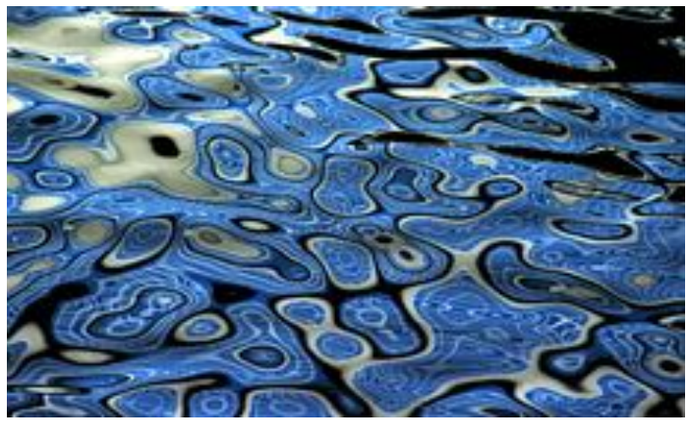

courtesy T. Saerbeck

INTRODUCTION TO NEUTRON REFLECTOMETRY FOR THE STUDY OF SURFACES AND INTERFACES

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Large Scale Structures & Soft Matter Science and Support
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Chair GIE UGA

NEUTRONS FOR SCIENCE

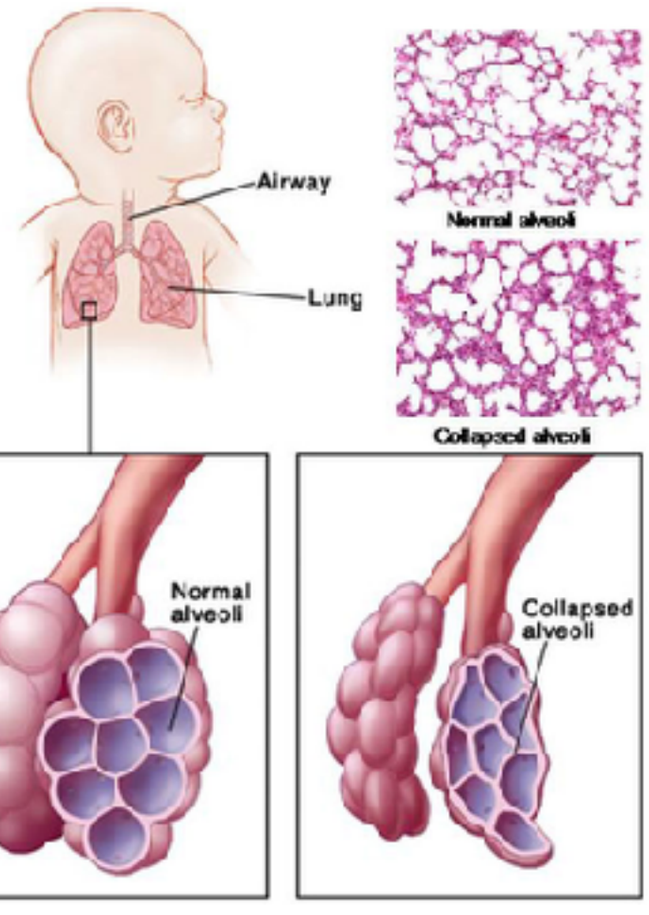
The importance of interfaces

They are everywhere: our body, food we eat, drinks, plants, animals, soil, atmosphere, manufacturing, chemical factories….

In many cases interfaces have a significant effect on the behaviour of a system

Examples:

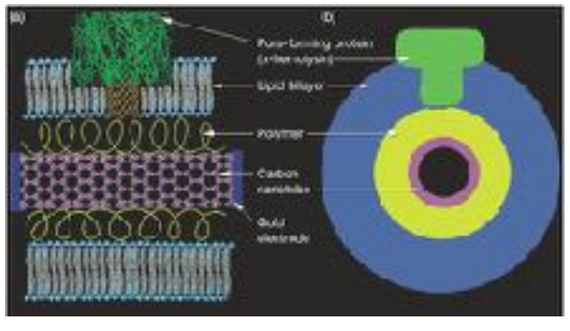
Inner lining of lung: surfactants prevent lung from collapsing at the end of expiration

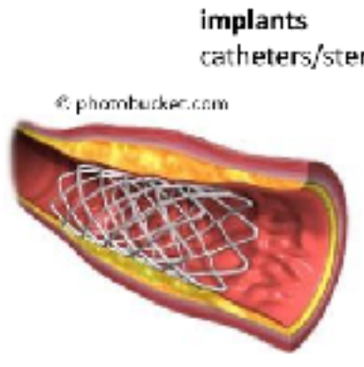


Nanotechnology: solid surfaces are the places where the processes of interest take place

Detergency

Biofouling





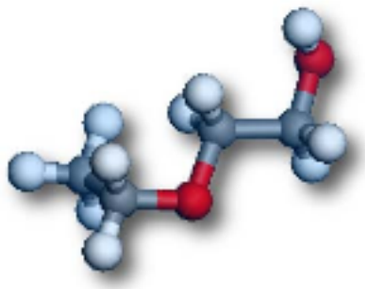
Specular Reflectometry

"Reflectometry is a technique used to determine the thickness and the internal structure of thin films at interfaces"

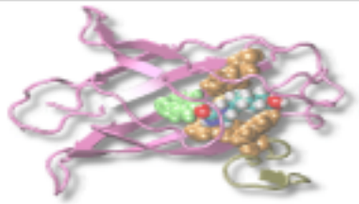
Characteristics of the film:

- Thickness comparable with the wavelength of the probe
- Visible for the probe i.e. with a good contrast with respect to the environment
- Allow the probe to penetrate across it i.e. low absorption for the given probe

Crystallography Microstructure Structure

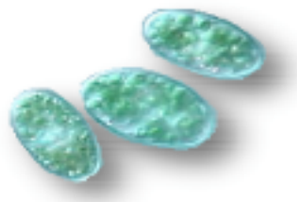


Atomic Structures

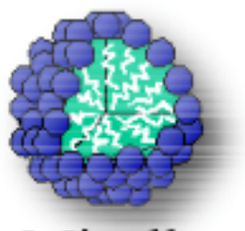


Proteins

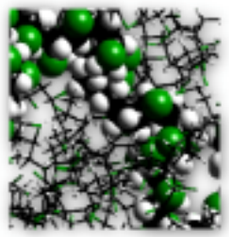
Viruses



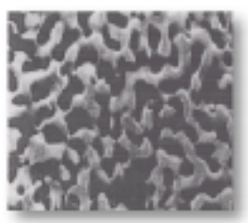
Bacteria



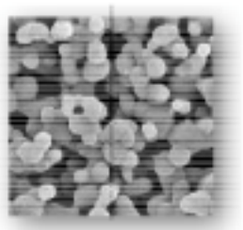
Micelles



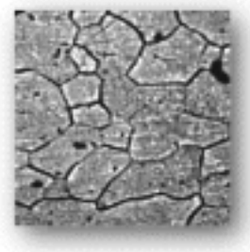
Polymers



Porous Media



Precipitates



Grain Structures

REFLECTOMETRY

TEM

USANS

DIFFRACTION

X-ray, n, e

SANS/SAXS

10-1000 Å

Optical microscopy

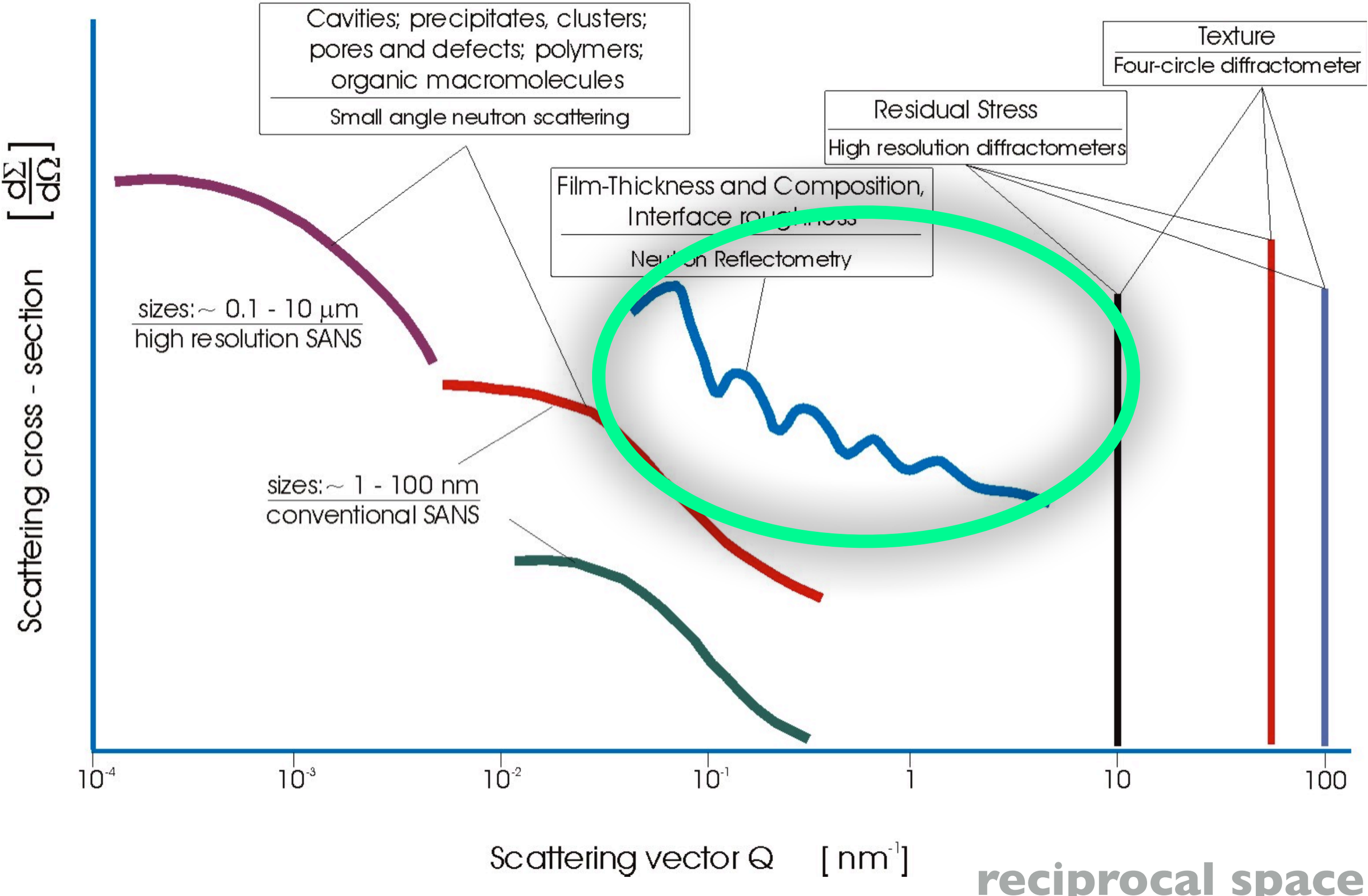
Light scattering

DLS

10^{-11} m 10^{-9} 10^{-7} 10^{-5} 10^{-3}

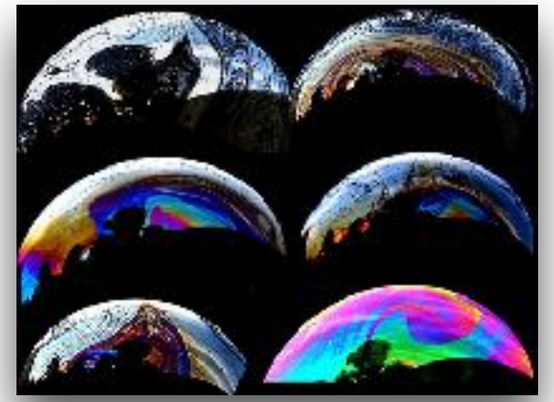
real space

Schematic view of elastic neutron scattering spectra

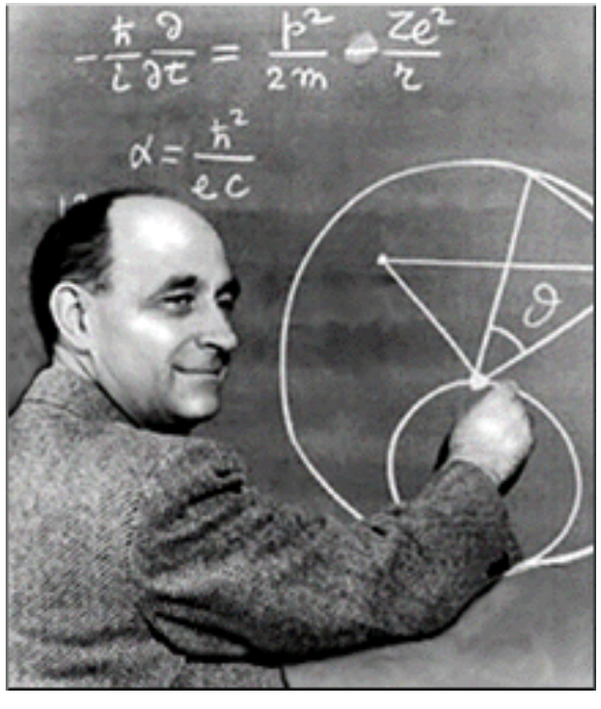


reciprocal space

1675 - *Newton* realised that the colour of the light reflected by a thin film illuminated by a parallel beam of white light could be used to obtain a measure of the film thickness. Spectral colours develop as a result of interference between light reflected from the front and back surfaces of the film.

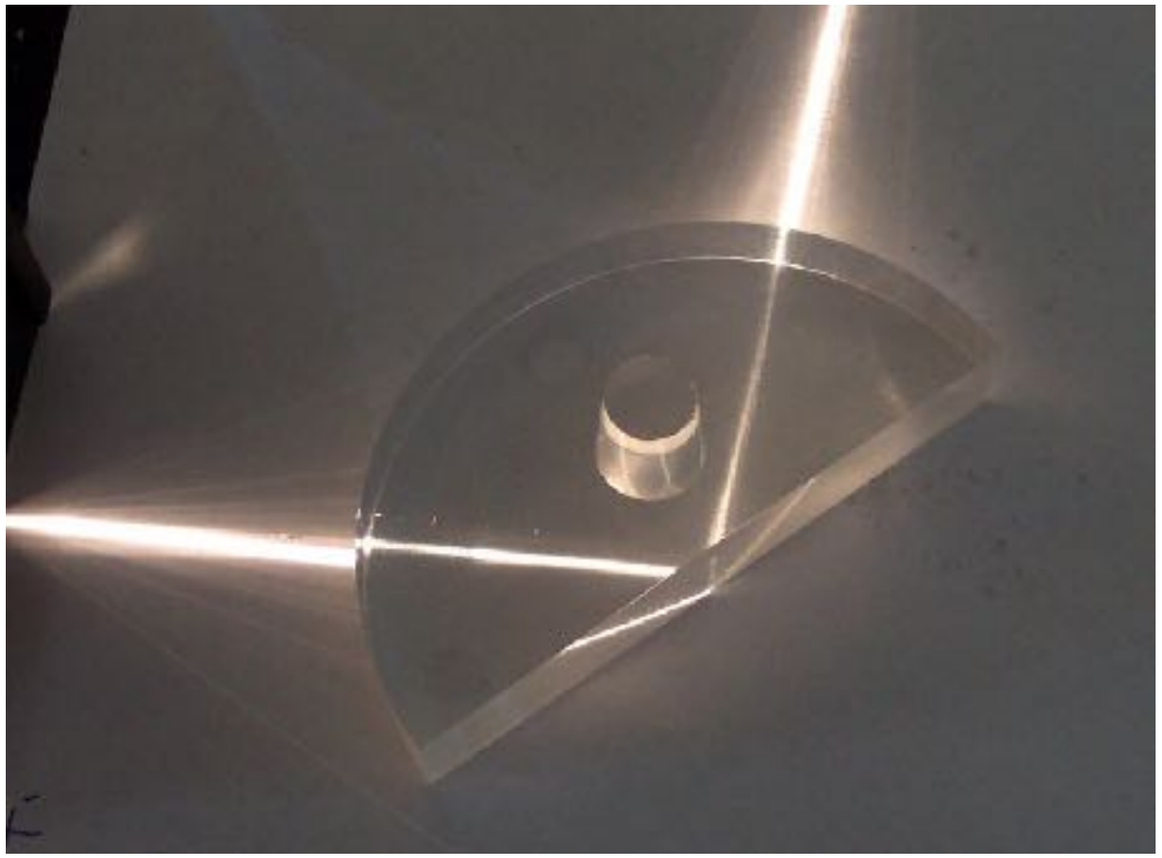


1922 - *Compton* showed that x-ray reflection is governed by the same laws as reflection of light but with different refractive indices depending on the number of electrons per unit volume.



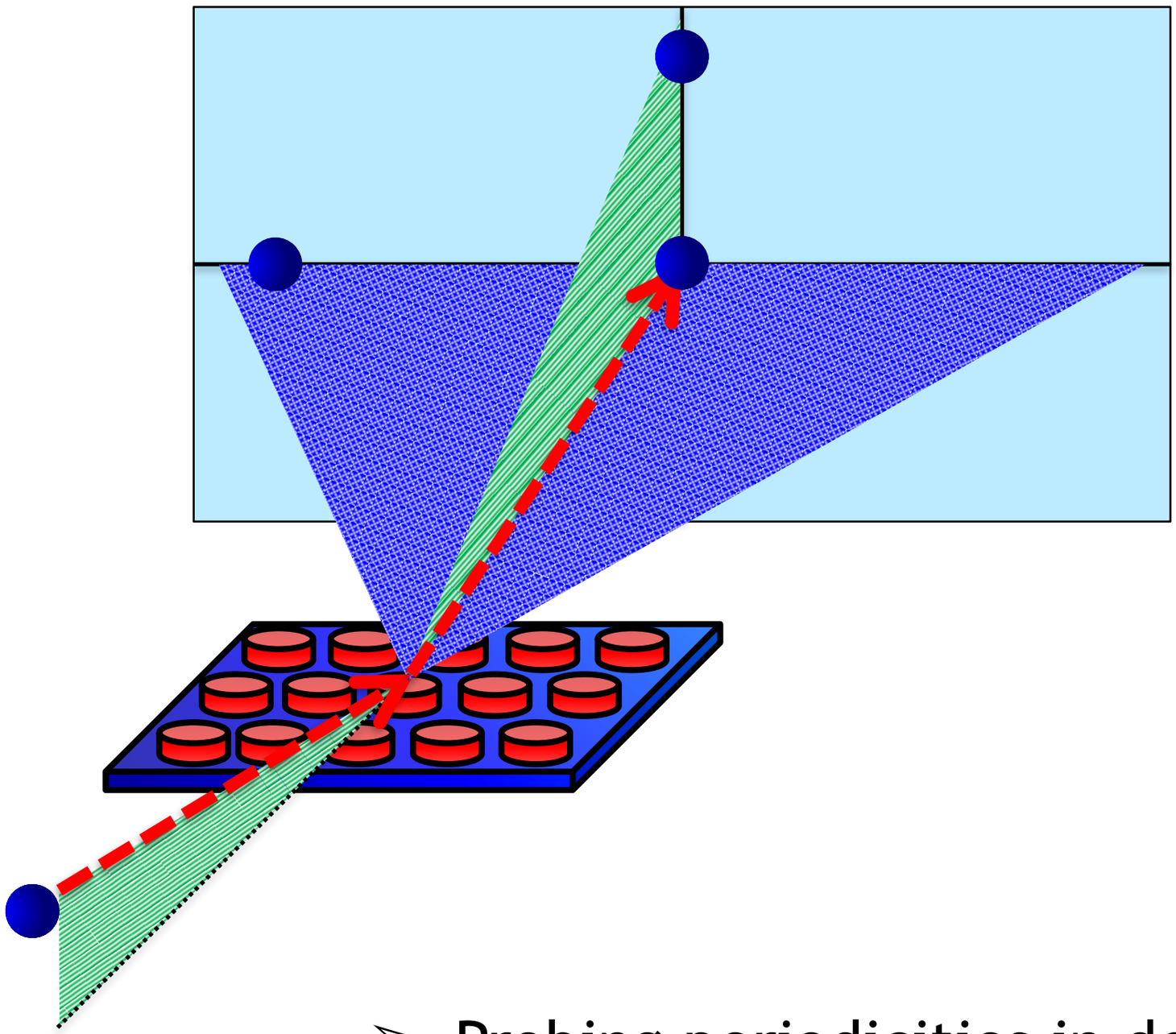
1944 - *Fermi* and ***Zinn*** first demonstrated the mirror reflection of neutrons. Again this follows the same fundamental equations as optical reflectivity but with different refractive indices.

For both kinds of radiation the refractive index is a function of the scattering length density and wavelength.



As with light, total reflection may occur when neutrons pass from a medium of higher refractive index to one of lower refractive index.

Reflectometry – OSS – GISAS



1) Specular Reflectivity
   → 1 nm < ξ < 300 nm

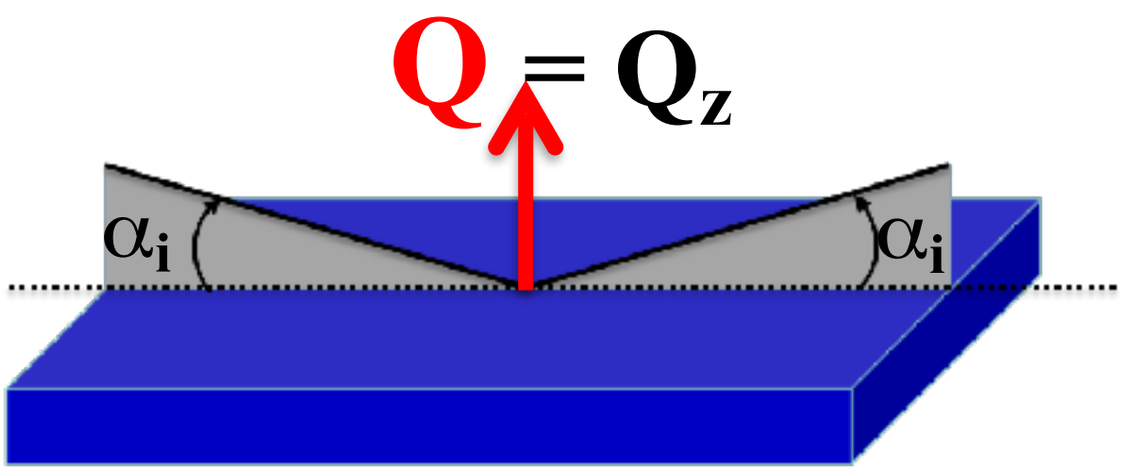
2) Off-Specular Scattering
   → 400 nm < ξ < 60 μm

3) Grazing Incidence
   Scattering
   → 1 nm < ξ < 200 nm

➢ Probing periodicities in depth and laterally on different length scales

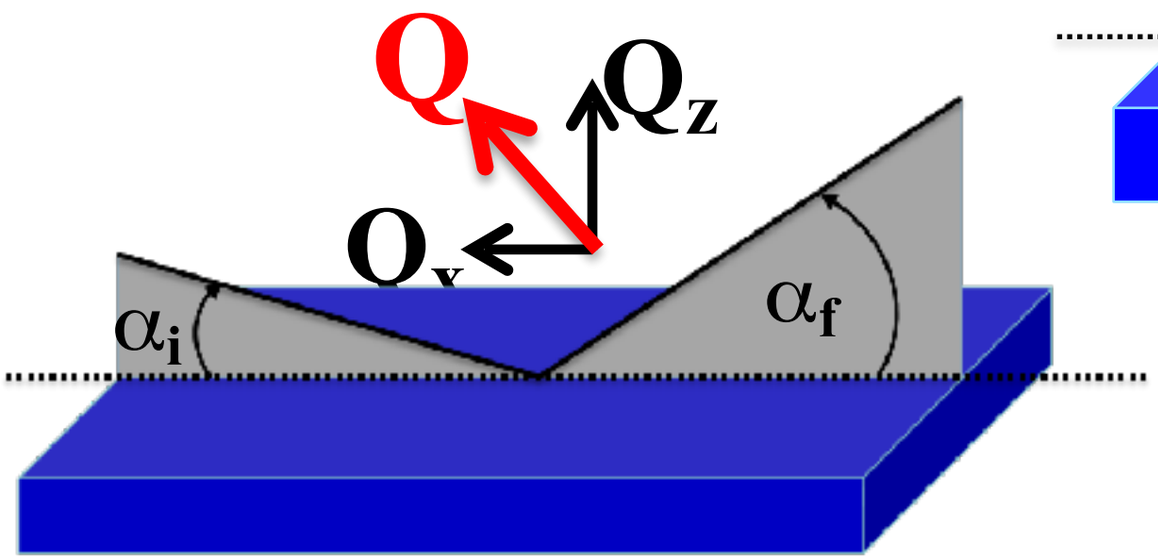
courtesy T. Saerbeck

Specular Reflection



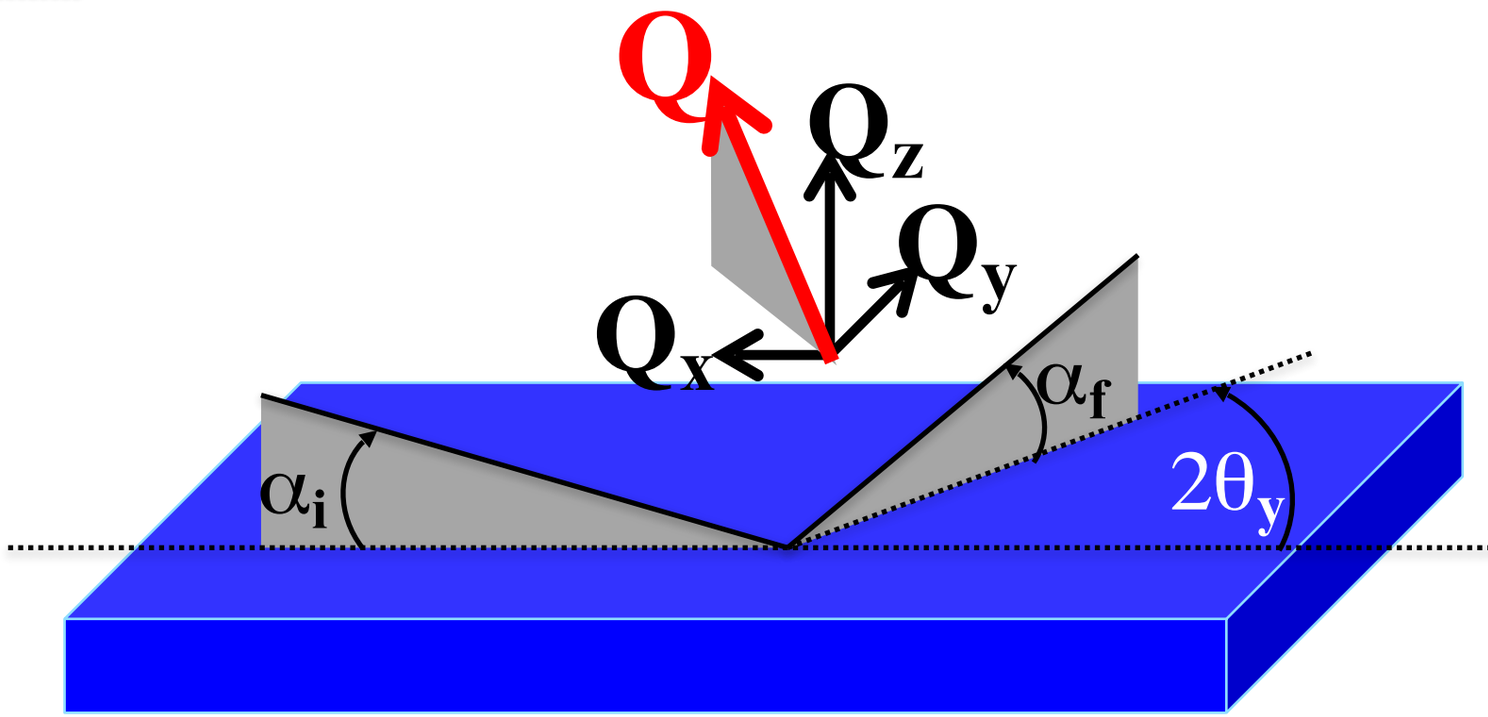
$$Q_Z = \frac{2\pi}{\lambda}(\sin\alpha_i + \sin\alpha_f)$$

