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The Equilibrium Shape of a Two-Dimensional Crystal between Parallel Planes

J. De Coninck,[1] J. Fruttero,[1,2] and A. Ziermann[1]

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By applying rather standard techniques for equilibrium crystal shapes (Wulff construction), we derive a construction for the equilibrium shape of a 2D crystal grown between two parallel plane substrates. The critical distance of the substrates at which this crystal splits into two parts is computed as a function of the wall free energy of the substrates. This may open new perspectives for the measurement of wall free energies.

KEY WORDS: Wulff shapes; Winterbottom and Summertop constructions; liquid bridge; wall attractions.

1. INTRODUCTION

This paper is devoted to the study of the shape of a crystal of phase B that grows between two parallel planar substrates and is in equilibrium with a surrounding phase A. A great variety of equilibrium shapes in the presence of substrates, namely the Winterbottom and Summertop constructions, has already been discussed in ref. 1. However, those constructions work only for scale-invariant situations. In the case of two parallel substrates, a Winterbottom construction does not work in general: the resulting shape solves the problem of minimal free energy only if it may be dilated so that it fits at the time the distance of the walls and the given volume, which is quite a particular case. In the present note we show how the idea of the Winterbottom and Summertop constructions may be extended to the case of two parallel substrates: a new geometrical construction is derived to compute the shape of these crystals.

[1] Université de Mons-Hainaut, B-7000 MONS, Belgium. Sconinck@Bmsueml1.Bitnet.
[2] Centre de Physique Théorique, CNRS Luminy, Case 907, 13288 Marseille Cedex 9, France.

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As a by product of our analysis, we have found a new interesting way, to our knowledge,[2] to measure wall free energies. Indeed, a droplet of fixed volume V that wets two parallel substrates splits into two parts if the distance between the substrates becomes large than a certain critical distance $d_c(V)$. In the present note we show how to compute $d_c(V)$ as a function of the wall free energies. This opens new perspectives to measure wall free energies in a partial wetting regime by using liquid bridges and measuring $d_c(V)$. It should be noticed that liquid bridges between completely wet substrates have already been used to measure surface tensions.[3-5] Complementary to those methods, we thus propose to use a liquid bridge of prismatic shape in a partial wetting regime.

2. RESULTS

Consider in two dimensions a crystal of B between two parallel planar substrates, in equilibrium with a surrounding phase A. The corresponding A/B interface is composed of two pieces which are usually at a macroscopic distance from each other. The equilibrium shape should then be given by two pieces of the equilibrium shape of a crystal of B surrounded by A, W_{AB} as indicated in Fig. 1, or a bubble of A surrounded by B (Wulff shapes).

For anisotropic media which can be described by lattice models, it is known that the contact angles should satisfy the generalized Young relation.[6] More precisely, if we denote by $\sigma^{AB}(\theta)$ the interfacial tension between A and B for an interface which makes an angle θ with the horizontal

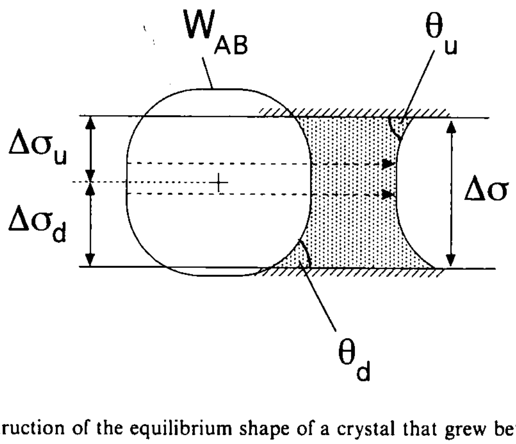

Fig. 1. The construction of the equilibrium shape of a crystal that grew between two parallel substrates for the case of large wall attractions ($\Delta\sigma > 0$). The corresponding Young relations imply acute contact angles, hence the resulting crystal shape is concave.

axis, and by θ_u (θ_d) the contact angle of the A/B interface with the upper (lower) substracte $U(D)$, the contact angles should satisfy

$$\sigma_{AB}(\pi+\theta_u)\cdot\cos(\pi+\theta_u)-\sigma'_{AB}(\pi+\theta_u)\cdot\sin(\pi+\theta_u)=\sigma_{BU}-\sigma_{AU} \quad (1)$$

and

$$\sigma_{AB}(\theta_d)\cdot\cos\theta_d-\sigma'_{AB}(\theta_d)\cdot\sin\theta_d=\sigma_{AD}-\sigma_{BD} \quad (2)$$

where we use σ_{PS} to denote the free energy contribution per unit area of a substrate S covered by the phase P. If A and B are fluids, we have an isotropic surface tension, hence σ'_{AB} vanishes and (1) and (2) become the well-known Young relations.

