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Modeling ternary mixtures by mean-field theory of polyelectrolytes: Coupled Ginzburg–Landau and Swift–Hohenberg equations

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1. Introduction

ABSTRACT

The purpose of this work is to model ternary mixtures using the theory of pattern formation and of polyelectrolytes, with mean-field approximations. The model has two local, non-conserved order parameters. In the free energy short-range and long-range nonlocal interactions between elements of the mixture are considered. The spatiotemporal dynamics of the system is described by coupling the time-dependent Ginzburg-Landau equation and the Swift-Hohenberg equation. These non-linear partial differential equations are solved with numerical methods to study the emergent spatially stable configurations. The model shows a large diversity of patterns, which permit an interpretation of the behavior of some biological systems and presents different growth lengths within its spatial structures.

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Many biological, chemical and physical systems present the property of spatial self-organization, which is the result of the interactions between its components. Examples are the pigmentation patterns of vertebrates (such as birds, fish and reptiles), biological lipid membranes, the formation of copolymeric and ferromagnetic layers, mixtures of binary and ternary liquids like suspensions, emulsions and microemulsions, convective phenomena, formation of ferromagnetic systems and binary alloys. In all these systems there are non-linear and symmetry breaking mechanisms whose behavior results in spatially stationary patterns [1,2].

There is a discussion about how to model the pigmentation patterns of some animals. On the one hand, there are mechanochemical models that reproduce the formation of skin patterns in birds by using coupled partial differential equations for modeling the interactions between dermis elements, meanwhile the epidermis is modeled by using a deformation matrix [1,3]. These models are capable of reproducing more complex patterns that those that do not use coupled terms, but they are difficult to analyze both analytically and numerically. On the other hand, there exist reaction–diffusion models with Turing instability for modeling some kinds of fish skin patterns [4–6]. They consist of linear, quadratic or cubic couplings of two Turing bi-dimensional systems. These models are easy to analyze both analytically and numerically, without losing the complexity of the generated patterns. However in this case the dermis and epidermis are assumed to constitute chemical substances (activator and inhibitor) or morphogens that react in forming spatial stable patterns.

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It is well known that in phenomena with domain coarsening (like in Rayleigh Bénard convection, diblock-copolymer melts, magnetic materials, or fluid binary mixtures), the characteristic length L(t), grows as a power law: $L(t) \sim t^{z}$. For instance in ferromagnetic systems, with uniform phases and nonconserved local order parameter that satisfies the timedependent Ginzburg-Landau equation [7,8], it is found that z = 1/2. In other work [9], the microemulsions are modeled as ternary mixtures with hydrodynamic effects, using two order parameters that are conserved ϕ y ρ . There ϕ represents the difference in the concentration of water and oil (for example), and ρ the surfactant density; again, in this case z = 1/2. In the models of ferromagnetic binary systems with conserved order parameter, z = 1/3 [7,8]. In systems that present spinodal decomposition [10-12], a lipid binary mixture is modeled using a conserved parameter and the value of z is 1/3, just like in the ferromagnetic theory for coarse-grained fluids with competing interactions [13]. However, in bi-dimensional ternary systems, for the case of spinodal decomposition modeled with two independent and conserved order parameters, a law is reported for the growth of the characteristic length with z = 1/3 [14,15]. Even more, in ternary systems for modeling microemulsions with two conserved order parameters and with a Ginzburg-Landau free energy functional, a slower growth power law $L(t) \sim \ln(t)$ [16,17] is found.

The specific proposal in this work, consists in the construction of a model for ternary mixtures with two local order parameters, both not conserved. Its free energy is the product of mean-field approximations in models of polyelectrolytes [18]. Furthermore we add terms of attractive interaction for short range and non local repulsive interactions for long range [19]. The morphology of the obtained patterns with this model show that this is convenient to use nonlinear dynamic approaches (Swift-Hohenberg lake models) instead like of lattice-gas models in which explicit molecular interaction potentials are used [14]. The results of this research analyzes the different length scales for the patterns obtained. Furthermore a wide variety of pattern morphologies are found. This is also a property of Turing and mechanochemical systems. However in Ref. [5] the disadvantages for models that couple reaction-diffusion systems and mechanochemical models are presented. When their dynamical equations are uncoupled, these can exhibit disadvantages like: the fact that the complexity of the patterns and its dynamics depend upon the choice of initial conditions, or the lack of patterns, which are not present in the model proposed. One inherent property of the proposed model is the wide variety of length scales. The model also provides the possible explanations of the nonlinear mechanisms that cause different stable biological patterns.

