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Equilibrium form of crystals and stable norm

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Abstract. The equilibrium form of a crystal is the shape which minimizes the total surface tension for a given volume. The surface tension itself is considered to be a function of the orientation of the crystal face within the crystal lattice. This function of orientation is identified with the stable norm on the second homology classes of a Riemannian 3-torus. Minimizing the total surface tension of the crystal leads to an equilibrium form which corresponds to the dual unit ball of the stable norm. We outline the connection between surface tension and stable norm and interpret the differentiability properties of the stable norm in terms of the crystal shape. The differentiability properties, in particular, prove Sohnke's reciprocity law estimating the size of crystal faces.

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1. Introduction

At the end of the last century Gibbs and Curie proposed regarding a crystal as a body which minimizes its total surface tension for a given volume. The solution of this isoperimetric problem (constant volume, minimal surface tension) goes back to the crystallographer G. Wulff and has been improved up to broad generality. The isoperimetric problem implicitly assumes the knowledge of the surface tension as a function of the orientation of the crystal face. In 1915 P. Ehrenfest suggested a means of characterizing the surface tension in a purely geometric fashion based on the coordination polyhedra of the crystal [6]. It was at the beginning of the 50^s that C. Herring and L. D. Landau established some differentiability properties of the surface tension as a function of the surface orientation [8, 9]. They considered Van der Waals interactions between surface steps which raise the surface tension. For a modern survey of such molecular effects see [6].

In our approach we go back to Ehrenfest's geometrical point of view and explain the same phenomena in a pure differential geometrical frame work. The Van der Waals interactions between the steps translate into a deformation of the local

space geometry. Instead of the additional interaction energy of a step we speak of an enlargement of the metric in $\mathbf{R}^3$. Instead of a single crystal face which locally minimizes the free energy we speak of a minimal surface with respect to the periodically deformed metric. The well-known differentiability properties of the surface tension turn out to be the consequences of the renormalization process in our geometrical interpretation (Section 2). Whether the surface tension exhibits a non-differentiability at a face orthonormal to some vector $\gamma \in \mathbf{R}^3$ depends on how the vector γ lies within the crystal lattice. The degree of the non-differentiability is equal to the rational dependency of the components of γ (cf. theorem 1 and 2). Solving the isoperimetric problem, the differentiability properties of the surface tension produce a surprisingly self-similar collection of faces of the minimizing body (Section 3). Finally, we describe a 3-dimensional example extending Ehrenfest's 2-dimensional one (Section 4).

From a crystallographical point of view, the importance of the crystal model discussed here consists in its simplicity and its power to explain some characteristic properties of crystal forms from a pure geometrical point of view. It is remarkable that the presence of a $\mathbf{Z}^3$-periodic crystal lattice alone provokes the typical face shape structure of a crystal and that it even induces Sohnke's reciprocity law. To explain the crystal shape in a first approximation it is in particular not necessary to understand any of the complex mechanisms of chemical reaction, condensation or diffusion.

From a mathematical point of view, our main contribution is to stress the close relationship between the *surface tension* of a crystal and the mathematical object of the *stable norm*. We consider the surface tension of a crystal as a function of the orientation of the corresponding crystal face. The crystal face itself may be seen as representing a 2-dimensional real homology class on the torus $T^3 = \mathbf{R}^3/\mathbf{Z}^3$. The surface tension then is a function on these homology classes, namely the stable norm on $H_2(T^3, \mathbf{R})$, the 2-dimensional real homology classes of (T^3, g), with respect to some metric g. Roughly speaking, the stable norm of such a homology class is the minimal (g-)area of a 2-cycle representing that class. There is a one-to-one correspondance between real 2-dimensional homology classes $v \in H_2(T^3, \mathbf{R})$ and normal vectors $\gamma \in \mathbf{R}^3$ which are normal to planes in $\mathbf{R}^3$ going through the origin. Note that the projection of a plane in $\mathbf{R}^3$ onto the torus T^3 represents a real 2-cycle in T^3 which is uniquely defined up to normalization. The normal vector $\gamma(v)$ corresponding to the homology class v is called *rotation vector* of v. For integer homology classes $v \in H_2(T^3, \mathbf{R})$, which have integer rotation vectors $\gamma(v) \in \mathbf{Z}^3$, the stable norm $\|v\|_{st}$ is the least area of a 2-dimensional subtorus in T^3 with rotation vector $\gamma(v)$. For rational homology classes the stable norm $\|v\|_{st}$ is obtained by a normalization procedure from the stable norm on integer classes and for real classes by an additional limit process.

The stable norm of a real homology class may also be obtained by lifting the metric g on the torus to a metric $\tilde{g}$ on $\mathbf{R}^3$ and by measuring the average $\tilde{g}$-area of the lifted minimal 2-cycle. Note that, due to the projection $\mathbf{R}^3 \to \mathbf{R}^3/\mathbf{Z}^3$, any

surface $\mathcal{F}_\gamma \subset \mathbf{R}^3$ homeomorphic to a plane and lying in a bounded strip orthogonal to γ, i.e. with $\mathrm{dist}(x, \mathcal{F}_\gamma) \leq \mathrm{const}$ for every $x \in \mathbf{R}^3$ with $x\gamma = 0$, represents a homology class v with rotation vector proportional to γ. Let us restrict ourselves to rotation vectors γ with Euclidean norm 1, $\gamma \in S^2 = \{x \in \mathbf{R}^3 : \|x\|_{Eucl.} = 1\}$, and let us moreover assume that the surface $\mathcal{F}_\gamma$ is $\tilde{g}$-minimal with respect to compact variations. Then the **stable norm** $\|v\|_{st}$ of the homology class v with rotation vecor $\gamma(v) \in S^2$ is the average ($\tilde{g}$-)area of $\mathcal{F}_\gamma$:

$$\|v\|_{st} = \lim_{r\to\infty} \frac{A_{\tilde{g}}(\mathcal{F}_\gamma \cap B^3_r)}{r^2\pi}\,, \quad v \in H_2(T^3, \mathbf{R}) \text{ with } \gamma(v) \in S^2\,, \tag{1}$$

where $A_{\tilde{g}}$ denotes the $\tilde{g}$-area and B^3_r denotes the unit ball $B^3_r = \{x \in \mathbf{R}^3 : \|x\|_{Eucl} \leq r\}$. Actually, the right-hand side of (1) defines the 'homotopical stable norm' rather than the 'homological stable norm', cf. [14]. Although the 'homological stable norm' of a vector v in general is smaller or equal than its 'homotopical stable norm', the two coincide for 'non-pathological' metrics.

