The Method of Selection Laws and its Applications to Crystallography

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***Abstract*—In physics, we often make use of the spatial properties of a system in order to choose a particular geometry to describe it. However, some geometric systems are so simple that we can hardly consider the possibility of their adoption in describing complex physical systems. It is known that, in areas such as crystallography, there are recurring problems involving discrete geometries, given the nature of the study subject. In this work, we show an alternative way of obtaining the atomic coordinates for a crystal using three steps: Finding a base geometric model, applying laws which help us in picking the adequate locations in this geometry and then applying a transformation which takes the geometric model and give us the final atomic coordinates. To illustrate this idea, we depart from the fundamental concepts of a particular model, the Manhattan Geometry, and will demonstrate how it can be a valuable tool in describing many structure types, from simple cubic to quasicrystalline lattices.**

***Index Terms*—Crystallography; Selection Laws; Computational Physics**

I. Introduction

NOWADAYS in crystallography, it is commonplace to utilize computational modelling to assist the interpretation of experimental results and predicting new ones. In this manner, computational physics represents a fundamental tool in diminishing costs and optimizing results all over the world, while also building a direct link between experimental data and the many theoretical models regarding the subject[1].

However, there is a myriad of unsolved puzzles in the computational crystallography, most of which can be reduced to reproducing crystalline structures by means of coordinates inside a digital data file[2]. From diffraction and microscopy experiments, we are able to find parameters that enable us to recreate these structures. But how, exactly? Today, what we do is to manually build a set of atoms which, when replicated through R^3, ends up with the desired crystalline shape [3,4]. Many are the problems associated to this method. To start with, we can highlight the great manual labor required to build the unit cell of the crystal we are dealing with, which might take hours or even days of manual calculations and tests involving several prototypes.

The most significant flaw of the unit cell replication method is that it only works for perfectly periodic crystals. Currently we know that there exists many kinds of materials which do not possess exact periodicity, ranging from amorphous materials (as is the case of glasses [5]) to more structured materials, such as liquid crystals[6] and quasicrystals[7]. All these materials are targets for recent scientific research in search of new technological solutions[8-10]. It would thus be interesting to have a more general method, also encompassing those cases.

We propose here another manner to build a structure we have in mind, be it crystalline or not. Initially we produce a grid containing every possible coordinate to be occupied by a hypothetical atom in a geometry suited to each problem, enabling us to then test such positions one by one against a condition, indicating whether or not it is adequate to model the desired structure. After that, a transformation would map the coordinates encountered to the final R^3 coordinates.

Although this idea seems complicated, when we speak of atoms in an ideal (non-relaxed and periodic) crystal, its atoms tend to occupy positions in a well known lattice, namely the Bravais Lattice. We can start from this lattice in order to choose a mathematical model which fits our problem. In spite of not being the most general model possible, we shall establish ahead how it is suitable to many problems.

II. Mathematical Foundations

Before we begin in earnest with the problem of building crystalline structures from computer models, we will see some basic ideas behind the method presented here. We will start by introducing the Manhattan Geometry, which is the mathematical model that we will use as an example. Then we

will shortly go through the Formation Laws, emphasizing their fundamental importance to the generality of the method.

A. Manhattan Geometry

Manhattan Geometry, or also Taxicab Geometry, is a geometric model introduced in the 19th century by lithuanian mathematician Hermann Minkowski[11]. The practical motivating problem for this geometry takes scene on the streets of Manhattan. A taxi driver receives a hypothetical call for a ride at a certain corner denoted A. Upon arrival, the passenger would ask the driver to drive to another corner, denoted B.

In this moment, the taxi driver starts to think what is the smallest possible path between the two corners on the streets. The roads found on the island of Manhattan are of a very particular geometry. A set of roads, parallel to each other, goes from south-southwest to north-northeast, being crossed by another set of roads, also parallel to each other, while also being orthogonal to the ones belonging to the first set. We might as well make use of such geometry in thinking about this problem, for it allows a simple interpretation: our taxicab has to move around the corners of a rectangular grid, going from point A to point B. This way, the car is kept from crossing diagonal paths in the squares of our grid, which clearly agrees with the real example given.

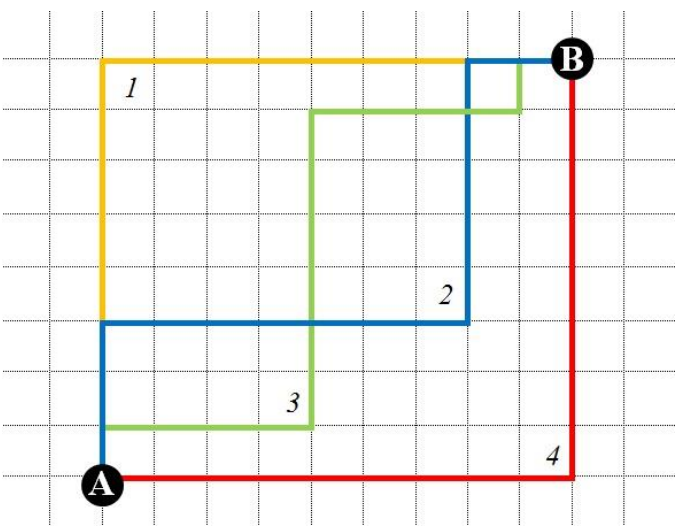

Figure 1: *Schematic representation of the problem: hypothetical trajectories 1, 2, 3 and 4 are possible paths that a taxicab can follow to reach corner B departing from corner A, moving toward B in every step.*

