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ISBN: 3-540-46488-4

Norbert Stribeck

X-Ray Scattering of Soft Matter

With 92 Figures and 6 Tables

 Springer

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Library of Congress Control Number: 2007922403

DOI 10.1007/978-3-540-69856-2

ISBN 978-3-540-69855-5 Springer Berlin Heidelberg New York

e-ISBN 978-3-540-69856-2

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Typesetting: Camera-ready copy from the author
Data conversion and production by LE- \TeX Jelonek, Schmidt & Vöckler GbR, Leipzig, Germany
Cover design: eStudio Calamar, Girona/Spain

SPIN 11533863 55/3100/YL - 5 4 3 2 1 0 Printed on acid-free paper

Springer Laboratory Manuals in Polymer Science

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Preface

Mehr Licht!

(J. W. v. Goethe)

The application of X-ray scattering for the study of soft matter has a long tradition. By shining X-rays on a piece of material, representative structure information is collected in a scattering pattern. Moreover, during the last three decades X-ray scattering has gained new attractivity, for it developed from a static to a dynamic method.

The progress achieved is closely linked to the development of both powerful detectors and brilliant X-ray sources (synchrotron radiation, rotating anode). Such point-focus equipment has replaced older slit-focus equipment (Kratky camera, Rigaku-Denki camera) in many laboratories, and the next step of instrumental progress is already discernible. With the “X-ray free electron laser” (XFEL) it will become possible to study very fast processes like the structure relaxation of elastomers after the removal of mechanical load.

Today, structure evolution can be tracked *in-situ* with a cycle time of less than a second. Moreover, if a polymer part is scanned by the X-ray beam of a microbeam setup, the variation of structure and orientation can be documented with a spatial resolution of 1 μm . For the application of X-rays no special sample preparation is required, and as the beam may travel through air for at least several centimeters, manufacturing or ageing machinery can be integrated in the beamline with ease.

On the other hand, the result of the scattering method is not a common image of the structure. There is not even a way to reconstruct it from scattering data, except for the cases in which either anomalous scattering is employed, or a diffraction diagram of an almost perfect lattice structure is recorded. Because most of the man-made polymer materials suffer from polydispersity and heterogeneity, the crystallographic algorithms of structure inversion are in general restricted to the field of biopolymers (e.g., protein crystallography). Thus the ordinary polymer scientist will deal with scattering data rather than with diffraction data. These data must be interpreted or analyzed. This book is intended both to guide the beginner in this field, and to present a collection of strategies for the analysis of scattering data gathered with modern equipment. Common misunderstandings are discussed. Instead, advanced strategies are advertised.

An advantage of a laboratory-oriented textbook is the fact that many technical aspects of our trade can be communicated¹. Their consideration may help to improve the quality and to assure the completeness of the recorded data. On the other

¹An example is the chapter entitled “It’s Beamtime, Phil”. It is written in the hope that in particular the practical work of students will benefit from it.

hand, the concept is restricting the presentation of the mathematical background to a terse treatment. For a field like the scattering that is virtually interpenetrated by mathematical concepts this is not unproblematic. As a consequence, it was impossible to present mathematical deductions, which could have been an assistance to methodical development by the reader. In this respect even the references given to original papers are not really helpful, because in such publications the fundamental mathematical tools are expected to be known. Nevertheless, this restriction may be advantageous from a different perspective. The terse scheme is enhancing the presentation of the fundamental ideas and their repetitive use in different subareas of the scattering technique.

This book with its special focus on application was stimulated by a suggestion of Prof. Dr.-Ing. W.-M. Kulicke. I greatly appreciate his support. Moreover, the manuscript has its roots in thirty years of practical work in the field of scattering from soft materials conducted in several labs and at several synchrotron sources. During this time the author has assisted many external groups with their practical work at the soft-matter beamlines of the Hamburg Synchrotron Radiation Laboratory (HASYLAB at DESY), supported evaluation of scattering data, and worked as a referee in the soft-condensed matter review-committee of the European Synchrotron Radiation Facility (ESRF) in Grenoble. The accumulated handouts prepared during twenty years of lecturing scattering methods at the University of Hamburg have been a valuable source for the book manuscript.

