Non-linear periodic structures

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It is well known that non-linear systems share the universal property of presenting symmetry-breaking bifurcations. Often, these processes lead to spatial periodic patterns that are both complicated and robust. In basic atomic processes, non-linear interactions could be important when forming a crystal or an amorphous solid from the melt. Furthermore, one is often interested in building periodic nano-structures. In this paper I present two different non-linear systems that produce periodic patterns. This theoretical study suggests that new experimental techniques could be devised to build solid state structures with specifically tailored geometrical properties.

Keywords: Non-linear systems, bifurcation, Turing patterns, statistical physics, nano-structures.

1. Introduction

In recent times, Solid State Physics has moved from studying basic quantum mechanical properties of crystals that Nature offers to creating new periodic structures with desired properties. This is particularly true in the nano-scale regime. There are currently many sophisticated techniques to fabricate nano-devices with extraordinary precision. The study of periodic arrays of quantum dots and quantum wires has opened new realms to solid state physicists. There are many devices that have been developed at a vertiginous pace using these techniques, such as ratchets, nano-engines, photonic arrays, and many others.

The purpose of this paper is to propose the idea that one could obtain solid state structures by using the properties of non-linear systems. Taking advantage of the fact that this field of research has been considerably developed in the past decade, particularly in the field of Mathematical Biology [2], one could try to make the bridge between the systems used in this field and solid state systems. This idea seems ambitious, and here I shall not pretend to give a magic recipe for everything, rather I shall restrict myself to pointing out some basic important features that might be useful for this task.

It is well known that complex systems, in which non-linear interactions are at play, share the universal feature of presenting spontaneous symmetry-breaking, driven by the manipulation of a certain external bifurcation parameter [1]. This results naturally in the appearance of spatio-temporal patterns. In certain systems these patterns present a characteristic length that could be controlled externally. This length could range from nanometers to several kilometers, depending on the system at hand. It is obvious that these virtues are particularly suitable to tailor artificial structures to customer requirements.

Of course, these general thoughts ought to be put into more precise form, and this is precisely the purpose of this paper. In order to be specific to Solid State interests, I shall show first that non-linear processes are present even in very common techniques used daily to grow solids, like sputtering or vapor deposition. Acknowledging this fact, one is able to work out non-linear models that allow one to predict the appearance of ordered periodic or quasiperiodic lattices.

Then I shall briefly revise some common techniques used when dealing with non-linear systems of differential equations. This is required to present two very different systems that produce robust periodic patterns. One is a simple system of reaction-diffusion equations proposed by us some time ago [3], which can be tuned to give a Turing instability [4]. This peculiar mechanism produces patterns that are stationary and regular in space, and models have been made in the past to be applied to biological phenomena, as morphogenesis, embryology, and wound healing. The other is the well known Faraday experiment [5], in which a liquid contained in a vase is agitated vertically with certain frequency and amplitude. This system produces regular patterns that are fixed in space but oscillate in time. I shall give examples of the applications of these models published elsewhere, and also give some ideas about the possible applications of these systems to the fabrication of solid state structures.

2. Analysis of non-linear systems

In general, one could write the equation representing the dynamical system as
\[
d\frac{V}{dt} = F_r(V, t),
\]
where \( V \) represents all the pertinent variables, \( r \) are the external parameters, and \( F \) are non-linear functions defining the interactions between variables. Eq.(1) represents either an infinite system of partial differential equation, or a discrete set of ordinary differential equations, since the associated phase space could be infinite and continuous or discrete and finite.

