Revealing the hidden microstructure of materials: *characterising surface and interfacial phenomena using reflectometry*

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Outline

- Motivation
  - The importance of interfaces
- Reflectivity
  - Introduction to the basic Ideas
  - Information contained
    - Specular/Off-specular
  - Practical Considerations
- Examples
- Outlook
  - Bright!

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Specular Scattering

Neutron and x-ray reflectivity

How do we connect the scattering length profile with the reflectivity

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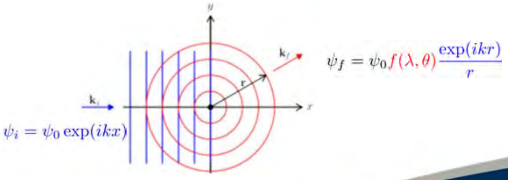
Scattering from a single (fixed) atom

- atomic nuclei via the short-range (fm) strong force;
- unpaired orbital electrons via a magnetic dipole interaction



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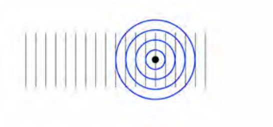
Scattering length

$$\sigma_{tot} = 4\pi b^2$$

Where *b* is the scattering length

- The sign of *b* is arbitrary
- A negative sign implies a change in the phase of the scattered wave
- *b* is sometimes complex and wavelength dependent due to resonant absorption
- *b* depends on the isotope
- *b* depends on the spin states of the neutron and nucleus



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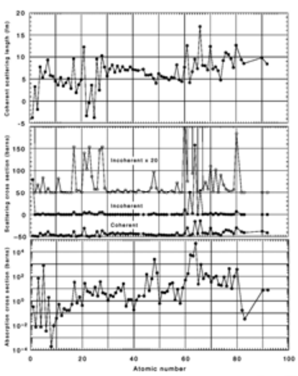

- Mass 1.67 x 10^{-27}kg 1.008665 atomic units
- Charge 0 (1.5 ±2.2) x 10^{-22}proton charge
- Spin ½
- Magnetic moment −1.913μ_N
- Electric dipole moment < 6 x 10^{-25}e-cm

$$\lambda = \frac{h}{mv}$$

$$E = \frac{h^2}{2m\lambda^2}$$

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Isotope Dependence

Nickel Isotope	Scattering length *b (fm)*
^{58}Ni	15.0(5)
^{60}Ni	2.8(1)
^{61}Ni	7.60(6)
^{62}Ni	-8.7(2)
^{64}Ni	-0.38(7)

Hydrogen Isotope	Scattering length *b(fm)*
1H	-3.7409(11)
2D	6.674(6)
3T	4.792(27)
O	5.803

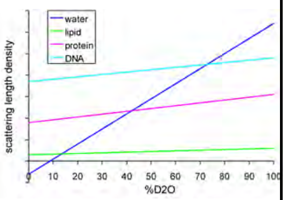
$$|11\rangle = \uparrow\uparrow$$
$$|10\rangle = (\uparrow\downarrow + \downarrow\uparrow)/\sqrt{2}$$
$$|1\ -1\rangle = \downarrow\downarrow$$
$$|00\rangle = (\uparrow\downarrow - \downarrow\uparrow)/\sqrt{2}$$

- Isotopic substitution for contrast
- Isotopic substitution to move peak positions in spectroscopy
- Incoherent scattering

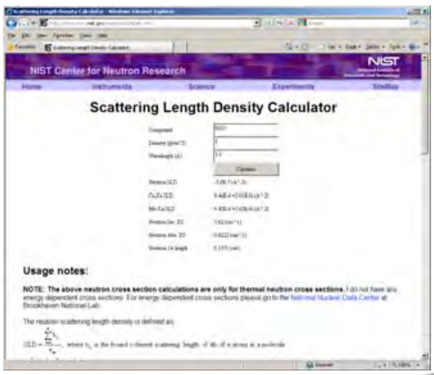
Scattering length density

$$SLD = \sum_i b_i \frac{DN_a}{M_w}$$

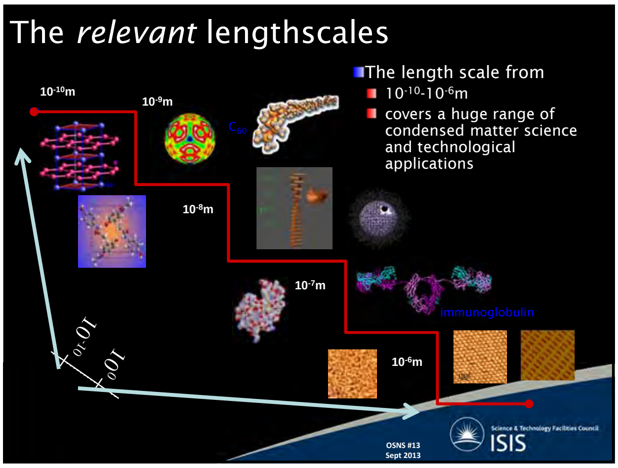
Solvent	ρ (h form) (×10^{10} cm^{-2})	ρ (d form) (×10^{10} cm^{-2})	Polymer	ρ (h form) (×10^{10} cm^{-2})	ρ (d form) (×10^{10} cm^{-2})
Water	−0.56	+6.38	PB	−0.47	+6.82
Octane	−0.53	+6.43	PE	−0.33	+8.24
Cyclohexane	−0.28	+6.70	PS	+1.42	+6.42
Toluene	+0.94	+5.66	PEO	+0.64	+6.46
Chloroform	+2.39	+3.16	PDMS	+0.06	+4.66
Carbon Tet.	+2.81		PMMA	+1.10	+7.22