There are many other people who have – in different respect – contributed to this work. The first to mention is my teacher, Prof. Dr. W. Ruland. I am grateful for his art of teaching the scattering. Wherever in this book I should have been able to explain something clearly and concisely, it is his merit. The second to mention is Prof. Dr. H. G. Zachmann. In his group I enjoyed to become involved in many practical issues of soft matter physics. In particular I appreciate many helpful comments on the manuscript that have been supplied by Prof. Dr. W. Ruland, Dr. C. Burger, Prof. Dr. A. Thünemann and Prof. Dr. S. Murthy. In addition, there are many other colleagues who have stimulated my work by fruitful cooperation, discussion and support. To mention them all would fill pages.

The complex task of writing a scientific manuscript has been significantly eased by authoring tools that keep track of the formal aspects of the growing manuscript. For this reason I thank the developers of LyX, Koma-Script and L^AT_EX (in particular Matthias Etrich and Markus Kohm) for their free and superb software. Moreover, I highly appreciate the excellent guidance and the distinguished manuscript editing by the team at Springer Publishers.

Last but not least I express cordial thanks to my wife Marie-Luise and to my children for their continuous support.

Hamburg, January 2007

N. Stribeck

List of Symbols and Abbreviations

The handling of polar coordinates is a general problem in a book on scattering, where the symbol θ that is normally used to indicate the polar angle is already used to indicate the Bragg angle. Too late I became aware of the problem and tried to introduce a consistent notation. Unfortunately the problem was more involved than I thought, as colleagues pointed out after proofreading the manuscript. Based on suggestions I finally tried to harmonize the nomenclature. Nevertheless, the reader should be aware of possible remnant inconsistencies concerning the use of the symbols ψ , φ and symbols of related angles.

$\langle \rangle$	Averaging operator
$\langle \rangle_V$	Irradiated volume average
$\langle \rangle_\omega$	Solid-angle average
\square	Slice mapping
$\{ \}$	Projection mapping
\star	Convolution operator
\star_φ	Angular convolution
\otimes	Correlation operator
\star_2	Autocorrelation operator
\ast	Complex conjugate. $z = a + ib$; $z^\ast = a - ib$
∇	Gradient operator
1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
$A(\mathbf{s})$	Scattering amplitude
\mathbf{a}	Scaling vector (anisotropic dilation)
a	Scaling factor (isotropic or 1D dilation)

a	In a lattice: edge length of unit cell, i.e., the distance between the $\delta(\cdot)$ -elements that make the abstract lattice $c(\cdot)$
α_i	Angle of incidence on the sample surface
α_e	Angle of exit from the sample surface
$B(h)$	Integral breadth of the distribution h
$c(\cdot)$	Comb function (abstract lattice)
CLD	Chord length distribution $g(r) = -\ell_p \gamma''(r)$
CCD	Charge-coupled device
CDF	Chord distribution function $z(\mathbf{r}) \propto -\Delta\gamma(\mathbf{r})$
$\delta(\cdot)$	DIRAC's delta function
Δ	Laplacian operator
DESY	D eutsches E lektronen- S ynchrotron (Hamburg, Germany)
DI	Digital image processing
D	Fractal dimension
d_{hkl}	Lattice repeat in WAXS (distance between net planes of a crystal indexed by hkl)
DDF	Distance distribution function
ESRF	E uropean S ynchrotron R adiation F acility (Grenoble, France)
ε	Mechanical elongation ($\varepsilon = l/l_0 - 1$)
$\exp(-\mu\ell)$	Linear absorption factor
$\mathcal{F}(\mathbf{s})$	Fourier transform
$\mathcal{F}_n(\cdot)$	n -dimensional Fourier transform
$\mathcal{F}_{-n}(\cdot)$	n -dimensional Fourier back-transform
f_P	Polarization factor
f_{or}	Uniaxial orientation parameter (HERMANS' orientation function)
<i>FIT2D</i>	Scattering data evaluation program by A. Hammersley (ESRF)
FLASH	Free Electron Laser Hamburg
FWHM	Full width at half-maximum