Off-Specular Scattering



$$Q_X = \frac{2\pi}{\lambda}(\cos\theta_y\cos\alpha_f - \cos\alpha_i)$$

Grazing Incidence Diffraction

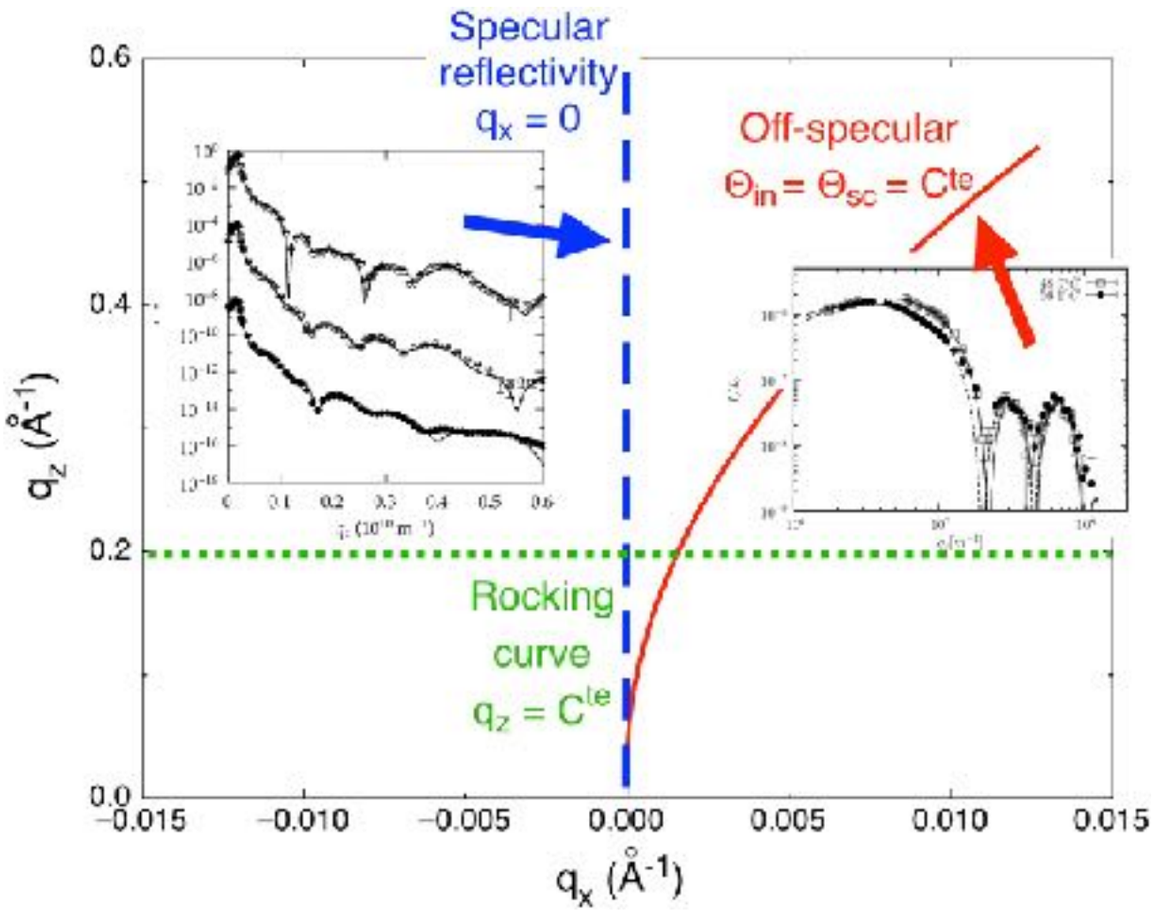


$$Q_Y = \frac{4\pi}{\lambda}(\sin\theta_y\cos\alpha_f)$$

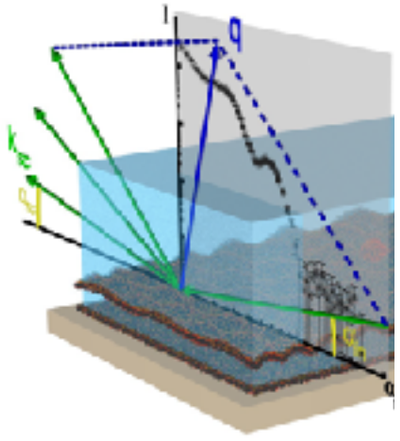
courtesy T. Saerbeck

Specular reflection most commonly used for soft and biological matter

- Thickness of layers at interfaces
- Roughness/interdiffusion
- Composition in the direction normal to the interface



In-plane features (height fluctuations, domains, holes ...) can be probed by **off-specular** measurements: for thin films synchrotron radiation is more suitable



Basic Principles of Neutron Reflection Theory

neutron scattering
A PRIMER

by Roger Pynn

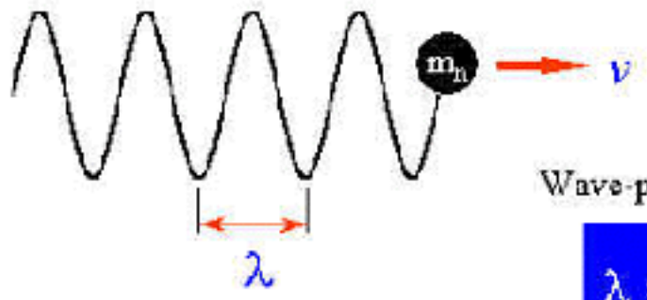
"Neutron man" personifies the neutron's dual nature, exhibiting wave and particle properties. Here he enters a crystal lattice as a plane wave (blue), interacts with the crystal lattice (green), and becomes, through interference effects, an outgoing plane wave (red) with a direction dictated by Bragg's law. His particle properties allow him to be absorbed by a helium atom in a neutron detector, and his time of flight is measured.

How can we determine the relative positions and motions of atoms in a bulk sample of solid or liquid? Somehow we need to see inside the material with a suitable magnifying glass. But seeing with light in an everyday sense will not suffice. First, we can only see inside the few materials that are transparent, and second, there is no microscope that will allow us to see individual atoms. These are not merely technical hurdles, like those of sending a man to the moon, but intrinsic limitations. We cannot make an opaque body transparent nor can we see detail on a scale finer than the wavelength of the radiation we are using to observe it. For observations with visible light this limits us to objects separated by about a micrometer (10^{-6} meter), which is more than a thousand times longer than the typical interatomic distance in a solid (about 10^{-10} meter or so).

X rays have wavelengths much shorter than those of visible light, so we might try using them to find atomic positions. For many crystalline materials this technique works quite well. The x rays are diffracted by the material, and one can work out the relative atomic positions from the pattern of spots the diffracted rays make on a photographic plate. However, not all atoms are equally "visible" to x rays:

"Neutron man" personifies the neutron's dual nature, exhibiting wave and particle properties. Here he enters a crystal lattice as a plane wave (blue), interacts with the crystal lattice (green), and becomes, through interference effects, an outgoing plane wave (red) with a direction dictated by Bragg's law. His particle properties allow him to be able to be absorbed by a He atom in a neutron detector, and his time of flight measured.

Neutrons can be treated as a wave:



Wave-particle duality

$$\lambda = \frac{h}{m_n v}$$

de Broglie (1924)

$m_n = 1.674 \times 10^{-27}$ kg

Thus: $\lambda \sim 10^{-10}$ m

$E \sim k_B T$

The Schroedinger equation is analogous to the wave equation for light and leads to neutrons showing characteristic optical behaviour such as total reflection and refraction.

The Schroedinger equation may be written as:

$$-\frac{h^2}{8\pi^2 m_n}\nabla^2\Psi + V\Psi = E\Psi$$

Where *V* is the potential to which the neutron is subject and *E* its energy

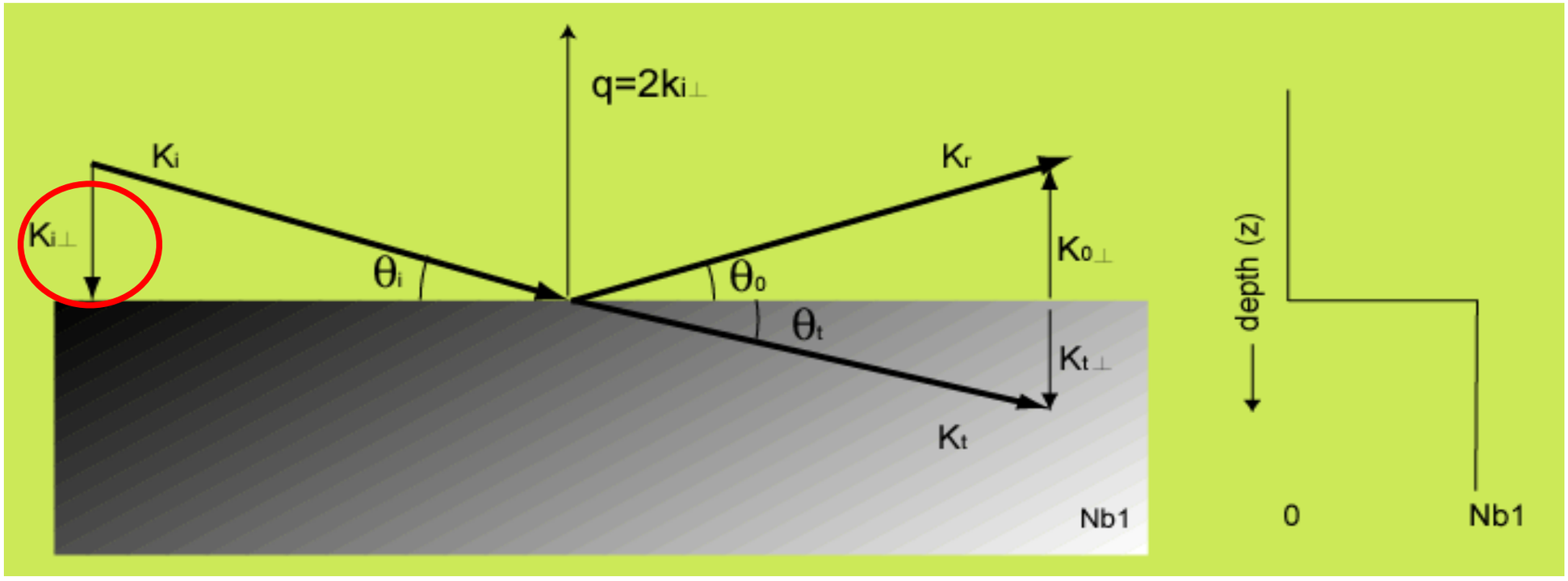
V **represents the net effect of the interactions between the neutron and the scatterers in the medium through which it moves.**

$$V = \frac{h^2}{2\pi m_n} N_b$$

$$N_b = \frac{\sum_j b_j n_j}{Vol}$$

scattering length density

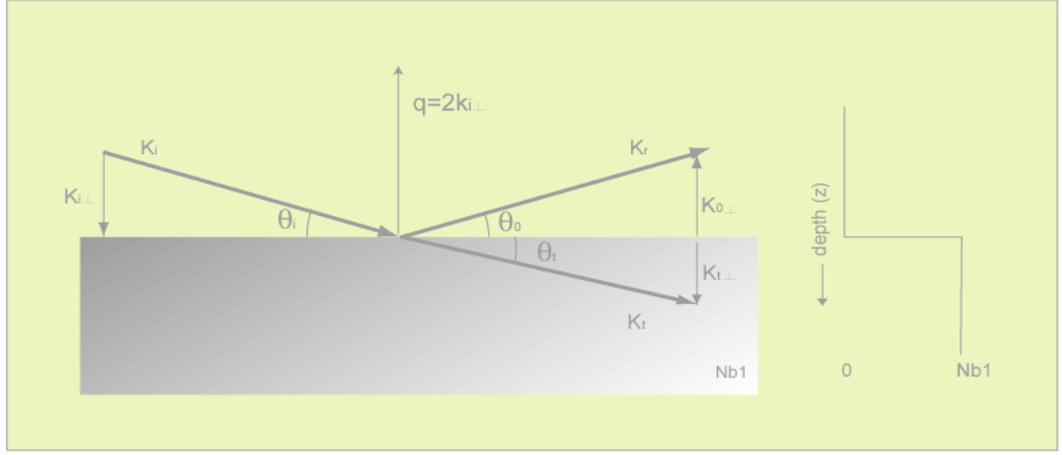
Let us consider *a beam approaching a surface with a bulk potential V*, infinitely deep



With no structure within the surface the only potential gradient and hence force is perpendicular to the surface.

Only the normal component of the incoming wave vector, k_i is altered by the barrier potential and it is the normal component of the kinetic energy $E_{i\perp}$ which determines whether the neutron is totally reflected from the barrier or not.

$$E_{i\perp} = \frac{(hk_i \sin\theta_i)^2}{8\pi^2 m_n}$$



If **$E_{i\perp}$<V then there is total reflection** and when $E_{i\perp} = V = \frac{h^2}{2\pi m_n} N_b$

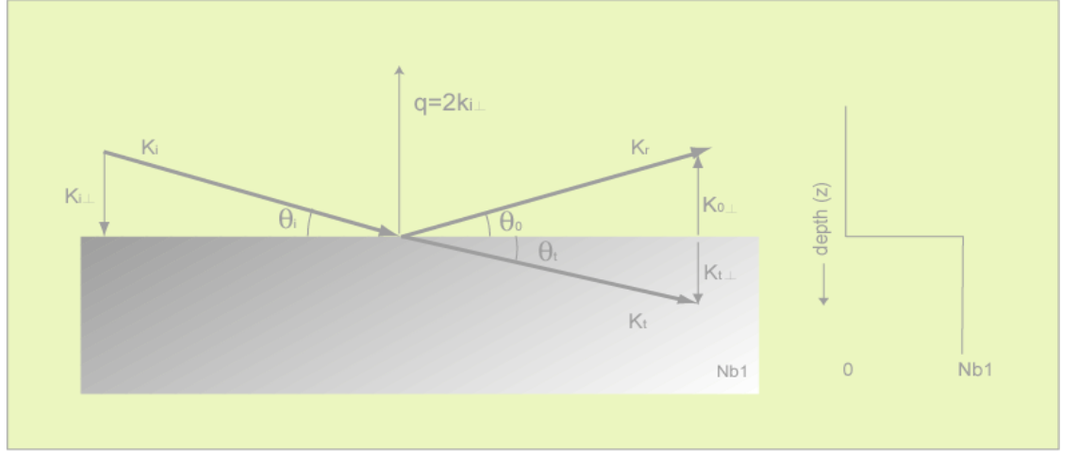
$$q_c = \sqrt{16\pi N_b} \quad \text{as} \quad q = 2k_i \sin\theta_i$$

If interaction is elastic then conservation of momentum and

$$\theta_i = \theta_o$$

***i.e.* the reflection is specular**

Provided the sample is static, any off specular reflection must be a result of potential gradients within the xy plane of the surface.



If $E_{i\perp}$>V, then the reflection is not total and the neutron can either be reflected or transmitted into the bulk of the material.

The transmitted beam, k_t with its normal component of kinetic energy reduced by the potential must change direction i.e. it is refracted.

The change in the normal wave vector is

$$k_{t\perp}^2 = k_{i\perp}^2 - 4\pi N_b$$

$$n^2 = \frac{k_t^2}{k_i^2} = \frac{k_{i//}^2 + (k_{i\perp}^2 - 4\pi N_b)}{k_i^2} = 1 - \frac{4\pi N_b}{k_i^2} = 1 - \frac{\lambda^2 N_b}{\pi}$$

Values of Refractive Index

$$n = 1 - \delta - i\beta$$

X-RAYS

$$\delta = \frac{\lambda^2}{2\pi} r_e \rho$$

NEUTRONS

$$\delta = \frac{\lambda^2}{2\pi} N_b$$

- Small difference in refractive index means that critical angles are small (less than 1 degree)
- As most n < 1, total external reflection is common. In optics n > 1
- Mixtures of isotopes can be used to match values of different materials
- β absorption coefficient small with neutrons

Quantum mechanical approach

The wavefunction describing the probability amplitude of a neutron near to the surface is:

$$\frac{\partial^2 \Psi_z}{\delta z^2} + k_\perp^2 = 0 \qquad \text{where} \qquad k_\perp^2 = \frac{2m_n}{\hbar^2}\left(E_i - V\right) - k_{//}^2$$

Solutions for this above and below the surface are:

$$\Psi_z = e^{ik_{i\perp}z} + re^{-ik_{i\perp}z} \qquad \& \qquad Y_z = te^{ik_{t\perp}z}$$

where r and t are the probability amplitudes for reflection and transmission.

Continuity of the wavefunction and its derivative gives the expressions:

$$1 + r = t \qquad\qquad k_{i\perp}\left(1 - r\right) = t\, k_{t\perp}$$

where the second relation only holds for $\mathbf{E_{i\perp} > V}$;

this leads directly to the classical ***Fresnel coefficients*** found in optics:

$$r = \frac{k_{i\perp} - k_{t\perp}}{k_{i\perp} + k_{t\perp}} \qquad \& \qquad t = \frac{2k_{i\perp}}{k_{i\perp} + k_{t\perp}}$$

Reflectivity is measured as a function of wavevector transfer or *q*

Note that what is measured is an intensity and thus is a function of the quantum mechanical probability amplitude squared.

$$R = r^2 = \left[\frac{q - \left(q^2 - q_c^2\right)^{1/2}}{q + \left(q^2 - q_c^2\right)^{1/2}} \right]^2$$

Fresnel reflectivity

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

Born Approximation

$q \gg q_c$

Ignored double scattering processes because these are usually very weak

$$q_c = \sqrt{16\pi N_b}$$

$$R(q) = \frac{16\pi^2}{q^4}\left|N_b(q)\right|^2$$

$$N_b(q) = \int_{-\infty}^{+\infty} \exp(iqz)\frac{dN_b}{dz}dz$$

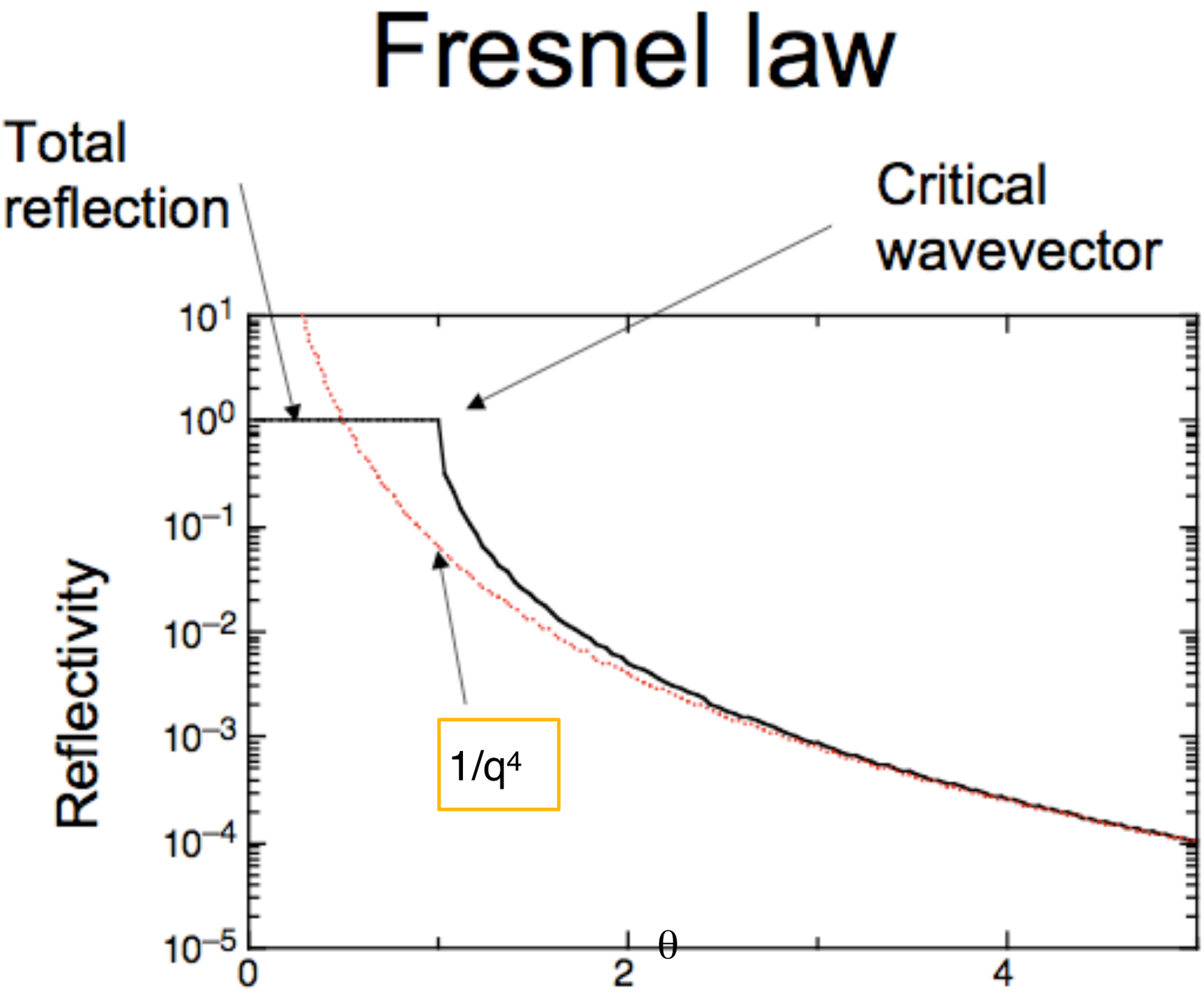
Scattering length density

$$N_b = \frac{\sum_i n_i b_i}{V}$$

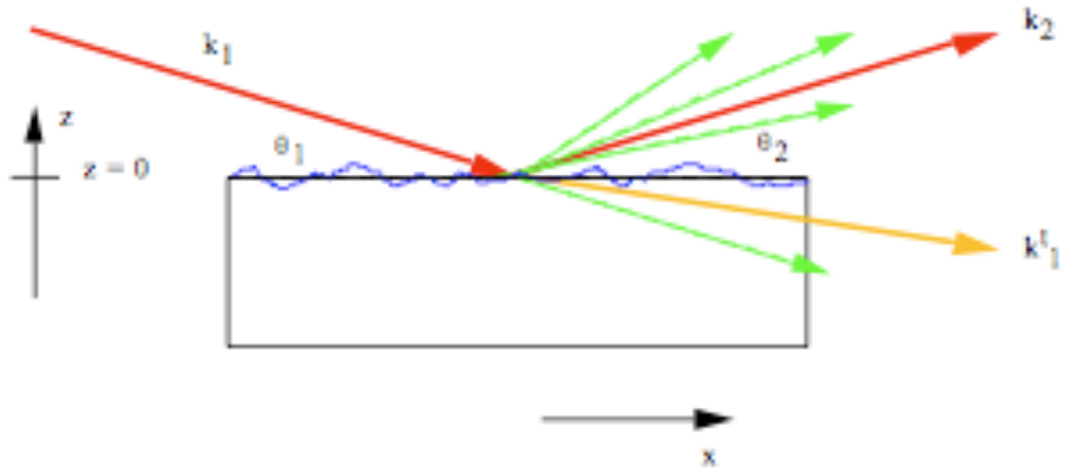
you can find it indicated also as ρ or SLD

$R = 1$ below q_{crit}

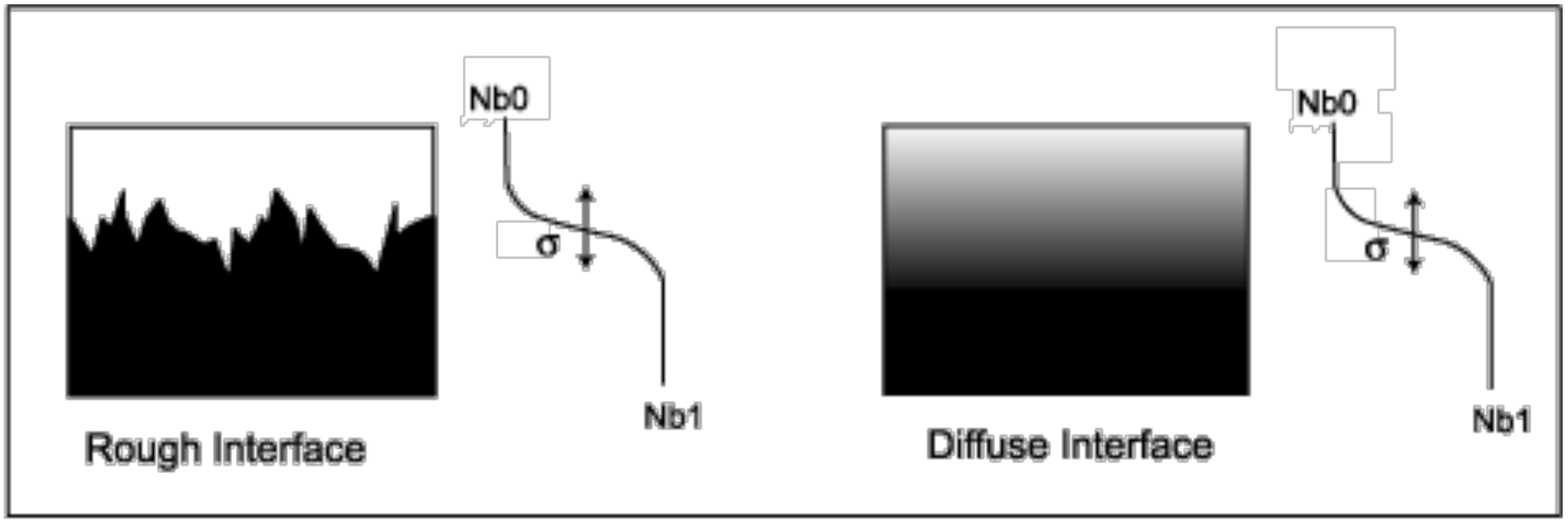
$\theta_c = \arccos(n_1/n_2)$



Roughness and Interdiffusion



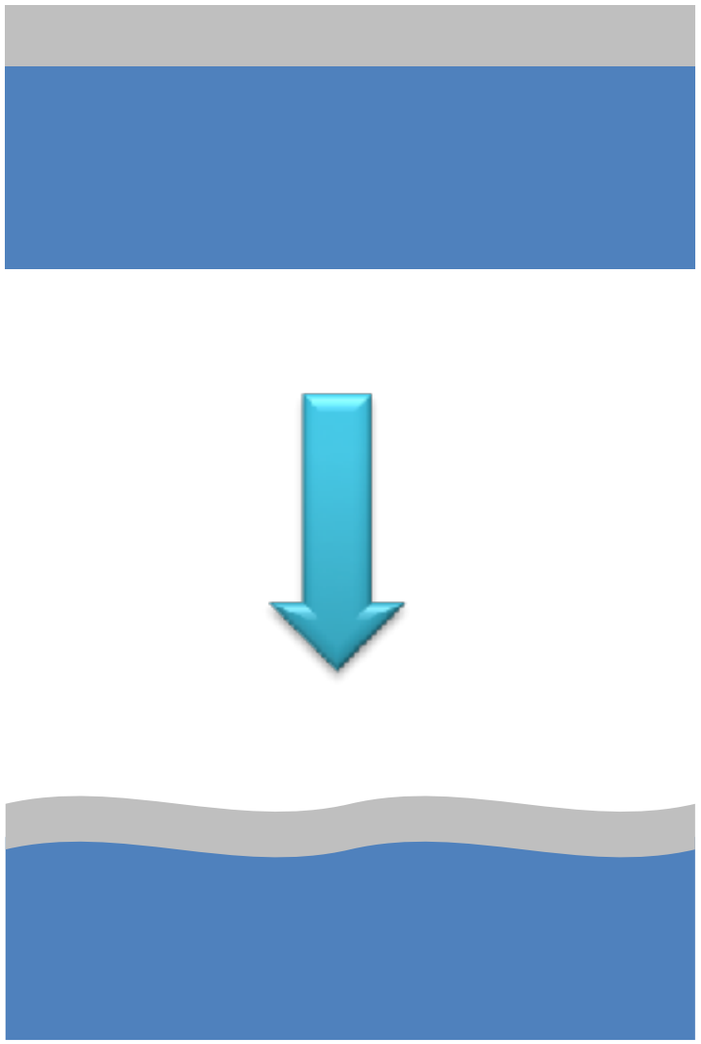
Both the rough and diffuse case the specular reflectivity is reduced by a factor very much like the Debye-Waller factor reduces scattered intensity from a crystal

