

Moving bands and moving boundaries in an hybrid model for the crystallization of polymers

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Abstract. Crystallization is a mechanism of phase change in polymeric materials; it consists of at least two processes, a nucleation (birth) process describing the time and location of spots in the material where crystals start to grow, and a growth process of the nucleated crystals.

Both processes are coupled to temperature, and viceversa the temperature field is coupled with the crystallization process due to the production of latent heat.

All processes described above are of a random nature since the birth process and the consequent geometry of the crystalline phase are random. However, under typical industrial conditions (many and small crystals), a multiple scale assumption can be made so that a deterministic approximation (homogenization) for the spatial density of the crystalline phase at the (macro)scale of the temperature field is possible.

Thus, at the macroscale, the whole crystallization process may be modelled as a reaction-diffusion system in which a deterministic ODE for the crystalline density is coupled with a deterministic PDE for the temperature field via the kinetic parameters of birth and growth on one hand and the latent heat on the other hand.

Numerical simulations of this reaction-diffusion system show that the solution exhibits an advancing moving band of crystallization in the mass distribution, accompanied by a moving boundary in the temperature field, both advancing with a decreasing velocity.

1. Introduction

Crystallization is a mechanism of phase change in polymeric materials; as for various similar processes, it consists of at least two processes, a nucleation (birth) process describing the time and location of spots in the material where crystals start to grow, and a growth process of the nucleated crystals.

Both processes are coupled to temperature, since the kinetic parameters of birth and of growth in general depend significantly upon the local temperature field, and viceversa the temperature field is coupled with the crystallization process due to the production of latent heat, and the possible dependence of the parameters of the heat conduction upon the phase (liquid or solid) [1].

Growth processes may be very complicated but in the following the restriction to the case of spherulitic growth is made, which is also a good assumption for the crystallization of relaxed polymer melts.

All processes described above are of a random nature since the birth process and consequent geometry of the crystalline phase are random. However, under typical industrial conditions, a multiple scale assumption can be made due to the fact that at the typical spatial scale of the temperature field (macroscale), many and small crystals are present, thus allowing a deterministic approximation (homogenization) at the macroscale for the spatial density of the crystalline phase and consequently of the temperature field. This approach has been carried out in a rigorous way in [7] via suitable “laws of large numbers”.

Thus, at the macroscale, the whole crystallization process may be modelled as a reaction-diffusion system in which a deterministic ODE for the crystalline density is coupled with a deterministic PDE for the temperature field via the kinetic parameters of birth and growth on one hand and the latent heat on the other hand. In particular, we have introduced a critical temperature above which no nucleation and no growth can take place. Also, we have taken into account the possibility that the rate functions may present a jump at the critical temperature. Numerical simulations of this reaction-diffusion system show that the solution exhibits an advancing moving band of crystallization in the mass distribution, accompanied by a moving boundary in the temperature field, both advancing with a decreasing velocity. The fact that the speed is not constant, that is, that two different space segments of same length have different times of crystallization, is a relevant aspect for the industrial process, and of great interest from the mathematical point of view.

On the other hand if we wish to obtain geometric information about the crystallization process such as the evolution equations for interface densities, we may couple the averaged deterministic temperature field with the stochastic birth-and-growth process (hybrid model) (see [14] and Sec.4).

2. A rigorous geometric approach

In this section we describe the crystallization process in a given deterministic field of temperature, neglecting at the moment the influence of the crystallization process on temperature, that we shall discuss later.

Crystallization is a stochastic process in time and space due to the combination of birth (nucleation) and growth of crystals. The first one is modelled as a marked point process, and the whole process is described by a dynamic Boolean model. The nucleation process is modelled as a stochastic spatially marked point process N on an underlying probability space (Ω, \mathcal{A}, P) , with marks in the physical space E , a compact subset of \mathbb{R}^d , $d = 1, 2, 3$ (we shall denote by $\mathcal{B}_{\mathbb{R}_+}$, resp. \mathcal{E} , the σ -algebra of Borel sets on \mathbb{R}_+ , resp. on E). The marked point process (MPP) N is a random measure given by $N = \sum_{n=1}^{\infty} \epsilon_{T_n, X_n}$ where T_n is an \mathbb{R}_+ -valued random

