Abstract
The relevance of nano sized structures and interfaces in upcoming technologies requires new non-destructive X-ray techniques exploiting attenuation as well as scattering. In the course of driving the resolution and the contrast of modern radiography into micro and nano metre dimension the inevitable scattering effects require increased attention. Several radiologists interpret the observed edge artefacts simply by "phase contrast" due to different X-ray path lengths within the sample and others refer to Fresnel scattering. The ultra small angle scattering is of high intensity and may reach the level of the primary beam. We present monochromatic synchrotron measurements on rather simply shaped objects (such as plates and cylinders) which prove clearly the dominance of refraction intensity over total reflection and coherent small angle scattering. The refraction conditions hold for angles of incidence of several degrees to the surface, but typical deflection angles range from several seconds to minutes of arc. Additionally to the concept of "phase contrast" of the primary beam its deflection becomes the essential issue. The appropriate removal of the attenuation contribution enables the imaging of inner surfaces and interfaces by refraction scanning topography. The presented measurements of reference particles demonstrate the reliability of laboratory refraction scanners applying X-ray tubes.

Keywords: X-ray refraction, Small angle scattering, Phase contrast radiography, Refraction topography, Nanostructures, Nanocracks

1. Introduction

Since the discovery of the wave character of light by Ch. Huygens [1] it is known that condensed matter deflects electromagnetic waves due to refraction which is driven by the phase shift accompanying the reduced speed of light. It took more than 200 years to find the same phenomenon regarding X-rays [2]. The only difference to visible light is the small negative deviation of the refractive index from unity in the range of some $10^{-6}$. This results in deflection angles of opposite sign. In 1987 Hentschel et al. [3] reported on refraction by cylindrical objects such as glass and polymer fibres and metallic wires, quantitatively, by presenting a scattering formula for the intensity distribution up to the limiting critical angle of total reflection, which may reach several minutes of arc. Furthermore, this discovery was exploited for establishing X-ray refraction topography in order to characterise interfaces and inner surfaces of materials non-destructively [4,5]. These scanning techniques employ the small angle scattering intensity typically separated within conventional Kratky cameras [6], well known in traditional crystallography.

Direct imaging of inner surface distributions and edge artefacts on 2D detectors was established by Mueller et al. [7] for the purpose of synchrotron refraction computed tomography taking advantage of the precise single crystal selection of the non-deflected beam. Even without single crystal imaging Wilkins et al. [8] observed similar edge artefacts in case of considerable object-detector-distance in high resolution polychromatic radiography interpreting them by “phase contrast”. Other authors prefer the explanation of edge effects by Fresnel diffraction [9]. The classical analytical techniques of coherent small angle scattering [10,11] are not considered here because of their weak scattering intensity which excludes their relevance for edge artefacts in radiography.

Beyond X-ray applications edge artefacts due to refraction and total reflection in neutron
radiography are reported by Strobl et al. [12]. In order to demonstrate the obviously analogue behaviour of X-rays we present measurements of the deflection of monochromatic synchrotron radiation by rather simply shaped homogeneous objects (such as plates and cylinders) within the typical angular scattering range of refraction and total reflection.

2. X-Ray Refraction by plane surface

Refractive X-ray deflection occurs, when X-rays interact with interfaces (cracks, pores, particles, phase boundaries) similar to visible light in transparent materials lenses or prisms. But the X-ray optical effects can be observed only at small scattering angles of between several seconds and a few minutes of arc as the refractive index \( n \) of X-rays is nearly unity (\( n \approx 1 - 10^{-5} \)). Let \( \delta \) be the real part of the complex index of refraction \( n \), \( \rho \) the electron density and \( \lambda \) the X-ray wavelength then \( n \) is

\[
n = 1 - \delta
\]

with \( \delta \approx \rho \cdot \lambda^2 \) and \( \delta \approx 10^{-6} \) for glass at 20 keV radiation (neglecting the imaginary part \( \beta \) which counts for absorption). From this follows, that the incident angle at which X-rays impinge on a surface should be small enough (very few degrees) in order to achieve a measurable deflection angle.

