

CLASSICAL ONE-PHASE STEFAN PROBLEMS FOR DESCRIBING POLYMER CRYSTALLIZATION PROCESSES*

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Abstract. A free boundary problem framework is proposed to approximate the solution of a deterministic nonisothermal polymer crystallization model in which crystallization fronts appear as the result of the combination of two heat transfer processes: the heat conduction due to the application of a cooling temperature below the polymer melting temperature threshold, and the latent heat production due to the phase change. When the latent heat is larger than the sensible heat of the crystallization process, a classical one-phase Stefan problem can be formulated which allows one to derive analytical approximations describing, for arbitrary applied cooling temperature profiles, the main features of the crystallization process: the relation between the latent heat and the specific heat capacity, the evolution of the temperature distribution, and the advance of the crystallization front. Analytical expressions of magnitudes of industrial interest such as the crystallization time are also derived, allowing the design of optimal cooling strategies for the applied temperature. The limits of the suitability of this framework are discussed, pointing out its applicability to other polymer crystallization models.

Key words. free boundary problems, nonlinear parabolic equations, numerical simulations, Stefan problem

AMS subject classifications. 35R35, 35K55, 65M06, 80A22

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1. Introduction. Polymer crystallization can be viewed as a phase change process whereby an initially amorphous molecular state evolves into an ordered crystalline state. When cooled below their melting temperature threshold, amorphous polymer molecular chains tend to curl and form ordered packages (crystals) held together by less ordered regions [5]. If the cooling temperature is kept below this threshold and above a second threshold (of vitrification), crystals continue to appear and grow until an almost fully ordered structure is reached, complete crystallization being impossible to achieve due to the amorphous inclusion of the crystalline elements [15]. Therefore, this process of molecular rearrangement takes place in a range of temperature (T_g, T_f) , where T_g is the vitrification threshold below which there is not enough molecular agitation to allow package formation (the polymer is just vitrified into an amorphous glass), and T_f is the freezing threshold above which the ordered structure remains disaggregated due to molecular agitation [2]. Amorphous solidification due to hypercooling is not considered in this paper.

Stefan problems are a classical mathematical tool for describing heat transfer phenomena in which two distinct phases are separated by a sharp moving boundary where the phase change takes place. It is well known that Stefan problems are not recommended in modeling polymer crystallization [1, 10, 16], due to the fact that phase changes described by Stefan problems take place at a given critical temperature, whereas polymer crystallization occurs in a wide range of temperatures [2, 18].

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Recently, a number of different models for polymers have been proposed [11, 5]. Among them, a deterministic nonisothermal model for the crystallization of polymers has been considered and studied in [12]. The model, borrowed from a stochastic particle model introduced in [5], consists of a reaction-diffusion system with two strongly coupled nonlinear partial differential equations, one for the temperature distribution and the other for the crystallinity (the volume fraction occupied by crystals). A special feature of the model is the truncation to zero of the nucleation and growth rate functions at the freezing temperature T_f when the temperature is greater than or equal to this value. Details of this choice were given in [12], and a similar treatment can be found in models of frontal polymerization processes (see, e.g., [8]).

The vanishing of the rate functions is the key ingredient of the model which gives rise to the formation of crystallization fronts, preserving at the same time the characteristic temperature range of phase change proper from polymer crystallization processes. Numerical results on the shape, width, and speed of these moving fronts were presented in [12]. Here, we show that the classical one-phase Stefan problem serves as a reduction of the model proposed in [12] and yields important clues about the polymer crystallization process.

More precisely, when the latent heat released by the growth of crystals is much larger than the sensible heat of the crystallization process, we will show that the classical one-phase Stefan problem describes quite accurately the evolution of the temperature distribution and the smooth part of the advance of the crystallization front and this, independently of the shape and the width of the front, for arbitrary applied cooling temperature profiles and along almost the entire crystallization process. This is done by formulating a free boundary problem (FBP) framework allowing us to derive analytical approximations of fundamental features of the model, such as the relation between the latent heat of the process and the specific heat capacity or the velocity of propagation of the crystallization front, and important properties from the viewpoint of industry, such as the total crystallization time and the optimal cooling strategy for the applied cooling temperature profile (see [13]). Finally, the limits of applicability of this framework are established, pointing out situations where the comparison between the polymer crystallization model and the corresponding one-phase Stefan problem is not appropriate.

The paper is organized as follows. In section 2, the model is introduced and solved numerically. Expressions defining the latent heat and the enthalpy functions are given. The jump of enthalpy across the crystallization front is derived. In section 3, the FBP framework is established, and a one-phase Stefan problem is formulated to approximate the solution of the polymer crystallization model. In section 4, the solution of the Stefan problem is compared with the numerical solution of the crystallization model for constant applied temperature, exponentially decreasing applied temperature, and for the general case of an arbitrary applied temperature. In all cases, the Stefan problem constitutes an excellent approximation of the crystallization process, provided the latent heat is large enough. The fundamental role of the latent heat to sensible heat relation is then derived from the crystallization model equations, and analytical estimates of the crystallization time are obtained. Conclusions and open problems are presented in section 5.

Let us remark that some important features of the model, such as the oscillatory behavior of the temperature field [12] and the effect of the size of the discontinuity in the nucleation and growth rate function, are not studied in the present work.

2. The deterministic model of polymer crystallization.

2.1. Model equations, conditions, and parameter values. Crystallization is here considered to consist of two processes: the nucleation process, which describes the birth of crystals (when and where some spots appear), and the growth process of these nucleated crystals. Both processes depend on the temperature and have a random nature; however, under usual industrial conditions, a multiple scale assumption can be made, and a deterministic approximation can be used [7, 12]. The experimental setup consists of a one-dimensional sample of a given material characterized by the thermal diffusivity and the rate functions of nucleation and growth. The sample is cooled by applying a low temperature at one of its sides.

At the macroscopic scale, the crystallization process may be modeled as a reaction-diffusion problem for the temperature distribution $T(x, t)$ and the degree of crystallinity $y(x, t)$, described by the following system of two coupled nonlinear partial differential equations:

$$(2.1) \quad y_t(x, t) = \left[Gy(x, t) + v_0 N(1 - y(x, t)) \right] (1 - y(x, t)) \theta(T(x, t)),$$

$$(2.2) \quad T_t(x, t) = \sigma T_{xx}(x, t) + a_G Gy(x, t)(1 - y(x, t)) \theta(T(x, t))$$

with the boundary and initial conditions

$$(2.3) \quad T(0, t) = u(t),$$

$$(2.4) \quad T_x(L, t) = 0,$$

$$(2.5) \quad y(x, 0) = 0,$$

$$(2.6) \quad T(x, 0) = T_0,$$

where L is the length of the sample and $u(t)$ is the cooling temperature applied at $x = 0$, whose typical values range from 0 to 100°C but can also be negative.

As we will show later, (2.1) and (2.5) preclude the possibility that the total crystallization ($y \equiv 1$) takes place. Equations (2.1) and (2.2) are coupled by the nucleation rate $b_N(T) = N\theta(T)$ and the growth rate $b_G(T) = G\theta(T)$, both depending on the instantaneous temperature through the exponentially decreasing rate function [7, 19]:

$$(2.7) \quad \theta(T) = \begin{cases} e^{-\beta T} & \text{if } T < T_f, \\ 0 & \text{if } T \geq T_f. \end{cases}$$

The critical temperature thresholds at which nucleation and growth processes are respectively triggered are assumed to be the same, namely, T_f . The fact that the rate function $\theta(T)$ vanishes above the crystallization threshold T_f is the key ingredient for the emergence of the main feature of the model, the formation of a crystallization front. Although $\theta(T)$ can be chosen to be continuous at T_f , we have used the more general case in which $\theta(T)$ exhibits a jump of size $e^{-\beta T_f}$; see [12], where this expression was first introduced.

An important quality of the model is that the contribution of the crystallinity and the temperature to the variation of the crystallinity are decoupled: (2.1) can be written as $y_t = \zeta(y)b_G(T) + v_0\kappa(y)b_N(T)$, where $\zeta(y) = y(1 - y)$ and $\kappa(y) = (1 - y)^2$ account for the onset of nucleation and the mechanisms of aggregation and saturation of nuclei [6].

Parameter values are oriented for isotactic polypropylene (i-PP), for which typical values of the sample length and the thermal diffusivity are 0.01 m and $10^{-7} \text{ m}^2 \text{ s}^{-1}$,

TABLE 2.1
Typical values and units of the parameters.

Symbol	Physical meaning	Typical value	Symbol	Physical meaning	Typical value
$u(t)$	applied temperature	0–100°C	v_0	initial mass	0.01
T_f	freezing temperature	70°C	N	nucleation factor	20 s ⁻¹
T_0	initial temperature	100°C	G	growth factor	5 s ⁻¹
σ	thermal diffusivity	0.002 m ² s ⁻¹	β	rate function exponent	0.1 (°C) ⁻¹
a_G	nonisothermal factor	2500°C	L	length of the sample	1 m

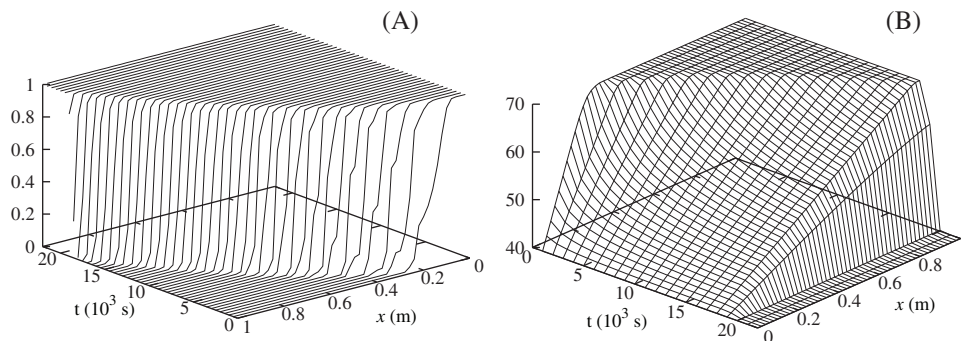


FIG. 2.1. Time evolution of (A) the degree of crystallinity $y(x, t)$ and (B) the temperature field $T(x, t)$ for $u(t) = 40^\circ\text{C}$ and the typical values reported in Table 2.1. Note that the axes have been inverted in (B).

respectively [4]. For numerical convenience and clearness in figures, the sample length is fixed to $L = 1$ m, so thermal diffusivity scales to 10^{-3} m² s⁻¹ in (2.2). The freezing temperature T_f in i-PP ranges from 130° to 170°C. We have used a wide range of values of the nucleation and growth rate coefficients G and N which, taken under the isokinetic assumption ($N/G = \text{constant}$), allowed us to keep the temperatures in the normalized interval $[0, 100]^\circ\text{C}$. The nonisothermal factor a_G is taken so that the hypercooling regime is avoided. The specific heat capacity c does not appear explicitly in the model. Parameters describing properties of the material are assumed to be constant and equal in both phases.

Parameter values used in our simulations are shown in Table 2.1. They have been adjusted with the aim of emphasizing the patterns and features exhibited by the model, which have shown to be quite stable and coherent for a wide range of values. Main features and extensive numerical simulations can be found in [12] and [13].

2.2. Numerical solution. Figure 2.1 shows the numerical solution of (2.1)–(2.7) for a constant applied temperature $u(t) = 40^\circ\text{C}$ and the parameter values of Table 2.1.

