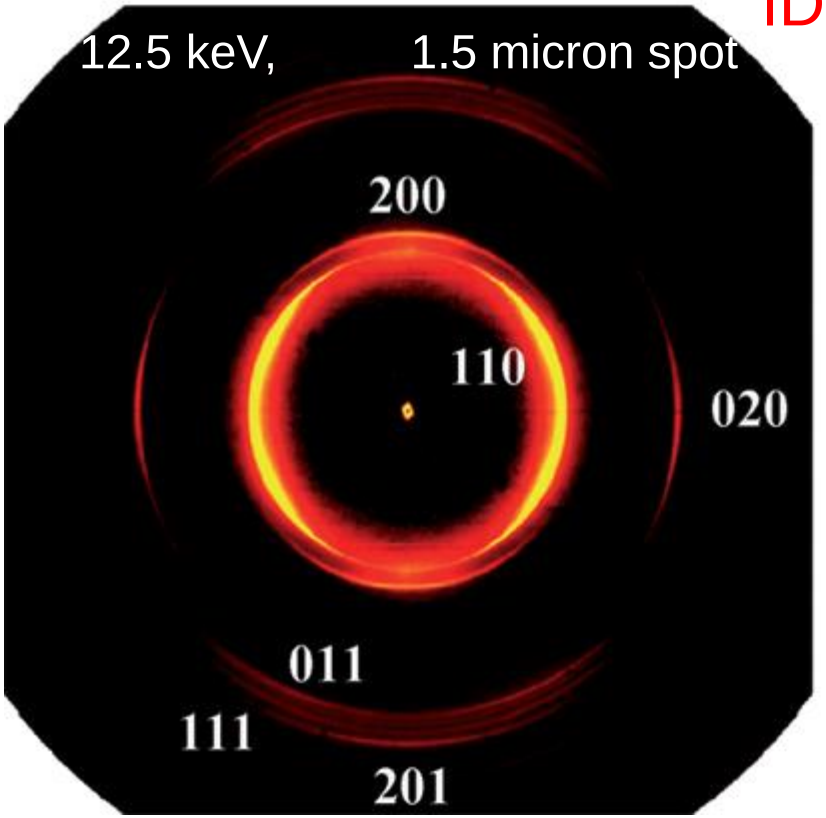




Scanning Micro-diffraction on HDPE spherulites

ID13





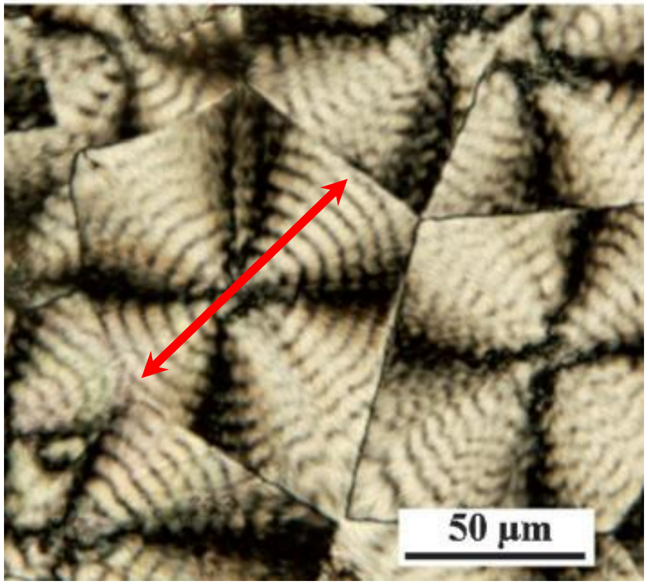
- **high density poly-ethylene**
- spherulites under polarized light banded structures indicating long range order

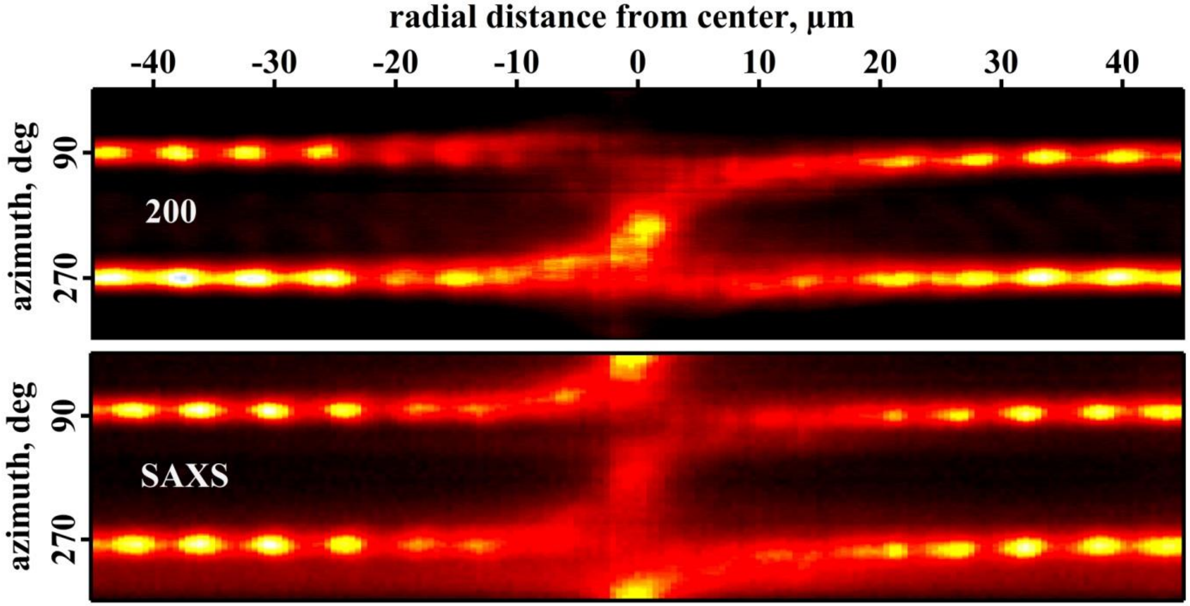
- **SAXS/WAXS** patterns
- line scans across the center reveal information on crystallite orientation

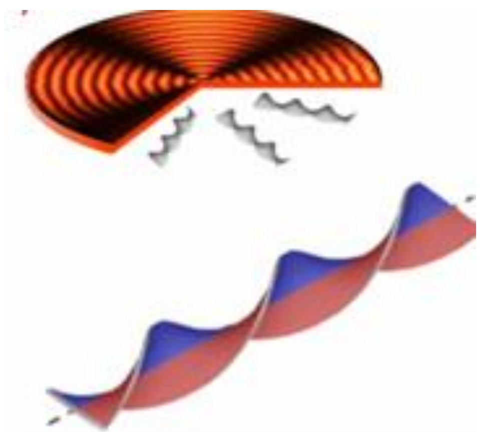
*M. Rosenthal et al., Angewandte Chemie, **123**, 9043-9047 (2011)*

