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

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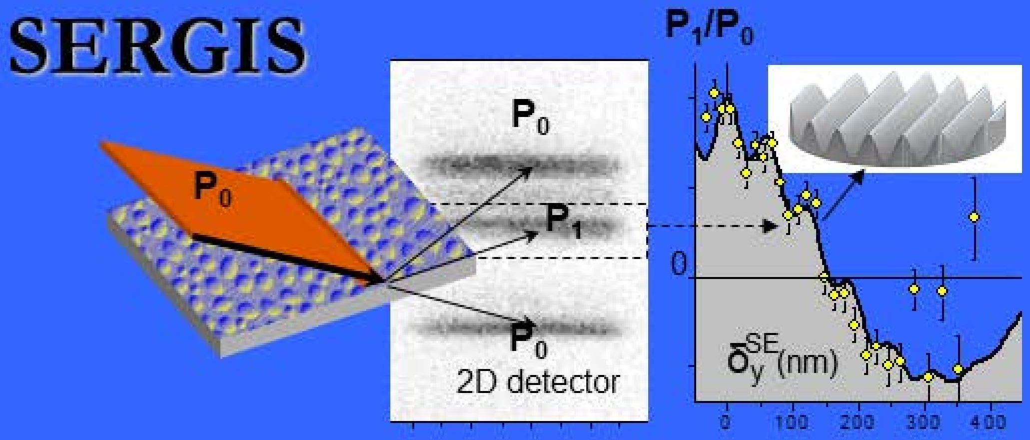
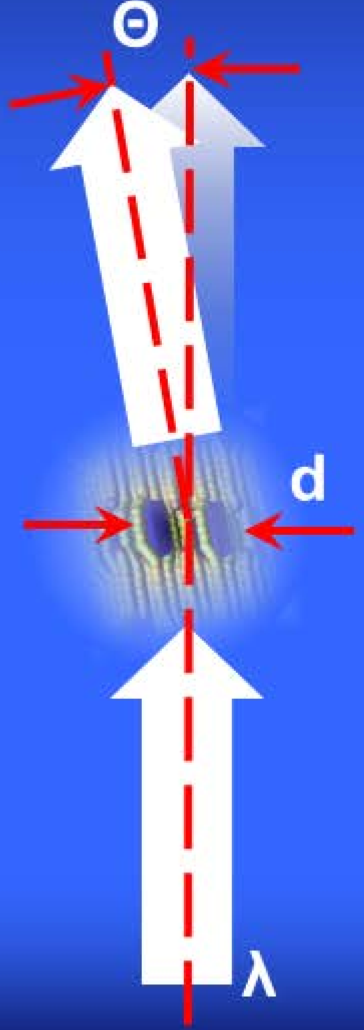


FORMULATION OF THE PROBLEM

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



$\lambda = 2d \sin\Theta$

if $d \gg \lambda \Rightarrow \Theta$ is small

- $\Rightarrow$ to measure small Θ one has to collimate both incident and scattered beams
- $\Rightarrow$ measured intensity will be very low
- $\Rightarrow$ 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

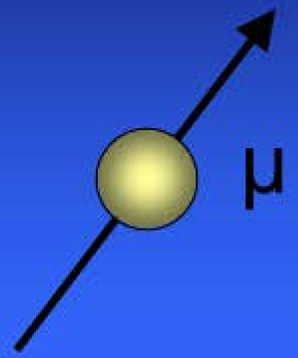
almost no collimation of the neutron beam is need

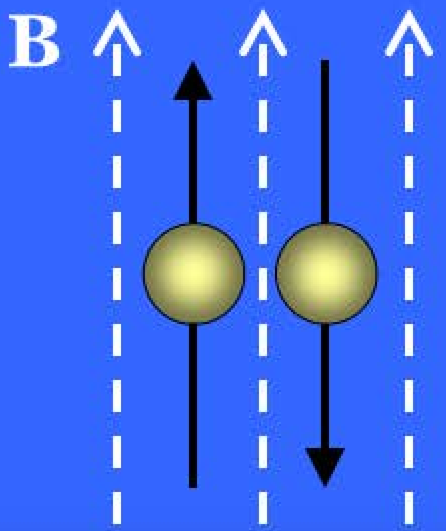
structural information about the sample is obtained in real space

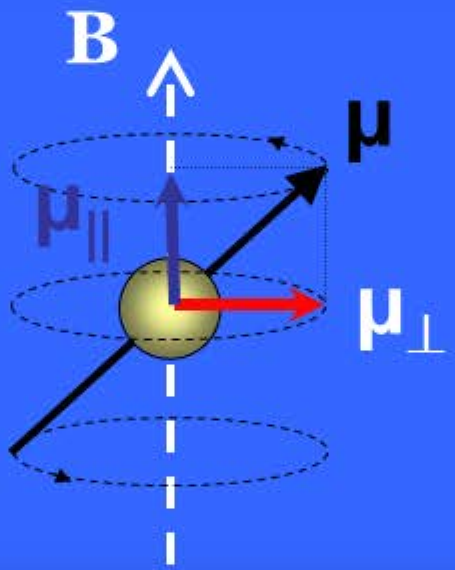
LARMOR PRECESSION

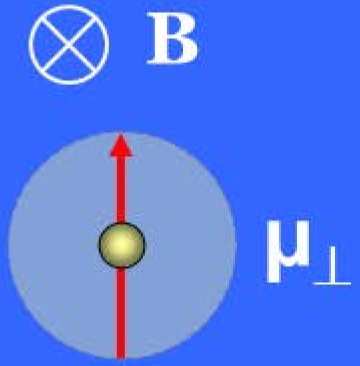
Neutron properties:

Mass $m=1.674928(1)\cdot 10^{-27}$ kg
Spin $s=-\hbar/2$
Magnetic moment $\mu=-9.649\cdot 10\text{-}27\ JT^{-1}$
ß-decay lifetime $\tau=886$ s



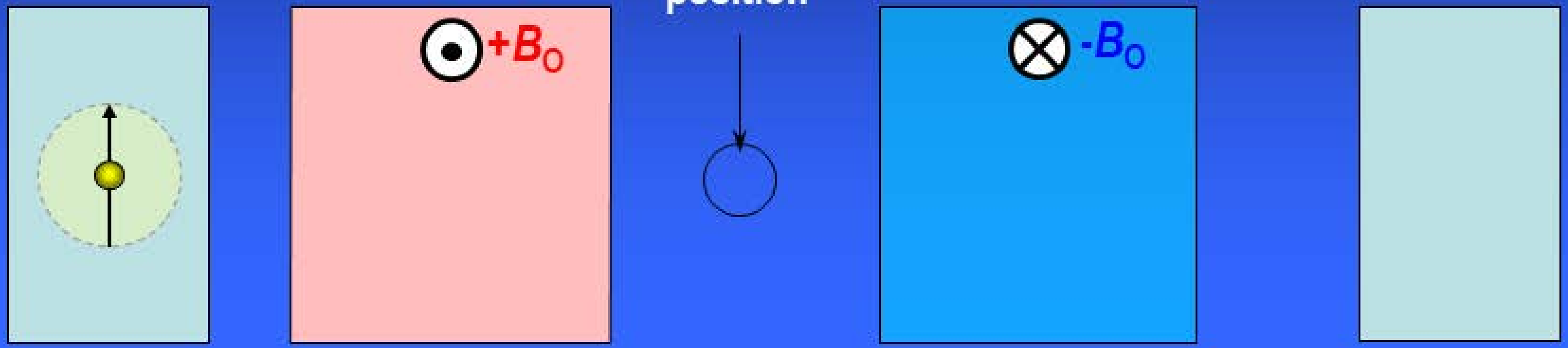






$\omega = \gamma B$
$\gamma = 2917$ Hz/Oe

CONVENTIONAL SPIN-ECHO FOR DYNAMIC STUDY



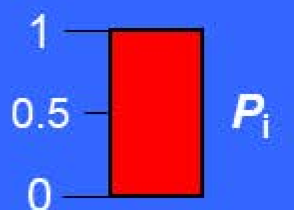
spin polarizer

1^{ST} precession arm

sample position

2^{ND} precession arm

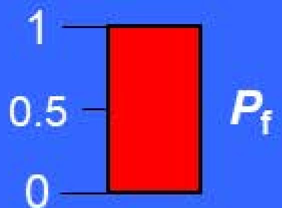
spin analyser



ALL SPINS
ARE VERTICAL:
FULL POLARIZATION

$$P_i = P_f$$

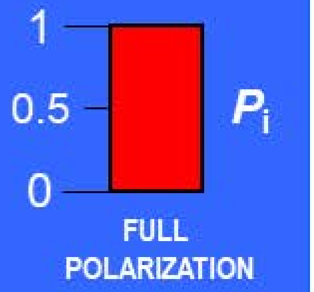
‘SPIN-ECHO’



ALL SPINS
ARE VERTICAL AGAIN:
POLARIZATION
IS BACK

INELASTIC SCATTERING

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



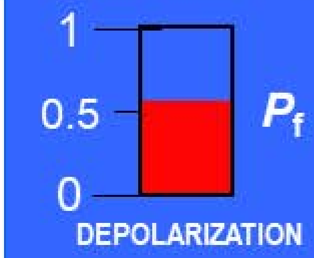
$$\xi_{tot} = \frac{\gamma B_1 L_1}{v_1} - \frac{\gamma B_2 L_2}{v_2}$$

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

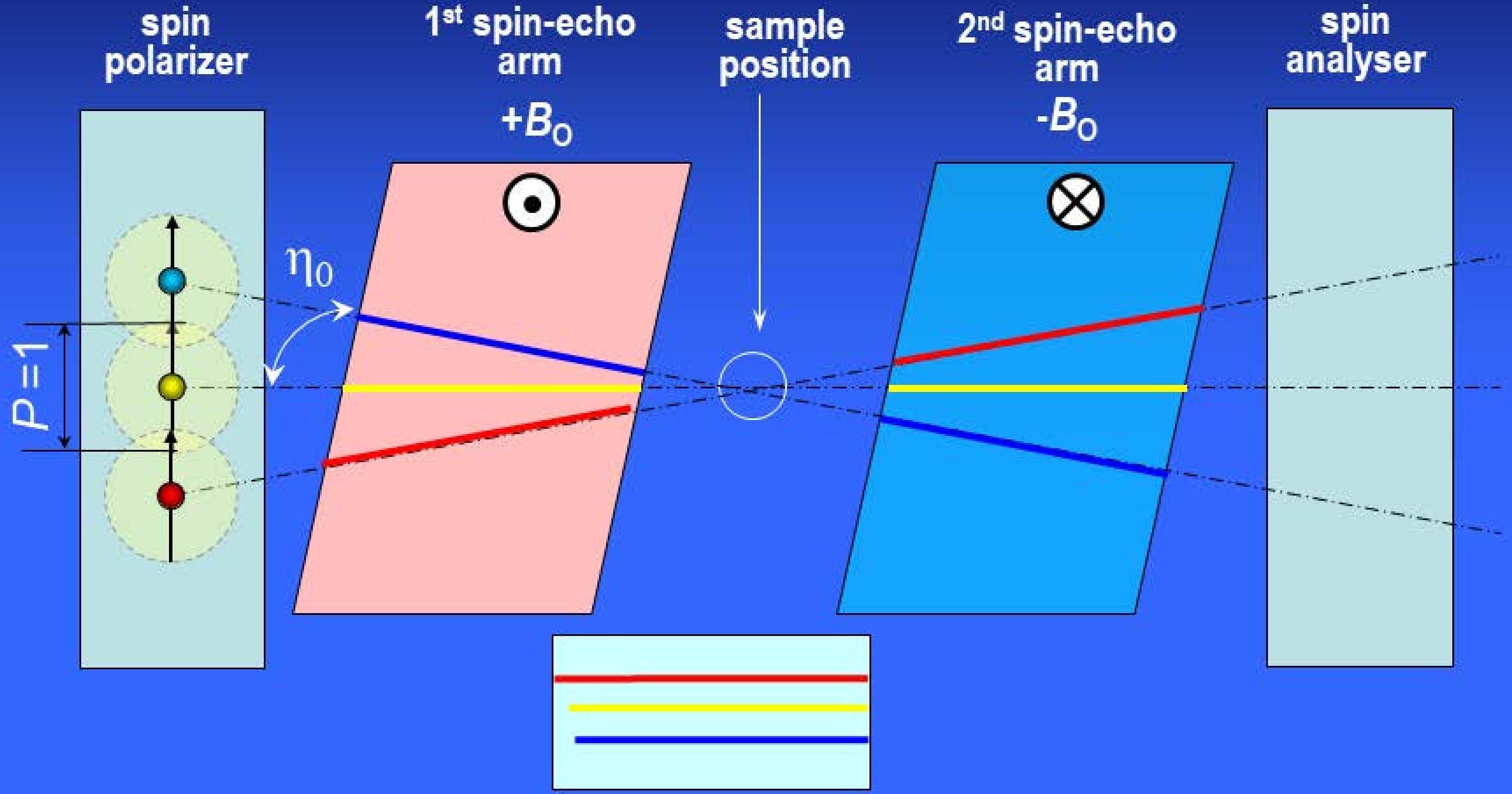
$$P = \langle \cos\xi \rangle = \frac{\int \cos\left(\frac{\gamma B L \hbar}{m v^3}\omega\right) S(q,\omega)\,\mathrm{d}\omega}{\int S(q,\omega)\,\mathrm{d}\omega} = S(q, t_{SE})$$

