Foreword

The reflection of x-rays and neutrons from surfaces has existed as an experimental technique for almost fifty years. Nevertheless, it is only in the last decade that these methods have become enormously popular as probes of surfaces and interfaces. This appears to be due to the convergence of several different circumstances. These include the availability of more intense neutron and x-ray sources (so that reflectivity can be measured over many orders of magnitude and the much weaker surface diffuse scattering can now also be studied in some detail); the growing importance of thin films and multilayers in both technology and basic research; the realization of the important role which roughness plays in the properties of surfaces and interfaces; and finally the development of statistical models to characterize the topology of roughness, its dependence on growth processes and its characterization from surface scattering experiments. The ability of x-rays and neutrons to study surfaces over four to five orders of magnitude in length scale regardless of their environment, temperature, pressure, etc., and also their ability to probe buried interfaces often makes these probes the preferred choice for obtaining global statistical information about the microstructure of surfaces, often in a complementary manner to the local imaging microscopy techniques. This is witnessed by the veritable explosion of such studies in the published literature over the last few years. Thus these lectures will provide a useful resource for students and researchers alike, covering as they do in considerable detail most aspects of surface x-ray and neutron scattering from the basic interactions through the formal theories of scattering and finally to specific applications.

It is often assumed that neutrons and x-rays interact weakly with surfaces and in general interact weakly enough so that the simple kinematic theories of scattering are good enough approximations to describe the scattering. As most of us now appreciate, this is not always true, e.g. when the reflection is close to being total, or in the neighborhood of strong Bragg reflections (e.g. from multilayers). This necessitates the need for the full dynamical theory (which for specular reflectivity is fortunately available from the theory of optics), or for higher-order approximations, such as the distorted wave Born approximation to describe strong off-specular scattering. All these methods are discussed in detail in these lectures, as are also the ways in which the magnetic interaction between neutrons and magnetic moments can yield information on the magnetization densities of thin films and multilayers. I commend the organizers for having organized a group of expert lecturers to present this subject in a detailed but clear fashion, as the importance of the subject deserves.

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Introduction

In his paper entitled "On a New Kind of Ray, A Preliminary Communication" relating the discovery of x-rays, which was submitted to the Würzburg Physico-Medical Society on December 28, 1895, Röntgen stated the following about the refraction and reflection of the newly discovered rays: "The question as to the reflection of the X-ray may be regarded as settled, by the experiments mentioned in the preceding paragraph, in favor of the view that ***no noticeable regular reflection of the rays takes place from any of the substances examined.*** Other experiments, which I here omit, lead to the same conclusion.[1]"

This conclusion remained unquestioned until in 1922 Compton[2] pointed out that if the refractive index of a substance for x-rays is less than unity, it ought to be possible, according to the laws of optics, to obtain total external reflection from a smooth surface of it, since the x-rays, on entering the substance from the air, are going into a medium of smaller refractive index. This was the starting point for x-ray (and neutron) reflectivity. The demonstration that the reflection of x-rays on a surface was indeed obeying the laws of electromagnetism was pursued by Prins[3] and others who investigated the role of absorption on the sharpness of the limit of total reflection and showed that it was consistent with the Fresnel formulae. This work was continued by Kiessig[4] using nickel films evaporated on glass. Reflection on such thin films gives rise to fringes of equal inclination (the "Kiessig fringes" in the x-ray literature) which allow the measurement of thin film thicknesses, now the most important application of x-ray and neutron reflectivity. It was, however, not until 1954 that Parratt[5] suggested inverting the analysis and interpreting x-ray reflectivity as a function of angle of incidence via models of an *inhomogeneous* surface-density distribution. The method was then applied to several cases of solid or liquid[6] interfaces. Whereas Parratt noticed in his 1954 paper that "it is at first surprising that any experimental surface appears smooth to x-rays. One frequently hears that, for good reflection, a mirror surface must be smooth to within about one wavelength of the radiation involved..." it soon appeared that effects of surface roughness were important, the most

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[1] A more complete citation of Röntgen's paper is given in an appendix to this introduction.

[2] A.H. Compton *Phil. Mag.* **45** 1121 (1923)

[3] J.A. Prins, *Zeit. f. Phys.* **47** 479 (1928); a very interesting account of these early developments is given in the famous book by R.W. James, "the optical principles of the diffraction of x-rays", Bell and sons, London, 1948.

[4] H. Kiessig *Ann. der Physik* **10** 715 and 769 (1931).

[5] L.G. Parratt, *Phys. Rev.* **95** 359 (1954).

[6] B.C. Lu and S.A. Rice, *J. Chem. Phys.* **68** 5558 (1978).

