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TUTORIAL REVIEW

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Why are quasicrystals quasiperiodic?
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In the past two decades significant progress has been made in the search for stable quasicrystals, the determination of their structures and the understanding of their physical properties.

Now, quasiperiodic ordering states are not only known for intermetallic compounds, but also for mesoscopic systems such as ABC-star terpolymers, liquid crystals or different kinds of colloids. However, in spite of all these achievements fundamental questions concerning quasicrystal formation, growth and stability are still not fully answered. This tutorial review introduces the research in these fields and addresses some of the open questions concerning the origin of quasiperiodicity.

1 Introduction

The first intermetallic compound identified as quasicrystal (QC)† was a rapidly solidified metastable Al–Mn phase with icosahedral diffraction symmetry.‡ Dan Shechtman obtained it on 8 April 1982 employing the melt-spinning method, which allows the quenching of melts within milliseconds. A few years later, it was shown that less rapidly solidified Al–Mn forms a metastable decagonal QC (DQC). Only in the case of even slower cooling rates a stable phase forms, which is periodic then.§ The faster crystallization of the icosahedral QC (IQC), compared to the periodic phase, was explained by its lower nucleation barrier because in the melt it is already existing in the icosahedral short-range order.¶ However, the easy nucleation of clusters with icosahedral symmetry does not necessarily imply quasiperiodic growth. The existence of QC approximants clearly demonstrates that the same kind of structural subunits (in the following called ‘cluster’⁷,⁸ or ‘quasi-unit cell’) can basically constitute both quasiperiodic and periodic structures.

In the year 1985, the first stable QC was identified in the system Al–Cu–Li,¹⁰ which has been overlooked in previous studies. This discovery showed that quasiperiodic order can be a thermodynamic equilibrium state of matter and motivated a systematic search for other stable QC in intermetallic systems, guided by certain expected valence-electron/atom ratios and the existence of approximants, if any.¹¹ The strongly differing compositional stability fields of the mostly ternary QC found so far are shown in Fig. 1.

The temperature stability ranges are differing largely as well, from a few to several hundred degrees. Unfortunately, due to the sluggish kinetics of phase transformations of intermetallics at low temperatures, it cannot be decided whether or not the quasicrystalline ordering state can be a ground state of matter.

Quasiperiodic structures and approximants have also been observed in some less metallic materials such as rapidly solidified borides¹³ or conventionally synthesized tellurides.¹⁴ However, in both cases particular preferred structural subunits favor random-tiling-like arrangements with non-crystallographic 10- and 12-fold symmetry, respectively.

In recent years, also an increasing number of ‘soft quasicrystals’ have been identified with self-assembled quasiperiodic structures on the mesoscale. Examples are supramolecular dendrimer liquid QC (LQC),¹² ABC-star terpolymers¹⁶ and surfactant-coated metallic nanoparticles in solution.¹⁷ Furthermore, forced quasiperiodic structures have been found for polystyrene particles

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† Originally it was called ‘icosahedral phase’, the term ‘quasicrystal’ was coined in 1984 by Levine and Steinhardt: “A quasicrystal is the natural extension of the notion of a crystal to structures with quasiperiodic, rather than periodic, translational order”. As described in Section 2.2, we focus on QC with non-crystallographic symmetry.

‡ Part of a themed issue on Quasicrystals in honour of the 2011 Nobel Prize in Chemistry winner, Professor Dan Shechtman.

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Every single atom tries to take on its energetically most favorable atomic environment type (AET) at the same time, which not only constrains the formation of the preferred AET of atom X with that of the neighboring atom Y, which is already part of the AET of X, but also all these individual AET can be geometrically very unfavorable for packing them space-filling in a crystal structure.

The simplest cases, where every atom has exactly the same AET, are the cubic and hexagonal close-packed structures. They have the highest possible coordination for equal spheres as well as the maximum space filling, locally and globally. However, much less metallic elements than one may expect crystallize in such structures, in particular, at higher pressures. The reason is anisotropic interaction potentials caused, for instance, by covalent bonding contributions, particular electronic and/or magnetic interactions and/or specific phononic contributions to entropy.

Crystal-chemical (atomic interactions) and geometrical constraints (stoichiometry and atomic size ratios) for structure formation can become quite complex in the case of multinary intermetallics. This limits the number of different compounds that are possible in a given intermetallic system. Indeed, this number decreases drastically going from binary to ternary or even higher multinary systems. The more complex the stoichiometry of an intermetallic compound becomes, the larger the number of different AET becomes and the more difficult their packing. Metastable metallic glasses (amorphous metals) represent the cases where all the irregular AET already present in the melt of a multinary alloy cannot be properly modified on the timescale of solidification for achieving lro. Thermal equilibration then usually leads to phase separation, where the individual phases have rather simple structures.

Complex structures of intermetallic phases frequently show larger structural subunits (‘clusters’), each of them constituted by several AET. The cluster formation can drastically reduce the number of different structural units to be optimized for packing (see, e.g., Dshemuchadse et al.25). Clusters are usually of higher symmetry than their constituting AET and their chemical composition is also closer to that of the compound. For an example see Fig. 2, where the cluster structure of the cubic 2/1-approximant \( \text{Cd}_{56}\text{Cd}_{13} \) of the Tsai-type IQC is shown together with the cluster-constituting \( \text{CaCd}_{16} \) polyhedron.

