Continuous and Discontinuous Models for Transport Phenomena in Polymers

A model for transport phenomena in polymers accompanied by morphological changes is presented that includes the essential features of a variety of seemingly disparate models available in the literature. The latter are classified as special cases of the model considered, and according to whether discontinuities of the morphology are or are not explicitly described. An ordering analysis is presented that indicates under which conditions one or more of the terms appearing in the differential equations can be neglected. A special subcase, termed surface crystallization, is shown to emerge in a well-defined asymptotic sense from the general model, and is also shown to yield predictions which are closely analogous to those of a model of Astarita and Sarti that has been very successful in correlating experimental data of the type called case II transport. The advantage of the surface crystallization model is that it is not an *ad hoc* model. The models considered result in hyperbolic differential equations, as is often the case when relaxation phenomena are taken into account. A procedure for numerically solving hyperbolic equations with great ease is presented.

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Introduction

Heat and mass transfer phenomena in solid polymers often occur at a macroscopic rate that is not adequately described by ordinary unsteady diffusion theory. Such phenomena are often accompanied by morphological changes, such as swelling, microcavity formation, crystallization, solid-solid phase transitions, and so on.

The observed phenomena can be broadly classified in two categories. The first encompasses phenomena where the morphological change appears to be abrupt, with an occasionally visible sharp front separating two regions of different morphology (Kwei and Zupko, 1969; Hopfenberg et al., 1969; Thomas and Windle, 1977; Enscore et al., 1977; Migliaresi et al., 1981). This category of phenomena has often been referred to as case II transport. As a general observation, at low enough times both the position of the front and the total amount of either mass or heat transported into the polymer are linear functions of time. The second category of phenomena is the one where no sharp morphological discontinuity is observed (and the existence of none needs to be assumed for ad hoc modeling), but the macroscopic transport rate exhibits marked anomalies (Bagley and Long, 1955; Long and Richman, 1960; Berens and Hopfenberg, 1978).

Numerous models have been presented in the literature to describe these phenomena. Work published up to 1979 is reviewed in detail by Joshi (1981); a concise review updated to about 1983 is also available (Astarita, 1987). These are all, in some sense, ad hoc models; in particular, those describing the first category of phenomena are based on physical assumptions that are different from those used in modeling the second category. The most successful models are all based on recognizing explicitly that there are two dependent variables to be considered. The first, θ, is temperature (for heat transfer) and either concentration or chemical potential (for mass transfer); the second, w, is some measure of the morphology of the polymer.

Joshi and Astarita (1979) have presented a model for the second category of phenomena where w is allowed to take values ranging anywhere between 0 and 1; this type of model will be called a continuous model. Astarita and Sarti (1978) give a model where only two possible morphologies are considered (say w is either 0 or 1), so that any morphological change is necessarily abrupt; this type will be called a discontinuous model. These two models have been reasonably successful not only for correlation, but also for prediction, in the sense that results of one type of experiment can be predicted from the models with parameter values extracted from fitting data of another type of experiment.

The question that arises is whether the two categories of phenomena are qualitatively different, or are simply manifestations of different values of some parameter in a yet to be determined more general model that encompasses the existing models as special cases. There is one piece of experimental evidence which seems to suggest that the second hypothesis is the correct one: the behavior observed for a given system may fall into one or the other category depending on the conditions of the experiment, and in particular on the sample size (Berens and Hopfenberg, 1978; Astarita and Joshi, 1978).

The two models referred to above are based on the same general idea, i.e., that in addition to a diffusion equation, one needs to write down a constitutive equation describing the intrinsic kinetics of the morphological change. This results in at least two dimensional parameters: a diffusion time, and some yardstick of the intrinsic rate of morphological change. In continuous models the latter is a characteristic time, but in discontinuous models it is a characteristic velocity; hence the two classes of models are seen to be even dimensionally at odds with each other.

Astarita and Kenny (1986) have recently presented a model for polymer crystallization that is continuous, and have shown rigorously that a discontinuous model emerges as an asymptote when a certain combination of parameters approaches zero. However, the discontinuous model that emerges is the most elementary one; it allows for a discontinuity of w across the front but not of θ. This is a conceptual difficulty, since the successful discontinuous models in fact are based on the assumption that both w and θ suffer a discontinuity at the front.

In this paper we present an attempt to develop a general model, one that, it is hoped, includes all the basic concepts of models existing in the literature. We consider specifically a heat transfer problem, but this entails no loss of generality since the mass transfer case is strictly analogous. The reader is referred to the paper by Astarita and Kenny (1987) both for a detailed discussion of the general approach to modeling relevant to the viewpoint taken in the present work, and for a review of the literature relevant to the heat transfer case.

Differential Equations

We consider a one-dimensional problem in Cartesian coordinates, i.e., physically, a slab of polymer of thickness $2L$, initially in the molten state at the equilibrium melting temperature T^*, both faces of which are brought to temperature T_0 at time zero. Let x be the coordinate orthogonal to the slab's external surfaces located at $x = 0$ and $x = 2L$. If Γ is the latent heat of crystallization, q the heat flux in the positive x direction, c the specific heat per unit volume, and w the degree of crystallinity, the energy balance is:

$$\partial q/\partial x + c\partial T/\partial t = \Gamma \partial w/\partial t \tag{1}$$

The boundary conditions are:

$$x = 0, t > 0, T = T_0 \tag{2}$$

$$t = 0, x > 0, T = T^*, \quad w = 0 \tag{3}$$

$$x = L, \quad q = 0 \tag{4}$$

and a dimensionless temperature θ is readily identified:

$$\theta = (T - T_0)/(T^* - T_0) = (T - T_0)/\delta T \tag{5}$$

Two constitutive equations are needed to close the problem: one for the rate of crystallization, and one for the heat flux. For the first equation we follow the approach of Astarita and Kenny and write:

$$\partial w/\partial t = f(w, \theta)/\tau \tag{6}$$

where τ is a parameter having units of time chosen in such a way that $f(0, 0) = 1$. With this choice, τ is recognized as the intrinsic time scale of crystallization under the imposed temperature driving force δT. f is zero if $\theta \geq 1$ and if $w = 1$; both $\partial f/\partial \theta$ and $\partial f/\partial w$ are nonpositive.

The crucial point of the present analysis is that we investigate the consequences of a somewhat peculiar assumption for the constitutive equation for the heat flux, i.e., that it has a form similar to the Maxwell equation for momentum flux in a viscoelastic fluid. Thus we write:

$$q + \phi \partial q/\partial t = -k\partial T/\partial x \tag{7}$$

with k as the conductivity and ϕ the thermal relaxation time.

As far as we have been able to find out, the first explicit mention in the literature of a constitutive equation for the heat flux of the form of Eq. 7 was published by Cattaneo in 1948. Cattaneo argued that a nonzero value of ϕ is implicit even in the simplest possible molecular model of a continuum, i.e., in the Maxwellian theory of gases regarded as a collection of material points endowed with finite mass but zero volume. This is in fact true. Truesdell (1983) shows that if a Maxwellian gas is kept at rest, the stress tensor relaxes toward its equilibrium value exponentially. Let $\boldsymbol{u}$ be the relative molecular velocity; the stress in a Maxwellian gas is the density times the distribution average of the diadic product $\boldsymbol{uu}$, while the heat flux is the density times the distribution average of $\frac{1}{2}u^2\boldsymbol{u}$; hence if the former exhibits relaxation phenomena, so does the latter. For a Maxwellian gas, ϕ is very small; but in the case of a polymer a much larger and hence macroscopically significant value of ϕ could easily be envisaged. Indeed, the possibility that the constitutive equation for the mass flux in a polymer could be of the form of Eq. 7 has been discussed in the literature (Neogi, 1983).

It is perhaps worth mentioning that Eq. 7 cannot be taken to be generally applicable, since the partial derivative with respect to time is not frame-invariant. Thus in general one should write a properly frame-invariant time derivative, and since there is an infinite variety of such derivatives, a whole spectrum of constitutive equations of the type of Eq. 7 could be considered. However, all such equations reduce to Eq. 7 in a stationary medium as considered here, and hence this point is irrelevant to the present discussion.

