Self-diffusion in random-tiling quasicrystals

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Abstract

The first explicit realization of the conjecture that phason dynamics leads to self-diffusion in quasicrystals is presented for the icosahedral Ammann tilings. On short time scales, the transport is found to be subdiffusive with the exponent $\beta \approx 0.57(1)$, while on long time scales it is consistent with normal diffusion that is up to an order of magnitude larger than in the typical room temperature vacancy-assisted self-diffusion. No simple finite-size scaling is found, suggesting anomalous corrections to normal diffusion, or existence of at least two independent length scales. A connection with transport in membranes is also noted.

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In addition to the uniform translations, quasiperiodic (incommensurate) crystals possess another Goldstone mode that is associated with relative translations between incommensurate components of density waves. This continuous zero-energy mode, the uniform phason displacement, does not generally correspond to a continuous, zero-energy path in the configuration space of the quasiperiodic crystal. For quasiperiodic structures with certain noncrystallographic symmetries (quasicrystals), a uniform phason displacement is necessarily mapped on a discrete rearrangement of particles in the configuration space. These rearrangements, which are called phason flips (see Fig. 1b), have interesting topological properties that suggest a novel mechanism of mass transport in quasicrystals. In particular, it was shown in Ref. that it is possible to make a closed path in the phason displacement space of a quasicrystal, such that starting from a quasicrystal structure in the real space one ends up with the identical structure except for a permutation of its atoms (see Fig. 1c).

These observations raise interesting questions regarding the mass transport in quasicrystals. First, can an atom be moved an arbitrarily large but finite distance in a quasicrystal by combining a finite number of phason flips? If the answer to this question is yes, then, what kind of transport results from the phason dynamics? By considering a perfectly quasiperiodic quasicrystal as a cut through a higher-dimensional periodic crystal (hypercystal), it was argued in that the answer to the first question is affirmative for nearly perfect quasicrystals whenever the hyperatoms of the associated hypercrystal are sufficiently extended. This was explicitly demonstrated for the transport of vertices in a nearly perfect octagonal tiling. A similar proof also exists for decagonal (Penrose) and icosahedral (Ammann) tilings. Furthermore, it was conjectured in that the phason dynamics would lead to a diffusive transport with a characteristic Arrhenius temperature dependence of the associated diffusion constant that crosses-over from one characteristic activation energy at low temperatures to a smaller activation energy at high temperatures.

The main motivation for this letter is to prove the high temperature limit of the above conjecture for quasiperiodic icosahedral Ammann tilings and their periodic approximants.
Their equilibrium properties have been extensively studied using the Monte Carlo phason dynamics, [9,10] which we also employ here. By measuring the mean square displacement of vertices $R^2$ as a function of time $t$ and size $L$ of periodic approximants of the Ammann tilings, shown in Fig. 2, we show that the long-time transport in the infinite Ammann tilings is diffusive, $R^2 = 0.0012(1) \, t$, with $R$ in units of the tile edge length $l$ and $t$ in units of the Monte Carlo sweeps (MCS). When translated into physical units, this gives a diffusion constant that can be an order of magnitude larger than the one obtained from vacancy-assisted mechanism at room temperature. This suggests that the phason flips might be the dominant mechanism of self-diffusion in quasicrystals, at least at temperatures where the effective energy for the flip creation begins to saturate. [7] We also find a universal, size-independent, subdiffusive short-time behavior, $R^2 \sim t^{0.57(1)}$.

We find a similar behavior for infinite periodic approximants of the Ammann tiling. Analyzing transport data shown in Fig. 2 for different finite periodic approximant sizes, we find that the data is not consistent with a simple finite-size scaling. This indicates a possible presence of corrections to scaling, existence of at least two independent length-scales (or physical mechanisms) governing the phason-assisted self-diffusion, or anomalous long-time correlations.

