Modeling of crystal morphology distributions. Towards crystals with preferred asymmetry

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A B S T R A C T

Exploitation of crystal symmetry is very important in formulation and efficient simulation of population balance models for crystal morphology. This work presents the first population balance model for morphology distribution considering the diversity of symmetry. In this model, we analyze the symmetry of a population of crystals using group theory and divide the population into various symmetry classes, which, in turn, is subdivided into various morphological forms. The internal coordinate vector for any given crystal can be symmetry reduced and can be grouped into various sets characterized by identical growth rates. It has been shown that the internal coordinate vector can be represented in such a way that only one internal coordinate needs to be treated dynamically for each set while all other coordinates remain invariant during growth. This leads to a very small number of dynamic internal coordinates and the effective dimensionality of the problem becomes very small, allowing simulation of a population of asymmetric crystals with minimal computational effort. It has been shown using this model that the concentration of more symmetric crystals invariably increases during the growth process. However, this natural gravitation of the crystal population towards more symmetric forms can be controlled by manipulating the supersaturation which has been shown using numerical examples.

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1. Introduction

We focus in this paper on cultivating, in a well-stirred crystallizer, geometrically asymmetric crystals with a preponderance of faces having properties of specific interest. The properties are linked to an application as, for example, in the promotion of bioavailability in pharmaceutical products, higher chemical activity of particles in synthetic catalysts, and so on. Asymmetric crystals, however, are constantly gravitating towards symmetry so that sustenance of asymmetry calls for ways to forestall this migration. We rely for this navigational effort only on the manipulation of supersaturation although other avenues have existed at least on an empirical basis particularly in industrial practice. However, the methodology we adopt will set the trail for more comprehensive approaches in a rational manner when quantitative understanding of other effects becomes available.

There is currently in the literature good understanding of the required mathematical framework for analyzing the behavior of a population of crystals growing in a stirred crystallizer (Dirksen and Ring, 1991; Zhang and Doherty, 2004; Ma et al., 2008; Borchert et al., 2009). However, such efforts have relied on the boons of symmetry so that the description of morphology requires only a very limited number of variables. The objective that we have set forth cannot, however, be met by imposing such constraints. We seek in this paper an approach built on exploiting basic features of an asymmetric crystal that serve to minimize the computational effort involved for cultivating asymmetric crystals. The strategy for this is built on minimizing the number of crystal dimensions that vary during growth. The appreciation of how such a minimization is actually accomplished requires geometrical insight of a faceted crystal.

It has been shown that a faceted crystal may be interpreted as the intersection of convex polyhedra, each bounded by a "family" of faces characterized by the same growth rate (in a common supersaturation environment), viz., the rate at which each face advances from an arbitrary reference point in a direction normal to itself. As the orientation of each crystal face remains fixed relative to crystal coordinates during growth, the interior angles between faces of the polyhedron representing a particular family is invariant with time. Since frequently some faces are slow growing relative to others, allowing the crystals to be viewed as two dimensional objects, we restrict our demonstrations to such
crystals for visual clarity. However, the methodology discussed in this article is not restricted to the two dimensional crystals alone and can readily be extended to three dimensional crystals by replacing polygons by polyhedra.

Our methodology consists in exploiting the symmetry properties of the polygons by elucidating the number of distinct time varying crystal dimensions. Towards this end, we provide a theoretical development that begins with defining a crystal state vector comprising all crystal faces and progress towards its description in terms of the minimum number of distinct time varying components in the vector. In what follows, various recent efforts for modeling crystal shape and morphology is recalled before attending to the issues of main concern in the paper.

2. Previous work

Control of crystal shape can be realized by changing the properties of the solution, namely by using additives (Weissbuch et al., 1991; Sangwal, 2007), changing the solvent (Davey et al., 1982) or in the simplest way by manipulating supersaturation (Liu and Bennema, 1994; Liu et al., 1995; Boerrigter, 2002). Thus the control of supersaturation presents an avenue for manipulating crystal shape towards a desired direction. However, a quantitative model based understanding of crystal growth is essential in order to achieve desired control in commercial applications.

Crystallizers are usually modeled using the population balance equation (Randolph and Larson, 1971; Myerson, 1993; Ramkrishna, 1985, 2000) considering only one internal variable. Often readily measurable quantities like volume, mass or diameter of the particle is used as an internal variable depending on the method of measurement used in the experiments. While such a simplistic one dimensional model is useful in predicting the size distribution of crystals, it has no means to predict crystal shape. Clearly, a multi-dimensional population balance model is required to describe the distribution of shape and size of a population of crystals.

Multidimensional model of a crystal population often recognizes crystals in terms of more than one characteristic dimension without invoking a faceted structure (Ma et al., 2002; Puel et al., 2003). However, recognition as a faceted structure is essential for applications like catalysis where it is advantageous to promote a specific face. Following the early work of Cardew (1985), Gadewar and Doherty (2004) considered crystals as faceted objects and a single crystal model was formulated considering appearance and disappearance of faces. Zhang and Doherty (2004) used this multidimensional description of a single crystal in a population balance model with the assumption that crystals of the same size must have the same shape. This assumption reduced the multidimensional description into a uni-dimensional PBE. Subsequently, Zhang et al. (2006) have explored many interesting features of the three dimensional single crystal model. Briesen (2006) described another technique for reduction of the two dimensional crystal population balance into a series of one dimensional PBEs.