The crystallinity distribution exhibits an advancing front with decreasing speed, accompanied by a free boundary separating two linear regimes in the temperature field. The temperature field results from the combination of two opposite thermal phenomena: the heat conduction, which contributes to reducing the temperature when the applied temperature $u(t)$ is lower than the freezing threshold T_f , and the reheating, produced by the latent heat $\mathcal{L}$ released by the change of phase from liquid to solid. The competition between these two processes gives rise to the oscillatory behavior exhibited by the temperature field, which in turn induces the advance by bumps of the most advanced crystallized point.

For parabolic equations, the speed of propagation of information is infinite. Hence, heat conduction affects instantaneously the whole sample and the decrease of temperature takes place everywhere in the sample when the applied cooling temperature is under T_f .

The key role of the truncated rate function $\theta(T)$ is that as soon as $T \geq T_f$, the information propagation is stopped ($y_t = 0$) and no nucleation or growth can occur, giving rise to the formation of the so-called crystallization band pattern shown in Figure 2.1(A), a moving thin interval where the phase change process takes place, separating two homogeneous regions of constant value: the upper region is the solid (or crystalline) phase, where y is almost equal to 1 (see section 2.5), and the lower region is the liquid (or amorphous) phase, where $y = 0$.

2.3. Latent heat function. Equation (2.2) describes the heat balance between heat conduction and latent heat production due to the growth of nuclei [4]. In non-isothermal polymer crystallization models, this relation is usually written as

$$(2.8) \quad T_t(x, t) = \sigma T_{xx}(x, t) + \frac{\Lambda}{c} y_t(x, t),$$

where Λ is the *latent heat* (J/Kg) and c is the specific heat capacity [11, 5, 7] (J Kg⁻¹°C⁻¹).

The latent heat may be understood as the heat produced at the point x during the time interval $[0, t]$, that is, the amount of heat produced by the phase transition which has made the degree of crystallinity grow from its initial value 0 to $y(x, t)$.

Equation (2.2) can in fact adopt this classical form, where the source term is proportional to the variation of the crystallinity: (2.1) is $(1 - y)\theta(T) = y_t/[Gy + v_0N(1 - y)]$, so

$$T_t = \sigma T_{xx} + a_G G y \frac{y_t}{Gy + v_0N(1 - y)} = \sigma T_{xx} + \frac{a_G y}{y + \delta(1 - y)} y_t = \sigma T_{xx} + \frac{\Lambda_\delta(y)}{c} y_t,$$

where $\delta = v_0N/G$ and $\Lambda_\delta(y)$ is the latent heat function of our framework. The function $\Lambda_\delta(y)$ is time- and space-dependent through the degree of crystallinity $y(x, t)$ and is a well-defined function, the denominator never being equal to zero because $\delta/(\delta - 1) \notin [0, 1]$ for the typical values of the parameters. As expected, $\Lambda_\delta(y)$ depends on the nucleation and growth parameters N and G , the initial mass of nuclei v_0 , and the nonisothermal factor a_G (times c).

In order to activate the mechanism which avoids the immediate nucleation in the entire liquid phase, the latent heat $\mathcal{L}$ released by the phase change must be large enough to raise the temperature from the cooling value $u(t)$ to the cutoff value T_f ; that is,

$$(2.9) \quad \mathcal{L} \gg c \max_t \{T_f - u(t)\}.$$

In this case, the reheating makes the temperature grow above T_f , thus stopping the advance of the crystallization band. Inside the band, the crystallinity grows and, once it becomes large enough to conduct the heat to the most advanced point of crystallization, the temperature falls under T_f and the nucleation and growth processes are again triggered.

When (2.9) does not hold, that is, when the latent heat is not large enough, the temperature falls rapidly under T_f in the whole sample and nucleation and growth take

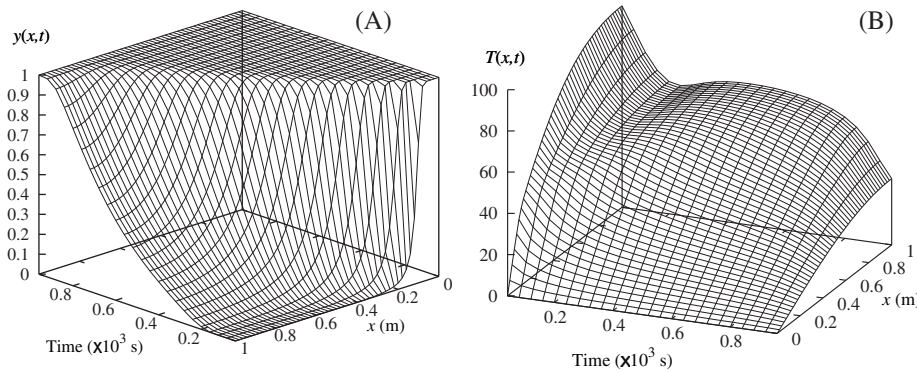


FIG. 2.2. Hypercooled sample with $u(t) \equiv 0^\circ\text{C}$ and values of Table 2.1 except $a_G = 200^\circ\text{C}$. Note that $T(x, t)$ falls under T_f at $t \approx 200$ s, making $y > 0$ in the whole sample, so that the typical band structure is not formed.

place everywhere in the sample, thus preventing the formation of the band structure; see Figure 2.2. A liquid cooled to so low a temperature is referred to as *hypercooled* [1].

Among other results, the study presented in this paper provides an analytical approximation of the relation between the latent heat released in the crystallization process and the specific heat capacity, which will allow us to obtain the conditions (values of the parameters) under which the crystallization band pattern is expected to emerge.

2.4. Equation for the enthalpy function. The enthalpy function $\mathcal{H}_\delta(y)$ associated to the latent heat $\Lambda_\delta(y)$ is given by

$$(2.10) \quad \mathcal{H}_\delta(y) \stackrel{\text{def}}{=} \int_0^y \Lambda_\delta(z) dz = \frac{c a_G}{1-\delta} \left(y - \frac{\delta}{1-\delta} \ln [(1-\delta)y + \delta] + \frac{\delta \ln \delta}{1-\delta} \right).$$

The latent heat and enthalpy functions allow us to write (2.2) in the form of the classical heat balance equation, which straightforwardly becomes

$$(2.11) \quad T_t(x, t) = \sigma T_{xx}(x, t) + \frac{1}{c} \frac{\partial}{\partial t} (\mathcal{H}_\delta(y(x, t))).$$

Integrating this equality with respect to time in $[0, t]$, we arrive at the main equation for the enthalpy function,

$$(2.12) \quad \frac{1}{c} \mathcal{H}_\delta(y(x, t)) = T(x, t) - \sigma \int_0^t T_{xx}(x, s) ds - T_0,$$

showing how the degree of crystallinity is related to the temperature field through the enthalpy function $\mathcal{H}_\delta$, whose jump across the region of phase change (the interface) is given by

$$(2.13) \quad \mathcal{H}_\delta(y) = \begin{cases} 0 & \text{if } y = 0 \text{ (the liquid phase),} \\ ca_G K_\delta & \text{if } y = 1 \text{ (the solid phase),} \end{cases}$$

where $K_\delta = [1 + \delta(\ln \delta - 1)]/(1 - \delta)^2$ is a dimensionless parameter.

When the interface is thin enough with respect to the size of the sample, as in Figure 2.1 but not as in Figure 2.2, an FBP framework can be set up in which (2.12) allows us to derive a Stefan condition for the evolution of the interface.

2.5. Maximum degree of crystallinity and complete crystallization time.

The degree of crystallinity shown in Figure 2.1(A) exhibits an upper plateau in which the crystallinity appears to have reached the maximum value $y = 1$. However, it is well known that due to the amorphous inclusion of the crystalline elements, the complete crystallization can never be achieved [15]. This feature is derived from (2.1) in the following result.

THEOREM 2.1. *For a given temperature distribution $T(x, t)$, $(x, t) \in [0, L] \times (0, \tau)$, there exists one and only one solution of (2.1):*

$$(2.14) \quad y(x, t) = 1 - \frac{1}{1 + \delta \left(e^{G \int_0^t \theta(T(x, s)) ds} - 1 \right)}.$$

Proof. In (2.1), we can separate the terms depending on y and T in the form

$$(2.15) \quad \theta(T) = \frac{y_t}{[Gy + v_0 N(1 - y)](1 - y)} = \frac{y_t}{G} \left[\frac{1 - \delta}{y + \delta(1 - y)} + \frac{1}{1 - y} \right].$$

Integrating this expression with respect to time in $[0, t]$, we get

$$\ln |\delta + (1 - \delta)y(x, t)| - \ln |\delta| - \ln |1 - y(x, t)| = G \int_0^t \theta(T(x, s)) ds.$$

Taking exponentials in this equality, we have

$$\delta + \frac{y(x, t)}{1 - y(x, t)} = \delta e^{G \int_0^t \theta(T(x, s)) ds}.$$

Rearranging terms yields (2.14). Note that x acts as a simple parameter in this expression. $\square$

For $\delta = 1$, the crystallinity at an arbitrary point x can be written as

$$(2.16) \quad y(x, t) = 1 - e^{-G \int_0^t \theta(T(x, s)) ds},$$

a classical expression found in the seminal works of Kolmogorov [20] and Avrami [3] (and also [7, 4]). Equation (2.16) shows that for large growth rates, the crystallinity reaches values close to the fully crystalline phase very quickly; see [4, p. 1044] for a multiple scale analysis.

Remark 1. As a consequence of (2.14) we can deduce that $y(x, t) \in [0, 1)$ for every $(x, t) \in [0, L] \times (0, \tau)$. Although the maximum value $y(x, t) = 1$ cannot be reached, the exponential in (2.14) becomes so large during numerical simulations that the full crystallization can be considered attained, that is, $y(x, t) \geq 1 - \epsilon_0$ for some small $\epsilon_0 > 0$ (we have used $\epsilon_0 = 10^{-16}$). For simplicity, from now on we will just say $y(x, t) = 1$, understanding it in this way. From this viewpoint, the complete crystallization ($y(x, t) = 1 \forall x \in [0, L]$) is reached at time $t_{\text{cryst}} = 22.475 \times 10^3$ s for the parameter values described in Table 2.1.

Another interesting property deriving from (2.14) is that in the liquid phase (where $y(x, t) = 0$), the temperature is such that $T(x, s) \geq T_f \forall s \in (0, t)$.

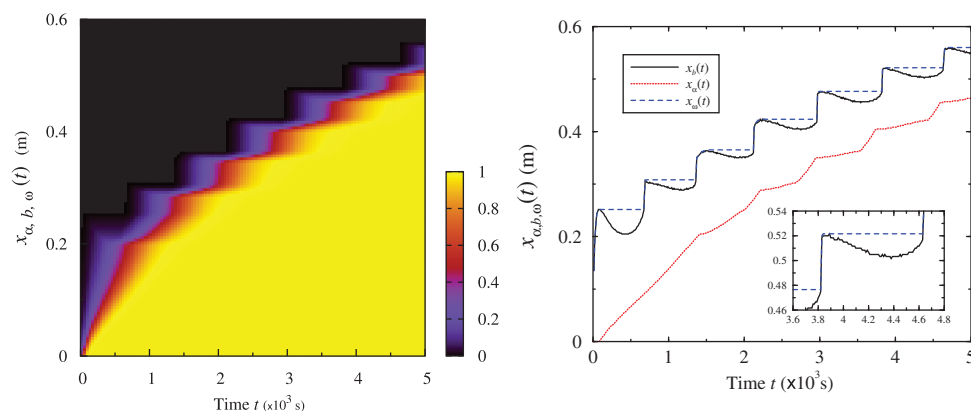


FIG. 3.1. Color map of the crystallinity $y(x, t)$ (left) and crystallization band characterization (right) corresponding to the case depicted in Figure 2.1(A). Parameter values are given in Table 2.1.

