

## Diffusion in 2D Quasi-Crystals.

D. JOSEPH (\*), M. BAAKE (\*)(\*\*), P. KRAMER (\*) and H.-R. TREBIN (\*\*)

(\*) *Institut für Theoretische Physik, Universität Tübingen*

*Auf der Morgenstelle 14, 72076 Tübingen, Germany*

(\*\*) *Institut für Theoretische und Angewandte Physik, Universität Stuttgart*  
*Pfaffenwaldring 57, 70550 Stuttgart, Germany*

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**Abstract.** – Self-diffusion induced by phasonic flips is studied in an octagonal model quasi-crystal. To determine the temperature dependence of the diffusion coefficient, we apply a Monte Carlo simulation with specific energy values of local configurations. We compare the results of the ideal quasi-periodic tiling and a related periodic approximant and comment on possible implications to real quasi-crystals.

Recently, Kalugin and Katz [1] proposed a possible mechanism for bulk self-diffusion in quasi-crystals. Their model is based on specific geometric properties of the quasi-crystalline structure. In ordinary crystals, the diffusion process depends on the presence of vacancies in the lattice and is activated by the vacancy production rate and the hopping of atoms in the neighbourhood. Both lead to a Brownian-like motion, and the temperature dependence of the diffusion coefficient thus obeys an Arrhenius law [2]. Due to additional degrees of freedom of quasi-periodic systems—the so-called phasons—one can construct an additional process for bulk diffusion in quasi-crystals. Based on general arguments, Kalugin and Katz conclude that the phason degree of freedom leads to a deviation of the diffusion coefficient from the Arrhenius law. Unfortunately, because of the general nature of their considerations, they were neither able to determine at which temperature these deviations are to be expected nor to estimate their order of magnitude.

In this article, we calculate the diffusion coefficient of the eightfold symmetric Ammann-Beenker tiling [3] quantitatively. We start from a mean-field model which takes the additional degrees of freedom into account and we apply a Monte Carlo method to estimate the phason contribution to the bulk diffusion in the quasi-periodic plane. We discuss general properties and similarities with the ansatz of Kalugin and Katz and compare the quasi-periodic tiling with a periodic approximant.

The Ammann-Beenker tiling is chosen because, on the one hand, it provides generic quasi-periodic properties while, on the other hand, it is as simple as possible. Nevertheless, all results stated below can easily be extended to other two-dimensional quasi-periodic tilings like the Penrose tiling [4] or the Tübingen triangle tiling [5]. The Ammann-Beenker tiling consists of squares and 45-degree rhombi which form (modulo operations of the dihedral group  $d_8$ ) 6 different vertex configurations. Combinatorially, another 10 (+3 mirror inverted) vertices are possible without gaps or overlaps, which were introduced and

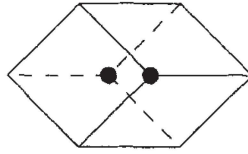


Fig. 1. – The simpleton flip in the octagonal Ammann-Beenker tiling.

investigated earlier as defects of the first kind [6]. One can easily show that all of them can be inserted locally in an ideal tiling. Regarding the ideal tiling as energetically favoured, one can follow a mean-field approach [6, 7], which assigns an average defect energy to each of the 10 (+3) forbidden vertex configurations due to nearest-neighbour interactions<sup>(1)</sup>. This approach has only one free parameter, compare eq. (3.1) and the following discussion in [6], which scales the measure of the elastic energy and plays the role of an activation energy. We fix this parameter to be  $E_0 = 2k\theta$ ,  $k$  the Boltzmann constant, and  $\theta$  the Debye temperature. The value is chosen to match specific-heat contributions of these defects with experimental findings [6, 7]. Taking a typical Debye temperature,  $E_0$  corresponds to approximately 0.05 eV.

The basic mechanism of the extraordinary diffusion (also called self-diffusion) is the simpleton flip [8], cf. fig. 1, the simplest representation of a phason degree of freedom. It can be seen as the geometric realization of local two-level systems with small excitation threshold. In fact, the rotating octagons used by Kalugin and Katz [1] can be realized as a sequence of eight simpleton flips. Starting from an ideal, defect-free Ammann-Beenker tiling we use the simpleton flips to randomize the tiling, cf. fig. 2. Gähler [9] has given an argument that the simpleton flip randomization should be ergodic (though not necessarily uniformly ergodic) on the tiling ensemble in this case. As a consistency check, we estimated the configurational entropy per tile  $S$  by integrating  $C_v/T$  over  $T$  and adding the ground-state contribution. This resulted in a value of  $S = 0.41(5)$  which is consistent with previous calculations [10]. During the randomization we keep the edges of the patch fixed. One can easily see that all 16 (+3) vertex configurations can be reached this way. Each new defect of the first kind corresponds to an energy cost in the mean-field approach above. Therefore, we can judge for each simpleton flip energetically whether it should be accepted or not in an importance sampling [11] by the classical Metropolis algorithm [12].

