Growth of Multiple Crystals in Polymer Melts

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Abstract

The aim of this paper is to develop a theory for the growth of multiple crystals in a polymer melt. This leads to nonlinear moving boundary problems for the heat equation, with normal growth speed of the boundaries depending on the temperature. Particular attention is paid to the effect of *impingement*, i.e., the event of two crystals hitting each other, which stops the growth on the contact interface.

In the case of spatial dimension one, the well-posedness of the growth model coupled to the heat equation is shown for an arbitrary number of crystals and the resulting evolution of a fixed crystal is compared to the single crystal case. In higher spatial dimensions, some basic features of the model and the main problems encountered in the attempt to prove a general well-posedness result are discussed. Finally, numerical methods for the computation of growth and heat conduction are presented, and applied to the simulation of impingement events between two crystals.
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1 Introduction

Crystallization of polymers is a solidification process taking place in a wide temperature range between the equilibrium melting point and the glass transition temperature of the material. The crystallization process consists of four main features:

- *Nucleation:* this term denotes the random birth of crystals from the melt.
- *Growth:* after the nucleation event, the crystal starts to grow, which is a process driven by temperature inside the material.
- *Impingement:* this term denotes the geometric effect taking place when two crystals hit each other and their growth is stopped on the contact surface.
- *Heat conduction:* heat conduction takes place inside the material during the crystallization process, usually with cooling at the boundary of the material. The heat conduction is a driving force for the crystallization process, but vice versa influenced by the growing crystals, since the material releases a heat source at the moment of phase change.

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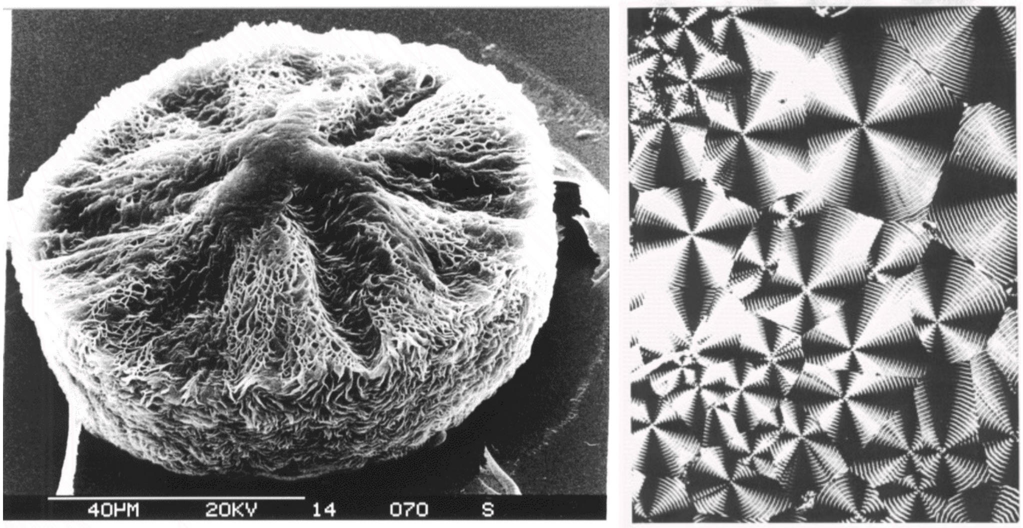

Figure 1: A polymeric crystal from a two-dimensional experiment (left) and the Johnson-Mehl tesselation of the space by a crystalline polymer (right), both taken from an experiment with Polyhydroxybutynate.

The growth of a single crystal in interaction with heat conduction has been investigated by Friedman and Velazquez [17] in the framework of moving boundary problems. Our aim in this paper is to investigate a situation with multiple crystals, which means in particular to include the effect of impingement. We shall see below that even for computing the growth of a fixed single crystal one cannot disregard the other crystals in the melt, because of their influence on temperature.

Models for polymer crystallization processes have been developed at many levels since Avrami [2] and Kolmogorov [18] first introduced their models in the case of constant temperature. For varying temperatures, a stochastic theory of crystallization can be developed based on marked point processes (cf. [10, 22]). Using averaging techniques, macroscopic models involving ordinary or partial differential equations can be derived (cf. e.g. [4, 5, 6, 12, 28]). In a practical situation with many small crystals, such averaged models provide a good approximation for the characteristic variables of the process such as the degree of crystallinity or the temperature. However, in order to obtain further insight into the formation of the material morphology, whic determines e.g. the mechanical properties (cf. [3, 33] for further details), microscopic models are needed, taking into account the interaction between the heat conduction and the solidification.

The paper is organized as follows: in Section 2 we review a model for the growth of crystals interacting with heat transfer and formulate two types of moving boundary problems for multiple crystals. These moving boundary problems in the case of spatial dimension are analyzed in Sections 3 (in the quasi-static case) and (4) (in the parabolic case). Section 5 is devoted to a discussion of the problems for multiple spatial dimensions, where well-posedness can be shown only in the absence of impingement events so far, which is mainly due to geometric singularities caused by the impingement. Numerical methods for the simulation of the moving boundary problems are presented in Section 6 and applied to situations with two crystals in Section 7. Finally, we draw conclusions and give an outlook to related open problems in Section 8.

2 A Model for Growth and Heat Conduction

In the following we assume that a finite number of nucleation events occurs in the time interval $[0,T]$ under consideration. We assume that the initial shape of each crystal is spherical with radius R_0 centered at $x_j \in \Omega$ $(j = 1,\dots,N)$ at given times of birth $t_j \in [0,T]$ $(j = 1,\dots,N)$. The crystals at time t will be represented by the open sets Θ_j^t in the following; the crystalline phase at time t is then given by

$$\Theta^t = \bigcup_{j=1,\dots,N} \Theta_j^t. \tag{2.1}$$

Its boundary, which represents the interface between the solid and liquid phase, will be denoted by $\Gamma(t) := \partial\Theta^t$.

The growth of polymeric crystals from a melt is an experimentally well-studied problem. If the temperature variation is negligible, it is well-known that the shape of a crystal is a sphere centered at the location of the nucleation event. For crystallization with a temperature gradient, Schulze and Naujeck [29] first observed that the growing crystal grows from its origin in such a way that it reaches each point in minimal time with a restriction on the speed of growth, which is a function of temperature. One can show that this minimum principle is equivalent to the growth law

$$\dot{x} = V_n n, \qquad \forall \mathbf{x} \in \partial\Theta^t, \tag{2.2}$$

where n denotes the outer normal and V_n is the normal growth speed. The normal speed V_n in $\Omega - \Theta^t$ is a material function of temperature (cf. [23, 25, 13]), i.e.,

$$V_n = G(u(x,t)), \qquad \forall\ (x,t) \in (\Omega - \Theta^t) \times [0,T]. \tag{2.3}$$

On $\partial\Omega$ the growth is stopped as well as at the contact interface to another crystal, i.e.,

$$V_n = 0, \qquad \forall\ (x,t) \in (\partial\Omega \cup \Theta^t) \times [0,T]. \tag{2.4}$$

In the remainder of this paper we will assume that $G \in C^1(\mathbb{R})$ and G is bounded and non-negative on $\mathbb{R}$.

The influence of the solidification on the thermal evolution is modeled by adding a source term in the heat equation, i.e.,

$$c\rho \frac{\partial u}{\partial t} = \text{div } (\kappa \nabla u) + L\rho \frac{\partial}{\partial t} I_{\Theta^t}, \tag{2.5}$$

where c is the heat capacity, ρ the density of the material, κ the heat conductivity and L is the so-called latent heat, which is released at the moment of phase change. I_{Θ^t} represents the indicator function of the crystalline phase, i.e.,

$$I_{\Theta^t}(x) := \begin{cases} 1 & \text{if } x \in \Theta^t \\ 0 & \text{else} \end{cases} \tag{2.6}$$

One can show that the source term is equal to $L\rho V_n \delta_{\Gamma(t)}$, i.e.,

$$\frac{\partial}{\partial t} \int_\Omega I_{\Theta^t}(x)\ \varphi(x)\ dx = \int_{\Gamma(t)} \varphi(x) V_n(x,t)\ d\sigma(x),$$

for any sufficiently smooth function φ. Unless further noticed we assume in the remainder of the paper that all parameters in the heat equation are constant. In practice, these parameters such as the conductivity or the density clearly differ in the liquid and solid phase and may in addition depend on temperature. However, the variation of the parameters is not very large and it seems therefore reasonable to neglect this effect at a first stage.

