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Are Layered Two-Dimensional Quasicrystals Periodic in the Third Direction?

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"Two-dimensional" quasicrystals have generally been believed to be quasiperiodic in the XY plane and periodic in the Z direction. This is not necessarily the case. A layered material with equidistantly spaced layers and a "random tiling" two-dimensional quasicrystal in each layer is shown to exhibit delta-function diffraction spots even when the phason strain fields in different layers are completely uncorrelated. Surprisingly, such a Z-aperiodic quasicrystal shows true δ-peaks, while a more ordered Z-periodic quasicrystal shows less sharp, power-law-decaying peaks.

KEY WORDS: Quasicrystals; aperiodic tilings.

The only experimental justification for the general belief that "two-dimensional" quasicrystals are periodic in the Z direction is the fact that their diffraction patterns exhibit sharp peaks which fill layers equidistantly spaced in Z. This experimental fact alone, however, is not sufficient to conclude the existence of periodicity in the Z direction. At a first glance, one would suspect that the absence of correlations between the layers would destroy peak sharpness. This would be the case if arbitrary rotations or translations in the XY plane were to occur. However, if the only disorder is associated with the phason mode, correlations between layers are not required for peak sharpness. This fact will be shown below in the framework of a layered tiling model. The result, however, is believed to be more general and could be obtained without requiring any tiling model assumptions.

The description of the model follows. The spacing between the layers in the Z direction is c. Atoms in every layer are situated on the sites of a

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rhombic tiling. Any rhombic tiling is known to be presented as a projection of a two-dimensional lattice surface in a higher-dimensional space $\mathbb{R}^D$ onto a tiling plane $\mathbb{R}^2_\parallel$, which is the plane of a layer. The task of averaging over the statistical ensemble of rhombic tilings (henceforth by $\langle \cdots \rangle$) can be performed in a continuous limit.[1,2] Specifically, the deviation of the strip from the plane $\mathbb{R}^2_\parallel$ is described by a continuous phason strain field $\mathbf{h}(\mathbf{x}_\parallel, z) \in \mathbb{R}^{D-2}_\perp$, where $\mathbb{R}^{D-2}_\perp$ is the space perpendicular to $\mathbb{R}^2_\parallel$ and z is an integer used to label the layers. The diffraction pattern of the layered quasicrystal will be calculated in the random tiling limit,[1-6] i.e., it will be assumed that all configurations of the tiles are nearly degenerate and, therefore, nearly equiprobable. This equiprobable ensemble is described by Elser's random tiling hypothesis,[1] which has not been proven analytically but has been confirmed by various computer simulations.[3-6] According to the hypothesis, the most probable (typical) configuration is quasiperiodic on average and possesses some high symmetry. More specifically, the typical two-dimensional lattice surface in $\mathbb{R}^D$ has an average slope

$$\lim_{x_\parallel \to \infty} \max_{\mathbf{x}_\parallel} (|\mathbf{h}(\mathbf{x}_\parallel)|)/x_\parallel = 0$$

although the deviation $\mathbf{h}(\mathbf{x}_\parallel) \in \mathbb{R}^3_\perp$ is unbounded: $\langle h^2 \rangle \propto \ln(\mathbf{x}_\parallel)$. The plane $\mathbb{R}^2_\parallel$ near which the surface fluctuates is selected so that the corresponding tiling has a rotational symmetry, octagonal, decagonal, and dodecagonal symmetries being found in various metallic alloys.

The diffraction intensity $I(\mathbf{q}, q_z)$ is given by

$$I(\mathbf{q}, q_z) = \sum \langle \exp(i\mathbf{q}(\mathbf{r}_z - \mathbf{r}'_{z'}) + iq_z(z - z')) \rangle \tag{1}$$

where $\mathbf{q}$ and q_z are the XY and the Z components of the diffraction vector, respectively, and the sum is taken over the coordinates of the tiling sites $\mathbf{r}_z$ and $\mathbf{r}'_{z'}$ and over all layers z and z'. Since the spacing between all the layers is the same, the diffraction peaks will be expected to occur in the planes $q_z = 2\pi m/c$, where c is the interlayer spacing. For these q_z the intensity becomes

$$I(\mathbf{q}) = L_z \sum_z \left\{ \sum_{\mathbf{r}, \mathbf{r}'} \langle \exp[i\mathbf{q}(\mathbf{r}_z - \mathbf{r}'_0)] \rangle \right\} \tag{2}$$

