introduction to SAXS for polymers
-a user view-

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outline

✓ basics of X-rays
  what are X-rays and how they work
  • generation of X-rays
  • interference of waves / Bragg’s law
  • the SAXS machinery

✓ morphological information from SAXS
  data interpretation
  • structure and form factor
  • polydispersity, lattice disorder

✓ what is in for you?
  examples

✓ summary
generation of X-rays

lab sources, synchrotron and nebulas
Hand mit Ringen (Hand with Rings):
first "medical" X-ray
(of Ms Röntgen)
commercial applications

material science

flight tube (vacuum) contains:
- sample
- detector
crab nebula

brightest source of X-rays…

(one of the) brightest source of X-rays…

that can be focused

synchrotron

synchrotron sources
typical experimental setup (WAXD)

- non-destructive
- no sample preparation
- time resolved (30 frames/s)
- space resolved (beam spot size limiting, 50nm)
- statistically sound information
- combination with other techniques possible
interference of waves

why do we use X-rays?
how are patterns formed?
basic interpretation: Bragg’s law
X-ray patterns: interference of electromagnetic waves

- X-rays scattering/diffraction patterns are the result of the *interference* between the incoming X-ray photons and the grating formed by the scatterers in the system (lattice)

- for positive interference, the wavelength should be of the order of the size/distance between scatterers

- crystals and molecules often have characteristic sizes ~ 10-1000 Å, just about the X-rays wavelength (→ they are suitable for investigation with X-rays)
interference of waves

single slit interference

two slit interference

N-slit interference

waves are scattered in phase when the path length difference is an integer number of wavelengths

\[ n \lambda = d \sin \theta \]

\( \theta \) is the angle where constructive interference takes place
examples

http://demonstrations.wolfram.com/FraunhoferDiffractionUsingAFastFourierTransform/

FraunhoferDiffractionUsingAFastFourierTransform-author.nb

http://demonstrations.wolfram.com/MultipleSlitDiffractionPattern/

MultipleSlitDiffractionPattern-author.nb
Bragg’s law

example of X-ray wave interference

when a sample is irradiated with X-rays: waves are scattered in phase (*constructive interference*) when the path length difference is an integer number of wavelengths

path length difference = $n \cdot \text{wavelength}$

$$2 \cdot d \sin \theta = n \cdot \lambda$$

W.L. Bragg 1890-1971
W.H. Bragg 1862-1942

Nobel Prize in Physics (1915)
application of Bragg’s law
length scales in SAXS and WAXD

\[ 2 \cdot d \sin \theta = n \cdot \lambda \]

typical length scales:

\[ d = \frac{\lambda}{2 \sin \theta} \]

- small angles (SAXS) → large d
- wide angles (WAXD) → small d

SAXS

\[ d = \frac{0.1 \text{nm}}{2 \sin(0.1/2)} \approx 60 \text{nm} \]

WAXD

\[ d = \frac{0.1 \text{nm}}{2 \sin(9/2)} \approx 0.60 \text{nm} \]
length scales
morphology of semi-crystalline polymers

macro scale
spherulites
10-100 µm

meso scale
lamellae
10-100 nm

micro scale
unit cells
1-10 Å

SAXS
\[ d = \frac{0.1\text{nm}}{2 \sin(0.1/2)} \approx 60\text{nm} \]

WAXD
\[ d = \frac{0.1\text{nm}}{2 \sin(9/2)} \approx 0.60\text{nm} \]

detailed information on the morphology of semi-crystalline polymers can be obtained with X-rays
morphological information from SAXS

modeling with form and structure factors
scattering is caused by etherogeneties in the electron density

\[ I(q) = \Delta \rho^2 \cdot (...) \]

2D scattered intensity is the Fourier transform of the electron density correlation function in real space

The SAXS signal

X-ray radiation

\( \rho_1 \)

\( \rho_2 \)

scattered X-rays

information on size, shape, content of the phases

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the SAXS signal

\[ \rho(x) \]