Remark 2. The initial conditions have been chosen to be constant temperature and zero crystallinity just for simplicity. For general conditions $T(x, 0) = T_0(x)$ and $y(x, 0) = y_0(x)$, the main results remain valid as, for instance, the crystallinity, which will obey

$$(2.17) \quad y(x, t) = 1 - \frac{1}{1 - \delta + \left(\frac{y_0(x)}{1 - y_0(x)} + \delta \right) e^{G \int_0^t \theta(T(x, s)) ds}}.$$

3. An FBP. A Stefan FBP framework for the crystallization process described by the model (2.1)–(2.6) is introduced and shown to provide analytical expressions of the crystallization front and the temperature field. By identifying the position of free boundary to the amount of crystallized polymer, a Stefan condition for the evolution of the free boundary is derived. The Stefan problem is solved in different experimental situations. The conditions under which this framework is valid are provided.

3.1. Characterization of the free boundary. Figure 3.1(A) shows a color map of the crystallinity depicted in Figure 2.1(A), where two homogeneous regions (separated by an oscillating band which evolves with a slightly decreasing velocity) can be clearly identified: the solid phase, located below the band, where the maximum degree of crystallization has already been reached ($y = 1$; see Remark 1), and the liquid phase, located above the band and where not even nucleation has taken place ($y = 0$).

Defining two time-depending abscissas $x_{\alpha} < x_{\omega}$,

$$(3.1) \quad x_{\alpha}(t) = \max\{x \in [0, L] : y(x, t) = 1\},$$

$$(3.2) \quad x_{\omega}(t) = \min\{x \in [0, L] : y(x, t) = 0\},$$

the solid phase is given by the interval $[0, x_{\alpha}(t)]$ and the liquid phase by $[x_{\omega}(t), L]$ [12]. Thus, the phase change is confined to the so-called crystallization band $[x_{\alpha}(t), x_{\omega}(t)]$. It is across this band that the enthalpy $\mathcal{H}_{\delta}$ experiences a jump.

The formulation of an FBP consists in characterizing a spatial coordinate $h(t)$ located inside the region where $\mathcal{H}_{\delta}$ grows abruptly as a representative of the whole region. The phase change is then considered to take place precisely at this point $h(t)$ and precisely at the critical temperature of freezing T_f . That is,

$$(3.3) \quad T(h(t), t) = T_f.$$

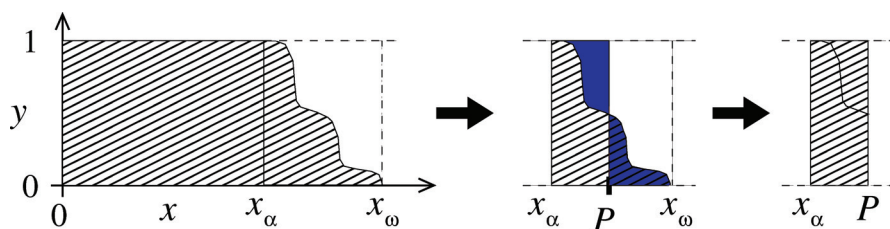


FIG. 3.2. *Instantaneous crystallization hypothesis: the crystallized area inside the band $[x_\alpha(t), x_\omega(t)]$ is instantaneously reorganized in $[x_\alpha(t), P(t)]$, where $y = 1$, as soon as nucleation takes place.*

The choice of $h(t)$ is especially delicate in the present case, because first, the width of the band is not necessarily small and the band can occupy more than 10% of the whole domain, and second, the crystallization band is not a traveling wave of constant shape or speed, due to the characteristic oscillatory behavior of the temperature field (induced by the competition between heat conduction and reheating). Indeed, the width of the band is not constant along the crystallization process.

A more appropriate characterization for the free boundary can be obtained by using the amount of polymer crystallized at a given time, $P(t)$:

$$(3.4) \quad P(t) \stackrel{\text{def}}{=} \int_0^L y(x, t) dx.$$

The fundamental magnitude $P(t)$ has been recently used by the authors to obtain the optimal cooling strategy in terms of reducing the time of total crystallization without using too low values of the applied temperature; see [13].

In [13] the following relation was obtained numerically:

$$(3.5) \quad P(t) \approx \kappa \sqrt{Q(t)},$$

where κ is a positive constant proved numerically to depend only on δ , a_G , and σ , and

$$(3.6) \quad Q(t) \stackrel{\text{def}}{=} \int_0^t (T_f - u(s)) ds.$$

In fact, it was shown, again numerically, that the amount of crystallized polymer $P(t)$ does not depend on the history of the applied temperature $u(t)$, provided $Q(t)$ remains unchanged. We will present here an analytical derivation of (3.5) and the explicit expression of κ .

Figure 3.2 illustrates the meaning of identifying the crystallization band $[x_\alpha(t), x_\omega(t)]$ with the amount of crystallized polymer $P(t)$. At every instant of the crystallization process, the amount of crystallized polymer inside the band can be reorganized in a narrower interval $[x_\alpha(t), P(t)]$, where the maximum degree of crystallinity has been reached, according to

$$(3.7) \quad \int_{x_\alpha(t)}^{x_\omega(t)} y(x, t) dx = \int_{x_\alpha(t)}^{P(t)} 1 dx = P(t) - x_\alpha(t),$$

exactly as if the maximum degree of crystallinity was instantaneously reached right after nucleation.

This *instantaneous crystallization hypothesis* consists then in identifying the position of the free boundary $h(t)$ with the amount of crystallized polymer $P(t)$:

$$(3.8) \quad h(t) \stackrel{\text{def}}{=} P(t) \quad \forall t > 0.$$

By construction, $h(t)$ is well defined and belongs to the band $[x_\alpha(t), x_\omega(t)] \forall t > 0$ and therefore is a good representative of the crystallization band. The suitability of (3.8) is also shown by the numerical observations carried out in [13] for different applied temperature profiles.

3.2. FBP framework. Once $h(t)$ is defined as the interface separating the two phases of the material, important simplifications can be made to establish the FBP framework.

The degree of crystallinity now satisfies

$$(3.9) \quad y(x, t) = \begin{cases} 1, & x \in [0, h(t)], \\ 0, & x \in (h(t), L], \end{cases}$$

which means that the width of the crystallization band may be considered negligible with respect to the distance traveled by the band and the distance it has to travel until the complete crystallization is achieved. Then, the area inside the band can be neglected with respect to the area covered by the crystalline phase.

The second ingredient of the FBP framework is the classical assumption used in one-phase Stefan problems (see, e.g., [1]) that the temperature in the liquid phase is constant and equal to the threshold temperature T_f . This assumption is quite reasonable for the industrial conditions for which the present model has been derived and for the typical parameter values we are using. This is shown by the following argument.

The temperature in the liquid region is determined by the heat equation

$$(3.10) \quad T_t(x, t) = \sigma T_{xx}(x, t) \quad \text{for } x \in (h(t), L]$$

with boundary conditions $T(h(t), t) = T_f$ and $T_x(L, t) = 0$. For the typical values used in this model, the heat conduction process is much faster than the crystallization process, that is, the distance x_d covered by conduction during a time Δt is much greater than the thickness of material crystallized during this time x_c [4]:

$$(3.11) \quad x_c \ll x_d.$$

Thus, the temperature in $(h(t), L]$ falls to T_f much faster than the advance of the crystallization band, allowing us to consider that the temperature is equal to T_f in this region, i.e.,

$$(3.12) \quad T(x, t) = T_f \quad \text{for } x \in (h(t), L].$$

The spatial scale x_d can be estimated to be $x_d = O(\sqrt{\sigma \Delta t})$. The solution of the Stefan problem will provide an expression of $h(t)$ from which it is possible to estimate the typical space scale of crystallization x_c . On the other hand, assumption (3.12) will be extended to the case of a semi-infinite liquid phase, allowing us to take advantage of the existence of closed-form explicit solutions of the Stefan problem [1]. This extension is quite reasonable, the boundary condition in $x = L$ being a zero heat flux boundary condition, meaning perfect thermal insulation (see [1, pp. 46, 50]).

3.3. A Stefan condition for the free boundary $h(t)$. Our aim in this section is to obtain an explicit equation for $h'(t)$, the velocity of the free boundary. For that purpose, we integrate (2.12) with respect to x in $[0, L]$:

$$(3.13) \quad \frac{1}{c} \int_0^L \mathcal{H}_\delta(y(x, t)) dx = \int_0^L T(x, t) dx - \sigma \int_0^L \int_0^t T_{xx}(x, s) ds dx - L T_0.$$

Combining (2.13) with (3.9) we have

$$(3.14) \quad \frac{1}{c} \int_0^L \mathcal{H}_\delta(y(x, t)) dx = \int_0^{h(t)} a_G K_\delta dx = a_G K_\delta h(t).$$

For the right-hand side of (3.13), interchanging the variables of integration in the double integral, and using the boundary condition $T_x(L, t) = 0$, we arrive at

$$(3.15) \quad \int_0^L \int_0^t T_{xx}(x, s) ds dx = \int_0^t (T_x(L, s) - T_x(0, s)) ds = - \int_0^t T_x(0, s) ds.$$

Taking into account (3.12), the resulting equation becomes

$$(3.16) \quad a_G K_\delta h(t) = \int_0^{h(t)} T(x, t) dx + T_f(L - h(t)) + \sigma \int_0^t T_x(0, s) ds - L T_0.$$

Now, time-differentiating (3.16) yields

$$a_G K_\delta h'(t) = T(h(t), t) h'(t) + \int_0^{h(t)} T_t(x, t) dx - T_f h'(t) + \sigma T_x(0, t).$$

Together with $T(h(t), t) = T_f$ and $T_t(x, t) = \sigma T_{xx}(x, t)$ for $x \in [0, h(t))$, this gives

$$a_G K_\delta h'(t) = \int_0^{h(t)} \sigma T_{xx}(x, t) dx + \sigma T_x(0, t),$$

which, calculating the integral and canceling terms, leads us to

$$(3.17) \quad a_G K_\delta h'(t) = \sigma T_x(h(t), t).$$

This expression can be viewed as the *Stefan condition* of a *classical Stefan problem*, exactly in the way that Lamé and Clapeyron [21] formulated it 58 years before Stefan.

