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Equilibrium Shapes of Crystals Attached to Walls

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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 a simple geometrical argument based on the isoperimetric inequality and monotonicity. Stability results in the form of Bonnesen inequalities are obtained in the two-dimensional case.

KEY WORDS: Wulff's construction; equilibrium crystal shapes; Winterbottom's construction.

1. INTRODUCTION

In this paper we present simple mathematical arguments allowing us to discuss the equilibrium shape of a droplet of a phase C, called 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 the presence of walls. While the many facets of statistical mechanics of equilibrium shapes are reviewed in refs. 18 and 22, for results concerning droplets in the presence of walls see, e.g., refs. 21, 23, and 24. 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

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simplify and improve results 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. It turns out that with the help of monotonicity arguments that are strongly reminiscent of those used in the method of "correlation inequalities" one can find optimal shapes for different arrangements of walls. We treat different cases solvable by this method in increasing order of complexity.

1.1. 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 $\tau_W(\mathbf{n})$ be its *support function* assigning to a unit vector $\mathbf{n}$ the value

$$\tau_W(\mathbf{n}) = \sup_{\mathbf{x} \in W} (\mathbf{x} \mid \mathbf{n}) \tag{1}$$

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

Considering a set $V \subset \mathbb{R}^d$ with a sufficiently smooth boundary[3] $\partial V = \gamma$, we define the functional

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

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

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

where $|W|$, $|V|$ denote 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

[3] 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 hypotheses which we need are those leading to the isoperimetric inequality [and such that the functional $\tau_W(\gamma)$ below be well defined]. It is not our intention to discuss this point here; see, e.g., ref. 10 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.

(I) is simple if presented in a geometrical language (see ref. 5 and for a general proof ref. 19). Namely, one first expresses the functional $\tau_W(\gamma)$ in a geometrical manner as

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

Here, $V + \varepsilon W$ denotes the union $\bigcup_{\mathbf{x} \in V} (x + \varepsilon W)$, and $\varepsilon W = \{\varepsilon \mathbf{x} : \mathbf{x} \in W\}$. The inequality (I) then follows by applying the Brunn–Minkowski inequality to $|V + \varepsilon W|$. 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 ref. 9.

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 $W' = W + \mathbf{a}$,

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

Another way of showing (3) is to observe that the change W into W' amounts to the change $\tau_W(\mathbf{n})$ into $\tau_{W'}(\mathbf{n}) = \tau_W(\mathbf{n}) + (\mathbf{a} \mid \mathbf{n})$, and that the integral $\int_\gamma (\mathbf{a} \mid \mathbf{n}(s))\, ds$ 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 $\tau_W(\mathbf{n})$ is positive for all $\mathbf{n}$.

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 geometrically close to W in a uniform way. Introducing

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

and

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

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

$$\frac{\tau_W(\gamma) - [\tau_W(\gamma)^2 - 4\,|W|\cdot|V|]^{1/2}}{2\,|W|} \leqslant r(\gamma) \leqslant R(\gamma)$$
$$\leqslant \frac{\tau_W(\gamma) + [\tau_W(\gamma)^2 - 4\,|W|\cdot|V|]^{1/2}}{2\,|W|} \tag{S}$$

Inequalities (S) are the generalized Bonnesen inequalities, which are proven in Theorem 2.5 in ref. 8.

1.2. Variational Problem

Our aim is to use (I) and (S) to find the ideal shape of the crystal C inside the medium M in the 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.[1,14,15] Let $\mathbf{n}$ be a unit vector in $\mathbb{R}^d$, and consider the situation with phases C and M coexisting over a hyperplane perpendicular to $\mathbf{n}$, $\{\mathbf{x}: (\mathbf{x} \mid \mathbf{n}) = a\}$. We use $\tau(\mathbf{n})$ to denote the interface free energy, or surface tension, corresponding to such an interface in the situation of the phase C occupying the half-space $\{\mathbf{x}: (\mathbf{x} \mid \mathbf{n}) \leqslant a\}$. We suppose that the surface tension τ is given and assume that it is strictly positive and lower semicontinuous, but we do not require the symmetry $\tau(\mathbf{n}) = \tau(-\mathbf{n})$. We denote by Γ 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

$$\tau(\gamma) := \int_\gamma \tau(\mathbf{n}(s))\, ds \tag{6}$$

We always suppose that the boundary γ of Γ is sufficiently smooth (see footnote 3). 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.[20] Notice first 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_τ be defined by the so-called *Wulff construction*

$$W_\tau = \{\mathbf{x} \in \mathbb{R}^d: (\mathbf{x} \mid \mathbf{n}) \leqslant \tau(\mathbf{n}) \text{ for every } \mathbf{n}\} \tag{W}$$

We show that *this set yields the optimal shape for the crystal.*

We first state some elementary properties of W_τ. The set W_τ is convex since it is given by the intersection of hyperplanes. If we extend the surface tension $\tau(\mathbf{n})$ to all $\mathbb{R}^d$ as a positively homogeneous function of degree one, we get

$$W_\tau = \{\mathbf{x} \in \mathbb{R}^d \colon \tau^*(\mathbf{x}) \leqslant 0\} \tag{7}$$

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

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

By the methods of convex analysis it can be shown that for almost all $\mathbf{x}$ one has

$$\tau^{**}(\mathbf{n}_\mathbf{x}) = \tau(\mathbf{n}_\mathbf{x}) \tag{9}$$

Equation (9) implies the important result that the values 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_τ (if the volume of the crystal is $|W_\tau|$).

Remarks. 1. It is expected from thermodynamic reasons that the equilibrium surface tension τ is in fact equal to the support function of the set W_τ defined above. In other words, the surface tension τ 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 τ satisfies the *pyramidal inequality*.[7,16] The convexity property of τ has been proven for several models of statistical mechanics.[16] However, in the present paper we do not assume that τ 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.[8,17]

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 the crystal differs from that 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 $\mathbf{n}$ be a unit vector in $\mathbb{R}^d$, and let

$$w(\mathbf{n}) = \{\mathbf{x} \colon (\mathbf{x} \mid \mathbf{n}) = a\} \tag{10}$$

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

$$\sigma(\mathbf{n}) = \tau_{cw}(\mathbf{n}) - \tau_{mw}(\mathbf{n}) \tag{11}$$

where $\tau_{cw}(\mathbf{n})$ and $\tau_{mw}(\mathbf{n})$ are the surface free energies of the phase C against the wall and of the phase M against the wall, respectively. Since $\sigma(\mathbf{n})$ is a difference of free energies, it may either be positive or negative. When $\tau_{cw}(\mathbf{n}) - \tau_{mw}(\mathbf{n}) \geqslant \tau(\mathbf{n})$ we have a *drying* situation: in equilibrium, it is preferable 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 $\tau_{cw}(\mathbf{n}) - \tau_{mw}(\mathbf{n}) \leqslant -\tau(\mathbf{n})$ 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 $\tau_{cw}(\mathbf{n}) - \tau_{mw}(\mathbf{n}) \geqslant 0$, and *partial wetting* if $\tau_{cw}(\mathbf{n}) - \tau_{mw}(\mathbf{n}) \leqslant 0$. Actually, at equilibrium, we have,[2] from thermodynamic reasons, the inequalities

$$|\sigma(\mathbf{n})| = |\tau_{cw}(\mathbf{n}) - \tau_{mw}(\mathbf{n})| \leqslant \tau(\mathbf{n}) \tag{12}$$

The physical situations described above have been studied rigorously in the Ising model, starting from first principles of statistical mechanics.[11-13]

Whenever the phase C is in contact with a wall with normal $\mathbf{n}$, we must replace the integrand $\tau(\mathbf{n})$ in the free functional (6) by $\sigma(\mathbf{n})$. Since the walls are fixed, the problem is no longer translation invariant, and the new functional, which we still denote by $\tau(\gamma)$, is

$$\tau(\gamma) = \int_\gamma \tau(\mathbf{x}(s), \mathbf{n}(s))\, ds \tag{13}$$

with

$$\tau(\mathbf{x}, \mathbf{n}) = \begin{cases} \sigma(\mathbf{n}), & \text{if} \quad \mathbf{x} \in w(\mathbf{n}) \\ \tau(\mathbf{n}), & \text{otherwise} \end{cases} \tag{14}$$

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 (13).

