ATOMIC SELF-DIFFUSION IN QUASICRYSTALS

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ABSTRACT

A molecular dynamics study on atomic self-diffusion in Frank-Kasper type dodecagonal quasicrystals is presented. It is found that the quasicrystal-specific flip mechanism for atomic diffusion, predicted by Kalugin and Katz, indeed occurs in this system. However, in order to be effective, this mechanism needs to be catalyzed by other defects, such as half-vacancies. For this reason, flip diffusion is difficult to distinguish from standard vacancy diffusion.

1. Introduction

There has recently been much interest in atomic self-diffusion in quasicrystals, mostly triggered by a paper by Kalugin and Katz[1], 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[1].

Flip diffusion has so far been studied in pure tiling models, without bothering about a specific atomic decoration of the tilings[2,3]. While such an approach may prove 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.

We therefore 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[4] 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[5,6].

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. We finally conclude in Section 4.

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2. Description of the Model Structures

The structure found by Dzugutov[4] 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 $AB A\bar{B}$ of a dodecagonal layer A and two hexagonal layers, B and $\bar{B}$, which are just rotated with respect to each other by 30°. 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[5,6]. The tiles occurring in the structure, together with their decorations, are shown in Fig. 1.

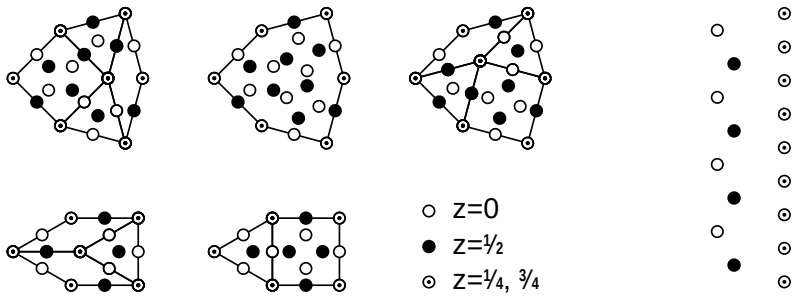

Fig. 1. The basic tiles with their decorations. Height coordinates are in fractions of the period length. Two elementary rearrangements of tiles and atoms are shown. One subdivision of a hexagon is replaced by a different one through an intermediate step (top line), and two rhombi are replaced by a square (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 small than that of the vertices. In our simulations, structures built on several different tilings are used, both perfectly ordered as well as disordered ones, each containing about 8000 atoms.

3. Results of the Molecular Dynamics Simulations

Our MD simulations were all done with a standard 4th-order predictor-corrector algorithm[7], at constant temperature and constant pressure. To keep atoms sufficiently mobile, a rather high simulation temperature of $T = 0.6$ (in Lennard-Jones units) was used, compared to a melting temperature of $T_m = 0.75$ for the idealized structures, and $T_m = 0.7$ for Dzugutov's structure, which was obtained in a simulation[4]. 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. 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, and since also Dzugutov's structure 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.

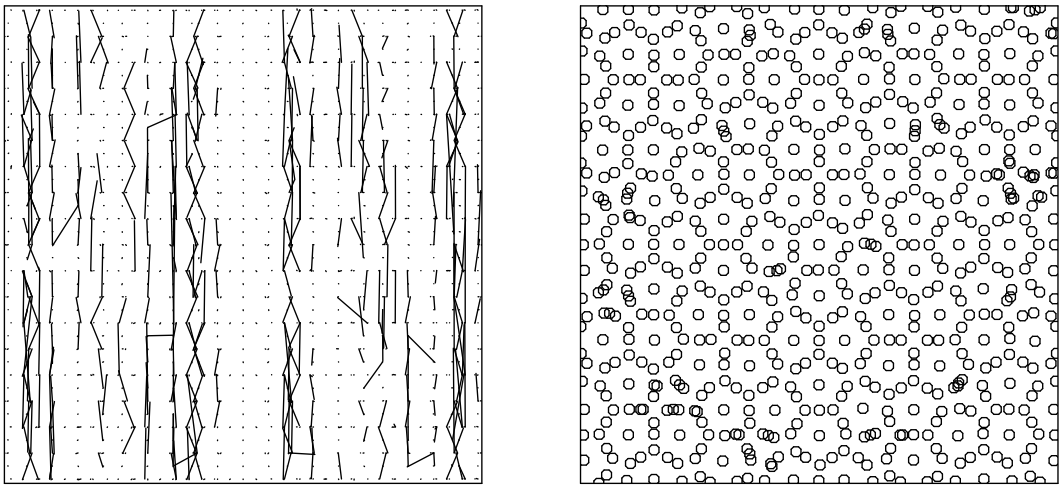

Fig. 2. Comparison of the initial configuration with the result after 100'000 simulation steps, for a structure based on a tiling with hexagons, containing about 2% vacancies inside hexagons. On the left, a projection on the xz-plane is shown, with initial and final positions connected. It can be seen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

