Study of interfaces and thin layers by X-ray and Neutron reflectivity

GUILLAUME BROTONS

09.17.2024

Légende

📚	Référence Bibliographique

Table des matières

I.Présentation

Module :

X-ray optics

Auteur(s) :

Guillaume BROTONS - Le Mans Université - Laboratoire de Physique de l'État Condensé (UMR 6087)

Résumé :

This course is devoted to the presentation of the theories used to calculate the specular reflectivity of an interface, a thin film or a more complex multi-layer. We underline with particular care the hypotheses which make it possible to apply a formalism historically developed for visible optics to x-ray and neutron beams which make it possible to probe smaller structural scales with very different contrasts and transparencies.

Mots-clés :

X-ray and neutron optics, reflectivity theory, interfaces, thin films and layers, multilayers

Pré-requis :

Physical optics (Fresnel optics), bases in quantum mechanics.

Objectif(s) pédagogique(s) :

Understand and know how to simulate (calculate, program) the phenomenon of reflectivity of x-rays or neutrons.

Analyze measurements and characterize interfaces, thin layers or multilayers.

Plan du cours :

- Introduction
- Theory of specular reflectivity of plane diopters and one-dimensional stratified media
- Use of simplifying Born approximations. Continuous kinematic formalism
- Calculation of the refractive indices of a material for X-rays and neutrons

Conception & production :

Le Mans Université

Licence :

---

[1] http://www.gnu.org/licenses/fdl.txt

II. Cours

This course is devoted to the presentation of the theories used to calculate the **specular reflectivity** of an interface, a thin film or a more complex multi-layer. We underline with particular care the hypotheses which make it possible to apply a formalism historically developed for visible optics to **X-ray** and **neutron** beams which make it possible to probe smaller structural scales with very different contrasts and transparencies.

The scientific community studying **interfaces** or **thin layers** expects these structural analysis techniques to allow the measurement of the thicknesses of the different materials encountered as well as the width and even the profile of the interfaces which separate them. Generally, adjustment procedures are used for this based on the optimization of a set of parameters making it possible to reproduce the measured reflectivity curve. For these procedures, the interaction potentials with radiation, the thicknesses and the widths of the interfaces are calculation parameters. We present here the bases of the theoretical models which allow these calculations of X-ray and neutron optics.

The scientific fields using these methods are numerous. Let us cite in particular the materials sciences which are interested in polymers and complex liquids (elastomers, rubbers, plastics, resins, glues, foams, etc.) with strong technological challenges coupled with original fundamental problems (*adhesion*, *wetting films*, *bio-compatibility*, *viscoelasticity*, etc.); the inorganic coatings and thin layers at the base of many microelectronics components (*semiconductors*, *magnetic multilayers for recording*, *thin liquid crystal films*, *nanocomposites* and *hybrid materials in thin layers*, etc.); the corrosion of metallic interfaces as well as more recently biology since many living phenomena take place at interfaces within complex solutions.

1. Theory of specular reflectivity of plane diopters and one-dimensional stratified media

1.1. Calculation of the reflectivity of X-rays or neutrons of thin films

We will introduce the theories commonly used to calculate the **reflectivity of X-rays** or **neutrons of thin films**. As these theories come from different formalisms such as classical optics or quantum mechanics, particular care will be taken to highlight the underlying hypotheses which define their domains of validity. The reflectivity phenomenon of laterally homogeneous thin films is studied first. The plane diopter constitutes the simplest reflective system and allows us to recall elementary notions of optics.

The phenomenon is approached firstly according to the **classical formalism of electromagnetic waves** which applies to X-rays and then according to the **quantum approach for massive particles** since this is the formalism used for neutrons.

The complementarity of the two approaches becomes evident when we describe with an original presentation the phenomenon of total reflection at small angles of incidence.

More complex systems but closer to the reality of systems studied in the laboratory or in industry are addressed next.

The simple case of a single thin layer is followed by that of stratified materials such as multilayer stacks. For these systems, the most common calculation methods are recalled within the framework of so-called dynamic formalisms respecting the laws of energy conservation.

The following part introduces the kinematic formalism based on the use of Born approximations. It is very practical when it can be applied, which is often the case for X-rays, since it simplifies calculations and allows you to work with analytical equations (as opposed to the matrix or iterative calculations introduced before).

The definitions of the quantities used to quantify the reflection and transmission of a material to X or neutrons are introduced in the last part.

1.2. Reflectivity on a plane diopter separating two semi-infinite homogeneous media.

The **plane diopter** constitutes the simplest physical system giving rise to the phenomena of reflection and transmission. It defines the interface between two media having different properties for wave propagation. The optical approach presented first is found in all academic works dealing with the propagation of waves at interfaces [1 [The Feynman Lectures on Physics], 2 [Theory of Reflection of Electromagnetic and Particles Waves], 3 [X-ray and Neutron Reflectivity : Principles and Applications]]. The quantum approach more appreciated by neutronics is rarely taught and will be carefully developed secondly. [4 [Neutron Optics, An introduction to the theory of Neutron Optical Phenomena and Their Applications], 5 [Theory of Neutron Scattering from Condensed Matter], 6 [Mécanique Quantique], 7 [Quantum mechanics]]. The phenomenon of total reflection is then discussed based on these two formalisms and following an original presentation.

a) Reminder of the concepts of the theory of wave propagation established by Maxwell

i Basic notions on the propagation of a wave when it meets a diopter

An electromagnetic, monochromatic, plane, infinite and homogeneous wave propagates in a homogeneous and isotropic material medium called incident (with index« *I* »). It falls on an infinite plane diopter constituting the separation with a medium denoted « *T* » where the speed of propagation of the wave is different.

The propagation speed in each of these media is an optical constant of the material and characterizes it sufficiently for the problem posed. In a material indexed I, this phase speed, v_I^{φ} , is equal to the ratio of the pulsation of the wave ω_I and the modulus of the propagation vector k_L.

Note that when we leave this optical approach to no longer deal with the case of light but of neutrons, the speed $\mathbf{v}$ of particles with mass is different from this phase speed.

For light, it is possible to obtain beams with almost perfect spectral resolution *(such as LASERs*), which is not the case for neutron beams. For neutrons, the notion of wave packet (Superposition of monochromatic waves of slightly different frequencies) is used and it is then necessary to define their group speed v_I^g which is the experimentally accessible quantity.

Définition

The first members of the following equations define these two speeds which are estimated respectively from the De Broglie relations and from the speed equation for neutrons introduced:

$$v_l^{\varphi} = \frac{w_l}{k_l} = \frac{C^2}{v} \quad \text{and} \quad v_l^g = \frac{dw_l}{dk_l} = v$$

Absolute refractive index n_I by the ratio of the phase speeds of the wave in the material I denoted v_I^{φ} and in the vacuum denoted C. This optical index specific to the monochromatic radiation considered is worth:

$$n_I = \frac{C}{v_I^{\varphi}} \quad \text{thus} \quad n_0 = 1$$

By comparing this expression to that of the propagation speed of a plane wave which follows, we define the relationship between the index and the permittivities:

$$v_I^{\varphi} = \frac{C}{\sqrt{\varepsilon_{r,I}\mu_{r,I}}}$$

where $\varepsilon_{r,I} and \mu_{r,I}$correspond to the electric and magnetic permeabilities relative to vacuum, thus $\varepsilon_{r,I} = \varepsilon_I/\varepsilon_0$and $\mu_{r,I} = \mu_I/\mu_0$ where $\varepsilon_0 = 1/(C^2 mu_0) = 8.854 \text{ in } (C^2 J^{-1} m^{-1})$ and $\mu_0 = 4\pi * 10^{-7} \text{ en } (J s^2 C^{-2} m^{-1})$ are specific to vacuum and $\varepsilon_I$and μ_I to material « I » and called absolute permittivities. Their unit is $\mathrm{F.m}^{-1}$. To simplify the writing we will no longer specify the index r in the following. So we link the optical index to these material constants:

$$n_I = \sqrt{\varepsilon_{r,I}\mu_{r,I}}$$

Définition

We also introduce the relative index n_{IT} of the dioptre between the two environments considered and suitable for propagation going from medium *I* (*incident*) to medium « *T* » (*transmitted*). It is equal to the ratio of absolute optical indices:

$$n_{IT} = \frac{n_T}{n_I} = \frac{v_I^{\varphi}}{v_T^{\varphi}} = \frac{k_T}{k_I} = \frac{\lambda_I}{\lambda_T} = \frac{\sqrt{\varepsilon_T \mu_T}}{\sqrt{\varepsilon_I \mu_I}} \quad \text{thus} \quad n_I = n_{0I}$$

For neutrons with vacuum speed v_0^g , we obtain:

$$n_I = \frac{v_I^g}{v_0^g} \quad \text{and} \quad n_{IT} = \frac{v_T^g}{v_I^g} = \frac{k_T}{k_I} = \frac{\lambda_I}{\lambda_T}$$

ii Use of Maxwell's equations for the continuity of fields at the passage of a dioptre

Rappel

Let us recall Maxwell's equations verified by a wave in a perfect dielectric material medium (i.e. with zero permanent volume densities of charge $\rho_{charges}$ and current *j*) which is homogeneous and isotropic (i.e. with dielectric permittivity ε and magnetic $\mu constants$).

Intrinsics :

Magnetic Flux Conservation : $\mathrm{div}(\vec{B})=0$

Maxwell-Faraday (MF) : $\vec{rot}(\vec{E})=\frac{-\partial\vec{B}}{\partial t}$

Depends on the environment : (ε, μ, j)

Maxwell-Gauss (MG) : $\mathrm{div}(\vec{D})=\rho_{charges}$

Maxwell-Ampère (MA) : $\vec{rot}(\vec{H})=\vec{j}+\frac{\partial\vec{D}}{\partial t}$

When a wave spreads in a medium I and reaches a diopter separating it from the middle T, there appears a wave in it. The equations binding the fields of these two waves are said **equations of continuity** and are derived from the Maxwell equations. They apply to the general case of **any polarization** of the incident electromagnetic wave where the fields $vec\ e$ and $vec\ b$ have simply characterized by a normal component (according to the unit vector perpendicular to the diopter $vec\ E_n$) and a **tangential component** with the diopter (according to the co -spanner unit vector at $vec\ e_t$) .

Complément

First, consider the flows of the two members of the first two Maxwell equations through the surface S_a*Delimited by the rectangular outline*C_a of Figure 1.

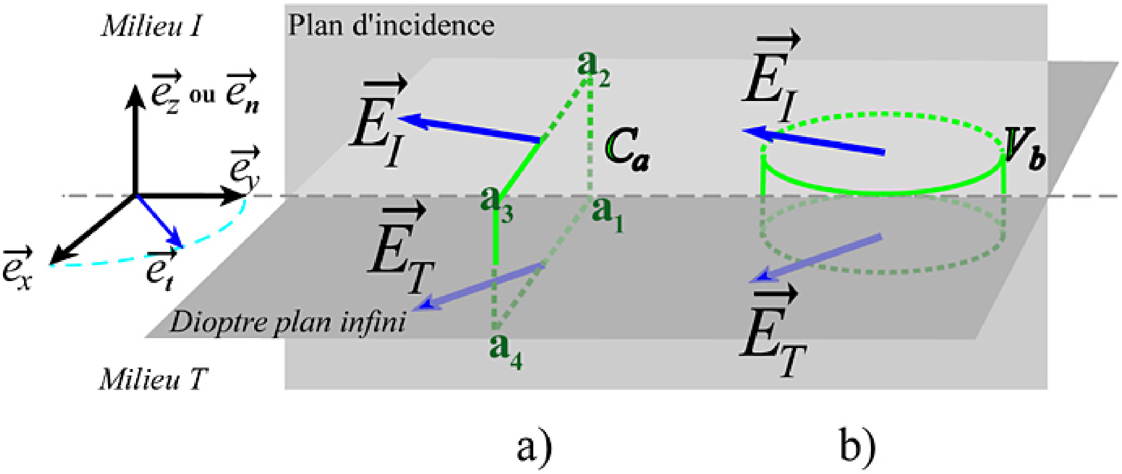


Figure 1 : Diopter Plan continuity equations

We introduce the rectangular contourC_a which delimits the surface S_a, and the cylindrical volume V_b surface S_b, both are involved in the demonstration of the continuity equations of the electromagnetic field at the separation surface of the two indexed media I et T. The height of the two constructions is infinitely small compared to the dimensions of their bases, parallel and on either side of the diopter.

The Maxwell-Faraday equation leads to : $\int\int_{Sa} \vec{rot}(\vec{E}).d\vec{S} = -\int\int_{Sa} \frac{\partial\vec{B}}{\partial t}.d\vec{S}$

According to the Stokes formula applied to the first member and since the derivative of the continuous function B is also, this relationship becomes : $\int_{Ca} \vec{E}.d\vec{l} = -\frac{d}{dt}\int\int_{Sa} \vec{B}.d\vec{S}$

The first term is obtained by considering only the tangential components of $\vec{E}$ including circulation on $a_1\bar{a}_2$ and $a_3\bar{a}_4$ are zero and constant on $a_2\bar{a}_3$ and $a_4\bar{a}_1$.

- The flow of $\vec{B}$ being infinitely small compared to $a_2\bar{a}_3$ we obtain : $E_{t,I}a_2\bar{a}_3 + E_{t,T}a_4\bar{a}_1$. This relationship is valid for this entire plan : $E_{t,I} = E_{t,T}$.

- Let us also give the relation obtained analogously with the Maxwell-Ampère equation : $\vec{rot}(\vec{B}) = \varepsilon\mu\frac{\partial\vec{E}}{\partial t} \Rightarrow \frac{B_{t,I}}{\mu_I} = \frac{B_{t,T}}{\mu_T}$

The Maxwell-Gauss relation $\mathrm{div}(\vec{D}) = 0$and the conservation of the magnetic flux $\mathrm{div}(\vec{B}) = 0$, are used with the cylindrical integration volume described in figure. Using Ostrogradski's theorem we arrive at the following equalities:

$$\int\int\int_{Vb}\mathrm{div}(\vec{D}).dV=\int\int_{Sb}\vec{D}.d\vec{S}=0$$

Only the components normal to the diopter need to be considered since the ratio of fluxes through the bases is infinitely large compared to that through the lateral surfaces and D is constant.

Thus the flows of each base must cancel each other which gives the following relation : $\varepsilon_I E_{n,I} = \varepsilon_T E_{n,T}$

Similar considerations applied to Maxwell's equation lead to the following second equation : $E_{n,I} = B_{n,T}$

1 Snell-Descartes laws

It is not useful to specify the nature of the wave as long as it is scalar, *i.e.* entirely characterized by a single variable (complex or real). When crossing the diopter, the waves can *a priori* undergo a phase change but this must be the same at all infinitely close points and on either side of the interface. At a point on the diopter ($z = 0$) this phase variation must be the same for the three waves I, R and T and we write:

$$d\varphi_I=-k_I\frac{\vec{k}_I}{\|\vec{k}_I\|}d(a_2\vec{a}_1),\quad d\varphi_R=-k_R\frac{\vec{k}_R}{\|\vec{k}_R\|}d(a_2\vec{a}_1)\quad\text{and}\quad d\varphi_T=-k_T\frac{\vec{k}_T}{\|\vec{k}_T\|}d(a_2\vec{a}_1)$$

$$\text{where}\quad k_I=k_0 n_I\quad\text{et}\quad k_T=k_0 n_T$$

By equalizing these expressions we obtain the relationships to be verified in $z = 0$ regardless of $d(a_2\vec{a}_1)$:

$$\text{For reflection :}\quad\left(\frac{\vec{k}_I}{\|\vec{k}_I\|}-\frac{\vec{k}_R}{\|\vec{k}_R\|}\right)=\vec{0}$$

$$\text{For refraction :}\quad\left(n_I\frac{\vec{k}_I}{\|\vec{k}_I\|}-n_T\frac{\vec{k}_T}{\|\vec{k}_T\|}\right)d(a_2\vec{a}_1)=0$$

Rappel

- From the second equality we obtain the **First Law of Refraction** : the refracted ray is in the plane of incidence,
- We also derive the **Second Law of Refraction** corresponding to the equality: $n_I\cos(\alpha_I) = n_T\cos(\alpha_T)$

  where α_I et α_T correspond respectively to the angles between $\vec{k_I}$ et $\vec{k_T}$ with the diopter.
- We also obtain the First Law of Reflection: the reflected ray is in the plane of incidence;
- As well as the Second law of reflection by rewriting the previous equation within the medium alone I and therefore considering the reflection as a refraction in a medium of

opposite index. It is stated as follows: the incident and reflected rays make right angles equal to the normal at the point of incidence $(\vec{e_n})$. The direction of reflection α_R is then called specular and corresponds to an outgoing angle equal to the incident angle $(\alpha_R = \alpha_I)$.

We will see only emptiness $(n_I = 1)$ towards a material (n_T),the transmitted light always deviates from the surface crossed since C is the limiting speed (matter is said to be more refractive than the vacuum to light $(n_T > n_I)$. On the contrary, an X-ray beam approaches the surface since the X-ray refractive indices are generally close to 1 minus 10^{-6} (or practically 1). The case of neutrons is more complex since both situations are possible depending on the materials crossed $(n_T > n_I$ ou $n_T < n_I)$.

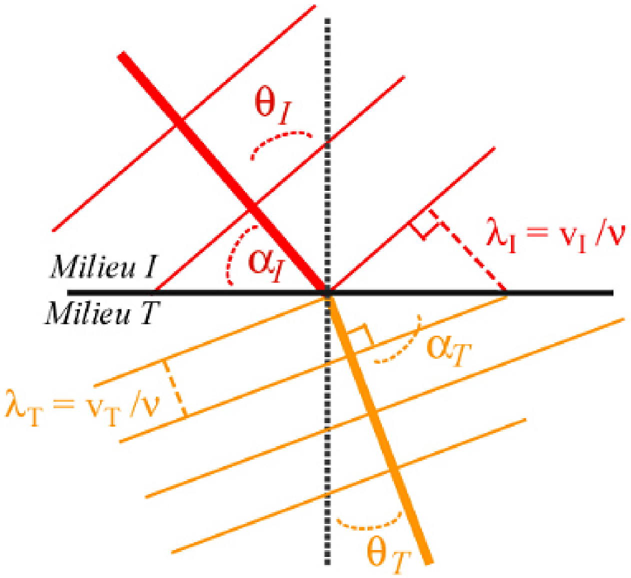


Figure 2 : Transition from medium I to a more refractive material (medium T) of visible light

Complément

The two right triangles represented with a common hypotenuse lead to the relation:

$$\left(\frac{\frac{v_T}{\nu}}{(\sin(\theta_T))}\right)=\left(\frac{\frac{v_I}{\nu}}{(\sin(\theta_I))}\right)$$

where ν is the frequency of the wave which remains constant during this elastic process (conservation of total energy). Speed v and the wavelength λ will, however, be different in each environment.

2 Helmholtz equation for the harmonic plane wave

The propagation of the electric and magnetic field of a wave (I) in any medium is governed by the **Helmholtz equation** obtained by combining Maxwell's equations. In case $\vec{j} = \vec{0}$ and $\rho = 0$:

$$\Delta^2(\vec{E}_I)-\frac{\varepsilon\mu}{C^2}\ddot{E}_I+\vec{\nabla}(\ln(\mu_I))\wedge(\vec{\nabla}\wedge\vec{E}_I)+\vec{\nabla}(\vec{E}_I\cdot\vec{\nabla}(\ln(\varepsilon_I)))=0$$

$$\Delta^2(\vec{H}_I)-\frac{\varepsilon\mu}{C^2}\ddot{H}_I+\vec{\nabla}(\ln(\varepsilon_I))\wedge(\vec{\nabla}\wedge\vec{H}_I)+\vec{\nabla}(\vec{H}_I\cdot\vec{\nabla}(\ln(\mu_I)))=0$$

For a medium with continuous properties (called homogeneous) such that ε and μ have zero gradients, the Helmoltz equation simplifies and we obtain:

$$\Delta(\vec{E}_l)+k_l^2\,\ddot{E}_l=\vec{0} \qquad \text{also noted :} \qquad \vec{\nabla}\wedge\vec{\nabla}\wedge\vec{E}_l-\left(\frac{n_l\,\omega_l}{C}\right)^2\ddot{E}_l=\vec{0}$$

$$\text{where} \quad k_l=\frac{\omega_l}{C}=k_0 n_l\,,k_0=\frac{2\pi}{\lambda_0}\,,n_l^2=\varepsilon_l\mu_I\,,v_l=\frac{C}{\sqrt{\varepsilon_l\mu_l}}$$

and $\ddot{E}_l$being the second derivative of the field with respect to time.

Attention

En pratique on peut considérer un matériau comme étant homogène lorsque ses caractéristiques affectant l'onde le parcourant (ε_l et μ_l) varient très peu sur des longueurs de l'ordre de la longueur d'onde λ_0 et peuvent être considérées comme constantes à l'échelle macroscopique. Homogène n'implique pas isotrope.