To determine the diffusion coefficient, we have to calculate the expectation value of the

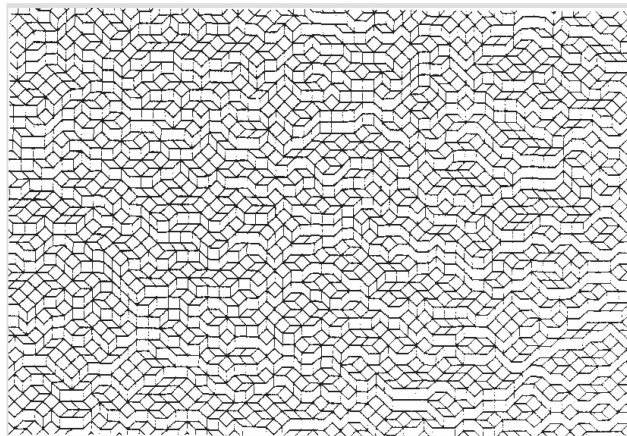


Fig. 2. – A random tiling produced via simpleton flips from the Ammann-Beenker tiling after 100 flips/vertex.

<sup>(1)</sup> Note that the ideal state is not a unique ground state in our model. More than half of the possible initial flips do not cause any change of energy.

squared distance a vertex has moved via simpleton flips as a function of time  $t$ , *i.e.* the number of attempted flips. For a Brownian motion one expects

$$\langle r^2 \rangle \sim D(T) \cdot t. \quad (1)$$

Here,  $D(T)$  is the diffusion coefficient as a function of the temperature  $T$ ,

$$D(T) = D_0 \exp\left[-\frac{\varepsilon}{T}\right], \quad (2)$$

where  $\varepsilon$  is the activation energy. In quasi-crystals, one expects an additional contribution due to the phason degree of freedom. Phenomenologically, both contributions can be summarized in a  $T$ -dependent activation energy, *i.e.*  $\varepsilon = \varepsilon(T)$ .

We will now focus on the phason-induced diffusion. Using the parameters as introduced above, we calculated  $\langle r^2 \rangle(t)$ . Figure 3 shows the result for a patch of  $10^4$  vertices with different temperatures  $T$ . For each temperature, we started with a thermalization<sup>(2)</sup> from an ideal patch, typically reached after 20 accepted flips per vertex. Only afterwards, we calculated  $\langle r^2 \rangle(t)$  by the usual techniques, where the random generator RAN1 from the Numerical Recipes [13] proved suitable.

The relation of eq. (1) is well fulfilled except for small times  $t$ . There, one can see sublinear growth because it is not possible to make smaller movements than the distance of a flip. One observes nearly straight lines up to several thousand flips per vertex without bending and without a change of the diffusion coefficient. Therefore, we can conclude that we do not see the influence of the boundary of the patch in the plot. This was also verified by using different patch sizes. Fitting straight lines to fig. 3 yields the Arrhenius plot for the diffusion coefficient ( $\log(D(T))$  vs.  $1/T$ ) which is shown in fig. 4a). We see three different regions. For  $T/\theta \leq 0.2$ , the diffusion coefficient shows a small increase only. Indeed, below 0.1 the diffusion coefficient is nearly constant due to the presence of zero-modes. At  $T/\theta \sim 0.20 \dots 0.25$ , the diffusion coefficient increases considerably until it reaches a point of saturation for  $T/\theta \geq 5$ .

The reason for the different regimes lies in the frequencies of the vertices arising during the randomization and in the way larger clusters (like the octagons) interpenetrate one another. For  $T/\theta \leq 0.2$ , we find, apart from the allowed vertices of the ideal tiling, only one or

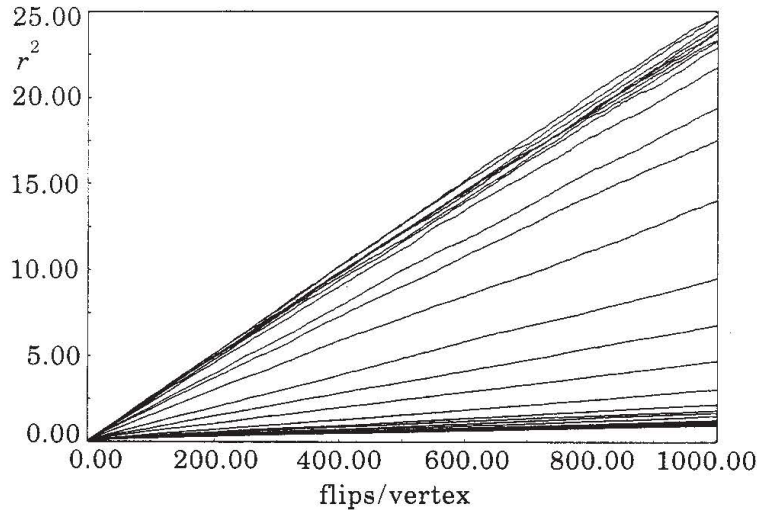


Fig. 3. – The expectation value of the squared distance  $\langle r^2 \rangle(t)$  a vertex has moved via simpleton flips as a function of time (number of attempted flips per vertex) after thermalization for different temperatures  $T$ .

