TECHNISCHE UNIVERSITÄT MÜNCHEN

Fundamentals of GISANS and Selected Examples

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Outline

- Fundamental Aspects of GISANS
- Selected Examples
- Monitoring the Ingression of Moisture into Hybrid Perovskite Thin Films with In-Situ GISANS

+ ACS LiveSlides video


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In Situ Monitoring the Uptake of Moisture into Hybrid Perovskite Thin Films

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Supporting Information

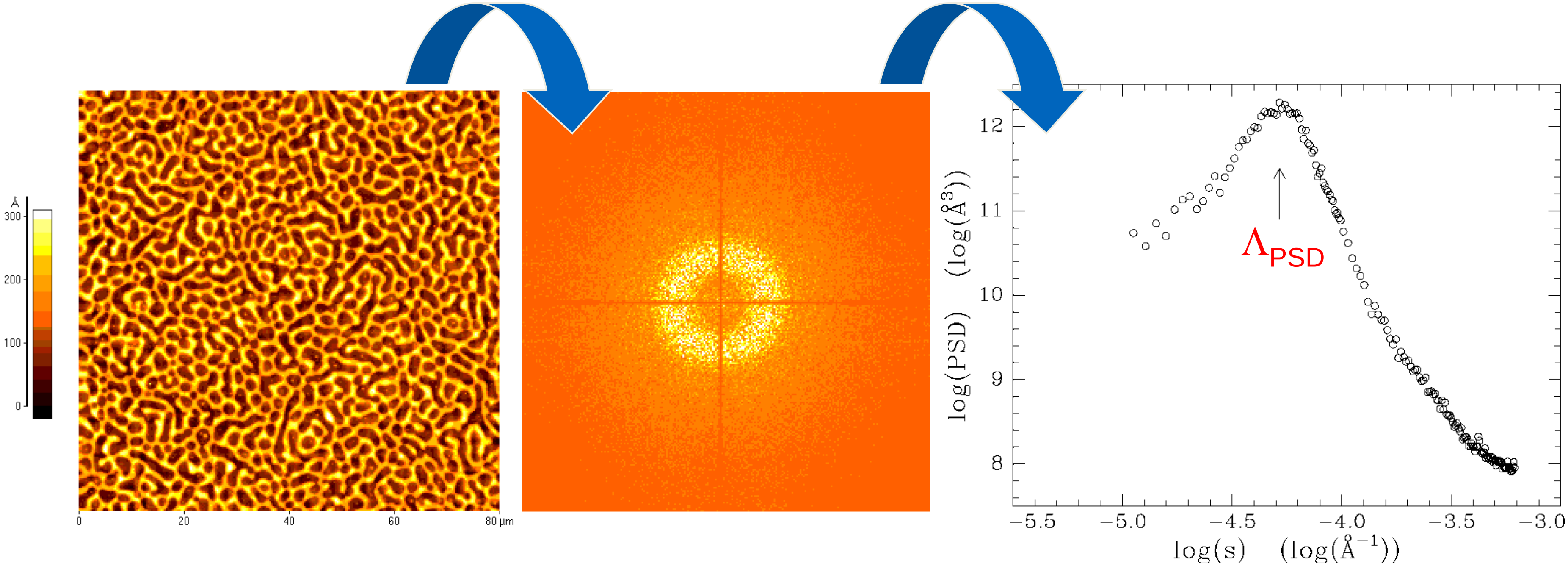
ABSTRACT: Solution-processed hybrid perovskites are of great interest for use in photovoltaics. However, polycrystalline perovskite thin films show strong degradation in humid atmospheres, which poses an important challenge for large-scale market introduction. With in situ grazing incidence neutron scattering (GISANS) we analyzed water content, degradation products, and morphological changes during prolonged exposure to several humidity levels. In high humidity, the formation of metastable hydrate phases is accompanied by domain swelling, which transforms the faceted crystals to a ...

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



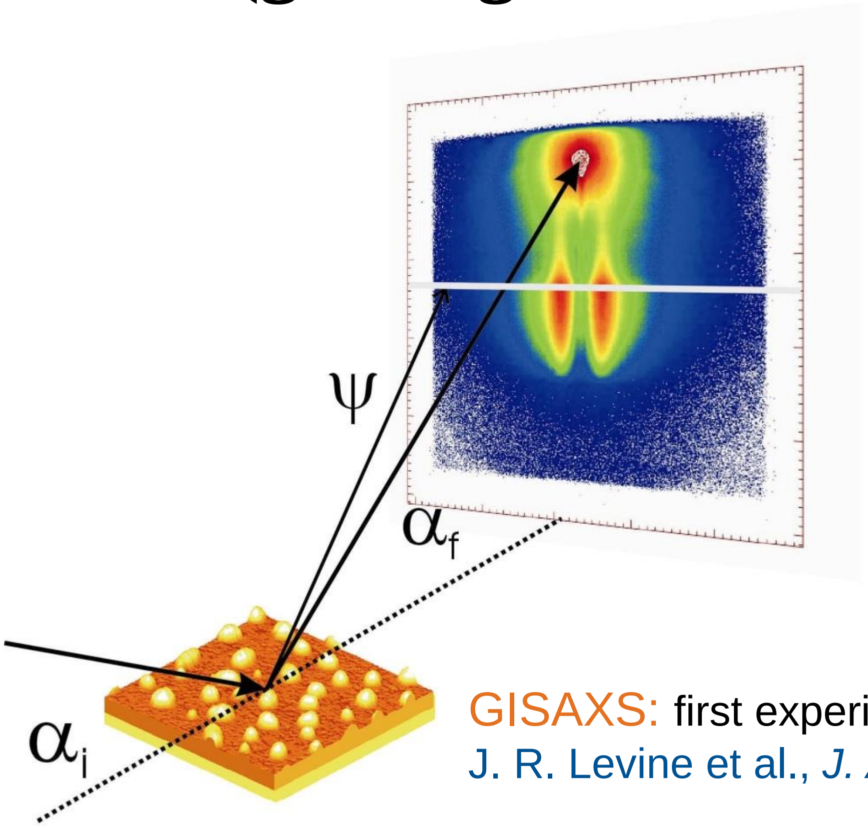
AFM data accessible with scan ranges up to ≈ 100 µm

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

→ only sample surface probed !

P. Müller-Buschbaum et al., *J. Macromol. Sci.*, **1999**, *B38*, 577

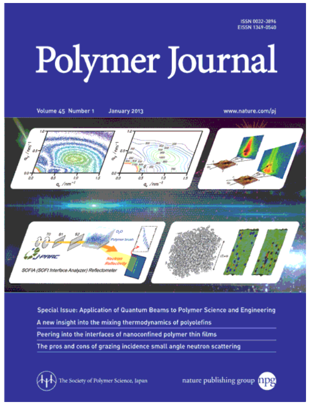
GISAS (grazing incidence small angle scattering)



- 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:
J. R. Levine et al., *J. Appl. Cryst.* **1989**, *22*, 528



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

Reviews: P. Müller-Buschbaum, *Polymer Journal* **2013**, *45*, 34
P. Müller-Buschbaum, *European Polymer Journal* **2016**, *81*, 470

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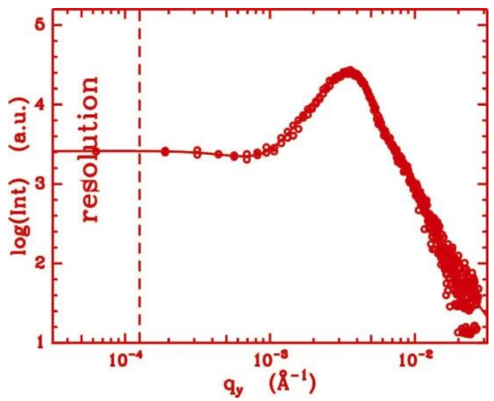
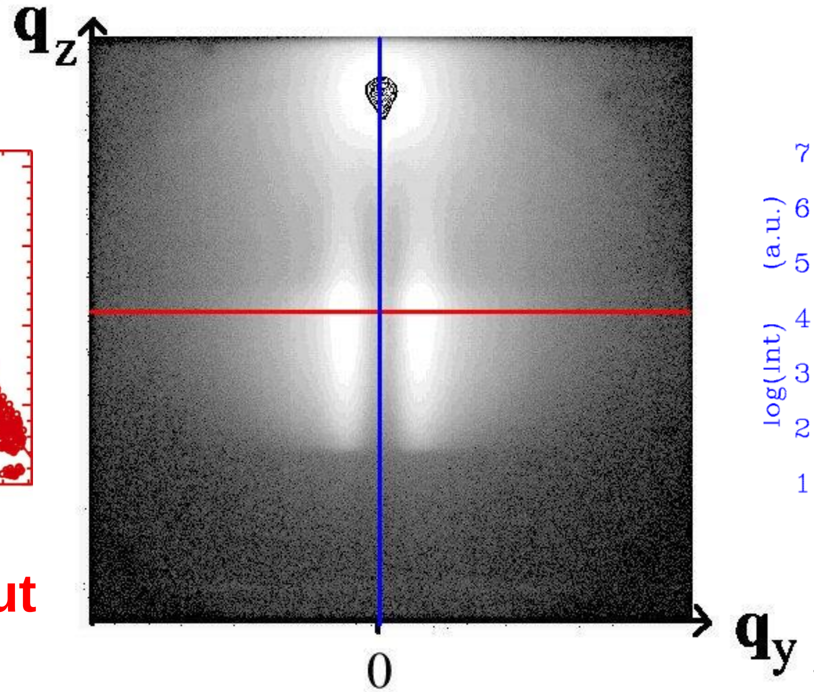
Line cuts

cut at constant q_z

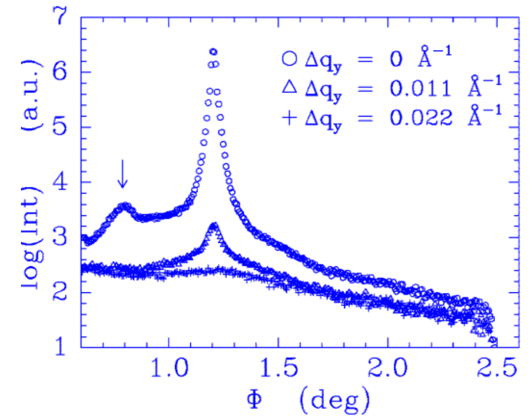


horizontal line cut

→ q_y-dependence:
in-plane structures



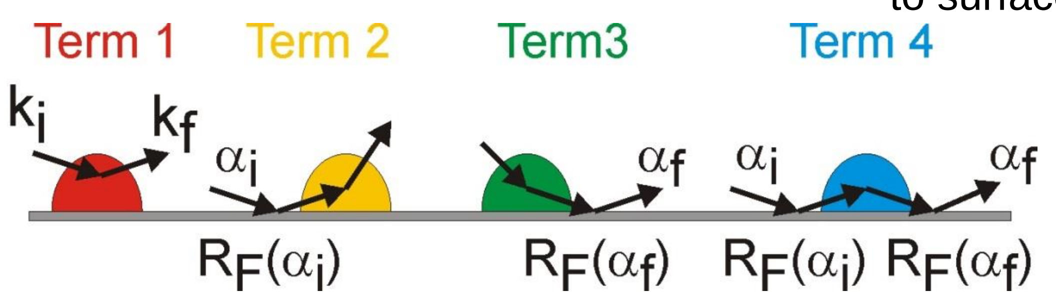
cut at constant q_y



vertical line cut

→ mainly q_z-dependence:
correlation perpendicular
to surface

distorted wave
Born approximation
(DWBA)

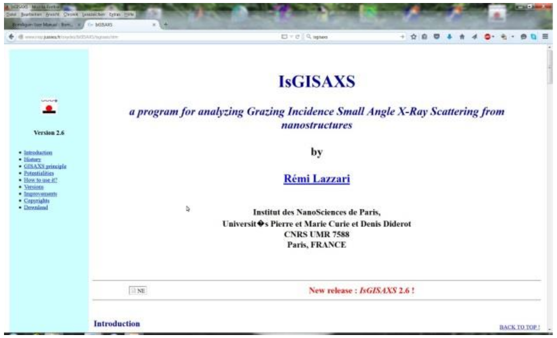


T. Salditt et al., *Phys. Rev. B* **1995**, *51*, 5617

Modelling of GISANS data

several software packages

IsGISAXS



R. Lazzari, *J. Appl. Cryst.* **2002**, *35*, 406

FitGISAXS

D. Babonneau, *J. Appl. Cryst.* **2010**, *43*, 929

HipGISAXS

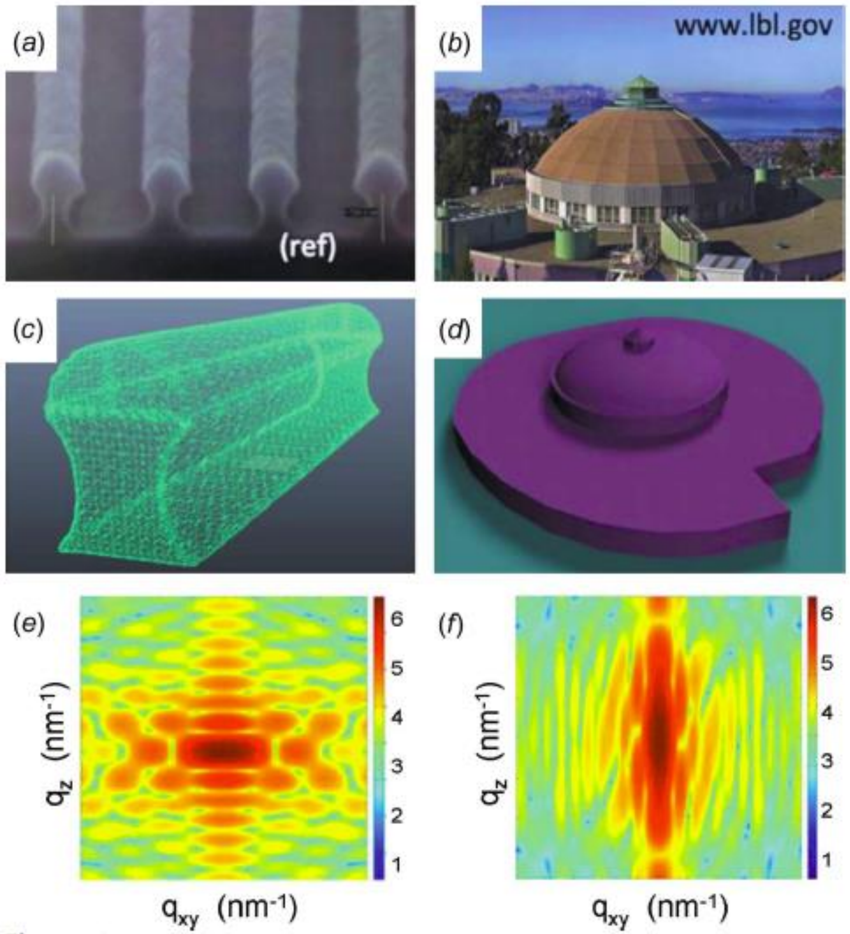
S. Chourou et al., *J. Appl. Cryst.* **2013**, *46*, 1781

