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A Simplified Model for Non–Isothermal Crystallization of Polymers

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Abstract

Recently, Burger and Capasso [M^3AS **11** (2001) 1029–1053] derived a coupled system of partial differential equations to describe non–isothermal crystallization of polymers. The system is based on a spatial averaging of the underlying stochastic birth–and–growth process describing the nucleation and growth of single crystals. In the present work we reconsider the scaling properties of the dimensional system as well as some special one–dimensional models. Moreover, using an appropriate scaling of the original system, we derive a simplified model which only consists of a reaction–diffusion equation with memory for the underlying temperature, such that the degree of crystallization can be explicitly given by a time integration of the temperature–dependent growth and nucleation rate. Numerical simulations indicate that the reduced model shows at least qualitatively the same behavior like the original model.

Keywords: Crystallization of Polymers, Scaling Properties, Inhomogeneous Wave Equation, Temperature Equation with Memory.

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1 Introduction

The control and optimization of polymer crystallization in industrial applications requires an appropriate understanding of the physical–chemical phenomena occurring during the process. Hence, the mathematical modeling and simulation is an important task and there exists a large variety of different approaches in this direction. A recent overview on such models can be found in [2].

In the present work we are concerned with a pure deterministic model for non–isothermal polymer crystallization recently proposed by Burger and Capasso in [1]. The model consists of a system of partial differential equations for the crystalline volume fraction $\xi = \xi(\bar{x}, \bar{t})$, the mean free surface distributions $v = v(\bar{x}, \bar{t})$ and $w = w(\bar{x}, \bar{t})$ of crystals as well as the underlying temperature field $T = T(\bar{x}, \bar{t})$.

The model is a mixed parabolic–hyperbolic system, in dimensional form given by

$$\frac{\partial T}{\partial \bar{t}} = \operatorname{div}_{\bar{x}}(D \nabla_{\bar{x}} T) + \frac{h}{c} \frac{\partial \xi}{\partial \bar{t}} \tag{1.1}$$

$$\frac{\partial \xi}{\partial \bar{t}} = (1-\xi) \bar{a}(T)\, \bar{v} \tag{1.2}$$

$$\frac{\partial \bar{v}}{\partial \bar{t}} = \operatorname{div}_{\bar{x}}(\bar{a} \bar{w}) + 2\pi \bar{a}(T)\, \bar{b}(T) \tag{1.3}$$

$$\frac{\partial \bar{w}}{\partial \bar{t}} = \nabla_{\bar{x}}(\bar{a} \bar{v}) \tag{1.4}$$

The system (1.1)–(1.4) is considered on the bounded domain $\Omega \subset \mathbb{R}^2$ and it is closed by the initial conditions

$$T(\bar{x}, 0) = T_0(\bar{x}) \tag{1.5}$$

$$\xi(\bar{x}, 0) = 0 \tag{1.6}$$

$$v(\bar{x}, 0) = 0 \tag{1.7}$$

$$w(\bar{x}, 0) = 0 \tag{1.8}$$

as well as the boundary conditions

$$-D \frac{\partial T}{\partial n} = \gamma_0 (T - T_{\text{out}}) \tag{1.9}$$

$$\bar{v} = -\bar{w}^T \cdot n \tag{1.10}$$

on the boundary $\partial \Omega$.

The parameters D, h, c and γ_0 denote the diffusion coefficient, the latent heat, the heat capacity and the heat transfer coefficient at the boundary, respectively. The temperature–dependent functions $\bar{a}$ and $\bar{b}$ are the growth and birth rates of a single crystal, respectively, and T_{out} is the cooling temperature at the boundary, which can be used to control the crystallization process.

Let us shortly explain the main steps to derive Eqns. (1.1)–(1.10), a detailed description can be found in [1]. The underlying model is a stochastic process for the crystallization of polymers, where crystals are generated according to a certain density in space and time and afterward grow with a specific growth rate. Applying a spatial averaging of the stochastic model on a mesoscopic scale lying between a typical size of the crystals and a typical scale for the heat transfer, one finally ends up with the deterministic system given above. The scaling property in space is obtained assuming certain relations between the nucleation rate of crystals and the diffusion of temperature. The Robin–type boundary condition (1.9) for the temperature field describes the cooling with an external temperature and Eq. (1.10) models the assumption that no nucleation of crystals occurs at the boundary.

