# EQUILIBRIUM SHAPES OF CRYSTALS ATTACHED TO WALLS

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Abstract. We discuss equilibrium shapes of crystals attached to walls. Optimal shapes for different configurations of walls are found and the minimality of the overall surface tension is proven with the help of simple geometrical argument based on the isoperimetric inequality and monotonicity. Stability results in a form of Bonnesen inequalities are obtained in the two-dimensional case.

*Key words and phrases.* Wulff's construction, equilibrium crystal shapes, Winterbottom's construction.

## Introduction

In this paper we present simple mathematical arguments allowing to discuss the equilibrium shape of a droplet of a phase $C$, called below the *crystal*, inside a phase $M$, called the *medium*, when $C$ and $M$ are two phases in equilibrium. The phase $C$ need not be a real crystal; when adopting this terminology we stress that we consider general anisotropic surface tension. In particular, we show that the corresponding variational problems can be solved by purely geometrical means also in presence of walls. While the many facets of Statistical Mechanics of equilibrium shapes are reviewed in [RW] and [Z], for existing results concerning droplets in presence of walls see e.g. [Wi, ZAT, Zi]. The method discussed in the present paper covers, in spite of its limitations, several cases of interest, which are treated in the literature. Not all results here are new, however, we present them in a unified manner using only several basic principles. In this way, we can simplify and improve results, already existing in the literature. Our conclusions are the strongest for dimension two — in that case we also have stability results.

All arguments are based just on the isoperimetric inequality and on monotonicity. We first recall this inequality and then formulate the basic variational problem, which we want to solve. Our results are then exposed in increasing order of complexity. Some comments of general nature and on recent related works are deferred to the conclusion at the end of the paper.

**Isoperimetric inequality.**

Different statements about optimal shapes of crystals are proven with the help of the isoperimetric inequality, which we state as follows. Let $W \subset \mathbb{R}^d$ be a convex body, and let $\tau_W(\boldsymbol{n})$ be its *support function* assigning to a unit vector $\boldsymbol{n}$ the value

$$\tau_W(\boldsymbol{n}) = \sup_{\boldsymbol{x}\in W} (\boldsymbol{x}, \boldsymbol{n}). \tag{1}$$

Notice that if the origin of the coordinates is outside the set $W$, the support function attains negative values for some directions $\boldsymbol{n}$. In (1) $(\boldsymbol{x}, \boldsymbol{n})$ is the Euclidean scalar product.

Considering a set $V \subset \mathbb{R}^d$ with a sufficiently smooth boundary[1] $\partial V = \gamma$, we define the functional

$$\tau_W(\gamma) = \int_\gamma \tau(\boldsymbol{n}(s))\, ds, \tag{2}$$

[1]The isoperimetric inequality can be proven for very general $V$. The purpose of the paper is to present some consequences of the isoperimetric inequality. Thus the hypothesis which we need are those leading to the isoperimetric inequality (and such that the functional $\tau(\gamma)$ below be well defined). It is not our intention to discuss this point here, see e.g. [Fo] for a recent paper on the subject. Having situations arising in physics in mind, we restrict ourselves to simple cases. For example in dimension two we may assume that the boundary of $V$ can be approximated by polygonal lines.

where $\boldsymbol{n}(s)$ is the exterior unit normal. The *isoperimetric inequality* is

$$\tau_W(\gamma) \geq d|W|^{\frac{1}{d}}\,|V|^{\frac{d-1}{d}}, \tag{I}$$

where $|W|$, $|V|$, denotes the (Lebesgue) volumes of $W$, $V$, respectively. The equality in (I) occurs only when $V$ equals, up to dilation and translation, the set $W$. The set $V$ need not be connected. The basic idea of the proof of (I) is simple if presented in a geometrical language (see [Di] and for a general proof [T]). Namely, one first expresses the functional $\tau_W(\gamma)$ in a geometrical manner as

$$\tau_W(\gamma) = \lim_{\epsilon\to 0} \frac{|V+\epsilon W| - |V|}{\epsilon}. \tag{G}$$

Here, $V+\epsilon W$ denotes the union $\cup_{\boldsymbol{x}\in V}(x+\epsilon W)$, and $\epsilon W = \{\epsilon\boldsymbol{x} : \boldsymbol{x}\in W\}$. The inequality (I) then follows applying the Brunn-Minkowski inequality to $|V+\epsilon W|$. When $W$ is the unit ball, the equality (I) is the classical isoperimetric inequality, and a proof of (G) for very general $V$ can be found in [F].

*Remarks.* 1. As an immediate corollary of the representation (G) we see that the functional will not change if we replace the set $W$ by its translation $W' = W + \boldsymbol{a}$,

$$\tau_{W'}(\gamma) = \tau_W(\gamma). \tag{3}$$

Another way of showing (3) is to observe that the change $W$ into $W'$ amounts to the change $\tau_W(\boldsymbol{n})$ into $\tau_{W'}(\boldsymbol{n}) = \tau_W(\boldsymbol{n}) + (\boldsymbol{a}|\boldsymbol{n})$, and that the integral $\int_\gamma (\boldsymbol{a}|\boldsymbol{n}(s))\,ds$ vanishes. We use such shifts in different situations.