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)*

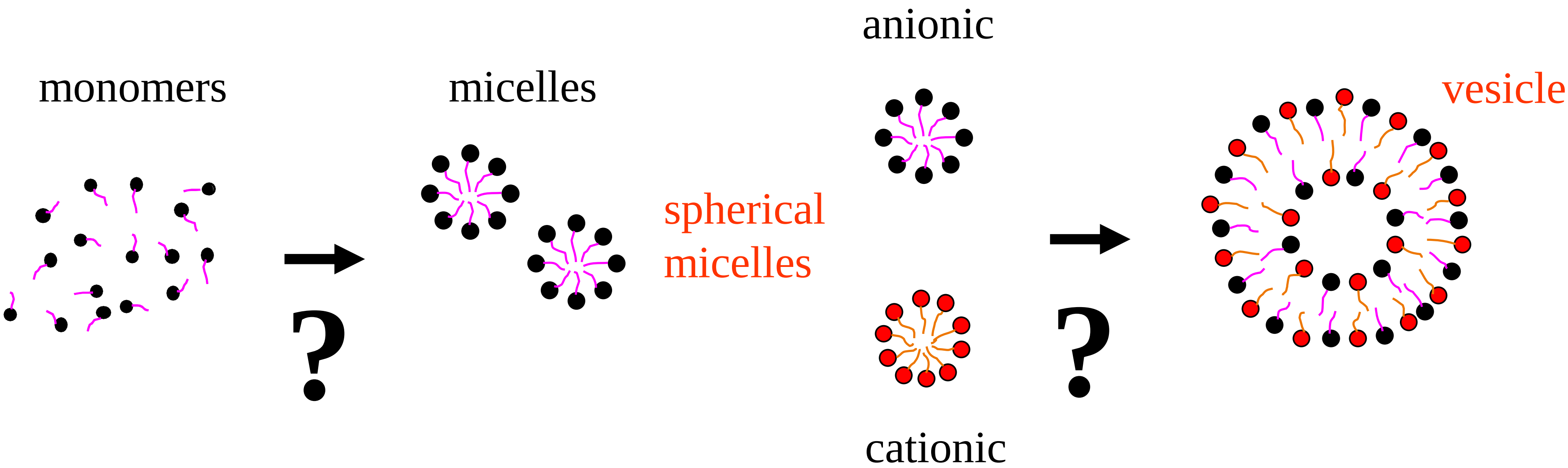
Soft Matter Self-Assembly

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

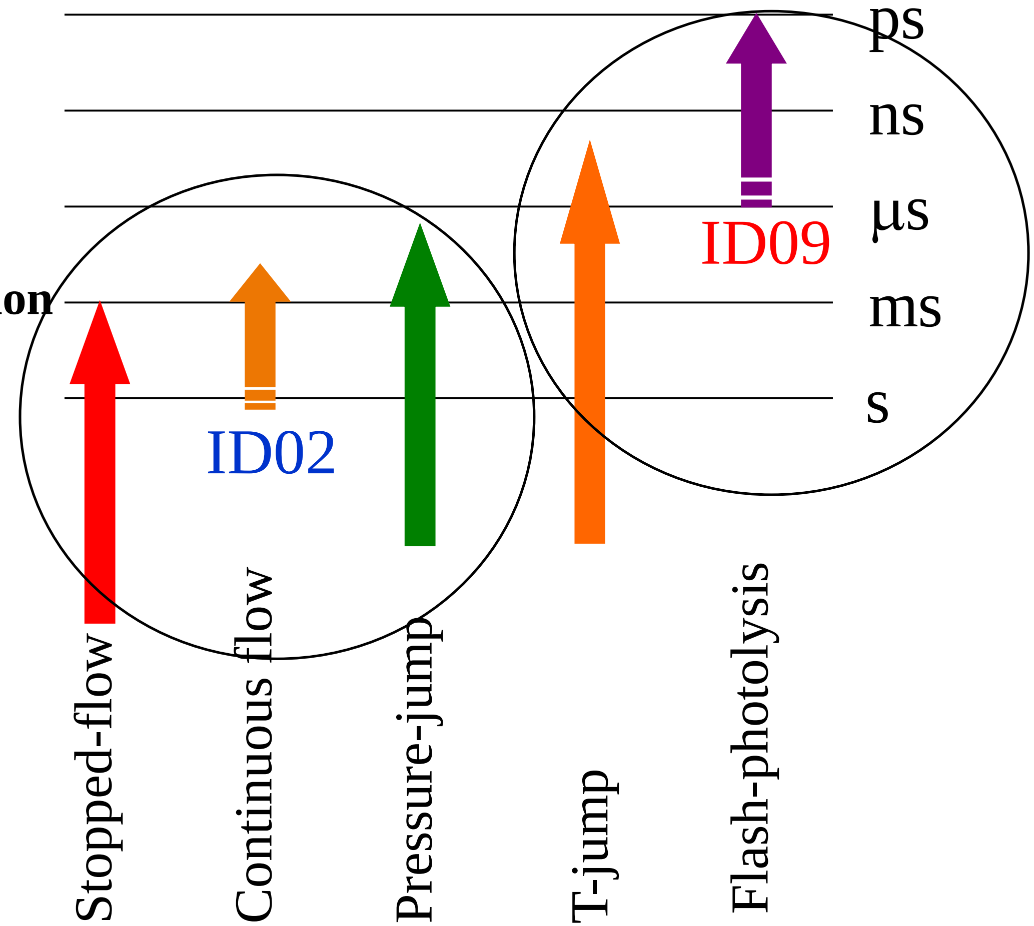
Triggering & Synchronization of Dynamic Processes

E.g. concentration/pH jump (rapid mixing)

