

Crystal Growth Simulations: a new Mathematical Model based on the Minkowski Sum of Sets

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Abstract. Realistic crystal growth simulators can give information on what would be the surface structure of a crystal grown under specific physical-chemical conditions, avoiding the real growth in a laboratory. By suitable upscaling, simulations can therefore be useful for industrial purposes to foresee and control the final product. We initially present Monte-Carlo micro-scale simulations based on spatial stochastic processes; we followed the Hartman and Perdok method for the classification of facets, using Growth Units with cubic shape. For a better description of a self-similar growth of a faceted surface, we propose a new mathematical micro-scale model based on the Minkowski sum of sets and we present some results obtained by the numerical implementations.

1 Introduction

The initial shape of a crystalline nucleus in homogeneous nucleation is the so called *Wulff Shape*, i.e. an equilibrium shape [1] [2]. The Wulff shape has been widely studied and has been described by means of various analytical and geometrical models [12] [14]. By slight modifications of the equilibrium conditions, the crystal can grow [3]. Hartman and Perdok [9] described a method to classify the possible surface structures depending on the energetic bonds available for the Growth Units close to the interface. According to the Kossel model we firstly consider the shape of the Growth Unit being squares (in 2D) or cubes (in 3D) and the surface of a growing crystal is classified in one of the three structures depicted in Fig. 1.

On the macro-scale, growth rates have been studied for the three surface structures, giving higher rates for kinked surfaces and lower rates for flat surfaces [1]. On the atomic scale, growth is the result of three simultaneous processes that bring Growth Units from the mother phase, that we assume to be gaseous, to the crystal (solid) phase. Specifically, Growth Units firstly attach to the surface of the crystal creating energetic bonds with other Units on the interface but without being directly absorbed (*adsorption*). Then they

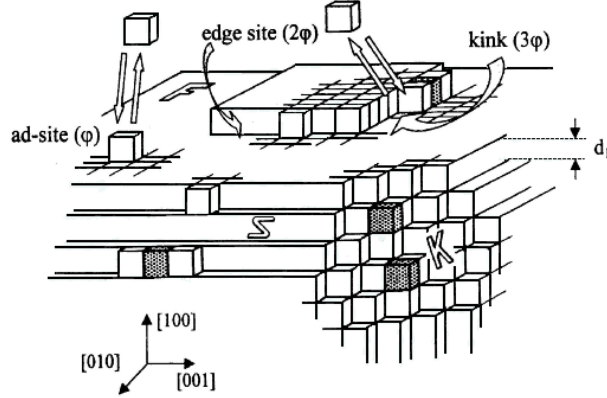


Fig. 1. The three surface structures according to the Hartman and Perdok method; K=Kinked, S=Stepped and F=Flat.

diffuse and collide on the surface, until they join together to form a more stable profile (*surface diffusion*). Finally they can possibly return to the mother phase (*desorption*).

On a macroscopic scale, the different surface growth rates can be summarized by assuming a space-time dependent growth field. Mathematical (multiple scales) models and simulations for macroscopic growth can be found in [6] [5] [11], with particular reference to polymer crystallization.

2 Simulation for Growth Units with cubic shape

In order to simplify the geometry of the problem we first consider Growth Units having cubic shape.

Russo and Smereka [15] proposed a deterministic simulator for faceted crystals based on Level Set methods. Gilmer and Bennema [8] implemented the crystal growth simulations by means of Monte-Carlo techniques, modelling only the adsorption and desorption of the Growth Units by the Ising model. Our approach is to describe the adsorption, the surface diffusion and the desorption via different stochastic processes, but still using Monte-Carlo techniques for simulations.

Adsorption We model the fall of the cubic Growth Units on a face of the crystal by a *spatial point process* [7]. The intensity of the process is not constant on the whole surface, but it depends on the surface free energy, i.e. on the number n of energetic bonds available for each site. Consider only the interactions with the nearest neighbours (according to Kossel), hence $n =$

$1, \dots, 5$. In particular, conditional upon the knowledge of the crystal surface at time t^- , the process is simulated at any time t with a non-homogeneous Poisson Process. Outcomes indicate the surface sites where the Growth Units are adsorbed [13].