BornAgain

→ bornagainproject.org

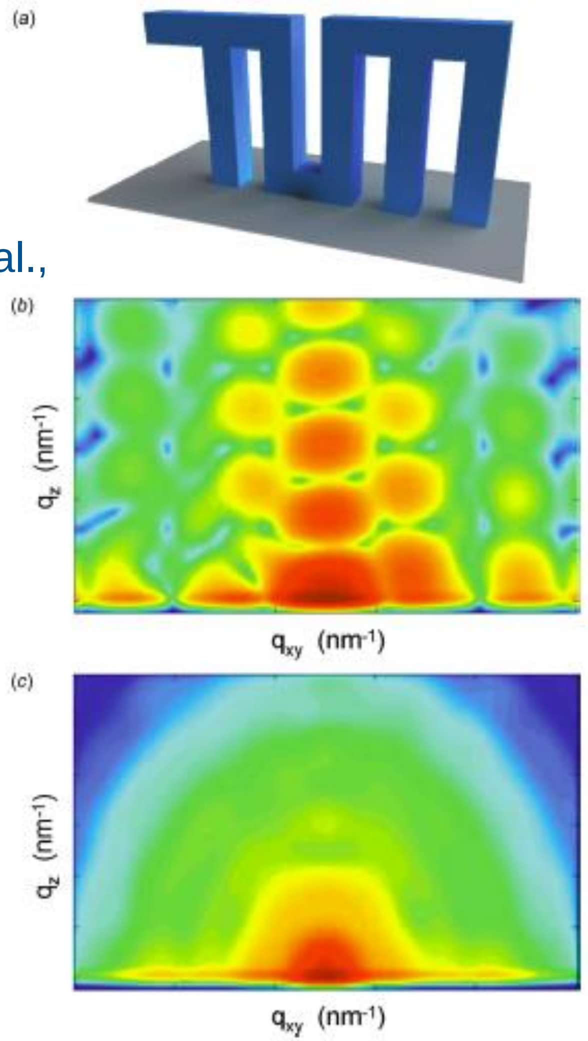
Modelling of complex samples

both for x-rays and neutrons



HipGISAXS from ALS

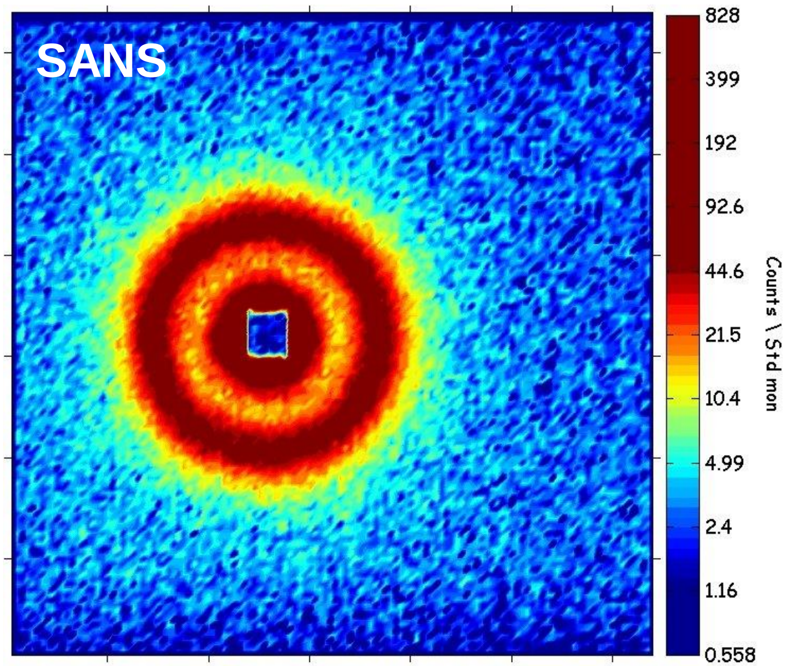
S. Chourou et al., *J. Appl. Cryst.* **2013**, *46*, 1781

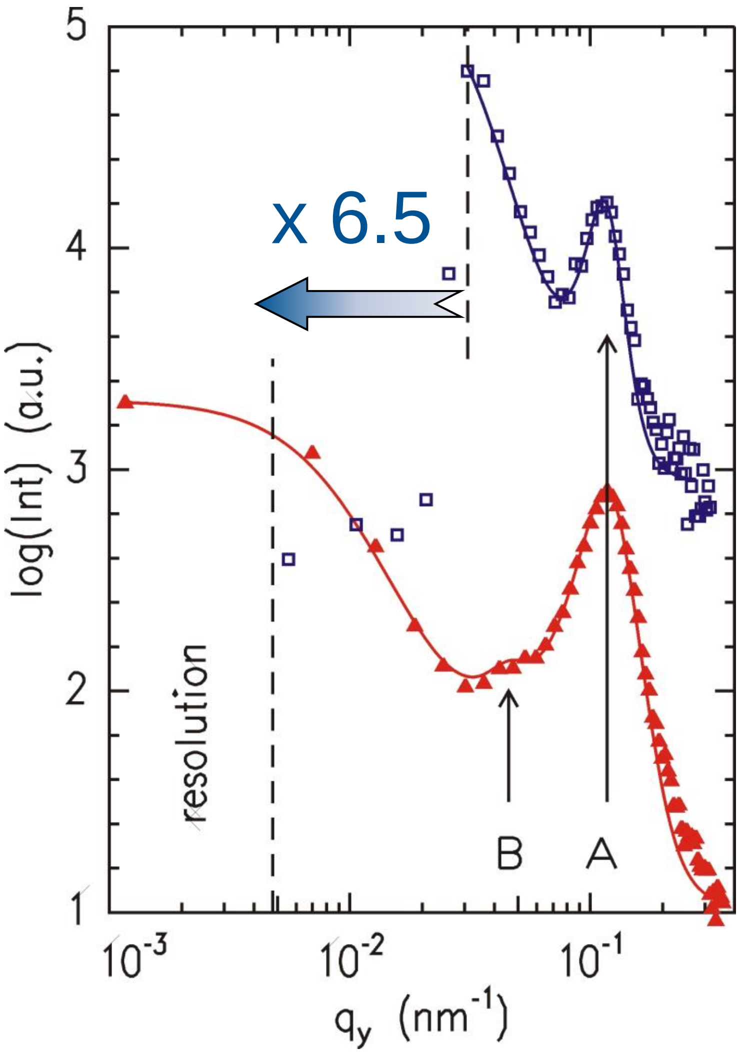


A. Hexemer, P. Müller-Buschbaum, *IUCrJ* **2015**, *2*, 106-125

Comparison SANS versus GISANS

thick tri-block copolymer film





SANS and GISANS yield lamellar spacing $L_o = \Lambda_A$ **= 47 nm**

GISANS has higher resolution
$\rightarrow$ second length Λ_B **= 300 nm**

P. Müller-Buschbaum et al., *Langmuir* **2006**, *22*, 9295

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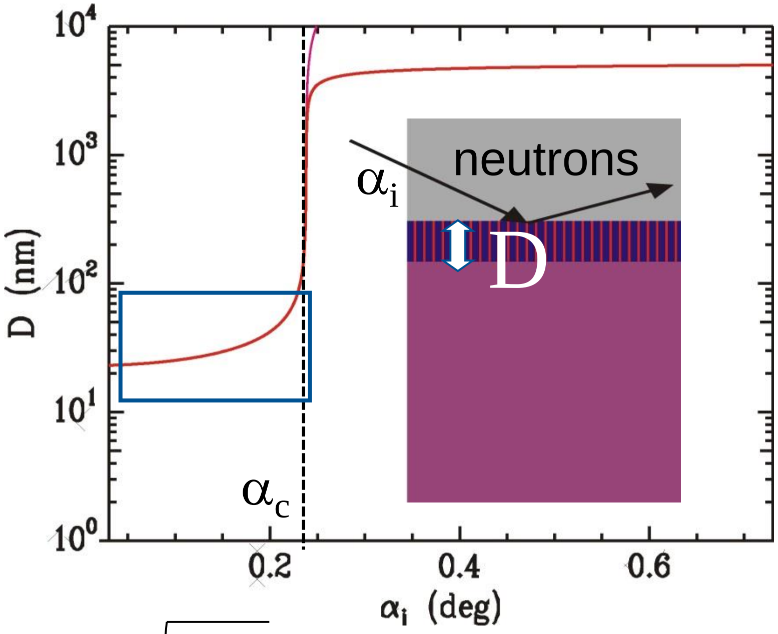
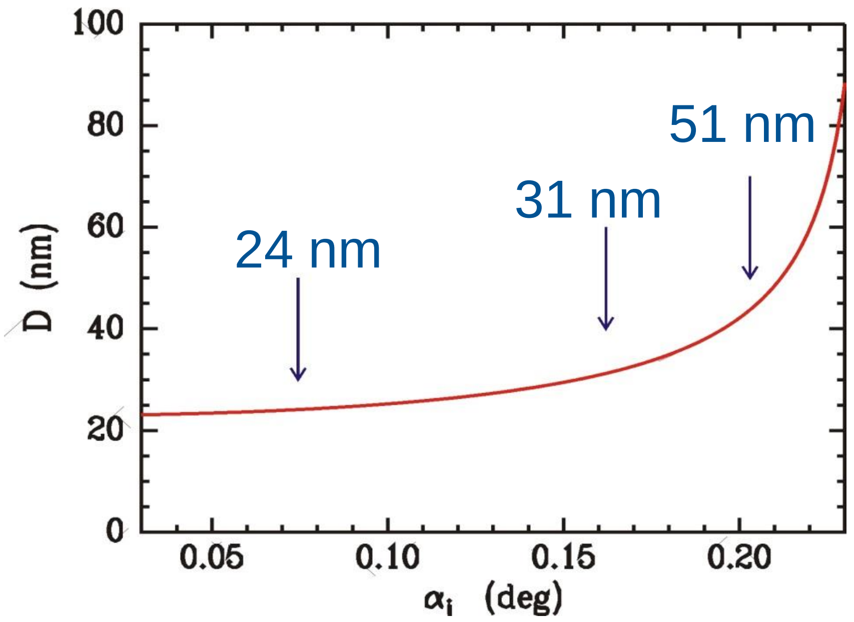
Surface sensitivity

scattering depth of neutrons

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





$$\alpha_c = \lambda\sqrt{\frac{\rho_{SLD}}{\pi}}$$

→ vary incident angle $\alpha_i < \alpha_c$ to probe interface near region

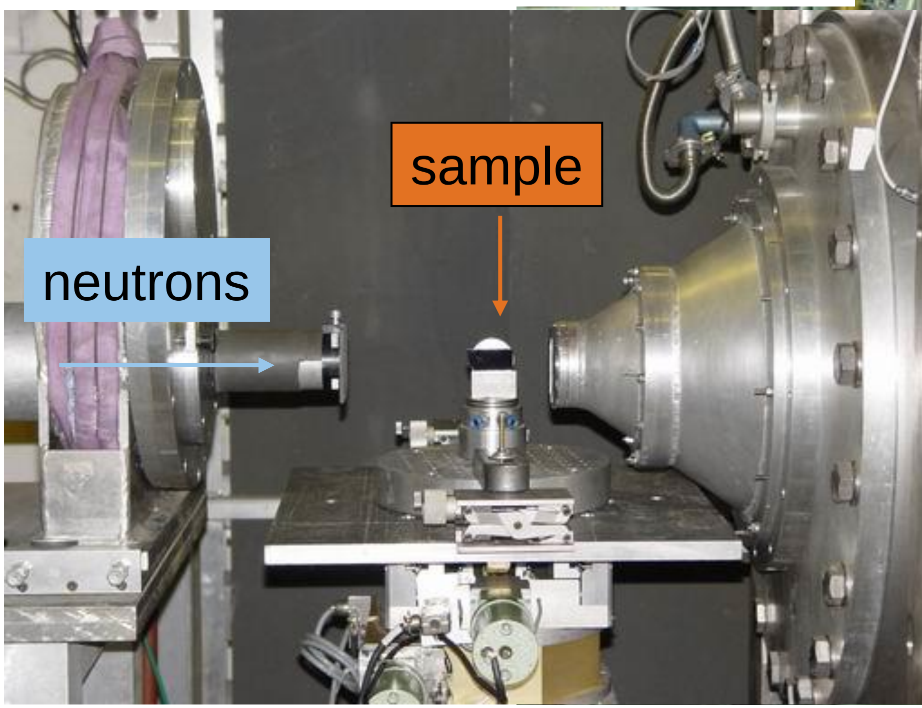
H. Dosch et al., *Phys. Rev. Lett.* **1986**, *56*, 1144

GISANS at D22

with R. Cubitt

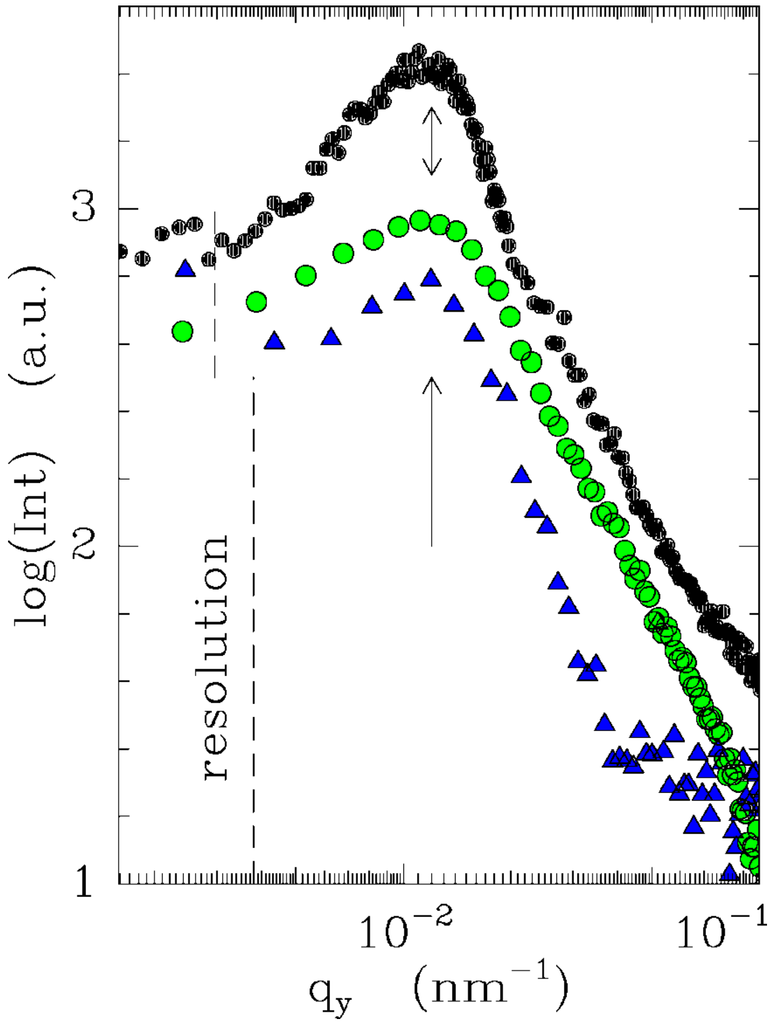
sample--detector distance 17.6 m
collimation length 17.6 m

slit 1*10 mm^2



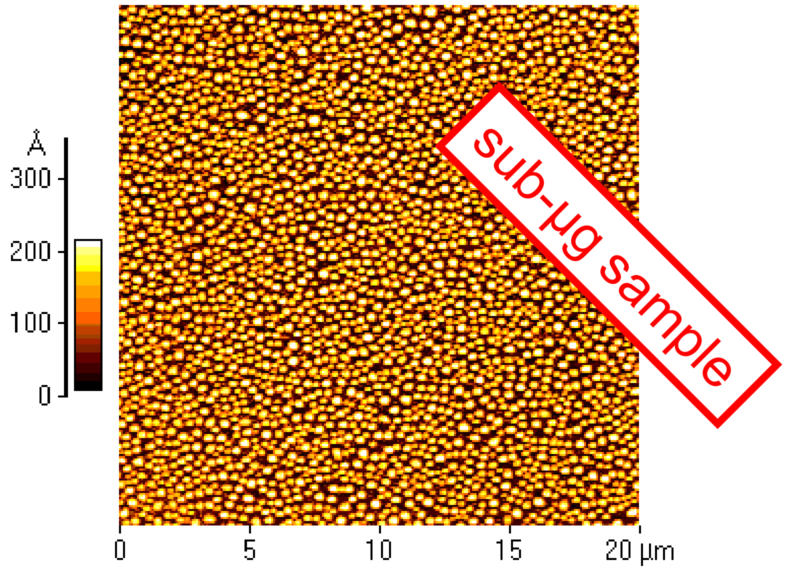
P. Müller-Buschbaum et al., *Physica B* **2000**, *283*, 53

