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Isothermic formation of spherulitic boundaries with equidistant time marks in a foil of polypropylene

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In a foil of polypropylene two circularly growing spherulites which touch each other and finally form a common grain boundary are regarded. Another grain boundary is formed by one circularly growing spherulite which makes contact with a growing band and with the growing interior of a circular ring. All possible grain boundary formations are systemized. This is done theoretically using analytical planar curves geometry, and is done in most cases, experimentally with equidistant time marks.

1. Introduction

Crystallization is studied in a foil of isotactic polypropylene. The polymer possesses an isotacticity of 96%, a mean molecular weight, M_w of 300.000 and a thickness of 4 μm, and contains neither stabilizers nor fillers. This foil melts at about 168 °C. During heat treatment the temperature is increased under exclusion of O_2 in an inert atmosphere to about 200 °C in order to reduce the number of athermic nuclei. The temperature is quickly reduced from 200 to 132 °C. In the supercooled melt at 132 °C, immediately many α-modified nuclei and some β-modified nuclei of polypropylene are formed which begin to grow simultaneously and circularly as α and β spherulites, respectively.

Fig. 1 shows a growing spherulite in which

1. the limiting circle between the spherulite and the undercooled melt is called the growth front,
2. the three circular marks in the interior of the spherulite are called thermic marks or time marks,
3. the radial rays from the nucleus to the growth front are called growth lines; these growth lines are approximately described by the fibrils.

In the metastable, undercooled and molten foil at 132 °C the α-modified spherulite grows at a constant growth rate of $v_\alpha = 3.3\ \mu\text{m min}^{-1}$, and the β-modified spherulite at a constant growth rate of $v_\beta = 4.3\ \mu\text{m min}^{-1}$. At 144 °C the growth rate of both α and β spherulites is reduced to about $0.3\ \mu\text{m min}^{-1}$. Growth of spherulites for 15 min at 132 °C, then for 4 min at 144 °C, again for 15 min at 132 °C, then for 4 min at 144 °C, and so on, leads to equidistant circular marks in the spherulites, as shown in Fig. 1 [1]. The different grey shading of the smaller circular marks is caused by the higher thickness of folded lamellae.

When two α nuclei start to grow at the same time as α spherulites, they make contact with each other during growth. At this moment of contact, a straight grain boundary begins to form. In Fig. 2 the development of this grain boundary is demonstrated at a later point of time; here, recognize a straight grain boundary and two symmetrical growth fronts which are circular arcs. Besides, two dynamic triple points exist at the two ends of the grain boundary.

With regard to the folded molecules of polypropylene, with a fold length of about 10^{-2}–10^{-1} μm, the 4 μm used foil is thick. On the other hand, the 4 μm used foil is thin with regard to spherulites having a radius of about 100 μm. Therefore, one can theoretically treat the spherulites in the thin foil using two dimensional analytical geometry. According to this, the spherulitic boundaries, which comprehend the movable growth fronts and the fixed grain boundaries, are theoretically treated with differential planar curve geometry.

In this paper the spherulitic boundaries for one growing spherulite is determined, which finally grows together with a growing

1. straight band,
2. second spherulite,
3. interior of a ring.

The two phases of the spherulite and of its growing partner can consist either of the same modification or of different modifications.

2. Discussion

2.1. Grain boundary produced by one spherulite and one straight band

2.1.1. The straight band and its production

A band is produced by transcrystallization [2]. Its fibrils are not arranged radially like those of spherulites, instead they possess parallel fibrils. Fig. 3 shows a growing band of α- and a growing band of β-modified polypropylene at 132 °C grown for 30 min. Of course, the growth rates v_α and v_β are the same for spherulites and bands.

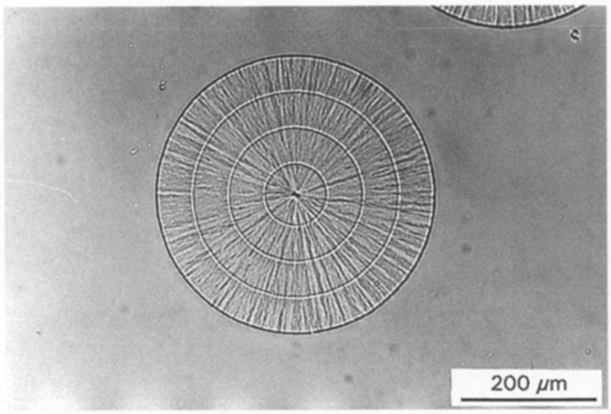

Figure 1 A growing spherulite in a polypropylene foil that contains three thermic marks. It is limited by a circular growth front and surrounded by undercooled melt.

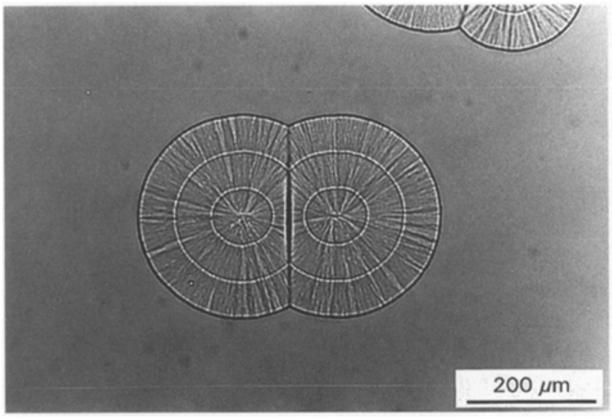

Figure 2 A straight grain boundary is formed between two α spherulites after 45 min growth at 132 °C. Both spherulites began their growth at the same time. They contain two time marks. The grain boundary is limited by two dynamic triple points where three two-dimensional regions meet: grain 1, grain 2 and the melt.

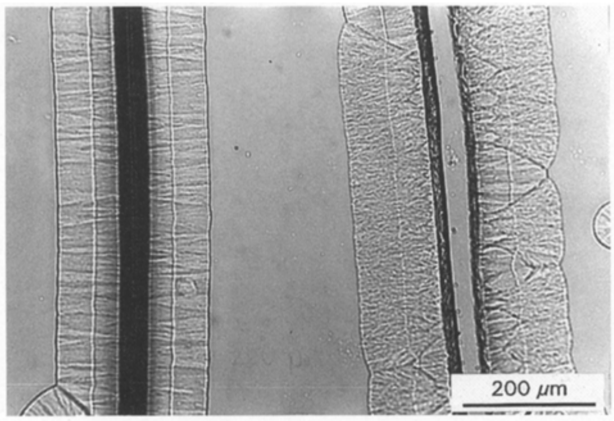

Figure 3 An α and a β band having begun to grow at the same time. Each band shows two symmetrical thermic marks set after 15 min growth and two growth fronts after 30 min growth which move in opposite directions. A growth rate ratio, v_β/v_α of 1.3 can be recognized.

The α band is made by putting a polyester filament onto the foil's surface before heat treatment begins. The temperature is increased to 200 °C for some minutes for homogenization of the melt. Then the

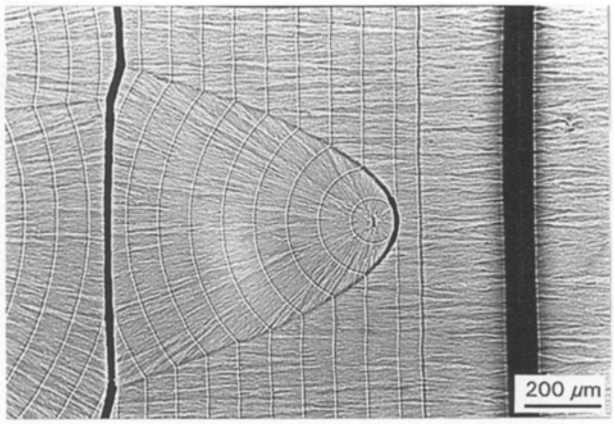

Figure 4 An α spherulite and an α band both having grown with the same growth rate of 3.3 μm min^{-1}. The grain boundary is a parabola. The point of time when the spherulite has begun its growth is marked by the first thermic mark in the band, the directrix. The next mark of time illustrates the moment of contact between spherulite and band. Then the marks are set every 15 min. This procedure is the same for Figs 5 and 6. A family of salient points defines the grain boundary.

temperature is decreased very quickly to 132 °C. A large number of α nuclei is formed at the border between liquid foil and solid filament. The nuclei are arranged like a string of pearls. The following, simultaneous growth of all nuclei, forms the desired straight band.