In analogy to visible optics the change of the beam direction after crossing a plane surface is described by Snell’s law:

\[
\cos \beta_1 / \cos \beta_2 = n
\]

where \( \beta_1 \) is the angle of incidence at the surface (in contrast to the complementary angle with respect to the surface normal) and \( \beta_2 \) is the surface angle inside the material, \( n \) is the refractive index of the penetrated material (in vacuum, i.e. \( n_1 = 1 \)). Therefore the deflection angle \( \theta \) of the beam at a single surface is

\[
\theta = \beta_1 - \beta_2
\]

and after (2)

\[
\theta = \beta_1 - \arccos (\cos \beta_1 / n)
\]

finally the incidence angle \( \beta_1 \) is separated as a function of the deflection angle \( \theta \):

\[
\beta_1 = \arctan[(1/n \times \sin \theta) - \cot \theta]
\]

Total reflection occurs for small angles of incidence below the critical angle \( \beta_{\text{crit}} \) when \( \beta_2 \) approaches zero. Eqs. (1) and (2) then reveal

\[
\beta_{\text{crit}} = \sqrt{2\delta} = 0.5 \, \theta_{\text{crit}}
\]

as the reflected beam takes two times the incident angle like from a mirror.

The functions corresponding to Eqs. (5) and (6) are plotted in Fig. 1, taking \( n = 1-1.3 \times 10^{-6} \) in case of E-glass and 20 keV radiation as applied below. The refraction phenomenon is experimentally demonstrated by parallel 20 keV synchrotron irradiation of a glass plate successively inclined within a range of ± 1 degree incidence angle at a 186 mm distance from a 14.5 µm pixel CCD-detector which was run as a line detector (Fig. 2). The synchrotron X-ray deflection by refraction and total reflection at the 1×5 mm² glass slide represents a direct test on Snell’s law for X-rays. On the left side a scheme of the...
The central dark stripe originates from sample absorption. The bright lines near the sample edge show the refracted intensity additional to the direct beam outside the sample area. The totally reflected intensity (which doubles the angle of incidence and thus gives a measure for the angles of deflection) appears at larger distance and at small tilt angles. The distance from the edge corresponds to the deflection angles. The intensity cut-off at the critical angle of total reflection directly reveals \( \delta \), which corresponds to tabulated values, e.g. given by Larsson as early as 1924 [2]. The relation between the incidence angles and deflection angles according to Fig. 1 and Eqs. (5) and (6) is obvious. The projected intensities reveal clearly the much stronger contribution of refraction compared to total reflection.

Figure 2. Synchrotron X-ray deflection by refraction and total reflection of a 5 mm glass slide; left: experimental set-up with beam geometry, detector position, and relevant angles; right: gray levels along horizontal lines correspond to horizontal detector intensity at sample tilt angles, central dark stripe: sample absorption shadow, bright lines near sample shadow: refracted intensity and totally reflected intensity near zero tilt angle.
Having in mind that since Huygens [1] the phenomenon of refraction is explained by the phase shift of electromagnetic waves in matter the presented edge intensities of Fig. 2 need no additional interpretation by "phase contrast".

3. X-Ray Refraction by cylindrical edges

Generally the interfaces of microstructures of materials are not as planar as in Fig. 2. Particles and fibres have rather round shapes but in contrast to optics the convex surfaces cause divergence of X-rays as \( n < 1 \).

Fig. 3 demonstrates the effect of small angle scattering by refraction of cylindrical “lenses” in a conventional small angle scattering camera: A bundle of 15 µm glass fibres (for composites) deflects a X-ray pencil beam within several minutes of arc. In fibres and spherical particles the deflection of X-rays occurs twice, when entering and when emerging from the object (insert of Fig. 3). The oriented intensity distribution is collected by an X-ray film or a CCD camera while the straight (primary) beam is blocked by a beam stop. In contrast to the symmetric scattering of completely exposed fibres in bundles the asymmetric scattering by a partially exposed single fibre disproves the phenomenon of diffraction (Fig. 3, upper left). The shape of the intensity distribution of such cylindrical objects (normal to the cylinder axes) is a universal function independent of materials, if normalized to the "critical angle" of total reflection (Fig. 4). The intensity of the deflected X-rays becomes nearly zero at the critical angle, with a small contribution from total reflection.

