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A superspace description for the morphology of quasicrystals
I. The Fibonacci chain of atoms

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ABSTRACT

An approach to determine the equilibrium morphology of quasicrystals by using a superspace embedding is investigated. We discuss the case of the Fibonacci chain of atoms, a one-dimensional structure that can be regarded both as a quasicrystal and as an incommensurately modulated crystal. Consequently, two different ways can be followed to find the equilibrium form. The results indicate that the description as a quasicrystal deals with the symmetry of the model in a more natural way. An analogous method is applied to the case of the two-dimensional octagonal quasicrystal. It is shown that the number of bonds cut by a crystallographic face depends on its position in both the one- and the two-dimensional case.

§ 1. INTRODUCTION

A common feature of classical crystals is their lattice translational symmetry in three independent directions. It can be described by a lattice spanned by three vectors \( \mathbf{a}_1, \mathbf{a}_2 \), and \( \mathbf{a}_3 \). For several decades, however, incommensurate crystal phases have been known as well (Janssen and Janner 1987 and references therein). These phases show long-range order, but unlike the classical crystals, there is no three-dimensional lattice periodicity. The class of incommensurate crystals includes the quasicrystals. In a first approximation, quasicrystals can be characterized as quasi-periodic space-filling patterns built from two or more structural units (Janssen and Janner 1987). Their X-ray diffraction patterns have symmetries that are not compatible with lattice periodicity in three dimensions. Five-, eight-, ten- and twelve-fold rotational symmetries have been observed. A detailed survey has been given elsewhere (Steurer 1990). These typical symmetries are also reflected in the morphology of the quasicrystals (Balzuweit, Meekes, van Tendeloo and de Boer 1993, Beeli and Nissen 1993 and references therein).

Another type of incommensurate crystal phase is formed by the incommensurately modulated crystals. These crystal phases can be obtained from a basic (non-modulated) crystal structure by means of a small periodic deformation, called modulation. If the period length of this modulation is not commensurate with any integral combination of \( \mathbf{a}_1, \mathbf{a}_2 \), and \( \mathbf{a}_3 \), lattice translational symmetry is lost in at least one direction. The crystal is then called incommensurate; otherwise, it is called commensurately modulated. Since the modulation is periodic, the average crystal structure can be described by the original basic structure. The spots in the X-ray diffraction patterns of incommensurately...
modulated crystals can be classified into main reflections, originating from the average structure, and satellite reflections, whose coordinates are not simple fractions with respect to the lattice of main reflections. On the other hand, the spots in the diffraction patterns of quasicrystals cannot be divided into main and satellite reflections since there is no average crystal structure which is lattice periodic.

Crystals can be characterized at a macroscopic level by their morphology. Many crystals are bounded by flat faces that can be labelled with a set of integral indices \((hkl)\). These indices represent a reciprocal lattice \(H_{hkl}\) perpendicular to the face:

\[
H_{hkl} = h\mathbf{a}^* + k\mathbf{a}_2^* + l\mathbf{a}_3^*,
\]

where \(\mathbf{a}_1^*\), \(\mathbf{a}_2^*\) and \(\mathbf{a}_3^*\) span the reciprocal lattice. A crystallographic face \((hkl)\) can be constructed by cutting \(1/h\) of \(\mathbf{a}_1\), \(1/k\) of \(\mathbf{a}_2\) and \(1/l\) of \(\mathbf{a}_3\) and taking the plane through these points. In each face \((hkl)\) a two-dimensional lattice can be defined. There exists a corresponding two-dimensional unit cell, the mesh area \(M_{(hkl)}\), which is very useful in the calculation of the stability of crystal faces.

Like the classical crystals, incommensurate crystal phases are often also bounded by flat faces. It has been observed (Janner, Rosing, Bennema and van der Linden 1980, Dam, Janner and Donnay 1985, Bennema et al. 1991 and references therein) that the faces of incommensurately modulated crystals with a one-dimensional modulation are perpendicular to vectors that are integral linear combination of four vectors from the reciprocal space. Consequently, these faces can be labelled with four integral indices \((hklm)\). Three of the four vectors, \(\mathbf{a}_1^*, \mathbf{a}_2^*\) and \(\mathbf{a}_3^*\), span the reciprocal lattice of the average structure, while the fourth is the modulation wave vector \(\mathbf{q}\). A face \((hklm)\), is thus perpendicular to the vector

\[
H_{hklm} = h\mathbf{a}_1^* + k\mathbf{a}_2^* + l\mathbf{a}_3^* + m\mathbf{q}.
\]

Suppose that \(\mathbf{q} = z\mathbf{a}_1^*\); the face then cuts the \(\mathbf{a}_1\) axis at \((h + mz)\). If the modulation is incommensurate, \(z\) is irrational.

Spots in the X-ray diffraction patterns of quasicrystals can be characterized by a set of more than three integers. This corresponds to the basic property that the wave vectors of the Fourier transform of the charge density have the following form:

\[
H_{h1...h_d} = h_1\mathbf{a}_1^* + h_2\mathbf{a}_2^* + \ldots + h_d\mathbf{a}_d^*, \quad d > 3.
\]

Faces of quasicrystals are perpendicular to these vectors. Thus, as in the case of incommensurately modulated crystals, more than three integral indices are needed to label such a face.

Neither in quasicrystals nor in incommensurately modulated crystals is there lattice translational symmetry in three independent directions. Therefore, it is generally not possible to define a planar elementary cell as a mesh area on a crystallographic face. Periodicity is used in explaining the equilibrium form of classical crystals. Therefore, a different explanation is needed for the equilibrium form of incommensurate crystals.

