GISAS for soft matter

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Outline

1. General introduction

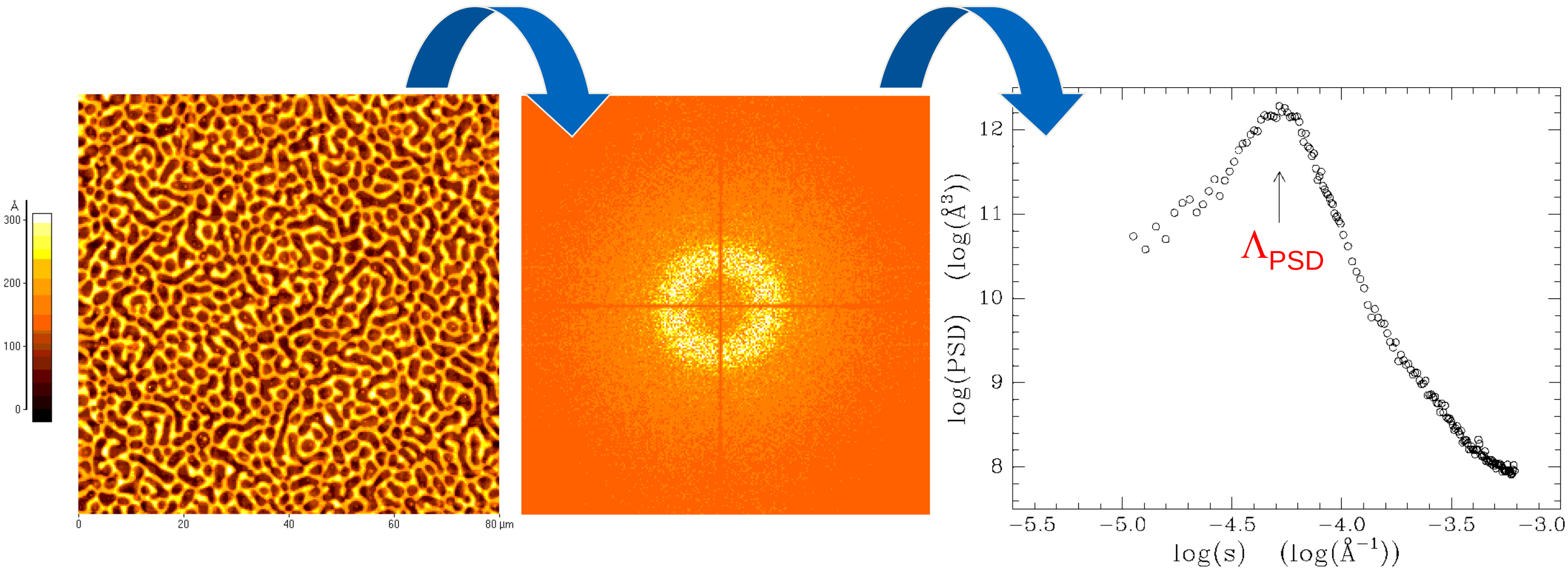
2. Selected X-Ray Examples

3. Selected Neutron Examples


German Black Forest Cherry Cake
looking for a more non-destructive way …

Statistical analysis of AFM data

isotropic structure → circular ring → well described by one in-plane length



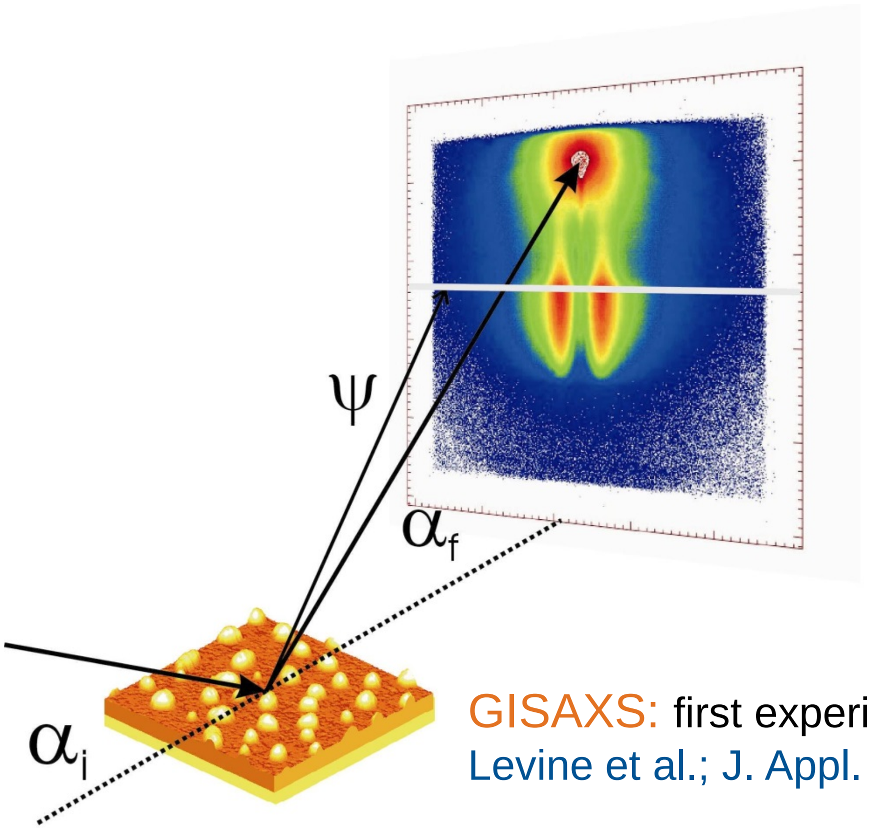
AFM data accessible with scan ranges up to ≈ 100 µm

→ determination of most prominent in-plane length Λ_{PSD}

→ only sample surface probed !

Müller-Buschbaum et al.; J. Macromol. Sci. **B38**, 577 (1999)

GISAS (grazing incidence small angle scattering)

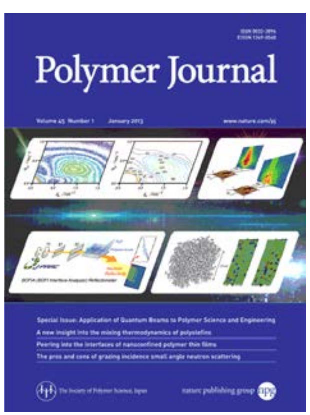


- fixed incidence angle α_i <<1°
- two high quality entrance cross-slits
- mostly evacuated pathway
- two dimensional detector array
- controlling sample position and orientation with respect to the beam

sample-detector distance determines resolution
→ **sub-nm up to several μm**

GISAXS: first experiment:
Levine et al.; J. Appl. Cryst. **22**, 528 (1989)

GISANS:
Müller-Buschbaum et al.; Colloid.Polym.Sci. **277**, 1193 (1999)



Review: Müller-Buschbaum; Polymer Journal **45**, 34 (2013)

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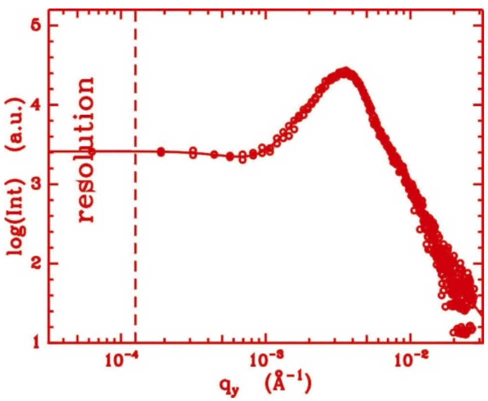
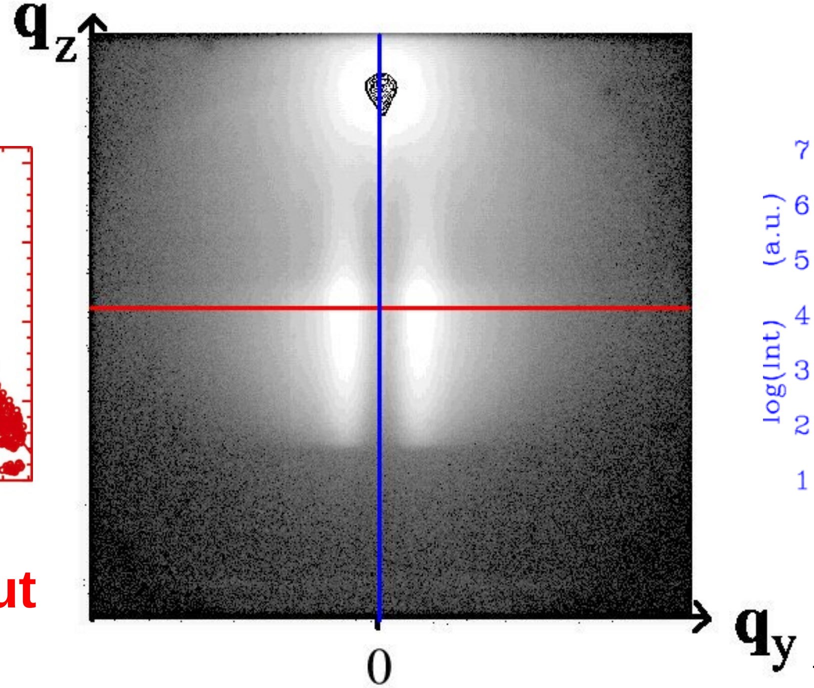
Line cuts