For the sake of simplicity we assume in the following that the domain Ω is a ball with radius R and the scaled temperature u satisfies a homogeneous Dirichlet boundary condition on $\partial\Omega$, i.e.,

$$u(x,t) = 0, \qquad \forall\ (x,t) \in \partial\Omega \times (0,T). \tag{2.7}$$

Moreover, we supply an initial condition of the form

$$u(x,0) = u_0(x), \qquad \forall\ x \in \Omega. \tag{2.8}$$

The scaling in the heat equation is assumed to be such that $\rho = 1$, $\kappa = 1$, $L = 1$ and $u_g < 0 < u_m$, where u_g and u_m represent the glass transition temperature and thermal melting point of the material, respectively.

If the heat capacity c is small, one can use a quasi-static approximation to the heat equation, i.e., put $c = 0$ in (2.5), which leads together with (2.7) to an evolution of elliptic boundary value problems. One observes that u satisfies the Laplace equation away from $\partial\Omega$, i.e.,

$$\Delta u = 0 \qquad \text{in } \Theta^t \cup (\Omega - \Theta^t). \tag{2.9}$$

The heat source can be rewritten as a jump condition on the solid-liquid interface, i.e.,

$$[u]\,(x,t) = \left[\frac{\partial u}{\partial n}\right](x,t) + G(u(x,t)) = 0, \qquad \forall\ x \in \Gamma(t), \tag{2.10}$$

where $[v]$ denotes the jump of a function v at $\Gamma(t)$ (the value outside minus the value inside).

This allows to formulate a moving boundary problem for the elliptic equation (2.9):

Problem (E): Find an evolution of the surface $\Gamma(t)$ and the temperature u on Ω satisfying (2.9), (2.10), (2.7) and the growth law (2.2) with normal speed defined by (2.3), (2.4).

In the parabolic case, i.e., for $c \neq 0$, we have to solve the transient heat equation

$$c\frac{\partial u}{\partial t}(x,t) - \Delta u(x,t) = 0 \qquad \text{for } t \in (0,t), x \in \Theta^t \cup (\Omega - \Theta^t). \tag{2.11}$$

The jump condition is the same as in the quasi-static case, namely (2.10). In addition, we have to supply the initial values (2.8) and boundary values (2.7). This leads to the following parabolic moving boundary problem:

Problem (P): Find an evolution of the surface $\Gamma(t)$ and the temperature u on Ω satisfying (2.11), (2.10), (2.7), (2.8) and the growth law (2.2) with normal speed defined by (2.3), (2.4).

3 The Quasi-Static Problem in $\mathbb{R}^1$

In the following we investigate the quasi-static problem for $\Omega = (-R, R) \subset \mathbb{R}^1$, which corresponds to experiments in cylindrical domains with small diameter (cf. e.g. [30]). In this case, all crystals are just intervals, denoted by $\Theta_j^t = (a_j(t), b_j(t))$, $j = 1, \ldots, N$. We assume that the crystals are ordered by their index, i.e.,

$$a_j(\tau) > b_{j-1}(\tau), \quad \text{with } \tau = \max\{t_{j-1}, t_j\}, \qquad j = 2, \ldots, N. \tag{3.1}$$

We only consider a_j and b_j after the nucleation event, i.e., in the time interval $[t_j, T]$; at $t = t_j$, the initial conditions are given by

$$a_j(t_j) = x_j - R_0, \quad b_j(t_j) = x_j + R_0, \quad j = 1, \ldots, N, \tag{3.2}$$

with $x_j \in [R + R_0, R - R_0]$.

Due to the absence of multiple directions (i.e., the outer normal equals either -1 or $+1$), the growth law (2.2) simplifies to

$$\frac{da_j}{dt}(t) = -V_n(a_j(t), t), \quad \frac{db_j}{dt}(t) = +V_n(b_j(t), t), \tag{3.3}$$

and we do not need to consider further geometric effects. In this section we assume that the normal growth rate G is monotonically decreasing, i.e., $G' \leq 0$. In practice, this assumption is realistic at least for a certain temperature range, which often appears in experiments. Since by a maximum principle for the heat equation we may deduce the nonnegativity of the temperature u, it suffices to assume $G'(u) \leq 0$ for $u \geq 0$. Moreover, we assume that G is globally bounded, i.e., there exists positive real number G_0 such that

$$|G(u)| \leq G_0, \qquad \forall\, u \in \mathbb{R}. \tag{3.4}$$

This assumption is motivated by the general form of the growth rate observed in experiments (cf. [5]).

The basic structure of our existence proof for problem (E) is as follows: First of all, we investigate the heat equation for given crystal boundaries, and show that this problem has a unique solution, which depends continuously on the boundaries. As a second step, we investigate the evolution of the boundaries, which are determined by a system of ordinary differential equations with the temperature contained in the right-hand side. The well-posedness of the problem finally follows from the Picard-Lindelöf Theorem.

3.1 An Auxiliary Elliptic Problem

We start our analysis with the solution of the elliptic equation

$$\frac{\partial^2 u}{\partial x^2} + G(u) \sum_{j=1}^{N} \left(\delta_{a_j} + \delta_{b_j}\right) = 0 \tag{3.5}$$

for given a_j and b_j, supplemented by the boundary conditions $u(-R, t) = u(R, t) = 0$.

Lemma 3.1. *Let $v \in C(S_1, S_2; H_0^1(\Omega))$ and let a_j, b_j be given functions in $C(S_1, S_2)$ satisfying (3.1). Then there exists a unique solution $u \in C(S_1, S_2; H_0^1(\Omega))$ of the equation*

$$\frac{\partial^2 u}{\partial x^2} = -G(v) \sum_{j=1}^{N} \left(\delta_{a_j} + \delta_{b_j}\right), \tag{3.6}$$

and the estimate

$$|u(.,t)|_{H^1(\Omega)} \le \sqrt{2R} N G_0 \qquad \forall\, t \in (S_1, S_2) \tag{3.7}$$

holds.

Proof. First of all, for fixed time t, there exists a solution $u(.,t) \in H_0^1(\Omega)$ of (3.6), since the right-hand side is an element of $H^{-1}(\Omega)$. Because of the continuity of the right-hand sides with respect to t, we may conclude that $u(.,t) \in C(S_1, S_2; H_0^1(\Omega))$.

In order to prove the estimate for the first derivative, we use the weak form of (3.6) and the Cauchy-Schwarz inequality to deduce

$$\begin{aligned}
\int_{-R}^{R} |\frac{\partial u}{\partial x}(x,t)|^2 \, dx &= \sum_{j=1}^{N} \left(G(v(b_j(t),t))u(b_j(t),t) + G(v(a_j(t),t))u(a_j(t),t)\right) \\
&\le 2NG_0\sqrt{2R}|u(.,t)|_{H^1(\Omega)}
\end{aligned}$$

where we have used the fact that $\|\varphi\|_{L^\infty(\Omega)} \le \sqrt{2R}|\varphi|_{H^1(\Omega)}$ for all $\varphi \in H_0^1(\Omega)$. $\square$

Theorem 3.2. *Let a_j, b_j be given functions in $C(S_1, S_2)$ satisfying (3.1). Then there exists a unique solution $u \in C(S_1, S_2; H_0^1(\Omega))$ of equation (3.5).*

Proof. Let t be fixed and consider the map $v \mapsto u$ induced by the solution of (3.6). Using similar arguments as in the proof of Lemma 3.1 we obtain that this map is continuous from $C(\Omega)$ to $H_0^1(\Omega)$. Since the embedding $H_0^1(\Omega) \hookrightarrow C(\Omega)$ is compact, we obtain that the map is completely continuous and (3.7) shows that it maps the ball with radius $\sqrt{2R}NG_0$ into itself. Hence, Schauder's fixed point theorem implies the existence of a fixed point $u(.,t)$ in this set, which is also a solution of (3.6).