As seen in Figure 1, trajectories that always follow the general direction of the final destination, with no turning back nor going further from point B, are of the same length. In the case of our scheme, should we consider the distance between two corners to be ξ, the total distance from A to B would be well described by 17ξ. To simplify this analysis and determine the uniqueness of shortest path lengths, Hermann Minkowski introduced the following metric:

$$d(A,B) = |x_B - x_A| + |y_B - y_A|$$

Where d(A,B) represents the distance between points $A = (x_A, y_A)$ and $B = (x_B, y_B)$, in a Z^2 grid, which means this pairs belong to the grid Z^2 contain integers. This notion is naturally extensible to the R^2 or R^3 spaces.

This metric can be obtained from more fundamental concepts, for instance, being induced by an internal product [12,13]. For now, we focus our attention solely on the metric.

The real meaning of this metric lies in the simplicity of summing minimal vertical displacement and minimal horizontal displacement in the grid, in order to move from point A to point B. Similar to what we have done in describing Figure 1, we denote by ξ the length of an edge (the minimal distance between *any* two distinct points), and then the function d(A,B) is restricted to values that are multiple of ξ. We can also consider, as means of making our equations easier (with no loss of generality), that ξ = 1. With this the distance from A to B in figure 1 is simply given by . Note now that the image of is N_0.

B. Formation Laws

Let us then submit our metric function to a first test. Our objective is to propose laws which utilize d(A,B) and the natural symmetries given by our model, so we will first suggest a two dimensional example to illustrate the idea. We start with the Z^2 plane, alongside a coordinate axis and a coordinate origin. The plane itself already gives us the first fundamental element: the set of every possible position. Based on its elements we shall apply the test. In our example, we can express this set formally as $N = \{(n_x, n_y) \mid n_x, n_y \in Z\}$.

Now we shall introduce a new function $\|\mathbf{n}\| = d(\mathbf{n},\mathbf{0})\}$, that is, given by the distance from $\mathbf{n}$ to the coordinate origin $\mathbf{0}$. Such function is very important in metric spaces.

Then, we proceed by considering the points in our set, and test if every single point meets the following condition: *"If the distance from point n to the coordinate origin is an even number, then n belongs to the so called 'Set of the Even Points' (N_{even})"*, which can be formally expressed as:

$$\mathbf{n} \in N_{even} \Leftrightarrow \|\mathbf{n}\|_{Z^3} = 2k\,;\, k = 0,1,2,...$$

That being done, we are going to plot in our Z^2 plane every point belonging in N_{even}. Figure 2 shows the final result.

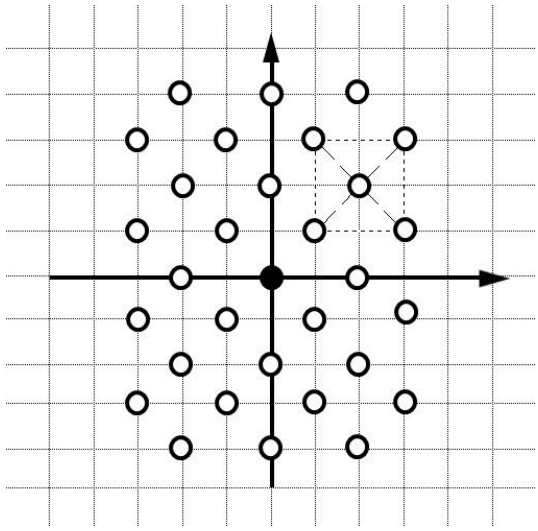

Figure 2: *Result of applying the proposed method over a simple 2D space, using as test the law for the Set of the Even Points.*

On Figure 2's first quadrant, we purposefully draw a set of edges linking a few points. Should one already have familiarity with common crystalline structures, one would already have noticed that such pattern appears on the surface of a unit cell for a face centered cubic (FCC) crystal. What seems to be a coincidence is a recurrence of the geometric model which perfectly fits these kinds of structures.

We can also choose a myriad of other laws, and test their results by comparing with structural models we would find in condensed matter. The more adequate the geometric model is to a problem, the simpler our laws tend to turn out. On the other hand, badly chosen models may difficult the coordinate adjusting, leading us to much more complicated laws. It is required to cautiously weight the situation, considering the difficulties we are willing to overcome in either dealing with a difficult law or a potentially long search for a simple one.

In supplementary material, we show this procedure has a great degree of generality and can be applied to create any set of points. We can affirm this, because every set containing known points has a selection law highlighting these points from a more encompassing set. The idea of such demonstration is also shown as supplementary material.

However, the fact is that each sequence has a formation law. Mathematicians seeking the so called formation law of prime numbers may find solace from this fact, given that we have a situation of the same nature: just as in the case of primes, for any other given set of points we are ensured of the existence of an associated formation law, no matter how sophisticated that law might be. Therefore it is worthy to contemplate the range of possibilities we are encompassing from this method.