If we can find a convex body W such that

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

for every γ, *where* τ_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 the monotonicity of $\alpha - (\alpha^2 - C)^{1/2}$ as a function of α (for $|\alpha| \geqslant \sqrt{C}$) 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.

For a basic illustration of the use of (M1) and (M2) [and thus of (I) and (S)], we first apply it in Section 2.1 to the well-understood case of a crystal on a single wall—Winterbottom shape.

The cases of partial wetting of an interface (Section 2.2) and partial wetting of an interface in the presence of a wall (Section 2.3) were (in a slightly different formulation and under more restrictive assumptions) discussed by Ziermann.[23] We include them here since they yield additional cases of the remarkably simple solution of the variation problem by our geometrical principle. Moreover, in the two-dimensional case we also get stability.

Section 2.4 is devoted to the case of a crystal in a corner. The case of convex droplet in a convex corner was presented in ref. 24—here, in Section 2.4.1, we again get the simple proof accompanied, for $d = 2$, by stability. The case of nonconvex angle discussed in Section 2.4.2 seems to be new, not discussed in the literature. It turns out that the optimal droplet does not touch both walls—it stays attached to only one of them.

In Sections 2.5 and 2.6 we discuss the case of a droplet between two parallel walls, restricting ourselves to the two-dimensional case. Since the distance of these two walls is fixed, one loses the standard rescaling argument used to adjust the given shape to the *a priori* fixed volume. Nevertheless, the optimal crystal can be found and shown to be bordered by the walls and properly chosen pieces of Wulff shapes.

During the completion of this work we received two papers[3,4] about numerical and analytical studies of the shape of droplets in a corner for different models of statistical mechanics. The problem mentioned at the end of Section 2.2 is treated in ref. 4. A double Wulff construction is used there.

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

$$\hat{\tau}(\gamma) = \int_\gamma \hat{\tau}(\mathbf{x}(s), \mathbf{n}(s))\, ds \tag{15}$$

with

$$\hat{\tau}(\mathbf{x}, \mathbf{n}) = \begin{cases} -\sigma(\mathbf{n}), & \text{if } \ \mathbf{x} \in w(\mathbf{n}) \\ \tau(-\mathbf{n}), & \text{otherwise} \end{cases} \tag{16}$$

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

2. PARTICULAR ARRANGEMENTS OF WALLS

2.1. Crystal on a Wall

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

$$\tau(\gamma) = \int_{\gamma_w} \sigma(\mathbf{n}^*)\, ds + \int_{\gamma_f} \tau(\mathbf{n}(s))\, ds \tag{17}$$

where the first integral is over the boundary of the crystal along the wall, $\gamma_w = \gamma \cap w(\mathbf{n}^*)$, 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 (13) with $\tau(\mathbf{x}, \mathbf{n})$ defined by (14).

The solution is well-known.[21,23] Let us briefly recall it. One first constructs the Wulff set,

$$W_\tau = \{\mathbf{x} \in \mathbb{R}^d : (\mathbf{x} \mid \mathbf{n}) \leqslant \tau(\mathbf{n}) \text{ for every } \mathbf{n}\} \tag{18}$$

which corresponds to the ideal shape of the free crystal. Then we take the

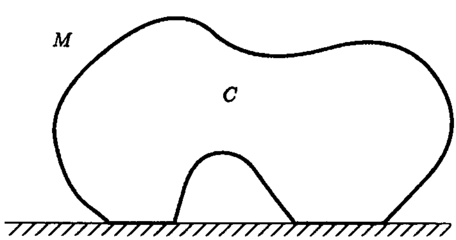

Fig. 1. A droplet of phase C in the half-space E.

intersection of this set W_τ with the half-space (which should not be mistaken for the half-space E)

$$\{\mathbf{x} \in \mathbb{R}^d \colon (\mathbf{x} \mid \mathbf{n}^*) \leqslant \sigma(\mathbf{n}^*)\} \tag{19}$$

and we get a new convex subset W, called the *Winterbottom shape* (see Fig. 2). Except for the case $\sigma(\mathbf{n}^*) \leqslant -\tau(\mathbf{n}^*)$, which corresponds to the complete wetting of the wall by the phase C, and in which the variational problem is degenerate [when $\sigma(\mathbf{n}^*) < -\tau(\mathbf{n}^*)$ the infimum of the functional is $-\infty$], the set W is a convex body, but not necessarily containing the origin.

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

$$\tau(\mathbf{x}, \mathbf{n}) \geqslant \tau_W(\mathbf{n}) \tag{20}$$

Therefore, the inequality (M1) is satisfied and the equality (M2) follows from (9). 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 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 ref. 8 only under the assumption that the origin belongs to W. We can always satisfy this assumption by applying a shift to W by, say, $(\tau_{cw} - \tau_{mw})\,\mathbf{n}_w$ or any $\mathbf{a}$ such that $(\mathbf{a} \mid \mathbf{n}_w) = \tau_{cw} - \tau_{mw}$. The new set W' contains the origin, but as 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 inter-

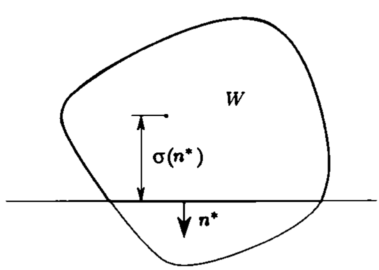

Fig. 2. The Winterbottom shape W.

face free energy on the wall to vanish and compensate for it by changing correspondingly the surface tension between the crystal and the medium.[23] This also shows that the minimum of the functional is strictly positive.