The β band is made by "cutting" the supercooled melt at the beginning of spherulitic growth at 132 °C with a fine scalpel. This causes mechanical stress and orientation of the polypropylene molecules, which leads to the growth of a band of β-modification at sufficient distance from the cut. Some other possibilities for producing bands can be found in [3–5], e.g. Notice that each straight band has two straightly growing growth fronts.

2.1.2. Overview of possible spherulitic boundaries

Here the growth of a growing spherulite and a growing band with a straight growth front making contact with each other and then forming a common grain boundary is investigated. It is the aim to observe experimentally the formation of this grain boundary and growth fronts. Theoretically, their shape is deduced using analytical planar curve geometry.

Between the spherulite and straight growth front there are three possible combinations of modifications; α–α as shown in Fig. 4, β–α as shown in Fig. 5 and α–β as shown in Fig. 6. It is deduced in the following that the shape of the grain boundary in Fig. 4 is a parabola, in Fig. 5 one branch of a hyperbola and in Fig. 6 a half ellipse continued by two arcs of a logarithmic spiral which meet in a vertex. The vertex is continued by an intrinsic grain boundary [6].

The α and β growth fronts, which belong to any point on the parabola, the hyperbola and on the half ellipse, are circular arcs for the spherulite and two straight lines for the growing front. Within the growth

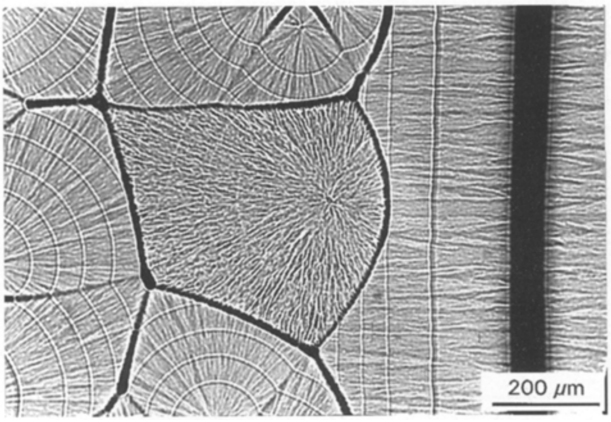

Figure 5 A β spherulite and an α band, with growth rate ratio of $v_\beta/v_\alpha = 4.3(\mu m\,min^{-1})/3.3(\mu m\,min^{-1}) \approx 1.3$. The grain boundary is a hyperbola.

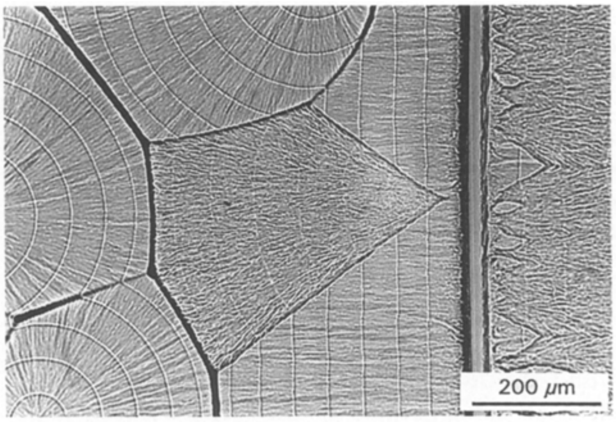

Figure 7 The nucleus of a β spherulite is placed directly on the directrix of a straight growth front of α-modified polypropylene. The grain boundary consists of two straight lines.

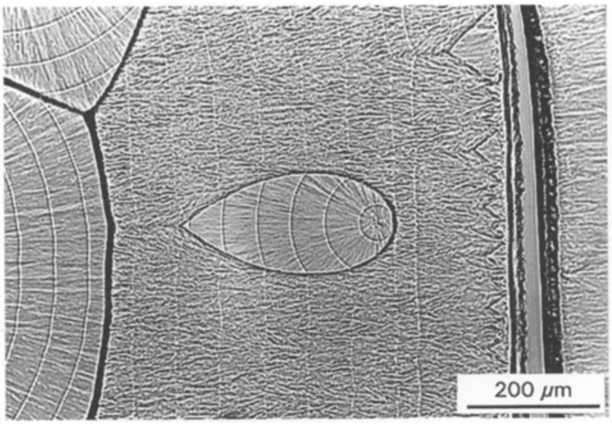

Figure 6 A β band is growing around an α spherulite. The photograph shows as grain boundary one-half of an ellipse continued by two arcs of a logarithmic spiral at both sides until these arcs meet in a vertex. Beginning in the vertex there runs an intrinsic grain boundary formed by two growth fronts which belong to the same band.

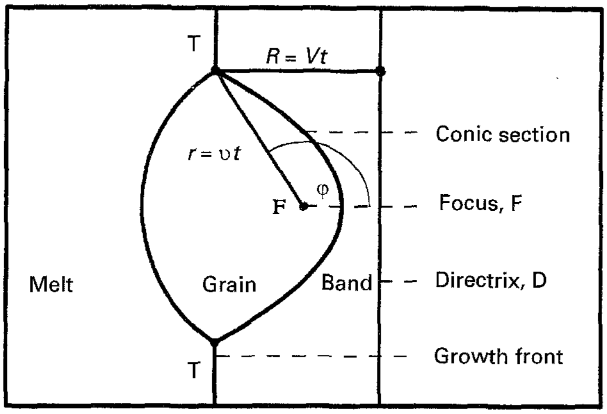

Figure 8 Schematical drawing of a conic section as grain boundary between both triple points, T: F, focus; D, the directrix of the conic section. The growth fronts are two straight lines and a circular arc with radius *r*.

shadow of Fig. 6, the growth fronts are evolvents of a logarithmic spiral.

A limiting case also has been investigated, where the nucleus of the β spherulite is placed directly on the directrix of a straight α growth front [3]. During growth a grain boundary is formed which consists of two straight lines. These straight lines are caused by degeneration of one branch of the hyperbola. The two straight lines form an angle of $2\cos^{-1}(v_\alpha/v_\beta)$. The growth fronts are two straight lines for the α front and a circular arc for the β spherulite. The experimental result is shown in Fig. 7.

2.1.3. Conic sections

Fig. 8 shows a schematic drawing for construction of conic sections. At point of time, t, $= 0$ the nucleus of a spherulite is formed at a place called the focus, F. The straight growth front at $t = 0$ is called the directrix, D. The constant growth rate of the spherulite is named υ, those of the straight grown front, V. The triple point, T, is the point where spherulite, band and supercooled melt coexist. T is a dynamic triple point. At T it is valid at point of time, t, that the spherulite has grown a distance υt from focus F, while the band has grown a distance Vt perpendicularly from directrix, D. Therefore it is true that

$$\frac{\overline{TF}}{\overline{TD}} = \frac{\upsilon t}{Vt} = \frac{\upsilon}{V} = \text{constant} = e$$

This means that the lengths $\overline{TF}$ and $\overline{TD}$ to every point T have the same ratio.

Where an α spherulite meets an α band, Fig. 4 shows the case that the growth rate is the same for spherulite and band. For any point on the grain boundary it holds that the distance between the grain boundary and the directrix equals the distance between the grain boundary and the nucleus of the spherulite. The ratio of these lengths amounts to one. In the theory of conic sections, this defines a parabola.