III. Application Regarding The Study Of Crystals

We have previously seen that we can use formation laws to fragment sets of points in a new set of possible positions. We have also plotted such points and verified they can give us structures similar to those found in crystals and other solids. Now, we will present test laws and how they can be useful in creating computational models for some kinds of crystals, after being properly scaled. As supplementary material, we show a small catalog of lattices for which we have already generated reasonably simplified laws. Here we will merely present the general aspect of the Bravais Lattices, to clarify how our proposed method is applied to those. Also, we shall give special attention to the case where we build a nearly periodic crystal using Manhattan Geometry as the starting point.

A. The Bravais Lattice

Auguste Bravais, in the year 1848, showed that crystals may be well described by periodic lattices carrying a geometry fixed by few parameters. We denote this structure by Bravais Lattice. In a certain way, if we put both models side by side, we can spot similarities bet ween them. Manhattan Geometry is a self sufficient starting point for the creation of perfect crystal prototypes, albeit lacking the characterizing Bravais Lattice parameters, such as the inclination of the unit cell (α, β and γ angles) and also the lattice parameters (lengths a, b and c) [14].

We are then able to build our ideal models in the first geometry indicated and later introduce a transformation $T : \mathrm{Z}^3 \to \mathrm{R}^3$ that will associate points in the ideal lattice, previously selected, to their corresponding points in the Bravais Lattice with the proper characteristic parameters.

In this work we will present some structures such that $\alpha = \beta = \gamma = \pi/2$, allowing us to write T as $\mathrm{T}(\mathbf{n}) = (\mathrm{a}_0\mathrm{n}_1, \mathrm{b}_0\mathrm{n}_2, \mathrm{c}_0\mathrm{n}_3)$. For the cases we work with, $\mathrm{a}_0 = \mathrm{b}_0 = \mathrm{c}_0 = \mathrm{qa}$, where a is the lattice parameter and q = 1/2 (In particular, for the diamond, we have q = 1/4).

However, at section 3.2, we present a structure completely different from the rest, where a major part of our plot is focused solely on a different T transformation. Such will be the case because in building the structure, we shall first pick points from a space with more than 3 dimensions, and T will then assume the role of projecting these points over R^3, as we shall see. This is required because the Bravais Lattice does not do a good job in describing that case, being based on the direct periodicity of the crystal, which is not always verified in nature.

With that in our hands, we have all the mathematical tools required to build crystal models.

1) Example: Face Centered Cubic Lattice (FCC)

This is the case of many metals at room temperature and noble gases at a high pressure. Examples are Au, Ag, Cu, Ni, Ce, Kr and Xe, among others. The set we are interested in regarding this system is the already defined *Set of Even Points*. In this way, the atomic species α must lie in positions such that:

$$\mathbf{n} \in N_\alpha \Leftrightarrow \| \mathbf{n} \|_{Z^3} = 2\,\mathrm{k},\ \ \mathrm{k} = 0,1,2,...$$

Then, we multiply the given coordinates by a proportionality constant (in this case, half the lattice parameter, $a_0/2$), arriving at the ideal model of the crystalline structure.

There are also metallic alloys possessing FCC geometry: Ni_3Au, Cu_3Au and CuAu, to mention a few. Here, when writing our law, we ought to pay attention to the proportion with which they appear in the lattice and distribute species in a way to preserve this proportion. Let us write the law for an $\alpha_3\beta$ molecule as example:

$$\mathbf{n} \in N_\alpha \Leftrightarrow \begin{cases} \| \mathrm{n} \|_{Z^3} = 2\,\mathrm{k}\,;\, \mathrm{k} = 0,1,2,... \\ \wedge \\ 2 \mid \mathrm{n_i}\ \textit{is true for all}\ \mathrm{n_i} \end{cases}$$

$$\mathbf{n} \in N_\beta \Leftrightarrow \begin{cases} \| \mathrm{n} \|_{Z^3} = 2\,\mathrm{k}\,;\, \mathrm{k} = 0,1,2,... \\ \wedge \\ 2 \mid \mathrm{n_i}\ \textit{is not true for at least one}\ \mathrm{n_i} \end{cases}$$

Based on this law, we can write expressions describing whatever structures of the type $\alpha_n\beta_m$ we wish. We also know, based on what we have already seen, that similar laws can be used for ternary alloys, but this is a more delicate problem that is not going to be discussed here.

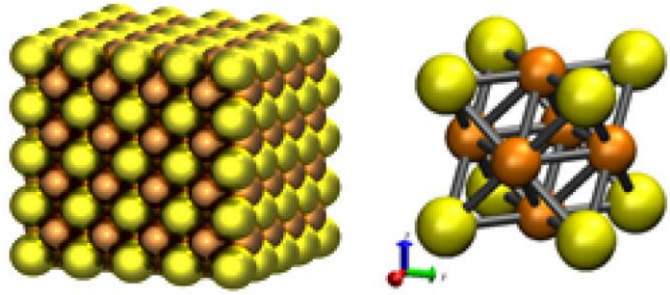

Figure 3: *Ilustration of the FCC model for a Cu3Au (type α3β) crystal. On the right, unit cell of the FCC lattice, naturally arrived as a consequence of the laws adopted in our method.*

B. Quasicrystals: the Penrose Tiling}

Quasicrystals, or also "nearly periodic crystals", are crystals of a homogeneous, ordered and isotropic structure, but a non periodic one. These materials surfaced from a experimental verification made by Dan Shechtman[15,16], who by 1982, while studying an Al-Mn alloy, noted the diffraction pattern of said material did not match the theoretical preview for classic crystals, even though it had a well defined structure. In 2011, this work gave Shechtman a Nobel Prize.

