statistical (liquid-like) fluctuations of the edge vectors of the lattice cells. From the two-dimensional SAXS analysis one learns, for instance, that during annealing the vector $a$, which expands between the centers of laterally adjacent mPC's, shows a decreasing fluctuation in chain direction 3. The structure becomes bimodal after a certain annealing time indicating that groups of mPC's cluster together within the lamellae with well-aligned fold surfaces (Loboda-Čačković, Hosemann & Čačković, 1971). From WAXS one learns that smaller mPC's recrystallize here to form larger ones.

The lateral grain boundaries of the mPC's proved by a combined SAXS and WAXS analysis play an important role in the understanding of the increase of the long period, $P$, with temperature. Surface premelting cannot explain this for polymers with a crystallinity below 0.5 (Yeh, Hosemann, Loboda-Čačković & Čačković, 1976). The paracrystalline model gives a direct answer: mPC's with unprotected lateral boundaries (e.g. at the end of lamellae) offer an excess free energy. They dissolve by solid-state diffusion and parts of their segments crystallize to form parts of the adjacent two lamellae (Hosemann, 1962). A true melting occurs solely in a rather narrow temperature range III near the melting point where the SAXS intensity decreases and isolated groups of bounded bundles of lamellae are imbedded in the melt. This can be shown directly on isotactic poly(1-butene) which in this range only melts partially; quenched to room temperature it recrystallizes to the unstable modification II (Haase, Hosemann & Renwanz, 1977). Even the so-called single crystals grown from dilute solution consist of specially aligned mPC's. Their degradation by $O_3$ or HNO$_3$ can only be understood in terms of the important role of the lateral grain boundaries of the mPC's (Schönfeld, Wilke, Höhne & Hosemann, 1972; Hosemann, Čačković & Loboda-Čačković, 1975).

The full paper will be published in *Journal of Materials Science*.

**References**


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**The Small-Angle Scattering of Distorted Lamellar Structures**

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*(Received 3 November 1977; accepted 31 May 1978)*

The effects of deviations from an ideal lamellar structure (infinite-size clusters of parallel layers of alternating electron densities) on the small-angle scattering curve are treated with the aid of the correlation function. If surrounded by a matrix of the average electron density, reduction of the size of the clusters in the direction of the layer normals leads to a simple modification of the one-dimensional correlation function. Distortions giving rise to structures containing concentric layers have little effect on this function, whereas corrugation of the surfaces causes minor modifications. Second-order defects are shown to reduce the three-dimensional correlation function of the ideal structure $\gamma(r)$ according to $\gamma(r) = \gamma^0(r) \exp\left(-2r/d\right)$, where $d$ is the 'distortion length'. This is the average length of the vectors for which the number of intersections with lamellar interfaces has changed by ±1 as a consequence of the distortions. Calculated diffraction curves show that the effects of reducing the cluster size and of increasing the width $\beta$ of the lamellar thickness distribution function are very similar. However, changes in $d$ and $\beta$ affect the scattering curves in a different way, which, other conditions being favourable, may enable these parameters to be determined from observed scattering curves.

**Introduction**

In nearly all calculations of the small-angle scattering of melt-crystallized polymers use is made of a structure model consisting of alternating parallel crystalline and amorphous layers in randomly oriented clusters, whose dimensions in all directions are large compared with those covered by the experiments. In the following this model will be referred to as the 'ideal lamellar model'. In the calculations two approaches have been followed; according to the first, and more general one, the one-dimensional intensity function $I_1$ from a cluster is obtained by squaring the corresponding one-dimensional amplitude function $F_1$, which in turn is obtained by Fourier transformation of the electron-density variations along the lamellar normal. A review of the literature about procedures and results, which also deals with the
limitations of the model, was given by Brämer (1973), whereas more recent studies were published by Crist (1973), Crist & Morosoff (1973), Kilian & Wenig (1974), and Hara (1976). The second method, which was put forward by Vonk & Kortleve (1967; hereafter referred to as paper I), consists of calculation of the one-dimensional correlation function \( \gamma_1 \) from the observed \( I_1 \), and comparison of this with correlation functions calculated from the model.

