An Introduction to *SESAME*: A New Neutron Scattering Technique for Studying the Structure of Soft Matter

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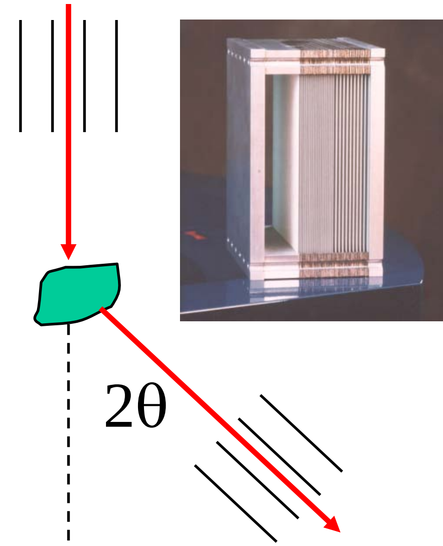
The Reason for the Experimental Difficulty:
The Resolution / Intensity Conundrum



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

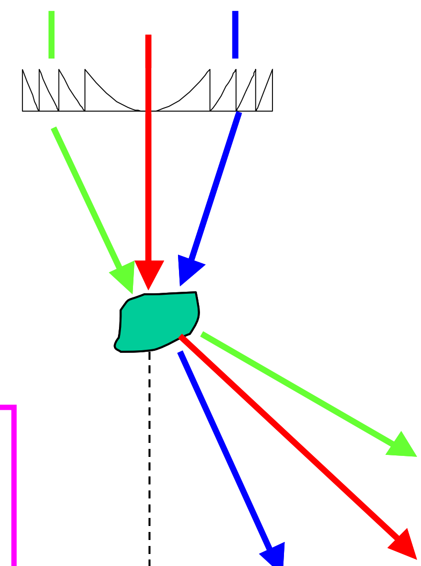
$$\lambda = 2d \sin\theta$$

- For soft matter, *d* >> λ so θ is small.

- To define θ with sufficient precision, the trajectories of both the incident & scattered beams are defined in traditional methods such as SANS

- But the measured intensity scales as ~ $\phi\,(\delta\theta)^2\,V$, so there is a conflict between high intensity and good resolution (i.e. small $\delta\theta$)

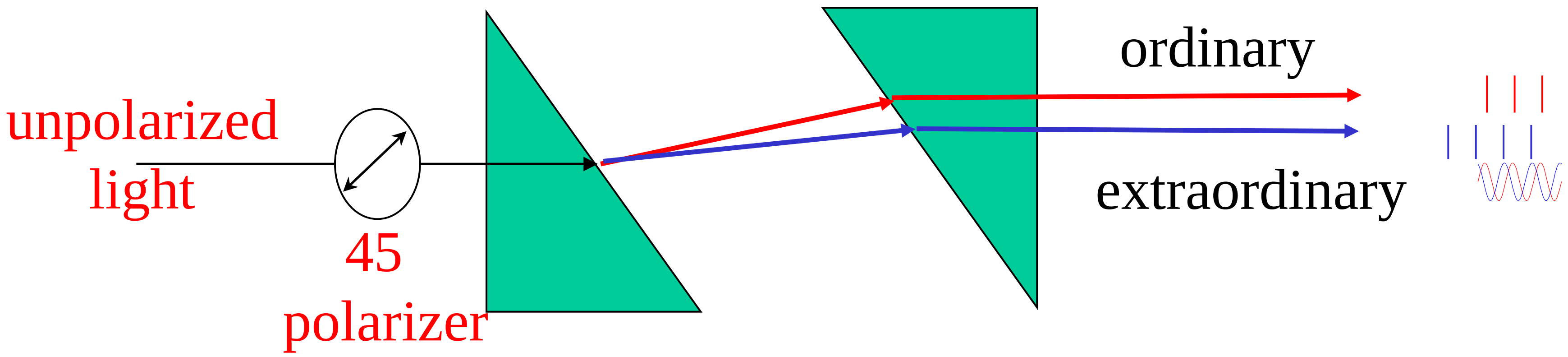
  – *SANS instruments are long so that V can be large while* $\delta\theta$ *is small*



We'd like to be able to measure 2θ accurately without having to collimate the beam or use a small sample

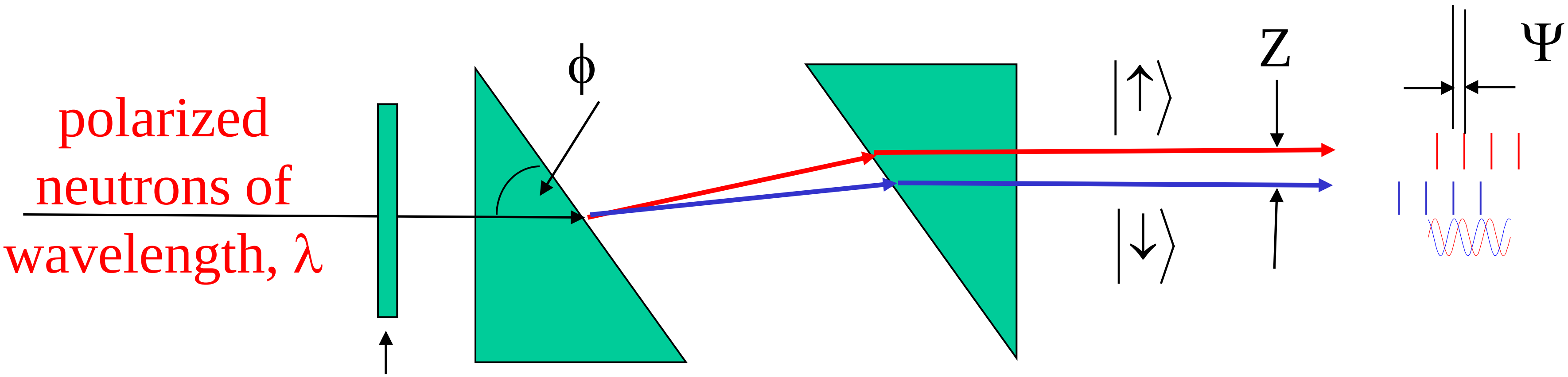
Calcite Prism Demonstration

- Two birefringent prisms produce parallel and separated ordinary and extraordinary rays
- With a 45° polarizer inserted, the O and E rays have a well defined phase separation



We Can do the Same Thing with Neutrons

- Birefringent prisms for neutrons are simply appropriately shaped magnetic-field regions

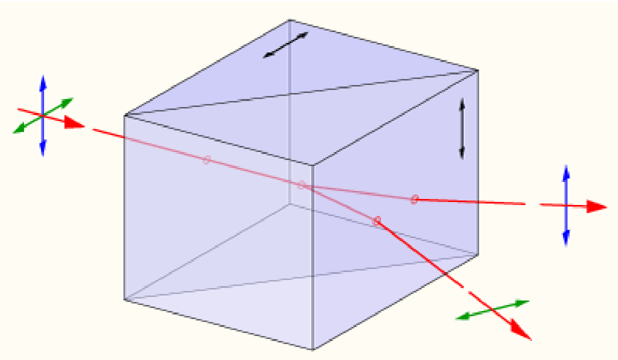


$\pi/2$ flipper
produces
$\left(|\uparrow\rangle + |\downarrow\rangle\right)/\sqrt{2}$

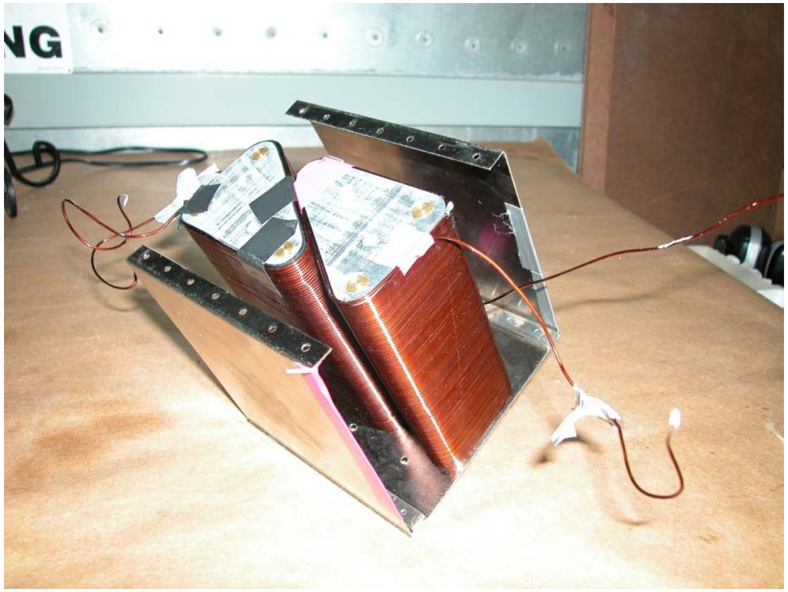
Using Snell's law we can show that
$d\Psi/d\phi = (2\pi/\lambda)\, Z$ for light or neutrons.
Z depends on geometry & materials.

Wollaston Prism: Invented Early 19th Century

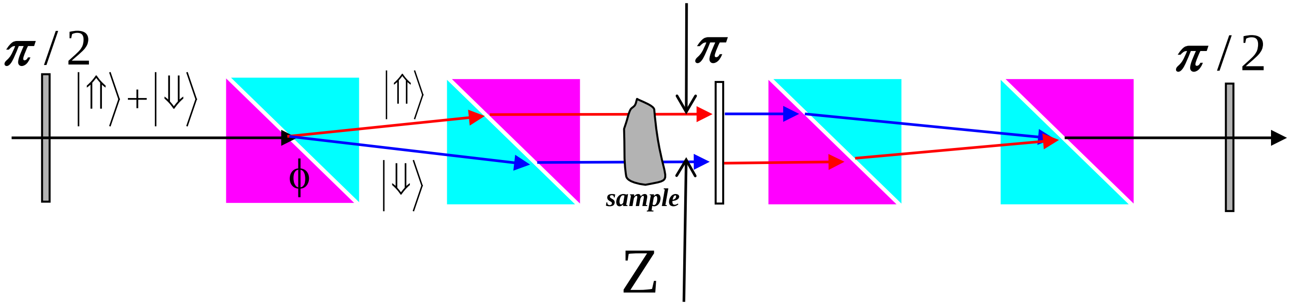
- *For light:* the refractive effect can be doubled by using a pair of prisms with perpendicular optic axes



- *For neutrons:* the refractive effect can be doubled by using a pair of triangular solenoids with opposite magnetic fields



Spin Echo Scattering Angle Measurement (SESAME)



- Neutron spin states are split and recombined by magnetic Wollaston prisms
- With no sample, the Larmor phase Ψ generated before sample is cancelled after the sample, independent of neutron incident angle, ϕ (this effect is called *neutron spin echo*)
- If scattering occurs, the phases generated before and after the sample are different (because ϕ is different) and the final neutron polarization is reduced because *P ~ cos(*Ψ*)*
- The neutron depolarization is weakly dependent on the incident value of ϕ so we don't need to collimate the beam

SESANS & SERGIS

- The SESAME method can be applied in two ways
  - *SESANS:* Spin Echo Small Angle Neutron Scattering (bulk samples)
  - *SERGIS*: Spin Echo Resolved Grazing Incidence Scattering (surface structure)
- Each allows large distance scales to be measured without excessive neutron beam collimation
  - Resolution is also independent of sample size
- SESAME is good for strong scattering because it incorporates multiple scattering naturally
  - Could be used for weak scattering if we can develop “dark-field SESANS”
- SESAME measures correlations in real space and provides different information from conventional scattering

Expression for Final Neutron Polarization

- Final neutron polarization, *P*, is given by the average of $\cos(\Psi_{tot})$ over all neutrons scattered. When we work through the math for SESANS we find:

$$\frac{P}{P_0} = e^{G(\zeta) - G(0)} \qquad G(\zeta) = \frac{\lambda^2}{4\pi^2}\frac{1}{A}\int_{-\infty}^{\infty} dQ_y \int_{-\infty}^{\infty} dQ_z \frac{d\sigma_s(0,Q_y,Q_z)}{d\Omega}\cos(Q_y\zeta)$$

$$\zeta = c\lambda^2 BL \cot\phi$$

(λ = neutron wavelength; B = magnetic field in each prism; L = separation of Wollaston prisms; ϕ = prism angle; A = sample area; c = constant)

- ζ is, to leading order, equal to the separation of rays (Z) in an earlier slide and is called the *spin echo length*. It is the distance probed in the sample.

- The expression for P/P_0 involves the single-scattering cross section and is correct even in cases of strong multiple scattering

- ζ is only weakly dependent on beam collimation. For $\phi_0 = 32°$, and $\Delta\phi = \pm 0.5°$, $d\zeta/\zeta \sim \pm 2.5\%$

$$\frac{d\zeta}{\zeta} \approx \frac{2\Delta\phi}{\tan\phi_0}$$

What does SESANS measure?

