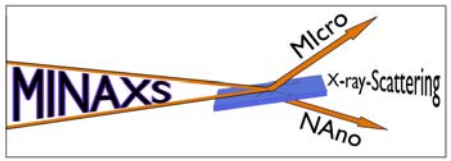
GISAXS

Development and applications using nanobeams, microbeams and tomography



Stephan V. Roth

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XDL-Workshop Cornell, June 27&28, 2011

HELMHOLTZ GEMEINSCHAFT

DESY

Outline

- ***G***razing ***I***ncidence ***S***mall-***A***ngle ***X***-ray ***S***cattering
  - Application to Metal-Polymer Nanocomposites
  - Optics
- Scanning experiments
  - Nanobeams – ID13 / ESRF

    Gradients [500nm]
    Classification [300nm]
  - Microbeams – BW4 / DESY

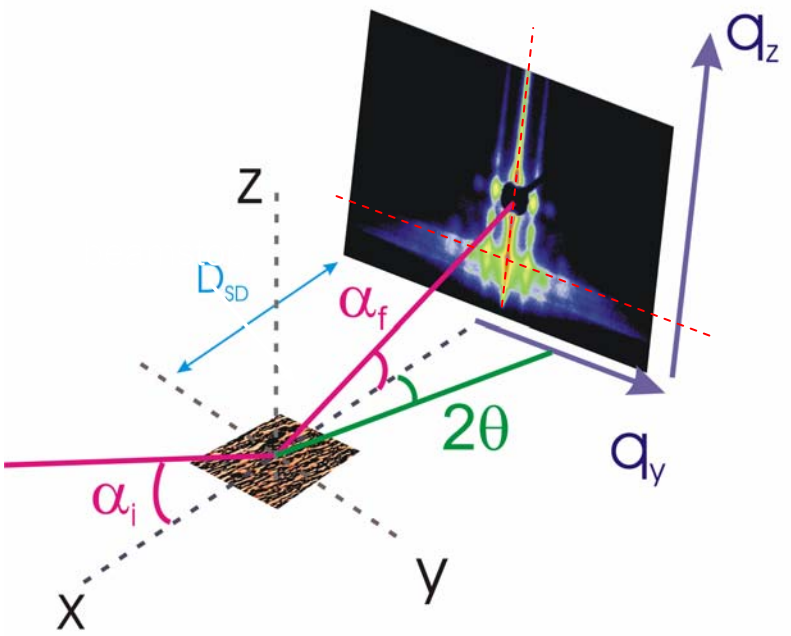
    Tomography – 30µm
- In-situ Kinetics
  - Nanobeams – droplet deposition [ID13 / ESRF – 300nm]
  - µGISAXS & imaging ellipsometry [MiNaXS / DESY – 10µm]
- Sputter deposition
  - In-situ observation of industrial style deposition of gold [MiNaXS / DESY – 10µm]
- Outlook
  - Nanofocus @ MiNaXS [300nm]

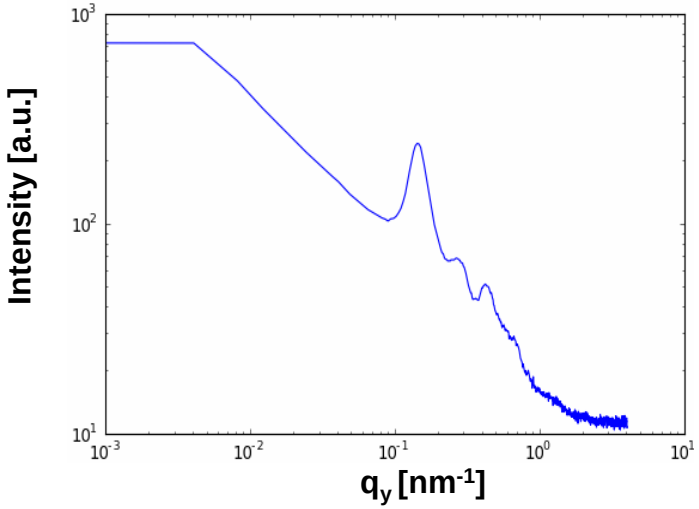
Grazing incidence small-angle x-ray scattering

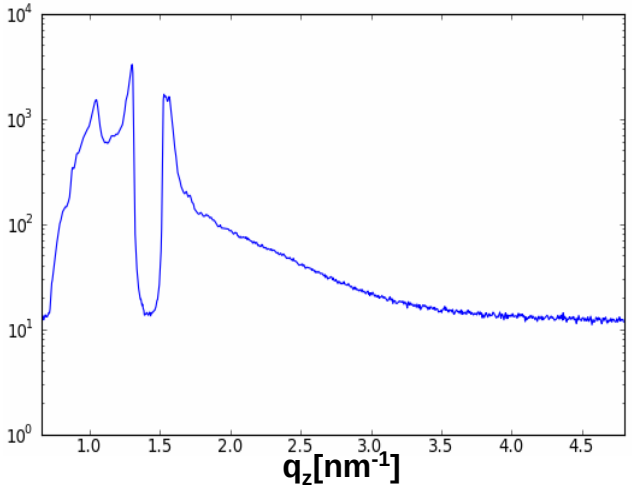
- X-ray µ/n-beam
- Scanning
  - Homogeneity
- Kinetics
  - Time resolution

2D detector:

- PILATUS 300k
- MARCCD 165







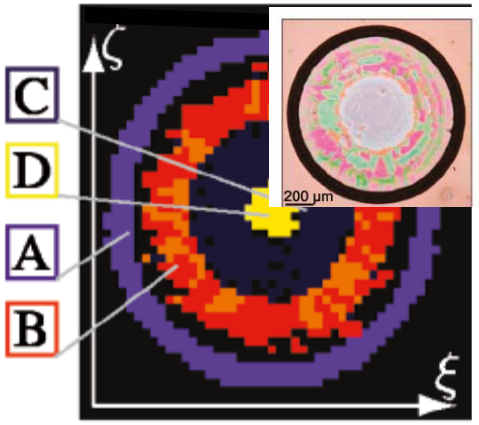
Mueller-Buschbaum, Springer Berlin, ISBN-13: 978-3-540-95967-0 (2009)

Roth et al., Rev. of Sci. Instr. **77**, 085106 (2006)

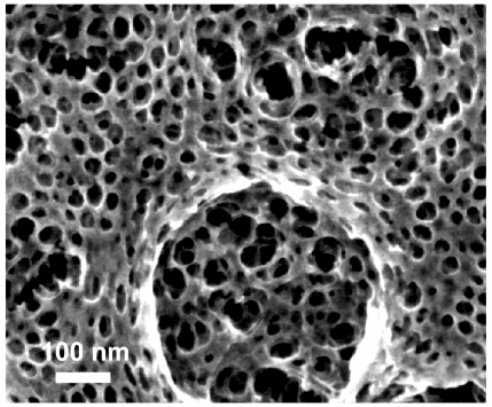
Motivation : Polymer-Metal nanocomposites

- Polymer:
  - low cost fabrication
  - mechanical flexibility, …
- Metal:
  - electronic properties
  - magnetic properties,
- Organic optics and electronics
- Hybrid sensors
- Photonics
- Use of colloids
- **Spray/spin coating solution casting**
- **Magnetron sputter deposition** Functional metal film

- Designed colloidal thin films and arrays:
  - Surface enhanced Raman scattering (SERS)
  - Inclusion of nanoparticles in photovoltaic devices:increase of light harvesting efficiency



Kuhlmann et al., Langmuir **25** 7241 (2009)



Kaune et al.,
ACS Appl. Mater. Inter.**1**, 2862 (2009)

- Fundamental issues
  - Nanocomposite structure?
  - Metal film growth mechanisms?
  - Interaction with the underlying polymer template?

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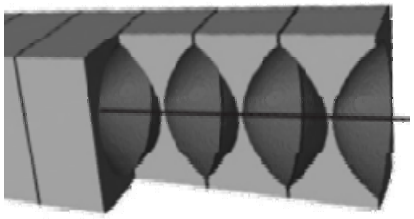
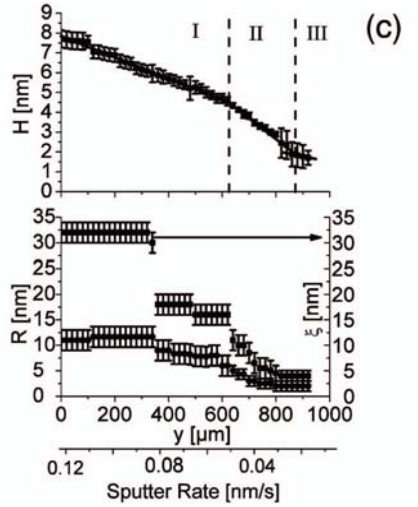
GISAXS and Microbeams

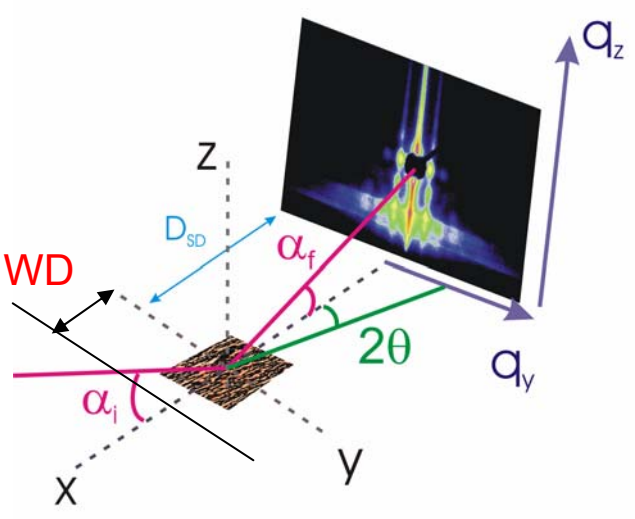
- Working distance (WD) ~ 10cm… >1m ➔ Low divergence
- We use Be CRL.
- Example: BW4, ID13, P03

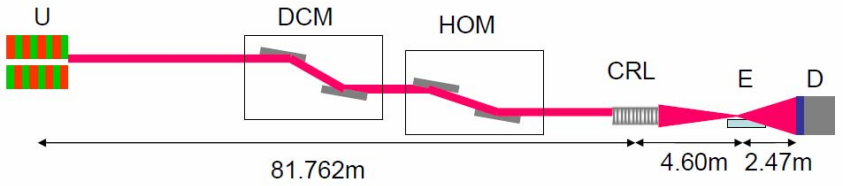


Schroer



Roth et al., Appl. Phys. Lett 88, 021910 (2006)