Rapid temperature or pressure change

Flash photolysis

ms – folding/self-assembly/nucleation

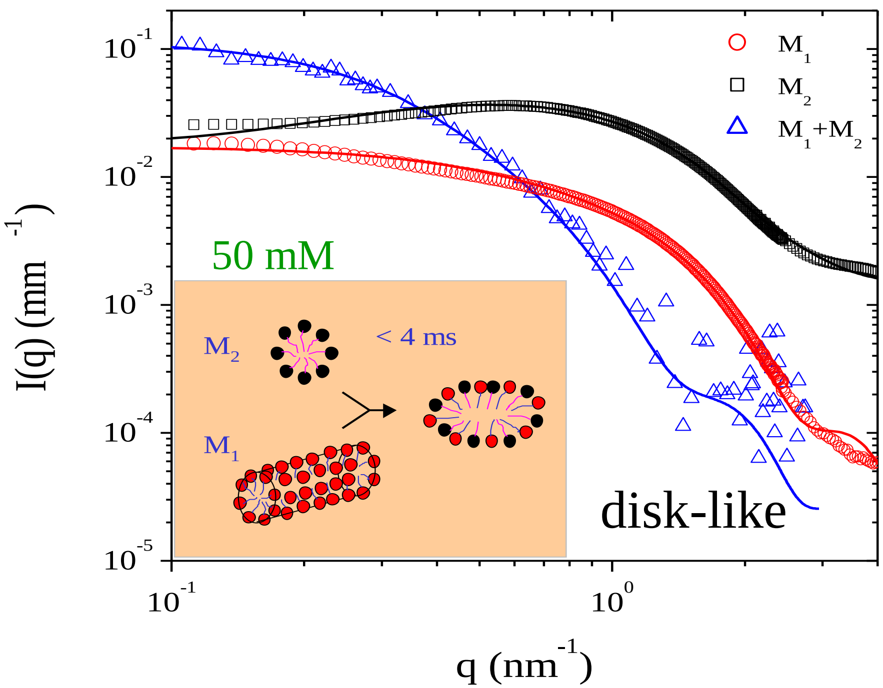


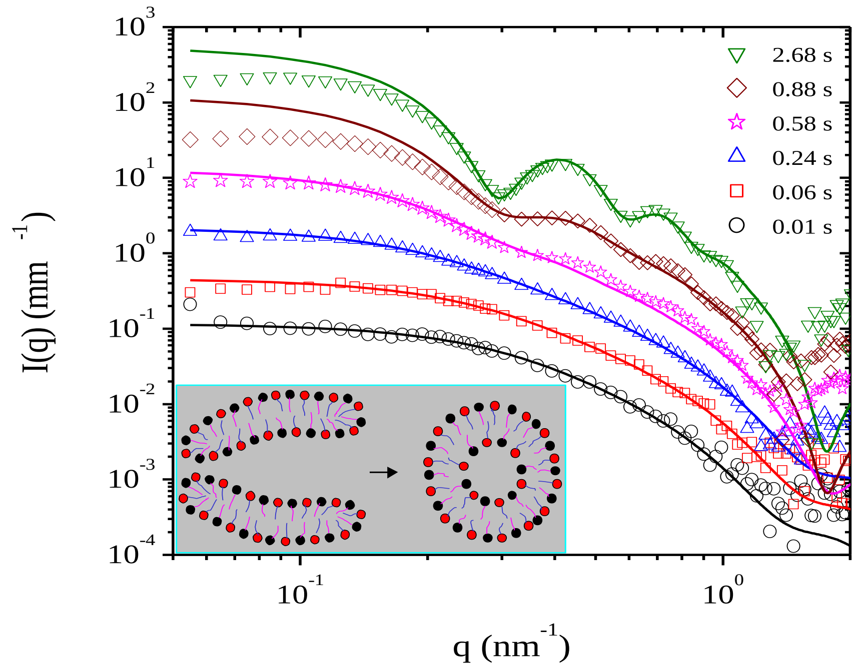
In water-like solvents

T. Narayanan *et al.*, Adv. Planar Lipid Bilayers & Liposomes (2014)

Micelle – Vesicle Transformation

Spontaneous self-assembly of small unilamellar vesicles





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

κ & $\bar{\kappa}$ - bending moduli

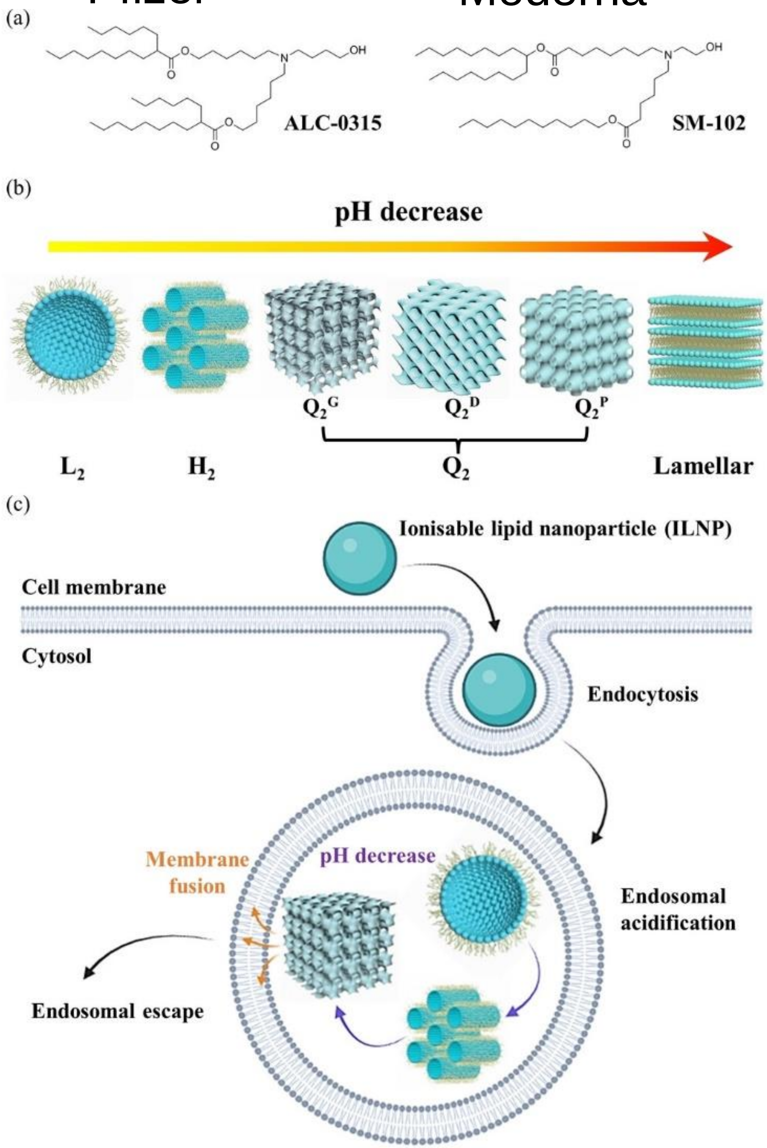
Λ - line tension

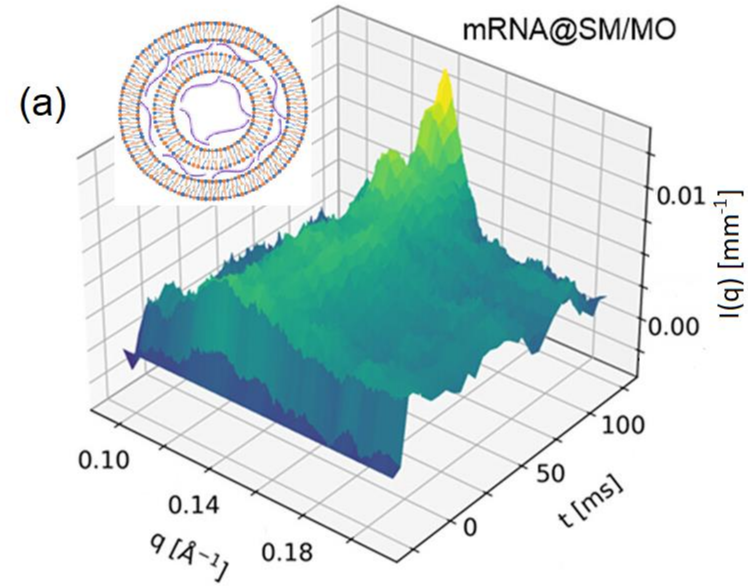
The whole evolution of the scattering curves can be described by a mechanistic model

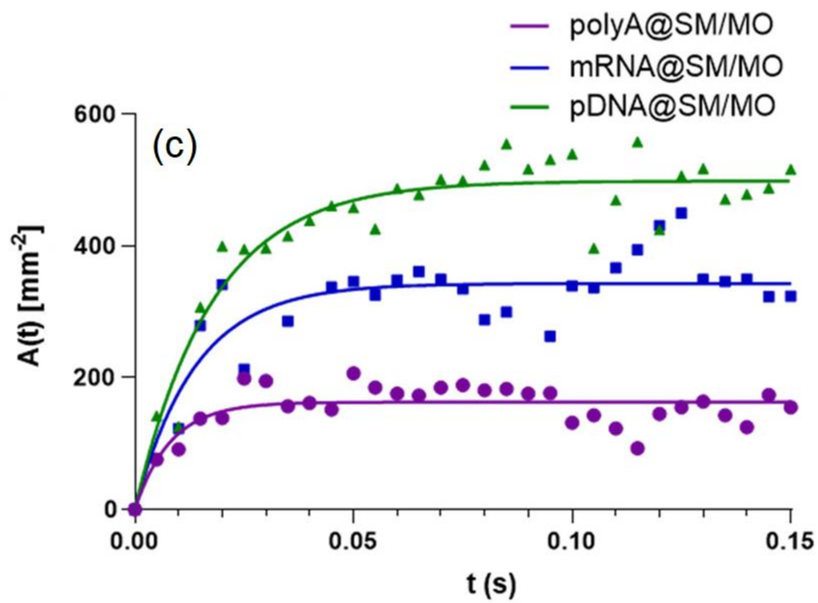
T.M. Weiss *et al.*, Phys. Rev. Lett. (2005), *Langmuir* (2008)

