

# Modelling Multi-dimensional Crystallization of Polymers in Interaction with Heat Transfer

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## Abstract

This paper is concerned with the mathematical modelling of crystallization processes in a general heterogeneous temperature field.

We present a new direct approach based on the coupling of the stochastic birth and growth process of crystallization (Avrami-Kolmogorov-Evans theory) with the evolution equation for temperature via enthalpy.

Later we provide conditions upon scales and parameters, under which averaging at a mesoscale leads to a classical deterministic model based on a system of partial differential equations of parabolic and hyperbolic type, modelling the evolution of volume and surface densities of crystals coupled with temperature.

**Keywords:** *Averaging, Diffusion, Growth, Nonlinear Evolution Equations, Nucleation.*

# 1 Introduction

A crystallization process is in general the superposition of two features, namely *nucleation* and *growth* of crystals. While the growth process may be considered deterministic (with speed  $G = G(x, t)$ , the *growth rate*), nucleation occurs randomly in space and time. We will consider a crystallization process in a bounded domain  $E \subset \mathbf{R}^d$  ( $d = 1, 2, 3$ ) and assume that nucleation takes place only in the interior of  $E$  with some rate  $\alpha = \alpha(x, t)$  (*nucleation rate*). In practice one must also expect *boundary nucleation* (cf. [9]), which is neglected almost completely in literature so far. Nevertheless we note that the approach presented here might also be adapted for the case of boundary nucleation, which will be an important future task.

In general, we will denote by  $\Theta^t$  the crystalline phase at time  $t$  and by  $\Theta^t(x_0, t_0)$  a crystal born at point  $x_0$  at time  $t_0$  and freely grown up to time  $t$ . In a crystallization process with nucleation events  $\{ (X_j, T_j) \mid 0 \leq T_1 \leq T_2 \leq \dots \}$ , the crystalline phase is given by

$$\Theta^t = \bigcup_{T_j < t} \Theta_j^T,$$

where  $\Theta_j^t$  denotes the crystal born at time  $T_j$  at  $X_j$  (again freely grown up to time  $t$ ). It has turned out (cf. [2, 8, 10]) that on a macroscopic scale the quantity

$$\xi(x, t) := E[I_{\Theta^t}(x)] = P(x \in \Theta^t), \quad x \in E, t \in \mathbf{R}_+$$

is suitable for the description of the crystallization process.

In the simple case of spatially homogeneous growth and nucleation rate, equations for  $\xi$  can be derived based upon the approaches by Avrami, Kolmogorov and Evans (cf. [1, 11, 13]). These models yield a good description of isothermal processes and have been investigated frequently in bounded and unbounded domains (cf. [4, 5, 9, 10, 14]).

We develop a model for heterogeneous growth based upon experimentally verified principles in Section 2. By using this growth model we can derive the crystallization kinetic equations for arbitrary growth and nucleation rates, which are given functions of time and space. This derivation uses a generalization of the classical theory by Avrami, Kolmogorov and Evans, the main tool being the *causal cone*. This theory cannot be extended easily to the case of interaction with temperature, since the causal cone cannot be defined in a deterministic way if the temperature field is random. In Section 5.3 we provide a formal derivation of the deterministic system by an approximation at different scales. A rigorous derivation will be left to subsequent work (cf. [7]).

## 2 Growth of a nucleus in an heterogeneous Field

The classical Kolmogorov-Avrami-Evans theory for isothermal crystallization heavily used the fact that crystals are of spherical shape if the growth rate is constant, the same is true if the growth

rate depends upon time only. In the case of heterogeneous growth, i.e., if the growth rate  $G$  depends on space and time, the shape of a polymeric crystal (before impingement) is no longer a ball centered in the origin of growth. In the case of a growth rate with constant gradient it has been verified experimentally that the growing nucleus is the union of lines (the *growth lines*) which lead to growth in minimal time (cf.[17]). This principle can be adapted for the case of arbitrary growth rates (cf.[18]).

**Assumption 2.1 (Minimal-time Principle).** A nucleus grows from its origin to any other point such that the needed time is minimal.

The minimal-time principle is obviously satisfied for homogeneous growth, since there the growth lines are just straight lines, whose union forms the shape. The growth of a nucleus in  $\mathbf{R}^2$  between its origin  $(x_0, y_0)$  and another point  $(x_1, y_1)$  due to Assumption 2.1 may be formulated as follows:

$$t_1 = \min_{(x,y,\phi)}$$

subject to

$$\begin{aligned} \dot{x}(t) &= G(x(t), y(t), t) \cos \phi(t) & t \in (t_0, t_1) \\ \dot{y}(t) &= G(x(t), y(t), t) \sin \phi(t) & t \in (t_0, t_1) \\ x(t_0) &= x_0, \quad y(t_0) = y_0 \\ x(t_1) &= x_1, \quad y(t_1) = y_1 \end{aligned}$$

The necessary first order conditions for this control problem (cf.e.g.[12]) lead to the following equation for the control variable  $\phi$ :

$$\dot{\phi} = \langle \nabla G(x, y, t), (-\sin \phi, \cos \phi)^T \rangle$$

For the growth of a nucleus in  $\mathbf{R}^3$  we obtain the control problem

$$t_1 = \min_{(x,y,\phi,\theta)}$$

subject to

$$\begin{aligned} \dot{x}(t) &= G(x(t), y(t), z(t), t) \cos \phi(t) \cos \theta(t) \\ \dot{y}(t) &= G(x(t), y(t), z(t), t) \sin \phi(t) \cos \theta(t) \\ \dot{z}(t) &= G(x(t), y(t), z(t), t) \sin \theta(t) \\ x(t_0) &= x_0, \quad y(t_0) = y_0, \quad z(t_0) = z_0 \\ x(t_1) &= x_1, \quad y(t_1) = y_1, \quad z(t_1) = z_1 \end{aligned}$$

which leads to the necessary conditions

$$\begin{aligned}\dot{\phi}(t) &= \langle \nabla G(x(t), y(t), z(t), t), (-\sin \phi(t), \cos \phi(t), 0)^T \rangle \\ \dot{\theta}(t) &= \langle \nabla G(x(t), y(t), z(t), t), (-\cos \phi(t) \sin \theta(t), -\sin \phi(t) \sin \theta(t), \cos \theta(t))^T \rangle\end{aligned}$$

By eliminating the angles we may deduce a second order ODE for the growth lines given by

$$\frac{d}{dt} \left( \frac{\dot{\mathbf{x}}}{G(\mathbf{x}, t)} \right) = -\nabla G(\mathbf{x}, t) + \left\langle \nabla G(\mathbf{x}, t), \frac{\dot{\mathbf{x}}}{G(\mathbf{x}, t)} \right\rangle \frac{\dot{\mathbf{x}}}{G(\mathbf{x}, t)}, \quad (1)$$

where  $\mathbf{x}$  denotes the vector  $(x, y)^T$  in  $\mathbf{R}^2$  and  $(x, y, z)^T$  in  $\mathbf{R}^3$ , respectively.