2. A consequence of the above remark is that the functional $\tau_W(\gamma)$ is always nonnegative. Indeed, it is always possible to shift the origin into the interior of $W$, and then $\tau_W(\boldsymbol{n})$ is positive for all $\boldsymbol{n}$.

3. From (I), or by a direct computation using (G), the minimum of the functional is

$$\min_{V:|V|=|W|} \tau_W(\partial V) = d|W|. \tag{4}$$

In addition to the isoperimetric inequality (I), the *stability* of the minimum in (I) can be controlled in the two-dimensional case. Namely, if $\tau_W(\gamma)$ is close to the minimal value on the right hand side of (I), the set $V$ is geometricaly close to W in a uniform way. Introducing,

$$r(\gamma) = \sup\{r\colon r\cdot W + x \subset V \text{ for some } x\in\mathbb{R}^2\} \tag{5a}$$

and

$$R(\gamma) = \inf\{R\colon R\cdot W + x \supset V \text{ for some } x\in\mathbb{R}^2\} \tag{5b}$$

to measure the geometrical resemblance of $V$ with $W$, one has

$$\frac{\tau_W(\gamma) - \sqrt{\tau_W(\gamma)^2 - 4|W|\,|V|}}{2|W|} \le r(\gamma) \le R(\gamma) \le \frac{\tau_W(\gamma) + \sqrt{\tau_W(\gamma)^2 - 4|W|\,|V|}}{2|W|}. \qquad \text{(S)}$$

Inequalities (S) are the generalized Bonnesen inequalities, which are proven in Theorem 2.5 in [DKS].

**Variational problem.**

Our aim is to use (I) and (S) to find the ideal shape of the crystal $C$ inside the medium $M$ in presence of one or several walls. Let us first recall the free situation. The shape of the crystal is obtained by minimizing the overall surface tension of the crystal [C], [G], [H]. Let $\boldsymbol{n}$ be a unit vector in $\mathbb{R}^d$, and consider the situation with phases $C$ and $M$ coexisting over a hyperplane perpendicular to $\boldsymbol{n}$, $\{\boldsymbol{x} : (\boldsymbol{x}|\boldsymbol{n}) = a\}$. We use $\tau(\boldsymbol{n})$ to denote the interface free energy, or surface tension, corresponding to such interface, supposing that it is the phase $C$ that is occupying the half-space $\{\boldsymbol{x} : (\boldsymbol{x}|\boldsymbol{n}) \le a\}$. We assume that the surface tension is strictly positive and that it is lower semicontinuous, but we do not require the symmetry $\tau(\boldsymbol{n}) = \tau(-\boldsymbol{n})$. We denote by $\Gamma$ the set of $\mathbb{R}^d$ occupied by the phase $C$, and its boundary by $\gamma = \partial\Gamma$. The overall interface free energy of the phase $C$ is given by

$$\tau(\gamma) := \int_\gamma \tau(\boldsymbol{n}(s))\, ds. \qquad (6)$$

We always suppose that the boundary $\gamma$ of $\Gamma$ is sufficiently smooth (see footnote above). The variational problem is to minimize (6) under the constraint that the total volume $|\Gamma|$ occupied by the phase $C$ is fixed. Given a set $W$, we say that a crystal has *shape* $W$, if after a translation and a dilatation, it equals $W$.

The solution of the variational problem is given below [W]. Notice that the problem is scale-invariant, so that if we can solve it for a given volume of the phase $C$, we get the solution for other volumes by an appropriate scaling. Let $W_\tau$ be defined by the so-called *Wulff's construction*

$$W_\tau = \{\boldsymbol{x} \in \mathbb{R}^d : (\boldsymbol{x}|\boldsymbol{n}) \le \tau(\boldsymbol{n}) \text{ for every } \boldsymbol{n}\}. \qquad \text{(W)}$$

We show that *this set yields the optimal shape for the crystal*. We first state some elementary properties of $W_\tau$ (for details see e.g. [DP]). The set $W_\tau$ is convex since it is given by the intersection of hyperplanes. If we extend the surface tension $\tau(\boldsymbol{n})$ to all $\mathbb{R}^d$ as a positively homogeneous function of degree one, we get

$$W_\tau = \{\boldsymbol{x} \in \mathbb{R}^d : \tau^*(\boldsymbol{x}) \le 0\}, \qquad (7)$$

where $\tau^*$ is the Legendre transform of $\tau$, $\tau^*(\boldsymbol{x}) = \sup_{\boldsymbol{n}}[(\boldsymbol{x}|\boldsymbol{n}) - \tau(\boldsymbol{n})]$. Actually $\tau^*(\boldsymbol{x}) = 0$ if $\boldsymbol{x} \in W_\tau$, and $\tau^*(\boldsymbol{x}) = +\infty$ otherwise. The support function of $W_\tau$ is given by

$$\tau_{W_\tau}(\boldsymbol{n}) = \tau^{**}(\boldsymbol{n}). \tag{8}$$

Another useful description of $W_\tau$ is in terms of the polar function of $\tau$,

$$\tau^\circ(\boldsymbol{x}) := \sup_{\boldsymbol{y}\neq 0}\left\{\frac{(\boldsymbol{x}|\boldsymbol{y})}{\tau(\boldsymbol{y})}\right\}. \tag{9}$$