We consider the ensemble of three dimensional random icosahedral Ammann tilings. [9] Each member of the ensemble is a tiling by prolate and oblate rhombohedra with edges parallel to the six five-fold symmetry axes of the icosahedral symmetry as shown in Fig. 1a. Furthermore, the orientational icosahedral symmetry of each tiling is guaranteed by the fact that prolate or oblate rhombohedra of all icosahedrally equivalent orientations appear with equal density, with the ratio of the overall densities of the prolates and oblates equal to $\phi = (1 + \sqrt{5})/2$. Starting from the perfect quasiperiodic Ammann tiling, members of the ensemble are constructed by successive phason flips (rearrangements of the rhombic dodecahedra) like the one shown in Fig. 1b. In equilibrium, these phason flips do not destroy long range order (quasiperiodicity) of the perfect Ammann tiling. [9,10]

We employ the discrete Monte Carlo dynamics of phason flips, that was also used to
equilibrate Ammann tilings. The random Ammann tiling is considered a plausible prototype of icosahedral quasicrystals. Moreover, several structure models of icosahedral or decagonal quasicrystals are based on atomic decorations of Ammann or Penrose tilings. In addition, although the real dynamics of atoms is certainly not Monte Carlo, the phason flip in a real crystal is likely to correspond to a movement of an atom (or a group of atoms) from one potential energy well to another, crossing an energy barrier. Thus, the “real” dynamics could be mapped to the Monte Carlo dynamics by relating the “real” time $t$ to the Monte Carlo time $t_{MC}$ by $t_{MC} = t \nu \exp(-\epsilon/k_BT)$, where $\nu$ is the attempt frequency for crossing the barrier and $\epsilon$ is the barrier energy.

Under the phason dynamics, vertices $r_i$ of a tiling perform walks that we characterize as phason-assisted self-diffusion. The diffusion can be quantified in the usual way, in terms of the time dependence of the average square end-to-end distance of the walks (i.e. of the displacements of vertices),

$$R^2 = \frac{1}{N} \sum_{i=1}^{N} |r_i(t) - r_i(0)|^2,$$

(1)

where $N$ is the number of vertices in the tiling. In addition to the time dependence of $R^2$, we are also interested in its dependence on the linear tiling size $L \sim N^{\frac{4}{3}}$. We start from periodic approximants of the Ammann tiling, the infinite periodic tilings related to the perfect Ammann tiling by approximating $\phi$ with its truncated continued fraction expansion, $\phi \approx F_n/F_{n-1}$, where $F_n$ is a Fibonacci number, $F_{n+2} = F_{n+1} + F_n$, $F_0 = F_1 = 1$.

These are cubic tilings with $N_n = 4(2F_n^3 + 3(F_n + F_{n-1})F_nF_{n-1})$ vertices per cubic unit cell of edge length $L_n = 2l(F_n\phi + F_{n-1})/\sqrt{\phi + 2}$. Then, for an approximant, we carry out the phason dynamics with periodic boundary conditions applied to a cubic unit cell of size $L = mL_n$ with $N = m^3 N_n$ vertices. In this way, not only can we investigate the infinite quasicrystal as $n \to \infty$, but for a given $n$ we can also investigate infinite crystals as $m \to \infty$.

The Monte Carlo phason dynamics is implemented in the following way. A vertex is selected at random and if it is of the type shown in Fig. 1b, it is flipped. Otherwise, the procedure is repeated. Since each vertex retains its identity in a single flip, and the dynamics
consists of a sequence of isolated flips, it is possible to follow a single vertex and measure its position \( \mathbf{r}(t) \) as a function of time. The unit of time is one Monte Carlo sweep, equal to \( N \) flip attempts. It should be noted that since we are interested here in the high temperature limit, we do not invoke any energetics in the flips.

