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# Reduction of a Mathematical Model for Polymer Crystallization

Ramón Escobedo and Vincenzo Capasso

MIRIAM (Milan Research center in Industrial and Applied Mathematics) and  
Dipartimento di Matematica, Università degli Studi di Milano, Via Saldini 50,  
20133 Milan, Italy. [escobedo@mat.unimi.it](mailto:escobedo@mat.unimi.it), [capasso@mat.unimi.it](mailto:capasso@mat.unimi.it)

**Abstract** A reduction of a recent model of crystallization is presented. After adimensionalization, we solve it numerically. The temperature field exhibits oscillations and the crystallization process exhibits jumps. In fact, there is an advancing front of crystallization outside which the degree of crystallinity is constant. For sufficiently large samples, the model (a PDE and a ODE) can be reduced to a pair of ODEs for the parameters which defines the front.

## 1 Introduction

Crystallization is a mechanism of phase change in polymeric materials. If an experiment is started with a liquid (the polymer melt) and the temperature is subsequently decreased below a certain point (the melting point of the material), crystals appear *randomly in space and time* and start to grow.

It is well known from experiments that the kinetic parameters of nucleation and growth strongly depend upon temperature. It is relevant to take this dependence into account when dealing with heterogeneous temperature fields.

A major difficulty arises in this context, due to the intrinsic randomness of the crystallization process that implies a random decomposition of the domain in which the process is taking place. This implies randomness in the temperature evolution due to the dependence of the parameters upon the phase and the dependence of the localization of the latent heat at the growing boundaries of the crystalline phase. All this implies a nontrivial double stochasticity on the crystallization process due to the announced dependence of the parameters of the nucleation-growth process upon temperature.

To overcome this complicacy we may take into account that, under typical industrial conditions (many and small crystals) the stochastic temperature field may be approximated with an averaged deterministic one. 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 deter-

ministic one, as in [CMS03], by using an interacting particle system coupled with the temperature field, and proceed via laws of large numbers [VC03].

A nonlinear reaction-diffusion system is obtained including an ODE for the degree of crystallinity  $y(x, t)$  and a PDE for the temperature field  $T(x, t)$ :

$$\frac{\partial y}{\partial t} = p(y) b_G(T) + v_0 q(y) b_N(T) \quad (1)$$

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

In this model morphologies and their geometrical properties are lost, in such a way that a symmetry in the  $y$ -direction may be assumed without a loss of generality to write the model in a one-dimensional form. Thus,  $(x, t) \in (0, L) \times (0, +\infty)$ , where  $L$  is the length of the material. The other parameters are as follows:  $\sigma$  is the diffusion coefficient,  $a_G$  is the non-isothermal factor,  $v_0$  is the initial mass, the function  $q(y)$  is the starting nucleation mechanism, and  $p(y)$  describes the growth process with a typical logistic expression due to consumption of the available liquid material:

$$p(y) = \begin{cases} y(1-y) & \text{in } [0, 1] \\ 0 & \text{outside} \end{cases}, \quad q(y) = \begin{cases} (1-y)^2 & \text{in } [0, 1] \\ 0 & \text{outside} \end{cases}. \quad (3)$$

The functions  $b_N(T)$  and  $b_G(T)$  express the dependence of the nucleation and growth rates upon temperature. They are typically given by exponential functions, e.g.  $b_N(T) = N e^{-\beta_N(T-T_{\text{ref}})}$ ,  $b_G(T) = G e^{-\beta_G(T-T_{\text{ref}})}$ , where  $T_{\text{ref}}$  is a temperature of reference, typically equal to zero. A recent argument [EC03] suggests the convenience of introducing explicitly a threshold crystallization temperature  $T_f$ , above which no nucleation nor growth can take place. Then, assuming that  $\beta_N = \beta_G = \beta$ , we can adopt the general form  $b_N(T) = N \theta(T)$  and  $b_G(T) = G \theta(T)$ , where

$$\theta(T) = \begin{cases} e^{-\beta(T-T_{\text{ref}})} & \text{if } T < T_f, \\ 0 & \text{if } T \geq T_f. \end{cases} \quad (4)$$

#### *Dimensionless Problem*

Numerical simulations in [EC03] have shown that a strong competition exists between two mechanisms: cooling at  $x = 0$  and heating due to the latent heat associated with the growth of crystals. It is then convenient to write the equations in a dimensionless form. For that, we define a frequency  $\nu = \beta a_G G e^{-\beta T_f} \approx 1.14 \text{ s}^{-1}$  and two dimensionless parameters  $\epsilon \ll 1$  and  $\delta \ll 1$ ,

$$\epsilon = \frac{1}{\beta a_G} = 4 \times 10^{-3} \quad \text{and} \quad \delta = \frac{v_0 N}{G} = 4 \times 10^{-2}, \quad (5)$$

and we scale the variables:  $\tilde{t} = \nu t$ ,  $\tilde{x} = \sqrt{\frac{\nu}{\sigma}} x$  and  $\tilde{T} = \beta(T - T_f)$ .  $(6)$

