Crystallization by stochastic flips

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Abstract. Tilings are often used as a toy model for quasicrystals, with the ground states corresponding to the tilings satisfying some local properties (matching rules). In this context, a challenging problem is to provide a theory for quasicrystals growth. One of the proposed theories is the relaxation process. One assumes that the entropy of a tiling increases with the number of tilings which can be formed with the same tiles, while its energy is proportional to the ratio of satisfied matching rules. Then, by starting from an entropically stabilized tiling at high temperature and by decreasing the temperature, the phason flips which decrease (resp. increase) the energy would become more and more favoured (resp. inhibited). Ideally, the tiling eventually satisfies all the matching rules, and thus shows a quasicrystalline structure. This paper describes a stochastic process inspired by this and discusses its convergence rate.

1. Introduction

The discovery of non-periodic metallic alloys whose diffraction patterns show sharp peaks – soon called *quasicrystals* – produced a paradigm shift in the fields of crystallography. Known mathematical notions, in particular *aperiodic tilings*, quickly turned out to provide a suitable model of such structures. On the one hand, so-called *matching rules*, which specify how tiles can be assembled, can model the *energetic stabilization* at low temperature. But this fails to explain *growth* of quasicrystals because of the bad dynamics of tiles assembly. On the other hand, the fact that quasicrystals correspond to the tilings allowing the most numerous rearrangements of tiles could explain their growth, at high temperature, by *entropic stabilization*. But this fails to explain the experimentally observed stability of quasicrystals at low temperature.

We are here interested in a *relaxation process*, as suggested *e.g.* by Janot [3]: can we obtain an energetically stabilized quasicrystal by cooling an entropically stabilized quasicrystal? This raises the questions of the cooling process and its rate, that we discuss here. Other important questions, *e.g.*, the existence of a *phase transition* during the cooling or the role of *boundary conditions* (which are assumed to be fixed) are however not discussed. This paper just aims to state the problem and describe first results.

The rest of the paper is organized as follows. We formally state in Sec. 2 the notions we need to describe in Sec. 3 the process we are interested in. Sec. 4 then provides examples of the way this process runs, namely on *dimer tilings* and on the *Penrose tiling*. Last, we consider in Sec. 5 a simplified process and we provide conjectures and some (partial) results about its convergence rate. This is a work in progress.

2. General settings

2.1. Canonical tilings

Let $\vec{v}_1, \ldots, \vec{v}_n$ be n non-colinear vectors of $\mathbb{R}^d$, $n > d \geq 1$. For each $\{i_1, \ldots, i_d\} \subset \{1, \ldots, n\}$, the *proto-tile of type* $\{i_1, \ldots, i_d\}$ is the compact set of $\mathbb{R}^d$ denoted by $T_{i_1, \ldots, i_d}$ and defined by:

$$T_{i_1, \ldots, i_d} = \{\lambda_1 \vec{v}_{i_1} + \ldots + \lambda_d \vec{v}_{i_d} \mid 0 \leq \lambda_1, \ldots, \lambda_d \leq 1\}.$$

Translated proto-tiles are called *tiles*. Coverings of $\mathbb{R}^d$ by tiles with non-intersecting interiors are called $n \to d$ *canonical tilings*, or simply $n \to d$ *tilings*. One also speaks about *partial* (resp. *finite*) tilings when only subsets (resp. finite subsets) of $\mathbb{R}^d$ are covered.

A $n \to d$ tiling is said to be *k-periodic*, $0 \leq k \leq d$, if it is invariant by translation along k linearly independant vectors. One simply says *periodic* if $k = d$, *non-periodic* otherwise.