In the case of entropy-driven substitutional (chemical) and/or displacive disorder, individual AET may become strongly distorted. In contrast, structural disorder can be easily accommodated in inner cluster shells without influencing the way of cluster packing. Another kind of disorder is caused by phason fluctuations, i.e., low-energy excitations in QC that lead to short-distance atomic jumps in double-well potentials (see Fig. 3(c)). With a few of them correlated, virtual jumps of whole clusters can result (see Fig. 9 of Coddens and Steurer27). To an extent, this kind of disorder (‘phasonic disorder’) can result in random-tile-like structures, where energy differences between allowed and forbidden tile configurations (in ideal quasiperiodic tilings) are overcompensated by the entropy gain.

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§ Roger Penrose, the creator of the quasiperiodic Penrose tiling, reminisces: ‘’...in the late 1970s and early 80’s I had often been asked to give lectures on these tiling patterns, and a question frequently posed to me after the lecture might be: ‘Does this not mean that there is a whole new area of crystallography opening up, with pentagonal and icosahedral symmetry allowed?’ My normal response would be: ‘In principle yes; but how on earth would Nature do it?’...the spontaneous growth of large regions of such quasi-crystalline five-fold symmetric substances had seemed to me virtually insurmountable.’”

Fig. 1 Compositional stability fields of (top) decagonal and (bottom) icosahedral QC (adapted from ref. 12). Note the different concentration ranges of the diagrams.
The QC-constituting clusters usually show ‘non-crystallographic’ 5-, 8-, 10- or 12-fold rotational symmetry. The densest possible packings of such clusters can be derived employing the higher-dimensional approach (see Section 2.2). Here, the basic underlying idea is illustrated on the example of a simple 1D quasiperiodic structure, the Fibonacci sequence (FS), and its approximants (Fig. 3). The vertices of the FS are separated by distances \( L \) and \( S \), with \( L = \tau S \). If the composition of the FS or an approximant differs from that of its constituting cluster, then it is obvious that it can only be achieved by allowing S-type overlaps. For the derivation of the sequence of overlaps that leads to the smallest deviation of the local from the global stoichiometry, we use the fact that the cluster (LS) can be obtained by the projection of the edges of a square in the strip-projection method. The projection of the sequence of vertex and edge connected shaded squares shown gives the FS plus some additional vertices (gray) at (phason) flip positions in a double-well potential (c). The width \( W \) of the strip defines the minimum distance between projected lattice points as well as the unit tile sequence; in our case, \( W \) is chosen so that the lowermost (gray) vertex of the yellow square is outside the strip. (d) A perp-space shear of the lattice (indicated by the arrow at right) leads to the \((LSL)\) approximant (modified from Steurer and Deloudi28).

Contrary to the structures of hard QC, those of soft QC are not cluster-based and follow other self-assembly mechanisms (see Section 4). Soft QC usually consist of just one type of building element such as micelles or other colloidal particles. In order to get something more complex than dense sphere packings, these ‘mesoscopic atoms’ must have complex interaction potentials providing two length scales, for instance. In the case of ABC-star terpolymers, additionally the stoichiometry \( A_B C \) plays a role for the kind of structure formed by the minimization of the interfacial area between the immiscible polymers \( A, B \) and \( C \).

Due to the specific interaction potentials on the mesoscopic scale, the resulting self-assembled quasiperiodic structures all show dodecagonal diffraction symmetry in contrast to the 5-fold symmetry prevalent in hard QC. The tetrahedrally close packed (tcp) structures resemble decorated random square–triangle tilings. Amazingly, simulations of dense packings of hard tetrahedra29 and trigonal bipyramids30 show dodecagonal diffraction symmetry and random-tiling-like arrangements of the polyhedra centers as well.

2.2 Structural description of quasicrystals and their rational approximants

Quasiperiodic structures are defined as having Fourier modules of rank \( n > d \), with \( d \) being the dimension of the structure. This definition includes incommensurately modulated structures (IMS) and composite structures (CS) with crystallographic symmetries, as well. Since IMS and CS can be described referring to one or more \( dD \) periodic basic structures, they are fundamentally different from quasiperiodic structures with non-crystallographic symmetry. Consequently, we mean by QC only those quasiperiodic structures that have non-crystallographic symmetry.

The classification of QC is based on their diffraction symmetry (\( N \)-fold axial symmetry or icosahedral symmetry), on one hand, and the type of clusters they consist of, on the other hand. In the case of IQC, the three different structure types are based on Mackay-, Bergmann- and Tsai-clusters, respectively. In the case of DQC, we distinguish between structures with 2-, 4-, 6- or 8-layer periodicity, and whether they are Al-based or of...
the Zn–Mg–RE (RE=rare earth element) class. The latter are related to the Frank–Kasper phases.

Basically, there are two ways of describing the structure of QC and their rational approximants (for a short introduction into the crystallography of QC see the review of Steurer and Deloudi, for instance, and for a comprehensive textbook see Steurer and Deloudi). The tiling- or ‘quasilattice’-approach, on one hand, is similar to the description of periodic structures by lattices decorated with atoms. In contrast to lattices, quasilattices have at least two different ‘unit cells’ (prototiles) that can be decorated by atoms or clusters (Fig. 4).

Partially overlapping ‘covering clusters’ allow us to describe the full quasiperiodic structure even by one type of cluster (‘quasi-unit cell’). In the case of the FS, the covering cluster corresponds to the sequence (LS) (Fig. 3), in the case of the Penrose tiling, the Gummelt decagon plays this role (Fig. 4 and 5).