Lipid Nanoparticle Formulation

Pfizer Moderna





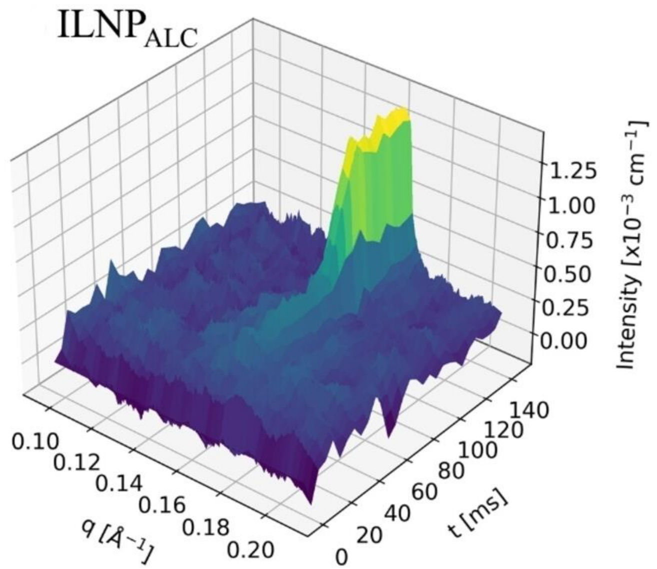


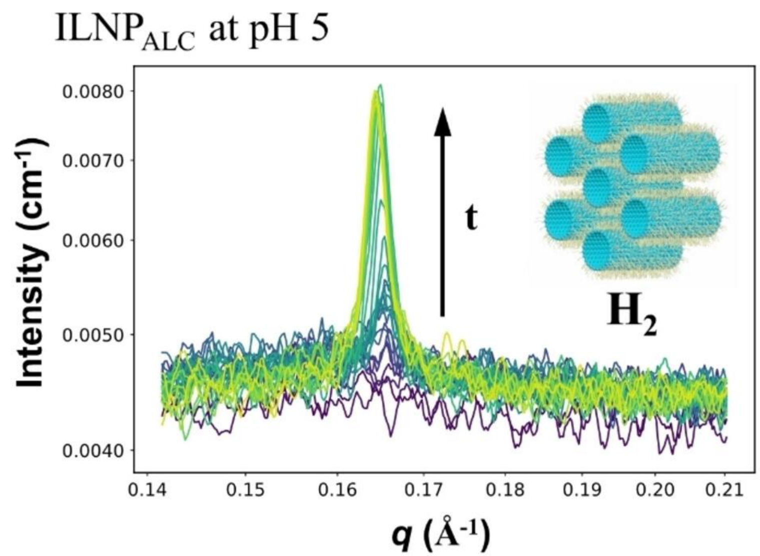
H. Yu *et al.*, Angew. Chem. (2023)

