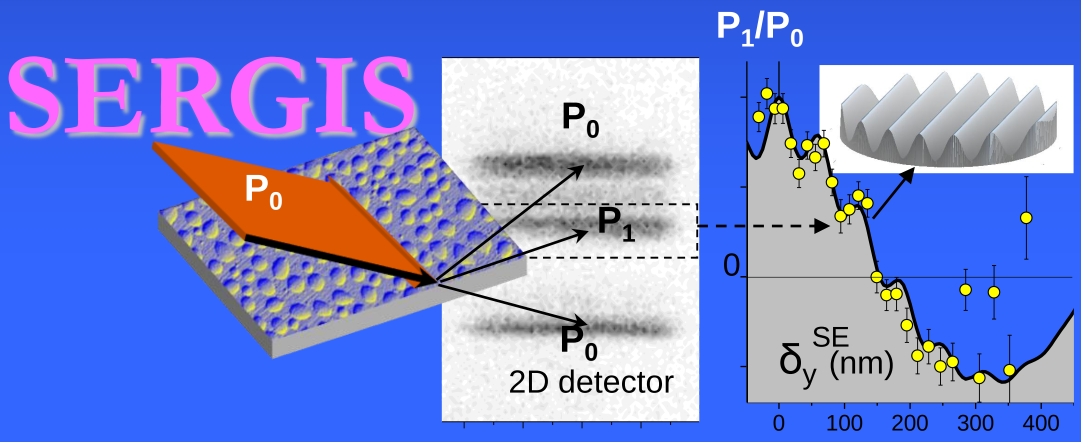
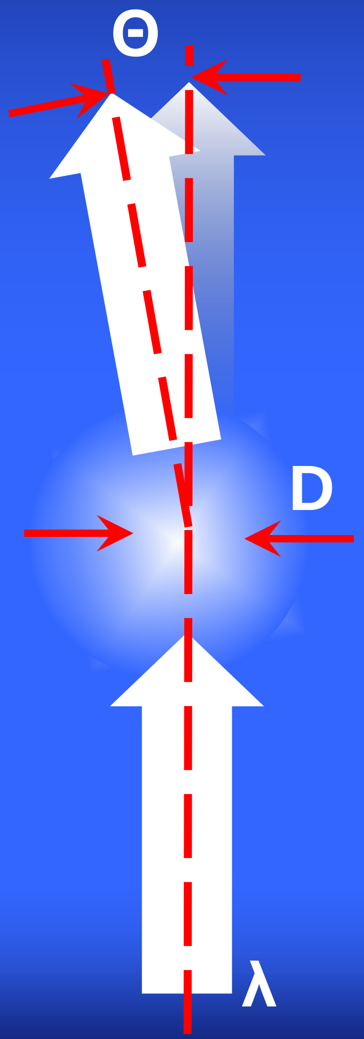
SPIN–ECHO CODING OF THE MOMENTUM TRANSFER IN GRAZING INCIDENCE SCATTERING



Алексей Воробьев

Университет Уппсала, Швеция

FORMULATION OF THE PROBLEM



Neutron scattering uses Bragg's law to measure a distance D within the sample

$\lambda = 2D \sin\Theta$

if D ‹‹ λ⇒ Θ is small

⇒ to measure small Θ one has to collimate neutron beams

⇒ measured intensity will be very low

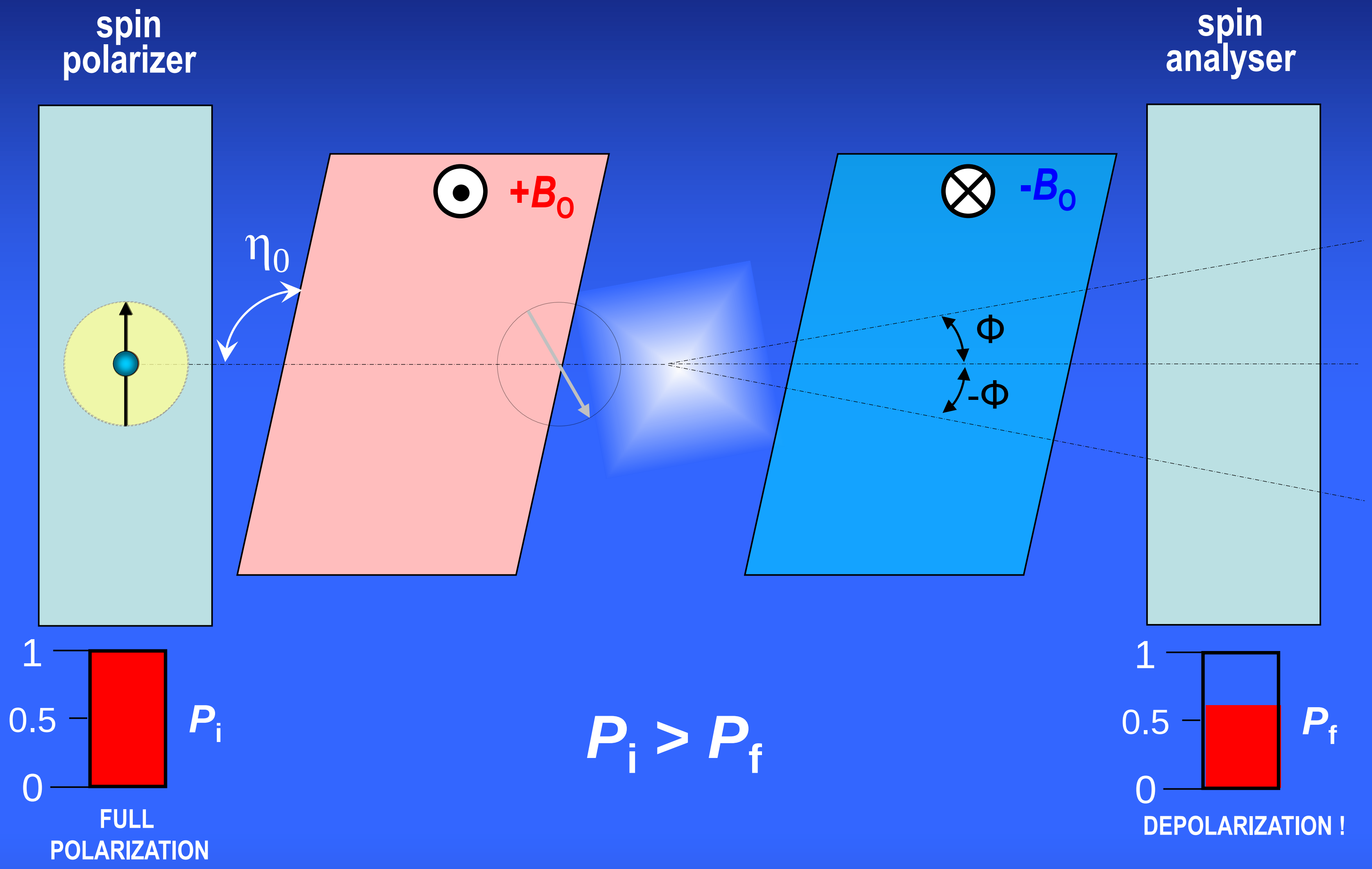
Proposed solution:

use spin-echo encoding of the momentum transfer

depolarization of the beam is measured instead of the scattering angle

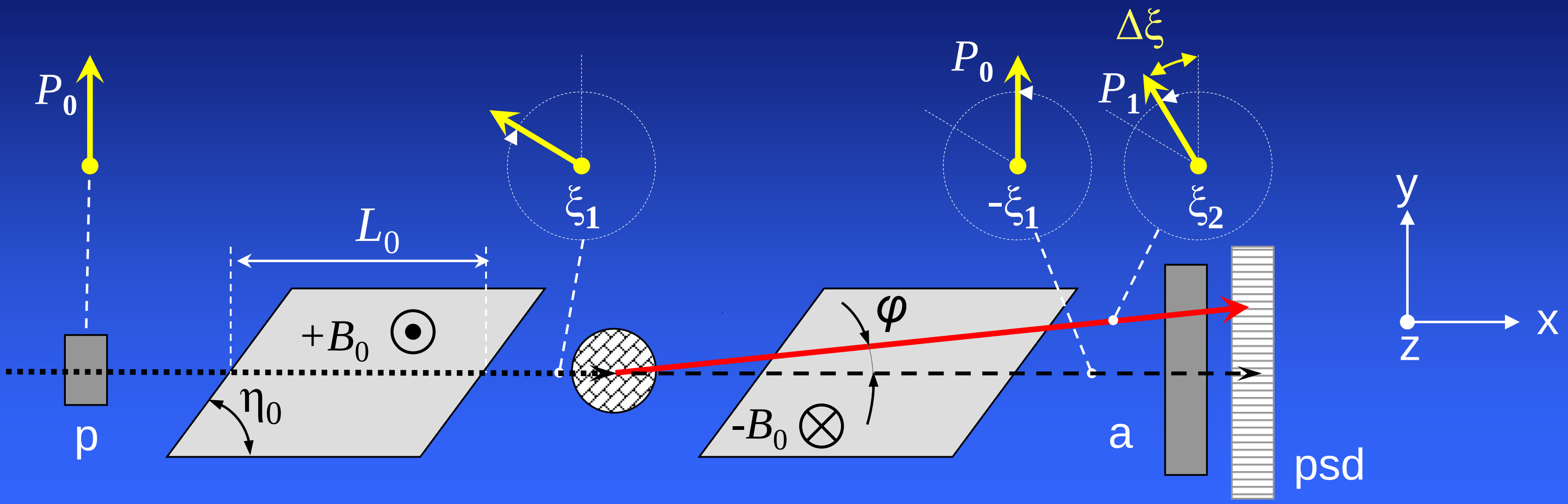
no collimation of the neutron beam is need

SCATTERING BY A STATIC SAMPLE



$$P_i > P_f$$

SPIN–ECHO GIVES RESULTS IN REAL SPACE



$$\Delta\xi = \xi_1 - \xi_2 = 2\pi\gamma_n B_0 \frac{L_0}{v}\left(1 - \frac{1}{\cos\varphi + \sin\varphi\cot\eta_0}\right) \cong \left(2\pi\gamma_n \frac{B_0 L_0}{v}\cot\eta_0\right)\sin\varphi =$$

$$= \left(\frac{\gamma_n B_0 L_0 \lambda^2}{K}\cot\eta_0\right)\left(\frac{2\pi}{\lambda}\sin\varphi\right) \equiv \delta_y^{SE} q_y$$

$$P_1 = P_0 \cos\Delta\xi\,.$$

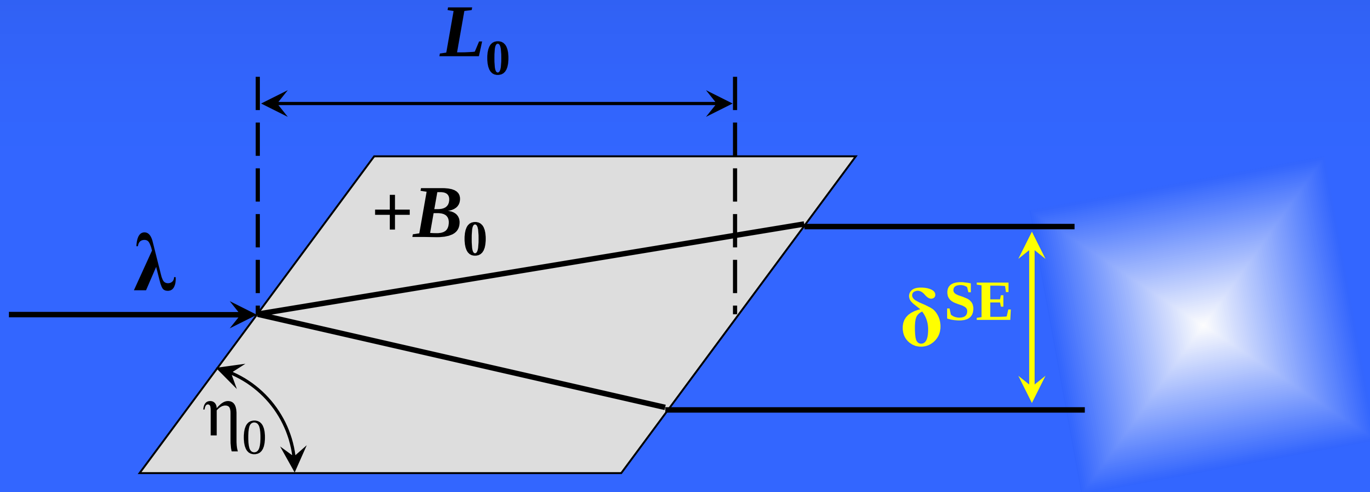
q_x=0

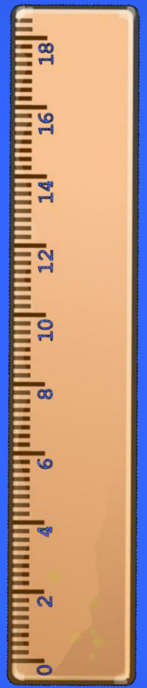
$$\frac{P_1}{P_0} = \langle\cos\Delta\xi\rangle \propto \frac{\int_{det} dq_y dq_z S(\mathbf{q})\cos(\delta_y^{SE} q_y)}{\int_{det} dq_y dq_z S(\mathbf{q})} = \int dx\,\Pi(x,y,0) \equiv G(y),$$

$$\Pi(\mathbf{R}) = \int d\mathbf{r}\,\rho(\mathbf{r})\rho(\mathbf{r}+\mathbf{R})$$