In two previous papers (Bennema, Kremers, Meekes, Balzuweit and Verheijen 1993, Kremers, Meekes, Bennema, Balzuweit and Verheijen 1994), a concept has been elaborated that deals with this problem for the case of incommensurately modulated crystals. This concept makes use of the embedding of modulated crystals in a so-called superspace (Janssen and Janner 1987), which has a dimension higher than three. The advantage of this superspace embedding is that the embedded structure has full lattice translational symmetry. The physical crystal is a three-dimensional section of the embedded structure. It is possible to generalize crystallographic faces to hyperfaces in
superspace. This generalization can be used to calculate the surface free energy of crystallographic faces in order to explain their stability.

In the present paper, we apply the method discussed above to the case of quasicrystals. First, we consider the simple case of the Fibonacci chain of atoms, which can be described both as a one-dimensional modulated crystal and as a one-dimensional quasicrystal. This duality allows us to compare the two types of incommensurate crystal phases. Sections 2 and 3 discuss the superspace description of the chain, regarded as a modulated crystal and as a quasicrystal, respectively. In §4 it is shown that these two descriptions are equivalent. Section 5 deals with the extension of the Wulff–Herring construction determining morphologies to include superspace descriptions. Model calculations are presented in §6. It is shown that both descriptions of the Fibonacci chain of atoms yield the same results. However, the description as a quasicrystal proves to be more natural.

Section 7 discusses how the superspace approach can be extended to the case of the two-dimensional octagonal quasicrystal in order to determine the average surface free energy of a grid of netplanes \((hkln)\). It was shown by Ho (1991) that the stability of a single crystal face in a two- or three-dimensional quasicrystal is independent of the position of the face if atoms and bonds are defined in a specific way. However, the results of §7 of the current paper demonstrate that, if other definitions are used, the surface free energy does depend on the position of the face. Part 1 of the paper (Heijmen, Kremers, Meekes and Janssen 1995) will present a method of determining the stabilities of single faces \((hlkm)\) in a two-dimensional octagonal quasicrystal.

§2. The Fibonacci Chain as a Modulated Structure

The Fibonacci chain of atoms is a one-dimensional crystal with two different interatomic distances. It contains a quasi-periodic ordering of long and short intervals between the atoms (Janssen and Janner 1987). The ratio of the long and the short interval lengths equals the golden ratio \(\tau = \frac{1}{2}(\sqrt{5} - 1)\).

In general, the atomic positions of a one-dimensional monoatomic modulated crystal are described in the following way. If, in the basic structure, the position of the atom in the \(n\)th unit cell is given by \(x_0 + na\), the corresponding position in the modulated structure is given by

\[x_n = x_0 + na + f(qna + \phi_0),\]  

with \(q = aa^*\), \(0 \leq a < 1\); \(f(y)\) is the periodic modulation function \(\phi_0\) is an arbitrary phase. The one-dimensional crystal with \(f(y) = \cos(y)\) has been discussed previously (Kremers et al. 1994, Bennema et al., 1993).

It is possible to define a lattice in a \(1 + 1\) dimensional superspace, spanned by the vectors

\[\mathbf{a}_s = (a, -ad) \quad \text{and} \quad \mathbf{d}_s = (0, d).\]  

The first coordinate of each of these vectors represents the component in the physical space, which is called external space in the superspace description, the second the component being in a perpendicular internal space; \(d\) is an arbitrary real number. The corresponding reciprocal lattice is spanned by

\[\mathbf{a}^* = (a^*, 0) \quad \text{and} \quad \mathbf{d}^* = (q, d^*),\]  

where \(aa^* = dd^* = 1\). Note that if \(d = 1/q\), the angle between \(\mathbf{a}\) and the physical space equals 45° and the unit of length in the internal space has the same periodicity as the
modulation wave in real space (Janner 1983). The Fibonacci chain of atoms, drawn in fig. 1, can be regarded as a one-dimensional crystal with saw-tooth shaped modulation. The positions of the atoms of such a structure are given by

\[ x_n = x_0 + na + b(1 - 2 \frac{q}{\lambda} + \delta_n + \phi_0). \]  

(7)

The function \( \frac{y}{\lambda} \) assigns to \( y \) the value \( y \) minus the largest integer smaller than or equal to \( y \). Equations (7) describes the positions of the atoms in the Fibonacci chain if the following values are assigned to the parameters \( a, b \) and \( \alpha \):

\[ a = 3\tau - 1, \quad b = \frac{1}{2}(1 - \tau), \quad \alpha = \tau. \]  

(8)

The atoms of the chain described by eqn. (7) can be embedded in the 1 + 1 dimensional superspace. The atomic positions are then given by

\[ r_s(n, \phi) = [na + b(1 - 2 \frac{q}{\lambda} + \delta_n + \phi_0), \phi], \]  

(9)

where \( \phi \) is a phase which runs along the internal axis. The equation describes an infinite set of (discontinuous) lines, called world lines, which represent the atoms in the superspace description. If the parameters \( a, b \) and \( \alpha \) are given the values of eqn. (8), then eqn. (9) describes the superspace embedding of the Fibonacci chain of atoms, as is shown in fig. 2. The section of the two-dimensional structure with the physical space yields the Fibonacci chain of fig. 1.

If the superspace description is to be used in explaining the equilibrium form of an incommensurate crystal, a number of crystallographic concepts have to be extended to superspace. These extensions have been discussed in detail by Kremers et al. (1994); a summary is given below.

