

MATHEMATICAL MODELLING AND SIMULATION OF NON-ISOTHERMAL CRYSTALLIZATION OF POLYMERS

MARTIN BURGER

*Industrial Mathematics Institute, Johannes Kepler University Linz,
Altenbergerstr. 69, A-4040 Linz, Austria*

VINCENZO CAPASSO

*MIRIAM (Milan Research centre for Industrial and Applied Mathematics),
Università di Milano, Via Saldini 50, 20133 Milano, Italy*

This paper is devoted to the study of mathematical problems arising in the modelling of nonisothermal polymer crystallization under industrial conditions. A review of the hybrid stochastic-deterministic modelling procedure, which yields an averaged model^{5,8}, is given and supplied by the study of mathematical problems arising from it.

Furthermore, multiple scale effects in the crystallization process are studied using different scalings, focussing either on the heat conduction or on the crystallization part. It is shown that in the limit of fast nucleation and slow growth, the model is equivalent to a direct extension of the classical Avrami-Kolmogorov model equations.

In addition, numerical simulations are presented to illustrate the behaviour during crystallization. Finally, open questions from mathematical and engineering view points are discussed.

Keywords: Crystallization, Growth, Nucleation, Nonlinear Evolution Equations, Polymers, Stochastic Geometry, Multiple Scales.

1. Introduction

The mathematical modelling of polymer crystallization under heat transfer conditions has become of great importance recently, especially because of the large amount of industrial applications and the need for mathematical tools to predict the quality of the final products^{12,20}.

Crystallization is a mechanism of phase change in polymeric materials. If an experiment is started with a liquid and the temperature is decreased subsequently below a certain point (the melting point of the material), crystals appear randomly in space and time and start to grow until they hit another crystal, which abruptly stops the growth at the interface (which is called *impingement*). Both these phenomena are driven by temperature; in the liquid phase nuclei are born randomly by a Poisson process with rate $\alpha = \alpha(x, t)$ (the so-called *free nucleation rate*), which depends on temperature (and temperature history) in some way. For many materials

like polypropylene, a standard model is ^{12,13}

$$\alpha(x, t) = \frac{\partial}{\partial t} \tilde{N}(T(x, t)). \quad (1.1)$$

Growth takes place at the surface of an individual crystal with normal speed $G = G(x, t)$ depending upon temperature via ^{12,13,23,25}

$$G(x, t) = \tilde{G}(T(x, t)). \quad (1.2)$$

Vice versa, growing crystals influence the heat transfer process by releasing energy as a consequence of phase change (which adds a source term to the heat equation). This source is usually called the *latent heat*.

The first mathematical model for a crystallization process (in that case for metals) was given by Kolmogorov ¹⁴ and independently by Avrami ² for processes homogenous in space and time. Kolmogorov's approach lead to the equation

$$\xi(t) = 1 - e^{-V(t)}, \quad (1.3)$$

where ξ represents the expected value of the crystalline fraction a domain and $V(t)$ is the expected volume of the crystals in absence of impingement. Avrami obtained the equivalent equation

$$\frac{d\xi}{dt}(t) = (1 - \xi(t)) \frac{dV}{dt}(t) = G(1 - \xi(t))S(t), \quad (1.4)$$

by the argument that the change of the crystalline volume fraction is proportional to the expected available surface of the crystalline phase $((1 - \xi)S)$, which can again be expressed in terms of the expected free surface S (in absence of impingement). The expected free surface S can be determined easily, e.g. in one spatial dimension, its twice the expected number of crystals, i.e.,

$$S(t) = 2 \int_0^t \alpha \, ds.$$

The last formula can also be rewritten as a differential equation, namely

$$\frac{dS}{dt} = 2\alpha. \quad (1.5)$$

It will turn out in the subsequent sections that this formula can be extended to heterogenous cases.

However, under industrial conditions, temperature and consequently nucleation and growth rates are almost never uniform in space, which causes a need for improved models to obtain information about the spatial distribution and morphology of crystals, which determine the mechanical properties of the final product ^{9,22}.

In the subsequent sections we will present an approach to obtain mathematical models either for stochastic simulations on the microscale or for the prediction of averaged quantities on larger scales. The paper is organized as follows: in Section 2

we derive a stochastic model for the crystallization process, which can be written as an initial-boundary value problem for a system of partial differential equations with random source. In Section 3 we show how this stochastic model can be approximated by the averaged deterministic model and discuss the effect of Bboundary nucleation as described e.g. by Eder ¹¹ and incorporate it into the model equations.

Section 4 is devoted to the study of multiple scales in the process and their implications on our averaged model, before presenting the results of numerical simulations of the crystallization process in Section 5. Finally, open and partially solved problems related to the mathematical modelling of polymer crystallization are discussed in Section 6.

2. The Stochastic Model of the Crystallization Process

From the stochastic point of view, crystallization can be modelled as a birth-and-growth process. Driven by some intensity α , crystals are born randomly and immediately start growing with normal speed G . The standard model adopted for the nucleation process is the one of a *stochastic spatially marked point process* (MPP), on an underlying probability space $(\Omega, \mathcal{A}, \mathcal{P})$

$$N = \sum_{j=1}^{\infty} \epsilon(X_j, T_j), \quad (2.6)$$

where T_j is the time of occurrence of the j -th nucleation and X_j denotes the space location of the j -th nucleus. T_j is a random variable valued in \mathbf{R}_+ and X_j is random variable valued in a Borel set $D \subset \mathbf{R}^d$, $d = 1, 2, 3$. We shall denote by \mathcal{B}_+ the σ -algebra of Borel sets in R_+ , and by \mathcal{C} the σ -algebra of Borel sets in D . For any $t \in \mathbf{R}_+$ and $x \in D$, $\epsilon(x, t)$ denotes the Dirac measure on $\mathcal{C} \times \mathcal{B}_+$, such that for any $B \in \mathcal{B}_+$ and $C \in \mathcal{C}$,

$$\epsilon(x, t)(C, B) = \begin{cases} 1 & \text{if } t \in B \text{ and } x \in C \\ 0 & \text{otherwise .} \end{cases} \quad (2.7)$$

In a crystallization process with nucleation events

$$\{ (X_j, T_j) \mid 0 \leq T_1 \leq T_2 \leq \dots \},$$

the crystalline phase at time t is given by

$$\Theta^t = \bigcup_{T_j < t} \Theta_j^t, \quad (2.8)$$

where Θ_j^t (a random set) denotes the crystal born at time T_j at location X_j freely grown up to time t . The real phase of the crystal may be a proper subset of Θ_j^t because of the effect of impingement, according to which growth is stopped at the common interface when two crystals hit each other. Nevertheless, impingement is included in (2.8), since the union over all crystals is taken.

The integer-valued random variable $N(A)$ counts the number of nucleation events in the region $A \in \mathcal{C} \times \mathcal{B}_+$ of space-time, i.e.,

$$N(A) = |\{ j \mid (X_j, T_j) \in A \}|, \quad (2.9)$$

whose randomness arises from the randomness of the nucleation events (X_j, T_j) .

Under the usual assumptions, the nucleation process is a MPP with intensity measure¹⁰

$$\nu(dx \times dt) = \alpha(x, t)(1 - I_{\Theta^t}(x))dxdt, \quad (2.10)$$

where $\alpha(x, t)$ is the mean number of new nuclei produced per unit volume and unit time at $(x, t) \in D \times \mathbf{R}_+$, independent of the actual crystalline phase Θ^t (with indicator function I_{Θ^t}).

The (deterministic) measure defined by the expected values

$$\Lambda(A) := E[N(A)], \quad A \in \mathcal{C} \times \mathcal{B}_+, \quad (2.11)$$

is known as the *intensity measure* of N . The following holds:

$$\Lambda(dx \times dt) = E[N(dx \times dt)] = E[\nu(dx \times dt)] = \alpha(x, t)(1 - \xi(x, t))dxdt.$$

where $\xi(x, t) := E[I_{\Theta^t}(x)]$ is the usual crystallinity function.

The average number of spherulites born up to time t per unit of volume at $x \in D$ is then

$$N_C(x, t) = \int_0^t \alpha(x, s)(1 - \xi(x, s)) ds.$$

2.1. *Evolution Equations with Random Source*

An equivalent description of the process can be obtained by using the (stochastic) indicator function f of the crystalline phase, defined by

$$f(x, t) = I_{\Theta^t}(x) \quad \forall t \in \mathbf{R}^+, x \in D, \quad (2.12)$$

so that the crystallinity function is given by

$$\xi(x, t) = E[f(x, t)], \quad \forall t \in \mathbf{R}^+, x \in D. \quad (2.13)$$

If we denote by f^j the indicator function of the single crystal Θ^j , we may write

$$f(x, t) = 1 - \prod_{t_j \leq t} (1 - f^j(x, t)). \quad (2.14)$$

Besides the actual volume distribution f , we may also define the *free volume distribution* f_{free} by

$$f_{free}(x, t) = \sum_{t_j \leq t} f^j(x, t), \quad (2.15)$$

the difference between f_{free} and f is obviously a measure of the relevance of impingement.

