GISAXS/SAXS Studies of Nanoparticle Assemblies at Solid/Fluid Interfaces

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- **Why GISAXS/SAXS and nanoparticles?**
- **Basics of GISAXS**
- **Nanoparticle assemblies**
  - solid surfaces
    - monolayers - tracking of self-assembly, surfactant removal
    - multilayers – the role of vertical correlation
  - liquid surfaces
    - time-resolved GISAXS – formation of monolayer
- **GISAXS in applied nanoparticle science**
  - solar cells, strain gauges, spintronics
- **Summary and outlook**

WINTER SCHOOL OF SYNCHROTRON RADIATION
31.1. - 4.2.2011 Liptovský Ján, Slovakia

Why GISAXS and nanoparticles?

The advantages of GISAXS:

- simple experimental setup
- large lateral *q*-space available (>10x)
- at $\alpha_i,\alpha_f > 3\alpha_c$ simple BA theory is valid

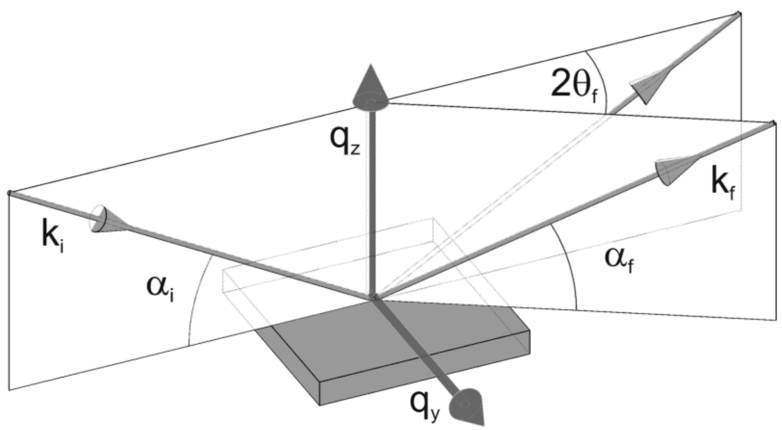
(we can avoid dynamic scattering processes like Yoneda peaks, etc.)

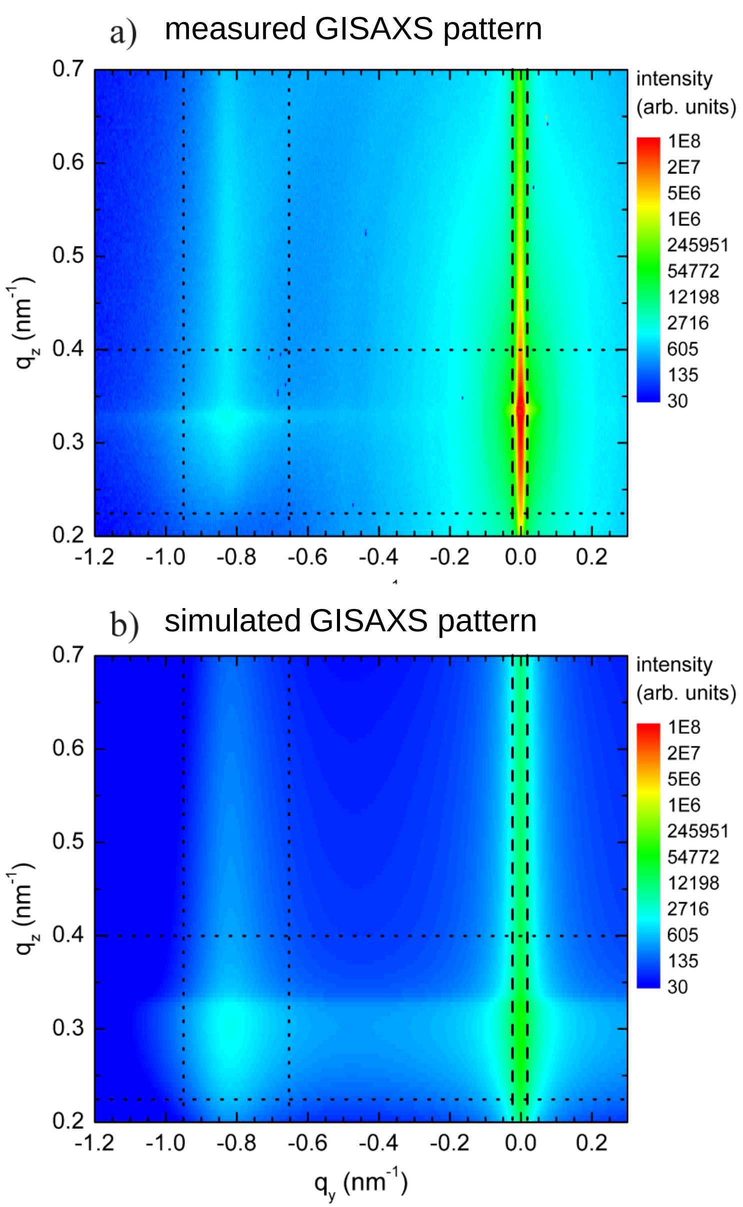
- laboratory table-top systems available

(Bruker Nanostar equipped with Incoatec IμS X-ray source, etc.)

Measurement geometry / GISAXS

(grazing-incidence small-angle X-ray scattering)





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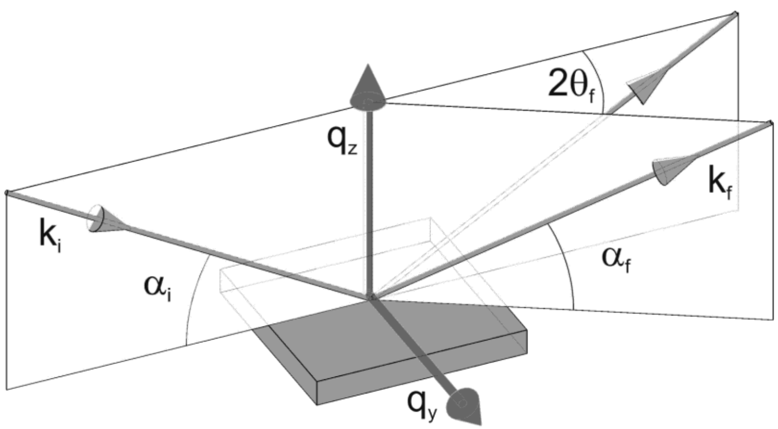
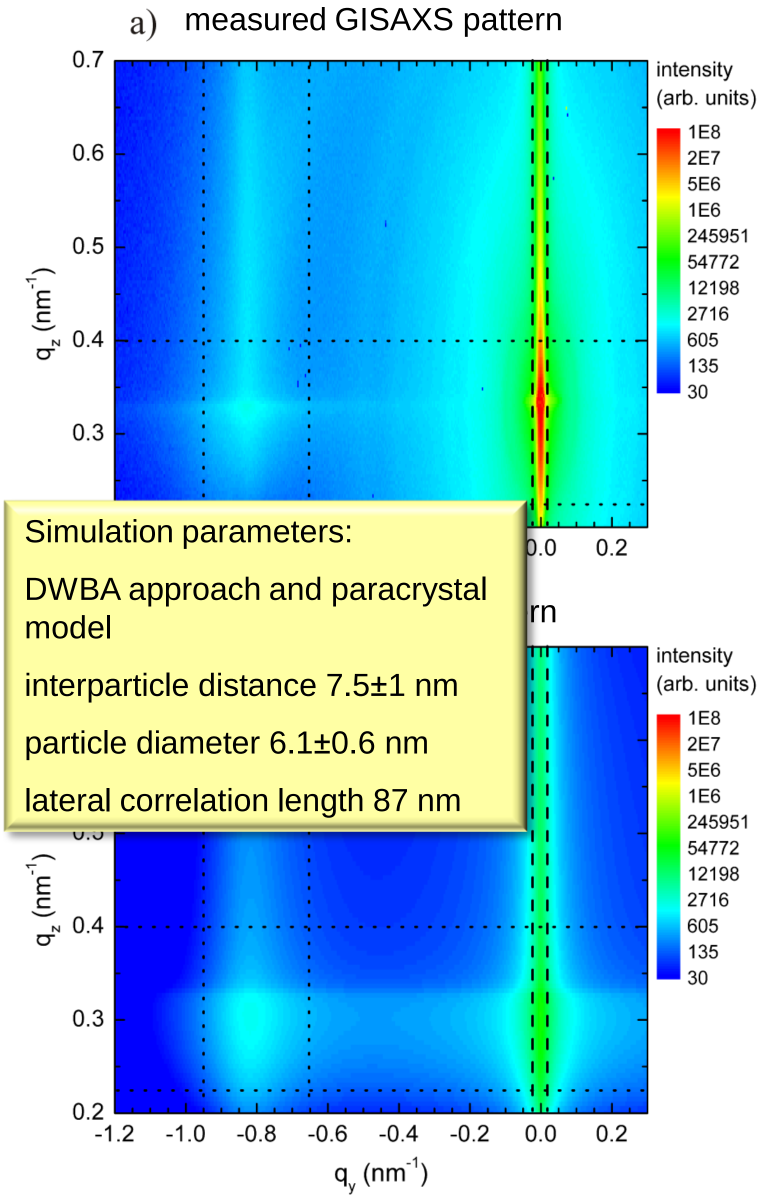




Simulation parameters:

DWBA approach and paracrystal model

interparticle distance 7.5±1 nm

particle diameter 6.1±0.6 nm

lateral correlation length 87 nm

Basics of GISAXS

Advantages:

- non-destructive technique allowing inspection of buried clusters and interfaces
- in contrast to microscopy we average over sample surface/volume
- working under all conditions (enables in-situ screening/control)
- due to small angle of incidence can be combined with many other techniques
- changing the incidence angle controls the penetration depth

Disadvantages:

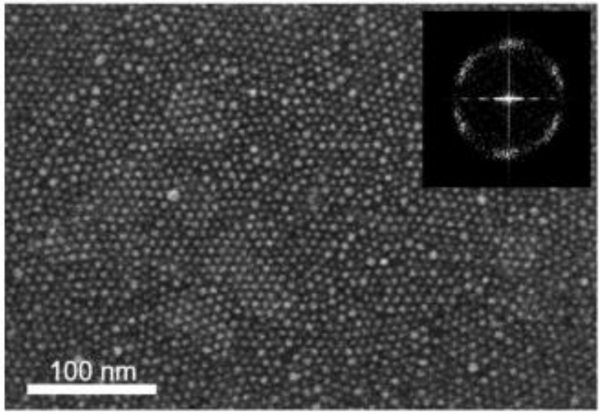
- transformation from reciprocal to real space needs an appropriate model
- we always measure statistical averages over ensemble of entities

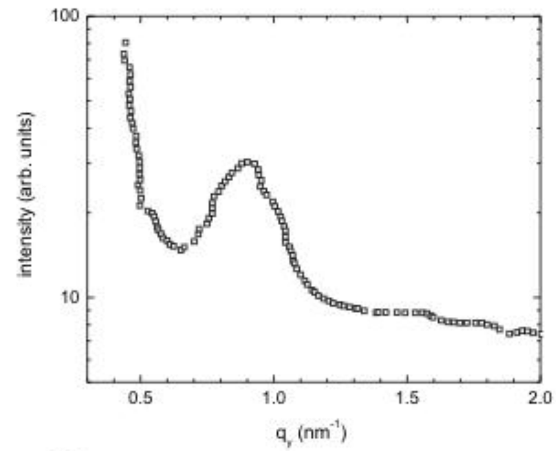
> As with most techniques, X-ray scattering also has some drawbacks:
>
> (i) The use of synchrotron radiation is nearly mandatory because the collected signal scales with the amount of material, which can be rather small (of the order of the monolayer).

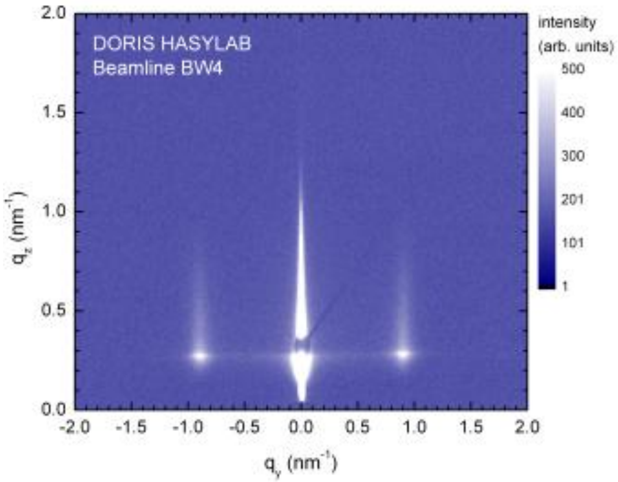
G. Renaud et al. / Surface Science Reports 64 (2009) 255380

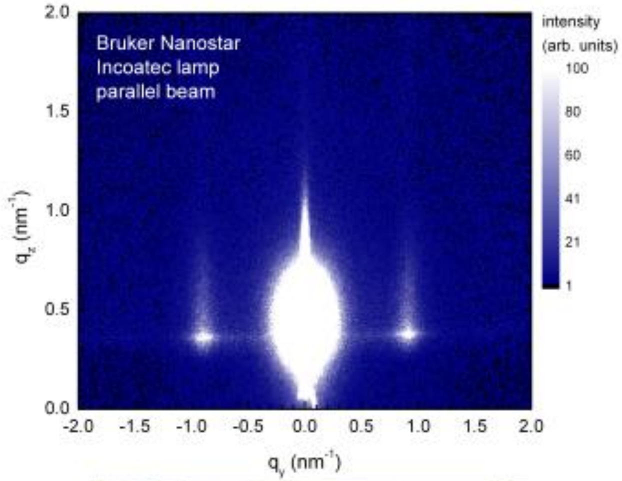
Basics of GISAXS / from synchrotron to table-top

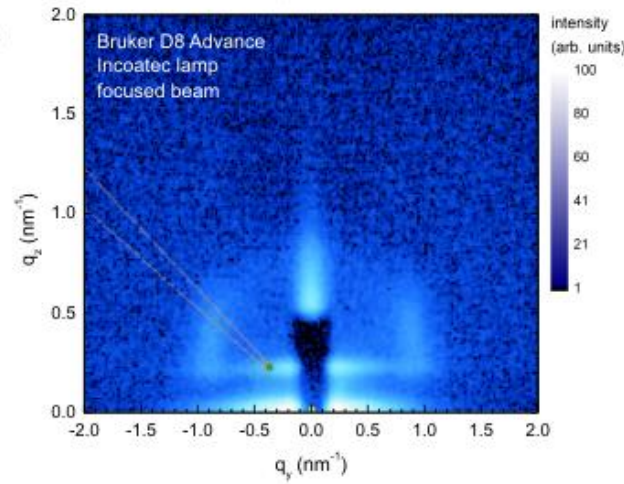
SEM image of self-assembled nanoparticle 2D array.





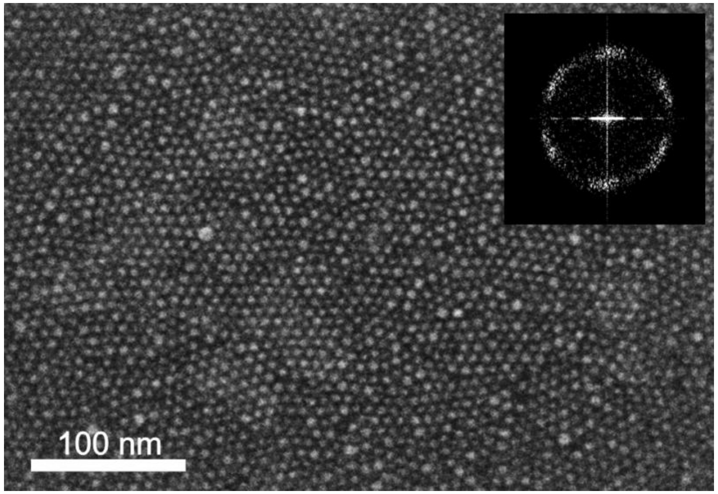




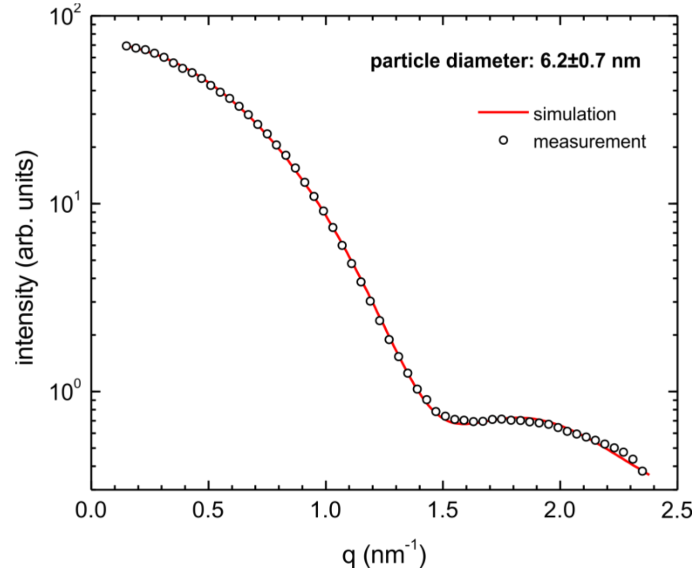


Nanoparticle self-assembly (SEM, SAXS, XRR, GID)

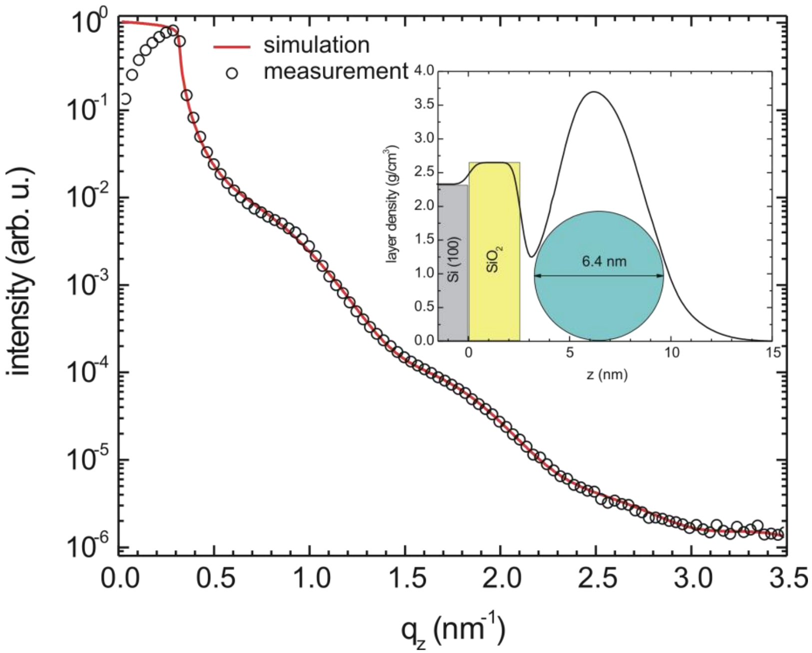
SEM image of self-assembled nanoparticle 2D array.



