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The Summertop Construction: Crystals in a Corner

R. K. P. Zia,[1] J. E. Avron,[2] and J. E. Taylor[3]

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Equilibrium shapes of crystals in contact with more than one substrate, e.g., droplets at a corner or the edge of two planes, are described. This generalizes a construction due to Wulff and Winterbottom and, unlike them, allows non-convex equilibrium shapes. Since this construction may require a central inversion of the Wulff plot, it is dubbed "the summertop construction."

KEY WORDS: Equilibrium crystal shapes; surface energy/tension.

1. INTRODUCTION

The shape of a macroscopic crystal of a given volume in equilibrium with its medium is governed by many factors. A simple model ignors all factors that cannot be incorporated into a single function $\sigma(\mathbf{n})$, the energy per unit area associated with the crystal–medium interface, expressed as a function of the surface normal $\mathbf{n}$. A geometric construction due to Wulff[(1)] and described below gives this equilibrium shape (assuming $\sigma > 0$) in the absence of external forces such as gravity or interaction with a substrate. This Wulff shape W corresponds to a region that has the least possible total surface energy compared to all other regions of the same volume. W is convex and has positive volume, denoted by $|W|$, which is a measure[(2)] of the total surface energy of the crystal. In d dimensions, the total energy is given by $d|W|^{1/d} V^{(d-1)/d}$, where V is the physical volume of the crystal. W is also unique up to translation.

A Wulff-type construction due to Winterbottom[(3)] and also described below gives W_1, the equilibrium shape of the crystal adsorbed on a substrate (an isotropic, homogeneous, and flat surface, e.g., table or wall),

[1] Center for Transport Theory and Mathematical Physics and Physics Department, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061.
[2] Physics Department, Technion, Haifa, Israel.
[3] Department of Mathematics, Rutgers University, New Brunswick, New Jersey 08903.

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provided the orientation of the latter is *fixed relative* to the crystalline axes. We specify this orientation by a constant vector $\mathbf{n}_1$, which is the exterior normal (one pointing *into* the substrate). The new ingredient here is σ_1, defined as the energy per unit area of the crystal–substrate interface minus that of the medium–substrate one. Since σ_1 is a difference, it can be negative, for substrates that "prefer" the crystal. If it is sufficiently negative, W_1 would be of zero volume or empty, leading to the phenomenon called complete wetting.(4),4 There the equilibrium shape becomes degenerate, spreading out to a microscopically thin film on the substrate. (The film might be infinitesimally corrugated rather than smooth.) The total surface energy may be zero or *infinitely* negative. Except for complete wetting, the adsorbed crystal is convex, with positive total energy.

For adsorption in edges and corners defined by two or more flat substrates, a special case (convex shape associated with a specific σ) has been thoroughly studied.(6) In this paper we extend the Winterbottom construction to include all crystals, i.e., for a given, *arbitrary* $\sigma(\mathbf{n})$. Further, we show that novel features can arise when the surface energy differences are sufficiently negative. A rich variety of shapes is possible, for example, a one-dimensional filament in a dihedral corner; a nonconvex, compact, and unique region; or degenerate but compact regions with no specific convexity. A familiar example is given by the shapes of water droplets attached to various substrates: convex ones on a flat table versus concave ones in a capillary tube. Unlike the single-substrate case, finite negative total surface energies are allowed, with the consequence of *negative* nucleation barriers.(7),5

Our construction is similar to that of Winterbottom. However, in the negative total surface energy case, we make use of central inversions. Therefore, we nickname our construction "summertop." The description will be given analytically, but the figures illustrate the construction geometrically and carry all the essential information. Proofs and mathematical details will be published elsewhere.(8)

2. THE CONSTRUCTIONS

2.1. Free Crystals and Crystals on a Substrate

For the sake of completeness and notation, we give a brief summary of the Wulff and Winterbottom constructions.

[4] For a recent review see, e.g., Ref. 5.

[5] An ordinary nucleation barrier (for the crystal phase) means that the medium phase is metastable against a potential difference favoring the crystal. "Negative" nucleation barriers are not barriers at all, in this sense. Instead, these negative energies can be associated with *stable* configurations when the potential favors the *medium*.

