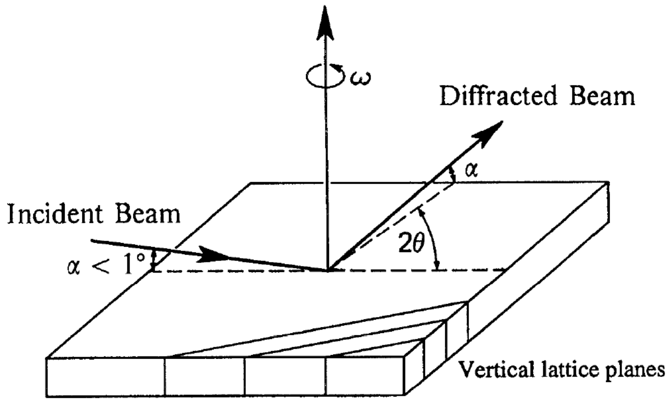
Grazing Incidence X-Ray Diffraction
A short introduction



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Ecole Thématique "Réflectivité des Rayons X et Neutrons"
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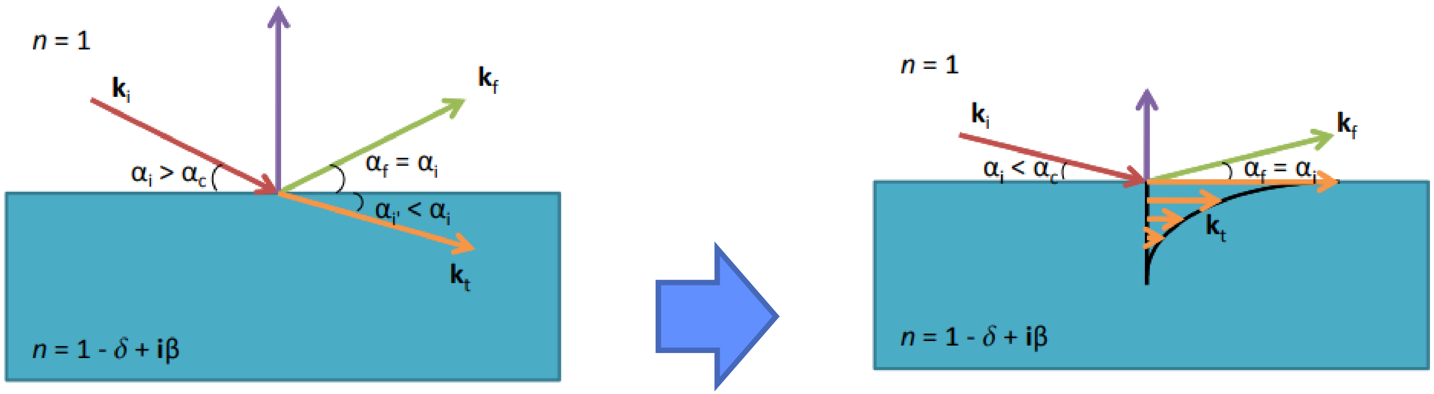
Grazing Incidence : why ??



Grazing incidence condition

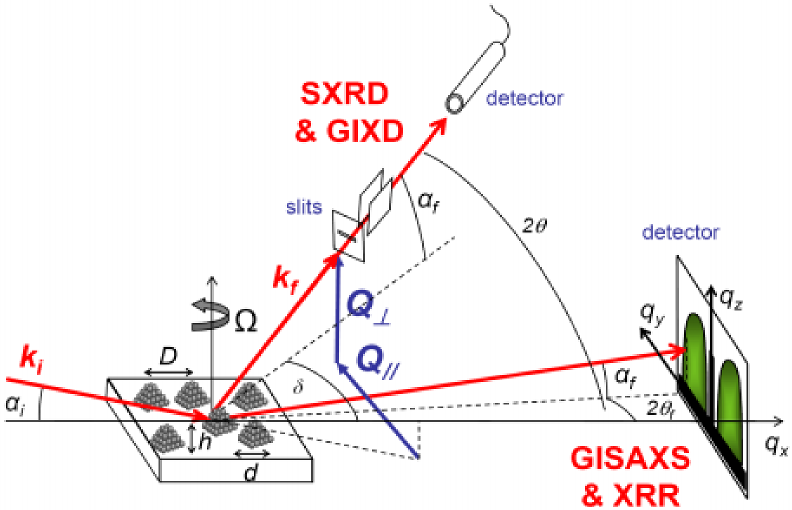
Maximize the contribution from the (near-)surface

Grazing Incidence : why ??

GIXRD, GIXS, Surface scattering, etc… use **grazing incidences** to illuminate the surface region specifically (total reflection)

Several geometries can be used depending on what is searched for:

- GIXS: in-plane or out-of plane
  → (atomic) structure of thin films
- GISAXS: small angles
  → large objects morphology



G. Renaud *et al.*, *Surface Science Reports* 64 (2009) 255–380

Outline

I. Fundamentals: Interaction light/matter, Scattering and Refractive index

II. Grazing incidence conditions: Boundary conditions, Penetration length

III. The Born Approximation and the Distorted Wave Born Approximation

IV. Reciprocal space of 3D & 2D crystal, Diffraction

V. The GIXS geometry: Crystal Truncation Rods and examples

VI. The GISAXS geometry and examples

VII. Some experimental setups

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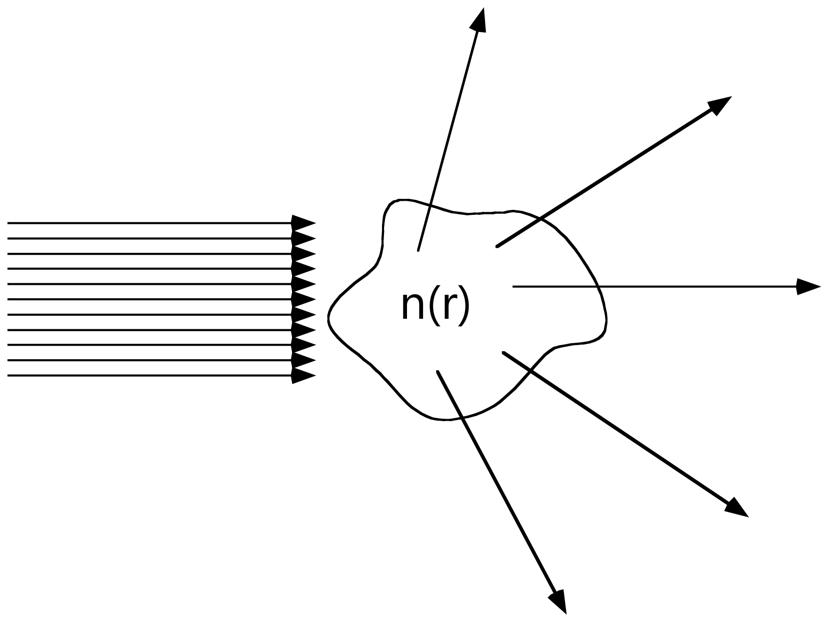
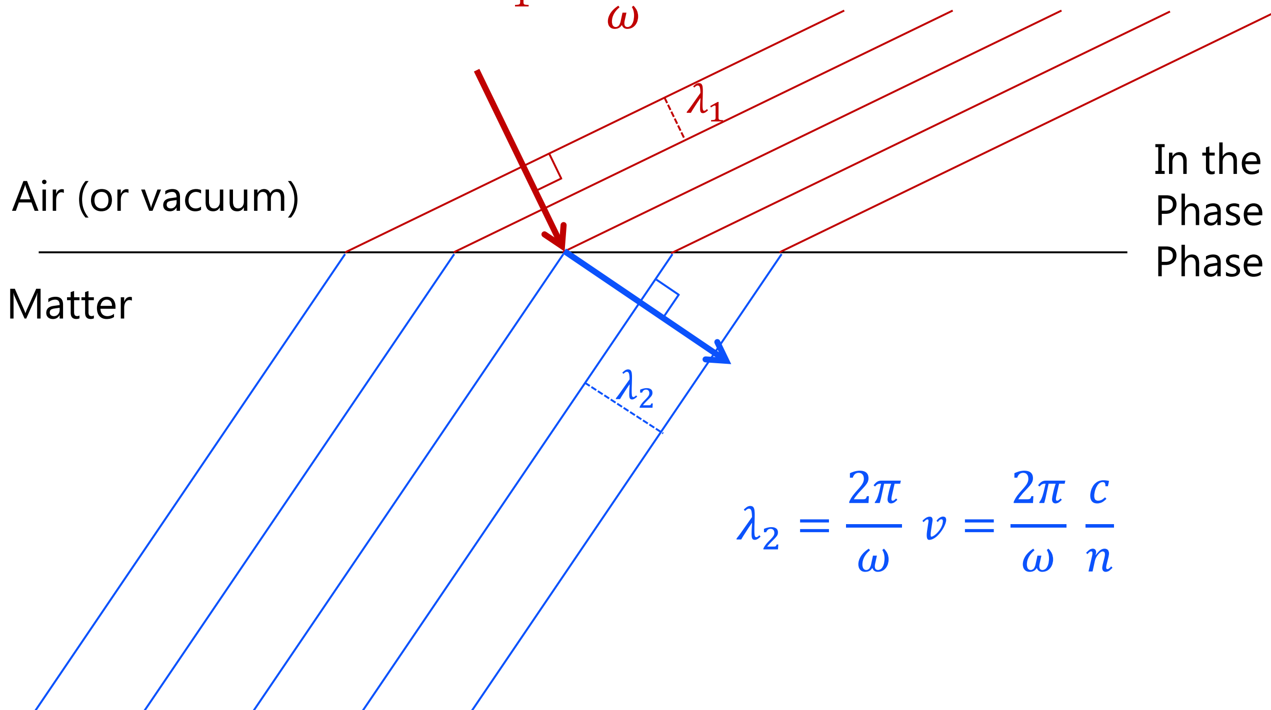
Light – matter interactions

- Atomic structure of materials
- Refractive index



Wave at an interface

$$\lambda_1 = \frac{2\pi}{\omega} c$$



In the same amount of time
Phase 1 must travel λ_1
Phase 2 must travel $\lambda_2 > \lambda_1$

$$\lambda_2 = \frac{2\pi}{\omega} v = \frac{2\pi}{\omega} \frac{c}{n}$$

$$n < 1$$

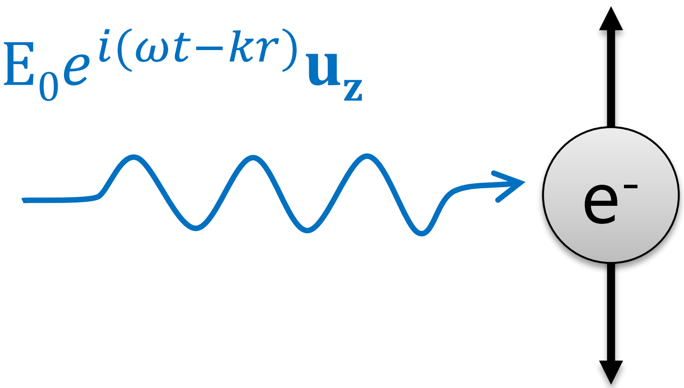
$$\boxed{n = \frac{kc}{\omega}}$$

$$k = \frac{2\pi}{\lambda}$$

Refractive index expression (X-rays)

Incident radiation = plane wave (linearly polarized // $\mathbf{u_z}$):

$$E_i = E_0 e^{i(\omega t - kr)} \mathbf{u_z}$$



$$E = E_0 e^{i\omega t} \mathbf{u_z}$$

(e⁻ at **r** = 0)

Electron = (damped) harmonic oscillator

Newton's second law of motion:

$$m\ddot{z} = -\gamma \dot{z} - \omega_0{}^2 z + qE$$

mass.acceleration

damping

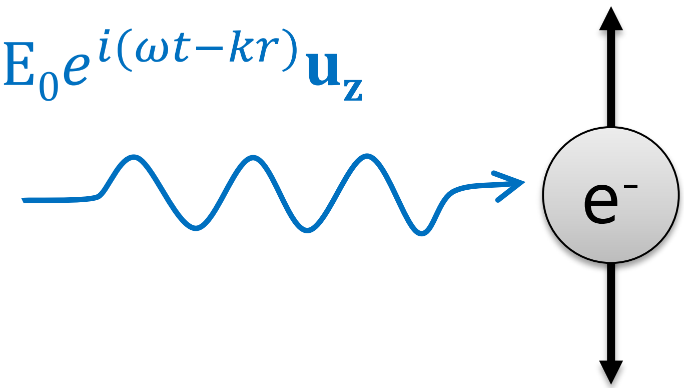
restoring force

excitation

Refractive index expression (X-rays)

Incident radiation = plane wave (linearly polarized // $\mathbf{u_z}$):

$$\mathrm{E_i} = \mathrm{E_0} e^{i(\omega t - kr)} \mathbf{u_z}$$



$$\mathrm{E} = \mathrm{E_0} e^{i\omega t} \mathbf{u_z}$$

(e^- at **r** = 0)

Electron = (damped) harmonic oscillator

Newton's second law of motion:

$$m(\ddot{z} + \gamma \dot{z} + {\omega_0}^2 z) = q\mathrm{E}$$

Solutions :

$$z = z_0 e^{i\omega t}$$

$$\boxed{z = \frac{q\mathrm{E_0}}{m(-\omega^2 + {\omega_0}^2 + i\gamma\omega)} e^{i\omega t}}$$

Refractive index expression (X-rays)

Field radiated by the oscillating charge:
Induced dipole: **p** = q**r**

$$\mathbf{r} = z\mathbf{u_z} = \frac{q\mathrm{E}_0}{m(-\omega^2 + {\omega_0}^2 + i\gamma\omega)} e^{i\omega t}\mathbf{u_z}$$

$$\mathbf{p} = \frac{q^2\mathrm{E}_0}{m(-\omega^2 + {\omega_0}^2 + i\gamma\omega)} e^{i\omega t}\mathbf{u_z}$$

$$\mathbf{p} = \frac{q^2}{m(-\omega^2 + {\omega_0}^2 + i\gamma\omega)} \mathbf{E}$$

$$\mathbf{p} = \alpha(\omega)\varepsilon_0\mathbf{E}$$

Atomic polarisability

$$\alpha(\omega) = \frac{q^2/m\varepsilon_0}{-\omega^2 + {\omega_0}^2 + i\gamma\omega}$$

Refractive index expression (X-rays)

In fact, there are multiple modes (electrons) per atom

$$\alpha(\omega) = \frac{q^2}{m\varepsilon_0}\sum_k \frac{f_k}{-\omega^2 + {\omega_{0,k}}^2 + i\gamma_k\omega}$$

Total polarization :
N = total number of atoms

$$\mathbf{P} = N\mathbf{p} = N\alpha(\omega)\varepsilon_0\mathbf{E}$$

… but what is the radiated field ??

Refractive index expression (X-rays)

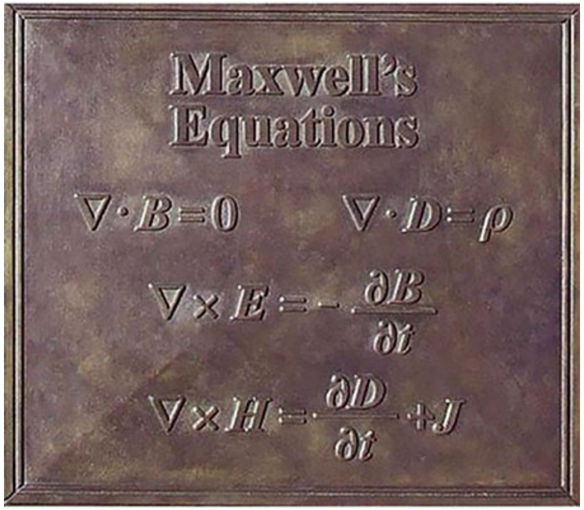
Solving Maxwell's equations

(a) $\mathbf{\nabla}.\mathbf{E} = \frac{-\mathbf{\nabla}.\mathbf{P}}{\varepsilon_0} = \frac{\rho}{\varepsilon_0}$

(b) $c^2\mathbf{\nabla}\times\mathbf{B} = \frac{\partial}{\partial t}\left(\frac{\mathbf{P}}{\varepsilon_0} + \mathbf{E}\right) = \frac{\mathbf{j}}{\varepsilon_0} + \frac{\partial \mathbf{E}}{\partial t}$

(c) $\mathbf{\nabla}\times\mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$

(d) $\mathbf{\nabla}.\mathbf{B} = 0$



With

$$\mathbf{E} = \mathrm{E}_0 e^{i(\omega t - kx)}\mathbf{u_z} = \mathrm{E_z}\mathbf{u_z}$$

Yields

$$-k^2\mathrm{E_z} + \frac{\omega^2}{c^2}\mathrm{E_z} = -\frac{\omega^2}{\varepsilon_0 c^2}\mathrm{P_z} = -\frac{\omega^2}{\varepsilon_0 c^2}\varepsilon_0 N\alpha \mathrm{E_z}$$

$$-k^2 E_z + \frac{\omega^2}{c^2} E_z = -\frac{\omega^2}{\varepsilon_0 c^2} \varepsilon_0 N\alpha E_z$$

Hence

$$k^2 = \frac{\omega^2}{c^2}(1 + N\alpha)$$

recall that $n = \frac{kc}{\omega}$

$$n^2 = (1 + N\alpha)$$

$$n^2 = 1 + N\alpha(\omega) = 1 + N\frac{q^2}{m\varepsilon_0}\sum_k \frac{f_k}{-\omega_k{}^2 + \omega_{0,k}{}^2 + i\gamma_k\omega}$$

Refractive index expression (X-rays)

This is quite complex, so for ω far from any $\omega_{0,k}$
i.e. far from resonances :

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

$$n = 1 - \frac{\lambda^2}{2\pi} r_e \rho_e - i\frac{\lambda}{4\pi}\mu$$

$$n^2 = \varepsilon_r$$

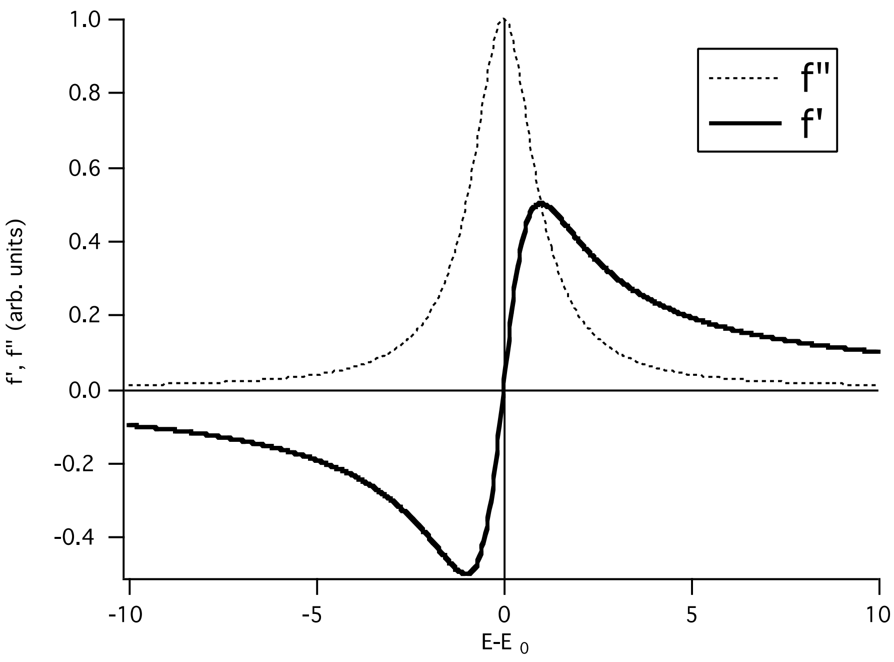
Classical radius of the electron

$$r_e = \frac{e^2}{4\pi\varepsilon_0 mc^2} \approx 2.818 \times 10^{-15} m$$

Refractive index expression (X-rays)

