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Small-Angle X-ray Scattering Functions in the Vicinity of Zero Scattering Angle with an Application to Polymer Blends

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ABSTRACT: The small-angle X-ray scattering (SAXS) of isotropic scatterers is studied in the region near zero scattering angles, where void scattering may contribute to the scattering power Q. Since Q is evaluated by an integration, the corresponding integrands $I_1(s)$ (for point collimation) and $\tilde{I}_1(s)$ (for slit focus) as well as the relations between them are studied. The properties of both their moments and their Taylor series expansions are discussed. For a lamellar two-phase system, which is frequently observed in semicrystalline or microphase-separated polymers, analytical equations are presented. They can help (1) to extrapolate $I_1(s)$ and $\tilde{I}_1(s)$ toward zero scattering angle, (2) to detect void scattering, and (3) to improve the modeling of the paracrystalline stack even in the case of considerable roughness of the layer surfaces. An example for a set of semicrystalline HDPE samples illustrates how to quantify void scattering and the effects of interfacial statistical structure.

Introduction

Many polymer samples exhibit an isotropic small-angle X-ray scattering (SAXS). If this curve can be ascribed to a two-phase system, the scattering power Q is given by a simple equation containing a few parameters of direct physical meaning. Q is evaluated by integration of one of the functions

$$I_1(s) = 2\pi s^2 I(s) \qquad (1)$$

or

$$\tilde{I}_1(s) = s\tilde{I}(s) \qquad (2)$$

where $s = (2/\lambda)\sin\theta$ is the magnitude of the scattering vector, $I(s)$ designates the absolute scattering intensity as measured with point focus, and $\tilde{I}(s)$ is the "slit-smeared" scattering intensity, measured, e.g., with a Kratky camera. [For ease of notation we write $I(s)$ and $\tilde{I}(s)$, where $I(s)/V$ and $\tilde{I}(s)/V$ would be more correct to write for the absolute intensities. Here V is the volume of the sample, which is irradiated by the primary beam.] Even for samples with fiber symmetry the scattering power is computed from $\tilde{I}_1(s)$ in the same manner, if the slit of the Kratky camera is oriented parallel to the fiber direction (Heikens[1]). The subject of this paper is the study of these one-dimensional intensity functions in the vicinity of zero scattering angle. To call these functions "one-dimensional" ones is suggestive, since the invariant Q is evaluated by a one-dimensional integral

$$Q = \int_{-\infty}^{\infty} I_1(s)\,\mathrm{d}s = \pi \int_{-\infty}^{\infty} \tilde{I}_1(s)\,\mathrm{d}s \qquad (3)$$

In order calculate Q, the integrands in eq 3 must be extrapolated beyond the interval covered by the measured data. To extrapolate toward wide scattering angles for a two-phase microstructure, one generally fits the decay of the intensities ($I(s)$ or $\tilde{I}(s)$) to Porod's law (A_P/s^4 or $\tilde{A}_P/s^3$) and uses this law as an analytical continuation.[2] No theoretical treatment of the extrapolation of the integrands toward zero scattering angle has previously been presented, although the need for such an extrapolation was emphasized early in experimental studies (cf., e.g., Hermans et al.[3]). On the other hand $I_1(0)$ has been discussed by Zernike and Prins[4] as well as by Blundell.[5]

Theoretical Results of General Validity

In order not to distract the reader, mathematical development has been relegated to an appendix, where it is shown that with respect to the one-dimensional intensity functions slit smearing can be treated in terms of a Mellin convolution. By using its properties one finds (1) that slit smearing moves the center of gravity of $\tilde{I}_1(s)$ to $\pi/4$ times the center of gravity of the unsmeared curve, $I_1(s)$ (eq 18), (2) that there is a relation between the intercepts,

$$\tilde{I}_1(0) = {}^1/_2 I_1(0) \qquad (4)$$

and (3) that the Taylor series expansion of $\tilde{I}_1(s)$ is

$$\tilde{I}_1(s) = \frac{I_1(0)}{2} + \sum_{k=0}^{\infty} a_{2k+1}|s|^{2k+1} \qquad (5)$$

One-Dimensional Intensities for the Model of Stacked Layers

To gain more information about the shape of the one-dimensional intensity functions at small scattering angles, one needs to consider special models.

