Random Tiling Model of Quasicrystalline Order

M. Widom

Department of Physics, Carnegie-Mellon University,
Pittsburgh, PA 15213, USA

Abstract. This paper reviews the theoretical and experimental evidence concerning the origins of thermodynamic stability of quasicrystalline structures. Random tiling models provide a compelling model of long range quasiperiodic order arising from tiling entropy. Theoretical predictions of this model are examined and contrasted with the quasiperiodic crystal and icosahedral glass models. Several experiments have been performed capable, in principle, of testing these models. The results have included a few surprises and in general tend to support the theory of random tilings.

1. Introduction

Shortly after the discovery by Shechtman, et al. [1] of icosahedral order in rapidly quenched metal alloys, theories of the nature and origin of the non-crystalline structures began to be proposed. Chief among these are the quasiperiodic crystal models [2], and the icosahedral glass models [3]. For reasons to be discussed, neither model proves entirely satisfactory as a description of real, thermodynamically stable, quasicrystalline alloys. Rather, there is a third type of model [4-6], based on random tilings, which shows great promise.

The three models differ both qualitatively and quantitatively in ways which are experimentally testable. Crudely speaking, the quasiperiodic crystal model makes sense when the quasicrystal forms the ground state of a system. The random tiling model is expected to apply when the quasicrystal is an equilibrium state at intermediate temperatures but not absolute zero. The icosahedral glass model is expected to apply when the quasicrystal phase is metastable. Many types of experimental tests of these models are possible. Scattering studies offer perhaps the most decisive tests. Thermodynamic measurements and microscopy are other types of experiments that could distinguish between the models as well. The remainder of this introduction describes the random tiling model. Then theoretical comparisons are made with the icosahedral glass and quasiperiodic crystal models in the following section. Section 3 discusses experimental tests which can distinguish between the models.

The random tiling models of quasicrystals are inspired in part by microscopic models of both real quasicrystal forming materials [7] and by theoretical systems which have been shown to have a quasicrystalline equilibrium state [8-9]. Let us consider this theoretical model. Figure 1a shows a pair of rhombic tiles. On each vertex of the tiles are placed atoms, either large or small. One can consider a few versions of this model with varying degrees of complexity. The most realistic version of this model ignores the rhombic tiles and allows long range interactions between the atoms, which move in the continuum. It may be observed, however, that low temperature states (figure 2a) are always sufficiently well ordered that the atoms form a well defined tiling (figure 2b). A cruder version of this model replaces the atoms with rigid tiles, and truncates the bonds at nearest neighbors.

These models are distinguished by a large entropy associated with the variety of ways the tiles can fill the plane. In the simplest truncated rigid tiling model the entropy re-

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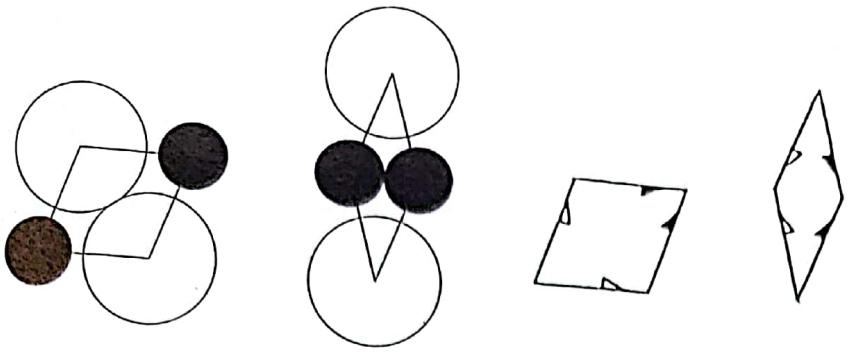

Figure 1. Large and small atoms decorate vertices of fat (72°) and thin (36°) rhombi (a). Arrows on tile edges must match to form Penrose tiling (b).

