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by

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Abstract

We study the reconstructive phase transformations in crystalline solids (i.e. transformations in which the parent and product lattices have arithmetic symmetry groups admitting no finite supergroup), the best known example of which is the bcc-to-fcc transformation in iron. We first describe the maximal Ericksen-Pitteri neighborhoods in the space of lattice metrics, thereby obtaining a quantitative characterization for weak transformations. Then, focussing for simplicity on a two-dimensional setting, we construct a class of strain-energy functions which admit large strains in their domain and are invariant under the full symmetry group of the lattice; in particular, we give an explicit energy suitable for the square-to-hexagonal reconstructive transformation in planar lattices. We present a numerical scheme based on atomic-scale finite elements and use it to analyze the effects of transformation cycling on a planar crystal, by means of our constitutive function. This example illustrates the main phenomena related to reconstructive phase changes: in particular, the formation of dislocations, vacancies and interstitials in the lattice.

1 Introduction

Reconstructive phase transformations in crystalline materials are characterized by the absence of a finite supergroup for the arithmetic symmetry

groups of the phases involved, as is the case for example in the well-known α-γ transformation in iron and other ferrous materials, which takes a body-centered cubic (bcc) to a face-centered cubic (fcc) structure. The term 'reconstructive' indicates that, at least in typical examples, the crystalline symmetry is initially reduced along the transformation path, (e.g. from bcc to face-centered tetragonal), and then increases when the final state is reached (e.g. from face-centered tetragonal to bcc). Such phase changes are outside the applicability range of the standard Landau theory of phase transitions.

Weak phase changes, in contrast, involve small lattice deformations, and admit a common finite supergroup for the symmetry groups of all the phases involved – see for instance Ericksen (1989). A special case of the latter are the symmetry-breaking transitions, whose phases have symmetry groups that are in a group-subgroup relation. The reconstructive transformations considered here are non-weak, and their properties are in general markedly different from those exhibited by the weak transitions.[1]

The current mathematical understanding of weak phase changes is based on nonlinear elasticity, and the underlying discrete symmetry derives from choosing a suitable finite subgroup within the full symmetry group of the crystal, which, a priori, is infinite and discrete, as was first pointed out by Ericksen (1970, 1977), Parry (1976). This line of thinking, initiated by Ericksen (1980) is compatible with the Laudau theory, and has proved remarkably successful especially in the investigation of symmetry-breaking martensitic transformations, with the related phenomena of twinning and microstructure formation, as they occur for example in shape-memory and magnetostrictive alloys (Ball and James, 1987, 1992, Luskin, 1996, Bhattacharya, 1997, Müller, 1999, James and Hane, 2000, Pitteri and Zanzotto, 2002). The significance and applicability range of the Landau theory have also been clarified by this approach.

A model for reconstructive transformations, however, proves harder to develop than for weak transitions. An explicit characterization of weak vs. reconstructive transformations is actually still missing; furthermore, one main problem is that the invariance of the strain-energy function of a material undergoing a reconstructive phase change is not described by a finite group, for in these cases one must take into account the full (infinite, discrete) symmetry group of the lattice – no choice of finite subgroups will suffice. As a consequence, the relaxed energy of a crystal only depends on the specific volume (Fonseca, 1987), which is a feature typical of fluids, not of solids. The relaxation must thus include slip-like processes and the creation and motion of dislocations, which, as we discuss below, are obtainable within

[1] The literature calls reconstructive also the transformations involving either large lattice distortions, or parent and product phases whose symmetry groups have no inclusion relation (Buerger, 1963, Tolédano and Dmitriev, 1996). The definitions coincide in all the main cases of interest.

a purely elastic framework if the energy density exhibits the full symmetry of the lattice. Finally, it is not clear which explicit functional forms the (unrelaxed) elastic energy density should have in order to exhibit such full lattice symmetry.[2]

These are, broadly, the questions of interest in this paper. To study these problems, we first characterize the domains in which the weak transformations occur; then, restricting ourselves to the two-dimensional case, we write a class of strain-energy functions with full lattice invariance, defined also for the large deformations that are typical of the reconstructive phase changes. We then consider an explicit constitutive function suitable for the square-to-hexagonal (s-h) transformation in planar lattices, and, by investigating numerically the evolution of an initially perfect lattice under repeated transformations, we observe twinning, slip-like processes, dislocations and other defects. These results put in evidence the main differences between the reconstructive and symmetry-breaking phase changes. The latter are often reversible, leading for instance to shape memory in some alloys. On the contrary, a reconstructive transformation may generate defects in the lattice, preventing the reversibility of the process. Such general effects are present both in two and three dimensions; we remark that two-dimensional periodic structures to which our analysis of the s-h transformation may be directly applicable occur in a number of physical systems, such as flux line lattices (Gammel et al., 1999) and vortex lattices (Chang et al., 1998) in superconductors, Wigner crystals in the two-dimensional electron gas (Holz, 1980, Ando et al., 1982), and skyrmion crystals in quantum Hall systems (Rao et al., 1997).

In Sect. 2 we recall some basic facts about the symmetry of two-dimensional (2-d) simple lattices (or 'Bravais lattices'). We introduce the classical action of the group $GL(2, \mathbb{Z})$ of 2 by 2 invertible integral matrices on the space $\mathcal{Q}_2^+$ of 2-d positive-definite quadratic forms (lattice metrics), and recall the ensuing subdivision of planar simple lattices and their metrics into five 'Bravais types'.[3] Following Engel (1986), we also describe the set of 'Lagrange-reduced forms' of lattice metrics, which is a fundamental domain for this action – see Table 1, and Figs. 1–2.

In Sect. 3 we recall a geometric result that introduces the 'Ericksen-Pitteri Neighborhoods' (EPNs) in the space of lattice metrics (see Ericksen,

[2]Other approaches to reconstructive phase transformations have been considered by a number of authors during the last decade; one method involves the extension of the Landau theory based on the adoption of a 'transcendental order-parameter' (see for instance Dmitriev et al., 1988, Horovitz et al., 1989, Tolédano and Dmitriev, 1996, Hatch et al., 2001). Numerically, such phenomena have also been investigated with molecular dynamics, see e.g. Morris and Ho (2001).