Polymer nano-droplets



dPS on Si/SiO_x h < 1/3 R_g

toluene vapor treatment



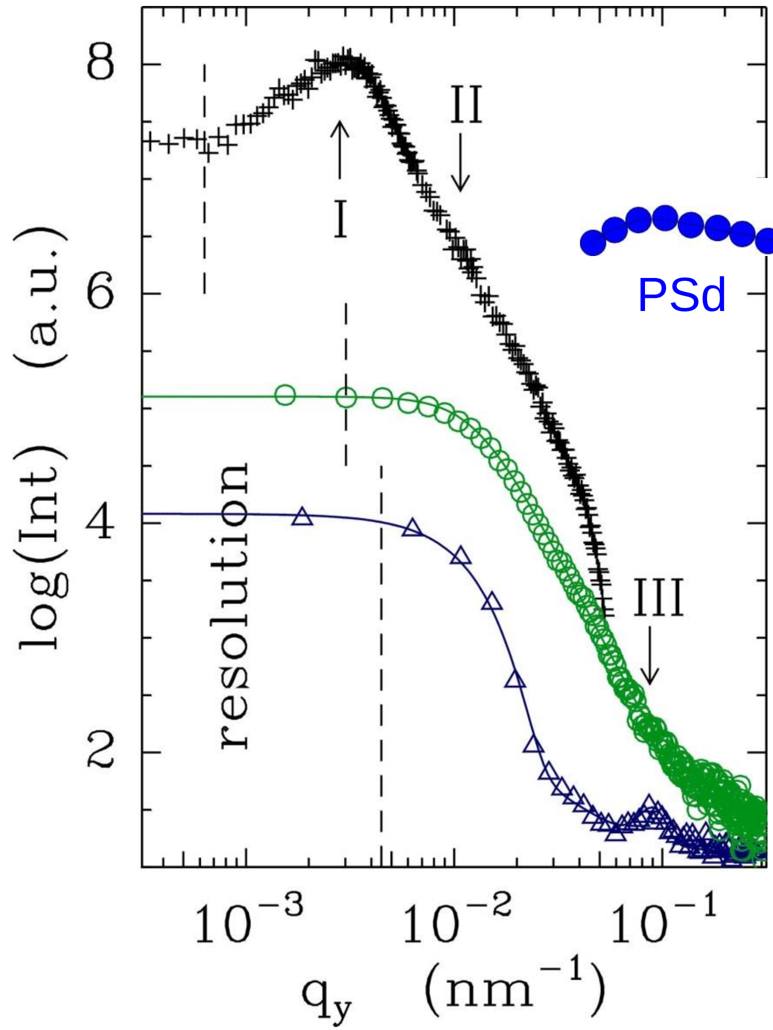
small droplets: prominent in-plane length scale of Λ_t = 522±5 nm
→ well pronounced peak in GISAXS and GISANS or in **AFM** data

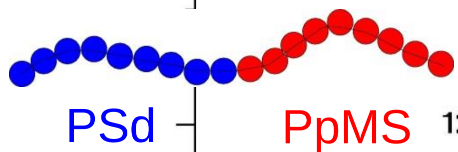
P. Müller-Buschbaum et al., *Phys. Chem. Chem. Phys.* **1999**, *1*, 3857

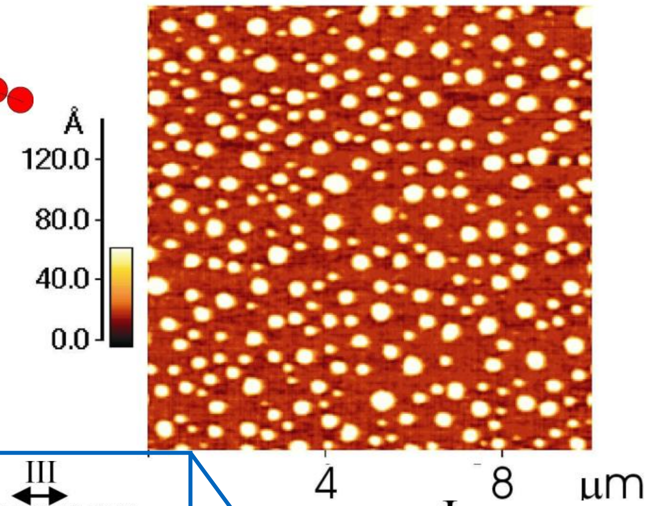
Internal nano-structure

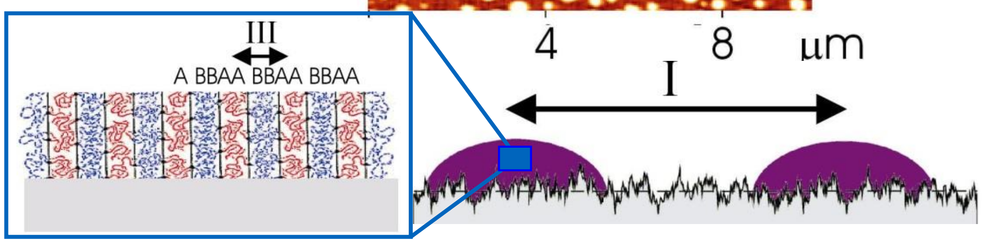
P(Sd-b-pMS) on Si/SiO_x h < 1/3 R_g

toluene vapor treatment 12h









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

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

P. Müller-Buschbaum et al., *Langmuir* **2001**, *17*, 5567

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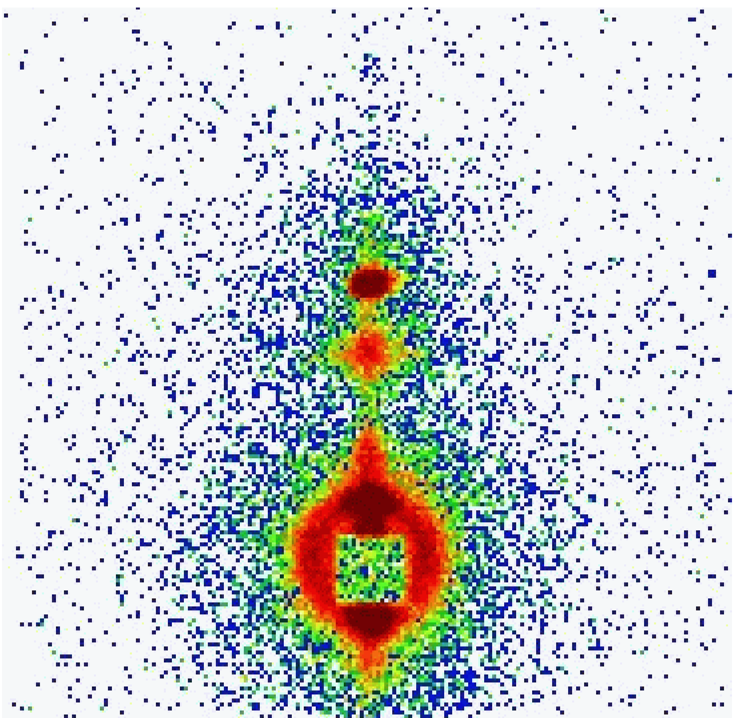
TOF-GISANS at REFSANS

48 h counting time, using 5 beams

sample-detector distance 10.7 m

wavelength range 0.25 – 1.49 nm



- select region of interest from 2D intensity
- TOF superposition of many wavelengths
- definition of individual time channels

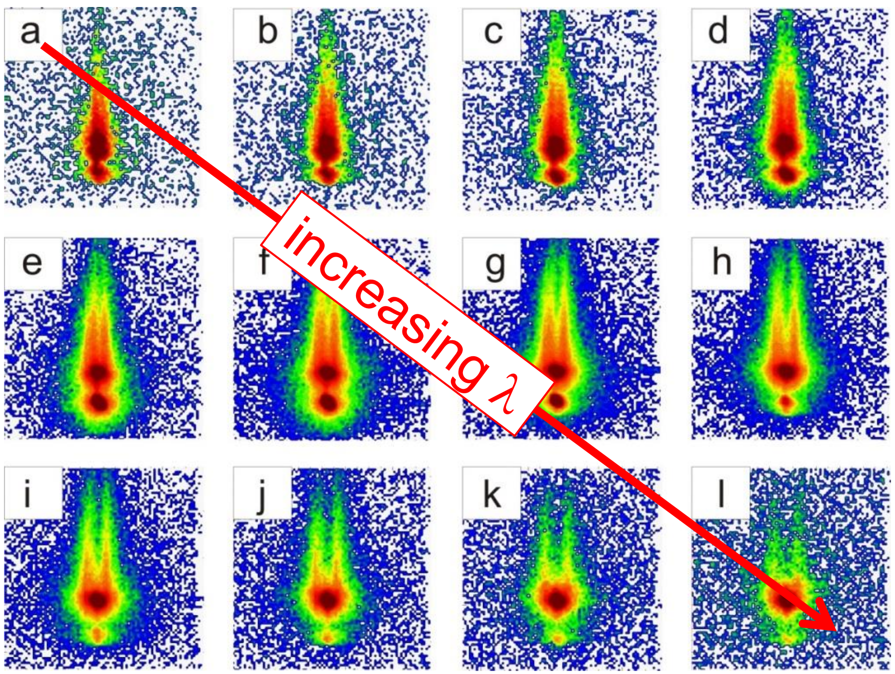
P. Müller-Buschbaum et al., *Eur. Phys. J. E ST.* **2009**, *167*, 107

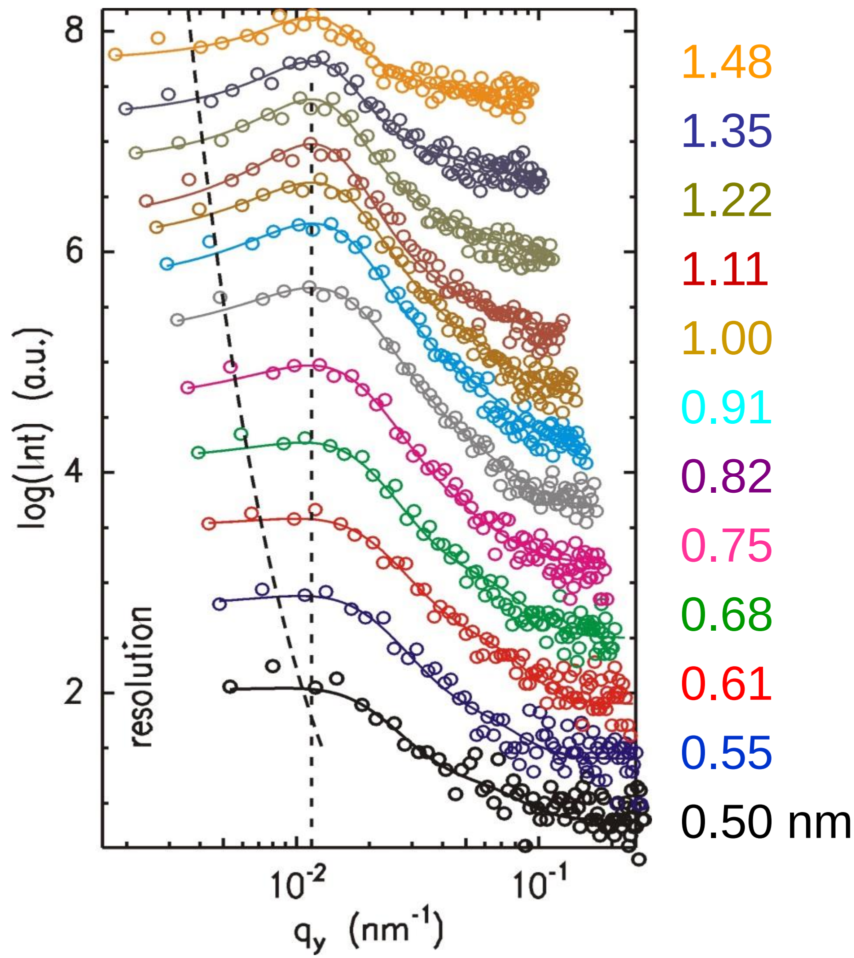
Polymer nano-droplets

$$\alpha_c = \lambda \sqrt{\frac{Nb}{\pi}}$$

dPS on top of Si/SiO_x $h < 1/3\ R_g$

toluene vapor treatment





structure factor of droplet assembly well resolved

P. Müller-Buschbaum et al., *Eur. Phys. J. E ST.*, **2009**, *167*, 107

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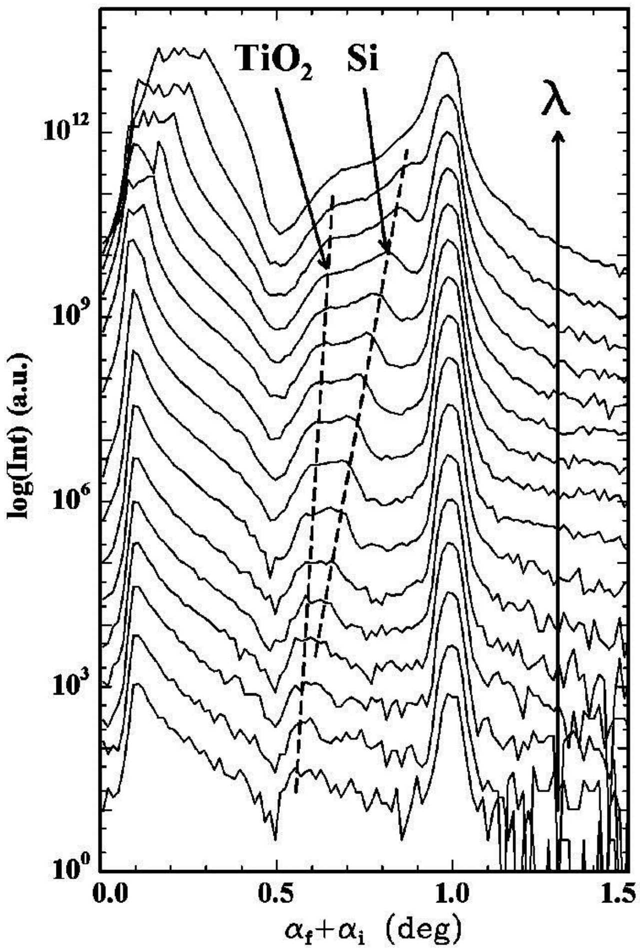
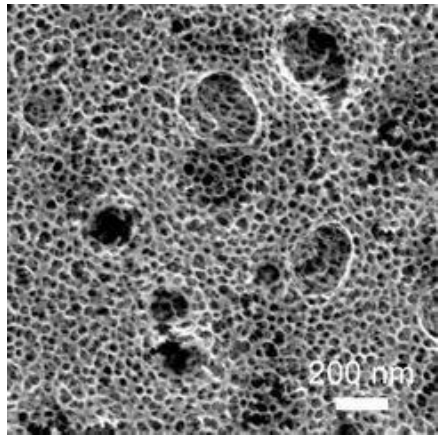
icis.com

