

Optimal cooling strategies in polymer crystallization

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Abstract An optimal control problem for cooling strategies in polymer crystallization processes described by a deterministic model is solved in the framework of a free boundary problem. The strategy of cooling both sides of a one dimensional sample is introduced for the first time in this model, and is shown to be well approximated by the sum of the solutions of two one-phase Stefan problems, even for arbitrary applied temperature profiles. This result is then used to show that cooling both sides is always more effective in polymer production than injecting the same amount of cold through only one side. The optimal cooling strategy, focused in avoiding low temperatures and in shortening cooling times, is derived, and consists in applying the same constant temperature at both sides. Explicit expressions of the optimal controls in terms of the parameters of the material are also obtained.

Keywords Optimal control · Stefan problem · Polymer crystallization

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1 Introduction

Optimization of cooling strategies is a fundamental part of modeling polymerization processes. A recent model of polymer crystallization [2,3] is being studied to derive the optimal cooling strategy in terms of the industrial main interests, focused in reducing the duration of the cooling process while avoiding excessively low temperatures.

The model consists of two non-linear partial differential equations for the degree of crystallinity $y(x, t)$, defined as the mean volume fraction of the space occupied by crystals, and the temperature field $T(x, t)$, coupled by means of the rate functions of nucleation and growth $b_N(T)$ and $b_G(T)$, the function of starting of nucleation $\kappa(y) = (1 - y)^2$, and the function of aggregation and saturation of nuclei $\beta(y) = y(1 - y)$:

$$y_t(x, t) = \beta(y(x, t))b_G(T(x, t)) + v_0\kappa(y(x, t))b_N(T(x, t)), \quad (1)$$

$$T_t(x, t) = \sigma T_{xx}(x, t) + a_G\beta(y(x, t))b_G(T(x, t)), \quad (2)$$

for $(x, t) \in Q_\tau = (0, L) \times (0, \tau)$, where L is the length of the sample and τ is the time at which the cooling process is stopped.

Equations (1)–(2) are solved with the following boundary and initial conditions:

$$T(0, t) = u_0(t), \quad T(L, t) = u_L(t), \quad t \in (0, \tau), \quad (3)$$

$$y(x, 0) = 0, \quad T(x, 0) = T_0, \quad x \in (0, L). \quad (4)$$

The nucleation and growth rate functions are such that $b_G(T)/G = b_N(T)/N = \theta(T)$, where

$$\theta(T) \stackrel{def}{=} \begin{cases} \exp(-\eta T) & \text{if } T < T_f, \\ 0 & \text{if } T \geq T_f. \end{cases} \quad (5)$$

The parameters $G, v_0, N, \sigma, a_G, \eta$ and T_f are positive real constants denoting the growth factor, the initial mass, the nucleation factor, the heat diffusion coefficient, the non-isothermal factor, the nucleation and growth exponent and the critical phase transition temperature (from liquid to solid), respectively. Typical values and more details of the model can be found in Refs. [2–4].

Condition (3) means that the injection of cold is applied at both sides of the sample, $x_0 = 0$ and $x_L = L$; we call this case a *double cooling* strategy. Previous strategies used in this model have only considered to cool one side of the sample (*single cooling*), using a thermally insulated boundary at the other side (e.g. $T_x(L, t) = 0$); see Refs. [3–5].

In the single cooling case, a crystallization front is formed close to the cooling side and moves towards the interior of the sample until the other side is reached. The front separates the liquid ($y = 0$) and the solid ($y = 1$) phases, and is not a travelling wave; instead, it is a *band of crystallization* which exhibits an oscillating advance with variable shape and velocity strongly dependent on the parameters of the material [3].

Under some conditions, the crystallization band can be identified with a thin interface where the nucleation and growth processes are confined and take place at the

freezing temperature T_f [5]. Then, a free boundary problem (FBP) framework can be used to describe the polymerization process by means of a one-phase Stefan problem [1]. Before this framework was established, numerical simulations were recently used to derive both the optimal applied temperature \bar{u}_0 and the cooling process duration $\bar{\tau}$ giving rise to the optimal single cooling strategy [4].