Surface diffusion Let (x, y) be the location on the surface of a Growth Unit at time t , Fig. 2. The location of the Growth Unit at time $t + \Delta t$ will be (x, y) with probability p_0 or one of the four neighbouring locations with probability p_1, \dots, p_4 , respectively.

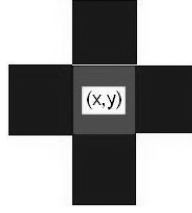


Fig. 2. Surface Diffusion

Probabilities p_0, p_1, \dots, p_4 depend on the surface free energy and therefore on the number of available energetic bonds, counted for each site at the call of the function, and on whether the neighbouring sites on (x, y) are free or not. For every temporal step of size Δt , i.e. an iteration, each unit can move up to one position; hence Growth Units diffuse with speed $\frac{1}{\Delta t}$. The probabilities p_0, p_1, \dots, p_4 depend also on the surrounding field through variables like temperature and supersaturation; the functional dependence could be made explicit through experimental laws or theoretical models that consider the mean velocity of a moving cell. For the simulation we allow the movement on the surface only to Growth Units that belong to the upper surface layer. Furthermore we allow the units to “fall” in case they move sideways on a site that does not belong to the upper surface layer. Finally we prevent the units from moving outside the study region by setting the probability of moving out equal to 0.

Desorption Growth Units are not immediately absorbed in the crystal volume, but they are firstly adsorbed and they possibly diffuse on the surface. Furthermore there exists a probability that the Units return to the mother phase. Probabilities of desorption are again chosen depending on the number of available energetic bonds for the site.

We run the simulation in 2 dimensions, Fig. 3, and 3 dimensions, Fig. 4.

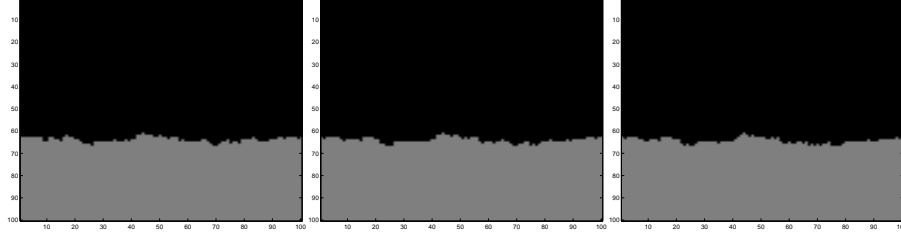


Fig. 3. 2D simulation at times $t = 51, 53, 55$ of an initially flat face (length=100).

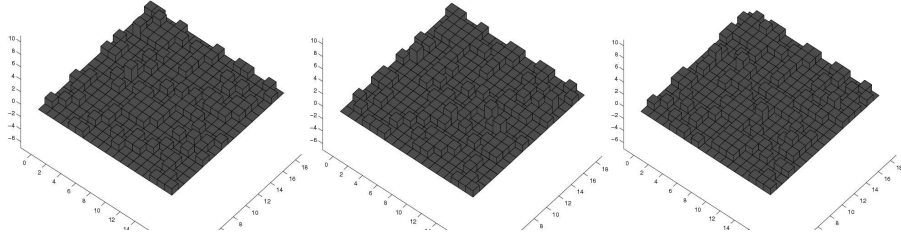


Fig. 4. 3D simulation at times $t = 7, 8, 9$ of an initially flat square face of dimension 18×18 .

In 3 dimensions we simulated the evolution of two adjacent non-coplanar faces, Fig. 5. In this case there arise problems for keeping the edges between adjacent facets; actually we solved the problem by a suitable interpolation that preserves the continuity of the facet.

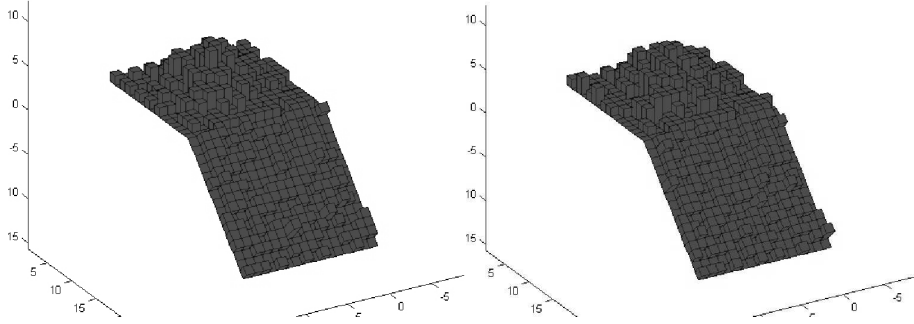


Fig. 5. Evolution of two adjacent facets, forming an angle of $\frac{3}{4}\pi$. One facet is initially flat, the second has a screw dislocation.