The concept of chemical bonds can be generalized to superspace by defining a density of bonds connecting the atoms in superspace with each other for each phase \( \phi \) along the internal axis. These bonds are defined parallel to the physical space. A (one-dimensional) crystallographic hyperplane \((hm)\) can be defined by taking a plane perpendicular to the vector\n
\[ H_{(hm)} = \hbar a^* + m d^* \]  

(10)

from reciprocal space. A grid of netplanes \((hm)\) can be constructed in superspace with interplanar distance

\[ d_{(hm)} = 1/|H_{(hm)}|. \]  

(11)

Related to the idea of interplanar distance is the concept of mesh area \( M \). It is defined as the surface area of a planar elementary cell of a hyperplane \((hm)\),

\[ M_{(hm)} = \frac{V^*_s}{d_{(hm)}}, \]  

(12)

where \( V^*_s \) is the area of the 1 + 1 dimensional unit cell of the lattice given by eqn. (5).

The surface free energy \( \Gamma \) can be used as a criterion for the stability of a crystal face:
The superspace embedding of the Fibonacci chain of atoms, regarded as a modulated crystal. The positions of the atoms are indicated by the full circles. In superspace, atoms are represented by discontinuous world lines. In the left part of the figure, the extension of the concept of chemical bonds to superspace is shown with the help of the dotted lines. In the right part, the principle of selective cuts is demonstrated for the face (11). The bonds that are selectively cut are indicated by the hatched areas. The mesh area $M_{\text{u,s}}$ is indicated by the symbol $M$.

The lower $I'$, the more stable the face. We make use of a broken-bonded model in which the surface free energy corresponds to the energy per unit area needed for cutting bonds in order to create the face from an infinitely large crystal. In equilibrium, the form of a crystal is such that the total surface free energy is minimal.

It has been discussed above that the bonds of the physical quasicrystal are represented in superspace by a uniform bond density. The lattice periodicity of the $1+1$ dimensional embedded structure implies that each bond in the physical crystal that is intersected by a grid of netplanes $(hm)_s$ is translationally equivalent to a bond in superspace intersected by one specific hyperplane $(hm)_s$. This is illustrated by fig. 2 for the grid of netplanes $(1\overline{1})_s$. The bonds of the physical quasicrystal that are intersected by the grid are therefore represented in superspace by the part of the uniform density of bonds that is intersected by a single hyperplane $(hm)_s$. Consequently, calculating the broken bond energy per mesh area of a single hyperplane $(hm)_s$ in superspace is equivalent to calculating the average energy of the bonds in the physical crystal that are cut by a grid of netplanes $(hm)_s$.

Figure 2 shows that the grid of netplanes $(1\overline{1})_s$ intersects only part of the dense set of bonds in superspace. In general, the ratio between the fractions of long and short bonds that are intersected is different for each grid of netplanes $(hm)_s$. Since the bond
energy is assumed to be only a function of the bond length, this implies that the broken bond energy per mesh area in superspace generally differs for each face \((hn)_s\). In the current paper, this so-called principle of selective cuts is used to discriminate between the stabilities of different faces on one- and two-dimensional quasicrystals.

Each phase \(\phi\) along the internal \(d\) axis corresponds to a crystal with a different phase factor \(\phi + \phi_0\) but with the same two periodicities which occur in the same ordering. The minimum surface free energy for each face \((hn)_s\), can therefore be found by varying the phase at which the corresponding hyperplane intersects the \(d\) axis. This is equivalent to varying the phase \(\phi_0\) in eqn. (9), has been discussed by Kremers et al. (1994).

§ 3. THE FIBONACCI CHAIN AS A QUASICRYSTAL

Since there a finite number (two) of intervals, which are ordered in a quasi-periodic way, the Fibonacci chain of atoms can be regarded as a one-dimensional quasicrystal. The procedure for embedding a quasicrystal in a higher-dimensional superspace is different from that for embedding an incommensurately modulated crystal (Janssen and Janner 1987). A lattice is defined which is spanned by two vectors

\[
e_{1s} = (\delta, 1) \quad \text{and} \quad e_{2s} = (1, -\delta),
\]

which are defined on an orthonormal basis \(\{\hat{e}_E, \hat{e}_I\}\), where \(\hat{e}_E\) and \(\hat{e}_I\) denote unit vectors along the external and internal axis, respectively. The correspondingly reciprocal lattice is spanned by

\[
e_{1s}^* = \frac{1}{1 + \delta^2} (\delta, 1) \quad \text{and} \quad e_{2s}^* = \frac{1}{1 + \delta^2} (1, -\delta).
\]

Atoms are represented in superspace by line elements, defined as the projection of the unit cell on the internal space. These line elements, generally called atomic surfaces, are attached with their centres at the vertices of the superlattice. The points of the \(1 + 1\) dimensional embedded structure are given by

\[
me_{1s} + ne_{2s} + (0, t), \quad m, n \text{ integers,} \quad t \in (- (1 + \delta)/2, (1 + \delta)/2].
\]

The superspace embedding of the Fibonacci chain of atoms, regarded as a one-dimensional quasicrystal, is shown in fig. 3.

The physical quasicrystal is the intersection of the embedded structure with the physical space; its atomic positions are

\[
x_{m,n} = m\delta + n, \quad -(1 + \delta)/2 < n\delta - m \leq (1 + \delta)/2.
\]

The definition of the atomic surfaces ensures that the number of intersection points does not change if the embedded structure is shifted with respect to the physical space. Equations (16) describes the atomic positions of the Fibonacci chain of atoms if \(\delta\) equals the golden ratio \(\tau\).