An interesting property of $n \to d$ tilings is that they can be seen as d-dimensional hypersurfaces living in a n-dimensional space. Indeed, let $(\vec{e}_1, \ldots, \vec{e}_n)$ denote the canonical basis of $\mathbb{R}^n$. The *lift* of a $n \to d$ tiling is the image by a map ϕ which is linear over tiles and defined for two connected vertices $\vec{x}$ and $\vec{x} + \vec{v}_k$ by $\phi(\vec{x} + \vec{v}_k) = \phi(\vec{x}) + \vec{e}_k$. Tiles are thus mapped onto d-dimensional hyperfaces of unit hypercubes of $\mathbb{Z}^n$ and tilings are mapped onto d-dimensional "stepped" hypersurfaces of $\mathbb{R}^n$.
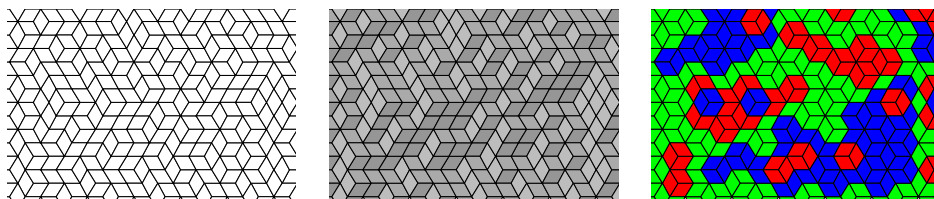
Figure 1. Three coloring of the same patch of a $3 \to 2$ canonical tiling: white tiles (left), shaded tiles making easy to see the lift in $\mathbb{R}^3$ (middle) and tiles colored according to the distance (modulo 3) of their lift to the V-cut defined by the hyperplane of normal vector $\vec{e}_1 + \vec{e}_2 + \vec{e}_3$ (right).

A $n \to d$ tiling is said to have *thickness* at most $k \geq 0$ if its lift lies into a "slice" $V + [0, k]^d$, where V is a d-dimensional affine space of $\mathbb{R}^n$. Tilings of thickness at most 1 are called V-*cuts*. They are the thinnest tilings (one indeed checks that thinner slices yield holes in the lift). Not every tiling has a well-defined thickness; those which have are said to be *perp-bounded*. Intuitively, a thick tiling corresponds (under the lift) to a bumby stepped surface, while a thin one corresponds to a straight stepped surface. In particular, the V-cuts correspond to the straightest stepped surfaces, and are therefore sometimes used as digitizations of affine spaces.

Physically, a tile model a stable local configuration of atoms, while tilings model the possible global configurations. Although this is only a toy-model, it is widely used and provides a good insight in some properties of crystals and quasicrystals, which are respectively modeled by periodic and non-periodic V-cuts. For example, with $\vec{v}_k = e^{\frac{2ik\pi}{n}}$ and V generated by the vectors

$$(\cos(2k\pi/n))_{0 \leq k < n} \quad \text{and} \quad (\sin(2k\pi/n))_{0 \leq k < n},$$

the obtained V-cut turns out to be the lift of a $n \to 2$ with having n-fold rotational symmetry. The *crystallographic restriction* ensures that such a tiling can be periodic only for $n \in \{2, 3, 4, 6\}$.

2.2. Matching rules

We call *decoration* of a tile a real function defined over the boundary of this tile. Two decorated tiles are said to *match* if their decorations take the same value in each intersecting point (if any). Intuitively, decorations can be seen as colors on facets of tiles, with two matching tiles sharing the same color where they meet. Note that decorations are not necessarily constant over facets[1].

Given a set τ of decorated proto-tiles, we denote by X_τ the set of tilings by the corresponding tiles in which any two tiles match. The tilings of X_τ are said to be *enforced by matching rules*. The case of a finite set τ is of special interest, since it provides a finite local description of X_τ. In this case, X_τ is said to have *finite type*.

It is easily seen that a periodic tiling has finite type. The first example of a finite type set of tilings which does not contain any periodic tiling has been constructed in 1966 [4]. Although rather complicated, this construction discarded the idea that a non-local property (non-periodicity) cannot be enforced by local constraints. Simpler examples have been since obtained (*e.g.*, [5, 2, 6, 7]), as well as some generic constructions [8, 9]. This is an active domain of research.

Physically, matching rules model the short-range interactions between atoms of adjacent tiles, with matching tiles corresponding to low-energy local configuration (some refinement considering that tiles can "more or less" match can be introduced). Hence, in this model, the internal energy of a tiling varies as the proportion of matching tiles, with minimal energy tilings (ground states) being thus enforced by matching rules. In particular, quasicrystals can be seen as ground states of matching rules enforcing non-periodic tilings.

