Review article



# Patterns in nature: more than an inspiring design

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#### Abstract

At all scales and both in animate and inanimate systems, nature displays a wide variety of colors, rhythms, and forms. For decades, these natural patterns and rhythms have been studied and used as a source of inspiration for the technological development and well-being of human beings. Today we understand that the design of these patterns responds to principles of functionality and efficiency. This article focuses on physicochemical aspects to show how the study of spatiotemporal patterns became such an important area of interest and research for natural sciences. In particular, we address some systems in which the formation of patterns is explained by the coupling between chemical and transport processes, such as chemical gardens, periodic precipitation and Turing patterns. © 2017. Acad. Colomb. Cienc. Ex. Fis. Nat.

Key words: Turing patterns; Morphogenesis; Periodic precipitation; Energy Economy; Bio-inspired processes.

#### Patrones en la naturaleza: más que un diseño inspirador

#### Resumen

En la naturaleza observamos una amplia variedad de colores, ritmos y formas, a toda escala y en sistemas animados e inanimados. Desde hace décadas los patrones y ritmos de la naturaleza han sido objeto de estudio y fuente de inspiración en el desarrollo tecnológico y en el bienestar del ser humano. Hoy entendemos que el diseño de los patrones de la naturaleza obedece a principios de funcionalidad y de eficiencia. En este artículo nos enfocamos en aspectos fisicoquímicos para mostrar cómo el estudio de los patrones espacio-temporales se convirtió en un área de gran interés e investigación en ciencias naturales. En particular, abordamos algunos sistemas donde la formación de patrones se explica mediante el acople entre procesos químicos y de transporte, tales como los jardines químicos, la precipitación periódica y los patrones de Turing. © 2017. Acad. Colomb. Cienc. Ex. Fis. Nat.

Palabras clave: Patrones de Turing; Morfogénesis; Precipitación periódica; Economía energética; Procesos bio-inspirados.

### Introduction

We have all felt overwhelmed when looking at the forms, colors, rhythms, and designs nature exhibits in all kinds of ways such as in coral reefs, schools of fish, flocks of birds, insect and microorganism colonies, insect wings, animal and fish skins, spider webs and even vegetables. For a long time, nature has inspired human beings to find solutions to technological challenges ranging from the design of textiles (Bar-Cohen, 2006; Helms, Vattam, & Goel, 2009), materials (**Bar-Cohen**, 2006; **Grzybowski**, 2009), reactor processes (Coppens, 2012), electrochemical cells (Armand, et al., 2009; Walish, et al., 2009) to means of transportation. One of these examples is the design of the Japanese bullet train's nose, inspired by the kingfisher's beak (Figure 1a), which allows the bullet train to reach speeds of over 300 km/h. reduce environmental noise and increase energy efficiency, thanks to the aerodynamic design which decreases the pressure shock waves generated when the train undergoes air resistance changes, such as when entering tunnels (Bar-Cohen, 2006; McKeag, 2012).

The silent flight of predatory birds such as the owl has also inspired the design of new materials. This bird's wing configuration allows it to cushion the air turbulence generated during the flapping, thus reducing the propagation of high frequency sound waves. The wings have a soft cover that dissipate the air flow over the surface, so when it reaches the end, the noise generated is minimal (**Tropea & Bleckmann**, 2012) (Figure 1b). This natural design inspired the modification of cooling fans and turbines blades, helicopters and airplanes propellers, as well as many other blade-based rotors, so apart from the design changes, blades are covered with a material that helps reduce air friction and noise and increase energy efficiency without compromising aerodynamic performance (**Clark**, *et al.*, 2016; **Tropea & Bleckmann**, 2012; **Xia & Jiang**, 2008). Another example is

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**Figure 1.** Examples of technologies inspired by nature. (a) Tokyo's Bullet Train inspired by the kingfisher's beak. Taken from flickr.com and commons.wikimedia.org with licenses CC BY 2.0 and CC BY-SA 4.0. (b) Hierarchical design with fractal distribution of the gas feeder (in blue color) to a catalytic reactor, inspired by the lung's bronchial structure. Taken from pixabay.com and commons.wikimedia.org with licenses CC0 and CC BY-SA 3.0. (c) Design of an artificial wing with efficient aerodynamics inspired by the owl. Taken from pixabay. com and commons.wikimedia.org with licenses CC0 and CC BY-SA 3.0. (d) Super hydrophobic material designed as a three-dimensional network of polymeric fibers with dispersed porous spheres, inspired by the hierarchical surface architecture of Lotus aquatic plant. Taken from pixabay.com, ca.wikipedia.org and flickr.com with licenses CC0 and CC BY 2.0.