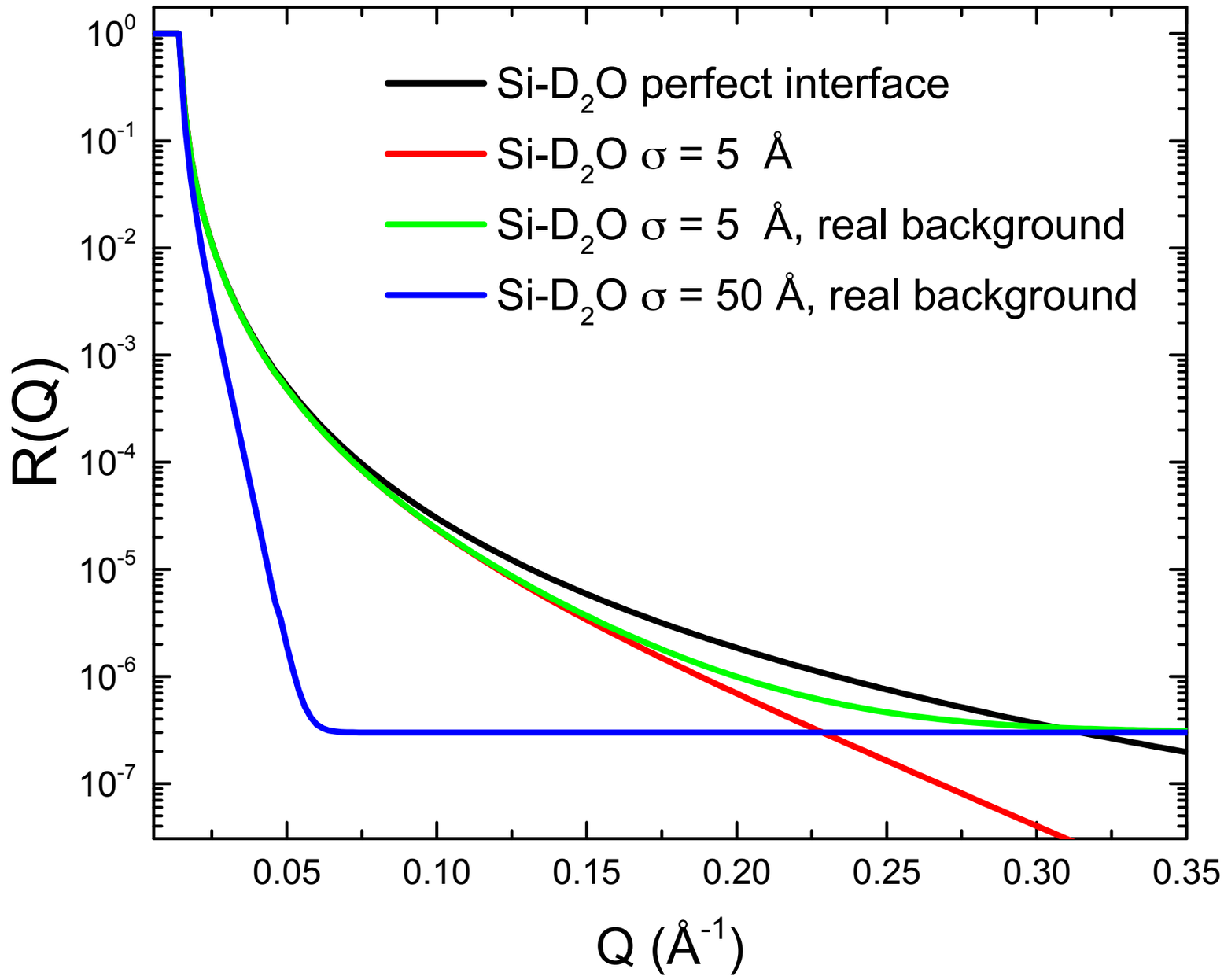


$$R \approx \left(\frac{16\pi^2}{q^4} N_b^2 \right) e^{-q_z^2 \sigma^2}$$

σ is a characteristic length scale of the layer imperfection

Real interfaces

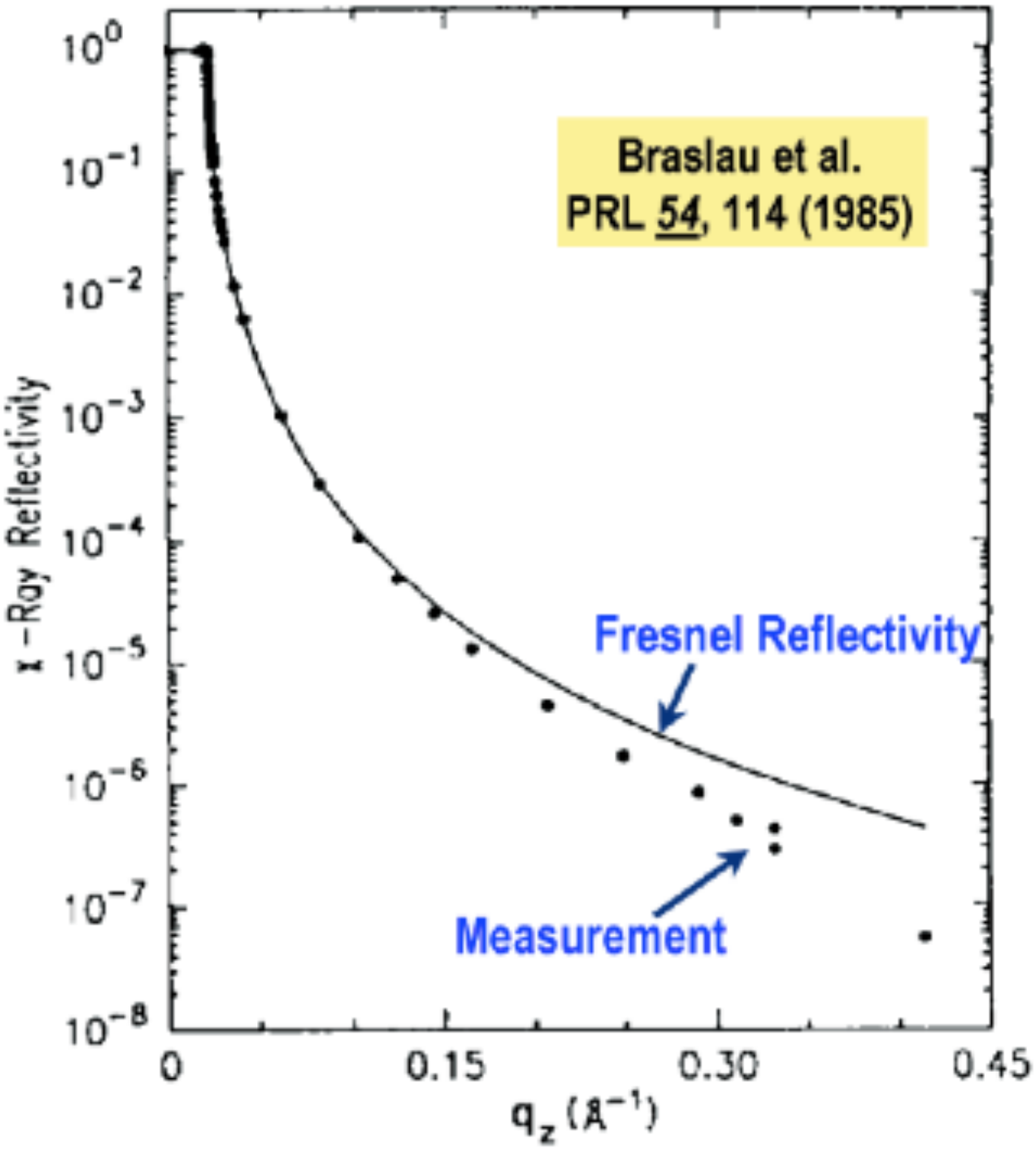


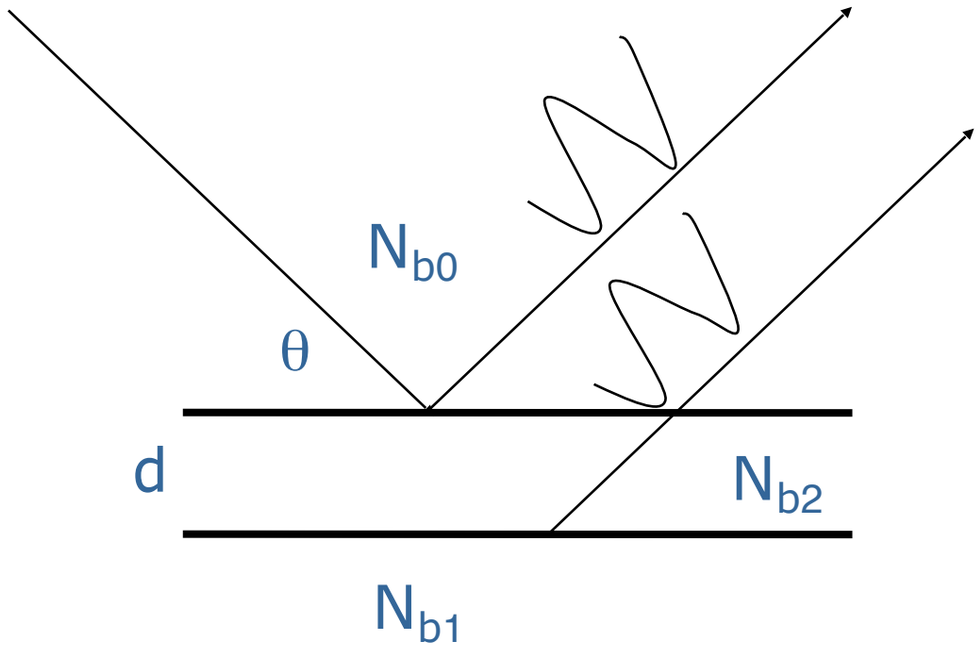


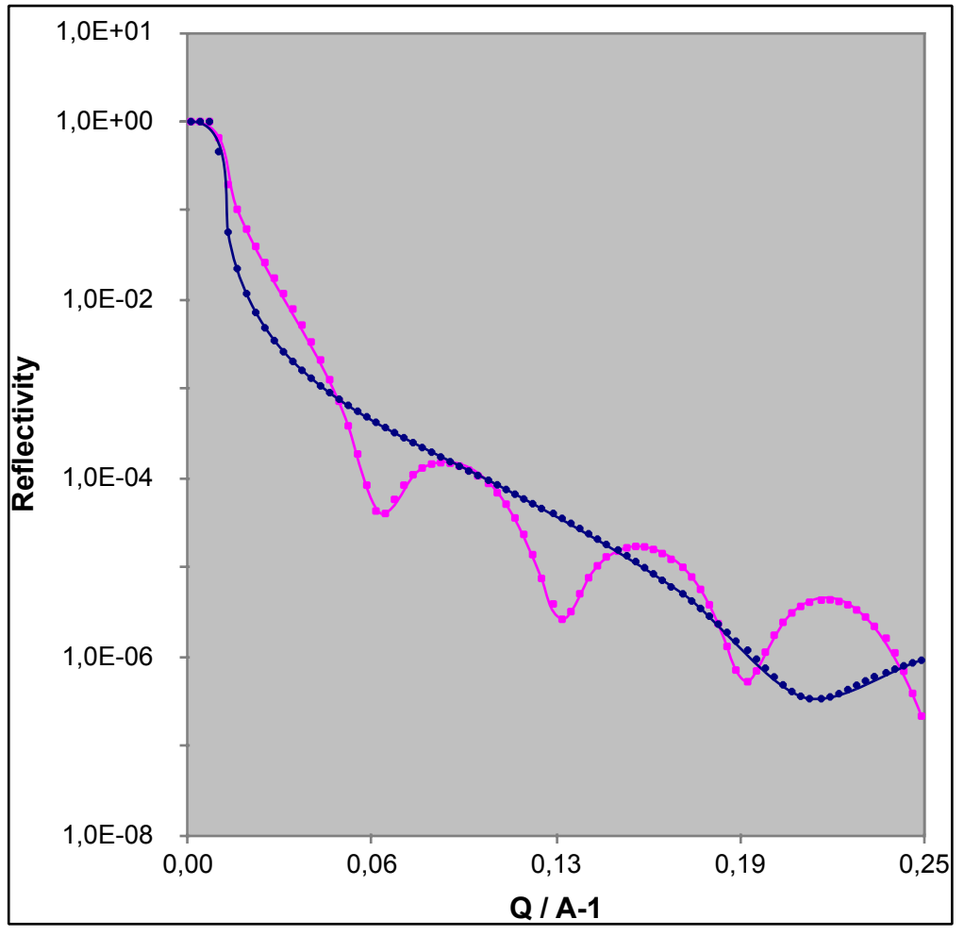
If interfaces are too rough reflectivity will decay quickly with loss of structural information on layer

courtesy Y. Gerelli

X-ray measurement of capillary wave amplitude on water (0.3nm)





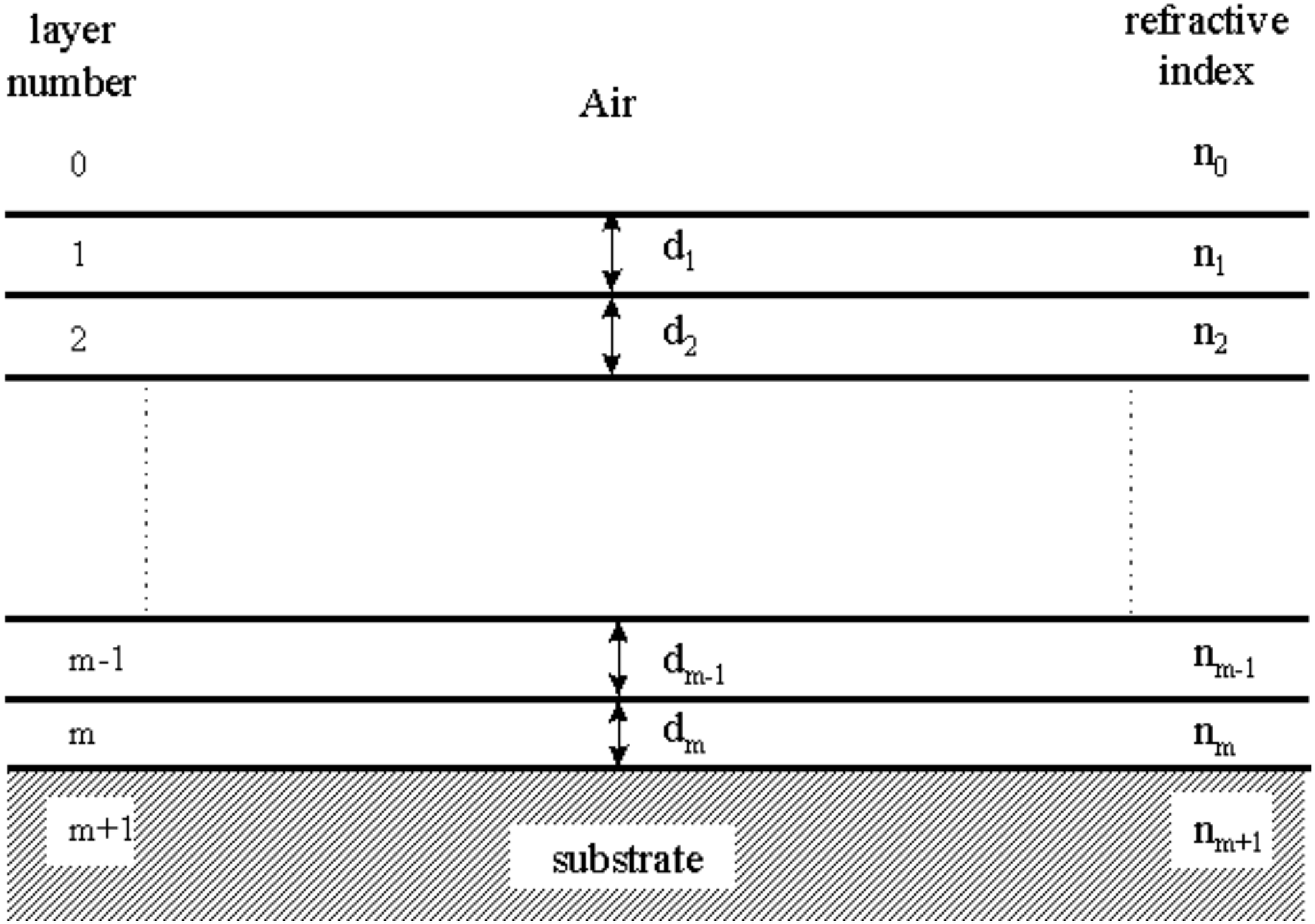


- Model calculation on smooth surface.
- Fringe spacing depends on thickness
- Fringe spacing ~ 2π/d

Model layer with ρ = 5 x 10^{-6} Å^2 on Si (2.07 10^{-6} Å $^{-2}$)
Blue 30 Å, Pink 100 Å. No roughness.

$$Rq^4 = [(N_{b2} - N_{b0})^2 + (N_{b1} - N_{b2})^2 + 2(N_{b2} - N_{b0})(N_{b1} - N_{b2})\cos(qd)]$$

Reflectivity from m layers



The reflection coefficient for the sample is calculated by firstly considering the coefficient between the substrate and the bottom layer, $r_{m,m+1}$, *i.e.* between the $(m+1)^{th}$ and m^{th} layers

$$r_{j,j+1} = \frac{n_j \sin\theta - n_{j+1} \sin\theta_{j+1}}{n_j \sin\theta + n_{j+1} \sin\theta_{j+1}}$$

The reflectivity coefficient between the (m-1)th and m^{th} is then given by:

$$r'_{m-1,m} = \frac{r_{m-1,m} - r_{m,m+1}\exp(2i\beta_m)}{r_{m-1,m} + r_{m,m+1}\exp(2i\beta_m)}$$

A phase factor, β_m, has also been introduced and represents an optical path length term for the mth layer, such that

$$\beta_m = (2\pi/\lambda) n_m d_m \sin\theta$$

where n_m and d_m are the refractive index and thickness respectively of layer m

This approach of calculating reflectivity is exact but extending it to multilayers is cumbersome.

A more general solution widely used is the **OPTICAL MATRIX METHOD** (Abeles).

$$c_m = \begin{bmatrix} \cos\beta_m & -(i/\kappa_m)\sin\beta_m \\ -i\kappa_m \sin\beta_m & \cos\beta_m \end{bmatrix}$$

An overall sample matrix is then defined as the product of the individual matrices:

$$M = \prod_{m=0}^{m} c_m = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix}$$

The reflectivity is simply related to the matrix elements from M by:

$$R = \left| \frac{(M_{11} + M_{12}k_{m+1})k_0 - (M_{21} + M_{22})k_{m+1}}{(M_{11} + M_{12}k_{m+1})k_0 + (M_{21} + M_{22})k_{m+1}} \right|^2$$

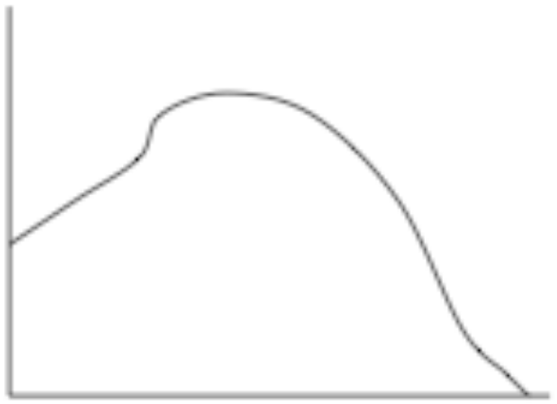
where m+1 denotes the substrate and 0 the air

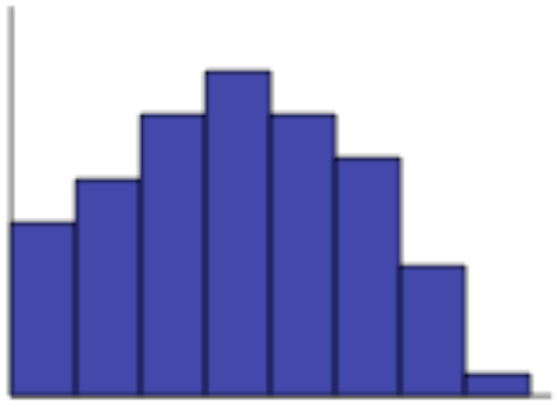
DATA ANALYSIS

Routine analysis of reflectivity data would ideally be solved by direct inversion of experimental data into either scattering length density, *Nb(z)*, or even volume fraction, f(z), profiles.

Generally, this cannot be achieved due to the loss of phase information, making this closely related to the phaseless Fourier problem.

Fitting data





Model

Layers

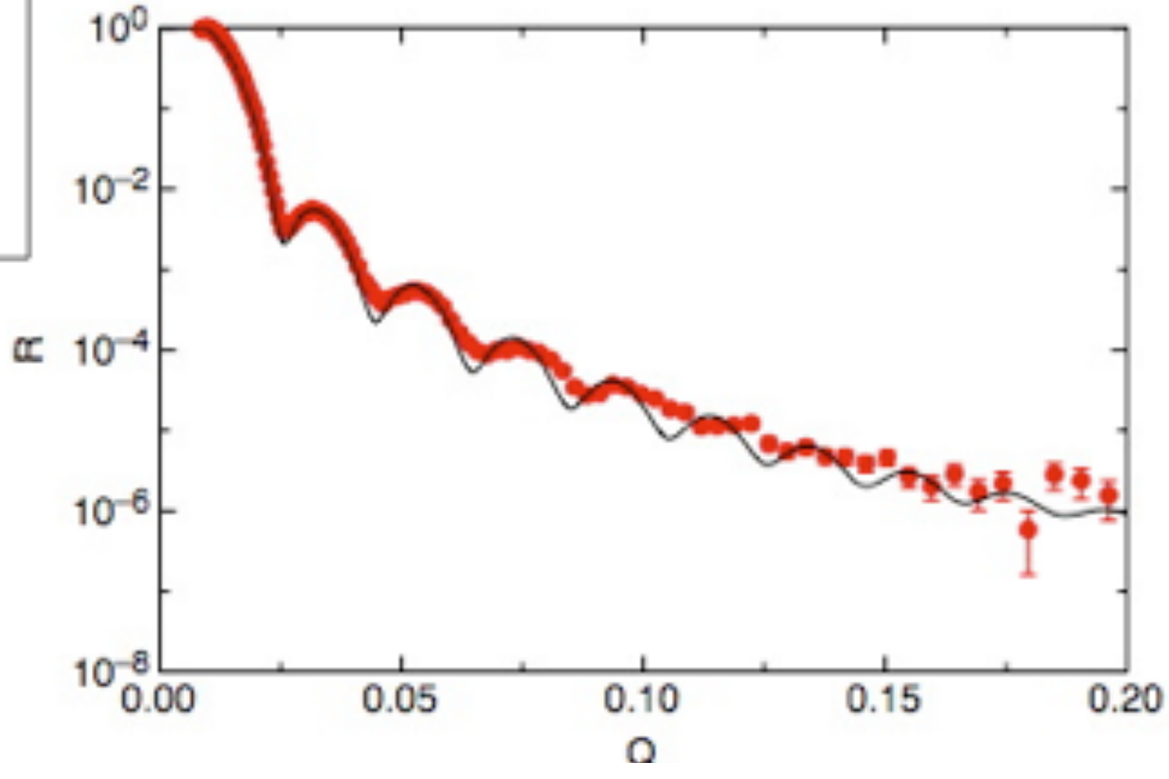
Calculated reflectivity

Goodness of fit (χ^2)

Best fit

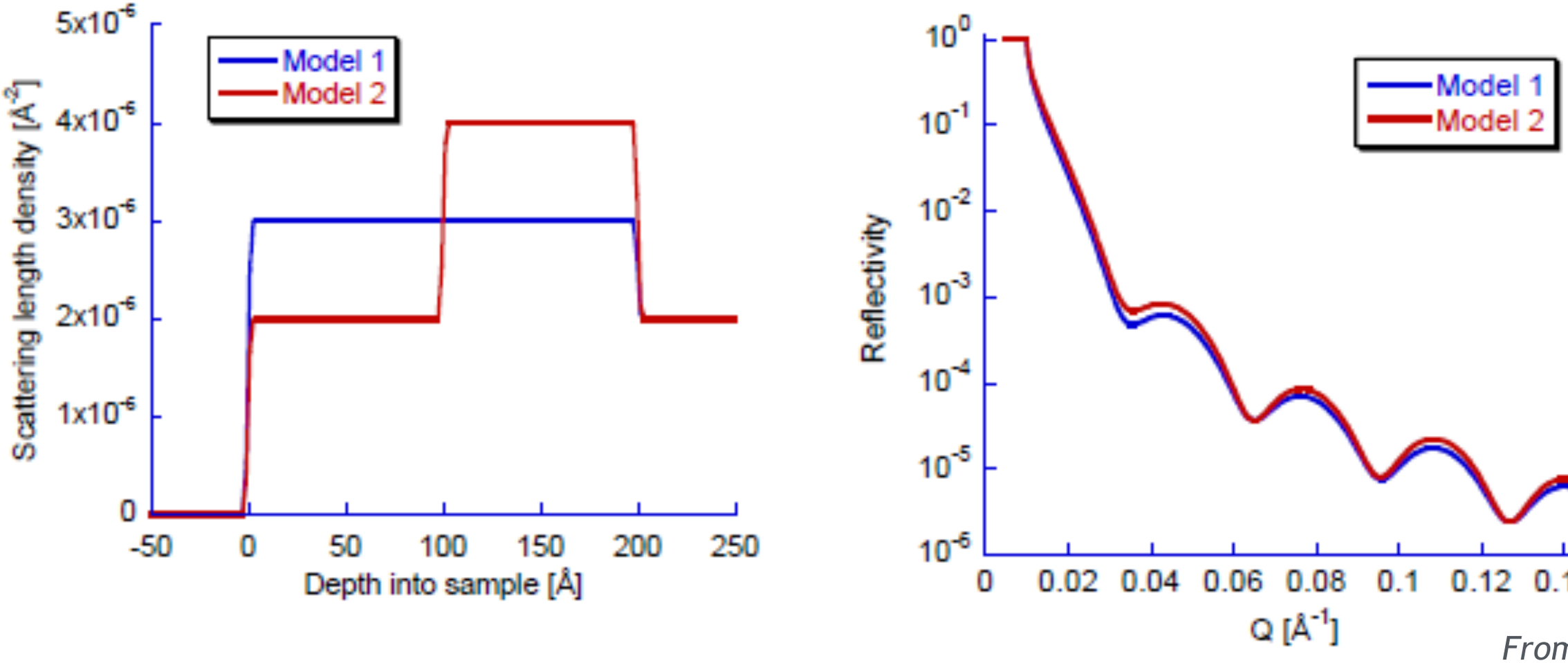
New parameters

Data (+errors)



Courtesy R. Jones

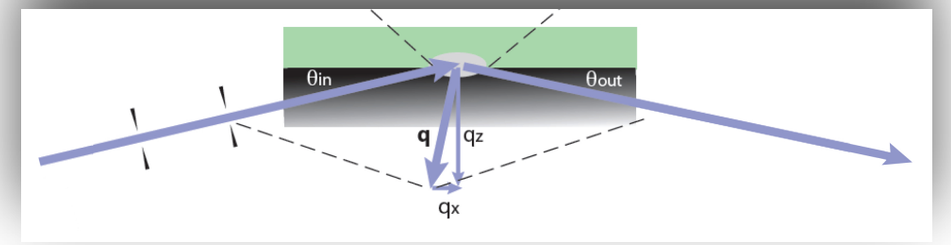
A common problem



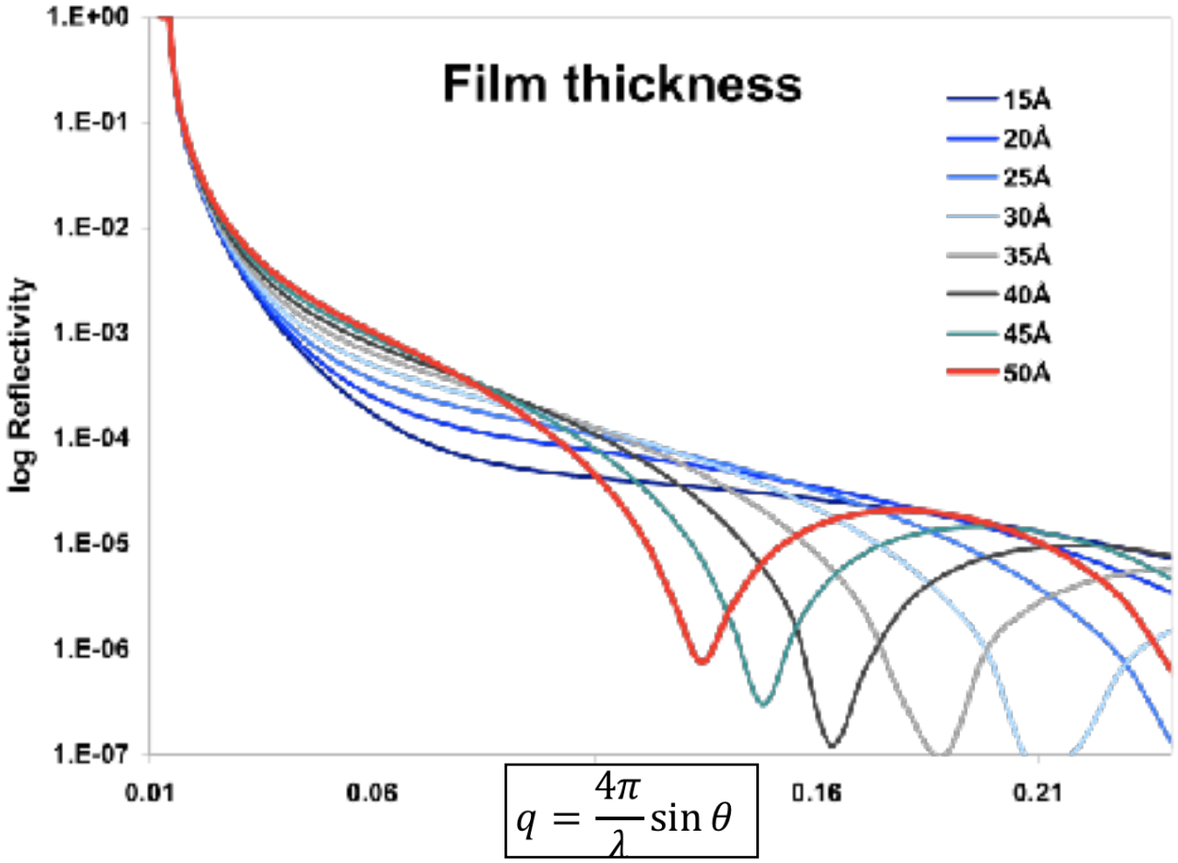
From R. Pynn

Contrast variation helps determining the right model

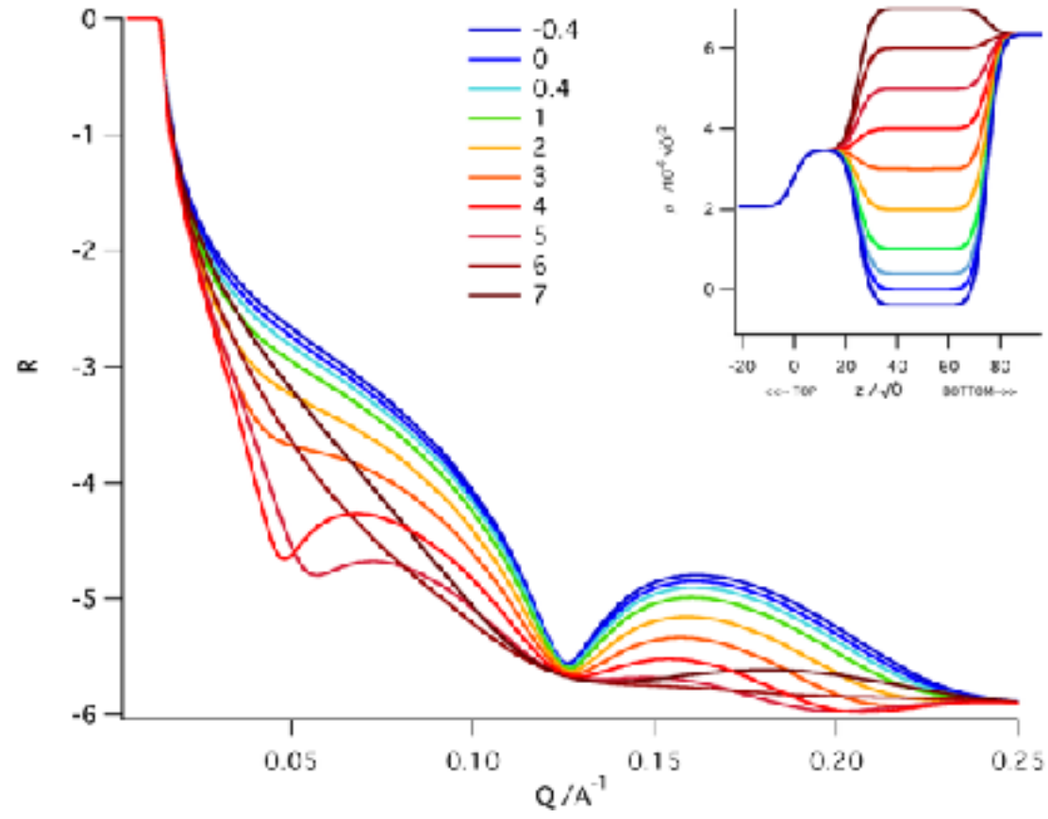
$$R(\vartheta,\lambda) = \frac{I_{out}(\vartheta,\lambda)}{I_{in}(\lambda)}$$