2.2. Partial Wetting of an Interface

This case is discussed in detail in ref. 23 (even though the variational problem in ref. 23 is slightly different and the assumptions more restrictive). We suppose that we have a system with three phases in equilibrium, M_1, M_2, C, and start with a situation in which the two phases M_1 and M_2 coexist in $\mathbb{R}^d$ and are separated by a stable flat interface perpendicular to $\mathbf{n}^*$, $I(\mathbf{n}^*) = \{\mathbf{x} \in \mathbb{R}^d: (\mathbf{x} \mid \mathbf{n}^*) = 0\}$, passing through the origin. Let $E^+ = \{\mathbf{x} \in \mathbb{R}^d: (\mathbf{x} \mid \mathbf{n}^*) < 0\}$ and $E^- = \{\mathbf{x} \in \mathbb{R}^2: (\mathbf{x} \mid \mathbf{n}^*) > 0\}$. The phase M_1 is in E^- and the phase M_2 is in E^+. The surface tension associated with this interface is $\tau_{1,2}(\mathbf{n}^*)$. We put a droplet of the phase C into the system. By inserting this droplet we can create "a hole" in the interface where the phases M_1 and M_2 do not touch directly. We denote by $\tau_j(\mathbf{n})$ the surface tension of an interface, perpendicular to $\mathbf{n}$, between the phase C and the phase M_j, $j = 1, 2$. The functional $\tau(\gamma)$ is similar, but not identical, to the functional (13). The surface ∂C of the droplet splits into two pieces, γ_1 and γ_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.

In the three-dimensional case, the surfaces γ_1 and γ_2 touch along a curve in I (in the two-dimensional case illustrated in the Fig. 3 they touch in a pair of points $\mathbf{a}$ and $\mathbf{b}$).

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

$$\tau(\gamma) = \int_{\gamma_1} \tau_1(\mathbf{n}(s))\, ds + \int_{\gamma_2} \tau_2(\mathbf{n}(s))\, ds - \tau_{1,2} \cdot L(\gamma) \tag{21}$$

The first two terms in (21) correspond to the surface tension between the

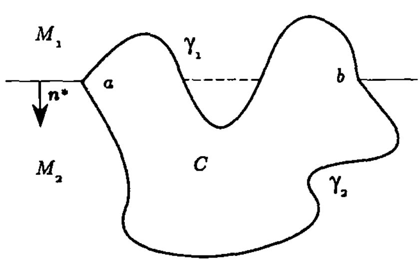

Fig. 3. The interface and a droplet of phase C.

crystal and the phases 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 area $L(\gamma)$ 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 surfaces γ,[4] called *compatible with the interface*:

1. γ_j, $j=1, 2$, are surfaces with a common boundary on a simple closed curve in $I(\mathbf{n}^*)$, $\partial(\gamma_1)=\partial(\gamma_2)\subset I(\mathbf{n}^*)$.
2. The infinite interface is broken inside $\partial(\gamma_1)=\partial(\gamma_2)$.
3. The surfaces γ_1 and γ_2 do not intersect outside their boundary— $(\gamma_1\backslash\partial\gamma_1)\cap(\gamma_2\backslash\partial\gamma_2)\neq\varnothing$.
4. The volume of the droplet with the boundary $\gamma=\gamma_1\cup\gamma_2$ is fixed.

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

$$\tau_1'(\mathbf{n})=\tau_1(\mathbf{n})+\tau_{1,2}\cdot(\mathbf{n}^* \mid \mathbf{n}) \tag{22}$$

we get

$$\int_{\gamma_1}\tau_1'(\mathbf{n}_s)\,ds=\int_{\gamma_1}\tau_1(\mathbf{n}_s)\,ds-\tau_{1,2}\cdot L(\gamma) \tag{23}$$

We can write (21) as

$$\tau(\gamma)=\int_{\gamma_1}\tau_1'(\mathbf{n}_s)\,ds+\int_{\gamma_2}\tau_2(\mathbf{n}_s)\,ds \tag{24}$$

Let W_j be the Wulff set defined by τ_j, $j=1, 2$. The set W_1' obtained by a translation of W_1 by $\tau_{1,2}\cdot\mathbf{n}^*$ is equal to the set which we get by performing the Wulff construction with τ_1'. Let

$$W:=W_1'\cap W_2 \tag{25}$$

If $\tau_{1,2}>\tau_1(-\mathbf{n}^*)+\tau_2(\mathbf{n}^*)$, 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 nonempty convex body.

We can solve the variational problem if the resulting shape W is compatible with the outside interface being held at a fixed level—namely, if the intersection of $\partial W_1'$ and ∂W_2 is contained in a plane orthogonal to $\mathbf{n}^*$.

Under this assumption, the optimal shape of a droplet of volume $|W|$ is

[4] Formulated here in the three-dimensional case.

given by W (Fig. 4). Moreover, in the two-dimensional case the stability condition (S) is satisfied.

If the size of the volume is different, then we get the solution by an appropriate scaling of the set W. Let τ_W be the support function of W. Inequality (M1) holds, since $\tau_W(\mathbf{n}) \leqslant \min(\tau_1'(\mathbf{n}), \tau_2(\mathbf{n}))$. Equality (M2) follows from (9). Let $r(\gamma)$ and $R(\gamma)$ be defined by (5a) and (5b) with W of (25). 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 γ as above, of volume $|W|$, we have

$$\int_\gamma \tau \geqslant \int_{\partial W} \tau_W = \int_{\partial W_2} \tau_2 \tag{26}$$

2. The condition that $\partial W_1' \cap \partial W_2$ lies in a plane $I(\mathbf{n}^*)$ is presumably rather restrictive in the three-dimensional case. Nevertheless, one may imagine it to be fulfilled due to a symmetry, getting thus a solution of the three-dimensional variational problem. If the intersection does not lie in a plane, one has to deform the shape W and possibly also the interface in the neighborhood of the droplet. The variational problem in this case is open.

3. In the two-dimensional case the condition above means that $\partial W_1'$ and ∂W_2 intersect in two points connected by a line orthogonal to $\mathbf{n}^*$. If this line were not orthogonal to $\mathbf{n}^*$, the shape W would still yield a solution to a slightly different variational problem—namely, to the

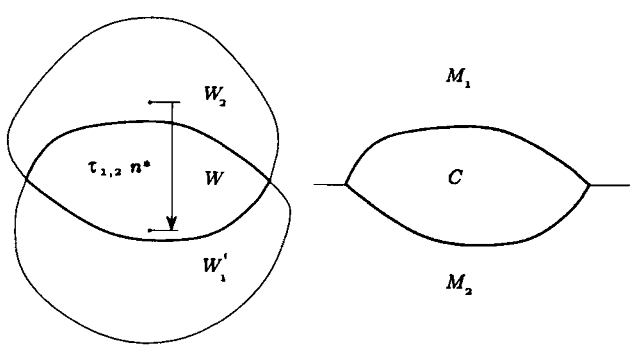

Fig. 4. Optimal shape W of the crystal in the interface.

problem where one does not fix the interface on both sides of the droplet to be on the same level, but adjusts these levels to minimize the overall surface tension.

