1.1. General considerations

Before addressing the specificity of the interaction between ions and condensed matter, it may be useful to note a selected number of physical properties of the ions used by the IBA techniques and compare them with those of electrons and photons used as a probe, particularly by electron microscopy and X-ray diffraction. For instance, the wavelengths of ions are much shorter than those of photons and electrons. The penetration depth is also very different when passing from ions to lighter particles. All these properties are highly dependent on the energy of particles and they define the contours of the practical use of ions for materials’ analysis.

1.1.1. Wavelengths of ions, electrons and X-rays

Regarding the techniques using X-ray photons, their wavelengths $\lambda$ can be easily deduced from the following equation:

$$\lambda = \frac{hc}{E}$$

[1.1]
Where $h$ is the Planck’s constant, $c$ the speed of light in vacuum and $E$ the photon’s energy. In the case of mass particles, electrons and ions, their wavelengths are given by the relationship of de Broglie:

$$\lambda = \frac{h}{m_o \nu \sqrt{1 - \frac{v^2}{c^2}}}$$  \[1.2\]

where $\lambda$ is the particle’s wavelength, $h$ is the Planck’s constant, $m_o$ is the rest mass, $\nu$ is its velocity and $c$ is the speed of light in vacuum. The associated wavelengths of electron, photon, proton and alpha particles are plotted in Figure 1.1 in the 1 eV–1 MeV range. In the same figure, the range of interatomic distances in solids (top gray area) and the range of nuclei radii (bottom gray area) are also indicated.

Figure 1.1. Photon wavelength and de Broglie wavelengths of different particles as a function of energy. The top gray area corresponds to the typical distances between atoms within a solid. The bottom gray area corresponds to the nuclear dimensions.
1.1.1.1. X-rays

Considering first the case of X-rays, we can observe that in the energy range used for structural analysis (2–25 keV), the associated wavelengths also correspond to the distance between atoms in solid materials. In this situation, the photons scattered by a crystal interfere with each other and produce a so-called diffraction pattern. The interpretation of this phenomenon was first proposed by William Lawrence Bragg and William Henry Bragg in 1913 [BRA 13]. If we consider an X-ray beam of wavelength $\lambda$ having an incidence angle $\theta$ on a family of crystal planes defined by their interplanar distance $d$, the Bragg’s law predicts the maximum intensities obtained at a $2\theta$ scattering angle with the following expression:

$$2 \ d \times sin(\theta) = n \times \lambda$$  \hspace{1cm} [1.3]

As shown in Figure 1.2, the geometrical interpretation of this law is to consider that photons scattered by adjacent planes cause constructive or destructive interferences depending on the scattering angle.

Figure 1.2. According to the \(2\theta\) deviation of the X-ray beam, the phase shift between photons scattered by adjacent planes causes constructive (left figure) or destructive (right figure) interferences.

In the typical use of X-rays, where the photon’s wavelength is actually smaller but close to the interplanar distances, the angular distance between
Diffraction peaks of different indices is large as shown in Figure 1.3 (left-hand side) for 10 keV X-rays diffracted by atomic planes spaced by 0.2 nm. The relative accuracy on the interatomic distances that can be reached by X-ray diffraction is better than $10^{-4}$.

![Figure 1.3](left) Maximum intensities of a 10 keV X-ray beam diffracted by atomic planes spaced by 0.2 nm according to Bragg's law ($\theta/2\theta$ configuration). (Right) Laue diffraction pattern of a Ge(111) wafer (European Synchrotron Radiation Facility, IF-BM32 beamline)

1.1.1.2. Electrons

Electrons in the typical energy range employed in transmission microscopy (50–500 keV) have a much shorter wavelength than photons, as shown in Figure 1.1. If we now consider a 200 keV electron beam, the wavelength of the particles is about 2.51 pm. The diffraction by a crystal with an interplanar distance of 0.2 nm leads to a much shorter angular distance between diffraction peaks ($0.36^\circ$ in this case) of different indices, as shown in Figure 1.4 (left-hand side). As a consequence, in Transmission Electron Microscopy (TEM), the diffraction pattern is visible in the forward direction with respect to the beam, contrary to X-rays. However, accurate structural information can be obtained with this technique with a high spatial resolution (basically given by the beam spot size on the sample).
1.1.1.3. **Light ions**

The wavelength of 100 keV protons is 90.5 fm and that of 100 keV helium ions is 45.4 fm. If, again, the Bragg conditions are calculated for the same crystal (d = 0.2 nm), the diffraction peaks of different indices are very close to each other, as shown in Figure 1.5 (0.007° for helium ions and 0.013° for protons). Under these conditions, the observation of ions’ diffraction patterns would need a very grazing beam incidence on the sample with a beam divergence of about 0.001°. Accordingly, the ion detection should also have the same angular accuracy.

Because of these strict conditions, the ion diffraction by a crystal has never been observed in the typical IBA energy range. However, recently and under specific conditions, diffraction patterns of very low energy atoms (using a neutralized helium ions beam) in grazing incidence on reconstructed surfaces have been observed simultaneously by two different groups [ROU 07, SCH 07]. This technique, called Grazing Incidence Fast Atom Diffraction (GIFAD), is dedicated to surface analysis and is briefly described in section 4.6.4.
1.1.1.4. Diffraction

The diffraction phenomenon, mainly obtained not only with X-rays but also with electrons, is the most commonly employed method to obtain structural information. However, when considering nanoscale crystals, the X-ray diffraction peaks are enlarged precisely because of the finite size of the diffracting structure. This enlargement $\Delta$ can be quantified by the Scherrer’s relationship [SCH 18] as follows:

$$\Delta = \frac{K \lambda}{\tau \sin(\theta)} \quad [1.4]$$

where $K$ is a dimensionless shape factor (its typical value is close to 0.9 but can vary depending on the crystallites shape [LAN 78]), $\lambda$ is the wavelength, $\tau$ is the mean size of the crystalline domains and $\theta$ is the Bragg’s angle. This line broadening comes in addition to the instrumental width of the diffraction peaks as well as possible inhomogeneities of the stress within the crystal. This effect is negligible for grain sizes beyond 100 nm but becomes a limiting factor for objects of a few nanometers, as shown in Figure 1.6.
Ion beam analysis, for its part, working in the real space, is not affected by this limitation and remains effective up to structures of sub-nanometer sizes.

