X-Ray Scattering from Soft-Matter Thin Films

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Materials Science and Basic Research

With 98 Figures

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Preface

Grazing-angle x-ray scattering and the physics of soft-matter films in general are fields of modern condensed-matter research which have grown rapidly in the past decades. This book is intended to give a review of the combination of the two. The state of the art in grazing-angle x-ray scattering from soft-matter thin films is reported.

At the beginning, an introduction to the formalism of x-ray reflectivity is given. Here my intention was to present a strict description for the case of rough interfaces because quite different schemes may be found in the literature. Other theoretical chapters of this book deal with new inversion techniques for x-ray reflectivity data, and off-specular and coherent x-ray scattering. Whereas the theory of off-specular scattering is outlined briefly, the description of x-ray scattering with coherent radiation is given in some more detail since it is a very young and promising research field, particularly for the investigation of soft-matter films.

The selection of the examples was mainly driven by the fact that x-ray scattering is almost the only possible way to obtain structural information on atomic length scales from these soft-matter films. Moreover, while the atomic dimensions are sampled, mesoscopic lengths up to several microns are accessible, too, owing to the high resolution in the regime of glancing angles. One of the aims of this book is to highlight this nice fact of x-ray scattering which makes this probe so unique and powerful. The underlying physics of all examples is quite different, showing the various research areas where x-ray scattering has been successfully applied to shed light on new phenomena.

All examples are discussed in great detail. Thus, many parts of this book may also be used for tutorial courses or lectures. This purpose is supported by many cross-references, particularly between the chapters dealing with experiments and theory, and a large bibliography, where I apologize for each piece of work which should have been quoted but which I accidently have overlooked.

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Kiel, August 1998 *Metin Tolan*

List of Acronyms

AFM	atomic force microscopy
APS	Advanced Photon Source
BS	Beckmann–Spizzichino
CdA	cadmium arachidate
DWBA	distorted-wave Born approximation
ESRF	European Synchrotron Radiation Facility
FWHM	full-width half-maximum
GID	grazing-incidence diffraction
HASYLAB	Hamburger Synchrotronstrahlungslabor
KPZ	Kardar–Parisi–Zhang
LB	Langmuir–Blodgett
MBE	molecular beam epitaxy
MCF	mutual coherence function
MOVPE	metalorganic vapor phase epitaxy
NC	Névot–Croce
NSLS	National Synchrotron Light Source
PEP	polyethylene–propylene
PMMA	polymethylmethacrylate
PS	polystyrene
PSD	power spectral density
PVP	polyvinylpyridine
RHEED	reflection high-energy electron diffraction
rms	root-mean-square
STM	scanning tunneling microscopy
TEM	transmission electron microscopy
UHP	upper half-plane
vdW	van der Waals
XPCS	x-ray photon correlation spectroscopy

Contents

1. Introduction

The investigation of surfaces and interfaces with x-ray scattering methods is a field that has grown enormously in the last three decades. Increasing surface quality, technological developments concerning sophisticated surface diffractometers and synchrotron radiation facilities, and a steady development of surface scattering theory have made this progress possible. Nowadays detailed and precise results from various liquid, glassy, and solid surfaces are available, and even complex layer structures can be characterized.

It is quite clear that there is also a large body of "competing" or complementary methods, such as various kinds of scanning tunneling microscopy, atomic force microscopy (AFM), and high-resolution transmission electron microscopy. Whenever possible, it is desirable to investigate surfaces with such complementary probes to obtain both real-space and reciprocal-space information. There is, however, one major advantage in favour of scattering methods: Soft-matter surfaces, i.e. the surfaces and interfaces of liquids, polymers, glasses, organic multilayers, etc., can be investigated on an atomic scale[1].

In our daily life soft-matter films are playing a more and more important role: Thin polymer films are used as coatings in many technological applications. The variety extends from their simple use as protection of surfaces against corrosion to the use of ultrathin films in semiconductor technology. Organic multilayers are promising materials for biosensors and liquid films are present in so many obvious contexts that there is no need to explain this here.

