1. Introduction

How do quasicrystals grow? This has been (and still is) one of the fundamental puzzles in the theory of quasicrystals, and despite the effort employed to provide an answer to this fascinating question, there is yet much to be understood. In this review, we want to show the problems one has to face, and present an overview on the ideas, the models, the methods, and the results that have been discussed in the literature to date.

But, after all, one may ask, what is so different about growing quasicrystals in comparison to the growth of (ordinary) crystals? Certainly, taking a thermodynamic point of view, one would expect that the basic theory of nucleation and crystal growth should be the same as for ordinary crystals; see e.g. [42] for an introductory textbook on this subject, and [27] for experimental results on undercooled melts of quasicrystalline alloys. In fact, the answer to this question lies in the structure of quasicrystals, and their relationship to ordered crystals, on the one hand, and disordered amorphous materials, on the other. An ideal crystal is constructed as a periodic arrangement of a single building block, the unit cell, forming a regular lattice. Thus, in order to understand why the atoms arrange in a crystalline fashion, it is sufficient to consider a small portion of the crystal containing a few of these unit cells. In amorphous systems, on the other hand, one only finds short-ranged local order, and one can quite easily imagine how such a structure can emerge in a process of aggregation.

For ideal quasicrystals (where “ideal” means perfect in the mathematical sense), however, the situation is completely different. Being aperiodic, they possess a long-ranged quasiperiodic order of the atomic positions. This quasiperiodic order, if it is perfect, is very restrictive, and one should not think of the quasiperiodic structure as being less ordered than the periodic structure that underlies crystals. In fact, structure models of quasicrystals are typically built on quasiperiodic tilings of space, where the tiles are decorated by the atomic positions. Such tilings can be obtained as sections through higher-dimensional periodic lattices, hence the degree of order in these periodic and quasiperiodic structures is comparable. But the lack of periodicity makes it much more difficult to build such a structure from its constituents.
(for example, to construct a quasiperiodic tiling by arranging the tiles like a puzzle) without violating quasiperiodicity, compare [54]. We cordially invite the reader to give it a trial, see [18] for details.

At first, the tile-by-tile growth of a quasicrystal may even seem to be an impossible task. However, for certain tilings, there exist collections of local conditions, so-called matching rules, that enforce quasiperiodicity. Nevertheless, these matching rules do not really solve the problem: they only state that if you managed to tile the space without violating the matching rules, you will indeed have constructed a quasiperiodic tiling. But they do not guarantee that a given finite “legal” patch (i.e., one that does not violate the rules) can in fact be extended to an infinite tiling of space. So, in this sense, matching rules are not sufficient to provide a simple algorithm for the construction of ideal quasiperiodic tilings.

With this in mind, one inevitably arrives at the question of how Nature solves this puzzle to grow real quasicrystals. Apparently, this seems to require non-local interaction among the constituents which we want to exclude on physical grounds. Of course, there is a rather easy way out of this dilemma – namely that in physical reality one never encounters real quasicrystals that are absolutely perfect in the mathematical sense. But the same is true for ideal crystals, and one can nowadays grow real quasicrystals that show at least comparable degrees of perfection to that of real ordinary crystals – judged, for instance, by the sharpness of their experimentally observed diffraction patterns. These high-quality quasicrystals are commonly called “perfect quasicrystals” regardless whether they resemble an ideal quasiperiodic tiling or a random tiling (see below).

Nevertheless, it turns out that the idea of building defects into the ideal quasiperiodic tilings is rather fruitful, being closely linked to the question of thermodynamic stability of quasicrystals. In principle, there are two possible scenarios: quasicrystals may either be true ground states of the many-particle Hamiltonian, and hence energetically stabilized (which means that they are thermodynamically stable at arbitrarily low temperatures), or they are high-temperature phases which are stabilized by entropic contributions to the free energy. In the latter case, which is tentatively favoured by experimental results (see [3, 4, 36]), the question of disorder in quasicrystals is crucial since disorder provides entropy. Examples are, for instance, defects and vacancies (as also frequently observed in crystals), configurational disorder (which can be described by randomizing the ideal quasiperiodic tiling, resulting in random tiling models), or chemical disorder (which emerges by interchanging atomic positions between different atomic species). Arguably, all these sources of entropy appear in quasicrystals, and there is experimental evidence that the description of quasicrystals as random tilings may be more appropriate than those based on ideal quasiperiodic tilings, see also [46]. Most of the models in the literature therefore do not describe the growth of ideal
structures, but rather try to grow tilings incorporating defects, or structures resembling random tilings.