1.1.2. Penetration depths of ions, electrons and X-rays

The penetration of ions in matter is much lower than that of electrons and photons. As an example, the penetration through silicon for photons, electrons and light ions is shown in Figure 1.7. In fact, the definition of the depth of penetration is different for each type of particle due to their specific behavior. Regarding photons, in the energy range under consideration (<50 keV), their trajectories are rectilinear and they propagate without any loss of energy until the full transmission of their energy to a single electron by the photoelectric effect. Therefore, the number of photons passing through the sample exponentially decreases with depth and the penetration into the material is approximated in this work by the absorption length. For electrons and ions, the penetration corresponds to the mean distance between the entry position in a sample and the position at which the particles stop. However, in the case of electrons, the stopping distance is spread over a very large area compared to ions.
As illustrated in Figure 1.7, the relatively weak penetration of light ions through matter, compared to electrons and photons, is due to their high stopping power as is discussed hereafter (in section 1.2.1). As an example, a 100 keV helium ion loses 206 eV per nm within silicon. Ion detectors, nowadays, are accurate enough to measure this energy loss and translate it to the depth of the ion/nucleus interaction down to the nanoscale.

The above-mentioned features, the analysis in real space and an accurate energy/depth relation, are specific to ion beam analysis and allow the use of these techniques in the field of nanoscience.

1.2. Basic physical concepts

1.2.1. Energy loss and range of ions in matter

When a charged particle penetrates in a material, it gradually loses its kinetic energy with depth until it finally stops. The energy loss is mainly due to inelastic Coulomb interactions with electrons of the material. Losses due to ion-nucleus collisions are at least two orders of magnitude lower (see Figure 1.8). For an ion of energy \( E \) traversing matter of density \( N \)
atoms \times \text{cm}^{-3}$, whose energy changes on average by $dE$ in a length $dx$, the stopping cross-section $\varepsilon(E)$ (eV $\times$ cm$^2$) is defined by the following equation:

$$\varepsilon(E) = -\frac{1}{N} \frac{dE}{dx}$$ \[1.5\]

Note that since energy is lost, $dE$ is negative so that $\varepsilon$ is a positive value. From measured stopping cross-sections, one may deduce the average energy loss per unit length $-dE/dx$ (eV $\times$ nm$^{-1}$). This is often referred to as the stopping power of the medium for the ion.

**Figure 1.8.** Stopping cross-section of: (top) protons in silicon [AND 77] – (bottom) alphas in silicon [ZIE 77]
Semi-empirical relations that are universally used for the stopping cross-sections of all elements of the periodic table for protons and alphas have been applied to the many experimental measurements of stopping powers available in the literature [ZIE 77, AND 77].

The stopping cross-section $\mathcal{E}_c$ of compounds composed of elements $i$ in elemental proportions $a_i$ ($\sum a_i = 1$) can be easily obtained from those of the components $\mathcal{E}_i$ through the Bragg-Kleemann law of additivity:

$$\mathcal{E}_c(E) = \sum_{i=1}^{n} a_i \mathcal{E}_i(E)$$  \hspace{1cm} [1.6]

As the ions are only slightly deflected by electrons, the penetration $R$ of an ion initially of energy $E_0$ in the material can be approximated by the distance $D$ traveled by the ion (see Figure 1.9 for helium and hydrogen penetration depth in silicon).

![Figure 1.9. Penetration depths of helium ions [ZIE 77] and hydrogen ions [AND 77] in silicon](image)

The traveled distance $D$ can be calculated by integrating the stopping cross-section as follows:

$$D = -\int_{E_0}^{0} \frac{1}{N} \frac{dE}{\mathcal{E}(E)}$$  \hspace{1cm} [1.7]
The average energy of the ion at depth $L$ is given by the following equation:

$$E_L = E_0 + \int_0^L \frac{dE}{dx} \, dx$$  \hspace{1cm} [1.8]

1.2.2. Energy straggling

These data on energy loss can provide, at a given depth in the sample, the average kinetic energy of the ions. However, the statistical processes involved in slowing down lead to energy loss fluctuations, commonly called energy straggling. In addition, as the ion energy decreases, ion-nucleus collisions become more probable causing significant changes in the particle trajectory, as shown in Figure 1.10. For this reason, the analysis techniques using ion beams are applied on depth ranges well below the penetration depth.

![Figure 1.10. Calculated trajectories of protons in the first micron of a silicon sample for two incident energies (left) 100 keV – (right) 2 MeV [AND 77]. The calculation was made using the SRIM software [ZIE 04]](image)

The distribution of kinetic energies at a given depth $L$ has a mean of $E_L$ and standard deviation of $\Omega$. In the vast majority of ion beam analytical situations the distribution is practically Gaussian, so that the full width at half maximum is given by the following relation: $FWHM = 2 \sqrt{2 \ln(2)} \Omega \approx 2.355 \Omega$. 
Bohr [BOH 48] calculated $\Omega$ for the case in which all of the electrons in the solid may be considered to be free, and found a simple formula, which does not depend on the energy of the ion:

$$\Omega^2_B = 4\pi Z_1^2 Z_2 e^4 N L$$  \[[1.9]\]

where $Z_1$ is the atomic number of the projectile, $Z_2$ is that of the target, $e$ is the elementary charge, $N$ is the density of target atoms and $L$ is the considered depth.

W.–K. Chu [CHU 76] refined this estimation of $\Omega$ through quantum mechanical calculations taking into account the binding energies of electrons to atoms, giving the energy-dependent values plotted in Figure 1.11.

