GEOMETRICAL ORDER IN NATURAL RANDOMNESS: LIESEGANG PATTERNS

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In the late 19th century, a German chemist and photographer achieved an interesting outcome with a simple mistake. He accidentally droped a few drops of silver nitrate solution onto the gelatin with potassium chromate. After a while, he observed the diffusion of the silver nitrate solution into the gelatin gel with dissolved potassium chromate, and surprisingly, obtained patterns that geometrically repeated themselves [1]. Those patterns were named after Raphael E. Liesegang, and thus, the first concrete step into the fascinating world of patterns was finally taken by accident.

Despite their late discovery, Liesegang patterns have already been in the real world, demonstrating that self-assembly systems have existed for centuries. For instance, colony developments of various bacteria, such as Bacillus (B.) subtilis, exhibited a typical concentric ring structure, similar to Liesegang patterns [2]. The bacterial colony was shaped by the impact of agar gel and nutrients that the bacteria needed to live. Additionally, Liesegang patterns were still visible in the culture medium. Thus, destroying such a ring-like life pattern altered cell metabolism, allowing Liesegang patterns to occur naturally among them [2].

Furthermore, following the discovery of the Liesegang phenomenon, geologists began to take it into account. Rocks are examples of such patterns that can emerge in nature. The analogies of Liesegang-type periodic patterning on the rock structures themselves raised a question of the origins of the various rock systems [2]. Mimicking natural systems with related chemicals leads to the development of models and laws that can be applied to these systems. In other words, the patterns that have existed for centuries partially preserve their mystery.

Liesegang patterns can also be produced in artificial settings, just like Raphael E. Liesegang did. They can be generated in 1D, 2D, or 3D, and remarkably, he first encountered the two-dimensional example with silver chromate by accident, as mentioned. Experimentally, tiny test tubes are preferred for 1D and petri dishes are proper choices for 2D samples. Cubes or spheres are mainly used for 3D sample preparation [3]. The chemistry behind this reaction-diffusion system can be enlightened by examining the chemistry of the components.

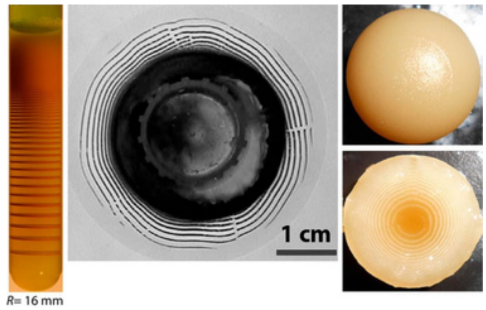


Figure 1. Respectively, One-Dimensional, Two-Dimensional, and Three-Dimensional Liesegang Patterns [3].

THE KEY CONCEPTS FOR UNDERSTANDING

Since the Liesegang phenomenon depends on familiar and basic concepts, all of them should be considered in detail. The logic behind such random systems can be clarified by revisiting and addressing related concepts, because in some cases, like this one, the complex ones are often hidden in the basics. Liesegang patterns are typically described as a specific type of reaction-diffusion system, implying that two distinct yet related principles are at play [3]. Diffusion is the spontaneous movement of molecules, atoms, or ions from areas of higher concentration to regions of lower concentration. Diffusion does not require any external energy; therefore, it is an irreversible process [4]. Moreover, the 'reaction' near the diffusion refers to the precipitation since the pattern bands are formed by the precipitation of ions in the system. To understand such reactions, a new subject emerges: solubility.

Solubility seems familiar yet essential, shaping the destiny of Liesegang patterns. As an easy-to-understand explanation of such concepts, a solution is a homogeneous mixture of two or more substances. Solvent is a significant solution component; it is present in large quantities compared to the others, whereas the solute is the matter dissolved in the solvent. The dissolution process is observed when the solute or solutes disperse homogeneously in the solvent and stabilize through interactions to form a solution [4]. Solubility determines the maximum amount of solute that a solvent can dissolve. Particularly, the solubility limits of most salts and compounds have been established by considering the pressure, temperature, nature of the solvent and solute, etc. These determinate limits are essential to follow the reaction because precipitation begins when the solubility limit is exceeded.