2.3. 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.[23] 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 here (but similarly as in Section 2, the results may be formulated for $d=3$ under a similar assumption). The interface is perpendicular to $\mathbf{n}^*$ as in Section 2, and the wall is perpendicular to $\hat{\mathbf{n}}$, $w(\hat{\mathbf{n}})=\{\mathbf{x}\in\mathbb{R}^2\colon (\mathbf{x}\mid\hat{\mathbf{n}})=0\}$. Without loss of generality we suppose that the wall is vertical, $\hat{\mathbf{n}}=(0,-1)$. The subspaces E^+ and E^- of Section 2 are now defined as $E^+=\{\mathbf{x}=(x_1,x_2)\in\mathbb{R}^2\colon (\mathbf{x}\mid\mathbf{n}^*)<0, x_1>0\}$ and $E^-=\{\mathbf{x}\in\mathbb{R}^2\colon (\mathbf{x}\mid\mathbf{n}^*)>0, x_1>0\}$. The phase M_1 is in E^-, and the phase M_2 is in E^+. We denote by $\sigma_j(\hat{\mathbf{n}})$, $j=1,2$, the free energies $\tau_{cw}(\hat{\mathbf{n}})-\tau_{m_jw}(\hat{\mathbf{n}})$, where $\tau_{m_jw}(\hat{\mathbf{n}})$ is the surface free energy of the phase M_j against the wall $w(\hat{\mathbf{n}})$. 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 $\sigma_j(\hat{\mathbf{n}})$ may be different for $j=1$ or $j=2$. For the sake of simplicity we consider crystals Γ whose boundaries γ are simple closed curves, and $\Gamma\cap w(\hat{\mathbf{n}})$ is an interval $[\mathbf{b},\mathbf{a}]$, with $a_2>b_2$. We denote by γ_1, resp. γ_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

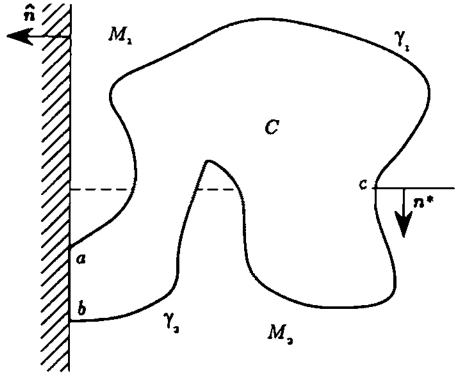

Fig. 5. A droplet of phase C with the wall and the interface.

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,

$$\tau(\gamma) = \int_{\gamma_1} \tau_1(\mathbf{n}(s))\, ds + \int_{\gamma_2} \tau_2(\mathbf{n}(s))\, ds - \tau_{1,2} \cdot L(\gamma)$$
$$+ \sigma_1(\hat{\mathbf{n}}) \cdot a_2(\gamma) - \sigma_2(\hat{\mathbf{n}}) \cdot b_2(\gamma) \tag{27}$$

where $L(\gamma)$ is the length of the portion of the interface which is missing, because of the presence of the phase C; we use $\tau_{1,2}$ to denote, as in Section 2, the interface free energy corresponding to a direct contact of phases M_1 and M_2 along a line orthogonal to $\mathbf{n}^*$. Notice that the last two terms in (27) may be positive or negative. They can be written

$$(\sigma_1(\hat{\mathbf{n}}) - \sigma_2(\hat{\mathbf{n}})) \cdot a_2 + \sigma_2(\hat{\mathbf{n}}) \cdot (a_2 - b_2)$$
$$= (\tau_{m_2 w}(\hat{\mathbf{n}}) - \tau_{m_1 w}(\hat{\mathbf{n}})) \cdot a_2 + \sigma_2(\hat{\mathbf{n}}) \cdot (a_2 - b_2) \tag{28}$$

If, for example, a_2 is negative, then the last term in (28) 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 γ, called *compatible*:

1. γ_j, $j = 1, 2$, are simple curves which do not intersect.
2. The interface is broken between the origin and a point $\mathbf{c}(\gamma)$.
3. $\gamma \cap w(\hat{\mathbf{n}})$ is an interval $[\mathbf{b}, \mathbf{a}]$, $a_2(\gamma) > b_2(\gamma)$.
4. The endpoints of γ_1 are $\mathbf{c}$ and $\mathbf{a}$.
5. The endpoints of γ_2 are $\mathbf{c}$ and $\mathbf{b}$.
6. The volume $|\Gamma|$ is given.

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

$$\tau_1'(\mathbf{n}) = \tau_1(\mathbf{n}) + \tau_{1,2} \cdot \frac{(\hat{\mathbf{n}}^\perp \mid \mathbf{n})}{(\hat{\mathbf{n}}^\perp \mid \mathbf{n}^*)} - \sigma_1(\hat{\mathbf{n}}) \cdot \frac{(\mathbf{n}^{*\perp} \mid \mathbf{n})}{(\mathbf{n}^{*\perp} \mid \hat{\mathbf{n}})} \tag{29}$$

and we change the surface tension $\tau_2(\mathbf{n})$ into $\tau_2'(\mathbf{n})$ by the shift

$$\tau_2'(\mathbf{n}) = \tau_2(\mathbf{n}) - \sigma_2(\hat{\mathbf{n}}) \cdot \frac{(\mathbf{n}^{*\perp} \mid \mathbf{n})}{(\mathbf{n}^{*\perp} \mid \hat{\mathbf{n}})} \tag{30}$$

After these shifts the functional becomes

$$\tau(\gamma) = \int_{\gamma_1} \tau_1'(\mathbf{n}(s))\, ds + \int_{\gamma_2} \tau_2'(\mathbf{n}(s))\, ds \tag{31}$$

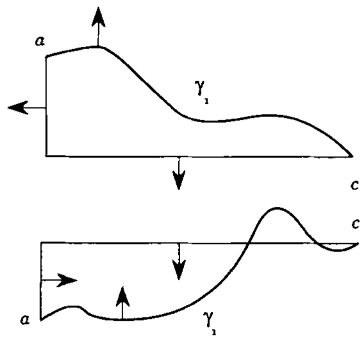

Fig. 6. The integration paths for proving (31).

To prove (31), we integrate, for example, $\tau_1'(\mathbf{n}(s)) - \tau_1(\mathbf{n}(s))$ along the two closed curves of Fig. 6 and we use the fact that the integral is zero. Notice the position of the normal $\mathbf{n}(s)$ in both cases.

We interpret the functional given by (31) as the integral along the closed curve formed by γ_1, the interval $[\mathbf{a}, \mathbf{b}]$, and γ_2. When we integrate along $[\mathbf{a}, \mathbf{b}]$ the surface tension is equal to zero. Therefore we define the set W as (Fig. 7)

$$W = W_{\tau_1'} \cap W_{\tau_2'} \cap \{\mathbf{x} \in \mathbb{R}^2 : (\mathbf{x} \mid \hat{\mathbf{n}}) \leqslant 0\} \tag{32}$$

If the set W is a nonempty convex body, and if its boundary defines a closed compatible curve γ, then the optimal droplet has shape W. This an immediate consequence of the monotonicity principle.

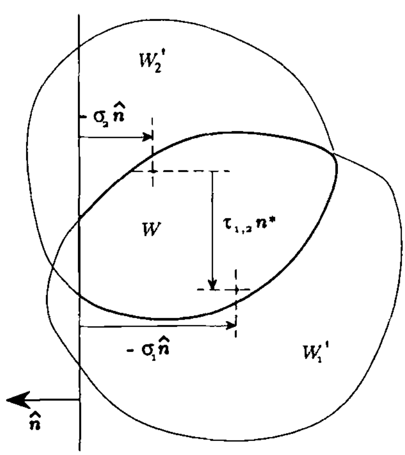

Fig. 7. The optimal shape W with a wall and an interface.

2.4. Droplet in a Corner

Here we have one droplet and two walls of different kinds. We consider the d-dimensional case, $d \geqslant 2$, and suppose that the walls are $(d-1)$-dimensional hyperplanes, and that their intersection has dimension $d-2$. The particular situation of two parallel walls is treated in the next section in the special case when $d=2$.