The connection between the stable norm and the surface tension is the following: We consider a $\mathbf{Z}^3$-periodic metric $\tilde{g}$ on $\mathbf{R}^3$ which is a small perturbation of the Euclidean metric. Such a perturbation will be interpreted as $\mathbf{Z}^3$-periodic distortion of the space metric which is introduced by presence of the crystal molecules. A crystal face orthogonal to some unit vector γ in $\mathbf{R}^3$ is identified with a bounded domain of a ($\tilde{g}$-)minimal surface $\mathcal{F}_\gamma$ as described above. The surface tension $\phi(\gamma)$ is obtained in a natural way as the average ($\tilde{g}$-)area of the 'crystal face' $\mathcal{F}_\gamma$ and thus is equal to the stable norm of the homology class corresponding to γ. The description of the surface tension in terms of the average area is a geometrical version of the notion of the *specific surface free energy* given in physical literature as e.g. [8]

The notion of the stable norm is directly related to the notion of the *minimal average action* which arises in the context of variational problems for non-parametrized minimal surfaces in the torus T^3. In this case one restricts to surfaces represented as graph of a (C°-)function $u : \mathbf{R}^2 \to \mathbf{R}$ and the variational problem consists in minimizing the integral $\int F(x, u, u_x)\; dx$ over all compact domains of $\mathbf{R}^2$. The variational integrand is a function $F : \mathbf{R}^2 \times \mathbf{R} \times \mathbf{R}^2 \longrightarrow \mathbf{R}$ which is $\mathbf{Z}^3$-periodic in the first 3 variables $(x_1, x_2, u) \in \mathbf{R}^3$ and which satisfies the Legendre condition and some further differentiability constraints, cf. [10, 11] For every 'rotation vector' $\alpha \in \mathbf{R}^2$ one defines the **minimal average action** by

$$A(\alpha) = \min_u \lim_{r\to\infty} \frac{1}{r^2\pi} \int_{B^2_r} F(x, u, u_x)\; dx,$$

where $B^2_r = \{\, x \in \mathbf{R}^2 \,:\, \|x\|_{Eucl} \leq r \,\}$ is the disc with radius r and center $0 \in \mathbf{R}^2$. The minimum is taken over all maps $u : \mathbf{R}^2 \longrightarrow \mathbf{R}$ with $|u(x) - \alpha \cdot x| \leq \mathrm{const}$, i.e. over all 'surfaces' lying in a bounded strip orthogonal to $(-\alpha, 1)$. The standard example is the Dirichlet integrand $F = \frac{1}{2}\|u_x\|^2_{Eucl}$ whose 'minimal solutions' u

are exactly the harmonic functions $u(x) = \alpha x + \text{const}$. Within this mathematical setting, the surface tension of a crystal face lying - with respect to the crystal lattice $\mathbf{Z}^3$ - orthogonal to $\gamma = (-\alpha, 1)$ is identified by the minimal average action $A(\alpha)/\|\gamma\|$. For a survey of the mathematical objects introduced here we refer to [4] and the citations therein.

Let us now specify the problem of crystal shape. Let $W \subset \mathbf{R}^3$ be any body with a fixed volume $\text{vol}_3 W$ and measurable boundary ∂W. Assume that to almost every boundary point $x \in \partial B$ the exterior normal $\gamma(x) \in S^2$ exists. According to the approach of Gibbs and Curie, the crystal with surface tension $\phi(\gamma)$ is realized by the **equilibrium form** $W \subset \mathbf{R}^3$ which minimizing the total surface energy

$$\int_{\partial W} \phi(\gamma(x))\, dx \stackrel{!}{=} \min, \qquad \text{under the constraint of } \text{vol}_3\, W \text{ being constant}. \quad (2)$$

The letter 'W' stands for 'Wulff crystal' and will be identified with the dual unit ball B_ϕ^* of the norm ϕ. Note that for $\phi \equiv 1$ this is the classical isoperimetric problem of finding the body with least surface and fixed volume.

We split the problem of finding the equilibrium form into the two parts:

A Determine from a geometrical point of view the typical properties of the surface tension $\phi(\gamma)$ as a function of the (outward) unit normal γ.

B Given $\phi(\gamma)$, determine the equilibrium form W of the crystal, i.e. find the solution of the corresponding isoperimetric problem (2).

While part B is well known and recently completed by a new elegant proof [5], our main contribution concerns part A.

2. Part A: Determination of the surface tension $\phi(\gamma)$

2.1. Geometrical definition of $\phi(\gamma)$ and differentiability properties

We think of a crystal lattice as an infinite set of identical molecules sitting at the sites $\mathbf{Z}^3 \subset \mathbf{R}^3$. A crystal face is determined by a cleavage face separating the molecules of the crystal lattice and passing through the locus of minimal interaction energy between these molecules. In a geometrical image, the energy to separate the crystal lattice is assumed to be proportional to the microscopic area of the crystal face passing closely to the molecules. The obstacle-effect of the crystal molecules may be modeled by a $\mathbf{Z}^3$-periodic metric $\tilde{g}$ on $\mathbf{R}^3$ which is large about points of $\mathbf{Z}^3$ and this enforces a minimal surface to turn around these sites. The average energy needed to separate the crystal lattice $\mathbf{Z}^3$ along some infinite surface is identified with the average ($\tilde{g}$-)area of that surface. Since the separation energy has to be minimized, such a cleavage face should be a minimal surface with respect to the $\mathbf{Z}^3$-periodically perturbed 'obstacle-metric'. The surface tension $\phi(\gamma)$ is obtained as the average area of a (smooth) minimal surface $\mathcal{F}_\gamma \subset \mathbf{R}^3$, the cleavage