In addition to the applications and use of soft-matter films in materials science, they are also of interest with respect to fundamental questions: In thin films liquids and polymers may be considered as trapped in a quasi-two-dimensional geometry. This confined geometry is expected to alter the properties and structures of these materials considerably.

On the one hand the typical film thicknesses are on the order of 20–1000 Å, and hence probes for their investigation have to be sensitive to this vertical length scale. Laterally even larger length scales ($> 10\,\mu$m) have to be covered,

[1] It is quite easy to investigate polymer surfaces with AFM. However, the extracted information is most reliable on larger length scales than those accessible by x-ray scattering.

since soft-matter films may possess long-range correlations due to capillary waves on their surfaces. On the other hand many fundamental properties are expected to be dominated by the regions close to the interfaces of the film, i.e. atomic resolution is needed for their investigation. X-ray scattering at grazing angles is a tool which meets these criteria, and hence soft-matter thin films have been extensively investigated by this method in the past. In this book, I review a small fraction of this work, where the focus is on x-ray reflectometry and off-specular diffuse scattering.

The surface sensitivity is based on the fact that for x-ray wavelengths ($\lambda \sim 1\,\text{Å}$) the index of refraction is slightly smaller than unity. Total external reflection occurs if the angle of incidence of the impinging x-rays is sufficiently small - more precisely, smaller than the critical angle of total external reflection. This limits the penetration depth and the scattering to the near surface region. However, this is not quite correct for x-ray reflectometry, since a reflectivity mainly consists of data taken at angles considerably larger than the critical angle, where the penetration depth is already on the order of thousands of angstroms. The sensitivity is then obtained by interference of x-rays scattered at different depths in the sample. In Chap. 2 the theory of x-ray reflectivity is discussed in terms of conventional optics. The basic principles are explained (Fresnel formulas, Parratt algorithm) as well as the more complicated topic of a *strict* inclusion of roughness into the formulas (comparison of "intuitively correct" results with exact results).

The next chapter deals with reflectivity experiments and is divided into two sections: In Sect. 3.1 setups to carry out reflectivity and diffuse-scattering measurements are described. I have taken the liberty of keeping the descriptions concise since nowadays all relevant information may be obtained within minutes by a few mouse clicks via the Internet[2]. Instead, the considerations about including the resolution in the data analysis are presented in more detail: In the specific case of scattering from liquid interfaces many important subtleties have to be taken into account. Section 3.2 contains several examples of soft-matter thin films that have been investigated by x-ray reflectometry. The examples range from the determination of the capillary wave roughness on top of polymer films to density profiles at the liquid/solid interface and structural properties of organic multilayers. Most of these examples again appear in Sect. 6.2 when diffuse-scattering experiments are discussed.

A major defect of x-ray scattering is the well-known phase problem. The data cannot be inverted, since the scattered signal is proportional to the modulus squared of the Fourier transform of the scattering length density, or, in other words, intensities rather than field amplitudes are measured by a detector. The considerations of Chap. 4 reveal that the situation is not as bad as anticipated for the one-dimensional problem of reflectometry. Reflectivity is re-discussed in Sect. 4.1, but within the kinematical theory of scattering.

[2] See e.g. *http://www.aps.anl.gov*, *http://www.esrf.fr*, *http://www.nsls.bnl.gov*, *http://www.desy.de/hasylab*, or *http://www.spring8.or.jp*.

It will be shown that for a system consisting of a layer of low density on top of a substrate with a sufficiently large density, the phase of the (complex) reflection coefficient is completely determined by its modulus, i.e. by the measured reflectivity. Fortunately this condition is valid for many soft-matter thin-film systems! A new data inversion method is proposed which is based on this fact and the inclusion of all a-priori knowledge of the system under investigation.

The second part of this book gives a review of a fraction of the works where diffuse x-ray scattering has yielded new information about soft-matter thin films. Before coming to the specific examples, a statistical description of surfaces and interfaces is given in Chap. 5 because the respective height–height correlation functions enter the scattering formulas. The definitions of correlation functions are recapitulated and surfaces with thermally excited capillary waves are considered in great detail. Also some of the formulas which have already appeared in Chap. 2 find their justification here.