Local Density | **Debye Correlation Function**

$$\rho(r) \longrightarrow \gamma(r)$$

SANS

$$I(Q) = 4\pi \int_0^\infty J_0(Qr)\gamma(r) r^2 dr$$

Fourier

SESANS

$$G(z) = \frac{2}{\xi} \int_z^\infty \frac{\gamma(r) r}{\sqrt{r^2 - z^2}} dr$$

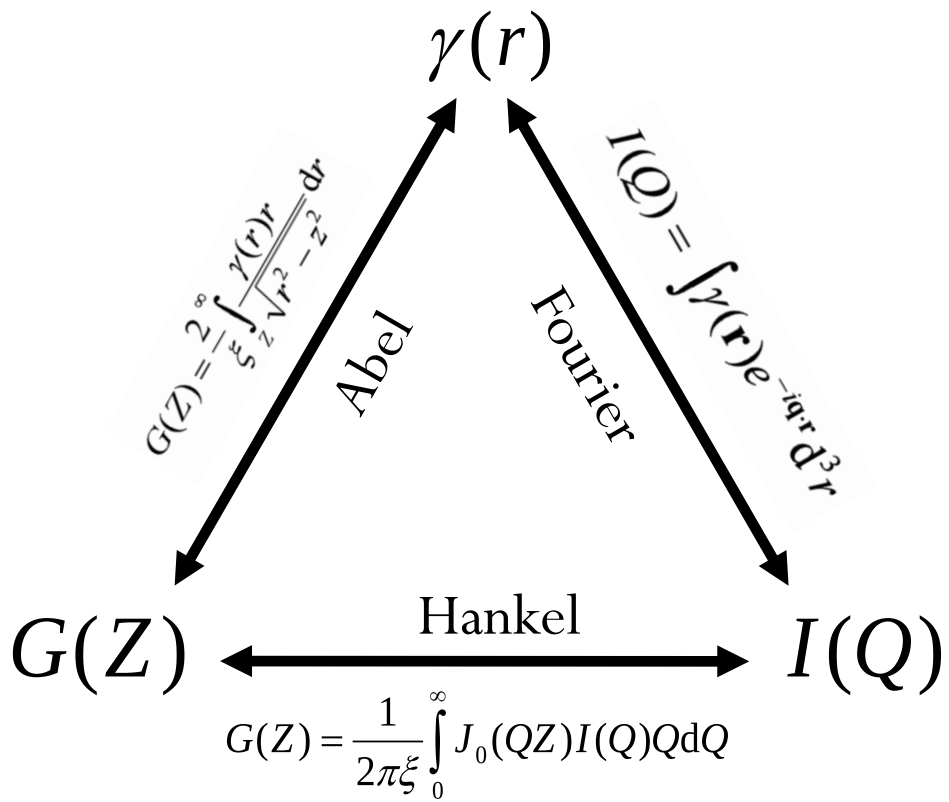
Abel*

$$\gamma(\mathbf{r}) = \frac{\int \rho(\mathbf{r} - \mathbf{r}')\rho(\mathbf{r}')d\mathbf{r}'}{\int \rho(\mathbf{r}')\rho(\mathbf{r}')d\mathbf{r}'}$$

* For an isotropic sample

Relationship Between SANS and SESANS

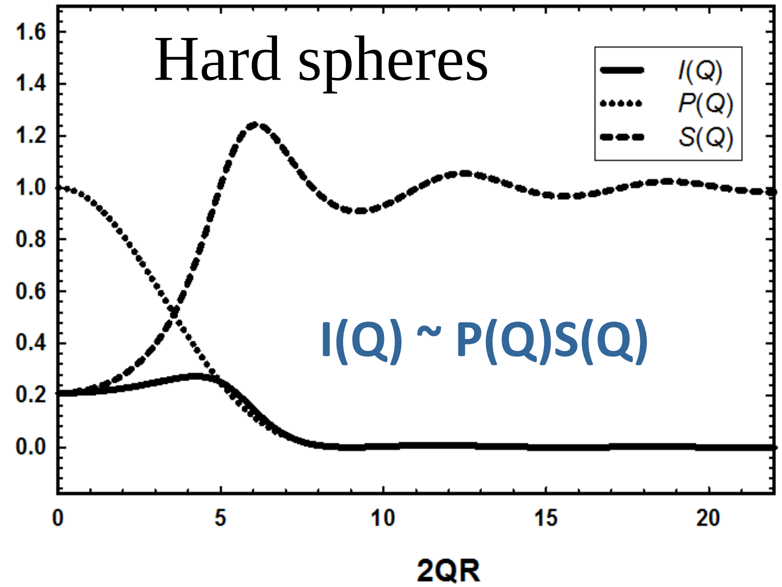
$$\gamma(\mathbf{r}) = \frac{\int \rho(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}')d\mathbf{r}'}{\int \rho(\mathbf{r}')\rho(\mathbf{r}')d\mathbf{r}'}$$



Sometimes measuring correlations in real space has advantages

SANS: A Product of Structural Information

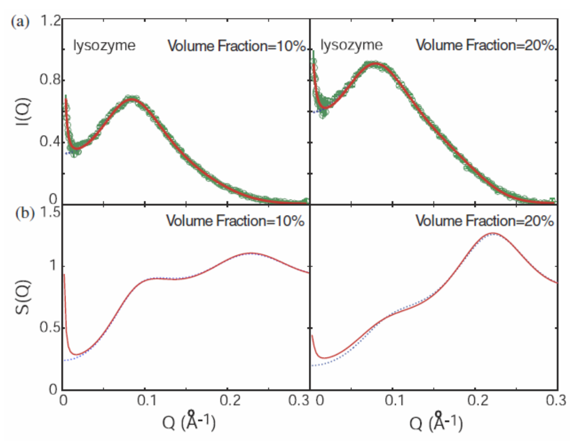
- The measured SANS intensity, *I(Q)*, is the product of:
  P(Q) – the particle form factor
  S(Q) – the structure factor



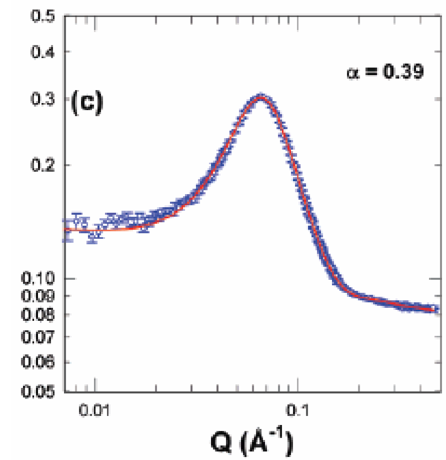
- The damping of the particle form factor at large Q obscures high Q structural information i.e. information about short range correlations

- In principle, *S(Q)* at large Q can be found if *P(Q)* is measured on a dilute sample. But noise is a problem.

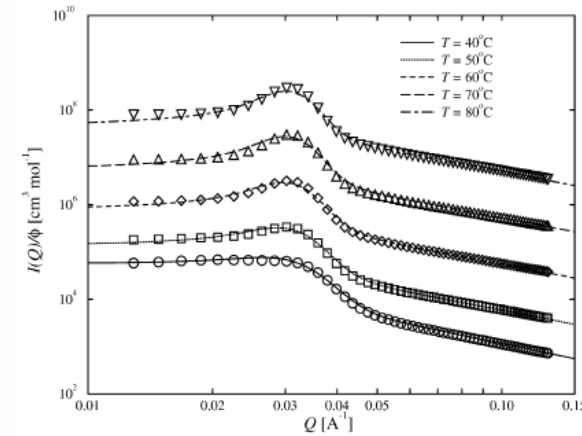
SANS I(Q) of Different Interacting Colloidal Systems



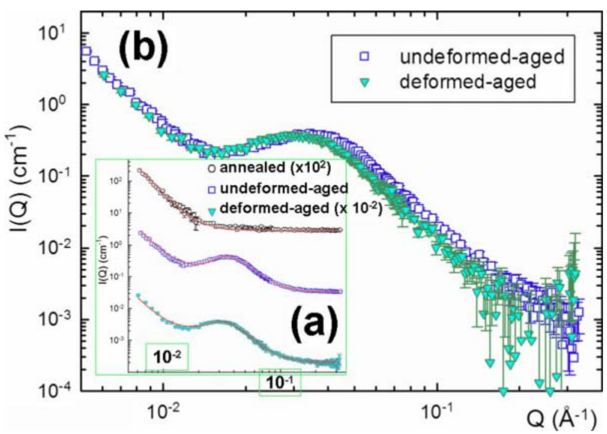
Liu *et al.* PRL **95** 118102 2005



Chen *et al.* Macromolecules **40** 5887 2007



Likos *et al.* PRE **58** 6229 1998

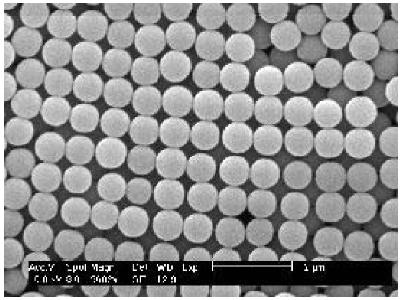


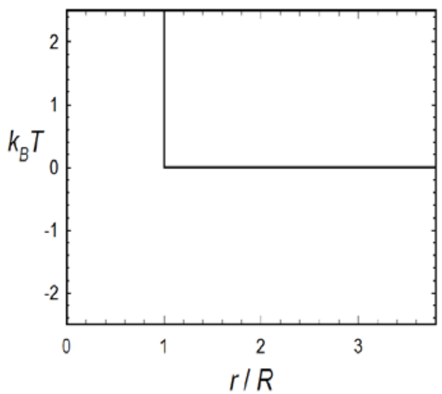
Huang *et al.* APL **93** 161904 2008

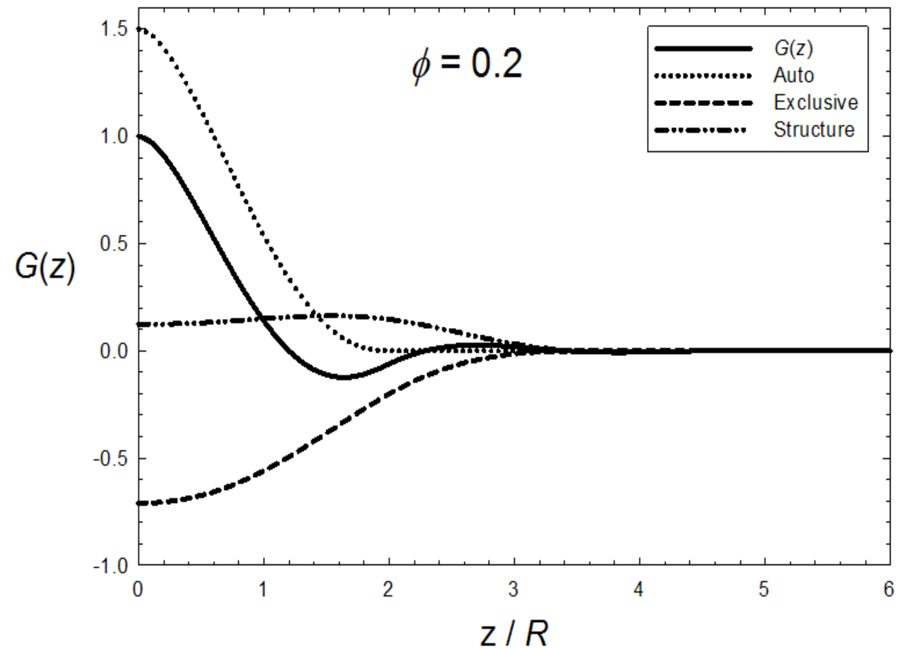
- Very different systems often show a broad peak in SANS.
- The interpretation is always that there is some sort of structure with a length scale of $1/Q_{peak}$.
- But we don't know what sort of structure it might be.

Viewgraph from Wei Ren Chen

SESANS: Superposition of Structural Information





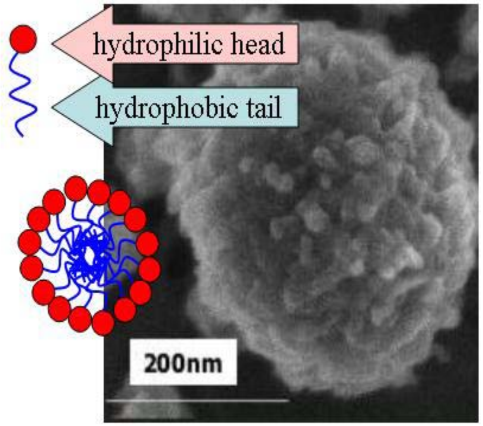


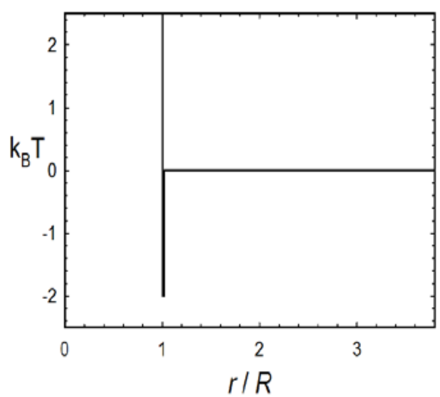
Li *et al., J. Chem. Phys.* **132** 174509 2010

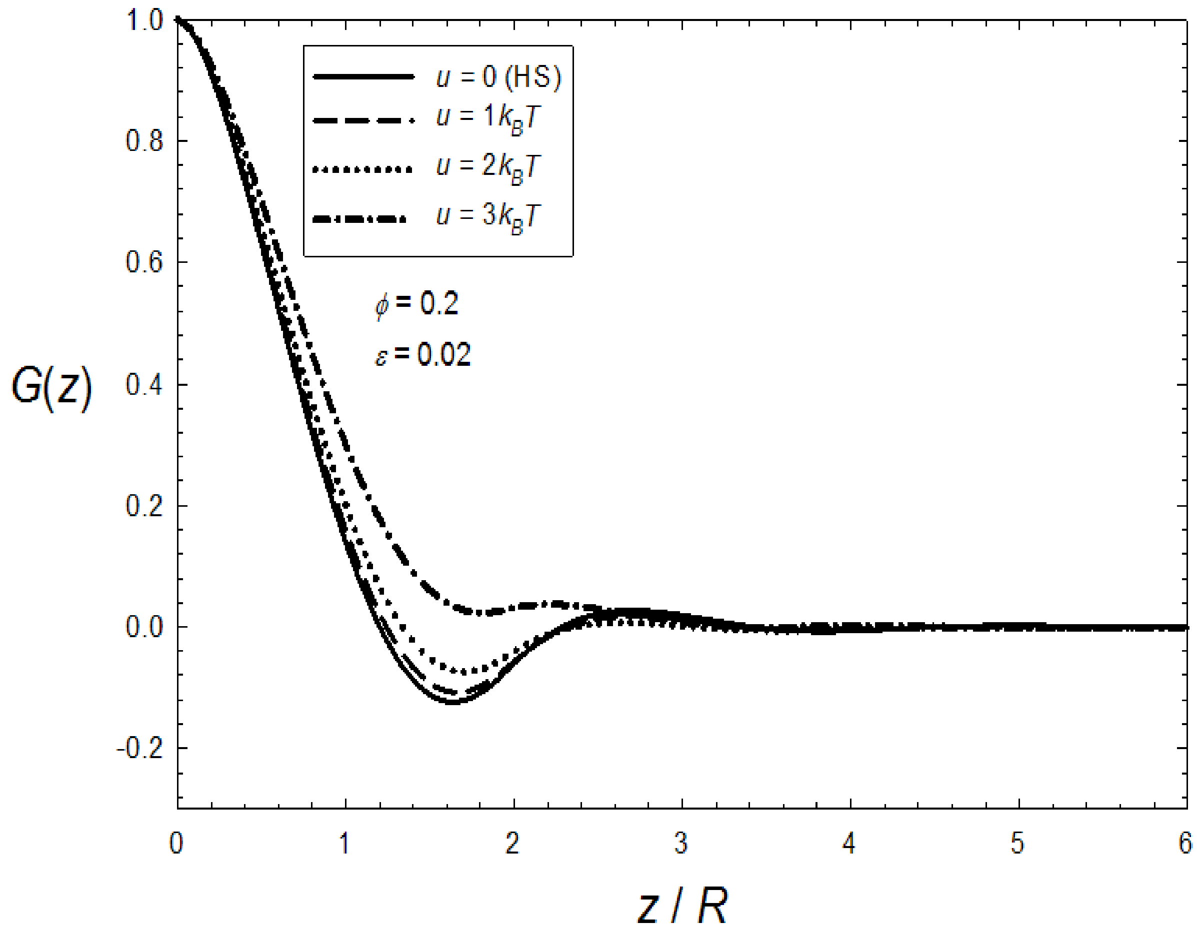
- For hard spheres, G(z) is the SUM of three terms:
  - an intraparticle term
  - an excluded volume term (i.e. the particles cannot overlap)
  - a correlation term