Starting from a perfect tiling we first equilibrate it for \( N \) MCS (the characteristic relaxation time for equilibration with the phason flip dynamics was found \([3,10]\) to scale with the system size as \( L^2 \sim N^{2/3} \)). Following this equilibration period, we record the position of each vertex \( \mathbf{r}_i(t) \) for the ensuing \( 2 \times 10^5 \) MCS at intervals of 5 MCS at short times and \( 10^5 \) MCS at long times. We investigated tilings with \( n \) up to 7 and \( m \) up to 4. For all cubic tilings, periodic boundary conditions that respect the cubic symmetry of the tiling can be imposed on simple cubic (sc), face centered cubic (fcc), and body centered cubic (bcc) unit cells that contain the primitive unit cell of the tiling. For each periodic tiling (i.e., each \( n \)), this leads to three families of periodic boundary condition unit cells with \( N = m^3 N_n \), with \( m \) equal to an integer, \( 2^{3/2} \) times an integer, or to \( 4^{3/2} \) times an integer, for sc, fcc, or bcc boundary conditions, respectively. Tilings with \( n = 1, 4, 7, \ldots \) (that is, those where both \( F_n \) and \( F_{n-1} \) are odd) are bcc, so that \( m \) takes the value \( 2^{-3/2} \) times an integer for the bcc boundary condition family. All other tilings are sc. In order to estimate the error bars, we repeat the simulation several times for each tiling ranging from 400 times, for \( n = 2 \), to 2 times, for \( n = 7 \). It can be shown that for \( n = 1 \) no vertex can be transported beyond a single flip and, therefore, we consider only \( n > 1 \).

We show in Fig. 2 the mean square displacement averaged over all vertices and samples as a function of time for all tilings with \( n = 2, 3, 4, 5, 6, \text{ and } n = 7, m = 2^{-3/2} \). The short time behavior is independent of the system size \( L \) and can be fitted to the power-law dependence \( R^2 = at^\beta \) with \( \beta = 0.57(1) \), and \( a = 0.0310(1) L^2 / \text{MCS}^\beta \). Independent of the periodic unit cell size, the long time behavior is consistent with a linear dependence of \( R^2 \) on time \( t \). We determine the diffusion constant, \( D \), by fitting \( R^2(t) \) between \( t = 10^5 \) MCS and \( 2 \times 10^5 \) MCS to the “normal” diffusion form.
\( R^2(t) = D_L t + C_L. \) (2)

\( D \) depends on \( L \), as shown in the inset in Fig. 2, and we extrapolate to the \( L \to \infty \) limit by a phenomenological fit, \( D_L = D_\infty + bL^{-2} \), obtaining \( D_\infty = 0.0012(1)l^2/MCS \) and \( b = 0.0433(1)l^4/MCS \). This extrapolated value, which does not depend appreciably on the particular algebraic form used, can be translated into the real, physical diffusion constant \( D = 0.0012(1)l^2\nu \exp(-\epsilon/k_BT) \). In principle, values of the attempt frequency \( \nu \) and the barrier energy \( \epsilon \) could be determined in a realistic quasicrystal model, for example, by using a molecular dynamic simulation.

In order to set a scale, the prefactor 0.0012(1) of the diffusion constant we obtained, can be compared with the analogous prefactor for vacancy-assisted self-diffusion, which is typically \( \sim 10^{-4} \) at room temperature. Generally, since the vacancy prefactor is essentially a Boltzmann factor associated with the vacancy activation energy, the difference between the prefactors should be most pronounced in real quasicrystals at temperatures at which the phason activation begins to saturate. For some quasicrystalline materials these temperatures are estimated at above 1000K, where the prefactors are comparable. However, because of the exponential dependence of the diffusion constants on activation energies, it is difficult to estimate them reliably for real quasicrystals.

A further complication may arise if the phason flip in a real quasicrystal involves a rearrangement of a larger group of atoms. This would not only limit the accuracy of our estimates, but in such case the phason flips might have to be accompanied with a vacancy motion to effect diffusion. The vacancy motion may also play an important role in facilitating phason flips, as suggested by a molecular dynamics simulation of a two dimensional, two component Lennard-Jones quasicrystal, which showed that vacancy motion in that system was strongly correlated with phason flips.