The crystal at time  $t$  is now given as the union of all growth lines, i.e.

$$\Theta_0^t = \{ \mathbf{x}(\tau) \mid \mathbf{x} \text{ solves (1), } \mathbf{x}(t_0) = \mathbf{x}_0, \tau \in (t_0, t) \}.$$

Each growth line is determined uniquely by its derivative at initial time, which may be written as

$$\dot{\mathbf{x}}(t_0) = G(\mathbf{x}_0, t_0) \mathbf{n}_0,$$

where  $\mathbf{n}_0$  is an arbitrary vector in  $\mathbf{R}^d$  with  $\|\mathbf{n}_0\| = 1$ . Thus, we may introduce a parametrization for the crystal based on the initial direction, namely, in  $\mathbf{R}^2$

$$\Theta_0^t = \{ \mathbf{x}(\tau, \gamma) \mid \tau \in (t_0, t), \gamma \in [0, 2\pi) \}, \quad (2)$$

where  $\mathbf{x}(\tau, \gamma)$  denotes the solution of (1) with initial values

$$\begin{aligned}\mathbf{x}(t_0) &= \mathbf{x}_0, \\ \dot{\mathbf{x}}(t_0) &= G(\mathbf{x}_0, t_0) (\cos \gamma, \sin \gamma)^T,\end{aligned}$$

and in  $\mathbf{R}^3$

$$\Theta_0^t = \{ \mathbf{x}(\tau, \gamma_1, \gamma_2) \mid \tau \in (t_0, t), \gamma_1 \in [0, 2\pi), \gamma_2 \in [-\frac{\pi}{2}, \frac{\pi}{2}] \}, \quad (3)$$

where  $\mathbf{x}(\tau, \gamma_1, \gamma_2)$  denotes the solution of (1) with initial values

$$\begin{aligned}\mathbf{x}(t_0) &= \mathbf{x}_0, \\ \dot{\mathbf{x}}(t_0) &= G(\mathbf{x}_0, t_0) (\cos \gamma_1 \cos \gamma_2, \sin \gamma_1 \cos \gamma_2, \sin \gamma_2)^T.\end{aligned}$$

Equation (1) yields a description of crystal growth based on growth lines, which are computed independently. The parametrizations introduced in (2) or (3) also provide another view upon the growing nucleus. For the sake of simplicity we concentrate on the case of a crystal in  $\mathbf{R}^2$ , but similar reasoning is possible in higher dimensions. By fixing the time  $t$  we obtain the set

$$\partial \Theta_0^t = \{ \mathbf{x}(t, \gamma) \mid \gamma \in [0, 2\pi) \},$$

which is called the *growth front*. In the following we will deduce equations for the crystal growth using information about the surface  $\partial\Theta_0^t$  and its normal vector, which will be denoted by  $\mathbf{n}(t, \gamma)$ .

Let  $\mathbf{x}'(t, \gamma)$  denote the derivative of  $\mathbf{x}$  with respect to  $\gamma$ . Then  $\|\dot{\mathbf{x}}\|^2 = G(\mathbf{x}, t)^2$  implies

$$\left\langle \frac{\dot{\mathbf{x}}}{G}, \frac{\partial}{\partial t} \mathbf{x}' \right\rangle = \langle \nabla G, \mathbf{x}' \rangle.$$

Multiplying (1) with  $\mathbf{x}'$  yields

$$\left\langle \frac{\partial}{\partial t} \frac{\dot{\mathbf{x}}}{G}, \mathbf{x}' \right\rangle = -\langle \nabla G, \mathbf{x}' \rangle + \langle \nabla G, \frac{\dot{\mathbf{x}}}{G} \rangle \left\langle \frac{\dot{\mathbf{x}}}{G}, \mathbf{x}' \right\rangle,$$

and by combining these equations we obtain the initial-value problem

$$\frac{\partial}{\partial t} \left\langle \frac{\dot{\mathbf{x}}}{G}, \mathbf{x}' \right\rangle = p(t) \left\langle \frac{\dot{\mathbf{x}}}{G}, \mathbf{x}' \right\rangle, \quad (4)$$

$$\left\langle \frac{\dot{\mathbf{x}}}{G}, \mathbf{x}' \right\rangle_{t=0} = 0, \quad (5)$$

where  $p(t) := \langle \nabla G, \frac{\dot{\mathbf{x}}}{G} \rangle$ . Since we may suppose that  $\dot{\mathbf{x}}$  and  $\mathbf{x}$  are known as the solutions of (1) we may interpret (4), (5) as an equation for the function  $\langle \frac{\dot{\mathbf{x}}}{G}, \mathbf{x}' \rangle$ , where  $\gamma$  is fixed now. If  $p(t)$  is sufficiently smooth we may conclude that the homogeneous initial-value problem (4), (5) has only the the trivial solution, i.e.,

$$\left\langle \frac{\dot{\mathbf{x}}}{G}, \mathbf{x}' \right\rangle(t, \gamma) = 0, \quad \forall t \geq t_0, \quad \forall \gamma \in [0, 2\pi).$$

Since  $\frac{\dot{\mathbf{x}}}{G}$  is a unit vector this immediately implies that  $\frac{\dot{\mathbf{x}}}{G}$  is just the normal vector of the growth front.

Consequently, we rewrite Equation (1) as the first-order system

$$\dot{\mathbf{x}}(t, \gamma) = G(\mathbf{x}(t, \gamma), t) \mathbf{n}(t, \gamma), \quad (6)$$

$$\dot{\mathbf{n}}(t, \gamma) = -\nabla G(\mathbf{x}(t, \gamma), t) + \langle \nabla G(\mathbf{x}(t, \gamma), t), \mathbf{n}(t, \gamma) \rangle \mathbf{n}(t, \gamma), \quad (7)$$

which clearly shows that the growth is determined by the actual normal direction of the growth front as well as by the growth rate and its gradient. The initial values are given by

$$\mathbf{x}(t_0, \gamma) = \mathbf{x}_0, \quad (8)$$

$$\mathbf{n}(t_0, \gamma) = (\cos \gamma, \sin \gamma)^T.$$

In  $\mathbf{R}^3$  equation (6) may be deduced in an analogous way by differentiating with respect to both angles separately, hence System (6), (7) still remains valid. The initial conditions are given by (8) and by

$$\mathbf{n}(t_0, \gamma) = (\cos \gamma_1 \cos \gamma_2, \sin \gamma_1 \cos \gamma_2, \sin \gamma_2)^T.$$

As opposed to the original minimal-time principle, the derivated System (6), (7) needs only information about the shape of the crystal at the actual time, but not about the history of growth. Hence, this description seems to be suitable not only for the case of growth in a given field, but also for growth in interaction with an evolving field.