Stacking Model. Since many phase-separated polymers form stacks of alternating layers of two different phases, the one-dimensional statistical stacking model is frequently used. Its principle was introduced by Zernike and Prins,[4] who pointed out that due to the inherent lack of long range correlation $I_1(0)$ is nonzero. Subsequently, it was substantially extended, discussed in terms of the "convolution polynomial", and for the first time, applied to polymers by Hermans.[6] Finally Hosemann[7] showed that the theory of analytic functions is an elegant tool for the deduction of the intensity equation. Brämer[8] has discussed several variants of the model and has shown the superiority of the case, in which the stacking of both kinds of layers is assumed to occur statistically independently. Assuming an infinite stack height, one obtains for this model

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$$I_1(s) = \frac{A_{P_1}}{s^2}\,\mathrm{Re}\left[\frac{(1 - H_1(s))(1 - H_2(s))}{1 - H_1(s)H_2(s)}\right] \qquad (6)$$

Here $A_{P_1} = \lim_{s\to\infty} s^2 I_1(s)$ is the one-dimensional Porod asymptote. The functions $H_i(s)$ are the Fourier transforms of the layer thickness distributions $h_i(x)$, and "Re" stands for the real part of a complex number. Equation 6 is valid for an ideal two-phase system with sharp phase boundaries and a constant density within each of the phases.

In general, the functions $H_i(s)$ are products of the harmonic function $\exp(2\pi i \bar{d}_i s)$ and an attenuating term, which describes the shape of the layer thickness distribution. $\bar{d}_i$ is the average thickness of the layers of phase i.

Intensity $I_1(s)$ in the Vicinity of Zero. Assuming $H_i(s) = \exp(2(\pi\sigma_i s)^2 + 2\pi i \bar{d}_i s)$, i.e. Gaussian layer thickness distributions with variances σ_i, one finds for the expansion of $I_1(s)$ about the origin (cf. Blundell[5])

$$I_1(s) = Q\bar{d}_P\left(\frac{\sigma_1^{\,2}}{\bar{d}_1^{\,2}} + \frac{\sigma_2^{\,2}}{\bar{d}_2^{\,2}}\right) + O(s^2) \qquad (7)$$

where the coefficient of the second-order term is too complicated to be of practical value. Here $\bar{d}_P = l_P/2$ is the one-dimensional equivalent of the average chord length in three dimensions, l_P, which governs the initial slope of the one-dimensional correlation function[9] $\gamma_1(x) = 1 - x/\bar{d}_P + O(x^2)$,

$$\bar{d}_P = \frac{\bar{d}_1\bar{d}_2}{\bar{d}_1 + \bar{d}_2} \qquad (8)$$

By analogy with the notion of a one-dimensional fluctuation of the electron density,[2,10] the zero-order term can be identified with a one-dimensional "layer thickness fluctuation". As expected, $I_1(0)$ only vanishes in the case of an ideal one-dimensional lattice.

By taking additional terms in the Taylor series expansion of $I_1(s)$, one can estimate how many terms are needed in order to extrapolate point focus curves with sufficient accuracy. Figure 1 shows that one should in general employ the expansion up to the fourth power term in s.

Intensity $\tilde{I}_1(s)$ in the Vicinity of Zero. As Figure 1 shows, the extrapolation of a slit-smeared intensity near zero angle is much less critical than that of a point focus curve. Here a linear extrapolation toward zero should, in general, be sufficient. Moreover, for the stacking model one finds a Taylor series expansion which is of some practical use

$$\tilde{I}_1(s) = \frac{1}{2}I_1(0) + \pi^2 A_{P_1}\frac{(\bar{d}_1\bar{d}_2)^2}{\bar{d}_1 + \bar{d}_2}s + O(s^2) \qquad (9)$$

As one observes, the slope of the extrapolation line is a function only of the stack composition and does not depend on the stacking statistics. Thus a perfect one-dimensional lattice exhibits the same initial slope in $\tilde{I}_1(s)$ as a stack with only short range order. Using the definitions of the scattering power Q and the Porod asymptote A_{P_1} one can finally rewrite the Taylor series expansion of eq 9 for the case of an ideal one-dimensional stacking model