ESRF

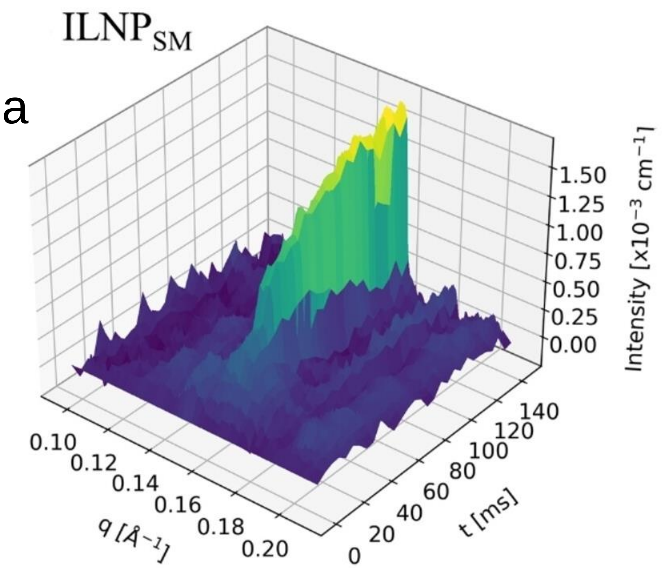
Lipid Nanoparticle Formulation

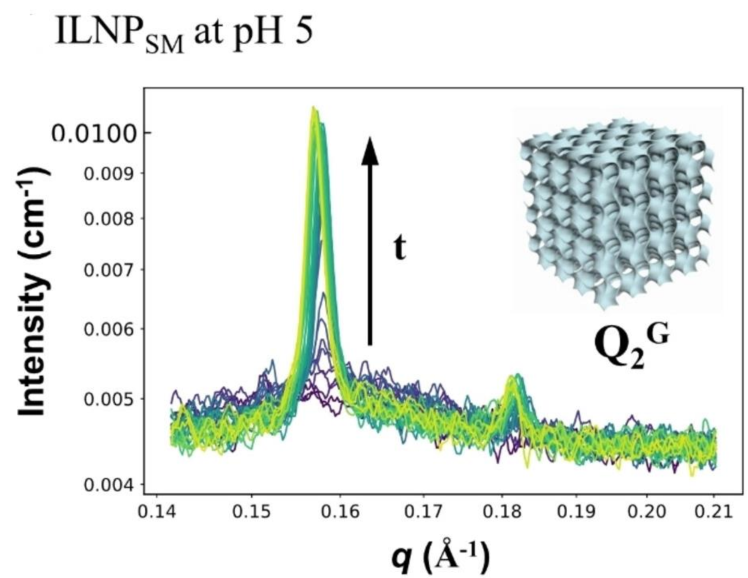
Pfizer





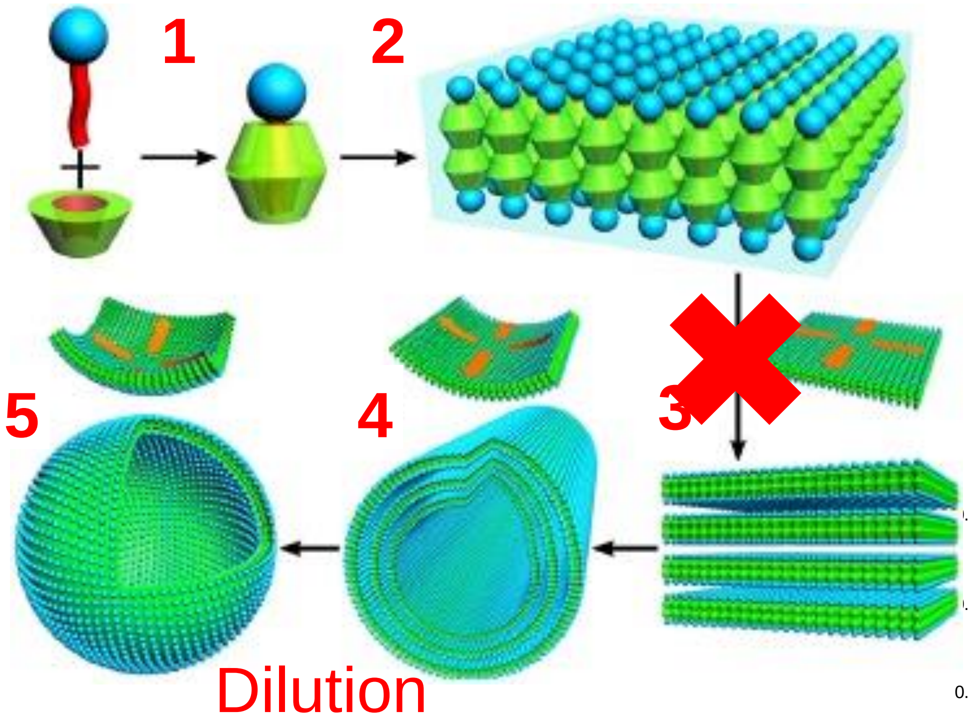
Moderna





H. Yu *et al.*, Angew. Chem. (2023)

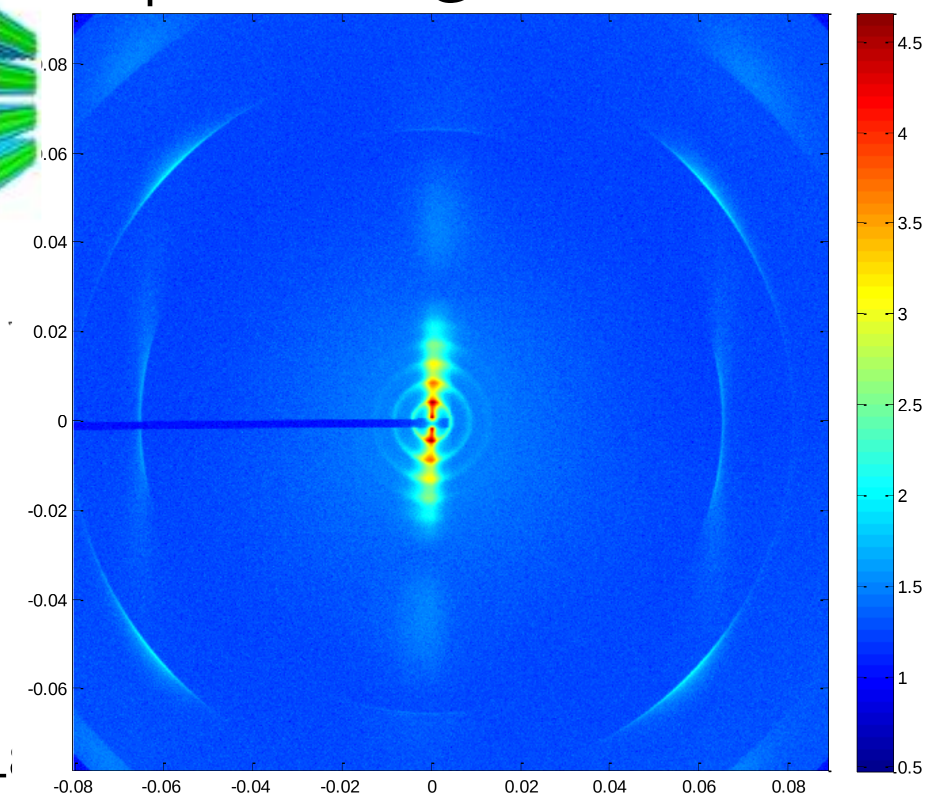
Multi-step hierarchical self-assembly of microtubules



Simple ingredients, a prototypical surfactant (SDS) and a naturally abundant polysaccharide (β-cyclodextrin) in water forming complex hierarchical structures.

L. Jiang et al., Soft Matter (2011)

2β-CD+SDS @ 75 ^{o}C → 25 ^{o}C

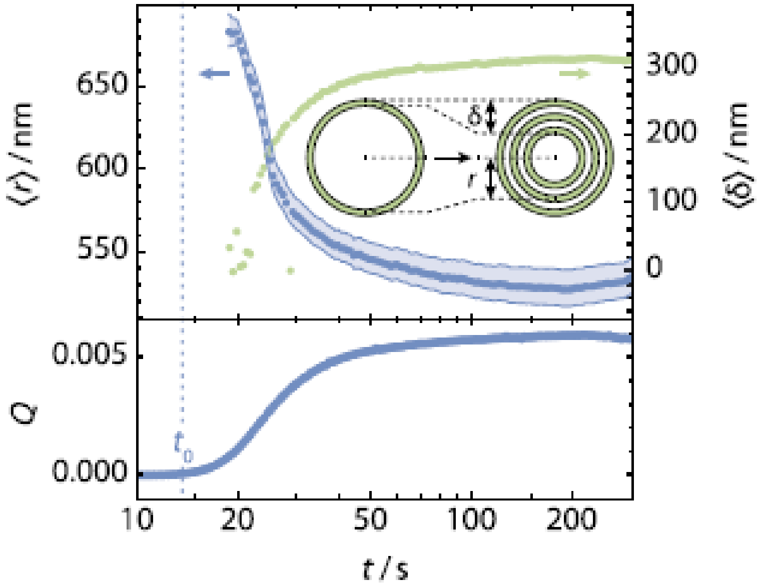


Spectacular self-assembly spanning size scales of 3 orders leading to formation of microtubules with a diameter of about 1.2 μm

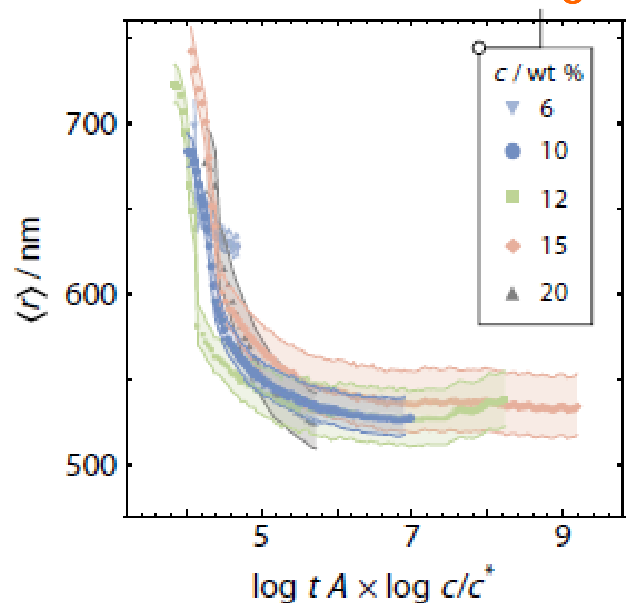
J. Landman *et al.*, Science Advances (201

