Long time solutions to the Seto–Frank equations

Marc L. Mansfield
Michigan Molecular Institute, 1910 W. St. Andrews Road, Midland, MI 48640, USA
(Received 4 December 1992)

A previously published solution to the Seto–Frank equations (Mansfield, M. L. *Polymer* 1988, **29**, 1755) that predicts an elliptical profile for the growing crystal can be derived using straightforward geometrical arguments and the known properties of trivial solutions. This simplified derivation clarifies several misconceptions generated by the original derivation.

(Keywords: Seto–Frank equations; crystallization; curved crystals)

INTRODUCTION

It has been generally assumed[1] for years that polymer crystals grow by a secondary nucleation process for which the following problem becomes relevant: begin with a flat substrate, as in *Figure 1a*. New nuclei appear on the substrate at a rate i per unit time and per unit substrate length. These new nuclei produce a pair of steps on the otherwise flat substrate, as in *Figure 1b*. New polymer stems are now able to add to the substrate at sites adjacent to the nucleus in a 'substrate completion' process, which is equivalent to permitting each step to move to the left or to the right, as in *Figure 1c*. Furthermore, it is assumed that all steps move with a uniform velocity $+g$ (right-steps) or $-g$ (left-steps). These steps continue to move with uniform velocity until a left- and a right-step collide and mutually annihilate. A number of questions then arise. For example, is it possible to predict the overall growth rate of the crystal? Furthermore, we can always assume values of i and g that would permit significant concentrations of steps on the face, which would of course also imply that the growing face is either rough or curved. Then, is it possible to predict the shape and roughness of the crystal as it grows?

Seto and Frank[2,3] have introduced a pair of coupled differential equations in order to describe this process. Let $l(x,t)\,dx$ and $r(x,t)\,dx$ represent, respectively, the number of left- and right-steps found in an element of substrate length dx at position x and at time t. The Seto–Frank equations read:

$$\frac{\partial r}{\partial t}+g\frac{\partial r}{\partial x}=i-2grl \qquad (1)$$

$$\frac{\partial l}{\partial t}-g\frac{\partial l}{\partial x}=i-2grl \qquad (2)$$

The left-hand side of the equations represent transport of density to either the right or the left, respectively. The term i on the right-hand side accounts for creation of steps due to nucleation, and the term $-2grl$ on the right accounts for the mutual annihilation of steps. If a length element dx contains $l\,dx$ left steps and $r\,dx$ right steps, and if each step contributes a height b, the height differential across the element is $b(l-r)\,dx$. Therefore, once the functions $r(x,t)$ and $l(x,t)$ are known, then the instantaneous profile $y(x,t)$ may be computed from the expression:

$$\frac{\partial y}{\partial x}=b(l-r) \qquad (3)$$

Finally, the temporal increase in the profile $y(x,t)$ is determined by the fluxes of both left and right moving steps through the point x. Obviously these fluxes are gl and gr, respectively, and we may write:

$$\frac{\partial y}{\partial t}=bg(l+r) \qquad (4)$$

A number of exact and approximate solutions to the Seto–Frank equations have appeared[2–8]. I published an asymptotically exact solution[4,5] several years ago that has met with some empirical success[9]. Unfortunately, certain subtle aspects of that derivation have been poorly understood and as a result, it has come under attack. Since that time, I have come upon a simpler version of the derivation, which should dispel some of the subtleties associated with the original version. In this paper I present the new version of the derivation, and I also answer some of the challenges that have been levelled at the solution.

As emphasized in the original publication[4], this solution is only asymptotically exact, which is to say that it only predicts a certain limiting form of the shape and growth of crystals, but that is hardly any reason to disparage it. The situation is a bit like the standard trick of replacing the form $n(n+1)$ with n^2. Obviously, this is not exact, but it is hardly correct to refer to it as 'erroneous'. The entire question hinges on a consideration of scale: over a scale of unity, this replacement is egregious; while over a scale of n^2, it is quite harmless, and is in