In the present work we discuss the scaling properties of the deterministic model and give a corrected solution for a simplified one–dimensional model considered in [1]: assuming a constant (temperature–independent) growth rate one may reformulate the model on the fast time scale of the nucleation process as an inhomogeneous wave equation on a bounded interval, which can be solved analytically using the method of characteristics. Moreover, we derive a simplified model which yields a single reaction–diffusion equation for the temperature field, which contains a memory term, i.e. the time history of the temperature field acts as a source term in the diffusion equation. The reduced model is valid as long as the time scale for the nucleation of crystals is (much) smaller than the time scale for the diffusion of temperature. Numerical simulations show that the simplified model yields at least qualitatively the same results as the original one given in [1].

The paper is organized as follows: in Section 2 we consider the dimensionless form of the deterministic model given above based on typical values for the space and time variables and reference values for the temperature, the mean surface distribution of crystals as well as the nucleation and growth rates. Based on the derivation of the model using an averaging procedures on three different space scales one may introduce different time scales, namely the scale of nucleation of crystals and a scale for the diffusion of temperature.

Assuming a constant growth rate and considering the fast time scale of nucleation one may derive an inhomogeneous wave equation, which is straightforward to solve analytically at least in the spatial one–dimensional case. This is done in Section 3 where we correct the analytic solution given in [1].

Section 4 deals with the derivation of a simplified model equation assuming that time scale of nucleation of crystals is (much) faster than the time scale for the diffusion of temperature. The relation between the different time scales is expressed in terms of a small parameter $\varepsilon \ll 1$. We give results obtained from a numerical simulation of the reduced model which qualitatively coincide with the one given in [1]. Finally we give some conclusions in Section 5.

2 Scaling Properties

Introducing the scalings $\bar{t} = t_0\, t$, $\bar{x} = x_0\, x$, $T = T_{\min} + \Delta T\, \theta$, $\bar{a} = a_0\, a$, $\bar{b} = b_0\, b$ and $(\bar{v}, \bar{w}) = v_0\, (v, w)$ we obtain the following dimensionless form of (1.1)–(1.4)

$$\dot{\theta} = \kappa\, \Delta\theta + L\dot{\xi} \tag{2.1}$$

$$\dot{\xi} = \gamma\, (1 - \xi)\, a(\theta)\, v \tag{2.2}$$

$$\dot{v} = \lambda\, \mathrm{div}_x(aw) + \delta\, a(\theta)\, b(\theta) \tag{2.3}$$

$$\dot{w} = \lambda\, \nabla_x(av) \tag{2.4}$$

with the dimensionless parameters

$$\kappa = \frac{D\, t_0}{x_0^2} \tag{2.5}$$

$$L = \frac{h}{c\Delta T} \tag{2.6}$$

$$\gamma = a_0 v_0 t_0 \tag{2.7}$$

$$\lambda = \frac{a_0 t_0}{x_0} \tag{2.8}$$

$$\delta = 2\pi \frac{a_0 b_0 t_0}{v_0} \tag{2.9}$$

The initial and boundary conditions for the temperature equation read as

$$\begin{aligned} \theta(x, 0) &= \theta_0(x) \\ -\frac{\partial\theta}{\partial n} &= \beta\, (\theta - \theta_{\mathrm{out}}) \end{aligned}$$

where $\beta = \gamma_0 x_0 / D$.

Some typical values for the parameters appearing in (2.5)–(2.9) are [1]:

Parameter	Symbol	Typical Value
Diffusivity	D	$10^{-7}\,\mathrm{m}^2\,\mathrm{s}^{-1}$
Length scale	x_0	$10^{-2}\,\mathrm{m}$
Growth rate	a_0	$10^{-5}\,\mathrm{m}\,\mathrm{s}^{-1}$
Nucleation density	b_0	$10^{12}\,\mathrm{m}^{-2}$
Temperature difference	ΔT	$150\,\mathrm{K}$
Latent heat	h/c	$50\,\mathrm{K}$

Table 1: Typical values for isotactic Polypropylene

Inspecting the reference values given in Table 1 we find that $\kappa/\lambda = O(1)$ indicating that diffusion and the growth of a single crystal take place on the same time scale. Furthermore one has $L = O(1)$.