Although the detailed morphological population balance model was formulated and solved (Ma et al., 2008; Wan et al., 2009; Borchert et al., 2009), quantitative modeling of real crystallizers could not be achieved as an essential property of particulate solid, asymmetry was ignored. Asymmetry is an important attribute of a particulate solid because along with size, it determines the specific surface for a given solid. The specific area of a symmetric shape is always less than the specific area of a corresponding asymmetric shape. Modeling of asymmetry using population balance has not been ventured so far as it is believed that considering asymmetry will lead to an unmanageable number of dimensions in the model. For example, Ma et al. (2008) considered symmetric crystals of potash alum which have 26 faces. They remarked that all 26 dimensions are needed if symmetry is not considered.

In this study, we model the growth process of asymmetric crystals using a population balance model. We demonstrate that the dimensionality of the population balance equation for growth does not necessarily increase by considering a population of asymmetric crystals. In order to formulate such a population balance model, we define and quantify the symmetry of a given crystal. Subsequently crystals are classified into various classes according to their symmetry. For each class, a separate population balance equation is written. It is shown that with this approach the dimensionality of the population balance equation does not exceed the number of independently growing faces.

This modeling effort also brings out the notion of evolution of symmetry of a population of crystals. It also shows that due to growth, a population of crystals always travels towards a more symmetric form. In the next section we shall discuss the model in detail, demonstrate the ideas using a numerical example, and present our conclusions.

3. Theory

Crystals are polyhedral objects which can have faces of more than one kind. Each kind is characterized by a distinct arrangement of atoms/molecules which leads to a specific growth rate. The faces that have identical arrangement of atoms grow at the same velocity and we shall refer to them as faces of the same family. Faces of different families grow at different rates and this difference in growth rates leads to morphological evolution.

Crystals are usually modeled in terms of a set of distances from an origin, the choice of which is closely related to the symmetry of the crystal. Symmetry of an object refers to the existence of one or more lines of symmetry about which rotation and/or reflection leaves the object unchanged. Maximum symmetry usually has a center of symmetry which can be chosen as the origin. For the less symmetric form, the choice of the origin depends on the extent of symmetry and will be discussed subsequently.

Now, consider a crystal comprising m families of faces with the ith family having fi faces, then the total number of faces of the crystal, denoted n, is given by

$$n = \sum_{i=1}^{m} f_i$$  \hspace{1cm} (1)

so that the vector of distances of all faces from a suitably chosen center, \( h \in \mathbb{R}^n \), may be written as a partitioned vector \( h = [h_1, h_2, \ldots, h_m] \). Where \( h_i \) represents the distances of faces of the ith family from the center and can be written as: \( h_i = [h_{i1}, h_{i2}, \ldots, h_{im}] \in \mathbb{R}^n \), \( i = 1, 2, \ldots, m \). If the growth rate of the kth face of the ith family is denoted \( H_{ik} \), then from the definition of the family, we have \( H_{1j} = H_{2j} = \cdots = H_{ij} = Z_j \). If further the crystal is symmetric, with the origin at the symmetry center, we would have \( h_{1j} = h_{2j} = \cdots = h_{ij} = Z_j \), \( i = 1, 2, \ldots, m \). In this case, the crystal state vector \( h \) may be replaced by the vector \( z \in \mathbb{R}^n \). Hence, there is a reduction of dimensionality of the crystal state vector from \( n \), which can be very large, to \( m \) which could be substantially smaller. We show below that this reduction in dimension is also enjoyed by asymmetric crystals, with a left-over time-invariant state vector whose dimension would depend on the extent of symmetry of the crystal.

Consider a completely asymmetric crystal with the ith family having \( f_i \) faces whose distances from some origin to be specified
are given by $h_{1,j}, h_{2,j}, ..., h_{k,j}$. By asymmetry, we imply that $h_{1,j} \neq h_{2,j} \neq ... \neq h_{k,j}$. From the definition of the family

$$H_{ij} = H_{kj}$$

(2)

from which we have, recognizing the dependence of the crystal face locations on time

$$\frac{d}{dt}(h_{ij} - h_{kj}) = 0$$

(3)

It is to be noted that the growth rate of a particular face is assumed to be independent of the size of the crystal which is true for most practical situations and is known as McCabe $\Delta L$ law. Now, integrating the above differential equation, we have

$$h_{ij} = h_{kj} + c_{ijk}$$

(4)

where $c_{ijk}$ is a constant of integration specific to the pair of $j$th and $k$th faces belonging to this $i$th family. Suppose we choose the $k$th face as a fixed reference face for the family and let $z_i = h_{kj}$, then we have $h_{ij} = z_i + c_{jk,i}$ and vectorially (suppressing the fixed index $k$)

$$h_i = z_i 1 + c_i, \quad 1 \equiv [1,1,...,1] \in \mathbb{R}^f, \quad c_i \in \mathbb{R}^f.$$  