variable representing the time of birth of the n -th nucleus; X_n is an E -valued random variable representing the spatial location of the nucleus born at time T_n ; $\epsilon_{t,x}$ is the Dirac measure on $\mathcal{B}_{\mathbb{R}_+} \times \mathcal{E}$. The crystalline phase at time $t > 0$ is given by a random set $\Theta^t = \bigcup_{T_j \leq t} \Theta_j^t$, (see [1], Sec.5.1) which is the union of all crystals

born at times T_j and locations X_j and freely grown up to time t . The integer valued random variable $N([0, t] \times B)$ counts the (random) number of nucleation events occurred in the time-space region $[0, t] \times B \in \mathcal{B}_{\mathbb{R}_+} \times \mathcal{E}$. We assume that the infinitesimal probability of birth of a new crystal during the time interval $[t, t + dt]$, in the free spatial interval $[x, x + dx] \subset E$, is given by (see also [14])

$$\nu_0(dt \times dx) = \alpha(x, t) dx dt.$$

The (*degree of*) *crystallinity*, $\xi(x, t)$, at location $x \in E$ and time $t > 0$ is the probability that, at time t , x is covered (or “captured”) by some crystal, i.e.

$$\xi(x, t) := P(x \in \Theta^t) = E[I_{\Theta^t}(x)].$$

Complementary to the degree of crystallinity (or probability of capture) $\xi(x, t)$ is the *survival function* or *porosity* of the point x at time t , which denotes the probability $p_x(t)$ that the point x is not yet crystallized at time t , i.e., $p_x(t) = P(x \notin \Theta^t) = 1 - \xi(x, t)$. Correspondingly we may define the *hazard function* $h(x, t)$ as the rate of capture, i.e., the rate of the capture probability,

$$h(x, t) = \lim_{\Delta t \rightarrow 0} \frac{P(x \in (\Theta^{t+\Delta t} \setminus \Theta^t))}{\Delta t}.$$

We can see [1] that

$$\frac{\partial}{\partial t} \xi(x, t) = (1 - \xi(x, t)) h(x, t)$$

Under the assumption of growth along the normal to the external surface due to a given field of growth rates $G(x, t)$, and assumptions of sufficient regularity of the field of birth rates $\alpha(x, t)$, it can be shown [5] that for almost any $x \in E$ and any $t \in \mathbb{R}_+$

$$h(x, t) = G(x, t) S_{ex}(x, t) \tag{1}$$

where S_{ex} is the mean value of the extended surface of the crystals, defined as follows in \mathbb{R}^d (λ^d denotes the usual Lebesgue measure).

$$S_{ex}(x, t) = \lim_{r \downarrow 0} E \left[\sum_{T_j < t} \frac{\lambda^{d-1}(\partial \Theta_j^t \cap B_r(x))}{\lambda^d(B_r(x))} \right].$$

Clearly $S_{ex}(x, t)$ represents the expected value of the spatial density of the sum of the surfaces of the individual crystals which are born and develop independently of each other. From the above considerations, we have in this case

$$\frac{\partial}{\partial t} \xi(x, t) = G(x, t) S_{ex}(x, t) (1 - \xi(x, t)).$$

This formula may be seen as an extension of the Kolmogorov-Avrami-Evans formula to the spatially heterogeneous case.

In order to obtain an explicit evolution equation for $\xi(x, t)$, we need to couple the previous one with an evolution equation for $S_{ex}(x, t)$. This has been done in [4] as follows.

