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MODELING GRAIN BOUNDARIES IN SOLIDS USING A COMBINED NONLINEAR AND GEOMETRICAL METHOD

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The complex arrangements of atoms near grain boundaries are difficult to understand theoretically. We propose a phenomenological (Ginzburg–Landau-like) description of crystalline phases based on symmetries and some fairly general stability arguments. This method allows a very detailed description of defects at the lattice scale with virtually no tunning parameters, unlike the usual phase-field methods. The model equations are directly inspired from those used in a very different physical context, namely, the formation of periodic patterns in systems out-of-equilibrium (e.g. Rayleigh–Bénard convection, Turing patterns). We apply the formalism to the study of symmetric tilt boundaries. Our results are in quantitative agreement with those predicted by a recent crystallographic theory of grain boundaries based on a geometrical quasicrystal-like construction. These results suggest that frustration and competition effects near a defect in crystalline arrangements have some universal features, of interest in solids or other periodic phases.

Keywords: Grain boundaries; pattern formation; geometrical frustration; quasicrystals; faceting.

1. Introduction

The structure and dynamics of grain boundaries in materials are still not well understood.[1,2] The possible relationships between the mesoscopic features of grain boundaries and their inner microscopic structure at the atomic scale remain unclear. The energies of some interfaces can be accurately described with continuous theories and topological arguments. But the study of other quantities (like mobilities), as well as short scale phenomena such as faceting, may require a deeper understanding of the microscopic structure, which directly reflects the discrete and anisotropic character of the lattice. Near a boundary, the crystal structure usually has no

simple periodic behavior and is therefore difficult to characterize. Any quantitative and sufficiently simple theory allowing a systematic characterization of the fine structure of grain boundaries at zero temperature could open the way toward a general description of these objects. Following such an approach requires going beyond usual continuous media approximations.

In this paper, we discuss a way of elucidating grain boundary microscopic structures within a theoretical framework that explicitly takes into account spatial variations at the atomic length scale. The models considered here have a very small number of parameters. They derive from very general energy and symmetry arguments. Although the nonlinear approach proposed below is fairly uncommon for crystals, it is largely used in a (apparently) completely different field of physics, namely, in pattern formation problems. Many physical systems driven out of equilibrium spontaneously form periodic structures, some of which are characterized by a crystal-like order.[3] Some well-known examples are the cellular structures formed in Rayleigh–Bénard convection of heated fluid layers or Turing patterns in reaction-diffusion processes. Pattern formation is ubiquitous in nature and has universal features. Some of these features may be of relevance to solid crystals as well. Striking analogies between pattern forming systems and dissipative processes taking place in solid crystals have been recently pointed out.[4,5] In Sec. 2, we briefly justify why some simple nonlinear models of pattern formation may be useful to study defects in crystals. We show in Sec. 3 that these models are very efficient to capture elementary competition and geometrical exclusion effects that probably take place in genuine grain boundaries. In particular, they are able to predict interface faceting, a feature still little understood from continuous theories.[6] The results obtained are in very good agreement with those given independently by a theory of grain boundaries developed recently, which is based on geometrical arguments and inspired from quasicrystals theory.[7]

2. Basics of Pattern Formation

We briefly recall some concepts of pattern formation that can be found in well documented reviews or textbooks.[3,8,9] Consider a spatially extended system described by a phenomenological, dimensionless local order parameter $\psi(\mathbf{x}, t)$ depending *a priori* on space and time variables. In convection problems, for instance, $\psi(\mathbf{x}, t)$ is related to the vertical velocity at the mid-plane of the convective cell. A uniform phase is characterized by the trivial solution $\psi = \mathrm{cst}(= 0)$. When a non-trivial stationary periodic pattern sets up in the system, e.g. above the onset of convection, ψ can be written in a first approximation as a sum of plane waves:

$$\psi(\mathbf{r}) = \sum_{n=1}^{N} A_n \cos(\mathbf{k}_n \cdot \mathbf{x}), \qquad (1)$$

where N is the number of wavevectors (of same modulus $|\mathbf{k}_n| = k_0 = 2\pi/\lambda_0$) characterizing the base pattern (in two spatial dimensions, $N = 3$ for hexagonal

symmetry and $N = 2$ for square symmetry). A perfect crystal is observed when the amplitudes A_n are all equal to a constant A_0. Figures 2 and 3 further show examples of the field ψ in gray scale in 2D (dark regions have $\psi(\mathbf{x}) \geq 0$, bright ones $\psi \leq 0$). We now look for a simple phenomenological isotropic partial differential equation satisfied by ψ. Keeping in mind the analogy with crystals, in addition to the periodicity λ_0, one wishes an equation that *imposes a symmetry* on the stationary solution (for instance hexagonal, $N = 3$). A linear wave equation like $(\Delta + k_0^2)\psi = 0$ is not acceptable as a superposition of any $N \geq 1$ waves would be the solution. Instead, we need to resort to a nonlinear equation, introducing a coupling between the different amplitudes A_n in Eq. (1). We consider here the well-known Swift–Hohenberg model (first introduced in the context of Rayleigh–Bénard convection), which also involve the time variable t:[3]

$$\frac{\partial \psi}{\partial t} = \epsilon \psi - \frac{1}{k_0^4}(k_0^2 + \Delta)^2 \psi + g_2 \psi^2 - \psi^3 \,, \qquad (2)$$

where $\epsilon \ll 1$ is a dimensionless control parameter, the reduced Rayleigh number in convection problems. If $\epsilon \leq 0$ in Eq. (2), $\psi = 0$ is the only stationary solution ($\partial \psi/\partial t = 0$) that is stable. The uniform solution $\psi = 0$ becomes unstable for $\epsilon > 0$. In that case, new solutions with broken symmetries appear, in the form of a periodic pattern characterized by a layer spacing $\lambda_0 = 2\pi/k_0$. The order parameter ψ can be approximated by a sum of the form (1) provided that $\epsilon \ll 1$. Nonlinear terms are responsible for mode combinations: given an arbitrary set of wavevectors $\{\mathbf{k}_n\}$, one can derive equations for their amplitudes A_n, these amplitudes being now coupled to each other. The A_n's happen to have stable non-zero solutions only in a very small number of cases that generally correspond to symmetric, crystal-like arrangements of the $\{\mathbf{k}_n\}$. For instance, Eq. (2) with $g_2 = 0$ leads to stripes formation ($N = 1$). On the other hand, if $g_2 \neq 0$ and $0 < \epsilon < 4g_2^2/3$, only hexagonal solutions are stable.[9]

Let us now point out one of the crucial properties of this type of model: the evolution equation (2) has a *potential structure*. One can associate an "energy" or Liapunov functional F to the system, such that Eq. (2) reads $\partial \psi/\partial t = -\delta F/\delta \psi$ (the right hand side representing a functional derivative). F is given in that case by

$$F = \int d\mathbf{x} \left[-\frac{\epsilon}{2}\psi^2 + \frac{\psi}{2k_0^4}(k_0^2 + \Delta)^2 \psi - g_2 \frac{\psi^3}{3} + \frac{\psi^4}{4} \right]. \qquad (3)$$

It is easy to show from Eq. (2) that $dF/dt \leq 0$: the quantity F always decreases with time. The dynamics is dissipative and converges toward stationary stable solutions that correspond to *local minima* of F in the configuration space. The absolute minimum of F corresponds to a perfectly regular pattern of the form (1), with wavenumber k_0 (a "perfect crystal"). Consider now an immobile grain boundary separating two differently oriented domains that are otherwise in the ground state: near the boundary, it is impossible to preserve the regular crystal structure imposed in the bulk. As a consequence, such a configuration must have a higher F.

