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A growing 2D spherulite and calculus of variations
Part I: A 2D spherulite in a linear field of growth rate

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Abstract: We propose to take the calculus of variations in order to compute the shape of a growing 2D spherulite in an uniaxial field of growth rate. We are concerned with the growth line (a path that is traveled in the shortest possible time from nucleus to a point (x_1, y_1), where a molecule just crystallizes) and the growth front (the times between spherulite and supercooled material). The Euler differential equation—a result of the calculus of variations—is derived for all uniaxial growth rates $v(x)$. Here we especially investigate $v(x) = px + q$.

Key words: 2D spherulite; growth; field of growth rate; calculus of variations; linear growth rate

1. Basic considerations

We regard a 4-μm-thick foil of polypropylene, which is in a supercooled state. First, we investigate the isothermal growth of a spherulite, which grows from a nucleus with a constant radial rate $v(x) = \text{constant}$.

Figure 1 shows such an isothermally growing spherulite. We see that the "growth lines" are radial rays from nucleus to growth front and that the "growth front" is a concentric circle.

The *growth line is a path that runs* from the nucleus to a point (x_1, y_1) of the growth front *in the shortest possible time*. This path is approximately described by the fibrils. An exact description of the growth line by the fibrils is not possible, because of the small-angle branching, which occurs on the tip of the touching fibril [1–3]. Of course, there exists an infinite number of growth lines.

In this study, we will investigate the spherulitic growth if the growth rate v depends on x only (uniaxial) but not on y. This $v(x)$ is isotropic, but constant in time. Isotropic means that at a point (x, y) the rate of growth is the same in all directions.

We investigate a growth line $y(x)$, which starts at the nucleus (0, 0) and ends at a point (x_1, y_1) of the growth front. *We propose* that the *growth line* is *always* the *path*, where *time is minimum.* Therefore, we must seek a time t that is minimum for the growth line $y(x)$. This $y(x)$ is principally determined by the *isotropic growth rate*, $v(x)$, of the spherulite.

This can be expressed mathematically by

$$t\langle y(x)\rangle = \int_{0,0}^{x_1,y_1} \frac{ds}{v(x)}$$

$$= \int_{x=0}^{x_1} \frac{\sqrt{1+y'^2(x)}}{v(x)}\,dx = \text{minimum} \qquad (1)$$

where $\sqrt{1+y'^2(x)}\,dx$ is an element of the growth line $y(x)$, $v(x)$ is the isotropic rate of growth at x, and t is the minimum time for the growth of line $y(x)$. (The element of the growth line path is

$$ds = \sqrt{dx^2 + dy^2} = \sqrt{1 + y'^2(x)}\,dx\,. \qquad (2)$$

The integral has the dimension "time.")

Our problem is thereby reduced to the calculus of variations [4, 5]: the growth line $y(x)$ is an extremal (minimum of time), and the growth front is an orthogonal to the extremals at t. The latter is orthogonal due to the isotropy of the growth rate $v(x)$. Therefore, the growth fronts are *always perpendicular* to the growth lines! (See e.g., Fig. 2.)