Besides the volume distribution of a crystal, we may also define the distribution of the surface metric density v^j or the oriented density w^j , which are generalized functions and can be defined via

$$\langle v^j, \phi \rangle = \int_{\partial\Theta^j \cap \bar{D}} \phi \, d|n|, \quad \forall \phi \in C(\bar{D}) \quad (2.16)$$

$$\langle w^j, \phi \rangle = - \int_{\partial\Theta^j \cap \bar{D}} \phi \, dn, \quad \forall \phi \in C(\bar{D}). \quad (2.17)$$

In one spatial dimension v^j (respectively w^j) is just the sum (respectively difference) of two Dirac δ -distributions located at the end points of the crystal. Similarly to f_{free} we can also define the free volume densities v_{free} and w_{free} as the sum over all v^j and w^j , respectively.

Now we consider an arbitrary closed set C and compute the crystalline volume in C at time t as

$$V(C, t) = \int_C f(x, t) \, dx = \sum_j \int_{\Theta_j^t \cap C} \prod_{k < j} (1 - f^k(x, t)) \, dx.$$

The time change of the crystalline volume can now be obtained in two ways:

$$\begin{aligned} \frac{\partial V}{\partial t}(C, t) &= \int_C \frac{\partial f}{\partial t}(x, t) \, dx \\ &= \langle I_C, \frac{\partial f}{\partial t} \rangle. \end{aligned} \quad (2.18)$$

and

$$\begin{aligned} \frac{\partial V}{\partial t}(C, t) &= \sum_j \frac{\partial}{\partial t} \int_{\Theta_j^t \cap C} \prod_{k < j} (1 - f^k(x, t)) \, dx \\ &= \sum_j \int_{\Theta_j^t \cap C} \operatorname{div} \left(W^j(x, t) \prod_{k < j} (1 - f^k(x, t)) \right) \, dx, \end{aligned}$$

where W^j is the speed with which the surface of crystal Θ^j moves. By applying Gauss' Theorem to the last identity we obtain

$$\frac{\partial V}{\partial t}(C, t) = \sum_j \int_{\partial\Theta_j^t \cap C} W^j(x, t) \prod_{k < j} (1 - f^k(x, t)) \, dn.$$

The modelling of crystal growth based upon experimentally verified minimum principles yields^{8,26}

$$W^j(x, t) = G(x, t)n(x, t), \quad \forall x \in \partial\Theta_j^t, t \in \mathbf{R}^+.$$

where n denotes the outer normal of the crystal's boundary. Furthermore, by definition we have $f^k = 0$ on $\partial\Theta_j^t$ for $k \geq j$, and consequently we may write

$$\begin{aligned} \frac{\partial V}{\partial t}(C, t) &= \sum_j \int_{\partial\Theta_j^t \cap C} G(x, t) \prod_k (1 - f^k(x, t)) d|n| \\ &= \sum_j \int_{\partial\Theta_j^t \cap C} G(x, t)(1 - f(x, t)) d|n| \\ &= \langle I_C, G(1 - f) \sum_j v^j \rangle. \end{aligned} \quad (2.19)$$

Since C is arbitrary in (2.18) and (2.19), we obtain (in the sense of generalized functions) with the free surface density $v_{free} = \sum v^j$:

$$\frac{\partial f}{\partial t} = G(1 - f)v_{free} = (1 - f)\frac{\partial f_{free}}{\partial t}, \quad (2.20)$$

which is a generalization of the *Avrami-formula* (1.4) to the spatially inhomogenous case.

In the distributional sense we may also compute the gradient of f via

$$\langle \nabla f(\cdot, t), \phi \rangle = -\langle f(\cdot, t), \operatorname{div} \phi \rangle, \quad \forall \phi \in C_0^\infty(D; \mathbf{R}^d).$$

This formula implies together with Gauss' Theorem

$$\begin{aligned} \langle \nabla f^j(\cdot, t), \phi \rangle &= -\int_D f^j(x, t) \operatorname{div} \phi(x) dx = -\int_{\Theta_j^t} \operatorname{div} \phi(x) dx \\ &= -\int_{\partial\Theta_j^t} \phi(x) dn(x) = \langle w^j(\cdot, t), \phi \rangle, \end{aligned}$$

and thus, we may conclude that

$$\nabla f^j = w^j. \quad (2.21)$$

By a similar technique as for f_t we may conclude that

$$\nabla f = (1 - f)w_{free}, \quad (2.22)$$

and a standard compatibility relation immediately yields

$$(w_{free})_t = \nabla(Gv_{free}). \quad (2.23)$$

So far, we have derived equations (2.20) and (2.23) for the evolution of f , v_{free} and w_{free} . Obviously we need a third evolution equations, thus we start by computing the time derivative of v^j in a distributional sense, i.e., for all $\phi \in C_0^\infty(D \times (0, t_*); \mathbf{R})$ we have

$$\begin{aligned} \langle v_t^j, \phi \rangle &= -\langle v^j, \phi_t \rangle = -\int_0^{t_*} \int_{\partial\Theta_j^t} \phi_t n dn dt \\ &= -\int_0^{t_*} \int_{\Theta_j^t} \nabla(\phi_t g) dx dt, \end{aligned}$$

where the last equality follows from Gauss' Theorem with g such that $g = n$ on $\partial\Theta_j^t$ and sufficiently smooth in the interior. Using the definition of f^j , integration by parts with respect to t and inserting the identity $f_t^j = Gv^j$ yields

$$\begin{aligned}
 \langle v_t^j, \phi \rangle &= \int_0^{t^*} \int_D \left(f_t^j \nabla(\phi g) + f^j \nabla(\phi g_t) \right) dx dt \\
 &= \int_0^{t^*} \int_D \left(Gv^j \nabla(\phi g) + \nabla(\phi g_t) \right) dx dt \\
 &= \int_0^{t^*} \int_{\partial\Theta_j^t} (G\nabla\phi + \phi n_t) dn \\
 &= -\langle Gw^j, \nabla\phi \rangle + \langle S_j^d, \phi \rangle \\
 &= \langle \nabla(Gw^j) + S_j^d, \phi \rangle,
 \end{aligned}$$

which implies

$$v_t^j = \nabla(Gw^j) + S_j^d \quad (2.24)$$

The generalized function S_j^d is the measure of the (stochastic) increase of free surface due to the birth of the j -th crystal at time T_j and location X_j . It can be computed explicitly, depending upon the space dimension $d=1,2$, as ⁸

$$\langle S_j^1, \phi \rangle = 2\phi_t(X_j, T_j) \quad (2.25)$$

$$\langle S_j^2, \phi \rangle = 2\pi G(X_j, T_j)\phi(X_j, T_j). \quad (2.26)$$

In \mathbf{R}^3 , the distribution S_j^3 is characterized by (cf. ⁸)

$$\left\langle \frac{\partial}{\partial t} S_j^3, \phi \right\rangle = 2G(X_j, T_j)\langle R_j^3, \phi \rangle \quad (2.27)$$

$$\langle R_j^3, \phi \rangle = 4\pi T_j G(X_j, T_j)\phi(X_j, T_j). \quad (2.28)$$

Summing up over all v^j in (2.24) we obtain

$$(v_{free})_t = \nabla(Gw_{free}) + \sum_{T_j=t} S_j^d. \quad (2.29)$$

Since the nucleation and growth rate depend on the temperature T , the above are coupled with

$$T_t = \operatorname{div}(D\nabla T) + \frac{h}{c}f_t, \quad (2.30)$$

with $D = \frac{\kappa}{\rho c}$, where κ denotes the heat conductivity, c the heat capacity and ρ the density. The constant h is called latent heat; it represents the energy released at the moment of the phase change. In general, κ , ρ and c depend on temperature and on the phase, i.e., in mathematical terms on T and f , but for many polymeric materials the variance of ρ and c is very small, so it seems reasonable to use constant values instead.

