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Double crystals

Brian Wecht,* Megan Barber and Jennifer Tice

c/o Professor Frank Morgan, Department of Mathematics, Williams College, Williamstown, MA 01267, USA. Correspondence e-mail: frank.morgan@williams.edu

The lowest-energy way to enclose and separate two planar regions of prescribed areas is found, where the energy is given by the l^1 norm ('Manhattan metric'), in which horizontal and vertical directions use less energy than other directions, as in some crystals. With the assumption that interfaces carry a fraction λ of the energy of exterior faces, it is proved that there are three possible types of energy-minimizing double crystals. The dependence of these three types on λ as well as the ratio of the areas of the two regions is discussed, and some paths for further study are suggested.

1. Introduction

There are situations that occur in nature in which one might have double crystals (bicrystals) of some material with an interface of positive energy. One such example is when a 'stacking fault' occurs (see, for example, Hammond, 1990). Here, there is a break in the translational symmetry which is caused by having one crystal translated by a vector that is not a lattice translation. Stacking faults occur when translations that break the symmetry are stable (although not global) equilibria. Usually, these occur by symmetry reasons for translations that are rational fractions of a lattice translation.

Another example of positive interface energy is in a merohedral twin, such as occurs in pyrite. Pyrite crystals form double crystals in which one crystal structure is rotated by 90° from the other around a twofold axis. These do not resemble our model (for pyrite, the interface is curved), although they are a good example of when double crystals in $\mathbf{R}^2$ could occur.

A final example of positive interface energy occurs when there are impurities along the interface. Thus, we have three simple situations for which our model applies: stacking faults, merohedral twins and impurities along the interface.

For our mathematical model, we determine the shape of energy-minimizing double crystals in the case where a single crystal (Wulff shape) is a square or cube, as in table salt. It is incidentally interesting to note that, as Gary Kuhnhenn (University of Eastern Kentucky) pointed out to us, the shape of single salt crystals might *a priori* be a result of cleavage instead of crystal growth. However, this would not explain why most grains are cubical rather than rectangular or our observation of double crystals. A version of the question of what energy-minimizing double crystals look like has been answered by the SMALL '93 Geometry Group (French *et al.*, 1993), included in Morgan *et al.* (1998). Under the hypothesis that the interface cost equals the exterior boundary cost, they found three types of minimizing double crystals when all ratios R of the areas B/A are explored at constant total area $A + B$. See Fig. 1.

To test their findings, they took some electron-microscope photos of double salt crystals (Fig. 2). These pictures match up with their results qualitatively and in Morgan *et al.* (1998) it was suggested that a model with deeper physical reality would assume that the interface carries a fraction λ of the energy of the exterior boundary. Physically, then, λ is the ratio of the interfacial energy per unit length $\gamma_{(AB)}$ to the surface energy per unit length $\gamma = \gamma_{(A)} = \gamma_{(B)}$ of the same material (A and B) (temperature is taken to be 0 K if not all directions are on the 2D Wulff shape).

In this paper, we consider this refined model. We seek the lowest-energy way to enclose and separate two regions of prescribed areas when the horizontal and vertical directions are cheaper than any other direction and the interface carries a fraction λ of the energy per unit length of the faces. That is, the energy of a face with unit normal (x_i) is proportional to $\sum |x_i|$ and the energy of an interface with unit normal (x_i) is proportional to $\lambda \sum |x_i|$, where $0 < \lambda \leq 1$.

We model our proof after that of Morgan *et al.* (1998). Existence and regularity generalize almost immediately; however, other proofs require new arguments. Our main theorem, Theorem 1, provides three types of minimizing double crystals. These minimizers are similar to the three types found in Morgan *et al.* (1998), but their dimensions depend on λ. In particular, when the interior boundary carries less energy than the exterior, the first two types have longer interfaces. The ratio R of areas at which the double crystal changes type also depends on the size of λ and, in fact, when λ is small enough, type II will not occur at all.