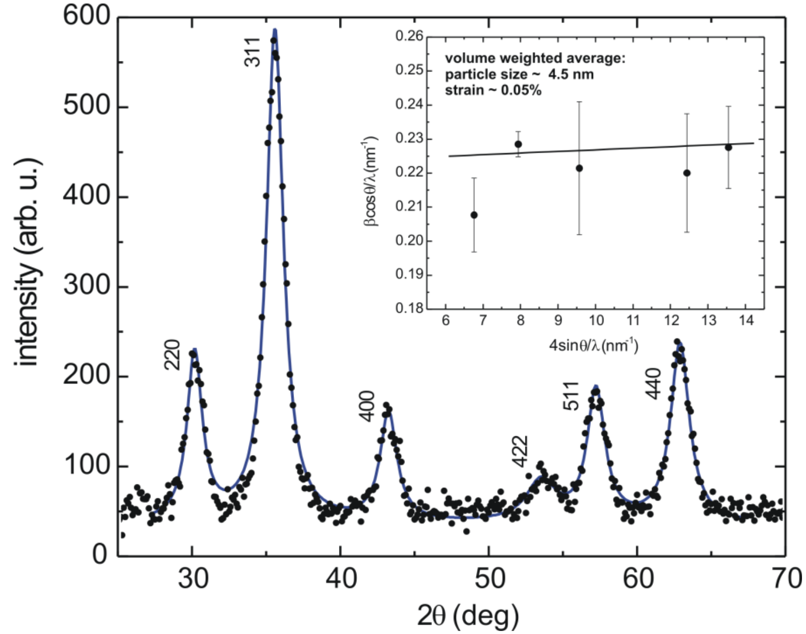
SAXS from diluted nanoparticle solution



X-ray reflectivity of nanoparticle 2D array



GI-XRD of nanoparticle multilayer

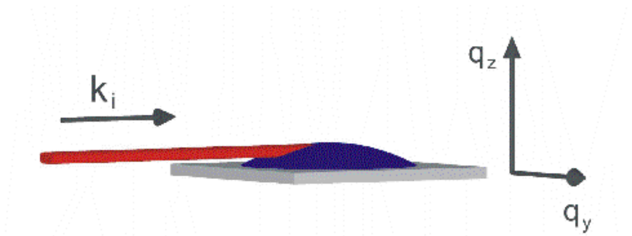


Tracking the origin of nanoparticle self-assembly

Observation of self-assembly of magnetic nanoparticles plays an important role in basic and applied research.

I. Dynamics of nanoparticles dispersed in slowly evaporating solvents (gold nanoparticles in water)

Static GISAXS allows for reciprocal space characterization of selected point of evaporating colloidal drop.



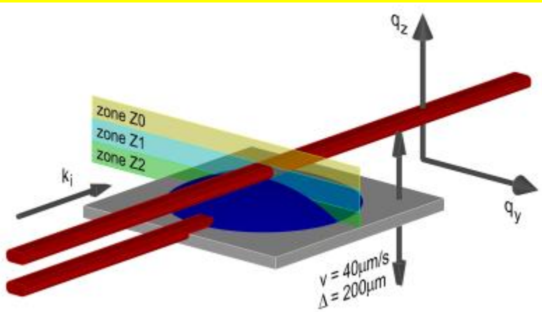
S. Narayanan et al., Phys. Rev. Lett. 93, 135503 (2004)

S. V. Roth et al., App. Phys. Lett. 91, 091915 (2007)

P. Siffalovic et al., Phys. Rev. B 76, 195432 (2007)

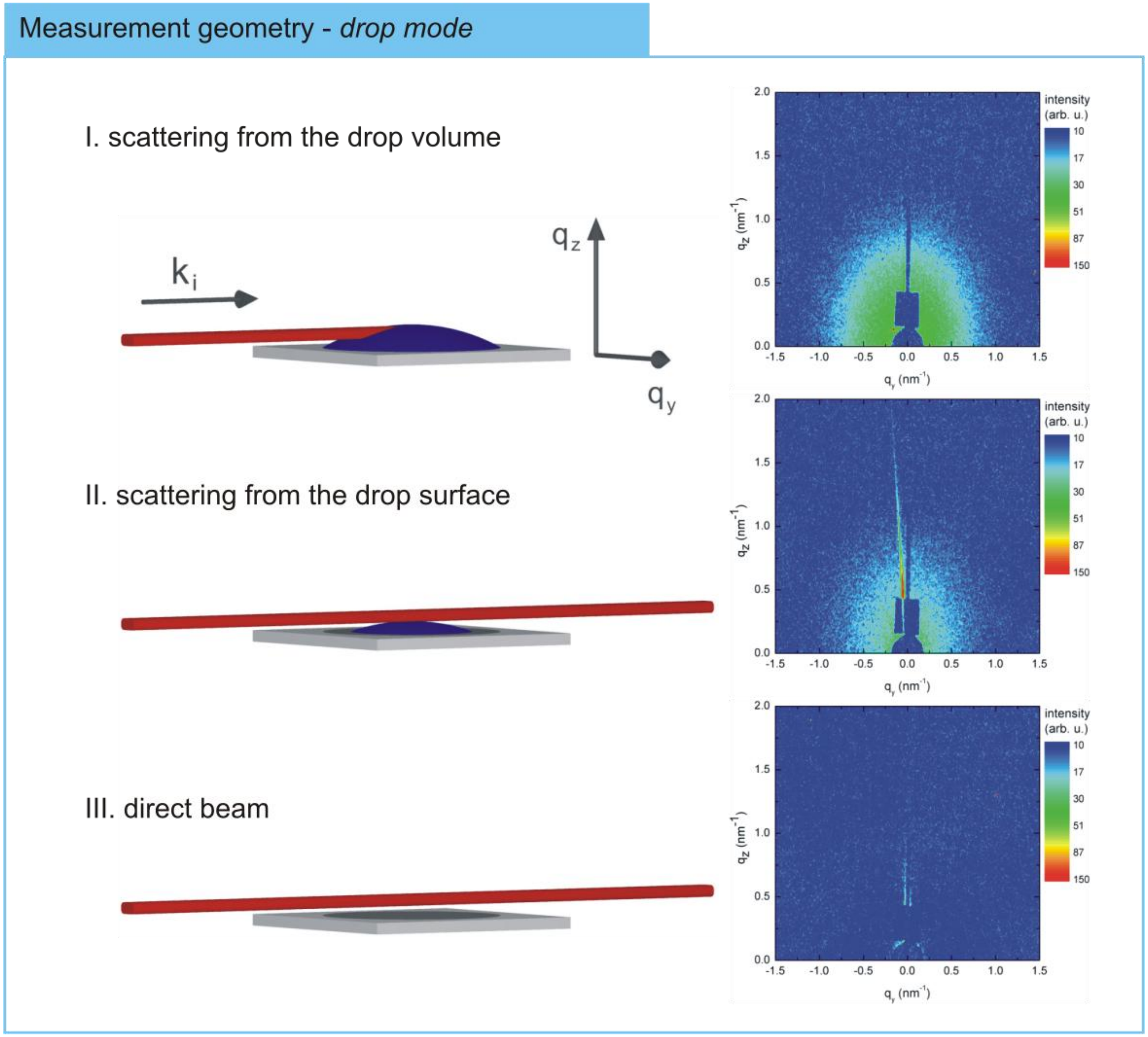
II. Dynamics of nanoparticles dispersed in rapidly evaporating solvents (iron oxide nanoparticles in toulene)

Scanning GISAXS scheme provides information on reciprocal space from various points located near the surface or inside the drop.



P. Siffalovic et al., Small 4 (12), 2222 (2008)

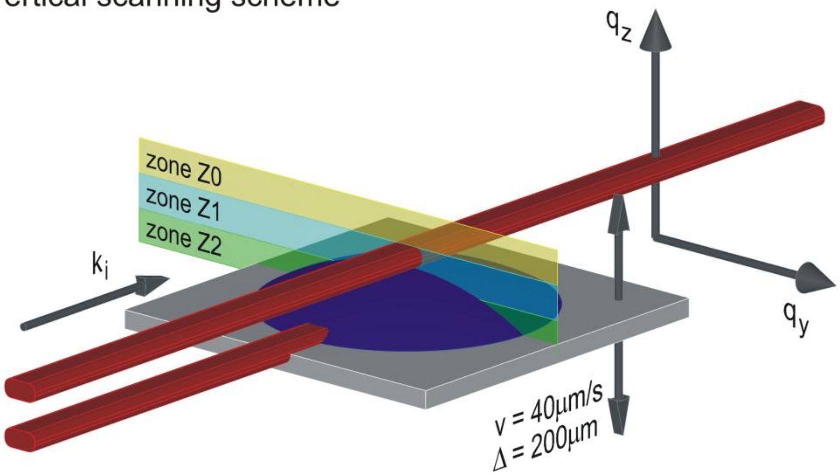
Static GISAXS mode

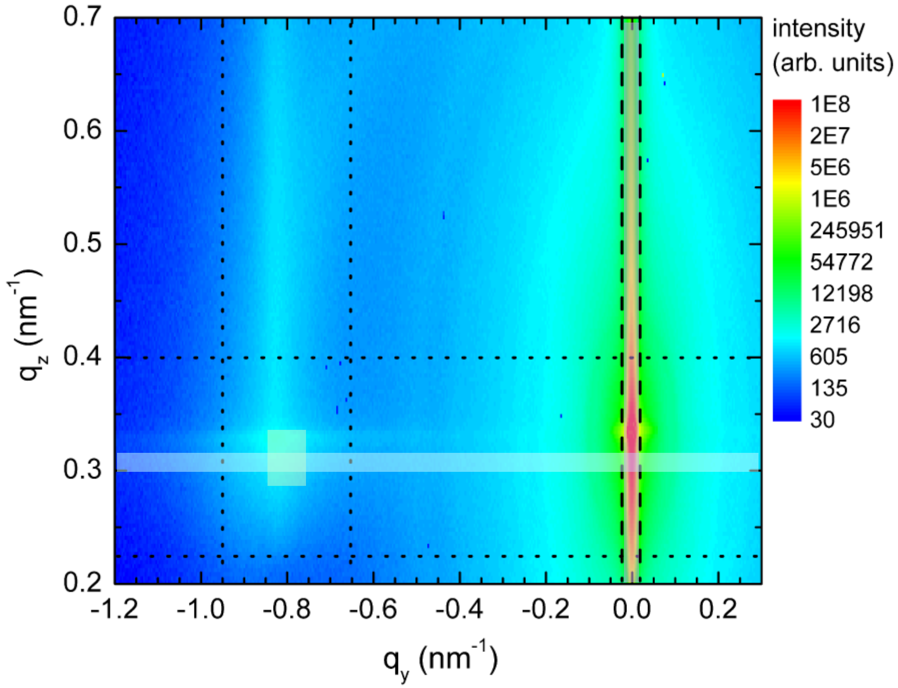


P. Siffalovic et al., Phys. Rev. B 76, 195432 (2007)

Scanning GISAXS mode – vertical scanning mode

Vertical scanning scheme





Legend:

QYT map - q_z integrated within <0.22, 0.4> nm^{-1}

QZT map - q_y integrated within <-0.02, 0.02> nm^{-1}

PIS plot - q_z integrated within <0.22, 0.4> nm^{-1}
- q_y integrated within <0.65, 0.95> nm^{-1}

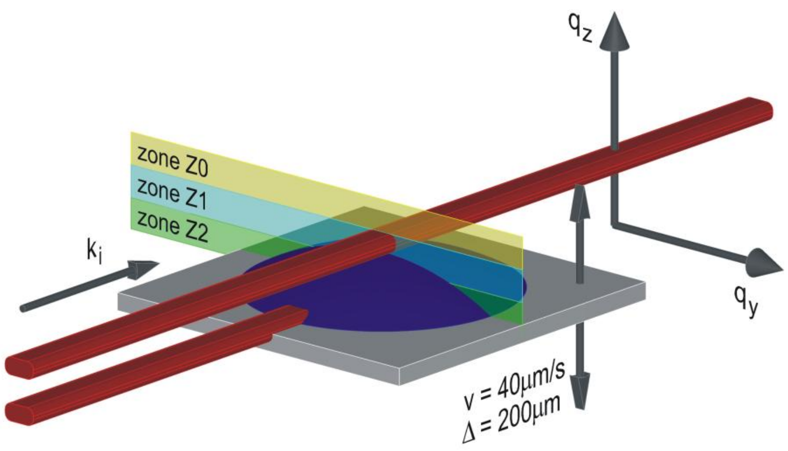
reflectivity plot
- q_y integrated within <-0.02, 0.02> nm^{-1}
- q_z integrated within <0.29, 0.35> nm^{-1}

ACOD - adjusted R^2 (coefficient of determination)

Short acquisition time compensates for spatial smearing which is in order of 1 μm for vertical scanning

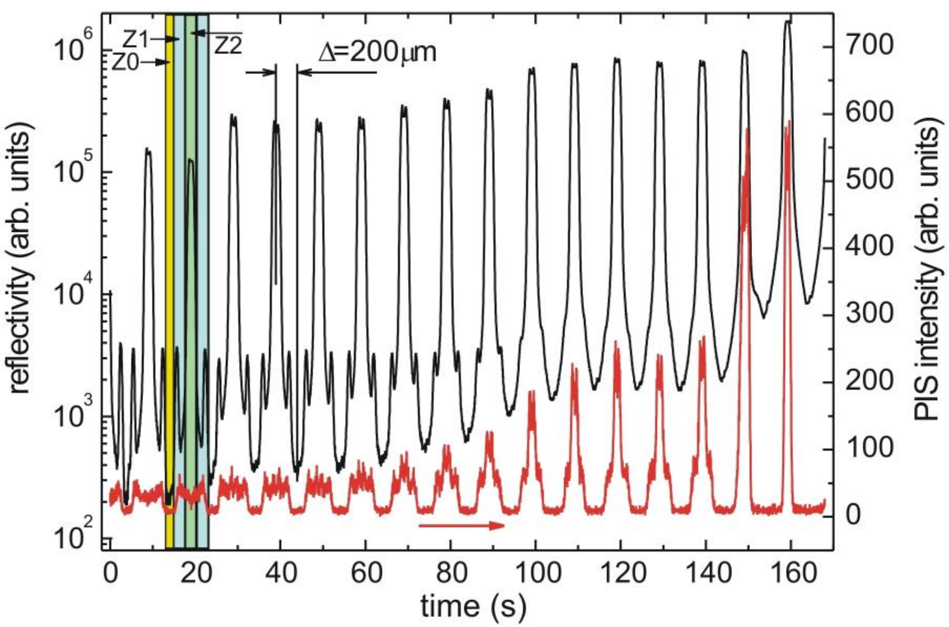
P. Siffalovic et al., Small 4 (12), 2222 (2008)

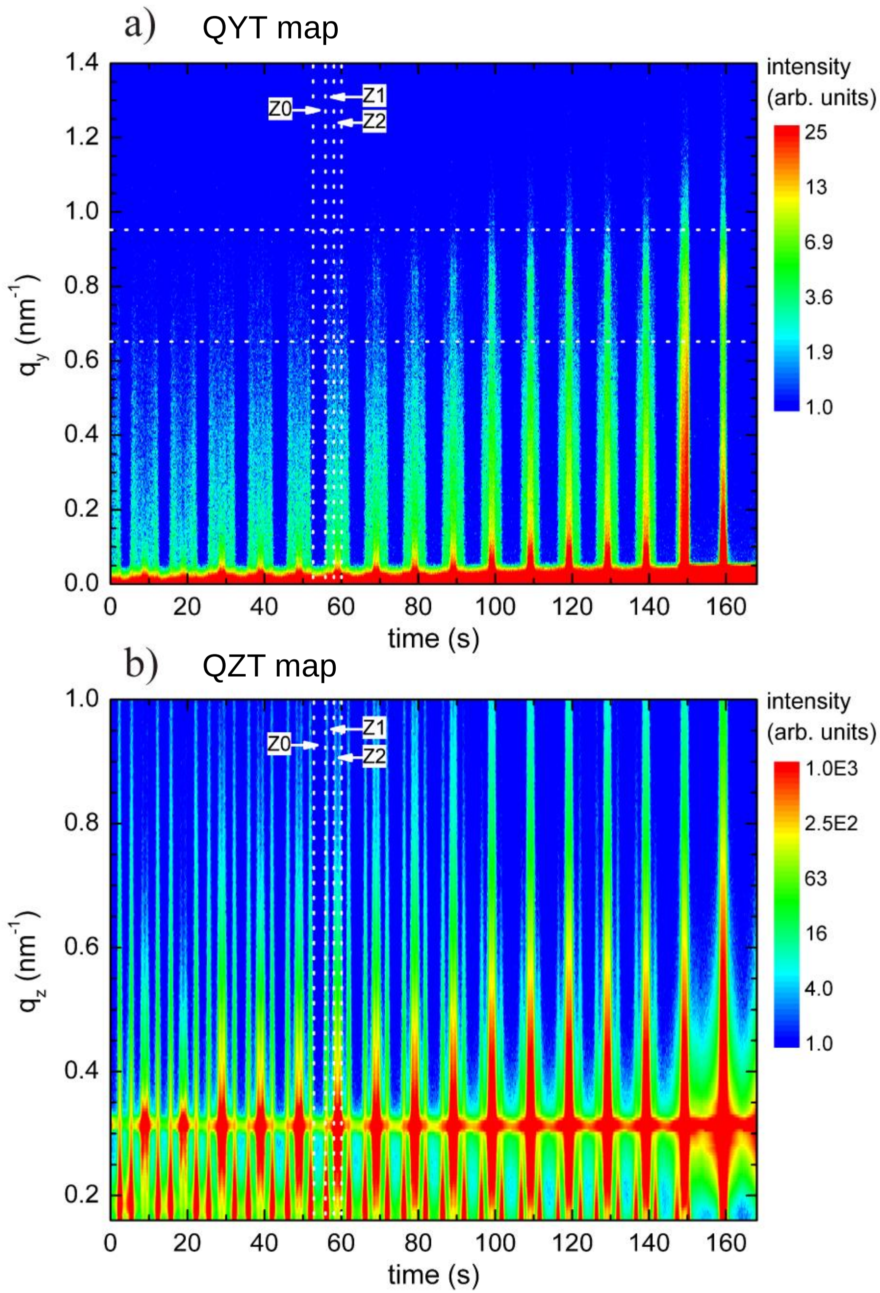
Scanning GISAXS mode – vertical scanning mode



