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Analysis of scattering from polydisperse structure using Mellin convolution

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This study extends a mathematical concept for the description of heterogeneity and polydispersity in the structure of materials to multiple dimensions. In one dimension, the description of heterogeneity by means of Mellin convolution is well known. In several papers by the author, the method has been applied to the analysis of data from materials with one-dimensional structure (layer stacks or fibrils along their principal axis). According to this concept, heterogeneous structures built from polydisperse ensembles of structural units are advantageously described by the Mellin convolution of a representative template structure with the size distribution of the templates. Hence, the polydisperse ensemble of similar structural units is generated by superposition of dilated templates. This approach is particularly attractive considering the advantageous mathematical properties enjoyed by the Mellin convolution. Thus, average particle size, and width and skewness of the particle size distribution can be determined from scattering data without the need to model the size distributions themselves. The present theoretical treatment demonstrates that the concept is generally extensible to dilation in multiple dimensions. Moreover, in an analogous manner, a representative cluster of correlated particles (*e.g.* layer stacks or microfibrils) can be considered as a template on a higher level. Polydispersity of such clusters is, again, described by subjecting the template structure to the generalized Mellin convolution. The proposed theory leads to a simple pathway for the quantitative determination of polydispersity and heterogeneity parameters. Consistency with the established theoretical approach of polydispersity in scattering theory is demonstrated. The method is applied to the best advantage in the field of soft condensed matter when anisotropic nanostructured materials are to be characterized by means of small-angle scattering (SAXS, USAXS, SANS).

1. Introduction

While a cohesive theory of scattering from polydisperse structure remains elusive, the mathematical concept of diffraction is well established: space is filled with matter by arrangement of identical structural units on the places defined by an abstract lattice. Mathematically, this procedure is realised by the translation operation inherent to the convolution integral. The result is an ideal lattice structure.

In a less ideal material, frequently many different but similar structural units can be found. This is the common notion of polydispersity (Higgins & Stein, 1978; Hosemann, 1950; Greschner, 1973; Glatter, 1980; Cohen & Thomas, 1987; Förster & Burger, 1998; Rieker *et al.*, 1999; Pedersen *et al.*, 2000; Keum *et al.*, 2005; Triolo *et al.*, 2005; Ruland & Smarsly, 2005). In the present work, polydispersity means that every structural unit in the sample is generated from a mean template by affine compression or expansion (dilatation). This building principle is mathematically governed by the Mellin convolution (*cf.* Appendix *A*), which splits the observed structure into a template structure and a size distribution. The determination of such 'domain' size distributions is a major goal in the area of materials science. Considering the more simple case of pure particle scattering, the sought size distribution is the particle dimension distribution (Fedorova & Schmidt, 1978). 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 parameter value describing the skewness of the sphere diameter distribution may become important in order to understand property variations in materials.

In experimental X-ray studies of special polymer materials, our group has been determining parameters of heterogeneous structure for several years. The corresponding methods are based on a simple concept of Mellin convolution theory valid in one dimension. Frequently, highly oriented materials have

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been investigated for which a one-dimensional sequence of lamellae (Stribeck *et al.*, 2003, 2004; Stribeck, 2004) or of domains in fibrils (Stribeck *et al.*, 1997) is described by a representative one-dimensional 'paracrystal'. Dilated images of such templates are considered to generate the observed heterogeneous structure. Moreover, the simple concept has been applied to experimental studies of isotropic lamellar systems (Stribeck, 1993*b*; Stribeck & Buchner, 1997; Flores *et al.*, 2001; Garcia-Gutierrez *et al.*, 2001; Wang *et al.*, 2002) or even to a material with diffuse particle scattering (Stribeck, 1999). In the present treatment, the concept is generalized to cover multi-dimensional multi-level dilation of a template structure. From the practical point of view, this generalization means that any reasonable kind of structure heterogeneity which may be detectable in anisotropic experimental scattering data can be described by the proposed general mathematical concept. An example is a complex nanostructure built from lamellae, in which both layer thickness and layer extension are polydisperse and, in addition, the 'clusters' of correlated lamellae themselves are only similar. The last-mentioned heterogeneity is identical to the classical notion of strain broadening. An approximative solution of this problem is the well known Warren–Averbach method (Warren & Averbach, 1950) that is restricted to the description of small heterogeneity.