The internal sum is calculated by lifting to $\mathbb{R}^D$ and making use of the continuous approximation in the usual manner:

$$\begin{aligned} I(\mathbf{q}) &= L_z^2 L_x L_y \sum_{\mathbf{Q}} |\Phi(\mathbf{Q}_\perp)|^2 \int F_{\mathbf{Q}}(x) \exp[i(\mathbf{q} - \mathbf{Q}_\parallel)\,\mathbf{x}]\, d^2\mathbf{x} \\ F_{\mathbf{Q}}(x) &= \frac{1}{L_z} \sum_z \exp\left\{ -\frac{1}{2} Q_\perp^2 \langle [\mathbf{h}(\mathbf{x}, z) - \mathbf{h}(0, 0)]^2 \rangle \right\} \end{aligned} \tag{3}$$

where $\mathbf{x} \in \mathbb{R}_{\|}^2$; $\mathbf{Q} \in \mathbb{R}^D$ are the reciprocal lattice vectors of the hyperlattice and $\Phi(\mathbf{Q}_\perp)$ is the Fourier transform of the strip form factor. [The form factor is $\Phi(x_\perp) = 1$ inside the strip, $\Phi(x_\perp) = 0$ outside the strip.] The anisotropy of the phason Debye–Waller factor $F_{\mathbf{Q}}$ is neglected for clarity. In the general case (not necessarily random tiling limit) the phason strain field correlator in (3) can be found using the free energy

$$F = c \sum_z \left\{ \frac{1}{2} (\nabla \mathbf{h}(\mathbf{x}, z), \mathbf{K} \nabla \mathbf{h}(\mathbf{x}, z)) + \frac{K_z}{2c^2} [\mathbf{h}(\mathbf{x}, z+1) - \mathbf{h}(\mathbf{x}, z)]^2 \right\} d^2\mathbf{x} \tag{4}$$

The first term is the quadratic form consistent with the symmetry of the tiling.[1,2] If K_z is nonzero, the phason correlator in (3) is finite. This fact becomes especially obvious if one substitutes the second term in (4) by its continuous analog $K_z(\partial \mathbf{h}/\partial z)^2/2$,[7]

$$\langle [\mathbf{h}(\mathbf{x}, z) - \mathbf{h}(0, 0)]^2 \rangle = T \cdot \text{const} \int \frac{(1 - e^{i\mathbf{q}\mathbf{x} + iq_z z})}{(\mathbf{q}, \mathbf{K}\mathbf{q}) + K_z q_z^2} d^2\mathbf{q}\, dq_z < \infty \tag{5}$$

Therefore, δ-function peaks at $\mathbf{q} = \mathbf{Q}_{\|}$ arise. They fill the planes $q_z = 2\pi m/c$ everywhere densely.

According to Elser's random tiling hypothesis,[1] in the random tiling limit the quadratic form $(\nabla \mathbf{h}, \mathbf{K} \nabla \mathbf{h})$ is positive definite and linear in T. In other words, the first term in (4) arises from the random tiling *entropy*. The second term tries to make neighboring layers similar (K_z is supposed to be positive) and is due to the layer–layer interaction *energy*. In the random tiling limit the energy is negligible in comparison with TS(S denotes the entropy). So, *in the random tiling limit K_z vanishes*. With $K_z = 0$ the phason correlator becomes

$$\langle [\mathbf{h}(\mathbf{x}, z) - \mathbf{h}(0, 0)]^2 \rangle = 2\langle \mathbf{h}^2 \rangle = 2v \ln(L/a) \tag{6}$$

where a is a typical lattice spacing and v a temperature-independent constant of order 1 that can easily be calculated if the specific form of the entropic quadratic form in (4) is given. The correlator (6) turns out to be $2\langle \mathbf{h}^2 \rangle$. This is in an agreement with the fact that the layers are uncorrelated when the interlayer coupling constant K_z is zero. The