This review is organized as follows. First, we concentrate on ideal quasiperiodic tilings, discussing the possibility of growing ideal Penrose tilings as an example. This will also clarify the question of non-locality in ideal quasiperiodic growth. After that, we will briefly address the basic problem of random growth models. Subsequently, a number of semi-realistic growth models is discussed which try to mimic the growth of defective quasiperiodic structures in different ways. We distinguish altogether four different classes of growth models, but we would like to stress that our somewhat arbitrary distribution of models into these groups serves mainly presentational purposes and is not meant as a real classification.

The first group consists of what we refer to as “atomistic” growth models, where single “atoms” are added to the growing cluster according to certain conditions. The second class contains (algorithmically motivated) “cluster-based” models, where the aggregation is driven by the requirement that certain preferred cluster configurations have to be completed. After this, we address more physically motivated cluster-based models, so-called “orientational glasses”, which are random packings of (symmetric) building blocks preserving relative orientations, and hence show orientational order. The last group of growth models in our list is based on the random tiling idea, starting from a fixed set of tiles. Finally, we conclude and give an outlook on future developments.

2. Growing Ideal Penrose Tilings

There has been a hot debate on the possibility of purely local growth algorithms for ideal quasiperiodic tilings (their inherent non-locality was first pointed out by V. Elser [11]), particularly after Onoda et al. [49] found an algorithm for the Penrose tiling and claimed that it was local (see the comment by Jarić and Ronchetti [30], the reply of Onoda et al. [50], and the beautiful article by Penrose [54]). In what follows, we shall discuss this algorithm, occasionally referred to as the “OSDS rules”, in some detail, compare also the rather nice presentation by Socolar [61], and review articles by Steinhardt [62] and DiVincenzo [6].

![Fig. 2.1. The Penrose rhombs with arrow decorations.](image)

As one may have guessed from our introductory comments, the algorithm is based on the matching rules for the Penrose tiling. These perfect matching
rules (see [2]) are most easily described in terms of two different types of arrows ("single" and "double" arrows) assigned to the edges of the two rhombs ("fat" and "thin" rhombs) as shown in Fig. 2.1. Starting with some initial patch, one successively adds single tiles to the surface obeying the matching rules. But, as mentioned above, this is not sufficient – in general, sooner or later, one arrives at the situation where a certain surface vertex cannot be completed without violating the matching rules.

Fig. 2.2. The eight vertex configurations of the Penrose tiling.

Thus, one has to be more careful about adding tiles, and in the OSDS rules, going back to a suggestion of Gardner [16], this is achieved by distinguishing two kinds of tile additions: so-called "forced" and "unforced" tiles. As the name suggests, the first kind of addition is one where there is only a single possibility of adding a tile (in general, there will be two) at this place without creating a vertex configuration that is not allowed in an ideal Penrose tiling (there are only eight such configurations, see Fig. 2.2).

Fig. 2.3. Two examples of a dead surface.

Growth according to the OSDS rules now proceeds in two sequential steps. In the first step, one only adds forced tiles at randomly chosen positions, until
the entire surface consists of unforced vertices, i.e., incomplete vertices at which no additions are forced. Such surfaces are termed “dead surfaces”, two small examples are shown in Fig. 2.3. There exist dead surfaces of arbitrary size which can be catalogued exhaustively, see e.g. [61].

Along the flat parts of a dead surface, one may add segments of so-called “worms” which consist of a linear chain of the two hexagons containing three rhombs (Fig. 2.4) arranged in a Fibonacci sequence (see [54] for details). The complete worm can be “flipped” without affecting the form or arrow decoration of its surface, hence it fits on the dead surface in both orientations, see Fig. 2.5 for an example.

While this shows the freedom one has to continue the growth process, simply adding worm segments of arbitrary orientations to a dead surface can lead to inconsistencies (there are “dangerous faces” of the dead surface) which may only show up after the addition of many more tiles, see [54]. Thus, in order to avoid this, one has to formulate a more restrictive rule for adding the next tile, and the second OSDS rule states that one should add a “fat”
rhomb at either side of an 108° corner of the dead surface, consistent with the vertex set of Fig. 2.2. This gives one possible rule that ensures that one never encounters inconsistencies (see [61] for a more thorough discussion). Note that any dead surface has at least two 108° corners, except for certain degenerate cases where two such corners merge to form a 36° corner.