(5)

Clearly, the time-variance of the vector $h_i$ is contained only in the scalar $z_i$ and therefore the number of differential equation needed to be solved in simulating the growth model is immensely reduced. However, the number density function is a density in $\mathbb{R}^f$, with $f_i - 1$ quantities in $c_i$ which, while invariant with time (for a specific crystal), can vary from crystal to crystal. Furthermore, the volume in $h_i$ space may be written as

$$dV = \prod_{j=1}^{k} dh_{ij} = dz_i \prod_{j=2}^{k} dc_{ji},$$

(6)

The argument presented above applies to each family of planes. The number of components in $c_i$ will depend on symmetry, an issue to which we will return following a discussion of the symmetry of the crystal. The largest face should be taken as the fixed reference face as it is the last face to disappear.

### 3.1. Symmetry of a crystal

The different arrangement of atoms on different planes originates from the different orientation of the planes that cut the crystal lattice. Although an infinite number of such planes can be imagined in a given crystal lattice, only a few of them are energetically favorable and hence only those planes need to be considered in any practical situation (Boerrigter et al., 2002). The orientation of the planes considered remains invariant during growth and hence the angular relationship between any two faces remains unaltered. This feature can be used to represent crystals in a unique and convenient way as in the discussion that follows.

Discussion of the symmetry of faceted crystals is simplified if we view such crystals as an intersection of polygons. If we consider only a particular family of planes, it is easy to see that such planes always form a polygon with known angles. Hence, a crystal can be thought of as a combination of intertwined polygons resulting from various families. We shall call the polygons generating a crystal as generating polygons or simply generators. Such a representation of a crystal consisting of only two families has been shown in Fig. 1.

In general, crystals can have complex shapes and a mathematical discussion and quantification of symmetry of such shapes is not straightforward. But the symmetry of a crystal can be discussed in terms of the symmetry of its generating polygons. The incentive for taking this approach lies in the ease with which the symmetry groups of polygons can be found. If the polygon is regular, its symmetry elements are readily available as the dihedral group (Lomont, 1959). If it is a non-regular polygon, symmetry exists for a few limited cases and symmetry groups for such cases can be found in a straightforward way. Hence, if we can establish a mathematical relation between the symmetry groups of the generating polygons to the symmetry of the crystal, we can readily find the symmetry of any crystal.

Now, consider the two generators, a square and a diamond, each having four lines of symmetry as shown in Fig. 2(a) and (b). We are concerned with a crystal which is produced from these two generators with a common geometric center. This situation is shown in Fig. 2(c). It is clear that the resulting crystal inherits all the symmetry axes of the generators and we shall refer to this situation as the case of 'maximum symmetry'. Now let us examine how various kinds of asymmetric shapes can be generated from these two generators. As the angle between any two kinds of planes is fixed during growth, the generators must be arranged in such a way that this angle remains the same. Thus, different arrangements differ only in the way one generator is translated with respect to the other. Hence, in order to explore various possible symmetry situations, we may start with the most symmetric case and translate one generator with respect to the other.

Translation of the diamond with respect to the square can happen in two possible ways: first, it may translate along any line of symmetry, as shown in Fig. 2(d). In this case the crystal will remain symmetric against this line of symmetry but loses all other lines of symmetry. It may also translate along a direction which is not a line of symmetry of either object. In that case, shown in Fig. 2(e), the crystal becomes completely asymmetric. Overall, this visual exercise shows the symmetry group of the crystal is the intersection of the symmetry groups of the generating polygons. This is an important conclusion and can be proved using group theory and is provided in Appendix.

![Fig. 1. Representation of an asymmetric crystal: (a) in terms of $h$-vector with respect to an origin; (b) and (c) in terms of polygons.](image-url)
3.2. Symmetry and the choice of origin

The choice of the origin is very important for a crystal of reduced symmetry. It not only produces the minimum possible dimension for \( h \) or \( c \), it also needs to be consistently defined from crystal to crystal. The choice is straightforward if the crystal contains two or more lines of symmetry where the intersection of the lines of symmetry is the natural choice. If the crystal contains only one line of symmetry, a suitable point can be chosen on that line as an origin. For example, the crystal shown in Fig. 2(d), the origin can be taken as the symmetry center of the rectangle that also lies on the line \( a_1 \). Even if the crystal is apparently asymmetric, as in Fig. 1(a), we have a unique choice which utilizes the symmetry of one of the generators. For this case, for example, the origin can be placed on the symmetry center of the rectangle.