We use $\mathbf{n}_j$, $j=1, 2$, to denote the unit vectors perpendicular to the considered walls. One can always suppose that the walls contain the origin and therefore the walls are

$$\{\mathbf{x} \in \mathbb{R}^d \colon (\mathbf{x} \mid \mathbf{n}_j) = 0\}, \qquad j = 1, 2 \tag{33}$$

We treat two cases. The space E containing the droplet is either *convex*,

$$E = \{\mathbf{x} \in \mathbb{R}^d \colon (\mathbf{x} \mid \mathbf{n}_1) \leqslant 0\} \cap \{\mathbf{x} \in \mathbb{R}^d \colon (\mathbf{x} \mid \mathbf{n}_2) \leqslant 0\} \tag{34}$$

or *nonconvex*,

$$E = \{\mathbf{x} \in \mathbb{R}^d \colon (\mathbf{x} \mid \mathbf{n}_1) \leqslant 0\} \cup \{\mathbf{x} \in \mathbb{R}^d \colon (\mathbf{x} \mid \mathbf{n}_2) \leqslant 0\} \tag{35}$$

The variational problem is to minimize the functional given by (13) and (14) for all simple (i.e., without self-intersection) closed hypersurfaces $\gamma = \partial \Gamma$ which are contained in E, and which are the boundary of a set $|\Gamma|$ of fixed volume. In order to avoid degenerate cases we also suppose that we have partial wetting for both walls,

$$|\sigma(\mathbf{n}_j)| \leqslant \tau(\mathbf{n}_j), \qquad j = 1, 2 \tag{36}$$

Let W_τ be the Wulff crystal and let

$$W = W_\tau \cap \{\mathbf{x} \in \mathbb{R}^d \colon (\mathbf{x} \mid \mathbf{n}_1) \leqslant \sigma(\mathbf{n}_1)\} \cap \{\mathbf{x} \in \mathbb{R}^d \colon (\mathbf{x} \mid \mathbf{n}_2) \leqslant \sigma(\mathbf{n}_2)\} \tag{37}$$

Several cases may occur.

2.4.1. *W* is Nonempty and *E* is Convex. If W is nonempty and E is convex, the solution of the variational problem is straightforward. (This case is considered in ref. 24.)

Namely, *the optimal droplet has the shape* W. The correct volume is obtained by an appropriate scaling. The point to notice is that any W can be rescaled in E to yield a droplet of any given volume (and the shape W). The answer to the variational problem is therefore a direct consequence of the monotonicity principle. Several possibilities for the intersection W yield the shapes of droplets as illustrated in Fig. 8. In cases (a)–(c) there is only one optimal droplet for a given volume, which lies in the corner. On the

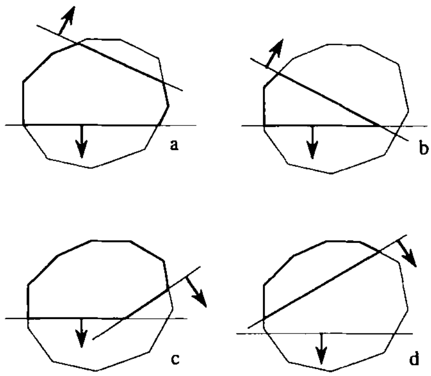

Fig. 8. Possible shapes of crystals.

other hand, in case (d) the droplet is repelled from the corner; it favors to be attached to only one wall—we get a Winterbottom shape.

In the dimension $d=2$, we have again the stability result in the form of Bonnesen's inequalities (S) with $\tau_W(\gamma)$ replaced by $\tau(\gamma)$.

2.4.2. *W* is Nonempty and *E* Nonconvex. Let W be nonempty, but E nonconvex. We use $w(\mathbf{n}_j)$ to denote the part of the boundary of E which is perpendicular to the vector $\mathbf{n}_j$ and W_j to denote the corresponding Winterbottom shape

$$W_j = W_\tau \cap \{\mathbf{x} \in \mathbb{R}^d: (\mathbf{x} \mid \mathbf{n}_j) \leqslant \sigma(\mathbf{n}_j)\} \tag{38}$$

The optimal shape of a droplet is given by that set W_j for which $|W_j| = \min\{|W_1|, |W_2|\}$.

The main point is to show that any optimal droplet cannot simultaneously touch both walls $w(\mathbf{n}_1)$ and $w(\mathbf{n}_2)$. Let Γ be the set occupied by the crystal C. There are two cases to be treated separately. First, the boundary γ of Γ may touch either only one wall or no wall at all. In this case we compare $\tau(\gamma)$ with a Winterbottom shape W_j of volume $|\Gamma|$ (and get our claim).

The second possibility is that γ touches both walls. In order to treat this case we reduce the situation to a convex one so that we can apply our monotonicity principle. To this end, we introduce an auxiliary wall $\hat{w}$, as shown in Fig. 9, which passes through $\{\mathbf{x} \in \mathbb{R}^d: (\mathbf{x} \mid \mathbf{n}_1) = 0\} \cap \{\mathbf{x} \in \mathbb{R}^d: (\mathbf{x} \mid \mathbf{n}_2) = 0\}$, so that the wall $\hat{w}$ splits the space E into two convex subsets E' and E''. In the "surface tension space," where we draw the surface tension plot, we consider the hyperplane $\hat{l} = \hat{l}(\hat{w})$ passing through $\{\mathbf{x} \in \mathbb{R}^d: (\mathbf{x} \mid \mathbf{n}_1) = \sigma(\mathbf{n}_1)\} \cap \{\mathbf{x} \in \mathbb{R}^d: (\mathbf{x} \mid \mathbf{n}_2) = \sigma(\mathbf{n}_2)\}$ and having the same

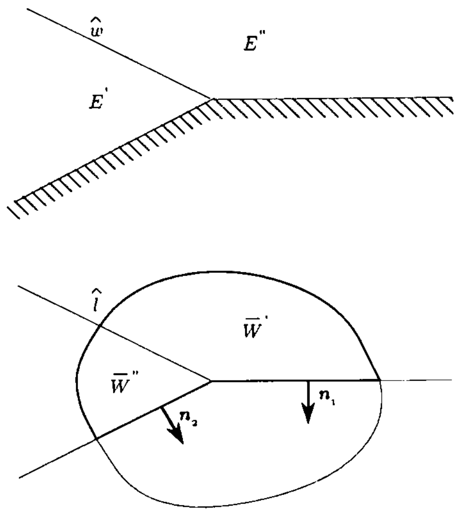

Fig. 9. The auxiliary wall $\hat{w}$ and the sets $\bar{W}'$ and $\bar{W}''$.

direction as $\hat{w}$. This hyperplane divides the set $\bar{W} = W_1 \cup W_2$ into two convex sets $\bar{W}'$ and $\bar{W}''$ (see Fig. 9).

