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Jumps in icosahedral quasicrystals

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Abstract. Atomic jumps in icosahedral (AlCu)Li quasicrystals and related structures have been studied by molecular dynamics simulations. In quasicrystalline structures jumps exists with jump vectors much shorter than an average nearest neighbor distance. This is a consequence of the phasonic degree of freedom. The jumps therefore are called flips and the sites connected by the jump vector are denoted alternative positions. We find that the atoms in the quasicrystal structures studied here do not flip to alternative positions as proposed and observed in decagonal or dodecagonal quasicrystals but jump to sites which are at least an ordinary interatomic distance apart. Furthermore we observe two diffusion regimes: below about 55% of the melting temperature only small (AlCu) atoms carry out ring processes whereas at higher temperatures both kinds of atoms contribute to long-range diffusion.

PACS. 61.44.Br Quasicrystals – 61.20.Ja Computer simulation of liquid structure

1 Introduction

Quasicrystals are translationally and rotationally well-ordered solids, but with non-crystallographic symmetries. The consequence are some unusual properties: for example, in a tiling description cells may be rearranged by flips. Kalugin and Katz [1] have demonstrated that the flips lead to a new type of diffusion mechanism if the vertices of the tiles are decorated with atoms. The situation becomes more complicated if we translate this picture to realistic structures: the flips occur by jump vectors that are usually shorter than the nearest neighbor atomic distance [2]. Therefore the two sites involved in the jump cannot be occupied simultaneously and are called alternative positions. If the structure is layered and the atoms in different layers are placed at alternative positions then the arrangement is called a split position in the two-dimensional projection. In addition to the new jump modes there are still the ordinary jumps which move an atom to a nearby vacancy. In summary, we find a broad spectrum of possible jumps for realistic quasicrystal models.

The flip and jump processes are very important for the mechanical and thermodynamical behavior of quasicrystals. Dislocations in quasicrystals are always accompanied by a stacking fault-like phason wall, which is nothing but an arrangement of flipped configurations. The phason wall weakens the structure and leads to the phenomenon that secondary dislocations follow the same track. Correlated flips are also involved in phase transitions. They can mediate a transition from a quasicrystal to an approximant phase or to a microcrystalline state. In spite of their importance, jumps and flips in quasicrystals are only poorly understood, at least on an atomic level. Our simulations are intended to help to understand diffusion in quasicrystals. Due to the complexity of the diffusion processes it will not be possible to study the long-time behavior, but we are able to determine the basic jumps.

In this paper we study the jumps in a class of three-dimensional icosahedral binary quasicrystals of the Frank-Kasper type using molecular dynamics simulations where we search directly for atomic jump processes by comparing the coordinates of the atoms at different times. If a sequence of time intervals is considered then this approach can be regarded as a coarse-grained version of the self-part of the van-Hove correlation function $G_\mathrm{s}(r,t)$.

The paper is organized as follows: First we describe the model quasicrystals (Sect. 2) and explain preparation of the samples and simulation parameters (Sect. 3). Then we present the results (Sect. 4) and discuss them in the final section.

2 Description of the models

The models which we have used to study single atom jumps are derived from the experimentally resolved structure of icosahedral AlCuLi and AlMgZn quasicrystals. Al and Cu in the first case and Al and Zn in the second are represented by small A atoms, Li and Mg by large B atoms. Thus we have transformed the originally ternary structure into a binary model. The three-dimensional structure models of these quasicrystals are based on the decoration of a quasilattice of standard icosahedral rhombohedra or on modifications thereof. It turned out that it is not possible in the molecular dynamics simulations

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to obtain an equilibrium structure model since this would involve an altered topology of the tiles and reordering of the atoms on a large scale. Therefore we have studied a number of configurations which could be considered as extreme cases or as a selection of local patterns of an unknown equilibrium model.

