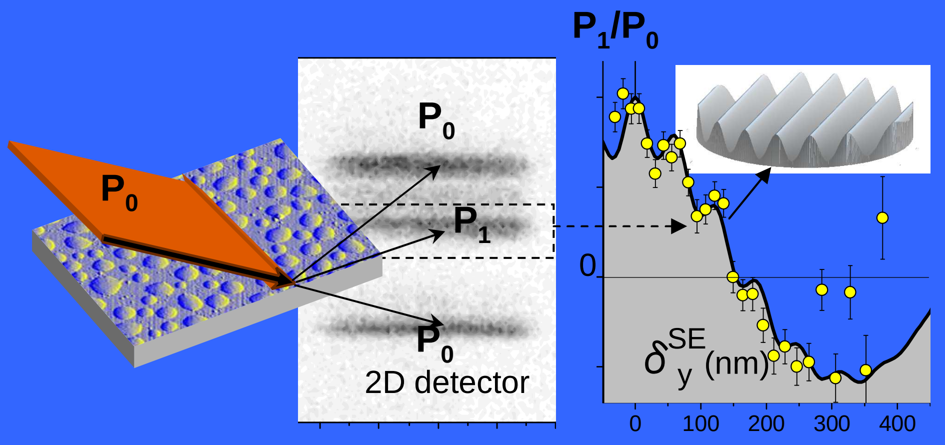
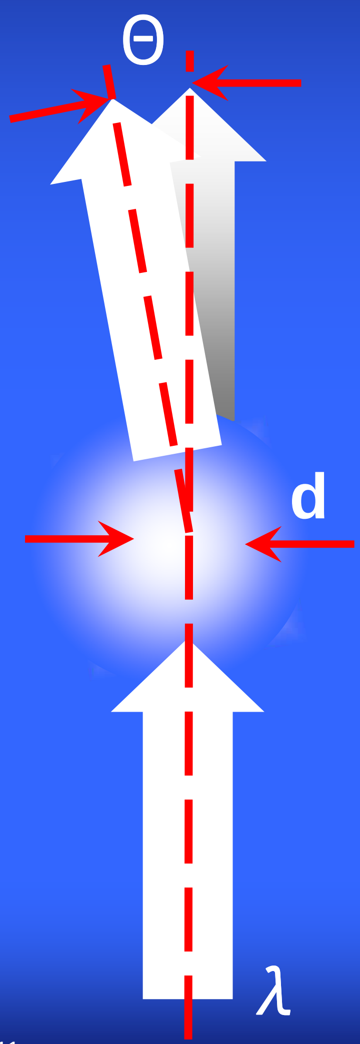
SPIN-ECHO CODING OF THE MOMENTUM TRANSFER IN GRAZING INCIDENCE SCATTERING

Alexei Vorobiev
ESRF



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 both incident and scattered beams**
- ⇒ **measured intensity will be very low**
- ⇒ **one should try to find a way to measure small angles without tightening of the beam**

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

structural information about the sample is obtained in real space

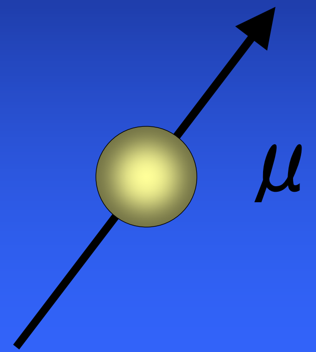
OUTLINE

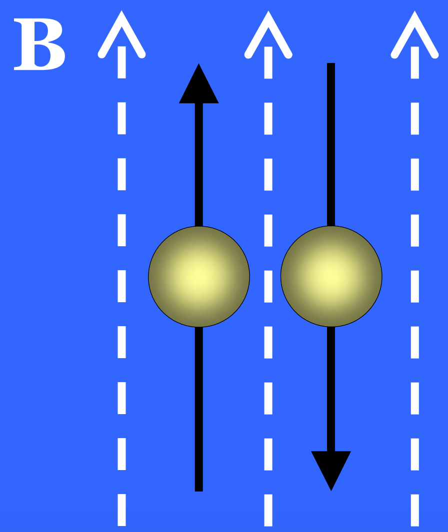
- **Basic principles of neutron spin echo (SE). Conventional SE for dynamic studies.**
- **SE angular coding for structural studies: transmission mode – SESANS; thick (3d) samples**
- **Experiments in reflection geometry: SERGIS (Spin-Echo Resolved Grazing Incidence Scattering); ultra thin (2d) samples**

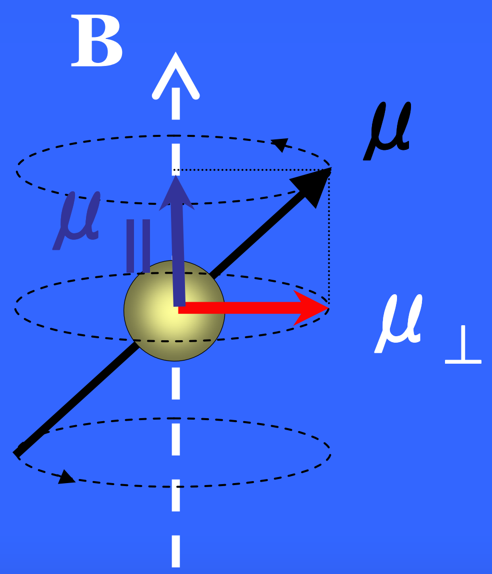
LARMOR PRECESSION

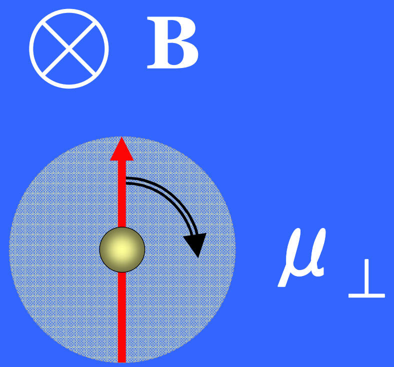
Neutron properties:

Mass m=1.674928(1)·10^{-27} kg
Spin s=-ħ/2
Magnetic moment μ =-9.649·10-27 JT^{-1}
ß-decay lifetime τ =886 s



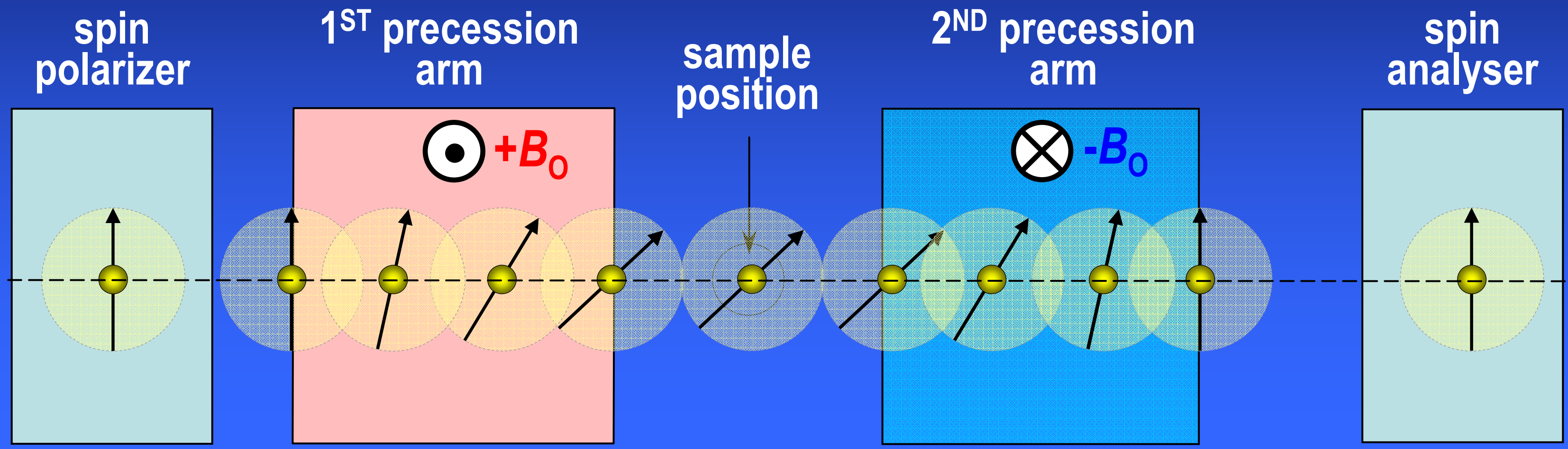


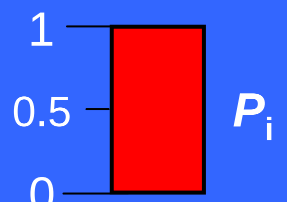




$\omega = \gamma$ **B**
γ **= 2917 Hz/Oe**

CONVENTIONAL SPIN-ECHO FOR DYNAMIC STUDY

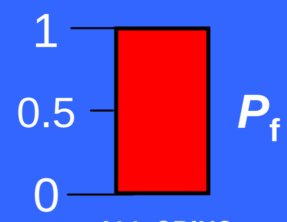




ALL SPINS ARE VERTICAL: FULL POLARIZATION

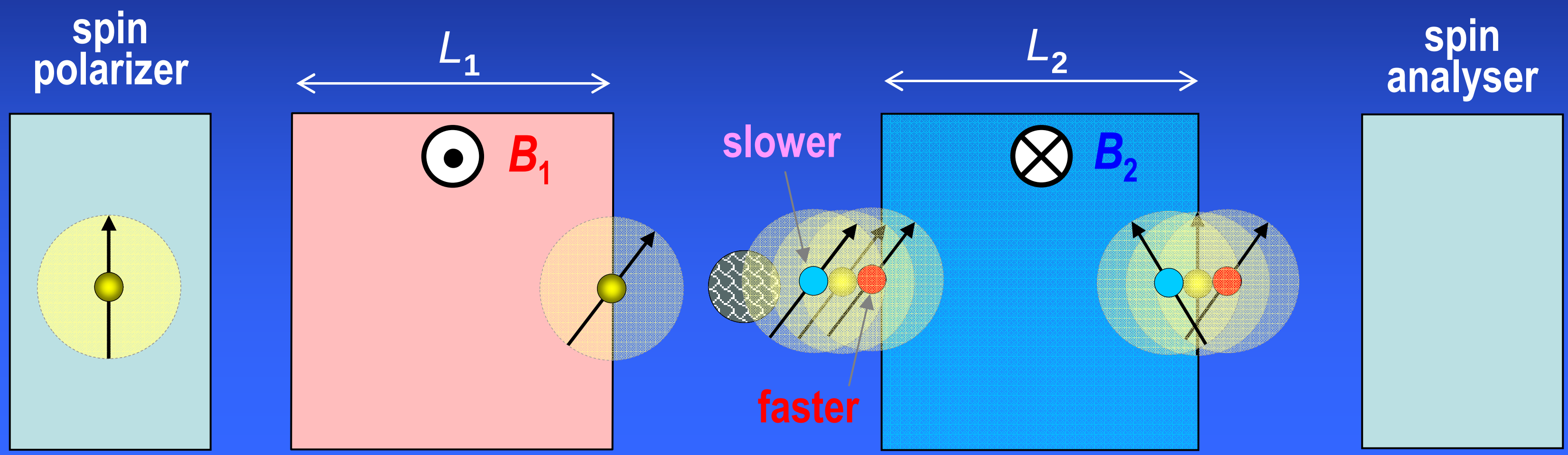
$P_i = P_f$

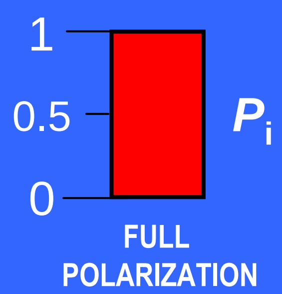
'SPIN-ECHO'



ALL SPINS ARE VERTICAL AGAIN: POLARIZATION IS BACK

INELASTIC SCATTERING





$$\xi_{tot} = \frac{\gamma B_1 L_1}{v_1} - \frac{\gamma B_2 L_2}{v_2}$$

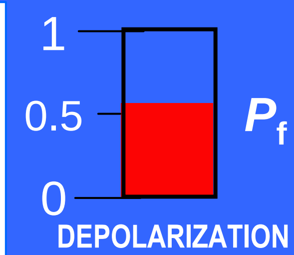
$$\xi_{tot} = \frac{\gamma B L \hbar}{m v^3}\omega$$

$$P = \langle \cos \xi \rangle = \frac{\int \cos\left(\frac{\gamma B L \hbar}{m v^3}\omega\right) S(q,\omega)\,\mathrm{d}\omega}{\int S(q,\omega)\,\mathrm{d}\omega} = S(q, t_{SE})$$

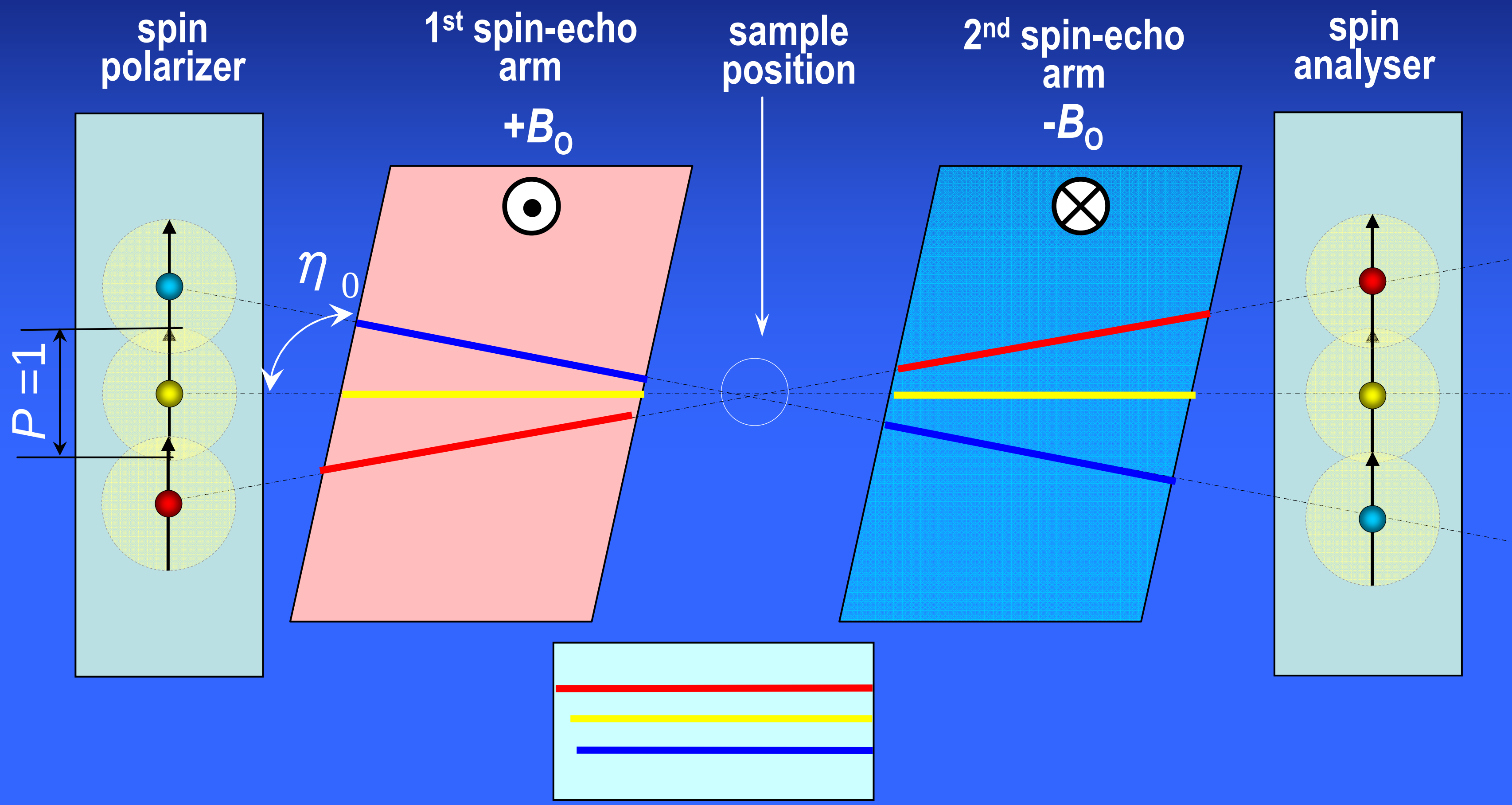
$$t_{SE} = \frac{\gamma B L \hbar}{m v^3} \propto \lambda^3$$