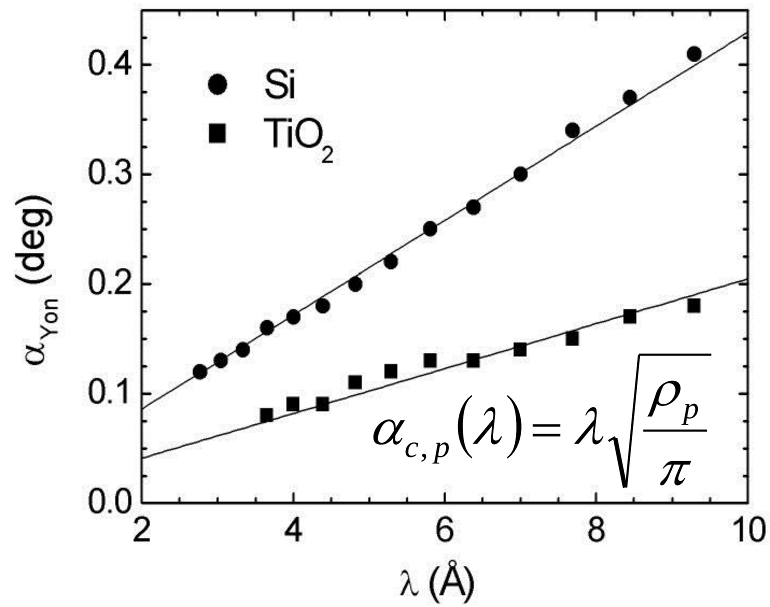
Porosity determination

TOF-GISANS: vertical cuts → extract Yoneda peak positions



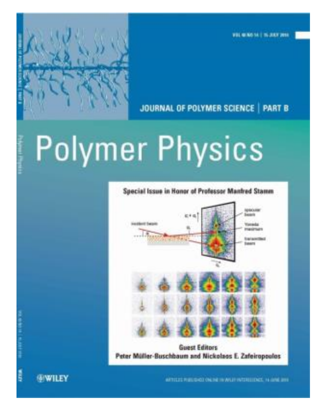


TiO_2 sponge-like morphology



→ porosity of 85%

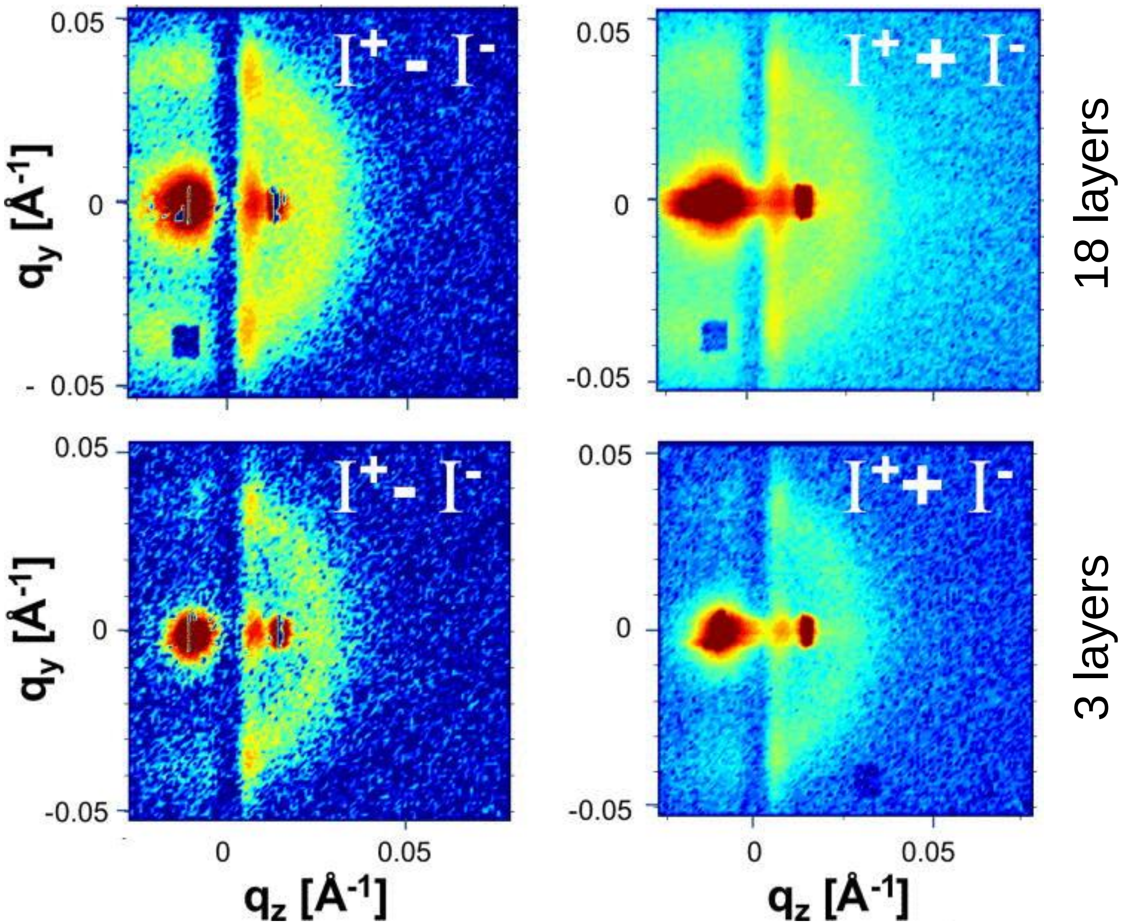
access to quantitative porosity of film



G. Kaune, P. Müller-Buschbaum et al., *J. Poly. Sci. Part B.* **2010**, *48*, 1628

Polarized GISANS

Co nanoparticles on Si/SiO_x at fields of 110 mT



D22, data taken with spin flipper in front of sample

Debye-Scherrer rings with strong magnetic contrast
→ short range lateral order of 13 nm nano-particles with Λ= 17 nm

K. Theis-Bröhl, et al., *J. Appl. Phys.* **2011**, *110*, 102207

Summary

GISANS opens new possibilities of advanced sample characterization

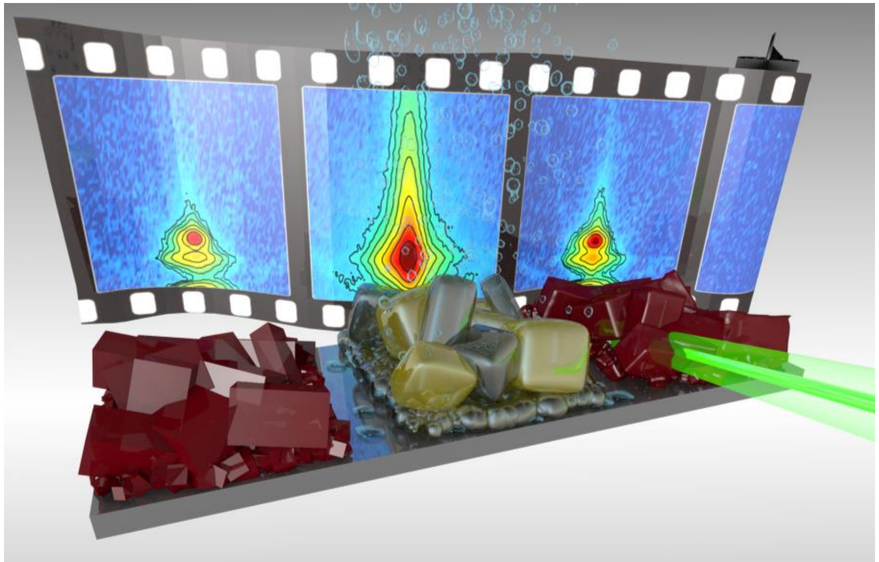
GISAS : reciprocal space analysis technique

- *non-destructive structural probe*
- sensitive to structures between 1 nm to 5 (or 21) 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

Monitoring the Ingression of Moisture into Hybrid Perovskite Thin Films with In-Situ GISANS



Johannes Schlipf[1],

L. Bießmann[1], L. Oesinghaus[2],

E. Berger[3], E. Metwalli[1], J. A. Lercher[3],

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1 Technische Universität München, Lehrstuhl für Funktionelle Materialien, Physik-Department, Garching (D)

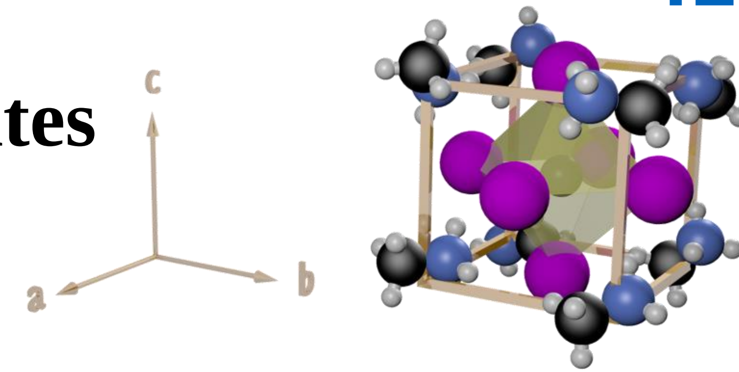
2 Technische Universität München, Physics of Synthetic Biological Systems, Physics-Dept., Garching (D)

3 Technische Universität München, Department of Chemistry and Catalysis Research Center, Garching (D)

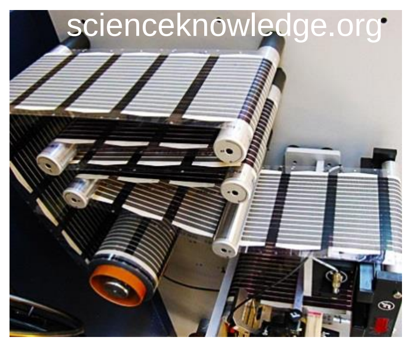
4 Institut Laue-Langevin (ILL), Beamline D22, Grenoble (F)

J. Schlipf et al., *J. Phys. Chem. Lett.* **2018**, *9*, 2015

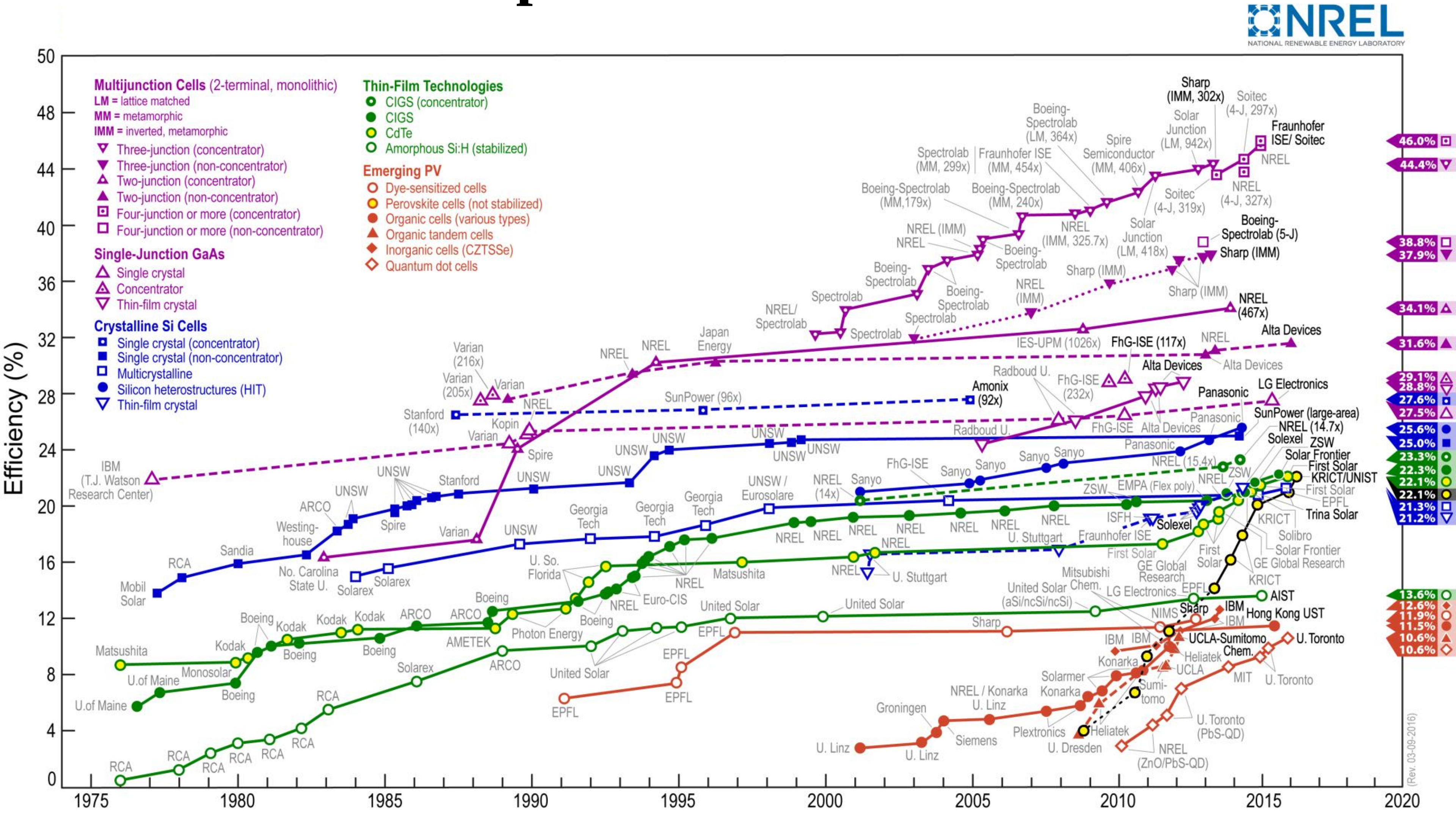
Properties of hybrid perovskites



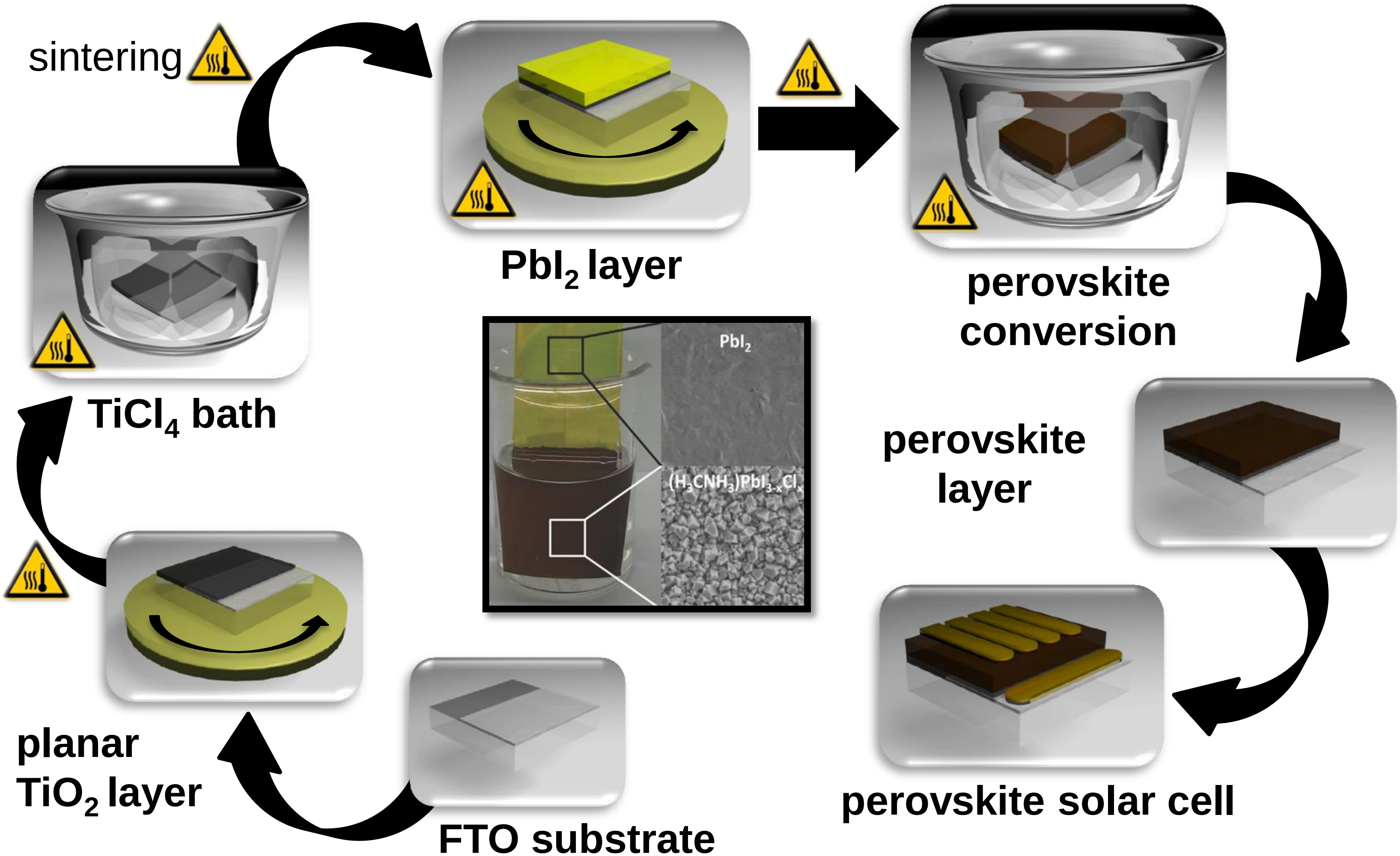
- ✓ exceptional optoelectronic properties
- ✓ photovoltaic efficiency > 20 %
- ✓ highly tunable by composition
- ✓ earth-abundant precursor materials
- ✓ solution processing
  - ➔ low production costs
- ✓ large-scale applicability
- ✓ device lifetimes
  - ≥ 1 year feasible[2]
- ✗ degradation with moisture