Namely, in terms of it we have

$$W_\tau = \{\boldsymbol{x} : \tau^\circ(\boldsymbol{x}) \leq 1\}. \tag{10}$$

Notice that $\tau \geq \tau^{**}$ and that the polar function of $\tau^{**}$ is $(\tau^{**})^\circ = \tau^\circ$ since $\tau^{**}$ and $\tau$ define the same Wulff's crystal $W_\tau$. These relations and the lower semicontinuity of $\tau$ imply the exitence of a vector of unit length $\boldsymbol{y}(\boldsymbol{x})$ for every $\boldsymbol{x} \in \partial W_\tau$, such that

$$\tau(\boldsymbol{y}(\boldsymbol{x}))\tau^\circ(\boldsymbol{x}) = (\boldsymbol{y}(\boldsymbol{x})|\boldsymbol{x}) = \tau^{**}(\boldsymbol{y}(\boldsymbol{x}))\tau^\circ(\boldsymbol{x}). \tag{11}$$

Therefore

$$\tau^{**}(\boldsymbol{y}(\boldsymbol{x})) = \tau(\boldsymbol{y}(\boldsymbol{x})) \tag{12}$$

The function $\tau^\circ$ being convex, $\tau^\circ$ is differentiable at $\boldsymbol{x}$ almost everywhere. The convexity of $\tau^{**}$ implies that $\tau^{**} = (\tau^{**\circ})^\circ$, which means that $\tau^{**}$ is the polar function of $\tau^{**\circ} = \tau^\circ$. Using the definition (9) of the polar function and the identity (11), we see that the supremum of the function $(\boldsymbol{y}(\boldsymbol{x})|\boldsymbol{z})/\tau^\circ(\boldsymbol{z})$ is attained at $\boldsymbol{x}$. Thus for almost all $\boldsymbol{x}$, the value $\boldsymbol{y}(\boldsymbol{x})$ is proportional to the gradient of $\tau^\circ$ at $\boldsymbol{x}$. Since the exterior unit normal to $\partial W_\tau$ at $\boldsymbol{x}$, $\boldsymbol{n}_{\boldsymbol{x}}$, is also proportional to the gradient of $\tau^\circ$ at $\boldsymbol{x}$, we have $\boldsymbol{y}(\boldsymbol{x}) = \boldsymbol{n}_{\boldsymbol{x}}$ whenever $\tau^\circ$ is differentiable, i.e. for almost all $\boldsymbol{x}$,and

$$\tau^{**}(\boldsymbol{n}_{\boldsymbol{x}}) = \tau(\boldsymbol{n}_{\boldsymbol{x}}). \tag{13}$$

Equation (13) implies the important result that the value of the functionals $\tau(\gamma)$ and $\tau_{W_\tau}(\gamma)$ coincide for $\gamma = \partial W_\tau$. The isoperimetric inequality implies that the optimal shape of a crystal $C$ inside the medium $M$ is indeed given by $W_\tau$ (if the volume of the crystal is $|W_\tau|$).

*Remarks.* 1. It is expected from thermodynamical reasons that the equilibrium surface tension $\tau$ is in fact equal to the support function of the set $W_\tau$ defined above. In other

words the surface tension $\tau$ can be extended to a positively homogeneous *convex* function of degree one to all $\mathbb{R}^d$. This statement is equivalent to the statement that $\tau$ satisfies the *pyramidal inequality* [DS] and [MMR]. The convexity property of $\tau$ has been proven for several models of Statistical Mechanics [MMR]. However, in the present paper we do not assume that $\tau$ can be extended to a convex function on $\mathbb{R}^d$.

2. Recently the above results for the shape of a droplet have been proven starting from a microscopic model and first principles of Statistical Mechanics [DKS], [P].

When walls are present, the variational problem has to be modified. Namely, the surface tension (or interface free energy) of a surface in contact with the medium surrounding crystal differs from that one arising in contact with the wall even when the corresponding orientations of the corresponding pieces of the boundary of the crystal $C$ are the same. Let $\boldsymbol{n}$ be a unit vector in $\mathbb{R}^d$, and let

$$w(\boldsymbol{n}) = \{\boldsymbol{x} : (\boldsymbol{x}|\boldsymbol{n}) = a\} \tag{14}$$

be a hyperplane describing a wall $w(\boldsymbol{n})$ perpendicular to $\boldsymbol{n}$ that is supposed to be in contact with the halfspace filled by the phase $C$. By convention the phase $C$ is supposed to occupy the half-space $\{\boldsymbol{x} : (\boldsymbol{x}|\boldsymbol{n}) < a\}$. The relevant physical quantity here is the difference

$$\sigma(\boldsymbol{n}) = \tau_{cw}(\boldsymbol{n}) - \tau_{mw}(\boldsymbol{n}), \tag{15}$$

