Population balance modeling of faceted asymmetric crystals

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Summary: Asymmetry is an important aspect of crystals that governs many properties like bulk density, surface area etc. However, modeling of asymmetric crystals is not trivial as it immediately calls for the quantification of symmetry. Also with the current models, the amount of computational effort required for solving population balance equation for asymmetric crystals is impractically high. In this report we systematically model a population of asymmetric crystals by analyzing and quantifying the symmetry of a population of crystals using symmetry groups of polygons. We also present a new strategy for simulation in which no extra computational effort is required for asymmetric crystals.

Keywords: CRE for pharmaceutical production, High value-added products, Multiphase and particulate reactors, Dynamics and control of chemical reacting systems.

In this paper we discuss a population balance model for asymmetric crystals produced in a batch cooling crystallizer. Crystals are often required to be grown up with some specific properties enhanced; for example, solubility, bioavailability etc. and such properties often depend on the shape of the crystal as well as on the degree of asymmetry. Although many factors affect shape and asymmetry of a crystal, probably the most important one is the supersaturation environment. At a given supersaturation, different faces of a crystal grow at their own characteristic rates and thereby modify the morphology of a crystal[1]. In this report we shall concentrate on controlling crystal shape and asymmetry by manipulating supersaturation.

The first step towards modeling of asymmetric crystals is to identify the symmetry group of a given crystal of any arbitrary shape. Crystals are composed of various kinds of faces and each kind signifies a specific family of fixed crystallographic directions. Hence, a crystal can be conveniently represented by using the polygons generated by various crystallographic families as shown in Fig. 1. With this representation, crystals become the intersecting zone of such polygons which maintains constant angularity. The symmetry group of a crystal therefore given by the intersection of the symmetry groups of the generating polygons. Symmetry groups of polygons being known[2], symmetry group of any given crystal can be found easily by using this procedure. Figure 1 shows two different combinations of the same kinds of crystallographic planes resulting in crystals of different symmetry aspects.

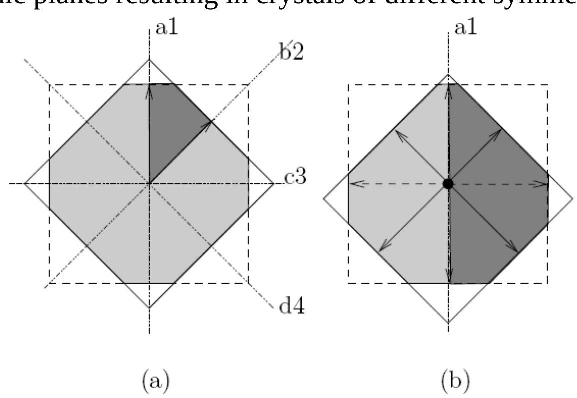

Figure 1: Representation of a crystal in terms of its generating polygons.

After the symmetry group of a crystal is known, we need to describe it by a set of internal coordinates. A crystal can be described conveniently by a set of distances[3] of all faces from a fixed center inside the

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crystal, (shown in Fig. 1), denoted by $\mathbf{h}$. The choice of center is critical as this determines the number of internal variables, which in turn determines the computational effort required. In all previous studies on morphology, presence of only the most symmetric form of crystal (e.g. Fig. 1(a)) is assumed because this enforces equality among distances and obviates the need for considering them as separate coordinates. For less symmetric or asymmetric cases, which we shall consider in our model, the center should be placed on a suitable location on the line of symmetry (Fig. 1(b)) if such a line exists. In absence of any symmetry line, the center should be placed by considering the symmetry of the polygon corresponding to a particular family of crystallographic planes. This strategy guarantees minimum number of internal coordinates for the crystal.

Even the minimum number of internal coordinates can be menacingly high for asymmetric crystals. But it is possible to reduce them dramatically using the following strategy. The faces of a given crystal can be classified into various crystallographic families characterized by identical growth rates. This feature leads to partitioning of $\mathbf{h}$ into $[\mathbf{h}_1, \mathbf{h}_2, ..., \mathbf{h}_m]$, where m families exist. Now, for i^{th} family, $\dot{H}_{1,i} = \dot{H}_{2,i} = \cdots = \dot{H}_{f_i,i}$ where $\dot{H}_{j,i}$ is the growth rate of j^{th} face of i^{th} family. Integrating the above relation, we get:

$$\dot{H}_{j,i} = \dot{H}_{k,i}$$

$$\frac{d}{dt}(h_{j,i} - h_{k,i}) = 0$$

$$h_{j,i} = h_{k,i} + c_{jk,i}$$

where $c_{jk,i}$ is the constant of integration. It can be clearly seen from the above equation that the vector $\mathbf{h}_i$ can be written in terms of only one representative time dependent coordinate and a set of time invariant coordinates. Denoting the time dependent coordinate for i^{th} family as z_i, we can write, $\mathbf{h}_i = [z_i, \mathbf{c}_i]$ where $\mathbf{c}_i$ is the vector of time invariant asymmetry dimensions. Hence, the internal coordinate space of a population of crystals can be written as $\mathbf{h} = [\mathbf{z}, \mathbf{c}]$ where the maximum length of $\mathbf{z}$ is given by number of crystallographic families present. The c-coordinates can be disregarded during computing the evolution and hence a population of asymmetric crystals can be simulated without any extra effort.

Following these strategies, the population balance model for asymmetric crystal can be developed easily. The entire population of crystals is divided into sub-populations according to symmetry and separate PBE is developed for each species. Faces with higher relative growth rates disappear from the crystal surface which leads to continuous flux of less symmetric crystals towards more symmetric form. This feature, although observed in experiments, predicted quantitatively for the first time. With this model we also suggest the optimum path for supersaturation for a preferred value of asymmetry related property.

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