One can now see the pattern formation process given by Eq. (2) from an alternate viewpoint, very useful for applications to materials: namely, as an *energy minimization* problem within some constraints. Stationary grain boundaries can be regarded as optimal solutions of a frustration problem of two competing lattices of different orientations. The free-energy functional imposes a fixed *periodicity* on the field ψ in the bulk, minimizing the term $\psi(k_0^2 + \Delta)^2\psi$ in the functional (3), as well as a given bulk *symmetry*, which is fixed by mode combination through the higher order terms. The equations for the amplitudes A_n show that the grain boundary is actually an interference pattern between the two crystals, with amplitudes not constant in space and not equal to each other.

Different choices of nonlinear terms can lead to different crystal symmetries in the bulk. Adding other cubic or higher order terms in the functional (3) generates new nonlinear terms in Eq. (2), modifying the relative coupling constants between the different amplitudes A_n in the solution (1). As a consequence, a crystal formerly unstable may become stable. For instance, a square crystal lattice ($N = 2$) can be obtained by choosing:[10] $F = \int d\mathbf{x}[-(\epsilon/2)\psi^2 + 1/(2k_0^4)\psi(k_0^2 + \Delta)^2\psi - g_2\psi^3/3 + \beta\psi^4/4 + (\gamma/4)\psi^2\Delta^2(\psi^2)]$, with $\beta < 0$ and $\epsilon > 16g_2^2(3\beta + 13\gamma)/(3\beta + 4\gamma)^2$. This free energy gives coefficients that depend on the angle between the wavevectors in the amplitude equations, such that they stabilize solutions with perpendicular wave numbers.

The energy (3) involves a Taylor series expansion of an order parameter, as usual in Ginzburg–Landau descriptions of phase transitions. This simple form suggests that geometrical frustration in crystalline phases with isotropic interactions is likely to have some universal features. Actually, numerical solutions of Eq. (2), or slight variants of it, are able to reproduce known features of crystals. The behavior of the energy F of grain boundaries as a function of misorientation angle follows a Read–Shockley law.[4] In addition, short-range pinning forces act on defects, a phenomenon analogous to the Peierls stress in crystals.[5]

In the following section, we emphasize the close relationships that exist between this pattern formation approach of grain boundaries and some space filling problems under constraints, that have been solved in Ref. 7 by the use of quasi-crystal methods. We briefly recall the main aspects of this second theory below.

3. Structures of Grain Boundaries

3.1. *A geometrical construction*

The main distinctive feature of this theory is that it considers interfaces and quasicrystals as a region in space where two or more interpenetrating crystal lattices compete for space. The final atomic positions are then decided by a modified version of the strip-projection proposed by Katz and Duneau[11,12] to study quasicrystals. Perhaps, the most important attribute of this approach is that it allows interfaces and quasicrystals to be described by the same set of equations, thus rendering them formally equivalent.

Given a completely arbitrary set of lattices and relative orientations the formalism produces ideal (minimum local strain) structures which are expected to play for grain boundaries the same role than the perfect crystal concept plays for crystals, i.e. they define defect free, reference structures analogous to Bravais lattices. Since strain minimization is a physical consideration, the formalism is endowed with a physical basis in spite of its geometrical formulation.

Full details of this method can be found in Ref. 7. Briefly, the crystal lattices are embedded in a higher dimensional space where they define an hyper lattice whose symmetry depends on that of the lattices and their relative orientation. This hyper lattice is then projected back to physical space to produce the actual interfacial structure or quasicrystal.