where $\tau_{cw}(\boldsymbol{n})$ and $\tau_{mw}(\boldsymbol{n})$ are the surface free energies of the phase $C$ against the wall and of the phase $M$ against the wall, respectively. Since $\sigma(\boldsymbol{n})$ is a difference of free energies, it may either be positive or negative. When $\tau_{cw}(\boldsymbol{n}) - \tau_{mw}(\boldsymbol{n}) \geq \tau(\boldsymbol{n})$ we have a *drying* situation: in equilibrium, it is preferrable that the phase $M$ occupies the place between the wall and the phase $C$, and consequently the phase $C$ is not in contact with the wall. On the other hand when $\tau_{cw}(\boldsymbol{n}) - \tau_{mw}(\boldsymbol{n}) \leq -\tau(\boldsymbol{n})$ we have a *(complete) wetting* situation: in equilibrium, the phase $C$ forms a layer between the wall and the medium $M$. Notice that *wetting* or *drying* are relative concepts. In the first case we have complete wetting of the wall by the phase $M$, and in the second case we have complete drying of the wall with respect to the phase $M$. In all other cases we speak of *partial drying* or *partial wetting*. If we consider the properties of the phase $C$, we say that we have *partial drying* if $\tau_{cw}(\boldsymbol{n}) - \tau_{mw}(\boldsymbol{n}) \geq 0$, and *partial wetting* if $\tau_{cw}(\boldsymbol{n}) - \tau_{mw}(\boldsymbol{n}) \leq 0$. Actually, at equilibrium, we have [Ca], from thermodynamical reasons, the following inequalities,

$$|\sigma(\boldsymbol{n})| = |\tau_{cw}(\boldsymbol{n}) - \tau_{mw}(\boldsymbol{n})| \leq \tau(\boldsymbol{n}). \tag{16}$$

The physical situations described above have been studied rigourously in the Ising model, starting from first principles of Statistical Mechanics in [FP1], [FP2], [FP3].

Whenever the phase $C$ is in contact with a wall with normal $\boldsymbol{n}$, we must replace the integrant $\tau(\boldsymbol{n})$ in the free functional (6) by $\sigma(\boldsymbol{n})$. Since the walls are fixed, the problem is not translation invariant any more, and the new functional, which we still denote by $\tau(\gamma)$, is

$$\tau(\gamma) = \int_\gamma \tau(\boldsymbol{x}(s), \boldsymbol{n}(s))\, ds \tag{17}$$

with

$$\tau(\boldsymbol{x}, \boldsymbol{n}) = \begin{cases} \sigma(\boldsymbol{n}), & \text{if } \boldsymbol{x} \in w(\boldsymbol{n}) \\ \tau(\boldsymbol{n}), & \text{otherwise.} \end{cases} \tag{18}$$

In simple situations the minimum of this new variational problem can be found using the following elementary *monotonicity principle*. Let $\tau(\gamma)$ be our functional (17).

*If we can find a convex body $W$ such that*

$$\tau(\gamma) \geq \tau_W(\gamma) \tag{M1}$$

*for every $\gamma$, where $\tau_W$ is the support function of $W$, and*

$$\tau(\partial W) = \tau_W(\partial W), \tag{M2}$$

*then both statements (I) and (S) remain true even after replacing $\tau_W(\gamma)$ by $\tau(\gamma)$.*

This fact is obvious for (I) and follows from monotonicity of $\alpha - \sqrt{\alpha^2 - C}$ as function of $\alpha$ (for $|\alpha| \leq \sqrt{C}$) for (S). Notice, however, that (M2) might be valid only for a particular location of $W$ and, as a consequence, the equality in (I) occurs only for a particular set $W$ (and not up to a translation). It is the purpose of the next sections to show examples where this method can be applied.

*Remark.* If we consider a droplet of phase $M$ inside the phase $C$, in presence of the walls, then the functional to minimize is the following one

$$\widehat{\tau}(\gamma) = \int_\gamma \widehat{\tau}(\boldsymbol{x}(s), \boldsymbol{n}(s))\, ds \tag{19}$$

with

$$\widehat{\tau}(\boldsymbol{x}, \boldsymbol{n}) = \begin{cases} -\sigma(\boldsymbol{n}), & \text{if } \boldsymbol{x} \in w(\boldsymbol{n}) \\ \tau(-n), & \text{otherwise.} \end{cases} \tag{20}$$

Here, of course, the set occupied by the phase $M$ is $\Gamma$ with boundary $\gamma = \partial\Gamma$.

## Particular arrangements of walls

**1. Crystal on a wall.**

Let us suppose that we have a planar wall $w(\boldsymbol{n}^*) = \{\boldsymbol{x} \in \mathbb{R}^d : (\boldsymbol{x}|\boldsymbol{n}^*) = a\}$ perpendicular to the unit vector $\boldsymbol{n}^*$ (see Fig. 1), and let $E = \{\boldsymbol{x} \in \mathbb{R}^d : (\boldsymbol{x}|\boldsymbol{n}^*) < a\}$ be the half-space where we have the phases $C$ and $M$ (the other halfspace is the wall). The overall interface free energy of a crystal $\Gamma$ is therefore

$$\tau(\gamma) = \int_{\gamma_w} \sigma(\boldsymbol{n}^*)\, ds + \int_{\gamma_f} \tau(\boldsymbol{n}(s))\, ds. \tag{21}$$

where the first integral is over the boundary of the crystal along the wall, $\gamma_w = \gamma \cap w(\boldsymbol{n}^*)$, and the second integral is over the remaining part of the boundary of the crystal, $\gamma_f = \gamma \cap E$. This is a problem with the functional $\tau(\gamma)$ of the form (17) with $\tau(\boldsymbol{x}, \boldsymbol{n})$ defined by (18).

