Vocabulary and fitting methods used in X-ray and neutron reflectometry

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Standardisation and Terminology

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Analysis and Methodology

- model dependent
  - (non-linear) least-squares analysis
  - genetic algorithm
  - simulated annealing
- model independent
  - multi-slice approach
  - DWBA
  - BA - charge flipping
  - Hilbert Transforms

Reflectometry is a relatively recent technique and is used by physicists, chemists, and biologists. Each group has developed its own terminology, which is one of the reasons why publications can sometimes be difficult to understand

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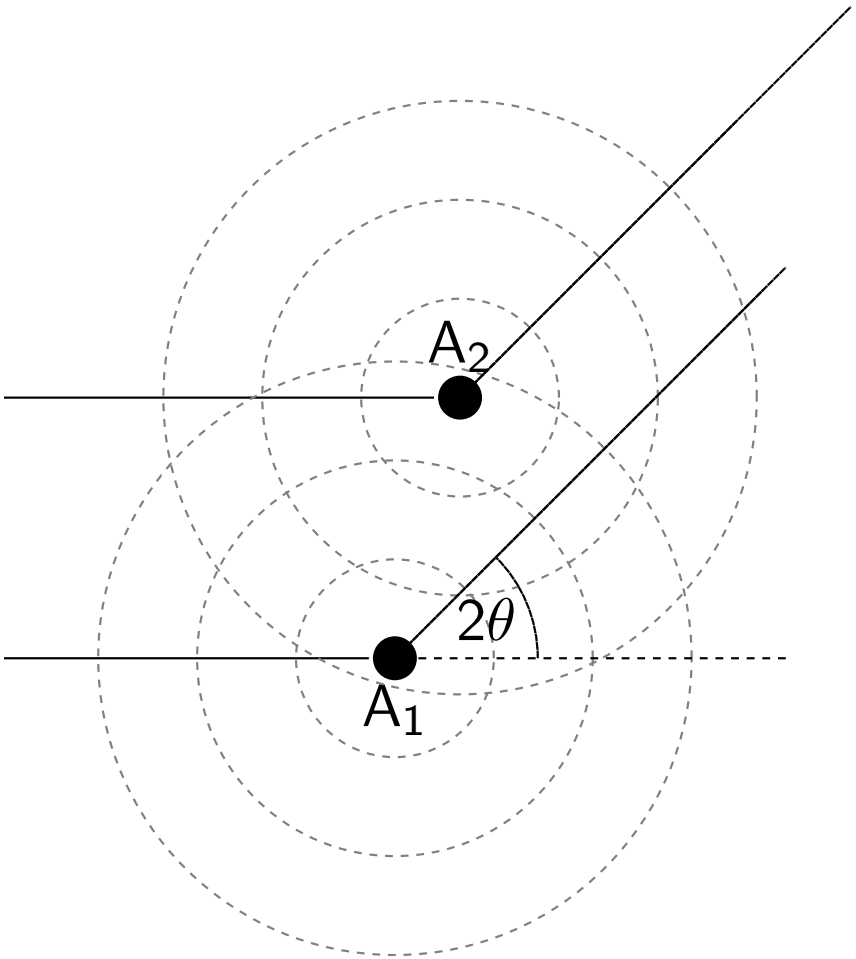
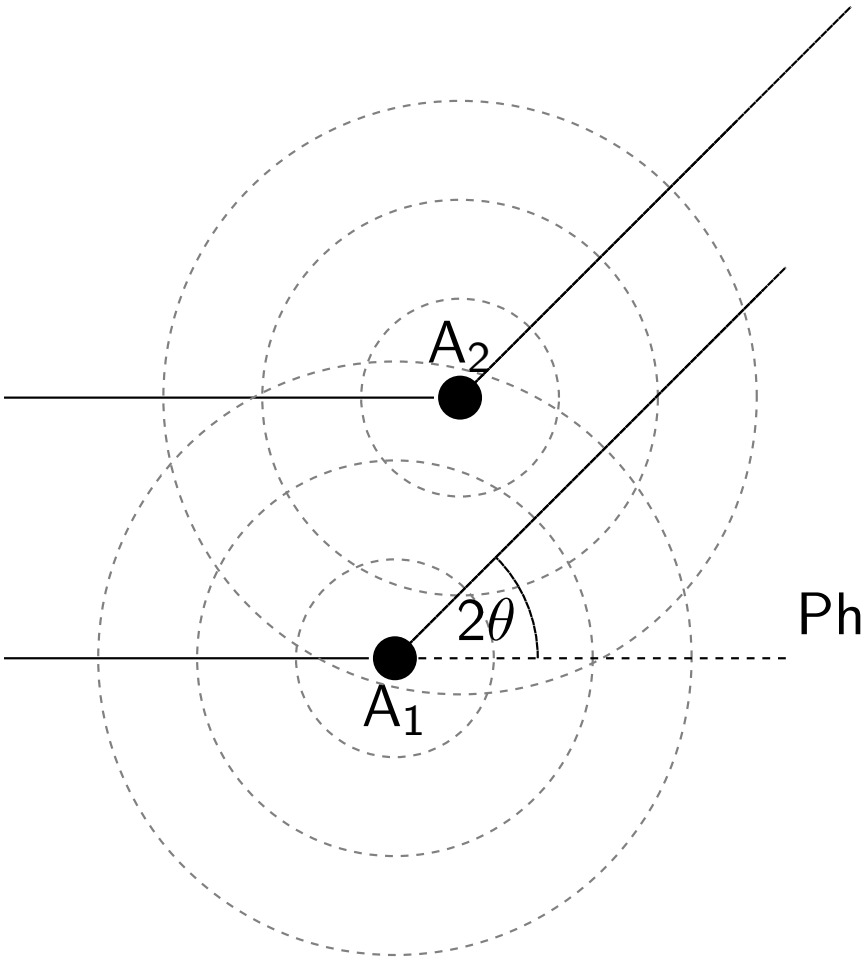
It is up to you to read and understand the different terminologies !

Some basic physics



Some basic physics

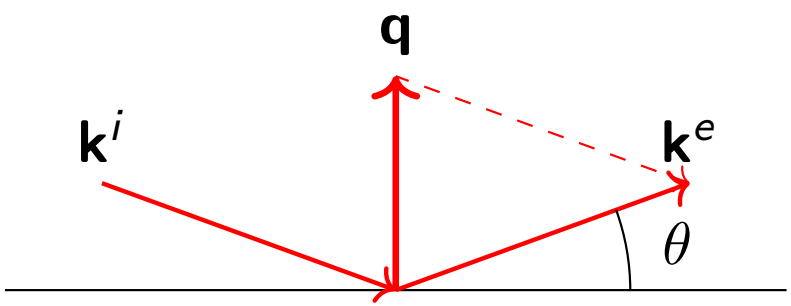


Photon - electron interaction is described by :

$$\psi''(k,z) + k^2\psi(k,z) = V(z)\psi(k,z)$$

(Schrödinger equation)

The scattering wave vector **k** and the wave number k

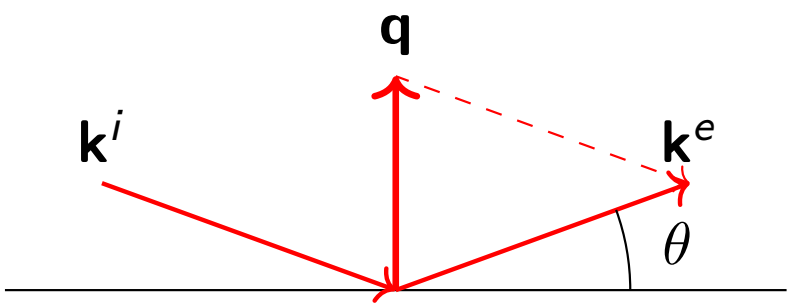


$k = k_0 \sin\theta = 2\pi \sin\theta/\lambda$

$q = 2k = |\mathbf{q}| = |\mathbf{k}^e - \mathbf{k}^i| = 4\pi \sin\theta/\lambda$