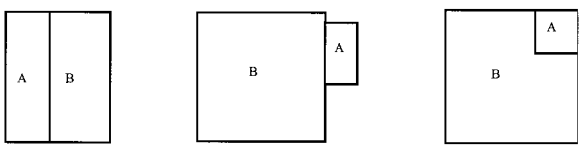


Figure 1
The three types of minimizing double crystals found in Morgan *et al.* (1998).

1.1. Plan

We will first present our main theorem (Theorem 1). Then we will discuss the open question concerning the shape of double crystals in $\mathbf{R}^3$. In particular, we will present some difficulties we have encountered in trying to generalize our findings in $\mathbf{R}^2$ to $\mathbf{R}^3$.

1.2. References

Additional references are provided by Taylor (1978, 1992), and Morgan (1998, ch. 10) and their bibliographies.

2. The main theorem

Theorem 1 provides the three types of double crystals and describes under what conditions each type will occur. Lemma 1 gives an example of how the proof of the more general case differs from the proof of the $\lambda = 1$ case.

Theorem 1. Consider two areas $0 < A \leq B$, a norm $\Phi(x_1, x_2) = |x_1| + |x_2|$ and a weighting factor λ $(0 < \lambda \leq 1)$. An energy-minimizing double crystal consisting of regions with areas A and B, where the energy (per unit length) of the boundary with unit normal n between either region and the exterior is $\Phi(n)$ and the energy (per unit length) of the boundary between the two regions is $\lambda\Phi(n)$, must be a type I, II or III, as shown in Fig. 3. Moreover, as the ratio R of areas (B to A) increases, as in Fig. 4, when

$$1 \geq \lambda > \lambda_0 = 1 + 2 \times 2^{1/2} - (5 + 4 \times 2^{1/2})^{1/2} \approx 0.56,$$

the crystal will change from a type I to a type II to a type III, and when $0 < \lambda \leq \lambda_0$, the crystal type goes directly from type I to type III and type II will not occur.

Remark 1. For the three types of Fig. 3, elementary calculus computations show that $x = [2(A + B)/(2 + \lambda)]^{1/2}$ and $y = (2A/\lambda)^{1/2}$. The shape ratios of width to height, $r_A^{\rm I} = (1 + \lambda/2)/(1 + R)$, $r_B^{\rm I} = (1 + \lambda/2)/(1 + 1/R)$ and $r_A^{\rm II} = \lambda/2$ all decrease as λ decreases and the cheaper interface gets longer.

Remark 2. Let R be the ratio between areas B and A. Elementary computations show that if $1 < \lambda \leq \lambda_0$ then, for

$$1 < R \leq R_\lambda = \{8 + 4\lambda + [(8 + 4\lambda)^2 - 16(\lambda^2 - 4\lambda - 12)]^{1/2}\}/8,$$

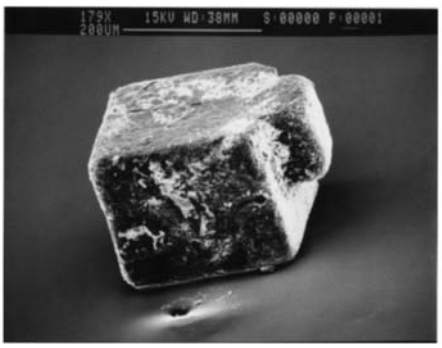
type I is cost-minimizing and, for $R \geq R_\lambda$, type III is cost-minimizing.

Let

$$\mu = [32 + 32(2\lambda)^{1/2} - 16\lambda + 40\lambda^2 - 8 \times 2^{1/2}\lambda^{5/2} - 12\lambda^3 + 8 \times 2^{1/2}\lambda^{7/2} - 2\lambda^4 - 2 \times 2^{1/2}\lambda^{9/2} + \lambda^5][16\lambda(\lambda - 2)^2]^{-1}.$$

If $\lambda_0 < \lambda \leq 1$, then, for $1 < R \leq 2/\lambda$, type I is cost-minimizing, for $2/\lambda < R \leq \mu$, type II is cost-minimizing and, for $R \geq \mu$, type III is cost-minimizing. See Fig. 4.

