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The width of Liesegang bands: A study using moving boundary model and simulation

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Abstract. The pattern formation in reaction–diffusion systems was studied by invoking the provisions contained in the moving boundary model. The model claims that the phase separation mechanism is responsible for separating the colloidal phase of precipitants into band and non-band regions. The relation between the band separation and its width are invariably related to the concentration of the reacting components. It was observed that this model provides critical condition for the band formation in semi-idealized diffusion systems. An algorithm for generating the band structure was designed, and the simulated pattern shows a close resemblance with the experimentally observed ones.

Keywords. Reaction–diffusion systems; Liesegang bands; pattern formation; moving boundary; simulation.

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1. Introduction

Nature has a wide storage of colourful patterns which are originated mostly by self-organized processes without the intervention of external templates [1]. The patterns tell us much about the dynamics, both at the macroscopic as well as at the microscopic levels of the underlying system. Because of its importance, pattern formation has received wide attention from people working in different areas of biology, chemistry, physics and geology. The spatio-temporal patterns observed in many reaction–diffusion systems provide an excellent area to study these phenomena, and the advanced computer techniques give scope for simulating the structures based on theoretical models. The quasiperiodic structure, reported first by Liesegang in 1896, is regaining its importance due to its applicability in engineering mesoscopic and microscopic structures [2]. These studies are opening up new possibilities in the control and design of structures by reversing the processing

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order from the bottom-up approach to top-down methods in microelectronic device fabrications [3]. In recent years the interest in self-organized structures is growing, triggered by the idea of cheap and fast production of nanoscaled devices. One of the promising effects for obtaining such devices in Liesegang pattern formation is based on reaction and diffusion processes. In addition, the Liesegang phenomenon is an interesting research topic on its own due to the simple patterns arising out of complicated reaction and diffusion processes. A scientific understanding of pattern formation seems to be one of the most exciting aspects of non-linear dynamics.

The diffusion of a chemical reagent into a medium, most generally a gel medium, and the subsequent precipitation with another component that the gel medium contains, will generate periodic patterns under favourable conditions. Pattern formation in a reaction–diffusion system is considered as a self-organization phenomenon and the patterns are stationary in the sense that the bands are ‘locked’ in the position once they are formed. In this context, some researchers have considered the Liesegang structures as Turing-type patterns [4–10]. Since the 1952 theoretical work of Alan Turing, it is known that self-activated reactions with long-range inhibition process can spontaneously lead to the formation of stationary symmetry breaking patterns [11]. Under appropriate conditions, a spatially homogeneous state can be stable in the absence of diffusion and unstable in the presence of diffusion. An appropriate reaction network is capable of exhibiting spatially inhomogeneous state, i.e. pattern. The phenomenon in which diffusion destabilizes a spatially homogeneous steady state is termed as diffusion-driven or Turing instability. But many experimental observations support the argument that the initial form of the precipitants appears as colloids and its coagulation plays a vital role during the early stages of Liesegang ring formation [12,13]. Flicker and Ross [14] describe the mechanism of chemical instability as a reason for the periodic pattern formation. In mean-field theories, reaction–diffusion (partial differential) equations can describe the dynamics of the system taking into account diffusion of electrolytes and nucleation and aggregation of the precipitant species. Randomizing impacts like thermal fluctuation, presence of impurities, etc., are usually ignored in these models. Altogether, it is evident that quite diverse mechanisms can be at the helm of affairs of chemically generated patterns. They may also include even more physical aspects like buoyancy instabilities, surface tension, non-linear colloidal dynamics, etc., as the list of attributes.

The patterns usually consist of a set of clearly separated zones of colloidal precipitants, the shape of which depends on the geometry of the system. In typical systems that produce Liesegang patterns, the reacting components diffuse from outside to the gel medium impregnated homogeneously with the oppositely charged electrolyte species. The sparingly soluble precipitate of the chemical reaction coagulates at specific locations resulting in a sequence of precipitate bands. Precipitate moves diffusively into the zone and the dynamics can be described by a set of equations. Earlier investigators have framed four quantitative relations characterizing the pattern structure.