In practice we can consider a material to be homogeneous when its characteristics affecting the wave traveling through it (ε_l and μ_l) vary very little over lengths of the order of the length wave $\lambda_0$and can be considered constant on the macroscopic scale. Homogeneous does not imply isotropic.

When the **wave is sinusoidal** it verifies:

$$\frac{1}{C^2}\ddot{E}\equiv\frac{1}{C^2}\frac{\partial^2\vec{E}}{\partial t^2}=\frac{-\omega^2}{C^2}\vec{E}=-k_0^2\vec{E}$$

$$\text{and} \qquad \Delta(\vec{E}_l)+k_l^2\,\vec{E}_l=\vec{0}$$

The electric fields (vector quantity) solutions of the differential equation are written :

$$\vec{E}_l=A_l e^{i(\omega t-\vec{k}_l\vec{r})}\vec{e}_l$$

Here $l = I, R$ et T denote the incident, reflected and transmitted fields.

Remarque

Note that the separation into three waves used to describe this phenomenon is artificial since it does not correspond to physical reality. It is in some way a convenient representation for calculating the electromagnetic field in the medium I which is obtained by interference (amplitude summation) of the waves I and R located in the environment of incidence.

We will now detail the meaning of the different useful quantities (represented in the complex plane in the following figure). First of all we recall that according to an elastic process the temporal dependence is known and defined by the pulsation w of the wave which is conserved ($\omega = 2\pi\nu$). To simplify the writing, we can eliminate this dependence by defining the complex amplitude $E_l = A_l e^{i\varphi_l}$(*called "phasor" by English speakers*). Here A_l is the real amplitude and φ_l is the time-independent phase which is included in the phase factor.$f = e^{i\varphi_l}$. The temporal dependence of the wave is simply restored when needed according to $E_{l,t} = \Re\left(E_l e^{+i(\omega t)}\right)A_l\cos(\omega t + i\varphi_l)$, where \Re designates the real part.

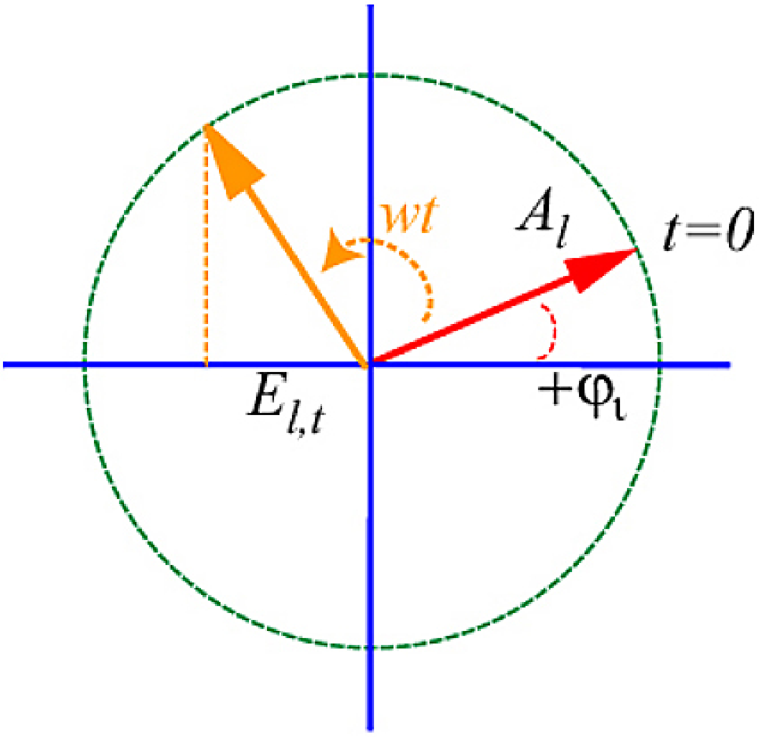


Figure 3 : Illustration of the phase of a traveling wave represented by a complex number

Complément

The quantity $E_I A_I$ rotating clockwise around the origin at angular velocity ω (also noted w) from an origin defined for $t = 0$ at which this vector forms the angle.

Let us study the case of a linearly polarized plane wave whose electric field is perpendicular to the plane of incidence (so-called polarization "TE" for **Electric Transverse**, noted " s" or "$\perp$"). A second polarization often studied corresponds to the wave whose magnetic field is perpendicular to the plane of incidence (so-called polarization"TM" for **Magnetic Transverse**, noted "p" or "$//$").

Remarque

Note that we can always decompose into a linear combination of these two polarizations (s and p) a wave polarized in any way (see figure 4).

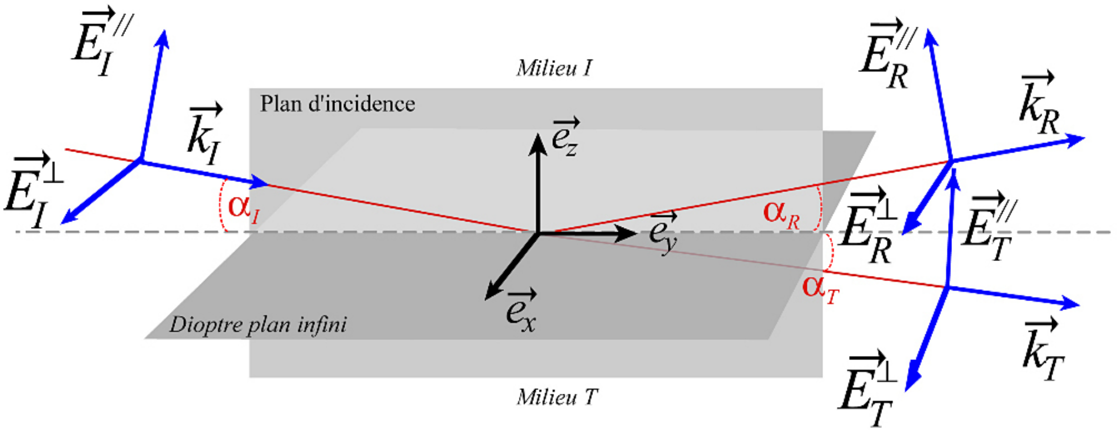


Figure 4 :

Figure 4: Representation of the axes along which we decompose the electric field of any polarization wave falling on the plane diopter ($z=0$) which separates the two semi-infinite mediums of indicesn_I and n_T. Vectors $\vec{e}_x, \vec{e}_y$ et $\vec{e}_z$ define a direct orthonormal trihedron. The so-called incidence plan is supported by$\vec{e}_y$ et $\vec{e}_z$.

Also, it is possible to transpose to the case of polarization "p"all the results that we will obtain for a polarization "s" due to the symmetries respected by Maxwell's equations and which lead to the following substitutions :

$$\begin{array}{ccccc} s\Rightarrow p & \text{with} & E\Rightarrow H & \text{and} & \varepsilon\Rightarrow\mu \\ p\Rightarrow s & \text{with} & -H\Rightarrow E & \text{and} & \mu\Rightarrow\varepsilon \end{array}$$

iii Fresnel coefficients in amplitude, reflectance r and transmittance t

1 Polarized wave TE

The incident wave "TE" for **Electric Transverse** (polarized "s") is taken according to $\vec{e}_x$. The variations of its vector electric field are :

$$\vec{E}_I(\vec{r},t)=E_{x,I}(\vec{r},t)\vec{e}_x=A_I\cos(\omega t-\vec{k}_I\vec{r})\vec{e}_x \quad \text{with} \quad \begin{array}{l}\vec{e}_x\vec{e}_x=1\\ \vec{e}_x\vec{k}_I=0\end{array}$$

From this expression we can identify a family of planes orthogonal to the direction $\vec{k}_I$ constituting the places where the electric field oscillates in phase ($\vec{k}_I\vec{r}$ is constant). Two of these consecutive planes are separated by the wavelength λ. The phase speed v_φ which defines the equiamplitude propagation along $\vec{k}_I$ is obtained according to the following differential equation where the coordinate s collinear with $\vec{k}_{I intervenes}$:

$$\frac{d}{dt}(\omega t-\frac{2\pi}{\lambda}s)=0$$

Let us apply the general relationships that this wave must respect when crossing the diopter shown in the figure below. We choose the frame of reference such that the propagation vector of the incident wave has only two components according to y and z : $\vec{k}_I = k_{y,I}\vec{e}_y + k_{z,I}\vec{e}_z$

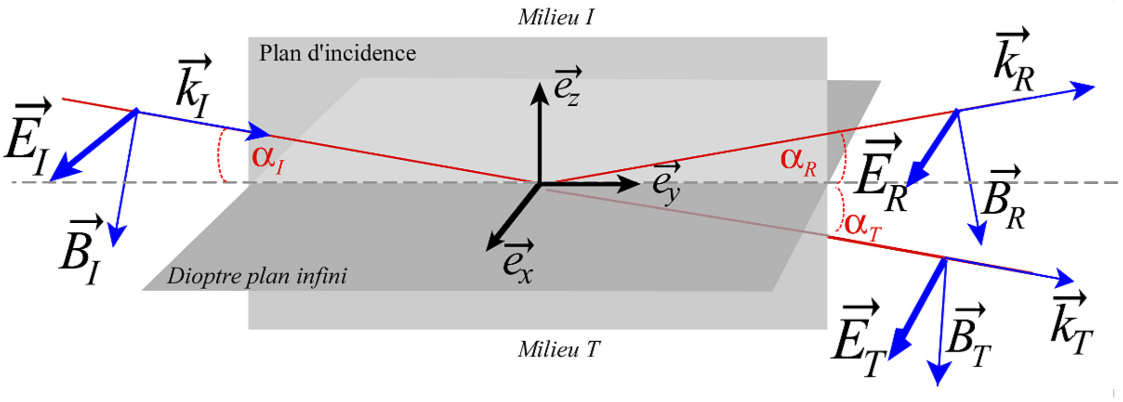


Figure 5 : Representation of the direct trihedron (k, E, B) for the TE wave (electric transverse, polarized "s")

According to Descartes' first laws, the wave vectors belong to the plane of incidence containing the normal to the diopter. The diffusion vectors of the reflected and transmitted waves are therefore written : $\vec{k}_I = k_{y,I}\vec{e}_y + k_{z,I}\vec{e}_z$ with $I = R$ ou T.

According to the second law known as Snell-Descartes the reflection is purely specular, that is to say at an outgoing angle equal to the incident angle ($\alpha_R = \alpha_I$). Considering that this process is elastic $\|\vec{k}_R\| = \|\vec{k}_T\| = \|\vec{k}_I\| = n_I k_0$ and according to the conservation of the tangential component of the wave vectors $k_{x,R} = k_{x,T} = k_{x,I}$, we obtain :

$$\vec{k}_I = k_0(\cos(\alpha_I)\vec{e}_y - \sin(\alpha_I))\vec{e}_z$$
$$\vec{k}_R = k_0(\cos(\alpha_I)\vec{e}_y + \sin(\alpha_I))\vec{e}_z$$

$$\vec{k}_T = n_{IT} k_0(\cos(\alpha_T)\vec{e}_y - \sin(\alpha_T))\vec{e}_z \quad \text{where} \quad n_{IT} = \frac{n_T}{n_I}$$

The continuity of the tangential electric field component (to the diopter) is written (according to Fresnel) :

$$(\vec{E}_I + \vec{E}_R)\cdot\vec{e}_x = \vec{E}_T\cdot\vec{e}_x \quad \text{either} \quad (A_I + A_R)e^{i(\omega t - \vec{k}_I\vec{r})} = A_T e^{i(\omega t - \vec{k}_I\vec{r})}$$

According to the expressions of the diffusion vectors, we obtain:

$$(A_I + A_R)e^{-i(y k_I \cos(\alpha_I))} = A_T e^{-i(y k_T \cos(\alpha_T))}$$

This relation being satisfied over the entire plane interface ($\forall x, y$ at $z = 0$), we obtain:

$$A_I + A_R = A_T \quad \text{and} \quad k_I\cos(\alpha_I) = k_T\cos(\alpha_T)$$

This latter relationship being known as the Snell-Descartes law. We should then specify for a defined diopter, that a different angle of refraction exists for each angle of incidence, i.e. $\alpha_T = f(\alpha_I)$.

The tangential component of the magnetic field is also preserved when crossing the diopter and we obtain its expression according to Maxwell's relation linking the magnetic field to the electric field:

$$\vec{rot}(\vec{E}) = \frac{-\partial\vec{B}}{\partial t} = i\omega\vec{B}$$

Note that a plane wave is said to be transverse because the vectors $\vec{E}$or $\vec{B}$ are in the wave plane which is perpendicular to the direction of propagation. These two vectors are also perpendicular to each other and form a direct trirectangular trihedron such as for our case:

$$\vec{B} = \frac{1}{v^{\varphi}}\vec{k}\wedge\vec{E}$$

By projection on the axis $\vec{e}_y$ we obtain the tangential component of $\vec{B}$equal to:

$$B_y = \vec{B}\cdot\vec{e}_y = \frac{\vec{rot}(\vec{E})\cdot\vec{e}_y}{i\omega} \quad \text{where} \quad \vec{rot}(\vec{E}) = \frac{\partial E_x}{\partial z}\vec{e}_y - \frac{\partial E_x}{\partial y}\vec{e}_z \quad \text{either} \quad B_y = \frac{1}{i\omega}\frac{\partial E}{\partial z}$$

Its continuity at the passage of the diopter is written:

$$(\vec{B}_I+\vec{B}_R)\cdot\vec{e}_y=\vec{B}_T\cdot\vec{e}_y \quad \text{either} \quad k_I(A_I-A_R)\sin(\alpha_I)=k_T A_T\sin(\alpha_T)$$

which leads to $(A_I - A_R)\sin(\alpha_I) = n_{IT}A_T\sin(\alpha_T)$

We thus obtain the Fresnel equations by introducing the reflection coefficients (r) and transmission (t).

Remarque

Note that these coefficients are in amplitude (complex numbers) and that they are often called reflectance and transmitance respectively.

The equation is rewritten:

$$1 + r_\perp = t_\perp \text{ où } r = \frac{A_R}{A_I} \text{ et } t = \frac{A_T}{A_I}$$

which becomes:

$$1 - r_\perp = n_{IT}t_\perp\frac{\sin(\alpha_T)}{\sin(\alpha_I)}$$

By combining relationships to r and for t, we obtain the Fresnel relations (1823) which can be simplified by using the Snell-Descartes relation leading to the second members below:

Fondamental

$$r_\perp = \frac{n_I\sin(\alpha_1) - n_T\sin(\alpha_T)}{n_I\sin(\alpha_I) + n_T\sin(\alpha_T)} = \frac{\sin(\alpha_I - \alpha - T)}{\sin(\alpha_I + \alpha_T)}$$

$$\text{et } t_\perp = \frac{2n_I\sin(\alpha_I)}{n_I\sin(\alpha_I) + n_T\sin(\alpha_T)} = \frac{2\sin(\alpha_I)\cos(\alpha_T)}{\sin(\alpha_I + \alpha_T)}$$

et $t_\perp = \dfrac{2n_I\sin(\alpha_I)}{n_I\sin(\alpha_I) + n_T\sin(\alpha_T)} = \dfrac{2\sin(\alpha_I)\cos(\alpha_T)}{\sin(\alpha_I + \alpha_T)}$

2 TM polarized wave

The same reasoning applied to the case of an electric field wave polarized parallel to the plane of incidence (called polarized"P") leads to :

Fondamental

$$r_\parallel=\frac{n_T\sin(\alpha_I)-n_I\sin(\alpha_T)}{n_T\sin(\alpha_I)+n_I\sin(\alpha_T)}=\frac{\tan(\alpha_I-\alpha_T)}{\tan(\alpha_I+\alpha_T)}$$

$$\text{and} \quad t_\parallel=\frac{2\,n_I\sin(\alpha_I)}{n_T\sin(\alpha_I)+n_I\sin(\alpha_T)}=\frac{2\sin(\alpha_I)\cos(\alpha_T)}{\sin(\alpha_I+\alpha_T)\cos(\alpha_I-\alpha_T)}$$

Attention

Experimentally, what is commonly called intensity is measured on the detector. This terminology is accurate when the measured beam arrives perpendicular to the detection surface. When we introduce an angle between this surface and a beam, it would be more accurate to speak of illumination.

In electromagnetic theory, this quantity corresponds to the integration of the energy flow vector of the wave $\vec{S}$ on the closed unit vector measurement surface defining its normal $\vec{n}$. Let us give the expression for the general intensity ($\vec{n}$ et $\vec{S}$ are collinear) and its expression developed for the particular case of plane waves :

and for a plane wave:

$$\vec{S}=\frac{C}{4\pi}\left(\vec{E}\wedge\vec{B}\right)$$

$$\vec{S}=\frac{C}{4\pi}\left(E\,B\,\vec{s}\right)=\frac{C}{4\pi}\left(E^2\sqrt{\frac{\varepsilon}{\mu}}\,\vec{s}\right)\quad \text{où}\quad \vec{s}=\frac{\vec{k}}{\left\|\vec{k}\right\|}$$

For a perfect dielectric ($\mu=1$), the module of this vector is $\frac{CnE^2}{4\pi}$ and corresponds to the light intensity in $\mathrm{J.s^{-1}.m^{-2}}$ spreading next $\vec{k}$. For the problem we are dealing with, let us estimate the quantity of diopter energy per unit area and time which is noted J. It is an illumination which has the unity of an intensity and which corresponds to the flux per surface common to the three beams considered in this approach (I, R et T).

$$J_I=S_I\sin(\alpha_I)=\frac{n_I C}{4\pi}|A_I|^2\sin(\alpha_I)$$
$$J_R=S_R\sin(\alpha_I)=\frac{n_I C}{4\pi}|A_R|^2\sin(\alpha_I)$$
$$J_T=S_T\sin(\alpha_I)=\frac{n_I C}{4\pi}|A_T|^2\sin(\alpha_I)$$

The quantities in which we are interested are thus completely defined:

Fondamental

$$R=\frac{J_R}{J_I}=\frac{|A_R|^2}{|A_I|^2}=r\,\tilde{r}$$
$$T=\frac{J_T}{J_I}=\frac{n_T\sin(\alpha_T)}{n_I\sin(\alpha_I)}\frac{|A_T|^2}{|A_I|^2}=\frac{n_T\sin(\alpha_T)}{n_I\sin(\alpha_I)}t\,\tilde{t}=\frac{k_{z,T}}{k_{z,I}}t\,\tilde{t}=n_{z,IT}\,t\,\tilde{t}$$

Remarque

The pre-factor of $tt*$ (*where the complex conjugate of t is denoted t* or*$\tilde{t}$) is $n_{z,IT}$ and comes from the fact that if the incident and reflected flows have the same section (perpendicular to the propagation), the transmitted flow does not spread over the same section. We can verify the energy conservation relation for the two defined polarizations:

$$R+T=1$$

iv Quantum theory for neutron reflectivity

The wave-particle duality of electromagnetic radiation materializes from a mathematical point of view by the resemblance between the Helmholtz equation governing the propagation of light and **the stationary Schrödinger equation specific to massive particles** such as neutrons.

By using the formalism of the reference works of quantum mechanics [4 [Neutron Optics, An introduction to the theory of Neutron Optical Phenomena and Their Applications], 5 [Theory of Neutron Scattering from Condensed Matter], 6 [Mécanique Quantique], 7 [Quantum mechanics]] we will deal with the case studied in the previous paragraph according to the classical wave theory and establish the connections between the expressions found according to these two approaches.

We will therefore look for the expression of the time-independent wave function specific to the particle subjected to the potential $V(r)$. The most general solution to the Schrödinger equation is :

$$\Psi(\vec{r},t)=\Psi(\vec{r})e^{\frac{-iEt}{\hbar}}$$

We deal with the elastic diffusion (without change of energy) of neutrons during a stationary phenomenon (independent of time). We will determine $\Psi(\vec{r})$, the **coherent stationary wave function of the non-relativistic quantum particle** used for all neutron optics phenomena. It is the solution of the Schrödinger equation known as a body with time-independent eigenvalues. :

$$\left(\frac{-\hbar}{2m}\Delta+V(r)\right)\Psi(\vec{r})=E\Psi(\vec{r}) \;\Rightarrow\; \nabla^2(\Psi(\vec{r}))+\frac{2m}{\hbar^2}(E-V(r))\Psi(\vec{r})=0$$

In a vacuum (taken as a medium of incidence I), the energy of the particle E_0 is purely kinetic. The module of **wave vector** is expressed according to this energy :

$$k_0=\sqrt{\frac{2m}{\hbar^2}(E_0)}=\frac{2\pi}{\lambda_0}$$

In a material (noted T), energy (E_T) is the sum of the kinetic energy of the particle (T_T) and potential energy (V_T) measuring its interaction energy with matter . The modulus of the wave vector is :

$$k_T=\sqrt{\frac{2m}{\hbar^2}(E_T-V_T)}$$

Following the conservation of energy associated with the encounter of a diopter, we obtain:

$$E_0=\frac{(\hbar k_0)^2}{2m}=\frac{(\hbar k_T)^2}{2m}+V_T$$

Fondamental

According to the optical formalism, the ratio of the modules of the diffusion vectors is the refractive index of the material with respect *T* to vacuum. What follows is the expression of this ratio and the equalities linking it to the quantities used in quantum formalism :

$$n_T=n_{0T}=\frac{n_T}{n_0}=\frac{k_T}{k_0}=\sqrt{1-\frac{V_T}{E_0}}=\sqrt{1-\frac{4\pi}{k_0^2}(\rho b)_T}=\sqrt{1-\frac{\lambda_0^2}{\pi}(\rho b)_T}$$

The product $(\rho b)_T$ is the material diffusion length density T (of inverse unit to a surface and often given in $[\mathring{A}^{-2}]$). In optics, the speed of propagation of radiation in a material I is translated into terms of optical index of the medium (n_I) which amounts to comparing this speed to that which the wave would have in a vacuum.