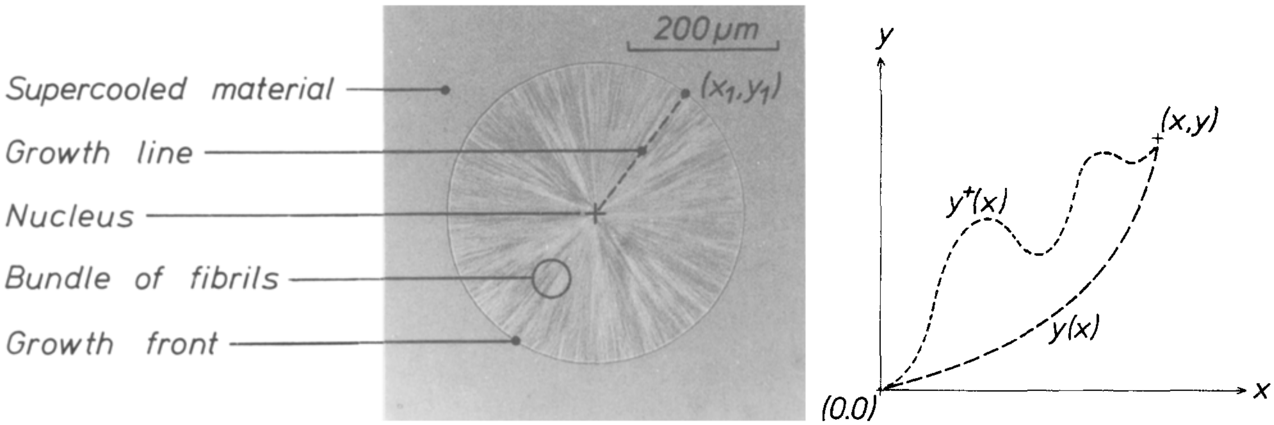

Fig. 1. a) An isothermal grown spherulite of polypropylene. We see a growth line, the growth front, fibrils, supercooled material, and the nucleus. b) The growth line $y(x)$ and a function $y^+(x)$. It holds $y(x) = y^+(x)$ at $(0, 0)$ and at (x, y)

2. Growth line $y(x)$ for $v(x) = px + q$

Equation (1) is solved in a manner given by Euler. We explain this method in Appendix A. The result is the Euler equation, Eq. (A10). With $v(x) = px + q$ the Euler equation is

$$\frac{y'(x)}{(px+q)\sqrt{1+y'^2(x)}} = c_1 \ . \tag{3}$$

Equation (3) is a differential equation for the growth line $y(x)$. Thereby it holds that the nucleus is arranged at $(0, 0)$ and the start angle of $y(x)$ amounts to $\phi(0)$. This is equal to the initial conditions $y(0) = 0$ and $y'(0) = \operatorname{tg}\phi(0)$. Now we solve Eq. (3) with the given initial conditions, but this is done in Appendix B. The result is $y(x, \phi(0))$, but in an implicit form:

$$\left(x + \frac{q}{p}\right)^2 + \left(y - \frac{q}{p}\operatorname{cotg}\phi(0)\right)^2 = \frac{q^2}{p^2 \sin^2\phi(0)} \ . \tag{4}$$

We see in this form that $y(x, \phi(0))$ describes a circle in x and y. The origin of this circle is arranged at $x_0 = -(q/p)$, $y_0 = (q/p)\operatorname{cotg}\phi(0)$ and its radius is

$$r = \frac{q}{p\,|\sin\phi(0)|} \ .$$

Two remarks are made about $y(x, \phi(0))$:

1) For physical reasons it holds that $v(x) = px + q \geq 0$, or $x \geq -(q/p)$. Therefore, we have only a *semicircle*, which is arranged to the right of the straight line $x_0 = -(q/p)$.
2) The start angle $\phi(0)$ can run from 0 to 2π. Therefore, a *family* of semicircles exists for $y_0 = (q/p)\operatorname{cotg}\phi(0)$.

Figure 2 shows these growth lines $y(x, \phi(0) = \text{constant})$ by *dotted* lines. The semicircle with $\phi(0) = (\pi/6)$ $(= 30°)$ is drawn in with $x_0 = -962\ \mu m$ (from the origin $x = 0$, where the nucleus is arranged), $y_0 = 962 \operatorname{cotg} 30° = 1666\ \mu m$, and $r(\pi/6) = 962/\sin 30° = 1924\ \mu m$.