The set Γ is the union of the sets $\Gamma' := E' \cap \Gamma$ and $\Gamma'' := E'' \cap \Gamma$, and we have

$$\tau(\partial\Gamma) \geqslant \tau_{\bar{W}'}(\partial\Gamma') + \tau_{\bar{W}''}(\partial\Gamma'') \tag{39}$$

[The contributions from $\partial\Gamma' \cap \hat{w} = \partial\Gamma'' \cap \hat{w}$ to $\tau_{\bar{W}'}(\partial\Gamma')$ and $\tau_{\bar{W}''}(\partial\Gamma'')$ compensate each other.] Without loss of generality we suppose that $|\Gamma| = |\bar{W}|$. Let us assume further that a wall $\hat{w}$ can be found in such a way that it splits Γ so that $|\Gamma'| = |\bar{W}'|$ and $|\Gamma''| = |\bar{W}''|$. From (39) and the isoperimetric inequality we have

$$\tau(\partial\Gamma) \geqslant \tau_{\bar{W}'}(\partial\bar{W}') + \tau_{\bar{W}''}(\partial\bar{W}'') = \tau_{\bar{W}}(\partial\bar{W}) = d\,|\bar{W}| \tag{40}$$

If the above hypothesis is not satisfied, a simple continuity argument shows that we can split the space E into a half-space, say E', and a convex cone E'', such that

$$|\Gamma'| := \lambda'\,|\bar{W}'|, \quad \lambda' > 1 \qquad \text{and} \qquad |\Gamma''| := \lambda''\,|\bar{W}''|, \quad \lambda'' < 1 \tag{41}$$

We proceed as above,

$$\begin{aligned}\tau(\partial\Gamma) &\geqslant \tau_{W'}(\partial\Gamma') + \tau_{W''}(\partial\Gamma'') \\ &\geqslant d(\lambda')^{(d-1)/d}\,|\bar{W}'| + d(\lambda'')^{(d-1)/d}\,|\bar{W}''| \\ &= \frac{d}{(\lambda')^{1/d}}\lambda'\,|\bar{W}'| + \frac{d}{(\lambda'')^{1/d}}\lambda''\,|\bar{W}''| \\ &\geqslant \frac{d}{(\lambda')^{1/d}}(\lambda'\,|\bar{W}'| + \lambda''\,|\bar{W}''|) \\ &= \frac{d}{(\lambda')^{1/d}}\,|\bar{W}|\end{aligned} \tag{42}$$

We can compare this lower bound with the one that can be attained by a set Ω_1 of the shape W_1 and of full volume $|\Omega_1| = |\bar{W}| = |\Gamma|$. Defining μ by $|\Gamma| = \mu\,|W_1|$, we have (since E' is a half-space) $|\Gamma| = \mu\,|W_1| = \mu\,|\bar{W}'| > \lambda'\,|\bar{W}'|$, and

$$\begin{aligned}\tau(\partial\Omega_1) &= d\,|\bar{W}|^{(d-1)/d}\,|W_1|^{1/d} \\ &= \frac{d}{\mu^{1/d}}\,|\bar{W}| \\ &\leqslant \frac{d}{(\lambda')^{1/d}}\,|\bar{W}|\end{aligned} \tag{43}$$

This finishes the proof.

Remark. In the case of convex E and empty W, a solution is proposed for $d=2$ in ref. 24 under the name "summertop construction," because it is a kind of dual construction to the Winterbottom construction. We can justify this result using our monotonicity principle for a *restricted* class of droplets. Some ideas as well as difficulties that would occur in our proof appear also in the next section. For that reason we do not present our partial results here.

2.5. Droplet Between Two Parallel Walls ($d=2$)

A new feature appears in this problem. Namely, in the preceding cases we were able to take into account the constraint on the volume of the droplet by rescaling the (correspondingly cut off) Wulff shape. Now, since the droplet is constrained to lie between two parallel walls of fixed distance, this is no longer possible. The confining aspect of the geometry of the problem changes the shape of the optimal droplet when its volume is large.

For the first time we use in this section the two-dimensional character of the space in all arguments; we suppose that the two walls are horizontal and are characterized by the surface free energy differences [cf. (11)] $\sigma(\mathbf{n}_1)$ and $\sigma(\mathbf{n}_2)$ with $\mathbf{n}_1 = -\mathbf{n}_2$. Further, let us suppose that

$$W = W_\tau \cap \{\mathbf{x} \in \mathbb{R}^2 : (\mathbf{x} \mid \mathbf{n}_1) \leqslant \sigma(\mathbf{n}_1)\} \cap \{\mathbf{x} \in \mathbb{R}^2 : (\mathbf{x} \mid \mathbf{n}_2) \leqslant \sigma(\mathbf{n}_2)\} \quad (44)$$

is a nonempty convex body.

The variational problem to solve is again the one given by (13) and (14), taking for $\gamma = \partial\Gamma$ a simple closed curve between two walls defined by the equations

$$\{x \in \mathbb{R}^2 : (\mathbf{x} \mid \mathbf{n}_1) = d\} \qquad \text{and} \qquad \{x \in \mathbb{R}^2 : (\mathbf{x} \mid \mathbf{n}_2) = -d\} \quad (45)$$

under the condition of a fixed volume $|\Gamma|$.

2.5.1. Complete Drying Case. Let us suppose first that Cahn's inequality (12) is saturated, i.e., $\sigma(\mathbf{n}_i) = \tau(\mathbf{n}_i)$, $i = 1, 2$. In this case we have

$$W = W_\tau \quad (46)$$

There exists the greatest value $|W^*|$ of the volume of a droplet W^* of shape W which can be put between the two walls. If $|\Gamma| \leqslant |W^*|$, *then the optimal shape of the droplet is* $W = W_\tau$. This follows from the monotonicity principle.

Let us therefore suppose that $|\Gamma| > |W^*|$ and let W^* be a droplet of shape W and volume $|W^*|$. We define the new set $\bar{W}$ by taking (see Fig. 10)

$$\bar{W} := \bigcup_{0 \leqslant x_1 \leqslant a} (W^* + (x_1, 0)) \quad (47)$$

Here the value a is chosen so that the volume of $\bar{W}$ is equal to $|\Gamma|$. If $|\Gamma| \geqslant |W^*|$, *then the optimal shape of the droplet is* $\bar{W}$.

To prove this fact, we first define $W_0^* = W^*$, $W_a^* = W^* + (a, 0)$, and also $\tilde{W} = \bigcup_{0 \leqslant x_1} (W^* + (x_1, 0)) \backslash W_0^*$. Using the translation invariance of the problem, we can always suppose that

$$\Gamma_0 := \Gamma \backslash \tilde{W} \quad (48)$$

has the Lebesgue measure $|W^*|$. The subset Γ_0 describes one or several droplets of total volume W^*, so that by the isoperimetric inequality

$$\tau(\partial\Gamma_0) \geqslant \tau(\partial W_0^*) \quad (49)$$

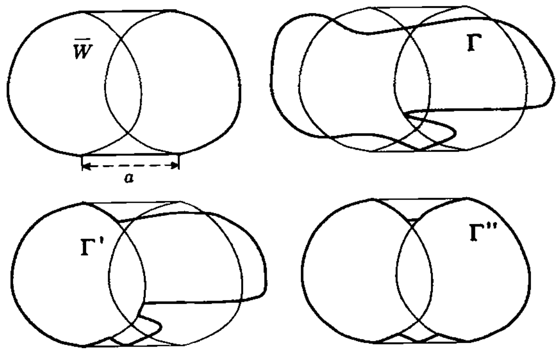

Fig. 10. The optimal shape $\bar{W}$ and the droplets Γ, Γ', Γ''.