The configurations studied are:

1. TI[1]: The vertices and mid-edge sites are decorated with atoms of type A. Further the prolate rhombohedron is filled with two large atoms placed on the long diagonal with distance ratios τ:1:τ where τ is the golden mean.
2. RTI: A random tiling version of the TI configuration.
3. BIA and BIB: The TI configuration contains pairs of adjacent oblate rhombohedra. These configurations are not very stable energetically and can be eliminated. A side-effect is the adjustment of the chemical composition closer to the experimental value. The pair of oblate rhombohedra together with a pair of neighboring prolate rhombohedra form the interior of a rhombic dodecahedron which is filled with a hexagonal bipyramid (Fig. 1). In the BIA[2] variant the tips of the bipryamid are occupied by small A atoms (as in AlMgZn quasicrystals), in the BIB variant they are filled with large B atoms (as in AlCuLi quasicrystals) [3].
4. CCA and CCB [5]: The BI configuration still contain single oblate rhombohedra. Their number can be minimized if one uses Henley's canonical cell (CC) configuration [4] as the basic space-filling structure. The canonical cells are decorated with rhombohedra and dodecahedra and finally filled with atoms. The difference between CCA and CCB is the same as between BIA and BIB, namely the different occupation of the tips of the hexagonal bipyramid in the rhombic dodecahedra.

If we go from the TI configurations *via* BI configurations to the CC configurations, A atoms are removed or replaced by B atoms. Thus the composition changes from $A_{764}B_{236}$ in the TI configurations to a phase with higher B atom content. The density of atoms on the other hand, decreases slightly.

There exists a further modification of the CC configurations: We know from experiment that the centers of the perfect truncated icosahedra clusters are empty. We have examined this modification, too, but we find that the vacancies at the centers of the icosahedra are completely immobile, at least on the time scales of a molecular dynamics simulation. The reason is obvious: the inner icosahedron is formed of A atoms only. Since the edge length of a perfect icosahedron is longer than the distance between the center and a corner, the bonds between the center and the corner atoms are compressed. If the central atom is removed, the corner atoms will relax inwards and the vacant site will be too small to accommodate an atom. This is the reason for the stability of the vacant site. We will not consider this modification in the remaining part of the paper, since the results are similar to those of the CCA and CCB configuration as expected due to the immobility of the vacancies.

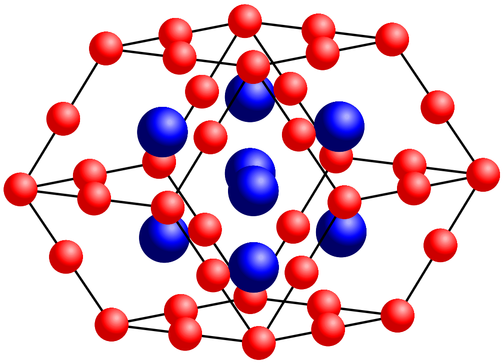

Fig. 1. The modified rhombic dodecahedron. The light atoms are small A atoms. The dark atoms in the interior are large B atoms.

2.1 Determination of the type of jumping atoms

In simple periodic crystals and in intermetallic alloys usually only a small number of different atomic environments exists, especially if topologically similar environments are not distinguished. For quasicrystals, however, we find a huge number of vertex types. In the icosahedral model described here there are about 50 different environments for the small A atoms if only nearest neighbors arrangements are distinguished. Most of the environments, however, need not be discussed in detail because the atoms at these sites do not jump. Nevertheless, we have developed a method which can be used to characterize the environment type of each atom. Since the structure model is a decoration of the standard rhombohedron tiling in three-dimensions we can exploit the properties and the results known about this tiling to determine the atom environments. The method for the vertex atoms is based on the results in reference [6], for mid-edge atoms on reference [7] which deals with generalized two-dimensional Penrose rhombi tilings[3]. This theory is applicable since a slab of rhombohedra all having one edge direction in common is equivalent to a generalized Penrose tiling in two dimensions. Basically our method amounts to computing distances between a certain atom and its neighbors or distances between the neighbors. Then we set up lists of the numbers of neighbors at a certain distance. Depending on the environment type more or less distances are needed to

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[1] TI stands for truncated icosahedra. Nowadays these polyhedra are better known as soccer balls. They have also been called Bergman clusters in contrast to the Mackay clusters found in other quasicrystals.