(*a*)



(*b*)

Figure 2
Electron-microscope photographs (Morgan *et al.*, 1998) of table salt crystals show shapes similar to those of Fig. 1.

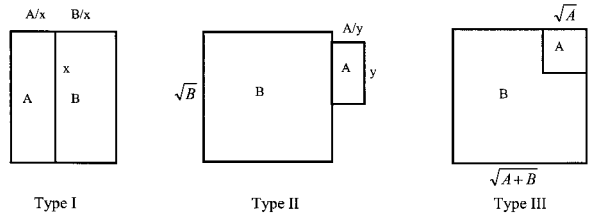


Figure 3
The three types of energy-minimizing double crystals for $0 < \lambda \leq 1$. For the type I crystal, $x = [2(A + B)/(2 + \lambda)]^{1/2}$ and, for the type II crystal, $y = (2A/\lambda)^{1/2}$.

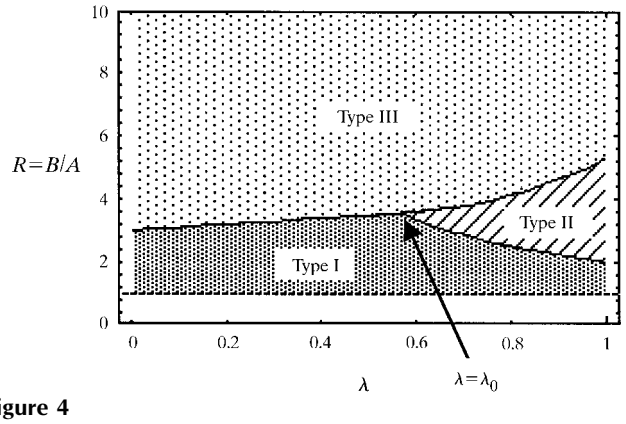


Figure 4
The cost-minimizing double crystal according to λ and $R = B/A$. The type indicated in each section of the graph represents the lowest-energy double crystal.

Proof sketch. The proof, given completely in Wecht *et al.* (1995), generalizes the proof of the special $\lambda = 1$ case of Morgan *et al.* (1998). First one shows for a general norm Φ that a minimizer exists and consists of portions of the Wulff shape and possibly other Φ-minimizing curves [Morgan *et al.* (1998, section 4); Wecht *et al.* (1995, section 3)]. For our special Manhattan norm, it is proved that all faces and interfaces may be taken to be horizontal or vertical. A proof that cost is a strictly increasing function of the area of either region of a double crystal implies that there are no empty spaces inside [Morgan *et al.* (1998, section 5); Wecht *et al.* (1995, section 4)], although at this point in the argument each crystal may have several component subregions. Certain 'simple subregions' are classified into 24 types [Morgan *et al.* (1998, Proposition 6.4); Wecht *et al.* (1995, Proposition 5.4)]. Most types are eliminated as in Lemma 1 below. Next it is shown that each crystal consists of just one simple subregion. These simple regions fit together only in the three ways of Fig. 3.

We now prove Lemma 1 as an example of the additional complications of not assuming $\lambda = 1$.

Lemma 1. A cost-minimizing double crystal has no simple subregion of the types shown in Fig. 5.

Proof. Suppose we have one of the two types of subregions mentioned in Lemma 1 for which the exterior boundary is the bold line of Fig. 6. Let the length of the left wall of the subregion be a and the length of the right wall be b. Then, if $\lambda a < 2b$, shift both the left and right walls to the right, maintaining area. By comparing the cost of the removed walls with the cost of the added walls, it is clear that this operation will reduce cost. Likewise, one can verify that, when $\lambda a > 2b$, moving the walls in the opposite direction from above will reduce cost. Finally, when $\lambda a = 2b$, one can move walls without reducing cost until either the right wall collides with another wall, reducing cost, or the subregion changes into a different combinatorial type. In the latter case, we have shown that similar operations can be performed on the new type of subregion, thus reducing cost. When the exterior boundary of the subregion is the nonbold line in Fig. 6, similar arguments also hold. Therefore, the original crystal was not cost-minimizing.