In order to show the uniqueness of the solution it suffices to prove uniqueness for the linearized equation

$$\frac{\partial^2 v}{\partial x^2} + G'(\hat{u})v \sum_{j=1}^{N} \left(\delta_{a_j} + \delta_{b_j}\right) = 0,$$

with given (arbitrary) $\hat{u} \in C(S_1, S_2; H_0^1(\Omega))$. If we consider this elliptic equation for fixed time $t \in [S_1, S_2]$, then we can show that the solution must satisfy

$$\int_{-R}^{R} |\frac{\partial v}{\partial x}(x,t)|^2 \, dx - \sum_{j=1}^{N} \left(G'(\hat{u}(a_j(t),t))v(a_j(t),t)^2 + G'(\hat{u}(b_j(t),t))v(b_j(t),t)^2\right) = 0,$$

and together with $G' \le 0$ this implies $v \equiv 0$. $\square$

Using the fact that the temperature satisfies $\frac{\partial^2 u}{\partial x^2} = 0$ in each crystal Θ_j^t and in the complement of the crystalline phase and is therefore affinely linear in and between the crystals, we may deduce that there exists a modification on a subset of Ω with zero measure (i.e., at the crystal boundary) such that $u(.,t) \in C^1([a_j(t), b_j(t)])$. Moreover, from estimate (3.7) and the fact that $\frac{\partial u}{\partial x}(x,t)$ is constant in $[a_j(t), b_j(t)]$ we may deduce the estimate

$$\sqrt{b_j(t) - a_j(t)}|\frac{\partial u}{\partial x}(x,t)| \leq \sqrt{2R}NG_0, \qquad \forall\, t \in [S_1, S_2], \forall\, j \in \{1, \ldots, N\}, \forall\, x \in [a_j(t), b_j(t)]$$

and together with $b_j(t) - a_j(t) \geq 2R_0$ for $t > t_j$ we obtain the following result:

Corollary 3.3. *Let a_j, b_j be given functions in $C(S_1, S_2)$ satisfying* (3.1)*. Then the unique solution u of* (3.5) *satisfies $u \in C(\overline{\Omega} \times [S_1, S_2])$ and (after modification on a subset of zero measure) $u(.,t) \in C^1([a_j(t), b_j(t)])$ for all $t \in [S_1, S_2]$ and $j = 1, \ldots, N$, Moreover, the stability estimate*

$$|\frac{\partial u}{\partial x}(x,t)| \leq \sqrt{\frac{R}{R_0}}NG_0, \qquad \forall\, t \in [S_1, S_2], \forall\, j \in \{1, \ldots, N\}, \forall\, x \in [a_j(t), b_j(t)] \tag{3.8}$$

holds.

Finally, we derive a system of algebraic equations characterizing the solution:

Lemma 3.4. *Let a_j and b_j be given values satisfying* (3.1)*. Then the unique solution $v \in H_0^1(\Omega)$ of*

$$-\frac{\partial^2 v}{\partial x^2} = G(v) \sum_{j=1}^{N} \left(\delta_{a_j} + \delta_{b_j}\right)$$

satisfies

$$v(x) = \sum_{j=1}^{N} \left(G(v(a_j))K(x, a_j) + G(v(b_j))K(x, b_j)\right), \tag{3.9}$$

where the continuous kernel K is defined by

$$K(x,y) = \begin{cases} \frac{1}{2R}(x+R)(R-y) & \textit{for } y \geq x \\ \frac{1}{2R}(y+R)(R-x) & \textit{for } y < x \end{cases} \tag{3.10}$$

Proof. The identity (3.9) can be verified either by straight-forward computation or by using the theory of Green functions for elliptic equations of second order in the special case of the one-dimensional Laplace operator. □

A direct consequence of Lemma 3.4 is that the values of v at the crystal interfaces a_j and b_j can be computed from a nonlinear system of algebraic equations. To see this, let $c_j := v(a_j)$ and $d_j := v(b_j)$. Then for the values $x = a_k$ and $x = b_k$ in (3.9) we obtain that

$$c_k = \sum_{j=1^N} \left(g(a_k, a_j)G(c_j) + g(a_k, b_j)G(d_j)\right) \qquad j = 1, \ldots, N \tag{3.11}$$

$$d_k = \sum_{j=1^N} \left(g(b_k, a_j)G(c_j) + g(b_k, b_j)G(d_j)\right) \qquad j = 1, \ldots, N. \tag{3.12}$$

The linearization of this system around given values $(\hat{c}_j, \hat{d}_j)$ is given by the linear system

$$c_k = \sum_{j=1^N} \Big(g(a_k, a_j) G'(\hat{c}_j) c_j + g(a_k, b_j) G'(\hat{d}_j) d_j \Big) \qquad j = 1, \dots, N \tag{3.13}$$

$$d_k = \sum_{j=1^N} \Big(g(b_k, a_j) G'(\hat{c}_j) c_j + g(b_k, b_j) G'(\hat{d}_j) d_j \Big) \qquad j = 1, \dots, N. \tag{3.14}$$

Using the monotonicity of the material function G one can show that the system matrix is positive definite with minimal eigenvalue bounded below by 1. This result will be used below to deduce stable dependence of the solution on the values a_j and b_j.

3.2 Coupling of Growth and Heat Conduction

After the preliminary studies on the heat equation in the preceding section, we shall now investigate the coupling of the heat conduction with the growth of the crystals. In the following we write

$$\gamma(t) := (a_1(t), b_1(t), \dots, a_N(t), b_N(t))$$

for the vector of crystal boundaries and u^γ for the corresponding solution of the heat equation (3.5). The evolution equation for the boundaries can be written as

$$\frac{d\gamma}{dt}(t) = F(u^\gamma(\gamma(t), t), \gamma(t)) =: \tilde{F}(\gamma(t), t), \tag{3.15}$$

with a function F that is continuously differentiable with respect to u and continuous with respect to γ. Moreover, F is differentiable with respect to γ for all times t that do not coincide with a nucleation or impingement event.

In order to prove existence and uniqueness of a solution of the ordinary differential equation (3.15), we have to show that the function $\tilde{F}$ is Lipschitz-continuous with respect to γ and continuous with respect to t. Due to the special form of $\tilde{F}$ and smoothness properties of F, this is equivalent to prove that the map $\gamma \mapsto u^\gamma(\gamma, t)$ is Lipschitz-continuous, which is the aim of the following lemma.

Lemma 3.5. *Let $\gamma \in \mathbb{R}^{2N}$ be such that* (3.1) *is satisfied. Then the map $\gamma \mapsto v^\gamma(\gamma)$ is Lipschitz continuous, where $v^\gamma \in H_0^1(\Omega)$ is the unique solution of the elliptic differential equation*

$$\frac{\partial^2 v}{\partial x^2} = G(v) \sum_{a \in \gamma} \delta_a.$$

Proof. Let γ and $\tilde{\gamma}$ be given. Then, due to (3.9), the difference w of the corresponding solutions, denoted by v and $\tilde{v}$ in following, satisfies

$$w(x) - \sum_{j=1}^{N} \Big(G'(\hat{c}_j) K(x, \alpha_j) w(\alpha_j) + G'(\hat{d}_j) K(x, \beta_j) w(\beta_j) \Big) = f(x),$$

where $\alpha_j = \max\{a_j, \tilde{a}_j\}$, $\beta_j = \min\{b_j, \tilde{b}_j\}$ and $\hat{c}_j$, $\hat{d}_j$ are real values such that

$$\min\{v(a_j), \tilde{v}(a_j)\} \le \hat{c}_j \le \max\{v(a_j), \tilde{v}(a_j)\}, \qquad \min\{v(b_j), \tilde{v}(b_j)\} \le \hat{d}_j \le \max\{v(b_j), \tilde{v}(b_j)\}.$$