![Figure 3](image)

Figure 3. Effect of oriented small angle scattering by refraction of glass fibres; \( n \) index of refraction, \( \delta \) real part of \( n \), \( \lambda \); asymmetric scattering by partially exposed single fibre disproves diffraction.

Applying a Kratky type high resolution small angle scattering camera with slit collimation a cross section of \( 10^{-3} \) of the fibre diameter contributes to the detectable intensity above typically 2 minutes of arc. Total reflection of X-rays occurs as well but only \( 10^{-6} \) of the cylinder diameter is involved and therefore negligible, but planar surfaces may scatter all the primary intensity if well aligned. Based on Snell’s Law the angular intensity distribution of cylinders has been modelled and fitted to measurements on very different fibres, as illustrated by Fig. 4. The refracted intensity \( I'_R \) of a cylinder (without absorption effects) can be expressed by (after [3]):
Figure 4. The normalized shape of the angular intensity distribution of cylindrical objects; PP: polypropylene (after [3]).

\[
I_R(2\theta') = \frac{J_0 \cdot 2R}{\delta} \sin^3 \left( \arctan \frac{\delta}{\theta} \right) \equiv \frac{J_0 \cdot 2R \cdot \delta^2}{\theta^3} \tag{7}
\]

\[
J_0 \text{ is the irradiation density of the incident X-rays, } R \text{ is the cylinder radius and } 2\theta' = \theta \text{ is the scattering angle. In case of spherical particles or pores } I_R \text{ becomes}
\]

\[
I_R(2\theta') \equiv \frac{J_0 \cdot 2R \cdot \delta^2}{\theta^4} \tag{8}
\]

The conventional understanding of "continuous" small angle X-ray scattering (SAXS) is governed by the interpretation of diffraction effects. Both, the well known Guinier's theory [10] for separated particles and Porod’s theory [11] of densely packed colloids are based on diffraction (Rayleigh or coherent scattering). Nevertheless, Porod approximates the same angular intensity decay as in Eq. (8). However both diffraction approaches refer to scattering objects two orders of magnitude smaller than the discussed ones.

A detailed investigation of the X-ray intensity distribution behind a cylindrical edge is performed by 20 keV parallel synchrotron radiation. Extraordinary intensity, additional to the direct beam appears in the vicinity of the attenuated projection of an acrylic glass cylinder of 75 mm diameter at 350 mm detector distance (Fig. 5, left end, area of \( \approx 0.9 \times 1 \text{ mm}^2 \)). The 3.4 \( \mu \text{m} \) detector pixel size determines the angular resolution of 2 seconds of arc, a necessary pre-condition for quantitative refraction measurement.

Figure 5. Intensity distribution of 20 keV parallel synchrotron radiation behind acrylic glass cylinder of 75 mm diameter at 350 mm detector distance (area app. 0.9 \( \times 1 \text{ mm}^2 \)) performing additional intensity at edge (angular resolution is 2 seconds of arc).
In order to model the “edge artefact” of overshooting intensity the radial attenuation profile of the cylinder is modified according to the refraction Eq. (4) by numerical dislocation of intensity from positions of incidence angles $\beta_1$ to the required position for the corresponding deflection angle $\theta$. The fit of the experimental intensity profile by this procedure agrees very well outside the cylinder area and gives the correct trend inside the area (Fig. 6). The range of local intensity dislocations corresponds to 1 minute of arc or 100 $\mu$m (30 pixels which is beyond the scope of “phase retrieval” procedures [13]).