P. Siffalovic et al., Small 4 (12), 2222 (2008)

Reflectivity and PIS plot





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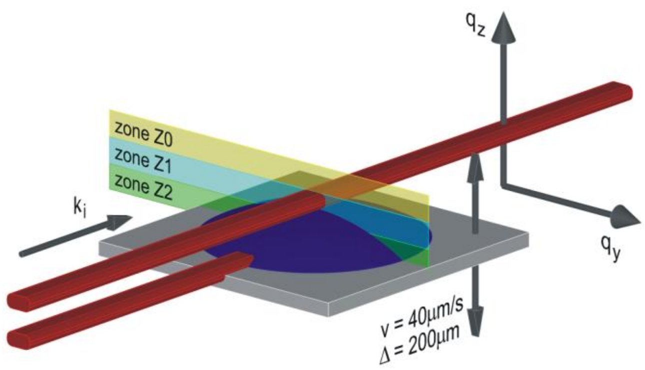
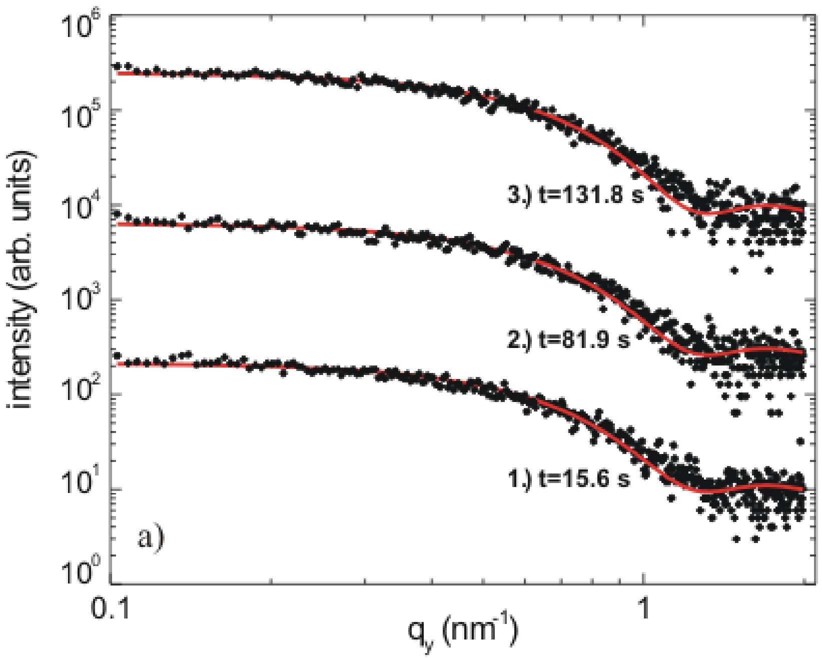
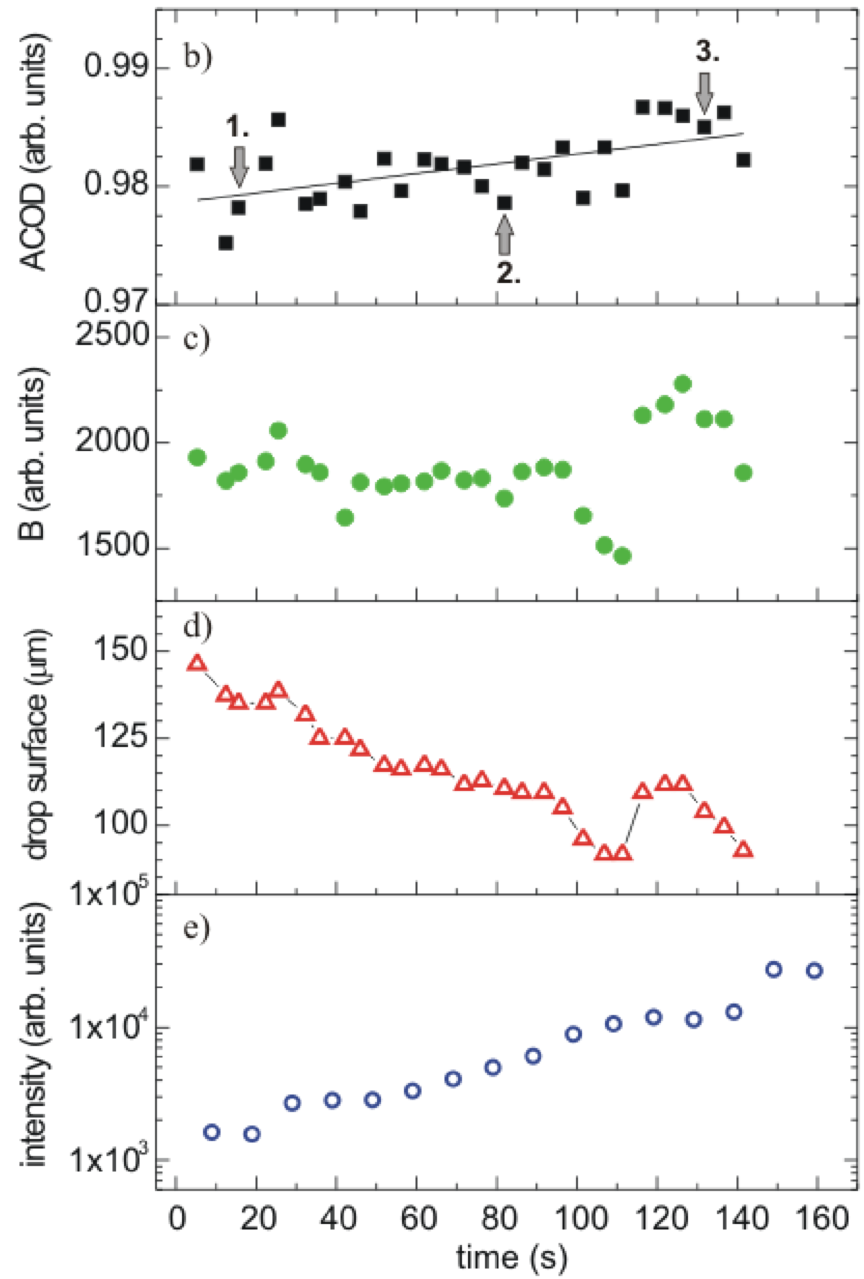


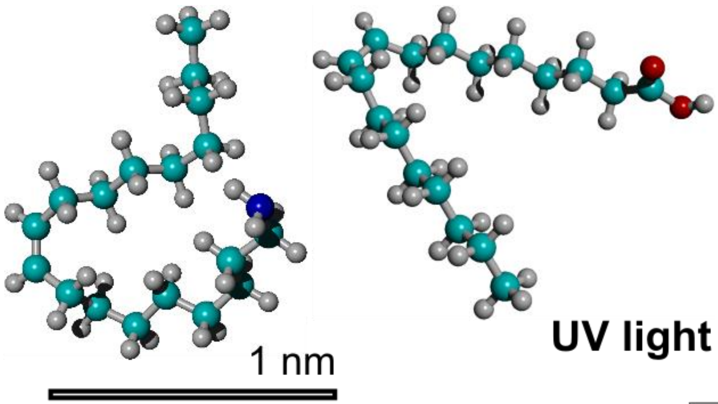
$$I(q_y) = A + B\left|F(q_y)\right|^2 S(q_y)$$

$$F(q_y) = 4\pi r^3\left[\sin(q_y r) - q_y r\cos(q_y r)\right]/(q_y r)^3$$





Photolysis and ozonolysis of nanoparticle surfactant

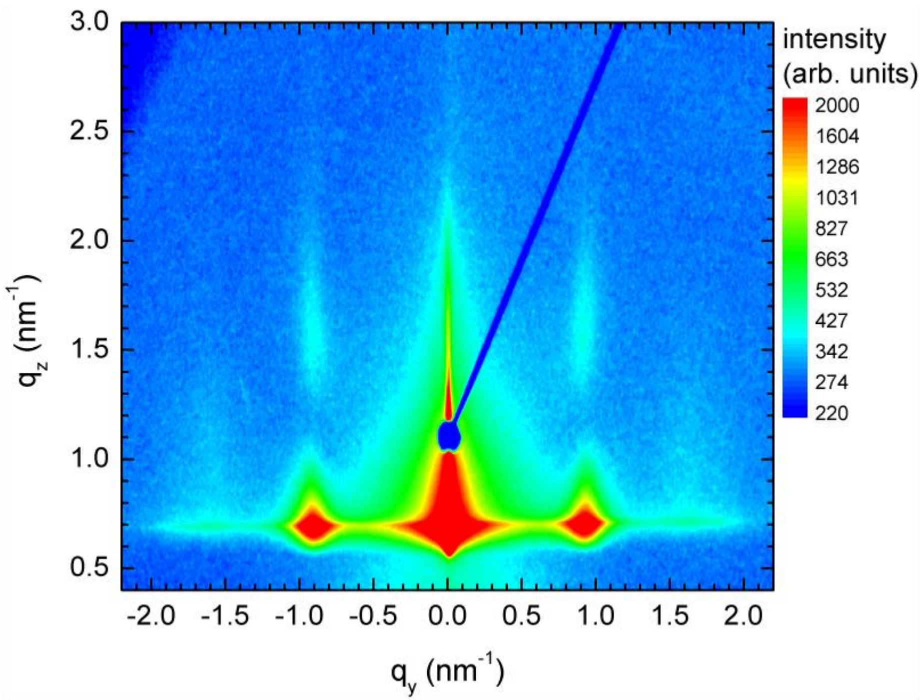


Nanoparticle surfactant:

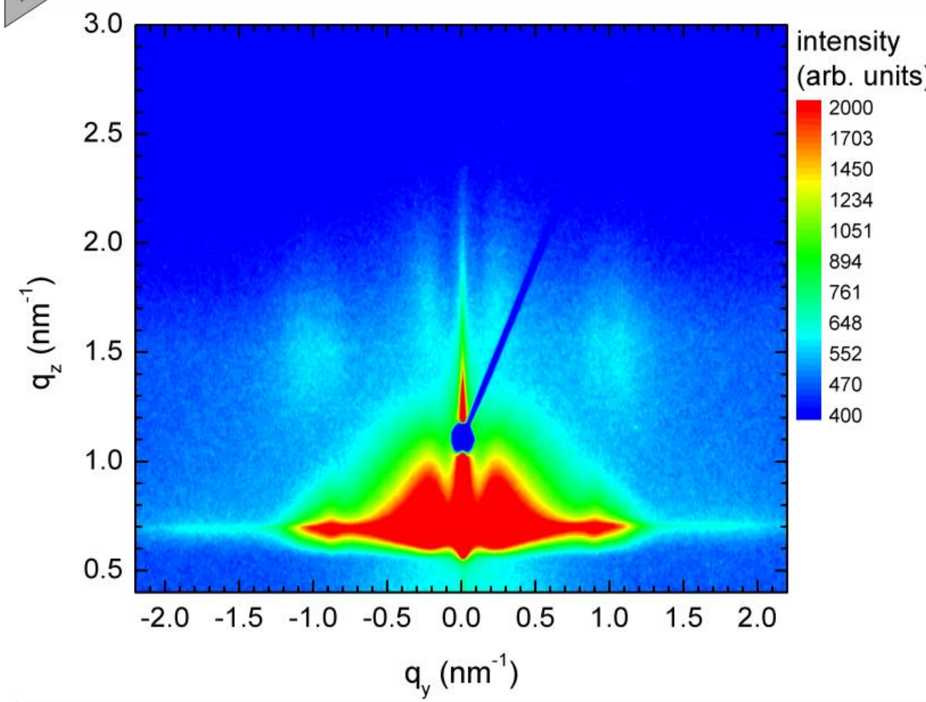
- oleic acid
- oleyl amine

UV light (4.9 eV, 6.7 eV) + O_3

Initial self-assembled state



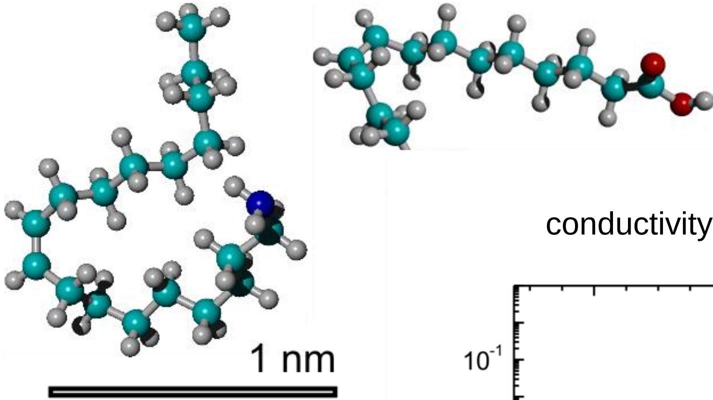
Final re-assembled state

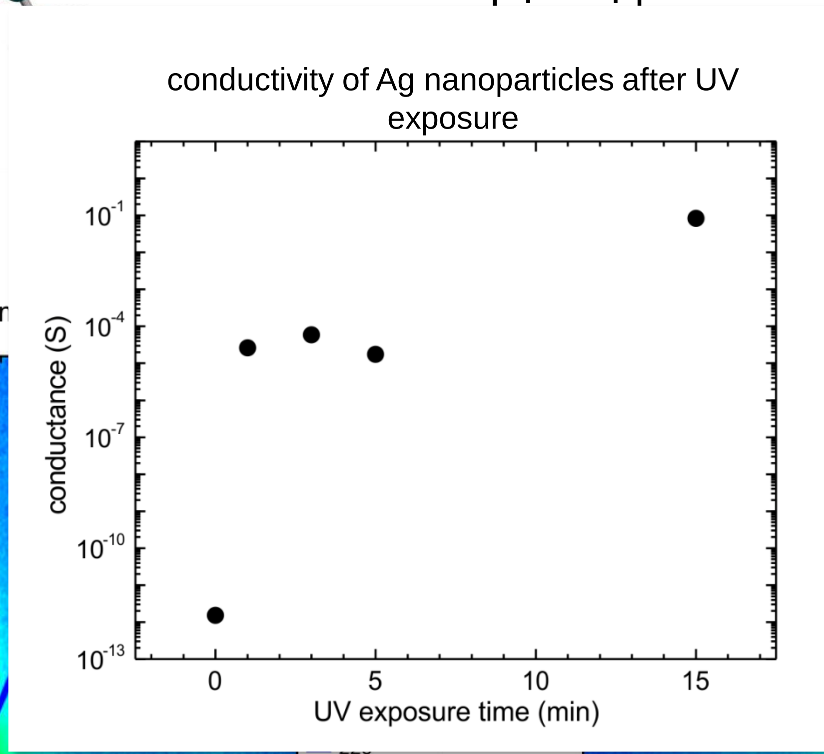


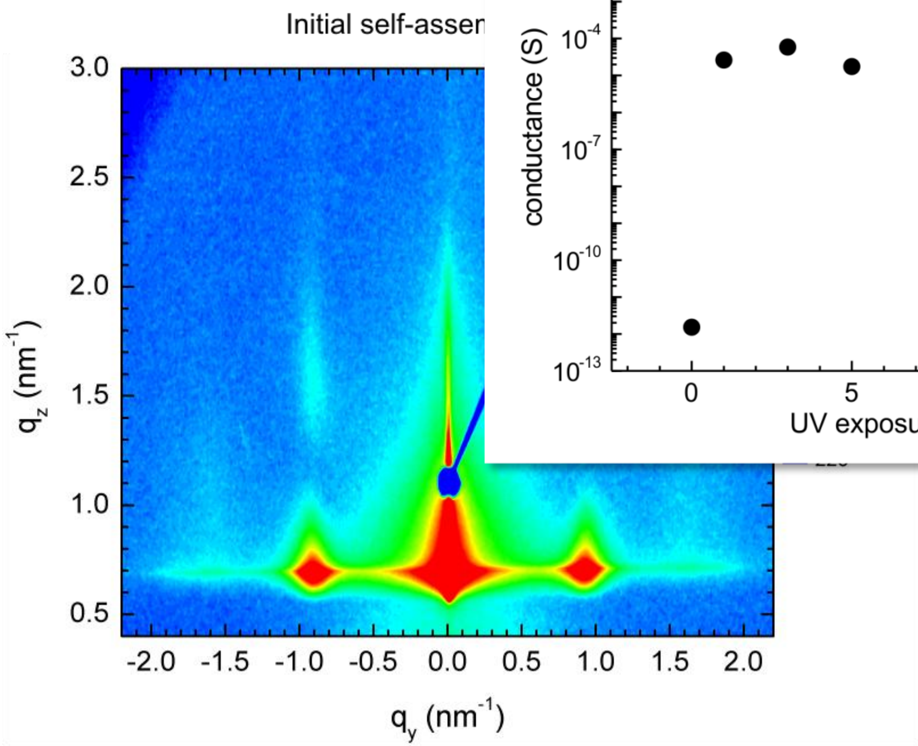
P. Siffalovic et al., Langmuir 26, 5451 (2010)

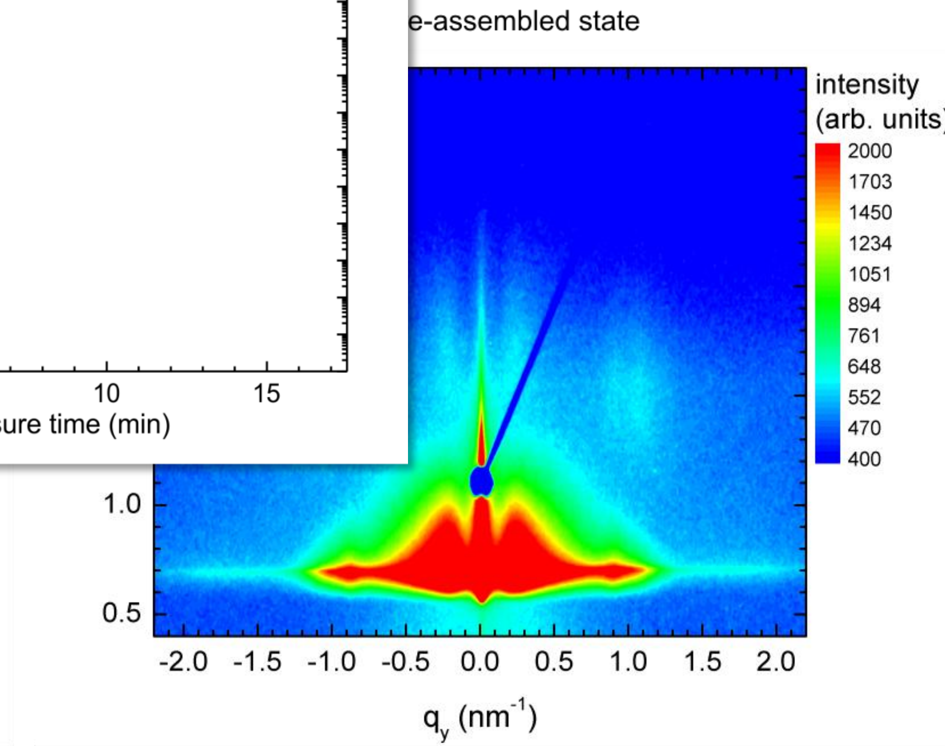
Photolysis and ozonolysis of nanoparticle surfactant

Nanoparticle surfactant:



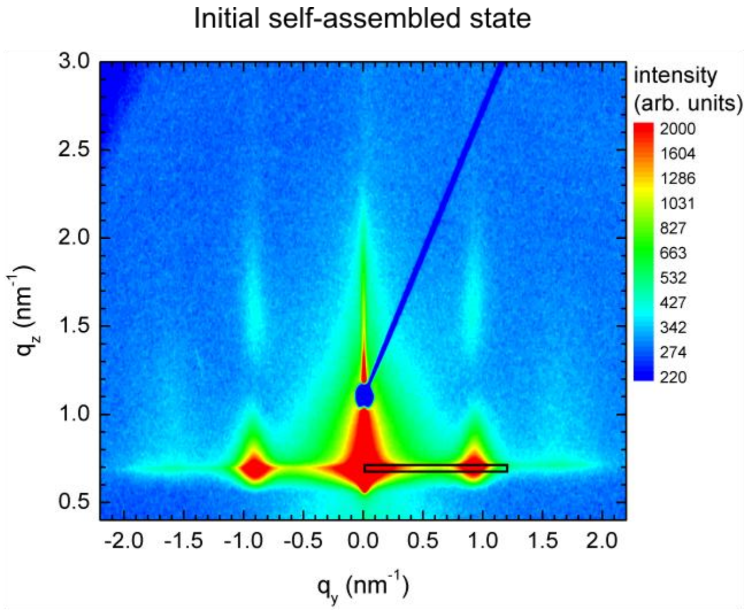


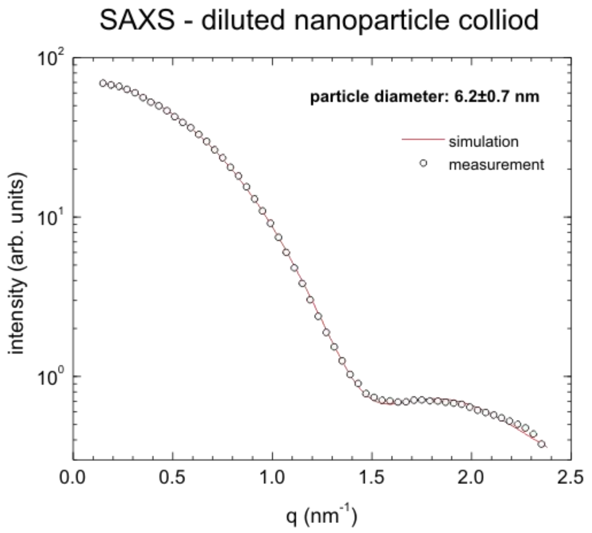


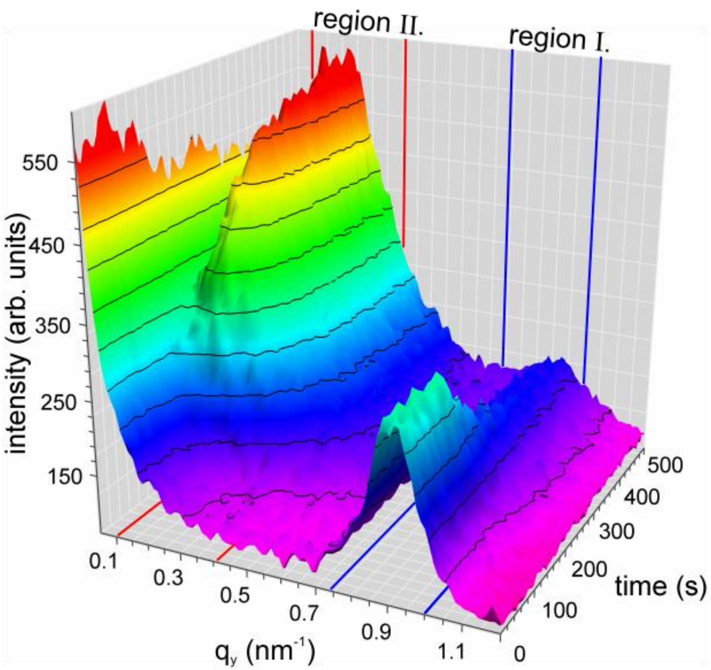


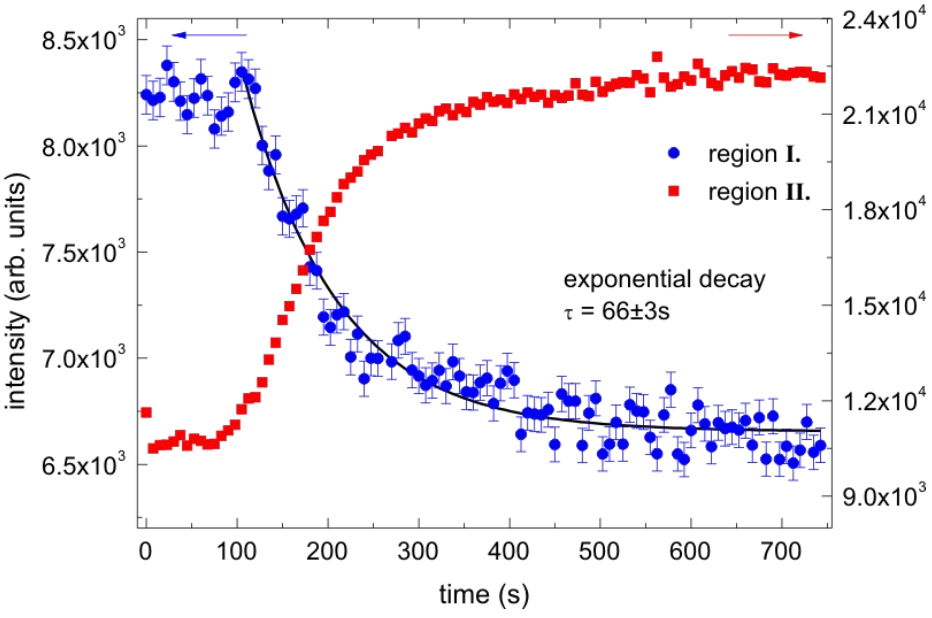
P. Siffalovic et al., Langmuir 26, 5451 (2010)

Photoinduced re-assembly of nanoparticles – reciprocal space

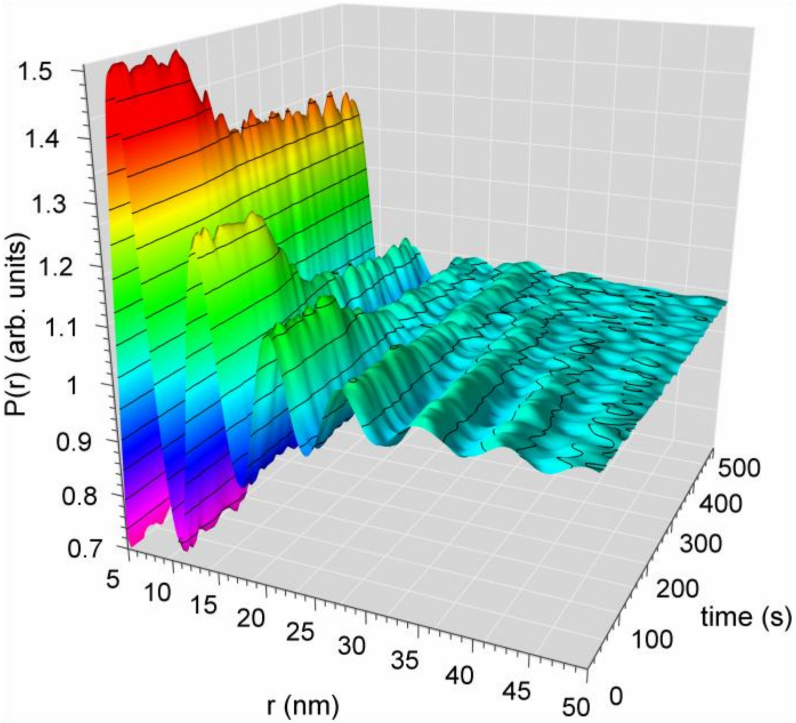


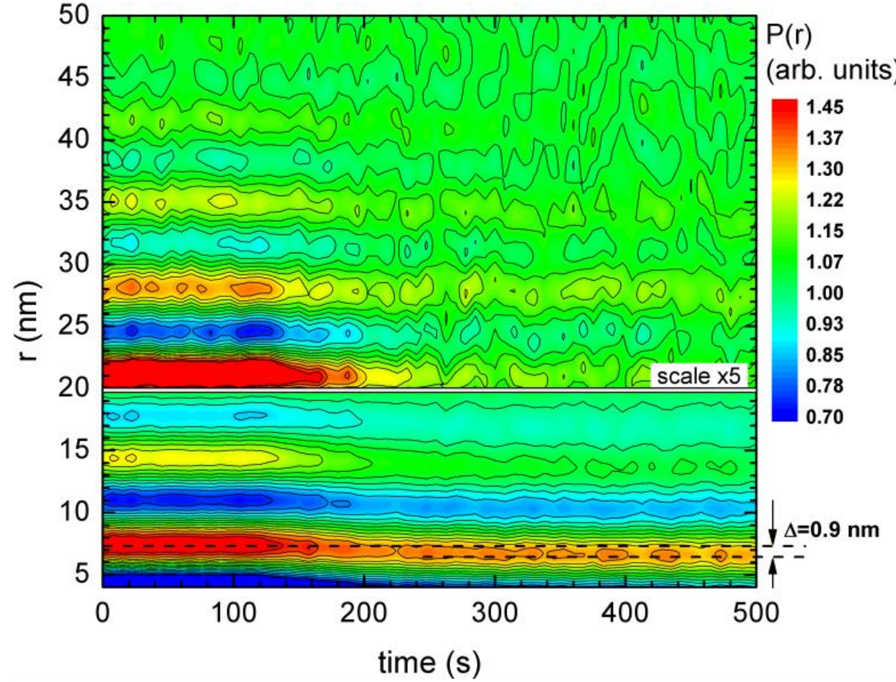






Photoinduced re-assembly of nanoparticles – object space





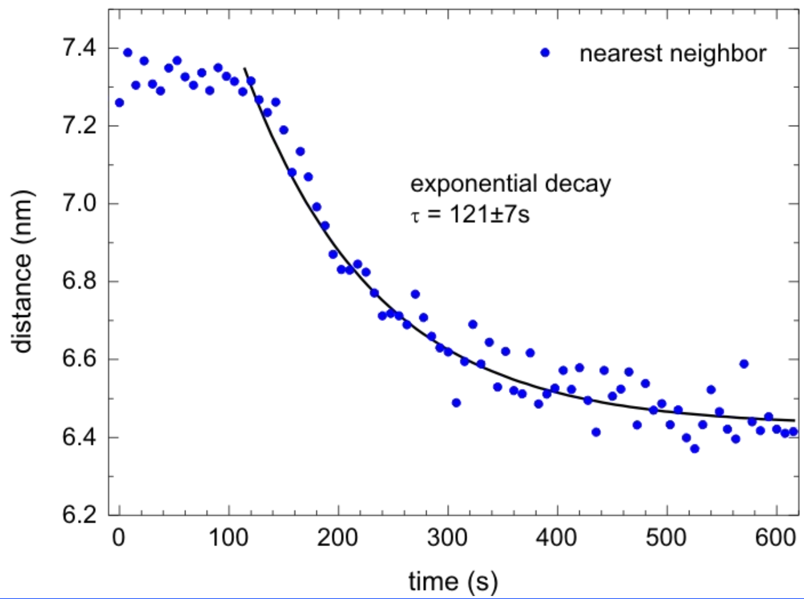
at constant k_z^i, k_z^f ; $q_{\|} = q_y$

$|F_s(q_{\|})|^2$ - form factor of full sphere

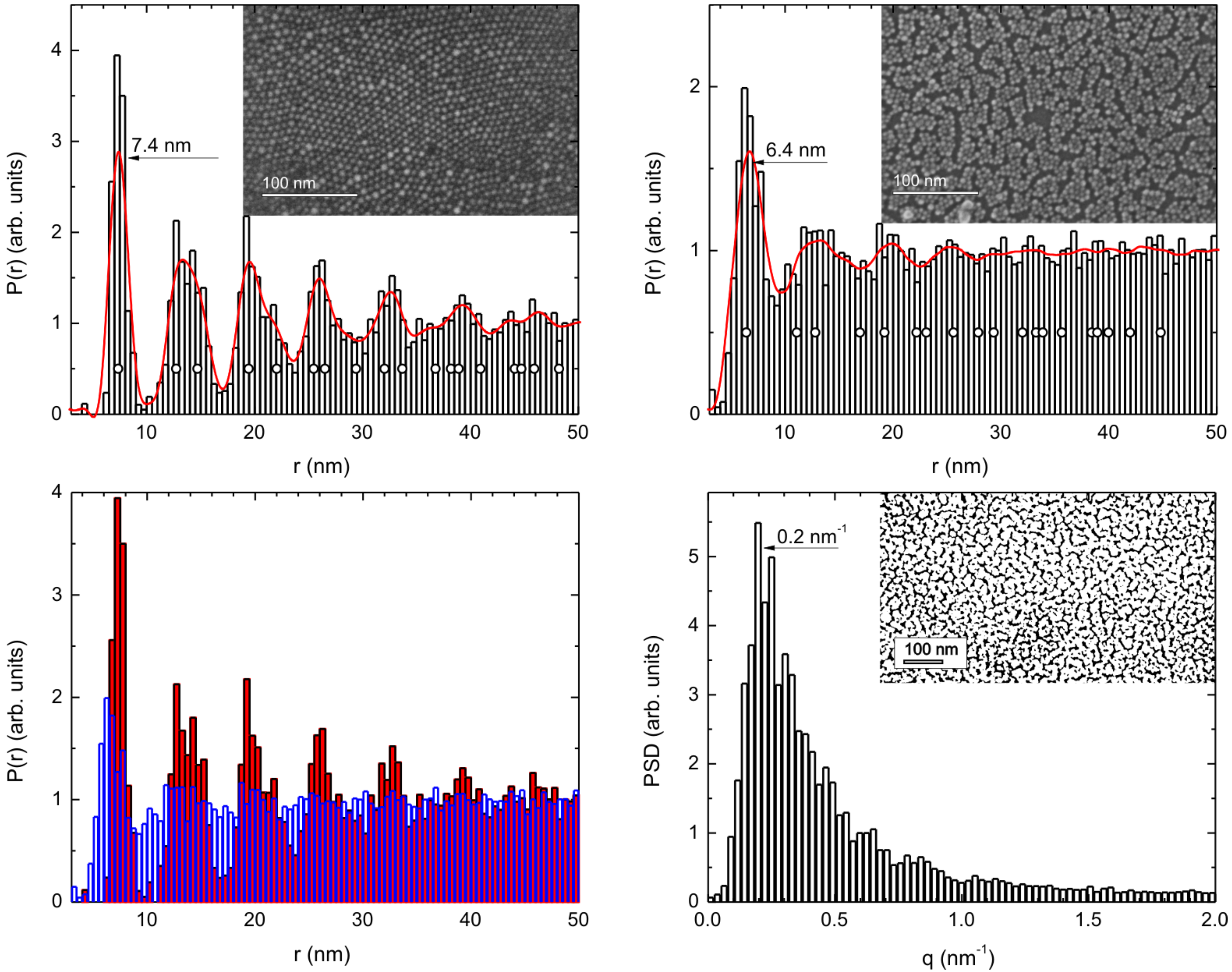
$$|F(q_{\|})|^2 = \int_0^\infty |F_s(q_{\|})|^2 e^{-\frac{(r_0-r)^2}{2\sigma^2}} dr$$

$$I(q_{\|}) \sim |F(q_{\|})|^2 \cdot S(q_{\|})$$

$$g(r_{\|}) = 1 + \frac{1}{2\pi\rho_s}\int_0^\infty (S(q_{\|})-1) J_0(q_{\|} r_{\|}) q_{\|} dq_{\|}$$

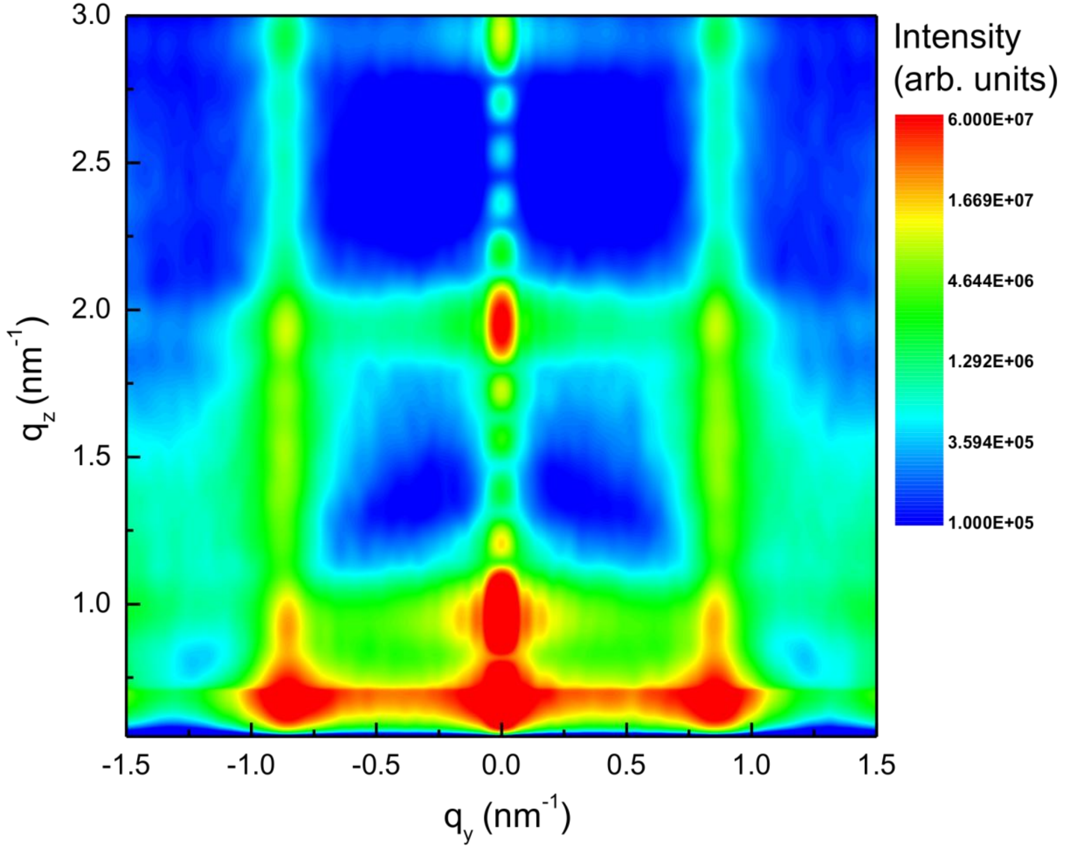


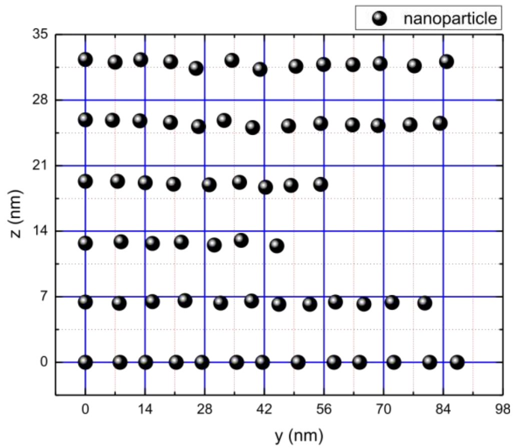
Pair correlation function of initial and final assembly - SEM