The first one relates the position of the ring (x_n) and its formation time (t_n) by a relation often called time law [15,16].

$$x_n = \alpha t_n^{1/2} + \beta, \tag{1}$$

where α and β are the constants. This relation is analogous to Einstein–Smoluchowski relation for Brownian motion, interpreted in terms of random walk in homogeneous space [17].

The time law reflects the diffusive behaviour of the electrolyte into the gel matrix. The second one called the spacing law, is due to Jablczynski [18], which relates another important property of the bands

$$\frac{x_{n+1}}{x_n} = (1 + p), \tag{2}$$

where $(1 + p)$ is the spacing coefficient and the factor p depends on the initial concentration of the reacting components. It has been observed in many experimental cases that p varies from 0 to 0.5 [19]. A detailed study of the dependence of p on concentration was made by Matalon and Packter [20,21].

According to them,

$$p = \Omega(b_0) + a_0^{-1}\Gamma(b_0), \tag{3}$$

where $\Omega(b_0)$ and $\Gamma(b_0)$ are two decreasing functions of their argument. Also the width or thickness (w_n) of the bands has some functional regularity [22]:

$$w_n = \varepsilon x_n, \tag{4}$$

where ε is a constant.

Many models, that provide theoretical prediction on the band formation was failed to provide conclusive suggestions on the domain size of the coagulated precipitants. Using cellular automata simulations, Chopard *et al* [23] have proposed

$$w_n = \varepsilon x_n^{\phi}, \tag{5}$$

where the width exponent ϕ depends on two constants a_0 and b_0. They have obtained theoretically the band structure for ϕ varying between 0.49 and 0.61. Later, Droz *et al* [24], combining the scaling properties of the density of precipitates in the bands, found that ϕ ranges from 0.90 to 0.99, which almost coincides with the linear dependence as suggested by eq. (4). Our goal here is to present an algorithm on pattern formation and predict the structure quantitatively with reasonably minimum inputs.

2. Theoretical methods

Several competing theories have been developed for describing the mechanism of Liesegang phenomena. All the theories share some common features to show how the diffusive reagents A and B turn into a final immobile precipitate D.

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{D}. \tag{6}$$

Some theorists strongly prefer to place an intermediate compound (C′) as an inevitable component formed before the end product is reached [25].

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C'} \rightarrow \mathrm{D}. \tag{7}$$

Theoretical models can be grouped into two main categories. The first termed the prenucleation model, suggest that band formation can be treated on the basis of a feedback mechanism between the nucleation and diffusion transport [26–28]. Nucleation is a nonequilibrium process, and it occurs when the local product of the ion concentrations of the reacting species reaches a saturation threshold value. The precipitation results in the reduction of the level of the supersaturation and no further nucleation is possible when the concentration product is less than the threshold limit. While the front proceeds further into the medium, the concentration product reaches the threshold level again and the nucleation of the precipitate is continuous. Repetition of this sequence results in periodic patterns. Theoretical predictions based on this model were made earlier by Wagner and Prager, and they assumed the existence of sharp periodic bands.

The second category, using Lifshitz–Sloyzov instability mechanism [29–31], suggests a post-nucleation droplet coarsening processes. The continuously advancing nucleation front produces an intermediate compound, which may be a homogeneous haze of colloids. The rate of production of colloid species is supposed to be proportional to the product of the local concentration of reactants. A first-order phase separation mechanism is assumed to take place inside the colloid-filled domain, separating them into regions of different matter densities. Such a process has the potential to generate a bunch of bands in a system when continuous domains of identical systems are perturbed. The precipitation bands arise by coagulation of the intermediate colloidal haze if certain critical electrolyte concentrations are exceeded [32]. The spatially distributed colloidal particles are unstable against perturbations [33]. Venzl [34] summarizes the process of Liesegang banding by three characteristic stages: the production of a continuous homogeneous colloid, the coarsening of the colloid and the dynamics of colloid particles resulting in pattern formation.

