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## Crystal shapes on striped surface domains

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Received 4 April 2004

Published 2 July 2004

Online at [stacks.iop.org/JPhysCM/16/4785](http://stacks.iop.org/JPhysCM/16/4785)

doi:10.1088/0953-8984/16/28/003

### Abstract

The equilibrium shapes of a simple cubic crystal in contact with a planar chemically patterned substrate are studied theoretically using an effective interface model. The substrate is primarily made of lyophobic material and is patterned with a lyophilic (easily wettable) stripe domain. Three regimes can be distinguished for the equilibrium shapes of the crystal. The transitions between these regimes as the volume of the crystal is changed are *continuous* or *discontinuous* depending on the strength of the couplings between the crystal and the lyophilic and lyophobic surface domains. If the crystal grows through a series of states close to equilibrium, the discontinuous transitions correspond to growth instabilities. These transitions are compared with similar results that have been obtained for a volume of liquid wetting a lyophilic stripe domain.

(Some figures in this article are in colour only in the electronic version)

### 1. Introduction

A chemically patterned substrate is a solid wall decorated with surface domains that exhibit different degrees of preference for a fluid or crystalline phase in contact with the wall. Chemically patterned substrates can be produced by a number of experimental methods; see [1] and references therein.

A liquid wetting a chemically patterned substrate can exhibit different morphologies and undergo transitions between them as the volume of liquid is changed. Such morphological wetting transitions have attracted a lot of interest in recent years. For example, instabilities affecting the shape of liquid channels on lyophilic (easily wettable) stripe domains have been studied in great detail [1–4].

In this paper, the case will be discussed in which the phase ‘wetting’ the patterned substrate is a crystal instead of a liquid. Let us therefore consider the differences between the shapes

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of liquid droplets and crystals. The spherical shape of a droplet in the absence of gravity is a manifestation that the surface tension of the vapour–liquid interface is isotropic. In contrast, the surface tension of a crystal is anisotropic; it depends on the orientation of the interface with respect to the lattice of the crystal. This explains why certain crystal planes are more favourable than others to form the faces of crystals, which gives them their characteristic appearance. Despite these differences, one may expect that surface domains which induce morphological transitions in liquid layers also induce such transitions if the phase wetting the substrate is a crystal.

The purpose of this paper is to study the equilibrium shapes and morphological transitions of a simple cubic crystal on a solid and planar chemically patterned substrate at zero temperature. The substrate is primarily made of lyophobic  $\delta$  material and is patterned with a lyophilic  $\gamma$  stripe domain. Here, equilibrium at zero temperature refers to stability under perturbation of the macroscopic variables that characterize the shape of the crystal. We will assume implicitly that there is always a microscopic mechanism that allows the crystal to attain a shape that corresponds to a local minimum of the free energy.

Because the main effect of temperature on the shapes of crystals is to round off their edges and corners, the morphological transitions in the shape of a simple cubic crystal at low temperature should not differ dramatically from the results for zero temperature.

This paper is organized as follows. In section 2, an effective interface model is introduced for crystals on chemically patterned substrates. In section 3, the equilibrium shapes are studied for a simple cubic crystal on a planar homogeneous (non-patterned) substrate. In section 4, the shapes are discussed for such a crystal located on a lyophilic stripe domain. Finally, section 5 compares the results for simple cubic crystals on lyophilic stripes with similar results that have been obtained for liquid channels wetting the same surface domains [4].

## 2. Effective interface model

For a crystal that is large compared to the unit cell of its lattice, an effective interface model can be used to investigate its equilibrium shapes. A similar model has been used to study the morphologies of a volume of liquid wetting chemically patterned walls; see, for example, the review in [5].

This paper focuses on the equilibrium shapes for a crystal in contact with a planar substrate. Any real substrate exhibits a lattice periodicity and an anisotropy that affect the shape of a crystal in equilibrium on its surface. In general, the misfits between the lattice of the crystal and the substrate introduce surface stresses that are neglected here. There are two particular cases in which this approximation is clearly appropriate:

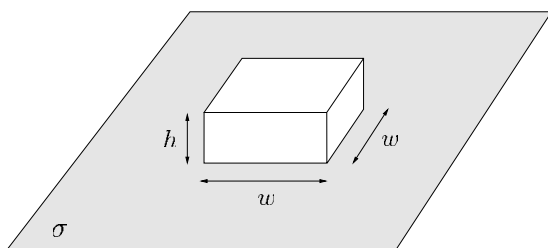
- (a) a structureless but patterned substrate in which the atoms are not ordered in a lattice (amorphous material);
- (b) a substrate patterned with surface domains that have strictly isomorphic lattices to the lattice of the crystal.

Furthermore, it is assumed that there are no elastic deformations of the bulk crystal.

In the two cases, (a) and (b), the equilibrium shape at a certain temperature for a macroscopic crystal in contact with the substrate is given by the minimization of the interfacial free energy  $F$  at constant crystal volume  $V_\beta$  [6], with

$$F = \int_{\mathcal{A}_{\alpha\beta}} \Sigma_{\alpha\beta}(\mathbf{n}) \, dA - \int_{\mathcal{A}_{\beta\sigma}} [\Sigma_{\alpha\sigma}(\mathbf{n}, \mathbf{x}) - \Sigma_{\beta\sigma}(\mathbf{n}, \mathbf{x})] \, dA, \quad (1)$$

where  $\alpha$ ,  $\beta$ , and  $\sigma$  correspond to the vapour, the crystal, and the substrate, respectively. The vapour–crystal and crystal–substrate interfaces are indicated by  $\mathcal{A}_{\alpha\beta}$  and  $\mathcal{A}_{\beta\sigma}$ , respectively.



**Figure 1.** Simple cubic crystal on a homogeneous substrate  $\sigma$ .

The normal vector  $\mathbf{n}$  characterizes the orientation of the crystal lattice plane or (isomorphic) lattice planes that meet at a certain point of the different interfaces. The vector  $\mathbf{x}$  indicates a point on the surface of the substrate. In equation (1), the effects of gravity and line tension have been neglected.