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dramatic of them being the asymmetric surface reflection known as Yoneda wings[7]. These Yoneda wings were subsequently interpreted as diffuse scattering of the enhanced surface field for incidence or exit angle equal to the critical angle for total external reflection. The theoretical basis for the analysis of this surface diffuse scattering was established in particular through the pioneering work of Croce et al.[8] In a context where coatings, thin films and nanostructured materials are playing an increasingly important role for applications, the number of studies using x-ray or neutron reflectivity dramatically increased during the 90's, addressing vitually all kinds of interfaces: solid or liquid surfaces, buried solid-liquid or liquid-liquid interfaces, interfaces in thin films and multilayers[9]. Apart from the scientific and technological demand for more and more surface characterisation, at least two factors explain this blooming of x-ray and neutron reflectivity. First, the development of neutron reflectometers (Chap. 5) has been decisive, in particular for polymer physics owing to partial deuteration (Chap. 9), and an equally important contribution of neutron reflectivity can be expected for surface magnetism. Second, the use of 2nd and 3rd generation synchrotron sources has resulted in a sophistication of the technique now such that not only the thicknesses but also the morphologies and correlations within and between rough interfaces can be accurately characterised for in-plane distances ranging from atomic or molecular distances to hundreds of microns. In parallel more and more accurate methods have been developed for data analysis.

This book follows a summer school on reflectivity held in Luminy (France) in June 1997. It is organised into two parts, the first one being devoted to principles and the second one to the discussion of examples and applications. Organising the school and now editing the book, we had in mind that an increasing number of non-specialists are now using x-ray and neutron reflectometry and that the need for a proper introduction to the field was not yet fulfilled. It is also true that even if the principle of a reflectivity experiment is extremely simple (one just has to measure the intensity of a reflected beam), the technique is in fact really demanding. An important purpose of this book is therefore also to warn the beginners of experimental problems, often related to the experimental resolution, which are not necessarily apparent but may lead to serious misinterpretations. This is done in the second part of the book where specific aspects related to the nature of the samples are treated. An equally important purpose is also to share with the reader our enthusiasm for the many beautiful recent developments in reflectivity methods, and for the physics that can be can be done with it, and to give him/her the desire to do even more beautiful experiments.

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7 Y. Yoneda, *Phys. Rev.* **131** 2010 (1963).

8 P. Croce, L. Névot, B. Pardo, *C. R. Acad. Sc. Paris* **274** 803 and 855 (1972).

9 For a recent review see for example S. Dietrich and A. Haase, *Physics Reports* **260** 1 (1995) and the numerous examples cited in the different chapters of this book.

As strongly suggested by the short historical sketch given above, most of the revolutions in the use of x-rays (not only for interface studies) arise by considering new potentialities[10] related to their nature of electromagnetic waves, which was so controversial in the days of Röntgen. The book therefore starts with a panorama of the interaction of x-rays with matter, giving both a thorough treatment of the basic principles, and an overview of more advanced topics like magnetic or anisotropic scattering, not only to give a firm basis to the following developments but also to stimulate reflection on new experiments. Then, a rigourous presentation of the statistical aspects of wave scattering at rough surfaces is given. This point, obviously important for understanding the nature of surface scattering experiments, as well as for their interpretation, is generally ignored in the x-ray literature (this chapter has been written mainly by a researcher in optics). The basic statistical properties of surfaces are introduced first. Then an ideal scattering experiment is described, and the limitations of such a description, in particular the fact that the experimental resolution is always finite, are discussed. The finiteness of the resolution leads to the introduction of ensemble averages for the calculation of the scattered intensities and to a natural distinction between coherent (specular, equal to the average of the scattered field) and incoherent (diffuse, related to the mean-square deviation of the scattered field) scattering. These principles are immediately illustrated within the Born approximation in order to avoid all the mathematical complications resulting from the details of the interaction of an electromagnetic wave with matter. These more rigorous aspects of the scattering theory are treated in Chaps. 3 and 4 for specular and diffuse scattering. The matricial theory of the reflection of light in a smooth or rough stratified medium and its consequences are treated in Chap 3. This is used in Chap 4 for the treatment of diffuse scattering. The Croce approach to the distorted-wave Born approximation (DWBA) based on the use of Green functions is mainly used. This theory is currently the most popular for data analysis and is extensively used in the second part of the book, which is devoted to applications, in particular in Chap 8. However, other methods used in optics are also shortly reviewed. The general case of a stratified medium with interface roughness or density fluctuations is discussed using this DWBA, and different dynamical effects are discussed. Then, the theoretical aspects of a finite resolution function (the experimental aspects are treated in the second part of the book) are considered, as well as their implications for reflectivity experiments. The last chapter of this first part, principles, is devoted to neutron reflectometry whose specific aspects require a separated treatment. After an introduction to neutron-matter interactions, neutron reflectivity of non-magnetic materials is presented and the characteristics of the neutron spectrometers are given. Examples follow with

[10] It is our opinion that fully exploiting the spectroscopic capabilities of x-rays in reflectivity experiments would lead to most interesting developments.

a particular emphasis put on the newly developed methods of investigation of magnetic multilayers using polarised neutrons.