Attractive System

Viewgraph from Wei Ren Chen



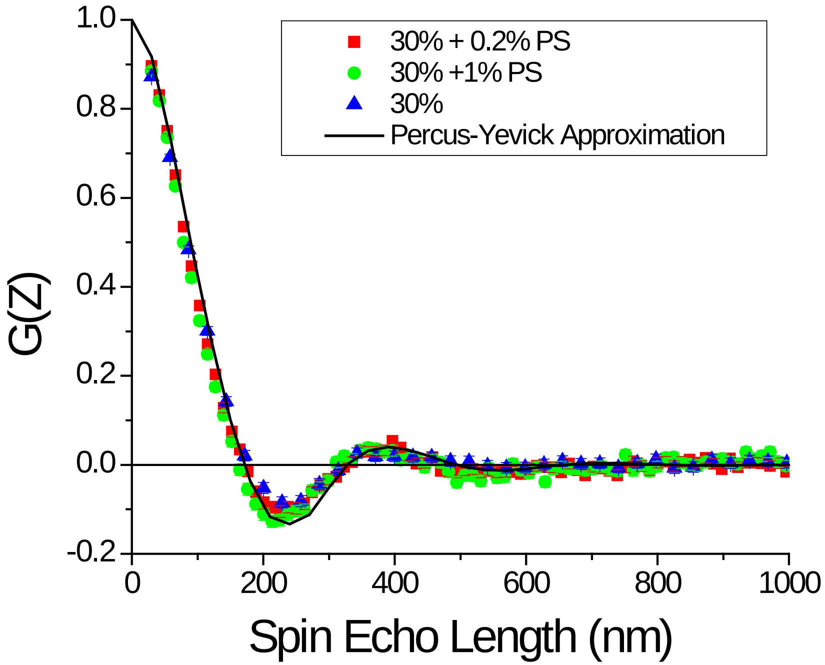




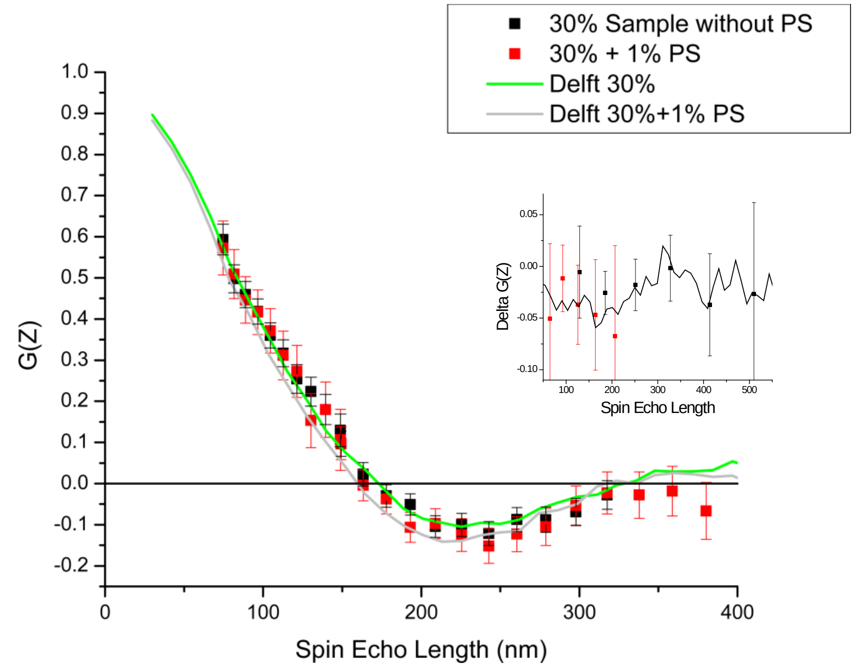
As the attractive part of the potential gets deeper, there is more chance of close contact so the dip gets less deep

Monodisperse PMMA Spheres

- DLS showed PMMA spheres in dodecane to be well described by Percus-Yevick hard-sphere model at low concentrations
- SESANS confirms this for high concentrations of 300 nm diameter spheres
- SESANS also shows the very weak effect of adding 1% PS to a 30% suspension of PMMA spheres – in the opposite direction to expected!

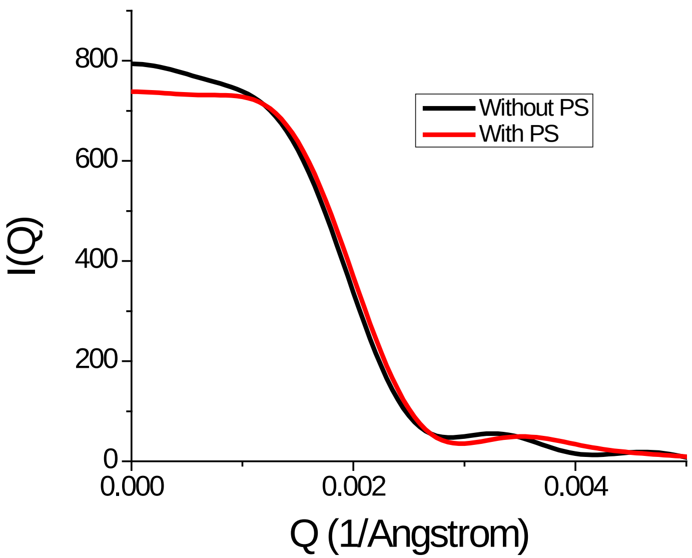


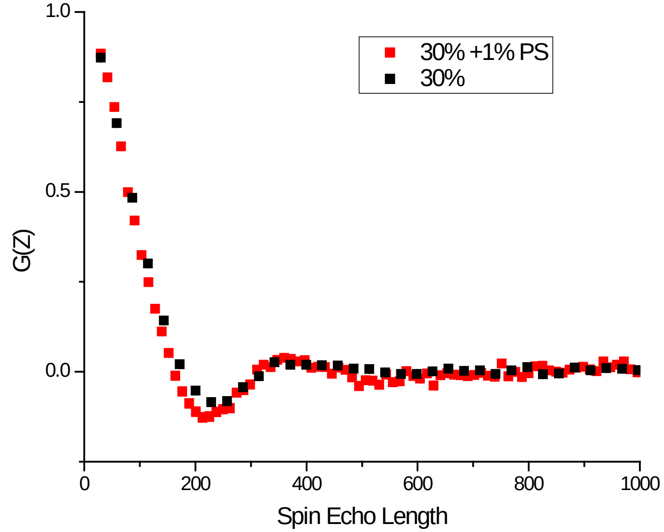
Data From Delft compared with PY



Lines are data from Delft (CW);
points from Asterix (TOF) with attenuated beam

The difference is less clear in Q space



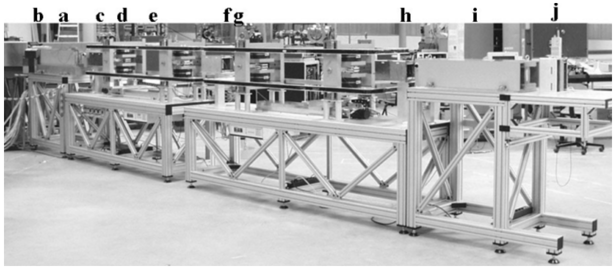


- The difference between PMMA and PMMA + 1% PS is much less clear in Q space as shown above
- It would be hard to look at I(Q) and know that the principal effect of adding PS is to decrease short range correlations

Available Instruments

- At LENS & at ASTERIX
  - Electromagnetic Wollaston Prisms
  - Max field ~ 300 Gauss; $\phi = 32°$; $\Delta\phi \sim \pm 0.5°$
  - Time of flight; SESANS and SERGIS
  - $\zeta_{max} \sim$ 5 μm (at λ = 1 nm)

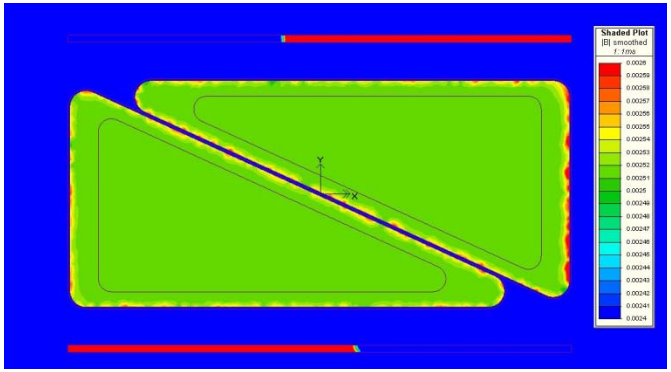
- At Delft
  - Permalloy foil flippers in iron core electromagnets
  - Max field is several kG; $\phi = 5.5°$; $\Delta\phi < \pm 0.1°$
  - Fixed wavelength λ = 0.21 nm : $\zeta_{max} \sim$ 20 μm
  - SESANS only



- OFFSPEC at ISIS
  - Adiabatic RF flippers (no material in beam)
  - Max field ~ 2 kG; $\phi > 60°$ and ; $\Delta\phi \sim 0.1°$
  - Time of flight; mainly SERGIS but some SESANS
  - $\zeta_{max} \sim$ 15 μm (at λ = 1 nm)

Design Criteria for Triangular Prisms

- For closed prisms, the field must be uniform – verified by FE calcs



Full scale is +/- 4%

$$\text{Larmor phase} = \omega_L t = \gamma B d / v$$

$$Z = c\lambda^2 BL \cot\phi; \quad c = 1.47x10^{14}\ T^{-1} m^{-2};$$

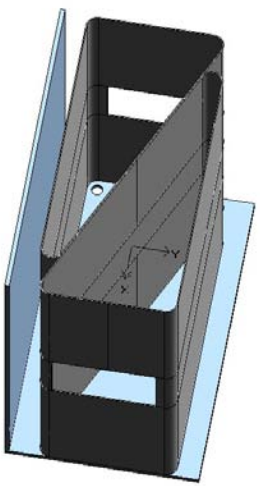
- Large *Z* => large *B.L* => large Larmor phases
  - Integrated Larmor phase (i.e. path integral of magnetic field) has to be the same for all "equivalent" neutrons: a small percentage error yields a large absolute error in Z at large *B.L*

- The interface between fields (hypotenuse) must be flat
  - Wires have to be positioned to within 0.1 mm to avoid aberrations in *BL* (different values for equivalent neutrons)

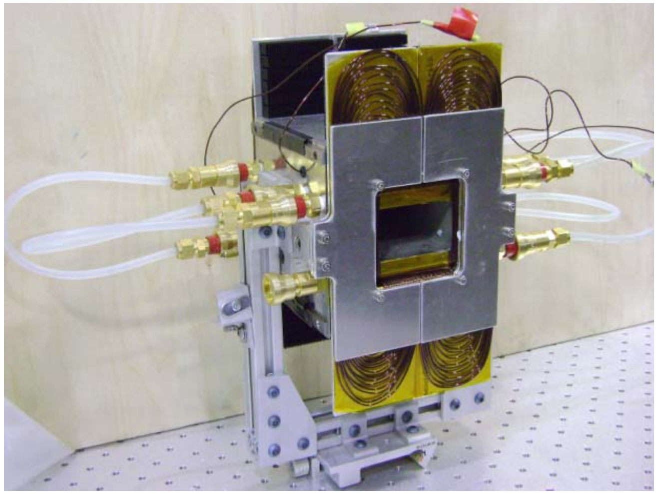
Key Difference Between Light and Neutrons

- It is easy to embed optically birefringent prisms in a non-birefringent medium
  - Harder for neutrons: need either constant B or B = 0

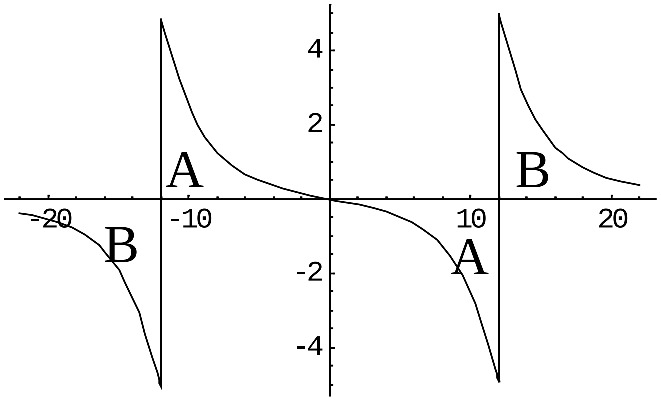
- Our approach has been to use guides fields and exploit symmetry to cancel aberrations in Larmor phase
  - This is also used at Delft and ISIS but with different architectures



Windings with gaps



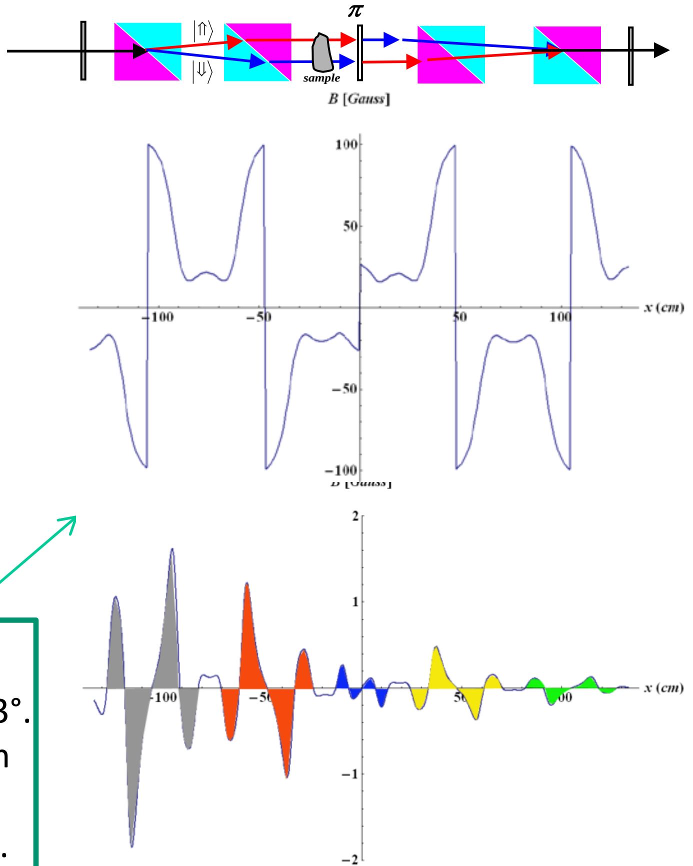
Water-cooled, gapped Wollaston prisms



Difference between field of Gapped and Ungapped Wollaston Prisms along Central path

Cancelling Field-Integral Aberrations

- Exploit symmetry to cancel aberrations in *B.L*
- Place “equivalent” field elements symmetrically about each pi flipper so that local cancellation is maximized
  - Guide fields designed like our flippers *decrease* aberrations *wrt* no guides
  - Changing the guide-field design can reduce the aberrations at $2\theta = 0$ even further
  - Contribution of gaps to spin-echo-length resolution is negligible compared to resolution obtained with closed prisms