the design of gas distribution systems inspired by the fractal geometry of the lung's bronchial tree, which improves mass transfer and increases the performance of industrial processes such as catalytic conversion of chemical substances into fluid bed reactors. The fractal distribution of gas in the medium not only ensures that the gas bubbles are small enough, but they are more likely to reach the places where they are most needed such as the interphase of the fluid-solid bi-phase, optimizing transfer and conversion processes (Coppens, 2012) (Figure 1c). There are other types of problems that have also benefited from natural inspiration, such as the design of super-hydrophobic and high adhesion surfaces (Xia & Jiang, 2008). The leaf of the lotus flower is wellknown for its high hydrophobicity, which allows it to float and stay dry and clean. Recent studies have shown that this property comes from the organization of different structures ranging from the macro to the nanoscale: leaf-papillaepores-cilia (Xia & Jiang, 2008). It is now know that there is a correlation between the properties exhibited by a material such as hydrophobicity and wettability, contact angle and roughness. This is how the natural design of the lotus flower's leaf inspired the synthesis of highly hydrophobic polymeric materials made up of porous microspheres dispersed in a three-dimensional network of nanofibers (Bar-Cohen, 2006; Xia & Jiang, 2008) (Figure 1d).

The previous examples illustrate how technological developments inspired by nature go beyond imitation and require discovering the fundamental principles that govern design's hidden efficiency. In the second law of thermodynamics we have a solid conceptual framework to evaluate the energy efficiency of a process, however, additional tools are required to connect form, patterns, geometry and design with the energy economy of processes (**Magnanelli**, *et al.*, 2016; **Walish**, *et al.*, 2009).

Adrian Bejan's constructal theory (Bejan & Marden, 2006; Bejan, 1995, 1997; Bejan & Lorente, 2006; Reis, 2006) states that any animate or inanimate natural system (including artificial ones) lasting for some time at the expense of flows must undergo form, architecture, design or pattern modification to ensure easier access to the currents that flow through it. This theory also postulates that by involving the energy and entropy balances in the analysis of how the flows going through the system direct design, all the criteria of optimal performance underlie; principle of minimum entropy production (**Prigogine**, 1967), maximum entropy production (Dewar, 2005; Lucia, 2012) or minimal flow resistance (Bejan, 1997). Thus, constructed theory is a theory involving a system's design, morphology or configuration to describe the fundamental principles that govern its performance.

In this article we present some of the systems that have contributed to the understanding of the formation of morphological patterns in nature, emphasizing some physicochemical aspects that allow their evaluation beyond design, such as their potential use in technological applications.

# Spatio-temporal structures and reaction-diffusion systems: first evidences

In 1896 the German chemist Raphael Liesegang found that a series of concentric rings defined a periodic precipitation pattern during the diffusion of a salt through a gel matrix with another saline substance dispersed in it (Figure 2a). Diffusion of a drop of silver nitrate solution,  $AgNO_2$ , through a gel matrix containing potassium dichromate,  $K_2Cr_2O_2$ , will lead to the periodic precipitation of silver dichromate, Ag<sub>2</sub>Cr<sub>2</sub>O<sub>2</sub> (Grzybowski, 2009; Liesegang, 1896). The initial explanation for this phenomenon was based on identifying two characteristics that the involved substances needed to satisfy: one of them is that the salt obtained as reaction product must have little solubility, that is to say, it must have a rather small ionic dissociation constant or solubility product constant (2.7x10<sup>-11</sup> for silver dichromate, (Lexa & Holba, 1993), and the other one is that the salts' diffusion rates were different.  $1.5 \times 10^{-9}$  m<sup>2</sup>/s for dichromate (**Rod &** Vacek, 1986) and  $1.5 \times 10^{-5}$  m<sup>2</sup> / s for nitrate (Yeh & Wills, 1970), at concentrations of sodium salts close to 0.1M and at 25 °C). Although Liesegang understood the reaction mechanism and the diffusive transport conditions, this was not sufficient to explain the origin of periodic precipitation: Periodic precipitation or band formation in a precipitation reaction- diffusion system is known as Liesegang bands, in honor of its discoverer (Liesegang, 1896).

In 1911 French biologist and chemist Stéphane LeDuc published his book, The Mechanism of Life, inspired by his experiments on the osmotic growth of structures obtained from inorganic salt mixtures. Mixtures of different salts with different proportions gave rise to a diversity of structures resembling a flower garden (Figure 2b). A classic experiment for these chemical gardens involves a 10% by mass aqueous solution of sodium silicate, Na<sub>2</sub>SiO<sub>2</sub>, to which ferric chloride, FeCl<sub>3</sub>, is added and instantly coating with a reddish ferric silicate membrane,  $Fe_2(SiO_3)_3$ ; this membrane allows the solvent to pass through it from a less concentrated medium, the outer sodium silicate solution, to a more concentrated medium, the inside of the iron chloride nuclei. This phenomenon is called osmosis and it causes the small nuclei to begin swelling and rapidly growing, imitating the growth of seedlings from seed germination (Barge, et al., 2015; Leduc, 2010). The patterns discovered by LeDuc grow under non-equilibrium conditions, where the mechanism involves three essential characteristics: molecular diffusion, chemical reaction and osmosis. Once the system reaches chemical and osmotic equilibrium, the process stops and the structures deteriorate (Barge, et al., 2015; Leduc, 2010).