To obtain a reference value v_0 for the surface density $\bar{v}$, we consider a two–dimensional sample of length x_0, which is fully crystallized with nucleation density

b_0, such that the total number of crystals is given by $N = b_0\, x_0^2$. Assuming a uniform crystallization with average radius r for each crystal, one has $\pi r^2 N = x_0^2$, i.e $r = 1/\sqrt{\pi b_0}$. The total surface of these crystals is given by $2\pi r N$ and we choose as a reference value for the surface density the value

$$v_0 = 2\pi r N / x_0^2 = 2\sqrt{\pi b_0}$$

Inserting the typical values from Table 1 gives $v_0 = 2\sqrt{\pi}\, 10^6\,\mathrm{m}^{-1}$.

One should remark that this reference value v_0 for the surface density determines the onset of impingement. As soon as $\bar{v} \approx v_0$, crystals start to touch each other and the quantity $\bar{v}$ looses its physical interpretation as surface density.

The reasoning given in [1] to obtain a value for v_0 by balancing the time derivative and the source term in (2.3) seems questionable, since then the scale for the surface density depends on the chosen time scale.

Summarizing the results for the three non–dimensional parameters, we obtain

$$\frac{\kappa}{\delta} = \frac{D}{\sqrt{\pi} a_0 \sqrt{b_0} x_0^2} \sim \frac{10^{-4}}{\sqrt{\pi}} = O(\varepsilon) \tag{2.10}$$

$$\frac{\gamma}{\delta} = \frac{a_0 v_0^2 t_0}{2\pi a_0 b_0 t_0} = 2 \tag{2.11}$$

Choosing in (2.1)–(2.4) the time scale of the nucleation process, i.e. $\delta = 1$ or $t_0 \sim 0.05\,\mathrm{s}$ we obtain the system

$$\dot{\theta} = \varepsilon\,\Delta\theta + L\dot{\xi} \tag{2.12}$$

$$\dot{\xi} = \gamma\,(1-\xi)\,a(\theta)\,v \tag{2.13}$$

$$\dot{v} = \varepsilon\,\mathrm{div}\,(a(\theta)w) + a(\theta)\,b(\theta) \tag{2.14}$$

$$\dot{w} = \varepsilon\,\nabla(a(\theta)v) \tag{2.15}$$

On the other hand, if we work on the time scale of the diffusion, which means $\kappa = 1$, we obtain $t_0 = 10^3\,\mathrm{s}$ and the system (2.12)–(2.15) can be easily rewritten on this time scale.

However, in industrial and technological applications one is usually more interested in the effects related to the nucleation and increase of crystallinity rather than in the mere diffusion process. Therefore we will focus in our subsequent discussion on the nucleation time scale.

3 An One–Dimensional Model

Restricting the system (2.12)–(2.15) with its boundary conditions to one spatial dimension $x \in [0,\, 1]$ and assuming the coefficients a and b to be independent of the underlying temperature field, Eqn. (2.12) decouples from the other three equations.

Introducing $u = -\ln(1-\xi)$ we obtain the system

$$u_t = \gamma a v \tag{3.1}$$

$$v_t = \varepsilon a w_x + \tilde{s} \tag{3.2}$$

$$w_t = \varepsilon a v_x \tag{3.3}$$

$$u(x,0) = 0 \tag{3.4}$$

$$v(x,0) = 0 \tag{3.5}$$

$$w(x,0) = 0 \tag{3.6}$$

$$v(x,t) = \pm w + 2\beta \qquad \text{for } x \in \{0,1\} \tag{3.7}$$

where β models the influence of boundary nucleation as described in Eqn. (3.60) of [1]. From (3.1) and (3.3) we obtain $u_x = \gamma w/\varepsilon$ and finally the following wave equation with source term for u