If applied to polymers of high or medium crystallinity, both methods in general lead to good agreement between calculated and observed one-dimensional intensity or correlation functions. However, at lower crystallinities, this is not always so. Some authors, using the first method, have tried to improve on it by limiting the number \( N \) of lamellae within each cluster. This model will be referred to as the 'finite-cluster model'. Values of \( N \), reported to have been obtained in this way, were in some cases very low, e.g. 1-5 (Kilian & Wenig, 1976). However, some of these calculations may be objected to as they are based on the assumption that the density of the material surrounding the clusters equals that of the amorphous fraction. If the clusters are to be space filling, the density of the material should be taken equal to the average density. As was recently shown by Schultz (1976), this difference between the preliminary assumptions may lead to appreciable differences between calculated scattering curves.

In this paper it will first be shown how, with the correct assumption being made about the density of the surrounding material, the one-dimensional correlation function for the finite-cluster model can be calculated by means of the second method. Next, the effect of the following deviations from the ideal lamellar structure will be discussed: deformations leading to concentric layers (Fig. 1), and lamellar distortions of both the first and second kinds. Lamellar distortions of the first kind are considered to consist of deviations of the lamellar surfaces, whereby short-range order is reduced, but the long-range order is preserved (Fig. 2b, c, top row); those of the second kind, on the other hand, cause destruction of the long-range order with preservation of the short-range order (Fig. 2d, top row). It should be emphasized that in the direction perpendicular to the layers the ideal lamellar model in general also shows second-order deviations, which are the deviations of the thicknesses of the layers from their average values. In this paper these deviations will be considered as inherent to the ideal lamellar model.

The finite-cluster model

As explained more fully in paper I, the one-dimensional correlation function \( \gamma_1 \) is obtained from the relation

\[
\gamma_1(x) = \langle \eta(x) \eta(x) \rangle / \langle \eta \rangle^2,
\]

where \( \eta \) is the local deviation of the electron density from the average value, \( AB \) is a vector of length \( x \) perpendicular to the layers, and \( \eta_P \) is the value of \( \eta \) at the point \( P \). Thus one
may think the one-dimensional correlation function to be obtained by averaging the products of the electron-density deviations at the beginning and end points of all vectors of length $x$ along a certain line normal to the layers.

If the stacks of lamella are of a finite thickness $L$, a certain part $q$ of the vectors of length $x$, for which $A$ is within a given stack, will have $B$ outside this stack. As the values of $\eta_A$ and $\eta_B$ pertaining to these vectors are no longer correlated, one may, in calculating $\langle \eta_A \eta_B \rangle$, assume the electron density outside the stack to have the average value of the sample, which means that here $\eta_B$ and the corresponding product $\eta_A \eta_B$ can be set equal to zero. The average value $\langle \eta_A \eta_B \rangle$ is therefore lowered by the ratio $q$, which is obviously given by

$$q = \begin{cases} 1 - |x|/L & \text{if } |x| < L \\ 0 & \text{if } |x| > L \end{cases}.$$  

(2)

The correlation function $\gamma_1$ for the finite-cluster model is then given by

$$\gamma_1 = \gamma_0 q,$$  

(3)

where $\gamma_0$ is the correlation function that would have been obtained from the corresponding ideal lamellar structure; this may be calculated according to the method described in paper I. The one- and three-dimensional intensity functions $I_1$ and $I$ may then be obtained from $\gamma_1$ with the aid of the general relations

$$I_1(s) = \mathcal{F}_1 \{ \gamma_1(x) \},$$  

(4)

and

$$I(s) = I_1(s)/(4\pi s^2),$$  

(5)

where $s$ is the radial coordinate in reciprocal space ($s = 2\sin\theta/\lambda$, $2\theta$ is angle of diffraction, $\lambda$ is wavelength of X-rays) and $\mathcal{F}_1$ is the operator for one-dimensional Fourier transformation.