By 1930, and based on his studies with algae, especially *Acetabularia* (Figure 2c), Danish-German biologist Joachim Hämmerling, proposed that the development of organisms is fully determined by DNA and that, additionally, there are certain substances responsible for defining an organism's form in its initial stages (**Haemmerling**, 1963). Hämmerling's work is considered the first to investigate on

the experimental basis of forms in living beings, thus creating a research area known as morphogenesis, which studies the forms of living beings also known as morphogenetic patterns (**Turing**, 1952).

In 1942, the Scottish biologist mathematician D'Arcy Thompson published the second edition of his book *On Growth and Form*. Thompson is credited for the creation of mathematical biology thanks to his efforts to explain



**Figure 2.** Examples of spatial distributed structures. (a) Liesegang Bands: one drop of a silver nitrate solution is added to a dry gel containing potassium dichromate to produce radial bands of silver dichromate and vertical bands of magnesium hydroxide. Taken from commons.wikimedia.org with licenses CC BY-SA 4.0 y CC BY-SA 3.0. (b) Osmotic growth in chemical garden experiments with carbonate, phosphate and silicate in basic medium. Given their characteristic form, they are called Leduc plants. Taken from commons.wikimedia.org with license CC 0 (c) *Acetabularia calycullus*, unicellular macroscopic algae; its peculiar umbrella shape has encouraged several studies on morphogenesis. Taken from commons.wikimedia.org with licenses CC BY-SA 3.0 (d) The leopard's dot pattern is an example of a naturally-occurring Turing pattern. Taken from pixabay.com with license CC 0.

morphogenesis in living beings. Thompson was emphatic in postulating that the origin of forms in living beings is guided by principles different from those directing forms in inanimate systems, such as those observed by Liesegang and LeDuc, and that therefore it is not possible to synthesize life, even if it is possible to imitate its forms (**Barge**, *et al.*, 2015; **Beloussov**, 2012; **Guiu-Souto**, 2014; **Maldonado**, 2004).

During the first half of the twentieth century, plenty of experimental evidence was gathered regarding the formation of structures, patterns, forms, both in inorganic and biological systems, leading to a growing interest towards discovering the principles that govern their evolution and formation. The mechanisms proposed some of the essential characteristics that pattern-exhibiting systems needed to satisfy, but it had not been possible to explain their genesis. In 1952, British mathematician Alan Turing proposed a chemical reaction mechanism gathering most of the existing experimental evidence, especially on genetic basis, and expressed it in a system of partial differential equations coupling diffusive processes with the reaction mechanism. Turing's mathematical model is known as reaction-diffusion system (Turing, 1952). Although Turing argued that his work set the chemical basis for morphogenesis, the impact of his work was more tangible in the second half of the twentieth century during the development of nonlinear chemical dynamics (Belousov, 1959; Zhabotinsky & Zaikin, 1970); a discipline dealing with the study of rhythms and patterns, so to say, their spatial-temporal dynamics. Turing established the conditions under which a system broke spatial symmetry giving rise to patterns; the reaction system is controlled by a positive feedback loop, where one of the species acts as a process activator and another species as an inhibitor; in addition, these species' specific diffusion rate must satisfy a certain mutual relationship (Hoang & Hwang, 2013; Peña Pellicer, 2002; Turing, 1952). In essence, Turing demonstrated that the system loses stability as a consequence of the free diffusion of the species involved in the reaction's positive feedback loop. In Turing's honor, static morphogenetic patterns, ie, those that continue to exist in time and space in open systems, such as zebra stripes and leopard spots (Figure 2d), are called Turing patterns (Ledesma Durán, 2012; R. Nagao & Varela, 2016; Peña Pellicer, 2002; Turing, 1952).