0032–3861/93/234904–04

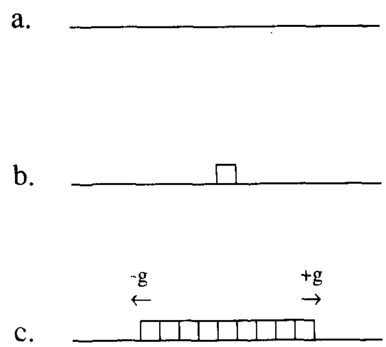

Figure 1 Schematic diagram of the nucleation and substrate completion processes

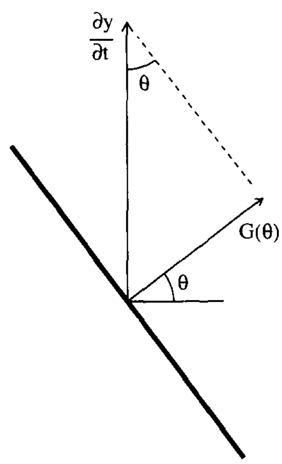

Figure 2 Relationship between the two velocities $G(\theta)$ and $\partial y/\partial t$ for a flat growth front growing according to the Seto–Frank equations

fact what one means by the expression 'asymptotically exact'.

PROPERTIES OF TRIVIAL SOLUTIONS TO THE SETO–FRANK EQUATIONS

The most trivial solution to the Seto–Frank equations is the solution $l=r=$constant. Then, obviously, we obtain:

$$l=r=(i/2g)^{1/2}=L_{\mathrm{F}}^{-1} \tag{5}$$

where the symbol L_{F} represents a quantity with the units of length, which we call the Frank length, $L_{\mathrm{F}}=(2g/i)^{1/2}$. Obviously, L_{F} is the scale of length between steps. Furthermore, equations (3) and (4) predict a uniformly level growth front $\partial y/\partial x=0$ that advances with time according to the equation:

$$\frac{\partial y}{\partial t}=2g(b/L_{\mathrm{F}})=G_{\mathrm{F}} \tag{6}$$

where we have introduced the Frank velocity, $G_{\mathrm{F}}=b(2ig)^{1/2}$. According to these equations, we expect a flat growth front, i.e. neither curved nor rough, since $\partial y/\partial x=0$. Obviously however, the functions $r(x,t)$ and $l(x,t)$ are coarse-grained averages. Local fluctuations of r and l away from their mean value of L_{F}^{-1} do, of course, exist, and therefore, the growth front is never completely flat. These equations really only mean that the growth front will appear to be flat when observed with resolutions much lower than L_{F}.

The next-least trivial solution is obtained by assuming that r and l are again constant, but not necessarily equal to each other. This also constitutes a valid solution, provided the two constants are related as follows:

$$rl=L_{\mathrm{F}}^{-2} \tag{7}$$

Obviously, $\partial y/\partial x$ and $\partial y/\partial t$ are again constants, so this solution also represents a non-curved, 'flat' growth front, moving with constant velocity, but now, since $\partial y/\partial x$ is generally non-zero, the growth front is inclined at an arbitrary angle. Let θ represent the direction normal to the growth front, i.e. the direction in which the front is progressing. (*Figure 2*). Let $G(\theta)$ represent the growth velocity when the growth front is proceeding in the direction θ. Then,

$$G(\theta)=\sin(\theta)\frac{\partial y}{\partial t}=bg(r+l)\sin\theta \tag{8}$$

Since $\theta-\pi/2$ is the angle of inclination of the growth front, we have

$$\frac{\partial y}{\partial x}=b(l-r)=\tan(\theta-\pi/2)=-\cot(\theta) \tag{9}$$

We can now combine equations (7), (8) and (9) to obtain an equation for $G(\theta)$, eliminating r and l. Perhaps the easiest way to proceed is to write $(r+l)^2-(r-l)^2=4rl$, and use equations (8), (9) and (7), respectively, to provide expressions for $(r+l)^2$, $(r-l)^2$ and rl. The result is:

$$G^2(\theta)=G_{\mathrm{F}}^2\sin^2\theta+g^2\cos^2\theta \tag{10}$$

Equation (10) has the general form:

$$r^2=b^2\sin^2\theta+a^2\cos^2\theta \tag{11}$$

which produces, in polar coordinates, curves such as the one shown in *Figure 3*.