SLD



http://www.ncnr.nist.gov/resources/sldcalc.html


The relevant lengthscales
The length scale from
10-10-10-6m
covers a huge range of condensed matter science and technological applications
10-10m
10-9m
10-8m
10-7m
10-6m
immunoglobulin
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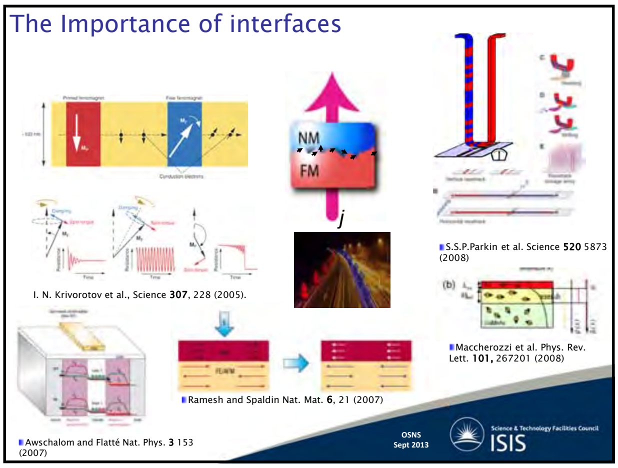
The Importance of interfaces
NM
FM
j
I. N. Krivorotov et al., Science 307, 228 (2005).
S.S.P.Parkin et al. Science 520 5873 (2008)
Maccherozzi et al. Phys. Rev. Lett. 101, 267201 (2008)
Ramesh and Spaldin Nat. Mat. 6, 21 (2007)
Awschalom and Flatté Nat. Phys. 3 153 (2007)
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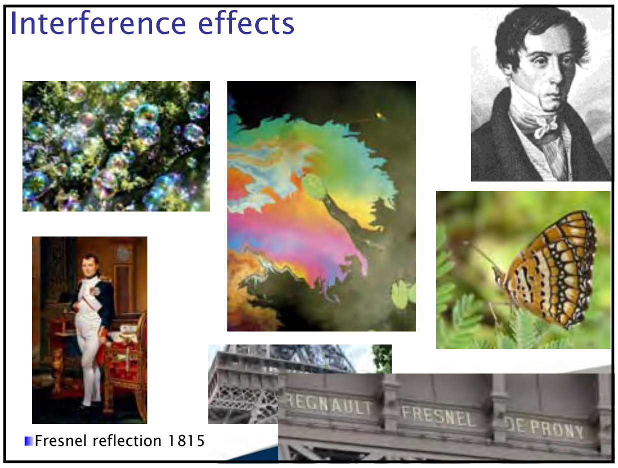
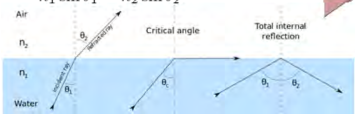

Interference effects
Fresnel reflection 1815
REGNAULT
FRESNEL
DE PRONY

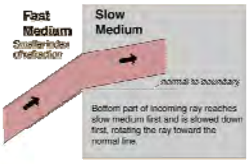
Refractive Index

$n = \frac{c}{v}$

- n varies with wavelength: dispersion

$n_1 \sin\theta_1 = n_2 \sin\theta_2$





http://hyperphysics.phy-astr.gsu.edu
en.wikipedia.org

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$$
\begin{aligned}
n &= 1 - \lambda^2 A - i\lambda B && (1)\\
A &= \frac{Nb}{2\pi} && (2)\\
B &= \frac{N(\sigma_a + \sigma_i)}{4\pi} && (3)
\end{aligned}
$$

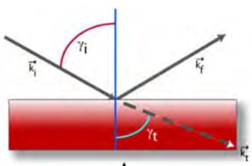
$$
\begin{aligned}
n &= 1 - \alpha - i\beta && (1)\\
\alpha &= \frac{N\lambda^2 |r_e}{2\pi} && (2)\\
\beta &= \frac{\lambda\mu}{4\pi} && (3)
\end{aligned}
$$

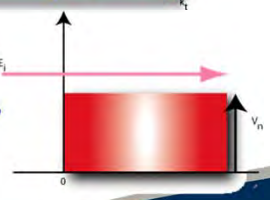
n <1 Total External reflection

Index of Refraction: Neutrons

$$
\begin{aligned}
n &= \frac{\sin\gamma_i}{\sin\gamma_t}\\
&= \frac{|\vec{k}_t|}{|\vec{k}_i|}\\
n^2 &= \frac{|\vec{k}_t|^2}{|\vec{k}_i|^2}\\
&= \frac{E_t}{E_i}\\
&= \frac{E_i - V_n}{E_i}\\
&= 1 - \frac{4\pi}{k_i^2} Nb
\end{aligned}
$$

$V_n = \frac{2\pi\hbar^2}{m_n} Nb$





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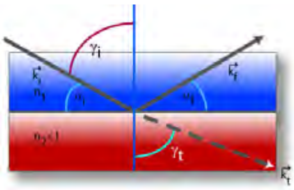
Critical Reflection

- $\frac{\cos\alpha_i}{\cos\alpha_f} = \frac{n_2}{n_1}$
- At the critical angle

  $\frac{\cos\alpha_i}{\cos 0} = n$

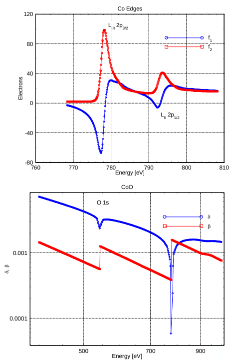
$$\begin{aligned} Q_c &= \frac{4\pi}{\lambda} 2k\sin\alpha_c \\ &= 2k\sqrt{1-\cos^2\alpha_c} \\ &= \sqrt{4k^2\left(1-n^2\right)} \\ &\cong \sqrt{4k^2\cdot 2\delta} \\ &= \sqrt{16\pi N b} \end{aligned}$$



Material	θ_c / Å
Ni	0.1
Cu	0.083
Al	0.047
Si	0.047
D_2O	0.082

- Q_c only depends on the material!