The moving boundary model [35] was suggested to deal with the problem slightly differently. Though it supports the formation of intermediate colloidal particles, it describes effectively the patterning process by considering a virtual migration of the boundary of the outer and the inner electrolytes. It also envisages a phase separation mechanism for the formation of the bands in the medium. The idea of formation of intermediate colloidal haze prior to patterning along with moving boundary model proved to be efficient in predicting the concentration dependence of the width of the spatio-temporal patterns. When the Liesegang patterns were studied by computer simulation, the usual method is to solve a set of coupled reaction–diffusion equations. We approach the task differentially by employing the results obtained directly from the moving boundary model. Once the boundary migration concept was introduced, the theory straight away upheld all the existing laws. Thus the moving boundary model is safer and simpler in many respects. It delineates scenery with distinctive assumptions and boundary conditions. Thus a better understanding of the basic facts of pattern formation and geometrical positioning of the bands is made possible with this model. The following are the basic approximations used in the moving boundary model.

(1) The initial concentration of the outer electrolyte C_{A0} is assumed to be much larger than the initial concentration C_{B0} of the inner electrolyte and it is also assumed that $C_{\mathrm{A}}(x = 0, t)$ is kept fixed at the junction point of the electrolytes. For experiments, $0.005 \leq C_{\mathrm{B0}}/C_{\mathrm{A0}} \leq 0.1$.

(2) The boundary which separates the outer and inner electrolytes (gel–solution interface) is located at $x = 0$, in the y–z plane. Also the type B ions are assumed to be uniformly distributed inside the gel medium and the initial concentrations are

$$C_{\mathrm{A}} = C_{\mathrm{A0}},\ C_{\mathrm{B}} = 0; \quad x < 0,\ t = 0 \tag{8}$$

and

$$C_{\mathrm{A}} = 0,\ C_{\mathrm{B}} = C_{\mathrm{B0}}; \quad x > 0,\ t = 0. \tag{9}$$

(3) As the reaction front advances into the medium in the positive x-direction, the concentration of type A ions varies and at the position of a band

$$C_{\mathrm{A}} = C_{\mathrm{A0}}; \qquad 0 < x \le x_n,\ t \sim t_n. \tag{10}$$

This assumption holds well as the reservoir concentration C_{A0} of type A ions is sufficiently large compared to the initial concentration C_{B0} of type B ions.

(4) The motion of the particles from one band to the other is assumed to be more or less uniform and therefore it can be assumed that the boundary layer shifts from one band to the next with uniform speed.

The concentration profile of type A ions in the gel is assumed to be [16]

$$C_{\mathrm{A}}(x,t) = C_{\mathrm{A0}} \exp\{-\beta(x - x_n(t))/\xi_{n+1}\}, \quad x_n \le x \le x_{n+1}, \tag{11}$$

where $\beta > 0$, is a constant for a given system and ξ_{n+1} is the separation between the nth and $(n+1)$th bands. For type B ions, the homogeneity of its concentration profile inside the gel column has been disturbed by the reaction process. It can be taken as

$$C_{\mathrm{B}}(x,t) = \eta C_{\mathrm{B0}} \exp\{-\gamma(x_n(t) - x)/\xi_n\} + C_{\mathrm{B0}}(1 - \eta' \exp\{-\gamma(x - x_n(t))/\xi_{n+1}\}). \tag{12}$$

Here γ is another constant. The first term on the right side of eq. (11) represents those components of B which have successfully penetrated the band in the negative x-direction. Since this fraction is very small, the coefficient η will be a very small positive quantity. The coefficient η' appearing in the second term signifies the factor of C_{B0} which had been eliminated from its initial level due to the formation of the reaction product C*. Applying the condition for band formation as stated in the ion product theory,

$$C_{\mathrm{A}}(x,t) C_{\mathrm{B}}(x,t) \mid x_n, t_n = \mathrm{C}^* \tag{13}$$

and

$$\partial/\partial x\{C_{\mathrm{A}}(x,t) C_{\mathrm{B}}(x,t)\} \mid x_n, t_n = 0. \tag{14}$$

Substituting the values of $C_{\mathrm{A}}(x,t)$ and $C_{\mathrm{B}}(x,t)$ from eqs (10) and (11) in eqs (12) and (13), we get

$$(\eta - \eta' + 1) C_{\mathrm{A0}} C_{\mathrm{B0}} = \mathrm{C}^* \tag{15}$$

and

$$\eta'(\beta/\gamma + 1) = \beta/\gamma + \eta(\beta/\gamma - \xi_{n+1}/\xi_n). \tag{16}$$