In the first part of Chap. 6 (Sect. 6.1) the theory of diffuse x-ray scattering is outlined. I have restricted the description to a simple kinematical treatment (a brief introduction into the so-called distorted-wave Born approximation can be found in Appendix A.2). However, again the subtleties which arise from long-range surface correlations lead to considerable complications in the treatment. In Sect. 6.2 experiments with polymer, liquid, and Langmuir–Blodgett films are presented. Another class of systems consists of polymer films on laterally structured surfaces. These particular substrates enable the quantitative investigation of roughness propagation by soft-matter thin films. Chapter 6 in a sense marks the end of the discussion of "classical" scattering experiments in this book.

A new, promising field for the future is x-ray scattering using coherent radiation. The high-brilliance third-generation synchrotron facilities are able to generate coherent beams with sufficiently high flux for surface investigations. In Chap. 7 a rigorous x-ray scattering theory for the case of (partially) coherent radiation is presented together with some examples of recent measurements. A critical discussion of the possibilities and difficulties is given and the scattering formulas for x-ray photon correlation spectroscopy are explicitly calculated.

At the end of this introduction it may be useful to mention some of the related topics that are not addressed in this book. Here all kinds of *diffraction* from soft-matter thin films have to be mentioned. Thus, diffraction from organic molecules on water surfaces is not addressed. The review of *Als-Nielsen et al.* [12] covers this subject. Grazing-incidence diffraction (GID) in general is not addressed. This method probes surfaces by keeping the incidence and exit angle small while measuring out of the scattering plane, e.g. Bragg reflections. Hence, the scattering is always limited to the first few atomic layers. The reviews of *Dosch* [103] and *Holý, Pietsch & Baumbach* [167] give an extensive overview of GID, where the former concentrates on the determination of critical phenomena in the near-surface region and the latter mainly deals with the structure of multilayers and dynamical scattering theory.

I also tried to avoid recapitulating the whole distorted-wave Born approximation theory of diffuse x-ray scattering, and hence have restricted myself to a description of the simple kinematical treatment. The recent review of *Dietrich & Haase* [94] contains calculations for almost all cases that may occur in experiments.

Finally, it should be mentioned that the field of neutron scattering is not touched in this article [40, 43, 116, 409]. However, all formulas may easily be translated to the case of neutron scattering, if the electron density is replaced by the scattering length density for neutrons. On one hand neutron reflectivity measurements often suffer from very low intensity, but on the other hand there is no better way to study many polymer/polymer and liquid/liquid interfaces yet. The field of neutron reflectivity in connection with soft-matter interfaces has been reviewed by *Russell* [303, 304] and *Stamm* [348], where further details may be found.

2. Reflectivity of X-Rays from Surfaces

The scattering of electromagnetic waves is used in basic research, materials science, and industry for investigations of surfaces and interfaces on length scales covering several orders of magnitude. Radar waves are scattered from the earth and other planets to create detailed maps of the respective surfaces, light scattering is a common technique to investigate the quality of silicon wafers in semiconductor technology on length scales on the order of microns, and x-ray scattering is a probe to investigate surfaces on angstrom scales.

This variety of quite different scattering problems can be described in the same way by introducing a refractive index and solving Maxwell's equations. The particular case of the reflection of hard x-rays (wavelengths on the order of angstroms, photon energies of approximately 10 keV) from matter will be discussed in the following sections.

2.1 Basic Principles

An electromagnetic plane wave given by its electric field vector $\boldsymbol{E}(\boldsymbol{r}) = \boldsymbol{E}_0 \exp(\mathrm{i}\,\boldsymbol{k}_\mathrm{i} \cdot \boldsymbol{r})$, which penetrates into a medium characterized by an index of refraction $n(\boldsymbol{r})$, propagates according to the Helmholtz equation

$$\Delta \boldsymbol{E}(\boldsymbol{r}) + k^2 n^2(\boldsymbol{r}) \boldsymbol{E}(\boldsymbol{r}) = 0 \,, \tag{2.1}$$

where $k = 2\pi/\lambda$ is the modulus of the wavevector $\boldsymbol{k}_\mathrm{i}$ and λ denotes the x-ray wavelength. In general, the index of refraction for an arrangement of N atoms per unit volume, which may be assumed to be harmonic oscillators with resonance frequencies ω_j, is expressed as [178]