In the theory of diffraction, heterogeneity was first discussed by Dehlinger & Kochendörfer (1939) and Kochendörfer (1944). As Kochendörfer was studying local tension in rolled copper material, he introduced ensembles of only similar lattices in order to describe the result of varying expansion or compression of crystal grains on the diffraction pattern. At the same time, Hosemann (1939) addressed the effect of polydispersity on the particle scattering of spheres. Besides Glatter's method of direct inversion (Glatter, 1980), there have been several proposals to solve the problem analytically (Roess, 1946; Greschner, 1973; Schmidt & Brill, 1967). Before Stribeck (1993*b*) studied the mathematical properties of the related integral transform in the special case of a one-dimensional two-phase structure, Roess (1946) and Schmidt & Brill (1967) came rather close to a Mellin convolution approach. Subsequently, several suggestions concerning a method to determine particle size distributions from scattering data were published, which were reviewed by Fedorova & Schmidt (1978) before they proposed an advanced method. Nevertheless, their proposed generalization was restricted to particles with a special contrast profile; thus, the goal of a cohesive theory of polydispersity was not reached.

2. Theory

2.1. The scattering of different similar 'particles'

Let us start with a generalization of the treatment on polydispersity given by Schmidt & Brill (1967). The sample contains an ensemble of independently scattering structural units which are similar to one another, *i.e.* they can be generated by scaling a template which is characterized by its excess electron density $\tilde{\rho}_{\mathrm{T}}(\mathbf{r}) = \rho_{\mathrm{T}}(\mathbf{r}) - \langle\rho\rangle_V$. Here $\rho_{\mathrm{T}}(\mathbf{r})$ is the density distribution of the template and $\langle\rho\rangle_V$ is the average density of the sample averaged over the volume V that is irradiated by the primary beam. The template may be any structure, in particular some single particle or an ensemble of particles with correlation among them. According to basic scattering theory, the scattering pattern of the template may be constructed in two steps. In the first step, its correlation function $\tilde{\rho}_{\mathrm{T}}^{*2}(\mathbf{r})$ is computed. The autocorrelation, because of its definition,

$$\begin{aligned} h^{*2}(\mathbf{r}) &= \int\limits_{-\infty}^{\infty} h(\mathbf{y})\, h(\mathbf{r} + \mathbf{y})\, \mathrm{d}^3 y \\ &= h(\mathbf{r}) * h(-\mathbf{r}), \end{aligned}$$

can be determined analytically by simple geometrical reasoning (*e.g.* Schmidt, 1995) for many particles with homogeneous density. The operator $*$ in the second line denotes the ordinary convolution. In the second step, the scattering intensity

$$\begin{aligned} I_{\mathrm{T}}(\mathbf{s}) &= \int\limits_{-\infty}^{\infty} \tilde{\rho}_{\mathrm{T}}^{*2}(\mathbf{r})\, \exp(-2\pi i\, \mathbf{rs})\, \mathrm{d}^3 r \\ &:= \mathcal{F}\big[\tilde{\rho}_{\mathrm{T}}^{*2}(\mathbf{r})\big](\mathbf{s}) \end{aligned}$$

is computed by Fourier transformation $\mathcal{F}()$ of $\tilde{\rho}_{\mathrm{T}}^{*2}(\mathbf{r})$. Let us now consider a structural unit

$$\tilde{\rho}_u(\mathbf{r}) = \tilde{\rho}_{\mathrm{T}}\left(\frac{\mathbf{r}}{\mathbf{a}}\right) \tag{1}$$

which is dilated by a scaling vector $\mathbf{a} \in \mathbb{R}^3_+$ with respect to the template. In Cartesian coordinates $\mathbf{a} = (a_1, a_2, a_3)$, this means that all components $a_i \in (0, \infty)$ are positive, and $\mathbf{r}/\mathbf{a} := (r_1/a_1,\, r_2/a_2,\, r_3/a_3)$. Thus we follow the notation conventions of Brychkov *et al.* (1992) (*cf.* Appendix *A*).