For bound electrons

$$n = 1 - \frac{\lambda^2}{2\pi} r_e \rho_a \left(f^0 + f'(\omega) + i f''(\omega) \right)$$



f′ and f′′ vary rapidly around absorption edges,
it can be used to enhance the contrast (*anomalous* effects)

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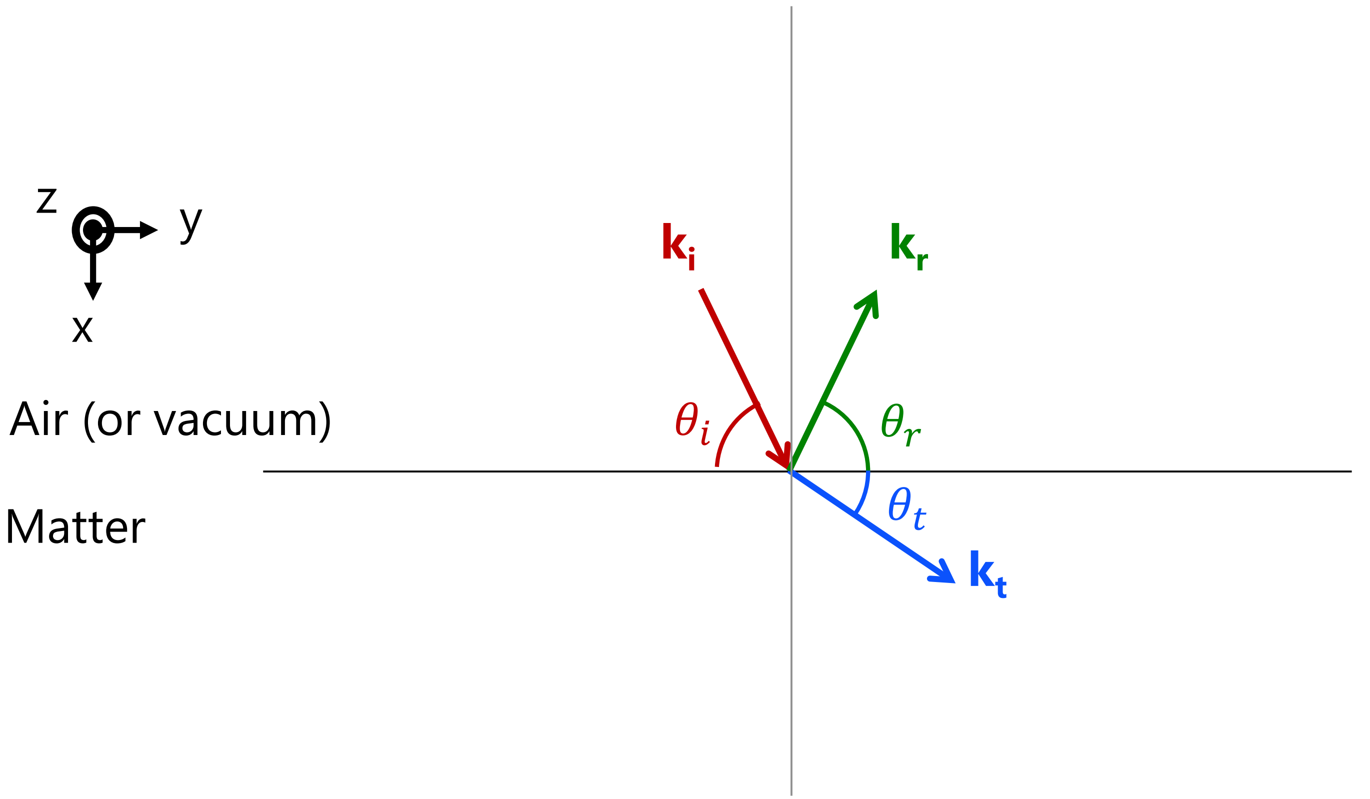

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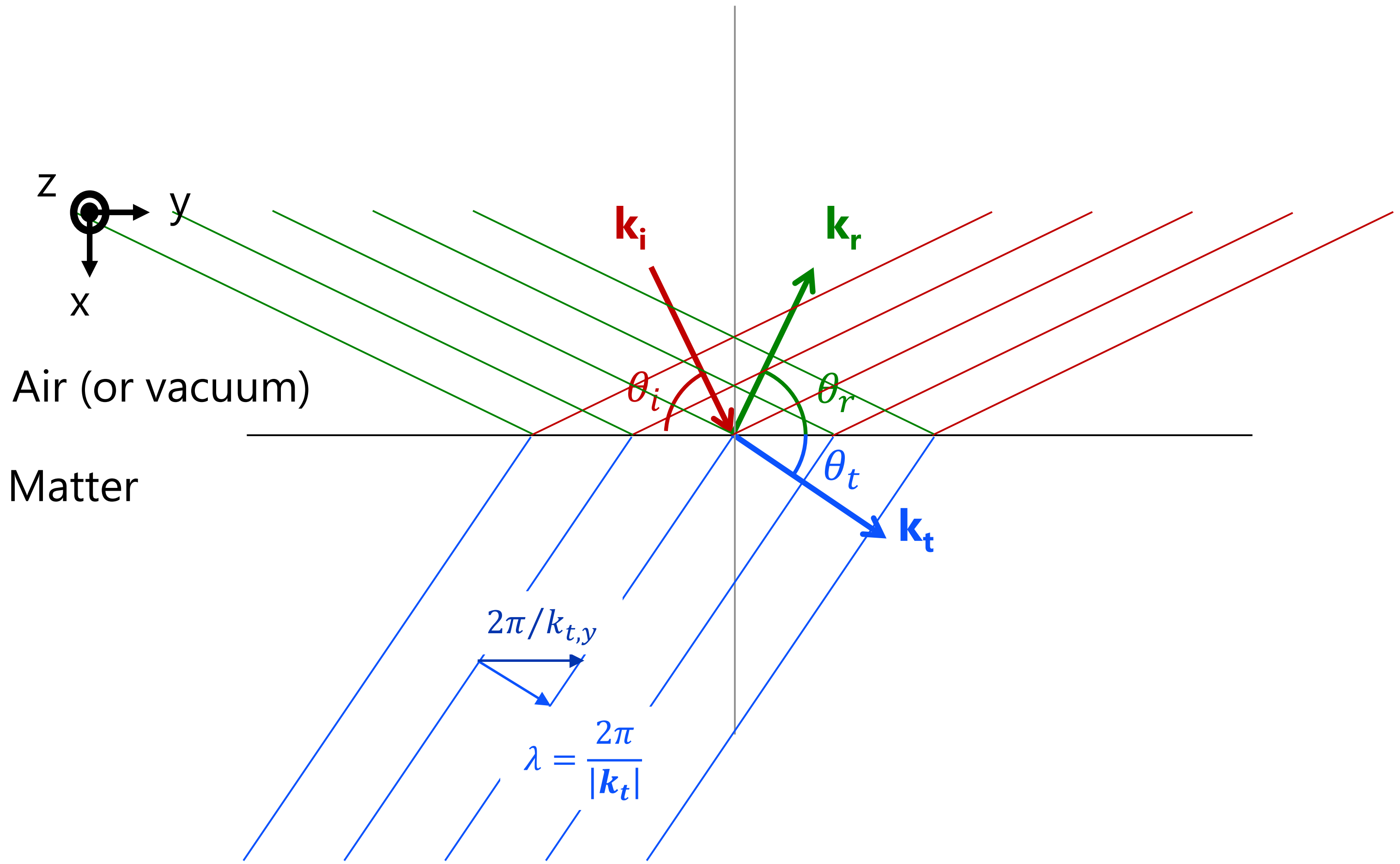

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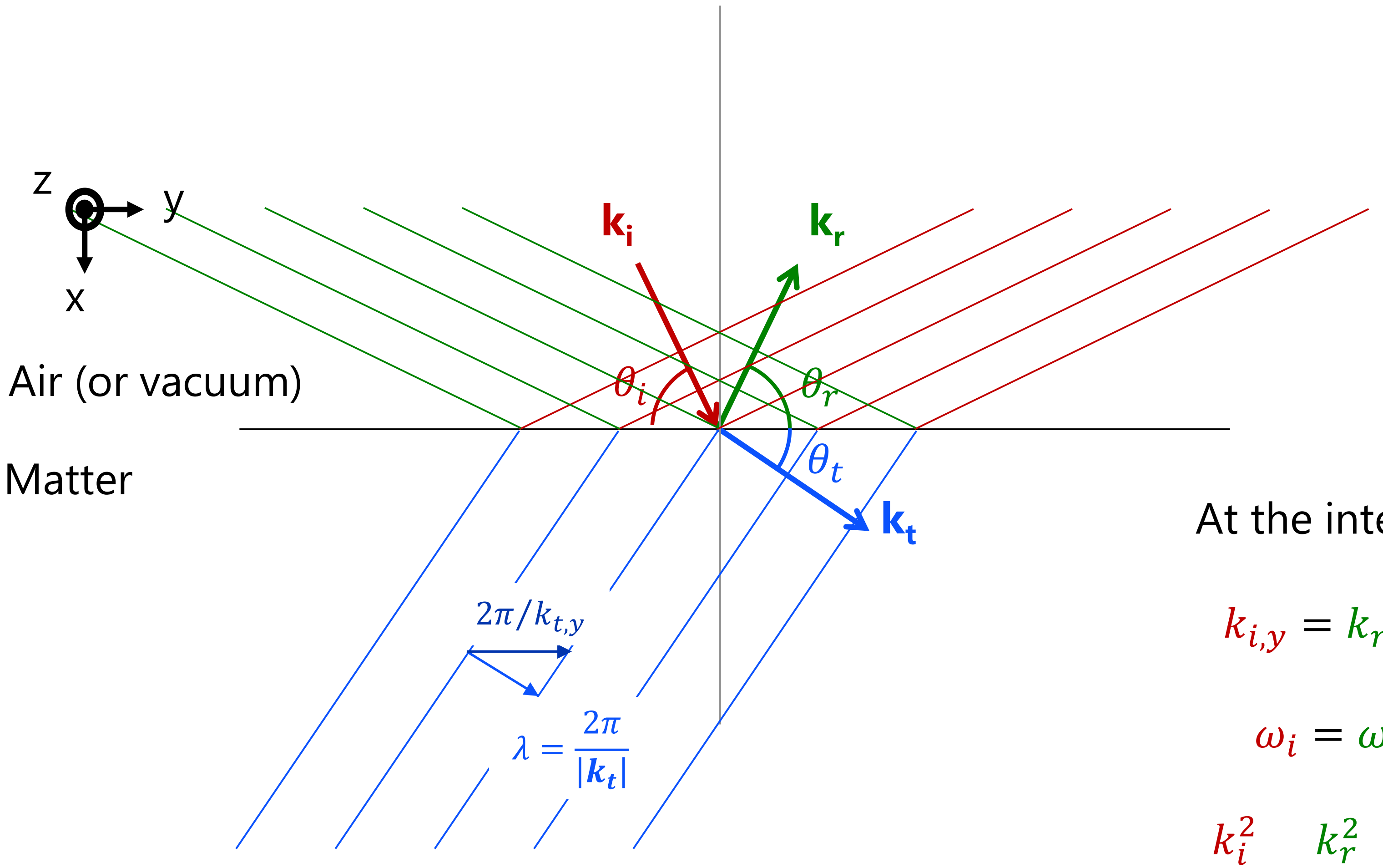


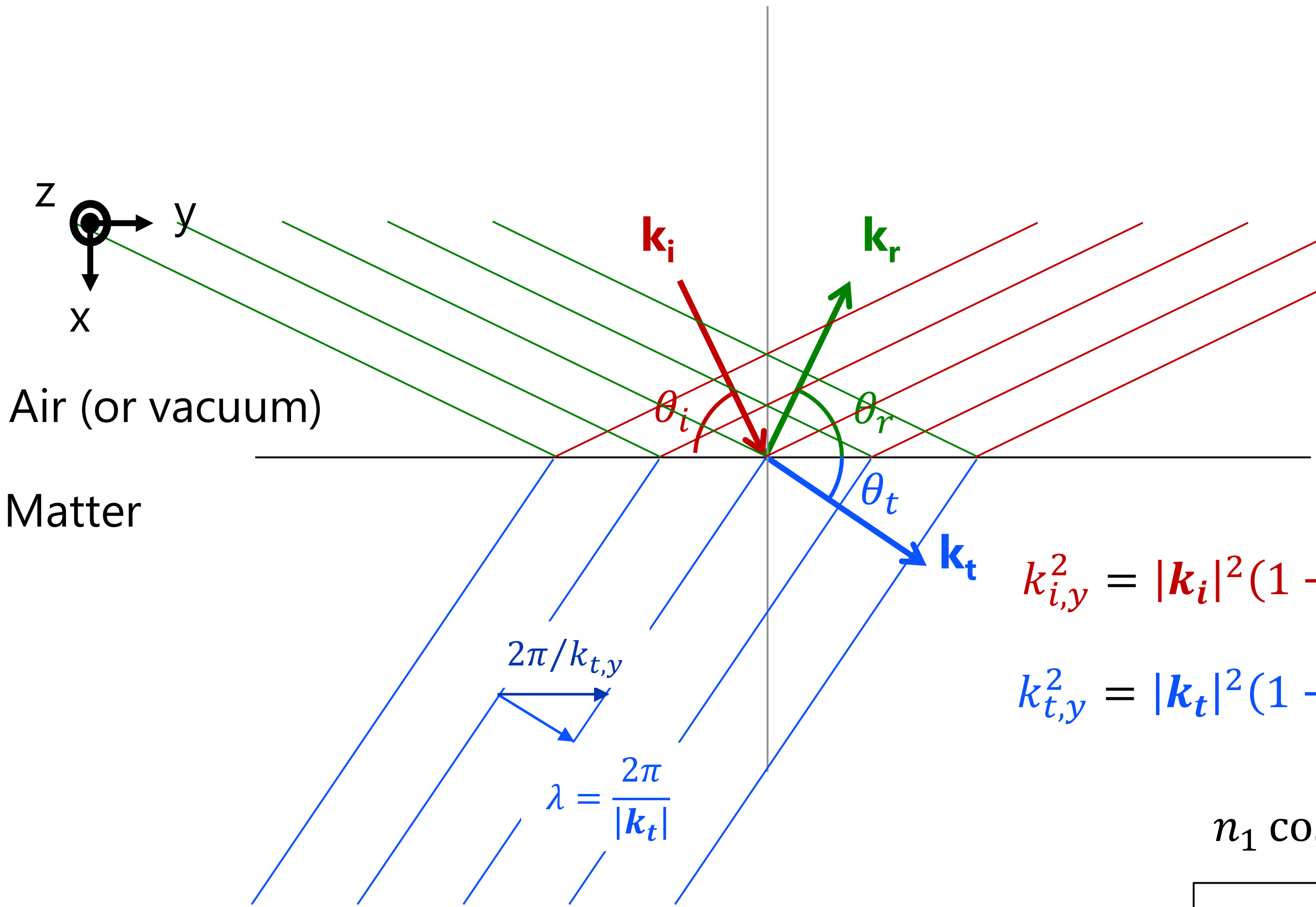
At the interface:

$$k_{i,y} = k_{r,y} = k_{t,y}$$

$$\omega_i = \omega_r = \omega_t$$

$$\frac{k_i^2}{n_1^2} = \frac{k_r^2}{n_1^2} = \frac{k_t^2}{n_2^2} = \frac{\omega}{c}$$

Reflection on a surface : Boundary conditions



$$k_{i,y}^2 = |\boldsymbol{k_i}|^2(1 - \sin^2\theta_i) = n_1^2 \frac{\omega^2}{c^2} \cos^2\theta_i$$

$$k_{t,y}^2 = |\boldsymbol{k_t}|^2(1 - \sin^2\theta_t) = n_2^2 \frac{\omega^2}{c^2} \cos^2\theta_t$$

$$n_1 \cos\theta_i = n_2 \cos\theta_t$$

$$\boxed{n_1 \sin\theta_1 = n_2 \sin\theta_2}$$

(angles defined from the normal)

Reflection and transmission coefficients

Fresnel coefficients

$$r = \frac{E_r}{E_i} = \frac{\sin(\alpha_i - \alpha_t)}{\sin(\alpha_i + \alpha_t)} \approx \frac{\alpha_i - \alpha_t}{\alpha_i + \alpha_t}$$

$$t = \frac{E_t}{E_i} = \frac{2\sin(\alpha_i)\cos(\alpha_t)}{\sin(\alpha_i + \alpha_t)} \approx \frac{2\alpha_i}{\alpha_i + \alpha_t}$$

$$n_1 \cos(\alpha_i) = n_2 \cos(\alpha_t)$$
$$n_1 \approx 1$$
$$n_2 \approx 1 - \delta$$

⇒

$$1 - \frac{\alpha_i^2}{2} = (1-\delta)\left(1 - \frac{\alpha_t^2}{2}\right)$$
$$\alpha_t^2 = \alpha_i^2 - 2\delta$$

Reflection and transmission coefficients

$$r \approx \frac{-\delta}{2{\alpha_i}^2+\delta}$$

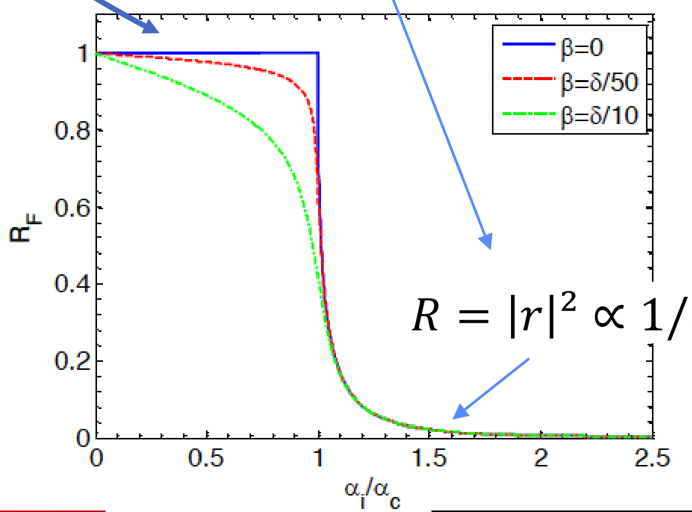
$$t \approx \frac{2{\alpha_i}^2}{2{\alpha_i}^2+\delta}$$