Remarque

To this characteristic quantity, the community of X-rays and neutrons prefers the diffusion length density whose expression does not depend directly on the wavelength although it is also specific to certain energy ranges of the radiation .

These two quantities are linked by the relationship above as well as with the critical angle measured from a vacuum following the relationship that we will introduce later.

We can also introduce into the expression the diffusion potential of the material T defined by:

$$F_T = \frac{k_0^2}{4\pi}\left(n_T^2 - 1\right) = -(\rho\, b)_T$$

For neutrons the potential V_T is obtained by integrating the **Fermi pseudo-potential** on the volume of the material T considered. In the energy range used, this potential makes it possible to quantify the bound neutron-nucleus interaction :

$$F^{Fermi}(r) = \frac{2\pi\hbar^2}{m} b_{core}\,\delta(r)$$

Note that the potential V_T is for this example considered constant in the material V assumed therefore to be homogeneous. After integration over the medium volume T, we obtain the macroscopic potential :

$$V_T = \frac{1}{Vol}\int_{Vol} V^{Fermi}(r)\,dr = \frac{2\pi\hbar^2}{m}(\rho\, b)_T$$

The plane diopter on which the reflection takes place separates two semi-infinite environments of constant potentials. We define :

$$V = V(z) = \begin{cases} V_I & \text{for} \quad z > 0 \\ V_T & \text{for} \quad z < 0 \end{cases}$$

By introducing the refractive index into the expression, we obtain:

$$\nabla^2(\Psi(\vec{r})) + n^2(\vec{r})\,k^2(\vec{r})\,\Psi(\vec{r}) = 0$$

La solution générale de cette équation s'exprime comme une superposition d'ondes planes :

$$\Psi(\vec{r}) = \sum_l A_l e^{-i\vec{k}_l\vec{r}}$$

In one dimension, the equation becomes :

$$\frac{\partial^2}{\partial z^2}(\Psi(z)) + k_0^2\left(n^2(z) - \cos^2(\alpha_I)\right)\Psi(z) = 0$$

where α_I corresponds is the angle of incidence of the wave on the diopter. This expression is called the reflectivity equation and its solutions (plane waves) are then of the type:

$$\Psi(r)=\begin{cases}\Psi_I+\Psi_R & \text{for} \quad z>0\\ \Psi_T \quad \text{for} \quad z<0\end{cases}$$

$$\text{where : for} \quad z>0:\begin{cases}\Psi_I=A_I e^{-i\vec{k}_I\vec{r}}\\ \Psi_R=A_R e^{-i\vec{k}_R\vec{r}}\end{cases} \quad \text{and for} \;\; z<0: \Psi_T=A_T e^{-i\vec{k}_T\vec{r}}$$

The continuity of this wave function and its derivative at the meeting of the diopter lead to :

$$A_I e^{-i\vec{k}_I\vec{r}}+A_R e^{-i\vec{k}_R\vec{r}}=A_T e^{-i\vec{k}_T\vec{r}}$$
$$\vec{k}_I A_I e^{-i\vec{k}_I\vec{r}}+\vec{k}_R A_R e^{-i\vec{k}_R\vec{r}}=\vec{k}_T A_T e^{-i\vec{k}_T\vec{r}}$$

Fondamental

we find the so-called "Fresnel" coefficients specific to the passage of the material I to the material T :

$$r_{IT}=\frac{A_R}{A_I}=\frac{k_{z,I}-k_{z,T}}{k_{z,I}+k_{z,T}}=\frac{Q_I-Q_T}{Q_I+Q_T}$$

$$\text{and} \quad t_{IT}=\frac{A_T}{A_I}=\frac{2k_{z,I}}{k_{z,I}+k_{z,T}}=\frac{2Q_I}{Q_I+Q_T}$$

where the modules of the diffusion vectors Q are twice the moduli of the wave vectors k.

Remarque

Quantum theory naturally leads us to a scalar quantity of the reflection coefficient r_{IT}. If we compare this coefficient to that obtained in the previous paragraph in the context of optical theory, we see that it corresponds to the reflection coefficient $r_\perp$. This explains the analogy often made between these two quantities.

It is accepted that we can neglect the differences between $r_\perp$ et $r_{//}$ when reflection occurs at low angles of incidence for non-polarized radiation.

These are the usual working conditions with X-ray beams used to characterize thin layers. Under these conditions, it seems to us that it would be more correct to calculate the different reflection coefficients corresponding to the polarizations of the beam. In a way, we consider a non-polarized beam as a beam containing all the polarizations and therefore as a set of waves which will reflect differently on the diopter considered. We have not carried out this calculation for which it is necessary to consider the interference between all these waves in order to obtain an effective reflection coefficient for the beam.

The accessible quantity being the particle flux, we apply the particle current density operator to the wave functions :

$$J_l=\frac{-i\hbar}{2m}\left[\tilde{\Psi}\frac{\partial}{\partial z}\Psi-\Psi\frac{\partial}{\partial z}\tilde{\Psi}\right]$$

For the incident wave :

$$\Psi_I = A_I e^{-i\vec{k}_I\vec{r}},\ \ \widetilde{\Psi}_I = \widetilde{A}_I e^{+i\vec{k}_I\vec{r}},\ \ \nabla(\Psi_I) = -i\vec{k}_I A_I e^{-i\vec{k}_I\vec{r}} \quad \text{et} \quad \nabla(\widetilde{\Psi}_I) = -i\vec{k}_I \widetilde{A}_I e^{+i\vec{k}_I\vec{r}}$$

$$\text{either}\ \ J_l = \frac{-i\hbar}{2m}\left[i\,2\,A_I\widetilde{A}_I\vec{k}_I\right] = \frac{\hbar\vec{k}_I}{m}|A_I|^2 = \frac{\vec{p}_I}{m}|A_I|^2 = \vec{v}_I|A_I|^2$$

For the reflected wave :

$$\text{either}\quad J_R = \frac{-i\hbar}{2m}\left[i\,2\,A_R\widetilde{A}_R\vec{k}_R\right] = \frac{\hbar\vec{k}_R}{m}|A_R|^2 = \frac{\vec{p}_R}{m}|A_R|^2 = \vec{v}_R|A_R|^2 = \vec{v}_R\, r\,\widetilde{r}\,|A_I|^2$$

And for the transmitted wave: Consider that the vector $\vec{k}_T$ can have complex components (this case is discussed later by introducing the absorption of radiation in the material). We pose $\vec{k}_T$ by defining the ratings :

$$\Re(\vec{k}_T) = \Re(\vec{k}_{y,T})\vec{e}_y + \Re(\vec{k}_{z,T})\vec{e}_z \quad \text{and} \quad \Im(\vec{k}_T) = \Im(\vec{k}_{y,T})\vec{e}_y + \Im(\vec{k}_{z,T})\vec{e}_z$$

We obtain :

$$\Psi_T = A_T e^{-i(\Re(\vec{k}_T)+i\Im(\vec{k}_T))\vec{r}} \ \ ; \ \ \widetilde{\Psi}_T = \widetilde{A}_T e^{(\Im(\vec{k}_T)+i\Re(\vec{k}_T))\vec{r}}$$

$$\nabla_z(\Psi_T) = A_T(\Im(k_{z,T}) - i\Re(k_{z,T}))e^{(\Im(\vec{k})-i\Re(\vec{k}))\vec{r}}$$

$$\text{and}\quad \nabla_z(\widetilde{\Psi}_T) = \widetilde{A}_T(\Im(k_{z,T}) + i\Re(k_{z,T}))e^{(\Im(\vec{k})+i\Re(\vec{k}))\vec{r}}$$

$$\text{either}\quad J_T = \frac{-i\hbar}{2m}\left[-i\,2|A_T|^2\Re(k_{z,T})e^{2\Im(\vec{k}_T)\vec{r}}\right] = \frac{-\hbar}{m}(t\,\widetilde{t}\,)|A_I|^2\Re(k_{z,T})e^{2\Im(\vec{k}_T)\vec{r}}$$

We will retain the following flows, for the incident, reflected and transmitted beam, respectively:

$$\vec{J}_l = \frac{\hbar\vec{k}_I}{m}|A_I|^2 \ \ ; \ \ \vec{J}_R = \frac{\hbar\vec{k}_R}{m}(r\,\widetilde{r}\,)|A_I|^2 \quad \text{and} \quad \vec{J}_T = \frac{-\hbar\Re(k_{z,T})}{m}\frac{\vec{k}_T}{\|k_T\|}(t\,\widetilde{t}\,)|A_I|^2 e^{2\Im(\vec{k}_T)\vec{r}}$$

and reflectivity and transmittance, as reported:

Fondamental

$$\begin{cases} R = \dfrac{|\vec{J}_R|}{|\vec{J}_I|} = r\,\tilde{r} = \left|\dfrac{k_{z,I} - k_{z,T}}{k_{z,I} + k_{z,T}}\right|^2 \\ T = \dfrac{|\vec{J}_T|}{|\vec{J}_I|} = \dfrac{\Re\left(k_{z,T}\right)}{k_I}\left(t\,\tilde{t}\right) e^{2\,\Im(\vec{k}_T)\vec{r}} = \dfrac{\Re\left(k_{z,T}\right)}{k_I}\left|\dfrac{2\,k_{z,I}}{k_{z,I} + k_{z,T}}\right|^2 e^{2\Im(\vec{k}_T)\vec{r}}\, k_{x,T} = k_{x,I} \end{cases}$$

Thus we find $R + T = 1$ when $\Im(\vec{k}_T) = \vec{0}$ (we often note : $\Im(k_T) = -\beta \mathrm{Im}\,(\vec{k}_T) \equiv -\beta$). When this is not the case, the exponential introduces a decrease linked to the absorption of the wave in the medium$T$. This case is discussed below.

v Total reflection from a critical angle

1 Cas d'un milieu non absorbant

Définition

Firstly consider that the refractive index n_{IT} is a pure real. According to the optical formalism, the **total reflection** ($R = 1$) takes place when the incident angle α_I is less than a critical value noted $\alpha_I^{(c,IT)}$ or $\alpha_I^{(c)}$ and corresponding to the establishment of a wave refracted tangentially at the interface α_T. The value of this critical angle (specific to the passage of the material I to the material T), can be obtained by the Snell-Descartes relation :

$$\cos\left(\alpha_I^{(c,IT)}\right) = \frac{n_T}{n_I} = n_{IT}$$

We can therefore distinguish the following two situations : $n_I < n_T$ et $n_I > n_T$.The first case can be illustrated by the passage of a light wave from the air $(n_I = 1)$ in water $(n_T = 1,33)$ and which can never be fully reflected. The second case is obtained when the propagation is from water to air, the **total reflection** takes place over a wide angular range ranging from 0 to $\alpha_I^{(c,IT)} = a\cos\,(1/1,54) = 49,51$.

Let us now consider what total reflection means in the context of quantum formalism. Mathematically, it is obtained according to when $Q^2 \leq 0$, $k^2(n^2 - \cos^2(\alpha_I)) \leq 0$. This inequality is respected when the kinetic energy of the particles has a component perpendicular to the interface ($E\,\sin^2(\alpha_I)$) below the potential barrier V_T. In this case the particles can no longer penetrate the material and are reflected. This is only possible when the group velocity of the particles would decrease if they passed through the material T (this medium is qualified as less refractive than the material $I(n_T < n_I)$). The total reflection in the incident medium can therefore only take place at the interface with a material of diffusion length density $(\rho b)_T$ higher (i.e. lower index).

Remarque

The **critical angle** of a diopter is a constant. It can be linked to optical indices or diffusion length densities which are simply calculated for a material.

It is useful to introduce these constants in the expression for the modulus of the wave vector in the material T which is a function of the wave vector in the medium$I$. We have :

$$\begin{cases} k_I^2=(k_{z,I})^2+(k_{x,I})^2=n_I^2 k_0^2 \\ k_T^2=(k_{z,T})^2+(k_{x,T})^2=n_T^2 k_0^2 \\ k_{x,T}=k_{x,I} \end{cases}$$

These equations give :

$$(k_{z,T})^2-(k_{z,I})^2=\left(n_T^2-n_I^2\right)k_0^2$$

It will also be useful to introduce the ratio of the perpendicular components :

$$n_{z,IT}=\frac{k_{z,T}}{k_{z,I}}$$

which leads to new expressions of the Fresnel coefficients :

$$\begin{cases} r=\frac{A_R}{A_I}=\frac{k_{z,I}-k_{z,T}}{k_{z,I}+k_{z,T}}=\left(\frac{1-n_{z,IT}}{1+n_{z,IT}}\right) \\ t=\frac{A_T}{A_I}=\frac{2k_{z,I}}{k_{z,I}+k_{z,T}}=\left(\frac{2}{1+n_{z,IT}}\right) \end{cases} \quad \text{where : } n_{z,IT}=\left(\frac{A_I-A_R}{A_T}\right)$$

At the critical angle, we have by definition :

$$\begin{cases} When\,\alpha_I=\alpha_I^{(c)} \\ k_{z,I}(\alpha_I)=k_{z,IT}^{(c)} \\ k_{z,T}(\alpha_I)=0 \end{cases}$$

Transferring this expression to the one seen just before, we obtain :

$$\left(k_{z,IT}^{(c)}\right)^2=\left(n_I^2-n_T^2\right)k_0^2$$

Following the expression linking the optical indices to the diffusion length densities of the materials and without any other approximation than those specific to the definition of the Fermi potential, we rewrite the expression :

$$\left(k_{z,IT}^{(c)}\right)^2=4\pi\left((\rho b)_T-(\rho b)_I\right)$$

This quantity, independent of angles, is specific to the interface between materials I and T and is attached in the middle I where reflection takes place. It is convenient to express the normal component of the diffusion vector in the material T according to this constant and its value in the material$I$. The equation becomes :

$$(k_{z,T})^2=(k_{z,I})^2-\left(k_{z,IT}^{(c)}\right)^2$$

If we want to understand the nature of the two reflectivity regimes delimited by $k_{z,IT}^{(c)}$, it is necessary to introduce this constant into the expression of the complex reflectivity coefficient. We formulate the equation differently by introducing $k_{z,I}^{(c)}$ given by:

$$\begin{cases} r_{IT} = \left(\dfrac{1 - n_{z,IT}}{1 + n_{z,IT}} \right) \\ n_{z,IT} = \dfrac{k_{z,T}}{k_{z,I}} = \sqrt{1 - \left(\dfrac{k_{z,IT}^{(c)}}{k_{z,I}} \right)^2} \end{cases}$$

Remarque

- When the angle of incidence is large enough to have $k_{z,I} > k_{z,IT}^{(c)}$,the Fresnel coefficient of the interface is real since $n_{z,IT}$ is a real number between 0 and 1. The reflectivity (i.e. the reflected intensity) decreases according to a law in $k_{z,I}^{(c)}$ (*This law is analogous to Porod's law in small angle diffusion*).
- At lower angles of incidence such as $k_{z,I} < k_{z,IT}^{(c)}$, becomes pure imagination. Using the classic notations associated with complex numbers and the sign conventions specific to phases, we rewrite r_{IT} by posing :

$$n_{z,IT} = -i\,\Im(n_{z,IT}) \quad \text{where} \quad \Im(n_{z,IT}) = \sqrt{\left| 1 - \left(\frac{k_{z,IT}^{(c)}}{k_{z,I}} \right)^2 \right|}$$

$$\text{either:} \qquad r_{IT} = \left(\frac{1 - n_{z,IT}}{1 + n_{z,IT}} \right) = \frac{1 + i\,\Im(n_{z,IT})}{1 - i\,\Im(n_{z,IT})} = |r_{IT}|\, e^{i\varphi}$$

When $k_{z,I}$ varies from 0 to $k_{z,IT}^{(c)}$, the module $|r_{IT}|$ worth 1 and the phase φ varies monotonically from π to 0. Reflectivity, presents a plateau at 1 in **this so-called total internal reflection regime (in the middle *I*) for the incident wave**. In the middle T, an inhomogeneous wave propagates parallel to the interface following, by definition, the direction normal to the equiphase planes. This wave is called evanescent because it decreases exponentially according to its distance from the interface, which defines "equiamplitude" planes parallel to it. O.Bryngdahl describes this phenomenon and its applications in optical imaging in detail in the reference [8 [Evanescent Waves in Optical Imaging]].

Conseil

To explain the total reflection of a plane wave of finite extension, it is necessary to consider that the energy enters the substrate through one of the edges of the incident wave and moves in the form of an evanescent wave along a trajectory parabolic type. It emerges at the other edge of the incident wave which generates a slight lateral movement of the plane of incidence. Averaging over time, the direction of the net energy flow is therefore parallel to the interface. This penetration makes it a volume phenomenon which is reduced to two dimensions (surface phenomenon) when the incident plane wave is considered of infinite extension.

2 Case of an absorbent medium

In order to calculate the reflectivity of an absorbing medium, we introduced an imaginary component to the index n_{IT} which is now called **complex refractive index**.

$$n_{IT}=\Re\left(n_{IT}\right)+i\,\Im\left(n_{IT}\right)$$

The **real part** is always called the refractive index and is often noted $1-\delta$. The **imaginary part** is here the opposite of the extinction coefficient βwhich is a positive real just like δ. We have $\Im(n_{IT})=-\beta$ according to the conventions we follow [9 [Ellipsometry and polarized light]]. The Snell-Descartes laws as well as the Fresnel relations are still applicable.

This writing leads us to also decompose the quantity according to a real and imaginary part :

$$n_{z,IT}=\Re\left(n_{z,IT}\right)+i\,\Im\left(n_{z,IT}\right)$$

and similarly we can also decompose :

$$\vec{k}_T=\Re\left(\vec{k}_T\right)+i\,\Im\left(\vec{k}_T\right)$$

So that this notation does not introduce any ambiguity, let us specify that :

$$\vec{k}_T=\left(k_{y,T}\right)\vec{e}_y+\left(k_{z,T}\right)\vec{e}_z=\left(\Re\left(k_{y,T}\right)+i\,\Im\left(k_{y,T}\right)\right)\vec{e}_y+\left(\Re\left(k_{z,T}\right)+i\,\Im\left(k_{z,T}\right)\right)\vec{e}_z$$

The expressions seen previously make it possible to eliminate α_T and introduce α_I in the expression for the wave vector T. We obtain:

$$\vec{k}_T=k_0\left(\cos\left(\alpha_I\right)\vec{e}_y-\left(\frac{A_I-A_R}{A_T}\right)\sin\left(\alpha_I\right)\vec{e}_z\right)$$

which according to the expression of $n_{z,IT}$ become :

$$\vec{k}_T=k_0\left(\cos\left(\alpha_I\right)\vec{e}_y-\left(n_{z,IT}\right)\sin\left(\alpha_I\right)\vec{e}_z\right)$$

By identifying the real and imaginary parts we obtain :

$$\begin{cases}\Re\left(k_{y,T}\right)=k_0\cos\left(\alpha_I\right)\\ \Im\left(k_{y,T}\right)=0\end{cases}\quad\text{and}\quad\begin{cases}\Re\left(k_{z,T}\right)=k_0\,\Re\left(n_{z,IT}\right)\sin\left(\alpha_I\right)\\ \Im\left(k_{z,T}\right)=k_0\,\Im\left(n_{z,IT}\right)\sin\left(\alpha_I\right)\end{cases}$$

The imaginary component of the transmitted wave therefore varies according to the depth z . $k_{z,I}$ is real (for example when the medium of incidence is a vacuum, $I=0$), we simply obtain :

$$\begin{cases}\Re\left(n_{z,0T}\right)=\left(1/k_{z,0}\right)\Re\left(k_{z,T}\right)\\ \Im\left(n_{z,0T}\right)=\left(1/k_{z,0}\right)\Im\left(k_{z,T}\right)\end{cases}\text{, with}\quad k_{z,0}=k_0\sin\left(\alpha_I\right)\quad\text{and}\quad k_0=2\frac{\pi}{\lambda_0}$$

These expressions can be injected into the expression established for the flow of transmitted particles which leads to :

$$\vec{J}_T=\frac{-\hbar\,\Re\left(k_{z,T}\right)}{m}\,\frac{\vec{k}_T}{\|k_T\|}\left|\frac{2k_{z,0}}{k_{z,0}+k_{z,T}}\right|^2\left|A_0\right|^2e^{-2\Im\left(k_{z,T}\right)z}$$

$$\text{and}\quad T=\frac{\Re(k_{z,T})}{k_0}\left|\frac{2k_{z,0}}{k_{z,0}+k_{z,T}}\right|^2 e^{-2\Im(k_{z,T})z}$$

since the imaginary component of the vector k_T only depends on z.