The dimensionless independent variables are defined as follows:

$$z = x/L \tag{9}$$

$$\sigma = t/\tau \tag{10}$$

so that the derivative $\partial w/\partial\sigma$ is by definition of order unity. This guarantees that no matter what the value of the other parameters may be, the field of integration extends at least up to $\sigma \approx 1$. With these definitions, three independent dimensionless groups emerge from the differential equations and boundary conditions: the Deborah number D, the Stefan number S, and the intrinsic time scale ratio ϵ:

$$D = \tau k/L^2 c \tag{11}$$

$$S = \Gamma/c\delta T \tag{12}$$

$$\epsilon = \tau/\phi \tag{13}$$

The Deborah number is the ratio of the crystallization time and the diffusion time, and has been considered previously by Astarita and Kenny; the Stefan number emerges also in the classical analysis of the freezing of water presented by Stefan (1891) almost 100 years ago. We believe that the dimensionless group ϵ has never been considered previously in the literature.

By cross-differentiation and substitution of the definitions, the differential equations and boundary conditions of the problem become:

$$D\partial^2\theta/\partial z^2 + S[\partial w/\partial\sigma + (1/\epsilon)\partial^2 w/\partial\sigma^2] = (1/\epsilon)\partial^2\theta/\partial\sigma^2 + \partial\theta/\partial\sigma \tag{14}$$

$$\partial w/\partial\sigma = f(w, \theta) = O(1) \tag{15}$$

$$z = 0, \sigma > 0, \theta = 0 \tag{16}$$

$$\sigma = 0, z > 0, \theta = 1, \quad \partial\theta/\partial\sigma = w = \partial w/\partial\sigma = 0 \tag{17}$$

$$z = 1, q = 0 \tag{18}$$

The boundary condition of Eq. 18 is imposed on the heat flux q, and as long as Eq. 7 is the constitutive equation for the heat flux, it does not by itself imply that the temperature gradient is zero. However, the symmetry of the problem is such that indeed one can write, instead of Eq. 18:

$$z = 1, \quad \partial\theta/\partial z = 0 \tag{19}$$

Classification of Previous Models

A number of models of unsteady heat conduction phenomena are available in the literature. In this section, we classify these models tentatively as subcases of the model considered here. The classification is based on the observation that there are three dimensional parameters in our model that could conceivably be set to zero without losing the problem altogether: the heat relaxation time ϕ, the crystallization time τ, and the latent heat Γ.

The two dependent variables are temperature, θ, and degree of crystallinity, w. A second criterion of classification is the type of discontinuity assumed, or predicted, by the different models for these two variables. We will call a shock a spatial discontinuity of the quantity considered itself, while a spatial discontinuity of the gradient (or of some higher order derivative with respect to z) of the quantity will be called a cusp. A smooth curve is one that has no shocks and no cusps.

The first category of models to be considered is that in which one sets Γ (and hence S) to zero. This has two important consequences. First, the differential equations for θ and w become uncoupled, and hence any model where the crystallization phenomenon is totally disregarded can be considered as a case where $S = 0$, at least as far as the distribution of θ is considered. For such models, σ is not the appropriate dimensionless time, since τ plays no role whatsoever in determining the temperature distribution. Hence for such models the appropriate dimensionless time is redefined as the ratio β of the actual time and the diffusion time:

$$\beta = kt/L^2 c = D\sigma \tag{20}$$

and the differential equation for θ becomes:

$$\partial^2\theta/\partial z^2 = (1/V^2)\partial^2\theta/\partial\beta^2 + \partial\theta/\partial\beta \tag{21}$$

where:

$$1/V^2 = D/\epsilon = k\phi/L^2 c \tag{22}$$

Let $\theta_0[z, \beta]$ be the temperature distribution calculated from a model in this category. The distribution of w can be calculated from the (by now ordinary) differential equation that is obtained from Eq. 15:

$$Ddw/d\beta = f(w, \theta_0[z, \beta]) \tag{23}$$

where z plays the role of a parameter. The Fourier and Cattaneo models belong to this category.

In the Fourier model ϕ is set to zero as well, and the classical heat diffusion equation is obtained, which has a well-known analytical smooth solution. The Cattaneo model is a general model of the $S = 0$ type. The differential equation for θ is thus Eq. 21, which is hyperbolic and therefore admits discontinuous solutions, with discontinuities propagating with speed V. Since a θ shock is imposed at $z = \beta = 0$, this shock propagates with velocity V until it reaches the plane $z = 1$ at $\beta = 1/V\,(1/\sigma^2 = \epsilon D)$. The solution up to that time is analytical, and the problem is the exact analog of the one obtained by considering the phenomenon of momentum transfer in a Maxwell fluid bounded by a flat plate located at $z = 0$ which at time zero is suddenly set in motion; that problem has been discussed in detail in the literature (Rayleigh, 1911; Astarita and Marrucci, 1974; Tanner, 1962). For the momentum transfer problem, the boundary condition at $z = 1$, which has been considered by Denn and Porteous (1971), is the analog of imposing $\theta = 1$; hence when the shock reaches $z = 1$, a new shock is imposed that is reflected backward and again propagates with speed V. In the problem considered here, when the shock reaches $z = 1$, the boundary condition of Eq. 19 only imposes a cusp, which is then reflected backward.

The second category of models is that in which crystallization is regarded as an instantaneous phenomenon, one that takes place abruptly and completely: the degree of crystallinity is allowed to take only two values: 0 (the molten state) and 1 (the crystalline state). The existence of a w shock is assumed in these models, which are in fact formulated as moving-boundary problems. Two boundary conditions need to be imposed at the moving boundary $z = s(\beta)$, since, in addition to the temperature distribution, the $s(\beta)$ function needs to be determined as well. The first boundary condition is simply a heat balance across the

shock front, which requires the rate of heat removal by unsteady conduction through the frozen layer to balance the localized rate of heat generation at the moving boundary. The latter is, in principle, made up of two parts: the latent heat generation due to the crystallization phenomenon, and the sensible heat generation due to a possible temperature shock at the moving boundary. If $\phi = 0$, this yields:

$$z = s(\beta) - 0, \quad \partial\theta/\partial z = (S + 1 - \theta_L)ds/d\beta \tag{24}$$

where θ_L is the temperature to the left of the front.

There are two models in this category, the Stefan model and the Astarita and Sarti model, which differ in what is written down as the second boundary condition. Both models, in addition to setting τ to zero, also assume that ϕ is zero, so that the heat balance boundary condition is indeed Eq. 24, and the differential equation for θ in the frozen layer becomes:

$$\partial^2\theta/\partial z^2 = \partial\theta/\partial\beta \tag{25}$$

In the Stefan model, which was published almost 100 years ago (1891), the second boundary condition is simply $\theta = 1$ at $z = s$, i.e., temperature is assumed not to undergo a shock. Thus Eq. 24 reduces to:

$$z = s(\beta) - 0, \quad \partial\theta/\partial z = Sds/d\beta \tag{26}$$

The solution of the Stefan problem is analytical, and the position of the freeze surface is given by:

$$s = K\sqrt{\beta}, \quad K = K(S) \tag{27}$$

It is important to realize that in the Stefan model, the freeze surface position is proportional to the square root of time; this result also holds for small times if one assumes parameters to depend on temperature. Hence a Stefan-type formulation cannot possibly describe the experimentally observed behavior that has been called case II transport, where s is linear in β, at least for small values of β. This was the point that prompted the formulation of the Astarita and Sarti (1978) model, which differs from the Stefan model only as far as the second boundary condition at the freeze surface is concerned. Instead of assuming that θ has no shock at $z = s$, Astarita and Sarti assumed that it has one, and that in fact the freeze surface advances at a rate governed by the local undercooling:

$$z = s(\beta) - 0, \theta = \theta_L < 1 \tag{28}$$

$$ds/d\beta = UF(1 - \theta_L) \tag{29}$$

where $F(0) = 0$, $F()$ is monotonically increasing, and the (dimensionless) characteristic velocity U is so chosen that $F(1) = 1$ (the corresponding dimensional intrinsic velocity is $U' = Uk/Lc$). Indeed, U is the initial rate of advance of the front, i.e., for sufficiently small β:

$$s = U\beta + O(\beta^2) \tag{30}$$

and the essential feature of case II transport is thus obtained.