$r = 1 \; for\, \alpha_i \ll \sqrt{2\delta}$

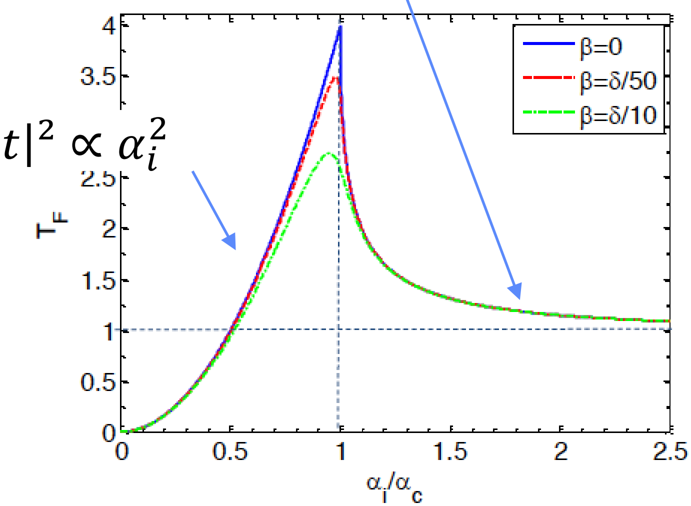
$r = -\delta/2{\alpha_i}^2 \; for\, \alpha_i \gg \sqrt{2\delta}$

$t = \alpha_i/\delta \; for\, \alpha_i \ll \sqrt{2\delta}$

$t = 1 \; for\, \alpha_i \gg \sqrt{2\delta}$



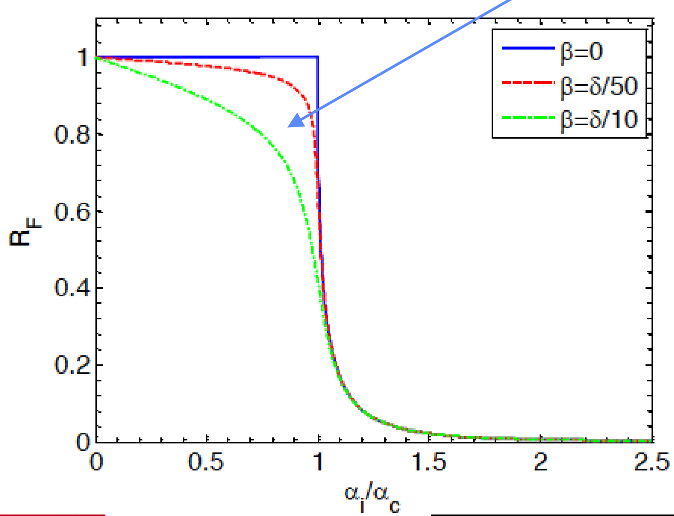
$R = |r|^2 \propto 1/\alpha_i^4$

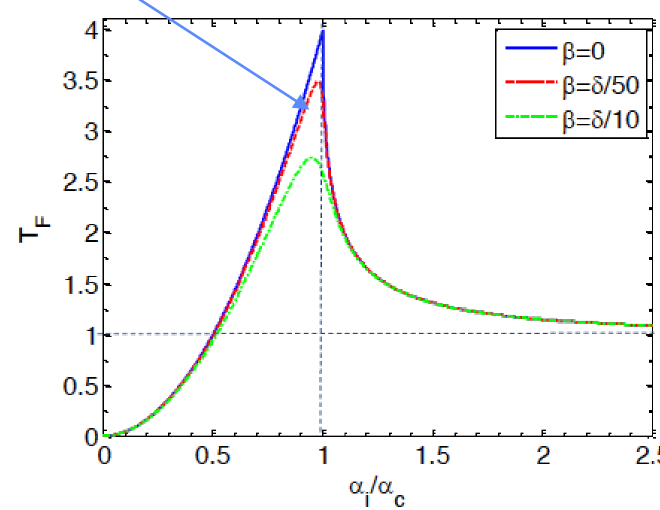


$T = |t|^2 \propto \alpha_i^2$

Reflection and transmission coefficients

Effect of absorption ($i\beta$)
→ Important below the critical angle





Total external reflection

For an interface air(vacuum)/material $\Delta n<0$:

$$\mathbf{n_1 \cos \theta_i = n_2 \cos \theta_t}$$

$$\cos \theta_t = n_1/n_2 \cos \theta_i$$

$$\cos \theta_t = \cos \theta_i /(1-\delta)$$

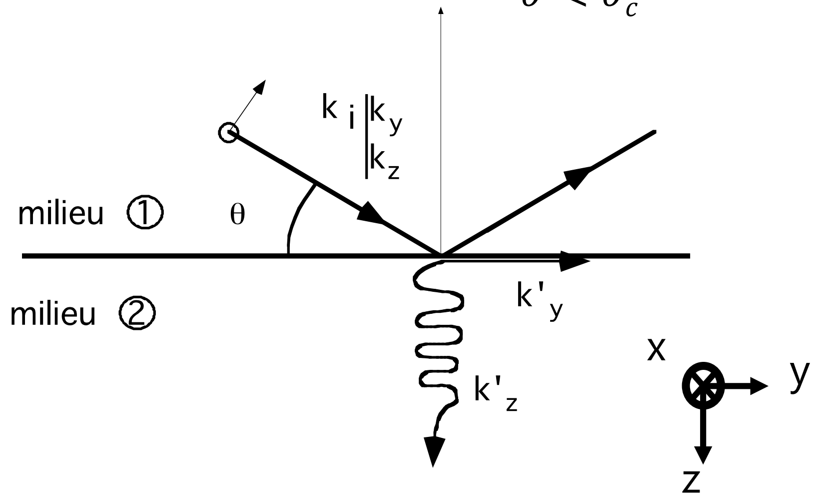
NB: or $\theta_i < \theta_c$ (such that $\mathbf{\cos \theta_c = 1-\delta}$), θ_t is not defined !

$$\cos \theta_c = 1 - \theta_c^2/2 = 1 - \delta$$

$$\boxed{\theta_c = \sqrt{2\delta}}$$

Boundary conditions

$\theta < \theta_c$



<u>At the interface</u>:

Conservation of the tangential component of E

$E_i \exp(i\mathbf{k_i r}) + E_r \exp(i\mathbf{k_r r}) = E_t \exp(i\mathbf{k_t r})$

<u>In each medium (Helmholtz equation):</u>

$$\frac{\partial^2 E_x}{\partial y^2} + \frac{\partial^2 E_x}{\partial z^2} + k_0^2 E_x = 0 \quad medium(1)$$

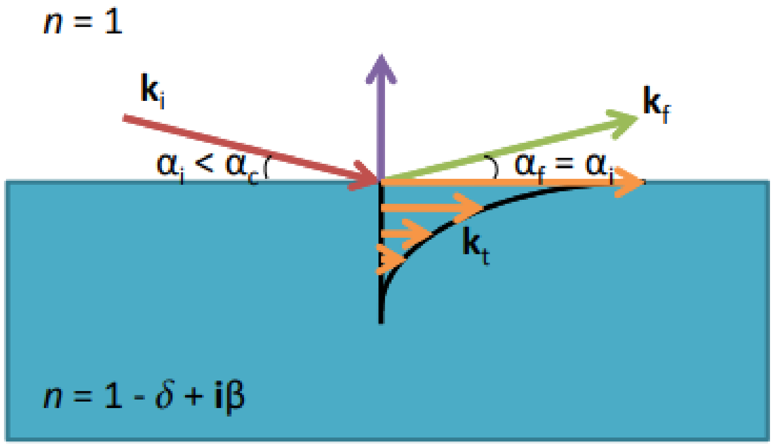
$$k_{t_z} = i\, k_0 \sqrt{\cos^2\theta - \cos^2\theta_c}$$

$$\frac{\partial^2 E_x}{\partial y^2} + \frac{\partial^2 E_x}{\partial z^2} + n^2 k_0^2 E_x = 0 \quad medium(2)$$

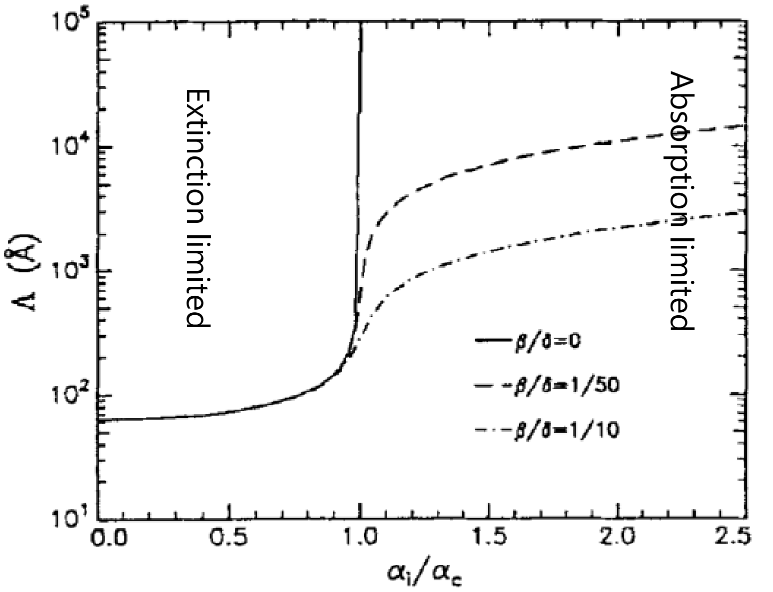
Penetration depth

$$I = I_0 \exp(-2k_z^{'} z) \Rightarrow \Lambda = \frac{1}{2k_z^{'}} = \frac{\lambda}{4\pi\sqrt{\theta_c^2 - \theta^2}}$$

For $\theta << \theta_c$ $\quad \Lambda = \dfrac{\lambda}{4\pi\theta_c} \approx 5\text{nm} = \textit{extinction}\ \text{length}$



Penetration depth on Si surface with λ=1.54A



In total reflection conditions:

-The “refracted” X-ray wave travels **parallel to the surface**

- It is **damped exponentially** with the distance to the surface (extinction length).

-> it can be used to probe specifically **the structure of the surface layer**

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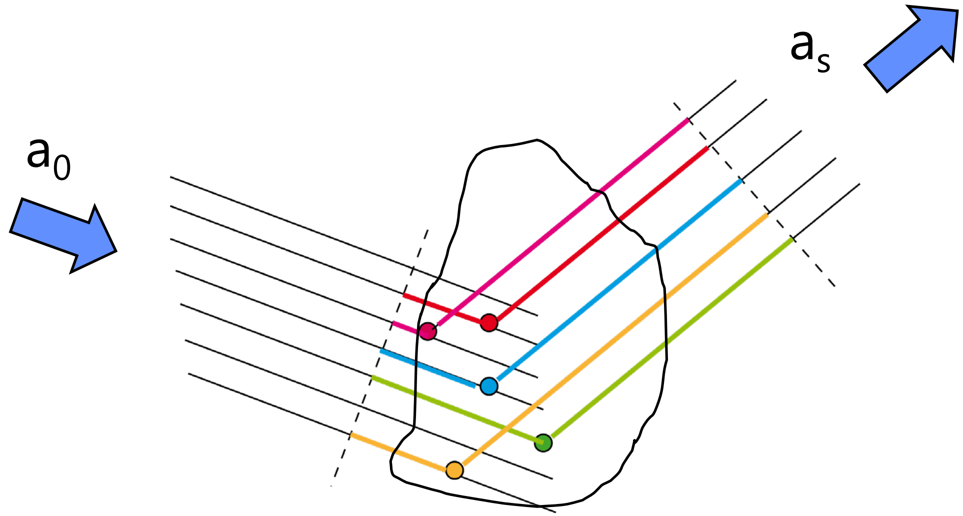
Born Approximation



The **scattered amplitude** in a given direction is obtained through **sum** of individual scattered amplitudes a_i with **phase** coefficients depending on position of scatterer *i*

$$a=a_1\exp(i\,j(r_1))+a_2\exp(i\,j(r_2))+a_3\exp(i\,j(r_3))+a_4\exp(i\,j(r_4))+\ldots$$

Kinematical/Born approximation

$a = a_1 \exp(i\, j(r_1)) + a_2 \exp(i\, j(r_2)) + a_3 \exp(i\, j(r_3)) + a_4 \exp(i\, j(r_4)) + \ldots$

When in far field, the phases read:

$$\varphi(r) = \boldsymbol{q}.\boldsymbol{r} \qquad \boldsymbol{q} = \boldsymbol{k}_f - \boldsymbol{k}_i$$

so that scattered amplitude reads

$$a(q) = \sum_{i=1}^{\infty} (a_i \exp i\boldsymbol{q}.\boldsymbol{r}_i) = \text{Fourier series}$$

Kinematical vs Dynamical scattering

- Kinematical theory (Born Approximation):
  - Assume all parts of the sample “see” the same incident wave
  - They scatter the beam depending only on their position(phase) and scattering cross section (→ Fourier Transform)
  - Multiple scattering is neglected

- Dynamical theory
  - Take into account the “screening” effect of the different parts of the sample

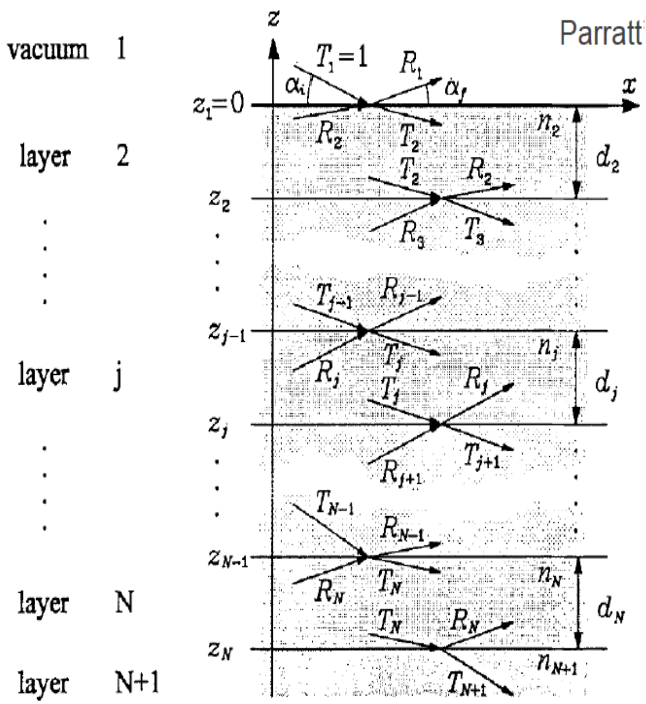
Grazing incidence conditions favor **dynamical** effects

- Total external reflection /refraction are in essence **dynamical** effects
  - The top layers prevent the bottom layers to see the incident beam
  - Strong variations of beam electric field with depth

How to handle that?

- Do a full calculation: only possible in simple cases, for example multilayers: r is a function only r(z), *e.g.* the Fresnel matrix “optical” formalism for calculating reflectivity (see previous courses)

- Use perturbation theory, starting from approximate exact solutions: DWBA= Distorted Wave Born Approximation



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Back to the Born Approximation: the reciprocal space etc…

In the kinematic approximation, the scattered amplitude is the Fourier transform of the electron density distribution r(r):

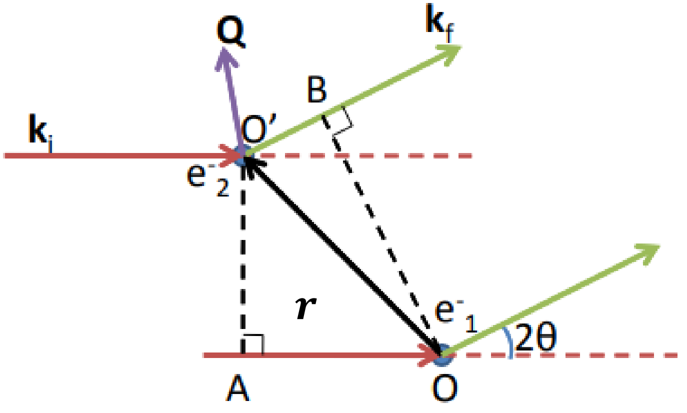
$$I(\mathbf{q}) = \left| F\{\rho(\mathbf{r})\} \right|^2 = \left| \int \rho(\mathbf{r}) e^{i\mathbf{q}.\mathbf{r}} d^3\mathbf{r} \right|^2$$

The angular distribution of scattered intensity has maxima for certain orientations of the scattering vector (certain “locations” in the reciprocal space)

Diffraction by a crystal

The phase difference of the scattered amplitude between 2 scatterers is:

$$\Delta\varphi = \frac{2\pi}{\lambda}(O'B - OA) = \boldsymbol{k_f}.\boldsymbol{r} - \boldsymbol{k_i}.\boldsymbol{r} = \boldsymbol{q}.\boldsymbol{r}$$



Consider a simple unit cell, the amplitude of the wave scattered is

$$F(\mathbf{Q}) = \sum_{atoms\ i} f_i(\theta, \lambda) e^{i2\pi \mathbf{Q}.\mathbf{r}_i}$$

Phase difference

Scattering "effectiveness"

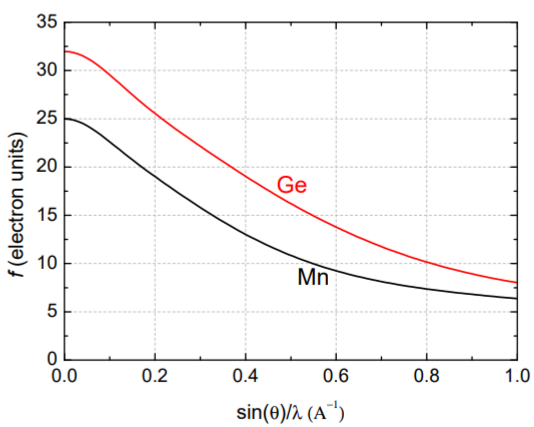
Diffraction by a crystal

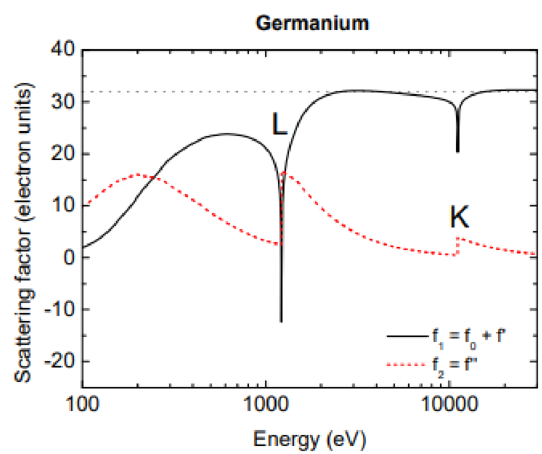
$$F(\mathbf{Q}) = \sum_{atoms\ i} f_i(\theta, \lambda) e^{i2\pi \mathbf{Q}.\mathbf{r}_i}$$