MEANING OF SPIN–ECHO LENGTH

$$\delta_y^{SE} = \left(\frac{\gamma_n B_0 L_0 \lambda^2}{K} \cot \eta_0 \right)$$

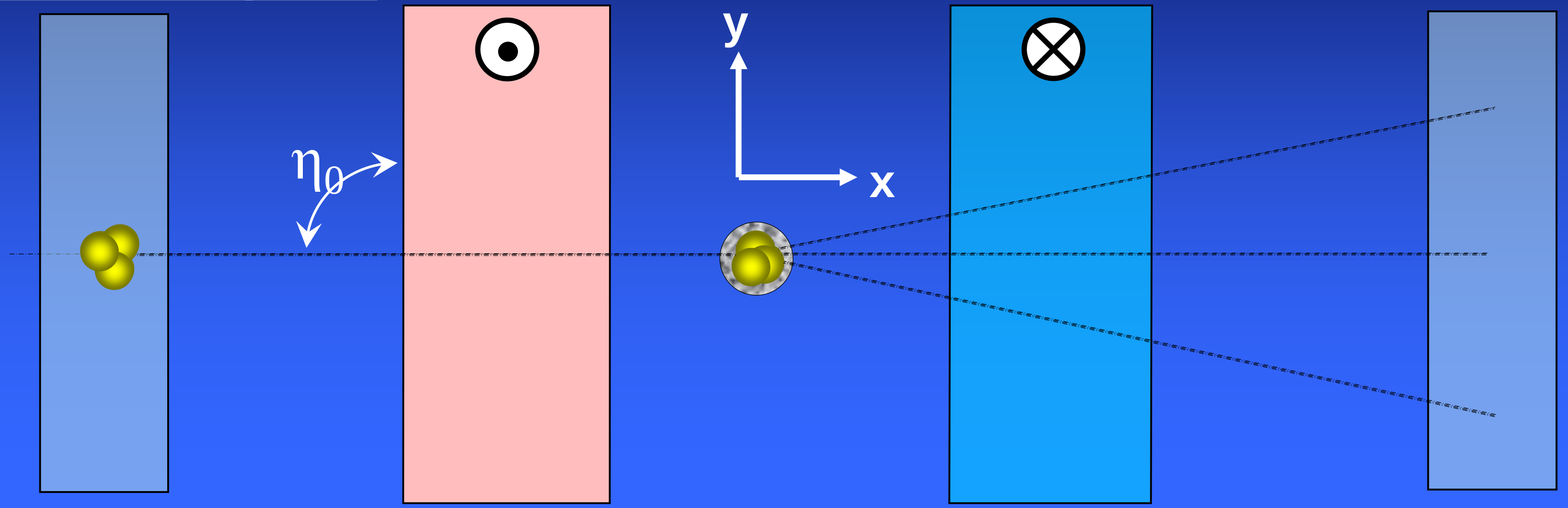


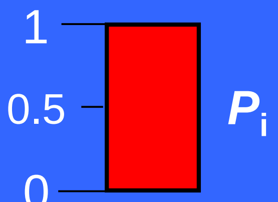


PARAMETERS: B_0, L_0, η_0, λ

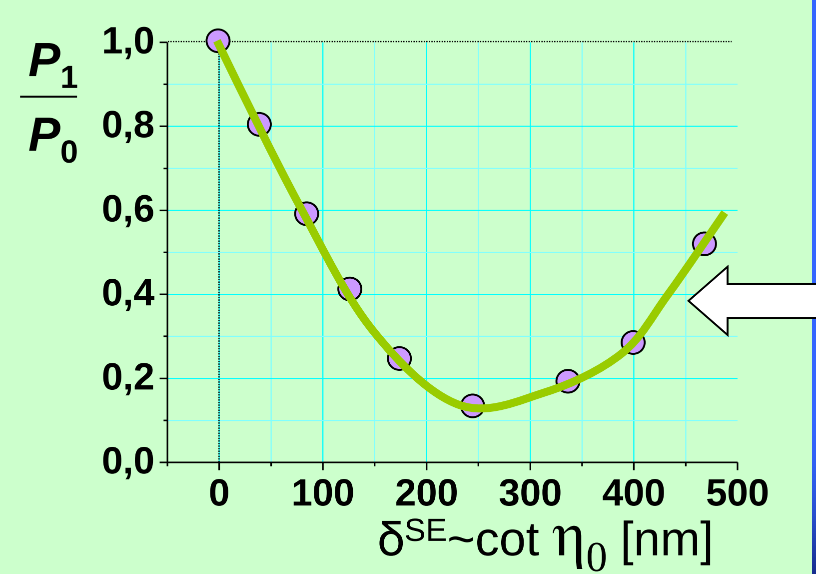
THE EXPERIMENT

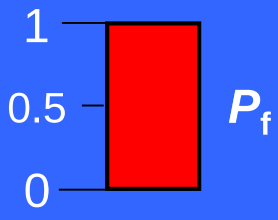
$$\frac{\gamma_n B_0 L_0 \lambda^2}{K} \cot \eta_0 \equiv \delta_y^{SE}$$





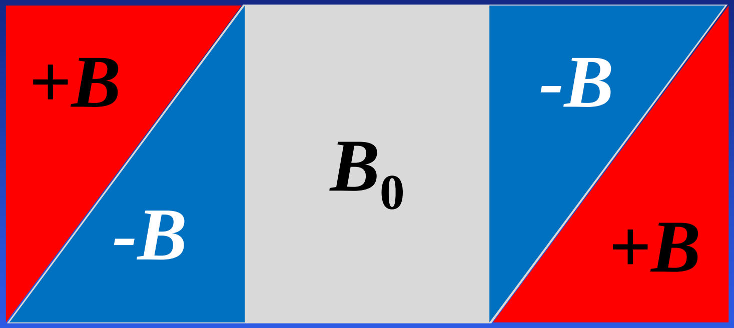
FULL POLARIZATION



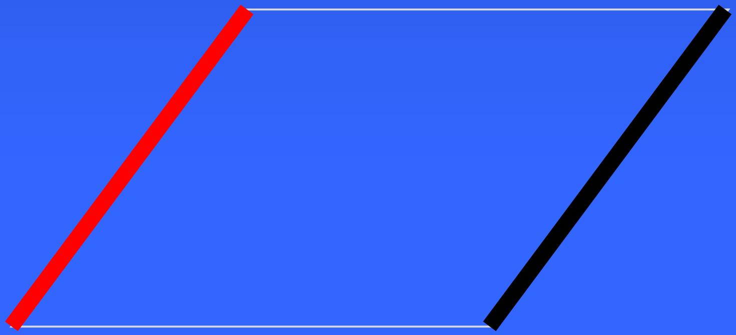


REAL-SPACE CORRELATION FUNCTION

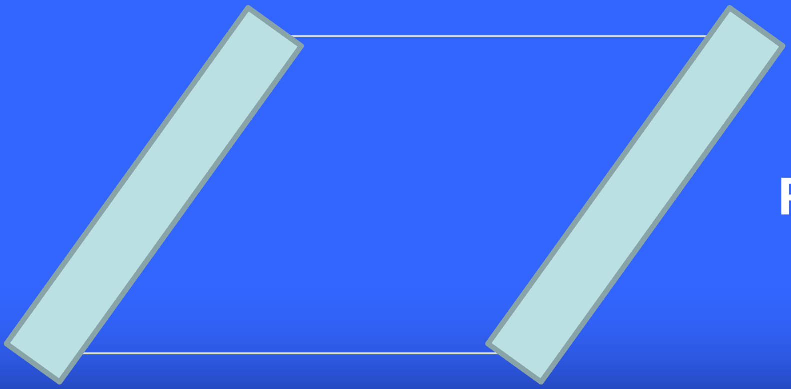
PRACTICAL REALIZATION



NON-ADIABATIC COILS FLIPPERS

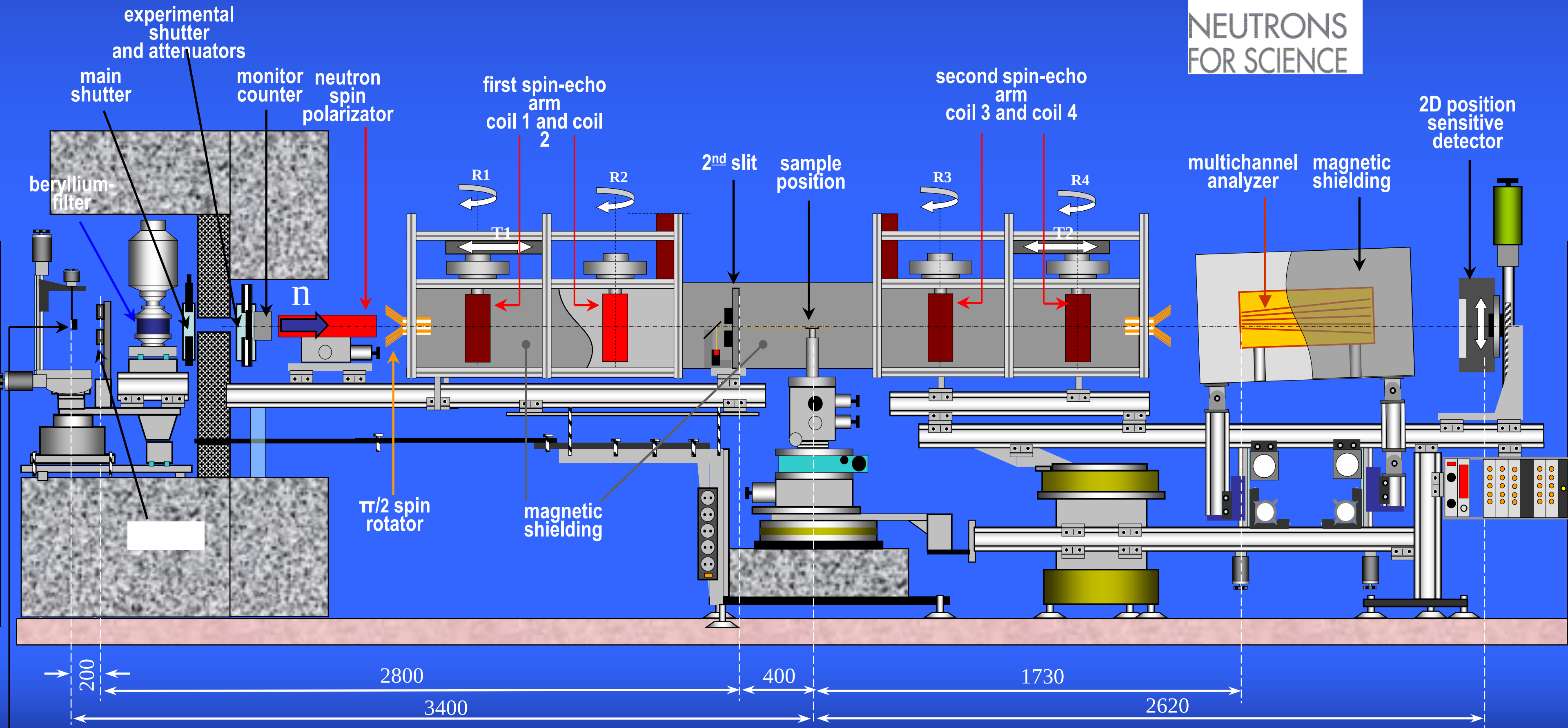


MAGNETIZED FOILS



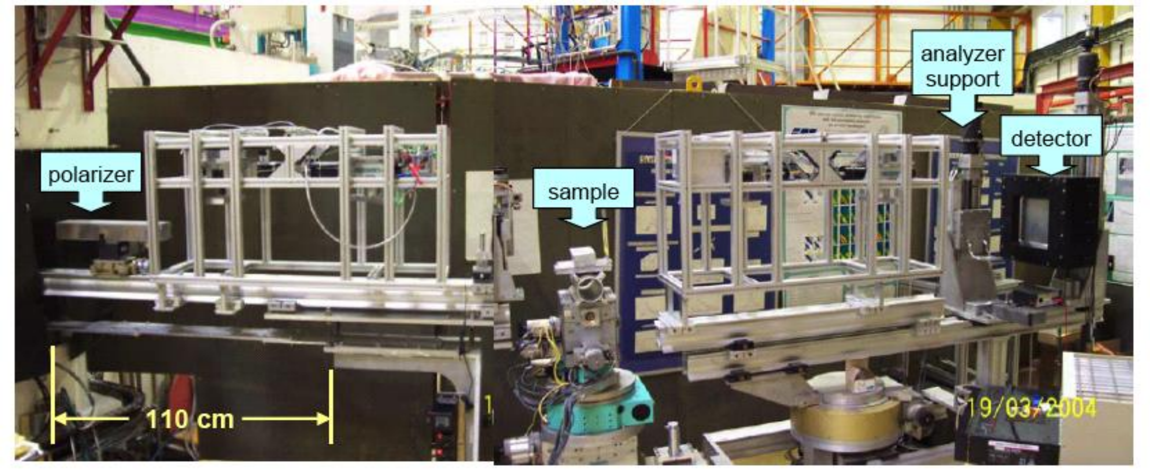
RESONANCE FLIPPERS

EVA REFLECTOMETER TRANSFORMED INTO A SERGIS PROTOTYPE INSTRUMENT



NEUTRONS FOR SCIENCE

EVA DURING THE TRANSFORMATION TO SERGIS



Beam size 50x5mm

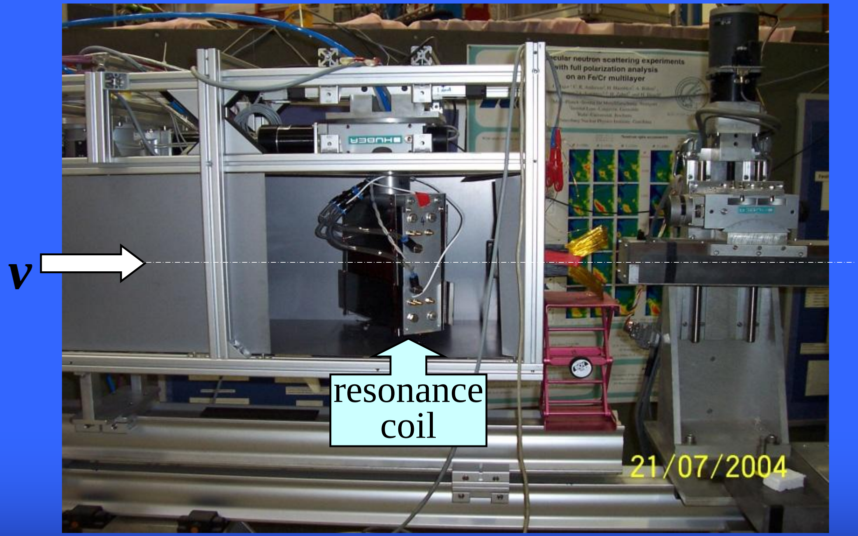
Wave numbers covered:

$1 \cdot 10^{-3}$ - $4 \cdot 10^{-2}$ Å^{-1}

Max. SE time in classical

configuration ($\eta_0=0$) 0.07ns

Max. spin echo length 4500 Å



$$\delta = \left\{ \frac{\gamma_n B d \lambda \cdot \cot \Theta}{v} \right\}$$

λ (neutron wavelength) 5.5 Å

v (neutron velocity) 720 m/s

Θ (tilt of precession coil) 50^o

B (magnetic field in leg) 310G

d (length of precession leg) 50 cm

EVA reflectometer transformed into a SERGIS prototype instrument

- λ 5.5 Å
- ν (velocity) 720 m/s
- η_0 (tilt of precession coil) 50^o
- B_0 (magnetic field) 310G
- L_0 (length of precession leg) 50 cm

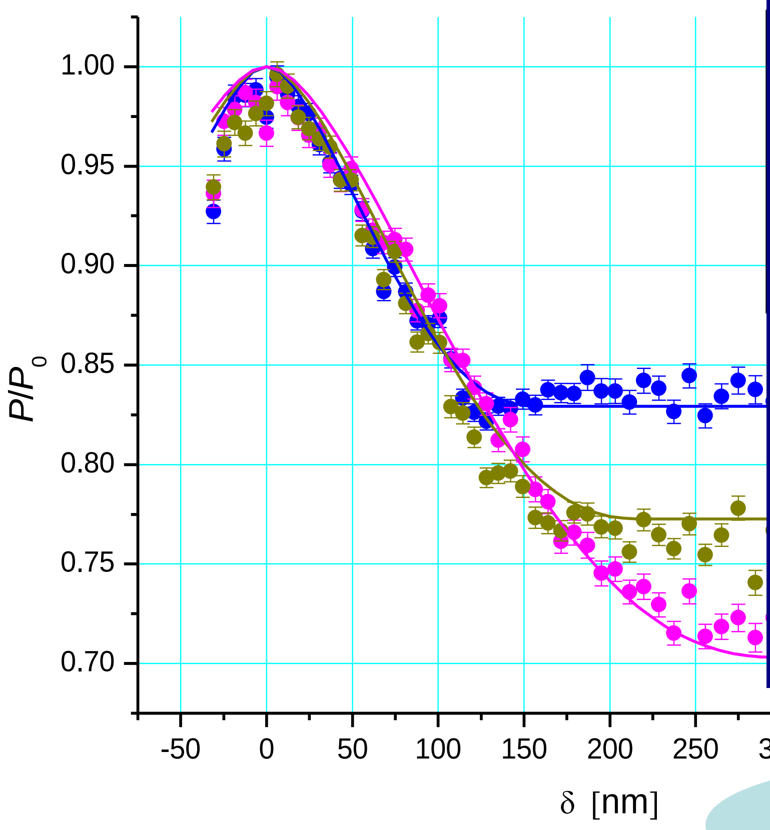
Max. spin echo length 4500 Å

SESANS experiments: polystyrene spheres

Test experiments in transmission mode

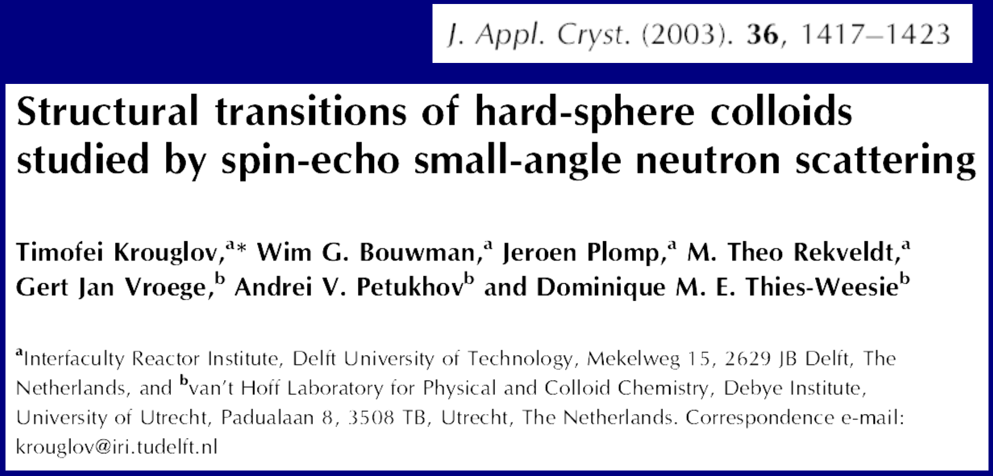
2.5% polystyrene balls in 3:1 D_2O/H_2O

2mm thick cell



Diameter 2R

The very first SESANS experiments in Delft



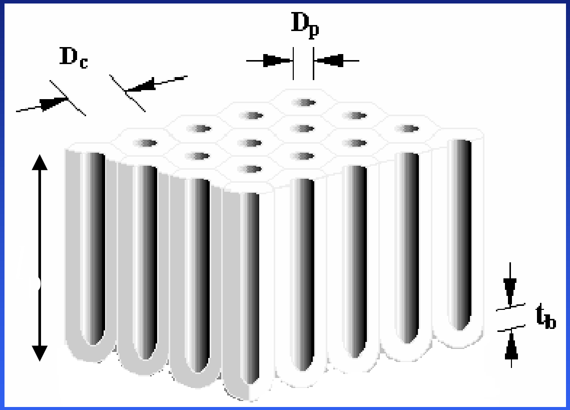
J. Appl. Cryst. (2003). **36**, 1417–1423

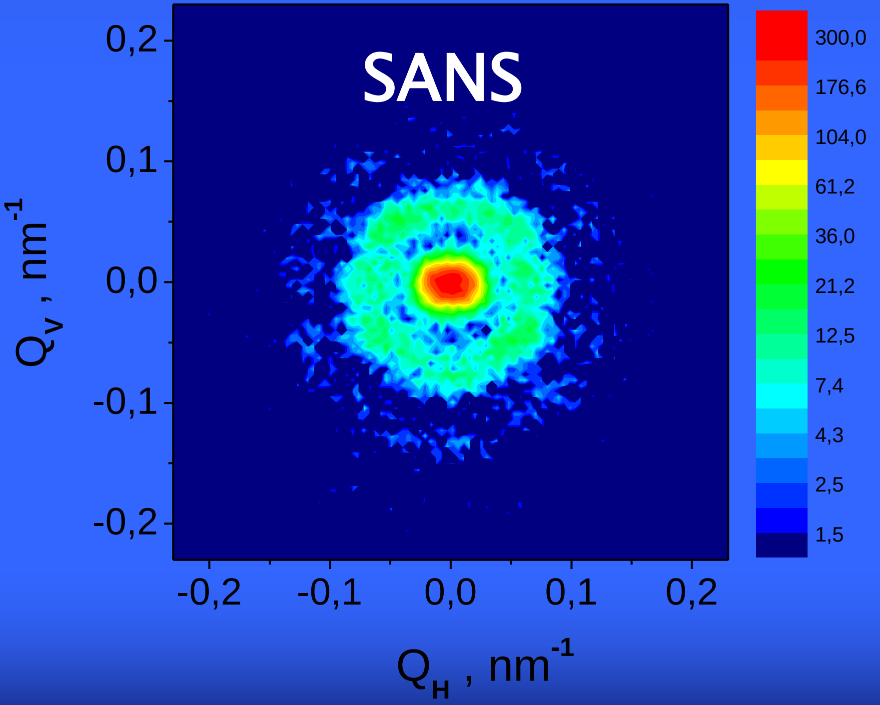
Structural transitions of hard-sphere colloids studied by spin-echo small-angle neutron scattering

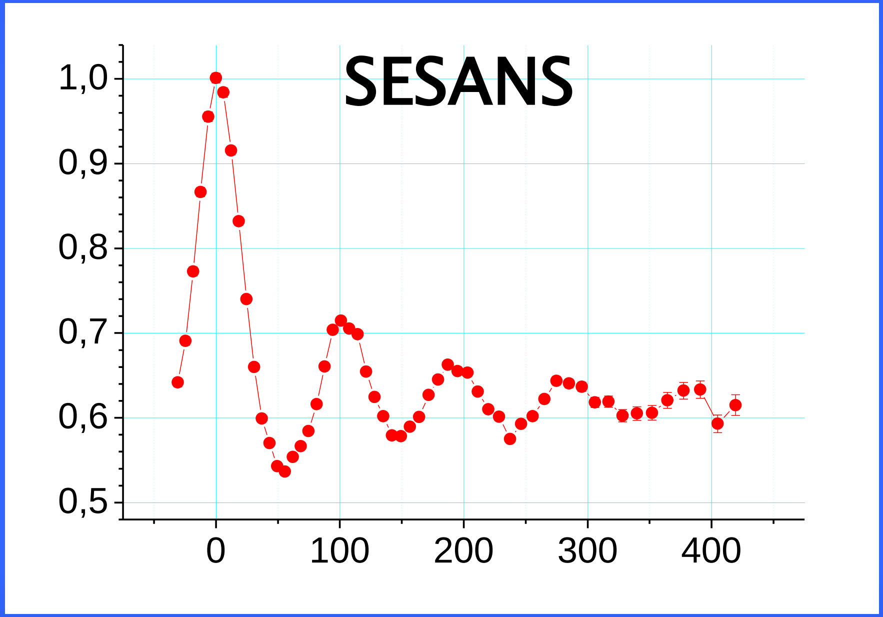
Timofei Krouglov,[a]* Wim G. Bouwman,[a] Jeroen Plomp,[a] M. Theo Rekveldt,[a] Gert Jan Vroege,[b] Andrei V. Petukhov[b] and Dominique M. E. Thies-Weesie[b]

[a]Interfaculty Reactor Institute, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands, and [b]van't Hoff Laboratory for Physical and Colloid Chemistry, Debye Institute, University of Utrecht, Padualaan 8, 3508 TB, Utrecht, The Netherlands. Correspondence e-mail: krouglov@iri.tudelft.nl

SESANS exp. : anodized aluminum oxide



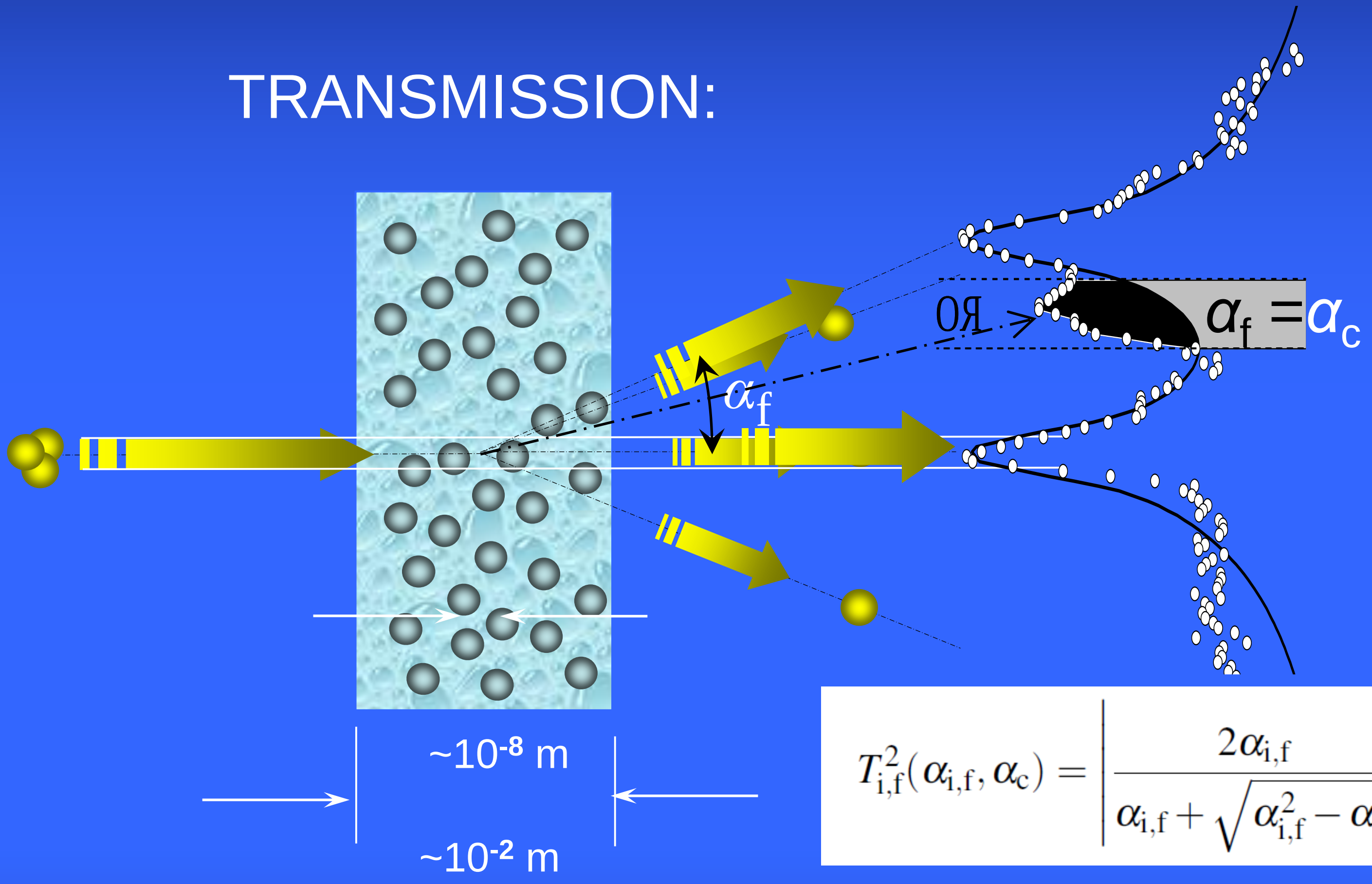




GRAZING INCIDENCE

TRANSMISSION:

PSD

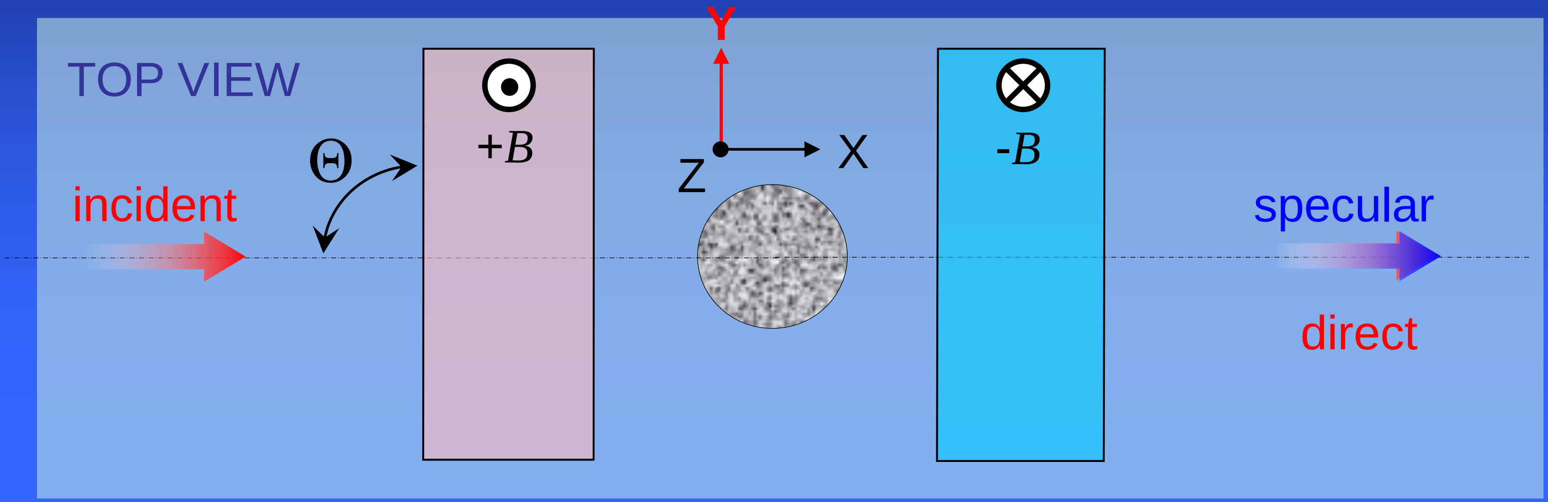


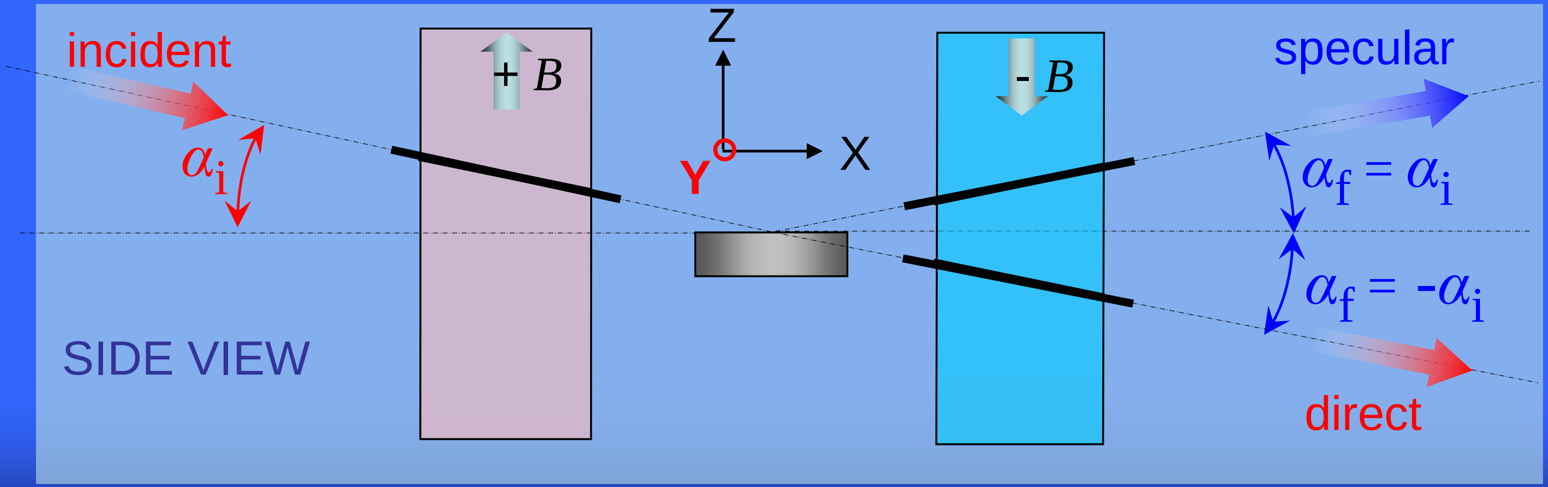
~10^{-8} m

~10^{-2} m

$$T^2_{\mathrm{i,f}}(\alpha_{\mathrm{i,f}}, \alpha_{\mathrm{c}}) = \left| \frac{2\alpha_{\mathrm{i,f}}}{\alpha_{\mathrm{i,f}} + \sqrt{\alpha^2_{\mathrm{i,f}} - \alpha^2_{\mathrm{c}}}} \right|^2$$