The exponential of this expression has a real argument and decreases with depth z. The term $\Im(k_{z,T})$ introduces the consideration of absorption and likewise the evanescence of the wave when $k_{z,I} < k_{z,IT}^{(c)}$. We define a characteristic length of the material called **depth of penetration** ($z_{1/e}$) beyond which the transmitted flow represents the fraction $1/exp(1) \sim 0,368$ of the incident flow.

$$\text{Either}\quad T=\frac{|\vec{J}_T|}{|\vec{J}_I|}=\frac{1}{e^1}\quad\text{giving}\quad z_{1/e}=\left|\frac{1}{2\Im(k_{z,T})}\right|=\left|\frac{1}{2\Im(n_{z,IT})k_{z,I}}\right|$$

Let us consider the consequences of considering absorption first from a mathematical point of view. We conclude that above the critical angle, the relationships defined previously remain true and taking absorption into account only results in the introduction of an attenuation factor. From the critical angle, the perpendicular components of the wave vectors were already complex which does not even modify the expressions introduced without absorption. From a physical point of view, the evanescent wave now propagates in a direction inclined relative to the surface. Indeed, the equiphase planes $\Re(\vec{k}_T) * \vec{r} = cst$ are no longer parallel to the equiamplitude planes $\Im(\vec{k}_T) * \vec{r} = cst$. In this case the time average of the energy flow which is also inclined is accompanied by a loss of energy in the absorbent material. Reflection is never complete again. The effects of absorption on reflectivity and transmission are illustrated in the following figures.

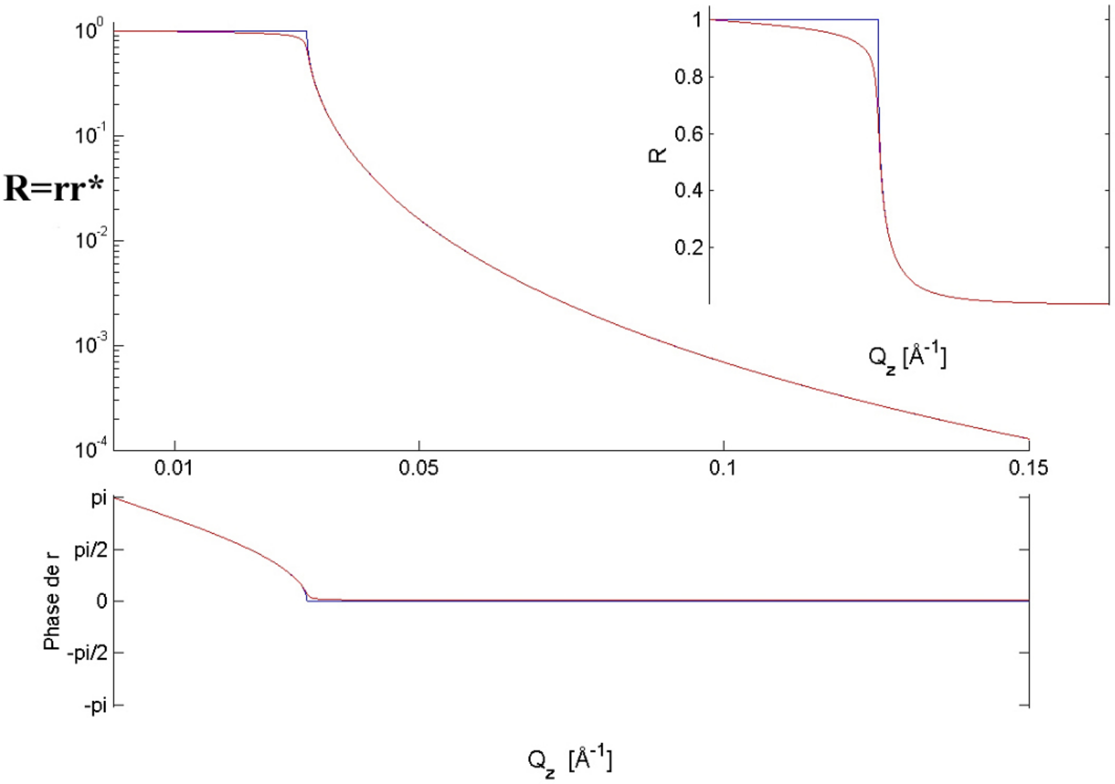


Figure 6 : Representation of reflectivities (R=rr) on a logarithmic and linear scale (in insert). The phase of r is shown below*

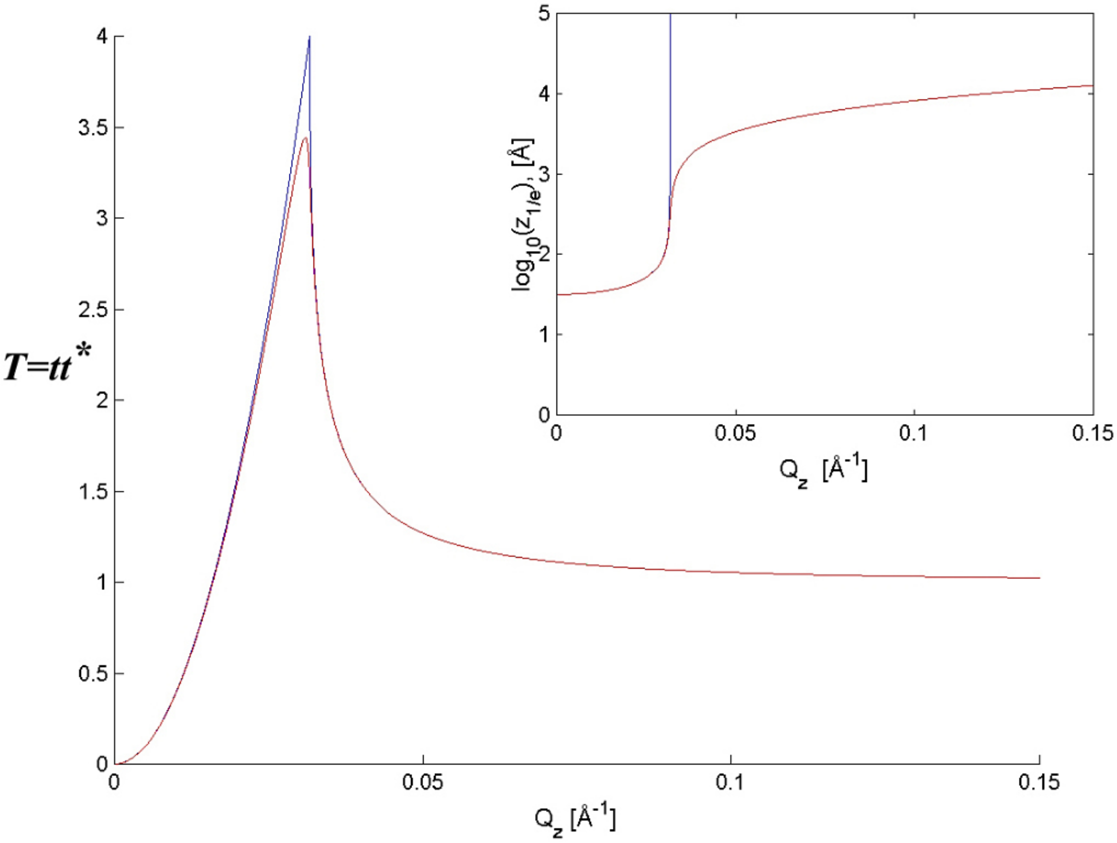


Figure 7 : Representation of the square of the module of the transmission coefficients (/t/2=tt)*

Figure 7 : Représentation du carré du module des coefficients de transmission ($|t|^2 = tt^*$)

Complément

The insert is the penetration depth ($z_{1/e}$) corresponding. These calculations are obtained for a silicon substrate ($\rho b = 1,992\ 10^{-05}\left[\mathring{A}^{-2}\right]$) and wavelength x-rays $\lambda = 1,54[\mathring{A}]$(either a copper anode). The blue curves are obtained when the absorption of the material is neglected. In the presence of absorption ($\mu = 1,425\ 10^{06}\left[\mathring{A}^{-1}\right]$) we obtain the red curves.

1.3. Reflectivity on a homogeneous thin layer of constant thickness

We are going to calculate the reflectivity of a **complete layer, of a homogeneous material** (*medium* 1), placed on a substrate (*medium* 2). The incident environment (*medium* 0) is assumed to be semi-infinite just like the substrate. This calculation is attributed to Airy [10 [Phil. Mag. 2]] from a formalism for visible optics. We will recall his demonstration which is taken up in numerous works including the reference [2 [Theory of Reflection of Electromagnetic and Particles Waves]]. It takes into account the interference of all waves emitted in the same direction (**towards the supposed detector at infinity**). The first reflection takes place on the upper free interface of the film (diopter noted 01*because between the medium* 0 *and the layer* 1) and is characterized by **the Fresnel reflection coefficient** :

$$r_{01}=\frac{k_{z,0}-k_{z,1}}{k_{z,0}+k_{z,1}}=\frac{Q_0-Q_1}{Q_0+Q_1}$$

At the level of the second interface (index diopter n_{12}), this coefficient is :

$$r_{12}=\frac{k_{z,1}-k_{z,2}}{k_{z,1}+k_{z,2}}=\frac{Q_1-Q_2}{Q_1+Q_2}$$

In this **dynamic approach**, multiple reflections are taken into account (they are illustrated in Figure 8).

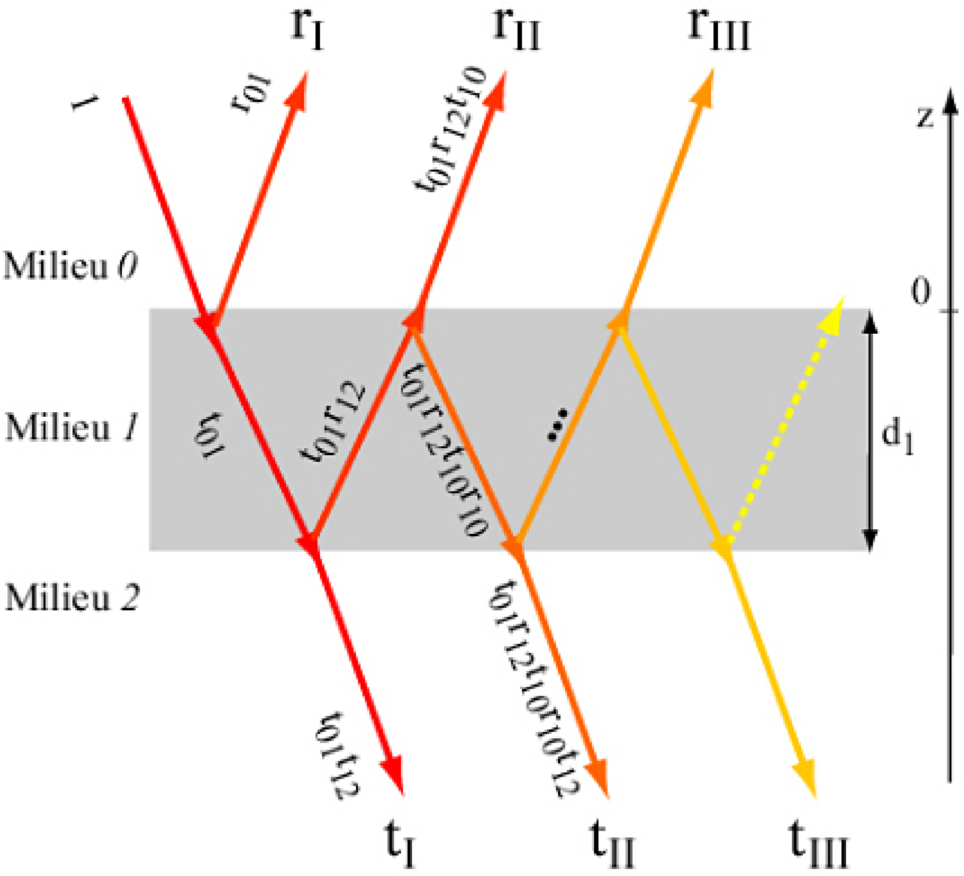


Figure 8).

Figure 8: **Schematic representation** of the multiple reflection phenomenon taking place within a homogeneous layer of thickness d_1. Only the Fresnel reflection and transmission coefficients are noted. Phase terms (of the type $\exp(\pm 2k_z d)$) are omitted for readability reasons.

The reflectivity coefficient (*complex*) of the film (all interferences) is obtained by the sum:

$$\tilde{r}_{01}=r_I+r_{II}+r_{III}+r_{IV}+\dots$$

$$\text{where}\quad\begin{cases} r_{01}=r_{01}\\ r_{II,IV,\dots}=t_{01}t_{10}r_{12}^{n-1}r_{10}^{n-2}e^{+inQ_{z,1}d_1}\\ r_{III,V,\dots}=t_{01}t_{10}r_{12}^{n-1}r_{10}^{n-2}e^{-inQ_{z,1}d_1}\end{cases}\quad\text{and}\quad\begin{cases} Q_{z,1}=Q_1=2k_{z,1}\\ \varphi=\pm i(n-1)Q_{z,1}d_1\end{cases}$$

where Q_l is the modulus of the **diffusion vector in layer** 1. The reflection here is purely specular (for plane and parallel interfaces) which makes it possible to identify Q_l to its component normal to the surface. Let us explain the terms of this sum:

$$\tilde{r}_{01}=(r_{01})+(t_{01}r_{12}e^{-i2k_{z,1}d_1}t_{10})+(t_{01}t_{10}r_{12}^2r_{10}e^{+i4k_{z,1}d_1})+(t_{01}t_{10}r_{12}^3r_{10}^2e^{-i6k_{z,1}d_1})+\dots$$

which allows us to use the following relationships : $\begin{cases} r_{10}=-r_{01}\\ t=1-r\end{cases}$ either : $t_{01}t_{10}=1-r_{01}^2$, we obtain :

$$\tilde{r}_{01}=r_{01}+(1-r_{01}^2)r_{12}e^{-iQ_{z,1}d_1}\left(\sum\nolimits_{n=II,III}(r_{10}^{n-2}r_{12}^{n-2})e^{\pm i(n-2)Q_{z,1}d_1}\right)$$

where the sum is equal to : $\dfrac{1}{1-r_{01}r_{12}e^{-iQ_{z,1}d_1}}$ since $|r_{01}r_{12}e^{-iQ_{z,1}d_1}|<1$ and $n\to\infty$.
This series is written:

$$\tilde{r}_{01}=r_{01}+\frac{t_{01}t_{10}r_{12}e^{-i2k_{z,1}d_1}}{1-r_{10}r_{12}e^{-i2k_{z,1}d_1}}\ \text{, either :}\quad \tilde{r}_{01}=\frac{r_{01}+r_{12}e^{-i2k_{z,1}d_1}}{1+r_{01}r_{12}e^{-i2k_{z,1}d_1}}$$

Analogous reasoning also makes it possible to obtain the transmission $\tilde{t}_{01}$ of the layer, and we retain:

$$\tilde{t}_{01}=\frac{t_{01}+t_{12}e^{-i2k_{z,1}d_1}}{1+r_{01}r_{12}e^{-i2k_{z,1}d_1}}$$

Reflectivity R and transmission T in intensity are obtained with the following relationships :

$$\begin{cases} R(Q_z)=\tilde{r}_{01}*Conj(\tilde{r}_{01})=\dfrac{r_{01}^2+r_{12}^2+2r_{01}r_{12}\cos(Q_1d_1)}{1+r_{01}^2r_{12}^2+2r_{01}r_{12}\cos(Q_1d_1)}\\ T(Q_z)=\left(\dfrac{k_{z,2}}{k_{z,0}}\right)\tilde{t}_{01}*Conj(\tilde{t}_{01})=\left(\dfrac{k_{z,2}}{k_{z,0}}\right)\dfrac{t_{01}^2t_{12}^2}{1+r_{12}^2r_{23}^2+2r_{12}r_{23}\cos(Q_1d_1)}\end{cases}$$

where $Q_z=Q_0=Q_{z,0}=2k_{z,0}$ is the relevant variable on which depend $r_{01},r_{12},r_{23},t_{01},t_{12}$ et Q_1.

a) General remarks from the expressions of R and T

The term phase $e^{-iQ_1 d_1}$ is introduced by the interference between the waves reflected at the two interfaces in turn constructive or destructive depending on the value of Q_1, that is to say according to the angle of incidence. The oscillations created by this interference have a period of $2\pi/d_1$ which allows direct measurement of the thickness of the layer. They are visible in the following figure and we call them "**Kiessig fringes**". Their amplitude depends on the optical index contrasts relating to the two interfaces and becomes maximum when the substrate (medium *2*) is the same material as the incident medium (medium 0).

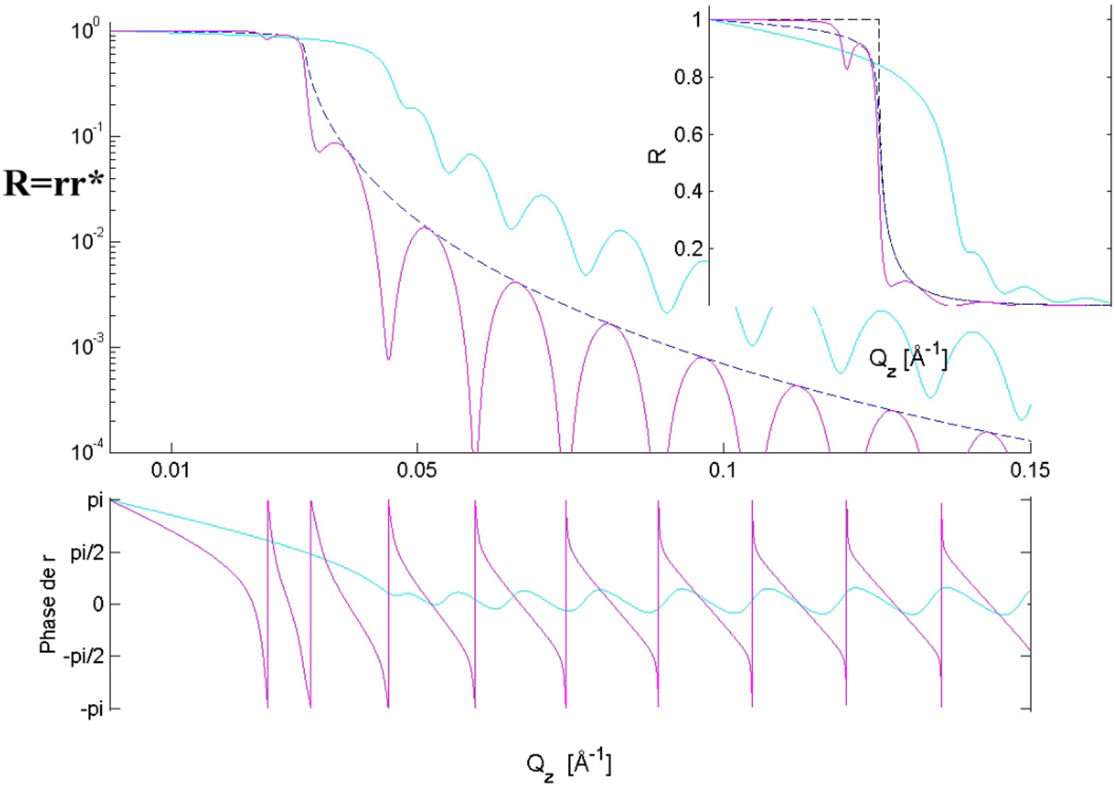


Figure 9: Reflectivities (R=rr) plotted on a logarithmic and linear scale of the system described*

Complément

The figure below corresponds to the phase of *r*. The reflectivity of the silicon substrate ($\rho b = 1{,}992.10^{-5}\left[\mathring{A}^{-2}\right]$) for X-rays of wavelength $\lambda = 1{,}54\left[\mathring{A}\right]$ is presented in dotted lines either in black when the absorption is neglected, or in blue when considering it ($\mu = 1{,}425.10^{-6}\left[\mathring{A}\right]$). The cyan curves are obtained for a 400[Å] layer of very absorbent maghemite (Fe2O3 with $\rho b = 3.99.10^{-5}\left[\mathring{A}^{-2}\right]$and $\mu = 1{,}065.10^{-5}\left[\mathring{A}^{-1}\right]$). The magenta curves correspond to a layer of the same thickness of the diblock copolymer studied. This material absorbs little (PS-PBMA with $\rho b = 3.99.10^{-5}\left[\mathring{A}^{-2}\right]$ and $\mu = 4.92.10^{-8}\left[\mathring{A}^{-1}\right]$).

b) Total Thinking Diet

If we are interested in the total reflection between the substrate and the layer, the expression of the critical angle must be rewritten according to the values accessible experimentally and therefore defined in the medium of incidence (medium I or 0). We note $k_{z,12}^{(0)}$ the particular value of $k_{z,0}$corresponding to the incident angle where this total reflection will appear. According to the expression seen previously we obtain:

$$\left(k_{z,12}^{(0)}\right)^2=\left(k_{z,0}^2\right)=\left(k_{z,01}^{(c)}\right)^2+\left(k_{z,12}^{(c)}\right)^2 \text{ , either : } \left(k_{z,12}^{(0)}\right)^2=4\pi\left((\rho b)_2-(\rho b)_0\right)$$

The total reflection between the layer and the substrate is therefore measured in the incident medium at the same angle as that obtained on the bare substrate $k_{z,02}^{(0)}$. On the other hand, in the presence of the layer, another particular value of $k_{z,0}$exists and corresponds to the phenomenon of total reflection on the layer in the incident medium. The corresponding critical angle is obtained with:

$$\left(k_{z,01}^{(c)}\right)^2=\left(k_{z,01}^{(0)}\right)^2=4\pi\left((\rho b)_1-(\rho b)_0\right)$$

Several cases can be considered when we compare these two critical angles, which amounts to comparing $(\rho b)_1$ and $(\rho b)_2$. Whatever the relationship between these two potentials, a total reflection plateau is measured at small angles so the overall reflection coefficient r must be of unit module.