cut at constant q_z

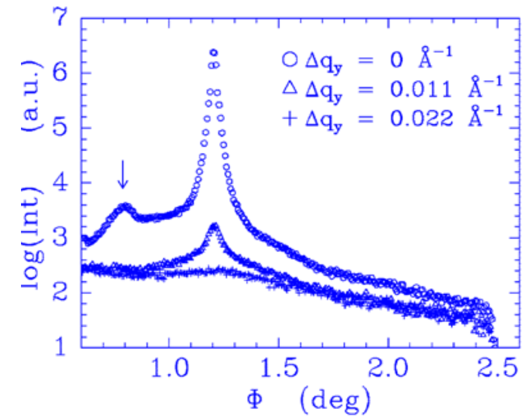


horizontal line cut

$\rightarrow$ q_y-dependence:
in-plane structures



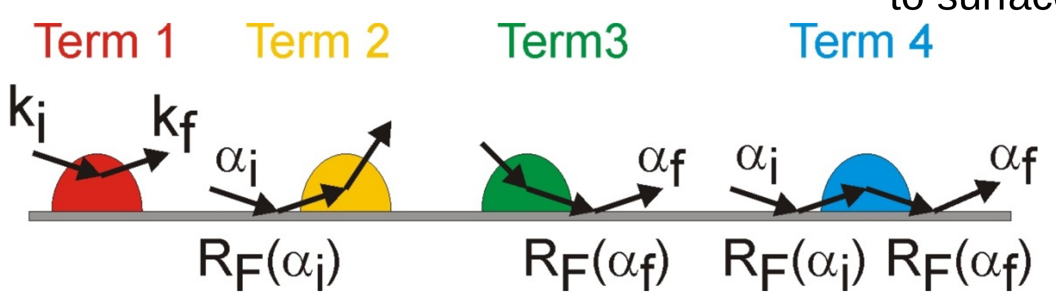
cut at constant q_y



vertical line cut

$\rightarrow$ mainly q_z-dependence:
correlation perpendicular to surface

Distorted-wave Born approximation:

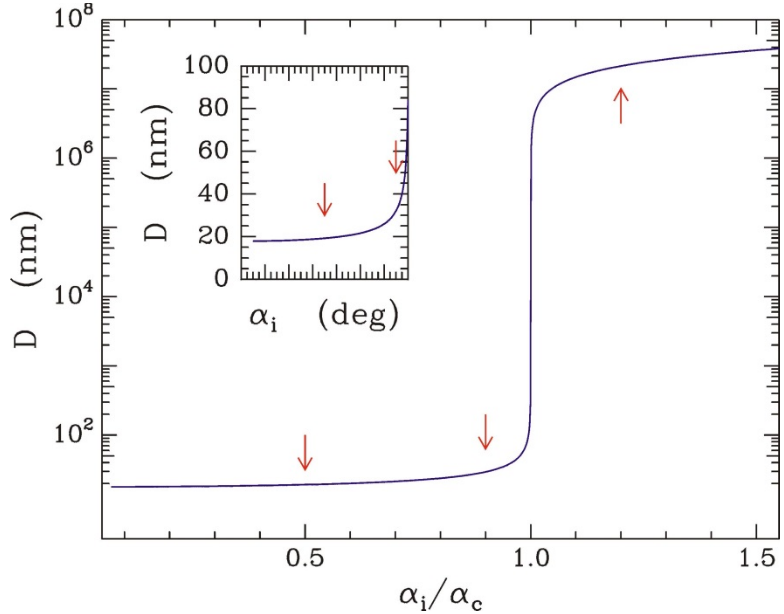


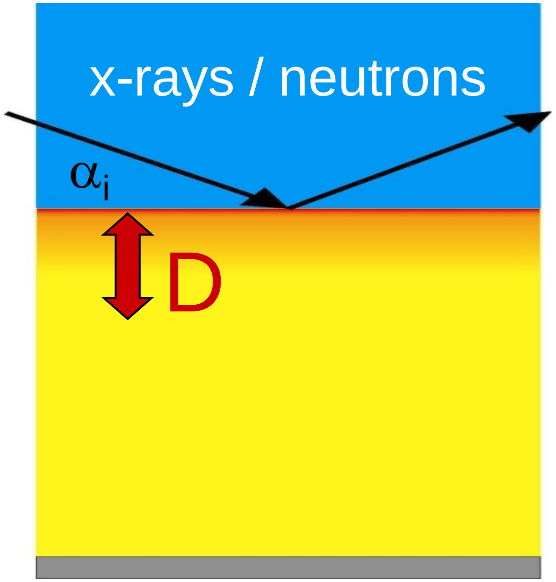
Salditt et al.; Phys.Rev.B **51**, 5617 (1995)

Surface sensitivity

scattering depth of x-rays or neutrons

$$D = \frac{\lambda}{\sqrt{2}\pi\left(l_i + l_f\right)} \qquad l_{i,f} = \left[\sin^2\alpha_c - \sin^2\alpha_{i,f} + \sqrt{\left(\sin^2\alpha_{i,f} - \sin^2\alpha_c\right)^2 + \left(\frac{\mu\lambda}{2\pi}\right)^2}\right]^{1/2}$$



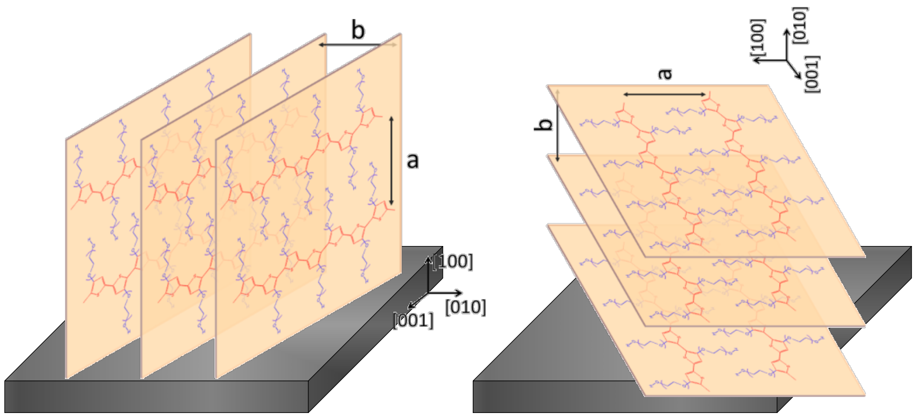


$\rightarrow$ vary incident angle $\alpha_i < \alpha_c$ to probe surface near region only or to penetrated large sample volume

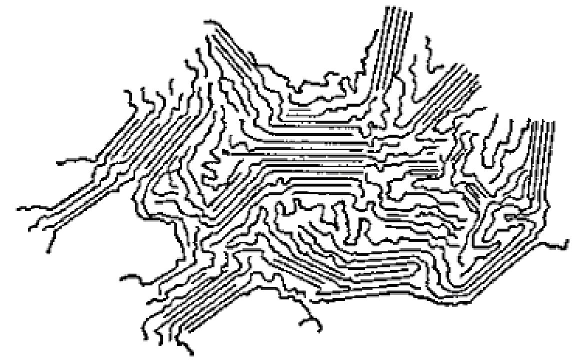
Dosch et al.; Phys. Rev. Lett. **56**, 1144 (1986)

GIWAXS (grazing incidence wide angle X-ray scattering)