[3]The analogous criterion in 3-d produces the well-known fourteen Bravais lattice types. These basic notions of crystallography can be given for any dimension n of the lattices – see for instance Engel (1986), Michel (1995, 2001).

1980, Pitteri, 1984). These regions are used to reduce in a rational way the domain of the energy functions of crystals, so that only finite crystallographic groups describe their invariance, as in the classical theories – see the references above on the elastic modeling of symmetry-breaking transformations in crystals. We then give a procedure (which works in any dimension $n \geq 2$) to construct maximal EPNs, thereby showing in a quantitative way the threshold between weak and non-weak transformations; we discuss some explicit examples of maximal EPNs for $n = 2$ (see Fig. 3).

In Sect. 4 we study a class of $GL(2,\,\mathbb{Z})$-invariant strain-energy functions on $\mathcal{Q}_2^+$ that can model the behavior of planar lattices undergoing reconstructive transformations. We give an explicit energy for the s-h phase change, that in suitable temperature ranges exhibits absolute minimizers with either square or hexagonal symmetry.[4] A proposal for producing $GL(2,\,\mathbb{Z})$-invariant constitutive functions on $\mathcal{Q}_2^+$, based on the use of the classical modular functions on the upper complex half plane, has been given by Parry (1998). Our energies, however, are constructed by 'patching' suitable polynomials of scaled variables, so as to obtain enough smoothness and the desired symmetry. We prefer this elementary method as it is quite straightforward for prescribing the correct minimizers in our model.

In Sect. 5 we present a numerical scheme which incorporates the $GL(2,\mathbb{Z})$-invariant energy, and use it to investigate numerically the effects produced on a lattice by taking it through two s-h-s transformation cycles, starting from a homogeneous configuration with square symmetry. We observe the development of twin bands when the system is transformed into the hexagonal phase (Figs. 6(b) and 6(d)), and the formation of dislocations or vacancies when the system is taken back to the square phase (Figs. 6(c) and 6(e)).

2 Crystallography

2.1 The arithmetic symmetry of simple lattices

A 2-d simple ('Bravais') lattice is an infinite and discrete subset of $\mathbb{R}^2$, given by:

$$\mathcal{L}(\mathbf{e}_a) = \left\{\, \mathbf{v} \in \mathbb{R}^2 \,:\, \mathbf{v} = v^a \mathbf{e}_a,\, v^a \in \mathbb{Z} \,\right\} \tag{1}$$

(hereafter the summation convention is understood). The independent vectors $\mathbf{e}_a$, $a = 1, 2$, are the lattice basis, and the metric (or 'Gram matrix') $C = (C_{ab})$ of $\mathcal{L}$ is

$$C_{ab} = C_{ba} = \mathbf{e}_a \cdot \mathbf{e}_b \quad (1 \leq a, b \leq 2). \tag{2}$$

[4] We notice that the resulting theory is not of the Landau type, as the potential is defined on all of $\mathcal{Q}_2^+$ (that is, also for large strains), and is not invariant under a typical crystallographic group. Its invariance reduces to the latter when the domain is cut down to an EPN. In particular, we remark that, as a consequence of $GL(2,\,\mathbb{Z})$-invariance, the elastic moduli relative to any energy-minimizing configuration exhibit the correct symmetry pertaining to that configuration.

The space $\mathcal{Q}_2^+$ of lattice metrics is the 3-d linear cone collecting all the positive-definite symmetric 2 by 2 real matrices.

Given a Bravais lattice, its basis and metric are not uniquely determined. Two bases $\bar{\mathbf{e}}_a$ and $\mathbf{e}_a$ generate the same lattice if and only if they are related by an invertible integral matrix; for the 2-d case one has:

$$\mathcal{L}(\mathbf{e}_a) = \mathcal{L}(\bar{\mathbf{e}}_a) \quad \Leftrightarrow \quad \bar{\mathbf{e}}_b = m_{ab}\mathbf{e}_a \text{ with } m = (m_{ab}) \in GL(2, \mathbb{Z}), \tag{3}$$

where $GL(2, \mathbb{Z})$ denotes the group of 2 by 2 invertible matrices with integral entries. Since each lattice determines its bases up to a transformation in this group, the latter is said to be the 'global symmetry group' of planar lattices. The change of basis in (3) induces, in obvious notation, the following change of the lattice metric C in (2):

$$\bar{C} = m^t C m, \tag{4}$$

where m^t denotes the transpose of a matrix m. Equation (4) defines a natural action of $GL(2, \mathbb{Z})$ on $\mathcal{Q}_2^+$, which is considered in crystallography for studying the arithmetic symmetry of simple lattices, also in the general case of n dimensions. The 'strata' of the action (4) subdivide the space of metrics (and hence the lattices themselves) into equivalence classes, the well-known 'Bravais types' (see Engel, 1986, Michel, 2001).

Explicitly, if C is the metric of a basis $\mathbf{e}_a$, let their 'lattice group' or 'arithmetic holohedry' be defined as

$$\begin{aligned} L(\mathbf{e}_a) &= \{m \in GL(2, \mathbb{Z}) \,:\, m_{ab}\mathbf{e}_a = Q\mathbf{e}_b,\, Q \in O(2)\} \\ &= \left\{m \in GL(2, \mathbb{Z}) \,:\, m^t C m = C\right\} \\ &= L(C). \end{aligned} \tag{5}$$

This group transforms by conjugacy under a change of basis (3) for the same lattice:

$$L(m_{ab}\mathbf{e}_a) = m^{-1} L(\mathbf{e}_b) m \quad \text{for all} \quad m \in GL(2, \mathbb{Z}); \tag{6}$$

a given lattice $\mathcal{L}(\mathbf{e}_a)$ therefore determines an entire conjugacy class of lattice groups in $GL(2, \mathbb{Z})$. One then defines two lattices $\mathcal{L}$ and $\mathcal{L}'$ as having the same Bravais type when they are associated to the same conjugacy class in $GL(2, \mathbb{Z})$. In an analogous way, one subdivides in Bravais types also the lattice metrics. A classical result in 2-d finds five Bravais lattice types in $\mathcal{Q}_2^+$, denominated *oblique, rectangular, rhombic (or centered-rectangular), hexagonal, and square* – see Theorem 7.8 in Engel (1986), or Michel (1995); see also Table 1.