In the presented model an important approximation is used: the supposition of the deterministic character of dynamical equations, in which noisy fluctuations are not considered. In stochastic models [20] the fluctuations are considered as additive or multiplicative noise. In order to distinguish between internal or external fluctuations, the origin of the noise must be taken into account. These stochastic models also present emergent patterns similar to that of the deterministic models. Examples are found in experimental, theoretical and numerical studies of hydrodynamic systems [21,22], chemical reactions [23] and biological systems like in the neuronal dynamics [24] or in the nature of calcium dynamic at cellular and tissue level [25].

The arguments mentioned before, are organized in the following sections: in Section 2 the construction of the model is presented, in Section 3 the numerical method for solving the dynamic equations is explained, in Section 4 the results are presented, in Section 5 there is a discussion of applications to biological systems, Section 6 refers to the conclusions and Section 7 is an Appendix with simulation details.

2. The model

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In the present section a model for ternary mixtures based on polyelectrolyte theory is shown. This model is more general, in the context of the morphogenesis, than the Ginzburg-Landau and Swift-Hohenberg models. The model considers a local order parameter ϕ , that represents the concentration difference of two polymeric solutions. This order parameter fulfills a nonlinear partial differential equation similar to the Ginzburg-Landau equation and it is coupled with an additional order parameter ψ , that forms modulated phases. This latter parameter satisfies a Swift–Hohenberg-like equation. The physical meaning of ψ is defined below.

The first step is to consider two non conserved order parameters that fulfill [26]:

$$\frac{\partial \phi}{\partial t} = -M_{\phi} \frac{\partial F[\phi, \psi]}{\partial \phi}
\frac{\partial \psi}{\partial t} = -M_{\psi} \frac{\partial F[\phi, \psi]}{\partial \psi}$$
(1)

where M_{ϕ} and M_{ψ} are two mobilities of the system, $F[\phi, \psi]$ is the Helmholtz free-energy functional and it is proposed as a functional of the type of Ginzburg-Landau, that contains a term similar to the Edwards free energy [18]:

$$F_{Edwards}[\phi,\psi] = \int dr \left\{ \frac{\beta}{2} |\nabla\phi(r,t)|^2 + \frac{\nu}{4} \phi^4(r,t) - \frac{\alpha}{2} \phi^2(r,t) \right\}.$$
 (2)

In this equation α is the chemical potential of the system and the coefficients β and ν are taken as unitary for consistency with the Ginzburg-Landau functional [7,8]. The first term of the Eq. (2) represents the short range interactions between elements of polymeric chains, the second term takes into account the excluded volume of a good solvent and the last term corresponds to the interactions of the monomer with the chemical potential (reservoir of the system). On the other hand, the free energy that refers to the solvent $F_{Solvent}$, depends on the nonconserved scalar order parameter, that represents the electrostatic potential of the solvent or its density. The free energy that takes into account the Coulomb's electrostatic contributions, is expressed as [18]:

$$F_{Solvent}[\phi,\psi] = \int dr \left\{ -\lambda |\nabla\psi|^2 + \left(-H\psi(r,t) + \frac{\mu}{2}\psi^2(r,t) - \frac{g}{3}\psi^3(\vec{r},t) + \frac{1}{4}\psi^4(\vec{r},t) \right) + \frac{\varepsilon}{2}\phi^2(\vec{r},t)\psi(\vec{r},t) \right\}.$$
(3)

Again, the first term represents the short range interactions, but in this case, the electrostatic interactions between the charges (small ions and charged monomers) are presented. The second term determines the concentration of the small ions and their interaction. At this point a fourth order series expansion is proposed. The third term represents the coupling of two scalar fields $\phi(\vec{r}, t)$ and $\psi(\vec{r}, t)$, and the parameter ε measures the relative strength of the coupling term. This parameter is associated with the reduced temperature of the system.

Lastly, the functional $F[\phi, \psi]$ has a free energy term, $F_{stretch}$, that does not permit the miscibility between the concentrations, represented by ϕ , and considers superficial deformations, like bending and stretching [19]. If the molecular order deformations are taken into account, the following equation is obtained:

$$F_{stretch}[\phi,\psi] = \int \mathrm{d}r \left\{ \frac{\sigma}{2} |\nabla\psi(\vec{r},t)|^2 + \frac{\lambda}{2} |\nabla^2\psi(\vec{r},t)|^2 + \Lambda\phi(\vec{r},t)\nabla^2\psi(\vec{r},t) \right\}.$$
(4)

In this equation, the meaning of ψ is the difference of the surface electrostatic potential that can be formed from a ternary mixture. The first term contains the superficial tension σ , the second term is the bending modulus λ and the last term is a measure of the elasticity Λ of the coupling term between the local curvature $\nabla^2 \psi$ and the polymeric order parameter ϕ . In this case we assume that the last term in $F_{stretch}$ is negligible, that is $\Lambda \approx 0$.