How does non-locality in growth manifest itself? The crux is hidden in the two-step process: in order to avoid mistakes, one first has to complete a dead surface before making an unforced choice. However, this implies that one has to inspect the entire surface of the patch. In other words, vertices at arbitrarily large distance have to be visited as the patch grows. In this sense, the OSDS growth algorithm is clearly non-local, as pointed out by Jarić and Ronchetti [30], by Penrose [54], and by Olami [48]. Beyond this, it is generally not possible to judge locally whether an unforced choice will yield inconsistencies or not, see [54].

However, it is indeed possible to derive a fully local algorithm if one is willing to pay the price of defects, for instance by allowing unforced choices with a very small probability. In this way, tilings with an arbitrarily low defect rate (depending on the chosen probability) can be grown. However, as observed in [58], the growth of the tiling shows a rather strange time-dependence: while forced tiles are added very quickly, growth becomes completely stalled when a dead surface is approached. Only after an unforced tile is chosen does rapid growth commence again. A number of more general growth rules, allowing defects of various types, was investigated by van Ophuysen et al. [51].

Let us close the discussion of ideal tiling growth with two remarks. The first is a warning concerning dead surfaces. It is by no means the case that nothing outside a dead surface is determined by the ideal structure – in general, large parts of the tiling beyond the worm segment are already fixed. The second remark concerns special kinds of defects, so-called “decapods”, which are decagons that cannot be filled without violating the matching rules. Starting from such a defect as an initial patch for the growth, one never encounters a dead surface, and forced growth of an (otherwise) ideal structure continues indefinitely, see [61].

3. Growth in the Random Scenario

Beyond the essentially deterministic growth of ideal tilings, non-locality usually poses no problem (for exceptions refer to Sect. 7). Instead of restrictive matching rules, one has to fulfill simple geometric constraints which guarantee symmetry, face-to-face conditions, etc. New atoms, clusters, or tiles can be attached to the growing surface using purely local information depending only on a limited number of neighbouring objects. The choices in the growth process correspond to the configurational entropy of the system.

Nevertheless, this scenario also has its drawbacks as was pointed out by Sekimoto [59] and by Kalugin [37]. The surface aggregation suffers from a
memory effect generating a considerable rise in the background strain of the “internal” (also referred to as “orthogonal”, “perpendicular”, or “phason”) coordinates, a so-called phason strain. This terminology refers to the embedding into higher-dimensional space, see [21, 2, 67] and the literature quoted therein. In fact, the corresponding phason fluctuations become size-dependent for three-dimensional (3D) quasicrystals. In practice, this means that a grown system shows strong systematic deviations from both ideal structure types (ideal quasiperiodic tilings and equilibrium random tilings) rather than the desired random fluctuations in the phason field alone. The behaviour can be modelled by a classical Ginzburg-Landau-Langevin equation for the coarse-grained phason field \( \Phi(r, z) \), \( z \) being the growth direction, \( r \) the surface coordinates,

\[
\frac{\partial \Phi(r, z)}{\partial z} = D \frac{\partial^2 \Phi(r, z)}{\partial r^2} + \rho(r, z),
\]

where \( \rho(r, z) \) represents a \( \delta \)-correlated noise term and \( D \) is the phason-diffusion constant. This diffusion equation leads to an asymmetry in the fluctuations of the phason coordinates and hence in the spectral density. The intensities of the Fourier spectrum of a grown 3D quasicrystal thus show a power-law decay, the fluctuations of the internal coordinates diverge logarithmically. Altogether, one ends up with an effective “\( D-1 \) model”, i.e., the system grown in \( D \) physical dimensions behaves like a \((D-1)\)-dimensional equilibrium system. For details, we refer to [59], an overview is given by Henley [21].

Most of the growth models discussed below belong to this class. Although divergent phason fluctuations have been reported for relatively-poor-quality quasicrystals, this is clearly not the case for very-high-quality quasicrystals. On the other hand, the quality of even the best samples benefits from annealing procedures, which means that internal rearrangements over time, after the quasicrystal is first grown, tend to increase the structural order. A possible scenario to avoid diverging phason strains is discussed in Sect. 7.