2.2 A fundamental domain

The question of how to select a representative metric for each orbit in $\mathcal{Q}_2^+$ (that is, for each Bravais lattice), is a natural one that arises also in the

Crystal system (International Symbol)	Lattice type (International Symbol)	Fixed set	Lattice group (up to inversion)
oblique (2)	oblique ($p2$)	$0 < C_{11} < C_{22}$ $0 < C_{12} < \frac{C_{11}}{2}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
rectangular ($2mm$)	rectangular ($p2mm$)	$0 < C_{11} < C_{22}$ $C_{12} = 0$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$
	rhombic or centered–rectangular ($c2mm$)	Fixed set I $0 < C_{11} = C_{22}$ $0 < C_{12} < \frac{C_{11}}{2}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$
		Fixed set II $0 < C_{11} < C_{22}$ $0 < C_{12} = \frac{C_{11}}{2}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 1 \\ 0 & -1 \end{pmatrix}$
square ($4mm$)	square ($p4mm$)	$0 < C_{11} = C_{22}$ $C_{12} = 0$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$
hexagonal ($6mm$)	hexagonal ($p6mm$)	$0 < C_{11} = C_{22}$ $0 < C_{12} = \frac{C_{11}}{2}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 & -1 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 1 \\ -1 & 0 \end{pmatrix}, \begin{pmatrix} -1 & 0 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 1 \\ 0 & -1 \end{pmatrix}, \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$

TABLE 1: The five Bravais types of simple lattices, and the fixed sets (sets of metrics with given lattice group) intersecting the fundamental domain $\mathcal{D}$ in (7), with the corresponding lattice groups (only one element of each pair $(m, -m)$ is tabulated). See also Fig. 1.

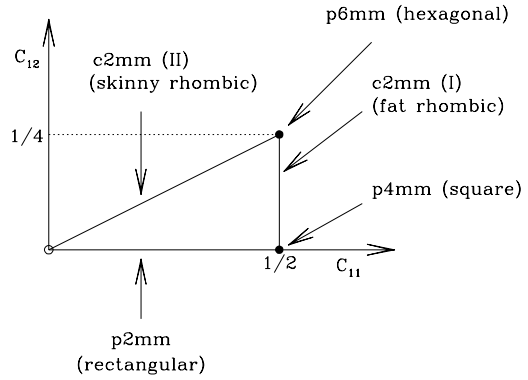


FIGURE 1: A two-dimensional representation of the intersection of the fundamental domain $\mathcal{D}$ in (7) with the plane $C_{11} + C_{22} = 1$, projected on the plane (C_{11}, C_{12}), projected on the plane (C_{11}, C_{12}). The five Bravais lattice types in $\mathcal{Q}_2^+$ are represented in $\mathcal{D}$ as shown (International Symbols are used). See Table 1 for a list of the corresponding lattice groups. Unlike the other four lattice types, the rhombic (or centered-rectangular) type is represented in $\mathcal{D}$ by two sets of metrics ('fat' and 'skinny' rhombi – see Footnote 8) with two distinct but arithmetically equivalent lattice groups. Details are given in Sect. 2.2 and Sect. 3.2.

arithmetic reduction of real quadratic forms, initiated by Lagrange and later pursued by many others, among whom Dirichlet, Jordan, Seeber. A 'fundamental domain' for the action (4) is a subset of $\mathcal{Q}_2^+$ such that each $GL(2,\,\mathbb{Z})$-orbit in $\mathcal{Q}_2^+$ has one and only one element in that subset. A simply connected fundamental domain in 2-d is the following:[5]

$$\mathcal{D} = \left\{ C \in \mathcal{Q}_2^+, \quad 0 < C_{11} \leq C_{22}, \quad 0 \leq C_{12} \leq \frac{C_{11}}{2} \right\}, \tag{7}$$

whose metrics are said to have the 'reduced form of Lagrange' (see Engel, 1986, Michel, 1995).[6] A representation of $\mathcal{D}$ is given in Fig. 1.

Given an arbitrary basis $\mathbf{e}_a$, the unique basis conjugate to it with metric in the fundamental domain $\mathcal{D}$ can be obtained in finitely many steps by iterating the following procedure: (i) if $|\mathbf{e}_1| \geq |\mathbf{e}_2|$, swap the two vectors; (ii) if $\mathbf{e}_1 \cdot \mathbf{e}_2 \leq 0$, change sign to $\mathbf{e}_2$; (iii) if $\mathbf{f} = \mathbf{e}_1 - \mathbf{e}_2$ is shorter than $\mathbf{e}_2$, replace $\mathbf{e}_2$ with $\mathbf{f}$. It is straightforward to restate the same procedure in terms of

[5]Fundamental domains have been explicitly described also in the 3-d case, see for instance Schwarzenberger (1972), Engel (1986), Terras (1988).

[6]Given any simple lattice $\mathcal{L}(\mathbf{e}_a)$, the definition in (7) corresponds to choosing a suitable 'reduced' basis $\bar{\mathbf{e}}_a$ for it, as follows: $\bar{\mathbf{e}}_1$ is a shortest lattice vector, $\bar{\mathbf{e}}_2$ is a shortest lattice vector non-collinear with $\bar{\mathbf{e}}_1$, with the sign chosen so that the angle between the two is acute. This basis always exists and is unique up to an inessential orthogonal transformation, so that its metric $\bar{C}$ is unique.