3 Modelling by the Minkowski sum of sets

We propose here another growth model which avoids the problems related to the preservation of edges in a self-similar growth process.

The growth of a crystal such that its shape is maintained in time, i.e. at every time t the crystal is similar to a fixed given set, may be modelled by the so called *Minkowski sum* of sets [10].

Definition 1. Given two sets A and B in \mathbb{R}^d , the Minkowski sum of A and B is defined as the set:

$$A \oplus B := \{a + b : a \in A, b \in B\}.$$

For simplicity we analyze the case when the crystal is a convex polygon in \mathbb{R}^2 , but the same arguments hold also in \mathbb{R}^d .

We remind that two polygons are said *similar* if they have equal angles and the corresponding sides are proportional.

Let Θ^t be the crystal at time t and θ be the “basic crystal”, i.e. the shape of the crystal we are referring to. The set θ is similar to Θ^t , but in scale small enough such that it may be used to represent the growth during an infinitesimal time interval Δt .

Let a and b be two sides of θ , and a' and b' be the two corresponding sides of Θ^t . (See Fig. 6). Let O be a given point in θ (even on the boundary) and fix it as the origin of a coordinate system in \mathbb{R}^2 . We assume that Θ^t e θ are equioriented.

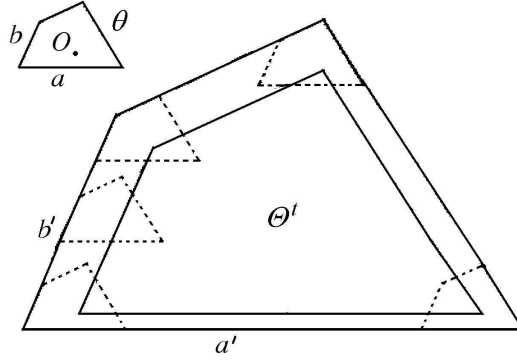


Fig. 6. Section of a growth

It follows that the set $\Theta^{t+\Delta t} := \Theta^t \oplus \theta$, obtained as Minkowski sum of Θ^t and θ (i.e. “overlapping” at every point of $\partial\Theta^t$, the set θ centered in O), is similar to Θ^t , since the corresponding angles are, obviously, congruent, and the sides

are proportional. In fact, if a'' and b'' are the two new sides corresponding to a and b , we have that $a'' = a + a'$, $b'' = b + b'$, and so

$$\frac{a''}{a} = 1 + \frac{a'}{a} = 1 + \frac{b'}{b} = \frac{b''}{b}.$$

Now, we relate this with the field of growth rates determining the growth.

CASE 1: the absolute value G of the growth rate is constant and it is the same in each direction perpendicular to the sides (*crystallographic directions*).

Let v_1, \dots, v_n be the vectors representing such directions. Then, the basic crystal θ is the convex polygon with n sides (if it exists), given by the intersections of the halfplanes H_1, \dots, H_n having normal unit vectors v_1, \dots, v_n , respectively, and each one with distance $G\Delta t$ from the origin (see Fig. 7).

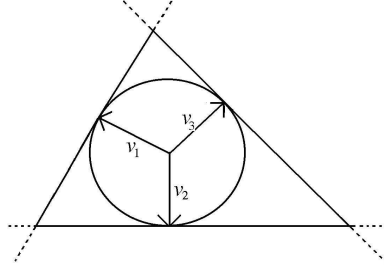


Fig. 7. An example of basic crystal obtained by the assumption of homogeneous growth in three directions.

In other words, we obtain a polygon that can be circumscribed about a circle with center in O ; thus the distance between a new side and the corresponding one is the same for each side, as expected by the assumption of homogeneous growth.

Summarizing, at a some time t_0 a crystal θ is born with incentrum O ; at time $t_1 = t_0 + \Delta t$ the crystal is given by $\Theta^1 = \theta \oplus \theta$; at time $t_k = t_0 + k\Delta t$, by $\Theta^k = \Theta^{k-1} \oplus \theta$, and so on. Time by time, Θ^k is similar to θ .

