introduction to SAXS for polymers
-a user view-

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Utrecht, June 1-2 2015

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

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generation of X-rays

lab sources, synchrotron and nebulas

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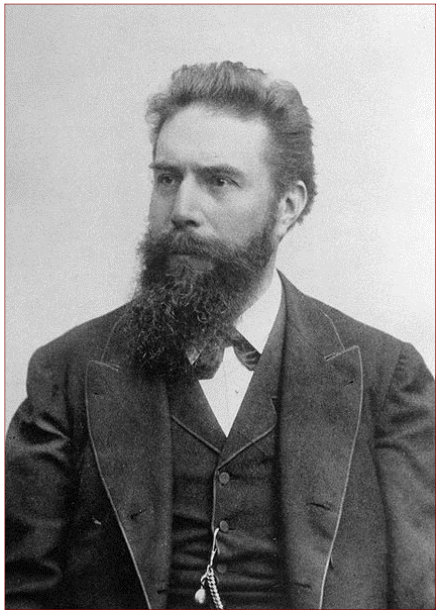
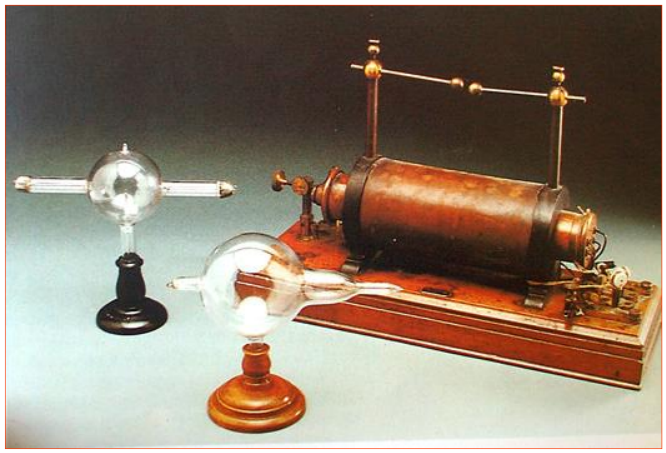
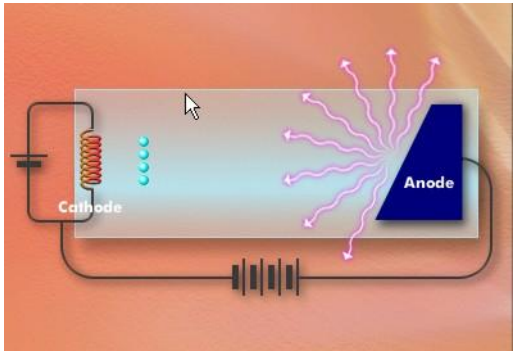
history



Wilhelm C. Röntgen
1845-1923
Nobel Prize in Physics (1901)





Hand mit Ringen (Hand with Rings):
first "medical" X-ray
(of Ms Röntgen)

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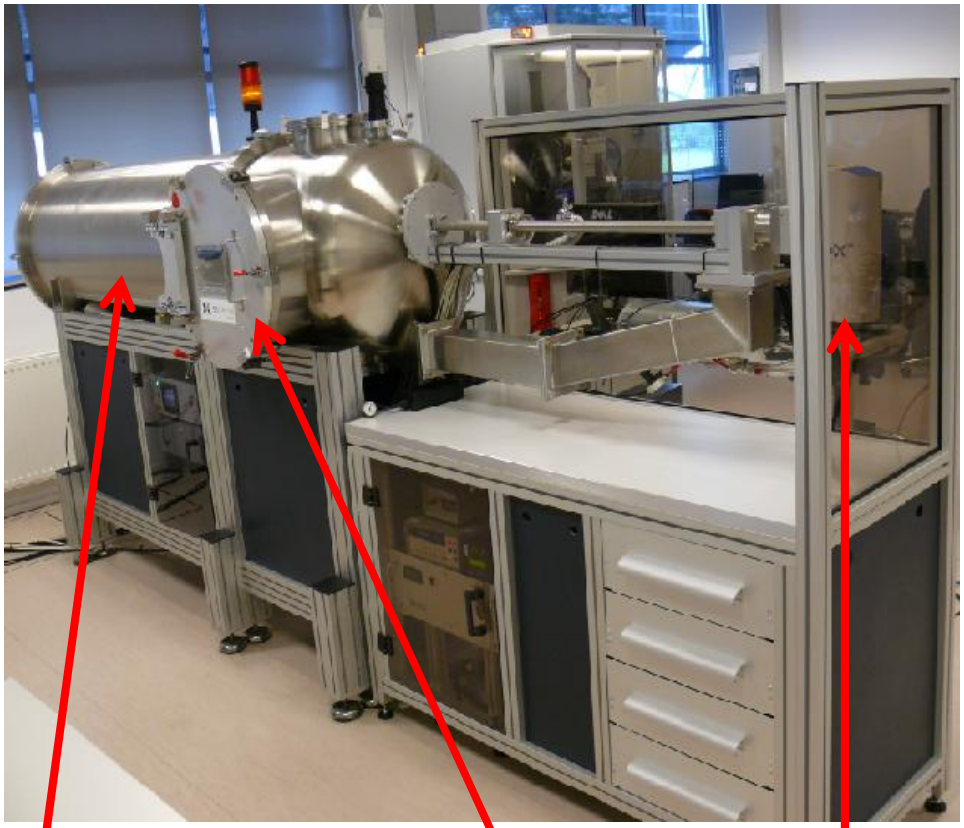
commercial applications

material science



flight tube (vacuum) contains:

- sample
- detector

sample/cell handling

generator

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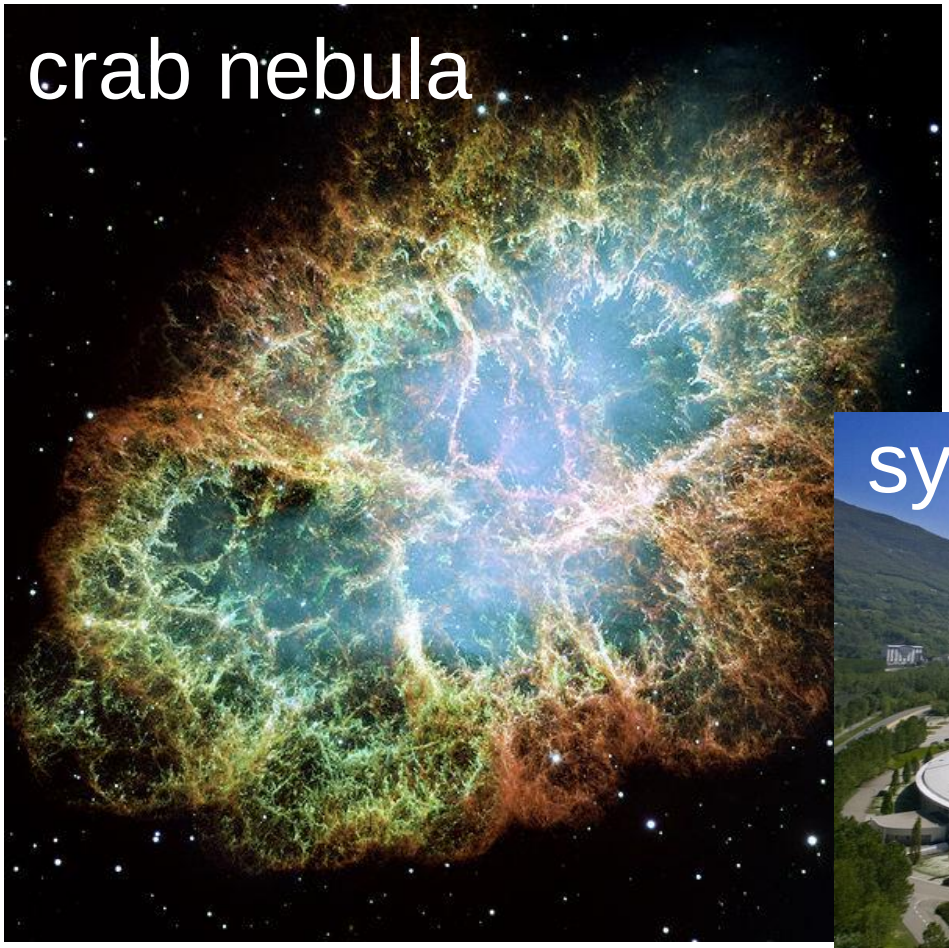
synchrotron sources