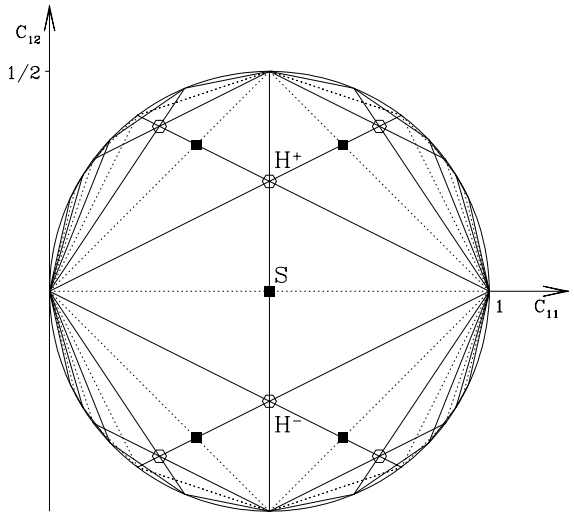


FIGURE 2: Section on the plane $C_{11} + C_{22} = 1$ of the space $\mathcal{Q}_2^+$ (with coordinates C_{11}, C_{12}), taken from Michel (1995). The $GL(2, \mathbb{Z})$-related copies of the fundamental domain $\mathcal{D}$ in Fig. 1 fill $\mathcal{Q}_2^+$. The full squares and empty hexagons indicate a few metrics with square and hexagonal symmetry, respectively. The dotted lines represent the rectangular metrics, the solid lines the rhombic metrics. The dense open set of the other points represents the generic (oblique) lattice metrics.

the lattice metrics, and check that it always converges to $\mathcal{D}$.[7] The fundamental domain $\mathcal{D}$ in (7) is subdivided into six subsets, the metrics in each of which are stabilized by six distinct lattice groups, as in (5); see Fig. 1 and Table 1. One obtains six subsets for five lattice types because the rhombic (or centered-rectangular) lattice type is represented by two distinct sets of Lagrange-reduced metrics, having two distinct (but arithmetically equivalent) lattice groups.[8] The fundamental domain $\mathcal{D}$ and its symmetry-related copies $m^t \mathcal{D} m$, $m \in GL(2, \mathbb{Z})$, cover the entire space $\mathcal{Q}_2^+$, as represented in Fig. 2. In the case of 3-d lattices, the explicit information of how the (six-dimensional) space of metrics is decomposed into copies of the fundamental domain does not seem to be available.

[7] Analogous, more complex, reduction schemes, due to Seeber, Selling, Niggli, Minkowski, exist also for the 3-d case – see Engel (1986).

[8] Geometrically, this happens because the unit cell of a rhombic lattice can be of two different kinds: (i) a 'skinny' rhombus, one of whose angles is smaller than 60 degrees, so that a diagonal is shorter than the side; (ii) a 'fat' rhombus, with angles all between 60 and 120 degrees, whose diagonals are both longer than the side. The Lagrange reduction inequalities (7) then select a reduced basis constituted by two side vectors for the 'fat' rhombi, and by a diagonal and a side for the 'skinny' ones. The intersection of these two sets of rhombic metrics gives the set of hexagonal metrics in $\mathcal{D}$, see Fig. 1.

3 Global and local symmetries of simple lattices

3.1 Ericksen-Pitteri neighborhoods (EPNs)

In Sect. 2 we have seen how the the action (4) of the group $GL(2, \mathbb{Z})$ on the space of lattice metrics $\mathcal{Q}_2^+$ describes the global symmetry of planar lattices. In this section we recall a result showing how such global symmetry reduces to the classical one given by the usual 2-d crystallographic groups. Indeed, within suitable 'Ericksen-Pitteri neighborhoods' (EPNs) in $\mathcal{Q}_2^+$ one needs only consider the action and invariance given by appropriate lattice (sub)groups of $GL(2, \mathbb{Z})$ as in (5). We remark that the notion of EPN holds in any dimension n.

Given any lattice metric C_0, an open neighborhood $\mathcal{N}$ of C_0 in $\mathcal{Q}_2^+$ is an EPN if the following properties hold:[9]

(i) for all $m \in L(C_0)$, $C \in \mathcal{N}$ implies $m^t C m \in \mathcal{N}$;

(ii) if C and $m^t C m$ are in $\mathcal{N}$, with $m \in GL(2, \mathbb{Z})$, then $m \in L(C_0)$.

Every $C_0 \in \mathcal{Q}_2^+$ has a nonempty EPN, see Pitteri (1984), Ball and James (1992). See also Duistermaat and Kolk (1999) for a general treatment of 'slices' of group actions. Pitteri and Zanzotto (2002) give a description of the local structure of the EPNs in (2- and) 3-d. As the metrics in an EPN are at most as symmetric as the 'center' metric C_0, these neighborhoods are the natural domains on which one analyzes symmetry-breaking transformations involving finite but not 'too large' lattice distortions, as in the literature mentioned in the Introduction. Indeed, the EPNs help formalizing the notion of a weak transformation, which is defined as a phase change completely taking place within one such neighborhood (Ericksen, 1989). As the metrics of the initial, final, and any intermediate states, belong to a single EPN, their symmetry groups are all included in the symmetry group of the neighborhood's center. Reconstructive transformations, in our definition, are necessarily non-weak.

3.2 Maximal EPNs

The above-mentioned existence results about EPNs do not give a quantitative measure for weak transitions. Typical examples of non-weak transitions are the (reconstructive) s-h or the bcc-fcc transformations, which both involve maximal lattice groups (i.e. not contained in any other lattice group in 2-d and 3-d, respectively). In general, however, one must know how large

[9] Equivalently:

(i) $m^t \mathcal{N} m = \mathcal{N}$ for all $m \in L(C_0)$;

(ii) $m^t \mathcal{N} m \cap \mathcal{N} = \emptyset$ for all $m \in GL(2, \mathbb{Z}) \setminus L(C_0)$.

the EPNs are in order to have an explicit criterion to differentiate between weak and non-weak phase changes. In this section we describe how, given a 'good enough' fundamental domain, one can construct maximal EPNs, that is, open EPNs not strictly contained in any other open EPN (this method works for any dimension $n \geq 2$).

Proposition 1. *Let $\mathcal{D}$ be a fundamental domain whose boundary has measure zero – as for instance in (7) –, and fix a metric $C_0 \in \mathcal{D}$. Let*

$$\Omega = \left\{ m^t C m : m \in L(C_0),\ C \in \mathcal{D} \right\}. \tag{8}$$

Then, the inner part Ω_0 of the set Ω is a maximal EPN of C_0.

We observe that every orbit has (at least) a representative in the closure of the maximal EPN Ω_0 considered in the Proposition. This representative is in general not unique, as each orbit in $\mathcal{Q}_2^+$ must have as many elements in an EPN $\mathcal{N}(C_0)$ as is dictated by the local symmetry given the lattice group $L(C_0)$ of the center C_0. On the other hand, it is clear that not every orbit can have a representative in Ω_0, as, for instance, the square and hexagonal metrics have symmetry groups with no finite common supergroup.