Where a β spherulite meets an α band, Fig. 5 shows the case that the ratio of the growth rates, υ/V, amounts to 1.3. This defines one branch of a hyperbola because the ratio is greater than one.

Where an α spherulite meets a β band, Fig. 6 shows a teardrop-shaped curve as a grain boundary. This teardrop consists of a half ellipse and two symmetrically arranged arcs of a logarithmic spiral and is continued by a straight intrinsic grain boundary.

1. The half ellipse: Fig. 6 shows in its first part a ratio of lengths of $\upsilon/V = 0.77$. In the theory of conic sections, this ratio smaller than one defines an ellipse of which only a half ellipse is realized here. The polar equation of conic sections [7] reads

$$r = \frac{p}{1 + e\cos\varphi}$$

with r the distance between grain boundary and nucleus of the spherulite, φ the angle between polar radius, r, and the polar axis, p, the parameter for $\varphi = \pi/2$, and e the known ratio. The right part of Fig. 9 and Fig. 10 show such a part of an ellipse with $e = 0.77$. The point H, the vertex of the ellipse, is given by $r_H = a$ and ϕ_H from $\cos(\pi - \phi_H) = b/a$. a and b are the half axes of the ellipse. In point H the half ellipse ends, their continuation is explained in the next section.

2. Two identical arcs of a logarithmic spiral: Fig. 6 shows a photograph of the experimental result with continuation of a half ellipse by two identical and symmetrically arranged arcs of a logarithmic spiral. The moment where the grain boundary is exactly described by a half ellipse is schematically shown in Fig. 9. In H, the growth lines of the straight β growth front lie tangential to the grain boundary. This means that in H a growth shadow originates. No point of the grain boundary inside the growth shadow can be reached from a straight growth line of the growing band. So, further continuation of the ellipse is not possible. For deduction of the run of the grain boundary inside the shadow one uses differential planar curve geometry. This is now proved using a polypropylene foil. The half ellipse must be continued by two arcs of a logarithmic spiral beginning in H. It is well known that a differential element of an arc, ds, yields in polar co-ordinates

$$\mathrm{d}s = [(\mathrm{d}r)^2 + r^2]^{1/2}(\mathrm{d}\varphi)$$
$$= \left[\left(\frac{\mathrm{d}r}{\mathrm{d}t}\right)^2 + r^2\left(\frac{\mathrm{d}\varphi}{\mathrm{d}t}\right)^2\right]^{1/2}\mathrm{d}t$$

This equation divided by dt yields

$$\dot{s} = (\dot{r}^2 + r^2\dot{\varphi}^2)^{1/2}$$

Fig. 10 shows that inside the growth shadow i.e. between points H and I, the β growth lines (the fibrils in the experiment) always lie tangential to the grain boundary and that the α growth lines are radial rays with origin in the α nucleus, F. Therefore one has $\dot{s} = \upsilon_\beta$ and $\dot{r} = \upsilon_\alpha$, which gives

$$\upsilon_\beta = \left[\upsilon_\alpha^2 + \left(r\frac{\mathrm{d}\varphi}{\mathrm{d}t}\right)^2\right]^{1/2}$$

or

$$\dot{\varphi} = \frac{(\upsilon_\beta^2 - \upsilon_\alpha^2)^{1/2}}{r}$$

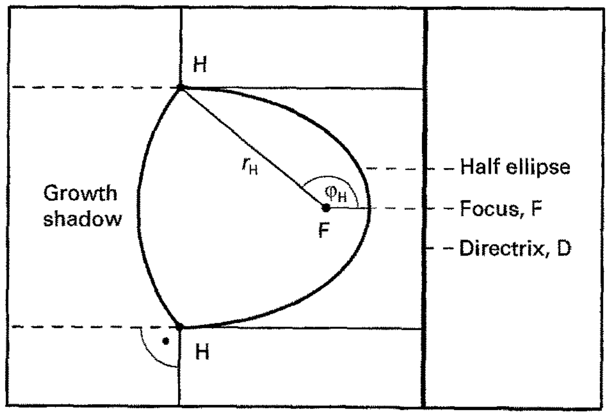

Figure 9 Schematical drawing of a half ellipse as grain boundary: F, is focus; D, directrix. The half ellipse ends in two symmetrically arranged points, H, the vertices of the ellipse. A shadow of growth originates in H because the growth lines of the growing β band in H are tangential to the grain boundary.

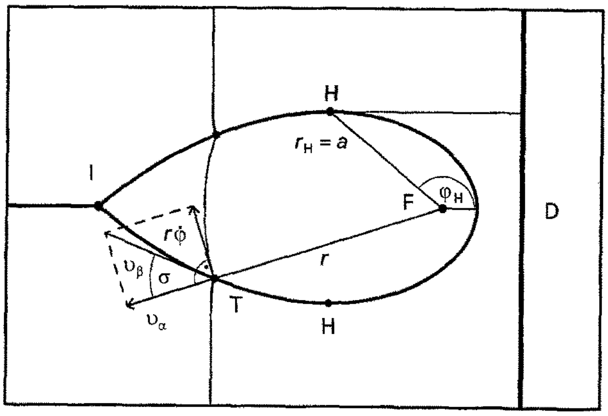

Figure 10 A band of the β modified polypropylene with greater growth rate and an α spherulite forming a common grain boundary. This schematic drawing corresponds to Fig. 6. The first part of the grain boundary is exactly a half ellipse with focus, F, and directrix, D. The half ellipse ends in the two symmetrically arranged points H, where a growth shadow originates. In this picture the grain boundary is continued by two arcs of a logarithmic spiral between H and I. T represents a triple point inside the shadow of growth with its corresponding fronts of growth. Beginning in I an intrinsic grain boundary is formed.

or

$$\mathrm{d}\varphi = (\upsilon_\beta^2 - \upsilon_\alpha^2)^{1/2}\frac{\mathrm{d}t}{r} = \left[\left(\frac{\upsilon_\beta}{\upsilon_\alpha}\right)^2 - 1\right]^{1/2}\frac{\mathrm{d}r}{r}$$

with $\mathrm{d}r = \upsilon_\alpha \mathrm{d}t$, which is integrated beginning in H

$$\varphi - \varphi_H = \left(\frac{\upsilon_\beta^2}{\upsilon_\alpha^2} - 1\right)^{1/2} \times \ln\frac{r}{r_H}$$

Eliminating the logarithm function,

$$r = r_H \exp\left[\frac{\upsilon_\alpha}{(\upsilon_\beta^2 - \upsilon_\alpha^2)^{1/2}}(\varphi - \varphi_H)\right] \qquad (1)$$

In mathematics the polar equation of a logarithmic spiral is well known [8] as

$$r = a\exp(\phi\cot\sigma) \qquad (2)$$

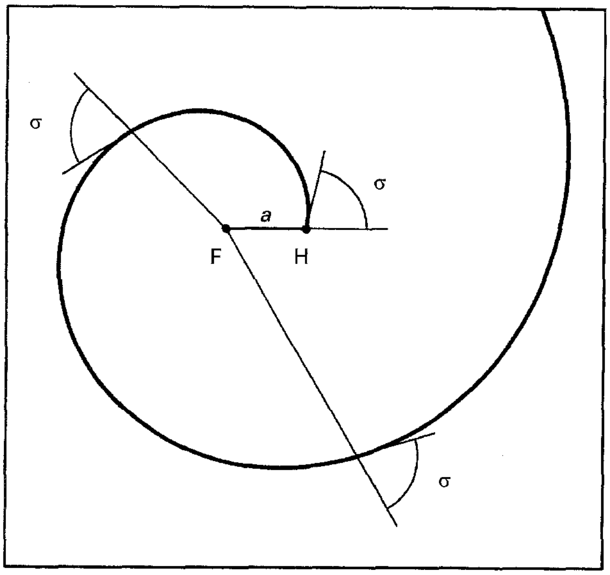

Figure 11 Part of a logarithmic spiral. At $\phi = 0$ there is $r = a$. It can be seen that the angle between the focus ray beginning in F and the logarithmic spiral is always the same and equals σ. In this picture $\sigma = 77°$ was chosen in order to have sufficient curvature of the logarithmic spiral. In experiment it holds that $\cot \sigma = v_\alpha/(v_\beta^2 - v_\alpha^2)^{1/2} = 3.3/2.76 = 1.2$, so $\sigma = 39.9° \approx 40°$.