In the present paper this FBP framework is used to characterize the solution of the double cooling problem (1)–(4) by means of two Stefan problems, allowing us to show that double cooling is always more effective than single cooling (injecting the same amount of cold), and to derive explicit expressions of the optimal controls $\bar{u}_0(t)$, $\bar{u}_L(t)$ and $\bar{\tau}$ giving rise to the optimal cooling strategy, expressions written in terms of the parameters of the material.

2 Stefan problems describing polymerization processes

The FBP framework for single cooling strategies consists in identifying a free boundary $h(t)$ with the instantaneous amount of crystallized polymer $P(t)$ defined by

$$P(t) \stackrel{\text{def}}{=} \int_0^L y(x, t) dx. \tag{6}$$

The free boundary $h(t)$ allows to consider the crystallinity as a step function in the whole sample, $y(x, t) = 1$ in $[0, h(t)]$ and $y(x, t) = 0$ in $[h(t), L]$, so that $P(t) = h(t)$. At the interface, the temperature is assumed to be precisely T_f , i.e. $T(h(t), t) = T_f$.

These assumptions allow us to derive a Stefan condition and the corresponding Stefan problem; details of the derivation and the solution of the Stefan problem for different applied temperature profiles will be presented elsewhere [5]. Here it suffices to say that the Stefan condition provides us with an explicit expression of the ratio of the latent heat \mathcal{L}_δ to the specific heat c in terms of the parameters of the material, $\mathcal{L}_\delta/c = a_G K_\delta$, where $K_\delta = [1 + \delta(\ln \delta - 1)]/(1 - \delta)^2$, $\delta = v_0 N/G$, and that the solution of the Stefan problem for arbitrary applied temperature profiles is given by the so-called *pseudo-steady state* (PSS) approximation, valid in the limit $Ste \ll 1$, where the Stefan number Ste is the ratio of the sensible heat $c\Delta T = c \max_t \{T_f - u(t)\}$ to the latent heat \mathcal{L}_δ [1]:

$$Ste \stackrel{\text{def}}{=} \frac{c\Delta T}{\mathcal{L}_\delta}. \tag{7}$$

2.1 Stefan problems for double cooling strategies

When both sides of the sample are cooled, two crystallization bands emerge and move towards each other until they merge somewhere in the interior of the sample.

We claim that a double cooling process can be seen as the sum of two single cooling processes, and therefore can be approximated by means of two Stefan problems for two free boundaries $h_0(t)$ and $h_L(t)$: for $i = 0, L$,

$$\frac{\partial T_i}{\partial t}(x, t) = \sigma \frac{\partial^2 T_i}{\partial x^2}(x, t), \quad x \in [0, h_i(t)], \quad t > 0, \quad (8)$$

$$T_i(x, t) = T_f, \quad x \in (h_i(t), +\infty), \quad t > 0, \quad (9)$$

$$T_i(0, t) = u_i(t), \quad t > 0, \quad (10)$$

$$T_i(h_i(t), t) = T_f, \quad t > 0, \quad (11)$$

$$\frac{\mathcal{L}_\delta}{c} h_i'(t) = \sigma \frac{\partial T_i}{\partial x}(h_i(t), t), \quad t > 0. \quad (12)$$

The PSS solution of these Stefan problems are, for $i = 0, L$ (see Refs. [1, 5]),

$$h_i^{\text{PSS}}(t) = \sqrt{\frac{2\sigma c}{\mathcal{L}_\delta} Q_i(t)}, \quad (13)$$

$$T_i^{\text{PSS}}(x, t) = \begin{cases} u_i(t) + \frac{T_f - u_i(t)}{h_i^{\text{PSS}}(t)} x & \text{if } x \leq h_i^{\text{PSS}}(t), \\ T_f & \text{if } h_i^{\text{PSS}}(t) \leq x, \end{cases} \quad (14)$$

where $Q_i(t)$ is the total amount of cold injected into the sample along the time interval $[0, t]$ through the boundary x_i :

$$Q_i(t) \stackrel{\text{def}}{=} \int_0^t (T_f - u_i(s)) ds, \quad \text{for } i = 0, L. \quad (15)$$

