Atomic Self-Diffusion in Quasicrystals: A Molecular Dynamics Study

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Abstract We present a molecular dynamics study on atomic self-diffusion in Frank-Kasper type dodecagonal quasicrystals. It is found that the quasicrystal-specific flip mechanism for atomic diffusion as predicted by Kalugin and Katz[2], indeed occurs in this system. However, in order to be effective, this mechanism needs to be catalyzed by other defects such as half-vacancies if the structure is truly three-dimensional. For this reason, flip diffusion is difficult to distinguish from standard vacancy diffusion. In a quasi-two-dimensional setup, however, the flips may occur without other defects. Activation energies and flip frequencies are also determined.

1 Introduction Quasicrystals are by now well-established in solid state physics. They exhibit non-crystallographic symmetries together with a number of unusual physical properties. Recent reviews may be found in Refs. [1].

There has recently been much interest in atomic self-diffusion in quasicrystals, mostly triggered by a paper by Kalugin and Katz[2] where a diffusion mechanism specific to quasicrystals was proposed. The elementary process in this *flip mechanism* consists of certain quasicrystal-specific rearrangements of atoms, where the initial and final configurations are energetically almost degenerate. In quasicrystals which are decorations of quasiperiodic tilings, the flip mechanism consists of a reshuffling of certain local tile configurations, along with their decorations [2].

Up to now experiments have not given a clear answer to the diffusion behaviour of quasicrystals. Coddens and his group [3] found atomic hopping of Cu and Fe in AlCuFe quasicrystals. The process can be regarded as flips but it behaves differently from the proposal of Kalugin and Katz. Tracer diffusion has been studied by Nakajima et al. [4]. Their results indicate an unusually low diffusivity of Mn in AlPdMn quasicrystals as compared to crystals of similar composition. To shed more light on these results one has to use simulations to find the elementary diffusion moves and their energetical properties.

Flip diffusion has so far been studied in pure tiling models, without bothering about a specific atomic decoration of the tilings [5]. While such an approach indeed proves that elementary flip processes do add up to diffusive behaviour, the physical feasibility of the flip mechanism and the magnitude of flip diffusion remain much less certain. In particular, activation energies of elementary flips cannot be estimated without a concrete atomic structure, and in a reshuffling of tiles atoms may have to move only much smaller distances than the vertices of the tiles. Those questions cannot be studied without having a specific atomic structure in mind. Some preliminary work treating this problem has been published in Ref. [6].

We propose to study the feasibility of flip diffusion in a concrete atomic model quasicrystal, by means of molecular dynamics (MD) simulations. For such a simulation, not only a realistic model structure, but also (short range) interatomic potentials stabilizing the model structure are needed. Fortunately, this has become available: Dzugutov [7] has found a one-component system with a simple potential, which solidifies into a quasicrystalline structure known already before as a realistic model of dodecagonal quasicrystals [8, 9].

In Section 2, we shall describe this model structure in more detail, along with some ideas on potential flip moves, before we present our MD simulation results in Section 3. In Section 4 activation energies and frequencies for the flips are given. We finally conclude in Section 5.

2 Description of the Model Structures The structure found by Dzugutov [7] in his MD simulation is a layered structure which, apart from some defects, is periodic in one direction, but quasiperiodic and 12-fold symmetric in the plane perpendicular to it. It basically is of Frank-Kasper type, i.e., it is mostly tetrahedrally close-packed, and can be described as a periodic stacking $ABA\bar{B}$ of a dodecagonal layer A and two hexagonal layers, B and $\bar{B}$, which are just rotated by 30° with respect to each other. The atoms in layer A form the vertices of a simple tiling of squares, triangles, asymmetric hexagons and 30° rhombi. The whole structure is, in fact, a decoration of such a tiling [8, 9]. The tiles occurring in the structure, together with their decorations, are shown in Fig. 1.