- When $(\rho b)_1 < (\rho b)_2$, the total reflection at the interface between the layer and the substrate will take place first when the angle of incidence decreases since $k_{z,12}^{(0)} > k_{z,01}^{(0)}$. Between these two particular values of $k_z^{(0)}$,there is total reflection on the substrate but not yet on the solid layer, thus $|r_{12}| = 1$ and r_{01} is real.

  Let's us set : $r_{12} = e^{i\delta}$, $r_{01} = \Re(r_{01})$ and $\Delta = \delta - Q_1 d$ to be able to reformulate : $r = \dfrac{\Re(r_{01}) + e^{i\Delta}}{1 + \Re(r_{01}) + e^{i\Delta}} = e^{-i\Delta}\dfrac{\Re(r_{01}) + e^{i\Delta}}{e^{-i\Delta} + \Re(r_{01})}$

  which leads to : $$R = r * Conj\,(r) = e^0\frac{(\Re(r_{01}) + e^{i\Delta})^2}{(\Re(r_{01}) + e^{i\Delta})^2} = 1$$

  At even lower angles, the total reflection on the first interface encountered also appears $|r_{01}| = 1$. In this case, Q_1 and Q_2 being pure imaginations, r_{12} is purely real but no longer has a unit module since all the energy of the evanescent wave penetrating the layer does not reach the substrate.

  Let's us set : $r_{01} = e^{i\delta}$ and $r_{12}e^{-iQ_1 d} = i$ a real, we obtain :

  $r = \dfrac{e^{i\delta} + i}{1 + e^{i\Delta}i}$,either $R = r * Conj\,(r) = rr^* = 1$

- When $(\rho b)_1 > (\rho b)_2$, the total reflection on the layer appears before that on the substrate when α_I decreases. For $k_{z,0}$ between $k_{z,01}^{(0)}$ and $k_{z,12}^{(0)}$ we therefore have $|r_{01}| = 1$ and an evanescent wave (*non-propagative mode*) extends to the substrate (Q_1 is pure imagination). As previously, the formalism used makes it possible to explain the presence of a total reflection plateau.

1.4. Reflectivity of laminated thin films (according to the normal to their free surface, z)

In the following paragraph, we will present the methods classically used for calculating the **specular reflectivity of thin films having depth-dependent index profiles**,that is to say having a diffusion length density function of their normal $(\rho b)_{(z)}$.

a) Optical matrix formalism introduced by Abeles

The introduction of **matrix formalism** is attributed to Herpin for the optics of homogeneous thin films [11 [Compt. Rend. Ac. Sc.]]. We start from Abelès' article [12 [Recherches sur la propagation des ondes électromagnétiques sinusoidales dans les milieux stratifiés. Applications aux couch.es minces]] which is included in numerous reference works in optics [13 [Principles of Optics], 14 [Light reflection from films of continuously varying refractive index]].

A laminated material optically introduces an asymmetry between the direction normal to the film z and directions x, y. Its characteristics are invariant by lateral translation, i.e. perpendicular to $z$and expressed by the refractive index (optical here) : $n_{(z)} = \varepsilon\mu$. We distinguish the following regions of the film :

$$\begin{cases}\text{For } \infty<z<0 : \epsilon=\epsilon_0 \wedge \mu=\mu_0 ,\ so : n=n_0 \\ \text{For } 0<z\leftarrow d_{tot} : \epsilon=\epsilon(z) \wedge \mu=\mu(z),\ so : n=n(z) \\ \text{For } -d_{tot}<z\leftarrow\infty : \epsilon=\epsilon_{N+1} \wedge \mu=\mu_{N+1},\ so: n=n_{N+1}\end{cases}$$

In this case, we must start from Maxwell's equations not yet simplified for the case of homogeneous materials and which are summarized for the polarization"s" studied ($E_y = E_z = 0$) to :

$$\begin{cases}(a): \dfrac{\partial H_z}{\partial y}-\dfrac{\partial H_y}{\partial z}+\dfrac{i\epsilon\omega}{C}E_x=0 \\ (b): \dfrac{\partial H_x}{\partial z}-\dfrac{\partial H_z}{\partial x}=0 \\ (c): \dfrac{\partial H_y}{\partial x}-\dfrac{\partial H_x}{\partial y}=0\end{cases} \qquad \begin{cases}(d): \dfrac{i\mu\omega}{C}H_x=0 \\ (e): \dfrac{\partial E_x}{\partial z}-\dfrac{i\mu\omega}{C}H_y=0 \\ (f): \dfrac{\partial E_x}{\partial y}+\dfrac{i\mu\omega}{C}H_z=0\end{cases}$$

Combined together, they lead to the Helmoltz equation (already stated in its general form) and which is simplified according to the relationships above to the expression :

$$\left(\frac{\partial^2 E_x}{\partial y^2}+\frac{\partial^2 E_x}{\partial z^2}\right)-d\frac{(\ln(\mu))}{dz}\frac{\partial E_x}{\partial z}+n^2k_0^2E_x=0$$

To show that this problem is one-dimensional (*selon*z), Abelès proposes as a solution to this equation, a field separable into two functions of the directions y and z :

$$E_x(y,z)=Y(y)U(z)$$

The expression becomes an equality with separable members :

$$\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}=\frac{-1}{U}\frac{\partial^2 U}{\partial z^2}-n^2k_0^2+\frac{d(\ln(\mu))}{dz}\frac{1}{U}\frac{\partial U}{\partial z}$$

This relation requires that its two members be equal to a constant, and Abelès poses:

$$\begin{cases} \dfrac{1}{Y}\dfrac{\partial^2 Y}{\partial y^2} = -K^2 \\ \dfrac{\partial^2 U}{\partial z^2} - \dfrac{d(\ln(\mu))}{dz}\dfrac{\partial U}{\partial z} + n^2 k_0^2 U = K^2 U \end{cases}$$

we will see that : $K^2 = k_0^2 S^2$

where K is a constant since $s = n(z)\cos(\alpha(z)) = n_I \cos(\alpha_I)$ is an invariant resulting from the conservation of the tangential component E_x at the passage of the different diopters of the multilayer (see previous relations).

The first differential equation has solutions of the type $Y = cst\, e^{i(\omega t - k_z S_y)}$. A similar reasoning for H_y et H_z leads for polarization"s" to solutions :

$$\text{S :} \begin{cases} E_x(y,z) = U(z)\, e^{i(\omega t - k_0 S_y)} \\ H_y(y,z) = V(z)\, e^{i(\omega t - k_0 S_y)} \\ H_z(y,z) = W(z)\, e^{i(\omega t - k_0 S_y)} \end{cases} \quad \text{with according to a), e) and f):} \quad \begin{cases} i k_0 \epsilon U = -i k_0 S W - \dfrac{\partial V}{\partial z} \\ i k_0 \mu V = \dfrac{-\partial U}{\partial z} \\ i k_0 \mu W = -i k_0 S U \end{cases}$$

These conditions simplify to two first order differential equations after elimination of W. We obtain:

$$s \;: \begin{cases} \dfrac{\partial U}{\partial z} = -i k_0 \mu V \\ \dfrac{\partial V}{\partial z} = -i k_0 \left(\epsilon - \dfrac{S^2}{\mu}\right) U \end{cases} \quad \text{which leads to :} \quad \begin{cases} \dfrac{\partial^2 U}{\partial z^2} - \dfrac{d(\ln(\mu))}{dz}\dfrac{\partial U}{\partial z} + k_0^2(\epsilon\mu - S^2) U = 0 \\ \dfrac{\partial^2 V}{\partial z^2} - \dfrac{d\left(\ln\left(\epsilon - \dfrac{S^2}{\mu}\right)\right)}{dz}\dfrac{\partial V}{\partial z} + k_0^2(\epsilon\mu - S^2) V = 0 \end{cases}$$

Note that for a polarized wave "p" such as $H_y = H_z = 0$, we obtain analogous relationships by directly using the substitutions seen previously on this equation.

For these two polarizations we obtain linear differential equations of the second order of type $\dfrac{\partial^2 y}{\partial z^2} + a(z)\dfrac{\partial y}{\partial z} + b(z) y = 0$. We deduce that each solution U et V decomposes into a linear combination of two particular solutions (U_1, U_2 ou V_1, V_2) satisfying the system of first order linear equations introduced above. We deduce the following systems :

$$\begin{cases} V_1 U_2^z - U_1^z V_2 = 0 \\ U_1 V_2^z - V_1^z U_2 = 0 \end{cases} \quad \text{either :} \quad \frac{\partial(Det)}{\partial z} = 0 \quad \text{where} \quad Det = \begin{vmatrix} U_1 & V_1 \\ U_2 & V_2 \end{vmatrix} = (U_1 V_2 - U_2 V_1)$$

where the exponent ^{z} refers to the differentiation according to z.

This equality implies that the determinant (Det) of any two solutions is independent of z. Let's use this result by selecting the following two particular solutions :

$$\begin{cases} U_1 = u_1(z) \\ V_1 = v_1(z) \end{cases} \quad \text{and} \quad \begin{cases} U_2 = u_2(z) \\ V_2 = v_2(z) \end{cases} \quad \text{such as} \quad \begin{cases} u_1(0) = v_2(0) = 0 \\ v_1(0) = u_2(0) = 0 \end{cases}$$

So the general solutions are of the type :

$$\begin{cases} U(z) = u_2(z)\,U(0) + u_1(z)\,V(0) \\ V(z) = v_2(z)\,U(0) + v_1(z)\,V(0) \end{cases}$$

either in matrix notation :

$$\begin{bmatrix} U(z) \\ V(z) \end{bmatrix} = \begin{bmatrix} u_2 & u_1 \\ v_2 & v_1 \end{bmatrix} \begin{bmatrix} U(0) \\ V(0) \end{bmatrix} \quad \text{with} \quad N(z) = \begin{bmatrix} u_2 & u_1 \\ v_2 & v_1 \end{bmatrix}$$

We obtain the value of the invariant reflecting the conservation of energy to the diopter $z = 0$:

$$Det(N(z)) = Det(N(0)) = u_2 v_1 - u_1 v_2 = 1$$

By reciprocity, we deduce the relationship :

$$\begin{bmatrix} U(0) \\ V(0) \end{bmatrix} = \begin{bmatrix} v_1(z) & -u_1(z) \\ -v_2(z) & u_2(z) \end{bmatrix} \begin{bmatrix} U(z) \\ V(z) \end{bmatrix} = M(z) \begin{bmatrix} U(z) \\ V(z) \end{bmatrix} \quad \text{with} \quad Det(M(z)) = 1$$

Remember that knowledge of U and V returns respectively to that of the fields E_x et H_y (for polarization "s"). Thus the determination of the **characteristic matrix** $M(z)$ **laminated material** makes it possible to determine the electrical and magnetic components of the sinusoidal wave in the different strata (depth z) when this wave is known in the incident medium. The square matrix $M(z)$ is unimodular and its elements M_{ij} depend only on the index $n(z)$ and therefore the structure of the film in depth.

b) Application to multilayer films. Discrete Dynamic Formalisms

A system that can be described as formed by the stacking of homogeneous layers of different optical indices is called multilayer. It is a particular laminated material whose optical index presents marked discontinuities along the axis z. Such a multilayer is shown in the following figure. Each of the N layers are numbered (hint l) from the middle of incidence of the beam corresponding to the index $l = 0$ to index substrate $l = N + 1$. All these strata of respective thickness d_l are homogeneous and characterized indifferently by their optical index n_l or their diffusion length density $(\rho b)_l$.

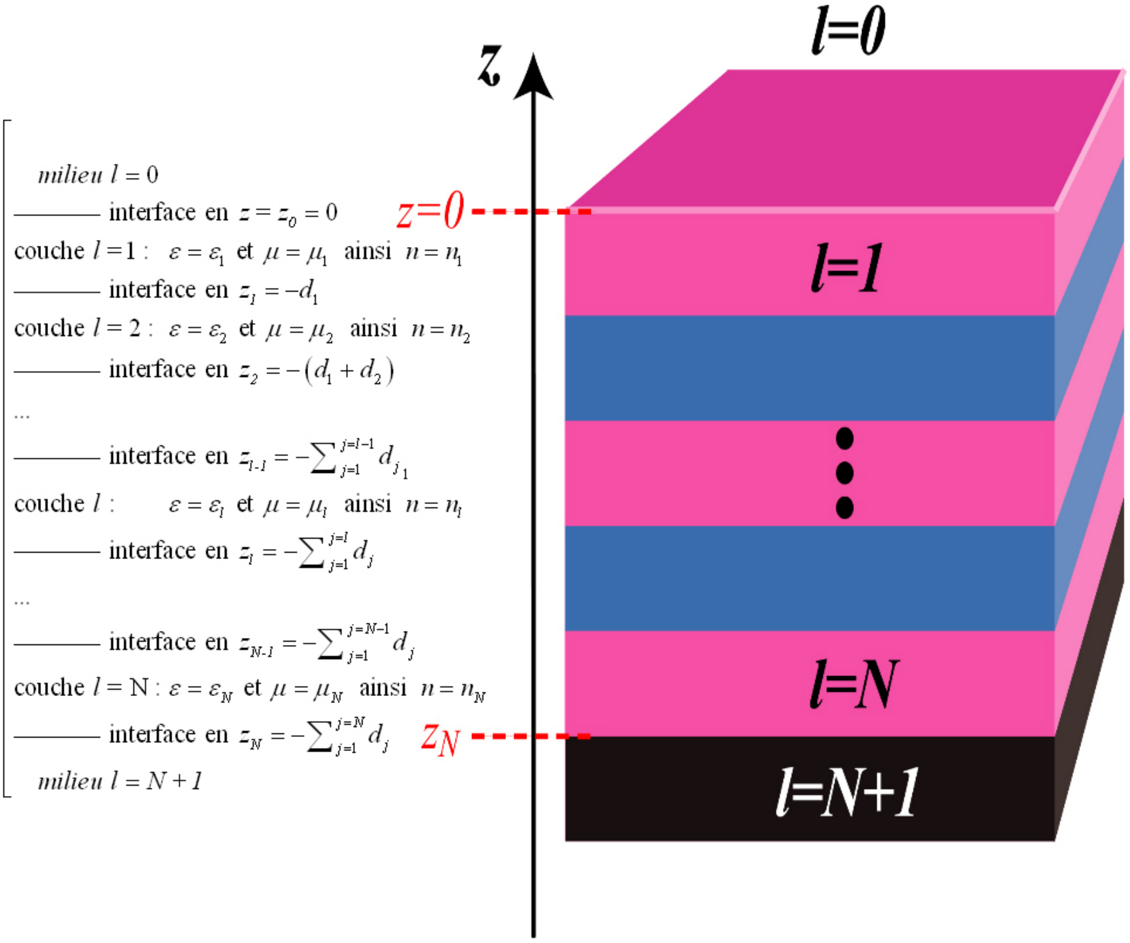


Figure 10 : Schematic representation of a multilayer

To calculate reflectivity R and transmittance T of this multilayer, we will first pursue the optical matrix formalism of Abelès. We will then detail the use of Parratt's recursive algorithm [15 [Surface Studies of Solids by Total Reflection of X-Rays]] introduced for the reflectivity of X-rays but resulting from the optical formalism proposed by Airy for a monolayer. Note that Lord Rayleigh dealt with this problem as early as 1912 in the context of the propagation of acoustic waves [16 [Proc. Roy. Soc.]].

These two calculation methods are dynamic and take into account refraction and multiple reflections. They conserve energy and can be considered accurate over the entire angular range when each interface of the multilayer stack satisfies the Fresnel conditions previously stated for a so-called "ideal" plane diopter. These two calculations lead to the same results for perfect dielectrics ($\mu = 0$).

c) Transition from laminated films to multilayers with the Abelès formalism

These two calculation methods are dynamic and take into account refraction and multiple reflections. They conserve energy and can be considered accurate over the entire angular range when each interface of the multilayer stack satisfies the Fresnel conditions previously stated for a so-called "ideal" plane diopter. These two calculations lead to the same results for perfect dielectrics (z) which are noted E_x and H_y. As we have seen, this expression makes it possible to link the components of these fields, at a given depth ($U(z)$ et $V(z)$), to their value in the environment of incidence which are accessible ($U(0)$ et $V(0)$). For this we must determine the matrix $M(z)$ which characterizes the multilayer studied.

In the case of a simple diopter, this matrix makes it possible to link the values of the fields in the medium of incidence I($U_I(z > 0)$ and $V_I(z > 0)$) to those in the material T ($U_T(z < 0)$ and $V_T(z < 0)$) by the relationship :

$$\begin{bmatrix} U_I(0) \\ V_I(0) \end{bmatrix} = M(z) \begin{bmatrix} U_T(z) \\ V_T(z) \end{bmatrix}$$

We generalize this relation for any **multilayer** characterized by the matrix $M(z)$ and we link the fields in the layer N ($U_N(z)$ and $V_N(z)$ for $z_{N-1} > z > z_N$) to those of the incident wave ($U_0(0)$ and $V_0(0)$ for $z \geq z_0$) by the relationship :

$$\begin{bmatrix} U_0(0) \\ V_0(0) \end{bmatrix} = M(z) \begin{bmatrix} U(z) \\ V(z) \end{bmatrix}$$

$$\text{with} \quad M(z) = [M_1(z_1)][M_2(z_2 - z_1)]\ldots[M_N(z - z_{N-1})] = \prod\nolimits_{l=1}^{l=N} M_l$$

$$\text{and} \quad M_l = M_l(z_l - z_{l-1}) = \begin{bmatrix} v_{1,l}(z) & -u_{1,l}(z) \\ -v_{2,l}(z) & u_{2,l}(z) \end{bmatrix}$$

and where the matrix M_l corresponds to the layer $z_{l-1} \leq z \leq z_l$ thick $d_l = |z_l - z_{l-1}|$.
Let's examine for a stretch l of this multilayer matrix M_l which characterizes it. Let's start from the system which becomes:

$$\begin{cases} \dfrac{\partial U}{\partial z} = -i k_0 \mu_l V \\ \dfrac{\partial V}{\partial z} = -i k_0 \left(\epsilon_l - \dfrac{S^2}{\mu_l} \right) U \end{cases} \quad \text{and which leads to :} \quad \begin{cases} \dfrac{\partial^2 U}{\partial z^2} + k_0^2 (\epsilon \mu - S^2) U = 0 \\ \dfrac{\partial^2 V}{\partial z^2} + k_0^2 (\epsilon \mu - S^2) V = 0 \end{cases}$$

Abelès indicates that the solutions satisfying these systems are of the type:

$$\begin{cases} U(z) = A \cos\left(k_0 (z - z_{l-1}) \sqrt{\epsilon_l \mu_l} \sin(\alpha_l)\right) + B \sin\left(k_0 (z - z_{l-1}) \sqrt{\epsilon_l \mu_l} \sin(\alpha_l)\right) \\ V(z) = \dfrac{1}{i} \sqrt{\dfrac{\epsilon_l}{\mu_l}} \sin(\alpha_l) \left[B \cos\left(k_0 (z - z_{l-1}) \sqrt{\epsilon_l \mu_l} \sin(\alpha_l)\right) - A \sin\left(k_0 (z - z_{l-1}) \sqrt{\epsilon_l \mu_l} \sin(\alpha_l)\right) \right] \end{cases}$$

where A and B are constants. We deduce the particular solutions introduced before and which lead us to the elements of the matrix $M_{l,ij}$characterizing the layer l :

$$M_l = \begin{bmatrix} M_{l,11} & M_{l,12} \\ M_{l,21} & M_{l,22} \end{bmatrix} \quad \text{by posing :} \quad \begin{cases} P_l = \sqrt{\dfrac{\epsilon_l}{\mu_l}} \sin(\alpha_l) \\ k_l = k_0 \sqrt{\epsilon_l \mu_l} \sin(\alpha_l) = n_0 k_{z,l} \end{cases}$$

$$\text{where}\quad \begin{cases} M_{l,11}=v_{1,l}=\cos\left(k_0\left(z-z_{l-1}\right)\sqrt{\epsilon_l\mu_l}\sin\left(\alpha_l\right)\right) \\ M_{l,12}=-u_{1,l}=i\sqrt{\dfrac{\mu_l}{\epsilon_l}}\dfrac{1}{\sin\left(\alpha_l\right)}\sin\left(k_0\left(z-z_{l-1}\right)\sqrt{\epsilon_l\mu_l}\sin\left(\alpha_l\right)\right) \\ M_{l,21}=-v_2=i\sqrt{\dfrac{\epsilon_l}{\mu_l}}\sin\left(\alpha_l\right)\sin\left(k_0\left(z-z_{l-1}\right)\sqrt{\epsilon_l\mu_l}\sin\left(\alpha_l\right)\right) \\ M_{l,22}=u_2=v_{1,l} \end{cases}$$

$$\text{either}\quad \begin{cases} M_{l,11}=v_{1,l}=\cos\left(k_l\left(z-z_{l-1}\right)\right) \\ M_{l,12}=-u_{1,l}=\dfrac{i}{P_l}\sin\left(k_l\left(z-z_{l-1}\right)\right) \\ M_{l,21}=-v_2=i\,P_l\sin\left(k_l\left(z-z_{l-1}\right)\right) \\ M_{l,22}=u_2=M_{l,11} \end{cases}$$

and where P_l **is called "characteristic admittance"** of the layer l by analogy with electronics [14 [Light reflection from films of continuously varying refractive index]]. We move on to the results of a polarization"p" by applying the substitutions ($s \longrightarrow p$).