Then, by dropping the  $\tilde{\cdot}$ 's, the dimensionless equations are written as follows:

$$\frac{\partial y}{\partial t} = \epsilon \left[ \delta + (1 - 2\delta)y + (\delta - 1)y^2 \right] \theta(T), \quad (7)$$

$$\frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial x^2} + y(1 - y)\theta(T), \quad (8)$$

$$\text{where } \theta(T) = \begin{cases} e^{-T} & \text{if } T < 0, \\ 0 & \text{if } T \geq 0, \end{cases} \quad (9)$$

and they may be solved subject to the initial and boundary conditions

$$y(x, 0) = 0 \quad \text{and} \quad T(x, 0) = 1, \quad \forall x \in [0, L]; \quad (10)$$

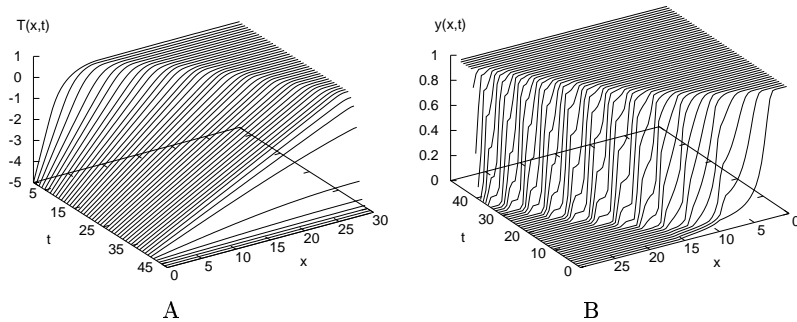
$$T(0, t) = T_{\text{app}} < 0 \quad \text{and} \quad \frac{\partial T(L, t)}{\partial x} = 0, \quad \forall t \geq 0. \quad (11)$$

These conditions correspond to the experimental situation in which the sample is cooled at one of its side ( $x = 0$ ) with an applied temperature  $T_{\text{app}}$ . The length scale is  $L = \sqrt{\nu/\sigma} \approx 23.87$ , and so is the size of the sample.

The slow time-scale  $\tau = \epsilon t$  shows that the temperature is almost all the time at its stationary state. Furthermore, in the regions where  $y = 0$  or  $y = 1$  the temperature is the solution of  $T_{xx} = 0$ , i.e. a straight line.

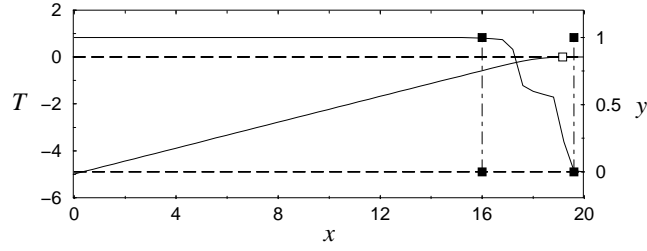
## 2 Numerical Solution

We have solved the problem (7)–(11) with  $\epsilon = 4 \times 10^{-3}$ ,  $\delta = 4 \times 10^{-2}$ ,  $T_{\text{app}} = -5$ ,  $T_{\text{ini}} = 1$  and  $L = 30$ , with a discretization of 301 spatial nodes (i.e.  $\Delta x = 0.1$ ) and a time-step  $\Delta t = 1.6 \times 10^{-5}$  which ensures that there will be no spurious oscillatory effects in the Crank-Nicholson scheme we used. The solution exhibits an oscillating moving boundary in the temperature field and a crystallization front which experiments stops in its advance. See Fig. 1.



**Fig. 1.** Solution of (7)–(11): (A) Oscillating moving boundary in the temperature field at height  $T \approx T_f = 0$ . (B) Crystallization front, exhibiting stops in its advance.

More details can be found in [EC03] and in [CES03], where a free boundary problem has been written for the moving boundary in the temperature field. There, the solution is characterized by three time-dependent parameters which determine the position of the boundary in  $T$  and the front in  $y$  (see Fig. 2).