q is called the *momentum transfer ve*

The scattering wave vector **k** and the wave number k



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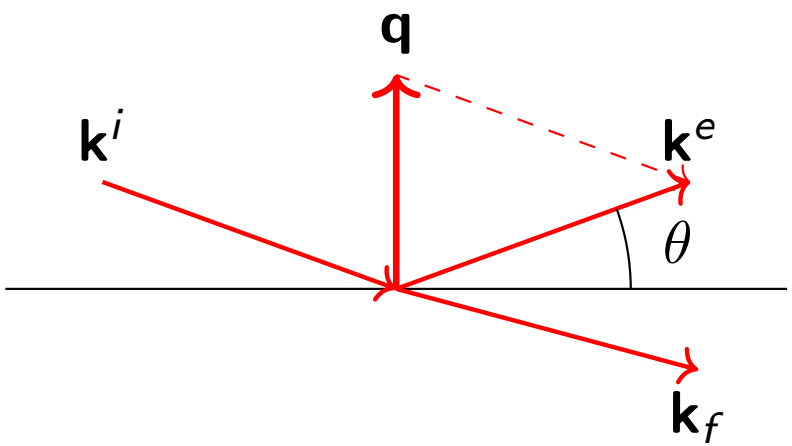
The scattering potential V

the scattering potential $V(z)$ is expressed, as k^2, $Å^{-2}$ units, but mostly the scattering length density (SLD) $\rho(z)$ is used :

$$V(z) = 4\pi\rho(z)$$

Rewrite the Schrödinger equation as :

$$\psi''(k,z) + (k^2 - V(z))\psi(k,z) = \psi''(k,z) + k_f^2\psi(k,z) = 0$$



vacuum $\Rightarrow V(z) = 0 \Rightarrow n(z) = 1$

layer $\Rightarrow \quad V(z) \neq 0 \Rightarrow n_f(z) \neq 1$

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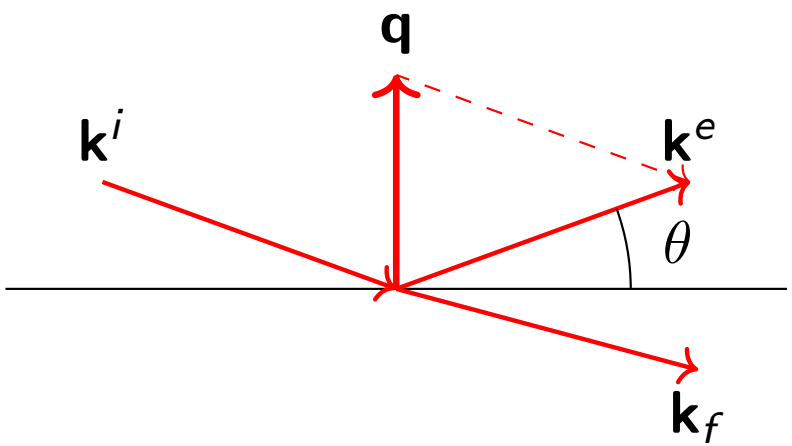

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The ratio between the vacuum wave number and the film wave number is the refractive index :

$$n(z) = k_f/k = \sqrt{1.0 - V(z)/k^2}$$

For X-rays ($0.2\text{Å} \lesssim \lambda \lesssim 6.0\text{Å}$) :

$$n(z) = 1.0 - \frac{\lambda^2}{2\pi}\rho(z) = 1.0 - \frac{\lambda^2 r_0}{2\pi}\sum n_j(z)(Z_j + f_j' + if_j'') = 1.0 - \frac{\lambda^2 r_0}{2\pi} N_A \rho_m \frac{\sum c_j(Z_j + f_j' + if_j'')}{\sum c_j A_j}$$

où :

- r_0 : classical radius of the electron (Thomson ; $r_0 = 2.8179.10^{-5}\text{Å}$)
- n_j : the number of atoms of element j per unit volume
- c_j : relative weight of element j in the chemical formula $c_1\text{A}c_2\text{B}c_3\text{C}\cdots$. Ex. :SiO2 $\Rightarrow$ c_{Si}=1 ; c_{O}=2
- Z_j : number of electrons of element j
- f_j',f_j'' : dispersion correction (real, imaginary) for element j

For neutrons the following equation should be used :

$$n(z) = 1.0 - \frac{\lambda^2}{2\pi}\rho(z) = 1.0 - \frac{\lambda^2}{2\pi}\sum n_j(z)(b_{j,\text{coh}} + ib_{j,\text{abs}})$$

où :

- ρ : scattering length density
- n_j : the number of atoms of element j per unit volume
- b_j : scattering length for nucleus j

Refractive index :

$$n = 1.0 - \delta - i\beta$$

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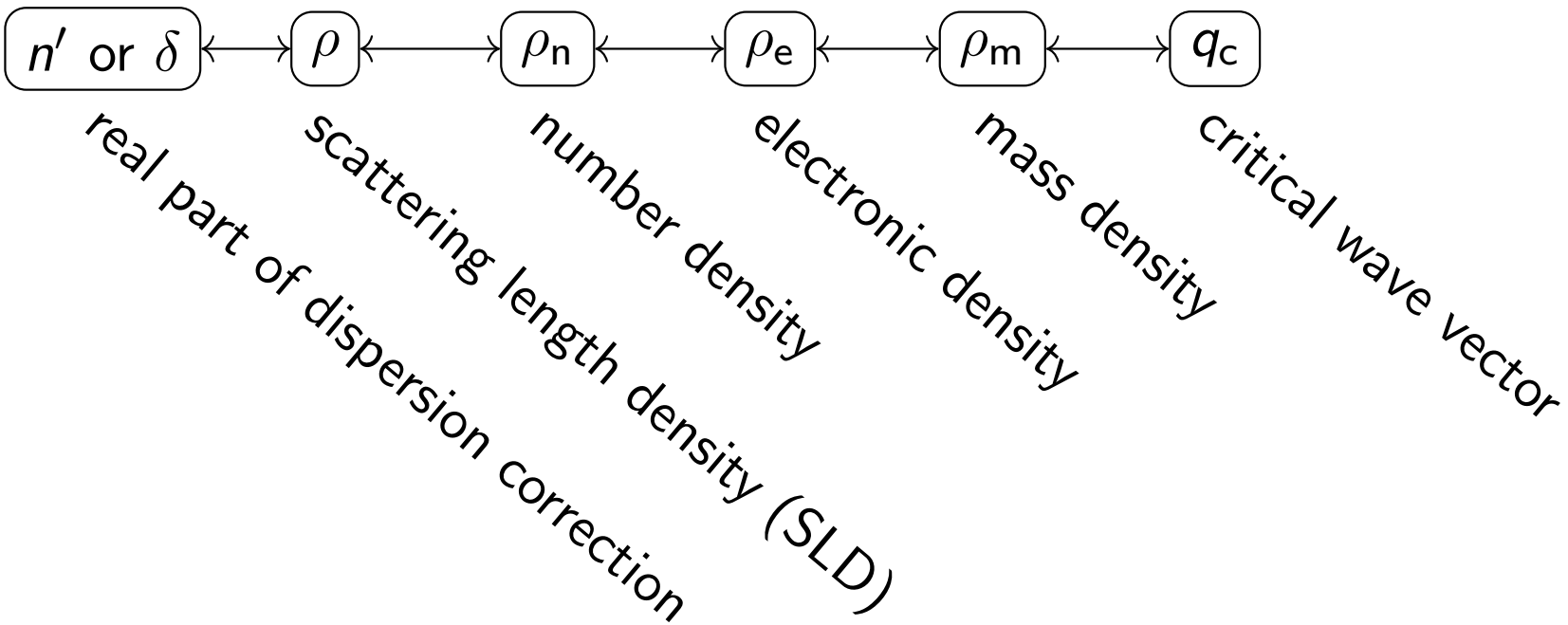
Real part of refractive index - main information



Conversion formula's between refractive index and densities

Refractive index $n = 1.0 - \delta - i\beta$; SLD $\rho = \rho' + i\rho''$

Between δ and ρ :

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

Entre δ et ρ_e :

$$\delta = \frac{\lambda^2}{2\pi} r_0 \rho_e$$

Entre δ et ρ_n :

$$\delta = \frac{\lambda^2}{2\pi} r_0 \rho_n \sum c_j (Z_j + f_j')$$

Entre δ et ρ_m :

$$\delta = \frac{\lambda^2}{2\pi} r_0 N_A \rho_m \frac{\sum c_j (Z_j + f_j')}{\sum c_j A_j}$$

Conversion formula's between refractive index and critical wave vector

Snell's law : $n\cos\theta' = \cos\theta$

Definition of critical angle (because $n < 1$) : $\cos\theta_c = n$

Taylor expansion : $\cos\theta_c \approx 1 - \theta^2/2$

Between θ_c and δ :