In the following, the effective interface model is applied to a crystal on a chemically patterned substrate that is primarily made of lyophobic  $\delta$  material but is patterned with a lyophilic  $\gamma$  surface domain. The physical properties of these two types of surface domains are homogeneous up to well defined boundaries between domains. In this case, it is convenient to separate the second integral of equation (1) into two integrals, one which integrates over the crystal–lyophilic interface ( $A_{\beta\gamma}$ ) and a second one which integrates over the crystal–lyophobic interface ( $A_{\beta\delta}$ ). Typically, at zero temperature the faces of a crystal present only the crystal planes which are energetically less costly, and the edges and corners are sharp. If all the faces between the crystal  $\beta$  and the vapour  $\alpha$  have equivalent lattice orientations, the surface tension  $\Sigma_{\alpha\beta}$  has a constant value for the whole surface of the  $\alpha\beta$  interface. In this case, one can drop the  $\mathbf{n}$  dependence from equation (1), which leads to

$$F = \Sigma_{\alpha\beta} (A_{\alpha\beta} - c_{\gamma} A_{\beta\gamma} - c_{\delta} A_{\beta\delta}). \quad (2)$$

The quantities  $A_{\alpha\beta}$ ,  $A_{\beta\gamma}$ , and  $A_{\beta\delta}$  stand for the areas of the corresponding interfaces. The material parameters  $c_{\gamma}$  and  $c_{\delta}$  characterize the coupling of the crystal with the lyophilic  $\gamma$  and lyophobic  $\delta$  surface domains, respectively, and are defined by

$$c_{\gamma} \equiv (\Sigma_{\alpha\gamma} - \Sigma_{\beta\gamma}) / \Sigma_{\alpha\beta} \quad \text{and} \quad c_{\delta} \equiv (\Sigma_{\alpha\delta} - \Sigma_{\beta\delta}) / \Sigma_{\alpha\beta}. \quad (3)$$

For a volume of liquid  $\beta$  partially wetting a planar wall  $\sigma$ , the Young equation, which is

$$\cos \theta = (\Sigma_{\alpha\sigma} - \Sigma_{\beta\sigma}) / \Sigma_{\alpha\beta}, \quad (4)$$

relates the contact angle  $\theta$  to a quotient of surface tensions. The *wettability* of the wall is the quantity defined as the right-hand side of equation (4). Notice that the dimensionless parameters  $c_{\gamma}$  and  $c_{\delta}$  are equal to the wettabilities of the lyophilic and lyophobic surface domains, respectively.

### 3. Crystal on a homogeneous substrate

Let us now consider a simple cubic crystal in equilibrium on a non-patterned wall that either is perfectly structureless or has the same lattice ordering and spacing as the crystal plane with Miller indices (100). In equilibrium at zero temperature, the faces of the crystal follow the easiest lattice planes, which are the planes (100), (010), and (001) of the simple cubic lattice. Hence, the crystal has the shape of a box of volume  $V_{\beta}$  with a square base of lateral side  $w$  and certain height  $h$  over the surface of the wall; see figure 1. In this case, the surface tension is equal in all the faces that form the vapour–crystal interface.

Let us assume that the unit length of the simple cubic lattice is very small compared to  $w$  and  $h$ , so that these variables can be regarded as continuous. The areas of the vapour–crystal and crystal–wall interfaces are  $A_{\alpha\beta} = w^2 + 4wh$  and  $A_{\beta\sigma} = w^2$ , respectively.

The free energy that has to be minimized at constant volume,  $V_\beta = w^2h$ , in order to find the shape of the crystal is

$$F = \Sigma_{\alpha\beta}(A_{\alpha\beta} - cA_{\beta\sigma}), \quad (5)$$

with the constant

$$c \equiv (\Sigma_{\alpha\sigma} - \Sigma_{\beta\sigma})/\Sigma_{\alpha\beta}. \quad (6)$$

The condition of stationarity, that the first derivative of  $F$  equals zero, together with the volume constraint yields

$$h/w = (1 - c)/2. \quad (7)$$

This equation characterizes the stationary crystal shape, and corresponds to a minimum of the free energy  $F$ . Let us call the *aspect ratio* the quotient of the height  $h$  of the crystal to the lateral size  $w$  of its base; see figure 1.

The right-hand side of equation (7) is a constant that only depends on the dimensionless combination of material parameters  $c$ . It is convenient to define the parameter

$$a \equiv (1 - c)/2, \quad (8)$$

because it has a more direct physical interpretation than  $c$ . From equation (7),  $a$  is equal to the equilibrium aspect ratio of the simple cubic crystal in contact with the wall,

$$h/w = a. \quad (9)$$

If the system is in equilibrium,  $\Sigma_{\alpha\sigma}$  can never exceed  $\Sigma_{\alpha\beta} + \Sigma_{\beta\sigma}$ , because if it did the system could always reach a state of lower free energy, namely, the state in which the wall  $\sigma$  is completely covered by the  $\beta$  phase, and in that case  $\Sigma_{\alpha\sigma} = \Sigma_{\alpha\beta} + \Sigma_{\beta\sigma}$ . Thus,

$$\Sigma_{\alpha\sigma} \leq \Sigma_{\alpha\beta} + \Sigma_{\beta\sigma}. \quad (10)$$

On the other hand, if there is a layer of vapour  $\alpha$  between the crystal  $\beta$  and the wall  $\sigma$ , two interfaces separate the crystal from the wall and  $\Sigma_{\beta\sigma} = \Sigma_{\alpha\beta} + \Sigma_{\alpha\sigma}$ . In equilibrium,  $\Sigma_{\beta\sigma}$  can never exceed  $\Sigma_{\alpha\beta} + \Sigma_{\alpha\sigma}$ , otherwise the system would prefer the situation with the crystal detached from the wall. Thus,

$$\Sigma_{\beta\sigma} \leq \Sigma_{\alpha\beta} + \Sigma_{\alpha\sigma}. \quad (11)$$

For a system in equilibrium, the inequalities (10) and (11) place limits to the values of the surface tensions of the different interfaces [7, 8]. From these relations, one has

$$-\Sigma_{\alpha\beta} \leq \Sigma_{\alpha\sigma} - \Sigma_{\beta\sigma} \leq \Sigma_{\alpha\beta}, \quad (12)$$