Hence, the model for the free energy functional of the ternary mixture is: $F = F_{Edwards} + F_{solvent} + F_{stretch}$. However, without loss of generality, we assume that the superficial tension energy is bigger than the bending modulus, for instance: $\sigma = 4\lambda$, $\mu = \lambda + \gamma$ and H = 0. So, taking into account the last assumption in Eq. (4), and substituting it and Eqs. (2) and (3) in *F*, the equation takes the form:

$$F[\phi,\psi] = \int dr \left\{ -\frac{\alpha}{2}\phi^2 + \frac{1}{4}\phi^4 + \frac{1}{2}|\nabla\phi|^2 + \frac{\varepsilon}{2}\phi^2\psi + \frac{\gamma}{2}\psi^2 - \frac{g}{3}\psi^3 + \frac{1}{4}\psi^4 + \frac{\lambda}{2}|(\nabla^2 + 1)\psi|^2 \right\}$$
(5)

that is the proposed model in this paper.

Finally, substituting the functional *F* in the Eqs. (1), the following equations are obtained:

$$\frac{\partial \phi}{\partial t} = \alpha \phi + \nabla^2 \phi - \phi^3 - \varepsilon \phi \psi$$

$$\frac{\partial \psi}{\partial t} = -\gamma \psi - \lambda (\nabla^2 + 1)^2 \psi - \frac{\varepsilon}{2} \phi^2 + g \psi^2 - \psi^3$$
(6)

where for simplicity $M_{\phi} = 1$ and $M_{\psi} = 1$. Eqs. (6) describe the dynamics of the whole system and are solved numerically.

3. Numerical method

In order to consider the spatial variations in the nonlinear partial differential equations, we need to solve the model numerically.

Eqs. (6) are solved using the semi-implicit pseudospectral method and we follow the procedure for the temporal integration described in Ref. [27]. An advantage is that the spatial term of the partial differential equations becomes a scalar. For instance, the function ψ obeys the relationship

$$\frac{\partial \psi}{\partial t} = e\psi - (\nabla^2 + 1)^2 \psi + N(\partial_x^2 \psi, \partial_y^2 \psi, \partial_x \psi, \partial_y \psi, \psi)$$
(7)

where *e* is a control parameter for the system, and *N* represents the nonlinear terms. We define its Fourier transform as well, as:

$$\tilde{\psi}(q_x, q_y, t) = \frac{1}{L_x L_y} \int_0^{L_x} \mathrm{d}x \int_0^{L_y} \mathrm{d}y \psi(x, y, t) \exp(-\mathrm{i}q_x x) \exp(-\mathrm{i}q_y y),$$

and applying the trapezoid rule to $\tilde{\psi}$. We can define the discrete Fourier transform as:

$$\tilde{\psi}(q_x, q_y, t) = \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \psi(x_i, y_j, t) \exp(-i(q_x)_i x_i) \exp(-i(q_y)_j y_j)$$

where $(q_x)_I = 2\pi I/L_x$, $(q_y)_J = 2\pi J/L_y$, $-(N_x/2 - 1) \le I \le N_x/2$ and $-(N_y/2 - 1) \le J \le N_y/2$ for a grid of $N_x \times N_y$. Then if we apply the Fourier transform $\tilde{\psi}$ to Eq. (7) it follows that:

$$\frac{\partial \psi}{\partial t} = b\tilde{\psi} + \tilde{N} \tag{8}$$

where $b = e - [1 - (q_x^2 + q_y^2)]^2$ and \tilde{N} represents the Fourier transform of the nonlinear terms. The term with the Laplacian has been transformed to a scalar in the complex Fourier space. Eq. (7) has been reduced to a time dependent nonlinear differential equation. The final step is to compute $\tilde{N}(\tilde{\psi})$, this is done approximating the nonlinear term by $\tilde{N} \approx \tilde{N}_0 + \tilde{N}_1(t - t')$ in the interval $t \le t' \le t + \Delta t$. For calculating \tilde{N}_0 and $\tilde{N}_1(t - t')$, it is necessary to solve Eq. (8) by using the integral factor method, for which the factor is $\exp(-bt)$. Subsequently the modified Euler method is applied and give the numerical solution: [27]