The crystallographic concepts discussed in the previous section can also be generalized to the superspace embedding of a quasicrystal. To extend the concept of chemical bonds to superspace, a density of bonds parallel to the physical space is defined between neighbouring atomic surfaces (see fig. 3). A bond from this dense set has the same length as either the long or the short bond in the physical crystal.

A crystallographic hyperplane \((hn)_s\) is defined perpendicular to the vector

\[
H_{(hn)_s} = he_{1s}^* + me_{2s}^*.
\]
The superspace embedding of the Fibonacci chain of atoms, regarded as a quasicrystal. The positions of the atoms are indicated by the full circles. In superspace, atoms are represented by line elements parallel to the internal space. In the left part of the figure, the extension of the concept of chemical bonds to superspace is shown with the help of the dotted lines. In the right part, the principle of selective cuts is demonstrated for the face (10). The bonds that are selectively cut are indicated by the hatched areas. The mesh area $M_{(10),s}$ is indicated by the symbol $M$.

The generalizations of the concepts of interplanar distance and mesh area are again given by eqns. (11) and (12), respectively.

Using the same arguments as in the previous section, it can be shown that the average energy of the bonds in the physical crystal that are cut by a grid of netplanes $(hm)_s$ is equal to the broken bond energy per mesh area of a single hyperplane $(hm)_s$ in superspace. The principle of selective cuts can again be used to discriminate between the stabilities of different faces $(hm)_s$. The principle is illustrated by fig. 3 for a grid of net planes $(10)_s$, which only intersect part of the dense set of bonds in superspace.

If the embedded structure in fig. 3 is shifted along the internal axis, its intersection with the physical space forms a quasi-periodic structure with the same ordering of long and short intervals as the original intersection. Therefore, we can again assume that it is legitimate to minimize the broken bond energy by varying the phase at which the hyperplane $(hm)_s$ intersects the internal axis.

§ 4. Equivalence of the two descriptions of the Fibonacci chain

A grid of netplanes $(hm)_s$ in superspace, embedding as a modulated crystal, divides the physical structure into intervals of length

$$d^\text{mod}_{hm} = 1/[ha^* + mq],$$

(18)
where $a^*$ and $q$ are the projections on the physical space of the vectors $a^*_r$ and $d^*_r$, respectively, as given by eqn. (6). On the other hand, a grid of netplanes $(hm)_s$ in the superspace, embedding as a quasicrystal, divides the physical structure into intervals of length

$$d^*_r = \frac{1}{|he^*_i + me^*_j|},$$

where $e^*_i$ and $e^*_j$ denote, respectively, the projections on the physical space of $e^*_s$ and $e^*_t$, given by eqn. (14).

It can be proved that eqn. (7) in § 2 is equivalent to eqn. (16) in § 3, i.e., it describes the atomic positions of the same structure, if the parameters of the former are given the following values:

$$a = (1 + \delta^2)/(1 + \delta), \quad b = \frac{1}{2}(1 - \delta), \quad \alpha = 1/(1 + \delta).$$

The corresponding expressions for $a^*$ and $q$ are

$$a^* = 1/a = (1 + \delta)/(1 + \delta^2) = e^*_i + e^*_j,$$

$$q = \alpha a^* = 1/(1 + \delta^2) = e^*_s.$$  

This implies that the physical crystal is cut at intervals of the same length by a grid of netplanes $(hm)_s$ in the embedding as a modulated crystal and a grid of netplanes $(h(h+m))_s$ in the embedding as a quasicrystal.

It has been discussed above that it is permissible to shift a grid of netplanes $(hm)_s$ with respect to the $1+1$ dimensional superlattice in order to find the minimum broken bond energy. Consequently, this minimum value depends only on the length of the intervals in which the grid cuts the physical crystal. Hence, the minimum broken bond energy is identical for both a grid of netplanes $(hm)_s$ in the embedding as a modulated crystal and a grid of netplanes $(h(h+m))_s$ in the embedding as a quasicrystal. Therefore, a face $(hm)_s$ in the former description is morphologically equivalent to a face $(h(h+m))_s$ in the latter. Figures 2 and 3 illustrate this for the faces $(11)_s$ and $(10)_s$, respectively. This equivalence corresponds to the fact that, since it is the same crystal that is embedded in superspace in two different ways, the equilibrium form of the crystal—as all physical properties—must be the same in either of the two descriptions.

§ 5. THE GENERALIZED WULFF–HERRING PLOT

A method for determining the equilibrium morphology from calculated surface free energies has been developed by Herring (1951, 1953). A radius vector is drawn for each crystallographic face. This vector has the same direction as the corresponding face normal, while its length is linearly proportional to the surface free energy. A plane is constructed perpendicular to this vector, through its tip. The resulting construction is called a Wulff–Herring plot. The equilibrium form of the crystal is determined by the points that can be reached from the origin without crossing any of the constructed planes. It is obvious that faces on the equilibrium form correspond to sharp cusps in the polar plot of the surface free energies. Bennema et al. (1993) have discussed how to extend this method in order to include superspace descriptions. They used as extended Wulff–Herring plot to determine the equilibrium form of modulated one-dimensional crystals.