Nucleation and Growth Mechanism

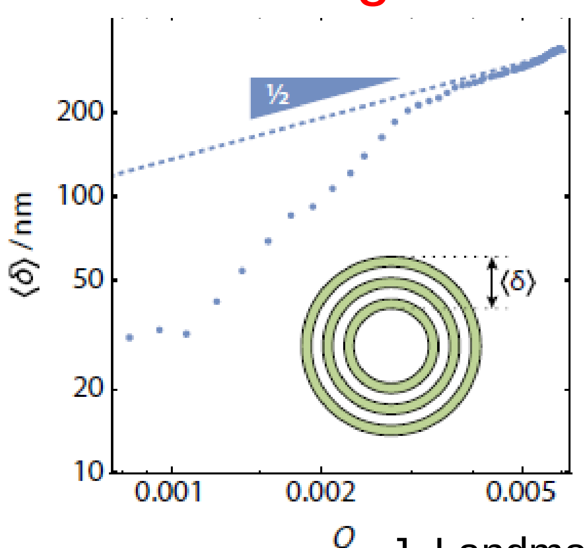
Central radius & wall thickness

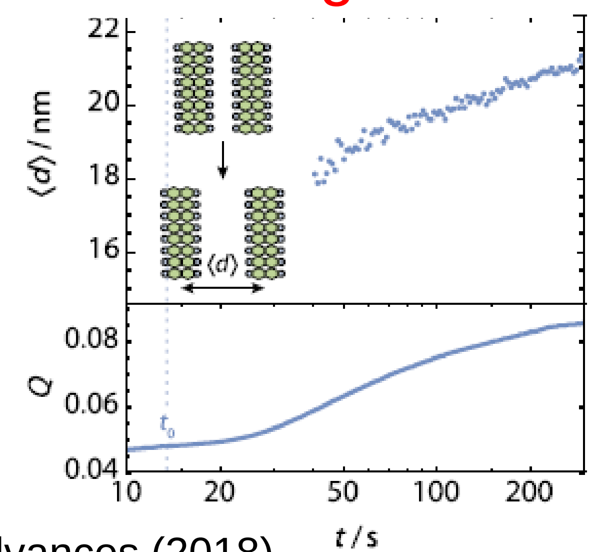


Concentration scaling



Inward growth of tubes by nucleation & growth





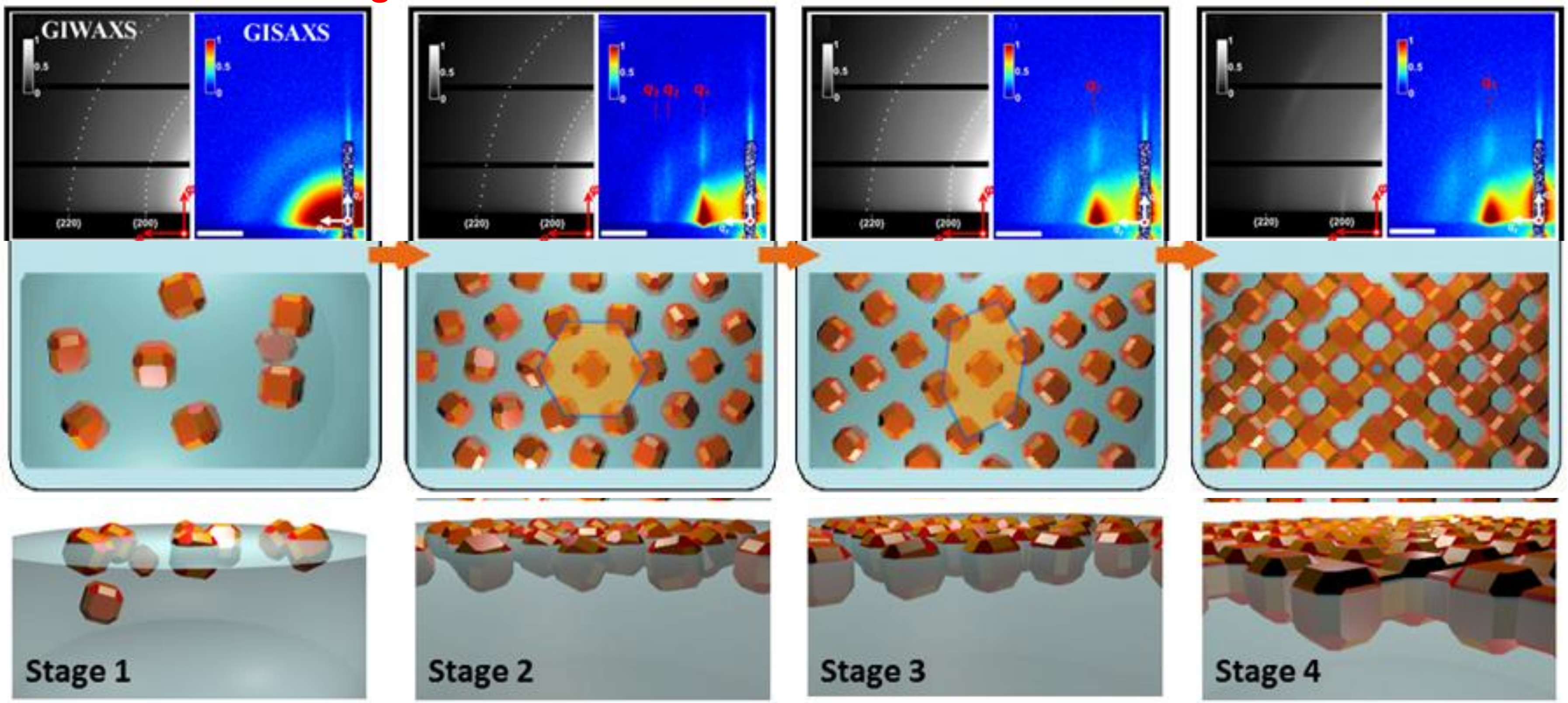
J. Landman *et al.*, Science Advances (2018)

Self-Assembly of 2D Superlattices

Formation mechanism of two-dimensional superlattices from PbSe nanocrystals at vapour/liquid interface

WAXS: Orientation/domain size
SAXS: Lateral organization

J.J. Geuchies, *et al.*, Nature Materials (2016)



Hexagonal array | Deformed array | Square lattice

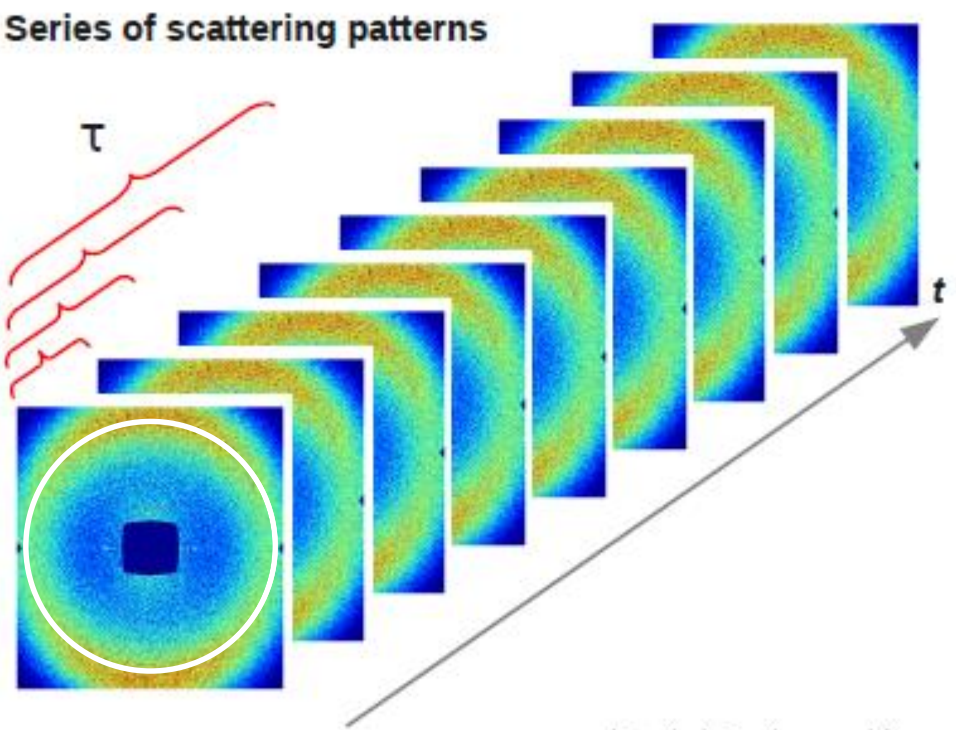
Crystalline bridges between the nanocrystals