THE SAME POLARIZATION IN DIRECT AND SPECULAR BEAMS





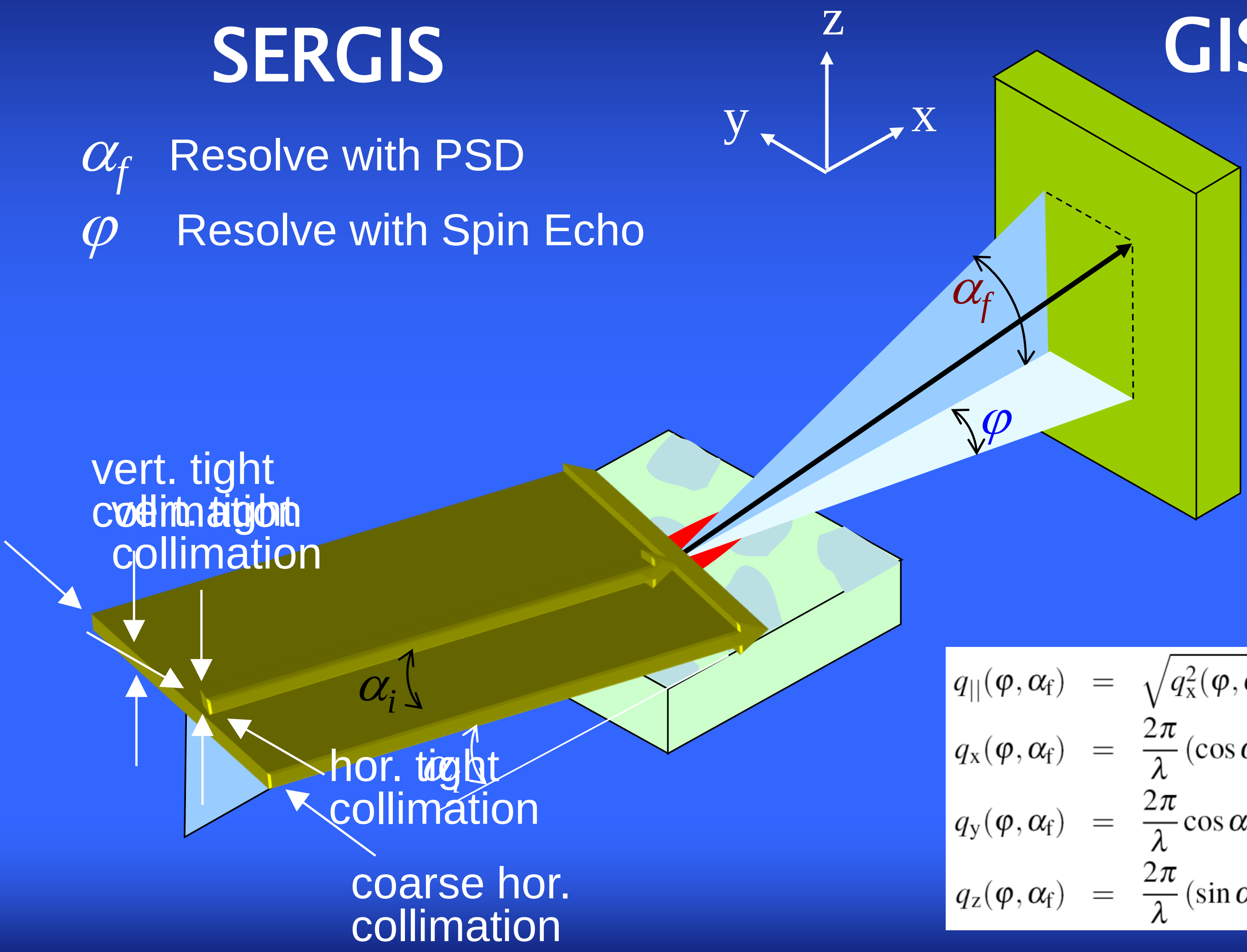
SERGIS vs. GISANS

SERGIS

GISANS

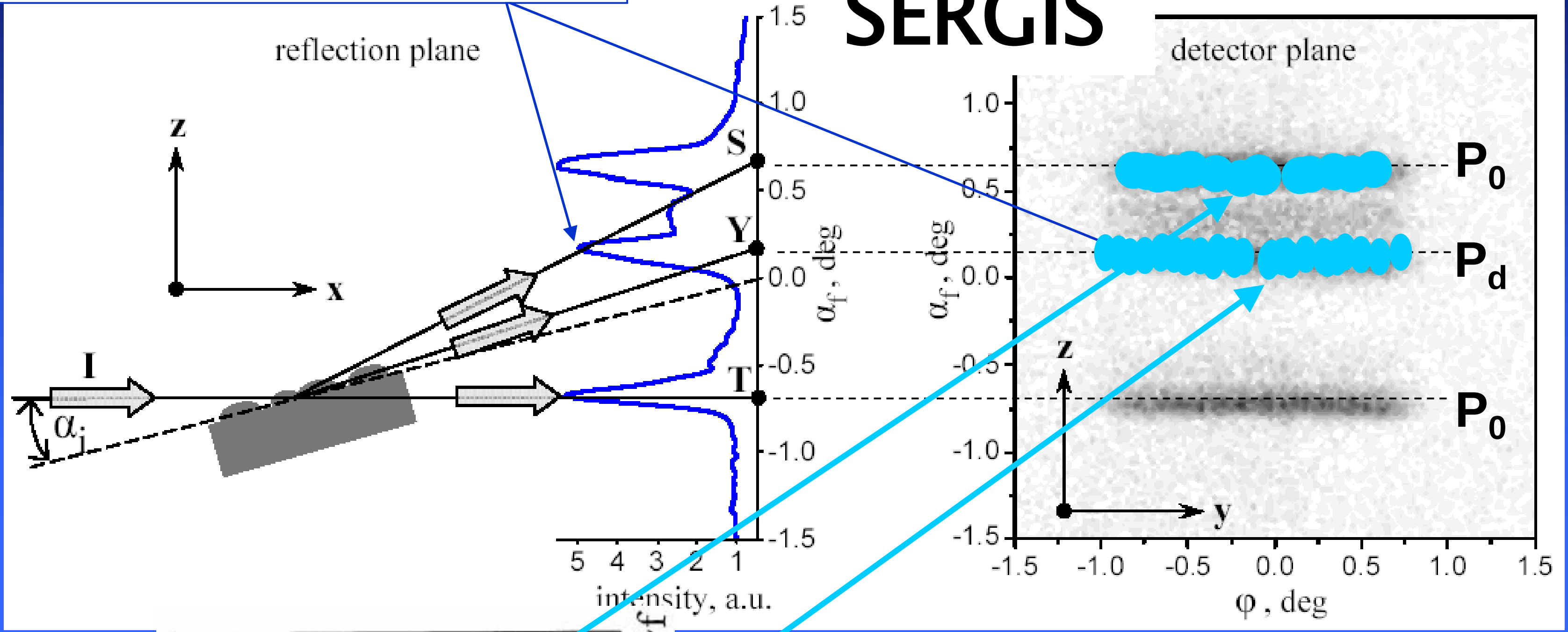
α_f Resolve with PSD

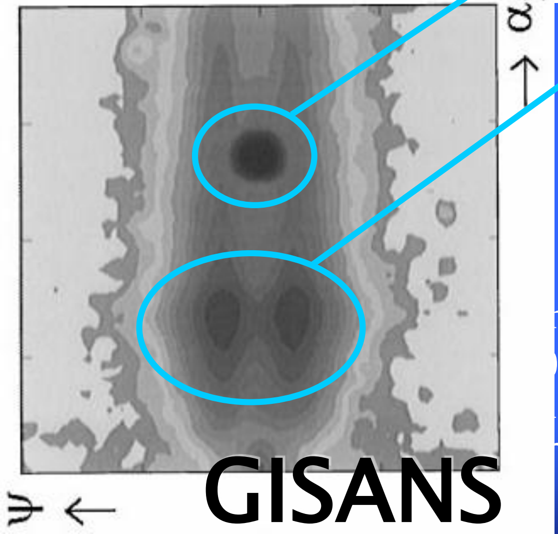
φ Resolve with Spin Echo



$$
\begin{aligned}
q_{||}(\varphi,\alpha_\mathrm{f}) &= \sqrt{q_\mathrm{x}^2(\varphi,\alpha_\mathrm{f})+q_\mathrm{y}^2(\varphi,\alpha_\mathrm{f})} \\
q_\mathrm{x}(\varphi,\alpha_\mathrm{f}) &= \frac{2\pi}{\lambda}\left(\cos\alpha_\mathrm{f}\cos\varphi-\cos\alpha_\mathrm{i}\right) \\
q_\mathrm{y}(\varphi,\alpha_\mathrm{f}) &= \frac{2\pi}{\lambda}\cos\alpha_\mathrm{f}\sin\varphi \\
q_\mathrm{z}(\varphi,\alpha_\mathrm{f}) &= \frac{2\pi}{\lambda}\left(\sin\alpha_\mathrm{f}+\sin\alpha_\mathrm{i}\right)
\end{aligned}
$$

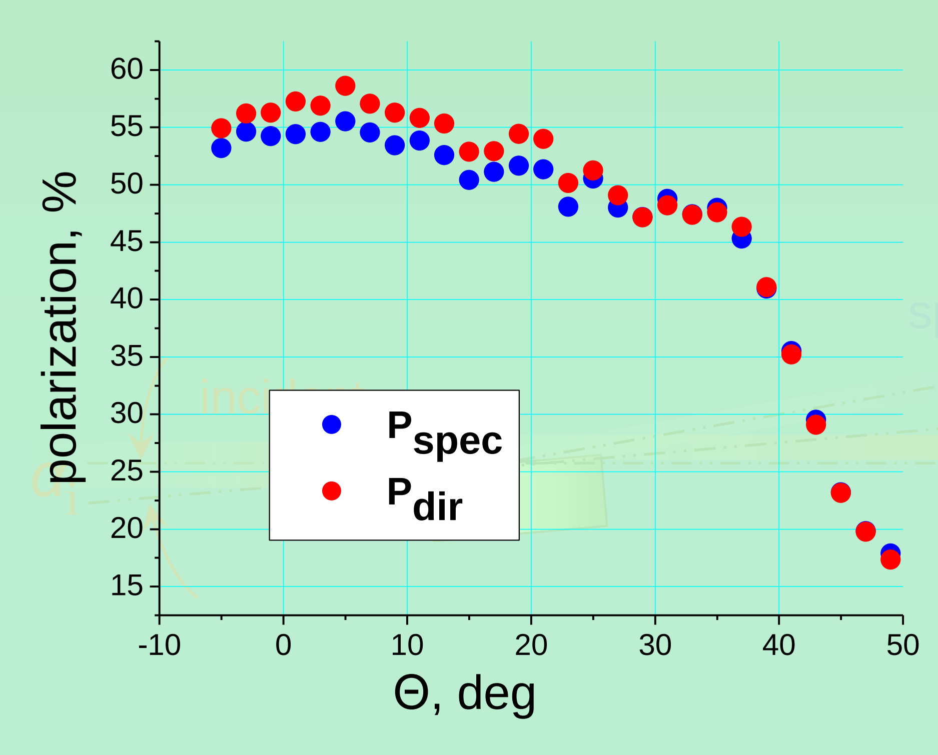
$$S(q) = |F_{\mathrm{BA}}|^2 \cdot T_{\mathrm{i}}^2(\alpha_{\mathrm{i}}) \cdot T_{\mathrm{f}}^2(\alpha_{\mathrm{f}})$$



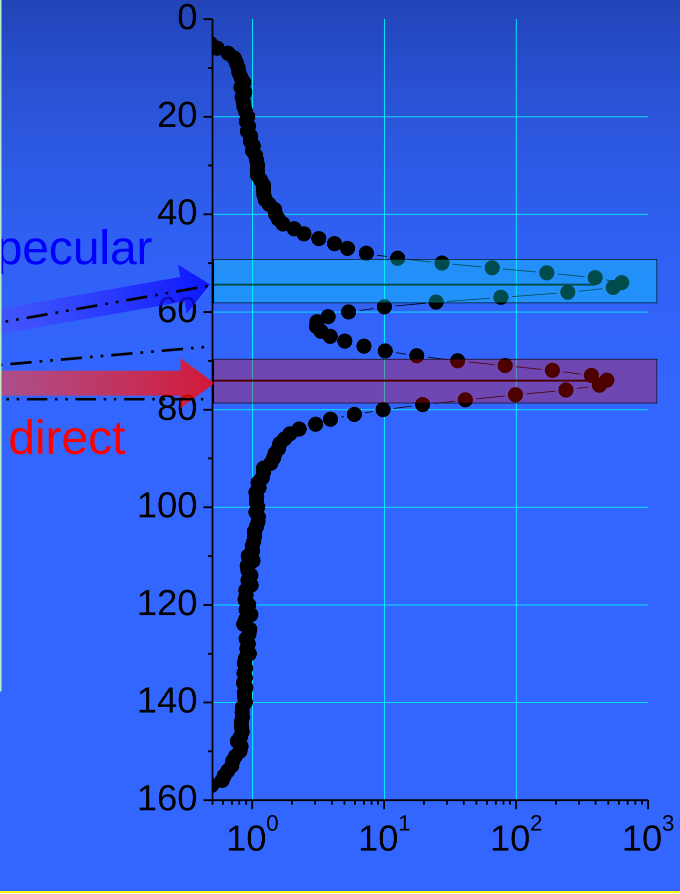


The sc m (I) impinges on the sample surface at a shallow angle α_i; transm intensities are simultaneously recorded by PSD. Image sional PSD during real experiment. The size of the incoming beam a n^2.

REFLECTIVITY REFERENCE MEASUREMENT



POLISHED SILICA CRYSTAL



possible reference data in reflection mode:

- separate scan with no sample
- separate scan with a reference sample
- direct beam (at high α_i)
- specular beam (at high α_i)

possible reference data in transmission mode:

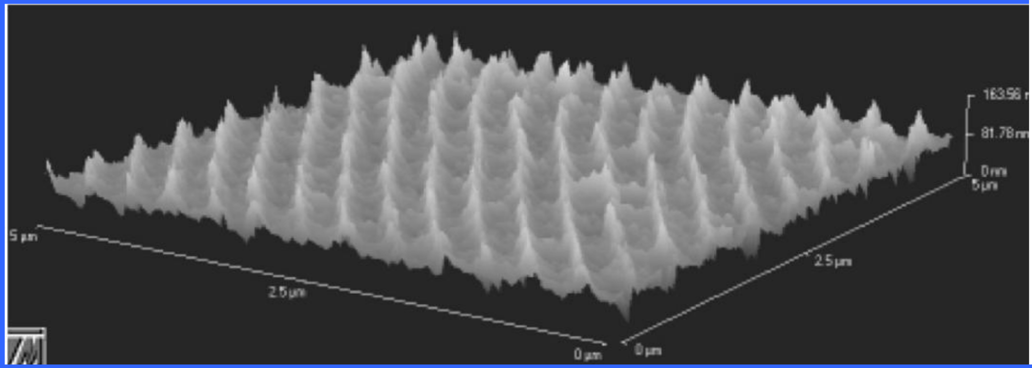
- separate scan with no sample

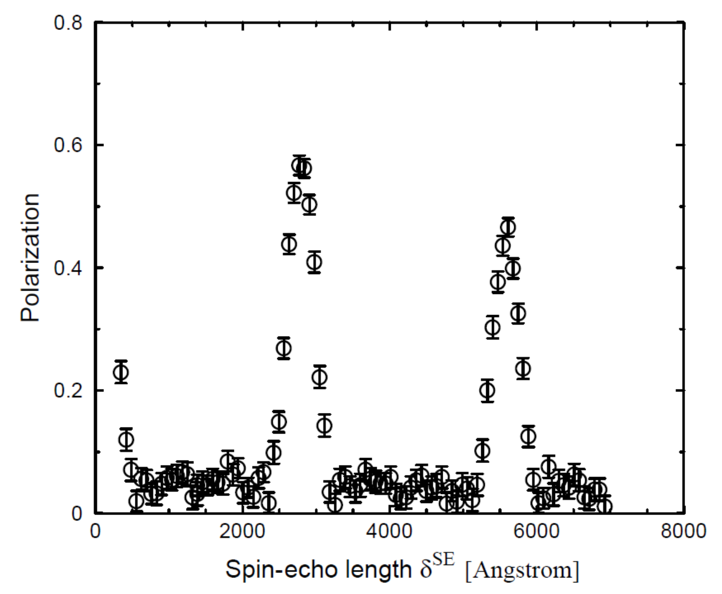
OPTICAL DIFFRACTION GRATING

Combining of neutron spin echo and reflectivity:
a new technique for probing surface and interface order

J. Major,, H. Dosch, G.P. Felcher, K. Habicht, T. Keller,
S.G.E. te Velthuis, A. Vorobiev, M. Wahl

Physica B 336 (2003) 8–15

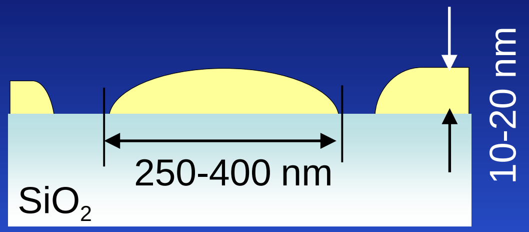




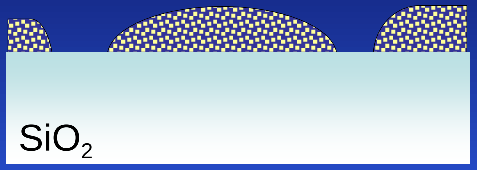
AFM

SERGIS

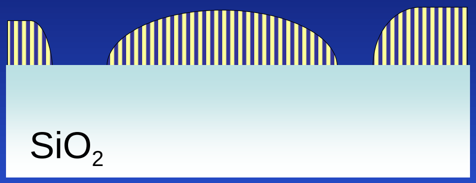
SAMPLES: DEWETED POLYMER FILMS



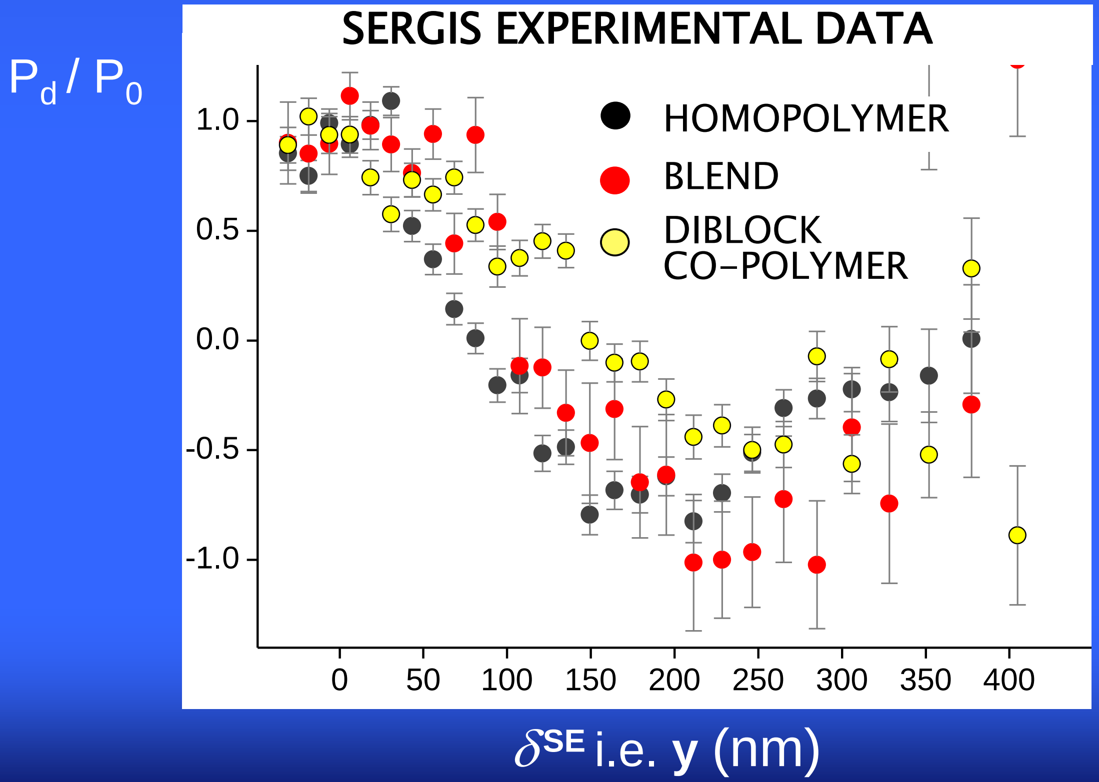
dPS
deuterated
polystyrene



polymer blend
PpMS:dPS = 3:2
polyparamethylstyrene
polystyrene



diblock
copolymer
poly(styren–block–
paramethylstyrene)
P(S–b–pMS)
regular phase
separation