Index of Refraction: Photons

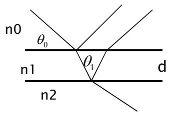


$$\begin{aligned} n &= 1-\delta-i\beta \\ &= 1-\frac{r_e}{2\pi}\lambda^2\sum_i n_i f_i(0) \\ f(0) &= f_1 + i f_2 \\ &= f_1 + i\frac{\sigma_a}{2r_e\lambda} \\ &= Z^* + \frac{1}{\pi r_e h c}\int_0^\infty \frac{\epsilon^2\sigma_a(\epsilon)}{E^2-\epsilon^2} \end{aligned}$$

http://www-cxro.lbl.gov/optical_constants/

Fresnel's law for a thin film

$$r_{ij} = \frac{p_i - p_j}{p_i + p_j}$$

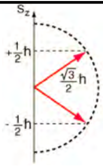


$$p_i = n_i \sin\theta$$

$$\beta_i = \frac{2\pi}{\lambda} n_i d_i \sin\theta_i$$

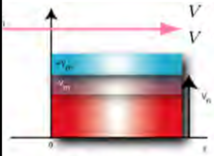
$$R(Q) = \left|\frac{r_{01} + r_{12}\exp(-2i\beta_i)}{1 + r_{01}r_{12}\exp(-2i\beta_i)}\right|^2$$

Using the neutron's spin



- The neutron is a spin ½ particle
- The neutron possesses an intrinsic magnetic moment: spin
- Caution…

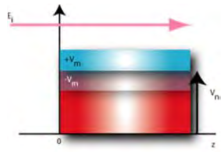
Nuclear Magnetic



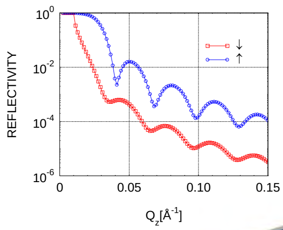
$$V = V_n + V_m \quad (1)$$
$$V = \frac{\hbar}{2\pi m} Nb - \mu \cdot \mathbf{B} \quad (2)$$
$$= -4\pi\mu_n \cdot M \quad (3)$$
$$= -\frac{2\hbar\pi^2}{m_n} p(z)\sin(\theta) \quad (4)$$
$$= \frac{2\hbar\pi^2}{m_n}\frac{M_p}{M_s}N\frac{m_n\mu_n\mu_0}{2\pi\hbar^2}\mu_s \quad (5)$$

$$\vec{\mu_n} = \gamma\mu_N\vec{\sigma}$$
$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

PNR from a single layer

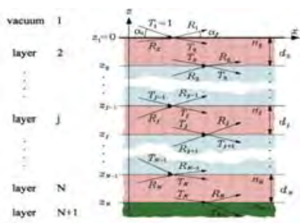


$$V = V_n + V_m \quad (1)$$
$$V = \frac{\hbar}{2\pi m} N(b \pm p) \quad (2)$$

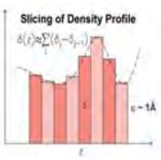


Parratt Iteration


Surface Studies of Solids by Total Reflection of X-Rays

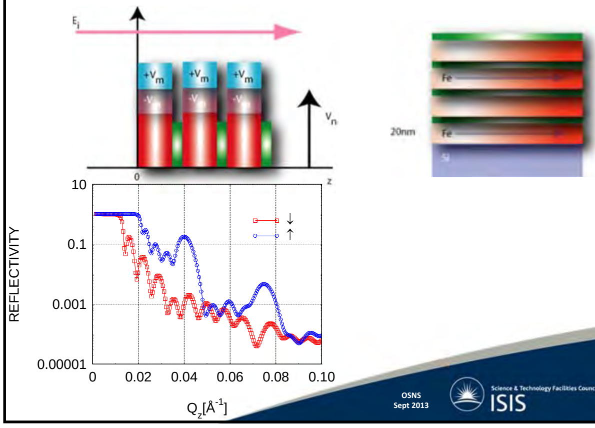


$$X_j = \frac{R_j}{T_j} = \exp(-2ik_{z,j}z_j)\frac{r_{j,j+1} + X_{j+1}\exp(2ik_{z,j+1}z_j)}{1 + r_{j,j+1}X_{j+1}\exp(2ik_{z,j+1}z_j)}$$



Can now simulate profile with a "*slice and dice*" approach

PNR from a multiple layers



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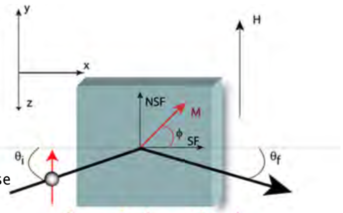
Spin dependent cross-section

- In-plane orientation of magnetisation obtainable from 4 spin dependent cross-sections

- Components of the magnetisation, m give rise to
- m||H: Non Spin Flip Scattering (NSF)
- m ⊥H: Spin Flip Scattering (SF)
- Dynamical analysis gives absolute depth dependence profile



$$b = b + p \sin\phi$$

$$p_m \cos\phi = p_x$$

$$\left[\frac{-\hbar^2}{2m_n}\nabla^2 + V(r)\right]\Psi^{\uparrow,\downarrow} = E\Psi^{\uparrow,\downarrow}$$