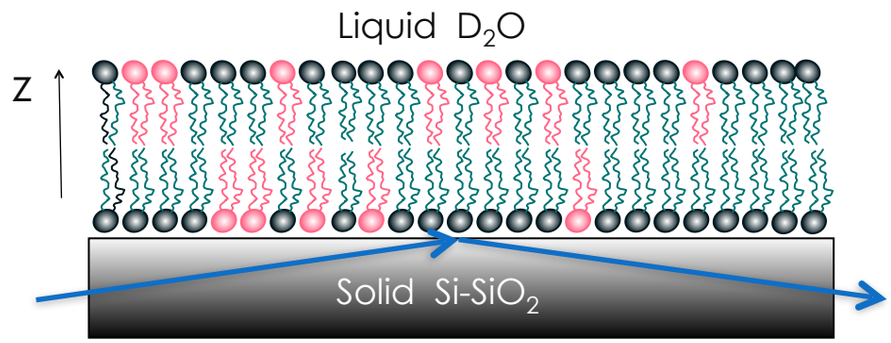


isotopic substitution



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



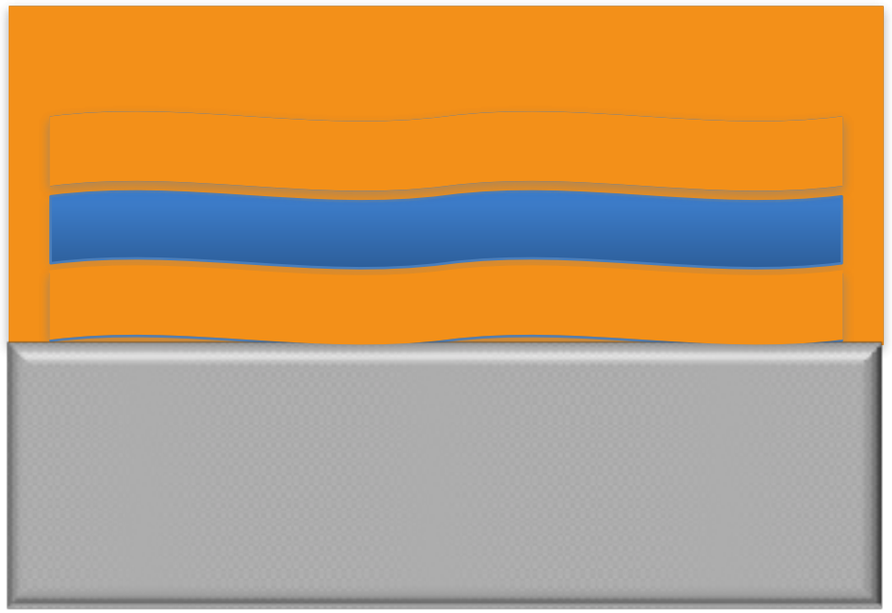


courtesy H.Wacklin

Isotopic substitution and contrast variation

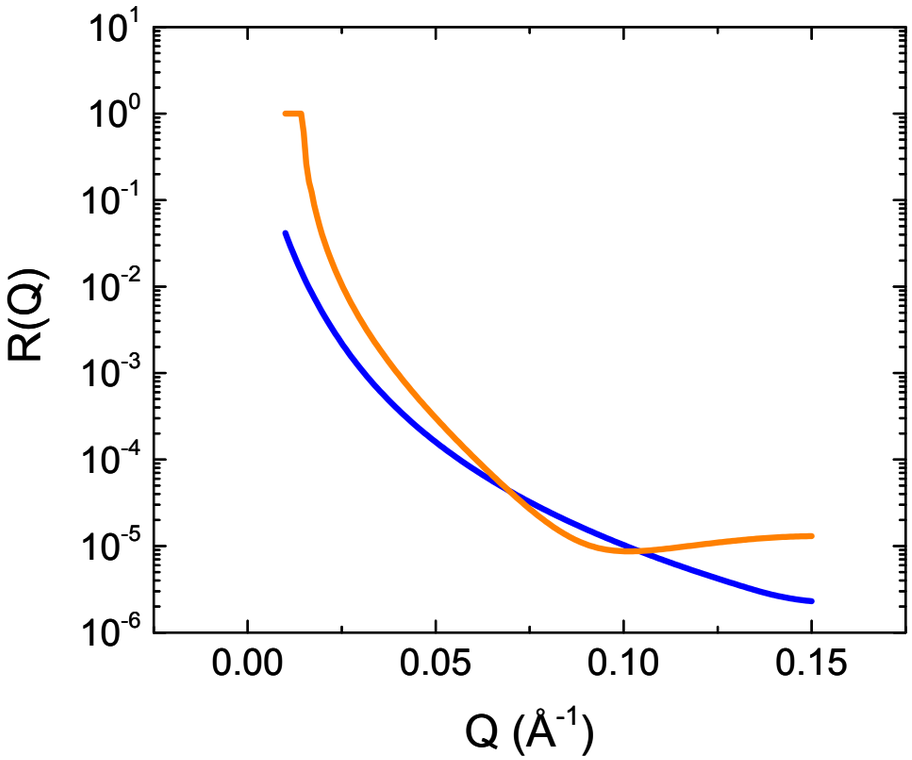
Possibilities by isotopic substitution:

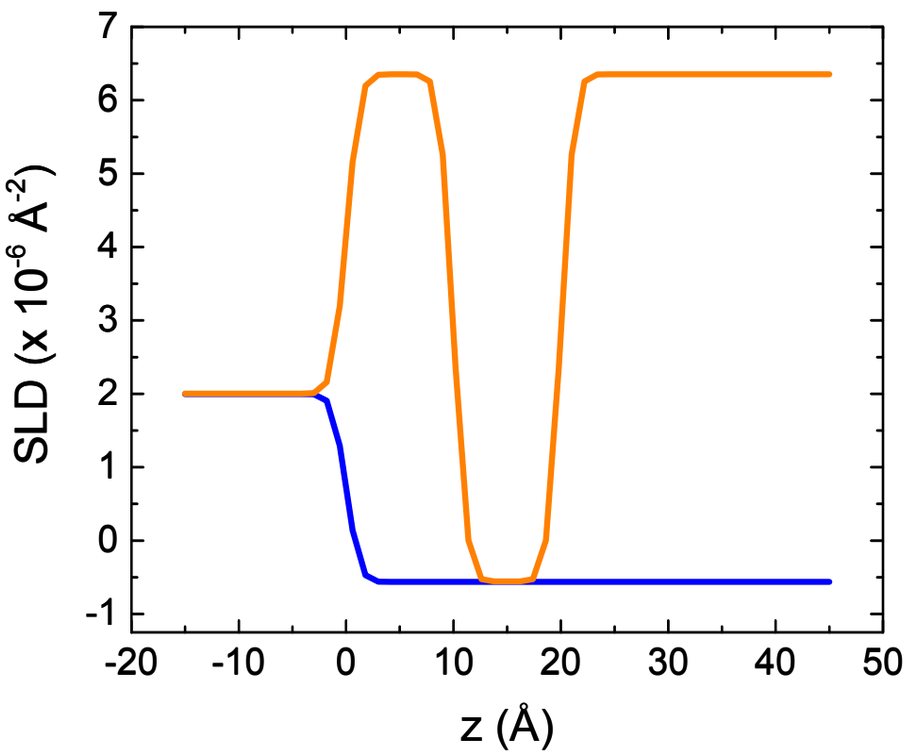
1. Change the SLD of one of the two bulk phases
2. Change the SLD of one of the components in your film
3. Both



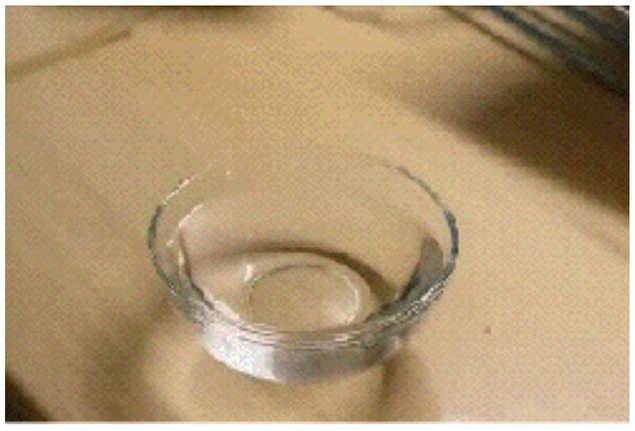
The reflectivity will change because the internal contrast of the film will change.

Possibility of detecting solvent penetration: the SLD of a region of the film changes because the material is hydrated by a different solvent.





courtesy Y. Gerelli



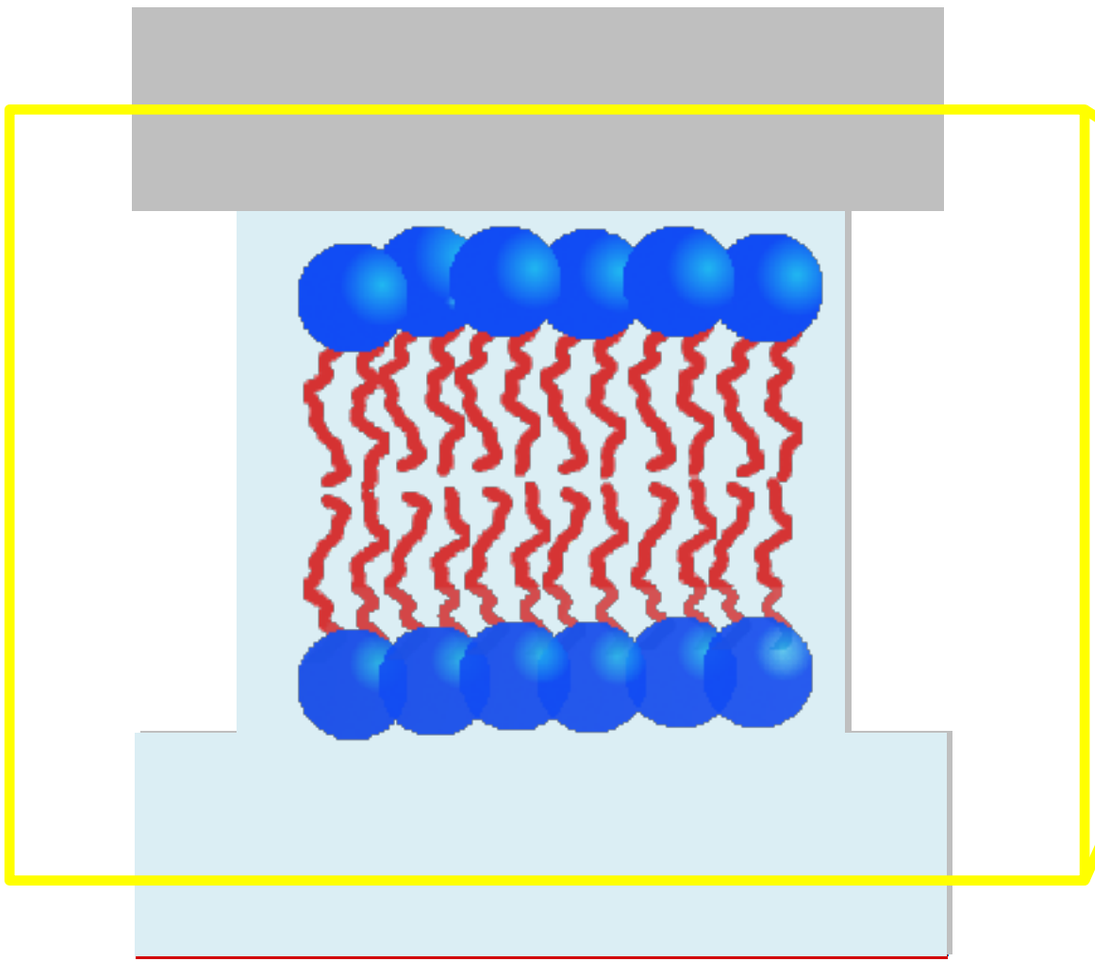
Contrast variation

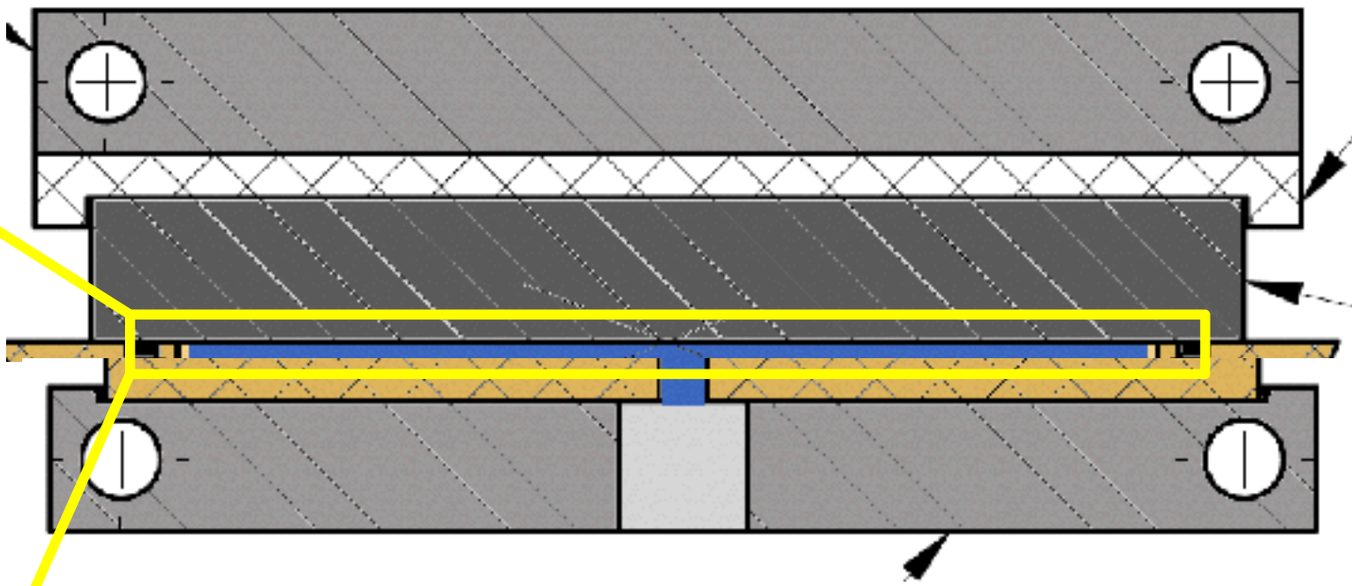
More than one model of $N_b(z)$ may give the same reflectivity profile – phase information is lost

Measurement with multiple ‘contrasts’ normally resolves ambiguity

Physical knowledge of system may define a unique model

Contrast variation

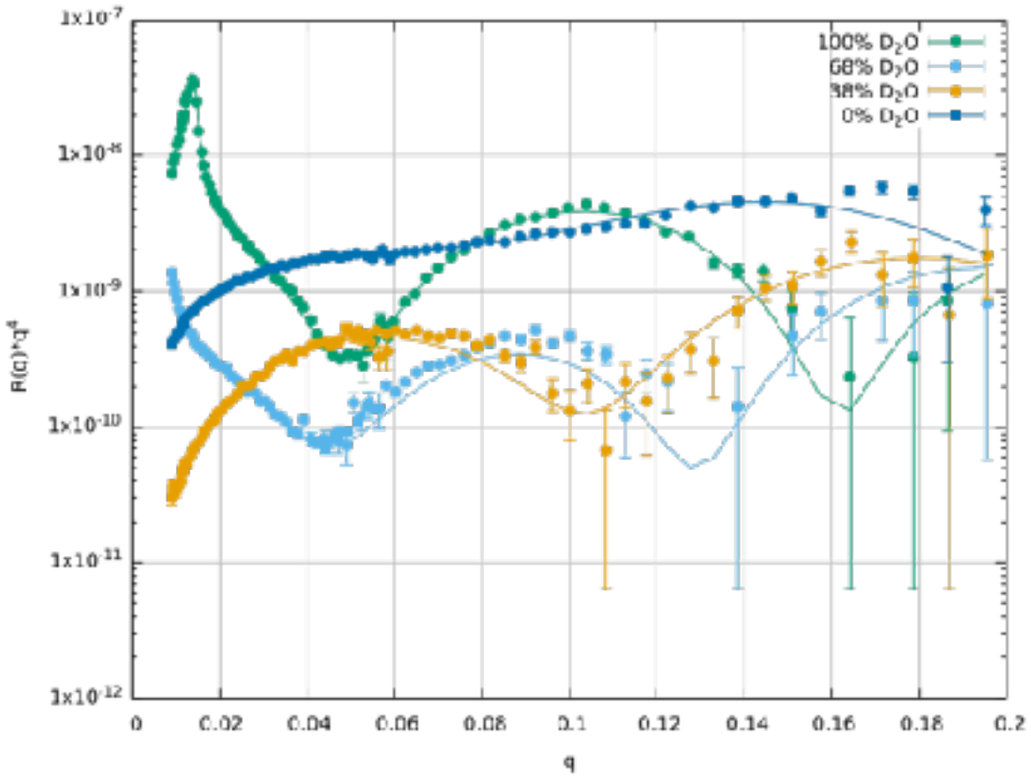




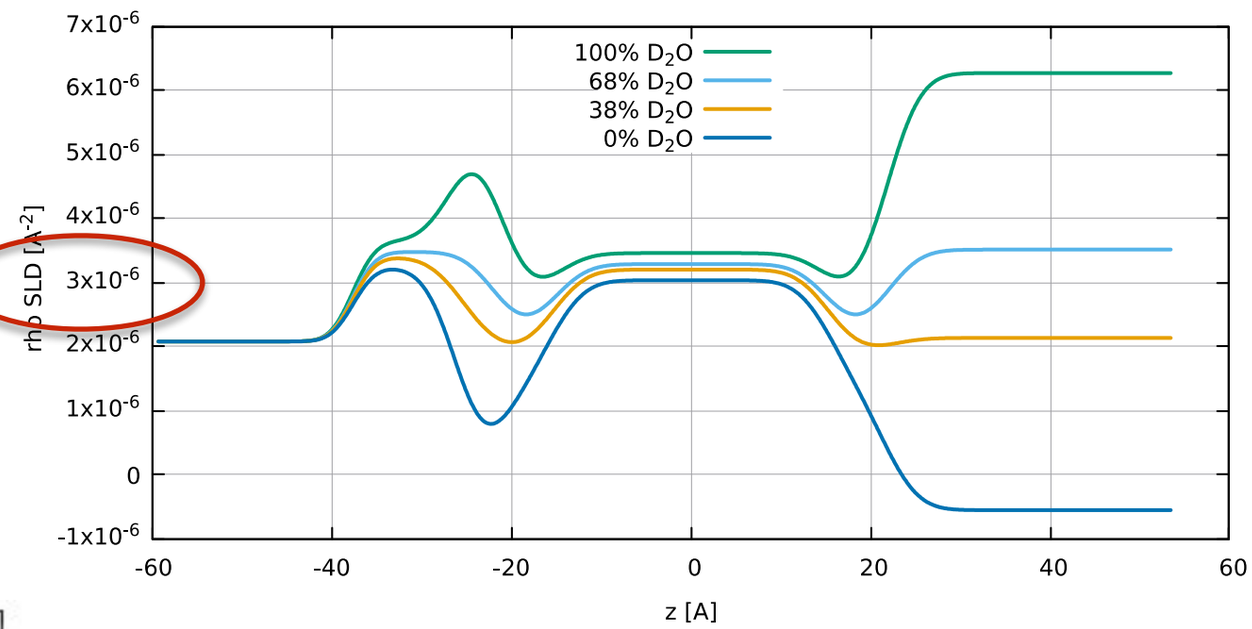
The system maintains the structure but reflectivity changes and signal from parts of the interface can be removed or enhanced

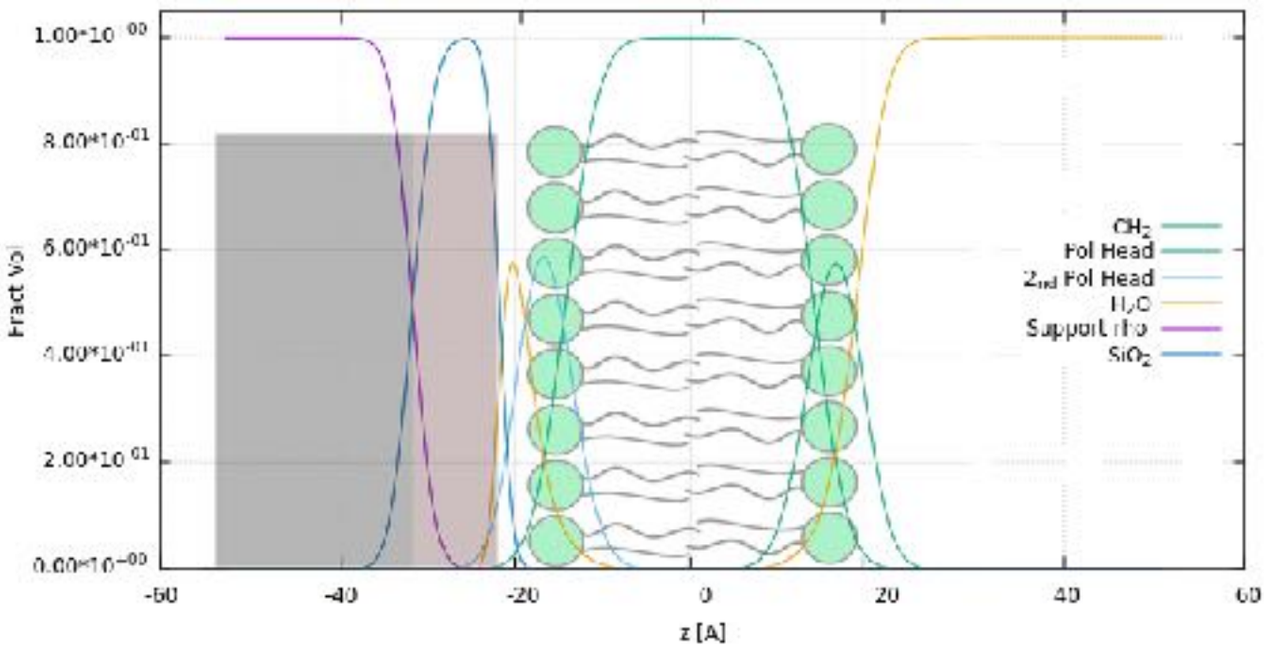
courtesy Y. Gerelli

Contrast variation

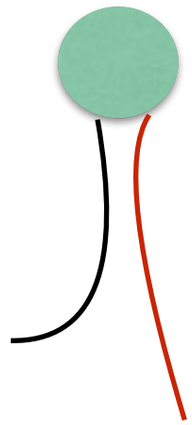


Scattering length density profile





Volume fraction profile



50% deuterated chains

courtesy G. Corucci

- ...there is a family of SL- e-density profiles that results into different $r(Q)$ but *exactly* into the same $R(Q)$.
- Even worse...many more ρ(z) that produce similar $r(Q)$.

The resulting profile can be non-unique.

Constraints and additional information about the sample must be put in place.

The Goal of Reflectivity Measurements Is to Infer a Density Profile Perpendicular to a Flat Interface

In general the results are not unique, but independent knowledge of the system often makes them very reliable

Frequently, layer models are used to fit the data

Advantages of neutrons include:
– Contrast variation (using H and D, for example)
– Low absorption –probe buried interfaces, solid/liquid interfaces etc
– Non-destructive
– Sensitive to magnetism
– Thickness length scale <5 Å – 3000 Å

• Issues include:
– Generally no unique solution for the SLD profile (use prior knowledge)
– Large samples (~10 cm^2) with good scattering contrast are needed

X-rays reflectivity
-Higher flux/resolution (synchrotron radiation)
-Smaller samples
-Smaller penetration length
-Available in the lab (not synchrotron radiation…)

Some useful references:

- V. F. Sears 'Neutron Optics', Oxford Press, Oxford (1989)
- Lekner J 1987 in: "*Theory of Reflection*" Martinus Nijhoff Dordrecht
- Born M and Wolfe E 1989 in: "*Principles of Optics*" Pergamon Press Eds. Oxford
- Penfold J and Thomas R K 1990 *J. Phys. Condens. Matter* **2** 1369
- Russell T. P. 1990 *Mat. Sci. Rep.* **5** 171
- Felcher G P 1981 *Phys. Rev. B* **24** 1995
- Sinha S K, Sirota E B, Garoff S and Stanley H B 1998 *Phys. Rev. B* **38** 2297
- Zhou X-L and Chen S-H 1995 *Phys. Rep.* **257** 223
- W. Williams 'Polarized Neutrons' , Oxford Press, Oxford (1989)
- Névot L and Croce P 1990 *Rev. de Phys. Appl.* **15** 761
- Daillant J and Gibaud A 1999 in:

"*X-ray and Neutron Reflectivity: Principles and Applications*" Springer Eds.

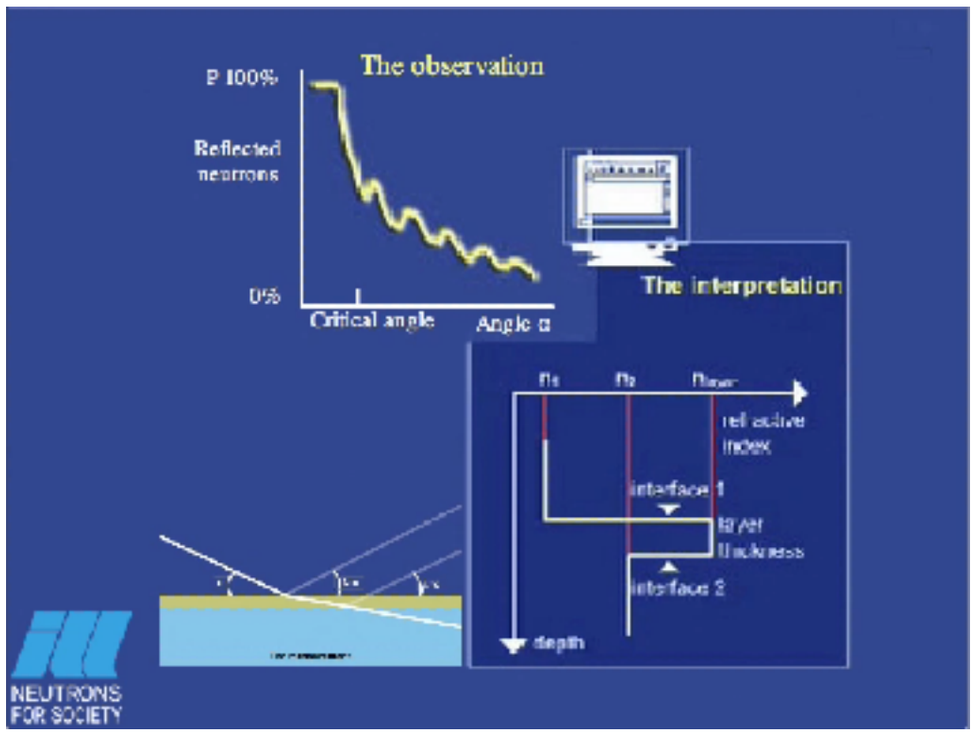
- Heavens O S 1955 in: "*Optical Properties of Thin Films*", Butterworths Eds. London

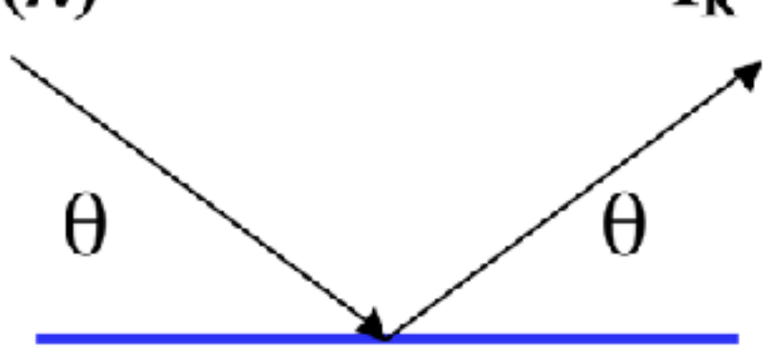
Web-sites:

http://www.mrl.ucsb.edu/~pynn/ (Roger Pynn)
http://www.pcl.ox.ac.uk/~rkt/ (Bob Thomas)

***Ref for this talk*:** Cubitt R. and Fragneto G. 2002 "*Neutron Reflection: Principles and Examples of Applications*", in *Scattering*, p. 1198-1208, Academic Press eds.