Since only bonds parallel to the physical space have been defined, a face parallel to this space cannot cut bonds. Consequently, the surface free energy for such a face
is equal to zero. The polar plot of surface free energies of a one-dimensional incommensurate crystal embedded in a 1 + 1 dimensional superspace therefore shows an infinitely deep cusp at \( \theta = \pm \pi/2 \), where \( \theta \) is the angle between the face normal and the physical space. Accordingly, the dimension of the equilibrium form is reduced from two to one, the dimension of the physical crystal. Each plane constructed in the extended Wulff–Herring plot intersects the physical crystal in a point. The equilibrium form is bounded by the faces that correspond to the planes for which the distance \( \gamma \) between their intersection with the physical crystal and the origin is minimal. The distance \( \gamma \) is related to the surface free energy \( \Gamma \) in the following way:

\[
\gamma = \frac{\Gamma}{|\cos \theta|}.
\]

The equilibrium form is thus bounded by two faces, opposite with respect to the origin, for which \( \gamma \) is minimal. In general, the value of \( \gamma \) is assumed to be inversely proportional to the morphological importance (MI) of a face.

§ 6. Calculations of Surface Free Energies

Calculations have been made of the surface free energies \( \Gamma_{(hm)} \) of a general one-dimensional quasicrystal with two different interatomic distances. Both superspace descriptions discussed above have been used. \( \Gamma_{(hm)} \) is defined as

\[
\Gamma_{(hm)} = \frac{\sigma |\cos \theta_{(hm)}|}{M_{(hm),s}} \int_{M_{(hm),s}} dM \Phi(l(M)),
\]

where \( \sigma \) denotes the bond density, taken to equal 1 m\(^{-1} \), \( \theta_{(hm)} \) the angle between the face normal and the physical space, \( M_{(hm),s} \) the mesh area of the hyperplane \( (hm) \), and \( \Phi(l) \) the energy of a bond, expressed as a function of its length:

\[
\Phi(l) = \chi/l.
\]

To calculate \( \Gamma_{(hm)} \), an integration is performed over one mesh area \( M_{(hm),s} \). Because of lattice periodicity, the mesh area of a (hyper)plane is translationally equivalent to those parts of the corresponding grid of netplanes that are found inside one unit cell. This is illustrated by fig. 4 for the hyperplane (21), in the superspace embedding of the Fibonacci chain of atoms, regarded as a modulated crystal. The superspace embedding on a square lattice, depicted in fig. 3, shows a third way to determine \( \Gamma_{(hm)} \). Integrating over one unit cell of this lattice is equivalent to integrating over one atomic surface if the bonds on only one side of the surface are counted.

Surface free energies \( \Gamma_{(hm)} \) have been calculated for crystallographic faces \( (hm)_s \), with \( -3 \leq h,m \leq 3 \), as a function of the parameter \( \delta \) of eqns. (16) and (20). Calculations have been performed for 50 values of \( \delta \) between 0 and 1. If the structure was regarded as a modulated crystal, \( \Gamma_{(hm)} \) was calculated according to eqn. (23); in the case where the structure was described as a quasicrystal, \( \Gamma_{(hm)} \) was determined by performing an integration over one atomic surface. In both cases, integrals were calculated by means of numerical integration over 750 points. The hyperplanes were shifted along the internal space with a phase \( \phi \), which was also varied over 750 values. The bond strength parameter \( \chi \) in eqn. (24) was taken equal to 1.

If \( \delta \) is varied from 0 to 1, all non-equivalent quasicrystals are considered. It is possible to show that a quasicrystal with \( \delta = \delta_0 \) is identical to a quasicrystal with \( \delta = -\delta_0 \); therefore only values of \( \delta \geq 0 \) have to be considered. A quasicrystal with \( \delta = \delta_0 \) is also equivalent to a quasicrystal with \( \delta = 1/\delta_0 \) if in the former the interval lengths are scaled by a factor \( \delta_0 \). Since energies are divided by the average energy 1/\( a \),
The line elements A and B represent the intersections of the grid of netplanes (21) with one unit cell in superspace. Together, these line elements are translationally equivalent with one mesh M(21), they are independent of the absolute length of the intervals and structures with \( \delta = \delta_0 \) and \( \delta = 1/\delta_0 \) are equivalent in our calculations. Consequently, \( \delta \) only has to be varied from 0 to 1, which corresponds to varying \( \gamma \) from \( \frac{1}{2} \) to 1, because of the relation \( \gamma = 1/(1 + \delta) \).

§ 7. Results

Figure 5 shows the generalized Wulff–Herring plot for the Fibonacci chain of atoms. The indexing of the faces corresponds to the superspace embedding of the chain as a modulated crystal; the indices according to the embedding as a quasicrystal are found by replacing \( (hm) \) with \( (h(h + m)) \). Results obtained from the two descriptions agree to a high extent. The two circles in the plot correspond to the case of a crystal with zero-amplitude modulation. The surface free energy \( \Gamma \) can be written as

\[
\Gamma(\theta) = \Gamma_0 |\cos \theta|.
\]

In this case, all faces \( (hm) \), have the same value of \( \gamma \) and, consequently, the same morphological importance. The line elements intersecting the circles represent the values of \( \Gamma_{(hm)} \) that have been obtained from our calculations on the Fibonacci chain by varying the phase \( \phi \); their end points correspond to the minimum and maximum values of \( \Gamma_{(hm)} \). Dashed lines have been drawn perpendicular to the face normal, from the end points corresponding to the minimum values. The distances between the origin and the intersection points of these lines with the physical space represent \( \gamma \), defined by eqn. (22).

In the broken-bond model, the faces \( (hm) \) and \( (\bar{h}\bar{m}) \), which are parallel, are morphologically equivalent. Hence, the right and the left sides of fig. 5 contain the same
Fig. 5

Extended Wulff–Herring plot for the Fibonacci chain of atoms. The faces have been labelled according to the description as a modulated crystal. The indices in the quasicrystal description are found by replacing \((hm)\) by \((h(h+m))\). Faces with indices up to 3 have been plotted.