SPIN-ECHO (FOURIER) TIME

F. Mezei
Z. Phys. **255** (1972) 146.

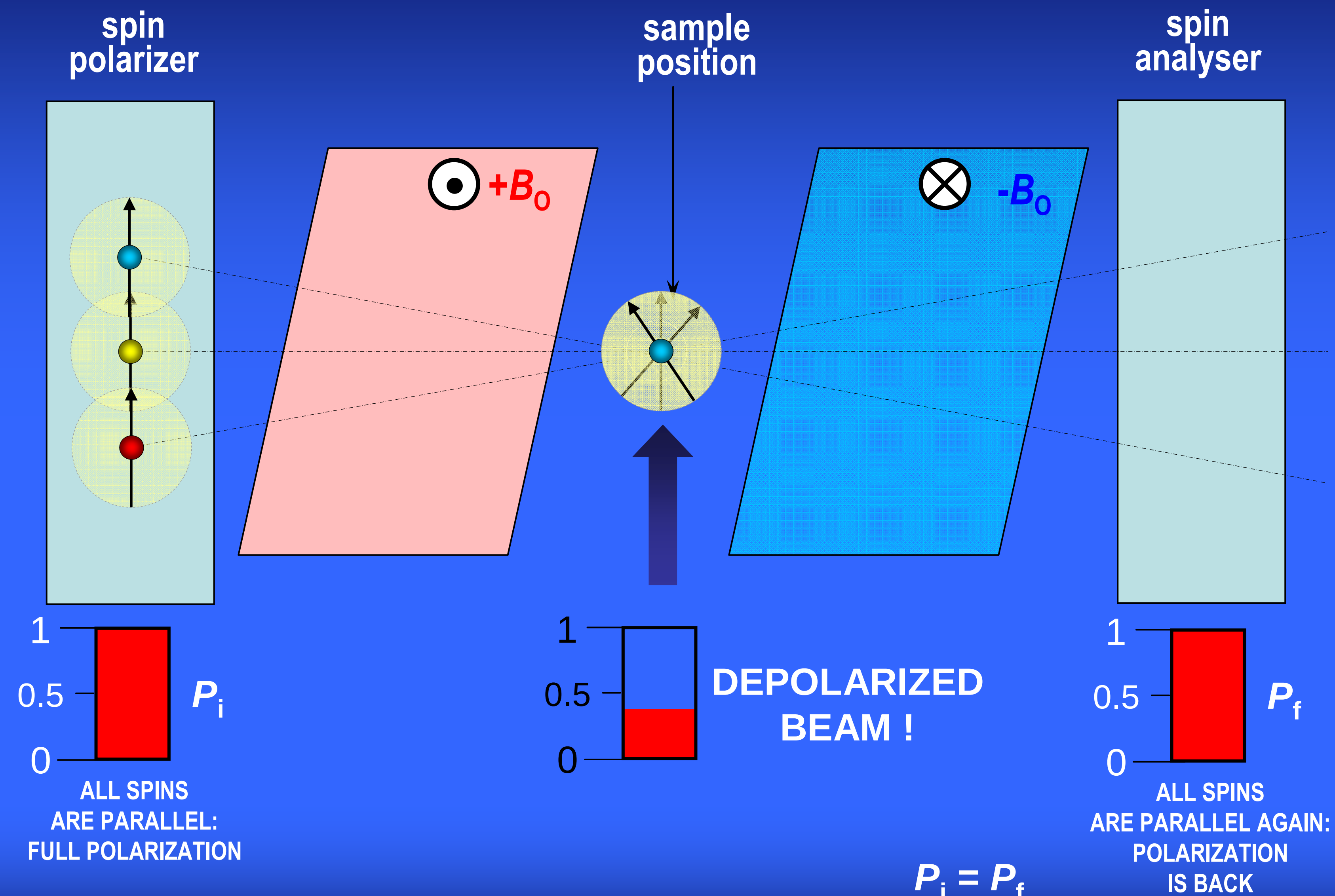


INCLINED BORDERS



DIFFERENT PATH LENGTHS FOR THE DIFFERENT TRAJECTORIES !

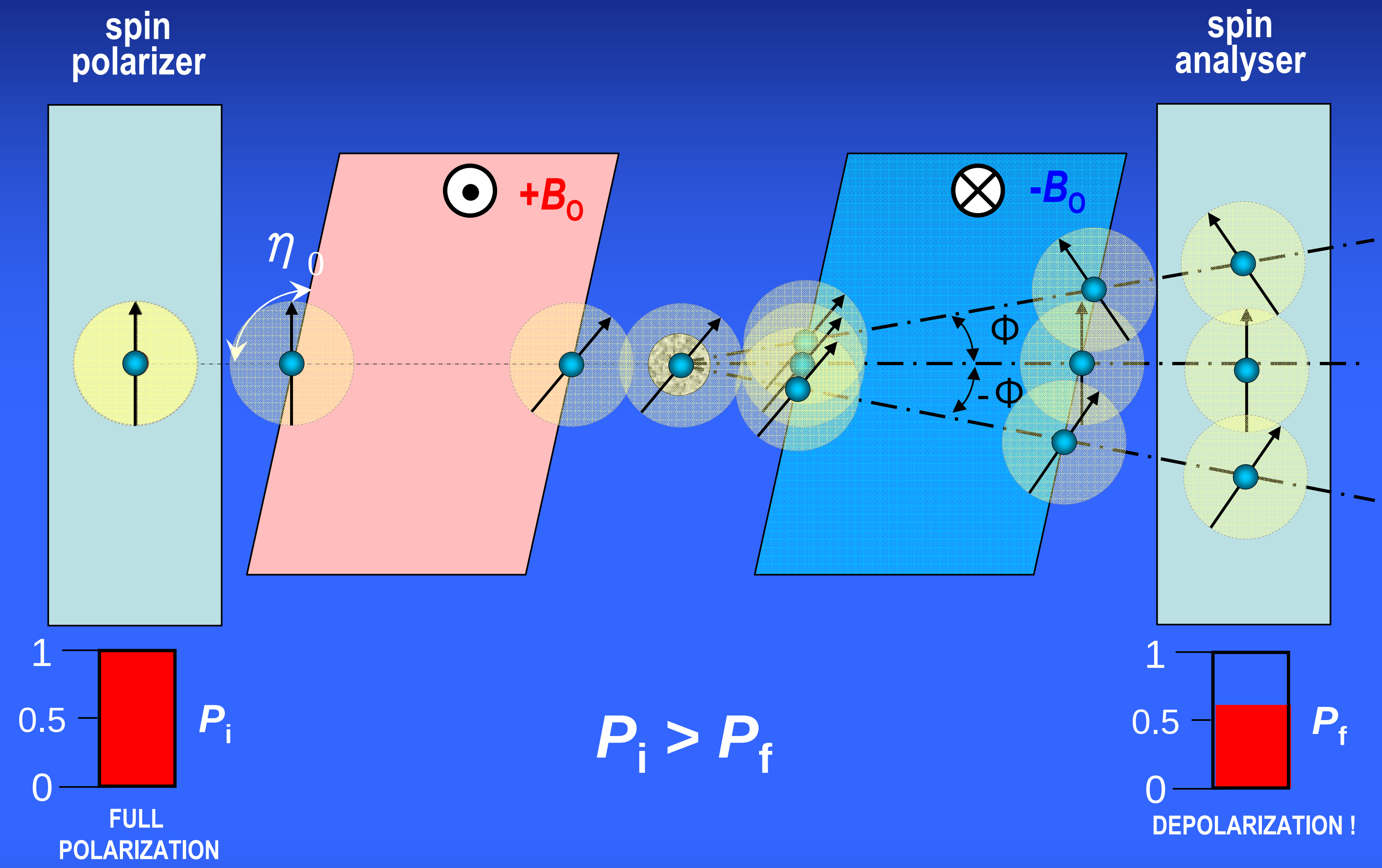
NO-SCATTERING CASE



$P_i = P_f$

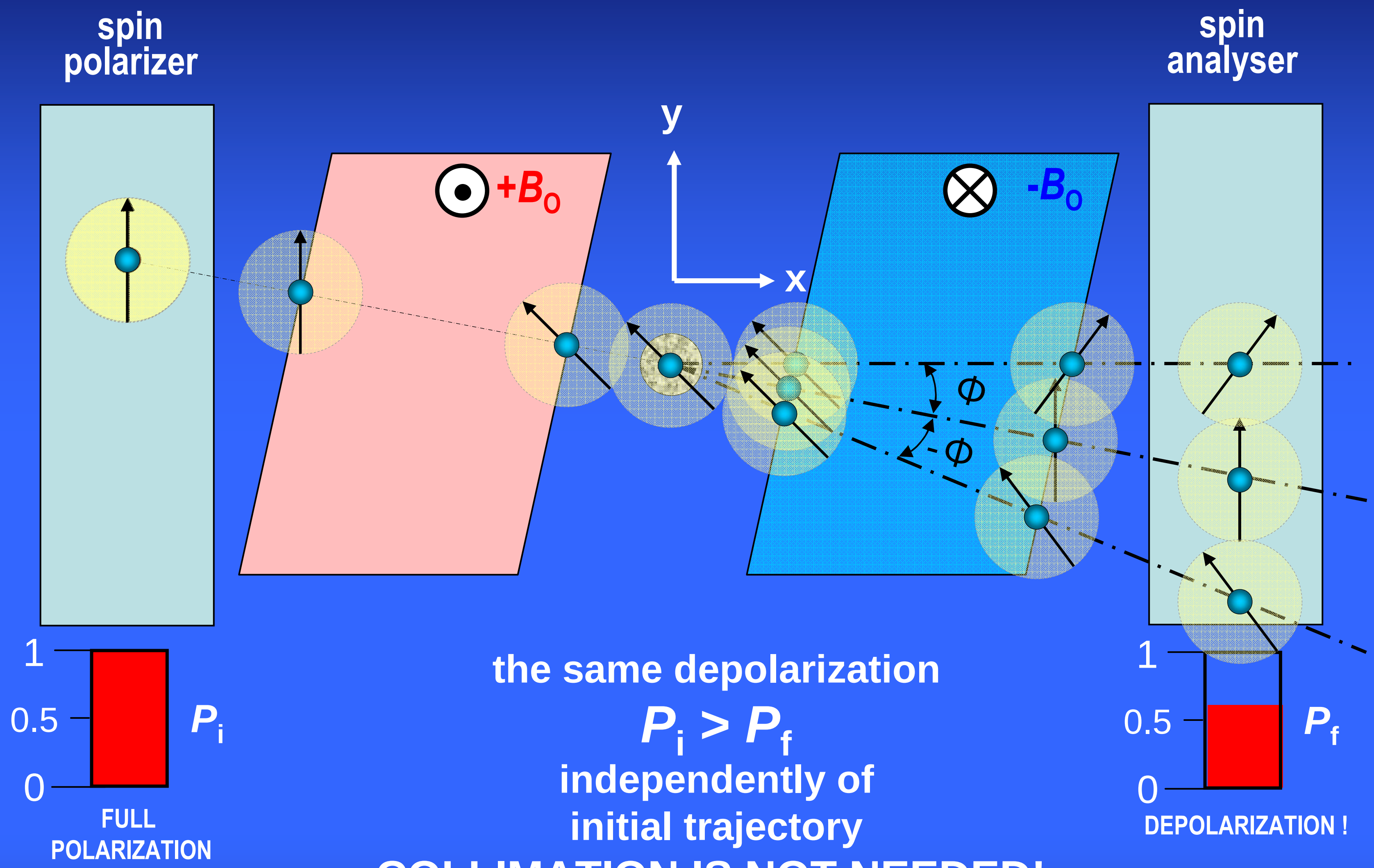
'SPIN-ECHO'

SCATTERING BY THE SAMPLE



$P_i > P_f$

SCATTERING BY THE SAMPLE



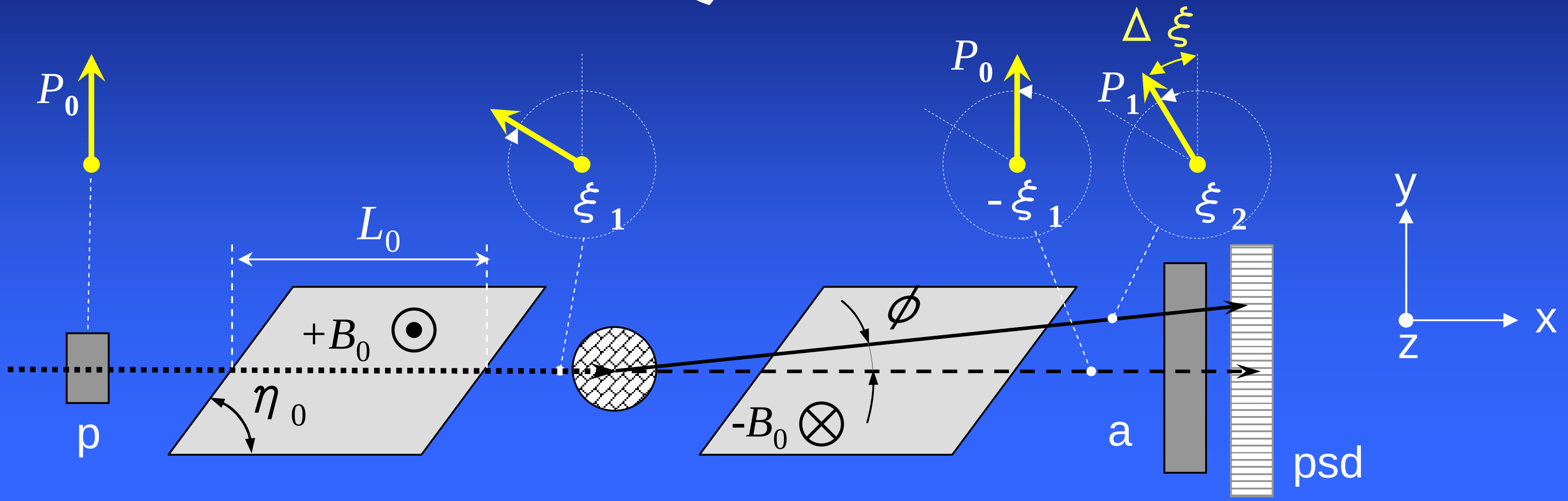
the same depolarization

$$P_i > P_f$$

independently of initial trajectory

COLLIMATION IS NOT NEEDED!