Equation (3.17) relates the size of the jump in the temperature field variation with the velocity of displacement of the free boundary $h'(t)$. Moreover, it allows us to formulate a *classical one-phase Stefan problem* which describes the evolution of the crystallization band and the temperature field of the polymer crystallization model (2.1)–(2.6):

$$(3.18) \quad T_t(x, t) = \sigma T_{xx}(x, t), \quad x \in [0, h(t)), \quad t > 0,$$

$$(3.19) \quad T(x, t) = T_f, \quad x \in (h(t), +\infty), \quad t > 0,$$

$$(3.20) \quad T(0, t) = u(t), \quad t > 0,$$

$$(3.21) \quad T(h(t), t) = T_f, \quad t > 0,$$

$$(3.22) \quad \frac{\mathcal{L}_\delta}{c} h'(t) = \sigma T_x(h(t), t), \quad t > 0,$$

where $\mathcal{L}_\delta$ represents the latent heat of the phase change process:

$$(3.23) \quad \mathcal{L}_\delta \stackrel{\text{def}}{=} \Lambda_\delta(1) K_\delta = c a_G K_\delta = \mathcal{H}_\delta(1).$$

3.4. Initial and final transients. The FBP framework requires a well-formed band to be a valid description of the crystallization problem (2.1)–(2.6). Two short transients exist during which this condition is not met: at the start, the band structure needs a certain amount of material to be fully crystallized, and at the end, the band structure is lost when it reaches the right end of the sample. We thus introduce two critical times t_1 and t_2 ,

$$(3.24) \quad t_1 = \min\{t > 0 : y(b_0, t) > 1 - \epsilon_1\}, \quad t_2 = \min\{t > 0 : y(L, t) > \epsilon_2\},$$

where t_1 is the time taken for the band to form and separate from the left end of the sample, t_2 is the instant at which the band reaches $x = L$, $b_0 > 0$ is an estimate of $x_\alpha(\tilde{t}_0)$, where $\tilde{t}_0$ is the time taken to develop a sharp interface, and $\epsilon_{1,2} > 0$ are two small real tolerances.

The next section shows that these transient times are really short, so that the Stefan problem accurately describes almost all the crystallization process. Note that b_0 (and therefore t_1) cannot be established a priori because the shape and width of the crystallization band are highly dependent on the parameters so that a specific value of b_0 is required for each case.

4. Solution of the one-phase Stefan problem. The Stefan problem (3.18)–(3.22) is solved for different applied temperature profiles $u(t)$. In all cases, the solution is shown to be an excellent approximation of the solution of the crystallization problem (2.1)–(2.6).

Section 4.1 presents two cases where the analytical solution of the Stefan problem is known. Measures of error are then defined, and a collection of examples presented. In section 4.2, the general case of arbitrary applied temperatures is solved by using the classical pseudo-steady state (PSS) approximation, and errors are estimated in terms of the Stefan number.

The excellent agreement is highlighted by means of detailed figures which, in combination with the measurement of errors, allow us to overcome the difficulties in analyzing the results due to the inherent oscillatory behavior of the temperature field.

4.1. Exact solution of the one-phase Stefan problem. Explicit analytical solutions of the one-phase Stefan problem (3.18)–(3.22) are available for a limited number of applied temperatures profiles $u(t)$ [9]. Two cases are of special interest: the case of constant temperature $u(t) \equiv u$, which is the simplest one and has been shown to correspond to the optimal cooling strategy [13], and the case of an exponentially decreasing cooling temperature, $u(t) = Ae^{\eta t} + B$, with $A < 0$ and $\eta > 0$, which leads to a free boundary advancing with a constant speed. Both cases were studied by Stefan in his seminal work (see [22]).

4.1.1. Constant cooling temperature: Neumann solution. The exact solution for constant boundary condition was sketched by Stefan [22] and generalized by Neumann (as explained in [23]).

Assume a particular solution of the form $T(x, t) = A \operatorname{erf}\{x/(2\sqrt{\sigma t})\} + B$, where A and B are constant and $\operatorname{erf}(\lambda)$ is the error function $\operatorname{erf}(\lambda) = 2/(\sqrt{\pi}) \int_0^\lambda e^{-z^2} dz$. Conditions (3.20)–(3.21) imply that $B = u$ and $\lambda = h(t)/(2\sqrt{\sigma t})$ is constant. Consequently, $A = (T_f - u)/\operatorname{erf}(\lambda)$. The parameter λ is obtained as the unique solution of the transcendental equation resulting from the Stefan condition (3.22),

$$(4.1) \quad \lambda e^{\lambda^2} \sqrt{\pi} \operatorname{erf}(\lambda) = \frac{c(T_f - u)}{\mathcal{L}_\delta}.$$

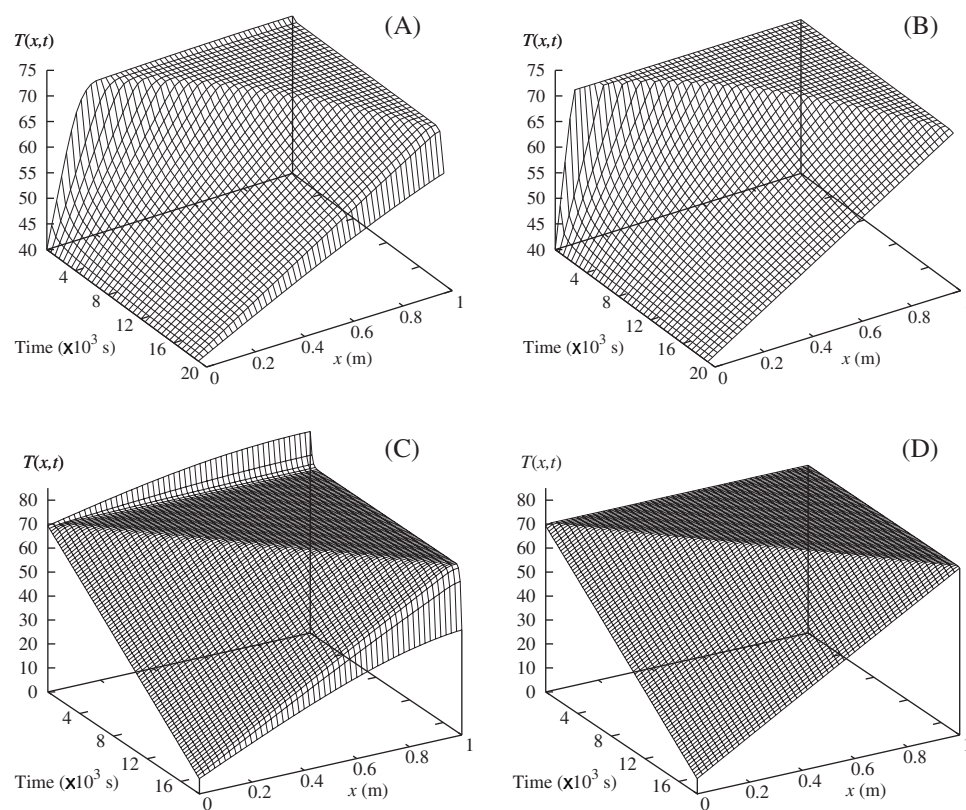


FIG. 4.1. Temperature field $T(x, t)$. (A) and (C) are a direct numerical simulation of (2.1)–(2.6). (B) and (D) are solution (4.2)–(4.3) of the one-phase Stefan problem (3.18)–(3.22). (A), (B) Constant applied temperature $u = 40^\circ\text{C}$, $\delta = 0.04$ ($N = 20\text{ s}^{-1}$; $G = 5\text{ s}^{-1}$, $v_0 = 0.01$), and $t \in [t_1, t_2]$. See Case 2 in Table 2.1. (C), (D) Exponentially decreasing applied temperature $u(t)$ given by (4.9) and $\delta = 0.04$. We have used $\gamma = 2.89 \times 10^{-2}$ in $[0, 17.5 \times 10^3]$.

Therefore, the unique solution of the one-phase Stefan problem (3.18)–(3.22) is given by the following expressions for the free boundary and the temperature field:

$$(4.2) \quad h(t) = 2\lambda\sqrt{\sigma t},$$

$$(4.3) \quad T(x, t) = \begin{cases} u + \frac{T_f - u}{\operatorname{erf}(\lambda)} \operatorname{erf}\left(\frac{x}{2\sqrt{\sigma t}}\right) & \text{if } x \leq h(t), \\ T_f & \text{if } x > h(t). \end{cases}$$

Figure 4.1 shows the excellent visual agreement between the temperature field obtained by direct numerical simulation of the polymerization problem model (2.1)–(2.6) and the solution of the one-phase Stefan problem (3.18)–(3.22).

The piecewise linear profile exhibited by the temperature field in Figures 2.1 and 4.1 is now explained in the light of expression (4.3). Under the FBP framework, the heat conduction and crystallization length scales are related by (3.11), so $x/(2\sqrt{\sigma t}) \ll 1$. Hence, the Taylor expansion of the error function $\operatorname{erf}(\lambda) = (2/\sqrt{\pi})\lambda + \mathcal{O}(\lambda^3)$ for $\lambda \ll 1$ allows to say that the fraction of error functions in

(4.3) behaves as $x/h(t)$,

$$(4.4) \quad \frac{1}{\operatorname{erf}(\lambda)} \operatorname{erf}\left(\frac{x}{2\sqrt{\sigma t}}\right) = \frac{\operatorname{erf}\left(\frac{x}{2\sqrt{\sigma t}}\right)}{\operatorname{erf}\left(\frac{h(t)}{2\sqrt{\sigma t}}\right)} \approx \frac{x}{h(t)},$$

therefore showing that the temperature profile is effectively almost piecewise linear:

$$(4.5) \quad T(x, t) \approx \begin{cases} u + \frac{T_f - u}{h(t)}x & \text{if } x \leq h(t), \\ T_f & \text{if } x > h(t). \end{cases}$$

Furthermore, (4.1) can be approximated by $2\lambda^2 = Ste$ when $\lambda \ll 1$, where

$$(4.6) \quad Ste \stackrel{\text{def}}{=} \frac{c(T_f - u)}{\mathcal{L}_\delta}$$

is the Stefan number, a dimensionless parameter which completely characterizes the phase change process, and which is referred to as the ratio of the sensible heat to the latent heat (see [1, p. 38]). We have thus arrived at the following approximation for the free boundary:

$$(4.7) \quad h(t) \approx \sqrt{2Ste\sigma t}.$$

The necessary condition for the latent heat to induce the formation of the crystallization band (2.9) can therefore be written in a classical way in terms of the Stefan number:

$$(4.8) \quad Ste \ll 1.$$

Expression (4.5) is a particular case of the PSS approximation of the solution of the Stefan problem for arbitrary boundary conditions at $x = 0$ (see section 4.2).

4.1.2. Exponentially decreasing cooling temperature. This case, also studied by Stefan in his original work [22], also has an explicit analytical solution. The relevance of this boundary condition is that the velocity of the free boundary is constant, thus highlighting the shape and behavior of the crystallization band under variations of the parameters (of special interest in optimal control problems dealing with the final spatial homogeneity of the material—band width, amplitude, frequency and regularity of temperature field oscillations).