In \mathbb{R}^d we introduce first the (stochastic) analogue $u(x, t)$ of $S_{ex}(x, t)$ such that for any $B \in \mathcal{B}_{\mathbb{R}^d}$, we have

$$\int_B u(x, t) \lambda^d(dx) = \sum_{T_j < t} \lambda^{d-1}(\partial\Theta_j^t \cap B).$$

In \mathbb{R}^2 , with given fields $\alpha(x, y)$ and $G(x, y)$, we have the following system for u

$$\left\{ \begin{array}{ll} \frac{\partial u}{\partial t} = \operatorname{div}(Gv) + \sum_{T_j=t} S_j^2 & \text{in } E \times \mathbb{R}_+ \\ \frac{\partial v}{\partial t} = \nabla(Gu) & \text{in } E \times \mathbb{R}_+ \\ u = 0 & \text{in } E \times \{0\} \\ v = 0 & \text{in } E \times \{0\} \\ u + v \cdot \mathbf{n} = 0 & \text{on } \partial E \times \mathbb{R}_+, \end{array} \right. \quad (2)$$

where the only source of stochasticity is due to nucleation $\sum_{T_j=t} S_j^2$; S_j^2 is the generalized function that describes the stochastic event of birth of the j -th crystal in \mathbb{R}^2 (system (2) has to be understood in a weak sense).

Since the system is linear and

$$S_{ex}(x, t) := E[u(x, t)],$$

we can obtain the deterministic equations

$$\left\{ \begin{array}{l} \frac{\partial S_{ex}}{\partial t} = \operatorname{div}(GE[v]) + E\left[\sum_{T_j=t} S_j^2\right] \\ \frac{\partial E[v]}{\partial t} = \nabla(GS_{ex}) \end{array} \right. \quad (3)$$

subject to the corresponding boundary and initial conditions. In \mathbb{R}^2 (see [4])

$$E\left[\sum_{T_j=t} S_j^2\right] = 2\pi G(x, t) \int_0^t \alpha(x, s) ds.$$

Once available the hazard function and the growth rate we may obtain further information about geometric measures regarding the crystallization process, such as the volume densities of interfaces of crystals at all Hausdorff dimensions (see [14] and [6]).

3. Coupling with temperature

In an experimental situation where spatial heterogeneities are caused only by the heat transfer in the material, we may assume that growth and nucleation rates are determined as material functions of the temperature [9].

$$G(x, t) = \tilde{G}(T(x, t)), \quad \alpha(x, t) = \tilde{\alpha}(T(x, t)). \quad (4)$$

Viceversa, the increase of the crystalline phase influences the heat transfer process in the material because of the release of latent heat, i.e., the temperature T is determined by the heat transfer model

$$\frac{\partial}{\partial t}(\rho c T) = \operatorname{div}(\kappa \nabla T) + \frac{\partial}{\partial t}(h \rho I_{\Theta^t}), \quad \text{in } \mathbb{R}^+ \times E, \quad (5)$$

$$\frac{\partial T}{\partial n} = \beta(T - T_{out}), \quad \text{on } \mathbb{R}^+ \times \partial E, \quad (6)$$

where $\frac{\partial}{\partial n}$ denotes the (outer) normal derivative on ∂E .

Here $\frac{\partial}{\partial t}(I_{\Theta^t})$ denotes the (distributional) time derivative of the indicator function I_{Θ^t} of the crystalline phase at time t , noting that Equation (5) has to be understood in the sense of distributional derivatives. The parameter ρ denotes the density, c the heat capacity, κ the heat conductivity, β the heat transfer coefficient and h the latent heat due to the phase change.

The parameters in the heat equation in general may depend upon the phase.

Thus the heat transfer model is now a random partial differential equation, since all parameters and the latent heat depend upon the random variable I_{Θ^t} . A direct consequence is the stochasticity of the temperature field, whose evolution influences (via (4)) the crystallization process itself (see also [3]).

Under these circumstances System (2) is *doubly* stochastic, and, as much nonlinear with respect to the operator E (expected value). In particular we notice that

$$E[\operatorname{div}(Gv)] \neq \operatorname{div}(E[G]E[v])$$

since now $G(T(x, t))$ is a stochastic quantity itself.

To overcome this complication we may take into account the fact that under typical industrial conditions (many and small crystals) we face a double scale process, so that one may approximate the stochastic model presented above in two ways. If we wish to obtain geometric information about the crystallization process such as the evolution equations for interface densities, we approximate the stochastic temperature field with an averaged deterministic one so to go back to the approach described in Section 2 (Hybrid model); if we are just interested in the evolution of the crystallinity (volume density of the crystal phase) then we may approximate the stochastic system with a fully deterministic one, as done in [7] by using an interacting particle system coupled with the temperature field, and proceed via suitable “laws of large numbers”.