$$\begin{aligned} u_{tt} &= \varepsilon^2 u_{xx} + s \\ u(0,x) &= 0 \\ u_t(0,x) &= 0 \\ u_t - \varepsilon u_x &= 2\beta \qquad \text{at } x = 0 \\ u_t + \varepsilon u_x &= 2\beta \qquad \text{at } x = 1 \end{aligned}$$

where we have replaced εa by $\tilde{\varepsilon}$ and dropped the tilde. Introducing $p = u_t + \varepsilon u_x$ and $q = u_t - \varepsilon u_x$ and setting $s = 1$ we can diagonalize the system

$$\begin{pmatrix} p \\ q \end{pmatrix}_t = \begin{pmatrix} \varepsilon & 0 \\ 0 & -\varepsilon \end{pmatrix} \begin{pmatrix} p \\ q \end{pmatrix}_x + \begin{pmatrix} 1 \\ 1 \end{pmatrix} \tag{3.8}$$

The initial and boundary conditions for (3.8) are

$$\begin{aligned} p(x,0) &= q(x,0) = 0 \\ q(0,t) &= p(1,t) = 2\beta \end{aligned}$$

Using the method of characteristics we readily obtain the solution

$$u(x,t) = \begin{cases} \dfrac{t^2}{4} + \dfrac{xt}{2\varepsilon} - \dfrac{x^2}{4\varepsilon^2} + \beta\left(t - \dfrac{x}{\varepsilon}\right) & \text{for } 0 \le x < \varepsilon t \\ \dfrac{t^2}{2} & \text{for } \varepsilon t \le x \le 1 - \varepsilon t \\ \dfrac{t^2}{4} + \dfrac{(1-x)t}{2\varepsilon} - \dfrac{(1-x)^2}{4\varepsilon^2} + \beta\left(t - \dfrac{1-x}{\varepsilon}\right) & \text{for } 1 - \varepsilon t < x \le 1 \end{cases} \tag{3.9}$$

which is valid up to time $t = 1/(2\varepsilon)$.

Figure 1 shows the results of the 1–D model with boundary nucleation (left) and without boundary nucleation (right). Note, that including the boundary nucleation (here shown for $\beta = 0.2$) leads to an unphysical overshoot of the crystallinity close to the boundary. Therefore it seems reasonable to exclude – at least in the 1–D model – the influence of boundary nucleation proposed in [1].

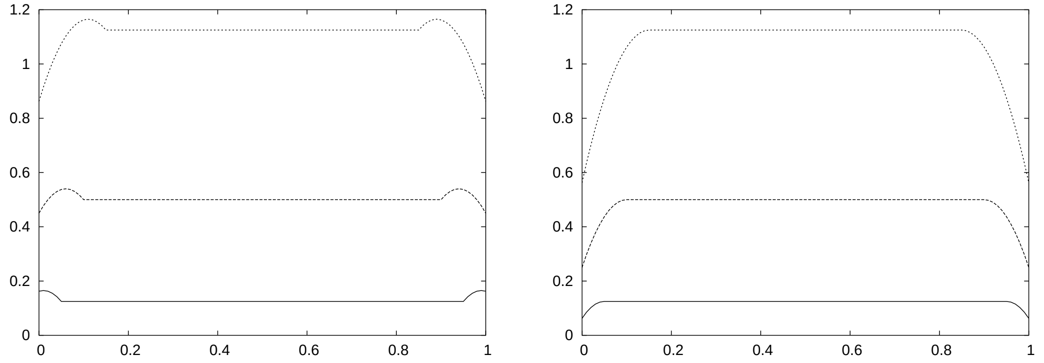

Figure 1: Solution of the 1–D model problem with boundary nucleation $\beta = 0.2$ (left) and without boundary nucleation $\beta = 0$ (right). In both cases we have chosen $\varepsilon = 0.1$ and plotted the solution for $t = 0.5,\ 1,\ 1.5$.