For a flat interface between an ordered (e.g., crystalline) material of fixed orientation and a surrounding medium (vapor, melt, or other solids), denote the normal pointing *into* the medium by $\mathbf{n}$. Let the surface energy per unit area of such an interface be given by the function $\sigma(\mathbf{n})$. Then Wulff's construction provides the equilibrium shape W of the crystal embedded in the medium. In three-dimensional space $\mathbb{R}^3$,

$$W = \{\mathbf{x} \in \mathbb{R}^3 \mid \mathbf{x} \cdot \mathbf{n} \leqslant \sigma(\mathbf{n}) \text{ for every } \mathbf{n}\} \tag{1}$$

(This construction is valid in any Euclidean space $\mathbb{R}^d$; we use $\mathbb{R}^3$ and $\mathbb{R}^2$ for ease of visualization and applicability.) In practice, this means that, for each direction specified by $\mathbf{n}$, go out a distance $\sigma(\mathbf{n})$ and discard the half-space beyond this point perpendicular to $\mathbf{n}$. The shape W is the remainder. See Fig. 1. "Equilibrium shape" here means that W has the least possible surface energy for the volume it contains.[9] The equilibrium shape for a crystal of volume V is obtained by scaling W with the factor $V/|W|$. The proof that such a scaled shape is of minimum energy relies on the scale invariance of the problem. Finally, we point out that WI, the central inversion of the Wulff shape (i.e., the image of W under the mapping $\mathbf{x} \to -\mathbf{x}$ for each $\mathbf{x}$), is the equilibrium shape of negative crystals, e.g., the crystal with a bubble of the medium embedded inside.

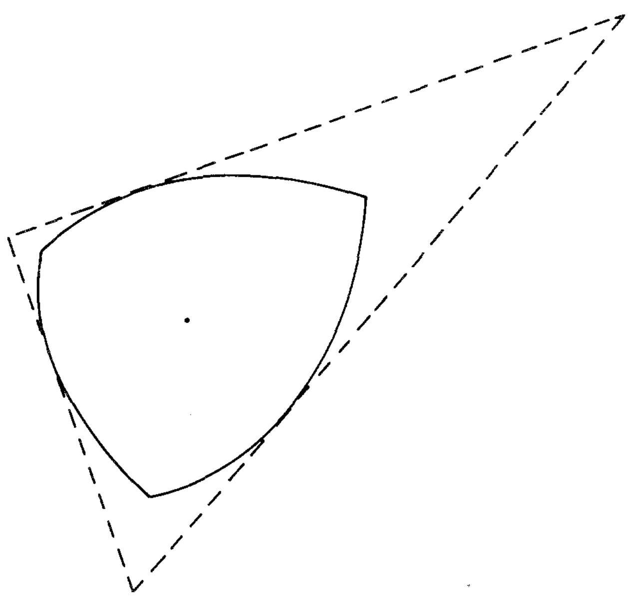

Fig. 1. An example of the Wulff construction in $\mathbb{R}^2$. The boundary of W is the solid line and σ is the dashed line. We have chosen an example with no symmetry under central inversion.

Winterbottom[3] gave a modification of this construction for a crystal that lies in a half-space: $R_1 = \{\mathbf{x} \mid \mathbf{x} \cdot \mathbf{n}_1 \leqslant 0\}$. This modification allows one to study the phenomenon of crystals adsorbed on a substrate in the absence of external forces, e.g., crystals sitting on a table without gravity. Set

$$W_1 = W \cap \{\mathbf{x} \mid \mathbf{x} \cdot \mathbf{n}_1 \leqslant \sigma_1\} \tag{2}$$

If $|W_1| > 0$ (see Fig. 2), the physical equilibrium shape is W_1 translated by $\sigma_1 \mathbf{n}_1$ (so that it lies in R_1) and scaled by $V/|W_1|$ (to satisfy the volume constraint). As for the free crystal, $|W_1|$ controls the total surface energy here. The proof that W_1 has least surface energy (for the volume it contains) is exactly the same as the proof for W, relying on scale invariance again. If $|W_1| = 0$, the equilibrium shape is degenerate and the crystal spreads out over the whole substrate as an infinitesimally thin (possibly infinitesimally corrugated) layer. This is known as complete wetting.[4,5] If σ_1 is sufficiently negative, W_1 is empty and complete wetting also occurs, with infinite negative total energy.

