Analysis of the small-angle X-ray scattering of linear polyethylene by a paracrystalline lattice model

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Abstract: Three paracrystalline lattice models for the interpretation of the small angle scattering of polyethylene are discussed: The "lattice model", the "stapel model" (often referred to as the lamellar stack model) and the "proportional model". While the applicability of the first model is restricted, the latter models differ in the statistical assumptions of lamellar and interlamellar thickness distributions. The principal advantage of the proportional model over the stapel model is its applicability through the adjustment of only three parameters: long period, crystallinity and one statistical parameter. Small angle X-ray curves of linear polyethylene are interpreted by the proportional model. The results are in good agreement with stapel model calculations.

Key words: small angle X-ray scattering, model calculations, paracrystal, polyethylene.

1. Introduction

One of the most common methods of analysing the small angle X-ray scattering of partially crystallized polymers is the calculation of theoretical curves by use of structure models. The aim of any model is to provide as much information about the system investigated as possible while keeping the number of parameters as low as possible.

Vonk and Kortleve [1, 2] derived a model where theoretically calculated correlation functions are compared to those obtained by Fourier-transformation of the intensity profile. This procedure, however, requires thoroughly measured curves and the model seems to be relatively insensitive towards parameter variation. Tsvankin [3–6] developed a structure model basing on the concept of the linear paracrystalline lattice. Buchanan [7] modified this theory and described an evaluation method that has been widely applied in the literature. Another paracrystalline model is that of Hosemann [8, 9] which has been repeatedly modified [10–15] to match the requirements of the various systems that had to be analysed. Christ [16, 17] and recently Blundell [18] have reviewed the various aspects of the model, especially the statistical functions used and the importance of the homogeneity of the sample. From these and other investigations [19] it is certain that the symmetry of the thickness distribution functions is of great importance.

In this paper we derive a modified paracrystalline lattice model where only three parameters have to be varied. This model is applied to interpret the small angle X-ray scattering of some linear polyethylene samples.

2. The one dimensional paracrystal

The small angle X-ray scattering of a superstructure composed of clusters containing crystal lamellae is produced by the density fluctuation \( \varrho_N \) within the cluster in the longitudinal direction (normal to the crystal surfaces). This fluctuation can be described by a one-dimensional lattice with varying occupation functions \( \varrho_n \) of the lattice cells:

\[
\varrho_N(r) = \sum_{n=1}^{N} \varrho_n (r - r_n).
\]
In most cases it can be assumed that the scattered intensity is generated by a large number of clusters having different inner structures and being randomly oriented, thus forming an isotropic structure. Furthermore the clusters are polydisperse in size which allows for neglect of the interparticle (cluster) interference terms. Hence the necessary averaging process can be carried out separately with respect to cluster orientation and structure. The averaging of the cluster orientations can be done by applying the Lorentzfactor $1/2(\pi s^2)$. In order to carry out the averaging of the cluster longitudinal structures, the number $N$ of the lattice cells and the different occupations $q_n$ have to be taken into account. If we assume that the inner structure of a cluster is dependent neither on its position in the sample or its environment nor on its size, including the number $N$ of lamellae, we get:

$$I = \frac{1}{2\pi s^2} \sum_N v_N I_N$$

where $v_N = $ distribution of number of lamellae per cluster

and

$$I_N(s) = \langle |\mathcal{Q}_N(r)e^{-2nis}dr|^2 \rangle$$

where $s = 2\sin \theta/\lambda$ and $2\theta = $ scattering angle.

Let $\alpha_{nm}$ be the structure parameter of the $n$-th lattice cell ($\mu = 1, \ldots, K$) and $H(\alpha_{nm})$ the statistical function which gives the relative probability of the representation of a specific set of structure parameters in a given lattice. Then

$$I_N = \int |\mathcal{Q}_N(1)e^{-2nis}|^2 H(\alpha_{nm})d\alpha_1\cdots d\alpha_K.$$  

A lattice is then paracrystalline if the following relations are satisfied:

$$H(\alpha_1, \ldots, \alpha_K) = \prod_{n=1}^{N} H_n(\alpha_{n1}, \ldots, \alpha_{nK}) \forall n$$

and

$$H_n(\alpha_{n1}, \ldots, \alpha_{nK}) = H_p(\alpha_1, \ldots, \alpha_K) \forall n$$

where $H_n$ and $H_p$ are normalized.

The first of these two relations expresses the lattice cells, from a statistical point of view, as independent structural units, e.g. the inner structure of the $n$-th lattice cell is completely independent of that of all neighbouring cells. The property of a single cell to be part of the lattice is designated only by the index $n$ of the lattice cell.

The second relation does not even contain this information: there is no distinction according to a one specifically designated cell. This makes clear that the paracrystalline model is an attempt to build up the lattice by employing one single cell-statistics. It should be noted that this procedure is relatively unproblematic for linear lattices. In case of a three-dimensional lattice, however, only very special structures fulfill the relations (5) and (6).

With this statistical interpretation of the lattice ensemble we derive an expression of the scattering function $I_N$. Separating the factors of (5) with respect to cell indices and using $z_n$ being the length of the $n$-th lattice cell

$$r_n - r_m = \sum_{v=1}^{n-1} z_v$$

we get

$$I_N = \sum_{n=1}^{N} \langle |F_n^2| \rangle + 2 Re $$

$$\left\{ \sum_{n=1}^{N} \sum_{m=1}^{n-1} \langle F_n H_n F_m e^{-2nis} \rangle H_m \frac{n-1}{\Pi_{v=m+1}^{n}} \langle e^{-2nis} \rangle H_v \right\}$$

with $F_n = \int \mathcal{Q}_n(z)e^{-2nis}dz$.

As has been stated in (6), the single terms are independent with respect to the indices. Hence the summation can be carried out and we finally get

$$I_N = N\langle |F|^2 \rangle H_p + 2 Re \left\{ \langle F \rangle H_p$$

$$\langle F_p e^{-2nis} \rangle H_p \left[ \frac{N}{1 - \langle e^{-2nis} \rangle H_p} - \frac{1 - \langle e^{-2nis} \rangle H_p}{(1 - \langle e^{-2nis} \rangle H_p)^2} \right] \right\}.$$  

(9) represents a paracrystalline lattice model where the only restrictions are to fulfill the relations (5) and (6). The widely used paracrystalline model, designated by Christ [16] as "restricted paracrystalline model" and as "general paracrystalline model" as well as the "general model" introduced by Blundell [20] incorporate the assumption of additional statistical independencies of the lattice cell parameters. Thus (9) proves to be a generalization of the above mentioned cases.

3. The lattice model

The first term in (9) describes the statistical scattering behaviour of the single lattice cells. The scattering of the lattice

$$G_N = Re \left\{ \frac{1 + \langle e^{-2nis} \rangle}{1 - \langle e^{-2nis} \rangle} \right\}$$

$$- 2\langle e^{-2nis} \rangle \frac{1 - \langle e^{-2nis} \rangle N}{(1 - \langle e^{-2nis} \rangle)^2} \right\}$$

(10)