The deduction of the corresponding scattering intensity does not require indirect reasoning (*cf.* Guinier & Fournet, 1955; Glatter & Kratky, 1982), but is readily established utilizing two basic theorems of Fourier transformation theory concerning dilatation {in one dimension: $\mathcal{F}[a\,H(as)] = h(r/a)$} and convolution $[\mathcal{F}(g * h) = G\,H]$. Thus, in Cartesian coordinates and with the definition $\mathbf{a} \cdot \mathbf{s} := (a_1 s_1, a_2 s_s, a_3 s_3) \in \mathbb{R}^3$,

$$I_u(\mathbf{s}) = a_1^2\, a_2^2\, a_3^2\, I_{\mathrm{T}}(\mathbf{a} \cdot \mathbf{s}) \tag{2}$$

is the scattering intensity of the dilated template. The template may as well be one of the simple homogeneous particles discussed in text books. In particular for the isotropic case with $a_i = a\, \forall\, i \in [1, 2, 3]$, we obtain the well known result (Schmidt & Brill, 1967)

$$I_u(\mathbf{s}) = a^6\, I_{\mathrm{T}}(a\mathbf{s}), \tag{3}$$

which is frequently cited when the meaning of the Guinier radius of a polydisperse material is discussed by referring to the unpleasant distorting multiplication by a high power of the scaling factor. Also easily established are the less distorting effects of uniaxial dilation ($a_1 = a_2 = 1$, $a_3 = a$) and lateral dilation ($a_1 = a_2 = a$, $a_3 = 1$) on the scattering intensity of the dilated particle. The cases of isotropic, lateral and uniaxial dilatation are the most important ones in the area of polydisperse structure.

2.2. Scattering and correlation function of the polydisperse material

There shall be no correlation among different structural units. Thus, the observed correlation function of the material,

$$\tilde{\rho}^{*2}(\mathbf{r}) = \int\limits_{\mathbb{R}^3_+} h_H(\mathbf{a})\, \tilde{\rho}_{\mathrm{T}}^{*2}\left(\frac{\mathbf{r}}{\mathbf{a}}\right) \mathrm{d}^3 a, \qquad (4)$$

is a superposition of dilated correlation functions with $h_H(\mathbf{a})$ being the size distribution of the structural units. Determination of this size distribution is the aim of research in the area of polydisperse materials.

Equation (4) is valid if upon dilatation the contrast is conserved. This means that the maximum and minimum excess densities are identical in every dilated image of the template. In a different subarea of polydispersity, one would assume that every 'particle' has the same excess mass (as in the case of monodisperse polymer chains in random coil conformation which are subjected to varying dilation). In this case, dilatation invariance of the mass is introduced by writing

$$\tilde{\rho}^{*2}(\mathbf{r}) = \int\limits_{\mathbb{R}^3_+} h_H(\mathbf{a})\, \tilde{\rho}_{\mathrm{T}}^{*2}\left(\frac{\mathbf{r}}{\mathbf{a}}\right) \frac{\mathrm{d}^3 a}{\mathbf{a}\cdot\mathbf{a}}, \qquad (5)$$

with, in Cartesian coordinates,

$$\frac{\mathrm{d}^3 a}{\mathbf{a}\cdot\mathbf{a}} = \frac{\mathrm{d}a_1}{a_1^2}\,\frac{\mathrm{d}a_2}{a_2^2}\,\frac{\mathrm{d}a_3}{a_3^2}.$$

From the observed correlation function, the scattering pattern is obtained by Fourier transformation. Obviously for both equation (4) and equation (5) the Fourier transformation will only act on the correlation function of the template, and with equation (2) we obtain the expected result

$$I(\mathbf{s}) = \int\limits_{\mathbb{R}^3_+} a_1^2\, a_2^2\, a_3^2\, h_H(\mathbf{a})\, I_{\mathrm{T}}(\mathbf{a}\cdot\mathbf{s})\, \mathrm{d}^3 a \qquad (6)$$

in Cartesian coordinates, assuming conservation of contrast.

Up to now all particles are considered to be perfectly oriented. High but imperfect orientation is not unusual in fibres or in injection-moulded materials. In this case, the remnant effect of misorientation can be eliminated by application of the Ruland streak method (Ruland, 1969, 1968; Perret & Ruland, 1969, 1970; Thünemann & Ruland, 2000).