Nanoparticle multilayers and the role vertical correlation

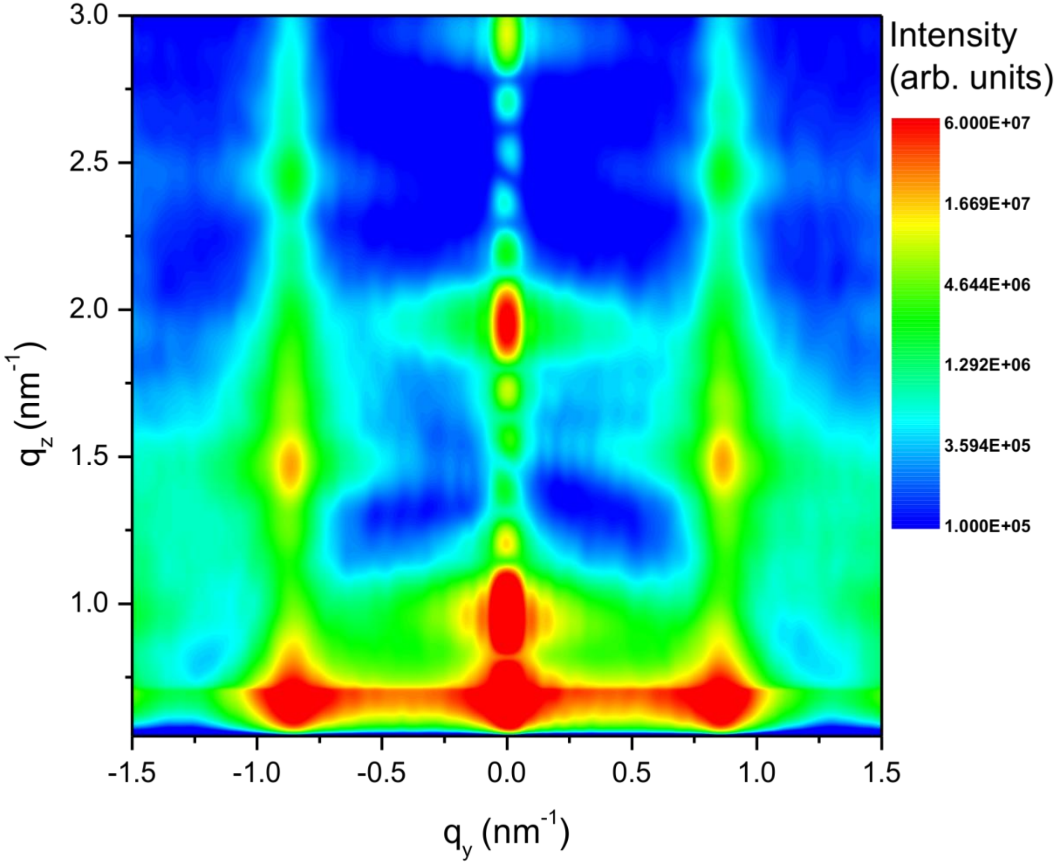
No shift between layers

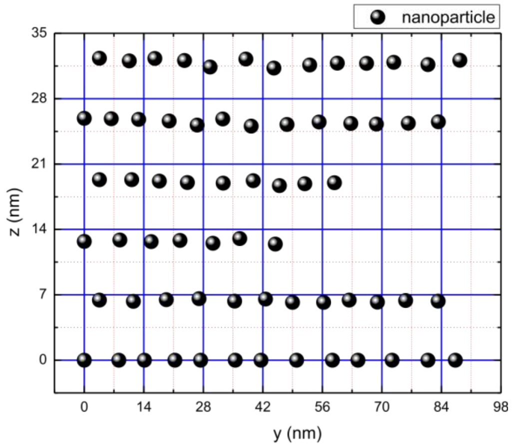




Nanoparticle multilayers and the role vertical correlation

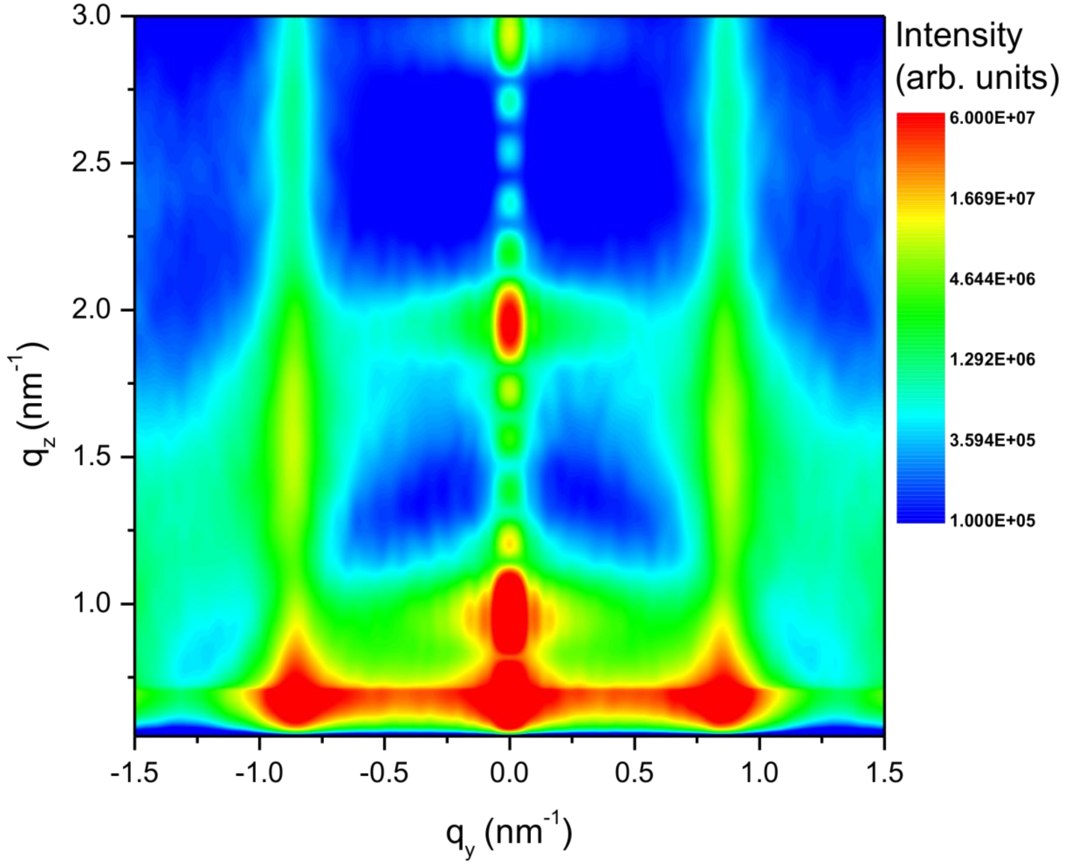
Alternate shift between layers

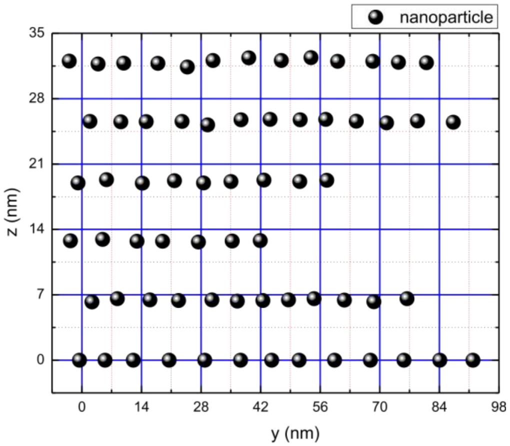




Nanoparticle multilayers and the role vertical correlation

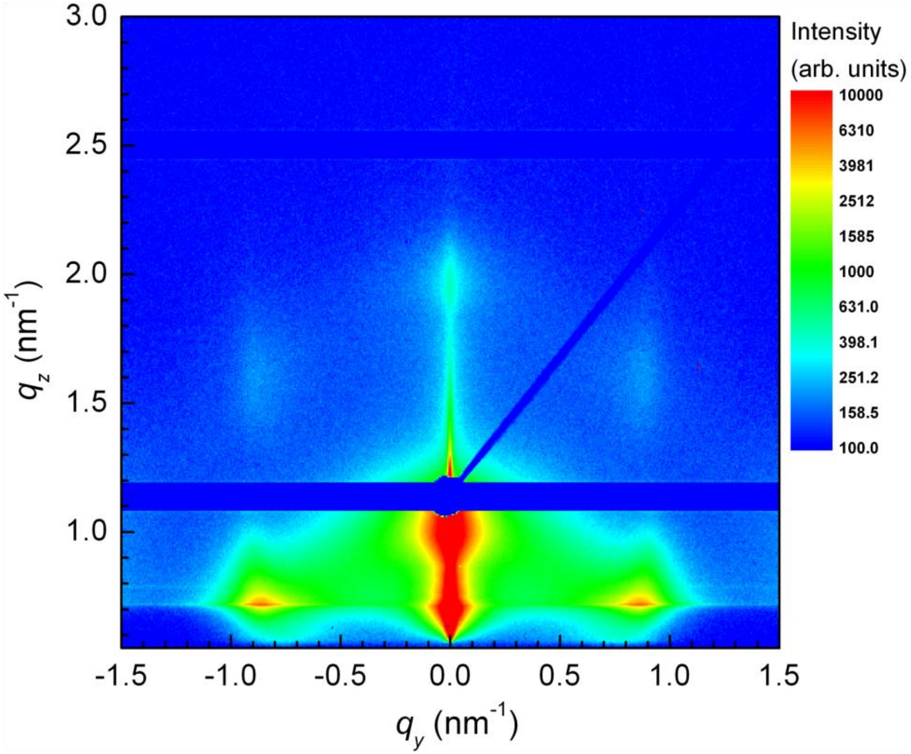
Uniform random shift between layers



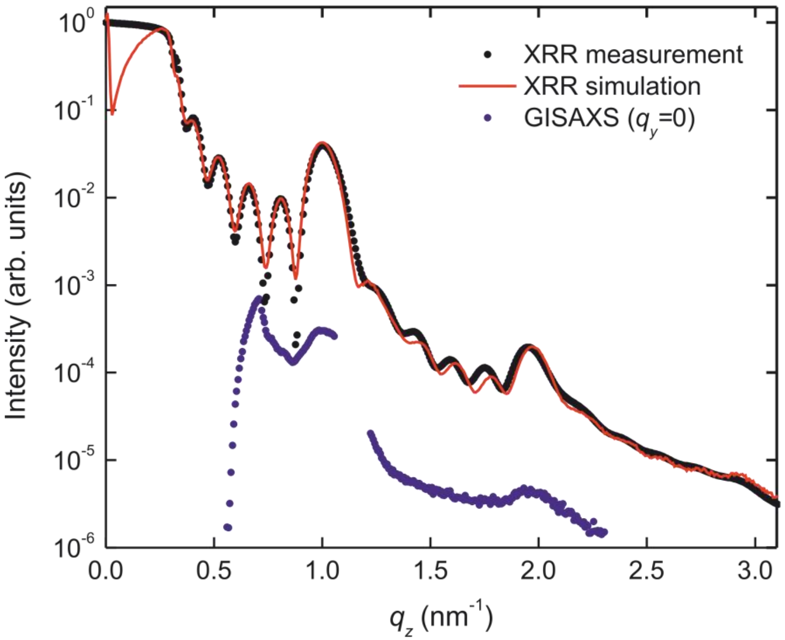


Nanoparticle multilayers / vertically uncorrelated system

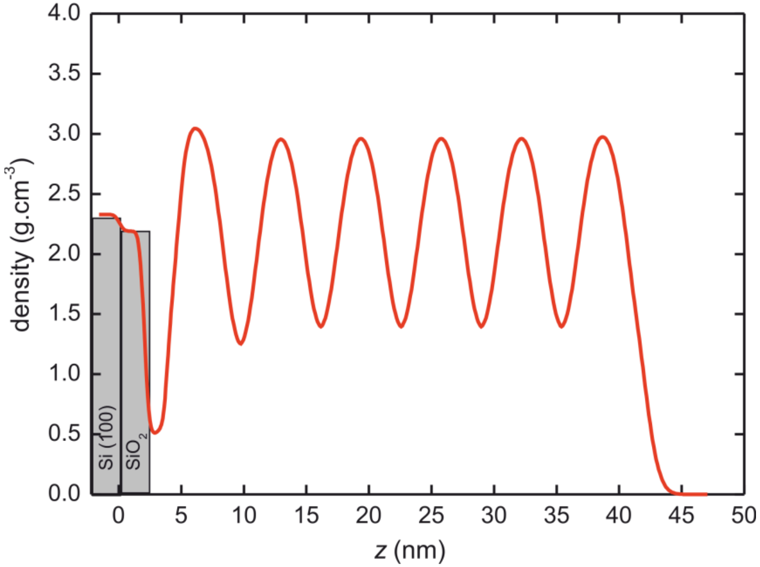
Measured GISAXS pattern for 6 uncorrelated layers



XRR measurement of 6 layers of nanoparticles

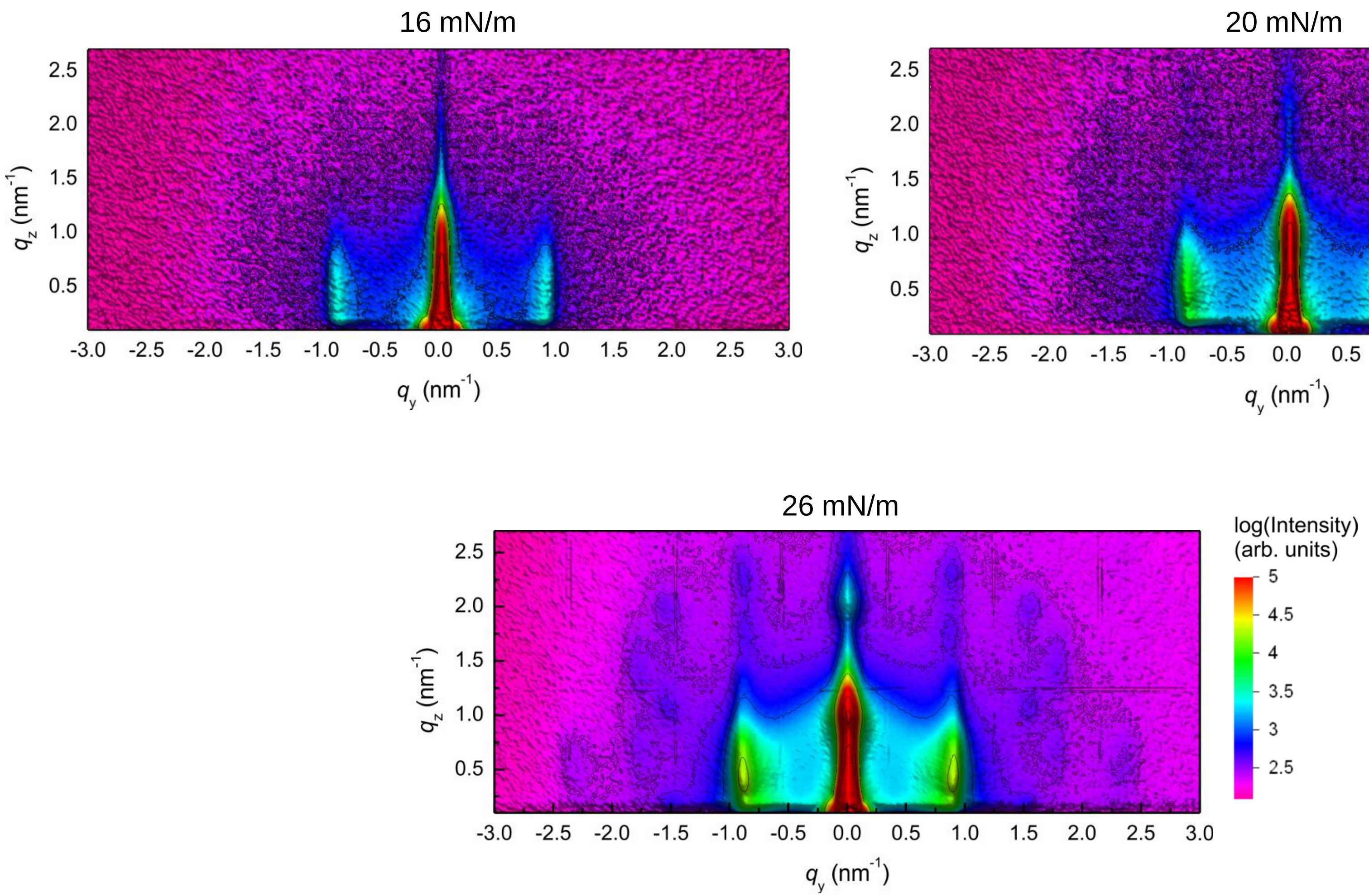


Density profile used for XRR simulation



Nanoparticle multilayers / vertically correlated system

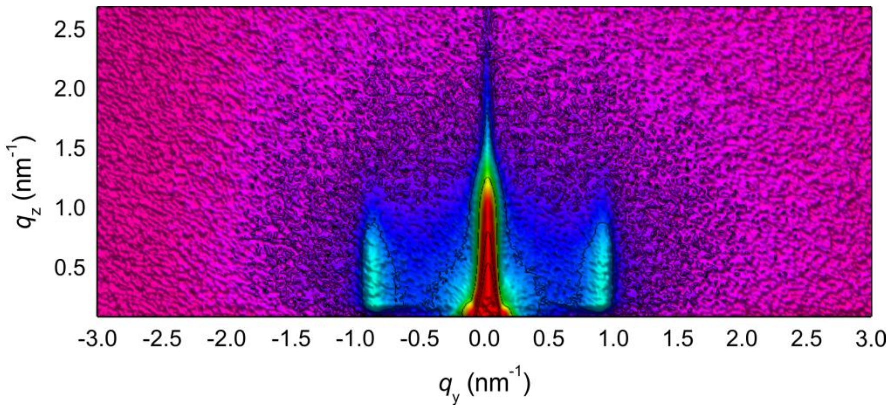
Measured GISAXS pattern for different surface pressures at Langmuir-Blodgett trough



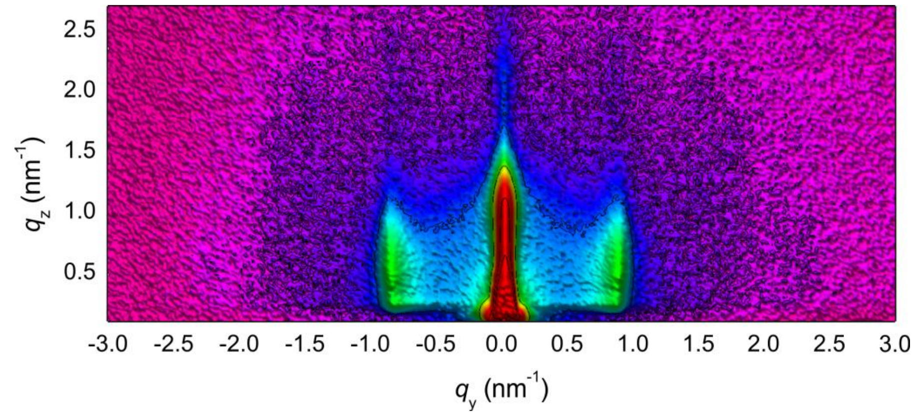
Nanoparticle multilayers / vertically correlated system

Measured GISAXS pattern for different surface pressures at Langmuir-Blodgett trough