It is interesting to focus on the geometrical meaning of these equations. Consider the crystal of B within A. Its equilibrium shape W_{AB} is given by the associated Wulff construction. Let ∂W_{AB} denote the boundary of this region W_{AB}. It is known that the points (x, y) which belong to this boundary are given by

$$x(\theta)=\sigma_{AB}(\theta)\sin(\theta)+\sigma'_{AB}(\theta)\cos(\theta) \quad (3)$$

$$y(\theta)=\sigma_{AB}(\theta)\cos(\theta)-\sigma'_{AB}(\theta)\sin(\theta) \quad (4)$$

where θ denotes the angle of the tangent to the boundary ∂W_{AB} at the point (x, y). Let then

$$\Delta_u\sigma=\sigma_{AU}-\sigma_{BU}$$

$$\Delta_d\sigma=\sigma_{AD}-\sigma_{BD}$$

$$\Delta\sigma=\Delta_u\sigma+\Delta_d\sigma$$

Let us first discuss the case $\Delta\sigma>0$. According to the Young relations (1) and (2) and their geometrical interpretation, to obtain the sought equilibrium shape, one has to cut W_{AB} by two vertical lines at the heights $\Delta_u\sigma$ and $-\Delta_d\sigma$ to represent the lower and the upper substrates, respectively. We shall use C_l (C_r) to denote the left (right) component of the intersection of ∂W_{AB} with the strip $\{(x, y)\in\mathbb{R}^2 \mid \Delta_d\sigma<y<\Delta_u\sigma\}$. The vertical size of C_l and C_r is $\Delta\sigma$. To obtain the two components of the surface of the sought equilibrium crystal that grew between two walls separated by a distance d, one has to rescale C_l and C_r by a factor $d/\Delta\sigma$. The rescaled curves will be denoted by C_l^d and C_r^d. After rescaling, one has to translate them horizontally so that C_l^d will be placed to the right of C_r^d and the volume between them will be equal to V. Hence we obtain a droplet given by two concave A/B interfaces.

If $\Delta\sigma < 0$, the sought equilibrium shape is composed analogously by the Wulff shape W_{BA}, which has to be cut by two horizontal lines at the heights $\Delta_d\sigma$ and $-\Delta_u\sigma$. Similarly as in the preceding case, one takes those pieces of W_{BA} which lie between those horizontal lines, rescales them by a factor $-d/\Delta\sigma$, and translates them horizontally to satisfy the fixed-volume constraint—but without exchanging the left and the right ones. The result is a convex droplet.

Of course, our construction leads to a physical solution only if the two components of the equilibrium shape do not touch or cross each other. This gives rise to the existence of a critical length $d_c(V)$ above which there exists no droplet of volume V that is in contact with both substrates. At this critical length, the two components of the surface of our construction touch each other, so that the droplet splits into two pieces. Hence the critical length $d_c(V)$ is defined by the condition

$$d_c(V) = \frac{\Delta\sigma\sqrt{V}}{\sqrt{W_c}} \tag{5}$$

where W_c is the volume of the droplet that is constructed by shifting C_l about a distance of $\sigma_{AB}(\pi/2) + \sigma_{AB}(-\pi/2)$, so that it touches C_r in one point (cf. Fig. 2).

We have

$$W_c = \Delta\sigma \cdot \left[\sigma_{AB}\left(\frac{\pi}{2}\right) + \sigma_{AB}\left(\frac{-\pi}{2}\right)\right] - \int_{+\Delta_d\sigma}^{\Delta_u\sigma} w(y)\, dy$$