Summing up, we have obtained the system

$$T_t = \operatorname{div}(D\nabla T) + \frac{h}{c}f_t \quad \text{in } D \times (0, t_*) \quad (2.31)$$

$$f_t = \tilde{G}(T)(1-f)v_{free} \quad \text{in } D \times (0, t_*) \quad (2.32)$$

$$(v_{free})_t = \nabla(\tilde{G}(T)w_{free}) + \sum_{T_j=t} S_j^d \quad \text{in } D \times (0, t_*) \quad (2.33)$$

$$(w_{free})_t = \nabla(\tilde{G}(T)v_{free}) \quad \text{in } D \times (0, t_*). \quad (2.34)$$

If we assume that the whole crystallization process starts at time $t = 0$ the initial values are given by

$$T = T^0 \quad \text{in } D \times \{0\} \quad (2.35)$$

$$f = 0 \quad \text{in } D \times \{0\} \quad (2.36)$$

$$v_{free} = 0 \quad \text{in } D \times \{0\} \quad (2.37)$$

$$w_{free} = 0 \quad \text{in } D \times \{0\}, \quad (2.38)$$

and because of the cooling from outside, the boundary condition

$$pfTn = \gamma_0(T - T_{out}) \quad \text{on } \partial D \times (0, t_*) \quad (2.39)$$

must be satisfied, where γ_0 denotes the heat transfer coefficient and T_{out} the temperature of the cooling material.

3. Averaging of the Stochastic Model

Under typical industrial conditions, several assumptions can be made, which allow to approximate the stochastic model (2.31)-(2.39) by a deterministic system:

- The nucleation rate and consequently the number of crystals is very large.
- The growth rate and consequently the sizes of the crystals are very small.
- The typical scale for diffusion of temperature (macroscale) is much larger than the typical crystal size (microscale).
- A *mesoscale* may be introduced, sufficiently small with respect to the macroscale of heat conduction so that temperature at that scale may be considered approximately constant, but large enough with respect to the typical scale of the size of individual crystals so that it contains a large number of them making the "law of large numbers" applicable.

A typical size x_{meso} on this mesoscale satisfies

$$x_{crystal} \ll x_{meso} \ll x_{temperature},$$

where $x_{crystal}$ and $x_{temperature}$ are typical sizes for single crystals and for the heat transfer process. If t_0 is a typical time, G_0 and D_0 are typical values for the growth rate and the diffusion coefficient, we may choose

$$x_{crystal} = G_0 t_0, \quad x_{temperature} = \sqrt{D_0 t_0},$$

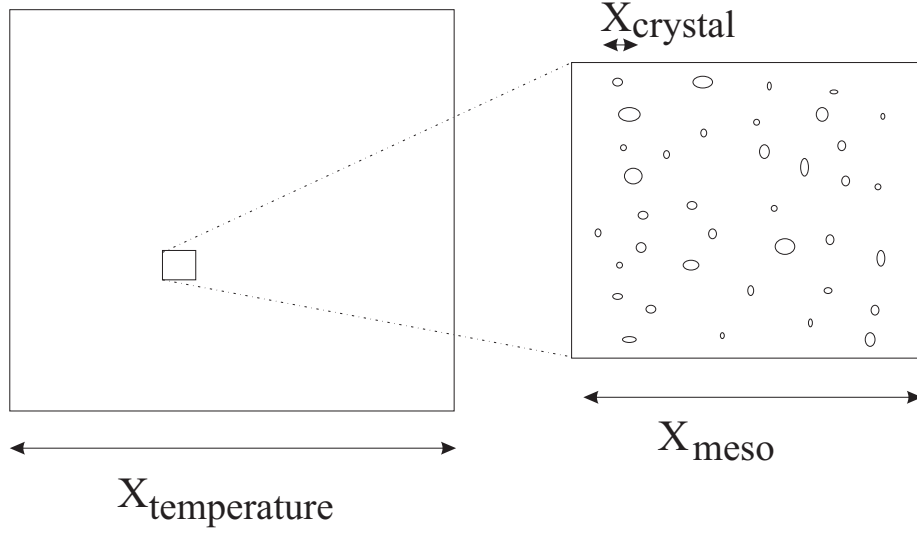


Fig. 1. The typical scales in the crystallization process.

which differ by several orders of magnitude under usual processing conditions. This typical feature of the process is illustrated in Figure 1.

If we take a sufficiently large volume C , than the number of crystals produced in C in the time interval $(t, t + \Delta t)$ can be approximated by its expected value, i.e. (note that overlapping of crystals is negligible since in an arbitrarily small time interval the new nuclei do not have a volume),

$$N(C \times (t, t + \Delta t)) \approx \int_t^{t+\Delta t} \int_C \alpha(x, s) dx ds. \quad (3.40)$$

If (3.40) is valid on a typical volume for this mesoscale, we can approximate the random source $\sum_j S_j^d$ by its local average in $C(x) \times (t, t + \Delta t)$ (where $C(x)$ is an appropriate neighbourhood of x), i.e. by

$$\begin{aligned} \frac{1}{\Delta t |C(x)|} \langle \sum_{T_j=t} S_j^1, I_{C(x) \times (t, t+\Delta t)} \rangle &\approx \frac{1}{\Delta t |C(x)|} E \left[\langle \sum_{T_j=t} S_j^1, I_{C(x) \times (t, t+\Delta t)} \rangle \right] \\ &= \frac{2}{\Delta t |C(x)|} E [N(C(x) \times (t, t + \Delta t))] \\ &= \frac{2}{\Delta t |C(x)|} \int_t^{t+\Delta t} \int_{C(x)} \alpha(y, s) dy ds \quad (3.41) \end{aligned}$$

$$\approx 2\alpha(x, t) = 2 \frac{\partial}{\partial t} \tilde{N}(T(x, t)) \quad (3.42)$$

By similar reasoning, one can deduce (cf. ⁸)

$$\begin{aligned} \frac{1}{\Delta t |C(x)|} \left\langle \sum_{T_j=t} S_j^2, I_{C(x) \times (t, t+\Delta t)} \right\rangle &\approx 2\pi G(x, t) \int_0^t \alpha(x, \tau) d\tau \\ &= 2\pi G(x, t) \tilde{N}(T(x, t)) \quad (3.43) \\ \frac{1}{\Delta t |C(x)|} \left\langle \sum_{T_j=t} S_j^3, I_{C(x) \times (t, t+\Delta t)} \right\rangle &\approx 8\pi G(x, t) \int_0^t G(x, \tau) \int_0^t \alpha(x, s) ds d\tau \\ &= 8\pi \tilde{G}(T(x, t)) \int_0^t \tilde{G}(T(x, \tau)) \tilde{N}(T(x, \tau)) d\tau \quad (3.44) \end{aligned}$$

The quantities we obtain from (2.31)-(2.39) with the source replaced by its local value, are mean quantities, i.e., they describe the mean behaviour in a volume of size $C(x)$, but cannot resolve smaller details. E.g., the indicator function f is replaced by the degree of crystallinity ξ , which approximates the expected value of f . The crystalline volume in a domain C_0 larger than $C(x)$ can still be approximated well by

$$V(C_0, t) \approx \int_{C_0} \xi(x, t) dx. \quad (3.45)$$

The averaged model we obtain (cf. ^{5,6,8}) is given by (here for crystallization in a domain $D \subset \mathbf{R}^2$, for $d = 1$ and $d = 3$ the source term in (3.48) is defined by (3.42) and (3.44), respectively)

$$T_{\bar{t}} = \operatorname{div}_{\bar{x}}(D \nabla_{\bar{x}} T) + \frac{h}{c} \xi_{\bar{t}} \quad \text{in } D \times (0, t_*) \quad (3.46)$$

$$\xi_{\bar{t}} = (1 - \xi) \tilde{G}(T) \bar{v} \quad \text{in } D \times (0, t_*) \quad (3.47)$$

$$\bar{v}_{\bar{t}} = \nabla_{\bar{x}}(\tilde{G}(T) \bar{w}) + 2\pi \tilde{G}(T) \tilde{N}(T) \quad \text{in } D \times (0, t_*) \quad (3.48)$$

$$\bar{w}_{\bar{t}} = \nabla_{\bar{x}}(\tilde{G}(T) \bar{v}) \quad \text{in } D \times (0, t_*), \quad (3.49)$$

supplied by the boundary conditions

$$\frac{\partial T}{\partial \bar{n}} = \gamma_0(T - T_{out}) \quad \text{on } \partial D \times (0, t_*) \quad (3.50)$$

$$\bar{v} + \bar{w}^T n = 0 \quad \text{on } \partial D \times (0, t_*), \quad (3.51)$$

and the initial conditions

$$T = T^0 \quad \text{in } D \times \{0\} \quad (3.52)$$

$$\xi = 0 \quad \text{in } D \times \{0\} \quad (3.53)$$

$$\bar{v} = 0 \quad \text{in } D \times \{0\} \quad (3.54)$$

$$\bar{w} = 0 \quad \text{in } D \times \{0\}. \quad (3.55)$$

Here T denotes the temperature, ξ the degree of crystallinity and \bar{v} , \bar{w} represent the mean free surface distributions of the crystals if they would grow freely. The

boundary condition (3.51) holds only if it is assumed that no nucleation event occurs on the boundary of D , its derivation will be discussed in detail in the following section. The capital $(T, \tilde{G}, \tilde{N})$ and overlined characters $(\bar{v}, \bar{w}, \bar{t}, \bar{x})$ represent dimensional quantities, only the degree of crystallinity ξ is dimensionless.