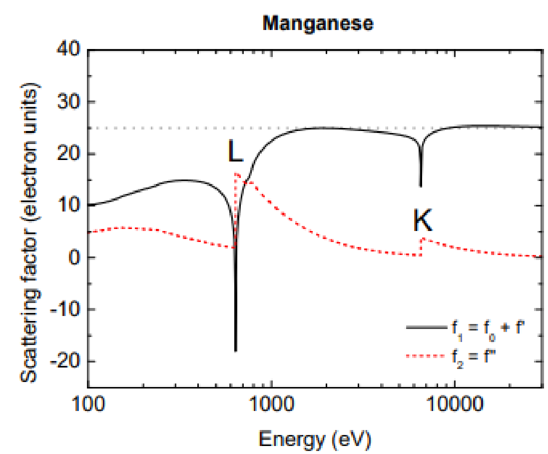
$$f_i(\theta, \lambda) = f_i^0\left(\frac{\sin\theta}{\lambda}\right) + f_i'(\lambda) + i f_i''(\lambda)$$

At the atomic scale, *i.e.* sum over all electrons :

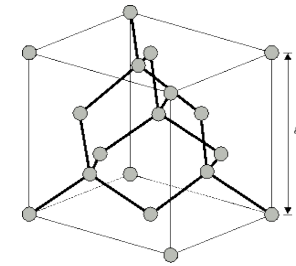
$$\begin{cases} f_e = \dfrac{\omega^2}{(\omega_0^2 - \omega^2 + ig\omega)} = 1 + f'(\omega) + if''(\omega) \\ f'(\omega) = \dfrac{\omega_0^2(\omega^2 - \omega_0^2) - g^2\omega^2}{(\omega_0^2 - \omega^2)^2 + g^2\omega^2} \\ f''(\omega) = \dfrac{g\omega^3}{(\omega_0^2 - \omega^2)^2 + g^2\omega^2} \end{cases}$$







Diffraction by a crystal



For example in Ge (8 atoms/unit cell):

$$\left\{(0,0,0);(0,\tfrac{1}{2},\tfrac{1}{2});(\tfrac{1}{2},0,\tfrac{1}{2});(\tfrac{1}{2},\tfrac{1}{2},0);(\tfrac{3}{4},\tfrac{1}{4},\tfrac{3}{4});(\tfrac{3}{4},\tfrac{3}{4},\tfrac{1}{4});(\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4});(\tfrac{1}{4},\tfrac{3}{4},\tfrac{3}{4})\right\}\times a$$

$$F(\mathbf{Q}) = f_{Ge}(\theta,\lambda)(1 + e^{i\pi(k+l)} + e^{i\pi(h+l)} + e^{i\pi(h+k)} + e^{i\frac{\pi}{2}(3h+k+3l)} + e^{i\frac{\pi}{2}(3h+3k+l)} + e^{i\frac{\pi}{2}(h+k+l)} + e^{i\frac{\pi}{2}(h+3k+3l)})$$

With **Q** projected in the convenient reciprocal basis:

$$\mathbf{Q} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

$$\mathbf{Q}.\mathbf{a} = h$$

$$\mathbf{Q}.\mathbf{b} = k$$

$$\mathbf{Q}.\mathbf{c} = l$$

$$\mathbf{a}^* = \frac{\mathbf{b}\times\mathbf{c}}{V}$$

$$\mathbf{b}^* = \frac{\mathbf{c}\times\mathbf{a}}{V}$$

$$\mathbf{c}^* = \frac{\mathbf{a}\times\mathbf{b}}{V}$$

$$V = \mathbf{a}.\mathbf{b}\times\mathbf{c}$$

Diffraction by a crystal

Extend to a full crystal: many, many cells

$$A(\mathbf{Q}) = \sum_{cell\ j} \sum_{atoms\ i} f_i(\theta,\lambda) e^{i2\pi\mathbf{Q}.(\mathbf{r}_i+\mathbf{R}_j)}$$
$$= \left(\sum_{cell\ j} e^{i2\pi\mathbf{Q}.\mathbf{R}_j}\right)\left(\sum_{atoms\ i} f_i(\theta,\lambda) e^{i2\pi\mathbf{Q}.\mathbf{r}_i}\right)$$
$$= D(\mathbf{Q})F(\mathbf{Q})$$

Form factor (encodes the shape of the crystal)

$$\mathbf{R}_j = n_x\mathbf{a} + n_y\mathbf{b} + n_y\mathbf{c}$$
$$\mathbf{Q}.\mathbf{R}_j = n_x h + n_y k + n_y l$$

$$D(\boldsymbol{Q}) = \sum_{-N_x/2}^{N_x/2} e^{i2\pi n_x h} \sum_{-N_y/2}^{N_y/2} e^{i2\pi n_y k} \sum_{-N_z/2}^{N_z/2} e^{i2\pi n_z l}$$

(N_x, Ny, Nz) : total number of cells

Diffraction by a crystal

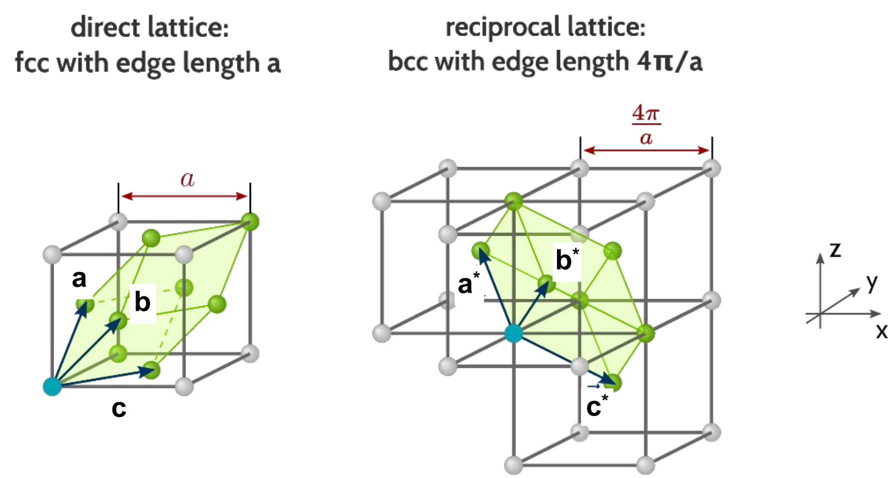
Extend to a full crystal: many, many cells

$$D(\boldsymbol{Q}) = \sum_{-N_x/2}^{N_x/2} e^{i2\pi n_x h} \sum_{-N_y/2}^{N_y/2} e^{i2\pi n_y k} \sum_{-N_z/2}^{N_z/2} e^{i2\pi n_z l}$$

$$D(\boldsymbol{Q}) = \frac{\sin \pi N_x h}{\sin \pi\, h} \frac{\sin \pi N_y k}{\sin \pi\, k} \frac{\sin \pi N_z l}{\sin \pi l}$$

If infinite: D(**Q**) is 3D Dirac comb with nodes at integer values of *h, k, l*

Diffraction by a crystal



The scattered intensity is also distributed along a 3D periodic structure **q** = **G** = h**a***+ k**b***+ l**c*** with **G** normal to net planes = "reciprocal space"

Reciprocal space is the analog of "dual" space in tensor mathematics or k-space in quantum mechanics.

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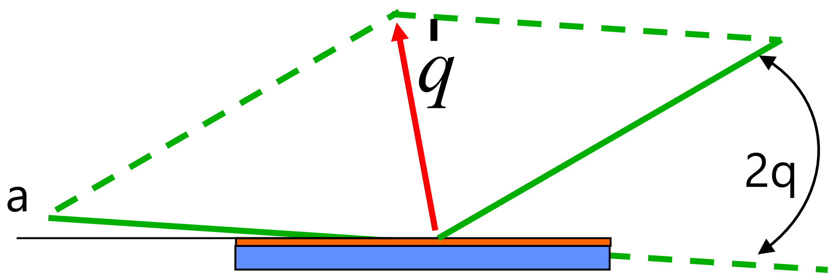
Grazing-incidence diffraction geometries

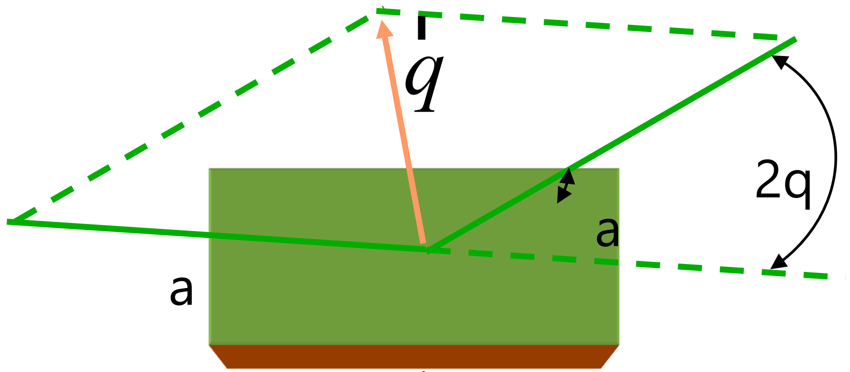
Grazing-incidence
out-of-plane diffraction



side view

Get information from the surface only,
Useful if disordered (powder-like) surface

Grazing-incidence
in-plane diffraction



top view

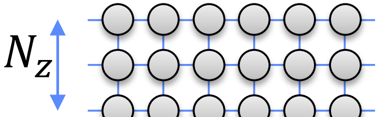
Get information from the surface only about the in-plane organization (texture, etc..)

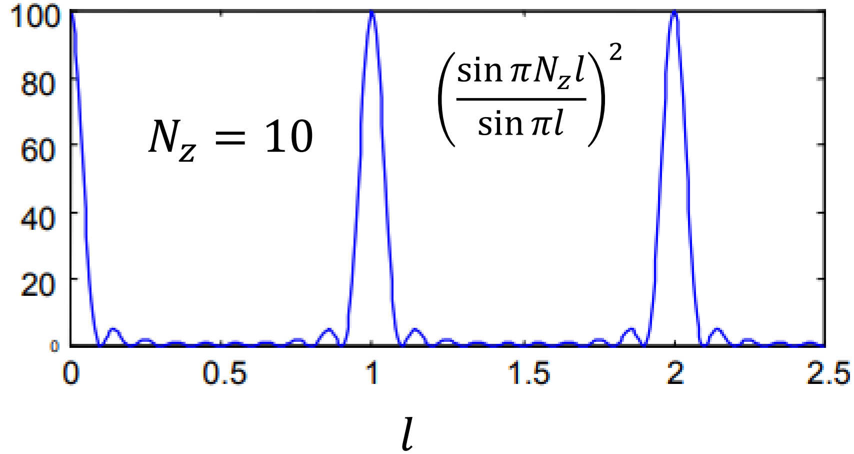
- Crystallinity of the deposited layer
- Mosaicity : distribution in-plane or out-of-plane
- Depth profiling of a given layer

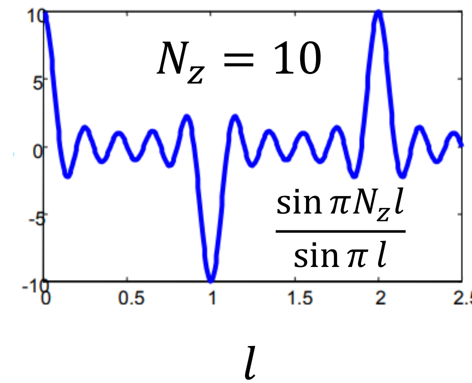
Slides adapted from D. Djurado

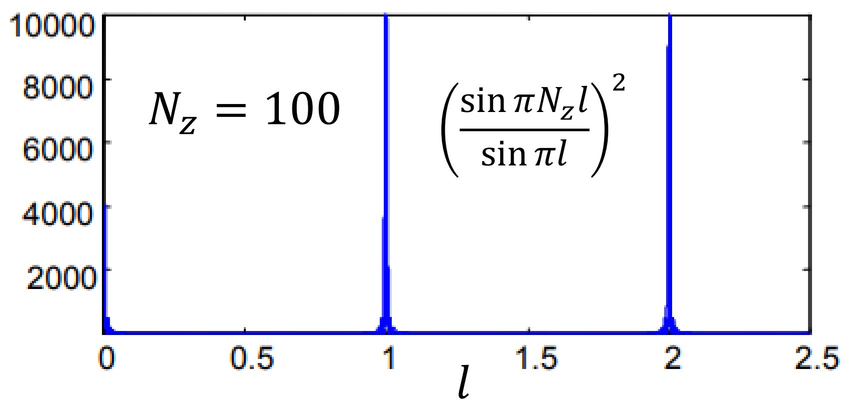
Finite crystal

$$D(\boldsymbol{Q}) = \frac{\sin \pi N_x h}{\sin \pi h}\frac{\sin \pi N_y k}{\sin \pi k}\frac{\sin \pi N_z l}{\sin \pi\, l}$$



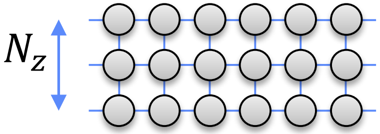


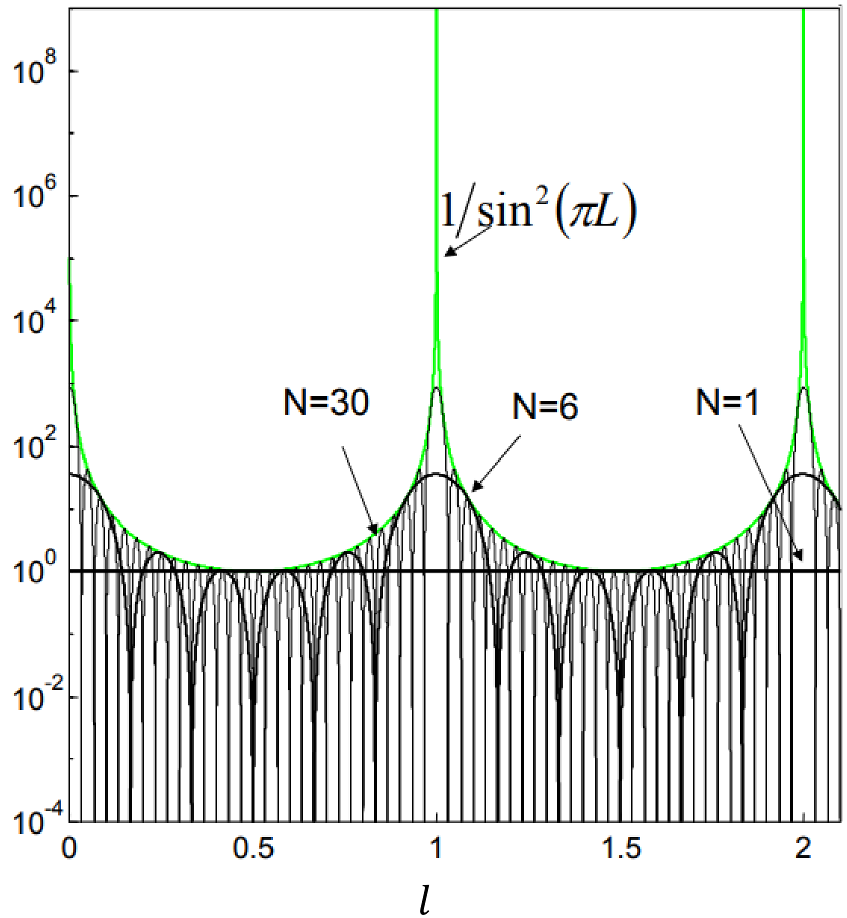




Slides adapted from T. Trainor

Semi-infinite crystal: the Crystal Truncation Rods (CTRs)



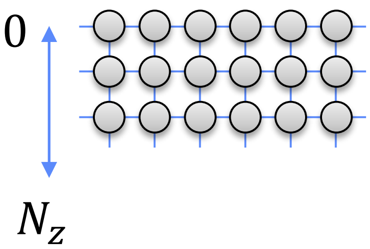


N = 1 : no oscillation

Finite size means intensity **between** the Bragg peaks

Slides adapted from T. Trainor

Semi-infinite crystal: the Crystal Truncation Rods (CTRs)



$$D(\boldsymbol{Q}) = \sum_{-N_x/2}^{N_x/2} e^{i2\pi n_x h} \sum_{-N_y/2}^{N_y/2} e^{i2\pi n_y k} \sum_{-\infty}^{0} e^{i2\pi n_z l}$$

= 1 for *h, k* integer
= 0 otherwise

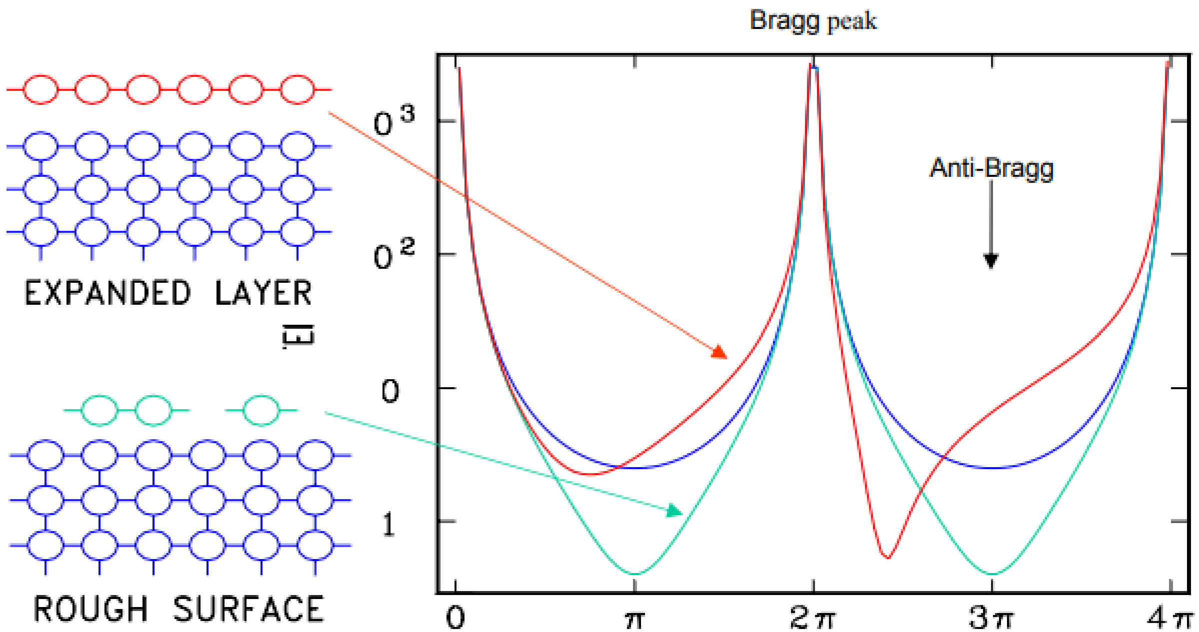
$$\sum_{-\infty}^{0} e^{i2\pi n_z l} = \frac{1}{(1 - e^{-i2\pi l})}$$

$$\left| \sum_{-\infty}^{0} e^{i2\pi n_z l} \right|^2 = \frac{1}{4\sin^2 \pi l}$$

Finite size means intensity **between** the Bragg peaks along l

Reciprocal space is not 3D Dirac anymore but includes 1D truncation rods

Semi-infinite crystal: the Crystal Truncation Rods (CTRs)

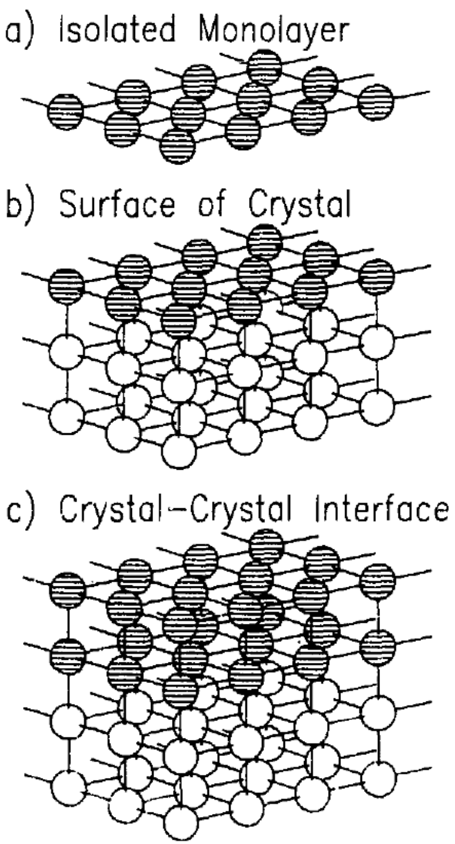


sensitive to the last unit cell in between Bragg peaks!