![Figure 1.11. Calculated values of straggling for protons and helium ions through different targets (data from [CHU 76])]
The correction becomes more important with decreasing energy of the incident particle as shown in Figure 1.11. It is already important to consider this correction for RBS analysis performed at a few MeVs, but it becomes crucial for MEIS analysis performed with ions of a few hundred keVs.

1.2.3. Elastic scattering

Elastic scattering of the ions on the nuclei of a sample to be probed is at the base of two techniques of ion beam analysis: RBS and MEIS [CHU 78]. RBS takes its name from Sir Ernest Rutherford who deduced from his scattering experiments the presence of an atomic nucleus in the early 20th Century. The first experiments of this type used radioactive sources emitting alpha particles before the onset of the Van de Graaff accelerator in the 1950s. During the spatial mission Surveyor V in 1967, the module landed on the moon in the sea of tranquility, had an alpha source and a surface barrier detector in order to study in situ the chemical composition of lunar rocks by RBS.

![Figure 1.12. Calculated trajectory of a 100-keV proton in the vicinity of a silicon nucleus with an impact parameter of 100 fm. The diameter of the Si nucleus, about 7.5 fm, and that of the proton (1.7 fm) are not to scale in this figure. The positions of the two nuclei over time are indicated by numbering from 1 to 6 corresponding to time intervals of $1 \times 10^{-4}$ fsec. In this simulation, the proton comes from the right-hand side of the figure and is scattered upward by the silicon nucleus initially at rest at the position $X = Y = 0$](image_url)
Indeed, when a sample is bombarded with an ion beam of energy higher than about 100 keV, most of the particles are found in the sample. However, a small fraction of the incident ions pass close enough to a nucleus to be deflected from their course by the Coulomb interaction and thus have a chance to emerge from the sample, as shown in Figure 1.12. Naturally, this only occurs if the mass of the ion is less than the target atoms. The measurement of the kinetic energy and of the direction of the emerging particles allows for analysis of the sample.

1.2.3.1. Kinematic factor

The energy of the backscattered particles at a given angle depends on two factors. First, the particles lose energy when they pass through the sample along the ingoing path, before the ion/nucleus collision, as well as during the outgoing path, up to the sample surface. The amount of energy lost depends on the stopping power of the material described in the previous paragraph. Second, the particle loses a fraction of its energy during the collision itself. Indeed, in the coordinate of the center of mass of the nucleus + ion system, kinetic energy and momentum are conserved but the movement of the collision frame with respect to that of the laboratory induces a decrease of ion energy due to the momentum transfer during the collision. The ratio between the energy of the projectile before and after the collision is called the kinematic factor. The energy range considered for ion beam analysis is much smaller than the rest mass of the proton (938 MeV) and a fortiori of the alpha particle. As a consequence, the kinematic factor $k$ can be calculated with a non-relativistic model in the laboratory frame and takes the following form:

$$k(\theta_s) = \frac{\sqrt{1-(M_1/M_2)^2 \sin^2 \theta_s} + (M_1/M_2) \cos \theta_s}{1+(M_1/M_2)}$$  \[1.10\]

This kinematic factor only depends on the scattering angle $\theta_s$ and on the mass ratio between the ion and the target atom, $M_1$ and $M_2$ respectively. By contrast, it does not depend on the energy of the incident ion. Its variation with atomic weight is shown in Figure 1.13 for helium ions scattered at different angles: 30°, 90° and 165°, respectively.
Figure 1.13. Variation of the kinematic factor for helium ions as a function of the mass of the target atoms for three different scattering angles (30°, 90° and 165°)

Figure 1.14 shows the variation of the kinematic factor with the scattering angle for helium ions scattered by four different nuclei. We also observe, in the same figure, that the energy transferred to the nucleus increases with the scattering angle. The kinematic factor has a direct influence on the mass resolution of the technique. In particular, we observe, still in Figure 1.14, that for very small scattering angles, we cannot separate chemical elements as the momentum transfer drops to zero with the scattering angle.

Figure 1.14. Variation of the kinematic factor for helium ions as a function of the scattering angle for four elements (C, Si, Ge and Hf)
1.2.3.2. **Scattering cross-section**

The elastic scattering cross-section is usually given in barn (1 barn = $10^{-24}$ cm$^2$), which is approximately the size of the atomic nucleus. The latter can be approximated by the relationship between nuclear radius $r_{\text{nucleus}}$ and atomic mass $A$ as follows [ZHA 02]:

$$r_{\text{nucleus}} [fm] \equiv 1.25 A^{1/3} \quad [1.11]$$

If we consider the collision as a two-body scattering, we find the following expression for the elastic scattering cross-section, also called the Rutherford cross-section, in the reference system of the laboratory:

$$\sigma(E, \theta_s) = \left( \frac{Z_1 Z_2 e^2}{4E} \right)^2 \frac{4}{\sin^4 \theta_s} \left[ \sqrt{1 - \left( \frac{M_1 \sin \theta_s}{M_2} \right)^2} + \cos \theta_s \right]^2 \quad [1.12]$$

From this expression, we can deduce the factors that play a dominant role in determining the scattering cross-section:

i) $Z_1^2$ dependence: the scattering cross-section $\sigma(E, \theta_s)$ is much larger for high atomic numbers of the projectile.

ii) $Z_2^2$ dependence: as shown in Figure 1.15, the high-Z atoms logically have a greater probability of scattering incident particles.

iii) $E^{-2}$ dependence: the swifter the incident particle is, the less it interacts with the target nucleus. The Coulomb interaction is the same as at lower speeds but the duration of the interaction is shorter.

iv) For small scattering angles, $\sigma(E, \theta_s)$ is approximately inversely proportional to the fourth power of the sine of $\theta_s$, causing a rapid increase of the cross-section with decreasing scattering angles, as shown in Figure 1.16. These events, in which the incident ion is only slightly deviated, are very likely but in fact correspond to collisions at large impact parameters for which the momentum transfer is very low. The extreme case of a zero scattering angle is “infinitely” likely but the kinematic factor is equal to 1 (according to equation [1.10]) and therefore the momentum transfer is zero. This is because the calculation of the Rutherford cross-section only
considers a single target nucleus but takes into account all possible collisions, even those where the ion passes very far from the scattering center.

