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Modeling decagonal quasicrystals: random assembly of interpenetrating decagonal clusters

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Abstract. — Conventional tiling models of quasicrystals imply the existence of two or more elementary cells (tiles). A new approach is proposed that allows a quasicrystal to be thought of as a random assembly of identical interpenetrating atomic clusters. This model is shown to be equivalent to a decagonal binary tiling. On applying a random tiling hypothesis, originally postulated by Elser, to the present cluster model it is found that the free energy as a function of the alloy composition has a cusp at a point exactly corresponding to the decagonal quasicrystal. This fact helps to explain an old mystery, namely, why a system is phase locked in a quasicrystalline state even though it is incommensurate.

Introduction.

The recent experimental progress made in the study of the thermodynamically stable decagonal quasicrystals Al-Cu-Co and Al-Ni-Co (believed to be isostructural) has revived an interest in the decagonal phase. These materials have been probed by high resolution electron microscopy (HREM) [4, 15, 16], scanning tunneling microscopy [3], powder [2] and single crystal X-ray diffraction [17-19]. However, the aim of the present article is not to determine the atomic structure of these particular alloys, AlCuCo and AlNiCo, but rather to develop a mathematical framework which might be used in determining their structure as well as that of other possible decagonal quasicrystals. The atomic model for AlCuCo and AlNiCo has been recently developed [20] making use of the above mentioned experimental data and the general approach described below. Although the decagonal cluster shown in figure 1 of the present paper is a cluster successfully describing AlCuCo, I will not discuss below why this is so, leaving the discussion to [20]. This is done, first, not to obscure geometry by crystallography and, second, to emphasize that AlCuCo might be merely one particular example of a class of decagonal quasicrystals. Besides, the general approach itself was developed before the experimental works [15-19] had been published.

The paper consists of two almost independent parts. The first, geometric, section provides a fresh insight into tiling models. The conventional interpretation of tiling models that decorates the two Penrose tiles [5] seems unconvenient to explain the high resolution electron
micrograms [4]. On contemplating these experimental images I discovered a new approach to their interpretation and to the atomic model itself. The new model proposed in this paper appears to be mathematically equivalent to one particular tiling model, i.e. a decagonal binary tiling [6-8]. Nevertheless, I believe that the present cluster model is more justified from a physical point of view and is more attractive because it uses only one decagonal atomic cluster instead of two or more rhomic tiles. In other words, by starting with a more general proposition than is usual [5] the binary tiling can be derived, in contrast with previous works in which it was taken as an axiom. Section 1 is devoted only to geometry and may be applied to either «random tiling» [6-9, 12] or «ideal», phason free, [10, 14] quasicrystals. A reader not interested in tiling geometry may skip the beginning of section 1, up to definition 3.

Fig. 1. — One of the possible examples of a decagonal atomic cluster, a cluster found in AlCuCo and AlNiCo. Circles : Al, squares : T-metal; white : z = 0, black : z = c/2 layer. Presence of two layers and, respectively, of two colors is not essential for the present theory.

Section 2 addresses the problem of phase locking in a quasicrystalline state. The random tiling approach is adopted in this section. Although the results of section 1 are used to derive a cusp in the free energy, this is done only to make calculations tangible. The main result, regarding the existence of a range of chemical potentials corresponding to a quasicrystalline phase, can be rederived for virtually any random tiling models, not necessarily decagonal and not necessarily two-dimensional. Moreover, I believe the result is still valid even beyond the framework of tiling models, provided that some generalized version of entropy stabilization hypothesis [12] holds.

Real materials are three-dimensional layered structures. Stacking of decagonal layers along the 10-fold axes is usually presumed periodic. Although there are certain doubts in stacking periodicity [21] this topic will not be discussed below. In AlCuCo there are two decagonal layers per vertical period c = 4.15 Å (they are shown by black and white in Fig. 1); however I will completely disregard this subtlety and consider a purely two-dimensional model.

1. Geometry of overlapping decagonal clusters.

Below is the description of the model. Atoms are allowed to form only one decagonal cluster (Fig. 1 is an example, the cluster found in AlCuCo [20]). One does not care about the particular positions of atoms, all one needs is decagonal or at least pentagonal symmetry for the atomic configuration inside the cluster. Clusters may intersect or share a side. The latter case will be referred to as a particular case of the former. The positions of atoms inside a region of intersection, although similar to those of a sole cluster, may not be exactly those. However, there is only one atomic decoration for each type of intersection region (Fig. 2).
DEFINITION 1. — A \( \left( \frac{\pi}{5}, 3 \frac{\pi}{5} \right) \)-covering is a covering of a plane by identical clusters such that

i) Every point of the plane belongs to at least one cluster.

ii) If two clusters intersect then it is either a \( \frac{\pi}{5} \) or a \( 3 \frac{\pi}{5} \) intersection (Fig. 2).