3.3. Classification of a population of crystals into various symmetry classes

From the previous discussion and Fig. 2 it emerges that the symmetry of a crystal is solely dependent on the symmetry of its generators and the way they are combined. Hence, to classify a population of crystals in terms of symmetry, we need to prepare an exhaustive list of possible generators and all possible combinations of such generators. As the generating polygons have fixed angles, there are only a limited number of such generators for a given family. For example, as all the angles between the planes of the rectangle family is \( \pi/2 \), it produces polygons which can either be regular (square) with four lines of symmetry or equiangular (rectangle) with two lines of symmetry. As in most situations the crystal is composed of two to three families of planes and the number of faces in a particular family is known, such combinations are readily obtained. For example, in the case of rectangle and diamond, only four kinds of generators are possible: regular-diamond (RD), irregular-diamond (ID), regular rectangle (RR) and irregular rectangle (IR). All possible combinations using these four generators are shown in Table 1.

For every combination of generators, the crystal can have a different number of symmetry axes depending on the way they are combined. This can be explored in a similar fashion as shown in Fig. 2 and therefore we can classify the entire population into several symmetry classes.

3.4. Using symmetry to determine minimum number of internal coordinates

Any reflectional symmetry of a crystal has the potential to reduce the number of internal coordinates. A line of symmetry creates images for each internal coordinates of a given family and if an internal coordinate becomes the image of another in the same family, only one of them needs to be considered. If an internal coordinate forms a distinct image, separate internal coordinate is needed for it. If a face is normal to the line of symmetry, the internal coordinate corresponding to that face lies along the line of symmetry. In this case, the internal coordinate and its image coincide and separate internal coordinate is also needed for this case.

The minimum number of internal coordinates for a given family can be found by using all lines of symmetry of the crystal in a recursive manner. Starting with the unreduced internal coordinate vector, the first line of symmetry can be applied to get a reduced set. Then the second line of symmetry is applied on the reduced set to reduce it further. This process continues until...
all symmetry axes are accounted for. We denote by $f_j^i$ the number of coordinates for the $i$th family after $j$ lines of symmetry have been accounted for, so that $f_0^i$ would represent the number of coordinates before accounting for any symmetry. We also denote by $f_0^{ij}$ the total number of internal coordinates either forming a distinct image or lying along the line of symmetry for the $j$th line of symmetry. Now, because a symmetry element divides the crystal into two identical halves, the recurrence relation for $f_j^i$ is given by:

$$f_j^i = \frac{f_{j-1}^i + f_0^{ij}}{2} \quad (7)$$

For a crystal with $s$ lines of symmetry the minimum number of internal coordinates for $i$th family is therefore given by $f_s^i$. In the foregoing discussion we will always describe a crystal using minimum number of coordinates. The symmetry-reduced internal coordinates for crystals with four and one line of symmetry are shown in Fig. 3.

### 3.5. Morphological forms of a symmetry class

Higher growth rate of one face of a crystal with respect to its neighboring faces often leads to disappearance of that face from the crystal transforming it into a vertex. Therefore, for the crystals in the same symmetry class dimensionality of $z$ and $c$ can be different if one or more faces become virtual. Such a difference calls for subdivision of the population of crystals of a symmetry class into different morphological forms.

Various morphological forms for a given symmetry class can be generated from a parent morphological form, which contains maximum number of faces, by allowing faces to become virtual due to growth. All possible morphological forms in a given symmetry class can be obtained by exhausting all possible combinations of internal coordinates and ensuring that the resulting crystal encloses a space. To enclose space, no two adjacent internal coordinates of the crystal can have an angle of $2\pi$ or larger. Fig. 4 shows all possible morphological forms for the symmetry class that has one line of symmetry and composed of the two regular generators.

### 3.6. Dynamics of symmetry: accumulation of more symmetric forms

As discussed above, generation of one morphological form from another occurs due to transformation of a face from real to virtual and vice versa. Such transformations may also lead to change in the symmetry property. For example, if the rectangular face grows further in Fig. 4(f), a diamond is created which has four lines of symmetry instead of one. Transformations among various symmetry classes and morphological forms for a population of crystals consisting of one, two and four lines of symmetry have been shown in Fig. 5. Various morphological forms of the same symmetry class are enclosed in a thick lined box. Completely asymmetric crystals and a few morphological forms have been omitted for clarity but can be included without difficulty.

Population fluxes between various morphological forms and symmetry classes are observed in a population of crystals due to real to virtual or virtual to real transition of crystal faces. The nature of the transition depends on the relative growth rates of crystal faces which in turn depend on the supersaturation. Various population fluxes for the current case have been shown in Fig. 5. We observe from Fig. 5 that two morphological forms in

![Fig. 3](image1.png)

**Fig. 3.** Reduction of number of internal co-ordinates by considering symmetry of the crystal which is produced by combining regular diamond and square. (a) Completely symmetric case: eight faces are represented by two internal co-ordinates; (b) one symmetry axis case: eight faces are represented by using five internal co-ordinates. The symmetry center of the square has been chosen as center.