Since the first observation of a quasicrystal, hundreds of others have been reported and confirmed. Albeit not so commonly, we can find these kinds of patterns in many metallic alloys and some polymers. Quasicrystals are found more frequently in Al based alloys (such as Al-Li-Cu, Al-Mn-Si, Al-Ni-Co, Al-Pd-Mn, Cu-Al-Fe, among others), but other compositions have also been identified (Cd-Yb, Ti-Zr-Ni, Zn-Mg-Ho, Zn-Mg-Sc, In-Ag-Yb, Pd-U-Si, and more).

Although this kind of pattern is relatively new to condensed matter physics, mathematicians have been studying it since the 1960's. Thus, we already possess knowledge of a myriad of nearly periodic and organized patterns to apply in the structure of matter.

Perhaps the most famous of mathematical nearly periodic patterns is the Penrose Tiling (also called Penrose Mosaic). It receives the name due to Roger Penrose [17], who studied it during the 1970's. Because it is a completely organized yet aperiodic tiling of the plane, this pattern is an extremely adequate model for a quasicrystal.

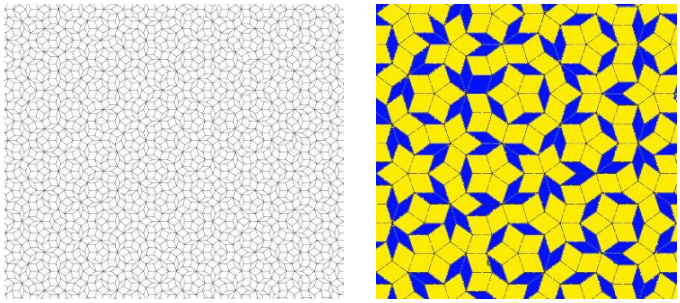

Figure 4: *In the figure to the left, we see the exemple of Penrose Mosaic, generated by the aforementioned methods. To the right, we zoom in on the pattern and separate between identical pieces integrating the tiling. It can then be noticed that the projection ends up creating a set of identical tiles that repeats itself across the plane in a nearly periodic manner.*

We will begin from results obtained by G. G. Naumis and J. L. Aragon[18], who have demonstrated a method with which we can project a grid of multiple dimensions over a plane, or even the R^3 space, enabling us to obtain quasicrystalline patterns such as Penrose's. The mathematical details behind the model suggested by them can be seen at the original article, and here the general idea about the model is going to be presented, displaying how it fits in our scheme.

For the case of a two dimensional pattern, we start by taking a set of points in a non real five dimensional space of integer coordinates (no more than a Manhattan Geometry, but in five dimensions). This is our *N* set. We could now apply a test law, but it would be a trivial one (in the model proposed by Naumis and Aragón, every point in *N* is valid in order to describe the quasicrystal).

In this moment, we apply the T transformation to each element in *N*, mapping them to points in R^2 corresponding to the vertices of the pattern (i.e. atoms of the quasicrystal). It is worthy of notice that a major part of the problem in spawning the coordinates is solved by T itself, and not by the law selecting points. This is such because the domain space of our transformation is already well adjusted to our problem, making our formation law not only simple, but also disposable. The five dimensions present are directly linked to the Bragg's law diffraction patterns we expect to see from these crystals, as well as what was originally observed by Shechtman.

The quasi-periodicity can also be related to the position we put the R^3 space relative to the space of tested points. A relation of this kind, where the unitary vectors in R^3 are the straight equivalents of 3 base vectors from a higher space, gives us a direct projection, spawning a simple cubic pattern. In the example here presented, the projection of unitary vectors in Z^5 Manhattan space results in five vectors corresponding to our edge coordinates of a pentagon with its center at the coordinate origin, causing the appearence of non trivial patterns over our projections. For a tridimensional quasicrystal, we can adopt a directly analogue treatment, for instance, using the directing vectors normal to the faces of a regular solid (such as a dodecahedron) as projections of unitary ones in a space with dimensionality higher than that of R^3.

In Figure 4 and 5, we can see simple cases of two dimensional quasicrystals spawned by means of this method.

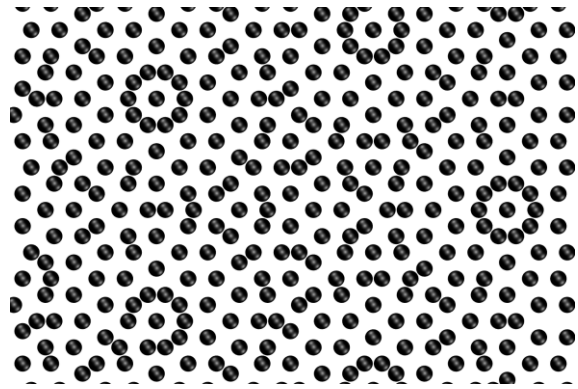

Figure 5: *2D structure of a simple quasicrystal built using the logic presented in here. It becomes evident that the repetition of a unit cell would not properly describe this pattern.*

IV. Conclusion

As we have seen, starting from a certain geometry, with a law selecting elements of a subset of it, and from a transformation relating the elements of such subset to coordinates in real space, we may build ideal models of atomic structures, taking advantage of some natural periodicities of Z^n in order to write such law. We have also seen that, once we have a good knowledge of the set's elements, it is always possible to write a test law describing these points, which opens the possibility of testing for ternary and quaternary alloys and quasicrystals, among many others.