A third category of models is that in which ϕ is set to zero. Of course the Fourier, Stefan, and Astarita and Sarti models also fall in this category. The general model in this category (i.e., the one in which $\phi = 0$ is the only assumption) has been presented by Astarita and Kenny (1987); the solution is easily obtained numerically, and both θ and w are smooth.

All the models that have been discussed are based on setting at least one of the three parameters of the model considered here to zero. The question that arises is of course that the limit where the value of a parameter approaches zero may be a singular one, so that the limit of the solution of the complete problem may not coincide with the solution obtained by setting the parameter to zero at the beginning.

Astarita and Kenny have considered (within the limitation of having set $\phi = 0$ at the start) the singular limit that arises when D approaches zero. They have shown that the Stefan model is recovered in a well-defined asymptotic sense: the expansion parameter in the singular limit is the ratio D/S, and the Stefan model represents the exact zero-order solution—i.e., deviations from the Stefan model solution are of order D/S. The first-order approximation is obtained via a boundary layer analysis, with the boundary layer (which is of thickness D/S) staying attached to the moving front that is assumed to exist in the Stefan model. The Astarita and Kenny analysis thus shows that if $\phi = 0$, when D/S approaches zero the w distribution approaches the condition of exhibiting a shock, and the θ distribution that of exhibiting a cusp. In no sense can the Astarita and Sarti model be recovered from the Astarita and Kenny model.

The singular limit considered by Astarita and Kenny is one where a smooth solution approaches asymptotically a discontinuous one. The converse situation arises in the Cattaneo model (where S is set to zero at the start) if the limit $\phi = 0$ is considered: the solution of the Cattaneo problem is discontinuous, but that of the Fourier problem (which is expected to hold asymptotically when $\phi = 0$) is smooth. This singular limit has been repeatedly studied in the mathematical literature (Lions 1973; Zlamal, 1959, 1960, 1963; Bobisud 1967; Widder 1975), and an estimate of the difference between the solutions of the Cattaneo and the Fourier models when ϕ is held fixed has been given recently by Caffarelli and Virga (1986).

A related problem has been considered by Tanner (1962), who analyzed the momentum transfer problem for an Oldroyd-B fluid. In this case, one obtains a differential equation that is the Cattaneo equation with an additional term on the lefthand side, $\delta\partial^3\theta/\partial z^2\partial\beta$. With δ finite, the solution is smooth; as δ approaches zero, the Cattaneo model is recovered asymptotically (perhaps in a well-behaved way), and the latter has of course discontinuous solutions. Hence the Tanner analysis is concerned with a singular limit of the same type as considered by Astarita and Kenny. Indeed, if one writes a constitutive equation for the heat flux in the form suggestd by Neogi (1983), and the lower limiting diffusivity is not neglected, one ends up with the analog of the Oldroyd-B fluid, and thus the Tanner analysis would apply to our problem as well. This is, however, the first step in a possibly infinite hierarchy of constitutive equations of increasing complication, and will not be considered here, since our attention is focused on the case where the simultaneous crystallization phenomenon plays a crucial role.

The whole discussion in this section is restricted to consideration of the several models available for the case in which the value of all parameters is taken to be constant. Of course, this is not in actual fact the case, and generalizations of the basic models that include variable-value parameters have been published. This will not be considered here.

Ordering Analysis

In this section we perform an ordering analysis of Eqs. 14 and 15. At sufficiently small times, the temperature wave has not yet reached the plane $z = 1$, and thus the temperature variation of unity is accomplished over a spatial distance of, say, h, where h is constrained to be ≤ 1. The derivative $\partial w/\partial\sigma$ is of order unity by definition. The five terms appearing in Eq. 14 thus have orders of magnitude estimated at:

$$D/h^2; \quad S; \quad S/\epsilon\sigma; \quad 1/\epsilon\sigma^2; \quad 1/\sigma \tag{31}$$

Now consider a neighborhood of time zero determined by the following condition:

$$\sigma \ll 1/S \tag{32}$$

This is certainly a neighborhood of pragmatic interest, unless S is very significantly larger than unity. If Eq. 32 is satisfied, the term of order $S/\epsilon\sigma$ can be neglected as compared to the term of order $1/\epsilon\sigma^2$, and the term of order S can be neglected with respect to the term of order $1/\sigma$; hence Eq. 14 degenerates into the Cattaneo equation:

$$D\partial^2\theta/\partial z^2 = (1/\epsilon)\partial^2\theta/\partial\sigma^2 + \partial\theta/\partial\sigma \tag{33}$$

One thus comes to the conclusion that the Cattaneo equation is guaranteed to be asymptotically valid in the neighborhood of time zero determined by the condition in Eq. 32. A temperature shock will propagate with dimensionless (z, σ) speed $\sqrt{(D\epsilon)}$, which corresponds to a dimensional speed $\sqrt{(k/c\phi)}$. This speed is constant in time, and $\theta = 1$ at z values to the right of the shock; it follows that $w = 0$ to the right of the shock.

Now consider a point located at some position z^* that satisfies the following condition:

$$z^* \ll \sqrt{(\epsilon D/S^2)} \tag{34}$$

Such a point will be reached by the θ shock at a time σ^* given by:

$$\sigma^* = z^*/\sqrt{(\epsilon D)} \tag{35}$$

which still satisfies the condition of Eq. 32. Hence, up to $\sigma = \sigma^*$ no crystallization has taken place. As the point considered is reached by the shock, it is suddenly exposed to a θ value less than unity, and hence crystallization starts at a finite rate. One thus concludes that the w distribution will present a cusp ($\partial w/\partial\sigma$ is discontinuous) but not a shock.

Now consider the case where the following condition is satisfied:

$$S^2 \ll D\epsilon \tag{36}$$

This guarantees that the condition of Eq. 34 is satisfied for every z^* in the integration field, and hence that the Cattaneo equation holds up to when the θ shock has reached the plane $z = 1$, which will happen at a time $1/\sqrt{(D\epsilon)}$. If furthermore:

$$1 \gg D\epsilon \tag{37}$$

the θ shock will reach the $z = 1$ plane at a time large as compared to the intrinsic time scale of crystallization ($\sigma \gg 1$), and hence when the shock does reach the plane $z = 1$ crystallization will be essentially complete: the phenomenon is, under these conditions, entirely governed by the speed of propagation of the θ shock predicted by the Cattaneo model.

It is of interest to consider how realistic it is that the conditions of both Eq. 36 and Eq. 37 are satisfied. The following condition:

$$1 \gg S^2 \tag{38}$$

guarantees that both Eq. 36 and Eq. 37 can be satisfied, but not that they in fact are. Condition 38 is certainly not unrealistic. Condition 36 is less realistic, although by no means impossible to conceive. The righthand side is $\tau^2 k/L^2 c\phi$, and even for very small values of ϕ the quantity $D\epsilon$ may not be extremely small in the case of very thin samples—for which most of the anomalous transport behavior reported in the literature has been observed.

As discussed before, the limit $S = 0$ is not a singular one, but the limits $D = 0$ and $1/\epsilon = 0$ are singular. We now turn attention to these two limits. Setting $1/\epsilon = 0$ at the start produces the Astarita and Kenny formulation; by analogy with the Caffarelli and Virga analysis (which is restricted to the case $S = 0$), it is presumable that indeed when ϕ approaches zero the solution of the equations of the complete model approaches that of the Astarita and Kenny one. The regularity of the limit could stand closer inspection, but this point will not be discussed in detail here. Rather, we focus attention on the case where D approaches zero; i.e., the intrinsic time scale of crystallization becomes very small as compared to the diffusion time.