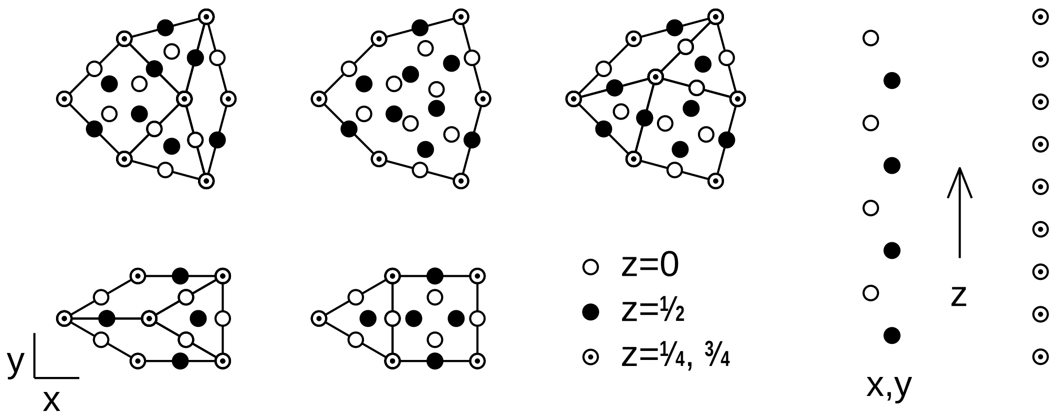

Figure 1: The basic tiles with their decorations. Height coordinates are in fractions of the period length. Two elementary rearrangements of tiles and atoms are shown. One subdivision of a hexagon is replaced by a different one through an intermediate step (top line), and two rhombi are replaced by a square (bottom line). In all these elementary steps, a whole column of (dotted) A layer atoms is replaced by a slightly jagged column of $B/\bar{B}$ layer atoms, or vice versa. These columns are shown on the right. A whole column thus has to move a quarter of a period length upwards or downwards.

All structures built on a tiling with squares and triangles only are perfectly tetrahedrally close-packed. Such structures are therefore very rigid, and there are also very few small groups of tiles that can be reshuffled. If hexagons or rhombi are present, however, some atoms are not close-packed: there are some octahedra occurring in the interior of hexagons, and near the obtuse corners of rhombi. Near those octahedra, the structure is much softer. Moreover, in such structures there are also many local tile configurations which can easily be reshuffled. Some of these tile flips are shown in Fig. 1. In all the moves, a whole column of atoms has to move upwards or downwards (Fig. 1), whereas other atoms move very little. Obviously, such a move is very unlikely, since the vertical distance of atoms is already rather small. If one introduces a vacancy in the column, however, the move becomes much easier. Since between two atom positions in a column there is another good atom position, a neighboring atom can then move half-way into the vacancy, effectively splitting it into two half-vacancies, which then can move up and down the column, thereby transforming it. Such half-vacancies therefore efficiently catalyze the moves shown in Fig. 1. They are responsible for the breaking of periodicity in z-direction. Note that the movement of atoms in the xy-plane is much smaller than that of the vertices. In our simulations, structures built on several different tilings are used, both perfectly ordered as well as disordered ones. Two different geometries have been studied: a cubic box with each sample containing about 8000 atoms and a flat tetragonal box with aspect ratio of about 7.5:1 containing 14040 atoms.

3 Results of the Molecular Dynamics Simulations Our MD simulations were all carried out with a standard 4th-order predictor-corrector algorithm[10], at constant temperature and constant pressure[11] using the constraint method. To keep atoms sufficiently mobile, a rather high simulation temperature of $T = 0.6$ (in reduced units) was used, compared to a melting temperature of $T_m = 0.9$ for the idealized structures, and $T_m = 0.7$ for Dzugutov's structure, which was obtained in a cooling simulation [7]. Since Dzugutov's structure contains many defects of all kinds, we decided to use, in our simulations, the idealized structures described in the last section, and to introduce defects in a controlled way where necessary. We will start with the description of the results of the cubic case, where the simulation box contains 10 double layers along the periodic direction. The pure square-triangle tiling structures turned out to be very stable, as predicted. The same is true for structures containing asymmetric hexagons. Regions with isolated rhombi are found to have a clear tendency to transform into hexagons, and then remain immobile. Only more disordered structures, where also pairs of rhombi occur, are somewhat more mobile. After very long simulations, these latter structures even developed vacancies, whereas the other structures only developed half-vacancies. In order to accelerate this process, and since Dzugutov's structure also contains many holes, we decided to introduce some vacancies artificially, in a controlled way, on different classes of sites. Vacancies are most effective when they are introduced on sites in the interior of hexagons, which are involved in the formation and disappearance of rhombi inside hexagons. When introduced on other sites, vacancies had a somewhat lesser effect. As expected, mobility is primarily in the periodic direction, whereas in the quasiperiodic plane atoms move much less (Fig. 2). It can clearly be seen, however, that the tiling is reshuffled, and periodicity is broken.