### 4. Atomistic Growth Models

Envisaging physical growth, the simplest model description grows a cluster atom by atom, for instance by a diffusion-limited aggregation process. In view of the peculiar properties of quasiperiodic structures, this approach appears to be problematic, because it is difficult to find simple assumptions (for example on interaction potentials) that will result in the growth of a quasicrystal rather than a periodic or a disordered structure. Monte Carlo investigations hint at the possibility of stable quasicrystalline order, see e.g. [68] for a two-component system with Lennard-Jones pair potentials. In fact, the models discussed below solve the problem by restricting the possible positions where new atoms may be added to the growing cluster, in this way...
trying to enforce non-crystallographic symmetries or, at least, preventing simple periodic arrangements. In some cases, these assumptions may appear rather artificial and hence unphysical. Clearly, as for all models based on random aggregation processes, one cannot expect to grow ideal quasiperiodic systems, but rather more or less disordered structures; and the degree of disorder present in the grown samples gives a first test of the relevance of the model.

The earliest model of this kind was inspired by the binary decoration of Penrose rhombs with two sizes of atoms. Equilibrium states of this system had been studied by Lançon et al. [40] and by Widom et al. [68]. Minchau et al. [43] and Szeto and Wang [66] consider a very simple growth model where atoms may stick to certain positions determined by the tile decoration of [40]. After being added to the growing cluster atoms remain frozen at their positions. The growth is forced to proceed “layer by layer”, new positions being taken into consideration only after a full surface layer has been completed. The possible sticking places for atoms are ordered according to an energy that is a sum of pairwise contributions from neighbouring atoms (“growth-priority parameters”), the available sites being filled successively according to this ordering. In this way, the only freedom occurs when several such places are degenerate in energy, in which case a random choice is made. As one might expect from such a simplistic model, the outcome is not very close to a realistic quasicrystalline structure. In most cases, the growing cluster generates “tears”. However, as shown in [66], for certain ranges of the energy parameters the layer-by-layer growth results in dense structures without holes or tears (Szeto and Wang [66] refer to these as “perfect structures”, a term that we want to avoid since it is prone to misinterpretation). However, these grown samples resemble multiply twinned crystalline structures much more than quasicrystals, showing huge local anisotropies.

The growth model by Olami [48] follows a somewhat different strategy. It starts from a small cluster of points from an ideal quasiperiodic set, which in this case was not the Penrose tiling, but a simpler pentagonal tiling obtained by projection. In such a finite patch, there will be straight lines in the pentagonal directions (“pentagonal lines”) that pass through a number of points in the set. As possible positions of new points only intersections of such pentagonal lines are considered; and a point is added on a randomly chosen intersection of pentagonal lines if, in fact, it falls on at least four lines. In addition, there is a rule that avoids short distances, discarding the point with the smaller “line number” if a new point comes too close to an existing point in the set (in the case that the maximum number, i.e. five, pentagonal lines pass through both points, both are kept). These growth rules are fully local, depending only on the environment of a chosen point up to a distance that is at most \( \tau^3 \) times the minimum distance of two points along a pentagonal line in the ideal structure (\( \tau \) is the golden mean). Provided one starts with a sufficiently large initial cluster (of about 30–100 points), one can grow large
patches with rather small fluctuations in the phason coordinates, resulting in very narrow diffraction peaks in the Fourier transform. Furthermore, the phason fluctuations grow extremely slowly with increasing system size, and the numerical data from five grown patches with up to $2 \cdot 10^4$ points suggest that they may stay bounded. Finally, Olami [48] points out that, in principle, a similar growth procedure could also be applied to the Penrose tiling. Due to the more complex shape of the acceptance domain one expects that grown patches will have larger disorder than in the simpler pentagonal case.

![Fig. 4.1. View along a threefold axis of a DLO grown cluster of about one million atoms (courtesy of V. Dmitrienko).](image)

As the last example is this category, we discuss the dodecahedral local ordering (DLO) model of Dmitrienko and Astaf’ev [7] for the growth of icosahedral quasicrystals. Here, DLO means that all closest neighbours of an atom are positioned at a subset of the vertices of a regular dodecahedron. Such a local ordering may result from a close packing of two kinds of atoms with different sizes. Again, atoms once stuck to the cluster are frozen and cannot move or be removed from the growing cluster. Starting from a seed of about 3–50 atoms, trial positions at all vertices of regular dodecahedra around all atoms are taken into account. The position for a new atom is then selected by an energy that is a sum of contributions for each atomic bond, depending
only on atomic distances. Dmitrienko and Astaf’ev [7] chose their energy parameters such that frustration between short- and medium-range interatomic forces results, mimicking oscillating interatomic potentials. In this way, the growth of crystalline structures is suppressed. Although the energy of a position can be obtained locally, the whole surface must be inspected to find the position of minimal energy. Fig. 4.1 shows an example of a large cluster grown with these rules. The obtained samples are faceted, they have a face-centered icosahedral structure, and their phasonic disorder depends on the particular interatomic potentials.