The higher-dimensional or $nD$ approach, on the other hand, allows us to describe $dD$ quasiperiodic structures based on periodic $nD$ hypercrystal structures ($n > d$). The $nD$ embedding space, $V = V' \oplus V'$, consists of the $dD$ physical or par(allel) space $V'$ and the $(n - d)D$ perp(endicular) or complementary space $V'$; $n$ corresponds to the rank of the Fourier module of the QC, i.e., the number of reciprocal basis vectors needed to index the reflections of a diffraction pattern with integers only. There are two equivalent methods, the strip-projection method and the embedding method. In the strip-projection method, illustrated in Fig. 3, those nodes of an $nD$ lattice are selected by a strip that give a quasiperiodic tiling, when projected onto the par-space. The width $W$ of the strip results from the projection of one $nD$ unit cell onto then perp-space. The embedding method is based on the description of a $dD$ quasiperiodic structure as the proper irrational section of a periodic $nD$ hypercrystal structure ($n > d$). In reciprocal space, this corresponds to a projection of the $nD$ reciprocal lattice onto the physical space.

Let us assume, now, that we have a 2D decagonal cluster, which can be described by a Gummelt decagon with its specific overlap regions. In a 2D packing, the decagon centers form a subset $T$ of a $Z$-module of rank $n = 5$. Since a $Z$-module of rank 5 can be created by projecting along a 5-fold axis a 5D hypercubic lattice onto 2D par-space, the subset $T$ corresponds to a connected portion of the 5D hypercubic lattice. These relationships are schematically illustrated in Fig. 5. For more details about the $nD$ cluster approach see the study of Steurer and Deloudi.

2.3 Complexity and periodicity versus quasiperiodicity

All experimentally observed intermetallic phases in thermal equilibrium are crystalline, with either periodic or aperiodic crystal structures. They all are characterized by Fourier spectra containing a dominant pure point component (set of Bragg peaks) beside a, usually much weaker, continuous part such as thermal, phason and disorder diffuse scattering.
Before entering the discussion on why particular materials are periodic and others are quasiperiodic, we first try to shortly summarize the benefits of periodicity, which must be enormous because almost all known crystals are periodic. Of course, real structures are never strictly (quasi)periodic, but only on average. In thermal equilibrium, the (quasi)periodicity is broken at least by the finite size of the crystals, thermal vacancies, phonons, and, particularly in complex intermetallics, frequently by structural disorder. However, these deviations from periodicity are usually small compared to interatomic distances.

Periodicity means that the energetically most favorable structural subunit (cluster or unit cell) acts as a building block leading to an energy- and entropy-optimized arrangement of atoms. Moreover, periodicity usually results in, due to the existence of Brillouin zones, simpler electronic band structures with well-defined band gaps.

One measure of the complexity of a structure is its generalized $R$-atlas, which describes the environment of a given atom within a sphere of radius $R$. If each atom in a structure has exactly the same $R$-atlas up to infinity, i.e., the number $N$ of different $R$-atlases equals one for any $R$, then the structure must be periodic and consist of one kind of atoms, only. In the case of a more complex, but still periodic structure, each of the $M$ atoms in the unit cell can have a different $R$-atlas. For the whole infinite structure the number of different $R$-atlases is still finite, $N = M$ for any $R$. In the case of quasiperiodic structures, however, the number of different $R$-atlases grows from $R$ to infinity, even for equally decorated vertices. From this point of view, QC seem to be much more diverse and complex than periodic crystals. According to the parsimony principle, periodic structures should be generally more favorable than quasiperiodic ones, consequently. This is the case, indeed.

However, the real complexity of QC is much lower than indicated by their $dD$ $R$-atlases. It is much more realistically reflected in the $nD$ description, where the number of different $nD$ $R$-atlases gets finite again for any $R$, reflecting the intrinsic correlations present in quasiperiodic structures. For instance, the 6D primitive hypercubic unit cell of the 3D Ammann$||$ tiling in the higher-dimensional description contains just one ‘hyperatom’ resulting in the simplest possible $R$-atlas with $N = 1$ for any $R$. Of course, it is difficult to quantitatively compare 3D and $nD$ $R$-atlases. The qualitative comparison, however, clearly shows that the number of different $R$-atlases is finite for any $R$, in both cases. Moreover, the $nD$ $R$-atlases of QC seem to be much simpler than many of the 3D ones of complex intermetallics.

Although for amorphous structures the $R$-atlases grow from $R$ to infinity, as well, it should be emphasized that QC are not intermediate between amorphous alloys and crystals, they are crystals! Even in the case of thermally equilibrated 3D QC that can be described based on random tilings, the autocorrelation function keeps a discrete part while it is continuous in the case of amorphous materials.

Another measure of complexity for comparing periodic structures is the number of atoms per unit cell, which for almost all structures is much smaller than 400 (Fig. 6). QC could be compared with each other by comparing the complexity of their clusters or quasi-unit cells. However, all QC known so far are of comparable complexity.

The number of intermetallic phases steeply decreases with increasing number of atoms. The small peak at $\approx 450$ atoms per unit cell mainly stems from a set of structures based on close packing of large clusters. There are only a few more structures left with more than 1000 atoms per unit cell. The so far largest structure of an intermetallic phase contains 23,134 atoms in its cubic unit cell with lattice parameter $a = 71.490 \text{ Å}$.35

The steeply decaying frequency distribution can be interpreted by decreasing benefits of periodicity with increasing unit cell dimensions, while the costs of maintaining periodicity, by packing more and more different AET, increase. Benefits of small unit cell periodicity are simple construction plans based on the packing of only a small number of different AET, a diffraction pattern with a high fraction of strong reflections indicating the existence of well-defined atomic layers parallel to lattice planes, repeating themselves with small distances.