Given a fixed constant $\gamma > 0$, we consider the applied time-dependent temperature

$$(4.9) \quad u(t) = T_f - \frac{\mathcal{L}_\delta}{c} \left(e^{\gamma^2 \sigma t} - 1 \right).$$

The corresponding exact solution of the Stefan problem (3.18)–(3.22) is then (see [1])

$$(4.10) \quad h(t) = \gamma \sigma t,$$

$$(4.11) \quad T(x, t) = \begin{cases} T_f - \frac{\mathcal{L}_\delta}{c} \left(e^{\gamma^2 \sigma t - \gamma x} - 1 \right) & \text{if } x \leq h(t), \\ T_f & \text{if } x > h(t). \end{cases}$$

As we imposed $u = 0^\circ\text{C}$ in Table 2.1 as a lower bound for the applied temperature $u(t)$ to be far from the hypercooling regime, the following condition must be satisfied:

$$(4.12) \quad \gamma^2 t \leq \frac{1}{\sigma} \ln \left(1 + \frac{cT_f}{\mathcal{L}_\delta} \right).$$

Inequality (4.12) shows the strong link between γ and the time interval where the Stefan problem (3.18)–(3.22) is a valid approximation of the crystallization problem (2.1)–(2.6). When γ is such that the crystallization time t_{cryst} verifies (4.12), the agreement is excellent; see Figure 4.1(C), (D) for $\gamma = 2.89 \times 10^{-2}$ along the time interval $[0, 17.5 \times 10^3]$, and errors calculated in the next section. The apparent linear shape of $u(t)$ there is due to the low value of γ , which gives rise to an approximate slope of -3.8×10^{-3} in $[0, 17.5 \times 10^3]$.

4.1.3. Comparison of solutions. Two features serve to evaluate the accuracy of the FBP framework: how well the free boundary describes the behavior of the crystallization band, and how similar the temperature fields of the Stefan problem and the crystallization model are.

The evolution of the free boundary $h(t)$ is compared with $P(t)$, which is the magnitude it approximates, by means of the difference

$$(4.13) \quad \xi_1(t) \stackrel{\text{def}}{=} h(t) - P(t),$$

where $h(t)$ is given by the Stefan problem and $P(t)$ is obtained by solving numerically the crystallization problem (2.1)–(2.6) and computing (3.4) with the extended Simpson's rule. When needed, λ is calculated with a bisection method until the error is such that $|\lambda^{i+1} - \lambda^i| < \epsilon$, where ϵ is a small positive tolerance (we have used $\epsilon = 10^{-8}$) and i is the iteration index.

Another measure of error, often used in phase change problems, consists in evaluating how well the free boundary satisfies (3.3), namely, $T(h(t), t) = T_f$, which usually defines the free boundary. For coherence with [12] and [13], we denote by $x_b(t)$ the numerical solution of (3.3). As the FBP framework is blind to which characterization of $h(t)$ is used, $x_b(t)$ adds a complete picture of how the crystallization band behavior is described by $h(t)$, because the temperature oscillations are visible in the behavior of $x_b(t)$ but not in the behavior of $h(t)$.

Therefore, this type of error is measured by

$$(4.14) \quad \xi_2(t) \stackrel{\text{def}}{=} h(t) - x_b(t).$$

The measurement of these two errors is carried out with the normalized L_2 and L_∞ norms, and the maximum relative error, respectively, for $i = 1, 2$:

$$\begin{aligned} \xi_i^{L_2} &= \frac{1}{L} \left(\frac{1}{t_2 - t_1} \int_{t_1}^{t_2} \xi_i^2(t) dt \right)^{1/2}, \\ \xi_i^\infty &= \frac{\|\xi_i\|_\infty}{L} = \frac{1}{L} \sup_{t \in [t_1, t_2]} \{|\xi_i(t)|\}, \quad \xi_i^{\text{rel}} = \sup_{t \in [t_1, t_2]} \left\{ \left| \frac{\xi_i(t)}{h(t)} \right| \right\}. \end{aligned}$$

With regard to the temperature field, the error is measured by the instantaneous pointwise error between $T^{\text{NUM}}(x, t)$ and $T^{\text{STEF}}(x, t)$, which are the respective solutions of the crystallization problem solved numerically and the Stefan problem:

$$(4.15) \quad \varepsilon(x, t) = T^{\text{NUM}}(x, t) - T^{\text{STEF}}(x, t).$$

TABLE 4.1
Normalized L_2 -error, L_∞ -error, and relative errors.

Case	u (°C)	δ —	$\xi_1^{L_2}$ (10^{-3})	ξ_1^∞ (10^{-3})	ξ_1^{rel} (10^{-2})	$\xi_2^{L_2}$ (10^{-2})	ξ_2^∞ (10^{-2})	ξ_2^{rel} (10^{-1})	ε_T (10^{-3})
1	60	0.04	2.17	6.49	3.02	1.07	3.91	1.57	0.28
2	40	0.04	2.68	8.1	3.52	3.27	8.43	3.08	1.35
3	0	0.04	3.37	14.17	7.64	7.13	14.49	7.73	5.42
4	60	4	0.93	2.94	1.08	0.40	0.91	0.33	0.56
5	40	4	3.79	4.57	2.05	1.93	4.77	4.39	7.62
6	0	4	12.17	13.6	8.31	4.23	8.1	9.2	19.4
7	exp.	0.04	1.60	2.44	2.26	4.37	7.01	5.08	0.89
8	exp.	4	8.80	10.1	3.69	1.86	2.11	1.69	0.53
2 ^a	40	0.04	2.02	6.24	3.9	0.23	1.51	0.88	0.74
3 ^b	0	0.04	102.6	154.6	39.5	25.2	54	11.7	43.8

2^a: $G = 50 \text{ s}^{-1}$ (instead of $G = 5 \text{ s}^{-1}$).

3^b: Hypercooled case ($a_G = 200$ instead of 2500°C).

The time evolution of the normalized L_2 -norm of this quantity is then used to obtain one single number ε_T expressing the accuracy of the temperature field approximation:

$$(4.16) \quad \varepsilon_T = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} \varepsilon_{L_2}(t) dt, \quad \text{where} \quad \varepsilon_{L_2}(t) = \frac{1}{T_f} \left(\frac{1}{L} \int_0^L \varepsilon^2(x, t) dx \right)^{1/2}.$$

The errors are calculated during the time interval $[t_1, t_2]$ to avoid the transients where the Stefan problem cannot be considered a valid approximation of the polymerization problem. Still, ξ_2 and ε are subject to the effects of the temperature field oscillations, especially when the band width and/or the amplitude of the oscillations is large. Decidedly, the numerical simulations exhibit a good agreement along almost all the crystallization process.

4.1.4. Examples (exact Stefan problem solution known). Errors are calculated for the following eight cases: (i) six cases of constant applied temperature, $u = 60, 40$, and 0°C , and two values of δ , 0.04 and 4 ($G = 5 \text{ s}^{-1}$ and, respectively, $N = 20$ and 2000 s^{-1}), and (ii) two cases of exponentially decreasing $u(t)$ with the same two values of δ as in (i), adjusting the value of γ to preserve the condition (4.12) until the crystallization time is reached.

Two more cases, analyzed in section 4.2, appear in the tables and figures: a case yielding a very thin band, where G is such that δ is one of the previous values ($\delta = 0.04$, with $G = 50 \text{ s}^{-1}$, $N = 200 \text{ s}^{-1}$), and the hypercooled case already depicted in Figure 2.2.

Comparisons are presented in Table 4.1, calculated with the transient times t_1 and t_2 given in Table 4.2. Table 4.2 also shows the crystallization time t_{cryst} and the percentages $\tilde{t}_i = 100(t_i/t_{\text{cryst}})\%$ ($i=1,2$) of the duration of the crystallization process during which the Stefan problem is a valid approximation. The time evolution of $h(t)$, $P(t)$, $x_b(t)$, $x_\alpha(t)$, and $x_\omega(t)$ is depicted in Figures 4.2 to 4.6. Two other hypercooled cases are depicted in Figure 4.7.

The first result is that errors are considerably small in almost all cases: $\xi_1^{L_2} = O(10^{-3})$, $\xi_1^\infty = O(10^{-3})$, $\xi_1^{\text{rel}} = O(10^{-2})$, and $\varepsilon_T = O(10^{-3})$. This shows that the Stefan problem is an excellent approximation to the solution of the crystallization model.

The second result is that $x_b(t)$ is a worthy representative of the crystallization band, with errors only one order of magnitude higher than those of $h(t)$, despite the large band width and temperature oscillations occurring in some cases.

TABLE 4.2
Crystallization times, approximations, errors, and initial and final transients.

Case	u (°C)	δ —	$\tilde{t}_1$ (%)	$\tilde{t}_2$ (%)	b_0 (m)	$t_{\text{cryst}}^{\text{NUM}}$ (10^3 s)	$t_{\text{cryst}}^{\text{STEF}}$ (10^3 s)	$t_{\text{cryst}}^{\text{PSS}}$ (10^3 s)	ϵ^{STEF} (10^{-2})	ϵ^{PSS} (10^{-2})
1	60	0.04	4	94	0.167	58.22	56.46	56.37	3.04	3.18
2	40	0.04	5	92	0.138	19.45	18.87	18.79	2.98	3.4
3	0	0.04	3	92	0.109	8.37	8.14	8.05	2.81	3.8
4	60	4	7	92	0.202	19.33	17.76	17.67	8.14	8.57
5	40	4	1	89	0.016	6.49	5.97	5.89	8	9.27
6	0	4	1	86	0.004	2.81	2.61	2.52	7.25	10.18
7	exp.	0.04	10	92	0.057	18.29	18.09	18	1.14	1.6
8	exp.	4	6	95	0.001	10.66	10.29	10.21	3.45	4.23
2 ^a	40	0.04	3	98	0.141	19.04	18.87	18.79	0.86	1.3
3 ^b	0	0.04	10	91	—	0.988	0.724	0.644	26.8	34.8

2^a: $G = 50 \text{ s}^{-1}$ (instead of $G = 5 \text{ s}^{-1}$).

3^b: Hypercooled case ($a_G = 200$ instead of 2500°C). In cases 7 and 8, the values $\gamma = 2.76 \times 10^{-2}$ and 4.86×10^{-2} were used, respectively.

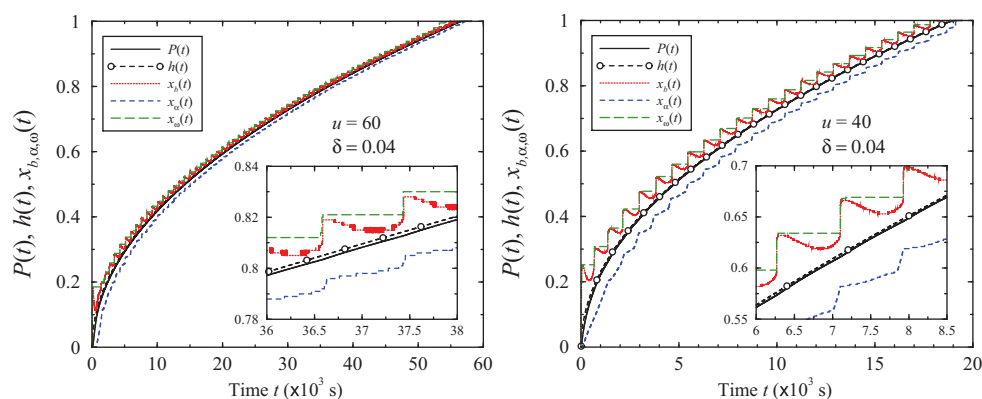


FIG. 4.2. Case 1 (left): $u = 60^\circ\text{C}$ and $\delta = 0.04$. Case 2 (right): $u = 40^\circ\text{C}$ and $\delta = 0.04$.