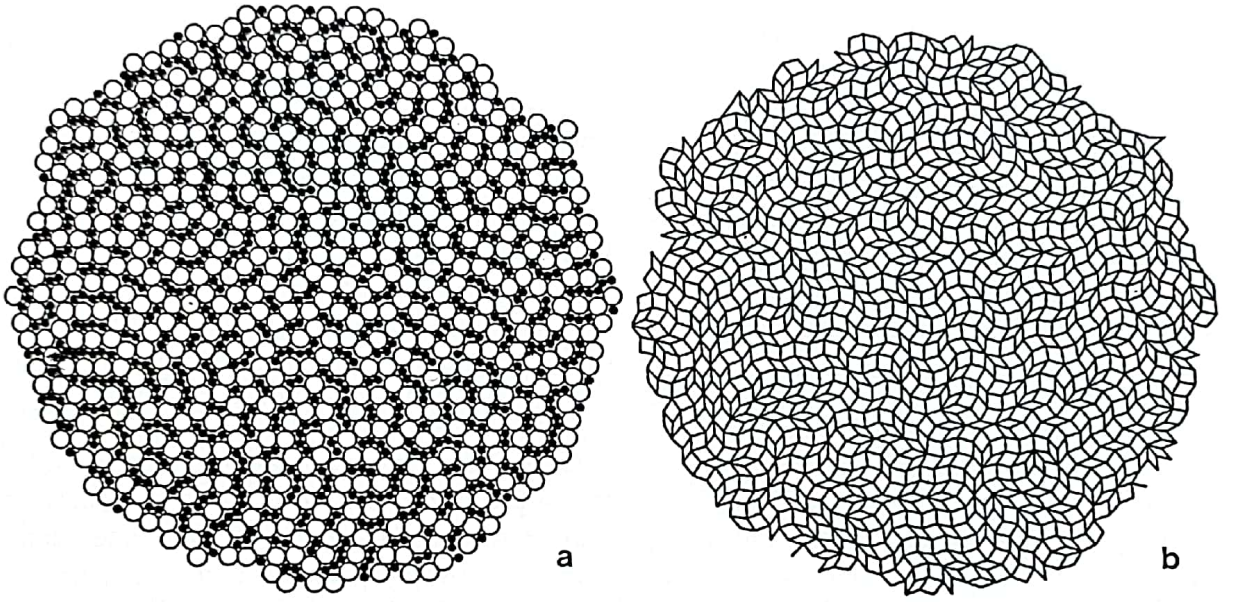

Figure 2. Atomic system in equilibrium at low temperature (a). Nearest neighbor large-small bonds define rhombus tiling (b).

flects an exact degeneracy. But even when the degeneracy is not exact the entropy can be large and significant. The entropy is made manifest in computer simulations [8,9] in which the structure is constantly fluctuating from one arrangement of atoms to another.

It is helpful to describe this model in the higher dimensional space projection language. Any rigid tiling of space can be thought of as a set of points in a fictitious space of finite but high dimensionality projected down into a lower dimensional physical space. Tilings of the plane by the rhombi shown in figure 1a correspond to a two dimensional surface of points in a five dimensional hypercubic lattice. Fluctuations between degenerate structures in the tiling correspond to fluctuations of this surface, which are also known as phasons. Local rearrangements of the tiles create a localized bump on the surface. Long wavelength phasons, which correspond to periodic undulations of the surface, require coherent rearrangement of tiles of large distances.

Defining the manner in which the system is quasicrystalline is somewhat problematic since the ordering is not perfect and there is no unique structure at all. Henley [4] suggested that if the entropy density of the tiling were to have a quadratic extremum as a function of

phason strain, with a maximum at zero strain, the tiling would have quasiperiodic long range order in three dimensions but only quasi-long range order in two dimensions. In the projection language, perpendicular space heights are bounded in three dimensions but diverge logarithmically in two dimensions. Subsequent transfer matrix [5] and Monte Carlo [6] calculations have confirmed that for short truncated rigid tiling models all these assertions are correct. The entropy density has a quadratic maximum at zero, and the curvatures of the entropy yield phason elastic constants. That follows because the phason part of the elastic free energy is given by

$$F = -TS.$$

Thus the curvatures of entropy density multiplied by temperature are phason elastic constants.

2. Theoretical Models

This section contrasts the random tiling model with the icosahedral glass and the quasiperiodic crystal models. These two models stand at opposite extremes from one another, with the random tiling model in some sense a compromise between the two. The icosahedral glass model offers hope of describing metastable quasicrystalline structures. The quasiperiodic crystal model presents the most exciting new physics of these models, but it appears unlikely to describe real materials correctly.

2.1 Icosahedral glass models

The name "icosahedral glass" was introduced to describe a particular model of quasicrystalline order [3] but, for the purposes of this paper, I will use it as a name for a family of models. The unifying feature of these models is that they seek not to describe a precise atomic structure in thermodynamic equilibrium, but rather a growth process which could lead to structures with diffraction patterns and certain physical properties similar to real quasicrystalline materials. Because the models are defined by nonequilibrium growth processes, it is unreasonable to expect them to describe stable structures such as AlCuFe. Rather, these models create metastable states and are more appropriately applied to growth out of equilibrium.