The limits of the complexity of intermetallic crystal structures are also indicated by the number of binary, ternary and quaternary intermetallic compounds known so far. From a combinatorial point of view, the number of different crystal structures should increase going from binary to higher multinary intermetallic systems. The opposite is true as already mentioned in Section 2.1. There are only a few truly quaternary phases known, which are not just superstructures of ternary or binary phases such as some Heusler phases or metastable ternary phases that are stabilized by the addition of a fourth element. Similar to that in the case of intermetallics with odd chemical compositions

Fig. 6 The number of intermetallic phases (on logarithmic scale) as a function of the number of atoms per unit cell (bin size 10). The data of the $\approx 43,000$ compounds have been extracted from Pearson’s Crystal Data43 (courtesy of J. Dhshemuchadse). Approximately twenty compounds with more than 1000 atoms have been omitted from the histogram to save space.

|| Also known as 3D Penrose tiling.
(complex stoichiometry, strongly differing atomic radii), in multinary phases many different AET are necessary to reach, on average, the global chemical composition; and the more different AET exist the more complex become their packings and the larger the resulting unit cells.

Periodicity has to be strongly disfavored in order to get a structure that is quasiperiodic or amorphous. How can this be achieved? One way is by mixing several elements with strongly differing atomic radii and rather rapid solidification of the melt in order to avoid phase separation and crystallization; thereby, amorphous materials can be obtained. Another way is to choose elements forming endohedral clusters with non-crystallographic symmetry whose densest packing is quasiperiodic (see Fig. 5). These clusters must be energetically favorable and they must allow specific cluster overlaps. Furthermore, electronic stabilization of the structure seems to be beneficial if not necessary.

An important feature, and used for the definition of crystals, is that both $\mathbf{dD}$ periodic and quasiperiodic structures show pure point (Bragg) spectra, corresponding to Fourier modules of rank $n$. In the case of a periodic structure the rank equals the dimension, $n = d$, in the case of a quasiperiodic structure it is larger, $n > d$. The Bragg reflection density is finite in the first case and infinite in the second. Related to the Bragg reflections in reciprocal space, in quasiperiodic structures a framework of ‘quasilattice planes’ exists, which can be seen as interfaces between adjacent parts of the structure (see Fig. 4 and 7). In the case of quasiperiodic structures, the non-crystallographic symmetry of the fundamental clusters coincides with the framework of quasilattice planes (see Fig. 7). In the case of its periodic approximant this is not the case.

The atomic layers on the quasilattice planes are important for the existence and propagation of phonons and of electron (Bloch) waves. Flat atomic layers correspond to strong Bragg peaks and therewith to well defined Brillouin zones; puckering decreases the intensity of Bragg peaks. Atomic layers also make possible faceted 3D crystal growth: all facets that grow at the same time independently from each other always fit together where they meet forming the crystal edges. The framework of atomic layers connects $\text{IRO}$ with $\text{LRO}$, and the internal symmetry of clusters with the global symmetry of the infinite structure.

In random-tiling based soft QC, quasilattice planes do not exist; however, this does not play a role for the entropy-driven ordering of LQC.

It is quite easy to transform a QC with non-crystallographic symmetry into a structurally closely related aperiodic structure with crystallographic symmetry. In reciprocal space, the respective distortion of the quasiperiodic structure corresponds to a change in the angles between the basis vectors. This kind of transformation does neither change the rank of the Fourier module nor does it make the structure periodic. A rational approximant can be obtained within the $\mathbf{nD}$ approach by a particular shear transformation of the hypercrystal structure (see Fig. 3). Thereby, the rank $n$ of the Fourier module is lowered to $\approx d$. In direct space, this structural phase transformation could be achieved locally by a correlated rearrangement of atoms (for a review see Steurer[26]) leading to a kind of nanodomain structure. It needs a first-order transformation to transform a QC into a periodic structure.

### 2.4 Model calculations

Model calculations are absolutely essential for gaining insight into the factors controlling structure, formation and stability of QC. Most commonly used are classical Monte Carlo (MC) or Molecular Dynamics (MD) simulations employing specific pair potentials for the interaction of atoms or particles (in the case of mesoscopic QC). On a larger hierarchy level, calculations based on tile Hamiltonians[35] have been proven useful for the study of medium range order (mro). Quantum mechanical calculations are computationally more expensive and therefore even more restricted by the model system size, let alone the periodicity conditions always needed. In other words, first principles calculations suffer most from the periodicity conditions because of the small possible model system size of a few hundred atoms per unit cell. Taking into account typical cluster sizes of $\approx 150$ atoms, this corresponds to just a few clusters per unit cell. Consequently, the quasiperiodic $\text{IRO}$, i.e., exactly the property that distinguishes QC from periodic crystals, cannot be modeled properly. With other words, the information obtained from all these calculations refers to approximant model structures and not to quasiperiodic ones.