Basic Principles of Reflection Measurement





Reflected beam deflected:
2θ

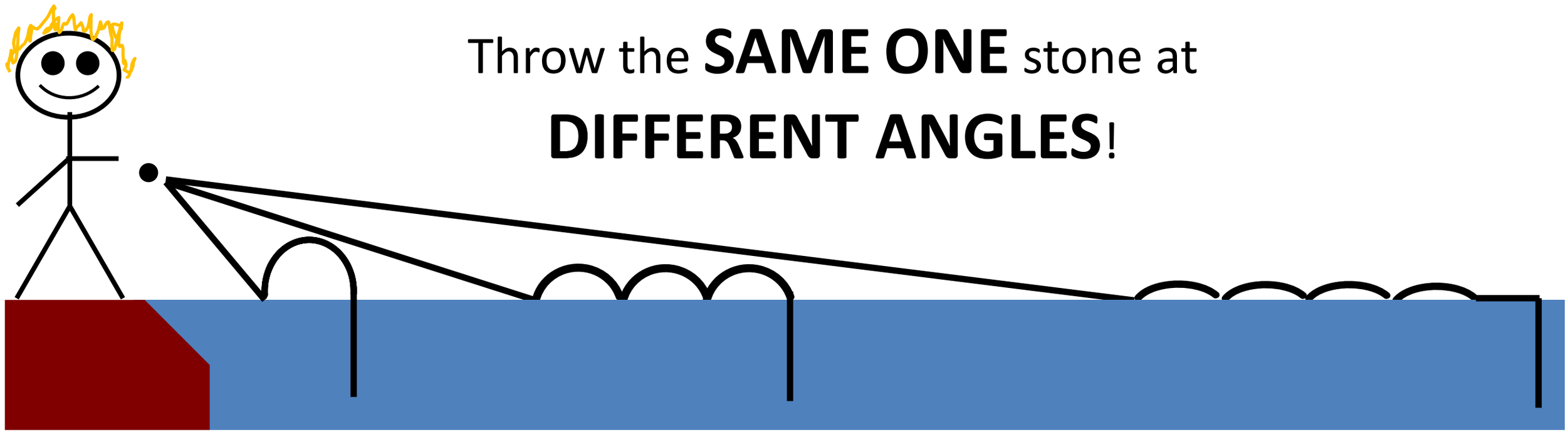
Reflectivity
$R(\theta, \lambda) = I_R/I_0(\lambda)$

Momentum transfer
$q = (4\pi/\lambda) \sin\theta$

Monochromatic

Throw the **SAME ONE** stone at

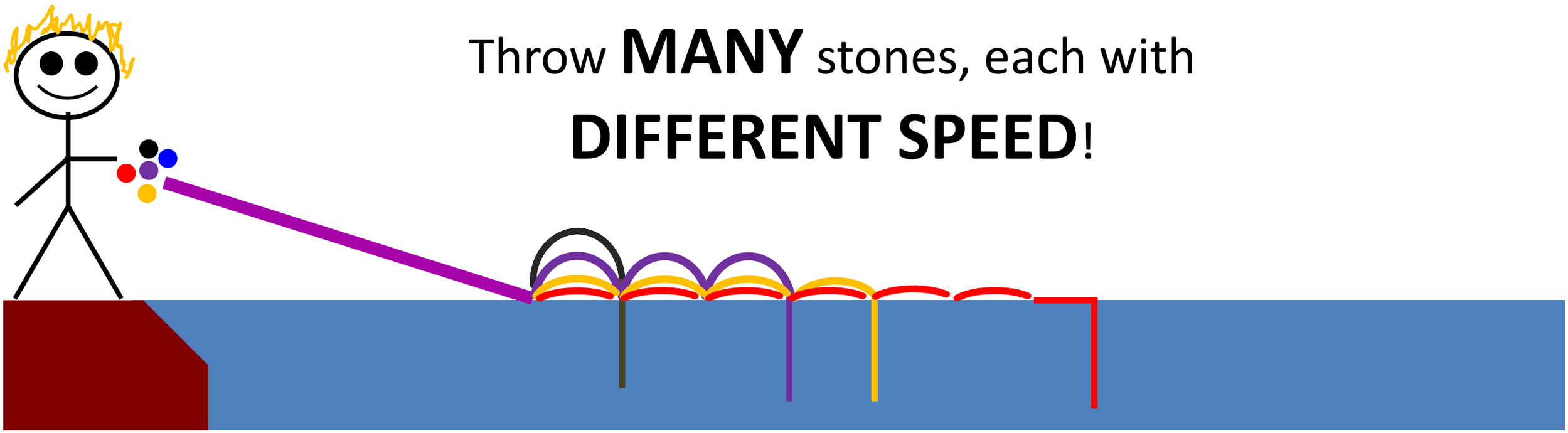
DIFFERENT ANGLES!



Time-of-Flight (ToF)

Throw **MANY** stones, each with

DIFFERENT SPEED!



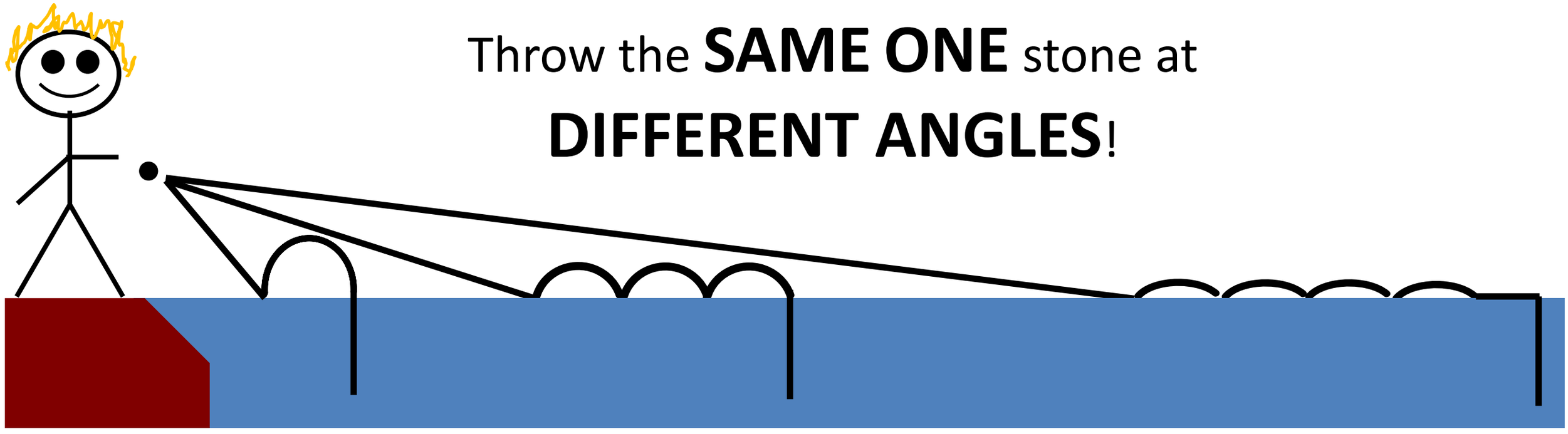
Saerbeck@ill.fr

courtesy T. Saerbeck

Monochromatic

Throw the **SAME ONE** stone at

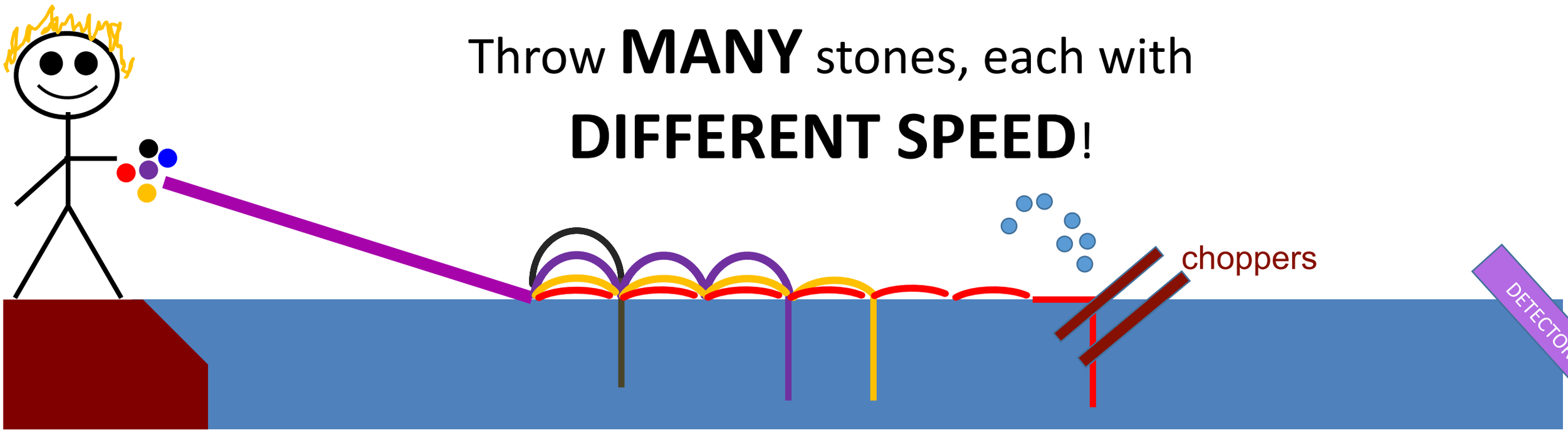
DIFFERENT ANGLES!



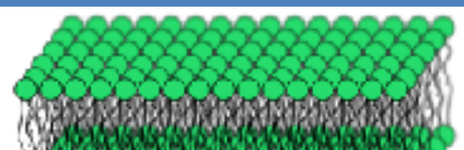
Time-of-Flight (ToF)

Throw **MANY** stones, each with

DIFFERENT SPEED!

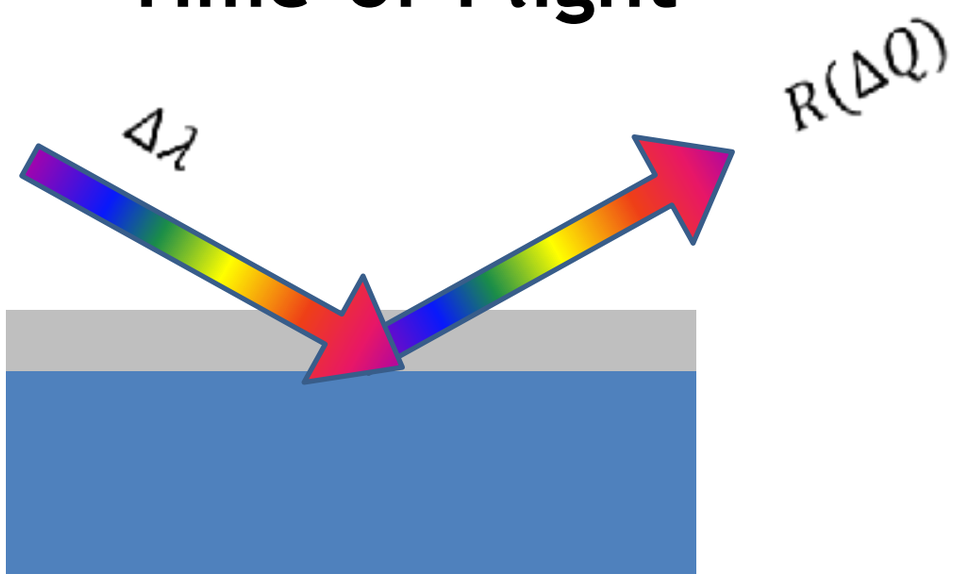


Saerbeck@ill.fr



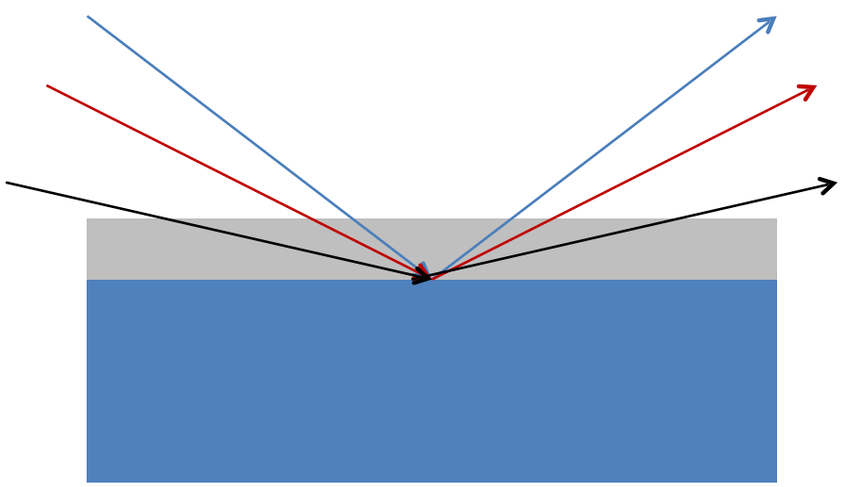
ToF and monochromatic modes

Time-of-Flight



- $\Delta Q = \frac{4\pi}{\Delta\lambda}\sin\vartheta$
- *Wide Q range covered in one shot*
- *ϑ can be changed*
  - *Moving the sample*
  - *Moving the beam and the detector*
- *Usually 1-3 angular configurations are enough to have a full curve*

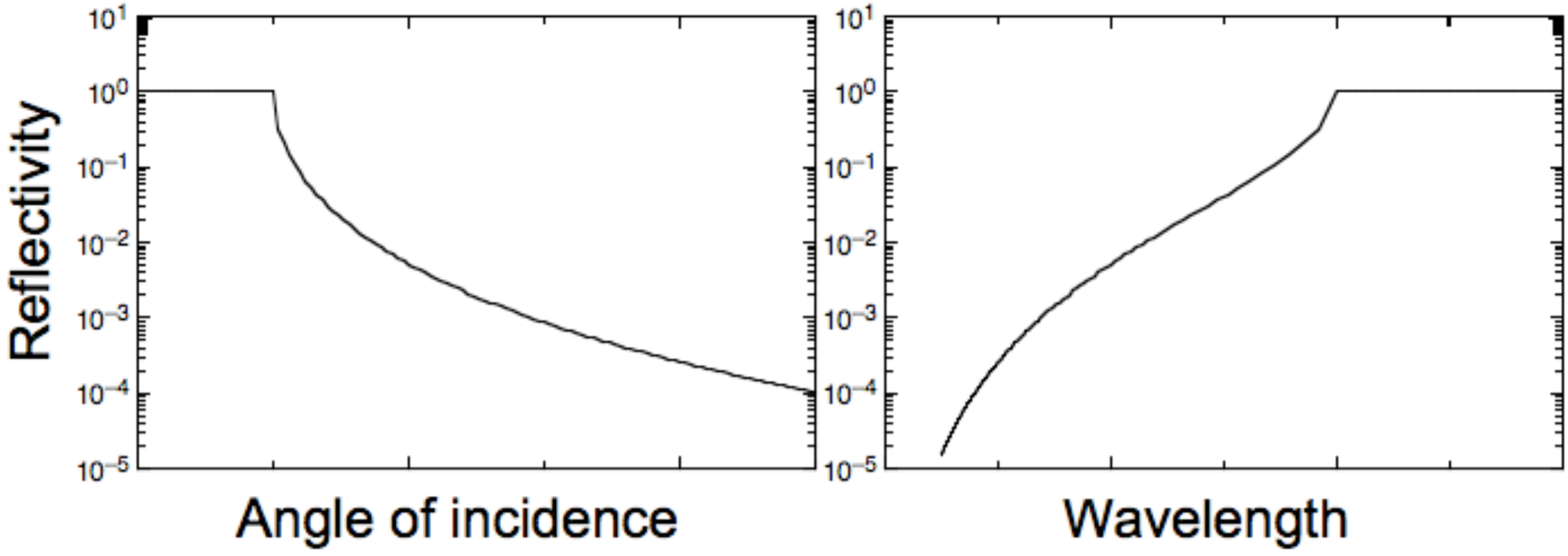
Monochromatic



- $Q = \frac{4\pi}{\lambda}\sin\vartheta$
- *Only one R(Q) point/angle*
- *ϑ can be changed moving the sample*
- *Many angular configuration (~100) needed*

Measurement can be done by:

varying θ at constant λ **measuring the TOF (⇒λ) at constant θ**



For the same resolution TOF is less efficient (flux at min and max λ up to two orders of magnitude smaller than at peak flux) *but* better for kinetics

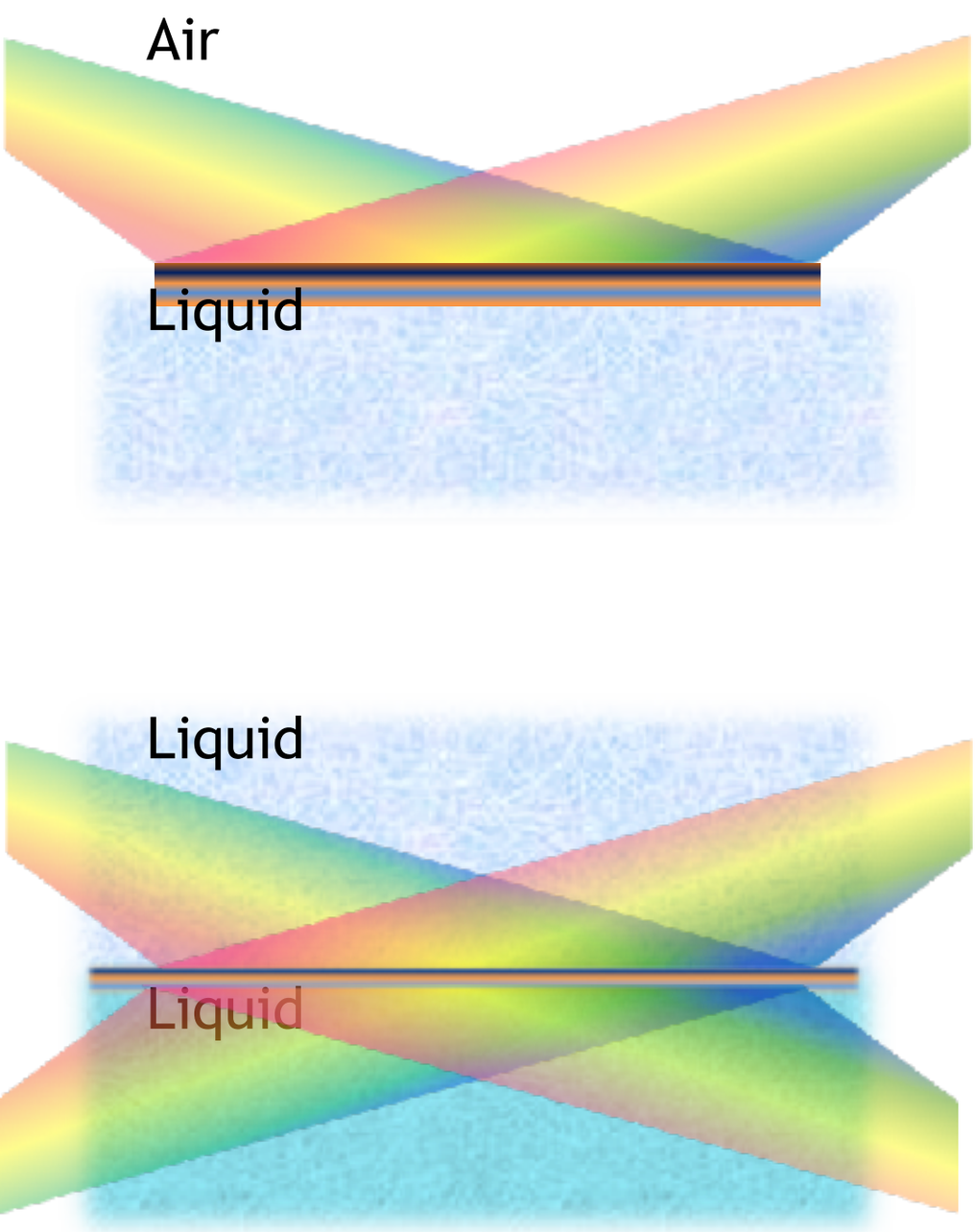
Classes of Interface

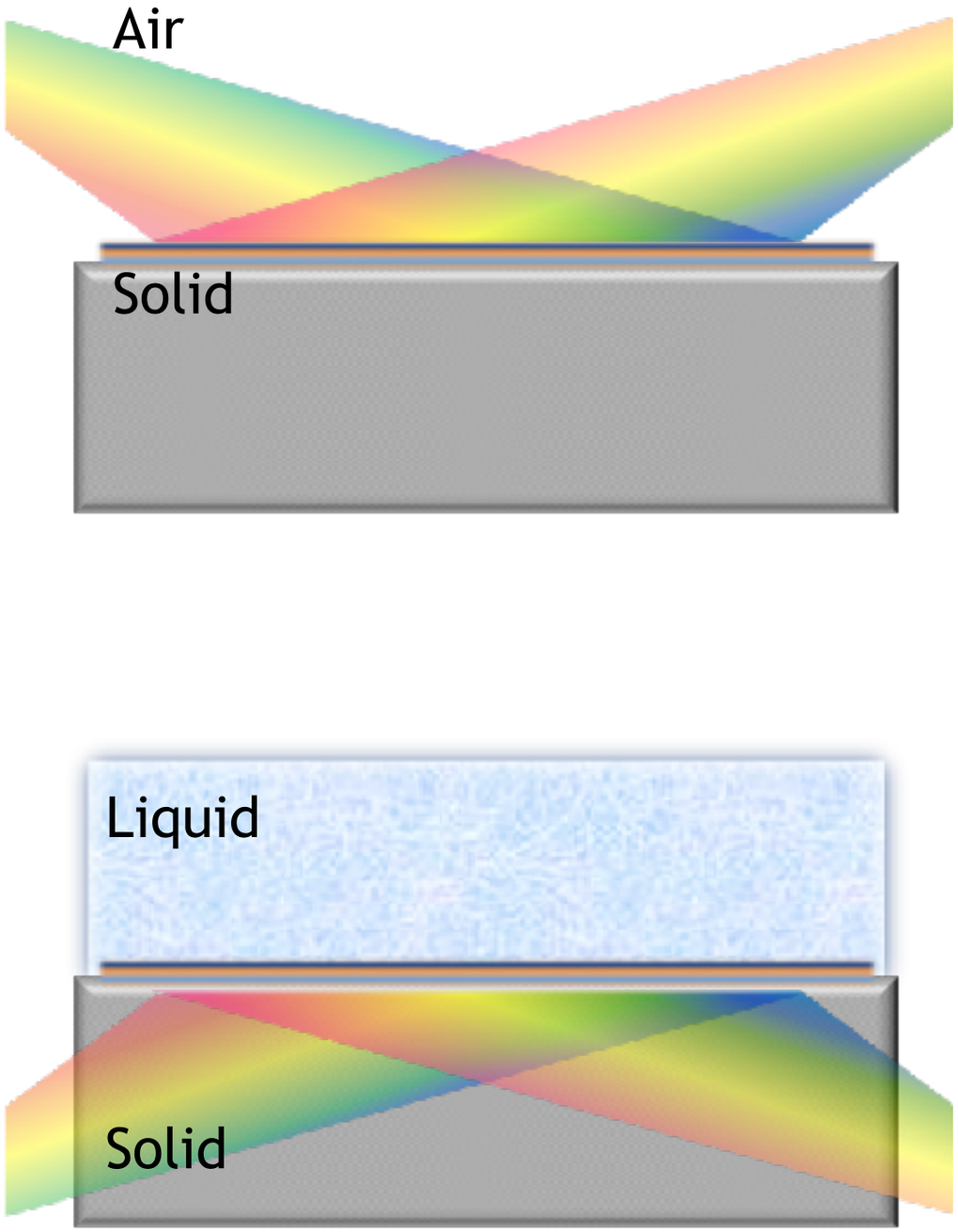
Air/Liquid Air/Solid	Samples can be limited by smoothness and by flatness (capillary waves amplitude is 0.3 nm)
Liquid/Solid Solid/Solid Liquid/Liquid	Constrained by passage through one phase. Signal can be limited by absorption or scattering background

Neutron reflection is an ideal tool to study buried interfaces because neutrons can penetrate solids (i.e. in solid/liquid systems), are not destructive, allow to gain information in the fraction of nanometer scale

Classes of Interface

The "incident" media must be as transparent as possible

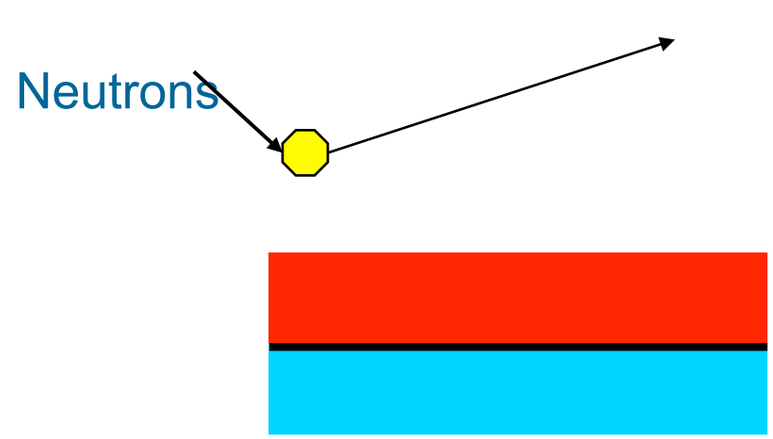




courtesy Y. Gerelli

Fate of a Neutron at an Interface

- Reflected
- Scattered/Diffracted from surface
- Absorbed
- Scattered from bulk (either side of surface)
- Other accidents



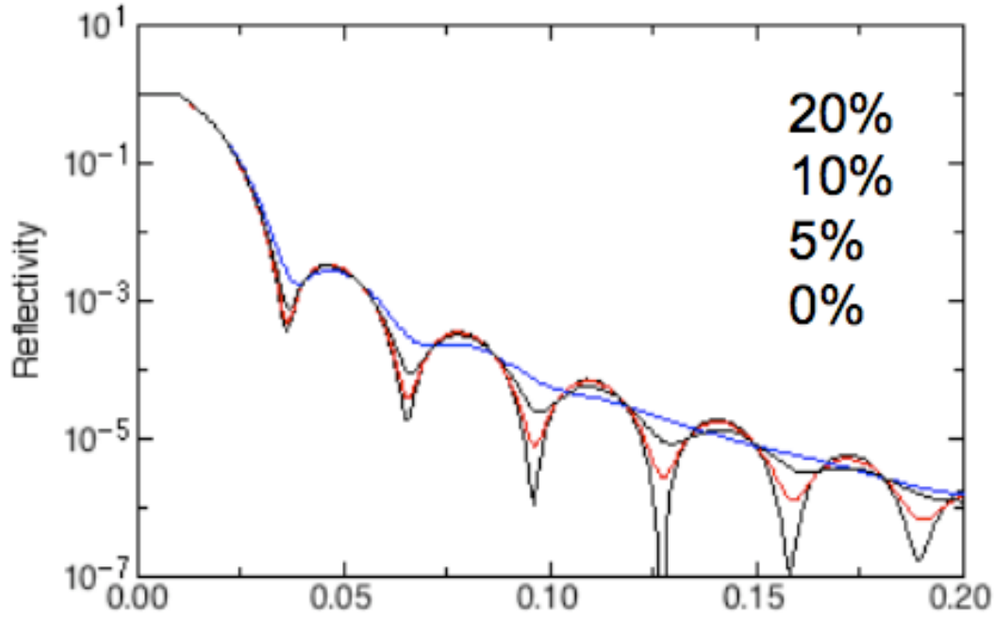
courtesy A. R. Rennie

Practical Issues

- Reflectivity drops quickly with increasing Q (or angle). Signal is easily ‘lost’ in background.