To prove Proposition 1, we first give two lemmas. In the following we denote by $m \circ C = m^t C m$ the natural action of $GL(n, \mathbb{Z})$ on $\mathcal{Q}_n^+$.

Lemma 1. *Given a metric C and a neighborhood I of C, there is an EPN of C contained in I.*

Proof. Let N be an EPN of C. The required set is

$$N \cap \bigcap_{m \in L(C)} \{ m \circ C :\ C \in I \}\ . \tag{9}$$

Lemma 2. *Let Ω be as in the statement of Proposition 1. If C, $C' \in \Omega$, with $C' = m \circ C$ for some $m \in GL(n, \mathbb{Z})$, then*

$$m \in L(C_0) L(C)\,. \tag{10}$$

Proof. By definition there are $\bar{m}$, $\bar{m}' \in L(C_0)$ such that $C = \bar{m} \circ \bar{C}$ and $C' = \bar{m}' \circ \bar{C}'$, with $\bar{C}, \bar{C}' \in \mathcal{D}$. The condition $C' = m \circ C$ becomes $\bar{C}' = ((\bar{m}')^{-1}\, m\, \bar{m}) \circ \bar{C}$, which by definition of $\mathcal{D}$ implies $\bar{C}' = \bar{C}$. Then we get $C' = \bar{m}'\, \bar{m}^{-1} \circ C$, which together with $C' = m \circ C$ gives the thesis.

Proof of Proposition 1. We first show that Ω_0 is an EPN of C_0. The first property of the EPNs (invariance under $L(C_0)$) is obvious. To verify the second one, let C, $C' \in \Omega_0$, with $C' = m \circ C$. If $L(C) \leq L(C_0)$, by Lemma 2 the thesis is verified. Otherwise, choose $\tilde{m} \in L(C) \setminus L(C_0)$, and let I be an EPN of C contained in Ω_0 (Lemma 1). We now choose in I a metric $\tilde{C}$

whose lattice group $L(\tilde{C})$ is minimal (i.e. for all $C'' \in \mathcal{Q}_n^+$, $L(\tilde{C}) \leq L(C'')$). Consider now $\tilde{C}$, $\tilde{m} \circ \tilde{C} \in I \subset \Omega$. By Lemma 2 we have

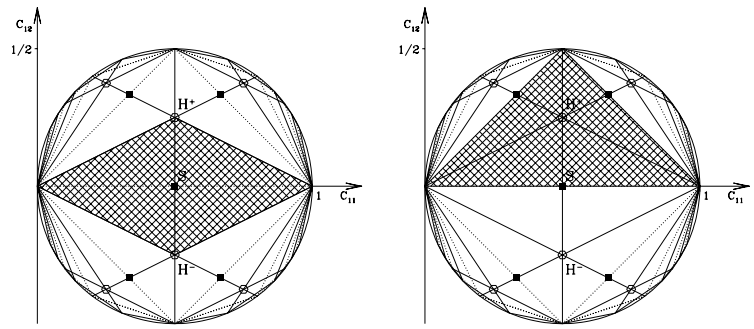
$$\tilde{m} \in L(C_0)L(\tilde{C}) = L(C_0), \tag{11}$$

which is a contradiction. It remains to show that Ω_0 is maximal. If not, there would be an open EPN Ω_1 which strictly contains Ω_0. Since Ω_1 contains at most finitely many copies of each metric (at most as many as is the cardinality of $L(C_0)$), copies of the boundary of $\mathcal{D}$ can cover only a zero-measure subset of $\Omega_1 \setminus \Omega_0$. Hence we can find C' with minimal symmetry in the interior of $\mathcal{D}$ and $m \in GL(2,\mathbb{Z})$ such that $m \circ C' \in \Omega_1 \setminus \Omega_0$. Since C' is in Ω_0 and $m \circ C'$ is not, m cannot be in $L(C_0)$. But since C' and $m \circ C'$ are both in Ω_1, m must be in $L(C_0)$. This gives the required contradiction and concludes the proof.

To give some explicit examples in 2-d, we represent any C belonging to the cone $\mathcal{Q}_2^+$ by means of the three coordinates C_{11}, C_{12}, C_{22}, with $C_{ii} > 0$ and $C_{12}^2 < C_{11}C_{22}$. Then, considering only the plane $C_{11} + C_{22} = 1$ (with coordinates C_{11} and C_{12}, $0 < C_{11} < 1$ and $|C_{12}| < C_{11}^{1/2}(1 - C_{11})^{1/2}$), amounts to giving the elements of $\mathcal{Q}_2^+$ up to a rescaling, which we will no longer mention in the rest of this section. On this plane, the trace of the fundamental domain $\mathcal{D}$ in (7) – still called $\mathcal{D}$ for simplicity – has a particularly simple form: it is the triangle with vertices $S = (1/2, 0)$, $H^+ = (1/2, 1/4)$, and $(0, 0)$, the latter not being included in $\mathcal{D}$ – see Fig. 1. The trace of $\mathcal{Q}_2^+$ on the plane $C_{11} + C_{22} = 1$ is covered by copies of $\mathcal{D}$ obtained by means of the action (4), as shown in Fig. 2.

Now, it is straightforward to describe some maximal neighborhoods in $\mathcal{Q}_2^+$. A maximal EPN for the square metric $S = (1/2, 0)$ is the open rhombus centered on S, composed by the four copies of $\mathcal{D}$ obtained through the action of the lattice group $L(S)$ on $\mathcal{D}$ (see Table 1 for a list of the elements in $L(S)$). As shown in Fig. 3(a), there are two distinct hexagonal metrics on the boundary of this maximal EPN. Analogously, for the hexagonal metric $H^+ = (1/2, 1/4)$ a maximal EPN is an open triangle containing six copies of $\mathcal{D}$, with three distinct square metrics on its boundary – see Fig. 3(b). For an oblique metric a maximal EPN coincides with the inner part of (the appropriate copy of) $\mathcal{D}$; for a rhombic or rectangular metric, a maximal EPN is composed by the two copies of $\mathcal{D}$ whose common boundary contains the given metric.