Information. The figure reveals that the faces \((10)\), \((01)\), \((1\bar{1})\), and \((1\bar{2})\), have the same (minimum) value of \(\gamma\). These four faces (which are not parallel in superspace) can be positioned in the embedded structure in such a way that only long bonds are cut. Since the bond energy is inversely proportional to the bond length, this situation corresponds to a minimum surface free energy. Obviously, it is possible to construct grids of netplanes \((hm)\), in superspace which intersect merely long bonds in the physical space, although the Fibonacci chain of atoms is only quasi-periodic. The faces \((10)\), \((01)\), \((1\bar{1})\), and \((1\bar{2})\), are labelled \((11)\), \((01)\), \((10)\), and \((1\bar{1})\), respectively in the description as a quasicrystal.

Figure 6 plots \(\gamma = \Gamma_{\text{min}}(hm)/\cos \theta\) as a function of \(\alpha = 1/(1 + \delta)\), where \(\Gamma_{\text{min}}(hm)\) denotes the minimum free surface free energy. The energies have been normalized, i.e., they have been divided by the average bond energy, which is proportional to \(1/\alpha = (1 + \delta^2)/(1 + \delta)\). Faces have been labelled according to the superspace embedding as a quasicrystal. The indices in the description as a modulated crystal are found by replacing \((hm)\) with \((h(h+m))\). There is a good agreement between the results obtained from the two descriptions.

The minimized surface free energies of the faces \((hm)\), and \((mh)\), labelled according to the quasicrystal description, are found to be equal. This is caused by a symmetry that is not directly obvious from the embedding as a modulated crystal, but which is understandable if the embedding as a quasicrystal is considered. Figure 7 shows this embedded structure, emphasizing the areas in which either long or short bonds are present. The hatched areas contain only short bonds while those that are not hatched comprise only long bonds. Both types of areas are square; their sizes are \(\delta \times \delta\) and \(1 \times 1\), respectively. Figure 7 reveals that there are fourfold axes of symmetry at the centres of the edges of the unit cell, i.e., at \((0, 1/2)^{\text{qc}}, (1/2, 0)^{\text{qc}}\) and at translationally equivalent positions. (The superscript \(\text{qc}\) denotes that the positions are defined with respect to the square superlattice, spanned by the vectors of eqn. (13).) Note that only the pattern of areas in which short and long bonds occur show this symmetry; the embedded structure
Normalized \( \gamma = \frac{\Gamma}{|\cos \theta|} \) values for 50z points, calculated by minimizing over 750 phases. The smallest value of \( \gamma \) corresponds to the highest morphological importance. The faces have been labelled according to the quasicrystal description. The indices in this description are found by replacing \((hm)\) by \((h(m - h))\). Faces with indices up to 3 have been plotted. The value \( \alpha \) for the Fibonacci chain is indicated.

Fourfold symmetry in the pattern of areas in which short (hatched) and long (not hatched) bonds occur in the Fibonacci chain of atoms, embedded as a quasicrystal. Fourfold symmetry axes have been indicated.
itself does not, because of the filling of the $1 + 1$ dimensional unit cell. The fourfold symmetry causes two faces $(hm)_s$ and $(m\bar{h})_s$, which are perpendicular, to cut long and short bonds in the same ratio. Since this ratio determines the surface free energy, the faces $(hm)_s$ and $(m\bar{h})_s$ have the same morphological importance. The grid of netplanes $(m\bar{h})_s$ generally divides the physical quasicrystal into intervals with a different length compared to the grid of netplanes $(hm)_s$. Nevertheless, the two grids intersect short and long bonds in the same ratio. This is another example of a symmetry aspect understood directly if the superspace description is used.

In quasicrystal description all faces, except $(11)_s$, $(10)_s$, $(1\bar{1})_s$ and $(01)_s$, start to cut only long bonds at a critical minimal value of $\alpha$. (The four exceptional faces can be positioned, for any value of $\alpha$, in such a way that they do not cut short bonds.) The critical value is relatively low for faces with low indices and relatively high for faces with high indices, as can be seen from fig. 6. Consequently, faces with low indices in the embedding as a quasicrystal generally have either a smaller or the same surface free energy compared to faces with high indices, and thus have a larger or equal morphological importance. This correlation is less obvious from the embedding as a modulated crystal. Since a description is preferred in which the faces with the lowest indices have the largest morphological importance, we state that a one-dimensional quasicrystal is embedded in superspace less naturally if it is regarded as a one-dimensional modulated crystal.

§ 8. THE TWO-DIMENSIONAL OCTAGONAL QUASICRYSTAL

The surface free energy in superspace of a face $(hm)_s$ in the Fibonacci chain of atoms proves to be dependent on its position. The current section examines whether this is also the case for a face in a two-dimensional octagonal quasicrystal. For this purpose, the superspace approach is used to calculate the average surface free energy of a grid of netplanes $(hk\bar{lm})_s$.

A model is used in which the atoms of the quasicrystal are located at the vertices of a quasi-periodic two-dimensional tiling. A tiling is a structure that is obtained if the space is quasi-periodically filled with tiles from a set of two or more. Tilings were described mathematically before quasi-crystalline phases were discovered (Penrose 1979).