### Pattern formation at all scales: main features

*Turing Patterns:* Turing patterns are static and stationary spatiotemporal structures that appear as a consequence of diffusive instabilities in reaction-diffusion systems (**Murray**, 2003b; **Peña Pellicer**, 2002; **Turing**, 1952). Alan Turing demonstrated that these structures can be described by the following mathematical model:

$$\frac{\partial u}{\partial t} = f(u, v) + D_u \frac{\partial^2 u}{\partial x^2} \tag{1}$$

$$\frac{\partial v}{\partial t} = g(u, v) + D_v \frac{\partial^2 v}{\partial x^2}$$
(2)

where *u* is an inhibitor and *v* an activator, *f* and *g* are the net change rates of these chemical substances and,  $D_u$  and  $D_v$  are the respective diffusion coefficients. Turing patterns appear when one of the solutions of the dynamic system, corresponding to a stable fixed point with no diffusivity, is unstable in the presence of diffusive processes (Nagao & Varela, 2016; Peña Pellicer, 2002). It is necessary to solve the following equations to find the system's solutions: f(u,v)=0 and g(u,v)=0. The solutions or fixed points are evaluated in the following homogeneous Jacobian matrix,

$$J_{0} = \begin{bmatrix} \frac{\partial f}{\partial u} & \frac{\partial f}{\partial v} \\ \frac{\partial g}{\partial u} & \frac{\partial g}{\partial v} \end{bmatrix}$$
(3)

to determine which ones correspond to stable solutions, that is, those that cause  $J_0$  to have all its eigenvalues with negative real part. Subsequently, the Jacobian matrix is constructed with diffusive terms,

$$J_D = J_0 + Dk^2 \tag{4}$$

where *D* is the diagonal matrix with the diffusion coefficients of the substances and *k* is the wave number. Finally, we verified which solutions grant that at least one eigenvalue is positive for all  $k \neq 0$ , that is, that the solution corresponds to an unstable fixed point (**Peña Pellicer**, 2002; **Serna**, 2016).

Turing patterns have been extensively studied from a theoretical point of view and in terms of numerical simulations; models like the Oregonator (Pullela, et al., 2009), cubic autocatalysis (Gray & Scott, 1983; Sel'kov, 1968) cubic autocatalytic reaction (A + 2B  $\rightarrow$  3B and FitzHugh-Nagumo (Murray, 2003a) have proven to be versatile systems for the study of pattern formation. Thus, it has been studied how the morphology of patterns depends on system parameters, such as kinetic constants, feed flows and system temperature (Gray & Scott, 1984, 1983; R. Nagao, et al., 2008; Nogueira, et al., 2014; Pearson, 1993; Simakov & Pérez-Mercader, 2013). In a recent work, we incorporated the energy balance into a reaction-diffusion system with cubic autocatalysis to study how the morphology of the pattern and its energy economy correlate under strictly nonisothermal conditions (Serna, 2016; Serna, et al., 2017).

An interesting attribute of Turing patterns is that the wavelength remains unchanged regardless of the size of the domain (**Murray**, 2003b); this is important for the design of structured surfaces, such as with Turing patterns, in materials of different sizes (Grzybowski, 2009). Another interesting attribute of Turing patterns is that they can be obtained on a wide variety of scales ranging from the nanoscale to the macroscopic scale. Patterns can be observed in leaves of plants and nano-Turing patterns were recently observed in the corneas of different arthropods (**Blagodatski**, *et al.*, 2015), Figure 3a; microscopic analysis of corneas from different insect families showed that there is a certain correlation

between families with similar evolutionary origins and the morphology of the observed pattern, enabling entomology to consider a new taxonomic criterion.

Experimental studies with Turing patterns dated from 1990, when **De Kepper**, *et al.* obtained specific patterns with the halogenation and oxidation reaction of malonic acid: chlorite ( $ClO_2$ ), iodide ( $I^-$ ) and malonic acid ( $CH_2$  (COOH)<sub>2</sub>). CIMA (chlorite-iodide-malonic acid) reaction was studied at 5 ° C in a setup including a flat gel film to which reactants were fed from its opposite sides, and then diffused at different rates into the gel forming static concentration patterns. Spatial periodicity of the first laboratory-obtained Turing patterns was of about 0.3 millimeters (**Castets**, *et al.*, 1990; **Lengyel & Epstein**, 1992)intrinsic wavelength(Figures 3b and 3c).

*Periodic precipitation:* Periodic precipitation is a current research topic motivated basically by three aspects: discovery of the mechanism (Müller & Ross, 2003), process control and scaling, in search of potential technological applications (Henisch, 1991; Jiang & Sakurai, 2016; Lagzi, 2012; Walliser, et al., 2015) and synthesis of monodisperse particles of materials (Badr & Epstein, 2017; Walliser, et al., 2015). Periodic precipitation experiments have not undergone big changes since the discoveries made by R. Liesegang. The reaction-diffusion process leading to periodic precipitation is caused by the chemical reaction between an electrolyte diffusing through a porous medium (gel), containing another dispersed electrolyte.