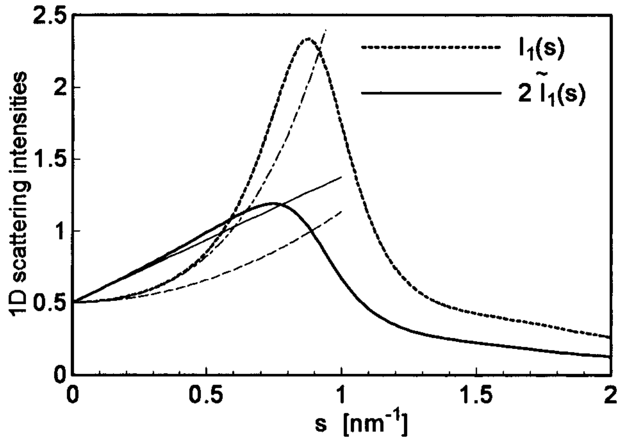

Figure 1. Model one-dimensional SAXS curves $I_1(s)$ (point focus) and $2\tilde{I}_1(s)$ (slit-smeared) for a stacking model (A_{P_1}, $\bar{d}_1 = 0.3$, $\bar{d}_2 = 0.7$, $\sigma_1/\bar{d}_1 = 0.7$, $\sigma_2/\bar{d}_2 = 0.3$) and a truncated Taylor series (up to second and up to fourth power, respectively, for $I_1(s)$; up to first power in s for $2\tilde{I}_1(s)$).

$$\tilde{I}_1(s) = \frac{\bar{d}_P}{2}\Delta\rho_{\mathrm{el}}^{\,2}\nu(1 - \nu)\left(\frac{\sigma_1^{\,2}}{\bar{d}_1^{\,2}} + \frac{\sigma_2^{\,2}}{\bar{d}_2^{\,2}}\right) + (\Delta\rho_{\mathrm{el}}\nu(1 - \nu)L)^2\, s + O(s^2) \qquad (9)$$

where $\Delta\rho_{\mathrm{el}}$ is the electron density difference between the two phases, ν is the volume fraction of one of the phases and $L = \bar{d}_1 + \bar{d}_2$ is the long period. Thus if the long period and density of a semicrystalline sample remain constant and the structure can be described using a statistical layer stacking model, the initial slope of the curve $\tilde{I}_1(s)$ should not change.

Application to Experiment

In Figure 2 we present slit-smeared one-dimensional scattering curves, which were recorded by us using a Kratky camera and discuss the shape of the curves in the vicinity of zero angle.

Figure 2 shows a subset of data recorded in a study of blends from HDPE and an SBS block copolymer. While, in general, the curves follow a straight line in the vicinity of zero angle, one of the blended samples shows some scattering, which may come from voids or imperfect blending on the mill, since the long period and density are the same for both samples containing 5% of SBS. The scattering power Q of the "irregular" sample will thus contain a considerable contribution to $\tilde{I}_1(s)$ resulting from voids or segregation. For the three "regular" samples the curves have been extrapolated to zero angle by extending the linear portion of the measured data. One observes that the intercept is indeed non-zero and the equation of the initial straight line in absolute units is given by

$$\tilde{I}_1(s) = 180\ \mathrm{e.u/nm^5} + 18 \times 10^3\ \mathrm{e.u./nm^4}\ s$$

Here "e.u." is the usual designation for "electron units".

At least for the pure PE samples one can assume that their SAXS arises from stacks built from crystalline and amorphous layers and that it is convenient to express it in terms of the parameters A_{P_1}, $\bar{d}_1$, $\bar{d}_2$, $\sigma_1/\bar{d}_1$, and $\sigma_2/\bar{d}_2$ (cf. eqs 6 and 7). A useful method in order to obtain values for these parameters is an IDF analysis,[11,12] which is performed (1) by transforming the slit-smeared scattering data to the "interface distribution function" (IDF) in physical space and (2) by fitting the resulting

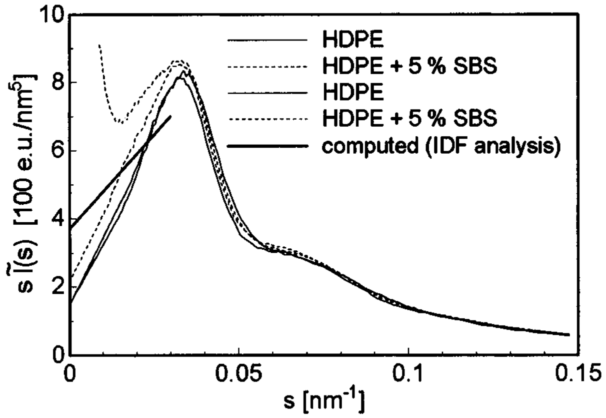

Figure 2. Reproducibility of sample preparation for blends from HDPE and SBS. The study of $\tilde{I}_1(s)$ facilitates the detection of improper blending or the creation of voids. The predicted line computed from eq 9 with the structure parameters obtained from an IDF analysis[11,12] of the four samples is shown in addition.