expression (6) diverges with the system size L, but only logarithmically. Substituting (6) into (3), one sees that the peaks are still δ-functions:

$$I_{\max} = I(0) \propto L_z^2 (L_x L_y)^{2-\eta/2} \propto L^{6-\eta}, \qquad \eta = vQ_\perp^2 \tag{7}$$

$$I(\mathbf{q}) \propto \max(L_z^2 (L_x L_y)^{1-\eta/2}, L_z L_x L_y) \propto \max(L^{4-\eta}, L^3) \tag{8}$$

The L^3 term is the intensity of the diffuse background. The ratio $I_{\max}/I(\mathbf{q})$ scales as L^2 for peaks with $\eta < 1$, and as $L^{3-\eta}$ for $1 < \eta < 3$. This is why I called the peaks δ-functions (there is no proper term for such peaks in the literature). One has to remember that they are δ-functional in the sense that their widths tends to zero as L tends to infinity. However, in contrast with the conventional δ-peaks, $I_{\max}$ scales not as L^6, but as $L^{6-\eta}$. Both (7) and (8) are only valid for peaks with not too big a $Q_\perp$, i.e., for $\eta = vQ_\perp^2 < 3$; otherwise, there is no peak at all. Therefore, the peaks do not fill the sheets $q_z = 2\pi m/c$ everywhere densely.

At first glance one might conclude that Eqs. (7), and (8) can be obtained from the free energy (3) with the second term omitted ($K_z = 0$). However, the first, entropic term in (3) is invariant under the transformation $\mathbf{h}(\mathbf{x}, z) \to \mathbf{h}(\mathbf{x}, z) + \mathbf{H}(z)$. So, the correlators of $\mathbf{H}(z)$'s and, therefore, of $\mathbf{h}(\mathbf{x}, z)$'s cannot be found unambiguously from the free energy (3) containing only the first term.[3] Retaining small but nonzero K_z in Eq. (3) allows one to find

$$\langle [\mathbf{H}(z') - \mathbf{H}(z)]^2 \rangle = \text{const} \cdot |z' - z|/(K_z L_x L_y) \tag{9}$$

One has to remember that in real quasicrystalline materials the random tiling limit is never achieved, and therefore K_z may be arbitrary small, but it remains nonzero. So, the denominator in (9) is extremely large. This physical argument establishes the following order of limits: first one has to put $L_x L_y \to \infty$ in (9), then find the correlator of the $\mathbf{H}(z)$'s and use it to obtain the correlator of the $\mathbf{h}(\mathbf{x}, z)$'s. Finally, one can put $K_z = 0$, which gives Eq. (6).

It is instructive to compare the diffracted intensities (7) and (8) which correspond to the case of uncorrelated phason fields in different layers with the diffraction intensities of a quasicrystal built by stacking identical copies of a two-dimensional random tiling. In this case $\mathbf{h}(\mathbf{x}, z) = \mathbf{h}(x, 0)$ and the correlator becomes

$$\langle [\mathbf{h}(\mathbf{x}, 0) - \mathbf{h}(0, 0)]^2 \rangle = 2v \ln(x/a) \tag{10}$$

[3] I thank C. L. Henley for pointing out this subtle but important point.

Substituting (10) into (3) gives a well-known result, namely, that the peaks are no longer δ-functions, but decay as a power law[2]:

$$I(\mathbf{q}) \propto L_z^2(L_xL_y)\,|\mathbf{q}-\mathbf{Q}_\parallel|^{(\eta-2)}, \qquad \eta = vQ_\perp^2$$
$$I_{\max} = I(0) \propto L_z^2(L_xL_y)^{2-\eta/2} \propto L^{6-\eta} \tag{11}$$

This formula is valid only for peaks with not too big a $Q_\perp$, i.e., for $\eta = vQ_\perp^2 < 2$; else, there is no peak at all. Note that the maximal intensity scales by the same law as in the uncorrelated case (7).