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

Between q_c and δ :

$$q_c = \frac{4\pi}{\lambda}\sqrt{2\delta}$$

Between q_c and ρ_e :

$$q_c = 4\sqrt{\pi\rho_e r_0} \approx 0.03763\sqrt{\rho_e}\text{Å}$$

Between q_c and ρ' :

$$q_c = 4\sqrt{\pi\rho'} \approx 7.088\sqrt{\rho'}$$

Les convertisseurs SLD $\rho \leftrightarrow \rho_m$

- SLD calculator : https://www.ncnr.nist.gov/resources/activation/
  - $\rho_m \longrightarrow$ SLD
  - X-rays (Cu et Mo) and neutrons
- *REFLEX*
  - $\rho_m \longrightarrow q_c$
  - X-arys and neutrons
  - database
- *REFLECTOOLS*
  - $\rho_m \longrightarrow$ SLD
  - SLD $\longrightarrow \rho_m$

Refractive index :

$$n = 1.0 - n' - in'' = 1.0 - \delta - i\beta$$

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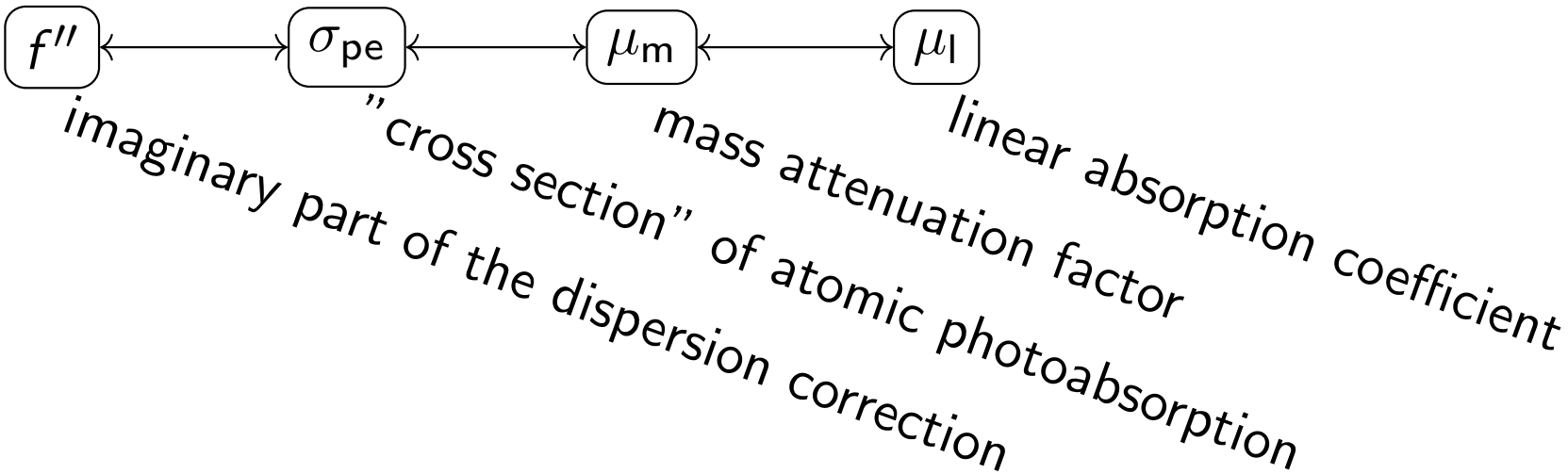
Absorption and X-rays : confusion !



Conversion formula's for absorption coefficients

The cross section of atomic photoabsorption (units : cm^2)

$$\sigma_{pe} = \frac{4\pi r_0 f''}{k_0} = 2\lambda r_0 f''$$

Mass attenuation factor (σ_{pe} per gram, units : cm^2/g) :

$$\mu_m = N_A \sigma_{pe}/A$$

Linear absorption coefficient (μ_m for a multi-element compound per unit volume , units cm^{-1}) :

$$\mu_l = \rho_n \sum c_j \sigma_{pe,j} = \rho_m \frac{\sum c_j A_j \mu_{m,j}}{\sum c_j A_j} = \rho_m \sum x_j \mu_{m,j}$$

Physical meaning : the reciprocal value of μ_l, the attenuation factor, is the length after which the incoming intensity is reduced by a factor 1/e.

Master relation

$$n(z) = 1.0 - \delta - i\beta = 1.0 - \frac{\lambda^2 r_0}{2\pi} N_A \rho_m \frac{\sum c_j (Z_j + f_j')}{\sum c_j A_j} - \frac{i\mu_l \lambda}{4\pi}$$

Critical angle :

$$\cos\theta_c = n$$

This equation gives, with $\cos\theta \approx 1.0 - \frac{\theta^2}{2}$:

$$\theta_c^2 = \frac{4\pi r_0}{k_0^2} N_A |\rho_m| \frac{\sum c_j (Z_j + f_j')}{\sum c_j A_j} = \frac{\lambda^2}{\pi} |\rho| = \frac{\lambda^2 r_0}{\pi} |\rho_{e|}$$

Relation between mass density and imaginary part of refractive index

$$n(z) = 1.0 - \delta - i\beta = 1.0 - \frac{\lambda^2 r_0}{2\pi} N_A \rho_m \frac{\sum c_j (Z_j + f_j')}{\sum c_j A_j} - \frac{i\mu_l \lambda}{4\pi}$$

$$n(z) = 1.0 - \delta - i\beta = 1.0 - \frac{\lambda^2}{2\pi}(\rho' + i\rho'')$$

$$\beta = \frac{\lambda^2 \rho''}{2\pi} = \frac{\mu_l \lambda}{4\pi} = \rho_m \frac{\lambda}{4\pi} \frac{\sum c_j A_j \mu_{m,j}}{\sum c_j A_j}$$

Two relations between the mass density and the obervables

$$q_c = \sqrt{16\pi r_0 N_A \rho_m \frac{\sum c_j (Z_j + f_j')}{\sum c_j A_j}}$$

$$\beta = \frac{\lambda^2 \rho''}{2\pi} = \frac{\mu_l \lambda}{4\pi} = \frac{\rho_m \lambda}{4\pi} \frac{\sum c_j A_j \mu_{m,j}}{\sum c_j A_j}$$

q_c and β (or ρ' and ρ'') are correlated !

Binary compound PQ_x

With q_c, β, determine x :

$$x = \frac{\beta\Gamma(Z_P + f'_P) - q_c^2 A_P \mu_P}{q_c^2 A_Q \mu_Q - \beta\Gamma(Z_Q + f'_Q)}$$

with

$$\Gamma = 64\pi^2 r_0 N_A/\lambda$$

$$n(E) = 1.0 - \delta - i\beta = 1.0 - \frac{\lambda^2 r_0}{2\pi} N_A \rho_m \frac{\sum c_j (Z_j + f_j'(E) + i f_j''(E))}{\sum c_j A_j}$$

Kramers-Kronig relation between $f'(E)$ et $f''(E)$:

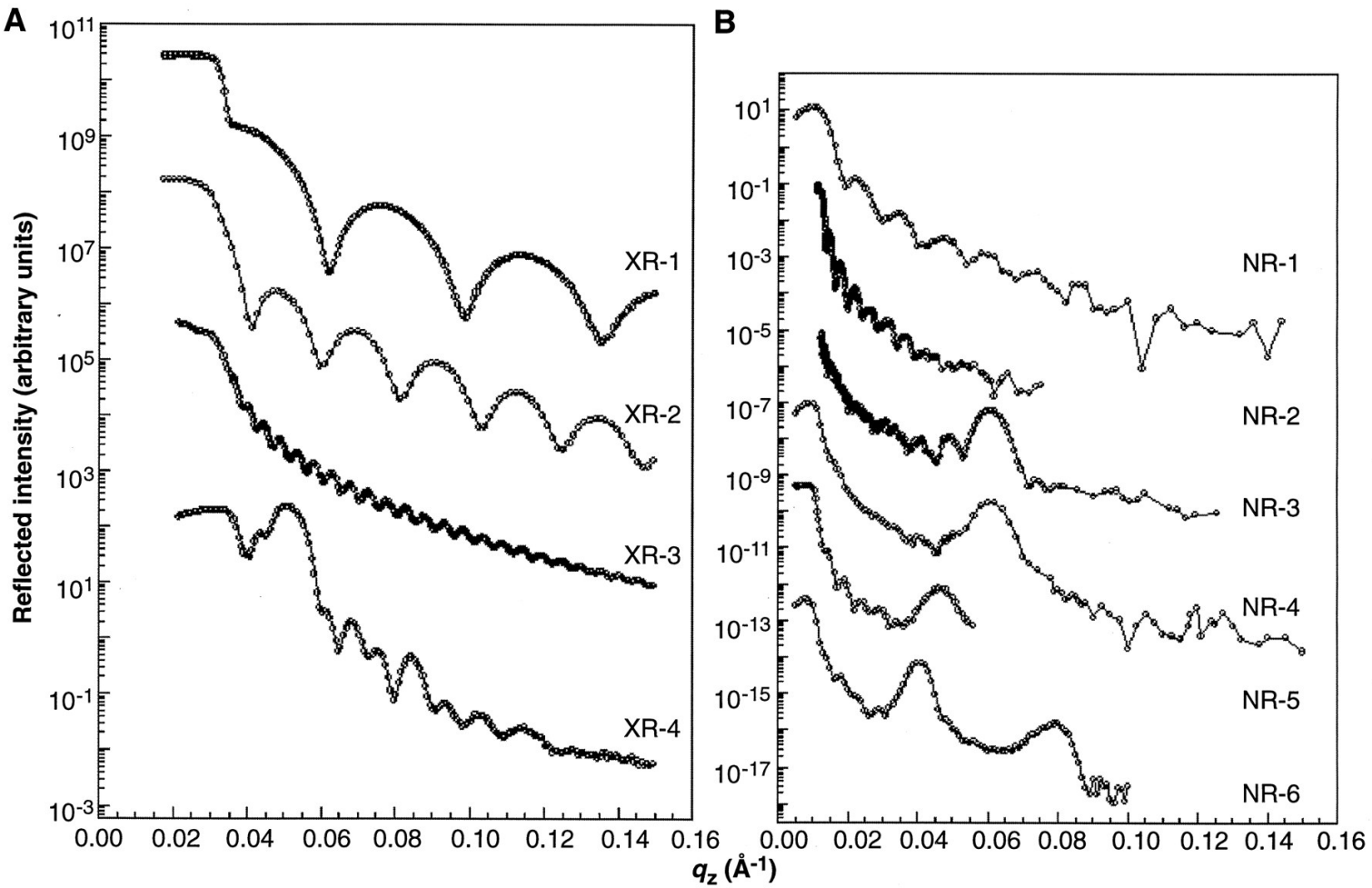
$$f'(E) = Z^* - \frac{2}{\pi} P \int_0^\infty \frac{x f''(x)}{x^2 - E^2} dx$$

How to use this correlation between q_c et β ?

- if the experimental data are not so good : nothing ! don't refine β
- if the data are excellent : use the relation as a validation tool
- for a binary compound PQ_x : possible to determine x

Verification with *REFLECTOOLS*

Once the reflectivity curve has been obtained, how to analyze it ?



The lost phases

In reflectivity, as in diffraction, one measures $I(\boldsymbol{q}) \propto |F(\boldsymbol{q})|^2$. The "structure factor" $F(\boldsymbol{q})$ is easy to calculate from the electronic density :

$$F(\boldsymbol{q}) \propto \int \rho(\boldsymbol{r}) e^{i\boldsymbol{q}\boldsymbol{r}} d\boldsymbol{r}$$

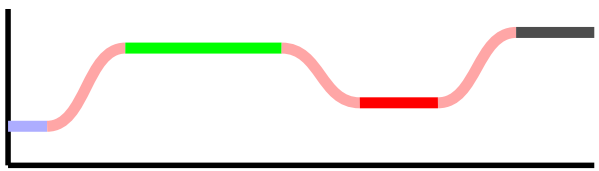
The model $\rho(\boldsymbol{r})$ to be found is directly related to the structure factor in the Born approximation (simple scattering) :

$$\rho(\boldsymbol{r}) \propto \int F(\boldsymbol{q}) e^{-i\boldsymbol{q}\boldsymbol{r}} d\boldsymbol{q}$$

$$F(\boldsymbol{q}) = |F(\boldsymbol{q})| e^{i\phi} \; ; \; \phi \text{ is not measured}$$

Classical analysis - model dependent

Initial model $\rho(z)$



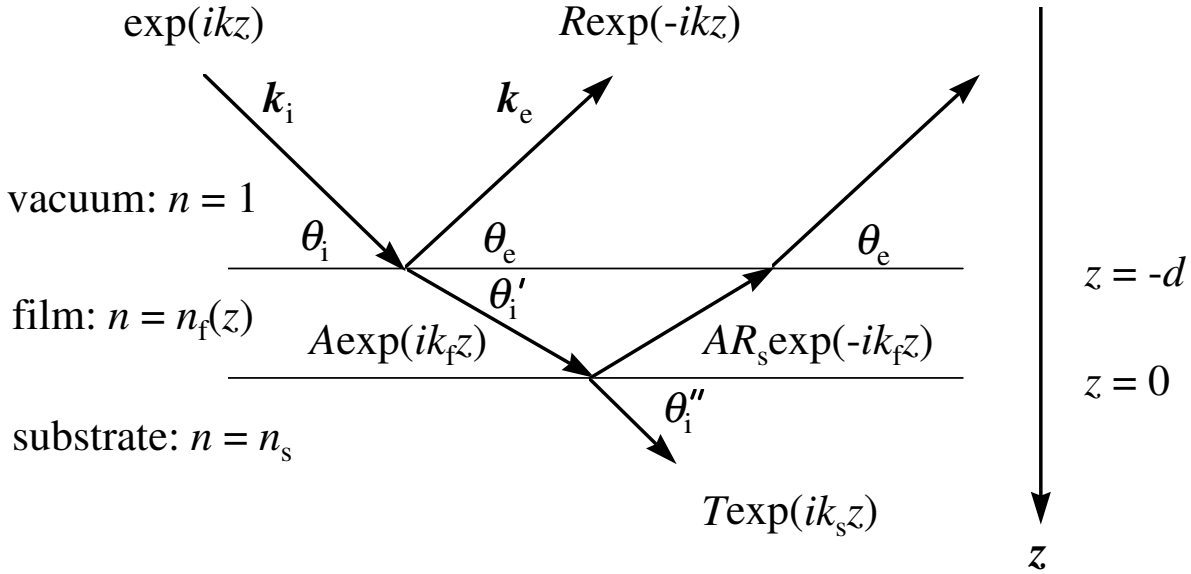
Minimisation $|r_{obs}(q)\text{-}r_{cal}(q)|$ ⟷ $r(q)$ (Parratt calculation)

How should the minimisation be carried out ?

- least squares
- simulated annealing
- monte carlo
- genetic algorithm
- machine learning/neural networks

The reflectivity is calculated - exactly - according to the Parratt formula.
It is a recursive formula and it is non-linear, which makes its use in classical optimisation algorithms difficult

Calculated reflectivity - Parratt's formula



$$\psi(z) = \exp(ikz) + R\exp(-ikz), \quad z \leq -d \tag{1}$$

$$\psi(z) = A[\exp(ik_f z) + R_s \exp(-ik_f z)], \quad -d \leq z \leq 0 \tag{2}$$