[2] BI stands for binary icosahedral. The third letter distinguishes the type of atoms at the tips of the bipyramid.

[3] In a generalized Penrose tiling the restriction of the sum of the shift-vectors of the grids to be zero has been removed.

determine the environment type unequivocally. The advantage of our procedure is that it is automatically rotationally invariant.

Here we list in more detail how our method works:

- For vertex atoms (type A) we first determine the number of tile edges which meet at a central atom. Since each edge contains three A atoms, two at the ends and one in the middle, we have to find all collinear pairs of A atoms at distances up to the length of the edge. To distinguish central atoms with the same number of edges but different arrangement of the tiles we also look for the neighboring B atoms (this determines the number of prolate rhombohedra), compute the distances between these B atoms and classify the environments of the central atom according to the numbers of distances. Note that not all of these parameters are really necessary to distinguish the environment types unambiguously.
- For the mid-edge atoms we simply compute all the distances between the neighboring B atoms. This is sufficient to distinguish all possible arrangements of rhombi and the types of the mid-edge atoms.
- For the large B atoms only four different environment types exist. A B atom may have from one up to four other B atoms as nearest neighbors, placed at the corners of a tetrahedron. The B atom environments differ by the number of B atoms at the corners of the tetrahedron. This determines the possible B environments completely.

3 Preparation of the samples

To determine the single atom jumps we at first prepared cubic approximants with about 12 000 atoms (the exact number depends on the configuration variant) and then determined atomic environments for all atoms.

3.1 The interactions

The interaction potentials are of the Lennard-Jones-type with equilibrium positions fitted to the average nearest neighbor distances for the different AA, AB and BB interaction types separately. Two sets of the strength of the interaction have been tested: in the first case we simulated a quasi-monoatomic situation where all interactions are of equal strength. In second case we chose the interaction between atoms of different type twice as strong as between atoms of the same type. It turns out that both sets yield only quantitative differences.

3.2 Simulation procedure

The starting samples are first "equilibrated" by molecular dynamics simulations at low constant temperature and low constant pressure. The resulting state does not represent a thermodynamical equilibrium in the usual sense, since such an equilibration would more or less convert the different starting configurations into one equilibrium model. What is achieved by procedure is a relaxation of the atoms and the volume. But we may still call this procedure "equilibration" since this is the term usually used in molecular dynamics. The samples are then equilibrated further at constant pressure at the higher simulation temperature.

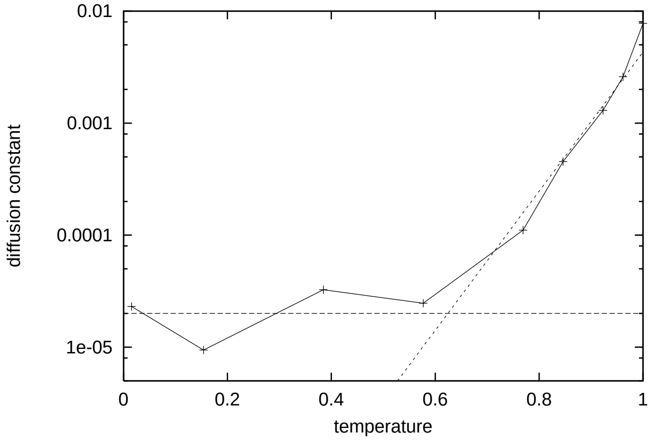

Fig. 2. Diffusion constant for the TI configuration. The temperature is scaled to the melting temperature. Below 55% of the melting temperature no diffusion could be observed.