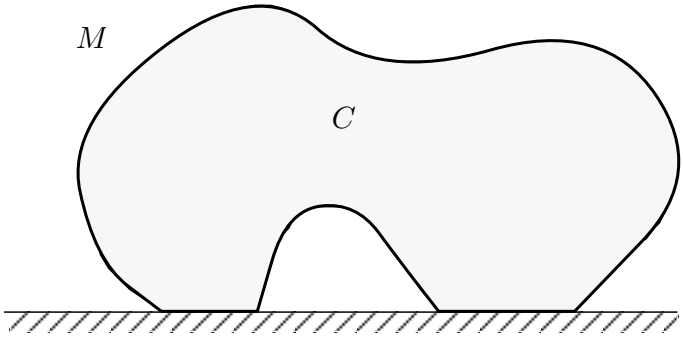


Fig. 1. A droplet of phase $C$ in the half-space $E$.

The solution is well-known [Wi], [Zi]. Let us briefly recall it. One first constructs the Wulff's set,

$$W_\tau = \{\boldsymbol{x} \in \mathbb{R}^d : (\boldsymbol{x}|\boldsymbol{n}) \le \tau(\boldsymbol{n}) \text{ for every } \boldsymbol{n}\}, \tag{22}$$

which corresponds to the ideal shape of the free crystal. Then we take the intersection of this set $W_\tau$ with the half-space (which should not be mistaken with the half-space $E$)

$$\{\boldsymbol{x} \in \mathbb{R}^d : (\boldsymbol{x}|\boldsymbol{n}^*) \le \sigma(\boldsymbol{n}^*)\}, \tag{23}$$

and we get a new convex subset $W$, called the *Winterbottom's shape* (see Fig. 2). Except for the case $\sigma(\boldsymbol{n}^*) \le -\tau(\boldsymbol{n}^*)$, which corresponds to the complete wetting of the wall by the phase $C$, and in which the variational problem is degenerate (when $\sigma(\boldsymbol{n}^*) < -\tau(\boldsymbol{n}^*)$

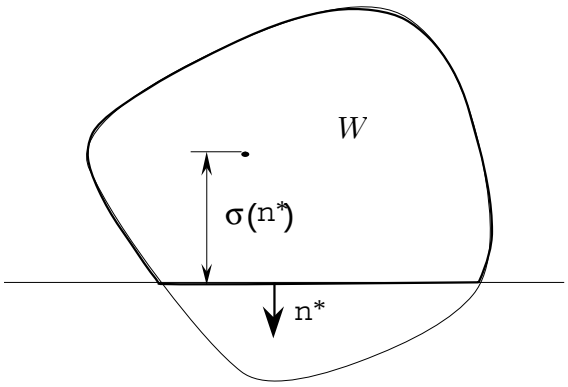


FIG. 2. THE WINTERBOTTOM'S SHAPE $W$.

the infimum of the functional is $-\infty$), the set $W$ is a convex body, but not necessarily containing the origin.

We claim that, in non-degenerate cases, the optimal form of the crystal is the Winterbottom's shape $W$. This is a simple consequence of the monotonicity principle. Let $\tau_W$ be the support function of the set $W$. Since $\tau(\boldsymbol{n})$ is always greater or equal to the support function of the set $W$, we have the inequality

$$\tau(\boldsymbol{x}, \boldsymbol{n}) \geq \tau_W(\boldsymbol{n}). \tag{24}$$

Therefore, the inequality (M1) is satisfied and the equality (M2) follows from (13). The constraint on the volume is satisfied by an appropriate scaling.

In the two-dimensional case we have a stability result. Let $r(\gamma)$ and $R(\gamma)$ be defined by (5a) and (5b) with $W$ the Winterbottom's shape. Then the Bonnesen inequalities (S) hold with the present functional $\tau(\gamma)$ in place of $\tau_W(\gamma)$. Notice that in the case $\tau_{cw} - \tau_{mw} < 0$ the origin does not belong to $W$. On the other hand the stability result (S) is proven in [DKS] only under the assumption that the origin belongs to $W$. We can always satisfy this assumption by applying a shift to $W$ by, say, $(\tau_{cw} - \tau_{mw})\boldsymbol{n}_w$ or any $\boldsymbol{a}$ such that $(\boldsymbol{a}|\boldsymbol{n}_w) = \tau_{cw} - \tau_{mw}$. The new set $W'$ contains the origin, but as already remarked in the introduction this procedure does not change the value of the functional. The shift in this particular case means that we set the interface free energy on the wall to vanish and compensate for it by changing correspondingly the surface tension between the crystal and the medium (cf. [Zi]). This also shows that the minimum of the functional is strictly positive.