- To observe fringes it will be necessary to measure over an appropriate range of Q and to have sufficient resolution (ΔQ small enough).

$$\left(\frac{\Delta Q}{Q}\right)^2 = \left(\frac{\Delta\lambda}{\lambda}\right)^2 + \left(\frac{\Delta\theta}{\theta}\right)^2$$



- Attenuation by reduced transmission (caused by scattering or absorption) may be significant

courtesy A. R. Rennie

Sources of background

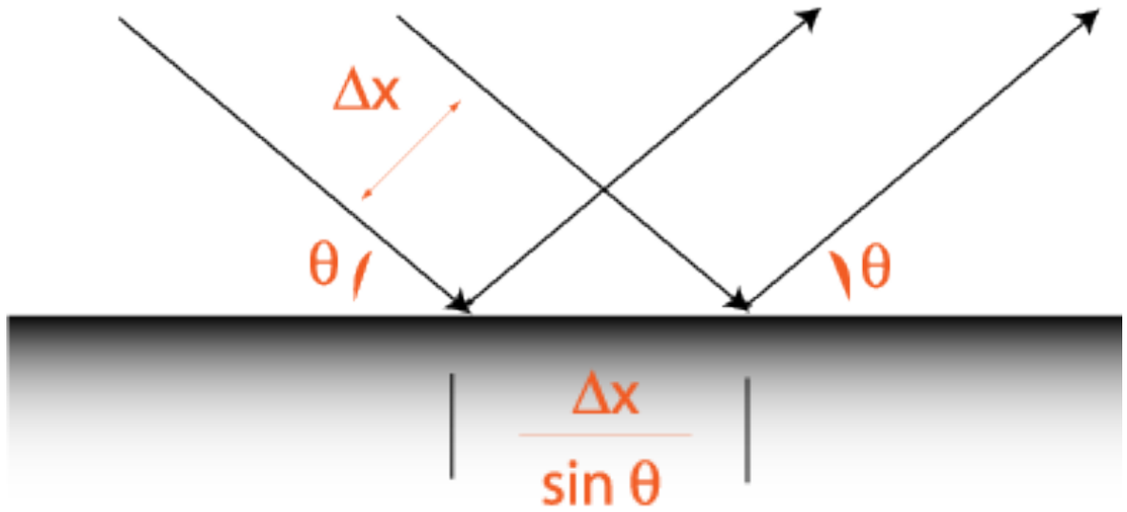
Electronics (negligible)

Scattering from other parts of the instrument
(can be efficiently shielded with B4C, Cd, etc.)

Sample:
Off-specular from roughness
or inhomogeneities

Incoherent scattering (liquids)

*The **coherence length** is essentially the separation distance on the specimen from which neutrons or x-rays emerging will interfere coherently at the detector*



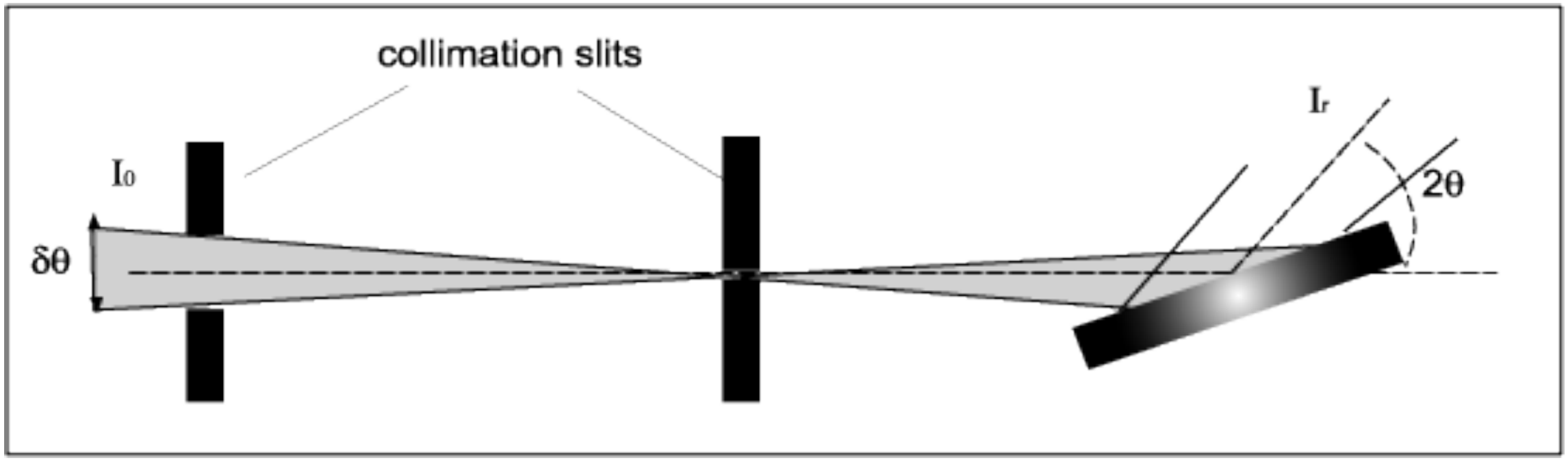
0.1 nm neutrons or x-rays
source divergence 0.005 deg

$\Delta k \Delta x = 2\pi$ $\Delta x = 600$ nm

$\theta = 1$
coherence length~30000 nm

The coherence length will depend on factors including:

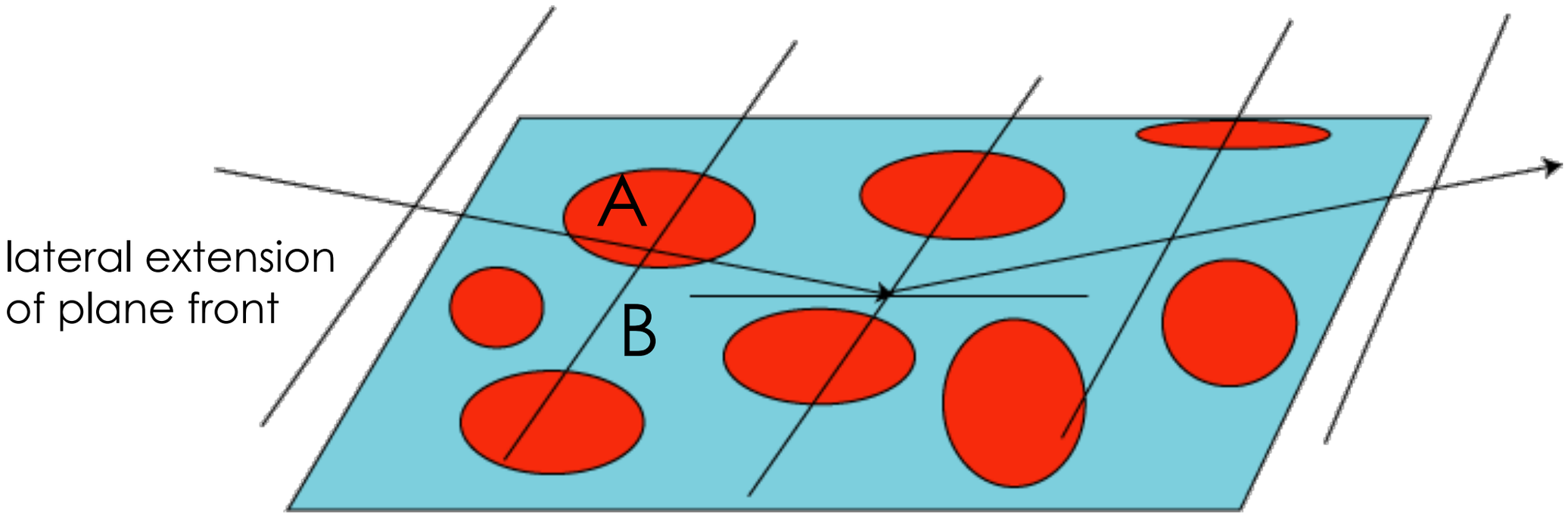
- wavelength of the incident radiation
- angle of incidence
- and beam divergence (instrument dependent)



Usually a slit defines the incident beam with good resolution in one dimension and poor normal to this

Inhomogeneous sample

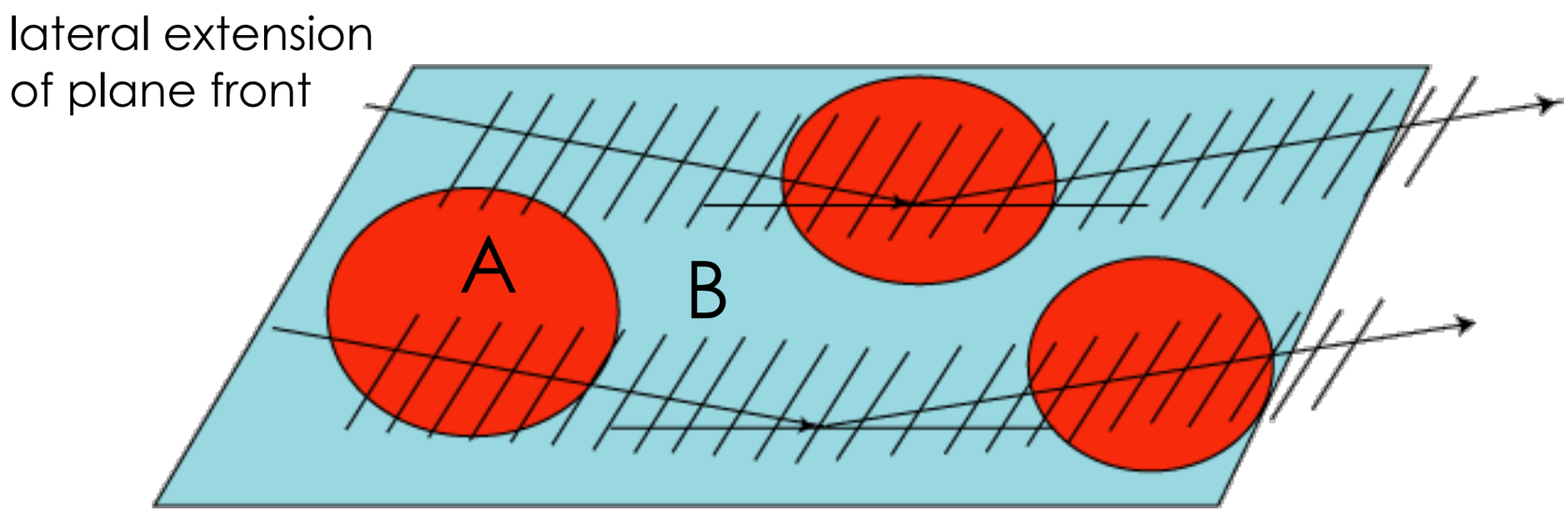
lateral coherence length of wave>>dimensions of regions A and B



$$|r|^2_{observed} = \left| \frac{4\pi}{iq} \int_0^L \Psi(z)\left[f_A N b_A(z) + f_B N b_B(z) \Psi_0 dz \right] \right|^2$$

Inhomogeneous sample

lateral coherence length of wave<<dimensions of regions A and B



$$|r|^2_{observed} = f_A|r|^2_A + f_B|r|^2_B$$

Rafts in membranes: can we see them with reflectometry?

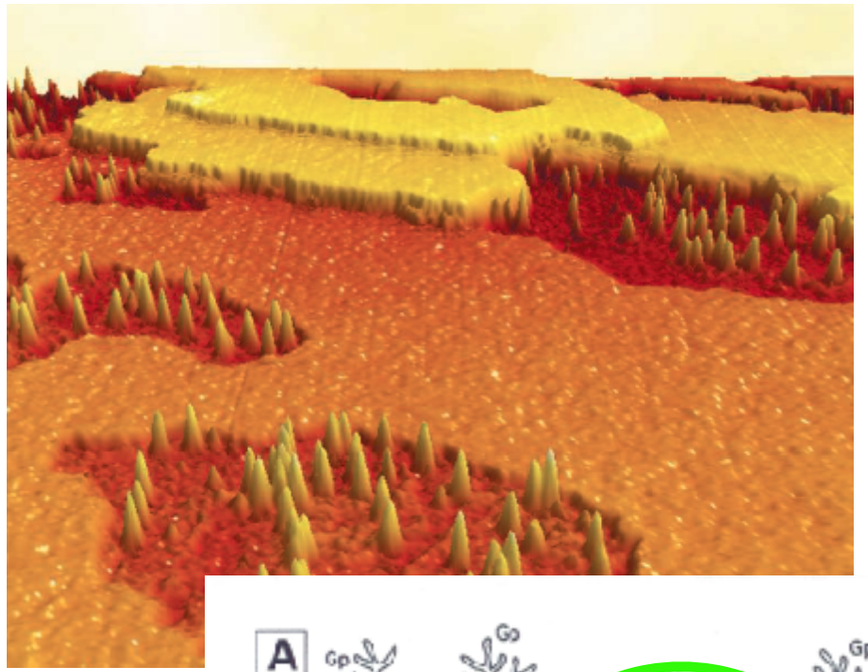
Lateral coherence length of neutron beam ~10 microns

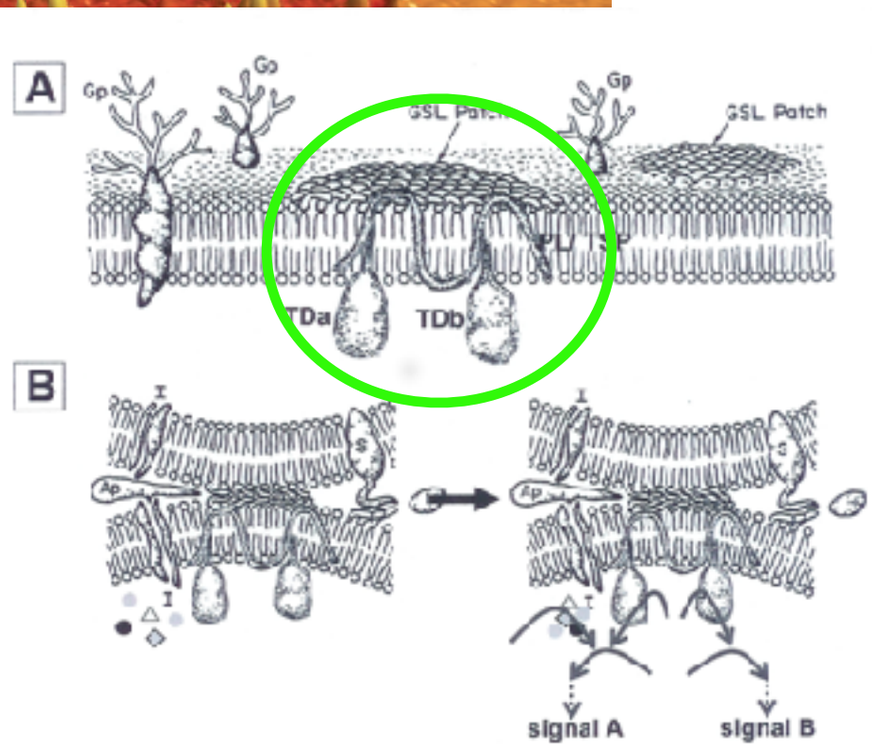
>>

Domain size ~100 nanometers

Signal will come from the averaged structure on the surface

Need to use GISANS



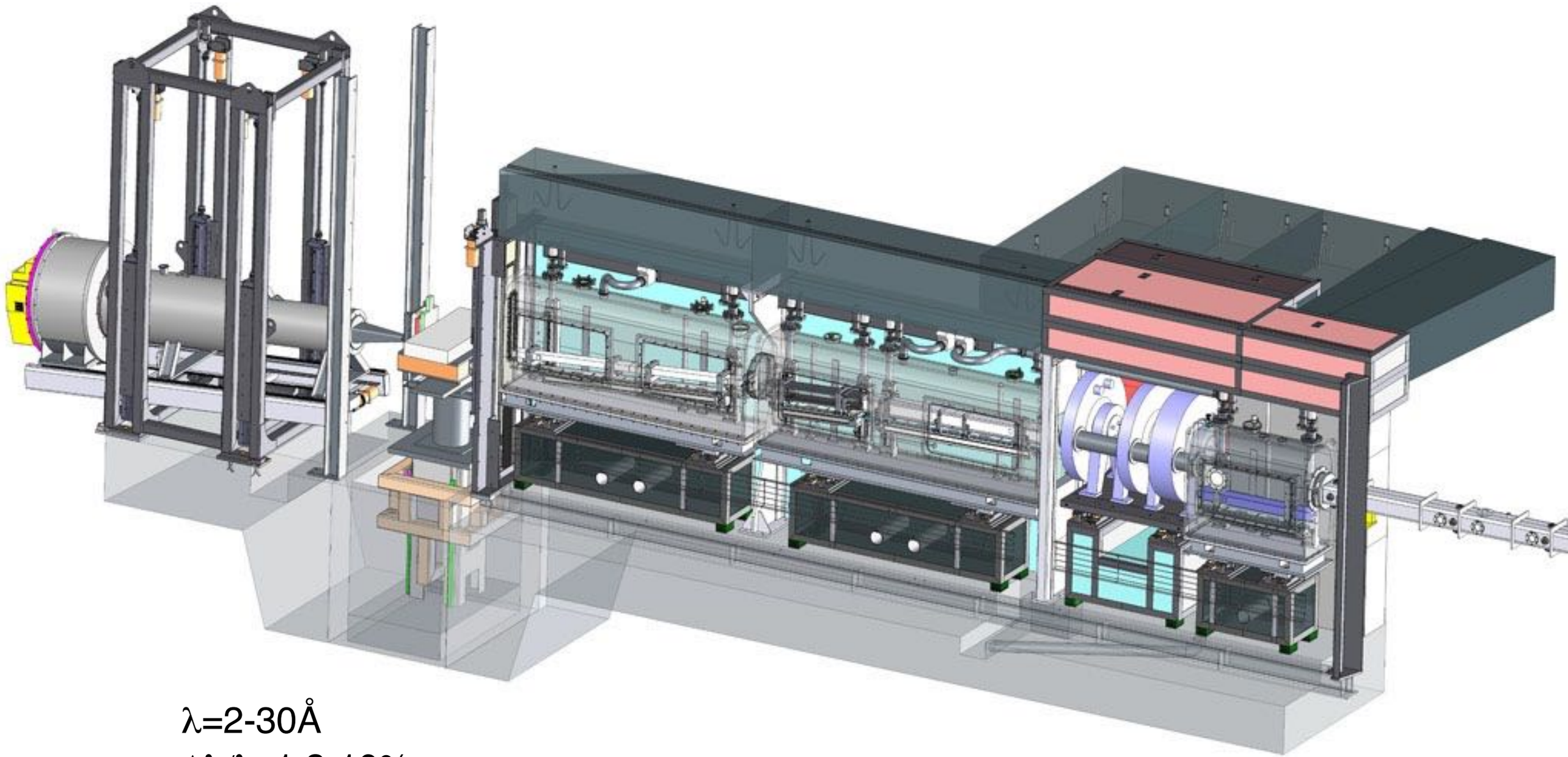


Example of reflectometer TOF mode:

The reflectometer FIGARO at the ILL

Fluid Interfaces Grazing Angles ReflectOmeter

FluidInterfaces Grazing Angles Reflectometer



λ=2-30Å

$\Delta\lambda/\lambda$ 1.2-10%

Beam strikes both sides of interfaces

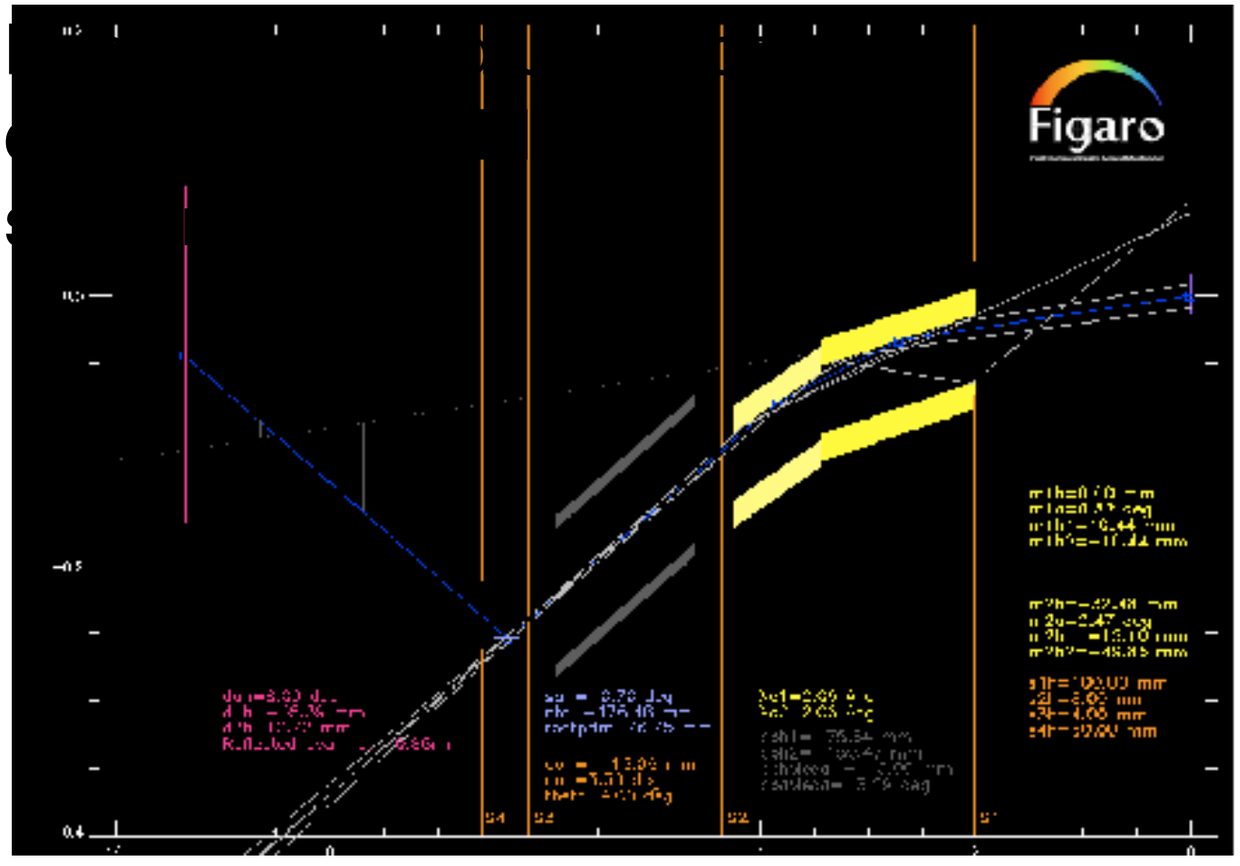
Figaro

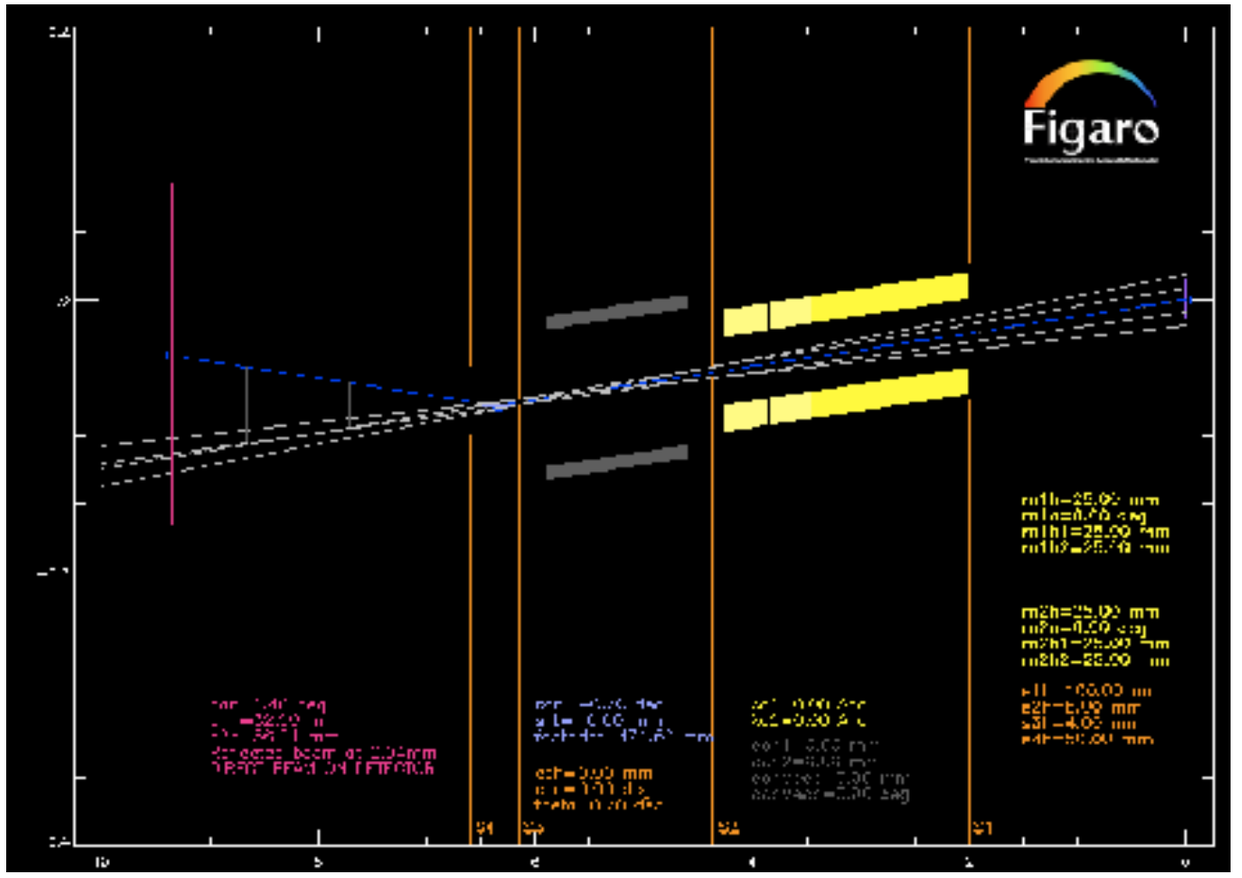
Fluid Interfaces Grazing Angles Reflectometer

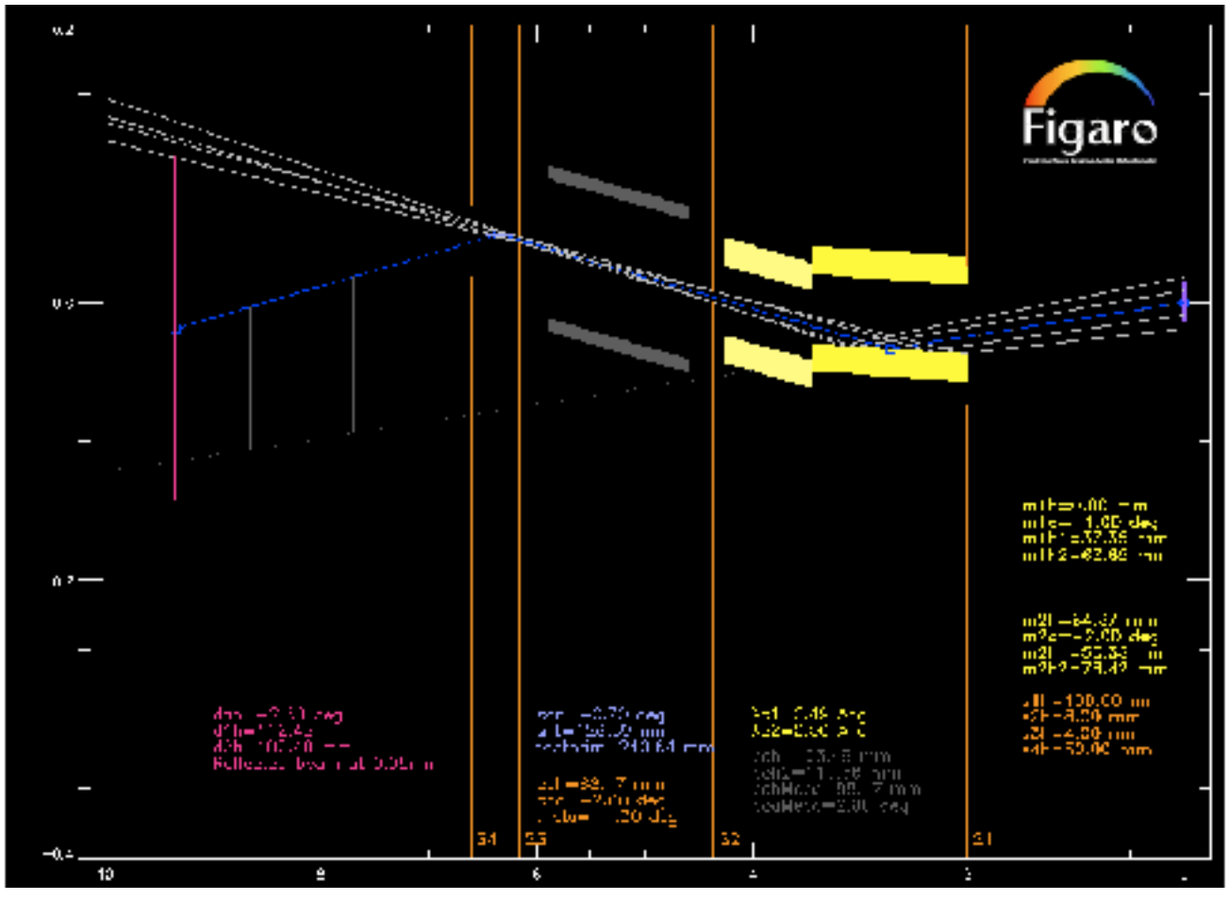
Loose resolution allows high flux and measurements of thin films and liquid/ liquid interfaces