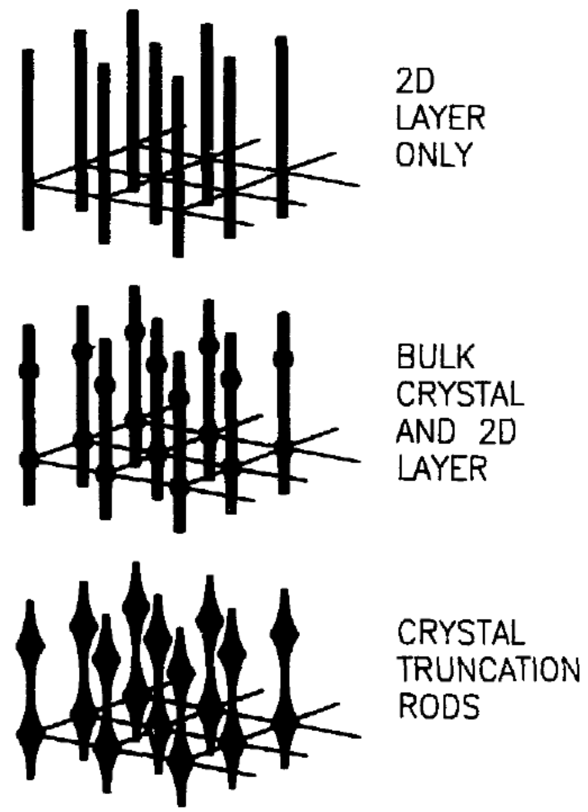
Slides adapted from T. Trainor

The structure of a crystal may be different close to the surface than in the bulk: relaxation, reconstruction

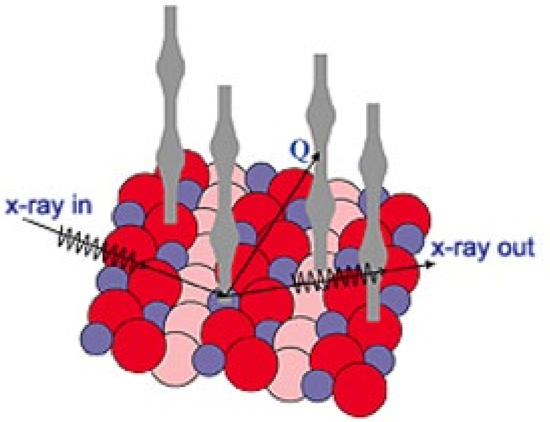
Real space

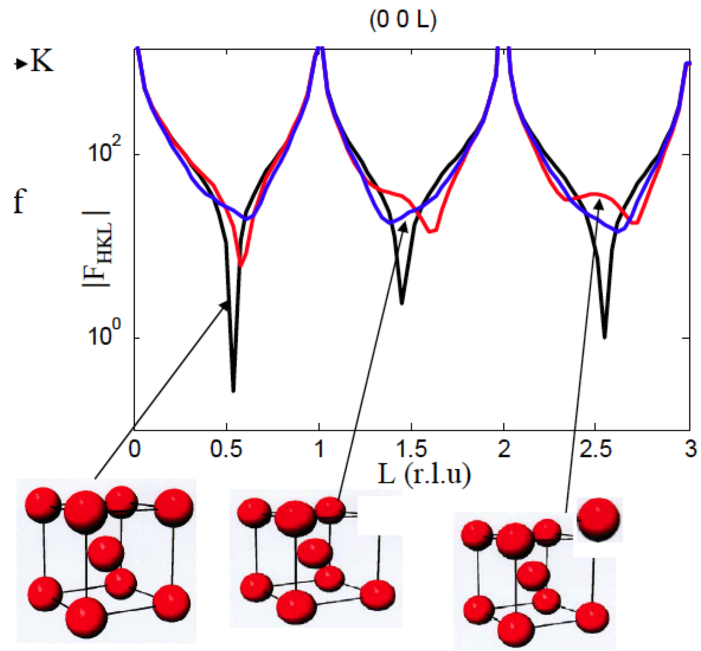


Reciprocal space



Surface relaxations through CTR analysis

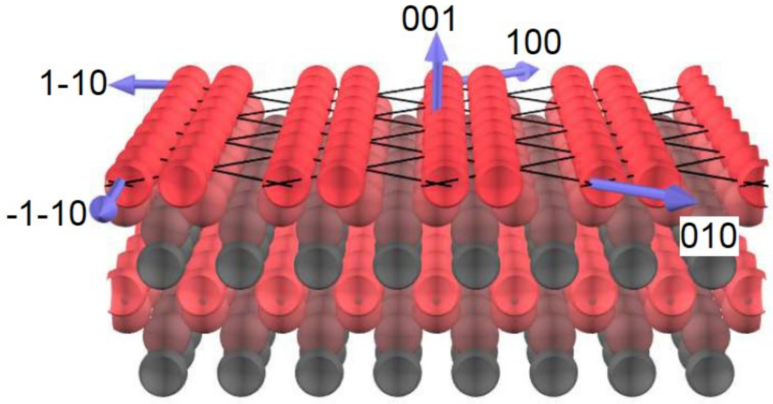




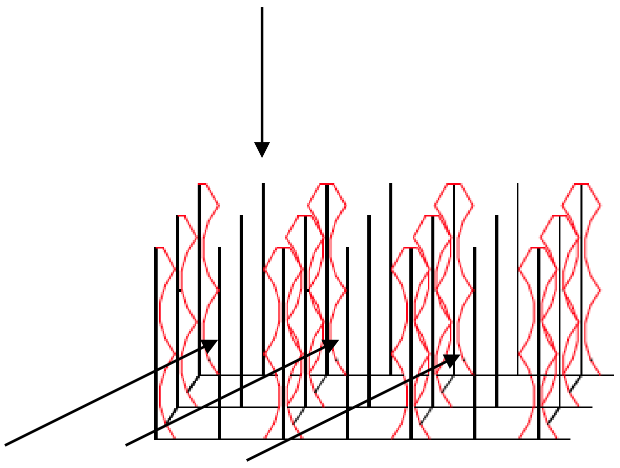
Slides adapted from T. Trainor

Surface reconstruction

Ex: 2x1 of silicon 001



“Superlattice” rods
“Fractional order” rods

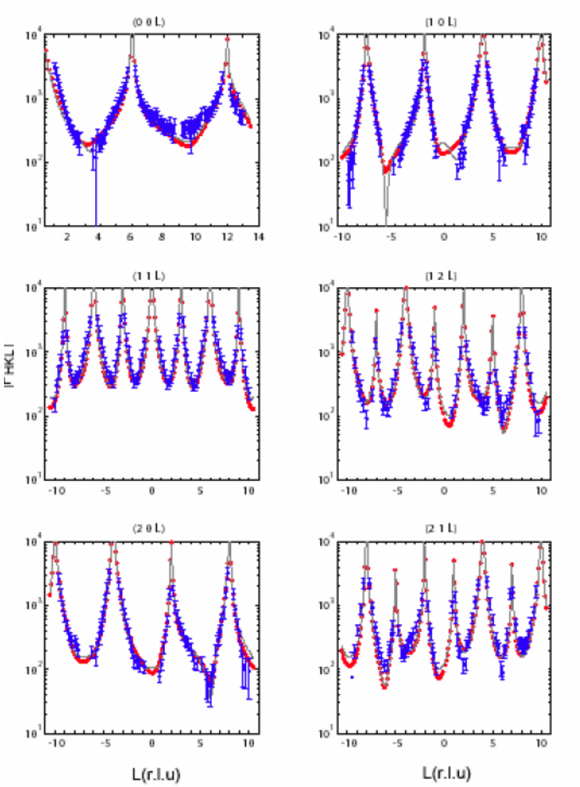


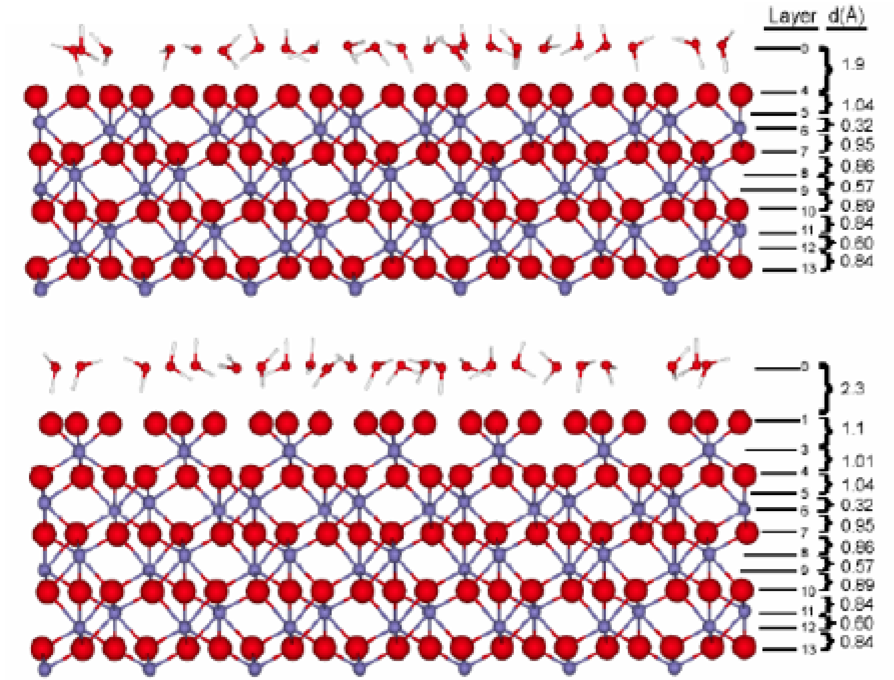
New peaks appears along 110

Example: Hematite/Water a-Fe_2O_3 (0001)

Models

CTRs

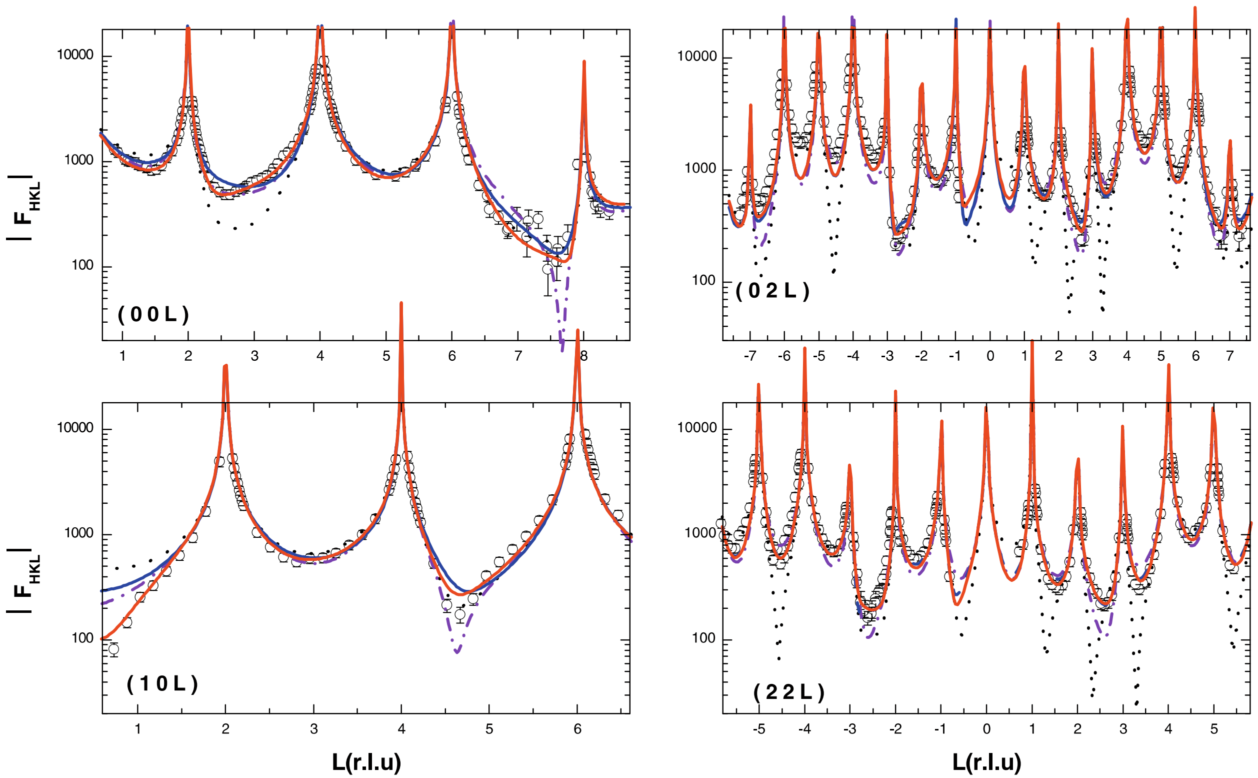




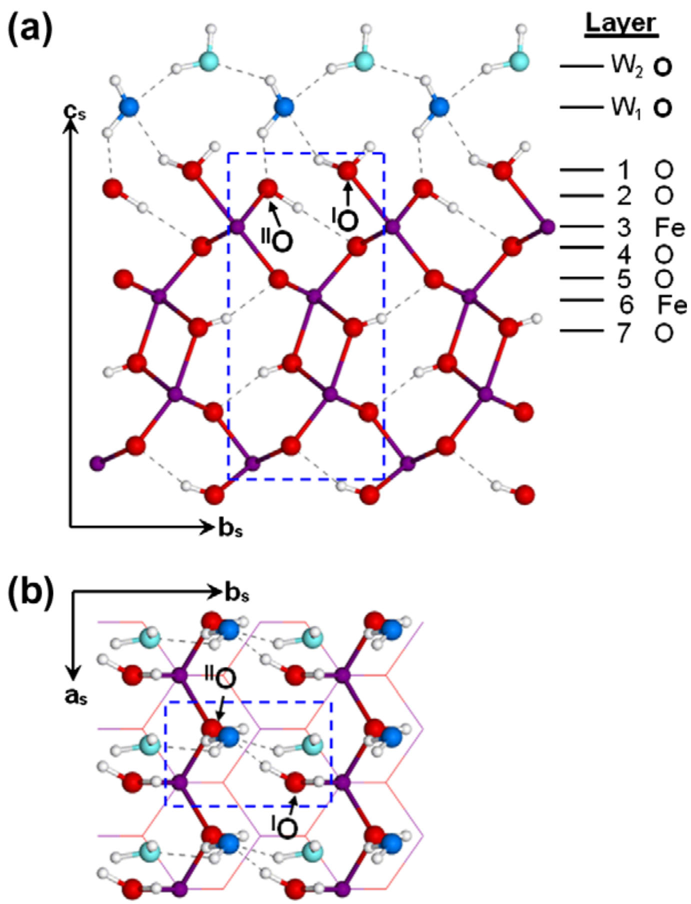
Trainor et al ., Surface Science, ***573,*** *204 (2004)*

Experimental observation is consistent with hydroxylated surfaces
Association with DFT to use the most stable configurations

Example: Goethite (a-FeOOH) (1 0 0) // water interface



Structure



Two ordered layers of water
Two layers of hydroxyl groups

$((H_2O)\text{-}(H_2O)\text{-}OH_2\text{-}OH\text{-}Fe\text{-}O\text{-}O\text{-}Fe\text{-}R)$

The two types of hydroxyls may explain interface reactivity

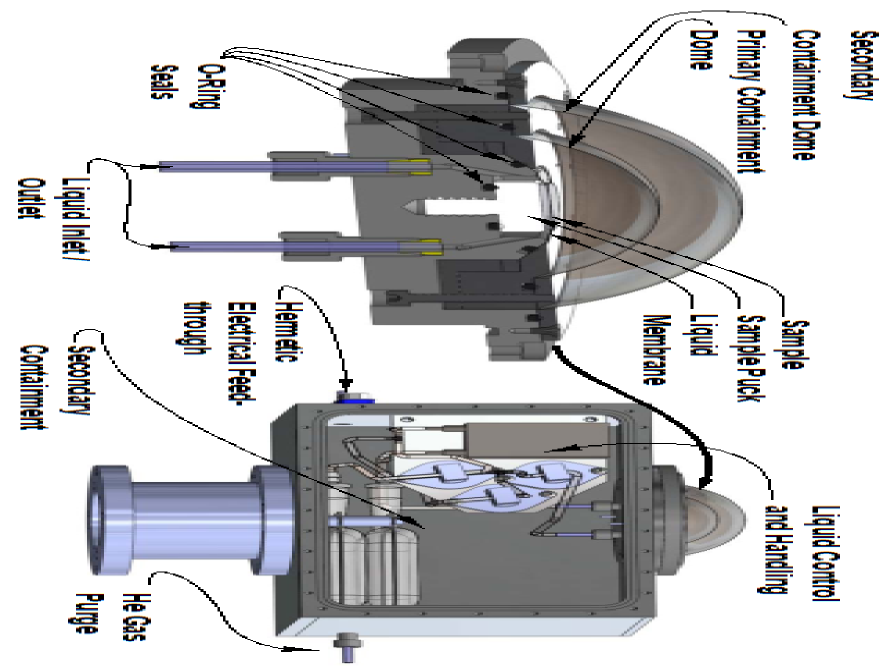
Association with DFT calculations to predict pKa