Hereby r and ϕ are the polar co-ordinates, a is the radius for $\phi = 0$ and σ the angle, under which the logarithmic spiral is intersected at every point from the rays beginning in the nucleus, F, as Fig. 11 shows. Comparison of Equations 1 and 2 yields $a = r_H$, $\sigma = \pi - \varphi_H$ and $\phi = \varphi - \varphi_H$. Therefore it holds for one branch of the grain boundary between H and I

$$r = r_H \exp\left[(\varphi - \varphi_H)\cot(\pi - \varphi_H)\right] \tag{3}$$

For the point I where the α–β grain boundary, $r(\varphi)$, ends and therefore the growth of the α spherulite is finished, it holds

$$r(\varphi = \pi) = r_H \exp\left[(\pi - \varphi_H)\cot(\pi - \varphi_H)\right]$$
$$= r_H \exp(\sigma \cot \sigma)$$

For $\sigma = 60°$

$$r(\varphi = \pi) = 1.83 r_H$$

3. The intrinsic grain boundary: Until now a grain boundary has been obtained which consists of a half ellipse which is continued by a pair of arcs of a logarithmic spiral, caused by a growing α spherulite and a growing straight β growth front of a band. The two arcs of logarithmic spirals hit in the point I. Therefore the angle between the tangents to these two arcs in I amounts to 2σ. The point I is also the beginning of a straight intrinsic β–β grain boundary as Fig. 10 schematically shows. It is called intrinsic because this grain boundary is formed by the same and single β band. The intrinsic grain boundary is attached symmetrically to the pair of logarithmic spirals.

It is noted that growth fronts of the spherulite are always circular arcs. The growth fronts of the band are

1. two straight lines if the grain boundary is either a branch of a hyperbola, a parabola or a half ellipse; or
2. two straight lines continued by evolvents of the logarithmic spirals if the grain boundaries are either logarithmic spirals or a straight intrinsic grain boundary.

2.2. Grain boundary produced by two spherulites

Four cases are distinguished in the plane

1. Two spherulites of the same modification begin their growth at the same time.
2. Two spherulites of the same modification begin their growth at different points of time.
3. An α and a β spherulite begin their growth at the same time.
4. An α and a β spherulite begin their growth at different points of time.

The α spherulite grows with the constant rate υ_α, the β spherulite with υ_β.

2.2.1. Two α spherulites (or two β spherulites) begin their growth at the same time

This case has been treated earlier. A straight grain boundary is formed, see Fig. 2.

2.2.2. Two α spherulites (or two β spherulites) begin their growth at different points of time

An α nucleus starts to grow at $t = 0$ as α spherulite. It has reached the radius Δr when the growth of the second α nucleus starts. When the two spherulites meet each other, the grain boundary begins to form. In the following, the grain boundary is one branch of a hyperbola. This can be proved by the equidistant marks of time in Fig. 12: two marks of the same time meet and form a salient point. All these salient points together represent the run of the grain boundary.The difference in distance between any salient point and the two nuclei, $r_1(t) - r_2(t)$, equals Δr which is independent of the chosen salient point; but this is the definition of a hyperbola. The fronts of growth are circular arcs with different radii, as Fig. 12 shows.

2.2.3. An α spherulite and a β spherulite start at the same time

Regard an α nucleus and a β nucleus which lie at a distance, D. The nuclei start to grow at the same time as circular spherulites with constant growth rates υ_α and υ_β. The ratio of the growth rates is $g = \upsilon_\beta/\upsilon_\alpha$. r_0 is the radius of the α spherulite at that point of time when the α spherulite makes contact with the β spherulite with radius $D - r_0$. Then

$$g = \frac{\upsilon_\beta}{\upsilon_\alpha} = \frac{D - r_0}{r_0} \text{ or } r_0 = \frac{D}{g + 1}$$

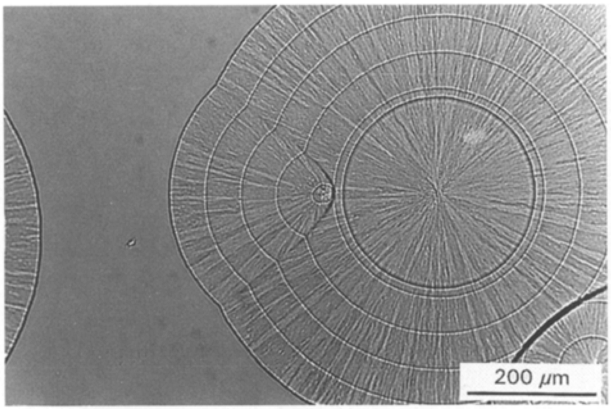

Figure 12 Two α spherulites which began their growth at different points of time. This fact can be easily recognized using the time marks. All salient points lie exactly on the grain boundary. The grain boundary is by definition a hyperbola.

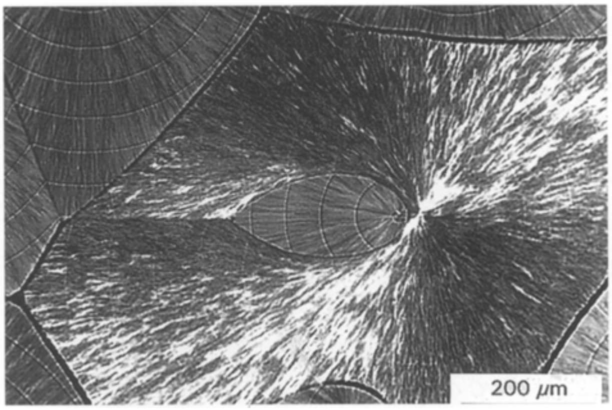

Figure 13 An α spherulite and a β spherulite of polypropylene start their growth at the same time at 132 °C. The photograph shows an α–β grain boundary, as a teardrop, an intrinsic β–β grain boundary and equidistant time marks. Crossed polarizers and a λ plate were used for emphasizing the run of the intrinsic grain boundary.

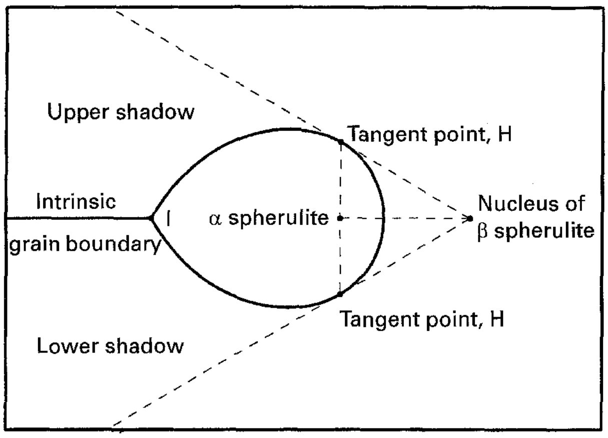

Figure 14 Schematic drawing of the experimental result shown in Fig. 13. The α–β grain boundary consists of an arc of a circle between the two tangent points, H, and two symmetrically arranged arcs of a logarithmic spiral between the points H and I inside the grown shadow. In I an intrinsic β–β grain boundary starts.