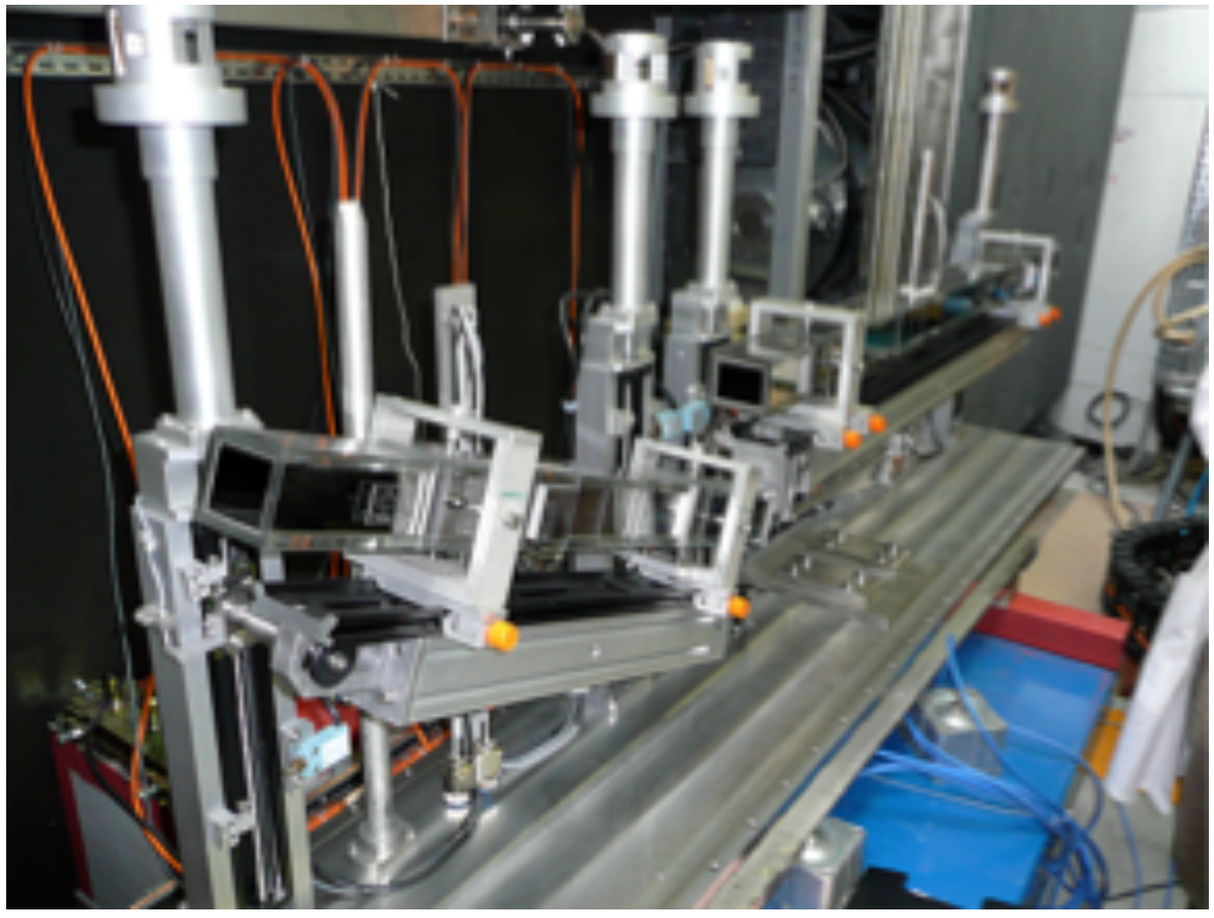
$$\frac{\delta t}{t} = \frac{D'}{D} + \frac{\phi \quad q}{2\pi\tau \quad q_{\min}}$$

$\Delta\lambda/\lambda$	Disc Numbers	Disc separation (mm)
10 %	1 & 4	800
8.8%	2 & 4	700
4.2%	1 & 3	350
3.0%	2 & 3	250
5.4%	3 & 4	450
1.2%	1 & 2	100


Figaro

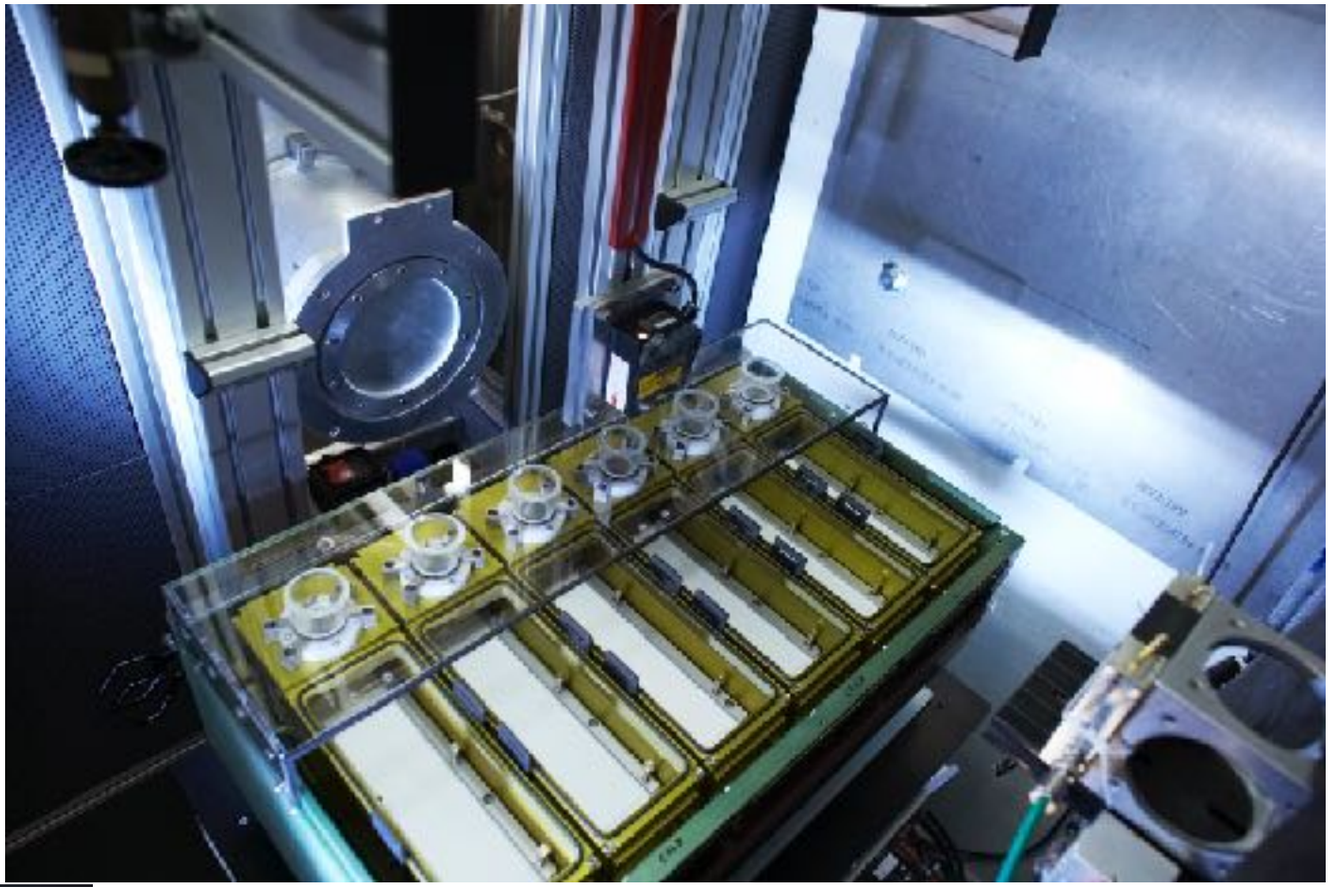

Figaro

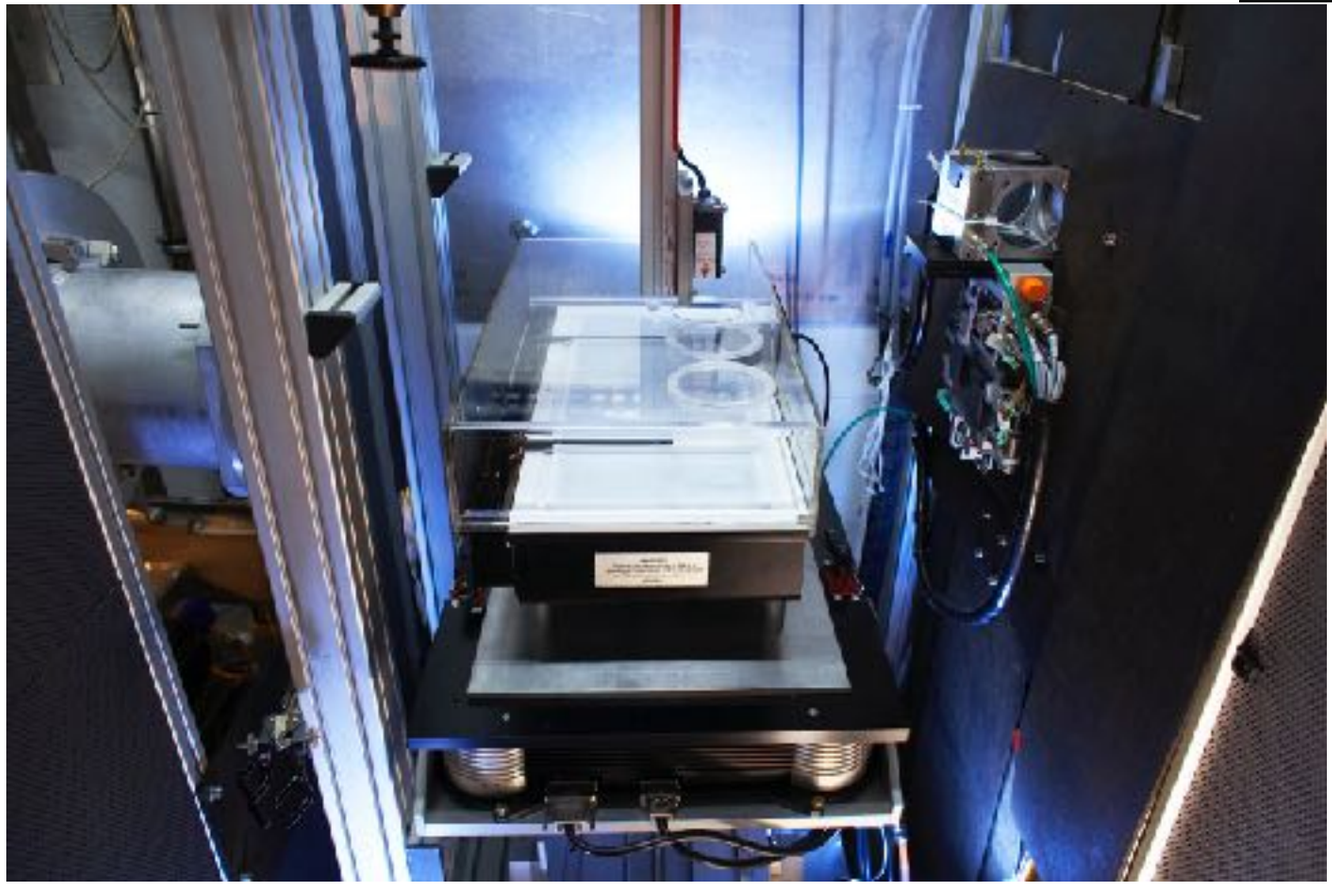

Figaro



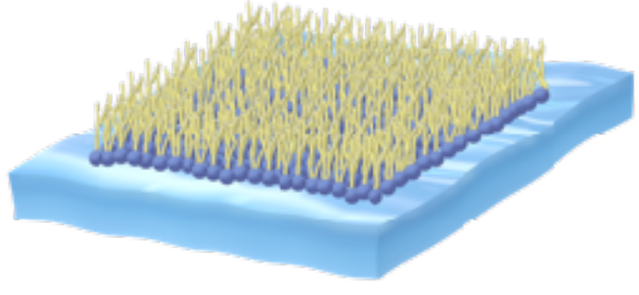
SAMPLE ENVIRONMENT

Adsorption troughs for adsorption from solution



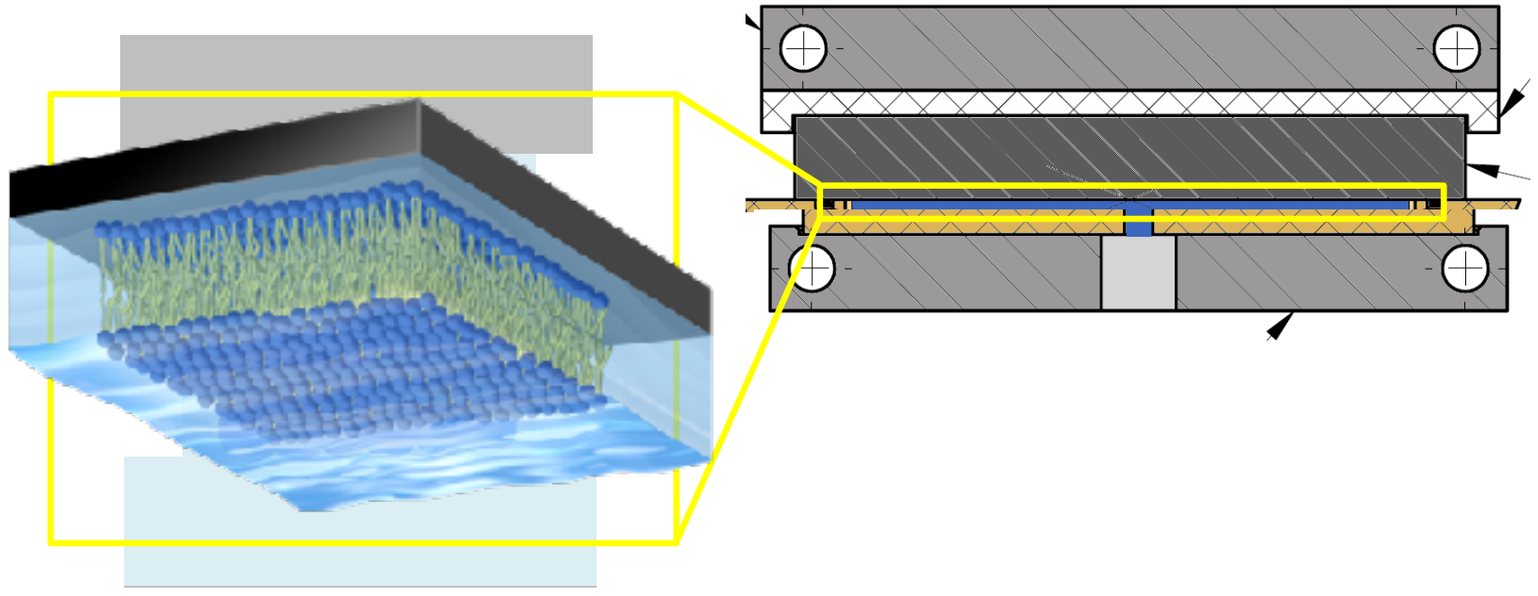


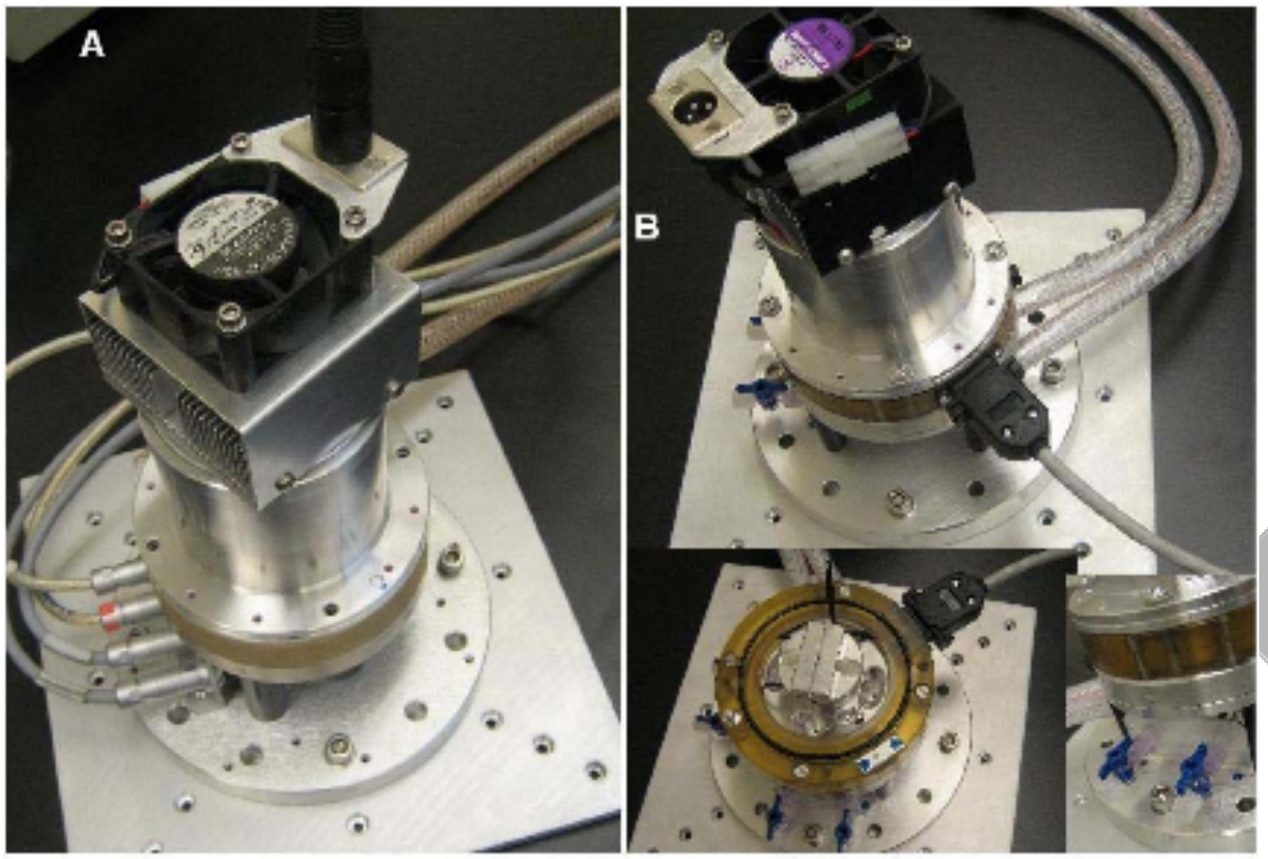
Langmuir trough for insoluble monolayers



SAMPLE ENVIRONMENT

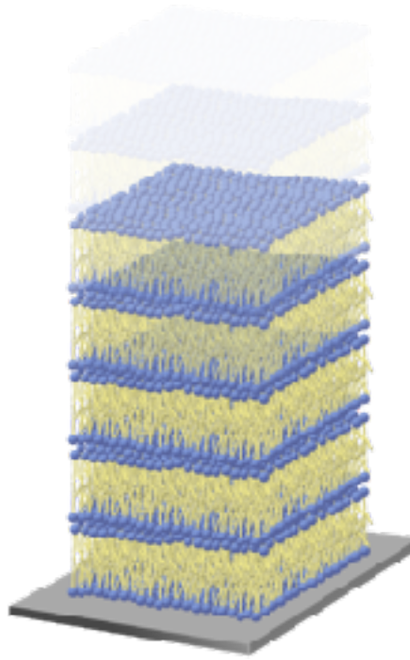
Solid/liquid cell for
adsorption on surfaces





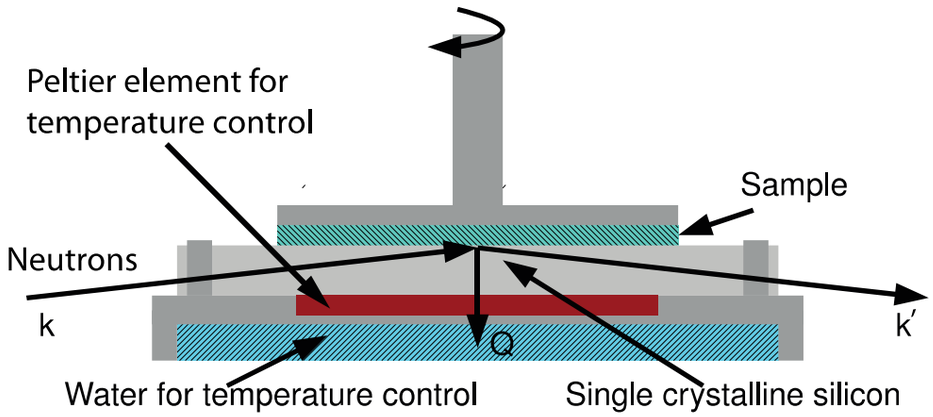
Humidity chamber

$$r.h.=100p(T_w)/p(T_s)$$

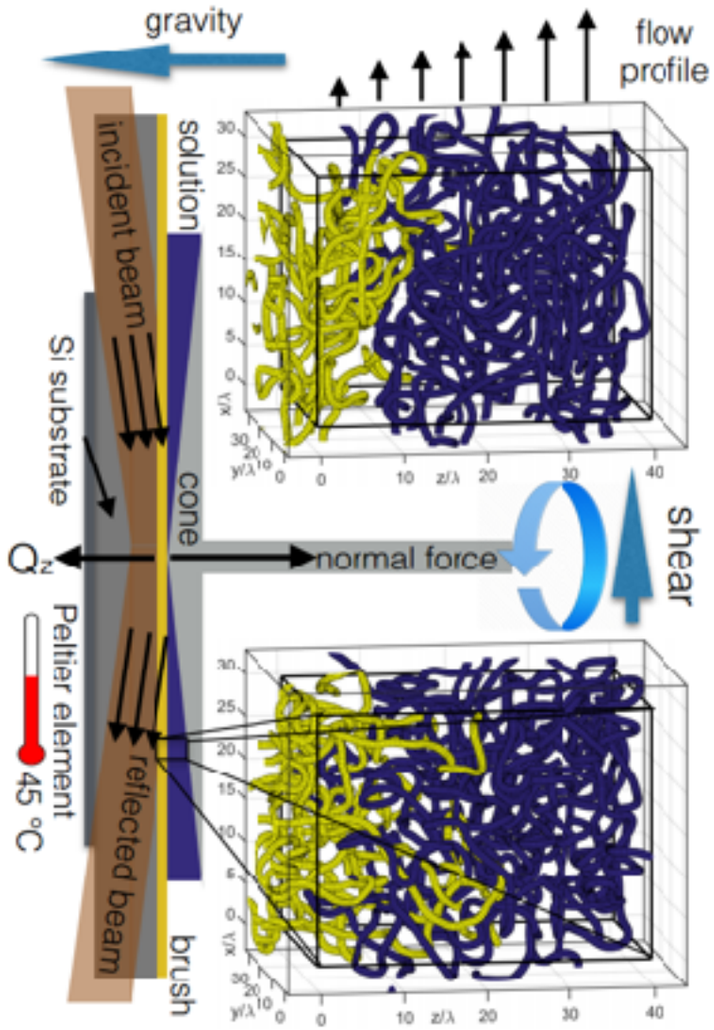


SAMPLE ENVIRONMENT

Rheometer

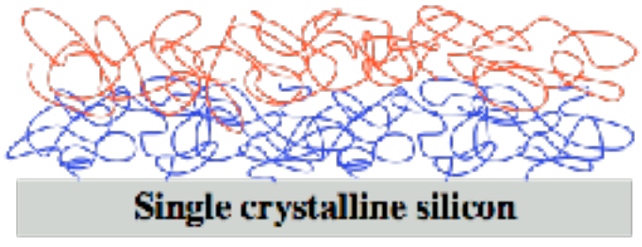


Temperature range: 15 - 160 °C
Shear rates up to 10^5 s^{-1}



d-PS in DEP

Grafted h-PS



brushes of greatly different chain lengths and grafting densities

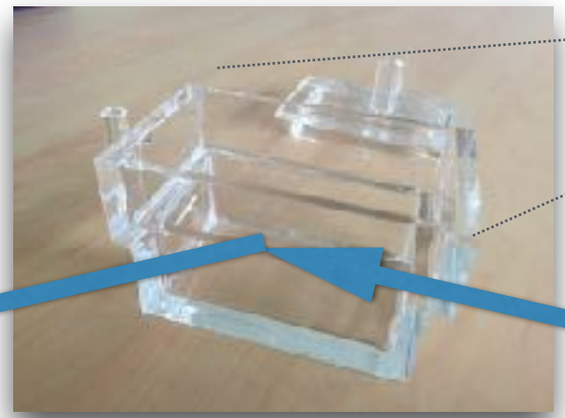
Korolkovas *et al.*, *Macromolecules* **50** (1215) 2017.

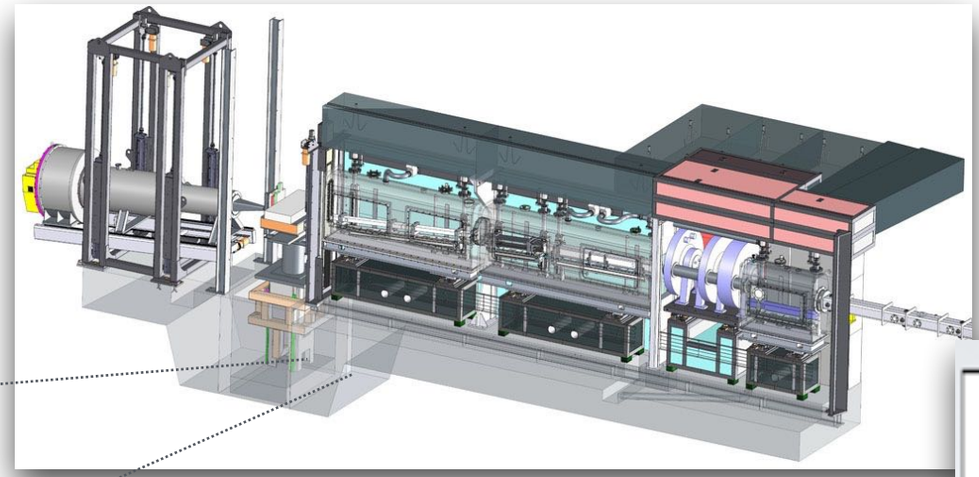
Polymer brushes can be made to be shear-responsive, here it is found that the brush dynamics were governed by the the free chains in solution rather than the brush itself. The phenomenon of the brush collapse has applications in the tailoring of nanosensors and as a way to dynamically control surface friction and adhesion.