CASE 2: the absolute value G of the growth rate depends only on the growth directions.

In this case we expect that θ can not, in general, be circumscribed about a circle centered at O (if $n > 3$), since the growth is not homogeneous and the crystal expand in different way in different directions.

Hence, now, θ is given by the intersection of the halfplanes H_1, \dots, H_n , with distance $G_1\Delta t, \dots, G_n\Delta t$ from the origin, respectively, where G_1, \dots, G_n are the absolute values of the growth rate in the different n crystallographic directions (see Fig. 8).

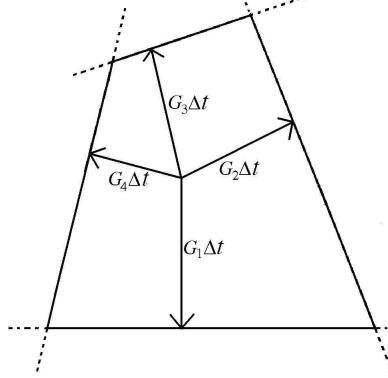


Fig. 8. An example of basic crystal obtained by the assumption of non homogeneous growth in four directions.

3.1 Inhomogeneous growth

Let us consider the case when the growth rate G of a crystal (convex polygon with n sides) does not depend any more only on the growth direction, but is varying in time and space: $G = G(x, t)$ $x \in \mathbb{R}^d$, $t \in \mathbb{R}_+$. Thus, we want now to adapt our model, by suitable Minkowski sums of sets, to more general situations, in which the shape of the crystal may change during its growth. In this case the crystal is not similar to a given fixed set any more, but the number of sides might even change.

The basic idea consists of summing time by time suitable sets depending on the growth law. If the change of shape depends only on time, then, at every fixed time t , we have to determine the set θ that we have to sum at every point of Θ^t as above. In other words, at time $t' = t + \Delta t$, we obtain $\Theta^{t'} = \Theta^t \oplus \theta_1$; at time $t'' = t' + \Delta t$, we obtain $\Theta^{t''} = \Theta^{t'} \oplus \theta_2$, and so on, where the sets θ_i 's will have a number of sides n_i having distance from the origin depending on time

$$\Delta r_j = \int_t^{t+\Delta t} G_j(s) ds, \quad j = 1, \dots, n_i.$$

Instead, if the growth rate depends also on the space location, we may not claim any more that, at time $t + \Delta t$, $\Theta^{t+\Delta t} = \Theta^t \oplus \theta$ for some θ .

Simulations in this very general cases could be quite complicated; nevertheless if the growth is locally homogeneous, then the model becomes more tractable, by representing it in a double scale framework (see also [6]).

Specifically, let us assume that, at any time t , Θ^t can be divided into a finite number of subsets $\Theta_1^t, \dots, \Theta_k^t$ which grow homogeneously, in such a way that we may apply, locally, the above models. Then, at a fixed time t , we have to determine only k suitable sets θ_i , $i = 1, \dots, k$, and so we obtain

$$\Theta^{t+\Delta t} = \bigcup_{i=1}^k \Theta_i^t \oplus \theta_i.$$

Note that if the growth field $G(x, t)$ may be controlled, then it is possible to forecast the shape of the final produced crystals (see [4] for an application to polymer crystallization).

Example 1. Let $v_1 = (1, 0)$, $v_2 = (0, 1)$, $v_3 = (-1, 0)$, $v_4 = (0, -1)$, and $G_1 = G_2 = G_3 = G_4 = 1$. Then it follows that θ is given by the square with side length $2\Delta t$, center $= (0, 0)$ and edges $(-\Delta t, -\Delta t)$, $(\Delta t, -\Delta t)$, $(\Delta t, \Delta t)$, $(-\Delta t, \Delta t)$. Suppose that both the v_i 's, and the G_i 's are constant, up to time \bar{t} . Thus, $\Theta^{\bar{t}}$ is given by the square with side length $2\bar{t}$ and edges $(-\bar{t}, -\bar{t})$, $(\bar{t}, -\bar{t})$, (\bar{t}, \bar{t}) , $(-\bar{t}, \bar{t})$. (See Fig. 9).