2.2. Crystals in a Corner in $\mathbb{R}^2$

In two dimensions, suppose that the crystal of a given "area" lies in the *intersection* of R_1 and R_2, two half-spaces with *distinct* exterior normals $\mathbf{n}_1$ and $\mathbf{n}_2$. The problem remains scale invariant if we exclude the case ($\mathbf{n}_1 = -\mathbf{n}_2$) where two parallel plates at a fixed distance sandwich a crystal. A corner is present in the physical region. As in Winterbottom's case, let the relative surface energies per unit "length" be given by σ_1 and σ_2. Define

$$W_{12} = W_1 \cap W_2 \tag{3}$$

where $W_2 = W \cap \{\mathbf{x} \mid \mathbf{x} \cdot \mathbf{n}_2 \leqslant \sigma_2\}$.

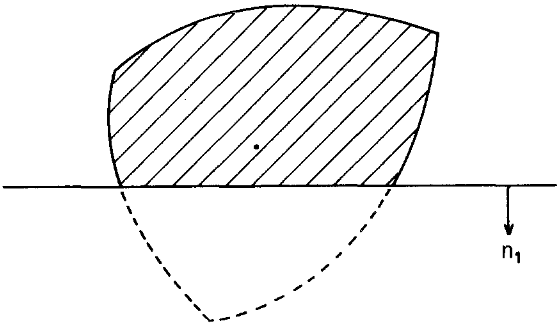

Fig. 2. The Winterbottom construction with a positive σ_1. Here W_1 is the shaded region.

If $|W_{12}| > 0$, then W_{12} is the equilibrium shape, when translated by $\sigma_1 \mathbf{n}_1 + \sigma_2 \mathbf{n}_2$ and scaled by $V/|W_{12}|$. The proof would run along the same lines as that for the previous constructions. Although this generalization of Winterbottom is straightforward, an interesting new feature may arise: The medium may become disconnected, so that the medium intervenes between the crystal and the corner (Fig. 3a).

If $|W_{12}| = 0$, one of the three following cases holds.

(a) At least one of the W_i is empty or has zero volume.

(b) Both $|W_i| > 0$, but W_{12} is a point.

(c) Both $|W_i| > 0$, but W_{12} is empty.

In case (a), the equilibrium shape is degenerate, with the crystal spreading over whichever substrate favors the crystal more. The other substrate might as well be absent and we have the Winterbottom construction again.

In case (b), we claim that the equilibrium shape is generically a triangle in the corner. Since the crystal–medium interface is allowed only one normal (the one associated with the single point in W), this is the third normal in the triangle. For the atypical case where W has a corner[6] at that point, the degeneracy of the two normals in W permits an infinite number of equilibrium shapes. Apart from a triangular region using only one normal, we may have regions using any appropriate combination of line segments with the two normals.[7] In particular, nonconvex regions and limiting cases with infinitesimally corrugated surfaces are also possible. One might term this "corner-induced faceting," in analogy with gravity-induced faceting.[(11)] The unifying feature of these manifestations is *zero* total surface energy. Unlike the Winterbottom case, vanishing $|W_{12}|$ need not imply complete wetting.

For case (c), e.g., Fig. 3b, we find a nontrivial extension of the Winterbottom construction, since W_{12} does not exist. We are able to prove that the equilibrium shape is the appropriate translation and scaling of a related

[6] Present physical theories for σ exclude the existence of a corner in W.[(10)] Similarly, there are difficulties with ridges in three-dimensional W's. Nevertheless, for the sake of mathematical completeness and future theories that allow corners, we discuss interesting consequences of assuming W's with missing normals.

[7] The varieties of shapes we present here are the solutions to the problem where a given functional is minimized. Further, we have assumed that corners and ridges do not contribute additional terms in the functional. Out of this infinite number of shapes, one or a few will be picked out if entropy is taken into account. Similarly, if corners and ridges contribute positively, shapes with only one facet will be favored.