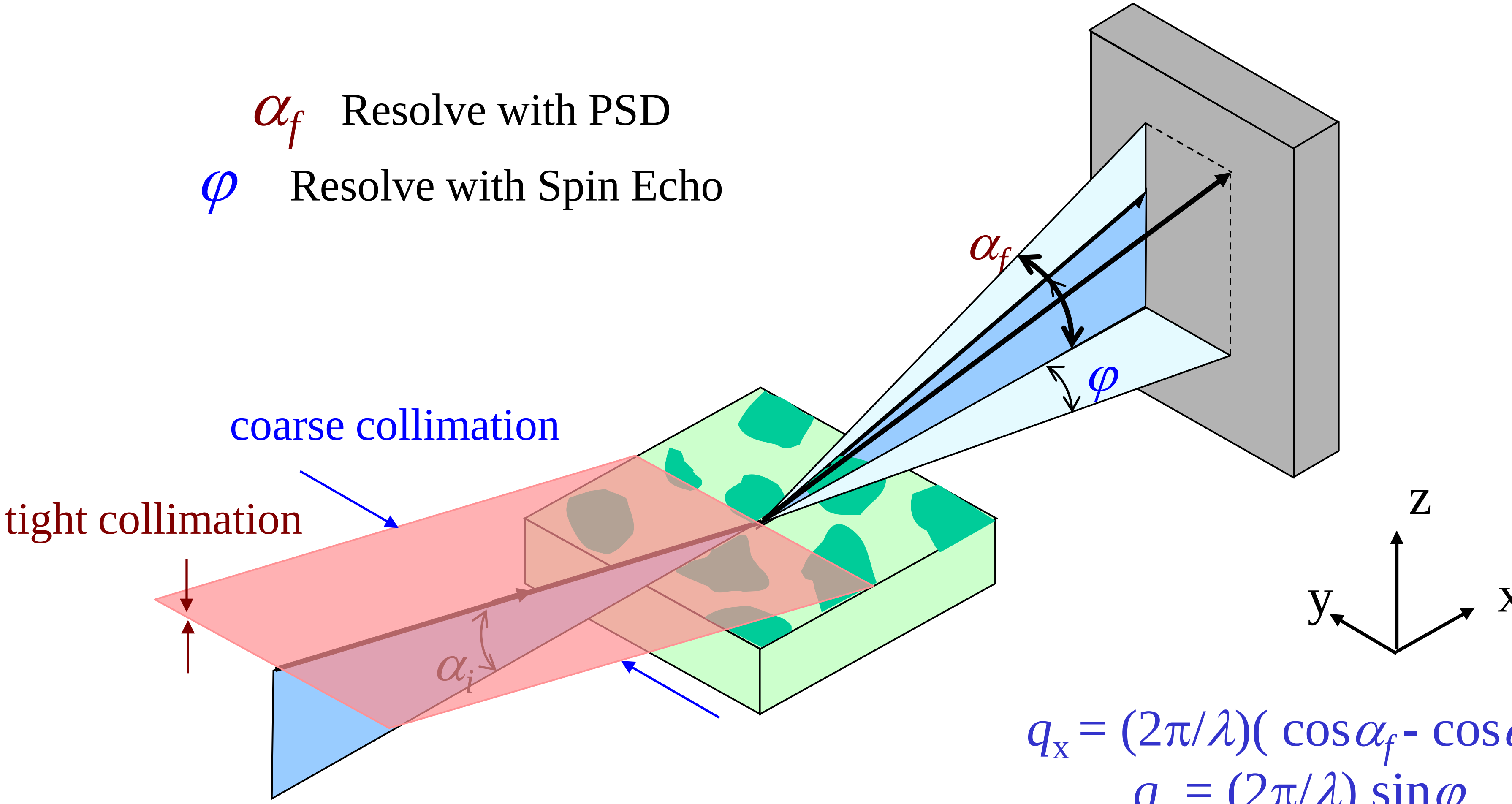


Upper plot shows field modulus. Lower plot is difference between field modulus in Gauss on axis and a trajectory with y = 0, z = -1 cm, $\phi = 0$, $\psi = 0.3°$. Grey integral is slightly +ve, red is slightly –ve: sum is very slightly +ve. Sum on right side is very slightly –ve. Near cancellation around a pi flipper, between adjacent pi’s & across central pi. Cancellation is exact if $\phi = \psi = 0$. Note the 50 fold difference in vertical scale of the two plots.

SERGIS: A Method for Studying GISANS

α_f Resolve with PSD

φ Resolve with Spin Echo

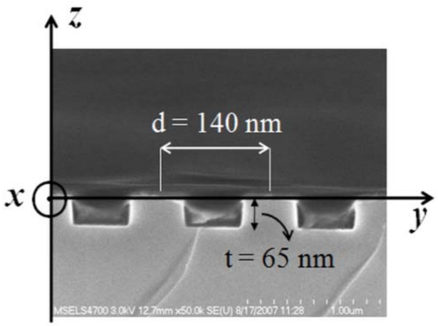


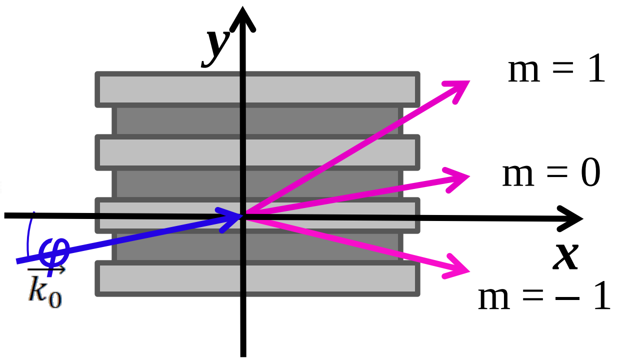
$$q_x = (2\pi/\lambda)(\cos\alpha_f - \cos\alpha_i)$$
$$q_y = (2\pi/\lambda)\sin\varphi$$

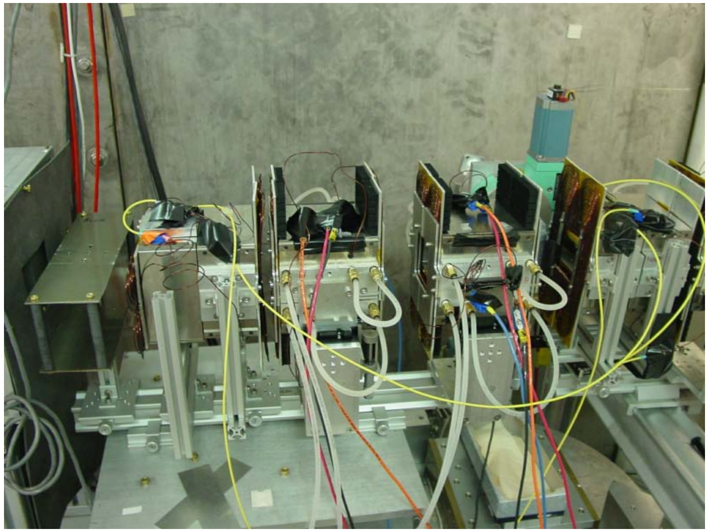
Note that scattering at a particular value of q is spread over larger angles α_f than ϕ

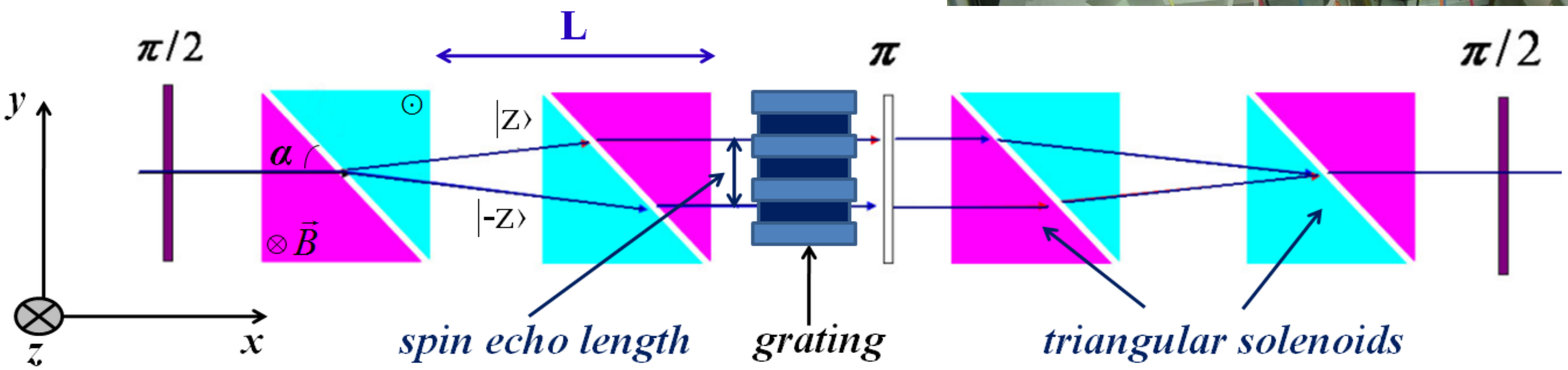
SERGIS Measurements of a Diffraction Grating

- First, let's look at something we understand (or do we?).

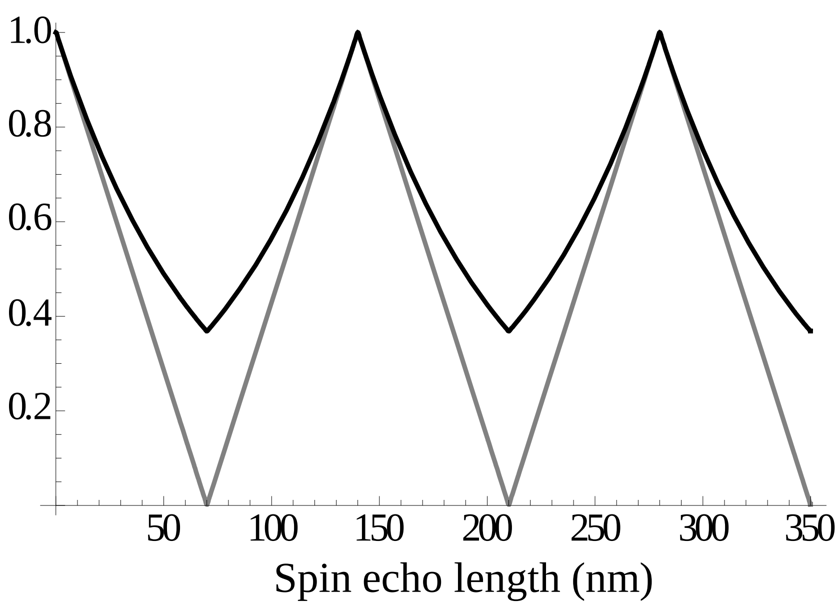






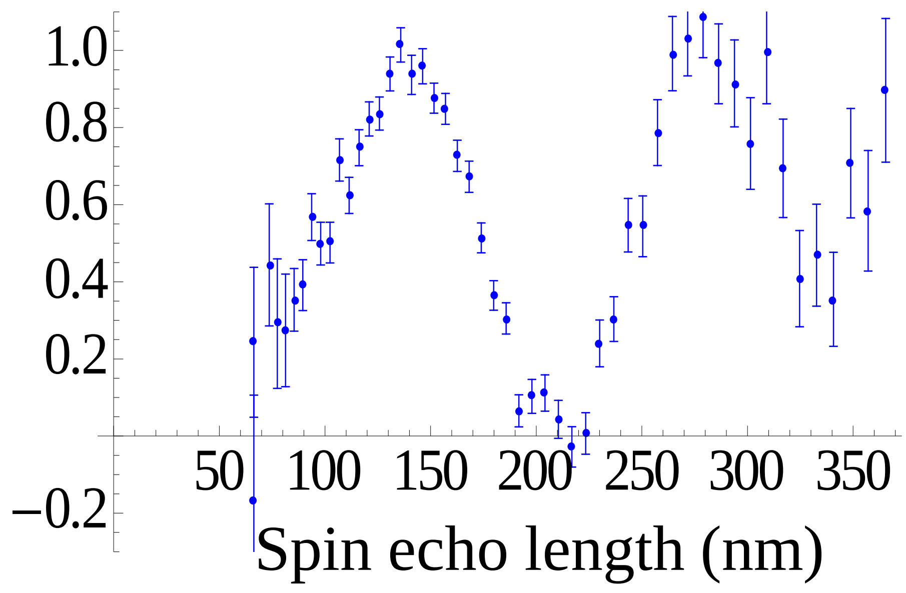


What should we expect?

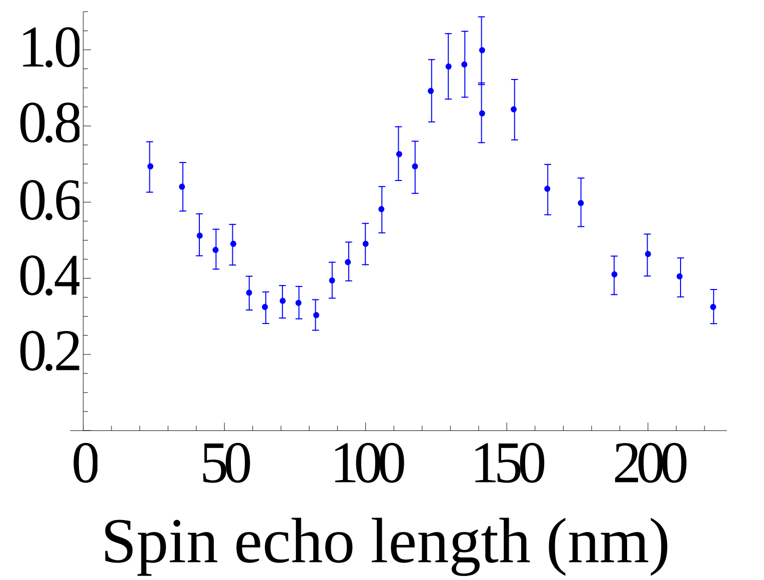


- P/P_0 is the FT of S(Q)
- Within DWBA, S(Q) ~ FT of height-height correlation function
- So, P/P_0 should look like the height auto-correlation function?

