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.

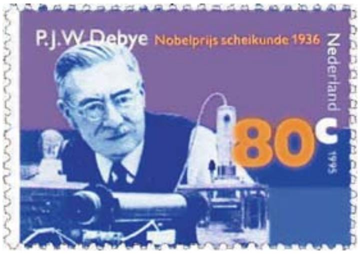

Figure 1.1. P. Debye (1884-1966) and his small-angle light-scattering device on a Dutch stamp

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 arrangement 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

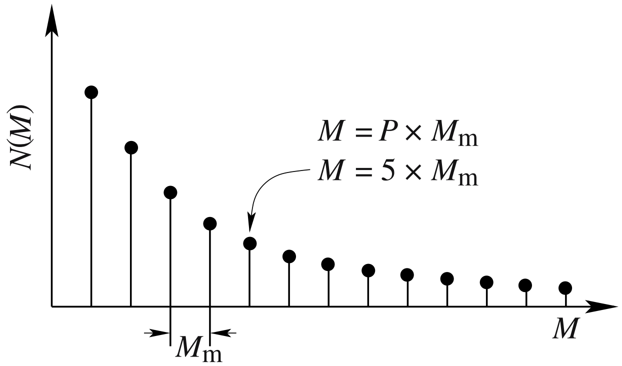

Figure 1.2. A number molecular mass distribution $N(M)$ of an ideal chain polymer. $N(M)$ is defined for integer multiples of M_m, the monomer mass. The integer factor, P, is called the degree of polymerization

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

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

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

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

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

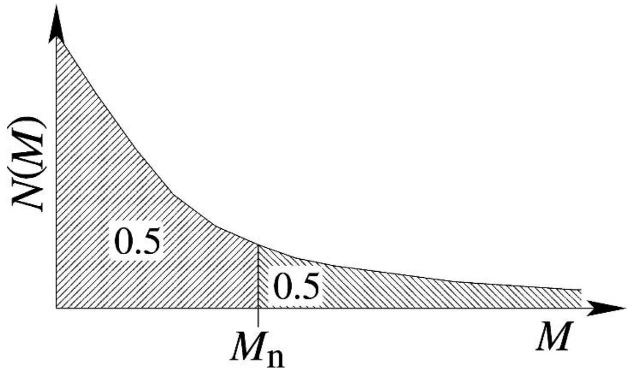

Figure 1.3. The number average molecular mass, M_n, is the position that divides the area under the corresponding distribution in equal parts

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 average[1], weight average (M_w), and centrifuge average (M_z)

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

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

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

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

$$\mu_i'(h) = \int x^i\, h(x)\,dx \tag{1.6}$$

(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

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[1] This 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

$$\mu_i(h) := \int (x - m(h))^i \, dx \tag{1.7}$$

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

$$\sigma^2(h) := \mu_2(h) \tag{1.8}$$

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 $\sigma_c/\bar{d}_c$ 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 $\sigma_c/\bar{d}_c$ 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.