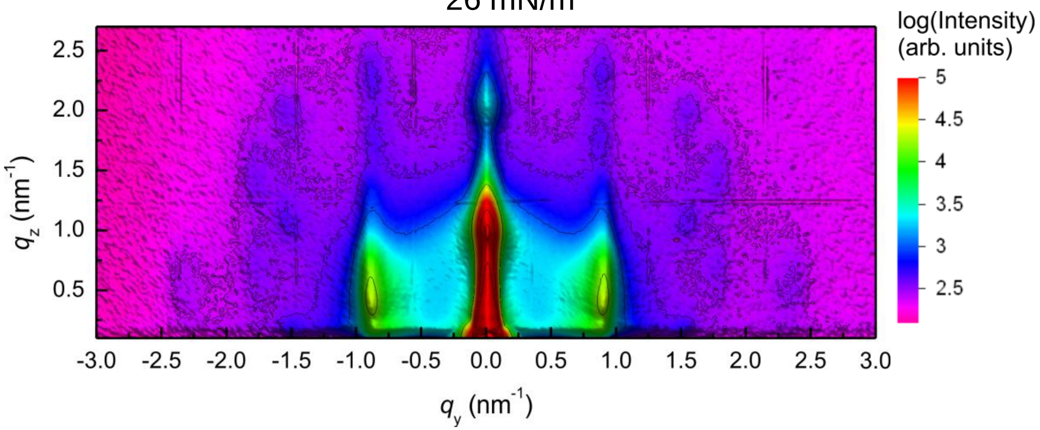
16 mN/m



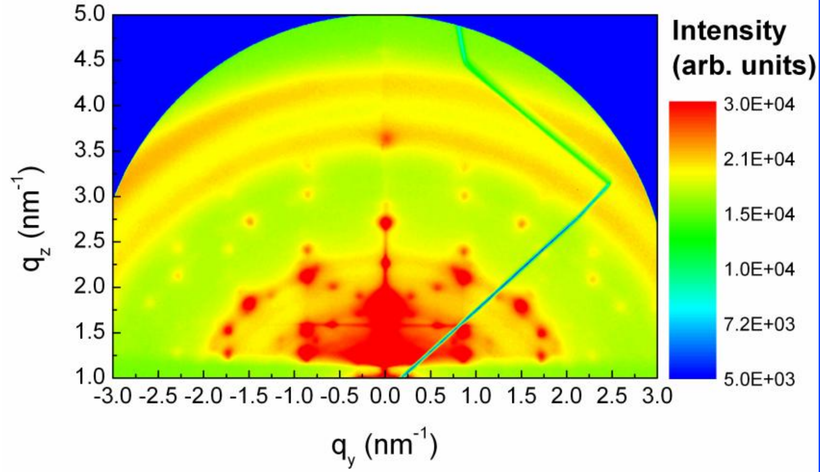
20 mN/m



26 mN/m

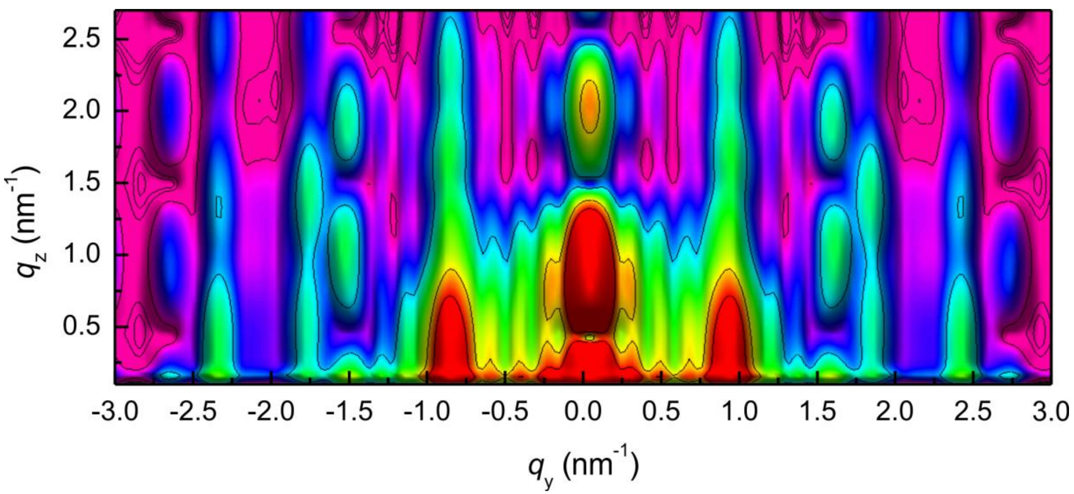


dropcast method

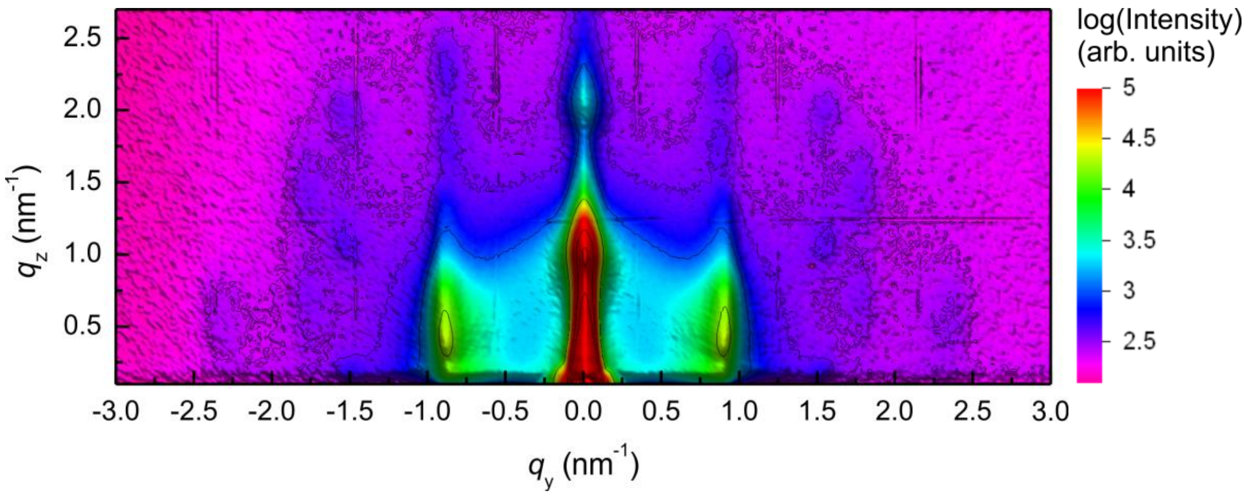


Nanoparticle multilayers / vertically correlated system

GISAXS simulation (2 monolayers)

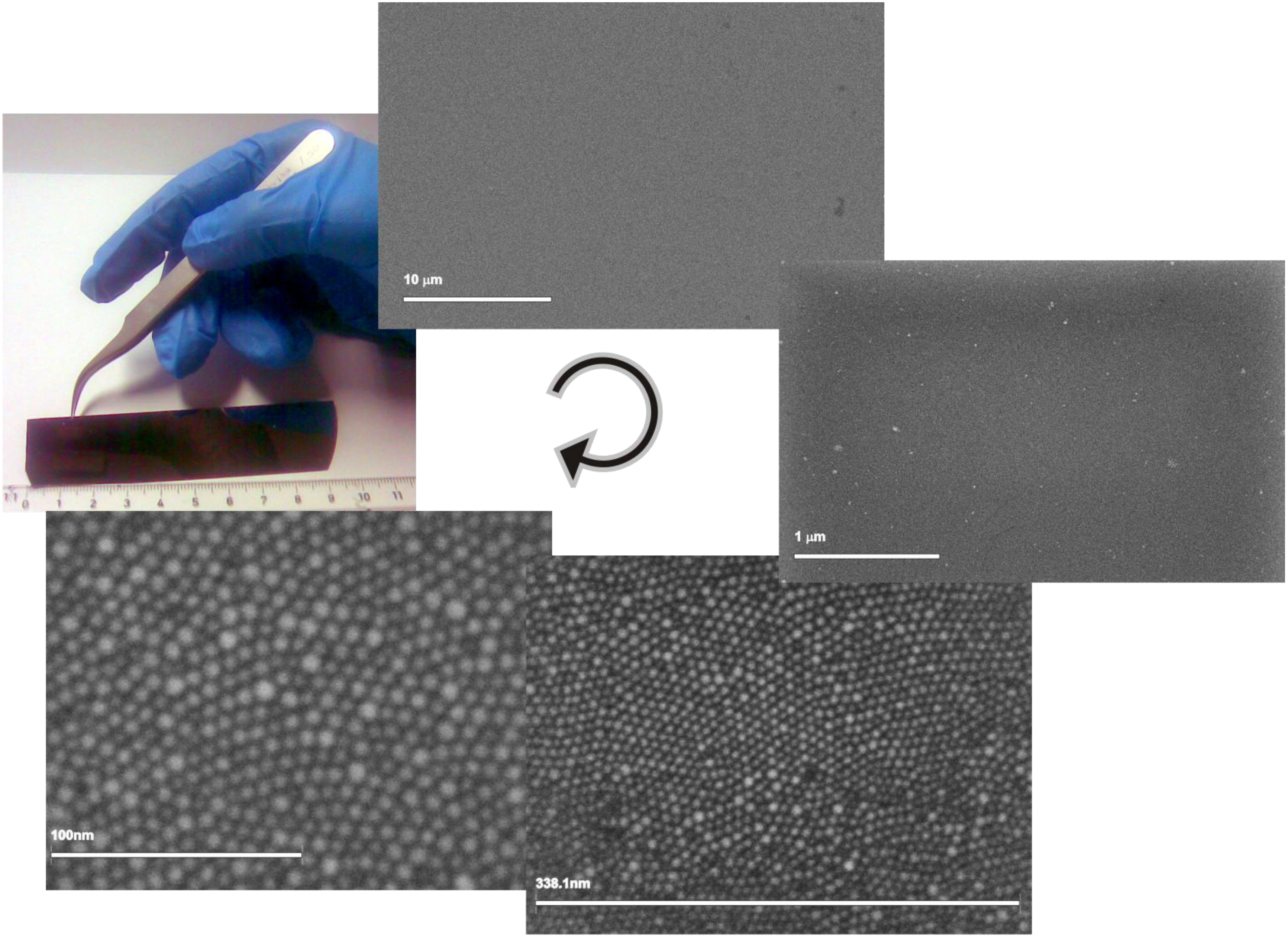


GISAXS measurement



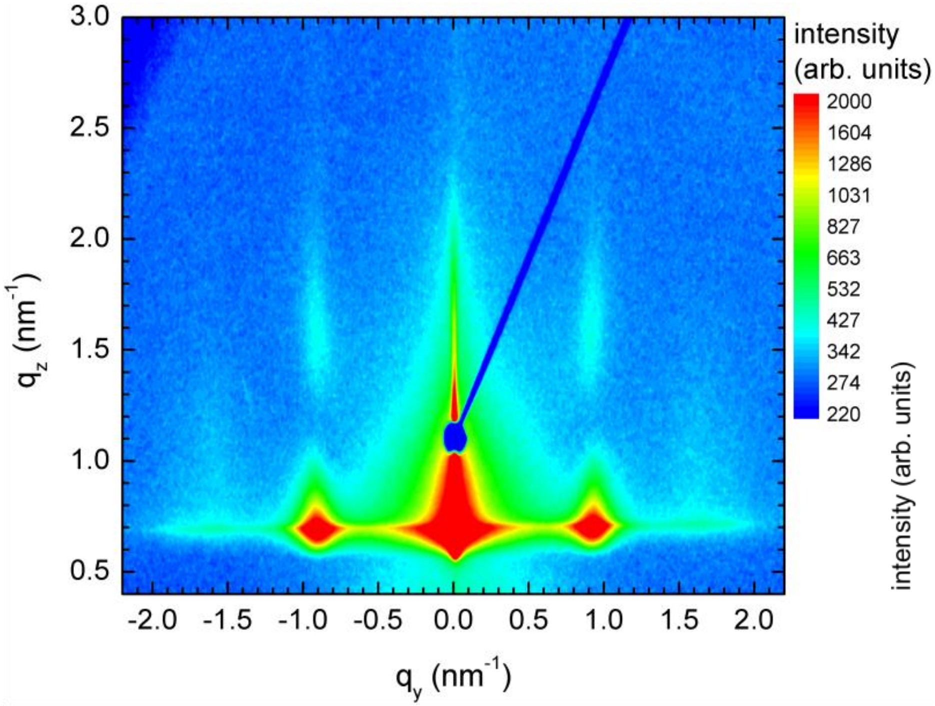
GISAXS in applied nanoparticle science

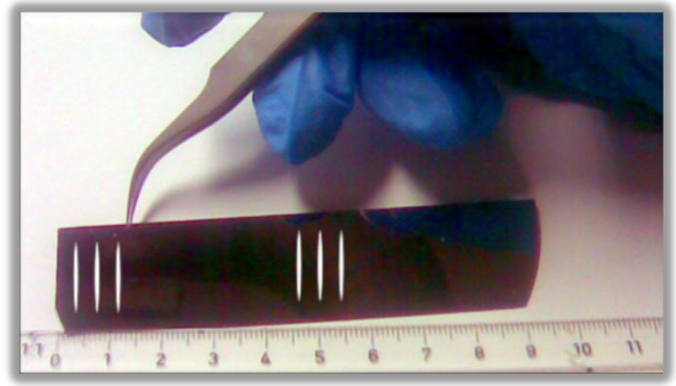
Homogenous large-scale nanoparticle deposition

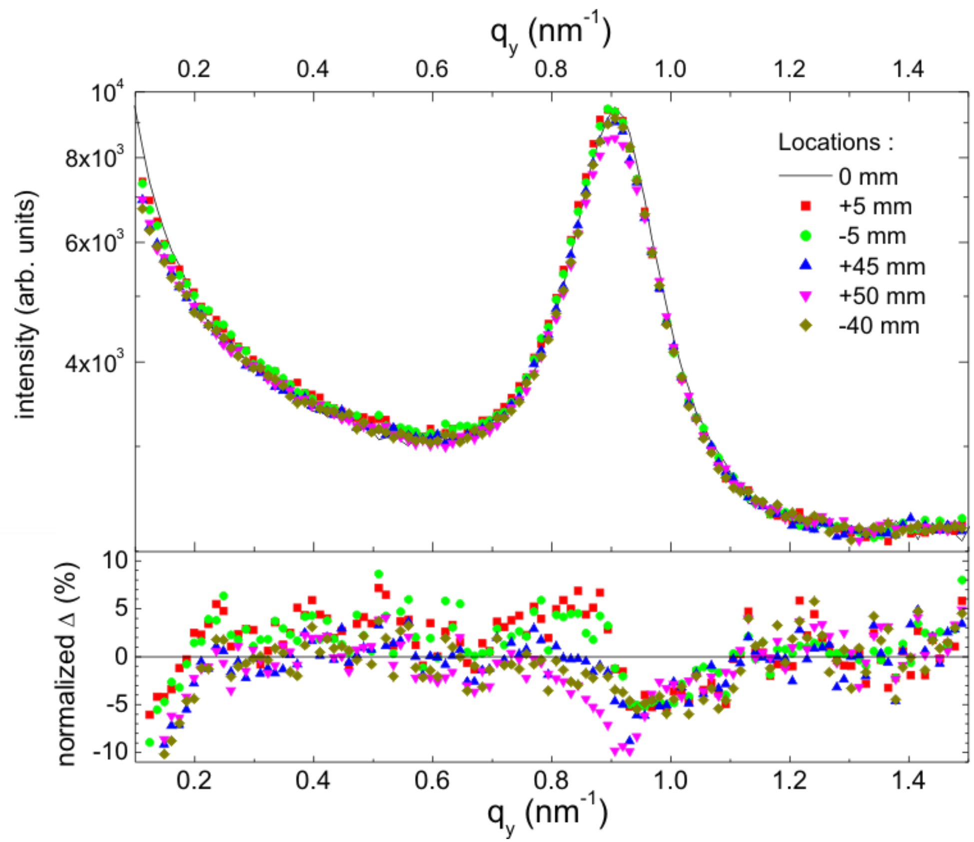


GISAXS in applied nanoparticle science

Homogenous large-scale nanoparticle deposition







L. Chitu, P. Siffalovic et al., Meas. Sci. Rev. 10, 162 (2010)

GISAXS in applied nanoparticle science / solar cells

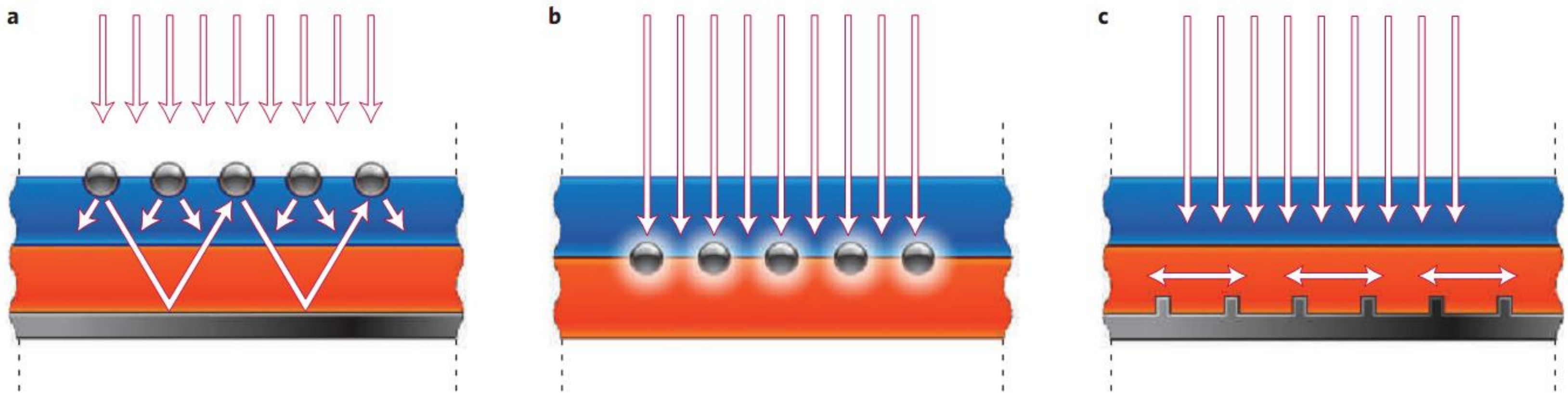


Figure 2 | Plasmonic light-trapping geometries for thin-film solar cells. a, Light trapping by scattering from metal nanoparticles at the surface of the solar cell. Light is preferentially scattered and trapped into the semiconductor thin film by multiple and high-angle scattering, causing an increase in the effective optical path length in the cell. **b**, Light trapping by the excitation of localized surface plasmons in metal nanoparticles embedded in the semiconductor. The excited particles' near-field causes the creation of electron-hole pairs in the semiconductor. **c**, Light trapping by the excitation of surface plasmon polaritons at the metal/semiconductor interface. A corrugated metal back surface couples light to surface plasmon polariton or photonic modes that propagate in the plane of the semiconductor layer.