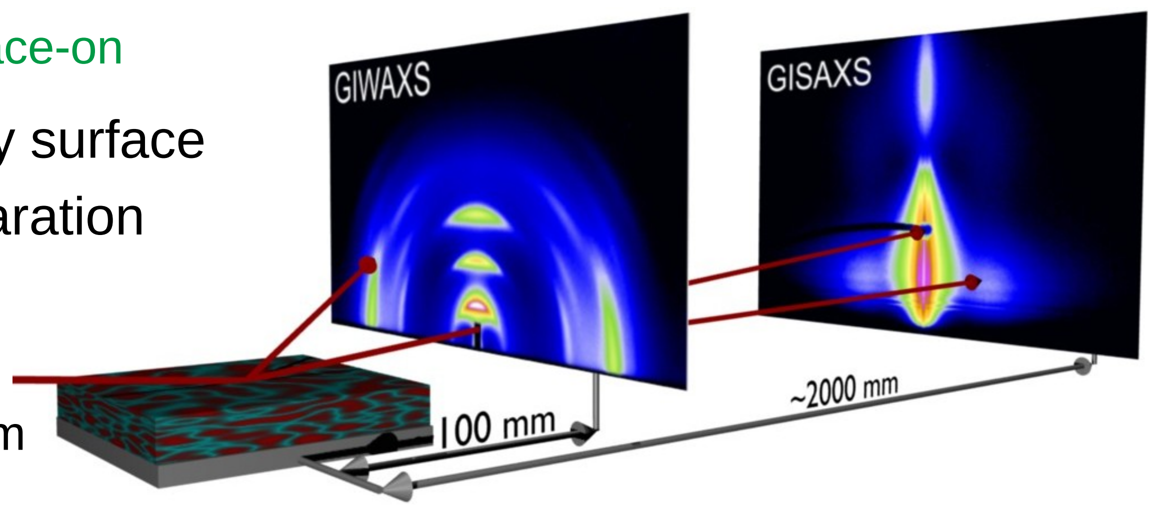
molecular order with respect to substrate



edge-on face-on



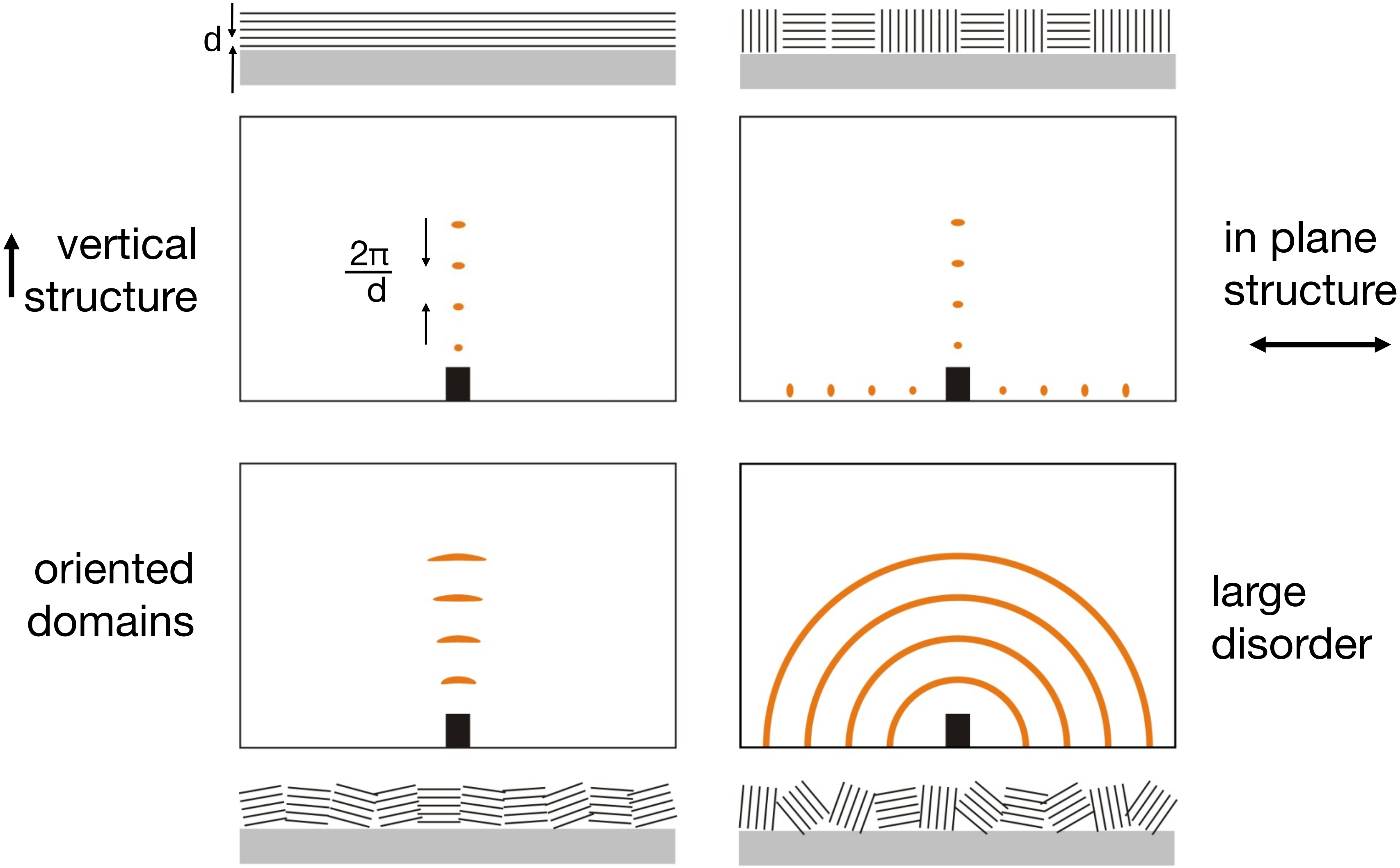
- inner structures, not only surface
- no special sample preparation



accessible length scales from
~0.1 nm to ~ 3.2 nm

Perlich, PMB et al.; Rev. Sci. Instr. **81**, 105105 (2010)

GIWAXS 2D pattern



Müller-Buschbaum; Adv. Mater. **26**, 7692-7709 (2014)

Outline

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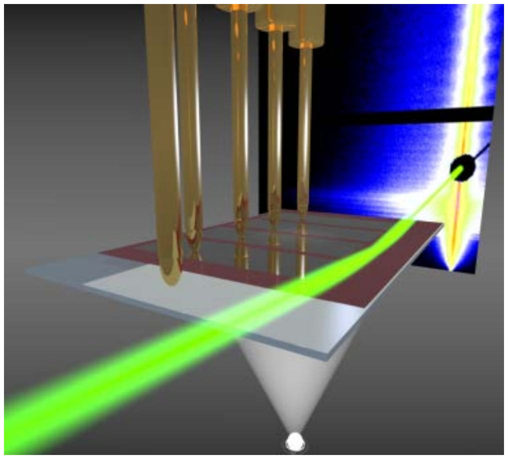
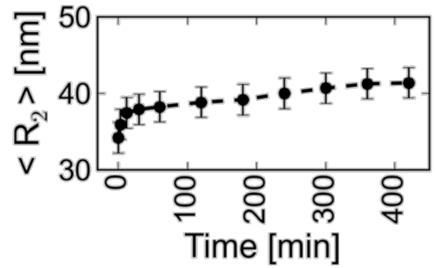
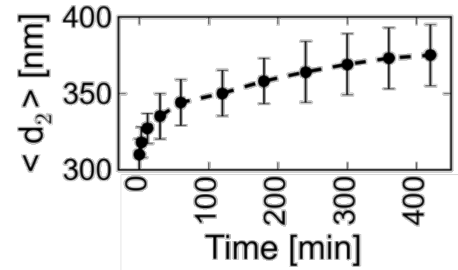
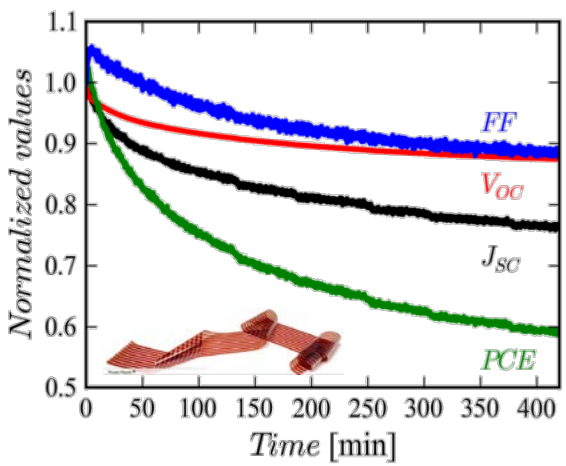
Structural degradation during operation