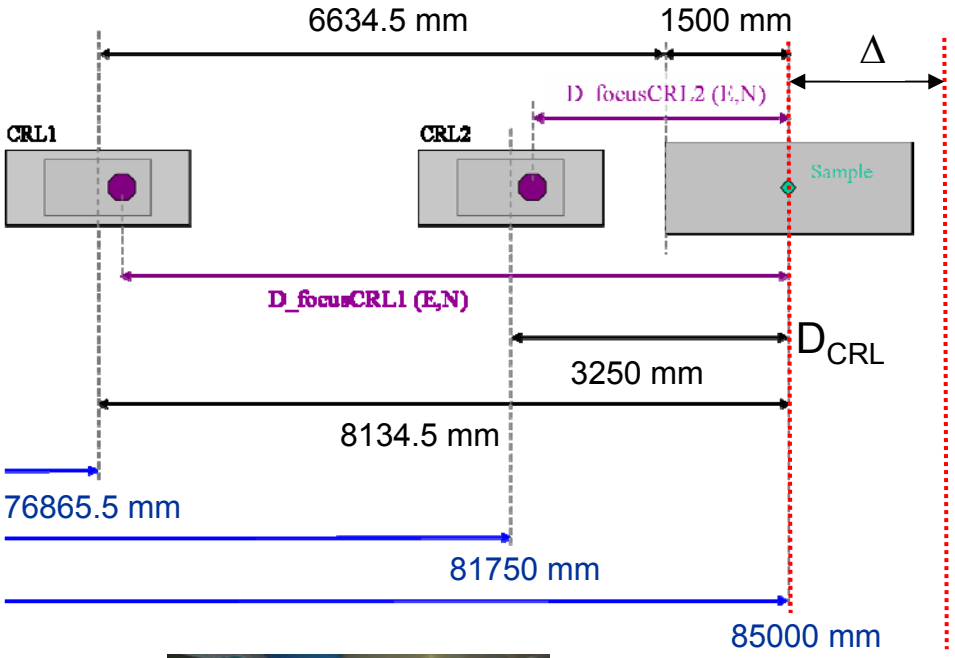


Roth et al., J. Phys.: Condens. Matter 23 (2011) 254208

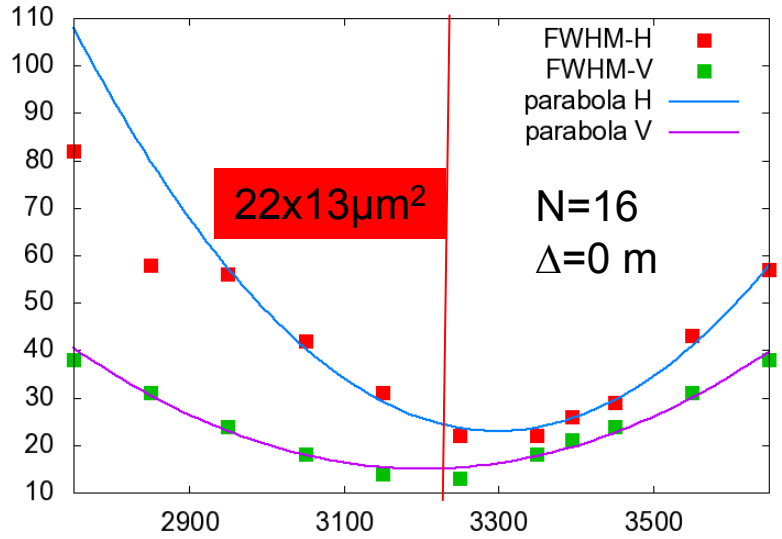
Roth et al., Rev. of Sci. Instr. 77, 085106 (2006)

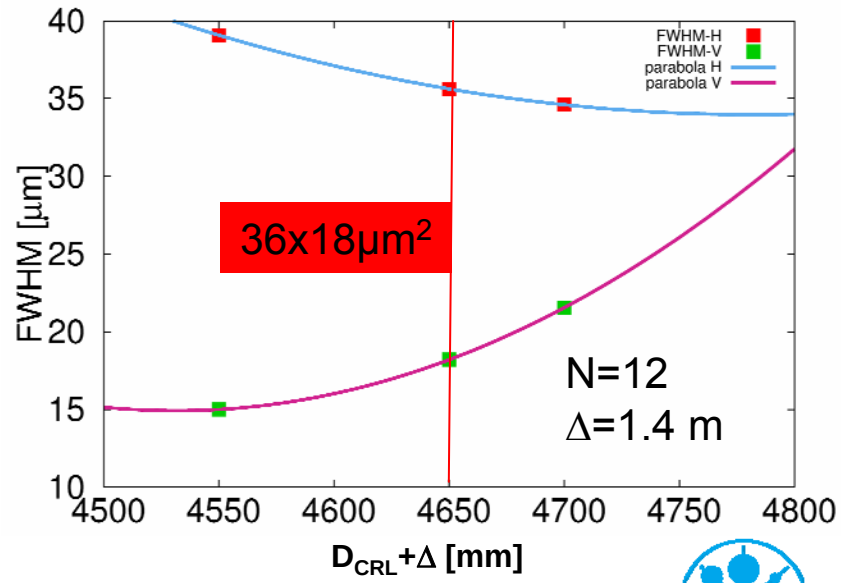
The nice thing about BeCRLs – the supertransfocator

- Optimizing the focal spot
  - Adjustable number of BeCRLs
  - Longitudinal translation (1m)
  - Fully automatic



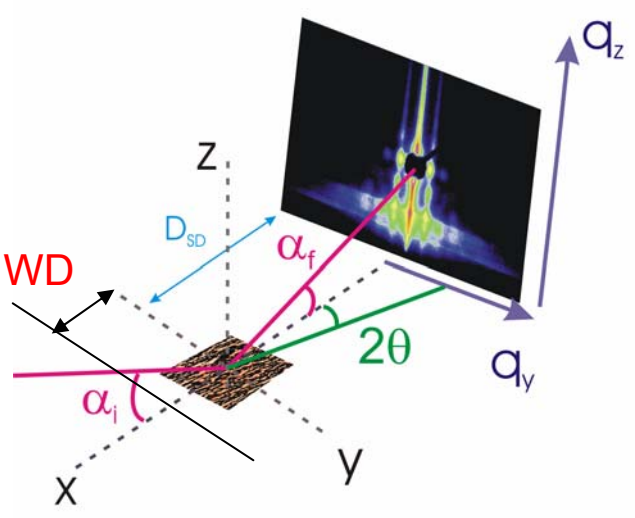
~5x10^{11} ph/s

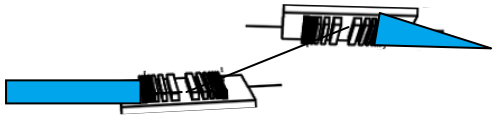


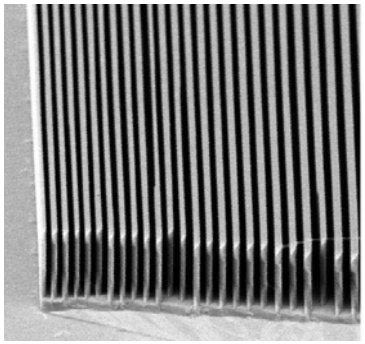


GISAXS and Nanobeams

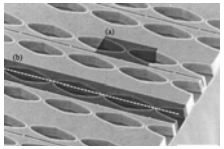
- Working distance (WD) ~ cm
- Possibilities:
  - FZP
  - NFL
  - KB mirrors

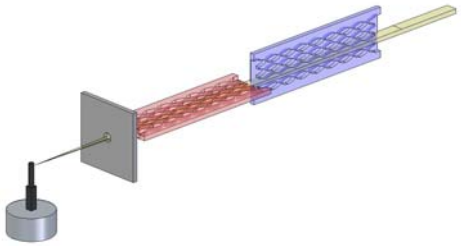






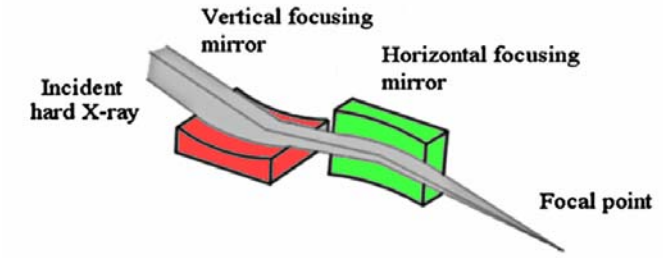
David et al., Micro. Eng.61–62 (2002) 987–992





Boye et al., J. Phys.: 186 (2009) 012063

Schroer et al., Appl. Phys. Lett. 82, 1485 (2003)



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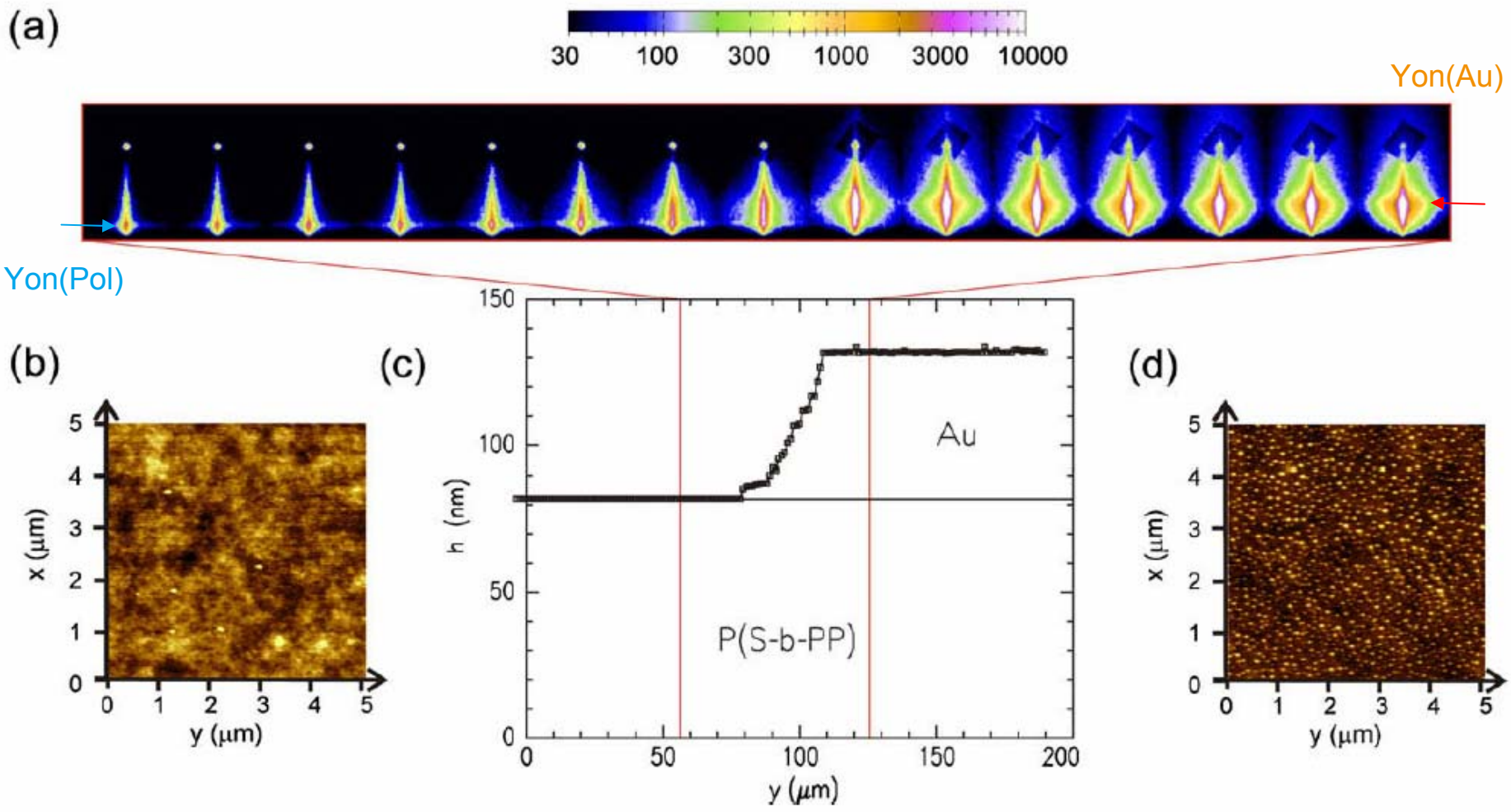
Gold contacts