![Fig. 4](image2.png)

**Fig. 4.** Various possible morphological forms that may be produced due to disappearance of one or more faces for crystals of one line of symmetry.
For example, the morphological form 2a occurs on the boundary (e.g. 2b and 4b), only one subscript is used. If the morphological form does not distinguished by another subscript to the number density. The symmetric morphological forms increases as a result of passage through various symmetry boundaries. And during the growth process, the concentration of more symmetric morphological forms increases as a result of passage of population through various symmetry boundaries.

The detail with which morphology has been characterized may perhaps appear to be excessive for practical applications. For example, the distinction between 1b, 2b and 4b may appear to be excessive for practical applications. For example, the distinction between 1b, 2b and 4b may appear to be more elaborate and more self-consistent notation. In the current case, \( z \) has two components and we shall denote the internal coordinates corresponding to square and diamond faces as \( z_1 \) and \( z_2 \) respectively. Only one \( c \)-coordinate is needed in this case (to represent species 2a and 2b), represented by \( c \). The notations for various morphological forms are summarized in Table 2.

### Table 2

Notations for various morphological forms.

<table>
<thead>
<tr>
<th>Morphological form</th>
<th>Notation</th>
<th>Label</th>
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<tbody>
<tr>
<td>2a</td>
<td>( n_{2,1}(z_1, c, t) )</td>
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</tr>
<tr>
<td>2b</td>
<td>( n_{2,2}(z, c) )</td>
<td>2b</td>
</tr>
<tr>
<td>2c</td>
<td>( n_{2,3}(z, t) )</td>
<td>2c</td>
</tr>
<tr>
<td>4a</td>
<td>( n_{4,1}(z_1, t) )</td>
<td>4a</td>
</tr>
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<td>4b</td>
</tr>
<tr>
<td>4c</td>
<td>( n_{4,3}(z_1, t) )</td>
<td>4c</td>
</tr>
</tbody>
</table>

![Image](image.png)

**Fig. 5.** Various symmetry classes and morphological forms present in the system and their boundary flux. The species corresponding to the same symmetry class are enclosed in a thick lined box.

3.7. Model equations

At this stage the PBEs for various morphological forms may be formulated. For brevity, we shall consider only the blocks 2 and 4 shown in Fig. 5. Different symmetry classes will be represented by using the number of symmetry axes as subscript to the population and various morphological forms in a symmetry class is distinguished by another subscript to the number density. The second subscript represents the boundary on which a particular morphological form occurs. If the morphological form does not occurs on a boundary (e.g. 2b and 4b), only one subscript is used. For example, the morphological form 2a occurs on the boundary \( \beta_1 \) and therefore, the number density will be written as \( n_{2,\beta_1} \). But the morphological form 2b occurs in the domain itself and will be written as \( n_2 \). In a subsequent generalization we shall introduce a more elaborate and more self-consistent notation. In the current case, \( z \) has two components and we shall denote the internal coordinates corresponding to square and diamond faces as \( z_1 \) and \( z_2 \) respectively. Only one \( c \)-coordinate is needed in this case (to represent species 2a and 2b), represented by \( c \). The notations for various morphological forms are summarized in Table 2.

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where the internal coordinate \( h_{ij} \) is dependent on its neighbors, \( h_{i,j-1} \) and \( h_{i,j+1} \) and \( z_1 \) and \( z_2 \) are the angles between \( h_{i,j} \) \( h_{i,j-1} \) and \( h_{i,j+1} \) respectively and \( z_{12} \) is the angle between \( h_{i,j} \) \( h_{i,j-1} \) \( h_{i,j+1} \). We will denote such relations for the ith boundary by \( \beta_i \). Notations for various boundaries are shown in Fig. 5. For the current case \( z_1 = \pi/4 \) and \( z_{12} = \pi/2 \) for all internal coordinates. Therefore, the relations between the internal coordinates at
various boundaries can be written as

\[
\begin{align*}
\beta_1 : z_2 &= \frac{2z_1 + c}{\sqrt{2}} \\
\beta_2 : z_2 &= \frac{z_1 + c}{\sqrt{2}} \\
\beta_3 : z_2 &= \frac{z_1}{\sqrt{2}} \\
\beta_4 : z_2 &= \frac{2z_1}{\sqrt{2}}
\end{align*}
\]

(9)

Now, we have to consider the population fluxes across all these boundaries. Population flux occurs across a boundary if the growth velocity is directed towards the boundary, i.e., \( \mathbf{Z} \cdot \mathbf{n}_{\beta_i} \geq 0 \) where \( \mathbf{n}_{\beta_i} \) is the unit normal towards the boundary \( \beta_i \). If the velocity is directed away from the boundary, a discontinuous change occurs in the number density at the boundary in which the population on the boundary moves into the higher dimensional domain. At this point \( (\mathbf{Z} \cdot \mathbf{n}_{\beta_i}) = 0 \), the number density in the higher dimensional domain must satisfy an extra boundary condition corresponding to the population at the boundary to be specified below.