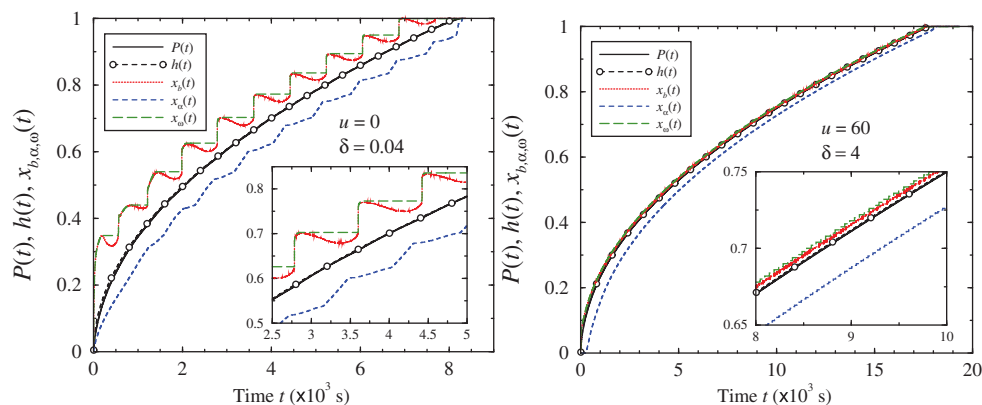


FIG. 4.3. Case 3: $u = 0^\circ\text{C}$ and $\delta = 0.04$. Case 4: $u = 60^\circ\text{C}$ and $\delta = 4$.

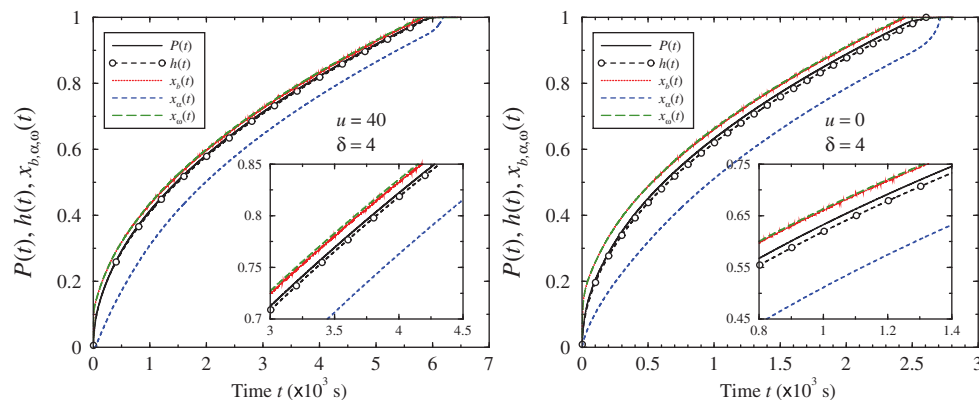


FIG. 4.4. Case 5: $u = 40^\circ\text{C}$ and $\delta = 4$. Case 6: $u = 0^\circ\text{C}$ and $\delta = 4$.

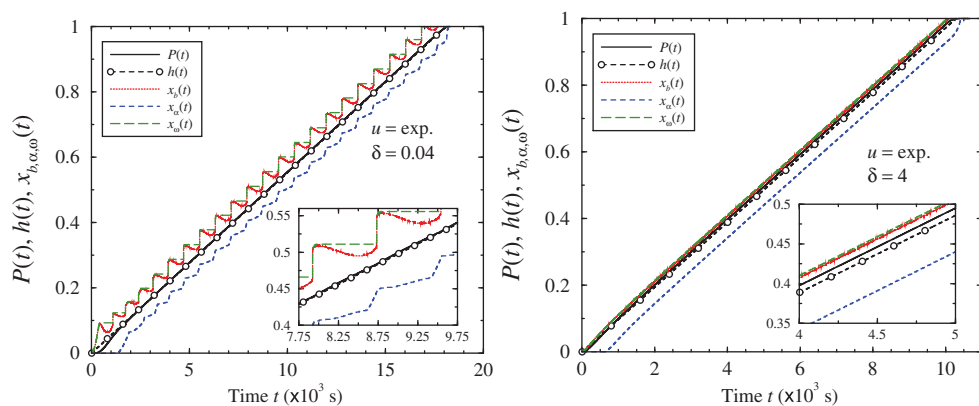


FIG. 4.5. Exponentially decreasing boundary condition. Case 7: $u = \text{exp.}$ and $\delta = 0.04$. Case 8: $u = \text{exp.}$ and $\delta = 4$.

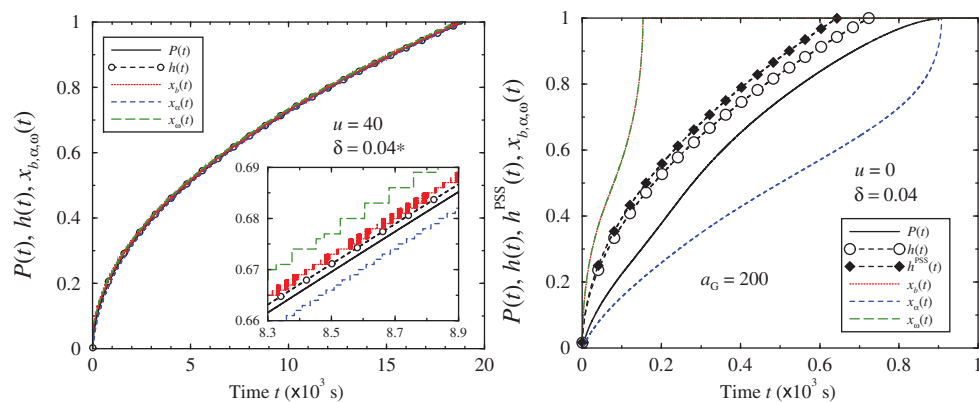


FIG. 4.6. Case 2^a: $u = 40^\circ\text{C}$ and $\delta = 0.04$ ($N = 200$, $G = 50$, $v_0 = 0.01$). Case 3^b (hypercooled case, also showing the PSS approximation): $u = 0^\circ\text{C}$, $\delta = 0.04$ ($N = 20$, $G = 5$, $v_0 = 0.01$), $a_G = 200^\circ\text{C}$. See also Figure 4.7.

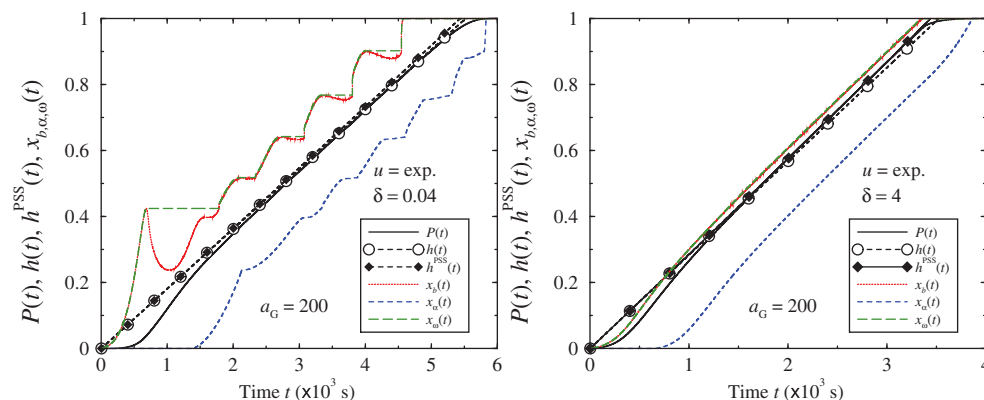


FIG. 4.7. Hypercooled cases: $a_G = 200^\circ \text{C}$. Free boundaries and crystallization band abscissas. Left: $u = \text{exp.}$, $\delta = 0.04$, $\gamma = 2.76 \times 10^{-2} \text{ m}^{-1}$. Right: $u = \text{exp.}$, $\delta = 4$, $\gamma = 4.86 \times 10^{-2} \text{ m}^{-1}$. (See also the right panel of Figure 4.6).

A third result from Table 4.2 is that the FBP framework is valid during 82% to 95% of the duration of the crystallization process, which is a quite representative proportion. Greater values of t_1 can reduce the averaged error ε_T , but to the detriment of the width of the interval $[t_1, t_2]$; see the transients in Table 4.2, e.g., case 6, where $\varepsilon_T = 19.4 \times 10^{-3}$ and $\tilde{t}_1 = 1\%$. For $\tilde{t}_1 = 14\%$, the error decreases, $\varepsilon_T = 6.79 \times 10^{-3}$, but the interval $[t_1, t_2]$ is reduced to 72% of the crystallization time and with no other benefits in the other errors. By contrast, in all cases a larger value of t_2 serves to enlarge $[t_1, t_2]$, without detriment of ε_T .

Errors and figures reveal other features of the crystallization process and how suitable the Stefan problem is to describe it. For example, in the exponential cases, ξ_1 is smaller in case 7 than in case 8, the opposite of what happens for ξ_2 , showing, as expected, that ξ_2 is more sensitive to oscillations than ξ_1 and, on the other hand, that in the sense of ξ_1 the free boundary $h(t)$ is closer to $P(t)$ in case 7 than in case 8, despite the fact that oscillations are more visible in case 7; see Figure 4.5.

4.2. PSS approximation for time-dependent boundary condition. Explicit analytical solutions of the Stefan problem are not available for arbitrary time-dependent imposed temperatures [1]. Thus, approximations are used, the simplest one being the PSS approximation [17, 1].

The PSS approximation is especially suitable in our framework, as it is based on the physical assumption that the sensible heat can be neglected with respect to the latent heat [1]. This assumption was precisely introduced in (2.9) as the necessary condition for the formation of the crystallization band pattern and therefore is the core assumption in our study.

4.2.1. PSS solution and its accuracy. The PSS estimate owes its name to the fact that the temperature is considered to remain at its stationary state, i.e., $T_t(x, t) = 0$, while the free boundary evolves in time. Hence, $T(x, t)$ is the solution of the equation

$$(4.17) \quad T_{xx}(x, t) = 0$$

with boundary conditions $T(0, t) = u(t)$ and $T(h(t), t) = T_f$. Therefore, the temperature profile at time t in $[0, h(t)]$ is a straight line which joins $u(t)$ at $x = 0$ with T_f at $x = h(t)$.

Using this approximation in the Stefan condition (3.22) leads to the expression of the free boundary and consequently to the PSS solution of the Stefan problem:

$$(4.18) \quad h^{\text{PSS}}(t) = \sqrt{\frac{2\sigma c}{\mathcal{L}_\delta} Q(t)} = \sqrt{\frac{2\sigma c}{\mathcal{L}_\delta} \int_0^t (T_f - u(s)) ds},$$

$$(4.19) \quad T^{\text{PSS}}(x, t) = \begin{cases} u(t) + \frac{T_f - u(t)}{h(t)}x & \text{if } x \leq h(t), \\ T_f & \text{if } x \geq h(t). \end{cases}$$

Note again that (4.18) was already found by Stefan for polar ice formation [22].

Since the free boundary $h(t)$ was defined as the approximation of the amount of crystallized polymer $P(t)$, expression (4.18) provides an analytical approximation of the value of the constant κ introduced here in (3.5) and obtained numerically in [13]:

$$(4.20) \quad \kappa = \sqrt{\frac{2\sigma c}{\mathcal{L}_\delta}}.$$

The approximation is remarkably good, as the value $\kappa = 1.33 \times 10^{-3} \text{ m (s } ^\circ\text{C)}^{-1/2}$ reported in [13] coincides exactly with the value arising from (4.20) for the values of the parameters of the problem used in [13] and shown in Table 2.1.