brightest source of X-rays…



(one of the) brightest source of X-rays…
that can be focused

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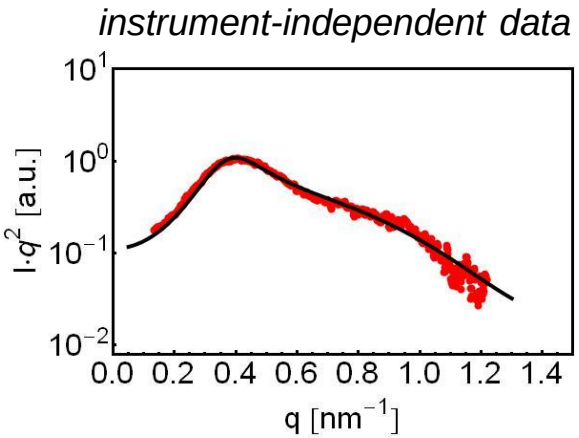
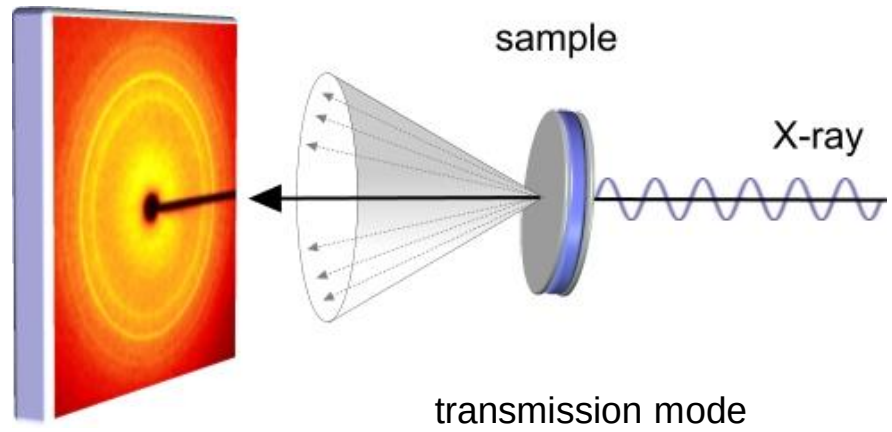
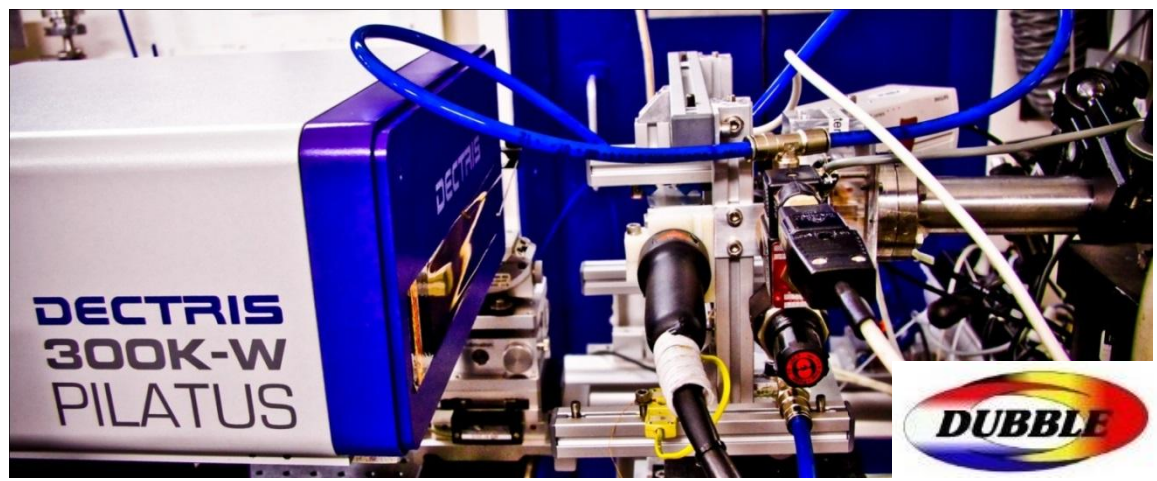
typical experimental setup (WAXD)



data reduction





- 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

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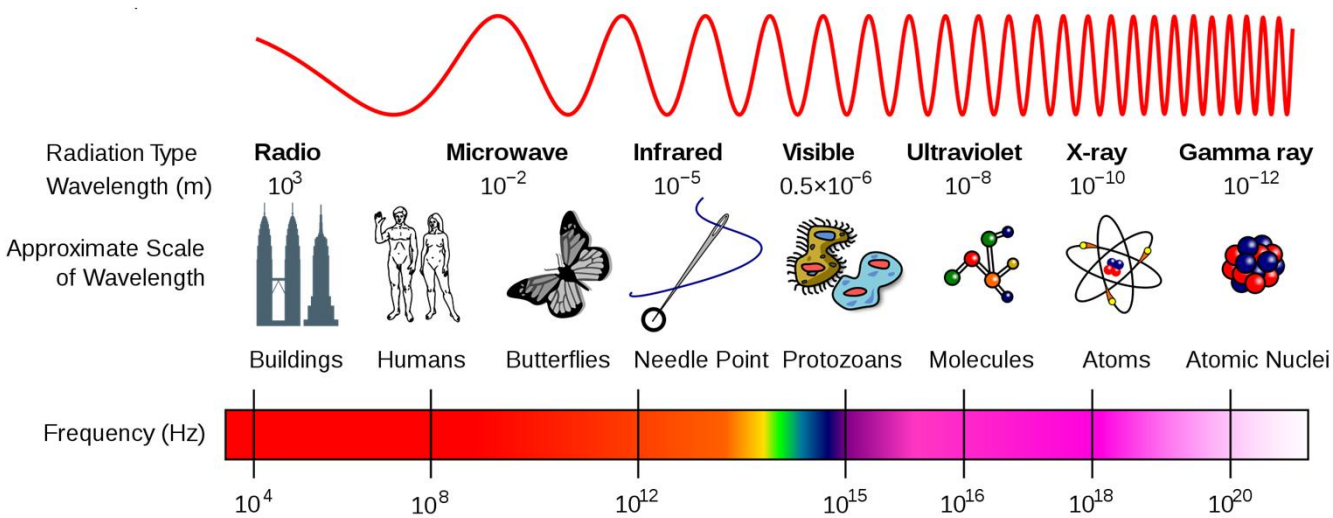
X-ray patterns: interference of electromagnetic waves

- 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)

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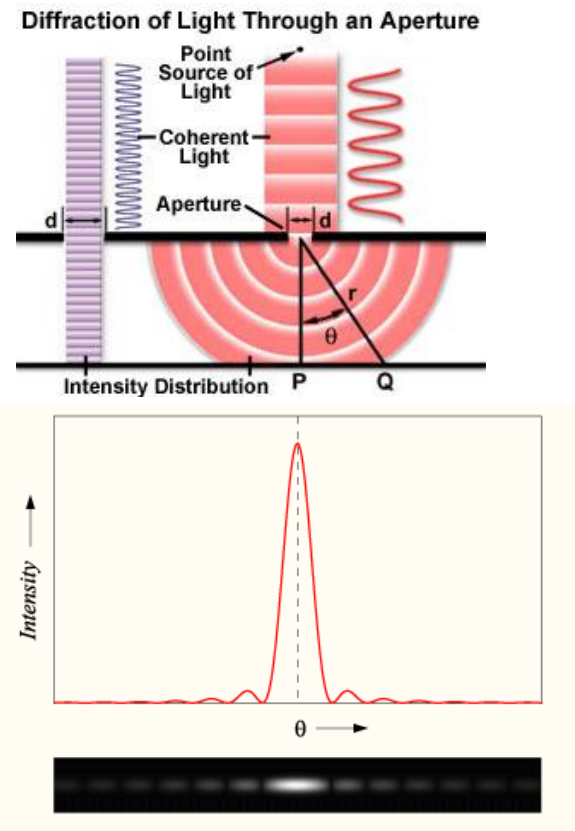
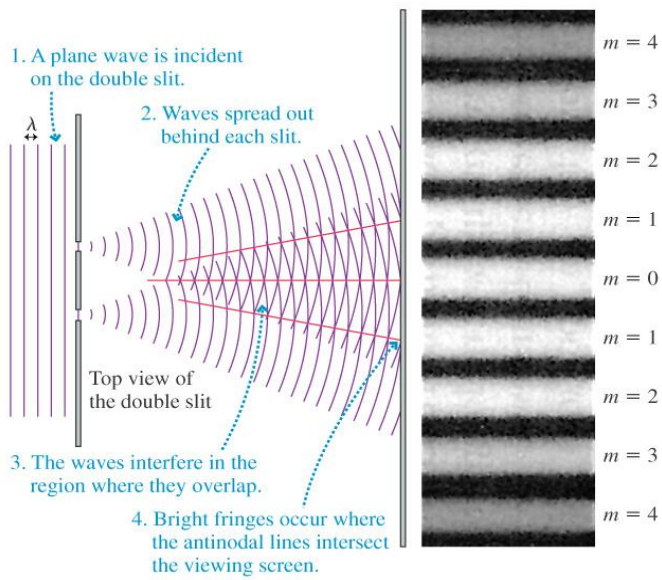
interference of waves

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

$$n\,\lambda = d\,\sin\theta$$

θ is the angle where constructive interference takes place

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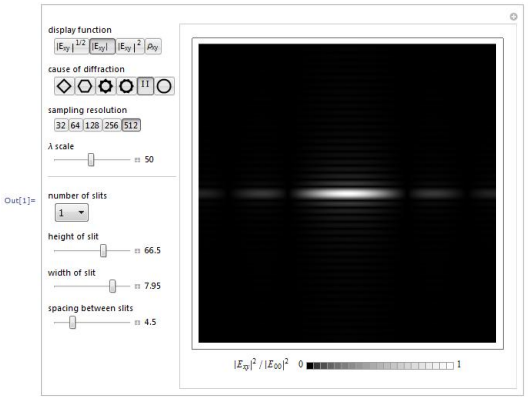
examples

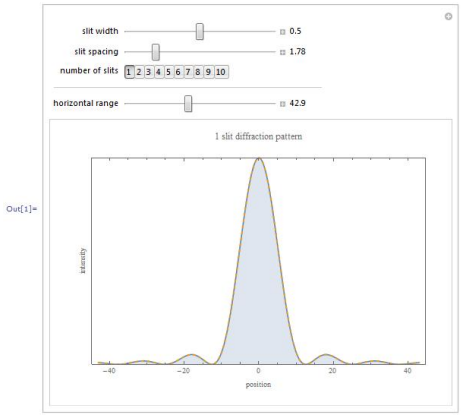
http://demonstrations.wolfram.com/FraunhoferDiffractionUsingAFastFourierTransform/