Best research cell power conversion efficiencies

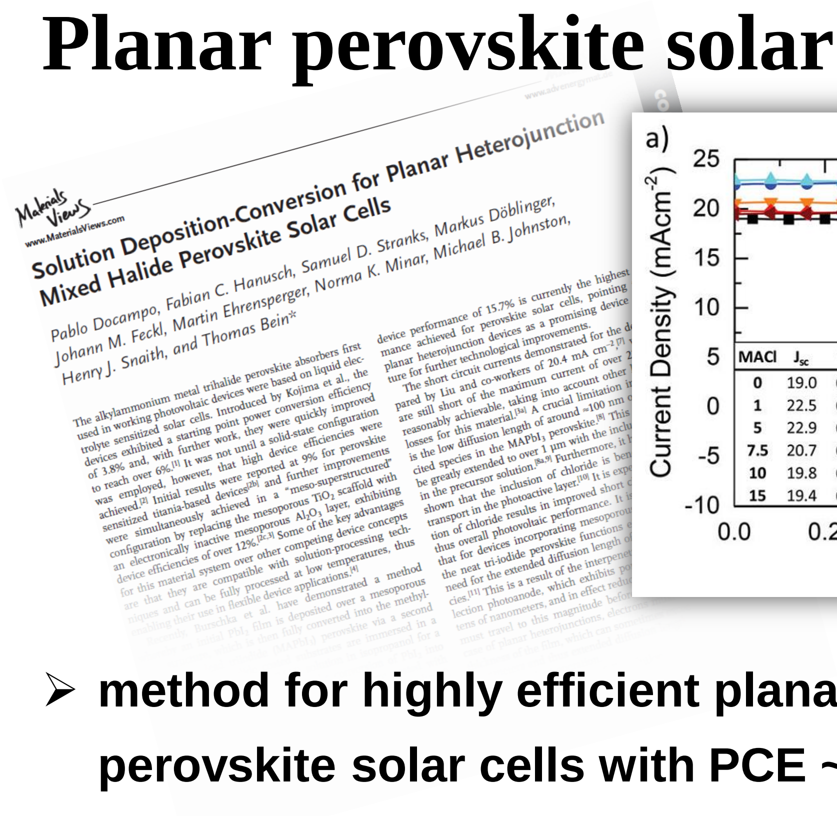


Preparation of planar solar cells



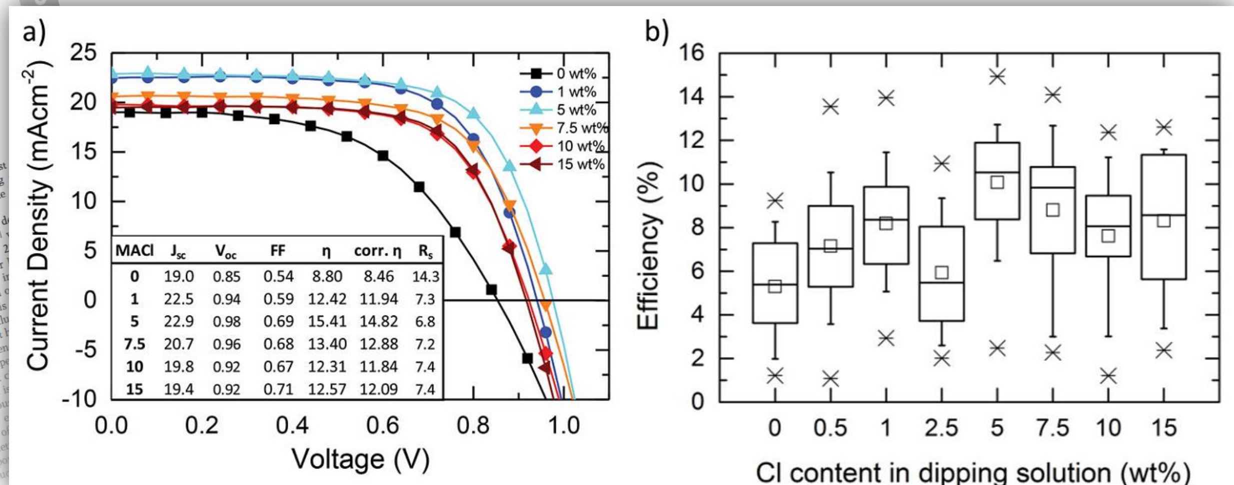
P. Docampo et al., *Adv. Energy Mater.* **2014**, *14*, 1400355

Planar perovskite solar cells


Materials Views
www.MaterialsViews.com

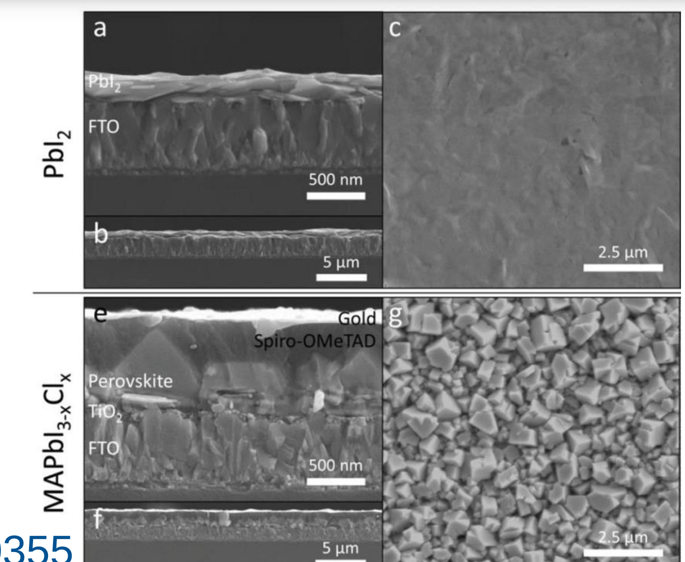
Solution Deposition-Conversion for Planar Heterojunction Mixed Halide Perovskite Solar Cells

Pablo Docampo, Fabian C. Hanusch, Samuel D. Stranks, Markus Döblinger, Johann M. Feckl, Martin Ehrensperger, Norma K. Minar, Michael B. Johnston, Henry J. Snaith, and Thomas Bein*



MACl	J_{sc}	V_{oc}	FF	η	corr. η	R_s
0	19.0	0.85	0.54	8.80	8.46	14.3
1	22.5	0.94	0.59	12.42	11.94	7.3
5	22.9	0.98	0.69	15.41	14.82	6.8
7.5	20.7	0.96	0.68	13.40	12.88	7.2
10	19.8	0.92	0.67	12.31	11.84	7.4
15	19.4	0.92	0.71	12.57	12.09	7.4

- **method for highly efficient planar perovskite solar cells with PCE ~15 %**
- dense, compact and homogeneous films
- Cl additive influences film growth and PCE
- **nowadays basis for many 2-step synthesis methods = model system**



P. Docampo et al., *Adv. Energy Mater.* **2014**, *14*, 1400355

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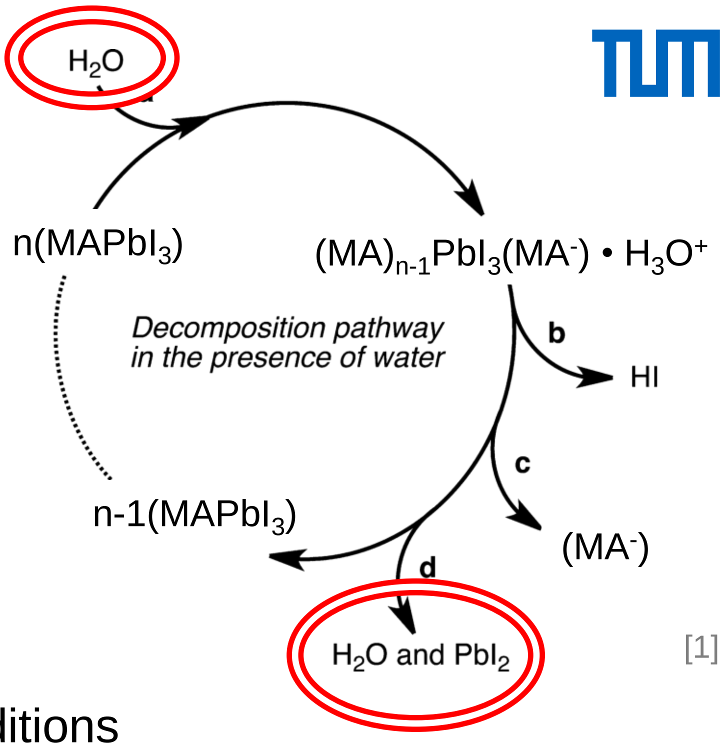
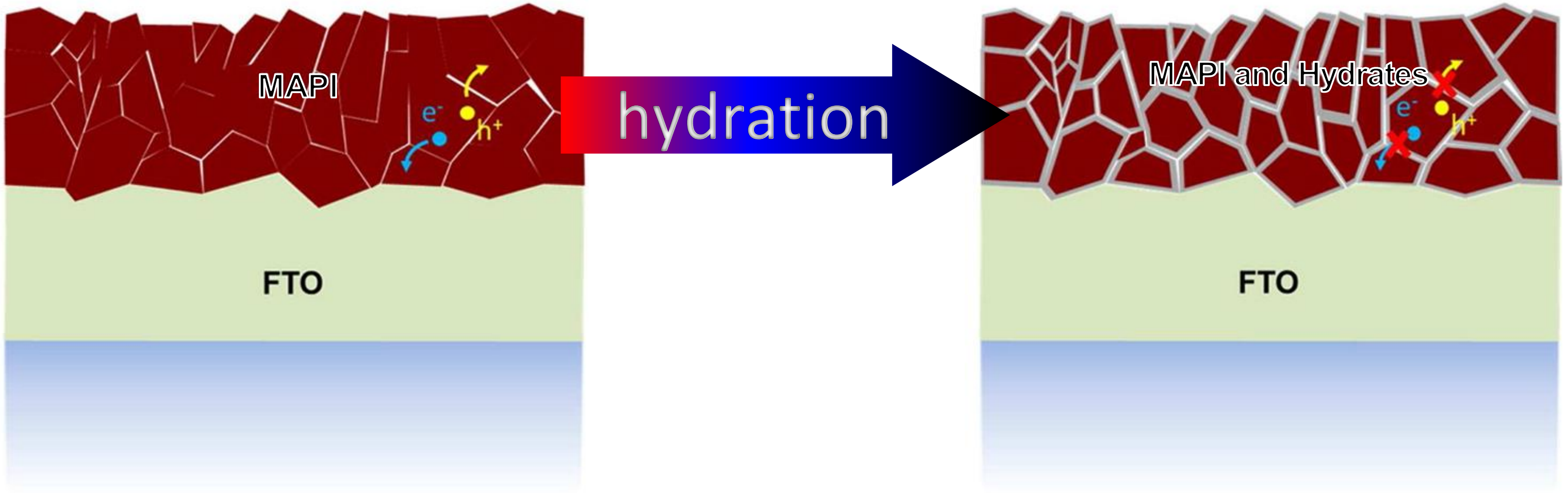
Degradation with moisture



[1]

- high ambient humidity detrimental for photovoltaic performance
- degradation to PbI_2 in self-sustaining reaction
- formation of metastable hydrate phases
- recovery of perovskite possible for certain conditions



[2]

[1] J. M. Frost et al., *Nano Lett.* **2014**, *14*, 2584; [2] A. M. A. Leguy et al., *Chem. Mater.* **2015**, *27*, 3397

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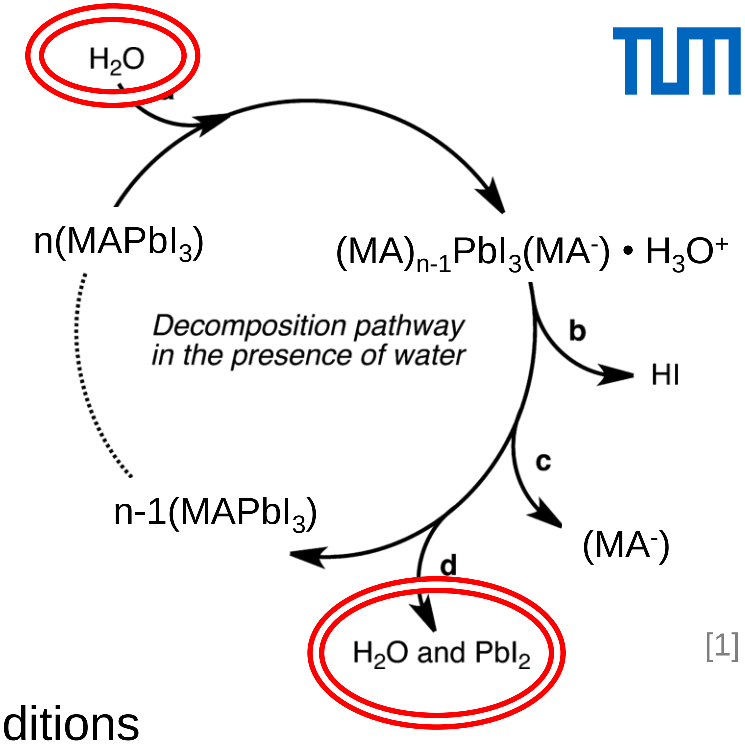
Degradation with moisture



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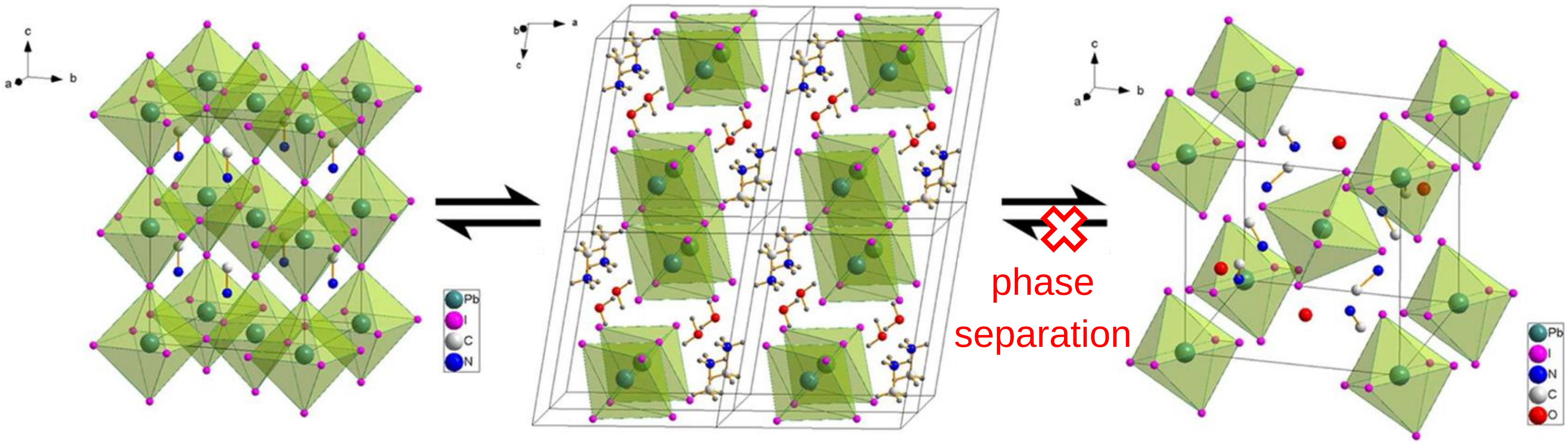
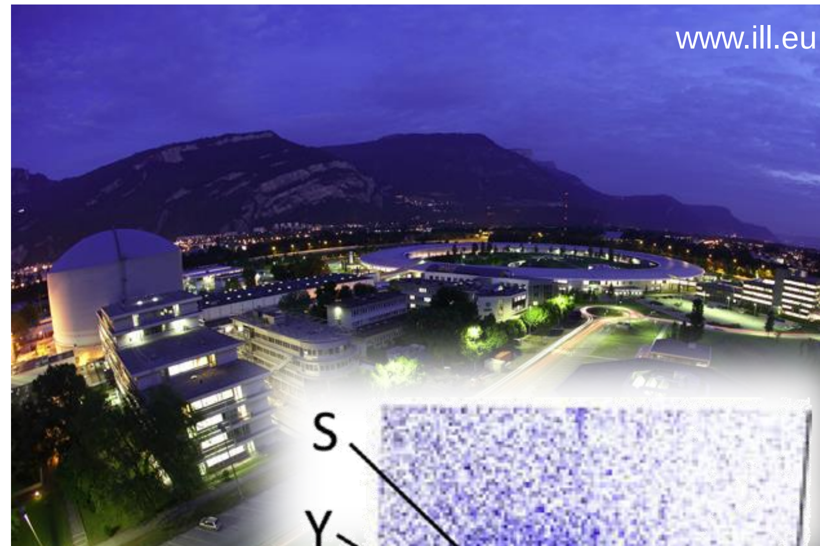