Then, the temperature and crystallinity profiles of the double cooling process can be approximated by the following functions: (see Fig. 1 and error estimates)

$$T^{\text{PSS}}(x, t) = T_0^{\text{PSS}}(x, t) + T_L^{\text{PSS}}(L - x, t) - T_f, \quad (16)$$

$$y^{\text{PSS}}(x, t) = \begin{cases} 0 & \text{if } x \in [h_0^{\text{PSS}}(t), L - h_L^{\text{PSS}}(t)], \\ 1 & \text{if not.} \end{cases} \quad (17)$$

An excellent agreement is also obtained for different applied temperatures profiles, as shown in Fig. 2, where we have depicted the time evolution of the free boundaries $h_0(t)$ and $h_L(t)$ together with their sum and the magnitude thus approximated, $P(t)$, for the case described in Fig. 1, a case where the applied temperature is variable in time, and a case of an asymmetric double cooling. Error estimates are obtained later.

2.2 Amount of crystallized polymer in double cooling strategies

According to the results obtained in the previous section, it turns out that the amount of crystallized polymer $P(t)$ can be accurately approximated by

$$P(t) = h_0^{\text{PSS}}(t) + h_L^{\text{PSS}}(t). \quad (18)$$

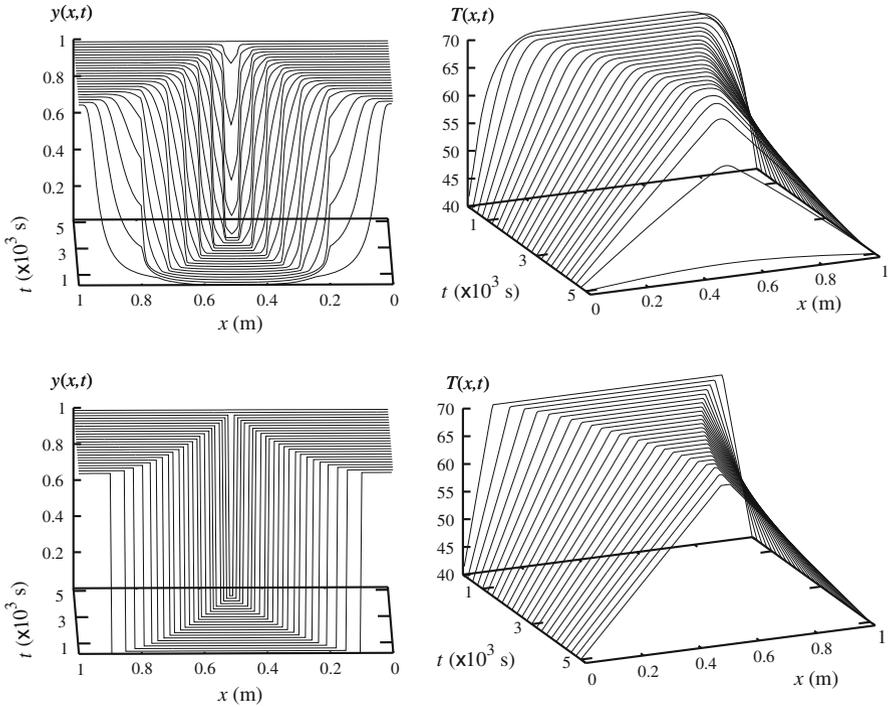


Fig. 1 Upper row: Crystallinity (left) and temperature field (right) obtained by direct simulation of the polymerization problem (1)–(4). Lower row: same as above but obtained by using (16)–(17) with the solution (13)–(14) of the Stefan problems (8)–(12). Parameter values are $u_0 = u_L = 40^\circ\text{C}$, $T_f = 70^\circ\text{C}$, $\sigma = 0.002\text{ m}^2\text{s}^{-1}$, $a_G = 2500^\circ\text{C}$, $G = 5\text{ s}^{-1}$, $N = 20\text{ s}^{-1}$, $v_0 = 0.01$, $\eta = 0.1$, $L = 1\text{ m}$ and $T_0 = 100^\circ\text{C}$. Resulting values are $\delta = 0.04$, $K_\delta = 0.902$ and $Ste = 0.013$. Note the symmetry with respect to $x = 0.5$