Fig. 13 shows an α spherulite with $g = 1.3$. Fig. 14 shows schematically such an α spherulite with $g = 2$ because of better drawing. Its α–β grain boundary begins with a circular arc between the two tangent points, H. It is continued by two symmetrical arcs of a logarithmic spiral between H and I because of the existence of a growth shadow [6, 9]. They intersect at point I of Fig. 14, where growth of the α spherulite has just finished. Beginning in I, a straight intrinsic β–β grain boundary is formed [6]. It is so called because it is formed by only one β spherulite. The complete mathematical derivation of the circular arc, the two arcs of a logarithmic spiral and the intrinsic grain boundary is given in [6].

The growth fronts of the α spherulite are always circular arcs. The growth fronts of the β spherulite are circular arcs which end at the circular α–β grain boundary. Later, when the radius of growth is larger than that radius belonging to the tangent points, H, they end at the limit of the growth shadow. Inside the shadow limit the β growth fronts are symmetrically continued by a family of evolvents of the arcs of logarithmic spirals.

2.2.4. An α spherulite and a β spherulite begin their growth at different points of time

Between an α nucleus and a β nucleus there is a distance, D. The nuclei start to grow at different points of time. r is the radius of the α spherulite just in that moment when it makes contact with the β spherulite, with a radius of $(D - r)$

Distinguish two intervals for r, i.e. $0 < r < r_0$ and $r_0 < r < D$. (At $r = r_0$ both nuclei start at the same time.) For $0 < r < r_0$, the α spherulite begins to grow later than the β spherulite. For $r_0 < r < D$, the α spherulite begins to grow earlier than the β spherulite.

Out of $0 < r < r_0$, $r = r_0/2$ and $g = 2$ were chosen for a demonstration in Fig. 15. The grain boundary begins with a fourth-order curve. At the two tangent points this curve is continued by two arcs of a logarithmic spiral. Where the arcs of logarithmic spiral hit, growth of the α spherulite is finished and the intrinsic grain boundary starts to grow. The intrinsic grain boundary is a straight line beginning in I in Fig. 15. Fig. 16 shows the experimental result.

For $r_0 < r < D$, $r = (D + r_0)/2$ and $g = 2$ were chosen for demonstration in Fig. 17. The grain boundary begins its growth with a change in curvature, as Fig. 17 shows. At the two symmetrical tangent points (seen from the position of the β nucleus) the curve is again continued by two arcs of logarithmic spiral. When they intersect, a straight intrinsic grain boundary begins to grow. Fig. 18 shows the experimental result.

In the case of $r = D$, the α spherulite has reached the growth radius, D, at exactly that moment when the β nucleus begins to grow. The grain boundary only consists of two symmetrically arranged arcs of a logarithmic spiral. Each arc of logarithmic spiral can be described by polar angles, α, between 0 and π. It is shown in Fig. 19 for $g = 2$.

The α growth fronts are always circles or circular arcs until the growth of the α spherulite has finished. The β growth fronts are always circles or circular arcs

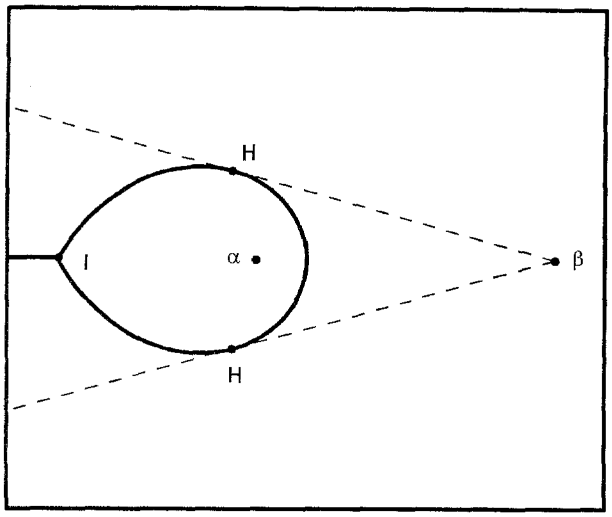

Figure 15 The grain boundary between an α spherulite and a β spherulite where the α spherulite began to grow later. $r = r_0/2$ and $g = 2$ were chosen for the schematic drawing. The tangent points are shown.

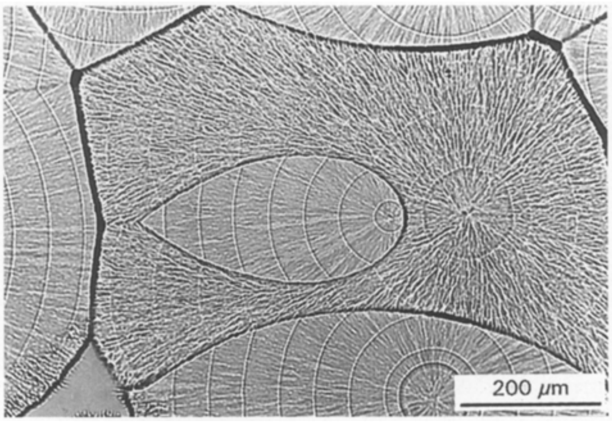

Figure 16 The experimental result for the situation presented in Fig. 15, but with $g = 1.3$, $r = (21 \pm 2)$ μm and $D = (110 \pm 2)$ μm.

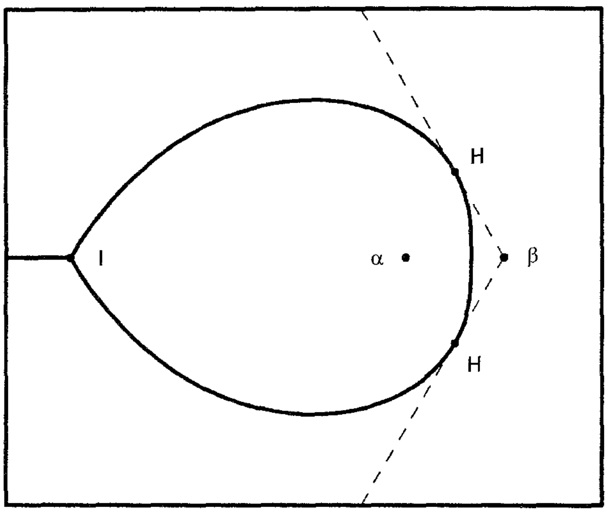

Figure 17 The grain boundary between an α spherulite and a β spherulite where the α spherulite began to grow earlier. $r = (D + r_0)/2$ and $g = 2$ were chosen for the schematic drawing.

until the β spherulite reaches the tangent points. Then the β growth fronts are circular arcs only outside the shadow of Figs 15 and 17. Inside the shadow, the circular arcs are continued by evolvents of the two

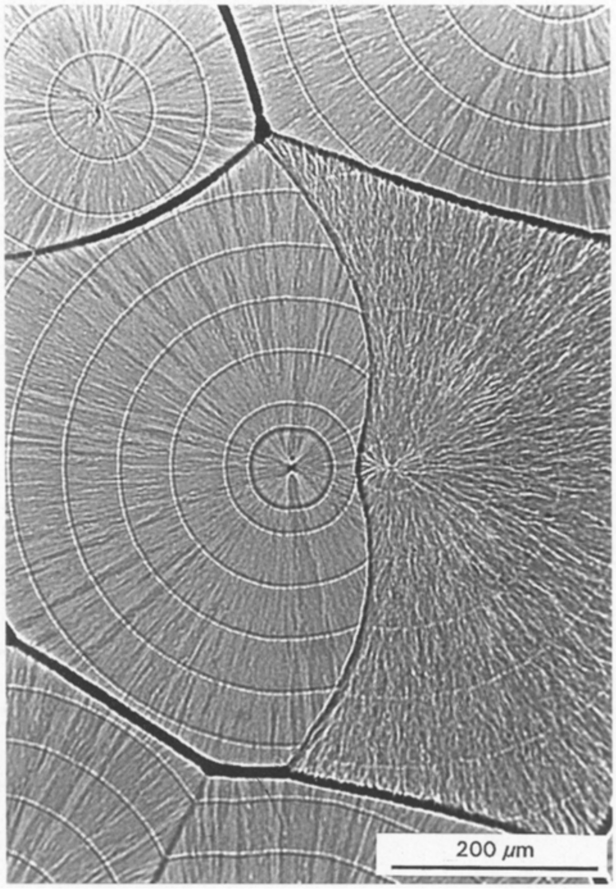

Figure 18 The experimental result for the situation presented in Fig. 17, but with $g = 1.3$, $r = (63 \pm 2)$ μm and $D = (93 \pm 2)$ μm. Only the first part of the grain boundary is visible.