## 2.1 Examples of Growing Crystals

For a first simulation of crystal growth in an heterogeneous field we used a typical parabolic temperature profile (i.e., the solution of the heat equation without source term) and data for the growth rate obtained by measurements of i-PP (cf. [15]). The results are presented in Figure 2, which shows the growth front in the first time steps. The deviation from the spherical shape obviously increases with time, nevertheless the crystals still remain convex and do not produce exotic shapes.

## 3 The Causal Cone Approach

A classical way of deducing model equations on a macroscopic scale is based on the investigation of the *causal cone*  $A(x, t)$ , i.e., the set of all points  $y$  and times  $s$ , such that nucleation at  $y$  at time  $s$  would lead to coverage of  $x$  at time  $t$ . The probability  $\xi(x, t)$  that the point  $x$  is covered at time  $t$  (which is the same as the expected value  $E[I_{\Theta^t}(x)]$ ) is substituted by the probability that no nucleation occurs in the causal cone.

This approach was successfully applied in the case of crystallization leading to the *Avrami-Kolmogorov-Evans* equation (cf.[1, 11, 13]). Recently, this approach has been generalized to heterogeneous crystallization (cf.[2, 8]). The growth rate  $G$  and the nucleation rate  $\alpha$  are usually treated as a given field, their kind of temperature-dependence being introduced a-posteriori. In the case of non-isothermal crystallization, this is a very delicate point, since growing crystals influence temperature and thus the growth rate. This problem will be discussed in detail in the following section.

### 3.1 The Structure of the Causal Cone

It has been shown (cf.[2, 8]) that the degree of crystallinity  $\xi$  satisfies

$$\begin{aligned}\xi(x, t) &= 1 - e^{-w(x, t)} \\ w(x, t) &= \int_0^t \left( \int_{\mathcal{E}(x, t, s)} \alpha(y, s) dy \right) ds\end{aligned}$$

with  $\mathcal{E}(x, t, s)$  defined by

$$\begin{aligned}\mathcal{E}(x, t, s) &= \{ y \in E \mid (y, s) \in A(x, t) \} \\ &= \{ y \in E \mid x \in \Theta^t(y, s) \}\end{aligned}$$

if the condition

$$P(x \notin \Theta^t) = P(\text{no nucleation occurs in } A(x, t)) \tag{9}$$

is satisfied. In order to verify (9), we have to show that any nucleation in the causal cone leads to coverage independent of the crystalline phase at that time. More precisely, we have to show that even if  $(x_1, t_1) \in A(x, t)$  is already covered by another crystal, the point  $x$  will be covered at time  $t$ . This can be done by comparing two crystals - the one already existing before (born at  $(x_0, t_0)$ ) and denoted by  $\Theta_0^t$  and the (virtual) new-born crystal  $\Theta_1^t$  (see Figure 2). We show that the later born will always stay 'inside' the other one. Defining the *cone of influence* by

$$\mathcal{I}(x_0, t_0) := \{ (x, t) \mid x \in \Theta_0^t \},$$

we can express this statement mathematically in the following Lemma:

**Lemma 3.1.** *If  $(x_1, t_1) \in \mathcal{I}(x_0, t_0)$ , then  $\mathcal{I}(x_1, t_1) \subset \mathcal{I}(x_0, t_0)$ .*

*Proof.* Suppose  $\mathcal{I}(x_1, t_1) \not\subset \mathcal{I}(x_0, t_0)$ . Then there exist  $t \geq t_1$  and  $\tilde{t} > t$  such that

$$\begin{aligned} \Theta_1^t &\subset \Theta_0^t \\ \Theta_1^s &\not\subset \Theta_0^s, \forall s \in (t, \tilde{t}). \end{aligned}$$

For all points  $x \in \partial\Theta_0^t \cap \partial\Theta_1^t$ , the normal with respect to both crystals must have the same direction, because otherwise there would exist a point  $\tilde{x}$  in  $\Theta_1^t - \Theta_0^t$ . By investigating the growth line  $y_0$  from  $(x_0, t_0)$  to  $(x, t)$  and the growth line  $y_1$  from  $(x_1, t_1)$  to  $(x, t)$ , the equality of the normal vector implies

$$\begin{aligned} y_0(t) &= x = y_1(t) \\ \dot{y}_0(t) &= G(x, t)\mathbf{n} = \dot{y}_1(t) \end{aligned}$$

Since  $y_0$  and  $y_1$  satisfy the second-order ODE (1), the uniqueness of the Cauchy-problem (for sufficiently smooth  $G$ ) implies  $y_0(s) = y_1(s)$  for all  $s \geq t$ . Hence, the crystal born at  $(x_1, t_1)$  can never grow beyond the boundary of the crystal born at  $(x_0, t_0)$ , i.e.,

$$\Theta_1^s \subset \Theta_0^s, \forall s \geq t_1,$$

a contradiction. □

Lemma 3.1 can be applied to any situation, where the growth rate  $G(x, t)$  is a given field independent of the actual crystalline phase, e.g. in the case of a nonhomogenous material, where  $G = G(x)$ . In the case of a really non-isothermal situation, this is not true anymore, since  $G$  depends upon temperature and the temperature depends upon the crystalline phase. Especially, two growing nuclei cannot be compared as in Lemma 3.1, since both influence temperature and consequently, their growth is driven by different growth rates. In a situation like that, even the causal cone cannot be defined independent of the process anymore, because of the reasons

described above it always depends on the pattern of the crystalline phase via the temperature. Nevertheless, the results obtained by this generalized Avrami-Kolmogorov-Evans theory yield good approximations under typical crystallization conditions as we will see in the following section.