3. Shortest time t for growth line to travel from start angle $\phi(0)$ to end angle ϕ

Now we investigate the time past t where the growth line has progressed from an angle $\phi(0)$ at $t = 0$ to an angle ϕ at t. For this we re-write Eq. (1) as

$$t\langle y(x)\rangle = \int_{(0,0)}^{x_1, y_1} \frac{ds}{v(x)}$$

$$= \int_{\phi(0)}^{\phi} \frac{\sqrt{(dx/d\phi)^2 + (dy/d\phi)^2}}{px(\phi) + q}\, d\phi \ . \tag{5}$$

We form $dx/d\phi$ and $dy/d\phi$ out of Eq. (B8). These are squared and then inserted in Eq. (5). Furthermore, we substitute the $x(\phi)$ from Eq. (B8) into

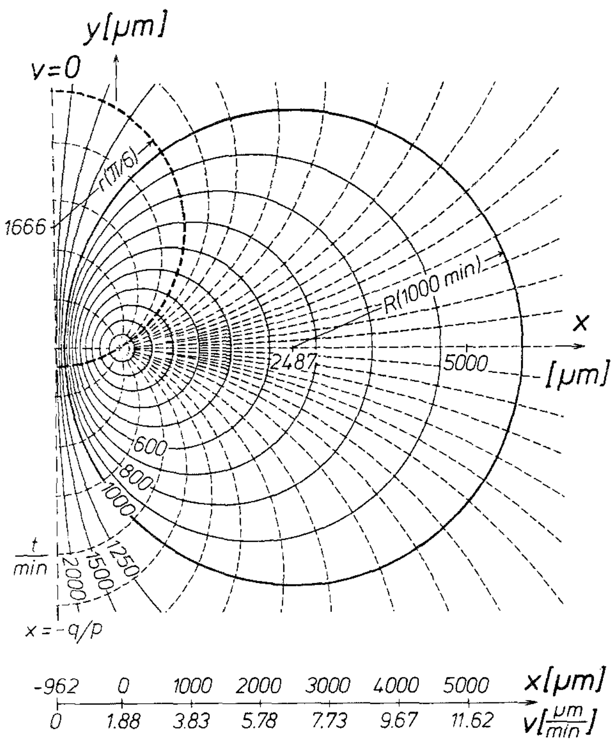

Fig. 2. Schematical representation of a spherulite, which grows with $v(x) = px + q$ ($p = 1.9498 \cdot 10^{-3}$ 1/min, $q = 1.8757$ µm/min). The growth lines are finally semicircles (dotted) and the growth fronts are always circles (solid lines). (Two growth lines that have angles $\phi(0)$ and $\phi(0) + \pi$, complete the growth lines to a semicircle)

Eq. (5) and obtain

$$t = \int_{\phi(0)}^{\phi} \frac{\sqrt{\left(\frac{q}{p\sin\phi(0)}\right)^2 \cos^2\phi + \left(\frac{q}{p\sin\phi(0)}\right)^2 \sin^2\phi}}{p\left(\frac{q}{p\sin\phi(0)}\sin\phi - \frac{q}{p}\right) + q}\, d\phi$$

$$= \frac{1}{p}\int_{\phi(0)}^{\phi} \frac{d\phi}{\sin\phi} = \frac{1}{p}\left\{\ln\left(\operatorname{tg}\frac{\phi}{2}\right)\right\}_{\phi(0)}^{\phi}$$

$$= \frac{1}{p}\ln\frac{\operatorname{tg}\frac{\phi}{2}}{\operatorname{tg}\frac{\phi(0)}{2}}. \tag{6}$$

This gives the shortest time $t(\phi, \phi(0))$ that a growth line travels from an initial angle $\phi(0)$ to an end angle ϕ. After rearrangement, we obtain

$$\operatorname{tg}\frac{\phi}{2} = \operatorname{tg}\frac{\phi(0)}{2} \cdot \exp(pt)\ . \tag{7}$$