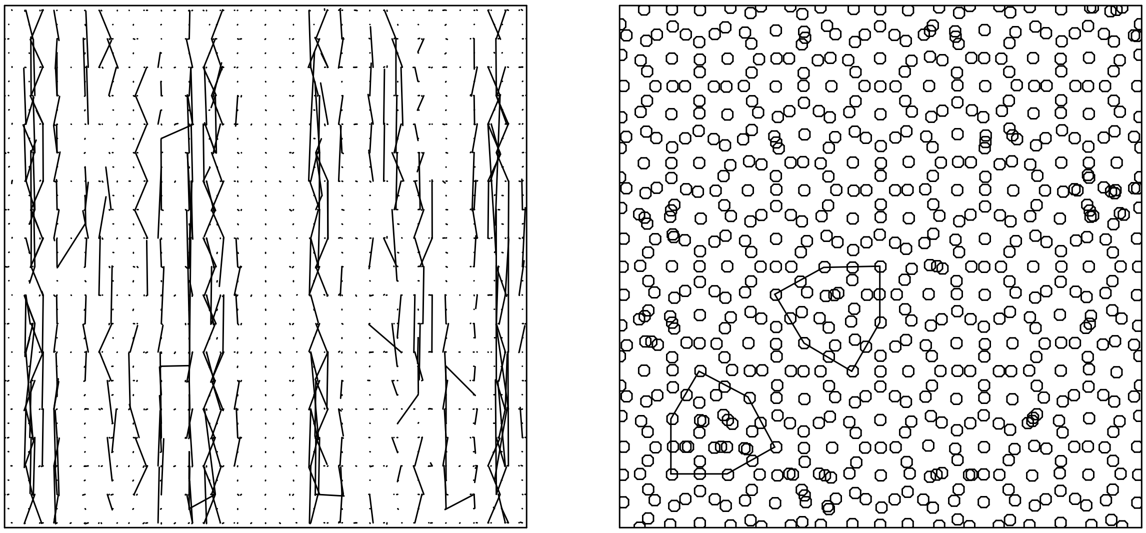

Figure 2: Comparison of the initial configuration with the result after 100,000 simulation steps, for a structure based on a tiling with hexagons, containing about 2% vacancies inside hexagons. On the left, a projection on the xz-plane is shown, with initial and final positions connected. It can be seen that atoms primarily move vertically, with small horizontal displacements (zig-zags). On the right, a projection of the final structure on the xy-plane is shown. The tiling has been reshuffled, and at different z-coordinates one has different tilings, so that periodicity is slightly broken. Atoms which have moved are primarily inside hexagons. Two of the hexagons are indicated.

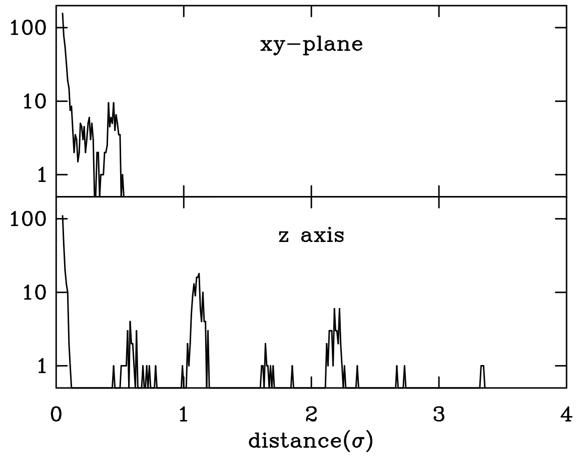

Figure 3: Histograms of distances between initial and final atom positions, after 100,000 simulation steps. Distances both in the (periodic) z-direction and within the (quasiperiodic) xy-plane are shown for a structure based on a tiling with hexagons and initial holes. In the periodic direction, atoms get much farther, and there are clear, discrete step sizes. In the quasiperiodic direction, step sizes are much smaller, but there are still discrete step sizes apparent.