Isotropy of the scattering pattern or even the template structure,

$$\tilde{\rho}^{*2}(r) = \int\limits_0^\infty h_H(a)\, \tilde{\rho}_{\mathrm{T}}^{*2}\left(\frac{r}{a}\right) \mathrm{d}a, \qquad (7)$$

results in considerable simplification. Nevertheless, even in the anisotropic case, the problem is generally simplified for practical reasons. If the template is not isotropic, it is most frequently assumed to show uniaxial symmetry (lamella, cylinder, rod). Similarly, the polydispersity is frequently discussed in terms of a 'length variation' which is independent of 'diameter variation'. This means that for the anisotropic case, $h_H(\mathbf{a}) = h_{H12}(a_{12})\, h_{H3}(a_3)$ decomposes into a product of simple functions in cylindrical coordinates $[a_{12} = (a_1^2 + a_2^2)^{1/2},\ r_{12} = (r_1^2 + r_2^2)^{1/2}]$. Finally, if the template structure $\tilde{\rho}_{\mathrm{T}}^{*2}(\mathbf{r}/\mathbf{a}) = \tilde{\rho}_{\mathrm{T}12}^{*2}(r_{12}/a_{12})\, \tilde{\rho}_{\mathrm{T}3}^{*2}(r_3/a_3)$ is suitably chosen,

$$\tilde{\rho}^{*2}(r_1 2, r_3) = \int\limits_0^\infty h_{H12}(a_{12})\, \tilde{\rho}_{\mathrm{T}12}^{*2}\left(\frac{r_{12}}{a_{12}}\right) \mathrm{d}a_{12} \times \int\limits_0^\infty h_{H3}(a_3)\, \tilde{\rho}_{\mathrm{T}3}^{*2}\left(\frac{r_3}{a_3}\right) \mathrm{d}a_3$$

is obtained. In this or a similar manner, polydispersity of anisotropic materials can frequently be split and treated as a set of quasi one-dimensional problems.

2.3. The chord distribution function of the polydisperse material

The notion of a chord length distribution (Méring & Tchoubar-Vallat, 1965, 1966, 1968; Tchoubar & Méring, 1969), an interface distribution function (IDF) (Ruland, 1977) or a multi-dimensional chord distribution function (CDF) (Stribeck, 2001), is commonly related to the special case of a two-phase system. Nevertheless, by application of the corresponding mathematical algorithms to a deliberate structure, the concept is readily extended.

The CDF

$$z(\mathbf{r}) = -\,[\nabla\tilde{\rho}(\mathbf{r})]^{*2} \qquad (8)$$

$$= -\,\Delta\big[\tilde{\rho}^{*2}(\mathbf{r})\big] \qquad (9)$$

$$= -\,\mathcal{F}\big[4\pi^2 s^2\, I(\mathbf{s})\big] \qquad (10)$$

is generally defined by the negative autocorrelation of the gradient of the excess electron density. As stated in the middle equation, it also represents the negative Laplacian of the correlation function. Finally, its close relation to the measured scattering pattern is established (Stribeck, 2001) by the Fourier-transform derivation theorem.

With equation (4) it follows that

$$z(\mathbf{r}) = \int\limits_{\mathbb{R}^3_+} h_H(\mathbf{a})\, \frac{1}{\mathbf{a}}\, z_{\mathrm{T}}\left(\frac{\mathbf{r}}{\mathbf{a}}\right) \frac{\mathrm{d}^3 a}{\mathbf{a}}. \qquad (11)$$

This is a genuine Mellin convolution of the size distribution $h_H(\mathbf{a})$ and a template function whose norm

$$\int \frac{1}{\mathbf{a}}\, z_{\mathrm{T}}\left(\frac{\mathbf{r}}{\mathbf{a}}\right) \mathrm{d}^3 r = c \qquad (12)$$

does not depend on the dilatation vector $\mathbf{a}$. If here we choose $c = 1$, the meaning of $\mathbf{a} = \mathbf{l}_{\mathrm{p}}$ as the general and three-dimensional equivalent to the common average segment length ℓ_{p} of two-phase materials becomes obvious.

In order both to verify this supposition and to relate equation (11) to existing theory, we consider the isotropic case

$$z(r) = \int\limits_0^\infty h_H(a)\,\frac{1}{a}\,z_\mathrm{T}\!\left(\frac{r}{a}\right)\frac{\mathrm{d}a}{a} \qquad (13)$$

with an integral chord length distribution $z_\mathrm{T}(r)$ of the template, and introduce the ordinary reduced radial correlation function $\gamma(r)$,

$$-z(r) = Q\,\gamma''(r) = Q\int\limits_0^\infty h_H(a)\,\frac{1}{a}\,\gamma''_\mathrm{T}\!\left(\frac{r}{a}\right)\frac{\mathrm{d}a}{a}, \qquad (14)$$