4. Growth front $y = y(x, t)$ at t = constant

Now we take again the growth line, Eq. (B8), which is described by two equations $x = x(\phi, \phi(0))$ and $y = y(\phi, \phi(0))$. With Eq. (7), $\phi = \phi(t, \phi(0))$, we obtain from Eq. (B8) $x = x(t, \phi(0))$ and $y = y(t, \phi(0))$. These two equations determine the function $y = y(x, t)$ if we eliminate $\phi(0)$. This is done in Appendix C. The result is the growth front $y = y(x, t)$ at t = constant, but in an implicit form, where

$$\left\{x + \frac{p}{q} - \frac{q}{p}\cosh(pt)\right\}^2 + y^2$$

$$= \left\{\frac{q}{p}\sinh(pt)\right\}^2 \tag{8}$$

We see in this form that $y(x, t)$ also describes a circle. The origin of this circle is at $x_0 = (p/q)[\cosh(pt) - 1]$, $y_0 = 0$ (always at the x-axis), and its radius $R = (q/p)\sinh(pt)$. $y = y(x, t = \text{constant})$ describes the end points of all growth lines at t = constant. These points represent the desired growth front at t = constant!

Figure 2 shows 10 growth fronts $y(x, t = \text{constant})$ for 10 values of constant by solid lines. The growth fronts and the growth lines hit perpendicular. Especially the circle with $t = 1000$ min is drawn in with $x_0 = 962\,[\cosh\ (195 \cdot 10^{-3} \cdot 1000) - 1] = 962 \cdot 2.5855 = 2487$ µm, $y_0 = 0$, and $R = 962 \cdot \sinh(1.95 \cdot 10^{-3} \cdot 1000) = 962 \cdot 3.4432 = 3312$ µm.

5. Field $v(x)$ and the temperature field

One question of concern is: what is the connection between $v(x) = px + q$ and the temperature field $T(x)$? For this reason we investigate the isothermal growth of a spherulite of polypropylene, and we measure its radial growth rate. We find that the growth rate is constant for an isothermal growth. This is calculated for eight different temperatures.

The result of the eight rate measurements is shown in Fig. 3. Moreover, Fig. 3 shows an exponentially fitted curve, $v(T) = \exp(a^+ T + b^+)$ with $a^+ = -0.208$ and $b^+ = 28.7$. This result is well known [6].

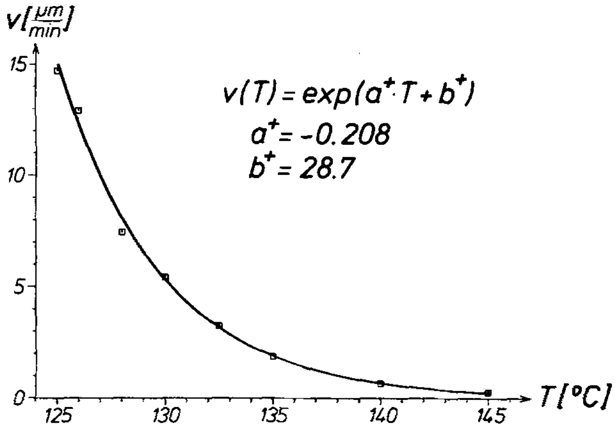

Fig. 3. Eight points of measurement and the fitted curve $v(T) = \exp(a^+ T + b^+)$

Because we know $v(x)$ and $v(T)$, we also know $T(x)$:

$$v(x) = px + q = \exp \ln(px + q) = v(T(x))$$
$$= \exp(a^+ T(x) + b^+) \; .$$

Therefore, we have

$$a^+ T(x) + b^+ = \ln(px + q)$$

and, consequently,

$$T(x) = (1/a^+)(\ln(px + q) - b^+)$$
$$= \ln(px + q)(1/a^+) - b^+/a^+ \; .$$

This uniaxial temperature field $T(x)$ exists if we have

$$v(x) = px + q \; .$$

Appendix A

Derivation of the Euler equation

We determine the function $y(x)$, which brings the integral

$$t\langle y(x)\rangle = \int_{x=0}^{x_1} \frac{\sqrt{1 + y'^2(x)}}{v(x)} dx$$
$$= \int_{x=0}^{x_1} f(x, y')\, dx \qquad \text{(A1)}$$

to minimum and makes the boundary conditions $y(0) = 0$ for $(0, 0)$ and $y(x_1) = y_1 =$ constant for (x_1, y_1).