To analyze the equilibrium structures in more detail, we first cooled them to zero temperature, then calculated the Voronoi and its dual Delaunay partitioning, and determined from the latter the distribution of the sizes of holes in the structure. In all cases, in addition to the small holes inside tetrahedra and octahedra also a number of half-vacancies had developed, and with less ordered initial structures, or when some initial holes were present, even an equilibrium distribution of full vacancies had formed. In the cases where only half-vacancies had formed, we probably still were away from equilibrium. It is particularly interesting that if in Dzugutov's structure all full vacancies were filled with additional atoms, a similar equilibrium distribution of vacancies formed again after a while. Some representative histograms of hole sizes are shown in Fig. 3.

In agreement with our theoretical picture, atoms indeed make discrete jumps in our simulations (Fig. 4). These jumps are much bigger in the periodic direction than in the quasiperiodic direction, but even in the latter they are still discernible, although atoms make only very few jumps and most don't move at all.

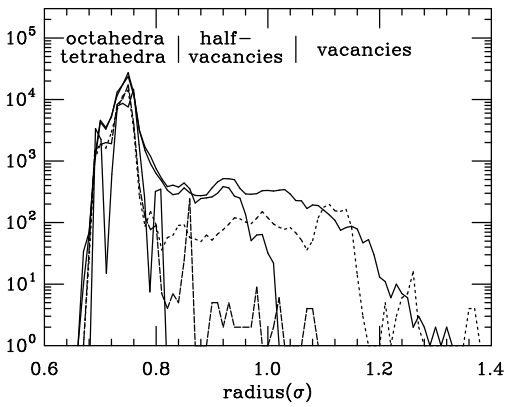

Fig. 3. Histogram of hole sizes for different structures, after cooling to zero temperature. There are holes inside tetrahedra, holes inside octahedra, half-vacancies, and full vacancies, where entire atoms fit in. The data of Dzugutov's structure is shown in solid, both before and after the full vacancies have been filled. The data for a structure based on a tiling with hexagons is shown dashed, after a very long simulation, both with (short dashed) and without (long dashed) initial holes.

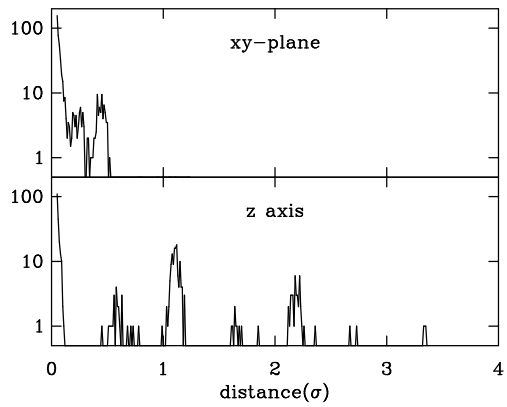

Fig. 4. Histograms of distances between initial and final atom positions, after 100'000 simulation steps. Distances both in the (periodic) z-direction and within the (quasiperiodic) xy-plane are shown for a structure based on a tiling with hexagons and initial holes. In the periodic direction, atoms 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.

4. Discussion and Conclusions

A careful analysis of the final states shows that flip moves indeed occur in our model quasicrystals. Such flip moves have also been observed by Dzugutov (private communication). Their activation energy is prohibitively high, however, unless there are other defects present as well, which can catalyze the flips. Particularly

efficient such catalyzers are half-vacancies and vacancies. We have found that a sizable density of such half-vacancies and vacancies 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 structure is left completely reshuffled after the passage of the vacancy.

Our model quasicrystal 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.

As is well known, molecular dynamics is too slow to reliably measure the diffusion constant directly in a simulation. It is a good tool, however, to identify the relevant moves, and to measure their activation energy. The actual diffusion constant then can be obtained from a Monte Carlo simulation, using the moves and activation energies determined in the MD simulation. This is planned for the future.

5. Acknowledgements

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6. References

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