SPIN–ECHO ANGULAR ENCODING: THE EQUATIONS



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

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

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

In our experiments:
SE length δ is tuned mechanically by changing η_0

SPIN-ECHO GIVES RESULTS IN REAL SPACE

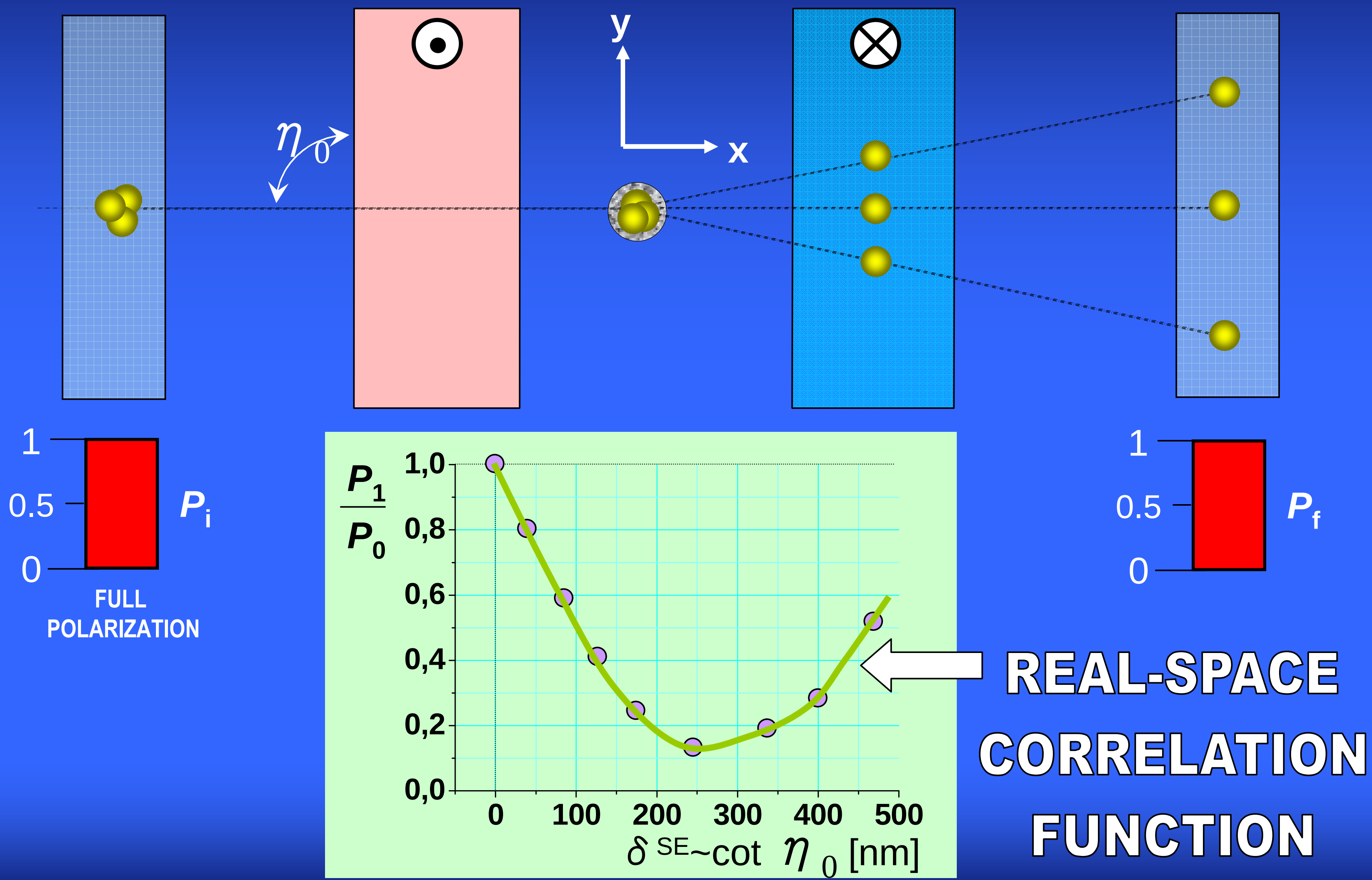
$$P_1 = P_0 \cos \Delta\xi \,.$$

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

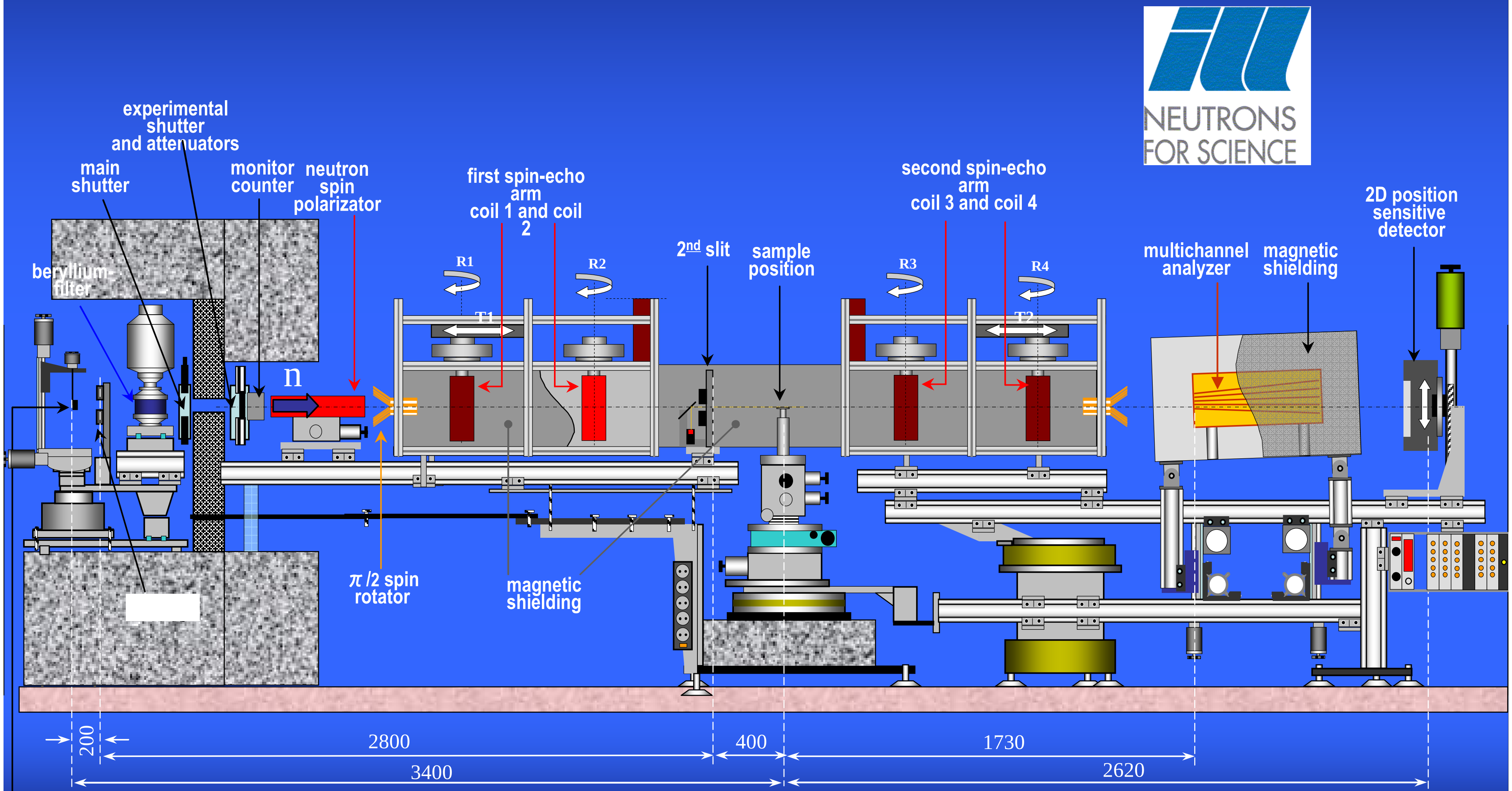
q_z=0

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

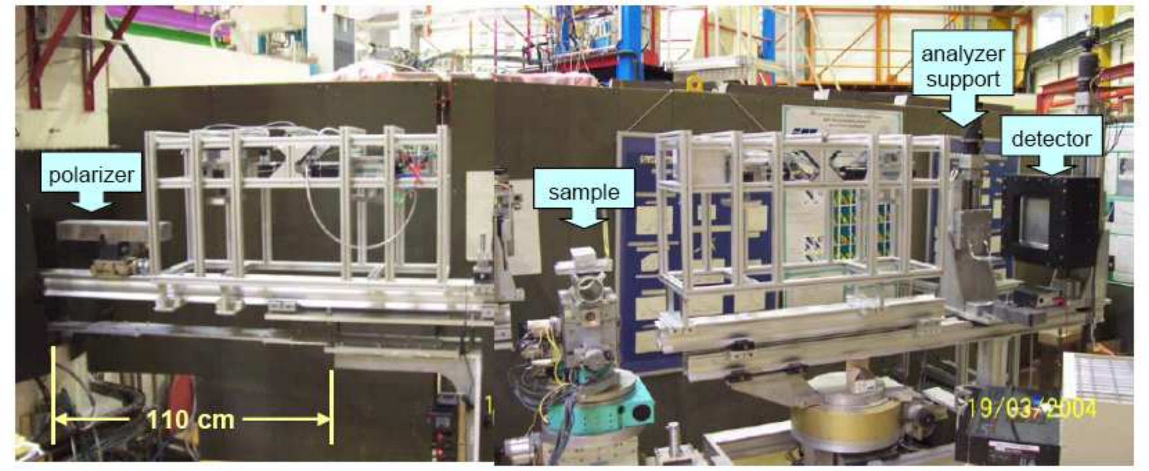
THE EXPERIMENT



EVA REFLECTOMETER TRANSFORMED INTO A SERGIS PROTOTYPE INSTRUMENT



EVA DURING THE TRANSFORMATION TO SERGIS



Beam size 50x5mm

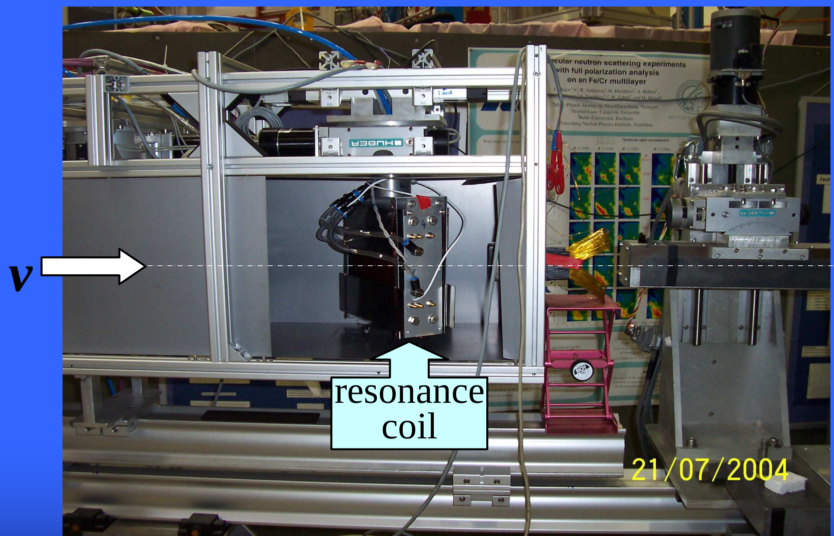
Wave numbers covered:

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

Max. SE time in classical configuration (η_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

ν (neutron velocity) 720 m/s

Θ (tilt of precession coil) 50°

B (magnetic field in leg) 310G

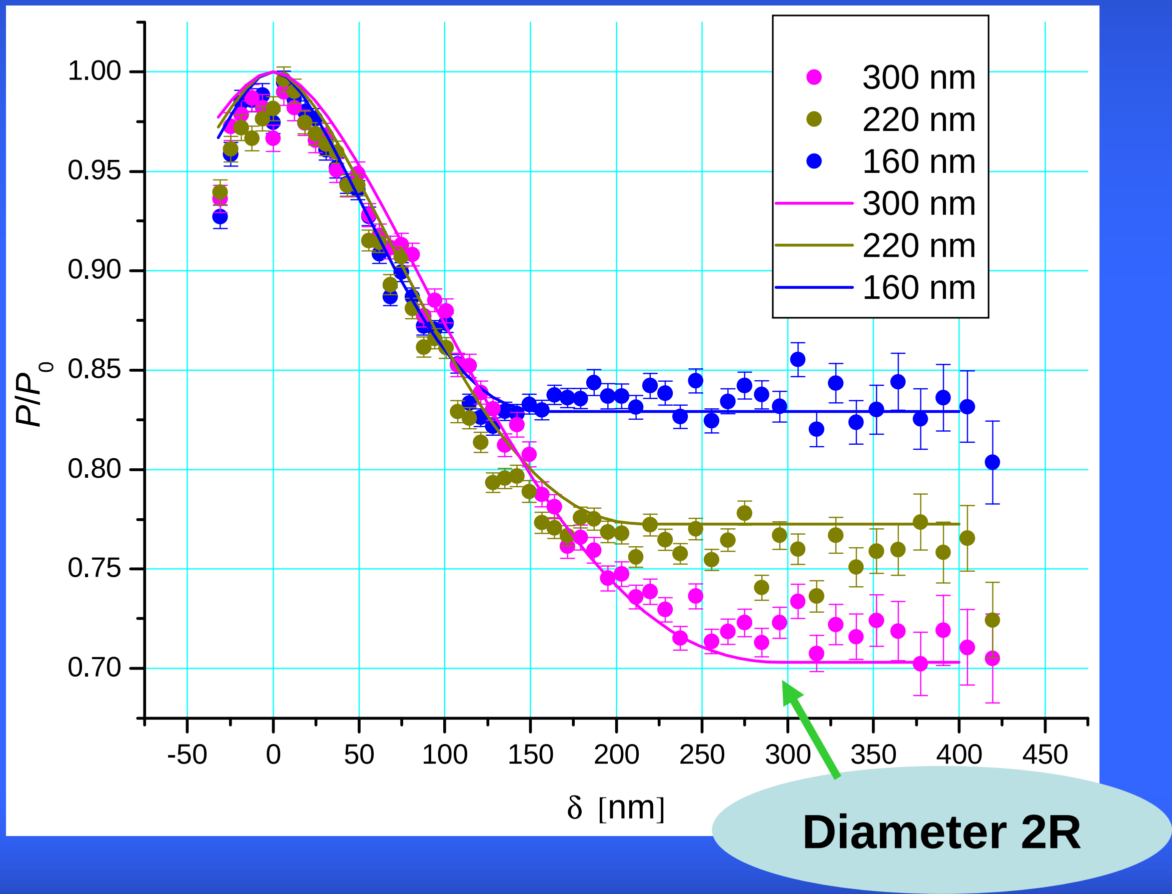
d (length of precession leg) 50 cm

EVA reflectometer transformed into a SERGIS prototype instrument

Test SESANS experiments: polystyrene spheres

2.5% polystyrene balls in 3:1 D_2O/H_2O

2mm thick cell



SESANS: first experiments, case of concentrated colloids

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

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

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[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

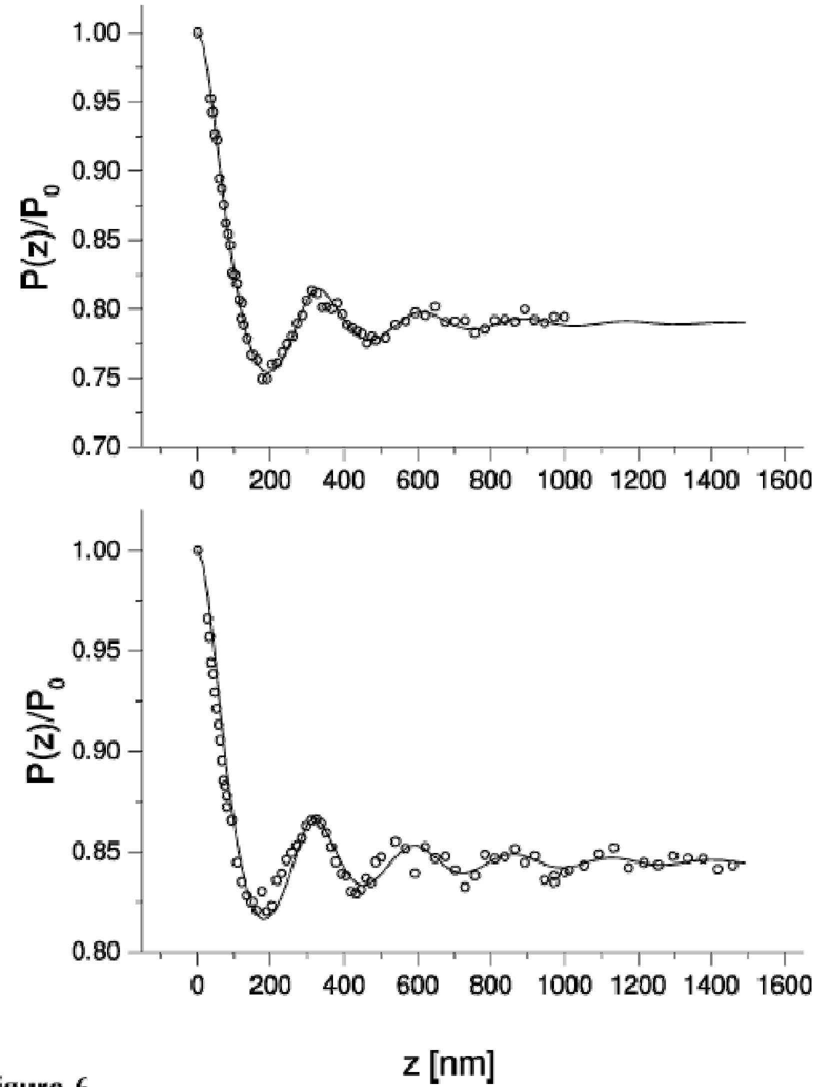
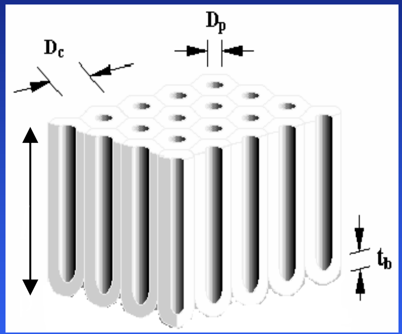


