



Surface techniques

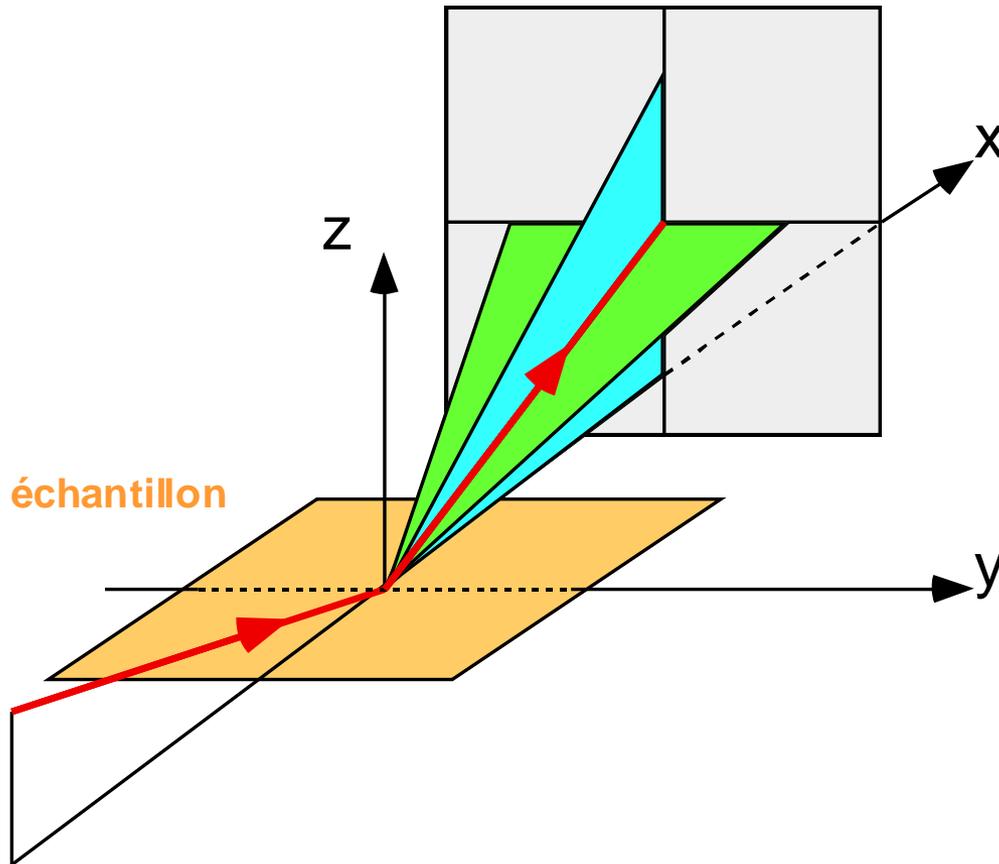
Frédéric OTT

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CEA Saclay FRANCE



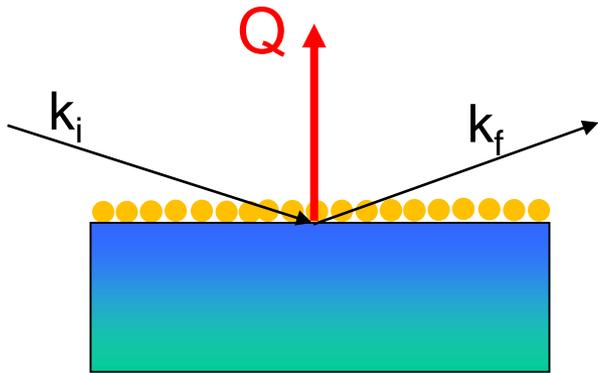
Scattering geometries



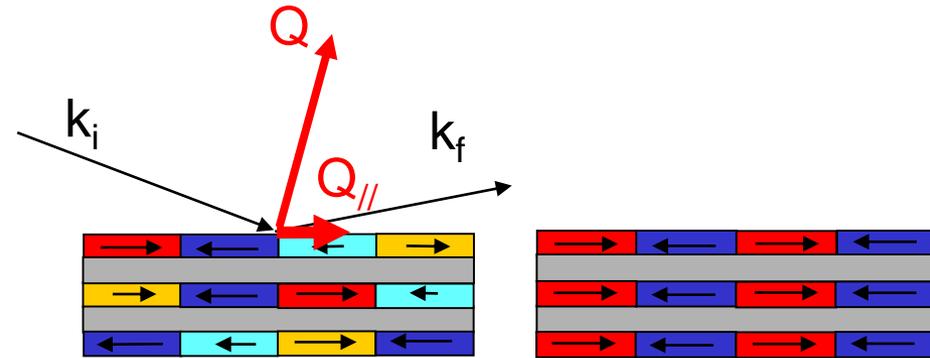
- **Specular reflection**
 $0.06 < Q_z < 3 \text{ nm}^{-1}$
 $3 \text{ nm} < \xi < 100 \text{ nm}$
- **Incidence plane (Off-specular)**
 $10^{-4} < Q_x < 10^{-2} \text{ nm}^{-1}$
 $600 \text{ nm} < \xi < 60 \text{ }\mu\text{m}$
- **⊥ incidence plane (GISANS)**
 $10^{-4} < Q_y < 3 \text{ nm}^{-1}$
 $3 \text{ nm} < \xi < 100 \text{ nm}$

The different techniques

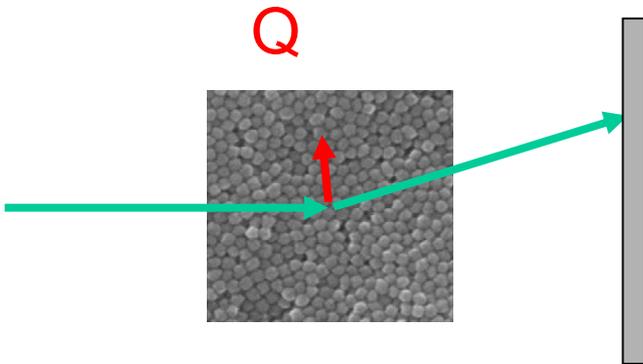
■ Reflectivity



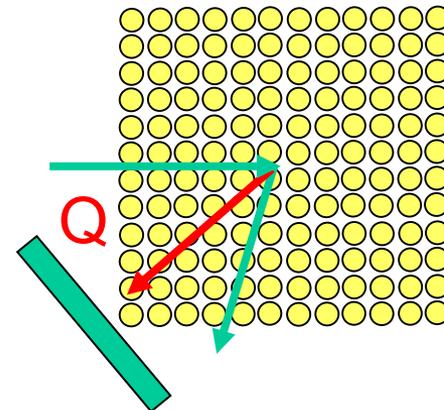
■ Off-specular



■ GISANS



■ Diffraction

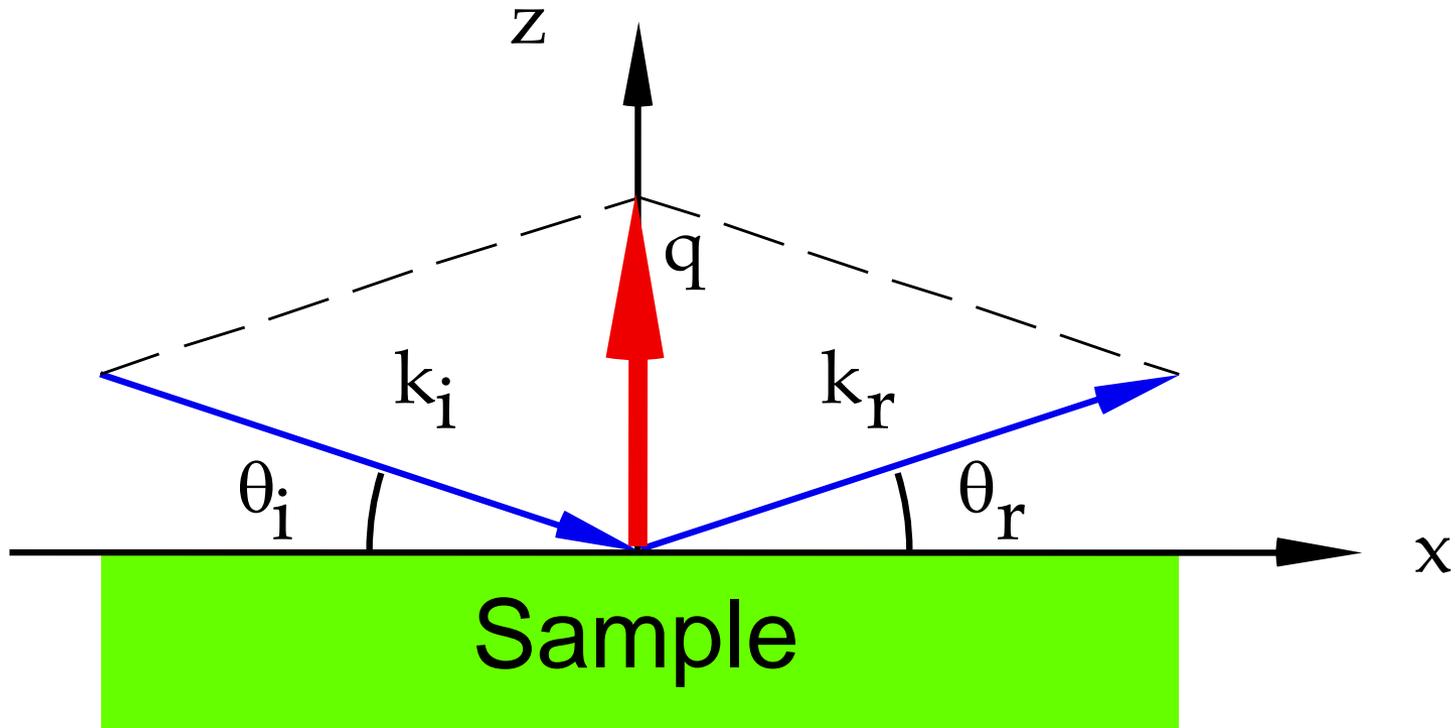


Reflectivity





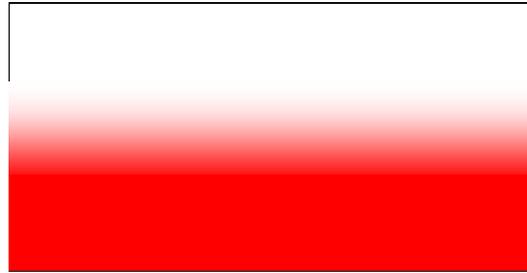
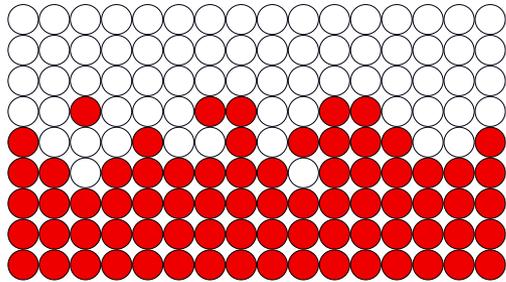
Neutron reflection



$$q = k_r - k_i = \frac{4\pi}{\lambda} \sin \theta$$



Optical approximation



$$b^{vol} = \frac{1}{vol} \sum_{i \in vol} b_i$$

$$f^{vol} = \frac{1}{vol} \sum_{vol} (f_i + f'_i)$$

- Interaction potential

$$V_n = \frac{\hbar^2}{2\pi m} SLD \quad \text{with} \quad SLD_n = \sum_i N_i b_i \quad SLD = \frac{1}{x} \sum_i N_i r_e (f_i + f'_i)$$

$$r_e = 2.81 \times 10^{-5} \text{Å}$$

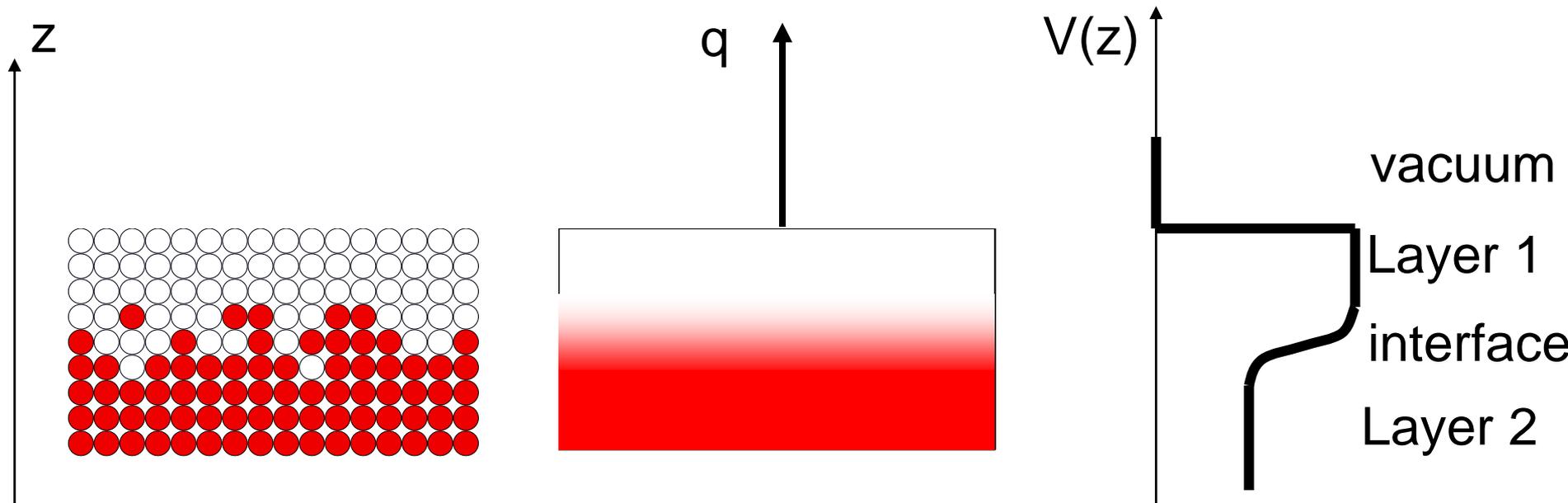
SLD is the Scattering Length Density

N_i is the atomic density of atomic species i



What information can be accessed ?

- Reflection on a thin film on a substrate



- In a first approximation :

$$R(\vec{q}) \propto \tilde{V}(\vec{q})$$

Characteristic length
scales
from 2 to 200nm



Derivation of the reflectivity

Interaction

$$V = \frac{2\pi\hbar^2}{m} SLD$$

Propagation eq.