Suppose that \( V_0 \) represents a stationary state, that is \( F_r(V_0, t) = 0 \), and one is interested in knowing the behaviour of the system subjected to a small perturbation \( V \to V_0 + \epsilon U \). Whatever the form of the functions \( F \), one could expect a linear response, represented by

\[
d\frac{dU}{dt} = L_r U,
\]
where \( L_r \) is a linear operator. The solution of Eq. (2) is

\[
U = \exp(s_n t) X_n,
\]
and one gets the eigenvalue equation

\[
L_r X_n = s_n X_n,
\]
where \( n \) labels the normal modes \( X \). If these eigenvectors form a complete set, then \( U = \sum_n A_n X_n \), and the time evolution of the perturbation is given by the behaviour of the amplitudes \( (A_n) \) of each mode \( X_n \).

\[
d\frac{dA_n}{dt} = s_n A_n.
\]

The complex eigenvalues \( s_n = \sigma_n + i \omega_n \) give valuable information about the solution, for instance: If \( \sigma_n > 0 \), then \( X_n \) is unstable, \( \sigma_n \leq 0 \), then \( X_n \) is stable. If \( \omega_n \neq 0 \) and \( \sigma_n > 0 \), there are oscillations in time. If \( \omega_n = 0 \) and \( \sigma_n > 0 \), there may be spatial fluctuations.

The general process described above is known as linear analysis, and it is extremely useful to predict the bifurcation points and also the nature of the instability. Examples relevant for our purposes are the Hopf bifurcation \( (s_n = |\sigma > 0, \omega \neq 0|) \), and the Turing instability \( (s_n = |\sigma > 0, \omega = 0|) \).

There are basic non-linear analysis techniques that could be applied to get information about the weakly non-linear behaviour of the system, but these are beyond the scope of this paper. In what follows, I will exemplify the usefulness of linear analysis to model the growth processes of solids, and then discuss two interesting examples of non-linear models.

3. The Stochastic Matrix Method: A theory of solid growth by agglomeration

A theory to model solid growth by agglomeration was initially put forward by R. Kerner (for a review see [6]). The theory assumes that in a melt there usually are basic units, which could be atoms, molecules or clusters, that make chemical bonds. As the temperature is lowered, the average size of the bonded clusters increases until one gets an infinite cluster that represents the solid. If there are two very different time scales in the process (as in glasses), where one time scale could be the lapse in which a chemical bond reaches equilibrium (very short) and the other could be the time spent by the whole system to relax to thermal equilibrium (very large), one could represent the solidification as individual additions of units to larger clusters, called agglomeration steps.

The dynamical process of agglomeration takes place at the surface of the clusters, and locally, the number of configurations in each step is finite, so one could ask for the time evolution of the probability of having any of these configurations. The fundamental idea is very simple and consists of representing the agglomeration process of units as a dynamical system in a properly defined phase space:

\[
p_i(t = 0) \longrightarrow p_i(\Delta t) = p_i(0) + v(0) \Delta t,
\]
where \( p_i \) is the probability of finding configuration \( i \), and all the relevant information is encoded in the velocity operator \( v(t) \), which in general could be derived only from dynamical considerations, without the need of a potential function.

When writing Eq.(5) for a specific model, one immediately realizes that non-linear terms become increasingly important as the agglomeration process advances, due to the fact that the velocity operator at a given time could depend on the probabilities at former times, a kind of memory effect.

If one observes that at any given time, the portion of the system that is relevant for the dynamical process is the surface, regardless of which processes took place to form the bulk, one could safely say that consecutive agglomeration steps do not influence each other. In this case, one could write each agglomeration process as a linear transformation,

\[
P' = SP,
\]
where \( P \) is a “vector” whose elements represent the proportions of each local configuration initially found at the surface, and \( P' \) is the resulting vector after one agglomeration event. The elements of matrix \( S \) should represent the transition probabilities for the occurrence of a given change. Naturally, \( S \) turns out to be stochastic, in the sense that the sum of its elements in any column is one. There is no need for the rows of the matrix to be normalized, as is the case for true transition matrices, since the transformation is not necessarily Hermitian or even reversible. Therefore, it is important to use “right vectors”, as in Eq.(6). The dimension of the space is exactly the number of distinguishable configurations.