Note that the existence of such values $\hat{c}_j$ and $\hat{d}_j$ is guaranteed by an application of the mean value theorem to the C^1-function G. The right-hand side f is given by

$$\begin{aligned} f(x) \quad = \quad & \sum_{a_j \neq \alpha_j} (K(x, a_j)G(v(a_j)) - K(x, \alpha_j)G(v(\alpha_j))) + \\ & \sum_{b_j \neq \beta_j} (K(x, b_j)G(v(b_j)) - K(x, \beta_j)G(v(\beta_j)) - \\ & \sum_{\tilde{a}_j \neq \alpha_j} (K(x, \tilde{a}_j)G(\tilde{v}(\tilde{a}_j)) - K(x, \alpha_j)G(\tilde{v}(\alpha_j))) - \\ & \sum_{\tilde{b}_j \neq \beta_j} (K(x, \tilde{b}_j)G(\tilde{v}(\tilde{b}_j)) - K(x, \beta_j)G(\tilde{v}(\beta_j))). \end{aligned}$$

Since the functions v, $\tilde{v}$ and K are Lipschitz-continuous, this right-hand side satisfies

$$\sup_{x \in \overline{\Omega}} |f(x)| \leq C_0 |\gamma - \tilde{\gamma}|$$

for some constant $C_0 \in \mathbb{R}^+$. Because of the well-posedness of the linearized equation (3.11), (3.12) we may derive the estimate

$$\sup_{x \in \overline{\Omega}} |w(x)| \leq C |\gamma - \tilde{\gamma}|$$

for some constant $C \in \mathbb{R}^+$.

Now let $j \in \{1, \ldots, N\}$ and assume without restriction of generality that $a_j \leq \tilde{a}_j$, then we have that

$$|v(a_j) - \tilde{v}(\tilde{a}_j)| \leq |v(a_j) - v(\tilde{a}_j)| + |w(\tilde{a}_j)|.$$

Both terms in the sum on the right-hand side are of order $\mathcal{O}(|\gamma - \tilde{\gamma}|)$, the first one because of the Lipschitz-continuity of v and the second one because of the above estimate for $|w(x)|$. Hence, the map $\gamma \mapsto v^\gamma(\gamma)$ is Lipschitz-continuous. □

Now we are able to prove a global existence and uniqueness result for the coupled problem in presence of impingement, which was the aim of this section:

Theorem 3.6. *Let $T \in \mathbb{R}^+$ be arbitrary and let $(X_j, T_j) \in \Omega \times [0, T]$, $j = 1, \ldots, N$ be given nucleation events. Then problem (E) has a unique solution $u \in L^\infty(0, T; H_0^1(\Omega))$ and $\gamma = (a_1, b_1, \ldots, a_N, b_N) \in L^\infty(0, T)^{2N}$, with $a_j, b_j \in C([T_j, T])$. Moreover, for each time interval $[S_1, S_2]$ that does not contain a nucleation or impingement event,the temperature satisfies $u \in C(S_1, S_2; H_0^1(\Omega))$ and the boundaries satisfy $a_j \in C^1([S_1, S_2])$ and $b_j \in C^1([S_1, S_2])$.*

Proof. We split the time interval into subintervals $[S_1, S_2]$ such that no nucleation event occurs in (S_1, S_2). To prove the assertion, it suffices to show that the problem has a solution in such time intervals, since at for each nucleation event γ is only modified by a step in a_j and b_j, which subsequently implies that also the temperature stays in the class $L^\infty(0, T; H_0^1(\Omega))$.

Now, we define S^* as the maximal time τ, such that no impingement event occurs in (S_1, τ). In the time interval (S_1, S^*), the evolution of the boundary γ is determined by (3.15) (with initial condition at time $t = S_1$), whose right-hand side $\tilde{F}$ is Lipschitz-continuous with respect to γ, which follows from Lemma 3.5. Thus, by the Picard-Lindelöf Theorem, (3.15) has a unique solution $\gamma \in C^1([S_1, S^*])$ and the corresponding temperature satisfies $u \in C(S_1, S^*; H_0^1(\Omega))$. At time $t = S^*$, we have one or more impingement events. For each index k such that $a_k(S^*) = b_{k-1}(S^*)$ we unite the k-th and $(k-1)$-th crystal to a single one given by $(a_{k-1}(S^*), b_k(S^*))$, decrease the number N to the new number of crystals, and restart the evolution in the time interval (S^*, S_2) until the next impingement event occurs. In an analogous way we proceed in the case of impingement at the boundary, i.e., if $a_1(S^*) = -R$ or $b_N(S^*) = R$. Here we only eliminate the heat source in (3.5) at the boundary point, but keep the crystal with time derivative of the boundary point identical zero (which is of course also a Lipschitz-function and does not disturb the well-posedness of (3.15)).

Since the possible number of impingement events is finite, this strategy must yield the existence and uniqueness for problem (E) in the time interval $[S_1, S_2]$ and by combining these intervals also in the full time interval $[0, T]$. □

3.3 Comparison to the Single Crystal Case

In the following we compare the growth of a crystal in the presence of other crystals to the previously investigated case of a single crystal growing from the melt. We shall show that the growth is faster in the single crystal case, which is due to the fact that each crystal causes a reheating effect. Our prove is heavily based on this physical reasoning, we first show a comparison result for the temperatures and then use this result to conclude that the crystal shape in presence of multiple crystals is always bounded by the shape in the single crystal case.

In the following let T_0 and X_0 denote time and location of the nucleation event for the crystal under investigation. We denote the crystal in presence of other crystals by $\Theta_0^t = (a(t), b(t))$ and in the single crystal case by $\tilde{\Theta}_0^t = (\tilde{a}(t), \tilde{b}(t))$. The other crystals in the first case are again denoted by Θ_j^t, $j = 1, \ldots, N$ and we denote by u the temperature, i.e., the solution of

$$-\frac{\partial^2 u}{\partial x^2} = G(u)\delta_{\gamma(t)} = G(u)\sum_{j=0}^{N} \delta_{\gamma_j(t)}, \tag{3.16}$$

with $\gamma_j(t) \in \Gamma_j(t) = \partial\Theta_j^t - \Theta^t - \partial\Omega$.

In the single crystal case, we denote the solution by $(\tilde{u}, \tilde{\Gamma})$; the heat equation reads

$$-\frac{\partial^2 \tilde{u}}{\partial x^2} = G(\tilde{u})\delta_{\tilde{\gamma}(t)} = G(\tilde{u})\delta_{\tilde{\gamma}_0(t)}, \tag{3.17}$$

with $\tilde{\gamma}_0(t) = \partial\tilde{\Theta}_0^t - \partial\Omega$.

Proposition 3.7. *Let $N > 0$, $T_1 \leq T_0$ and let $u, \tilde{u} \in L^\infty(0, T; H_0^1(\Omega))$ satisfy (3.16) and (3.17), respectively, for arbitrary $t > 0$. Then, the comparison result*

$$u(x,t) < \tilde{u}(x,t), \qquad \text{for } x \in \{\tilde{a}(t), \tilde{b}(t)\} \tag{3.18}$$

holds for $t \in (T_0, T_0 + \tau)$ with τ sufficiently small.