The higher dimensional $6D$ space is schematically represented in Fig. 1. It is divided in two sets of orthogonal $3D$ subspaces: (V_1, V_2) and $(E^\parallel, E^\perp)$. V_1 and V_2 contain the lattices L_1 and L_2 of the two crystals, and $E^\parallel$, $E^\perp$ contain respectively, the actual interfacial structure and the strain field across the interface. $E^\perp$ is actually the Bollmann's displacement space or b-space.[1]

Only those hyperpoints contained within a small region around $E^\parallel$ (see Fig. 1) called the strip[11,12] are projected. The size of the strip is chosen to include pairs of atoms that occupy incompatible positions, these atoms are then replaced in $E^\parallel$ by a single atom at their average position. Given two interpenetrating lattices in
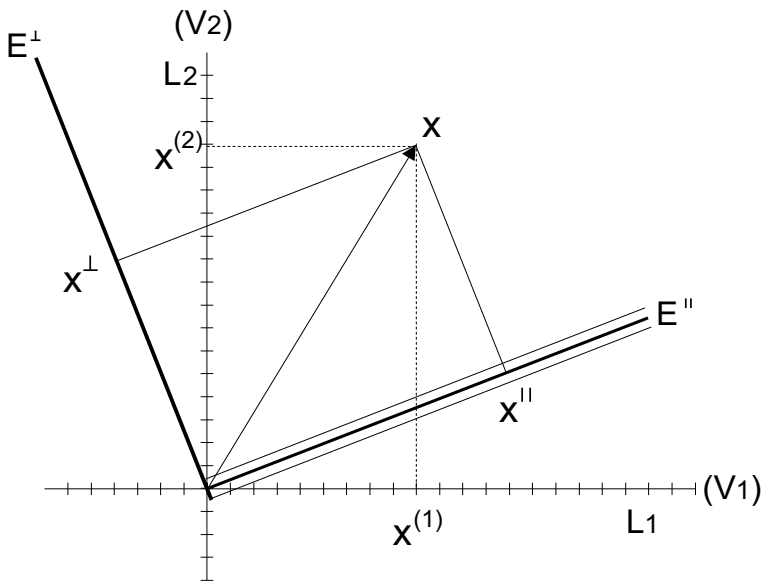

Fig. 1.   Schematic representation of 6D space showing the orthogonal 3d subspaces V_1, V_2, $E^\parallel$, $E^\perp$ as 1D lines. The crystal lattices L_1 and L_2 are respectively contained in V_1, V_2. The interface is defined as the set of points $x^\parallel$ that are projections of the hyperlattice points located inside a small region around $E^\parallel$. This region is called the strip and is delimited by the two thin lines (see text).

physical space, the method constructs an ideal, best fit, minimum strain lattice as the set of points of $E^{\parallel}$. By adopting the average position, atoms at the interface act as a strain buffer between the crystals on each side of the interface. The component in $E^{\perp}$ is a measure of the local strain or frustration between two nearly coincident (overlapping) atoms from each lattice.

This method allows the construction of a complete bicrystal with the parent crystals separated by a unique, fully 3D structure called the interfacial layer (IL), arising from the projection of hyperpoints within the strip. The role of the IL, whose structure is different from that of either crystal is to resolve the positional incompatibilities that occur at the interface. Since grain boundaries are usually 2D, a suitable IL plane (or manifold) must be selected in order to model any particular boundary plane, of given relative orientation to the parent crystals. A bicrystal can then be built by filling the space on either side of the boundary with crystal sites projected from (V_1) and (V_2). Note this approach is unique in that the grain boundary always contains atomic (IL) sites, which makes it susceptible to crystallographic analysis.

We recall now the definition of the O-lattice, a concept that will be useful in the next section. Given two crystal lattices, L_1, L_2 and a transformation $\mathbf{A}$, such that $L_2 = \mathbf{A}L_1$, in the absence of translations, the O-lattice is defined as the set of points $x^{(o)}$ that satisfy