### 3.2 Model Equations in the Multi-dimensional Case

As we have seen in the previous section, the degree of crystallinity is given by

$$\begin{aligned}\xi(x, t) &= 1 - e^{-w(x, t)}, \\ w(x, t) &= \int_0^t \int_{\mathcal{E}(x, t, s)} \alpha(y, s) dy ds \\ &= \int_0^t \int_E \chi(x, t, y, s) \alpha(y, s) dy ds,\end{aligned}$$

where  $\chi$  is the indicator function of the  $s$ -section of the causal cone of  $(x, t)$ , more precisely

$$\chi(x, t, y, s) = I_{\mathcal{E}(x, t, s)}.$$

In the preceding paper [2] we have deduced the hyperbolic initial-boundary value problem

$$\begin{aligned}\left(\frac{1}{G}w_t\right)_t &= (Gw_x)_x + 2\alpha \quad \text{in } E \times \mathbf{R}^+, \\ w_t + Gw_n &= 0 \quad \text{on } \partial E \times \mathbf{R}^+, \\ w = w_t &= 0 \quad \text{in } E \times \{0\},\end{aligned}\tag{10}$$

in the case of  $E \subset \mathbf{R}^1$  by applying a method of characteristics upon  $\chi$ . In the following, we will deduce similar model equations in the multidimensional case, making use of Equations (6), (7).

Since the solution  $x(t, \gamma)$  of (6), (7) represents the surface on which the value 1 of the indicator function is propagated,  $\chi$  satisfies

$$\begin{aligned}\chi_t + G\langle \nabla \chi, \theta \rangle &= 0 \\ \langle \nabla \chi, \theta^\perp \rangle &= 0 \\ \langle \theta, \theta \rangle &= 1\end{aligned}$$

for  $t > s$ , with initial values

$$\begin{aligned}\chi(x, t, y, t) &= 0 \quad \text{for } x \neq y \\ \chi(x, t, x, s) &= 1 \quad \text{for } t > s.\end{aligned}$$

In the above equations,  $\theta = \theta(x, t, y, s)$  represents the outer normal of the causal cone with respect to  $x$ .

The same technique as applied to the growth of one nucleus yields

$$\begin{aligned}\chi_t &= G\chi^1 \\ \chi_t^1 &= \nabla_x \cdot (G\chi^2) + \psi_d \\ \chi_t^2 &= \nabla_x (G\chi^1)\end{aligned}$$

in  $\mathbf{R}^d$ , where  $\chi^1$  and  $\chi^2$  may again be interpreted as densities of the boundary of the causal cone and  $\psi_d(x, t)$  is the functional

$$\langle \psi_2(x, t), \phi \rangle := 2\pi \int_0^t \phi(x, s) ds.$$

for  $d = 2$ , respectively

$$\langle \psi_3(x, t), \phi \rangle := 4\pi \int_0^t G(x, s) \int_0^s \phi(x, \tau) d\tau ds.$$

for  $d = 3$ .

Now we may easily verify that  $w$  is a solution of the system

$$w_t = Gu \tag{11}$$

$$u_t = \nabla \cdot (Gv) + \langle \psi_d, \alpha \rangle \tag{12}$$

$$v_t = \nabla(Gu) \tag{13}$$

with homogenous initial values for  $u$ ,  $v$  and  $w$ .

In a similar way we may also derive the boundary condition

$$u(x, t) + \langle v(x, t), n(x, t) \rangle = 0, \quad \text{for } x \in \partial E.$$

(assuming that no boundary nucleation occurs), where  $\frac{\partial}{\partial n}$  denotes the normal derivative with respect to  $\partial E$ .

It turns out that System (11)-(13) can be transformed to the form of (10) if  $G > 0$ . We note that also the higher-dimensional model contains the well-known system of rate equations derived by Schneider et al. [16] for the space-homogeneous case.

## 4 Interaction with Heat Transfer

In an experimental situation, where heterogeneities are caused only by the heat transfer in the material, we may model growth and nucleation rates as certain temperature-dependent material functions (cf. [9])

$$\begin{aligned}G(x, t) &= \tilde{G}(T(x, t)), \\ \alpha(x, t) &= \frac{\partial}{\partial t} \tilde{N}(T(x, t)).\end{aligned}$$

Vice versa, the growing crystalline phase influences the heat conduction process in the material as follows

$$\begin{aligned}(\rho c T)_t &= \nabla \cdot (\kappa \nabla T) + (h I_{\Theta^t})_t && \text{in } E \times \mathbf{R}^+ \\ T_n &= \beta(T - T_{out}), && \text{on } \partial E \times \mathbf{R}^+\end{aligned}$$

where again the derivative of the indicator function  $I_{\Theta^t}$  has to be understood in a weak sense. Here  $\rho$  denotes the density,  $c$  the heat capacity,  $\kappa$  the heat conductivity,  $\beta$  the heat transfer coefficient and  $h$  the latent heat released at the moment of phase change.

The parameters in the heat equation may depend upon the phase, i.e., if  $\rho_1, c_1, \kappa_1$  and  $\beta_1$  denote the parameters of the crystallized material and  $\rho_2, c_2, \kappa_2$  and  $\beta_2$  the ones of the non-crystallized, we may write

$$\begin{aligned}\rho &= I_{\Theta^t} \rho_1 + (1 - I_{\Theta^t}) \rho_2 \\ c &= I_{\Theta^t} c_1 + (1 - I_{\Theta^t}) c_2 \\ \kappa &= I_{\Theta^t} \kappa_1 + (1 - I_{\Theta^t}) \kappa_2 \\ \beta &= I_{\Theta^t} \beta_1 + (1 - I_{\Theta^t}) \beta_2\end{aligned}\tag{14}$$

This heat transfer model is a random differential equation, since all parameters depend upon the random variable  $I_{\Theta^t}$ . A direct consequence is the stochasticity of temperature, whose evolution depends upon the geometry of the crystalline phase.

The typical scale of the heat transfer problem is given by

$$x_T = \sqrt{\frac{\kappa_0 t_0}{\rho_0 c_0}}\tag{15}$$

where  $t_0$  is the length of the considered time interval,  $\kappa_0$ ,  $\rho_0$  and  $c_0$  are typical scales for  $\kappa$ ,  $\rho$  and  $c$ . The typical scale for the growth of a nucleus is given by

$$x_G = G_0 t_0,\tag{16}$$

where  $G_0$  is a typical value for the growth rate  $G$ . In practical applications it turns out that  $x_T \gg x_G$ , which is due to the fact that crystal growth is very slow, whereas the heat conduction is rather fast. This means that there exist two significant scales in the problem, i.e.

- Microscale  $x_G$  for growth.
- Macroscale  $x_T$  for heat conduction.