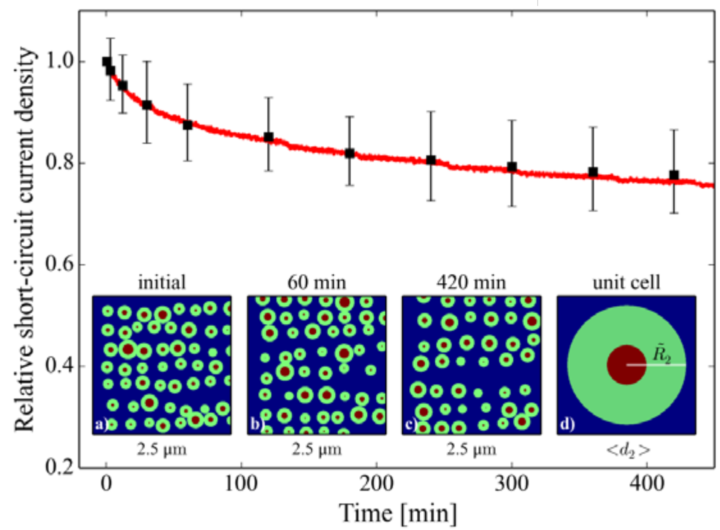
In-operando study of P3HT:PCBM BHJ solar cell in vacuum











J_{SC} - from model

J_{SC} - measured

morphological degradation as consequence of demixing reduces short-circuit current J_{SC}

Schaffer, PMB et al.; Adv. Mat. **25**, 6760-6764 (2013)

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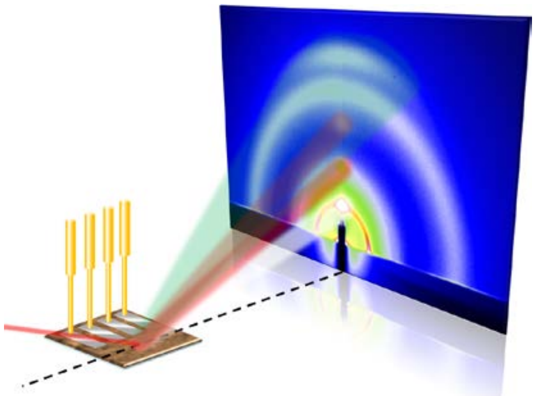
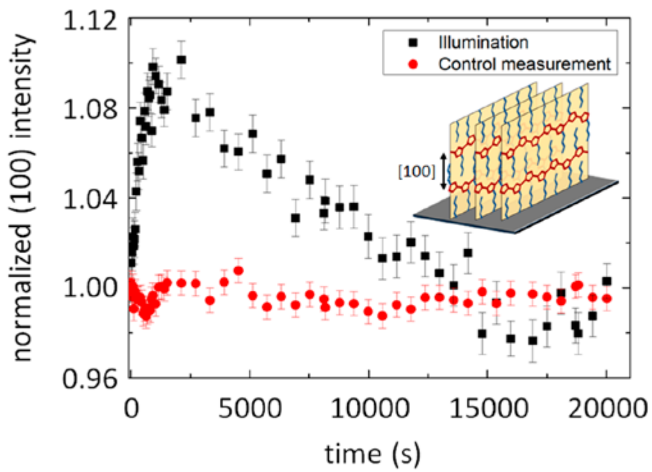
In-operando study of changes in crystalline parts

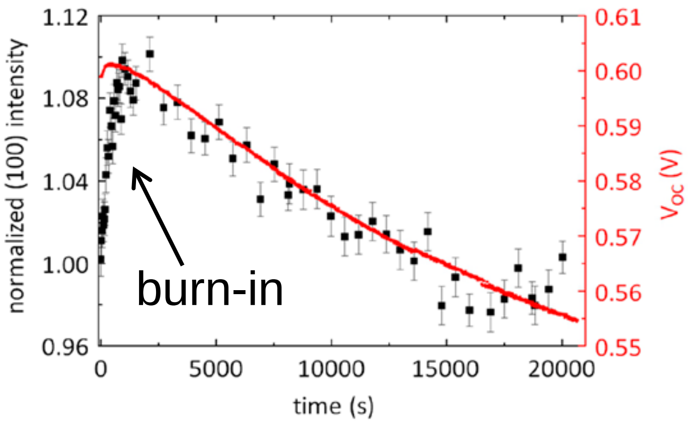
P3HT:PCBM BHJ solar cell: GIWAXS + IV tracking in air





illumination:
increase of FWHM and change in intensities

control (dark):
no change of crystalline P3HT parts



longtime exposure to light:
degradation mechanisms like oxidation, photobleaching reduce crystallinity

link between crystalline state and photovoltage

Moseguí González, PMB et al.; ACS Appl. Mater. Interfaces **9**, 3282-3287 (2017)

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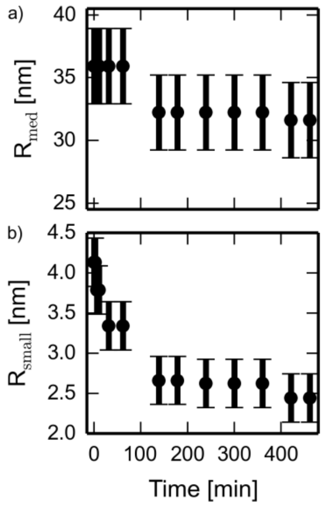
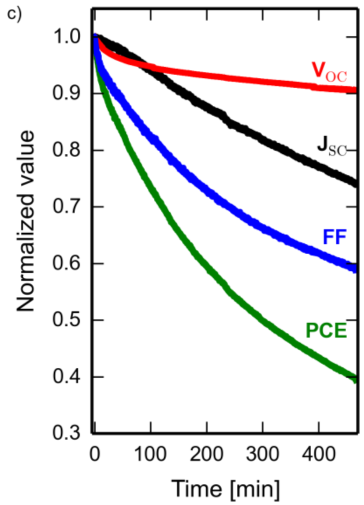
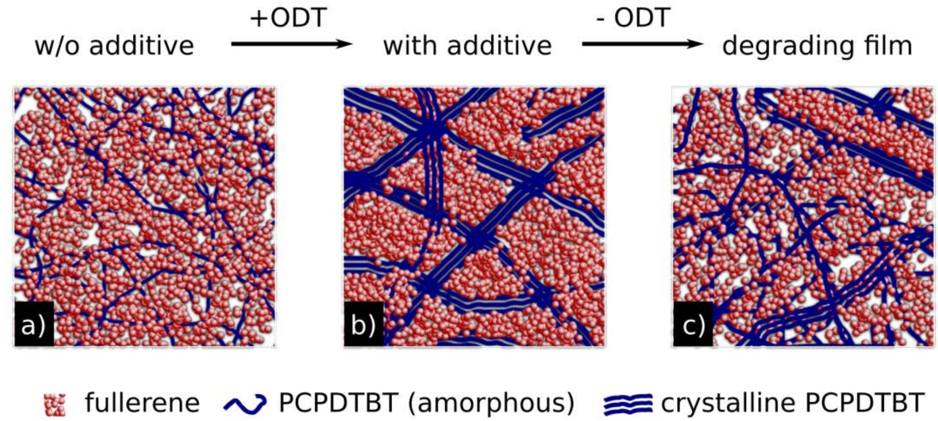
Morphological degradation in low bandgap polymer solar cells

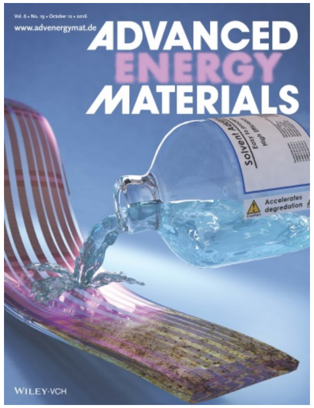
In-operando study of PCPDTBT:$PC_{71}BM$ + 3 v% 1,8-octanedithiol (ODT)