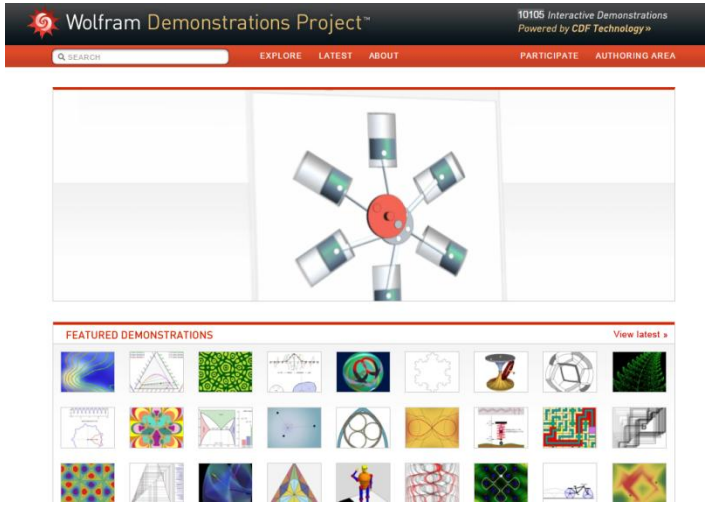
FraunhoferDiffractionUsingAFastFourierTransform-author.nb



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

MultipleSlitDiffractionPattern-author.nb





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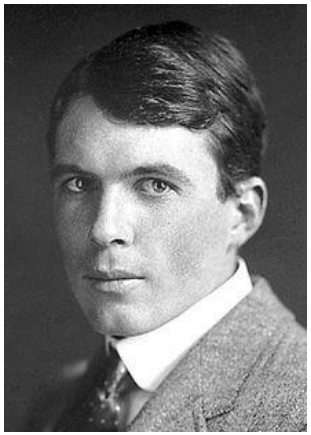
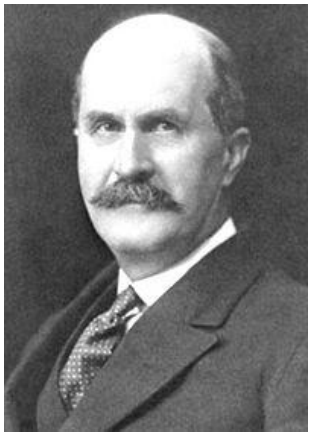
Bragg's law

example of X-ray wave interference



W.L. Bragg
1890-1971



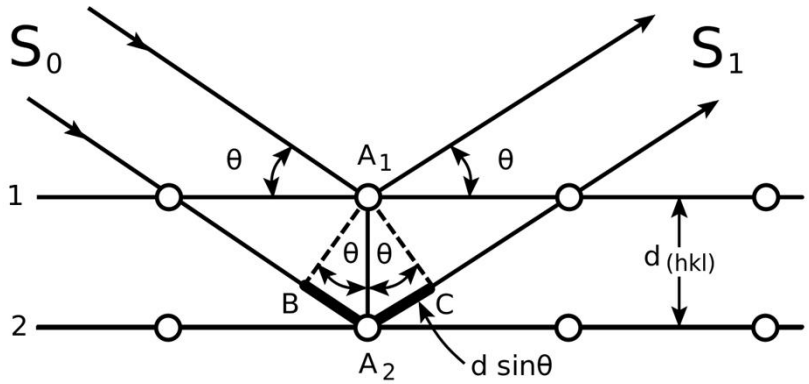
W.H. Bragg
1862-1942

Nobel Prize in Physics (1915)

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·wavelength

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



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application of Bragg's law

length scales in SAXS and WAXD

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

typical length scales: $d = \dfrac{\lambda}{2\sin\theta}$

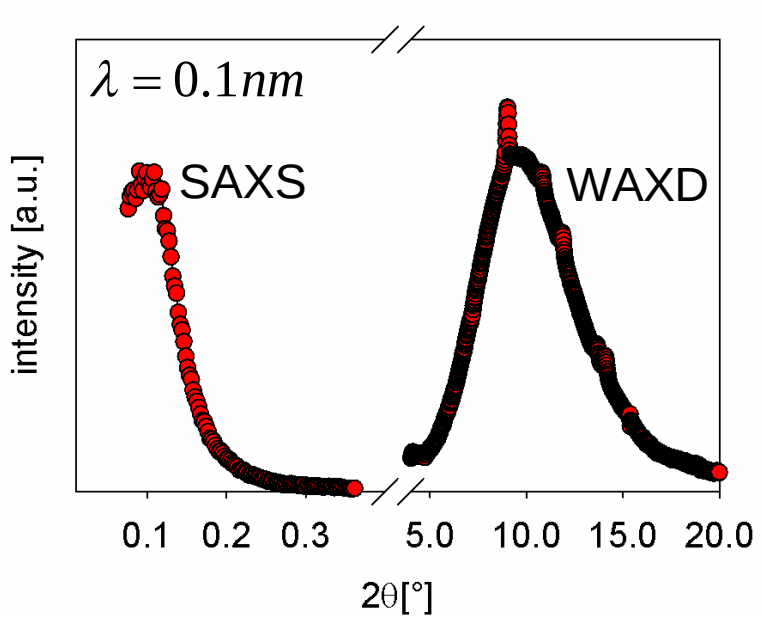
- small angles (SAXS) → large d
- wide angles (WAXD) → small d

SAXS

$$d = \frac{0.1nm}{2\sin(0.1/2)} \cong 60\,nm$$

WAXD

$$d = \frac{0.1nm}{2\sin(9/2)} \cong 0.60\,nm$$



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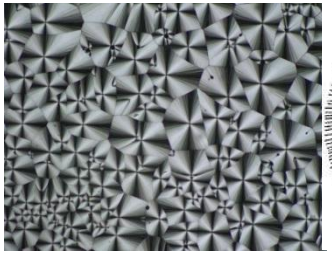
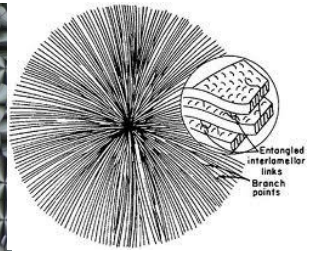
length scales

morphology of semi-crystalline polymers

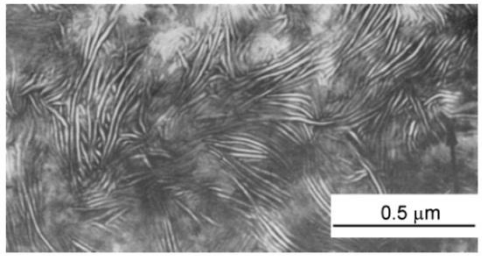
macro scale
spherulites





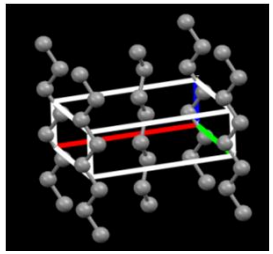
10-100 µm

meso scale
lamellae



10-100 nm

micro scale
unit cells



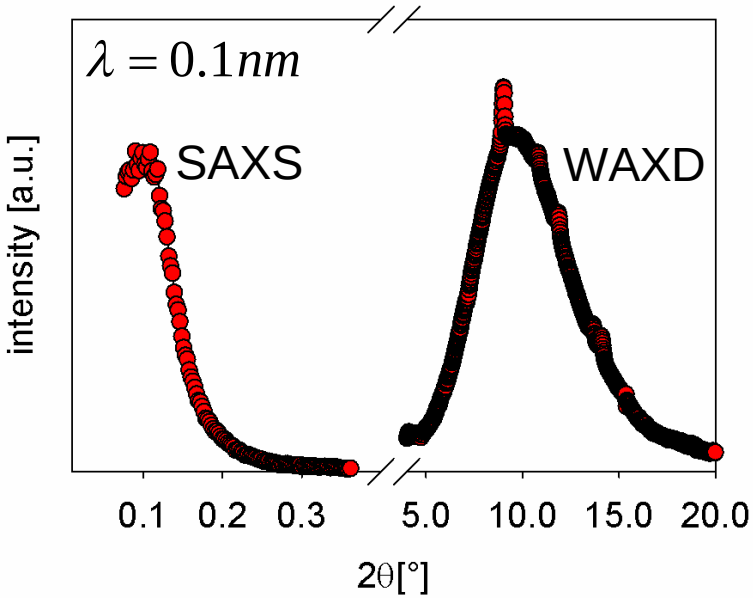
1-10 Å

SAXS

$$d = \frac{0.1nm}{2\sin(0.1/2)} \cong 60\,nm$$

WAXD

$$d = \frac{0.1nm}{2\sin(9/2)} \cong 0.60\,nm$$



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

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morphological information from SAXS