The reduced equation, obtained from Eq. 14 by setting $D = 0$, has the following trivial solution:

$$\theta = 1; \quad w = 0 \tag{39}$$

which satisfies both Eq. 14 and Eq. 15, as well as all boundary conditions except Eq. 16.

Since the phenomenon considered cannot reach equilibrium in a time shorter than the heat diffusion time L^2c/k, i.e., $\sigma = 1/D$, one is interested in a σ time range well in excess of unity. Now near the $z = 0$ plane $\theta \approx 0$, and hence crystallization is complete over a time range $\sigma \approx 1$. It follows that a crystallized layer is guaranteed to exist near $z = 0$ at $\sigma \gg 1$, where the second and third terms on the lefthand side of Eq. 14 are zero simply because, when $w = 1$, $\partial w/\partial\sigma = 0$. The Cattaneo equation holds in the crystallized layer:

$$D\partial^2\theta/\partial z^2 = (1/\epsilon)\partial^2\theta/\partial\sigma^2 + \partial\theta/\partial\sigma \tag{40}$$

Let s be the thickness of the crystallized layer. The three terms appearing in Eq. 40 have the following orders of magnitude:

$$D/s^2; \quad 1/\epsilon\sigma^2; \quad 1/\sigma \tag{41}$$

Two subcases arise now, according to the value of the parameter ϵ, i.e., $\epsilon \geq 1$, and $\epsilon \ll 1$. Notice that the whole analysis developed here has to do with the case where τ is very small, so that the first subcase is one where ϕ is very small as well; this, for reasons that will become clear later, will be called the Stefan limit. The second case does not require ϕ to be large in comparison to the

diffusion time, but only in comparison with the (implicitly small) crystallization time τ; this second case will be called the case II limit.

In the Stefan limit, since one restricts attention to σ values well in excess of unity, it follows that $\epsilon\sigma \gg 1$, and hence the first term on the righthand side of Eq. 40 can be neglected with respect to the second one; heat conduction through the crystallized layer is thus governed by the ordinary Fourier unsteady diffusion equation. Since the lefthand side and the righthand side of Eq. 40 need to be equal, one concludes that:

$$s = 2M(S)\sqrt{(D\sigma)} = 2M(S)\sqrt{\beta} \tag{42}$$

with M a constant to be determined; i.e., the thickness of the crystallized layer is proportional to the square root of time, as it is in the Stefan model.

In the case II limit, one may first restrict attention to a time range defined by:

$$1 \ll \sigma \ll 1/\epsilon \tag{43}$$

which in this limit is guaranteed to exist. In this time range, the second term on the righthand side of Eq. 40 can be neglected, and one now obtains:

$$s = N(S)\sigma\sqrt{(D\epsilon)} = N(S)\beta\sqrt{(\epsilon/D)} \tag{44}$$

with, again, N a constant yet to be determined; i.e., the thickness of the crystallized layer is proportional to the first power of time, as it is in the case II theory for low enough times.

The initial rate of advance of the front, which according to Eq. 44 is constant in time, is given by:

$$ds/d\beta = N(S)\sqrt{(\epsilon/D)} \tag{45}$$

It follows that if the Astarita and Sarti model is in some sense compatible in an asymptotic sense with the present model, the dimensionless characteristic velocity U appearing in Eq. 29 is $N(S)\sqrt{(\epsilon/D)}$. The dimensional characteristic velocity U' is identified as:

$$U' \equiv N(S)\sqrt{(k/\phi c)} \tag{46}$$

Equation 46 shows that if a case II transport model endowed with a characteristic velocity is to emerge in any asymptotic sense, the heat flux relaxation time ϕ needs to be different from zero.

Canonical Formulation

The Cattaneo constitutive equation for the heat flux results in a diffusion equation that is hyperbolic. Hyperbolic problems are best formulated in canonical form, with only first-order derivatives; this is easily obtained by skipping the elimination of q between Eqs. 1 and 7. Let g be the dimensionless heat flux in the z direction, which is defined as:

$$g = qL/k\delta T \tag{47}$$

so that Eq. 7 takes the form:

$$g + (D/\epsilon)\partial g/\partial\beta = -\partial\theta/\partial z \tag{48}$$

Equation 1 takes the following form:

$$\partial g/\partial z + \partial\theta/\partial\beta = S\partial w/\partial\beta = (S/D)f(w, \theta) \tag{49}$$

and the boundary conditions are:

$$\theta(z, 0) = 1; \quad g(z, 0) = 0; \quad w(z, 0) = 0 \tag{50}$$

$$\theta(0, \beta) = 0; \quad g(1,\beta) = 0 \tag{51}$$

i.e., Riemann jump boundary conditions are imposed on the hyperbolic set. Thus a shock wave is generated, and jump balance conditions need to be written down. These need to be considered carefully in the limit $D = 0$.

The jump balance conditions can be obtained as follows. Let V be the speed of propagation of the shock, $s(\beta)$ the instantaneous position of the shock (so that $ds/d\beta = V$), and let z' be defined as:

$$z' = s - z \tag{52}$$

Given any quantity $\Omega = \Omega(z, \beta) = \Omega^*(z', \beta)$, one has:

$$\partial\Omega/\partial z = -\partial\Omega^*/\partial z'; \quad \partial\Omega/\partial\beta = \partial\Omega^*/\partial\beta + V\partial\Omega^*/\partial z' \tag{53}$$

Equation 53 is substituted in the canonical set, and the integral over z' ranging from $-\Phi$ to $+\Phi$ is taken of all terms in the set; the limit for Φ approaching zero is then taken. Let $[\Omega]$ represent the jump of Ω, i.e., the difference of the values of Ω to the right and to the left of the shock. Terms of the type $\partial\Omega^*/\partial\beta$, as well as any finite term, yield in the limit $\Phi = 0$ a value of zero; terms of the type $\partial\Omega^*/\partial z'$ reduce to $[\Omega]$. Hence one obtains, for the set of Eqs. 48 and 49:

$$DV[g]/\epsilon = [\theta] = 1 - \theta_L \tag{54}$$

$$[g] = V([\theta] - S[w]) \tag{55}$$

Now in the case where $D = 0$, crystallization is abrupt, and hence $[w] = -1$, and Equation 55 reduces to:

$$[g] = V(S + [\theta]) \tag{56}$$

For the time being, attention will be restricted to the case $D = 0$ (but D/ϵ is finite); this case will be called the surface crystallization limit.

Equation 56 is somewhat peculiar and should be discussed in some detail. The jump balance conditions in their classical form (Truesdell and Toupin, 1961) are based on the hypothesis that any source term (and $S\partial w/\partial\beta$ is of course a source term in the heat diffusion equation) is everywhere bounded. This would reduce Eq. 56 to $[g] = V[\theta]$, and the jump balance conditions would be formulated in the classical form known as Kotchine's theorem. Foraboschi (1974) has considered the case of a localized source term that represents a finite rate of generation per unit area of the shock surface, and he writes (the appropriate generalized equivalent of) Eq. 56, which he calls the generalized Kotchine theorem, by directly considering such a surface generation term in the jump balance equations.

The jump conditions, Eqs. 54 and 56, furnish immediately the appropriate boundary conditions for the Stefan model. In fact,

when $D/\epsilon = 0$, Eq. 54 implies that $[\theta] = 0$, i.e., the assumption that no θ shock exists at the freeze surface is shown to be correct. With $[\theta] = 0$, Eq. 56 reduces to $VS = [g]$, which is equivalent to Eq. 26; both boundary conditions of the Stefan model are thus recovered.

