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Convex optimization for shape manipulation of multidimensional crystal particles

Naim Bajcinca[a,b], Ricardo Perl[a], Kai Sundmacher[a,c]

[a]*Max-Planck Institute for Dynamics of Complex Technical Systems, Sandtorstr.1, 39106 Magdeburg, Germany*
[b]*Technische Universität Berlin, Einsteinufer 17, 10857 Berlin, Germany*
[c]*Otto-von-Guericke Universität Magdeburg, Universitätsplatz 2, 39106 Magdeburg, Germany*

Abstract

A convex formulation of the optimal control problem leading to global optimal solutions and efficient algorithms for crystal shape manipulation is proposed in this paper. These results build on the preceding work [1] of the authors, where several useful properties of the minimum-time trajectories in the state-space have been devised. In particular, it has been shown that minimum time switching trajectories consist of a number of subsequent growth and dissolution sections with different constant supersaturation levels. Such a shaping strategy employs the unequal growth and dissolution rate quantities in order to achieve crystal morphologies which otherwise do not result directly from a pure growth scenario only. The main outcome of the paper are strategies for constructing minimum-time trajectories with an arbitrary number and sequence of switching phases. Optimal trajectories involving a growth and a dissolution phase only are shown to be unique. In all other cases infinity many optimal trajectories exist, all sharing the same globally unique process time scope. The resulting shaping strategy is shown to be dual to the ones proposed in [1].

Keywords: Crystal shape manipulation, convex optimization, optimal control, batch processes, multidimensional crystal particles

1. Introduction & Motivation

Crystal shape manipulation is a critical engineering venture in numerous industries. It has been shown that many properties of dispersed phase products are strongly linked to their shape, see [7]. For instance, dissolution rate or catalytic activity may depend on the ratio of the face area of a crystal particle. From the engineering point of view, manipulation of the crystal morphology is therefore essential, [2]. In contrast to the traditional techniques that utilize chemical additives for blocking or promoting of certain crystal faces despite the undesired chemical impurities (see [6]), here, shape manipulation by means of temperature control only is considered. This ideas presented in this article are strongly based on the results of the work in [1], where diverse optimal control strategies for crystal shape manipulation have been proposed. Here we suggest a convenient reformulation of the minimum-time problem as a *convex optimization problem*, this being a result of a natural modification of constraints in the optimization problem in [1]. Indeed, while the two switching manifolds in state-space have been introduced there for switching between the subsequent trajectory sections, here, instead a *switching region* is arbitrarily specified to include all switching points in its interior. The content of the paper is of a rather theoretical nature, however, the problem formulation and proposed strategies allow for diverse practical demands. The discussion focuses on shape manipulation of a single crystal particle only, but it has been already shown that the suggested ideas, in principle, can be easily extended to populations of crystal particles, too.

2. Problem formulation

2.1. Particle shape dynamics

Crystallization process involves a natural negative feedback structure [refer to Figure 1] in that any temperature change ΔT distorting the process equilibrium invokes a supersaturation σ of the opposite sign to force the crystal particles to grow ($\Delta T < 0, \sigma > 0$) or dissolve ($\Delta T > 0, \sigma < 0$) until the equilibrium conditions are restored ($\sigma = 0$). The three blocks in the simplified model setting (*e.g.,* nucleation has been neglected) in Figure 1 are described by the following standard set of equations

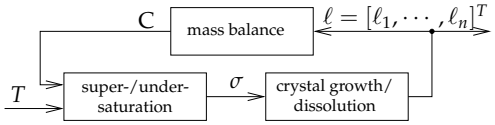

Figure 1: Crystallization feedback loop

$$\text{growth: } \mathrm{d}\ell_i/\mathrm{d}t = k_{g_i}\sigma^{g_i} =: G_i,\ \ \sigma \geq 0,\ k_{g_i} > 0,\ g_i > 0,\ i = 1,2,\ldots,n \tag{1a}$$

$$\text{dissolution: } \mathrm{d}\ell_i/\mathrm{d}t = k_{d_i}(-\sigma)^{d_i} =: G_i,\ \ \sigma \leq 0,\ k_{d_i} < 0,\ d_i > 0,\ i = 1,2,\ldots,n \tag{1b}$$

$$\text{supersaturation: } \sigma := C/C_{\text{sat}} - 1,\ C_{\text{sat}} = a_0 + a_1 T + a_2 T^2, \tag{1c}$$

$$\text{mass balance: } C = C_0 - \rho_C/V_t M \cdot \Delta V_C,\ \ V_C = V_C(\ell_1, \ell_2, \ldots, \ell_n) \tag{1d}$$

where $\ell = [\ell_1, \ell_2, \ldots, \ell_n]^T$ includes the n-lengths of the multi-dimensional crystal particle, C stands for the concentration, C_{sat} for the saturation concentration, $\Delta V_C = V_C - V_{C,0}$ for crystal volume change, $V_{C,0}$ for the initial crystal volume, ρ_C for crystal mass density, M is the solvent molar mass, and V_t the solvent volume. For notation simplicity we collect the equations (1a-1b) in the vector form

$$\mathrm{d}\ell/\mathrm{d}t =: G(\sigma) := [G_1(\sigma), G_2(\sigma), \ldots, G_n(\sigma)]^T. \tag{1e}$$