Factors such as temperature, the gel's three-dimensional network and the distribution and size of the pores, the nature and concentration of the electrolytes, are decisive in the occurrence and structure of periodic precipitations (Figure 2a). Two experimental parameters govern the behavior of



**Figure 3.** Examples of natural and laboratory patterns. (a) Autumn leaf red-green patterns observed in many plants. Taken from en.wikipedia.org with licenses CC BY-SA 2.0. (b) Micro-pattern exhibited by an optical disk while recording. Taken from commons. wikimedia.org with licenses CC BY-SA 3.0. (c) Simulated relaxed Turing pattern observed in CIMA reaction. Taken from flickr.com with license CC BY 2.0.

reaction-diffusion systems with precipitation; one of them is the system's supersaturation index,  $s, s = [A^{m+}]^a [B^{n-}]^b/k_{ns}$ which is a measure of how far the system is from heterogeneous thermodynamic equilibrium, and the other one is the stoichiometric difference in initial concentrations between the gel-dispersed electrolyte and the diffusing electrolyte,  $\Delta = \frac{1}{h} [B^{n-}] - \frac{1}{a} [A^{m+}]$ . Parameters s and  $\Delta$  define the metrics to understand the system's dynamics (Müller & **Ross**, 2003), from very low values for both parameters, to very high values. At the its lower ends, the chemical reaction between A and B produces local changes in electrolyte concentration, accompanied by a slow diffusive process during which particles,  $A^{m_+}{}_b B^{n_-}{}_a$ , grow and mature in the presence of local concentration gradients according to the size of the colloidal particles, so the presence of a precipitate is explained by the autocatalytic competition between colloidal particles of different sizes, which can be understood as a Turing type spatio-temporal instability. At high values of s and  $\Delta$ , the system is in the domain of periodic precipitations of Liesegang rings: both the position in time and space and the structure of the rings depend on the specific system that produces the precipitate and on s and  $\Delta$  values. Experiments show that colloidal particles form continuously and that the process of particle maturation and growth and the formation of the rings can be explained by a Turing type autocatalytic instability, so larger particles grow faster at the expense of their smaller-sized neighbors (George & Varghese, 2002; Henisch, 1991; Lebedeva, et al., 2004; Nakouzi & Steinbock, 2016).

As for the scaling of the process, another question regarding the study of periodic precipitations is the gel's limit thickness in the formation of periodic precipitations.

It has been recently demonstrated (**Jiang & Sakurai**, 2016) that a gel film with a thickness of a few tenths of a nanometer allowed the formation of micrometer-scale bandwidth Liesegang rings. At this scale, it is already feasible to consider potential applications for periodic precipitations in terms of nanotechnological developments as it is possible to synthesize materials with different physical properties through reaction-diffusion processes (**Lagzi**, 2012; **Walliser**, *et al.*, 2015).

Another interesting aspect of Liesegang rings or bands is the synthesis of monodisperse nanomaterials (**Lagzi**, 2012; **Walliser**, *et al.*, 2015). It was experimentally demonstrated that Liesegang's periodic precipitation system, with a structure of rings that are spatially separated in a sequence determined by  $x_{n+1}/x_n$  has also a local structure in each band at a micro-nano-metric scale. Each band is made up of a series of monodisperse particles, with diameters established according to the band's appearing sequence (**Badr & Epstein**, 2017; **Walliser**, *et al.*, 2015).

These findings are of great interest for the synthesis of nanomaterials, since at this scale, most properties are clearly associated with the size of the particles, which is a critical control factor in synthesis processes.

*Morphogenesis.* Since Hämmerling and Turing, there has been a large number of research aimed at explaining patterns in living beings (Brachet, et al., 1964; Haemmerling, 1963; Hunding, et al., 1990; Needham, 1935). Bacterial dendritic growth is a good example of patterns in living beings morphogenesis; the fractal geometry of patterns maximizes contact area between bacteria and the culture medium in order to optimize substrate uptake for the colony. These dendrites have sizes ranging from just a few micrometers to several millimeters (Figure 4a). The mechanisms of morphogenesis have been widely studied along the years. Self-assembly and reaction-diffusion are the most accepted mechanisms by the scientific community. The first one states that there are many fundamental parts, i.e. molecules, which have the sufficient information in the way they interact each other (potential energy) to determine the structure they generate at the steady state or at the thermodynamic equilibrium (Davies, 2013). The second approach explains the emergence of the shapes as a consequence of dynamical instabilities due to diffusional effects (Beloussov, 2012; Gierer & Meinhardt, 1972)starting from almost homogeneous tissue. It will be shown that relatively simple molecular mechanisms based on auto- and cross catalysis can account for a primary pattern of morphogens to determine pattern formation of the tissue. The theory is based on short range activation, long range inhibition, and a distinction between activator and inhibitor concentrations on one hand, and the densities of their sources on the other. While source density is expected to change slowly, e.g. as an effect of cell differentiation, the concentration of activators and inhibitors can change rapidly to establish the primary pattern; this results from auto- and