Ruderer et al., Nucl. Instr. Meth. B **268**, 403 (2010)

> Au on diblock film

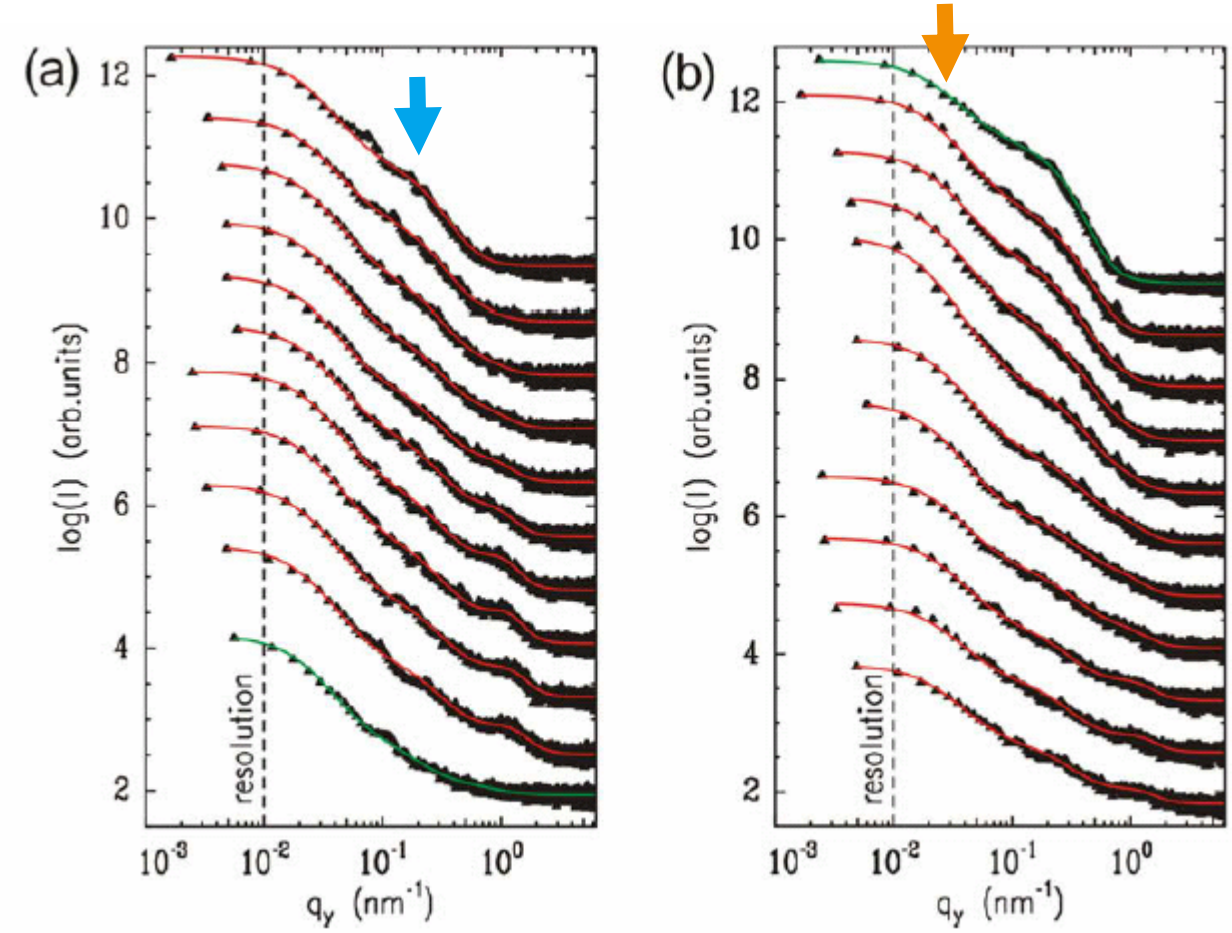


Results – selective doping

Ruderer et al., Nucl. Instr. Meth. B **268**, 403 (2010)

> Different length scales:

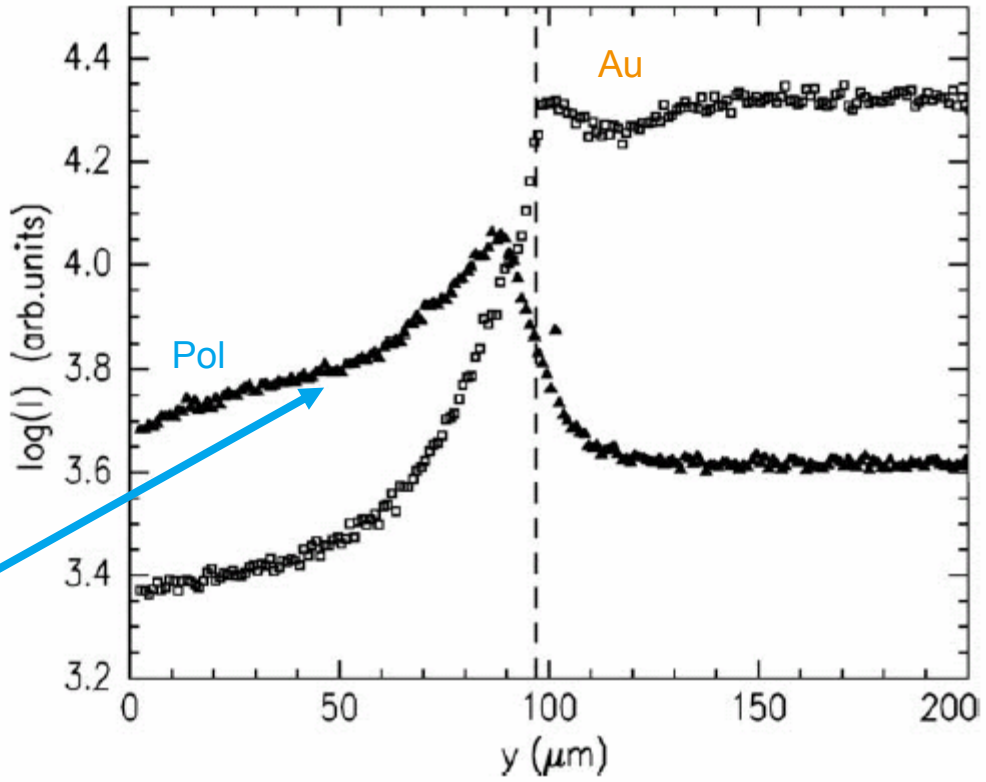
- **d_1(Pol)=19nm**
- **d_1(Au)=200nm**



Results – selective doping

Ruderer et al., Nucl. Instr. Meth. B **268**, 403 (2010)

- Different length scales:
  - **d_1(Pol)=19nm**
  - **d_1(Au)=200nm**
- increase in internal contrast
- diffusion of gold atoms inside the P(S-b-PP) film
- selective attraction of gold to one of the two blocks: increase in internal contrast



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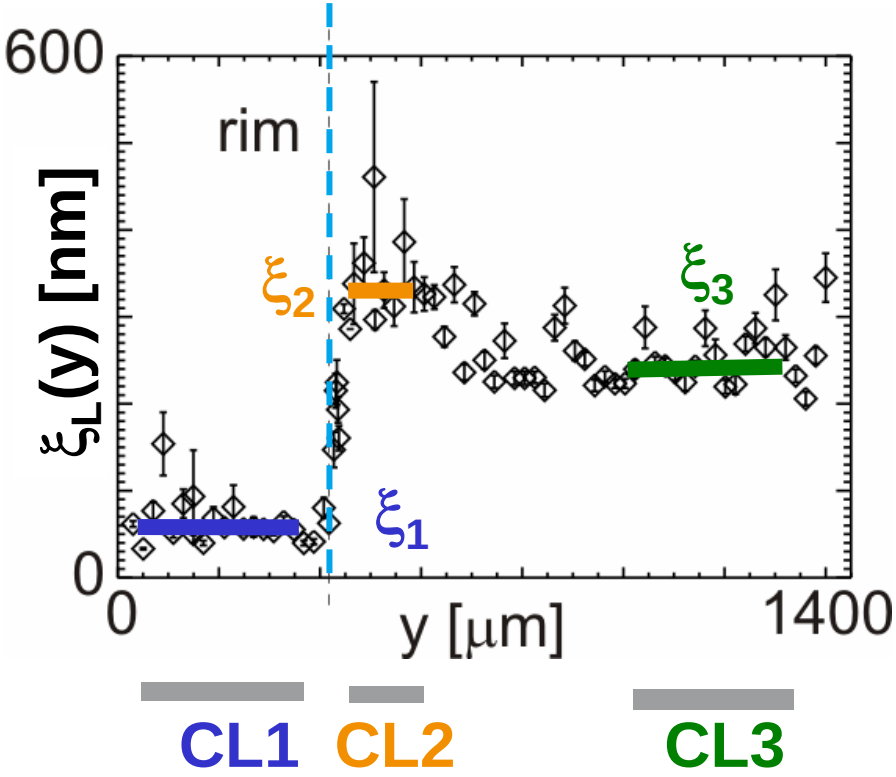
Supervised classification

Roth et al., Langmuir 26, 1496 (2010)
Müller-Buschbaum et al., J. Phys. Cond Matter **23**, 184111 (2011)