Writing $\xi_{n+1}/\xi_n = 1 + p$ and $\beta/\gamma = \alpha$, one obtains

$$\eta(\alpha - (1 + p)) + \alpha = \eta'(\alpha + 1). \tag{17}$$

Eliminating η' from eq. (14) and by substituting in eq. (16),

$$p = K\mathrm{C}^*/\eta C_{\mathrm{B0}}^2 + K\alpha C^* - (1+2\eta)C_{\mathrm{B0}}^2/C_{\mathrm{A0}}(K\eta C_{\mathrm{B0}}), \tag{18}$$

where $K = C_{\mathrm{A0}}/C_{\mathrm{B0}}$ which obviously is the Matalon–Packater law. It is now desirable to calculate the values of the positive constants η and η' which were mentioned earlier. For this, substitute the value of C* in eq. (17) and approximate the two concentration profile indices as the same. This will lead to

$$p = C_{\mathrm{B0}}^2\alpha(\eta - \eta' + 1) - (1+2\eta)/\eta C_{\mathrm{B0}}^2 \tag{19}$$

and finally to

$$p = (1 - 2\eta')/\eta. \tag{20}$$

If we assume the upper limit for p as 0.5, then the two constants η and η' will become 0.05 and 0.493 respectively. On the other hand, if p assumes the lowest range, i.e., $p \sim 0$ as in the case of equidistant band system, one of the constants becomes $1/2(\eta)$ and the other ambiguous. Thus the limiting ranges of the two new constants involved in the above calculation can be fixed. Using this value we may get a picture of the reaction mechanism. When η' approaches 0.493, 49.3% of C_{B0} had been eliminated from its initial level, due to the formation of the reaction product (C*). This seems to be a large value, but generally in the precipitation band structure thick bands observed near the interface, nevertheless signifies this approximation. The value of η which is small describes the intensity of penetration of type B ions into the negative direction. Here, in the approximation, $\eta \sim 0.05$ proposes a very low penetration of the B ions in the backward $(-x)$ direction.

An analysis of the width law is also possible at this juncture using the moving boundary concept. One of the main features of the intermediate species theory is that the substance to be precipitated is formed first as a continuous homogeneous colloidal dispersion [32,36,37]. A phase separation mechanism, the reason for which is not yet clear, occurs in the medium which segregates, the colloidal precipitants into a band. Different techniques were proposed to explain the phenomenon of phase separation. Droz *et al* analysed the phenomenon by employing spinoidal decomposition processes [38,39] and by the action of a moving reaction front. The reaction front produces colloidal particles and small clusters of particles nucleate and aggregate behind the front. The phase separation mechanism distributes the homogeneous colloidal particles of uniform initial concentration c_0 into two parts: a band having concentration c_{b} and a gap having concentration c_{g}. Applying the rules of matter conservation we write

$$w_n c_{\mathrm{b}} + (\xi_n - w_n)c_{\mathrm{g}} = \xi_n c_0, \tag{21}$$

where w_n is the width of the nth band.

The width of the nth band as a function of the concentration is

$$w_n = (c_0 - c_{\mathrm{g}})/(c_{\mathrm{b}} - c_{\mathrm{g}})\xi_n, \tag{22}$$

or

$$w_n = f_{\mathrm{c}}\xi_n, \tag{23}$$

where

$$f_{\mathrm{c}} = (c_0 - c_{\mathrm{g}})/(c_{\mathrm{b}} - c_{\mathrm{g}}) \tag{24}$$

is the width coefficient, which will be more or less constant for a steady pattern. Thus the width of the precipitation bands depends exclusively on the concentration of the intermediate colloidal particles.

For the evaluation of the values of f_c, the following approximations are useful:

(1) During the diffusion processes, type A particles will move towards the positive x-direction and a fraction of type B particles will move towards the negative x-direction. The remaining type B particles with concentration $(1-\eta)C_{B0}$, available in the diffusion zone, are capable of initiating the reactions.
(2) The quantity of colloidal precipitants formed will be a further fraction of the available electrolytes. Hence we proceed to assume $\mu(1-\eta)C_{B0}$ as the amount of the colloidal particles generated.
(3) The colloidal particles which segregate on the band is yet another fraction $\lambda(1-\eta)C_{B0}$ of the total colloidal particles generated.
(4) All the remaining particles will present in the gap.

