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## Equilibrium, alternating surfaces and polymorph structures of 2D model crystals: discrete and continuous polar diagrams

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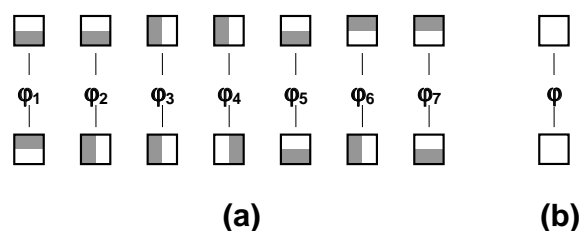
**Abstract.** The equilibrium of large two-dimensional (2D) model crystals with polymorph structures (screw, bilayer and monochess) and asymmetrical interactions are investigated microscopically using two different atomistic approaches: the method of Stranski and Kaischew and the Wulff construction which is based on the polar diagram of surface energy. Each model proposes at least two structurally different surfaces (periphery rows), some of them being alternating. Accounting for nearest neighbour interactions, it is established that only some of the alternating surfaces belong to the equilibrium forms. The equilibrium surfaces of a 2D Kossel crystal appear as a limiting case.

The orientation dependence of the specific surface energy  $\sigma$  for these models is determined by mathematical induction in a discrete  $\sigma(m, n)$  presentation of the polar diagram. The usual continuous presentation  $\sigma(\theta)$  has the meaning only of fitting curves, not all points of which have a physical meaning. These  $\sigma(\theta)$  dependencies cannot be constructed without in advance analysing the discrete  $\sigma(m, n)$  presentations. The latter allows determination not only of the number of fitting curves, but also of their unknown coefficients.

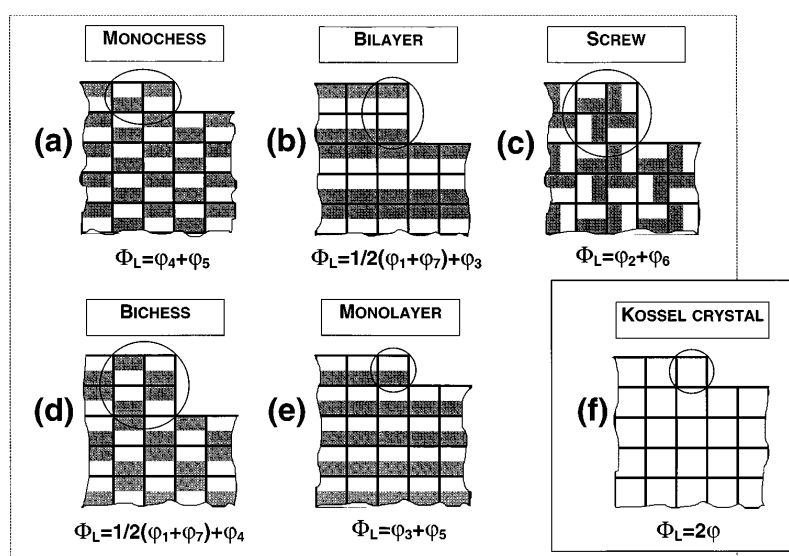
### 1. Introduction

There exist two different atomistic approaches for treating the problem of crystal equilibrium on a microscopic level. The first approach, developed by Stranski and Kaischew [1], is based on comparison of the work for separation of atoms on the crystal surface with their energy in the half crystal position (the lattice energy) for large crystals or with the mean separation work for small crystals (see also [2]). The second approach, originating from Ehrenfest [3], Yamada [4] and Landau [5], is based on the dependence of the specific surface energy  $\sigma$  on the orientation angle  $\theta$  ( $\sigma(\theta)$ , called the polar diagram). As shown by Stranski and Kaischew [1], Wolff [6], Mullins [7] and Bennema [8], this approach offers a principal possibility for correlating the intermolecular bond with the surface free energy. A general expression for the polar diagram in terms of broken bonds energy is proposed by Wolff [6]. The used formalism is based on an atomistic version of the definition of Born and Stern [9] of surface energy. It is applied to many real structures. For example, in the instructive case of a two-dimensional (2D) Kossel crystal with nearest neighbour interactions in the lattice it is demonstrated that the polar diagram  $\sigma(\theta)$  can be constructed by knowing the bond energy  $\varphi$  only [8].