$$\tilde{\psi}(t+\Delta t) = \exp(b\Delta t)\tilde{\psi}(t) + \tilde{N}_0 \left[\frac{1-\exp(b\Delta t)}{b}\right] + \tilde{N}_1 \left[\frac{\exp(b\Delta t) - (1+b\Delta t)}{b^2\Delta t}\right]$$
(9)

where $\tilde{N}_0 = \tilde{N}(\tilde{\psi}(t))$ and $\tilde{N}_1 = \tilde{N}(\tilde{\psi}_{temp}(t + \Delta t)) - \tilde{N}(\tilde{\psi}(t))$. We can obtain $\tilde{\psi}_{temp}$ letting $\tilde{N}_1 = 0$ in Eq. (9). Δt is the time step, that in this case can be larger than in the typical Euler methods, because the discrete Fourier transform tends to converge faster with each iteration.

To calculate $\psi(t + \Delta t)$, we compute the inverse transform of $\tilde{\psi}(t + \Delta t)$, after that $N(\psi(t + \Delta t))$ is obtained and Eq. (9) is iterated.

In the remainder of this section we deduce the approximated solution for the equation system (6), using the method described above. So we define the ϕ and ψ correspondent Fourier transforms as:

$$\widetilde{\phi}(\vec{q},t) = \int_{-\infty}^{\infty} d\vec{r} \exp(-\vec{q} \cdot \vec{r}) \phi(\vec{r},t)$$

$$\widetilde{\psi}(\vec{q},t) = \int_{-\infty}^{\infty} d\vec{r} \exp(-\vec{q} \cdot \vec{r}) \psi(\vec{r},t)$$
(10)

where \vec{r} is a point in the grid. The inverse transforms of Eqs. (10) are:

$$\begin{split} \phi(\vec{r},t) &= \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} d\vec{q} \exp(\vec{q} \cdot \vec{r}) \tilde{\phi}(\vec{q},t) \\ \psi(\vec{r},t) &= \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} d\vec{q} \exp(\vec{q} \cdot \vec{r}) \tilde{\psi}(\vec{q},t). \end{split}$$
(11)

Using Eqs. (10) and (11) we can see that Eqs. (6) are transformed in the Fourier space as:

$$\frac{\partial \tilde{\phi}}{\partial t}(q,t) = c(\alpha, q_x, q_y) \tilde{\phi}(q,t) + \tilde{N}(\phi(q,t), \psi(q,t))$$

$$\frac{\partial \tilde{\psi}}{\partial t}(q,t) = d(\gamma, q_x, q_y) \tilde{\psi}(q,t) + \tilde{N}'(\phi(q,t), \psi(q,t))$$
(12)

where $c(\alpha, q_x, q_y) = \alpha - q^2$ and $d(\gamma, q_x, q_y) = -(\gamma + \lambda [1 - q^2]^2)$ with $q^2 = q_x^2 + q_y^2$, $\tilde{N} \approx \tilde{N}_0 + \tilde{N}_1(t - t')$, $\tilde{N}' \approx \tilde{N}_0' + \tilde{N}_1'(t - t')$, $\tilde{N}_0 = -\varepsilon \widetilde{\phi \psi}(q, t) - \widetilde{\phi^3}(q, t)$ and $\tilde{N}_0' = -\varepsilon \widetilde{\phi^2}(q, t)/2 + g \widetilde{\psi}^2 - \widetilde{\psi}^3$. Applying the same algorithm to Eq. (9) we conclude that Eqs. (12) can be solved approximately in the $[t_0, t_0 + \Delta t]$ interval, such that they fulfill:

$$\tilde{\phi}(t + \Delta t) = \exp(c\Delta t)\tilde{\phi}(t) + \tilde{N}_0 \left[\frac{1 - \exp(c\Delta t)}{c}\right] + \tilde{N}_1 \left[\frac{\exp(c\Delta t) - (1 + c\Delta t)}{c^2\Delta t}\right]$$

$$\tilde{\psi}(t + \Delta t) = \exp(d\Delta t)\tilde{\psi}(t) + \tilde{N}_0' \left[\frac{1 - \exp(d\Delta t)}{d}\right] + \tilde{N}_1' \left[\frac{\exp(d\Delta t) - (1 + d\Delta t)}{d^2\Delta t}\right]$$
(13)

if $\tilde{\phi}_{temp}$ and $\tilde{\psi}_{temp}$ correspond to $\tilde{\phi}(q, t_0 + \Delta t)$, $\tilde{\psi}(q, t_0 + \Delta t)$, which are obtained where $\tilde{N}_1 = 0$ and $\tilde{N}'_1 = 0$ in Eq. (13). Finally the $\tilde{N}_1, \tilde{N}'_1$ coefficients are given by:

$$\begin{split} \tilde{N}_{1} &= -\left\{ \left[\varepsilon(\widetilde{\phi\psi})_{temp} + \widetilde{\phi^{2}}_{temp} \right] (q, t_{0} + \Delta t) - \left[\widetilde{\phi\psi} + \widetilde{\phi^{2}} \right] (q, t_{0}) \right\} \\ \tilde{N}_{1}' &= -\left\{ \left[\frac{\varepsilon}{2} (\widetilde{\phi^{2}})_{temp} - g\widetilde{\phi^{3}}_{temp} + \widetilde{\psi^{3}}_{temp} \right] (q, t_{0} + \Delta t) - \left[\frac{\varepsilon}{2} \widetilde{\phi^{2}} - g\widetilde{\phi^{3}} + \widetilde{\psi^{3}} \right] (q, t_{0}) \right\}. \end{split}$$

Then, Eqs. (13) are the way to compute the numerical solutions for the system (6).

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Fig. 1. Patterns obtained from Eqs. (6) with parameters fixed in Table 1 of Appendix.

4. Results

Numerical solutions of Eqs. (13) are obtained discretizing on a square grid of mesh size $\Delta x = 1$ with 256 × 256 nodes, and the wavelength is set to $\lambda_0 = 8 \Delta x$. This value is suitable for bi-dimensional pattern formation of coarsening stripe phases [28,29] and grain boundaries in solids [30]. Also, the result of stability analysis [31] defines the critical wave number $q_0 = 2\pi / \lambda_0$, which strips leads to pattern formation. The temporal evolution of the system is performed with a time step $\Delta t = 0.1$. The initial conditions for ϕ and ψ are random variables with a Gaussian distribution of zero averages and variances $\langle \phi^2 \rangle = 0.1$ and $\langle \psi^2 \rangle = 0.1$.

In Fig. 1 the results obtained by Eqs. (13) with $\epsilon = 0$ and the other parameters with values listed in Table 1 of Appendix are shown. The morphology of the patterns can be associated with Turing systems [5,32], time dependent Ginzburg–Landau [7,8,10,19] and Swift–Hohenberg [28,30,29] models. Fig. 1a shows a stripe phase pattern for field ψ , which is similar to spatial configurations obtained by Turing systems [5,32] and the Swift–Hohenberg model [29]. The pattern in picture 1b is like a glassy dynamic patterns that is also obtained by the Swift–Hohenberg model [28]. Fig. 1d and e show the patterns that have been reported in the study of grain boundaries [30], ferromagnetic [7,8] and polymeric [10,19] systems.

On the other hand, the emergent patterns obtained from Eqs. (13), also present many similitudes with spatially stationary configurations obtained experimentally in biological, physical and chemical systems. Ref. [2] displays a picture of marine angelfish, *Pomacanthus imperatur* in adult form. This picture and a section of the pattern in Fig. 1a, show that they are similar. A picture of the domain formation in the stripe phase of ferromagnetic garnet is shown in the Ref. [19]. Again, similarity between this pattern and Fig. 1b is observed, which is a typical spatial configuration produced by the Swift–Hohenberg model [28]. Finally, the hexagonal arrays experimentally obtained and shown in Ref. [33], compare well with the pattern of Fig. 1c. Fig. 1(c) can simulate a polymeric film (*SiN_x*) coating the surface of a semiconductor layer (*GaAs*), after the polymeric layer is removed a hole pattern on the semiconductor surface is produced.



Fig. 2. Diversity of patterns obtained from Eqs. (13) for different parameter values (see Table 2 of Appendix).

4.1. Morphologies and similarities with biology and chemical systems

The most interesting case is obtained when $\epsilon \neq 0$, Fig. 2 displays three different types of temporal evolutions (up to t = 10,000 adimensional units). Fig. 2a shows patterns for the fields ϕ and ψ at different times. The field ϕ is characterized by two phases, positive (here in blue) and negative (white), where both are slightly modulated by a hexagonal phase. Even we can observe that this modulation is responsible for sharp edges or linear edges in the positive phase domain. For the field ψ , we find that the pattern is characterized by two microphases, positive (white) and negative (gray), which are composed by points and small stripes, also slightly modulated by a hexagonal phase.

Another interesting pattern is shown in Fig. 2b (with parameter values listed in Appendix). The most important characteristic of the pattern corresponds to the field ϕ : it is composed of two uniform phases, one positive (blue) and another negative (white). This pattern presents an interfacial structure between different phase domain (light blue). Now, for the field ψ , the pattern is dominated by a phase positive and an interfacial structure corresponding to the domain boundaries in ϕ . Fig. 2b shows the field ψ in gray scale.