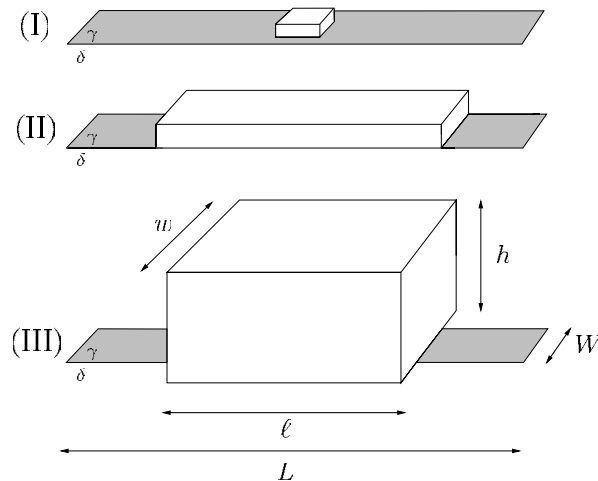
which implies that the physically meaningful values of the material parameters  $c$  and  $a$  are limited to the intervals

$$-1 \leq c \leq 1 \quad \text{and} \quad 0 \leq a \leq 1. \quad (13)$$

For  $c = -1$  or  $a = 1$ , the crystal is a perfect cube detached from the wall, while for  $c = 1$  or  $a = 0$  the crystal is completely spread on the wall. Notice that in the latter case, because the finite size of the lattice unit cell is not taken into account in our calculations, there is no limit for the area that the crystal can cover when it is completely spread on the wall.

Using in equation (5) the condition of stationarity (7) and the volume constraint,  $V_\beta = w^2h$ , one obtains that the equilibrium free energy for a crystal of volume  $V_\beta$  is

$$F(V_\beta) = 6\Sigma_{\alpha\beta}a^{1/3}V_\beta^{2/3}. \quad (14)$$



**Figure 2.** Three different regimes for a crystal on a lyophilic stripe domain. Regimes I, II, and III are characterized by  $w < W$ ,  $w = W$ , and  $w > W$ , respectively. In all three cases,  $L$  is much larger than  $\ell$ .

#### 4. Crystal on a lyophilic stripe domain

In this section, the equilibrium shapes at zero temperature are studied for a simple cubic crystal of finite volume  $V_\beta$  in contact with a planar lyophobic substrate patterned with an infinitely long lyophilic stripe domain. It is assumed that the lyophilic  $\gamma$  stripe domain and lyophobic  $\delta$  surface have lattices that are strictly isomorphic to the lattice of the crystal. The surface of the substrate corresponds to the (001) plane of the simple cubic lattice, and the lyophilic stripe is oriented along one of the two main lattice directions parallel to the wall.

The couplings between the crystal and the lyophilic  $\gamma$  and lyophobic  $\delta$  surfaces are

$$a_\gamma \equiv (1 - c_\gamma)/2 \quad \text{and} \quad a_\delta \equiv (1 - c_\delta)/2, \quad (15)$$

respectively, where  $c_\gamma$  and  $c_\delta$  are given by equation (3). Because the  $\gamma$  domain is more attractive for the crystal than the  $\delta$  surface, one has that  $a_\gamma < a_\delta$ . From equations (15) and (2), the free energy of the crystal is

$$F = \Sigma_{\alpha\beta} (A_{\alpha\beta} - A_{\beta\sigma} + 2a_\gamma A_{\beta\gamma} + 2a_\delta A_{\beta\delta}), \quad (16)$$

with  $A_{\beta\sigma} \equiv A_{\beta\gamma} + A_{\beta\delta}$ .

The contact line is the boundary at which the vapour  $\alpha$ , the crystal  $\beta$ , and the wall  $\sigma$  meet. For a simple cubic crystal in equilibrium on the lyophilic stripe domain, three regimes can be distinguished that depend on the location of the contact line with respect to the boundaries of the stripe. These regimes are defined by comparing the width  $w$  of the crystal to the width  $W$  of the stripe; see figures 2(I)–(III).

- *Regime I.* At low volumes  $V_\beta$ , the contact line is located within the lyophilic stripe domain. The crystal has a square base with lateral side  $\ell = w$  smaller than the width  $W$  of the stripe,  $w < W$ .
- *Regime II.* For intermediate volumes  $V_\beta$ , the base of the crystal is a rectangle of width  $w$  equal to the width  $W$  of the stripe,  $w = W$ . In this regime, two opposed sides of the contact line are located on top of  $\gamma\delta$  domain boundaries.

- *Regime III.* The crystal has the shape of a box of width  $w$  larger than the width  $W$  of the stripe,  $w > W$ . In this case, part of the base of the crystal is on the lyophilic stripe and part of it is on the lyophobic surface.

At zero temperature, a simple cubic crystal in stable equilibrium on a lyophilic stripe domain is necessarily in one of the regimes I, II, or III. Other states with the crystal having a different shape are not stable states. For example, starting with a crystal in regime III of volume  $V_\beta$  one could add a ‘deformation’ of volume  $V_d$  that covers a longer area of the lyophilic stripe (similar morphologies have been observed in a volume of liquid wetting a lyophilic stripe [2]). In order to find the equilibrium shape of the whole crystal, one has to minimize its free energy at constant volume  $V_\beta + V_d$ . As a result, one finds that in equilibrium the deformation is indistinguishable from the rest of the crystal and the final shape is as in figure 2(III).

#### 4.1. Crystal in regime I

In regime I, the contact line is located within the lyophilic stripe domain, the width  $w$  of the crystal is smaller than the width  $W$  of the stripe and is equal to the length  $\ell$  of the crystal along the stripe,  $\ell = w < W$ ; see figure 2(I).