The vertices of an octagonal tiling form a rank four module $M$ that is spanned by four vectors which point, together with their opposites, to the vertices of a regular octagon. The positions of the vertices of the tiling are given by vectors $n$, defined on an orthonormal basis:

$$n = \sum_{i=1}^{4} n_i a_i, \quad n_i \text{ integers},$$

$${a_1} = (1, 0), \quad {a_2} = \frac{1}{2}\sqrt{2}(1, 1),$$

$$a_3 = (0, 1), \quad a_4 = \frac{1}{2}\sqrt{2}(-1, 1).$$

The tiling can be built from two prototiles, a square one and a rhombic one with angles of $45^\circ$ and $135^\circ$. The edges of both prototiles are equal; their length is that of the basis vectors $\{a_i\}$. Figure 8 shows a part of an octagonal tiling.
A part of a two-dimensional octagonal tiling. If we assume that the vertices of the tiling correspond to atomic positions and the edges of the tiling to chemical bonds, this figure also represents the two-dimensional octagonal quasicrystal.

The superspace embedding of the four generators \( \{ a_i \} \) of the vector module \( M \) with respect to an orthonormal basis is given by (Janner 1991):

\[
\begin{align*}
    a_{1s} &= (1, 0; 1, 0), \\
    a_{2s} &= \frac{1}{2} \sqrt{2} (1, 1; -1, 1), \\
    a_{3s} &= (0, 1; 0, -1), \\
    a_{4s} &= \frac{1}{2} \sqrt{-1} (1, 1).
\end{align*}
\]

The first two coordinates of these vectors represent the component in the physical space, the last two the component in the internal space. Note that the lattice is hypercubic since the basis \( \{ a_{is} \} \) is orthogonal and its vectors all have the same length.

The following procedure is adopted to embed a two-dimensional octagonal quasicrystal in superspace (Janner 1991). Two-dimensional atomic surfaces are attached to the vertices of the 2 + 2 dimensional hypercubic lattice. These atomic surfaces, representing the atoms in the embedded structure, are defined as the projection of the unit cell on the internal space. Consequently, they have no component in the physical space. The surfaces are attached to the vertices of the lattice in their 'centres of gravity'. Accordingly, the embedded structure is given by

\[
V_p = \left\{ \mathbf{x} \in V | \mathbf{x} = \sum_{i=1}^{4} \lambda_i a_{is}, \lambda_i \in \left[-\frac{1}{2}, \frac{1}{2}\right] \right\},
\]

where \( V_p \) represents the atomic surfaces; \( a_{is} \) denotes the internal component of the vector \( a_{is} \). The octagonal quasicrystal is formed by the intersection of the embedded structure with the physical space. Note that an atomic surface intersects the physical space in, at most, a single point.

The atoms of the two-dimensional quasicrystal can be connected by bonds in several
Morphology of quasicrystals

ways. In the current paper, we only define bonds between atoms separated by one of the vectors \( \{a_i\} \) of eqn. (26). In other words, each edge of the tiling is equivalent to a bond. An edge of the tiling in the physical space corresponds to an edge of a hypercubic unit cell in superspace. Accordingly, only bonds are defined between atoms corresponding to atomic surfaces connected by an edge of a hypercubic unit cell. Our definition of bonds is therefore a natural choice in the superspace description. It is discussed above that all edges of the tiling have the same length. Since the bond energy is only a function of the bond length, all bonds have the same energy.

The concept of chemical bonds can be extended to the 2 + 2 dimensional superspace by defining a density of bonds of equal length connecting the atomic surfaces in superspace with each other for each pair of phases \((\phi_1, \phi_2)\) along the two internal axes. As in the one-dimensional case, these bonds are defined parallel to the physical space. A bond between two atoms along an edge of the two-dimensional tiling in the physical space corresponds to a dense set of bonds between two first-nearest neighbours in superspace, where first-nearest neighbours are atomic surfaces whose centres of gravity are connected by an edge of a unit cell. Since the unit cell of the superlattice is 2 + 2 dimensional, each atomic surface has first-nearest neighbours in four directions. Hence, there are four different types of bonds between an atomic surface and its first-nearest neighbours. In contrast with the one-dimensional case, bonds are only found in specific sections of the superspace. Inside these sections, the bond density is uniform.

Analogously to the one-dimensional case, a number of crystallographic concepts can be extended to the 2 + 2 dimensional superspace. A three-dimensional crystallographic hyperplane \((hklm)\) is defined perpendicular to the vector

\[
H_{(hklm)} = ha_1 + ka_2 + la_3 + ma_4.
\]

The extensions of the concepts of interplanar distance and mesh area are analogous to eqns. (11) and (12), respectively. A grid of netplanes \((hklm)\), with interplanar distance \(d_{(hklm)}\) can be constructed in superspace. The intersection of such a grid with the physical space forms an infinite set of equidistant lines.

Owing to the lattice periodicity of the 2 + 2 dimensional embedded structure, each bond in the physical space that is intersected by a grid of netplanes \((hklm)\), is translationally equivalent to a bond in superspace intersected by one specific hyperplane \((hklm)\). Therefore, the part of the uniform density of bonds this hyperplane intersects represents the bonds in the physical space that are intersected by the grid of netplanes \((hklm)\). Analogously to the one-dimensional case, this implies that calculating the broken bond energy per mesh area of a single hyperplane \((hklm)\), is equivalent to calculating the average surface energy of the intersection of the grid of netplanes \((hklm)\), with the physical space.