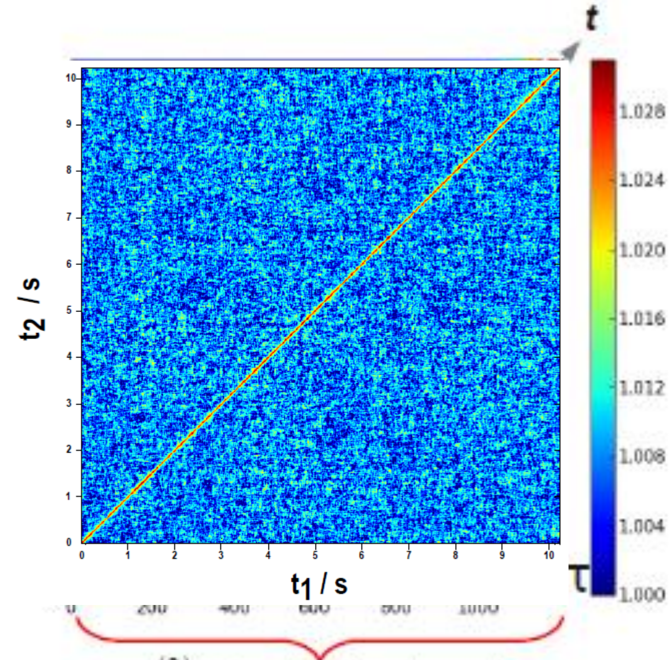
Out-of-equilibrium dynamics

Soft Matter: Out-of-equilibrium Dynamics

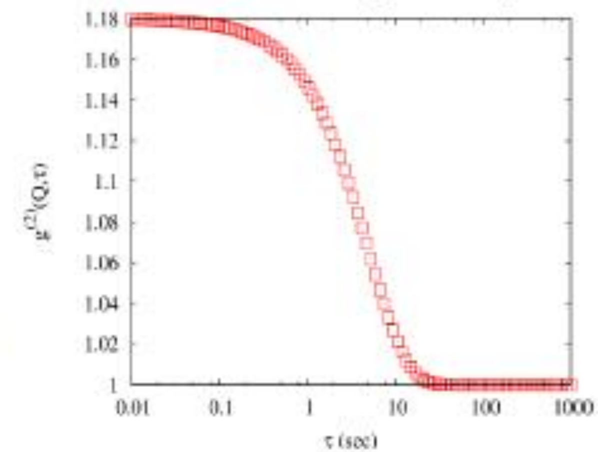
Out-of-equilibrium dynamics of systems far away from equilibrium

Multi-speckle XPCS





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



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

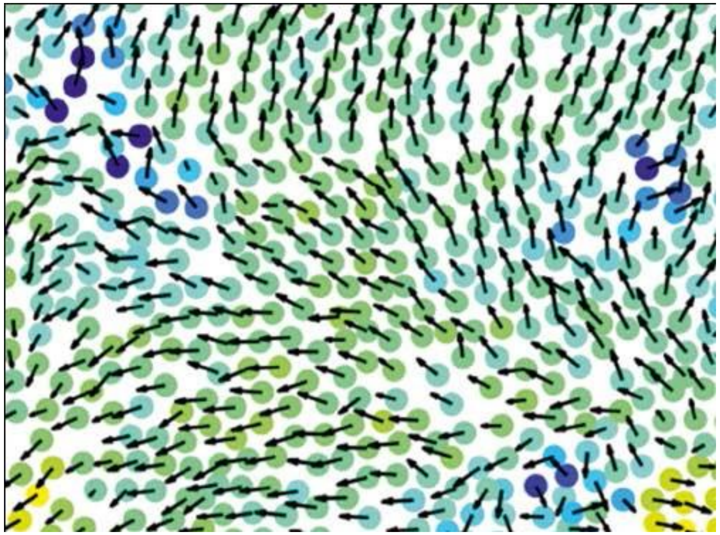
Time resolved correlation function

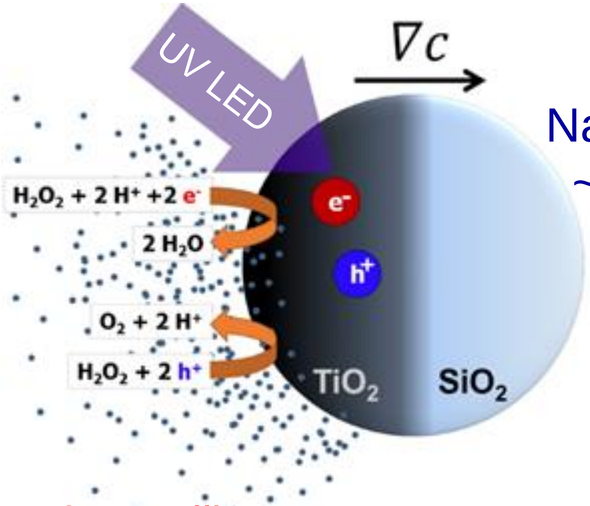
Dynamics of Active Particles

Active matter: understanding the physics of life from complex systems perspective

Complex systems

Self-propelled particles





Nanomotor
~ 500 nm

Micro-swimmers (microorganisms or Janus particles in a catalytic medium)

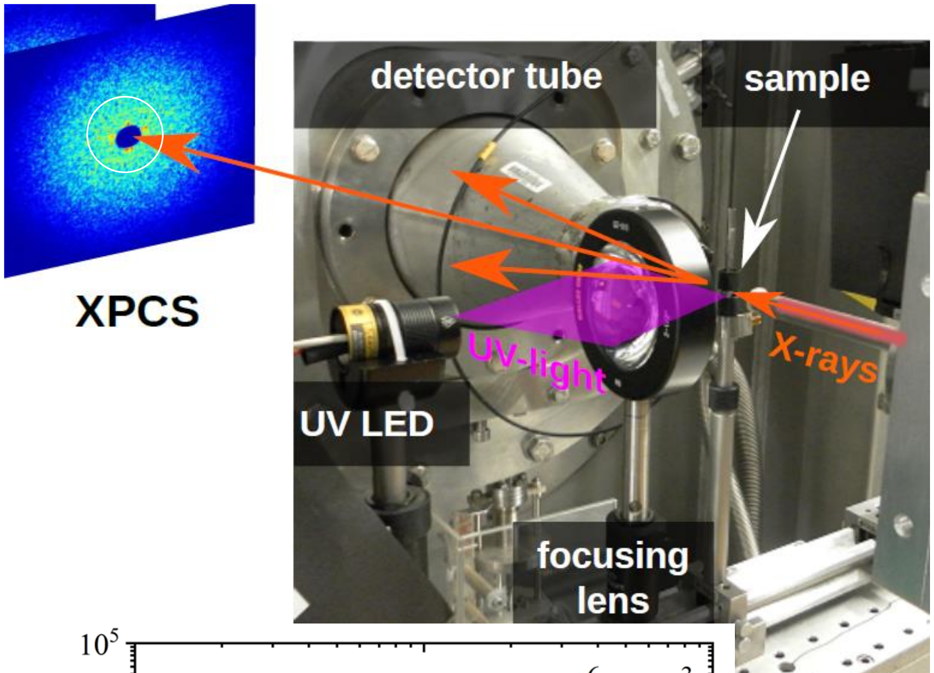
Diffusiophoresis

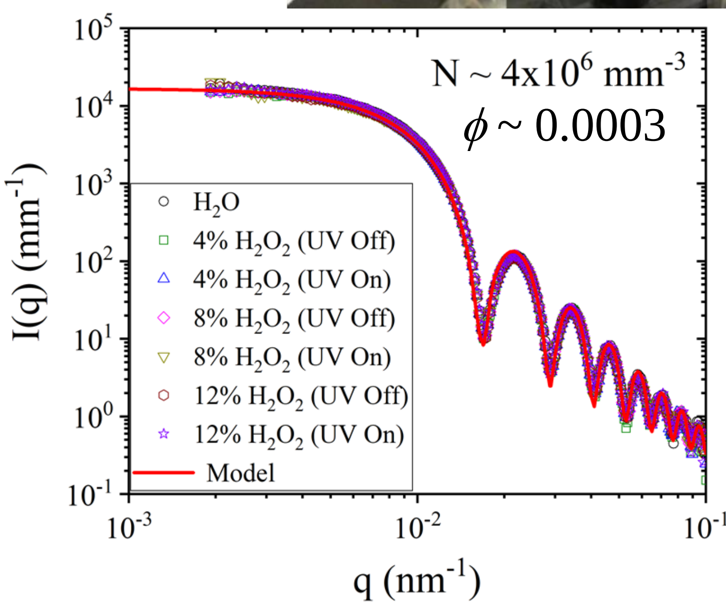
Probe the emergent dynamics by XPCS

Control parameter, Péclet number (Pe)