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

SPIN-ECHO (FOURIER) TIME

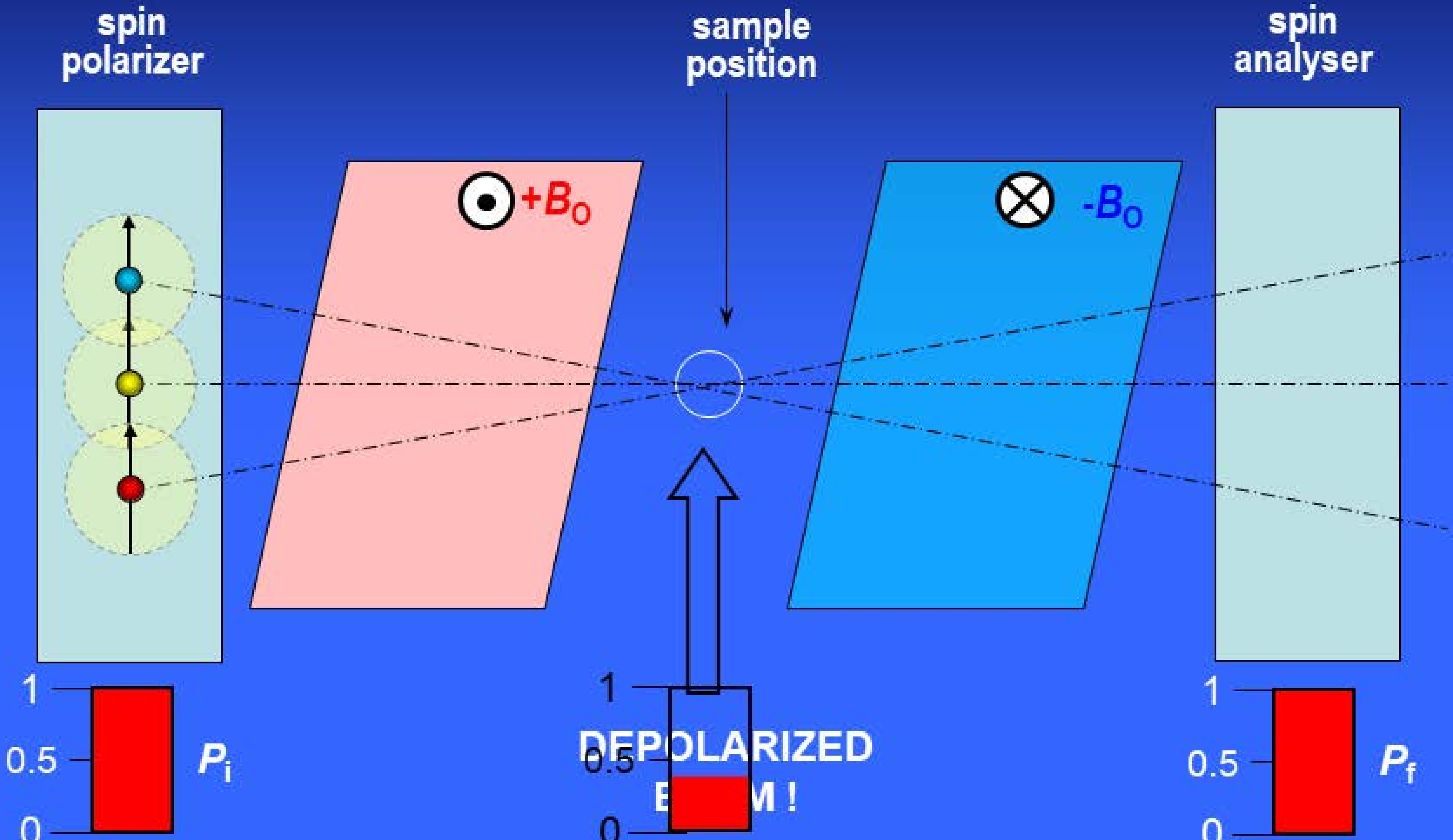


INCLINED BORDERS



DIFFERENT PATH LENGTHS FOR THE DIFFERENT TRAJECTORIES !

NO-SCATTERING CASE



spin polarizer

sample position

spin analyser

$+B_0$

$-B_0$

1

0.5

0

P_i

DEPOLARIZED BEAM !

P_f

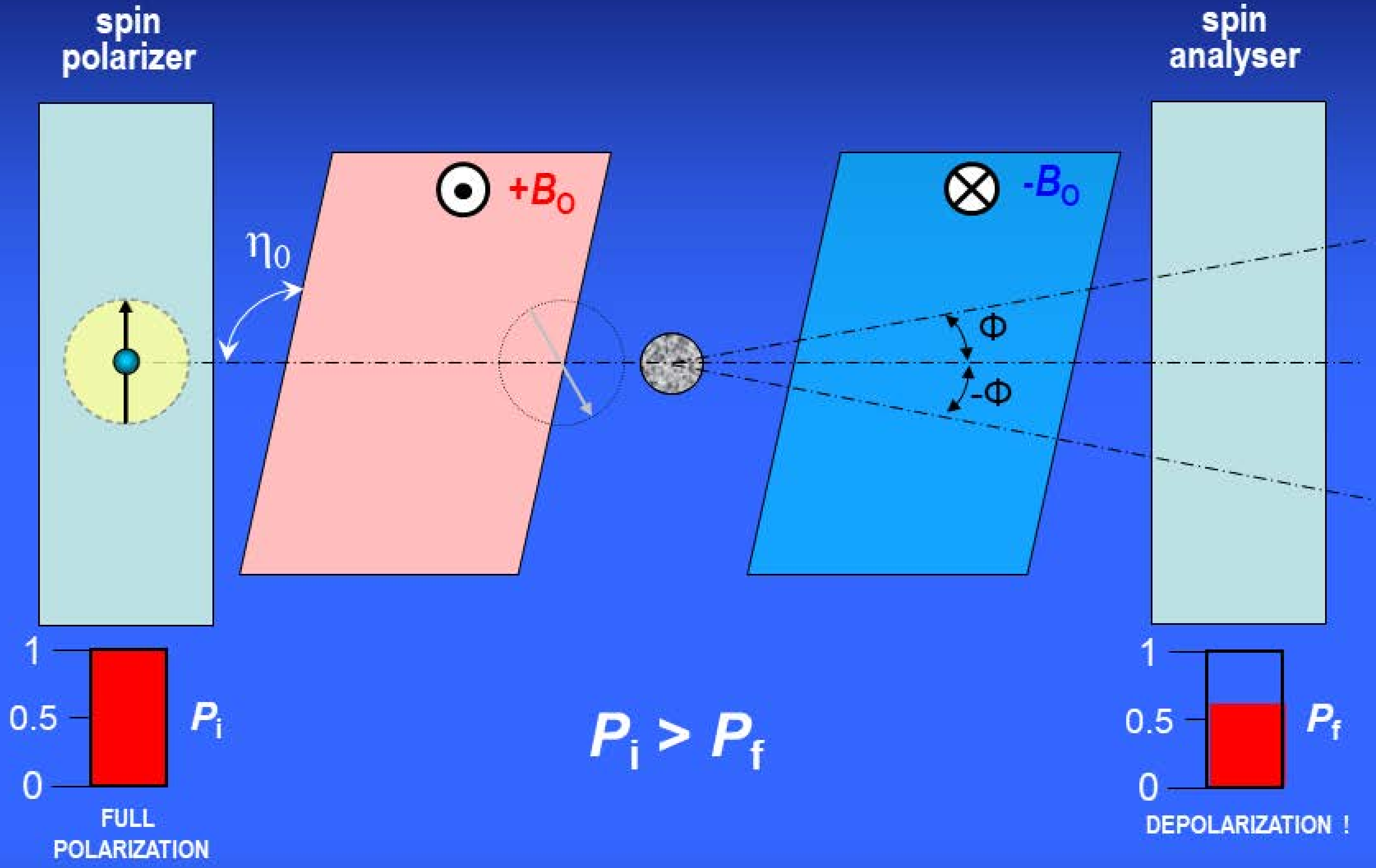
ALL SPINS
ARE PARALLEL:
FULL POLARIZATION

$P_i = P_f$

'SPIN-ECHO'

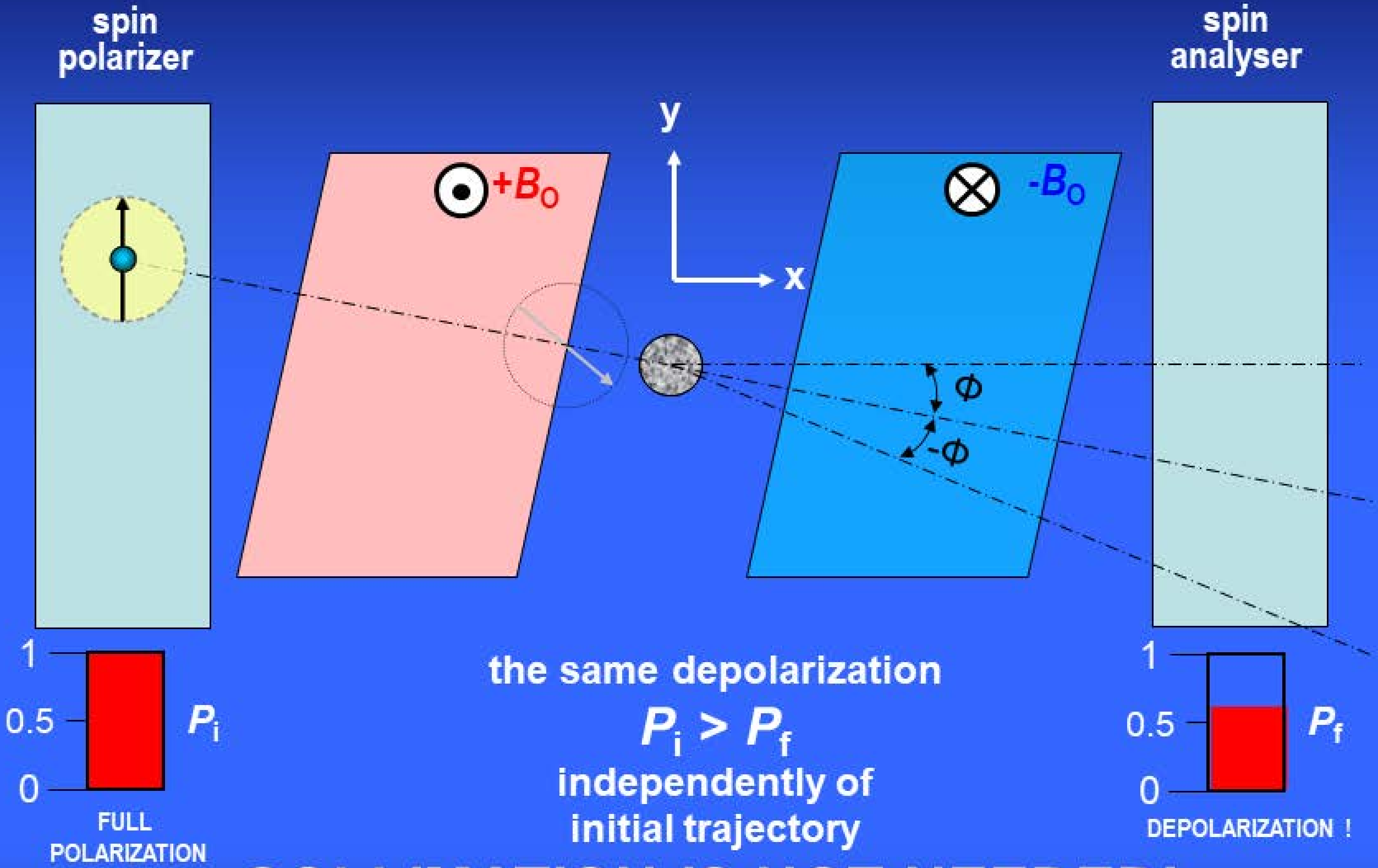
ALL SPINS
ARE PARALLEL AGAIN:
POLARIZATION
IS BACK

SCATTERING BY THE SAMPLE



$P_i > P_f$

SCATTERING BY THE SAMPLE



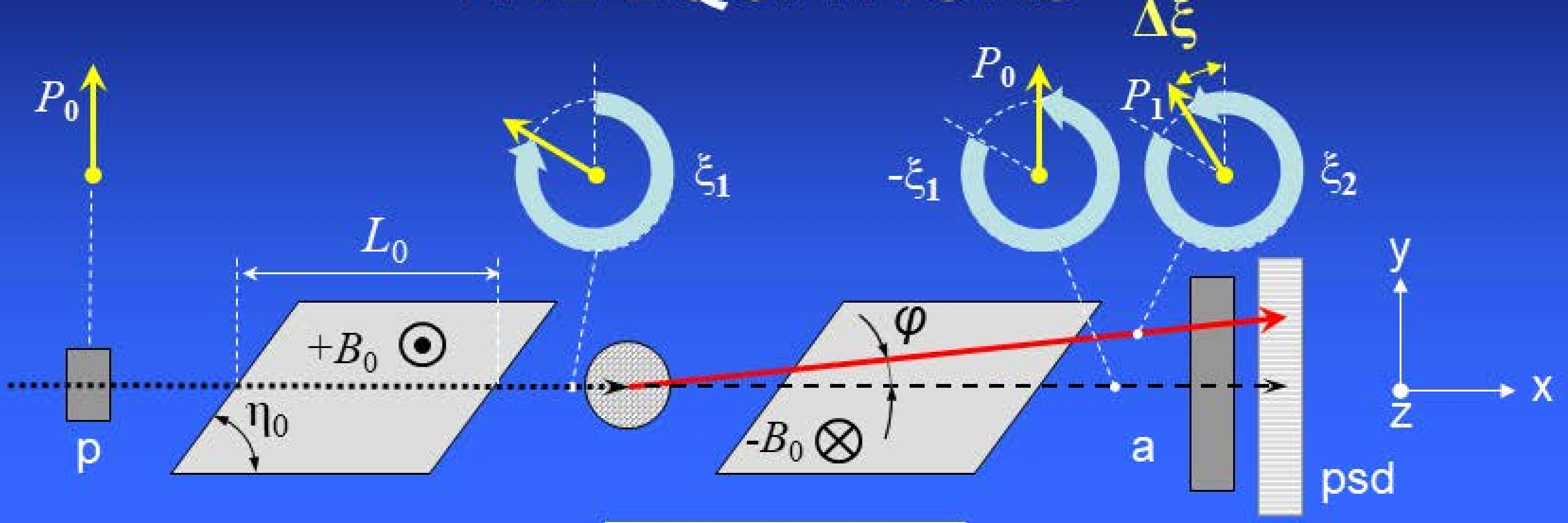
the same depolarization

$$P_i > P_f$$

independently of initial trajectory

COLLIMATION IS NOT NEEDED!