2.2. Optimal control problem

Particle shape manipulation can be seen as a trajectory planing problem in the state-space $\mathbb{R}^n_+$ defined by $\ell_i > 0$ for $i = 1, \ldots, n$. Since for a given particle morphology not just any $\ell > 0$ [componenent-wise!] may make sense, the state-space is, in fact, a subset of $\mathbb{R}^n_+$. Throughout the paper we assume $k_{g_i} \neq |k_{d_i}|$, $i = 1, \ldots, n$, that is, the growth and dissolution vectors are assumed to be unequal for symmetric supersaturation levels. This is mandatory for to produce a lateral motion in the state-space as a result of shape manipulation scenarios with a number of subsequent growth and dissolution sections. In this article we primairly focus on switching trajectories of this art only, in order to achieve crystal morphologies which do not result directly from a pure growth scenario. Indeed, the growth rate vector $G = \mathrm{d}\ell/\mathrm{d}t$, as defined in (1e), is constrained to lie within an "interval" parameterized by the state-dependent supersaturation level σ, which is confined between a minimal and maximal value, see Figure 2. The limiting values of supersaturation may be determined by the temperature constraints $T_{\min} \leq T \leq T_{\max}$, as carried out in [1], or may be directly given, *i.e.* $\sigma_{\min} \leq \sigma \leq \sigma_{\max}$, as utilized in this article. Notice the corresponding qualitative differences in the reachability region: supersaturation constraints produce a conical region, whereas for temperature constraints the latter warps (dashed indicated for $g_2 > g_1$). Obviosuly, morphologies outside such reachability regions are attainable only by means of subsequent growth and dissolution sections, this being the focus in the present work.

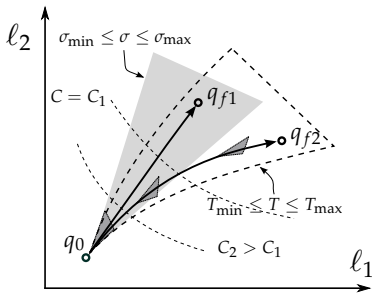

Figure 2: Rechability analysis

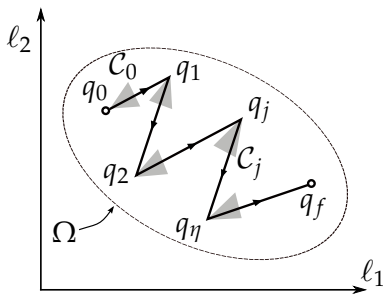

Figure 3: Optimal switching path

Two results are borrowed from [1]. First, using the minimum principle it has been shown that switched minimum-time trajectories are composed of a number of straight segments, corresponding to constant supersaturation sections, as indicated in Figure 3. And secondly, given a trajectory of the crystal particle in the state-space, we use the dynamic inversion algorithms from [1] to compute the temperature profile $T = T(t)$. This turns out to be primarily useful as it converts dynamic optimization problem into a static nonlinear program. With this said, we are ready to formulate the optimization problem as follows

$$\underset{\ell(t)\in\Omega,\, t\in[0,t_f]}{\text{minimize}}\ t_{\text{process}} = t_f - t_0 \ \text{ subject to } \begin{matrix}\sigma_{\min} \le |\sigma| \le \sigma_{\max} \\ \ell(t_0) = q_0, \ell(t_f) = q_f\end{matrix} \tag{2}$$

In addition to adopting supersaturation constraints, the striking difference with respect to the optimization problems of [1] in (2) is loosening of the two bouncing manifold constraints in the state-space by the switching region Ω, which is ought to host the entire particle trajectory, see Figure 3.

