Phason-elastic energy in a model quasicrystal

Ulrich Koschella, Franz Gähler, Johannes Roth, and Hans-Rainer Trebin

Institut für Theoretische und Angewandte Physik, Universität Stuttgart, D-70550 Stuttgart, Germany

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Abstract

The standard two-dimensional decagonal binary tiling quasicrystal with Lennard-Jones potentials is metastable at zero temperature with respect to one phason strain mode. By calculating the frequencies of local environments as a function of phason strain, a correction for the potentials is predicted, which stabilizes the quasicrystal.

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1. Introduction

In a previous paper [1] we have measured the five generalized phason-phonon elastic constants at zero temperature for the standard two-dimensional decagonal binary tiling quasicrystal with Lennard-Jones potentials, using molecular dynamics relaxation simulations. One of the phason elastic constants turned out to be negative, rendering the system metastable. Lee et al. [2] have shown, that the ground state of this system is a phase separation into various crystalline states without any five- or tenfold motifs.

To improve on those results, we analyze in Section 2 the phason elastic constants in dependence of the two-body interaction potentials, by counting the frequencies of atomic neighborhoods as a function of phason strain. These calculations suggest a modification of the potentials, presented in Section 3, which stabilizes the binary tiling quasicrystal. For these new potentials the elastic constants are determined with the same simulation method as in [1]. The elastic constant for stoichiometry preserving phason

strains becomes positive, and the system is stable.

The ground state structure for both potentials is obtained by Monte-Carlo cooling simulations, briefly discussed in Section 4. With the unmodified Lennard-Jones potentials the results of Lee et al. [2] are reproduced, whereas the modified potentials strongly prefer tenfold clusters. The cooling simulations yield a ground state structure which is a supertile random tiling with mainly doubly inflated thick Penrose rhombs.

2. Calculation of the zero temperature phason elastic constants

We consider here a model quasicrystal without phonon strain or local relaxations of atom positions, but with an arbitrary phason strain. Such structures include both periodic approximants and the perfect quasicrystal. If we consider a cutoff radius R_c for the atomic interactions, the potential energy E_i of a single atom depends only on the potentials ϕ and the atomic configuration inside the ball B_{R_c, x_i} with radius R_c around the position x_i of the atom. There-
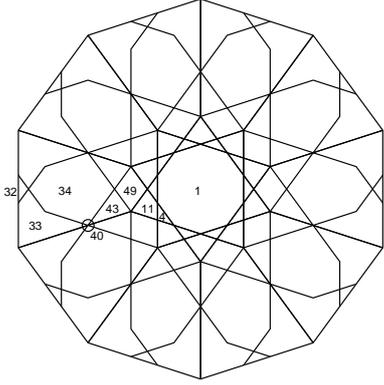
Fig. 1. Acceptance domains for the environments of a big atom ($R_c = 1.92$). The atomic configurations are shown in Fig. 2. An analogous subdivision existst for the acceptance domain of the small atoms.

Fig. 2. Local environments of big atoms appearing in the standard binary tiling quasicrystal ($R_c = 1.92$). (No. 40 doesn't exist in the perfect quasicrystal, but appears at infinitesimal phason strain.)

fore, we can calculate the total potential energy by adding the potential energies of the central atoms of each local environment, multiplied with the number of occurrences of the environment. In the same manner we can express the total volume by the Voronoi volumes of the central atoms of the occuring environments, and finally get for the potential energy density

$$e_{\mathrm{pot}} = \frac{E_{\mathrm{pot}}}{V} = \frac{\sum_i N_i E_i}{\sum_i N_i V_i} = f\,(T = 0)\,. \qquad (1)$$

We can easily rewrite this in terms of the frequencies n_i of the environments. These, on the other hand, are proportional to the areas of the acceptance domains A_i of the environments:

$$f = \frac{\sum_i n_i E_i}{\sum_i n_i V_i} = \frac{\sum_i A_i E_i}{\sum_i A_i V_i}\,. \qquad (2)$$

The energy E_i of an atom with a given environment depends only on the potentials ϕ, the corresponding acceptance domain A_i depends on the phason strain χ, and the Voronoi volumes V_i are fixed and known, so that we have derived the zero temperature free energy density $f\,(\chi; \phi)$ as a function of phason strain, parameterized by the values of the potentials at the occuring distances.