Non-periodic finite type tilings can thus model the *structure* of quasicrystals, but they however fail to model their *growth*. Indeed, whenever a set of decorated tiles can form only non-periodic tilings, aggregating one decorated tile at time such that it matches with the previous ones often yields a *deception*, *i.e.*, a finite configuration which cannot be extended to a tiling of the whole space without introducing mismatches [10]. Some refinements seem to avoid this problem [11], but a non-local inspection at each time is needed (what could be seen as physically unrealistic).

2.3. Flips

Whenever a vertex x of a $n \to d$ tiling belongs to exactly $d+1$ tiles, one gets a new tiling of the same subset by translating each of these tiles by the vector which belongs to the d other tiles. This local rearrangement of tiles is called a *flip* or *phason-flip*, said to be performed *around x*.

Figure 2. Flips on $n \to 2$ and $n \to 3$ tilings respectively involve three parallelogram tiles (left, in $\mathbb{R}^2$) and four parallelepiped tiles (right, in $\mathbb{R}^3$), which still fill the same space in both cases.

A tiling is said to be (finitely) flip-accessible from another tiling if the former can be obtained by performing a (finite) sequence of flips on the latter[2]. It is proven [12] that two finite $n \to 2$

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[1] One checks that this allows, for example, to model the celebrated arrow-matching for Penrose tilings.
[2] Flip-accessibility is also sometimes called *ergodicity*.

tilings covering the same subset are mutually finitely flip-accessible. A characterization of flip-accessibility among infinite $n \to 2$ tilings is also known [13]. Flip-accessibility turns out to not always hold for $n \to 3$ tilings [14], but a complete characterization still remains to be obtained.

Physically, flips model local rearrangements of atoms that have been experimentally observed [15, 16]. They provide a mechanism for moving atoms (of controversial importance, however), allowing to explore different structures of the matter, *i.e.*, different tilings. Let us stress that, although theoretically defined as translations of tiles, flips do not necessarily need many moves of atoms: small variations of atoms positions can correspond to such rearrangements of tiles.

3. Crystallization by stochastic flips
The stochastic process we are interested in is the Markov chain $(x_t)_{t=0,1,\dots}$ defined as follows.

(i) We introduce a non-negative parameter T - the temperature. It starts from a very high initial value T_0 and then varies in a specified way (*temperature schedule*) up to reach zero.

(ii) We start from a finite decorated $n \to d$ tiling x_0 whose tiles do not necessarily all match, but can do it up to some rearrangement (which do not modify the covered subset of $\mathbb{R}^d$).

(iii) Given $x = x_t$ and $T > 0$, we choose uniformly at random a flippable vertex of x and we denote by y the tiling obtained by performing this flip. We then choose uniformly at random $\alpha \in [0, 1]$, and we set $x_{t+1} := y$ or $x_{t+1} := x$, depending whether or not α is lower than

$$\frac{\exp(-E(y)/T) \times F(x)}{\exp(-E(x)/T) \times F(y)},$$

where $E(z)$ and $F(z)$ respectively denotes the number of mismatches and the number of flippable vertices of a tiling z.

Roughly, the flips decreasing the number of mismatches are all the more favoured since the temperature is low. This naturally raises the "(quasi)crystallization" question: does this process converge towards a mismatch-free tiling when the temperature goes to zero, and at which rate? Note that the hypothesis on the initial tiling x_0 is a necessary condition for such a convergence. This convergence (and its rate) would moreover depends on the temperature schedule and on x_0.

Let us give a brief "physical justification" for the study of such a process. Recall that the stability of a material at temperature T is governed by the minimization of its *free energy* $F = U - TS$, where U and S respectively denote its *internal energy* and its *entropy*. In terms of tilings, internal energy and entropy are usually defined as follows: the internal energy of a finite decorated tiling is proportional to its number of mismatches, while its entropy is proportional to the logarithm of the number of different tilings which can be obtain by rearranging tiles (without modifying the covered subset of $\mathbb{R}^d$). In the light of this, our process turns out to be, when T is fixed, a Metropolis-Hasting algorithm drawing samples from the Boltzmann distribution. Moreover, according to the so-called *random tiling hypothesis* [17], the initial tiling x_0 of our process has, under some conditions, maximal entropy among tilings with the same number of tiles. It can thus be seen as rather stable at the initial temperature of our process since, at high temperature, minimizing the free energy roughly means maximizing the entropy.