3. Convex optimization solutions

3.1. Convex optimization program

Without loss of generality, consider a two-dimensional particle (*i.e.* $n = 2$), and a trajectory with η switchings. Let q_0 and q_f denote the given initial and target particle morphologies in the state-space (ℓ_1, ℓ_2), see Figure 3. The points $q_j = [q_{j1}, q_{j2}]^T$, $j = 1, 2, \ldots, \eta$ in the figure denote the switching points, where jumps in the supersaturation (*i.e.* temperature) profile are exerted. By introducing the decision parameter $q := [q_1, \ldots, q_\eta]^T := [q_{11}, q_{12}, \ldots, q_{\eta 1}, q_{\eta 2}]^T$, and setting $q_{\eta+1} := q_f$ (see Figure 3), it can be shown that the net process time length τ reads

$$\tau(q) = \sum_{j=1}^{\eta+1} K_j \cdot (q_{j1} - q_{j-1,1})^{\frac{\gamma_{j2}}{\gamma_{j2}-\gamma_{j1}}} \cdot (q_{j2} - q_{j-1,2})^{\frac{-\gamma_{j1}}{\gamma_{j2}-\gamma_{j1}}}, \tag{3}$$

where $K_j = M^{-\gamma_{j1}}/2k_{\gamma_{j1}} + M^{-\gamma_{j2}}/2k_{\gamma_{j2}}$ and $M = (k_{\gamma_{j1}}/k_{\gamma_{j2}})^{1/(\gamma_{j2}-\gamma_{j1})}$ with $k_{\gamma_{j1}} = k_{g1}$, $k_{\gamma_{j2}} = k_{g2}$, $\gamma_{j1} = g_1$, $\gamma_{j2} = g_2$ for a growth phase, and $k_{\gamma_{j1}} = k_{d1}$, $k_{\gamma_{j2}} = k_{d2}$, $\gamma_{j1} = d_1$, $\gamma_{j2} = d_2$ for a dissolution phase. Clearly, the exponential parameters γ_{j1} and γ_{j2}, as well as K_j in (3) are all positive constants.

Notice that q takes values in $\Theta \subseteq \mathbb{R}_+^{2\eta}$, which, referring to Figure 3, for a scenario beginning with a growth and ending with a dissolution phase, is defined by

$$\Theta := \{q \in \mathbb{R}_+^{2\eta} : q_0 \le q_1, q_2 \le q_1, q_2 \le q_3, \ldots, q_\eta \le q_{\eta-1}, q_\eta \le q_f\}. \tag{4}$$

It is an easy exercise to see that this domain is convex and closed. To examine the convexity of the objective function $\tau = \tau(q)$ in (3), the hessian $\text{hess}(\tau) := \partial^2\tau/\partial q^2$ in Θ is to be investigated. Therefore, it is instructive to consider the summing terms in (3) separately. It is obvious that two sort of terms can be discriminated therein: the initial and the final terms, involving two decision parameters [q_0 and q_f are fixed!], and the terms in between involving four decision parameters. It turns out that [technical details are omitted, due to the limited space!] all but one $(2\eta - 1)$ eigenvalues of each hessian are nil $(= 0)$, and one is

strictly positive, equal to the trace of the hessian term at hand. Moreover, it can be shown that the net hessian hess(τ) posseses itself at least one zero-eigenvalue, *i.e.* it is positive semi-definite, too, this indicating that the function $\tau = \tau(q)$ is convex, *but not* strictly convex! As we shortly see, this is helpful in constructing the optimal trajectories.
Referring to the optimization problem (2) the supersaturation level at each switching section is confined to lie within an interval $\sigma_{\min,j} \leq \sigma_j \leq \sigma_{\max,j}$, where for growth phases: $\sigma_{\min,j} = \sigma_{\min}$, $\sigma_{\max,j} = \sigma_{\max}$, and for dissolution phases: $\sigma_{\min,j} = -\sigma_{\max}$, $\sigma_{\max,j} = -\sigma_{\min}$. Hence, considering equation (1e) (but also Figure 2) it is obvious that each point q_j can be associated a cone, as depicted in Figure 3, defined by

$$\mathcal{C}_j := \left\{ x \in \mathbb{R}^2_+ : x = q_j + \lambda_1 G^{(j)}_{\min} + \lambda_2 G^{(j)}_{\max},\ \lambda_1 \geq 0, \lambda_2 \geq 0 \right\},\ j = 0,1,2,\ldots,\eta.$$

where $G^{(j)}_{\min} := G^{(j)}(\sigma_{\min,j})$, and $G^{(j)}_{\max} := G^{(j)}(\sigma_{\max,j})$, with $G^{(j)}$ referring to the section j, see (1e). Obviously, $q_{j+1} \in \mathcal{C}_j$ and the supersaturation constraints of each phase $\sigma_{\min,j} \leq \sigma_j \leq \sigma_{\max,j}$ are mapped to linear constraints in $\mathbb{R}^{2\eta}_+$

$$\Gamma^{(j)}(q) := \left[G^{(j)}_{\min} \mid -G^{(j)}_{\max} \right]^T \cdot (q_j - q_{j-1}) \leq 0,\ \ j = 1,2,\ldots,\eta+1. \tag{5}$$

The discussion thus far leads us to the conclusion that the optimization problem (2) can be posed as a convex optimization problem in terms of the decision parameter $q \in \Theta \cap \Omega^\eta$ as follows

$$\underset{q \in \Theta \cap \Omega^\eta}{\text{minimize}}\ \tau(q)\ \text{ subject to } \Gamma^{(j)}(q) \leq 0,\ j = 1,2,\ldots,\eta+1. \tag{6}$$