The local environment of an atom is determined by the set of its neighbors inside a ball of radius R_c. The acceptance domain of a local environment thus

is the intersection of the projections of the atomic surfaces of all the atoms inside this ball. The atomic surface of the central atom is thereby divided into different areas, each belonging to one local environment in physical space (Fig. 1). Applying phason strain deforms perpendicular space, and in particular the atomic surfaces, along with their subdivisions according to the local environments. The sizes of the different subdomains of the atomic surfaces, and thus the frequencies of the local environments, therefore depend on the phason strain.

From now on we choose the interaction cutoff radius $R_c = 1.92$. This is rather small, but includes all bonds of the characteristic tenfold cluster (Fig. 2). For this cutoff radius there are 299 inequivalent (up to symmetry operations) local environments in a totally randomized binary tiling. 19 of them exist in the perfect quasicrystal, and 4 more occur already at infinitesimal phason strain. The remaining 276 only show up at phason strains with absolute values greater than 0.1. As we are only interested in small phason strains, and are doing linear phason elasticity theory, these latter environments are neglected.

After calculating the acceptance domains of the 23 environments of interest and the Voronoi volumes and potential energies of the central atoms, (2) leads to

r_1	$1/\tau$	0.62	
r_2	1	1.00	
r_3	$2s/\tau$	1.18	
r_4	$\sqrt{4-\tau}$	1.54	
r_5	τ	1.62	
r_6	$2s$	1.90	
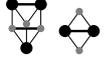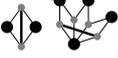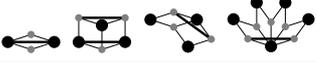
Table 1. Atomic distances smaller than $R_c = 1.92$ occuring in binary tiling quasicrystals ($\tau = \frac{\sqrt{5}+1}{2}, s = \sin\frac{2\pi}{5}$).

$$f = f_0 + \frac{1}{2}\lambda_7\chi_6^2 + \frac{1}{2}\lambda_9\chi_8^2 + O\left(\chi^3\right) \tag{3}$$

$$\begin{aligned}
\lambda_7 = & -0.47\phi_{AA}\left(r_3\right) - 2.38\phi_{AA}\left(r_6\right) \\
& + 0.76\phi_{BB}\left(r_1\right) - 0.68\phi_{BB}\left(r_3\right) \\
& \qquad - 3.47\phi_{BB}\left(r_5\right) - 0.91\phi_{BB}\left(r_6\right) \\
& + 0.58\phi_{AB}\left(r_2\right) + 4.40\phi_{AB}\left(r_4\right) \\
\lambda_9 = & \quad 0.47\phi_{AA}\left(r_3\right) - 1.02\phi_{AA}\left(r_6\right) \\
& - 0.76\phi_{BB}\left(r_1\right) - 2.72\phi_{BB}\left(r_3\right) \\
& \qquad - 4.22\phi_{BB}\left(r_5\right) - 4.27\phi_{BB}\left(r_6\right) \\
& - 0.58\phi_{AB}\left(r_2\right) + 2.40\phi_{AB}\left(r_4\right).
\end{aligned}$$

The free energy density is a quadratic form in the phason strain modes. We get the two phason elastic constants as a function of the potential values at six occuring distances, shown in Table 1.

If we evaluate the phason elastic constants from (3) for the Lennard-Jones potentials usually used for the binary tiling quasicrystal, we get

$$\lambda_7 = -2.40, \qquad \lambda_9 = 1.03,$$

while our molecular dynamics relaxation simulations [1] resulted in

$$\lambda_7 = -2.70, \qquad \lambda_9 = 0.80.$$

The cutoff radius used for the simulations ($R_c = 7$) was bigger than the one used for the analytic expression. However, variations of the simulations show, that the difference between the obtained phason elastic constants is mainly due to atomic relaxations allowed in the simulations, while the atom positions are fixed in the analytic calculations presented here.

3. Modification of the potentials

The nearest neighbor interaction terms for the two phason elastic constants λ_7 and λ_9 have the same weights, but opposite sign (first column in (3)). This is due to the fact, that all binary tilings with the same stoichiometry have the same potential energy, if only nearest neighbor interactions are assumed. For all plausible potentials the nearest neighbor part of λ_7 is negative, while the one of λ_9 is positive. Since the phason strain mode χ_6 increases the relative number of small atoms while χ_8 decreased it, this describes the dependence of the potential energy density on bond density.