On *ASTERIX* at *LANSCE*

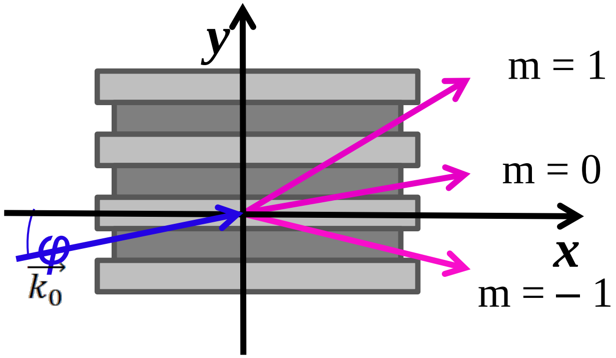


On *AND/R* at *NCNR*

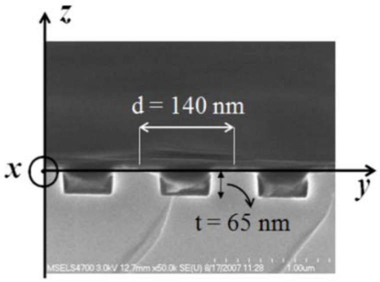


Exact Dynamical Theory Calculation by Rana Ashkar

- Expand wavefunction in terms of Bloch waves
- Solve boundary conditions at interfaces between air, modulated layer and substrate



- Find: $$\frac{P(\zeta)}{P_0} = \sum_m \tilde{p}_m \cos(mg\zeta)$$
  where $g = 2\pi/d$, m is the order of Bragg reflection from the grating and the coefficients p_m are found from the calculation

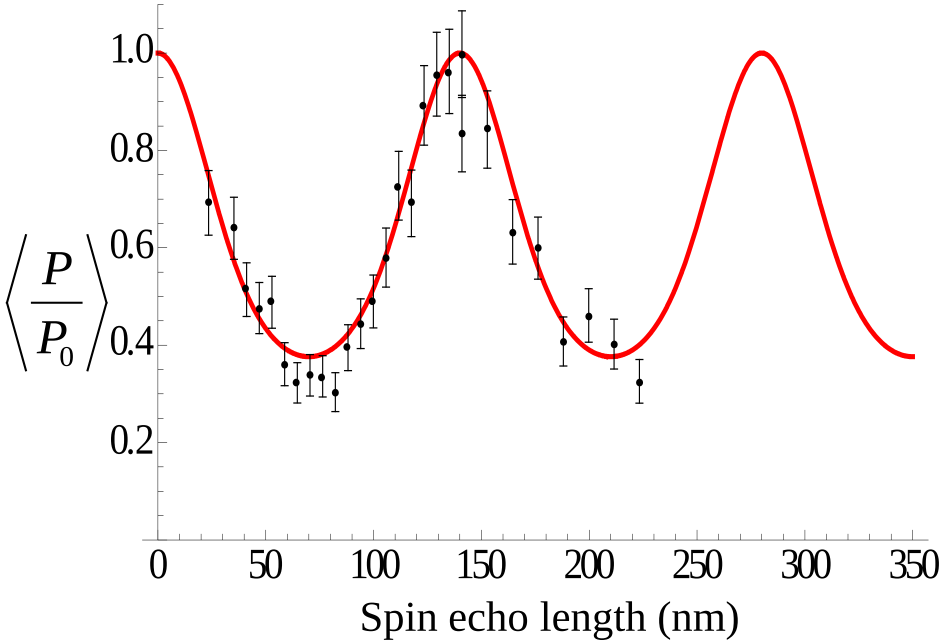


- The calculation is stable to any Bragg order and easily extended to other grating shapes
  – Mathematica code

Comparison of Theory and Experiment

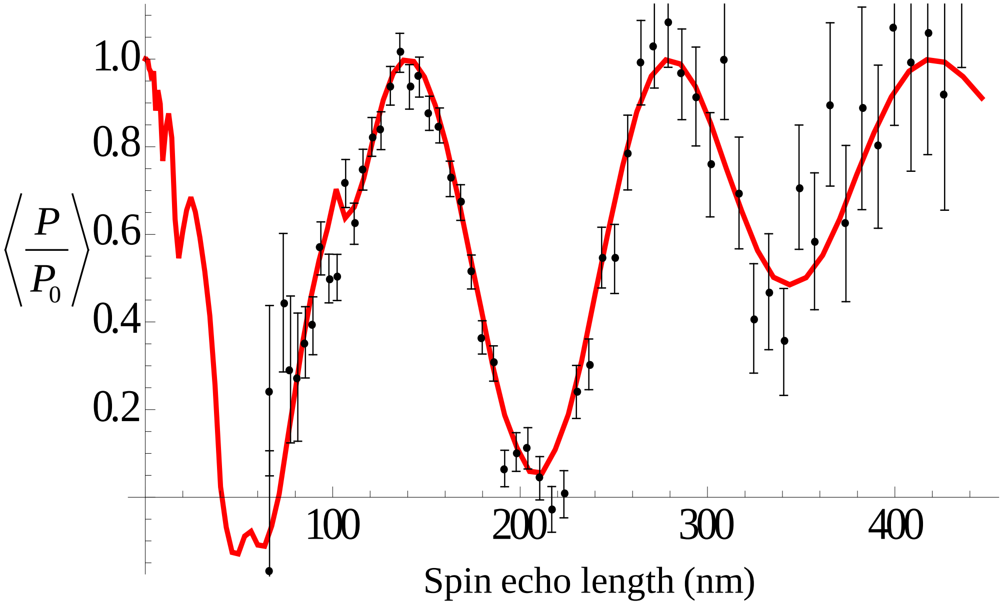
Data from a Fixed-Wavelength Source (NCNR)

- Spin-echo length varies as a function of the current in the triangular solenoids:
  - P/P_0 peaks at integer multiples of the grating period, as expected
- Numerical calculations are very sensitive to beam divergence (in this case FWHM = 0.4°)



Data from a Pulsed Source (LANSCE)

- Spin-echo length is wavelength dependent: $\zeta = 551 \times \lambda^2$
- Current in triangular solenoids is kept constant
- Analytical calculations (with all variables set to their experimentally observed values) and experimental data are again in good agreement



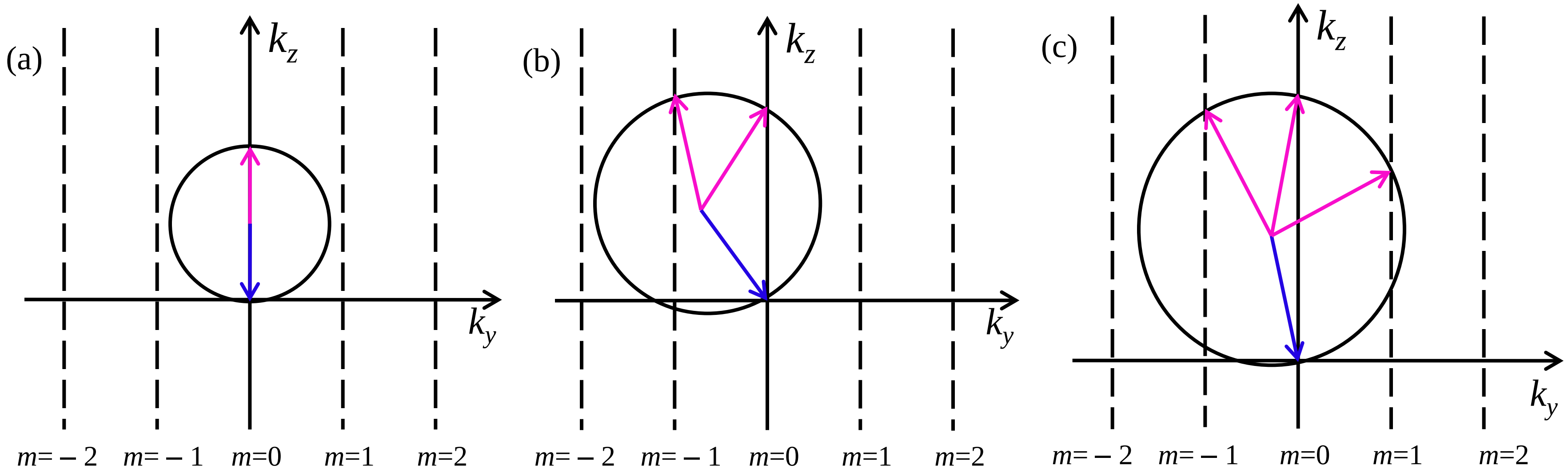
19-beam approximation

Again the theory *explains* the lack of periodicity of the spin-echo polarization

$$\frac{P(\zeta)}{P_0} = \sum_m \tilde{p}_m \cos(mg\zeta)$$

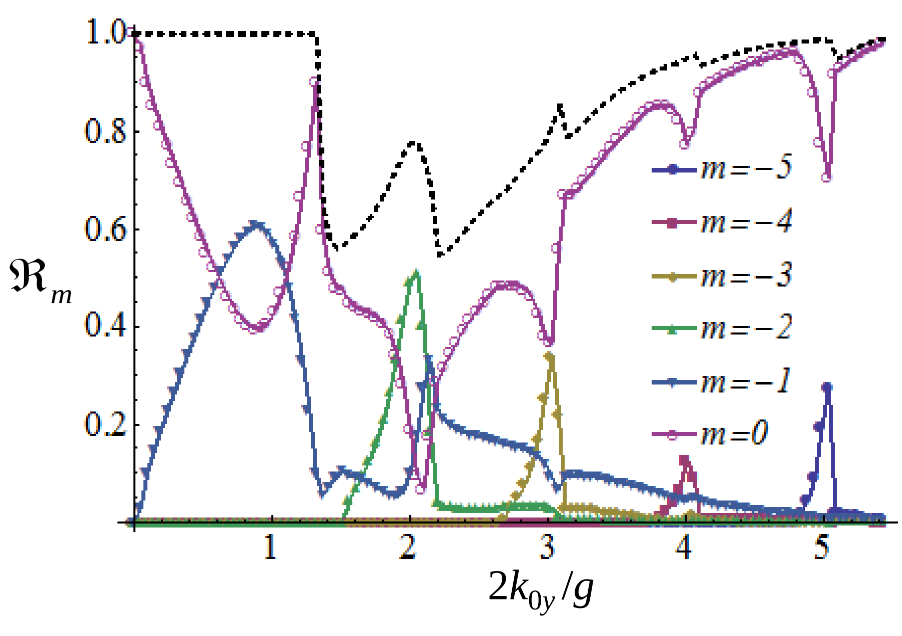
Wavelength-dependent

Outcomes of the Dynamical Theory



1. Number of allowed states in the theory is consistent with the Ewald construction

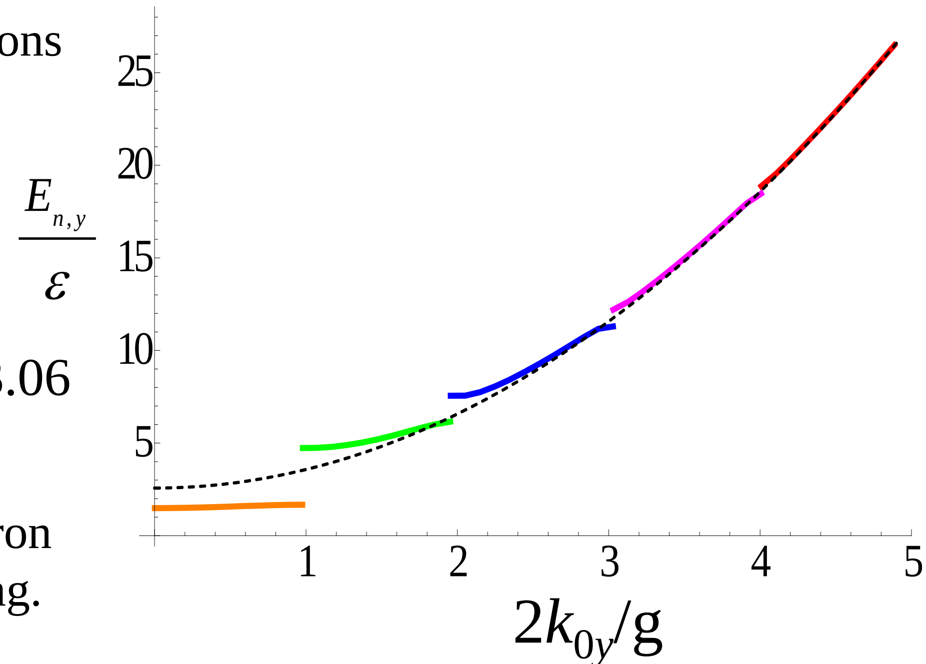
2. Theory confirms the *turn on* points of the allowed reflected beams



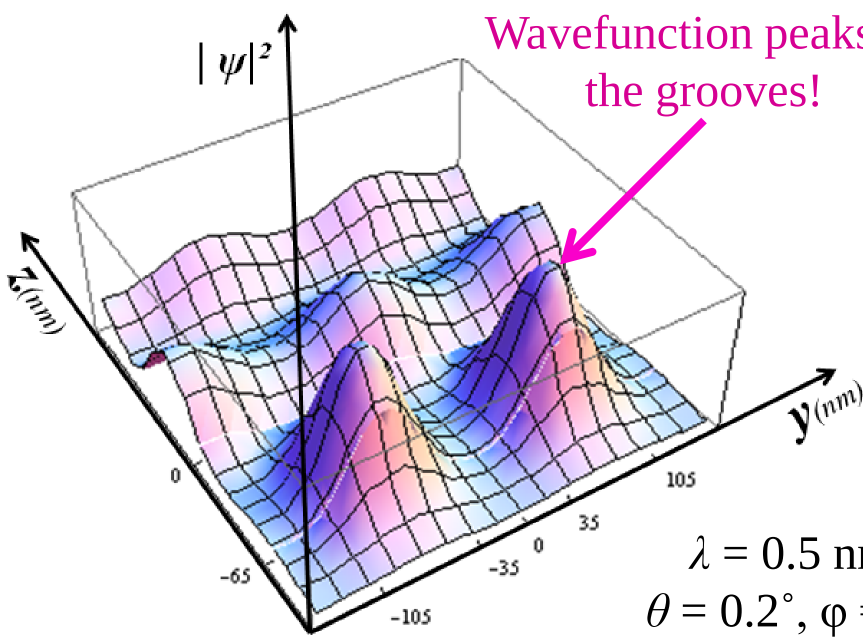
5. Theory predicts the band structure of neutrons in the 1D periodic potential.

$$v_l = \frac{1}{d}\int_{-d/2}^{d/2} dy e^{-ilgy} v_{mod}(y) = \frac{v_{silicon}}{l\pi}\sin(fl\pi)$$

$$\text{Band Gap} = 2v_1 = 2v_{Si}/\pi = 3.27 \longleftrightarrow v_{exact} = 3.06$$