**2. Partial wetting of an interface.**

This case is discussed in detail in [Zi]. (The variational problem in [Zi] is slightly different, the methods are different and the assumptions more restrictive.) We suppose that the dimension of the space is two, and that we have a system with three phases in equilibrium, $M_1$, $M_2$, $C$. We start with a situation in which the two phases $M_1$ and $M_2$ coexist in $\mathbb{R}^2$ and are separated by a stable flat interface perpendicular to $\boldsymbol{n}^*$, $i(\boldsymbol{n}^*) = \{\boldsymbol{x} \in \mathbb{R}^2 : (\boldsymbol{x}|\boldsymbol{n}^*) = 0\}$, passing through the origin. Let $E^+ = \{\boldsymbol{x} \in \mathbb{R}^2 : (\boldsymbol{x}|\boldsymbol{n}^*) < 0\}$ and $E^- = \{\boldsymbol{x} \in \mathbb{R}^2 : (\boldsymbol{x}|\boldsymbol{n}^*) > 0\}$. The phase $M_1$ is in $E^-$, and the phase $M_2$ is in $E^+$. The surface tension associated with this interface is $\tau_{1,2}(\boldsymbol{n}^*)$. We put a droplet of the phase $C$ into the system. By inserting this droplet we can break the interface between the points $\boldsymbol{a}$ and $\boldsymbol{b}$ into two pieces as in the Fig. 3. We denote by $\tau_j(\boldsymbol{n})$) the surface tension of an interface, perpendicular to $\boldsymbol{n}$, between the phase $C$ and the phase $M_j$, $j = 1, 2$. The functional $\tau(\gamma)$ is similar, but not identical, to the functional (17). For the sake of simplicity we suppose that the boundary $\gamma$ of the droplet is a simple closed curve, and we denote by $\gamma_1$, $\gamma_2$, the parts of the boundary in contact with the phase $M_1$, $M_2$, respectively. Notice that, because of the presence of the droplet of phase $C$, the phase $M_1$ may occupy a part of the half-space $E^+$, as in Fig. 3.

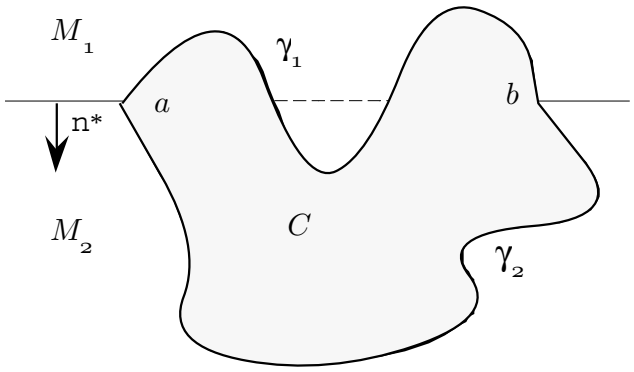


FIG. 3. THE INTERFACE AND A DROPLET OF PHASE $C$.

The interface free energy of the droplet consists of three terms,

$$\tau(\gamma) = \int_{\gamma_1} \tau_1(\boldsymbol{n}(s))\, ds + \int_{\gamma_2} \tau_2(\boldsymbol{n}(s))\, ds - \tau_{1,2} \cdot L(\gamma). \tag{25}$$

The first two terms in (25) correspond to the surface tension between the crystal and the phase $M_1$, $M_2$, respectively, and the third one to the loss of surface tension $\tau_{1,2}$ between phases $M_1$ and $M_2$ over the length $L(\gamma)$ of the portion of the interface which is missing,

because of the presence of the phase $C$. We want to minimize this functional among the following class of simple closed $\gamma$, called *compatible with the interface*:

(1) $\gamma_j$, $j = 1, 2$, are simple curves which don't intersect;
(2) the infinite interface is broken between the points $\boldsymbol{a}(\gamma)$ and $\boldsymbol{b}(\gamma)$;
(3) the end-points of $\gamma_j$ are $\boldsymbol{a}$ and $\boldsymbol{b}$, $j = 1, 2$;
(4) the volume of the droplet with the boundary $\gamma$ is given.

Changing, say, the surface tension $\tau_1(\boldsymbol{n})$ by the shift

$$\tau_1'(\boldsymbol{n}) = \tau_1(\boldsymbol{n}) + \tau_{1,2} \cdot (\boldsymbol{n}^* | \boldsymbol{n}), \tag{26}$$

we get

$$\int_{\gamma_1} \tau_1'(\boldsymbol{n}_s)\, ds = \int_{\gamma_1} \tau_1(\boldsymbol{n}_s)\, ds - \tau_{1,2} \cdot L(\gamma). \tag{27}$$

We can write (25) as

$$\tau(\gamma) = \int_{\gamma_1} \tau_1'(\boldsymbol{n}_s)\, ds + \int_{\gamma_2} \tau_2(\boldsymbol{n}_s)\, ds \tag{28}$$

Let $W_j$ be the Wulff's set defined by $\tau_j$, $j = 1, 2$. The set $W_1'$ obtained by a translation of $W_1$ by $\tau_{1,2} \cdot \boldsymbol{n}^*$ is equal to the set which we get by performing the Wulff's construction with $\tau_1'$. Let

$$W := W_1' \cap W_2 \tag{29}$$

If $\tau_{1,2} > \tau_1(-\boldsymbol{n}^*) + \tau_2(\boldsymbol{n}^*)$, the set $W$ is empty, and the problem is degenerate, the infimum of the functional being $-\infty$. This situation corresponds to a complete wetting of the interface by the droplet of phase $C$. Let us therefore suppose that $W$ is a non-empty convex body. *We can solve the variational problem if the closed simple curve $\gamma = \partial W$ is compatible with the interface, where $\gamma_1$ is the part of the boundary of $W$ belonging to $W_1'$, and $\gamma_2$ is the part of the boundary of $W$ belonging to $W_2$.*