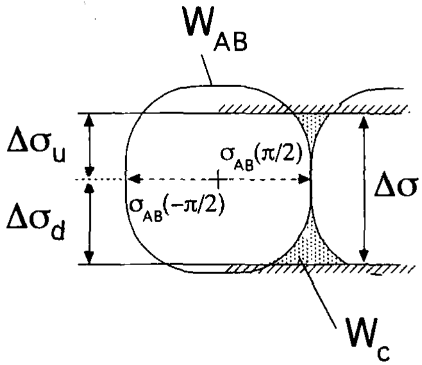

Fig. 2. The definition of W_c. The curve C_l has been shifted to the right about a distance $\sigma_{AB}(\pi/2) + \sigma_{AB}(-\pi/2)$ so that C_l and C_r touch each othner and the resulting droplet splits into two disconnected parts.

where $w(y)$ is the length of the intersection of W_{AB} with a horizontal line at the height y. For the case of a liquid [i.e., $\sigma_{AB}(\theta)=\sigma=\text{const}$]. we have a spherical Wulff shape with $w(y)=2(\sigma^2-y^2)^{1/2}$. For W_c we get

$$W_c = 2\sigma \cdot \Delta\sigma - \sigma^2 \left[f\left(\frac{\Delta_u \sigma}{\sigma}\right) - f\left(\frac{-\Delta_d \sigma}{\sigma}\right) \right] \tag{6}$$

where the function f is defined as $f(t) = -\arccos t + t(1-t^2)^{1/2}$. In Fig. 3 we display the wall attraction of two identical substrates ($\Delta_u\sigma = \Delta_d\sigma$) as a function of the critical distance for the case of water.

As an application, let us mention that the results presented above may also be applied to a droplet modeled by an Ising ferromagnet in an horizontal strip $\mathbb{Z} \times \{1,..., d\}$, where the interaction with the walls is represented by an external field which is equal to a real parameter a if the lattice site $i=(i_1, i_2)$ is such that $i_2=0$ or $i_2=d$ and zero elsewhere. Phases B and A are represented by positive and negative density of magnetization, respectively. Let β be the inverse temperature and let J be the coupling constant. The wall attractions have been computed[7] as a function of the field a; one has

$$\Delta_d \sigma(a) = \beta^{-1} \operatorname{arcosh} \left[\frac{\cosh^2(2\beta J)}{\sinh(2\beta J)} - \frac{\omega + 1/\omega}{2} \right]$$

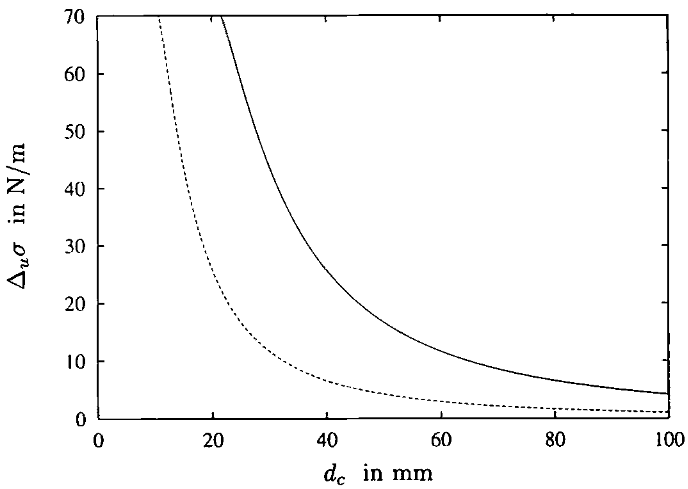

Fig. 3. The wall attraction $\Delta_u\sigma$ of two parallel walls of identical material, $\Delta_u\sigma = \Delta_d\sigma$, as a function of the critical length, where a droplet splits into two parts. We plotted $\Delta_u\sigma$ for the case of pure water with $\sigma = 70\ \text{Nm}^{-1}$ for prismatic droplets of cross sections $100\ \text{mm}^2$ (full line) and $25\ \text{mm}^2$ (dashed line).

where

$$\omega = e^{2\beta J}[\cosh(2\beta J) - \cosh(2\alpha\beta J)]/\sin(2\beta J)$$

For the Ising Wulff shape we have[8,9]

$$w(y) = 2\beta^{-1} \operatorname{arcosh}[\cosh^2(2\beta J)/\sinh(2\beta J) - \cosh(y\beta)]$$

Hence W_c and d_c may be computed numerically, which allows a full description of the equilibrium crystal. The graph of the wall attraction as a function of the critical distance obtained for the Ising ferromagnet is qualitatively the same as the graph shown in Fig. 3.