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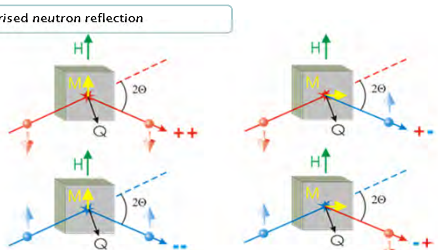
Polarisation

Polarised neutron reflection



Non spin flip
++ measures b + M_z
- - measures b - M_z

Spin flip
+ - measures M_x + iM_y
- + measures M_x - iM_y

By fitting all components the direction and strength of the magnetic moment can be measured as a function of depth

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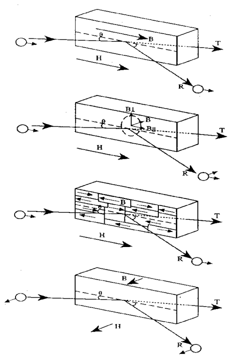
Effects of magnetisation on neutron reflectivity



(a) Spin dependent reflectivity, potential is Zeeman split

(b) Rotation of the neutron polarisation. Resonance or spin flip channel

(c) Average of the 2 spin states

(d) Pure nuclear, the component of B normal to the surface is continuous across the surface

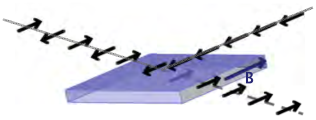
$$\nabla \cdot \vec{B} = 0$$

G.P. Felcher, Physica B, **192**, (1993), 137

Polarisation

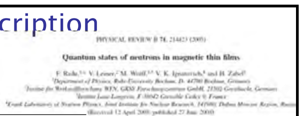
Polarising supermirrors

Magnetic materials have a spin dependent term in their refractive index



An ~60%/40% Fe/Co mirror works well at saturation

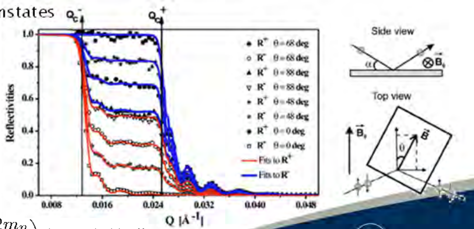
Caveat to Classical Description



- CD predicts a continous variation of critical edge

$$\frac{4\pi \sin(\alpha_c^{\pm})}{\lambda} = Q_c^{\pm} = \sqrt{\frac{2m_n}{\hbar^2}\left(V_n \pm |\mu|\,|B_s|\cos(\theta)\right)}$$

- Stern-Gerlach effect? Only 2 eigenstates



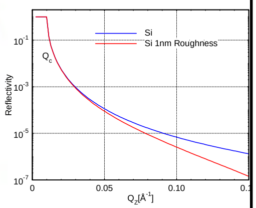
$$k_{\pm}^2 = \left(\frac{2m_n}{\hbar^2}\right)(V_n \pm |\mu|\,|B|)$$

Roughness

Structural and magnetic interfacial phenomena

Structural Roughness

$$R(Q) = R_F \exp\left(-Q^2\sigma^2\right)$$



PHYSICAL REVIEW B VOLUME 38, NUMBER 4 1 AUGUST 1988

X-ray and neutron scattering from rough surfaces

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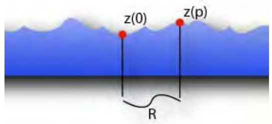
H. B. Stanley†
University of Maryland, College Park, Maryland 20742
(Received 30 November 1987)

$$C(R) = \left\langle \left[z(x,y) - z(x',y')\right]^2 \right\rangle$$
$$= \sigma^2 \exp(-r/\xi)^{2h}$$



- σ= roughness
- ξ= cut-off length:
  - for R > ξ, interface appears smooth,
  - for R < ξ, interface appears rough, fractal behaviour
- h=3-D Hurst parameter for jaggedness(0<h<1)
  - smooth: D=2, h=1
  - very rough D=3, h=0

Simulation Packages

Simulation Packages: neutron

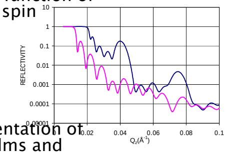
- Neutron
  - Polly
    - http://www.isis.rl.ac.uk/LargeScale/CRISP/data_analysis_software.htm

Simulation Packages: photon

- X-ray
  - http://sergey.gmca.aps.anl.gov/
  - ESRF
  - RefTool

Spin polarised Neutron Reflectivity

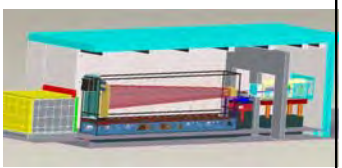
- Measure the reflected neutrons as a function of their perpendicular momentum and spin eigenstate
- $k^{\pm} = \sqrt{k - 4\pi N(b \pm cB)}$



- Can observe the magnitude and orientation of atomic magnetic moments in thin films and multilayer media.
- Probe length scale (<1nm to >1000nm): covers many aspects of thin film structure and magnetism
- Complementary to:
  - VSM/SQUID
  - MOKE average magnetisation over the sample thickness
  - SEMPA, Lorentz surface domain magnetisation
  - XMCD/XRMS-element specific
- PNR gives the microscopic *in-plane vector* magnetisation *depth* profile.