Experimentally, the accessible quantities are found in homogeneous media considered as semi-infinite indexed 0 (*above the film*) and $N+1$ (*above the film*) where the measurement is carried out. The sizes $U(z=0)$ and $V(z=0)$ correspond to the fields in the first medium which can be obtained by decomposition of these into the sum of two contributions corresponding to an incident wave (of electric field amplitude E_0^-) and to a wave reflected by the multilayer (of electric field amplitude E_0^+). Which results in equalities:

$$\begin{cases} U_0(0)=E_0^-+E_0^+ \\ V_0(0)=P_0\left(E_0^--E_0^+\right) \end{cases} \quad\text{and}\quad \begin{cases} U_{N+1}(z)=E_{N+1}^- \\ V_{N+1}(z)=P_{N+1}E_{N+1}^- \end{cases} \quad\text{linked by}\quad \begin{bmatrix} U_0(0) \\ V_0(0) \end{bmatrix}=M\begin{bmatrix} U_{N+1}\left(z_{N+1}\right) \\ V_{N+1}\left(z_{N+1}\right) \end{bmatrix}$$

$$\text{either}\quad \begin{cases} U_0(0)=E_0^-+E_0^+=\left(M_{11}+P_{N+1}M_{12}\right)E_{N+1}^- \\ V_0(0)=P_0\left(E_0^--E_0^+\right)=\left(M_{21}+P_{N+1}M_{22}\right)E_{N+1}^- \end{cases}$$

Cette description du phénomène permet de revenir aux coefficients de réflexion $\tilde{r}_{01}$ et de transmission $\tilde{t}_{NN+1}$des milieux extrêmes :

$$\begin{cases} \tilde{r}_{01}=\left|\tilde{r}_{01}\right|e^{i\varphi_{01}}=\left(\dfrac{E_0^+}{E_0^-}\right)=\dfrac{P_0\left(M_{11}+P_{N+1}M_{12}\right)-\left(M_{21}+P_{N+1}M_{22}\right)}{P_0\left(M_{11}+P_{N+1}M_{12}\right)+\left(M_{21}+P_{N+1}M_{22}\right)} \\ \tilde{t}_{NN+1}=\left|\tilde{t}_{NN+1}\right|e^{i\varphi_{NN+1}}=\left(\dfrac{E_{N+1}^+}{E_0^-}\right)=\dfrac{2P_0}{P_0\left(M_{11}+P_{N+1}M_{12}\right)+\left(M_{21}+P_{N+1}M_{22}\right)} \end{cases}$$

We deduce the reflectivity R and transmission $T$of the multilayer (in the middle $I = 0$) :

$$\begin{cases} R(Q_z)=\tilde{r}_{01}*Conj(\tilde{r}_{01}) \\ T(Q_z)=\frac{P_{N+1}}{P_0}\tilde{t}_{01}*Conj(\tilde{t}_{01}) \end{cases} \quad \text{where} \quad \frac{P_{N+1}}{P_0}=\sqrt{\frac{\epsilon_{N+1}}{\mu_{N+1}}\frac{\mu_0}{\epsilon_0}}\frac{\sin(\alpha_{N+1})}{\sin(\alpha_0)}$$

i Case of a homogeneous layer of perfect dielectric

Suppose that the layer described by the previous figure is non-magnetic ($\mu_l = 0$) and purely dielectric. We then obtain:

$$\begin{cases} M_{1,11}=v_{1,1}=\cos(k_1 d_1) \\ M_{1,12}=-u_{1,1}=\frac{-i}{P_1}\sin(k_1 d_1) \\ M_{1,21}=-v_2=-i\,P_1\sin(k_1 d_1) \\ M_{1,22}=u_2=M_{1,11} \end{cases} \quad \text{where} \quad \begin{cases} P_1=n_1\sin(\alpha_I)=\frac{k_1}{k_0}=\frac{n_1}{n_0}=\frac{n_0}{k_0}k_{z,1} \\ k_1=k_0 n_1\sin(\alpha_I)=n_0 k_{z,1} \end{cases}$$

These elements are introduced into the equations giving the reflection and transmission amplitude coefficients of each interface. We obtain the expression of the reflectivity and transmission coefficients of the film (noted with a tilde). They are simplified by introducing the Fresnel coefficients of the interfaces. For the diopter separating the middle$I$ and T, these coefficients become:

$$r_{IP} = r_{\perp} = \frac{n_I\sin(\alpha_I) - n_T\sin(\alpha_T)}{n_I\sin(\alpha_I) + n_T\sin(\alpha_T)} = \frac{P_I - P_T}{P_I + P_T}$$

and $$t_{\perp} = \frac{2n_I\sin(\alpha_I)}{n_I\sin(\alpha_I) + n_T\sin(\alpha_T)} = \frac{2P_I}{P_I + P_T}$$

$$\text{either :} \quad \tilde{r}_{01}=\frac{r_{01}+r_{12}e^{-i2k_{z,1}d_1}}{1+r_{01}r_{12}e^{-i2k_{z,1}d_1}} \quad \text{and} \quad \tilde{t}_{01}=\frac{t_{01}+t_{12}e^{-i2k_{z,1}d_1}}{1+r_{01}r_{12}e^{-i2k_{z,1}d_1}}$$

By introducing r_{12}, r_{23} and t_{12}, t_{23} in the expressions of $\tilde{r}_{01}$ and $\tilde{t}_{01}$ we find the expressions of reflectivity R and Transmission T already seen :

d) Recurrent Parratt algorithm

For this iterative method, the reflectivity is calculated from interface to interface while respecting the continuity equations of the electromagnetic fields and taking into account the interference between the waves reflected and refracted at the different interfaces. The reflectivity coefficient of the deepest interface corresponds to the local Fresnel coefficient since no waves return from the substrate:

$$\tilde{r}_{N\,N+1}=r_{N\,N+1}=\frac{k_{z,N}-k_{z,N+1}}{k_{z,N}+k_{z,N+1}}=\frac{Q_N-Q_{N+1}}{Q_N+Q_{N+1}} \quad \text{where} \quad Q_l=Q_{z,l}=2k_{z,l}$$

We start from this reflectivity coefficient ($N/N+1$) to the substrate and go back to the reflectivity in the medium $0$where the measurement takes place, following the recurrent method already introduced for the calculation of a single layer. We thus obtain an analogous expression which is for the $l^{ième}$ interface (located between layers $l-1$ and l) :

$$\tilde{r}_{l-1l}=\frac{r_{l-1l}+\tilde{r}_{ll+1}e^{-iQ_l d_l}}{1+r_{l-1l}\tilde{r}_{ll+1}e^{-iQ_l d_l}}$$

It takes into account the interference between waves reflected at the underlying interfaces and makes it possible to obtain the reflection coefficient of the interface ($l-2\,l-1$):

$$\tilde{r}_{l-2l-1}=\frac{r_{l-2l-1}+\tilde{r}_{l-1l}e^{-iQ_{l-1}d_{l-1}}}{1+r_{l-2l-1}\tilde{r}_{l-1l}e^{-iQ_{l-1}d_l-1}}$$

Here we decrement l (from N to 0) up to the first interface (between the medium of incidence 0 and the layer 1). The reflectivity and transmission of the multilayer are:

$$\begin{cases} R(Q_z)=\tilde{r}_{01}*Conj(\tilde{r}_{01}) \\ T(Q_z)=1-R(Q_z) \end{cases}$$

e) Expressions of diffusion vectors for their calculation

The programming of the two formalisms presented (matrix or iterative) always involves the calculation of the wave vectors in the different layers. These quantities can be complex, we will start by defining them and highlighting a common source of error for their programming. Let us first return to the relations of continuity of the electromagnetic fields at the interfaces which link the expressions of the wave vectors of the radiation propagating on either side of a diopter. So the **diffusion vector in index layer** $l+1$ is obtained from its value in the previous middle of index l by the relation already seen :

$$(k_{z,T})^2=(k_{z,I})^2-(k^{(c)}_{z,IT})^2$$

Let us express the module of this vector differently for its calculation:

$$k_{z,l+1}=\sqrt{(k_{z,l})^2-(k^{(c)}_{z,ll+1})^2}=\sqrt{(k_{z,0})^2-\sum_{i=1}^{i=l+1}(k^{(c)}_{z,i-1i})^2}$$

where the critical angle attached to the diopter between layers l and $l+1$ is identified by the value of the module of the corresponding wave vector : $k^{(c)}_{z,ll+1}$. To calculate this complex quantity we use the relationships linking it to the diffusion length indices or densities. Let us expand the sum as a function of the diffusion length densities:

$$\sum_{i=1}^{i=l+1}(k^{(c)}_{z,i-1i})^2=\sum_{i=1}^{i=l+1}\left(4\pi\left((\rho b)_i-(\rho b)_{i-1}\right)\right)=4\pi\left((\rho b)_{l+1}-(\rho b)_0\right) \;=\; (k^{(c)}_{z,0l+1})^2$$

Depending on the optical indices we obtain:

$$\sum_{i=1}^{i=l+1}(k^{(c)}_{z,i-1i})^2=\sum_{i=1}^{i=l+1}\left((n_{i-1}^2-n_i^2)k_{z,0}^2\right)=(n_0^2-n_{l+1}^2)k_{z,0}^2 \;=\; (k^{(c)}_{z,0l+1})^2$$

In :

$$k_{z,l+1}=\sqrt{k_{z,0}^2-\left(k_{z,0l+1}^{(c)}\right)^2} \quad \text{with} \quad \left(k_{z,i-1i}^{(c)}\right)^2=4\pi\left((\rho b)_i-(\rho b)_{i-1}\right)$$

or again:

$$k_{z,l+1}=k_0\sqrt{\left(\left(n_{l+1}^2-n_0^2\right)+1-\cos^2(\alpha_0)\right)} \quad \text{where} \quad n_{l+1}=n_{0T}=\frac{k_{l+1}}{k_0}=\sqrt{1-\frac{4\pi}{k_0^2}(\rho b)_{l+1}}$$

For these expressions : $k_0=\frac{2\pi}{\lambda_0}$, $k_{z,0}=k_0\sin(\alpha_0)$ and $\alpha_0=\alpha_{I,0}$ is the angle of incidence of the beam in the medium $l=0$ (*empty*) on the surface.

Let us recall that the 2$^{\text{ième}}$ Descartes' law imposes the conservation of the transverse component of the wave vectors, namely:

$$k_{y,l+1}=k_{y,0}=k_0\cos(\alpha_0)=k_{l+1}\frac{n_0}{n_{l+1}}\cos(\alpha_0)=k_{l+1}\cos(\alpha_{l+1})=\frac{k_{z,l+1}}{\tan(\alpha_{l+1})}$$

Attention

Programming these relationships is not as simple as it seems.

For a material with no absorption and at angles less than its critical angle, the quantity under the root of the wave vector expression becomes negative. The wave vector in the material is then a pure imaginary whose sign must be negative in accordance with the conventions adopted for the temporal and spatial dependence of electric fields. Software such as MATLAB [17 [Matlab]] will systematically take this imagination as positive. To avoid this, you must specify in the calculation that you use its complex conjugate. In the case where absorption exists, the diffusion vector always includes an imaginary part which fixes its sign unambiguously. The effects of these errors are rarely spectacular in reflectivity calculations because they only affect the imaginary part of the reflection coefficients. They are more important under the critical angle and when calculating interference between reflected waves.

This is one of the reasons why we have systematically plotted the phases of complex reflectivity coefficients (r) in the sequel.

2. Use of simplifying Born approximations. Continuous kinematic formalism

Jens Als-Nielsen popularized the use of **Born approximations** for calculating the specular reflectivity of X-rays. Its objective was to determine the average electronic distribution $(\rho b)(z)$ normal to the surface of a nematic liquid crystal solution [18 [Smectic-A Order at the Surface of a Nematic Liquid Crystal: Synchrotron X-Ray Diffraction], 19 [Physica B]]. The expression relating the depth potential profile to the measured reflectivity is:

$$R(Q_z)\approx R_{Fresnel}(Q_z)\left|\frac{1}{(\rho b)_{Volume}}\int_{-\infty}^{+\infty}dz\,\frac{d\langle(\rho b)(z)\rangle}{dz}\,e^{iQ_z z}\right|^2=R_{Fresnel}(Q_z)\left|S(Q_z)\right|^2$$

where $S(Q_z)$ is the local structure factor of the interface and $R_{Fresnel}(Q_z)$ corresponds to the theoretical expression of the Fresnel reflectivity expected for an ideal free interface (*abrupt, flat and of infinite lateral extension*).

2.1. Born approximations

The use of Born approximations in diffusion is common and justified when the radiation interacts little with matter [18 [Smectic-A Order at the Surface of a Nematic Liquid Crystal: Synchrotron X-Ray Diffraction], 19 [Physica B]]. They are particularly appreciated when they make it possible to simplify the formalism to the point of making the writing of analytical expressions possible for R and T. Mainly they amount to neglecting:

- multiple thoughts
- refraction in materials
- phase variations due to changes in the propagation speed when passing from one medium to another.

The second and third of these simplifications can be called "*kinematic approximations*", since the conservation is only verified for the velocity vector along the particle's trajectory. On the contrary, the previous ("dynamic") models respect the laws of mechanical conservation.

For multilayer films, the integral of the previous expression becomes a discrete sum. When the origin of the odds ($z = 0$) is taken at the free surface of the film, we obtain:

$$R(Q_z) = r * Conj(r) \quad \text{where} \quad r(Q_z) \approx 4\pi \sum_{l=0}^{(N-l)\,interfaces} \frac{\left((\rho b)_{l+1} - (\rho b)_l\right)}{Q_z^2} e^{iQ_z z_l}$$

By applying Born approximations, we traced the reflectivities of the sample presented previously following dynamic theory. We see in the figure that these approximations are not valid in the region which extends from very small angles to several times the critical angle of the film (i.e. small diffusion vectors Q with $Q = Q_z$ under specular conditions). This limitation makes the use of Born approximations difficult when the reflected intensity drops quickly with Q_z.

Remarque

These approximations are therefore rarely used for neutrons since the range of the diffusion vector analyzed rarely goes beyond $Q_z \sim 0,3\ \text{Å}^{-1}$.

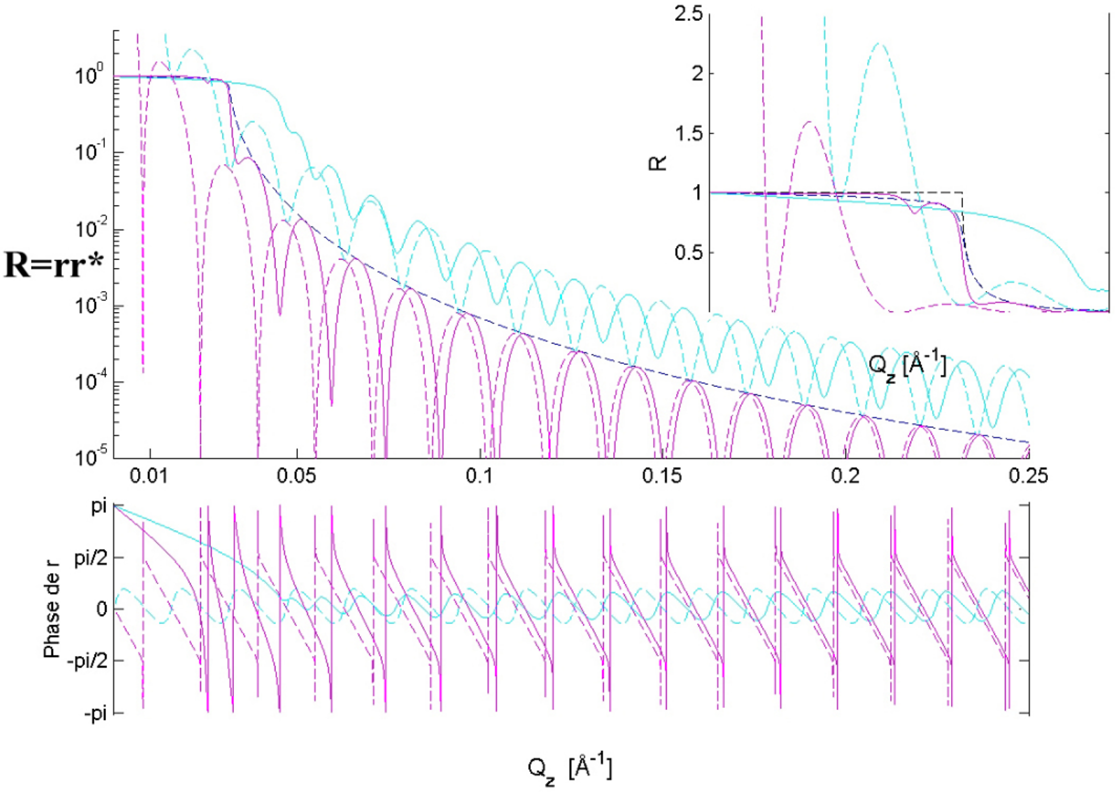


Figure 11 : Comparison of reflectivities plotted with a kinematic theory based on the use of Born approximations (dotted lines) and with a dynamic theory (solid lines)

Complément

The dynamic calculations are presented in a previous figure. The curves corresponding to the bare substrate without a film on it are calculated according to dynamic theory and plotted in black dotted lines (with and without absorption)

3. Calculation of the refractive indices of a material for X-rays and neutrons

We will see how to calculate the **refractive index of a material for x-rays and neutrons**,this from its isotopic composition and using data tabulated in the literature.

It is convenient to decompose the refractive index (n) from a material into a real component ($1-\delta$) and an imaginary component ($-\beta$) :

$$n=1-\delta-i\beta \quad , \text{ with } \quad \begin{cases} \Re(n)=1-\delta \\ \Im(n)=-\beta \end{cases}$$

The components δ and β respectively characterize the **broadcast** and the **absorption** of a material on the macroscopic scale, that is to say when the components of the diffusion vector Q are large compared to the dimensions of the atomic cells projected into the reciprocal space. These values depend on the nature and wavelength of the radiation used. They are obtained from constants accessible in the literature or on the internet. For example, we can use the **diffusion length density**(ρb) and the **linear absorption coefficient**(μ) material with expressions:

$$\begin{cases} \delta = \dfrac{(\rho b)\lambda_0^2}{2\pi} \\ \beta = \dfrac{\mu \lambda_0}{4\pi} \end{cases}$$

L'expression de δ is only valid when $(\rho b)$is weak. This is generally the case for neutrons and X-rays since the materials have a diffusion length density (ρb) of the order of 10^{-6} à $10^{-5}\left[\mathring{A}^{-2}\right]$, but this is not the case for visible light for example. Thus, the link between δ, β and respectively (ρb) and μ is not as simple as this relationship indicates (François de Bergevin discusses it in the reference [3 [X-ray and Neutron Reflectivity : Principles and Applications]]). We will see that it is possible to remove this approximation while retaining the use of the values usually calculated or tabulated for (ρb) and (μ). These two constants characterizing a material are particularly appreciated for the following reasons:

- The **diffusion length density**(ρb) is independent of the wavelength in the range of energies that we usually consider for X-rays in the laboratory or Neutron beams (except in the case of the use of very specific techniques well beyond the scope of this course). When the relationships linking δ to (ρb) and β to μ above are valid and when the absorption of the material is low, the Snell-Descartes law relates δ_T at the **critical angle of the material** T by the simple relationship : $\alpha_{0T}^{(c)} \approx \sqrt{2\delta_T}$
- The **linear absorption coefficient**μ has here the same meaning as that used in the Beer-Lambert law for visible light. Transmission through a thickness x of a material corresponds to the ratio of the transmitted flux relative to the incident flux. Either : $T = \dfrac{J_T}{J_I} = e^{-\mu x}$

  So the opposite of μ corresponds to the thickness crossed giving a reduction in the intensity of the beam by a factor $\exp(1) \approx 2,72$, either $\Delta J / J_I = (J_I - J_T)/J_I = 63,2$. This greatness $(1/\mu)$is called the **average free path without absorption** (*in meters*).