Also from these assumptions, we equate the total concentration of colloidal precipitants produced c_0 and the concentration of the precipitants on the band c_b as,

$$c_0 = \mu(1-\eta)C_{B0}, \tag{25}$$

$$c_b = \lambda(1-\eta)C_{B0}. \tag{26}$$

Upon substituting these values in eq. (23) it becomes,

$$f_c = \lambda/(2\lambda - \mu). \tag{27}$$

Majority of the colloidal particles appear to segregate on the bands and the void region contains practically very few colloidal particles. When $\lambda = 0$, f_c also becomes zero, which gives the no-band condition. Between the values $0 \le \lambda \le 0.5$, f_c becomes negative and band formation is forbidden. The width coefficient f_c has an anomalous behaviour at $\lambda = 0.5$ and it takes the value 0.5 asymptotically. We may conclude that for sustained band formation, $\lambda \ge 0.5$, which is somewhat a critical condition. Hence it may be safer to approximate

$$f_c \approx 1/2 \tag{28}$$

when $\mu \ll \lambda$ and $\lambda = 1$ as special case and we simulate the patterns for this case. This gives an immediate conclusion

$$w_n = \xi_n/2. \tag{29}$$

The widths of the bands become half the separation distance and this is true only for small values of n. When n becomes larger, the contribution of μ in eq. (26) becomes considerably large and the widths of the bands become lesser than this value.

3. Experimental methods

An experiment was carried out to obtain precipitation bands. This consists of silver dichromate precipitation bands in gelatin gel. The concentration of the outer (silver nitrate) and

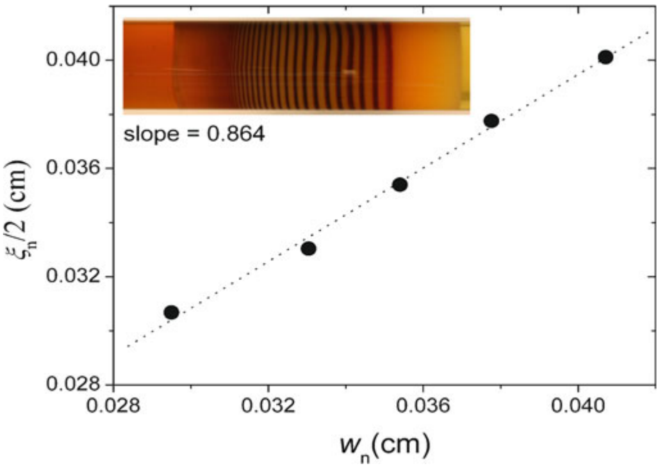

Figure 1. Dependence of the half-separation distance on the width of the band for the first five bands in silver dichromate system in 12.5 wt% gelatin gel. The concentration of the outer (silver nitrate) and the inner (potassium dichromate) electrolytes are 0.25 M and 0.0036 M, respectively. The obtained spacing coefficient is 0.074. The size of the experimental picture is 5.6 cm × 1.7 cm.

the inner (potassium dichromate) electrolytes are 0.25 M and 0.0036 M, respectively. Well-defined bands were seen at regular intervals in the gel column depicting the geometric sequence of Liesegang patterns. The width of the bands was approximately half of the interband separation (figure 1), supporting the theoretical predictions made on the basis of the moving boundary model.

4. Simulation

The algorithm of the program for simulation contains the following procedures:

(1) Assuming the values of p, compute the constants η and η'.
(2) Compute the position of the first band using spacing law, assuming $x_0 = 1$.
(3) Continue the process for ten successive steps by assuming the concentration C_{A0} as fixed.
(4) Compute the separation distance for each band and hence calculate the width of the bands using eq. (29).
(5) Then plot the bands using the above steps.

On the basis of this algorithm, two-dimensional band structures were generated by a Matlab programme, resembling Liesegang-type patterns. The geometry of the pattern bears all distinguishable features of the experimentally observed structure. These two-dimensional patterns are obtained for $p = 0.077$ and 0.5, respectively (figures 2 and 3). The pattern in the figure shows fixed values for y-axis, maximum or zero. The maximum corresponds to the initial concentration of outer diffusant (C_{A0}). This parameter does not vary between x_n and $x_n + w_n$ (shown as the shaded region) as envisaged in the moving boundary model.