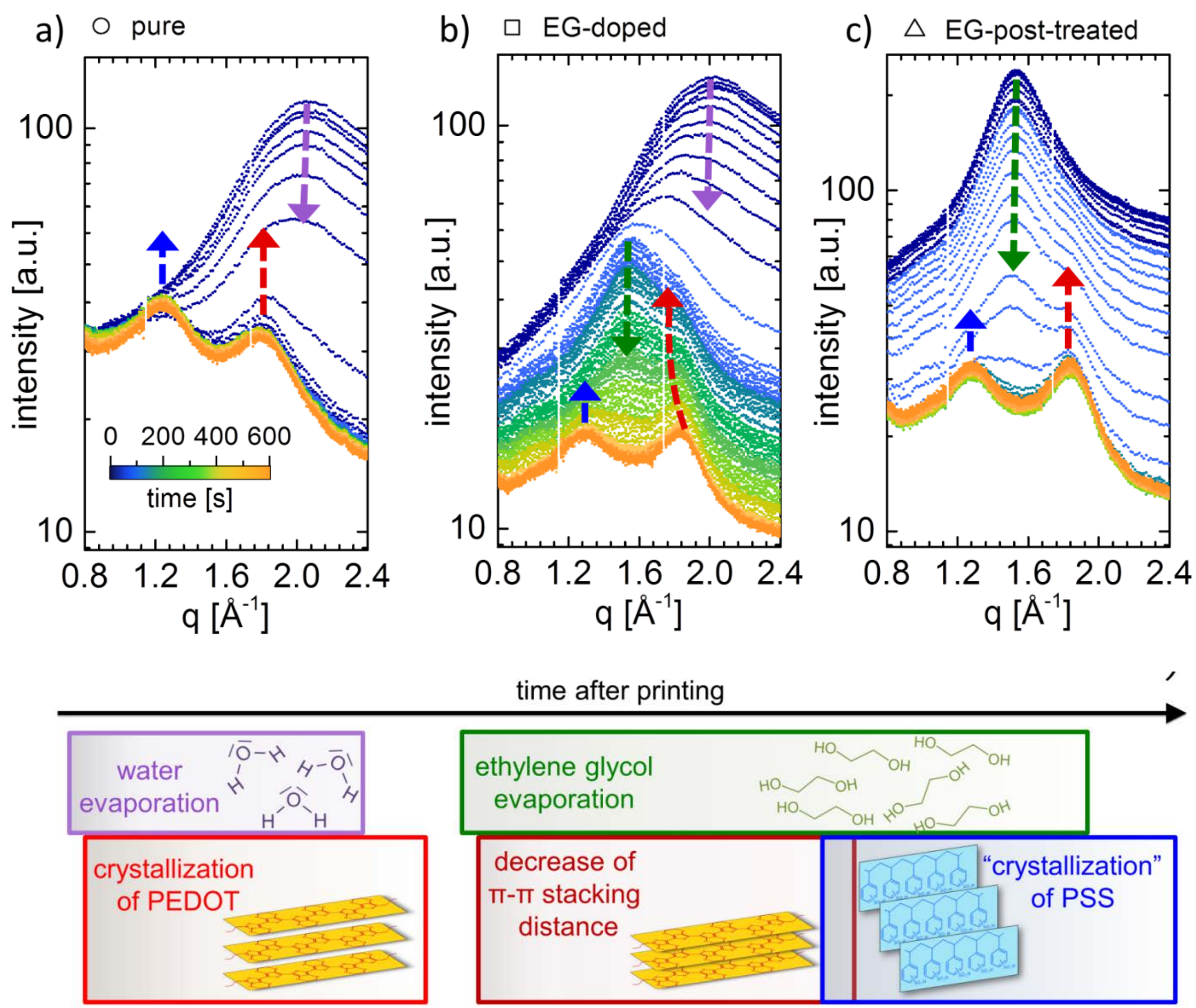
shrinking domains lose their connection to interpenetrating network
→ charge carriers get trapped in isolated domains
→ amplification of recombination lowers fill factor



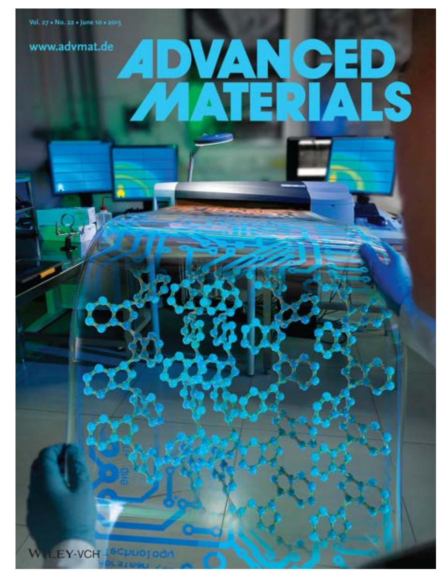
one none-equilibrium state changes into another without ODT

Schaffer, PMB et al.; Adv. Energy Mater. **6**, 1600712 (2016)

Printing of PEDOT:PSS electrodes



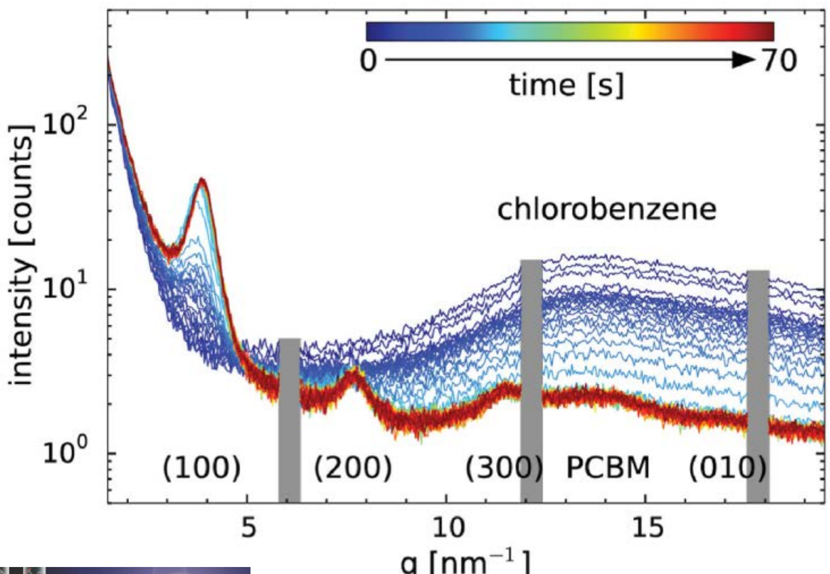
information on:
- solvent evaporation
- polymer crystallization
- film formation times & processes

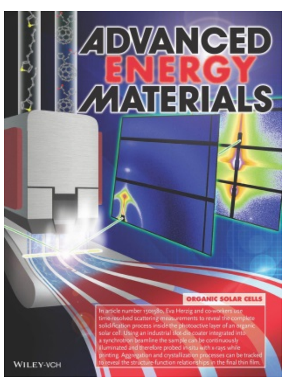


Palumbiny, PMB et al.; Adv. Mat. **27**, 3391-3397 (2015)

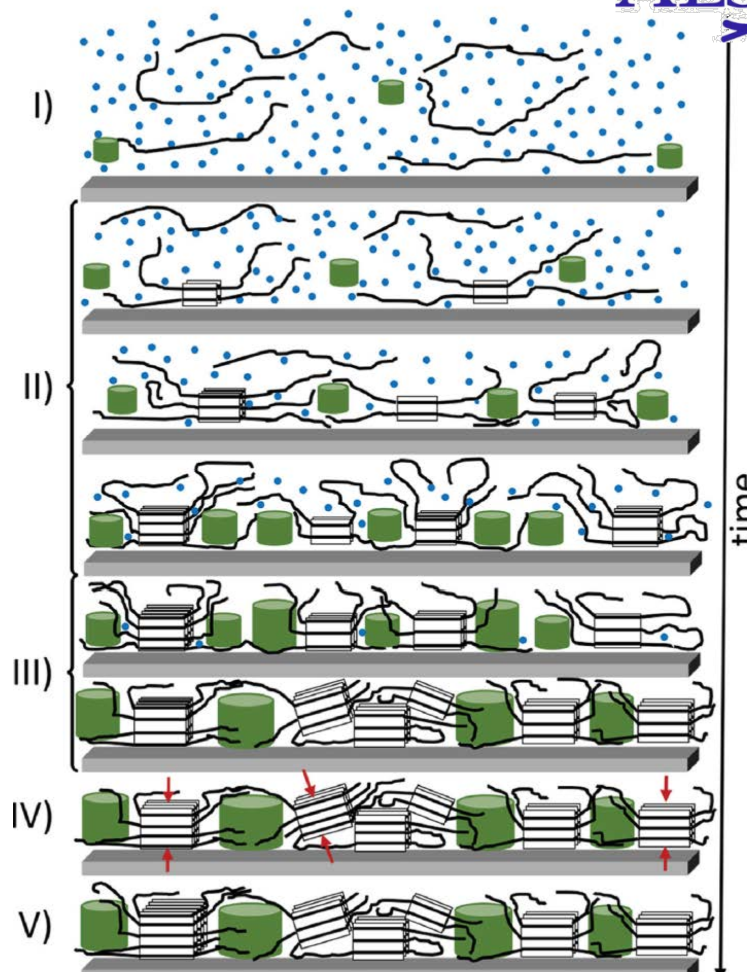
Printing of P3HT:PCBM active layers

from chlorobenzene





initial slow formation of P3HT crystallites in well-aligned edge-on orientation followed by a rapid crystal growth