It is a direct consequence that if one is interested only in local microscopic effects, temperature variations can be neglected, whereas for a pure macroscopic description the growth effects are not important (see Fig 3). The scale of real interest in polymer processing is a mesoscale between  $x_T$  and  $x_G$ , which is fine enough for morphological details without paying attention to each microscopic crystal. In the subsequent sections we will derive a hybrid model on such a mesoscale.

## 5 A Random PDE Model

A different approach to the computation of  $\xi$  by 'looking back' via the causal cone is to investigate the crystalline phase directly and take expected values later, using the so-called *method of characteristics* (cf.[18]). The aim is to write a differential equation for the indicator function of the nucleus, which grows at its boundary with growth rate  $G$ . Since the non-continuous indicator function cannot satisfy such an equation in a classical sense, characteristics are used.

### 5.1 The evolution of a single crystal

We first consider the crystal  $\Theta_j^t$  born at time  $t = T_j$  and point  $x = X_j$ , its indicator function will be denoted by  $f^j$ . The evolution of  $f^j$  is determined by the first-order PDE (cf.[2])

$$f_t^j + G\|\nabla f^j\| = 0, \quad (17)$$

for  $x \in E$ ,  $t > T_j$  with additional conditions

$$\begin{aligned} f^j(x, T_j) &= 0 & \text{for } x \neq X_j, \\ f^j(X_j, t) &= 1 & \text{for } t > T_j. \end{aligned}$$

We may also consider the same equation for  $t < T_j$  with the additional condition  $f^j(X_j, t) = 0$ .

Equation (17) may be written equivalently as

$$\begin{aligned} f_t^j + G\nabla f^j \cdot \mathbf{n} &= 0 \\ \nabla f^j \cdot \mathbf{n}^\perp &= 0 \\ \mathbf{n} \cdot \mathbf{n} &= 1, \end{aligned} \quad (18)$$

where  $\mathbf{n}$  is the normal vector of the growth front. As the normal vector multiplied by the growth rate is just  $\dot{x}$ , we have

$$\frac{df^j}{dt}(x(t, \gamma), t) = f_t^j + \nabla f^j \cdot \dot{x} = f_t^j + G\nabla f^j \cdot \mathbf{n} = 0,$$

i.e.,  $f^j$  is constant along the growth lines.

For any smooth function  $\phi = \phi(x)$  we have

$$\begin{aligned} \frac{\partial}{\partial t} \int_E f^j(x, t) \phi(x) dx &= \frac{\partial}{\partial t} \int_{\Theta_j^t} \phi(x) dx \\ &= \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \left[ \int_{\Theta_j^{t+\Delta t}} \phi(x) dx - \int_{\Theta_j^t} \phi(x) dx \right] \\ &= \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{\Theta_j^{t+\Delta t} - \Theta_j^t} \phi(x) dx \\ &= \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{\partial \Theta_j^t} \phi(x) d\sigma(x) G(x, t) \Delta t \\ &= \int_{\partial \Theta_j^t} G(x, t) \phi(x) d\sigma(x) \end{aligned}$$

If we consider the crystal  $\Theta_j^t$  as an open set, i.e.  $1 - f^j$  equals 1 on  $\partial\Theta_j^t$ , this yields

$$\frac{\partial}{\partial t} \int_E f^j(x, t) \phi(x) dx = \int_{\partial\Theta_j^t} (1 - f^j(x, t)) G(x, t) \phi(x) d\sigma(x).$$

Let us denote by  $u^j$  the density of the crystal surface, that is

$$u^j(x, t) dx = \nu^{d-1}(\partial\Theta_j^t \cap dx)$$

where  $\nu^{d-1}$  is the Lebesgue measure on  $\mathbb{R}^{d-1}$ . We have that

$$\begin{aligned} \langle u^j, \phi \rangle &= \int_{\mathbb{R}^d} u^j(x, t) \phi(x) dx \\ &= \int_{\partial\Theta_j^t} \phi(x) d\sigma(x), \end{aligned}$$

for any sufficiently smooth function  $\phi$ . We may write, in a weak sense,

$$f_t^j = (1 - f^j) G u^j. \quad (19)$$

Let the function  $v$  be the density of the surface direction, i.e.

$$v^j(x, t) dx = -\mathbf{n}(x, t) \nu^{d-1}(\partial\Theta_j^t \cap dx),$$

so that

$$\langle v^j, \phi \rangle = - \int_{\partial\Theta_j^t} \phi(x) \mathbf{n}(x, t) d\sigma(x).$$

Note that  $u^j$  and  $v^j$  satisfy the compatibility condition

$$v^j \cdot \mathbf{n} = -u^j.$$

From Eq.(18) and (19), we obtain

$$G \nabla f^j \cdot \mathbf{n} = -f_t^j = (1 - f^j) G u^j = (1 - f^j) G v^j \cdot \mathbf{n},$$

and we may conclude

$$\nabla f^j = (1 - f^j) v^j.$$

With the above definitions for  $u^j$  and  $v^j$ , we may write

$$f_t^j = (1 - f^j) G u^j, \quad (20)$$

$$\nabla f^j = (1 - f^j) v^j. \quad (21)$$

By deriving (20) with respect to the space variable and (21) with respect to time, we have

$$\begin{aligned}
\nabla(f_t^j) &= -\nabla f^j G u^j + (1-f^j)\nabla(G u^j) \\
&= -(1-f^j)v^j G u^j + (1-f^j)\nabla(G u^j) \\
&= (1-f^j)(\nabla(G u^j) - v^j G u^j), \\
(\nabla f^j)_t &= -f_t^j v^j + (1-f^j)v_t^j \\
&= -(1-f^j)G u^j v^j + (1-f^j)v_t^j \\
&= (1-f^j)(v_t^j - G u^j v^j).
\end{aligned}$$

For the compatibility condition,  $u^j$  and  $v^j$  must satisfy

$$v_t^j = \nabla(G u^j). \quad (22)$$

The time derivative of  $u^j$  can be calculated as

$$\begin{aligned}
\frac{\partial}{\partial t} \langle u^j, \phi \rangle &= \lim_{\Delta t \rightarrow 0} \left[ \int_{\partial \Theta_j^{t+\Delta t}} \phi(x) d\sigma(x) - \int_{\partial \Theta_j^t} \phi(x) d\sigma(x) \right] \\
&= \lim_{\Delta t \rightarrow 0} \int_{\partial \Theta_j^t} \left[ \phi(x + G \mathbf{n} \Delta t) - \phi(x) \right] d\sigma(x) \\
&= \lim_{\Delta t \rightarrow 0} \int_{\partial \Theta_j^t} \left[ \phi(x) + G \, dt \mathbf{n} \cdot \nabla \phi(x) - \phi(x) \right] d\sigma(x) \\
&= \int_{\partial \Theta_j^t} G(x, t) \mathbf{n}(x, t) \nabla \phi(x) \, d\sigma(x) \\
&= -\langle G v^j, \nabla \phi \rangle \\
&= \langle \nabla \cdot (G v^j), \phi \rangle,
\end{aligned}$$

for  $t > T_j$  which implies

$$u_t^j = \nabla \cdot (G v^j) \quad (23)$$

in a distributional sense.