**Systematic distortions**

An important type of deformation of an ideal lamellar structure, which can be expected in polymers containing ringed spherulites, consists in buckling and distortion of large clusters as a whole. As mentioned in paper I, this type of deformation may be expected to have little effect on the one-dimensional correlation function as long as the layers can be considered to be concentric. In view of the importance of this point in the present discussion, the arguments involved will be presented here.

Fig. 1 shows a section through an ideal lamellar structure, together with the structure that can be obtained by bending the ideal structure around $O$. Also presented is the cross section through a sphere of radius $AB = r$. If $\eta_A$ and $\eta_B$ represent the electron density deviations at $A$ and $B$, and the sample contains curved layers in all orientations, the value of the three-dimensional correlation function at distance $r$ will be determined by the sum total of all $\eta_A \eta_B$ values on the surface of the sphere, averaged over all positions of $A$. It is clear that after the bending of the layers the sphere will be intersected by the same layers as before. Also, the contributions of the various types of products $\eta_A \eta_B$ will not have been changed much by the deformation; the figure shows that the contributions from the vectors ending in the segments 1 and 3 are nearly offset by those in the sectors 2 and 4. As to magnitude and sign, the small residual contribution depends on the position of $A$ relative to the surrounding layers, and will cancel out in averaging over all positions of $A$. These arguments no longer hold if the midpoint of bending $O$ lies within the sphere around $A$, in other words, if $r > R_c$, where $R_c$ is the radius of curvature. As information from the correlation function is usually significant only at values of $r$ for which $r < 2D$ ($D$ is the average distance of periodicity in the direction perpendicular to the layers), it was stated in paper I that buckling of the layers has little effect on the correlation function as long as $R_c > 2D$.

**Distortions of the first kind**

In ideal lamellar structures showing disorder of the first kind, the long-range order in the direction parallel to the lamellae is preserved, whereas the short-range order in this direction is disturbed by irregularities in the lamellar surfaces. If the size of the details in the roughened surfaces is small compared to the size of the heterogeneities giving rise to small-angle scattering in general, the surfaces can be thought to be replaced by a transition layer of thickness $E$ (Fig. 2b), in which the electron density varies gradually between the two extreme values. As was discussed before (Vonk, 1973), this leads to a non-zero value of the second derivative of $\gamma_1(x)$ at the origin, and to intensities deviating from Porod’s law (Ruland, 1971).

In discussing the effect of coarser corrugations, such as shown in Fig. 2(c), we first consider the vectors $AB$ which are parallel to the average lamellar surfaces. If $x, y, z$ are the rectangular coordinates of the correlation function, these vectors correspond to points in the plane $x = 0$. In the ideal structure these vectors all begin and end in the same phase, for which in this plane $y = 1$ at all points. In the corrugated structure, however, parts of these vectors are within the irregular surface layers; their contribution to $\langle \eta_A \eta_B \rangle$ will decrease as $AB$ increases. As a result, in the $x = 0$ plane the correlation function will fall off with increasing distance from the origin; however, as the greater part of the vectors giving contributions in the $x = 0$ plane is still well within the interior of the layers, it will not fall off to zero.

The correlation function in the $x$ direction ($y = 0, z = 0$) can be calculated by the method presented in paper I, provided the distribution functions $P_x$ and $P_z$ of the lamellar thicknesses $x_1$ and $x_2$ are replaced by those of the corresponding chord lengths $x_1$ and $x_2$ (see Fig. 2c). Furthermore it can be shown that in all planes $x = c$, for which $c > E$, the correlation function is independent of $y$ and $z$. It will thus be a one-dimensional function, except for the origin peak that falls off in all directions, as shown schematically in the bottom part of Fig. 2(c). Consequently the three-dimensional correlation function which is obtained by averaging this function over all directions will show a larger first derivative at the origin $(d^2/dr^2)_{r=0}$ than the three-dimensional correlation function of the corresponding ideal structure. This can be connected with the larger specific surface of the corrugated structure, this surface being equal to $4\pi(1 - \phi)(d^2/dr^2)_{r=0}$, where $\phi$ is the volume fraction of crystalline material in the sample.