$g(r)$	(Radial) chord length distribution (CLD)
$g_1(x)$	(One-dimensional) interface distribution function (IDF)
GEL	Image data format returned by image plate scanners
$\gamma(\mathbf{r}) = \rho^{*2}(\mathbf{r})/k$	Normalized correlation function
HASYLAB	Hamburg Synchrotron Radiation Laboratory
$h()$	Some kind of distribution function
hkl	MILLER's index of a crystal reflection in reciprocal space
(h)	Order of a reflection, line or peak. Short for hkl
$H()$	Fourier transform of the distribution $h()$
$h_H(a)$	Size distribution (of particles, clusters)
$\Im()$	Imaginary part of a complex number
$I(\mathbf{s}) = \mathcal{F}_3(\rho^{*2}(\mathbf{r}))$	Scattering intensity
I_0	Incident intensity (i.e. primary beam intensity)
I_t	Transmitted intensity behind the sample
IDL	Commercial programming system for image data processing
ImageJ	Open-source programming system for image data processing
$J(s_3) = [\{I\}_2(s_2, s_3)]_1(s_3)$	Slit-smearred scattering intensity
J_i	Bessel function of the first kind and order i
$k = \int I(\mathbf{s}) d^3s = \rho^{*2}(0)$	Scattering power
L	Lattice repeat (in SAXS: long period, in WAXS identical to d_{hkl} according to Bragg's law)
ℓ	Path of the photon through the sample
ℓ_p	Chord length related to size of crystals or domains
l	In straining experiments: actual length of the sample
l_0	In straining experiments: initial length of the sample
λ	X-ray wavelength
λ_d	Draw ratio $\lambda_d = l/l_0 = \varepsilon + 1$
Linac	Linear accelerator

M	Molecular mass
MAXS	Middle-angle X-ray scattering
$\mathcal{M}()$	Mellin transform
μ	Linear absorption coefficient
μ_i	i -th central moment of a distribution function
μ'_i	i -th moment about origin of a distribution function
OTOKO	Scattering curve evaluation program by M. Koch (EMBL, Hamburg)
<i>pv-wave</i>	Commercial programming system for image data processing
$P(\mathbf{r}) = \rho^{*2}(\mathbf{r})$	Patterson function
$p(r)$	(Radial) distance distribution function $p(r) = r^2\gamma(r)$
$\Phi(\mathbf{s})$	Fourier transform of a shape function $\Phi(\mathbf{s}) = \mathcal{F}(Y(\mathbf{r}))$
$\mathbf{q} = 2\pi\mathbf{s}$	Alternate scattering vector
$Q = k/V$	Invariant (SAXS)
Q_P	Polarization quality (of a synchrotron source)
\mathbb{R}	The set of real numbers
\mathbb{R}^n	The n -dimensional vector space
$\Re()$	Real part of a complex number
R	Sample-to-detector distance
R_g	Guinier radius (i.e. radius of gyration)
$\mathbf{r} = (r_1, r_2, r_3)$	Real space vector
r_e	COMPTON's classical electron radius ($2.818 \times 10^{-15}\text{m}$)
ROI	Region of interest (from Digital Image Processing)
ρ_m	Mass density
$\rho(\mathbf{r})$	Electron density (in the field of SAXS: deviation of the electron density from the average electron density)
$\rho^{*2}(\mathbf{r}) = k\gamma(\mathbf{r})$	(SAXS) correlation function
$\langle\rho\rangle_V$	Average electron density