In agreement with our theoretical picture, atoms indeed make discrete jumps in our simulations (Fig. 3). These distances covered are much bigger in the periodic direction than in the quasiperiodic direction since in the first case an atom may jump several times during the simulation. In the latter case jumps are still discernible, although only few atoms jump and most don't move at all.

The behaviour of the structural changes is different in the flat tetragonal sample containing only three double layers along the periodic direction. Now the flips occur in *all* configurations and they do not terminate, and we observe an equilibrium structure containing squares, triangles, hexagons and single rhombi. Even in the pure square-triangle tiling the atoms become mobile but only if we increase the simulation temperature up to $T = 0.8$. Several mobility processes can be distinguished at the tiling level (Fig. 4): pairs of rhombi are eliminated immediately. The reason for this will be discussed in the next section. If there are untilable defects then they disappear after about 16,000 time steps. The equilibrium density of hexagons and single rhombi, established by their transition into one another, is reached after about 70,000 time steps, but the number of hexagons keeps showing large fluctuation and a very slow relaxation during the whole simulation run (up to 700,000 time steps).

On the atomic scale we observe phason hopping. This represents the motion of the atoms corresponding to the tile flip. The hopping is in almost all cases only local, back and forth. It does not lead to long range diffusion. Furthermore nearest neighbour jumps typical for ordinary vacancy diffusion have been found. A few long-range diffusion processes in the periodic plane have been found, the overwelming part of diffusion however is along the periodic direction as seen already in the cubic cell simulations. Therefore the diffusion in this model seems to be maximally anisotropic.

4 Activation Energy and Flip Frequency For the flat sample it is possible to describe the flipping process more quantitatively. A jump of an atom chain along the periodic direction occurs every 110,750 time steps. The cosine of the angle between the directions of two successive jumps of the same atom is -0.169 on average, which means that successive jumps are nearly uncorrelated. The frequencies for the jumps are the following: a jump of any tile occurs every 12,283 time steps, a jump of a rhombus every 21,123 and a jump of a hexagon every 29,288 steps. For rhombus-hexagon-rhombus the branching ratio between the backward and the two forward jumps is 4:1:1, and for a hexagon-rhombus-hexagon jumps it is 13:4. To determine the activation energies we have optimized the potential energy of small samples containing the flipable configurations. The energy of the configuration with the pairs of rhombi (bottom of Fig. 1) is about 5.4 (in reduced units) per period higher than the energy of the square-triangle configuration. The energy of the hexagon with the symmetric interior is nearly identical to the hexagon containing a rhombus (it is 0.1 per period lower). If there are three rhombi in the hexagon the energy increases by 6.4 per period. Therefore this configuration does not occur. The barrier energies can be found by molecular static calculations [13]. The jumping atoms are slowly dragged from one configuration to the other, while monitoring the energy along this path. In this way it is possible to find the saddle point configurations and their energies. Special care is needed, however, to avoid introducing artificial constraints, which might increase the energy. For the configurations in Fig. 1 it turns out that the pairs of rhombi actually display saddle point configurations. That is the reason why they disappear immediately at the beginning of the simulation. The barrier for the flipping process shown in the upper part of Fig. 1 is too low to be determined accurately, the barrier for the opposite process (not shown) transforming a hexagon into a second hexagon via a common central rhombus is also very low: 0.5. If we take the geometry of the simulation cell into account we find that there are percolating clusters of hexagons sharing a rhombus. Therefore long range tile diffusion should be possible.