<sup>(2)</sup> A detailed description of this procedure can be found in [11].

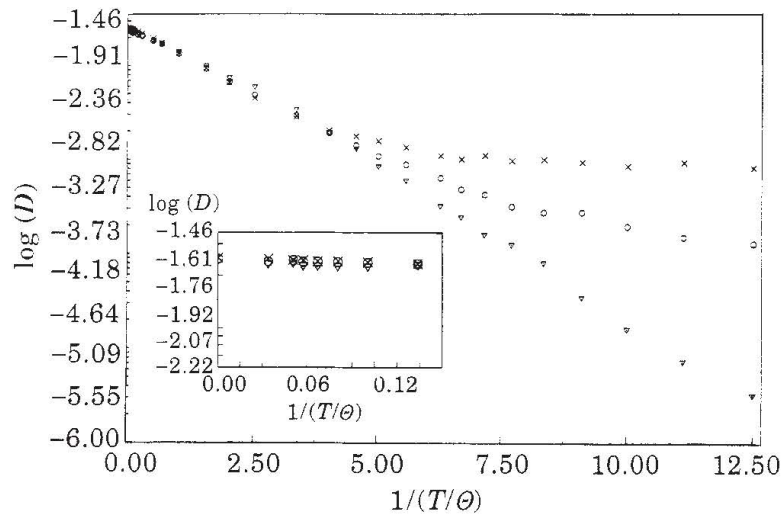


Fig. 4. – Arrhenius plot of the quasi-periodic diffusion coefficient: *a*) for the Ammann-Beenker pattern, *b*) for the periodic approximant with the unit cell of fig. 5, *c*) for the Ammann-Beenker tiling with the mean-field model plus a flipping barrier of  $0.1E_0$ .

two defective vertices in the tiling with sufficiently high probability. These vertices act like zero-modes for the diffusion mechanism because of their low energy costs (0 for the allowed ones,  $0.11$  or  $0.14E_0$  for the defects) and result in a nearly constant diffusion coefficient. From the above simulation one can conclude that because of these zero-modes the vertices are *not* confined to a finite region as in the picture of Kalugin and Katz. Nevertheless, at  $T/\theta \sim 0.20 \dots 0.25$  we see a percolation limit in the sense that the probability for infinite diffusion paths is suddenly increased<sup>(3)</sup> by additionally excited vertices. At this point, nearly all defects occur with a frequency of at least a few in one thousand. Therefore, above this point, phase space of a moving vertex is enlarged considerably. Beyond another threshold, all phason degrees of freedom are effectively activated, which causes saturation.

For comparison, we also calculated the diffusion coefficients starting from the periodic approximant with the elementary cell of fig. 5. Practically, we took enough copies of such a cell to get a patch of size equal to the quasi-periodic patch, and then fixed the boundary. In this large patch of a periodic tiling there is also an extraordinary diffusion possible because the fundamental cells allow simpleton flips. Note, however, that the simpleton flips will destroy the periodicity. Figure 4*b*) shows the Arrhenius plot after thermalization. Above the percolation point, there is no difference between the quasi-periodic and the periodic starting points of the randomization. Only for temperatures below the percolation limit one can distinguish the two cases. A start from the Ammann-Beenker tiling leads to a much higher diffusion coefficient than a start from the periodic approximant. Again, this behaviour is caused by the interpenetration of the octagons, which is more frequent in the quasi-periodic case.

It is worthwhile looking at the shape of some diffusion paths of the vertices at a specific temperature in this sensitive region. Figure 6 shows the trace of a typical vertex at  $T/\theta = 0.1$  for the randomized Ammann-Beenker tiling and for the randomized periodic tiling. Due to the specific geometric structure of the ideal quasi-periodic tiling, *i.e.* the allowed vertices are arranged in penetrating elementary octagons, a typical vertex can move over a much

<sup>(3)</sup> Percolation paths are in principle allowed by the zero modes, but with very low probability. In models with unique ground state, it is around this point of probability increase where we expect the opening of true percolation paths.