4 Temperature Equation with Memory

According to the different time scales discussed in Section 2 we reconsider for $\varepsilon \ll 1$ the initial–boundary value problem

$$\dot\theta = \varepsilon\,\Delta\theta + L\dot\xi \tag{4.1}$$

$$\dot\xi = \gamma(1-\xi)av \tag{4.2}$$

$$\dot v = \varepsilon\ \operatorname{div}(a(\theta)w) + a(\theta)b(\theta) \tag{4.3}$$

$$\dot w = \varepsilon\,\nabla(a(\theta)v) \tag{4.4}$$

with initial conditions

$$\theta(x,0) = \theta_0(x) \tag{4.5}$$

$$\xi(x,0) = 0 \tag{4.6}$$

$$v(x,0) = 0 \tag{4.7}$$

$$w(x,0) = 0 \tag{4.8}$$

and boundary conditions

$$-\frac{\partial\theta}{\partial n} = \beta(\theta - \theta_{\mathrm{out}}(x)) \quad (\beta > 0) \tag{4.9}$$

$$v = -w^T n \tag{4.10}$$

for $x \in \partial\Omega$.

Introducing the function $u(x,t) = -\ln(1-\xi(x,t))$ the first two equations of the system above may be written in the form

$$\dot\theta = \varepsilon\Delta\theta + \gamma L e^{-u} a(\theta)v \tag{4.11}$$

$$\dot u = \gamma a(\theta)v \tag{4.12}$$

Eq. (4.12) yields together $u(x,0) = 0$ (cf. Eq. (4.6)) the expression

$$u(x,t) = \gamma \int_0^t a(\theta(x,t))v(x,t)\,ds \tag{4.13}$$

such that x simply acts as a parameter in (4.13).

If we define

$$\Phi(x,t) = (v(x,t), w_1(x,t), w_2(x,t))^T$$

we may formulate (4.3) and (4.4) as a quasilinear first order system given by

$$\dot{\Phi} + \sum_{i=1,2} A_i(\theta;\varepsilon)\Phi_{x_i} = B(\Phi,\theta,\nabla\theta;\varepsilon) \tag{4.14}$$

with

$$\begin{aligned} A_1 &= -\varepsilon \begin{pmatrix} 0 & a(\theta) & 0 \\ a(\theta) & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\ A_2 &= -\varepsilon \begin{pmatrix} 0 & 0 & a(\theta) \\ 0 & 0 & 0 \\ a(\theta) & 0 & 0 \end{pmatrix} \end{aligned}$$

and

$$B = (a(\theta)b(\theta) + \varepsilon a'(\theta)\nabla\theta \cdot w, \varepsilon a'(\theta)v\nabla\theta)^T$$

The system (4.14) is hyperbolic in time (strictly, as long as $a(\theta) \neq 0$) and may be solved using the method of characteristics.

Assuming $a'(\theta) = O(1)$ and $\nabla\theta = O(1)$ we obtain for $t = O(1)$ the relations

$$\begin{aligned} v(x,t) &= \int_0^t a(\theta)b(\theta)\,ds + O(\varepsilon^2) \\ w(x,t) &= O(\varepsilon) \end{aligned} \tag{4.15}$$

Substituting (4.15) into (4.11) and (4.13) yields (up to higher order terms in ε) the following temperature equation with memory

$$\dot{\theta} = \varepsilon\Delta\theta + \gamma L e^{-u} a(\theta) \int_0^t a(\theta)b(\theta)\,ds \tag{4.16}$$

where $u = u(x,t)$ is now defined by

$$u(x,t) = \gamma \int_0^t a(\theta) \left(\int_0^s a(\theta)b(\theta)\,d\tau \right) ds \tag{4.17}$$

Hence, for $\varepsilon \ll 1$, the initial–boundary value problem given by the system (4.1)–(4.10) may be substituted by the single reaction–diffusion equation (4.16) with memory together with (4.17) and initial and boundary conditions (4.5) and (4.9), respectively.

For the crystalline volume fraction $\xi = \xi(x,t)$ one has – again up to higher order terms in ε – the formula

$$\xi(x,t) = 1 - \exp\left(-\gamma \int_0^t a(\theta)\left(\int_0^s a(\theta)b(\theta)\,d\tau\right)ds\right)$$

In the following we present some numerical results obtained from a finite–difference approximation of (4.16) with (4.17), (4.5) and (4.9). As numerical scheme we use a first order explicit time integration together with a standard 5–point stencil for the Laplace operator. The boundary values at the time level $n+1$ are computed using a first order difference approximation of the normal derivative at the boundary. To ensure stability of the scheme and non–oscillating modes in the numerical approximates we should satisfy the condition $\varepsilon^2 k/h^2 < 1/8$, where k and h denote the step size in time and space, respectively. Because we apply a first order time integration the time step is chosen much smaller than given by the condition above in order to obtain a sufficiently accurate integration of the source term in the temperature equation.