Moreover, the normalized L_2 -norm of the error can be calculated from the data in [13] for a large variety of time-depending applied temperature. For all the cases analyzed there, we obtained the following value of an error based on the L_2 -norm:

$$(4.21) \quad E_1(\tau_1) = \frac{1}{\tau_1} \int_0^{\tau_1} \left| \kappa \sqrt{Q(t)} - P(t) \right|^2 dt = O(10^{-5})$$

for a value $\tau_1 = 1.5 \times 10^4 \text{ s}$. Defining the quantity ξ_3 for the free boundary determined by the PSS approximation as

$$(4.22) \quad \xi_3(t) \stackrel{\text{def}}{=} h^{\text{PSS}}(t) - P(t)$$

and writing $t_1 = 0$ and $t_2 = \tau_1$, we have $\xi_3^{L_2} = \sqrt{E_1(\tau_1)} = O(10^{-3})$, showing that the PSS approximation is excellent for the cases studied in [13] (see Figure 4 therein).

This excellent order of magnitude of the L_2 -error is also reached in the cases presented in section 4.1.4, where the exact solution of the Stefan problem is known; see Table 4.3. The measures of error also have the same order of magnitude as those obtained for ξ_1 . With regard to the temperature, defining as before the quantity $\varepsilon_T^{\text{PSS}}$ as the L_1 -norm of $\varepsilon_{L_2}^{\text{PSS}}(t)$ in $[t_1, t_2]$, where $\varepsilon^{\text{PSS}}(x, t) = T^{\text{NUM}}(x, t) - T^{\text{PSS}}(x, t)$, the same order of magnitude is again reached: $\varepsilon_T^{\text{PSS}} = O(10^{-3})$.

Table 4.3 shows that the PSS approximation is an accurate approximation of the crystallization problem at almost the same level as the exact solution of the Stefan problem. Moreover, in some cases (namely, cases 5–8), ξ_3 yields lower values than ξ_1 , so that the position of the free boundary is better described by the PSS solution. As we will explain later, this is due to the fact that the PSS approximation overestimates the position of the free boundary: as $h(t)$ is below $P(t)$ in these cases, $h^{\text{PSS}}(t)$ can be closer to $P(t)$ than $h(t)$, therefore yielding smaller errors; see the insets in Figures 4.4 and 4.5.

TABLE 4.3
Errors for the PSS approximation.

Case	u (°C)	δ —	$\xi_3^{L_2}$ (10^{-3})	ξ_3^∞ (10^{-3})	ξ_3^{rel} (10^{-2})	$\varepsilon_T^{\text{PSS}}$ (10^{-3})
1	60	0.04	1.38	6.65	3.09	0.34
2	40	0.04	3.70	8.61	3.74	1.87
3	0	0.04	8.34	15.12	8.15	7.88
4	60	4	2.35	3.57	1.32	0.75
5	40	4	3.06	3.68	1.35	9.27
6	0	4	9.63	7.85	6.69	27.5
7	exp.	0.04	0.88	2.61	2.31	1.46
8	exp.	4	7.59	7.63	3.57	1.52
2 ^a	40	0.04	3.03	6.59	4.12	1.33
3 ^b	0	0.04	642.38	183.5	45.5	60.76

2^a: $G = 50 \text{ s}^{-1}$ (instead of $G = 5 \text{ s}^{-1}$).

3^b: Hypercooled case, with $a_G = 200$ instead of 2500°C .

This does not happen in the case of the temperature field: $\varepsilon_T^{\text{PSS}}$ is always greater than ε_T . The time evolution of $\varepsilon_{L_2}^{\text{PSS}}(t)$ and $\varepsilon_{L_2}(t)$ shows that the exact solution of the Stefan problem is always a better description of the numerical solution of the polymerization problem than the PSS approximation, which, in the exponential cases, loses accuracy as t grows. This is related to condition (4.12) and will be explained later.

4.2.2. The fundamental role of the sensible heat to latent heat relation.

The reason for the high accuracy with which the PSS approximation (4.18) describes the crystallization process lies in that the parameter values used in Table 2.1 (also used in [13]) are such that the condition (2.9), namely, $c \max_t \{T_f - u(t)\} \ll \mathcal{L}_\delta$, is largely satisfied.

For $\delta = 0.04$, we have $\mathcal{L}_\delta/c = 2254.9^\circ\text{C}$, and for $\delta = 4$, we have $\mathcal{L}_\delta/c = 706.99^\circ\text{C}$, so $Ste \approx 0.031$ for $\delta = 0.04$ and $Ste \approx 0.099$ for $\delta = 4$. Therefore, in both cases, $Ste \ll 1$. However, when the latent heat is not large enough and condition (2.9) is not satisfied, the PSS approximation is no longer valid; this is what happens in the hypercooled case depicted in Figure 2.2 and denoted by 3^b in Tables 4.1 to 4.4. In this case, $a_G = 200^\circ\text{C}$, so $Ste \approx 0.39$ for $\delta = 0.04$ and $Ste \approx 1.24$ for $\delta = 4$, i.e., $Ste \not\ll 1$.

In fact, not only is the PSS approximation not valid, but the whole Stefan problem framework should be rejected as a description of the polymerization problem: as Figure 4.6 shows, $h^{\text{PSS}}(t)$ is too far from the free boundary $h(t)$, and none of them are close to $P(t)$.

The fundamental role of the sensible heat to latent heat relation (2.9) can be clarified by deriving the PSS approximation directly from the initial statement (2.1)–(2.4) and using the hypotheses in a slightly different way.

Let us start from (3.16), to which we arrived from (2.1)–(2.4) just by assuming that a free boundary $h^*(t)$ exists such that $y(x, t) = 1$ if $x < h^*(t)$, $y(x, t) = 0$ if $x > h^*(t)$, and $T(x, t) = T_f$ if $x \geq h^*(t)$. Assuming now that the temperature profile is linear with respect to x in the solid phase, we have

$$T(x, t) \approx u(t) + x \left(\frac{T_f - u(t)}{h^*(t)} \right)$$

for $x < h^*(t)$. Substituting this expression in (3.16) with $h = h^*$, we get

$$\begin{aligned}
 \frac{\mathcal{L}_\delta}{c} h^*(t) &= \int_0^{h^*(t)} T(x, t) dx + T_f(L - h^*(t)) + \sigma \int_0^t T_x(0, s) ds - LT_0 \\
 &= u(t)h^*(t) + \frac{1}{2} [T_f - u(t)] h^*(t) + T_f [L - h^*(t)] \\
 &\quad + \sigma \int_0^t \frac{T_f - u(s)}{h^*(s)} ds - LT_0 \\
 (4.23) \quad &= \frac{1}{2} [u(t) - T_f] h^*(t) + \sigma \int_0^t \frac{T_f - u(s)}{h^*(s)} ds + (T_f - T_0)L.
 \end{aligned}$$

Time-differentiating this expression yields

$$(4.24) \quad \frac{\mathcal{L}_\delta}{c} \frac{dh^*(t)}{dt} = \frac{1}{2} \frac{d}{dt} [(u(t) - T_f)h^*(t)] + \sigma \frac{T_f - u(t)}{h^*(t)}.$$

By introducing the auxiliary function $z(t) = \frac{1}{2}[h^*(t)]^2$, this gives rise to the following differential equation for $z(t)$:

$$(4.25) \quad \left(\frac{\mathcal{L}_\delta}{c} + \frac{T_f - u(t)}{2} \right) z'(t) = z(t)u'(t) + \sigma(T_f - u(t)).$$

This linear ODE can be solved with the initial condition $z(0) = 0$ to obtain the following explicit expression of the free boundary:

$$(4.26) \quad h^*(t) = \frac{\sqrt{\frac{2\sigma c}{\mathcal{L}_\delta} \int_0^t [T_f - u(s)] \left[1 + \frac{c(T_f - u(s))}{2\mathcal{L}_\delta} \right] ds}}{1 + \frac{c(T_f - u(t))}{2\mathcal{L}_\delta}}.$$

Defining a kind of instantaneous Stefan number $Ste^*(t) = c[T_f - u(t)]/\mathcal{L}_\delta$, the free boundary coordinate can finally be written as

$$(4.27) \quad h^*(t) = \frac{1}{1 + \frac{1}{2}Ste^*(t)} \sqrt{\frac{2\sigma c}{\mathcal{L}_\delta} \int_0^t [T_f - u(s)] \left[1 + \frac{1}{2}Ste^*(s) \right] ds}.$$

Let us remark that the above derivation was obtained assuming some regularity with respect to time for $u(t)$ —i.e., at least the existence of $u'(t)$). Nevertheless, this assumption can be avoided by using a classical approximation result, arriving again at (4.27) for almost every t , from the corresponding one for regular cooling temperatures.

Expression (4.27) can be interpreted as a correction of the PSS approximation result $h^{\text{PSS}}(t)$: when $\max_t \{Ste^*(t)\} \ll 1$, expression (4.27) becomes (4.18). However, the error $h^*(t) - P(t)$ does not always yield better results than ξ_1 , due to the nonlinear effect of $Ste^*(t)$ in (4.27). When $u(t) = u$ is constant, we have $Ste^*(t) = Ste$ and (4.27) becomes

$$(4.28) \quad h^*(t) = \frac{\sqrt{2Ste \sigma t}}{\sqrt{1 + \frac{1}{2}Ste}} = \frac{h(t)}{\sqrt{1 + \frac{1}{2}Ste}},$$

showing that $h^*(t)$ is always smaller than $h(t)$.

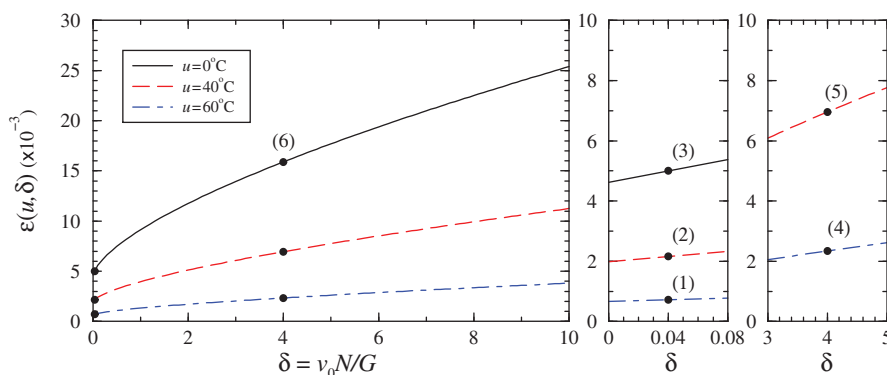


FIG. 4.8. Relative error $\varepsilon(u, \delta)$ for three values of u and $\delta \in [0, 10]$. Small panels: zoom at $\delta = 0.04$ and 4. Numbered dots denote the six cases for different values of u and δ used in section 4.1.4.

This alternative derivation of the equation of the free boundary reveals the fundamental role of condition (2.9) and corroborates the fact that the PSS approximation is valid whenever the Stefan number is small, that is, either if the sensible heat is small compared to the latent heat or if the cooling temperature $u(t)$ is just below the freezing temperature T_f (see [17]).