Fourier transform

\[ F(q) \]

(can be complex, not measurable (X-rays have too high frequency))

\[ |F(q)|^2 \]

(loss of information (phase), intrinsic feature of the data recording process)

ensemble average (polydispersity)

orientation average

measured intensity

\[ I(q) = \Delta \rho^2 \cdot (...) \]

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Strieck N - X-ray scattering of Soft Matter
Schultz JM – Diffraction for Material Scientists
Glatter O and Kratky O – Small Angle X-ray Scattering
Balta-Calleja FJ and Vonk CG- X-ray scattering of synthetic polymers and more...
	hanks{B. Lotz}
modelling, how?

system with identical particles:

\[ P(q) = S(q) = 1 \]

\[ I(q) = n \Delta \rho^2 V^2 P(q) S(q) \]

- \( n \): number of scatterers
- \( \Delta \rho \): density difference (contrast)
- \( V \): particle volume
- \( P(q) \): form factor (often \( |F|^2 \))
- \( S(q) \): structure factor

Guinier A and Fournet G – Small Angle Scattering of X-rays
Pedersen JS – Adv Colloid Interface Sci 70 (1997), 171
modelling, how?

form factor

homogeneous sphere with sharp boundary

\[ F(q) = \int_0^\infty \rho(x) \frac{\sin(qx)}{qx} x^2 dx = \frac{1}{q} \int_0^R \sin(qx) x dx \]

\[ F(R, q) = 3 \frac{\sin qR - qR \cos qR}{(qR)^3} \]

\[ P(R, q) = F^2(R, q) \]

- many form factors available in literature -
modelling, how?

form factor

homogeneous spheres with polydisperse radius

\[ \langle P(\bar{x}, q) \rangle = \int_0^\infty P(x, q) h(x) \, dx \]

h(x) distribution function

polydispersity can be introduced by averaging the form factor over the size distribution

spheres with Gaussian distribution of radii

\[ \langle P(\bar{R}, q) \rangle = \int_0^\infty \left[ 3 \frac{\sin qR - qR \cos qR}{(qR)^3} \right]^2 \frac{1}{\sqrt{2\pi}\sigma} \text{Exp} \left[ -0.5 \left( \frac{R - \bar{R}}{\sigma} \right)^2 \right] \, dR \]

\[ P(x, q) \]

\[ h(x) \]

for certain h(x), several \( \langle P(R, q) \rangle \) have analytical expressions, see:

Pedersen JS – Adv Colloid Interface Sci 70 (1997), 171


.....
modelling, how?

**form factor**

homogeneous spheres with polydisperse radius

\[
\langle P(\bar{x}, q) \rangle = \int_0^\infty P(x, q) h(x) \, dx \\
\]

**distribution function**

polydispersity can be introduced by averaging the form factor over the size distribution

spheres with Gaussian distribution of radii

![Graphs showing form factor and Gaussian distribution](image)

- monodisperse, \( R = 1 \)
- Gauss, FWHM = 0.1
- Gauss, FWHM = 0.5

![Gaussian distribution](image)
modelling, how?

structure factor for *disordered* systems

\[ S(q) = 1 \]  
dilute system with randomly distributed particles

\[ I(q) = n\Delta \rho^2 V^2 P(q)S(q) \]

\[ \frac{I(q)}{n\Delta \rho^2 V^2} = P(q) \]

the intensity scattered by a dilute system with randomly distributed particles represents the form factor of the scatterers

asymptotes (Guinier, Porod) recovered in the low and high q limits
modelling, how?

structure factor for ordered systems

ideal systems

SC (Pm3m)  
BCC (Im3m)  
FCC (Fm3m)  
HCP (P6/mmc)