5. Algorithmically Motivated Cluster Growth Models

The importance of clusters for the understanding of the structure and the physical properties of quasicrystals was recognized immediately after their discovery; but particularly over the past few years there have been increasing research activities on a cluster-based description of quasicrystals, see e.g. [28, 31, 9]. While, at first, this may seem to be in conflict with the tiling picture, this is clearly not the case. On the one hand, one may decorate tilings such that certain atomic clusters predominate the local arrangements of atoms. On the other hand, at least some quasiperiodic tilings, as for instance the Penrose tiling, can alternatively be described in terms of a covering of space by a single cluster, see [10, 19, 20]. That is, in contrast to the tiling picture, only a single tile is used, but different kinds of overlaps may occur. For the example of the Penrose tiling, it has been shown that a suitable restriction on the possible overlaps of regular decagons is in fact equivalent to the perfect matching rules. The corresponding picture of a quasicrystal is physically very attractive as one may imagine the quasicrystal as sort of a densely-packed conglomerate of very stable clusters. Recently, it was argued that a quasicrystalline structure may even result from a maximization of certain cluster configurations (see [15, 63, 32, 23]), which may also give some new insight into quasicrystal formation. The growth models considered here are of a different nature – they are based on the addition of single “atoms” guided by conditions that certain cluster configurations have to be completed. In this sense, they are in fact “atomistic” models. However, the role of clusters as the fundamental entities of the structure is strongly pronounced, which is the reason why we want to consider them separately.

The first model we want to mention here, the so-called decahedral-recursive (DR) model, was considered in a series of papers by Romeu and coworkers [56, 1, 57]. In a sense, this model bears some similarity to the DLO model [7], but it is more closely tied to the cluster idea. The growth according to the DR model proceeds in two steps. First, there is a “decahedral stage”, in which atoms are added to an initial seed (which the authors chose to be magic number clusters of atoms, known to be particularly stable) such that they complete irregular decahedra (pentagonal bipyramids).
This process is carried out with atoms of one size until, due to geometric frustration, it becomes necessary to use a second type of somewhat (about 5%) smaller atoms, hence at least two atomic species are required. Note that frustrations necessarily appear due to the different lengths of the edges and the outer radius of an icosahedron (dodecahedron). During this growth, certain atomic positions (“O points”) on the surface occur that may act as new nucleation centers. These are located at the center of (distorted) icosahedra. These O points have the property that, shifting the whole cluster into them, a large number of coincidences are created. This is exploited to enlarge the cluster further (discarding overlapping atoms), until one arrives at particular O points (“nodes”) which give rise to a larger percentage of coincidences than others. The cluster obtained in this way is considered the “basic cluster” of the structure, and further growth proceeds by shifting this basic cluster into its nodes that maximize the fraction of coinciding atomic positions. Thus, the grown structure may be thought of as a packing by overlapping copies of the basic cluster. The DR model can, in principle, lead to quasicrystalline (in particular decagonal and icosahedral) and to crystalline approximant structures, depending heavily on the initially chosen seed. The DR growth process can be interpreted in terms of a cut-and-projection scheme with a peculiar window function, and the diffraction pattern of DR structures consists, in general, of Bragg peaks together with a diffuse background.

The second model in this category, proposed by Janot and Patera [29] recently, is much simpler than the DR model. Here, growth commences from a given seed which determines a “star” of atomic bondings, for instance a decagonal star if the initial cluster is a decagon with one atom in its center. This vector star then defines the only possible translations, relative to the surface atoms, for adding new atoms to the cluster. Growth through the star short-distance scheme (SSDS) then proceeds as follows. Choosing an arbitrary surface atom, atoms forming a shifted copy of the basic initial cluster are added around it. Those of the new atoms that are too close to already existing sites (the allowed minimum distance is a parameter of the model) are rejected. Due to the randomness in the choice of the surface atom, this leads to a family of slightly different structures. Details on the possible structures, and their dependence on the choice of the star and the short-distance threshold are still to be investigated; but it was already shown that also twinned crystals may result.

6. Physically Motivated Cluster Growth Models

While the previously presented models use structureless “atoms” to build up the growing cluster, we now turn to models whose building blocks already contain information about the symmetry. More specifically, the orientational models discussed below are random arrangements of symmetric
building blocks (regular decagons or icosahedra) subject to certain constraints on relative orientations and distances.