[2]

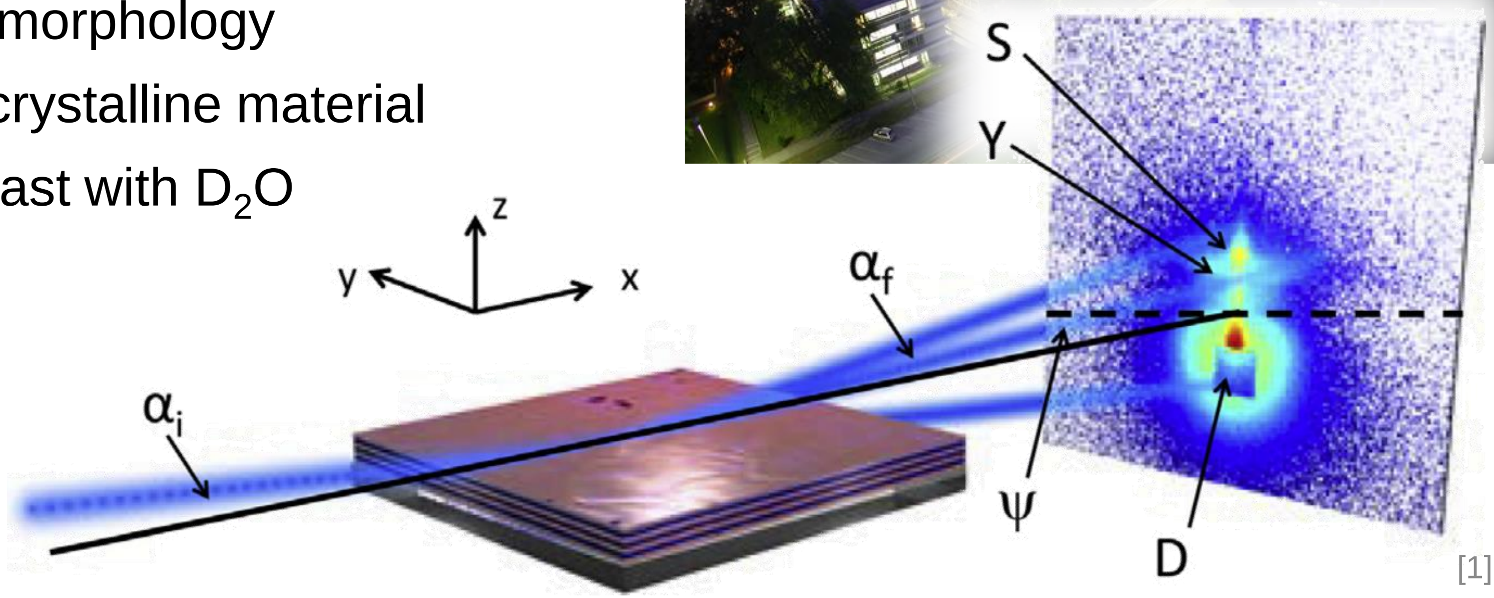
[1] J. M. Frost et al., *Nano Lett.* **2014**, *14*, 2584; [2] A. M. A. Leguy et al., *Chem. Mater.* **2015**, *27*, 3397

In-situ GISANS in humid atmosphere

- ✓ non-destructive
- ✓ probing large sample volume
  ➔ high statistics
- ✓ high flux ➔ 10 min/frame
- ✓ inner film morphology
- ✓ also non-crystalline material
- ✓ high contrast with D_2O

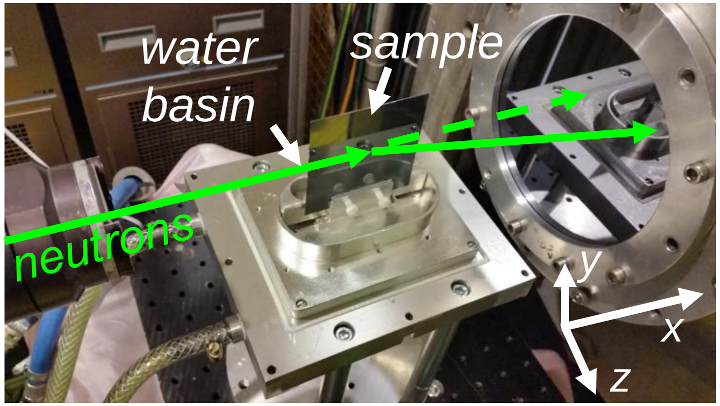


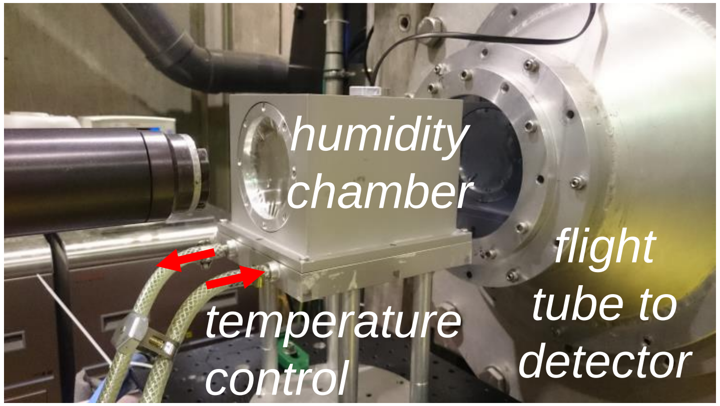
NEUTRONS FOR SCIENCE®



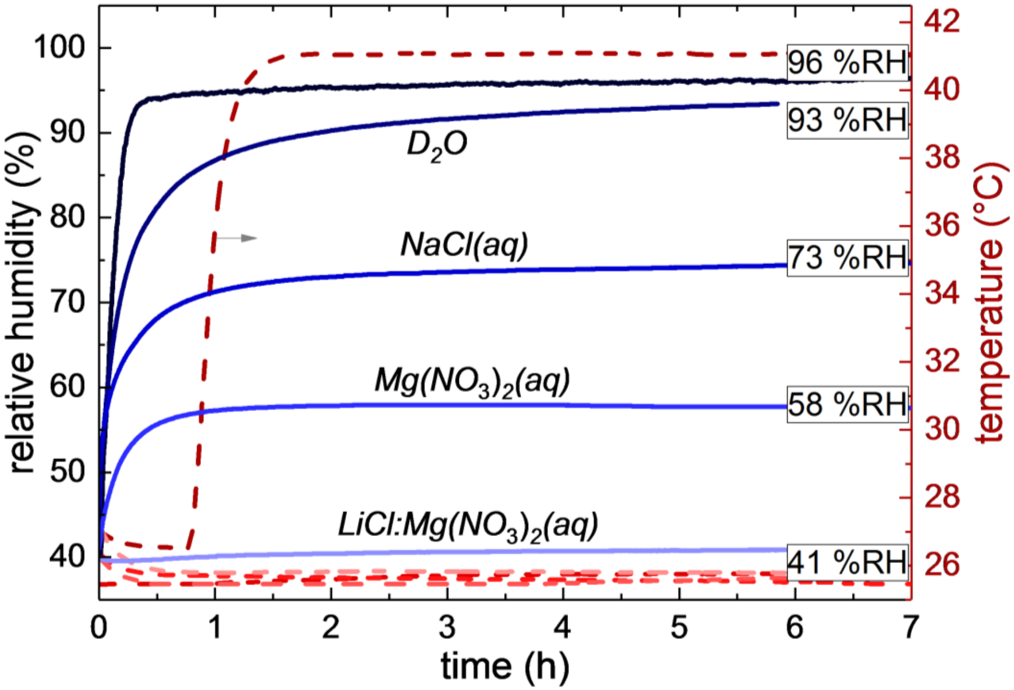
[1] P. Müller-Buschbaum, *Eur. Polym. J.* **2016**, *81*, 470

In-situ GISANS – experiment design



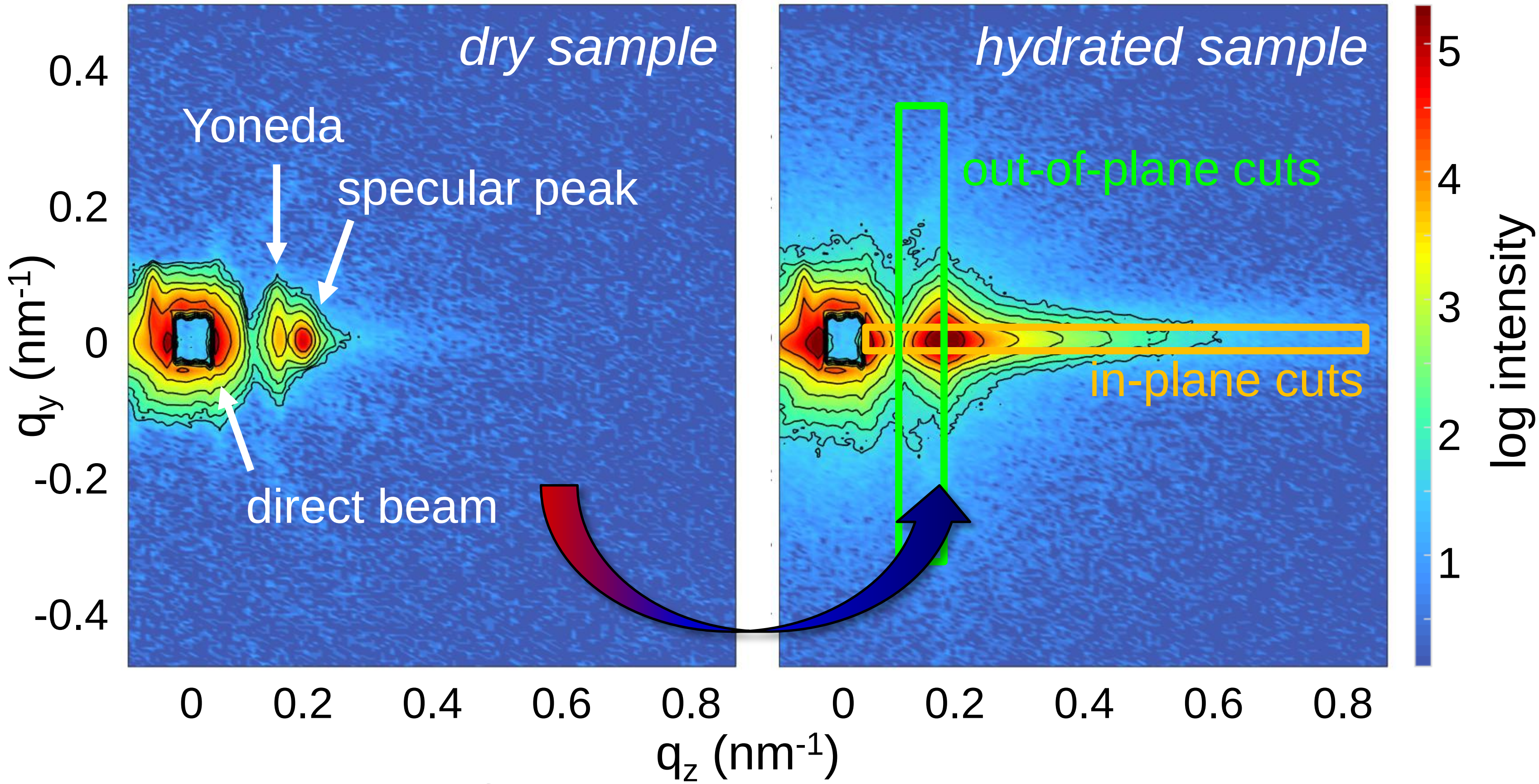


- inject D_2O or salt solutions into chamber
- control temperature, monitor humidity



J. Schlipf et al., *J. Phys. Chem. Lett.* **2018**, *9*, 2015

In-situ GISANS – data acquisition and treatment

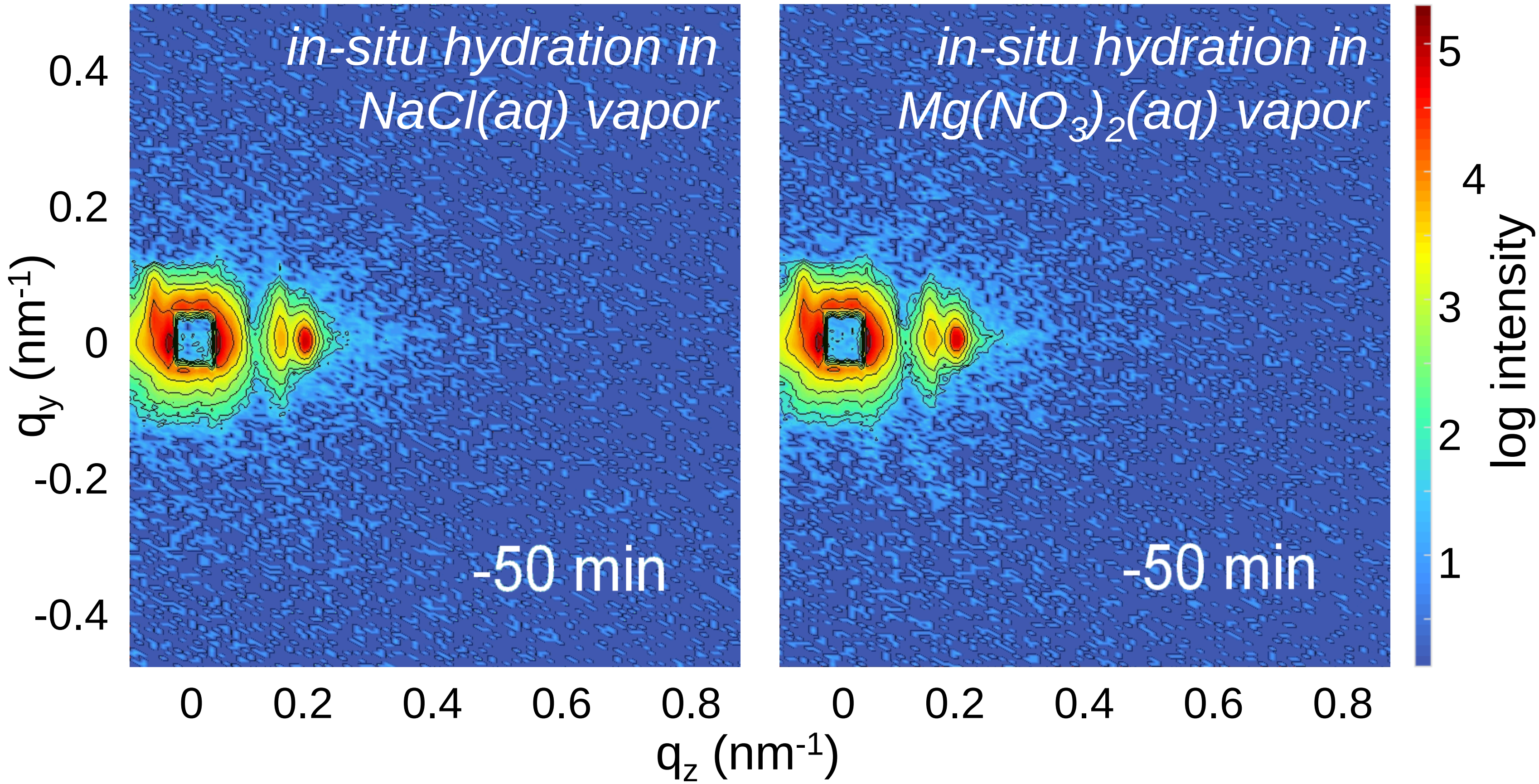


refractive index: $n = 1 - \delta$

$\Rightarrow$ scattering length density: $Nb = \frac{2\pi}{\lambda^2}\delta$ $\Rightarrow$ critical angle: $\alpha_c = \lambda\sqrt{\frac{Nb}{\pi}}$