We assume that there is a function

$$y^+(x) = y(x) + \varepsilon\eta(x) \; , \qquad \text{(A2)}$$

whereby ε is a parameter and

$$\eta(0) = \eta(x_1) = 0 \qquad \text{(A3)}$$

is true. Figure 1b describes $y^+(x)$ and $y(x)$. Due to Eqs. (A1) and (A2), the equation

$$t\langle y^+(x)\rangle = \int_{x=0}^{x_1} f(x, y'(x) + \varepsilon\eta'(x))\, dx \qquad \text{(A4)}$$

is true. With this, $t\langle y^+(x)\rangle$ assumes the function $t(\varepsilon)$. Therefore we obtain

$$\frac{dt(\varepsilon)}{d\varepsilon} = \int_{x=0}^{x_1} \frac{df}{d\varepsilon} dx$$
$$= \int_{x=0}^{x_1} \frac{df}{d(y' + \varepsilon\eta')} \cdot \frac{d(y' + \varepsilon\eta')}{d\varepsilon} \cdot dx \; . \qquad \text{(A5)}$$

For $\varepsilon = 0$ the $t(\varepsilon)$ reaches its minimum. It holds that $dt(\varepsilon)/d\varepsilon = 0$ and we obtain with Eq. (A5)

$$\int_{x=0}^{x_1} \frac{df}{dy'} \cdot \eta' dx = 0 \; . \qquad \text{(A6)}$$

We can do nothing with Eq. (A6). Nevertheless we can use the integration of a product

$$\int_{x=0}^{x_1} uv'\, dx = uv\,|_{x=0}^{x_1} - \int_{x=0}^{x_1} u'v\, dx \; .$$

With Eq. (A3), whereby $uv\,|_{x=0}^{x_1} = 0$, there remains of Eq. (A6)

$$-\int_{x=0}^{x_1} \frac{d}{dx}\left(\frac{df}{dy'}\right)\eta(x)\, dx = 0 \; . \qquad \text{(A7)}$$

Equation (A7) is, in general, only true if

$$\frac{d}{dx}\left(\frac{df(x, y')}{dy'}\right) = 0 \qquad \text{(A8)}$$

is valid, or integrated as

$$\frac{df(x, y')}{dy'} = c \; . \qquad \text{(A9)}$$

With Eqs. (A9) and (A1), we obtain

$$\frac{df(x, y')}{dy'} = \frac{d\dfrac{\sqrt{1 + y'^2(x)}}{v(x)}}{dy'}$$
$$= \frac{d\sqrt{1 + y'^2(x)}}{v(x)\, dy'}$$

$$= \frac{y'(x)}{v(x)\sqrt{1+y'^2(x)}} = c\,. \tag{A10}$$

Equation (A10) is the desired Euler equation, with which we calculate the growth line $y(x)$.

Appendix B

Solution of the Euler equation

We have to solve

$$\frac{y'(x)}{(px+q)\sqrt{1+y'^2(x)}} = c_1\,. \tag{B1}$$

Therefore, it is advisable to make the substitution

$$y'(x) = \operatorname{tg}\phi\,. \tag{B2}$$

Because

$$\frac{\operatorname{tg}\phi}{\sqrt{1+\operatorname{tg}^2\phi}} = \sin\phi\,,$$

it follows from Eq. (B1) that

$$x = \frac{\sin\phi}{pc_1} - \frac{q}{p}\,. \tag{B3}$$

We differentiate Eq. (B3) with respect to ϕ and obtain

$$\frac{dx}{d\phi} = \frac{\cos\phi}{pc_1}\,. \tag{B4}$$

Because of the substitution of Eq. (B2) and because of Eq. (B4), we have

$$dy = \operatorname{tg}\phi\,dx = \operatorname{tg}\phi\frac{\cos\phi}{pc_1}d\phi = \frac{\sin\phi}{pc_1}d\phi\,.$$