3.1. Boundary Nucleation

The effect of boundary nucleation as described e.g. by Eder ¹¹ has not been included in our averaged model so far. Contrary to other models, which are based on systems of ODEs, our averaged model can incorporate this behaviour easily in the boundary conditions.

We first consider the case without boundary condition to derive (3.51). The change of the free volume density f_{free} in a boundary point x in an arbitrarily small time interval $(t, t + dt)$ is given by the sum of the volume densities of the crystals arriving at x in the time interval $(t, t + dt)$. This sum can be splitted into those crystals which already exist at time t and the ones which are born in $(t, t + dt)$. Since a crystal that is born in $(t, t + dt)$ and reaches x before time $t + dt$ must have its origin in a space region with distance less than $G(x, t)dt + \mathcal{O}(dt^2)$, we can write

$$\begin{aligned} f_{free}(x, t + dt) - f_{free}(x, t) &= f_{free}(x - G(x, t)ndt, t) - f_{free}(x, t) + \\ &V(B(x, G(x, t)dt) \times (t, t + dt)) + \mathcal{O}(dt^2), \end{aligned}$$

where V is the free volume density created by new crystals and n is the outer normal. If there is no boundary nucleation, i.e., no nucleation takes place in the point $x \in \partial D$ with lower-dimensional intensity, we have

$$V(B(x, G(x, t)dt) \times (t, t + dt)) = o(dt).$$

If we now change to the mean field quantity \bar{f}_{free} for the free volume, we have

$$\bar{f}_{free}(x, t + dt) - \bar{f}_{free}(x, t) = \bar{f}_{free}(x - G(x, t)ndt, t) - \bar{f}_{free}(x, t) + o(dt).$$

Dividing by dt and the limit $dt \rightarrow 0$ yield

$$(\bar{f}_{free})_t + G(\nabla \bar{f}_{free})^T n = 0. \quad (3.56)$$

Noticing that

$$\begin{aligned} \xi_t &= (1 - \xi)(\bar{f}_{free})_t = G(1 - \xi)\bar{v} \\ \nabla \xi &= (1 - \xi)\nabla \bar{f}_{free} = (1 - \xi)\bar{w}, \end{aligned}$$

we can transform (3.56) into (3.51).

If we have boundary nucleation with intensity

$$\nu_{\partial D}(d\sigma(x) \times dt) = \beta(x, t)(1 - f(x, t))d\sigma(x)dt, \quad (3.57)$$

the volume density of the crystals born in time $(t, t + dt)$ in a boundary segment $d\sigma(x) = o(dt)$ is of order dt and for the mean free density we obtain analogously

$$G\bar{v} + \bar{w}^T n = \lim_{dt \rightarrow 0} E(V(d\sigma(x) \times dt)) \quad (3.58)$$

$$= \overline{S}_{free}^d(\beta), \quad (3.59)$$

where \overline{S}_{free} is the mean free surface (with rate β) defined in \mathbf{R}^d by

$$\overline{S}_{free}^1(\beta) = 2\beta(x, t) \quad (3.60)$$

$$\overline{S}_{free}^2(\beta) = 2\pi G(x, t) \int_0^t \beta(x, s) ds \quad (3.61)$$

$$\overline{S}_{free}^3(\beta) = 8\pi G(x, t) \int_0^t G(x, s) \int_0^s \beta(x, \tau) d\tau ds \quad (3.62)$$

3.2. Solution in a Special Case

In this section we consider the case G constant and $D \subset \mathbf{R}^1$, which enables us to derive an explicit formula for the solution of the crystallization kinetic equations. Since we can easily express ξ in terms of \overline{f}_{free} by using the generalized Avrami-Kolmogorov formula

$$\xi = 1 - e^{-\overline{f}_{free}}, \quad (3.63)$$

which is a direct consequence of (2.20) and $\xi(x, 0) = 0$. In the case of no boundary nucleation, we have to solve a system of the form (with the notation u for the free volume f_{free})

$$u_t = Gv \quad \text{in } D \times (0, t_*) \quad (3.64)$$

$$v_t = Gw_x + 2\alpha \quad \text{in } D \times (0, t_*) \quad (3.65)$$

$$w_t = Gv_x \quad \text{in } D \times (0, t_*) \quad (3.66)$$

$$v = -wn \quad \text{on } \partial D \times (0, t_*) \quad (3.67)$$

$$u = v = w = 0 \quad \text{in } D \times \{0, t_*\}. \quad (3.68)$$

Since from (3.64) and (3.66) we may derive $u_x = w$, we can directly obtain an initial-boundary value problem for u , namely

$$u_{tt} = G^2 u_{xx} + 2G\alpha \quad \text{in } D \times (0, t_*) \quad (3.69)$$

$$u_t = -Gu_x n \quad \text{on } \partial D \times (0, t_*) \quad (3.70)$$

$$u = 0 \quad \text{in } D \times \{0, t_*\}. \quad (3.71)$$

By Kirchhoff's formula (cf. e.g. Kythe¹⁶), a solution of the wave equation (3.69) with homogenous initial value is given by

$$\tilde{u}(x, t) = \int_0^t \int_{D(x, t, s)} \alpha(y, s) dy ds, \quad (3.72)$$

with $D(x, t, s) = D \cap (x - G(t - s), x + G(t - s))$. A straightforward computation shows that \tilde{u} also satisfies the boundary condition (3.70) and thus, it solves (3.69)-(3.71). In the case of boundary nucleation with rate $\beta(t)$ on ∂D , one easily verifies that the solution is given by

$$\tilde{u}(x, t) = \int_0^t \int_{D(x, t, s)} \alpha(y, s) dy ds + \int_0^{\max(0, t - \tau(x))} \beta(s) ds, \quad (3.72)$$

with

$$\tau(x) = \frac{1}{G} \min_{y \in \partial D} |x - y| = \frac{1}{G} d(x, \partial D).$$

As usual for hyperbolic problems, the boundary condition has only influence to other points in a layer around the boundary, which grows in time. This layer of size Gt represents exactly those points which can be reached by a crystal born on ∂D , since points with larger distance from the boundary such a crystal cannot influence the crystalline volume.

In this special case, we can also give a more rigorous mathematical justification for the averaging procedure. Let \tilde{u} be the solution of (3.69)-(3.71) given by (3.72) and let \tilde{u}^N be the (real) free volume of a crystallization process with growth rate G and N crystals randomly born at $\{(X_j, T_j)\}_{j=1, \dots, N}$ (with nucleation rate α). Then for any $\phi \in L^1(D \times (0, t_*))$ we have

$$\begin{aligned} \langle \tilde{u}^N, \phi \rangle &= \int_0^T \int_D \phi(x, t) \left(\sum_{X_j \in D(x, t, T_j)} 1 \right) dx dt \\ &= \sum_{j=1}^N \int_{T_j}^T \int_{D(X_j, T_j, t)} \phi(x, t) dx dt. \end{aligned}$$

Furthermore we have

$$\langle \tilde{u}, \phi \rangle = \int_0^T \int_D \alpha(y, s) \left(\int_s^T \int_{D(y, s, t)} \phi(x, t) dx dt \right) dy ds$$

If we split the time interval and the domain D into

$$(0, t_*) \times D = \bigcup_{k=1}^M I_k \times D_k,$$

such that $|I_k| < \epsilon$, $|D_k| < c\epsilon$, we obtain

$$\begin{aligned} \langle \tilde{u} - \tilde{u}^N, \phi \rangle &= \sum_{k=1}^M \left(\int_{I_k} \int_{D_k} \alpha(y, s) \left(\int_s^T \int_{D(y, s, t)} \phi(x, t) dx dt \right) dy ds - \right. \\ &\quad \left. \sum_{T_j \in I_k, X_j \in D_k} \int_{T_j}^T \int_{D(X_j, T_j, t)} \phi(x, t) dx dt. \right) \\ &\leq \sum_{k=1}^M \left(\left| \int_{I_k} \int_{D_k} \alpha(y, s) dy ds - N(I_k \times D_k) \right| + o(\epsilon^2) \right) \\ &\quad \int_0^T \int_D |\phi(x, t)| dx dt, \end{aligned}$$

where $N(I_k \times D_k)$ denotes the number of nucleation events in $I_k \times D_k$. Since $\epsilon^1 = \mathcal{O}(M^{-1})$, we obtain for $\|\phi\|_{L^1} = 1$,

$$\langle \tilde{u} - \tilde{u}^N, \phi \rangle \leq \sum_{k=1}^M |N(I_k \times D_k) - E[N(I_k \times D_k)]| + \delta(M),$$

where $\delta(M) \rightarrow 0$ for $M \rightarrow \infty$. Hence the term on the left hand side is small, if M is large enough that $\delta(M)$ is small and on the other hand small enough such that we have a sufficiently high number of nucleations in $I_k \times D_k$ (and by the law of large number $|N(I_k \times D_k) - E[N(I_k \times D_k)]|$ is small). The estimate

$$\|\tilde{u} - \tilde{u}^N\| \leq C \sup_{\|\phi\|_{L^1(D)}=1} \langle \tilde{u} - \tilde{u}^N, \phi \rangle$$

also implies an error bound in the L^2 -norm.

