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Crystal structure and crystal growth: I. The influence of internal structure on morphology: a reply

ERIC DOWTY

Department of Geological and Geophysical Sciences
Princeton University, Princeton, New Jersey 08540

The following points raised by Hartman seem to require some clarification.

(1) As the method of computing attachment energy in the PBC method has been changed since the original publication (Hartman and Perdok, 1955), and is now the same as in the direct method I proposed (Dowty, 1976; this method will be referred to as the surface-of-least-bonding or SLB method), the predictions of the two methods are ideally expected to be the same in the majority of cases. The numerical evaluations of "HP attachment energy" in the specific examples given in my paper are invalid, as is my objection to the PBC method on the grounds that it does not take full account of the symmetry. It should be noted, however, that early explanations of the success of the Donnay-Harker method published by Hartman and Perdok (*e.g.* Hartman and Perdok, 1956) are not completely correct, since they introduce unnecessary assumptions.

(2) Aside from the fact that the template fraction is measured across an explicitly-defined surface of least bonding, it differs from the Hartman attachment energy in being divided by the crystal energy (the total bond energy in a slice was intended to include the bonds holding that slice to the substrate). Such values are readily converted to physically meaningful attachment energies for individual faces by multiplying by an empirically-derived crystal energy. Attachment energies derived in this way should be much more accurate than those derived by direct crystallographic calculation, when the model used for bond energies is incomplete (*e.g.* first-order bonds only in an ionic crystal).

(3) My use of a slice of indefinite thickness was probably an error. In modern growth theory, layers are usually assumed to have thickness *d* or less, and visible steps are attributed to the pile-up of such layers.

(4) My hypothesis that "the number of blocks which go to make up a layer nucleus will be about the same on all faces" is probably also incorrect, as suggested by Hartman (personal communication). It is consistent neither with classical nucleation theory, nor with the concept that relative growth rates of faces can be predicted from the template fractions.

(5) As Hartman correctly points out, my Figure 1 does not illustrate a redefinition of *F*-, *S*- and *K*-faces, but the roughening of a face which is structurally an *F*-face. My conception of *S*- and *K*-faces follows that given by Hartman in his discussion. Nevertheless, these face types can be redefined using template fractions only, as follows: If a face can be constructed from two and only two other faces in such a way that the template fraction of the combination is less than that of the smooth or complete face, the face will be an *S*-face; if the template fraction of a combination of three or more faces is less than that of the smooth face or the combination of two faces, the face will be a *K*-face; otherwise it will be an *F*-face. The compound faces are constructed in the way illustrated in several papers on the PBC method and elsewhere (*e.g.* Hartman, 1973).

These definitions merely specify approximately the conditions under which sub-faces would ideally be set up in the midst of the face in question if we started, for example, with a smooth polished surface. Alternative and possibly more precise definitions could be made on the basis of the Wulff construction (Bennema, 1973). As in the PBC theory, such compound faces are not likely to be present on a crystal grown continuously from a small seed. Thus if one is concerned with predicting the ideal growth shape using the Wulff construction and template fractions or attachment energies (*e.g.* Hartman, 1973), it is unnecessary to recompute the template fraction for *S*- and *K*-faces, since that for the smooth (non-compound) face can only be higher than that for the compound face.

However, a purely structural definition of the different types of faces does not necessarily predict the mode of growth in all cases, because the entropy factor is neglected; *F*-faces may grow by a rough or non-singular mechanism at high temperature.

(6) I believe the utility of the SLB method remains unchallenged; its chief merit lies in the fact that it is a

relatively rapid, direct, and objective method of determining quantities used in crystal-growth analyses, and it can be carried out without the time- consuming and arbitrary process of defining periodic bond chains. I do not concede that the SLB method in principle has any limitations which are not also present in the PBC method. In both methods, preliminary results (ranking of faces, identification of surface levels) are obtained using first-order bonds. More exact evaluations of bond energies in ionic crystals can subsequently be carried out by complete electrostatic summation in either method, although a direct summation is appropriate in the SLB method, whereas a modified Madelung method can be applied in the PBC method. Such direct summations are in progress for some simple crystals. The current limitation of the SLB computation methods to planar surfaces can be overcome by consultation of projections, when necessary.

Since the final ranking of forms is done in the PBC method by comparing attachment energies, and since these energies (no matter how they are defined) may be calculated directly without the necessity of defining periodic bond chains, I contend that PBC's do not have fundamental importance in crystal growth. PBC's are not necessary to predict the surface structure or mode of growth either, as explained above in point 5. This is not to imply that PBC analyses are invalid; the bond chains can obviously be used as an intermediate step in more quantitative calculations, and they have some value in qualitatively understanding the morphology. Again, the predictions of the two methods are expected to be the same in most cases.

I developed the SLB method as an alternative to the PBC method for several theoretical and practical reasons. One of the theoretical reasons, the method of computing attachment energies, has been shown by Hartman to be no longer valid, but most of the other theoretical reasons, and all the practical reasons are, I believe, unchanged.

References

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