It was also shown that a fine tuning can be done, picking among geometries which simplify the laws describing elements in the desired subset of Z^n, as seen in the formation laws presented for cubic lattices. However, at times it might be more useful to keep a more complex transformation, using a simple space to solve a problem with complicated symmetry, like the case for the 2D quasicrystal following the Penrose Pattern.

But we may also question ourselves as to what news all this brings to crystallography or to the modelling of crystals. In fact, we already know efficient techniques to the construction of periodic crystal lattices for simulations, mainly by means of replicating a basic building block which would spawn the whole structure from its repetition. The method introduced here in reality brings a more general approach: instead of looking for a unit cell and repetition directions, we search for a law giving us the position of every atom in an alternative geometry space and use a transformation to spawn coordinates in real space

through that set. Thus, we gain a tool which does not only attack the problem of building periodic structures, but that could also create any type of atomic structure, be it organized or not. Such safety arrives exactly from the fact that any subset of points has a law picking them from a more general set, which in our case is the Manhattan space.

Logically, this new technique involves a cost: the simplicity of the test law is closely related to the one building it and his or her ability of recognizing numerical patterns, or implementing code which is able to do that. We also face the problem of writing the appropriate transformation, adequating the level of complexity of each part in our model, so it can work in a simple manner and reduce possible difficulties in its implementation.

It is also important to note that this method does not necessarily solve the current problems of crystallography, but indicates a different way to attempt solving them. If a computational crystallographer, for example, tries to find the structure that has generated a given pattern in a X-ray diffraction, he can now construct a code which starts with a simple geometric system and then applying various formation laws, generate a set of digital samples. Making theoretical diffraction patterns, one could compare the patterns found computationally with previous data and then finally point out which ones are the formation laws which led to structures closer to the real one.

Fortunately, we recall here that for the cases presented in this work, everyone may straight ahead make use of the results shown. That being another practical facet of the method: the logical effort of choosing an initial geometry, the formation law for points and a transformation over to real space, is only required once. After being cataloged, the result can be used again. With that, we have significant gains in terms of computational time and effort in building structures, mainly in the case of complex alloys (whose unitary cells are simply too big and difficult to manually build) and quasicrystals (where the original idea of replicating basic units falls flat).

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REFERENCES

[1] A. T. Brünger, M. Nilges, *Quarterly Reviews of Biophysics.* 26 (1993) 49-125

[2] G. Langer, S. X. Cohen, V. S. Lamzin, A. Perrakis, *Nature Protocols.* 3, (2008) 1171 - 1179

[3] J. Bettini, F. Sato, P. Z. Coura, S. O. Dantas, D. S. Galvão, D. Ugarte, *Nature Nanotechnology* . 1, (2006) 182 - 185

[4] R. Salomon-Ferrer, D. A. Case, R. C. Walker, *WIREs Comput. Mol. Sci*. . 3, (2013) 198-210

[5] M. Okunoa, N. Zotovb, M. Schmückerc, H. Schneiderc, *Journal of Non-Crystalline Solids*. 351, (2005) 1032–1038

[6] J. L. Finney, *Structural Chemistry* . 13, (2002) 231-243

[7] W. Steurer, S. Deloudi, *Crystallography of Quasicrystals: Concepts, Methods and Structures*. Springer Series in Materials Science, Vol. 126

[8] A. Ledermann, L. Cademartiri, M. Hermatschweiler, C. Toninelli, G. A. Ozin, D. S. Wiersma, M. Wegener, G. von Freymann, *Nature Materials*. 5, (2006) 942 - 945

[9] A. J. Snell, K. D. Mackenzie, W. E. Spear, P. G. LeComber, A. J. Hughes, *Applied physics*. 24 [4] (1981) 357-362

[10] Z. Minevski, C. L. Tennakoon, K. C. Anderson, C. J. Nelson, F. C. Burns, D. J. Sordelet, C. W. Haering, D. W. Pickard, *MRS Proceedings.* (2003) 805

[11] H. Minkowski, *Gesammelte Abhandlungen*. B. G. Teubner, Berlin 1911

[12] E. L. Lima, *Espaços Métricos*. IMPA, Rio de Janeiro 2003

[13] C. Ekici, I. Kocayusufoglu, Z. Akça, *Tr. J. of Mathematics.* 22, (1998) 295-307.

[14] N. W. Ashcroft, N. D. Mermin, *Solid State Physics*. Saunders College, Saunders 1976

[15] D. Shechtman, I. Blech, D. Gratias, J. Cahn, *Physical Review Letters.* 53, (1984) 20.

[16] D. Shechtman, *Physica Scripta* . 49, (1988) 49.

[17] R. Penrose, *Bulletin of the Institute of Mathematics and its Applications*. 10, (1974) 266–271.

[18] G. G. Naumis, J. L. Aragon, *Z. Kristallogr*, 218, (2003) 1–3.