4. The deterministic reaction-diffusion model

In the deterministic model the geometry is lost. We can make use of this fact assuming that a symmetry exists in the y -direction so that the model can be studied in the one-dimensional case. For completeness, we reproduce here the model obtained in [1]. It consists of the following equations for the crystallinity $y(x, t)$ and the temperature $T(x, t)$, for $x \in [0, L]$ and $t > 0$,

$$\frac{\partial y}{\partial t} = \beta(y) b_G(T) + v_0 \kappa(y) b_N(T) \quad (7)$$

$$\frac{\partial T}{\partial t} = \sigma \frac{\partial^2 T}{\partial x^2} + a_G \beta(y) b_G(T), \quad (8)$$

and of the initial and boundary conditions

$$y(x, 0) = y_{\text{ini}}(x), \quad x \in [0, L], \quad (9)$$

$$T(x, 0) = T_{\text{ini}}(x), \quad x \in [0, L], \quad (10)$$

$$T(0, t) = T_{\text{app}} \quad \forall t \geq 0, \quad (11)$$

$$\frac{\partial T(L, t)}{\partial x} = 0 \quad \forall t \geq 0, \quad (12)$$

where $\kappa(y)$ and $\beta(y)$ reproduce the features of crystallization phenomena, respectively, the start of the nucleation, and the aggregation and saturation of nuclei (see [7]):

$$\beta(y) = \begin{cases} y(1-y) & \text{in } [0, 1] \\ 0 & \text{outside} \end{cases}, \quad \kappa(y) = \begin{cases} (1-y)^2 & \text{in } [0, 1] \\ 0 & \text{outside} \end{cases}. \quad (13)$$

The constants σ , v_0 and a_G are the diffusion coefficient, the initial mass and the non-isothermal factor respectively. The functions $b_N(T)$ and $b_G(T)$ are the nucleation and growth rates respectively for a temperature T ; they are typically given by exponential functions with a negative exponent:

$$b_N(T) = N_0 e^{-\beta_N(T-T_{\text{ref}})}, \quad b_G(T) = G_0 e^{-\beta_G(T-T_{\text{ref}})}, \quad (14)$$

where N and G are the nucleation and growth factors, β_N and β_G the nucleation and growth exponents, and T_{ref} is a temperature of reference (usually $T_{\text{ref}} = 0$). They have been obtained via statistical regression analysis in [7] and Ref. 6 therein.

It has been shown in [10] that a threshold temperature of freezing T_f must be introduced, above which no nucleation and no growth can take place: $b_N(T \geq T_f) = b_G(T \geq T_f) = 0$. The reason is that without this threshold, the full crystallization of the sample would be only a matter of time for every applied temperature, something that may be not realistic. The introduction of T_f can be done simply by truncating the exponentials in (14), so that the rate functions will be discontinuous functions of T , or by modifying (14) to make the exponentials to decay continuously to $(T_f, 0)$. At our understanding, there is no experimental basis to decide which option is the most realistic one. The second option can be preferred because of the continuity, but Nature is sometimes not continuous, and the discontinuous option is in fact the general case (the other one being a particular case

of discontinuity of size 0), and it is mathematically more interesting, the casuistry being (not surprisingly) more rich.

For simplicity, we can assume that both rate functions can be reduced to a general rate function $\theta(T)$ such that $b_N(T) = N_0 \theta(T)$ and $b_G(T) = G_0 \theta(T)$, where

$$\theta(T) = \frac{1}{1 - a_0 e^{-T_f/10}} \begin{cases} e^{-\beta T} - a_0 e^{-\beta T_f/10} & \text{if } T < T_f \\ 0 & \text{if } T \geq T_f \end{cases}, \quad (15)$$

where a_0 is a measure of the discontinuity of θ at $T = T_f$.