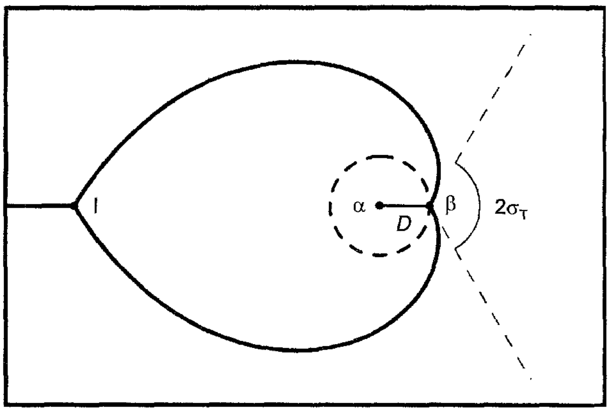

Figure 19 When the α spherulite has exactly reached the position of the β nucleus, $r = D$, the β spherulite starts to grow. One sees two symmetrical branches of a logarithmic spiral as grain boundary for $g = 2$.

arcs of logarithmic spiral. These curves run from the shadow limit to the α–β grain boundary, later to the intrinsic grain boundary.

2.3. Grain boundary produced by one spherulite and the interior of one circular band (ring)

2.3.1. Production of one circular band (ring)

An α ring is produced in a polypropylene foil in the following way. The liquid foil is undercooled at

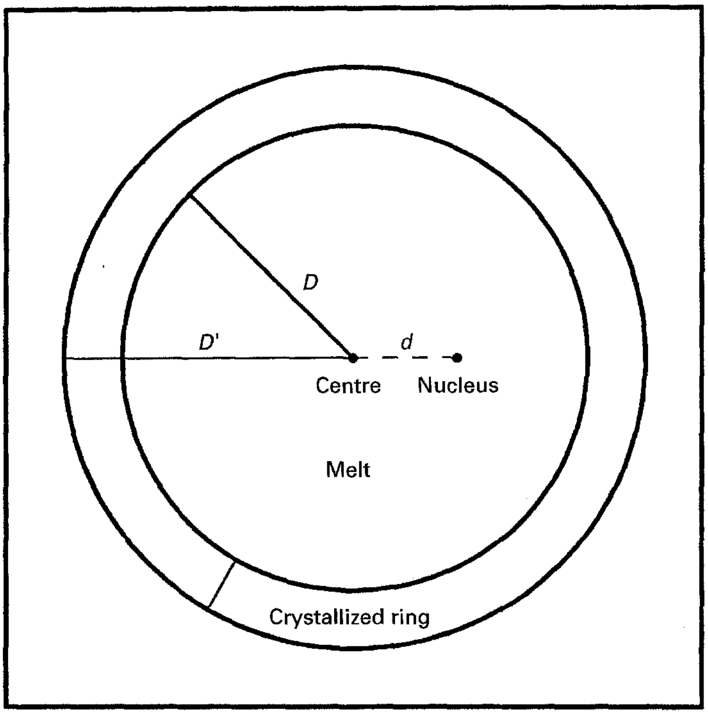

Figure 20 A crystallized ring with radii D and D'. Its interior consists of melt. The inner radius of the ring is D' when growth of the ring begins, and D at that point of time, when the nucleus of the spherulite is formed. The nucleus lies at a distance, d, from the centre of the ring. Of course it holds that $D \geq d$. This is the starting position of Fig. 21.

132 °C. Thereby, some α nuclei are formed and they start to grow immediately as grains with a growth rate of 3.3 μm min^{-1}. When the grain has a radius of about $D = 250$ μm, the temperature is increased to 144 °C. The grain then grows with a growth rate of about 0.3 μm min^{-1}. After 90 min of growth at 144 °C, the temperature is increased to 169 °C for 20 min. During this time the interior of spherulites with a radius of 250 μm melts, but the ring grown at 144 °C during 90 min remains stable. This is so because with increasing temperature the thickness of the lamellae also increases, which again causes a higher melting temperature of some tens of degrees.

In this paper, only the interior of the ring is updated. The exterior of the ring shows the same growth habits as a spherulite. This is shown in section 2.2.

2.3.2. Nucleus within the interior of a ring

After 20 min at 169 °C, the temperature is decreased to 126 °C for a very short time in order to obtain one nucleus in the molten circular area within the crystallizing ring. Fig. 20 shows this situation schematically. Then the temperature is increased to 132 °C, where the α nucleus grows as a spherulite within the ring; while the ring grows circularly with decreasing radius with the same growth rate. The increasing radius of the exterior of the ring is not of interest here.

Theoretically the following combinations of ring and spherulite are possible

1. α ring and α spherulite,
2. β ring and β spherulite,
3. β ring and α spherulite, and
4. α ring and β spherulite.

Practically only the first case has been realized. Cases two and three are not possible in polypropylene because of neocrystallization: instead of melting the β spherulites transform into a large number of very small α spherulites [10]. Although it is possible in principle Case four has not been found.

2.3.3. An α ring and an α nucleus (grain boundary is an ellipse)

Regard a growing α ring and a growing α spherulite which just meet each other [11]. This is schematically shown in Fig. 21. R_0 is the radius of the ring at that moment when the grain boundary begins to grow. r_0 is the radius of the spherulite at the same moment.

Since the radius, R, of the inner ring decreases with time, t, $R(t) = R_0 - \upsilon_\alpha t$, and since the radius, r, of the spherulite increases with time, t, $r(t) = r_0 + \upsilon_\alpha t$, one obtains

$$R(t) + r(t) = (R_0 - \upsilon_\alpha t) + (r_0 + \upsilon_\alpha t)$$
$$= R_0 + r_0 = \text{constant}$$

This is the mathematical expression for the Gardener construction of an ellipse if the rays r and R run from the two focii in the centre of the ring and of the spherulite to any point of the ellipse.

The growth fronts are circular arcs both for the ring and for the spherulite. Fig. 22, quoted from [11], shows a grain boundary which is an ellipse with three time marks.

2.3.4. A β ring and an α nucleus

Although this case does not exist because of neocrystallization of polypropylene, it is treated. With the

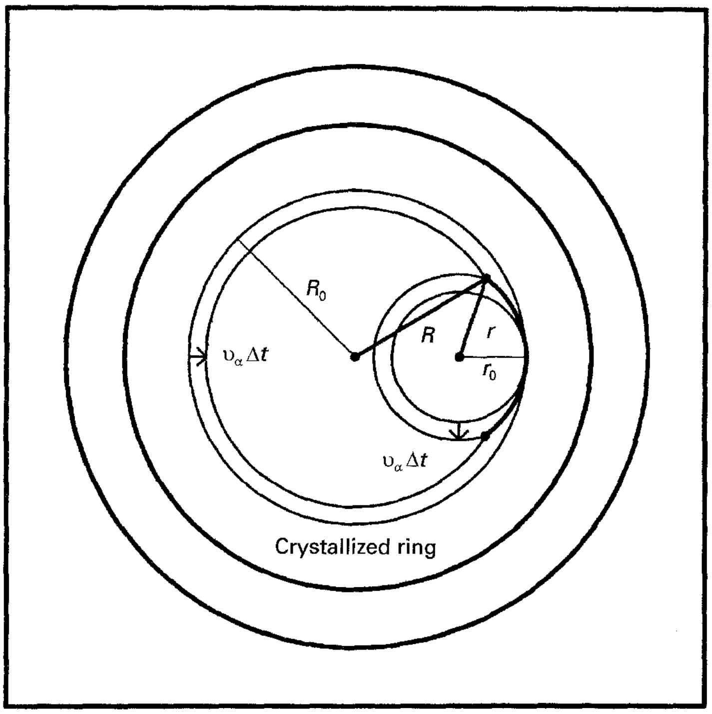

Figure 21 Schematic drawing of that point of time when α ring and α spherulite meet each other with radii R_0 and r_0, respectively. At a later point of time the radii are R and r, respectively. This leads to the Gardener construction of an ellipse because of the same growth rate.