Using these two atomistic approaches, this paper investigates the equilibrium of some 2D model crystals with asymmetrical nearest neighbour interactions. The models considered propose a great variety of polymorph structures and different surface structures, including alternating ones. (The surface of the 2D crystal to be investigated here is the line of its



**Figure 1.** Interaction energy  $\varphi_i$  between nearest neighbour building elements of (a) 2D model crystals and (b) a 2D Kossel crystal. For concreteness,  $\varphi_1 > \varphi_2 > \varphi_3 > \varphi_4 > \varphi_5 > \varphi_6 > \varphi_7$  is used.



**Figure 2.** Examples of 2D model crystals with different polymorph structures: (a) monochess, (b) bilayer, (c) screw, (d) bichess, (e) monolayer and (f) model of a 2D Kossel crystal. The building blocks: monomer (e), (f), dimer (a), (b) and quadrumer (c), (d), outlined by ovals, are located in the corresponding half crystal position. The calculated values of the lattice energy  $\Phi_L$  are denoted.

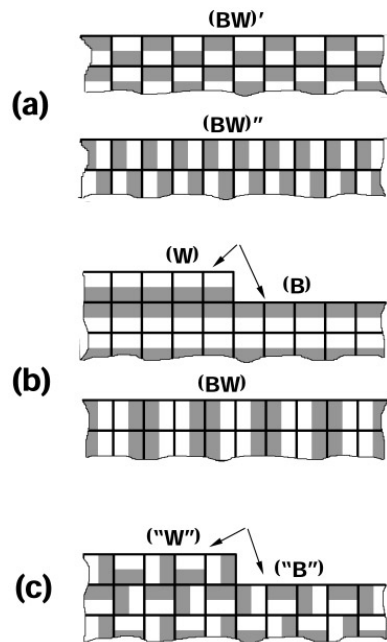
periphery.) Appropriate algorithms are proposed for construction of their polar diagrams in a discrete presentation, respectively for atomistic determination of the coefficients in a continuous presentation. The influence of the asymmetry of interaction forces on the equilibrium form as well as of the existence of alternating surfaces is discussed for three polymorph crystals. The advantage of the discrete polar diagrams is considered.

## 2. Model description

The 2D models of crystals with asymmetrical interactions are constructed by using identical building elements represented graphically as black–white squares (figure 1). The interaction energy between two elements is assumed to be highest ( $\varphi_1$ ) and lowest ( $\varphi_7$ ) when they are oriented to each other with, respectively, their black sides and white sides. As shown in figure 2, a great variety of such polymorph structures can be created: monolayer, bilayer, monochess, bichess, screw etc (one of them, the 2D screw lattice, was discussed in detail in

our previous papers [10]). Different blocks are used as building blocks (outlined by ovals in figure 2): monomer (single building element)—figure 2(e), dimers (two neighbour building elements)—figures 2(a), (b), and quadrumers (four neighbour building elements located in a square)—figures 2(c), (d). Such a lattice appears to be a generalization of the well known 2D Kossel crystal (figure 2(f)) [1, 2].