SHAPE OF A GROWING CRYSTAL AT LONG TIMES

Assume that we begin with an arbitrarily shaped crystal at $t=0$, and ask what shape will be assumed at long times, assuming the growth is governed by the Seto–Frank equations. Obviously, as time progresses, the growth front at any arbitrary angle θ becomes progressively flatter, and eventually, its radial growth velocity will be given by equation (10). However, equation (10) itself does not predict the shape of the crystal. It states that the growth front travelling in the direction θ will be at a distance $tG(\theta)$ from the origin at time t. Each of these growth fronts defines a straight line

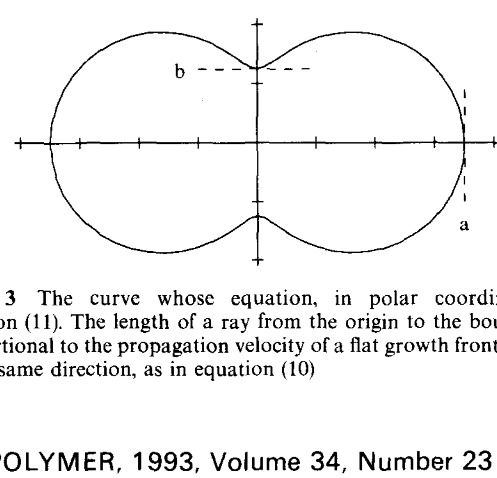

Figure 3 The curve whose equation, in polar coordinates, is equation (11). The length of a ray from the origin to the boundary is proportional to the propagation velocity of a flat growth front growing in the same direction, as in equation (10)

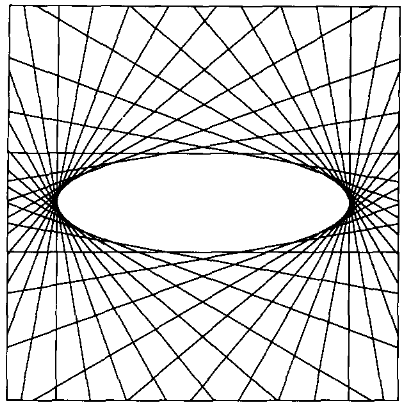

Figure 4 The form of the crystal is the curve that is simultaneously tangent to all possible growth fronts at time t

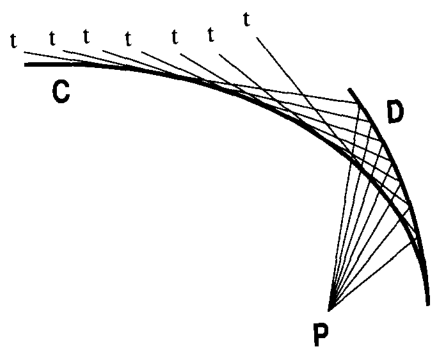

Figure 5 Pedal-point construction of a curve D from a given curve C with respect to the point P

in the plane, and obviously, the form of the crystal at time t will be the curve that is simultaneously tangent to all these lines, i.e. the envelope of the set of straight lines, as shown in *Figure 4*. Below it is shown that the envelope of these lines is the ellipse described in the original paper[4].

The construction of an ellipse from curves such as those shown in *Figure 3* is known, in classical geometry, as a pedal-point construction[10]. Given a curve C and a point P, we draw tangents to C, the lines t in *Figure 5*. Then for each tangent, we draw the perpendicular that passes through the point P. The locus of intersections between the tangents and their perpendiculars defines a second curve, D. Then D is called the pedal curve of C with respect to the point P. Conversely, C is called the inverse or the negative pedal of D with respect to P. Intuitively, the pedal is the curve traced out by the vertex of a carpenter's square when one edge of the square is constrained to be tangent to the original curve and when the other edge is constrained to lie on the point P. Obviously, every curve has a unique pedal and negative-pedal (with respect to a particular point). We are left, then, with the problem of determining the negative-pedal with respect to the origin of the curve whose equation in polar coordinates is equation (11), which I assert is the ellipse whose equation is:

$$\left(\frac{x}{a}\right)^2+\left(\frac{y}{b}\right)^2=1 \qquad (12)$$

The proof of this assertion is probably found somewhere in the classical literature on conic sections. For example, MacLaurin propounded extensively in the 18th century on the theory of pedals[11]. However, since I have been unable to find the proof, I give it in the Appendix.