The so called Stochastic Matrix Method (SMM) is nothing else other than the linearization of the original non-linear model, and Eq.(6) represents a linear Markov process. Then, \( S \) has at least one eigenvalue with norm one and all the others have norms less than one. Since the solid could be regarded as the result of applying the transformation matrix many times \( (\lim_{N \to \infty} [S^N]) \), the eigenvector with eigenvalue one represents the final configuration of the infinite solid, since all other distributions die out exponentially.

A specific model of growth could be constructed if one has information about three features: 1) which units form the
solid, 2) which surface configurations are dynamically relevant (the number of vector components), and 3) which physical knowledge one should need to take into account, that is, the specific reaction terms encoded in the elements of S.

This method has been applied to covalent glasses [7, 8] and the results are strikingly useful, for instance, one can predict the behaviour of the glass transition temperature as one adds a modifier that changes the local configuration of the chemical bonds. A curious case is boron oxide (B$_2$O$_3$), whose Raman spectrum shows a very sharp peak. This is assumed to be the signature of regular six-fold rings called boroxol rings. By applying the SMM to this system [9], one gets the result that about 80% of boron atoms are in boroxol rings, a prediction later confirmed by inelastic neutron scattering experiments.

Another interesting application of the SMM is the study of the formation of two-dimensional tiles. We investigated the fixed points of the stochastic matrix using equilateral triangles and squares as basic units. We obtained all the known crystalline tilings, and two new non-periodic structures, which turned out to be hexagonal quasicrystals whose existence was unsuspected before [10]). Quasicrystals are extremely interesting because some of the elementary excitations in solids, as phonons, could be localized in space, as it has been shown in Penrose tiles [11].

When modeling glass formation, one can use the composition of the melt to extract relevant information, such as the temperature of homogeneous growth ($T_g$), which could be verified experimentally in numerous binary and ternary covalent glasses. When modeling solid growth by deposition, the situation is exactly the opposite since one does not control the composition to modify the temperature of solid formation, but one usually controls the temperature of the substrate where all the relevant agglomeration processes take place, and the final composition of the film depends on that. Results of this kind for the epitaxial growth of a Ge : H alloy have been published elsewhere [12].

This discussion of the SMM gives a basic idea of the way one could use very common techniques of non-linear systems to investigate the properties of materials. In the following section, I shall present a model that has not been used in Solid States, but that presents very useful features.

4. Generic Turing Model

In 1952, the mathematician Alan M. Turing wrote a magnificent paper [4] proposing a theory for “morphogenesis”, that is, the ways in which a highly symmetrical zygote evolves to acquire an anatomical shape. He showed that a system of reacting and diffusing chemicals could break the symmetry of a state, initially homogeneous, into a spatial pattern of chemical concentrations, by a process called “diffusion-driven instability”. The Turing instability has been reproduced in the laboratory in a real chemical reactor [13], although the existence of Turing patterns in biology is still a controversial issue (see Ref. 14 for a review).

We have proposed a general form of reaction-diffusion equations with two chemicals with concentrations $U$ and $V$ that present a Turing instability [3], which is

$$\frac{\partial U}{\partial t} = D\delta \nabla^2 U + \alpha U(1 - r_1 U^2) + v(1 - r_2 U)$$

$$\frac{\partial V}{\partial t} = \delta \nabla^2 V + \beta V(1 + \frac{\alpha r_1}{\beta} U V) + u(\gamma + r_2 V)$$

where $\delta$ is a scaling factor, $U = U - U_c$ and $V = V - V_c$, so the uniform stationary solution of Eq. (7) is at the point $(U, V) = (0, 0)$, which is the only one if $\alpha = -\gamma$. The linear

![Figure 1](image-url)
analysis when this condition is not met has been made elsewhere [15]. In the absence of diffusion, the eigenvalues of the linear operator in Eq. (2) are

\[ s_{\pm} = (\alpha + \beta)/2 \pm \sqrt{(\alpha + \beta)/2} - \alpha(\beta + 1). \]

whose real part is negative for certain values of the kinetic parameters \( \alpha \) and \( \beta \), and the uniform solution is stable. When diffusion is added, the solutions have the form \( X_k = e^{kr} \), and there is a dispersion relation

\[ s(k)^2 - Bs(k) + C = 0 \]  