Now turn attention again to the general case where D/ϵ is finite. $[g]$ can be eliminated between Eqs. 54 and 56 to yield:

$$DV^2/\epsilon = (1 - \theta_L)/(S + 1 - \theta_L) \tag{57}$$

Several important observations can be made concerning Eq. 57. First, for the case $S = 0$ (which is known to be equivalent to the original Cattaneo model), $DV^2/\epsilon = 1$, i.e., the shock propagates with constant speed $V = \sqrt{(\epsilon/D)}$, although θ_L does change in time. This guarantees that the Cattaneo model is recovered asymptotically in a regular way.

The second observation is that the initial rate of propagation of the shock is finite. Indeed, at $\beta = 0$, $\theta_L = 0$, and thus:

$$U = V(0) = 1/\sqrt{[D(S + 1)/\epsilon]} \tag{58}$$

which is in perfect agreement with Eq. 45. The function $N(S)$ has now been determined to be:

$$N(S) = 1/\sqrt{(S + 1)} \tag{59}$$

It is also worth noticing that this initial speed of propagation is smaller than that resulting from the Cattaneo model: the crystallization phenomenon slows down the speed of propagation.

Another important point to be stressed is that when S is different from zero, the shock propagates at a speed that is not constant in time, since, as time progresses θ_L increases from its initial value of zero to its asymptotic value of unity. Since $dV/d\theta_L$ is negative when S is nonzero, the speed of propagation decreases with increasing time, and it thus stays smaller than the Cattaneo value at all times. Two observations are important in this regard. First, a speed of propagation of the shock that is not constant is obtained without allowing the parameters to be variable. Second, the stability or entropy criterion that the shock wave speed should not exceed the wave speed is satisfied.

Finally, one is now in a position to assess the status of the Astarita and Sarti model. First compare the equation for the speed of propagation of the shock wave, Eq. 57, with Eq. 29, which is the assumption of the Astarita and Sarti model. With U identified as in Eq. 58, the function F appearing in Eq. 29 is identified with:

$$F^2 = (S + 1)(1 - \theta_L)/(S + 1 - \theta_L) \tag{60}$$

This is indeed, at least at fixed S, a function only of $1 - \theta_L$, which has a value of 1 if $\theta_L = 0$ and of 0 if $\theta_L = 1$. However, the value of F does depend on S, which was not considered by Astarita and Sarti. Also, if formulated as a moving-boundary problem, the lefthand side of Eq. 24 should be written as $-g$, not as $\partial\theta/\partial z$, as was done by Astarita and Sarti. Finally, it should be considered that the diffusion equation in the crystallized layer should be the hyperbolic Cattaneo equation, not the parabolic Fourier equation written by Astarita and Sarti.

One thus comes to the conclusion that the Astarita and Sarti model is an *ad hoc* model that cannot emerge in any rigorous asymptotic sense. However, it presents qualitative features that are loosely but closely analogous to those of the surface crystallization model: an initial finite rate of propagation of the front that eventually decreases, and a θ shock strictly related to the instantaneous shock propagation speed. It is therefore presumable that the success of the Astarita and Sarti model in correlating and predicting experimental data would be enjoyed also by the surface crystallization model.

Simplified Formulation

Before analyzing in detail the characteristics of the solution to the general model equations, it is useful to simplify the formulation by making use of the following considerations. As long as ϕ is finite, a θ shock will propagate at a finite speed, and the values of θ and w to the right of the shock are simply the initial ones, $\theta = 1$ and $w = 0$. It follows that boundary condition Eq. 18 (or, equivalently, Eq. 19) is never actually used until the θ shock reaches the plane $z = 1$. It is therefore best to formulate the problem by considering a semiinfinite slab of polymer ($L = \infty$), since the solution to this simpler problem will coincide with that of the finite slab problem up to the time the shock reaches the midplane. Of course, the case $L = \infty$ has one less dimensional parameter, and thus also one less dimensionless group.

Since in the simplified formulation the problem has no intrinsic length scale, the new dimensionless variables are defined as:

$$y = x\sqrt{(c/\phi k)} \tag{61}$$

$$\alpha = t/\phi \tag{62}$$

$$p\delta T = q\sqrt{(\phi/kc)} \tag{63}$$

so that the canonical set becomes:

$$\partial p/\partial y + \partial\theta/\partial\alpha = S\partial w/\partial\alpha \tag{64}$$

$$\partial p/\partial\alpha + \partial\theta/\partial y = -p \tag{65}$$

$$\partial w/\partial\alpha = f(w, \theta)/\epsilon \tag{66}$$

$$p(y, 0) = w(y, 0) = 0, \quad \theta(y, 0) = 1 \tag{67}$$

$$p(\infty, \alpha) = \theta(0, \alpha) = 0 \tag{68}$$

The set is hyperbolic, and the imposed jump thus propagates with speed $W = d\mu/d\alpha$, with $\mu(\alpha)$ the instantaneous position of the jump. The jump conditions are:

$$W[p] = [\theta] \tag{69}$$

$$[p] = W([\theta] - S[w]) \tag{70}$$

If the rate of crystallization is finite, $[p] = [\theta]$, $W = 1$; in the classical hyperbolic problem, the speed of propagation is constant unless the parameters are allowed to be variable. When ϵ approaches zero, so that crystallization occurs completely and abruptly as soon as θ becomes even differentially smaller than unity, $[w] = -1$, and Eq. 70 becomes:

$$[p] = W([\theta] + S) \tag{71}$$

and, by elimination of $[p]$:

$$W^2 = [\theta]/(S + [\theta]) \tag{72}$$

Surface Crystallization

In the simplified formulation discussed in the preceeding section, the initial speed of propagation of the w shock is given by:

$$W_0^2 = 1/(S + 1) \tag{73}$$

However, the shock eventually propagates at a progressively smaller speed. Therefore, the position of the front is not known in advance, and thus the problem needs to be formulated as a classical moving-boundary problem, as discussed below.

Numerical solution of a hyperbolic set of differential equations presents several difficulties (Lax and Wendroff, 1960; Alexander et al., 1979; Miller and Miller, 1981). The difficulties are of course connected with the existence of discontinuities, and are particularly severe when the position of the discontinuity is not known in advance, as in the case at hand.

Since $[w] = -1$, at $y < \mu(\alpha)$ crystallization is complete ($w = 1$), and therefore $\partial w/\partial\alpha = 0$, so that Eq. 64 reduces to:

$$\partial p/\partial y + \partial\theta/\partial\alpha = 0 \tag{74}$$

The solution to the system of Eqs. 65–74 is sought for $0 \le y < \mu(\alpha)$, with $\mu(0) = 0$, i.e., in the hatched area in Figure 1. For $y > \mu(\alpha)$, $\theta = 1$ and $w = p = 0$, so that the temperature to the left of the front is $1 - [\theta]$, and the heat flux to the left of the front is $-[p]$. The boundary conditions are:

$$\theta(0, \alpha) = 0 \tag{75}$$

$$(d\mu/d\alpha)p(\mu, \alpha) = \theta(\mu, \alpha) - 1 \tag{76}$$

which, together with Eq. 71 and the condition $\mu(0) = 0$ determine both the p and θ distributions and the boundary $\mu(\alpha)$.