The shape of a crystal in regime I is not affected by the lyophobic part of the substrate. Thus, the problem of finding the equilibrium shapes in regime I is equivalent to the problem of finding the equilibrium shapes for a crystal on a homogeneous wall with coupling constant equal to the coupling  $a_\gamma$  on the lyophilic stripe domain. From equation (9), the condition of stationarity in regime I is

$$h/w = a_\gamma. \quad (17)$$

As for a crystal on a non-patterned substrate, the stationary shape given by condition (17) corresponds to a minimum of the free energy. From equation (14), the free energy of a stable crystal of volume  $V_\beta$  in regime I is given by

$$F_I(V_\beta) = 6\Sigma_{\alpha\beta}a_\gamma^{1/3}V_\beta^{2/3}. \quad (18)$$

The condition of regime I,  $w < W$ , together with equation (17) impose a restriction on the volumes  $V_\beta$  available for a stable crystal in this regime. Only a crystal with volume  $V_\beta < V_0$ , where

$$V_0 \equiv a_\gamma W^3, \quad (19)$$

can be stable in regime I.

#### 4.2. Crystal in regime II

In regime II, the width  $w$  of the crystal is equal to the width  $W$  of the stripe,  $w = W$ ; see figure 2(II). A crystal in regime II has volume  $V_\beta \geq V_0$ , with  $V_0$  as defined in equation (19).

For a crystal in regime II, equation (16) gives

$$F(h, \ell) = 2\Sigma_{\alpha\beta}(\ell h + hW + a_\gamma \ell W). \quad (20)$$

Using the volume constraint,  $V_\beta = \ell h W$ , to eliminate one of the variables,  $\ell$  or  $h$ , the free energy can be written as a function of the other variable and the parameters  $\Sigma_{\alpha\beta}$ ,  $a_\gamma$ ,  $W$ , and  $V_\beta$ . In a stationary state, the derivative of  $F$  with respect to the remaining variable,  $\ell$  or  $h$ , at constant volume  $V_\beta$  is zero. From this condition, one has

$$h/\ell = a_\gamma. \quad (21)$$

In regime II, the shape that satisfies the stationarity condition (21) corresponds to a minimum of the free energy. The free energy of a stable crystal of volume  $V_\beta$  in regime II is given by

$$F_{\text{II}}(V_\beta) = 2\Sigma_{\alpha\beta} \left[ \frac{V_\beta}{W} + 2\sqrt{a_\gamma W V_\beta} \right]. \quad (22)$$

#### 4.3. Crystal in regime III

In regime III, the crystal has the shape of a box of width  $w$  larger than the width  $W$  of the stripe,  $w > W$ , and length  $\ell$  along the stripe larger than the width  $w$ ,  $\ell > w$ ; see figure 2(III).

In this regime, equation (16) gives

$$F(h, \ell, w) = 2\Sigma_{\alpha\beta}[wh + \ell h + a_\gamma W\ell + a_\delta(w - W)\ell]. \quad (23)$$

The volume constraint,  $V_\beta = h\ell w$ , can be used to eliminate one of the variables ( $h$ ,  $\ell$ , or  $w$ ). Say that one eliminates  $h$ , then one has  $F(\ell, w; V_\beta)$ . The stationarity conditions, which correspond to the zeros of the partial derivatives of  $F(\ell, w; V_\beta)$  with respect to  $w$  and  $\ell$ , are

$$h/w = a_\delta \quad (24)$$

and

$$h/\ell = a_\gamma[W/w] + a_\delta[(w - W)/w], \quad (25)$$

respectively. In these stationary conditions, the volume constraint,  $V_\beta = h\ell w$ , has been used to introduce  $h$  again, because writing the equations in this way makes their interpretation easier. The condition (24) is similar to (17). The condition (25) is a linear combination of two relations of the kind of (21) weighted with the fraction of the base of the crystal lying on the lyophilic stripe,  $W/w$ , and on the lyophobic surface,  $(w - W)/w$ , respectively.

Using the stationarity conditions and the volume constraint in equation (23), one obtains that the free energy for a stationary crystal of volume  $V_\beta$  in regime III is

$$F_{\text{III}}(V_\beta) = 2\Sigma_{\alpha\beta} \left[ 2a_\delta[w(V_\beta)]^2 + \frac{V_\beta}{w(V_\beta)} \right]. \quad (26)$$

The function  $w = w(V_\beta)$  relates the width of a stationary crystal in this regime to its volume.

From the stationarity conditions, (24) and (25), and the volume constraint,  $V_\beta = h\ell w$ , one obtains an equation that relates  $w$  to  $V_\beta$  in the stationary states in regime III,

$$g(w; V_\beta) \equiv w^4 - \frac{V_\beta}{a_\delta}w + \frac{a_\delta - a_\gamma}{a_\delta^2}V_\beta W = 0. \quad (27)$$

This equation defines implicitly  $w$  as a function of the volume  $V_\beta$ ,  $w = w(V_\beta)$ . If one scales the variable  $w$ , doing the variable transformation

$$w = \left[ \frac{a_\delta - a_\gamma}{a_\delta^2} V_\beta W \right]^{1/4} y, \quad (28)$$

equation (27) becomes

$$y^4 - Dy + 1 = 0, \quad (29)$$

with the dimensionless parameter

$$D \equiv \left[ \frac{a_\delta^2}{(a_\delta - a_\gamma)^3} \frac{V_\beta}{W^3} \right]^{1/4}. \quad (30)$$

We are interested in the real solutions of equation (27) with  $w > W$  or, equivalently, we are interested in the real solutions of equation (29) with  $y > y_1$ , where  $y_1$  is the value of  $y$



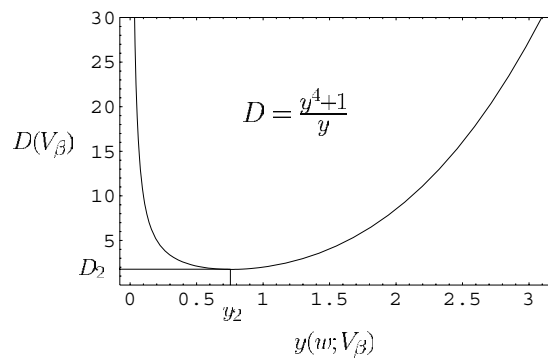


Figure 3. Plot of equation (34).