**Distortions of the second kind**

A structure containing distortions of the second kind, of which a cross section is shown schematically in Fig. 2(d), is characterized by a loss of long-range order in the directions parallel to the lamellae, the short-range order being preserved. A problem in discussing a structure of this kind is that there is no obvious way to relate it to an ideal la-
mellar structure. In the following we will, however, assume that such an ideal structure can be assigned, and afterwards, from the imposed requirements, derive the relation between the ideal and the actual structures.

In the following derivation it is assumed that at each point in the deformed structure one can recognize the layer structure sufficiently well to assign a preferential direction \( x_a \) of the layer normals. One may then imagine a three-dimensional correlation function of cylindrical symmetry to be built up of many local contributions of products \( \eta_{AB} \) corresponding to vectors \( AB \), in which all \( x_a \) directions are made to coincide in a common \( x \) direction. This function will be referred to as the 'locally oriented correlation function', \( \Gamma(r) \). In the bottom part of Fig. 2 schematic representations of this function as pertaining to the ideal lamellar model (to be indicated by \( F^0 \)), and to the deformed structure are given. The value of \( F^0(x) \) is equal to that of \( \gamma^0(x) \).

Next, it is assumed that each point within the actual structure corresponds to a point in the corresponding ideal lamellar structure in such a way that the structures in the near vicinity of the point are nearly equal, whereas the agreement decreases with increasing distance from the point at a rate that is independent of the direction with respect to \( x \). In order to translate this into a mathematical equation, we note that the contribution \( \eta_{AB} \) of a vector \( AB \) to the correlation function is determined by the number \( k \) of intersections the vector makes with the interfaces: if \( k \) is odd, this contribution is negative, if \( k \) is even, it is positive. Corresponding vectors in the actual and ideal structures may differ in \( k \) values by \( IAkI = 0, 1, 2 \ldots \). The above assumption implies that the average of \( |\Delta k| \) will increase with increase of the vector length \( r \) in a way that is independent of \( \psi \) (Fig. 2a). We will assume that the increases in the average of \( |\Delta k| \) and \( r \) are proportional to each other; this implies that the jumps in \( |\Delta k| \) are distributed at random over the lengths of the vectors. The average increase in length of a vector that is needed to increase \( |\Delta k| \) by 1 will be called the 'distortion length' \( d \). As will be shown in the Appendix, these assumptions lead to the relation

\[
\Gamma(r) = F^0(r) \exp \left( -2r/d \right),
\]

which, after averaging over all directions, yields

\[
\gamma(r) = \gamma^0(r) \exp \left( -2r/d \right).
\]  

We note that the value of \( k \) of vectors perpendicular to \( x \) in the ideal lamellar structure is zero, and that consequently in the corresponding distorted structure the intersections themselves are distributed at random over these vectors. In view of this, the distortion length may be visualized as follows: through any point \( P \) within the structure consider a plane that is parallel to the nearest interface (see Fig. 2d); in all directions within these planes find the length \( l \) between \( P \) and the nearest intersection with an interface; then \( d \) is the average of all these lengths \( l \), taken over all points within the structure.