$$\psi(z) = T\exp(ik_s z) \quad z \geq 0 \tag{3}$$

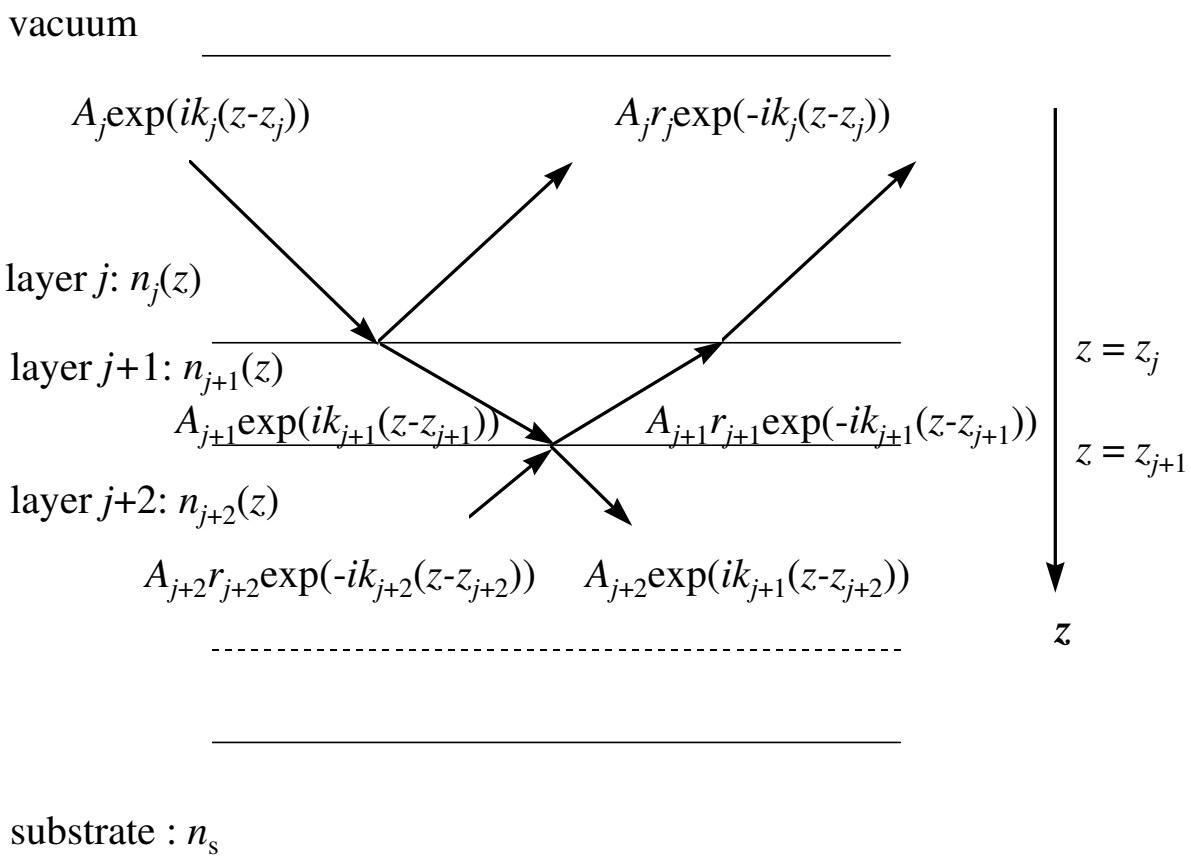
$$k_f = \sqrt{k_i^2 \sin^2\theta - k_i^2(1-n_f)^2} \tag{4}$$

$$R = \frac{R_F + R_s e^{2ik_f d}}{1 + R_F R_s e^{2ik_f d}} e^{-2ikd}, \tag{5}$$

where R_s and R_F are the Fresnel reflectivities of the substrate and the layer :

$$R_s = \frac{k_f - k_s}{k_f + k_s}, \tag{6}$$

$$R_F = \frac{k - k_f}{k + k_f} \tag{7}$$



The Fresnel reflectivity for each sublayer :

$$R_{F,N+1} = \frac{q_N - q_{N+1}}{q_N + q_{N+1}}, \qquad q = 2k$$

$$R_j = \frac{R_{F,j+1} + R_{j+1} e^{iq_{j+1}\Delta z_{j+1}}}{1 + R_{F,j+1} R_{j+1} e^{iq_{j+1}\Delta z_{j+1}}}$$

Start with the substrate $j = N$ where $R_{N+1} \equiv 0$ and, consequently :

$$R_N = \frac{q_N - q_s}{q_N + q_s}$$

Calculate $R_{N-1} \cdots R_0$ and then $r = |R_0|^2$

$$R_j = \frac{R_{f,j+1} + R_{j+1} e^{iq_{j+1}\Delta z_{j+1}}}{1 + R_{f,j+1} R_{j+1} e^{iq_{j+1}\Delta z_{j+1}}}$$

where the fitting parameters are :

- thickness : Δz_{j+1}
- density : $q_j = q_0 n_j$
- roughness : $R_j \Rightarrow R_j \exp(-q_{j-1} q_j \sigma_j^2)$

Least-squares difficulties for Parratt

- non-linear iterative methods
- trapping in false minima
- starting point should be close to the final solution
- maximum number of layers : $N = 3$
- adjustment very often done manually

Comparison of algorithms

Multidimensionnal radius of convergence

$$\tau = \sqrt{\sum_i \left(\frac{p_i - p_{im}}{p_{im}}\right)^2}$$

τ	d	ρ	σ_1	σ_2	GA1	GA2	SA	S'plex	*F'4c*	*P32*	*IMD*
0.4	240.0	1.20	12.0	8.0	yes	yes	yes	yes	yes	yes	no
0.5	150.0	0.75	7.5	3.75	yes	yes	yes	yes	yes	no	no
2.5	450.0	2.25	22.5	11.25	yes	yes	yes	no	no	no	no
7.0	900.0	4.50	45.0	22.5	yes	yes	yes	no	no	no	no
15.0	1700	8.50	85.0	42.5	yes	yes	no	no	no	no	no

Initial model : $d = 200$, $\rho = 0.861$, $\sigma_1 = 10.0$, $\sigma_2 = 5.0$

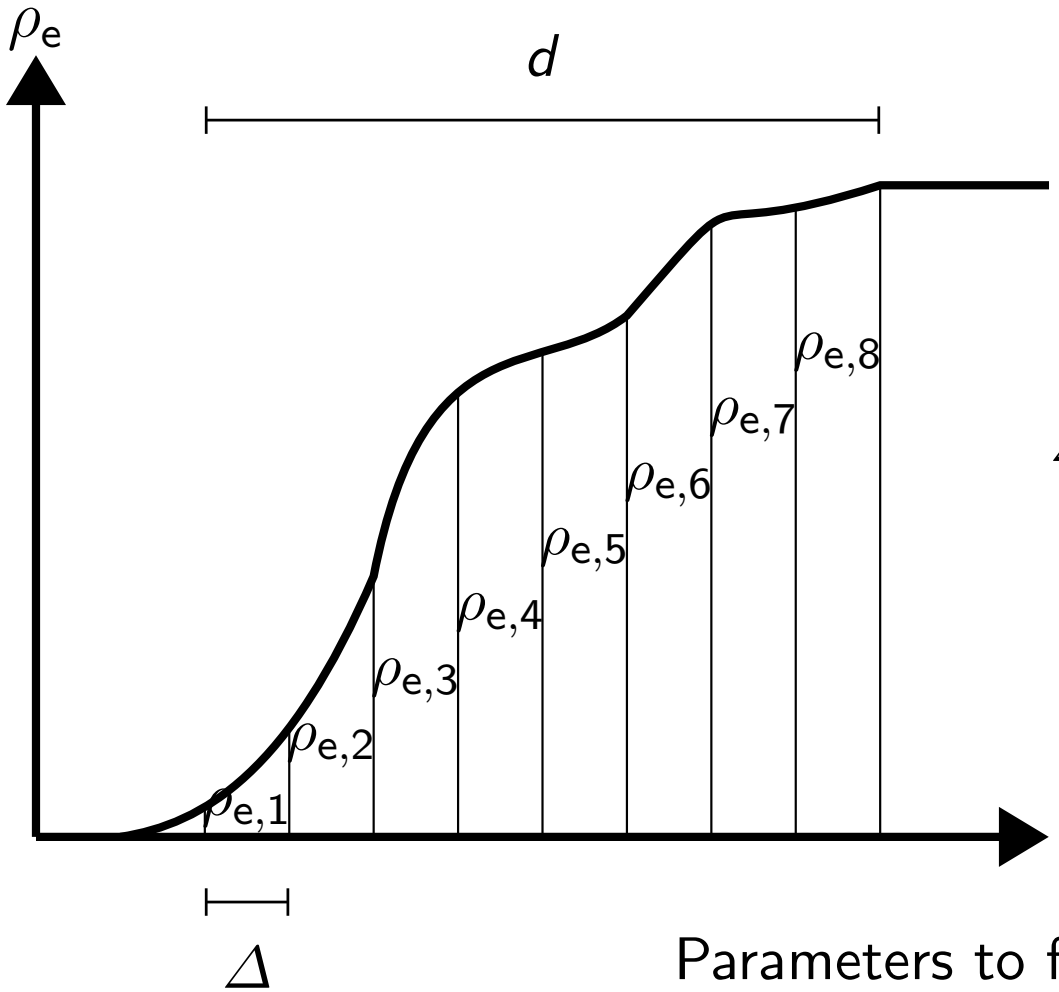
Conclusion with respect to classical algorithmes