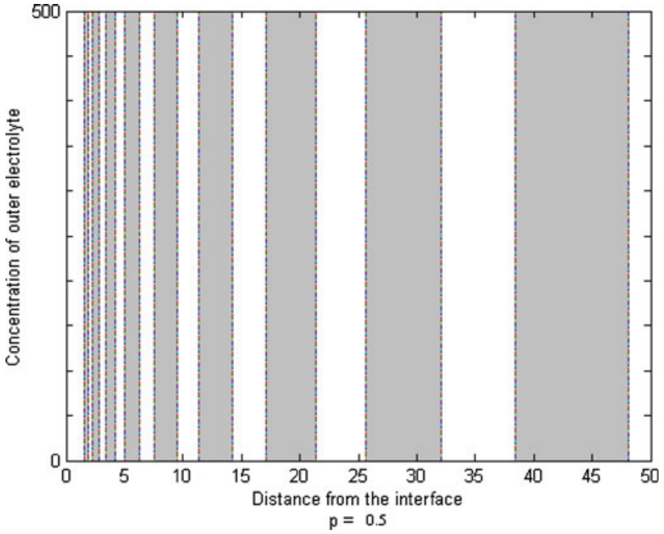

Figure 2. Computer simulated pattern for spacing coefficient $p = 0.5$. The concentrations taken on y-axis represent millimoles per litre and the distance on x-axis is in cm.

Beyond this point the concentration of type A ions falls to zero (blank region). This repeats periodically in space and hence the system is obtained. However, it does not mean that concentration of type A ions has a discontinuous regime before the precipitation zone. As p

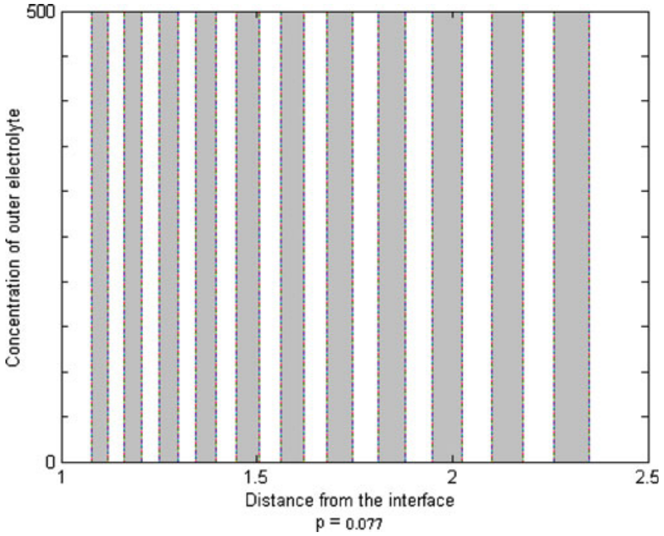

Figure 3. Computer simulated pattern for spacing coefficient $p = 0.077$. The concentrations taken on y-axis represent millimoles per litre and the distance taken on x-axis is in cm.

increases, the spacing and hence the width of the bands increases. Hence different patterns may be obtained for different concentrations of electrolytes. Plotting may also be possible for λ values ranging from 0.5 to 1. Three-dimensional patterns can also be obtained by a similar analysis.

5. Conclusions

The moving boundary model provides a reasonable conclusion on the spatial positioning of the periodic band structure observed in reaction-limited diffusion systems. The theoretical calculations based on the model suggest that the width of the precipitation bands depends exclusively on the concentration of the intermediate colloidal particles. Also the theory could stipulate a critical condition for sustained band formation in the reaction–diffusion systems. This idea was sequentially developed to generate patterns in a Matlab program. The algorithm for this was prepared entirely on the basis of moving boundary concept and the simulated patterns bear the characteristic nature of the experimentally observed Liesegang patterns. The intermediate colloid formation hypothesis was once again ascertained in the model and it seems to be useful in illustrating many other phenomena, in particular, the self-sustained steady patterns.

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