In general, the critical length d_c may be computed as a function of the wall free energies once one knows the surface tension as a function of the inclination angle. This might be used for an alternative aproach to determine wall attractions by measuring the critical length where a concave droplet splits into two convex droplets. Let us finally comment on the corresponding experimental conditions: to apply our two-dimensional results directly, one has to use a liquid bridge formed by a prismatic droplet, or for isotropic liquids, one may use the fact that the corresponding shape is rotationally invariant and thus replace the volume V which appears in our formulas by $V/2\pi$.

3. OUTLINE OF THE PROOF

For completeness we present here the main ideas of the proof of the validity of our construction. We shall concentrate on the case $\Delta\sigma > 0$.

The main ingredients of the proof are the following.

Let $\bar{W}_{AB}$ be that part of W_{AB} which lies between the horizontal lines at the heights $-\Delta_d\sigma$ and $\Delta_u\sigma$ (an analog of the Winterbottom construction for two walls) and let $|\bar{W}_{AB}|$ be its volume. The free energy of a bubble of phase A surrounded by phase B of fixed volume

$$V^* = |\bar{W}_{AB}| \frac{d^2}{(\Delta\sigma)^2} \tag{7}$$

is minimized by $\bar{W}_{AB}$ after rescaling it by a factor $d/\Delta\sigma$. Here (7) ensures that there exists a rescaling factor by which the Winterbottom shape $\bar{W}_{AB}$ may be dilated at the same time to the wall distance and to the fixed volume V^*. The validity of this construction may be proved in the same manner as the Wulff construction[10] and the Winterbottom construction for nonparallel walls.[1]

A second ingredient of the proof is the fact that the free energy of a unit-volume Winterbottom droplet equals twice the square root of the volume of the nonrescaled Winterbottom shape.[10,1] [For instance, the free energy of a bubble of phase A of volume V^* which is in contact with both substrates U and D and the shape of which is given by $\bar{W}_{AB}$ equals $2|\bar{W}_{AB}|^{1/2}(V^*)^{1/2}$.] From this we obtain the inequality

$$F_{ABU} \geqslant F_{ABDU} \qquad \text{for} \quad \Delta\sigma > 0 \tag{8}$$

where we use F_{ABU} (F_{ABDU}) to denote the free energy of a unit-volume Winterbottom bubble of phase A surrounded by phase B and in contact with the substrate U (the substrates U and D). As we supposed that $\Delta\sigma > 0$, we shall use the fact that the free energy of a bubble of phase A of volume V^* takes its minimum on the shape $\bar{W}_{AB}$ to prove the validity of our construction. Since the surface of a droplet that is in contact with the two walls plits into two components, we may vary them independently. The validity of our construction is proved if we show that the free energy of all droplets with a fixed right (left) component is minimized by the droplet, the left (right) component of which is given by C_r^d (C_l^d). We have to minimize the free energy

$$F(\Gamma) = \int_{\Gamma_l} \sigma_{AB}(\theta(l))\, dl + \int_{\Gamma_r} \sigma_{AB}(\theta(l))\, dl - (u_r - u_l)(\Delta_u \sigma) - (d_r - d_l)(\Delta_d \sigma)$$

Here we used u_r to denote the x coordinate of the point where Γ_r touches the upper substrate. The real numbers u_l, d_l, and d_r are defined analogously. The idea of the proof is to consider the left component Γ_l of a given droplet Γ as the right part of the surface of a bubble Γ^* of phase A of volume $V^* = |\bar{W}_{AB}| \cdot (d/\Delta\sigma)^2$ [cf. (7)] surrounded by phase B the left part of which is equal to C_l^d (cf. Fig. 4).

For the free energy $F^*(\Gamma^*)$ of the droplet Γ^* we have

$$F^*(\Gamma^*) = \int_{C_l^d} \sigma_{AB}(\theta(l))\, dl + \int_{\Gamma_l} \sigma_{AB}(\theta(l))\, dl + (u_l - u_l^*)(\Delta_u \sigma) + (d_l - d_l^*)(\Delta_d \sigma) \tag{9}$$

One may easily convince oneself that, since we keep Γ_r fixed, $F^*(\Gamma^*) - F(\Gamma)$ is a constant. For the same reason, fixing the volume of the drop Γ is equivalent to fixing the volume of the droplet Γ^*. Hence the free energy of Γ with fixed volume V is minimized if the free energy of Γ^* with fixed volume V^* is minimized, i.e., when Γ^* is equal to the $d/\Delta\sigma$ times rescaled shape $\bar{W}_{AB}$. Thus, the free energy of all droplets Γ with fixed Γ_r is minimized by the droplet for which $\Gamma_l = C_r^d$.