**Fig. 2.** Profiles of  $T(x, t)$  and  $y(x, t)$  at a given instant of time in which the front has advanced sufficiently far from the cooling point  $x = 0$ . Horizontal dashed lines are the respective zero-axis. The white square is  $x_b$ , the moving boundary of  $T(x, t)$ , and the black squares denote the mass front  $[x_\alpha, x_\omega]$ . See (12), (13) and (14) below:

$$x_b(t) = \min_t \{x \in [0, L] / T(x, t) \geq T_f\}, \quad (12)$$

$$x_\alpha(t) = \max_t \{x \in [0, L] / y(x, t) = 1\}, \quad (13)$$

$$x_\omega(t) = \min_t \{x \in [0, L] / y(x, t) = 0\}. \quad (14)$$

### 3 Reduction of the Model

In the asymptotic limit of a very large sample, the following argument may be applied. Let  $t_0$  be a fixed instant of time at which the mass front is moving in the interior of the sample. Then, splitting the area under  $y(x, t_0)$  we obtain

$$\begin{aligned} \int_0^1 y(x, t_0) dx &= \int_0^{x_\alpha(t_0)} y(x, t_0) dx + \int_{x_\alpha(t_0)}^{x_\omega(t_0)} y(x, t_0) dx + \int_{x_\omega(t_0)}^1 y(x, t_0) dx \\ &= x_\alpha(t_0) + \int_{x_\alpha(t_0)}^{x_\omega(t_0)} y(x, t_0) dx, \end{aligned} \quad (15)$$

where use has been made of that  $y = 1$  in  $[0, x_\alpha(t_0)]$  and  $y = 0$  in  $[x_\omega(t_0), L]$ .

If the front is sufficiently far from the cooling point  $x = 0$ , its width can be neglected with respect to the travelled distance (see Fig. 2), so that the integral can be dropped in (15). Then,

$$x_\alpha(t_0) \approx \int_0^L y(x, t_0) dx. \quad (16)$$

Deriving this expression with respect to time and using Eq. (7) yields:

$$\dot{x}_\alpha(t) \approx \frac{\partial}{\partial t} \int_0^L y(x, t) dx = \int_{x_\alpha}^{x_\omega} \epsilon [\delta + (1 - 2\delta)y + (\delta - 1)y^2] \theta(T) dx. \quad (17)$$

Splitting again the integral, and using the values of  $y$  in each interval, we obtain

$$\dot{x}_\alpha(t) \approx \int_{x_\alpha(t)}^{x_\omega(t)} \epsilon [\delta + (1 - 2\delta)y + (\delta - 1)y^2] \theta(T) dx + \int_{x_\omega(t)}^L \epsilon \delta \theta(T) dx. \quad (18)$$

Here  $T(x, t)$  is a monotone function of  $x$  which in  $[x_b, L]$  is greater than  $T_f$  (see [CES03]) so  $\theta(T) = 0$  in this interval. On another hand,  $\delta$  can be neglected with respect to 1 (but not with respect to  $y$ , which may be zero). Then,

$$\dot{x}_\alpha(t) \approx \epsilon \int_{x_\alpha(t)}^{x_b(t)} [\delta + y(1 - y)] \theta(T) dx. \quad (19)$$

A similar argument can be used for  $T(x, t)$ . At a given time  $t_0$ ,  $T(x, t_0)$  is made of two straight lines (recall the argument of the slow time scale). Then,

$$\int_0^L T(x, t_0) dx \approx \frac{1}{2} T_{\text{app}} x_b(t_0). \quad (20)$$

As before, derive, replace with Eq. (8) and split the integral to obtain:

$$\frac{1}{2} T_{\text{app}} \dot{x}_b(t) \approx \left. \frac{\partial T}{\partial x} \right|_0^L + \int_{x_\alpha(t)}^{x_b(t)} y(1 - y) \theta(T) dx. \quad (21)$$

The slope of  $T(x, t)$  at  $x = L$  is given by the b.c. (11), and at  $x = 0$  by the straight line which joins  $(0, T_{\text{app}})$  with  $(x_b, 0)$ , that is,  $-T_{\text{app}}/x_b$ . Then,

$$\dot{x}_b(t) \approx \frac{2}{x_b(t)} + \frac{2}{T_{\text{app}}} \int_{x_\alpha(t)}^{x_b(t)} y(1 - y) \theta(T) dx. \quad (22)$$

The first term of the *RHS* of (22) is always positive, and the second term is always negative; this explains that  $x_b$  could move backwards, producing the oscillations observed numerically in the temperature field.

The reduced model (19)-(22), which describes the crystallization process in a large sample when the front is advancing far from the cooling point, can also be a proof of the fact that the physics of the crystallization process happens mainly in the interior of the band  $[x_\alpha, x_b]$ . It is also a sustain for the formulation of a free boundary problem in the temperature field (see [CES03]).

Further directions on this problem include to obtain approximations the temperature field and the mass distribution in the interior of the band, in order to find a closed system of equations to obtain  $x_b$ , which is the parameter of main interest for industry.

## References

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