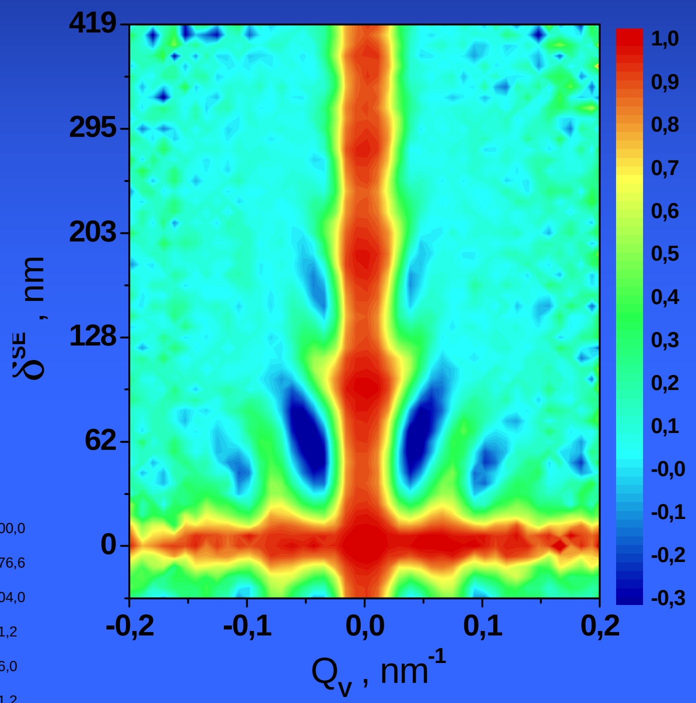
Figure 6
The solution from Fig. 5 after two weeks at rest. The top graph corresponds to the top of the sediment. The lower graph corresponds to the bottom of the sediment. Lines: Percus–Yevick solution for a hard-sphere liquid with $\varphi_V = 0.4$ (top) and $\varphi_V = 0.5$ (bottom). $R = 149$ nm.

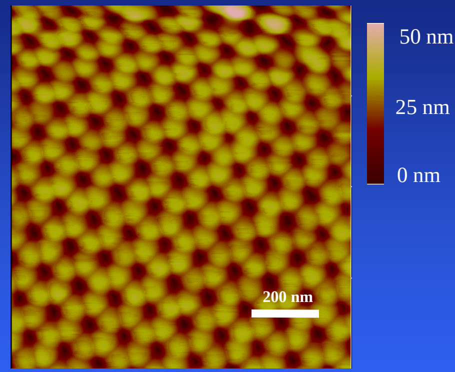
SESANS EXAMPLE: Anodized Aluminum Oxide



AAO scheme

RECIPROCAL & REAL
SPACE DATA (SESANS)



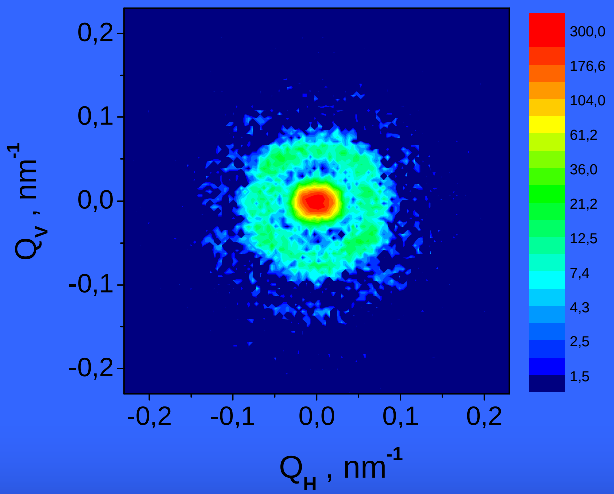


REAL SPACE (AFM)

D_C, pore-to-pore distance = 120nm

D_P, pore diameter = 50÷60 nm

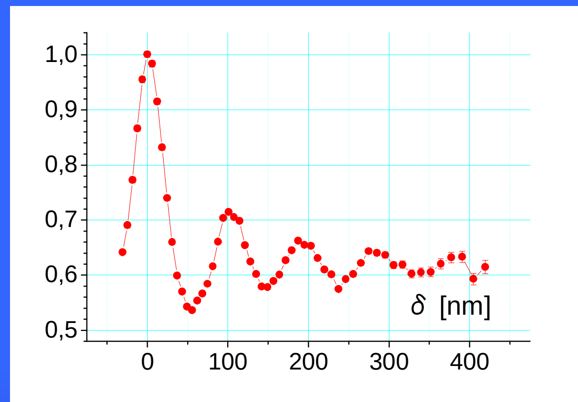
RECIPPROCAL SPACE (SANS)



SANS:

$D_C = 2\pi / \Delta Q = 100$ nm

RECIPROCAL^2 SPACE (SESANS) =
REAL SPACE CORRELATION FUNCTION

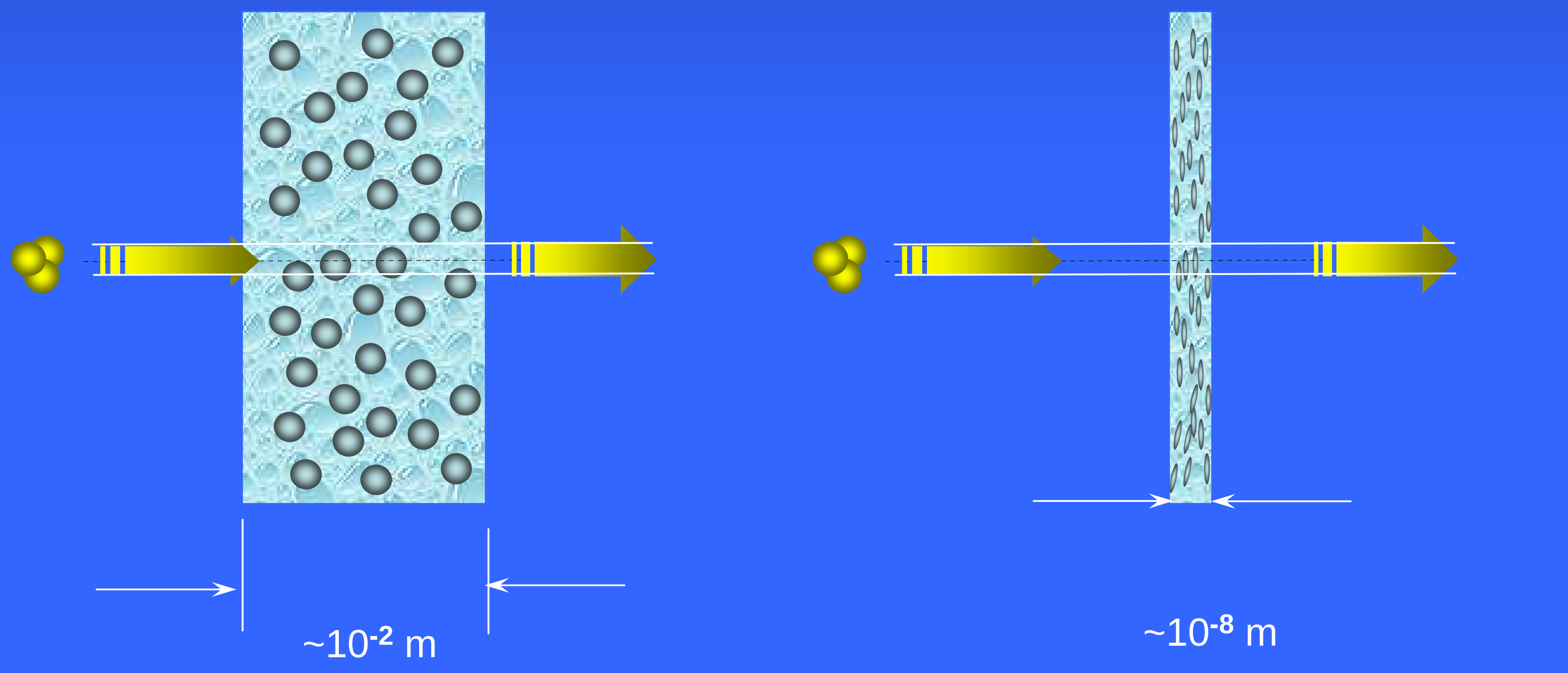


SESANS:

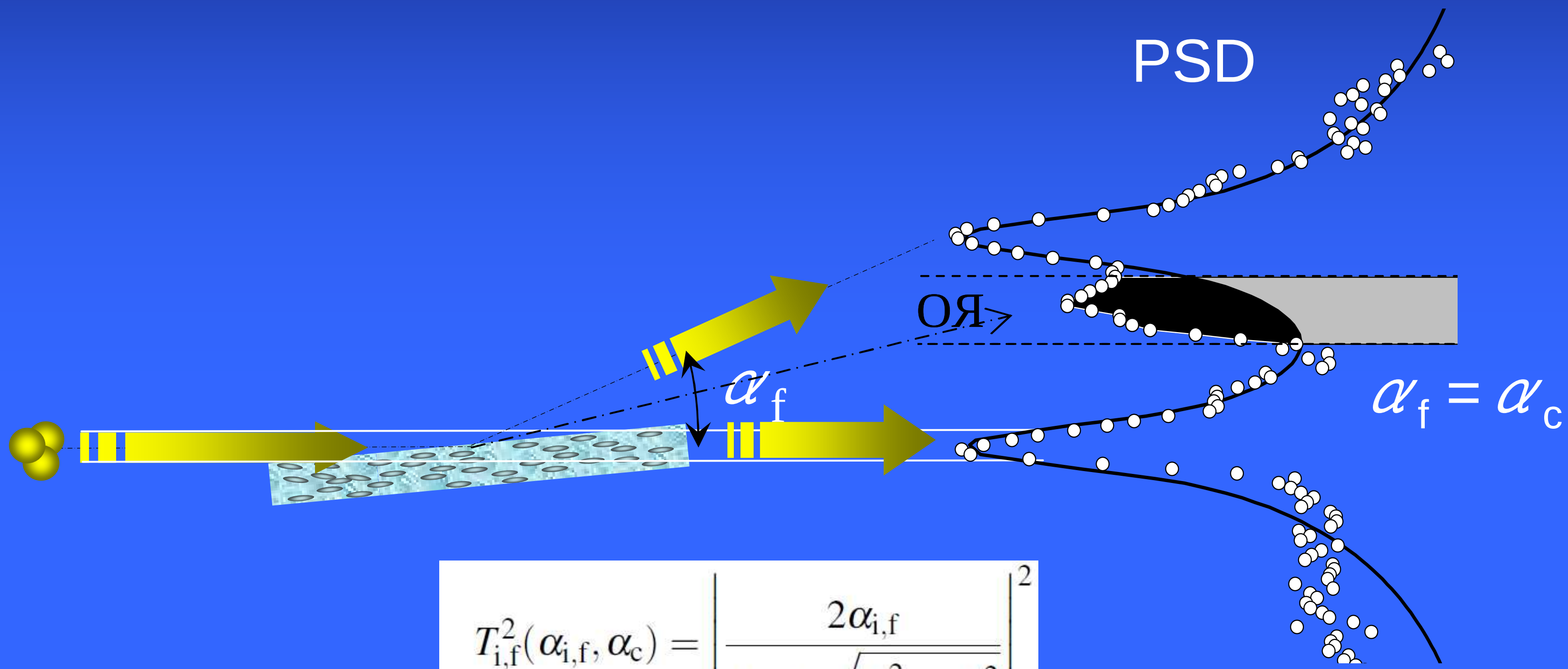
D_C = 100 nm

GRAZING INCIDENCE

TRANSMISSION:
what to do with a very thin sample?



GRAZING INCIDENCE

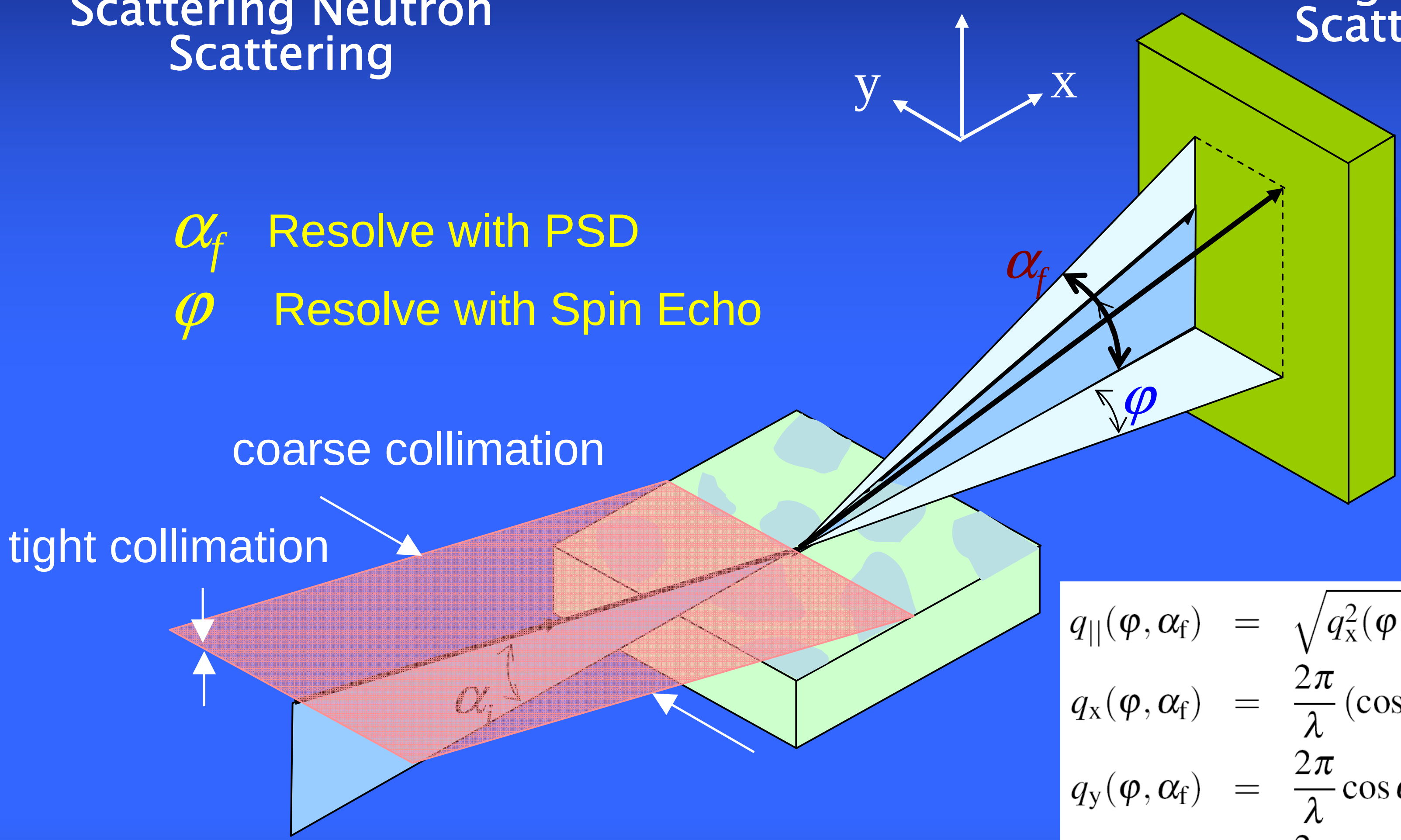


$$T^2_{i,f}(\alpha_{i,f}, \alpha_c) = \left| \frac{2\alpha_{i,f}}{\alpha_{i,f} + \sqrt{\alpha^2_{i,f} - \alpha^2_c}} \right|^2$$