Genetic algorithms are preferable, but the layers should be well defined

A comparison of modern data analysis methods for X-ray and neutron specular reflectivity data

A. van der Lee, F. Salah, B. Harzallah, *J. Appl. Cryst.* (2007). **40**, 820-833

Multislice method



$$\Delta \geq 1/2q_{max} = \frac{\lambda}{8\pi \sin\theta_{max}}$$

Parameters to fit : $\rho_{e,i}$

Born (kinematical) approximation

- Only valid for angles $\theta > 3\theta_c$
- Relation between density $\Longleftrightarrow$ structure factor F by a Fourier transform

$$r = \left(\frac{4\pi\rho_\infty}{q^2}\right)^2 \left|\frac{1}{\rho_\infty}\int \frac{d\rho}{dz} e^{iqz} dz\right|^2 \propto \frac{1}{q^4}$$

$$r = \left(\frac{4\pi}{q^2}\right)^2 \left|F[\rho'(z)]\right|^2 = R_F^2 \left||F|e^{i\phi}\right|^2$$

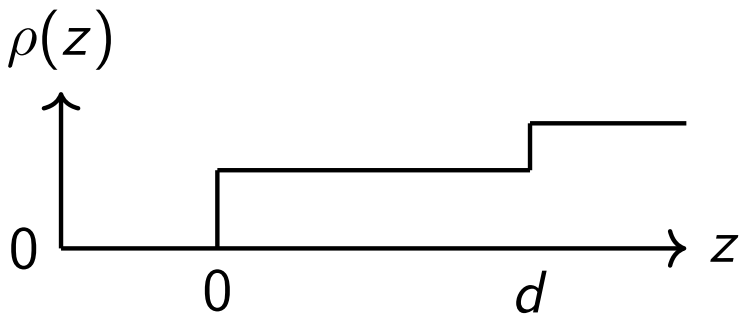
- Inverse Fourier transform gives access to $\rho'(z)$ at the condition that ϕ is known !

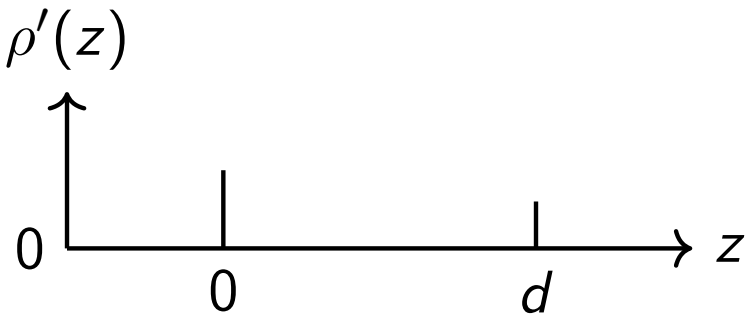
$$|F| = \sqrt{r/R_F^2} \rightarrow |F|e^{i\phi} = \mathcal{F}[\rho'(z)]$$

$$\rho'(z) = \mathcal{F}^{-1}\mathcal{F}[\rho'(z)] = \mathcal{F}^{-1}[|F|e^{i\phi}]$$

Derivative of the density function ?

- $\rho'(z) = 0$ for $z < 0$ and $z > d$

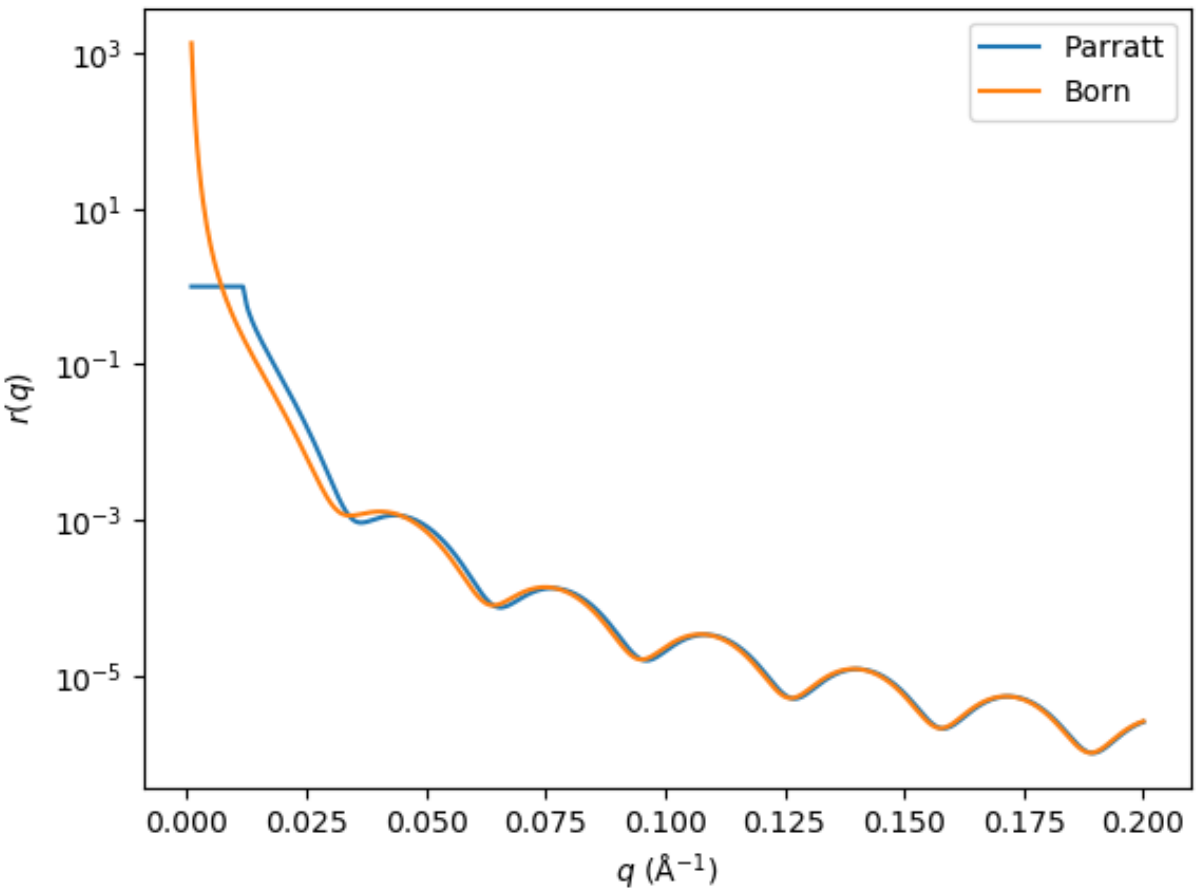




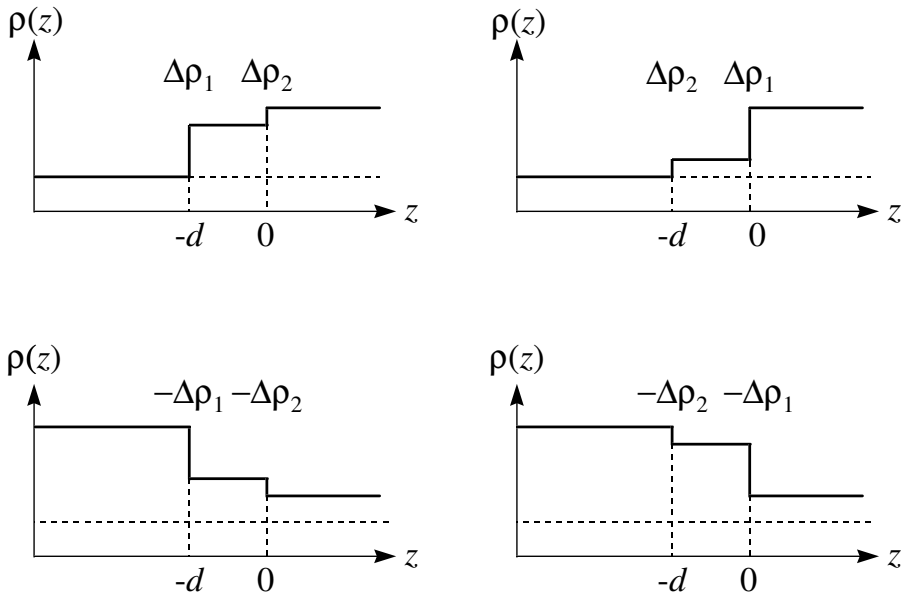
Three important points :

- The derivative of the density profile is 'atomic-like'
- The derivative of the density profile is bounded
- The sensitivity to the first derivative indicates the importance of the change of the density profile to the reflectivity curve.