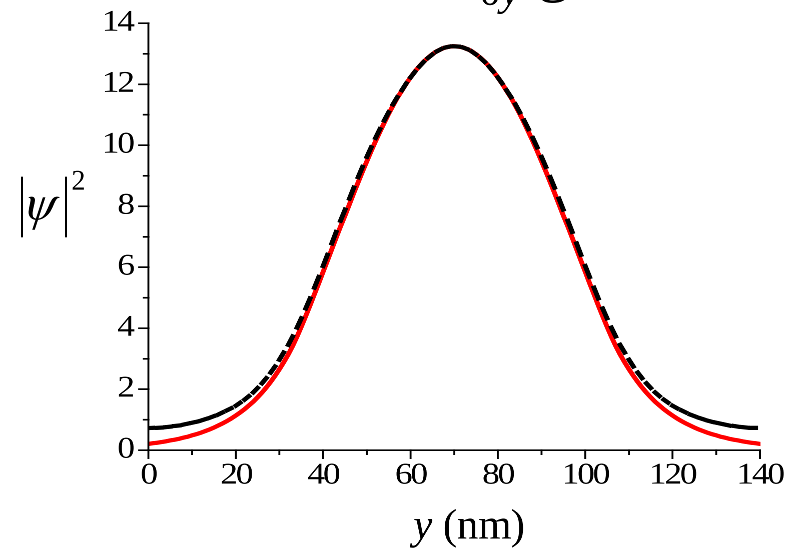


6. Theory explains the behavior of the neutron wavefunction in the vicinity of the grating.



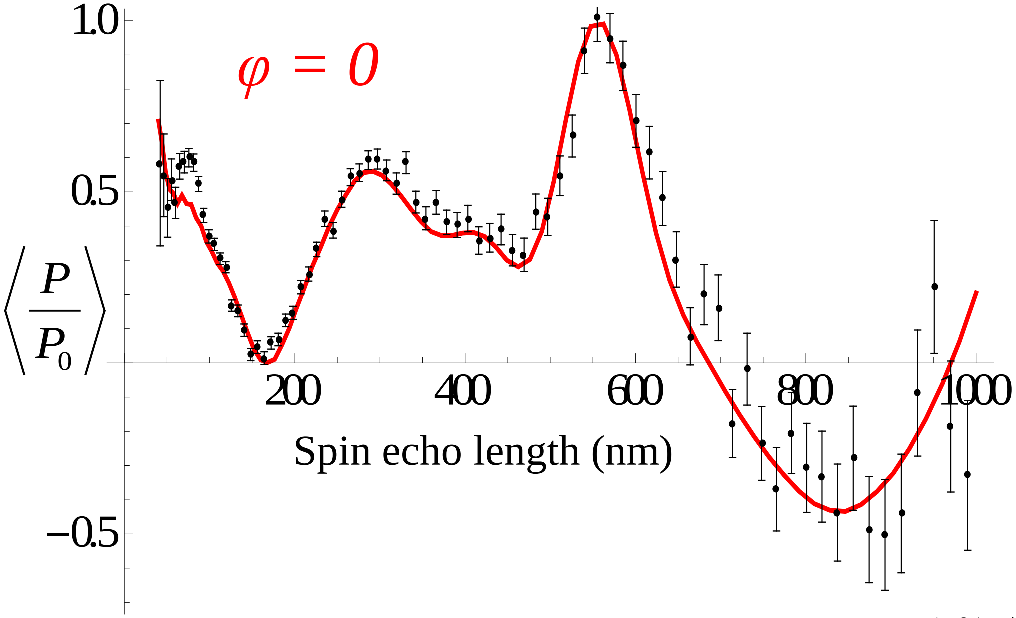
Wavefunction peaks in the grooves!

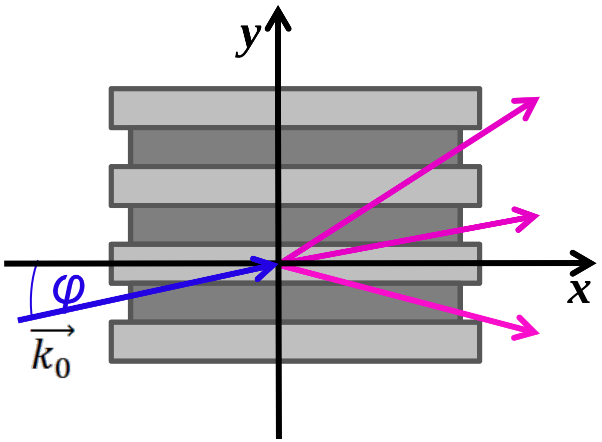
λ = 0.5 nm
θ = 0.2°, φ = 0°



z = – 45 nm, λ = 0.5 nm and θ = 0.2°

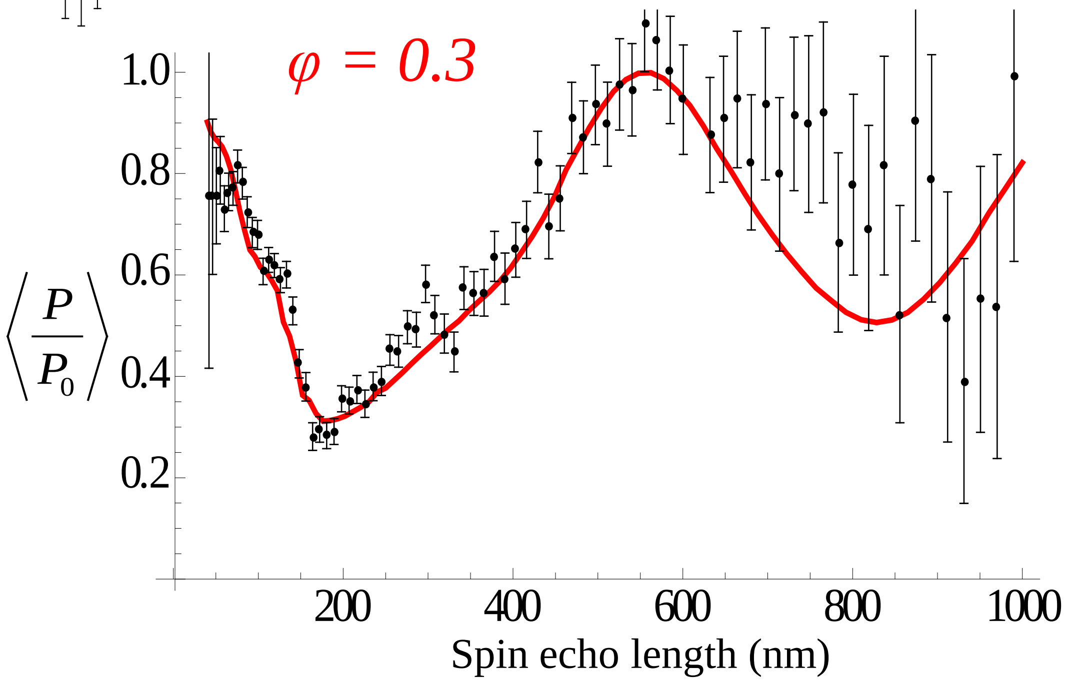
Sensitivity to the scattering geometry

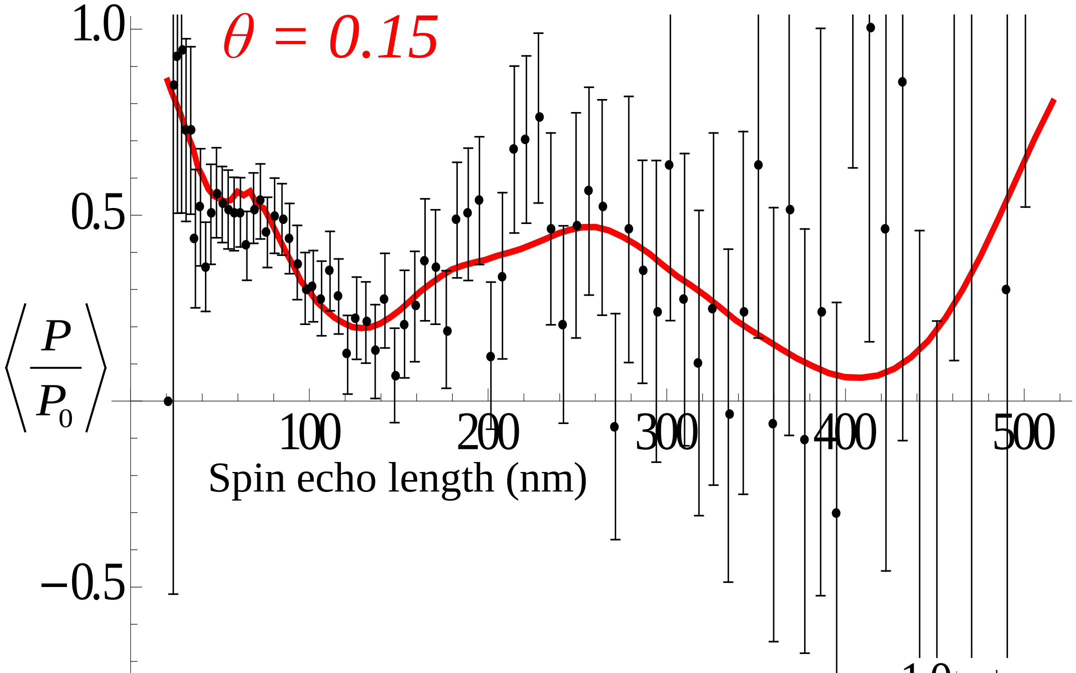


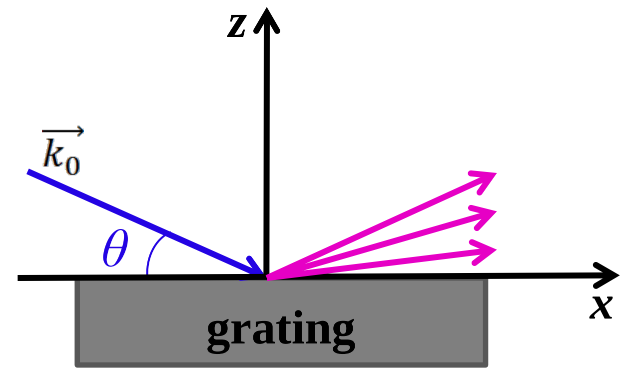


d = 556 nm, t = 110 nm, f = 0.5

$\theta = 0.15$

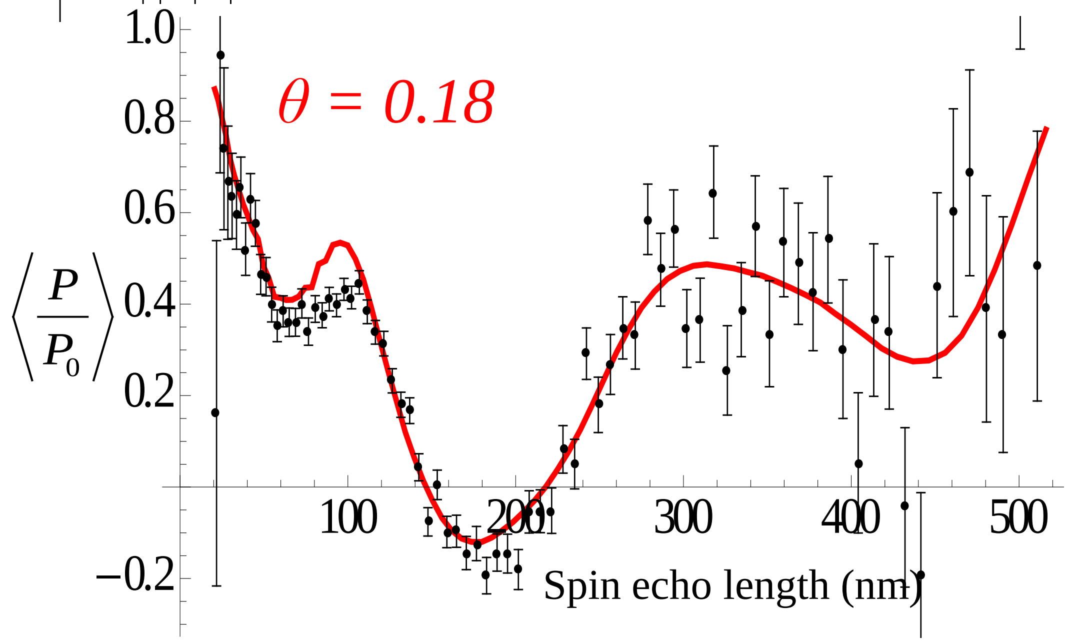




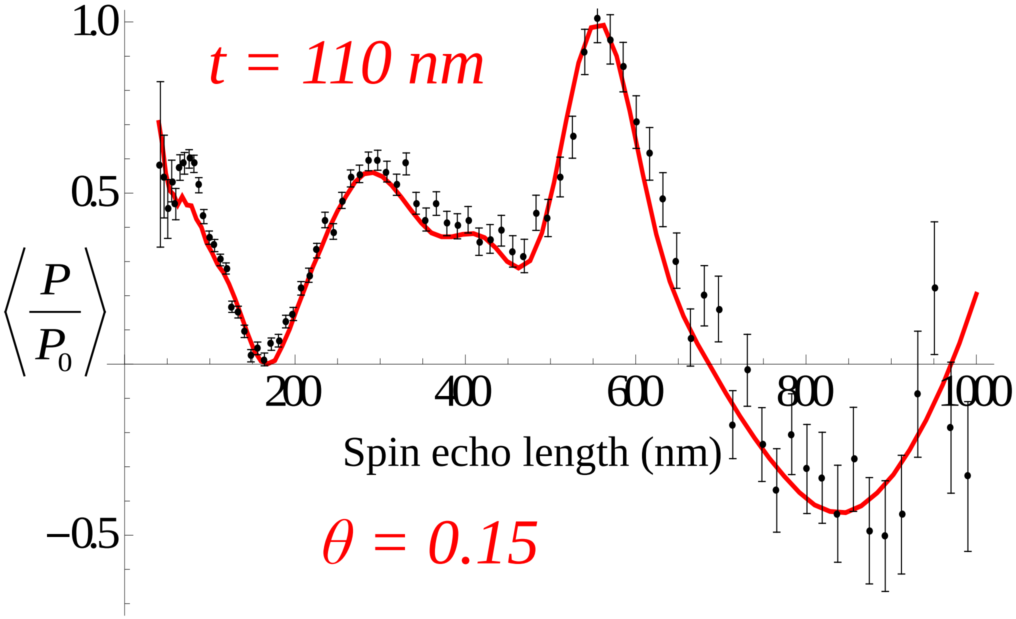


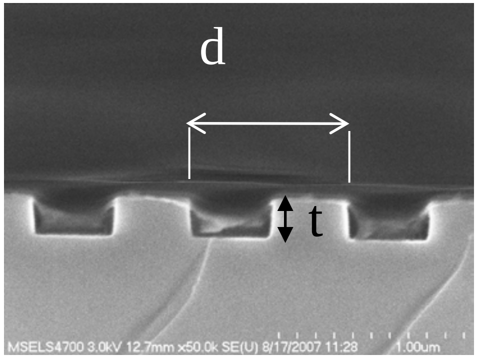
$d = 556\ nm,\ t = 140\ nm,\ f = 0.5$

$\varphi = 0$



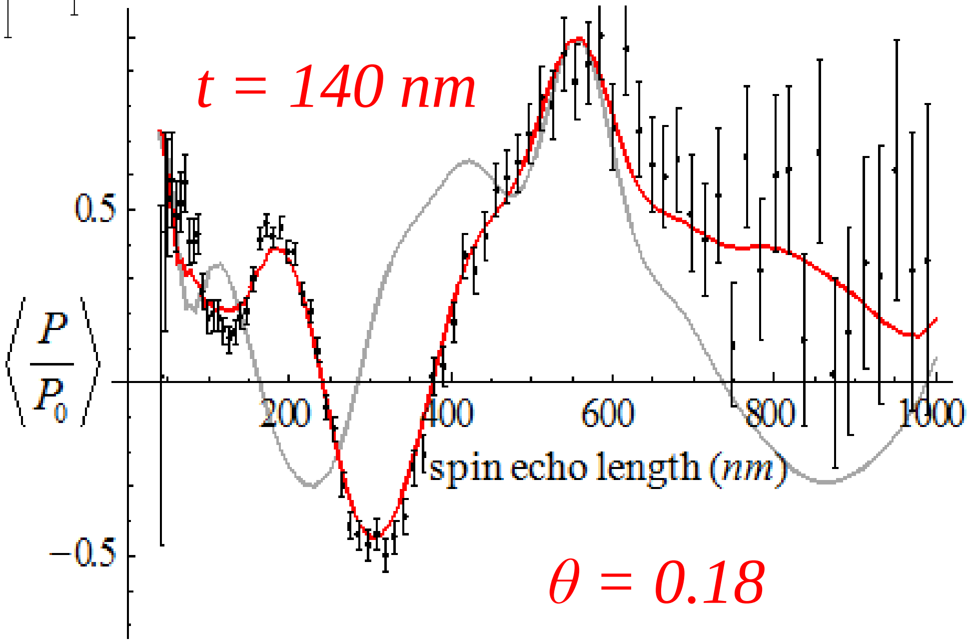
The result appears to be very sensitive to groove depth