face, which lies in a strip between two affine planes orthogonal (in the Euclidean sense) to γ. Notice that this last condition may be seen as a boundary condition with boundary at infinity. The term 'minimal' states that an arbitrary smooth variation of the surface $\mathcal{F}_\gamma$ supported on a compact domain is area-increasing or at least indifferent. The term 'average' refers to normalization with the area of an Euclidean disc (cf. Fig. 1). Denoting by $A_{\tilde{g}}$ again the $\tilde{g}$-area and abbreviating $B_r^3 = \{x \in \mathbf{R}^3 : \|x\|_{Eucl} \leq r\}$, our geometrical definition of the **surface tension** $\phi(\gamma)$ is

$$\phi(\gamma) \doteq \lim_{r\to\infty} \frac{A_{\tilde{g}}(\mathcal{F}_\gamma \cap B_r^3)}{r^2\pi}\,, \quad \gamma \in S^2\,. \tag{3}$$

For small $\mathbf{Z}^3$-periodic perturbations of the Euclidean metric this is equivalent to the stable norm $\|v\|_{st}$ given in (1), where $v \in H_2(T^3, \mathbf{R}) \simeq \mathbf{R}^3$ is the real homology class with coefficients $\gamma(v) = \gamma$.

The existence of minimal surfaces $\mathcal{F}_\gamma$ for $\gamma \in S^2$ is proved in [3]. One shows that for large $\mathbf{Z}^3$-periodic perturbations of the metric $\tilde{g}$ there are regions in $\mathbf{R}^3$ where no minimal surface $\mathcal{F}_\gamma$ passes for any $\gamma \in S^2$ [2]. These regions represent the sites of the crystal molecules with high interaction energy such that no cleavage face will pass there. The question of how much the metric is allowed to be perturbed until such regions arise where no $\mathcal{F}_\gamma$ passe is related to stability problems and is quite delicate [11].

In order to describe qualitatively the solution of the isoperimetric problem $\int_{\partial B} \phi(\gamma)$ one needs to know about the differentiability properties of the surface tension $\phi(\gamma)$. First, let us extend the function $\phi(\gamma)$ homogeneously from S^2 to $\mathbf{R}^3$ by defining $\phi(\lambda\gamma) \doteq \lambda\phi(\gamma)$ for all $\lambda > 0$ and all $\gamma \in S^2$. Moreover, we define for $\gamma \in \mathbf{R}^3$ the subspace

$$V_\gamma \doteq \operatorname{span}_{\mathbf{R}} \{k \in \mathbf{Z}^3 : k\gamma = 0\}\,,$$

in $\mathbf{R}^3$ which is orthogonal to γ. Notice that $\dim V_\gamma = 2$ if and only if γ is a rational direction, i.e. $\mathbf{R}^+\gamma \cap \mathbf{Q}^3 \neq \emptyset$. Conversely, $\dim V_\gamma = 0$ if and only if the components of γ are rationally independent. One has $\dim V_\gamma = 1$ if there is, up to dilatation, exactly one integer vector ($\neq 0$) in the orthogonal complement of γ. We will see that the body B solving the isoperimetric problem has a face of dimension $\dim V_\gamma$ orthogonal to γ. This is essentially due to the fact that ϕ is *not* differentiable at γ in the directions lying in V_γ while it is differentiable in any direction orthogonal we define to V_γ.

Let $V_\gamma^\perp$ denote the orthogonal complement of V_γ in $\mathbf{R}^3$ (with respect to the Euclidean metric) and let the term $(D_\beta + D_{-\beta})\phi(\gamma)$ denote the difference of right- and left-sided derivative of ϕ at γ in the direction β. (Recall that, if $D_\beta\phi$ defines the directional derivative in the direction β, the left-sided derivative in the direction β is given by $-D_{-\beta}\phi$.)

Theorem 1. *Let $\beta, \gamma \in \mathbf{R}^3 \setminus \{0\}$ and suppose that there is a region in $\mathbf{R}^3$ where*