$$n^2(\boldsymbol{r}) = 1 + N \frac{e^2}{\varepsilon_0 m} \sum_{j=1}^{N} \frac{f_j}{\omega_j^2 - \omega^2 - 2\mathrm{i}\,\omega\,\eta_j} \,, \tag{2.2}$$

where ω is the frequency of the incoming electromagnetic wave, e is the charge and m the mass, respectively, of the electron, the η_j are damping factors, and the f_j denote the forced oscillation strengths of the electrons of each single atom. It should be noted that in general the f_j are complex numbers, $f_j = f_j^0 + f_j'(E) + \mathrm{i} f_j''(E)$, where $f_j'(E)$ and $f_j''(E)$ take into account dispersion and absorption corrections depending on the radiation energy E [394]. For x-rays $\omega > \omega_j$, and Eq. (2.2) may be replaced by

$$n(\boldsymbol{r}) = 1 - \delta(\boldsymbol{r}) + \mathrm{i}\beta(\boldsymbol{r}) \, , \tag{2.3}$$

with the dispersion and absorption terms

$$\delta(\boldsymbol{r}) = \frac{\lambda^2}{2\pi} r_e \varrho(\boldsymbol{r}) \sum_{j=1}^{N} \frac{f_j^0 + f_j'(E)}{Z} \tag{2.4}$$

and

$$\beta(\boldsymbol{r}) = \frac{\lambda^2}{2\pi} r_e \varrho(\boldsymbol{r}) \sum_{j=1}^{N} \frac{f_j''(E)}{Z} = \frac{\lambda}{4\pi} \mu(\boldsymbol{r}) \, . \tag{2.5}$$

It should be emphasized that $\delta(\boldsymbol{r})$ is always positive. In Eqs. (2.4) and (2.5) we have introduced the classical electron radius[1] $r_e = e^2/(4\pi\varepsilon_0 mc^2) = 2.814 \times 10^{-5}$ Å; the total number of electrons $Z = \sum_j Z_j$, where Z_j denotes the number of electrons of each component of the material; the electron density $\varrho(\boldsymbol{r})$ as a function of the spatial coordinates $\boldsymbol{r} = (x, y, z) = (\boldsymbol{r}_\parallel, z)$; and the linear absorption coefficient $\mu(\boldsymbol{r})$. The quantities f_j^0 are $\boldsymbol{q}$-dependent, where $\boldsymbol{q} = \boldsymbol{k}_f - \boldsymbol{k}_i$ is the wavevector transfer ($\boldsymbol{k}_i$, $\boldsymbol{k}_f$ are the wavevectors of the incident and scattered plane x-ray waves). This has to be taken into account when measurements over a large q region are analyzed [394]. However, in the region of glancing incident and exit angles, α_i and α_f, respectively, the wavevector transfer is small, and f_j^0 may be approximated with high accuracy by $f_j^0 \approx Z_j$. In the case of a homogeneous medium and far away from absorption edges, one may simplify the expression for the refractive index to

$$n = 1 - \frac{\lambda^2}{2\pi} r_e \varrho + \mathrm{i} \frac{\lambda}{4\pi} \mu \, . \tag{2.6}$$

Scattering length densities $r_e \varrho$ for some materials are listed in Table 2.1.

The values in Table 2.1 yield $\delta = r_e \varrho \lambda^2/(2\pi) \sim 10^{-6}$ for x-rays, i.e. the real part of the refractive index is slightly smaller than unity. The absorption β is usually one or two orders of magnitude smaller[2].

For a single vacuum/medium interface the law of refraction gives $\cos\alpha_i = (1 - \delta)\cos\alpha_t$, where α_t is the exit angle of the refracted radiation (see Fig. 2.1)[3]. Thus, if $\alpha_t = 0$, and since δ is very small, the critical angle is

$$\alpha_c \approx \sqrt{2\delta} = \lambda\sqrt{r_e \varrho/\pi} \, . \tag{2.7}$$

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[1] Also known as the Thompson scattering length of the electron.