SPIN–ECHO ANGULAR ENCODING: THE EQUATIONS



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

$$\Delta\xi = \xi_1 - \xi_2 = 2\pi\gamma_{\mathrm{n}} B_0 \frac{L_0}{v}\left(1-\frac{1}{\cos\varphi+\sin\varphi\cot\eta_0}\right) \cong \left(2\pi\gamma_{\mathrm{n}}\frac{B_0L_0}{v}\cot\eta_0\right)\sin\varphi =$$

$$= \left(\frac{\gamma_{\mathrm{n}} B_0 L_0 \lambda^2}{K}\cot\eta_0\right)\left(\frac{2\pi}{\lambda}\sin\varphi\right) \equiv \delta_{\mathrm{y}}^{\mathrm{SE}} q_{\mathrm{y}}$$

SPIN-ECHO GIVES RESULTS IN REAL SPACE

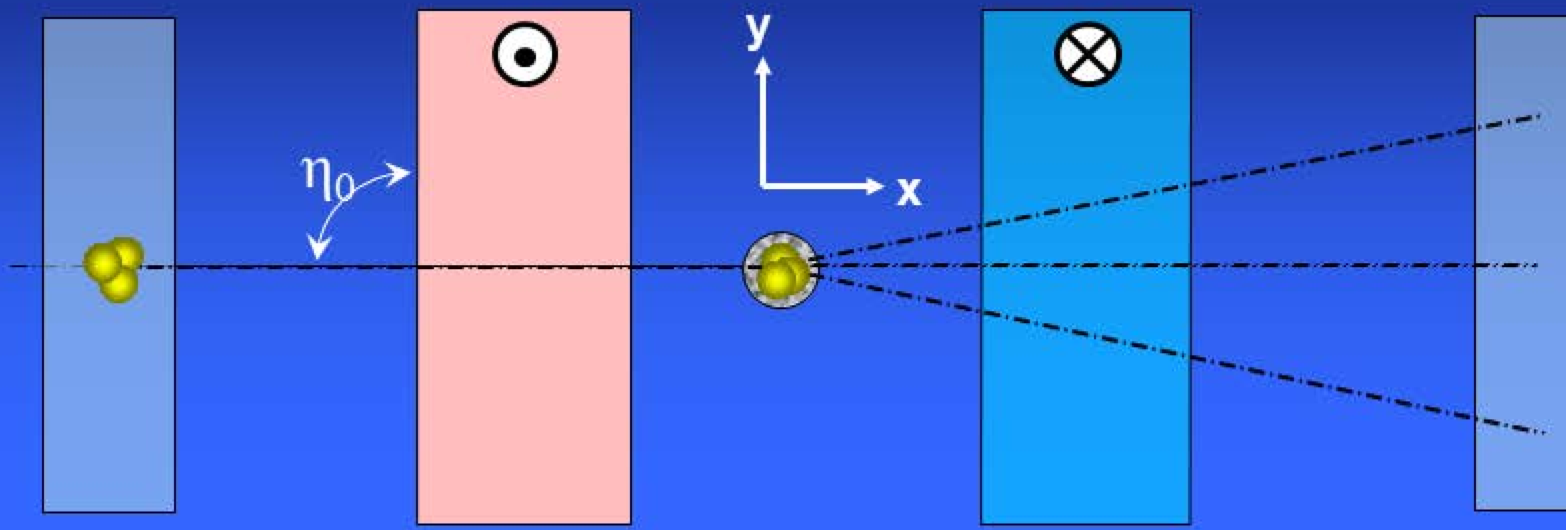
$$P_1 = P_0 \cos \Delta\xi \,.$$

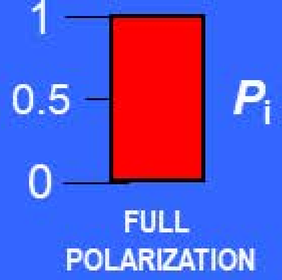
$$\frac{P_1}{P_0} = \langle \cos \Delta\xi \rangle \propto \frac{\int_{\mathrm{det}} \mathrm{d}q_{\mathrm{y}} \mathrm{d}q_{\mathrm{z}} S(\mathbf{q}) \cos(\delta_{\mathrm{y}}^{\mathrm{SE}} q_{\mathrm{y}})}{\int_{\mathrm{det}} \mathrm{d}q_{\mathrm{y}} \mathrm{d}q_{\mathrm{z}} S(\mathbf{q})} \underset{\uparrow}{=}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

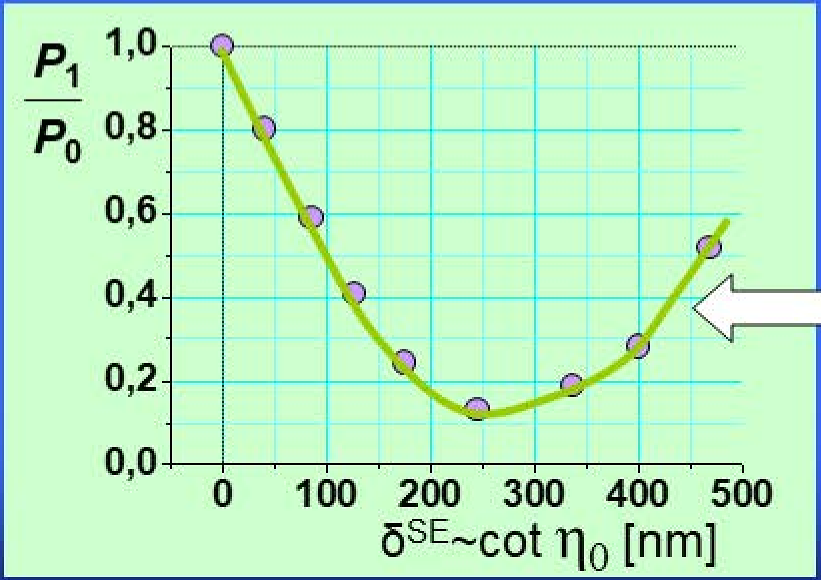
$q_z=0$

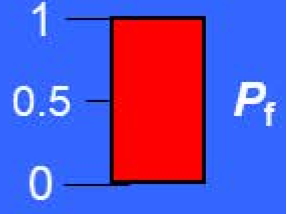
$$\Pi(\mathbf{R}) = \int \mathrm{d}\mathbf{r} \rho(\mathbf{r}) \rho(\mathbf{r} + \mathbf{R})$$

EXPERIMENT: SE length scan





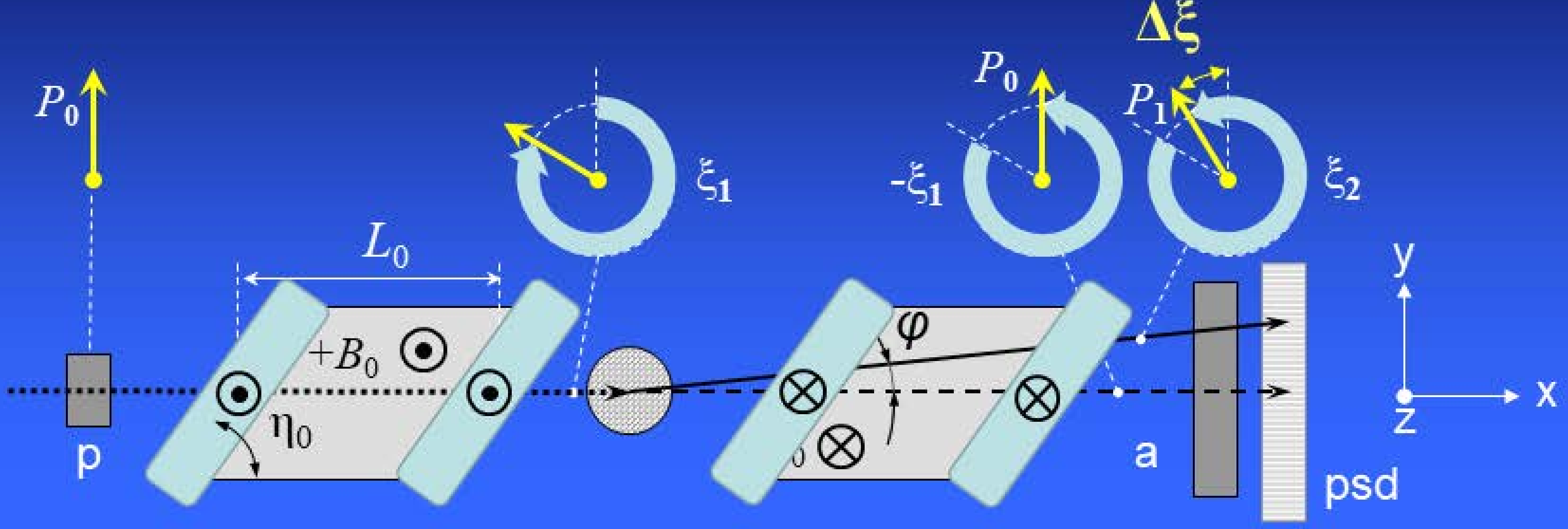




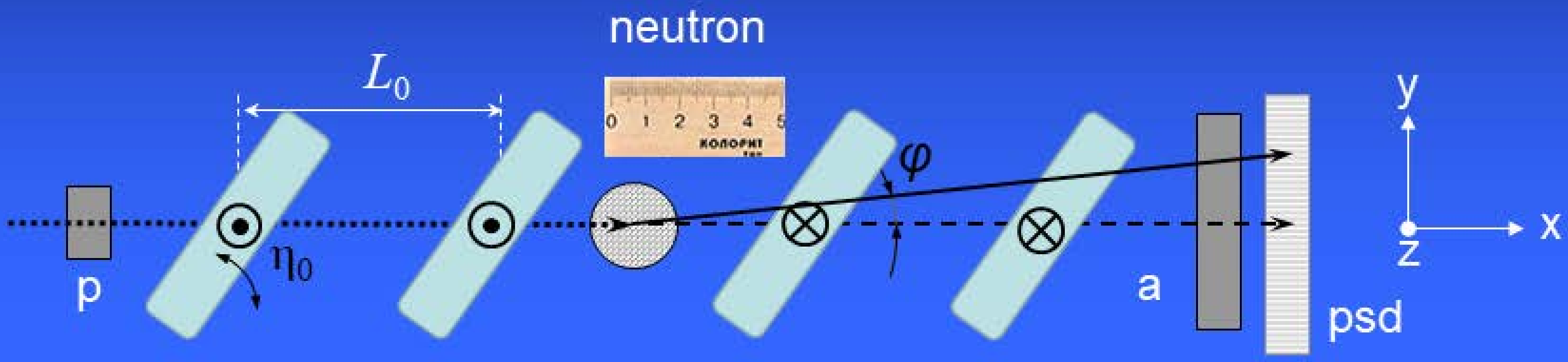
REAL-SPACE CORRELATION FUNCTION

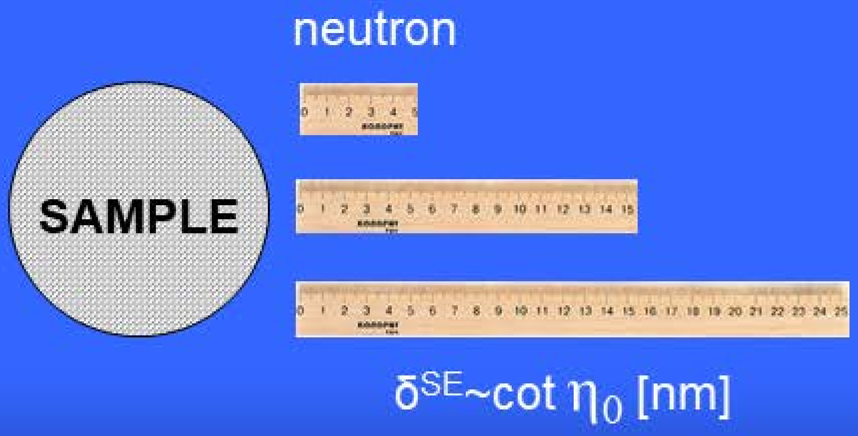
$$\left(\frac{\gamma_n B_0 L_0 \lambda^2}{K}\cot\eta_0\right)$$

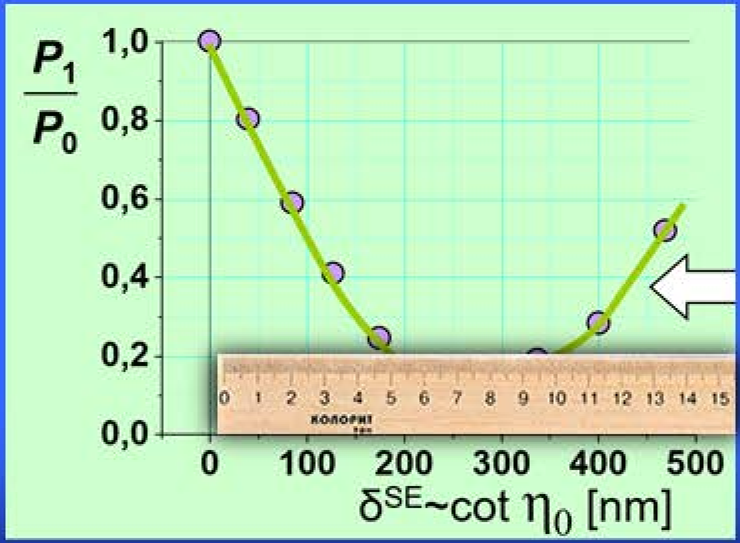
SPIN–ECHO ANGULAR ENCODING



SPIN-ECHO ANGULAR ENCODING:

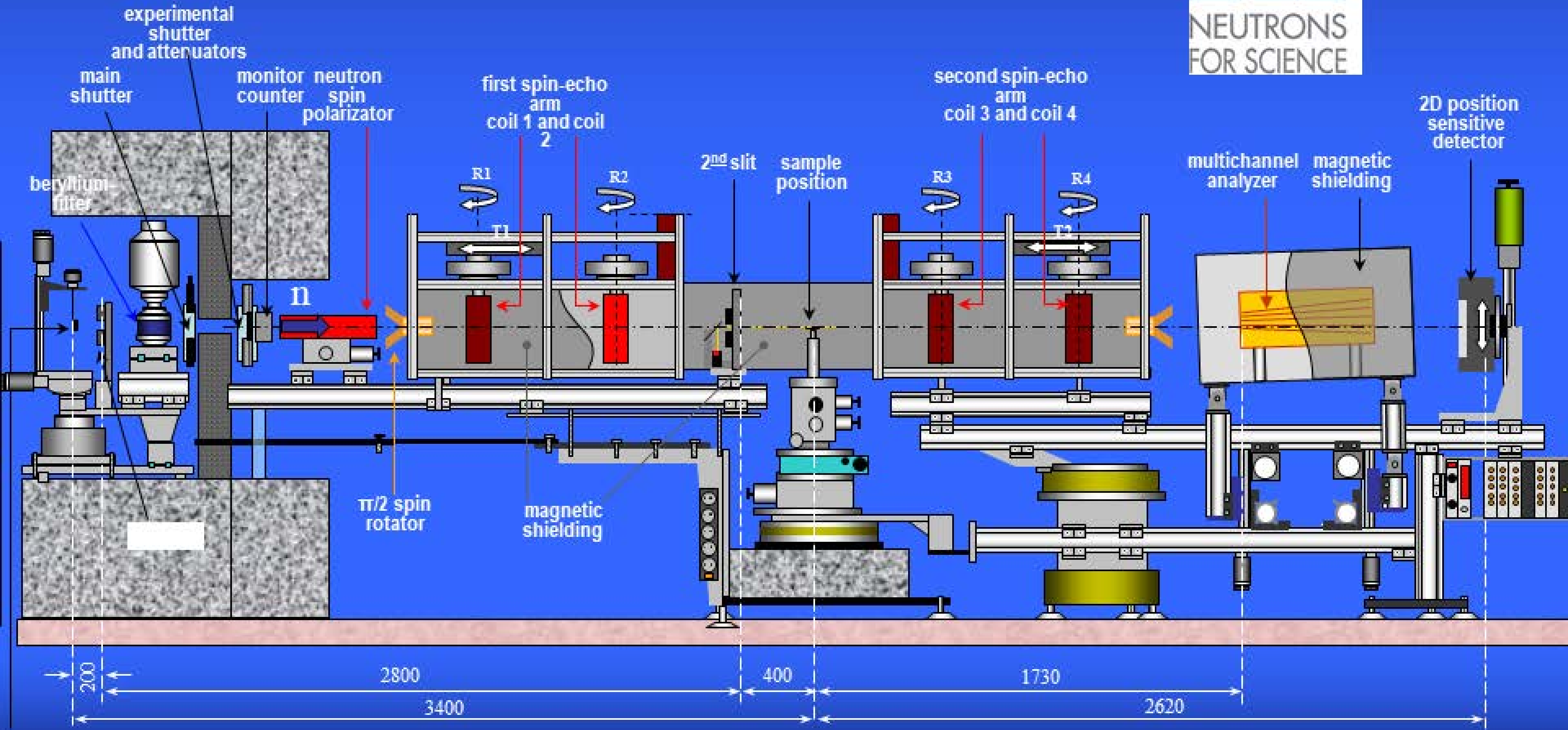






EVA REFLECTOMETER TRANSFORMED INTO A SERGIS PROTOTYPE INSTRUMENT

NEUTRONS FOR SCIENCE



experimental shutter and attenuators

main shutter

beryllium-filter

monitor counter

neutron spin polarizator

first spin-echo arm coil 1 and coil 2

2nd slit

sample position

second spin-echo arm coil 3 and coil 4

multichannel analyzer

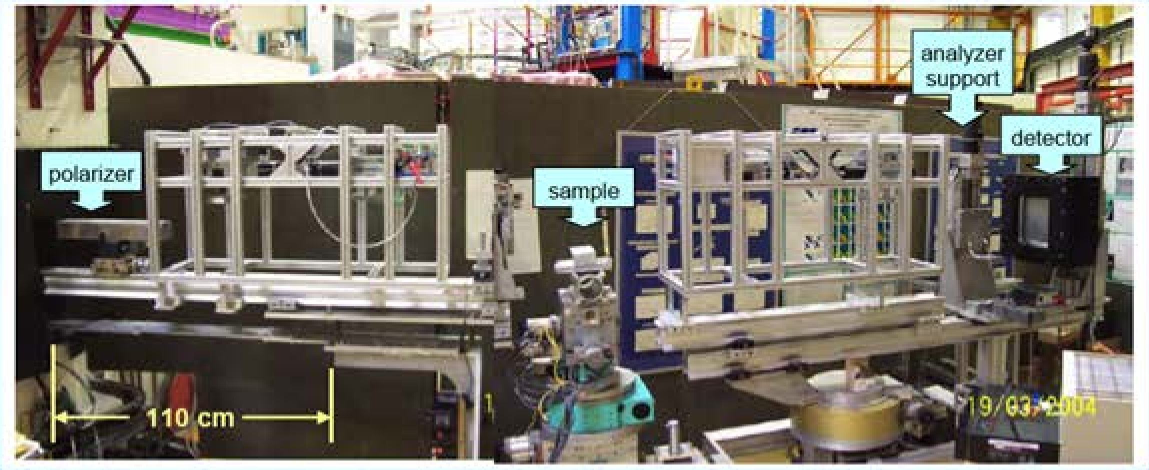
magnetic shielding

2D position sensitive detector

π/2 spin rotator

magnetic shielding

EVA DURING THE TRANSFORMATION TO SERGIS



Beam size 50x5mm

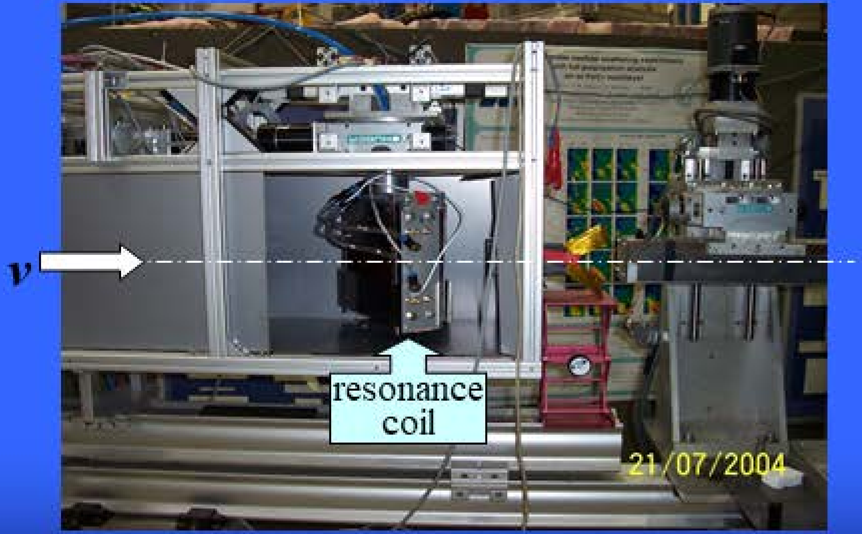
Wave numbers covered:

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

Max. SE time in classical

configuration (η_0=0) 0.07ns

Max. SE length



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

4500 Å

λ (neutron wavelength) 5.5 Å

ν (neutron velocity) 720 m/s

Θ (tilt of precession coil) 50°

B (magnetic field in leg) 310G

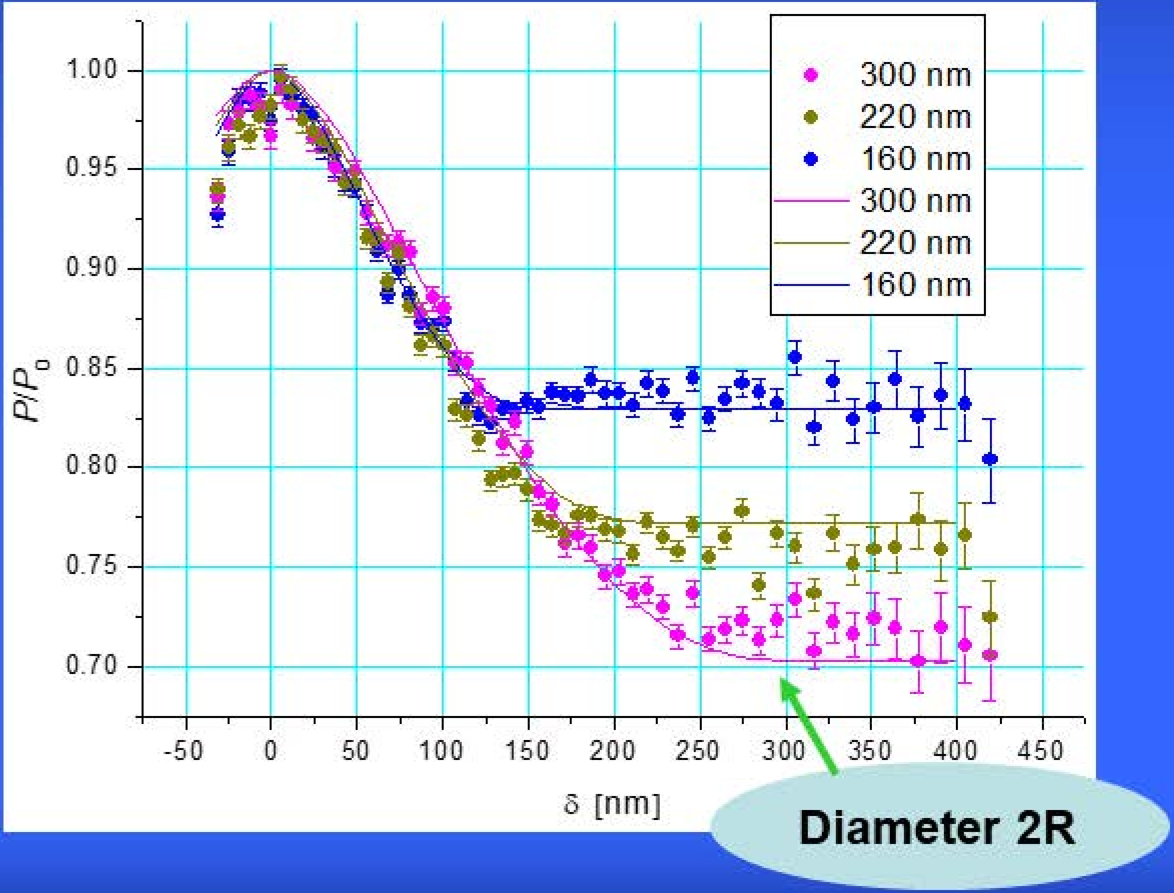
d (length of precession leg) 50 cm

EVA reflectometer transformed into a SERGIS prototype instrument

Test SESANS experiments: polystyrene spheres

2.5% polystyrene balls in 3:1 D_2O/H_2O

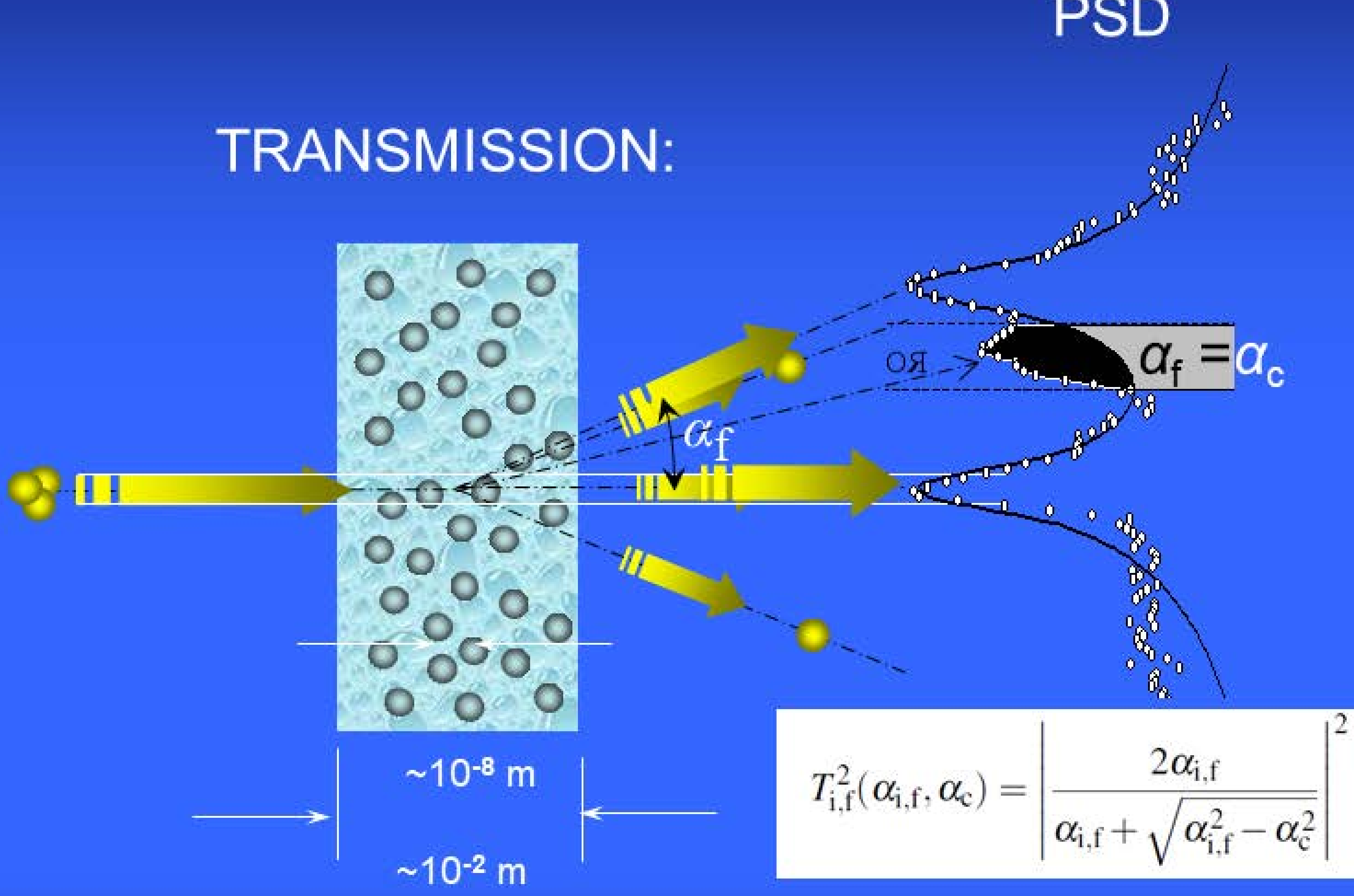
2mm thick cell



Diameter 2R

GRAZING INCIDENCE

TRANSMISSION:



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

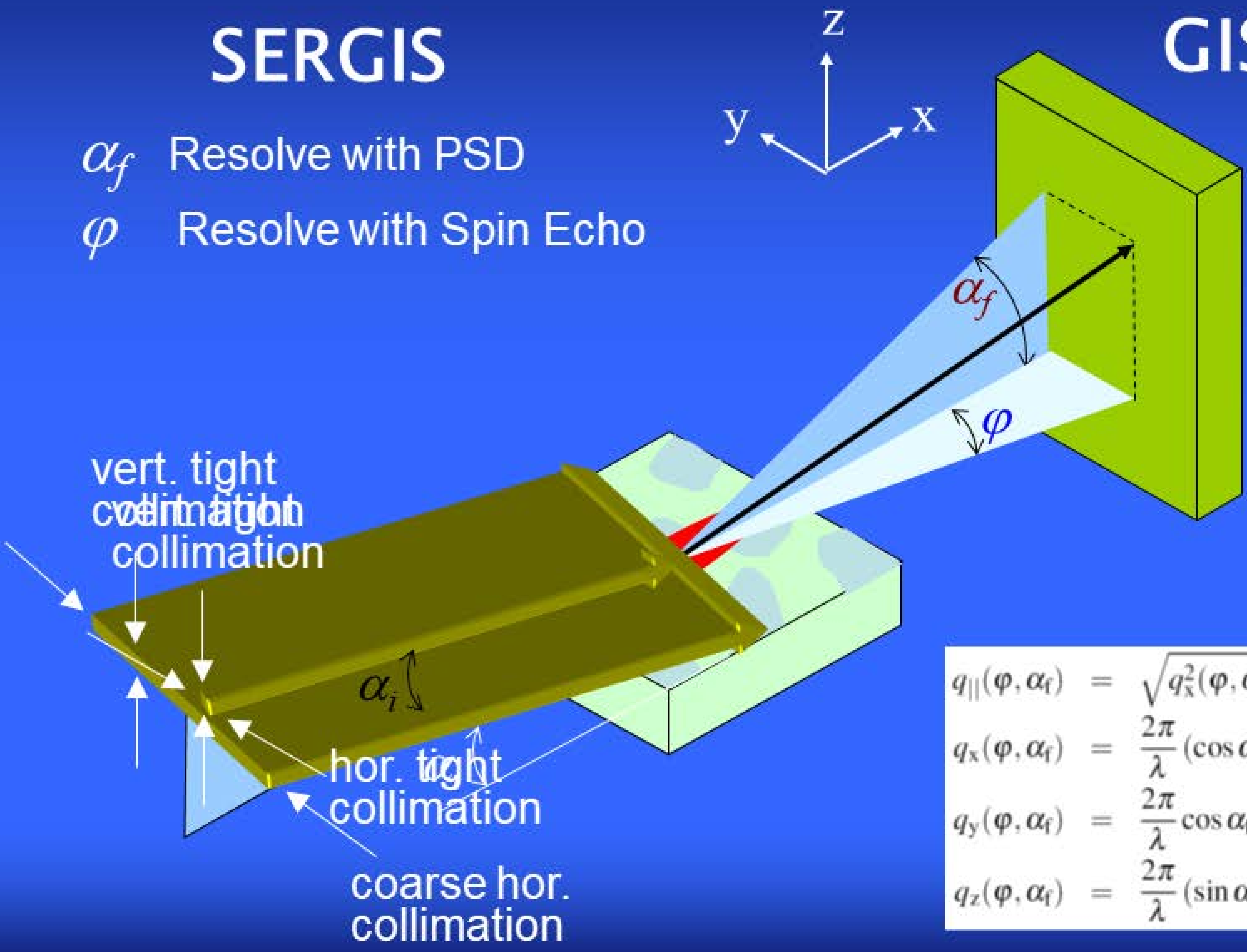
SERGIS vs. GISANS

SERGIS

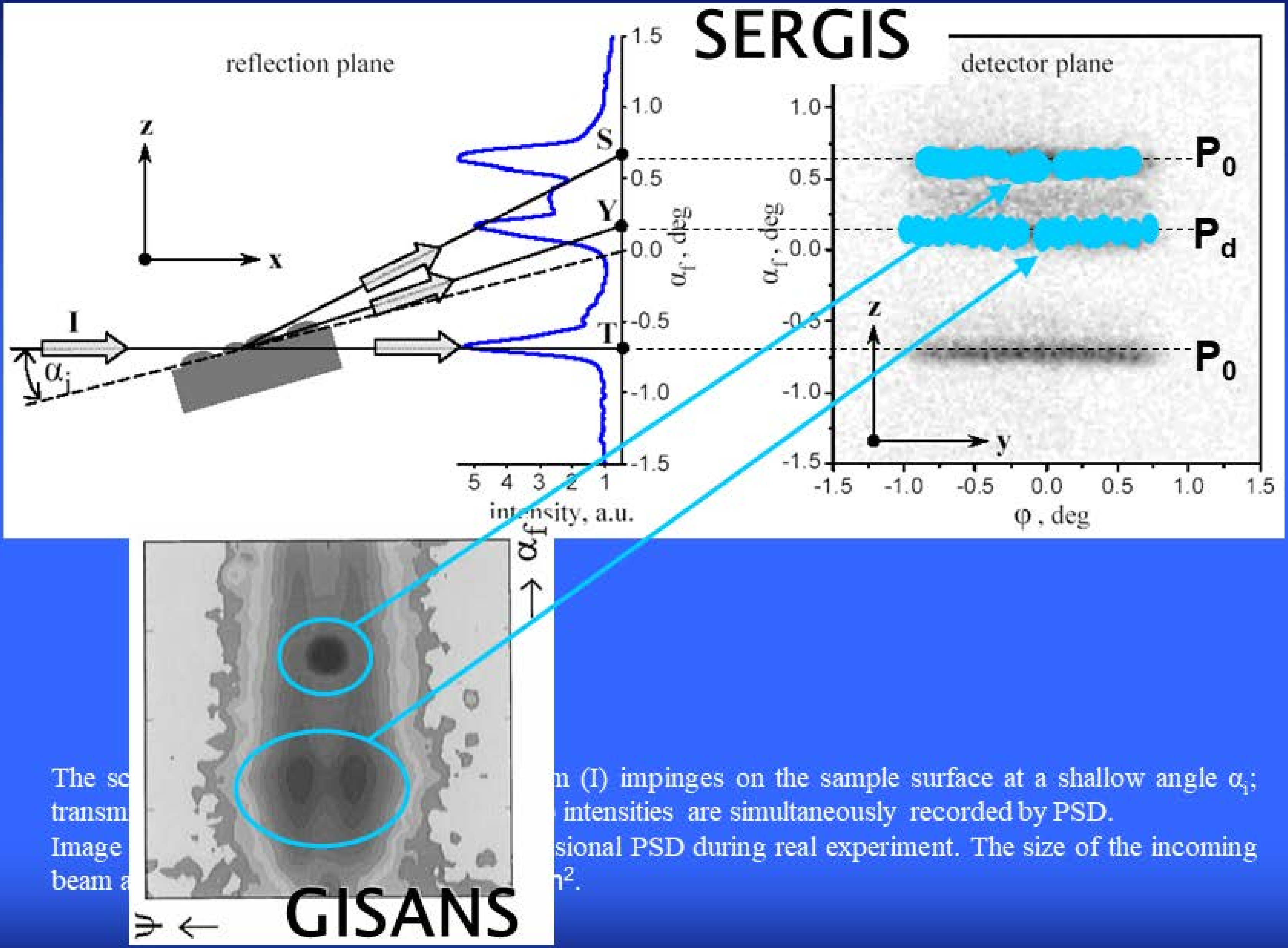
α_f Resolve with PSD

φ Resolve with Spin Echo

GISANS

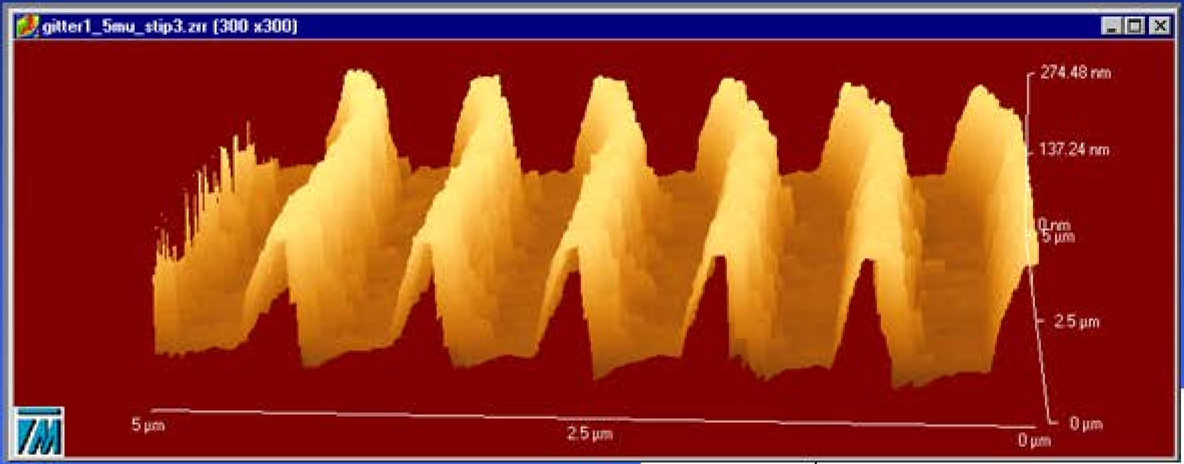


$$
\begin{aligned}
q_{||}(\varphi,\alpha_f) &= \sqrt{q_x^2(\varphi,\alpha_f)+q_y^2(\varphi,\alpha_f)}\\
q_x(\varphi,\alpha_f) &= \frac{2\pi}{\lambda}(\cos\alpha_f\cos\varphi-\cos\alpha_i)\\
q_y(\varphi,\alpha_f) &= \frac{2\pi}{\lambda}\cos\alpha_f\sin\varphi\\
q_z(\varphi,\alpha_f) &= \frac{2\pi}{\lambda}(\sin\alpha_f+\sin\alpha_i)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

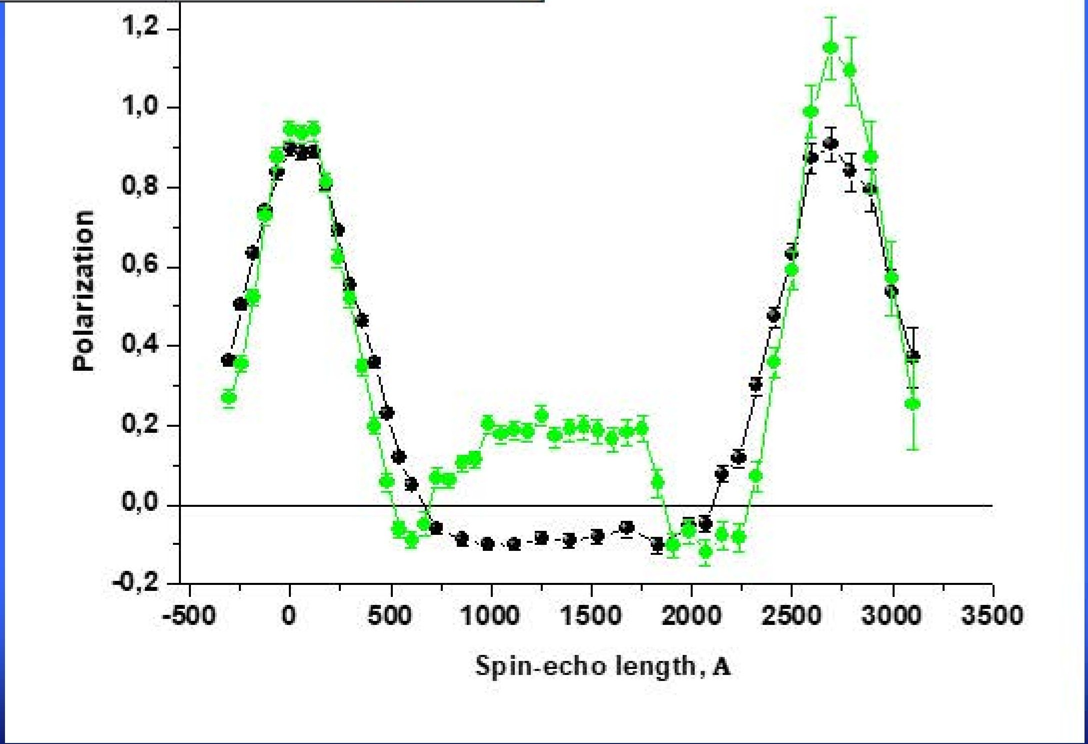


The sc m (I) impinges on the sample surface at a shallow angle α_i; transm intensities are simultaneously recorded by PSD.
Image sional PSD during real experiment. The size of the incoming beam a ^{2}.

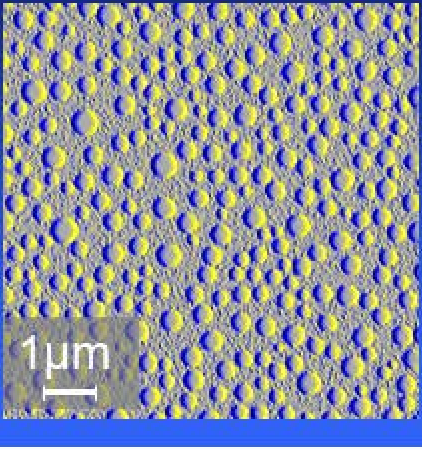
OPTICAL DIFFRACTION GRATING



3600/mm
2780 Å period

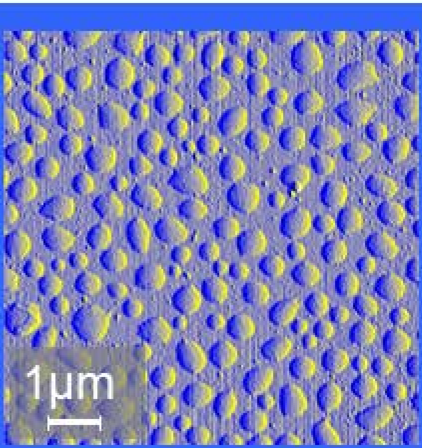


SAMPLES: DEWETED POLYMER FILMS



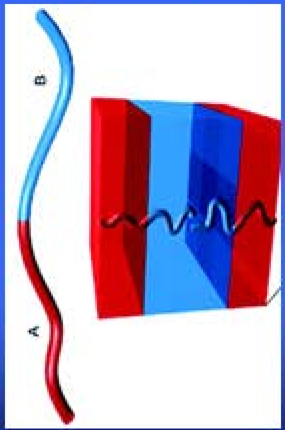
polymer blend

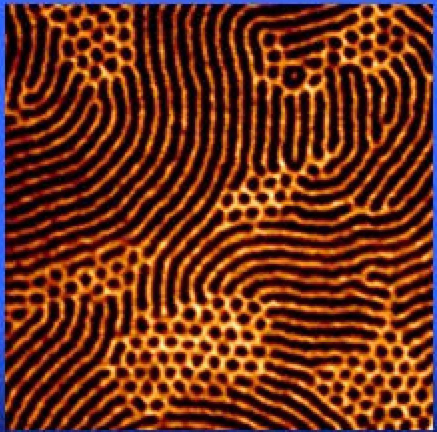
PpMS:dPS = 3:2
polyparamethylstyrene
d-polystyrene



diblock copolymer

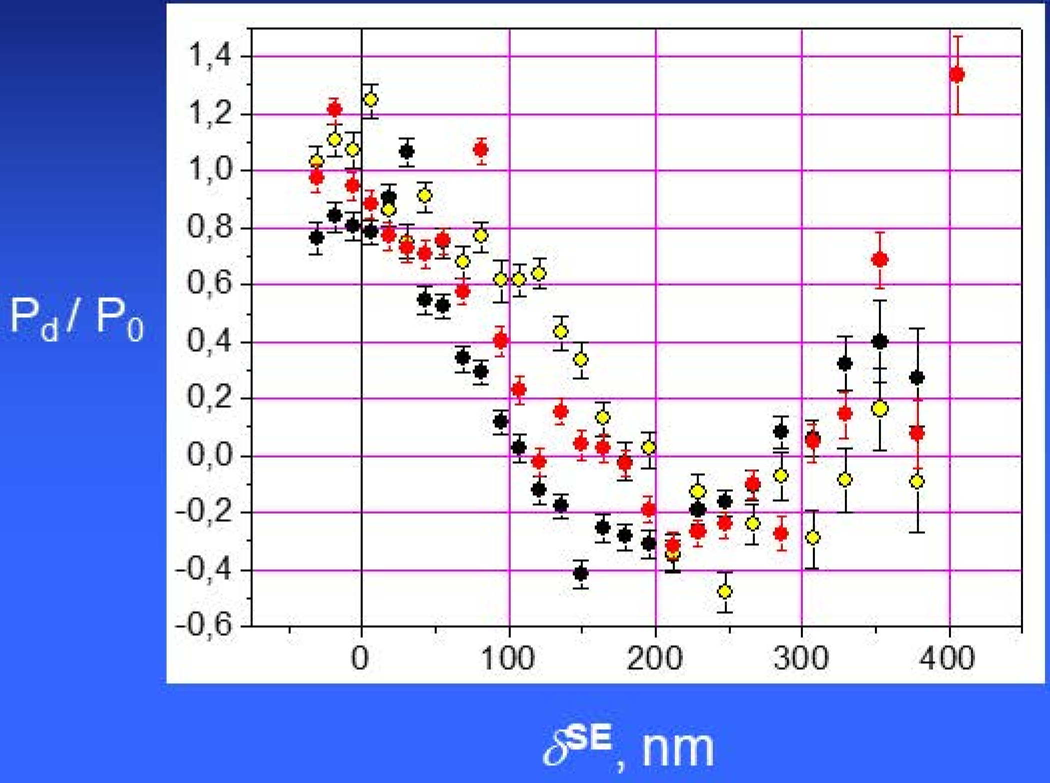
poly(styren-block-paramethylstyrene)
P(S-b-pMS)





regular lamellar phase separation

SERGIS EXPERIMENTAL DATA



- ● **HOMOPOLYMER** pancake-type droplets
- ● **BLEND** pancake-type droplets
- ○ **DIBLOCK** 'spherical' droplets