The idea of such a model goes back to Shechtman and Blech [60]. They tried to explain the observed diffraction patterns of icosahedral quasicrystals by describing their structure as random packings of icosahedra, joined along their edges or at their vertices while preserving orientational symmetry. Albeit their clusters were rather small (containing about 1000 icosahedra), the computed diffraction pattern of the vertex-connected random packing gave reasonable qualitative agreement with experimental results.

This idea was followed up by Stephens and Goldman [65] (see also the review article by Stephens [64]). Besides vertex- and edge-connected “icosahedral glasses”, they also considered face-connected packings. In particular, they investigated the size-dependence of the peak widths, performing simulations of up to 109,454 sites in a sample of cubic shape. The intrinsic peak widths they obtained turned out to be very small and comparable to those observed experimentally for icosahedral AlMn. For the majority of peaks, the cluster size was still insufficient to resolve the internal width.

Though these results look quite encouraging, Robertson and Moss [55] point out that these simple models based on non-interpenetrating random packings of clusters are unrealistic in several aspects. First, their density is far too low — only about 60% of the bcc packing density. Another, unrelated problem is the low, filamentary connectivity of the cluster network. Even reasonably connected networks were found to be broken up by “tears” into domains. Accordingly, the phason components behave rather irregularly, and there is a large increase in the phason fluctuations with growing patch size. Finally, the peak positions and the peak shapes calculated from the grown samples do not agree with experimental powder diffraction patterns of high-quality quasicrystals.

Clearly, to improve the situation, one wants to increase connectivity and suppress the generation of tears. Prior to Robertson and Moss [55], Elser, in a series of papers [12, 13, 14], and Nori et al. [47] had already discussed a scenario that strongly improves the quality of the grown clusters. The main idea, first introduced by Elser for a 2D random packing model of regular decagons [12], consists in introducing a finite temperature into the growth process, thus allowing rearrangements close to the surface of the growing sample. More precisely, Elser distinguishes a “growth region” with a non-uniform temperature field, and a “frozen” region where no further rearrangements are allowed. A lattice gas Hamiltonian with pairwise interactions, including a next-nearest-neighbour term, was chosen to facilitate the formation of nicely connected networks. In particular, the allowed cluster-neighbour relationships were taken from observed approximant phases. The quasicrystal was grown, starting from a single seed, by moving the growth region with its linear temperature profile with constant velocity, and applying a Monte Carlo procedure to the lattice gas Hamiltonian. The whole procedure eas-
ily translates to the icosahedral case, and the simulations of Elser [13, 14] show that this growth mechanism, with suitable choices of the parameters, produces well-packed, icosahedrally ordered structures with intrinsic phason fluctuations that are in good agreement with the behaviour of peak widths observed in diffraction experiments. However, due to the anisotropy of the growth conditions, a small but finite phason strain cannot be avoided.

A somewhat different route was followed by Robertson and Moss [55], imposing additional local constraints on the neighbourhood of an icosahedron, in this way trying to suppress the formation of tears and to increase the connectivity. The main idea consists in allowing a cluster to have only a discrete set of neighbour distances within its local environment of a certain size. By suitably tuning their parameters, Robertson and Moss reach packing fractions and connectivities that are comparable to Elser’s, but they also find a remaining phason strain that does not seem to vanish with increasing system size.

Finally, we would like to point out that facet formation is not a domain of crystals or ideal quasiperiodic tilings but may also occur in random tilings and certain classes of bond-oriented glasses (see [25, 26, 24, 41] for discussions of the possible $T = 0$ equilibrium shapes of systems with icosahedral symmetry). Some simple examples are shown in Fig. 6.1.

7. Random Tiling Growth Models

Soon after ideal quasiperiodic tilings came into fashion as geometric models of quasicrystals, Elser [11] pointed out that one may relax the mathematical
constraints of these tilings without losing their most important features, as for instance their sharp diffraction peaks. This remark led the way to the so-called random tiling theory (see [21] for an overview) where tiles are packed randomly without gaps or overlaps. In a hydrodynamic description, elastic constants and configurational entropy were introduced. The new degrees of freedom were (in analogy to modulated crystals) called phasons, which are long-wavelength modes of the orthogonal coordinates of the quasicrystal. The difference between the physical properties of these random tilings compared to those of the ideal quasiperiodic ones – although mathematically essentially different – are so small, that even today it is hard to distinguish between them experimentally, see [3, 4, 34, 36]. The local character of the random tiling scenario made it attractive to growth modelling, having in mind a cluster decoration of the tiles or the vertices.