For the growth and nucleation rates we use

$$a(\theta) = b(\theta) = e^{-\kappa(\theta-\theta_{\mathrm{ref}})}$$

which describes the temperature dependence of the growth and nucleation rate observed in experiments at least qualitatively, see [3].

We perform two different simulations on the rectangle $[0,1]\times[0,2]$: in the first one we use the constant cooling temperature $\theta_{\mathrm{out}} = 0$, in the second one the cooling temperature is $\theta_{\mathrm{out}} = 0$ on the left and upper as well as $\theta_{\mathrm{out}} = 1$ on the right and lower boundary of the rectangle. The initial temperature is homogeneous on the rectangle, i.e. $\theta(x,0) = 2$, and we use the parameters $L = 1/3$, $\beta = 10$, $\kappa = 3$ and $\theta_{\mathrm{ref}} = 1/2$. The step size in space is given by $h = 1/40$, the time step equal to $k = 0.16$ and, finally, $\varepsilon = 10^{-4}$.

Figures 2 and 3 show the temperature and crystalline volume fraction for the two different profiles of the cooling temperature mentioned above. In both cases one observes a sharp front in the crystalline volume fraction moving in time from the boundary into the interior domain. Like in [1] we do not observe such a moving front in the temperature fields, which indicates that the cooling at the boundary dominates the effect of latent heat during the crystallization process and confirms the validity of our asymptotic induced model reduction. We even observe that the temperature is not monotonically decreasing although our results do not show a significant temperature overshoot close to the boundary like given in Fig. 5 of [1].

The influence of a non–uniform cooling temperature along the boundary is clearly indicated comparing the results shown in Fig. 2 and 3. Whereas the results in Fig. 2

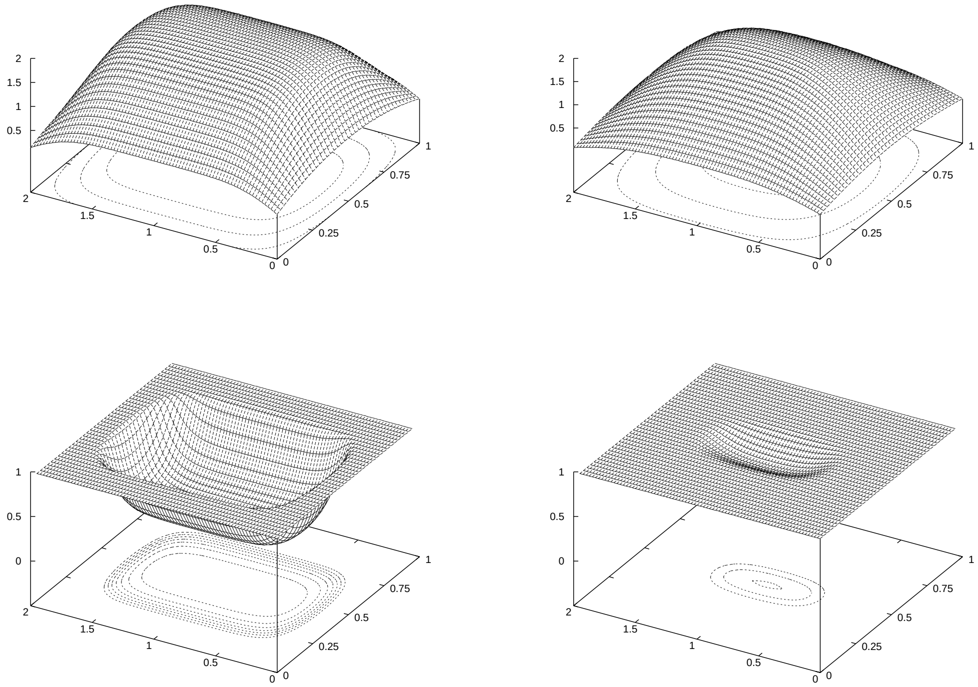

Figure 2: Temperature (up) and crystalline volume fraction (down) for $t = 400, 800$.

seem to be completely symmetric with respect to the line $y = 1$, the non–uniform cooling temperature yields a shift of the higher crystalline volume fraction toward the lower cooling temperature at two boundary segments.