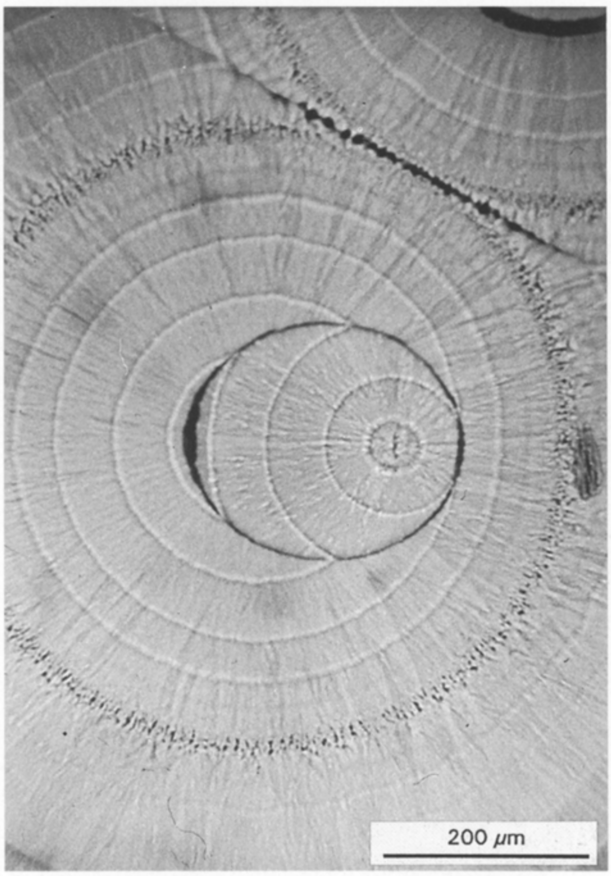

Figure 22 An ellipse as grain boundary with three time marks.

symbols d and D with $0 < d < D$ of Fig. 20, one has to distinguish three cases

1. $D/d = \upsilon_\beta|\upsilon_\alpha = g$: The α spherulite reaches exactly the centre of the ring when its growth has finished. There, the grain boundary has a point with an infinitely small radius of curvature. This is the limiting case for the existence of a growth shadow and separates the two cases presented in items two and three below. Fig. 23 shows an example with $g = 2$.

2. d varies between D and D/g: One finally has a growth shadow which causes two arcs of logarithmic spiral. The logarithmic spirals intersect and the growth of the α spherulite finishes. Grain boundary formation is continued by an intrinsic grain boundary until the centre of the ring is reached. Fig. 24 shows this for $(D + D/g)/2 = d$ with $g = 2$.

3. d varies between D/g and 0: Growth shadow cannot exist. The grain boundary of the spherulite is a closed curve without any sharp salient point. Fig. 25 shows this case for $d = D/2g$ with $g = 2$. At $d = 0$ the grain boundary of the spherulite is a circle with radius

$$\frac{\upsilon_\alpha}{\upsilon_\alpha + \upsilon_\beta} D$$

2.3.5. An α ring and a β spherulite

To distinguish between $d = 0$, $d = D$ and $0 < d < D$

1. $d = 0$ means that the grain boundary of the spherulite is a circle with radius

$$\frac{\upsilon_\beta}{\upsilon_\alpha + \upsilon_\beta} D$$

2. $d = D$ means that the β nucleus is positioned exactly on the limit of the ring. At this point, the grain boundary has a vertex with an angle of $2\cos^{-1}(\upsilon_\alpha/\upsilon_\beta)$.

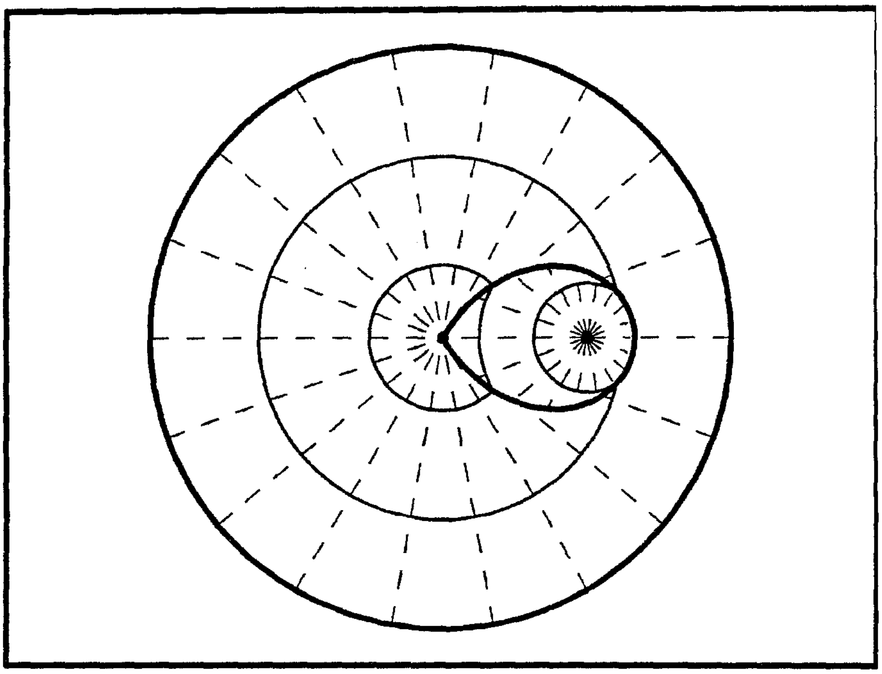

Figure 23 An α spherulite and a β ring. $D/d = v_\beta/v_\alpha = g = 2$ were chosen construction.

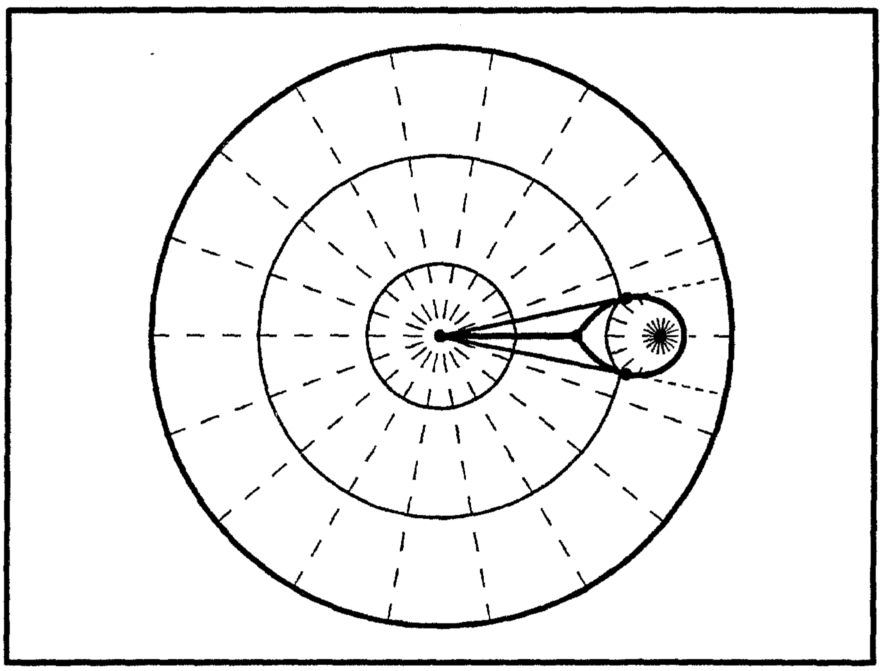

Figure 24 An α spherulite and a β ring. $d = (D + D/g)/2$ and $g = 2$ was chosen for construction.