HEX (P6/mm)  
SQ (P4/mmm)  
LAM

non-ideal systems

\[ \beta(q), G(q) = 1 \]

\[ S(q) = Z_0(q) \]

\[ \beta(q), G(q) \leq 1 \]

lattice factor

\[ Z_0(q) = \frac{\text{const}}{q^{d-1}} \sum_{hkl} m_{hkl} f_{hkl}^2 L_{hkl}(q) \]

probability to find a particle in certain (hkl) direction

structure factor

\[ S(q) = 1 + \beta(q)[Z_0(q) - 1]G(q) \]

\[ \beta(q) \quad \text{polydispersity} \]

\[ G(q) \quad \text{positional disorder} \]

modelling, how?

example: structure factor of an hexagonal lattice

\[ S(q) = Z_0(q) \]

\[ S(q) = 1 + \beta(q)[Z_0(q) - 1]G(q) \]

\( \beta(q) \) polydispersity
\( G(q) \) positional disorder

\( q \) [nm\(^{-1}\)]

\[ S(q) \]

polydispersity
positional disorder

what is in it for you?

examples:
• growth of shish-kebabs
• phase separation of (dissolution type) nucleating agents
• crazing during cyclic loading
• spatial heterogeneity in injection molded parts
modeling growth of shish-kebabs

- material: iPP
- isothermal at 165 °C
- shear time 0.188 s
- wall stress~ 0.16 MPa
- wall shear rate~ 750 s⁻¹
modeling growth of shish-kebabs


all identical particles (monodisperse system)

form factor (sharp interfaces)

structure factor (perfect orientation)

\[
I(\vec{s}) = F^2(\vec{s}) \cdot Z(\vec{s}) \quad \vec{s} = \{s_1, s_2, s_3\}
\]

\[
F(s_{12}, s_3) = \frac{\pi D^2}{4} \frac{2J_1(\pi D s_{12})}{\pi D s_{12}} \frac{\sin(\pi T s_3)}{\pi T s_3}
\]

\[
Z(s_3) = \text{Re} \left[ \frac{1 + H_L(s_3)}{1 - H_L(s_3)} \right]
\]
modeling growth of shish-kebabs


polydisperse system

\[ I(\vec{s}) = \langle F^2(\vec{s}) \rangle + \langle F(\vec{s}) \rangle^2 \left[ Z(\vec{s}) - 1 \right] \]

spatially averaged form and structure factors
(can be complicated formulas but they are)
available in literature !!!

modeling growth of shish-kebabs


\[
\text{% shishes} = 100 \frac{2 \text{ area shish}}{\text{area unit cell}} = 100 \frac{2\pi D_k^2}{(3\sqrt{3}/2)D_s^2 k} \approx 3 \%
\]

detailed kinetic information → hint for the formation mechanism
crazing during cyclic loading

Poly(ethylene terephthalate), PET

Reflection from craze-bulk interfaces

Scattering from fibrils and voids

Failure initiation under loads

crazing during cyclic loading

Poly(ethylene terephthalate), PET

phase separation of (dissolution type) nucleating agents

iPP+1% DMDBS

$T = 246.585^\circ C$

(total scattered intensity (invariant)) $Q = 2\pi^2 \cdot x(1-x)\Delta \rho^2$

DMDBS phase separates $\rightarrow$ invariant increases due to the e\textsuperscript{-} density difference

Balzano et al. - Macromolecules 2008, 41, 399-408
phase separation of (dissolution type) nucleating agents

iPP+1% DMDBS

phase diagram

Balzano et al. - Macromolecules 2008, 41, 399-408
spatial heterogeneity in injection molded parts

isotactic polypropylene, iPP

cooling rate vs stress as function of the position
SAXS is a relatively simple technique that can be used to extract morphological information in static and dynamic conditions.

The SAXS signal comes from electron density differences and can be seen as the Fourier transform of the real-space morphology.

SAXS data can be modeled in terms of form and structure factors (also in other ways...)

- mathematical complexity should not scare you! Very many form and structure factors are tabled in literature.
- modeling provides qualitative and quantitative information on size, size distribution and morphology of scatterers.
- results are model dependent.
- model assumptions need to be validated by other techniques.

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