Each 2D block lattice results in at least two structurally different  $\{10\}$  and/or  $\{01\}$  surfaces (periphery rows), some of them being alternating (figure 3). For example, the surface structures of the bilayer lattice (figure 3(b)) are white (W), black (B) and black–white (BW), according to the orientation of their surface located building elements. The screw lattice surfaces (figure 3(c)) are predominantly white ('W') or predominantly black ('B'), and the monochoess lattice surfaces are two different kinds of black–white—(BW)' and (BW)". The so called alternating surfaces are crystallographically identical and replace alternatively one another when an additional 'layer' (periphery row) is attached to the lattice or separated from it. The couples of alternating surfaces are indicated by arrows in figure 3: (W) and (B) in figure 3(b) and ('W') and ('B') in figure 3(c).

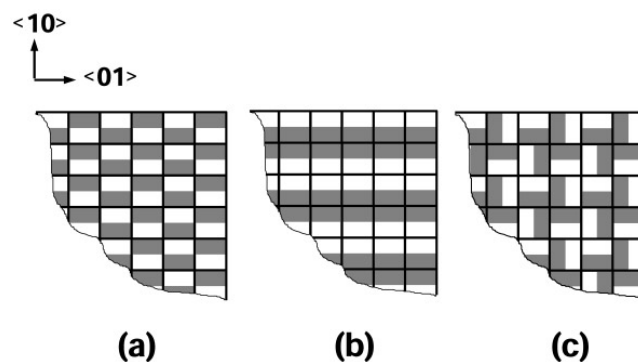


**Figure 3.**  $\{10\}$  and/or  $\{01\}$  surfaces (periphery rows) of 2D polymorph crystals: (a) monochoess, (b) bilayer and (c) screw. The different surface structures are called: white (W), 'white' ('W'), black (B), 'black' ('B') and different types of black–white—(BW), (BW)' and (BW)". The couples of alternating surfaces are indicated by arrows: (W) and (B) in case (b), and ('W') and ('B') in case (c).

### 3. Separation work and equilibrium of the 2D model crystals

According to Stranski [11], the equilibrium of a crystal with its environment is determined by the lattice energy  $\Phi_L$  (per one element). This energy can be estimated at low temperatures, analogously to the case of Kossel crystal [1], as the work done for separation of the appropriate building block (monomer, dimer, quadramer etc) from the half crystal position (figure 2) and for

the subsequent dissociation of this block into single elements [10]. Following the well known method of Stranski and Kaischew [1], the equilibrium of a large 2D crystal can be determined by comparison of  $\Phi_L$  with the separation energy of the building elements from different sites in the periphery [10]. The obtained equilibrium surfaces for three of the polymorph structures, monochess, bilayer and screw (figure 2(a)–(c)), are shown in figure 4. Obviously, the equilibrium large 2D Kossel crystal [2] follows as a limiting case when one returns to a central symmetry of interaction.



**Figure 4.** Equilibrium surfaces of large 2D crystals with polymorph structures: (a) monochess— $\{10\}$  (BW)' and  $\{01\}$  (BW)''; (b) bilayer— $\{10\}$  (W) and  $\{01\}$  (BW)—and (c) screw— $\{10\}$  ('W') and  $\{01\}$  ('W').

Only one from the two possible 'white' and 'black' surfaces (see figure 3(c)), alternating in  $\langle 10 \rangle$  and  $\langle 01 \rangle$  directions, namely the 'white' ('W') one, belongs to the equilibrium large 2D screw crystal (figure 4(c)) [10]. The same is valid for the white (W) surface, alternating in the  $\langle 10 \rangle$  direction, of the equilibrium large 2D bilayer crystal (see figures 3(b) and 4(b)). As seen, its equilibrium surface in  $\langle 01 \rangle$  direction is structurally different, black–white (BW), but not alternating (figures 3(b) and 4(b)). To the large 2D monochess crystal belong two equilibrium surfaces: (BW)' in  $\langle 10 \rangle$  direction and (BW)'' in the  $\langle 01 \rangle$  direction, which are the only possible surfaces for this structure (see figures 3(a) and 4(a)). The consecutive steps of obtaining equilibrium forms of large and small 2D crystals will be described in more detail separately. Obviously, the applied procedure chooses only one of the possible alternating surfaces (the so-called white or 'white' one). The physical reason for this choice becomes clear from the atomistic investigation of the equilibrium with the help of the concept of polar diagram of surface energy.