In classical MC or MD simulations a certain chemical composition and density are predefined. This implicitly forces a particular arrangement of the energetically favorable AET into larger subunits (clusters) as well as a particular ordering of the resulting clusters themselves. Whether periodic or quasiperiodic order results in a lower free energy for a given composition and density depends on the cluster packing optimization rather than directly on pair potentials.
This said, what kind of useful information can be obtained employing the methods mentioned above? First principles calculations can give insight into the local chemical bonding of energetically favorable cluster shells. They can clarify whether structure stabilizing pseudo-gaps in the electronic density of states (eDOS) at the Fermi level originate from hybridization of atoms in the innermost cluster shells or rather from a Hume-Rothery mechanism (Fermi surface nesting). However, it should be kept in mind that this information refers rather to a low approximant than to a quasiperiodic system; furthermore, disorder of any kind is not included in stability calculations of this kind.

Although the model size is rather small, local disorders such as phason flips can be studied quite well in classical MC and MD simulations, which can be based on system sizes up to millions of atoms. The strength of these methods is their capability in investigating the role of pair potentials for the stabilization of clusters and their preferred arrangements, \textit{i.e.}, the local evolution of quasiperiodic order and the kind and role of disorder even as a function of temperature.

In the case of mesoscopic systems MC and MD simulations can give much deeper insight into the self-assembly mechanisms of mesoscopic systems than in the case of intermetallics. There, the interaction potential is given by the structure of the micelles and does only change with density and temperature. For instance, it was demonstrated by \( T = 0 \) MD simulations that even in monatomic systems structures with decagonal and dodecagonal diffraction symmetry can be stabilized if particular double-well potentials are used.\(^{38}\) One has to keep in mind, however, that these were 2D model systems, only.

However, it is important to emphasize that the models that work quite well for mesoscopic systems cannot be directly transferred to intermetallic QC; the underlying mechanisms are too different, in particular the kind of bonding and electronic stabilization. This is reflected in the prevalence of 5-fold symmetry and good quasiperiodic order in the case of hard QC and 12-fold symmetry and random-tiling-like order in the case of soft QC. The pair potential for interactions between micelles is exclusively defined by the individual micelle and fully transferable between different structures. In contrast, due to multibody interactions and the existence of itinerant electrons, the pair potentials of atoms in intermetallic phases strongly depend on the kind and arrangement of neighboring atoms as well as on the structure as a whole.\(^{39}\)

### 3 Intermetallic (‘hard’) quasicrystals

Up to date, stable intermetallic QC could be synthesized as (pseudo)binary or ternary phases with either decagonal or icosahedral diffraction symmetry, only. Furthermore, there is one, probably stable, semimetallic dodecagonal QC known, Ta\(_{1.6}\)Te, with a lubricant-like layer structure,\(^{40,41}\) which can be seen to take an intermediate position between hard and soft QC. Furthermore, a number of metastable octagonal and dodecagonal intermetallic phases have been prepared by rapid solidification techniques.

From their electronic structure, two classes of hard QC can be distinguished, Al–TM (TM—transition metal) based QC where d-orbitals play a crucial role and Mg–Zn based QC (Frank–Kasper type) with s- and p-electrons dominating metallic bonding. While in the first case pair potentials with Friedel oscillations seem to be appropriate for modeling,\(^{42}\) in the latter case even simple Lennard-Jones potentials have been found to stabilize QC structures (see, \textit{e.g.}, Roth and Henley\(^{43}\) and citations therein).

The question is why no hard QC with other non-crystallographic symmetries are known, in contrast to the findings for soft QC (see Section 4). For instance, there are ternary borides that can be seen as approximants of heptagonal QC;\(^{44,45}\) however, neither stable nor metastable hard QC with this symmetry have been observed ever.

Concerning the stability of intermetallic QC, it is interesting to note that only a few of them seem to be truly ternary phases. Most of them are pseudobinaries, needing a particular amount of a third element just for tuning the electron concentration, stabilizing particular AET or increasing the entropy by chemical (substitutional) disorder. For instance, the metastable IQC Al–Mn can be stabilized by substituting a part of Al and Mn by Pd. It is also remarkable that all quasiperiodic structures determined so far show a clear cluster substructure, with just a few topologically differing clusters. In the case of decagonal and icosahedral phases the underlying quasilattice (quasiperiodic tiling) is closely related to the 2D Penrose tiling and the 3D Ammann tiling.

The typical structural units of decagonal quasicrystals can be described based on the so-called Gummelt clusters\(^{33,46}\) that are decorated in a particular way. In the case of icosahedral quasicrystals, the structures can be seen to consist of subunits which can be inscribed into triacontahedra. Both types of clusters can be described as proper projections of \( n \)D hypercubes, with \( n = 5 \) and \( n = 6 \), respectively.\(^{28}\)

#### 3.1 Decagonal quasicrystals (DQC)

So far, stable DQC have been found in ternary intermetallic systems only, while metastable DQC have also been obtained by rapid solidification of binary phases (Fig. 1) (for a review on DQC see Steurer\(^{47}\)). There are a few systems known such as Al–Mn–Pd and Zn–Mg–Dy, where both stable DQC and IQC with slightly different compositions exist.

The structures of DQC show 2D quasiperiodicity perpendicular to the tenfold axis and periodicity along it. Geometrically, they can be described as periodic stackings of quasiperiodic layers. However, from a crystal-chemical point of view DQC are by no means layer structures as indicated already by their needle-like growth morphology. The interatomic distances within layers and between layers are on the same scale. Therefore, DQC should better be described as packings of each other partially overlapping columnar clusters. Amazingly, all structures of DQC analyzed so far can be described as variations of cluster-decorated Penrose tilings. A typical example is shown in Fig. 4.