In summary one can conclude that our reduced model equation yields qualitatively the same results like the full deterministic model proposed by Burger and Capasso.

5 Conclusion

In the previous sections we discussed a deterministic model to describe the crystallization process of polymers. Referring to a recent work of Burger and Capasso we reconsidered the scaling properties of the model and gave a corrected solution for the one–dimensional version assuming that the growth and nucleation rate of crystals is independent of the temperature. In particular we showed that the boundary nucleation proposed by Burger and Capassso yields an unphysical overshoot of the crystalline volume fraction close to the boundary.

Our main result is the reduction of the original model to a single reaction–diffusion equation with memory for the underlying temperature field. In the reduced model the crystalline volume fraction is obtained by integrating growth and nucleation rate over the temperature history. Our numerical results showed that

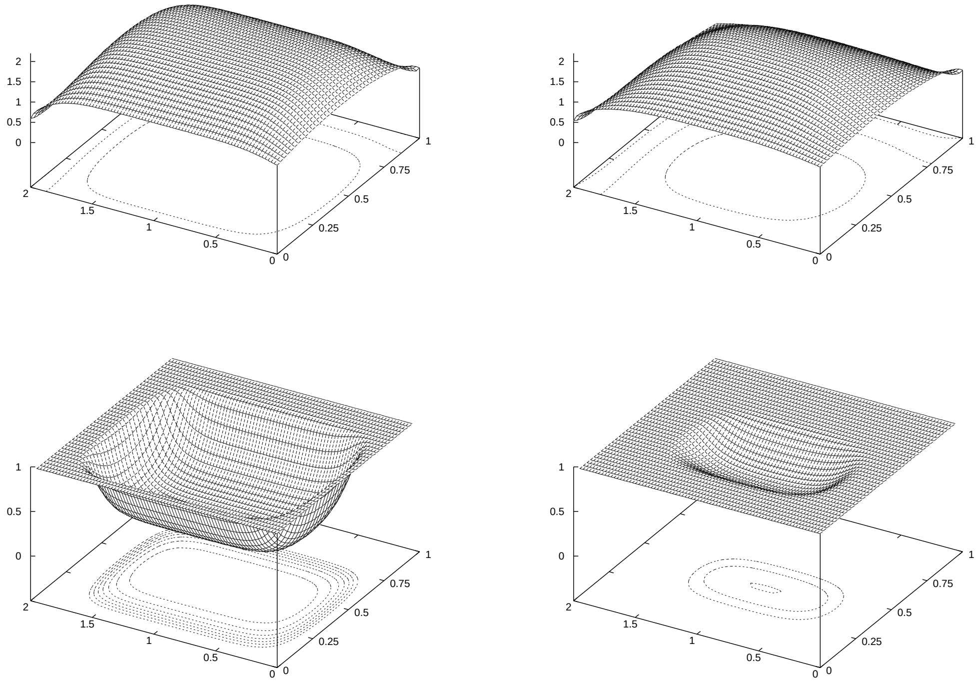

Figure 3: Temperature (up) and crystalline volume fraction (down) for $t = 400, 800$.

the reduced model shows at least qualitatively the same behavior like the original model.

A major goal in the mathematical modeling of polymer crystallization is the computation of an optimal control, in our case the cooling temperature along the boundary of the spatial domain, such that the crystallization is as uniform as possible. Here one may use our simplified model which may reduce the theoretical as well as numerical work when applying optimization strategies for partial differential equations. Results on the optimal control problem are currently under investigation.

A problem from a mathematical point of view, which we did not discuss in the present work, is to obtain an existence and uniqueness result for the reduced model formulated in (4.16) and (4.17).

Acknowledgment

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