Schrödinger

$$-\frac{\hbar^2}{2m} \Delta\varphi + V\varphi = E\varphi$$

Helmoltz propagation eq.

$$\Delta\mathbf{U} + k^2\mathbf{U} = 0$$

$$k^2 = \frac{2m}{\hbar^2} (E - V)$$

$$n^2 = \frac{k^2}{k_0^2}$$



Optical index

- The optical index is given by

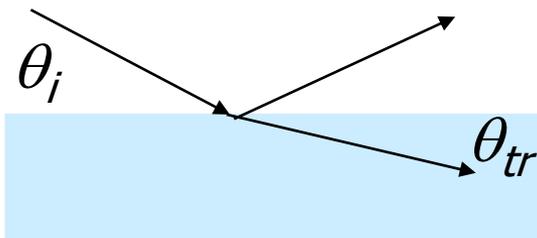
$$n^2 = \frac{k^2}{k_0^2}$$

$$n^2 = 1 - \frac{V}{E} = 1 - \frac{\lambda^2}{\pi} SLD$$

$$n \approx 1 - \frac{\lambda^2}{2\pi} SLD$$

- Snell's law :

$$\cos \theta_i = n \cos \theta_{tr}$$



Total reflection : $\theta_{tr} = 0$

$$\theta_c = \sqrt{\frac{SLD}{\pi}} \lambda$$

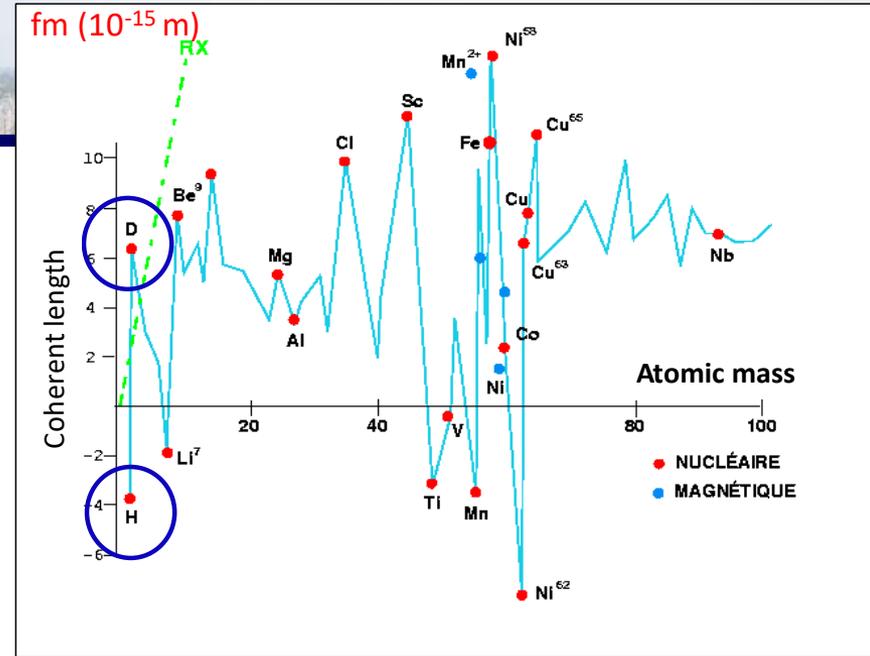
$$\text{For Ni : } \theta_c = 0.1^\circ / \text{\AA}$$

Neutron – X-rays SLD



$$SLD = \sum_i N_i b_i$$

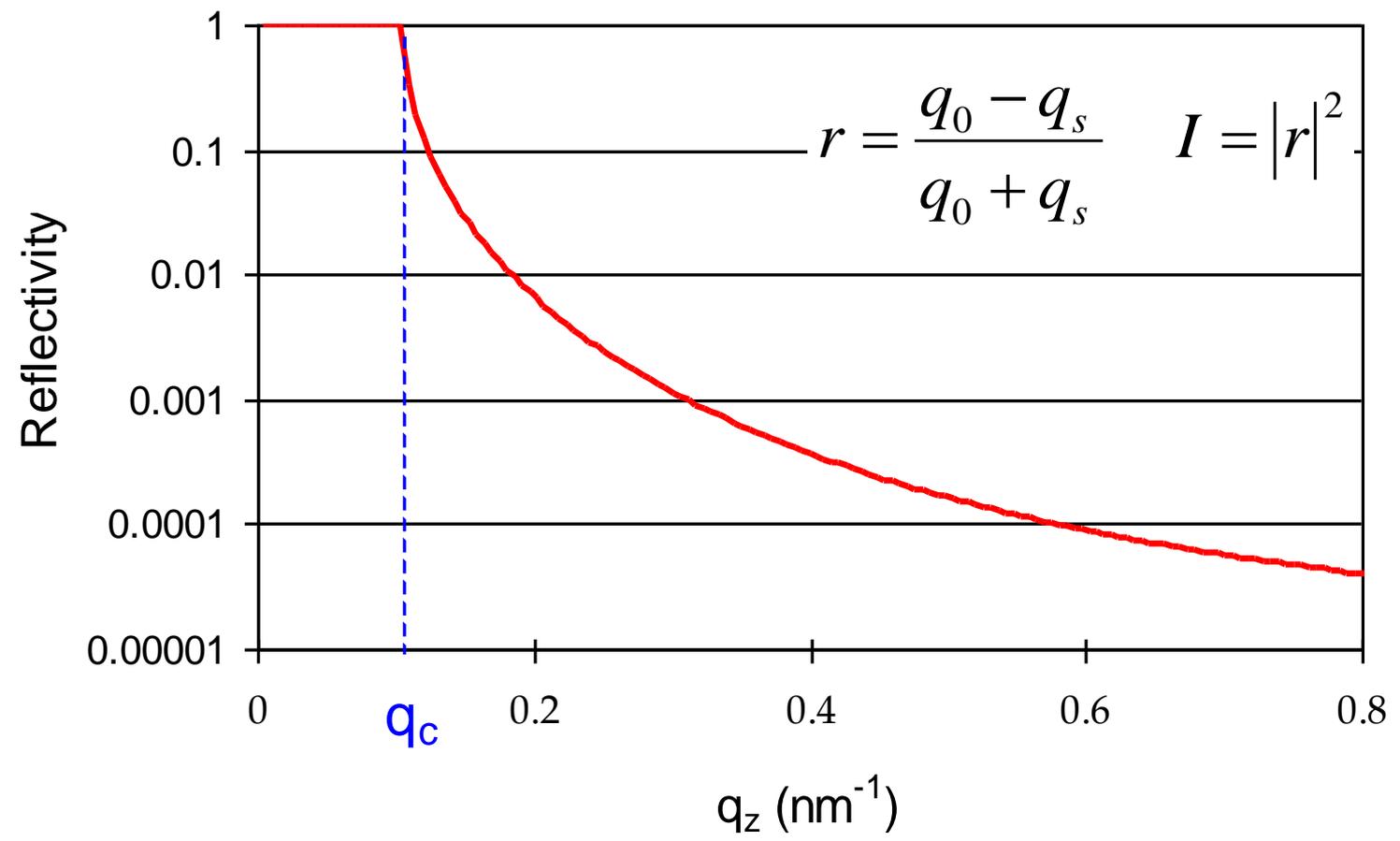
$$SLD = \sum_i N_i r_e (f_i + f_i')$$



	Neutrons (10^{-6} \AA^{-2})	X-rays (10^{-6} \AA^{-2})	X-rays imag. (10^{-6} \AA^{-2})
H ₂ O	-0.56	9.4	0.03
D ₂ O	6.4	9.4	0.03
PS-h	1.42	9.2	0.01
PS-d	6.5	9.2	0.01
Si	2.08	19	0.4
Fe	9.2	68	9
Pt	6.3	137	13

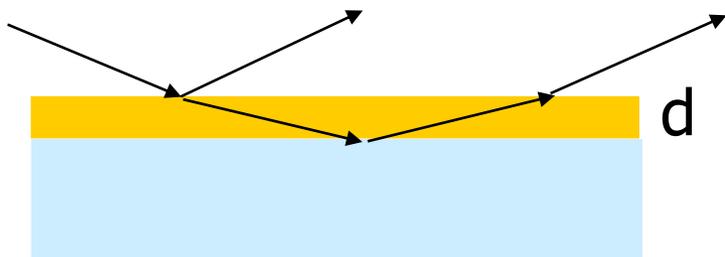
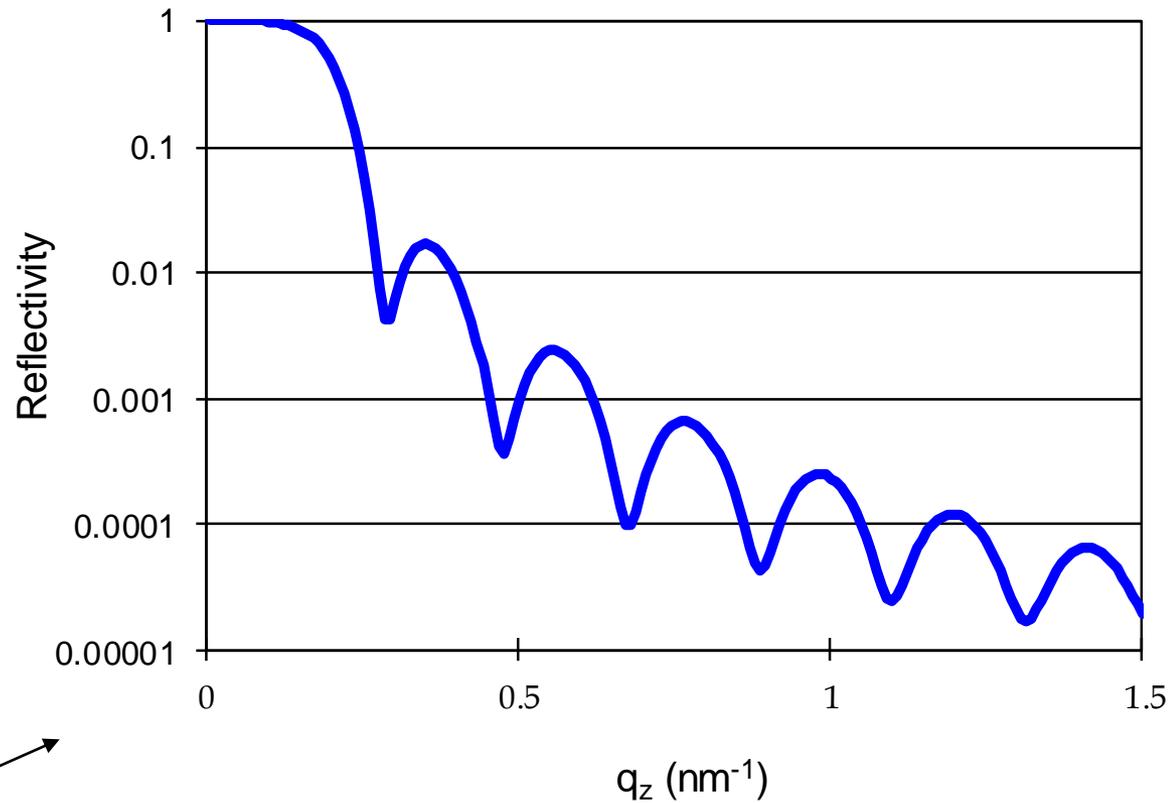


Case of a semi-infinite medium





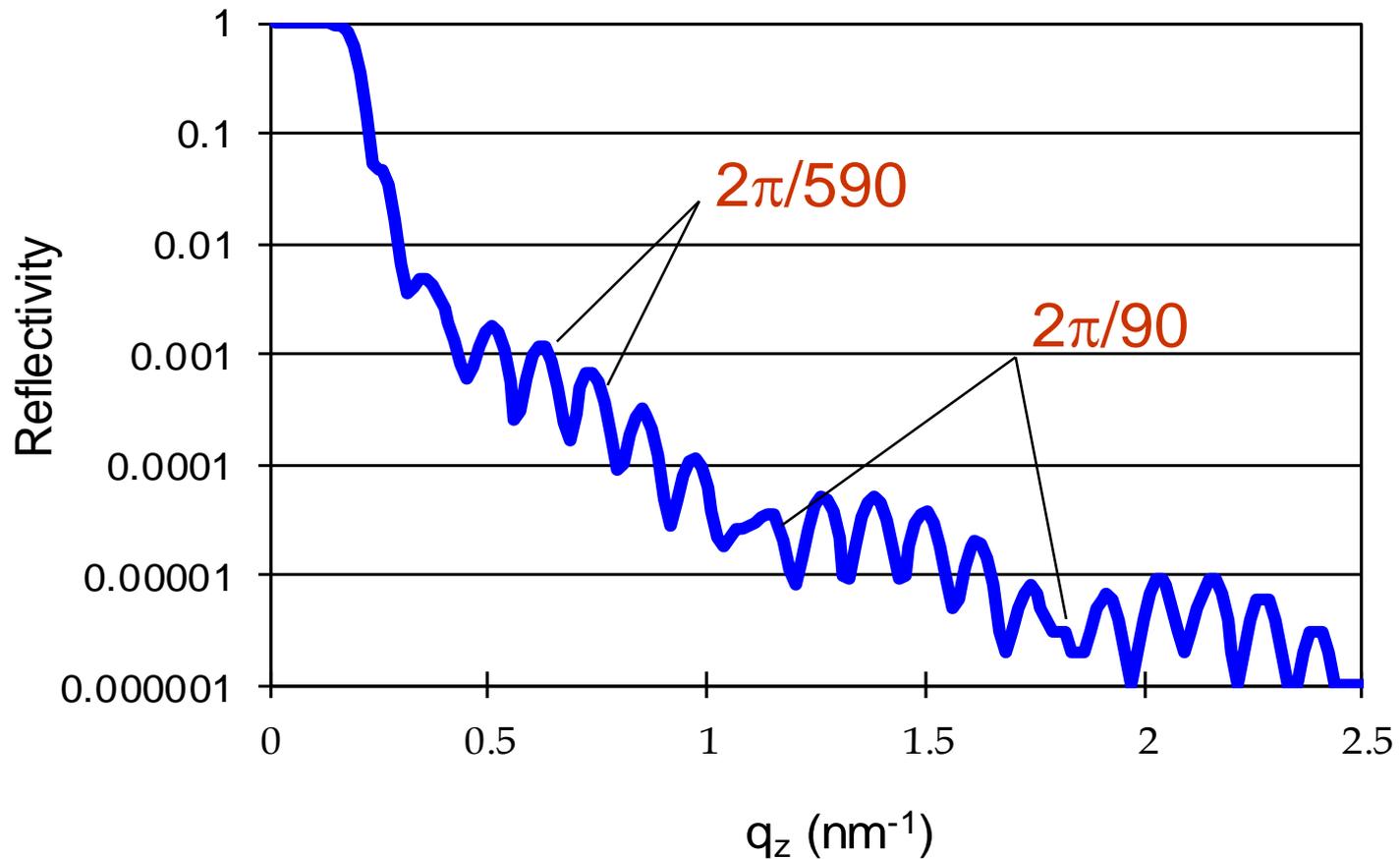
Reflection on a thin film deposited on a substrate



$$d = \frac{2\pi}{\Delta q}$$



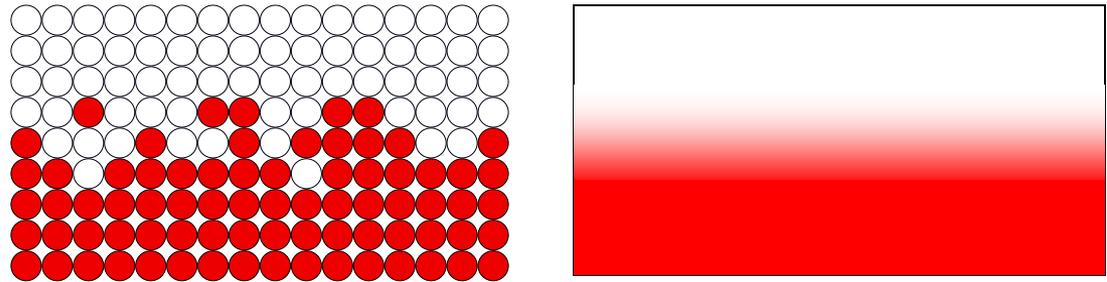
Example Cu(500 Å)/Cr(90 Å) on silicon



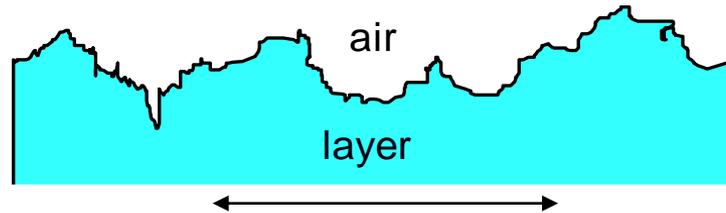


Roughness effects

- **Roughness at the atomic level** : interdiffusion between the thin films, $\xi < 100$ nm.