Inter

- Designed for the study of chemical interfaces, with a particular emphasis on the air-water interface
- >10 times the flux of SURF
- Much wider dynamic range
- Tuneable resolution

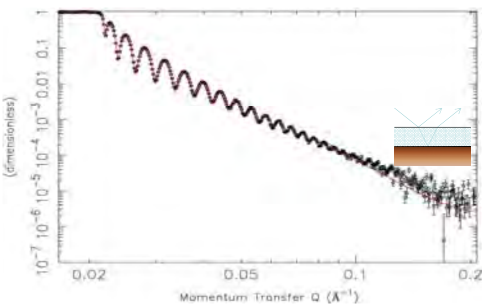


Scientific Opportunities

- Biology

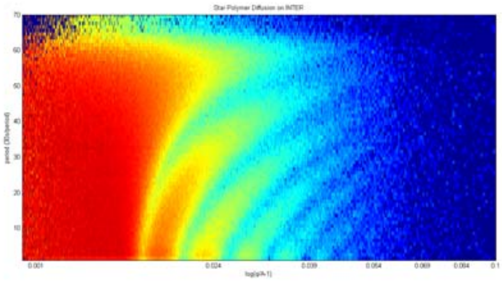
D-spacing range	1 – 16 (22) Å
Moderator	Coupled s-CH_4 grooved – 26K
Primary flight path	17m (m=3 supermirror guides)
Secondary flight path	3-7 m
Beam size	60(h) x 30(v) mm
Flux at sample	~10^7 n/s/cm^2

First Results 29 sep 08



First reflectivity measured on INTER. Nickel/Carbon film (1216 Å) on glass

Kinetics



- Star Polymer
- D.G. Bucknall *(2010)*

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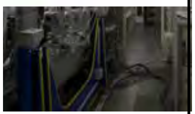
PolRef

- Wavele
- Unpola
- Polariz
- Source
- Beam i
2.3°
- Well shielded Helium tube
- 640 channel linear gas detector with 0.5mm pixel
- Vertical 2θ 7.5°
- Horizontal 2θ 22°



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Reflectometry Village

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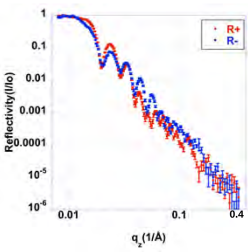
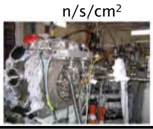


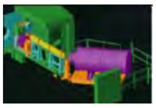
ASF08 T=10K, 3 angles (θ=0.4, 1.6, 3.2)

Reflectometers

- Continuous or tof mode of operation
- 5Å Monochromator (6Å Polarised)
- White beam flux 9.6×10^9 n/s/cm^2



- The CRISP reflectometer at ISIS is a white beam time of flight (tof) polarised neutron reflectometer viewing a 20K hydrogen moderator.



http://www.ill.fr/YellowBook/D17/

http://www.ill.fr/YellowBook/ADAM/

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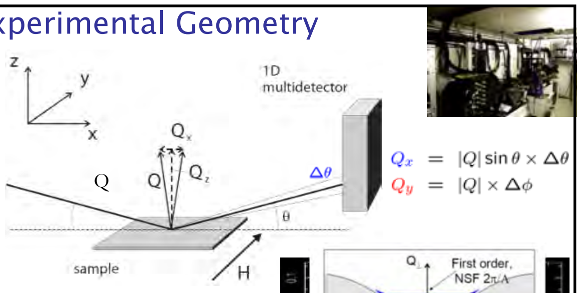
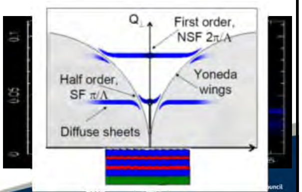
Off-specular scattering

Probing in-plane lengthscales

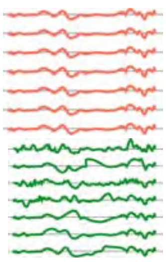
Experimental Geometry

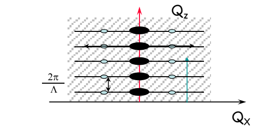


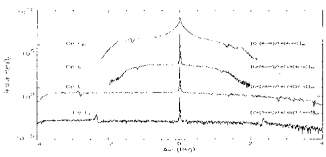
- λ range 0.5-6.5Å
- 1-d Detector
- Typical acquisition~2hours/field
- Measured coherence length ~30μm



Diffuse scattering







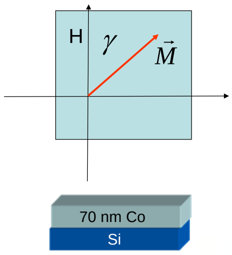
(Ce/Fe) Tixier, Mannix et al.

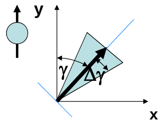
Holý and Baumbach, prb, 49, 10668, (1994)

Domains and the coherence volume

Many thanks to H. Zabel for slides

Simulation of a Co film on a substrate



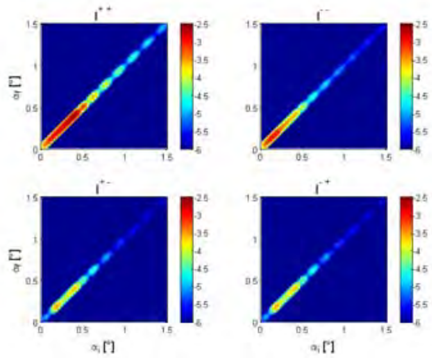


$\langle \cos\gamma \rangle = 0.7; \langle \sin^2\gamma \rangle = 0.25;$

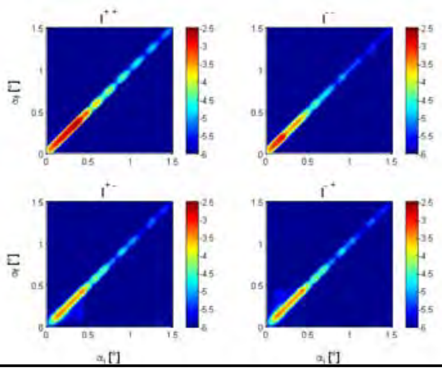
$\langle \cos\Delta\gamma \rangle; \langle \sin^2\Delta\gamma \rangle$