**Figure 1.15.** Scattering cross-sections as a function of the atomic number at a scattering angle of 90° for an incident helium beam of different kinetic energies (0.1, 0.2, 1 and 2 MeV)

**Figure 1.16.** Scattering cross-section of silicon as a function of the scattering angle for an incident helium beam at different energies (0.1, 0.2, 1 and 2 MeV)
Values of the cross-section may deviate from those given by the Rutherford cross-section (equation [1.12]) in some particular cases. For example, at low energies we must take into account the partial screening of the nuclear charge by the electrons of the atom target. We then apply a correction coefficient of the effective section defined as follows:

\[ \sigma(E, \theta) = F \sigma_{Ruth}(E, \theta) \]  

\[ \text{[1.13]} \]

For scattering angles greater than 80°, one can use the correction factor given by L’Ecuyer et al. [LEC 79]:

\[ F_{L'Ecuyer} = \left( 1 - \frac{0.04873 Z_1 Z_2^{4/3}}{E_{CM}} \right) \]  

\[ \text{[1.14]} \]

\( E_{CM} \) is the kinetic energy in keV of the ion in the coordinate of the center of mass of the ion/nucleus system.

For scattering angles smaller than 80°, the impact parameter of the collision is larger which means that the ion passes farther from the scattering nucleus and therefore the screening effect is more important. In this case, we prefer to use the correction factor given by Andersen et al. [AND 80] which, unlike the correction given by L’Ecuyer, is dependent on the scattering angle:

\[ F_{Andersen} = \frac{\left( 1 + \frac{V_1}{2 E_{CM}} \right)^2}{\left\{ 1 + \frac{V_1}{E_{CM}} + \left[ \frac{V_1}{2 E_{CM} \sin(\theta_{CM}/2)} \right]^2 \right\}^2} \]  

\[ \text{[1.15]} \]

\( \theta_{CM} \) is the scattering angle in the coordinate of the center of mass and the increase of kinetic energy \( V_1 \) of the projectile due to the screening of the nucleus charge by core electrons is given by the following relation:

\[ V_1 [keV] = 0.04873 Z_1 Z_2 \left( Z_1^{2/3} + Z_2^{2/3} \right)^{1/2} \]  

\[ \text{[1.16]} \]

The dependence of the correction factor given by Andersen as a function of scattering angle \( \theta \) for \(^4\)He particles scattered by gold is shown in
Figure 1.17 for different energies of the incident beam. The dotted lines correspond, in this figure, to the correction factor independent of the scattering angle given by L’Ecuyer. We note that, for large scattering angles, the correction factors given by L’Ecuyer and Andersen are similar. However, for small scattering angles, the Andersen’ correction becomes very important and that of L’Ecuyer greatly underestimates the deviations from the Rutherford cross-section.

![Figure 1.17. Angular dependence of the screening correction factors of the Rutherford cross-section for an incident helium beam scattered by gold at different energies (0.25, 0.5, 1 and 2 MeV). The dotted lines correspond to the correction, independent of the scattering angle, given by L'Ecuyer et al. [LEC 79] (equation [1.14]) and the solid lines correspond to the correction factor, dependent of the scattering angle, given by Andersen et al. [AND 80] (equation [1.15])](image.png)

Under normal conditions of the use of the RBS technique, i.e. with helium ions of energy greater than or equal to 1 MeV and measuring the scattered ions at large angles, the two correction factors merge and are close to the unit. In contrast, the MEIS technique is practiced at lower energies for which these corrections are no longer negligible. In addition, some MEIS experiments are sometimes practiced with smaller scattering angles and the angular dependence of this correction must be taken into account.
Furthermore, at high energies, the minimum distance between the incident particle and the target nucleus approaches or even reaches the size of the nucleus itself. In this case, the strong interactions modify the Coulomb scattering cross-section. However, for energies of the order of MeVs and below, the latter deviation is minor and can be neglected.

### 1.3. Channeling, shadowing and blocking

#### 1.3.1. Channeling

The channeling effect is observed when the incident ion beam is aligned with a crystal axis or plane of the sample to be analyzed. In this geometry, the ions, which are not scattered by the surface nuclei, are repelled by the rows of nuclei and have oscillating trajectories in the crystal, as schematically shown in Figure 1.18. Indeed, when the ion approaches an atomic row, it undergoes a series of elastic scattering at small angles (and therefore at large impact parameters) that does not allow this ion to get close enough to a nucleus in order to undergo a backscattering event. The consequence of this is that the yield of the backscattered ions, which is nothing but a RBS or MEIS spectrum, is drastically reduced (by a factor of about 25–30 for silicon at room temperature). This reduction factor of the scattered yield is noted $\chi_{\text{min}}$. However, if interstitial atoms are found in the crystal due to the presence of structural defects or due to ion implantation, the scattering yield of these atoms is the same as the one observed in a random geometry. Comparing both spectra obtained under channeling conditions (in two different orientations) to a spectrum obtained in a random geometry, allows one to quantify and profile the displaced atoms in the sample. This method makes it possible to produce profiles of defects and may also, under favorable conditions, locate an interstitial atom in the crystal lattice.

Channeling may also be observed if the incident beam is slightly disoriented with respect to the considered crystal direction. The angular tolerance can be quantified by calculating the critical angle given in radians by the following formula [LIN 64]:

$$\psi_c = \sqrt{\frac{Z_i Z_e e^2}{2\pi e_0 E d}}$$  \[1.17\]
where $Z_i$ is the atomic number of the incident ion, $\bar{Z}$ is the average atomic number of the considered material, $e$ is the elementary charge, $\varepsilon_0$ is the dielectric constant of vacuum, $E$ is the kinetic energy of the ions and $d$ is the average distance between atoms along atomic rows.