(8)

where

\[ B = \delta k^2 (1 + D) - (\alpha + \beta), \]

and

\[ C = (\alpha - D k^2)(\beta - \delta k^2) + \alpha. \]

If the condition \( \alpha - 2\sqrt{\alpha D} > \beta D \) is met, then there are states in which \( \text{Re}(s(k)) > 0 \) for a certain range of \( k \), and the states in this range (called the Turing space) become unstable. This is the reason why this phenomenon is called “diffusion driven instability”, which is remarkable, since diffusion usually tends to produce the opposite, namely, it smears out any structure. We discovered that cubic or quadratic interactions favour patterns with stripes or spots, respectively [3].

In Fig. 1 there are numerically obtained patterns with two different sets of parameters. Observe that the characteristic length of the ones shown on the left hand side is larger than the length of those on the right hand side, since the corresponding region of \( k \), in which the dispersion relation has a positive real part is smaller for the former. In three dimensions, there are more possibilities; one could have ordered spheres, disordered spheres, lamellae, tunnels, layered patterns, and labyrinthine patterns [16].

In 1995, Kondo and Asai [17] published an astonishing paper based on a one-dimensional calculation, suggesting that the coat pattern of certain marine fish of the order Pomacanthus really was a Turing pattern. These fish in their juvenile form present the semicircular stripes, common to all species in the order, (the reason for this is to prevent selective predation by the adult cannibal fish). When they grow, the pattern changes dramatically to the specific colors and forms of the different species. In Fig. 2 we show the pattern of the fish Pomacanthus imperator, (taken from Ref.18).

We decided to study this problem properly, both theoretically and experimentally. We used the model of Eq. 7 to simulate the skin pattern of this fish when it was growing, and compared our calculations with observations of the changes of the skin on a real fish. These observations lasted for 4 years because the fish did not grow. It is well known that this kind of fish can stop growing if there is not enough space. When the fish was changed to a 3 m³ tank, it had enough space and grew in a matter of weeks. In Fig. 3 we show a series of snapshots of the fish during a time span of 3 months.

There have been numerous applications of this model to various biological systems, for example, the study of the general mechanisms of transformation of Turing patterns in growing and curved domains [20] to be applied to the pattern changes of lizards, patterns on a spherical surface to model
the very regular shapes encountered in many small organisms, such as radiolarian and viruses [21], patterns on the different species of lady birds and butterflies, modeling the heartbeat [22], and many others.

However, it has always been a deception to realize that Turing patterns are too simple to be compared with real patterns in Nature. A long time ago we suggested that one could obtain complicated patterns by coupling two Turing systems [3], and we were able to reproduce the coats of many other fish. In Fig. 4 we show a few examples (Taken from Ref.18).

In recent years, there have been many efforts to produce complicated patterns. One of the most successful ones has been proposed in a series of papers by Epstein et al. [23], consisting of linearly coupling two Turing systems and ensuring that the modes that are parametrically enhanced have two very different wavelengths, and they resonate. In this fashion they demonstrate that one can obtain “white eyes”, “black eyes”, patterns with stripes containing dots, or vice-versa, or spirals within dots, and many others.

![Figure 4](image)

**Figure 4.** Patterns obtained by coupling two Turing models of Eq.(7) in different ways. The theroretical patterns resemble the ones exhibited by animals.

![Figure 5](image)

**Figure 5.** (a) Pattern obtained by cubically coupling two Brusselator models, using a coupling strength of 0.09. (b) A pattern of “boats” obtained in the same system using a coupling strength of 0.15

Of course, one could experimentally study these coupled systems by setting up two layered reactors, separated by an intermediate membrane that allows diffusion of chemicals from one reactor to the other. One such experiment has been published [24]. These models could also be used to describe semiconductor bilayer systems or even complicated biological membranes.