with $Q = \tilde{\rho}^{*2}(0)$ representing the scattering power. We map $a \longmapsto \ell_\mathrm{p}$ and identify

$$-\frac{1}{\ell_\mathrm{p}}\,\gamma''_\mathrm{T}\!\left(\frac{\ell}{\ell_\mathrm{p}}\right) = g_\mathrm{T}(\ell) \qquad (15)$$

as the renormalized chord length distribution (Porod, 1982). It is renormalized because $\int g_\mathrm{T}(\ell)\,\mathrm{d}\ell = 1$ is no longer a function of ℓ_p. Such renormalization is generally required in order to eliminate any dependency of the norm of the template function from the scaling vector $\mathbf{a}$.

Finally

$$z(\mathbf{r}) = \int\limits_{\mathbb{R}^3_+} h_H(\mathbf{a})\,g_\mathrm{T}\!\left(\frac{\mathbf{r}}{\mathbf{a}}\right)\frac{\mathrm{d}^3a}{\mathbf{a}}, \qquad (16)$$

the observed CDF, is a multi-dimensional Mellin convolution. It combines the generalized and normalized chord distribution $g_\mathrm{T}(\mathbf{r})$ with the size distribution $h_H(\mathbf{a})$ of the structural units.

After Fourier transformation of equation (16), we obtain for the scattering pattern, in Cartesian coordinates,

$$4\pi^2 s^2\,I(\mathbf{s}) = -\int\limits_{\mathbb{R}^3_+} h_H(\mathbf{a})\,a_1a_2a_3\,G_\mathrm{T}(\mathbf{a}\cdot\mathbf{s})\,\frac{\mathrm{d}a_1}{a_1}\frac{\mathrm{d}a_2}{a_2}\frac{\mathrm{d}a_3}{a_3}, \qquad (17)$$

which is no longer a Mellin convolution.

2.3.1. Discussion. It has been demonstrated that the CDF is advantageously utilized if polydispersity is accounting for a considerable effect. The main advantage is its plain relation to the size distribution. A second advantage arises from the simple mathematical relation (15) that permits computation of segment distributions $g_\mathrm{T}(\mathbf{r})$ for simple and more complicated geometrical bodies which are of practical interest (spheres, cylinders, *etc.*). Analytical results are reported in the literature.

Although the correlation function according to equation (7) seems not to be far from a genuine Mellin convolution, the same problem as with the scattering intensity becomes obvious upon renormalization of the template function: finally, the contributions of the largest 'particles' are governing not only the scattering intensity, but also the correlation function. The reason is the assumed conservation of the contrast amplitude of the structural units. This overemphasis is removed by employing the gradient operator, as it is sensing the differential of the contrast.

2.4. A general pathway for the analysis of polydisperse structure

2.4.1. Outline. Why should it be advantageous to describe polydispersity by Mellin convolution? The reason is the simplicity by which each moment

$$\mu'_i(f \odot h) = \mu'_i(f)\,\mu'_i(h) \qquad (18)$$

of the Mellin convoluted function $f \odot h$ is expressed by the moments of its partner functions f and h (Stribeck, 1993*b*). Obviously this property indicates a straightforward strategy for the determination of the structural parameters which are describing the polydispersity of the sample.

Provided that we have either measured the scattering intensity of a monodisperse sample or that the template shape is known, we can compute first $g_\mathrm{T}(\mathbf{r})$, and, second its series of moments, either by numerical integration or by analytical mathematics, respectively. This list of numbers is set aside for later use.

After measuring the scattering intensity of a polydisperse sample, its CDF $z(\mathbf{r})$ is computed (Stribeck, 2001). Then the moments of $z(\mathbf{r})$ are determined by numerical integration. Equation (18) shows how the moments of the size distribution are computed by simple arithmetic. Finally, from these moments the structure parameters of heterogeneity are readily assessed (Stribeck, 1999).

2.4.2. Analytical determination of the template function. For two-phase materials, simple geometrical reasoning based on the 'particle-ghost construction method' (Guinier & Fournet, 1955, pp. 12–19; Brumberger, 1995, pp. 16–20) results in the analytical form of the correlation function of the representative particle. Several solutions concerning spheres, hollow spheres, circles and cylinders can be found in the literature (Letcher & Schmidt, 1966; Schmidt, 1967; Fedorova & Schmidt, 1978; Jánosi, 1986), and a comprehensive collection is presented by Pedersen (2002). For a more general material, the solution may require more involved reasoning. In this case, equation (15) or an analogon adapted for two- or one-dimensional isotropy is used to compute the template function $g_\mathrm{T}(r)$.