SERGIS EXPERIMENTAL DATA

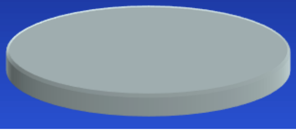
$$\frac{P_d}{P_0} = \langle \cos \Delta\xi \rangle \propto$$

$$\frac{\int_{\mathrm{det}} dq_y dq_z S(\mathbf{q}) \cos(\delta_y^{\mathrm{SE}} q_y)}{\int_{\mathrm{det}} dq_y dq_z S(\mathbf{q})} =$$

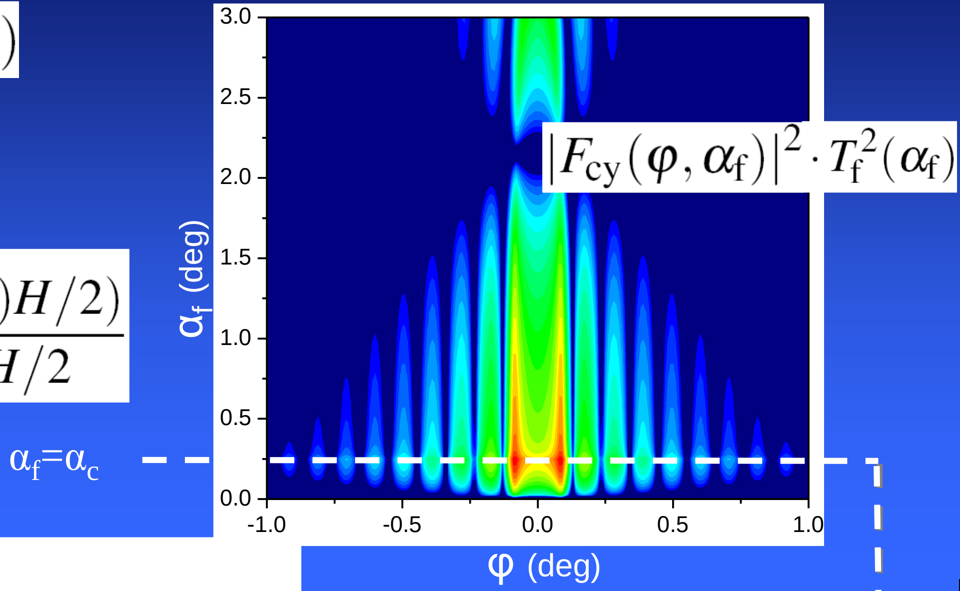
$$= \int dx \Pi(x, y, 0) \equiv G(y),$$

SCATTERING INTENSITY DISTRIBUTION

$$S_{\mathrm{cy}}(\varphi,\alpha_{\mathrm{f}}) = M_{\mathrm{c}}|F_{\mathrm{cy}}(\varphi,\alpha_{\mathrm{f}})|^2 \cdot I_{\mathrm{H}}(\varphi,\alpha_{\mathrm{f}})$$

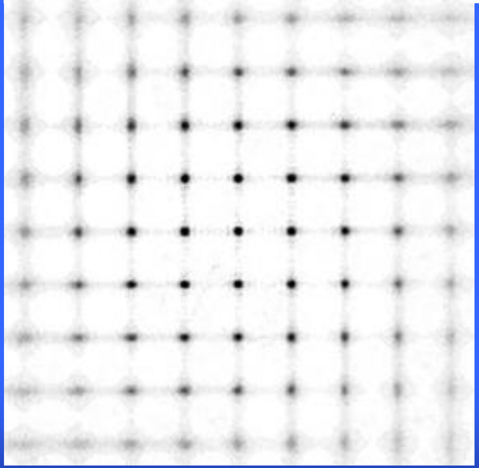


$$|F_{\mathrm{cy}}(\varphi,\alpha_{\mathrm{f}})| = \frac{J_1\left(q_{||}(\varphi,\alpha_{\mathrm{f}})R\right)}{q_{||}(\varphi,\alpha_{\mathrm{f}})R}\,\frac{\sin\left(q_{\mathrm{z}}(\varphi,\alpha_{\mathrm{f}})H/2\right)}{q_{\mathrm{z}}(\varphi,\alpha_{\mathrm{f}})H/2}$$



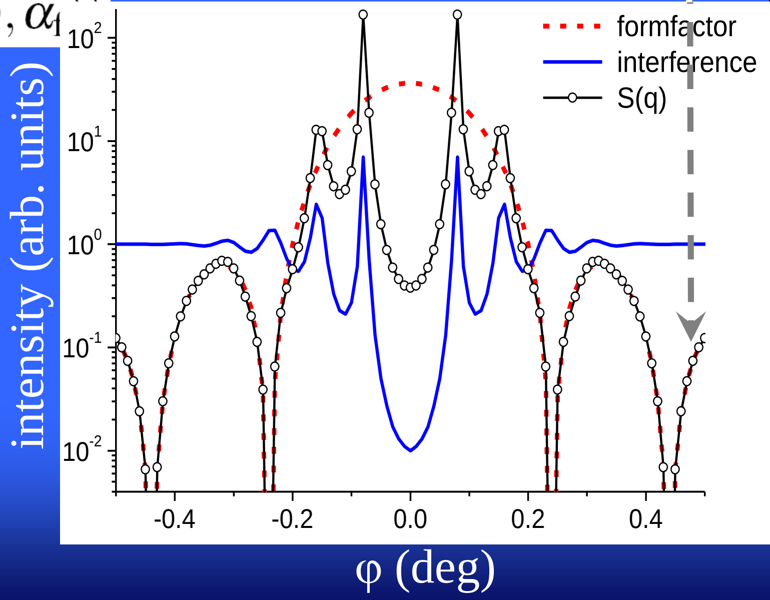
$$|F_{\mathrm{cy}}(\varphi,\alpha_{\mathrm{f}})|^2 \cdot T_{\mathrm{f}}^2(\alpha_{\mathrm{f}})$$

$$I_{\mathrm{H}}(\varphi,\alpha_{\mathrm{f}}) = \frac{1-\mathrm{e}^{-q_{||}(\varphi,\alpha_{\mathrm{f}})\sigma^2}}{1+\mathrm{e}^{-q_{||}(\varphi,\alpha_{\mathrm{f}})\sigma^2}-2\mathrm{e}^{-\frac{1}{2}q_{||}(\varphi,\alpha_{\mathrm{f}})\sigma^2}\cos\big(Dq_{||}(\varphi,\alpha_{\mathrm{f}}}$$



D – the mean value of the lattice parameter
σ– its standard deviation if the disorder factor obeys Gaussian distribution

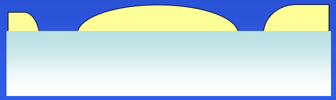
Hosemann, R.; Bagchi, S. N. *Direct Analysis of Diffraction by Matter* (North-Holland Publishing Company: Amsterdam, 1962).

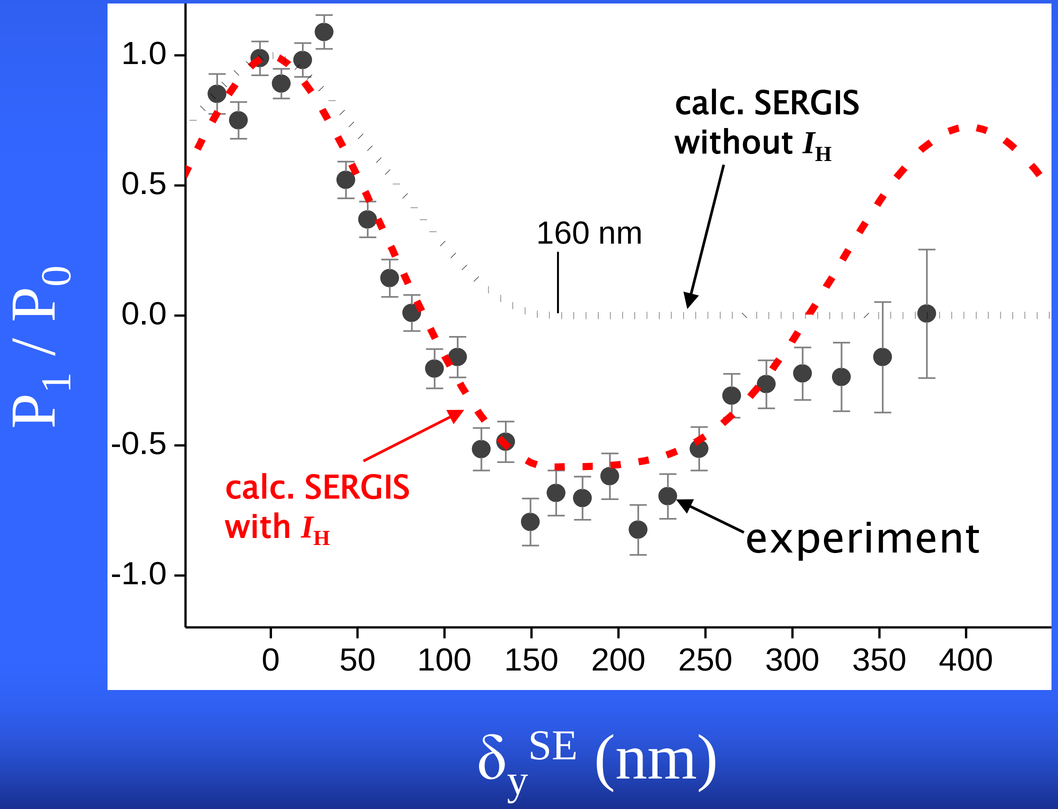


Simulated SERGIS signal for dPS sample

$$\frac{P_1}{P_0}(\delta_y^{SE}) = \frac{\int_{-\varphi_{lim}}^{\varphi_{lim}} S_{cy}(\varphi,\overline{\alpha}_f)\cos(\delta_y^{SE},\varphi)\,d\varphi}{\int_{-\varphi_{lim}}^{\varphi_{lim}} S_{cy}(\varphi,\overline{\alpha}_f)\,d\varphi}$$