An example from nuclear science

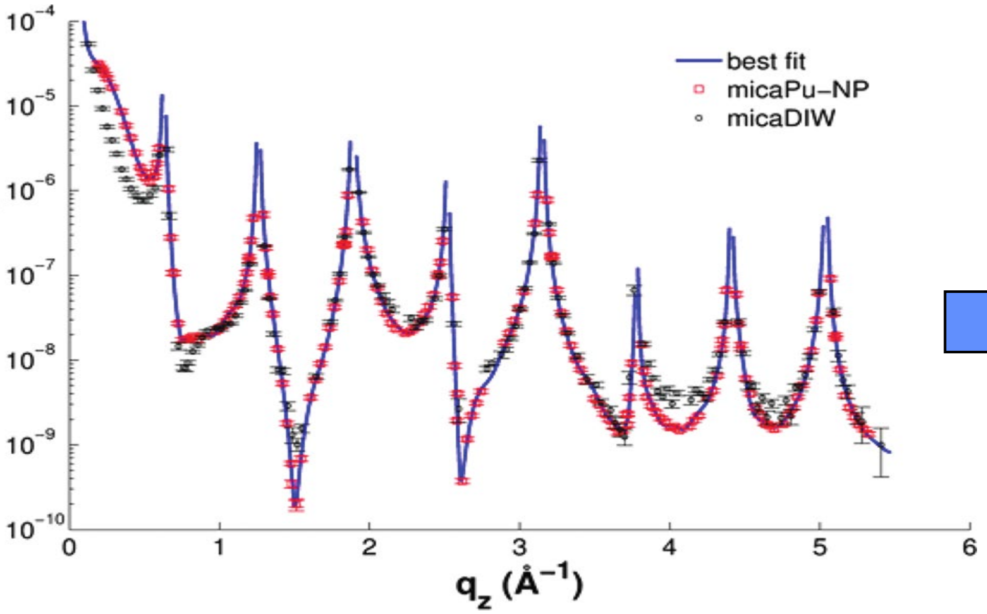
- Interaction of Pu^{3+} solution / Mica surface:

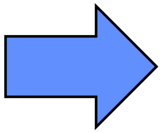
- In-situ study

Schmidt, Eng, Stubbs, Fenter, and Soderholm (2011) Rev. Sci. Inst. 82:075105



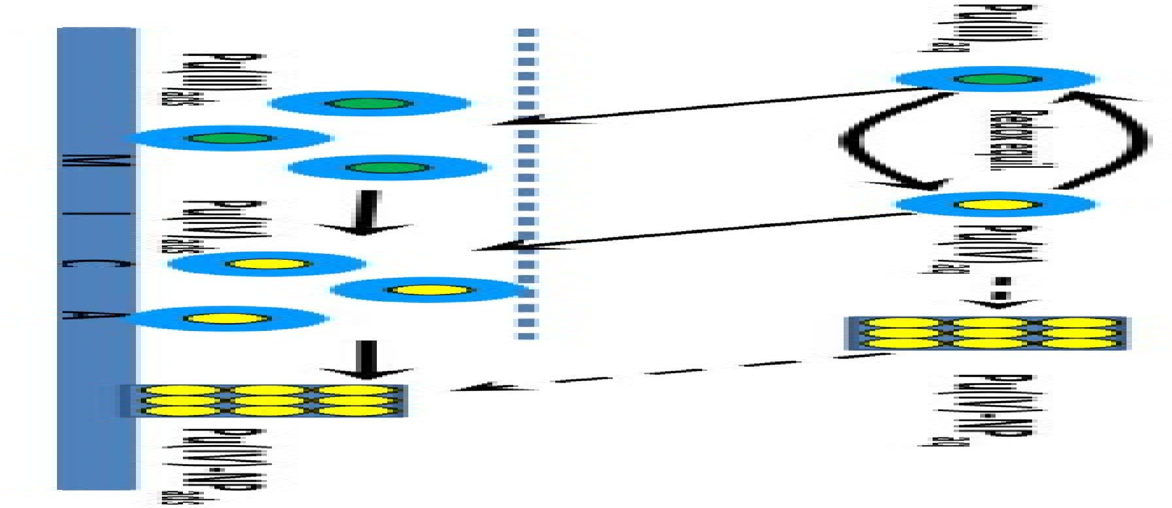
CTR analysis





- *M. Schmidt, S. Lee, R.E. Wilson, K.E. Knope, F. Bellucci, P.J. Eng, J.E. Stubbs, L. Soderholm, P. Fenter, "Surface-Mediated Formation of Pu(IV) Nanoparticles at the Muscovite-Electrolyte Interface", ES&T* ***47(24)*** *14178-14184 (2013)*
- *M. Schmidt, R.E. Wilson,S.Lee, L. Soderholm, and P. Fenter, « Adsorption of Plutonium Oxide Nanoparticles », Langmuir* ***28*** *2620–2627 (2012).*

Formation of Pu(IV)O nanoparticles



- Surface catalyzed formation of Pu NP
- Agreement with anomalous reflectivity at the Pu L_{III} edge and AFM measurements
- Surface concentration of NP is in agreement with charge compensation

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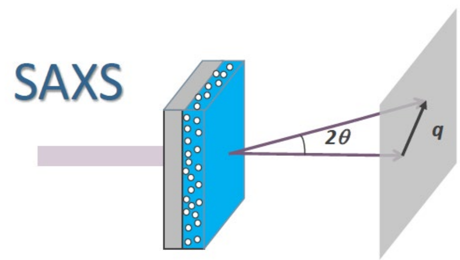
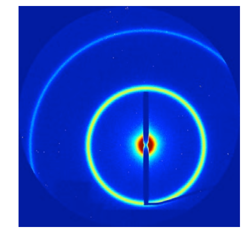
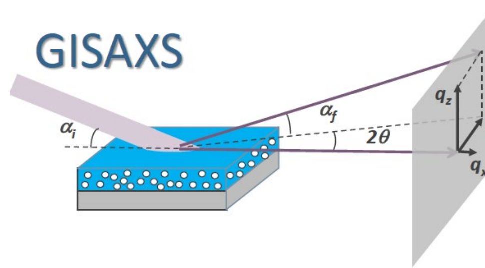
GISAXS

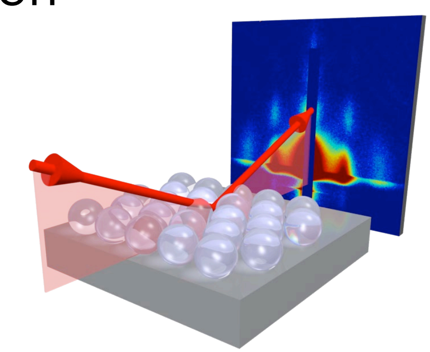
- SAXS
  - Usually transmission geometry



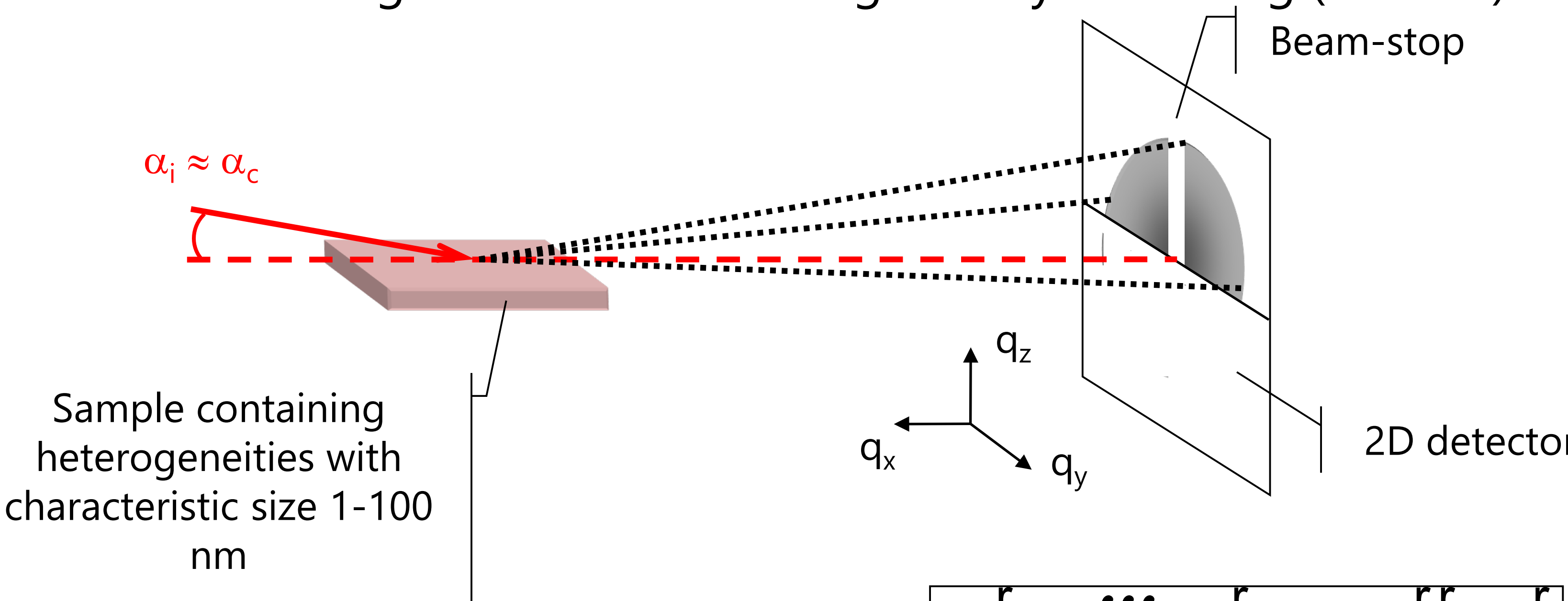


- GISAXS
  - Reflection geometry → take into account refraction

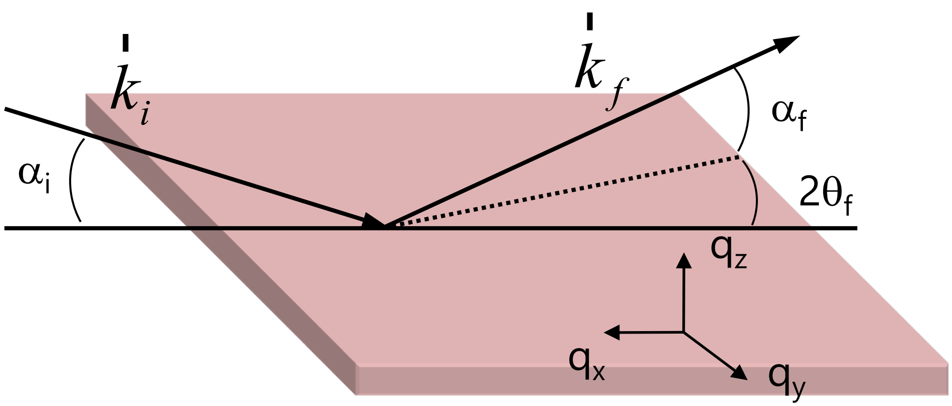




Grazing Incidence Small-Angle X-ray Scattering (GISAXS)



$$A(\vec{q}) \propto \iiint \rho_e(\vec{r})\exp(-i\vec{q}\vec{r})d^3\vec{r}$$

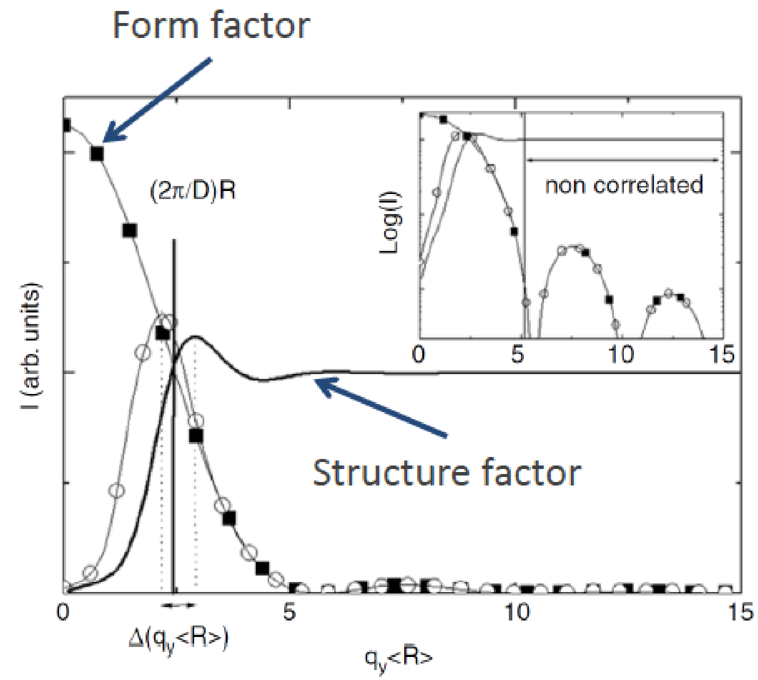


$$\vec{q} = \vec{k}_f - \vec{k}_i = \begin{pmatrix} q_x \\ q_y \\ q_z \end{pmatrix} \approx \frac{2\pi}{\lambda}\begin{pmatrix} 0 \\ \sin 2\theta_f \\ \sin\alpha_f + \sin\alpha_i \end{pmatrix}$$

Slides adapted from D. Babonneau

GISAXS: Form factor (F(q)) & Structure factor (S(q))

$$\left(\frac{d\sigma}{d\Omega}\right) \cong \langle |F(q)|^2 \rangle S(q)$$



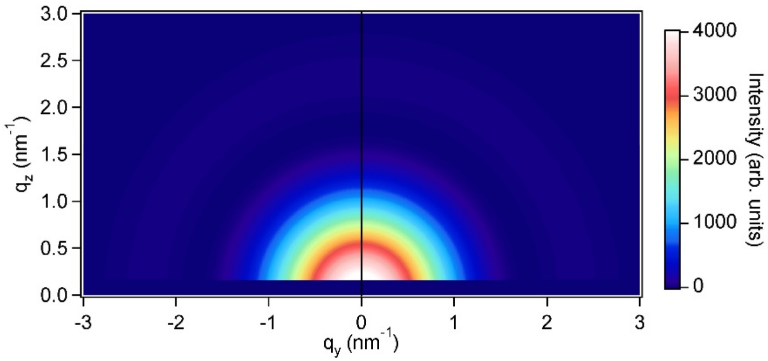
Nanostructure morphology
– Form factor *F*, *P*: size, shape, facets etc.
– Structure factor *S*: inter-particle correlations, distances

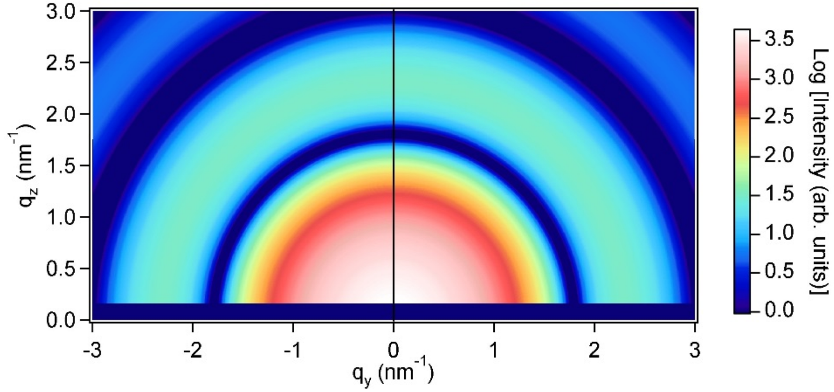
Isolated object

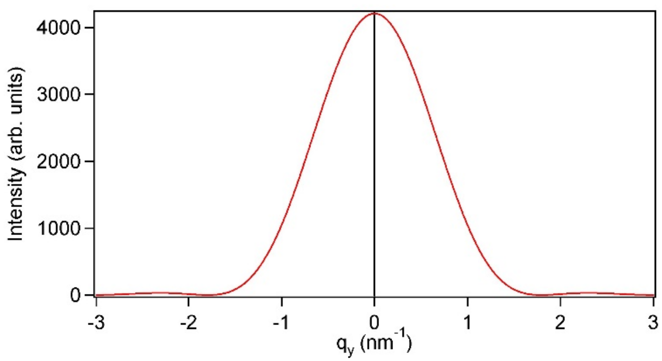
$$I(q_y,q_z) \propto \left|F(q_y,q_z)\right|^2$$

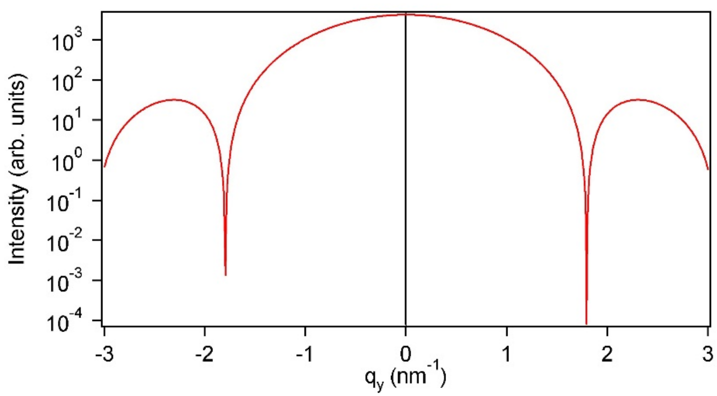
Form factor = FT(shape)