- **Intermediate roughness** (ξ de $0.1 \mu\text{m}$ à $50 \mu\text{m}$).



- **A large scale roughness** ($\xi > 100 \mu\text{m}$).





Roughness effects

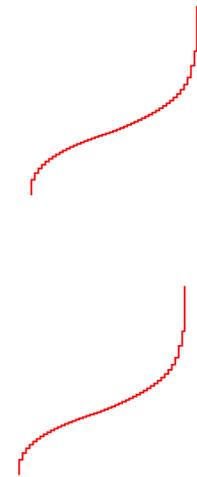
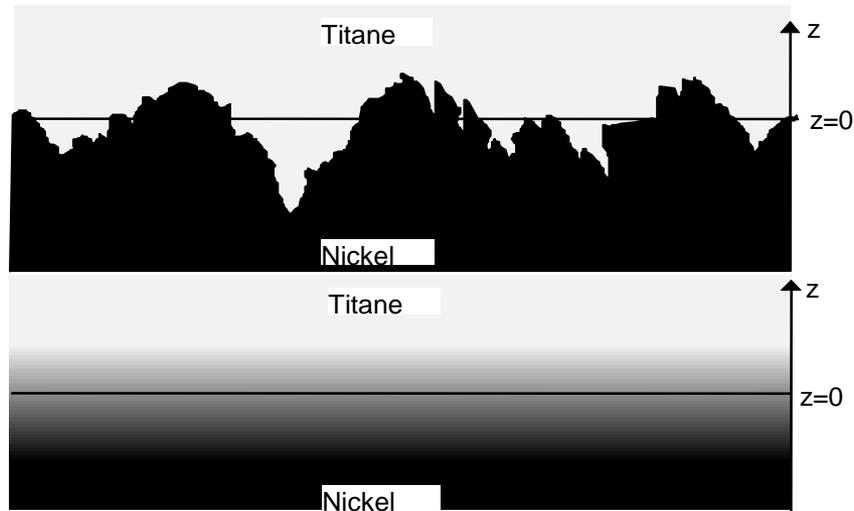
Nb

Roughness

Gives off-specular scattering

Interdiffusion

No off-specular scattering



Indistinguishable effects with specular reflectivity

Nb profile described by :
$$\operatorname{erf}\left(\frac{z - z_{m/m+1}}{\sigma_{m/m+1}}\right) = \frac{2}{\sqrt{\pi}} \int_0^{(z - z_{m/m+1})/\sigma_{m/m+1}} e^{-t^2} dt$$

Debye -Waller like factor:
$$R = R_F \exp(-4q_m q_{m+1} \sigma_{m/m+1}^2)$$

Practical aspects



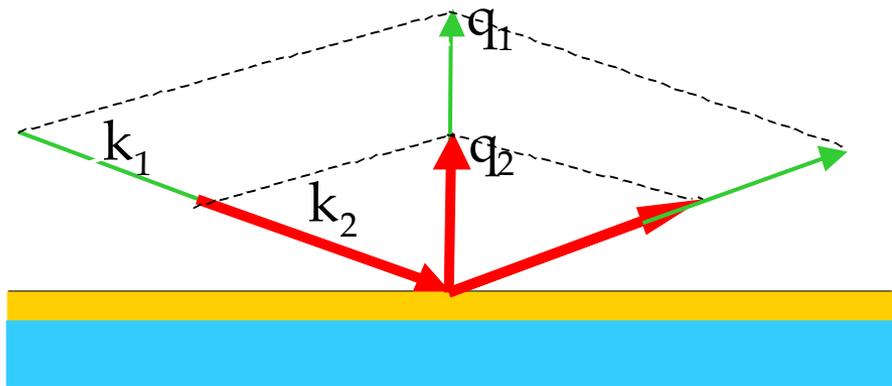
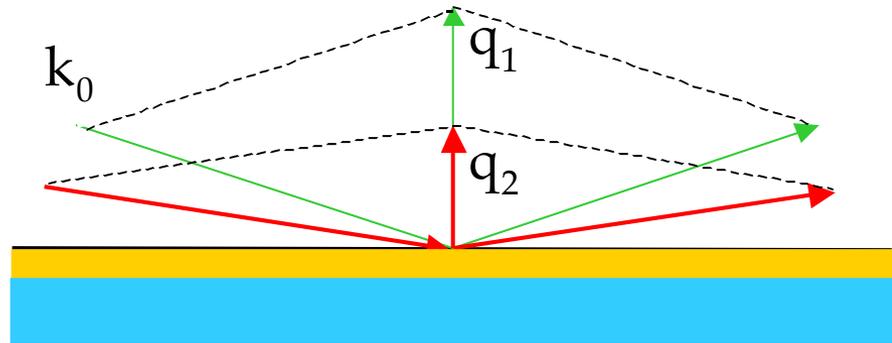


Reflectivity measurements

- 2 ways of varying the scattering wave-vector
 - Angular scan $\theta - 2\theta$

$$Q = \frac{4\pi}{\lambda} \sin \theta$$

- Time-of-flight





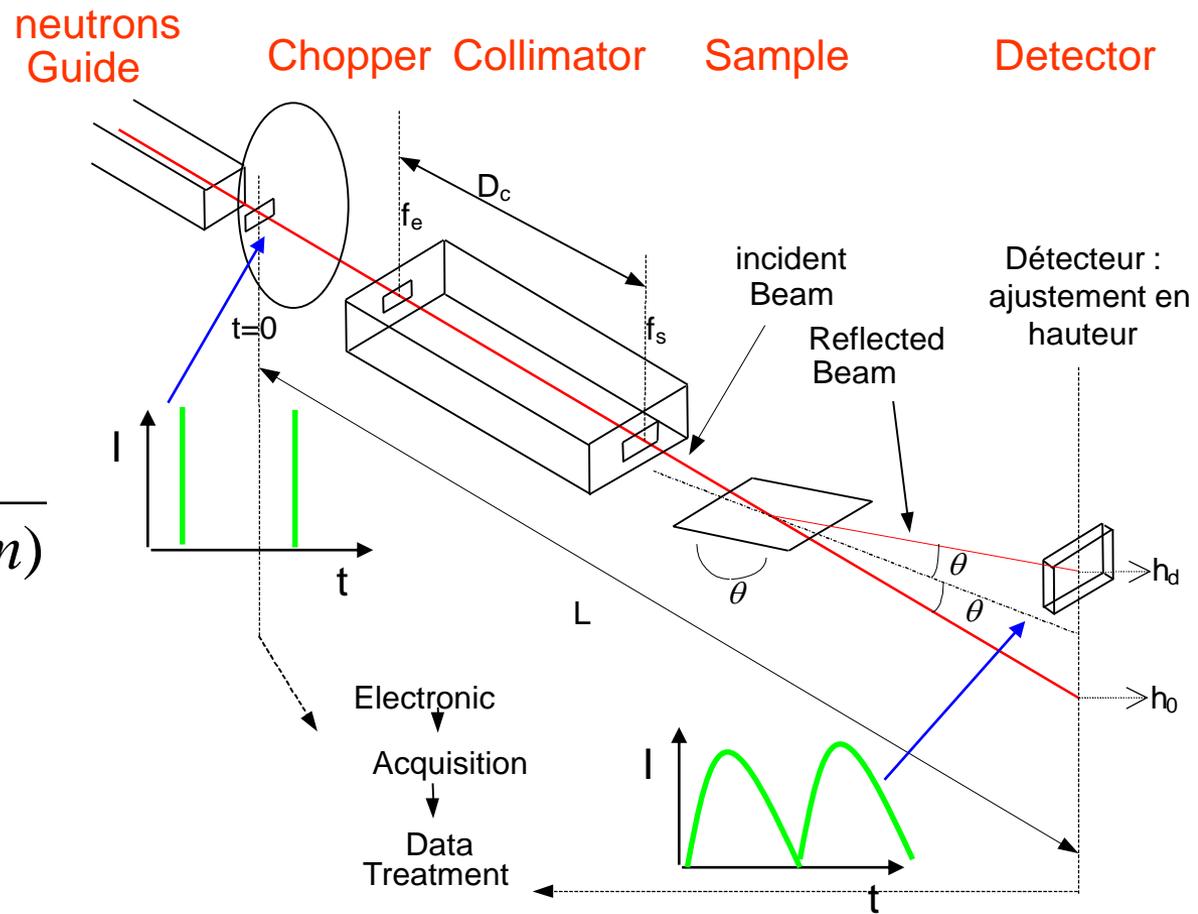
Time of Flight spectrometer



$$q = \frac{4\pi}{\lambda} \sin\theta$$

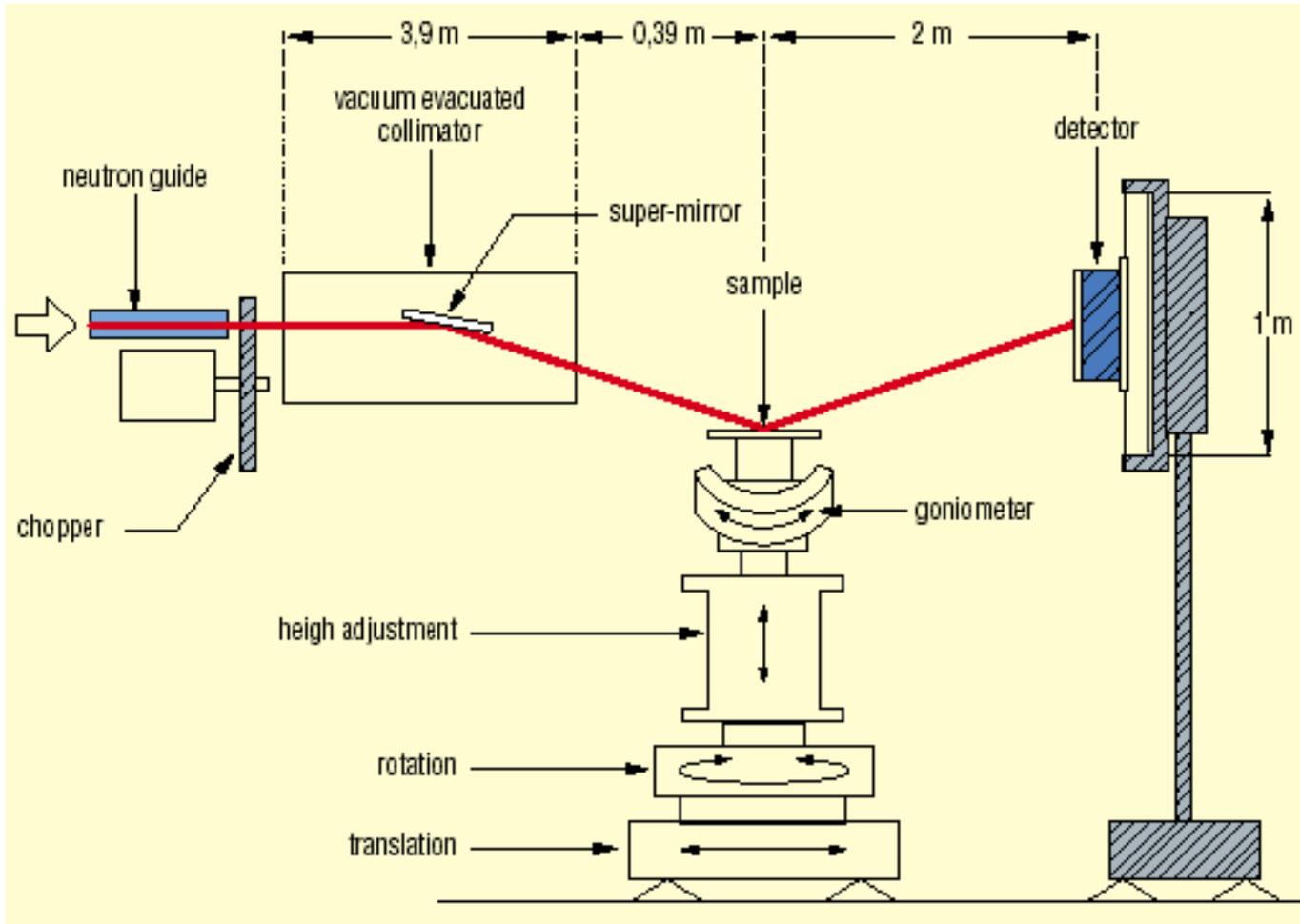
$$\lambda(\text{\AA}) = \frac{t(\mu\text{s})}{252,7L(m)}$$

$$R = \frac{I_r}{I_0}$$



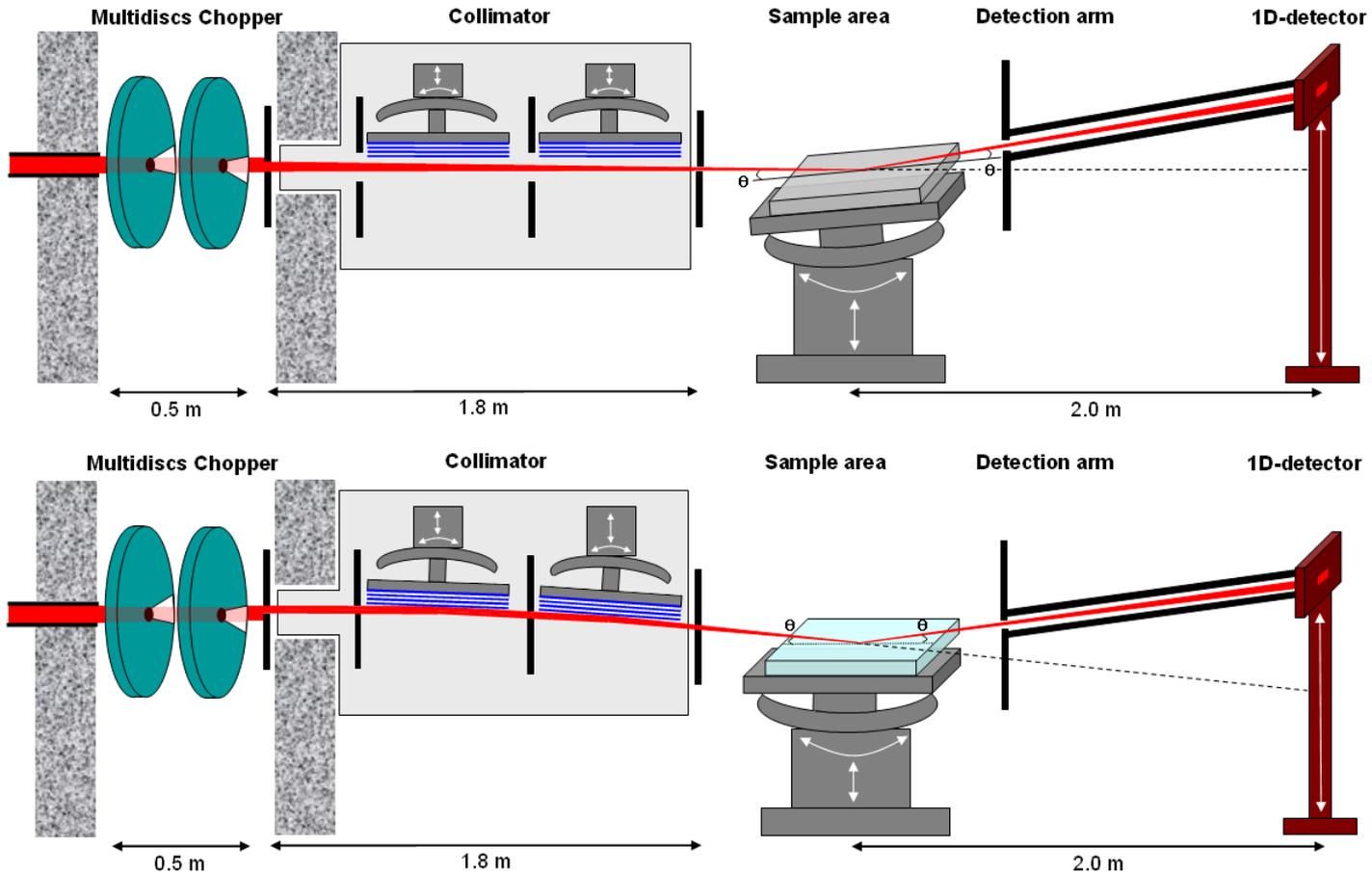


ToF reflectometer : EROS





Time of Flight spectrometer



(Eros, LLB)