The \( (\pi/5, 3 \pi/5) \)-coverings will also be referred to as allowed coverings. Every allowed covering (Fig. 3) is characterized by the set \( \Gamma \) of the cluster centers. One can examine this set and the Voronoi decomposition associated with it. Let the cluster radius be equal to 1. According to definition 1 the distances between intersecting clusters take two values only (Fig. 2):

\[
\ell = 2 \cos (\pi/10) \quad \text{or} \quad s = 2 \cos (3 \pi/10).
\]

Note that \( \ell/s = \tau = (\sqrt{5} + 1)/2 = 1.618... \), the golden mean. Connecting the centers of the intersecting clusters is a graph (Fig. 3) with bonds of the two lengths, \( \ell \) and \( s \). We shall call this graph an \( \ell \)-s graph. Note that the above given definition of both the \( \pi/5 \) and \( 3 \pi/5 \) intersections implies that if two clusters intersect then their axes of symmetry are parallel. This is possible if, and only if, the angles between the bonds are of the form \( \pi n/5 \), i.e. the bonds of the \( \ell \)-s graph are oriented along a symmetric 5-star.

It is useful to distinguish between « real » and « fake » \( \ell \)-bonds. If a \( \pi/5 \)-intersection does not belong to a \( 3 \pi/5 \)-intersection then the corresponding \( \ell \)-bond is called real (long solid lines in Fig. 3a). The interval perpendicular to a real \( \ell \)-bond at its center is a side of some Voronoi domain. If a \( \pi/5 \)-intersection belongs to a \( 3 \pi/5 \)-intersection then the corresponding \( \ell \)-bond is called fake (dashed lines in Fig. 3a). The perpendicular to a fake \( \ell \)-bond is not a side of a Voronoi domain, it is « beaten » by nearby \( s \)-bonds. For this reason fake \( \ell \)-bonds play no significant role and will be ignored in what follows. It is clear that there are no fake \( s \)-bonds, i.e. an interval perpendicular to any \( s \)-bond at its center is the side of a Voronoi domain.
Below are some useful properties of $l$-s graphs which could be easily observed in figure 3. If contemplating figures is not convincing strict mathematical proofs can be found in the preprint version [22] of the present work.

i) The Voronoi decomposition associated with any \( \left( \frac{\pi}{5}, 3 \frac{\pi}{5} \right) \) covering is constructed of only 6 Voronoi domains shown in figure 4.

ii) The only allowed multiple cluster intersection other than a single point is a triple intersection.

iii) An $l$-s graph corresponding to any \( (\pi/5, 3 \pi/5) \) covering forms the tiling of a plane by three tiles: a triangle, a trapezoid and a regular pentagon (Fig. 3).

Triangle-trapezoid-pentagon tiling is not convenient for our purposes. However, this tiling is known to be equivalent [11] to different, more convenient tiling, namely a binary tiling. One may recall a definition of the latter [6]. Consider a tiling of a plane by two Penrose tiles (a thin rhombus with $\pi/10$ and $4 \pi/10$ angles and a fat rhombus with $2 \pi/10$ and $3 \pi/10$ angles).

**DEFINITION 2.** — A vertex of a tiling is called even (odd) if all angles made by tiles meeting at this vertex are of the form $N \pi/10$, where $N$ is even (odd). A tiling of a plane by two Penrose tiles such that any vertex is either even or odd is called a binary tiling.

The central result of section 1 (and the only one we will need in the following) is:

**Proposition 1.** — A set of all \( \left( \frac{\pi}{5}, 3 \frac{\pi}{5} \right) \) coverings is equivalent to the set of all binary tilings.

The mapping between the two models is illustrated by figure 3b (if Fig. 3b is not convincing strict mathematical proofs can be found in the preprint version [22] of the present work):

— odd vertices of a binary tiling are centers of decagonal clusters;
— even vertices of a binary tiling are corners of decagonal clusters, common for two overlapping clusters (Fig. 2);
— binary tiling's side length equals the cluster radius;
— \(\pi/5\) overlappings are associated with thin Penrose tiles (Fig. 2), true \(\ell\)-bonds being long diagonals of thin tiles;
— 3 \(\pi/5\) overlappings are associated with thick Penrose tiles, \(s\)-bonds being short diagonals of thick tiles.