J. Schlipf et al., *J. Phys. Chem. Lett.* **2018**, *9*, 2015

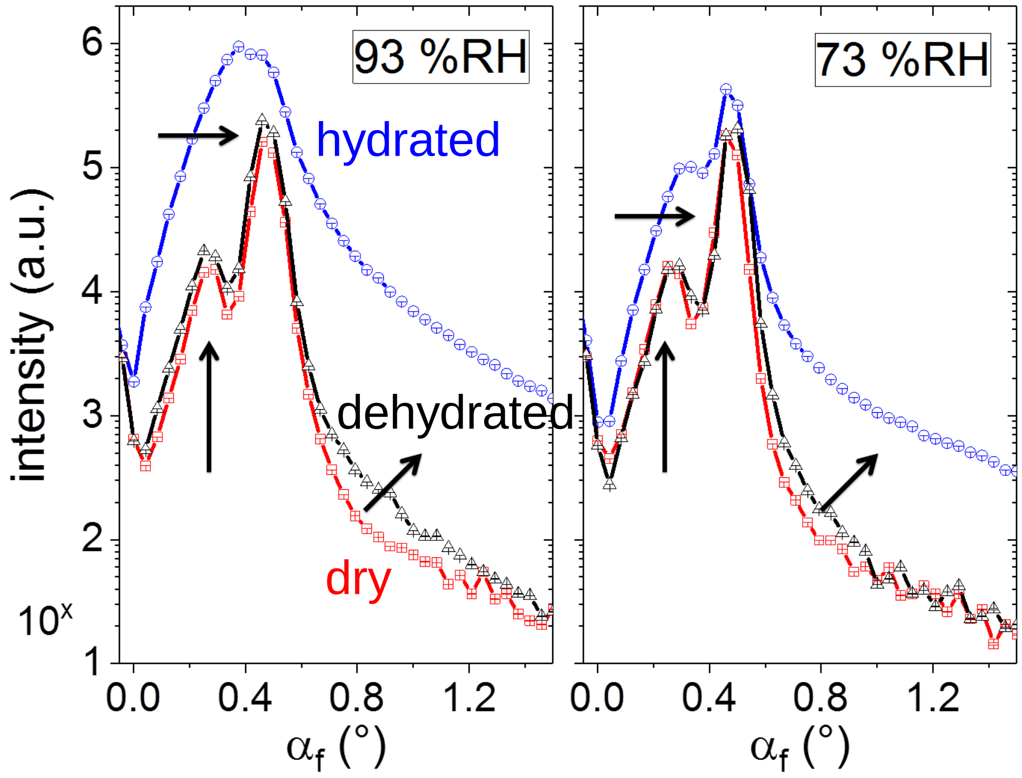
In-situ GISANS – high vs. low humidity conditions



J. Schlipf et al., *J. Phys. Chem. Lett.* **2018**, *9*, 2015

Snapshots from the highest humidity levels

in-plane cuts



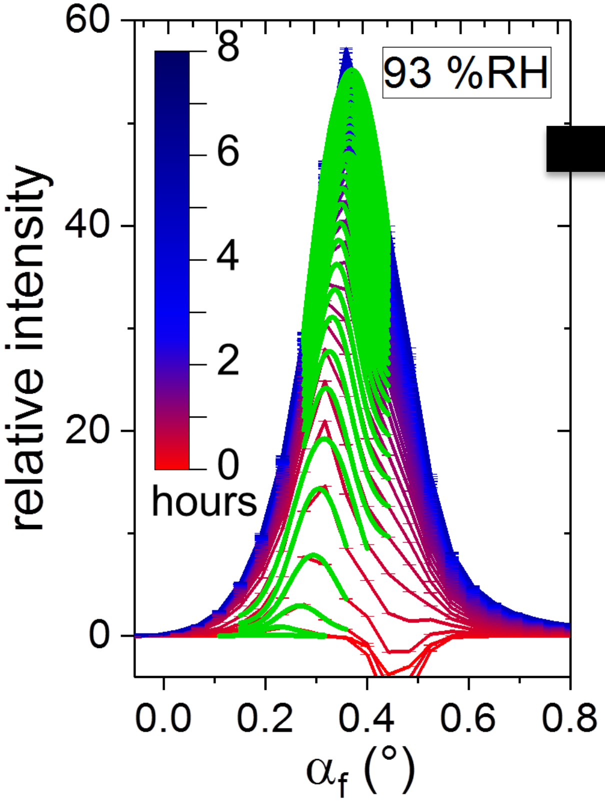
- strong shift of Yoneda peak for hydrated films
- higher roughness in dehydrated films than in dry ones
- PbI_2 formed for 93 %RH
- MAPI recovered for 73 %RH

➔ permanent morphological changes for high humidity levels

J. Schlipf et al., *J. Phys. Chem. Lett.* **2018**, *9*, 2015

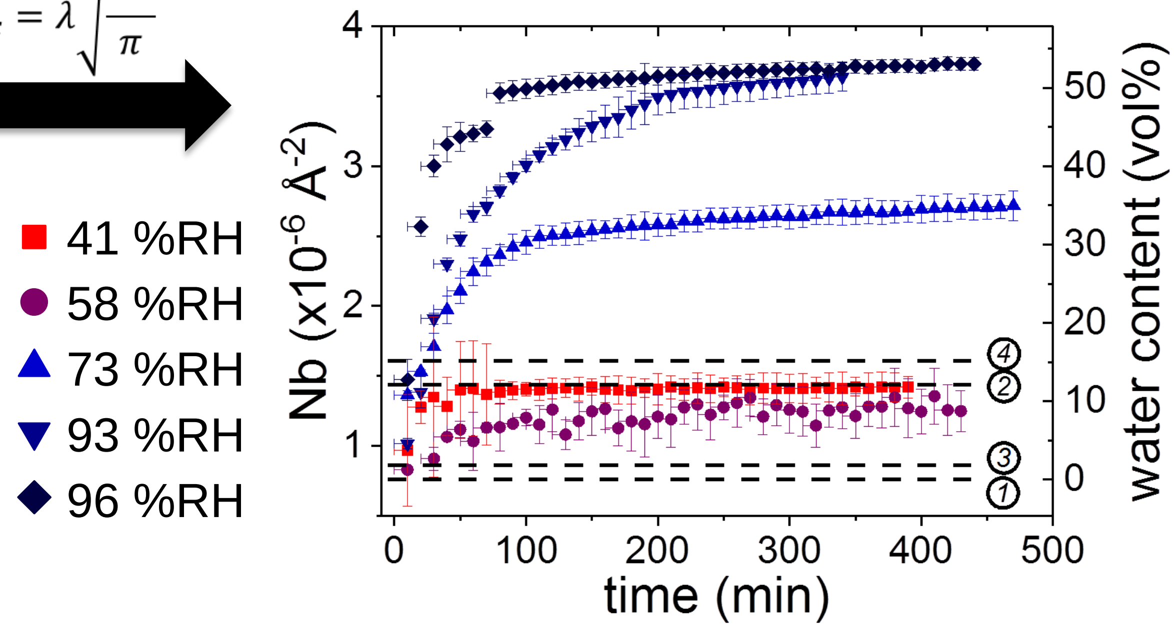
Following water uptake in situ

in-plane cuts – 1st frame



$$\alpha_c = \lambda \sqrt{\frac{Nb}{\pi}}$$

$$x \cdot Nb_{D2O} + (1 - x) \cdot Nb_{MAPI} = Nb_{mix}$$



- up to 50 vol% water uptake
- 10 vol% water uptake for low humidity

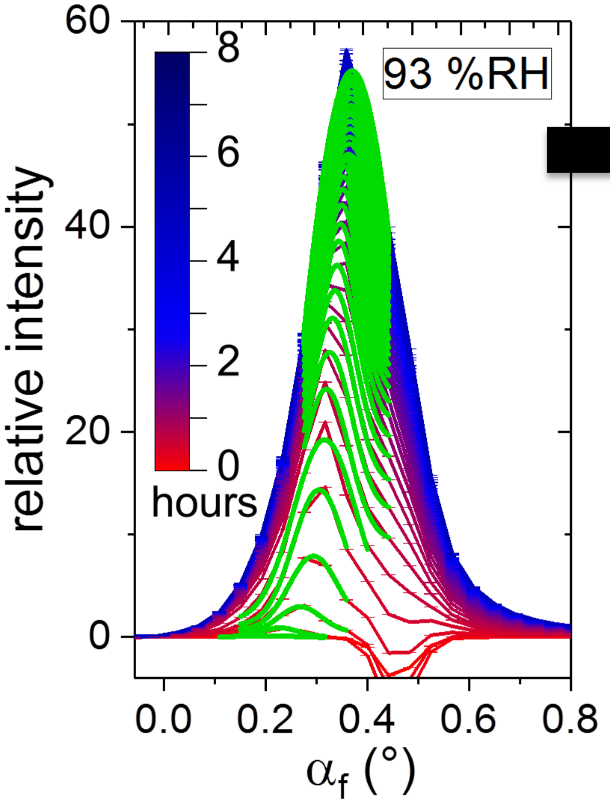
❶ MAPI ❸ dihydrate

❷ monohydrate ❹ PbI_2

J. Schlipf et al., *J. Phys. Chem. Lett.* **2018**, *9*, 2015

Following water uptake in situ

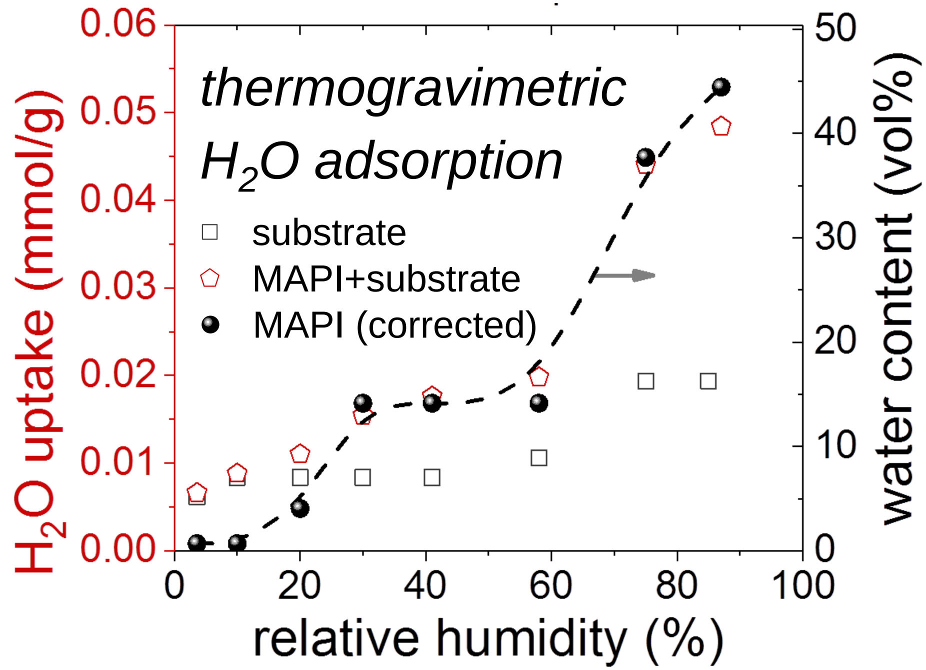
in-plane cuts – 1st frame



$$\alpha_c = \lambda \sqrt{\frac{Nb}{\pi}}$$

41 %RH
58 %RH
73 %RH
93 %RH
96 %RH

$$x \cdot Nb_{D2O} + (1 - x) \cdot Nb_{MAPI} = Nb_{mix}$$



❶ MAPI
❷ monohydrate
❸ dihydrate
❹ PbI_2

- up to 50 vol% water uptake
- 10 vol% water uptake for low humidity
- plateau ➔ intermediate saturation level

J. Schlipf et al., *J. Phys. Chem. Lett.* **2018**, *9*, 2015

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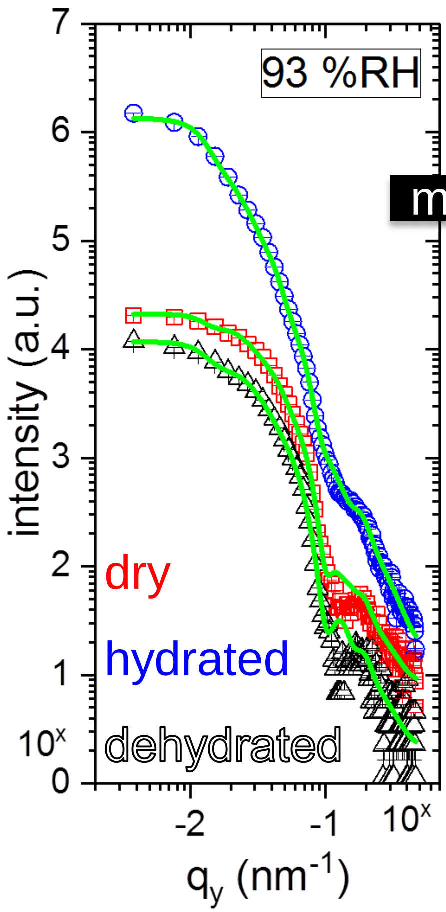
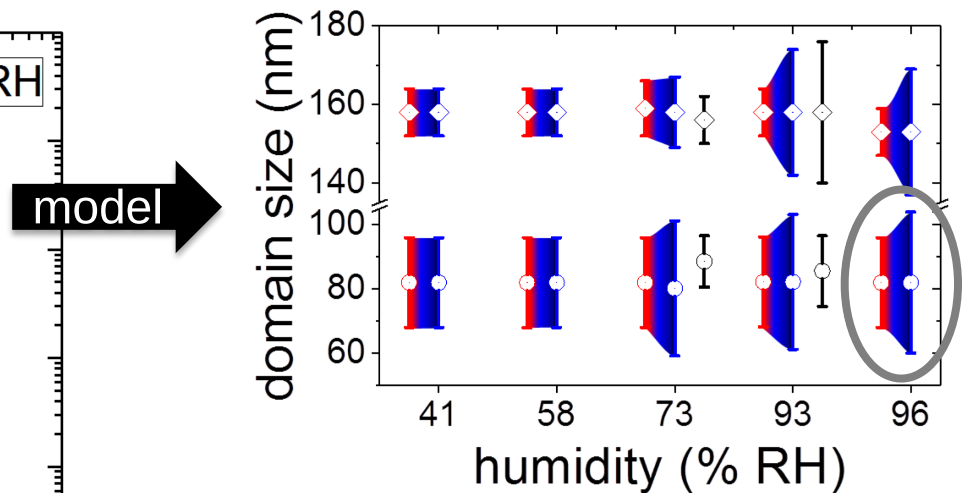
Morphological changes due to hydration