Time-of-flight Vs $(\theta, 2\theta)$

Time of Flight

- Easy for Liquids
(fixed angle)
- Kinetics Measurements
- Gravity (if horizontal)

$(\theta, 2\theta)$

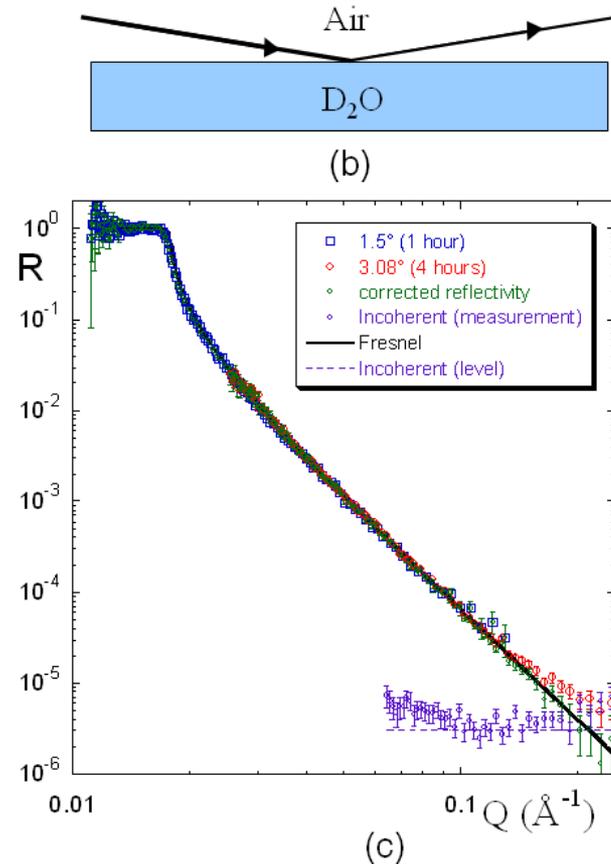
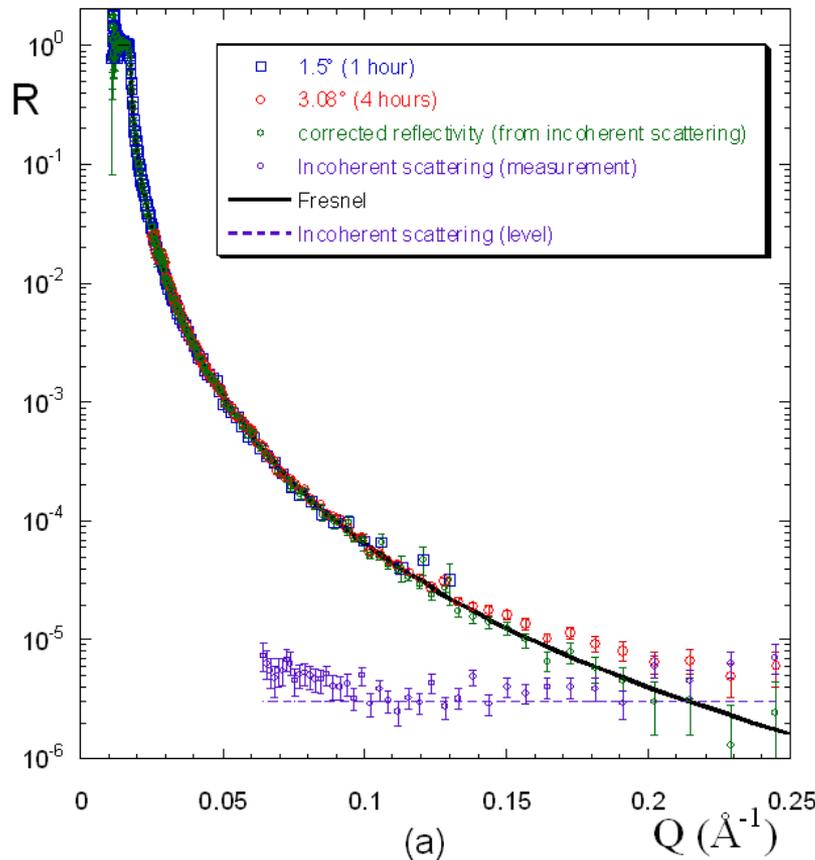
- No gravity problem
- Kinetics measurements impossible
- Difficult to handle with liquids

For Soft Matter, Time of Flight is preferable

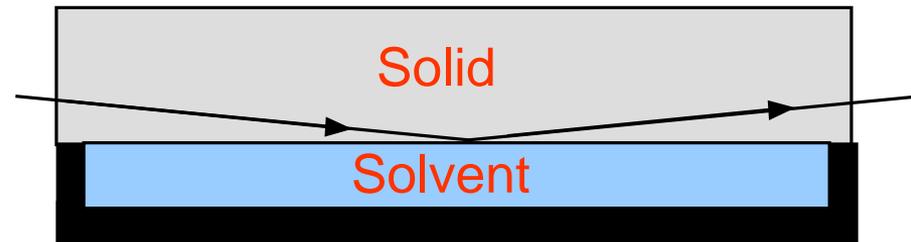
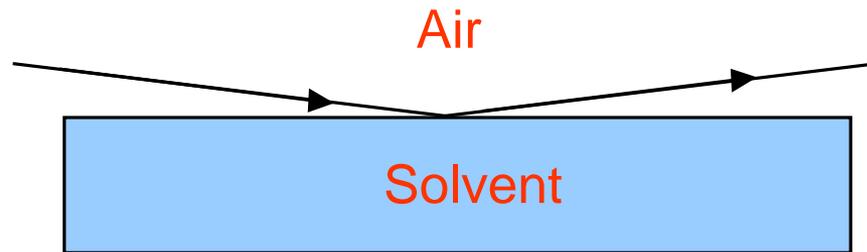
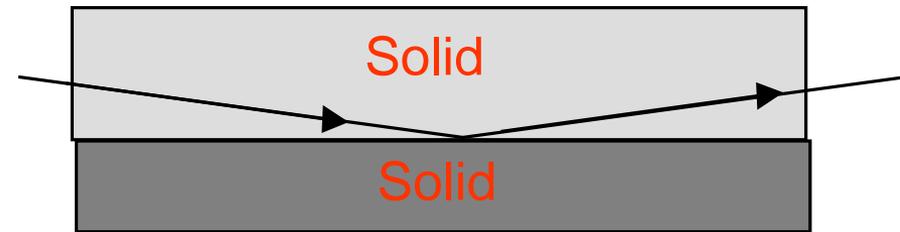
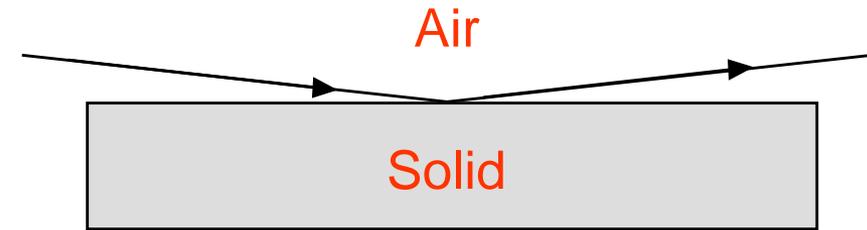


NR: Incoherent Scattering

Incoherent scattering looks as a background,
usually negligible at large R,
but becomes important at small R : **intrinsic limitation**



Possible geometries for measurements

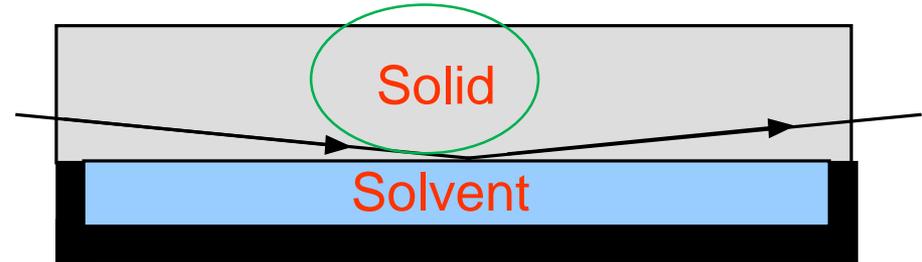
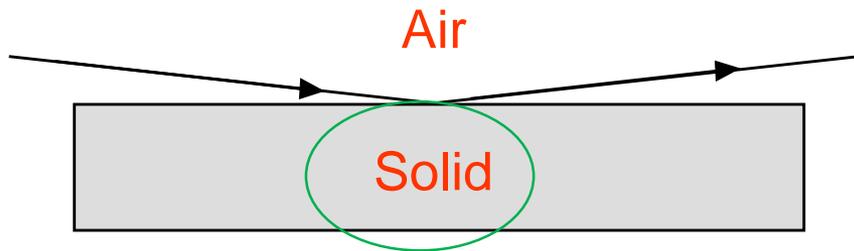


Sample size: a few cm^2
Good flatness required

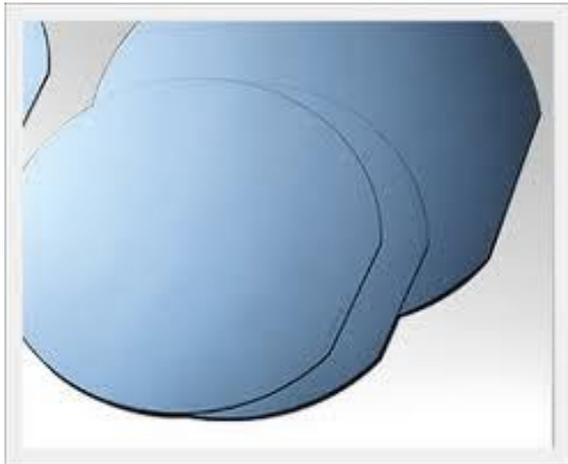
For liquid samples : a few ml

For solid samples : no bending (rigid substrates)

Possible geometries for measurements



Silicon wafers :



- No incoherent scattering
- Almost no absorption
- Good mechanical properties ($t > 1\text{mm}$)
- rms roughness (a few Å)
- Easy chemical surface modification
- Easy to purchase

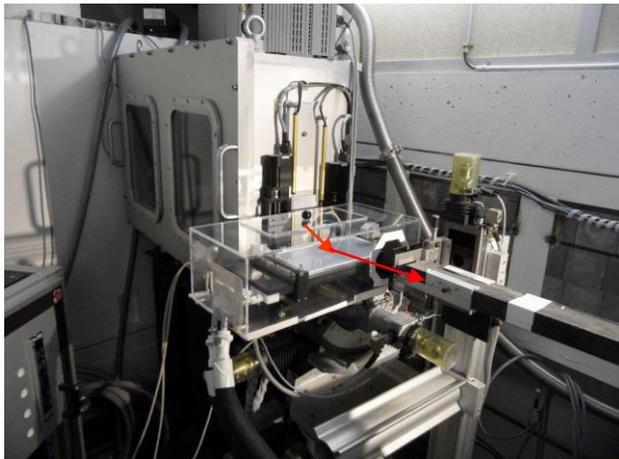


Around 90% of experiments on solid substrates..

Possibilities of samples environments

Since neutrons are barely absorbed/scattered by matter, various samples environments for *in-situ* measurements are easy to design

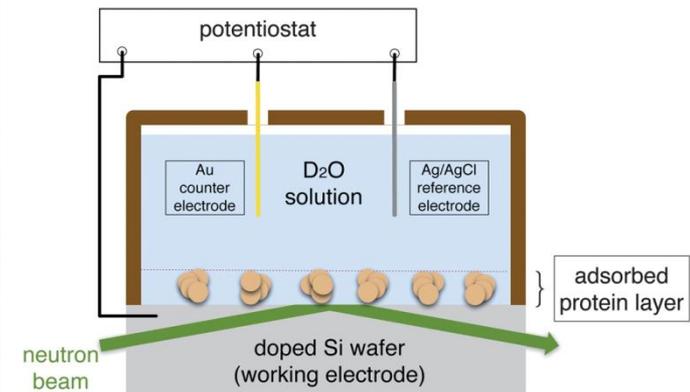
Langmuir trough



Rheometer



Electric Cell



+ Air/liquid cells, solid/liquid cells, humidity chambers, controlled pressure cells, etc ...

Data modelling





Modelling of the data : problem of unicity of the fit

In a NR experiment, the phase information is lost.

Several Nb profiles may correspond to a single given NR curve !

How to make modelling unambiguous ?