There is a last difficulty with the numerical solution of the model equations, and that is connected with the fact that the initial field of integration has a zero extension along the y axis. This difficulty is circumvented as follows. In a neighborhood of time zero, a solution valid within $O(\alpha)$ is easily obtained:

$$\mu = \alpha/\sqrt{Q} \tag{77}$$

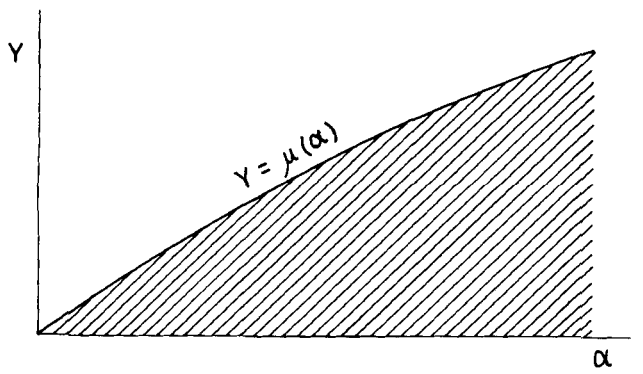

Figure 1. Domain of integration.
For the hyperbolic problem, the whole positive quadrant; for the moving boundary form, only the hatched area.

$$\theta = ay \tag{78}$$

$$p = -\sqrt{Q} + b\alpha \tag{79}$$

where $Q = S + 1$. The heat balance differential equation, Eq. 74, and the boundary condition at the exposed surface, Eq. 75, are satisfied exactly for any choice of the constants a and b; the differential constitutive equation, Eq. 65, can only be satisfied to within $O(\alpha)$, and it requires that $a + b = \sqrt{Q}$. Should one choose to satisfy exactly Eq. 76, which is the jump condition emerging from the constitutive equation, one would need to have $a = b = \sqrt{Q}/2$ and the heat balance at the front, Eq. 71, would be satisfied to within $O(\alpha)$. Alternatively, one may choose to satisfy the latter exactly with $a = Q\sqrt{Q}/(Q + 1)$, $b = \sqrt{Q}/(Q + 1)$, and Eq. 76 is satisfied to within $O(\alpha)$. Satisfying exactly the balance equations seems the appropriate choice, which we have used as the starting distribution for our numerical calculation.

In our finite-difference scheme, the field of integration $0 < y < \mu$ was divided into ten intervals. Since at the starting point of the calculation μ is small, so is the interval δy, and should the numerical stability condition valid for the parabolic diffusion equation, $\delta\alpha \le \delta y^2/2$, also hold in this case, one would need to use an extremely small initial time interval. However, it turns out that this condition can be grossly violated without running into any problem of numerical stability. As μ approaches the value of unity, the stability criterion for the diffusion equation needs to be satisfied, but this now corresponds to large time intervals and no difficulty arises. Details on the numerical procedure are given in a thesis soon to be completed (Ocone 1987).

For the case $S = 0$, an analytical solution is available, so that a check of the correctness of the procedure is possible for this case. The calculated temperature distributions agreed to within no more than 1% difference with the theoretical values.

Figure 2 gives plots of the position of the crystallization front vs. time for three values of S: 0.2, 1, and 5. Several observations are in order. First, the initial constant speed of propagation given by Eq. 73 is observed up to rather large values of α. This is in agreement with the experimental observation that the linear behavior of case II transport is observable over a wide range of

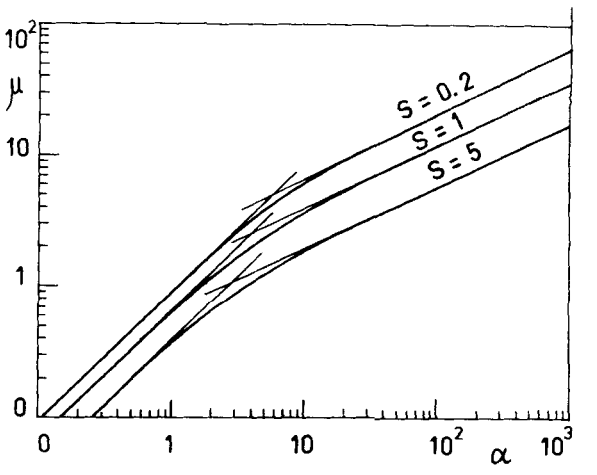

Figure 2. Front position as a function of time.
Lines of slope 1 on the left calculated from Eq. 73; lines of slope ½ on the right calculated from the Stefan model. The curves are obtained numerically.

parameters. Following this, a smooth transition occurs during which $0.5 < d \ln \mu / d \ln \alpha < 1$; again, this is in agreement with experimental observations (in the literature, the situation where $d \ln \mu / d \ln \alpha$ is between 0.5 and 1 has been termed anomalous diffusion). At very long times, the curves for any finite value of S asymptotize to lines of slope 0.5. This is not surprising, since at sufficiently long times a Stefan-type behavior is expected: $\partial p / \partial \alpha$ becomes negligible as compared to p in Eq. 65, while in Eq. 71 [θ] becomes negligible as compared to S, and thus the model equations approach those of the classical Stefan problem, for which μ is proportional to $\sqrt{\alpha}$. Indeed, the straight lines of slope 0.5 in Figure 2 are not fitted to the numerically calculated data, but are obtained from the solution of the Stefan model.

Figure 3 gives temperature distributions at three different times for the case $S = 1$. Figures 2 and 3 should be compared with Figures 1–4 of Astarita and Sarti (1978) to realize that the predictions of the two models are qualitatively very similar (the analog of S is the q parameter in the Astarita and Sarti analysis).

A final observation is in order. The technique of transforming a hyperbolic problem into a moving-boundary problem, with boundary conditions deduced from the jump conditions, appears to be applicable to all hyperbolic problems; this technique enormously reduces the difficulties of the numerical solution, since in the actual domain of integration there are no discontinuities.

Boundary Layer Analysis

The $\epsilon = 0$ limit is singular, as can be seen by writing the canonical set for the $y - \sigma$ variables:

$$\partial w / \partial \sigma = f(w, \theta) \tag{80}$$

$$\epsilon \partial p / \partial y + \partial \theta / \partial \sigma = S \partial w / \partial \sigma \tag{81}$$

$$\partial p / \partial \sigma + \epsilon \partial \theta / \partial y = -\epsilon p \tag{82}$$

Singular limits of this type are dealt with by following the classical boundary layer expansion procedure. First, an "outer" solution is obtained for the reduced equations, i.e., those obtained by setting $\epsilon = 0$. Since the highest order derivative is lost, not all boundary condition can be satisfied. For the case at hand, the outer solution is, trivially:

$$p = w = 0, \theta = 1 \tag{83}$$

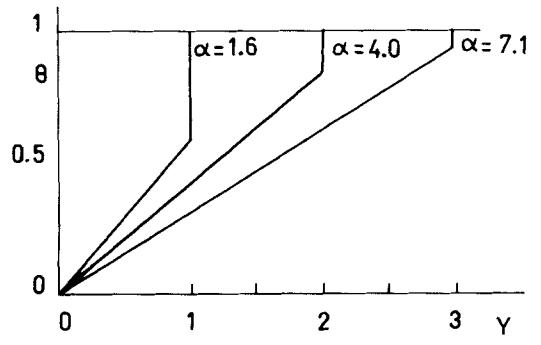

Figure 3. Temperature distributions at three different times for $S = 1$.

which satisfies the differential equations as well as all the boundary conditions except $\theta(0, \sigma) = 0$.

A rather subtle question about the validity of this outer solution is as follows. As ϵ approaches zero, the rate of crystallization becomes very large, say of order $1/\epsilon$, unless either w or θ is extremely close to unity. At the same time, as long as ϵ is finite a θ discontinuity propagates with constant speed $W = 1$, and therefore at $y < \alpha$ the temperature is necessarily less than unity—so that there may be some difficulty in accepting the outer solution given by Eq. 83. However, as shown in the Appendix, in the region between the discontinuity predicted by the surface crystallization model and the actual discontinuity located at $y = \alpha$, the value of θ differs from unity by an amount that is negligibly small even as compared to ϵ, and hence Eq. 83 is indeed the correct outer solution.

One is now tempted to assume that a boundary layer exists near the $y = 0$ surface, where the boundary condition is violated by the outer solution. However, at $y = 0$ the initial rate of crystallization is unity in the σ time scale, and hence at α values well in excess of ϵ a crystallized layer will exist near the exposed surface. This layer will have a thickness $\mu(\alpha)$, and within it the differential equations are Eqs. 65 and 74, subject to $\theta(0, \alpha) = 0$ and to matching conditions at $y = \mu$ which are expected to emerge from the boundary layer analysis. The boundary layer is sandwiched between the crystallized and the molten layers; it is expected to have a small thickness δ, through which w changes steeply but continuously from 0 on the right to 1 on the left.