Consider the morphological form 2b for which the population balance equation in \( n_{2b}(\mathbf{Z},t) \), can be written as

\[
\frac{\partial n_{2b}(\mathbf{Z},t)}{\partial t} + \mathbf{Z} \cdot \nabla n_{2b}(\mathbf{Z},t) = 0
\]

(10a)

This particular morphological form has two boundaries \( (\beta_1 \text{ and } \beta_2) \) as shown in Fig. 5. These two boundaries will produce two boundary conditions when the population moves away from these boundaries, given by

\[
\begin{align*}
@\mathbf{Z} \cdot \mathbf{n}_{\beta_1} &= 0 : \nabla_{\mathbf{Z}} n_{2b}(\mathbf{Z},t) |_{\beta_1} = n_{2b}(z_1, t) \delta\left(z_2 - \frac{2z_1 + c}{\sqrt{2}}\right) \\
@\mathbf{Z} \cdot \mathbf{n}_{\beta_2} &= 0 : \nabla_{\mathbf{Z}} n_{2b}(\mathbf{Z},t) |_{\beta_2} = n_{2b}(z_1, t) \delta\left(c - z_2 - z_1\right)
\end{align*}
\]

(10b)

(10c)

We notice that the number density corresponding to the population on a boundary is written as a density on the corresponding coordinate planes rather than on the boundary itself. Hence, it is necessary to project the number density on the boundary to one on the coordinate plane. The corresponding factor is given by \( \nabla_{\mathbf{Z}} \mathbf{h} \) where \( \mathbf{h} \) and \( \mathbf{Z} \) represent the boundary and the coordinate plane respectively. We also need to establish dimensional consistency between number densities defined in the spaces of different dimensionality using Dirac-delta function as shown in Eqs. (10b) and (10c). Similarly, the equations for the morphological forms 2a and 2c can be written as

\[
\begin{align*}
2a: & \quad (\mathbf{Z} \cdot \mathbf{n}_{\beta_i} \geq 0) \quad \frac{\partial n_{2a}(\mathbf{Z},t)}{\partial t} + \mathbf{Z} \cdot \nabla n_{2a}(\mathbf{Z},t) = \mathbf{v}_{\beta_i} \cdot \nabla_{\mathbf{Z}} n_{2a}(\mathbf{Z},t) |_{\beta_i} \\
2c: & \quad (\mathbf{Z} \cdot \mathbf{n}_{\beta_i} \geq 0) \quad \frac{\partial n_{2c}(\mathbf{Z},t)}{\partial t} + \mathbf{Z} \cdot \nabla n_{2c}(\mathbf{Z},t) = \mathbf{v}_{\beta_i} \cdot \mathbf{n}_{\beta_i} n_{2a}(\mathbf{Z},t) |_{\beta_i}
\end{align*}
\]

(11)

(12)

We notice that although the morphological form 4a occurs at a boundary of 2c, it does not imply a boundary condition corresponding to the receding boundary because the flux is one way. The equations for the morphological forms 4a, 4b and 4c can be written in a similar fashion

\[
\begin{align*}
4a: & \quad (\mathbf{Z} \cdot \mathbf{n}_{\beta_i} \geq 0) \quad \frac{\partial n_{4a}(\mathbf{Z},t)}{\partial t} + \mathbf{Z} \cdot \nabla n_{4a}(\mathbf{Z},t) = \mathbf{v}_{\beta_i} \cdot \mathbf{n}_{\beta_i} n_{4a}(\mathbf{Z},t) |_{\beta_i} \\
4b: & \quad (\mathbf{Z} \cdot \mathbf{n}_{\beta_i} \geq 0) \quad \frac{\partial n_{4b}(\mathbf{Z},t)}{\partial t} + \mathbf{Z} \cdot \nabla n_{4b}(\mathbf{Z},t) = \mathbf{v}_{\beta_i} \cdot \mathbf{n}_{\beta_i} n_{4b}(\mathbf{Z},t) |_{\beta_i} \\
4c: & \quad (\mathbf{Z} \cdot \mathbf{n}_{\beta_i} \geq 0) \quad \frac{\partial n_{4c}(\mathbf{Z},t)}{\partial t} + \mathbf{Z} \cdot \nabla n_{4c}(\mathbf{Z},t) = \mathbf{v}_{\beta_i} \cdot \mathbf{n}_{\beta_i} n_{4c}(\mathbf{Z},t) |_{\beta_i}
\end{align*}
\]

(13)

Now, to complete the set of equations, we need to provide the mass balance equation relating the concentration in the solution phase with the population. As the volume change of dissolution may be considered small, the total dispersion volume can be considered constant. Hence, the concentration of solute in the solvent phase, \( x(t) \), can be expressed in terms of population density as

\[
x(t) = \frac{m_{\text{total}} - \rho V_s(t)}{V_s(t)}
\]

(14)

where \( m_{\text{total}} \) is the total mass of solid per unit volume (in solution and as particles), which remains constant throughout the process. \( V_s \) is the volume of a particle per unit volume of crystallizer and \( \rho \) is the density of the solid. \( V_s \) can be expressed in terms of population density as

\[
V_s(t) = \int \int \int n_{2a}(z_1, c, t)V(z_1, c, t) dz_1dc + \int \int \int n_{2b}(z_1, c, t)V(z_1, c, t) dz_1dc + \int \int \int n_{2c}(z_1, c, t)V(z_1, c, t) dz_1dc
\]