The latent heat (over c) in the right panel of Figure 4.6 is not small, $\mathcal{L}_\delta/c = 180.39^\circ\text{C}$, but the sensible heat (over c) is large, $T_f - u = 70^\circ\text{C}$, so the approximation is not valid. The latent heat has the same value in the left panel of Figure 4.7 and is even smaller in the right panel of Figure 4.7 (where $\mathcal{L}_\delta/c = 56.57^\circ\text{C}$), but in these cases the sensible heat is very small during a large part of the time (especially at the beginning); this is why, in the exponential case, the PSS approximation can be accepted.

Condition (2.9), in which all the parameters of the problem $u(t)$, T_f , a_G , σ , N , G , and v_0 appear explicitly, can therefore serve to anticipate the emergence of the crystallization band pattern.

4.2.3. PSS approximation for $u(t)$ constant. The examples described in section 4.1.4 show that the structure of the crystallization band is strongly dependent on the values of the applied temperature and the parameter δ , which in turns affects the accuracy with which the Stefan problem describes the crystallization process. The suitability of the PSS approximation for a given constant applied temperature u and a given value of δ can be evaluated by calculating the relative error between the Stefan number Ste and the solution of the transcendental equation (4.1), λ :

$$(4.29) \quad \varepsilon(u, \delta) = \frac{\left| \sqrt{Ste(u, \delta)} - \sqrt{2\lambda(u, \delta)} \right|}{\sqrt{Ste(u, \delta)}}.$$

The variation of $\varepsilon(u, \delta)$ is depicted in Figure 4.8 for three values of u representing the range of temperatures $[0, T_f]$ and for δ in $[0, 10]$; the six cases corresponding to the different values of u and δ used in section 4.1.4 are labeled with their number.

Figure 4.8 shows that the relative error $\varepsilon(u, \delta)$ is small when expected, that is, when the sensible heat is small (i.e., when u is close to T_f), and when the latent heat is great (i.e., when δ is small; note that K_δ is a decreasing function of δ , so $\mathcal{L}_\delta$ increases

TABLE 4.4
Latent heat over c , transcendental parameter, Stefan number.

Case	u (°C)	δ —	K_δ —	λ —	$\sqrt{Ste/2}$ —	ε (10^{-3})	$\mathcal{L}_\delta/c$ (°C)	Ste —
1	60	0.04	0.902	0.0471	0.0471	0.74	2254.9	0.004
2	40	0.04	0.902	0.0814	0.0816	2.21	2254.9	0.013
3	0	0.04	0.902	0.1239	0.1246	5.11	2254.9	0.031
4	60	4	0.283	0.0839	0.0841	2.34	706.99	0.014
5	40	4	0.283	0.1446	0.1457	6.96	706.99	0.042
6	0	4	0.283	0.219	0.2225	15.9	706.99	0.099
3 ^b	0	0.04	0.902	0.4156	0.4405	5.66	180.39	0.39

3^b: Hypercooled case with $a_G = 200$ instead of 2500°C .

when δ decreases). For the typical values we are using, $\varepsilon(u, \delta)$ is smaller than 10^{-2} , proving again that the PSS approximation is excellent.

Figure 4.8 also gives good insight into the relative quality of the errors, which from best to worse are 1, 2, 4, 3, 5, and 6.

Table 4.4 shows that the same order arises in terms of the Stefan number, which therefore should be considered the fundamental parameter to evaluate the accuracy of the PSS approximation, by means of the fundamental relation (2.9), rewritten equivalently as $Ste \ll 1$; in the hypercooled case depicted in Figure 2.2 (case 3^b in Table 4.4), $Ste = 0.39 \ll 1$.

4.2.4. PSS approximation for $u(t)$ exponential. In the case of the exponentially decreasing boundary condition (4.9), the PSS approximation gives the following expression for the free boundary:

$$(4.30) \quad h^{\text{PSS}}(t) = \sqrt{\frac{2}{\gamma^2} (e^{\gamma^2 \sigma t} - 1)} - 2\sigma t.$$

Expression (4.30) is a valid approximation of the exact solution (4.10), provided $\gamma^2 \sigma t \ll 1$.

When $\gamma^2 \sigma t \ll 1$ holds, the Taylor expansion of $e^{\gamma^2 \sigma t}$ can be truncated after the third term, thus reproducing (4.10):

$$(4.31) \quad h^{\text{PSS}}(t) \approx \sqrt{\frac{2}{\gamma^2} \left(\gamma^2 \sigma t + \frac{1}{2} \gamma^4 \sigma^2 t^2 \right)} - 2\sigma t = \gamma \sigma t.$$

Assuming a nonnegative applied temperature $u(t)$, equivalently (4.12), a sufficient condition for $\gamma^2 \sigma t \ll 1$ is $\ln(1 + \frac{cT_f}{\mathcal{L}_\delta}) \ll 1$ or, equivalently, $cT_f \ll \mathcal{L}_\delta$.

When t grows, the condition $\gamma^2 \sigma t \ll 1$ fails and the PSS approximation worsens. Therefore, the interval of time where the PSS approximation is valid is strongly dependent on γ , its length being much smaller than $1/(\sigma\gamma^2)$. As the error $h(t) - h^{\text{PSS}}(t)$ does not provide a useful explicit expression, it is difficult to determine how much of the accuracy of the PSS approximation relies on the latent heat to sensible heat ratio or on the value of γ , both magnitudes being related through (4.12).

4.2.5. Estimates of the total crystallization time. Explicit expressions such as (4.18) are especially relevant from the practical viewpoint, as they reveal fundamental features of the physical phenomenon and allow us to derive important magnitudes of industrial interest.

Expressions (3.5) and (4.20) show that the amount of crystallized polymer $P(t)$ depends only on the magnitude $Q(t)$, whatever the history of the applied cooling temperature $u(t)$. Thus, the profile of the applied temperature $u(t)$ has no effect on the duration of the crystallization process t_{cryst} , provided $Q(t)$ remains unchanged. Consequently, the full crystallization of a sample of length L , that is, the production of an amount of crystallized polymer $P(t_{\text{cryst}}) = L$, will require a cooling strategy such that

$$(4.32) \quad Q_0 \equiv Q(t_{\text{cryst}}) = \frac{\mathcal{L}_\delta}{2\sigma c} L^2.$$

That Q_0 does not depend on the profile of $u(t)$ is something a priori not expected, as first noticed in [13].

Notably, expression (4.32) constitutes a characterization of the crystallization time in terms of the fundamental parameters of the material, $\mathcal{L}_\delta$, σ , c , and L .

Moreover, when $u(t) < T_f$ for every t , upper and lower bounds can be derived for t_{cryst} by using the extreme values of the applied temperature $u_M = \max_t u(t)$ and $u_m = \min_t u(t)$. Then, the total crystallization time is such that

$$(4.33) \quad \frac{Q_0}{T_f - u_m} \leq t_{\text{cryst}} \leq \frac{Q_0}{T_f - u_M}$$

or, equivalently,

$$(4.34) \quad \frac{L^2}{2\sigma Ste_m} \leq t_{\text{cryst}} \leq \frac{L^2}{2\sigma Ste_M},$$

where we have defined the Stefan numbers $Ste_M = c(T_f - u_M)/\mathcal{L}_\delta$ and $Ste_m = c(T_f - u_m)/\mathcal{L}_\delta$.

However, as the PSS approximation ignores the sensible heat, all the heat is employed in driving the phase change. Thus, the PSS approximation often overestimates the free boundary location (see [1, p. 126]), so that only the lower bound is valid.

When u is constant, we have $Q_0 = (T_f - u)t_{\text{cryst}}$ and the PSS approximation yields

$$(4.35) \quad t_{\text{cryst}}^{\text{PSS}} = \frac{L^2}{2\sigma Ste},$$

which, as shown previously by calculating the relative error $\varepsilon(u, \delta)$, compares very well with the value given by the Stefan problem (also an approximation of the real value):

$$(4.36) \quad t_{\text{cryst}}^{\text{STEF}} = \frac{L^2}{4\sigma\lambda^2}.$$

When $u(t)$ is an exponentially decreasing function, then $t_{\text{cryst}}^{\text{STEF}} = L/(\gamma\sigma)$, and $t_{\text{cryst}}^{\text{PSS}}$ is the unique solution of the following transcendental equation for λ (see (4.30)),

$$(4.37) \quad e^{\gamma^2\sigma\lambda} = \gamma^2\sigma\lambda + \frac{\gamma^2 L^2}{2} + 1,$$

which, approximated again with the first three terms of the Taylor expansion of the exponential (provided $\gamma^2\sigma\lambda < 1$), yields precisely $t_{\text{cryst}}^{\text{STEF}}$.

Table 4.2 shows the values of the relative errors for the cases presented in section 4.1.4,

$$(4.38) \quad \epsilon^{\text{STEF}} = \frac{|t_{\text{cryst}}^{\text{NUM}} - t_{\text{cryst}}^{\text{STEF}}|}{t_{\text{cryst}}^{\text{NUM}}}, \quad \epsilon^{\text{PSS}} = \frac{|t_{\text{cryst}}^{\text{NUM}} - t_{\text{cryst}}^{\text{PSS}}|}{t_{\text{cryst}}^{\text{NUM}}},$$

which yield excellent estimates (of order 10^{-2}) except, logically, in the hypercooled case.

The estimates of the crystallization time based on the PSS approximation provide an analytical support to the optimal control problem solved numerically in [13].

5. Conclusions and open problems. An FBP framework has been proposed for a polymer crystallization model which develops advancing crystallization fronts for typical values of the parameters. The FBP framework consists in using a physical magnitude, the amount of crystallized polymer $P(t)$, as a representative of the position of the crystallization front, under a hypothesis of instantaneous crystallization. This allowed us to describe the crystallization process as the evolution of a free boundary separating the polymer sample into two regions, the crystalline phase and the amorphous one.

Under this framework, we have derived an evolution equation for the free boundary which turned out to be a Stefan condition. Then we formulated a classical one-phase Stefan problem that was solved for different boundary conditions corresponding to the typical applied cooling temperature profiles, obtaining analytical expressions for the evolution of the free boundary and the temperature distribution, first for two cases where they are available, and second for the general case (arbitrary time-dependent boundary condition) by using the PSS approximation.

We have compared the solution of the Stefan problem with the numerical solution of the polymer crystallization problem, showing that the former is a quite accurate approximation of the latter, for the description of the evolution of the crystallization front (normalized L_2 -norm error of order 10^{-3}) and the temperature distribution (global error of order 10^{-3}), during almost all the crystallization process (82% to 95%). Moreover, we have obtained explicit expressions of important features of the model such as the latent heat, given by (3.23), and the Stefan number, defined in (4.6), relating all the parameters of the crystallization model for which the FBP framework yields a valid approximation; see expression (2.9).

The relevance of our approach has been illustrated by deriving analytical approximations of important properties from the viewpoint of industry, such as the crystallization time (error of order 10^{-2}). The FBP framework has been shown to be especially effective in determining the optimal cooling strategy in one-dimensional samples, both in the one-sided cooling case [13] and in the two-sided cooling case [14]. In both cases, the optimal applied temperature profile and the total time of the cooling process are obtained.

Let us finish by mentioning two main directions for future work: first, the extension to other geometries of higher dimension (one-sided and two-sided cooling in cylindrical and two-dimensional samples), and second, the extension to other polymer crystallization models, especially those exhibiting a heat balance equation of the form of (2.8). We also hope that our work will help in finding the optimal cooling strategy in all these situations.

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