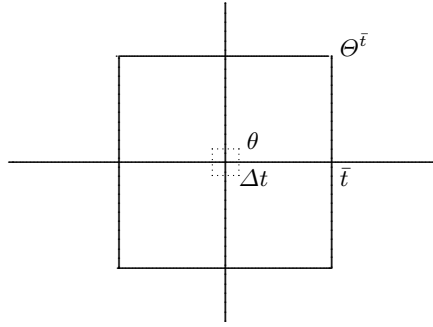


Fig. 9. Crystal as in Example 1 at time \bar{t} .

Suppose now that, at time \bar{t} , the v_i 's are unchanged, while

$$G_2 = 1, \quad G_4 = 0, \quad G_1 = \begin{cases} 1 & \forall (x, y), x < 0 \\ 5 & \forall (x, y), x \geq 0 \end{cases}, \quad G_3 = \begin{cases} 2 & \forall (x, y), x < 0 \\ 1 & \forall (x, y), x \geq 0 \end{cases}.$$

Hence, we may divide $\Theta^{\bar{t}}$ into two parts, both growing homogeneously during $[\bar{t}, \bar{t} + \Delta t)$. So, at every point of $\partial\Theta^{\bar{t}}$ with $x < 0$, we sum the rectangle θ_1 with edges $(-2\Delta t, 0)$, $(\Delta t, 0)$, $(\Delta t, \Delta t)$ and $(-2\Delta t, \Delta t)$; while at the other points of the boundary we sum the rectangle θ_2 with edges $(-\Delta t, 0)$, $(5\Delta t, 0)$, $(5\Delta t, \Delta t)$ and $(-\Delta t, \Delta t)$. In conclusion, at time $\bar{t} + \Delta t$, $\Theta^{\bar{t}+\Delta t}$ is given by the rectangle with edges $(-\bar{t} - 2\Delta t, -\bar{t})$, $(\bar{t} + 5\Delta t, -\bar{t})$, $(\bar{t} + 5\Delta t, \bar{t} + \Delta t)$ and $(-\bar{t} - 2\Delta t, \bar{t} + \Delta t)$. (See Fig. 10).

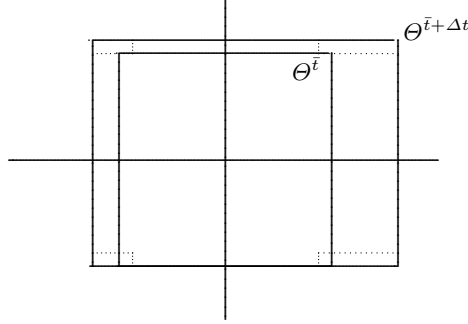


Fig. 10. Crystal as in Example 1 at times \bar{t} and $\bar{t} + \Delta t$. The dotted rectangles represent θ_1 and θ_2 .

3.2 Simulations

We consider again the three processes of adsorption, surface diffusion and desorption for bi-dimensional simulations. We assume that the growth starts from a nucleus having triangular shape, which grows by deposition of triangular Growth Units. The initial nucleus and the Growth Units are similar triangles (i.e. same angles and proportional sides) and the shape can be freely chosen by the user. Growth directions are perpendicular to the facets and the growth is homogeneous with respect to time. Furthermore we allow to choose the attach point of the Growth Units, so that we can simulate the growth for a spatially non-homogeneous velocity field. Note that, due to the surface diffusion process, some Growth Units may “jump” from a side to the neighbouring one.

With this new model, angles are kept during the growth, as it can be seen in Figs. 11, 12, 13.

We leave to subsequent papers simulations when the growth rate varies both in space and time, according to the model of Section 3.1.

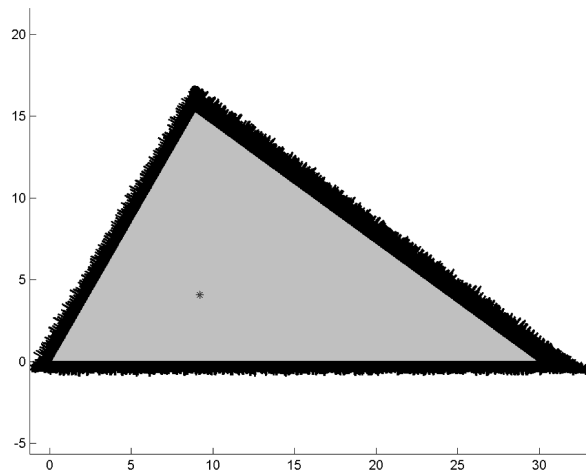


Fig. 11. Growth by only adsorption. The side on the x-axis measures 30 and the two adjacent angles measure $\pi/3$ and $\pi/5$ respectively. The star represents the attach point referred to the Growth Units. The number of iteration is 700.