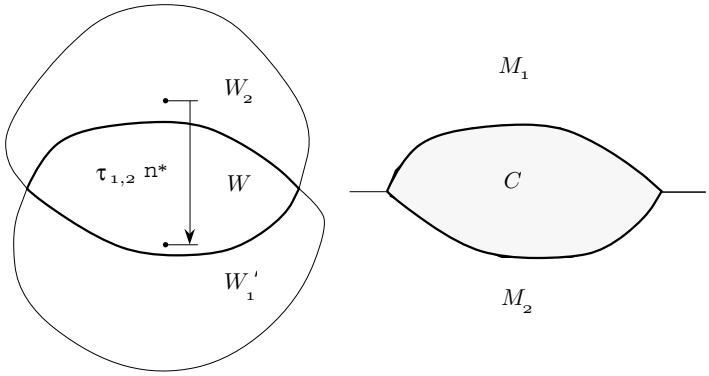


FIG. 4. OPTIMAL SHAPE $W$ OF THE CRYSTAL IN THE INTERFACE.

*The optimal shape of a droplet of volume $|W|$ is given by $W$.* If the volume is different, then we get the solution by an appropriate scaling of the set $W$. Let $\tau_W$ be the support function of $W$. Inequality (M1) holds, since $\tau_W(\boldsymbol{n}) \le \min(\tau_1'(\boldsymbol{n}), \tau_2(\boldsymbol{n}))$. Equality (M2) follows from (13). Let $r(\gamma)$ and $R(\gamma)$ be defined by (5a) and (5b) with $W$ of (29). Then the Bonnesen inequalities (S) hold after replacing $\tau_W(\gamma)$ by $\tau(\gamma)$.

*Remark.* 1. If the intersection is either $W = W_1'$, or $W = W_2$, we have the situation of drying of the interface with respect to the phase $C$. Putting a droplet of phase $C$ into the system, the optimal shape is that of a droplet inside phase $M_1$, or $M_2$. This is again a consequence of the monotonicity principle. Let $W = W_2$, and let $\tau_W = \tau_{W_2}$ be the support function of $W$. Then for any $\gamma$ as above, of volume $|W|$, we have

$$\int_\gamma \tau \ge \int_{\partial W} \tau_W = \int_{\partial W_2} \tau_2. \tag{30}$$

2. If the intersection of the boundaries is, say, in two pairs of points, or in a pair of points $P_1$ and $P_2$, such that the segment $[P_1, P_2]$ is not perpendicular to $\boldsymbol{n}^*$, then the resulting shape is not consistent with a single interface perpendicular to $\boldsymbol{n}^*$. The above construction does not give the solution to the variational problem.

3. The difficulties in the three-dimensional case are of similar nature. However if the intersection of the sets $W_1'$ and $W_2$ happens to lie in a plane perpendicular to $\boldsymbol{n}^*$, then the shape yielding the crystal with minimal interface free energy is given by the set $W$.

**3. Partial wetting of an interface boundary in presence of a wall.**

This variational problem is inspired by a very closely related problem considered by Ziermann [Zi]. We have a crystal in contact with a wall and an interface (see Fig. 5). We suppose that we have partial wetting, and therefore it is preferable for the droplet to stick to the wall.

We restrict ourselves to the two-dimensional case. The interface is perpendicular to $\boldsymbol{n}^*$ as in Section 2, and the wall is perpendicular to $\widehat{\boldsymbol{n}}$, $w(\widehat{\boldsymbol{n}}) = \{\boldsymbol{x} \in \mathbb{R}^2 : (\boldsymbol{x}|\widehat{\boldsymbol{n}}) = 0\}$. Without loss of generality we suppose that the wall is vertical, $\widehat{\boldsymbol{n}} = (0, -1)$. The subspaces $E^+$ and $E^-$ of section 2 are now defined as $E^+ = \{\boldsymbol{x} = (x_1, x_2) \in \mathbb{R}^2 : (\boldsymbol{x}|\boldsymbol{n}^*) < 0,\ x_1 > 0\}$ and $E^- = \{\boldsymbol{x} \in \mathbb{R}^2 : (\boldsymbol{x}|\boldsymbol{n}^*) > 0,\ x_1 > 0\}$. The phase $M_1$ is in $E^-$, and the phase $M_2$ is in $E^+$. We denote by $\sigma_j(\widehat{\boldsymbol{n}})$, $j = 1, 2$, the free energies $\tau_{cw}(\widehat{\boldsymbol{n}}) - \tau_{m_j w}(\widehat{\boldsymbol{n}})$, where $\tau_{m_j w}(\widehat{\boldsymbol{n}})$ is the surface free energy of the phase $M_j$ against the wall $w(\widehat{\boldsymbol{n}})$. Since the media $M_j$ are different, it is possible that the free energies of the phases $M_j$ against the wall are different, and therefore $\sigma_j(\widehat{\boldsymbol{n}})$ may be different for $j = 1$ or $j = 2$. For the sake of simplicity we consider crystals $\Gamma$ whose boundaries $\gamma$ are simple closed curves, and $\Gamma \cap w(\widehat{\boldsymbol{n}})$ is an interval

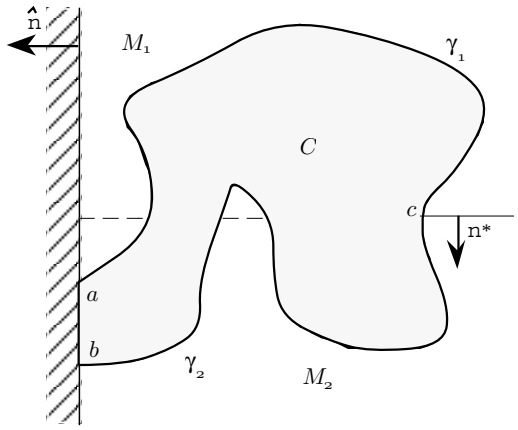


FIG. 5. A DROPLET OF PHASE $C$ WITH THE WALL AND THE INTERFACE.