DATA ANALYSIS via MODELING

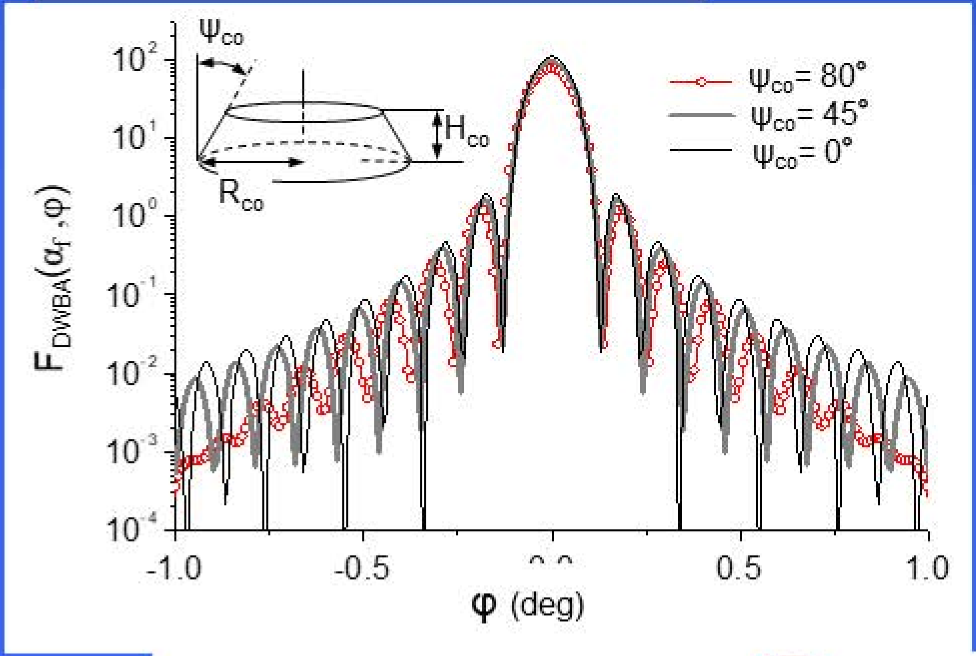
$$\frac{P_1}{P_0} = \langle \cos \Delta\xi \rangle \propto \frac{\int_{\mathrm{det}} \mathrm{d}q_y \mathrm{d}q_z S(\mathbf{q}) \cos(\delta_y^{\mathrm{SE}} q_y)}{\int_{\mathrm{det}} \mathrm{d}q_y \mathrm{d}q_z S(\mathbf{q})}$$

CONE FORM FACTOR IN THE CASE OF PANCAKE-LIKE OBJECTS

$$F_{\mathrm{co}}(\varphi,\alpha_{\mathrm{f}}) = \int_0^{H_{\mathrm{co}}} Z_{\mathrm{r}}^2(z,\psi_{\mathrm{co}}) \frac{J_1\left(q_{||}(\varphi,\alpha_{\mathrm{f}})\cdot Z_{\mathrm{r}}(z,\psi_{\mathrm{co}}\right)}{q_{||}(\varphi,\alpha_{\mathrm{f}})\cdot Z_{\mathrm{r}}(z,\psi_{\mathrm{co}})})\exp\left(\frac{\mathrm{i}}{2}q_{\mathrm{z}}(\varphi,\alpha_{\mathrm{f}})z\right)$$

$$Z_{\mathrm{r}}(z,\psi_{\mathrm{co}}) = R_{\mathrm{co}} - z/\cot\psi_{\mathrm{co}}$$

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



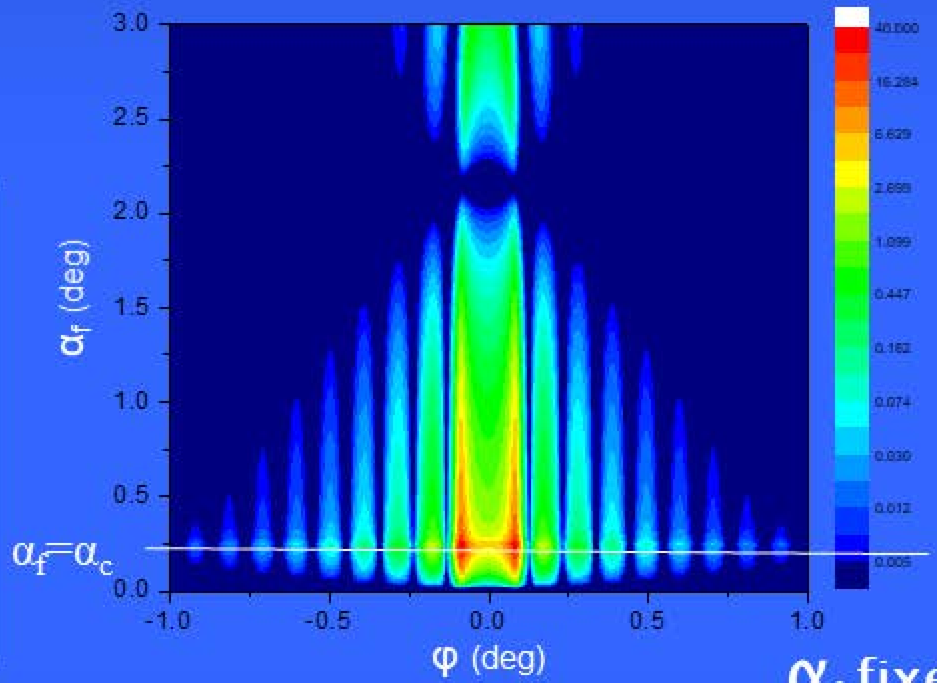
$\psi_{\mathrm{co}} = 0°$ **cylinder**

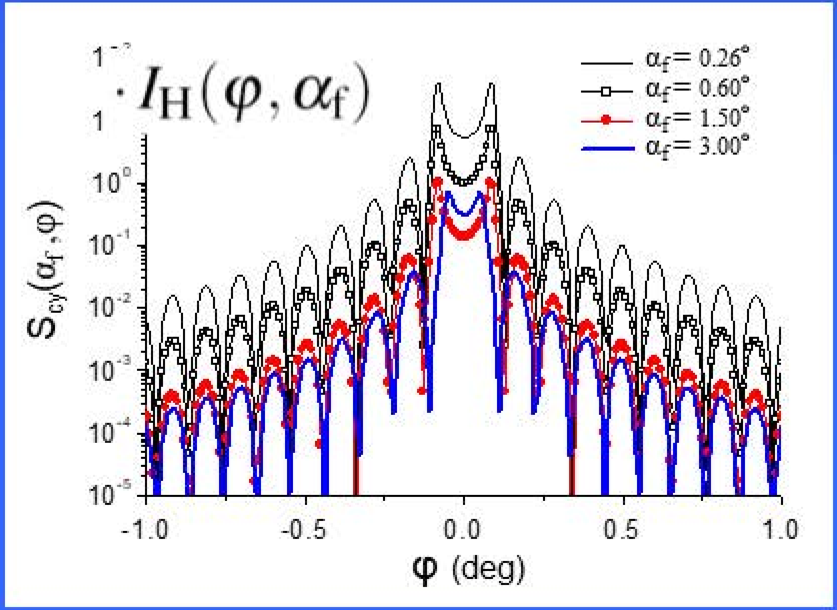
$$|F_{\mathrm{cy}}(\varphi,\alpha_{\mathrm{f}})| = \frac{J_1\left(q_{||}(\varphi,\alpha_{\mathrm{f}})\boxed{R}\right)}{q_{||}(\varphi,\alpha_{\mathrm{f}})R}\frac{\sin\left(q_{\mathrm{z}}(\varphi,\alpha_{\mathrm{f}})\boxed{H}/2\right)}{q_{\mathrm{z}}(\varphi,\alpha_{\mathrm{f}})H/2}$$

CYLINDER FORM FACTOR AS SEEN IN THE 2d DETECTOR

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

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





α_i fixed

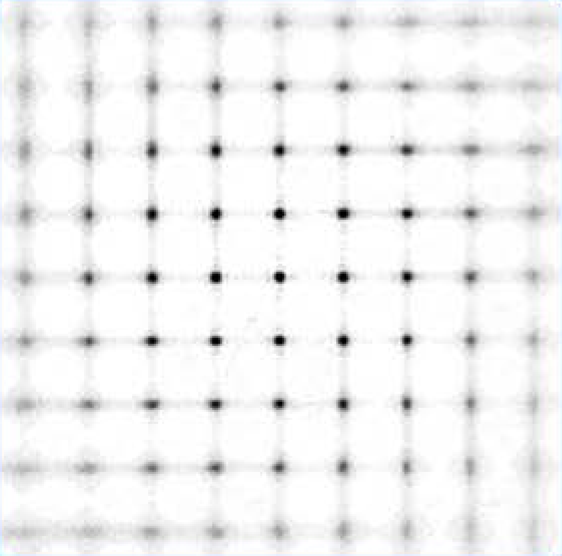
$\alpha_f = \alpha_c$ fixed

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



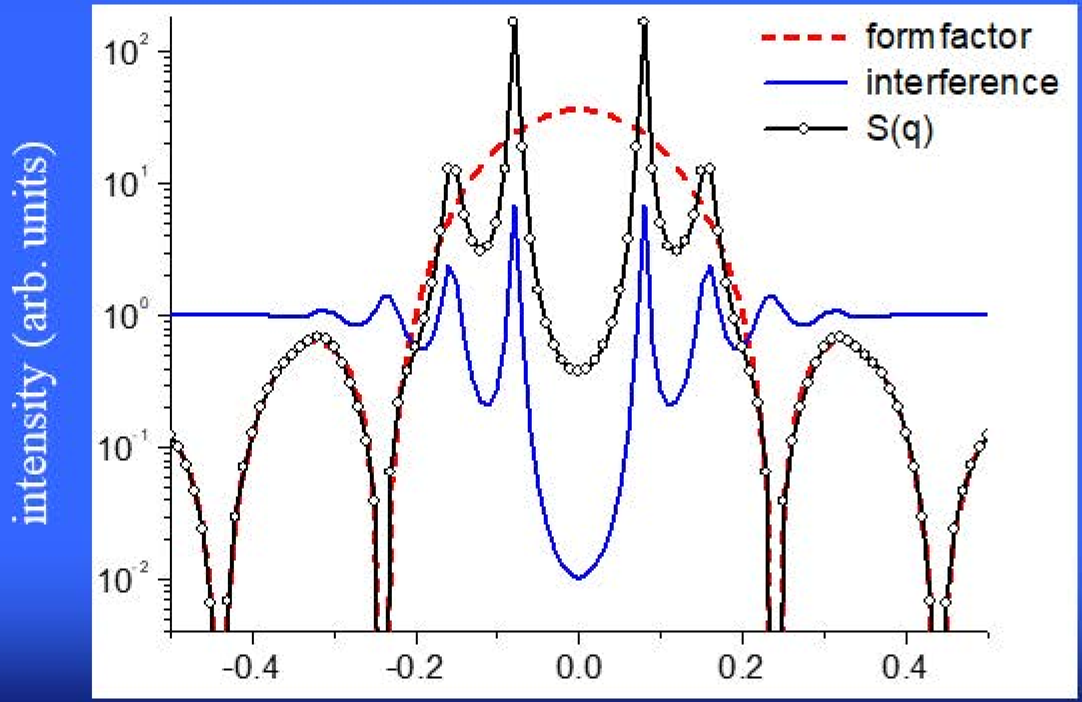
Hosemann, R.; Bagchi, S. N. *Direct Analysis of Diffraction by Matter* (North-Holland Publishing Company: Amsterdam, 1962).

SCATTERING INTENSITY DISTRIBUTION

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

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

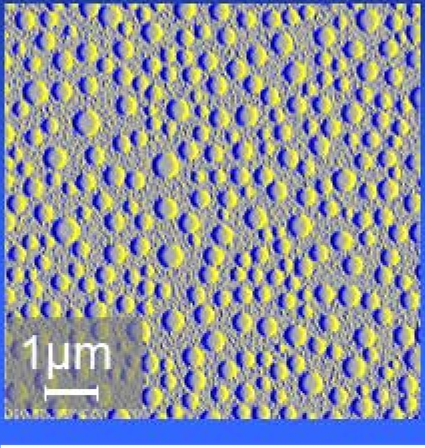
$$I_{\mathrm{H}}(\varphi, \alpha_{\mathrm{f}}) = \frac{1 - \mathrm{e}^{-q_{||}(\varphi, \alpha_{\mathrm{f}}) \sigma^2}}{1 + \mathrm{e}^{-q_{||}(\varphi, \alpha_{\mathrm{f}}) \sigma^2} - 2\mathrm{e}^{-\frac{1}{2} q_{||}(\varphi, \alpha_{\mathrm{f}}) \sigma^2} \cos\left(D q_{||}(\varphi, \alpha_{\mathrm{f}})\right)}$$