Proof. We use again the representation (3.9) and the mean value theorem applied to G to deduce that $v := u - \tilde{u}$ satisfies (with fixed time t)

$$\begin{aligned} v(x) - K(x, \tilde{a}_0)G'(c)v(\tilde{a}_0) - K(x, \tilde{b}_0)G'(d)v(\tilde{b}_j) &= A_0 + B_0 \\ + \sum_{j=1}^{N} \left(K(x, a_j)G(u(a_j)) + K(x, b_j)G(u(b_j))\right), \end{aligned} \tag{3.19}$$

with

$$\begin{aligned} A_0 &= K(x, \tilde{a}_0)G(u(\tilde{a}_0)) - K(x, a_0)G(u(a_0)) \\ B_0 &= K(x, \tilde{b}_0)G(u(\tilde{b}_0)) - K(x, b_0)G(u(b_0))). \end{aligned}$$

Now consider the above formula for v evaluated at $x = \tilde{a}$ and $x = \tilde{b}$, which leads to a system of linear equations (3.19) for $v(\tilde{a})$ and $v(\tilde{b})$, whose system matrix is monotone. Using the Lipschitz-continuity of K, G and u, we may deduce that

$$|A_0| + |B_0| \leq C(|\tilde{a} - a| + |\tilde{b} - b|),$$

for some constant C. Thus, for $|\tilde{a} - a|$ and $|\tilde{b} - b|$ sufficiently small, which is the case in a sufficiently small time interval $(T_0, T_0 + \tau)$, we obtain that the right-hand side in the system (3.19) for $v(\tilde{a})$ and $v(\tilde{b})$ is positive, which implies that also its solution is positive, i.e., (3.18) holds. □

Now we are able to prove a comparison result for the crystals Θ_0^t and Θ_1^t.

Theorem 3.8. *Under the assumptions of Proposition 3.7 we have that $\Theta_0^t \subset \tilde{\Theta}_0^t$ with proper inclusion in a sufficiently small time interval $(T_0, T_0 + \tau)$.*

Proof. We use Proposition 3.7 to deduce that $u(\tilde{a}(t), t) > \tilde{u}(\tilde{a}(t), t)$ for $t \in [T_0, T_0 + \tau)$ and with the monotonicity of G, this implies that $G(u(\tilde{a}(t), t)) < G(\tilde{u}(\tilde{a}(t), t))$. Hence, the crystal Θ_0^t must be a proper subset of $\tilde{\Theta}_0^t$. □

4 The Parabolic Problem in $\mathbb{R}^1$

In the following we will use the same notations for the nucleation events and the crystals as in Section 3. For simpler notation we assume that $c = 1$. For the initial value we assume the weak regularity $u \in H_0^1(\Omega)$.

Our aim is to prove the existence and uniqueness of a solution to problem (P); the basic strategy of the proof is the same as in the quasi-stationary case, i.e., we first investigate the properties of the parabolic heat equation

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} + G(u) \sum_{j=1}^{N} \left(\delta_{a_j} + \delta_{b_j}\right) \tag{4.1}$$

for given a_j, b_j, and subsequently apply the results to the evolution equation of the boundary, which will lead to a system of nonlinear Volterra integral equations of the second kind. Because of the strong analogies to the quasi-static case we shall not give detailed proofs for some results that require only minor modifications with respect to the analysis of problem (E).

4.1 An Auxiliary Parabolic Equation

We start our analysis with the parabolic initial-boundary value problem (4.1), (2.8), (2.7). As in the elliptic case we can find an a-priori bound on the solution of the nonlinear problem and show the complete continuity of the map $v \mapsto u$ defined by the linear equation

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} + G(v) \sum_{j=1}^{N} \left(\delta_{a_j} + \delta_{b_j}\right)$$

on the space $L^2(S_1, S_2; H_0^1(\Omega)) \cap L^2(S_1, S_2; H^{-1}(\Omega)$ (where we use the compact embedding of this space into $L^2(S_1, S_2; C(\Omega))$, which can be shown using a result by Aubin and Lions, cf. [32]). Together with a standard proof of additional regularity with respect to the time variable this allows to deduce the following result:

Theorem 4.1. *Let a_j, b_j be given functions in $C(S_1, S_2)$ satisfying* (3.1) *and let $u_1 \in H_0^1(\Omega)$. Then there exists a unique solution $u \in C(S_1, S_2; H_0^1(\Omega))$ of equation* (4.1) *supplemented by the initial condition $u(., S_1) = u_1$.*

In the quasi-static case we have used elliptic potential theory to deduce a system of algebraic equations characterizing the complete solution, which was piecewise continuous between the crystal interfaces in that cases. In the parabolic case, the last statement is not true anymore, but it is still possible to reduce the complexity of the problem, namely to a system of Volterra integral equations:

Proposition 4.2. *There exist a continuous functions $K, K_1 \in \mathbb{R}^3$, which are Lipschitz-continuous with respect to the first two variables, such that the unique solution u of* (4.1) *satisfies*

$$\begin{aligned} u(x,t) &= \int_{S_1}^{t} \sum_{j=1}^{N} \left(K(x, a_j(s), t-s) G(c_j(s)) + K(x, b_j(s), t-s) G(d_j(s))\right)\, ds + \\ &\quad \int_{\Omega} K_1(x,y,t) u_1(y)\, dy \end{aligned} \tag{4.2}$$

where $c_j(s) = u(a_j(s), s)$ and $d_j(s) = u(b_j(s), s)$.

Proof. The existence of such functions K and K_1 follows from the theory of Green functions for the parabolic heat equation, they can be obtained from rescaling the heat kernels presented by Cannon [9] in the case of the unit interval to the domain $\Omega = (-R, R)$. □

Now we can plug the special values $x = c_k(t)$ and $x = d_k(t)$ into the representation (4.2), which yields a system of $2N$ Volterra integral equations of the second kind for the $2N$ functions c_j and d_j, $j = 1, \ldots, N$, which admits a unique solution. Moreover, using the Lipschitz-continuity of the heat kernels, one obtains the Lipschitz-continuity of u with respect to the spatial variable.

4.2 Growth and Heat Conduction

In the following we shall show the existence and uniqueness of a solution to the growth model coupled to the nonlinear heat equation (4.1). Our basic strategy is the same as in the quasi-static case, we first restrict our attention to a time interval without impingement and nucleation events and then put these intervals together.

Using the notations of the previous section, the growth in absence of impingement and nucleation is determined by

$$a_j(t) = a_j(S_1) - \int_{S_1}^{t} G(c_j(s))\, ds, \qquad j = 1, \ldots, N, \tag{4.3}$$

$$b_j(t) = b_j(S_1) + \int_{S_1}^{t} G(d_j(s))\, ds, \qquad j = 1, \ldots, N. \tag{4.4}$$

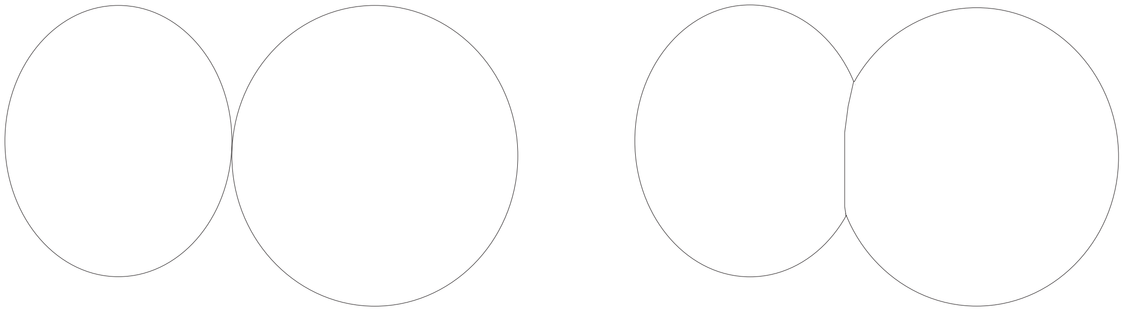

Figure 2: Schematic representation of an impingement event between two crystals leading to boundary points with less regularity.