Since the boundary layer is around $y = \mu(\alpha)$, a stretched coordinate is defined as follows:

$$u = (y - \mu)/\delta \tag{84}$$

The coordinate transformation from y, α to u, α leads to:

$$\partial / \partial y = (\partial / \partial u)/\delta \tag{85}$$

$$(\partial / \partial \alpha)_y = (\partial / \partial \alpha)_u - (W/\delta)\partial / \partial u \approx -(W/\delta)\partial / \partial u \tag{86}$$

which show that, to within $O(\delta)$, a similarity solution to the boundary layer equations exists (i.e., $\partial / \partial u \approx d/du$).

With this transformation, the differential equations become:

$$dp/du - W d\theta/du = -SW(\epsilon/\delta) dw/du \tag{87}$$

$$d\theta/du = W dp/du \tag{88}$$

and, since by definition the source term on the right must be of the same order of magnitude as the terms on the left, one concludes that $\delta = \epsilon$. Thus the constitutive equation for the rate of crystallization becomes:

$$-W dw/du = f(w, \theta) \tag{89}$$

If Eq. 89 is integrated over u ranging from $-\infty$ to $+\infty$ (i.e., over the thickness of the boundary layer), one obtains:

$$W = \int f(w, \theta)\, du \tag{90}$$

while integration of Eqs. 87 and 88 produces:

$$W(p_R - p_L) = \theta_R - \theta_L \tag{91}$$

$$p_R - p_L = W(S + \theta_R - \theta_L) \tag{92}$$

where the subscripts R and L identify conditions to the right and left of the boundary layer. Therefore differences such as those appearing on the lefthand side of Eq. 92 can be interpreted as jumps, and hence Eqs. 91 and 92 reproduce the jump conditions, Eqs. 69 and 70. This result guarantees that the zero-order approximation of the surface crystallization model is approached regularly.

It is now useful to rescale p and θ as follows:

$$r = (p - p_L)/(p_R - p_L) \tag{93}$$

$$m = (\theta - \theta_L)/(\theta_R - \theta_L) \tag{94}$$

so that the differential equations in the boundary layer collapse to:

$$dr/du = dm/du = -dw/du \tag{95}$$

which has the trivial solution:

$$r = m = 1 - w \tag{96}$$

and hence, after algebraic rearrangement:

$$1 - \theta = W[p]w \tag{97}$$

which upon substitution into Eq. 89 reduces it to an ordinary differential equation that can be integrated for any assigned form of the function $f(w, \theta)$. The simplest such form that satisfies the constraints is:

$$f(w, \theta) = (1 - w)(1 - \theta) \tag{98}$$

for which integration of Eq. 89 yields:

$$\ln [w/(1 - w)] = -[p]u \tag{99}$$

Thus an explicit analytical solution of the differential equations in the boundary layer has been obtained. This, coupled with the trivial "right" solution, and with the "left" solution obtained from the zero-order approximation, represents a full first-order approximation.

We finally consider the case where ϵ is of order unity, so that the full system of Eqs. 64–66 needs to be integrated. This can again be formulated as a moving boundary problem, and in fact a particularly simple one, since when ϵ is finite $[w] = 0$, so that the jump conditions imply a constant speed of propagation $W = 1$, and hence the moving boundary is simply $\mu = \alpha$. Thus the set of equations needs to be integrated over the triangular domain $0 \le y \le \alpha$, and no discontinuities will appear within this domain. At the boundary $y = \alpha$, the jump condition of Eq. 71 reduces to:

$$y = \alpha - 0, \quad -p = 1 - \theta \tag{100}$$

while of course:

$$y = \alpha - 0, \quad w = 0 \tag{101}$$

Again, in order to perform a numerical integration one needs initial distributions valid at sufficiently small values of α. The following distributions are easily calculated as an $O(\alpha)$ approximation:

$$p = -1 + Sy/\epsilon + [\alpha(1 - S/\epsilon)]/2 \tag{102}$$

$$\theta = y[(1 + S/\epsilon)]/2 \tag{103}$$

$$w = (\alpha - y)/\epsilon \tag{104}$$

which satisfy Eqs. 64, 100, and 101 exactly, and Eqs. 65 and 66 to within $O(\alpha)$.

In order to perform a numerical calculation, a specific form for the function $f(w, \theta)$ needs to be assumed; we have chosen the simple form of Eq. 98. The domain of integration $0 \le y \le \mu$ was divided into 40 intervals. This is needed because very significant gradients of w and θ are observed only in a comparatively small fraction of the field of interpretation. Some of the results are presented in Figures 4 and 5; all results presented are for $S = 1$.

Figure 4 presents the distributions of w and θ at $\alpha = 3.20$ for the case $\epsilon = 1$. The temperature profile exhibits just a hint of the sigmoid shape which, in the limit $\epsilon = 0$, would degenerate into a temperature discontinuity; it is barely visible in the plot, but numerically the existence of two inflection points is clearly observed. The w distribution presents a much more marked sigmoid shape, as expected.

Figure 5 presents the profiles of w and θ at $\alpha = 0.8$ for $\epsilon = 0.02$. In this case the sigmoid shape of both profiles, and the existence of a nearly molten layer where θ is almost unity, is clearly visible; indeed, the temperature discontinuity at $y = \alpha$ has become so small that it is not visible in the figure (the calculated value of $[\theta]$ is less than 10^{-6}). This shows that indeed the "outer" solution, Eq. 83, is very closely approached even at a

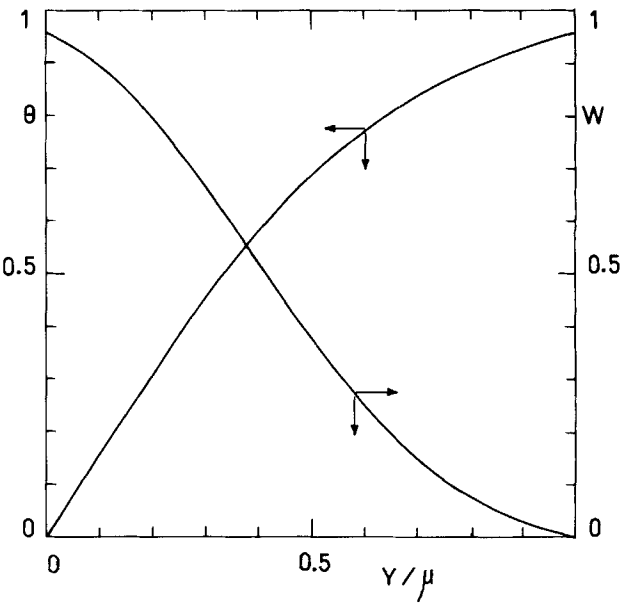

Figure 4. Distributions of temperature and degree of crystallinity.
$S = 1, \epsilon = 1, \alpha = 3.20$.

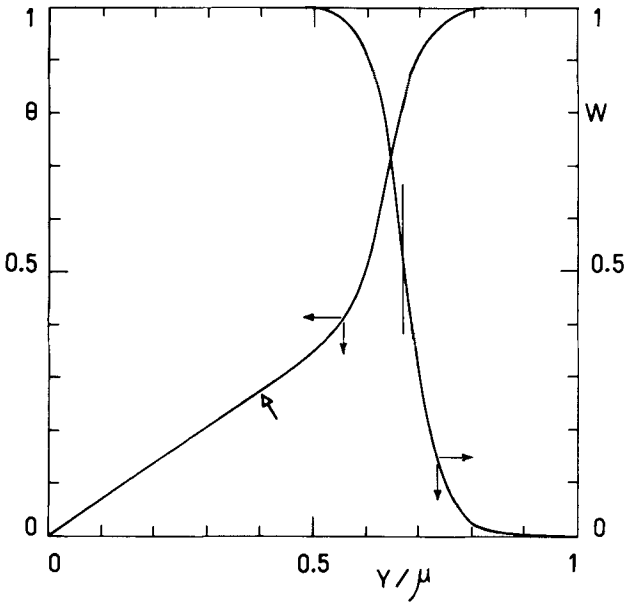

Figure 5. Distributions of temperature and degree of crystallinity.