Chemical precipitation is the process in which ions or molecules in a solution form a precipitate with significantly low solubility under suitable conditions [5].

When a solution contains more solute than it can dissolve, it becomes unstable and supersaturated. If that solution reaches the solubility limit, it gathers and forms a precipitate. The solubility limit is the key to this process because it marks the exact point at which precipitation begins. In other words, precipitation is quantitatively followed by concentration using the solubility product constant, Ksp [5]. Therefore, the concentrations of free ions become variables in this process when the instantaneous product of ion concentrations of a sample reaches the Ksp value; precipitation begins.

Although Liesegang patterns form randomly by simultaneous diffusion and precipitation, they follow a periodic rule: a geometric series. A geometric series (Sn) is the ratio of each two consecutive terms of the series, which is a constant function [6]. Namely, the consecutive terms are proportional to each other. Considering an is the nth term of the series, and r is the constant ratio, the general empirical formulas are given below [6]:

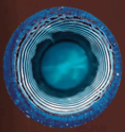
$$S_n = a_1 + a_2 + a_3 + ... + a_n \, (1)$$

$$S_n = a_1 + r.a_1 + r^2.a_1 + ... + r^{n-1}.a_1 \, (2)$$

$$\frac{a_2}{a_1} = r \, (3)$$

REVISITING CONCEPTS

In Liesegang pattern formation, two solutions with different media are used. The outer medium consists of only ions dissolved in distilled water, whereas the inner medium comprises a gel (hydrogel) that can retain water and dissolved ions. In other words, the inner medium has a more compact structure. So, Liesegang systems combine the two systems and the diffusion between them. Therefore, water is a liquid solvent; however, hydrogels are different. Hydrogels consist of water and gel matter, which mostly have a polymer web structure, being smooth but not fluid, allowing them to exhibit distinctive chemical and physical properties.



They are not completely liquid or solid, but rather have a gel-like consistency, similar to soft matter that can be easily shaped or molded without complex processes [7]. Additionally, their three-dimensional crosslinked polymer network renders them more solid than a liquid; however, their ability to retain water imparts flexibility and softness [8]. Namely, the gel medium is more compact than the aqueous solution, leading to a diffusion-controlled precipitation process.

In regular precipitation reactions, when the two water-soluble salts in an aqueous medium are mixed, the cation of one and the anion of the other would interact and form a precipitate. This precipitate will likely coalesce and accumulate at the bottom of the container because the aqueous phase provides a suitable environment for molecules to migrate and coalesce or to assemble and be transported. This accumulation of solids is called sedimentation [3]. However, when the gel medium is used, and the diffusion controls the precipitation process, particles cannot move freely as they would in aqueous media due to the compact structure of the gel medium; therefore, they cannot collect and accumulate instantaneously. So, ion mobility is also controlled by the gel medium. This is where the secret of Liesegang patterns begins to emerge gradually.

For a better understanding, the processes emerging from the pattern formation should be followed moment by moment. As an artificial one-dimensional example of Liesegang pattern formation, cobalt (II) hydroxide systems can be examined. In a real experimental procedure, cobalt (II) chloride was incorporated into the gelatin as the inner electrolyte, and an aqueous sodium hydroxide solution was prepared as the outer electrolyte in a thin test tube [9]. The concentration of the outer electrolyte, sodium hydroxide, was ten times greater than that of the inner electrolyte, cobalt chloride. Since the gel environment restricted ionic movement, the concentration of the outer S electrolyte that could diffuse into the gel was reduced, allowing the precipitation reaction to occur in a more limited space. After the diffusion started from the diffusion front, the amount of hydroxide from the outer electrolyte increased gradually in the gelatin. The first band emerged when the concentration of constituent ions reached the Ksp of cobalt(II) hydroxide, $Co(OH)_2$ accumulated in this region, resulting in the exhaustion of hydroxide ions. When the anion amount decreased, precipitation also drastically reduced, and no precipitation band appeared in that space, known as a depletion zone. No band formation was observed until the amount of hydroxide ions was replenished, which was possible by diffusion, since neither diffusion nor back-diffusion could compensate for the concentration to reach the Ksp threshold [9]. This reaction-diffusion pattern repeated itself periodically, leading to the formation of bands.