From this, it follows that at long times, the crystal form predicted by the Seto–Frank equations is the ellipse whose equation is:

$$\left(\frac{x}{tg}\right)^2+\left(\frac{y}{tG_{\mathrm{F}}}\right)^2=1 \qquad (13)$$

It is important to note, however, that this argument breaks down as we move towards $\theta=0$ or $\pm\pi$. For example, if θ is small, then we can show that $r\simeq(b\theta)^{-1}$ and $l\simeq b\theta L_{\mathrm{F}}^{-2}$, which means that $r\gg l$ and that $rb\gg 1$. To maintain such a small value of θ we must insert many more right-steps than left-steps, in fact, we must insert many right-steps at each site. Obviously, if so many right-steps are piled up at the same site, then they present a lateral substrate surface lying at a right angle to the original substrate, and upon which an equivalent growth process can occur. Therefore, each growth front of the growing crystal must be thought of as possessing its own elliptical section, with orientation dictated by the inclination of the growth front, and shape dictated by equation (13) using values of G_{F} and g that appertain to that growth front. Then the overall crystal shape is given, not by a single ellipse, but by the intersection of several ellipses. *Figure 6*, for example, demonstrates how this analysis might be applied to predict the form of a polyethylene crystal. *Figure 6* shows three ellipses, A, B and C. (B and C have large aspect ratios, and are therefore only shown in section.) Ellipse A belongs to the (200) faces of the polyethylene crystal, and has been drawn assuming $(g, G_{\mathrm{F}})=(1.333, 0.5)$ in arbitrary units. Ellipses B and C belong to the (110) faces, and have been drawn assuming $(g, G_{\mathrm{F}})=(100, 1)$ and rotated $\pm 60°$ relative to ellipse A.

The previous publication[4] shows that there is actually some rounding of the elliptical sections in the vicinity of the points of intersection P. However, this rounding extends only over distances comparable to L_{F}, and therefore becomes unimportant when t is large.

FURTHER DISCUSSION

Relationship to the velocity h

The original derivation began by solving the Seto–Frank equations in the interval $(-ht, ht)$, where h is the component of the velocity of the points P parallel to the x-axis (*Figure 6*), and took h as an independent variable, it being assumed that the value of h is dictated by growth on the adjoining face[4]. In the present case, the value of h is determined after the fact, by constructing intersecting ellipses as in *Figure 6*. Since the form of the ellipse proves to be independent of h, the present derivation could have been anticipated from the former:

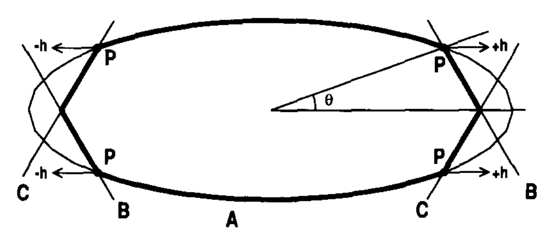

Figure 6 The overall crystal form is expected to be the intersection of several ellipses, one belonging to each crystal face

the absence of a parameter from a given formula generally indicates that the formula can be derived without recourse to the parameter.

Vanishing transport terms in the Seto–Frank equations

The trivial, constant-r, constant-l solutions to the Seto–Frank equations discussed above share a property with the solution as given here or in reference 4, which is that the transport terms [the left-hand sides of equations (1) and (2)] are effectively zero. This fact has led to a few misconceptions about the general solution[5,7,8]. Confusion results from the mistaken belief that if these transport terms are zero for any given solution, then that solution must not correctly treat the transport of steps, and must therefore be erroneous. However, as the trivial solutions indicate, the transport terms also vanish if the $r(x)$ and $l(x)$ profiles are uniform. These solutions still exhibit transport of steps, since, as equation (4) indicates, it is only by the flux of steps past a point x that the profile grows.

For the solution given here, these transport terms only vanish asymptotically, in proportion to $1/t$, since it is only at long times that the ellipse becomes much larger than L_F and that the $r(x)$ and $l(x)$ profiles become featureless over length scales comparable to L_F.