(15)

where \( V(z, c, t) \) is the volume of a crystal with internal coordinates given by \( z,c \), the expression for which can be found in Cardew (1985). The supersaturation is expressed as:

\[
s(t) = \frac{x(t) - x^s}{x^s}
\]

(18)

where \( x^s \) is the solubility of the solute. The growth rates of various faces are observed to have complex functionality with supersaturation and generally expressed as a combination of several power law functions of the type \( Z_i = a \rho^{b_i} \) over the range of supersaturation. We shall discuss specific forms of growth functions in the next section. This complete set of equations can be solved for a given initial asymmetric seed population and detail morphological evolution can be traced.

4. Case study: evolution of a population of asymmetric crystals

To simulate the growth of a population containing crystals with two types of faces, namely square and diamond, we need the supersaturation dependent growth rates of both the faces. For this purpose, we have taken growth functions which are similar to the 110 and 011 faces of Acetamophen crystals respectively (Ristic et al., 2001) and are shown in Fig. 6. Other parameters needed for simulations are shown in Table 3. The model equations (Eqs. (10)–(18)) contain both integral and partial differential equations. The partial differential equations have been solved by using the method of characteristics and an iterative approach has
been taken to converge it with the mass balance equation. In the following, we shall first consider a seeded batch cooling crystallizer under isothermal condition and then discuss the effects of various temporal profiles of temperature during growth.

4.1. Seeded batch cooling crystallizer under isothermal condition

\( T = 348 \text{ K} \)

In this crystallizer, the small seed particles of a given mass and size distribution grow up to a specified final mass. During this process the temperature is held constant and supersaturation drops due to consumption of material. The initial seed has been considered to be purely of morphological form \( n_2(z, c, t) \) \((2b)\), normally distributed in its domain with mean and variance given in Table 3. During crystal growth, various boundary fluxes are observed which lead to changes in the populations of various morphological forms. The changes in the zeroth moments of various populations have been considered as a suitable measure of evolution and expressed as the number fraction of a given morphological form. The evolution of the zeroth moments for the current case has been shown in Fig. 7 where the fractional numbers have been plotted against the relative change in the mass of the crystals given by

\[
\frac{m(t) - m_0}{m_f - m_0} = \frac{m(t)}{m_f}
\]

where \( m_0 \) and \( m_f \) are initial and final mass of crystals and \( m(t) \) is the mass of crystals at any given time. The corresponding time evolution of supersaturation has been shown in Fig. 8.

It can be noted from Fig. 6 that the rectangular face grows faster than the diamond face at initial supersaturation, \((\sigma \sim 0.18)\). This gives rise to a flux of population through the boundaries \( b_2 \) and \( b_3 \) which creates the morphological forms \( n_2, b_2(z, t) \) and \( n_4, b_3(z, t) \) respectively. This has been shown in the left most portion of Fig. 7. As growth continues, the supersaturation depletes and when the supersaturation reaches a value of \( \sim 0.13 \), a switch in growth rate occurs (see Fig. 6). At this point the diamond face starts to grow at a faster rate than the square face and a flip in the directionality of the flux occurs. Due to this reverse flux, the total population of \( n_2, b_2(z, t) \) are added to the domain of \( n_2(z, c, t) \) in a discontinuous manner as shown in Fig. 7. Similarly, \( n_4, b_3(z, t) \) convert into \( n_4(z, t) \) instantaneously. Although

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density of solid</td>
<td>1200 kg/m³</td>
</tr>
<tr>
<td>Saturation concentration at ( T = 348 \text{ K} )</td>
<td>1 kg/m³</td>
</tr>
<tr>
<td>Number of seed crystals</td>
<td>( 1.4678 \times 10^7 \text{ m}^{-3} )</td>
</tr>
<tr>
<td>Initial seed distribution ( n_2(z, c, 0) )</td>
<td>((5 \times 10^{-4}, 5 \times 10^{-4}, 2.5 \times 10^{-5}, \sigma^2 = 10^{-6}))</td>
</tr>
<tr>
<td>Initial volume fraction of seed</td>
<td>( 6.608 \times 10^{-6} )</td>
</tr>
<tr>
<td>Initial mass of seed crystals</td>
<td>( 7.5129 \times 10^{-3} \text{ kg/m³} )</td>
</tr>
<tr>
<td>Final mass of crystalline solids</td>
<td>( 120 \times 10^{-3} \text{ kg/m³} )</td>
</tr>
<tr>
<td>Parameters for Van’t Hoff’s plot</td>
<td></td>
</tr>
<tr>
<td>(equilibrium solubility vs. temperature)</td>
<td>( \frac{D S_{diss}}{R} = 5.77, \frac{D H_{diss}}{R} = 3674 \text{ K}^{-1} )</td>
</tr>
</tbody>
</table>
4.2. Seeded batch crystallizer operating at a fixed value of supersaturation ($\sigma = 0.1$)