4. Two examples
Let us first consider the $3 \to 2$ tiling with 6-fold rotational symmetry. There is only one tile up to rotation, usually called a *dimer* because it covers exactly two cells of the triangular grid. This tiling can model only crystals since it is periodic.

This tiling is easily enforced by matching rules: decorations shall simply make that two translation-equivalent tiles which are adjacent along an edge do not match. One checks that the number of mismatches can vary from -6 to 6 by performing a flip. Fig. 3 provides an example.
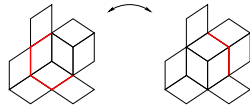

Figure 3. Here, performing a flip on the central vertex decreases (from left to right) or increases (from right to left) by 2 the number of mismatches (emphasized by the thick lines).

Fig. 4 shows the evolution of a random initial tiling x_0 when the temperature linearly decreases as a function of the number of performed flips. Tiles are colored as in Fig. 1, left. Mismatch-free regions thus correspond to unicolor regions.
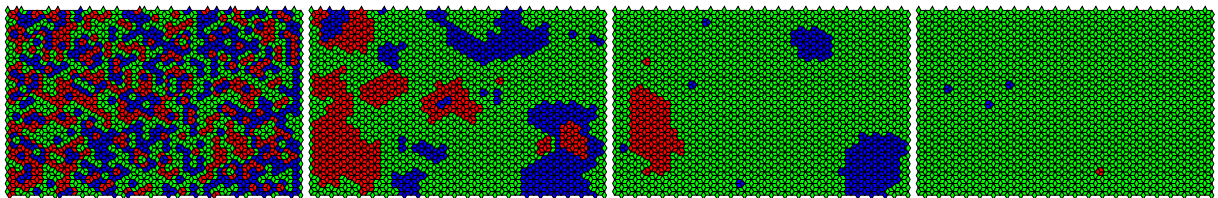
Figure 4. Snapshots (every 3000 flips) of the cooling of a dimer tiling.

Let us now consider the $5 \rightarrow 2$ tiling with 5-fold rotational symmetry. This is a non-periodic tiling of finite type, called the *Penrose tiling*. Unfortunately, mismatches turn out to be sparse, instead of forming level sets as in the $3 \rightarrow 2$ case (what allowed, by choosing suitable colors, a nice visualization of mismatch-free regions). This is because the lift of this tiling is a 2-dim. surface living in a 5-dim. space. We hence just assign different colors to the thin and fat rhombs. Fig. 5 shows the evolution of a random initial tiling x_0 when the temperature linearly decreases.
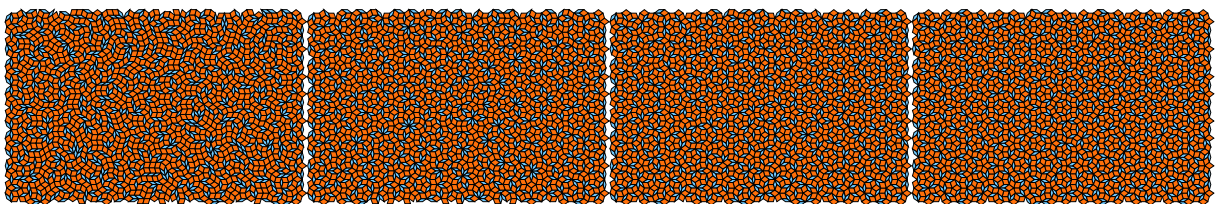
Figure 5. Snapshots (every 10000 flips) of the cooling of a Penrose tiling.

5. Towards theoretical results

Obtaining bounds on the number of steps of the process described in Sec. 3 and characterizing the corresponding optimal temperature schedules would be theoretical results of great interest. This however seems very hard. We thus chose to first consider the following simplified process. There is no more temperature parameter. We still start from a tiling x_0 satisfying the same hypothesis and we proceed step by step. Given the tiling x_t, we choose uniformly at random a flip which does not increase the number of mismatches. If there is no such flip, the process stops. Otherwise, x_{t+1} is the tiling obtained by performing this flip.

This new Markov chain experimentally runs similarly as the previous one, only faster and without the "noise" due to sparse flips creating isolated mismatches. Ergodicity is however no more ensured by the flip-accessibility results recalled in Sec. 2.3 because some flips are now forbidden. The notion of *constrained* flip-accessibility shall be investigated.