modeling with form and structure factors

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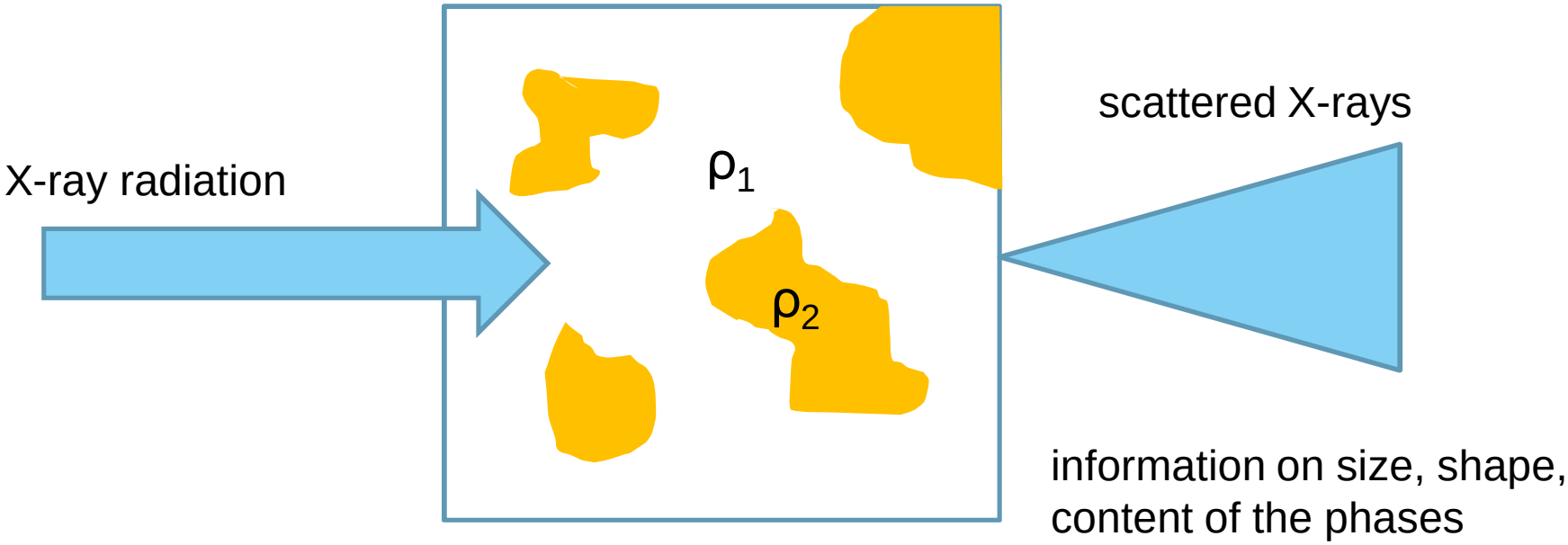
the SAXS signal



- scattering is caused by etherogeneties in the electron density $I(q) = \Delta\rho^2 \cdot (\ldots)$
- 2D scattered intensity is the Fourier transform of the electron density correlation function in real space

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the SAXS signal

density profile $\rho(x)$

↓ Fourier transform

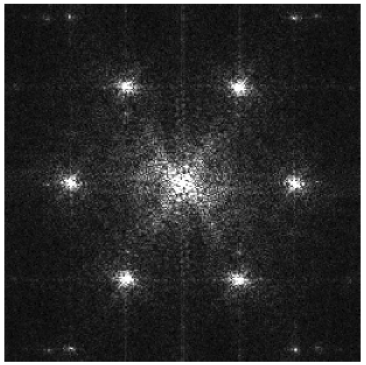
scattering amplitude $F(q)$
(amplitude of the form factor)

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

↓ square

scattering intensity $|F(q)|^2$
(form factor)

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



↓ ensemble average (polydispersity)
orientation average

measured intensity $I(q)$ $\quad I(q) = \Delta\rho^2 \cdot (\ldots)$

thanks B. Lotz

Stribeck 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...

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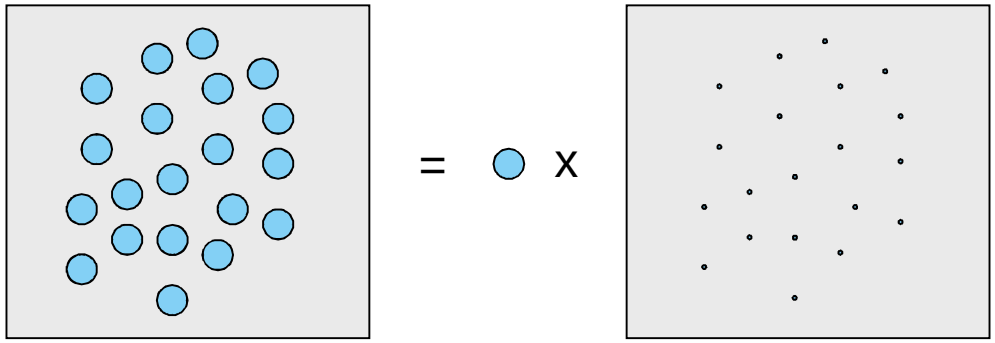
modelling, how?

system with identical particles:



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

n	number of scatterers
Δρ	density difference (contrast)
V	particle volume
P(q)	form factor (often $\lvert F \rvert^2$)
S(q)	structure factor

P(q=0)=S(q=0)=1

Guinier A and Fournet G – Small Angle Scattering of X-rays
Pedersen JS – Adv Colloid Interface Sci 70 (1997), 171
Förster S et al – J Phys Chem B 2005, 109, 1347

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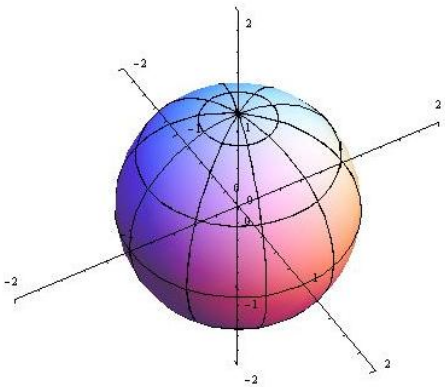
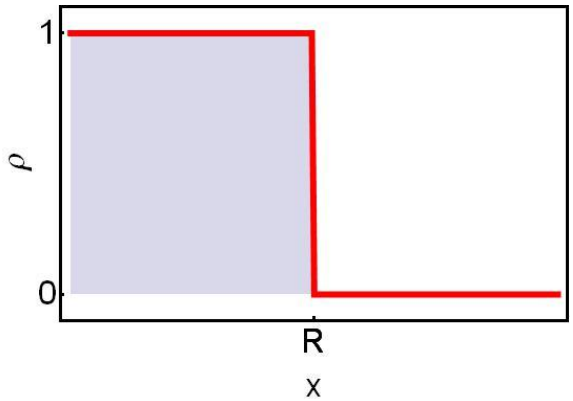
modelling, how?

form factor



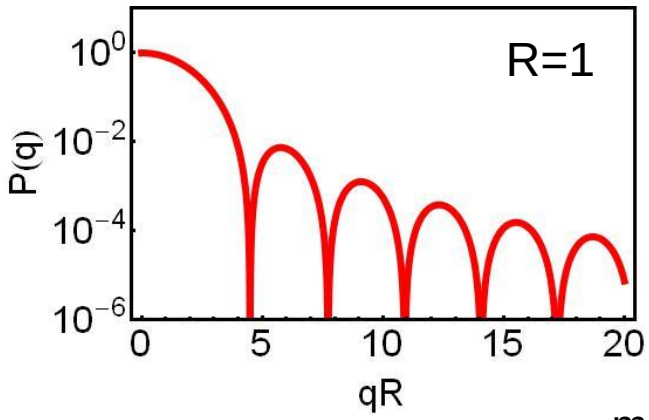
homogeneous sphere with sharp boundary

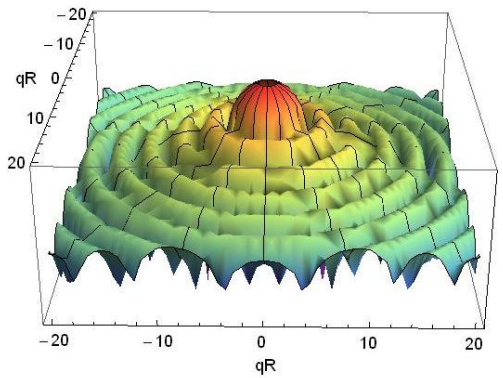
$$F(q) = \int_0^\infty \rho(x) \frac{\sin(qx)}{qx} x^2 dx = \frac{1}{q} \int_0^R \sin(qx) x dx$$



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

$$P(R,q) = F^2(R,q)$$





- 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

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

for certain h(x), several <P(R,q)> have analytical expressions, see:

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

Förster S et al – J Phys Chem B 2005, 109, 1347

....

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modelling, how?