We will now consider the relation between an actual, distorted structure and the corresponding ideal lamellar structure. The assumption that at each point within the actual structure the \( x \) direction can be recognized allows us to construct the locally oriented correlation function \( \Gamma(x) \) in the \( x \) direction. The procedure is the same as described in paper I, except that in equation (14) of paper I the distribution functions \( P_i(x) \) and \( P_i(x) \) of the lamellar thicknesses have to be replaced by distribution functions of the chord lengths in the \( x \) direction. According to equation (6) the corresponding ideal lamellar structure would have to yield a one-dimensional correlation function that is related to \( \Gamma(x) \) by \( \Gamma^0(x) = \Gamma(x) \exp (2r/d) \). Thus, the question to be answered is whether a one-dimensional structure of the same crystallinity as the actual structure can be assigned for which the correlation function equals \( \Gamma^0(x) \). In connection with this we note that, because of the factor \( \exp (2r/d) \), the oscillations in \( \Gamma^0(x) \) will be stronger and less damped out than those in \( \Gamma(x) \). As such, the effect of this factor is much the same as the effect brought about by narrowing the distribution functions. It therefore seems reasonable to suppose that by narrowing \( P_i \) and \( P_i \) with respect to the functions used in calculating \( \Gamma(x) \) (and, if necessary, by adjusting their shapes), one may in principle find distribution functions which, if applied in calculating the one-dimensional correlation function, would yield \( \Gamma^0(x) \). The structure based on these functions can be considered as the ideal lamellar structure in question.

Relation (7) will also be applicable to structures with non-sharp phase boundaries, as long as the width of the transition is small compared with the distortion length. The function \( \Gamma^0 \) for such structures may be calculated with the aid of relations given earlier (Vonk, 1973).

**Application to model structures**

In Fig. 3 a number of calculated intensity curves are shown, such as would be obtained from isotropic samples with the aid of pinhole collimation. These were obtained by first calculating \( \gamma^0(x) \) for an ideal lamellar structure from equation (14) of paper I. In the calculations for the finite-cluster model this function was modified by applying equations (2) and (3), after which the final curves were obtained with the
Fig. 4. Calculated scattering curves, ideal lamellar model, \( \varphi = 0.5 \), \( \delta E = 0 \); \( P_c \) and \( P_a \); Poisson functions. Inset: shape of \( P_c \) and \( P_a \) for the different values of \( \beta \).

The results of this work show that the interpretation of the small-angle scattering data from polymers in terms of a model consisting of a very limited number of parallel crystalline and amorphous layers (finite-cluster model) does not necessarily imply the physical reality of such a structure. Probably the effect of a reduction of the cluster thickness on the scattering curve can just as well be brought about by an increase of the width of the lamellar-thickness distribution functions. Distortions however affect the scattering curve in a different way. As a result, conditions being otherwise favourable, the degree of the distortions can in principle be determined from the scattering curve. Confirmation with experimental data, obtained from polymers during isothermal crystallization, is in progress now.

The author is grateful to Mr N. Masic, of the Institute Rudor Boskovic, Zagreb, who during his visit to our laboratory produced a large stream of experimental results that initiated this work.

APPENDIX

Calculation of the correlation function of a lamellar structure

Let \( p_{0m}(r) \) represent the fraction of all those vectors \( AB = r \) in the ideal layer structure that have \( A \) in phase \( l \) and at the same time have \( B \) in phase \( m \). From equations (9)-(16) of Debye, Anderson & Brumberger (1957), one may then derive:

\[
\Gamma^0(r) = p_{00}^c(r) + p_{00}^a(r) + 1. \tag{41}
\]

The distortions will cause a redistribution of the vectors \( r \); over these types, the new fractions being indicated by \( p_{nm}(r) \). If \( k \) is the number of intersections a vector makes with the interfaces between the layers, then the redistribution may be expressed in terms of the fraction \( \sigma(k) \) of the vectors \( r \) for which \( k \) has changed by an odd number \( \Delta k \). On the assumption that \( x \) is isotropic and equal for vectors of different types, the following relations are obvious:

\[
p_{n}^a(r) = p_{n}^c(r) - \alpha(r)p_{n}^a(r) + \alpha(r)p_{n}^0(r)
\]

and

\[
p_{n}^c(r) = p_{n}^c(r) - \alpha(r)p_{n}^a(r), \quad \text{for different values of } \beta.
\]
\[ p_{ad}(r) = p_{ad}^0(r) - \alpha(r) p_{ad}^0(r) + \gamma(r) p_{ad}^0(r). \]