GISANS vs. SERGIS

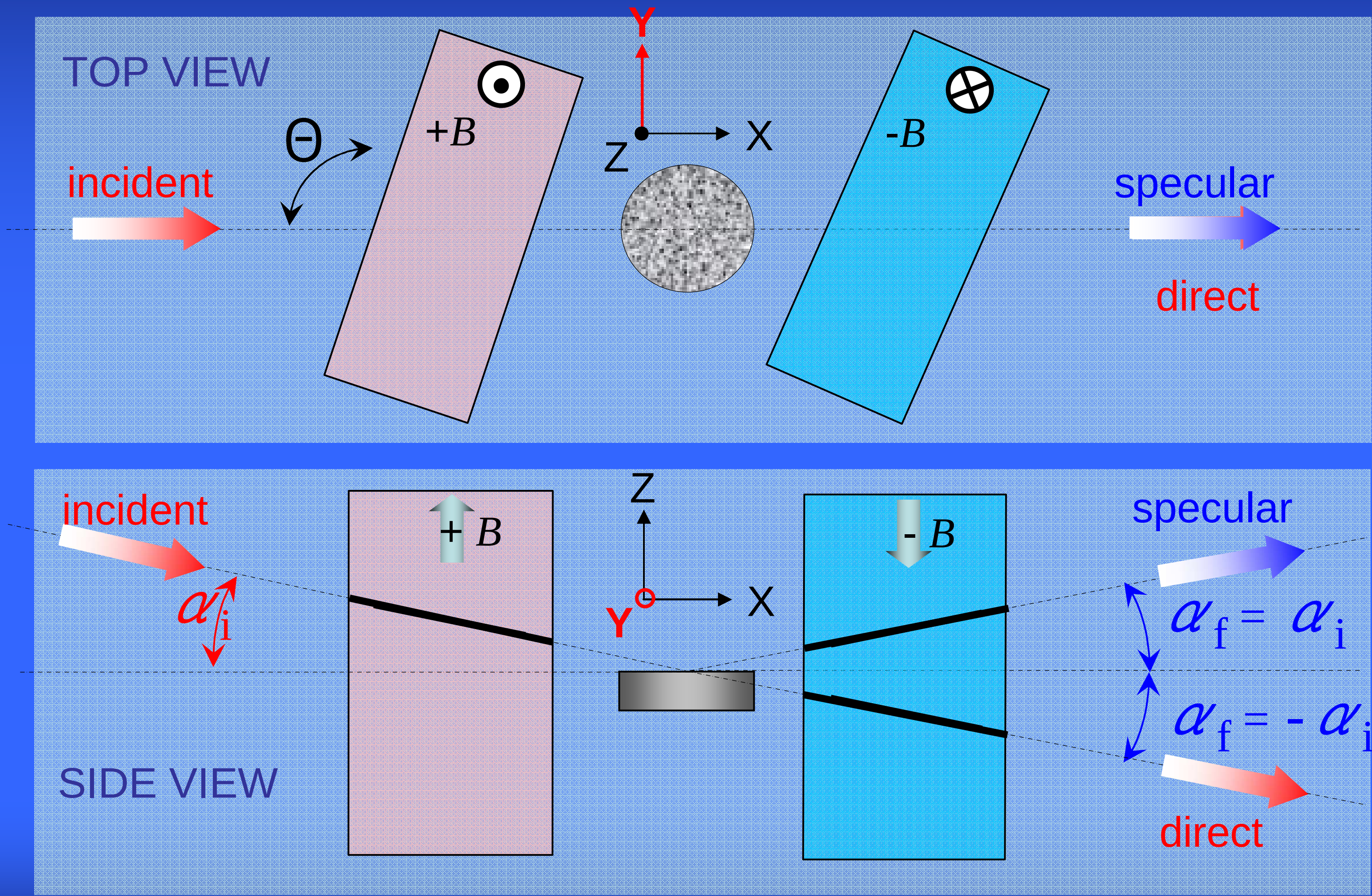
Grazing Incidence Scattering Neutron Scattering

Spin-Echo Resolved Grazing Incidence Scattering

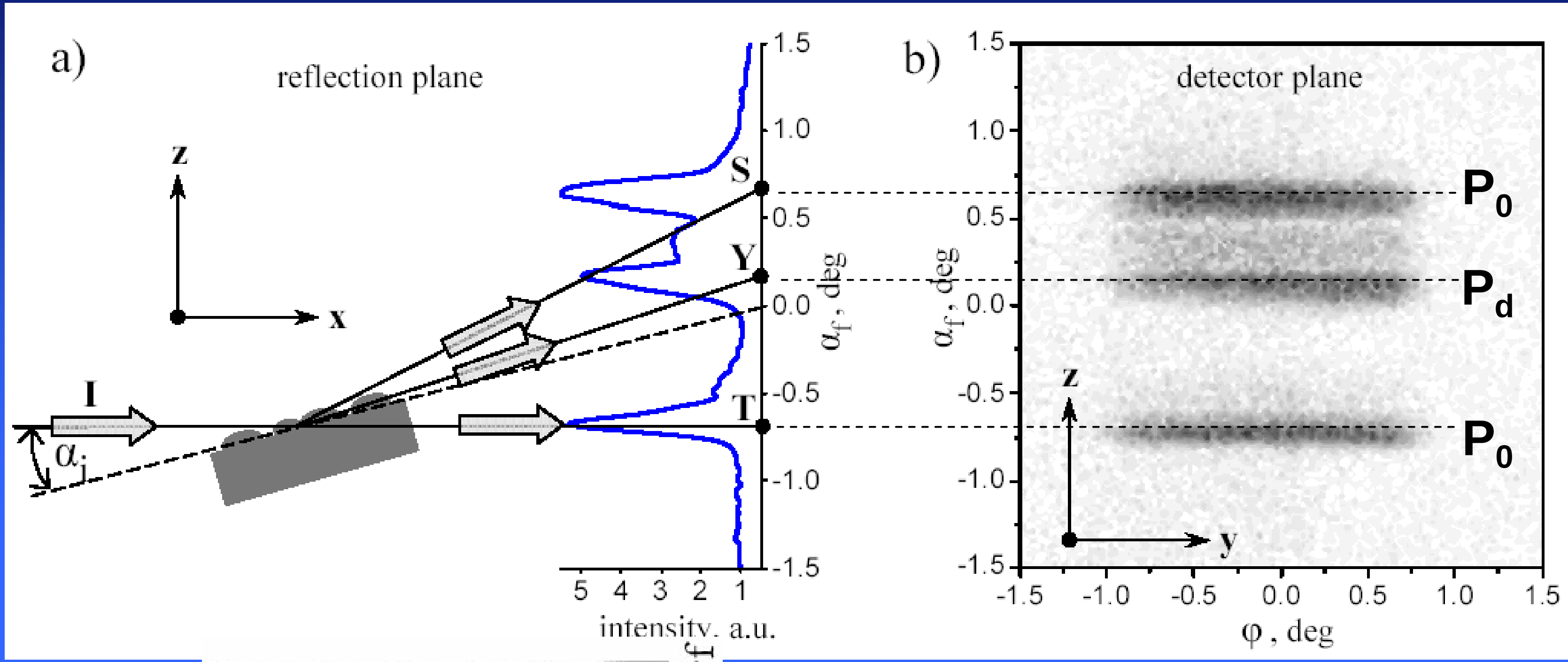


$$
\begin{aligned}
q_{||}(\varphi,\alpha_f) &= \sqrt{q_x^2(\varphi,\alpha_f)+q_y^2(\varphi,\alpha_f)} \\
q_x(\varphi,\alpha_f) &= \frac{2\pi}{\lambda}(\cos\alpha_f\cos\varphi-\cos\alpha_i) \\
q_y(\varphi,\alpha_f) &= \frac{2\pi}{\lambda}\cos\alpha_f\sin\varphi \\
q_z(\varphi,\alpha_f) &= \frac{2\pi}{\lambda}(\sin\alpha_f+\sin\alpha_i)
\end{aligned}
$$

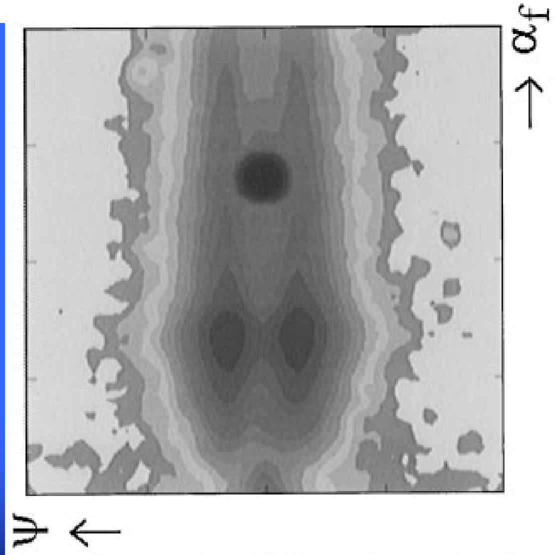
THE SAME POLARIZATION IN DIRECT AND SPECULAR BEAMS



SERGIS

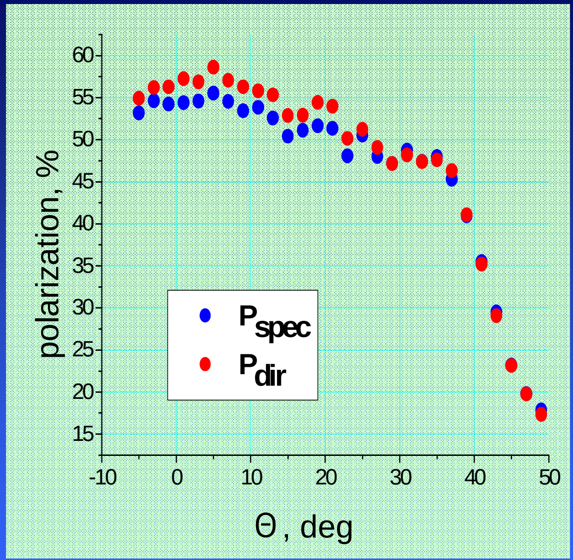


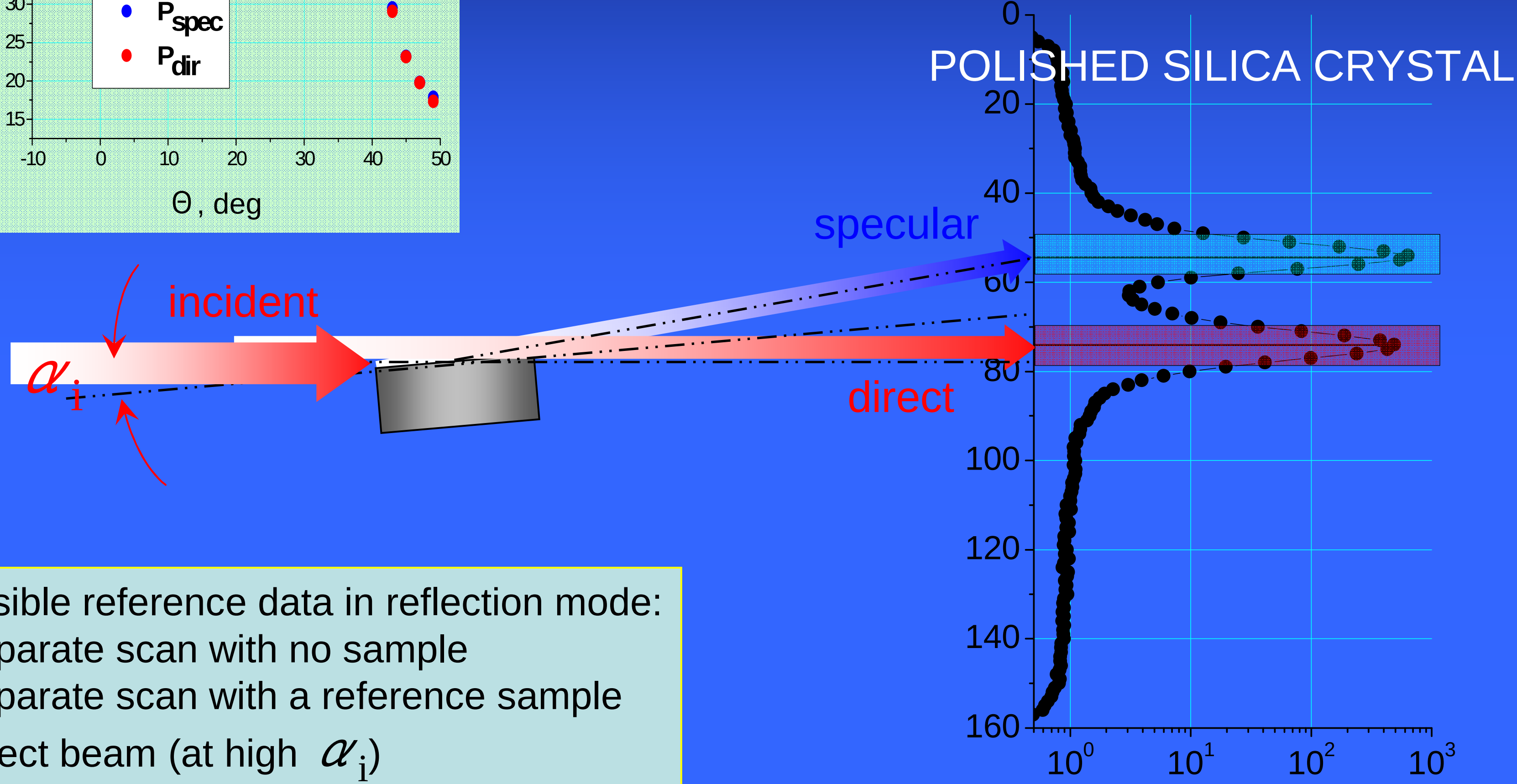
GISANS



a) The scattering geometry. The incident beam (I) impinges on the sample surface at a shallow angle α_i; transmitted (T), specular (S) and diffuse (Y) intensities are simultenuously recorded by PSD. b) Image taken by 2-dimensional PSD during real experiment. The size of the incoming beam at the sample position was 30×2 mm^2.