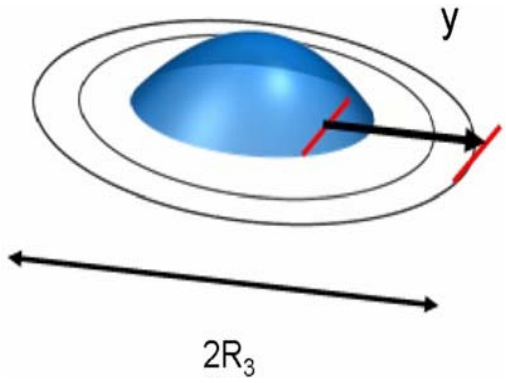
> Scanning, 5nm colloids

$$\xi_L(y)=P_1(y)\xi_1+P_2(y)\xi_2+P_3(y)\xi_3$$



> Grouping into three classes

> Probability: $P_{1,2,3}(y)$



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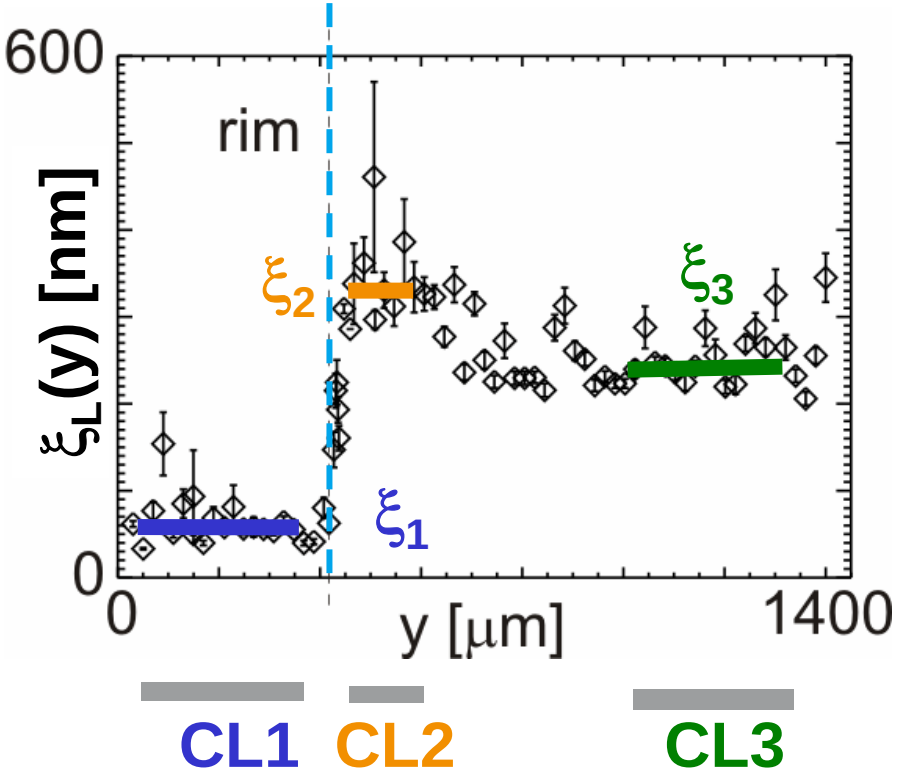

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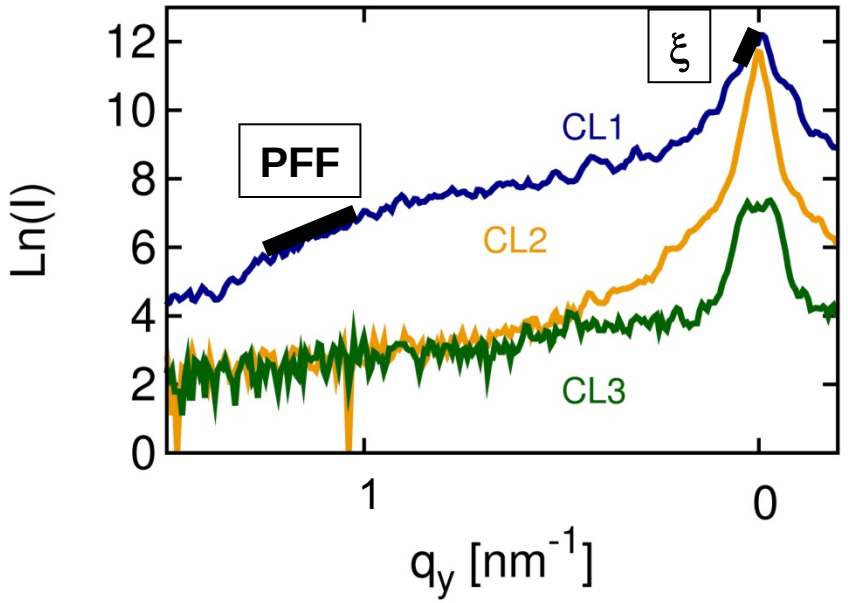

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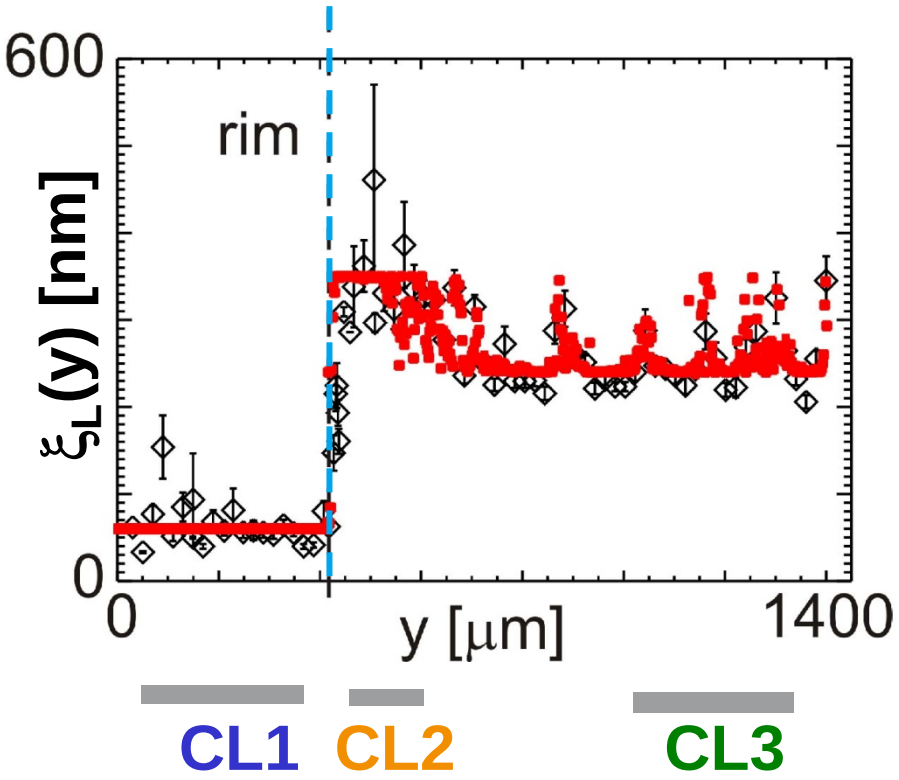

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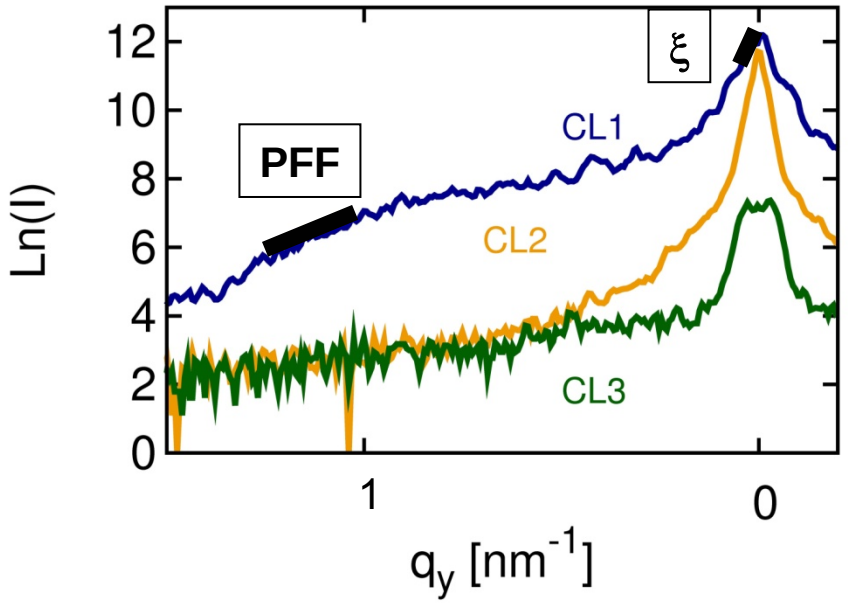

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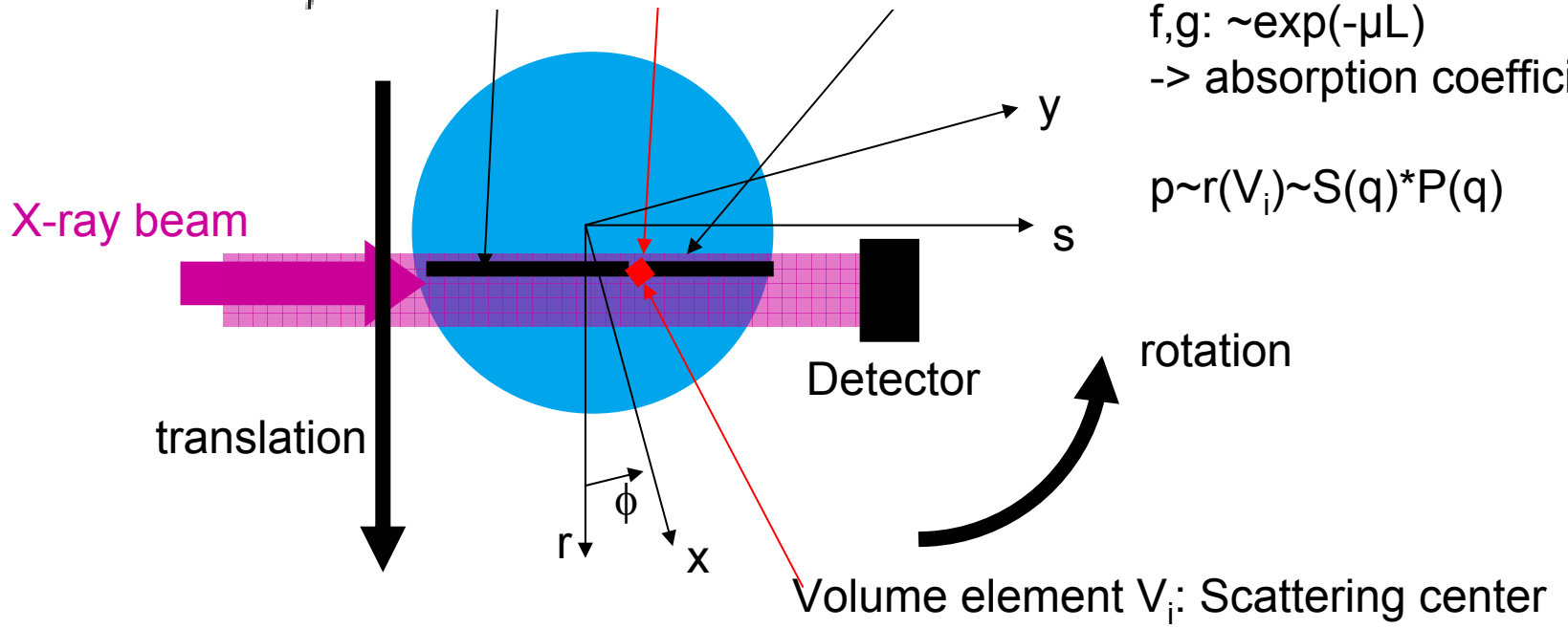
SAXS-Tomography