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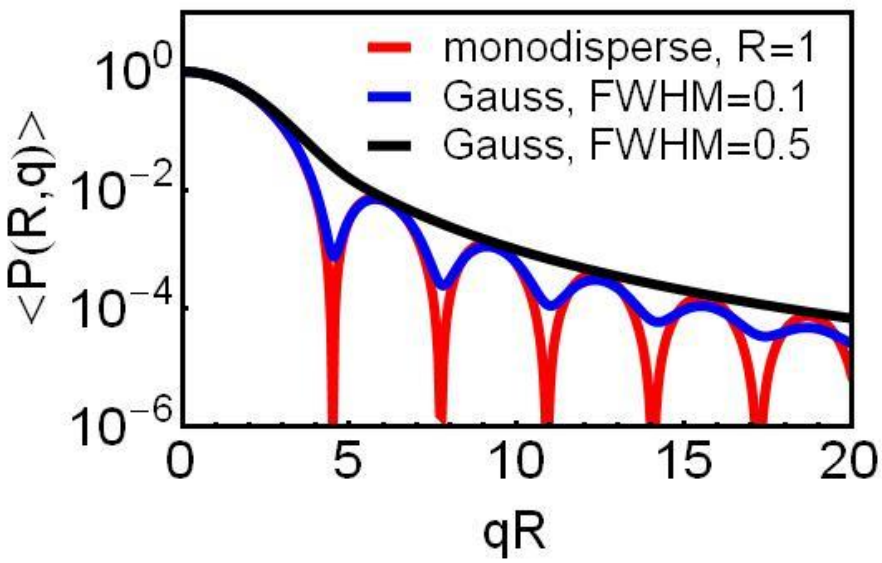
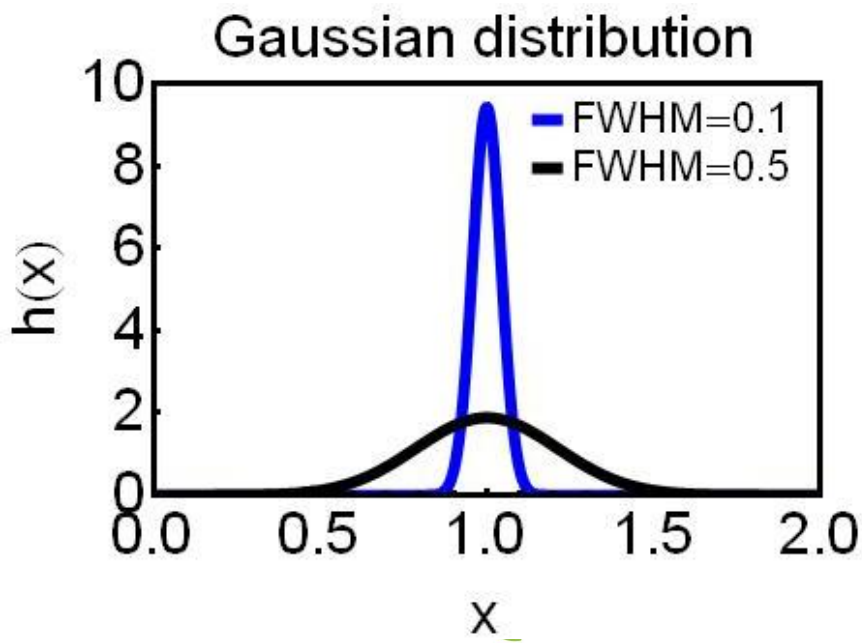




modelling, how?

structure factor for *disordered* systems

$$S(q) = 1$$

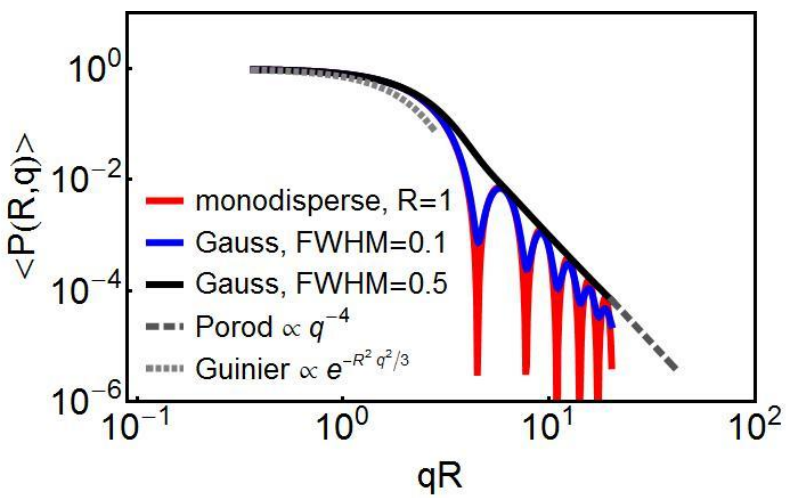
dilute system with randomly distributed particles

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

$$\downarrow$$

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

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

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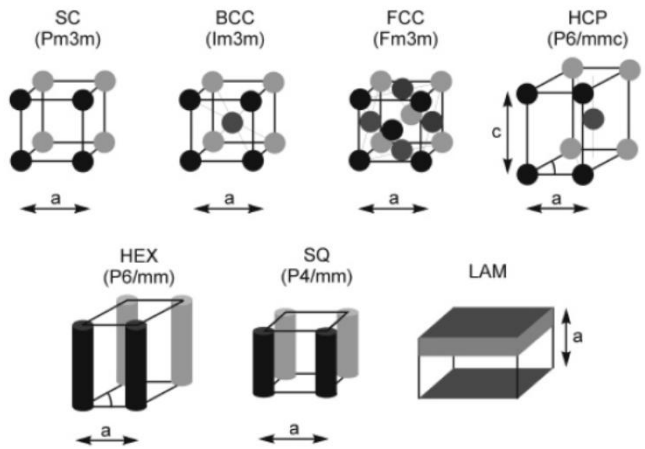
modelling, how?

structure factor for *ordered* systems

ideal systems



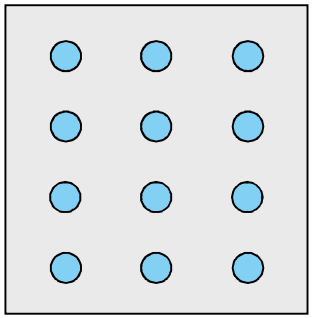
lattice factor

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

probability to find a particle in certain (hkl) direction

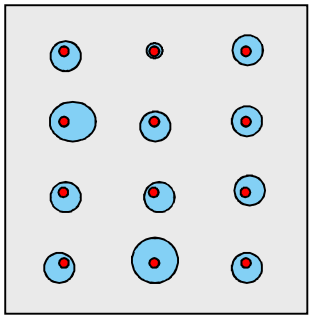
non-ideal systems

$\beta(q), G(q) = 1$



$S(q) = Z_0(q)$

$\beta(q), G(q) \leq 1$



structure factor

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

$\beta(q)$ polydispersity

$G(q)$ positional disorder

Förster S et al – J Phys Chem B 2005, 109, 1347

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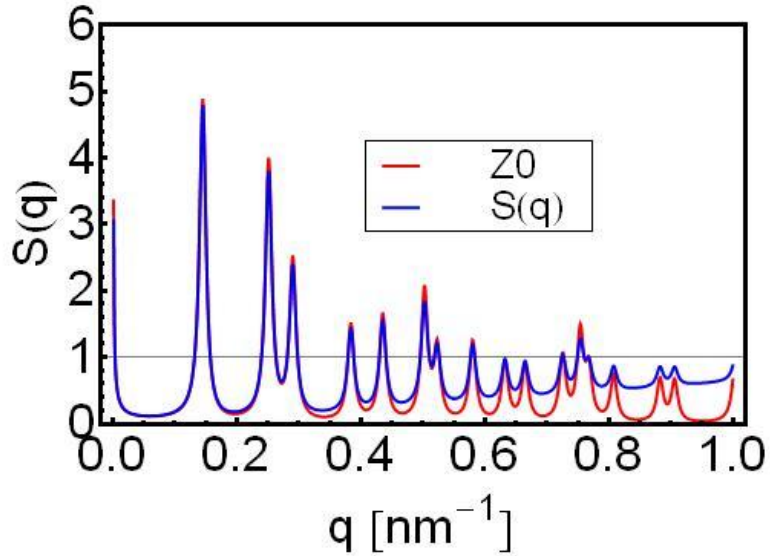
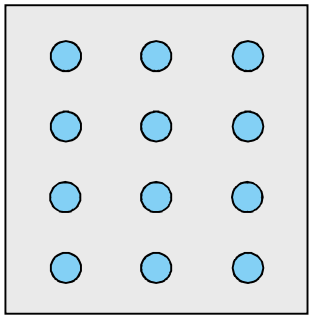
modelling, how?

example: structure factor of an hexagonal lattice



non-ideal systems

$\beta(q), G(q) = 1$



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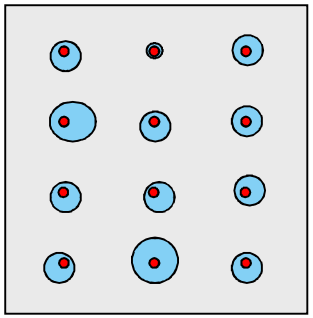

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Förster S et al – J Phys Chem B 2005, 109, 1347

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

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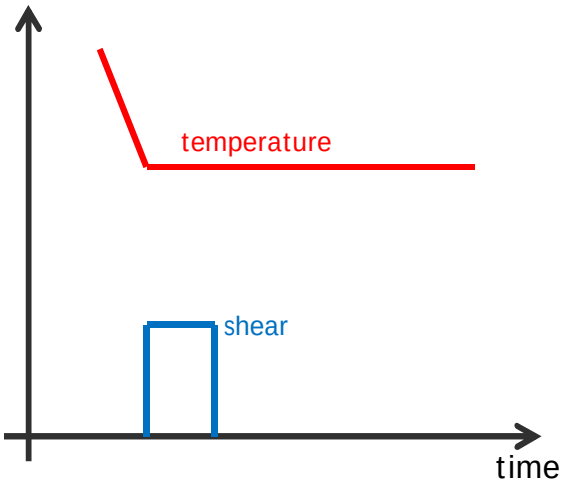
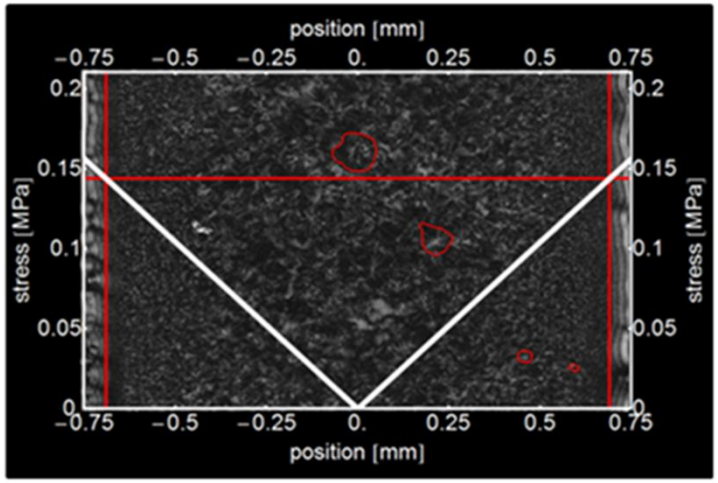
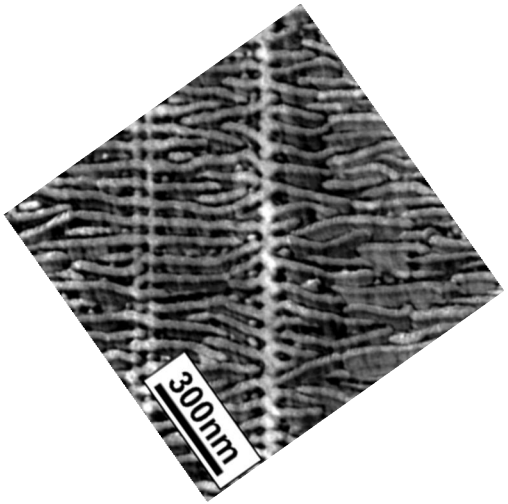
modeling growth of shish-kebabs