To collect the jump statistics we carried out simulation runs with up to 10^6 time steps at constant volume in the temperature range between $T = 0$ and the melting temperature.

For the evaluation we stored the atom positions at regular time intervals [8]. To remove dynamic displacement of the atoms from their equilibrium position we then minimized the total energy of the samples at $T = 0$. The frequency of the jumps is displayed graphically in histograms. The dependence on the environment type of the atom is listed in tables. For the icosahedral quasicrystals the jumps can easily be separated from the vibrations of the atoms around their equilibrium position even if the samples are not quenched since the jumping distances are of the order of the nearest neighbor distances. This is in contrast to other decagonal models [9] for example, if atoms move to alternative positions less than a half the nearest neighbor position apart.

Correlations between the jumps of neighboring atoms can be determined from projections of three-dimensional pictures where the initial and final position of an atom are connected by a straight line.

4 Results

Dependent on the temperature of the samples we arrive at the following picture: in all configurations only small A atoms jump if the temperature is lower than about 55% of the melting temperature T_m[4] (see Fig. 2). Since the jumps

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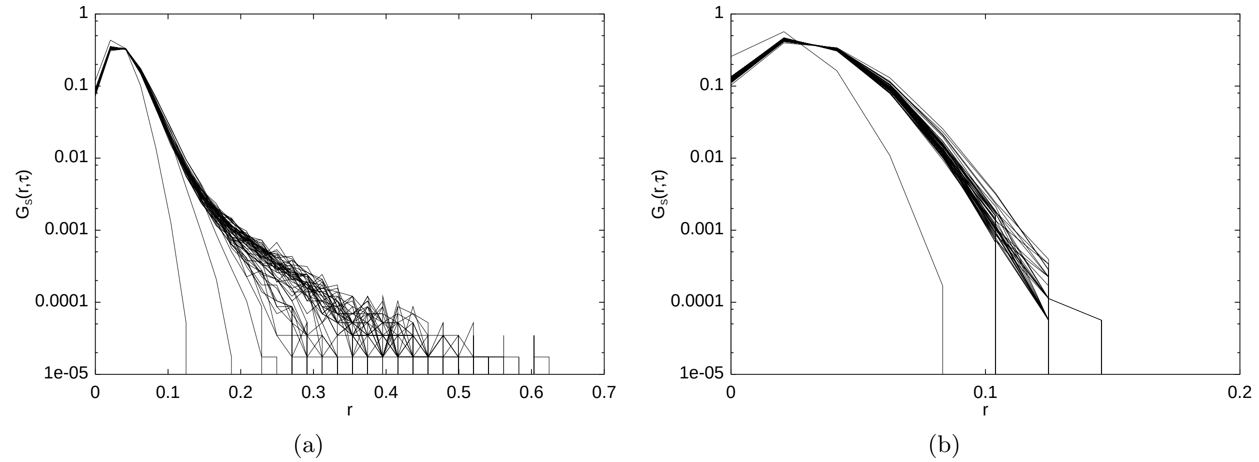
[4] All results are given in Lennard-Jones units. The unit of energy is the depth of the AB interaction.



(a) (b)

Fig. 3. Histogram of the atomic jumps at low temperatures. (a) A atoms, (b) B atoms. The different line paths represent different time intervals, the line paths move to the right with time. Comparing the pictures one finds that only A atoms are jumping whereas B atoms only vibrate around their equilibrium position.

themselves depend on the type of the configuration we will discuss them in detail later. If the temperature is between 0.55 T_{m} and T_{m} ordinary diffusion sets in where atoms of all types and of all environments take part (Fig. 3).

Below $T_{\mathrm{m}} = 0.55$ we only observe isolated jumps. Therefore we do not know if these jumps will lead to long range diffusion or if the atoms jump only back and forth. Above $T_{\mathrm{m}} = 0.55$ the jumps leading to diffusion clearly dominated. The fact that diffusion constant in Figure 2 is more or less constant below $T_{\mathrm{m}} = 0.55$ should not be mistaken: in this range the diffusion rate is too low to be resolved by molecular dynamics.

