The Wulff construction goes low symmetry

Paul Erhart[1] and J. Magnus Rahm[1,2]

[1] *Department of Physics, Chalmers University of Technology, SE-41296, Gothenburg, Sweden* *
[2] *Compular AB, Vasagatan 5B, SE-41124, Gothenburg, Sweden*

An apparent quirk of mathematics draws on a symmetry and resolves the issue of how to determine the equilibrium shape of crystals of two-dimensional materials with asymmetric terminations.

The striking geometrical simplicity of naturally occurring minerals has inspired human imagination for millennia, suggesting the emergence of order in an otherwise seemingly amorphous world. The appearance of spinel, quartz or topaz crystals that exhibit faceting visible to the naked eye is the direct result of the arrangement of the atoms inside these materials on a (crystal) lattice. The latter can be terminated in countless distinct ways, yet each surface formed by such a cut is associated with a different energy cost. As shown already by Gibbs [1] and Curie [2], the equilibrium shape of a crystallite is the one that minimizes the total surface energy. A formal geometric procedure to determine the shape given by this condition was introduced by Wulff [3] and later proven for example by Laue [4]. The Wulff construction has been extremely successful for understanding the shapes of both two and three-dimensional materials, all the way from the macroscopic to the nanoscale [5], as one has to approach the sub-10 nm size regime in order to observe deviations [6].

In the two-dimensional equilibrium shape, the distance from one point inside the crystal to each edge is proportional to the edge energy in that direction, in the same fashion as for the three-dimensional Wulff construction. Thus, knowledge of the direction-dependent edge energy is necessary to construct the equilibrium shape. Nowadays, edge energies are routinely calculated with density functional theory by comparing the energy of ribbons with the fully periodic system. For crystals lacking symmetry, however, such ribbons will always expose two symmetrically inequivalent edges with potentially different energetics, and density functional theory calculations can only provide the average energy of two such edges. In fact, Cahn and coworkers pointed out already in the 1970s that in some such cases, edge energies even escape a proper definition and cannot be determined, even in principle [7]. It appears as though the construction devised by Wulff is of no use when searching for equilibrium shapes of crystals with low symmetry.

Now, writing in Nature Computational Science, Luqing Wang and colleagues demonstrate how the lack of a definition of edge energies in low-symmetry crystals can be circumvented when constructing the equilibrium shape [8]. The approach turns out to be pleasantly simple: just assume values for edge energies that are otherwise undefined. As long as these "auxiliary energies"

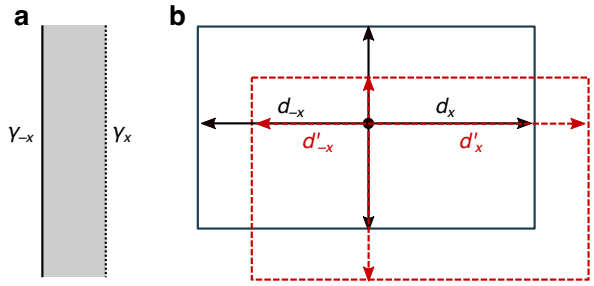

FIG. 1. A simple example of a Wulff construction for an asymmetric crystal. (a) If facets with normals x and $-x$ are inequivalent, only their sum can be calculated using a ribbon. (b) As long as this sum and any other well-defined edge energies are respected, we can make an ansatz for the undefined energies and obtain a Wulff construction. A different ansatz merely leads to a translated version of the same shape having different distances d_x and d_{-x} but the same sum $d_x + d_{-x}$.

fulfill all well-defined relationships between the edge energies, a valid equilibrium shape will result. A simple example is illustrated in Figure 1. If the crystal edges with normals x and $-x$ are inequivalent, only the sum of their edge energies, $\gamma_{-x} + \gamma_x$, can be calculated using a ribbon (Figure 1a). A Wulff construction can still be made by assuming a value for, say, γ_x, because this choice only leads to a translation of the resulting shape. The only physically well-defined energy, namely the sum $\gamma_{-x} + \gamma_x$, corresponds to the total distance $d_x + d_{-x}$, which remains unchanged when γ_x is varied (Figure 1b). In other words, Wulff constructions with undefined edge energies are possible because one shape corresponds to an infinite set of possible surface energies. Thus, an apparent quirk of mathematics draws on a symmetry and beautifully resolves, as happens so often in nature. This insight is crucial as the asymmetric edge character of many two-dimensional materials of current and potential future interest, including cases as diverse as SnS, $GeAs_2$, $VOBr_2$, and $LiBH_4$, has so far prevented a systematic analysis of their equilibrium shapes and edges.

The ability to construct equilibrium shapes of two-dimensional materials is not only of academic interest but has immediate applications. The edges of transition metal dichalcogenides for example are known to exhibit different electronic properties depending on orientation and termination [9], which can be exploited, for example, in catalysis [10]. Edges can also support plasmonic modes with a strong impact on the optical properties

* erhart@chalmers.se

of flakes of two-dimensional materials [11]. All of these properties become amenable to tuning if the edge structure and composition can be consciously controlled. This is where the ability to predict equilibrium shapes can make a strong impact. Future research can now for example address how the environment or the segregation of dopants or alloyants impacts edge energetics and hence the shapes of flakes, leading the way to further expanding the potential and impact of two-dimensional materials.

ACKNOWLEDGMENTS

This work was funded by the Swedish Research Council (grant numbers 2018-06482, 2020-04935, 2021-05072) and the Excellence Initiative Nano at Chalmers.

COMPETING INTERESTS

The authors declare no competing interests.

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