#### 4. Polar diagram and equilibrium of the 2D model crystals

According to Born and Stern [9], the surface energy of a 2D crystal surface is defined as half the work  $W(\theta)$  done in dividing a large crystal along the corresponding crystallographic plane. In continuous presentation the specific surface energy  $\sigma$  is determined as a macroscopic quantity which depends on the given geometric orientation, crystallographic and non-crystallographic, characterized by polar angle  $\theta$ . The equilibrium form can be deduced from the polar diagram  $\sigma(\theta)$  by means of the Wulff construction (see [2–8]). Following Wolff [6], the work  $W$  (respectively  $\sigma$ ) can be calculated microscopically as the total energy of broken bonds (per unit area). In such a discrete presentation, the orientation dependence of the specific surface energy  $\sigma(m, n) = \sigma[\tan^{-1}(m/n)]$  can be determined for each crystallographic orientation of

the large 2D crystal. Here  $m$  and  $n$  are the numbers of broken periphery bonds along the  $\langle 10 \rangle$  and  $\langle 01 \rangle$  crystallographic axes. The used  $(m, n)$  notation of surfaces characterizes not only their crystallographic orientation but also their step structure. For more complicated structures, however, one needs additionally to know the exact position of the cross section with respect to the alternating surfaces, because some parallel sections cut bonds with different energy.

#### 4.1. Discrete presentation

Treating microscopically the polar diagram of large 2D model crystals, we start from the well known macroscopic orientation dependence of  $\sigma$  for the 2D Kossel crystal (see [3–8])

$$\sigma(\theta) = \sigma_0(\cos \theta + \sin \theta). \quad (1)$$

Bennema [8] put in (1) the coefficient  $\sigma_0 = \varphi/2r_0$ , where  $\varphi$  and  $r_0$  are respectively the interaction energy and the distance between nearest neighbour building elements (see figures 1(b) and 2(f)). Using a mathematical induction, we can transform (1) in terms of a discrete  $(m, n)$  presentation (upon assuming that  $r_0$  is unity):

$$\begin{aligned} \sigma_{\{10\}} &= \sigma_{\{01\}} = \varphi/2 \\ \sigma(m, n) &= (\varphi/2)(m+n)/(m^2+n^2)^{-1/2}. \end{aligned} \quad (2)$$

Orientation dependencies  $\sigma(m, n)$ , corresponding to the general expression of Wolff [6], can be obtained in discrete presentations in a similar way also for the more complicated models from the great family of proposed 2D polymorph crystals. We have demonstrated this approach on the three polymorph structures discussed in section 3.

In the case of a large 2D monochess crystal, the orientation dependence of  $\sigma$  is characterized by a single series of  $\sigma(m, n)$  values, obtained by mathematical induction and given by

$$\begin{aligned} \sigma_{\{10\}}^{(BW)'} &= \varphi_5/2 \\ \sigma_{\{01\}}^{(BW)''} &= \varphi_3/2 \\ \sigma(m, n) &= m\varphi_5/2(m^2+n^2)^{-1/2} + n\varphi_3/2(m^2+n^2)^{-1/2}. \end{aligned} \quad (3)$$

The polar diagram, obtained in discrete presentation, is shown in figure 6(a) by circles.