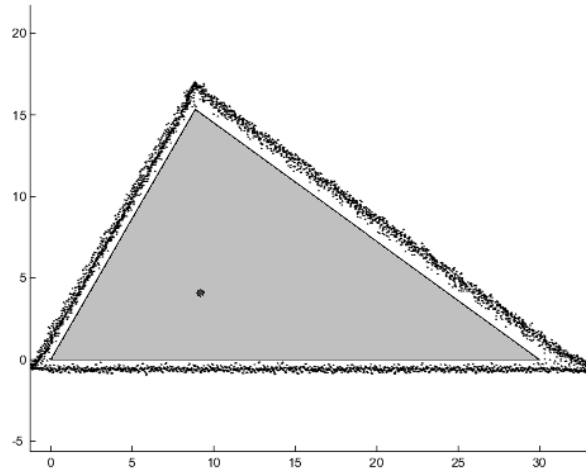


Fig. 12. The same as before, except that only the layer of Growth Units on the interface is depicted.



Fig. 13. Growth by adsorption, surface diffusion and desorption.

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References

1. F. Abbona, La crescita delle facce. In: Meccanismi della crescita cristallina: fondamenti e applicazioni, D. Aquilano, G. Artioli, M. Moret (eds), *Università degli Studi di Milano*, Milano, 2003.
2. D. Aquilano, G. Sgualdino, L'equilibrio cristallo-fase madre: introduzione ai concetti base e implicazioni sulla crescita. In: Meccanismi della crescita cristallina: fondamenti e applicazioni, D. Aquilano, G. Artioli, M. Moret (eds), *Università degli Studi di Milano*, Milano, 2003.
3. R. F. Brebrick, Phase equilibria. In: Handbook of crystal growth, vol. 1, D. T. J. Hurle (ed), *North Holland*, 1993.
4. M. Burger, V. Capasso, A. Micheletti, Optimal control of polymer morphologies, *J. Engineering Math.*, vol. 49, pp. 339-358, 2004.
5. M. Burger, V. Capasso, C. Salani, Modelling multi-dimensional crystallization of polymers in interaction with heat transfer, *Nonlinear Analysis: Real World Applications*, vol. 3, pp. 139-160, 2002.
6. V. Capasso (ed), Mathematical Modelling for Polymer Processing. Polymerization, Crystallization, Manufacturing. Serie "Mathematics in Industry", vol. 2, *Springer*, 2002.
7. N. A. C. Cressie, Statistics for Spatial Data, *Wiley*, New York, 1993.
8. G. H. Gilmer, P. Bennema, Computer simulation of crystal surface structure and growth kinetics, *Journal of Crystal Growth*, vol. 13/14, pp. 148-153, 1972.
9. P. Hartman, W. G. Perdok, On the relations between structure and morphology of crystal, *Acta Crystallogr.*, vol. 8, pp. 49-52, 1955.
10. G. Matheron, Random sets and integral geometry, *John Wiley and Sons*, New York, 1975.
11. A. Micheletti, M. Burger, Stochastic and deterministic simulation of nonisothermal crystallization of polymers, *J. Math. Chem.*, vol. 30, pp. 169-193, 2001.
12. S. Osher, B. Merriman, The Wulff shape as the Asymptotic Limit of a Growing Crystalline Interface, *UCLA CAM report*, 97-30, 1997.
13. S. Patti, Modelli Matematici e Simulazione Numerica della Crescita di Cristalli, MSc thesis, *Università degli Studi di Milano*, 2004.
14. D. Peng, S. Osher, B. Merriman, H. Zhao, The geometry of Wulff Crystals Shapes and its relations with Riemann problems, *UCLA CAM Report*, 98-51, 1998.
15. G. Russo, P. Smereka, A level set method for the evaluation of faceted crystals, *Siam J. Sci. Comput.*, vol. 163, No. 1, pp. 51-67, 2000.