In order to extend the equations to the whole time domain  $t > 0$  we examine the time derivatives at  $t = T_j$  using

$$\frac{\partial}{\partial t} \langle u^j, \phi \rangle|_{t=T_j} = \frac{\partial}{\partial t} \int_{\partial \Theta_j^t} \phi(x, t) \, d\sigma(x)|_{t=T_j}, \quad k = 0, 1, 2. \quad (24)$$

Since at time  $t = T_j$ , the grain  $\Theta_j^t$  reduces to the point  $X_j$ , we may expand the function  $\phi(x, t)$  in a neighborhood of  $(X_j, T_j)$ , thus obtaining

$$\begin{aligned}
\phi(x, t) &= \phi(X_j, T_j) + \phi_t(X_j, T_j)(t - T_j) + \nabla \phi(X_j, T_j) \cdot (x - X_j) + o(t - T_j) \\
&= \phi(X_j, T_j) + \phi_t(X_j, T_j)(t - T_j) \\
&\quad + \nabla \phi(X_j, T_j) \cdot G(X_j, T_j) \mathbf{n}(x, t)(t - T_j) + o(t - T_j).
\end{aligned}$$

By substituting in (24), we have

$$\frac{\partial}{\partial t} \langle u^j, \phi \rangle |_{t=T_j} = \frac{\partial}{\partial t} \left( \phi(X_j, T_j) |\partial \Theta_j^t| + \phi_t(X_j, T_j) (t - T_j) |\partial \Theta_j^t| + o((t - T_j)^d) \right) |_{t=T_j},$$

because  $|\partial \Theta_j^t| = \mathcal{O}((t - T_j)^{d-1})$  and, for the isotropy of  $\mathbf{n}$  around the nucleus,

$$\lim_{t \rightarrow T_j} \int_{\partial \Theta_j^t} \mathbf{n}(x, t) d\sigma(x) = 0.$$

In  $\mathbb{R}^1$  we have  $|\partial \Theta_j^t| = 2$  and consequently

$$\frac{\partial}{\partial t} \langle u^j, \phi \rangle |_{t=T_j} = 2\phi_t(X_j, T_j).$$

In  $\mathbb{R}^2$ ,  $|\partial \Theta_j^t| = 2\pi r(X_j, T_j; t) + o(t - T_j)$ , where

$$r(X_j, T_j; t) = \int_{T_j}^t G(X_j, s) ds$$

and thus

$$\frac{\partial}{\partial t} \langle u^j, \phi \rangle |_{t=T_j} = 2\pi G(X_j, T_j) \phi(X_j, T_j).$$

In  $\mathbb{R}^3$  we have  $|\partial \Theta_j^t| = 4\pi r(X_j, T_j; t)^2 + o((t - T_j)^2)$ , hence

$$\begin{aligned} \frac{\partial}{\partial t} \langle u^j, \phi \rangle &= \frac{\partial}{\partial t} \left( \phi(X_j, T_j) 4\pi r(X_j, T_j; t)^2 + o((t - T_j)^2) \right) \\ &= 4\pi \phi(X_j, T_j) r(X_j, T_j; t) \frac{\partial}{\partial t} \int_{T_j}^t G(X_j, s) ds + o(t - T_j) \\ &= 8\pi \phi(X_j, T_j) r(X_j, T_j; t) G(X_j, T_j) + o(t - T_j) \end{aligned}$$

and, since  $r(X_j, T_j; T_j) = 0$ ,

$$\frac{\partial}{\partial t} \langle u^j, \phi \rangle |_{t=T_j} = 0.$$

With the notation

$$\frac{\partial}{\partial t} \langle u^j, \phi \rangle = \langle G \hat{u}^j, \phi \rangle$$

where

$$\langle \hat{u}, \phi \rangle = 8\pi \phi(X_j, T_j) r(X_j, T_j; t)$$

and thus

$$\frac{\partial}{\partial t} \langle \hat{u}^j, \phi \rangle |_{t=T_j} = 8\pi G(X_j, T_j) \phi(X_j, T_j),$$

we obtain

$$\frac{\partial^2}{\partial t^2} \langle u^j, \phi \rangle |_{t=T_j} = G(X_j, T_j) \frac{\partial}{\partial t} \langle u^j, \phi \rangle |_{t=T_j} = 8\pi G(X_j, T_j)^2 \phi(X_j, T_j).$$

Similar reasoning yields that (22) is satisfied at  $t = T_j$ , without any point source, which is due to the isotropy of the additional factor  $n(x, t)$  at the point of birth of the nucleus.

Obviously (22) and (23) hold for  $0 < t < T_j$  with homogeneous initial values at  $t = 0$ , since both distributions are equal to zero in this region.

Hence, we have shown that in a distributional sense, in  $\mathbb{R}^d$   $d = 1, 2$ ,

$$\begin{cases} \begin{cases} u_t^j = \nabla \cdot (Gv^j) \\ v_t^j = \nabla(Gu^j) \end{cases} & t > T_j \\ \begin{cases} u_t^j = S_j^d \\ v^j = 0 \end{cases} & t = T_j \\ \begin{cases} u^j = 0 \\ v^j = 0 \end{cases} & t \leq T_j \end{cases} \quad (25)$$

where  $S_j^d$  is the generalized function defined by

$$\langle S_j^d, \phi \rangle = \frac{\partial}{\partial t} \langle u^j, \phi \rangle |_{t=T_j}.$$

In  $\mathbb{R}^3$ , (25) has to be replaced by

$$\begin{cases} \begin{cases} u_{tt}^j = \nabla \cdot (Gv^j)_t \\ v_t^j = \nabla(Gu^j) \end{cases} & t > T_j \\ \begin{cases} u_{tt}^j = GS_j^3 \\ u_t^j = 0 \\ v^j = 0 \end{cases} & t = T_j \\ \begin{cases} u^j = 0 \\ v^j = 0 \end{cases} & t \leq T_j \end{cases} \quad (26)$$

where  $S_j^3$  is the generalized function defined by

$$\langle S_j^3, \phi \rangle = \frac{\partial}{\partial t} \langle \hat{u}^j, \phi \rangle |_{t=T_j}.$$

## 5.2 The evolution of the union of the crystals

Based on the equations for  $f^j$  we may deduce a system for the indicator function  $f$  of the whole crystalline phase in order to investigate the crystallization process directly and take expected values later.