The values of (ρb) and of μ of a material are different for light, X-rays and neutrons. On the other hand, we can compare these quantities with each other $(\rho b)_{Neutrons}$ or $(\rho b)_{RX}$ which allows, among other things, to know whether it is better to use X-ray or neutron radiation to study a given sample. We generally look for the greatest contrast between successive layers (difference of (ρb)) which results in more marked interference fringes in the signal R analysis. Experimental considerations must also be taken into account when choosing the technique and will be discussed in another chapter. We will now present their calculation.

3.1. Photons X

The reduction in propagation speed experienced by a light wave arriving from a vacuum in matter can be explained with simple arguments: the periodic electric field of the incident wave exerts a force on the electrons in the medium. This force causes the electrons to oscillate at the same frequency as the incident wave, which results in the emission of an electromagnetic wave of the same frequency. The resulting total field is the coherent superposition of the fields of the incident wave and the wave emitted by the medium. The interference of these waves leads to slower propagation in the material medium than in a vacuum. The same reasoning applies to the propagation of X-rays in matter.

X-rays interact with the electrons of the atom. The X-ray refractive index of a material is obtained from the **classical phenomenological model of the elastically bound electron.**. The fundamental equation of dynamics applied to the electron takes into account a Lorentz force due to the local electromagnetic field induced by the incident wave, an electron-nucleus restoring force (with a spring constant $m_é \omega_{l,m}^2$) and viscous type braking of its movements (of friction constant ζ_i). The pulsation of the electron m of the atom l is noted $\omega_{l,m} \left(\sim 10^{15}\ [\mathrm{rad/s}]\right)$ and is infinitely weaker than that of the incident electromagnetic wave $\omega \left(\sim 10^{19}\ [\mathrm{rad/s}]\right)$. We therefore assume that the electron will vibrate under the influence of the incident field at the forced pulsation ω. This model leads to the following expression for the refractive index [22 [Neutron and Synchrotron Radiation For Condensed Matter Studies]] :

Fondamental

$$n_l^2 = 1 + \frac{N_l^{atoms} e^2}{\epsilon_0 m_e} \sum_m^{electrons} \left(\frac{f_{l,m}}{\omega_{l,m}^2 - \omega^2 - i\,\omega\,\zeta_{l,m}} \right)$$

where $m_é$ is the mass of an electron ($9,109.10^{-31}$ kg) and e is his charge ($1,602.10^{-19}$ C).

The **complex diffusionfactor**$f_{l,m}$ can be decomposed into the sum of three terms for the atom l : Z_l, f_l, m' et $if_{l,m}$'' which are accessible in the literature for each atom or ion [23 [Relativistic Calculation of Anomalous Scattering Factors for X Rays], 24 [Determination of the Dispersive Correction f'(E) to the Atomic Form Factor from X-ray Reflection]]. These are respectively the total number of electrons, the real part and the imaginary part of the anomalous scattering factor .Only the second and third term depend on the wavelength of the X-rays used. In practice, the number of atoms per unit volume is obtained from the mass density ρ_l in atoms $l$and from the atomic mass A_l, with the expression : $N_l^{atoms} = Na\rho/A_l$, où Na is Avogadro's constant equal to $6,022.10^{23}$.

For a material consisting solely of the chemical element l we obtain for X-rays:

$$\begin{cases} (\rho\, b)_l^{RX} = r_0 (\rho\, b)_l^{electron} = r_0 N_l^{atoms} (Z_l + f'_l) \\ (\mu)_l^{RX} = 2\,\lambda_0 r_0 N_l^{atoms} (f''_l) \end{cases}$$

where $r_0 = e^2/(4\pi\varepsilon_0 m_é C^2) = 2,814.10^{-15}\ m$ and corresponds to **classical electron radius**. This constant quantifies the strength of the interaction of an electron with an X-ray photon.

Remarque

In these expressions, f'_l appears as a correction to the total number of electrons Z_l of the atom l in the expression of the electron density of the material andf_l'' introduces the presence of absorption thresholds at particular wavelengths.

These two corrections strongly depend on the wavelength and can be very important.

3.2. Neutrons and pseudo-Fermi potential

Neutrons interact mainly with the nucleus of the atom. Within the framework of quantum theory, the study of the diffusion of a neutron by a fixed atom involves the search for the wave function Ψ solution of Schrödinger's equation. Analogous to the treatment of scalar diffusion according to the optical formalism presented, the wave function Ψ is expressed from the interference of an incident wave (Ψ_l) and a diffused wave (Ψ_{Dif}). We then pose the following conditions:

$$\begin{cases} H\Psi = E\Psi \\ \text{Solution : } \Psi = \Psi_l + \Psi_{Dif} \end{cases} \quad \text{with} \quad \begin{cases} H_0\Psi_l = E\Psi_l \\ \Psi_{Dif} = G\,V\,\Psi \end{cases}$$

where the wave functions are written Ψ_l for the incident plane wave, Ψ_{Dif} for the scattered wave assumed to be spherical and Ψ for the solution sought. H_0 is the Hamiltonian of the system in the absence of interactions with the neutron, E is the energy of the system that is conserved during diffusion and$G$ is a so-called delayed Green function for the spherical wave. The solution must satisfy the Lippmann-Schwinger equation which involves determining the transition operator T (*equation 2.1.5 reference [*25 [Neutron Scattering lengths and cross sections]*]*) :

$$\Psi = (1 + G\,T)\,\Psi_l$$

Fermi in 1936 proposed the following expression for the transition operator:

$$T(r) = \frac{2\pi\hbar^2}{m_N} a_{core}\,\delta(r)$$

where a is a diffusion length equal to the first term of the expansion of the diffusion amplitude $f = -a + ik_0a^2 + O(k_0^2)$ and of which it is the low energy limit (*equation 2.3.38 of the reference [*25 [Neutron Scattering lengths and cross sections]*], the different terms of f are defined after equation 2.2.27*). This result was extended to the case of bound atoms, assuming that at the instant of the collision, interatomic interactions were negligible. This so-called "Impulse approximation" hypothesis has since been justified since interatomic forces are typically of the order of 1eV over a distance of $1\mathring{A}$, while the neutron-nucleus interaction potential is estimated at nearly 40.10^6 eVwithin a radius of a few fm. The Fermi pseudo-potential makes it possible to quantify the bound neutron-nucleus interaction and has the expression:

$$V^{Fermi}(r) = T(r) = \frac{2\pi\hbar^2}{m_N} b_{core}\,\delta(r)$$

In this expression we have substituted for the constant a of the operator the constant b_{core} called **bound diffusion length**. These constants are linked by the relation:

$$b_{core} = \left(\frac{A_{core}/(m_N+1)}{A_{core}/m_N}\right) a \quad \text{, where} \quad A_{core} \quad \text{is the atomic mass of the nucleus.}$$

This substitution (*from a to b*) corresponds to the transition from the frame of reference attached to the center of mass to that attached to the laboratory. The word bond does not refer to chemical bonding and these quantities are both applicable to monatomic gases for example. The expression of V is a hard-core central pseudo-potential describing an interaction of very weak spatial extension ($r = |\vec{r} - \vec{r}_{core}| = 10^{-5}\,\mathring{A}$) with the neutron located at the position

$\vec{r}$. The interaction is centered on the position of the nucleus $\vec{r}_{core}$ like a dirac $\delta(r)$ and is repellent ($V^{Fermi} > 0$) for positive values of b_{core}. This phenomenological quantity is determined experimentally and evaluates, in some ways, the strength of the neutron-matter interaction.

For neutrons, we introduced into the framework of the elementary theory of diffusion the refractive index of the material by the expression:

$$n_l=\frac{n_l}{n_0}=\frac{k_l}{k_0}=\sqrt{1-\frac{V_l}{E_0}}=\sqrt{1-\frac{4\pi}{k_0^2}(\rho b)_l}=\sqrt{1-\frac{\lambda_0^2}{\pi}(\rho b)_l}$$

A more rigorous formalism which we will not explain here due to its complexity introduces corrections to the local field [25 [Neutron Scattering lengths and cross sections]]. It is often possible to separate the optical index into two contributions while maintaining excellent precision. Likewise, the diffusion length of the bound nucleus also separates into a real part and an imaginary part leading to the expression:

$$b=\Re(b)-i\,\Im(b)$$

Remarque

To explain the origin of these two contributions, we must recall that neutrons are sensitive to magnetism and have a spin $s = 1/2$ able to interact with nuclear spins I atoms encountered. The linked diffusion length therefore becomes dependent on I and its most general expression (*rotation invariant*) is :

$$b=b^{Coh}+\frac{2\,b^{Inc}}{\sqrt{I(I+1)}}\vec{s}\,\vec{I}$$

When the nuclei or neutrons are not polarized, the average over time and over all possible orientations of the spin vectors cancels the second term of this sum. We therefore obtain the Coherent diffusion length : $\langle b\rangle = b^{Coin}$. On the other hand, the expression of the square of the fluctuations of b preserves for this average a part dependent on the spins and is expressed as : $\langle|\Delta b|^2\rangle = \langle|b|^2\rangle - |\langle b\rangle|^2$, where $\langle|b|^2\rangle = \left(b^{Inc}\right)^2$. **Diffusion cross sections** say **coherent and inconsistent** are obtained from these quantities. Their sum corresponds to the total effective diffusion section:

$$\sigma^{Dif}=\sigma^{Coh}+\sigma^{Inc} \quad \text{, with :} \quad \begin{cases} \sigma^{Coh}=4\pi\left(b^{Coh}\right)^2 \\ \sigma^{Inc}=4\pi\left(\left(b^{Inc}\right)^2-\left|b^{Coh}\right|^2\right) \end{cases}$$

Rappel

A material consisting of a single chemical element is generally a mixture of isotopes with different spins. To the orientation disorder of the spin vectors is then added an isotopic disorder. A crude approach to this dependence of cross sections as a function of spins is to consider that a neutron will probe a material with a uniform interaction potential as if this medium were constituted by a single effective scatterer characterized by b^{Coch} and that there are random fluctuations (time and space) of this interaction giving rise to a **so-called incoherent isotropic diffusion** and characterized by b^{Incoin}.

According to the elementary theory of diffusion, the absorption cross section σ^{Ab} simply worth μ/ρ. In reality the coherent wave is also attenuated by diffusion, which is taken into account in the so-called rigorous dispersion theory. We find in the reference [25 [Neutron Scattering lengths and cross sections]] the absorption cross sections for different elements calculated for a wavelength of $1,798\,\mathring{A}$. the absorption cross sections for different elements calculated for a wavelength of σ^{Ab} and λ et b" is :

$$\sigma^{Ab}=2\lambda\langle\Im(b)\rangle$$

where the statistical average is carried out on the spins of neutrons and nuclei.

Exemple

To illustrate this discussion, consider the case of **Hydrogen**, ${}_{1}H$ spin ½.

$$\begin{cases} b_H^{Coh}=-3{,}8\,10^{-15}\,m \\ b_H^{Inc}=25{,}3\,10^{-15}\,m \end{cases} \text{, either } \begin{cases} \sigma_H^{Coh}=1{,}8\,bn \\ \sigma_H^{Inc}=80\,bn \end{cases} \text{, so } \quad \sigma^{Dif}=81{,}8\,bn$$

For its double mass isotope, the **Deutérium**, ${}_{2}D$ spin 1, the values obtained are very different :

$$\begin{cases} b_D^{Coh}=6{,}67\,10^{-15}\,m \\ b_D^{Inc}=4{,}04\,10^{-15}\,m \end{cases} \text{, either } \begin{cases} \sigma_D^{Coh}=5{,}6\,bn \\ \sigma_D^{Inc}=2{,}03\,bn \end{cases} \text{, so } \quad \sigma^{Dif}=7{,}67\,bn$$

Thus the diffusion of H is almost eight times stronger than that of D but is on the contrary mainly incoherent. The isotope D will therefore lead for the same molecular structure to a much more advantageous coherent signal to noise (incoherent) ratio than H and to a much greater amplitude of coherent interaction. In the sense defined here, it is this which makes it possible to obtain structural information. In neutron reflectivity the incoherent contribution is often assimilated to an additional source of background noise.

We can take into account the loss of intensity due to the incoherent diffusion of a material by assuming that it sums to the absorbed intensity (*neutrons captured in the sample*). To do this, we substitute for the absorption cross section its sum with the incoherent diffusion cross section which is also found in the literature. For the calculation we will use:

$$\begin{cases} (\rho\, b)_l^{Neutrons}=N_l^{isotope}\, b_l^{Coh} \\ (\mu)_l^{Neutrons}=N_l^{isotope}\,\sigma_l^{Ab} \end{cases}$$

These terms are found in the literature for each isotope and for the average value obtained from the natural isotopic abundances of isotopes of an element. This average includes all those that should be carried out for non-polarized neutrons in the context of elastic diffusion.

3.3. Using tables to calculate indices

Some values are given in the following tables for common chemical elements. Likewise, the critical angles and corresponding diffusion vectors appear in the last table.

Méthode

For a chemical compound of molecular mass M_Σ and volume density ρ_Σ, we must consider all the elements that constitute it, that is to say all the different isotopes.

Macroscopic quantities, (ρb) et μ, are obtained by summations of these isotopes weighted by their volume fractions Φ_1 respective. We can also weight by the fractions in number of the different diffusers (*ex* : for silicon oxide SiO₂ : $\Phi_{Si}^{N} = 1/2$, $\Phi_{0}^{N} = 2/3$ since $N_{Si} = 1$ et $N_0 = 2$). In the general case we retain:

$$\begin{cases} (\rho\, b)_{\Sigma}^{RX} = r_0(\rho_{\Sigma}^{electron}) = r_0(Na\,\rho_{\Sigma}) \sum_{l}^{atoms} \dfrac{\phi_l}{A_l}(Z_l + f\,'_l) \\ (\mu)_{\Sigma}^{RX} = 2\,\lambda_0 r_0 (Na\,\rho_{\Sigma}) \sum_{l}^{atoms} \dfrac{\phi_l}{A_l}(f\,''_l) \end{cases}$$

and

$$\begin{cases} (\rho\, b)_{\Sigma}^{Neutrons} = Na\left(\dfrac{\rho_{\Sigma}}{M_{\Sigma}}\right) \sum_{l}^{isotopes} N_l b_l^{Coh} \\ (\mu)_{\Sigma}^{Neutrons} = Na\left(\dfrac{\rho_{\Sigma}}{M_{\Sigma}}\right) \sum_{l}^{isotopes} N_l b_l^{Abso} \end{cases}$$

Remarque

Note that $b_H^{Coh} < 0$ which allows, through mixtures or substitution between isotopes H and D, to obtain a whole range of neutron diffusion length densities $(\rho b)^{Neutrons}$ including zero value.

This operation is called contrast variation by isotopic substitution and is widely used, for example, by mixing light water (H_2O) and heavy water (D_2O). With X-rays it is possible to choose radiation whose energy corresponds to an intense electronic absorption threshold of an element of the sample and also to create a variation in contrast by so-called anomalous diffusion. The physical origin of these two phenomena is very different.

Pour λ_0 = 1,798 [Å]		Rayons-X, *(diffusion)*	Rayons-X, (a*bsorption*)	Neutrons, Diffusion Cohérente.	Neutrons, Diffusion Incohérente.	Neutrons, Diffusion totale.	Neutrons, Absorption.
Eléments chimiques et composition isotopique (Spins).	A [g/mol]	$\sum_{j}^{atomes} Z_j$ en électrons et f'	f'' et μ/ρ en cm^2/g	(b_{Coh}) en Å et σ_{Coh} en bn	(b_{Inc}) en Å et σ_{Inc} en bn	σ_{Dif} en bn	σ_{Abs} en bn
Hydrogène = 99,985% $_1$H (½) +0,015% $_2$D (1) +(12,32 a) $_3$T (½)	1,008	1 et ?	?	-3,739 10^{-5} et 1,7568	25,27 10^{-5} et 80,26	82,02	0,3326
100% $_1$H (½)	1	1 et ?	?	-3,7406 10^{-5} et 1,7583	25,27 10^{-5} et 80,27	82,03	0,3326
100% $_2$D (1,)	2	1 et ?	?	6,671 10^{-5} et 5,592	4,04 10^{-5} et 2,05	7,64	0,0005
100% $_3$T (½)	3	1 et ?	?	4,792 10^{-5} et 2,89	-1,04 10^{-5} et 0,14	3,03	0
Carbone = 98,9% $_{12}$C (0) + 1,10% $_{13}$C (½)	12,011	6 et 0,017	0,009 et 3,9	6,64 10^{-5} et 5,550	-0,52 10^{-5} ($_{13}$C) et 0,001	5,551	0,0035
Oxygène = 99,762% $_{16}$O (0) + 0,038% $_{17}$O (5/2) + 0,2% $_{18}$O (0)	16,004	8 et 0,47	0,032 et 10,5	5,80 10^{-5} et 4,23	0,004 10^{-5} ($_{17}$O) et 0,000	4,232	0,00019
Silicium = 92,23% $_{28}$Si (0) + 4,67 $_{29}$Si (½) +3,10% $_{30}$Si (0)	28,09	14 et 0,244	0,330 et 61,5	4,149 10^{-5} et 2,16	0,09 10^{-5} ($_{29}$Si) et 0,004	2,167	0,171
Soufre = 95,02% $_{32}$S (0) +0,75 $_{33}$S (3/2) +4,21% $_{34}$S (0) +0,02% $_{36}$S (0)	32,092	16 et 0,319	0,557 et 90,8	2,804 10^{-5} et 1,0186	1,5 10^{-5} ($_{33}$S) et 0,007	1,026	0,53
Fer = 5,8% $_{54}$Fe (0) +91,7% $_{56}$Fe (0) +2,2% $_{57}$Fe (½) +0,3% $_{58}$Fe (0)	55,85	26 et −1,179	3,204 et 300,1	9,45 10^{-5} et 11,22	- et 0,3	1,0	2,56

***Tableau I** : Caractéristiques de la diffusion des neutrons et des rayons-x de quelques éléments chimiques. Pour chaque élément : A est sa masse atomique. 1 bn = 100 fm^2 = 10^{-4} Å^2. Issues des tables de référence. Les ? marquent les valeurs qui n'ont pas été reportées.*

Table I: Characteristics of the diffusion of neutrons and x-rays of some chemical elements. For each element: A is its atomic mass. 1 bn = 100 fm2 = 10-4 Å2. From reference tables. THE ? mark the values which have not been reported