Below are some useful properties of binary tilings. Any binary tiling can be lifted to a five-dimensional space in the standard manner [5-10, 14]. Any vertex of the tiling can be presented in the form:

\[
\mathbf{R} = \sum_{j=1}^{5} X_j \mathbf{A}_j
\]

(2)

where \(\mathbf{A}_j\) denotes five vectors directed along the tile sides (\(\mathbf{A}_i\) form a regular 5-star) and where \(X_j\) denotes five integers. So, any vertex of a tiling is mapped unambiguously to a point of \(\mathbb{Z}^5\). The tiling itself can be viewed as a projection of a two-dimensional lattice surface in a five-dimensional space onto the tiling (physical) plane \(\mathbb{R}^2\). One may project vertices of this lattice surface onto a space \(\mathbb{R}^3\) which is perpendicular to \(\mathbb{R}^2\). Since the sum of five vectors \(A_j\) is zero, an integer vector \(\mathbf{B} = (1, 1, 1, 1)\) belongs to \(\mathbb{R}_1^3\). This means that projections of vertices onto \(\mathbb{R}_1^3\) cannot fill \(\mathbb{R}_1^3\) everywhere densely, projected points are situated on layers perpendicular to \(\mathbf{B}\):

\[
X_B = \frac{1}{\sqrt{5}} \sum_{j=1}^{5} X_j.
\]

(3)

Proposition 2. — (Widom, Deng, Henley [9]) The projection of any odd vertex of a binary tiling onto a vector \(\mathbf{B} = (1, 1, 1, 1) \in \mathbb{R}_1^3\) equals zero (under proper choice of the origin). The projection of any even vertex onto \(\mathbf{B}\) equals \(\pm 1/\sqrt{5}\).
« One may show that in a thin tile the sum of the $X_j$'s is the same for both its vertices with a $\pi/10$ angle. In fact, the coordinates of the second vertex may be derived from the coordinates of the first one by adding $A_1 - A_4$, $A_2 - A_5$ or, generally, $A_i - A_j$. After lifting to a 5-D space this corresponds to changing $X$ by a vector consisting of three 0's, one $+1$ and one $-1$. So, the sum of the $X_j$'s is unchanged. An analogous statement holds for a fat tile: both vertices with a 3 $\pi/10$ angle have the same sum of the $X_j$'s. If an odd vertex of a binary tiling is taken as the origin then the sum of the $X_j$'s at that point is zero. Since this is a binary tiling, only the 3 $\pi/10$ angle of a fat tile and the $\pi/10$ angle of a thin tile can meet at the origin. Therefore, the zero sum of the $X_j$'s spreads to adjacent $\pi/10$ and 3 $\pi/10$ vertices, which are also odd. Then considering new tiles adjacent to the latter vertices one sees that the zero sum of the $X_j$'s spreads out over all odd vertices (Fig. 3b). Even vertices are obtained by adding or subtracting one $A$ vector from a nearest odd neighbor whose sum of the $X_j$'s is zero, which in 5-D corresponds to the addition of a vector with four 0's and one $+1$ or four 0's and one $-1$.

The present model allows a generalization useful for applications [20]. Consider clusters of decagonal shape but decorated by atoms so that the decorated cluster possesses only 5-fold symmetry, as is the case for AlCuCo (Fig. 1). Such a symmetry reduction may be viewed as a coloring of cluster corners, in which black and white corners alternate as one goes around the cluster. Since cluster corners are mapped to even vortices of a binary tiling, this procedure creates a colored binary tiling. The problem of existence arises immediately: is it possible to color a given binary tiling so that when one goes around any odd vertex the corners' colors alternate? The answer is affirmative. All even vertices for which the sum of the five integer coordinates equals $+1$ must be colored, say, white, whereas, the others, whose coordinate sum equals $-1$, are colored black. Since two opposite even vertices of a tile always have different sums (one is $+1$, the other is $-1$, see the proof of proposition 2) they will be colored in different colors. Two even vertices are either nearest neighboring corners of a cluster ($\pi/5$ intersection) or third neighbors ($3\pi/5$ intersection), which implies that the alternation rule is fulfilled (Figs. 1, 3). Note that all the decagonal clusters are colored the same way.