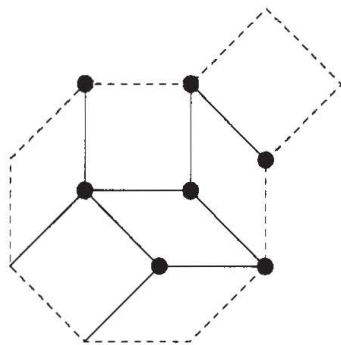


Fig. 5.

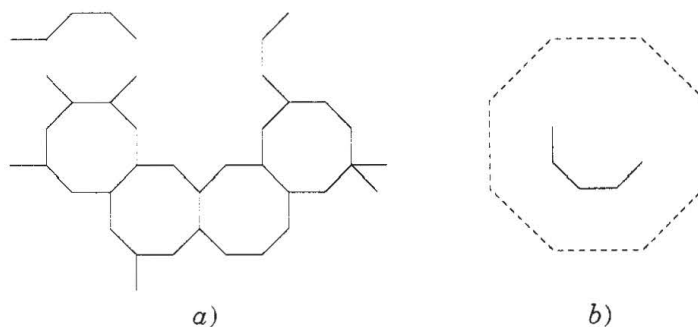


Fig. 6.

Fig. 5. – The vertices and the shape of the unit cell of the smallest approximant. There are simpleton flips possible which will destroy periodicity during randomization.

Fig. 6. – *a*) A typical trace of a vertex moving in Ammann-Beenker random tilings at  $T/\theta = 0.1$ . *b*) A typical trace of a vertex moving in randomized approximants of fig. 5 at  $T/\theta = 0.1$ , shown within the shape of an elementary octagon. The time scale is the same for both pictures.

longer distance than in the case of the randomized tiling starting from the periodic patch, where this penetration is not present. In the ideal tiling, the vertex can move via the vertices of low energy through these interpenetrating octagons whereas in the periodic tiling the vertices are more or less confined to the unit cells. Figure 6 provides a hint on the typical shape of the trace of a moving vertex. The traces are dominated by small octagons which lie inside the octagonal cages of the tiling. This is the Monte Carlo analogue of the elementary diffusion step proposed by Kalugin and Katz [1].

In conclusion, we have calculated the phasonic bulk diffusion of the octagonal Ammann-Beenker tiling by randomizing the tiling via simpleton flips. A mean-field model for the defects together with the Metropolis algorithm allowed us to estimate the typical behaviour of the Arrhenius plot of the diffusion coefficient. We found a percolation limit and a point of saturation of the diffusion where all additional degrees of freedom are activated and, therefore, the quasi-periodic diffusion is not increased any further. Below the percolation limit, the diffusion process depends sensitively on the initial conditions, *i.e.* we could distinguish between random tilings produced from the ideal quasi-periodic tiling and those produced from a related periodic tiling. This region is dominated by the frequencies and the distribution of tiles and clusters in the original tiling.

The question whether the quasi-periodic diffusion or the usual vacancy diffusion will dominate cannot be answered with confidence. It depends, in our model, on the strength of the activation energy  $E_0$  in the mean-field model. Although the typical behaviour of the Arrhenius plot for the quasi-periodic diffusion does not depend on the choice of  $E_0$ , the ratio between quasi-periodic and usual diffusion does. A possible mechanism which could suppress the quasi-periodic diffusion is the following. The mean-field model above assigns a total energy to the vertex configurations before and after the flip. It could be modified by using an additional term which takes the energy threshold of a 2-level system (*i.e.* the simpleton flip) into account. Using this threshold, one can assign another flipping probability (a kind of tunnelling through a barrier in the quantum-mechanical sense) which does not primarily depend on the initial and the final configuration but on the barrier height. As an example we simulated the diffusion for the presence of a low barrier together with the mean-field model, *i.e.* at least a barrier of  $0.1E_0$  was present at every flip. Figure 4c) shows the result for the simulation starting from the Ammann-Beenker tiling. Again, above the percolation point there is no difference for the mean-field model with or without the barrier, but below, the threshold will suppress the zero-modes of the mean-field model and the diffusion goes to zero

for vanishing  $T/\theta$ . If such a barrier for the elementary flip is very high, the quasi-periodic diffusion channel will be suppressed completely so that only the ordinary vacancy diffusion will remain. Molecular-dynamics calculations indicate that this is possible [14]. Here, experiment has to decide whether the quasi-periodic diffusion is visible or not.

The main limitation of our approach is the presence of zero-modes. Very recently, a simple cluster approach has been found [15] which makes the Ammann-Beenker tiling to a unique ground state. Though more complicated, simulations for this model look promising and will be presented in a forthcoming publication.

The obvious next step will then be the investigation of three-dimensional examples and the calculation of thermodynamic properties. An interesting candidate is the standard rhombohedral tiling with icosahedral symmetry [16] which should allow a cluster approach like that of [15].

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