There are situations in which the intermediate layer could be chemically active. The inter-layer interaction can involve more than a simple selective diffusion of chemicals, as catalysis. We have carried out extensive numerical calculations in two Brusselator models, as the ones used in Ref. 23, coupled cubically. Guided by linear analysis, one could search for new complex patterns. A non-linear coupling means that the coupling layer is not inert as in the case of linear coupling, but there is a possibility of having a chemically active layer. To our knowledge, no other study has addressed this question. In Fig. 5 we show two extraordinary patterns obtained this way by varying the coupling strength parameter(Taken from Ref. 25.

![Figure 6](image)

**Figure 6.**

In pattern (a) one notices the presence of irregular stripes inside dots arranged in a nearly perfect hexagonal lattice. These features resemble the ones observed when one makes the interaction of the Abrikosov lattice of magnetic quanta of layered high-$T_c$ superconductors, with a matching hexagonal lattice of iron dots (see for instance Ref. 26). The boat-shaped pattern on (b) is quite remarkable. Observe that the symmetry of the pattern is two-fold, very different from the triangular patterns usually obtained with simple Turing systems, and that the lattice is perfectly periodic. I propose that reactors of this kind could be used a pre-patterns to fabricate nanostructured materials. In fact, there have been intents to build two-layered semiconductor devices in which the spatial scale could be easily modified.

I could envisage Turing systems being used in the future to develop new techniques to prepare structured materials in which the length scale and the geometry could be easily controlled.
5. The Faraday experiment

Here I shall present another non-linear system that is potentially important for investigating new phenomena in Solid State Physics. It is the famous experiment made by Faraday in 1831 [5]. This experiment is deceptively simple; it consists in agitating vertically a vessel containing a liquid. Then, the uniform steady state that corresponds to a flat surface is disturbed by agitation, and the surface acquires a complicated shape. This is illustrated in Fig. 6.

The theoretical treatment of this phenomenon, in the linear regime, was first made by Lord Rayleigh, who described surface waves, which are known as Rayleigh waves ever since. In a cylindrical container, the linear solutions are Bessel functions of the first kind.

Much more interesting are the non-linear solutions, and we repeated the experiment in a Petri dish using a rare liquid (fluorinert FC-75), chosen to enhance the non-linear interactions, namely a high density and a very low surface tension coefficient (σ). We discovered that the non-linear patterns are centro-symmetric, and that their symmetry depends on the bifurcation parameter, which is a combination of the amplitude and the frequency. We published a model based on the Euler equation with friction for the linear liquid, adding a non-linear mechanism resulting from the interaction between the vertical and horizontal velocity fields [27]. The final model reads

\[ \frac{\partial^2 \phi}{\partial t^2} = gh_0 \left(1 - \frac{A}{h_0} \sin(\omega t)\right) \nabla^2 \phi - \frac{\sigma' h_0}{\rho} \nabla^2 \phi - C A \omega (\cos \omega t) \sin(q \phi) + \gamma' \nabla^2 \phi \frac{\partial \phi}{\partial t}. \]  

(9)

Here, the velocity field is defined as \( \mathbf{v} = -\nabla \phi \), \( g \) is the gravity, \( \rho \) is the density of the liquid, \( \gamma' \) is related to the kinematic viscosity coefficient, \( C \) and \( Q \) are constants related to the size of the molecules, and \( \sigma' = \sigma - gh_0^2/3 \) is an effective surface tension coefficient, which for FC-75 is exactly zero at \( h_0 = 1.6 \text{ mm} \). The first two terms represent a parametric pendulum (Mathieu’s equation).