2.4.3. Particle clusters and cumulated polydispersity. If no correlations are observed among the individual particles from the polydisperse ensemble, this paragraph may be skipped. Otherwise, the correlations have to be modelled, resulting in the mathematical description of a complex structural unit. In this paper, such a complex structural unit is addressed as a 'cluster', not in the restricting sense of coagulated particles, but in the general sense of an ensemble of correlated particles. For poor correlation, short-range-order models may suffice, which are generated using the principle developed by Zernike & Prins (1927) and refined by Hermans (1944) and Hosemann (1949). For highly ordered materials, which are of interest in nanotechnology, appropriate models are presently constructed by Ruland and Burger (Ruland & Smarsly, 2002, 2004, 2005; Smarsly *et al.*, 2005; Gelfer *et al.*, 2004; Chen *et al.*, 2005).

If, in a kind of cumulated polydispersity, the particle clusters themselves are not identical but similar only, the ultimately observed structure is, again, described by a Mellin convolution. In this case, the partner functions are the cluster template function and the cluster size distribution. At this point it is, in principle, possible to carry out the Mellin convolution numerically using a model cluster size distribution (Stribeck, 1993*a*,*b*) in order to consider the effect of heterogeneity on the scattering data.

2.4.4. Determination of polydispersity. In order to determine heterogeneity or polydispersity, it is not necessary to model the size distribution if the template function of the representative structural unit is known analytically. Then the series of moments $\mu_i'(g_{\rm T})$ of $g_{\rm T}$ can be computed (Stribeck, 1999). This is conveniently achieved by programming the Mellin transformation in *Mathematica* (Wolfram Research, Champaign). Thereafter, the moments $\mu_i'(z)$ of the experimental CDF are numerically determined and equation (18) is used to compute the corresponding moments of the dilation distribution $h_H(r)$ and related structural parameters (for an example, *cf.* Stribeck, 1999). The most simple case for the application of this method is the polydispersity introduced by isotropic dilatation in isotropic scattering curves.

3. Conclusion

The presented considerations demonstrate how the Mellin convolution approach can be utilized in order analytically to describe and to analyse polydispersity and heterogeneity in general scattering data. This approach adds a new tool to the toolbox of scattering theory. An analytical method based on the Mellin convolution can easily handle particle scattering. Moreover, even more complex cases appear to be manageable. An example is the description and study of anisotropic scattering patterns with preferred orientation and anisotropic dilatation.

The advantage of the deduced method is that no modelling of the size distribution (of particles or clusters, respectively) is required. The general approach is based on the same set of assumptions as the established Glatter method (Glatter, 1980) for the analysis of isotropic scattering curves from polydisperse particle systems. If raw isotropic scattering curves can be directly analysed, Glatter's method is to be preferred. On the other hand, the proposed analysis involves little extra effort if a stepwise analysis is required because the scattering pattern of a non-ideal two-phase system must be pre-treated in order first to compute the scattering pattern of the ideal two-phase system and, second, to check the CDF for correlations among the particles. For the case of pure particle scattering, this has been demonstrated in previous experimental work (Stribeck, 1999). It appears worth mentioning that the directly measured scattering images are not analysed. Instead, the analysed CDF must be computed. This is similar to the situation in tomography, where it is not the absorption images that are analysed, but a three-dimensional image that has been computed from the absorption images. Only complete low-noise scattering patterns can be converted into a CDF. Completeness means that reciprocal-space data must be available for every direction, at least up to a scattering vector $s_{\max}$ that is in the region of un-modulated decay of Porod's law. Computation is carried out in several automated steps (Stribeck, 2001). In particular, the step of background determination by low-pass filtering of the scattering pattern is critical, because the filter function cannot be founded on analytical mathematics. It is only adjusted in such a way that the resulting CDF reproduces several simple model data well (Stribeck, 2001).

On the basis of the deduced theoretical Mellin convolution approach, it may become possible to tackle another question of fundamental interest, namely what is happening both to the scattering and to the structure if the scaling distribution becomes broader and broader. Obviously the structural units can only coexist side-by-side in the irradiated volume as long as the support of the scaling distribution is limited. Thus an infinitely broad scaling-factor distribution should force the structure to become fractal.