![Figure 1.18](image1.jpg)

**Figure 1.18. Schematic representation of the trajectories of channeled protons (the vertical distance scale has been greatly expanded in this figure to allow visualization of trajectories)**

For example, the critical angle is $0.5^\circ$ for 2 MeV $^4$He ions in the [001] direction of silicon and $2.2^\circ$ under the same conditions but for an energy of 100 keV. The evolution of the critical angle with respect to the incident energy is plotted in Figure 1.19 for silicon in the [001] direction.

![Figure 1.19](image2.jpg)

**Figure 1.19. Critical angle of [001] channeling in silicon as a function of ion beam energy**
The trajectory of each ion does not oscillate with exactly the same wavelength depending on, first, the angle between the velocity of the ion and the channeling direction and, second, the impact parameter with nuclei located at the sample surface. Nevertheless, we can define an average half-wavelength of the characteristic oscillations of ions that can be estimated by the simple relation given below expressing the critical angle in radians [DAV 78]:

$$\lambda_{1/2} \approx \frac{d}{\psi_{1/2}}$$  \[1.18\]

where $d$ is the average spacing between atoms in the channeling direction. This half-wavelength of oscillation in silicon is about a few nanometers at low energy and can reach several tenths of nanometers in the MeV range, as shown in Figure 1.20.

![Figure 1.20. Channeling half-wavelength in the [100] direction of silicon as a function of ion beam energy](image)

The ratio of the scattering yield in a channeling direction with respect to a random one, $\chi_{\min}$, can be expressed as follows [FEL 82]:

$$\chi_{\min} = C_1 N d \pi \rho^2 \sqrt{1 + \left(\frac{\psi_{1/2}d}{C_2 \rho}\right)^2}$$  \[1.19\]
In the above equation, $N$ is the atomic density; $\rho$ is the amplitude of thermal vibrations; and $C_1$ and $C_2$ are empirical coefficients that must be chosen to fit the experimental observations. For example, in a perfect silicon crystal at room temperature, the amplitude of thermal vibrations perpendicular to the [110] direction is 0.08 Å [KEP 91], $d$ is 3.84 Å and $N$ is $4.9748 \times 10^{22}$ atoms $\times$ cm$^{-3}$. The experimental $\chi_{\text{min}}$ values obtained by different experiments can be adjusted by equation [1.19] using $C_1 = 4.52$ and $C_2 = 2.5$, plotted in Figure 1.21.

![Figure 1.21. $\chi_{\text{min}}$ values for protons and helium ions channeled in silicon along the <110> direction](image.png)

**1.3.2. Shadowing**

The impact parameters of the incident ions reaching the surface of the crystal are randomly distributed. Interactions of incident ions with the atoms of the first atomic layer will have the same scattering yield as if the target was amorphous. This is the reason why, at each chemical element present on the surface of a crystalline sample, there is a correspondence with a surface peak in the channeled spectrum. However, in this channeling geometry, the initial nuclei in a row will, by deflecting the incoming ions, prevent them from reaching the following nuclei as shown in Figure 1.22, and is at the origin of a shadow cone.
This shadowing effect is only due to the scattering on the first atomic layer for a perfect crystal at 0 K. This is no longer true at room temperature because the thermal vibrations allow atoms from deeper layers to come out of the shadow cone generated by the surface atoms. To take this effect into account one can compare the amplitude of thermal vibration, noted $\rho$, with the radius of the shadow cone. The radius $R$ of the shadow cone is defined as the minimum distance of approach between the ingoing ion and the atoms of the second deeper layer as schematically shown in Figure 1.23.
This radius can be calculated, considering a pure Coulomb potential between ion and nuclei, using the following formula [FEL 82]:

\[ R_c = 2 \sqrt{\frac{Z_1 Z_2 e^2 d}{4 \pi \varepsilon_0 E}} = 2 d \psi_{1/2} \]  

[1.20]

where \( Z_1 \) and \( Z_2 \) are the atomic numbers of the ion and the target nucleus, \( e \) is the elementary charge, \( d \) is the distance between atoms in a row and \( E \) is the ion’s kinetic energy.

Nevertheless, the charge of the target nucleus seen by the incoming ion is not equal to its atomic number due to the screening by the core electrons. The relation between the radius of the shadow cone \( R_M \) and \( R_C \), considering a screened potential, is shown in Figure 1.24 as a function of \( R_C/a \).

![Figure 1.24. Ratio of the shadow cone radius from the screened potential \( R_M \) to the unscreened potential \( R_C \) as a function of \( R_C/a \) (data from [FEL 82])](image)
In this figure, parameter $a$ is the Thomas-Fermi screening distance given by equation [1.21] where $a_o = 0.529177249$ Å, which is the Bohr radius [BOH 13b].

$$a(Å) = 0.8853 a_o \left(Z_1^{1/2} + Z_2^{1/2}\right)^{-2/3}$$  \[1.21\]

The evolution of this screening distance with the atomic number of the target nucleus is shown in Figure 1.25.

![Figure 1.25. Thomas Fermi screening distance as a function of the atomic number of the target nucleus](image)

The surface peak area can be obtained experimentally for various bulk materials and in different channeling directions. The results, expressed as a number of atoms per row, are plotted on Figure 1.26 as a function of a single parameter: the ratio between the amplitude of thermal vibrations $\rho$ and the
radius of the shadow cone $R_M$. Remarkably, the experimental evidence follows a universal dependence of the peak area versus the ratio $\rho/R_M$ [FEL 82].

![Figure 1.26. Experimental values of the surface peak intensity for various crystals expressed in number of atoms per row as a function of the ratio between the thermal vibration amplitude and the radius of the shadow cone. The continuous curve was generated from numerical simulations (data from [FEL 82])](image)

We can note that for values of the ratio $\rho/R_M$ below 0.35, only the outermost atoms interact with the incoming ions in close encounter processes. As an example, in a silicon crystal at room temperature, the
amplitude of thermal vibrations perpendicular to the [110] direction is about 0.078 Å [KEP 91]. The number of atoms per row seen by helium ions as a function of their kinetic energy is plotted on Figure 1.27. One can observe that, for He$^+$ below 150 keV aligned on the [110] direction, all the atoms are hidden below the surface atoms. Taking advantage of this specific feature, one can choose a crystallographic structure-dependent incident angle in order to only observe the first atomic layers, as schematically shown in Figure 1.28. Indeed, in these particular geometries, the incident ions have a high probability of scatter on the initial atomic layers, while the nuclei of deeper layers are hidden behind the surface layers. This technique is often used in conjunction with the blocking effect with the objective of analyzing surface reconstructions.