5 Discussion and Conclusions A careful analysis of the final states has shown that flip moves indeed occur in our model quasicrystals. Such flip moves have also been observed by Dzugutov[12]. Their activation energy is prohibitively high if the periodic direction is long, unless there are other defects present as well, which can catalyze the flips. Half-vacancies and vacancies are particularly efficient such catalyzers. We have found that a sizeable density of such half-vacancies and vacancies (up to 2%) is always present in equilibrium, which therefore makes flip diffusion possible. Unfortunately, due to the (necessary) presence of vacancies and half-vacancies, the contributions of flip diffusion and classical vacancy diffusion are very hard to separate. We should emphasize, however, that the flip mechanism, although catalyzed by vacancies, is qualitatively different from vacancy diffusion, in that the passage of a vacancy without flips associated with it leaves the structure unchanged, whereas with the flips the struc-

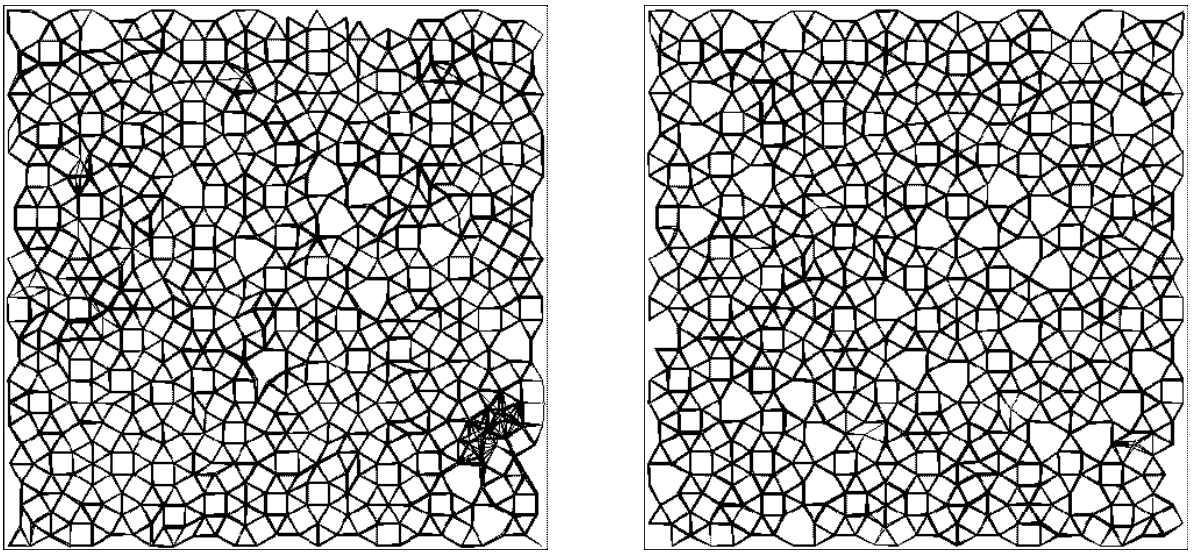

Figure 4: Projection of the initial (left) and final (right) state of the tiling after 700,000 simulation steps for the flat sample. A Comparison shows how the tiling has been reshuffled in many places.

ture is left completely reshuffled after the passage of the vacancy. If a flat geometry is chosen it is possible to study tiling flips and their dynamics explicitly. If the starting configuration contains untilable defects, it is possible to observe tiles move finite distances. In most of the cases, however, the tiles and the associate atoms move only back and forth as they do in a two-well-potential. For geometrical reasons it is not clear why this should happen, since it is possible for the tiling moves to percolate. Maybe the long-range diffusion process is too slow to be seen in molecular dynamics. Since we have determined all the energetical parameters for the flips it should be possible to use them in a Monte Carlo simulation to clarify these questions and to calculate the diffusion constants accurately. This is planned for the future.

Our model quasicrystals are somewhat untypical in that they are periodic in one direction, which causes problems because isolated flips have to break periodicity and thus lead to larger mismatches. Moreover, our models are mostly tetrahedrally close-packed, which makes them very rigid, and which is also not very typical for quasicrystals. Still, we believe that our results are relevant also for (stable) icosahedral quasicrystals, which are completely non-periodic and not Frank-Kasper like.

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