APPENDIX *A*
Mellin convolution and scattering theory

A1. Mellin convolution

A1.1. Definition. The integral equations of polydispersity, (4) and (5), are closely related to Mellin convolution. In the multidimensional case it is defined as (Brychkov *et al.*, 1992; Sneddon, 1994)

$$f(\mathbf{r}) = \int\limits_0^\infty h(\mathbf{r}) f_{\rm T}\left(\frac{\mathbf{r}}{\mathbf{x}}\right) \frac{{\rm d}^n x}{\mathbf{x}} \qquad (19)$$

$$:= h(\mathbf{r}) \odot f_{\rm T}(\mathbf{r}), \qquad (20)$$

with $\mathbf{x} \in \mathbb{R}_+^n$. The Mellin convolution shall be represented by the symbol $\odot$. Most frequently, the Mellin convolution is used in one dimension (Titchmarsh, 1948, p. 53; Marichev, 1983; Feigin & Svergun, 1987, p. 304):

$$f(r) = \int\limits_0^\infty h(x) f_{\rm T}\left(\frac{r}{x}\right) \frac{{\rm d}x}{x}. \qquad (21)$$

The Mellin convolution describes the uncorrelated superposition of similar functions derived from a template $f_{\rm T}$ under the assumption that the norm of the dilated images of $f_{\rm T}$ is conserved (Stribeck, 1993*b*). In measure theory, the term ${\rm d}x/x$ is named the multiplicative Haar measure. It is invariant under dilatation $x \longmapsto ax$, so that ${\rm d}(ax)/ax = {\rm d}x/x$. The relation of the Mellin convolution to the ordinary convolution is readily established by substituting the variables by their logarithms.

A1.2. Consistency considerations. In the established scattering theory, one-dimensional particle size distributions are not modelled by the Mellin convolution, but by the ordinary convolution (Hermans, 1944; Hosemann, 1949). If the Mellin convolution is consistent with the established theory, a neutral element $\delta(x-1)$ for the Mellin convolution must exist with $\delta(x)$ being the Dirac delta distribution. This means that the equation

$$h(x) = h(x) \odot \delta(x-1) \qquad (22)$$

must hold. The validity of this equation is obvious because of the dilatation invariance of Mellin convolution and can be verified by Mellin transformation using the identity $\mathcal{M}[\delta(x-a)] = a^{s-1}$. For materials science, this means that, *e.g.* a layer thickness distribution $h(x)$ can as well be thought of as a Mellin convolution of a representative unit lamella $\delta(x-1)$ with $h(x)$.

With respect to the Fourier transformation, the Mellin convolution is also consistent with scattering theory. The polydispersity relation is conserved since only one of the partner functions is affected by the Fourier transformation.

A2. Mellin transformation and moments

The function

$$\tilde{H}(s) = \int_0^\infty x^s\, h(x)\, \frac{\mathrm{d}x}{x} \tag{23}$$

$$:= \mathcal{M}[h(x)] \tag{24}$$

is the Mellin transform of $h(x)$. The Mellin transform is the integration using a kernel x^s with respect to the multiplicative Haar measure. Its inverse transform is defined by

$$h(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \tilde{H}(s)\, x^{-s}\, \mathrm{d}s \tag{25}$$

$$:= \mathcal{M}^{-1}\big[\tilde{H}(s)\big]. \tag{26}$$

Equation (23) shows that the Mellin transform is an extension to the definition of moments (Abramowitz & Stegun, 1968, ch. 26),

$$\mu_i'(h) = \int x^i\, h(x)\, \mathrm{d}x, \tag{27}$$

of a distribution $h(x)$. The structure parameters of a polydisperse structure that concern the engineer are closely related to these moments. $\mu_0'(h)$ is the norm and $m(h) := \mu_1'(h)$ is the mean of the distribution on which the definition of central moments,

$$\mu_i(h) := \int [x - m(h)]^i\, \mathrm{d}x, \tag{28}$$

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

$$\sigma^2(h) := \mu_2(h), \tag{29}$$

or the standard deviation $\sigma(h)$. $\mu_3(h)/\sigma^3(h)$ is the skewness of the distribution (Abramowitz & Stegun, 1968, ch. 26).

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