Since the phason Goldstone mode requires correlated flips of infinitely many rhombic dodecahedra arranged in families of continuous sheets, isolated phason flips would generically require a non-zero energy. However, as pointed out in [14], this would have a negligible
effect in an equilibrated quasicrystal at sufficiently high temperature where a random tiling description becomes appropriate. On the other hand, this implies that the new mechanism of self-diffusion is, at a sufficiently high temperature, not so much a consequence of the existence of the phason Goldstone mode, i.e. of incommensurability, but of a particular tiling character of the structure. Therefore, the same mechanism should also be effective at a sufficiently high temperature in periodic crystal approximants of the quasicrystal. In fact, the diffusion constants \( D_2 = 0.0010(1)l^2/MCS \) and \( D_3 = 0.0011(1)l^2/MCS \) that we determined for the infinite \((m \to \infty)\) periodic approximants with \(n=2\) and \(3\), although slightly smaller than what we found for the Ammann tiling, are consistent with \( D_\infty = \lim_{n \to \infty} D_n \).

It is interesting to examine if there is a simple scaling form that describes all of our data. Since the short time behavior that we observed is independent of the system size, the scaling, if it exists, should take the form \( R_L^2 = \tau_L^{\beta} g(t/\tau_L) \), where \( \tau_L \) is a characteristic diffusion time that depends on the system size \( L \), and the scaling function \( g \) should have the asymptotic form \( ax^\beta \) for \( x \ll 1 \). On the other hand, the normal diffusion in the long time limit demands that \( g(x) = dx + c \), for \( x \gg 1 \). This, in turn, implies that \( D_L^{\beta/(1-\beta)} C_L \) should be independent of \( L \), where \( D_L \) and \( C_L \) are determined from the long time behavior Eq. (2). Our measured values are inconsistent with this conclusion since \( C_L \) changes sign as \( L \) is increased. It is possible that our systems are not sufficiently large and the discrepancy is due to the corrections to scaling. Another possible explanation for the apparent lack of a simple finite-size scaling is that there are two mechanisms, or two distinct length scales, responsible for the diffusion. Using the six-dimensional representation, where the tiling is a fluctuating three dimensional membrane, it is tempting to associate the two mechanisms with the decomposition of the membrane fluctuations into the relative and the center of mass motions. Indeed, it is the relative motion of the membrane that is responsible for permutations of vertices. In the physical space, such motions can be viewed as a cloud of phason flips that must accompany the permutation motion of a vertex. The size of this cloud would be finite, on the order of unity for Ammann tilings, and independent of \( L \) in the scaling limit. Similarly, the characteristic time for the short time correlated motion of
vertices in the cloud, at which the short time subdiffusive transport $t^\beta$ crosses over to the normal diffusion, would approach a finite value $\tau_\infty = (a/D_\infty)^{1/(1-\beta)}$ in the scaling limit $L \to \infty$. These conclusions are consistent with $D_L$ approaching a finite, non-zero value $D_\infty$ in this limit and with the characteristic time $\tau_\infty = 1.9(4) \times 10^{3}$MCS comparable to the average time needed to permute vertices inside the rhombic icosahedron in Fig. 1c.

Alternatively, the discrepancy could arise from anomalous corrections to the normal diffusion $[Ct^{1/\mu},$ with $1 < \mu < 2, C\sqrt{t\ln t}$, or $C\sqrt{t}$, instead of $C$ in Eq. (2)] due to any long-time correlations. [17] It is also difficult to rigorously rule out a possibility that the long time transport is anomalous with $R^2 \sim Dt/\ln t$, or $R^2 \sim Dt^\mu$ and $\mu$ very close to one. [18] The waiting time distribution provides a valuable tool for further clarification of these possibilities, and our preliminary analysis shows that the distribution could be consistent with a $\mu$ close to 2.