ex. : 5 nm sphere



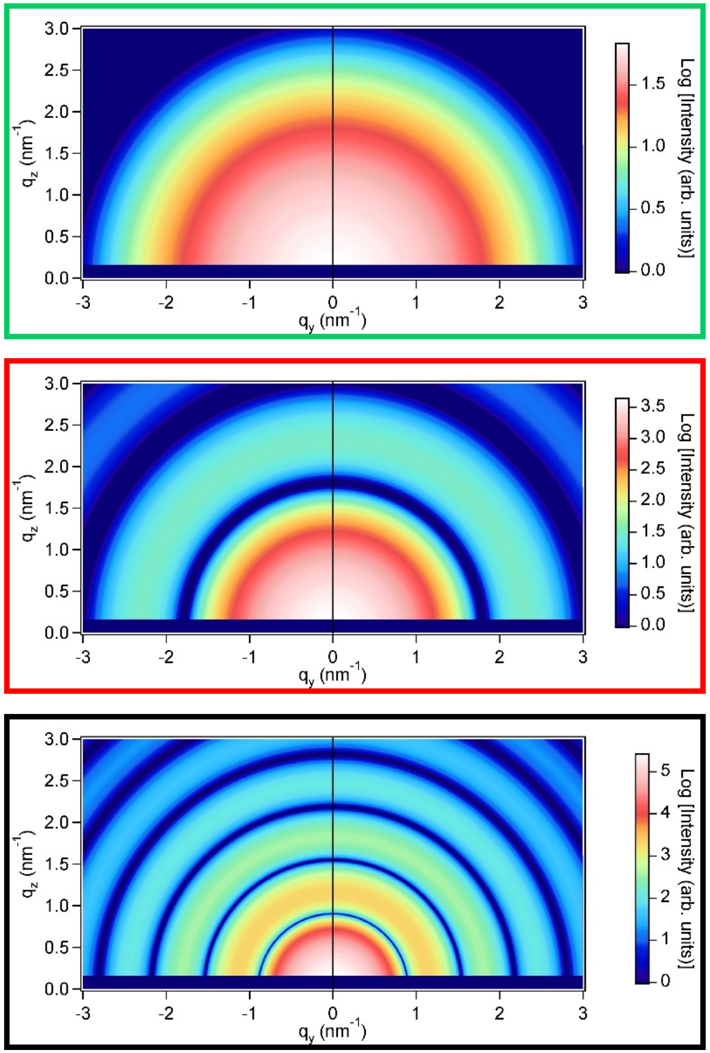


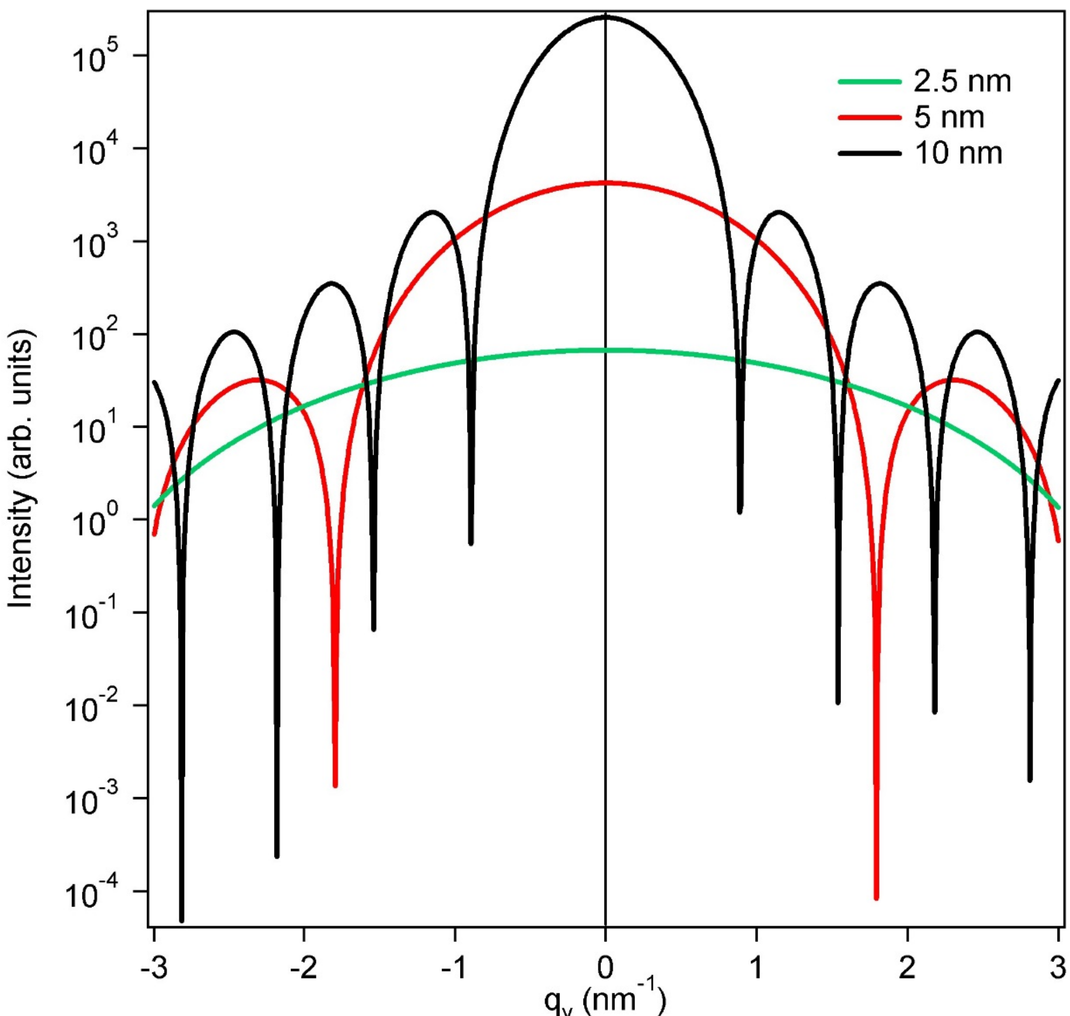




Slides adapted from D. Babonneau

Size effect

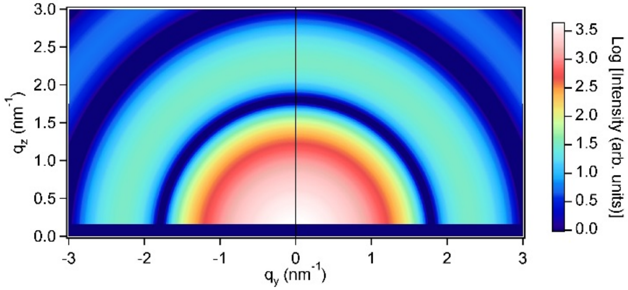




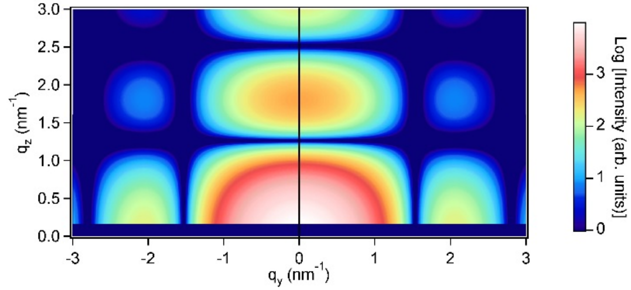
Slides adapted from D. Babonneau

Shape effect

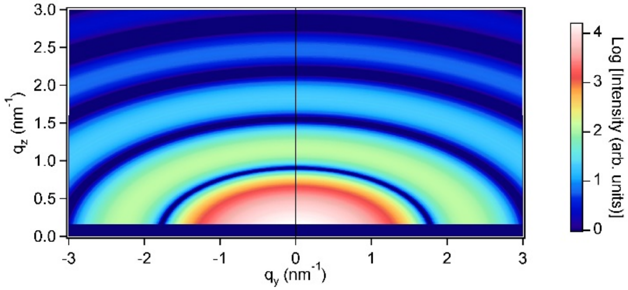
5 nm Sphere



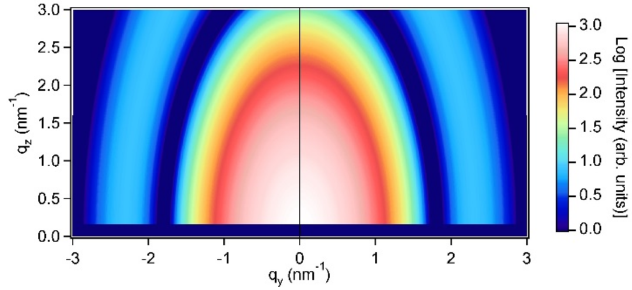
5 nm x 5 nm Cylinder



5 nm, H/D 2 Ellipsoid

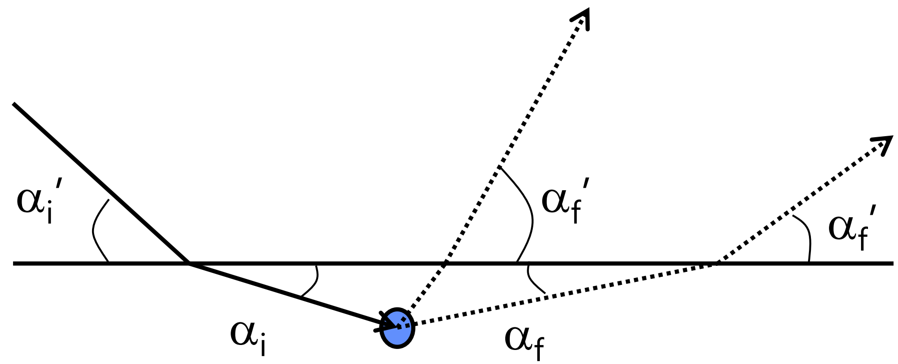


5 nm, H/D 0.5 Ellipsoid



Slides adapted from D. Babonneau

Refraction effect



$$\cos\alpha_i' = n\cdot\cos\alpha_i$$

$$\cos\alpha_f' = n\cdot\cos\alpha_f$$

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

Scattering vector *seen* by the sample

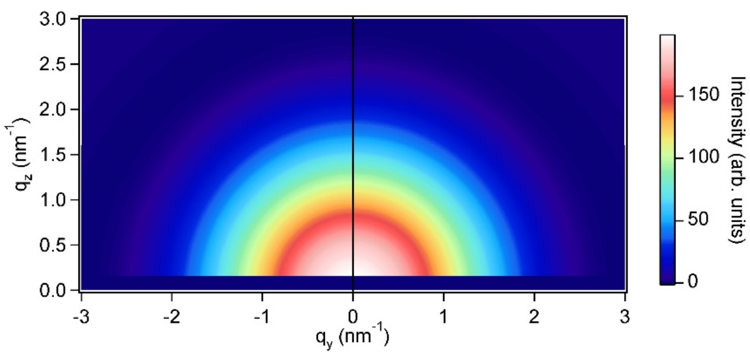
$$q_z = \frac{2\pi}{\lambda}\left(\sin\alpha_f + \sin\alpha_i\right)$$

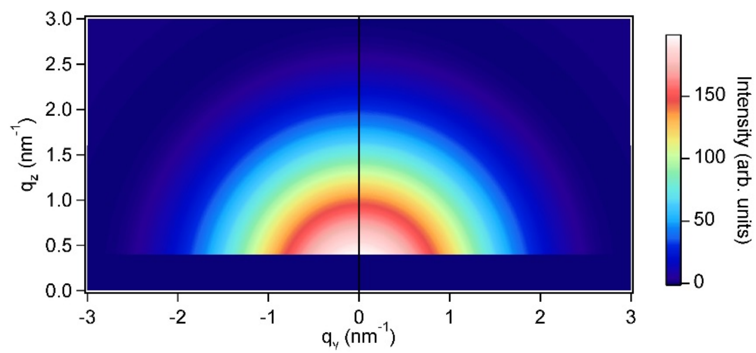
$$q_z^{\min} = \frac{2\pi}{\lambda}\left(\sin\alpha_i\right)$$

Scattering vector *seen* by the detector

$$q_z' = \frac{2\pi}{\lambda}\left(\sin\alpha_f' + \sin\alpha_i'\right)$$

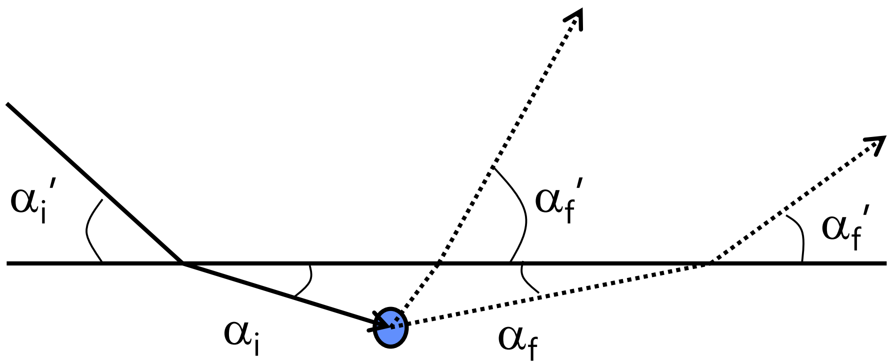
$$q_z^{\min}{}' = \frac{2\pi}{\lambda}\left(\sin\alpha_c + \sin\alpha_i'\right)$$



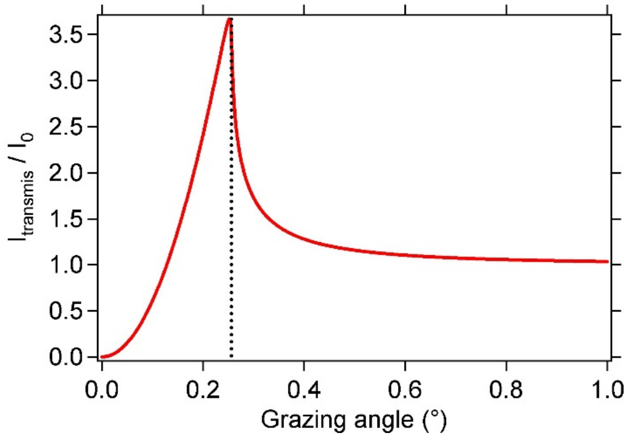


Slides adapted from D. Babonneau

Transmission effect

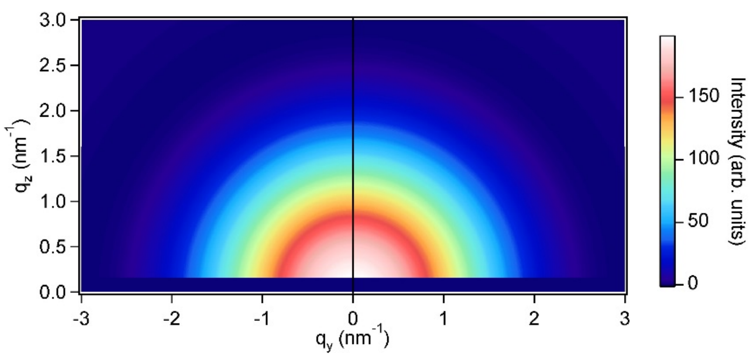


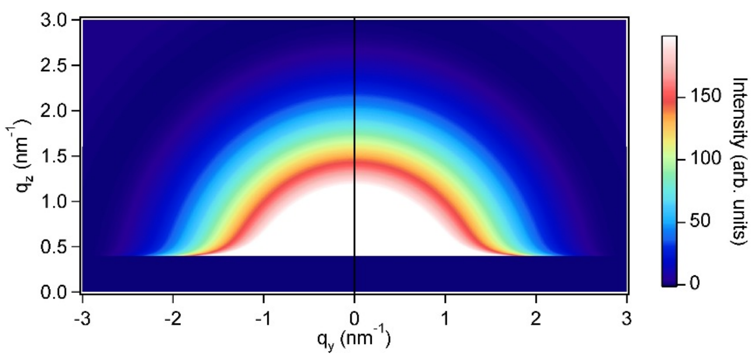
$$n = 1 - \delta - i\beta$$



$$I_{détecteur} = \left|T(\alpha_i')\right|^2 \left|T(\alpha_f')\right|^2 \times I_{échantillon}$$

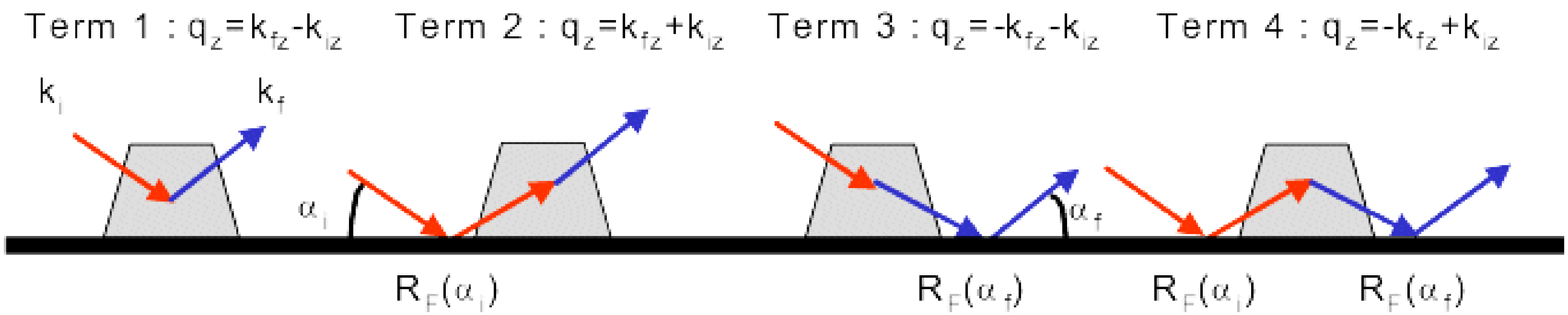
$$q_z' = \frac{2\pi}{\lambda}\left(\sin\alpha_f' + \sin\alpha_i'\right)$$





Slides adapted from D. Babonneau

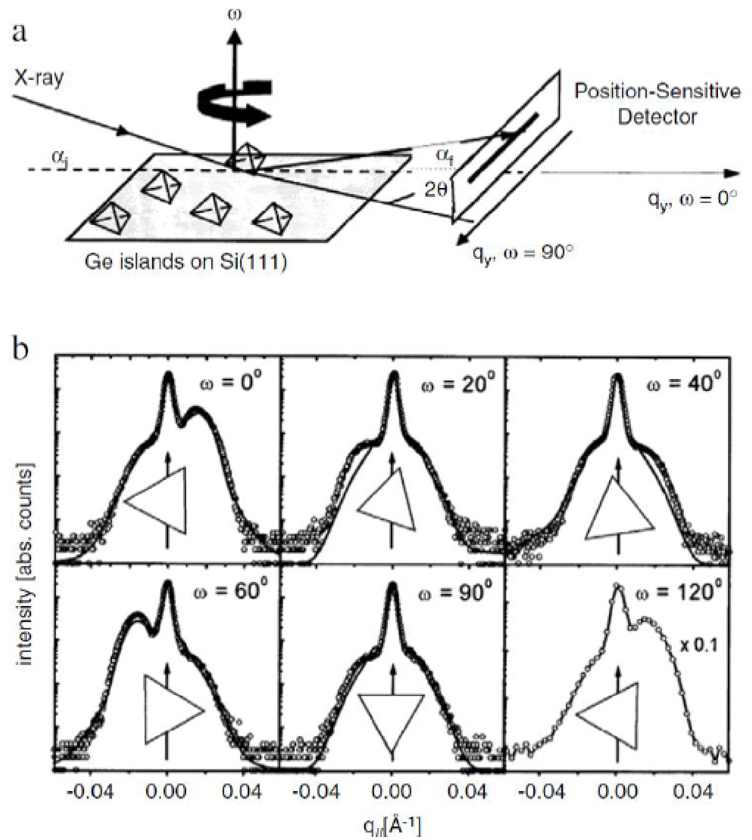
DWBA



$$
\begin{aligned}
F(q_y, k_z^i, k_z^f) = F(q_y, k_z^f - k_z^i) \\
+ R(\alpha_i) F(q_y, k_z^f + k_z^i) \\
+ R(\alpha_f) F(q_y, -k_z^f - k_z^i) \\
+ R(\alpha_i) R(\alpha_f) F(q_y, -k_z^f + k_z^i)
\end{aligned}
$$

Slides adapted from D. Babonneau

Example= Ge islands on a Si (111) substrate

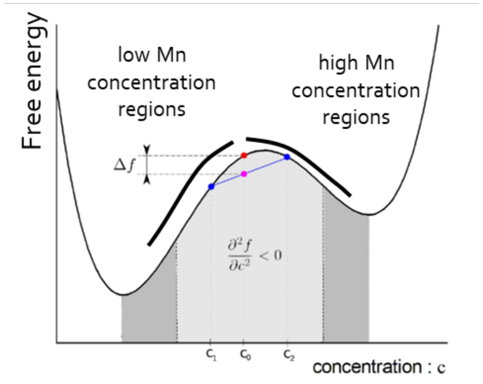


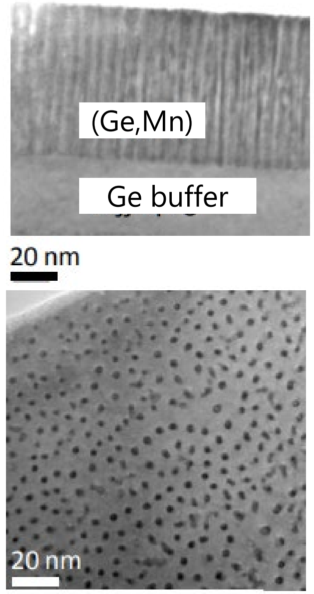
Pyramids are oriented: scattering depend on orientation