$$(\mathbf{I} - \mathbf{A}^{-1})^{-1}l^{(1)} = x^{(o)} \tag{4}$$

where $\mathbf{I}$ is the identity matrix, and $l^{(1)} \in L_1$. Geometrically, the O-lattice corresponds to points in space (not necessarily lattice points) of minimum strain i.e. the minimum misfit between L_1 and L_2. Another interesting property of the O-lattice is that if $l^{(i)*}$ and $(\mathbf{A}l^{(i)})^*$ with $i = 1, 2, 3$ are the base vectors of the reciprocal lattices of L_1 and L_2 respectively, then

$$(l^{(i)*} - (\mathbf{A}l^{(i)})^*) \cdot x^{(o)} = n \tag{5}$$

with integer n. This equation establishes a relationship between the O-lattice and the Moiré pattern formed by the superposition of L_1 and L_2.

3.2. *Results*

In this section we study symmetric tilt grain boundaries in two-dimensional (2D) crystals. The initial condition $\psi(\mathbf{x}, t = 0)$ in Eq. (2), or its analogue for square patterns, is made of two crystals rotated by θ_{mis}, the interface being directed along the vertical axis (see Ref. 5 for more details). We introduce an angle θ that either corresponds to the misorientation angle θ_{mis} or to $90° - \theta_{mis}$ (for square patterns), depending on the orientation of the symmetric boundary plane. Note that $0 \leq \theta_{mis} \leq 45°$ and $0 \leq \theta \leq 90°$. For each rotation θ_{mis}, there are two possible boundary orientations (with different structure) that lead to a symmetric interface. The angle θ represents the angle formed between two atomic planes that are symmetric with respect to the boundary.
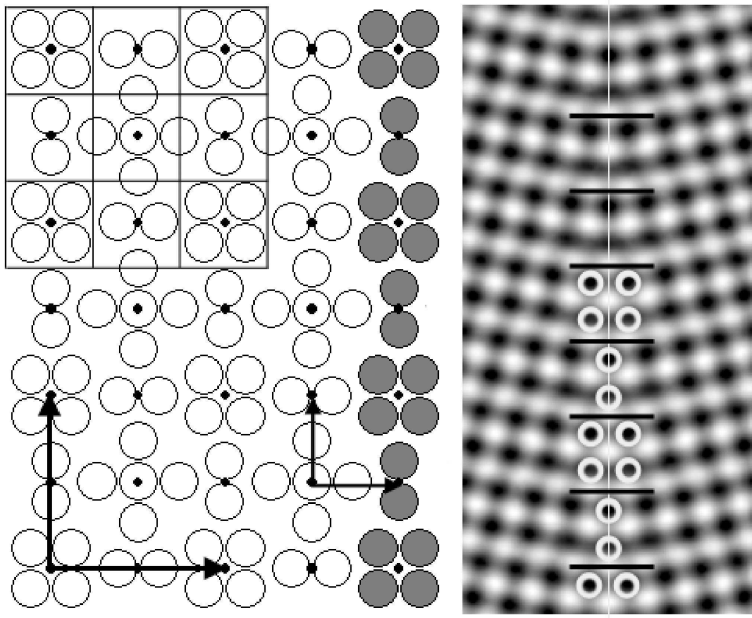
Fig. 2. Singular tilt boundary with $\theta = 28.072°$ ($\Sigma 17$). Right: ψ in gray scale given by the nonlinear model. Left: $E^{\parallel}$ from the construction of Sec. 3.1. See text for legend.

We analyze the stationary (minimum energy) fields obtained at large times by solving Eq. (2) numerically, and compare their structures with those given by the method described in Sec. 3.1.

Figure 2 displays (on the right) a boundary obtained by solving the Swift–Hohenberg equation for square patterns, with an angle $\theta = 2\tan^{-1}(1/n)$, where n is an integer (4 in this case). Such interfaces are singular[7] and characterized by a simple repeating pattern, as emphasized by the bright circles.