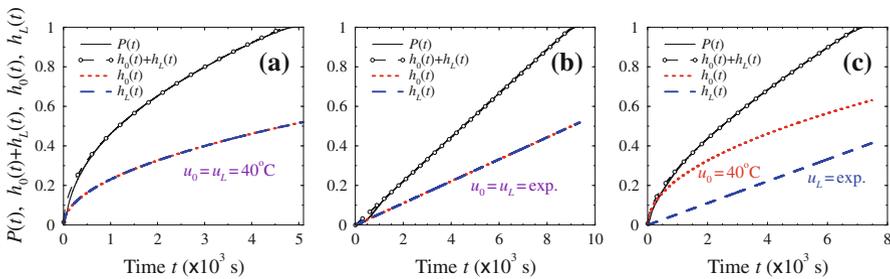


Fig. 2 Total amount of polymer $P(t)$ (solid line) compared with the sum of the two free boundaries $h_0(t) + h_L(t)$ (solid line with circles); also depicted are $h_0(t)$ and $h_L(t)$ (dotted and dashed lines respectively). **a** $u_0 = u_L = 40^\circ\text{C}$, **b** $u_0 = u_L = T_f + \mathcal{L}_\delta(1 - e^{\gamma^2\sigma t})/c$. **c** $u_0 = 40^\circ\text{C}$, $u_L = T_f + \mathcal{L}_\delta(1 - e^{\gamma^2\sigma t})/c$ (asymmetric cooling). We have used $\gamma = 2.76 \times 10^{-2}\text{ m}^{-1}$

Therefore, a given amount of cold $Q(t) = Q_0(t) + Q_L(t)$ injected into the sample with a double cooling strategy will produce an amount of polymer given by

$$P(t) = \sqrt{\frac{2\sigma c}{\mathcal{L}_\delta} Q_0(t)} + \sqrt{\frac{2\sigma c}{\mathcal{L}_\delta} Q_L(t)} \quad (19)$$

$$\geq \sqrt{\frac{2\sigma c}{\mathcal{L}_\delta} [Q_0(t) + Q_L(t)]} \quad (20)$$

$$\geq \sqrt{\frac{2\sigma c}{\mathcal{L}_\delta} Q(t)} \stackrel{\text{def}}{=} \bar{P}(t), \quad (21)$$

where $\bar{P}(t)$ is the amount of crystallized polymer produced by injecting an amount of cold $Q(t)$ by cooling only one side of the sample, showing that double cooling always produces a greater or equal amount of crystallized polymer than single cooling.

Moreover, the maximal production of crystallized polymer achievable by injecting a given amount of cold $Q(t)$ is reached when a double cooling strategy with $Q_0(t) = Q_L(t) = Q(t)/2$ is used. In this case,

$$P(t) = \sqrt{2} \bar{P}(t). \quad (22)$$

2.3 Crystallization time in double cooling strategies

The total crystallization is reached when $P(t_{\text{cryst}}) = L$. Thus, the PSS approximation provides us with the following equation to estimate the crystallization time:

$$\left(\sqrt{Q_0(t_{\text{cryst}}^{\text{PSS}})} + \sqrt{Q_L(t_{\text{cryst}}^{\text{PSS}})} \right)^2 = \frac{\mathcal{L}_\delta}{2\sigma c} L^2. \quad (23)$$

When the same constant temperature u is applied at both sides, expression (23) yields

$$t_{\text{cryst}}^{\text{PSS}} = \frac{L^2}{8\sigma Ste}, \quad (24)$$

where $Ste = c(T_f - u)/\mathcal{L}_\delta$, showing that the time needed for complete crystallization when cooling both sides at a given constant applied temperature is a quarter of the time needed when cooling only one side with the same temperature, and that the double cooling requires only one half of the amount of cold required by the simple cooling.