Born approximation versus Parratt formalism



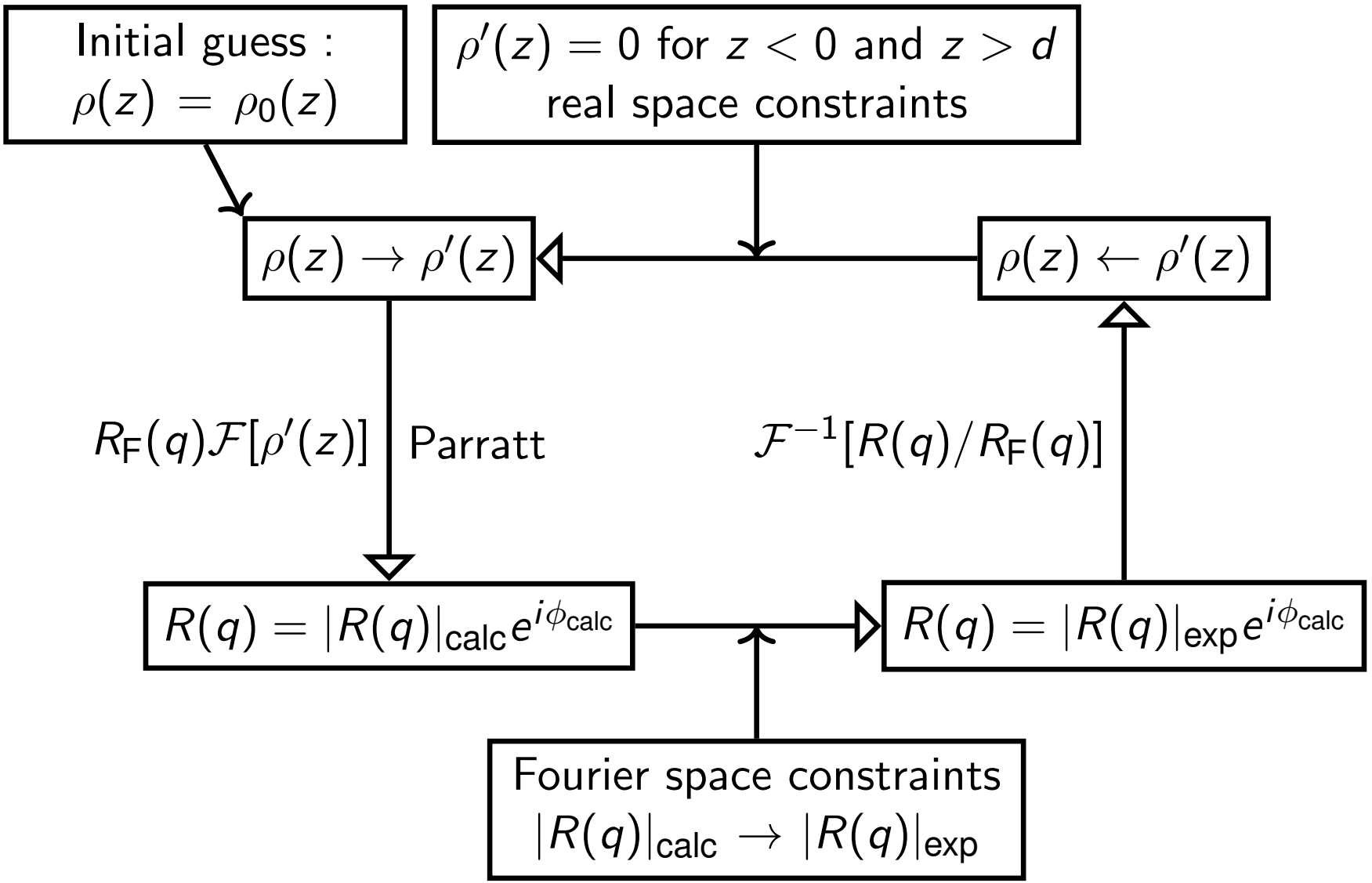
Born is not unique !



$$|F(q)|^2 = |\Delta\rho_1 + \Delta\rho_2 e^{iqd}|^2 = \Delta\rho_1^2 + \Delta\rho_2^2 + \Delta\rho_1\Delta\rho_2 \cos(2qd)$$

$$r(q) = r_F(q)|F(k)|^2 = \frac{16\pi^2}{q^4}(\Delta\rho_1^2 + \Delta\rho_2^2 + \Delta\rho_1\Delta\rho_2 \cos(2qd))$$

Iterative method in direct and Fourier space



Machine learning

research papers

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Fast fitting of reflectivity data of growing thin films using neural networks

Alessandro Greco,[a] Vladimir Starostin,[a] Christos Karapanagiotis,[b] Alexander Hinderhofer,[a]* Alexander Gerlach,[a] Linus Pithan,[c] Sascha Liehr,[d] Frank Schreiber[a]* and Stefan Kowarik[d]*

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Deep learning approach for an interface structure analysis with a large statistical noise in neutron reflectometry

Hiroyuki Aoki[1,2]✉, Yuwei Liu[2] & Takashi Yamashita[3]

Machine learning

topical reviews

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Machine learning for scattering data: strategies, perspectives and applications to surface scattering

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research papers

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Neural network analysis of neutron and X-ray reflectivity data: automated analysis using *mlreflect*, experimental errors and feature engineering

Alessandro Greco,[a] Vladimir Starostin,[a] Evelyn Edel,[a] Valentin Munteanu,[a] Nadine Rußegger,[a] Ingrid Dax,[a] Chen Shen,[b] Florian Bertram,[b] Alexander Hinderhofer,[a]* Alexander Gerlach[a] and Frank Schreiber[a]*

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Agreement factors and residual fit

Global fit agreement :

$$wR_{\text{curve}} = \sqrt{\frac{\sum_i w_i (\log_{10} r_{\text{obs},i} - \log_{10} r_{\text{cal},i})^2}{(\sum_i w_i \log_{10} r_{\text{obs},i})^2}}$$

The 'best' fit agreement :

$$wR_{\text{exp}} = \sqrt{\frac{N}{(\sum_i w_i \log_{10} r_{\text{obs},i})^2}}$$

χ^2 :