The more complicated structure of the large 2D bilayer crystal needs an additional explanation (see figure 5). This structure allows parallel cross sections, cutting different combinations of bonds. These are the so-called alternating surfaces. Naturally, this leads to different values of  $\sigma(m, n)$ . For example, dividing the large crystal along the  $\langle 01 \rangle$  direction, we create two identical surfaces, both black (line AA, figure 5) or both white (line BB, figure 5), cutting bonds with energy either  $\varphi_7$  or  $\varphi_1$ . Along the  $\langle 10 \rangle$  direction we cut bonds with energy  $\varphi_3$  and create surfaces with a black–white structure (line CC, figure 5). Thus, for each type of cross section we obtain different  $\sigma$  values ( $\sigma_{\{10\}}^{(B)}$ ,  $\sigma_{\{10\}}^{(W)}$  or  $\sigma_{\{01\}}^{(BW)}$ ) given by the first three of the following equations:

$$\begin{aligned} \sigma_{\{10\}}^{(B)} &= \varphi_1/2 \\ \sigma_{\{10\}}^{(W)} &= \varphi_7/2 \\ \sigma_{\{01\}}^{(BW)} &= \varphi_3/2 \end{aligned}$$

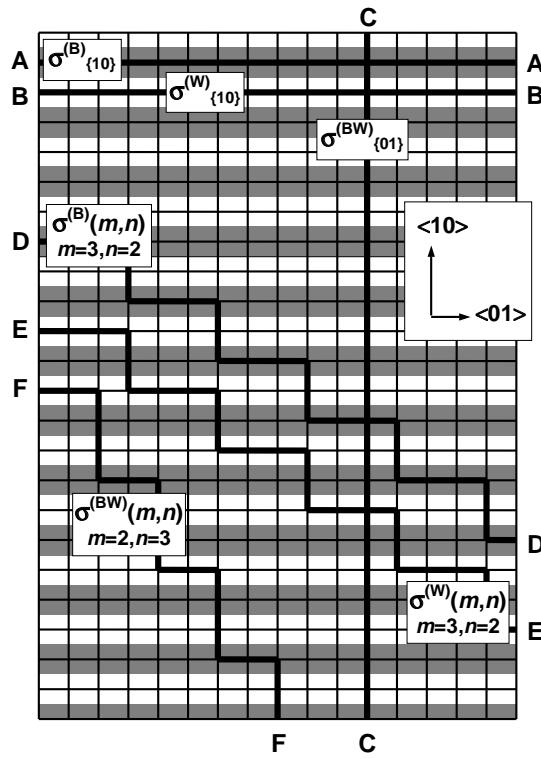


Figure 5. Application of the microscopic version of the Born and Stern definition of  $\sigma(m, n) = (\tan^{-1}(m/n))$  to the case of a 2D bilayer crystal.

$$\begin{aligned}
 \sigma^{(B)}(m, n) &= m\varphi_1/2(m^2 + n^2)^{-1/2} + n\varphi_3/2(m^2 + n^2)^{-1/2} & (n = \text{odd number}) \\
 \sigma^{(W)}(m, n) &= m\varphi_7/2(m^2 + n^2)^{-1/2} + n\varphi_3/2(m^2 + n^2)^{-1/2} & (n = \text{odd number}) \\
 \sigma^{(BW)}(m, n) &= m(\varphi_1 + \varphi_7)/4(m^2 + n^2)^{-1/2} + n\varphi_3/2(m^2 + n^2)^{-1/2} & (n = \text{even number}).
 \end{aligned}
 \tag{4}$$

Here, for convenience, the upper index of  $\sigma$  is used to indicate the most often cut types of surfaces—black (B), white (W) or black–white (BW). The other types of cross sections in figure 5 cut different combinations of bonds. As seen, these are bonds with energies  $\varphi_1$  and  $\varphi_3$  only (line DD), or  $\varphi_7$  and  $\varphi_3$  only (line EE), while in the case of line FF the cut bonds are with energies  $\varphi_1$ ,  $\varphi_3$  and  $\varphi_7$ . The corresponding values of  $\sigma^{(B)}(m, n)$  and  $\sigma^{(W)}(m, n)$ ,  $n$  being an odd number, and of  $\sigma^{(BW)}(m, n)$ ,  $n$  being an even number, are presented in the last three rows of (4) obtained also by mathematical induction. The polar diagram for a bilayer crystal is shown in discrete presentation by circles in figure 6(b).