2.4 Errors estimates

To check how accurate our approximation is, the following error estimates, introduced in Ref. [5] to test the FBP framework, are used:

Table 1 Error estimates and crystallization times for the cases depicted in Fig. 2

	u_0 (°C)	u_L (°C)	$\xi_{L_2}(10^{-3})$	$\varepsilon_T (10^{-3})$	$\epsilon (10^{-2})$	$t_{\text{cryst}}^{\text{NUM}}(10^3 \text{ s})$	$t_1(10^3 \text{ s})$	$t_2(10^3 \text{ s})$	%
A	40	40	5.34	3.73	8.1	5.11	0.23	4.55	84.6
B	exp.	exp.	2.30	0.18	3.5	9.37	1.1	8.9	84.7
C	40	exp.	5.60	2.16	6.2	7.49	0.22	6.66	85.9

$$\xi(t) = P(t) - \left(h_0^{\text{PSS}}(t) + h_L^{\text{PSS}}(t) \right), \tag{25}$$

$$\varepsilon(x, t) = T^{\text{NUM}}(x, t) - T^{\text{PSS}}(x, t), \tag{26}$$

where T^{NUM} denotes the temperature obtained by solving the polymerization problem (1)–(4) numerically. They are measured with the normalized L_1 and L_2 norms,

$$\xi_{L_2} = \frac{1}{L} \left(\frac{1}{t_2 - t_1} \int_{t_1}^{t_2} \xi^2(t) dt \right)^{1/2}, \tag{27}$$

$$\varepsilon_T = \frac{1}{(t_2 - t_1)T_f} \int_{t_1}^{t_2} \left(\frac{1}{L} \int_0^L \varepsilon^2(x, t) dx \right)^{1/2} dt, \tag{28}$$

where t_1 and t_2 correspond to the short transient times at the beginning and the end of the polymerization process, during which the crystallization band is not formed [5].

Moreover, $t_{\text{cryst}}^{\text{PSS}}$, the solution of (23), can be also compared with the crystallization time $t_{\text{cryst}}^{\text{NUM}}$, obtained numerically by solving $P(t_{\text{cryst}}^{\text{NUM}}) = L$, by using the relative error

$$\epsilon = \frac{|t_{\text{cryst}}^{\text{NUM}} - t_{\text{cryst}}^{\text{PSS}}|}{t_{\text{cryst}}^{\text{NUM}}}. \tag{29}$$

Error estimates ξ_{L_2} , ε_T and ϵ are calculated for the three cooling strategies depicted in Figs. 1 and 2, and are reported in Table 1.

The results show that error estimates are of the same order, but twice the value, than those obtained when describing single cooling strategies under the FBP framework sketched above [5], thus confirming that the double cooling polymerization process is accurately described by the sum of the two Stefan problems. A priori, this seems quite surprising, due to the nonlinear character of the polymerization problem.

Note that we are intentionally not using the exact solution of the Stefan problems (available when the applied temperature is constant or exponentially decreasing [1]) because our goal consists in proving that the PSS approximation is accurate enough to describe the double cooling polymerization process.

3 The optimal control problem

The optimal control problem of the single cooling case was solved numerically in Ref. [4]. The FBP framework allows us to rewrite the solution in terms of the parameters of the material, and to derive the corresponding optimal controls for the double cooling case.

3.1 Single cooling

Expression (8) from Ref. [4] shows the relation between the amount of crystallized polymer $P(t)$ and the amount of injected cold $Q(t)$, obtained numerically:

$$P(t) \approx \alpha \sqrt{Q(t)}, \quad (30)$$

where α is a positive real constant. Expression (13) provides us with its analytical expression, $\alpha = \sqrt{2\sigma c/\mathcal{L}_\delta}$, and consequently with the analytical expression of the optimal controls \bar{u} and $\bar{\tau}$, see [4]:

$$\text{if } \sigma_2 > \sigma_1 T_f^2: \quad \bar{u}(t) \equiv 0, \quad \bar{\tau} = \frac{\mathcal{L}_\delta}{2\sigma c T_f} L^2, \quad (31)$$

$$\text{if } \sigma_2 \leq \sigma_1 T_f^2: \quad \bar{u}(t) \equiv T_f - \sqrt{\frac{\sigma_2}{\sigma_1}}, \quad \bar{\tau} = \sqrt{\frac{\sigma_1}{\sigma_2}} \frac{\mathcal{L}_\delta}{2\sigma c} L^2, \quad (32)$$

where the control problem and the set of admissible controls U_{ad} were defined as follows,

$$\left\{ \begin{array}{l} \text{Min } J(u, \tau) = \sigma_1 \int_0^\tau (T_f - u(t))^2 dt + \sigma_2 \tau, \\ (u, \tau) \in U_{ad} = \left\{ (u, \tau) \in L^2(0, \tau) \times [0, +\infty) : u(t) \in [0, T_f], \text{ a.e., } P(\tau) = L \right\}, \end{array} \right. \quad (33)$$

and σ_1 and σ_2 are non-negative weights fixed to balance the contribution of each term.