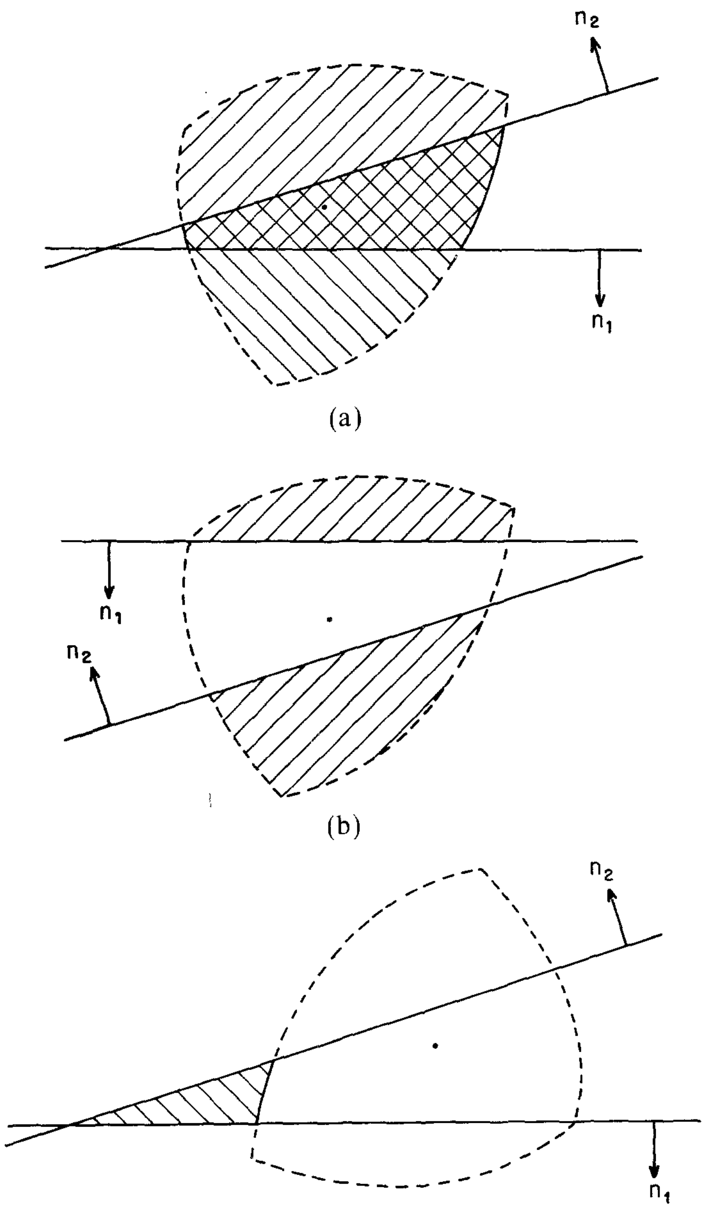

Fig. 3. Crystals in a corner in $\mathbb{R}^2$. (a) Intervening medium in the corner. W_i are shaded, while W_{12} is represented by the cross-hatch. (b) An example with W_{12} empty. W_i are shaded. (c) The summertop construction: W_{12}^* is shaded. Note that the dashed line is an *inverted* Wulff shape, with WI being the region *outside*.

region, W_{12}^*. To construct it, recall WI, the central inversion of the Wulff shape. Then,

$$W_{12}^* = \text{bounded connected component of}$$
$$WI \cap \{\mathbf{x} \mid \mathbf{x} \cdot \mathbf{n}_1 \leqslant -\sigma_1 \text{ and } \mathbf{x} \cdot \mathbf{n}_2 \leqslant -\sigma_2\} \tag{4}$$

See Fig. 3c. Immediately, we recognize a qualitatively different aspect: unlike W and the various W_1, this equilibrium shape is *not convex*. This counterintuitive picture is related to another novel feature: a *finite* and *negative* total surface energy, proportional to $-|W_{12}^*|^{1/2}$. Again, "negative" is relative to a system with substrates and medium only. Here, the gain due to the interaction with the substrates more than compensates the "loss" due to crystal–medium surface. Inversions in several senses occur naturally in this construction, hence the title. A heuristic argument may be given for W_{12}^*: it has all the correct local properties (contact angles, constant weighted curvature). Thus, it is stationary. In a later paper, we will present a detailed proof that all possible minima have been specified.

We have discussed only the restricted case where the angle at the corner is less than π, by specifying the intersection of two half-spaces. For angles greater than π, the global minimum will always be the crystal adsorbed on only one substrate, namely W_1 or W_2, whichever has smaller area. A construction similar to (3) might suggest the union of the W's, corresponding to the crystal surrounding a pointed tip. Although this shape is stationary, it is not clear whether it is even a local minimum of the energy, i.e., a metastable state. On the other hand, experimental observations[12] of these shapes lend support to the possibility of metastability. We are investigating this issue.