**Figure 4.** (a) *Pseudomonas* motility and bacterial dendritic growth with different length scales. Taken from commons.wikimedia.org and en.wikipedia.org with licenses CC BY-SA 3.0. (b) Detail on the hydra's tentacles. Taken from commons.wikimedia.org with licenses CC BY-SA 3.0 and CC BY-SA 3.0-D.E.

cross catalytic effects on the sources, spreading by diffusion or other mechanisms, and degradation. Employing an approximative equation, a criterium is derived for models, which lead to a striking pattern, starting from an even distribution of morphogens, and assuming a shallow source gradient. The polarity of the pattern depends on the direction of the source gradient, but can be rather independent of other features of source distribution. Models are proposed which explain size regulation (constant proportion of the parts of the pattern irrespective of total size. The latter is going to be detailed in this paper.

In 1969, Brian Goodwin and Morrel Cohen made a significant contribution to developmental biology (Goodwin & Cohen, 1969), by proposing a mathematical model to describe cellular-scale morphogen concentration profiles for pattern formation. The model suggests the wave-like propagation of morphogen concentrations in a three-stage scheme arranged in spatial order: a) a propagation frequency gradient establishes the location of early- development areas and the direction of propagation, b.) a slow propagation stage results in local pattern formation, and c.) a pattern regulation step leads to independently sized structures. In their works, and based on this model, Goodwin & Cohen study: a) the development and regeneration of hydra, an animal with small tentacles ranging from 10mm to 17mm in length (Solomon, et al., 2013) (Figure 4b), positioning in the early amphibian embryo, which has a development rate ranging from just a few millimeters to 6 cm (Solomon, et al., 2013), and c.) the development of the amphibian visual system, which has an average size of around 0.7cm (Solomon, et al., 2013).

In 1972, Gierer and Meinhardt evaluate the subject in order to formulate a general theory on the formation of spatial patterns in tissues of living beings. Their main goal was to model the process of cellular differentiation, in which a type of cells, stem cells, adopt different forms and functions resulting in entirely spatially self-organized tissue, (**Gierer & Meinhardt**, 1972). The generalized cellular differentiation model is based on the interaction of two substances, an activator and an inhibitor, and on quadratic-order rate laws, so depending on the initial conditions and the values of the model parameters, the system may have different stable stationary states corresponding to different states of cellular differentiation.

In 1974 Gunther Werz preformed a detailed analysis to understand morphogenesis of *Acetabularia* (Werz, 1974). Werz concluded that in addition to DNA-contained morphogenetic information, the apical region of the algae carries sufficient information for the development of the cap (umbrella); he also described some precise aspects regarding its morphology, especially the nucleus and the chloroplasts. *Acetabularia* is a giant unicellular green algae; its 0.5cm to 10cm in length (Solomon, et al., 2013). Its peculiar umbrella shape (Figure 2c) was, and still is one of the greatest challenges in the mathematical modeling of morphogenesis (Goodwin & Pateromichelakis, 1979; Sandakhchiev, et al., 1972). In 1975, Rommelare and Hiernaux proposed a mathematical model for the positional differentiation of the cap in *Acetabularia*, which considered the algae to be a onedimensional domain with one end representing the nucleus and the other end representing the apical region (**Rommelaere & Hiernaux**, 1975). The model includes three fundamental elements: 1.) a linear mRNA gradient that increases from the nucleus to the apical region and codes for a lytic enzyme that initiates the cap formation process, 2.) the presence of another substance which acts as an unmasking factor and which is in its active and inactive forms, and 3.) an inhibitor that originates in the nucleus and inactivates the unmasking factor. The four-stage mechanism leads to the following equations:

$$\frac{\partial D_a(x)}{\partial t} = -k_1 D_a(x) I^n(x) + k_2 D_i(x)$$
(5)

$$\frac{\partial I(x)}{\partial t} = -nk_1 D_a(x) I^n(x) + nk_2 D_i(x) - k_3 I(x) + \Delta_I \frac{\partial^2 I(r)}{\partial x^2}$$
(6)

$$\frac{\partial E(x)}{\partial t} = -\epsilon k_4 (mARN)^x_M D^y_a(x)a - k_5 E(x)$$
(7)

where  $D_a$  is the unmasking factor concentration, I is the inhibitor concentration, E is the lytic enzyme concentration,  $D_a + D_i = D_0$ , where  $D_a$  and  $D_i$  are the unmasking factor active and inactive form concentrations and  $D_0$  is the total concentration, which remains constant.  $k_1$ ,  $k_2$ ,  $k_3$ ,  $k_4$  and  $k_5$ are kinetic constants,  $\Delta_l$  is the inhibitor diffusion coefficient,  $\alpha$  is an enzyme precursor,  $(mARN)_M^x = ax + b$  represents mRNA's increasing profile, with a, for the initial nucleus concentration and, b a model adjustment parameter. Finally, n and v are adjustable stoichiometric coefficients. With this model, it was possible to understand morphogen's spatiotemporal dynamics and stationary concentration profiles during the process of cap formation from a semi-quantitative point of view. Later, Goodwin and Pateromichelakis studied the fundamental role of electric fields and ions in morphogenesis of Acetabularia, and concluded that ions  $Mg^{+2}$  and  $Ca^{+2}$  reversibly inhibit the formation of the cap without compromising the longitudinal growth of the algae (Goodwin & Pateromichelakis, 1979).