s	Magnitude of the scattering vector
$\mathbf{s} = (s_1, s_2, s_3)$	Scattering vector in Cartesian coordinates
$\mathbf{s} = (s, \phi, \psi)$	Scattering vector in polar coordinates (ϕ polar angle, ψ azimuthal angle). – See the preamble to this “List of Abbreviations”
SAXS	Small-angle X-ray scattering
S/N	Signal-to-noise ratio
SSRL	Stanford Synchrotron Radiation Laboratory
σ	Standard deviation
σ^2	Variance
t	Sample thickness
t_{opt}	Optimum sample thickness
TIFF	Tagged Image File Format
TOPAS	Scattering curve evaluation program by N. Stribeck
θ	Bragg angle (half of the scattering angle)
2θ	Scattering angle
θ_c	Critical angle of total reflection
USAXS	Ultra small-angle X-ray scattering
USB	Universal Serial Bus (an interface to couple external devices to computers)
V	The sample volume irradiated by the X-ray beam
VFC	Voltage-to-frequency converter
VUV	Vacuum ultra-violet light
W	Beam cross-section of the incident X-ray beam
x	Principal axis of uniaxial structure, depth in which a photon is scattered
XFEL	X-ray free electron laser
$Y(\mathbf{r})$	Shape function ($Y(\mathbf{r}) = 0$ outside the body, $Y(\mathbf{r}) = 1$ inside)
$Y_H(x)$	Heaviside function. $Y_H(x > 0) = 1$, $Y_H(x < 0) = 0$. $\partial Y_H(x) / \partial x = \delta(x)$
WAXS	Wide-angle X-ray scattering
$z(\mathbf{r}) = -\Delta P(\mathbf{r})$	Chord distribution function

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1 Polydispersity and Heterogeneity

The heterogeneity immanent to materials that show scattering but not diffraction patterns should not be ignored. An assessment concerning the significance of results can only be expected if the collected data are complete (cf. Sect. 8.4.2) and show low noise (exposure time long enough). Whenever a measured parameter value is discussed, heterogeneity results in fundamental questions to be answered: What kind of average does my method return? Is it possible to determine the width and skewness of the parameter value distribution? A brief review of such “probability distributions” and their moments is given for later reference.

1.1 Scattering, Polydispersity and Materials Properties

Except for biopolymers, most polymer materials are polydisperse and heterogeneous. This is already the case for the length distribution of the chain molecules (molecular mass distribution). It is continued in the polydispersity of crystalline domains (crystal size distribution), and in the heterogeneity of structural entities made from such domains (lamellar stacks, microfibrils). Although this fact is known for long time, its implications on the interpretation and analysis of scattering data are, in general, not adequately considered.

DEBYE & MENKE (1931) [1]: “It is futile to draw distinct conclusions if genuine scattering curves are not at hand. It is insufficient under any circumstances if authors state that an interference maximum or several of them exist at certain angular positions. Only a continuous scattering pattern can be the fundament of proper reasoning. Concerning the abundant reports on disordered materials it must unfortunately be stated that they are unsatisfactory in this respect. Although even in this way, by mere accumulation of data and comparison of

data from materials with similar chemical composition, some valuable conclusion was drawn with a higher or a lower level of significance. This situation is the result of the fact that we are insufficiently informed on the theory of the arrangement of molecules in a fluid. Only if it were possible to theoretically describe this arrange-

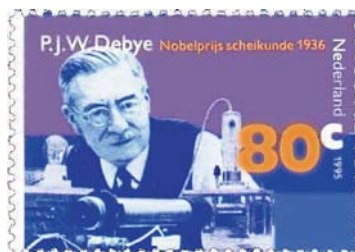


Figure 1.1. P. Debye (1884-1966) and his small-angle light-scattering device on a Dutch stamp

ment in a similar manner as can be done for the arrangement of atoms in a crystal, it would be sufficient to report interference maxima.”

Heterogeneity. In reality, structure is frequently heterogeneous. For example, if colloidal crystals have been produced by means of nanotechnology, it must be assumed that the material is not perfect. Thus it is of some importance to describe the deviation of the individual sample from the ideal material. For such purposes scattering methods are frequently employed and the scattering patterns are *qualitatively* interpreted. Nevertheless, the mechanisms of structure formation remain obscured as long as the amount of heterogeneity cannot be determined *quantitatively* during the structure formation process.

Different kinds of heterogeneity can be imagined. In the most simple case only a few differing structural entities are found to coexist without correlation inside the volume irradiated by the primary beam. In this case it is the task of the scientist to identify, to separate and to quantify the components of such a multimodal structure. In an extreme case heterogeneity may even result in a fractal structure that can no longer be analyzed by the classical methods of materials science.