We notice from Fig. 6 that the growth rate of the rectangular surface becomes smaller than that of the diamond surface below relative supersaturation 0.14 and therefore if we can keep the supersaturation to a value lower than that, mostly the diamond face will grow and the population will traverse towards the morphology $n_{2b}^1(z_2,c,t)$ from the parent form $n_2(z,c,t)$. In this case no morphological form with four lines of symmetry is created. The evolution of various morphological forms due to growth at a fixed supersaturation of 0.1 is shown in Fig. 9. In this figure we notice that only the less symmetric form $n_{2b}^1(z_1,c,t)$ has been created and no crystal with four lines of symmetry has been formed. To keep the supersaturation at a fixed value, the temperature has been varied according to the saturation curve of the crystalline solid. The temperature dependence of solubility is given by Van’t Hoff’s plot necessary parameters for which are provided in Table 3. The corresponding variation in temperature has been shown in Fig. 10.

4.3. Control of symmetry related properties in a seeded batch crystallizer

In many practical applications, symmetry related properties like surface area and sphericity are important. For example, for pharmaceutical powders, the bioavailability of a particular face might be more than the other faces and higher fractional coverage of that face is desirable. In the current model, we consider the rectangular face to have some favorable property and in the following example we investigate the variation of the fractional coverage of the rectangular surface for different mode of operation of the crystallizer.

In Fig. 11 we have plotted the evolution of the fractional surface area of the rectangular surfaces for the isothermal case along with two cases of fixed supersaturation. For the isothermal case, the initial supersaturation is high and the growth rate of rectangular surface is higher. Therefore, the relative importance of the rectangular face decreases until the supersaturation reaches below $\sim 0.14$. After this point, the rectangular face dominates and reaches a value of 100%. If the value of the supersaturation is held at a value higher than this critical value of 0.14, the rectangular surface always grows faster than the diamond surface and its morphological importance reduces monotonicly. Similarly, if the supersaturation is held at a value higher than this critical level, the morphological importance increases monotonicly to 100%.

Another important property of the particulate solid which affects downstream processing is sphericity. The evolution of the average sphericity of the crystal population for the three cases considered has been shown in Fig. 12. It may be noted that for all three cases, the average sphericity of the population evolves to a value which is close to that of a square from the higher sphericity of octagons. However, the transient behavior of the system is very different depending on the supersaturation environment. For the case of $\sigma = 0.1$, the initial population quickly goes to the limiting value whereas for the case of $\sigma = 0.18$, this approach is much gradual and retains a much higher value of sphericity for a considerably long time. For the isothermal growth, the sphericity
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varied symmetry, crystals are classified into several symmetry classes and morphological forms. Although the theory requires a morphological characterization which may be too elaborate from a practical viewpoint, a suitable regrouping of populations can always be made so that the classifications are experimentally resolvable.

This strategy has been used to simulate a population of asymmetric crystals efficiently. It has been shown that during the growth, the crystals of lower symmetry transferred into more symmetric morphological forms due to appearance and disappearance of faces. However, the reverse is shown to be impossible and therefore the number density of more symmetric crystals monotonically increases inside the crystallizer. We have demonstrated that it is possible to drive a population of asymmetric crystals towards a desired symmetry by controlling the supersaturation. Different temperature profiles have been considered and it has been shown that the control of sphericity and fractional coverage of a desired surface can be achieved using this model.

Acknowledgments

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Appendix. Symmetry group of the region common to two polygons

Let us consider two polygons $P_1$ and $P_2$ which can be thought of as an infinite set of points and hence the common region of both the polygons can be denoted by $P_c$ where $P_c = P_1 \cap P_2$. The symmetry groups of regular polygons are known as dihedral groups and are well documented in the literature (Lomont, 1959).

The matrix representations of such symmetry groups are also available. Now, let us assume that the cardinality of the symmetry groups of $P_1$ and $P_2$ are $n$ and $m$ respectively. We can now denote the symmetry group of $P_1$ by $S_1 = \{s_{11}, \ldots, s_{1n}\}$ and that of $P_2$ by $S_2 = \{s_{21}, \ldots, s_{2m}\}$.

Let us assume that $P_c$ is symmetric with respect to the operation $s_1$, where: $s_1 \in S_1 - (S_1 \cap S_2)$. Now, let us consider a point $p$ such that $p \in P_c$ and let us denote the image of the point $p$ after the symmetry operation $s_1$ as $p'$. Now, the symmetry operation $s_1$ ensures that $\{p, p'\} \in P_c \forall p$ but as $s_1 \notin S_2$, the condition $\{p, p'\} \in P_2$ is not necessarily satisfied unless $s_2 \in (S_1 \cap S_2)$.

Hence, $s_2$ is a symmetry operation of $P_c$ if $s_2 \in (S_1 \cap S_2)$.

References