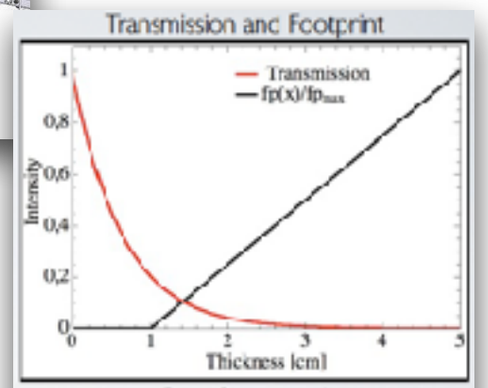
Liquid-liquid interfaces…

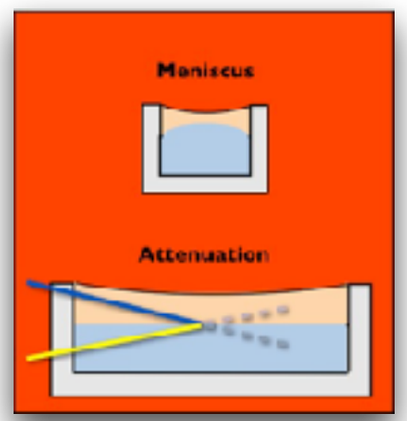
Use FIGARO unique reflection down option : fluorinated oil highly transmitting and denser than water for example

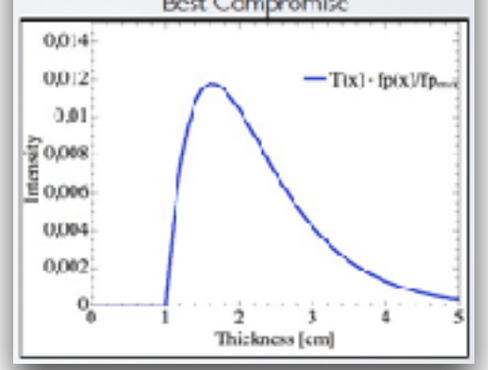
Scoppola et al., Angew. Chem. Int. Ed., 2016







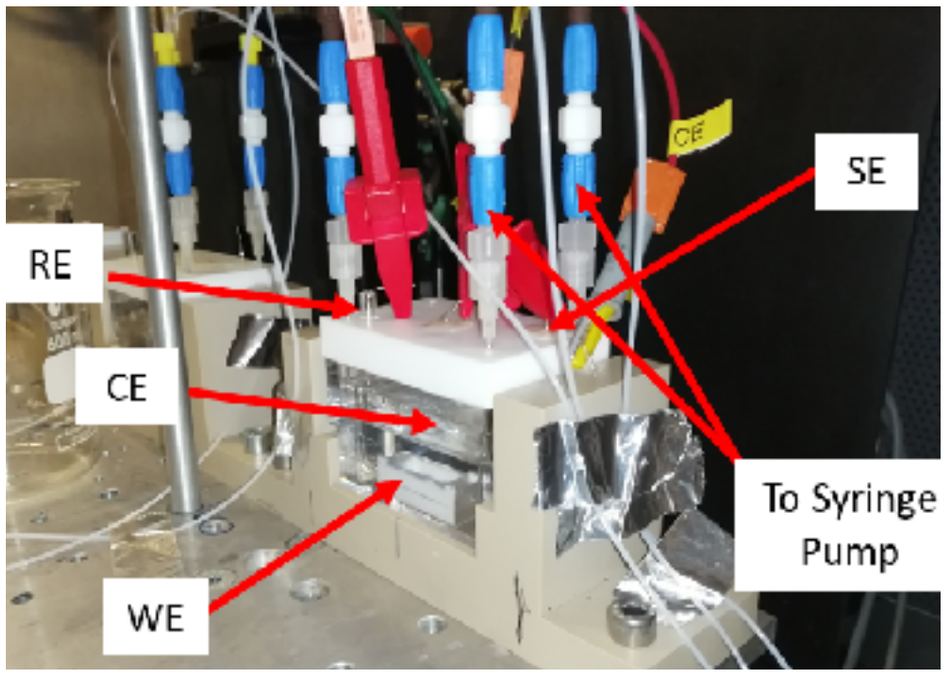


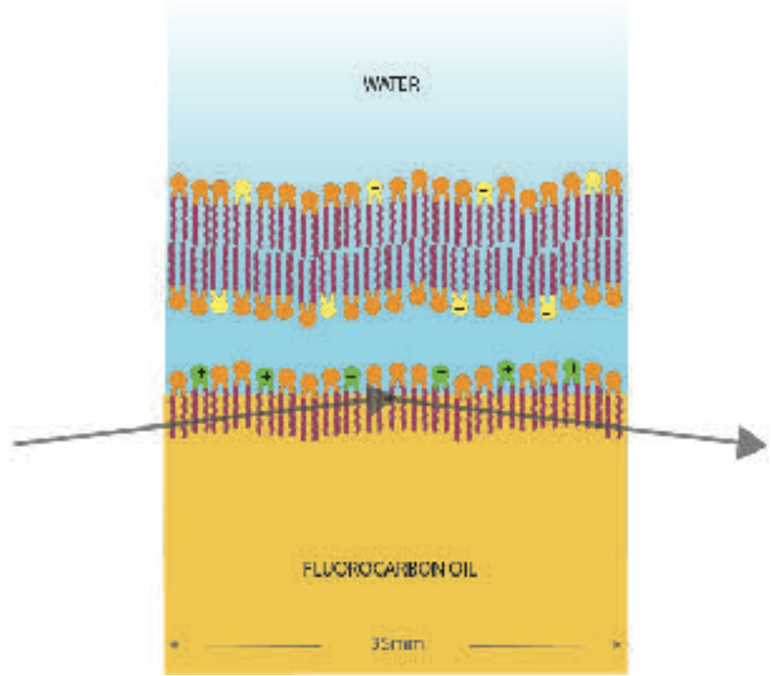


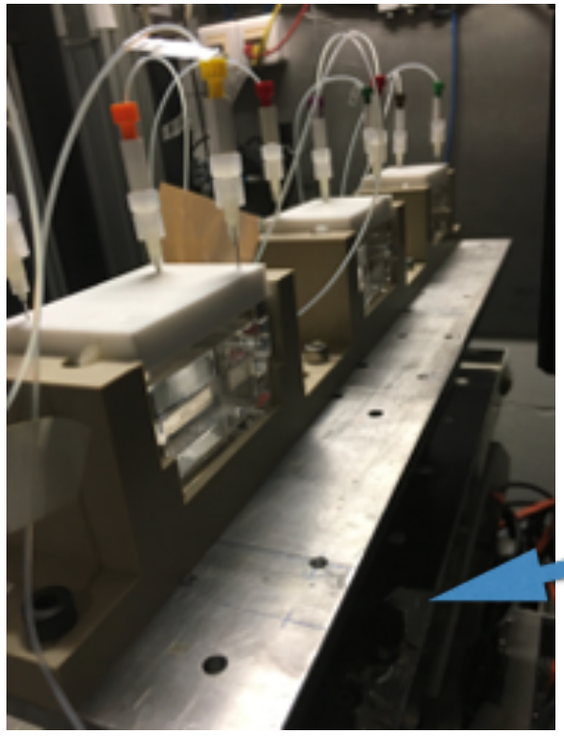
Neutrons cross 35mm of bottom liquid bulk phase (deuterated or fluorinated oil)

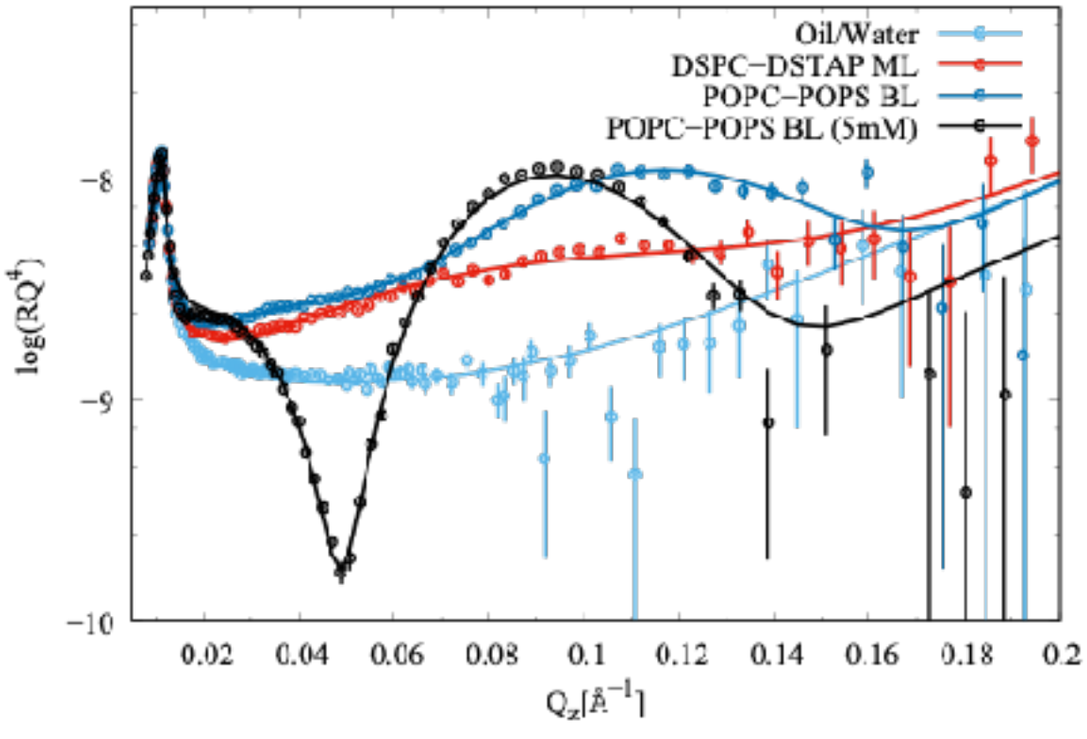
Cell used also for synchrotron radiation crossing the 70 mm top liquid phase

BILAYERS AT LIQUID-LIQUID INTERFACES



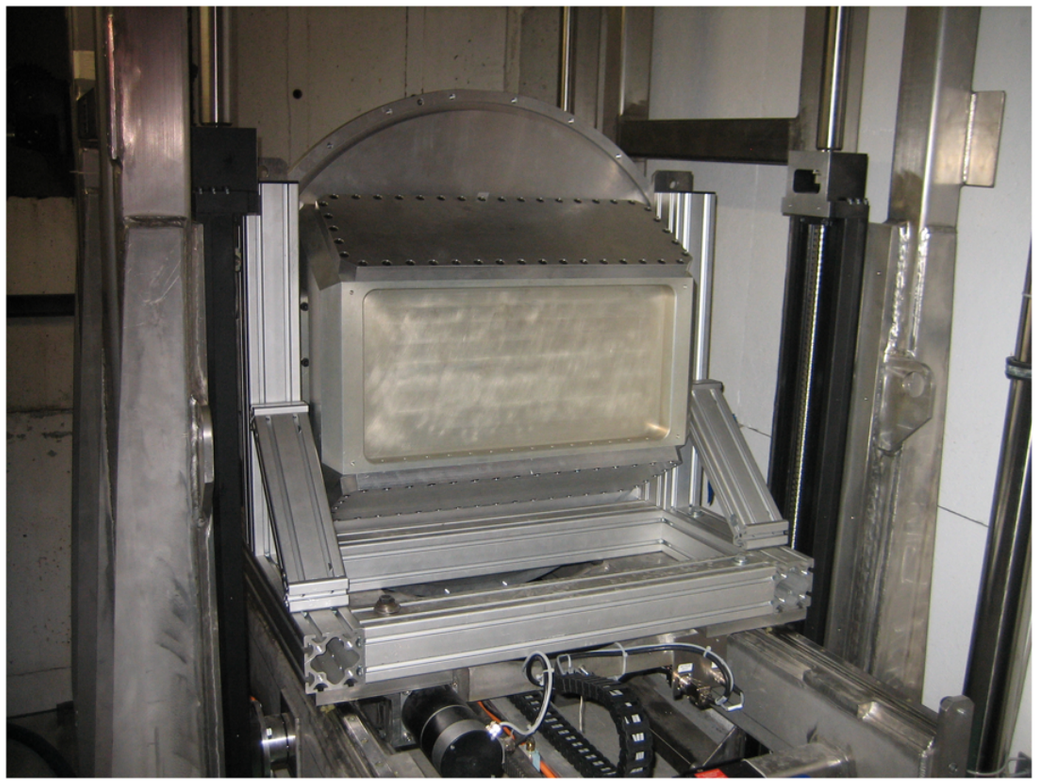


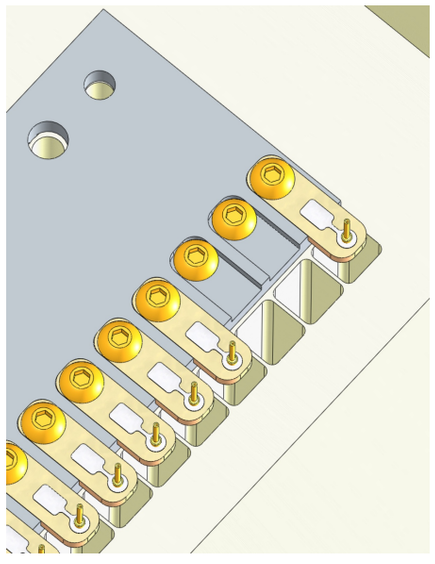




Tummino et al. Electrochim. Acta 2021

2-D DETECTOR: simultaneous access to off-specular/GISANS *(the latter after optimisation of instrument settings)*





Neutrons have mass but no electrical charge. Because of this they cannot directly produce ionization in a detector, and therefore **cannot be directly detected.**

This means that neutron detectors must rely upon a conversion process where an incident neutron interacts with a nucleus to produce a secondary charged particle. These charged particles are then directly detected and from them the presence of neutrons is deduced.

BF_3 filled detectors that utilize the fission of the ^{10}B atom to provide the charged particle

$$n + {}^{10}_{5}B \rightarrow \begin{cases} \alpha + {}^{7}_{3}Li + 2.310\ \text{MeV}\ (94\%) \\ \alpha + {}^{7}_{3}Li + 2.792\ \text{MeV}\ (6\%) \end{cases}$$

Planning a Reflectivity Measurement

- **Simulation of reflectivity profiles is essential**
  – Can you see the effect you want to see?
  – What is the best substrate? Which materials should be deuterated?

- **If your sample involves free liquid surface you will need to use a reflectometer with a vertical scattering plane**

- **If you want to follow a changes with time (kinetics) better to use a time-of-flight instrument.**

- **Preparing good (i.e. low surface roughness) samples is key**
  – Beware of large islands

- **Layer thicknesses between <10 Å and 5000 Å**
  – But don't mix extremes of thickness

For a list of neutron reflectometers and programs to analyze the data:

http://material.fysik.uu.se/Group_members/adrian/reflect.htm#Instruments
by Adrian Rennie (Uppsala University)

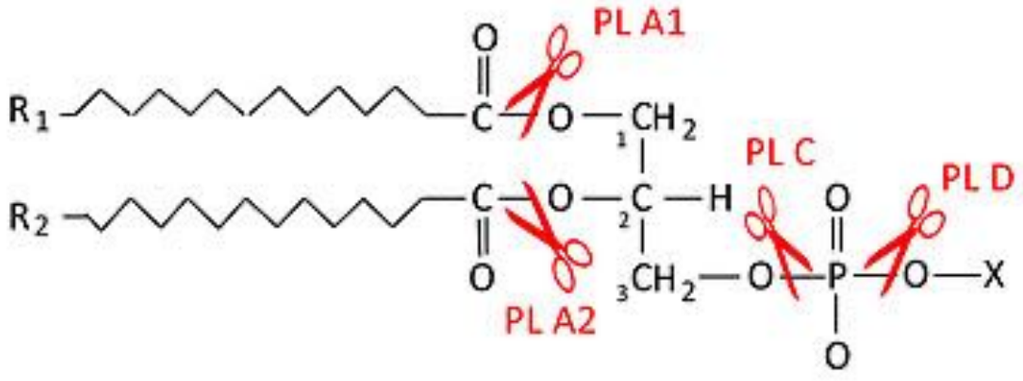
Complementary Measurements

- Ellipsometry is really important for pre-characterization measurements
- Brewster Angle Microscopy for interpretation of off-specular features
- Quartz Crystal Microbalance with dissipation monitoring
- Lab-based XRR
- MD-simulations

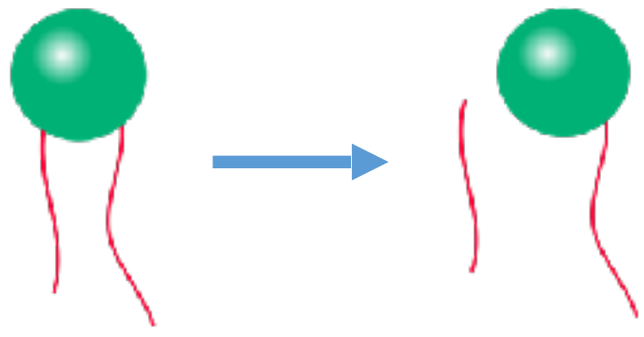
Soft-bio applications include:

Polymer films
Thin films under shear
Lipid bilayers
Protein and surfactant adsorption
Oil/water interfaces
Polyelectrolyte/surfactant interactions
Chemistry at interfaces
Adsorption from solution
Insoluble monolayers
……..

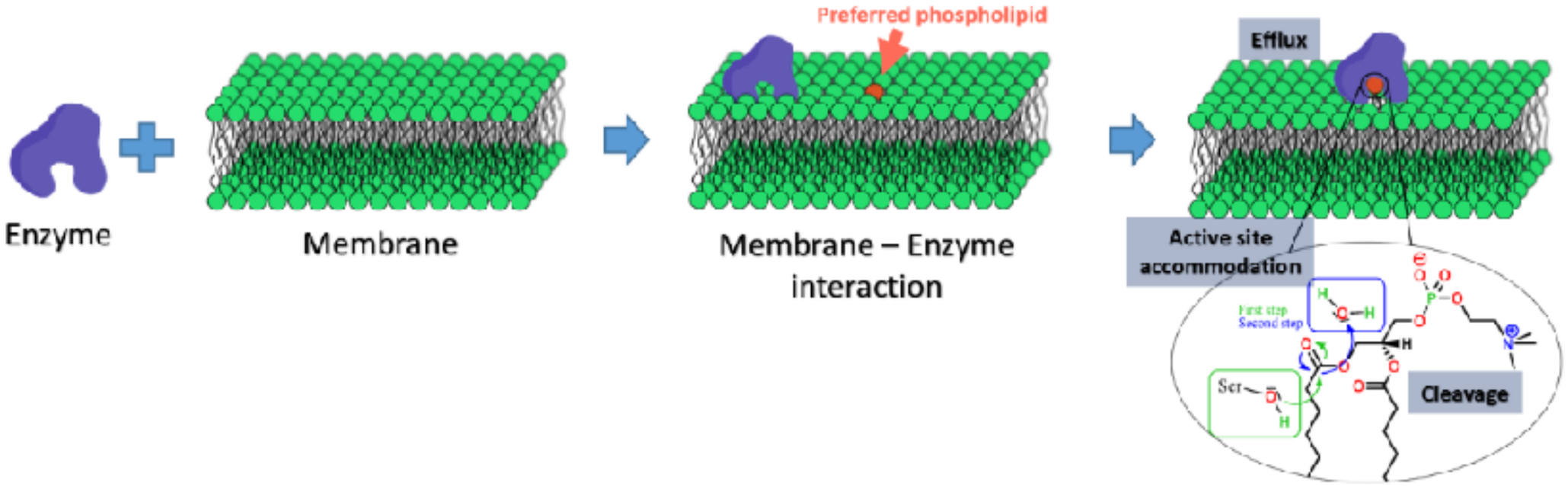
Factors that influence the substrate specificity of phospholipases



PLA= enzyme that cleaves phospholipids



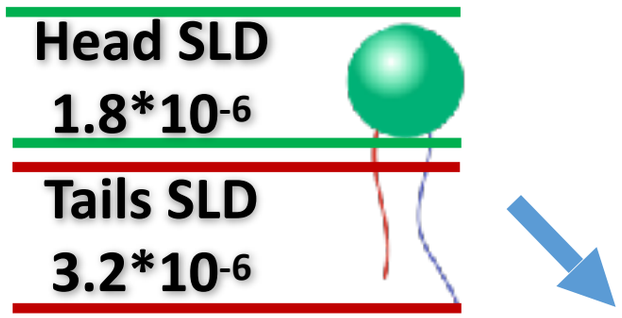
Catalytic mechanism

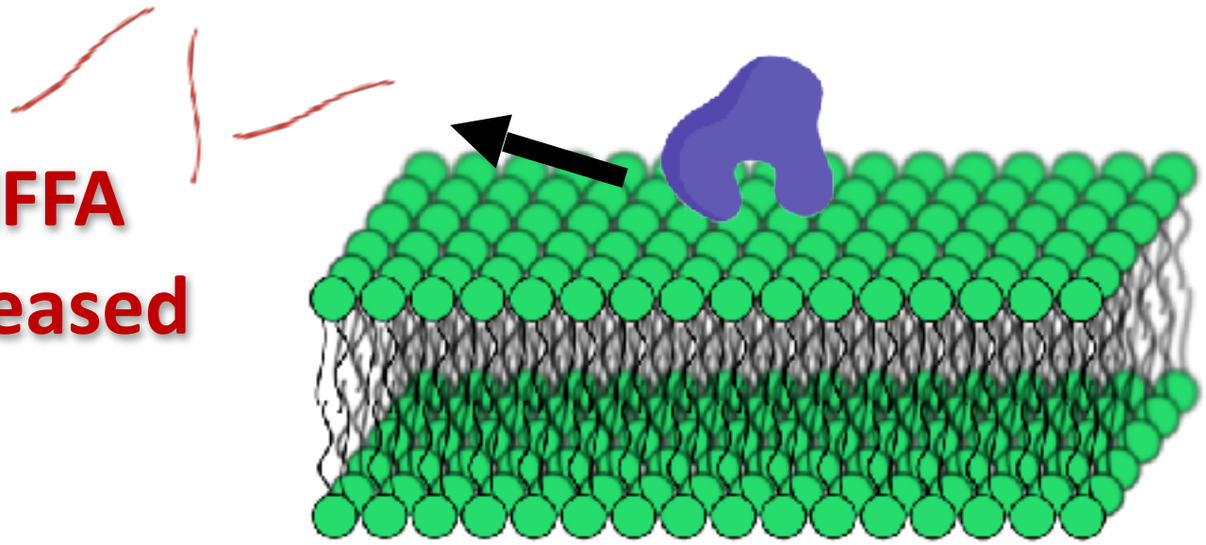


courtesy G. Corucci

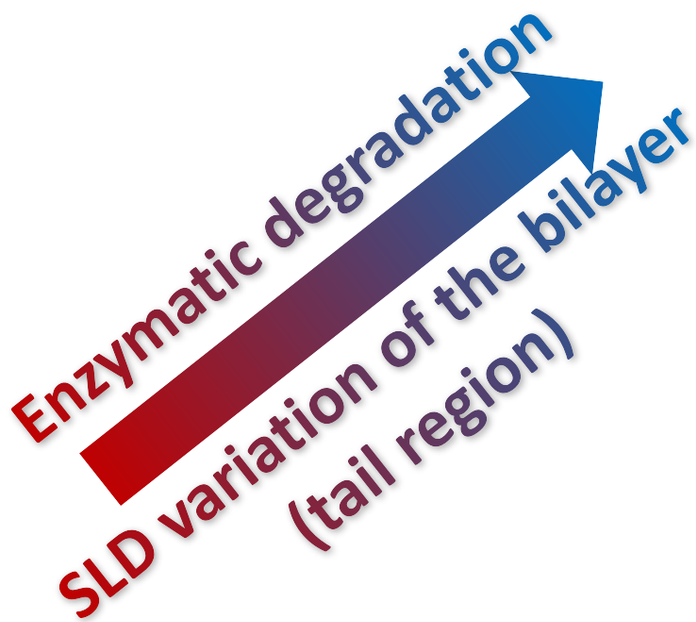
Why partially deuterated phospholipids?

Deuterated FFA released in the bulk solution

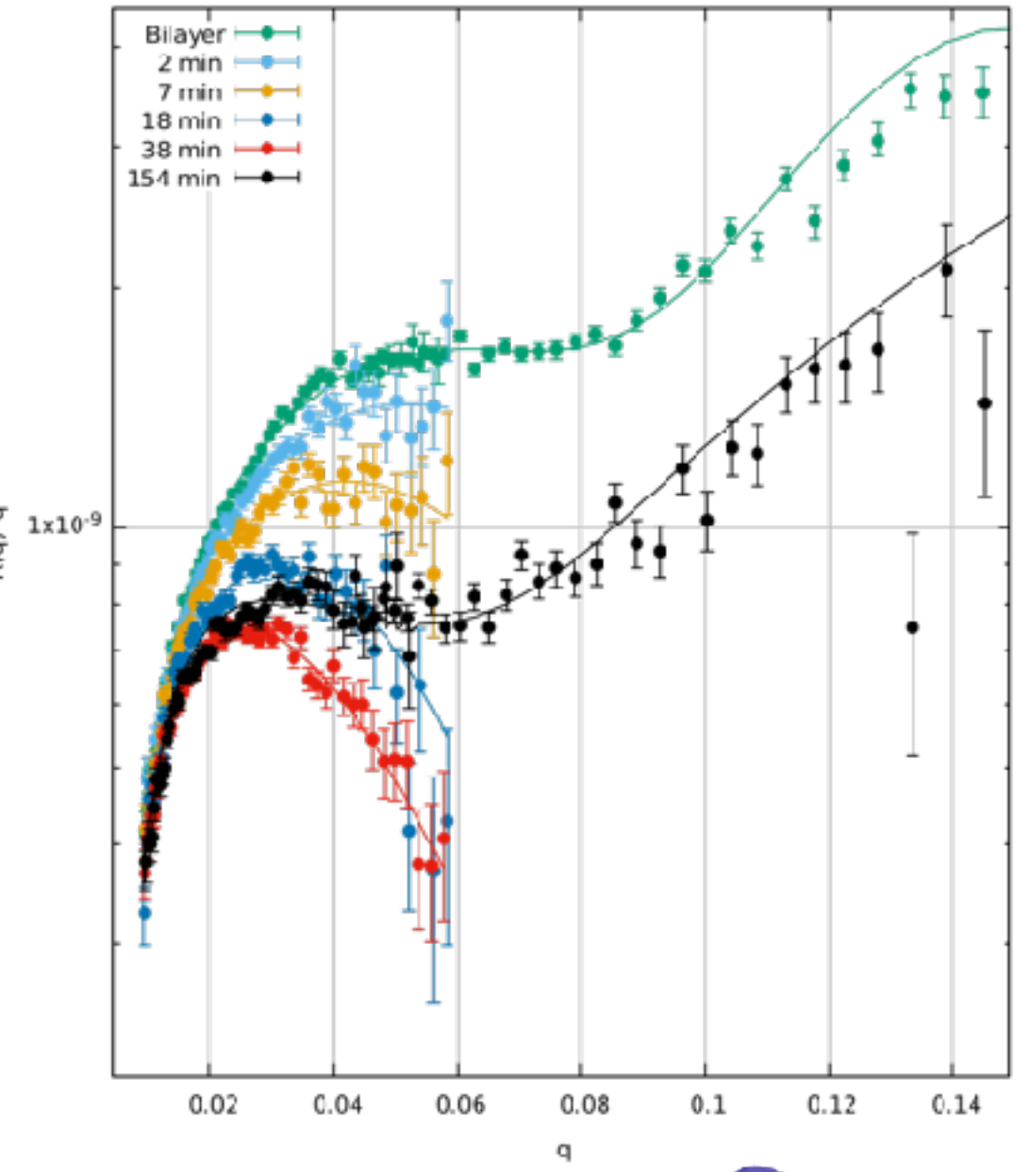


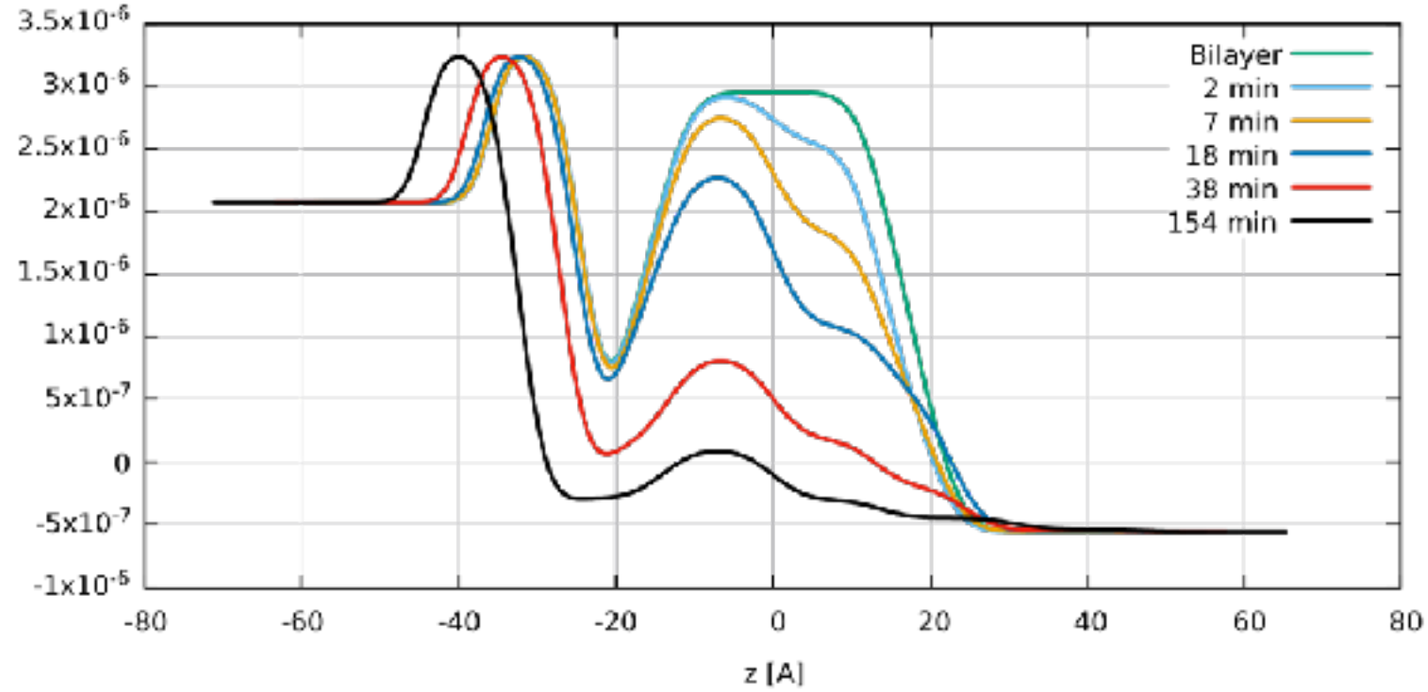


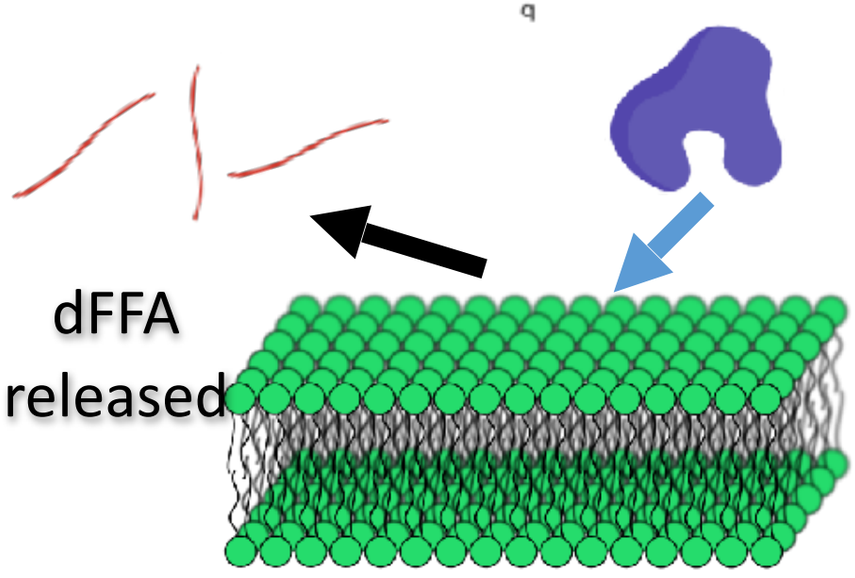
CONTRAST VARIATION



16:0 18:2 PC







Possibility to follow the kinetics, determine the variation in composition of the membrane and the amount of deuterated FFA released in the bulk solution

courtesy G. Corucci

Conclusions

- Neutron and x-ray reflectometry remains an essential tool for the study of structure at the nanometer level of soft self-assembled systems at interfaces.

- Complementary to x-ray and synchrotron radiation, advantages of neutrons include high penetration, sensitivity to light elements (H, C, O, N, …) and isotopic labelling/contrast variation.

- Possibility to work in real (physiological) conditions

- Possibility for in-situ studies of systems under deformation.

- Need optimised sample preparation

- Perspectives in soft matter and biology are very numerous.