			Rayons-x			Neutrons	
Pour $\lambda_{Cu\text{-}K\alpha}$=1,54[Å]	Masse	Densité	Electronique	Diffusion	Absorption	Diffusion	Absorption
	M g/mol	g/cm^3 et V_{Elem} Å^3	$\sum_{j}^{atomes} Z_j$ et ρ^{elec} Å^{-3}	$(\rho\, b)^{elec}\ \mathring{A}^{-2}$ et δ_{RX}	μ_{RX} Å^{-1}, ($1/\mu_{RX}$) et β_{RX}	$(\rho\, b_{Coh})\ \mathring{A}^{-2}$ et δ_N	μ_N Å^{-1}, ($1/\mu_N$) et β_N
Silicium (Si)	28,1	2,32 et 20,1	14 et 0,7	19,92 10^{-6} et 7,55 10^{-6}	1,425 10^{-6}, 70 µm et 0,175 10^{-6}	2,14 10^{-6} et 0,808 10^{-6}	8,5 10^{-11}, 1,17 m et 1,05 10^{-11}
Oxyde de silicium (SiO_2)	60,1	2,05 et 48,7	30 et 0,616	18,06 10^{-6} et 6,81 10^{-6}	7,03 10^{-7}, 14,2 µm et 8,6 10^{-8}	3,23 10^{-6} et 1,228 10^{-6}	3,5 10^{-11}, 2,84 [m] et 4,3 10^{-12}
Eau (H_2O)	18	1 et 30	10 et 0,335	9,88 10^{-6} et 3,73 10^{-6}	9, 3 10^{-8}, 1,08 mm et 1,34 10^{-8}	-5,614 10^{-7} et 2,119 10^{-7}	4,4 10^{-11}, 2,26 [m] et 4,49 10^{-11}
Psh (Polymère Polystyrène hydrogéné) (C_8H_8)	104,15	1,05 et 164,7	56 et 0,34	9,96 10^{-6} et 3,67 10^{-6}	4,15 10^{-8}, 2,41 mm et 5,08 10^{-9}	1,41 10^{-6} et 5,32 10^{-6}	1,6 10^{-10}, 0,61 m et 2,00 10^{-11}
Psd (Polymère Polystyrène deutéré) (C_8D_8)	112,2	1,13 et 164,9	"	"	"	6,46 10^{-6} et 2,44 10^{-6}	1,95 10^{-12}, 51,3 m et 2,4 10^{-13}
PBMAh ($C_8H_{14}O_2$) Polymère	142,2	1,052 et 224,5	78 et 0,3475	9,91 10^{-6} et 3,74 10^{-6}	5,7 10^{-8}, 1,75 mm et 6,99 10^{-9}	0,55 10^{-6} et 2,07 10^{-7}	2,08 10^{-10}, 0,48 m et 2,55 10^{-11}
PBMAd ($C_8H_{14}O_2$) Polymère	156,3	1,154 et 224,9	"	"	"	7,03 10^{-6} et 2,65 10^{-6}	1,6 10^{-12}, 63,1 m et 1,94 10^{-13}
Maghémite (γ-Fe_2O_3)	159,7	5 et 53	76 et 1,43	39,9 10^{-6} et 1,5 10^{-5}	1,06 10^{-4}, 0,94 [µm] et 1,3 10^{-6}	6,84 10^{-6} et 2,58 10^{-6}	1,0 10^{-9}, 0,10 m et 1,18 10^{-10}

Tableau II. *Caractéristiques liées à la diffusion des matériaux pour quelques exemples. Pour chaque matériau : M est sa masse molaire en g/mol, ρ est sa densite massique en g/cm³, V_{Elem} est le volume de l'élément unitaire constitutif Å³, Σz_i est le nombre d'électrons, $\rho^{élec}$ est sa densite électronique en électrons/Å³, les (ρb) sont les densitées de longueur de diffusion électroniques (rayons-x) ou cohérente (neutrons), les δ et β sont les décréments et les parties imaginaires des indices de réfraction et les µ sont les coefficients d'absorption lineaire électronique ou neutronique.*

Table II. Characteristics linked to the diffusion of materials for some examples. For each material: M is its molar mass in g/mol, ρ is its mass density in g/cm3, VElem is the volume of the constituent unit element Å3, ΣZi is the number of electrons, ρélec is its electron density in electrons/Å3, the (ρb) are the electronic (x-rays) or coherent (neutrons) diffusion length densities, the δ and β are the decrements and imaginary parts of the refractive indices and µ are the electronic or neutron linear absorption coefficients

L'angle critique et son vecteur de diffusion associé sont obtenus à partir de ces valeurs :

	Rayons-x		Neutrons	
$Q_{0T}^{(c)}$ est indépendant de la longueur d'onde, pas calculé pour $\lambda_{Cu\text{-}K\alpha}$=1,54 Å. $\alpha_{0T}^{(c)}$	$Q_{0T}^{(c)}$, en 1/Å	$\alpha_{0T}^{(c)}$, degrés	$Q_{0T}^{(c)}$, 1/Å	$\alpha_{0T}^{(c)}$, degrés
Silicium (Si)	0,0316	0,222	0,0102	0,0715
Oxyde de silicium (SiO_2)	0,0301	0,2116	0,0127	0,0895
Eau (H_2O)	0,0222	0,1564	0	0
Polymère PSh (C_8H_8)	0,0220	0,154	0,00842	0,0591
Polymère PSd (C_8D_8)	"	"	0,0180	0,126
Polymère PBMAh ($C_8H_{14}O_2$)	0,0222	0,156	0,053	0,037
Polymère PBMAd ($C_8D_{14}O_2$)	"	"	0,019	0,132
Maghémite (γ-Fe_2O_3)	0,045	0,314	0,0185	0,13

Tableau III. *Angles critiques* $\alpha_{0T}^{(c)}$ *dans le vide (0) des différents matériaux considérés pour une longueur d'onde* λ_0 *~1,54 [Å], et vecteurs de diffusion associés* $Q_{0T}^{(c)}$.

.

Table III

III.Exercices

These exercises aim to put into practice some fundamental notions covered in the course.

1. Comparison of neutron and X-ray refractive indices

Take silicon as an example (*isotopic mixture*) widely used in microelectronics. Its mass density is $\rho_{Si} = 2,32\ \mathrm{g/cm^3}$ and atomic mass $A_{Si} = 28,1\ \mathrm{g/mol}$. This is studied with neutron or X-ray radiation of equal wavelength: $\lambda_0 = 1,54\mathring{A}$ (corresponding for X-rays to emission lines K_α Copper widely used in the laboratory).

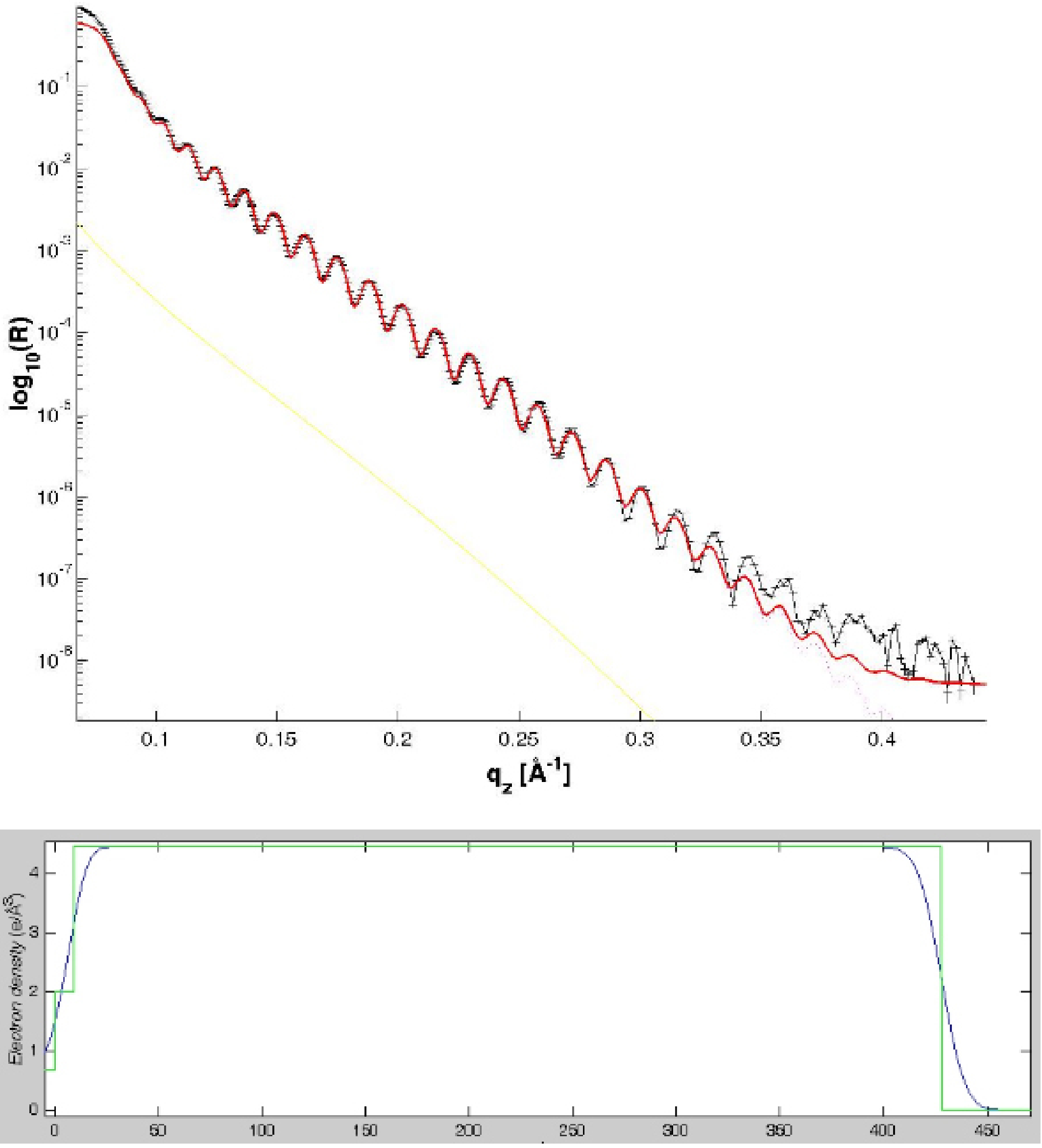
Question

[*Solution n°1 p 54*]

Using the characteristics of chemical elements given in the course tables, calculate the refractive indices (real and imaginary part) for X-rays and neutrons.

2. Determination of the electron density and thickness of a thin layer of gold by specular X-ray reflectivity

We will determine the thickness of a thin layer of gold deposited on a glass substrate (type SiO_2). The figure shows the X reflectivity curve measured in blue and the red curve is obtained following a dynamic calculation of the reflectivity using the Parratt algorithm introduced in the course. By adjusting the parameters of the model we obtain the red curve leading to the thickness, the roughness and the electronic density of the gold layer as well as the electronic density of the substrate and its roughness (taking into account the roughness in the calculation is not presented in this chapter of the course).



Couches	**Vecteur diffusion Critique, q_c en Å^{-1}**	**Absorption : μ x10^{-7}**	**Rugosité Gaussienne (rms), σ en Å**	**épaisseur, d en A**
Air	0	0	0	∞
Au	0.079167 *	48.9 *	9	419
SiO_2	0.030814 *	0.92 *	6	∞

Figure 12

Model Fit Parameters that are set to expected values are marked with a star in the table. They are calculated for an energy of $8050,9122\,\text{eV}$ (either $\lambda_0 = 1,540\AA$), either $Z_{Au}^{eff} = 74.9851$ effective electrons (gold has 79 electrons but the anomalous correction f' to Z decreases the effective value of the number of electrons participating in the interaction with X-radiation).

Question 1

[*Solution n°2 p 54*]

Calculate from the parameters resulting from the reflectivity analysis, the following properties of the gold layer:

- The critical angle in degrees from the critical diffusion vector of the gold layer.

- Its diffusion length density (in $\mathring{A}^{-2}$) from its critical angle.
- Its electron density in $\text{électrons}/\mathring{A}^3$.
- Its atomic density.

Question 2

[Solution n°3 p 55]

From the measured reflectivity, it is possible to determine the thickness of the dense gold layer quite precisely simply from the period of the oscillations. In the present case, there are 7 oscillations between the angle of incidence $1,040$ and $1,809$. Deduce the thickness of the gold layer.

Solution des exercices

>Solution n°1 *(exercice p. 51)*

For neutrons, the elementary scatterers are the nuclei of the atom whose volume density is $N_{Si}^{atoms} = Na\rho / A_l = 5.10^{22}$ diffusers/cm^3. For X-rays, the scatterers are electrons whose volume density is 14 times higher since $Z_{Si} = 14$. The "scattering force" of elementary scatterers is quantified in terms of effective scattering length. That of the electron diffusing the X-rays is: $r_0 \equiv b_{\acute{e}} = 2,82.10^{-5}\mathring{A}$ while that of the silicon nucleus diffusing neutrons is valid here: $b_{Si}^{Coh} = 4,15.10^{-5}\mathring{A}$. The product of the densities of scatterers by their diffusion length leads us to the diffusion length densities, they are here respectively $(\rho b)_{Si}^{RX} = 1,992.10^{-5}\mathring{A}^{-2}$ and $(\rho b)_{Si}^{Neutrons} = 2,14.10^{-6}\mathring{A}^{-2}$. So for Silicon, it is the density of diffusers which is mainly at the origin of the difference between these two values. Therefore, the X-ray critical angle $\alpha_{0\,Si}^{(c,Rx)}$ will be larger than neutrons $\alpha_{0\,Si}^{(c,Neutrons)}$ by about a factor:

$$\rho_{Si}=2{,}32\,g/cm^3$$

If we compare the absorptions of silicon for these two radiations, we can consider that X-rays are quickly absorbed while neutrons are very penetrating, in fact : $\frac{1}{\mu_{Si}^{RX}} \approx 7\,\mu\,\mathrm{m}$ and $\frac{1}{\mu_{Si}^{Neutrons}} \approx 1,17\,\mathrm{m}$

This remark applies to the majority of elements constituting common materials, however there are particular isotopes that are very absorbent for neutrons (*Li*, ^{113}Cd,...). As an example, the ^{113}Cd has an effective absorption section of 20600 barns whereas it is only $0,34$ for ^{114}Cd. The isotope 113 is often used as a neutron absorber.

>Solution n°2 *(exercice p. 52)*

Under so-called specular measurement conditions, the diffusion vector is linked to the angle of incidence of the beam following the relationship:

$$A_{Si}=28{,}1\,g/mol$$

It allows you to approximately calculate the parameter δ_{Au} and to deduce the diffusion length density of gold:

$$\lambda_0=1{,}54\,\mathring{A}$$

We obtain $(\rho b)_{Au}^{RX} \approx 2\pi\frac{\delta}{\lambda_0^2} \approx 124,72 * 10^{-6}\mathring{A}^{-2}$

The electron density of gold is obtained by dividing (ρb) by the classical electron radius $r_0 = 2,8179.10^{-5}\mathring{A}$. We obtain : $(\rho)_{Au}^{electrons} = 4,426\ \mathrm{electrons}/\mathring{A}^3$.

We can also deduce one:

- Atomic density : $\rho_{Au}^{At} = 0.0590\ \mathrm{Au}/\mathring{A}^3$.
- Mass density : $\rho_{Au}^{Weigth} = 19.3\ \mathrm{g/cm^3}$.

- Volume density : $\rho_{Au}^{Vol} = 0.0980\ \mathrm{mol/cm^3}$.

with $M_{Au} = 196,967\ \mathrm{g/mol}$. All these values are consistent with the structure of the expected dense gold (here the orientation of the gold layer is 111 and is obtained by measuring the diffraction peaks at the largest angles).

>Solution n°3 *(exercice p. 53)*

We deduce the period of the oscillation in degrees: $(1,809 - 1,040)/7 \sim 0,10971$. It corresponds to a period in diffusion vector equal to:

$$K_\alpha$$

The formula given in the course for calculating the reflectivity of a homogeneous layer on a substrate makes it possible to relate this period in reciprocal space to the thickness of the layer in real space following the calculation:

$$N_{lf}^{atoms} = Na\,\rho / A_l = 5,10^{22}$$

Bibliographie

[Compt. Rend. Ac. Sc.] A.Herpin , *Compt. Rend. Ac. Sc. 225* , - , - , 1947, 182.

[Determination of the Dispersive Correction f'(E) to the Atomic Form Factor from X-ray Reflection] F.Stanglmeier, B.Lengeler, W. Weber, H.Gobel and M.Schuster , *Determination of the Dispersive Correction f'(E) to the Atomic Form Factor from X-ray Reflection* , Acta Cryst. 1992. A48, 626-639.

[Ellipsometry and polarized light] R.M.A.Azzam and N.M.Bashara , *Ellipsometry and polarized light* , - , - , 1977. Conventions adoptées par les participants de la conférence internationale de 1968 sur l'éllipsométrie tenue à l'université de Nebraska. Elles sont liées notamment à une dépendance temporelle en exp(+iwt).

[Evanescent Waves in Optical Imaging] Olof Bryngdahl , *Evanescent Waves in Optical Imaging* , Progress in optics XI, - , - , 1973, 169-221.

[Light reflection from films of continuously varying refractive index] R.Jacobsson, *Light reflection from films of continuously varying refractive index*, Progress in Optics, Vol. 5, ed. E.Wolf, Amsterdam, North Holland Publishing Company and New York, J.Wiley and Sons, 1965, p. 247.

[Mécanique Quantique] A. Messiah , *Mécanique Quantique* , Dunod-Paris , - , 1958.

[Neutron and Synchrotron Radiation For Condensed Matter Studies] HERCULES , *Neutron and Synchrotron Radiation For Condensed Matter Studies* , Springer-Verlag–Les éditions de Physique , Vol.1, 1999.

[Neutron Optics, An introduction to the theory of Neutron Optical Phenomena and Their Applications] Varley F.Sears , *Neutron Optics, An introduction to the theory of Neutron Optical Phenomena and Their Applications* , Oxford University Press , - , 1989.

[Neutron Scattering lengths and cross sections] Varley F.Sears , *Neutron Scattering lengths and cross sections* , Neutron News , Vol. 3, No. 3, 1992.

[Phil. Mag. 2] G.B.Airy , *Phil. Mag. 2* , 20, - , - , 1833.

[Physica B] Jens Als-Nielsen , Physica B , -, 126, 1984, 145-148.

[Principles of Optics] M.Born and E.Wolf , *Principles of Optics* , Pergamon , London , First Published 1959, 7th edition, 1999.

[Proc. Roy. Soc.] Lord Rayleigh , *Proc. Roy. Soc.* , 1912, 96A, 207.

[Quantum mechanics] C.Cohen-Tannoudji,B.Diu,F.Laloe , *Quantum mechanics* , - , - , 1977, Vol.1&2.

[Recherches sur la propagation des ondes électromagnétiques sinusoidales dans les milieux stratifiés. Applications aux couch.es minces] F.Abelès , *Recherches sur la propagation des ondes électromagnétiques sinusoidales dans les milieux stratifiés. Applications aux couch.es minces* , -, -, 1950, Annales de physique 5 , 596-640 , 706-782.

[Relativistic Calculation of Anomalous Scattering Factors for X Rays] Don T.Cromer and D.Liberman , *Relativistic Calculation of Anomalous Scattering Factors for X Rays* , The Journal of Chemical Physics , Vol.53, 5 , 1970.

[Smectic-A Order at the Surface of a Nematic Liquid Crystal: Synchrotron X-Ray Diffraction] Jens Als-Nielsen, F.Christensen, and P.S.Pershan , Smectic-A Order at the Surface of a Nematic Liquid Crystal: Synchrotron X-Ray Diffraction , Phys. Rev. Lett. 48, 1107, 1982.

[Surface Studies of Solids by Total Reflection of X-Rays] L.G.Parratt , *Surface Studies of Solids by Total Reflection of X-Rays* , Phys. Rev. 95 359, 1954. S.H.

[The Feynman Lectures on Physics] Feynman, *The Feynman Lectures on Physics*, Leighton and Sands, InterEditions, Paris, 1979.

[Theory of Neutron Scattering from Condensed Matter] Stephen W.Lovesey, *Theory of Neutron Scattering from Condensed Matter* , Clarendon Press , Oxford Science Publications , 1984, Vol.1.

[Theory of Reflection of Electromagnetic and Particles Waves] J.Lekner, *Theory of Reflection of Electromagnetic and Particles Waves*, Nijhoff, Dordrecht, 1987.

[X-ray and Neutron Reflectivity : Principles and Applications] J.Daillant and A.Gibaud (Eds.) , *TX-ray and Neutron Reflectivity : Principles and Applications* , Springer-Verlag , Berlin Heidelberg , 1999.

Webographie

[Matlab] Matlab. *The Math Works*, Inc.

Crédit des ressources

Figure 1 : Diopter Plan continuity equations *p. 8*

Figure 2 : Transition from medium I to a more refractive material (medium T) of visible light *p. 10*

Figure 3 : Illustration of the phase of a traveling wave represented by a complex number *p. 12*

Figure 4 : *p. 12*

Figure 5 : Representation of the direct trihedron (k, E, B) for the TE wave (electric transverse, polarized "s") *p. 13*

Figure 6 : Representation of reflectivities (R=rr*) on a logarithmic and linear scale (in insert). The phase of r is shown below *p. 25*

Figure 7 : Representation of the square of the module of the transmission coefficients (|t|2=tt*) *p. 26*

Figure 8). *p. 27*

Figure 10 : Schematic representation of a multilayer *p. 34*

Figure 11 : Comparison of reflectivities plotted with a kinematic theory based on the use of Born approximations (dotted lines) and with a dynamic theory (solid lines) *p. 41*

Table I: Characteristics of the diffusion of neutrons and x-rays of some chemical elements. For each element: A is its atomic mass. 1 bn = 100 fm2 = 10-4 Å2. From reference tables. THE ? mark the values which have not been reported *p. 48*

Table II. Characteristics linked to the diffusion of materials for some examples. For each material: M is its molar mass in g/mol, ρ is its mass density in g/cm3, VElem is the volume of the constituent unit element Å3, ΣZi is the number of electrons, ρélec is its electron density in electrons/Å3, the (ρb) are the electronic (x-rays) or coherent (neutrons) diffusion length densities, the δ and β are the decrements and imaginary parts of the refractive indices and µ are the electronic or neutron linear absorption coefficients *p. 49*

Table III *p. 50*

Figure 12 *p. 52*