Broadly speaking these models create a quasicrystal by randomly aggregating icosahedral or other shaped clusters [10] along axes of high symmetry. The clusters may be thought of as groups of atoms which clump together in the liquid phase. Or else one may consider them to be individual atoms for which the equilibrium structure would have a large degree of icosahedral order so that the icosahedral cluster formation is a part of the aggregation process. The most important success of this model is it showed how one could obtain long range orientational order and fairly sharp peaks without requiring long range translational order. By invoking the Hendricks - Teller mechanism it was understood why many diffraction peaks appeared superficially to be sharp even though the range of translational order was limited. In the projection picture of quasicrystals, the icosahedral glass model corresponds to a wildly fluctuating and torn surface. The fluctuations provide entropy, but the tears raise the energy to a point where the model is unlikely to be in equilibrium.

Much attention has focussed on the dependence of the peak width on phason momentum [11]. Icosahedral glass models tend to show peak widths depending quadratically on phason momentum $q_\perp$. Models in which there is basically a well ordered quasicrystal structure with frozen in dislocations and phason strains, in contrast, show widths growing linearly in $q_\perp$. Experiments on AlMn have tended to find a linear dependence at least for $q_\perp$ not too large. But this should not be taken as discrediting the icosahedral glass scenario, because there is surely some improved growth rule for which the proper dependence can be obtained

over the range of $q_{\perp}$ which is measured. That assertion is, in a sense, tautology since it is certain that the quasicrystal state of AlMn is metastable and thus obtainable through some nonequilibrium growth process.

It is reasonable to put into the category of icosahedral glass models the recent growth algorithms devised by Onoda, et al. [12]. These algorithms generate almost perfect quasicrystalline order via local growth rules. They naturally fall into the icosahedral glass category because they grow the structure out of equilibrium. There are no rearrangements allowed once a tile is attached. The existence of such rules clearly shows that icosahedral glass models can cover a wide spectrum of degrees of disorder.

2.2 Quasiperiodic crystal models

The Quasiperiodic crystal model [2] is the most prominent model of quasicrystalline order. I will argue shortly that it is unlikely to be correct in certain important respects. But, because this model captures the essence of the structure of thermodynamically stable quasicrystals, and provides an especially simple description of atomic locations in infinite structures, the model is probably a sensible starting point for calculating physical properties of quasicrystalline materials.

In general the quasiperiodic crystal model states that the arrangement of atoms is similar in nature to that of a crystal - a superposition of a small number of periodic mass density waves - but that the periods may be incommensurate and the symmetry noncrystallographic [13]. In ordinary crystals the existence of an underlying crystal lattice leads to the recognition of a unit cell. The entire crystal structure may be described by a tiling of space with the unit cell once the atomic decoration of a single unit cell is found. Quasiperiodic crystals may be similarly described, but the space to be tiled is of a higher dimension than physical space.

In physical space it is natural to consider tiling models of quasicrystals such as the Penrose tiling model which fills the plane with two packing units. But as soon as we try to pack these units in physical space we are faced with a problem tiling quasiperiodically. There must be rules which guarantee that our tiling will be quasiperiodic. Such rules were found by Penrose and are shown in figure 1b by arrows along the edges of the tiles. The result of tiling the plane by these rules is a tiling which is every bit as ordered as an ordinary crystal, but is quasiperiodic instead of periodic. The diffraction pattern of such a structure contains delta function peaks and no diffuse scattering [2].

An implicit assumption in such a model is that the tiling rules are implemented in real materials by interactions among the atoms which decorate the tiles. Violations of the rules should raise the system energy so that the Penrose tiling forms a ground state. One of the failures of the quasiperiodic crystal model is that no simple, physically plausible, system is known which forces Penrose or other similar tiling rules. Indeed there is some reason to question whether such a feat is possible in principal. In an aperiodic structure each atom has an environment distinct from every other atom if far enough neighbors are considered. That suggests that the binding energy of each atom should vary. Some atoms will have low (favorable) energies and others will have slightly higher energies. If possible the system would like to minimize its energy by removing the sites of higher energy, leaving behind the low energy sites. Only in periodic structures can all sites, or a subset of sites, be absolutely equivalent in binding energy. This is the basis of arguments suggesting that ground states of matter may always be spatially periodic [14].

A further assumption is that the ground state is stable against thermal fluctuations at low temperatures. That is, there could be a phase transition out of the quasiperiodic crystal state at T = 0 into some other phase. In the projection language a two dimensional quasiperiodic crystal corresponds to a perfectly flat surface. Thermally excited phasons can cause this surface to fluctuate, but as long as the height remains bounded (in a probabilistic sense) one is still in the quasiperiodic crystal phase. If the surface roughens so that the height diverges logarithmically the system changes phase into a random tiling state. Penrose tilings with arrow rules have been studied and it appears that the roughening temperature is at T = 0 so that the Penrose tiling is unstable at all finite temperatures [15].