REFLECTIVITY
REFERENCE MEASUREMENT

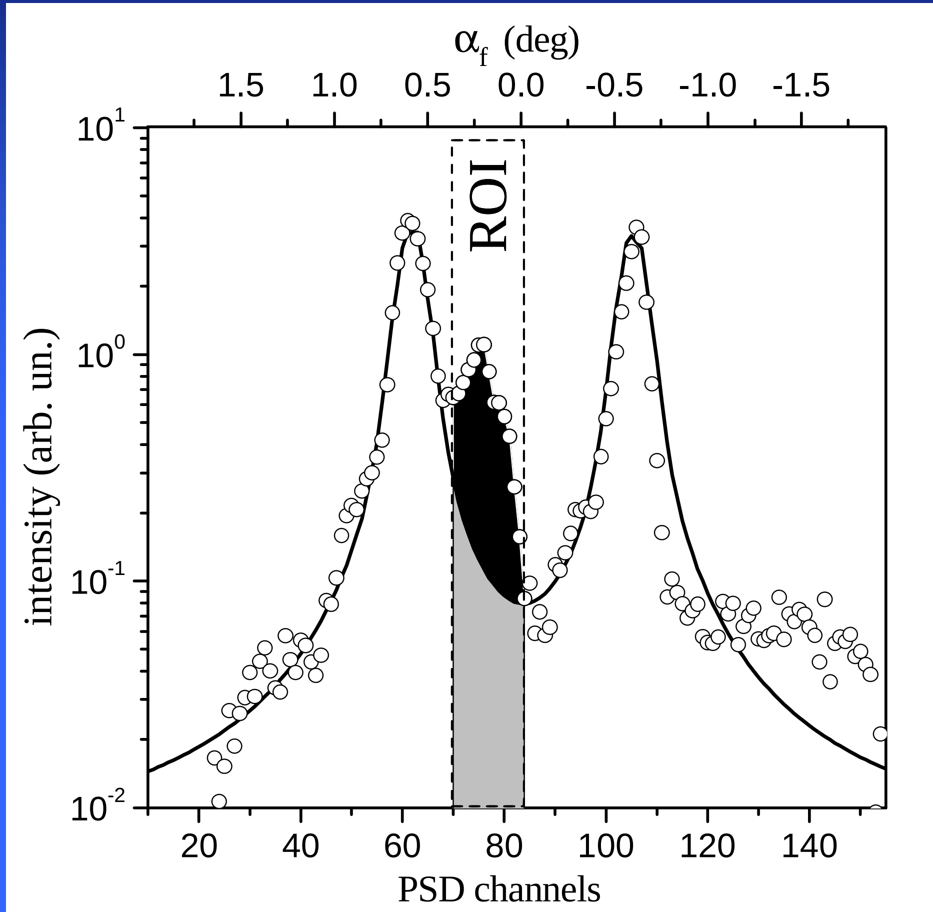




possible reference data in reflection mode:
- separate scan with no sample
- separate scan with a reference sample
- direct beam (at high α_i)
- specular beam (at high α_i)

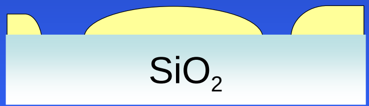
possible reference data in transmission mode:
- separate scan with no sample

“PURIFICATION” OF THE SIGNAL

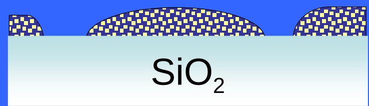


$$\frac{P_d}{P_0} = \frac{P_{ROI}}{P_0} - \frac{1}{C}\left(1 - \frac{P_{ROI}}{P_0}\right)$$

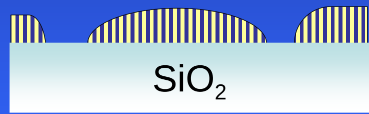
SAMPLES: DEWETED POLYMER FILMS



dPS
deuterated
polystyrene



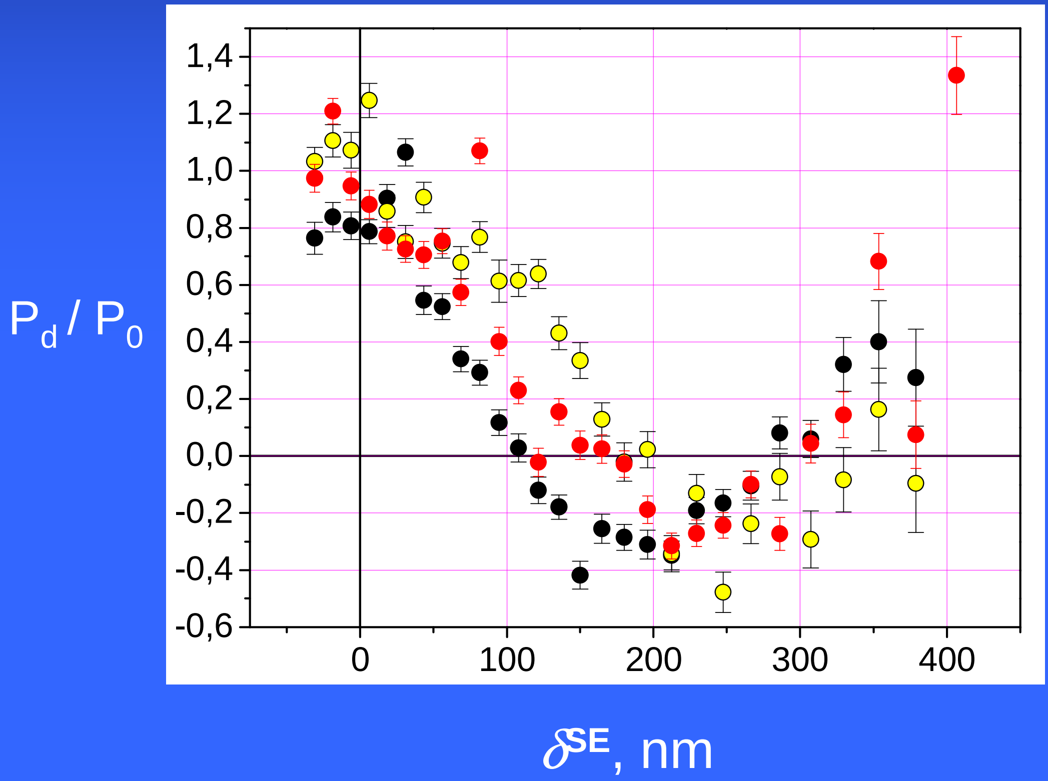
polymer
blend
PpMS:dPS = 3:2
polyparamethylstyrene
polystyrene



diblock
copolymer
poly(styren-block-
paramethylstyrene)
P(S-b-pMS)

regular phase
separation

SERGIS EXPERIMENTAL DATA



- HOMOPOLYMER pancake-type droplets
- BLEND pancake-type droplets
- DIBLOCK 'spherical' droplets

DATA ANALYSIS IN SERGIS

Modeling of the scattering from the dewetted polymer droplets

$$\frac{P_1}{P_0} = \langle \cos \Delta\xi \rangle \propto \frac{\int_{\mathrm{det}} \mathrm{d}q_{\mathrm{y}} \mathrm{d}q_{\mathrm{z}} S(\mathbf{q}) \cos(\delta_{\mathrm{y}}^{\mathrm{SE}} q_{\mathrm{y}})}{\int_{\mathrm{det}} \mathrm{d}q_{\mathrm{y}} \mathrm{d}q_{\mathrm{z}} S(\mathbf{q})} = \int \mathrm{d}x \Pi(x,y,0) \equiv G(y),$$

Specific of grazing incidence scattering: framing of the form-factor by the Fresnel transmission coefficients

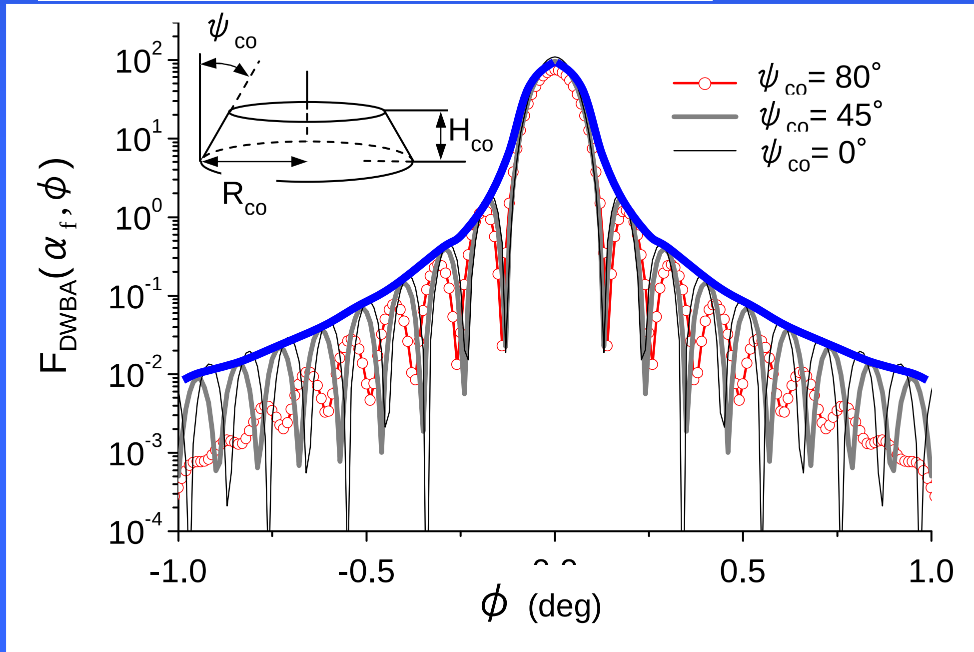
$$S(q) = |F_{\mathrm{BA}}|^2 \cdot T_{\mathrm{i}}^2(\alpha_{\mathrm{i}}) \cdot T_{\mathrm{f}}^2(\alpha_{\mathrm{f}}) \quad \cdot I_{\mathrm{H}}(\varphi, \alpha_{\mathrm{f}})$$

CONE FORM FACTOR IN THE CASE OF PANCAKE-LIKE OBJECTS

$$F_{co}(\varphi,\alpha_f) = \int_0^{H_{co}} Z_r^2(z,\psi_{co}) \frac{J_1\left(q_{||}(\varphi,\alpha_f)\cdot Z_r(z,\psi_{co})\right)}{q_{||}(\varphi,\alpha_f)\cdot Z_r(z,\psi_{co})}) \exp\left(\frac{i}{2} q_z(\varphi,\alpha_f) z\right)$$

$$Z_r(z,\psi_{co}) = R_{co} - z/\cot\psi_{co}$$

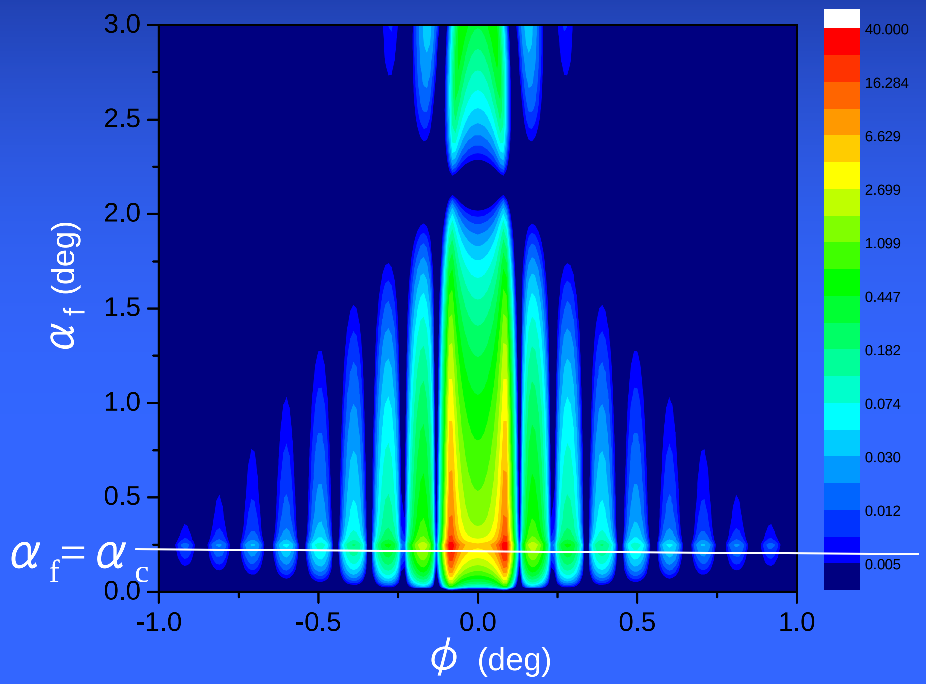
R_{co}=150 nm
H_{co}=10 nm

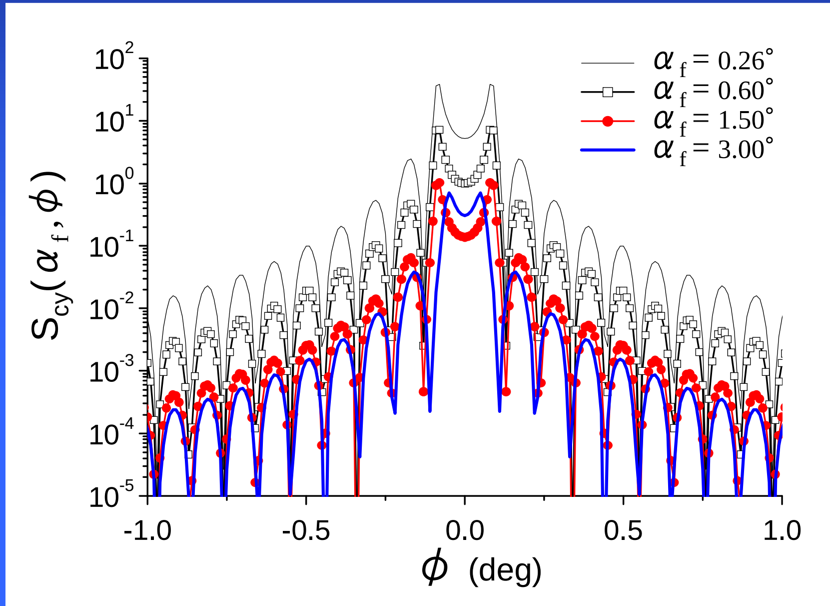


$\psi_{co} = 0°$ cylinder

$$|F_{cy}(\varphi,\alpha_f)| = \frac{J_1\left(q_{||}(\varphi,\alpha_f)R\right)}{q_{||}(\varphi,\alpha_f)R} \frac{\sin\left(q_z(\varphi,\alpha_f)H/2\right)}{q_z(\varphi,\alpha_f)H/2}$$

CYLINDER FORM FACTOR AS SEEN IN THE 2d DETECTOR





α_i fixed

$\alpha_f = \alpha_c$ fixed

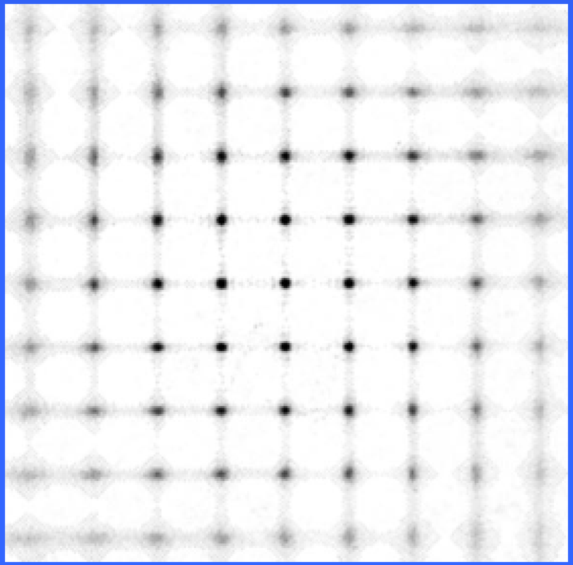
DATA ANALYSIS IN SERGIS

Choice of the interference function – structure factor of one-dimensional ideal paracrystal (Hosemann and Bagchi)

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

D – the mean value of the lattice parameter

σ – its standard deviation if the disorder factor obeys Gaussian distribution

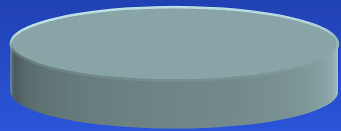


Hosemann, R.; Bagchi, S. N. *Direct Analysis of Diffraction by Matter* (North-Holland Publishing Company: Amsterdam, 1962).