The orientation dependencies  $\sigma(m, n)$  for the large 2D screw crystal are obtained in an analogous way and are given by the expressions

$$\begin{aligned}
 \sigma^{(B')}_{\{10\}} &= \sigma^{(B')}_{\{01\}} = \varphi_2/2 \\
 \sigma^{(W')}_{\{10\}} &= \sigma^{(W')}_{\{01\}} = \varphi_6/2 \\
 \sigma^{(B'')}_{(m, n)} &= (m + n)\varphi_2/2(m^2 + n^2)^{-1/2}
 \end{aligned}$$

$$\begin{aligned}
& (m = \text{even}, n = \text{even numbers}) \\
\sigma^{(W)}(m, n) &= (m+n)\varphi_6/2(m^2+n^2)^{-1/2} \\
& (m = \text{even}, n = \text{even numbers}) \\
\sigma^{(B)}(m, n) &= m(\varphi_2 + \varphi_6)/4(m^2+n^2)^{-1/2} + n\varphi_2/2(m^2+n^2)^{-1/2} \\
& (m = \text{even}, n = \text{odd numbers}) \\
\sigma^{(W)}(m, n) &= m(\varphi_2 + \varphi_6)/4(m^2+n^2)^{-1/2} + n\varphi_6/2(m^2+n^2)^{-1/2} \\
& (m = \text{even}, n = \text{odd numbers}) \\
\sigma^{(B)}(m, n) &= m\varphi_2/2(m^2+n^2)^{-1/2} + n(\varphi_2 + \varphi_6)/4(m^2+n^2)^{-1/2} \\
& (m = \text{odd}, n = \text{even numbers}) \\
\sigma^{(W)}(m, n) &= m\varphi_6/2(m^2+n^2)^{-1/2} + n(\varphi_2 + \varphi_6)/4(m^2+n^2)^{-1/2} \\
& (m = \text{odd}, n = \text{even numbers}) \\
\sigma^{(B)}(m, n) &= \sigma^{(W)}(m, n) = (m+n)(\varphi_2 + \varphi_6)/4(m^2+n^2)^{-1/2} \\
& (m = \text{odd}, n = \text{odd numbers}). \tag{5}
\end{aligned}$$

These dependencies are also related both to the complicated crystal structure and to the surfaces alternating in  $\langle 10 \rangle$  and  $\langle 01 \rangle$  directions with ‘black’ (‘B’) and ‘white’ (‘W’) structures. The cutting bonds here are with energies  $\varphi_2$  and  $\varphi_6$ , respectively, or different combinations of them. The obtained polar diagram for a screw crystal in discrete presentation is shown in figure 6(c) by circles.

#### 4.2. Continuous presentation

In order to obtain the polar diagrams in the usual continuous description (like (1)), the coefficients before the trigonometric functions are determined from the corresponding series of discrete values (3)–(5) by their transformation in expressions having the form of (1). These transformations are equivalent to fitting procedures.

The continuous presentation of polar diagram of the 2D monochess crystal, obtained on the basis of the series of discrete values (3), is given by

$$\sigma(\theta) = (\varphi_5/2) \cos \theta + (\varphi_3/2) \sin \theta. \tag{6}$$

This single curve (6) is drawn with a dashed line in figure 6(a) at  $\theta \in [0, \pi/2]$ .