Let  $f(x, t) := I_{\Theta^t}(x)$ ,  $f^j(x, t) := I_{\Theta_{T_j}^t}(x)$ , then

$$1 - f(x, t) = \prod_{T_j < t} (1 - f^j(x, t)),$$

since  $f$  equals 0 if and only if all  $f^j$  are 0.

Defining the sum of densities

$$u = \sum_{T_j < t} u^j$$

$$v = \sum_{T_j < t} v^j$$

we may write

$$\begin{aligned} f_t &= \sum_{T_j < t} f_t^j \prod_{k \neq j} (1 - f^k) \\ &= \sum_{T_j < t} (1 - f^j) G u^j \prod_{k \neq j} (1 - f^k) \\ &= G \sum_{T_j < t} u^j \prod_{T_k < t} (1 - f^k) = G(1 - f)u \end{aligned}$$

and, similarly,

$$\nabla f = (1 - f)v.$$

As an immediate consequence of the fact that  $u$  and  $v$  are linear superpositions of the functions  $u^j$  and  $v^j$ , respectively, the quantities  $u$  and  $v$  can be computed directly by solving, for  $E \subset \mathbb{R}^d$ ,  $d = 1, 2$ ,

$$\begin{aligned} u_t &= \nabla \cdot (Gv) + \sum_{T_j = t} S_j^d && \text{in } E \times \mathbb{R}^+ \\ v_t &= \nabla(Gu) \\ u + \langle v, n \rangle &= 0 && \text{on } \partial E \times \mathbb{R}^+ \\ u &= 0 && \text{in } E \times \{0\}. \\ v &= 0 \end{aligned} \tag{27}$$

For  $E \subset \mathbb{R}^3$ , Equations (27) become

$$\begin{aligned} u_{tt} &= \nabla \cdot (G_t v) + \nabla \cdot (G v_t) + \sum_{T_j = t} G S_j^d && \text{in } E \times \mathbb{R}^+ \\ v_t &= \nabla(Gu) \end{aligned} \tag{28}$$

The distributions  $u$  and  $v$  are of special interest by themselves, since they provide additional information about the morphology of the material, e.g. the total surface of nuclei in a domain  $B$  in the absence of impingement is given by

$$\int_B u \, dx := \langle u, I_B \rangle = \sum_{T_j < t} \int_{\partial \Theta_j^t} I_B(x) d\sigma(x) = \sum_{T_j < t} \nu^{d-1}(\partial \Theta_j^t \cap B).$$

The expected value of  $u$  is just the *mean free metric density*, which has been introduced in [6] as one of the most important measures for the morphology of the final material.

### 5.3 Averaging

By coupling with temperature we obtain, in  $\mathbb{R}^1$  and  $\mathbb{R}^2$  the system

$$\begin{cases} \begin{cases} f_t = \tilde{G}(T)(1-f)u \\ v_t = \nabla(\tilde{G}(T)u) \\ u_t = \nabla \cdot (\tilde{G}(T)v) + \sum_{T_j=t} S_j^d \\ (\rho c T)_t = \nabla \cdot (\kappa \nabla T) + (hf)_t \end{cases} & \text{in } E \times \mathbb{R}_+ \\ \begin{cases} u + \langle v, n \rangle = 0 \\ T_n = \beta(T - T_{out}) \end{cases} & \text{on } \partial E \times \mathbb{R}_+ \\ \begin{cases} f = 0 \\ u = 0 \\ v = 0 \\ T = T^0 \end{cases} & \text{in } E \times \{0\}, \end{cases} \quad (29)$$

whose stochasticity is caused by the sources  $S_j^d$  only (we obtain an analogous system in  $\mathbb{R}^3$ , coupling (28) with the temperature).

At this point, by the remarks made in Sec.4, we may consider a multiple scale approach, in order to obtain a deterministic system from (29).

At the level of the mesoscale, it makes sense to consider a region  $B$  small enough that the space variation of temperature inside  $B$  may be denied and such that there is a sufficiently high number of “small” crystals in  $B$ , so that a law of large numbers allows the approximation

$$\sum_{X_j \in B} \sum_{T_j \leq t} S_j^d \approx E \left[ \sum_{X_j \in B} \sum_{T_j \leq t} S_j^d \right], \quad (30)$$

i.e. we may approximate the source term by its expected value, which is the mean rate of surface production.

In Equation (29), at each time  $t$ , there is the contribution of the nuclei born exactly at that time. But at every time  $t$ , the probability of birth of a nucleus is zero, so that for a rigorous interpretation of (29), we need to use an integral version of it and introduce the approximation in

(30):

$$\begin{aligned}
\int_B \phi(x, t) u(x, t) dx &= \int_B \phi(x, 0) u(x, 0) dx \\
&+ \int_0^t \int_B \nabla \cdot (\tilde{G}(T) v(x, s)) \phi(x, s) dx ds + \sum_{T_j \leq t} \sum_{X_j \in B} \langle S_j^d, \phi \rangle \\
&\approx \int_B \phi(x, 0) u(x, 0) dx \\
&+ \int_0^t \int_B \nabla \cdot (\tilde{G}(T) v(x, s)) \phi(x, s) dx ds + E \left[ \sum_{T_j \leq t} \sum_{X_j \in B} \langle S_j^d, \phi \rangle \right] \\
&\approx \int_B \phi(x, 0) u(x, 0) dx \\
&+ \int_0^t \int_B \nabla \cdot (\tilde{G}(T) v(x, s)) \phi(x, s) dx ds + \int_0^t \int_B \mathcal{F}_d[\tilde{G}, \tilde{\alpha}, T(x, s)] dx ds. \tag{31}
\end{aligned}$$