Stoichiometry preserving phason strains satisfy $\chi_6^2 = \chi_8^2$, and thus have the phason elastic constant

$$\begin{aligned}
\frac{1}{2}\left(\lambda_7 + \lambda_9\right) = & -1.70\phi_{AA}\left(r_6\right) - 1.70\phi_{BB}\left(r_3\right) \\
& - 3.85\phi_{BB}\left(r_5\right) - 2.59\phi_{BB}\left(r_6\right) \\
& + 3.40\phi_{AB}\left(r_4\right). \tag{4}
\end{aligned}$$

The Lennard-Jones potentials are attractive at all distances r_1 to r_6. Thus all terms in (4) are positive, except for the last one. This term drives the system with the Lennard-Jones potentials unstable. A repulsive component in the potential between different atoms at distance r_4 makes the last term of (4) positive and leads to stabilization. We have chosen a mixed Lennard-Jones and Dzugutov [3, 4] potential for the modification, which has a minimum of -2 at distance r_2 and a maximum of $+0.25$ at approximately r_4 (Fig. 3).

The new potentials result in the following phason elastic constants:

$$\lambda_7 = -0.31, \qquad \lambda_9 = 2.17,$$
$$\left(\lambda_7 + \lambda_9\right)/2 = 0.93.$$

We also reran our molecular dynamics relaxation simulations with the modified potentials, which resulted in

$$\lambda_7 = -0.88, \qquad \lambda_9 = 1.34,$$
$$\left(\lambda_7 + \lambda_9\right)/2 = 0.23.$$

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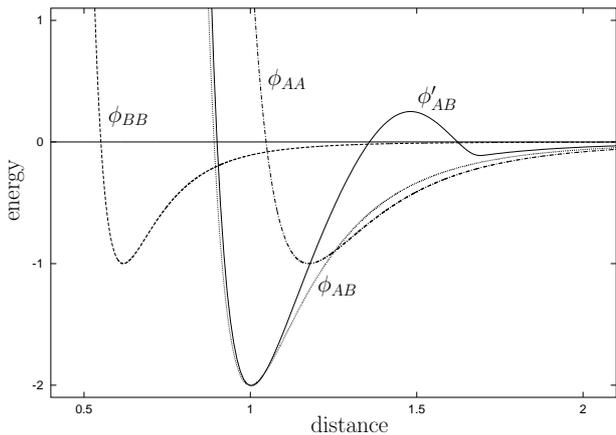
Fig. 3. Original Lennard-Jones potentials ϕ_{AA} (dash-dotted), ϕ_{BB} (dashed), ϕ_{AB} (dotted), and modified potential ϕ'_{AB} (solid), a mixed Lennard-Jones and Dzugutov potential.

With the potential modification described above, we were able to drive the phason elastic constant for constant stoichiometry positive, but the phason elastic constant λ_7 remains negative. The calculated and simulated values of the phason elastic constants still have the same order of magnitude and the same sign, but differ more than those for the Lennard-Jones potentials. If we enlarge the repulsive part of ϕ_{AB} further, for example to 0.5, we obtain from the analytic expressions phason elastic constants which are all positive, but the simulations lead to completely different results. So, if the repulsive part is too strong, atomic relaxations overshadow completely the effect of the energy dependence on the frequencies of local environments, and the calculation is no longer realistic.

4. Monte Carlo Simulations

In order to obtain the ground state structure, we have also performed Monte-Carlo cooling simulations, both with the Lennard-Jones potentials and the modified potentials. In the Lennard-Jones case we could reproduce the results of Lee et al. [2]. The ground state then is a phase separation into several crystalline states, without any five- or tenfold local environments. For the modified potentials, on the other hand, we obtain a super-tile random tiling structure, where the diameter of the super-tiles is of the same order as our cutoff radius. We expect to get a similar structure with bigger super-tiles if we enlarge the cutoff radius. An interesting question is, whether a qualitatively different behavior is found, if the cutoff radius is increased beyond the matching rule radius, which is about 8 for the present model [5]. According to the locked state theory [6] one should then find non-analytic linear terms in the free energy denstiy. However, the method presented here is computationally too demanding for such large cutoff radii, but there may be modifications with which one could reach the matching rule radius.

5. Conclusion

We have presented a way to compute the phason elastic constants at temperature zero as a function of the potential values at certain distances occurring in the quasicrystal. This enabled us to predict a modification of the potentials, improving the stability of the quasicrystal. One phason elastic constant remains slightly negative, but the corresponding phason strain changes stoichiometry, so that a discussion of the free energy dependence on this phason strain without chemical potentials is incomplete anyway. For the phason strain directions which leave stoichiometry constant, the stabilization criteria are fulfilled. The comparison of the analytic results with relaxation simulation results are important, because the analytic calculations do not take atomic relaxations into account. The analytic calculations are meaningful only if the effect of the relaxations on total potential energy is small compared with that of the variation of the frequencies of local environments.

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