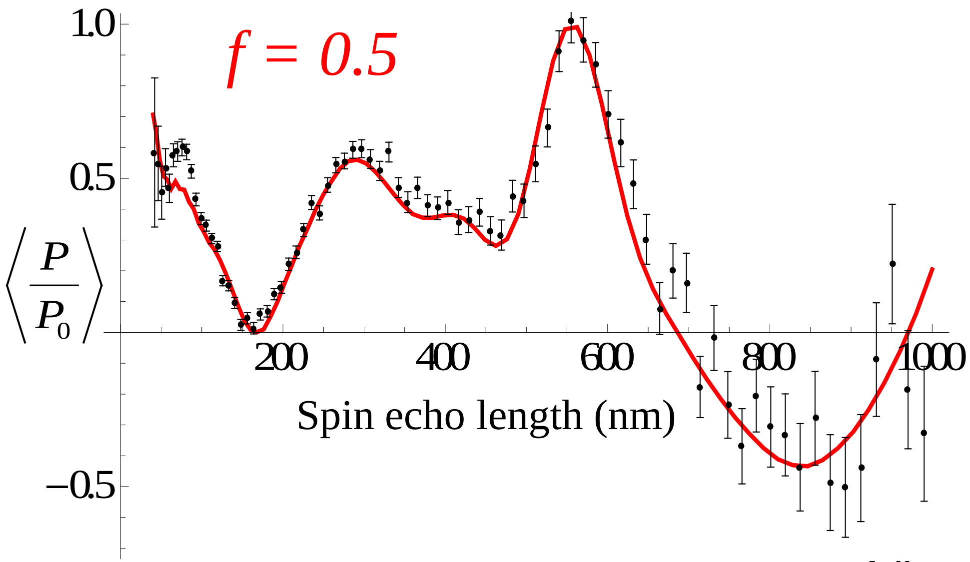


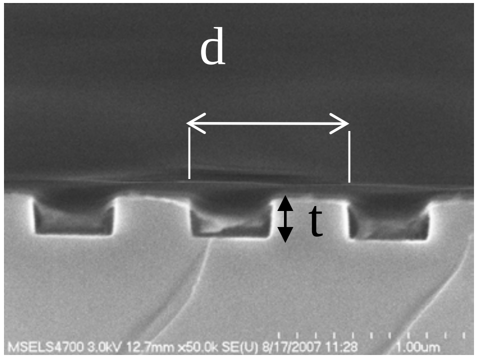
d = 556 nm, f = 0.5

Grey curve on the right is
for t = 110 nm and $\theta = 0.18°$



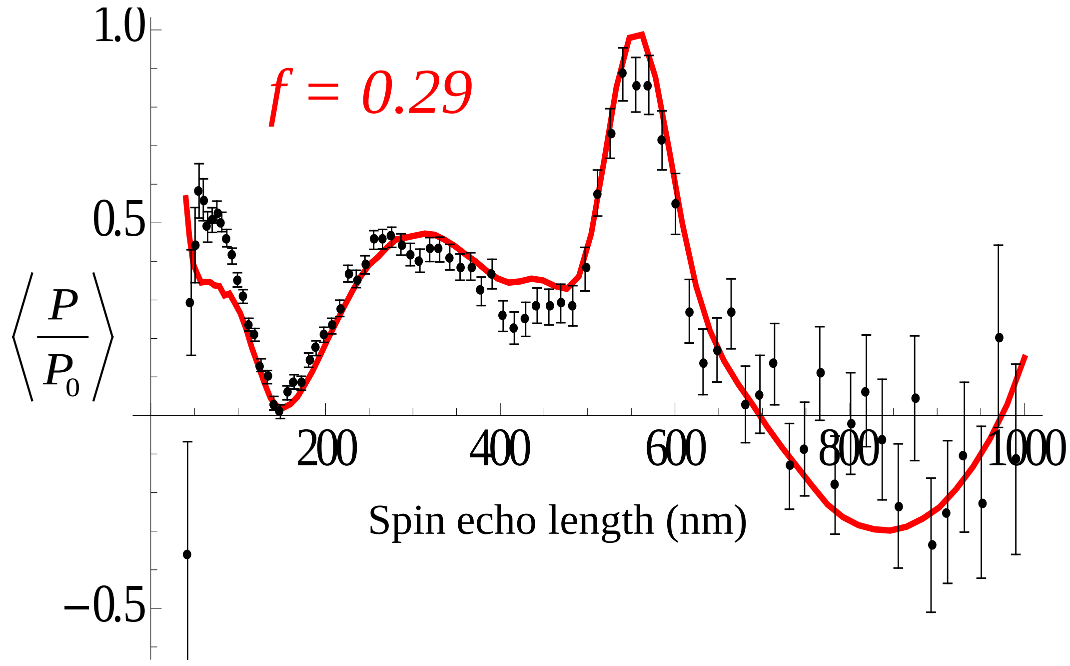
The result is not very sensitive to fill factor





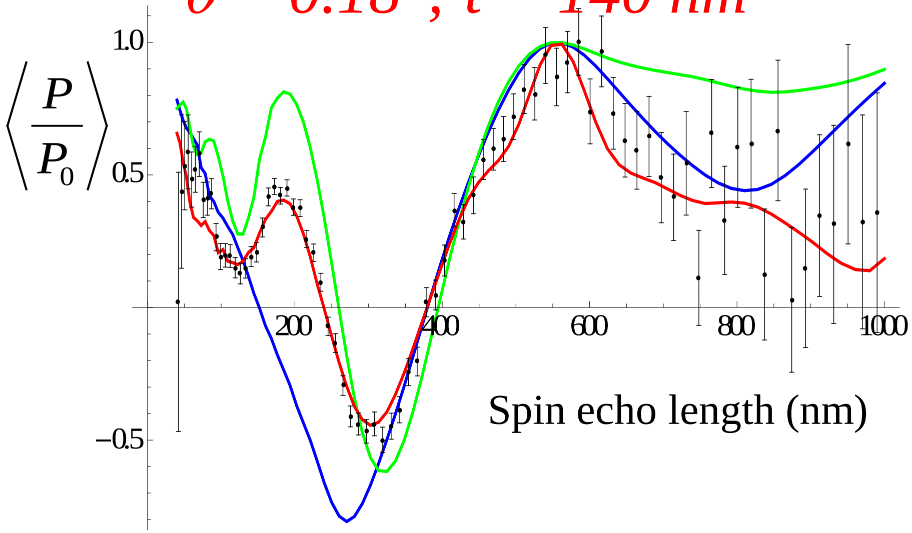
$d = 556$ nm, $t = 110$ nm

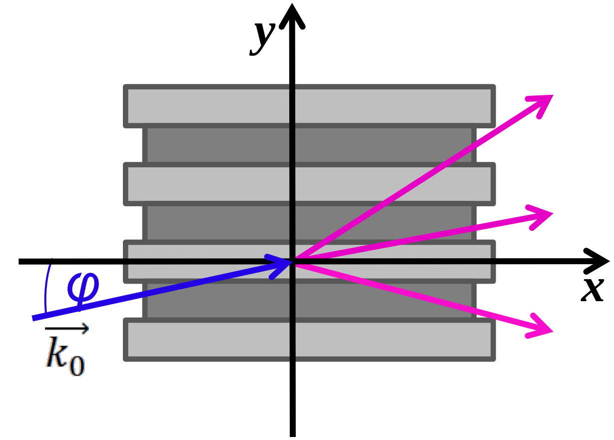
$\theta = 0.15$, $\varphi = 0$



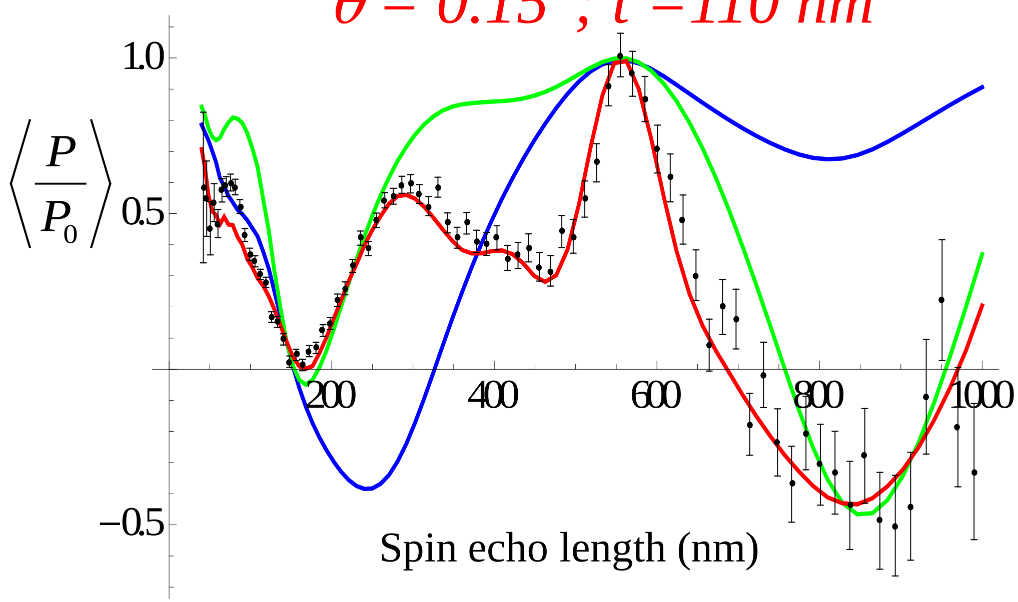
Comparison with POA (Green) and DWBA (Blue)

$\theta = 0.18\ ;\ t = 140\ nm$





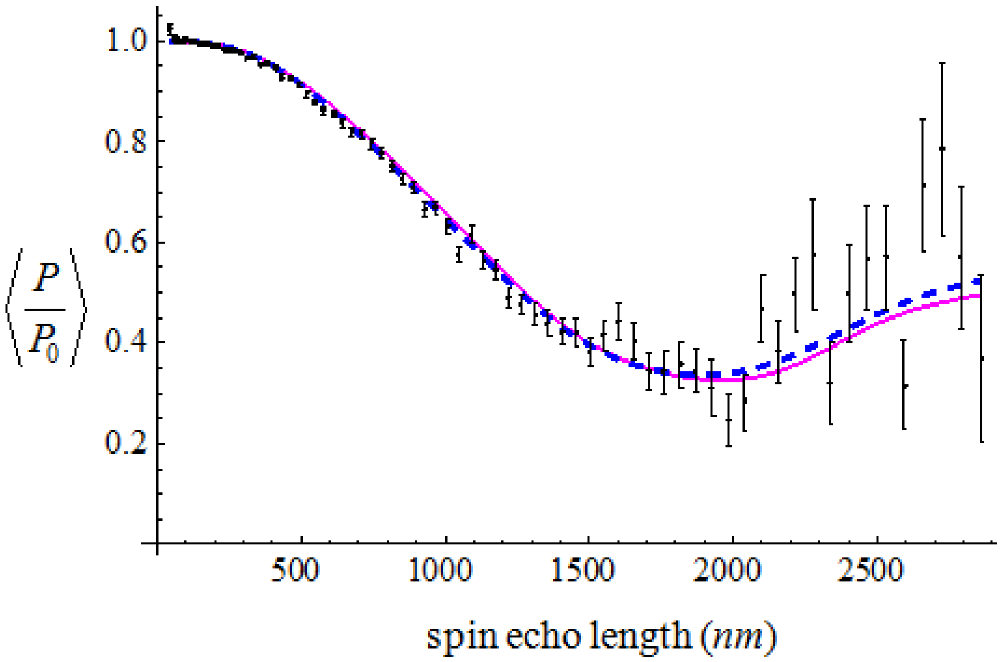
$\theta = 0.15\ ;\ t = 110\ nm$



$d = 556\ nm,\ f = 0.5,\ \phi = 0$

Sometimes approximate theories work; sometimes they don't

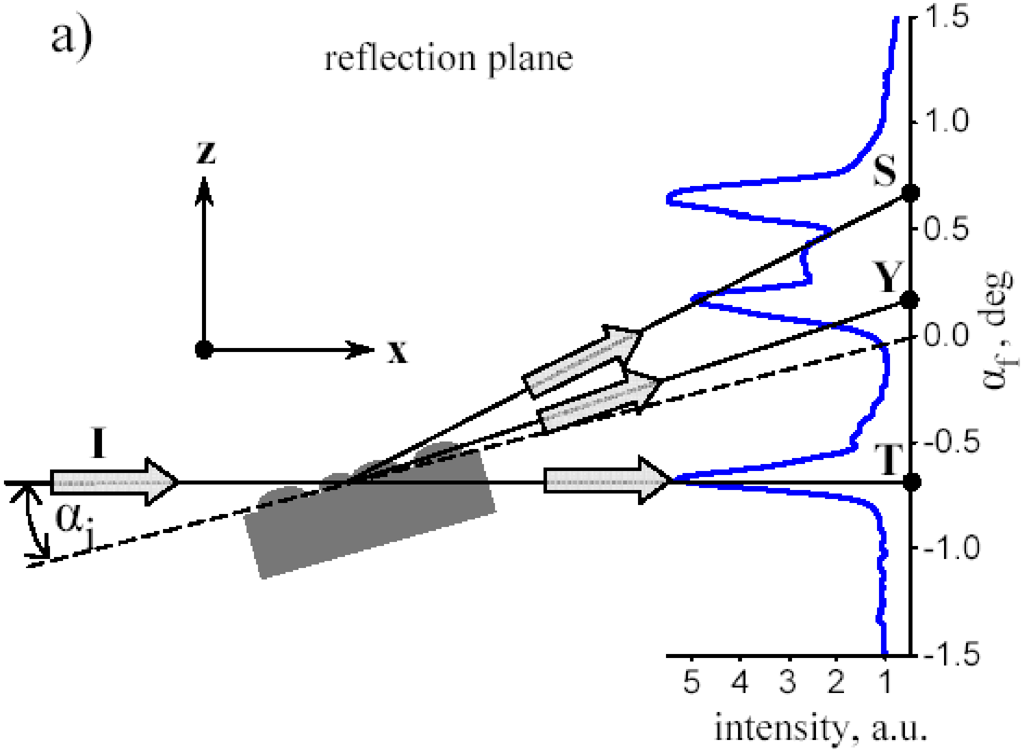
The POA (blue) Works as well as the DT (red) for Transmission through a Grating