In three dimensions the issue is somewhat less clear because both the Penrose tiling and the random tiling have bounded fluctuations. One possible difference lies in their elasticity. The energy of a Penrose tiling (in 2-D) is known to grow linearly with phason strain, leading to a breakdown of conventional elasticity at absolute zero. If this is also true of 3-D tilings one could use the form of the elastic free energy as a distinguishing tool. If, on the other hand, the 3-D tiling does have ordinary quadratic dependence of energy on phason strain the elastic constants should be determined from the matching rule energy. In particular they must be independent of temperature. Random tiling models, on the other hand acquire their stability against phason strain from entropy. Therefore their phason elastic constants grow linearly with temperature. For the remainder of this paper I will assume that the quasiperiodic crystal model is stable at finite temperature and does possess conventional elasticity.

3. Experimental Tests

It is of great interest to test experimentally whether real equilibrium quasicrystals are better described by the random tiling model, the quasiperiodic crystal model, or perhaps neither. Several tests are conceivable. This section describes tests involving x-ray scattering, microscopy, and thermodynamic measurements. Many of the experiments have been performed already. The results generally support the random tiling model or lack sufficient resolution to be sure. What stands out most clearly is the need for further experimentation.

3.1 X-Ray diffraction

High resolution x-ray scattering probes long range order in a material. Such experiments provided the first evidence of the lack of long range order in rapidly quenched AlMn, as well as the presence of such order in AlCuFe. That is, the scattering peaks appeared to be delta functions to within instrumental resolution suggesting translational correlation lengths of more than 30000 Angstroms [16]. Diffuse scattering tails on the delta functions reveal that the ordering is not perfect despite being of infinite range.

Let us remind ourselves of the predictions of the models. The Debye-Waller effect leads to temperature dependent peak intensities

$$I = I_0 \exp\left\{\left(\frac{-T}{2}\right)\left[\frac{q_\perp^2}{K_\perp} + \frac{q_\parallel^2}{K_\parallel}\right]\right\}$$

where $K_\parallel$ and $K_\perp$ are combinations of elastic constants. The intensity lost from the peaks goes into diffuse scattering in qualitative agreement with experiments. At any finite fixed temperature the quasiperiodic crystal model and the random tiling model are indistinguishable. That is the Debye-Waller effect on peak intensities has identical form in the random tiling model and the quasiperiodic crystal model.

To distinguish the models one must vary the temperature. The quasiperiodic crystal model predicts simple exponential decay of each peak with temperature because the elastic

constants are all independent of temperature. The random tiling model, on the other hand predicts that the phason elastic constants should increase linearly with temperature. This leads to instability of the quasicrystal state at low temperatures due to either coupling between phonons and phasons [17] or an instability in the phason elasticity by itself [18]. In any case the system should enter the quasicrystal phase through a first order phase transition as temperature is increased, followed by monotonic increase of intensity for peaks with large $q_\perp$. At high temperatures $K_\perp$ becomes proportional to temperature (within the harmonic approximation) so that peaks with large $q_\perp$ will level off at constant intensity.

Such remarkable behavior has indeed been seen in experiments by P. Bancel [16]. One note of caution is in order. Several other researchers have been unable to confirm this result, and Bancel finds it in only four out of five samples studied. Or course, to observe the effect it is essential that equilibrium be maintained throughout the experiment. Otherwise the phasons will be frozen and the large $q_\perp$ peaks will have constant intensity. In fact, perhaps the most remarkable finding of Bancel's experiment is the discovery that phasons can relax on laboratory time scales far below the melting temperature. Another important point is that the quasicrystal concentration regime is rather small and many attempts at confirmation have not been at precisely the correct concentration.

X-ray scattering has not yet been exploited to its fullest. In particular the diffuse scattering has not been studied. All eigenvalues of the hydrodynamic matrix can be measured, in principle, from the diffuse scattering lineshapes [19]. This information would allow unambiguous identification of an elastic instability. Perhaps it would even be possible to determine whether the instability is driven by phonon-phason coupling or is instead intrinsic to the phason degrees of freedom.