dPS sample





R=80 nm
H=10 nm
D=390 nm
σ= 25 nm

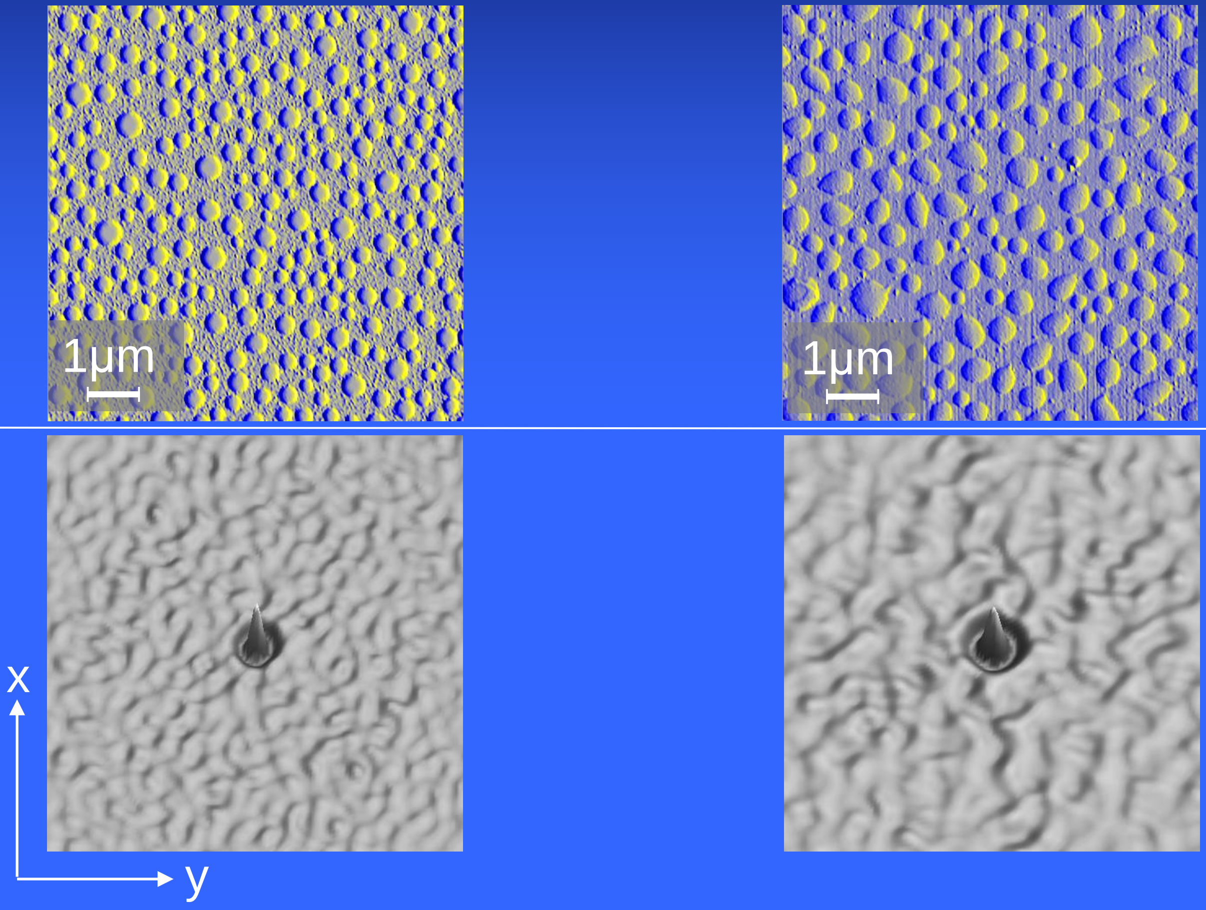
COMPLIMENTARY DATA – AFM

polymer blend

diblock copolymer

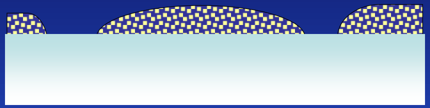
AFM raw data

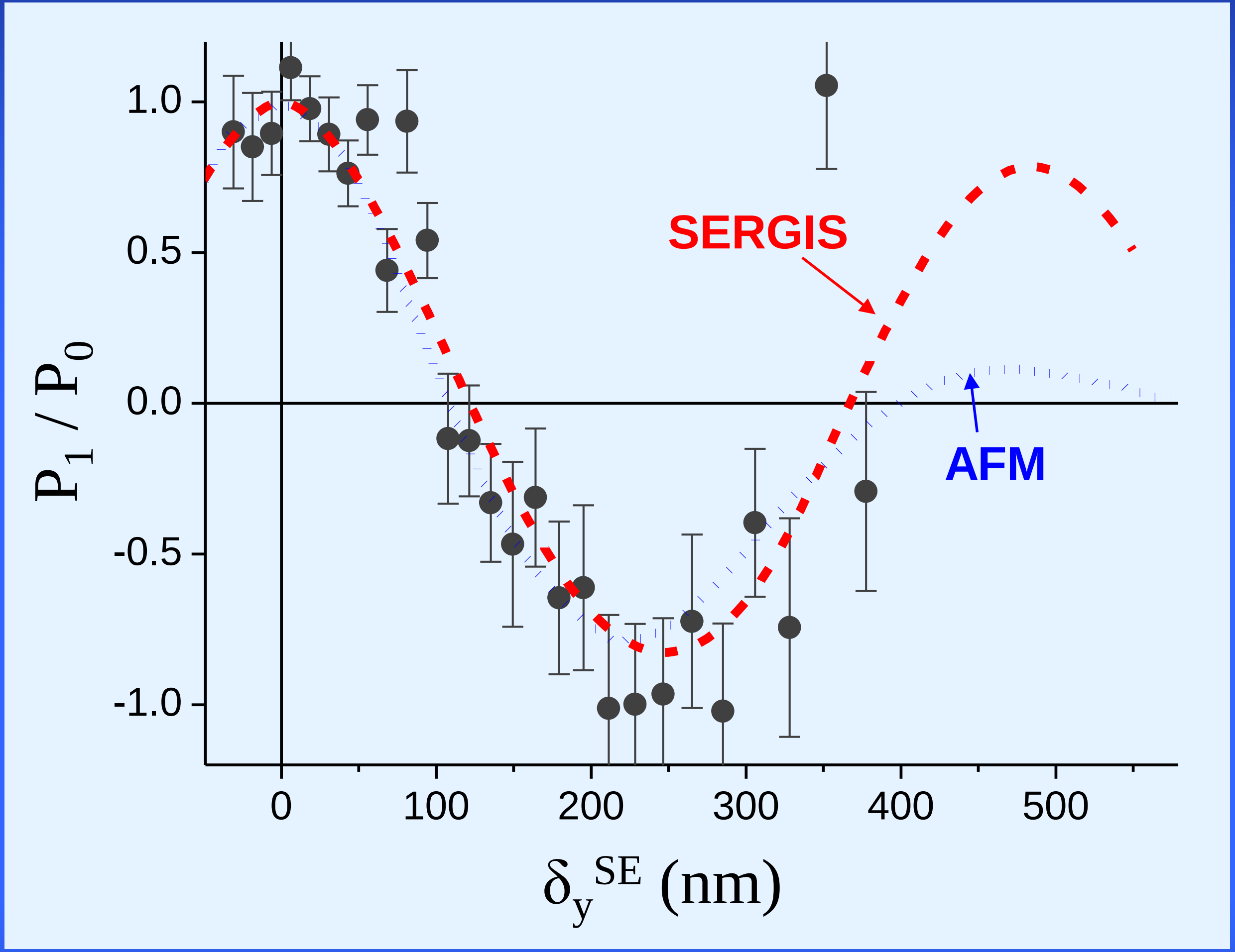
ACF



$$\Pi(\triangle a_1,\triangle a_2)=\sum\widetilde{f}(a_1,a_2)\cdot\sum\widetilde{f}(a_1+\triangle a_1,a_2+\triangle a_2)$$

POLYMER BLEND



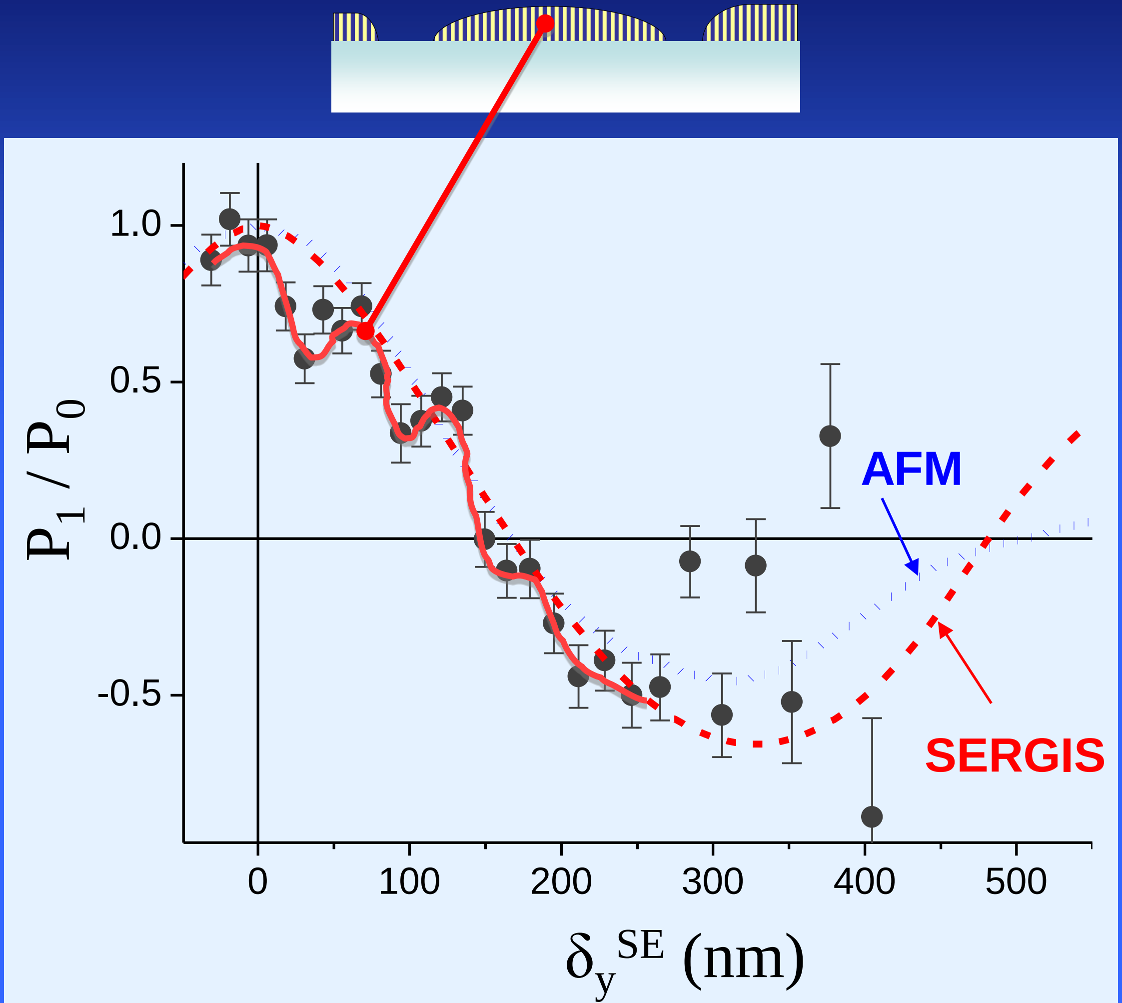


SERGIS
model:
R=170 nm
H=20 nm
D=480 nm
σ= 50 nm

AFM:
D=450 nm

GISANS/GISAXS:
D=500 nm

DIBLOCK COPOLYMER



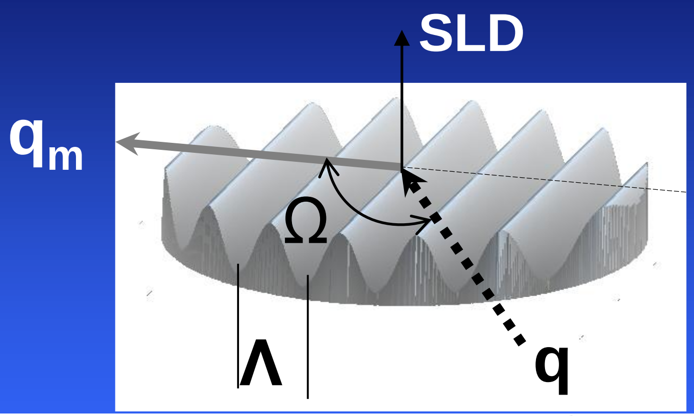
SERGIS
model:
R=230 nm
H=10 nm
D=600 nm
$\sigma/D=0.17$

AFM:
D=630 nm

GISANS/GISAXS:
D=600 nm

AFM and X-rays can not see internal structure,
GISANS can see and does see. What about SERGIS?

MODULATED DROPLETS



SLD contrast

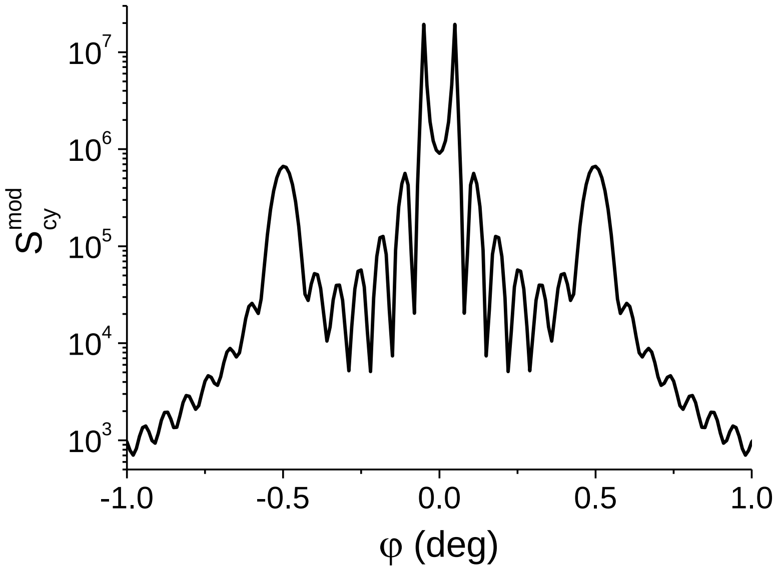
$$f_m(\mathbf{r}) = \overline{\rho} + \frac{\Delta\rho}{2}\cos(\mathbf{q}_m \cdot \mathbf{r})$$