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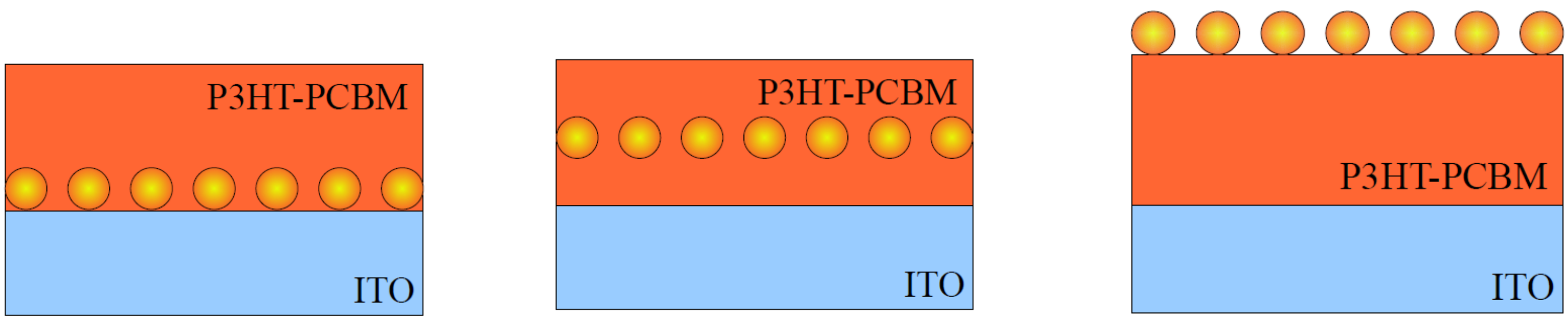
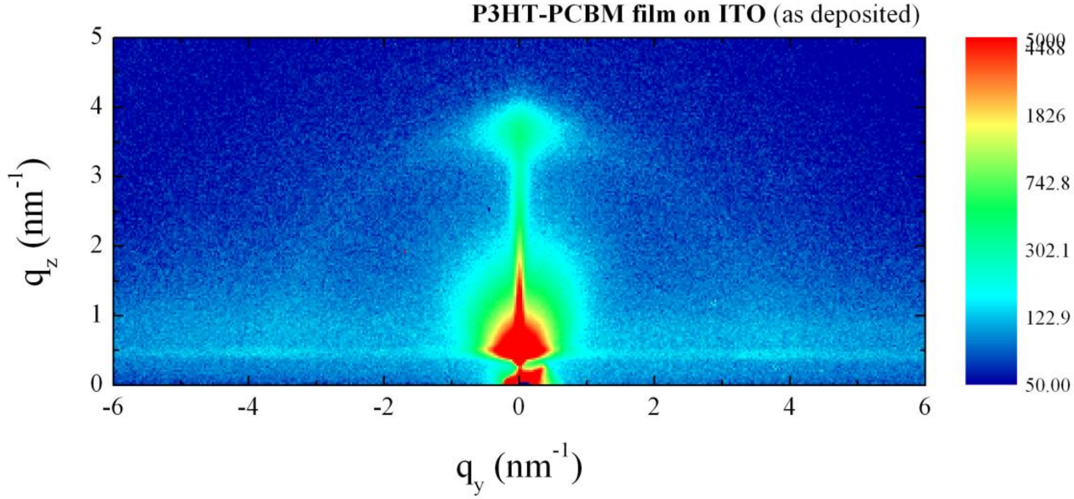
Ag nanoparticle inclusion into the polymer solar cells

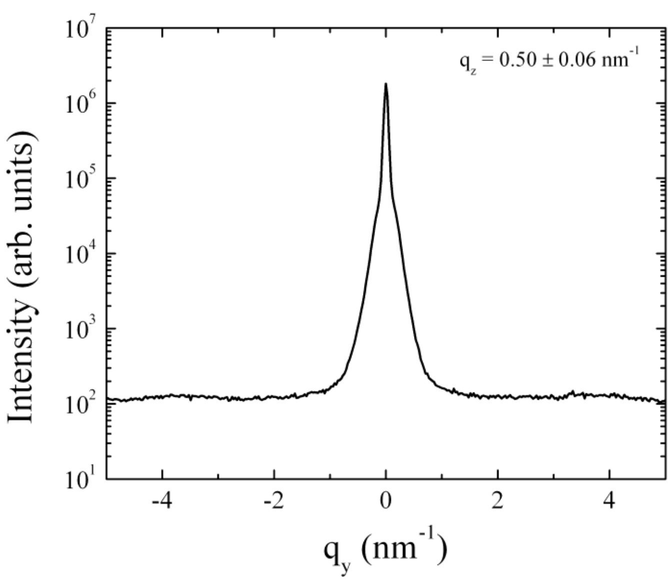


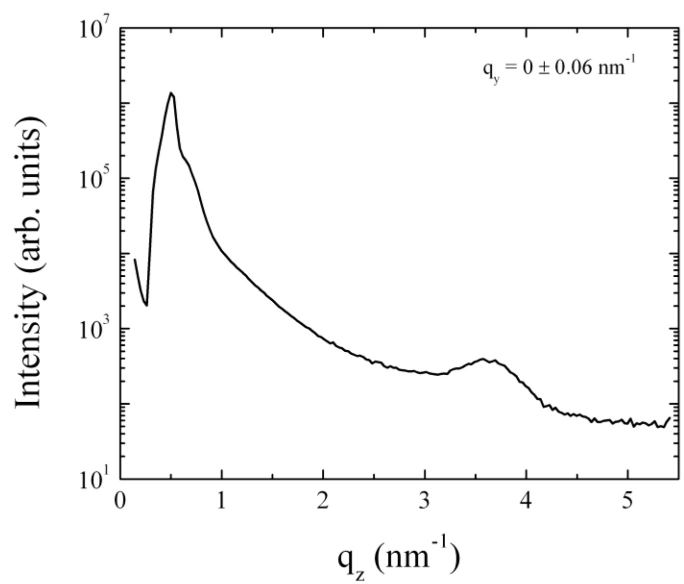
GISAXS in applied nanoparticle science / solar cells

Ag nanoparticle inclusion into the polymer solar cells



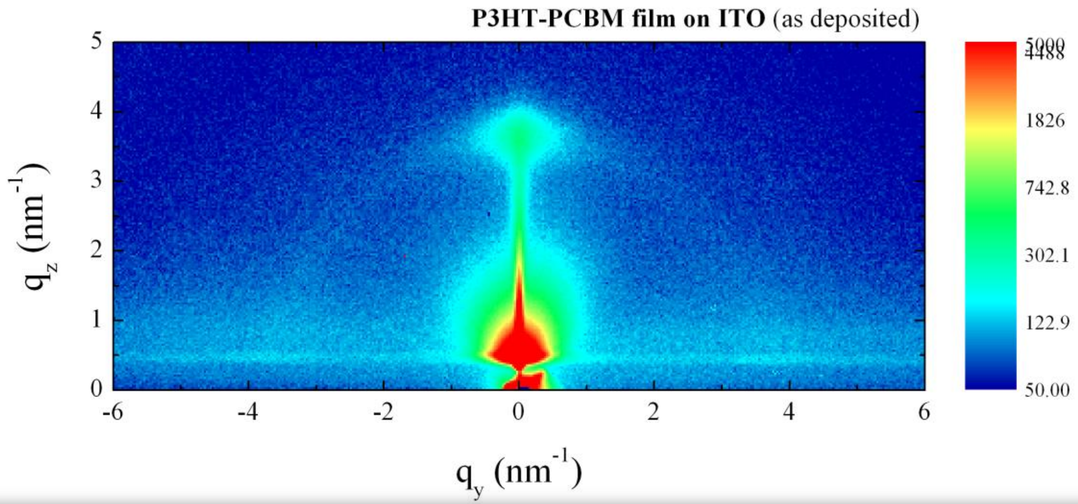
Molecular separation: **1.7 nm** (3.65 nm^{-1})

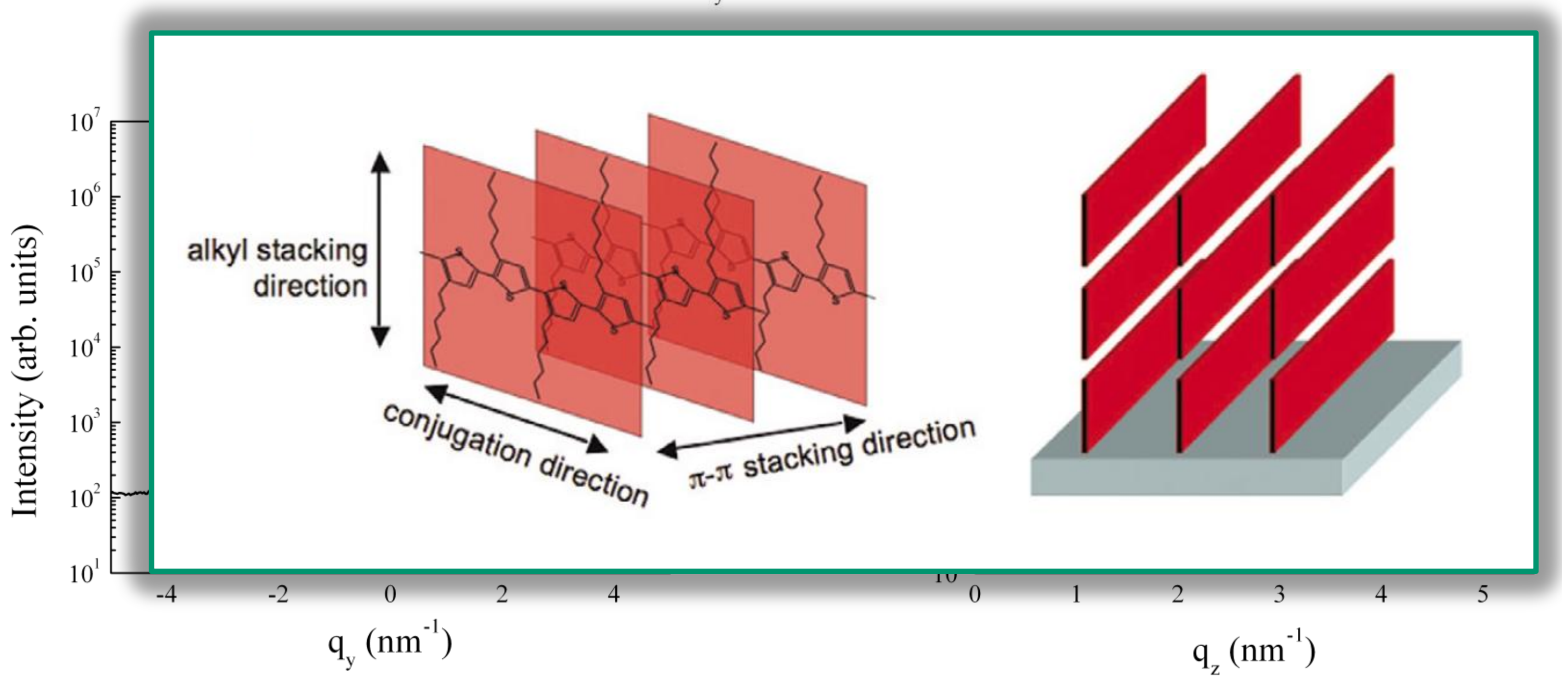




GISAXS in applied nanoparticle science / solar cells

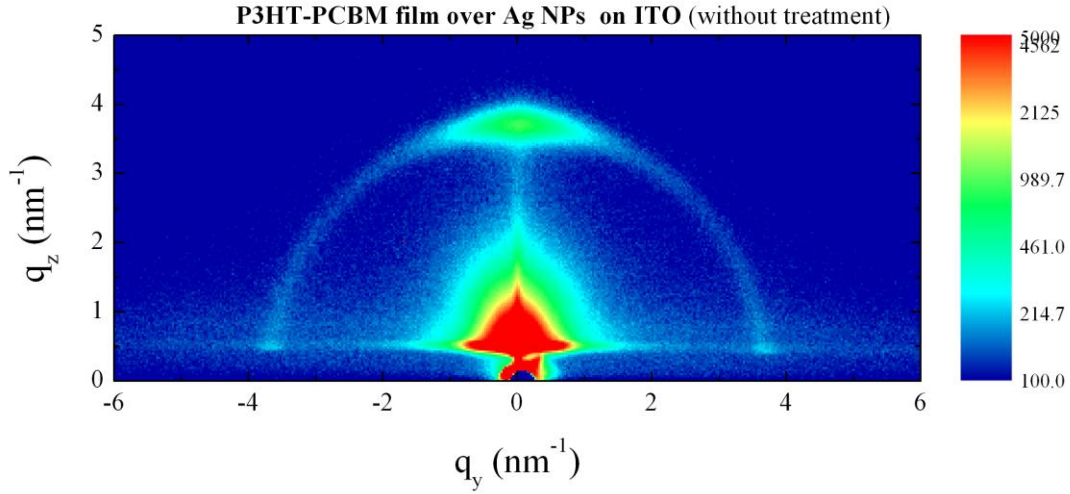
Ag nanoparticle inclusion into the polymer solar cells

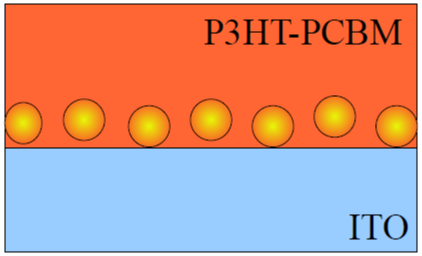


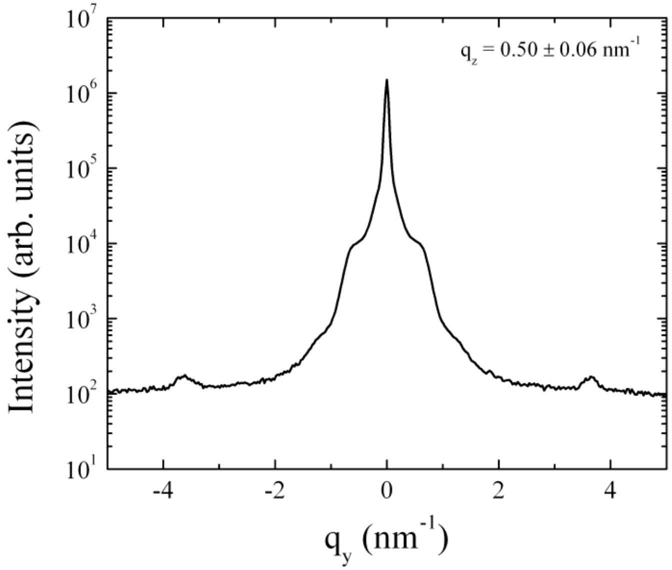


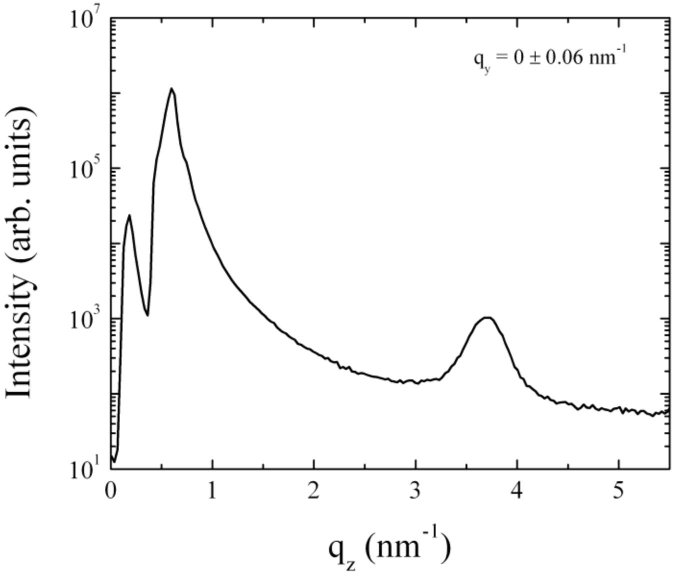
GISAXS in applied nanoparticle science / solar cells

Buried Ag nanoparticle template at the ITO/active layer interface









SAXS in applied nanoparticle science / strain gauges

Strain gauge sensors based on nanoparticle assemblies

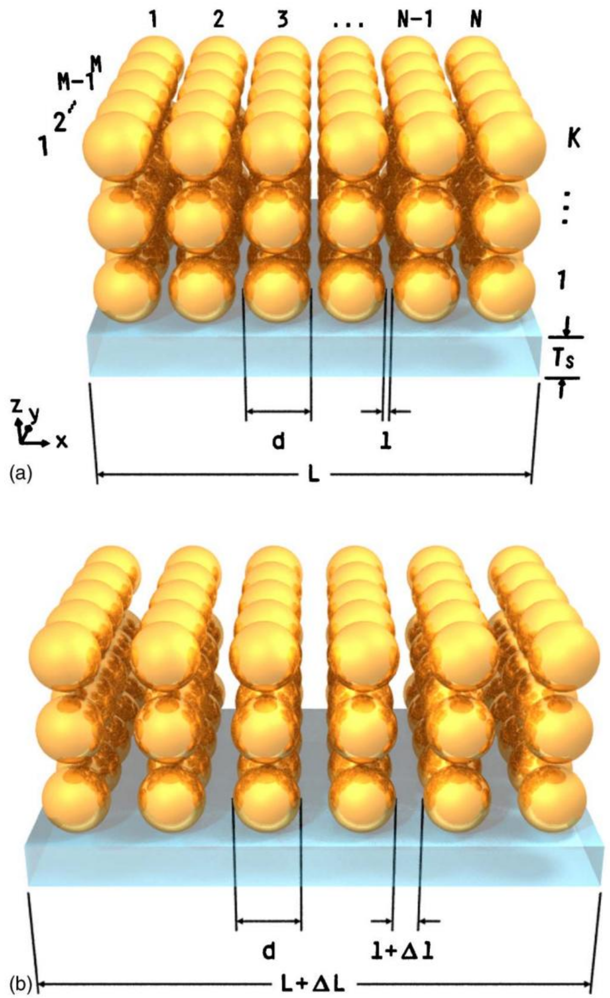
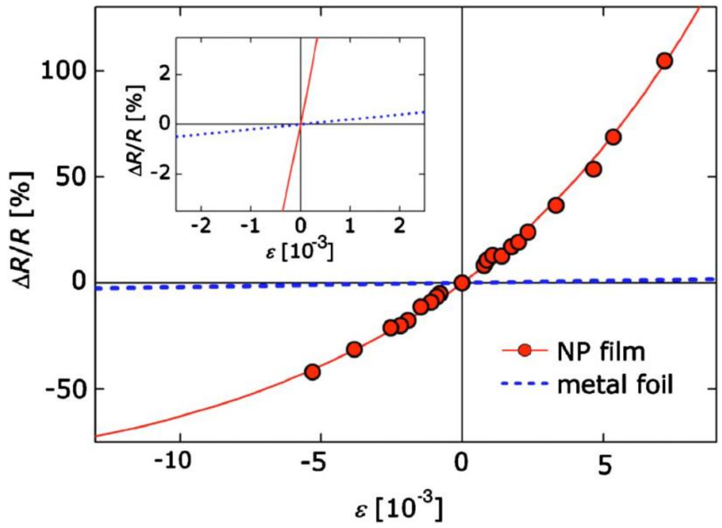


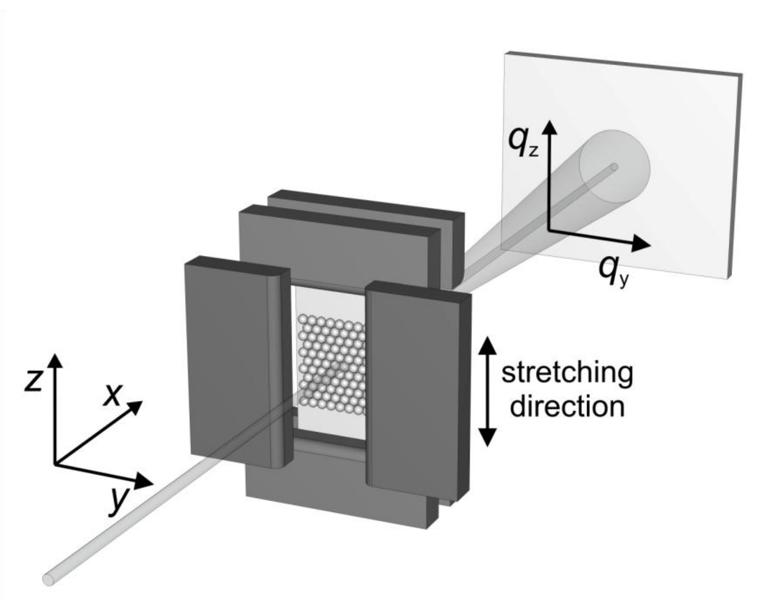
FIG. 1. (Color online) Schematic illustration of the geometry of the NP film. When the unstrained film (a) is subjected to a mechanical stress along the x direction, the overall film length L changes by ΔL (b). In our model, this strain is predominantly caused by changes in the interparticle separation gap l.