3.2 Microscopy

Microscopy attempts to image the structure and thereby give direct structural information. So far, however, these techniques have not been able to resolve the quasicrystal model issue. In particular, distinguishing between models requires observing the temperature dependence of the short wavelength phason fluctuations. But these fluctuations have not been observed at all through microscopic techniques. It is possible that they are not present in any appreciable numbers which would be a certain vindication of the quasiperiodic crystal model. But it seems far more likely that resolution and interpretation problems plague the experiments.

Lattice imaging, such as performed by Hiraga [20], show beautiful patterns with essentially no phason strain evident. But the phason strains which can be imaged clearly by this technique are long wavelength strains which show up regardless of resolution. Recall that the localized phason fluctuations do not destroy long range translational order. Therefore it is necessary to clearly resolve local atomic arrangements to observe these strains. High resolution imaging has been done, but here there is still a problem. The high resolution image is not actually a picture of atoms and is actually rather difficult to interpret.

Three effects make interpretation difficult. First of all, not all the scattered electrons are used in forming the image. Rather a ring of bright spots is recombined, excluding much of the diffuse scattering. It is well known that simply superposing plane waves with symmetrically arranged wave vectors yields pictures which greatly resemble the electron micrographs [13]. Secondly, the sample is of finite thickness so that the image is the result of averaging a structure over many atomic layers. Such averaging will tend to cancel strains of wavelength less than the sample thickness [20]. Finally, the problem of multiple scattering obscures the connection between the observed image and the real structure so that sophisticated image

simulations are needed to connect the two. It would be of great interest to carry out such a calculation for a random tiling to see whether these experiments actually can observe local phason strains.

Electron microscopy is well suited to studying symmetries of materials. M. Audier [21] has performed similar analysis of AlCuFe samples annealed at 600C. His results suggest that the structure is not quasicrystalline at all, but rather microcrystalline with a unit cell of 8.9 Angstroms. This result is consistent with the observation of Bancel that the quasicrystal peaks disappear at 670C, and the observation of broadened x-ray peaks in samples annealed at 600C by Goldman [22]. These results tend to support the random tiling picture by showing that the quasicrystal is a high temperature phase while the ground state is a conventional crystal.

Scanning tunneling microscopy overcomes the problems faced by electron microscopy of connecting the atomic locations to the image. That is, the technique really does give direct information about the spatial variation of surface height with resolution adequate to locate individual atoms. So far the technique has been used [23] to demonstrate the existence of long range order, and to identify certain local atomic arrangements, but a serious search for phason fluctuations has not been made.

3.3 Thermodynamic measurements

The random tiling model predicts a few effects of a thermodynamic nature. One of these is that the system should transform from a crystal into a quasicrystal as temperature is increased. The other is that the quasicrystal phase should have an entropy significantly enhanced by tiling fluctuations. The quasiperiodic crystal model also makes a novel prediction. That is, the nonelectronic contribution to the specific heat should be enhanced by the presence of phason excitations leading to a T^3 term of twice the amplitude one would expect from phonons alone.

These predictions of the random tiling model have been confirmed by Sheild and Goldman [24]. A sample of AlCuFe was annealed at 600C then quenched to room temperature. Upon heating, a DTA scan revealed an endothermic peak at 670C. Thus the quasicrystal (high temperature) phase has a higher energy than the low temperature phase. Since the free energies must be equal at the point of phase change, the quasicrystal has a higher entropy. Of course, it is not certain that the higher entropy is the result of tiling fluctuations rather than, say, vacancies. It will be of great interest to measure the entropy change and compare to the entropies of three dimensional binary random tiling models.

4. Conclusions

This paper discusses three qualitatively different models of quasicrystalline order. The icosahedral glass model is, essentially by definition, an appropriate model for describing nonequilibrium quasicrystals. The other two models, the random tiling model and the quasiperiodic crystal model, share much in common. They both attempt to describe equilibrium structures. They both predict similar types of ordering at finite temperatures. But they are distinguishable and have a very different physical basis.

The quasiperiodic crystal model suggests that energetics favor quasiperiodicity. The ground state is a perfect quasicrystal. At finite temperature phason fluctuations are allowed, but they fail to destroy long range translational order. The random tiling model suggests that

quasiperiodicity is favored by entropy. Phason fluctuations provide a source of entropy, with short wavelength phason fluctuations actually providing the mechanism for eliminating the long wavelength fluctuations and guaranteeing long range translational order.

Experimentally the models can be distinguished by x-ray diffraction, microscopy, and thermodynamic measurements. Many of these experiments have been performed. Where effects are seen the experiments tend to favor the random tiling model. But duplication of results among research groups has proven difficult and further work is needed. Experiments need to be repeated in different laboratories to ensure reproducibility. And some types of experiment, such as a study of diffuse scattering, are still needed.

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