We have demonstrated that phason dynamics does indeed result in self-diffusion of vertices of the icosahedral Ammann tiling, in agreement with a general scenario conjectured for quasicrystals. [7] On short time scales, we found that the transport is subdiffusive with the exponent $\beta \approx 0.57(1)$. We determined the diffusion constant to be $D = 0.0012(1)I^2\nu \exp\left(-\frac{\xi}{\kappa_B T}\right)$, and we concluded that, in a real quasicrystal, it could be an order of magnitude larger than the room temperature vacancy-assisted diffusion constant with comparable parameters. The two mechanisms are expected to enhance each other, especially at lower temperatures where vacancies would be more effective in randomizing the phason field. However, a study of the low-temperature diffusion in energetically stabilized Ammann tilings or its approximants, is a significantly more complex problem which will have to be studied separately. Such study should also shed a light on the pinning-depinning transition in phason dynamics. If the phason-assisted self-diffusion is significant in a quasicrystal, then a strong change in the diffusion constant should be experimentally observed at its depinning transition. Additional work is also needed to resolve the questions about the finite size scaling for the phason-assisted diffusion.

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REFERENCES

[1] P. Bak, Rep. Prog. Phys. 45, 587 (1982); *ibid.* Phys. Rev. Lett. 54, 1517 (1985).

[2] P. Kalugin, A. Yu. Kitaev, and L. C. Levitov, Pis’ma. Zh. Eksp. Teor. Fiz. 41, 119 (1985) [JETP Lett. 41, 145 (1985)].

[3] P. Bak, Phys. Rev. Lett. 56, 861 (1986).

[4] D. M. Frenkel, C. L. Henley, and E. D. Siggia, Phys. Rev. B 34, 3649 (1986).

[5] A. Katz, in *Quasicrystals*, edited by M. V. Jarić (World Scientific, Singapore, 1990), p. 200.

[6] P. A. Kalugin, Europhys. Lett. 9, 545 (1989).

[7] P. A. Kalugin and A. Katz, Europhys. Lett. 21, 921 (1993).

[8] P. A. Kalugin, (unpublished).

[9] L. H. Tang, Phys. Rev. Lett. 64, 2390 (1990).

[10] L. J. Shaw, V. Elser, and C. L. Henley, Phys. Rev. B 43, 3423 (1991).

[11] M. V. Jarić and S. Y. Qiu, Phys. Rev. B (submitted).

[12] S. Burkov, J. Phys. I France, 2, 695 (1992).

[13] M. V. Jarić and S.-Y. Qiu, J. Non-Cryst. Solids 153&154, 181 (1993).

[14] P. A. Bancel, Phys. Rev. Lett. 63, 2741 (1989); G. Coddens et al., Europhys. Lett. 23, 33 (1993).

[15] M. Ronchetti, M. Bertagnolli, and M. V. Jarić in *Geometry and Thermodynamics*, edited by J. C. Tolédano (Plenum Press, New York, 1990), p. 141.

[16] V. Elser, Phys. Rev. Lett. 54, 1730 (1985).

[17] J.-P. Bouchaud and A. Georges, Phys. Rep. 195, 127 (1990).
[18] E. W. Montroll and H. Scher, J. Stat. Phys. 9, 101 (1973).
FIGURES

FIG. 1. (a) The six icosahedral five-fold symmetry directions of the Ammann tilings (arrows) and the two types of Ammann rhombohedra with edges along these directions. (b) Phason flip in the Ammann tiling as a rearrangement of a rhombic dodecahedron. (c) The vertices inside a rhombic icosahedron (emphasized by larger spheres) that are separated by a short rhombus diagonal can be permuted as a result of ten successive phason flips.

FIG. 2. Log-log plot of the average square vertex displacement versus time, for several crystal approximants. The inset shows extrapolation to the infinite Ammann tiling limit of the resulting diffusion constants $D_L$. 