Note that a factor of λ comes into the proof, since changing a wall from an interior to an exterior boundary alters its cost. For the $\lambda = 1$ case, plainly no such consideration was necessary. Thus, in the proof of this lemma, it was necessary to make alterations in the work that had been performed for the simpler case.

Remark 3. One could also consider a model for two different crystals in which the exterior of the first, the exterior of the second, and the interface between them all had different costs a, b and c. Note that now the surface energies per unit length are different: $a = \gamma_{(A)} \neq b = \gamma_{(B)} \neq c = \gamma_{(AB)}$. Physically, this is the most general case. At the MAA Student Workshop on Soap Bubbles and Salt Crystals by Frank Morgan in Orlando in January 1996, students Laura Glaessger and Mike Nimchek computed that, for two adjacent congruent rectangles of unit area, each should have

$$\text{width}^2 = (a + b + c)/(2a + 2b)$$

and

$$\text{height}^2 = (2a + 2b)/(a + b + c).$$

More generally, if $R = B/A > 1$, then

$$\text{height}^2 = [2A(a + Rb)]/(a + b + c)$$

and (for A)

$$\text{width}^2 = [A(a + b + c)]/[2(a + Rb)].$$

Thus, the width/height ratio of A is $(a + b + c)/[2(a + Rb)]$. Notice that, again, as the interface energy c decreases, the length of the interface (the height of the crystal) increases. One suggestion for further research is to take this more general case into account and find a result similar to Theorem 1.

3. The 3D conjecture

The shape of double crystals in $\mathbf{R}^3$ remains an open question. Some preliminary work has been performed on this problem by Megan Barber, Eric Boeckx, Chris Connell, Brad Lackey, Trevis Litherland, Joe Shive, Jennifer Tice and Brian Wecht, at the 1995 Institute for Mathematics and its Applications (IMA) graduate conference at the University of Illinois at Urbana–Champaign. Using elementary calculus arguments, they proved Theorem 2, which gives the dimensions for the three-dimensional analogs of types I, II and III planar double crystals.

Theorem 2. Consider two volumes A and B ($A \leq B$), the norm $\Phi = |x| + |y| + |z|$ (so that now three orthogonal planar directions are cheaper than any others), and the weighting factor λ ($0 < \lambda < 2$) on the area of the interfaces. Here, λ is defined as before: if the surface energy per unit area is $\gamma = \gamma_A = \gamma_B$ and the interface energy per unit area is γ_{AB}, then $\lambda = \gamma_{AB}/\gamma$. Assume that the cost-minimizing double

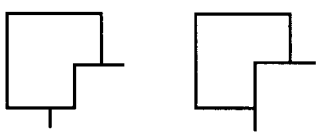


Figure 5
Two types of simple subregions that cannot occur in a cost-minimizing double crystal.

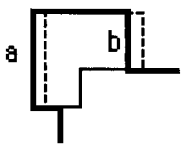


Figure 6
The subregion of Lemma 1 where $\lambda a < 2b$, and the exterior is the bold line.

crystal is one of the three types of double crystal of Fig. 7. If the crystal is type I, it consists of two connected rectangular boxes with dimensions

$$x = [2(A + B)/(\lambda + 2)]^{1/3}$$

$$y = [(\lambda + 2)^2 B^3/4(A + B)^2]^{1/3}$$

$$z = [(\lambda + 2)^2 A^3/4(A + B)^2]^{1/3}.$$

If the crystal is type II, it has a rectangular box of dimensions $d = (2A/\lambda)^{1/3}$ and $e = (\lambda^2 A/4)^{1/3}$ on the face of a cube. If the crystal is type III, then it consists of a cube in the corner of a larger cube. Furthermore, as in the planar case, the value of λ and the volumes of the two regions will determine which of these three double crystals is cost-minimizing.