Polydispersity. Quite frequently many *different but similar* structural entities can be found in a material. This is the common notion of polydispersity. Thus polydispersity means that every structural unit in the sample can be generated by compression or expansion (dilation) from a template. This building principle is mathematically governed by the Mellin convolution [2], which generates the observed structure from the template structure and its size distribution. The determination of the latter is a major goal in the field of materials science. Considering the simple case of pure particle scattering, the searched size distribution is the particle dimension distribution [3]. If, for example, the studied particles are spheres, the number distribution of sphere diameters would be of interest, and the material would advantageously be characterized by the mean diameter and the variance of the sphere diameters. Moreover, even a value describing the skewness of the sphere diameter distribution may become important in order to understand property variations of different materials.

1.2 Distribution Functions and Physical Parameters

A general principle is governing the relation between physical parameters and underlying distribution functions. Its paramount importance in the field of soft condensed matter originates from the importance of polydispersity in this field. Let us recall the principle by resorting to a very basic example: molecular mass distributions of polymers and the related characteristic parameters.

1.2.1 The Number Molecular Mass Distribution

In the basic molecular mass distribution, $N(M)$, the number N of molecules in a sample is plotted vs. their molecular mass, M . Figure 1.2 presents a sketch of a

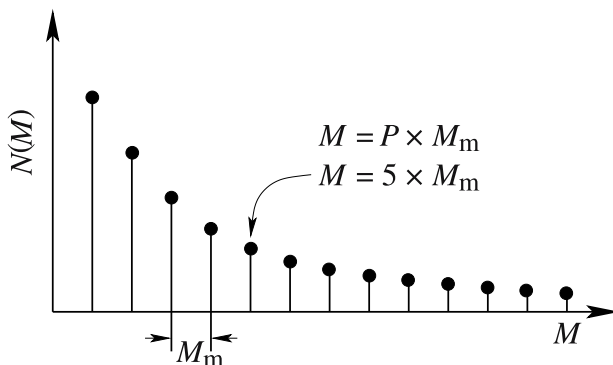


Figure 1.2. A number molecular mass distribution $N(M)$ of an ideal chain polymer. $N(M)$ is defined for integer multiples of M_m , the monomer mass. The integer factor, P , is called the degree of polymerization

molecular mass distribution. For ideal chains the distribution is a discrete function which is only defined for integer multiples of the monomer mass, M_m . The function is called the *number* molecular mass distribution, because it exhibits the number of molecules with a certain molecular weight M .

The function $N(M)$ can be considered a continuous function, if the average molecular weight of the chains is high enough. In this case we draw a continuous line through the points in Fig. 1.2.

It is reasonable to normalize $N(M)$ with respect to the total number of molecules in the sample

$$n(M) = N(M) / \int_0^{\infty} N(M) dM. \quad (1.1)$$

Now the function displays the number fraction of molecules with a certain molecular mass. Its integral is 1 by definition. Nevertheless, we still call it the number molecular weight distribution because the factor $\int N(M) dM$ is nothing but a constant.

1.2.2 The Number Average Molecular Mass

The obvious definition of the number average, M_n , of the distribution is the position on the M -axis that divides the area under the $n(M)$ -curve in equal parts (cf. Fig. 1.3). Because of the fact that $n(M)$ is normalized to 1, each of the subareas is equal to 0.5. As 50% of all the molecules are shorter than M_n , the other 50% are longer than M_n . Bearing in mind the normalization, the number average molecular mass is

$$M_n = \int_0^{\infty} M n(M) dM. \quad (1.2)$$

This equation is, as well, the definition of the mean (cf. ABRAMOWITZ [4] chap. 26) – the first moment of the distribution $n(M)$ about origin. In fact, with respect to a