Figure 1.27. Calculated values of the surface peak area for silicon channeled in the [110] direction expressed in the number of atoms per row as a function of the ion beam energy.
Figure 1.28. Schematic view of shadowing geometries employed to enhance the scattering yields of the initial atomic layers with respect to deeper layers.
1.3.3. Blocking

The effect of blocking consists of an anisotropy of the angular distribution of scattered ions in a crystal. This effect is similar to the shadowing effect observed for the incident beam. Indeed, in an ordered structure, the ions scattered by a nucleus are “blocked” by the nuclei closer to the surface, which causes a reduction of the scattering yield at a characteristic angle called “blocking dip”. In other words, the blocking effect is nothing but a second Coulomb scattering, which inevitably occurs if the trajectory of the scattered particle is aligned to another nucleus in the output path of the sample. The second scattering will, once again, create a shadow cone in the distribution of backscattered ions, as shown in Figure 1.29.

![Figure 1.29. Schematic view of the shadowing and blocking effects](image)

The angular position of the blocking dip reveals the relative position of atoms within the crystal. The angular width $\omega$ of the blocking dip can be
calculated from the radius of the shadow cone \( R_M \), the amplitude of thermal vibrations \( \rho \) and the distance \( d \) between the blocking atom and the scattering center as follows:

\[
\omega \approx 2 \arctan \left( \frac{\rho + R_M}{2d} \right)
\]  

[1.22]

The dependence of the blocking dip width with respect to the scattered energy for helium ions in silicon along the [110] direction is shown in Figure 1.30. In this figure, the straight line is the result of a calculation in which only the contribution of the screened Coulomb potential to the blocking dip width is taken into account. If we also consider the enlargement due to the amplitude of thermal vibrations (\( \rho = 0.078 \) Å for silicon at 300 K in a plane perpendicular to the [110] direction [KEP 91]), we obtain the dotted line of Figure 1.30. We observe that, above 1 MeV, the thermal contribution dominates the blocking dip width. By contrast, at lower energies, the width is more sensitive to the Coulomb contribution.

![Figure 1.30. Blocking dip width versus scattered energy for helium ions in silicon along the <110> direction neglecting (straight line) or taking into account (dotted line) the thermal vibration amplitude at 300 K](image_url)
The same calculation can be done for protons in silicon along the <110> direction. The results are plotted on Figure 1.31.

\[ \frac{c}{a} = \tan(\theta) \]  

Figure 1.31. Blocking dip width versus scattered energy for protons in silicon along the <110> direction neglecting (straight line) or taking into account (dotted line) the amplitude of thermal vibration at 300 K

In a single crystal, any deformations of the structure induced by elastic strain is visible by a shift in the angular position of these blocking dips, as shown in the diagram of Figure 1.32. For instance, in the (110) direction of a cubic structure, the relation between the angular position of the blocking dip is given by the simple following relation:
This effect can be employed to produce depth strain profiles within crystalline layers. The method consists in measuring a two-dimensional spectrum of the scattered ions with respect to the scattering angle and the scattered energy in the vicinity of a crystalline direction of the sample. Different angular cuts are made at different energies to determine the relative position of atoms in the crystal at different depths. This method can be applied to all chemical elements in the sample, if it is possible to separate their contributions to the energy spectrum. One or more similar cuts are made in the substrate or in a reference layer of which the strain is known. The comparison between the deformation observed in the analyzed layer and that of the reference allows a quantitative determination of the deformation. In favorable cases, this technique allows direct measurements of strain profiles element by element with a depth resolution of a single atomic layer.

A refinement of the above technique, also called double alignment technique, consists in taking advantage of both the shadowing and the blocking effects. The incident beam is channeled into one crystallographic
direction to promote the scattering yield of a limited number of atomic layers and the scattered ions are observed around another crystallographic direction. This method, shown schematically in Figure 1.33, is used to analyze surface structures.

![Figure 1.33. Schematic view of the shadowing/blocking geometry used to analyze surface structures (from the Surface Physics Group at the University of York (UK))](image)

1.4. 1D layers: limits to depth resolution

Spatial resolution is a central element that determines the usefulness of a given measurement method with respect to a given physical system. Ideally, nanometric systems require nanometric or even sub-nanometric spatial resolutions. However, defining usefully what we mean by resolution is a subtle task. In this work, we will consider depth resolution along just one spatial dimension – the case of laterally homogeneous thin films. This is both useful for the numerous cases where this is indeed the system to be studied and also provides a simple introduction to basic ideas of depth resolution.

The first objective definition of resolution comes from optics. Lord Rayleigh [RAY 79] defined resolution as being that distance between the ideal diffraction-limited images of two point objects for which the diffraction patterns, which are Airy functions for point objects observed with a
rotationally symmetrical optics system, are separated such that the maximum of one lies at the first minimum of the other. This is shown in Figure 1.34(a), where intuitively it can be seen that the image of the two points is composed of two overlapping peaks separated by a modest valley. The eye could probably distinguish two bright spots in the image. In ion beam analysis, the instrument function can often be taken to be Gaussian, for which the Rayleigh criterion cannot be applied because there is no minimum. Practitioners often then apply the criterion that two point sources are resolved when their images are separated by the full width at half maximum (FWHM) of the Gaussian instrument function. This is shown in Figure 1.34(b), where we see that the Gaussian FWHM criterion is a little less severe than the Rayleigh criterion, in that the valley between the two peaks is less pronounced.