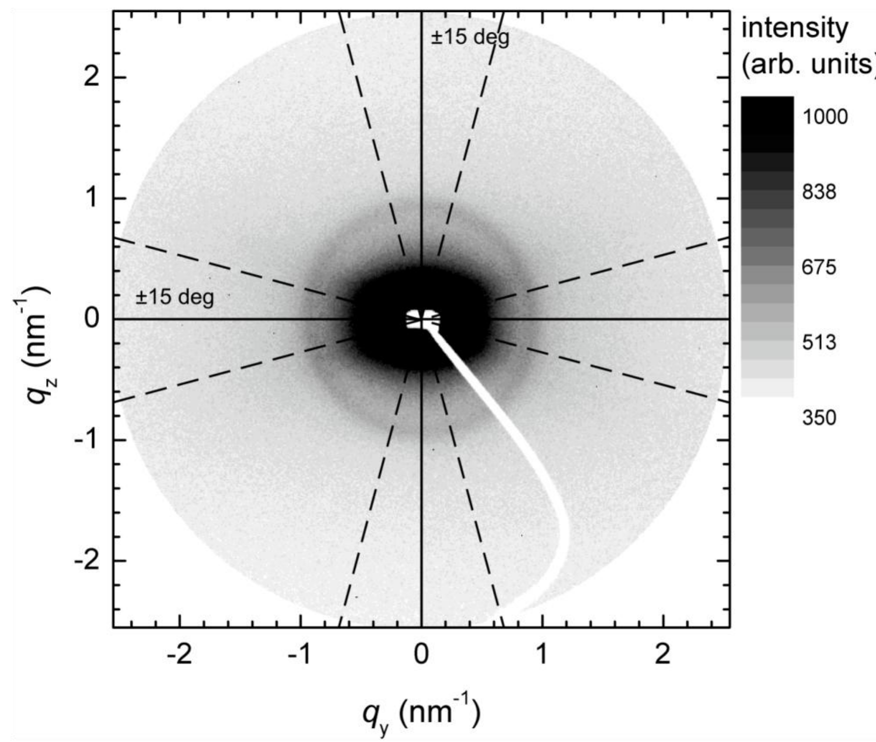


J. Herrmann et al., Appl. Phys. Lett. 91, 183105 (2007)

SAXS in applied nanoparticle science / strain gauges

Strain gauge sensors based on nanoparticle assemblies

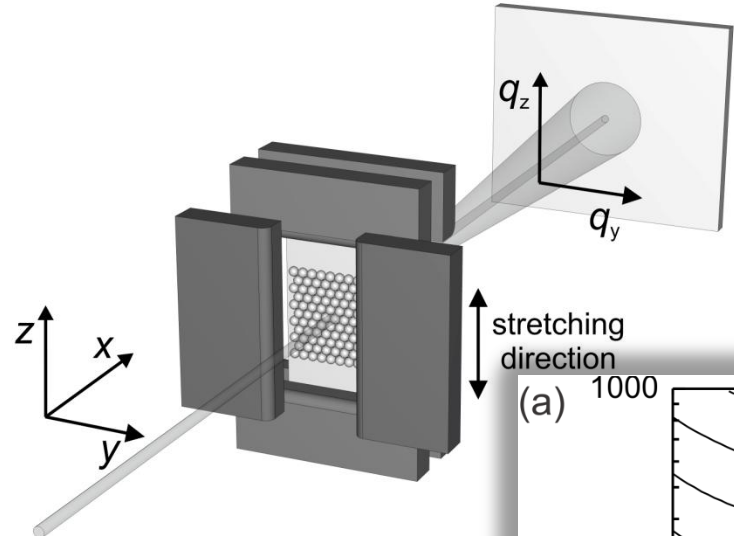


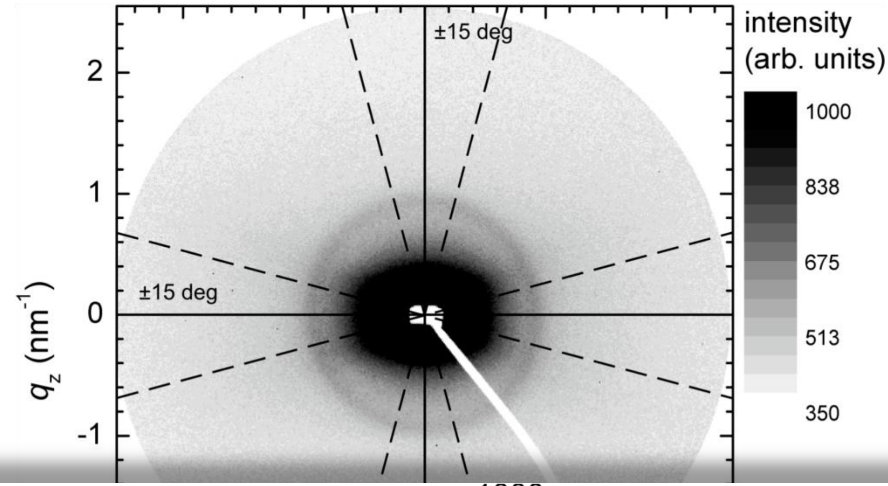


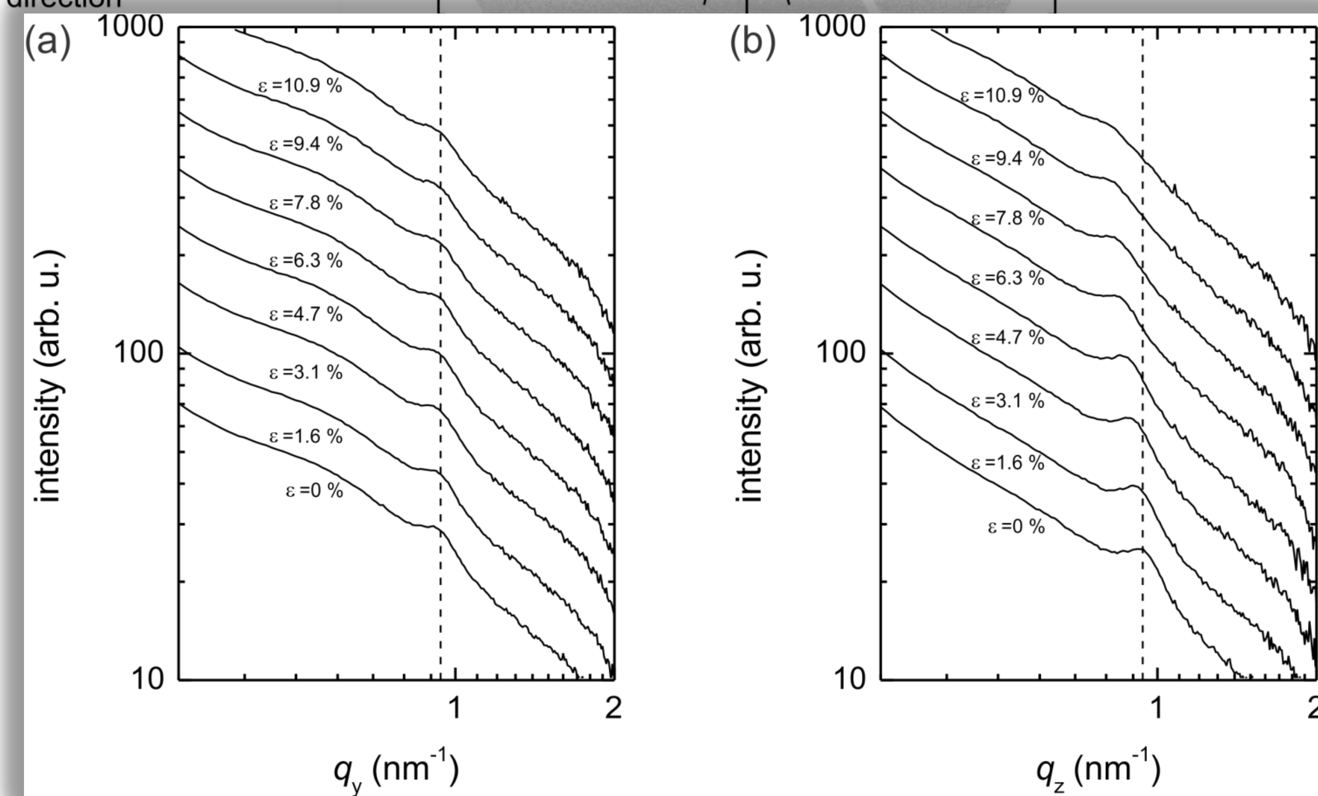
P. Siffalovic et al., Nanotechnology 21, 385702 (2010)

SAXS in applied nanoparticle science / strain gauges

Strain gauge sensors based on nanoparticle assemblies

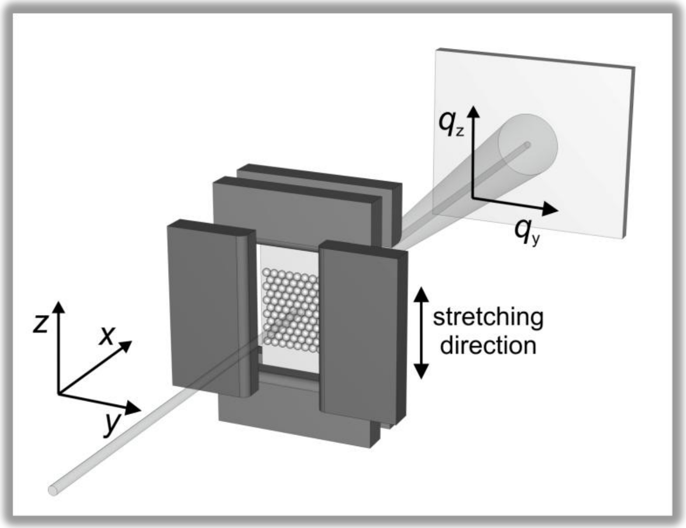


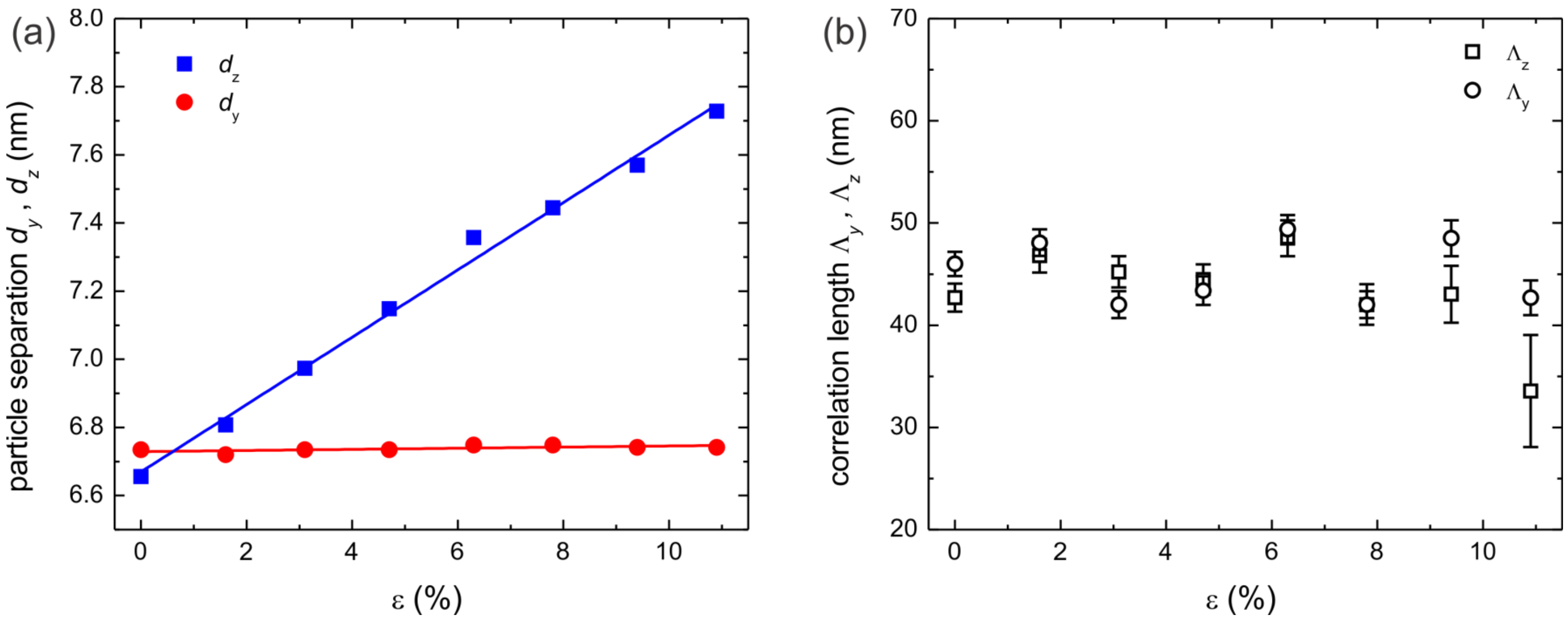




SAXS in applied nanoparticle science / strain gauges

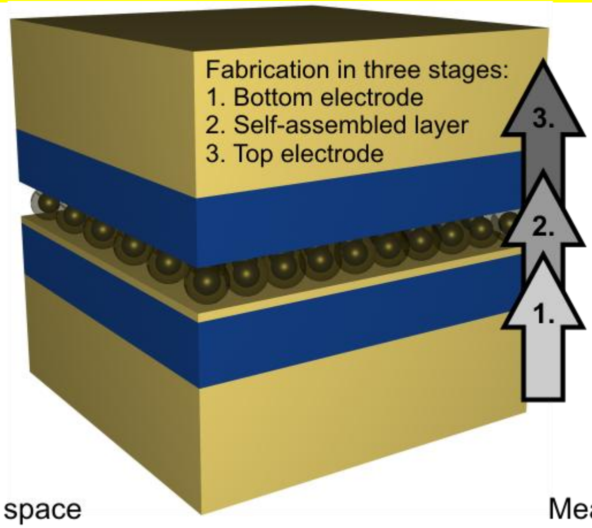
Strain gauge sensors based on nanoparticle assemblies



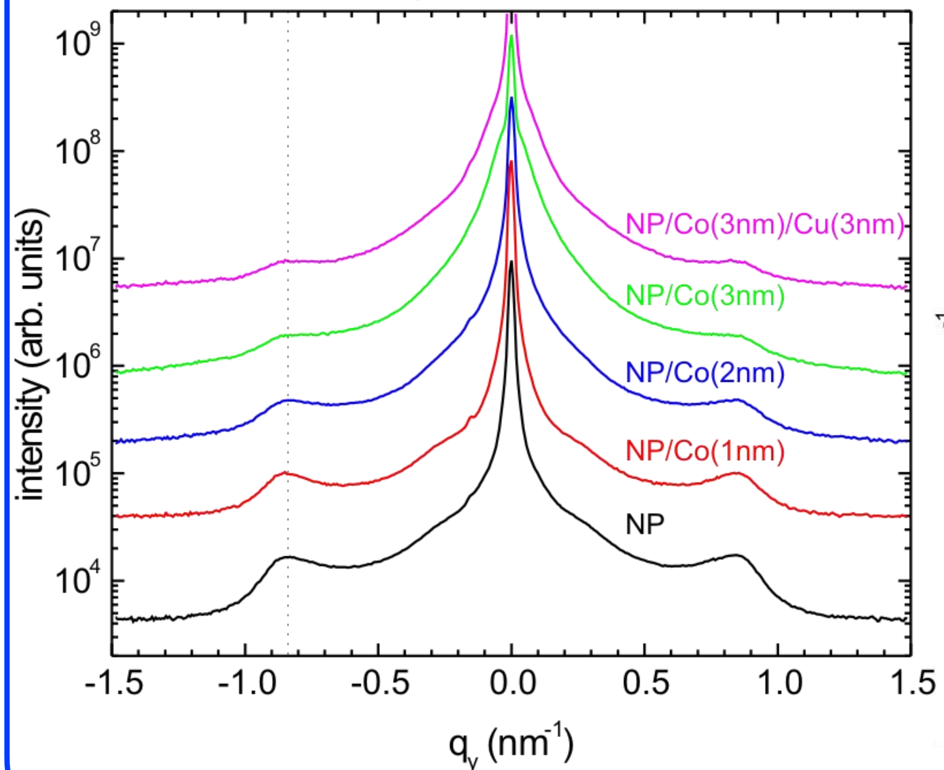


P. Siffalovic et al., Nanotechnology 21, 385702 (2010)

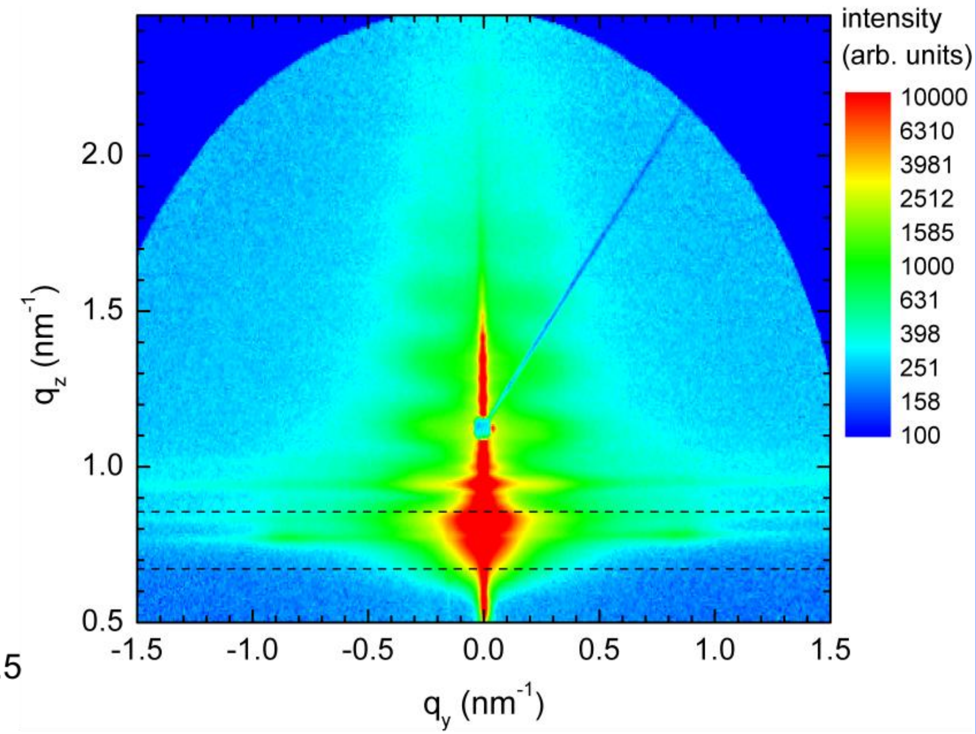
GISAXS in applied nanoparticle science / nanospintronics



Evolution of scans in reciprocal space with increasing thickness of top electrode



Measured GISAXS pattern of complete hybrid TMR structure



Summary

- GISAXS together with XRR provide unique set of measurements for characterization of buried nanoparticles at interfaces and their replication
- GISAXS provide possibility for ex-situ measurements and in-situ monitoring of nanoparticle layer growth

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