$S = 1, \epsilon = 0.02, \alpha = 0.8$. Vertical line at $y/\mu = 0.67$ is front position that would be observed at $\epsilon = 0$. Arrow indicates first point of inflection of temperature profile.

comparatively large value of ϵ. The vertical line at $y/\mu = 0.67$ represents the position of the discontinuity calculated from the surface crystallization model: the sigmoid shape of the w distribution is indeed centered at that spatial position. Finally, it is worth pointing out that we have not used Eq. A4 as a boundary condition in the numerical calculation, which was set up as sketched in this section. This affords an independent check of the procedure, since the values of $1 - \theta_L$ obtained numerically could be compared with the theoretical values given by Eq. A4. The two values compared to within better than 1%, even in the most severe case tested ($S = 1$, $\epsilon = 0.02$, $\alpha = 8$), for which θ_L differs from unity by less than 10^{-16}.

Conclusions

The general model discussed in this paper seems to encompass all the essential physical assumptions made in the formulation of a variety of *ad hoc* models presented in the literature. The model degenerates, in the $\phi = 0$ case, into the Astarita and Kenny model, which in turn is known to encompass asymptotically the Stefan model. For the $\gamma = 0$ case, one obtains the surface crystallization model, which has been shown to be qualitatively, if not rigorously, analogous to the Astarita and Sarti model. The status of different models in relation to the present one is presented schematically in Figure 6. Arrows connecting two different models are single lines when the regularity of the approach to the limiting case has not yet been proven rigorously, they are double lines when it has been proven, or when the limit is not a singular one.

The surface crystallization limit, $\epsilon = 0$, is a singular limit, but a boundary layer analysis shows that it is approached regularly, and in fact a full analytical solution of the boundary layer equations can be obtained.

The possibility of recovering asymptotically a model that analogously to the Astarita and Sarti model allows a discontinu-

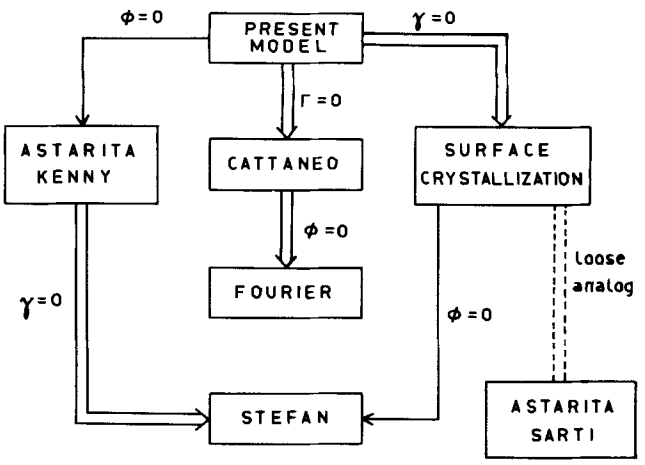

Figure 6. Status of different models.

ity of the potential at the front, is crucially related to the consideration of a finite value of the flux relaxation time ϕ. This conclusion is independent of the specific form of the kinetic equation that is considered. Introduction of a nonzero value of ϕ leads to model equations that are hyperbolic, and hence present significant difficulties of numerical integration. However, by setting up the problem in canonical form (i.e., by not eliminating the flux between the constitutive and the balance equations), it can be transformed to a moving-boundary problem that can be integrated numerically with ease and precision.

Acknowledgment

We are grateful to G. C. Sarti of the University of Bologna, who gave us advice on the formulation of the surface crystallization model in canonical form, and to T. Bruno of the University of Naples, who helped with several mathematical technicalities.

Notation

a = constant, Eq. 78
b = constant, Eq. 79
c = specific heat, kcal/m^3 · K
D = Deborah number, $D = \gamma k/cL^2$
$F()$ = function, Eq. 29
$f()$ = function, Eq. 6
g = dimensionless heat flux, $g = gL/k\delta T$
h = thickness over which θ is significantly different from unity
K = constant, Eq. 27
k = thermal conductivity, kcal/ms · K
L = sample thickness, m
M = constant, Eq. 42
m = rescaled temperature, Eq. 94
N = constant, Eq. 44
p = dimensionless heat flux, $p\delta T = q\sqrt{(\phi/kc)}$
Q = $Q = S + 1$
q = heat flux, kcal/m^2 · s
r = rescaled heat flux, Eq. 93
s = dimensionless front position, z variable
S = Stefan number, $S = \Gamma/c\delta T$
T = temperature, K
T_0 = cold surface temperature, K
T^* = equilibrium crystallization temperature, K
t = time, s
U = initial dimensionless front speed, $z - \sigma$ variables
U' = initial dimensional front speed, $U' = Uk/Lc$, m/s
u = relative molecular velocity, m/s
u = stretched coordinate, Eq. 84
V = front speed, $z - \beta$ variables
V_0 = initial value of V

W = front speed, $y - \alpha$ variables
W_0 = initial value of W
w = degree of crystallinity
x = position, m
y = dimensionless position, $y = x\sqrt{(c/\phi k)}$
z = dimensionless position, $z = x/L$
$z' = z' = s - z$

Greek letters

α = dimensionless time, $\alpha = t/\theta$
β = dimensionless time, $\beta = kt/L^2c$
Γ = latent heat, kcal/m^3
τ = crystallization time, s
δ = thickness of boundary layer, y variable
δT = imposed temperature differnce, K
ϵ = time scale ratio, $\epsilon = \tau/\phi$
θ = dimensionless temperature
θ_L = value of θ to left of front
$\theta_0()$ = temperature distribution for $S = 0$
μ = dimensionless front position, y variable
σ = dimensionless time, $\sigma = t/\mu$
ϕ = heat flux relaxation time, s
Ω = any quantity

Operator; Subscripts

[] = jump value
L = to left of boundary layer or front
R = to right of boundary layer or front

Appendix

Consider the region of nearly molten polymer which, at sufficiently low values of ϵ, is present between the quasi discontinuity predicted by the boundary layer analysis and the actual discontinuity of θ located at $y = \alpha$. We wish to develop an estimate of the rate of crystallization in this region, and in order to do so we first determine the value of θ_L. The following equations are obvious:

$$d\theta_L/d\alpha = d\theta(\alpha, \alpha)/d\alpha = \partial\theta/\partial y + \partial\theta/\partial\alpha \qquad \text{(A1)}$$

$$dp_L/d\alpha = dp(\alpha, \alpha)/d\alpha = \partial p/\partial y + \partial p/\partial\alpha \qquad \text{(A2)}$$

where all partial derivatives are to be calculated at $y = \alpha$. Substitution of Eqs. 64–66 and 101 into Eqs. A1 and A2 yields the following differential equation for θ_L:

$$2d\theta_L/d\alpha = (S/\epsilon)f(0, \theta_L) + 1 - \theta_L \qquad \text{(A3)}$$

which is an ordinary differential equation for $\theta_L(\alpha)$, subject to the initial condition $\theta_L(0) = 0$. (Incidentally, the solution of Eq. A3 could be used as a boundary condition at $y = \alpha$ for the moving-boundary problem emerging when ϵ is finite.) Now consider the special case where Eq. 98 holds. Equation A3 integrates to:

$$1 - \theta_L = \exp\,[-\alpha(1 + S/\epsilon)/2] \qquad \text{(A4)}$$

The initial rate of crystallization at $y = \alpha$ (i.e., the rate when the actual θ discontinuity has just passed the point considered) is:

$$\partial w/\partial\alpha = (1 - \theta_L)/\epsilon \qquad \text{(A5)}$$

which, in view of Eq. A4, becomes negligibly small when ϵ approaches zero provided α is significantly in excess of ϵ. Thus the outer solution given by Eq. 93 is in fact correct in the limit $\epsilon = 0$.

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