Below, the mapping between ($\pi/5, 3\pi/5$)-coverings and binary tilings (proposition 1) and the lifting of binary tilings onto a 5-D space ((Eqs. (2), (3)) and proposition 2) is exploited to establish a one-to-one correspondence between cluster coverings and two-dimensional lattice surfaces in a five-dimensional space.

**Definition 3.** — A two-dimensional lattice surface in a five-dimensional space is called a surface with an average slope if there exists a two-dimensional subspace $\mathbb{R}_5^2$, called a grid plane, such that

$$
\lim_{R \to \infty} \max (|h(R)|) \forall R = 0
$$

where $h(R) \in \mathbb{R}_5^1$ is the transversal deviation of the lattice surface from the grid plane $\mathbb{R}_5^2$ at the point $R \in \mathbb{R}_5^2$.

It is useful to choose the following normalized orthogonal basis of $\mathbb{R}_5^2$:

$$
t_1 = \frac{1}{\sqrt{10}} (2, \tau^{-1}, -\tau, -\tau, \tau^{-1}) \in \mathbb{R}_5^2
$$

$$
t_2 = \frac{1}{\sqrt{2(\tau + 2)}} (0, \tau, 1, -1, -\tau) \in \mathbb{R}_5^2
$$

$$
p_1 = \frac{1}{\sqrt{10}} (2, -\tau, \tau^{-1}, \tau^{-1}, -\tau) \in \mathbb{R}_5^3 \setminus \mathbb{R}_5^2
$$

(5)
Cluster Model of Decagonal Quasicrystal

\[ \mathbf{p}_2 = \frac{1}{\sqrt{2(\tau + 2)}} (0, 1, \tau, -1) \in \mathbb{R}_\perp^3 \backslash \mathbb{B} \]

\[ \mathbf{b} = \frac{1}{\sqrt{5}} (1, 1, 1, 1) \in \mathbb{R}_\perp^3, \quad \mathbf{b} = \mathbf{B}/\mathbb{B}. \]

A grid plane can be specified by two vectors \( \mathbf{A}_1, \mathbf{A}_2 \) spanning \( \mathbb{R}_g^2 \):

\[ \begin{align*}
\mathbf{A}_1 &= a_{11} \mathbf{t}_1 + a_{12} \mathbf{t}_2 + e_{11} \mathbf{p}_1 + e_{12} \mathbf{p}_2 \\
\mathbf{A}_2 &= a_{21} \mathbf{t}_1 + a_{22} \mathbf{t}_2 + e_{21} \mathbf{p}_1 + e_{22} \mathbf{p}_2
\end{align*} \]

where the term \( \beta \mathbf{b} \) is omitted because we are interested in binary tilings only which, according to proposition 2 do not deviate from \( \mathbf{B} \). The \( \alpha \)-matrix has to be chosen such that \( \det \mathbf{A} = 1 \), the best choice is \( \mathbf{a}_{\perp} = 3 \mathbf{a}_{\parallel} \).

The phason strain matrix.

Zero \( \mathbf{e} \) corresponds to \( \mathbf{R} \), the tilling itself in this case is called a decagonal binary tiling because its diffraction pattern is decagonally symmetric [6-9].

**Proposition 3.** If the basis \( \mathbf{A}_1, \mathbf{A}_2 \) of the grid plane \( \mathbb{R}_g^2 \) of a binary tiling is given by equation (6) then the cluster density \( \rho \) of the corresponding \((\pi/5, 3 \pi/5)\) covering is

\[ \rho = \frac{\tau}{5 \sin (\pi/5)} + \frac{\det e_{ij}}{5 \tau^2 \sin (\pi/5)} \]  

The cluster density of a decagonal tiling \((\mathbb{R}_g^2 = \mathbb{R}_g^2, \ e_{ij} = 0)\) is \( \rho_0 = \tau/5 \sin (\pi/5) \).