These two widely used definitions make the most sense when the images of the two source objects are given by exactly the same instrument function, the two sources are of equal intensity, and the response is measured without uncertainty. Although useful for defining and discussing resolution, this is seldom the case in real life. A most useful and well-tested program for calculating the ideal IBA depth resolution [SZI 95] according to the Gaussian FWHM criterion may be found at http://www.kfki.hu/~ionhp/doc/prog/wdepth.htm.

Figure 1.34. Theoretical response functions for two point sources resolved according to a) the Rayleigh criterion and b) the Gaussian FWHM criterion. In each case, the single central peak is the response when the two point sources are not separated at all.
In Figure 1.35, we show some simulated RBS spectra for more realistic cases in which two delta-function gold layers separated by a silicon layer (this would correspond for example to two ideal delta-doped Au layers in a silicon wafer) are in principle resolved according to the FWHM criterion, but in which their relative intensities and the precision of the measurement are varied. Firstly, we may note that the signal from the deeper gold layer has a slightly lower peak than that at the surface. This is due to the energy straggling of 3 keV of the incident beam in the silicon between the first and the second Au layers, which effectively broadens the instrument function for the deeper gold layer compared to the first. This is a small effect here, but when very high energy resolutions can be obtained, for example in MEIS and narrow resonance profiling, this effect can be dominant. Secondly, we can see that when the two delta functions which are to be resolved have very different intensities, the intuitive idea that there needs to be some kind of valley between two observable peaks is no longer a useful concept for defining depth resolution. Indeed, in the case where one of the Au layers is 1/10th the intensity of the other, even with an ideal measurement, it would be difficult to differentiate between a sample constituted by the two delta-layers and a sample in which there is a continuous depth distribution (one layer, with some diffusion into the silicon). Finally, we also see that the inherent statistical noise of the measurement – the number of particles detected in each energy channel follows a Poisson distribution of standard deviation equal to the mean – influences the real resolving power of a given measurement. With very high counting statistics (and thus narrow Poisson distributions) resolution close to the idealized Gaussian FWHM criterion can be obtained, but with low counting statistics there is greater uncertainty as to whether or not the two delta-doped layers are resolved by the measurement.

The point of the above discussion is to highlight the limitations of a simple approach to deciding what the resolution of a given measurement is. In fact, the idea of resolution is a first order reply to the question “what information, with what uncertainty, is contained in my spectrum?”. The general answer to this question is very case-dependent and difficult to express analytically and succinctly. It depends, as seen above, on the counting statistics, but also on many other instrumental factors such as adequate energy calibration of the spectrum, determination of detection efficiency and solid angle, underlying physical models and data such as stopping powers, straggling calculations and so on, each with their associated uncertainties. It also depends on what information can be brought
to bear to constrain the possible sample structures that could give rise to the observed spectrum. For example, if it may safely be assumed that the Au is contained in just two delta-layers (e.g. as determined from TEM examination) then even from a spectrum such as that of Figure 1.35(d) the amounts of gold in each layer can be confidently deduced. On the other hand, if it can be assumed that the gold has a continuous distribution, then the same spectrum could be used to obtain a continuous concentration profile.

![Graphs showing simulated RBS spectra for nominally resolved Au delta-doped layers in Si, of equal intensity (a and c) and of ten times different intensities (b and d) with good (a and b) and poor (c and d) statistics.](image)

**Figure 1.35.** Simulated RBS spectra for nominally resolved Au delta-doped layers in Si, of equal intensity (a and c) and of ten times different intensities (b and d) with good (a and b) and poor (c and d) statistics.

It is worth noting that further information may be brought to bear from additional measurements – for example, using two or more particle detectors at different detection angles, or measuring the ion-induced characteristic X-ray spectrum as well as the charged particle spectra.
To adequately answer the question “what information, with what uncertainty, is contained in my spectrum?”, it is necessary to explore the entire set of possible sample structures compatible with the measured spectrum (or spectra) and determine the sensitivity of the optimum sample structure to the uncertainties of each element involved in the chain that ties the observed spectra to the sample structure. This requires a detailed statistical analysis and advanced spectrum fitting procedures that can include constraints on the solution space (such as the assumption that the Au is present in two delta functions rather than as a continuous distribution). Fortunately, computer programs exist for RBS, NRA and PIXE which allow this. The most widely used is the IBA DataFurnace [BAR 97, JEY 03], which contains a well-tested physics engine and uses a simulated annealing algorithm to search the solution space and determine the sample structure that is optimally compatible with any measured backscattering, NRA and PIXE spectra. Due to the statistical procedures used in the DataFurnace, uncertainties on determined parameters (layer thickness, composition, etc.) are also produced.

1.5. 2D and 3D objects: aspects of lateral resolution

The lateral resolution is the ability to distinguish information coming from closely separated objects, such as adjacent nanostructures, in a plane perpendicular to the ion beam. In the case of swift ion beam techniques, this resolution is simply governed by the beam spot size on the sample. In what follows we will discuss the possibility of reducing the size of the ion beam but above all why we cannot reduce it at the nanoscale.

1.5.1. Beam focusing

The minimum beam size that can be obtained practically is limited by three factors:

– The finite emittance of the ion beam. The emittance of a beam is the volume of the beam in the particle position and momentum phase space (x, p_x, y, p_y, z and p_z). Due to Liouville’s theorem, the volume in phase space is conserved for conservative forces. While it may change shape, the total volume is conserved. If the motion of the particles in the beam in each direction is independent of each other, the emittance is conserved in each direction separately. The emittance is also expressed as the distribution of
the following product: the distance between a particle and the center of the beam multiplied by the angle of its velocity with respect to the beam direction. As a direct consequence of this finite value of the emittance, all the particles cannot be focused at the same point as illustrated in Figure 1.36 and this effect limits the minimum size of the ion beam spot on the sample.