It is instructive to consider in this picture the phase transformations of a lattice. For instance, a (weak) square-to-rhombic transition involves the parent square metric $S = (1/2, 0)$ and two product rhombic metrics $R^{\pm} = (1/2, \pm r)$, with $0 < r < 1/4$; the choices $\pm$ correspond to the two rhombic metrics ('variants') that exist in an EPN of S, which belong to the same $L(S)$-orbit. In the homogeneous configuration with metric S the basis vectors of the lattice are orthogonal: $r = \mathbf{e}_1 \cdot \mathbf{e}_2 = 0$; when the lattice is



(a) (b)

FIGURE 3: Examples of maximal EPNs in $\mathcal{Q}_2^+$, indicated as dashed areas. (a) Maximal EPN for a square lattice metric, and (b) for a hexagonal lattice metric. See Sect. 3.2 for details.

transformed to one of the configurations with metrics $R^{\pm}$, the distortion breaks the orthogonality relation $r = 0$, but leaves the basis vectors of equal length. This transformation is weak as for not too-large r the metrics involved do not exit from the maximal EPN of S constructed above (twinning arises when the lattice deforms in a piecewise linear fashion to a configuration involving both the variants $R^{\pm}$). If the system is made to transform back to the square phase, it is reasonable to assume that it will all go back to the metric S, due to strong energy barriers in the direction of any other square metric, which are 'far-away' from (that is, they are not in any EPN containing) the metrics S, $R^{\pm}$. This reasoning is the basis of the mathematical theory of the shape-memory effect – see the literature quoted in the Introduction.

If, on the other hand, the homogeneous lattice configuration is transformed from S to one or both of the variants $H^{\pm} = (1/2, \pm r)$, with $r = 1/4$, the strain is so large that the deformed system with metric H^+ has actually gained full hexagonal symmetry: we have a reconstructive transformation (which cannot be weak because the metrics S, $H^{\pm}$ cannot all belong to a single EPN). Also in this case there can be twinning and the formation of microstructure in the transformed lattice, as its cells may find themselves either in the variant H^+ or H^- (see Fig. 3(a)). However, things differ considerably from the weak case on going back to the square phase. In this instance, neglecting elastic interactions, the cells in the configuration H^+ have in principle equal chances of going to any of the three neighboring square metrics $S_1 = S = (1/2, 0)$, $S_2 = (1/3, 1/3)$ or $S_3 = (2/3, 1/3)$; likewise for H^- (Fig. 3(b)). In a large-enough lattice one expects that all these five square choices may be present in different parts of the crystal. Transformation cycling can thus have the result of moving different parts of the

sample from S_1 to four other square metrics. This generates defects which can be either localized (interstitials, vacancies) or long-range (dislocations). An energetic model for these effects is presented and discussed in the rest of this paper.

4 Elastic potentials for reconstructive phase changes and the square-to-hexagonal transformation

The free energy ϕ of a lattice per unit mass depends on the basis vectors $\mathbf{e}_a$, and due to Euclidean invariance, it actually depends only on their inner products, that is, on the lattice metric C, besides the temperature θ:

$$\phi = \phi(C, \theta). \tag{12}$$

From the discussion in the preceding section, we see that the phenomenological description of reconstructive transformations in (2-d) crystals entails energies ϕ whose domain in $\mathcal{Q}_2^+$ is large enough to contain metrics not all belonging to a single EPN. These state functions also ought to identify the different basis representations of the same lattice, so that, in the 2-d case, their invariance should be dictated by the action (4) of $GL(2, \mathbb{Z})$:

$$\phi(C, \theta) = \phi(m^t C m, \theta) \tag{13}$$

for all θ, all C, and all $m \in GL(2, \mathbb{Z})$. This invariance requirement is achieved by setting

$$\phi(C, \theta) = \phi_0(C_R, \theta)\,, \tag{14}$$

where ϕ_0 is a function defined on the fundamental domain $\mathcal{D}$ in (7), and, for any $C \in \mathcal{Q}_2^+$, $C_R \in \mathcal{D}$ is the corresponding Lagrange-reduced form obtained as discussed in Sect. 2.2. One may choose any parametrization of ϕ_0 in (14) – e.g. Fourier coefficients, polynomial expansions, etc. –, but in order to ensure suitable regularity of ϕ one needs to impose appropriate conditions on the boundary of $\mathcal{D}$, as discussed for instance by Parry (1976).

This procedure is simplified if one starts from a maximal EPN, as smoothness on most of the boundary of $\mathcal{D}$ is then a consequence of the symmetry with respect to the lattice group of the center. In the following we require the continuity of the first and second derivatives of ϕ, which makes the elastic moduli of the lattice continuous. Since the determinant is invariant under $GL(2, \mathbb{Z})$, one can decouple the volumetric and the shape-dependent parts of the energy by using scaled variables, i.e. writing ϕ_0 as a function of $\det C$ and $C/\det^{1/2} C$. We will do so in our model, and assume the dependence on the latter variables to be polynomial.

We start by studying polynomials in the three variables C_{11}, C_{12}, C_{22}, with $C_{ii} > 0$ and $C_{12}^2 < C_{11}C_{22}$ as in Sect. 3.2 (no planar section of $\mathcal{Q}_2^+$

is taken here). We first focus on a maximal EPN $\mathcal{N}(\bar{H}^+)$ of the unimodular hexagonal metric $\bar{H}^+ = (1, 1/2, 1)$, whose lattice group $L(\bar{H}^+)$ is the hexagonal group in Table 1. A polynomial in C is invariant under $L(\bar{H}^+)$ if and only if it can be written as a polynomial in the following hexagonal invariants (see Smith and Rivlin, 1958):

$$\begin{aligned} I_1 &= \frac{1}{3}(C_{11} + C_{22} - C_{12}), \\ I_2 &= \frac{1}{4}(C_{11} - C_{22})^2 + \frac{1}{12}(C_{11} + C_{22} - 4C_{12})^2, \\ I_3 &= (C_{11} - C_{22})^2(C_{11} + C_{22} - 4C_{12}) - \frac{1}{9}(C_{11} + C_{22} - 4C_{12})^3 . \end{aligned} \tag{15}$$