Hobbs, J.K. et al. Macromolecules 2001

time= 0. s

- material: iPP
- isothermal at 165 °C
- shear time 0.188 s
- wall stress~ 0.16 MPa
- wall shear rate~ 750 s^{-1}

*Balzano L et al PRL **2008***
*Balzano L et al Macromolecules **2011***

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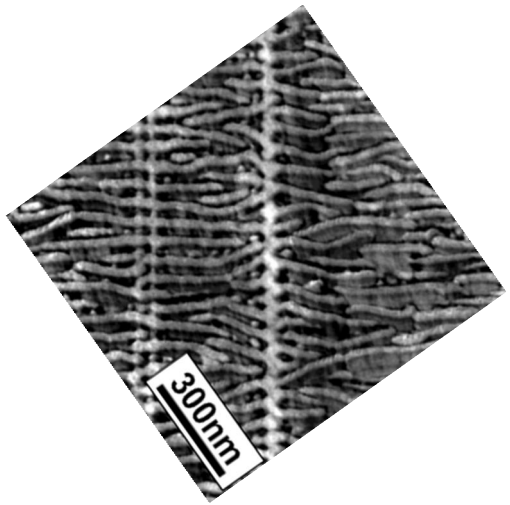
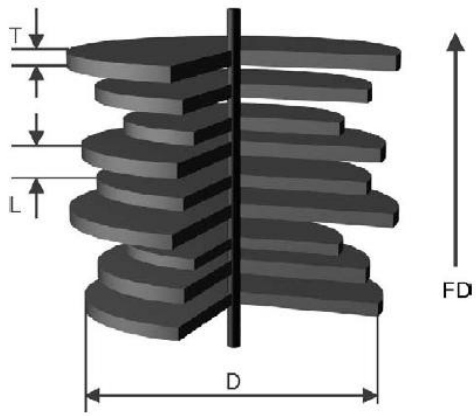
modeling growth of shish-kebabs



Hobbs, J.K. et al. Macromolecules 2001

idealization →



all identical particles
(monodisperse system)

$$I(\vec{s}) = F^2(\vec{s}) \cdot Z(\vec{s}) \qquad \vec{s} = \{s_1, s_2, s_3\}$$

form factor
(sharp interfaces)

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

structure factor
(perfect orientation)

$$Z(s_3) = \mathrm{Re}\left[\frac{1 + H_L(s_3)}{1 - H_L(s_3)}\right]$$

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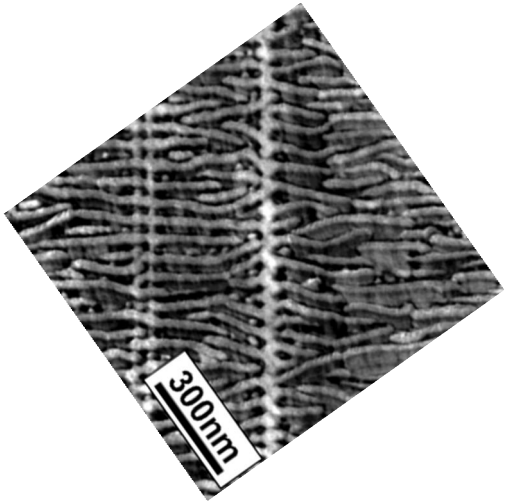
modeling growth of shish-kebabs



Hobbs, J.K. et al. Macromolecules 2001

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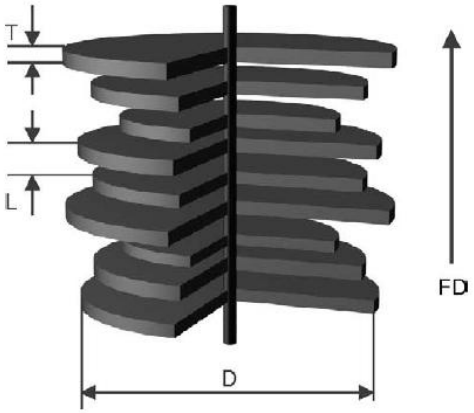

polydisperse system $$I(\vec{s}) = \langle F^2(\vec{s}) \rangle + \langle F(\vec{s}) \rangle^2 \left[Z(\vec{s}) - 1 \right]$$

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

J. K. Keum et al. Progress in Colloid and Polymer Science, vol. 130, pp. 114-126 , 2005.

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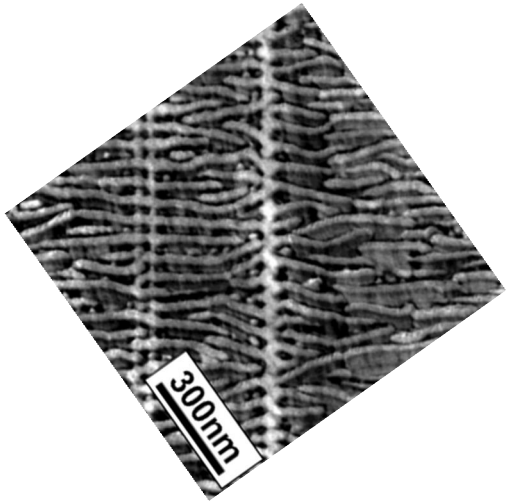
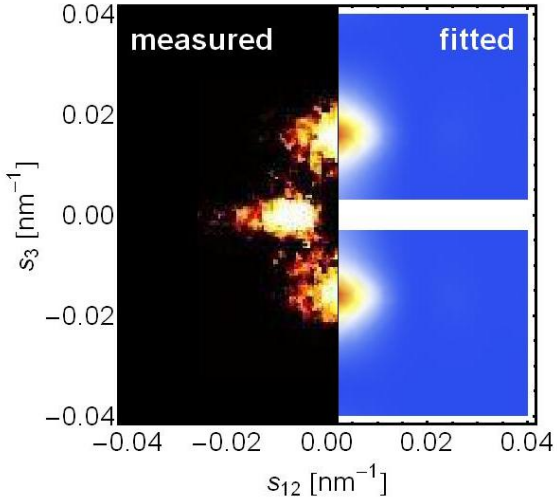
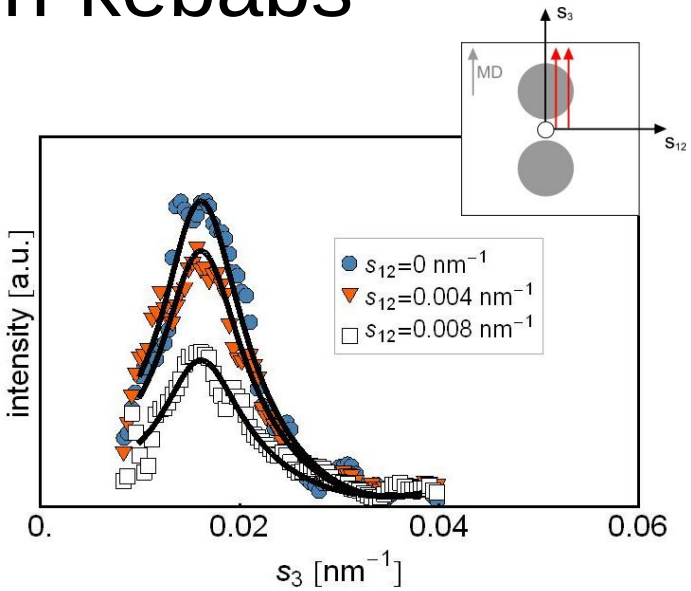
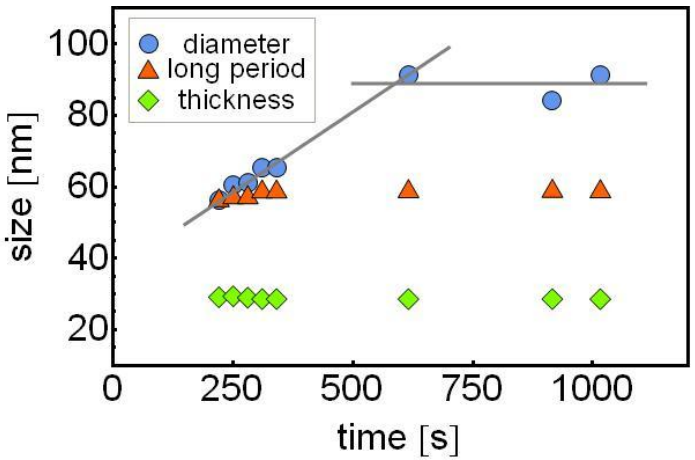
modeling growth of shish-kebabs