The last case considered in this work is obtained by changing the values of the parameters γ and ε (see Fig. 2c and Appendix). It is important to mention that we use a grid of 512 × 512 nodes, in this case for each field of ϕ and ψ , to discretize the space. The pattern of the field ϕ is composed by a majority of positive phase (light blue) and two more phases, one positive (blue) and another negative (white). The two phases (positive and negative) form domains in which there is a fourth phase (pale blue). On the other hand for the field ψ we get a dominant phase (light gray) and a negative phase (dark gray), which form domains in which there is another phase inside.

There are biological systems with similar patterns as those described above. Namely a membrane composed of lipid bilayers, skin patterns of certain reptile species and random patterns in ternary membranes. Fig. 3a and b, are the skin patterns of a Gila monster (a certain reptile species) that can be depicted as a field ϕ which is lightly modulated by an other field ψ with dots and stripes. The pattern in Fig. 3b is obtained by plotting the difference between the fields ϕ and ψ and its present edges, which form the perimeter of the positive phase (blue spots) that is inside a dominant negative phase (white). Both phases and domains have point arrays slightly modulated by a hexagonal phase (sky blue or white). The morphology of this pattern is similar to obtained one in the Ref. [2].

Fig. 2b, presents typical patterns for microemulsion ternary systems [16,17] (for instance water, oil and some surfactant at t = 100,1000-10,000), in which there is a structure of the third species (surfactant) between the positive and negative phases. The models in microemulsions have applications in Biology, for instance for explaining the mechanisms of formation of lipid membranes [11]. Another important aspect about the dynamics of those ternary systems, is that they are determined by the superficial tension in the interfacial phase; the result is that the total energy of the system decrease when temperature increases [9,34,35]. Fig. 2b corresponds to a pattern with very low superficial tension (almost zero). At least qualitatively our model corresponds to experimental observation [36].

The pattern that explains the mechanism of formation in ternary membranes with unordered bulk domains is shown in Ref. [12]. The same reference, shows a structure of a membrane obtained by atomic force microscopy (AFM), which is a cut of a real membrane [12]. The conditions for forming this membrane require a certain quantity of water salinity and a low temperature (close to zero ⁰C). This suggests that the salinity corresponds to parameter γ whereas ε can be associated to the system's temperature, see Eqs. (6). The parameters ε and γ in the case of the pattern in Fig. 5a. One final comment is that the domains of the membrane are porous, which implies that the picture shown in Ref. [12] is a 3D pattern whose associated image shows similarities with Fig. 5a.

An important chemical system that shows experimental evidence of Turing patterns, is the chlorite-iodide-malonic-acid (CIMA) reaction, reported in Ref. [37]. The CIMA reaction presented in this reference occurs in a two-dimensional layer constituted by an activator (iodide) and an inhibitor (chlorite) leading to stripe or/and dot morphologies. The layer of dots and stripes are quite similar to the patterns of Fig. 2(a) that correspond to spatial configuration of the order parameter ψ , and the patterns with stripes only correspond to the Fig. 1(b) for ψ . This suggests that ψ is related to a concentration difference between activator and (malonic acid) indicator, ϕ being the inhibitor in this case.

4.2. Coarsening and correlations length

At this point only qualitative aspects have been analyzed, characterizing the patterns morphologically. This section studies coarsening phenomena and defines some length scales to describe the evolution of partially ordered systems. If $\phi(\vec{x}, t)$ is a nonconserved order parameter, we define the correlation function as $C(\vec{r}, t) = \langle \phi(\vec{x} + \vec{r}, t)\phi(\vec{x}, t) \rangle$ (where \vec{x} is a point on the grid) or its Fourier transform, the structure factor, $S(\vec{k}, t) = \langle \phi(\vec{k}, t)\phi(-\vec{k}, t) \rangle$. Similar equations are defined for the field ψ .

It is well known that the growth of order in many binary systems far from equilibrium (i.e. ferromagnetic domains and spinodal decomposition of binary mixtures) fulfill a dynamic scaling law. This property can be enunciate as:

...at late times, a single characteristics length scale L(t) such that the domain structure is (in a statistical sense) independent of time when lengths are scaled by L(t). [7]

L(t) can be a correlation length, defined through Eq. (14). The dynamic scaling hypothesis states that L(t) is the unique important length in the system, given that the structure remain the same statistically, if all lengths are scaled by L(t). Also, the scaling length is proportional to the curvature radius or to the distance between the domains in the same phase. Beginning from a random initial condition, the length grows like a power law, and in many cases takes the form: $L(t) \sim t^{z}$.