$[\boldsymbol{b}, \boldsymbol{a}]$, with $a_2 > b_2$. We denote by $\gamma_1$, resp. $\gamma_2$, the part of the boundary in contact with the phase $M_1$, resp. $M_2$. Because of the presence of the phase $C$, the phase $M_1$ may occupy a part of the subspace $E^+$, or the phase $M_2$ a part of the subspace $E^-$. The interface free energy of the crystal consists of five terms,

$$\tau(\gamma) = \int_{\gamma_1} \tau_1(\boldsymbol{n}(s))\, ds + \int_{\gamma_2} \tau_2(\boldsymbol{n}(s))\, ds - \tau_{1,2} \cdot L(\gamma) + \sigma_1(\widehat{\boldsymbol{n}}) \cdot a_2(\gamma) - \sigma_2(\widehat{\boldsymbol{n}}) \cdot b_2(\gamma), \quad (31)$$

where $L(\gamma)$ is the length of the portion of the interface which is missing, because of the presence of the phase $C$. Notice that the last two terms in (31) may be positive or negative. They can be written

$$\begin{aligned} &(\sigma_1(\widehat{\boldsymbol{n}}) - \sigma_2(\widehat{\boldsymbol{n}})) \cdot a_2 + \sigma_2(\widehat{\boldsymbol{n}}) \cdot (a_2 - b_2) = \\ &(\tau_{m_2 w}(\widehat{\boldsymbol{n}}) - \tau_{m_1 w}(\widehat{\boldsymbol{n}})) \cdot a_2 + \sigma_2(\widehat{\boldsymbol{n}}) \cdot (a_2 - b_2). \end{aligned} \quad (32)$$

If, for example, $a_2$ is negative, then the last term in (32) is the contribution to the free energy of the crystal against the wall, and the first term is the contribution to the free energy against the wall due to the phase $M_1$ in the subspace $E^+$, where we had the phase $M_2$ before introducing the crystal. As in Section 2 we minimize the functional $\tau(\gamma)$ among the following class of simple closed $\gamma$, called *compatible* :

(1) $\gamma_j$, $j = 1, 2$, are simple curves which don't intersect;
(2) the interface is broken between the origin and a point $\boldsymbol{c}(\gamma)$;
(3) $\gamma \cap w(\widehat{\boldsymbol{n}})$ is an interval $[\boldsymbol{b}, \boldsymbol{a}]$, $a_2(\gamma) > b_2(\gamma)$;
(4) the end-points of $\gamma_1$ are $\boldsymbol{c}$ and $\boldsymbol{a}$;
(5) the end-points of $\gamma_2$ are $\boldsymbol{c}$ and $\boldsymbol{b}$;
(6) the volume $|\Gamma|$ is given.

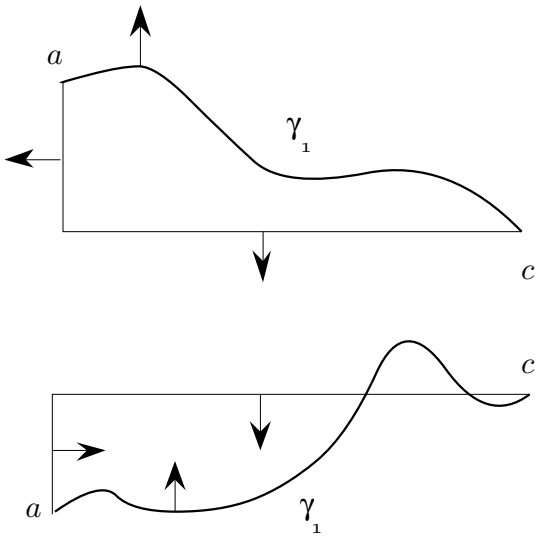


FIG. 6. THE INTEGRATION PATHS FOR PROVING (35).

We perform two shifts. Let $\boldsymbol{n}^{*\perp}$, resp. $\widehat{\boldsymbol{n}}^{\perp}$, be two unit vectors perpendicular to $\boldsymbol{n}^*$, resp. $\widehat{\boldsymbol{n}}$. We change the surface tension $\tau_1(\boldsymbol{n})$ into $\tau_1'(\boldsymbol{n})$ by the shift

$$\tau_1'(\boldsymbol{n}) = \tau_1(\boldsymbol{n}) + \tau_{1,2} \cdot \frac{(\widehat{\boldsymbol{n}}^{\perp}|\boldsymbol{n})}{(\widehat{\boldsymbol{n}}^{\perp}|\boldsymbol{n}^*)} - \sigma_1(\widehat{\boldsymbol{n}}) \cdot \frac{(\boldsymbol{n}^{*\perp}|\boldsymbol{n})}{(\boldsymbol{n}^{*\perp}|\widehat{\boldsymbol{n}})}, \tag{33}$$

and we change