> Tomography => 3D reconstruction of objects

$$I_{\mathbf{q}}(r,\phi) = I_0 \int ds f(\phi,s,r) p_{\mathbf{q},\phi}(x,y) g(\phi,s,r)$$



f,g: ~exp(-μL)
-> absorption coefficient μ

p~r(V_i)~S(q)*P(q)

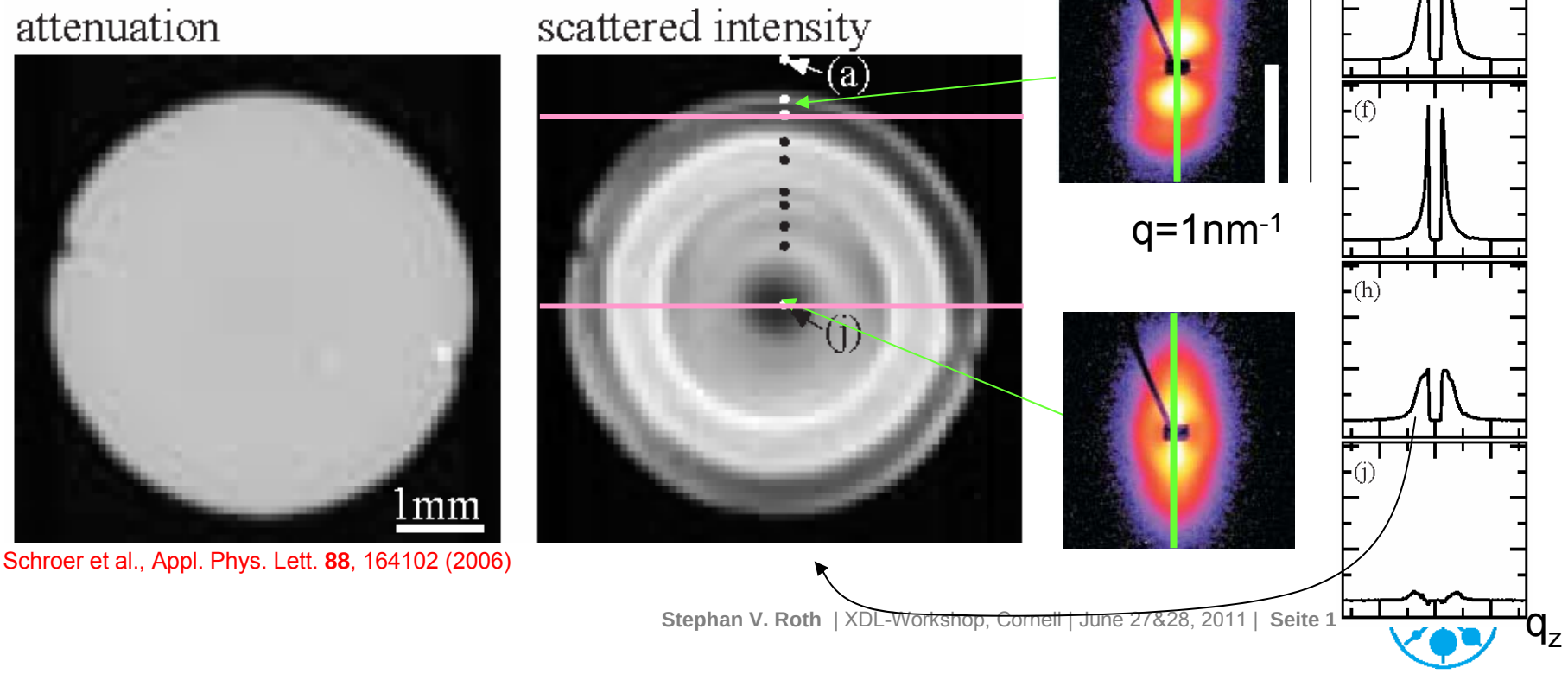
- Greek: *tomé* (cut) & *gráphein* (write, draw)
- Produce a virtual cut through object without actual slicing
- Mathematical technique for extracting a certain feature, e.g. absorption coefficient from the object, starting from integral of this feature.

Results

- For each translation and rotation (r,ϕ) => one value for $I_q(r,\phi)$
- Solve system of linear equations to extract $p_{q,\phi}$
- Integral of curve = grey scale

$$I_{\mathbf{q}}(r,\phi) = I_0 \int dsf(\phi,s,r)p_{\mathbf{q},\phi}(x,y)g(\phi,s,r)$$

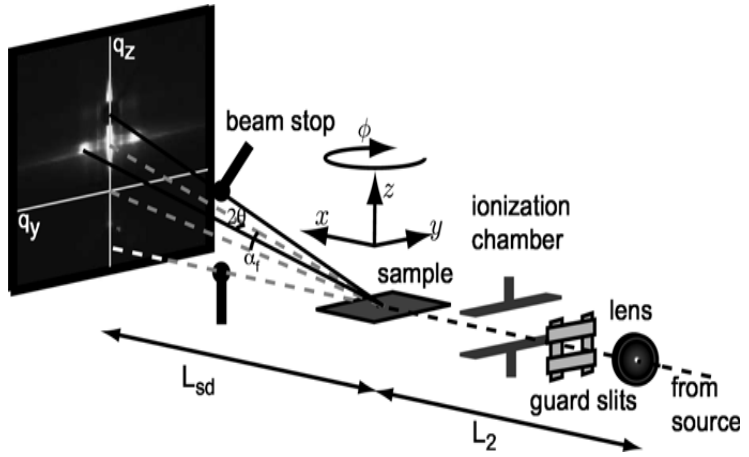
SAXS cross section



Schroer et al., Appl. Phys. Lett. **88**, 164102 (2006)

GISAXS-tomography - microbeam

- Colloidal PS spheres
- Ring-like structure
- Different arrangements



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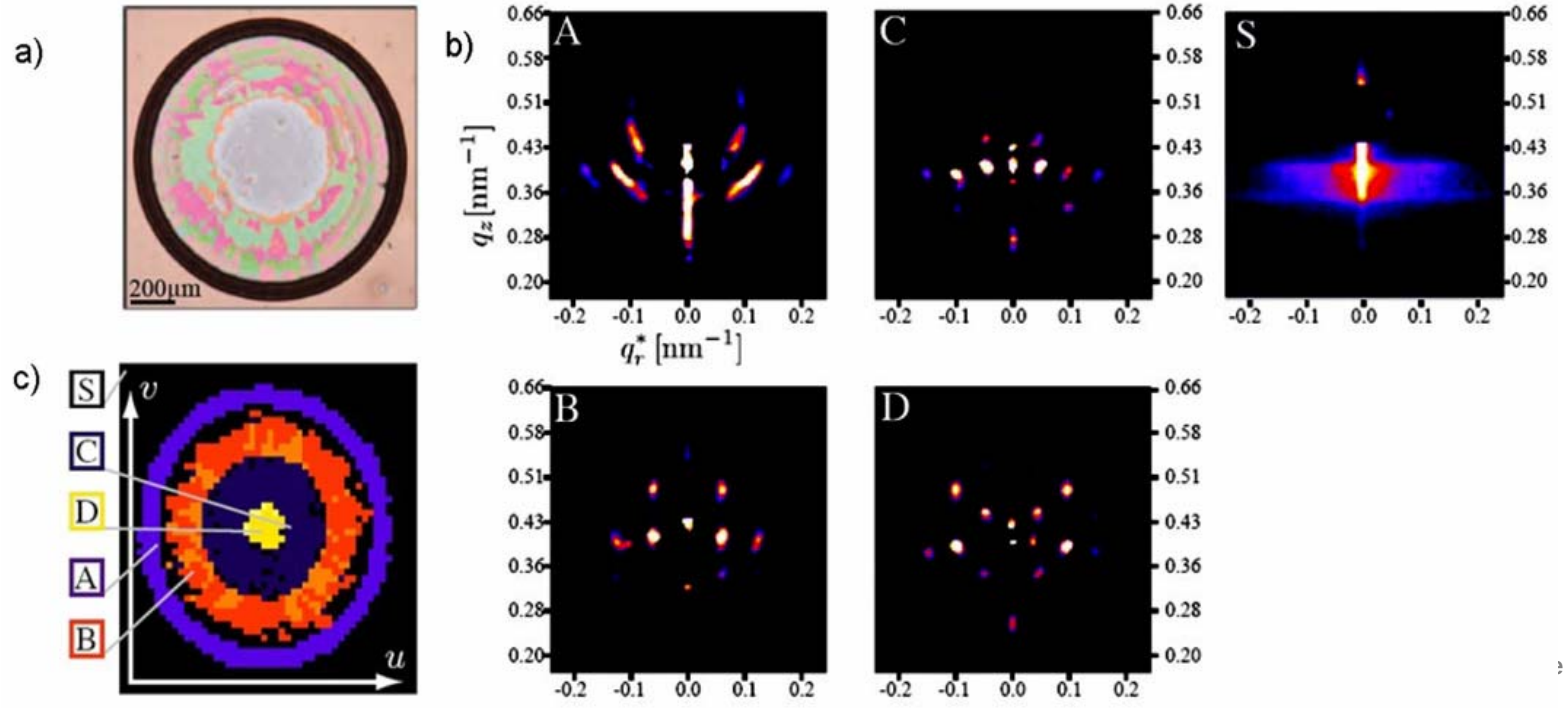

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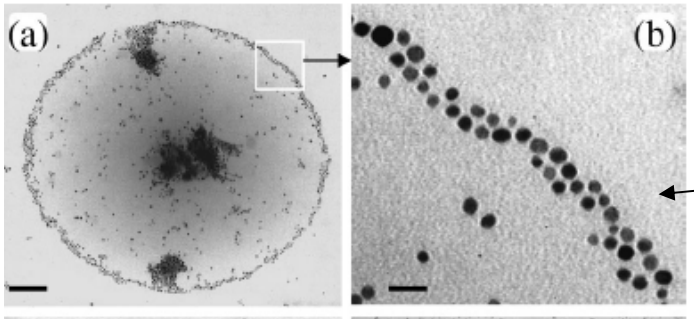
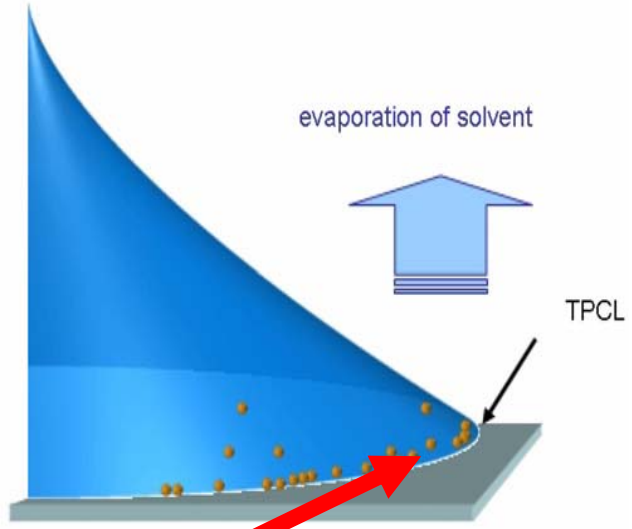
In-situ nanostructuring from solution