In general, a grid of netplanes \((hklm)\), intersects only part of the dense set of bonds in superspace. Therefore, the surface free energy \(\Gamma\) in superspace is generally different for each hyperplane \((hklm)\). This selectivity principle can be used to distinguish between the stabilities of different grids. The principle implies that \(\Gamma\) generally depends on the position of the origin. Consequently, the minimum value of \(\Gamma\) can be found by shifting the hyperplane with respect to the origin.

Analogously to the one-dimensional case, a quantity \(\gamma_{\text{grid}}\) can be defined as

\[
\gamma_{\text{grid}} = \frac{\Gamma}{|\cos \theta|},
\]

where \(\theta\) denotes the angle between the normal vector \(H_i\) in superspace and its projection
Calculated values of \( \gamma_{\text{grid}} \) for the two-dimensional octagonal quasicrystal. Only faces that are not symmetry equivalent are shown.

<table>
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on the physical space. The value of \( \gamma_{\text{grid}} \) has been taken as a measure for the morphological importance of a face \( (hklm) \).

Calculations have been done for faces \( (hklm)_s \) for which \(-2 \leq h,k,l,m \leq 2\). Integrations have been performed numerically. In order to minimize \( \Gamma \), hyperplanes have been shifted along their normal vectors over 750 different phases.

The plane symmetry of a two-dimensional octagonal tiling is 8 mm (Steurer 1990). Because of the eightfold symmetry axis, the face \( (hklm)_s \) is equivalent to the face \( (mhlk)_s \); because of the two mirror operations, the face \( (hklm)_s \) is equivalent to both the face \( (mikh)_s \) and the face \( (lkhi)_s \). The number of morphologically non-equivalent faces is largely reduced by this symmetry.

Calculations have shown that the values of \( \gamma_{\text{grid}} \) depend on the position of the grid. In other words, \( \gamma_{\text{grid}} \) generally alters if the grid of netplanes is shifted in the direction of the normal vector. The calculated minimum values of \( \gamma_{\text{grid}} \) are listed in the table. It is seen that faces with the same orientation in the physical space have different minimum values of \( \gamma_{\text{grid}} \). Compare, for example, the faces \( (0110)_s \), \( (1001)_s \), and \( (1111)_s \); in table 1, the face \( (0110)_s \) is represented by the face \( (1100)_s \), which is equivalent because of the eightfold symmetry.

§ 9. DISCUSSION

The morphology of the two-dimensional pentagonal quasicrystal has been discussed by Ho (1991). The quasicrystal was represented there by a Penrose tiling. Each tile was regarded as an atom, and bonds were defined between neighbouring tiles with bond directions perpendicular to the edges of the tiling. It was shown that the surface free energy of an arbitrary face is independent of its position for this structure. The argument
leading to this conclusion is also valid for the two-dimensional octagonal tiling. Therefore, the surface free energy in a two-dimensional octagonal quasicrystal would not depend on the position of the face if atoms were represented by tiles and if bonds are defined between neighbouring tiles, with bond directions perpendicular to the edges of the tiling.

In the current paper, atoms are represented by the vertices of the tiling and each edge is considered to be a bond. It has been found that, in this case, the surface free energy of a grid of netplanes \((hklm)_s\) is dependent on the position of the grid. If the surface free energy of a single face \((hklm)_s\) were independent of its position, \(\gamma_{\text{grid}}\) would not depend on the position of the grid. Thus, it is proved that in our model the surface free energy of a single face is dependent on its position. Therefore, the result found by Ho is a consequence of the definitions of atoms and bonds used. In general, it will not hold if other definitions are used. Since the surface free energy of a single face \((hklm)_s\) depends on its position, grids of netplanes \((hklm)_s\) which have the same orientation in the physical space generally have different surface free energies, as is shown by table 1. This result will be used in part II of the paper (Heijmen et al. 1995) to determine the surface free energy of a single face \((hklm)_s\).

§ 10. Conclusions

The present paper shows that the superspace description for the morphology of one-dimensional incommensurately modulated crystals can be generalized to the case of one-dimensional quasicrystals.

The Fibonacci chain of atoms can be embedded in a \(1 + 1\) dimensional superspace in two different ways. The two descriptions prove to be equivalent in determining the stabilities of crystal faces. Crystallographic faces are labelled with different indices in the quasicrystal embedding compared to the embedding as a modulated crystal. Calculated surface free energies indicate that low-index faces are more stable than high-index faces in the quasicrystal description. This correlation is less strong in the description as a modulated crystal.

Several symmetry aspects concerning the equilibrium forms of quasicrystals can be explained more easily if the superspace description is used. It is found that a one-dimensional quasi-periodic chain of atoms can be cut in intervals of equal length in such a way that only long bonds are broken. In addition, the superspace description as a quasicrystal shows that the grids of netplanes \((hm)_s\) and \((mh)_s\) intersect long and short bonds in the same ratio, although the two grids generally have different interplanar distances in the physical space.

The superspace approach can be extended to the case of the two-dimensional octagonal quasicrystal. In the present paper, it is used to calculate the average surface free energies of grids of netplanes. The results provide evidence that the stability of a single crystal face depends on its position. On the other hand, Ho (1991) has found that the stability is independent of the position of the face if specific definitions of atoms and bonds are chosen. Obviously, the problem of determining the stability of crystallographic faces in quasicrystals is more complex than Ho’s approach suggests.

The superspace description of quasicrystals proves to be of great help in solving this problem. In part II of the present paper (Heijmen et al. 1995), we will use this description to give an explanation for the equilibrium form of the two-dimensional octagonal quasicrystal. Our final aim is a theory, based on the superspace description, which enables us to deal with three-dimensional quasicrystals for arbitrary definitions of atoms and chemical bonds.
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