Let \( \rho \) be the number of clusters per unit area, \( F \), the density of fat Penrose tiles (72°-angle) and \( T \), the density of thin Penrose tiles (36°-angle). Obviously

\[ A_F F + A_T T = 1, \quad A_F = \sin 72°, \quad A_T = \sin 36° \]

Since \( A_F/A_T = \sin 72°/\sin 36° = \tau \)

\[ (\tau F + T) A_T = 1. \] (8)

Fat rhombi are projections of 12, 23, 34, 45 and 51 two-dimensional facets of a five-dimensional cube. Thin rhombi are projections of 13, 24, 35, 41 and 52 facets. To calculate the density of the \( ij \) rhombi, one considers a large but finite portion of the grid plane in the shape of a parallelepiped with sides along the basis \( \mathbf{A}_1, \mathbf{A}_2 \). The number of the \( ij \)-rhombi inside this region is proportional to the area of the projection of this region onto the \( ij \)-plane. So, the density of the \( ij \)-rhombi is

\[ f_{ij} = \alpha \begin{vmatrix} A_1 & A_{1j} \\ A_2 & A_{2j} \end{vmatrix} \]  

where \( \alpha \) is some coefficient independent of the \( i, j \) indices. Thus, the densities of the fat and thin rhombi are:

\[ \begin{align*}
F &= \alpha (f_{12} + f_{23} + f_{34} + f_{45} + f_{51}) \\
T &= \alpha (f_{13} + f_{24} + f_{35} + f_{41} + f_{52})
\end{align*} \] (10)

Equations (9) and (10) define bilinear antisymmetric forms for \( F \) and \( T \):

\[ F = \alpha (\mathbf{A}_1, \mathbf{FA}_2), \quad T = \alpha (\mathbf{A}_1, \mathbf{TA}_2). \] (11)
The easiest way to find $\alpha$ is to employ equation (8):

$$\alpha = \left[ \tau (A_1, F A_2) + (A_1, T A_2) \right]^{-1}$$

Substituting $A_1$, $A_2$ from equations (5), (6) and the operators $F$ and $T$ from equations (9), (10) into equation (11) one obtains

$$F = \left( \frac{\tau}{\tau + 2} + \frac{1}{\tau + 2} \det \varepsilon_{ij} \right) A_F \tag{12}$$

$$T = \left( \frac{1}{\tau + 2} + \frac{\tau}{\tau + 2} \det \varepsilon_{ij} \right) A_T .$$

Next one expresses the density of clusters $\rho$ in terms of the densities of fat and thin tiles. According to proposition 1 $\rho$ equals the density of odd vertices of a binary tiling. Both even and odd vertices are shared by fat and thin tiles. One $3 \pi/5$ angle of a fat tile contains $(3 \pi/5)/2 \pi = 3/10$ths of an odd vertex, the whole fat tile contains $3/5$ths of an odd vertex. Similarly, a thin tile contains $1/5$th of an odd vertex. Therefore, the cluster density is:

$$\rho = \frac{3}{5} F + \frac{1}{5} T . \tag{13}$$

Finally, making use of equation (12) one can obtain an expression (7) for the cluster density. »

2. Random cluster assembly and phase locking in quasicrystalline state.

Below the statistical physics of $(\pi/5, 3 \pi/5)$-coverings is considered. Following Elser and Henley, we postulate that all coverings have the same energy, which, without any restrictions, can be taken to be zero. This assumption, at least at a first glance, does not look justified from a physical point of view. However, there is evidence [12, 6-9, 4, 15, 16] that it might be a reasonable approximation. The dispute between adherents of « random tiling » and « matching rules » approaches is far from completion and I am not going to argue below for the random version. A final theory should account for both entropy and energy. The aim of the present section is to demonstrate that even when the energy is neglected the entropy alone provides phase locking in quasicrystalline state.

Consider a statistical ensemble of all the coverings entering the partition function with equal probability. The free energy becomes $F = -TS$, where the entropy $S$ is temperature independent (both $F$ and $S$ are per unit area). Proposition 1 establishes a one-to-one correspondence between $(\pi/5, 3 \pi/5)$-coverings and binary tilings, the latter being easily lifted up to the five-dimensional space ((Eq. (2)), proposition 2). So, one can consider an ensemble of the corresponding two-dimensional lattice surfaces in $\mathbb{Z}^2$. To be precise, one has to introduce the entropy of the ensemble of surfaces with fixed average slope (definition 3). The grid plane $\mathbb{R}_g^2$ can be specified by four independent coordinates, namely the elements of the matrix of the phason strain $\varepsilon_{ij}$ defined by equation (6). We denote this entropy henceforth as $S(\varepsilon_{ij})$.

A RANDOM TILING HYPOTHESIS (Elser [12]). — The entropy $S(\varepsilon_{ij})$ for small $\varepsilon_{ij}$ is a negative definite quadratic function of the phason strain $\varepsilon_{ij}$.