Figure 6. 20 keV synchrotron radiation edge artefact of a 75 mm polyacryl cylinder at 350 mm detector distance; measurement: overshoot of 25% above primary beam at 10000 cps intensity; cylinder simulation: attenuation profile of cylinder; simulation: repositioned intensity according to Eq. (4).

The isolated “edge artefact” due to refraction is demonstrated by Fig. 7, which displays the difference between the measured intensity and the calculated cylindrical attenuation profile. The averaged cross section provides the typical refraction profile of a cylinder edge.

Figure 7. Refraction image and profile near edge of cylinder without attenuation: difference of the measured intensity to the calculated cylindrical attenuation profile.

Unfortunately, the demonstrated additional intensity at edges of radiographic images result in negative density, when the data are conventionally interpreted by the Lambert-Beer’s law of attenuation. The above procedure for the intensity correction is not very convenient in general.
applications since it requires prior knowledge of the boundary conditions regarding material and geometry. Therefore an edge correction of the density (instead of intensity) radiographs is proposed. The procedure aims at adapting the requirements for vanishing density outside the projected object region.

The phenomenon of “negative density” due to refractive intensity overshoot at the cylinder edge is demonstrated by Fig. 8 at its left side. The removal of this artefact can be performed by a relatively simple convolution procedure which can be adapted to the specific boundary conditions of materials and radiation. The procedure employs a symmetric non-linear saw-tooth function of selectable length which is convolved with the first derivative of the density radiograph. The convolution product is then added to the radiograph, principally similar to the derivation given by Paganin et al. [13] but of considerable larger operating range.

![Figure 8. “Negative density” in the radiograph due to refractive intensity overshoot at cylinder edge.](image)

The successful application of the saw-tooth convolution to the radiograph of Fig 8 is demonstrated by the profile plots of Fig. 9. The negative density outside the cylinder projection is removed as indicated by the red refraction plot. Inside the projected cylinder area the approximation of the cylinder profile is improved.

![Figure 9. Removal of negative density indications at the cylinder edge by application of the saw-tooth convolution to the radiograph (Fig. 8).](image)
4. Quantitative exploitation of refractive scattering

Beyond the above statements about the nature of radiographic edge artefacts and the possibilities of their removal in order to improve the true attenuation of materials, the edge scattering can be exploited in order to measure the geometry and quantity of the boundaries. This is performed by separate measurement of the primary radiation and the deflected radiation, well known from the small angle X-ray scattering techniques (SAXS) in analytical crystallography.

A modified SAXS instrumentation with X-ray fine structure tube and Kratky camera is employed for performing defined scattering and spatial resolution by one technique. The camera needs an additional scattering foil for the primary beam attenuation measurement and a micro manipulation device for the sample (Fig. 10). For practical measurements the refraction detector remains at a fixed scattering angle $2\theta'$, so that the relative surface density $C$ of the specimen can be measured according to [5]:

$$C = \frac{1}{d} \left( \frac{I_R \cdot I_{A0}}{I_{R0} \cdot I_A \cdot d} - 1 \right) \tag{9}$$

Intensities $I_R$ and $I_{R0}$ refer to the refraction detector with and without sample respectively, $I_A$ an $I_{A0}$ to the absorption detector, and $d$ is the wall thickness of the sample. Apart from the choice of materials the relative surface density $C$ depends merely on the scattering angle and the radiation wavelength.

The absolute “inner surface density” (specific surface, surface per unit volume) is determined by comparison with a known calibration standard at unmodified boundary conditions (wavelength and scattering angle) [14]. A prove of the linearity of the refraction value $C$ according to Eq. (9) and the surface density $\Sigma$ is realised by measuring densely packed uniform size spheres of diameters between 0.25 µm and 8 µm. The linearity holds typically for two orders of magnitude and materials of different attenuation and $\delta$ (after normalizing to the squared density).