> Circuits, solar cells -> printing: electrodes, cost reduction



Govor et al., Phys. Rev. E **69**, 061609 (2004)



Decreased temperature

Increased nanoparticle concentration
Convective flow

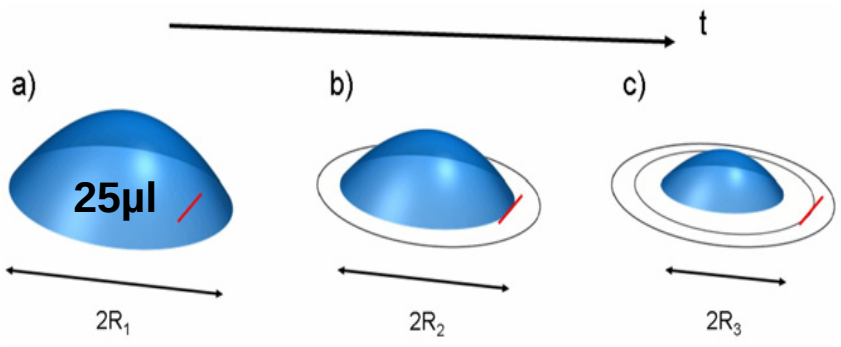
Capillary forces / dewetting

> Control drying-up of colloidal solution layer during inkjet printing

> Critical step: Transfer of order to substrate

Real-time results: nanoGISAXS/ ID13 ESRF

Roth et al., Appl. Phys. Lett. **91**, 091915 (2007)



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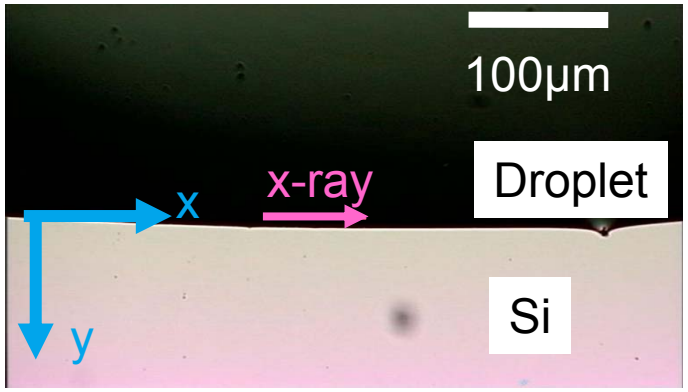

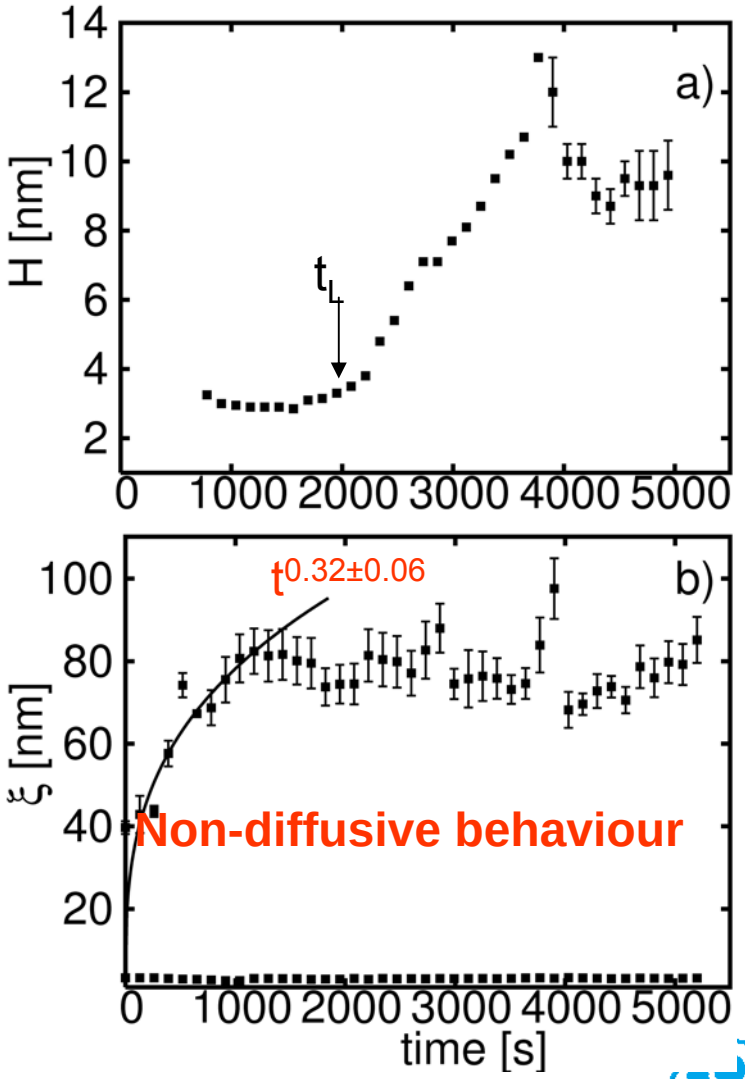

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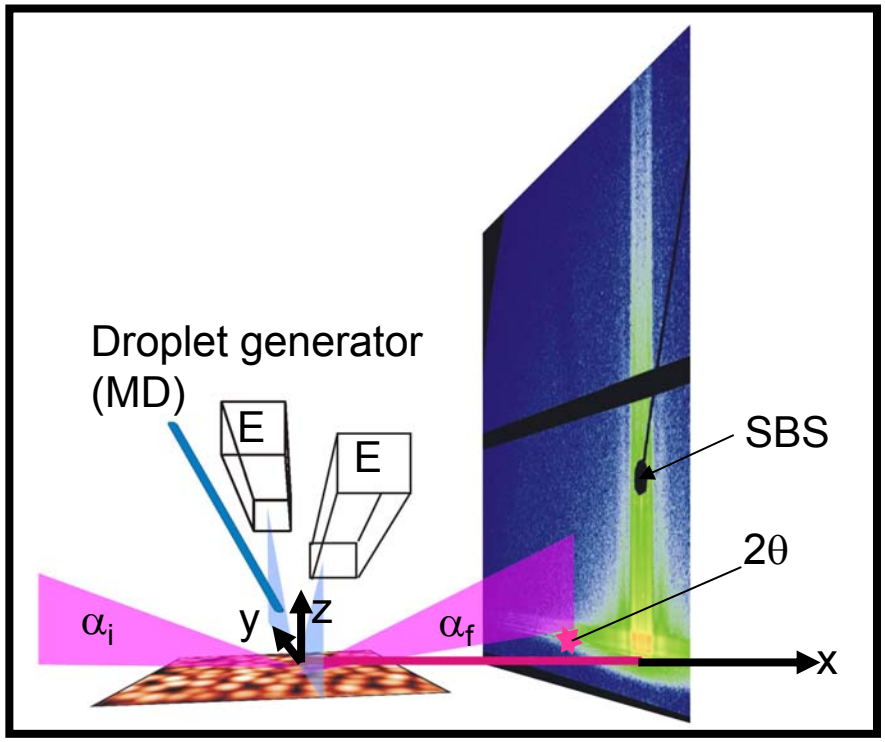
µGISAXS & Imaging ellipsometry

> µGISAXS

- Visualization of nanostructure



- α_i=0.45°
  λ=0.096 nm, t_{acq}=5 s
  D_{SD}=2470 mm
  Beam size (HxV): 35x22 µm^2

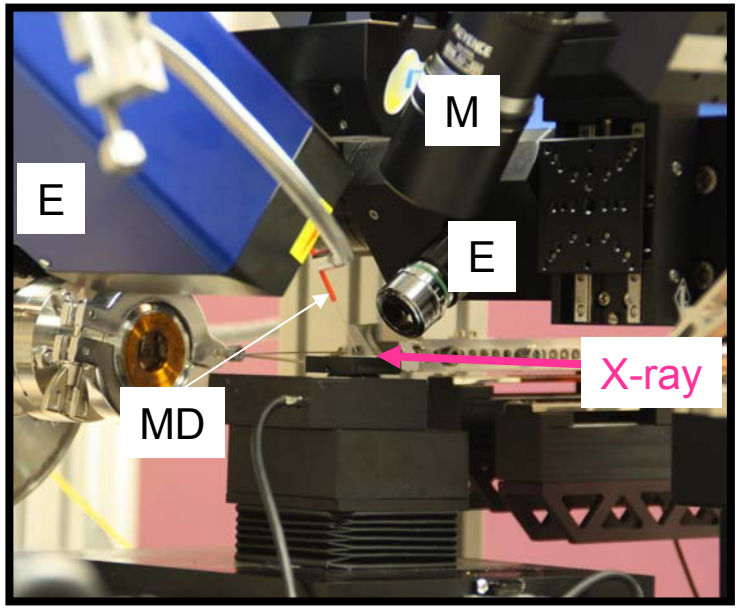
Körstgens et al.,Anal. Bioanal. Chem. **396**, 139 (2010)

Roth et al., J. Phys.: Condens. Matter **23**, 254208 (2011)

> Imaging Ellipsometry

- Real space visualization
- Optical parameters

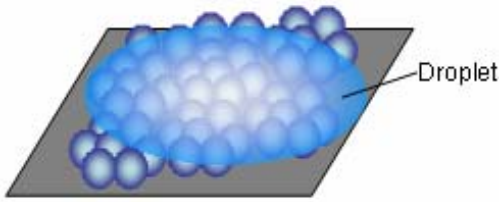
(BMBF-Verbundforschung, TUM: P. Müller-Buschbaum)