In the geometrical method, any grain boundary structure is a 2D manifold (a plane, usually) included in the 3D IL. The most likely manifolds are *a priori* the ones that run along directions that maximize the density of IL sites. Such dense planes must clearly intersect perpendicular IL planes along directions that have also a high density of sites. In the particular case of a tilt boundary configuration, the planes of the IL normal to the tilt boundary constitute the model's prediction for the so called twist boundary. Hence, in the geometrical approach, twist boundaries do provide information about the possible directions that a perpendicular (tilt) boundary may run along. We will hence focus on the structure of twist planes below.

The left part of Fig. 2 shows the twist interface corresponding to the example above, obtained using the approach of Sec. 3.1 for a cubic lattice. It is a plane normal to the $\langle 001 \rangle$ direction in the cubic $(100)/\langle 001 \rangle$ twist interface. As indicated above,

this plane is a map of all the possible transverse conformations (or trajectories) of a tilt grain boundary between two grains of given misorientation angle. A particular trajectory is indicated in gray. Large disks represent atomic positions, or interfacial sites. The short and long arrows indicate the O-lattice (OL) and coincidence sites lattice (CSL) base vectors, respectively. Note that the interface is composed of identical domains centered at O-points (small dots) that are points of zero strain. Atomic domains are separated by a network of primary screw dislocations.[1] The intersection of these dislocations with the boundary plane is highlighted by a square grid in the figure.

The predicted atomic positions (grayed dots) match nearly exactly the (black) regions where ψ is maximum in the nonlinear model. The short horizontal lines on the figure mark the positions of dislocations. These are edge dislocations, with Burger's vectors normal to the boundary line. A similar remarkable agreement was obtained in every case for a variety of angles θ chosen arbitrary, in square and hexagonal symmetries. Non-singular interfaces are characterized by more complicated interfacial patterns (not shown).

Since elastic strain is minimized near O-points, it is expected that tilt interfaces *of low angles* θ tend to run along directions that follow the O-lattice, preserving this way the structure of the domains around the O-points. The O-lattice has the same symmetry as the crystal (see Fig. 2, left), but a distinct period λ_O, given by $\lambda_O = \lambda/[2\sin(\theta/2)]$ independently of the symmetry[7] (λ is the period of the crystal; $\lambda_O > \lambda$ at low angles). Therefore, the grain boundaries separating two symmetric grains along the vertical axis should be located at some discrete x-positions, separated from each other by λ_O (Fig. 2, left). On the other hand, a weakly nonlinear analysis of Eq. (2) allows the derivation of the law of motion of straight grain boundaries.[5] It is found analytically that interfaces feel a pinning potential, periodic along the x-direction. Strikingly, the nonlinear model agrees perfectly with the geometrical construction: The periodicity of the pinning potential is $\lambda/[2\sin(\theta/2)]$ and coincides with λ_O. In the nonlinear model, the derivation of this formula follows from a solubility condition that imposes particular combinations of the modes $\mathbf{k}_n$. The result is formally equivalent to the the formula (5) above. The lines going through points of the O-lattice thus correspond to minima of a pinning potential in the nonlinear model.

Figure 3 (on the right) represents a configuration obtained at time $t = 2000$ from the same nonlinear model, with a *high* angle $\theta = 73.74°$. The initially straight interface quickly destabilizes into a broken-symmetry phase, characterized by facets of short period. This faceting instability is not observed for low θ boundaries, for instance that of $\theta = 90 - 73.74$, the other symmetric boundary orientation in this bicrystal.