Together with the equations for c_j and d_j arising from (4.2), this is a nonlinear system of Volterra equations of the second kind. The Lipschitz-continuity of all the functions involved implies the existence of a solution and with the same technique as in the quasi-static case, we may prove the following result:

Theorem 4.3. *Let $T \in \mathbb{R}^+$ be arbitrary and let $(X_j, T_j) \in \Omega \times [0,T]$, $j = 1,\dots,N$ be given nucleation events. Then problem (P) has a unique solution $u \in L^\infty(0,T;H_0^1(\Omega))$ and $\gamma = (a_1, b_1, \dots, a_N, b_N) \in L^\infty(0,T)^{2N}$, with $a_j, b_j \in C([T_j,T])$. Moreover, for each time interval $[S_1, S_2]$ that does not contain a nucleation or impingement event,the temperature satisfies $u \in C(S_1,S_2;H_0^1(\Omega))$ and the boundaries satisfy $a_j \in C^1([S_1,S_2])$ and $b_j \in C^1([S_1,S_2])$.*

5 Towards a Multi-Dimensional Theory

In the presence of multiple spatial dimensions, the growth model (2.2) is of a different structure as in the one-dimensional case, since the crystal boundary does not consist of a finite number of points anymore and there are infinitely many possible directions for the normal vector. The evolution of the normal vector can be computed either by using derivatives of the boundary points with respect to a parametrization or by the differential equation

$$\frac{\partial n}{\partial t} = -\nabla_x V_n(x,t) + (n.\nabla_x V_n(x,t))n, \tag{5.1}$$

which has been deduced in [6].

If local parametrizations are used, e.g. $x_3 = f(x_1,x_2)$, then the growth equation (2.2) is equivalent to (cf. [17])

$$\frac{\partial f}{\partial t} = \sqrt{1 + |\nabla_{(x_1,x_2)} f|^2} V_n. \tag{5.2}$$

In the single crystal case, a method of characteristics for this formulation of the growth model can be employed to prove the existence of solutions for the problems (E) and (P) locally in time (cf. [17]). The ideas employed for this proof carry over to the case of multiple crystals for small time intervals before impingement.

In order to supplement the above discussion by more rigorous arguments, we consider problem (E) in $\Omega = R^d$, $d = 2,3$, with some initial boundary $\Gamma(0)$, whose connected components are of class $C^{2+\alpha}$ for some $\alpha > 0$. In this particular case, the temperature satisfies

$$u(x,t) = \int_{\Gamma(t)} u(y,t) K(x-y)\ d\sigma(y), \qquad \forall\, x \in \mathbb{R}^2, \tag{5.3}$$

where K is the fundamental solution of the Laplace equation, i.e.,

$$K(x) = \begin{cases} -c_2 \ln|x| & \text{for } d = 2 \\ c_3|x|^{-1} & \text{for } d = 3 \end{cases} \tag{5.4}$$

with appropriate constants c_2 and c_3. Consequently, the temperature along the moving boundary $\Gamma(t)$ is determined by an integral equation of the second kind with weakly singular kernel. An existence theorem for a time interval without impingement can be obtained by similar reasoning as in [17]. I.e., we define a fixed point map on the space of boundaries $\Gamma_S = (\Gamma(t))_{t\in[0,S]}$ of class $C^{2+\alpha}$ with time derivative of class $C^{1+\alpha}$, which is a metric space when equipped with the Hausdorff metric (cf. [11] for metrics on shapes). The fixed-point map is the concatenation of the maps $\Gamma_S \mapsto u$, where u is the solution of the elliptic moving boundary problem (2.9), (2.10), (2.7), and the map $u \mapsto \tilde{\Gamma}_S$, where $\tilde{\Gamma}_S$ is the domain evolution obtained from (2.2), (2.3) for given temperature u.

Using elliptic potential theory one can show that u can be extended to a function of class $C^{2+\alpha}$ in a neighbourhood of Θ^t (with time derivative in $C^{1+\alpha}$), whose dependence on Γ_S is continuous. For given temperature u, one can show that the system of ordinary differential equations (2.2) and (5.1) has a unique solution $(x,n) \in C^1([0,S])$ for each initial value $(x(0),n(0)) \in \Gamma(0)$. Using local parametrizations, one can then verify that this solution is of the same regularity class as Γ_S. Finally, by similar reasoning as Friedman and Velazquez, now with multiple crystals, one can show that for small time S, the fixed point operator is contractive and maps some bounded set into itself, which implies the existence and uniqueness of the solution in a small time interval.

However, this technique only yields well-posedness for an arbitrarily small time interval and heavily relies on the strong regularity of the boundary. If an impingement event occurs, there are further difficulties due to a possible singularity at the new boundary (of the union of the crystals). If two crystals Θ_1 and Θ_2 hit each other at time τ and location ξ, then the boundary of their union is probably of less regularity at this point, even if the boundaries of the single crystals are smooth (see Figure 2). Moreover, there appears some kind of discontinuity with respect to time, since for any time $t > \tau$, the contact interface between the two crystals is of positive $d-1$-dimensional measure and thus,

$$\text{int}\ (\Theta_1^t \cup \Theta_2^t) \neq \text{int}\ \Theta_1^t \cup \text{int}\ \Theta_2^t.$$

The kind of regularity we can expect after an impingement event is at most of Lipschitz-type and thus, a methodology using more regularity cannot produce reasonable results. A theory with Lipschitz-type regularity could be based on the same idea in principle, i.e., to construct a fixed-point map on a space of Lipschitz boundaries equipped with the Hausdorff metric, which consists of the following ingredients:

1. The map $\Gamma_T \mapsto u$, mapping into an appropriate space of functions that are Lipschitz-continuous on $\overline{\Theta^t}$. This map can be analyzed similar to the one of class $C^{2+\alpha}$ in the preceding discussion.

2. The map $u \mapsto \tilde{\Gamma}_T$, now into a space of Lipschitz-continuous boundaries. In this case, we cannot show the existence and uniqueness of a solution of the ordinary differential equations (2.2), (5.1), since the term $\nabla_x G(u)$ that appears in (5.1) is not even continuous in general. Therefore, an equation for a parametrization like (5.2), which is a Hamilton-Jacobi equation on the domain of the parameter, seems to be of advantage. Using results for Lipschitz-continuous solutions of Hamilton-Jacobi equations such as the one recently presented by Ley [19, Theorem 4.1], it might be possible to prove existence and uniqueness for this equation, with appropriate continuity estimates implying contractivity of the fixed-point map for small time.

The ideas presented above are only the starting point to a detailed investigation of impingement events in the multi-dimensional case, with many associated questions such as the regularity for the arising contact interfaces or the influence of impingement on the normal speed.

6 Numerical Simulation

For the numerical solution of the moving boundary problems we first have to decide which type of numerical integration we use for the growth model, which is a system of ordinary differential equations. We assume that our discretization times $0 = t_0 < t_1 < \ldots < t_n$ cover all nucleation events, then we have two main possibilities:

- *Explicit time discretization of* (2.2)*:* in this case we evaluate the right-hand side of (2.2) with the values at time $t = t_j$ and perform a time step to t_{j+1}. At the new time step we can now solve the heat equation before we perform the next time step, i.e., this discretization strategy implies also a decoupling and partial linearization of the original problem. The stability bounds for such methods are usually of the form $(t_{j+1} - t_j)V_n(x) \leq h$ for all values x obtained from a spatial discretization, and h is the fineness of the spatial discretization. For typical polymeric materials, this stability bound is not restrictive, since the absolute values of G and consequently of V_n are rather small.

- *Implicit time discretization of* (2.2)*:* in this case the position of the crystal boundaries and the temperature after each time step t_{j+1} have to be computed simultanously, using information at time $t = t_j$ mainly for the discretization of time derivatives. A considerable advantage of such an approach is that stability bounds can be avoided, but this is compensated by a high numerical effort, which is needed for the solution of a coupled nonlinear problem in each time step.

At least in the case of an explicit discretication technique for (2.2), we have a second choice for the construction of a numerical method, namely the way of discretizing the growth law with respect to space:

- *Lagrangian methods:* the Lagrangian approach to the numerical solution of (2.2) consists in interpreting the growth model as an evolution equation for a (possibly parametrized) curve or surface consisting of the points x. A typical example are front-tracking methods, where the initial crystal boundary is first parametrized (e.g. in polar coordinates) and then discretized with respect to this parameter. Since this does not lead to a grid-based method, the coupling with the heat equation can only be realized in a reasonable way if a boundary integral method using formulas like (3.9) or (4.2) is applied for its numerical solution.