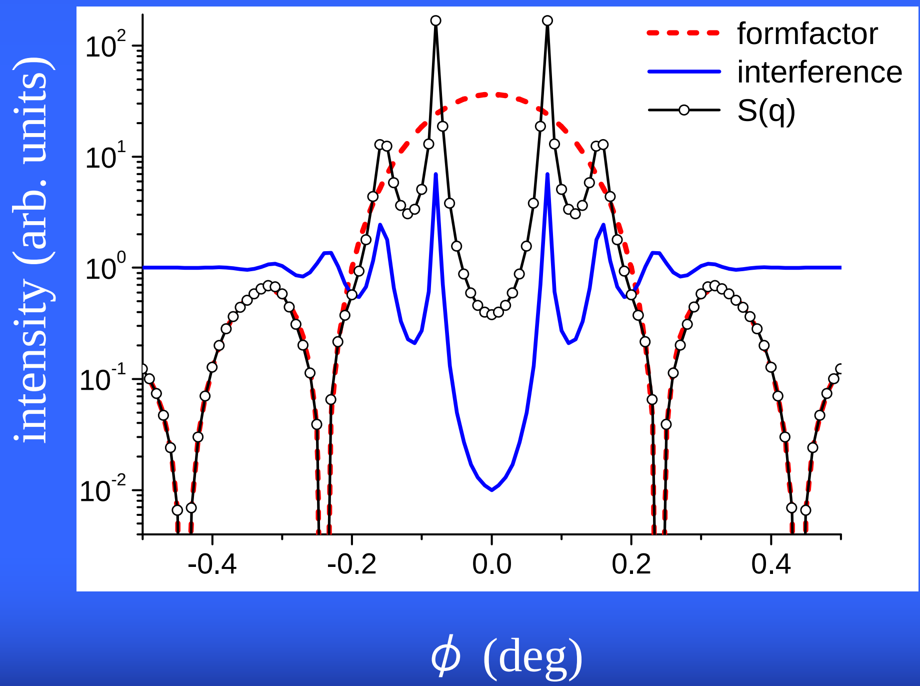
SCATTERING INTENSITY DISTRIBUTION

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

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

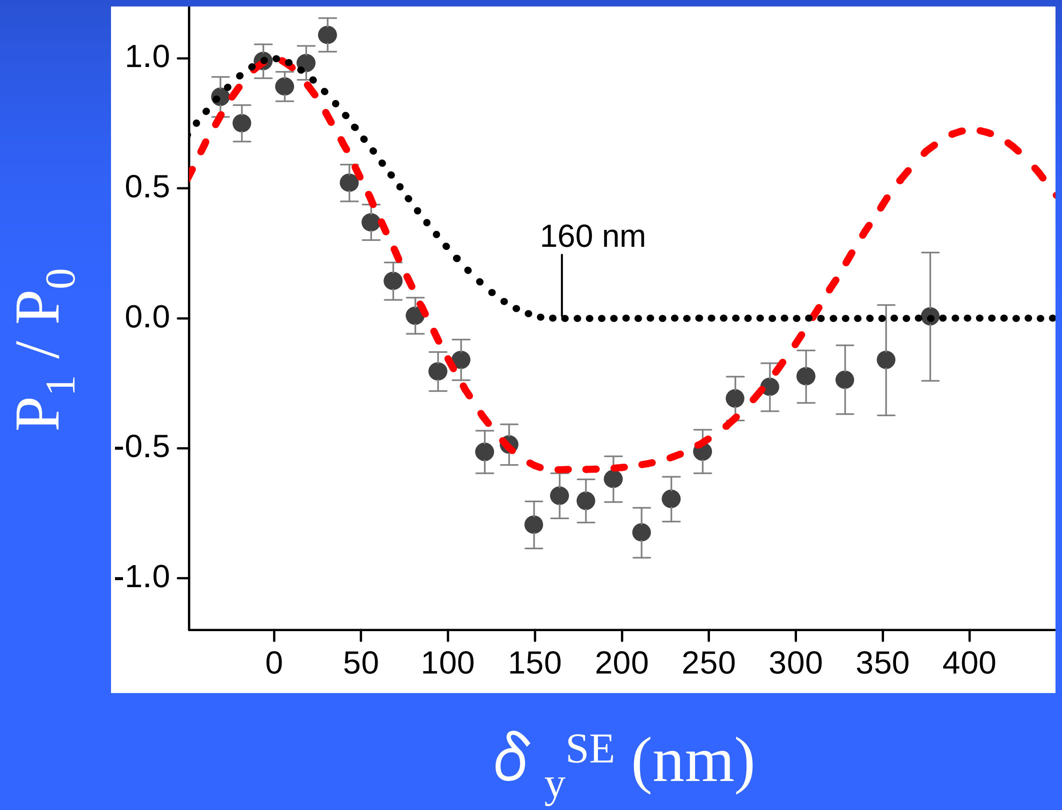


$$I_{\mathrm{H}}(\varphi,\alpha_{\mathrm{f}}) = \frac{1-\mathrm{e}^{-q_{||}(\varphi,\alpha_{\mathrm{f}})\sigma^2}}{1+\mathrm{e}^{-q_{||}(\varphi,\alpha_{\mathrm{f}})\sigma^2} - 2\mathrm{e}^{-\frac{1}{2}q_{||}(\varphi,\alpha_{\mathrm{f}})\sigma^2}\cos(Dq_{||}(\varphi,\alpha_{\mathrm{f}}))}$$