More precisely, for a test function  $\phi(x, t)$  smooth enough and s.t.  $\phi(x, t) = 0$  on  $\partial B$ ,

$$\begin{aligned}
\sum_{X_j \in B} \sum_{T_j \leq t} \langle S_j^1, \phi \rangle &\approx E \left[ \sum_{X_j \in B} \sum_{T_j \leq t} 2\phi_t(X_j, T_j) \right] \\
&= \int_0^t \int_B 2\alpha(x, s) \phi_t(x, s) dx ds \\
&= -2 \int_0^t \int_B \alpha_t(x, s) \phi(x, s) dx ds \\
\sum_{X_j \in B} \sum_{T_j \leq t} \langle S_j^2, \phi \rangle &\approx E \left[ \sum_{X_j \in B} \sum_{T_j \leq t} 2\pi G(X_j, T_j) \phi(X_j, T_j) \right] \\
&= 2\pi \int_0^t \int_B \alpha(x, s) G(x, s) \phi(x, s) dx dt \\
\sum_{X_j \in B} \sum_{T_j \leq t} G(X_j, T_j) \langle S_j^3, \phi \rangle &\approx E \left[ \sum_{X_j \in B} \sum_{T_j \leq t} 8\pi G^2(X_j, T_j) \phi(X_j, T_j) \right] \\
&= 8\pi \int_0^t \int_B \alpha(x, s) G^2(x, s) \phi(x, s) dx ds
\end{aligned}$$

So we have that the source terms in (31) are defined by

$$\begin{aligned}
\mathcal{F}_1[\tilde{G}, \tilde{\alpha}, T](x, t) &:= -2\tilde{\alpha}(T(x, t))_t \\
\mathcal{F}_2[\tilde{G}, \tilde{\alpha}, T](x, t) &:= 2\pi\tilde{G}(T(x, t))\tilde{\alpha}(T(x, t)) \\
\mathcal{F}_3[\tilde{G}, \tilde{\alpha}, T](x, t) &:= 8\pi\tilde{G}^2(T(x, t))\tilde{\alpha}(T(x, t)).
\end{aligned}$$

In (31), all randomness is eliminated and we obtain a nonlinear initial-boundary value problem

for a system of one parabolic and one hyperbolic equation:

$$\frac{\partial \xi}{\partial t} = \tilde{G}(\tilde{T})(1 - \xi)\tilde{u} \quad (32)$$

$$\frac{\partial \tilde{u}}{\partial t} = \nabla \cdot (\tilde{G}(\tilde{T})\tilde{v}) + \mathcal{F}_d[\tilde{G}, \tilde{\alpha}, \tilde{T}] \quad (33)$$

$$\frac{\partial \tilde{v}}{\partial t} = \nabla(\tilde{G}(\tilde{T})\tilde{u}) \quad (34)$$

$$\frac{\partial}{\partial t}(c\rho\tilde{T}) = \nabla \cdot (k\nabla\tilde{T}) + \frac{\partial}{\partial t}(h\xi), \quad (35)$$

in  $E \times \mathbb{R}^+$ ,  $E \in \mathbb{R}^d$ ,  $d = 1, 2$ , supplemented by the boundary conditions

$$\tilde{u} + \langle \tilde{v}, n \rangle = 0, \quad (36)$$

$$\frac{\partial \tilde{T}}{\partial n} = \beta(\tilde{T} - T_{out}), \quad (37)$$

on  $\partial E \times \mathbb{R}^+$  and initial values given by

$$\xi = 0 \quad (38)$$

$$\tilde{u} = 0 \quad (39)$$

$$\tilde{v} = 0 \quad (40)$$

$$T = T^0 \quad (41)$$

in  $E \times \{0\}$ , usually with  $T^0(x) \geq T_m$  for all  $x \in E$ . In order to express the essential difference between the (generalized) functions  $f$ ,  $u$ ,  $v$  and  $T$  and their equivalents in the averaged equations we now write  $\xi$ ,  $\tilde{u}$ ,  $\tilde{v}$  and  $\tilde{T}$ .

In  $\mathbb{R}^3$ , introducing the variable  $\tilde{w} = \frac{\partial \tilde{u}}{\partial t}$ , the system becomes

$$\frac{\partial \xi}{\partial t} = \tilde{G}(\tilde{T})(1 - \xi)\tilde{u}$$

$$\frac{\partial \tilde{u}}{\partial t} = \tilde{w}$$

$$\frac{\partial \tilde{w}}{\partial t} = \nabla \cdot \left( \frac{\partial}{\partial t} \tilde{G}(\tilde{T})\tilde{v} \right) + \nabla \cdot \left( \tilde{G}(\tilde{T}) \frac{\partial}{\partial t} \tilde{v} \right) + \mathcal{F}_3[\tilde{G}, \tilde{\alpha}, \tilde{T}]$$

$$\frac{\partial \tilde{v}}{\partial t} = \nabla(\tilde{G}(\tilde{T})\tilde{u})$$

$$\frac{\partial}{\partial t}(c\rho\tilde{T}) = \nabla \cdot (k\nabla\tilde{T}) + \frac{\partial}{\partial t}(h\xi).$$

The parameters  $c$ ,  $\rho$ ,  $k$ ,  $h$  are consequently averaged by substituting  $\xi$  to  $I_{\Theta}$  in (14).

For a rigorous derivation of (33) as a limit of a suitable stochastic counterpart, the reader is referred to [7].

## 6 Conclusions

We have seen that the Avrami-Kolmogorov-Evans theory is applicable to any crystallization process, where the growth and nucleation rates are arbitrary functions of time and temperature, but

independent of the actual crystalline phase. If the rates depend upon the actual pattern of the crystalline phase by some reason, e.g. because of interaction with temperature, the theory fails, since the causal cone cannot be defined anymore as a deterministic region. Nevertheless, the results obtained that way yield a good approximation under typical conditions, which is confirmed by the alternative direct approach presented in Section 5, which clearly shows the averaging included in the model using the different scales of the process. In addition, the direct approach seems to be more flexible for other situations, like age-dependent growth, too.

We note that the averaging procedure presented in this paper was only qualitative, a quantitative estimation of the error made by using the averaged model seems to be an important task for future work. Together with this estimate, one might also examine other possible simplifications of the model, since perturbations of the same order as the model error can obviously be disregarded, too. Especially the terms including spatial derivatives with the 'small' factor  $G$  might possibly be disregarded.

Another important task for future investigations will be the identification of model parameters from temperature measurements and phase observations in (32)-(41). In the past, this problem had been treated only in the case of one-dimensional crystallization (cf. [3])

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## Figure captions

**Figure 1:** Crystal shapes in a typical temperature field.

**Figure 2:** Two hitting crystals in the situation of Lemma 3.1.

**Figure 3:** Schematic representation of the scales in polymer crystallization.