This observation has important consequences for experiments: remember that we do not create vacancies in our structure. Obviously thermal expansion alone generates enough free space that the atoms can start to diffuse. This is even more astonishing since the structure is rather close packed. At the moment we can only speculate what the mechanisms for this kind of diffusion are: it is unlikely that it is an interstitial mechanism. We assume that the jumps are initiated by unstable Frenkel pairs which are created when an atom moves to an alternative site. Another atom can jump into the vacant place and then move on.

In the following we will describe the jump processes at low temperatures in detail for each of the configurations (see Fig. 3).

In the TI configuration edges exist which are common to ten oblate rhombohedra. Alternating mid-edge and vertex atoms form polygonal rings with ten edges. The most common jump processes in the TI decoration are jumps around these rings. The atoms move successively from one position to the next. Therefore we call it a ring process (Fig. 4). During a simulation time of about 10^6 steps no complete rotations have been observed. The atoms have moved at most half around the ring. Therefore we do not know for sure whether the ring processes lead to percolation and to long-range diffusion of the small A atoms, however, it is rather unlikely. The TI configuration contains complete rings and ring fragments. The rings are separated. Some of the fragments are connected, but they do not form an extended network. Therefore, without additional jump modes which link the rings and the fragments the ring processes alone cannot lead to long-range diffusion.

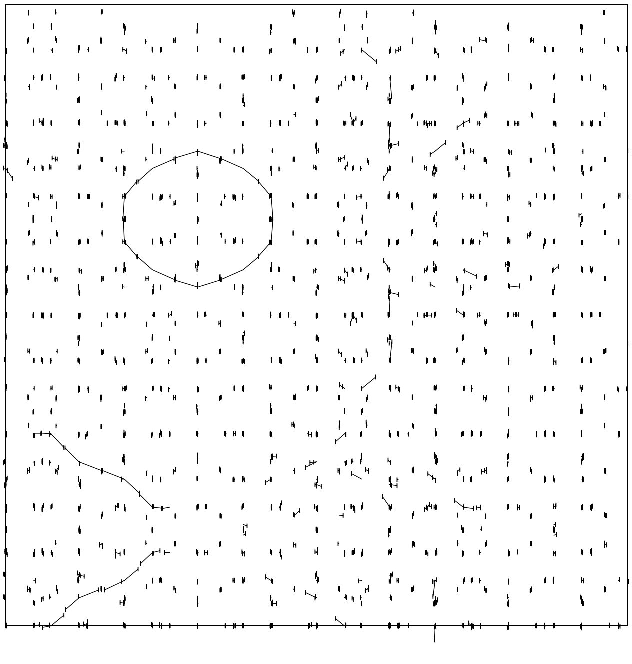


Fig. 4. Comparison of the atom positions. The lines connect identical atoms at the beginning and at the end of a simulation. In the upper left-hand part a ring process can be observed, in the lower left-hand part two ring processes are visible edge-on.