![Figure 1.36. Schematic illustration of the particle trajectories in an ion beam of finite emittance](image)

- The quality and the alignment of the optical devices (steerers, lenses, acceleration stages, etc.) within the beamline. The effect of optical devices on an ion beam can be calculated using simulation programs (some examples are given in section 1.5.1.1). The stability of the ion beam energy (any slight fluctuation of the beam energy induces some small trajectory changes) can also be an important factor depending on the accelerator technology.

- The space charge of the ion beam. An ion beam in vacuum is a region of space containing particles of identical charge states. The Coulomb interaction tends to repulse every particle from each other. This effect, strongly dependent on the current density, is at the origin of a beam broadening. Considering a selected beam diameter, or beam spot size on target, we can calculate the maximum beam intensity beyond which the spot size is enlarged by charge space. Figure 1.37 shows this maximum intensity as a function of the beam diameter for protons of 10, 100 and 1000 keV calculated for a focusing lens positioned at 1 m from the target sample.
For swift ion beam analysis, the beam intensities commonly used range from a few nA to a few tens of nA, far below the limitations induced by the space charge effect. However, this effect is dominant in the limitation of the beam emittance within the ion source and in the first stage of acceleration when the ion’s velocity is still weak.

Actually, the main reason to limit the decrease of the beam spot size on the sample does not arise from optical consideration. Basically, it comes from the damage induced by the ion beam within the sample. For instance, if we consider the initial 10 nm of a silicon wafer exposed to a helium ion beam, we can calculate the number of displaced silicon atoms per incoming ion using SRIM [ZIE 04]. For a 100-keV energy beam, this value is about 0.15 displaced atoms/helium ion within 10 nm. At 1 MeV, this value falls to about 0.015. Now, if the beam intensity is 10 nA, a typical value in IBA, we can then calculate the time to displace 10% of the silicon atoms within the initial 10 nm. The result, plotted in Figure 1.38, shows that for a beam diameter of 1 mm, this time exceeds 1 hour. By contrast, if we consider a
beam spot of a micron, this duration drops below 1 second. Certainly, this
calculation overestimates the damages since it does not take into account the
possible recombination between a displaced atom and a vacancy (created by
a different collision). Moreover, in systems equipped with a microprobe, the
ion beam is scanned laterally but the exposure time of a single spot and/or
the beam intensity must be adjusted carefully to avoid excessive damages.

Figure 1.38. Time to displace 10% of the silicon atoms in the first
10 nm with a 10 nA helium ion beam of 100 keV and 1 MeV
respectively according to SRIM calculations [ZIE 04]

More generally, the beam-induced damages in the sample are sensitive
not only to many parameters such as the mass of the incident particle, its
speed and its angle of incidence but also to the nature of the sample and its
temperature. More details on this subject can be found in [VIC 11].

For the above-mentioned reason, in most of the IBA facilities the spot
size is in the millimeter range and only some ion microprobes have specific
focusing devices that can decrease the spot size on the target down to about
0.2–1 micron. As a consequence, in nanosciences, the probe size remains
larger than the objects under investigation.
1.5.1.1. Further resources: ion beam optics

A large number of simulation programs can be used to predict ion beam behavior in acceleration stages or optical devices. A short selection of widely used codes is given below:

– SIMION:

An easy-to-use program to calculate trajectories of charged particles in electromagnetic fields.

http://simion.com

– POISSON/SUPERFISH:

A collection of programs for calculating static, magnetic and electric fields and radio-frequency electromagnetic fields.

http://laacg.lanl.gov/laacg/services/download_sf.phtml

– A selected number of schools in beam physics and accelerator technology are organized by:

- The CERN Accelerator School: http://cas.web.cern.ch/cas/
- The U.S. Particle Accelerator School: http://uspas.fnal.gov/

1.5.1.2. Further reading: ion beam optics

– Theory and design of charged particle beams:


http://www.lepp.cornell.edu/~ib38/tmp/reading/reiser/0471306169.pdf

– Charged particle beams:


1.5.2. Simulation of nanostructures

Since the probe size provided by the ion beam facilities is not small enough to give any side information on the sample at the nanoscale, the ion beam techniques do not analyze a single nano-object but give chemical or structural information on an assembly of nanostructures and thus offer a global view of the nature of the sample.

However, if we look closer at the scattering events within the sample, we can observe a basic difference between a 2D system and a set of 3D objects. As it is schematically described in Figure 1.39, in a 2D layer, the path length of an ion scattered by all the nuclei located at a selected depth remains the same whatever their lateral position may be. For this reason, the average ion energy loss can be directly translated into depth within the sample.

![Figure 1.39. Schematic illustration of the particle trajectories in a continuous layer (left) and in a set of 3D objects (right)](image)

If we now consider a set of 3D objects at the sample surface, the situation is quite different. The ingoing and/or outgoing path lengths are dependent on the lateral position of the scattering center within the nanostructure. The clear relation between the depth and the energy of the scattered particle is no longer direct.

The best way to accurately analyze the data from RBS or MEIS measurements consists in calculating a large number of projectile trajectories, considering a random lateral position of the incoming ion, in order to take into account all the possible geometrical situations. This can be done with the Monte Carlo method applied to IBA techniques. Nowadays a unique code of that kind, called PowerMEIS, has been developed by M.A. Sortica et al. [SOR 09]. The code can simulate RBS or MEIS spectra of any nanoparticle geometry and areal density. Size distribution of the nanostructures can also be accounted for. An efficient use of such
calculations is to introduce any geometrical information, extracted from other available techniques such as Atomic Force Microscopy (AFM), SEM or TEM in the simulation in order to precisely refine the chemical profiling.

Alternatively, a way to determine the shape of a nanoparticle through the MEIS technique is to look at all different scattering angles available since each geometrical shape has a typical angular dependence on the backscattering yield, as shown in Figure 1.40.

![Figure 1.40](image_url)

**Figure 1.40.** 2D map of scattered ion intensities as a function of the scattering angle and scattered ion energy for normal incidence of 100 keV He\(^+\) ions calculated for a 2D layer (top left) or for three nanoparticle shapes: sphere (top right), hemisphere (bottom left) and cylinder (bottom right) [SOR 09]