4. Multiple Scale Effects

In the previous section we have used the different scales of temperature and crystallinity to derive the deterministic model (3.46)-(3.55). We normalize the minimal length using the new space variable $x = \frac{1}{x_0}\bar{x}$ and introduce a new time variable $t = \frac{1}{t_0}\bar{t}$. Temperature and the other free variables are scaled by

$$\theta = \frac{1}{\theta_0}(T - T_{min}) \quad v = \frac{1}{v_0}\bar{v} \quad w = \frac{1}{w_0}\bar{w},$$

and the parameter functions are transformed to

$$a(\theta) = \frac{1}{G_0} \tilde{G}(T) \quad \|a\|_{C^1} = \mathcal{O}(1) \quad (4.74)$$

$$b(\theta) = \frac{1}{N_0} \tilde{N}(T) \quad \|b\|_{C^0} = \mathcal{O}(1) \quad (4.75)$$

The arising initial-boundary value problem reads

$$\theta_t = D\Delta\theta + L\xi_t \quad \text{in } D \times (0, t_*) \quad (4.76)$$

$$\xi_t = (1 - \xi)\gamma av \quad \text{in } D \times (0, t_*) \quad (4.77)$$

$$v_t = \epsilon\nabla(a(\theta)w) + \delta a(\theta)b(\theta) \quad \text{in } D \times (0, t_*) \quad (4.78)$$

$$w_t = \nabla(a(\theta)v) \quad \text{in } D \times (0, t_*), \quad (4.79)$$

with boundary conditions

$$\frac{\partial\theta}{\partial n} = \beta(\theta - \theta_{out}) \quad \text{on } \partial D \times (0, t_*) \quad (4.80)$$

$$v = -w^T n \quad \text{on } \partial D \times (0, t_*), \quad (4.81)$$

and initial conditions

$$\theta = \theta^0 \quad \text{in } D \times \{0\} \quad (4.82)$$

$$\xi = 0 \quad \text{in } D \times \{0\} \quad (4.83)$$

$$v = 0 \quad \text{in } D \times \{0\} \quad (4.84)$$

$$w = 0 \quad \text{in } D \times \{0\} \quad (4.85)$$

The parameters in the new system are given by

$$\begin{aligned} \beta &= \gamma_0 x_0 & \gamma &= G_0 t_0 v_0 & \delta &= 2\pi \frac{G_0 N_0 t_0}{v_0} \\ \epsilon &= \frac{G_0 t_0}{x_0} & D &= \frac{a_0 t_0}{x_0^2} & L &= \frac{h}{c\theta_0}. \end{aligned} \quad (4.86)$$

Table 1. Typical values for isotactic Polypropylene (cf. ^{27,28}).

Parameter	Symbol	Typical Value
Diffusion coefficient	a_0	$10^{-7} \text{ m}^2 \text{ s}^{-1}$
Latent heat	$\frac{h}{c}$	50 K
Growth rate	G_0	10^{-5} m s^{-1}
Nucleation rate	N_0	10^{12} m^{-2}
Typical length	x_0	10^{-2} m
Typical temperature	θ_0	150 K

It seems reasonable to balance v and the source term in the hyperbolic part of the system, i.e.,

$$1 = \delta = 2\pi \frac{G_0 N_0 t_0}{v_0} \quad \text{or} \quad v_0 = 2\pi G_0 N_0 t_0, \quad (4.87)$$

for the other free parameters we have several choices dependent on which scale we are interested in.

4.1. Diffusion Time Scale

In order to balance the heat transfer process, we choose t_0 such that the diffusion coefficient is scaled to 1, i.e.,

$$1 = D = \frac{a_0 t_0}{x_0^2}, \quad (4.88)$$

which implies a typical time scale of

$$t_0 = \frac{x_0^2}{a_0} \sim 10^3 \text{ s}. \quad (4.89)$$

If the latent heat is ignored and the heat transfer coefficient is sufficiently large, t_0 is a good approximation for the time which is needed to decrease the temperature from its initial value to an equilibrium determined by the cooling temperature T_{out} . In the presence of the latent heat as a heating source, the cooling is obviously slower, but the numerical simulations show that this effect is not very strong.

On the diffusion time scale, the hyperbolic part has an almost scaled 'wave number', i.e. $\epsilon \sim 1$, which represents the fact that the growth of nuclei can be important for large time scales. The coefficient γ in equation (4.77) is very large $\gamma \sim 10^{12}$, which means that the degree of crystallinity grows strongly in a typical time interval for diffusion. Solving (4.77) for ξ and using the initial condition $\xi(t=0) = 0$ yields

$$\xi(x, t) = 1 - e^{-\gamma \int_0^t av \, d\tau}. \quad (4.90)$$

This means, that with the growth of $\int_0^t av \, d\tau$, the second term tends to zero and ξ tends to 1 very fast.

4.2. *Fast Time Scale*

If one is interested in the effects of the crystallization on a typical time scale one should rather normalize the parameters γ and δ than the diffusion coefficient D . From $\gamma = \delta = 1$ we obtain

$$t_0 = \frac{1}{G_0 \sqrt{2\pi N_0}} \quad (4.91)$$

$$v_0 = \sqrt{2\pi N_0}. \quad (4.92)$$

We note that t_0 is rather small compared to the diffusion time scale. Furthermore, $\epsilon = \frac{1}{x_0 \sqrt{2\pi N_0}}$ is very small now ($\epsilon \sim 10^{-5}$). Thus, (4.76)-(4.85) is a singularly perturbed problem, and we have to expect a boundary layer since the boundary conditions are not satisfied by the solution of the reduced problem. In addition, the diffusion coefficient is rather small ($D \sim 10^{-3}$), which expresses the slowness of diffusion.

We analyze the asymptotic properties of the hyperbolic part as $\epsilon \rightarrow 0$ with an

arbitrary source term s , i.e.

$$v_t = \epsilon \nabla (aw) + s \quad \text{in } D \times (0, t_*) \quad (4.93)$$

$$w_t = \epsilon \nabla (av) \quad \text{in } D \times (0, t_*) \quad (4.94)$$

$$v = -w^T n = 0 \quad \text{on } \partial D \times (0, t_*) \quad (4.95)$$

$$v = w = 0 \quad \text{in } D \times \{0\}. \quad (4.96)$$

In the limiting case $\epsilon = 0$ we obtain a reduced problem whose unique solution is given by (cf. Burger ³ for a proof of existence and uniqueness of solutions of the reduced problem)

$$v^0(x, t) = \int_0^t s(x, \tau) d\tau \quad (4.97)$$

$$w^0(x, t) = 0. \quad (4.98)$$

Hence, the reduced problem is a straightforward extension of the classical Avrami model (1.4), (1.5). We will now prove weak convergence of the solutions as $\epsilon \rightarrow 0$ by similar techniques as Lions ¹⁹.

Theorem 4.1. *Let $\epsilon \rightarrow 0$ and let (v^ϵ, w^ϵ) denote the solution of (4.93)-(4.96). Then*

$$(v^\epsilon, w^\epsilon) \rightharpoonup (v^0, w^0) \text{ in } L^2(Q) \times L^2(Q).$$

Proof. The solution of (4.93)-(4.96) satisfies the a-priori estimate (cf. Burger ⁴)

$$\|v\|_{L^2(Q)}^2 + \|w\|_{L^2(Q)}^2 \leq c \|s\|_{L^2(Q)}^2, \quad (4.99)$$

which is uniform in ϵ . Thus, as $\epsilon \rightarrow 0$, for any sequence ϵ_k there exists a subsequence ϵ_n such that $(v^{\epsilon_n}, w^{\epsilon_n})$ converges weakly. One easily shows that the weak limit is a solution of the reduced equation and because of the uniqueness of the solution (v^0, w^0) , a standard subsequence of subsequences argument implies the convergence of $(v^\epsilon, w^\epsilon) \square$.