Inspired by the structural similarity between the dodecagonal and the $\sigma$ phase of VNi and VNiSi alloys (which can be described as a periodic net of squares and equilateral triangles), Kuo et al. [39] considered a growth model of dodecagonal quasicrystals based on the same building blocks, i.e., a square-triangle random tiling. The ensemble consists of squares and equilateral triangles only, see [52]. The growth process proceeds in attaching complete tiles to a seed following three rules: (1) only the two tiles considered above are used, (2) squares prefer triangles on all sides, and (3) when two triangles face each other they are surrounded by four squares. Whereas rules (1) and (2) – according to the authors – yield a modified random tiling with motifs very similar to those found in high-resolution transmission electron microscopy (HRTEM) images of dodecagonal phases, the addition of rule (3) results in a periodic $\sigma$ phase.

In order to obtain a 3D icosahedral random tiling with two linkages and a high packing density, Henley [22] developed the so-called canonical cell tiling (CCT). Its tiles are two irregular tetrahedra, one irregular square-pyramid and one equilateral prism. Unfortunately, the CCT is much harder to treat than the primitive icosahedral tiling [38]. Motivated by transfer matrix techniques, Newman et al. [45] introduced a method to produce towers of CCTs with periodic boundary conditions in two dimensions. The tower construction resembles a growth model. Starting on a layer of canonical cells which span the entire cross-section, new vertices of the canonical cells are constructed, without gaps or overlaps, respecting the boundary conditions. In order to avoid wrong moves and to save computer time, preference was given to the deepest lying vertex (w.r.t. the surface). For the majority of such growing surfaces, there is at least one move that is forced by the surrounding geometry. Following the forced moves, one ends at locally dead surfaces where every crevice can be filled at least in two different ways. Here, one has to make a choice to proceed. The surface is only locally dead, i.e., in some cases one ends up with a defective vertex later on. The catalogue of these dead surfaces is the key feature to derive estimates for the elastic and entropic properties of
the CCT, see [44]. The appearance of forced moves and dead surfaces reminds one of the growth algorithm for the ideal Penrose tiling described in Sect. 2. However, the canonical cells do not have matching rules, and their possible arrangements contain a finite entropy density.

Motivated by the question how close one can approach an equilibrium random tiling via a growth process, Joseph and Elser [35] took a different approach to the square-triangle random tiling. To every vertex $i$ of a tiling, two variables are associated: a uniform chemical potential $\mu$ and an angle variable $\Omega_i$. The chemical potential describes the energy difference of a bulk vertex relative to the liquid/vapour phase. The angle $\Omega_i$ mimics the influence of the surface: it is nothing but the portion of the full angle around a vertex that is covered by already completed tiles. Both enter a simple Hamiltonian

$$H = \sum_i (\mu - \Omega_i), \quad (7.1)$$

where the sum extends over all vertices of the tiling. In this way, each bulk vertex has an energy $\mu - 2\pi$, whereas surface vertices have energies $\mu - 2\pi n/12$ with $n = 0, 2, 3, 4, \ldots, 9$ (the case $n = 10$ does not occur because the “missing” triangle is always complete, and hence the corresponding vertex belongs to the bulk). Attaching or removing vertices gives rise to a change in bulk and surface energies. The system will try to minimize its surface with respect to the bulk. Using (7.1) as a penalty function in a Monte Carlo simulation, the authors proposed the first reversible growth model with a fluctuating surface, i.e., vertices may be attached or removed, and detailed balance is always fulfilled. In the case of the square-triangle tiling, the geometric constraints were minimal: the minimal distance between vertices is given by the bond length, and completed tiles may only be squares or equilateral triangles, while their relative frequency may vary freely.

Starting from a seed, on the plane or a cylinder, Joseph and Elser [35] derived a growth/melting boundary of the form $\mu = 2\pi + TS_0$, where $S_0$ is the entropy of the equilibrium system. The temperature $T$ enters the simulation through the Boltzmann factor of the Monte Carlo simulation. In this way, it is possible to measure equilibrium properties of a system via a non-equilibrium process like growth. For a given temperature $T < 2\pi/3$, the system develops tears for all $\mu < 2\pi + TS_0$; and their separation $\lambda_{\text{tear}}$ follows a scaling law

$$\lambda_{\text{tear}} \sim (2\pi + TS_0 - \mu)^{-1} \quad (7.2)$$

that is predicted by a phason instability at the surface. Furthermore, the model shows that the asymmetry in the phason fluctuations (see Sect. 3) vanishes when approaching the growth limit. Therefore, in the limit of vanishing growth velocities (i.e., $\mu \to 2\pi + TS_0$), it is possible to produce a grown random tiling that is, on a given length scale, indistinguishable from a member of the equilibrium ensemble. When approaching the growth limit, the system must exploit all its entropy to grow at all. Thus, it must align its phason strain closer and closer to zero. In practice, the system is growing and
retreating repeatedly until large, accidental phason fluctuations are erased. Using this property, even the modelling of surface annealing is possible, see [33].