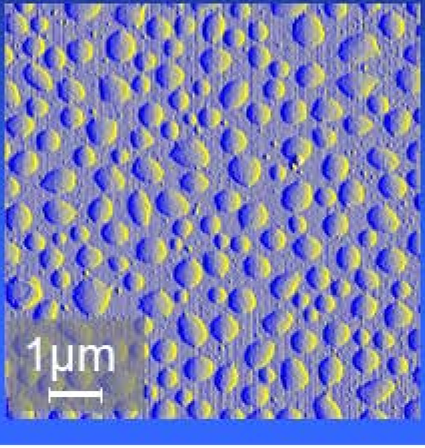


COMPLIMENTARY DATA – AFM

polymer blend

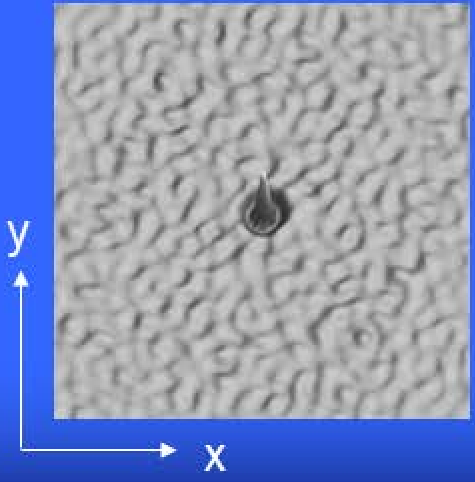
diblock copolymer

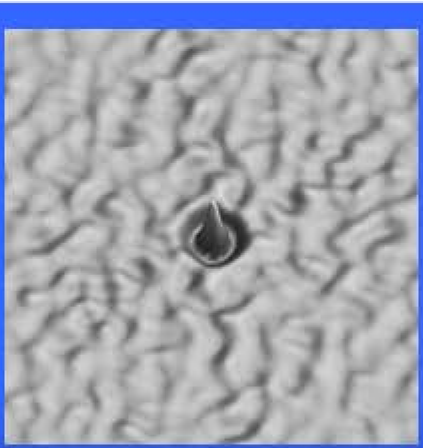




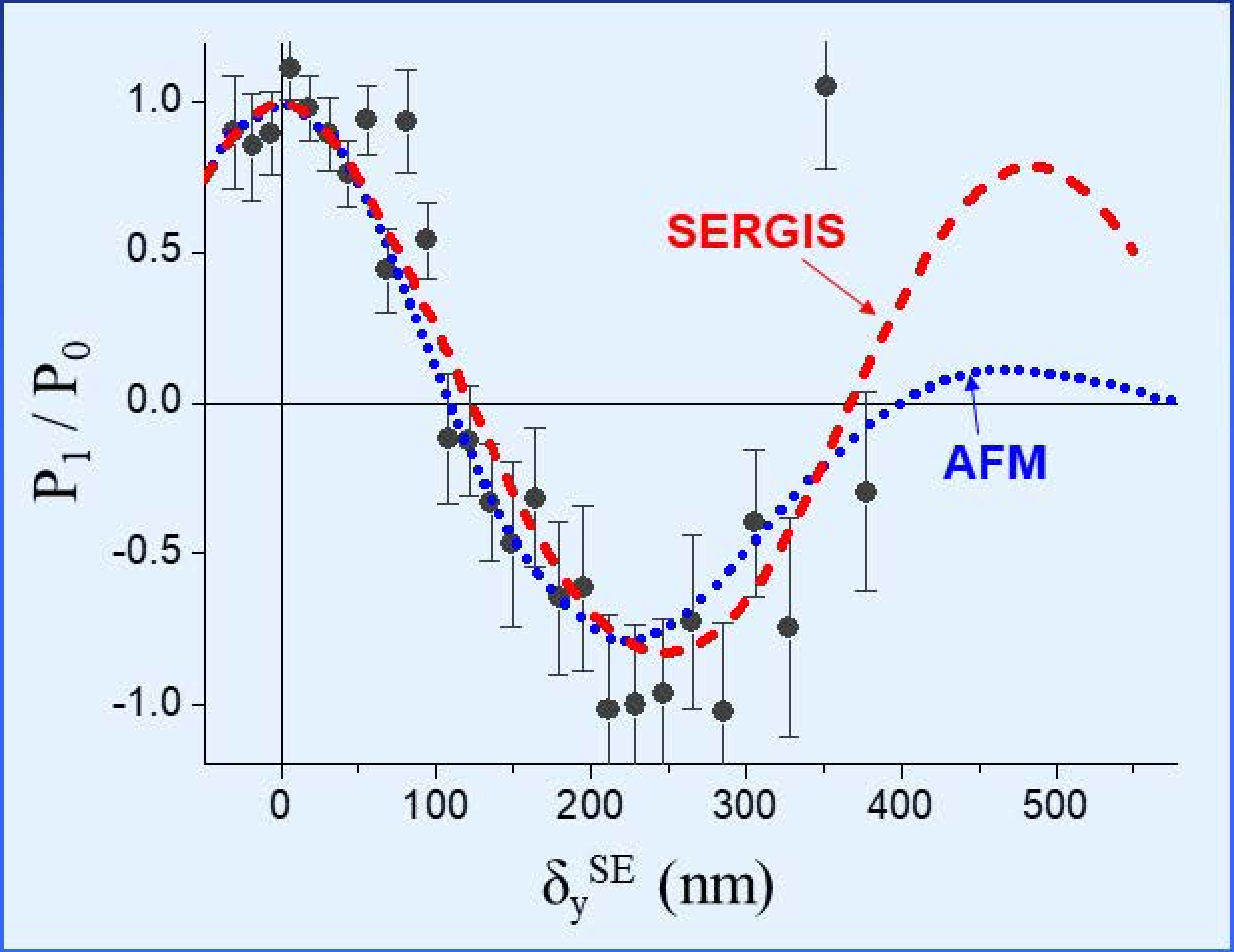
ACF

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





POLYMER BLEND

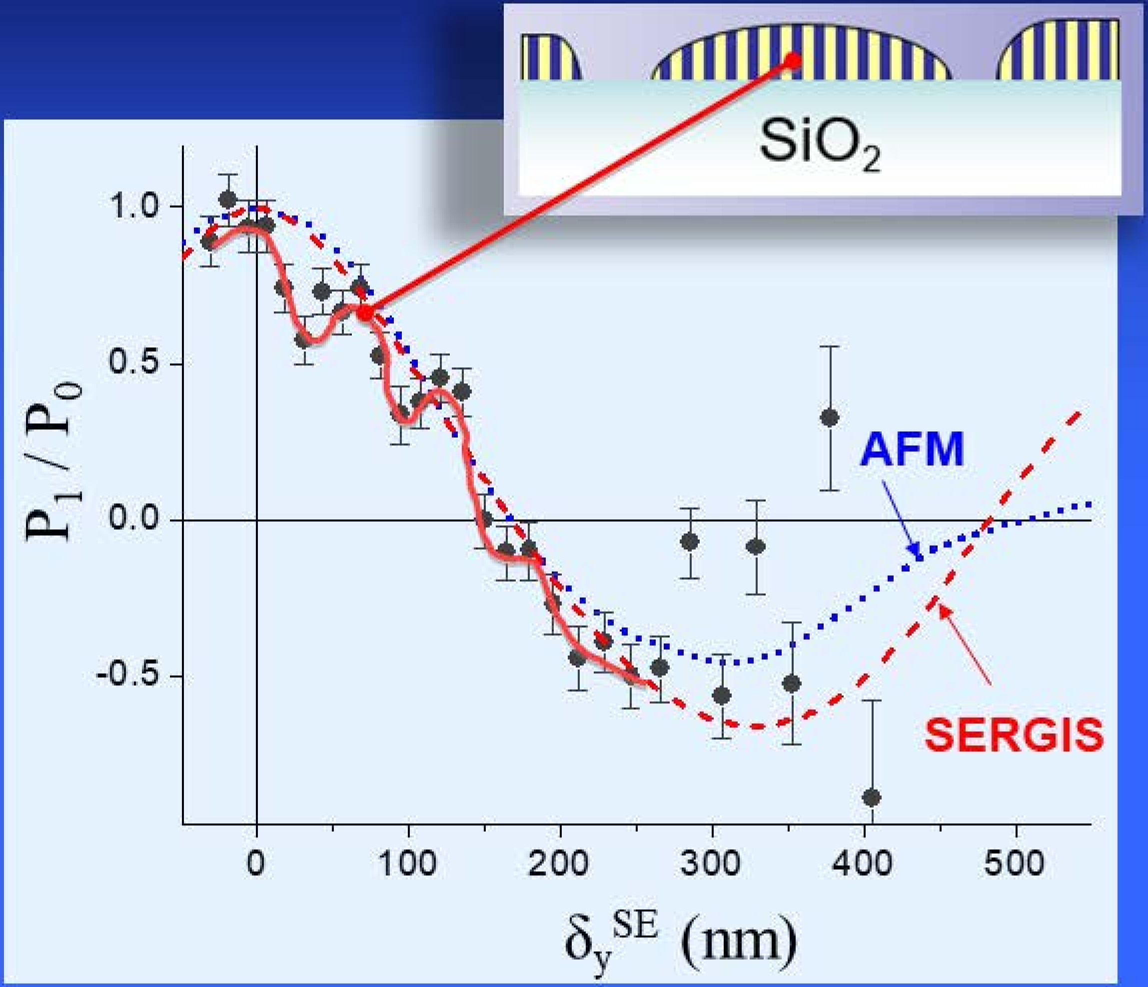


SERGIS model:
R=170 nm
H=20 nm
D=480 nm
σ= 50 nm

AFM:
D=450 nm

GISANS/GISAXS:
D=500 nm

DIBLOCK COPOLYMER



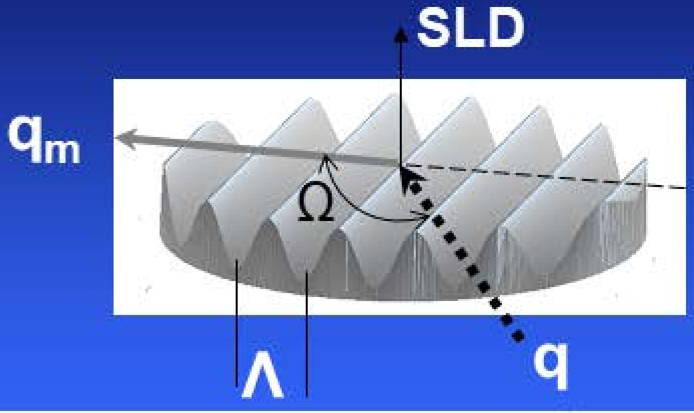
SERGIS model:
R=230 nm
H=10 nm
D=600 nm
$\sigma / D = 0.17$

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

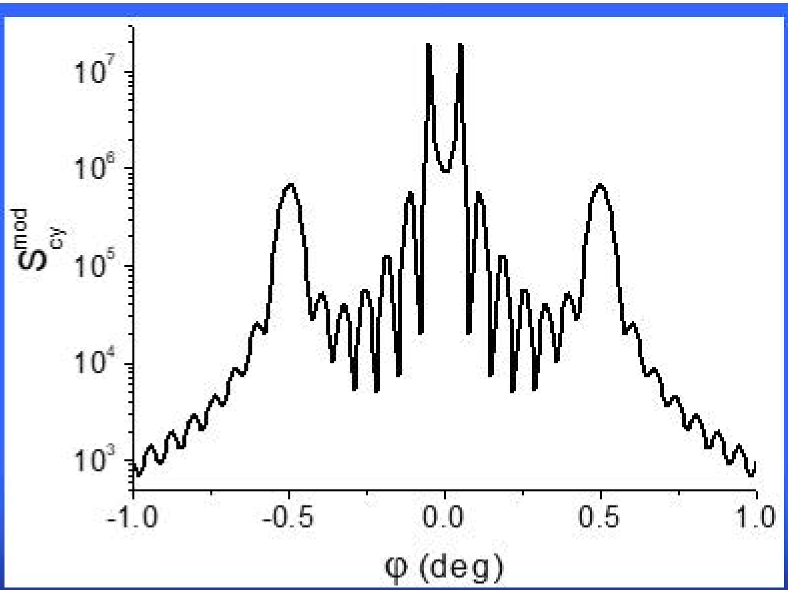
$$f_m(\mathbf{r}) = \overline{\rho} + \frac{\Delta\rho}{2}\cos(\mathbf{q}_m \cdot \mathbf{r})$$

mean SLD

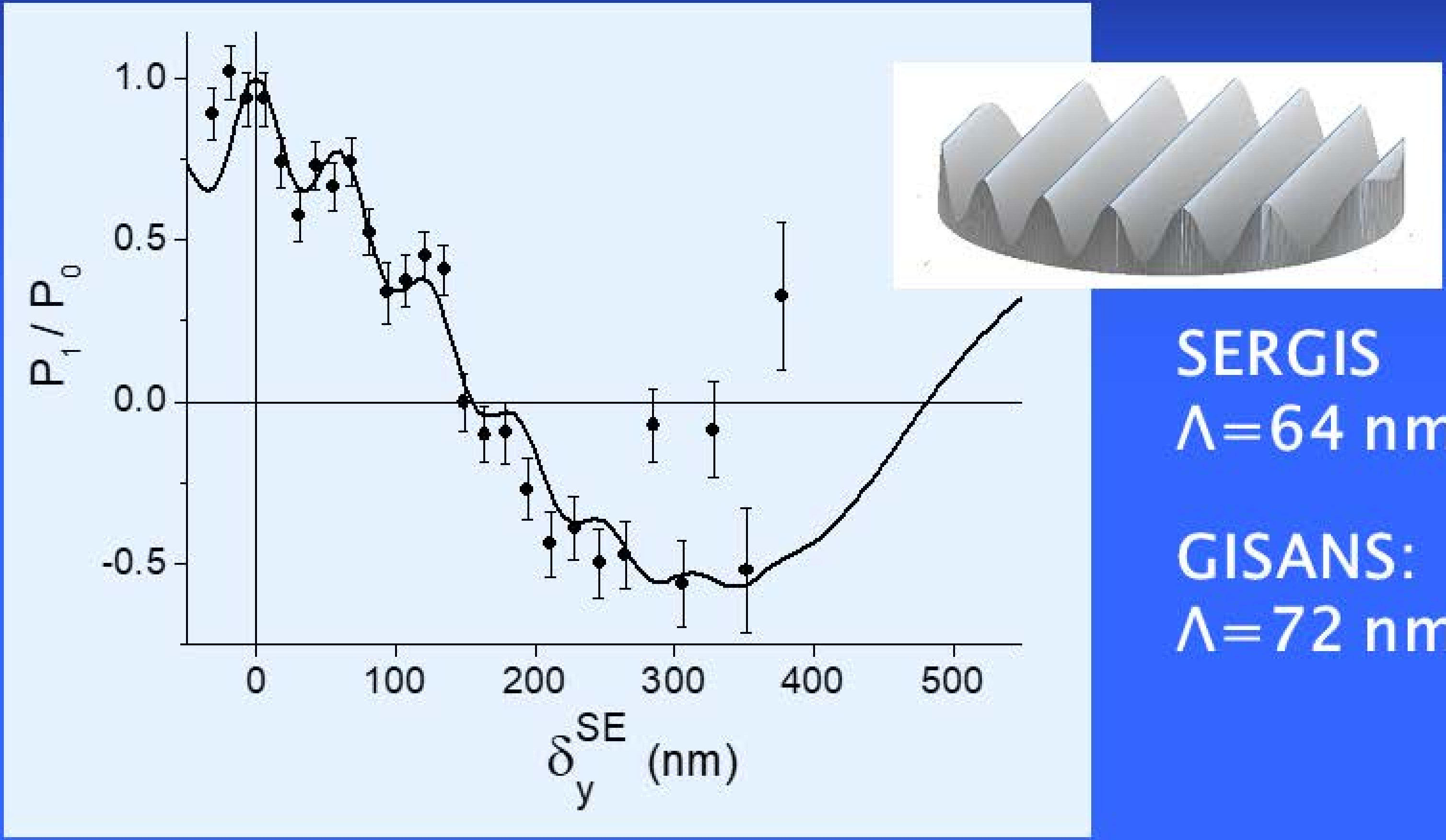
$$|F_{\mathrm{cy}}^{\mathrm{mod}}(\mathbf{q})| = \overline{\rho}|F_{\mathrm{cy}}(\mathbf{q})| + \frac{\Delta\rho}{4}\left(\frac{J_1\left(|\mathbf{q}_{||} - \mathbf{q}_m|R\right)}{|\mathbf{q}_{||} - \mathbf{q}_m|R} + \frac{J_1\left(|\mathbf{q}_{||} + \mathbf{q}_m|R\right)}{|\mathbf{q}_{||} + \mathbf{q}_m|R}\right)\frac{\sin\left(q_z(\varphi,\alpha_{\mathrm{f}})H/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