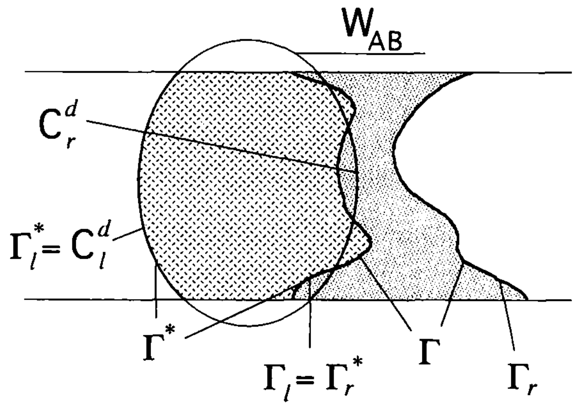

Fig. 4. Illustration of the proof of our construction for the case $\Delta\sigma > 0$. The left part of the surface of a given crystal is considered to be part of the surface of a bubble of the fluid phase A surrounded by the condensed phase B. The volume of this bubble is fixed and the second part of the surface of this bubble is considered to be a part of the Winterbottom shape of such a bubble for the case of parallel substrates. Hence, to minimize the free energy, Γ_l must also be a part of that Winterbottom shape.

Up to now this argument works only if the left part of Γ does not intersect the left part of Γ^*, so that Γ^* forms one droplet. In the opposite case we have to show that Γ is not the minimal droplet. Let us discuss the simplest case of only one intersection where the curve Γ touches the lower and upper substrates to the left and to the right of Γ_l^*, respectively. We shall again use (9), but to do this, we have to interpret Γ^* in a different way. Namely, that part of Γ_l that lies to the left of Γ_l^* forms together with a part of Γ_l^* a droplet of phase B surrounded by phase A that wets partially the lower substrate (cf. Fig. 5). We shall use V_B to denote its volume. This corresponds to the fact that $d_l - d_l^*$ becomes negative, hence the term $(d_l - d_l^*)(\sigma_{AD} - \sigma_{BD})$ in (9) should be interpreted as the free energy contribution of a part of the substrate D of length $d_l^* - d_l$ covered by phase B. That part of Γ_l which lies at the right to Γ_l^* forms together with Γ_l^* a droplet of phase A surrounded by phase B that wets partially the upper substrate. To denote its volume, we shall use $\check{V}_A$. We have $V^* = V_A - V_B$. The free energy of those two droplets may be estimated from below by the free energy of the according Winterbottom droplets. We have

$$F^*(\Gamma^*) \geq F_{ABU}(V_A)^{1/2} + F_{BAD}(V_B)^{1/2} > F_{ABDU}(V^*)^{1/2} = 2\,|\bar{W}_{AB}|^{1/2}(V^*)^{1/2}$$

The last inequality follows from the inequality (8) and the fact that $V^* = V_A - V_B < V_A$. Hence the free energy of Γ^* is larger than the minimal free

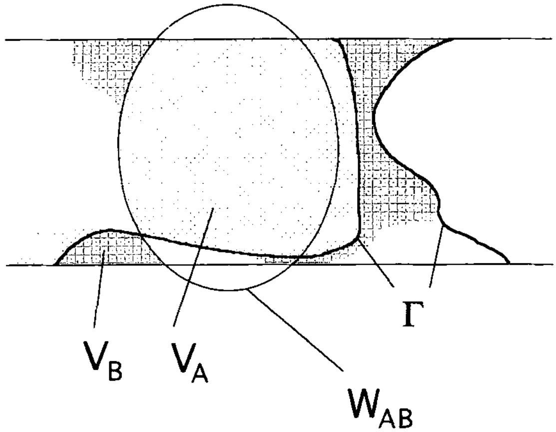

Fig. 5. Illustration of the case of Γ_l intersecting the curve Γ_l^*. We interpret the free energy of Γ^* as the sum of the free energies of a crystal of B surrounded by A and a bubble of A included in B.

energy of a bubble of phase A and fixed volume V^*. In view of (9), this implies that Γ is not the equilibrium droplet. The case of more than one intersection may be treated in a similar way.

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