3.2 Double cooling

For the optimal control of double cooling strategies, the control parameters are the applied temperatures $\vec{u}(t) = (u_0(t), u_L(t)) \in (L^2(0, \tau))^2$ and the duration of the cooling process $\tau \in [0, +\infty)$. Following the same argument used in [4], a cost functional $J(\vec{u}, \tau)$ promoting a short duration of the cooling process and avoiding excessively low applied temperatures can be written as

$$(CP) \left\{ \begin{array}{l} \text{Min } J(\vec{u}, \tau) = \sigma_1 \left[\int_0^\tau (T_f - u_0(t))^2 + (T_f - u_L(t))^2 dt \right] + \sigma_2 \tau, \\ (\vec{u}, \tau) \in U_{ad}, \end{array} \right. \quad (34)$$

$$\text{where } U_{ad} = \left\{ (\vec{u}, \tau) \in (L^2(0, \tau))^2 \times [0, +\infty) : \vec{u}(t) \in [0, T_f]^2, \text{ a.e., } P(\tau) = L \right\}.$$

As in the single cooling case, the rate σ_2/σ_1 is a measure of the relative cost of the two opposite contributions to the cost functional: to avoid low temperatures (σ_2/σ_1 small) and to shorten the cooling time (σ_2/σ_1 large). The cost of double cooling is considered symmetric, that is, cooling at $x_0 = 0$ has the same cost than cooling at $x_L = L$.

Optimal controls. Let (\vec{u}, τ) be an admissible control; then, complete crystallization is reached at $t = \tau$ and expression (23) means

$$\left(\sqrt{Q_0(\tau)} + \sqrt{Q_L(\tau)}\right)^2 = \frac{\mathcal{L}_\delta}{2\sigma c} L^2. \tag{35}$$

Therefore, (CP) can be reformulated as the following optimization problem:

$$(OP) \begin{cases} \text{Min } J(\vec{u}, \tau) = \sigma_1 \left[\int_0^\tau (T_f - u_0(t))^2 + (T_f - u_L(t))^2 dt \right] + \sigma_2 \tau, \\ (\vec{u}, \tau) \in V_{ad}, \end{cases} \tag{36}$$

where $V_{ad} = \left\{ (\vec{u}, \tau) \in \left(L^2(0, \tau) \right)^2 \times [0, +\infty) : \vec{u}(t) \in [0, T_f]^2 \text{ a.e., and (35) holds} \right\}$.

The admissibility condition $(\vec{u}, \tau) \in V_{ad}$ implies that there exists a lower bound for τ , corresponding to $u_0 = u_L = 0^\circ\text{C}$:

$$\tau \geq \hat{\tau} \stackrel{\text{def}}{=} \frac{\mathcal{L}_\delta}{8\sigma c T_f} L^2. \tag{37}$$

Theorem 1 Assume that $\sigma_1 \in [0, +\infty)$ and $\sigma_2 \in (0, +\infty)$. Then,

- a) If $\sigma_2 > 2\sigma_1 T_f^2$, the unique solution of the optimization problem (OP) is given by

$$\bar{u}_0(t) = \bar{u}_L(t) \equiv 0, \quad \bar{\tau} = \frac{\mathcal{L}_\delta}{8\sigma c T_f} L^2. \tag{38}$$

- b) If $\sigma_2 \leq 2\sigma_1 T_f^2$, the unique solution of the optimization problem (OP) is given by

$$\bar{u}_0(t) = \bar{u}_L(t) \equiv T_f - \frac{1}{2} \sqrt{\frac{2\sigma_2}{\sigma_1}}, \quad \bar{\tau} = \sqrt{\frac{\sigma_1}{2\sigma_2}} \left(\frac{\mathcal{L}_\delta}{4\sigma c} L^2 \right). \tag{39}$$