The structure of DQC shows atomic layers not only perpendicular to the tenfold axis but also inclined to it. Consequently, those slightly puffed layers connect the periodic and the quasiperiodic directions. This coupling constrains the evolution of quasiperiodic order during QC growth (see Steurer\(^{47}\) and references therein). It favors strict quasiperiodic order because
any deviation from it would hinder the growth of the inclined atomic layers. Consequently, 2D growth models of 3D models assuming stackings of largely independent 2D quasiperiodic layers are not realistic. They would lead to random-tiling-like structures, indeed. It has been demonstrated by matching-rule-based Monte Carlo (MC) simulations that a 2D rhomb Penrose tiling, existing as a ground state at \( T = 0 \), transforms more and more into a random tiling with increasing temperature.\(^{48}\) The phason fluctuations appear to be unbounded, showing a logarithmic divergence on increasing system size. This means that at \( T > 0 \) in thermodynamic equilibrium randomized Penrose tiling possesses only quasi-bro. Its Fourier spectrum would not contain a pure point contribution (Bragg reflections) anymore.

While macroscopic single crystals of Al-based DQC easily form, this is different for Zn–Mg-based ones. In the system Zn–Mg–Dy, for instance, Frank–Kasper-type DQC and IQC exist at slightly differing compositions. While macroscopic single crystals of the IQC can be quite easily obtained, in the case of the DQC it took 10 months annealing time at \( \approx 650 \) K, indicating a rather sluggish, diffusion based solid state reaction.

### 3.2 Dodecagonal quasicrystals (DDQC)

On the atomic scale, there is just one, probably stable, dodecagonal QC known, \( dd\)-Ta\(_{1.6}\)Te, with a layer structure based on a triangle–square tiling.\(^{39,41}\) The layer structure causes its soft lubricant-like appearance. A detailed structure model of the fundamental building cluster (\( \Theta \approx 20.5 \) Å) could be only derived from its approximant \( aP62c\)-Ta\(_{0.7}\)Te.\(^{14}\) The Ta-substructure is amazingly similar to that of the spherical Ta-substructure can be seen as tcp structure. The Te-atoms \( d_{Ta-Te} = 2.95 \) Å, \( d_{Ta-Te} = 3.05 \) Å and that of weak Te–Te interactions \( d_{Te-Te} = 3.34 \) Å. The Ta-substructure can be seen as scp structure. The Te-atoms correspond to the periodic average structure (PAS) of the square–triangle tiling of the Ta-atoms at the centers of the hexagonal Ta-antiprisms (see Fig. 3 of Zeng et al.).\(^{13}\) The structure of the DDQC has been also described as modulated hexagonal structure with its origin in a charge-density wave (CDW).\(^{39}\)

Due to the quite anisotropic layer structure of \( dd\)-Ta\(_{1.6}\)Te, this quasiperiodic structure is much closer to a quasiperiodic system than those of DQC. Consequently, one could expect a lower degree of quasiperiodic \( l\)ro. Indeed, this DDQC is of rather poor quality as indicated in Fig. 1 of Krumeich et al.\(^{41}\) It shows periodic nanodomains, mainly composed of square tiles, beside some random-tiling-like ones. Overall, the structure resembles that of entropy-stabilized random tilings.\(^{50}\) In thermal annealing experiments for several weeks, the DDQC appeared stable for \( T = 1070 \) K and transformed into approximant (?) structures for \( T > 1800 \) K.\(^{40}\) However, there is not enough experimental information so far to decide on the thermodynamic stability of \( dd\)-Ta\(_{1.6}\)Te.

### 3.3 Icosahedral quasicrystals (IQC)

IQC represent the largest fraction of stable QC. There are binary and ternary IQC known so far (Fig. 1). Contrary to 2D quasiperiodic systems, phason fluctuations in 3D quasiperiodic tilings remain bounded with increasing temperature. This has been demonstrated by MC simulations on a 3D Ammann tiling.\(^{51}\) Consequently, the thermodynamic equilibrium randomized 3D Ammann tiling is on average still quasiperiodic resulting in a Fourier spectrum containing both Bragg peaks and continuous diffuse scattering.

In an X-ray diffraction study on icosahedral Al–Cu–Fe with very large dynamic intensity range, it was estimated that the amplitude of phason fluctuations reaches \( \approx 7\% \) of the diameter of the largest atomic surface (perp-space component of the 6D hyperatoms) and \( \approx 19\% \) of the smallest one. This means that more than 20\% of all atoms are involved in phasonic (including chemical) disorder.\(^{52}\) This indicates a disordered quasiperiodic structure rather than a random-tiling-like one, where this fraction would be much higher.

### 4 Mesoscopic (soft) quasicrystals

In recent years an increasing number of soft QC has been identified with self-assembled structures on the mesoscale. Examples are structures of supramolecular dendrimer LQC,\(^{15}\) ABC star terpolymers\(^{36}\) and colloidal micelles in solution\(^{19}\) (for reviews see the publications of Dotera,\(^{20}\) Ungar et al.\(^{31}\) and Dotera\(^{53}\)). Furthermore, mesoscopic quasicrystals were also obtained by self-assembly of surfactant-coated metallic nanoparticles.\(^{17}\) Contrary to hard QC, some soft QC can self-assemble from just one type of particles.