The only function of this type consistent with the symmetry of $\mathbb{R}_g^2$ is [9]:

$$S(\varepsilon_{ij}) = S_0 - \left[ \frac{1}{2} C_1 \varepsilon_{ij}^2 + C_2 \det \varepsilon_{ij} \right] \tag{14}$$
where \( S_0 \) is the entropy of a random decagonal binary tiling, \( C_1 \) and \( C_2 \) are called phason elastic constants. The random tiling hypothesis has not been proven exactly, but has been confirmed by many numerical calculations [6-9]. The elastic constant \( C_1 \) has been found to be 0.6, the second constant \( C_2 \) has not yet been determined. The quadratic form (14) is negative definite if and only if \( C_1 + C_2 > 0 \) and \( C_1 - C_2 > 0 \). These conditions have not even been checked numerically. But it will be shown below that for physical applications it is of no importance whether or not the form is negative definite and also that the value of \( C_2 \) is irrelevant. In fact, the free energy and the entropy are functions of the density of clusters \( \rho \). According to proposition 3

\[
\rho = \rho_0 + \frac{1}{K} \det \epsilon_{ij}, \quad K = 5 \tau^2 \sin(\pi/5)
\]

and, therefore, if the density \( \rho \) is fixed then the four variables \( \epsilon_{ij} \) are not independent. Denoting \( \Delta \rho = \rho - \rho_0 \), equation (14) becomes:

\[
S_\rho(\epsilon_{ij}) = S_0 - \left[ \frac{1}{2} C_1 \epsilon_{ij}^2 + C_2 K \Delta \rho \right], \quad \det \epsilon_{ij} = K \Delta \rho.
\] (15)

The distribution (15) is Gaussian. Diagonalizing the form by

\[
\begin{align*}
  u_1 &= \epsilon_{11} + \epsilon_{22} & u_3 &= \epsilon_{11} - \epsilon_{22} \\
  u_2 &= \epsilon_{12} - \epsilon_{21} & u_4 &= \epsilon_{12} + \epsilon_{21}
\end{align*}
\]

gives

\[
S_\rho(u_i) = S_0 - \left[ \frac{1}{4} C_1 (u_1^2 + u_2^2 + u_3^2) + C_2 K \Delta \rho \right], \quad u_1^2 + u_2^2 - u_3^2 - u_4^2 = 4 K \Delta \rho.
\] (16)

Keeping \( \Delta \rho \) fixed one averages equation (16) over the three independent \( u_i \) weighted by the probability \( \exp(-S(u_i)/A) \), where \( A \) is the sample area, to obtain.

**Proposition 4.** — The dependence of the free energy and the entropy on the cluster density \( \rho \) has a cusp at \( \rho = \rho_0 \), where \( \rho_0 \) is the cluster density of a decagonal quasicrystal:

\[
S(\rho) = S_0 - (C_1 |\Delta \rho| + C_2 \Delta \rho) K \Delta \rho = \rho - \rho_0.
\] (17)

It is worth noting that only \( C_1 \) enters the distribution (16) in earnest, at fixed \( \Delta \rho \) the second constant \( C_2 \) is completely irrelevant. The only condition mandated by the requirement of stability is \( C_1 > 0 \). The inequality \( C_1 > 0 \) has not been proven analytically, but has been checked numerically: \( C_1 = 0.6 \) [7-9].

As is usually the case, the cusp in \( F(\rho) \) indicates a « phase locking » at \( \rho = \rho_0 \). Considering a grand canonical ensemble of clusters with a chemical potential \( \mu \):

\[
G(\mu) = \min_\rho (F(\rho) - \mu \rho)
\] (18)

and substituting (17) into (18) gives:

**Proposition 5.** — A decagonal random tiling quasicrystal is thermodynamically stable in a nonzero interval of the chemical potential

\[
\mu \in [(C_2 - C_1) KT, (C_2 + C_1) KT].
\] (19)

Small non-harmonic corrections to equation (14) will slightly change the interval of
stability, but as long as they are small they will not wash out the cusp. Proposition 5 is the main result of this paper, it gives a plausible explanation of an old mystery, namely, why a system is phase locked in a quasicrystalline state even though it is incommensurate.