SERGIS signal

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



dPS sample

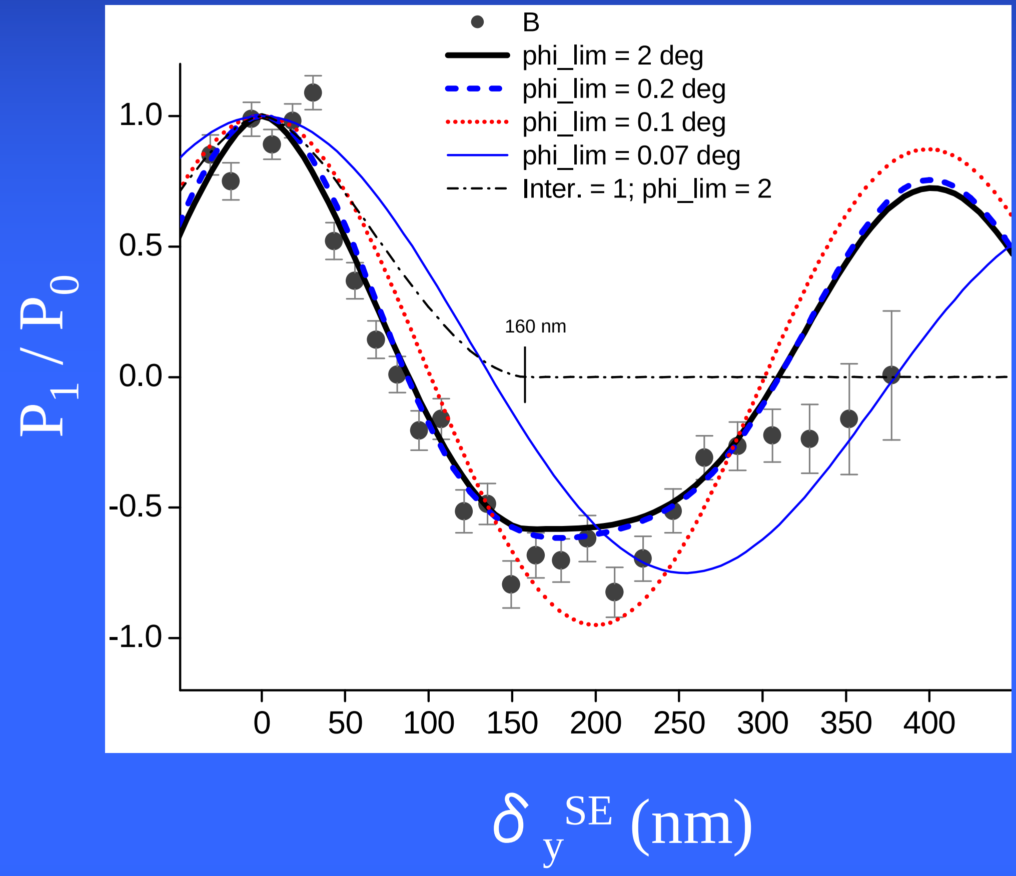
R=80 nm

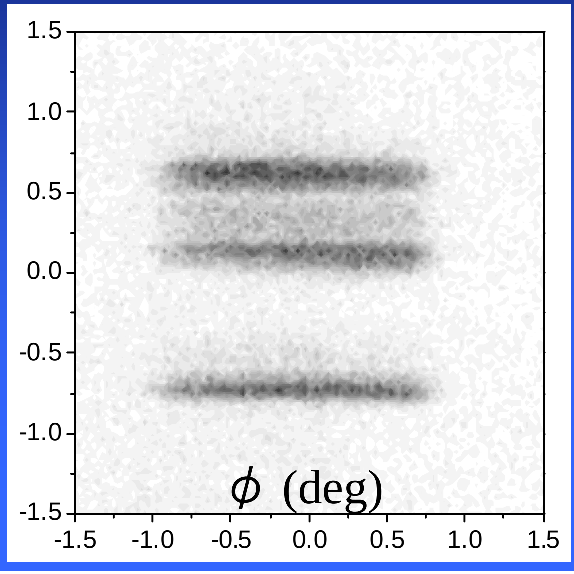
H=10 nm

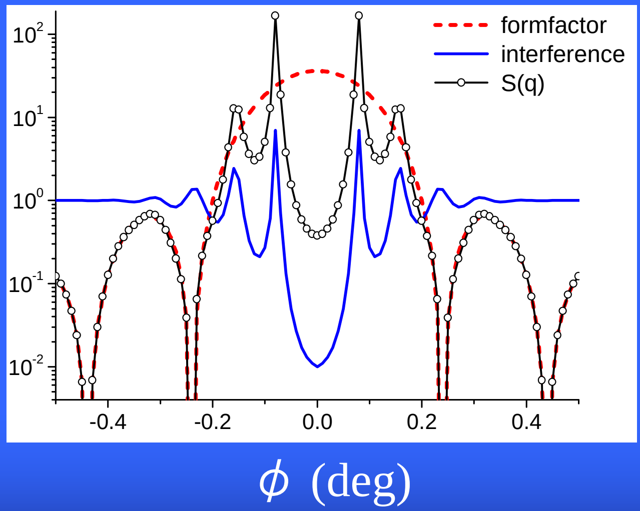
D=390 nm

σ = 25 nm

POSSIBLE EFFECT OF THE LIMITED SIZE OF THE DETECTOR ON THE SERGIS DATA

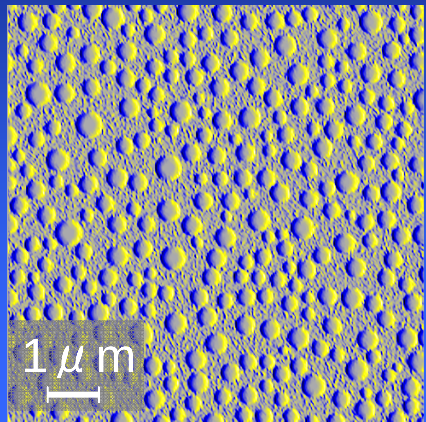


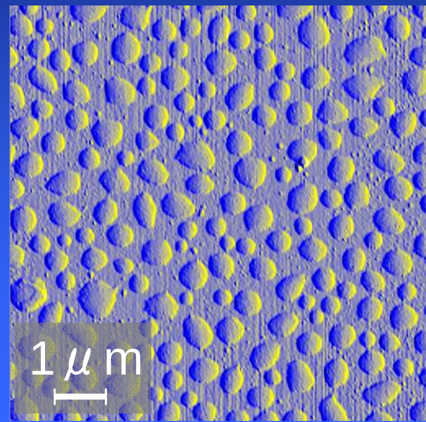




COMPLIMENTARY DATA – AFM

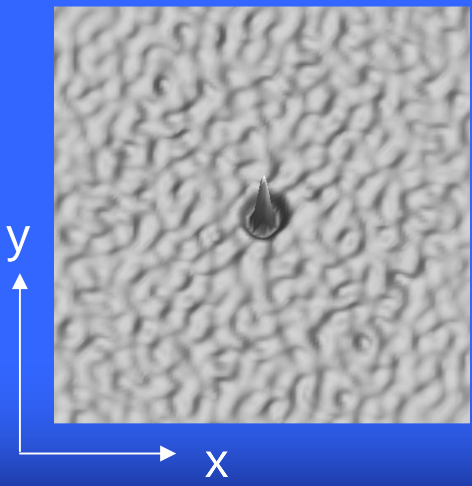
polymer blend | diblock copolymer

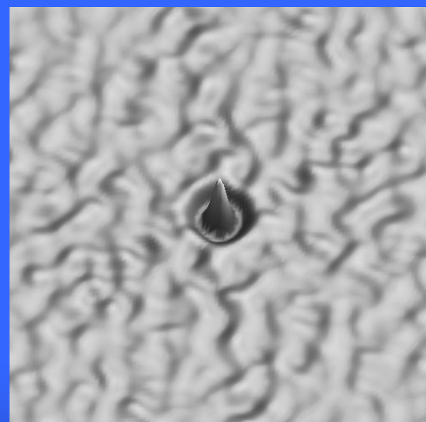




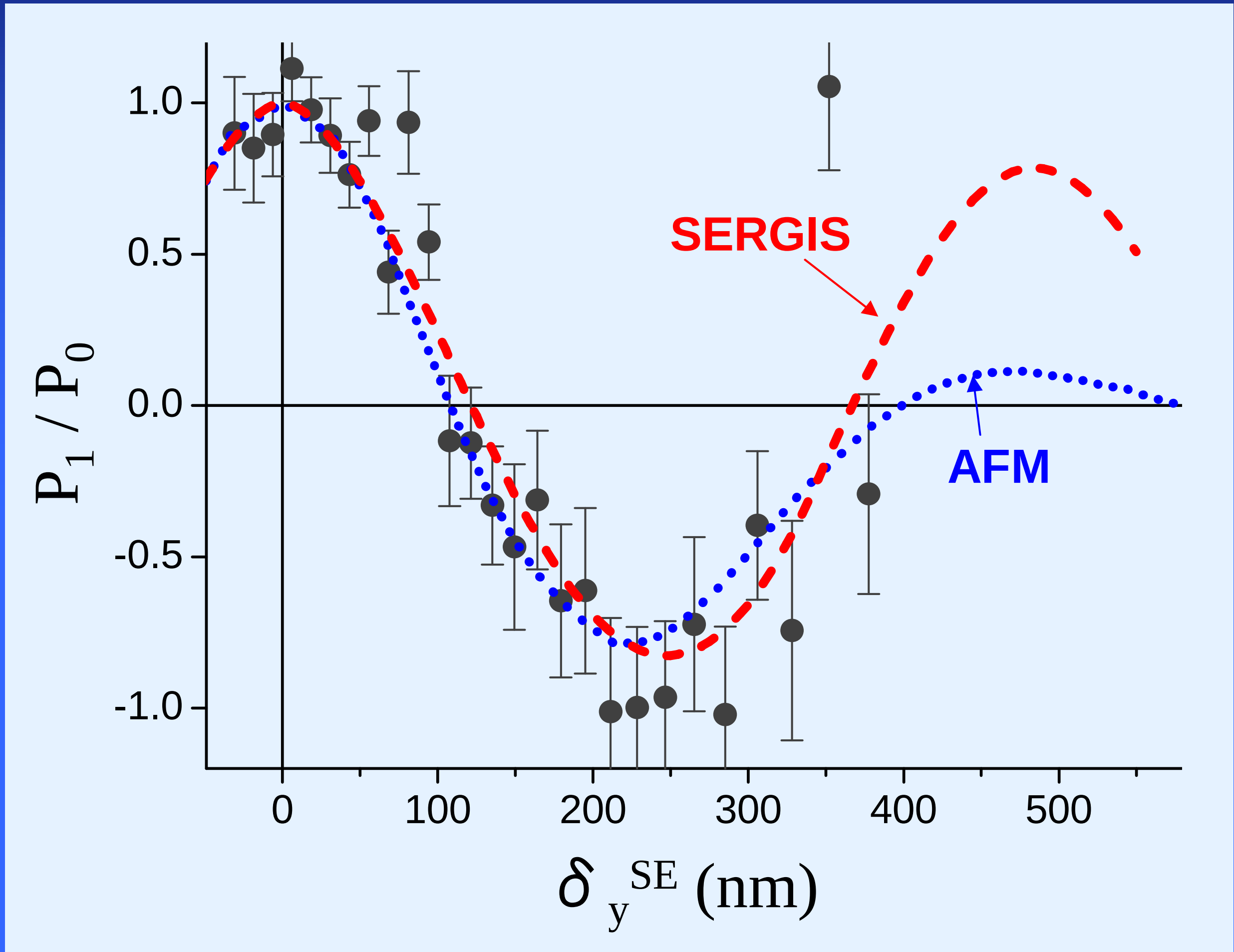
ACF

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





POLYMER BLEND

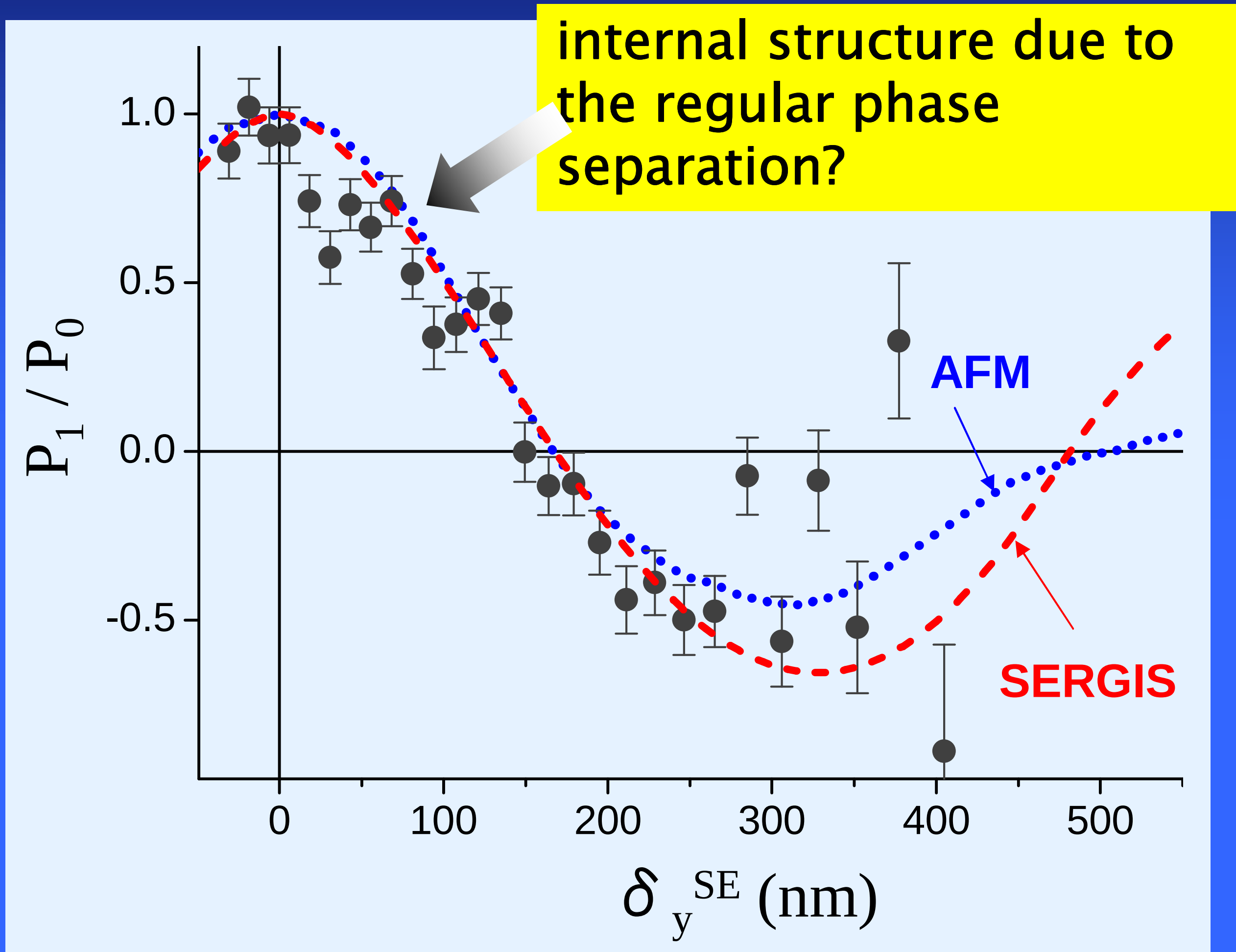


SERGIS model:
R=170 nm
H=20 nm
D=480 nm
σ = 50 nm

AFM:
D=450 nm

GISANS/GISAXS:
D=500 nm

DIBLOCK COPOLYMER



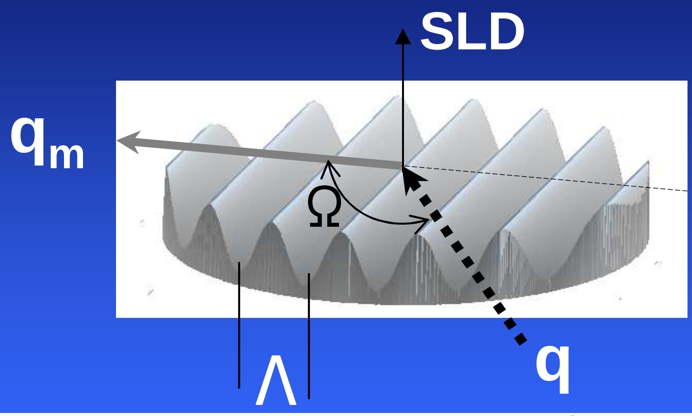
SERGIS model:
R=230 nm
H=10 nm
D=600 nm
σ /D=0.17

AFM:
D=630 nm

GISANS/GISAXS:
D=600 nm

AFM and GISAXS can not see internal structure, GISANS can see and does see. What about SERGIS?

MODULATED DROPLETS



SLD contrast

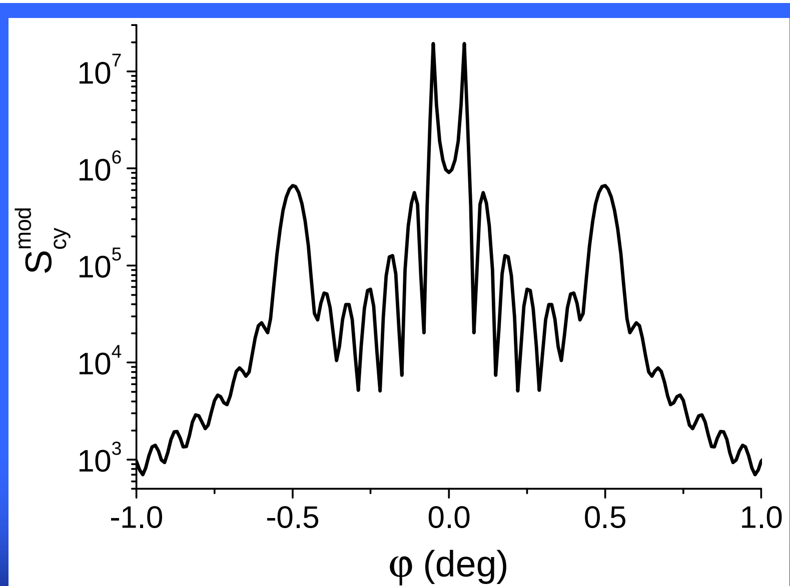
$$f_m(\mathbf{r}) = \overline{\rho} + \frac{\Delta\rho}{2}\cos(\mathbf{q}_m \cdot \mathbf{r})$$

mean SLD

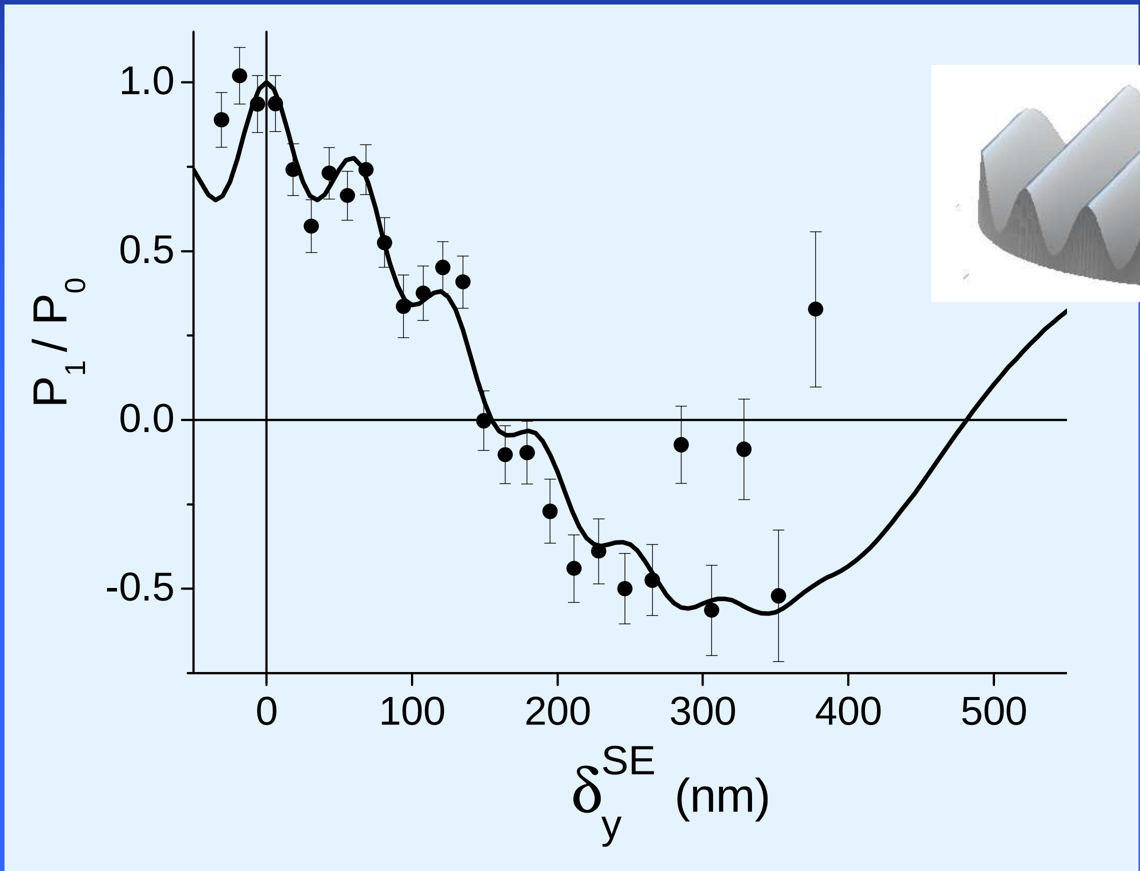
$$|F_{\mathrm{cy}}^{\mathrm{mod}}(\mathbf{q})| = \overline{\rho}|F_{\mathrm{cy}}(\mathbf{q})| + \frac{\Delta\rho}{4}\left(\frac{J_1\left(|\mathbf{q}_{||} - \mathbf{q}_m|R\right)}{|\mathbf{q}_{||} - \mathbf{q}_m|R} + \frac{J_1\left(|\mathbf{q}_{||} + \mathbf{q}_m|R\right)}{|\mathbf{q}_{||} + \mathbf{q}_m|R}\right)\frac{\sin\left(q_{\mathrm{z}}(\varphi,\alpha_{\ma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

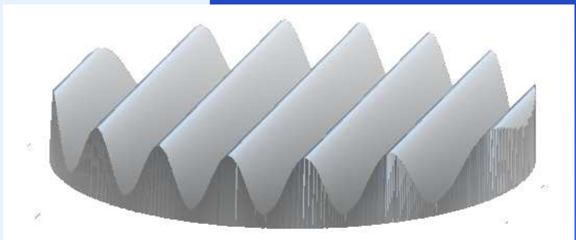
$$\overline{|F_{\mathrm{cy}}^{\mathrm{mod}}(\mathbf{q})|^2} = \frac{1}{\pi}\int_{-\pi/2}^{\pi/2}|F_{\mathrm{cy}}^{\mathrm{mod}}(\mathbf{q})|^2 \mathrm{d}\Omega$$

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



DIBLOCK COPOLYMER – MODULATED DROPLETS

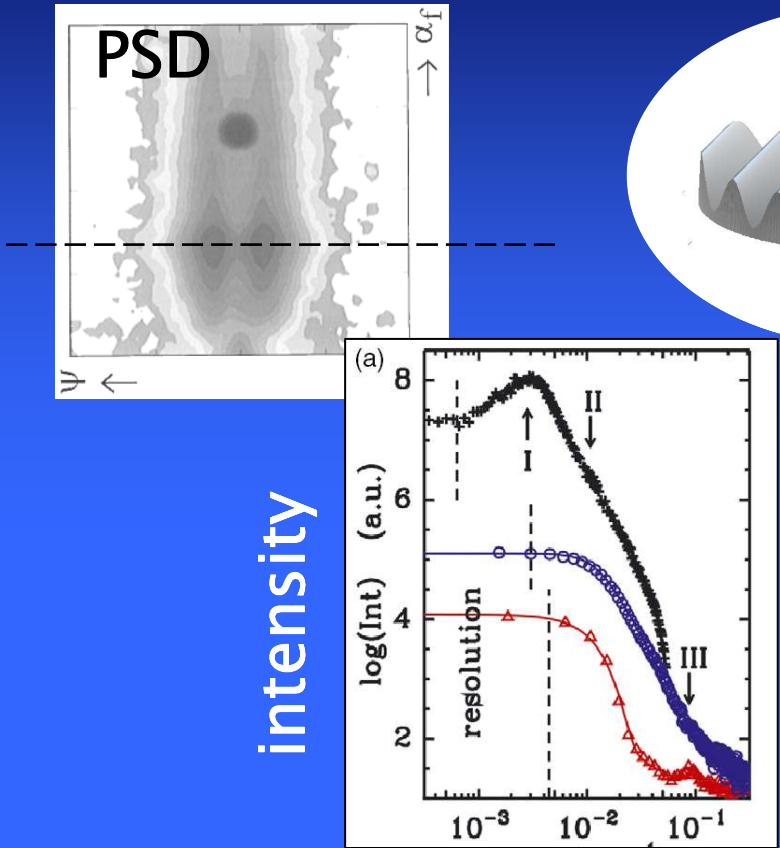




SERGIS
Λ =64 nm

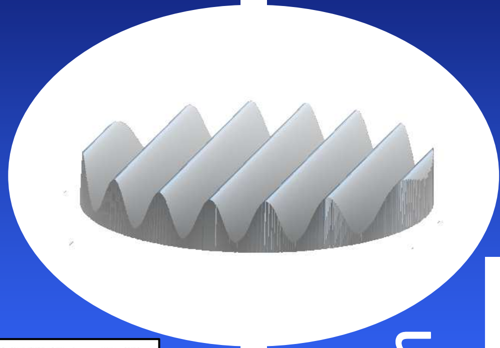
GISANS:
Λ =72 nm

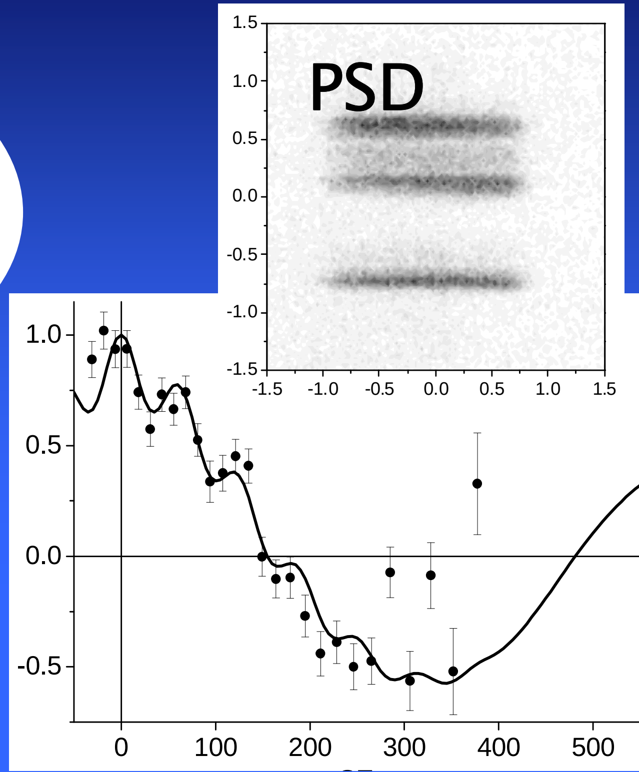
GISANS vs. SERGIS



intensity

q_y (nm^{-1})





polarization

y (nm)

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.

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