The dominating factors determining whether a structure gets periodic or quasiperiodic are the chemical composition and cluster shape in the case of intermetallic QC. In the case of colloidal QC, hard-core–soft-shell potentials seem to be decisive while in the case of polymeric QC the shape (terpolymer) and stoichiometry plays a role again. In all cases, double-well potentials favoring two length scales (see Fig. 8(c)) appear to be responsible for the formation of the structural subunits. In the case of colloidal QC the temperature determines whether a periodic or quasiperiodic structure forms, in the other cases it is mainly the stoichiometry.

Without an external field, all QC-forming mesoscopic phases assemble themselves in structures based on either periodic Archimedean or quasiperiodic dodecagonal tilings. In both cases, the prototiles are triangles and squares with frequencies according to the kind of tiling and depending on composition and/or temperature.

In contrast to hard QC, where this symmetry has never been observed, micrometre-sized polystyrene particles, dispersed in water, self-assemble with 7-fold quasiperiodic symmetry if they are exposed to a weak potential created by interference of seven Laser beams.\(^{18}\) The authors relate the probability of the formation of quasiperiodic structures with 2-fold symmetry to the density of high-symmetry stars (local 2-fold symmetry), which deceses with \( n \). Holographic trapping of silica microspheres in aqueous solution was used to assemble QC with 5-, 7- and 8-fold symmetry.\(^{54}\) Another study suggests that the probability of the existence of a QC with 2-fold symmetry decreases with increasing dimensionality \( d_{AS} \) of the atomic surfaces (AS) of the embedded quasiperiodic structure. For \( n = 5, 8, 10 \) and 12 the dimensionality \( d_{AS} = 2 \), for icosahedral
Fig. 8 Self-assembly of ABC-star terpolymers. (a) The polymer chains, linked together at a single junction point, form a 67 tiling for equal amounts of the monomers A, B and C. In the case of different monomer ratios, structures form based on the triangle–square tilings (b) 4.6.12, (c) 4.82 and (d) 32.4.3.4. A vertex configuration \( n^* \) is defined by the kind of polygons arranged along a circuit around a vertex. The unit cells are outlined. (e) Dodecagonal tiling formed by a hypothetical ABC-star terpolymer with concentrations of C > A > B. The black arrows mark the two length scales \( a \) and \( a\sqrt{2 + \sqrt{3}} = 1.93a \).

QC \( d_{AS} = 3 \), for \( n = 7 \) and 9 \( d_{AS} = 4 \), for \( n = 15 \) \( d_{AS} = 6 \), for \( n = 11 \) and 13 \( d_{AS} = 8 \) and 10, respectively. Indeed, there are also colloidal structures known that order with 9-fold symmetry in an external field.59

4.1 Three-component systems – ABC star terpolymers

These three-arm star-shaped copolymers consist of three different immiscible polymers A, B and C of similar molecular weight linked at a junction point. In the liquid state, phase-separated columnar nanodomains are formed with the junction points lining up along their axes, where the three interfaces between A/B, B/C and C/A meet. The cross sections of the solidified terpolymers show polygonal structures related to Archimedean tilings16 (Fig. 8). Depending on the frequencies of triangles and squares in the skeleton of the tiling, which can be varied by changing the arm lengths (volume fractions) of A, B or C, either periodic Archimedean tilings or on average quasiperiodic, dodecagonal random tilings result. The three different nanodomains A, B, and C correspond to the regular polygons in the Archimedean tilings shown in Fig. 8(b–d).

The driving force for the formation of these structures is seen in the minimization of the interfacial area. Phason fluctuations, which would lead to a particular reshuffling of the unit tiles, are kinetically hindered by the prismatic morphology of the nanodomains.

MC simulations based on the diagonal-bond method revealed a phase sequence \( 4.8^2 \rightarrow 3^2.4.3.4 \rightarrow DDQC \rightarrow 4.6.12 \) with increasing C content.53 Thereby the skeleton connecting the C nano domains changes from a square tiling (4-fold symmetry) to a triangle tiling (6-fold symmetry) via square–triangle tilings. The \( 3^2.4.3.4 \) Archimedean tiling has a ratio \( r = N_t / N_s = 2 \) of the numbers of triangles and squares compared to the ratio for the dodecagonal tiling \( r = 4/\sqrt{3} \approx 2.309 \). Consequently, the crucial factor for the formation of the quasiperiodic structure is the right value for the ratio \( r \). A prerequisite is further the constraint that only triangular and square arrangements of the nano domains are possible due to the usage of star terpolymers with specific interaction potentials, which, however, do not essentially change by changing the volume fraction of C.

In terms of the phenomenological Landau theory it was found that the third-order terms in the free energy favor these kinds of tiling structures.55 This can also be modeled by the Lifshitz–Petrich equation, which requires two characteristic length-scales and effective three-body interactions.56,57

4.2 Two-component systems – surfactant-coated metallic nanoparticles

A large variety of different structures can form by self-assembly of surfactant-coated nanoparticles depending on their size ratios and concentration. The surfactant molecules, which usually have long hydrocarbon chains, prevent aggregations of the nanoparticles by a soft repulsive potential counter-balancing van der Waals interactions. In a similar way as that of soft colloidal quasicrystals (see Section 4.3), they form tcp structures, periodic as well as quasiperiodic ones. Examples are mixtures of surfactant-coated nanoparticles of Fe2O3 (\( \Phi 134 \) Å) and Au (\( \Phi 50 \) Å). As a function of the ratio of these two kinds of nanoparticles all kinds of structures self-assemble, which can be described as decorated triangle–square tilings when connecting the centers of the Fe2O3 nanoparticles;17 from the triangle tiling \( 3^2 \), via the Archimedean tiling \( 3^2.4.3.4 \) (related to the Frank–Kasper \( \sigma \) phase, see Fig. 9), and the dodecagonal tiling to the square tiling, 41. Each triangle is centered by one Au nanoparticle and each square by a cluster of six. For a ratio of the number of triangles to the number of squares of \( N_t / N_s = 4/\sqrt{3} \approx 2.31 \), what also means that the area covered by triangles and squares is equal, the random dodecagonal tiling has its ideal composition.58