curve with the one-dimensional stacking model. From such a fit one computes

$$\tilde{I}_1(s) = 370 \text{ e.u./nm}^5 + 11 \times 10^3 \text{ e.u./nm}^4 \; s$$

This prediction is shown in Figure 2 as a bold line. One observes that only the order of magnitude of both analyses coincides. The observed discrepancy probably results from the influence of the statistical structure of the interface between the two phases[13,14] on the parameters evaluated from the IDF. For samples with a considerable and uncorrected layer surface roughness one observes two effects on the layer thickness distributions determined from an IDF analysis. Firstly, it broadens the widths of the distributions and thus leads to an underestimation of the long range order in the stack. Secondly, it moves the centers of gravity of both distributions to smaller values and thus underestimates the long period L.

Together, both effects lead to the crossover observed in Figure 2 with the three regular curves, since the initial slope of $\tilde{I}_1(s)$ is not affected by the surface roughness of the layers. Finally, this comparison may show a way to quantify the background scattering effects related to the statistical nature of the interface in lamellar two-phase samples:

(1) Verify that the initial linear shape of $\tilde{I}_1(s)$ is governed only by the two-phase system (no voids, no segregation).

(2) Determine the constants in eq 9 and thus two constraining equations for the structural parameters of the stack.

(3) Model the statistical structure of the interface in the IDF by an additional narrow distribution in the vicinity of zero and fit the IDF with a one-dimensional paracrystalline model with the established constraints.

Conclusions

It has been shown that the mathematical treatment of slit smearing in terms of Mellin convolutions leads to novel insight into the properties of the integrands, from which the SAXS invariant is calculated. Considering the physical parameters which determine the initial slope and intercept of $\tilde{I}_1(s)$ (in terms of the stack composition and its range of order), a measurement with slit collimation may sometimes be more convenient than one with point collimation.

Appendix A

It is obvious that in the Taylor series expansion of $I_1(s)$ about the origin all the terms with odd powers of s vanish, since $I_1(s)$ is continuous, even, and differentiable everywhere, i.e.

$$I_1(s) = \sum_{i=0}^{\infty} a_{2i} s^{2i} \qquad (10)$$

Moment Expansion of $\tilde{I}_1(s)$. Using the slit-smearing equation for infinite slit length, one obtains a relation between the slit-smeared and the unsmeared one-dimensional intensity

$$\tilde{I}(s) = \int_{-\infty}^{\infty} I(\sqrt{s^2 + y^2})\, dy = \frac{1}{\pi}\int_0^{\infty} \frac{I_1(\sqrt{s^2 + y^2})}{s^2 + y^2}\, dy$$

which after the variable substitution $s^2/u^2 = s^2 + y^2$ may be expressed in terms of a Mellin convolution[12,15]

$$\tilde{I}_1(s) = \tilde{S}_1(s) \otimes I_1(s) \qquad (11)$$

defined by the equation

$$f(x) \otimes g(x) = \int_0^{\infty} f(y) g\left(\frac{x}{y}\right) \frac{dy}{y} \qquad (12)$$

In eq 11 $\tilde{S}_1(s)$ is a characteristic function which mediates slit smearing for a class of one-dimensional functions in reciprocal space under the Mellin convolution. It is given by

$$\tilde{S}_1(s) = \frac{1}{\pi} \frac{s}{\sqrt{1 - s^2}}\, \Theta(1 - s) \qquad (13)$$

with

$$\Theta(x) = \begin{cases} 0 & x < 0 \\ 1 & x > 0 \end{cases}$$

being the Heaviside function.

From the definition of the Mellin transformation as a generalized moment expansion

$$Mf(t) = \int_0^{\infty} f(y) y^{t-1}\, dy \qquad (14)$$

the Mellin-convoluted function enjoys the property that its nth moment about the origin, $\mu'_{n,f\otimes g}$, is the product of the corresponding moments of its constituents,

$$\mu'_{n,f\otimes g} = \mu'_{n,f}\, \mu'_{n,g} \qquad (15)$$

From the Mellin transform of $\tilde{S}_1$ given by

$$M\tilde{S}_1(t) = \frac{1}{2\sqrt{\pi}} \frac{\Gamma\left(\frac{t+1}{2}\right)}{\Gamma\left(\frac{t+2}{2}\right)}$$

one may therefore study the relation between the moments of the smeared and the unsmeared one-dimensional intensities

$$\mu'_{n,\tilde{I}_1} = \frac{1}{2\sqrt{\pi}} \frac{\Gamma\left(\frac{n+2}{2}\right)}{\Gamma\left(\frac{n+3}{2}\right)} \mu'_{n,I_1} \tag{16}$$