![Figure 10. Refraction scanner, a scanning SAXS instrumentation with collimated X-ray beam, sample manipulator, a refraction detector for refracted intensity $I_R$ with sample or $I_{R0}$ without sample and an absorption detector for the attenuation intensity $I_A$ or $I_{A0}$ of the primary beam.](image)

Beyond the average inner surface of pores and particles, interfaces and cracks like fibre debonding in composites can be determined as well [4] without imaging the individual interfaces.. The investigated interface structures may go well below micrometers as the typical X-ray wavelengths applied by the crystallographic fine structure equipment ranges between 0.07 and 0.15 nanometer, remaining below 20 keV photon energy.
Figure 11. Prove of the linearity of the refraction value as a function of the known surface density of densely packed uniform spheres.

For the investigation of engineering or natural materials the homogeneity of their microstructure might be essential for their function. An obvious example is the homogeneity of membranes, in particular filters, in which the pore structure is the essential quality parameter. Therefore the spatial investigation by scanning may image and measure the material homogeneity with respect to the density or the specific surface.

Figure 12. Topographs of dense packings of monodisperse glass spheres of different radii ($R_1=0.25 \mu m$, $R_2=1.2 \mu m$). The porosity is measured by absorption and indicates the mass density which is equal for both radii (middle). However refraction topography (bottom) reveals a specific surface which is 5 times larger for the small radius spheres (expected factor $R_2/R_1$).
The essential difference of the two material parameters can be obtained from Fig. 12 in which the scanning topographs of densely packed uniform glass spheres of different radii ($R_1=0.25 \, \mu m$, $R_2=1.2 \, \mu m$) are compared (Fig. 12, top, schematically). The porosity is measured by absorption and indicates the mass density which is nearly the same for both radii (middle). However, the specific surface (additionally measured by the refraction detector) is 5 times larger for the small radius spheres. This is the factor $R_2/R_1$ which is to be expected for pure geometric reasons (same packing density provided). Again in contrast to all radiographic requirements the spatial resolution in this kind of refraction topography as determined by the scanning steps and the beam width, is much lower than the individual size of the particles. They need no individual imaging in order to be characterised in the average geometry.

Beyond the ability of refraction topography to image the specific surface and interface distribution the related orientation patterns can be imaged as well which is a straight consequence from the oriented scattering examples of Fig. 3 [15]. This is of specific relevance for fibre composites characterisation and crack tensor fields as a result of impacts.

5. Conclusion

Edge artefacts are an interesting disturbance in radiography. For standard applications they might cause wrong attenuation indications of X-rays near edges and need considerable efforts for their removal. But they provide the advantage of improved edge indications in case of poorly contrasting materials, e.g. plastic and organic tissues. Artefacts of very small range may be removed by the “phase retrieval” procedure. The refractive nature of broader artefact patterns has been proven by high angular resolution synchrotron radiographs and their numerical modelling in terms of deflected intensity according to Snell’s law. Furthermore, procedures for the complete removal of the edge artefacts (the constructive refractive signal) outside the sample are given and improved accordance with the theoretical attenuation profile inside the cylinders is reached based on the related excitation sites of the refractive signal.

Apart from radiographic edge artefacts their scattering can be exploited in order to measure the geometry and quantity of boundaries by separate measurement of the primary radiation and the deflected radiation, well known from small angle X-ray scattering (SAXS) techniques in analytical crystallography. Scanning refraction topography with X-ray tubes reveals spatial resolution of the homogeneity of material micro structures like pores, cracks and interfaces and of their quantity at the same time, even without imaging the individual elements of the substructure.

Advantage can be taken from the selectivity of refractive X-ray scattering for the orientation of interfaces or inner surfaces. As the useful wavelength of X-rays is always smaller than an atom and therefore smaller than any kind of crack the limitations for micro and nano crack detection arise only for single cracks of small surface. This problem can be solved in most cases by applying synchrotron techniques with sources of much higher intensity and better alignment.

The complementary approaches of radiography and refraction topography require complementary correction procedures in order to give exact values for either density or boundary properties.

Radiography has to omit scattering.
Scattering has to omit attenuation.
References
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