Strategy 1 : use of several contrasts for a given condition

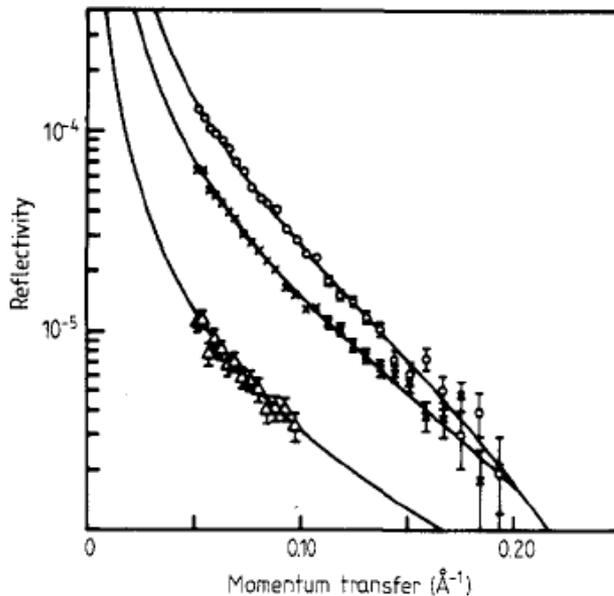


Figure 10. Observed and calculated specular reflectivity profiles of isotopic species of 0.05 M decyltrimethylammonium bromide (DTAB) in null reflecting water (background subtracted). In order of decreasing reflectivity the isotopic species are dDdTAB, dDhTAB and hDdTAB. The continuous curves are profiles calculated for the structure shown in figure 12(a) [17].

J. Phys.: Condens. Matter 2 (1990) 1369–1412. Printed in the UK

REVIEW ARTICLE

The application of the specular reflection of neutrons to the study of surfaces and interfaces

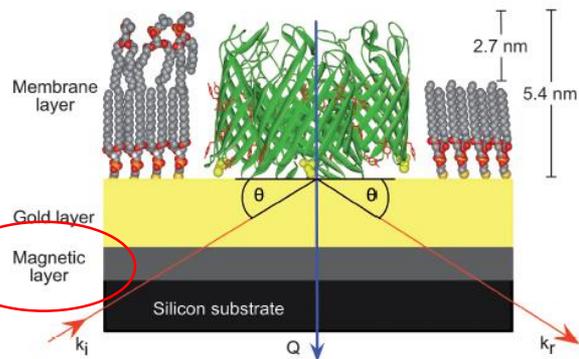
J Penfold† and R K Thomas‡

† Neutron Science Division, Rutherford Appleton Laboratory, Chilton, Oxfordshire, UK

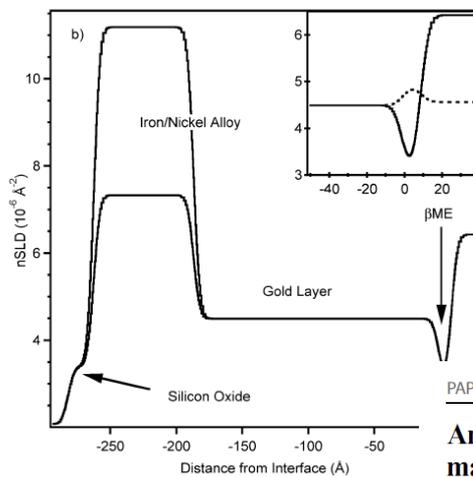
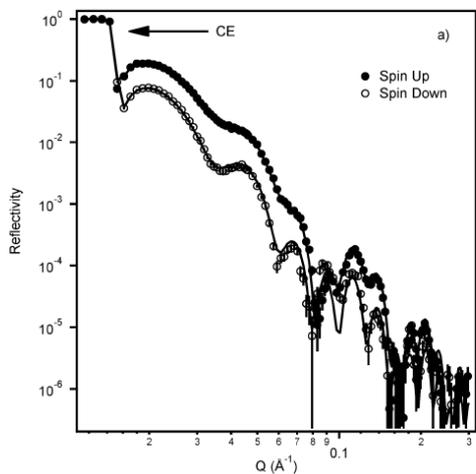
‡ Physical Chemistry Laboratory, Oxford University, South Parks Road, Oxford, UK



Modelling of the data : problem of unicity of the fit



Strategy 2 : polarized neutron reflectometry



PAPER

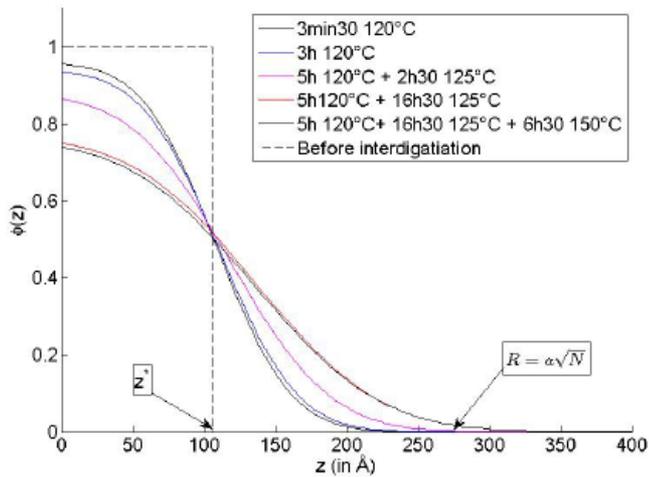
www.rsc.org/softmatter | Soft Matter

An ion-channel-containing model membrane: structural determination by magnetic contrast neutron reflectometry[†]

Stephen A. Holt,^{*,a} Anton P. Le Brun,^b Charles F. Majkrzak,^c Duncan J. McGillivray,^{‡,c} Frank Heinrich,^{cd} Mathias Lösche^{cd} and Jeremy H. Lakey^b

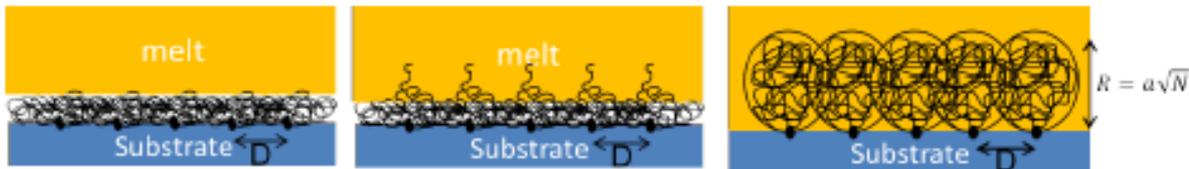


Modelling of the data : problem of unicity of the fit



Strategy 3 : Consistency of data

Volume conservation !



Increasing annealing time →

Courtesy of Chennevière *et al*

Example 1

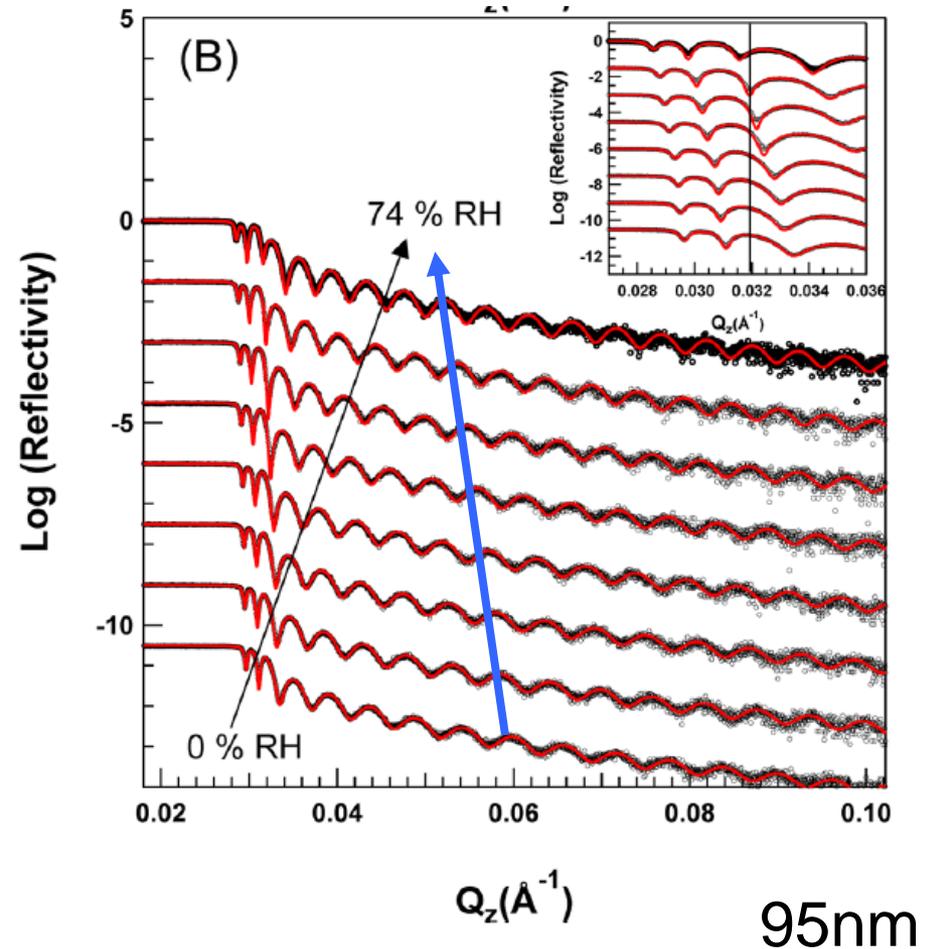
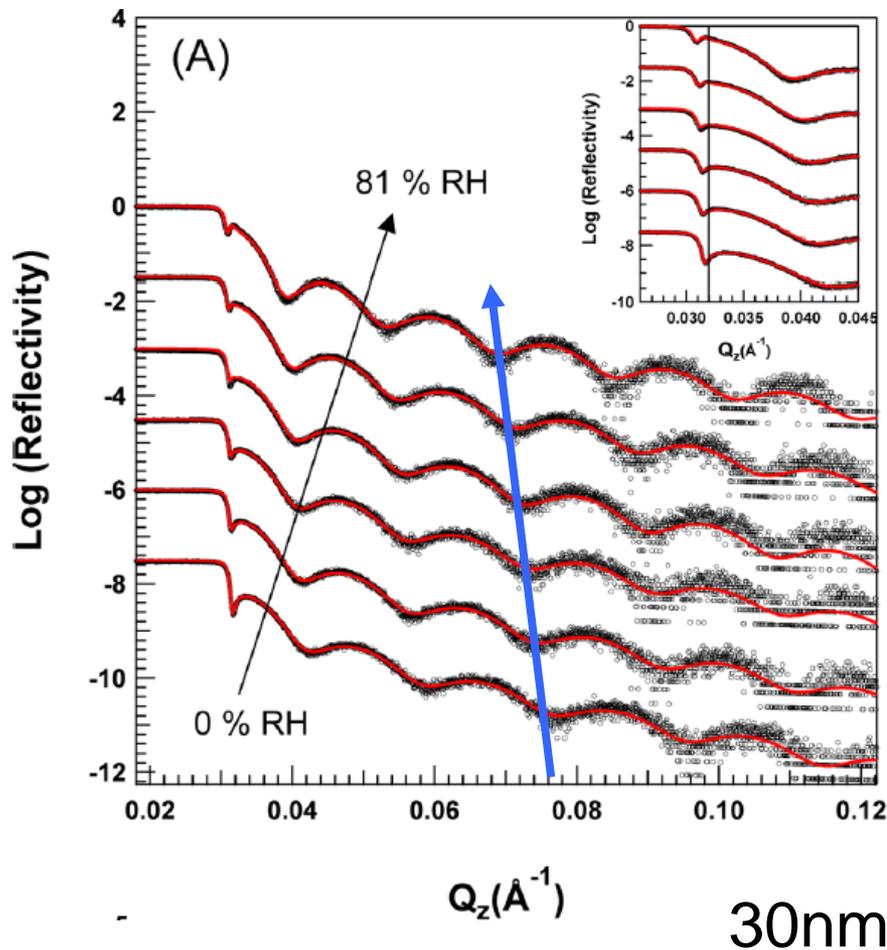
Reflectivity on fuel cells





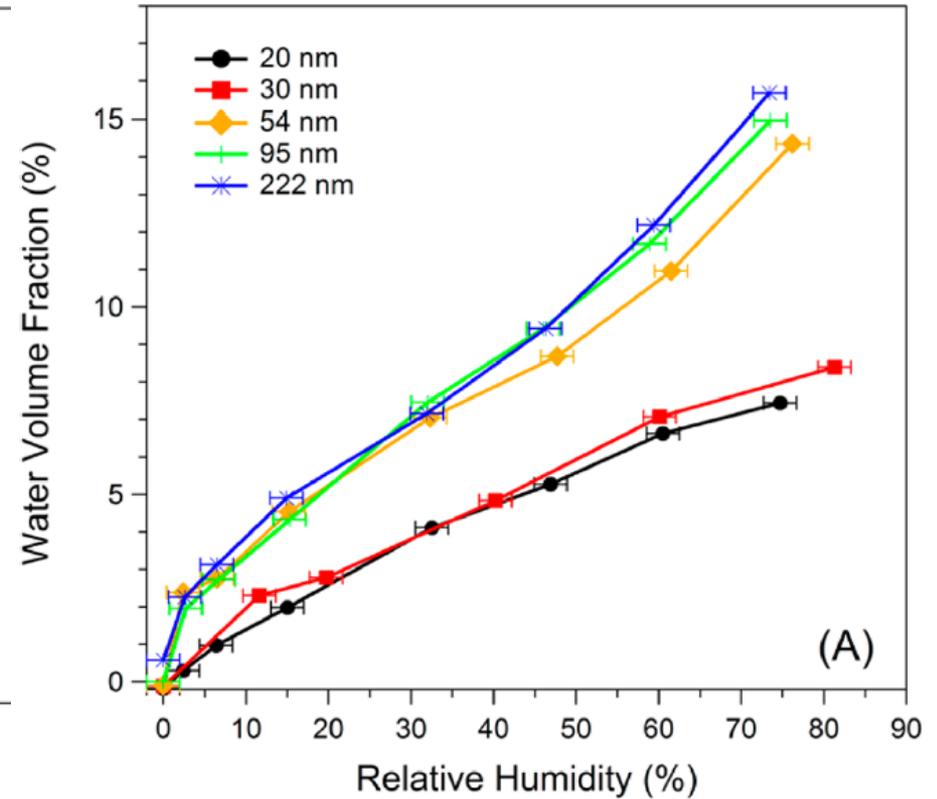
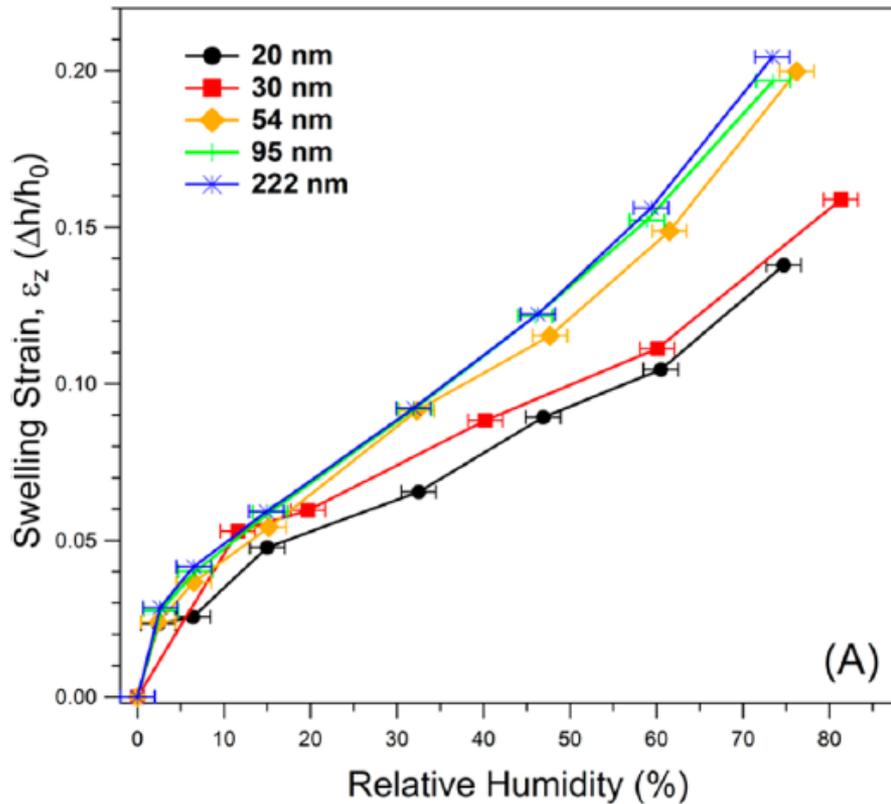
Water in confined Nafion thin films