One may try to distinguish between the correlated and the uncorrelated cases experimentally by measuting peak profiles, looking for the presence or absence of the power-law tails. However, phonons may produce power-law tails of a similar kind. One needs to separate them carefully. There is another, straightforward possibility to check whether the system is periodic or not: to make an HREM image of the XZ or YZ plane. Although many valuable experiments on the decagonal phase have been carried out (see refs. 8–12 and references therein), none of them has questioned the stacking periodicity.

The obtained result looks a bit surprising: a less correlated system has sharper diffraction peaks. Nevertheless, this fact does not contradict any fundamental principle. By qualitative reasoning one might mistakenly conclude that the absence of correlations between layers results in random phases destroying the Bragg diffraction. However, one has to take into account that the only existing randomness is associated with the phason mode. According to Elser's random tiling hypothesis,[1] the most probable configuration is the configuration with no phason strain at all. So, the tilings in all the layers are close to this most probable tiling, which is known to be symmetric (octagonal, decagonal, or dodecagonal). Therefore, even without imposed interlayer correlations the material becomes close to Z-periodic *on the average* due to the phason fluctuations in the layers. Nevertheless, the layers differ from one another and the material is not periodic microscopically. This closeness to periodicity on the average may also be responsible for the fact that high-resolution electron micrograms[8,9] exhibit symmetric quasiperiodic patterns.

The present result helps to apply the random tiling hypothesis to real alloys. The classic random tiling approach[1–6] deals with tilings of a plane, whereas real "two-dimensional" quasicrystals[8–12] are layered materials. In general (not necessarily in the random tiling limit) the interlayer coupling is described by Eq. (4). Three cases should be distinguished: $K_z = 0$ (uncorrelated layers), $K_z = \infty$ (exact periodicity along z), and finite K_z. As has been already mentioned, K_z arises from the layer–layer interaction

energy, whereas K may be deduced from the tiling configurational *entropy*.[1–6] A natural generalization of the random tiling hypothesis to layered structures is to neglect *all* energetic contributions, including the second term in Eq. (4). This explains my interest in the case of $K_z = 0$. However, nobody knows for sure whether or not nature has chosen entropy to stabilize real quasicrystals. Therefore, two other cases deserve to be considered. The diffraction intensities for the periodic stacking ($K_z = \infty$) are given by Eq. (11). However, *Z-periodicity is incompatible with the entropic stabilization.* In fact, the entropy of such a Z-periodic structure would simply equal the entropy of the in-plane random tiling which would scale proportionally to $L_x L_y$. Any energy associated with the structure would scale as L^3 and thus would not be negligible in comparison with the entropy. However, if the layers were uncorrelated ($K_z = 0$) the entropy would simply be the in-plane entropy multiplied by L_z. Thus, the entropy of the layered system would scale as L^3 and could therefore dominate over the energy. The case of finite, nonzero K_z (regardless of the K_z origin: from coupling energy, growth algorithms, conditional probabilities, etc.[7]) is rather trivial: the free energy scales as L^3, allowing entropic stabilization and, according to Eq. (5), the peaks are true δ-functions. The phason degree of freedom would manifest itself in phason Debye–Waller factors $\exp(-BQ_\perp^2/4)$ with B routinely found from Eqs. (3)–(5):

$$B = \frac{T}{4\pi^2}\left\{\frac{a^2}{K}\ln\left(1+\frac{Kc^2}{K_z a^2}\right)+\frac{2ac}{(KK_z)^{1/2}}\,\mathrm{tg}^{-1}\left[\left(\frac{K_z a^2}{Kc^2}\right)^{1/2}\right]\right\} \tag{12}$$

If $K_z \to 0$, the coefficient B increases indefinitely, but only logarithmically:

$$B = \frac{a^2 T}{4\pi^2 K}\left[\ln\left(\frac{Kc^2}{K_z a^2}\right)+2\right] \tag{13}$$

The intensities of *true* δ-peaks become zero at $K_z = 0$, which does not mean disappearance of the peaks. It only means that the intensities of *conventional* δ-peaks, i.e., those scaled as L^6, vanish. At $K_z = 0$ the maximal intensity scales anomalously, as $L^{6-\eta}$ [Eq. (7)].

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