Pröller, PMB et al.; Adv. Energy Mater. **6**, 1501580 (2016)

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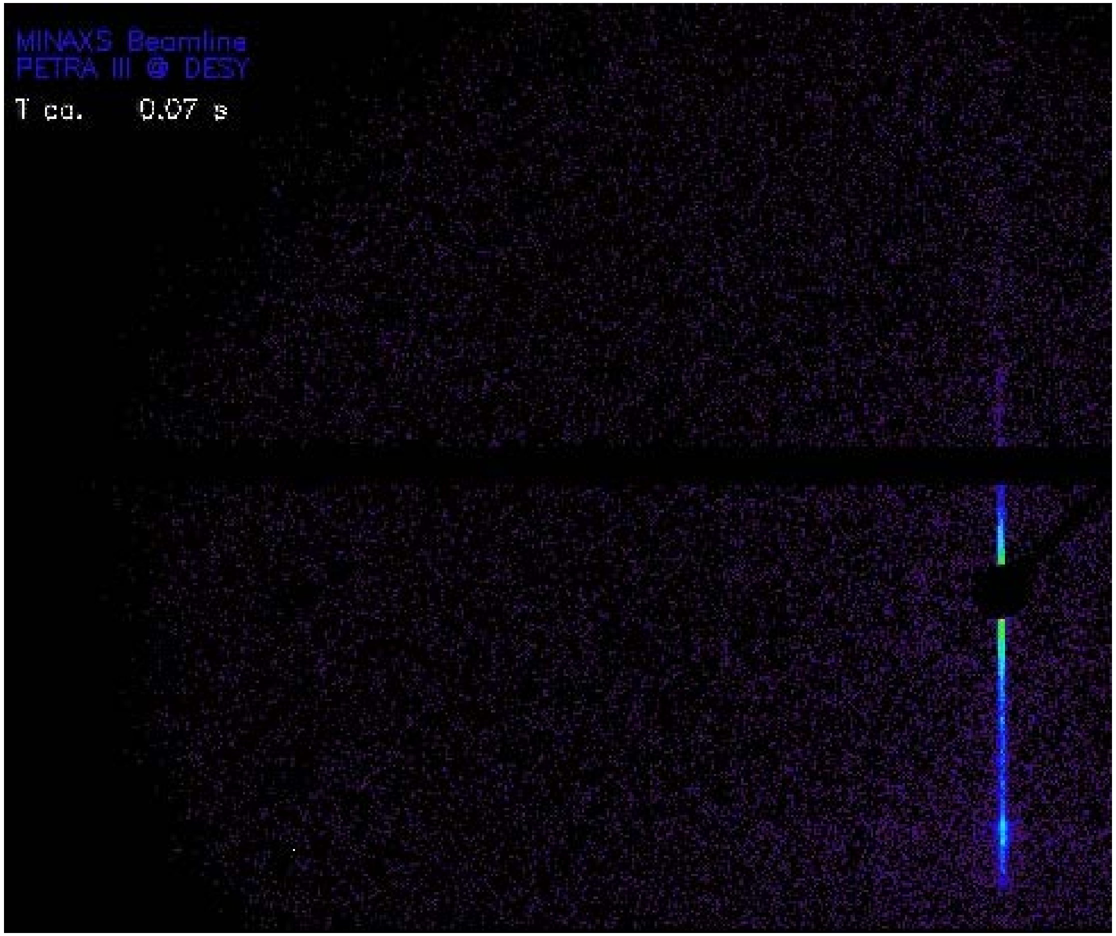
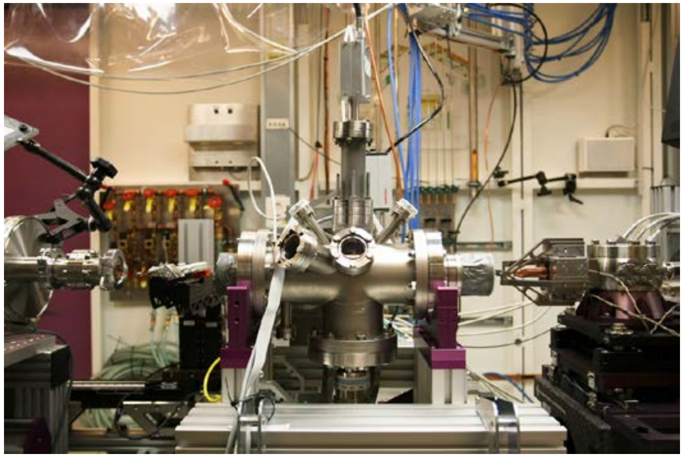
Metal top contact deposition

In-situ GISAXS during sputter deposition of gold



sputter rate = 12 nm/min



α_i=0.41°

counting time 10 ms

exposure period 15 ms

10000 frames

Schwartzkopf, PMB et al.; Nanoscale **5**, 5053 (2013)

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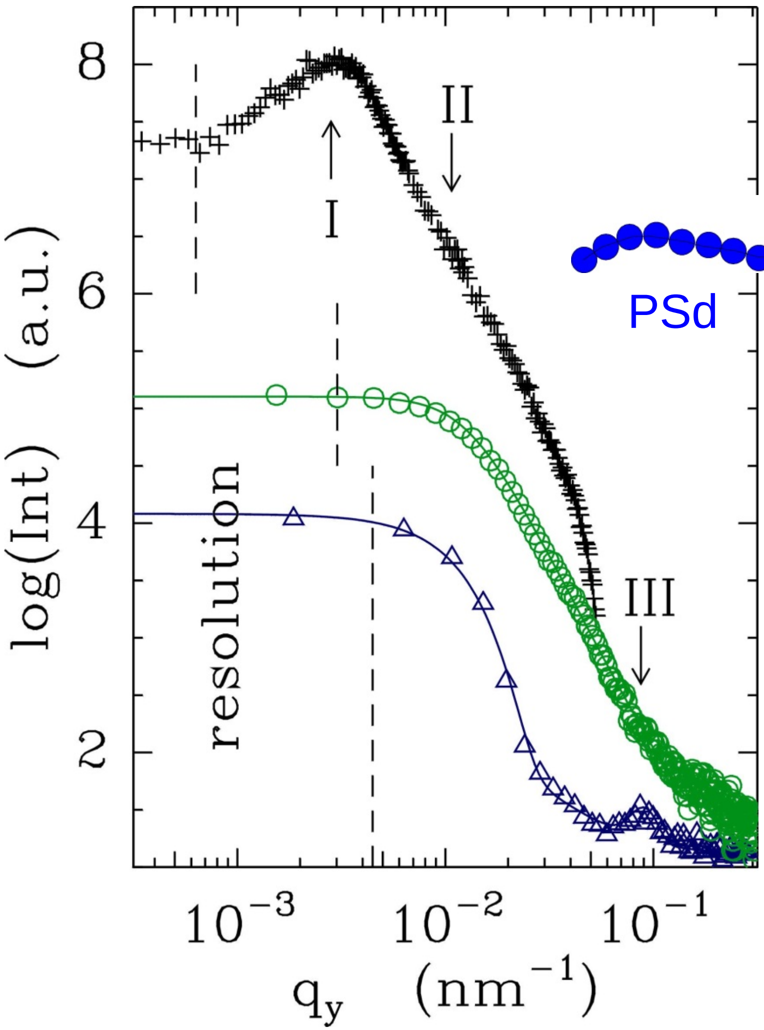
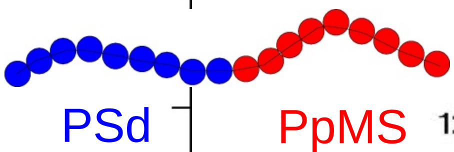
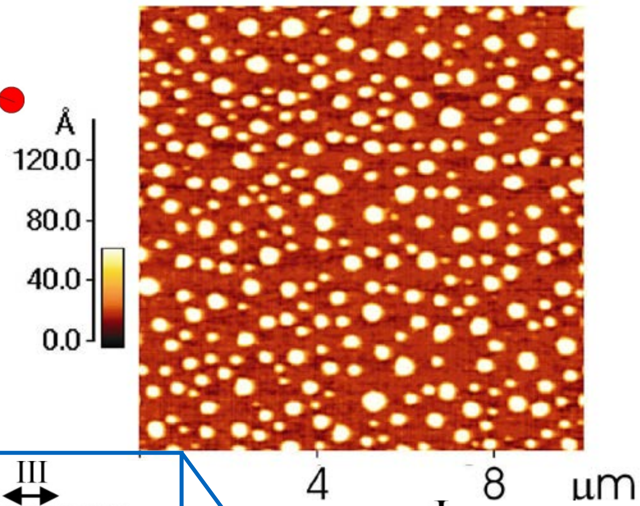
Internal nano-structure

