Mechanisms of bands and spirals formation during the drying of watery solutions of mercury (II) chloride with agar-agar

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Abstract. It is proposed two mechanisms to explain the formation of periodic and non periodic bands and spirals as thin films of gelatinous aqueous solutions of mercury (II) chloride are dried. The first mechanism supposes an homogeneous drying, where the height of the film decreases at constant rate, forming Liesegang bands. The second mechanism implies a non homogeneous drying where an evaporation front drives the formation of periodic bands and spirals.

1. Introduction
It is well know that crystals of any substances can grow as dendritic forms. The crystal can be developed by drying of aqueous solutions. The deposition of solid onto a surface via the drying of a aqueous solution or a waterborne dispersion is a fundamental process in nature and in many technologies. Latex, paints, inks, floor waxes, cosmetics, correction fluid, slurries of glass and ceramic frits for glazes or enamels, biofilms, and some pharmaceuticals rely on this process [1].

If the growth is limited to a bidimensional surface and the solution is gelatinous, the morphology could be notably complex [2, 3, 4, 5, 6], and fractal geometry is needed to characterize [7]. There are some models that explain the morphologies of structures that result of an interaction among particles[2, 8], i.e. Diffusion Limited Aggregation (DLA) [2, 9] and Ballistic Deposition (BD) [2, 8].

Yasui et al [3] and Suda et al [4, 5] have observed and explained the patterns developed in gelatinous solutions of salts where the evaporation rate is low.

In previous work [6], it was observed the formation of periodic bands and spirals in crystal growth of mercury (II) chloride in thin film of gelatinous solutions when the drying rate was high. The spirals appears as a consequence of little particles in the film [6, 10].

We can noticed that a qualitative change in the patterns developed as the evaporation rate increases. At low rates, the growing is continuous. If the rate is higher, periodic bands are developed (see figure 6). That is, a bifurcation is presented.

Why an homogeneous solution develops non homogeneous patterns of crystallization, as bands and spirals? As this system is far from equilibrium, we could expect more complex self-organization phenomena at higher evaporation rate than those observed at lower one, as it is the case. In this work, we propose simple mechanisms than can explain the developing of spiral and periodic and no periodic bands. And they can clarify the causes of the bifurcation in the crystallization patterns.
2. Mechanisms

According with the patterns observed in the experiments, two mechanisms can be proposed for a crystallization of mercury chloride in an aqueous thin film: one for homogeneous drying and the other for non homogeneous drying.

2.1. Homogeneous drying

Consider the case when the liquid evaporate slowly and the contact line is not pinned to the glass surface. Then, the contact angle remains constant. This is the homogeneous evaporation of the film.

![Figure 1. Height profile of the liquid film.](image)

A periodic temporal and horizontal spatial profile of salt concentrations in the film is needed for a periodic crystallization. Nevertheless, in homogeneous evaporation, it is not possible to fulfill these conditions, as it is showed below.

Consider a profile of a liquid film as a set of \( n \) cells (see figure 1). The volume \( V(n) \) of the cell is:

\[
V(n) = \frac{L \cdot l \cdot [h(n) + h(n + 1)]}{2}
\]

(1)

Where \( l \) is the length of the cell in the longitudinal direction of the crystal growing. \( L \) is the length of the cell in the transversal direction, it can be assumed as a number of high value, so the effects of the edges in transversal direction can be disregarded. Let

\[
\tan \theta = \frac{h(n)}{nl}
\]

(2)

Where \( h(n) \) is the film height through the distance at time zero, so that \( h(0) = 0 \) at \( t = 0 \). Then

\[
h(n) = nl \tan \theta
\]

(3)

The salt concentration is:

\[
C(n) = \frac{m(n)}{V(n)}
\]

(4)

Where \( C(n) \) is the salt concentration in the \( n \) cell, \( m(n) \) is the salt mass in the \( n \) cell. As the agar limits the diffusion in the film, the mass \( m(n) \) can be considered constant in the cell.

As the area of any of the cells is \( A = L \cdot l \), then:

\[
V(n) = \frac{A[h(n) + h(n + 1)]}{2}
\]

(5)
\[ h(n+1) = h(n) + c \sin \theta \]  

(6)

The mass is, from equations (2), (3), (4) and (5):

\[ m(n) = \frac{C_0 A_l (2n+1) \tan \theta}{2} \]

(7)

Where \( C_0 \) is the concentration of the salt at \( t=0 \)

And, due to homogeneous evaporation,

\[ \frac{dV}{dt} = -kA_s \]

(8)

Where \( A_s \) is the superficial area,

\[ A_s = A / \cos \theta \]

(9)

From the figure 1 and combining the equations (5), (6), (8) and (9), results:

\[ \frac{dh(n)}{dt} = -\frac{k}{\cos \theta} \]

(10)

On a glass surface, the contact angle of agar aqueous solutions must be near zero, so the equation (10) can be reduced to:

\[ \frac{dh(n)}{dt} = -k \]

(11)

That is:

\[ h(n) = h_0(n) - kt \]