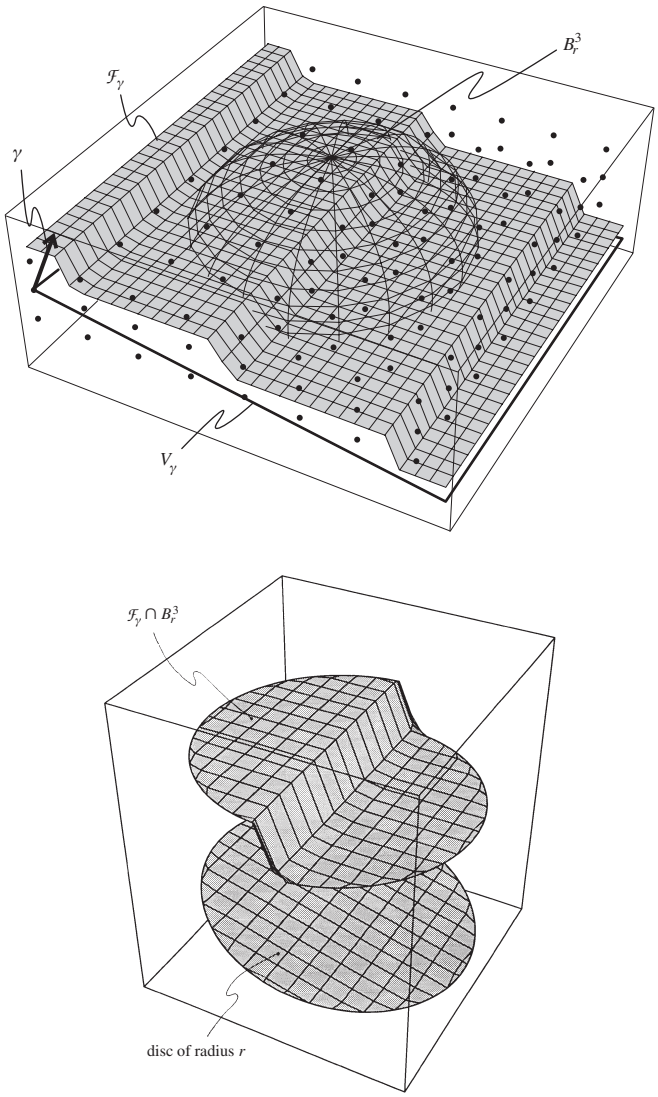

Figure 1.
The definition of the surface tension or average area $\phi(\gamma)$ according to (3). Above: The metric in $\mathbf{R}^3$ is enlarged $\mathbf{Z}^3$-periodically around the dots which are interpreted as crystal molecules. With respect to this metric, $\mathcal{F}_\gamma \subset \mathbf{R}^3$ represents a minimal surface which lies between two affine planes orthonormal to $\gamma = \frac{1}{\sqrt{17}}(1, 0, 4)$. Below: The part of $\mathcal{F}_\gamma$ cut out by the 3-dimensional ball B_r^3 of radius r. The ratio of its area (measured with respect to the deformed metric) and the area of a disc of radius r (measured with respect to the Euclidean metric) yields in the limit $r \to \infty$ the surface tension $\phi(\gamma)$.

no minimal surface $\mathcal{F}_\gamma$ (with respect to a smooth periodic metric) passes. Then

$$(D_\beta + D_{-\beta})\phi(\gamma) \begin{cases} = 0 & \textit{if } \beta \in V_\gamma^\perp \\ > 0 & \textit{else} \ . \end{cases}$$

A rigorous proof of the corresponding theorem in the nonparametric case is found in [15, theorem 2].

Let us interpret the theorem in terms of boundary singularities of the unit unit ball $B_\phi \doteq \{x \in \mathbf{R}^3 : \phi(x) \leq 1\}$. Suppose that the metric on $\mathbf{R}^3$ is $\mathbf{Z}^3$-perturbed such that the condition in the theorem holds for any $\gamma \in S^2$. Let $\partial B_\phi \doteq \{x \in \mathbf{R}^3 : \phi(x) = 1\}$ be the boundary of the unit ball and let us put $\mathbf{R}^+ \doteq \{x \in \mathbf{R} : x > 0\}$. Then, the theorem states that the unit ball B_ϕ of ϕ is differentiable at the boundary point $\partial B_\phi \cap \mathbf{R}^+\gamma \ = \frac{\gamma}{\phi(\gamma)}$ if and only if γ is not rationally dependent, i.e. iff $\dim V_\gamma = 0$.

To quantify the singularities we say that a boundary point is 0-, 1- or 2-**singular** iff the tangent cone to B_ϕ at $\partial B_\phi \cap \mathbf{R}^+\gamma$ contains exactly 0, 1 or 2 linear independent straight lines. Thus, a boundary point on B_ϕ is 0-, 1- or 2-singular iff its tangent cone is a genuine cone, a 'wedge-like' cone or a plane, respectively. The theorem states that the boundary point $\partial B_\phi \cap \mathbf{R}^+\gamma$ is $(2-s)$-singular (s=0, 1, 2) if and only if there are exactly s linear independent integer directions orthogonal to γ, i.e. iff $\dim V_\gamma = s$. According to [1], this is an example of a convex body with most possible singularities in the sense of measure: To get all s-singular points $(s = 0, 1, 2)$ of the boundary ∂B_ϕ one has to take the union of countable *infinitely* many compact sets of finite s-dimensional Hausdorff measure.

To give the mathematical bases of Sohnke's reciprocity law (cf. Section 3) we estimate $(D_{e_i} + D_{-e_i})\phi(\gamma)$ from above, where e_i, $i = 1, 2, 3$, are the standard unit vectors in $\mathbf{R}^3$:

Theorem 2. *There is a constant const>0 depending on the periodically perturbed metric such that for any 'shortest' vector $\gamma = (p^1, p^2, p^3) \in \mathbf{Z}^3$ (i.e. with $gcd(p^1, p^2, p^3) = 1$) and any $\lambda > 0$ one has*

$$0 \leq (D_{e_i} + D_{-e_i})\phi(\lambda\gamma) \leq \ const \cdot \frac{1}{|p^i|} \ , \quad 1 \leq i \leq 3 \ , \ p^i \neq 0 \ .$$

In the nonparametric case, the theorem corresponds to [15, theorem 3].

Remark. The components p^i are interpreted as the *Miller indices* of the corresponding crystal face orthonormal to γ.

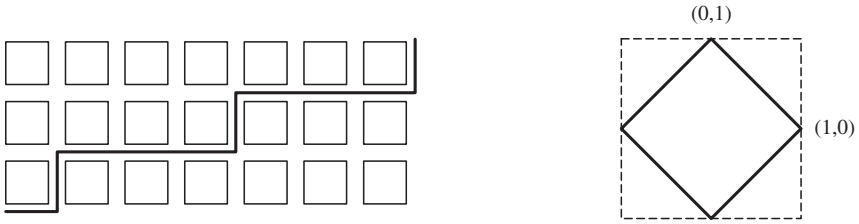

Figure 2.
Left: The Ehrenfest model of a 2-dimensional crystal. The fat line is a shortest path in diagonal direction and represents a crystal 'face' with the same direction in the large. The distance along the path divided by the distance in bee-line is equal to the surface tension ϕ of this crystal 'face'. Right: The unit ball B_ϕ of the Ehrenfest model (thick) represents the bee-line distances which may be reached by a paths of length 1. The Wulff crystal B_ϕ^* (dotted) is the dual of B_ϕ.