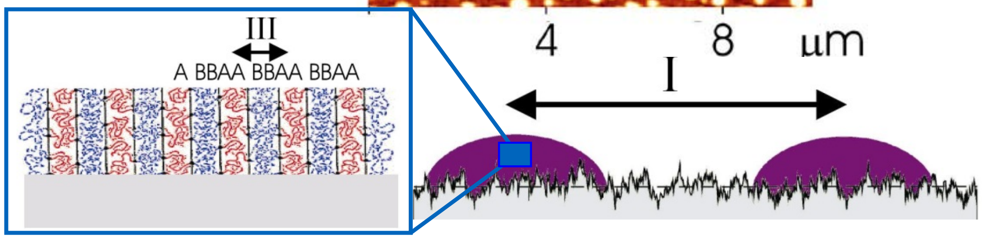
$P(Sd\text{-}b\text{-}pMS)$ on Si/SiO_x $h < 1/3\ R_g$

toluene vapor treatment 12h







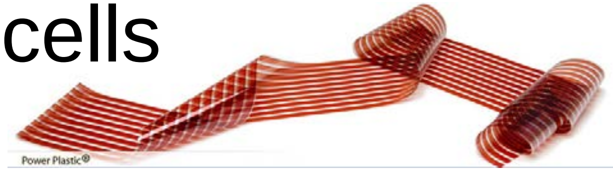


large drops (I) only resolved by **AFM**

small structure (III) only visible with GISANS not with GISAXS

Müller-Buschbaum et al.; Langmuir **17**, 5567 (2001)

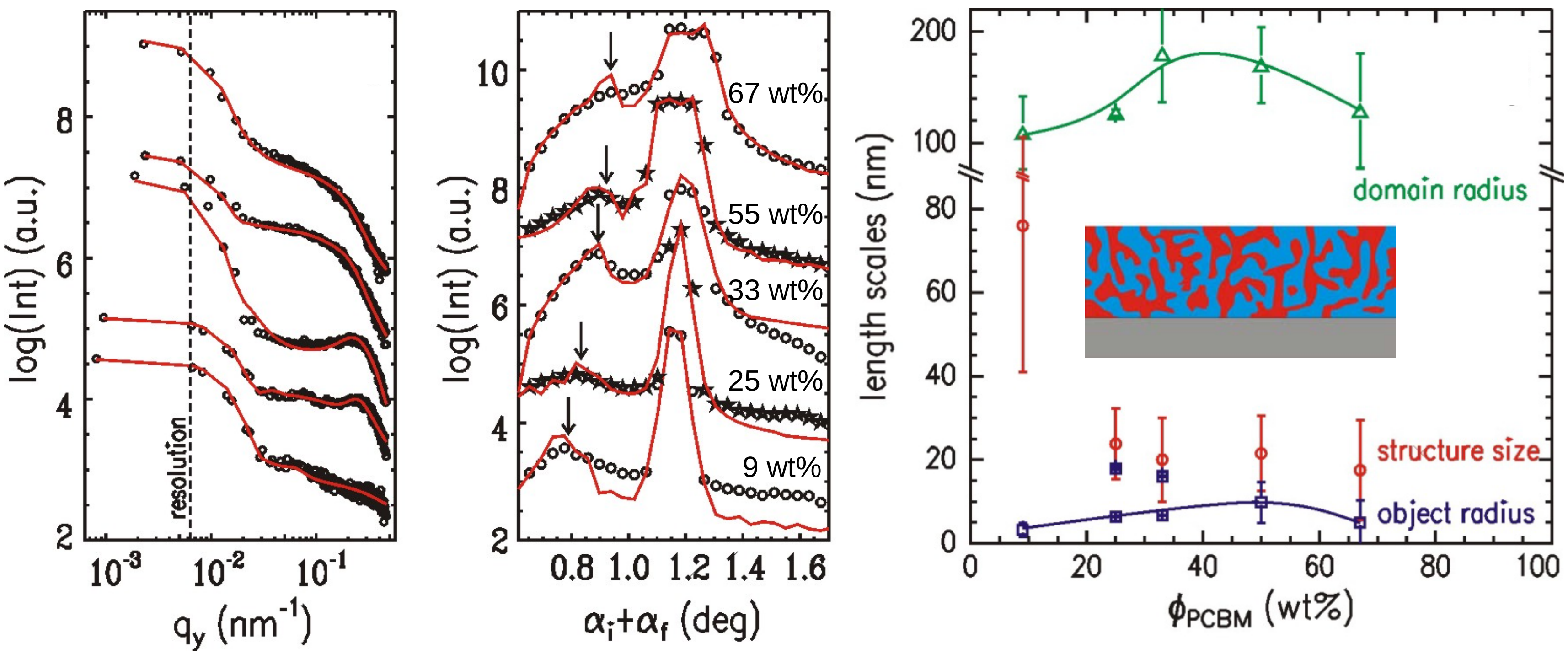
Active layer of organic solar cells



NEUTRONS FOR SCIENCE®

P3HT:PCBM on Si/SiO_x

horizontal cut | vertical cut | lateral structures



at most efficient blend ratio → structure size ~ exciton diffusion length

→ largest PCBM objects – charge transport

Ruderer, PMB et al.; J. Phys. Chem. Lett. **3,** 683 (2012)

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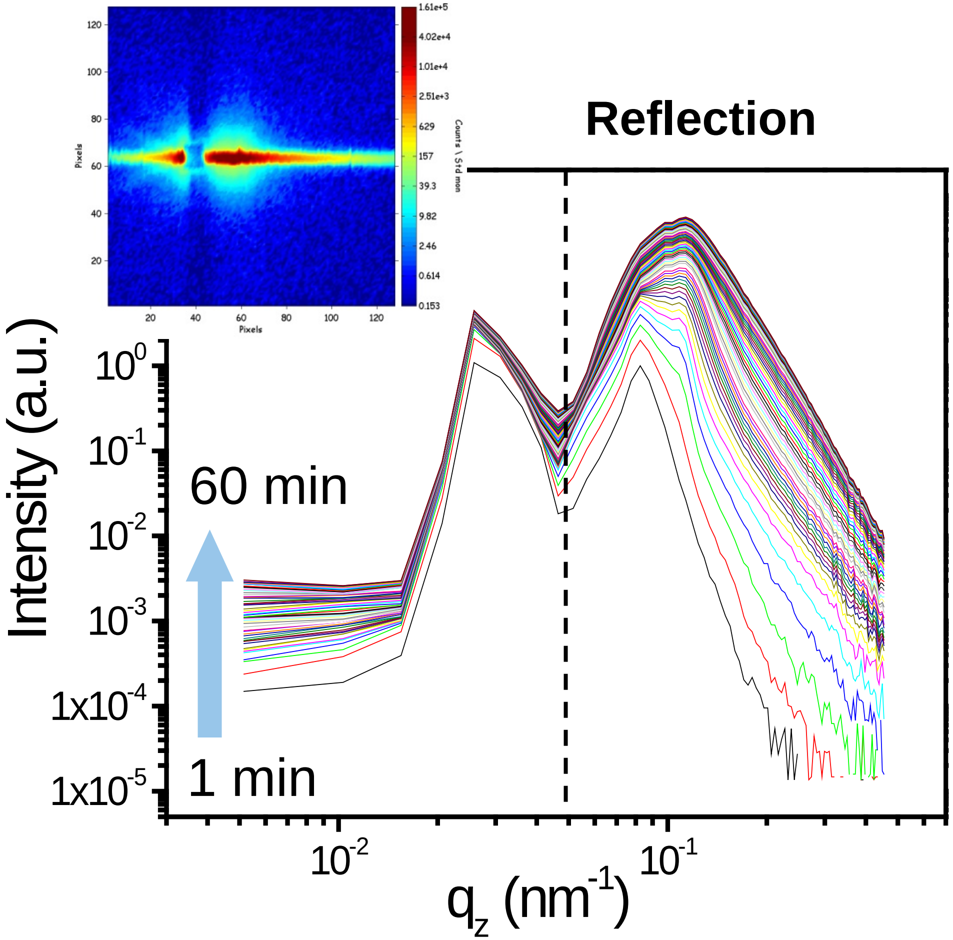
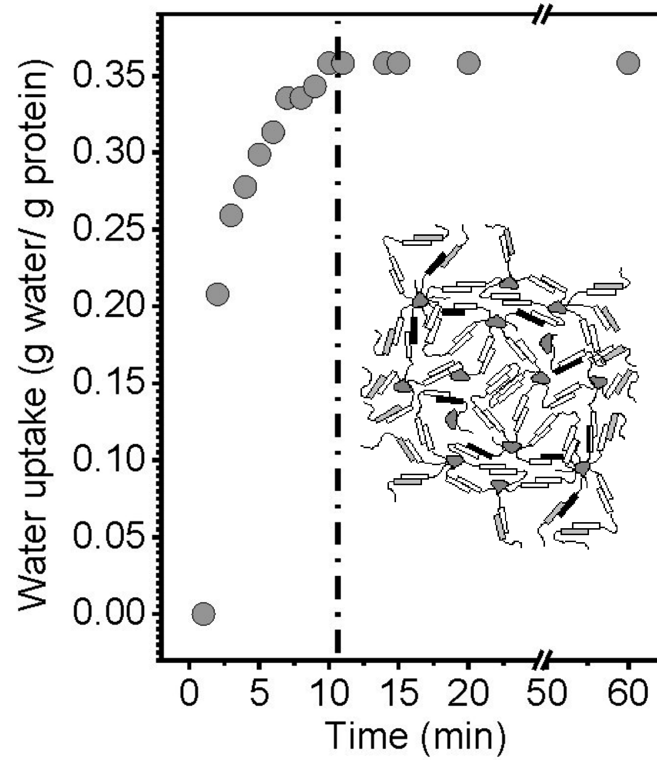
Time resolved GISANS