Note 1. Here, as in $\mathbf{R}^2$, the area of the interface increases as λ decreases. For type I, the shape ratios

$$r_A^{\mathrm{I}} = (z/x) = (1 + \lambda/2)/(1 + R)$$

and

$$r_B^{\mathrm{I}} = (y/x) = (1 + \lambda/2)/(1 + 1/R),$$

where $R = B/A$. For Type II, $r_A^{\mathrm{II}} = e/d = \lambda/2$.

Proving that the minimizer is one of the three types in Fig. 7 appears to be quite difficult. First of all, we do not know, as we do for the planar case, that every surface in the double crystal must be either Φ-minimizing or a portion of the boundary of the Wulff shape. Even for soap bubble clusters in $\mathbf{R}^3$, which have a simpler norm, it is apparently not true that all surfaces are either Φ-mimimizing (area-minimizing) or a portion of the boundary of the spherical Wulff shape.

Even if we did know that every surface was Φ-minimizing or a portion of a cube, we could not conclude that each Φ-minimizing surface may be replaced by a finite number of surfaces oriented in cheap directions, as we did for the curves in $\mathbf{R}^2$. Consider a Φ-minimizing tilted rectangular region bounded by four line segments, as in Fig. 8(*a*). We could replace the Φ-minimizing surface with a series of 'stairs' of surfaces oriented in cheap directions for two opposing line segments, but then we would violate the boundary given by the other two line segments (Fig. 8*b*).

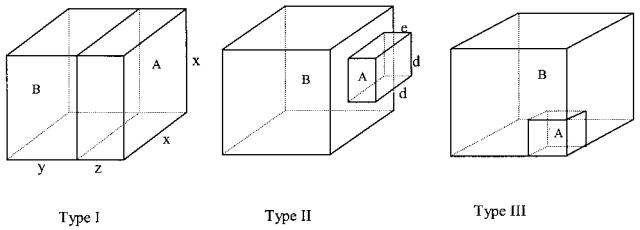


Figure 7
The three conjectured cost-minimizing double crystals in $\mathbf{R}^3$.

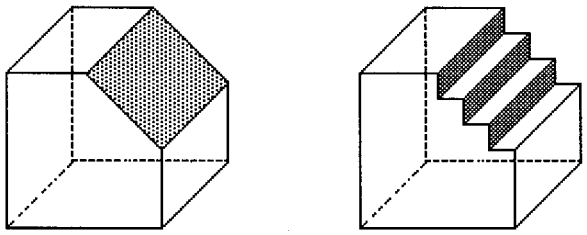


Figure 8
We cannot replace the Φ-minimizing surface shaded in (*a*) with stairs as in (*b*) since the new surface will no longer be enclosed by the same boundary.

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References

French, C., Albrethsen, K., Arthur, C., Curnutt, H., Greenleaf, S. & Kollett, C. (1993). *The Planar Double Wulff Cluster.* NSF SMALL Undergraduate Research Geometry Group Report, Frank Morgan, advisor. Williams College, Williamstown, MA, USA.

Hammond, C. (1990). *Introduction to Crystallography*. New York: Oxford University Press.

Morgan, F. (1998). *Riemannian Geometry: a Beginner's Guide*, 2nd ed. Wellesley: A. K. Peters.

Morgan, F., French, C. & Greenleaf, S. (1998). *J. Geom. Anal.* **7**, 97–115.

Taylor, J. (1978). *Bull. Am. Math. Soc.* **84**, 568–588.

Taylor, J. (1992). *Acta Metall. Mater.* **40**, 1475–1485.

Wecht, B., Barber, M. & Tice, J. (1995). *Double Salt Crystals.* NSF SMALL Undergraduate Research Geometry Group Report, Frank Morgan, advisor. Williams College, Williamstown, MA, USA.