Fig. 7.1. The unrestricted tenfold rectangle-triangle tiling grown according to the model of Joseph and Elser [35] at temperature $T = \frac{\pi}{2}$ with chemical potential $\mu = 2\pi + 0.160\pi/2$ (rapid growth). For this case, the growth/melting boundary is $\mu \approx 2\pi + 0.175\pi/2$ [17].

The extension to other tilings is straightforward. In Figs. 7.1 and 7.2, we show two cylindrical patches of the unrestricted tenfold rectangle-triangle random tiling (see [5]), grown at different growth velocities. Although this tiling ensemble can be treated by Bethe-ansatz methods [17], it has not yet been understood in terms of the conventional random-tiling description, see [53]. On the other hand, a restricted (binary) version of this tiling, which is used to model the decagonal phase of AlPdMn [53], can be treated with random tiling theory without problems. However, it shows a growth instability due to its binary restriction which acts as a non-local constraint on the tiling ensemble [33]. Hence growth without leaving the ensemble appears impossible.
The model of Joseph and Elser [35] shows that, in principle, there is no need for collective bulk rearrangements after growth and that uniform phason strains can be made arbitrarily small on macroscopic length scales. Usually, bulk rearrangements (in the form of flips, zippers, . . .) are needed to approach equilibrium, but they can be kinetically very slow.

Fig. 7.2. Same as in Fig. 7.1, but this patch was grown slowly at a chemical potential $\mu = 2\pi + 0.174\pi/2$.

8. Concluding Remarks

To date, it is fair to state that the growth of quasicrystals has not been understood, and there is still a lot of work to be done in order to arrive at a physical picture of the growth process that can account for the experimental observations. It appears impossible to grow ideal quasiperiodic structures by purely local algorithms without incorporating a certain amount of defects. The structure of quasicrystals may be better described in terms of random
tilings (or other models including a stochastic component), which points at the importance of entropic contributions in the formation of quasicrystals.

As we have demonstrated, there are a number of different approaches towards an understanding of quasicrystal growth. Most models concentrate on the question of how quasiperiodic order is established, using a greatly simplified set of degrees of freedom. Clearly, some remnants of the orientational symmetry are already implicit in all these models, for instance by allowing only certain atomic positions or directions of atomic bonding. In this sense, the long-ranged orientational order in the grown samples is not surprising. What one really would like to see is a more pronounced order of atomic positions that can account for the sharp diffraction peaks observed in experiments. The question whether quasicrystals can be grown by local deposition of atoms of different species or by attachment of pre-formed clusters alone remains to be attacked.

Almost all models discussed above employ non-reversible dynamics in their growth algorithms. Usually, this is said to be motivated by the rapid quenching processes used to produce quasicrystals, particularly in the early days (many quasicrystals are still produced by melt-spinning, with quenching rates of about $10^5$K/s, but these samples contain many defects; and only after annealing at about 20–50K below their melting point, they become “good” quasicrystals). However, the current picture of growth for crystals suggests diffusion and fluctuation processes on the surface during growth. There is no reason to believe that quasicrystals are different in this respect. In our view, this is probably the reason why most of these models suffer from large anisotropies or phason fluctuations, creating structures that are far from ideal quasicrystals or equilibrium random tilings. Introducing temperature, and allowing reorganization to occur at least at the surface, the growing bulk is given the possibility to reconnoiter the configurational phase space, making full use of its entropy. In this way, structures that resemble equilibrium random tilings may be realized by a physical growth process.

Finally, we emphasize that the inflation properties of quasiperiodic structures allow, in principle, for several physical interpretations of these models (e.g., “atoms” in what we call atomistic models may be thought of as real atoms, but equally well may be considered as clusters containing groups of atoms, or even clusters of such clusters). Thus, also rather simplistic models might well capture the important ingredients that render possible the formation of quasicrystals.

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Note added

After completion of this review, Dmitrienko et al. [8] published a modified version of the growth model discussed in Sect. 4 [7]. They replaced the non-local energy minimization by a local Monte Carlo step.

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