- Eastman et al, *Macromolecules* 2012, 45, 7920–7930



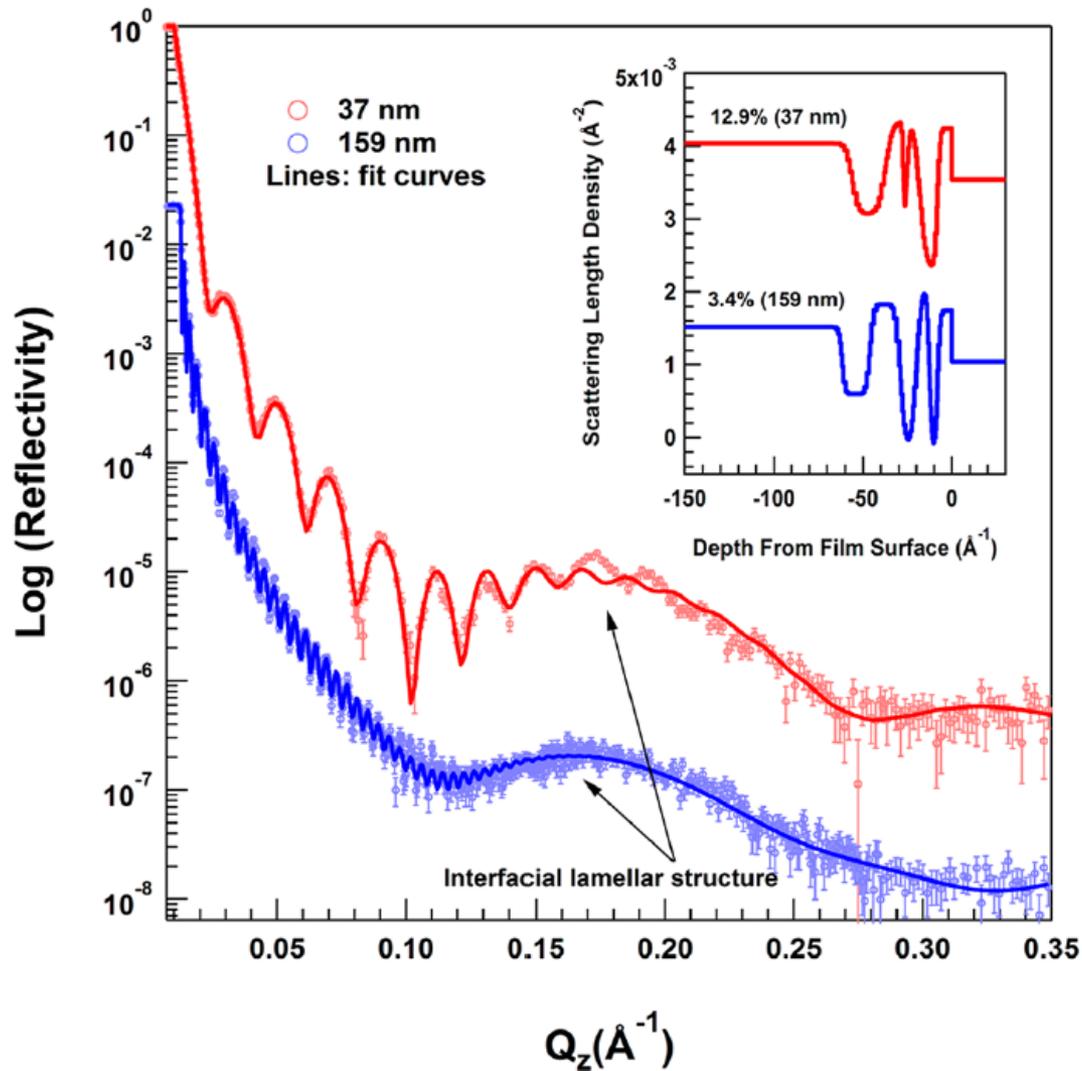


Water in confined Nafion thin films



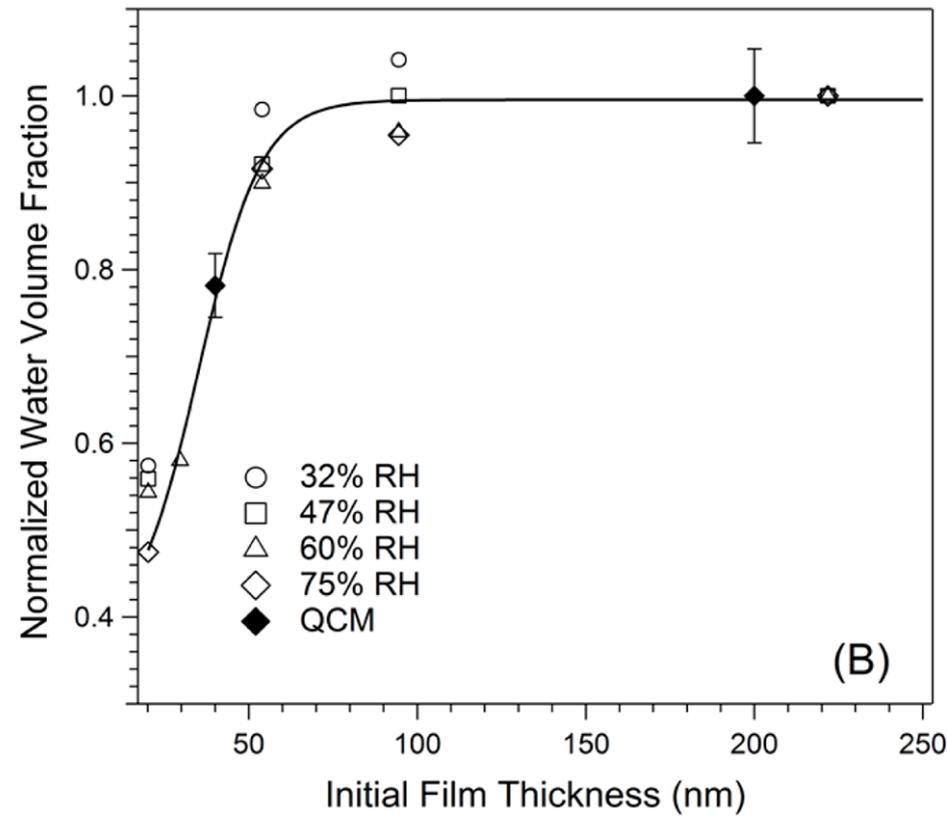


Water in confined Nafion thin films





Water in confined Nafion thin films



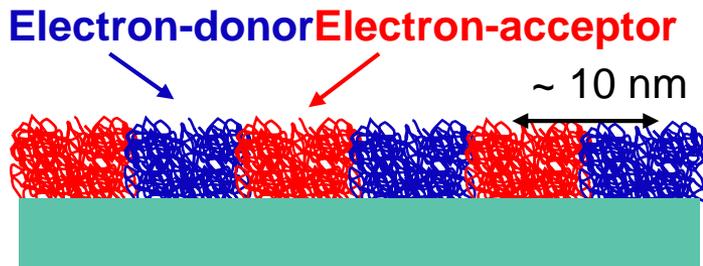
Example 2

Organic photovoltaics for solar cells



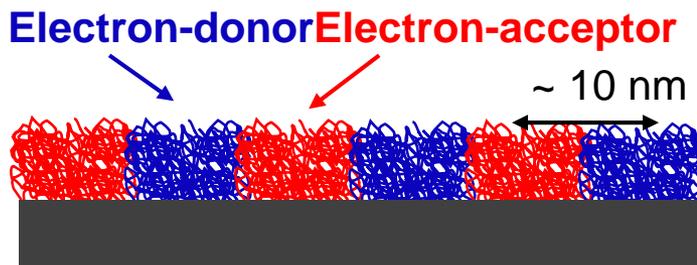
Organic photovoltaics for solar cells

E. Pavlopoulou et al, Organic Electronics 14 (2013) 1249–1254



Hole transport layer
(PEDOT:PSS)

(conventional solar cells)
Or

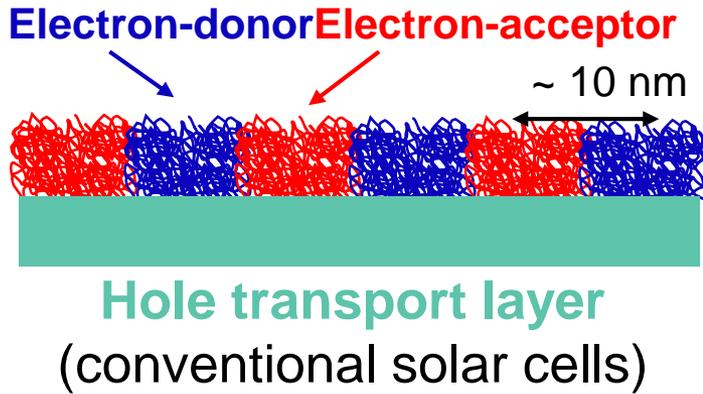


Electron transport layer (TiO₂)
(conventional solar cells)

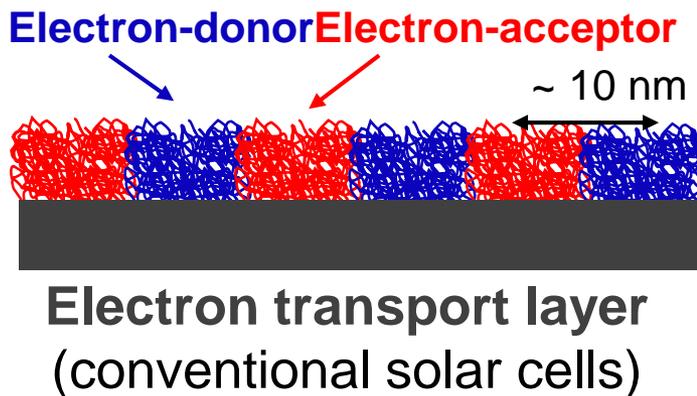
Blends of polymers

PCBM – P3HT

Organic photovoltaics for solar cells

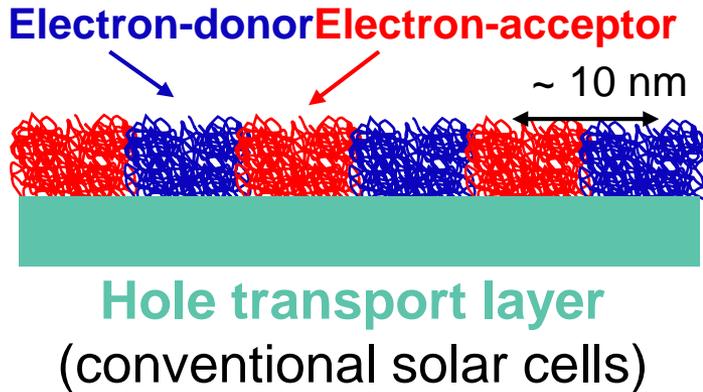


or

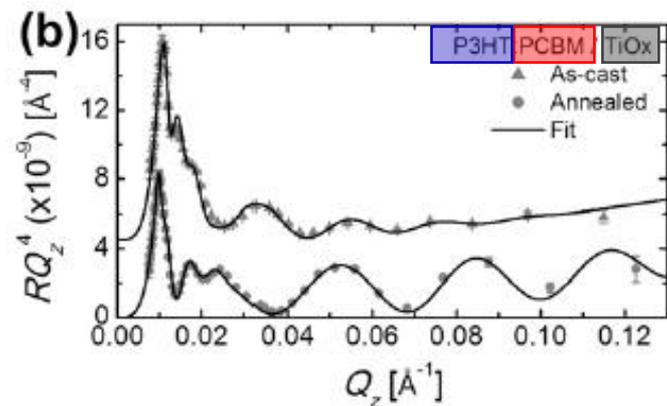
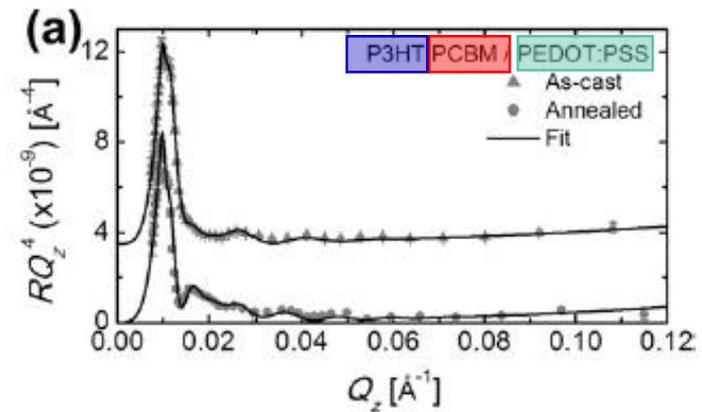
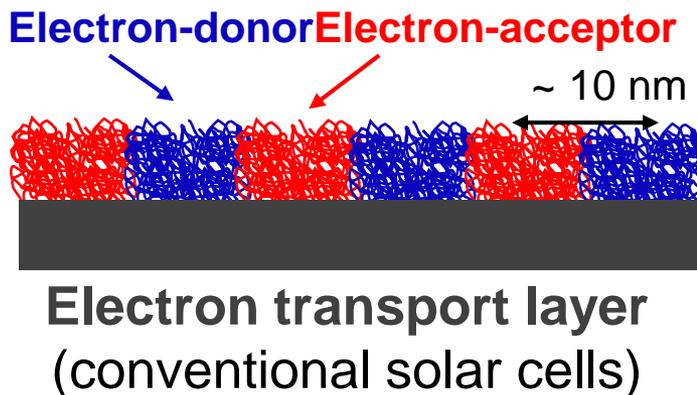