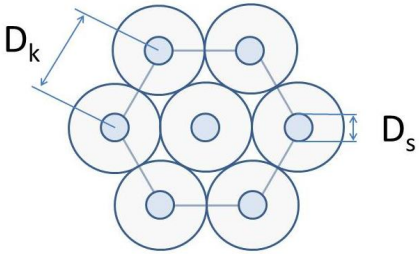






Hobbs, J.K. et al. Macromolecules 2001





$$\%\ shishes = 100\frac{2\ area\ shish}{area\ unit\ cell} = 100\frac{2\pi D s^2/4}{(3\sqrt{3}/2)Dk^2} \cong 3\ \%$$

➡ detailed kinetic information → hint for the formation mechanism

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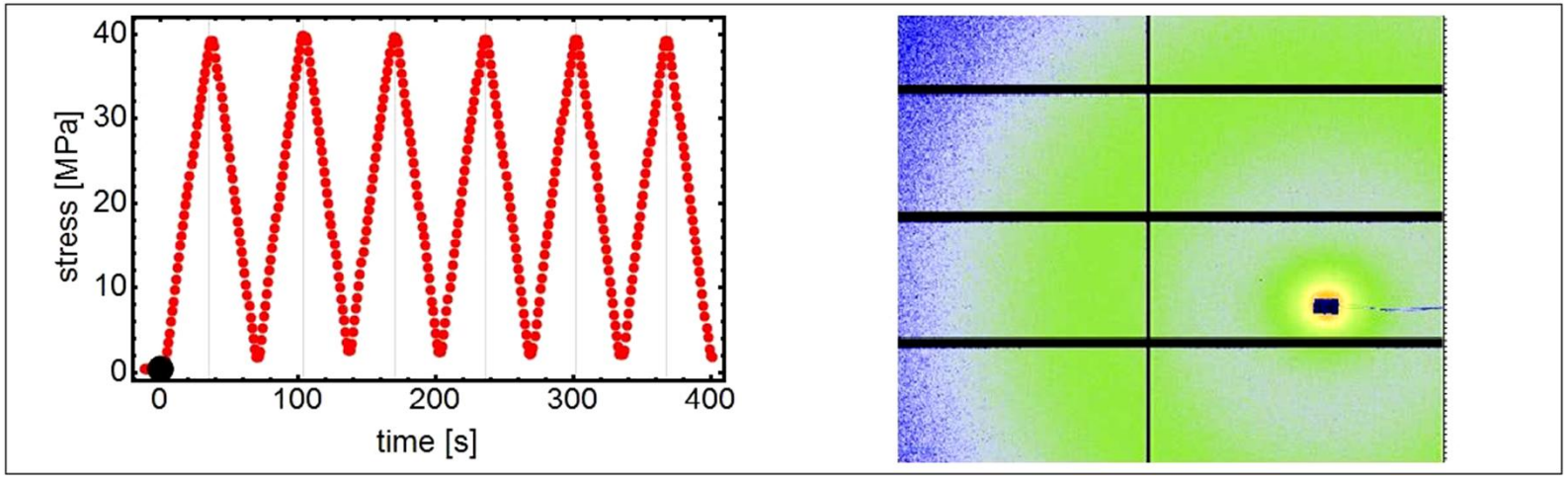
crazing during cyclic loading

Poly(ethylene therephtalate), PET



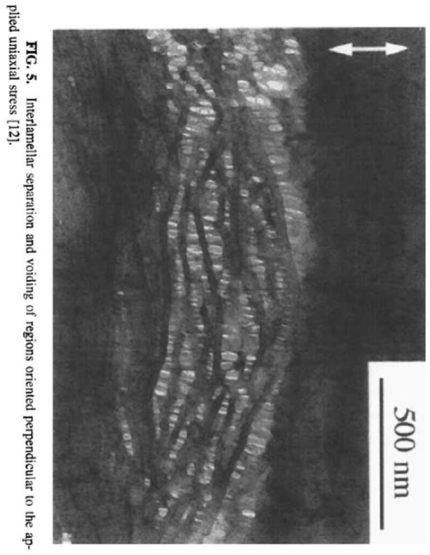
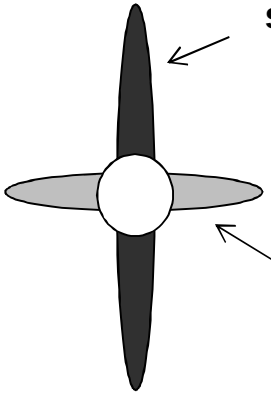


FIG. 5. Interlamellar separation and voiding of regions oriented perpendicular to the applied uniaxial stress [12].



scattering from fibrils and voids

reflection from craze-bulk interfaces

failure initiation under loads

H.Kausch et al. – J. Macromol. Sci. Part B,38, 1999, 803
R.Bubeck, D.Buckley, E.Kramer, H.Brown – Journal of Materials Science 26, 1991, 6249

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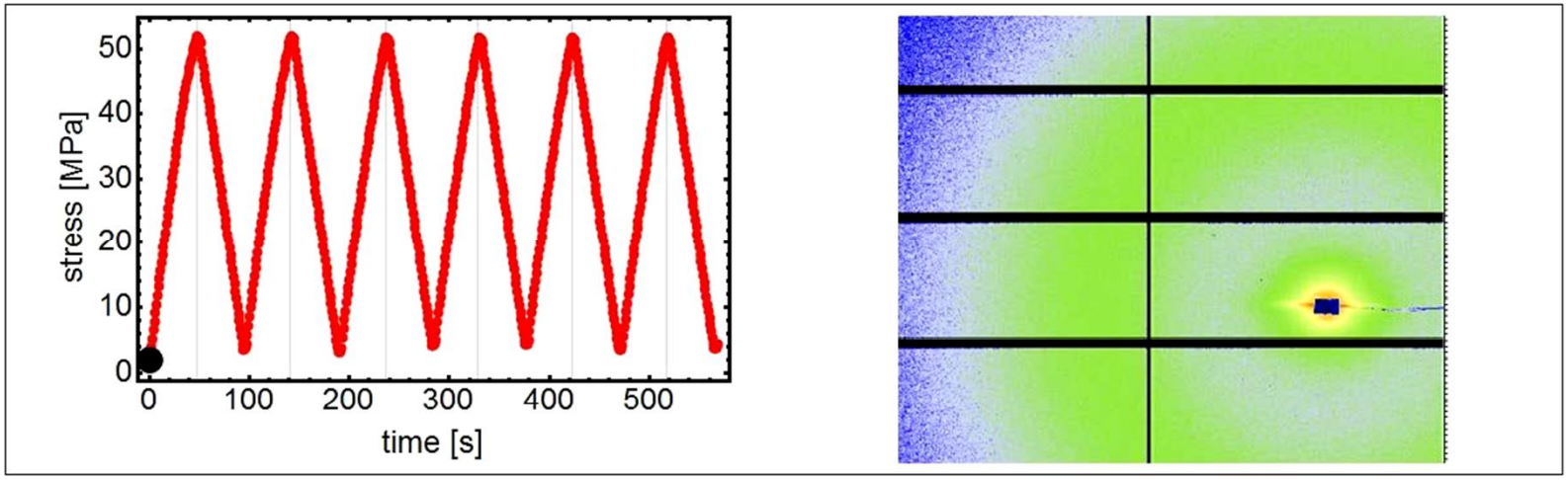

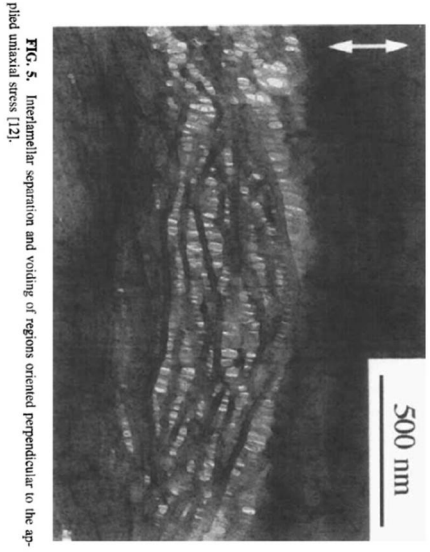

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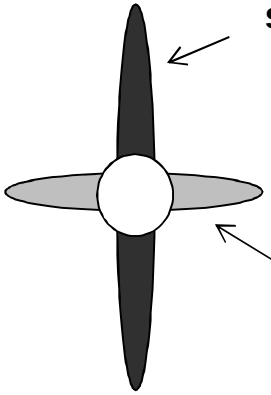

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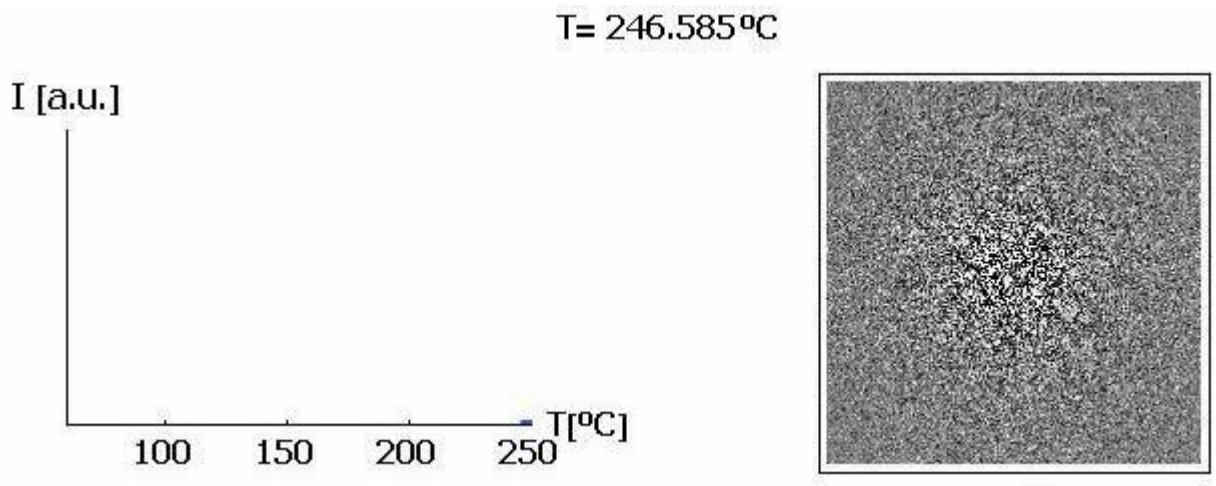
phase separation of (dissolution type) nucleating agents

