Soft Matter Studies with X-rays

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Outline

• What is Soft Matter?

• Some general features

• Different X-ray techniques employed

• Self-assembly & complexity

• Out-of-equilibrium phenomena

• Summary and outlook
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 Studies seek to address the link between microscopic structure/interactions and macroscopic properties.

- 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 ($\sim k_B T$)
  - Characteristic size scale or microstructure $\sim 100 - 1000$ nm
  - Shear modulus, $G \sim$ Energy/Free volume $\gg 10^9 - 10^{12}$ smaller

  - Low shear modulus ($G$) $\gg$ 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.
Sustainable development and supply of consumer products
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
• **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.
Elucidating the pathways of self-assembly
Small-Angle X-ray Scattering (SAXS)

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

Measured Intensity:  
\[ I_S = i_0 T_r \varepsilon \Delta \Omega \left( \frac{d\sigma}{d\Omega} \right) \]

- \( i_0 \) - incident flux
- \( T_r \) - transmission
- \( \varepsilon \) - efficiency
- \( \Delta \Omega \) - solid angle

Differential scattering cross-section

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

Beamline – ID02
Beamline ID02

Sample-detector distance: 1 - 31 m

Energy range: 8–20 keV
q – range: 10^{-3} – 50 nm^{-1}
\Delta q: 5 \times 10^{-4} \text{ nm}^{-1} \text{ (FWHM)}
Time resolution: < 100 \mu s
Ultra SAXS/SAXS/WAXS

Beamline ID02

2\pi/q (nm)

Time (s)
Size scales probed by SAXS & related techniques

2\pi/q

Colloids
Polymers
Surfactants
Liquid crystals
Etc.
Size scales probed by SAXS & related techniques

2\pi/q

10^{-10} m 10^{-9} m 10^{-8} m 10^{-7} m 10^{-6} m 10^{-5} m 10^{-4} m 10^{-3} m 10^{-2} m

0.1 nm 1 nanometer (nm) 0.01 \mu m 10 nm 0.1 \mu m 100 nm 1 \mu m 100 \mu m 1 millimeter (mm) 1,000,000 nanometers = 1 millimeter (mm)

Soft x-ray Ultraviolet Visible Infrared Microwave

10^{-10} m 10^{-9} m 10^{-8} m 10^{-7} m 10^{-6} m 10^{-5} m 10^{-4} m 10^{-3} m 10^{-2} m

10^{-10} m 10^{-9} m 10^{-8} m 10^{-7} m 10^{-6} m

Glucose Hemoglobin Ribosome Virus Mitochondria Bacteria Erythrocyte

C-C bond

10^{-10} 10^{-9} 10^{-8} 10^{-7} 10^{-6} length [m]

The European Synchrotron
Modeling or simulation required to extract quantitative information

Silica particles (\(\phi \sim 0.01\), size \(~ 600\) nm, \(p \sim 2\%\))

Model (\(R_{\text{Mean}} = 303\) nm, \(\sigma_R = 6.2\) nm & \(\Delta q = 0.001\) nm\(^{-1}\))

SAXS from dilute spherical particles
Form & Structure Factors

Differential scattering cross-section per unit volume

\[ I(q) = N(\Delta \rho^* V)^2 P(q) \quad S_M(q) \]

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

\[ \phi < 0.001 \]
Structure Factors at high packing fractions

E.g. 60%

Glass

Crystal
Core Shell Structures

$I(q) \text{ [cm}^{-1}\text{]}$
$q \text{ [nm}^{-1}\text{]}$

BSA

Unloaded

Loaded

$D \rho(r) \text{ [nm}^{-3}\text{]}$
$r \text{ [nm]}$

Unloaded

Loaded

BSA

$I(q) \text{ [cm}^{-1}\text{]}$
$q \text{ [nm}^{-1}\text{]}$
X-ray Photon Correlation Spectroscopy (XPCS)

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

Beamline – ID10

Silica microspheres in water
\[ d=0.49\pm0.02\mu m, \quad q=0.09 \text{ nm}^{-1} \]

\[ \frac{1}{\tau_C} = D_0 \cdot q^2 \]

Mean-square displacement
\[ \langle \Delta r^2(\tau) \rangle = 6D_0\tau \]

Diffusion constant
\[ D_0 = \frac{k_B T}{6\pi \eta R} \]

(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

J. Moeller, et al. (2016)
Multi speckle XPCS at low angles, $10^{-3} \leq q \leq 10^{-2} \text{ nm}^{-1}$

Simultaneous static & dynamic scattering

Intensity autocorrelation function

Diffusive dynamics

J. Moeller, et al. (2016)
Soft Matter: out-of-equilibrium dynamics

Multi-speckle XPCS

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

Time resolved correlation function
Soft Matter: out-of-equilibrium dynamics

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

Multi-speckle XPCS
X-ray Photon Correlation Spectroscopy (XPCS)
Grazing Incidence Small-Angle X-ray Scattering

Beamline – ID10

\[
q_{x,y,z} = \frac{2\pi}{\lambda} \begin{cases} 
\cos \alpha_f \cos \theta_f - \cos \alpha_i \cos \theta_f \\
\cos \alpha_f \sin \theta_f - \cos \alpha_i \sin \theta_f \\
\sin \alpha_i + \sin \alpha_f
\end{cases}
\]
Soft Interfaces Scattering Beamline (ID10)

**PS-PMMA:** blocks length ratio →

![X-ray Reflectivity Chart](image)

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

**E.g.:**

PS-PMMA (1:1) & (2:1)

The beat 2D order at:

- **PS-PMMA (1:1)**
  - π = 12 mN/m
Soft Interfaces Scattering

Beamline ID10

Interfacial cavities for reaction
Varying the penetration depth

Water @ $\lambda = 1.55 \text{ Å}$

Penetration depth $\Lambda$, Å

$\alpha_i \approx 0.1 ^\circ$ at 8 keV

Atomic layering
Accumulation of ions

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)*
• 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.

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

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

• 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)
Growth of disk-like micelles

I(q) (mm$^{-1}$) vs q (nm$^{-1}$)

Bending energy vs Edge energy

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

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

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

$\kappa$ & $\overline{\kappa}$ - bending moduli

$\Lambda$ - line tension

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

Growth of disk-like micelles

Free energy of a bend bilayer

\[
\ln\left(\frac{F}{A}\right) \quad \text{[kT/nm}^2\text{]} \quad \ln(F/A [kT/nm^2])
\]

Disk, lense, Vesicles

\[
R_d [\text{nm}] \quad R_v = 1/c [\text{nm}]
\]

Disk area \(\pi R^2\)

\[
RC = \frac{1}{C^2} - \frac{R^2}{4}
\]

Radius of curvature

\(\kappa\) & \(\bar{\kappa}\) - bending moduli

\(\Lambda\) - line tension

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