Proof Using that $2(a + b) \geq (\sqrt{a} + \sqrt{b})^2$ in expression (35) yields

$$Q_0(\tau) + Q_L(\tau) \geq \frac{\mathcal{L}_\delta}{4\sigma c} L^2. \tag{40}$$

Thanks to Hölder's inequality (for $i = 0, L$)

$$\sqrt{\tau} \left(\int_0^{\tau} (T_f - u_i(t))^2 dt \right)^{1/2} \geq \int_0^{\tau} (T_f - u_i(t)) dt, \quad (41)$$

we get, $\forall(\vec{u}, \tau) \in V_{ad}$:

$$\left(\int_0^{\tau} (T_f - u_0(t))^2 dt \right)^{1/2} + \left(\int_0^{\tau} (T_f - u_L(t))^2 dt \right)^{1/2} \geq \frac{\mathcal{L}_\delta}{4\sqrt{\tau}\sigma c} L^2. \quad (42)$$

Using again $2(a + b) \geq (\sqrt{a} + \sqrt{b})^2$, we have

$$\int_0^{\tau} (T_f - u_0(t))^2 dt + \int_0^{\tau} (T_f - u_L(t))^2 dt \geq \frac{1}{2\tau} \left(\frac{\mathcal{L}_\delta}{4\sigma c} L^2 \right)^2. \quad (43)$$

Consequently,

$$J(\vec{u}, \tau) \geq \psi(\tau), \quad \forall(\vec{u}, \tau) \in V_{ad}, \quad (44)$$

where we have used the auxiliary real function

$$\psi(\tau) = \frac{\sigma_1}{2\tau} \left(\frac{\mathcal{L}_\delta}{4\sigma c} L^2 \right)^2 + \sigma_2 \tau, \quad \tau \in [\hat{\tau}, +\infty). \quad (45)$$

Elementary calculus shows that $\psi(\tau)$ has a unique global minimum at $\bar{\tau}$ in $[\hat{\tau}, +\infty)$, where

$$\bar{\tau} = \begin{cases} \hat{\tau} & \text{if } \sigma_2 > 2\sigma_1 T_f^2, \\ \sqrt{\frac{\sigma_1}{2\sigma_2}} \left(\frac{\mathcal{L}_\delta}{4\sigma c} L^2 \right) & \text{if } \sigma_2 \leq 2\sigma_1 T_f^2. \end{cases} \quad (46)$$

Then, it is quite easy to verify that if $\sigma_2 \leq 2\sigma_1 T_f^2$,

$$J(\vec{u}, \tau) \geq \psi(\tau) \geq \psi(\bar{\tau}) = J\left(T_f - \frac{1}{2}\sqrt{\frac{2\sigma_2}{\sigma_1}}, T_f - \frac{1}{2}\sqrt{\frac{2\sigma_2}{\sigma_1}}, \bar{\tau}\right), \quad \forall(\vec{u}, \tau) \in V_{ad}, \quad (47)$$

meanwhile, if $\sigma_2 > 2\sigma_1 T_f^2$,

$$J(\vec{u}, \tau) \geq \psi(\tau) \geq \psi(\hat{\tau}) = J(0, 0, \hat{\tau}), \quad \forall(\vec{u}, \tau) \in V_{ad}. \quad (48)$$

To prove the uniqueness, let us assume that $(\vec{u}^*, \tau^*) \in V_{ad}$ is another solution of (OP) , i.e. $J(\vec{u}^*, \tau^*) = J(\vec{u}, \bar{\tau})$. In any case it is easy to deduce from previous estimations that $\psi(\tau^*) = \psi(\bar{\tau})$. Since ψ is strictly convex, we get that $\tau^* = \bar{\tau}$.