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

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



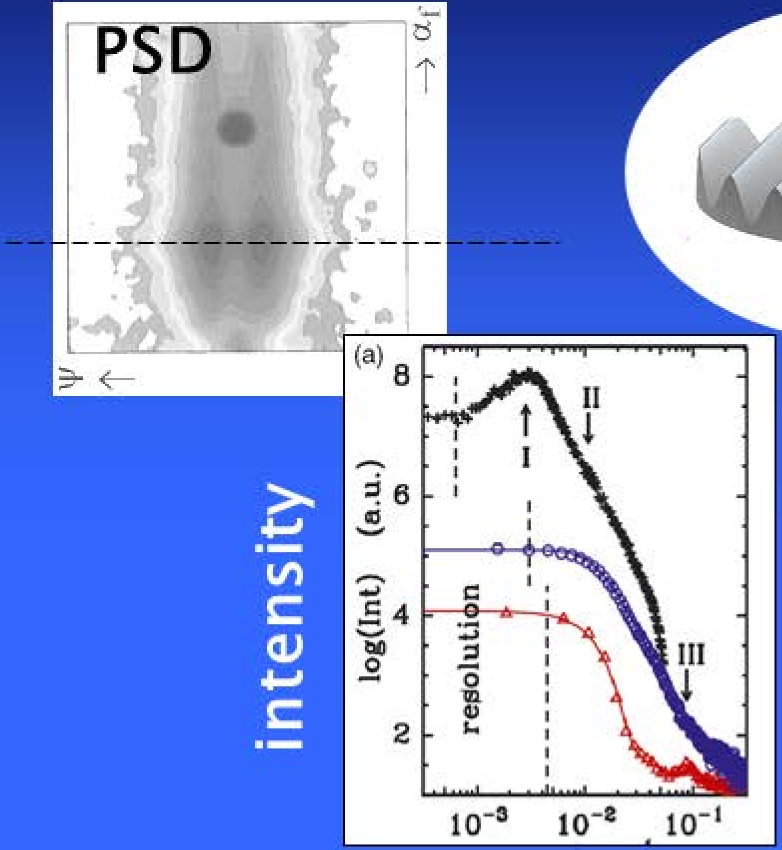
DIBLOCK COPOLYMER – MODULATED DROPLETS



SERGIS
Λ=64 nm

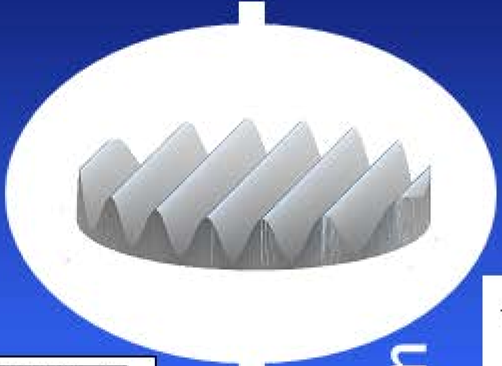
GISANS:
Λ=72 nm

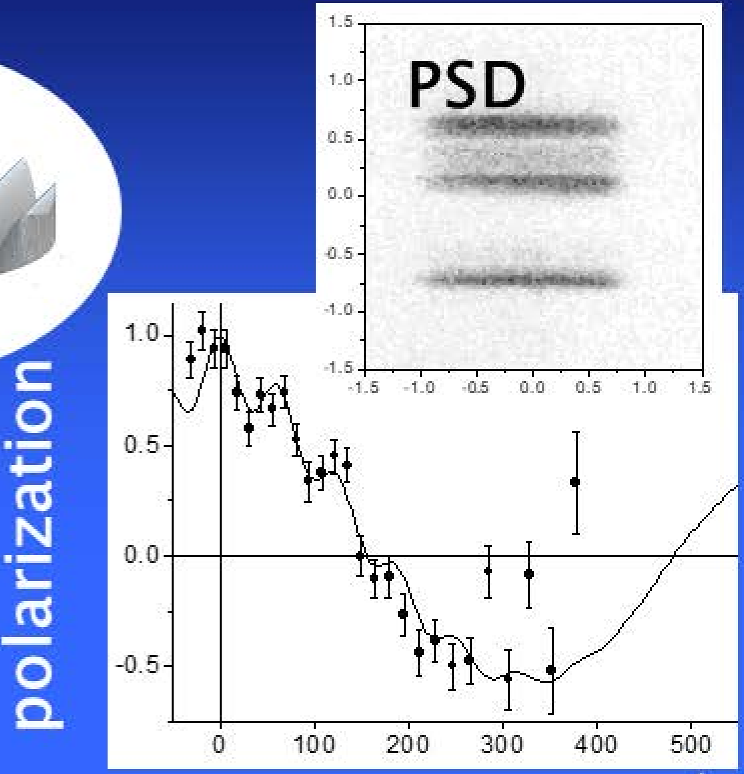
GISANS vs. SERGIS



$\longrightarrow q_y\ (nm^{-1})$

measuring time T_m:
8 hours at D22, ILL





$\longrightarrow y\ (nm)$

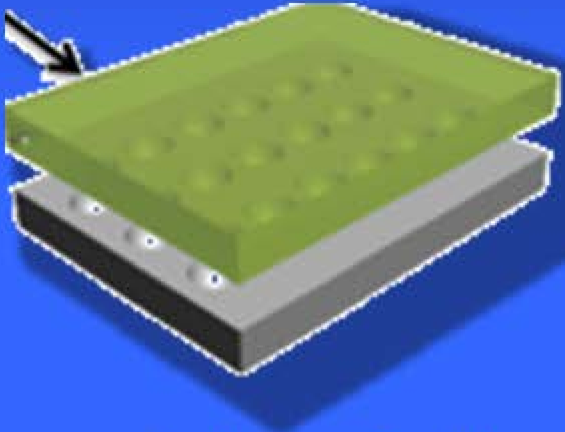
T_m: 12 h at EVA

improvements:	time factor:
monochromator Δλ/λ 5%	/5
improved polarization circuit	/2
improved measuring algorithm (one component, less points)	/10

12 h / 100 ≈ 10 min

APPROPRIATE SAMPLES

burred or fragile interface

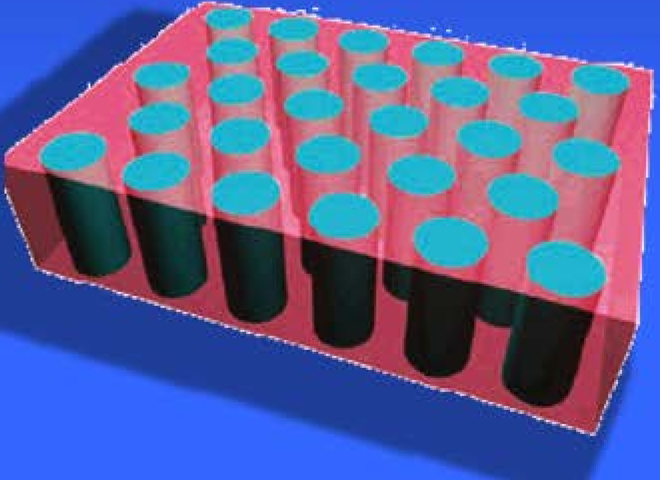


cupping layer or liquid

~~SEM~~

~~AFM~~

block copolymers



isotope contract: D vs. H

CONCLUSION

The SERGIS scattering technique can be especially advantageous for studying
- very soft or liquid surfaces
- buried interfaces

with length scales from few nanometers to few micrometers.

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

Phase and Microphase Separation of Polymer Thin Films Dewetted from Silicon – SERGIS Study

A. Vorobiev et al.
J. Phys. Chem. B **115** (2011) 5754-5765

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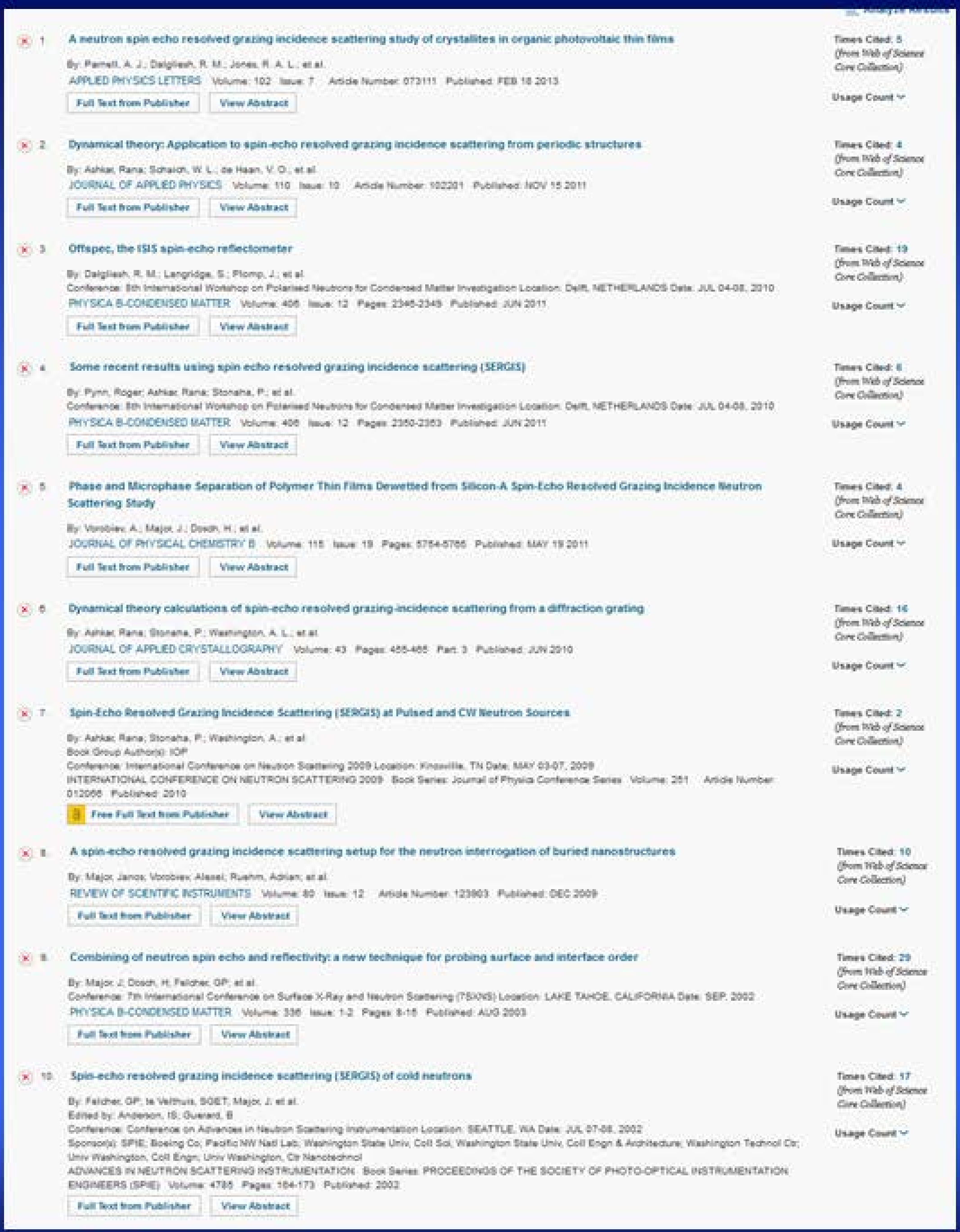

1 **A neutron spin echo resolved grazing incidence scattering study of crystallites in organic photovoltaic thin films**
By: Parnell, A. J.; Dalgliesh, R. M.; Jones, R. A. L.; et al.
APPLIED PHYSICS LETTERS Volume: 102 Issue: 7 Article Number: 073111 Published: FEB 18 2013
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2 **Dynamical theory: Application to spin-echo resolved grazing incidence scattering from periodic structures**
By: Ashkar, Rana; Schaich, W. L.; de Haan, V. O.; et al.
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Times Cited: 4 *(from Web of Science Core Collection)*

3 **Offspec, the ISIS spin-echo reflectometer**
By: Dalgliesh, R. M.; Langridge, S.; Plomp, J.; et al.
Conference: 8th International Workshop on Polarised Neutrons for Condensed Matter Investigation Location: Delft, NETHERLANDS Date: JUL 04-08, 2010
PHYSICA B-CONDENSED MATTER Volume: 406 Issue: 12 Pages: 2346-2349 Published: JUN 2011
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PHYSICA B-CONDENSED MATTER Volume: 406 Issue: 12 Pages: 2350-2353 Published: JUN 2011
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5 **Phase and Microphase Separation of Polymer Thin Films Dewetted from Silicon-A Spin-Echo Resolved Grazing Incidence Neutron Scattering Study**
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By: Ashkar, Rana; Stonaha, P.; Washington, A.; et al.
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INTERNATIONAL CONFERENCE ON NEUTRON SCATTERING 2009 Book Series: Journal of Physics Conference Series Volume: 251 Article Number: 012066 Published: 2010
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8 **A spin-echo resolved grazing incidence scattering setup for the neutron interrogation of buried nanostructures**
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Times Cited: 29 *(from Web of Science Core Collection)*

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Edited by: Anderson, IS; Guerard, B
Conference: Conference on Advances in Neutron Scattering Instrumentation Location: SEATTLE, WA Date: JUL 07-08, 2002
Sponsor(s): SPIE; Boeing Co; Pacific NW Natl Lab; Washington State Univ, Coll Sci; Washington State Univ, Coll Engn & Architecture; Washington Technol Ctr; Univ Washington, Coll Engn; Univ Washington, Ctr Nanotechnol
ADVANCES IN NEUTRON SCATTERING INSTRUMENTATION Book Series: PROCEEDINGS OF THE SOCIETY OF PHOTO-OPTICAL INSTRUMENTATION ENGINEERS (SPIE) Volume: 4785 Pages: 164-173 Published: 2002
Times Cited: 17 *(from Web of Science Core Collection)*