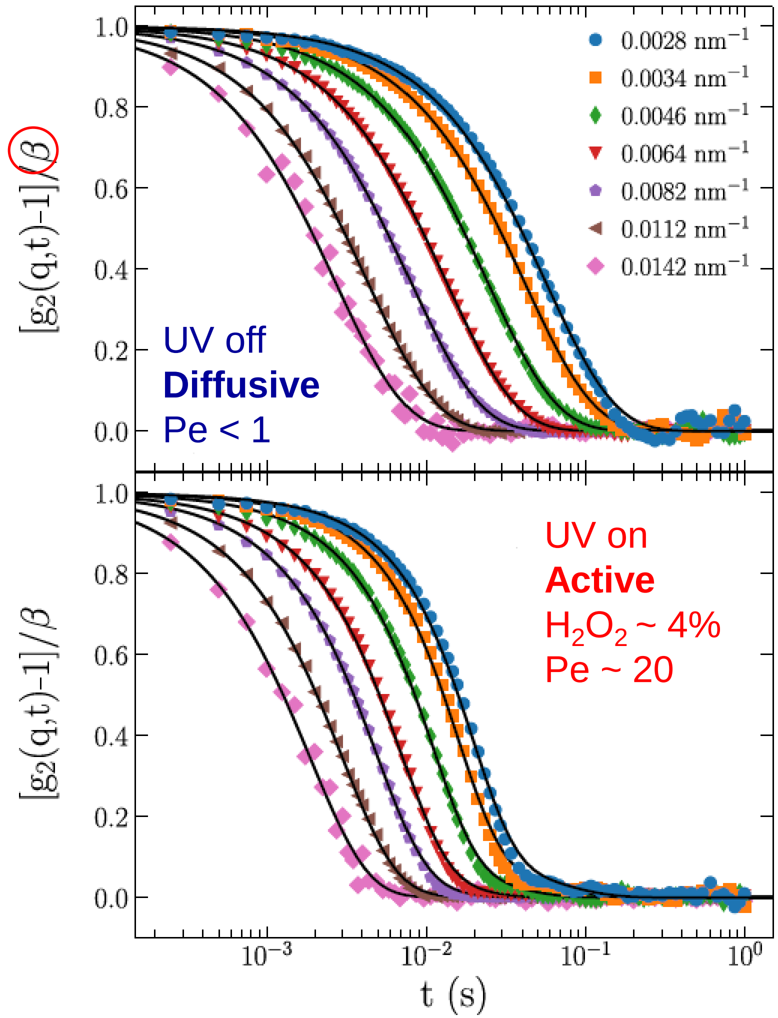
MPI for Intelligent Systems, Stuttgart (P. Fischer)

Multispeckle XPCS Study of Active Dynamics





Self-propulsion & associated dynamics



Weaker q-dependence – tendency towards superdiffusive behavior

T. Zinn *et al.*, New J. Phys. (2022)

Emergent Active Dynamics

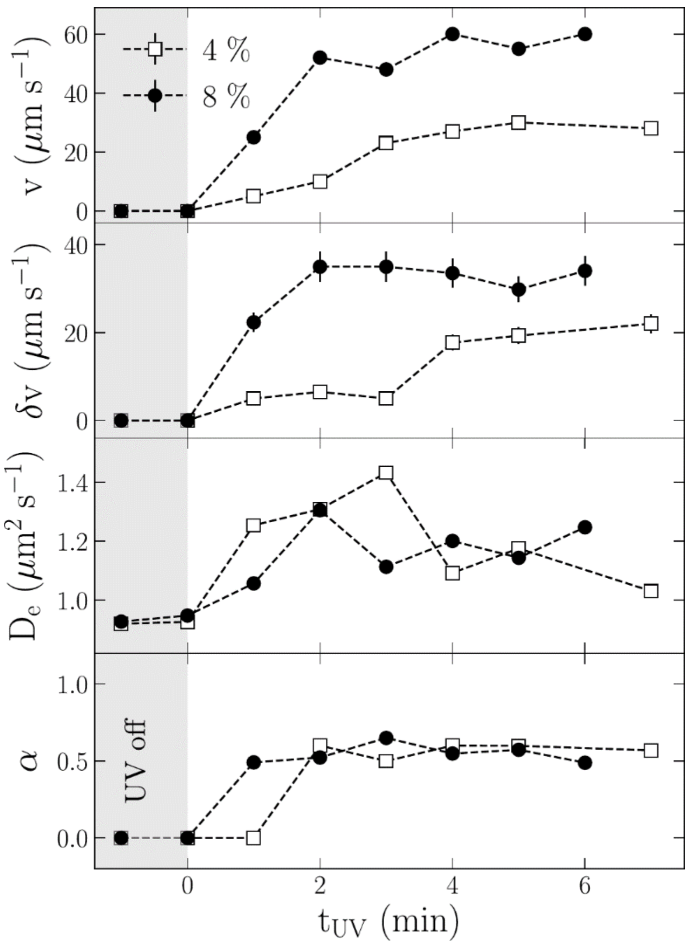
propulsive

diffusive

transit

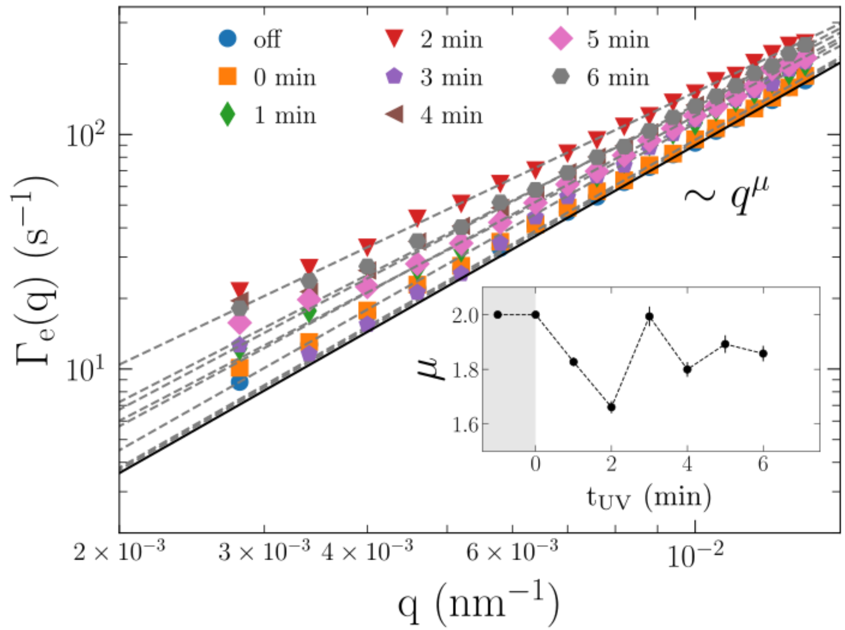
Gaussian $(\Delta v.\mathrm{q})^2$ — Exponential Dq^2 — Gaussian v

$$|g_1(q,t)|^2 = \left|g_{1,A}(q,t)\right|^2 \times \left|g_{1,D}(q,t)\right|^2 \times \left|g_{1,T}(t)\right|^2$$



Mean velocity (**v**) and it's variance (**δv**)

Effective diffusion coefficient (D_{eff})



Large **δv** – strong number fluctuations

Weaker q-dependence of (Γ_e)

T. Zinn *et al.*, New J. Phys. (2022)

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 multicomponent systems and radiation sensitive specimen.

- The emphasis has become on quantitative studies of highly complex systems by exploiting the coherence properties of extremely bright synchrotron sources. In particular to problems related to the Physics of Life.