for which  $w = W$  and which can be obtained from the following argument. The solution of equation (27) for  $w = W$  is

$$V_\beta = V_1 \equiv (a_\delta^2/a_\gamma)W^3. \quad (31)$$

Hence,  $y_1$  is the value of  $y$  given by relation (28) for  $w = W$  and  $V_\beta = V_1$ ,

$$y_1 \equiv [a_\gamma/(a_\delta - a_\gamma)]^{1/4}. \quad (32)$$

From equation (30), the value of  $D$  for  $V_\beta = V_1$  is

$$D = D_1 \equiv a_\delta / [(a_\delta - a_\gamma)^3 a_\gamma]^{1/4}. \quad (33)$$

Solving equation (29) for  $D$ , one has

$$D = (y^4 + 1)/y. \quad (34)$$

Figure 3 shows a plot of the parameter  $D$  as a function of  $y$ . Notice that, on the one hand,  $y$ , defined in equation (28), is a function of  $w$  and  $V_\beta$ ,  $y = y(w; V_\beta)$ . On the other hand,  $D$ , defined in equation (30), is a monotonic function of  $V_\beta$ ,  $D = D(V_\beta)$ , and increases for increasing  $V_\beta$ .

The minimum of equation (34) occurs for  $y = y_2$  and  $D = D_2$ , where

$$y_2 \equiv 3^{-1/4} \quad \text{and} \quad D_2 \equiv 4/3^{3/4}; \quad (35)$$

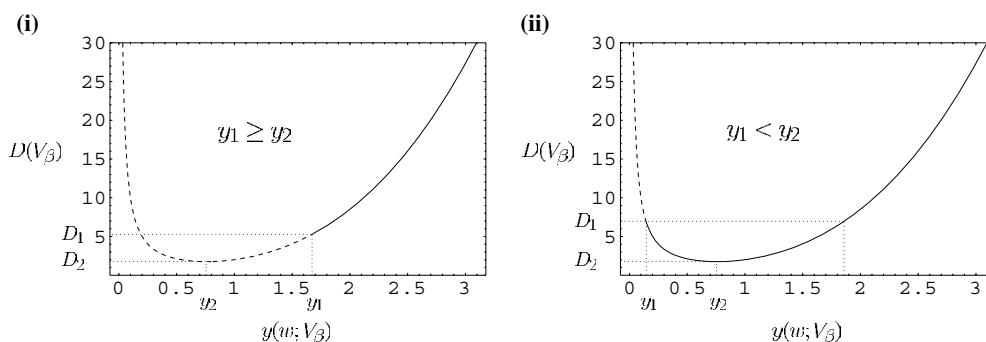
see figure 3. These values correspond to  $w = w_2$  and  $V_\beta = V_2$ , with

$$w_2 \equiv \frac{4(a_\delta - a_\gamma)}{3a_\delta} W \quad \text{and} \quad V_2 \equiv \frac{4^4(a_\delta - a_\gamma)^3}{3^3 a_\delta^2} W^3. \quad (36)$$

In figure 3, each value of  $D$  larger than  $D_2$  corresponds to two real values of  $y$ , one smaller and one larger than  $y_2$ . Thus, using the relations (28) and (30), each value of  $V_\beta$  larger than  $V_2$  corresponds to two values of  $w$ , one with  $w < w_2$  and one with  $w > w_2$ . One should also take into account that, by the definition of regime III, only solutions of equation (29) with  $y > y_1$  (or  $w > W$ ) correspond to this regime.

*Two different scenarios in regime III.* In order to classify the stationary states in regime III, let us distinguish two different scenarios that depend on the number of real solutions of equation (29) for  $y > y_1$  (or  $w > W$ ):

- (i) If  $y_1 \geq y_2$ , which is equivalent to  $a_\delta/4 \leq a_\gamma$ ; see figure 4(i):
- For  $V_\beta \leq V_1$  (or, equivalently,  $D \leq D_1$ ), the real solutions of equation (29) correspond to  $w \leq W$  and, thus, there is no solution in regime III.



**Figure 4.** Two different scenarios: (i)  $y_1 \geq y_2$  and (ii)  $y_1 < y_2$ . The solid curve stands for the real solutions of equation (29) with  $y > y_1$  (or  $w > W$ ), which correspond to stationary states in regime III. The dashed curve stands for the real solutions of equation (29) without physical meaning in regime III ( $y \leq y_1$  or  $w \leq W$ ).

- For  $V_\beta > V_1$  (or  $D > D_1$ ), there is a single real solution in regime III ( $w > W$ ).
- (ii) If  $y_1 < y_2$ , which is equivalent to  $a_\gamma < a_\delta/4$ ; see figure 4(ii):
- For  $V_\beta < V_2$  (or  $D < D_2$ ), equation (29) has no real solution.
  - For  $V_\beta = V_2$  (or  $D = D_2$ ), there is a single real solution in regime III,  $y = y_2$ , which corresponds to  $w = w_2$ .
  - For  $V_2 < V_\beta < V_1$  (or  $D_2 < D < D_1$ ), there are two real solutions in regime III.
  - For  $V_\beta \geq V_1$  (or  $D \geq D_1$ ), there is a single real solution in regime III.

Once we know the stationary states in regime III, we have to analyse their stability by studying the second derivative of the free energy  $F$ . In both scenarios, (i) and (ii), if there is a single real solution of equation (29) with  $w > W$  (or  $y > y_1$ ) it corresponds to a minimum of the free energy in regime III. In scenario (ii), for  $V_\beta$  within the interval  $V_2 < V_\beta < V_1$  there are two solutions in regime III: the one with  $W < w < w_2$  (or  $y_1 < y < y_2$ ) corresponds to a maximum of  $F$  and the one with  $w > w_2$  (or  $y > y_2$ ) corresponds to a minimum of  $F$ .