From the mathematical point of view, this model defines a Free Boundary Problem (FBP) for the temperature field. Let us illustrate this by means of a simple model of heat diffusion. Let $L = \pi/2$ and $u(x, t)$ be the solution of

$$u_t - u_{xx} = 0, \quad (16)$$

$$u(x, 0) = \sin x, \quad (17)$$

$$u(0, t) = 0, \quad (18)$$

$$u_x(L, t) = 0. \quad (19)$$

In this problem it is not difficult to establish the existence, the uniqueness and the monotonicity of the solution. In fact, u is given by $u(x, t) = e^{-t} \sin x$. Then, for a given value $a \in (0, 1)$ and for each $t \in [0, \ln \frac{1}{a}]$, there exists a unique abscissa $x_b(t) \in [0, L]$ such that $u(x_b(t), t) = a$:

$$x_b(t) = \arcsin(ae^t). \quad (20)$$

At a given instant of time, $x_b(t)$ determines a boundary in the interval $[0, L]$, in the sense that it separates $[0, L]$ in two intervals with some qualitative difference, namely, the sign of $u - a$. Eq. (20) gives the time evolution of this boundary value. In this case, x_b evolves with an always positive and increasing velocity, and it reaches the end of the interval at $t = \ln \frac{1}{a}$. See Fig. 1.



FIGURE 1. Left: Solution $u(x, t)$ of the heat equation at four instants of time. At height $a = 0.3$ the boundary point $x_b(t)$ moves with an increasing velocity and arrives to $x = \frac{\pi}{2}$ at $t \approx 1.2$. Right: time evolution of $x_b(t)$.

In a similar way, a boundary value $x_b(t)$ is expected to be found in the polymer crystallization temperature field. Our ideal resolution of the polymer problem is to provide the same description than in the simple heat diffusion problem. Nevertheless, for such a problem it is more complicated to obtain analytical expressions or even estimates of the velocity and the arrival time.

A first attempt in this direction has been recently presented in [10], where Eqs. (7) and (8) have been solved numerically with the conditions (9)–(12) and the parameter values shown in Table 1.

TABLE 1. Typical values and units of the parameters.

Symbol	Physical meaning	Typical value	Units
T_{app}	applied temperature	0–100	°C
σ	diffusion coefficient	0.01	$\text{m}^2 \text{s}^{-1}$
T_{ini}	initial temperature	100	°C
y_{ini}	initial crystallinity	0	–
T_f	nucleation temperature	40	°C
T_G	growth temperature	40	°C
T_{ref}	reference temperature	0	°C
N_0	nucleation factor	1000	s^{-1}
G_0	growth factor	0.5	s^{-1}
β_N	nucleation exponent	0.1	$(\text{°C})^{-1}$
β_G	growth exponent	0.1	$(\text{°C})^{-1}$
v_0	initial mass	0.01	–
a_G	non-isothermal factor	2500	°C
L	length of the sample	10^{-3}	m

The result is that the temperature field exhibits an advancing boundary point at height T_f approximately. This moving boundary is accompanied by an advancing front of crystallization in the mass distribution. Assuming that $T(x, t)$ is a monotone increasing function of x at every time t , as in the simple heat diffusion problem, $x_b(t)$ can be defined as the unique value such that

$$T(x_b(t), t) = T_f.$$

We can also define two abscissas to describe the mass front,

$$x_\alpha(t) = \max_t \{x / y(x, t) = 1\} \quad (21)$$

$$x_\omega(t) = \min_t \{x / y(x, t) = 0\}, \quad (22)$$

in order to characterize the solution in terms of the time evolution of these three parameters.

It appears now clearly that a Free Boundary exists in the temperature field, in the sense that $x_b(t)$ divides the interval $[0, L]$ in two parts, depending on the degree of crystallization: at time t , the part $x < x_b(t)$ is almost fully crystallized ($y = 1$), whereas the part $x > x_b(t)$ is almost empty of crystals ($y = 0$).