We define the new droplet Γ' of total volume larger than or equal to $|\Gamma|$ by taking

$$\Gamma' := W_0^* \cup (\Gamma \backslash \Gamma_0) \tag{50}$$

Since $\partial \Gamma_0 \backslash \partial \Gamma \subset \partial W_0^*$, we have

$$\tau(\partial \Gamma) \geqslant \tau(\partial \Gamma') \tag{51}$$

Notice that Γ' is connected. We transform now also the set Γ' in a similar manner with the help of W_a^*. The Lebesgue measure of the set

$$\Gamma_a' := \Gamma' \backslash (\bar{W} \backslash W_a^*) \tag{52}$$

is greater than or equal to $|W^*|$, and we define

$$\Gamma'' := W_a^* \cup (\Gamma' \backslash W_a^*) \tag{53}$$

For the same reason as above, taking into account that $|\Gamma_a'| \geqslant |W_a^*|$, the isoperimetric inequality shows that

$$\tau(\partial \Gamma') \geqslant \tau(\partial \Gamma'') \tag{54}$$

Now, let us consider the set $\bar{W} \backslash \Gamma''$. We use Ω_1 to denote the union of the connected components of $\bar{W} \backslash \Gamma''$ that are connected to the wall $\{\mathbf{x} \in \mathbb{R}^2 \colon (\mathbf{x} \mid \mathbf{n}_1) = d\}$, and Ω_2 to denote the union of the connected components that are connected to the wall $\{\mathbf{x} \in \mathbb{R}^2 \colon (\mathbf{x} \mid \mathbf{n}_2) = -d\}$. These sets may be empty, but in any case we have $\Omega_1 \cap \Omega_2 = \varnothing$, because the set Γ is connected and therefore the same is true for Γ''. If the set Ω_1 is nonempty, then it describes one or several droplets of the phase M inside the phase C.

The surface free energy of the droplets is given by (15) and (16), and is equal to $\hat{\tau}(\partial\Omega_1)$. Taking into account our assumption that $\sigma(\mathbf{n}_i)=\tau(\mathbf{n}_i)$, we have $\hat{\tau}(\partial\Omega_1)\geqslant 0$. This last assertion is first proven in the case where $\sigma(\mathbf{n}_j)=\tau(\mathbf{n}_j)-\varepsilon$, by comparison with a Winterbottom shape of volume $|\Omega_1|$. Then we let ε vanish. The boundary $\partial\Omega_1\equiv\omega_1$ of Ω_1 can be decomposed into $\omega_1' := \omega_1\cap\partial\Gamma''$ and $\omega_1'' := \omega_1\cap\partial\bar{W}$. We get

$$\hat{\tau}(\partial\Omega_1)=\int_{\omega_1'}\tau(\mathbf{n}(s))\,ds-\sigma(\mathbf{n}_1)\cdot|\omega_1''|\geqslant 0 \tag{55}$$

where $|\omega_1''|$ is the length of ω_1''. A similar inequality can be derived for the set Ω_2. Thus

$$\tau(\gamma)\geqslant\tau(\partial\Gamma'')\geqslant\tau(\partial\bar{W})+\hat{\tau}(\partial\Omega_1)+\hat{\tau}(\partial\Omega_2)\geqslant\tau(\partial\bar{W}) \tag{56}$$

This finishes the proof.

2.5.2. Partial Wetting Case. If only one wall, say the wall $\{\mathbf{x}\in\mathbb{R}^2\colon(\mathbf{x}\mid\mathbf{n}_1)=d\}$, is partially wetted, then all results of Section 2.5.1 hold true with

$$W=W_\tau\cap\{\mathbf{x}\in\mathbb{R}^2\colon(\mathbf{x}\mid\mathbf{n}_1)\leqslant\sigma(\mathbf{n}_1)\} \tag{57}$$

Let consider the case when both walls are partially wetted, and let us assume that W is a nonempty convex body. We can define the set W^* exactly as in Section 2.5.1. The results for droplets with $|\Gamma|\geqslant|W^*|$ are similar to those of Section 2.5.1 and are proved in exactly the same manner. Let us consider the range of volumes $|\Gamma|<|W^*|$. We sketch the main arguments.

We first introduce the following subset of W^*. Let R be the maximal rectangle of the form

$$\{\mathbf{x}\in\mathbb{R}^2\colon b'\leqslant x_1\leqslant b'',\ -d\leqslant x_2\leqslant d\} \tag{58}$$

that can be placed inside W^*. Removing this rectangle from W^* and gluing together the two remaining parts, we define the set $\hat{W}$ of volume $|\hat{W}|$; see Fig. 11.

For the range of volumes $|\hat{W}|\leqslant|\Gamma|\leqslant|W^*|$ there are three possibilities for the position of γ, which are treated separately. In each of these cases, we find a lower bound for $\tau(\gamma)$, and then compare the results for all three cases. First of all, the droplet may touch no wall at all, or it may touch only the wall $\{\mathbf{x}\in\mathbb{R}^2\colon(\mathbf{x}\mid\mathbf{n}_1)=d\}$. By the monotonicity principle, we have

$$\tau(\gamma)\geqslant\tau_{W_1}(\gamma) \tag{59}$$

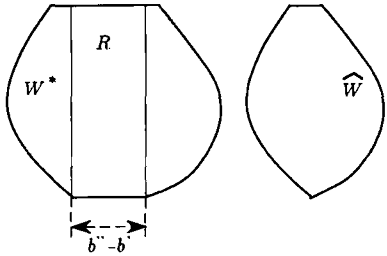

Fig. 11. The sets W^* and $\hat{W}$.

where W_1 is the Winterbottom shape

$$W_1 = W \cap \{\mathbf{x} \in \mathbb{R}^2 \colon (\mathbf{x} \mid \mathbf{n}_1) = \sigma(\mathbf{n}_1)\} \tag{60}$$

Similarly we may have a droplet which does not touch the walls or touches only the wall $\{\mathbf{x} \in \mathbb{R}^2 \colon (\mathbf{x} \mid \mathbf{n}_2) = -d\}$. We have

$$\tau(\gamma) \geqslant \tau_{W_2}(\gamma) \tag{61}$$

Finally we have to consider the case of droplets that touch both walls. By an obvious surgery we can transform such a droplet into a droplet of volume $|W^*|$, by "adding a rectangle" of volume $|W^*| - |\Gamma|$ of phase C. After this construction the horizontal length of the new droplet has increased by k, with $2dk = |W^*| - |\Gamma|$. More precisely, the new droplet whose boundary we denote by $\bar{\gamma}$ is obtained by shifting the right-hand portion of the boundary γ connecting both walls by the appropriate horizontal vector of the length k. We have

$$\tau(\bar{\gamma}) = \tau(\gamma) + k(\sigma(\mathbf{n}_1) + \sigma(\mathbf{n}_2)) \geqslant \tau(\partial W^*) = 2\,|W^*| \tag{62}$$