2.2. Comparison with the work of Ehrenfest and Herring

Let us compare these results with the model proposed by Ehrenfest [6]. He suggested a simple example of a 2-dimensional crystal with square-shaped molecules filling the plane (Fig. 2). In his example, the specific 'surface' free energy $\phi(\gamma)$ with $\gamma \in S^1$ is the average length of a minimizing path with global direction orthonormal to γ and passing along the boundary of the molecules. Extending ϕ homogeneously to $\mathbf{R}^2$, the unit ball B_ϕ is calculated to be (cf. Fig. 2).

$$B_\phi = \{(x^1, x^2) \in \mathbf{R}^2 : |x^1| + |x^2| \leq 1\} \,. \tag{4}$$

In contrast to the situation in theorem 1 and 2, the metric $\tilde{g}$ which would model the impenetrability of the square-shaped obstacle would be discontinuous. However, the model explains in a simple way how e.g. at the point $(0, 1)$ the non-differentiability of the specific 'surface' energy ϕ arises: For any direction $\gamma \in S^1$, $\gamma \neq \pm e_i$, a crystal 'face' orthonormal to γ consists of an infinity of horizontal *and* vertical segments of length 1. If the direction of the crystal face approximates a unit direction e_i, the possibility of short-cutting decreases linearly with the proportion of horizontal and vertical segments. This linear digression is responsible that the point e_1 represents a corner of B_ϕ. Indeed, by homogeneity of $\phi(\gamma)$, the right- and left-sided derivatives of ϕ at e_1 in the direction e_2 are given by

$$\begin{aligned} D_{e_2}\phi(e_1) &= \lim_{h \downarrow 0} \frac{1}{h}(\phi(e_1 + he_2) - \phi(e_1)) = \lim_{s \to \infty} (\phi(se_1 + e_2) - \phi(se_1)) = 1 \\ -D_{-e_2}\phi(e_1) &= \lim_{h \downarrow 0} \frac{1}{h}(\phi(e_1) - \phi(e_1 - he_2)) = \lim_{s \to \infty} (\phi(se_1) - \phi(se_1 - e_2)) = -1 \end{aligned}$$

and thus do not coincide! Note that $\phi(se_1) = s$ and $\phi(se_1 \pm e_2) = s + 1$ and that for Ehrenfest's example one in general has $\phi(\alpha e_1 + \beta e_2) = |\alpha| + |\beta|$ for

any α, $\beta \in \mathbf{Z}$. In turn, at any point $\gamma \in S^2$ not equal to $\pm e_1$ or $\pm e_2$ the one-sided derivatives orthogonal to γ coincide. Setting $\gamma = (\cos\alpha, \sin\alpha)$ one calculates $\phi(\gamma) = |\cos\alpha| + |\sin\alpha|$ which indeed is non-differentiable exactly for $\alpha = 0,\ \pi,\ \pm\frac{\pi}{2}$. The boundary of the unit ball B_ϕ is obtained as

$$\partial B_\phi = \{\ \frac{\gamma}{\phi(\gamma)}\ :\ \gamma \in S^1\ \} = \{\ \frac{(\cos\alpha, \sin\alpha)}{|\cos\alpha| + |\sin\alpha|}\ :\ 0 \le \alpha < 2\pi\ \}$$

which agrees with (4).

After the initial work of Ehrenfest in 1915 it was Yamada [18] and then Herring [8] and Landau [9] who took up again the problem of equilibrium forms about 1950. Their results, deduced from the interaction energy between molecular steps, phenomenologically may directly be obtained as geometrical properties of the underlying periodic metric on $\mathbf{R}^3$. Refining Ehrenfest's model, the interaction energies seem to have the same effect to the surface tension as the assumption that the molecules do not need anymore to be impenetrable. This impenetrability, mathematically formulated as an out-smoothing of the periodic metric $\tilde{g}$ on $\mathbf{R}^3$, leads to an intriguing picture of differentiability properties or, dually, to a surface structure as drawn e.g. in Fig. 3. We were very surprised to discover qualitatively our theorems 1 and 2 in the cited works. We give the wording of such a striking passage from [8, p. 21] (the notation of the surface tension is adapted):

We conclude therefore that at the absolute zero (of temperature) the $\phi(\gamma)$-plot of a crystal will have a point cusp of finite angle at every rational orientation. Of course, the discontinuity in the derivatives of $\phi(\gamma)$ with respect to the angle will be extremely minute for all except a few of the low-index orientations, but in principle it is still present. A similar argument leads to the conclusion that knife-edge cusps will occur for all orientations with a rational ratio of any two Miller indices. This is an interesting example of a function occuring in physics with discontinuous derivatives at an everywhere dense set of points.

The **Miller indices** of a rational plane orthogonal to some $\gamma \in \mathbf{Q}^3 \setminus \{0\}$ are defined by the components p^1, p^2 and p^3 of the shortest vector in $\mathbf{R}^+\gamma \cap \mathbf{Z}^3$. For large absolute values of Miller indices p^1, p^2, p^3 the discontinuity in the derivatives of ϕ at $\gamma = \lambda \cdot (p^1, p^2, p^3)$ indeed is minute: According to theorem 2 it holds $(D_{e_i} + D_{-e_i})\phi(\gamma) \le \text{ const} \cdot \frac{1}{|p^i|}$ for any $\lambda > 0$ and any i with $p^i \neq 0$. According to theorem 1, indeed a knife-edge cusp may occur if the degree $\dim V_\gamma$ of rational dependency of γ is only 1.

We emphasize that the underlying crystal model describes an idealized crystal at 0° Kelvin without any surrounding medium. If the temperature is raised, the 'extreme minute' cusps will disappear by thermal fluctuations and only cusps of the low-index orientations will survive.

3. Part B: Determination of the equilibrium form B_ϕ^*

Once the surface tension $\phi(\gamma)$ is known, the minimizing body W of the isoperimetric problem may easily be described: Up to dilatation, the body with minimal surface energy $\int_{\partial W}\phi(\gamma)$ and prescribed volume $\mathrm{vol}_3 W$ =const is given by the dual unit ball or **Wulff crystal**

$$W = B_\phi^* = \{\, y \in \mathbf{R}^3 : y\cdot x \le 1 \quad \forall\, x \in B_\phi \,\}\,.$$

Motivated from the thermodynamical point of view, B_ϕ^* is called the **equilibrium form** of the crystal. The isoperimetric result has a long history. In 1901, G. Wulff gave an explicit construction of the surface-energy-minimizing body as the intersection of half-spaces according to

$$B_\phi^* = \bigcap_{\gamma\in\ S^2} \{\, y \in \mathbf{R}^3 : y\cdot\gamma \le \phi(\gamma) \,\}\,.$$

A new general proof that the Wulff crystal B_ϕ^* is surface-energy-minimizing recently was found by J.E. Brothers and F. Morgan [5].