Supplementary Material to

The Method of Selection Laws and its Applications to Crystallography

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***Abstract*—This is a supplementary material that seeks to expose and clarify some concepts and results seen in the main paper. In the first section, we show some applications of the proposed method in the structures with cubic crystalline lattice. Then we will make a more mathematical development of the concepts involved when we speak of Manhattan Geometry, starting from the fundamental concept of a Metric Space. Finally, we demonstrate the generality of the formation law in a very simplistic (but formal) way.**

***Index Terms*—Crystallography; Selection Laws; Computational Physics**

I. Practical Examples: Other Cubic Structures

A. Simple Cubic (SC)

As example of cubic structures we can cite Nitrogen (at a temperature of approximately 20K). We note that taking the whole of $\mathbb{Z}^3$ already gives us the desired symmetry for this system. We can now face the matter of describing diatomic SC crystals, a very common case among salts and oxides. As example we consider here the proportion type $\alpha\beta$ (as in the case of NaCl crystals) and write a law:

$$\mathbf{n} \in \mathbf{N}_\alpha \Leftrightarrow \|\mathbf{n}\|_{\mathbb{Z}^3} = 2k+1; \quad k = 0,1,2,\ldots$$

$$\mathbf{n} \in \mathbf{N}_\beta \Leftrightarrow \|\mathbf{n}\|_{\mathbb{Z}^3} = 2k; \quad k = 0,1,2,\ldots$$

What we see is no more than α belonging to the Set of Odd Points and β belonging to the Set of Even Points, both defined in the paper. It also gives rise to the fact that if we completely remove either species, we end up with the FCC lattice.

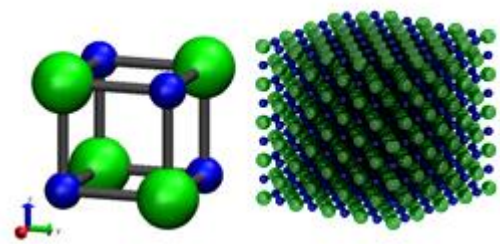

Figure 1: *Illustration of the SC model for a* NaCl *(type $\alpha\beta$) crystal. On the left, unit cell of the SC lattice, naturally arrived as a consequence of the laws adopted in our method.*

B. Body Centered Cubic (BCC)

This crystal is usually made up by Alkaline elements under low temperatures (~5K) and some transition metals such as Cr, Nb, Mo and W, among others. For pure crystals, we consider the set:

$$\mathbf{n} \in \mathbf{N}_\alpha \Leftrightarrow n_1 \bmod 2 = n_2 \bmod 2 = n_3 \bmod 2$$

At first glance, this formation law is very different from the previous ones: the points which interest us are the ones where every coordinate is even or every coordinate is odd. We can use this in our favor and build a law for a type $\alpha\beta$ crystal, As in the case of NiTi. It follows that:

$$\mathbf{n} \in \mathbf{N}_\alpha \Leftrightarrow n_1 \bmod 2 = n_2 \bmod 2 = n_3 \bmod 2 = 0$$

$$\mathbf{n} \in \mathbf{N}_\beta \Leftrightarrow n_1 \bmod 2 = n_2 \bmod 2 = n_3 \bmod 2 = 1$$

This case also allow us to see how quickly these laws can become sophisticated compared to the very simple FCC lattice.

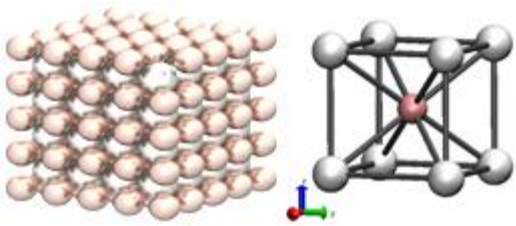

Figure 2: *Illustration of the BCC model for a* NiTi *(type αβ) crystal. On the right, unit cell of the BCC lattice, naturally arrived as a consequence of the laws adopted in our method.*

C. Diamond

A crystal with a diamond-type stacking has a very resilient structure, such as crystalline silica, the Si crystal or diamond itself, which gave the shape its name. This structure is a little bit more complicated and has a formation law even more distinguished from the last ones:

$$\mathbf{n} \in \mathbf{N}_\alpha \Leftrightarrow \begin{cases} n_1 \bmod 2 = n_2 \bmod 2 = n_3 \bmod 2 = 0 \\ \qquad \textbf{and } (n_1 + n_2 + n_3) \bmod 4 = 0 \\ \\ \textbf{OR} \\ \\ n_1 \bmod 2 = n_2 \bmod 2 = n_3 \bmod 2 = 1 \\ \qquad \textbf{and } (n_1 + n_2 + n_3) \bmod 4 = 0 \end{cases}$$

It might look confusing at first sight, but such law gives us precisely the appropriate elements in $\mathbb{Z}^3$ that, when scaled, inform the positions of atoms inside a diamond crystal. If we take the first condition to α and the second for β, that law can also be useful to build zinc blende type structures.