Fig. 9 (a) Structure of the Frank–Kasper phase \( \sigma - \text{Al}_{40}\text{Ta}_{60} \) projected along [001] (Al—gray, Ta—black). The centers of the hexagonal antiprismic columns form the Archimedean square–triangle tiling \( 3^2.4.3.4 \) (outlined red). (b) Icosahedral AET (blue, and marked also blue in (a)) appear in the \( \sigma \)-phase along the tile edges, where the hexagonal antiprismic columns meet. In the case of an idealized colloidal DDQC, the atoms are replaced by spherical micelles and the triangular and square unit tiles are arranged like in Fig. 8(e).
Since similar structures are also found in other nanoparticle systems, the authors assume the DDQC to be, for this composition, the "most stable, highest entropy quasicrystal phase of very weakly attractive spherical particles".17

MD simulations of systems consisting of micelles with mobile surface features and a significant fraction of dimers, with aspect ratio 1.5 for disfavoring close-packed structures, lead to DDQC as well, even when using simple, purely repulsive potentials.59 While double-well potentials such as the Dzugutov potential60 can lead to energy-stabilized DDQC, this technique yields entropy-stabilized DDQC.

4.3 Single-component systems – colloidal quasicrystals and hard polyhedra

It has been shown in several experimental and theoretical studies that colloids in solution can self-assemble into rather complex structures, from Frank–Kasper phases to dodecagonal QC. Examples are supramolecular dendrimer LQC15,21 and colloidal micelles in solution.19 The decisive factors for the formation of the different structures, periodic or quasiperiodic, are specific interaction potentials as well as the temperature. The pair potential of a micelle is characterized by a strongly repulsive (hard) core, a van-der-Waals attraction at the core boundary and an exponentially decaying (soft) repulsive interaction in the outer part (shell) (see, e.g., Barkan et al.57).

An important feature for the suppression of close packings is the formation of icosahedra centered at sites where the hexagonal antiprisms share vertices (Fig. 9).

It has been shown by MD simulations that rather simple double-well Lennard-Jones-Gauss interaction potentials can lead to quasiperiodic structures.38 Depending on the locations of the first and the second minimum, which define two competing nearest-neighbor distances, pentagonal, decagonal or dodecagonal structures evolve. The dodecagonal structure has the highest density of all these quasiperiodic phases. An alternative mechanism is solely based on particle functionalization and shape in order to disfavor all kinds of close packings, encouraging the formation of structures with low surface contact area.59

The formation of periodic or quasiperiodic tcp structures that are known from transition metal compounds is explained by the hard-core–soft-shell potential of the colloidal particle. In a similar way, transition metals with their slowly decaying d and f orbitals (less-localized electrons than in s or p orbitals) can be seen as spheres with a soft shell. Such spheres energetically prefer tcp structures over other close-packed structures, which have octahedral voids in addition to the much smaller tetrahedral ones.21

It has been shown in several model simulations that entropy driven, on-average dodecagonal quasiperiodic ordering can result under certain conditions for hard complex objects such as tetrahedra or dimers of tetrahedra.29,30 In these cases, the two length scales are provided by the shape of the particles, which also disfavors cubic or hexagonal close packings.

5 Summary

What are the ingredients needed for the formation of quasi-periodic structures in both atomic and mesoscopic systems? First of all, the fundamental building units, atoms, micelles, surfactant-coated nanoparticles or columnar nanodomains must have interaction potentials forcing the formation of particular structural subunits such as clusters or patches of unit tiles. Model calculations have shown that particularly suitable can be double-well potentials defining two different length-scales characteristic for particular quasiperiodic structures. In the case of intermetallic QC, Friedel-oscillations in the pair potentials fulfill this criterion, in the case of mesoscopic QC, they result from the hard-core–soft-shell structure of the building units.

Whether these energetically favorable structural units are packed periodically or quasiperiodically depends on the following factors: their shape and the relationship between their chemical composition and that of the whole phase as well as the electronic band structure in the case of hard QC, while it is mainly composition and temperature in the case of soft QC.

In both cases, entropic contributions from phason fluctuations and/or other kinds of disorder can be crucial for the stability of the quasiperiodic phase. The much weaker interactions on the mesoscopic scale increase the weight of entropic contributions leading to random(ized) tiling based structures. The prevalence of 12-fold symmetry in soft QC results from the preference of their soft-shell particles for tetrahedrally-close-packings. A somehow similar behavior shows the hard QC dd-Ta1.6Te, with the substructure of “soft” Ta atoms close to a tcp packing. For all other hard QC, the 5-fold symmetry of their fundamental building clusters forces the formation of QC with 5-fold symmetry axes (DQC, IQC).

Finally, I want to emphasize that the origin of quasiperiodicity is already much better understood for mesoscopic QC than for intermetallic QC. What is still needed to understand QC formation and growth on the atomic scale is a growth simulation for intermetallic QC under realistic conditions, i.e., with large model system sizes (up to millions of atoms) and the full atom dynamics at the high temperature of formation.

References