By integration, we find

$$y = -\frac{\cos\phi}{pc_1} + c_2\,. \tag{B5}$$

Now we determine c_1 and c_2 at (0, 0) from Eqs. (B3) and (B5):

$$0 = \frac{\sin\phi(0)}{pc_1} - \frac{q}{p}$$

and

$$0 = -\frac{\cos\phi(0)}{pc_1} + c_2\,.$$

This yields

$$c_1 = \frac{\sin\phi(0)}{q} \tag{B6}$$

and

$$c_2 = \frac{p}{q}\operatorname{cotg}\phi(0). \tag{B7}$$

Thereby Eqs. (B3), $x = x(\phi, \phi(0))$, and (B5), $y = y(\phi, \phi(0))$, give the results

$$x + \frac{q}{p} = \frac{q}{p\sin\phi(0)}\sin\phi$$

and (B8)

$$y - \frac{q}{p}\operatorname{cotg}\phi(0) = \frac{-q}{p\sin\phi(0)}\cos\phi\,.$$

These two equations squared and added yield one equation: $y = y(x, \phi(0))$, whereby

$$\left(x+\frac{q}{p}\right)^2 + \left(y - \frac{q}{p}\operatorname{cotg}\phi(0)\right)^2 = \frac{q^2}{p^2\sin^2\phi(0)}, \tag{B9}$$

which was desired.

Appendix C

Calculation of the growth front

We must first change all terms with the arguments ϕ and $\phi(0)$ in Eq. (B8) into terms with the arguments $\phi/2$ and $(\phi(0))/2$, because of Eq. (7). This yields

$$\sin\phi = \frac{2\operatorname{tg}(\phi/2)}{1+\operatorname{tg}^2(\phi/2)}$$

and

$$\cos\phi = \frac{1-\operatorname{tg}^2(\phi/2)}{1+\operatorname{tg}^2(\phi/2)}\,.$$

Correspondingly, the same holds for $\phi(0)$. An example is

$$\operatorname{cotg}\phi(0) = \frac{\cos\phi(0)}{\sin\phi(0)} = \frac{1-\operatorname{tg}^2(\phi(0)/2)}{2\operatorname{tg}(\phi(0)/2)}\,.$$

After a short calculation, we obtain from the

Eq. (B8)

$$x + \frac{q}{p} = \frac{q}{p} \frac{(1 + \mathrm{tg}^2(\phi(0)/2)) \exp(pt)}{1 + \mathrm{tg}^2(\phi(0)/2) \cdot \exp(2pt)} .$$

Rearranged this yields

$$x + \frac{p}{q} - \frac{q}{p} \cosh(pt)$$

$$= \frac{q}{p} \sin h(pt) \frac{1 - \mathrm{tg}^2(\phi(0)/2) \exp(2pt)}{1 + \mathrm{tg}^2(\phi(0)/2) \exp(2pt)} , \quad \text{(C1)}$$

if the equations $\sinh z = 1/2(e^z - e^{-z})$ and $\cosh z = 1/2(e^z + e^{-z})$ are introduced.

From the second Eq. (B8) we obtain after a calculation

$$y = \frac{q}{p} \sinh(pt) \frac{2\mathrm{tg}(\phi(0)/2) \exp(pt)}{1 + \mathrm{tg}^2(\phi(0)/2) \exp(2pt)} . \quad \text{(C2)}$$

Squared and added, these two Eqs. (C1) and (C2) yield

$$\left\{ x + \frac{q}{p} - \frac{q}{p} \cosh(pt) \right\}^2 + y^2$$

$$= \left\{ \frac{q}{p} \sinh(pt) \right\}^2 . \quad \text{(C3)}$$

This is the desired equation of the growth front at t, which is so because

$$\frac{\{1 - \mathrm{tg}^2(\phi(0)/2) \exp(2pt)\}^2 + \{2\mathrm{tg}(\phi(0)/2) \exp(pt)\}^2}{\{1 + \mathrm{tg}^2(\phi(0)/2) \exp(2pt)\}^2} = 1 ,$$

which is easy to show.

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