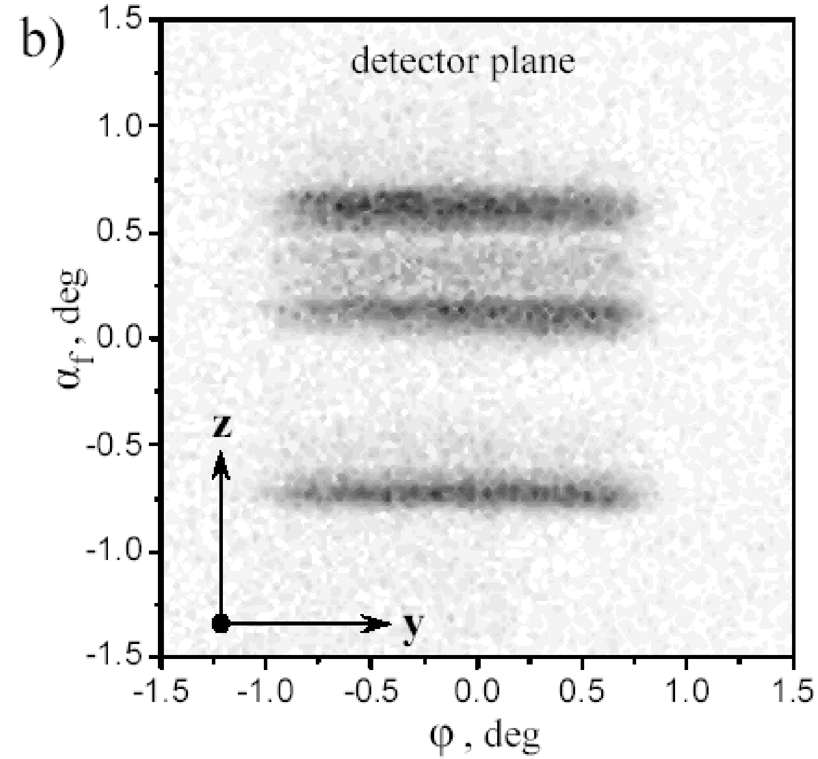


$d = 11.5\ \mu m$
$h = 46.1\ \mu m$

This is not unexpected. The Phase Object Approx was originally used for TEM. Also, in transmission the phase of the neutron wavefunction does not vary very much over the sample: it does in reflection.

What Happens for a "Rough" Sample in Reflection?



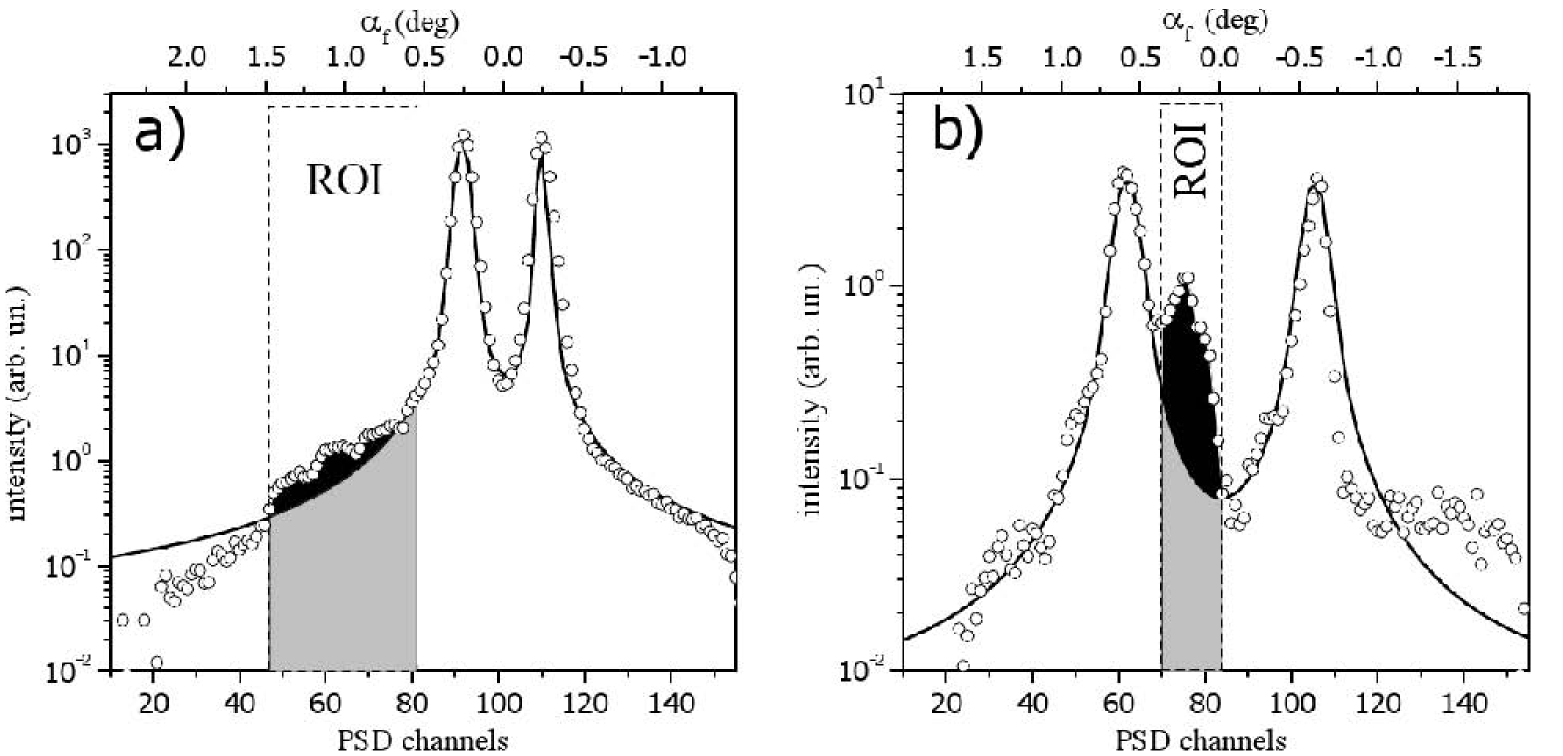


a) scattering geometry. The incident beam (I) impinges on the sample surface at a shallow angle α_i; transmitted (T), specular (S) and diffuse (Y) intensities are simultaneously recorded by PSD.

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.

Pictures from Vorobiev et al

The Useful Signal



(a) Incident angle less than critical angle; (b) Incident angle ~ 3 x critical

Pictures from Vorobiev et al

- Grey background (S + T) is fully polarized (P_0)
- Black area is diffuse scattering due to dewetted polymer
- P/P_0 over ROI is the weighted sum of the polarizations of black + grey
- Condition (b) is better because we want to find P/P_0 for black area

An Example: Dewetted Polymers on Silicon

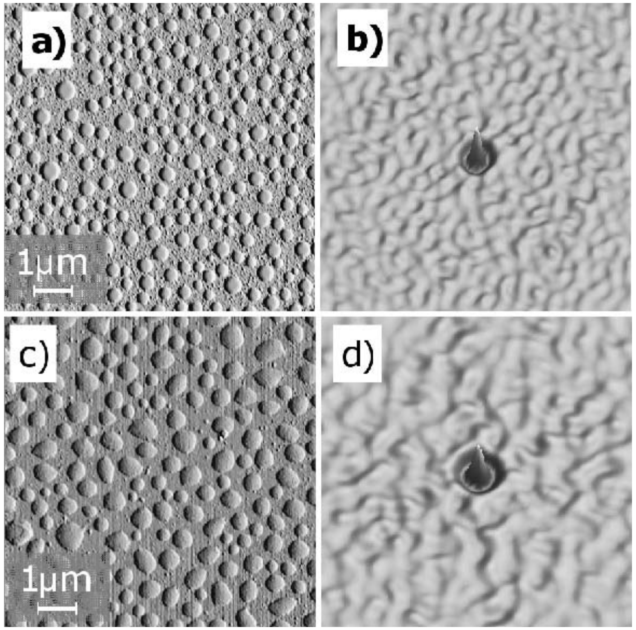
(Vorobiev et al: to be published)

- Three samples:

  (i) homo-polymer (d-PS);

  (ii) blend (d-PS + PpMS);

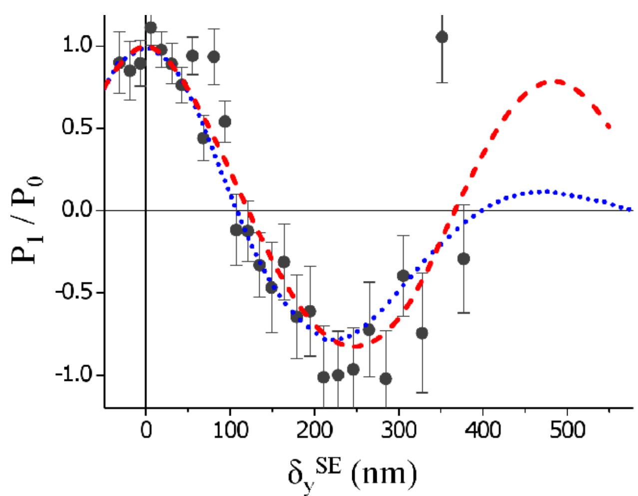
  (iii) symmetric BCP P(S-b-PMS)



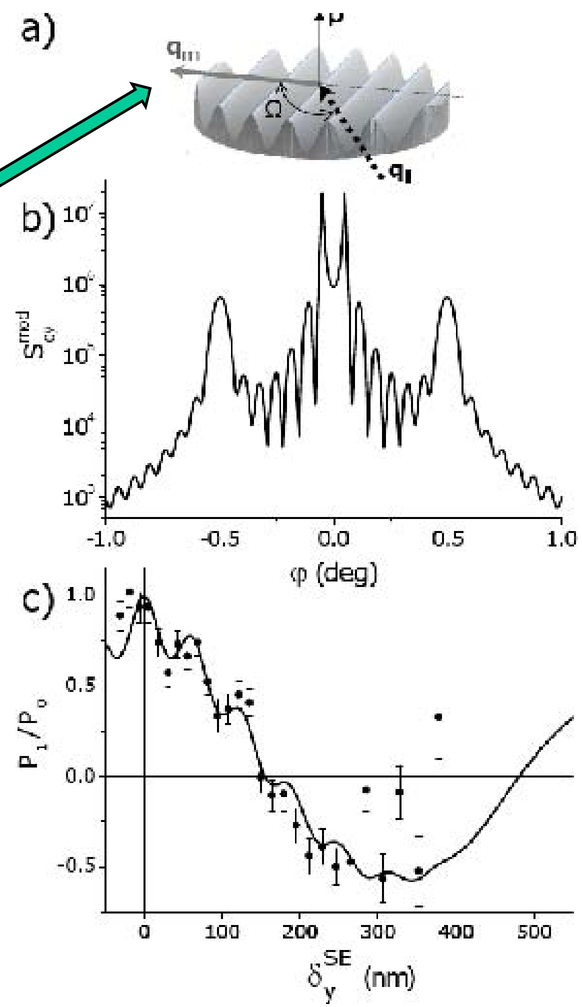
a) AFM of sample (ii)
b) Autocorrelation function of (a)
c) AFM of (iii)
d) Autocorrelation function of (c)

SERGIS Results on Dewetted Polymers

- Results for BCP show structure that is not present for the blend
- A model with lamellae oriented perpendicular to the surface (a) explains the data (c)



Polymer blend: SERGIS experiments plus model (red) and ACF (blue) from AFM

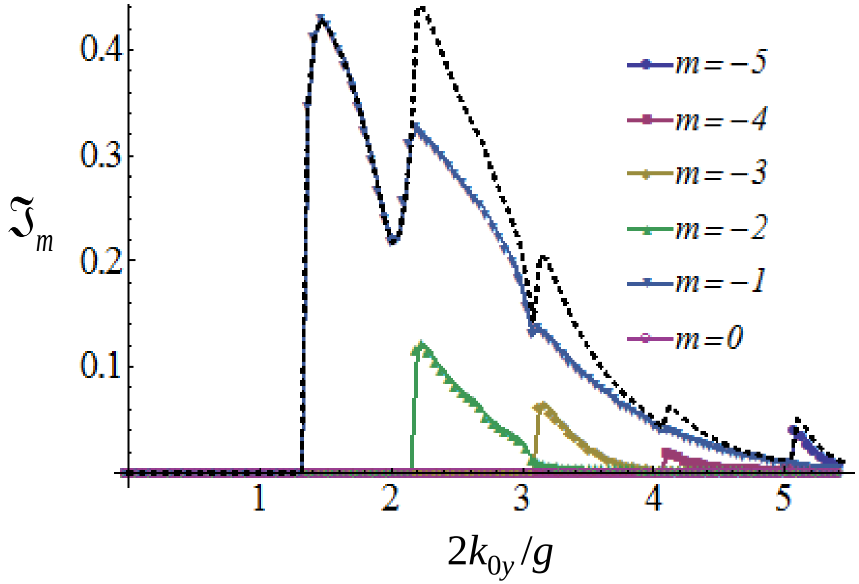


Can we use SERGIS to Study Surface Structure?

- Yes –if we can see Yoneda scattering
  - This means that there has to be SLD contrast on the several micron length scale in addition to the length scales of interest (50 nm – 500 nm)
  - The gain in measurement time is roughly the ratio of the collimations needed for traditional and SERGIS measurements
  - SERGIS yields a real space correlation function rather than S(Q)
- The problem for GISANS is that diffuse scattering is spread out in the specular plane making weak scattering hard to separate from background
  - A possible solution is to measure the scattering in the transmitted beam when the incident angle is well above critical – but this requires that we find a way to eliminate the unscattered beam – dark-field SESAME
- For now, the proven uses of SESAME are:
  - SESANS on strongly scattering samples
  - SERGIS on periodic samples with in-plane SLD contrast which give Yoneda peaks.

END

3. Theory determines the *turn on* points of the allowed transmitted beams



4. Theory obeys the optical theorem