We conclude that $\vec{u}^*(t) = \vec{u}(t)$, a.e. $t \in (0, \bar{\tau})$, by seeing that

$$\begin{aligned} & \int_0^{\bar{\tau}} (u_0^*(t) - \bar{u}_0)^2 dt + \int_0^{\bar{\tau}} (u_L^*(t) - \bar{u}_L)^2 dt \\ &= \int_0^{\bar{\tau}} ((u_0^*(t) - T_f) + (T_f - \bar{u}_0))^2 dt + \int_0^{\bar{\tau}} ((u_L^*(t) - T_f) + (T_f - \bar{u}_L))^2 dt \\ &= \int_0^{\bar{\tau}} (u_0^*(t) - T_f)^2 dt + \int_0^{\bar{\tau}} (T_f - \bar{u}_0)^2 dt - 2(T_f - \bar{u}_0) \int_0^{\bar{\tau}} (T_f - u_0^*(t)) dt \\ &\quad + \int_0^{\bar{\tau}} (u_L^*(t) - T_f)^2 dt + \int_0^{\bar{\tau}} (T_f - \bar{u}_L)^2 dt - 2(T_f - \bar{u}_L) \int_0^{\bar{\tau}} (T_f - u_L^*(t)) dt \\ &= 2 \int_0^{\bar{\tau}} (T_f - \bar{u}_0)^2 dt - 2(T_f - \bar{u}_0) \int_0^{\bar{\tau}} (T_f - u_0^*(t)) dt + 2 \int_0^{\bar{\tau}} (T_f - \bar{u}_L)^2 dt \\ &\quad - 2(T_f - \bar{u}_L) \int_0^{\bar{\tau}} (T_f - u_L^*(t)) dt \leq 0, \end{aligned}$$

where we have used the inequality (40) for $(\vec{u}^*, \bar{\tau})$ and the equality

$$\int_0^{\bar{\tau}} (T_f - u_0^*(t))^2 dt + \int_0^{\bar{\tau}} (T_f - u_L^*(t))^2 dt = \int_0^{\bar{\tau}} (T_f - \bar{u}_0)^2 dt + \int_0^{\bar{\tau}} (T_f - \bar{u}_L)^2 dt. \tag{49}$$

□

Noticeably, the remarks written in Ref. [4] about the choice of the ratio σ_2/σ_1 for the single cooling are also in order in the double cooling case.

4 Conclusion

We have analyzed a recent polymer crystallization model for a new kind of cooling strategy, consisting in cooling the sample at both sides. By means of a free boundary problem framework whose main features have been presented here, we have shown that the double cooling crystallization process can be approximated by the sum of two Stefan problems. Explicit expressions of the solution have been derived and errors

estimates have revealed a quite high accuracy, both in reproducing the behaviour of the crystallization front and the distribution of the temperature field. Also, important magnitudes such as the crystallization time and the amount of crystallized polymer with respect to the single cooling case have been derived explicitly.

The characterization of the double cooling crystallization process by means of two Stefan problems has then be used to find the optimal cooling strategy when both sides can be cooled. The solution of the control problem is obtained explicitly in terms of the parameters of the material, and shows that the optimal strategy consists in first, using a symmetric strategy, that is, applying the same cooling temperature at both sides of the sample, and second, using a constant temperature, thus recovering the result obtained for the single cooling case.

The free boundary problem framework has therefore shown to be quite effective in the analysis of cooling strategies in polymerization processes and could be used in higher dimension problems in future works.

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References

1. V. Alexiades, A.D. Solomon, *Mathematical Modeling of Melting and Freezing Processes* (Hemisphere Publishing Co., Washington DC, 1993)
2. V. Capasso, in *Mathematical Models for Polymer Crystallization Processes*, ed. by V. Capasso, H. Engl, J. Periaux. Computational Mathematics Driven by Industrial Problems (Springer, Berlin, 2000), pp. 39–67
3. R. Escobedo, V. Capasso, Moving bands and moving boundaries with decreasing speed in polymer crystallization. *Math. Mod. Meth. Appl. Sci. (M3AS)* **15**(3), 325–341 (2005)
4. R. Escobedo, L.A. Fernández, Optimal control of chemical birth and growth processes in a deterministic model. *J. Math. Chem.* **48**, 118–127 (2010)
5. R. Escobedo, L.A. Fernández, A classical one-phase Stefan problem for describing a polymer crystallization process (2010, submitted)