In 1985 Goodwin and Brière proposed a viscoelastic model for the cytoplasmic medium with the purpose of explaining Acetabularia's mechanical properties (B C Goodwin & Briere, 1994). The model includes the cytoskeleton coupled with the evolution of ion concentration and its inhibitory effect on the cap formation (Davies, 2013; Goodwin & Trainor, 1985) we investigate the nature of the spatial ordering which arises from Ca2+ regulation of the viscoelastic properties of the cell cortex. From a survey of the empirical information available on the effect of free Ca<sup>2+</sup> on the elastic and viscous properties of the cell cortex, and on the mechanisms of strain-induced Ca2+ release, we derive a set of coupled, non-linear equations using first order theory of elastic and viscous response to stress fields, in effect extending previous work of **Odell**, et al. (1981). Later, in the 1990s, this complex model could be solved using the finite element method with remarkable results (Goodwin & Briere, 1994).

Finally, a very recent approach of biochemical and mechanical coupling has been proposed in the last decade. A nice example of this coupling can be found in the biochemical regulation of cytoskeletal mechanics. The actin or tubulin polymerization is joined to the motor protein activity in order to influence the mechanics of the cellular tissue due to an advective-mechanic transport of the regulating components, which creates a feedback loop between the chemical reactions of intracellular regulation and the internal movement of microtubules (**Davies**, 2013; **Heisenberg & Bellaiche**, 2013; **Howard**, *et al.*, 2011).

# Dynamic and thermodynamic considerations of space-time self-organization

At all scales, nature displays a great variety of structures such as the crystalline structure of minerals, the geometric form of some rocks carved by water currents, the sinuous bed of rivers, the mountain formations, etc. All of the above are examples of equilibrium structures resulting from matter and energy dissipative processes which ultimately become independent. Classical thermodynamics describes equilibrium structures by evaluating the change in thermodynamic potentials up to the equilibrium state throughout all the process coordinates, for example  $\frac{\partial G_{r,0}}{\partial r} \leq 0$  (Adrian Bejan, 1997; Callen, 1985). However, the network of filaments that form some fungi, the color maps on butterfly wings, the skin's network of cellular tissues and even the cellular membrane, are examples of non-equilibrium structures that originated and sustained at the expense of matter and energy dissipative processes (Nicolis & Prigogine, 1977). When a system in equilibrium is subjected to forces or gradients that move it away from its original state, resulting flows and currents carry the system to non-equilibrium states.

Depending on the nature of the dynamics, some chemical, physical or mixed instabilities may take place within the system (**Guiu-Souto**, *et al.*, 2013; **Nagao & Varela**, 2016; **Nicolis & Prigogine**, 1977; **Satnoianu**, *et al.*, 2010; **Schwarzenberger**, *et al.*, 2014; **Strogatz**, 2001), and as a result, state-specific fluctuations are amplified resulting in a breaking of spatial symmetry and thus leading to the occurrence of structures and patterns. Non-equilibrium processes and states are studied through the formalism of non-equilibrium thermodynamic or thermodynamics of irreversible processes, either to determine transport coefficients described by the flows or to evaluate entropy generation through coordinates  $\frac{\partial \sigma}{\partial r} > 0$  (**De Groot & Mazur**, 1984; **Eu**, 2016; **Kjelstrup & Bedeaux**, 2008; **Nicolis & Prigogine**, 1977).

The theory of non-linear dynamical systems (**Murray**, 2003b; **Strogatz**, 2001) allows us to study the nature of instabilities (chemical, thermal, transport, hydrodynamic, etc.) and to model the systems' spatial-temporal evolution. When studying Turing patterns, nonlinear dynamics allows to establish the restrictions that must be imposed on the system in order to generate morphogenetic patterns and provides us

with evaluation tools. On the other hand, non-equilibrium thermodynamics allows to evaluate the dissipative nature of processes, determine transport coefficients, quantify energy efficiency and to perform a general analysis of evolutionary aspects (**Al-Ghoul & Eu**, 1996; **Eu**, 2016). However, there is still no unified theory accounting for both the dynamic, kinetic, and thermodynamic aspects of processes and non-equilibrium states. In this sense, it is worth mentioning the valuable contributions of the school of Ilya Prigogine, Lars Onsager, Adrian Bejan, Byung Chan Eu, John Ross, Dick Bedeaux, Signe Kjelstrup, Miguel Rubí, among others (**Bejan**, 1995; **Eu**, 2016; **Kjelstrup & Bedeaux**, 2008; **Nicolis & Prigogine**, 1977; **Onsager**, 1931).