For the Ehrenfest model the Wulff crystal B_ϕ^* corresponding to the unit ball (4) is given by the intersection of the 4 half-spaces $\{y \in \mathbf{R}^2 : y\cdot(\pm e_i) \le 1\}$, where e_1 and e_2 denote the standard unit vectors (cf. Fig. 2, right). Thus,

$$B_\phi^* = \{(y^1, y^2) \in \mathbf{R}^2 : |y^i| \le 1\,,\ i = 1, 2\}\,.$$

In the 3-dimensional case, the differentiability properties of the (convex) unit ball $B_\phi \subset \mathbf{R}^3$ translate to the dual properties of B_ϕ^* as follows:

- A singular point (i.e. a 'non-differentiability point') of ∂B_ϕ with a genuine tangent cone corresponds to a genuine affine face of B_ϕ^*.
- A singular point of ∂B_ϕ with a 'wedge-like' tangent cone corresponds to a piece of an affine line in ∂B_ϕ^*.
- A regular point (i.e. a 'differentiability point') of ∂B_ϕ corresponds to an extreme point (i.e. a 0-dimensional face) of ∂B_ϕ^*.

If the condition in theorem 1 holds for a $\mathbf{Z}^3$-periodic metric, the theorem predicts a quite strange surface structure of B_ϕ^*: For every rational direction $\gamma \in \{\frac{x}{\|x\|_{Eucl}} : x \in \mathbf{Q}^3\}$ the Wulff crystal B_ϕ^* has a 2-dimensional face orthonormal to γ. In general, if the rational dependency of $\gamma \in S^2$ $(= \dim V_\gamma)$ is $s = 0, 1, 2$, there is a s-dimensional face of the Wulff crystal B_ϕ^* orthogonal to γ. Moreover, the affine faces are distributed in such a way that the Wulff crystal B_ϕ^* even is smooth! The smoothness of B_ϕ^* is just the dual property of the *strict* convexity of B_ϕ (for a smooth periodic metric $\tilde{g}$) which may be showed in an analogous way as in [13]. In a different setting F. Vallet [17] calculated the boundary structure of a

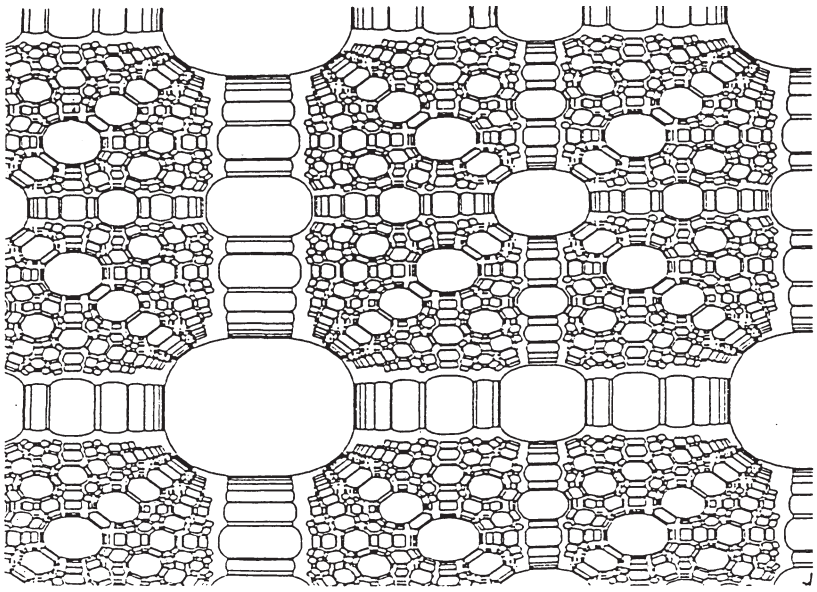

Figure 3.
A possible surface structure of the Wulff crystal B_ϕ^* after unrolling to the plane. The system of the convex regions defines a self-similar structure on $\mathbf{R}^2$. The convex regions correspond to affine faces of B_ϕ^* with an integer normal direction γ, $\mathbf{R}^+\gamma \cap \mathbf{Z}^3 \neq \emptyset$. In general, a s-dimensional face ($s = 0, 1, 2$) of the dual body B_ϕ^* corresponds to $(2-s)$-singular of point B_ϕ . According to theorem 1, the dimension s of a face of B_ϕ^* with normal γ is equal to the number $\dim V_\gamma$ of linear independent integer directions orthogonal to γ. I would like to thank F. Vallet for the permission to enclose his plot from [17].

convex function having the same typical properties as the boundary structure of B_ϕ^*, see Fig. 3. Between any two pretendedly neighboring faces there is again a face since between two rational normal directions there is again a rational direction. Iterating this argument, the collection of affine faces of B_ϕ^* is shown to define some self-similar structure.

Finally, we point out that theorem 2 may be seen as an exact formulation of the well-known **reciprocity law** due to L. **Sohnke** from 1888. In the original paper the corresponding passage runs as follows [16, p.221]:

Hiernach scheint es also in der That nothwendig, dass die verschiedenen möglichen Krystallflächen an der wirklichen Begrenzung des Krystalls im Allgemeinen in dem Maasse geringeren Theil nehmen, als ihre Flächendichtigkeiten geringere sind.

If the Miller indices of a crystal face are $(p^1, p^2, p^3) = \gamma \in \mathbf{Z}^3$, the 'Flächendichtigkeit', i.e. the density of lattice points within the plane $\langle\gamma\rangle^\perp$ orthogonal to

γ, is given by $\frac{1}{\sqrt{(p^1)^2+(p^2)^2+(p^3)^2}}$ and thus is reciprocal to the (absolute values of the) Miller indices. According to Sohnke, the size of the crystal face should be estimated by an similar reciprocal factor. Indeed, Sohnke's reciprocity law is confirmed by theorem 2: Let e_i' denote the projection of e_i to $\langle\gamma\rangle^\perp$. According to the theorem, the right- and left-sided tangent to ∂B_ϕ at the point $\partial B_\phi \cap \mathbf{R}^+\gamma$ in the direction e_i' differ at most by an angle of order $\frac{1}{|p^i|}$. For the dual unit ball B_ϕ^* this means that the face orthogonal to γ is bounded in the direction e_1' by $\frac{1}{|p^i|}$, $i = 1, 2, 3$.