2.3. Crystals in a Dihedral Angle in $\mathbb{R}^3$

Consider two planar substrates under circumstances like those specified in the $\mathbb{R}^2$ problem. Following the procedures above, we construct W_1, W_2, and W_{12}. If $|W_{12}| > 0$, or if case (a) holds, there is no qualitative difference between the two-dimensional solution and the one here. Unlike the above situation (Fig. 3a), the medium will always be connected, even when the crystal is not in contact with the corner. A liquid (special case of isotropic σ) droplet squeezed between two nearly parallel planes is a familiar example. We have also received reports of an experiment with Ru crystals adsorbed on oxide surfaces[12] in which such phenomena have been observed.

Qualitative differences do occur for situations like (b) or (c) above. Instead of assuming nonconvex shapes, the crystal will spread out as an infinitely long and thin filament in the dihedral corner. Since the crystal wets neither substrate completely, it seems appropriate to call this phenomenon "corner-induced complete wetting," the isotropic case of which was found mathematically and experimentally by Concus and Finn.[13]

2.4. Crystals in an Interior Corner Formed by Three Planes in $\mathbb{R}^3$

Specify the three substrates by the exterior normals $\mathbf{n}_i$ and denote the relative surface energies by σ_i ($i = 1, 2, 3$). Labeling the half-spaces R_i, we consider configurations with a corner only, i.e., crystals lying in the octant $R_1 \cap R_2 \cap R_3$. Define

$$W_{123} = W_1 \cap W_2 \cap W_3 \tag{5}$$

where each W_i is as before. If $|W_{123}| > 0$, it determines the unique equilibrium shape, for reasons by now familiar. The case of a disconnected medium (such as Fig. 3a) is again possible. With ^{4}He crystals, it should be easy to observe this phenomenon, where a region of liquid develops in a corner spontaneously in the approach to equilibrium.

If $|W_{123}| = 0$, we have four possibilities:

(α) At least one of the W_i is empty or has zero volume.

(β) $|W_i| > 0$, but one of the W_{ij} is empty or has zero volume.

(γ) $|W_i|$ and $|W_{ij}| > 0$, but W_{123} is a point.

(δ) $|W_i|$ and $|W_{ij}| > 0$, but W_{123} is empty.

Case (α) corresponds to complete wetting of the appropriate substrate. Case (β) represents corner-induced complete wetting of a dihedral corner. Like the two-dimensional triangular solution, we find a tetrahedron in the corner for case (γ), with the same possibility of rich variations if W_{123} is a corner or part of an edge in W (see footnotes 4 and 5). For the last case, we need a "summertop" construction, in complete analogy with (c) above.

3. SUMMARY AND CONCLUSION

We have exploited scale invariance to find equilibrium shapes of crystals in contact with more than one flat substrate. Typically, we follow the lines of Wulff and Winterbottom. For cases where the Winterbottom-like construction comes up with an empty set, novel features abound. Generic situations include corner-induced complete wetting, where the crystal speads out as an infinitely thin line in a dihedral angle, and non-convex compact shapes, where central inversion of the Wulff shape is needed. In both cases, the total surface energy is negative, with an important consequence of negative nucleation barriers for physical systems. Other new features are more accidental, when the construction results in a single point. The crystal may be a triangle (in $\mathbb{R}^2$), a tetrahedron (in $\mathbb{R}^3$), or more bizarre. The total energy here is zero.

The emergence of such a variety of shapes may possibly be traced to *confinement*, an essential difference between the effect of many substrates on the crystal and that in a single-substrate case. For example, there is a variety of shapes associated with a water droplet in a capillary (of, say, triangular cross section), depending on their relative sizes. However, confinement typically breaks scale invariance, so that Wulff-like constructions fail. In the cases we consider, confinement occurs only in angular variables and scale invariance is preserved.

Apart from explicit length scales like the one introduced in the water droplet example above, there are more subtle sources in physical systems. Thus, our construction, like Winterbottom's, works only for flat, homogeneous substrates (or ones where any departure from flatness is confined to a region so small that it is completely engulfed by the constructed region). Only such substrates provide us with scale-invariant boundary conditions. Similarly, external forces (e.g., gravity) involve length scales and spoil the geometric constructions.

Finally, we could extend our construction to cases where more planes are present, *provided* all planes go through a point physically *and* with just the correct σ_i for them to go through a point in the Wulff plot. Such conditions are imposed so as to preserve scale invariance. Except for some special cases (e.g., isotropic σ and identical planes), these circumstances would not occur generically in the laboratory. Naturally, it is possible to generalize these results to higher dimensional spaces.

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