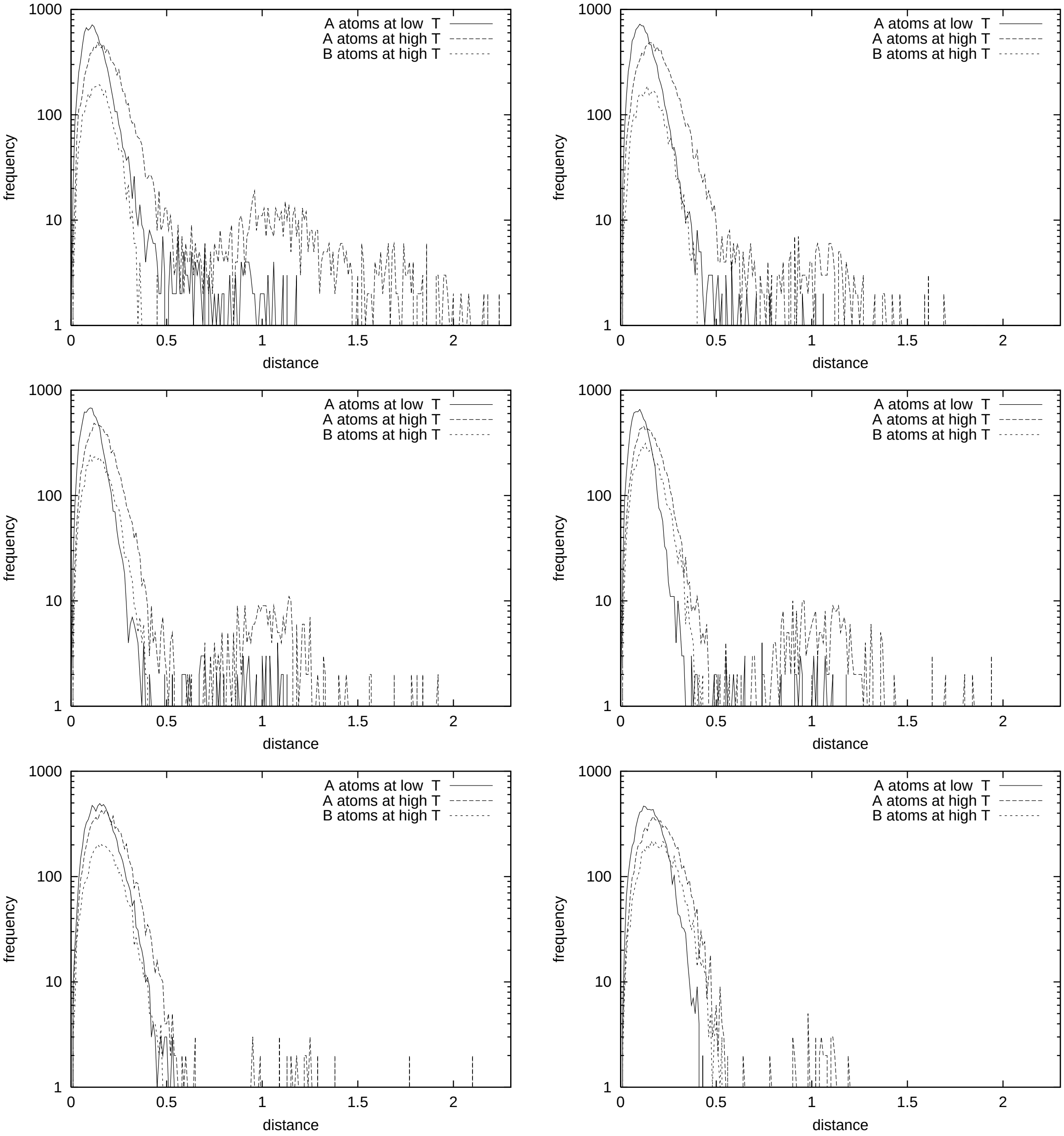


Fig. 5. Histogram of the atomic jumps of the TI, RTI, BIA, BIB, CCA and CCB configurations after 10^6 time steps (from left to right and downwards).

In all the other modifications the ten-membered rings are destroyed. In the RTI configuration this is achieved by flips which reduce the number of pairs of flat rhombohedra from 23 down to 15%. In the other configurations some of the small A atoms of the ten-membered rings are replaced by large B atoms. This change stops the ring processes very effectively. In the BI and CC configurations all pairs of oblate rhombohedra have been removed. But there are still pair exchanges which involve mid-edge and vertex atoms of the oblate rhombohedra. Therefore the number of jumps in the BI configurations is larger than in the CC configurations since the latter contain fewer single oblate rhombohedra. Other jumps are observed at the tips of the hexagonal bipyramid, but only in the BIA and CCA configurations. The reason is that the site is too large for small A atoms and should be occupied by large B atoms. Jumps of this type do not occur in the TI and RTI configuration. They are isolated like the bipyramid and do not lead to long-range diffusion.