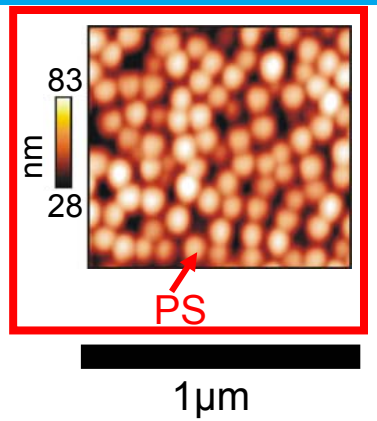


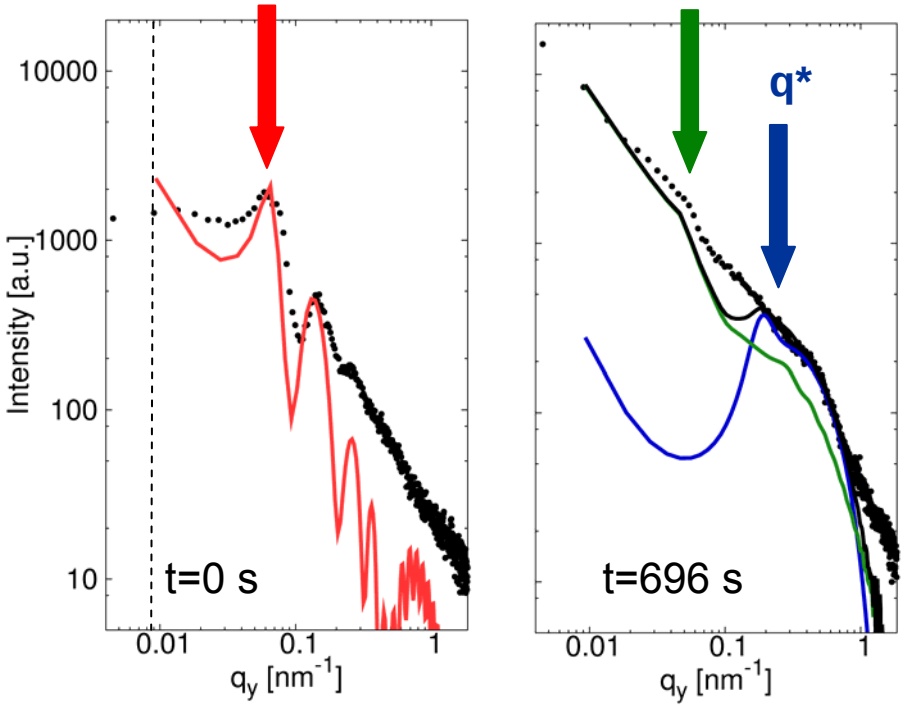
- AOI = 55°
  λ_{LASER}: 532 nm
  FOV: 201 µm x 263 µm
  PCSA configuration

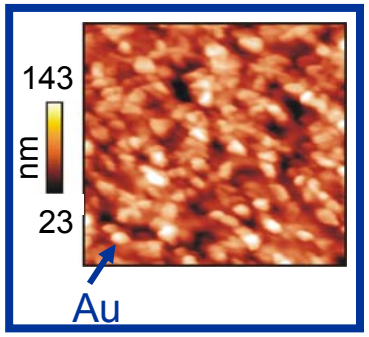
Structural characterization – solution casting

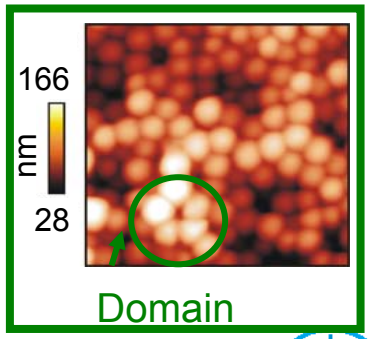
- Droplet Au(20 nm) / H_20 on PS colloidal template
- Colloidal particles
  - Domain ordering
  - Clear identification in µGISAXS and AFM







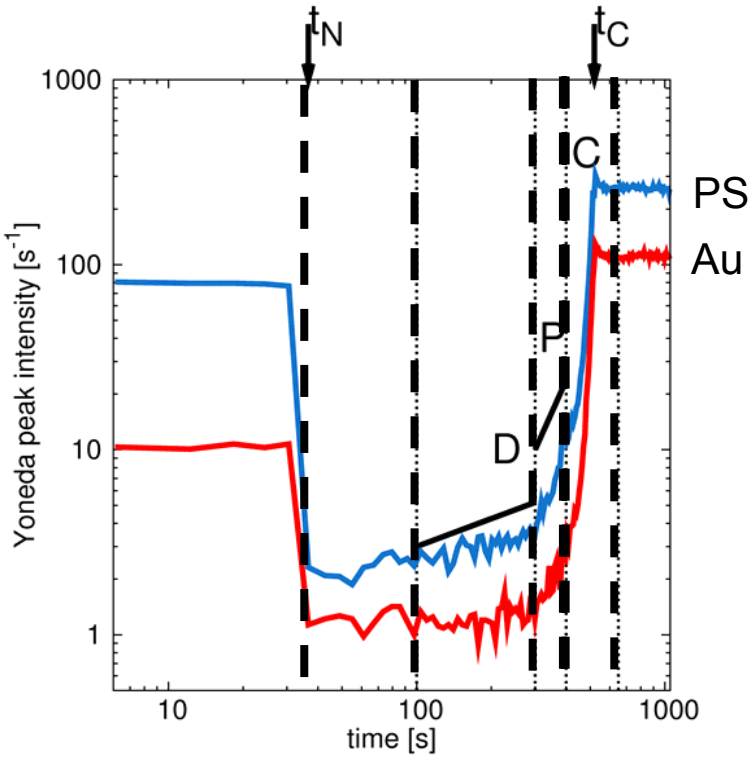




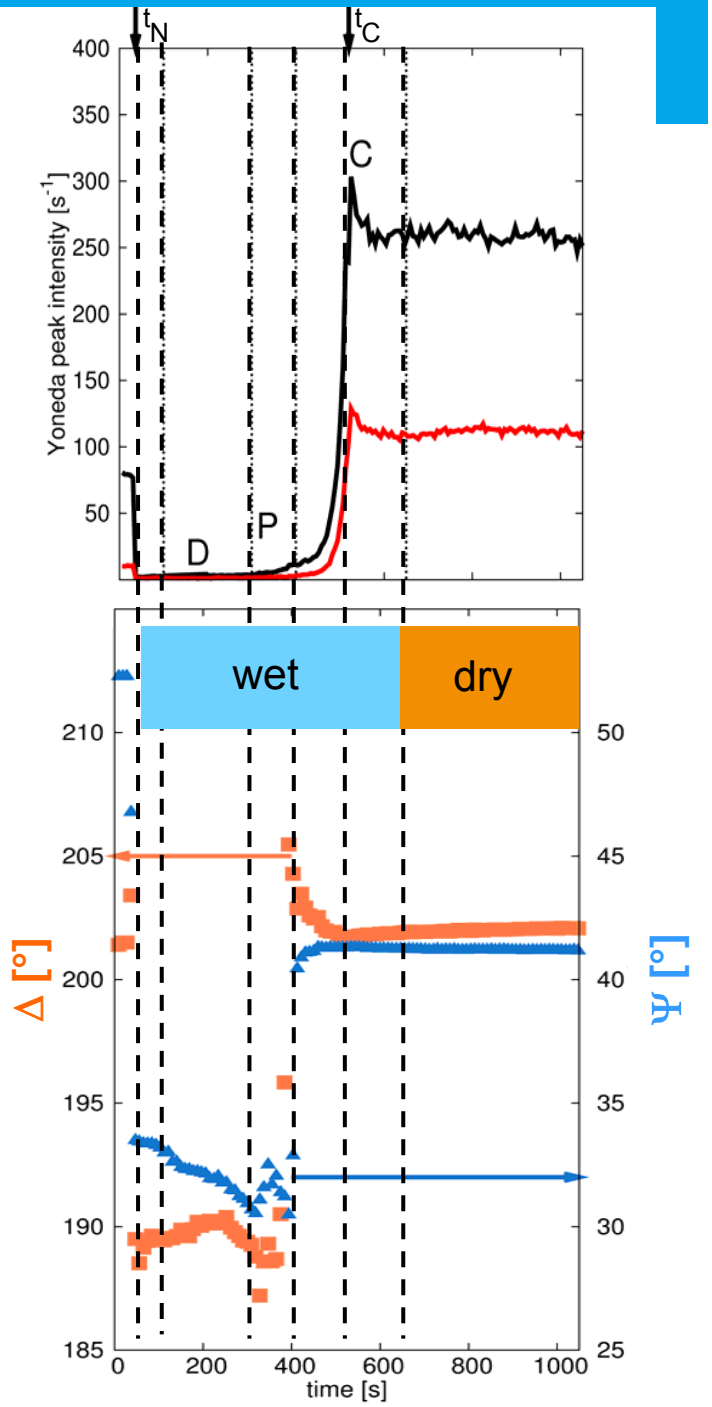
Software IsGISAXS: Lazzari et al., J. Appl. Cryst. **35**, 406 (2002)

Roth et al., J. Phys.: Condens. Matter **23**, 254208 (2011)

Kinetics of drying process



- Diffusional rearrangement (D) ~ $t^{0.5}$
- Precipitation Au (P) ~ t^3
- Compaction (C)
- Agreement with ellipsometric data



Roth et al., J. Phys.: Condens. Matter **23**, 254208 (2011)

Outline

- ***G***razing ***I***ncidence ***S***mall-***A***ngle ***X***-ray ***S***cattering
  - Application to Metal-Polymer Nanocomposites
  - Optics
- Scanning experiments
  - Nanobeams – ID13 / ESRF

    Gradients [500nm]
    Classification [300nm]
  - Microbeams – BW4 / DESY

    Tomography – 30µm
- In-situ Kinetics
  - Nanobeams – droplet deposition [ID13 / ESRF – 300nm]
  - µGISAXS & imaging ellipsometry [MiNaXS / DESY – 10µm]
- Sputter deposition
  - In-situ observation of industrial style deposition of gold [MiNaXS / DESY – 10µm]
- Outlook
  - Nanofocus @ MiNaXS [300nm]