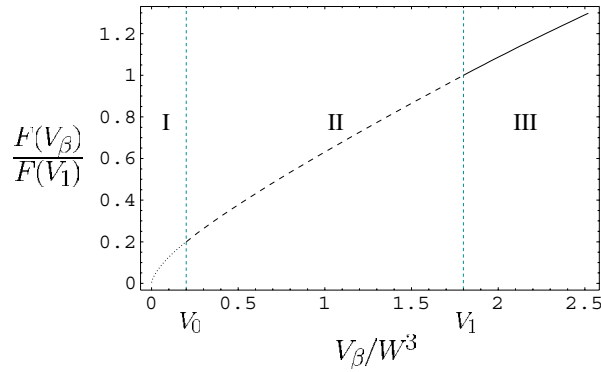
#### 4.4. Transitions between regimes

*Transitions between regime I and II.* Let us consider a simple cubic crystal that grows on a substrate patterned with a lyophilic stripe domain. Assuming that the crystal is always close to its equilibrium shape, it undergoes morphological transitions between regimes I, II, and III.

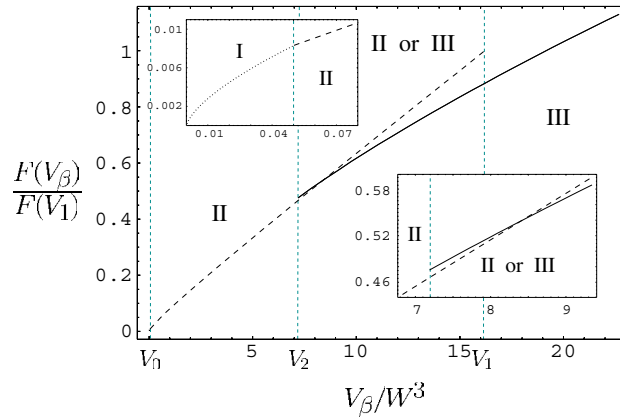
At low volumes, the width of the crystal is smaller than the width of the stripe,  $w < W$ , and the crystal is in a state belonging to regime I. If one increases the volume  $V_\beta$  of the crystal, the transition between regime I ( $w < W$ ) and regime II ( $w = W$ ) occurs for  $V_\beta = V_0$ , where  $V_0$  is the volume defined in equation (19).

The interfacial free energies of the crystals in equilibrium in regimes I and II,  $F_I$  and  $F_{II}$ , are given by equations (18) and (22), respectively. These free energies and their first derivatives with respect to the volume  $V_\beta$  are equal for  $V_\beta = V_0$ ,  $F_I(V_0) = F_{II}(V_0)$  and  $F'_I(V_0) = F'_{II}(V_0)$ . Therefore, the transitions between regimes I and II are always *continuous* for any values of the couplings  $a_\gamma$  and  $a_\delta$  with the substrate; see the numerical examples in figures 5 and 6.

*Transitions between regimes II and III.* The maximum size of a crystal in regime II corresponds to the volume  $V_\beta$  at which both stationarity conditions of regime III, (24) and (25), are satisfied by a crystal of width  $w = W$ . This occurs for  $V_\beta = V_1$ , where  $V_1$  is the volume defined in equation (31).



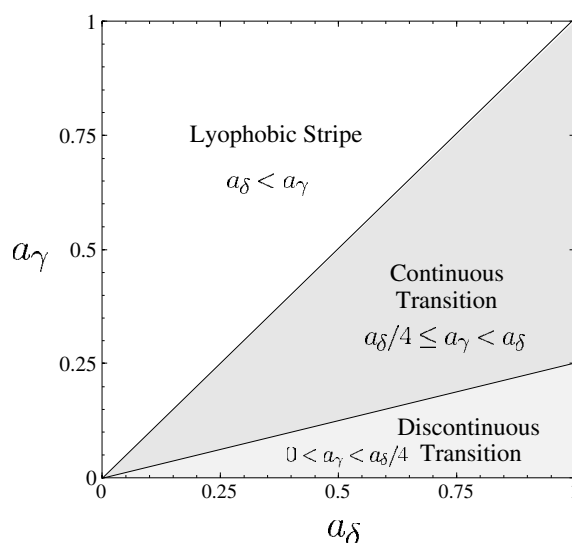
**Figure 5.** Numerical example for scenario (i) ( $a_\delta/4 \leq a_\gamma < a_\delta$ ). Continuous transitions between regimes I and II, and between regimes II and III. The free energy  $F(V_\beta)$  is normalized to its value for  $V_\beta = V_1$ . The coupling constants are  $a_\gamma = 0.2$  and  $a_\delta = 0.6$ .



**Figure 6.** Numerical example for scenario (ii) ( $0 < a_\gamma < a_\delta/4$ ). Continuous transition between regimes I and II, and discontinuous transition between regimes II and III. The free energy  $F(V_\beta)$  is normalized to its value for  $V_\beta = V_1$  in regime II. The coupling constants are  $a_\gamma = 0.05$  and  $a_\delta = 0.9$ .

First, let us consider the case  $a_\delta/4 \leq a_\gamma < a_\delta$ , which corresponds to the scenario (i) described in section 4.3. In this case, the free energies in regimes II and III are equal for  $V_\beta = V_1$ ,  $F_{\text{II}}(V_1) = F_{\text{III}}(V_1)$ . The free energy  $F_{\text{III}}$ , as given by equation (26), is a function of the volume  $V_\beta$  and the width  $w(V_\beta)$  of the crystal. Given a certain volume  $V_\beta$ ,  $w(V_\beta)$  is a real solution of equation (27) with  $w(V_\beta) > W$ . Using the theorem of the implicit function in equation (27), one can compute the derivative  $dw/dV_\beta$  for the stationary states in regime III. Applying the chain rule to equation (26), one obtains  $dF_{\text{III}}/dV_\beta$ . From these results, one has that the first derivatives of  $F_{\text{II}}$  and  $F_{\text{III}}$  with respect to the volume  $V_\beta$  are equal for  $V_\beta = V_1$  (and  $w = W$ ),  $F'_{\text{II}}(V_1) = F'_{\text{III}}(V_1)$ . In conclusion, in the case  $a_\delta/4 \leq a_\gamma < a_\delta$  the transition between regimes II and III is *continuous* and occurs for volume  $V_\beta = V_1$ ; see figure 5.