$L_c \approx 100\mu m$

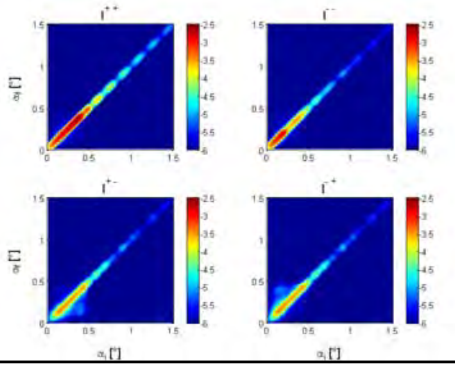
Domain size: 100 μm (> L_c)



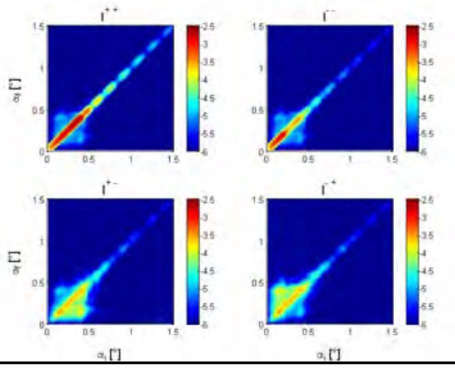
Domain size: 100 μm



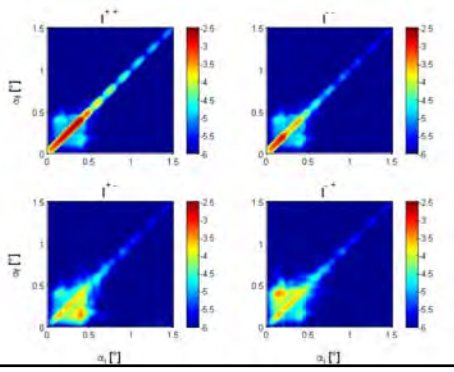
Domain size: 50 μm



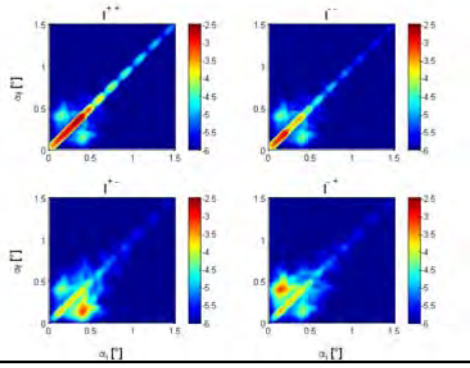
Domain size: 10 μm



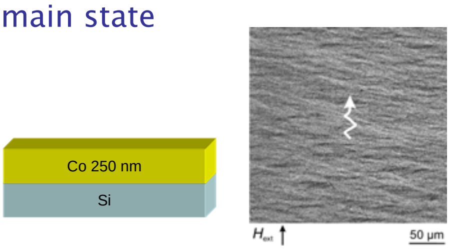
Domain size: 5 μm



Domain size: 1 μm

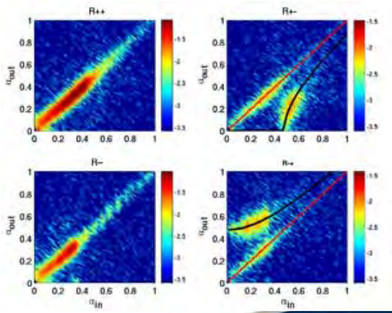


Single ferromagnetic film in the domain state

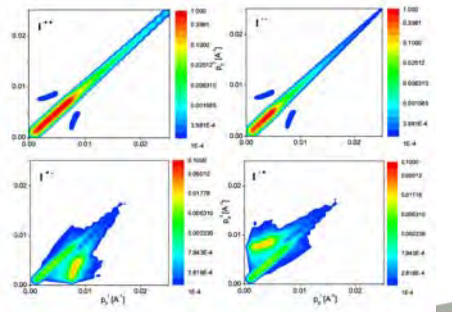


- F. Radu *et al*, J. Phys.: Condens. Matter **17** (2005) 1711-1718

Banana shape off-specular scattering from domain state



Simulation of domain state



- B.P. Toperverg Physica B **297** (2001) 160-168

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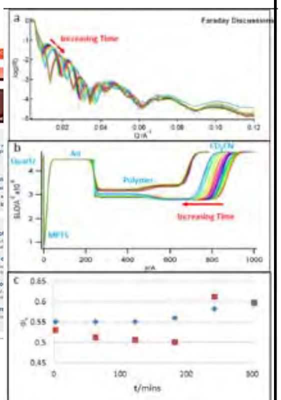

- Combining Figaro and INTER

A. R. Hillman et al. Faraday Discussions (2013).

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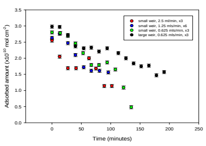
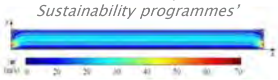
Kinetics of surface desorption

Kinetics of anionic surfactant desorption followed by neutron reflectivity on INTER

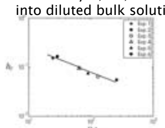
Small trough, d-LAS4/nrw



'Understanding and optimising surfactant rinse mechanisms important for Sustainability programmes'



Diffusion from a near-surface stagnant layer, Hc, into diluted bulk solution



Kinetics determined by Hc (from mathematical model) and scales with Peclet number (flow conditions)

C. Morgan, C. Breward, I. Griffiths, P. Howell, J. Penfold, R. Thomas, I. Tucker, J. T. Petkov, and J. R. P. Webster, Langmuir **28**, 17339 (2012).