Organic photovoltaics for solar cells

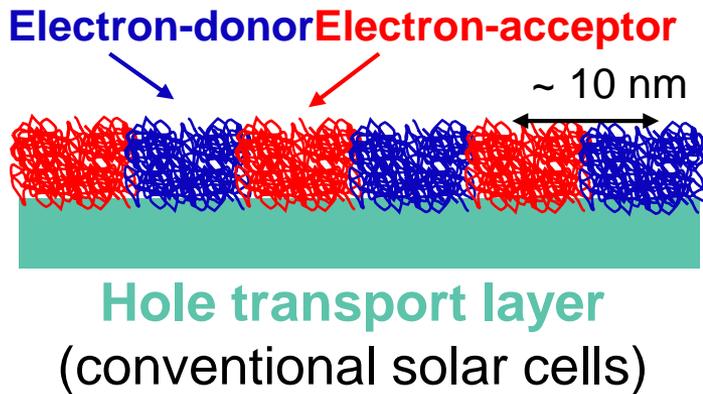
R.Q⁴



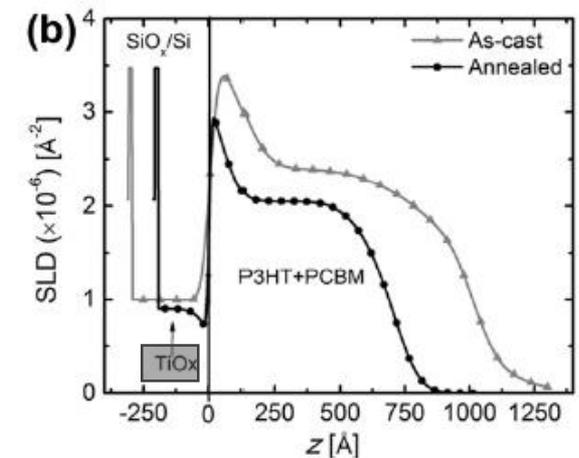
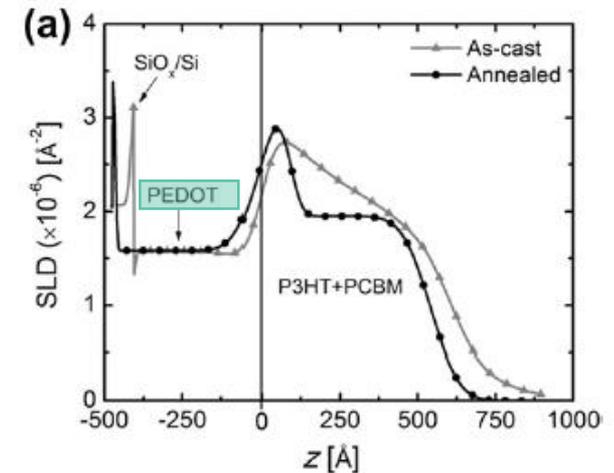
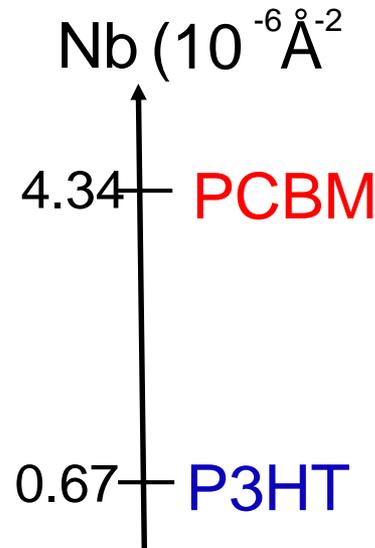
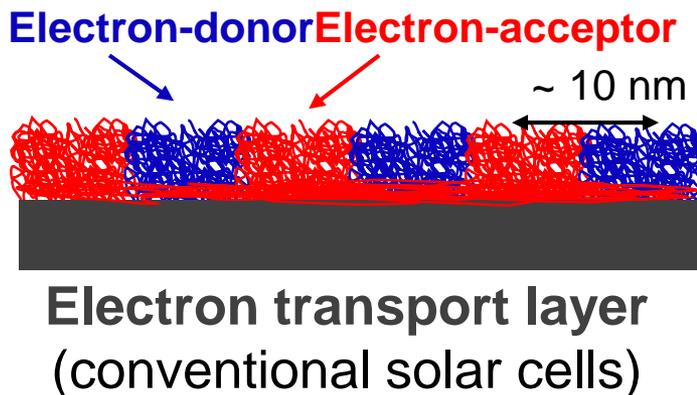
or



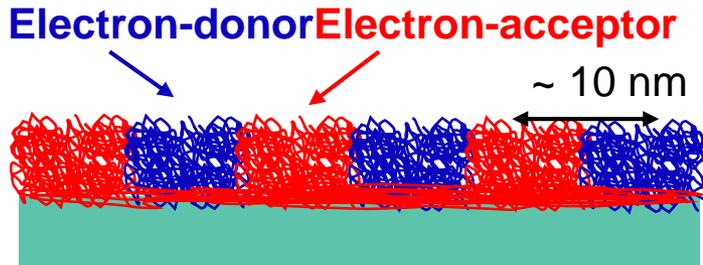
Organic photovoltaics for solar cells



or

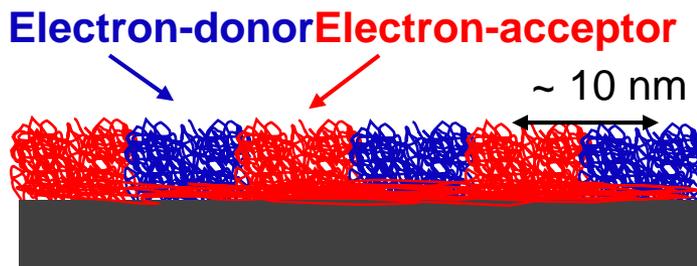


Organic photovoltaics for solar cells

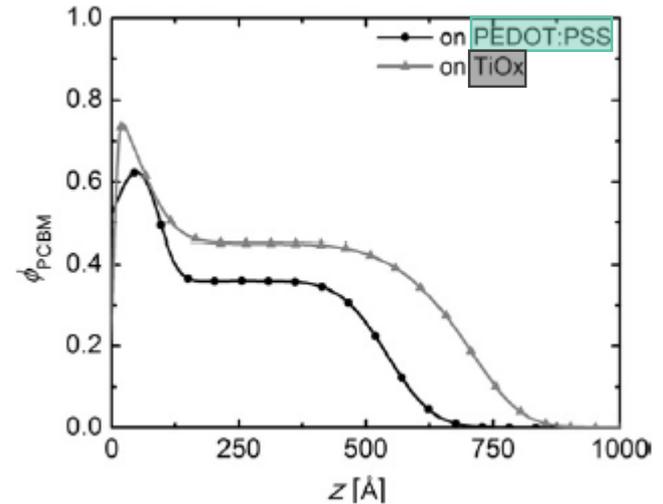


Hole transport layer
(conventional solar cells)

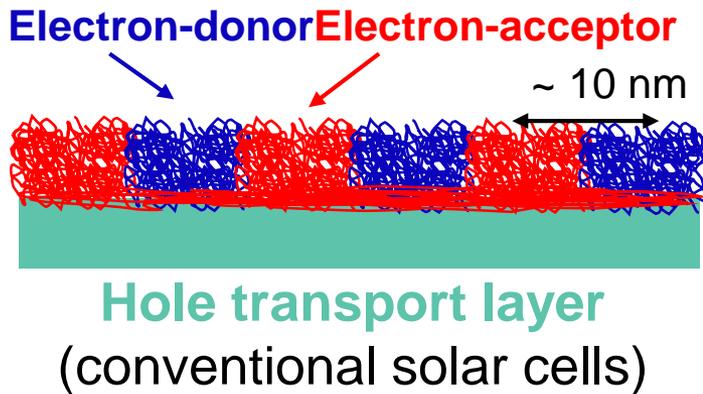
or



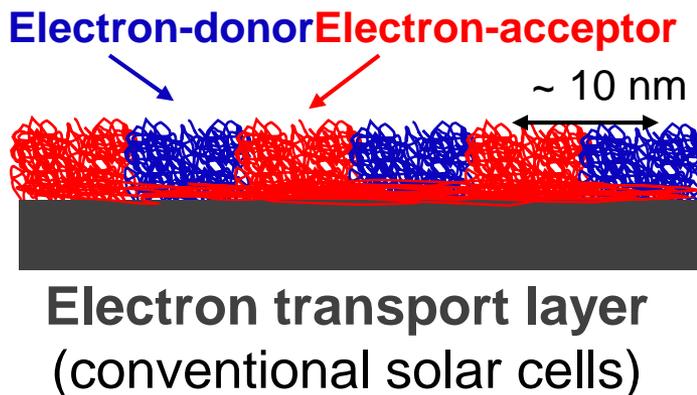
Electron transport layer
(conventional solar cells)



Organic photovoltaics for solar cells



or



Charge collection → Efficiency

Charge collection → Efficiency

Example 3

Adsorption of asphaltene





Adsorption of asphaltene under shear rate

Y. Corvis Eur. Phys. J. Special Topics 213, 295–302 (2012)

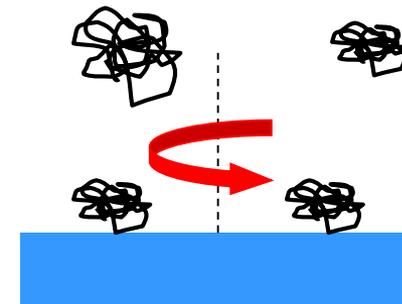
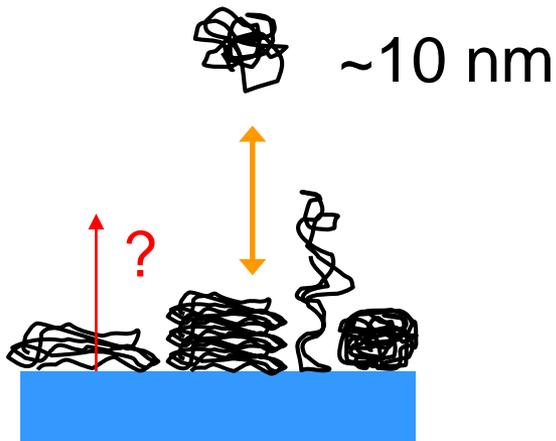


Adsorption of asphaltene from crude oils ?

aromatic dense core and a aliphatic shell

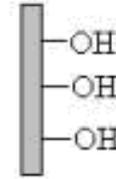
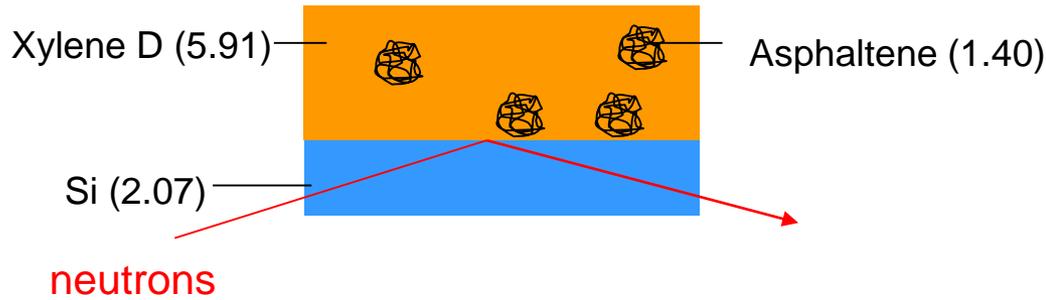


Blockage of pipes ?

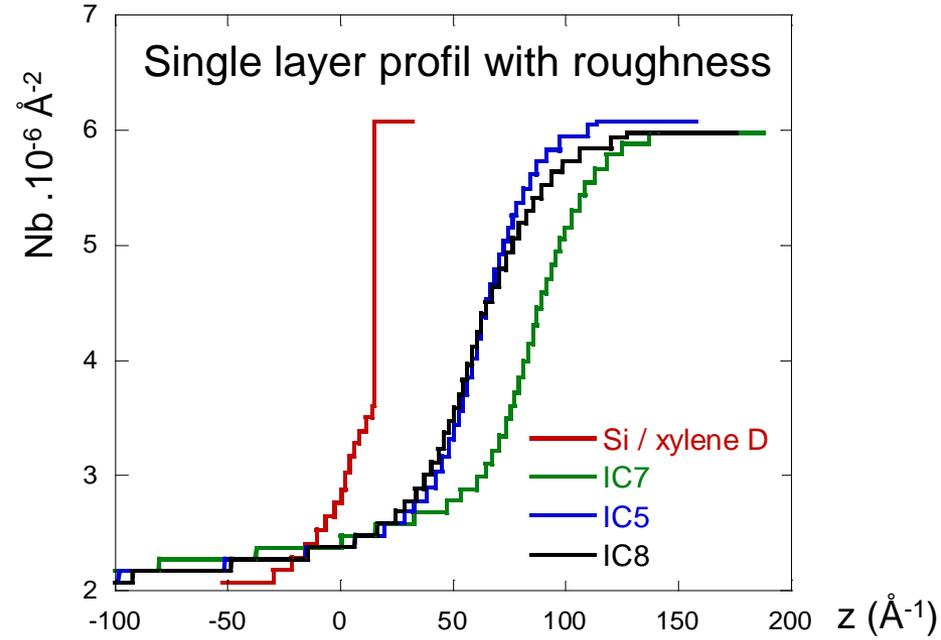
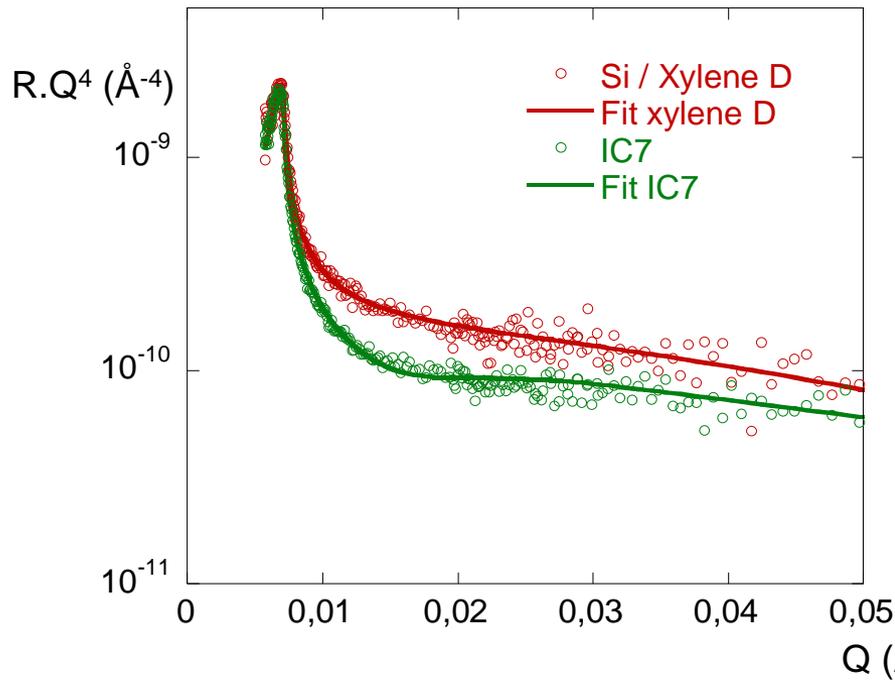




Adsorption of asphaltene under shear rate



Hydrophilic
(70/30 H₂O₂/H₂SO₄)