Proposition 5 could be reformulated in a language more appropriate for alloys; for the sake of simplicity we restrict ourselves to the case of a binary alloy. We assume that there is a unique, fixed decoration of the cluster by atoms of two types: A and B (e.g., Al and TM of Fig. 1). Vacancies, interstitial and substitutions are prohibited (which is, unfortunately, far from the case in reality). The atomic composition

\[ x = \frac{N_B}{N_A + N_B} \]  

is obviously a rational function of the cluster density. To draw a phase diagram for the binary alloy in question one needs to know the free energy as a function of the composition \( x \). Substituting \( \rho \) as a rational function of \( x \) into the free energy \( F(\rho) = -TS(\rho) \), where \( S(\rho) \) is given by equation (17), one sees that \( F(x) \) also has a cusp at \( x = x_0 \), where \( x_0 \) is a composition corresponding to a decagonal quasicrystal. Note that because of proposition 3 the decagonal quasicrystal \( (\varepsilon_{ij} = 0) \) can only exist at \( \rho = \rho_0 \) and, consequently, at \( x = x_0 \). Any change in composition would result in a non-zero phason strain \( \varepsilon_{ij} \) and a deviation from decagonal symmetry.

We have found \( F(x) \) for a quasicrystalline phase. As usual, information about one phase is not enough to draw a phase diagram. One needs to know \( F(x) \) for competing crystalline phases. This task is beyond the reach of the present theory. For example, some simple crystalline structure might have an energy much lower than the energy of a quasicrystal, calculated above. In this case the quasicrystal would not exist at all. But if for some temperature region the free energies are like those shown in figure 5a, then according to the standard rules for the thermodynamics of alloys [13] the decagonal quasicrystal is a «line compound» in this temperature region (Fig. 5b). This means that if one mixes together A and B atoms with composition \( x \) from «\( d + \alpha \)» region then the sample will separate into two phases, one will be a decagonal quasicrystal with the composition \( x_0 \) and the other a crystal \( \alpha \)

![Fig. 5. — a) Free energy as a function of the alloy composition, b) «Line compound» phase diagram (d-quasicrystalline phase, \( \alpha \) and \( \beta \)-competing crystalline phases).](image-url)
with composition \( x_0 \) (Fig. 5b). In an experiment nobody can mix ingredients with the composition exactly equal to \( x_0 \) (which is, incidently, irrational!), but the presence of the cusp in the free energy (proposition 4), which results in the « line compound » type of the phase diagram, offers a possible explanation of self-fine-tuning to an exact irrational composition \( x_0 \), which is necessary for a decagonal quasicrystal to exist in nature. It should be emphasized that, although the main result regarding a cusp at \( x = x_0 \) has been derived for the particular model of overlapping decagonal clusters, it is easy to believe that it should hold for virtually any random tiling model. Indeed, the only things we need for the derivation are:

i) the free energy is quadratic in phason strain tensor \( \epsilon_{ij} \) (random tiling hypothesis or, may be, even more general situation);

ii) the atomic composition \( x \) is rational in \( \det \epsilon_{ij} \) (obvious geometry);

iii) the correct thermodynamic function for an alloy is \( F(x) \), not \( F(\epsilon_{ij}) \); it is obtained by averaging over components of the tensor \( \epsilon_{ij} \) while one variable \( x \) is kept fixed. This process would always produce a term in \( F(x) \) proportional to \( \| x - x_0 \| \).

I want to emphasize that the conclusion of a « line compound » phase diagram has been drawn on the assumption that there are neither substitutions nor vacancies. The theory allowing for such defects is to be developed. However, it is not very difficult to imagine, even in that theory, that the cusp in the free energy would survive. If so, the phase diagram would be similar to figure 5b, but the decagonal quasicrystal would be stable in a tiny interval of compositions around \( x_0 \). Recent experimental results [23] indicate that the region of stability of the best quasicrystals is actually extremely small, of the order of 0.1 at. % or even less.

Recently new HREM images have become available [15, 16]. They show clusters of about 20 Å in diameter overlapping in accordance with the present theory. Moreover, the quality of Hiraga's images allows one to discern odd and even vertices of the binary tiling. Reference [16] is devoted to rational approximants of the decagonal tiling, which are also made of the same clusters, however, arranged periodically. One can also find overlapping clusters in the atomic images obtained by the Patterson analysis and subsequent refinement [17, 18]. Employing these experimental data and the above mathematical framework leads to the developing of a rather successful atomic model of AlCuCo/AlCoNi [20].

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