Figure 5 displays an overview of the jumps frequency in all configurations. The parameters are the following: low temperature is 0.374 for TI and RTI configurations, 0.331 for BI and 0.580 for CC configurations. The high temperature was 0.654 for TI and RTI configurations, 0.580 for BI and 0.745 for CC configurations. The simulation times

Table 1. Simulation times of the histograms in Figure 5. The first column names the configurations, the second and third column contain the number of timesteps/the number of jumps per 10^5 time steps at the low and at the high temperature.

configuration	T_{low}	T_{high}
TI	650 000 / 33	260 000 / 302
RTI	100 000 / 73	250 000 / 194
BIA	560 000 / 35	330 000 / 122
BIB	580 000 / 24	330 000 / 112
CCA	250 000 / 23	250 000 / 79
CCB	200 000 / 14	670 000 / 124

and number of jumps per 100 000 time steps are given in Table 1. The number of jumps in the RTI configuration at low temperature is no quite representative since it may still contain transient effects due to the short simulation time.

Although the behavior of the A atoms in the TI and BI configurations looks quite similar, the jumps are of different origin. In the TI configuration the jumps form ring processes, whereas this is not the case in the BI configurations. The jumps in the RTI configuration indicate that the ring processes can also take place on the ring fragments.

Below 55% of the melting temperature we never observed large B atoms to jump which implies that atoms of different type never interchange their position. If they are exchanged forcibly the structure is destroyed and becomes amorphous. As mentioned already, there are no qualitative differences in the jumping modes for the two sets of interaction parameters. We conclude that the different size of the atoms is more important for jumps modes to occur then a different interaction strength. Obviously the energy landscape does not depend strongly on the specific interaction which tells us that the results for the Lennard-Jones interactions are meaningful.

We did not observe true flips, *i.e.* jumps with distances less than the average interatomic distance. Rearrangements of the tiles have also not been observed. If we construct possible tiling flips we find that they involve of the order of 10 atoms at least. A correlated rearrangement of such a large number of atoms is clearly rather unlikely. A recent study [10] of the TI configuration shows that if a new tile (a twin of two rhombic dodecahedra) is introduced, flips may become more likely.

5 Discussion

The simulation results for the icosahedral quasicrystals of the densely packed Frank-Kasper type may be summed up as follows: We observe ring processes which by themselves are not specific for quasicrystals. The length of the shortest cycles (10 steps) may appear large, but such moves are also required for ordinary diffusion processes in complex intermetallic alloys. All jump processes observed in our simulations involve atom environments which are high in their local potential energy and have a density below average. They furthermore have a low local symmetry. It has been found by Hafner *et al.* [11] that there are localized phonon modes centered at the following sites: at the flip vertex in the center of the dodecahedron, at the tips of the oblate rhombohedra, and at the mid-edge and vertex atoms of the oblate rhombohedra.

All the jump processes at low temperatures occur without the presence of vacancies. Therefore the ring processes and the pair exchanges have to be considered as a consequence of the quasicrystalline structure. The jumps take advantage of free volume which does not occur in ordinary crystals. At temperatures higher than 0.55 T_{m} there are still no vacancies available because their creation is suppressed by the periodic boundary conditions. The simulations have been carried out at constant pressure, and therefore the volume of the samples grows with temperature. The newly created free volume permits the generation of unstable vacancies and enables the atoms to jump.