If the source s is smooth with respect to x , we can even show a quantitative estimate in the L^2 -norm:

Theorem 4.2. *Let $\nabla s \in H^{-1}(I; L^2(\Omega))$ and let (v^ϵ, w^ϵ) denote the solution of (4.93)-(4.96). Then there exist constants C_1 and C_2 independent of ϵ , such that*

$$\|(v^\epsilon, w^\epsilon) - (v^0, w^0)\|_{L^\infty(I; L^2(D))^2} \leq C_1 e^{C_2 \epsilon} \sqrt{\epsilon} \quad (4.100)$$

as $\epsilon \rightarrow 0$.

Proof. if $\nabla s \in H^{-1}(I; L^2(\Omega))$, one can easily show that $v^0 \in L^2(I; H^1(D))$ and $s \in L^2(\partial D \times I)$; furthermore $w^0 = 0$ holds. Thus, the difference between the

solutions for the perturbed and the reduced problem satisfies

$$\begin{aligned}(v^\epsilon - v^0)_t &= \nabla \cdot (w^\epsilon - w^0) \\ (w^\epsilon - w^0)_T &= \nabla(v^\epsilon - v^0) + \nabla v^0\end{aligned}$$

in $D \times I$ with homogenous initial conditions and boundary condition

$$(v^\epsilon - v^0) + (w^\epsilon - w^0) = -v^0$$

on $\partial D \times I$. A standard energy inequality as in Theorem 4.1 (cf. Burger ⁴) yields

$$\|v^\epsilon - v^0\|^2 + \|w^\epsilon - w^0\|^2 \leq ce^{2C_2\epsilon t_*} \epsilon (\|v^0\|_{L^2(I; H^1(D))}^2 + \|v^0\|_{L^2(\partial D \times I)}^2),$$

for some constant c depending on a and D only. Since the above norms of v^0 are bounded and independent of ϵ , we immediately obtain (4.100) by taking the square root \square .

We note that in our case the assumption $\nabla s \in H^{-1}(I; L^2(\Omega))$ is not restrictive, it can be easily verified (in spatial dimensions $d = 1, 2, 3$) if $b \in C^2(\mathbf{R})$. Thus, we have an error bound in the L^2 -norm. Nevertheless, we have to expect a boundary layer, as we will see below.

Example 4.3. In order to obtain more insight into the behaviour of the boundary layer we consider again the simple one-dimensional example (3.64)-(3.68) Introducing again $u = \log(1 - \xi)$ we obtain after scaling the equivalent initial-boundary value problem

$$u_{tt} = \epsilon^2 u_{xx} + s \quad \text{in } (0, 1) \times (0, t_*) \quad (4.101)$$

$$u_t = \epsilon u_x \quad \text{in } \{0\} \times (0, t_*) \quad (4.102)$$

$$u_t = -\epsilon u_x \quad \text{in } \{1\} \times (0, t_*) \quad (4.103)$$

$$u = 0 \quad \text{in } (0, 1) \times \{0\} \quad (4.104)$$

$$u_t = 0 \quad \text{in } (0, 1) \times \{0\}. \quad (4.105)$$

The solution of this system can be computed explicitly as

$$u(x, t) = \frac{1}{2\epsilon} \int_0^t \int_{D_\epsilon(x, t, \tau)} s(y, \tau) d\tau dy, \quad (4.106)$$

where $D_\epsilon(x, t, \tau) = (x - \epsilon(t - \tau), x + \epsilon(t - \tau)) \cap (0, 1)$. Since u is the solution of the Cauchy problem for the wave equation in the cone \mathcal{C} defined by

$$\mathcal{C} := \{(x, t) \mid \epsilon t \leq x \leq 1 - \epsilon t\}, \quad (4.107)$$

the boundary layer occurs only in a region, where the distance from the boundary is less or equal ϵt . A remarkable effect of the hyperbolicity of the problem is that the boundary layer grows with time (here linearly because of the constant growth rate). The boundary conditions have no effect on the behaviour of the system in

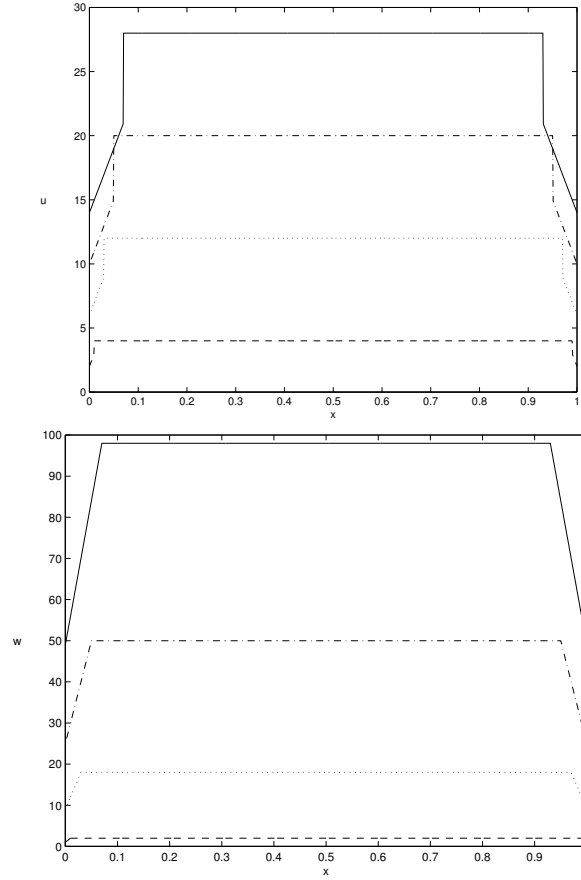


Fig. 2. The functions v (top) and u (bottom) in Example 4.3 at different time steps.

the domain \mathcal{C} , which is bounded by the characteristics starting at $x = 0$ and $x = 1$. In the general case of a non-constant coefficient $\epsilon a(x, t)$, the region \mathcal{C} is bounded by the characteristics

$$\dot{x}_0(t) = \epsilon a(\theta(x_0(t), t)), \quad x_0(0) = 0 \quad (4.108)$$

$$\dot{x}_1(t) = -\epsilon a(\theta(x_1(t), t)), \quad x_1(0) = 1, \quad (4.109)$$

more precisely

$$\mathcal{C} := \{(x, t) \mid \epsilon x_0(t) \leq x \leq x_1(t)\}. \quad (4.110)$$

This feature can be observed even more clearly if s is constant, e.g. $s = 1$, then

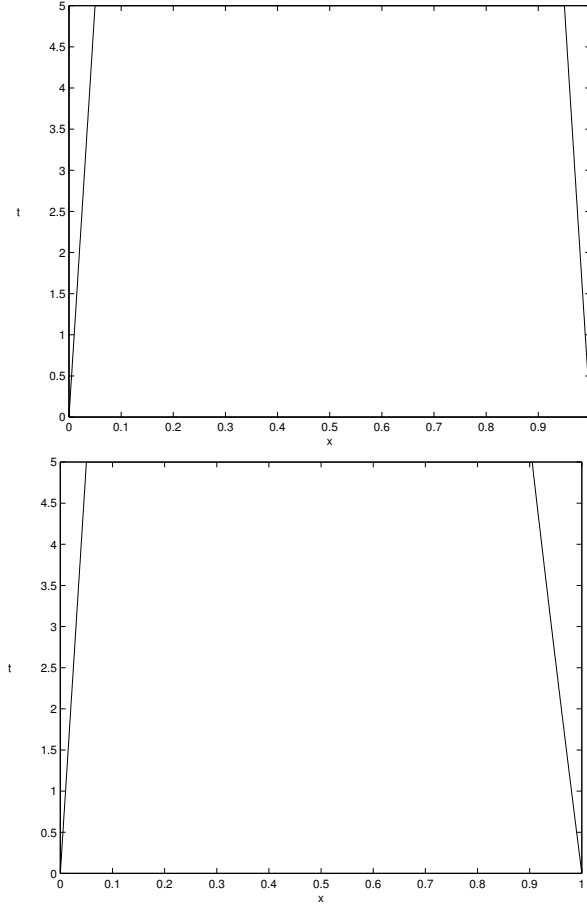


Fig. 3. The development of the boundary layer in time for constant growth rate (top) and varying, non-uniform growth rate (bottom).

the solution is given by

$$u = \begin{cases} 2t^2 & \text{if } x \in [\epsilon t, 1 - \epsilon t] \\ t^2 + \frac{x t}{\epsilon} & \text{if } x \in [0, \epsilon t] \\ t^2 + \frac{(1-x)t}{\epsilon} & \text{if } x \in (1 - \epsilon t, 1] \end{cases}, \quad (4.111)$$

i.e. the size of the boundary layer is exactly ϵt .