Recall from the introduction that we are interested in the rate of our cooling process. Indeed, quasicrystals can be experimentally grown, *e.g.* by the Bridgman-Stockbarger technique, with low cooling rates, but not *too* low. In particular, a cooling time exponential in the tiling's size would make our model highly unrealistic. We thus focus on the *convergence time* of our process.

The *convergence time* is the random variable $C(x_0) := \min\{t \mid E(x_t) = 0\}$, where $E(z)$ denotes the number of mismatches of z. Let also $\langle z \rangle$ denotes the set of tilings which can be obtained by rearranging tiles of a tiling z without modifying the covered subset of $\mathbb{R}^d$. The *worst convergence time* $\widehat{C}$ and, given a distribution μ_{x_0} over $\langle x_0 \rangle$, the *mean convergence time* $\overline{C}$ are the random variables defined by

$$\widehat{C}(x_0) := \max_{x \in \langle x_0 \rangle} C(x) \quad \text{and} \quad \overline{C}(\mu_{x_0}) := \sum_{x \in \langle x_0 \rangle} C(x) \mathrm{d}\mu_{x_0}(x).$$

We are interested in asymptotics of their moments (at least their expected value $\mathbb{E}$) when the size $|x_0|$ of x_0 goes to infinity, in particular when μ_{x_0} is the uniform distribution U_{x_0} over $\langle x_0 \rangle$.

- For $n \to 1$ tilings, numerous simulations led us to conjecture $\mathbb{E}(\widehat{C}(x_0)) = O(|x_0|^3)$ and $\mathbb{E}(\overline{C}(U_{x_0})) = O(|x_0|^{5/2})$. We have so far proven both bounds for $2 \to 1$ tilings in [18].
- For $n \to 2$ tilings, numerous simulations led us to conjecture $\mathbb{E}(\widehat{C}(x_0)) = O(|x_0|^2)$ and $\mathbb{E}(\overline{C}(U_{x_0})) = O(|x_0|^{3/2})$. We have so far proven $\mathbb{E}(\widehat{C}(x_0)) = O(|x_0|^3)$ for $3 \to 2$ tilings.

Note that bounds for $n \to 2$ tilings are smaller that for $n \to 1$ tilings. We do not have yet considered $n \to 3$ tilings, but we expect lower bounds.

References
[1] Shechtman D, Blech I, Gratias D and Cahn J W 1984 *Phys. Rev. Lett.* **53** 1951–54
[2] Penrose R 1974 *Bull. Inst. Maths. Appl.* **10** 266
[3] Janot C 1992 *Quasicrystals, a Primer* (Oxford: Oxford University Press)
[4] Berger R 1966 *Memoirs of the American Mathematical Society* **66** 1–72
[5] Robinson R M 1971 *Inv. Math* **12** 177-90
[6] Kari J 1996 *Discrete Mathematics* **160** 259–64
[7] Socolar J E S 1990 *Comm. Math. Phys.* **129** 599–619
[8] Mozes S (1989) *J. D'Analyse Math.* **53** 139-86
[9] Goodman-Strauss C (1998) *Annals of Mathematics* **147** 181-223
[10] Dworkin S and Shieh J I 1995 *Comm. Math. Phys.* **168** 337–52
[11] Onoda G Y, P J Steinhardt, DiVincenzo D P and Socolar J E S 1988 *Phys. rev. lett.* **60** 2653–56
[12] Kenyon R 1993 *Algorithmica* **9** 382–97
[13] Bodini O, Fernique Th and Rémila É 2008 *Information and Computation* **206** 1065–73
[14] Desoutter V and Destainville N 2005 *J. Phys. A: Math. Gen.* **38** 17–45
[15] Lyonnard S, Coddens G, Calvayrac Y and Gratias D 1996 *Phys. Rev. Lett B* **53** 3150–60
[16] Adagawa K, Mandal P, Hosono K,3, Suzuki K, and Takeuchi S 2004 *Phys. Rev. Lett B* **70**
[17] Henley C 1990 *Quasicrystals: The State of the Art* ed D. P. DiVincenzo et P. J. Steinhardt (Singapore: World Scientific)
[18] Bodini O, Fernique Th and Regnault D 2010 *Proc. of ANALCO'10*