swelling of dry casein film in D_2O

$\Delta t = 60$ s





Metwalli, PMB et al.; Langmuir **25**, 4124-4134 (2009)

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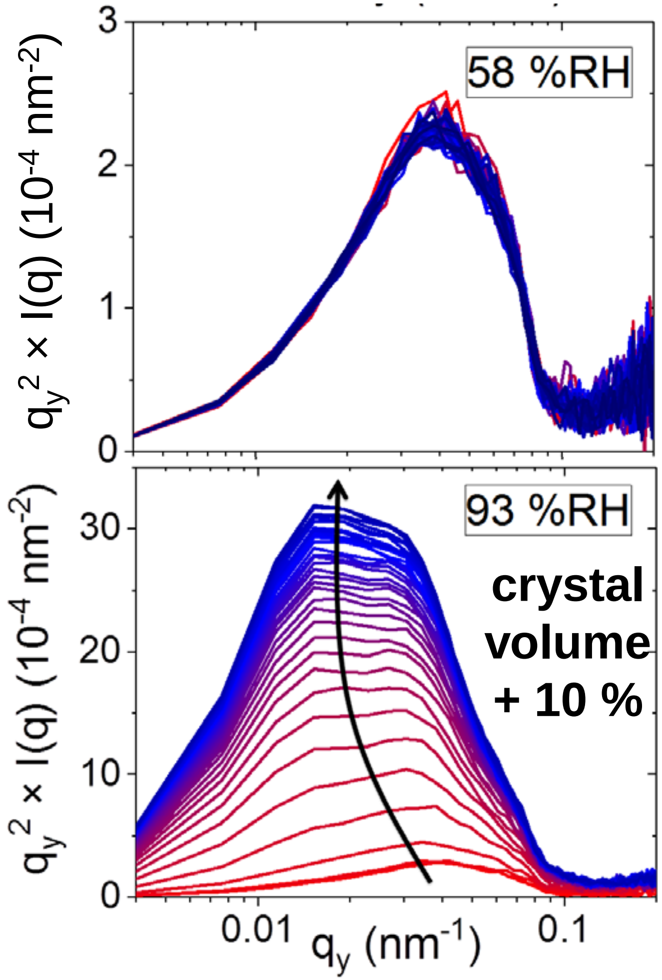
Ingression of moisture into hybrid perovskite thin films



in-situ GISANS with Δt= 600 s

- ingression of moisture at low %RH
  → level of monohydrate
  → no morphological changes
  → most water adsorbed

- sponge-like behavior at high %RH
  → strong morphological changes of crystal domains for ≥ 73 %RH
  → formation of di-hydrates

recovery of perovskite possible for certain conditions

Schlipf, PMB et al.; J.Phys.Chem.Lett. **9**, 2015-2021 (2018)

Summary

GISAXS/GISANS open new possibilities of advanced sample characterization

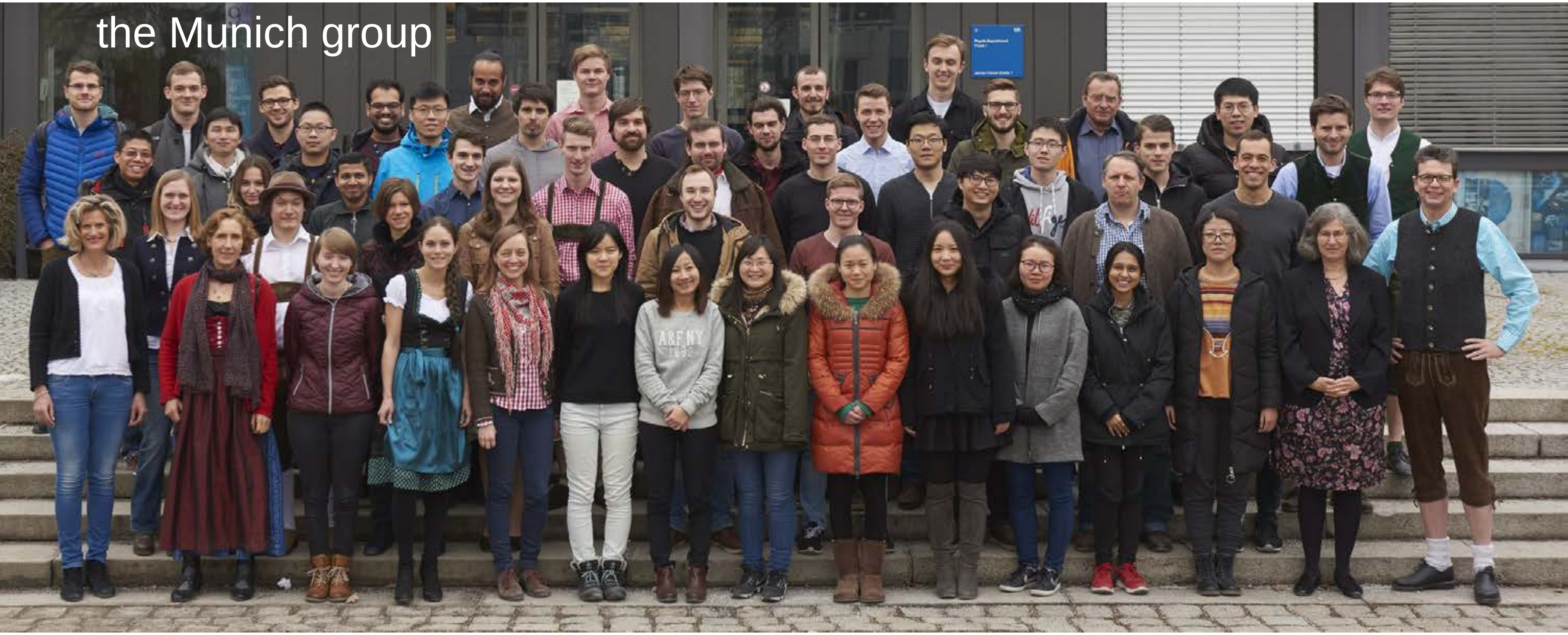
GISAXS/GISANS : reciprocal space analysis technique

- *non-destructive structural probe*
- sensitive to structures between nm to μm
- does not require a special sample preparation
- *yields excellent sampling statistics*

  (averages over macroscopic regions to provide information on nanometer scale)

- buried structures: object geometry, size distributions and spatial correlations

Acknowledgments



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