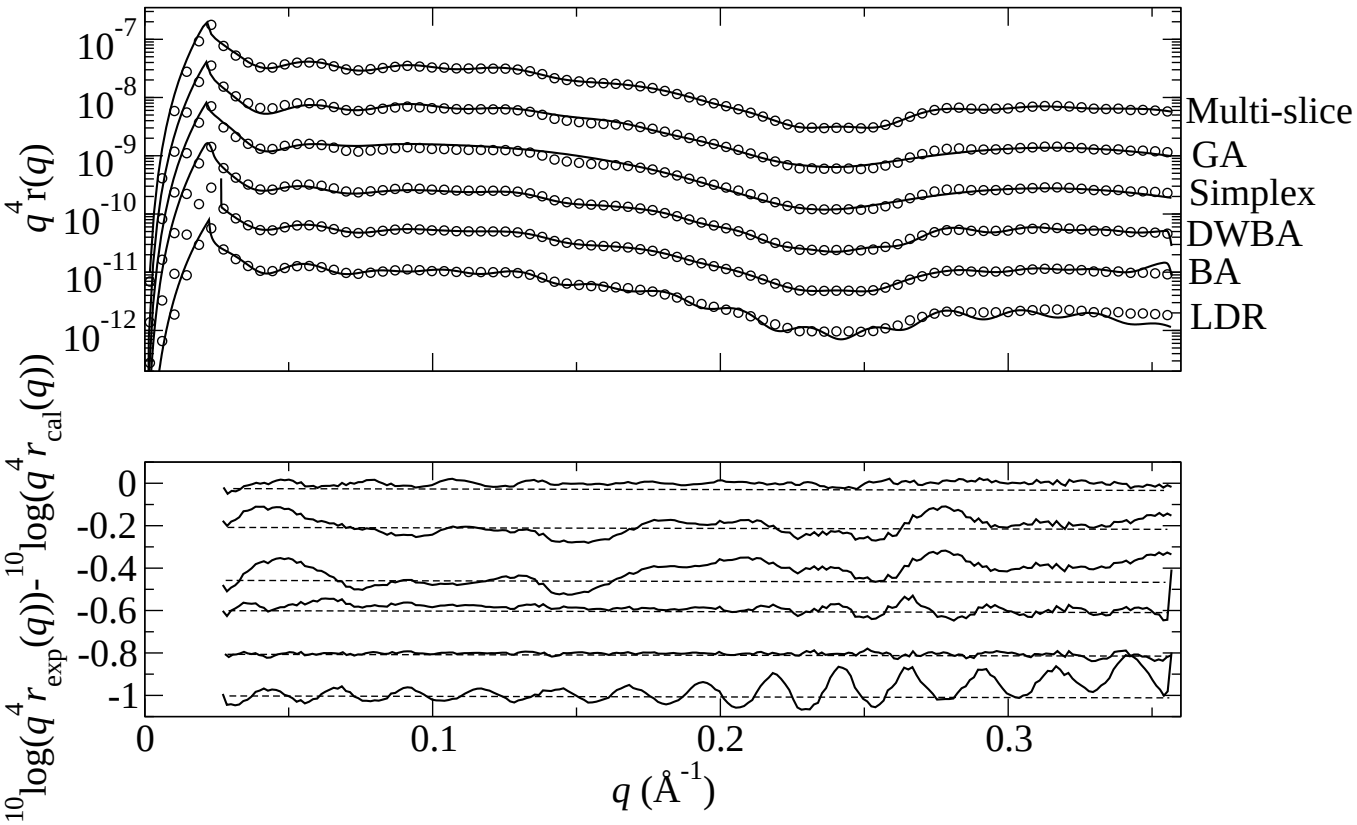
$$\chi^2 = (wR_{\text{curve}}/wR_{\text{exp}})^2$$

Agreement factors and residual fit

Local fit agreement :

$$\Delta(q_i) = \log_{10} r_{\text{obs}}(q_i) - \log_{10} r_{\text{cal}}(q_i)$$

$$\Delta(q_i) = \log_{10} q_i^4 r_{\text{obs}}(q_i) - \log_{10} q_i^4 r_{\text{cal}}(q_i)$$



Software

How to do the minimisation ?

- *REFLEX*
  - specular (neutron & rayons-X)
  - differents optimisation (classical, genetic)
  - optical tables
  - fit on q_c, β, SLD, thickness, roughness
  - correlated fitting between real and imaginary part
  - fit and calculation on non-model parameters - scale factor etc.
  - single and multilayers
  - correction for geometric effects
  - soft X-rays : reflectivity depends on polarisation

Software

How to do the optimisation ?

- *STOCHFIT*
  - specular
  - multi-slice refinement (permits to detect density gradients)
  - least-squares fit , stochastic fit
  - fit on SLD, thicknesses

Reporting an X-ray or neutron reflectometry experiment

The final structural model depends on :

- the instrumental parameters, including the scale factor
- the initial model
- the fixed and the free parameters
- the lower and upper bound of the free parameters
- constraints and restraints between parameters

These details should be mentioned in the manuscript or the supplementary information.

Reporting an X-ray or neutron reflectometry experiment

Report :

- Instrument used for data collection
- Data collection parameters
- Fitting program used
- Prior knowledge used
- Experimental and calculated curves (make available as supplementary material)
- Difference curves and agreement factors
- All optimisation details (see preceding slide)
- Final model parameters with esd's - if available

A Bayesian approach (see McCluskey *et al.* - publication and *REFNX* software - is probably the best way to deal with this.

Software workshop

Demonstration and exercises

- Demonstration of the use of *REFLEX*
- Simulations
  - influence of thickness on q_c
  - influence of β on q_c
  - effect of instrumental parameters on the calculated reflectivity
  - effect of roughness on the reflectivity
  - upper limit of detectable thicknesses
- Classical fits
  - organic layer of 1000 Å on Si - simulated data
  - single ZnS layer on Si
  - silica layer of 1000 Å on Si - experimental data
  - oxydized niobium layer on sapphire
  - ideal periodic W/Si multilayer on Si
  - detection of fine details - *STOCHFIT*

What is the difference between small-angle techniques ?

X-rays and neutrons

- Reflectivity
- GISAS
- Off-specular

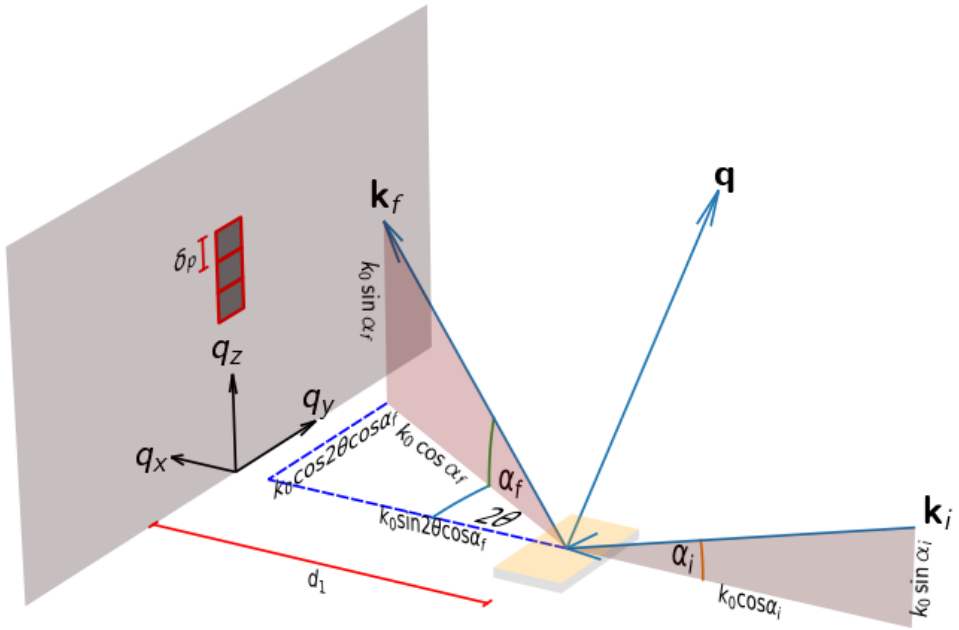
All is defined by the momentum transfer q !

Geometry of small-angle scattering techniques

$\mathbf{q}=\mathbf{k}_f-\mathbf{k}_i$

$|\mathbf{k}_f| = |\mathbf{k}_i| = k_0 = 2\pi/\lambda$

$$\begin{pmatrix} q_x \\ q_y \\ q_z \end{pmatrix} = \begin{pmatrix} k_0(\cos 2\theta \cos\alpha_f - \cos\alpha_i) \\ k_0(\sin 2\theta \cos\alpha_f) \\ k_0(\sin\alpha_f + \sin\alpha_i) \end{pmatrix}$$



GISAS: $q_x = 0 \rightarrow q_{||} \approx 2k_0\theta, q_\perp \approx k_0(\alpha_f + \alpha_i)$

Off-specular: $q_y = 0, 2\theta = \alpha_i + \alpha_f = \text{Cst} \rightarrow q_{||} \approx k_0(\alpha_i^2 - \alpha_f^2)/2, q_\perp \approx 2k_0\alpha_f$

Reflectivity: $q_x = 0,\ q_y = 0, \alpha_i = \alpha_f \rightarrow q_\perp \approx 2k_0\alpha_f$

Key points to remember

- Angles are small → small wavevector transfer ($0.0001 < q < 1$ nm^{-1})
- Reflectivity → probe density profile perpendicular to surface
- Off-specular → probe density correlations along q_x
- GISAS → probe morphology parallel with the surface (along q_y) and perpendicular to it (along q_z)
- GISAS and off-specular scans are not the same (although both probe fluctuations parallel to the surface) !
  - GISAS, $q_{||} = q_y$ is of first order with respect to in-plane angle Θ_f → intermediate distances (1 nm - 100 nm)
  - off-specular, $q_{||} = q_x$ is of second order with respect to out-of-plane angle α_f → long distances (100 nm - 1μm)

Grazing incidence diffraction : α_i small, α_f and Θ_f large