5. Numerical Simulations

For numerical simulation of the crystallization one has to solve the coupled system (3.46)-(3.55), consisting of nonlinear hyperbolic and parabolic equations. If we perform a simultaneous implicit time discretization of both equations, this leads to nonlinear systems, whose solution is rather difficult. A simple strategy to avoid

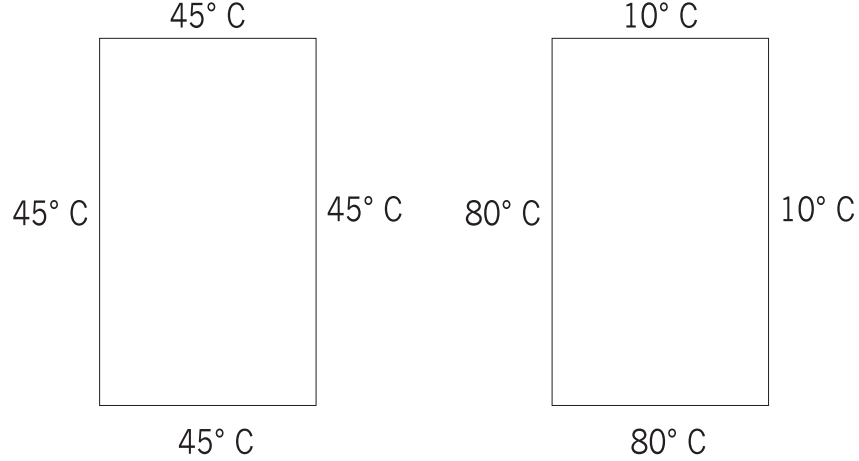


Fig. 4. Setup of the numerical examples.

such problems is an explicit discretization of the hyperbolic part, which yields (in semidiscrete form)

$$\xi^{j+1} = \xi^j + \tau^j (1 - \xi^j) \tilde{G}(T^j) v^j \quad (5.112)$$

$$v^{j+1} = v^j + \tau^j (\nabla(\tilde{G}(T^j) w^j) + \mathcal{F}(T^j)) \quad (5.113)$$

$$w^{j+1} = w^j + \tau^j (\nabla(\tilde{G}(T^j) v^j)), \quad (5.114)$$

where \mathcal{F} is the source term including the nucleation rate, which depends on the space dimension. The index j denotes the function at time t^j and $\tau^j = t^{j+1} - t^j$ is the j -th time step. For the spatial discretization any appropriate method like Lax's method for problems with source terms (c.f. Niessner²⁴) can be used. The stability bound for this hyperbolic equation is given by

$$\tau^j \leq 2 \frac{h}{G^j}, \quad (5.115)$$

where h denotes the mesh size and $G^j = \max G(x, t^j)$ (c.f. e.g. Kröner¹⁵ or Niessner²⁴). Because of the small size of G , this bound is not very restrictive and still allows a good performance of the algorithm. The explicit Euler method is of first-order in time, this could be improved by using a second-order methods like the Lax-Wendroff scheme (cf. e.g. Lax¹⁷), which can be adapted for hyperbolic problems with source term^{24,29}. For the numerical solution of the parabolic part one can then use standard discretization methods like the Crank-Nicholson scheme, since the source including ξ is known at $t = t^{j+1}$.

In our numerical simulations we considered crystallization in a rectangular domain, whose length is twice the width, i.e., $\Omega = (0, L) \times (0, 2L)$. We performed simulations with two different choices for the temperature of the cooling material,

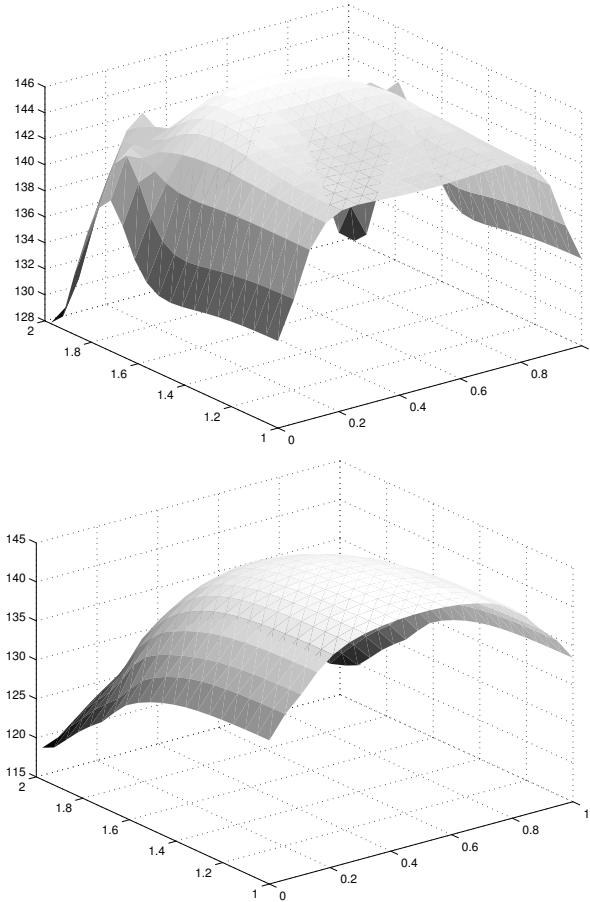


Fig. 5. Temperature in Example 1 after 5 and 10 minutes. Because of the symmetry, only the upper part of the rectangle $((0, L) \times (L, 2L))$ is plotted.

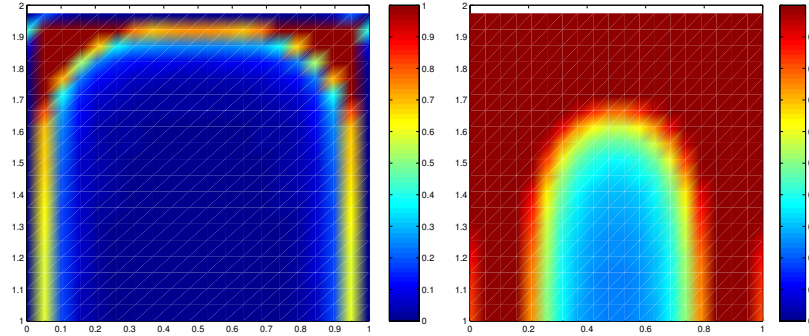


Fig. 6. Degree of crystallinity in Example 1 after 5 and 15 minutes.

using a uniform temperature T_{out} (Figures 5 and 6) and a temperature T_{out} which is lower on two boundary segments (Figures 7 and 8). For all material parameters we used measurements for isotactic polypropylene. The heat transfer coefficient and the outer temperature were chosen such that the assumptions about nucleation and growth are satisfied, but cooling is still slow compared to industrial conditions.

The results (which were performed without boundary nucleation) clearly show the boundary layer in ξ (Figures 6 and 8), but there is no such effect in the temperature, which is due to the fact that cooling at the boundary is much stronger than the reheating effect caused by the latent heat. A comparison of the left and right hand side in Figure 5 shows that the reheating effect in the interior is more significant, the temperature is not necessarily monotone decreasing in time there.

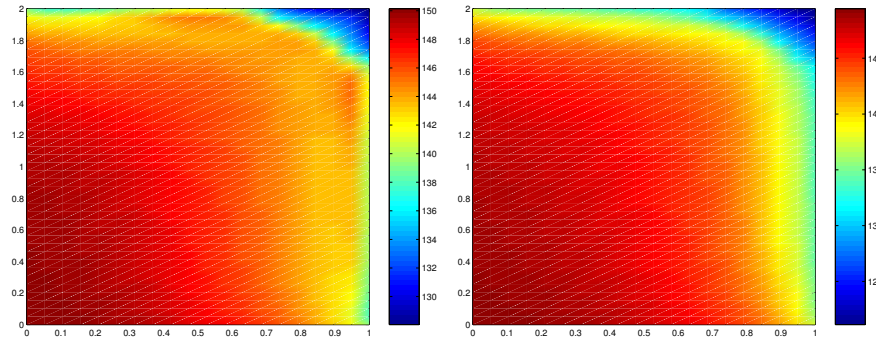


Fig. 7. Temperature in Example 2 after 6 and 9 minutes.