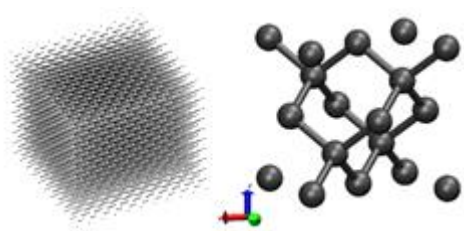

Figure 2: *Illustration of the diamond crystal model. Structure size is purposefuly upgraded to show how we can build any amount of atoms, once a proper formation law is found. On the right, unit cel of the diamond lattice, naturally arrived as a consequence of the laws adopted in our method.*

II. Metric Spaces

Definition 1. *We denote by Metric Space a set* $\boldsymbol{S}$ *allied by a function* $d: \boldsymbol{S} \times \boldsymbol{S} \to \mathbb{R}$ *which obeys the following properties:*

(i) $d(x, y) \geq 0$

(ii) $d(x, y) = 0 \Leftrightarrow x = y$

(iii) $d(x, y) = d(y, x)$

(iv) $d(x, z) \leq d(x, y) + d(y, z)$

For all $(x, y) \in \boldsymbol{S} \times \boldsymbol{S}$. *In this manner,* d *is said to be the distance function, or metric of* $\boldsymbol{S}$.

A. Manhattan Metric

Though we have already introduced a function d which describes a metric relationship, we will now present a more fundamental concept:

Definition 2. *Let* $\alpha = (a_1, a_2)$ *and* $\beta = (b_1, b_2)$, *such that* α, $\beta \in S$, *then:*

$$\langle \alpha, \beta \rangle_S = \begin{cases} +|a_1, b_1| + |a_2, b_2|; & \alpha \text{ and } \beta \text{ lie in the same quadrants} \\ -|a_1, b_1| + |a_2, b_2|; & \alpha \text{ and } \beta \text{ lie in neighbor quadrants, such that } a_1 b_1 < 0 \text{ and } a_2 b_2 > 0 \\ +|a_1, b_1| - |a_2, b_2|; & \alpha \text{ and } \beta \text{ lie in neighbor quadrants, such that } a_1 b_1 > 0 \text{ and } a_2 b_2 < 0 \\ -|a_1, b_1| - |a_2, b_2|; & \alpha \text{ and } \beta \text{ lie in the opposit quadrants} \end{cases}$$

We are adopting $\boldsymbol{S}$ as two dimensional and its elements as an ordered pair of elements in $\mathbb{R}$. It is important for the reader to observe that this treatment is a mere convenience for our case, where we will soon set $\boldsymbol{S} = \mathbb{Z}^n$.

Such relation defines $\langle \alpha, \beta \rangle_S$ as an *inner product* of $\boldsymbol{S}$. An inner product must verify hermitian symmetry, distributivity, homogeneity and positivity. The proof of these properties for the case of this product is not shown here, but can be seen in details on **The Norm in Taxicab Geometry** - C. Ekici, I. Kocayusufoglu & Z. Akça - *Tr. J. of Mathematicas*, **22** (1998), pages 295-307.

Definition 3. *Let* $\alpha = (a_1, a_2) \in \boldsymbol{S}$, *then:*

$$\|\alpha\|_S = \sqrt{\langle \alpha, \alpha \rangle_S + 2|a_1 a_2|}$$

We define $\|\alpha\|$ as the Norm of α in $\boldsymbol{S}$ space. It's simple to observe that:

$$\|\alpha\|_S = \sqrt{{a_1}^2 + {a_2}^2 + 2|a_1 a_2|} = |a_1| + |a_2| = d(\alpha, 0)$$

However, we still did not show that $\|\alpha\|$ is, in fact, a norm.

Theorem 1. $\|\alpha\|_S$ *is a norm in* $\boldsymbol{S}$.

Proof. As we are particularly interested in discrete $\boldsymbol{S}$, it is true if $\|\alpha\|_S$ verifies the following properties:

(i) $\|\alpha\|_S \geq 0$

(ii) $\|\alpha\|_S = 0 \Leftrightarrow \alpha = (0,0)$

(iii) $\|k\alpha\|_{\boldsymbol{S}} = |k|\|\alpha\|_{\boldsymbol{S}} \ \forall k \in \mathbb{Z}$
(iv) $\|\alpha + \beta\|_{\boldsymbol{S}} = \|\alpha\|_{\boldsymbol{S}} + \|\beta\|_{\boldsymbol{S}}$
Let's show these properties:

(i) $\|\alpha\|_{\boldsymbol{S}} = |a_1| + |a_2| \geq 0$

(ii) $\|\alpha\|_{\boldsymbol{S}} = |a_1| + |a_2| = 0 \Leftrightarrow \ a_1 = a_2 = 0 \ \Leftrightarrow \alpha = (0,0)$
(iii) $\|k\alpha\|_{\boldsymbol{S}} = \|(ka_1, ka_2)\|_{\boldsymbol{S}} = |k|(|a_1| + |a_2|) = |k|\|\alpha\|_{\boldsymbol{S}}$
(iv) $\|\alpha + \beta\|_{\boldsymbol{S}} = \|(a_1, a_2) + (b_1, b_2)\|_{\boldsymbol{S}} =$
$= \|(a_1 + b_1, a_2 + b_2)\|_{\boldsymbol{S}} = \cdots \leq \|\alpha\|_{\boldsymbol{S}} + \|\beta\|_{\boldsymbol{S}}$

In (iv), we omit some calculations which demonstrate the triangle inequality. The full proof includes a detailed analysis of every possible sign for the coordinates α andβ. Such analysis can be easily found in literature. Along with the previously mentioned work, the reader can find the proof in other books, some of which are cited as bibliography.