(12)

Where \( h_0(n) \) is the level of liquid of the \( n \) cell at \( t=0 \)

From the equations (3), (4), (5), (7) and (12), the concentration is defined by:

\[ C(n,t) = \frac{C_0 (2n+1) \tan \theta}{(2n+1)l \tan \theta - 2kt} \]

(13)

**Figure 2.** Liesegang bands on a slide. The concentration of HgCl\textsubscript{2} was 0.1 M, the agar concentration was 0.50 %, temperature was 30 °C

Because the equation (13), it is not possible that temporal and spacial variation of salt concentrations get to be periodical. So it is not possible to obtain the same profile of concentrations as the liquid evaporates along the film. As a consequence, the periodic patterns of crystallization are
forbidden. Nevertheless, Liesegang patterns are permitted, and they were actually observed in the edges of the slide, when the film is thicker. These sections are the last in drying (figures 2 and 3).

**Figure 3.** Profile of the thin film on the slide. The square remarks the edges of the slide, where non periodic bands developed. The periodical bands appears in the center of the slide.

2.2. Non homogeneous drying

The model 2 suppose that the evaporation is not really homogeneous, a front of drying is advancing along the slide. This possibility is based in the models of drying of thin films of polymeric colloids, proposed by Winnik *et al* [11] and extended by Routh *et al* [1, 12]. It can be explained by a flux of liquid from the solution to the crystallized region. This flux can be due to evaporation in the edges of wet film [13, 14 and 15] and residual evaporation in the dried film [1, 11, 12].

In this model exists three regions of drying, as in the figure 4. In $\varepsilon_1$, the film is wet, and in $\varepsilon_2$ is dry. The region $\varepsilon_3$ is where the evaporation is fast due to crystallization. In $\varepsilon_1$, although the salt has cristallized, the evaporation continue. Due to evaporation in $\varepsilon_1$ and fast evaporation in $\varepsilon_2$, there is a flux ($f$) of liquid from $\varepsilon_1$ to $\varepsilon_3$ to compensate the loss of fluid. As a consequence, the region $\varepsilon_2$ moves to $\varepsilon_3$ as a drying front.

A drying front can force to reproduce the same profile of salt concentrations along the film during the evaporation, so it is possible to develop periodical patterns of crystallization. This mechanism is more probable in the flat film observed in the center of the slide (see figure 3). To reach this non homogeneous drying is necessary a front of crystallization than can appear as the salt is supersaturated in solution after a period of homogeneous evaporation of the flat film.

**Figure 4.** Regions of evaporation in the non homogeneous drying.
We propose the following mechanism to explain the periodic bands. The profile of the thin film around the front of crystallization is the showed in the figure 5. As in the mechanism for homogeneous drying, the transversal direction is not relevant to the phenomenon. For the sake of simplicity, let $L = 1$. C is the dried crystallized region, whose boundary with the wet region A is in the position x. A is the region of crystallization and rapid evaporation. The liquid is fixed (pinned) to the crystal of C. Region C is growing toward A due crystallization. There is a flux of liquid from B to A to compensate the evaporation. But the limit of this flux is in the boundary between B and D. Due to this flux, the film height decreases from the boundary A-B to the boundary B-D, and then rises before the surface becomes a flat one. The distances $a$ and $b$ are constant during the process; as a consequence, the regions A and B are moving in the direction of the crystallization and some liquid volume is passing from D to B.

A similar profile (in form of N) is predicted in the model of Routh for a nonuniform drying [12].

As the evaporation rate by volume unity in A is considerably higher than in the other regions, we can consider them as negligible.

Let $V_m$ be the total volume of the regions A and B. Then:

$$V_m = \frac{1}{2} \left[ a(h_1 + h_2) + b(h_2 + h_s) \right]$$

(14)

where $h_1$ is the film height in the boundary C-A, $h_2$ is the film height in the boundary A-C, and $h_s$ is the film height in the boundary B-D. As $h_1$ must be considered as a constant value, the derivative of $V_m$ respect time is:

$$\frac{dV_m}{dt} = \frac{1}{2} \left[ (a + b) \frac{dh_2}{dt} + b \frac{dh_s}{dt} \right]$$

(15)

Let $V_s$ be the liquid volume that pass from D to B as the front of crystallization is advancing, $V_c$ be the liquid volume passing to C as crystal, and $V_e$ be the volume of the evaporated liquid at A, in a time interval. According to this:

$$\frac{dV_m}{dt} = \frac{dV_s}{dt} - \frac{dV_c}{dt} - \frac{dV_e}{dt}$$

(16)

The variation of crystal volume is
\[
\frac{dV_c}{dt} = h_1 \frac{dx}{dt} \tag{17}
\]

And, as \(a + b\) is a constant value:
\[
\frac{dV_s}{dt} = h_s \frac{dx}{dt} \tag{18}
\]

Then, combining equations (16), (17) and (18):
\[
\frac{dV_m}{dt} = (h_s - h_1) \frac{dx}{dt} - \frac{dV_c}{dt} \tag{19}
\]

In the conditions near the front, the salt concentration is supersaturated. Let suppose that the crystallization rate \(\frac{dV_c}{dt}\) is directly proportional to the flux from B to A. If \(V_f\) is the liquid volume acquired to A by the flux, then
\[
h_1 \frac{dx}{dt} = k_1 \frac{dV_f}{dt} \tag{20}
\]

where \(k_1\) is a proportionality constant. Here \(k_1 \leq 1\) because only a fraction of \(V_f\) is transformed in crystal.