Using the scaling hypothesis, the correlation function and the structure factor have the form:

$$C(\vec{r},t) = f\left(\frac{r}{L(t)}\right), \qquad S(\vec{k},t) = L^d g(kL(t))$$
(14)



Fig. 3. Fig. (a) is a section of a Gila monster's skin. The pattern of Fig. (b) is obtained from the fields $\phi - \psi$, after numerically solving Eqs. (12) with fixed values for the parameters (see Table 2). Fig. (c), presents the structure factor S(k, t) for the field ϕ . The graph (d) show the collapse of structure factor curves in the scaling function. The graphs (e) and (d) represents the growth curves for the fields ϕ and ψ , with the exponent z = 0.02 for the field ϕ and z = 0.18 for ψ .

where *d* is the spatial dimension of the system and g(kL) the Fourier transform of f(r/L). Both *f* and *g* are time independent scaling functions.

Solving Eq. (13) numerically, the circular average of the factor $S(\vec{k})$ to $|\vec{k}|$ is calculated by using the discrete Fourier transform method. It is defined $\langle |\vec{k}| \rangle_{\phi}$ as in Ref. [8]: $\langle |\vec{k}| \rangle_{\phi} = \int d\vec{k}S(\vec{k}, t)k/\int d\vec{k}S(\vec{k}, t)$, it is supposed that $\langle |\vec{k}| \rangle_{\phi}$ scales as 1/L(t) or

$$L(t) \propto \frac{1}{\langle |\vec{k}| \rangle_{\phi}}.$$
(15)

For a modulated phase with wave number k_0 (which is often the case of ψ , here), one can define an other characteristic length as

$$L(t) \propto \frac{1}{\langle |\vec{k} - \vec{k}_0| \rangle_{\psi}} \tag{16}$$

and $\langle |\vec{k} - \vec{k}_0| \rangle_{\phi} = \int d\vec{k} S(\vec{k}, t) (k - |\vec{k}_0|) / \int d\vec{k} S(\vec{k}, t) 4.$

The rest of the section shows the scaling laws for the correlation lengths in the patterns mentioned above.

Fig. 3 presents the results for the pattern with morphological similarities to the Gila monster's skin (see Fig. 3a and b). Fig. 3c and d display the structure factors for the fields ϕ and ψ respectively, for time from t = 40 up to t = 10,000. The plot of the correlation length L(t) for the field ϕ is shown in Fig. 3(e) and we get approximately that $L(t) \sim t^z$ with an extremely slow growth, $z = 0.02 \pm 0.005$ for t > 100 (from a least squares fit).

Fig. 3f represents a growth plot for the correlation length of the field ψ as a function of time and a growth exponent $z = 0.18 \pm 0.03$ is found. Using Eqs. (15) and (16) for the fields ϕ and ψ , it is concluded that there exist several length scales describing the system evolution and only one characteristic length for ψ , which do not obey typical scaling laws. This fact can be understood qualitatively as follows: the coupling term gives an origin to spatial modulations with a slightly hexagonal phase when $\varepsilon \neq 0$, which have the effect of a disordered blocking black potential. Then, the dots act like a potential barrier that inhibits the growth of the two field bistable ϕ phases. This result means that the system has extremely slow dynamics with metastable disordered or glassy states.

The analysis of the patterns similar to the membranes composed by lipids are shown in Fig. 4. The Eqs. (14) and (15) are computed only be solved for the field ϕ in this case, as ψ does not from modulated phases. Fig. 4c shows the structure factors plotted when *t* goes from 50 up to 3000, and the scaling function in which the structure factors plots collapses. Fig. 4d shows the growth of the correlation length L(t) for which we find $L(t) \sim t^z$ where $z = 0.54 \pm 0.01$. Furthermore, when the value of ε decrease and the of γ increase (see values of this parameters in Fig. 4d), it is found that $z = 0.33 \pm 0.05$. This behavior of growth lengths corresponds to the typical scaling laws [7,8,16,17]. The decrease in the value of *z* is due to the decrease of free energy (see parameters ε and γ in Table 2). This happens because the interfacial structure of the field ψ , is blocking the dynamics of the uniform phases of ϕ . Another implication, is that the interfacial structure takes the form of a bilayer, which is shown in Fig. 4e.