The more complicated polar diagram of the 2D bilayer crystal is described by three continuous curves given by

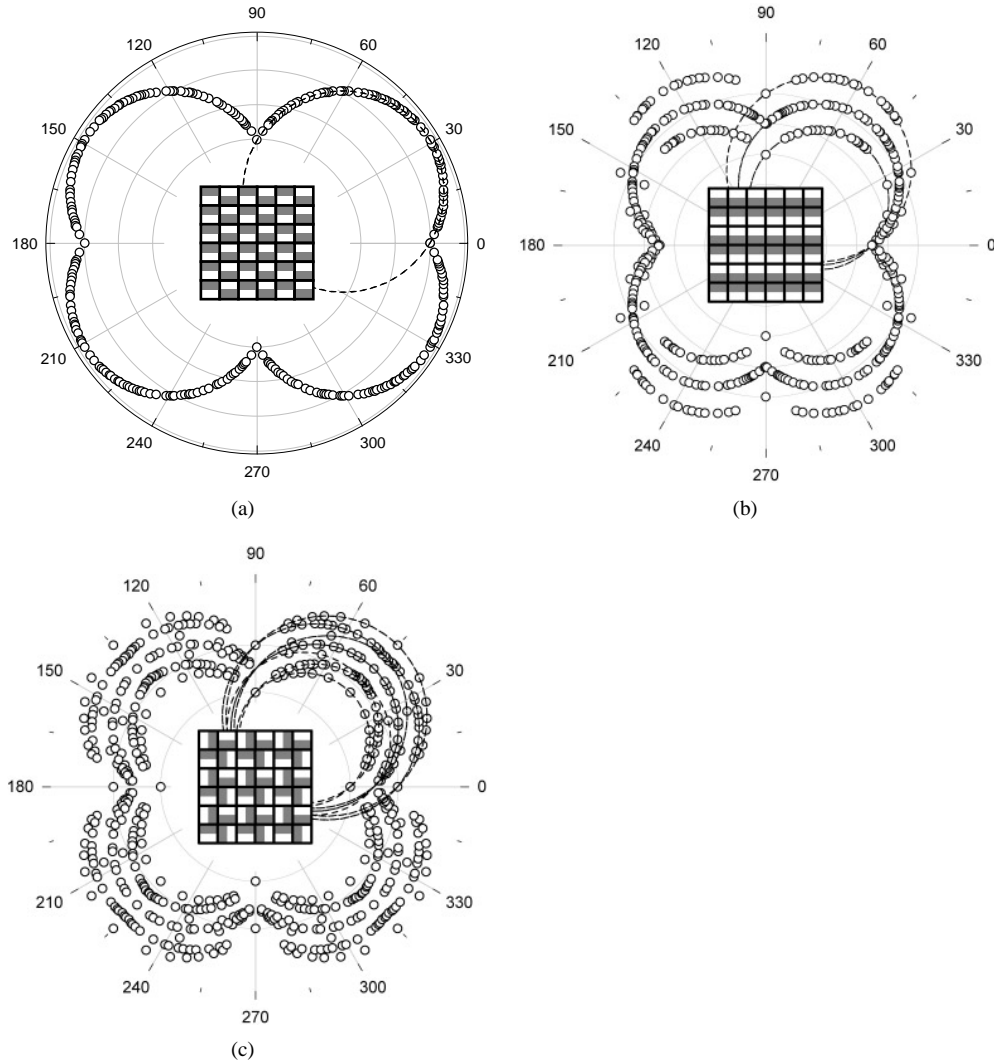
$$\begin{aligned}
\sigma^{(B)}(\theta) &= (\varphi_1/2) \cos \theta + (\varphi_3/2) \sin \theta \\
\sigma^{(W)}(\theta) &= (\varphi_7/2) \cos \theta + (\varphi_3/2) \sin \theta \\
\sigma^{(BW)}(\theta) &= [(\varphi_1 + \varphi_7)/4] \cos \theta + (\varphi_3/2) \sin \theta. \tag{7}
\end{aligned}$$

These curves are presented in figure 6(b) with dashed lines at  $\theta \in [0, \pi/2]$ .