Moreover, we can reasonably assume that the flux rate is
\[
\frac{dV_f}{dt} = k_2 \frac{dV_c}{dt} \tag{21}
\]

Here \(k_2 \leq 1\) because the flux of liquid can not be higher than the evaporation.

Then, from equation (17):
\[
\frac{dx}{dt} = \frac{k_1 k_2 dV_c}{h_1} \tag{22}
\]

Combining equations (19) and (22), we obtain the next relation:
\[
\frac{dV_m}{dt} = \left[ k_1 k_2 \left( \frac{h_s - h_1}{h_1} \right) - 1 \right] \frac{dV_c}{dt} \tag{23}
\]

Examining the figure 5, we can notice that in case of a decrease of \(V_m\), the heights \(h_2\) and \(h_s\) can decrease too. But the drop of \(h_s\) is more probable than of \(h_2\) due to the flux of liquid moving away \(h_s\) to \(h_2\). So we can consider \(h_2\) as a constant value. And from equations (15) and (23) we obtain:
\[
\frac{dh_s}{dt} = \frac{2}{b} \left[ k_1 k_2 \left( \frac{h_s - h_1}{h_1} \right) - 1 \right] \frac{dV_c}{dt} \tag{24}
\]

Here \(k_1 k_2 < 1\), but \(k_1 k_2 \left( \frac{h_s - h_1}{h_1} \right)\) can be greater than 1 if \(h_s\) is considerably greater than \(h_1\). But our equations fails in this regime because actually \(h_s\) can not grow without limit. In this case, as the growing of \(h_s\) will be damped and the system will return to the regime where these equations apply.

The fixed point, where \(h_s\) is constant, is not stable. \(h_s\) will tend to increase (and its increasing will be damped and \(h_s\) will be near constant) or it will tend to decrease. And the decreasing rate of \(h_s\) will depend strongly on the evaporation rate.

As a result, we obtain the following:

- If the evaporation rate is low, \(\frac{dh_s}{dt}\) must be low too, and the front of crystallization will advance for a long distance before stops and no bands will be noticed.
• If the evaporation rate is high, $\frac{dh_s}{dt}$ must be high too, so $h_s$ will decrease quickly and a hole will be formed between B and D. As a consequence the front of crystallization will advance for only a short distance before stops. But the hole will create forward a new profile similar to the figure 5, crystal will grow again and the process will recur. This form, the periodic bands of crystallization will be developing.

• The bands could be wider if the evaporation rate is lower. So, we can pass from a continuous crystallization to a periodic bands as we vary the evaporation rate. This can explain how the bifurcation occurs. In our experiments, this was the case (see figure 6).

Figure 6. Crystallization patterns at different conditions (evaporation rate is increases with temperature).

a) Continuous crystallization. The concentration of HgCl$_2$ was 0.10 M, the agar concentration was 0.75 %, temperature was 30 ºC

b) Periodic crystallization. The concentration of HgCl$_2$ was 0.10 M, the agar concentration was 0.75 %, temperature was 30 ºC

c) Periodic crystallization. The concentration of HgCl$_2$ was 0.10 M, the agar concentration was 0.50 %, temperature was 70 ºC. Some spirals can be observed to.

Although (a) and (b) developed at the same temperature, (a) took eight times more than (a) in drying.
A particle in the film can be presented by crystallization or contamination (figure 7). This particle can generate a spiral pattern of crystallization around it (figure 8). The nature of this particle is not important: a chlorofluorocarbon particle can produce a spiral [23]. The cause is only a mechanical effect that blocks the flux of liquid from region B to A. Then, the front of crystallization will try to surround the particle, but due to instabilities, instead of forming concentric circles, a spiral develop.

**Figure 7.** A particle in the wet region of the film.

**Figure 8.** Spiral on a slide. The concentration of HgCl₂ was 0.05 M, the agar concentration was 0.20 %, temperature was 50 ºC.

3. Conclusions
The mechanisms proposed here can explain some patterns observed in crystal growth on a glass slide. Non-periodic bands can be formed due to an homogeneous drying of the film. Instead, periodic bands and spirals can develop if the drying of film is not homogeneous: that is, if the evaporation rate is considerably higher around a front of crystallization than in the rest of the film.

These mechanisms are very simplified, but we think that they capture the essential of the process. More work is necessary to verify the mechanisms. The constants of equation (24) can be determined. It is needed to examine the effect of the temperature on the crystallization rate. And the model could be refined to take account the damping of $h_s$ growth.

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