Combining these with equation (41), and observing that \( p_{ad}^0 = 1 - p_{ad}^0 \), and \( p_{ad}^0 = 1 - \gamma(r) p_{ad}^0 \), one finds

\[ I(r) = I^0(r) \left( 1 - 2\alpha(r) \right). \]  \hspace{1cm} (42)

As the changes, \( \Delta k \), of the number of intersections with lamellar interfaces are assumed to be distributed at random over the vectors, the lengths of the vectors for which \( |\Delta k| = 1 \) must show a Poisson distribution:

\[ f_n(r) = \frac{1}{d} \exp \left( -\frac{r}{d} \right). \]  \hspace{1cm} (A3)

Here, \( d \) is the 'distortion length', mentioned before. The distribution of the vectors for which \( |\Delta k| = n \) can be obtained by \( n \) successive convolutions of equation (A3), which leads to:

\[ f_n(r) = r^n \left[ \frac{1}{(n-1)!} \frac{d^n}{d^n} \right] \exp \left( -\frac{r}{d} \right). \]  \hspace{1cm} (A4)

At a given value of \( r \), the integral

\[ \int_0^r f_n(q) dq \]

gives the fraction of the vectors for which \( |\Delta k| = n \) or more. The fraction \( F_n \), for which \( k \) has changed by no more or less than \( n \) times, can therefore be found from

\[ F_n(r) = \int_0^r \{ f_n(q) - f_{n+1}(q) \} dq, \]

which, combined with equation (A4) leads to

\[ F_n(r) = \frac{1}{n!} \left( \frac{r^n}{d^n} \right) \exp \left( -\frac{r}{d} \right). \]  \hspace{1cm} (A5)

The definition of \( \alpha \) given before requires that

\[ \alpha(r) = \sum_{n=1, 3, 5} F_n(r), \]

which, with the aid of equations (42) and (A5), yields

\[ I(r) = I^0(r) \left\{ 1 - 2 \exp \left( -\frac{r}{d} \right) \sum_{n=1, 3, 5} \frac{1}{n!} \left( \frac{r}{d} \right)^n \right\}. \]

By developing \( \exp \left( -\frac{r}{d} \right) \) into a series, and multiplying this with the summation, one can verify that this is equivalent to equation (6).

References


Small-Angle X-ray Diffraction Studies and Morphology of Microporous Materials and Their 'Hard' Elastic Precursors

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(Received 3 November 1977; accepted 16 March 1978)

Changes in small-angle X-ray diffraction when microporous materials, formed from hard elastic precursors, are immersed in liquids has established that the interlamellar fibrils are crystalline. It is concluded that the stabilization of the extended void structure is due to crystallization of the fibrils.

The superstructure of hard elastic materials such as polypropylene fibers and films has been shown to consist of well oriented lamellae. The small-angle pattern of the 'as-extruded' materials has the character of a narrow fan on the meridian, indicating the existence of a distribution of long spacings and thus lamellar thicknesses along the extrusion direction and of very large lateral lamellar dimensions. With increasing annealing temperature, the meridional fan increases in intensity, it becomes shorter and eventually the lamellar thickness (long spacing) becomes so uniform that in addition to the basic spacing the second-order scattering is visible. This is easily observed when annealing in the temperature range 130–150 °C. The details of the preparation of these materials, their diffraction pattern as function of extrusion and annealing conditions have been published elsewhere (Noether & Whitney, 1973; Park & Noether, 1975).

A characteristic feature of these highly crystalline, highly oriented materials is the fact that they can be extended 50–100%, this extension being practically completely and immediately reversible. Small-angle and wide-angle X-ray diffraction (SAXR and WAXR) and electron-microscopy data show that these fibers or films, on extension beyond 20 25°, rupture in the interlamellar regions to form elongated voidy regions parallel to the lateral lamellae direction. The void size in the stretch direction is proportional to