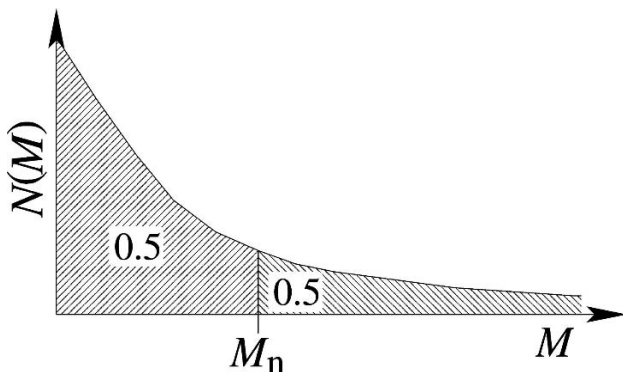


Figure 1.3. The number average molecular mass, M_n , is the position that divides the area under the corresponding distribution in equal parts

normalized distribution ($\int n(M) dM = 1$) the mean is the *center of gravity* of the distribution.

In order to describe the discussed distribution function, three characteristic parameters are used in polymer science. They are named number average¹, weight average (M_w), and centrifuge average (M_z)

$$M_n = \frac{\int M^1 n(M) dM}{\int M^0 n(M) dM} \quad (1.3)$$

$$M_w = \frac{\int M^2 n(M) dM}{\int M^1 n(M) dM} \quad (1.4)$$

$$M_z = \frac{\int M^3 n(M) dM}{\int M^2 n(M) dM} \quad (1.5)$$

This series of equations demonstrates a general principle in physics, namely how measurable materials parameters are generated from moments of the related distribution function.

1.3 Moments

The i -th *moment* (about origin) of a distribution $h(x)$ is defined by

$$\mu'_i(h) = \int x^i h(x) dx \quad (1.6)$$

(ABRAMOWITZ [4] chap. 26). We have demonstrated that the structure parameters of a polydisperse structure are closely related to these moments. $\mu'_0(h)$ is the norm

¹This is the center of gravity of the distribution $n(M)$.

and $m(h) := \mu'_1(h)$ the mean of the distribution on which the definition of *central* moments

$$\mu_i(h) := \int (x - m(h))^i dx \quad (1.7)$$

is based. As a measure of distribution width it is common to report the variance

$$\sigma^2(h) := \mu_2(h) \quad (1.8)$$

or the standard deviation, $\sigma(h)$. $\mu_3(h)/\sigma^3(h)$ is known as skewness of the distribution (ABRAMOWITZ [4] chap. 26).

Application in the Field of Scattering. Let us consider two important distribution functions, $h_c(x)$ and $h_L(x)$. These functions shall describe the thicknesses of crystalline layers and the distances (long periods) between them, respectively. In this case we take into account polydispersity of the crystalline layers, if (at least) the two parameters \bar{d}_c and σ_c/\bar{d}_c are determined which are defined as the average thickness of the crystalline layers,

$$\bar{d}_c = \frac{\mu'_1(h_c)}{\mu'_0(h_c)},$$

and the relative standard deviation of the crystalline layer distribution,

$$\frac{\sigma_c}{\bar{d}_c} = \frac{\sigma(h_c)}{\bar{d}_c}.$$

In the classical treatment of the paracrystal, HOSEMANN [5] refers to the quantity σ_c/\bar{d}_c as “g-factor”.

If we knew that the long periods are varying from stack to stack, but not within one and the same stack, the quantities

$$\bar{L} = \frac{\mu'_1(h_L)}{\mu'_0(h_L)}$$

(average long period) and

$$\frac{\sigma_L}{\bar{L}} = \frac{\sigma(h_L)}{\bar{L}}$$

(relative standard deviation of the long periods, which is another HOSEMANN g-factor) describe the polydispersity of this material.

2 General Background

Interpretation of scattering data requires understanding of the general dimensions of the field and a general background of scattering theory which is reviewed in this chapter. Reference is given to textbooks and original work, where detailed discussion would extend beyond the scope of this book.

2.1 The Subareas of X-Ray Scattering

Scattering experiments are carried out in four different angular regions which will be frequently addressed in this book. In Table 2.1

the subareas are identified by the typical distance R between the sample and the detector. The wavelength selected for the example is close to the historical wavelength of an X-ray tube equipped with a copper anode (CuK_α radiation with $\lambda = 0.15418 \text{ nm}$).