- *Eulerian methods:* the Eulerian view-point is to fix some points in space and to observe the crystal boundaries passing through these points. In mathematical terms, such an approach is realized by *level set methods* (cf. [31] for an overview), which relate the curve or surface Γ to the zero level set of a smooth function ϕ, i.e.,

$$\Gamma(t) := \{ \ x \in \Omega \mid \phi(x,t) = 0 \ \}. \tag{6.1}$$

In the case of normal growth, the evolution of the level set function can be computed from the Hamilton-Jacobi equation

$$\frac{\partial \phi}{\partial t} + V_n |\nabla \phi| = 0 \qquad \text{in } \Omega \times (0,T). \tag{6.2}$$

For the heat equation in the parabolic case it seems natural to use some kind of implicit discretization such as the Crank-Nicholson scheme, which does not lead to a stability bound. For an explicit time discretization, the stability bound would be of the form $t_{j+1} - t_j \leq ch^2$, which is very restrictive for the choice of appropriate time steps. In the case of the quasi-static approximation an implicit time discretization seems natural anyway from the physical interpretation that the diffusion is much faster than the growth process.

Below we shall split our discussion again into a spatially one-dimensional and a multi-dimensional case.

6.1 Numerical Solution in $\mathbb{R}^1$

In the case of one spatial dimension a Lagrangian formulation seems favorable for the design of numerical methods, since each grid can be easily adapted such that it covers the crystal boundaries, and the growth of the crystals can be computed easily from this formulation. Moreover, with the representations (3.9) and (4.2) it is possible to design a numerical method for the coupled problem without using a spatial grid.

In the quasi-static case, one can just use some implicit discretization scheme in the time interval (t_{k-1}, t_k) for the ordinary differential equations

$$\frac{da_j}{dt} = -G(c_j), \qquad \frac{db_j}{dt} = G(d_j), \qquad j = 1, \ldots, N, \tag{6.3}$$

and then solve the nonlinear system, which arises together with the algebraic equations (3.11), (3.12), for $a_j(t_k), b_j(t_k), c_j(t_k), d_j(t_k)$, e.g. by a Newton-type method. After solving this problem one has to check whether $b_{j-1}(t_k) \leq a_j(t_k)$ for $j = 2, \ldots, N$. If this is not the case, we decrease the time step until this condition is satisfied, e.g. by bisection. Since one cannot expect to find a time t_k with the exact equality $b_{j-1}(t_k) = a_j(t_k)$, we unite the crystals Θ_{j-1} and Θ_j as soon as $b_{j-1}(t_k) - a_j(t_k)$ is below some small threshold value.

In the parabolic case we can just discretize the system of Volterra integral equations defined by (4.2) for $x = a_j$ and $x = b_j$ coupled to (4.3) and (4.4) by a standard scheme such as an implicit Runge-Kutta method (cf. e.g. [14, 20]). The arising sequence of nonlinear algebraic systems can then be solved numerically by a Newton-type method.

We want to mention that such an approach enforces only the solution of n nonlinear systems of size $4N \times 4N$. A grid-based method for the heat equation with m spatial nodes would enforce the numerical solution of n nonlinear systems of size $m \times m$. Since the grid size must be much smaller than the size of the crystals in order to obtain a reasonable accuracy, we need that $m << N$ and therefore the numerical effort would probably be much higher for such an approach.

6.2 Multi-Dimensional Simulation

In the multi-dimensional case, we can use a similar numerical algorithm as presented in the previous section if the kernel K is known, which is the case if Ω is a ball or equal to $\mathbb{R}^d$. If Ω is a general domain, the corresponding Green function might be unknown and the method cannot be realized in a simple way. Moreover, the Lagrangian formulation is less efficient in the numerical solution of normal growth compared to level set methods.

Therefore, we construct a numerical method in the multi-dimensional case as follows: first of all, we represent each crystal via level sets, i.e.,

$$\Theta_j^t = \{ \ x \in \Omega \mid \phi_j(x,t) > 0 \ \}, \tag{6.4}$$

the crystal boundary is then the zero level set of ϕ_j. At time $t = T_j$, the level set function ϕ_j is initialized such that the zero level set is the ball with radius R_0 (cf. [31] for initialization strategies for level set functions). In each time interval (t_{k-1}, t_k), we solve the level set equation (6.2) using an explicit time discretization (cf. [31] for numerical schemes for level set equations) and compute the new crystal boundaries.

At the new time step $t = t_k$ we can now compute numerically the solution of the heat equation either by solving a nonlinear elliptic equation with given crystal boundaries (in the stationary case) or by performing an implicit time step for the parabolic heat equation (in the parabolic case) using the Crank-Nicholson method (cf. [24]), which again results in a nonlinear elliptic equation similar to the stationary case. The discretization of these elliptic equations can be carried out by standard methods such as finite elements or finite differences, resulting again in a (sparse) nonlinear system of algebraic equation. This nonlinear system can now be solved using a Newton-type method with sparse solvers for the linearized problem to be solved in each iteration step.

The remaining ingredient for a numerical algorithm with multiple crystals is a technique that allows to take impingement effects into account. First of all, one observes that an interface between two crystals Θ_1^t and Θ_2^t can be detected from the corresponding level set functions, e.g. as the zero level set of the function

$$\psi_{1,2}(x.t) := \max\{\phi_1(x,t)^2, \phi_2(x,t)^2\}. \tag{6.5}$$

Due to numerical imprecision, we have to use again some thresholding in order to compute the values of $\psi_{1,2}$ at the grid points. Moreover, the overall crystalline phase Θ^t can be computed via

$$\overline{\Theta^t} = \{ \ x \in \Omega \mid \ \min\{\phi_j(x,t)\}_{j=1,\ldots,N} \geq 0 \ \}, \tag{6.6}$$

which allows to judge whether (2.3) or (2.4) have to be used on a crystal boundary. In the grid points not belonging to the boundary we use an appropriate extension velocity for V_n (cf. [1] for efficient constructions) and therefore we have all information to proceed to the next time step with an explicit solution of the level set equations.

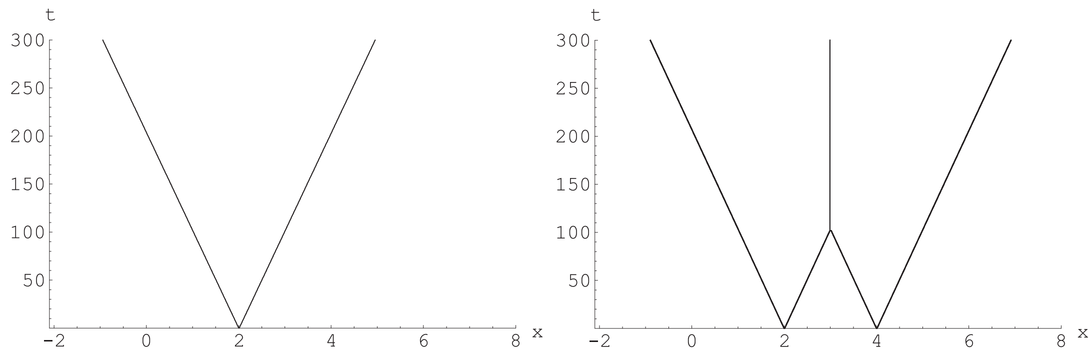

Figure 3: The single crystal $\tilde{\Theta}_0$ (left) and the crystals Θ_0 and Θ_1 (right), for growth parameters $p = 10^{-4}$ and $q = 10^{-2}$.

7 Numerical Experiments with Two Crystals

In the following we present the results of numerical simulations with two crystals and compare them to the single crystal case. We start with the quasi-static case in $\Omega = (-R, R)$ with $R = 20$ and two crystals nucleated at time $t = 0$ at the locations $X_0 = 2.05$ and $X_1 = 4.05$; the initial radius is $R_0 = 0.05$. For simplicity we use a linear growth rate G of the form

$$G(u) = -p\, u + q, \tag{7.1}$$

which allows to compute an analytic solution of (3.11), (3.12) in terms of a_j and b_j. The remaing system of ordinary differential equations is then solved numerically by an implicit Runge-Kutta scheme.