mean SLD

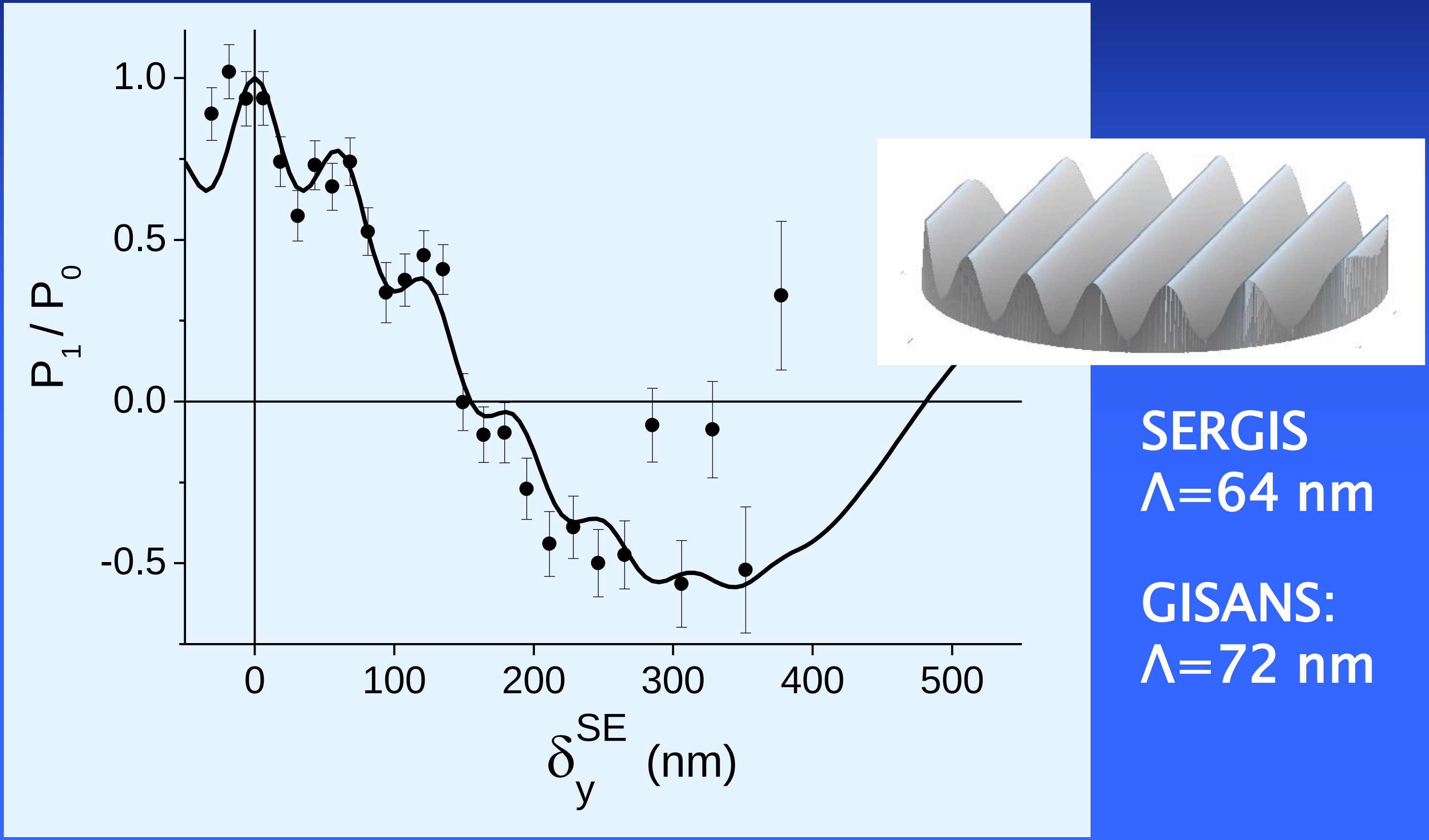
$$|F_{\mathrm{cy}}^{\mathrm{mod}}(\mathbf{q})| = \overline{\rho}|F_{\mathrm{cy}}(\mathbf{q})| + \frac{\Delta\rho}{4}\left(\frac{J_1\left(|\mathbf{q}_{||} - \mathbf{q}_m|R\right)}{|\mathbf{q}_{||} - \mathbf{q}_m|R} + \frac{J_1\left(|\mathbf{q}_{||} + \mathbf{q}_m|R\right)}{|\mathbf{q}_{||} + \mathbf{q}_m|R}\right)\frac{\sin\left(q_z(\varphi,\alpha_{\mathrm{f}})H/2\right)}{q_z(\varphi,\alpha_{\mathrm{f}})H/2}$$

$$\overline{|F_{\mathrm{cy}}^{\mathrm{mod}}(\mathbf{q})|^2} = \frac{1}{\pi}\int_{-\pi/2}^{\pi/2}|F_{\mathrm{cy}}^{\mathrm{mod}}(\mathbf{q})|^2 d\Omega$$

$$S_{\mathrm{cy}}^{\mathrm{mod}}(\mathbf{q}) = c\overline{|F_{\mathrm{cy}}^{\mathrm{mod}}(\mathbf{q})|^2}I_{\mathrm{H}}$$



DIBLOCK COPOLYMER – MODULATED DROPLETS

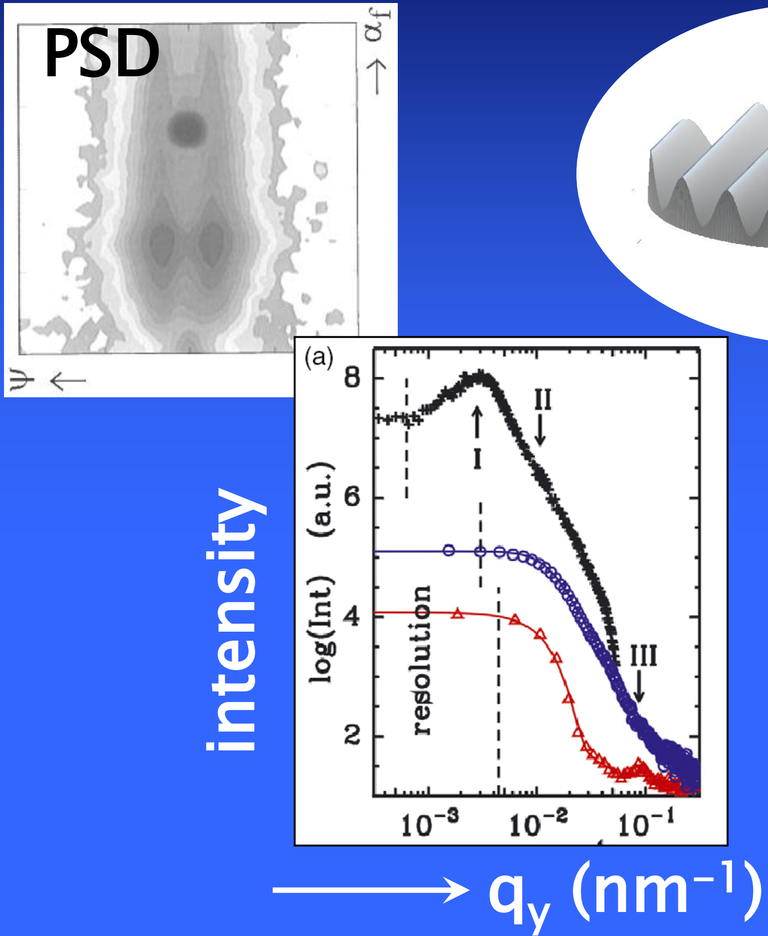


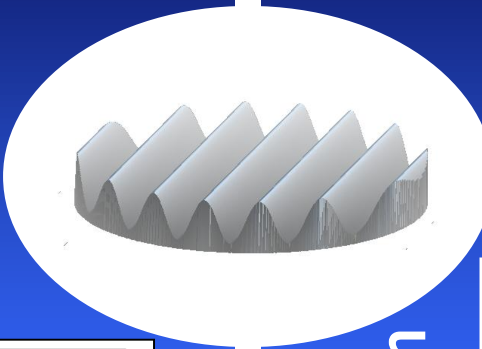
SERGIS
Λ=64 nm

GISANS:
Λ=72 nm

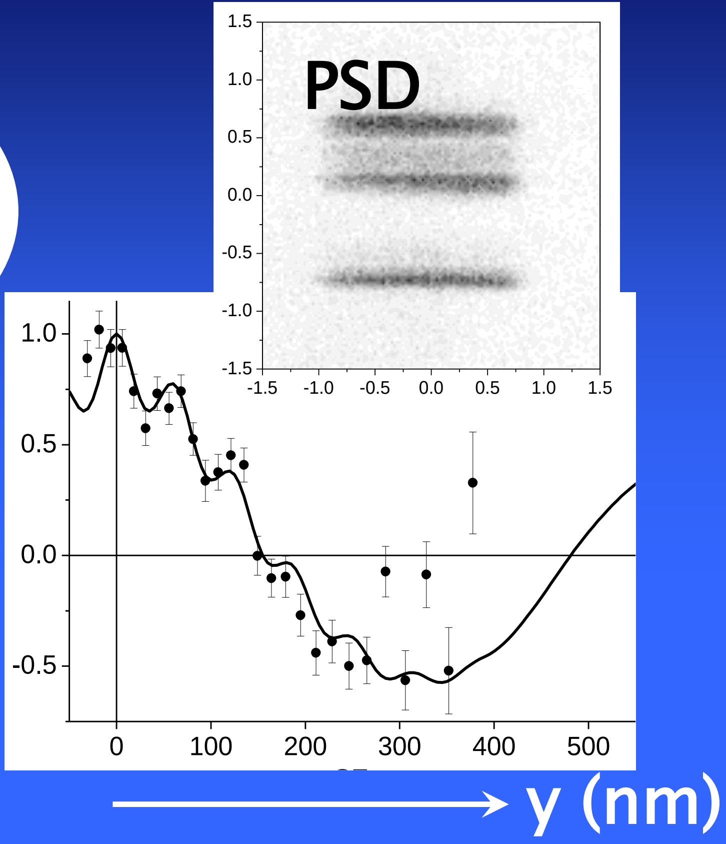
"Phase and microphase separation of polymer thin films dewetted from silicon – a spin-echo resolved grazing incidence neutron scattering study"
J. Phys. Chem. B 2011, 115, 5754-5765

GISANS vs. SERGIS





polarization



measuring time T_m :
8 hours at D22, ILL

T_m : 12 h at EVA

improvements:	time factor:
monochromator $\Delta\lambda/\lambda$ 5%	/5
improved polarization circuit	/2
improved measuring algorithm (one component, less points)	/10

12 h / 100 ≈ 10 min

CONCLUSION

The SERGIS scattering technique can be especially advantageous for studying

- very soft,
- fragile,
- and liquid surfaces
- as well as buried interfaces

structured on length scales varying from nanometers to sub-micrometers.

Alternative techniques, such as AFM and SEM, cannot be applied for such kinds of objects.

Due to the grazing angle geometry, structural information about surfaces/interfaces can be obtained with adjustable depth resolution.

ACKNOWLEDGEMENT

J. Major M. Wahl, M. Mezger, R. Maier, B. Nickel, H. Dosch (*MPI-MF*)

G. P. Felcher, S. G. E. te Velthuis (*ANL*)

P. Falus (*ILL*)

P. Müller-Buschbaum (*TU München*)

Roger Pynn (*LANL*)

Thomas Keller (*MPI-FF*)

SUPPLIMENTARY INFO

Publications record

SESANS: 70–80

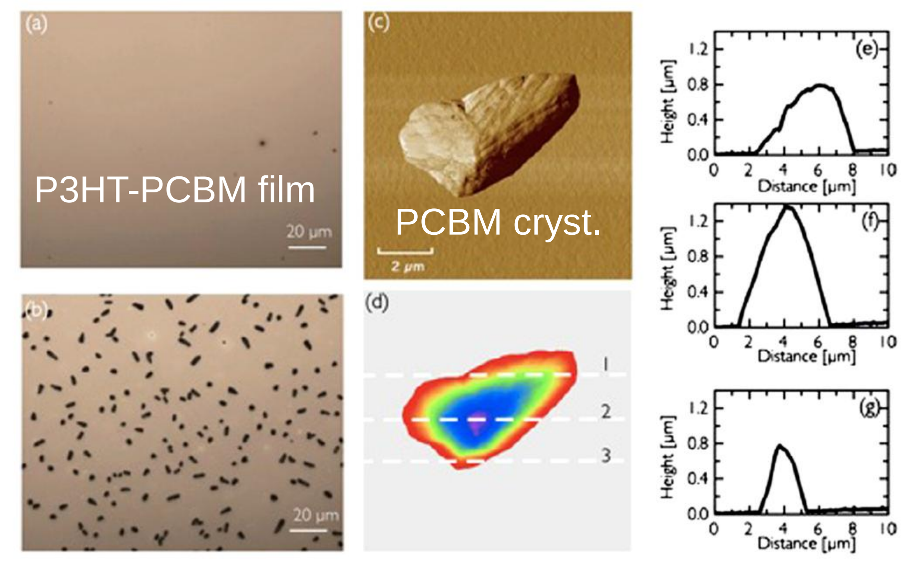
SERGIS: < 15 (2 scientific)

SERGIS SCIENTIFIC PUBLICATION №2

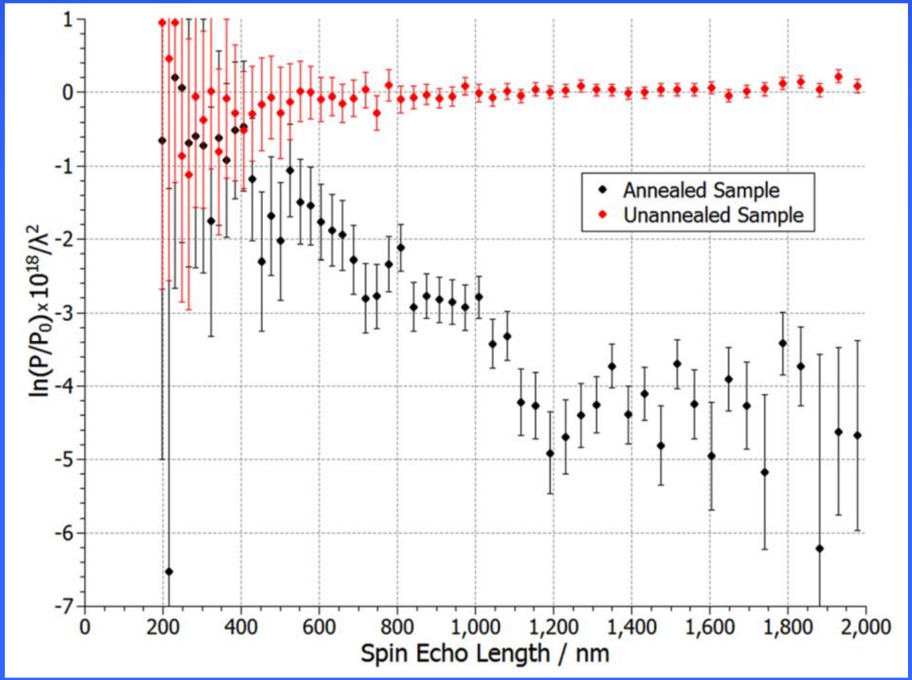
A neutron spin echo resolved grazing incidence scattering study of crystallites in organic photovoltaic thin films

A. J. Parnell, R. M. Dalgliesh, R. A. L. Jones, and A. D. F. Dunbar

Applied Physics Letters 102, 073111 (2013)



AFM



SERGIS