The following Free Boundary Problem can be formulated:

The free boundary $x_b(t)$ is a time-dependent parameter which divides $[0, L]$ in two intervals $I_1 = [0, x_b]$ and $I_2 = [x_b, L]$. Inside each interval, the temperature

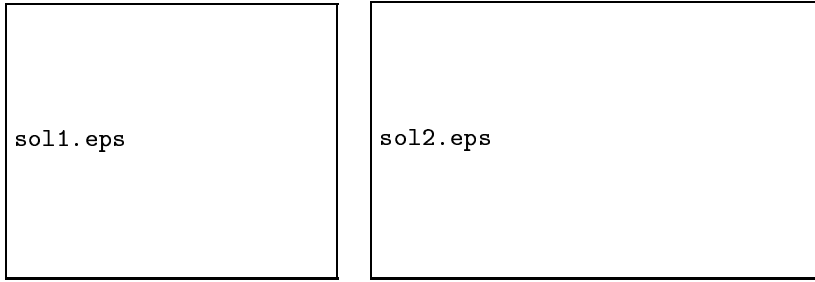


FIGURE 2. Left: Time evolution of the three coordinates which characterize the solution: the moving boundary $x_b(t)$ of the temperature field and the mass band $(x_\alpha(t), x_\beta(t))$. The velocity is slightly decreasing. Right: Crystallization time for two strategies of cooling in a slightly different case ($\sigma = 0.002$, $T_f = 70$, $N_0 = 20$ and $G_0 = 5$): cooling only at one side of the sample (solid line), and at both sides (dot-dashed line).

$T(x, t)$ solves the heat equation $T_t = \sigma T_{xx}$ with initial condition (10) and boundary conditions (11) and (12). The degree of crystallinity is such that $y = 1$ in I_1 and $y = 0$ in I_2 , and $x_b(t)$ describes the crystallization process depicted in Fig. 2.

Still needed are an equation for the evolution of $x_b(t)$ and the boundary conditions for $T(x, t)$ at $x_b^+(t)$ and $x_b^-(t)$. The difficulty for completing the formulation lies in that the regions where $y = 1$ and $y = 0$ are in fact separated by a narrow band whose width may not allow us to reduce the mass front to a point. It has been shown numerically that the mass front may be considered more a band than a layer [10], and an asymptotic argument for sufficiently large samples has recently established that what happens in the interior of the band can not be neglected [11].

Fig. 2(A) shows the monitoring of the crystallization process by means of the three abscissas defined above. It is noticeable that both the band of crystallization and the boundary in the temperature field advance with a decreasing velocity, which implies that two different space segments of same length have different times of crystallization. Also numerically, we have obtained the arrival time defined in the simple heat diffusion problem; see Fig. 2(B). The variation of the crystallization time as a function of the applied temperature is, as expected, monotonically increasing, but not linear. Thus, a better strategy of cooling can be suggested: to cool the sample at both sides with a smaller (i.e. less expensive) temperature. The difference with the first strategy is greater as smaller is the applied temperature, that is, as smaller is the time (i.e. the money!) spent in the process.

Analytical results are more difficult to obtain. For instance, we have provided a numerical temperature field to be used in the hybrid stochastic model. We have used this field in a stochastic simulation of model (2), and we have depicted the result in Fig. 3, where we represent the degree of crystallization at different times.

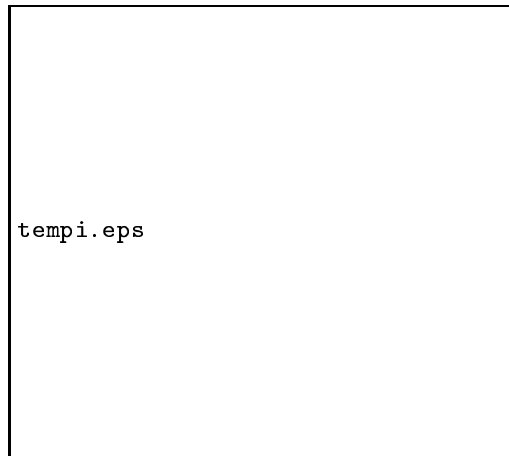


FIGURE 3. Evolution of the crystalline phase.

At the beginning of the process crystals develop randomly where the temperature is lower than T_f , but after a short time interval (less than 10 sec.), the crystallization front becomes deterministic and follows the evolution of the temperature field. In Figure 4 we can see the crystalline front compared with the moving boundary $x_b(t)$ of the temperature field.

FIGURE 4. Crystalline front (solid line) and moving boundary $x_b(t)$ of the temperature field (dotted line).

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