For a first simulation, we choose $p == 10^{-4}$ and $q = 10^{-2}$, i.e., the variance of the growth rate with respect to temperature is relatively low. The evolving crystal boundaries in the case of a single crystal as well as in the case of multiple crystals are shown in Figure 3. One observes that the crystal boundaries are almost straight line, which is due to the low variance of the growth rate with respect to temperature. In the case of two crystals an impingement event occurs at time $t = 102$ and stops the growth at this point. A comparison of the results is shown in figure 4. In the left part, the evolution of the crystal boundaries of $\tilde{\Theta}_0$ (blue) and Θ_0 (red) are plotted. For the particular growth rate we have used here, the results are very similar (apart from the impingement effect), at the left boundary a difference can be seen by eye only for large time. From the second plot in Figure 4, which shows the temperatures $\tilde{u}(., t)$ and $u(., t)$ at the fixed time $t = 90$ (before impingement), one can observe a significant difference of the single and multiple crystal case, namely with respect to temperature, which is much higher in presence of a second crystal. This confirms the results of Proposition 3.7numerically. Moreover, the crystal Θ_0 lies inside $\tilde{\Theta}_0$ for all times t, which was predicted by Theorem 3.8.

Our second example deals with faster growth and stronger variation of the growth rate with respect to temperature, i.e., with the choice $p = q = 10^{-1}$, which causes a more significant nonlinearity in the evolution of the crystal boundaries. This can be seen from Figure 5, the moving boundaries deviate significantly from a linear evolution in both cases. A comparison of the boundaries of $\tilde{\Theta}_0$ and Θ_0 (plotted vs. time in Figure 6) shows now a significant difference already for small time, which increases during the evolution.This numerical result confirms

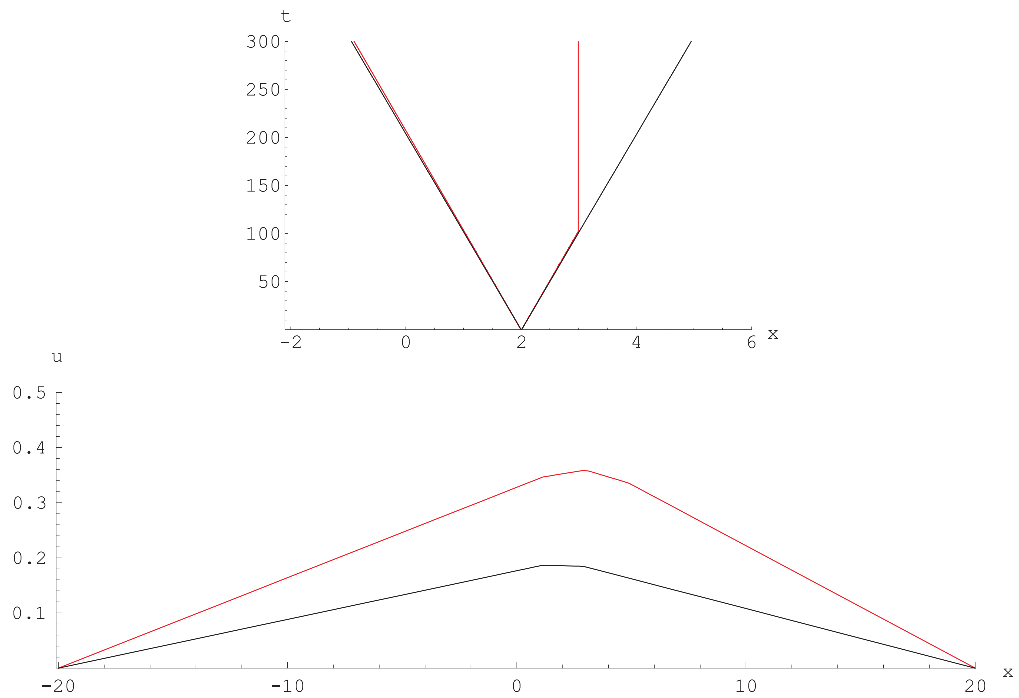

Figure 4: Comparison of the evolving crystals $\tilde{\Theta}_0$ and Θ_0 (red) in the above plot. The second figure shows a comparison of the temperatures $\tilde{u}$ and u at time $t = 90$.

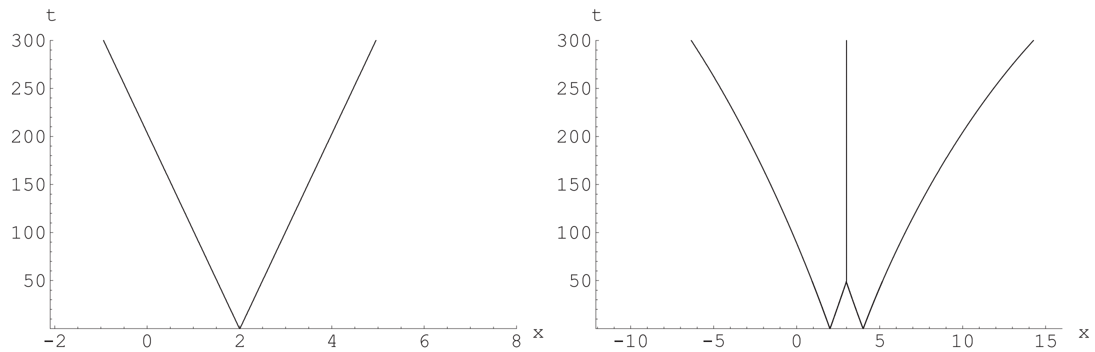

Figure 5: Evolution of the single crystal $\tilde{\Theta}_0$ (left) and of the crystals Θ_0 and Θ_1 in the second example.

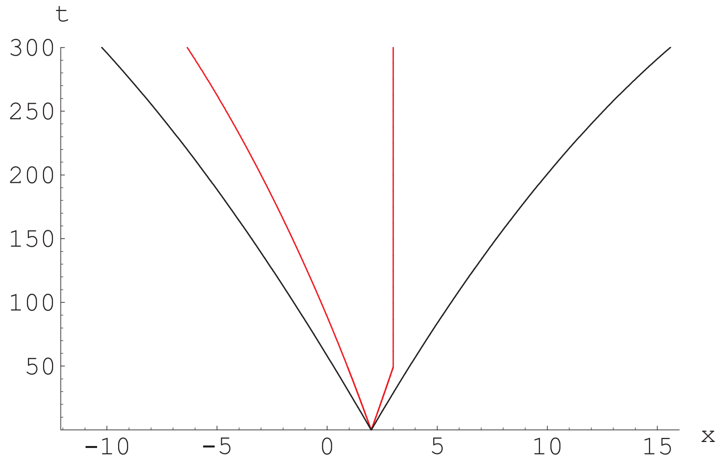

Figure 6: Comparison of the evolving crystals $\tilde{\Theta}_0$ and Θ_0 (red) in the second example.

the motivation of this paper, i.e., the necessity to consider growth processes with multiple crystals, since simulations with single crystals may predict larger crystals.

8 Conclusions

We have formulated a growth model for multiple crystals in a polymer melt in the framework of moving boundary problems, which led to moving boundary problems for an elliptic (in the quasi-static case) and a parabolic partial differential equation. This represents an attempt to a rigorous mathematical treatment of moving boundary problems with multiple growth fronts. Though of tremendous practical importance, such problems have been attacked so far only computationally (cf. [8] for dendritic crystals and [21] for polymer crystals) or by mean-field models, whereas a lot of research has been carried out for the single crystal case.

We have performed a detailed analysis in the spatially one-dimensional case, in higher dimensions only preliminary results could be shown so far. We want to stress that the analysis of multi-dimensional situations including questions such as the shape and regularity of contact interfaces is an important and challenging problem for future research, not only in the case of polymeric crystals but also for other materials and various growth modes, such as crystal growth problems in semiconductor technology (cf. [7, 31]), metal homoepitaxy (cf. [26]) or protein crystallization (cf. [16, 27] and the references therein).

Another important topic in this context is the numerical computation of growing crystals and the arising contact interfaces. We have discussed efficient solution methods in this paper, theoretical elaborations of these methods are still left open for future research.

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