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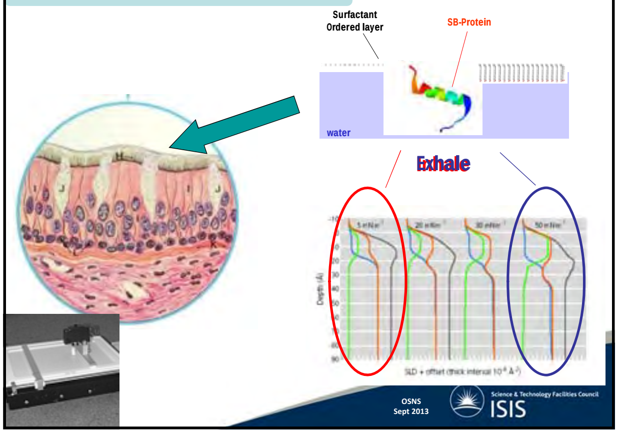
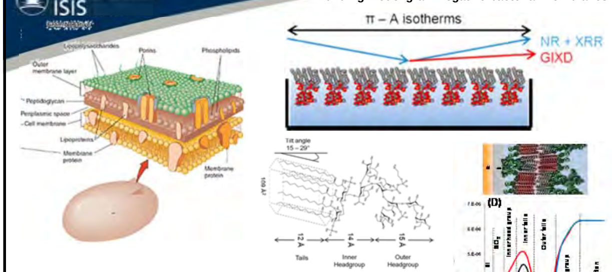
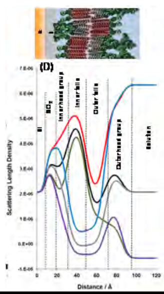
Breathe easy: Surfactants in the lungs



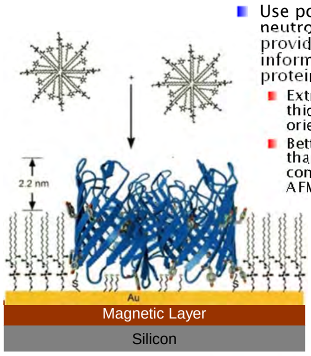
Building model gram negative bacterial membranes



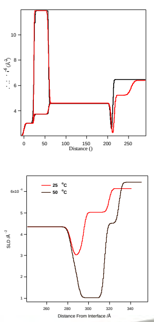
- Gram negative bacteria due to their increasing antibiotic resistance and their role in biotechnological processes.
- The asymmetric membrane is the outer surface.
- Work has been on going to produce accurate models of the gram negative bacterial membrane using extracted bacterial lipopolysaccharides for future use in biophysical studies on membrane behaviour and interactions.



Polarised Neutrons for Biology



- Use polarised neutrons to provide additional information for protein absorption
  - Extract protein thickness and orientation
  - Better resolution than conventional AFM studies

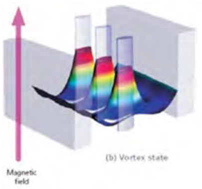


Superconducting Spintronics

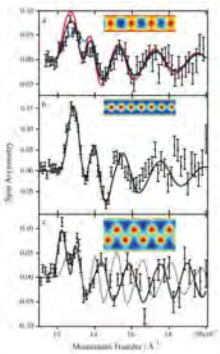
Generation of spin-triplets

Visualising the Flux distribution

$d = 195nm$



$d = 250nm$



A Drew *et al* Phys. Rev. B. **80** 134510 (2009)

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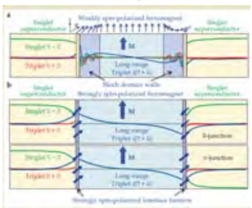
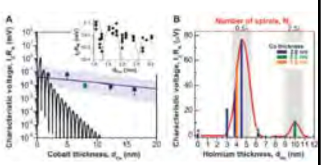
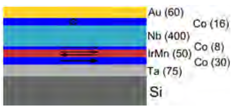
Generating a triplet state







- first found in heavy fermion materials such as UGe_2 or URhGe
- *orbital* and *spin* components of the wavefunction are both *even* with respect to electron exchange, thus they must be an *odd-frequency*, odd with respect to time reversal
- non-collinear magnetism within a distance of the coherence length required

- Robinson et al *Science* **329**, 59 (2010)
- M. Eschrig Physics Today (2011)

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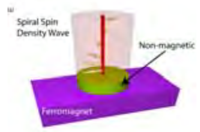
Motivation

Bulk Spin Transfer Torque

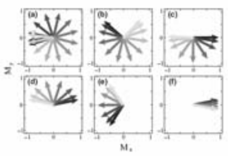
- PRL **96**, 256601 (2006)
- PRB **79**, 104433 (2009)



$$|f| = (1/2\pi J\hbar)\sqrt{(C_{23}j_3)^2 - (6K_6^{'6})^2}$$

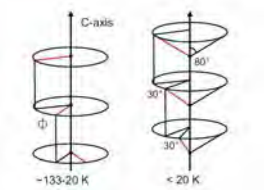
Exotic Phase

- PRB **78**, 020402(R) (2008)
- PRB **79**, 134420 (2009)

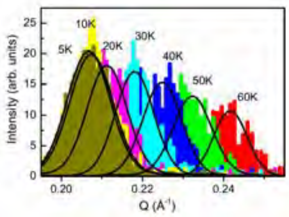


- Spin-triplet SC Science, **329**, 59 (2010)
- RMP **77** 1321 (2005)

Magnetic Spirals in Holmium thin films

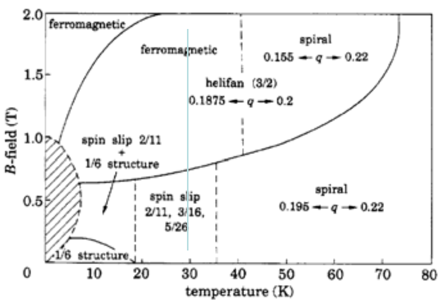


The representative magnetic structure of bulk Ho below its Néel temperature (left) and below its Curie temperature (right).