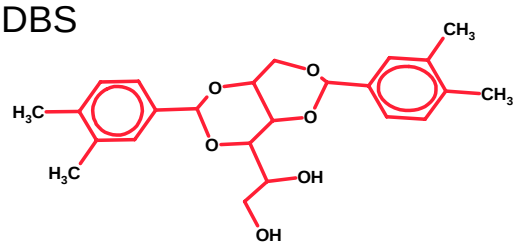
iPP+1% DMDBS

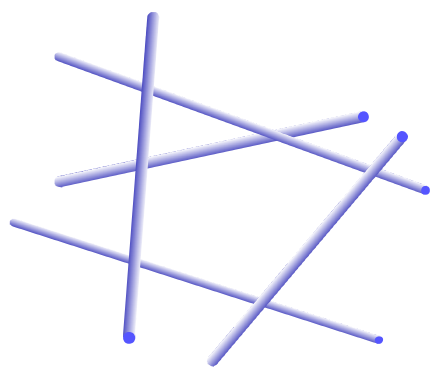


total scattered intensity (invariant) $Q = 2\pi^2 \cdot x(1-x)\Delta\rho^{\ 2}$

DMDBS phase separates → invariant increases due to the e^- density difference

DMDBS





Balzano et al. - Macromolecules 2008, 41, 399-408

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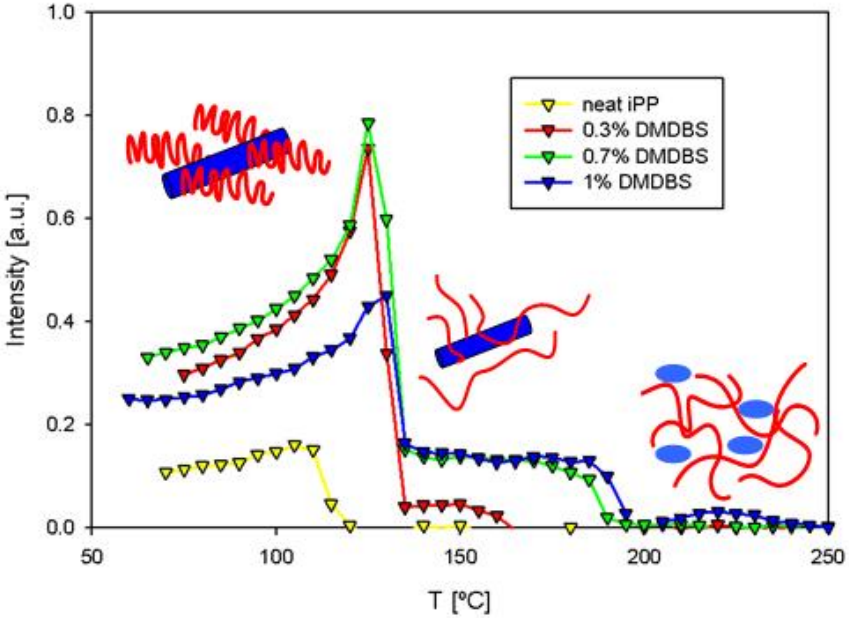

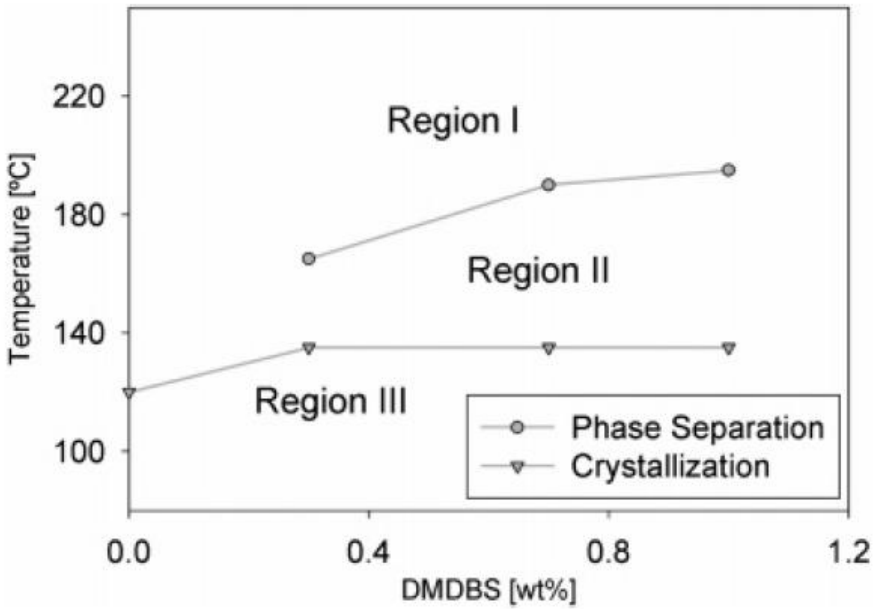

phase diagram

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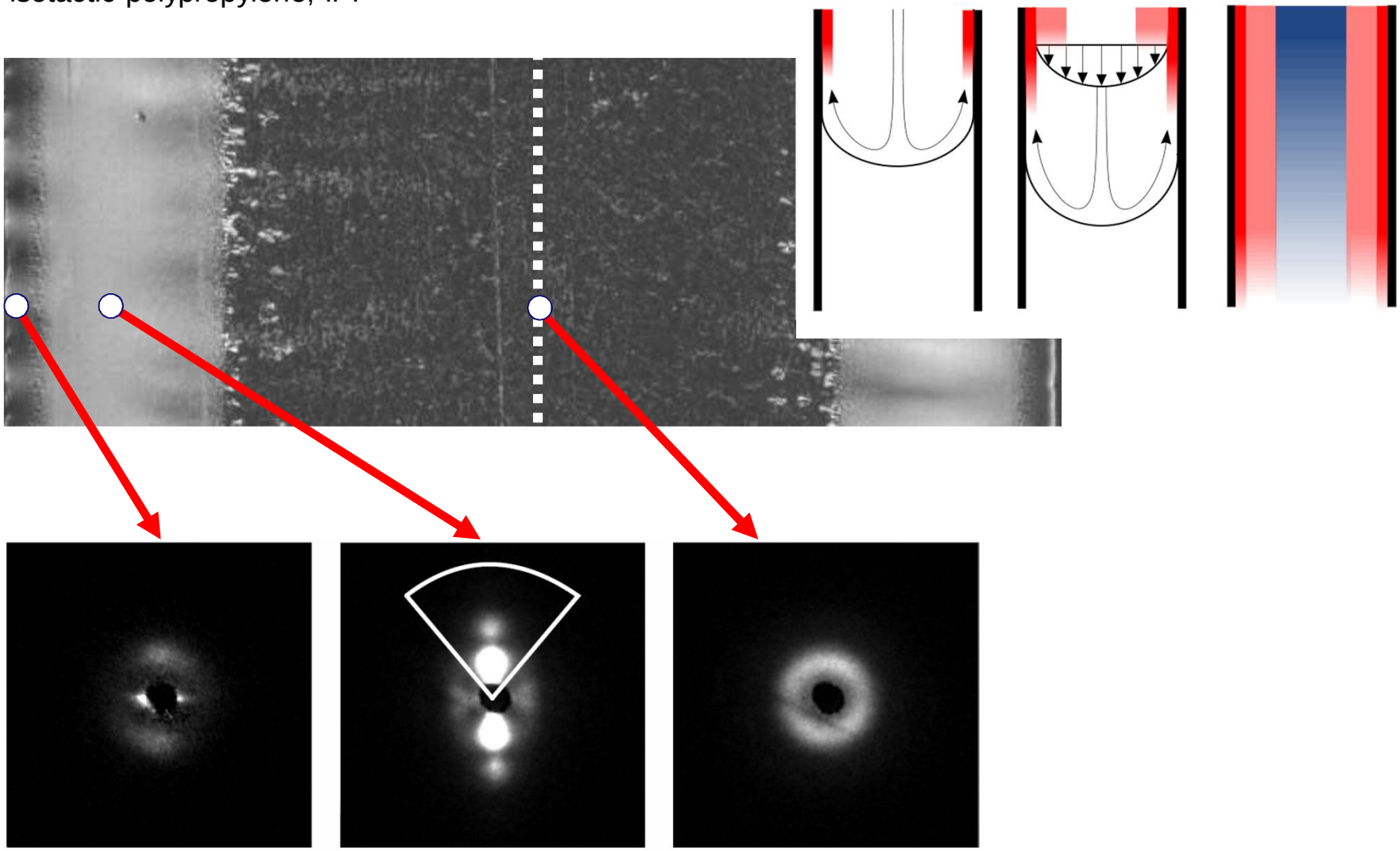
spatial heterogeneity in injection molded parts

isotactic polypropylene, iPP



cooling rate vs stress as function of the position

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take away

SAXS is a relatively simple technique that can be used to extract morphological information in static and dynamic conditions

the SAXS signal comes from e^- 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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