4. The extended Ehrenfest model

We consider a 3-dimensional generalization of the Ehrenfest model now, again with a discontinuous metric $\tilde{g}$. Instead of a 2-dimensional square, the coordination polyhedron of the crystal molecule is assumed to be the octahedron (cf. Fig. 4)

$$\mathcal{O} \doteq \text{ conv}\left\{(\pm\frac{1}{2},0,0),(0,\pm\frac{1}{2},0),(0,0,\pm\frac{1}{2})\right\} ,$$

where 'conv' denotes the convex hull. Thus, the crystal lattice is given by the integer translates of $\mathcal{O}$. The interaction forces between two octahedron-shaped crystal molecules are supposed to vanish compared with the forces within a single octahedron (molecule). Thus, a cleavage face giving rise to a face of the crystal will avoid the octahedron-shaped regions. In the mathematical model the impenetrability of the coordination polyhedra for a cleavage face again is simulated by setting the metric inside the polyhedra infinitely large. Outside, the Euclidean metric is retained.

The surface tension $\phi(\gamma)$ of a macroscopic crystal face orthogonal to $\gamma \in S^2$ still is defined by (3) where $\mathcal{F}_\gamma$ is a cleavage face which has finite distance to the affine plan $\langle\gamma\rangle^\perp$. Due to the infinitely large metric inside the coordination polyhedra, $\mathcal{F}_\gamma$ remains outside and $A(\mathcal{F}_\gamma \cap B_r^3)$ is the same as its Euclidean area.

We first look for the vertices of the unit ball B_ϕ. Since we only enlarged the metric, the average area of a cleavage face ($\equiv$ minimal surface) is greater or equal than 1: $\phi(\gamma) \geq 1$ for all $\gamma \in S^2$. Using periodicity arguments one shows that $\phi(\gamma) = 1$ if and only if the corresponding cleavage face $\mathcal{F}_\gamma$ is an affine plane avoiding the coordination octahedra. These γ will give rise to the vertices of B_ϕ. Taking into account the orientation of these planes one gets 26 possible orthonormal vectors $\gamma \in S^2$: Either γ is one of the 6 directions from the midpoint to the vertices of the octahedron $\mathcal{O}$ or one of the 12 directions orthogonal to its edges or one of the 8 directions orthogonal to its faces (see Fig. 4).

For all remaining $\gamma \in S^2$ the cleavage face $\mathcal{F}_\gamma$ is only piecewise affine. There is a finite list of affine pieces such that any $\mathcal{F}_\gamma$ may be clustered together by integer translates of them. The pieces are obtained by intersecting the 26 planes (with

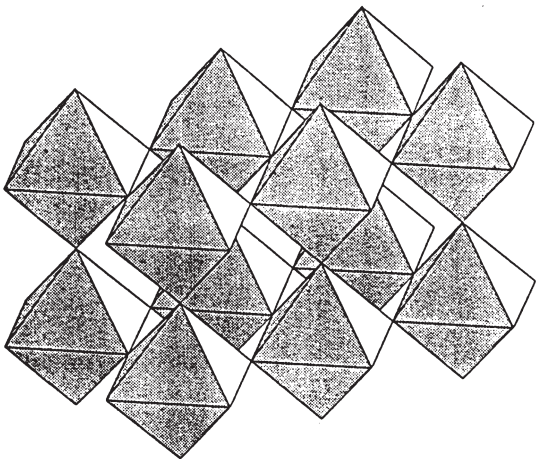

Figure 4.
The coordination polyhedra for the extended Ehrenfest model. Within a polyhedron the interaction energy is supposed to be infinite. In a mathematical formulation, the polyhedra are the regions where the metric is infinitely large while the cleavage faces avoiding the polyhedra correspond to the minimal surfaces with respect to this degenerated metric.

orientation) with their $\mathbf{Z}^3$-translates. For an arbitrary cleavage face $\mathcal{F}_\gamma$ the affine pieces constituting $\mathcal{F}_\gamma$ exhibit at most 3 of the 26 different normal unit vectors. The maximally 3 normal directions correspond to the 3 vertices of B_ϕ nearest to γ. If a cleavage face $\mathcal{F}_\gamma$ exhibits exactly 3 normal directions, say γ_1, γ_2 and $\gamma_3 \in S^2$, the boundary point $\gamma/\phi(\gamma)$ of B_ϕ lies within the convex hull of γ_1, γ_2 and γ_3: Setting $\gamma = \mu_1\gamma_1 + \mu_2\gamma_2 + \mu_3\gamma_3$ the components $\mu_i > 0$ give the relative amount (in the sense of average area) of the pieces of $\mathcal{F}_\gamma$ with normal vector γ_i. The sum $\mu_1 + \mu_2 + \mu_3$ therefore has to be equal to $\phi(\gamma)$. This shows that $\gamma/\phi(\gamma)$ lies in the affine face of B_ϕ spanned by the γ_i.

Precising these arguments one proves that the unit ball B_ϕ consists of the convex hull of the 26 centrally symmetric points on S^2 determined above. Thus (cf. Fig. 5, left),

$$B_\phi = \operatorname{conv}\Big\{(\pm1,0,0),(0,\pm1,0),(0,0,\pm1),\frac{1}{\sqrt{2}}(\pm1,\pm1,0),\frac{1}{\sqrt{2}}(\pm1,0,\pm1),\\ \frac{1}{\sqrt{2}}(0,\pm1,\pm1),\frac{1}{\sqrt{3}}(\pm1,\pm1,\pm1)\Big\}.$$

According to the general solution of the resulting isoperimetric problem, the crystal shape is the dual B_h^* of this unit ball B_ϕ (see ch. (3)). By Wulff's construction, B_ϕ^* is the intersection of the 26 half-spaces $\{y \in \mathbf{R}^3 : y\gamma_i \le 1\}$, where $\gamma_1, \ldots, \gamma_{26} \in S^2$ are the vertices of B_ϕ (Fig. 5). Recall that the γ_i are the normal unit directions for which there is an affine plane through the octahedron-shaped