[2] For neutrons the refractive index can be written as $n = 1 - \delta_n + \mathrm{i}\beta_n$, too. Whereas δ_n is on the same order as for x-rays, the absorption β_n is essentially negligible ($\beta_n \sim 10^{-12}$).

[3] In the x-ray literature all angles are measured towards the surface and not, as usual in optics, with respect to the surface normal.

Table 2.1. Scattering length densities $r_e\varrho$, dispersions δ, linear absorption coefficients μ, and critical angles α_c for x-rays with $\lambda = 1.54$ Å (CuKα radiation, from *Stamm* [348] and [394])

	$r_e\varrho\,(10^{10}\text{cm}^{-2})$	$\delta(10^{-6})$	$\mu\,(\text{cm}^{-1})$	$\alpha_c(°)$
Vacuum	0	0	0	0
PS $(C_8H_8)_n$	9.5	3.5	4	0.153
PMMA $(C_5H_8O_2)_n$	10.6	4.0	7	0.162
PVC $(C_2H_3Cl)_n$	12.1	4.6	86	0.174
PBrS $(C_8H_7Br)_n$	13.2	5.0	97	0.181
Quartz (SiO_2)	18.0–19.7	6.8–7.4	85	0.21–0.22
Silicon (Si)	20.0	7.6	141	0.223
Nickel (Ni)	72.6	27.4	407	0.424
Gold (Au)	131.5	49.6	4170	0.570

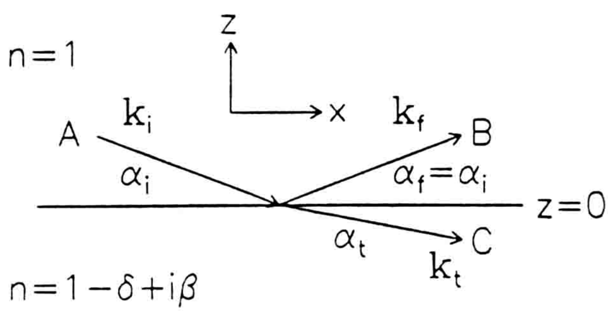

Fig. 2.1. A plane electromagnetic wave with wavevector $\boldsymbol{k}_i$ hits a surface at a grazing angle α_i. The wave splits into a reflected ($\alpha_f = \alpha_i$) and a refracted wave transmitted at the angle α_t

For incident angles $\alpha_i \leq \alpha_c$ the phenomenon of total external reflection occurs. The x-rays do not penetrate far into the medium. Instead, all incoming radiation is reflected (with small losses due to absorption). The critical angle α_c is usually several tenths of a degree for most materials (see Table 2.1).

Now the reflectivity of a single perfectly smooth vacuum/medium interface will be calculated and the situation shown in Fig. 2.1 is considered. A plane wave in vacuum, $\boldsymbol{E}_i(\boldsymbol{r}) = (0, A, 0), \exp(\mathrm{i}\,\boldsymbol{k}_i \cdot \boldsymbol{r})$ with wavevector $\boldsymbol{k}_i = k(\cos\alpha_i, 0, -\sin\alpha_i)$, hits at a grazing angle α_i a flat surface of a medium with refractive index $n = 1 - \delta + \mathrm{i}\beta$. The reflected and transmitted fields may be described by $\boldsymbol{E}_r(\boldsymbol{r}) = (0, B, 0)\exp(\mathrm{i}\,\boldsymbol{k}_f \cdot \boldsymbol{r})$, with $\boldsymbol{k}_f = k(\cos\alpha_i, 0, \sin\alpha_i)$, and $\boldsymbol{E}_t(\boldsymbol{r}) = (0, C, 0)\exp(\mathrm{i}\,\boldsymbol{k}_t \cdot \boldsymbol{r})$, where the components of $\boldsymbol{k}_t = (k_{t,x}, 0, k_{t,z})$ are given by the law of refraction. Here the case of s-polarization is considered, i.e. the impinging wave is linearly polarized with the electric field vector in the y direction perpendicular to the (x, z) scattering plane. From the fact that the tangential components of the electric and magnetic fields have to be continuous at the surface $z = 0$, the (complex) reflection and transmission