Now, let us consider the case  $0 < a_\gamma < a_\delta/4$ , which corresponds to the scenario (ii) described in section 4.3. A numerical example for this case is shown in figure 6. In this figure, the end point (maximum volume) of the branch of stable states in regime II corresponds to  $V_1$ , and the end point of the branch of stable states in regime III (minimum volume) corresponds to  $V_\beta = V_2$ , where  $V_2$  is the quantity defined in equation (36). The transition between regimes



**Figure 7.** Diagram indicating the continuity or discontinuity of the transition between regimes II and III for a simple cubic crystal on a lyophilic stripe domain. The parameters  $a_\gamma$  and  $a_\delta$  are the dimensionless couplings of the crystal with the lyophilic stripe and with the lyophobic surface, respectively.

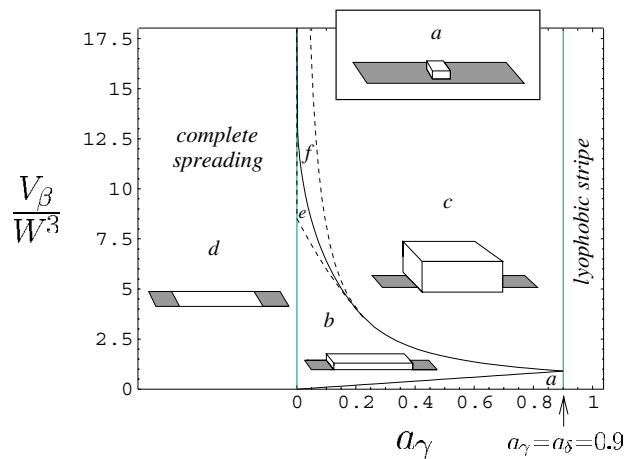
II and III for  $0 < a_\gamma < a_\delta/4$  is *discontinuous*. Thus, there is *hysteresis* in the volume at which the transition occurs if one goes from regime III to regime II decreasing the volume  $V_\beta$ , or if one goes from regime II to regime III increasing  $V_\beta$ ; see figure 6.

In summary, the continuity or discontinuity of the transition between regimes II and III depends on the strength of the couplings of the crystal with the lyophilic ( $a_\gamma$ ) and lyophobic ( $a_\delta$ ) surface domains. Two different cases can be distinguished. For  $a_\delta/4 \leq a_\gamma < a_\delta$  (scenario (i)), the transition is continuous and occurs at  $V_\beta = V_1$ ; see figure 5. For  $0 < a_\gamma < a_\delta/4$  (scenario (ii)), the transition is discontinuous and there is hysteresis in the volume at which it occurs; see figure 6.

In both scenarios, (i) and (ii), irrespective of the continuity or discontinuity of the transitions between regimes II and III, the morphologies of stable crystals with volume  $V_\beta$  larger than  $V_1$  always belong to regime III. Figure 7 shows a plot of  $a_\delta$  versus  $a_\gamma$  in which the regions have been indicated that correspond to continuous and discontinuous transitions between regimes II and III. For  $a_\gamma > a_\delta$ , the stripe domain is less attractive for the crystal than the rest of the wall, thus the stripe is lyophobic. The case  $a_\gamma > a_\delta$  is out of the scope of this paper.

#### 4.5. Bifurcation diagram

This section is devoted to the diagram of morphologically stable states for a simple cubic crystal on a lyophilic stripe domain. In figure 8, this diagram has been plotted for  $a_\delta = 0.9$ . The complete diagram is a three dimensional cartesian graphic with  $a_\gamma$  versus  $a_\delta$  in two of the axes and  $V_\beta/W^3$  in the third axis. For a different value of  $a_\delta$ , figure 8 does not change qualitatively. However, the range of  $a_\gamma$  in which the stripe is lyophobic ( $a_\gamma > a_\delta$ ), the range in which the transition between regimes II and III is continuous ( $a_\delta/4 \leq a_\gamma < a_\delta$ ), and the range in which this transition is discontinuous ( $0 < a_\gamma < a_\delta/4$ ) are shifted when  $a_\delta$  is changed. The full bifurcation diagram can be obtained from composing the information contained in figures 7 and 8.



**Figure 8.** Bifurcation diagram for a simple cubic crystal on a lyophilic stripe domain. Different regions indicate different regimes for the stable shapes of the crystal; see the text.  $a_\delta = 0.9$ .

In figure 8, the *solid curves* between regions (a) and (b), between (b) and (c), and between (e) and (f) indicate the volumes  $V_\beta$  for which the free energies in two different regimes are equal. The *dashed curves* indicate the limits of stability ('spinodal' lines) for the branches of locally stable states in regions of the diagram in which there is another minimum with lower free energy.

The stable states corresponding to the regions indicated in figure 8 are as follows.

- There is a single minimum, which corresponds to a crystal of square base that lies within the stripe,  $w < W$  (regime I).
- The crystal has the shape of a box of width  $w = W$  and certain height  $h > 0$  over the surface of the wall (regime II).
- The crystal is detached outward from the boundaries of the stripe,  $w > W$  (regime III).
- For  $a_\gamma = 0$ , the crystal is in regime II,  $w = W$ , but it is completely spread on the surface of the stripe,  $h = 0$ . The coupling  $a_\gamma$  cannot be negative; see section 3.
- In this area of the diagram, for every volume  $V_\beta$  there are two local minima of the free energy, one in regime II and one in regime III. The minimum in regime II is the global minimum.
- Identical situation to that in (e), but in (f) the global minimum is in regime III.

The dashed curve between regions (f) and (c) corresponds to the maximum volume of a crystal in regime II,  $V_\beta = V_1$ , where  $V_1$  is the quantity defined in equation (31). This curve goes to infinity as  $a_\gamma$  approaches 0, meaning that for any  $a_\gamma > 0$  a stable crystal in regime II can only exist for  $V_\beta < V_1$ .

The solid curve between regions (e) and (f) corresponds to the volume at which the free energies in regimes II and III are equal, and also goes to infinity as  $a_\gamma$  goes to 0.