Then, let $\phi_1(C)$ be a generic sixth-order polynomial for $C \in \mathcal{D}$, expressed in terms of the I's, and define $\phi(C)$ outside of $\mathcal{D}$ by $GL(2,\mathbb{Z})$-symmetry as in (14). As the same polynomial form is retained in all of $\mathcal{N}(\bar{H}^+)$, we only need to impose C^2 smoothness on the $C_{12} = 0$ boundary (see Fig. 3 (b)). The extension through the latter is generated by a reflection, hence we need to require C^2 smoothness for $\phi_1(C_{11}, |C_{12}|, C_{22})$ around $C_{12} = 0$. This is equivalent to

$$\left.\frac{\partial \phi_1}{\partial C_{12}}\right|_{C_{12}=0} = 0, \tag{16}$$

as the second derivative is automatically continuous. By imposing (16) to the sixth-order polynomial ϕ_1, we obtain a 10-dimensional linear space, for which, as $\det C$ is $GL(2,\mathbb{Z})$-invariant, three basis vectors are trivially given by the determinant, its square and cube. The remaining basis vectors are, for instance:

$$\begin{aligned} \psi_1 &= {I_1}^4 I_2 - \frac{41\,{I_2}^3}{99} + \frac{7\, I_1 I_2 I_3}{66} + \frac{{I_3}^2}{1056}, \\ \psi_2 &= {I_1}^2 {I_2}^2 - \frac{65\,{I_2}^3}{99} + \frac{I_1 I_2 I_3}{11} + \frac{{I_3}^2}{264}, \\ \psi_3 &= \frac{4\,{I_2}^3}{11} + {I_1}^3 I_3 - \frac{8\, I_1 I_2 I_3}{11} + \frac{17\,{I_3}^2}{528}, \\ \psi_4 &= \frac{9\,{I_1}^5}{2} - 4\,{I_1}^3 I_2 + I_1 {I_2}^2 - \frac{I_2 I_3}{48}, \\ \psi_5 &= 48\,{I_1}^5 - 24\,{I_1}^3 I_2 + {I_1}^2 I_3, \\ \psi_6 &= 21\,{I_1}^4 - 5\,{I_2}^2 + I_1 I_3, \\ \psi_7 &= -\frac{5\,{I_1}^3}{2} + I_1 I_2 - \frac{I_3}{48}, \end{aligned} \tag{17}$$

where the I's are expressed in terms of C as in (15). The general sixth-order polynomial ϕ_1 in C meeting (16) can thus be written as a linear combination of the above-mentioned ten basis vectors.

We can use this result to obtain energies ϕ_0 which are polynomials in the scaled variables $C/\det^{1/2} C$, and have a generic dependency on $\det C$. Indeed, since the ψ_i are homogeneous the scaling of C with respect to $\det C$ gives a factor that we can incorporate into the coefficient. We obtain:

$$\phi_0(C) = h(\det C) + \sum_{i=1}^{7} \beta_i(\det C)\psi_i\left(\frac{C}{\det^{1/2} C}\right), \tag{18}$$

which still satisfies (16) and hence can be extended with C^2 smoothness to $\mathcal{Q}_2^+$. In particular, for constant coefficients β_i the above energy function ϕ_0 completely decouples into the sum of a volumetric term and a deviatoric one.

In order to obtain a model energy for the s-h (first-order) transformation, we seek numerical values of β_i in (18) such that the global minimum is always either the square or the hexagonal state, and when changing a parameter, the system goes through the following three regimes: (i) the square state is the minimum, and the hexagonal is unstable; (ii) both the square and the hexagonal states are local minima; (iii) the hexagonal is the minimum, and the square is unstable (see Fig. 4). This leads to an underdetermined set of restrictions on the coefficients β_i, which are met for instance by choosing $\beta_3 = 1$, $\beta_2 = \beta_4 = \beta_5 = \beta_6 = \beta_7 = 0$, and $-1/4 \leq \beta_1 \leq 4$. The parameter β_1 now plays the role of 'temperature', hence we call it θ in the final form of our energy:

$$\phi_0(C, \theta) = \theta\psi_1\left(\frac{C}{\det^{1/2} C}\right) + \psi_3\left(\frac{C}{\det^{1/2} C}\right) + (\det C - 1)^2, \tag{19}$$

where the volumetric part has been taken to be quadratic. It is straightforward to verify that due to the $GL(2, \mathbb{Z})$-invariance of ϕ, the elastic moduli of the square and hexagonal energy minimizers, have square and hexagonal symmetry, respectively.

5 Transformation cycles: dislocations and plasticity phenomena

Some numerical examples illustrate how this model is useful in the study of reconstructive transformations in a planar crystal, with the associated phenomena of microstructure and dislocation formation. We take as reference a portion of the simple lattice (1), and assume its strain-energy density to be as in (19). The numerical approach we use for computing the total energy of any deformation of the reference lattice is based on a set of atomic coordinates, from which the deformation gradient is constructed using linear finite elements. Precisely, let $\{\mathbf{r}_i\}_{i=1\ldots N}$ be the position vectors of the N atoms considered. The lattice is first subdivided into triangles, with vertices

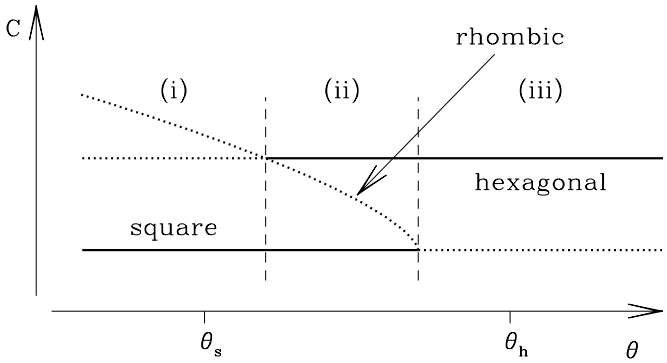


FIGURE 4: Bifurcation for the energy (19): dotted and solid lines indicate unstable and stable critical points respectively. The bifurcation between the square and rhombic critical points is transverse in our C^2 energy, but would be the usual pitchfork for C^3 and smoother energies. The other bifurcation is generically 'transcritical' (i.e. transverse). The pattern shown here repeats itself according to $GL(2,\mathbb{Z})$-symmetry, so that three [two] rhombic branches meet each hexagonal [square] branch at the bifurcation point.