Classical X-ray diffraction and scattering is carried out in the subarea of wide-angle X-ray scattering (WAXS). The corresponding scattering patterns yield information on the arrangement of polymer-chain segments (e.g., orientation of the amorphous phase, crystalline structure, size of crystals, crystal distortions, WAXS crystallinity).

The subarea of middle-angle X-ray scattering (MAXS) covers the characteristic scattering of liquid-crystalline structure and rigid-rod polymers.

In the small-angle X-ray scattering (SAXS) regime the typical nanostructures (in semicrystalline materials, thermoplastic elastomers) are observed. Because of the long distance between sample and detector time-resolved measurements can only be carried out at synchrotron radiation sources (Sect. 4.2.1.2).

Table 2.1. Subareas of scattering as a function of the sample–detector distance R assuming an X-ray wavelength of $\lambda \approx 0.15 \text{ nm}$

Subarea	R [m]	Focus
WAXS	0.05 – 0.2	arrangement of chain segments
MAXS	0.2 – 1	liquid-crystalline structure
SAXS	1 – 3	nanostructure 3 nm – 50 nm
USAXS	6 – 15	nanostructure 15 nm – 2 μm

The ultra small-angle X-ray scattering (USAXS) extends the accessible structure towards the micrometer range. Time-resolved measurements require a synchrotron beam that is intensified by an insertion device (Sect. 4.2.2).

2.2 X-Rays and Matter

2.2.1 General

X-rays are electromagnetic radiation with short wavelengths of about 0.01 to 10 nm. $\lambda \approx 0.15$ nm is the typical wavelength for the study of soft condensed matter. Whenever X-rays are interacting with matter, their main partners are the electrons in the studied sample. Thus X-ray scattering is probing the distribution of electron density, $\rho(\mathbf{r})$, inside the material.

As scattering intensity is computed from $\rho(\mathbf{r})$ in this book, the symbol $\rho(\mathbf{r})$ has two different meanings. Only in the field of WAXS it is identical to the plain *electron density*. However, in the area of SAXS it indicates the *electron density difference*¹, i.e., the deviation of the local electron density from the average electron density $\langle \rho(\mathbf{r}) \rangle_V$ in the irradiated volume V .

Electron Density Computation. The average² electron density of a material or of a specific phase within a material,

$$\rho = Z_m \rho_m = N_A \frac{Z_M}{M_M} \rho_m, \quad (2.1)$$

is computed from the respective average mass density, ρ_m , by multiplication with the “number of electrons per gram”, Z_m , given by Avogadro’s number, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$, the number of electrons per molecule or monomer unit, Z_M , and the molecular weight of molecule or monomer unit, M_M .

For polybutadiene with the chemical composition C_4H_6 we have a molecular weight of $M_M = 54.092 \text{ g/mol}$ and $Z_M = 30 \text{ e.u.}$ (electrons in “electron units”). If the mass density is $\rho_m = 0.90 \text{ g/cm}^3$, the electron density becomes $\rho = 300.6 \text{ e.u./nm}^3$.

2.2.2 Polarization

Polarization is a relevant issue, because we are dealing with transversal waves (GUINIER [6], p. 10-11). Polarization correction should be carried out for MAXS and WAXS data. It is less important for SAXS and USAXS patterns. In particular, if synchrotron radiation is used, the polarization correction is quite involved and based on the degree of polarization. For the purpose of reliable correction it is thus recommended to let a polarization monitor measure the actual degree of synchrotron beam polarization.

¹In many publications the electron density difference is addressed as $\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \langle \rho(\mathbf{r}) \rangle_V$.

²*Exercise:* Compute the average electron density $\langle \rho \rangle_V$ of a sample from pure poly(ethylene terephthalate) (PET) with a mass density of 1.38 g/cm^3 . The chemical formula of PET is $\text{C}_{10}\text{H}_8\text{O}_4$. Because PET is most probably in the semicrystalline state, it makes sense to stress that the computed electron density is a volume average $\langle \rangle_V$.