This norm may also be denoted by "L_1 Norm" or "1-Norm", just as the euclidean norm is denoted by "L_2 Norm" or "2-Norm". (In a more general sense, the "L_P Norm" or "P-Norm" is defined as $\|\mathbf{x}\|_P = (\sum_{i=1}^{n} |x_i|^P)^{\frac{1}{p}}$.)

■

With this, we are at last able to build a metric induced by the norm:

$$d(\alpha, \beta) := \|\alpha - \beta\|_{\boldsymbol{S}} = |a_1 - b_1| + |a_2 - b_2| \quad \forall \alpha, \beta \in \boldsymbol{S}$$

And that is the Manhattan Metric.

B. The $\mathbb{Z}^3$ Case

Our objective from now on is to utilize the Manhattan Metric for the $\mathbb{Z}^3$ set. In other words, for every $\mathbf{n} = (n_1, n_2, n_3)$ and $\mathbf{m} = (m_1, m_2, m_3)$ contained in $\mathbb{Z}^3$, we may seek $d(\mathbf{n}, \mathbf{m})$ from the definition:

$$d(\mathbf{n}, \mathbf{m}) = |n_1 - m_1| + |n_2 - m_2| + |n_3 - m_3|$$

We can naturally obtain a norm as well, defined by:

$$\|\mathbf{n}\|_{\mathbb{Z}^3} = |n_1| + |n_2| + |n_3|$$

It is important to mention that, in fact, the values for the metric and norm are actually to be taken as elements in the field of real numbers ($\mathbb{R}$), but for this case, they assume values exclusively in $\mathbb{Z}$. This treatment might justifiably sound unsettling, for $\mathbb{Z}$ is not even properly defined as a field in the same sense as $\mathbb{R}$ is. Nonetheless, that does not modify by any means what was developed until here, though it is reassuring to mention we can actually define a "metric space over $\mathbb{Z}$" with no great loss of properties, as long as we are able to adapt the metric, which is our case. Even then, we will maintain our rigour in defining structures.

We denote the $\mathbb{Z}^3$ space, equipped with the metric $d(\mathbf{n}, \mathbf{m})$, by Manhattan Space. This metric space is the one we will work with from now on.

III. Genetality of the Selection Law

Theorem 2. *All known set of points in a metric space has at least one law of selection.*

Proof. We will suppose that we know all the elements for a generic subset$\boldsymbol{C}$, that is, $\boldsymbol{C} = \{\boldsymbol{c}_1, \boldsymbol{c}_2, \boldsymbol{c}_3, \dots, \boldsymbol{c}_n\}; \boldsymbol{c}_i \in \boldsymbol{S} \ \forall i = 1,2,3, \dots, n$. We intend to realize how we can create a mathematical law verified solely by these elements.

This is a strong result, for it implies that every set should have a law associated to its elements. In fact, this is a well known result for sequences: every sequence has a law of formation, regardless of our capacity of actually describing it mathematically. Also, we know that for the case of numerical sequences, we can always write such law as a mathematical expression, which motivates, for example, the search for a law associated to the prime number sequence.

Let us start by ordering the elements in $\boldsymbol{C}$ (i.e as the subset was defined before, we just we need to create an order relation, no matter what. The order itself is irrelevant, being a mere tool for the demonstration). We initially consider the truncated sequence $\boldsymbol{C}^1 = \{\boldsymbol{c}_1\}$. This sequence has the trivial formation law:

$$\mathbf{n} \in \boldsymbol{C}^1 \Leftrightarrow \ \mathbf{n} = \boldsymbol{c}_1$$

Now, we rewrite this expression in a way more convenient to our demonstration:

$$\mathbf{n} \in \boldsymbol{C}^1 \Leftrightarrow d(\mathbf{n}, \boldsymbol{c}_1) = 0$$

Which, from the properties of $d(\mathbf{n}, \mathbf{m})$, goes straight back to our first expression. Let us now consider another set, truncated now at the k-th element, that is, the set $\boldsymbol{C}^k = \{\boldsymbol{c}_1, \boldsymbol{c}_2, \boldsymbol{c}_3, \dots, \boldsymbol{c}_k\}$. We are then able to easily generalize the previously seen expression as:

$$\mathbf{n} \in \boldsymbol{C}^k \Leftrightarrow \prod_{i=1}^{k} d(\mathbf{n}, \boldsymbol{c}_i) = 0$$

Writing the formation law for our proposed sequence, we have shown that, once we know the terms belonging to a set and have defined a metric in the corresponding space, a law that will only be verified by the elements of that set can be

built. The extension of this to the case of infinite sets is more delicate and will not be discussed here, but the core concepts remain the same.

■

The expressions we presented before do not assume the form of the last one, and it is so because in some cases, the formation laws can be written in highly simplistic ways. Here we arrive at a delicate matter on the method: obtaining the adequate law for a set (or crystal). We cannot give a clear recipe to obtain such expression, this task being very dependent of recognizing specific numerical patterns or writing software that can test through a variety of candidates for laws, by means of AI or genetic algorithms (simple examples like the FCC lattice, the law is easily found manually. But in the case of ternary alloys, a computational approach is highly recommended). It is important to recall that we have already shown the search is not in vain, for a law will surely always exist, albeit it might not be a simple one.