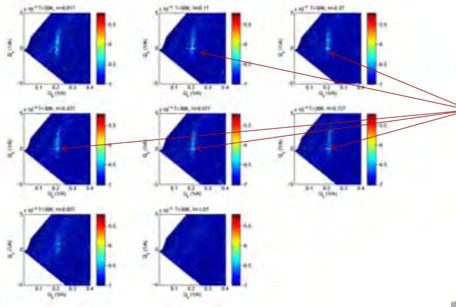
The momentum transfer versus the intensity of the magnetic diffraction peak for the 50 nm thick Ho sample as a function of temperature.

Bulk Ho Field Phase diagram



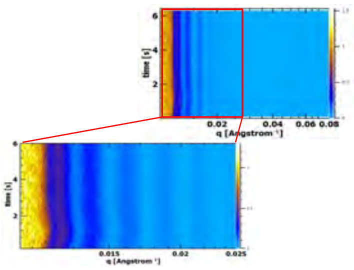
D. A Jehan *et al.*, Europhys. Letts. 17 553 (1992)

Polref: Diffuse scattering from a holmium spin spiral: 7.5T



J. D. S. Witt et al. J Phys: Condens Matter **23**, 416006 (2011).

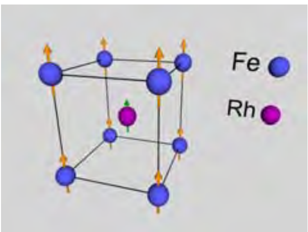
New capability, new science

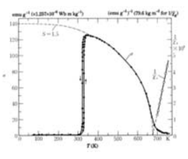


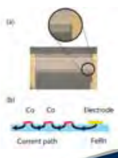
- Visible change in Q_c and shift in Kiessig fringes

- Stroboscopic measurement on INTER
- Courtesy of A. Glidle *et al.*
- Time slices are 200 milliseconds
- Polymer redox system

FeRh: Bulk Properties







D. Arena, BNL

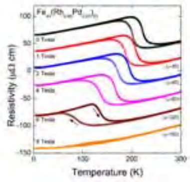
- CsCl structure
  - a~2.99Å
  - α' phase
- 300K: Type G AF
- Fe: ~3.3 μ_B
- Rh: no moment
- FM alignment within <111> planes
- AF alignment between <111> planes
- 350 K: AF → FM
- Fe: ~3.1 μ_B
- Rh: ~1 μ_B

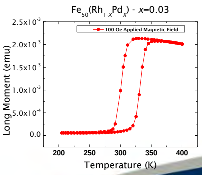
- J. S. Kouvel and C. C. Hartelius, JAP, **33**, 1343 (1962).
- G. Shirane *et al.* Phys. Rev. **134**, A1547 (1964)
- T. Naito et al., J Appl Phys **109**, 07C911 (2011)
- R. Fan, SL et al. Phys Rev B **82**, 184418 (2010).

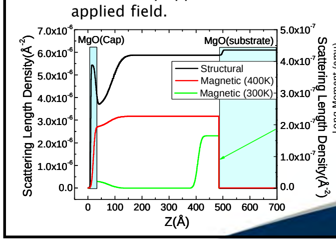
Pd doping

- Transition temperature is tuneable via doping and field
  - T_{AF-F} can be increased by doping with Ir and Pt and decreased by doping with Pd and Ni.
  - Shift to lower temperatures observed by application of applied field.

- P. Kushwaha, A. Lakhani, R. Rawat, and P. Chaddah, Physical Review B **80**, (2009)







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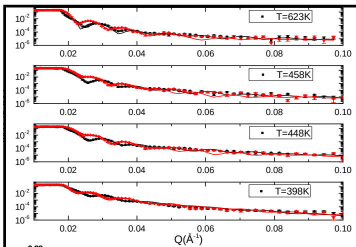

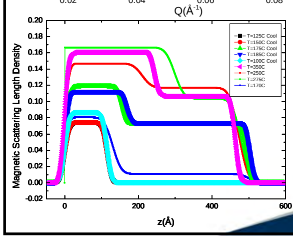

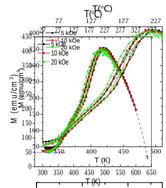

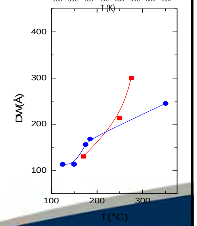

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Summary

- Can take advantage of (*i.e.* control) the refractive index (polarised neutrons, deuteration, isotopic substitution)
- Can extract magnetic structures
- Realistic sample environments
  - Time resolution
- Sub nm resolution for structural systems
- Lengthscales (out of plane) monolayer to ~100nm

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References

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- Theory of Magnetic neutron and photon scattering, E. Balcar & S.W. Lovesey, Oxford (1988)
- Introduction to Thermal Neutron Scattering, G.L. Squires, Cambridge (1978)
- Elements of Modern X-Ray Physics, Als-Nielsen and McMorrow, Wiley & Sons (2001)
- Magnetism: from fundamentals to nanoscale dynamics, Stohr and Siegmann, Spinger (2006)
- www.ill.eu
- www.isis.stfc.ac.uk
- www.esrf.eu
- www.diamond.ac.uk



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