The second part of the book is devoted to examples of the physics that can be done using x-ray and neutron reflectivity. The first three chapters are related to solid surfaces and multilayers, whereas the last two chapters deal with soft condensed matter. In both cases, a statistical description of the surfaces and of their properties is given first (Chap 6 and beginning of Chap 9) and examples follow. In Chap 7, the complete characterisation of the roughness of a single solid surface is considered. The experimental geometry, diffractometers, resolution functions are introduced first. Then, examples are given and and the x-ray results are compared to the results obtained using complementary techniques like transmission electron microscopy and atomic force microscopy. More complicated cases of multilayers are discussed in Chap 8. The experimental setups are described and examples of reflectivity studies and non-specular scattering measurements are discussed with the aim of reviewing all the important situations that can be encountered. Examples include rough multilayers, stepped surfaces, interfaces in porous media, the role of roughness in diffraction experiments and multilayer gratings. Examples in soft condensed matter include liquid interfaces and polymers. This is a domain where the impact of reflectivity measurements has been very large because many of the very powerful complementary techniques which can be used with solid surfaces require high vacuum, and cannot be used for the characterisation of liquid interfaces. The specific aspects of liquid interface studies (mainly using x-rays) are discussed first. Experimental setups for the study of horizontal interfaces are described, and the implications of the specific features of liquid height-height correlation functions for reflectivity experiments are described. Examples include liquid-vapour interfaces, organic films at the air-water interfaces, liquid metal surfaces, and finally buried liquid-liquid interfaces. Finally, polymers at interfaces are considered in a last chapter. This is a domain where neutron reflectivity has made an invaluable contribution, in particular owing to the transparency of many materials to neutrons and to the possibility of contrast variation.

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Appendix: Röntgen's report on the reflection of x-rays.

"With reference to the general conditions here involved on the other hand, and to the importance of the question whether the X-rays can be refracted or not on passing from one medium into another, it is most fortunate that this subject may be investigated in still another way than with the aid of prisms. Finely divided bodies in sufficiently thick layers scatter the incident light and allow only a little of it to pass, owing to reflection and refraction; so that if powders are as transparent to X-rays as the same substances are in mass–equal amounts of material being presupposed–it follows at once that neither refraction nor regular reflection takes place to any sensible degree. Experiments were tried with finely powdered rock salt, with finely electrolytic silver-powder, and with zinc-dust, such as is used in chemical investigations. In all these cases no difference was detected between the transparency of the powder and that of the substance in mass, either by observation with the fluorescent screen or with the photographic plate... The question as to the reflection of the X-ray may be regarded as settled, by the experiments mentioned in the preceding paragraph, in favor of the view that no noticeable regular reflection of the rays takes place from any of the substances examined. Other experiments, which I here omit, lead to the same conclusion.
One observation in this connection should, however, be mentioned, as at first sight it seems to prove the opposite. I exposed to the X-rays a photographic plate which was protected from the light by black paper, and the glass side of which was turned towards the discharge-tube giving the X-rays. The sensitive film was covered, for the most part, with polished plates of platinum, lead, zinc, and aluminum, arranged in the form of a star. On the developing negative it was seen plainly that the darkening under the platinum, the lead and particularly the zinc, was stronger than under the other plates, the aluminum having exerted no action at all. It appears, therefore, that these metals reflect the rays. Since, however, other explanations of a stronger darkening are conceivable, in a second experiment, in order to be sure, I placed between the sensitive film and the metal plates a piece of thin aluminum-foil, which is opaque to ultraviolet rays, but it is very transparent to the X-rays. Since the same result substantially was again obtained, the reflection of the X-rays from the metals above named is proved. If we compare this fact with the observation already mentioned that powders are as transparent as coherent masses, and with the further fact that bodies with rough surfaces behave like polished bodies with reference to the passage of the X-rays, as shown as in the last experiment, we are led to the conclusion already stated that regular reflection does not take place, but that bodies behave toward X-rays as turbid media do towards light."