In particular, after evaluating the norm and mean of $\tilde{S}_1$, one obtains for the norm and mean of the smeared 1D intensity

$$\mu'_{n,\tilde{I}_1} = \frac{1}{\pi}\mu'_{n,I_1}$$

$$\mu'_{n,\tilde{I}_1} = \frac{1}{4}\mu'_{n,I_1} \tag{17}$$

and here the relation between the norms is simply a restatement of eq 3. Combining the relations for the norm and the mean, one deduces a relation between the centers of gravity, μ'_1/μ'_0, of the intensities $\tilde{I}_1(s)$ and $I_1(s)$

$$\frac{\mu'_{1,\tilde{I}_1}}{\mu'_{0,\tilde{I}_1}} = \frac{\pi}{4} \frac{\mu'_{1,I_1}}{\mu'_{0,I_1}} \tag{18}$$

If, as in the case of a two-phase structure, $I_1(s)$ obeys Porod's law, all its moments beginning with the second one diverge. Then its Mellin transform does not exist and the useful properties of the Mellin convolution cannot help to solve the smearing integral transform analytically.

Taylor Series Expansion of $\tilde{I}_1(s)$. The Fourier transformation of $I_1(s)$ is related to the one-dimensional correlation function,[9] $\gamma_1(x)$

$$FI_1(x) = Q\gamma_1(x) = 2\int_0^\infty I_1(s) e^{2\pi i x s}\, ds$$

Thus after Fourier transformation of eq 11 one obtains

$$\tilde{\gamma}_1(x) = \tilde{X}_1(x) \otimes \gamma_1(x) \tag{19}$$

This again is a Mellin convolution with the function $\tilde{X}_1$ being given by

$$\tilde{X}_1(x) = \frac{1}{\pi} \frac{1}{x\sqrt{x^2 - 1}} \Theta(x + 1) \tag{20}$$

Its Mellin transform can easily be computed

$$M\tilde{X}_1(t) = \frac{1}{2\sqrt{\pi}} \frac{\Gamma\left(\frac{2-t}{2}\right)}{\Gamma\left(\frac{3-t}{2}\right)} \tag{21}$$

and setting $t = n + 1$, one can study the nth moments of $\tilde{X}_1(x)$ about $x = 0$, $\mu'_{n,\tilde{X}_1}$. One now can use the relation between the moments of a function and the coefficients in the Taylor series of its Fourier transform, in our special case written as

$$\tilde{I}_1(s) = Q\sum_{k=0}^{\infty} \frac{\mu'_{k,\tilde{\gamma}_1}}{k!}(2\pi i s)^k \tag{22}$$

and deduce

$$\tilde{I}_1(0) = {}^1/_2 I_1(0) \tag{4}$$

from $\mu'_{0,\tilde{X}_1} = {}^1/_2$. Thus the value of the smeared one-dimensional intensity at zero scattering angle is half the value of the corresponding unsmeared intensity.

Further consideration of eq 21 yields

$$\mu'_{n,\tilde{X}_1} = 0 \qquad n \in \{2, 4, 6, ...\} \tag{23}$$

and

$$\frac{1}{\mu'_{n,\tilde{X}_1}} = 0 \qquad n \in \{1, 3, 5, ...\} \tag{24}$$

from the values of the Γ function at zero and at negative whole number arguments. For practical applications one deduces from eq 23 that in the Taylor series expansion of $\tilde{I}_1(s)$ about the origin all the terms with even and positive powers of s vanish, as long as the corresponding terms in the series expansion of $I_1(s)$ are finite. From eq 24 one finds that in the Taylor series expansion of $\tilde{I}_1(s)$ about the origin all the terms with odd powers of s are finite, only if the limit

$$\lim_{t \to k} \frac{M\gamma_1(t)}{1/M\tilde{X}_1(t)} \tag{25}$$

exists for even values of k. Using l'Hopital's rule, one can easily verify that the derivative of the "denominator" yields finite and nonzero values (e.g., $\lim_{1\to 2}$ $(d/dt)(2\sqrt{\pi}\Gamma((3 - t)/2)/\Gamma((2 - t)/2)) = -\pi$).

In summary of the previous considerations, $\tilde{I}_1(s)$ can be expanded in odd positive powers of $|s|$ plus a well-defined constant

$$\tilde{I}_1(s) = \frac{I_1(0)}{2} + \sum_{k=0}^{\infty} a_{2k+1}|s|^{2k+1} \tag{5}$$

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