The run of the closed grain boundary is shown in Fig. 26 for $g = 2$.

3. $0 < d < D$ means that the grain boundary is always a closed curve without vertex as shown in Fig. 27 for $d = D/2$ and $g = 2$.

3. Conclusions

When two growth fronts touch each other, a point of the grain boundary is formed. The authors have investigated the grain boundary which is built by the growth front of a spherulite with a growth front of a straight band, of another spherulite, and of a circular band.

The work surpasses the hithero existing results of Varga [3, 12, 13] in the following ways

1. The formation of growth fronts is investigated using a series of equidistant time marks, which are also called thermic marks. The equidistant time marks represent a series of past growth fronts.

2. The formation of the grain boundary is investigated by the intersection points of the equidistant time marks. So it is easy to obtain the mathematical expression for most grain boundaries.

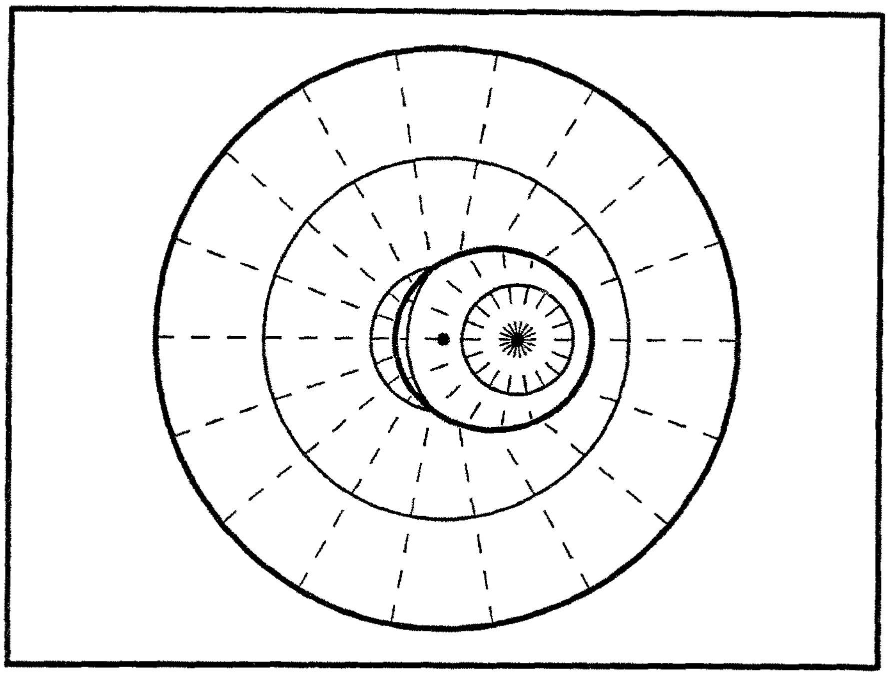

Figure 25 An α spherulite and a β ring. $d = D/(2g)$ and $g = 2$ were chosen for construction. One emphasizes that the grain boundary cannot be described by any ellipse.

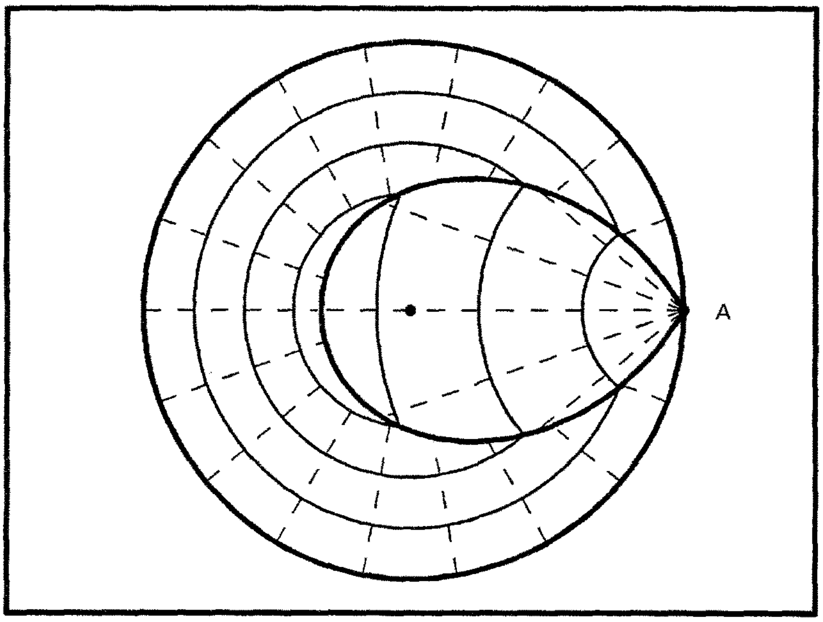

Figure 26 A β spherulite with the nucleus in point A, and an α ring. $d = D$ and $g = 2$ were chosen for construction.

3. The growth shadow has been introduced. Within the region of the growth shadow the growth lines are curved and the growth fronts can be described by evolvents of the grain boundary.
4. Within the growth shadow, finally two symmetrical arcs of a logarithmic spiral end in a vertex. Beginning in the vertex an intrinsic grain boundary is formed.
5. The work in Section 2.3. is completely new. An α spherulite in an α ring gives an ellipse as a grain boundary.

In this paper the authors have deduced theoretically, and in most cases shown experimentally, the formation of spherulitic boundaries. For further information and detailed calculations of all curves presented in this paper see [14].

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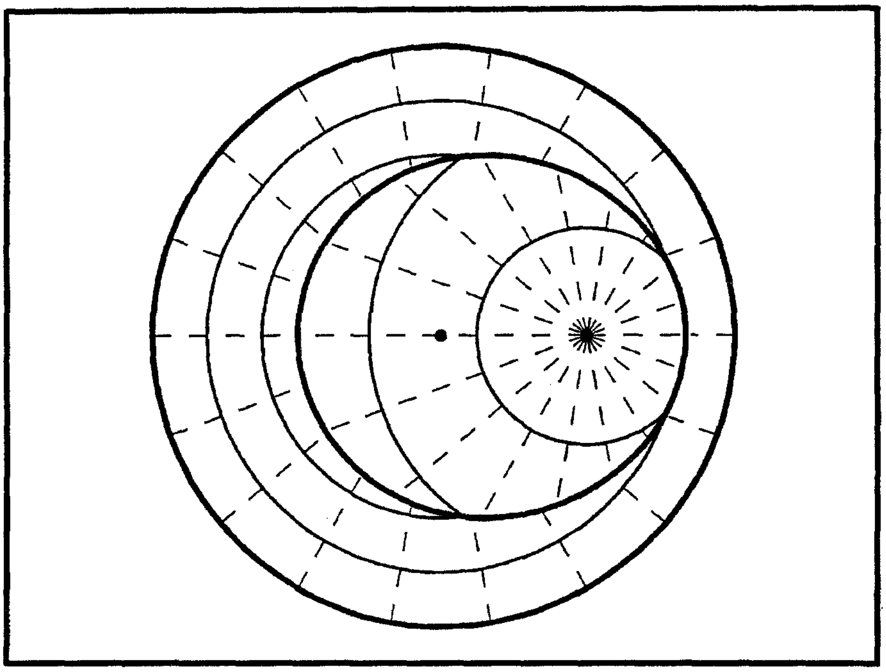

Figure 27 A β spherulite and an α ring. $d = D/2$ and $g = 2$ were chosen for construction. It has to be emphasized that the grain boundary cannot be described by any ellipse.

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