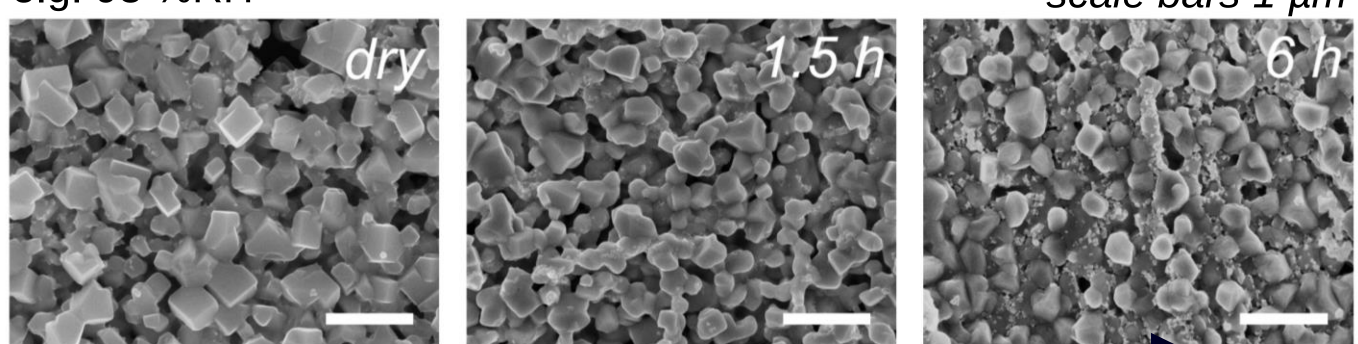


out-of-plane cuts

σ of Gaussian size distribution

e.g. 93 %RH

scale bars 1 µm



➔ domains become less defined for humidity levels ≥ 73 %RH

J. Schlipf et al., *J. Phys. Chem. Lett.* **2018**, *9*, 2015

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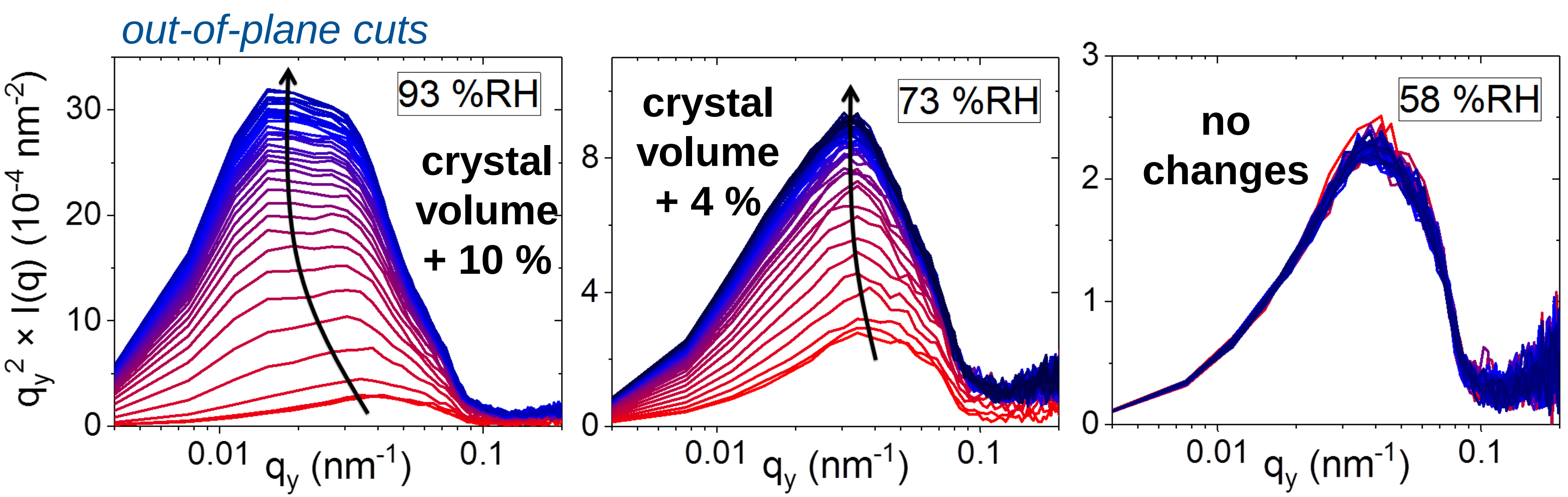
Crystal inflation reveals composition

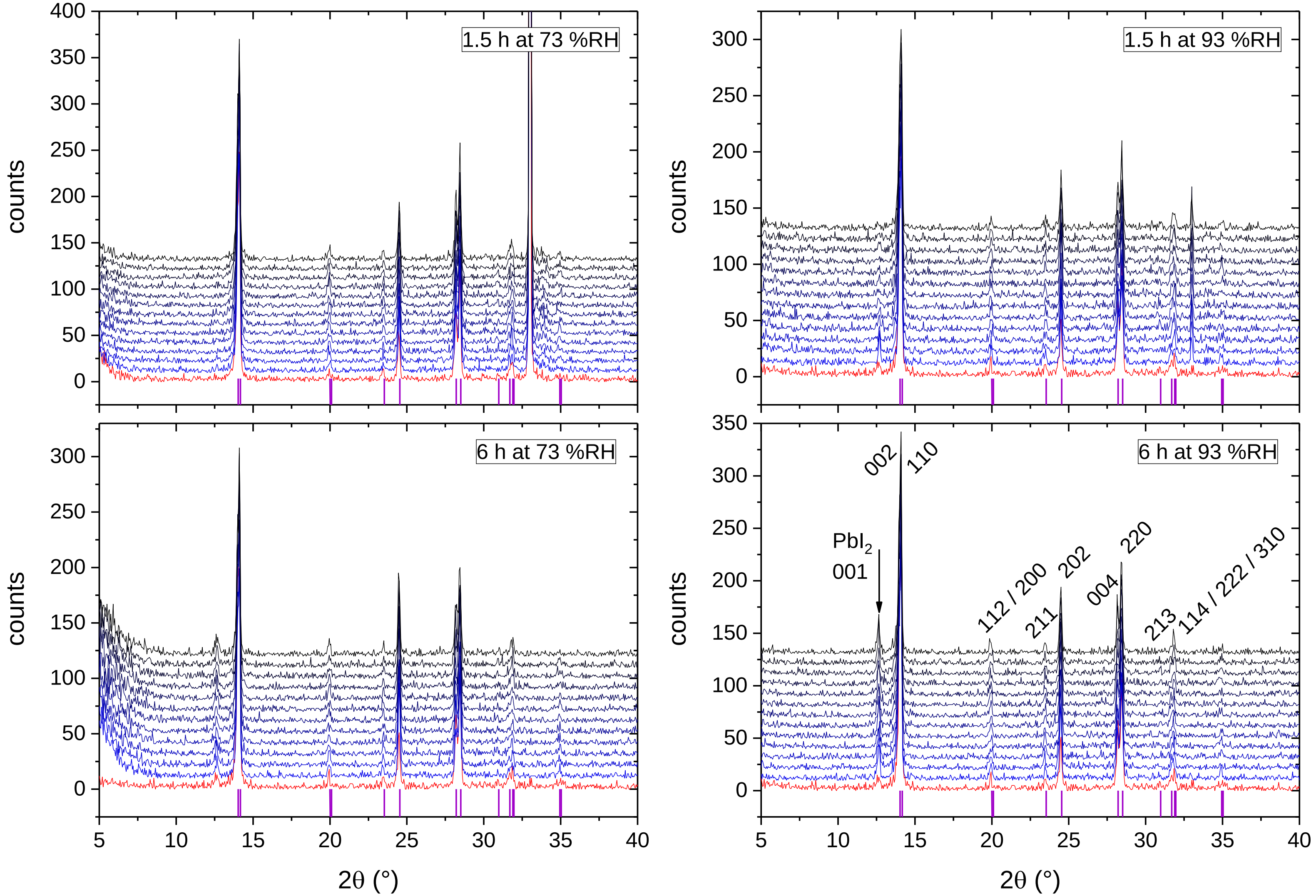


- Kratky representation reveals slight crystal inflation for first 1.5 h
- mostly monohydrate = MAPI volume + 7 % vs. dihydrate = MAPI × 250 %
- no apparent changes for humidity ≤ 58 %RH ➔ no monohydrate

➔ water for low humidity not incorporated into crystals

J. Schlipf et al., *J. Phys. Chem. Lett.* **2018**, *9*, 2015

In-situ XRD during dehydration



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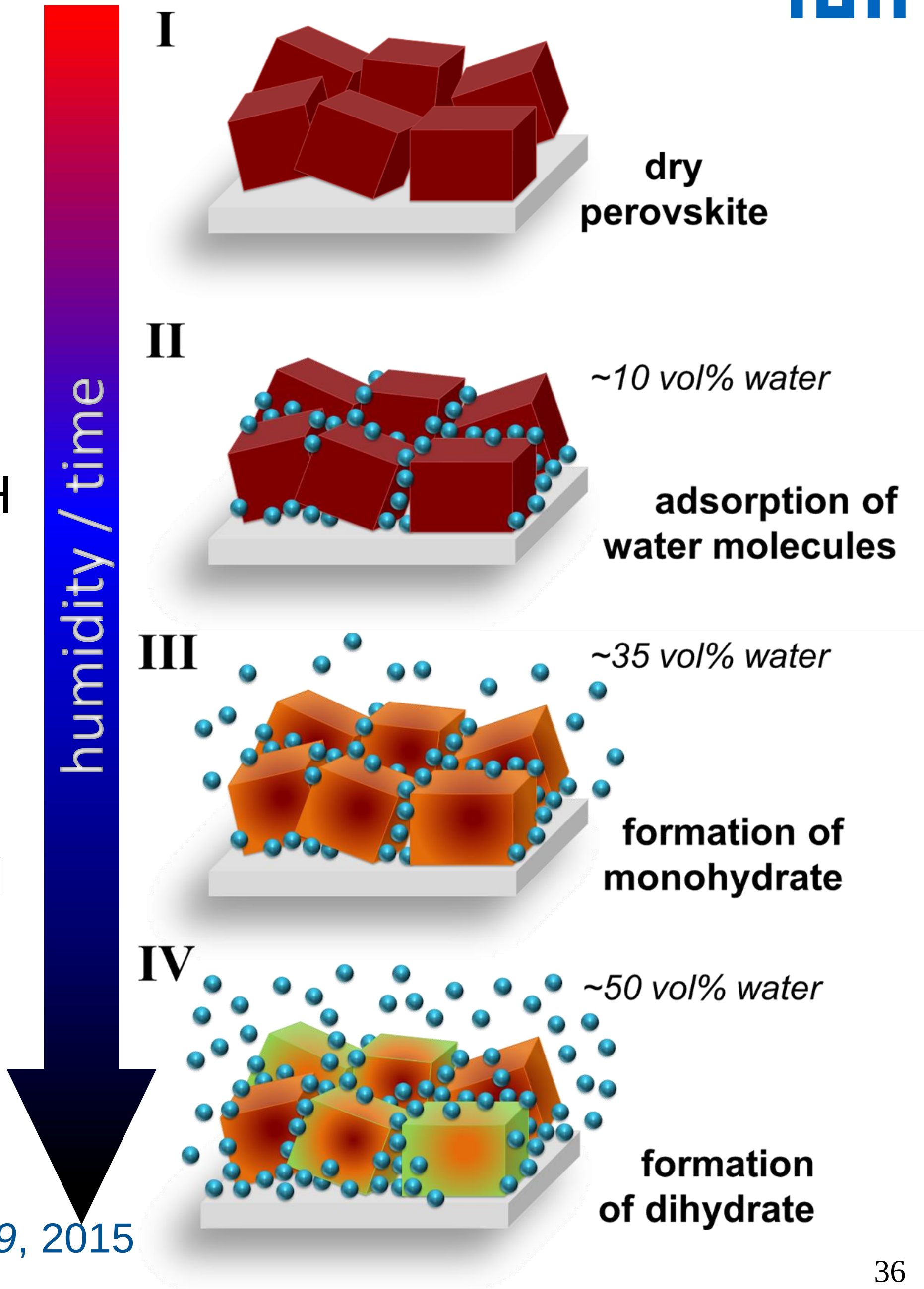
Conclusions

- in-situ GISANS with high time resolution
- ingression of moisture at low %RH
  ➔ level of monohydrate
  ➔ no hydrates formed
  ➔ most water adsorbed
- sponge-like behavior at high %RH
  ➔ strong morphological changes of crystal domains for ≥ 73 %RH
  ➔ formation of hydrates



J. Schlipf et al., *J. Phys. Chem. Lett.* **2018**, *9*, 2015

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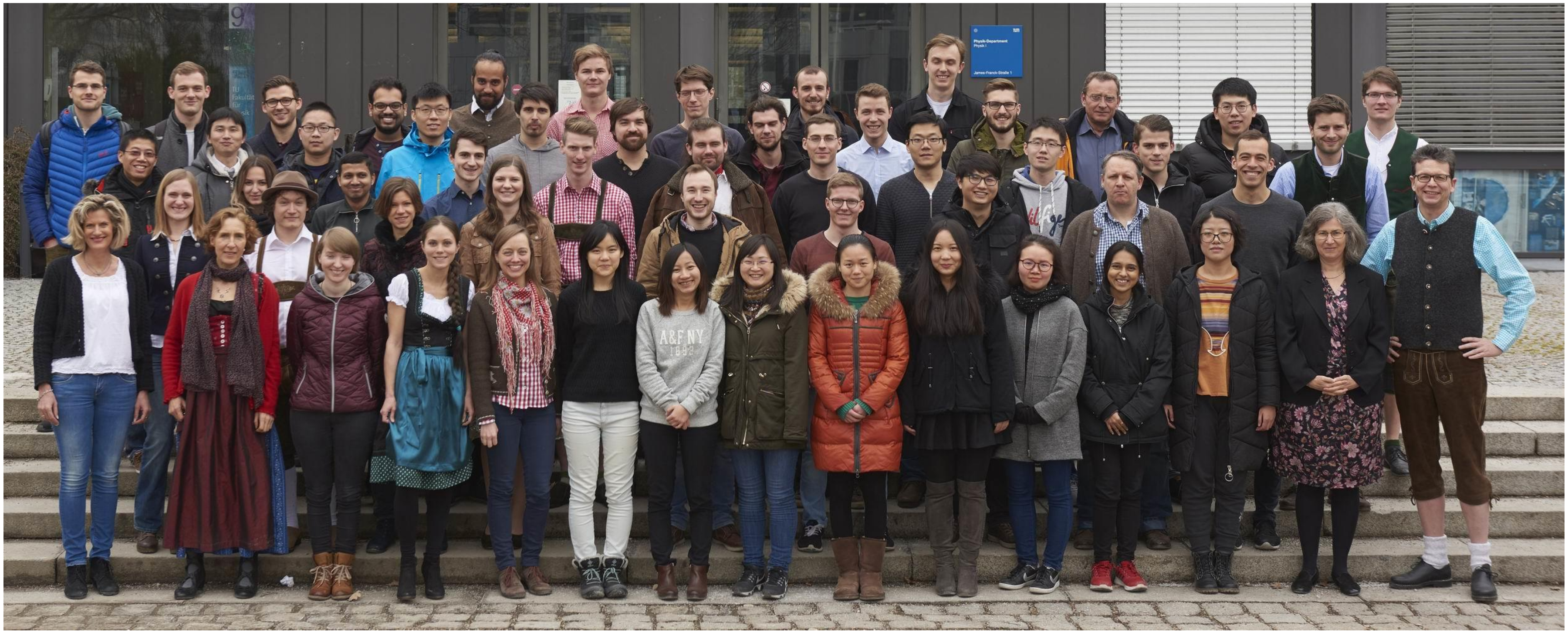

Federal Ministry of Education and Research

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