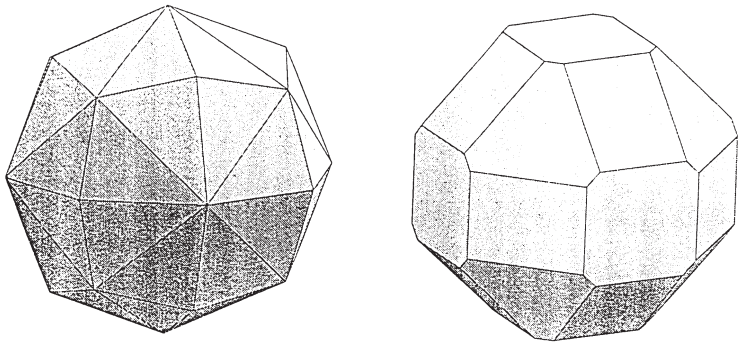

Figure 5.
Left: The unit ball B_ϕ for the extended Ehrenfest model. A point γ at the boundary of B_ϕ is a vertice if and only if γ is normal to an affine plane which passes through the packing of octahedra (fig. 3) without cutting an octahedron in two.
Right: The Wulff crystal B_ϕ^* of the extended Ehrenfest model is obtained by sliding all vertices and edges of an octahedron normally down to its in-ball. The habit of the crystal is a combination of the 3 crystal forms 'cube', 'octahedron' and 'rhomb-dodecahedron' and is therefore of highest symmetry class m3m.

packing (Fig. 4). Thus, up to dilatation, B_ϕ^* is obtained by cutting of the vertices of the octahedron $\mathcal{O}$ tangentially down to its in-ball. B_ϕ^* is calculated to be the convex hull of 48 points (cf. Fig. 5, right):

$$B_\phi^* = \mathrm{conv}\{(\pm\alpha, \pm\beta, \pm 1), (\pm\beta, \pm\alpha, \pm 1), (\pm\alpha, \pm 1, \pm\beta), \\ (\pm\beta, \pm 1, \pm\alpha), (\pm 1, \pm\alpha, \pm\beta), (\pm 1, \pm\beta, \pm\alpha)\}\ ,$$

where $\alpha = \sqrt{3} - \sqrt{2} \approx 0.318$ and $\beta = \sqrt{2} - 1 \approx 0.414$.

We again ask what happens if the cleavage face is allowed to cut of the vertices and edges of the coordination polyhedra. In the mathematical terminology this corresponds to smoothing out the (degenerated) periodic metric $\tilde{g}$ defined by the octahedra-shaped obstacles. At a first glance one could expect that the unit ball B_ϕ will get smooth as well. However, according to theorem 1, just the opposite happens! For a smooth $\mathbf{Z}^3$-periodic metric on $\mathbf{R}^3$ the unit ball B_ϕ typically has a dense set of singular points! Correspondingly, the Wulff crystal B_ϕ^* would exhibit faces for a dense set of orthonormal directions on S^2 which, however, would get tiny with increasing Miller indices and B_ϕ^* itself would get smooth (cf. Sect. 3).

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References

[1] R. D. Anderson and V. L. Klee, Convex functions and upper semi-continuous collections. *Duke Math. J.* **19** (1952), 349-357.

[2] V Bangert, The existence of gaps in minimal foliations. *Aequationes Mathematicae* **34** (1987), 153-166.

[3] V. Bangert, Laminations of 3-tori by least area surfaces. In: *Analysis, et cetera*, eds P.H.Rabinowitz and E.Zehnder, Academic Press 1990.

[4] V. Bangert, Minimal Foliations and Laminations, *Proceedings of the International Congress of Mathematicians, Switzerland 1994*, pp. 453-464, Birkhäuser Verlag, Basel 1995.

[5] J. E. Brothers and F. Morgan, The Isoperimetric theorem for General Integrands. *Mich. U. Math. J.* **41** (1994), 419-431.

[6] Ehrenfest P., Zur Kapillaritätstheorie der Kristallgestalt. *Annalen der Physik* **48** (1915), 360-368.

[7] P. Hartmann (ed.), *Crystal growth: an introduction*. North-Holland, Amsterdam 1972.

[8] C. Herring, The Use of Classical Macroscopic Concepts in Surface-Energy Problems. In: *Structure and Properties of Solid Surfaces*, eds R.Gomer and C.S. Smith, Univ. of Chicago Press 1952.

[9] L. D. Landau, The Equilibrium Form of Crystals, In: *Collected Papers of L.D. Landau*, pp. 540–545. Gordon and Breach, Science Publishers 1965.

[10] J. Moser, Minimal solutions of variational problems on a torus. *Ann. Inst. Henri Poincaré - Analyse non linéaire* **3** (1986), 229-272.

[11] J. Moser, A stability theorem for minimal foliations on a torus. *Ergod. Th. & Dynam. Syst.* 8^*, (1988), 251-281.

[12] P. Nozières, Shape and Growth of Crystals, In: *Solids Far from Equilibrium*, ed. C. Cordèche, Cambridge 1992, 1-154.

[13] W. Senn, Strikte Konvexität für Variationsprobleme auf dem n-dimensionalen Torus. *Manuscripta mathemathica* **71** (1991), 45-65.

[14] W. Senn, Differentiability properties of the minimal average action. Dissertation (Adviser: V. Bangert), Universität Bern, Sidlerstr. 5, CH-3012 Bern, 1993.

[15] W. Senn, Differentiability properties of the minimal average action. *Calc. Var.* **3** (1995), 343-384.

[16] L. Sohnke, Über Spaltungsflächen und natürliche Krystallflächen. *Zeitschrift f. Kryst.* **13** (1888), 214-235.

[17] F. Vallet, Thermodynamique unidimensionelle et structures bidimensionelles de quelques modèles pour des systèmes incommensurables. Thèse de Doctorat (Adviser: S. Aubry), Université Paris 6, 1986.

[18] M. Yamada, Über die Kristallformen und Kristallgitter. *Physik. Zeitschrift* **12** (1924), 289-296.

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