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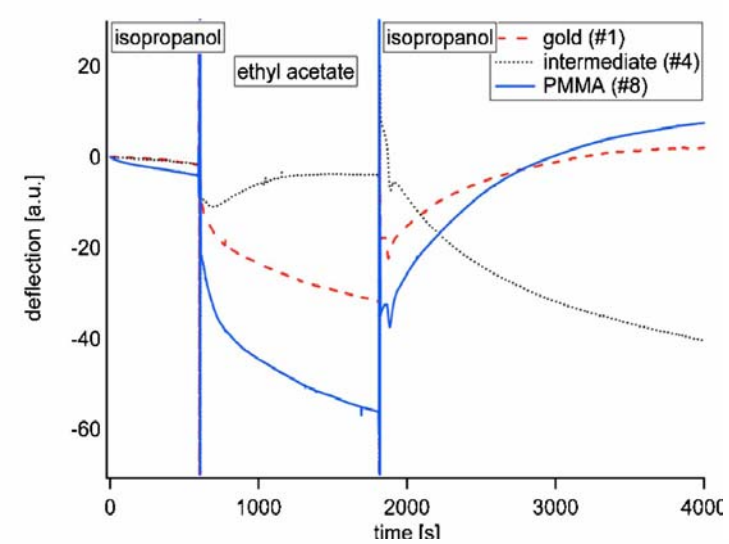
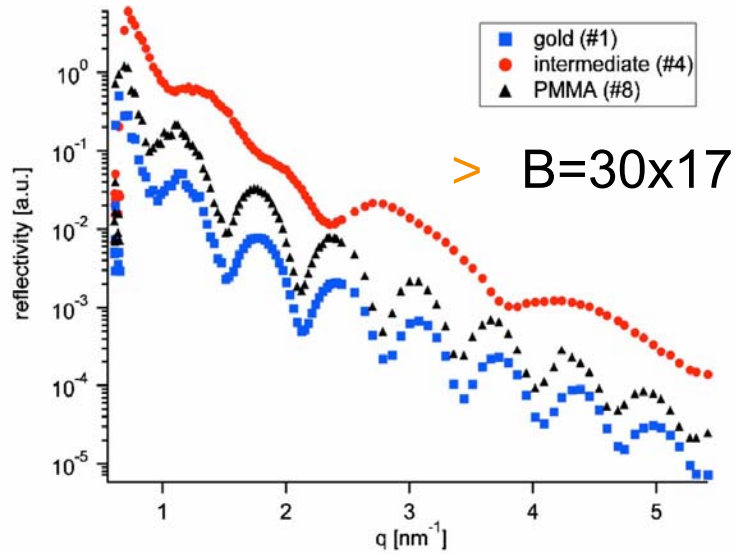
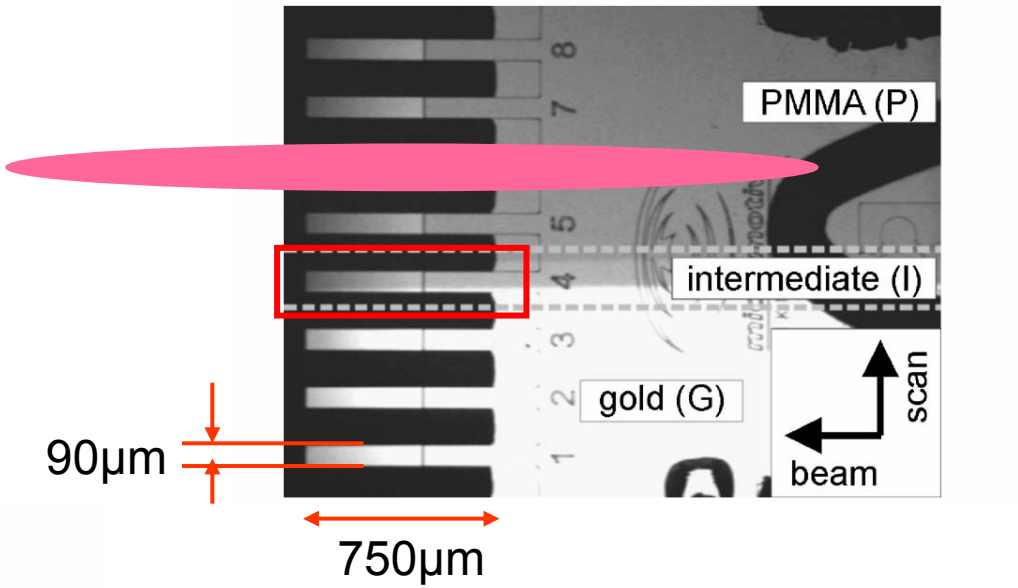
Outlook – nanofocus at MiNaXS (KB, 300nm)





> B=30x17µm^2



> Beam: 100nm

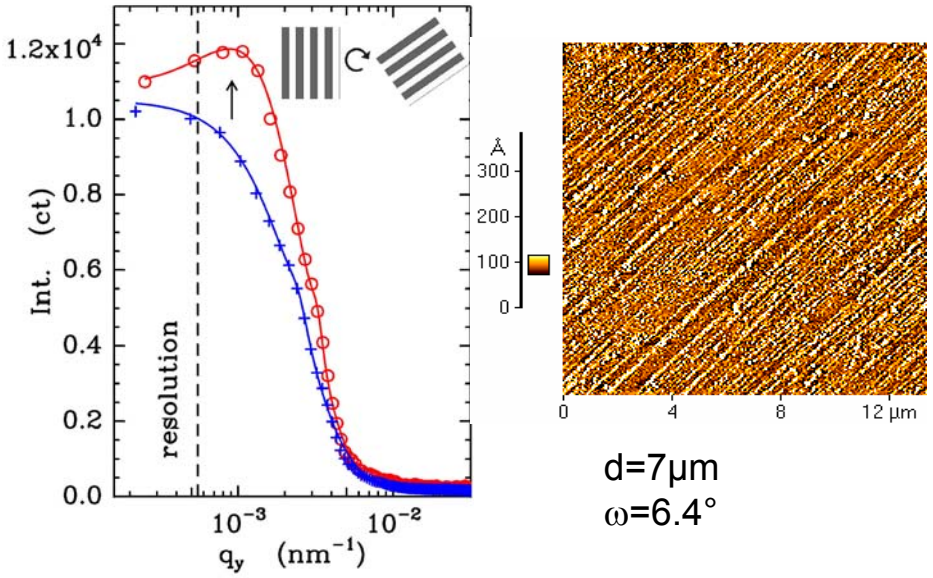
> In-situ response

> nanoGISAXS

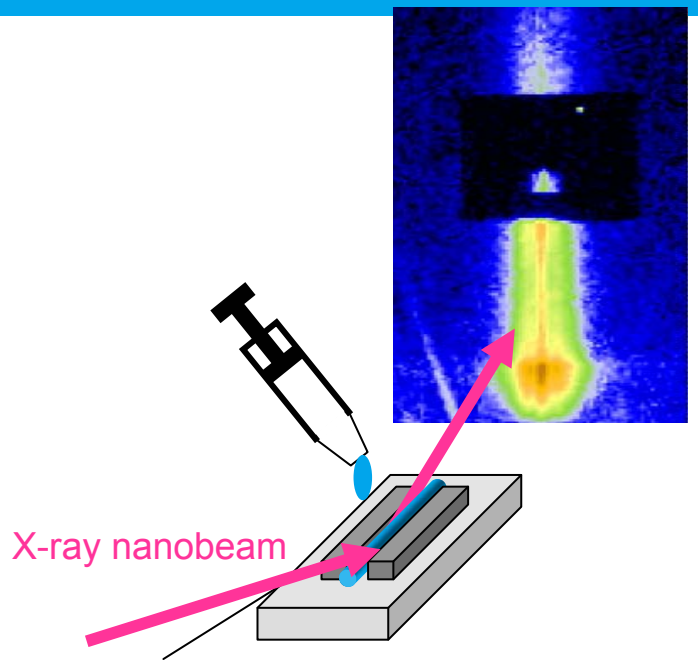
Wolkenhauer et al., Appl. Phys. Lett. **89**, 054101 (2006)

Polymeric nanochannels

- Electronic chip production
- Fabrication of bioanalytical assays



d=7µm
ω=6.4°



- Kinetics in single nanochannel
- Flow/ drying → Nanofluidics/ -wires
- Optical spectroscopy, ellipsometry

Müller-Buschbaum et al., Appl. Phys. Lett. **88**, 083114 (2006)
HASYLAB – highlight, www.hasylab.desy.de (2006/2007)

Outlook & Summary

> Wide variety of application

- Nano
  Roth et al., Appl. Phys. Lett. **91**, 091915 (2007)
  Ruderer et al., Nucl. Instr. Meth. B **268**, 403 (2010)
  Roth et al., Langmuir **26**, 1496 (2010)
- Micro
  Roth et al., Appl. Phys. Lett 88, 021910 (2006)
  Roth et al., Rev. of Sci. Instr. **77**, 085106 (2006)
  Körstgens et al.,Anal. Bioanal. Chem. **396**, 139 (2010)
  Buffet et al., Adv. Eng. Mat. **12**, 1237 (2010)
  Roth et al., J. Phys.: Condens. Matter **23**, 254208 (2011)
- Tomography
  Schroer et al., Appl. Phys. Lett. **88**, 164102 (2006)
  Kuhlmann et al., Langmuir **25** 7241 (2009)

} GISAXS
Müller-Buschbaum et al., J. Phys. Cond Matter **23**, 184111 (2011)

> Complementary methods / in-situ

- Solution casting and
- Ellipsometry

Acknowledgement

> *MiNaXS Team:*
A. Buffet, M.M. Abul Kashem, B. Heidmann, G. Benecke(*), R. Döhrmann, G. Herzog, R. Mannweiler, J. Risch, K. Stassig

> *FS-DO & FS-PE & HASYLAB:*
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A. Rothkirch, T. Kracht

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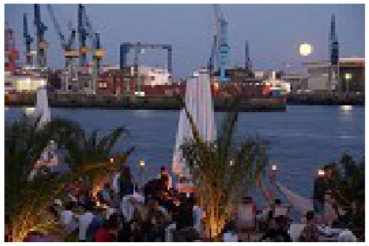
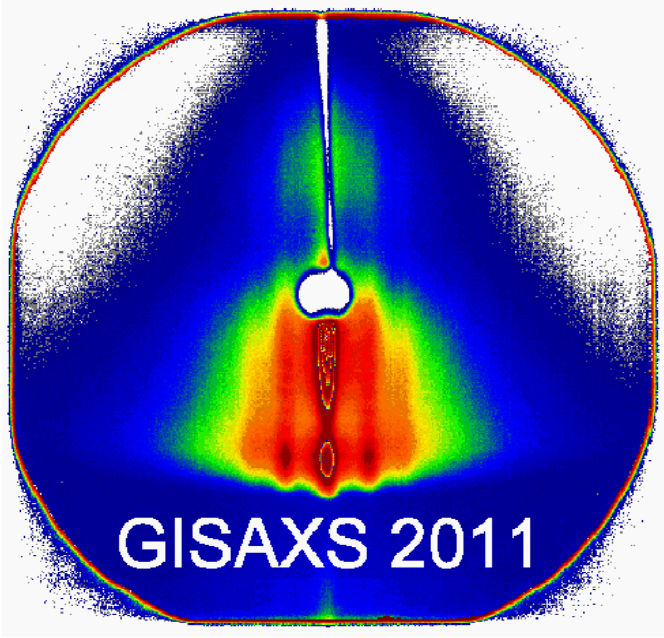
> *TU Dresden:*
C. Schroer and group

> *ESRF:*
C. Riekel, M. Burghammer

(*) & … and many more…

10.-12. October 2011

List of invited speakers:

David Babonneau (Universite de Poitiers, France)
Tilo Baumbach (KIT, Karlsruhe, Germany)
Sigrid Bernstorff (ELETTRA, Trieste, Italy)
Tiberio A. Ezquerra (CSIC, Madrid, Spain)
Alexander Hexemer (ALS, Berkeley, US)
Byeongdu Lee (APS, Argonne, US)
Hiroshi Okuda (Univ. Kyoto, Japan)
Markus Rauscher (MPI, Stuttgart, Germany)
Gilles Renaud (CEA, Grenoble, France)
Tim Salditt (Univ. Göttingen, Germany)
Jin Wang (APS, Argonne, US)

organized by
S.V. Roth + R. Gehrke (DESY)
&
P. Müller-Buschbaum (TU München)

TECHNISCHE UNIVERSITÄT MÜNCHEN

HELMHOLTZ GEMEINSCHAFT

DESY

Invited lectures, contributed posters session, visit to PETRAIII & hands-on practical training at BW4, from theory and simulation to actual real experiments

http://gisaxs2011.desy.de