The dashed curve between regions (e) and (b) indicates the minimum volume of a crystal in regime III,  $V_\beta = V_2$ , which has been defined in equation (36). For  $a_\gamma = 0$ , the volume  $V_2$  is finite,  $V_2(a_\gamma = 0) = (4^4/3^3)a_\delta W^3$ . Thus, for  $a_\gamma = 0$  a stable crystal in regime III can only exist for  $V_\beta > (4^4/3^3)a_\delta W^3$ . Actually, the results for  $a_\gamma = 0$  should be taken with caution. In this limit, the model predicts complete spreading on the lyophilic stripe for a crystal in regime II (the height  $h$  of the crystal goes to 0), but in a real system the finite size of the molecules limits the spreading of the crystal on the wall.

To conclude this section, let us emphasize that the transitions between regimes II and III that occur by changing the volume  $V_\beta$  at constant  $a_\gamma$  and  $a_\delta$  are continuous (no hysteresis) for  $a_\delta/4 \leq a_\gamma < a_\delta$  and discontinuous (hysteresis) for  $0 < a_\gamma < a_\delta/4$ . In the continuous transitions, the free energy has only one minimum that moves ‘continuously’ between regimes II and III when the volume  $V_\beta$  is changed across the curve that separates regions (b) and (c) in figure 8. In the discontinuous transitions, in contrast, close to the transition line, i.e., near the solid curve separating regions (e) and (f) in figure 8, the free energy has two minima for every volume  $V_\beta$ , one in regime II and one in regime III. Along the transition line between regions (e) and (f), both minima have equal depth.

The *bifurcation point* at which the transition between regimes II and III changes from continuous to discontinuous, occurs for  $a_\gamma = a_\delta/4$  and volume  $V_\beta = 4a_\delta W^3$ . In figure 8, the bifurcation point is the point where regions (b), (c), (e), and (f) meet. In the space of the couplings,  $a_\gamma$  and  $a_\delta$ , plotted in figure 7, the equation  $a_\gamma = a_\delta/4$  corresponds to the line of bifurcation points that separate the region in which the transition between regimes II and III is continuous from the region in which it is discontinuous.

## 5. Outlook: comparison with liquid channels

Let us finally compare the results for crystals on lyophilic stripe domains with the results for liquid morphologies wetting these surface domains. In [4], Brinkmann and Lipowsky have studied morphological transitions of liquid channels wetting a lyophilic stripe domain, and they have obtained a bifurcation diagram similar to figure 8. In this analogy, a crystal in regime I corresponds to a spherical cap of liquid located within the stripe domain, a crystal in regime II corresponds to a liquid channel extended along the stripe with almost constant cross-section and the contact line attached to the boundaries of the domain, and a crystal in regime III corresponds to a channel with a bulge that collects an important amount of the volume of liquid.

In the case of a crystal on a lyophilic stripe domain, for a given value of  $a_\delta$  the transition between regimes II and III is continuous or discontinuous depending on the value of  $a_\gamma$ . Likewise, for a given value of the contact angle on the lyophobic surface  $\theta_\delta \geq \pi/2$  the transition between a liquid channel and a channel with a bulge is continuous or discontinuous depending on the value of the contact angle on the lyophilic stripe  $\theta_\gamma$  [4]. Despite these similarities, the transitions in these two cases differ in several respects.

One should notice that, in the case of liquid wetting a lyophilic stripe, the transition from a channel to a channel with a bulge does *not* necessarily involve the detachment of the contact line from the boundaries of the stripe. In contrast to this, the transition from regime II to regime III for a simple cubic crystal always involves the detachment of the contact line.

Another important difference between the transitions in liquid channels and crystals on lyophilic stripes is the following. From the definition of  $a_\gamma$  and the Young equation, one has that

$$\cos \theta_\gamma = 1 - 2a_\gamma. \quad (37)$$

A stable crystal in regime II can only grow to volume  $V_1 \equiv (a_\delta^2/a_\gamma)W^3$ . For a crystal of volume  $V_\beta > V_1$  located on a lyophilic stripe with  $a_\gamma > 0$ , which corresponds to  $\theta_\gamma > 0$ , regime II is unstable and regime III is preferred. In contrast, for an infinitely long lyophilic stripe with  $\theta_\gamma < 38.24^\circ$  patterned on a lyophobic substrate with  $\theta_\delta \geq \pi/2$ , a liquid channel that grows along the stripe does *not* produce a bulge as the volume of liquid is increased [4].

A complete bifurcation diagram for liquid channels on lyophilic stripes including the curves that correspond to the detachment of the contact line from the boundaries of the

lyophilic stripe, and a study of the cases for different values of  $\theta_\delta$  are still open questions and may require extensive numerical computations. A more detailed comparison between morphological transitions in liquid channels and simple cubic crystals on lyophilic stripes has to wait to have these questions answered.

### Acknowledgments

The author would like to thank Martin Brinkmann, Gerhard Gompper, Stefan Klumpp, Peter Lenz, Reinhard Lipowsky, André Moreira, and Peter Swain for useful discussions and comments. Funding from the Deutsche Forschungsgemeinschaft through the SFB-448 and from the Max-Planck-Gesellschaft are gratefully acknowledged.

### Appendix. List of Symbols

$\alpha$	low density phase (vapour)
$\beta$	crystal or liquid phase
$\gamma$	lyophilic surface domain
$\delta$	lyophobic surface domain
$\theta$	contact angle of a droplet on a wall
$\theta_\gamma, \theta_\delta$	contact angle on a $\gamma$ and $\delta$ domain
$\Sigma_{ij}$	surface tension of the $ij$ interface
$\sigma$	substrate or wall
$\mathcal{A}_{ij}$	surface region of the $ij$ interface
$A_{ij}$	area of $\mathcal{A}_{ij}$
$a_\gamma, a_\delta$	aspect ratio of a crystal on a $\gamma$ and $\delta$ domain
$c_\gamma, c_\delta$	see equation (3)
$D$	see equation (30)
$F$	interfacial free energy
$h$	height of the crystal on the wall
$L$	length of the lyophilic stripe domain
$\ell$	length of the crystal along the lyophilic stripe
$\mathbf{n}$	vector normal to a crystal plane
$V_\beta$	volume of the crystal
$W$	width of the lyophilic stripe domain
$w$	width of the crystal across the lyophilic stripe
$\mathbf{x}$	surface coordinate on the wall
$y$	see equation (28)

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