3.2. Optimal solutions

The optimization problem for $\eta = 1$ [a trajectory with one switching only!] and $\Omega = \mathbb{R}^2_+$ turns out to be particularly important, since for a fixed crystallization sequence (e.g., growth phase followed by dissolution) its solutions $q = q^*$ and $\tau^* = \tau(q^*)$ turn out to be *unique*. The rigorous proof of this fact [which we again must omit!] uses the dual Lagrange function of the optimization problem (6), and is basically a consequence of the fact that in this case hess($\tau(q)$) is strictly positive definite, and, hence, $\tau = \tau(q)$ is *strictly convex*. The corresponding two optimal supersaturation levels σ^*_+ (growth phase) and σ^*_- (dissolution phase) are indeed important computational outcomes, as it turns out that with the sequence interchanged (i.e., now growth follows dissolution), q^* changes, but τ^*, σ^*_+ and σ^*_- don't.
Now consider the case with $\eta > 1$, and, again, for simplicity, disregard Ω^η by setting $\Omega^\eta = \mathbb{R}^{2\eta}_+$. As expected, the problem is not strictly convex, therefore, optimal solutions $q = q^*$ are no longer unique. Less obvious are probably the outcomes that $\tau^* = \tau(q^*)$ is identical as in the case $\eta = 1$, and, moreover, that in all growth and dissolution phases the corresponding optimal supersaturation levels match exactly to those σ^*_+ and σ^*_- of $\eta = 1$. This holds for any $\eta > 1$, independently of the switching sequence. Hence, the unique optimal solution of the minimum-time trajectory with one switching only can be indeed used for construction of all optimal solutions of any number or sequence of switchings. Any continuous piecewise linear trajectory connecting q_0 and q_f and consisting of a finite number of segments with the two slopes defined by σ^*_+ and σ^*_- is a *minimum-time trajectory*.
Figures 4 and 5 provide numerical results comparing the convex optimization algorithm (dashed lines) presented in this paper, with those proposed in the preceding work [1] (black-colored). The task consists in constructing minimum-time trajectories which lie in the area bounded by the two manifolds depicted by thin dashed lines in Figure 4. Figure 5 demonstrates clearly the fact that the global minimum time provided by convex optimization is

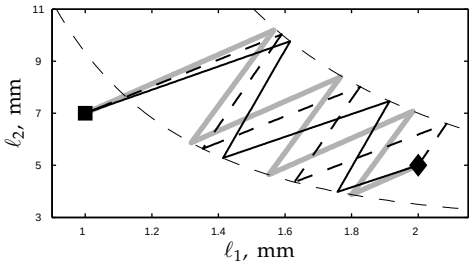

Figure 4: Path profile

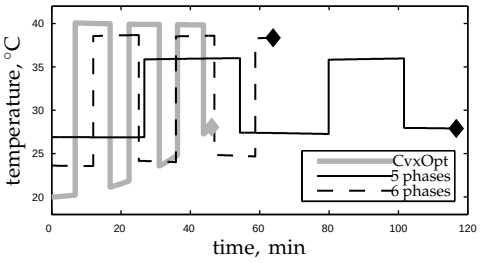

Figure 5: Temperature profile

notably smaller. Avowedly, it comprises more phases, and, additionally, it does not necessarily bounce at the switching manifolds [indeed, hard to see in the figure], which has been a requisite for the trajectories constructed by the algorithms in [1]. Note that seven has been the minimum number of phases of the convex optimal solution which could be hosted by the area specified by the switching manifolds in the figure. Compared to the counterpart shape manipulation algorithm of [1], the resulting strategy is somehow dual: while in [1] the switching conditions are defined by two concentration values [corresponding to the two bouncing manifolds!], and the optimization problem consists in optimizing the supersaturation levels within its limits, here, the supersaturation itself can take two values only, and the computational task consists in switching at the appropriate concentration level.

4. Conclusions

A strategy for crystal shape manipulation of multidimensional crystal particles based on a convex optimization formulation is proposed in this article. Optimal scenarios with subsequent growth and dissolution phases have been investigated. The resulting strategy is a bimodal constant supersaturation control policy, which is popular in practical crystallization engineering. The underlying two supersaturation levels are uniquely defined by problem data. The algorithms are developed for a two-dimensional single crystal particle, however, the extension to a population of crystal particles is basically a solved problem, too, a result which is to be published. On the other hand, shape manipulation for particles of a higher dimension can always be recast as a two-dimensional problem. This is due to the fact that the supersaturation is uniquely determined by the projection of the higher-order trajectory nto a two-dimensional plane, see [1].

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