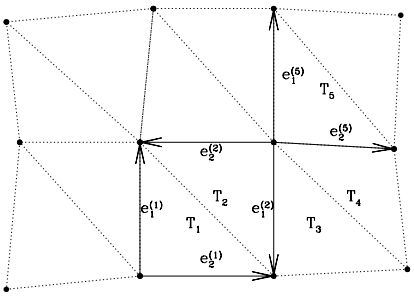


FIGURE 5: Decomposition of the crystal in triangles, and construction of the basis vectors used in the numerical computations (see Sect. 5).

on the atoms; for example, the triangle T_k has vertices $(\mathbf{r}_{\alpha_k}, \mathbf{r}_{\beta_k}, \mathbf{r}_{\gamma_k})$. (The topology of this decomposition remains fixed during the computation.) In each triangle T_k the deformation $\mathbf{u}_k$ is defined by means of the linear interpolation between the positions of the vertices. The corresponding basis vectors are given by

$$\mathbf{e}_1^{(k)} = \mathbf{r}_{\beta_k} - \mathbf{r}_{\alpha_k}, \qquad \mathbf{e}_2^{(k)} = \mathbf{r}_{\gamma_k} - \mathbf{r}_{\alpha_k}, \tag{20}$$

and $C_{ij}^{(k)} = \mathbf{e}_i^{(k)} \cdot \mathbf{e}_j^{(k)}$, for $i, j = 1, 2$ (see Fig. 5). The energy density at temperature θ is then given by $\phi(C^{(k)}, \theta)$ in each triangle, and the total energy is obtained as a Riemann sum over the triangles in the reference

configuration.[10] The invariance properties of the energy guarantee that any permutation of $\{\alpha_k, \beta_k, \gamma_k\}$ in (20) will not change $\phi(C^{(k)}, \theta)$, and that any subdivision of a Bravais lattice will also produce the same energy.[11] The gradient of the energy with respect to the atomic positions can be computed analytically, but its explicit expression is rather cumbersome and is not given here. Our code is then based on a mixture of gradient flow and random displacements. More precisely, we perform gradient flow, and periodically displace randomly all atoms by a small fraction (around 2%) of the atomic spacing, to accelerate the exploration of the phase space. Note that the model on which our code is based on nonlinear elasticity, and thus markedly different from the pair-potential or embedded-atom models typical of numerical investigations of analogous phenomena performed with molecular dynamics (see, e.g., Morris and Ho, 2001).

By using this method, we now observe the quasistatic evolution of the lattice through two s-h transformation cycles. We start at $\theta = \theta_s = -0.2$, with the crystal in a homogeneous square configuration, which realizes a (homogeneous) minimizer of the energy functional, as in Fig. 6(a). Fig. 6(b) shows a state obtained by computing with the hexagonal energy ($\theta = \theta_h = 3.5$) starting from (a). We observe the formation of a twinned microstructure involving two hexagonal variants and two different lamination directions (the ground state would involve only one such direction). In Fig. 6(c) the crystal is brought back to the square phase, by computing with $\theta = \theta_s$ starting from (c). Here we observe the formation of several defects: a dislocation in the lower-right part of the crystal, and a bulk and a surface interstitial in the upper-right part. In Fig. 6(d) we show the result obtained by starting a second transformation cycle from (c), with the hexagonal energy. Again, we observe different twinned microstructures in different parts of the sample, and some strains arising from kinematic incompatibility. Finally, Fig. 6(d) shows the end of the second cycle, in which the sample accumulates defects in the square phase.

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[10] In agreement with ideas by Ericksen (1997, 1999), Friesecke and Theil (2002), our total energy computation for the crystalline body makes no assumptions relating atomic movements to macroscopic deformations, such as the 'Cauchy-Born hypothesis' (Ericksen, 1984, Zanzotto, 1992, 1996).

[11] By the same invariance there is here no need for relabeling, or equivalently for dynamic neighbor lists. This is the reason why we can keep the topology of the grid fixed during the transformation.

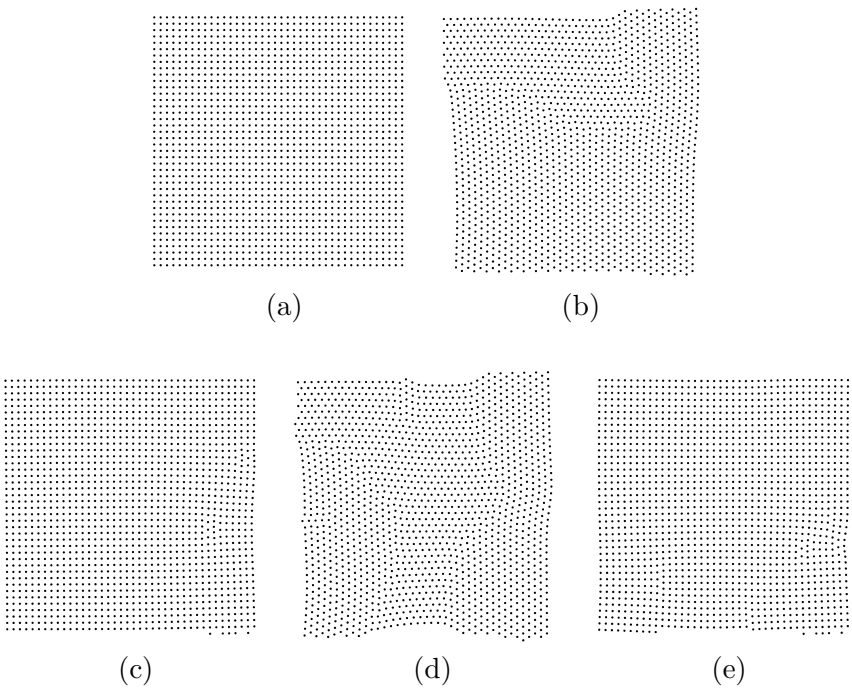

FIGURE 6: Positions of the atoms in the numerical computation described in Sect. 5. (a) The initial square configuration. (b) A state obtained by evolving with the hexagonal energy ($\theta = \theta_h$) starting from (a). (c) The result of evolution with $\theta = \theta_s$, starting from (b). (d) The result of evolution with $\theta = \theta_h$, starting from (c). (e) The result of evolution with $\theta = \theta_s$, starting from (d).

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