LAWS FOR PATTERN FORMATION

There are three empirical laws describing Liesegang pattern formation. These laws help characterize and demonstrate the mathematical basis of spontaneous band formation. Since band characteristics repeat themselves regularly in a sample, certain variables and laws are derived based on this dependence.

The spacing law is about the distance of the nth and (n+1)th bands from the gel-outer electrolyte interface. The distances between the positions of bands xn and xn+1 are measured from the exact point of the diffusion front [9]. Recalling the main feature of the geometric series, the ratio between the two adjacent elements should be equal and a constant function [6]. The consecutive distances satisfy that rule as follows [10]:

$$1+p=\frac{x_{n+1}}{x_n}(4)$$

Now, a new parameter appears. The ratio 1+p is called the spacing coefficient, which depends on the external and internal conditions rather than being a universal, definite number. Thankfully, scientists successfully turned it into a law with one type of function: concentration. The functional link between distance and concentration enables scientists to discover and characterize other parameters. This law, which was named after Matalon and Packter, is given below [3]:

$$p = F\left(b_0\right) + G\left(b_0\right)\frac{b_0}{a_0}(5)$$

In this context, F and G are monotonically decreasing functions of the inner electrolyte concentration, b0. a0 in the equation refers to the outer concentration, the ion is in the aqueous medium [3]. Moreover, it should be noted that the concentration of the outer electrolyte is inversely proportional to the p value when b0 is kept constant, indicating that a decrease in the outer electrolyte concentration results in higher p values and increased spacing. By the functions and equations, experimental and computational studies can be conducted.

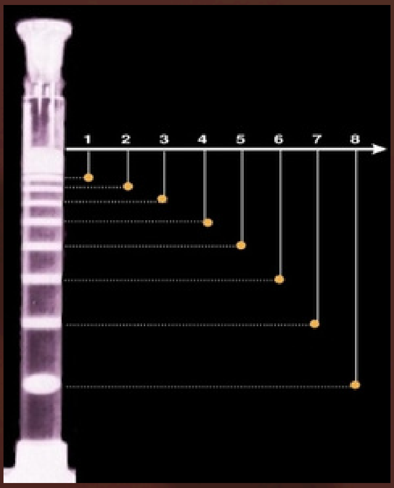


Figure 2. Geometrical representation of the spacing law [10].

The width law is another important law that states the width refers to the numerical extent of the bands. Surprisingly, band widths also follow a pattern on their own.

Now, another parameter, the quotient of the width series, is used to describe it, where wn and wn+1 are the bandwidths of the nth and (n+1)th bands, respectively [10]:

$$Q = \frac{W_{n+1}}{W_n}(6)$$

Lastly, the crucial law concerns that time dependency of the pattern formation resulting from the diffusion factor. The time law states that the time tn when the nth band is formed, and the square of the position xn is proportional to each other [3]:

$$\frac{{x_n}^2}{t} = k\,(7)$$

This law is derived by considering the diffusion process, where k is a constant. This relationship describes various aspects of the Liesegang patterns. Considering all the spacing, width, and time laws, the mathematical order of reaction-diffusion systems can be determined quantitatively.

FURTHER RESEARCH AND APPLICATIONS

Considering the versatility of external impacts on pattern formation, Liesegang systems are open to discovery through changes in conditions, such as concentration, gel media, and the presence of different types of ions [11]. Also, temperature has a considerable impact on the patterns [12]. Researchers try to develop new combinations and observe how they behave. Fortunately, with the development of technology, the analysis and characterization of reaction-diffusion systems have become convenient. Instruments such as scanning electron microscopy aid in investigating the macrostructures of systems and their microstructures on a small scale [2].

Through such instrumentation, research on Liesegang patterns is expected to gain interest, and new, challenging discoveries are likely to be made. Practically, Liesegang patterns can be utilized in the design of bioceramic materials. Since they are mineralized hydrogels, they can be used for bone regeneration in humans by using appropriate ions and gels [13].

The versatility of ions, precipitates, and gel combinations, combined with the sensitivity of external conditions, offers a wide range of research opportunities. This world of orderly, yet scattered patterns, has opened the doors to a different world for scientists who strive to explore it. We wish everyone interested a pleasant journey into this world.

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