We have studied a number of extreme configurations of an icosahedral model. It was not possible to reach the equilibrium state. This is in contrast to the results for another, geometrically quite similar dodecagonal model [8] which is also of the Frank-Kasper type. In the dodecagonal model we started with two configurations: a pure square-triangle configuration, and a configuration with a maximum content of hexagonal tiles. After a long simulation time the two configurations converged more ore less to an equilibrium configuration with a reduced number of hexagons. We do not expect that this can happen for the icosahedral model, even if we reduce the size of the simulation box and increase the simulation time considerably. The reason is that the dodecagonal model is monatomic and a few jumps are sufficient to change the topology of the tiling. In the icosahedral model a large number of correlated jumps of two types of atoms would be necessary to change the tiling.

The procedure of the jumps in the dodecagonal model is also different: one-dimensional chains of jumping atoms parallel to the periodic direction are observed. In connection with these jumps tiling flips occur in the quasiperiodic plane. Although it is not sure that the flips propagate (since the simulation time of up to 10^7 time steps was still too short to find such processes) there is no principal obstacle which would forbid it. An important reason for the difference between the icosahedral and the dodecagonal model is again that the latter monatomic. Any pair of atoms can switch places without introducing chemical disorder. A further reason for the different behavior is the periodicity of the dodecagonal model.

The behavior of the icosahedral models is also completely different from the decagonal AlCuCo quasicrystals [2]. In this case we observe flips which involve pairs of atoms and lead to tiling flips. But the AlCuCo decagonal quasicrystals do not belong to the Frank-Kasper quasicrystal class according to Henley. The structures in the AlCuCo class are not densely packed, but contain octahedra or prisms as building elements. Icosahedral quasicrystals in this class include AlCuFe and AlPdMn. Nothing is known about atomic jumps in these structures from molecular dynamics up to now, but we speculate that the behavior may be similar to the decagonal AlCuCo quasicrystals. In these quasicrystals there exist pseudo-Mackay-clusters with a first shell of seven or possibly eight atoms which can be rearranged by flips. This is similar to AlCuCo where we have a decagon with three atoms in a first shell. In a model proposed by Elser [12] a second level of jumps exists which connect the first clusters, and thus percolation of the flips seems possible. If it is the case we should see a difference between AlCuFe, AlPdMn and AlCuCo quasicrystals and the Frank-Kasper-type quasicrystals with respect to diffusion. But from experiment we only have diffusion data for the first class, and these data indicate that ordinary vacancy diffusion is the dominating process.

The consequences of our results for macroscopic atom diffusion in the Frank-Kasper-type icosahedral quasicrystals are that flip diffusion as introduced by Kalugin and Katz should not play a role for this class. This is a clear distinction to the AlCuFe class quasicrystals where flip diffusion should be observable if other dominating diffusion modes could be suppressed. A further consequence is that phason relaxation should be much harder to achieve for Frank-Kasper-type quasicrystals. Until recently this was a clear case since the highest quality for quasicrystals was achieved for AlPdMn. But the discovery of phason-strain free rare-earth quasicrystals may call this conclusion into question.

The standard tiling flips in the TI (and RTI) configuration are the exchange processes of the interior atoms of the rhombic dodecahedron. Two large B atoms have to move a distance of about 1.7 interatomic distances to switch their position with two A atoms. A further A atom has to jump a distance of 1.3 interatomic distances. Such moves have never been observed. If the flips are broken up into nearest neighbor exchanges the structure will become chemically disordered.

Up to now we do not know the tiling flips for the BI and CC configurations, but they are certainly more complicated than the flips in the TI and RTI configurations. The flips would involve a rather huge number of atoms if chemical disorder should be avoided. If the flips involve the interchange of atoms of different types then they would be energetically rather costly at low temperatures even in the case where the interactions differ only by the equilibrium atom distance and not by the interaction strength.

Very recent results [10] indicate that flips are possible in the BI configurations, if the replacement condition that all the oblate rhombohedra pairs have to be removed is relaxed and a new tile, which is a twin of two rhombic dodecahedra is introduced. Now it is possible that the oblate rhombohedra move around and that the rhombic dodecahedra change their places. But the new moves still involve a large number of atoms which have to change their place and are therefore still rather unlikely.

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