Since $|\hat{W}| \leqslant |\Gamma|$, we must have $b'' - b' \geqslant k$. Therefore, we can remove from W^* a rectangle $R(k)$ of volume $2dk$ and we get a new set called $\bar{W}(k)$. By definition of this set,

$$\tau(\partial \bar{W}(k)) = \tau(\partial W^*) - k(\sigma(\mathbf{n}_1) + \sigma(\mathbf{n}_2)) = 2\,|W^*| - k(\sigma(\mathbf{n}_1) + \sigma(\mathbf{n}_2)) \tag{63}$$

and thus

$$\tau(\gamma) \geqslant \tau(\partial \bar{W}(k)) \tag{64}$$

We can now compare the minima in the three cases reaching the values $2\,|\Gamma|^{1/2}\,|W_1|^{1/2}$, $2\,|\Gamma|^{1/2}\,|W_2|^{1/2}$, and (63), and find the smallest one yielding the optimal shape of the droplet of volume $|\Gamma|$. This procedure works because $b''-b'\geqslant k$. The case $b''-b'=k$ corresponds to the case $|\Gamma|=|\hat{W}|$. Here the optimal shape is the Winterbottom shape W_i with $|W_i|=\min\{|W_1|,|W_2|\}$. Indeed, by definition of $\hat{W}$ there is at least one of the walls which has only one point in common with $\hat{W}$. If, for example, this is the wall $\{\mathbf{x}\in\mathbb{R}^2: (\mathbf{x}\mid\mathbf{n}_2)=-d\}$, then we have

$$\tau(\partial\hat{W})\geqslant\tau_{W_1}(\partial\hat{W}) \tag{65}$$

and therefore the optimal shape is a Winterbottom shape.

For $|\Gamma|\leqslant|\hat{W}|$ we were not able to show, using the above method, that the optimal shape is a Winterbottom shape. However, if $|\Gamma|$ is sufficiently small, an *a priori* estimate shows that we always have a Winterbottom shape as the optimal one.

2.6. Droplet Between Two Parallel Walls with a Lid

In this final example we consider the situation described in the preceding section restricted further by a third perpendicular wall (the lid) closing the strip

$$S=\{\mathbf{x}\in\mathbb{R}^2: |(\mathbf{x}\mid\mathbf{n}_1)|\leqslant d\} \tag{66}$$

at one, say the left-hand side (see Fig. 12). Even though more general cases can be analyzed, for simplicity we will restrict ourselves to the situation of Section 2.5.1 with $\sigma(\mathbf{n}_i)=\tau(\mathbf{n}_i)$, $i=1,2$, and suppose the fourfold symmetry $\tau(\mathbf{n})=\tau(\varepsilon\mathbf{n})$, where $\varepsilon\mathbf{n}$ is any coordinate reflection of $\mathbf{n}$.

Consider, again, the Winterbottom shape

$$W=W_\tau\cap\{\mathbf{x}\in\mathbb{R}^2: (\mathbf{x}\mid\mathbf{n}_3)\leqslant\sigma(\mathbf{n}_3)\} \tag{67}$$

and W^*, the maximal rescaling of this shape that matches into the strip S,

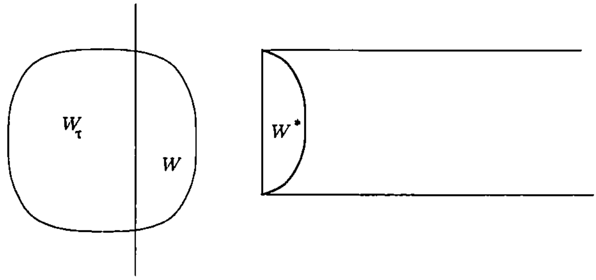

Fig. 12. Winterbottom droplet W and its rescaling W^* matching the strip.

as well as W_τ^*, the maximal rescaling of the full Wulff shape W_τ matching into S.

Let us suppose first that the lid is strongly wetted, $-\tau(\mathbf{n}_3) < \sigma(\mathbf{n}_3) \leqslant 0$. We will distinguish three cases:

(a) $|\Gamma| < |W^*|$.

(b) $|\Gamma| \in [|W^*|, \frac{1}{2}|W_\tau^*|]$.

(c) $|\Gamma| > \frac{1}{2}|W_\tau^*|$.

(a) Clearly, if $|\Gamma| \leqslant |W^*|$, *the optimal shape is the appropriately rescaled Winterbottom shape W attached to the lid.*

(b) For each $A: |W^*| \leqslant A \leqslant \frac{1}{2}|W_\tau^*|$, consider the intersection $W(A) = W_\tau \cap \{\mathbf{x} \in \mathbb{R}^2: x_1 \geqslant x_1(A)\}$, where $x_1(A) \leqslant |\sigma(\mathbf{n}_3)|$ is uniquely chosen so that the area of the rescaled set $W(A)^*$ equals A. Here $W(A)^*$ is the shape $W(A)$ rescaled to match accurately into S. *The optimal shape for $|\Gamma| \in [|W^*|, \frac{1}{2}|W_\tau^*|]$ is the shape $W(|\Gamma|)^*$ attached to the lid.*

To verify this, we just notice that for all curves γ containing all the length $2d$ of the lid one has $\tau(\gamma) \geqslant \tau_{W(A)}(\gamma)$ by monotonicity. Notice that this is true even in the class of curves not restricted to the strip S. At the same time, clearly, $\tau(\partial W(A)^*) = \tau_{W(A)}(\partial W(A)^*)$.

(c) In a similar way one can verify that *for $|\Gamma| > \frac{1}{2}|W_\tau^*|$, the optimal droplet consists of a rectangle of the area $2kd$, $k = (2|\Gamma| - |W_\tau^*|)/4d$, with half of the set W_τ^* attached on the right-hand side of it.*

See Fig. 13 for a sequence of droplets with growing areas through stages (a)–(c).

If $0 < \sigma(\mathbf{n}_3) \leqslant \tau(\mathbf{n}_3)$, partial drying, there are only two cases:

(a) $|\Gamma| \leqslant |W^*|$.

(b) $|\Gamma| > |W^*|$.

The optimal shape in case (b) consists of W^* with the rectangle $2kd$

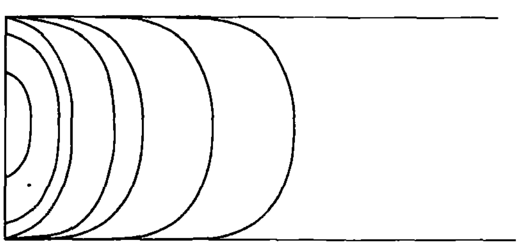

Fig. 13. A sequence of crystals of different volumes in a tube with lid in the case of partial wetting.

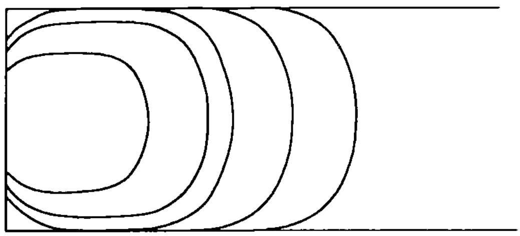

Fig. 14. A sequence of crystals of different volumes in a tube with lid in the case of partial drying.

inserted in a similar way as in the construction of $\bar{W}$ in Section 2.5.1. See Fig. 14 for a sequence of growing droplets. Notice that the corners where the lid is touching the walls stay always dry.

In all cases above we have also the stability (S). The symmetry condition of τ was assumed only for the ease of the formulation. A straightforward generalization to a less symmetric W_τ (for example, the one on Fig. 2) can be easily formulated.

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