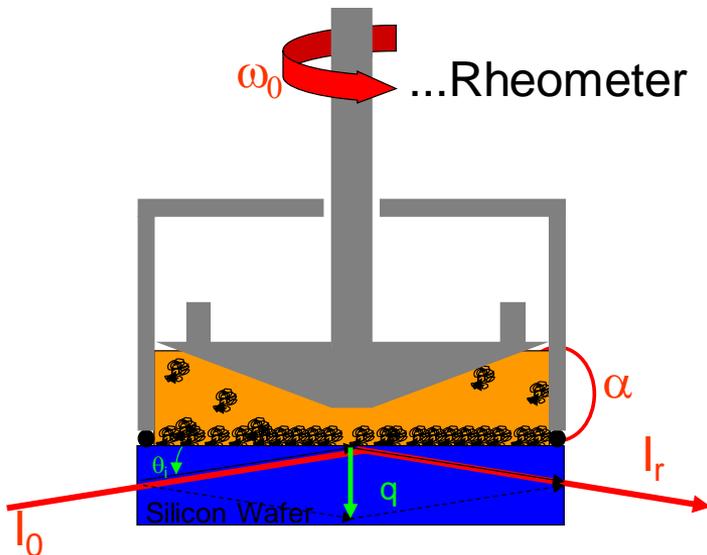
Monolayer - $e \sim R_g$ - density $\sim 70\%$ of asphaltenes - IC5~IC7~IC8

Adsorption of asphaltene under shear rate

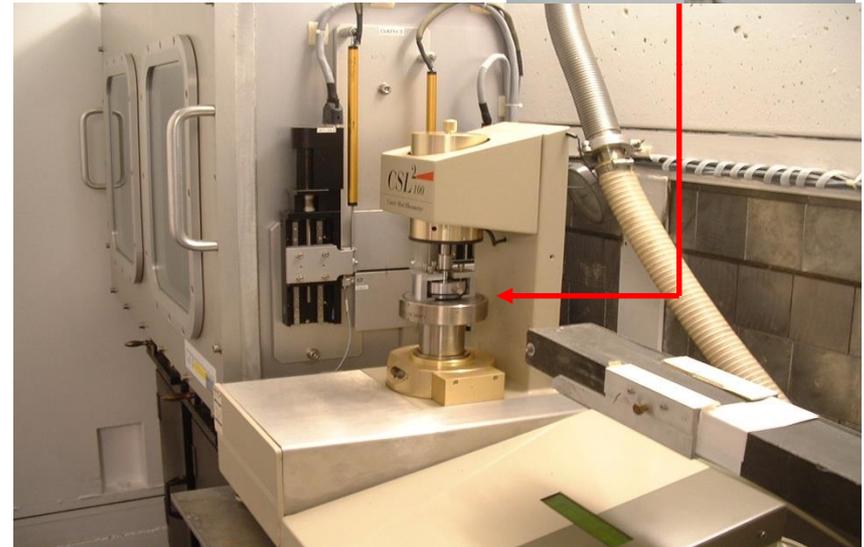
Y. Corvis et al, Euro. Phys. J ST **213** (2012) 295-302

Adsorption under dynamic conditions

The Rheo-reflectivity set-up



EROS reflectometer

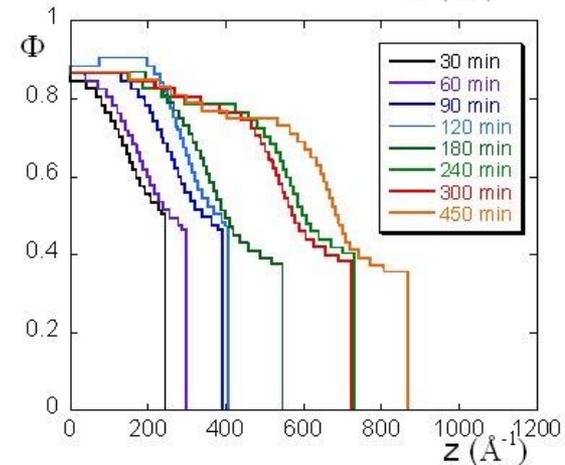
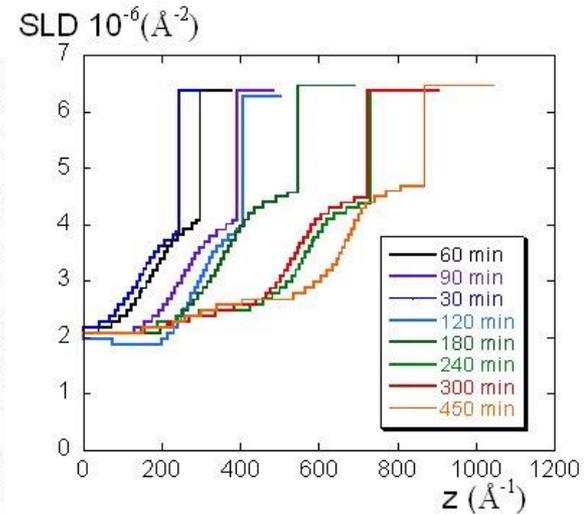
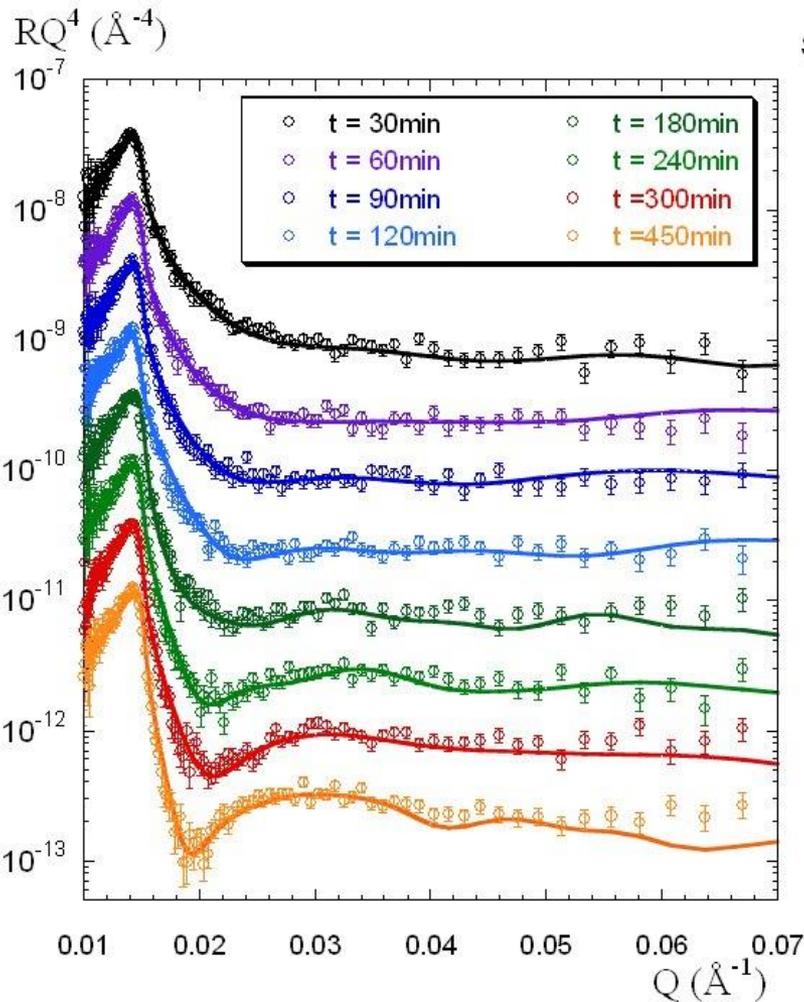


Effect of shear-rate : $\dot{\gamma} = 1200 \text{ s}^{-1}$; $\dot{\gamma} = 2600 \text{ s}^{-1}$

Effect of time : from 0 to 270 min.

$$\dot{\gamma} = \frac{\omega_0}{\alpha}$$

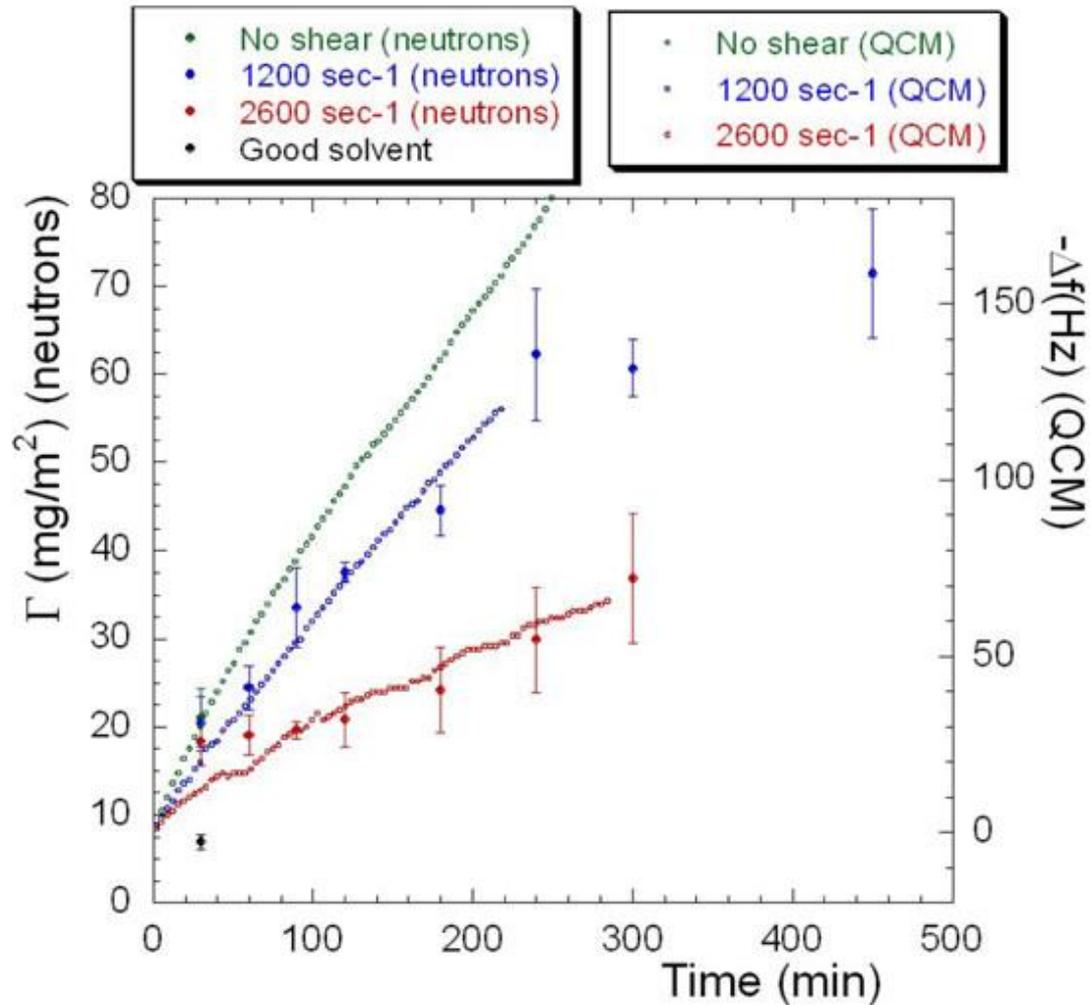
Adsorption of asphaltene under shear rate



1200s^{-1}

Adsorption of asphaltene under shear rate

1200s⁻¹



Conclusions



Comparison neutrons – xrays

Neutrons

- + Isotopic labelling
- + Cross Section known accurately
- + Wide range of sample environments
- Low flux
- Not element specific
- No resonant scattering

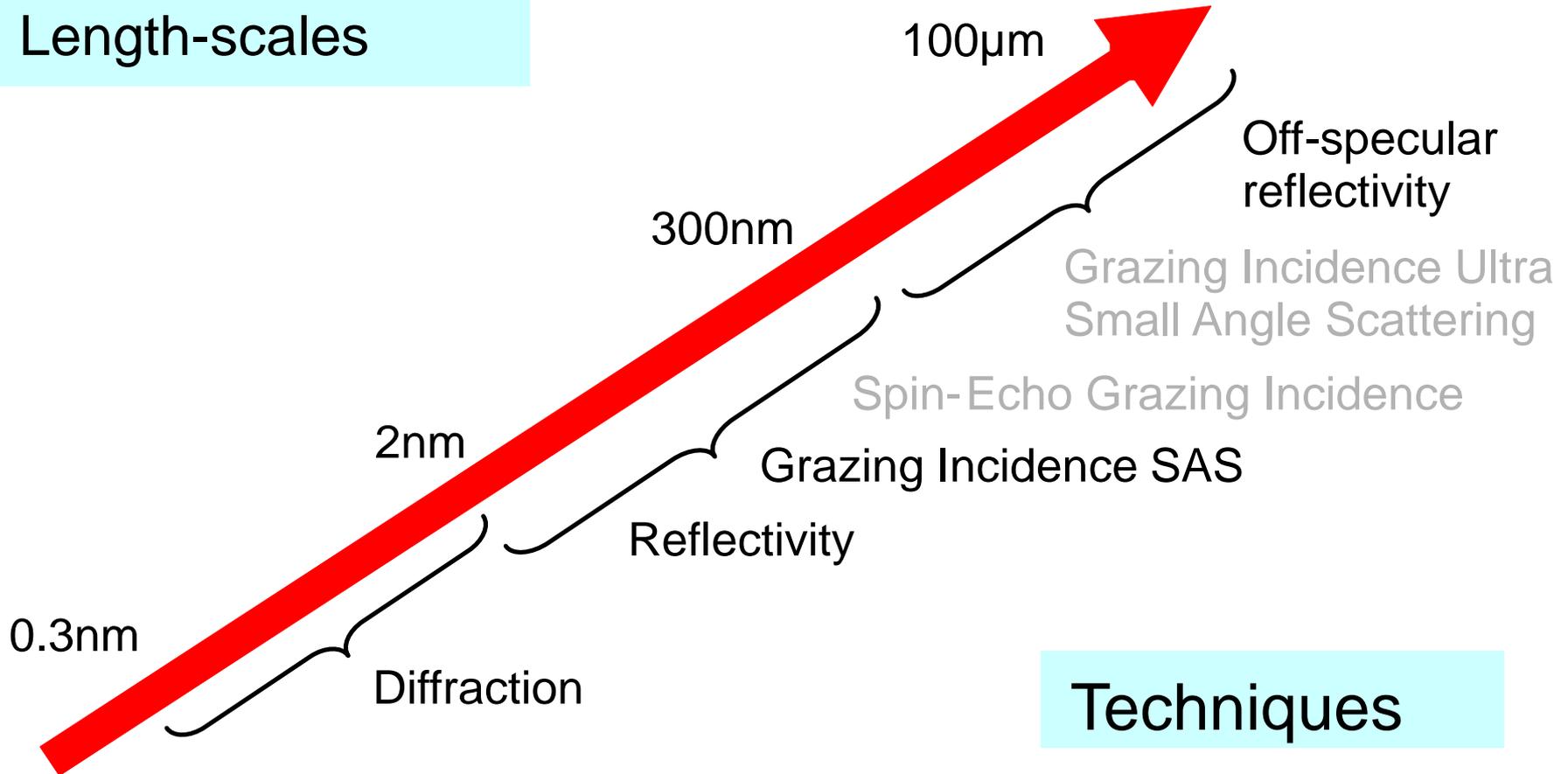
X-rays

- + High flux and large q
- + Can do kinetic experiments
- + Element Specific
- Indirect probe of the magnetisation
- Measure interference term between charge and magnetism
- Penetration depth



A panel of techniques

Length-scales



Techniques