The faceted structure is also visible from the geometrical construction of $E^{\parallel}$ (left). In this configuration, a straight tilt grain boundary would run vertically, i.e. along the diagonal of the domains of best fit of size 3 or 4, where the distance
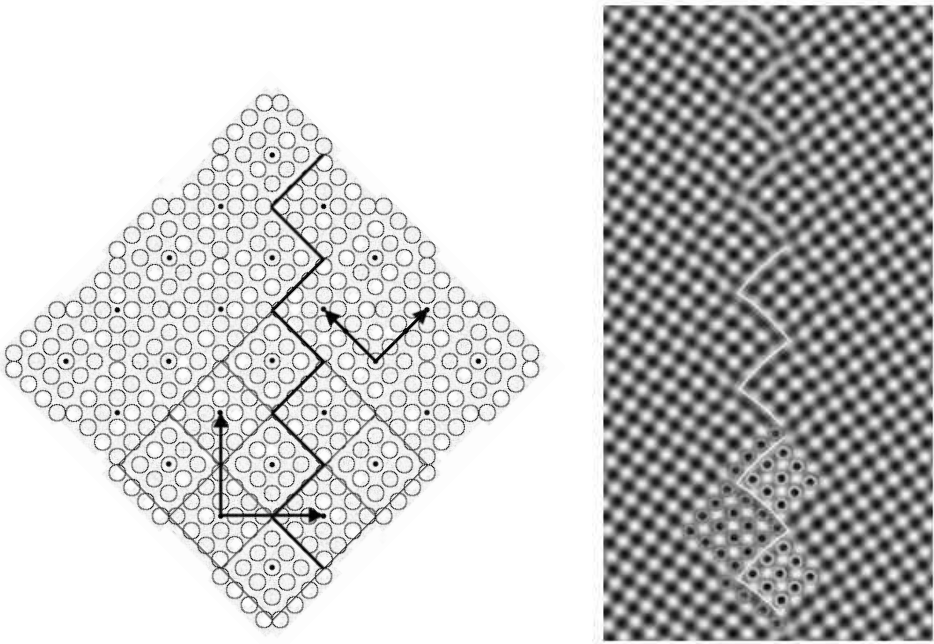
Fig. 3. Facet formation. Right: Nonlinear model with at $\theta = 73.74°$ ($\Sigma25$). Left: Geometrical construction.

between O-points is larger. In order to keep the structure of these domains anyway, the interface becomes faceted instead. It runs along the core lines of the screw dislocation network. In this case, the interface is locally aligned with the Burgers vectors of the dislocations that compose it. Along this line, a repeated structure of 4 atoms facing 3 atoms of the other grain appears, as correctly reproduced by the nonlinear method. Note that the geometrical map of Fig. 3 (left) also contains the structure of symmetric tilt boundaries with the angle $\theta = 90 - 73.74 = 16.26°$. The direction of these interfaces is now inclined of $45°$ with respect to the vertical direction in Fig. 3 (left): the most likely trajectories are straight and run along a line of maximum O-point density (or pinning potential minimum), as confirmed by nonlinear calculations (not shown). If an interface with such an orientation destabilized, it would find it difficult to develop the same "Chinese hat" facets as observed for the other orientation $\theta = 73.74°$. Hence, low θ grain boundaries are probably less likely to facet. In conclusion, when the average orientation of a boundary is not parallel to the O-lattice, the boundary *may* become faceted.

Preliminary numerical results on the nonlinear model for square patterns show that the faceting instability does not occur for misorientation angles lower than a characteristic value $\theta_c \approx 60°$. This value can be interpreted qualitatively as follows: For $\theta \geq \theta_c$, the periodicity of the pinning potential $\lambda/[2\sin(\theta/2)]$ becomes similar to that of the crystal making it easier for the interface to deform under stress.

The configuration of Fig. 3 (right) has a relatively high elastic stress. After a sufficiently long time, it starts to slowly evolve into more complicated patterns, with longer facet lengths in order to relieve the initial stress.

4. Conclusions

We have presented a theory of crystals based on a local order parameter description and general stability and symmetry principles. The theory is well suited for the description of short scale phenomena, in particular the intricate spatial distributions of atoms in grain boundaries. The results compare very well with those given independently by a generic geometrical theory of grain boundaries. The nonlinear nature of the model naturally incorporate some underlying topological structures, such as the O-lattice, which in this theory is interpreted as the set of boundary pinning sites.

Acknowledgments

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