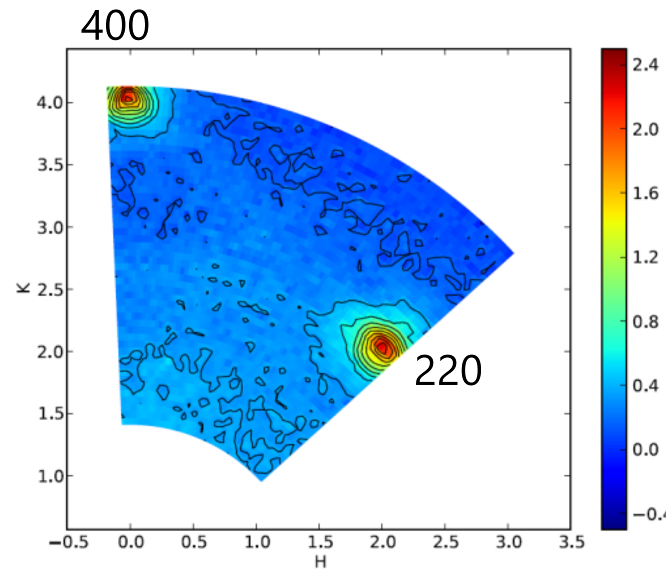
see Metzger, *Thin solid films (1998)*

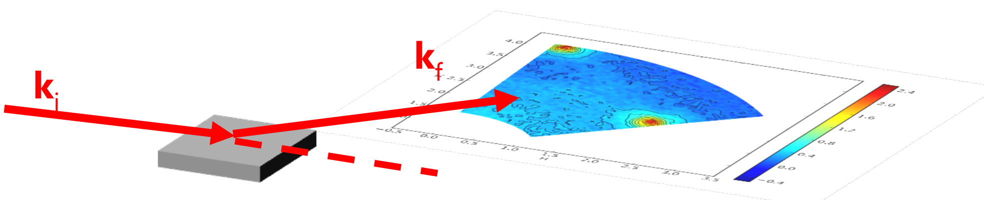
Combining Diffraction and GISAXS (*Bragg-GISAXS)*

in (Ge,Mn) nanocolumns



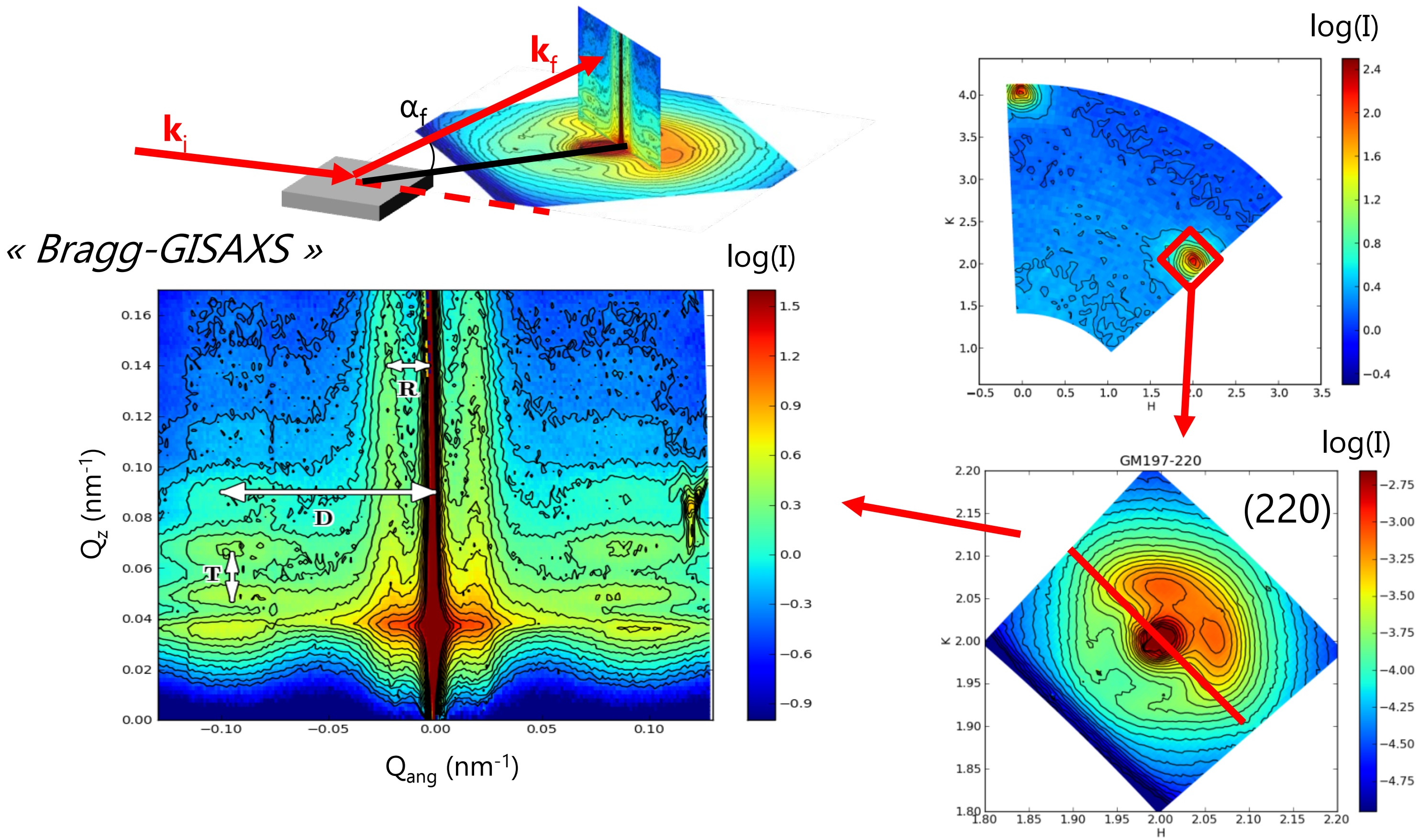






« Bragg-GISAXS »

Combining Diffraction and GISAXS (*Bragg-GISAXS)*



R: Surface roughness correlations at distance ~40 nm
D: Inter-nanocolumns correlations at distances ~10 nm
T: Layer thickness ~60 nm

S. Tardif et al., PRB 82, 104101 (2010)

Outline

I. Fundamentals: Interaction light/matter, Scattering and Refractive index

II. Grazing incidence conditions: Boundary conditions, Penetration length

III. The Born Approximation and the Distorted Wave Born Approximation

IV. Reciprocal space of 3D & 2D crystal, Diffraction

V. The GIXS geometry: Crystal Truncation Rods and examples

VI. The GISAXS geometry and examples

VII. Some experimental setups

VIII. References

Instruments: 4-circle diffractometers

@ ESRF: French Collaborative Research Groups (CRGs)

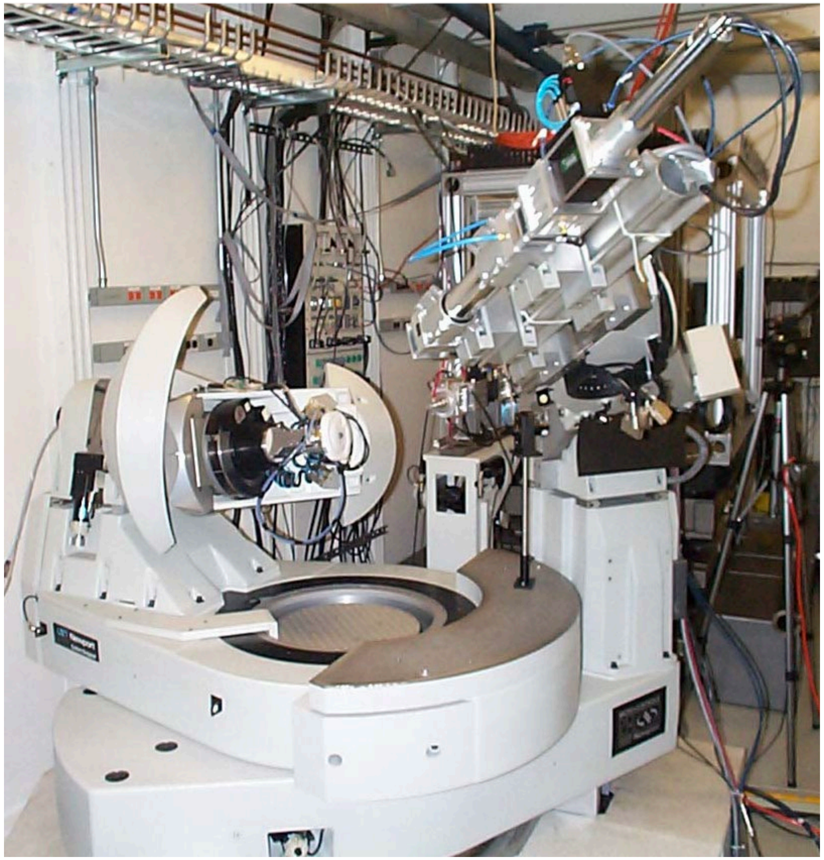
- BM32/IF : INS2
- BM32/IF: GMT
- BM2/D2AM

@ Soleil

- SIXS

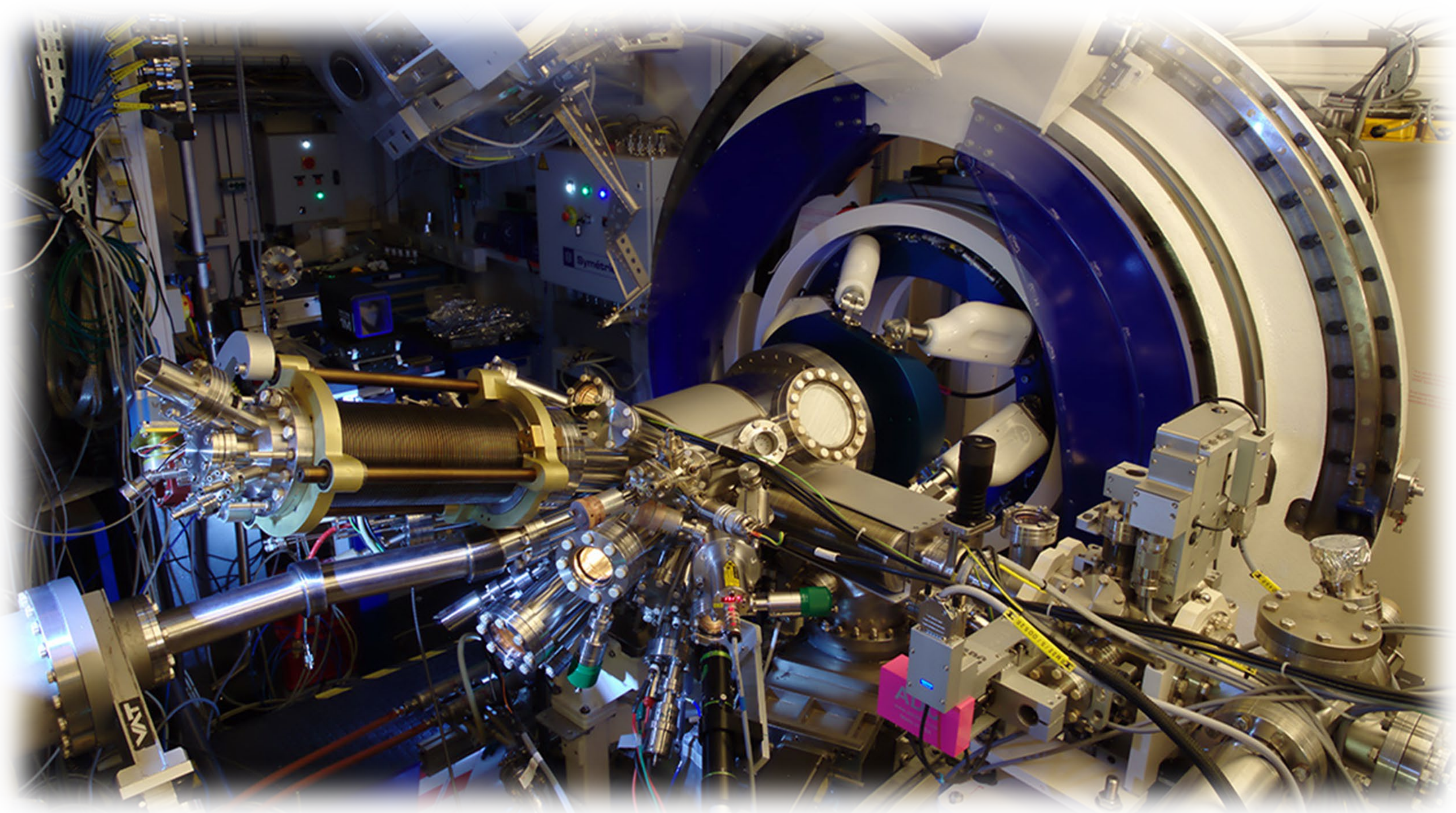
@ other synchrotron (APS, Hamburg)

D2AM goniometer (BM2 beamline @ESRF)



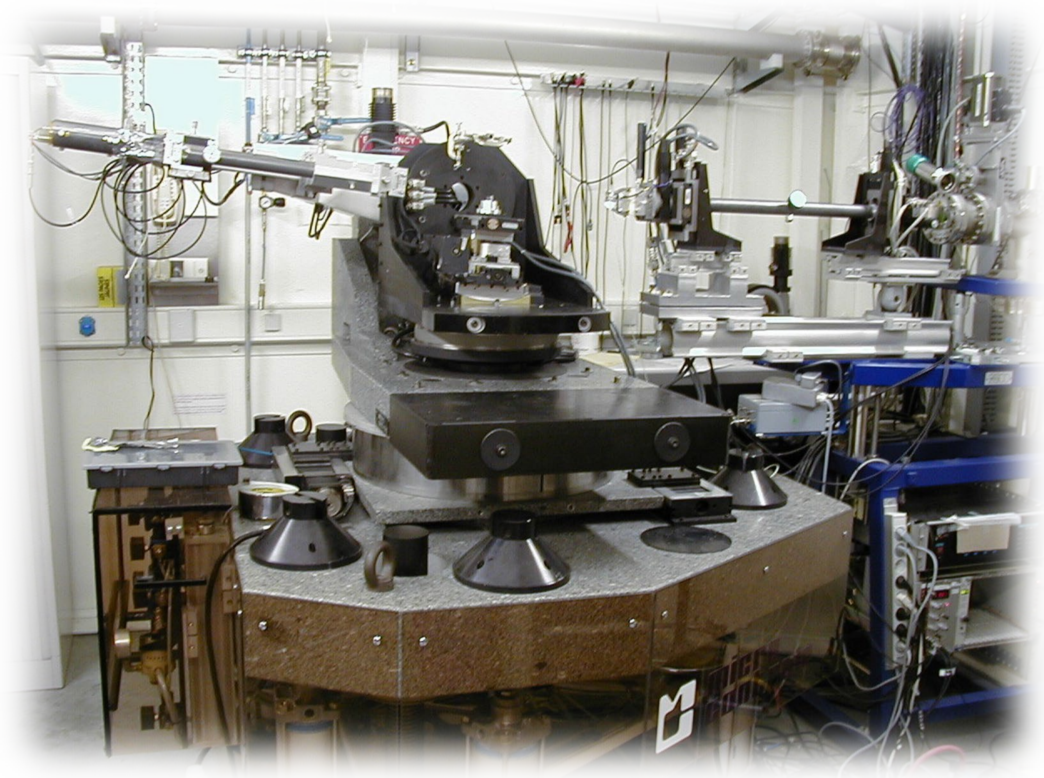
Kappa geometry

Surface diffractometer for UHV in-situ surface studies



INS2 – IF beamline (BM32 @ ESRF)

Surface diffractometer/reflectometer



GMT – IF beamline (BM32 @ ESRF)

Outline

I. Fundamentals: Interaction light/matter, Scattering and Refractive index

II. Grazing incidence conditions: Boundary conditions, Penetration length

III. The Born Approximation and the Distorted Wave Born Approximation

IV. Reciprocal space of 3D & 2D crystal, Diffraction

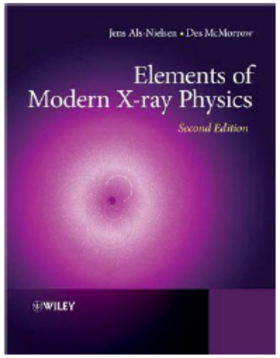
V. The GIXS geometry: Crystal Truncation Rods and examples

VI. The GISAXS geometry and examples

VII. Some experimental setups

VIII. References

Bibliography

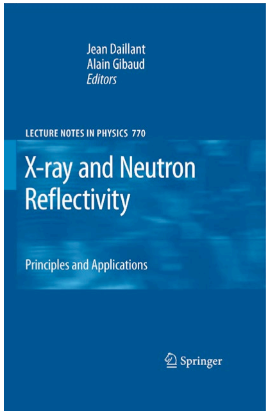


Books

- Als-Nielsen J. and McMorrow D. (2001) *Elements of Modern X-ray Physics*
- J. Daillant, A. Gibaud, *X-ray and Neutron Reflectivity: Principles and Applications*

A few GIXRD papers:

- Robinson I. K. (1986) Phys. Rev. B 33(6), 3830-3836. (original reference)
- Andrews S.R. and Cowley R.A. (1985) J. Phys C. 18, 642-6439. (original reference)
- Vlieg E., et. al. (1989) Surf. Sci. 210(3), 301-321.
- Vlieg E. (2000) J. Appl. Crystallogr. 33(2), 401-405. (rod analysis code)
- Trainor T. P., et. al.. (2002) J App Cryst 35(6), 696-701. (rod analysis code)
- Fenter P. and Park C. (2004) J. App Cryst 37(6), 977-987.
- Fenter P. A. (2002) Reviews in Mineralogy & Geochemistry 49, 149-220.



Reviews on GIXRD

- Werzer, O., Kowarik, S., Gasser, F. *et al.,* "X-ray diffraction under grazing incidence conditions" *Nat Rev Methods Primers* **4**, 15 (2024)
- Fenter P. and Sturchio N. C. (2005) Prog. Surface Science 77(5-8), 171-258.
- Renaud G. (1998) Surf. Sci. Rep. 32, 1-90.
- Robinson I.K. and Tweet D.J. (1992) Rep Prog Phys 55, 599-651.
- Fuoss P.H. and Brennan S. (1990) Ann Rev Mater Sci 20 365-390.
- Feidenhans'l R. (1989) Surf. Sci. Rep. 10, 105-188.

Bibliography

GISAXS

Supported nano-objects

- Rauscher et al, J. Appl. Phys. 86, 6763 (1999) (IsGISAXS)
- Lazzari, J. Appl. Cryst. 35, 406 (2001)

Nanostructures in supported single layer film

- Lee et al., Macromolecules 38, 3395 and 4311 (2005)
- Tate et al., J. Phys, Chem. B 110, 9882 (2006)

Depth-dependence structures in films

- Babonneau et al., Phys. Rev. B 80, 155446 (2009)
- Jiang, et al., Phys. Rev. B 84, 075440 (2011)

Some GISAXS analysis softwares

IsGISAXS, FitGISAXS, BornAgain, HipGISAXS