In Example 2 the temperature after 6 and 9 minutes is shown in Figure 7, the evolution of the degree of crystallinity (after 6, 9, 12 and 15 minutes) is plotted in Figure 8. Here the crystallization process seems to behave almost like a two-phase

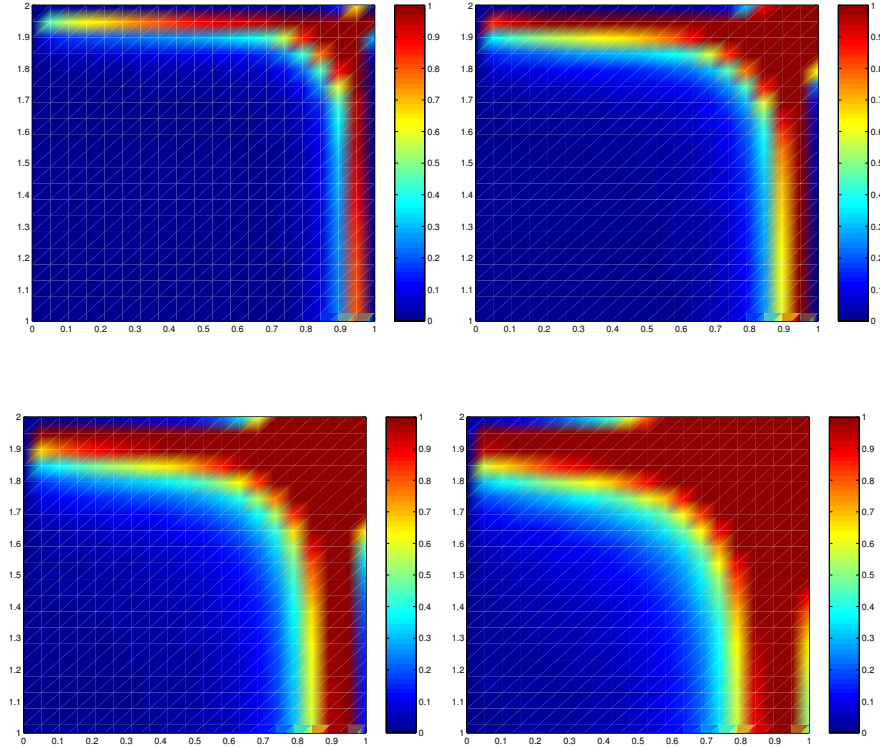


Fig. 8. Degree of crystallinity in Example 2 after 6 and 9 minutes.

problem, the crystalline phase propagates from the corner with lowest temperature to the interior. This corresponds very well to earlier modelling approaches, approximating crystallization by a two-phase process ²¹.

6. Open Problems

In this final section we want to give an overview of open mathematical problems in the context of crystallization, which may motivate future work in this area. First of all, many problems in the analysis of the modelling procedure, e.g. a rigorous convergence proof of the stochastic to the deterministic model is still unsolved. Furthermore, mathematical properties of the averaged model such as existence and uniqueness of solution have not been shown except in the one-dimensional case (cf. Burger ⁴).

Another essential problem for the applicability of the model is the identification of unknown parameters in the model, where especially the nucleation rate \tilde{N} and the growth rate \tilde{G} are of interest as material dependent/specific functions of temperature. In experiments one can measure the temperature at the boundary of

the domain during the whole time interval and observe the final morphology. This problem is an ill-posed parameter estimation problem, many difficulties arise from instabilities due to errors in the data. The estimation of nucleation rates in one spatial dimensions has been investigated by the authors^{4,7}.

A lot of future work remains in the modelling of the crystallization process under different operating conditions, e.g. crystallization under pressure (cf. e.g. Mancini²⁰) or shear stress (cf. e.g. Liedauer et al.¹⁸). Together with all this modelling problems, industry also addresses the need for certain optimal control process, e.g. the control of the cooling temperature on the boundary such that the final distribution of crystal sizes is as uniform as possible.

Acknowledgment

This work has been carried by the Austrian Fonds zur Förderung der wissenschaftlichen Arbeit, Project P 13478-INF and SFB F 013 / F 1308, by the EU under the TMR-Network *Differential Equations in Industry and Commerce* and by ASI (Italian Space Agency), contract ARS-97-121.

Useful and stimulating discussions are acknowledged to Dr. Alessandra Micheletti and Dr. Claudia Salani, University of Milano, and Dr. Walter Zulehner, University of Linz. We also want to thank the Referees for their useful comments.

References

1. L.Arkerd, J.Bergh, P.Brenner, R.Pettersson, **Progress in Industrial Mathematics at ECMI 98** (Teubner, Stuttgart, Leipzig, 1999).
2. M.Avrami, *Kinetics of phase change I-III, J.Chem.Phys.* **7**(1939), 1103-1112; **8**(1940), 212-224; **9**(1941), 177-184.
3. M.Burger, *Mathematical Modelling and Inverse Problems in Polymer Processing* (Diploma Thesis, University Linz, 1998).
4. M.Burger, *Iterative regularization of an identification problem arising in polymer crystallization* (1999), submitted.
5. M.Burger, V.Capasso, G.Eder, *Modelling crystallization of polymers in temperature fields* (1998), submitted.
6. M.Burger, V.Capasso, G.Eder, H.W.Engl, *Modelling and parameter identification in non-isothermal crystallization of polymers*, in Arkerd et al.¹, 114-121.
7. M.Burger, V.Capasso, H.W.Engl, *Inverse problems related to crystallization of polymers, Inverse Problems* **15** (1999), 155-173.
8. M.Burger, V.Capasso, C.Salani, *Modelling multi-dimensional crystallization of polymers in interaction with heat transfer* (1999), submitted.
9. V.Capasso, I.Gialdini, A.Micheletti, *Stochastic modelling and morphological features of polymer crystallization processes*, in M.Brons, ed., **Proceedings of the Eight European Conference on Mathematics in Industry** (Teubner, Stuttgart, 1996).
10. V.Capasso, C.Salani, *Stochastic birth-and-growth processes modelling crystallization of polymers with spatially heterogenous parameters, Nonlinear Analysis*, in press.
11. G.Eder, *Crystallization kinetic equations incorporating surface and bulk nucleation, ZAMM Z.angew.Math.Mech.* **76**(1996), S4, 489-492.
12. G.Eder, *Fundamentals of structure formation in crystallizing polymers*, in K.Hatada, T.Kitayama, O.Vogl, eds., **Macromolecular Design of Polymeric Materials**

- (M.Dekker, New York, 1997), 761-782.
13. G.Eder, *Mathematical modelling of crystallization processes as occurring in polymer processing, Nonlinear Analysis* **30** (1997), 3807-3815.
 14. A.N.Kolmogorov, *On the statistical theory of the crystallization of metals, Bull. Acad.Sci.USSR, Math.Ser.* **1** (1937), 355-359.
 15. D.Kröner, **Numerical Schemes for Conservation Laws** (Wiley & Teubner, Chichester, Stuttgart, 1997).
 16. P.K.Kythe, **Fundamental Solutions for Differential Operators and Applications** (Birkhäuser, Boston, Basel, Berlin, 1996).
 17. R.LeVeque, **Numerical Methods for Conservation Laws** (Birkhäuser, Basel, Boston, Berlin, 1990).
 18. S.Liedauer, G.Eder, H.Janeschitz-Kriegl, P.Jerschow, W.Geymayer, E.Ingolic, *On the Kinetics of Shear Induced Crystallization in Polypropylene, Intern. Polymer Processing* **8** (1993), 236-244.
 19. J.L.Lions, **Perturbations Singulières dans les Problèmes aux Limites et en Contrôle Optimal** (Springer, Berlin, Heidelberg, New York, 1973).
 20. A.Mancini, *A model for the crystallization of polypropylene under pressure*, in Arkeryd et al. ¹, 146-153.
 21. S.Mazzullo, M.Paolini, C.Verdi, *Polymer crystallization and processing: free boundary problems and their numerical approximation, Math. Engineering in Industry* **2** (1989), 219-232.
 22. A.Micheletti, V.Capasso, *The stochastic geometry of polymer crystallization processes, Stoch. Anal. Appl.* **15** (1997), 355-373.
 23. B.Monasse, J.M.Haudin, *Thermal dependence of nucleation and growth rate in polypropylene by non-isothermal calorimetry, Colloid & Polymer Sci.* **264** (1986), 117-122.
 24. H.Niessner, *Stability of Lax-Wendroff methods extended to deal with source terms, ZAMM Z.angew.Math.Mech.* **77** (1997), Suppl. 2, S637-S638.
 25. E.Ratajski, H.Janeschitz-Kriegl, *How to determine high growth speeds in polymer crystallization, Colloid Polym. Sci.* **274** (1996), 938-951.
 26. J.A.Sethian, **Level Set Methods. Evolving Interfaces in Geometry, Fluid Mechanics, Computer Vision, and Materials Science** (Cambridge Univ. Press, Cambridge, 1996).
 27. P.Supaphol, J.E.Spruiell, *Thermal properties and isothermal crystallization of syndiotactic polypropylenes: differential scanning calorimetry and overall crystallization kinetics, Journ. Appl. Polym. Sci.* **75** (2000), 44-59.
 28. D.W.Van Krevelen, *Properties of Polymers* (5th ed., Elsevier, Amsterdam, 1990)
 29. Y.Zhang, B.Tabarrok, *Modifications to the Lax-Wendroff scheme for hyperbolic systems with source terms, Int. J. Numer. Methods Eng.* **44** (1999), 27-40.