# What advantages do static patterns bring to the system?

From a morphological point of view, Turing patterns can be classified into four types of structures: 1.) Hexagonal (direct) (Figure 5a), 2.) Striped (direct) (Figure 5b), 3.) Striped (inverse) (Figure 5c), 4.) Hexagonal (inverse) (Figure 5d), (**Guiu-Souto**, *et al.*, 2012). Likewise, it is possible to estimate the dissipation cost that each pattern requires to sustain itself in relation to matter and energy flows; for this reason, it is possible to achieve a complete morphological and thermodynamic characterization of the patterns (**Serna**, *et al.*, 2017).

One of the most promising aspects of Turing patterns is the study of the transitions between different structures, for example, from an inverse striped pattern to a direct hexagonal pattern. These morphological transitions can be experimentally achieved by adjusting control parameters, but we have recently shown that it is possible to induce these transitions under non-isothermal conditions by adjusting ambient temperature. Something interesting about these thermally induced transitions is that non-equilibrium thermodynamics shows that they occur at a lower energy cost (**Serna**, *et al.*, 2017).

It seems clear that there is a correlation between the patterns and the energy performance of a system, as shown by some applications where the energy efficiency and productivity of a process are improved by imposing spatio-temporal structures on physical-chemical processes (**Coppens**, 2012; **Coppens & Froment**, 1996; **Nagao**, *et al.*, 2013).

Nature seems to provide some evidence for the above. Figure 6 shows a chameleon in two well-differentiated moods: a state of calmness and a state of euphoria. This color change can be understood as a morphological phase transition between a direct striped pattern and a reverse striped pattern. These morphological transitions, which do not involve abrupt changes in the structure of the pattern, are more favorable for the energy economy of the system (**Serna**, *et al.*, 2017). For the chameleon, this correlation between morphology and energy economy must be somewhat favorable; the mood change prior to a fight against another individual, whether for territorial defense or mating, must take place under the most favorable energy conditions. Rev. Acad. Colomb. Cienc. Ex. Fis. Nat. 41(160):349-360, julio-septiembre de 2017 doi: http://dx.doi.org/10.18257/raccefyn.481



Figure 5. Turing's thermal patterns obtained by computational simulation. (a) Hexagonal (direct) pattern. (b) Striped (direct) pattern. (c) Striped (inverse) pattern. (d) Hexagonal (inverse) pattern. (Serna, 2016)



**Figure 6.** Chameleon's mood-induced color changes understood as a direct-to-inverse pattern morphology change. Taken from pixabay. com and pxhere.com with licenses CC 0.

In addition to the above observation, recent studies on the chameleon's color change mechanism reveal some closely related thermal regulation processes (**Chou**, *et al.*, 2015; **Ohtsuka**, *et al.*, 2015; **Teyssier**, *et al.*, 2015; **Walton & Bennet**, 1993), which in a way allows us to accept the fact that it is more favorable to induce morphological changes through temperature variations.

Thus, the presence of patterns in living beings can be indicators of their evolutionary history and their adaptability, as suggested by some recent studies (**Blagodatski**, *et al.*, 2015). Regarding inert systems, pattern formation results in the design of efficient bio-inspired technologies, in particular the design of structured-surface solids with appropriate patterns for specific applications (**Bensemann**, *et al.*, 2005) and the design of chemical processes that emulate organic systems of living beings, such as the respiratory and circulatory systems (**Coppens**, 2012)

### Conclusions

Evolution has led natural systems to adopt forms that guarantee optimal process efficiency according to environment conditions. In this critical review on the subject, we show how the study of forms, structures and patterns first started in laboratories; this is the case for some of the most studied systems such as chemical gardens, periodic precipitations and Turing patterns. We have shown the main physical-chemical aspects that characterize these system's dynamics and how research reveals their potential application in technological developments.

Our main objective was to draw attention on the fact that it is possible to establish a correlation between patterns seen in nature and the energy efficiency of systems, and that for these correlations to be more evident. It is necessary to understand all the biological, chemical and physical aspects involved in pattern design.

### **Author contributions**

H. S. and D. B. conceived of the presented and discussed ideas. H. S. designed the figures and performed the computational simulations to obtain Turing patterns in Figure 5. H.S. and D. B. wrote the manuscript.

# **Conflicts of interest**

We have no conflict of interest to declare.

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