As follows from (5), the  $\sigma(\theta)$  dependence for the 2D screw crystal is described by equations

$$\begin{aligned}
\sigma^{(B)}(\theta) &= (\varphi_2/2) \cos \theta + (\varphi_2/2) \sin \theta \\
\sigma^{(W)}(\theta) &= (\varphi_6/2) \cos \theta + (\varphi_6/2) \sin \theta \\
\sigma^{(B)}(\theta) &= [(\varphi_2 + \varphi_6)/4] \cos \theta + (\varphi_2/2) \sin \theta \\
\sigma^{(W)}(\theta) &= [(\varphi_2 + \varphi_6)/4] \cos \theta + (\varphi_6/2) \sin \theta \\
\sigma^{(B)}(\theta) &= (\varphi_2/2) \cos \theta + [(\varphi_2 + \varphi_6)/4] \sin \theta
\end{aligned}$$





**Figure 6.** Polar diagram of the specific surface energy  $\sigma$  for 2D model crystals with polymorph structures: (a) monochess, (b) bilayer and (c) screw. The discrete values of  $\sigma(m, n)$ , calculated from (a) equations (3), (b) equations (4) and (c) equations (5) are presented as circles. The fitting curves are drawn for  $\theta \in [0, \pi/2]$  with dashed lines according to (a) equation (6), (b) equations (7) and (c) equations (8). The used values of the interaction energies are  $\varphi_1 = 1$ ,  $\varphi_2 = 0.72$ ,  $\varphi_3 = 0.7$ ,  $\varphi_5 = 0.6$ ,  $\varphi_6 = 0.56$  and  $\varphi_7 = 0.3$ . The illustrations in the centre of each polar diagram show the equilibrium surfaces of the corresponding large 2D crystals.

$$\begin{aligned}\sigma^{(W')}(\theta) &= (\varphi_6/2) \cos \theta + [(\varphi_2 + \varphi_6)/4] \sin \theta \\ \sigma^{(B')}(\theta) &= \sigma^{(W)}(\theta) = [(\varphi_2 + \varphi_6)/4] \cos \theta + [(\varphi_2 + \varphi_6)/4] \sin \theta.\end{aligned}\quad (8)$$

The curves (8) are presented in figure 6(c) with dashed lines at  $\theta \in [0, \pi/2]$ .

On the bases of the obtained polar diagrams in discrete (3)–(5) or continuous (6)–(8) presentation, we determine the equilibrium surfaces, following the Wulff procedure [2, 8]. As one can see from the inset illustration in the centre of figure 6(c), the equilibrium surfaces of the large 2D screw crystal are the ‘white’ ones only. Two different equilibrium surfaces

belong to the large 2D bilayer crystal (see the inset in figure 6(b)) but again only one of the two alternating surfaces is equilibrium, the white one. In the case of a large 2D monochess crystal the equilibrium form is trivial (see the inset in figure 6(a)). These results are identical with those obtained by the method of Stranski and Kaischew [2] and shown in figures 4(a)–(c).

## 5. Conclusion

As shown above, for the 2D model crystals with alternating surfaces (like bilayer and screw ones) there is no single continuous curve describing the transition between neighbour orientations. In such cases there exist neighbour orientations for which the values of  $\sigma(m, n)$  and of  $\sigma(m \pm 1, n)$  or  $\sigma(m, n \pm 1)$  belong to different continuous curves. Therefore, it is clear that not all points of the usual continuous presentation  $\sigma(\theta)$  of the polar diagram have a physical meaning. It is not possible for one to construct the  $\sigma(\theta)$  presentation without in advance analysing the discrete  $\sigma(m, n)$  presentations. The discrete presentations allow one to determine not only the number of fitting curves but also the unknown coefficients.

As can be expected, both atomistic methods of investigation (by the separation work and by the polar diagram) lead to identical results for the equilibrium forms of large 2D model crystals. It is demonstrated also how the polar diagram (and, respectively, the equilibrium form) is affected by the intermolecular forces and their asymmetry. The models used in this paper allow comparison of the equilibrium forms of polymorph structures.

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