We also showed that Eq.(9) could be written as a Turing system by defining an auxiliary field \( \psi \). The “diffusion coefficients” are \( \alpha + \gamma' \) and \( -\alpha \), where

\[ \alpha = \frac{1}{2} \left(-\gamma' + \sqrt{\gamma'^2 - 4\sigma' h_0/\rho}\right). \]

Observe that if the surface tension is small (\( \sigma' \approx 0 \)), the coefficients are very different, as required for a Turing instability. For details, the reader should consult Ref. 27.

Extensive numerical calculations predicted patterns that could be verified experimentally. In this form, we were able to choose the symmetry axis of the bifurcation, and since we were interested in quasicrystalline symmetries, we followed the bifurcation tree of symmetry 5 (in fact, quasicrystalline patterns have been obtained in the Faraday experiment [28]). The important observation, made by M. Torres, is that the patterns obtained following this bifurcation tree are very similar to the shells of sea urchins in subsequent geological times of evolution. The actual photographs from the experiment are reproduced in Fig. 7.

One may ask at this point: What is the relation between the evolution of animals and the disturbed surface of a liquid? The most suitable answer could be taken from Faraday himself, who pointed out that the universality of a theory, as the Classical Theory of Vibrations, allows a deep understanding of the phenomena being modeled, regardless of the nature of the particular system. In the present case, we could infer that the mechanisms acting on the evolution of species could be better described following the bifurcations of a non-linear system. The far reaching consequence is that one needs to rethink the meaning of natural selection and adaptability.

Five-fold symmetry is remarkable, not only because of the existence of quasicrystals, but also because all known vertebrates in this planet present in the development of their members the following scheme of symmetry-breaking processes \( 1 \to 2 \to 5 \) (see for instance [2]). Furthermore, 5-fold symmetry is not only seen in sea urchins, but in all the phylum echinodermata.
Therefore, it is important to investigate the robustness of symmetry 5 in finite domains. We performed a series of numerical calculations using the same Turing model of Eq. (7) in a circular domain in two dimensions varying its radius [29]. This can be easily done by manipulating $\delta$ in Eq (7). In Fig. 8, we show a histogram with the results. Observe that for a wide range of small radii, the patterns are 5-fold, and then they go to the more frequently found 6-fold. Our prediction would be that if one is able to delay the appearance of the primary podia in the circular belly of the urchin until it reaches a bigger size, the animal should present a 6-fold symmetry.

So far I have described the Faraday experiment in a liquid, and shown the appearance of exceedingly robust non-linear patterns (in fact, one could stir the liquid with a finger and the pattern persists), but there is more to it. Faraday himself repeated his experiment using sand, but the theory of the forces involved in a granular system is much more complicated.

I suggest that Faraday patterns could be produced in quantum systems, as in a two-dimensional gas of electrons or phonons. These systems exist nowadays, for example, electrons driven to the surface of liquid helium could crystallize in a Wigner lattice, or phonons could be localized in planes in superlattices.

The main idea being that if the quantum states are well separated in the perpendicular direction, one could have spatial arrangements of quantum states which could be both, very robust and easily controlled.

The difficulty is that in the case of an electron, it is extremely difficult to set a system in which non-linear interactions and dissipative terms are sizable. This is not the case of phonons, since anharmonic terms could be easily enhanced. In fact, a paper in which Faraday patterns are seen in a Bose-Einstein condensate has very recently been published [30].

6. Conclusions

The main purpose of this paper was to show how non-linear models can be used in applications in Solid State Physics. For that, I have described some of the work that I have been doing in recent years, and suggested the ways in which such models could be transplanted to other systems, whenever possible. I provide no proofs of my claims, but simply express some punctual ideas to be developed and demonstrated in the future.

I examined the properties of two different models and showed that they share many common features. I analyzed the mechanisms leading to spatial and oscillatory patterns in different domains and conditions, illustrating several applications to various problems, ranging from the patterns on coats of marine fish to the evolution of the form and morphogenesis of sea urchins.

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15. C. Varea, D. Hernández, and R.A. Barrio, Phase decomposition leading to stationary patterns (to be published).