Limitations to the validity of the Seto–Frank equations

The Seto–Frank equations predict significant curvature whenever $G_F \cong g$, since then the ellipse has an aspect ratio near 1. Straight edges are expected when $g \gg G_F$. But $G_F \cong g$ implies $L_F \cong b$ [cf. equation (6)]. As is well-known, $L_F \gg b$ is a condition for the validity of the Seto–Frank equations[2,3]. Therefore, the elliptical profiles of high curvature are suspicious, not because they are invalid solutions of the Seto–Frank equations, but because the Seto–Frank equations themselves are beginning to lose validity. We are currently examining lattice growth models to better understand the limits of validity of these equations, and will be preparing a report of that work shortly.

ACKNOWLEDGEMENT

Partial financial support was provided by the National Science Foundation, Grant no. DMR-8822934.

REFERENCES

1 Hoffman, J. D., Davis, G. T. and Lauritzen Jr, J. I. in 'Treatise on Solid State Chemistry' (Ed. N. B. Hannay), Vol. 3, Plenum, New York, 1966
2 Seto, T. *Rep. Prog. Polym. Phys. Jpn* 1964, **7**, 67
3 Frank, F. C. *J. Crystal Growth* 1974, **22**, 233
4 Mansfield, M. L. *Polymer* 1988, **29**, 1755
5 Mansfield, M. L. *Polym. Commun.* 1990, **31**, 285
6 Toda, A. *Polymer* 1991, **32**, 771
7 Point, J. J. and Villers, D. *J. Crystal Growth* 1991, **114**, 228
8 Point, J. J. and Villers, D. *Polymer* 1992, **33**, 2263
9 Hoffman, J. D. and Miller, R. L. *Macromolecules* 1989, **22**, 3038
10 Hilbert, D. and Cohn-Vossen, S. 'Geometry and the Imagination', Chelsea Publishing, New York, 1956
11 Taylor, C. 'Geometry of Conics', Cambridge University Press, Cambridge, 1881, p. 345

APPENDIX

Here we show that the ellipse, equation (12), is the negative-pedal with respect to the origin of the curve whose equation in polar coordinates is equation (11). Given an ellipse, we construct the tangent at an arbitrary point (x, y) on the ellipse, as in *Figure A1*. Then from the

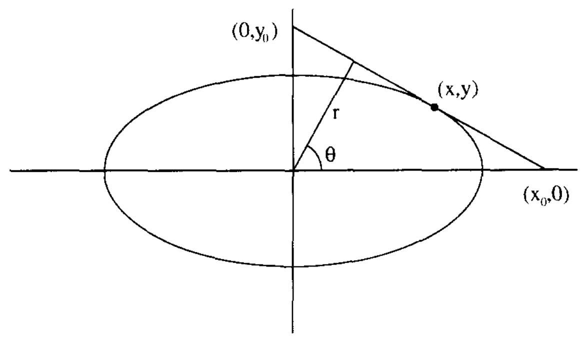

Figure A1 Schematic diagram showing that when a tangent is drawn through an arbitrary point (x, y) on the ellipse of equation (12), the distance of the tangent from the origin, r, is given by equation (11)

tangent we drop a perpendicular to the origin. Assume that the perpendicular has length r and is inclined at the angle θ. Then it is necessary to show that r and θ obey equation (11). Obviously, the tangent has x and y intercepts $x_0 = a^2/x$ and $y_0 = b^2/y$, respectively. Twice the area of the triangle whose edges are the tangent and the two coordinate axes can be written in two equivalent ways:

$$x_0 y_0 = r(x_0^2 + y_0^2)^{1/2}$$

The above expression rearranges to:

$$r^2 = \frac{a^4 b^4}{a^4 y^2 + b^4 x^2}$$

We now multiply this by $1 = (x/a)^2 + (y/b)^2$, and then divide numerator and denominator by $x^2 y^2$ and obtain:

$$r^2 = \frac{a^2 y_0^2 + b^2 x_0^2}{x_0^2 + y_0^2}$$

or

$$r^2 = a^2 \cos^2 \theta + b^2 \sin^2 \theta$$

since x_0^2 and y_0^2 are, respectively, proportional to $\sin^2 \theta$ and $\cos^2 \theta$.

Note added in proof

Professor A. Toda has independently obtained similar results. His report is scheduled to appear in *Faraday Discussions of the Chemical Society*, 1993.