Finally the last case presents more complex morphologies (see Fig. 5a). In Fig. 5b and in the inset of Fig. 5c the structure factors for *t* units are plotted, when *t* varies from 50 up to 6000 in intervals of 100, and every 1000 time units for 1000 < t < 10, 000. Also the growth laws for the fields ϕ and ψ are presented in Fig. 5d and e. In this case, the exponent of the growth law is $z = 0.33 \pm 0.02$ for the field ϕ and $z = 0.8 \pm 0.1$ for ψ . The growth law for the field ϕ , corresponds with results obtained experimentally [12]. The scaling function is shown in Fig. 5c. Instead, for the field ψ there is not scaling function (dynamical scaling from), although it has a correlation length.

5. Discussion

A framework over the layers that constitute the skin of animal vertebrate (fishes, reptiles or chick embryos), is shown in the Refs. [3,4]. These works considered only three outer layers that form the skin: epidermis, dermis and basal laminar. The latter couples and allows the interactions among the other two skin layers. On the other hand, has been demonstrated that the dermis determines the location, size, number and structure of skin appendage, while its orientation is defined by the epidermis [38]. The outcomes are perspectives for skin modeling: the coupling reaction-diffusion systems and a mechanochemical model coupled to a reaction-diffusion system. The first one considers that the dermis and epidermis are formed as activator-inhibitor (morphogens), both are modeled by a nonlinearly coupled reaction-diffusion system with Turing instability [4–6]. In the second perspective, considering the epidermis as previously explained, the dermis is modeled by conservation equations, which are coupled by a mechanical force balance equation [1,3,39]. In relation to Eqs. (6) of the model proposed, a possible interpretation is that ϕ represents the dermis, which consists of morphogens, and the field ψ represents the density the density of dermis (as well as their constituents). Additionally, the interaction between ϕ and ψ is related to the experimental behavior reported: the dermis has an influence on the epidermis (for instance ψ modulates the dynamic of ϕ in the pattern of the Gila monster's skin). Another important result has been published in Ref. [21], where it is demonstrated that the conservation flows equations of Navier-Stokes are reduced by a linear combination that come out to be the field ψ . So, the equation for ψ is analogous in its behavior to the equations of the mechanochemical model. The previous arguments suggest that Eqs. (6) are other ways for modeling the skin with reaction-diffusion and mechanochemical equations.

On the other hand, an important aspect of the interpretation for the fields ϕ and ψ , is that these give more information for the mechanism of membrane formations. Previously, it has been stated that the experimental and simulation results, in which the scalar field ϕ is associated to polymeric density [10,12]. Ref. [12] does not explain the causes of the deformation in the membrane pores, compared with the pattern obtained by AFM. Instead in the present study, Eqs. (6) explain that ϕ is responsible for the deformations and spatial patterns of the pores and ψ represents the local electric potential and modulates the curvature energy. So, the deformation of the pores is due to the interaction between the polymeric density and scalar potential of the solvent (or its density). Additionally, this explains that in each pore the value of electric potential



Fig. 4. Fig. (a) is a final pattern obtained with the difference of fields $\phi - \psi$, where ϕ and ψ are the numerical solutions of Eqs. (13). Fig. (b) is the pattern of field ψ . Fig. (c) shows the collapse of structure factor curves on the scaling function when $z = 0.54 \pm 0.01$. Graph (d) in log–log, present the growth length and the exponent *z* for different parameter values. The graph (e), represents a concentration profile of the field ψ , where *y*-coordinate is fixed (y = 80).

is greater than outside. It is represented by gray scale of ψ patterns (see Fig. 3a). Again, this suggests the mechanism by which the charged particles (positive or negative) are attracted or repelled in the membrane pores.

In the case of CIMA reaction previously mentioned, there is another study [40], for which a transition of patterns between the morphologies of stripes and dots was presented. This behavior of the patterns, is probably implicit in the Eqs. (6), because the equations exhibit a wide variety of spatial stable configurations. This point well motivate future studies.

The mechanism of the additive noise described in the Fitz–Nagumo equations, can originate instabilities from which emerge a state of synchronization in the whole system. In such state, there is a characteristic spatial frequency associated to the spatially stable pattern. These behaviors are characteristic of calcium dynamic [24] and neuronal dynamics [25]. The spatial dynamics of these systems depend a lot on the noise intensity. When the noise is very intense, the dynamics



Fig. 5. The pattern of Fig. (a), is obtained by numerical simulation of Eqs. (13) (see the values of the parameters in Table 2). Fig (b) presents the structure factor S(k, t) for the field ψ . Graph (c), represents the collapse of structure factor curves on the scaling function (18 curves for different times from t = 50 up to t = 6000). Figs. (d) and (e), show the growth lengths for the fields ϕ and ψ , with the exponent value: z = 0.8 for ψ and z = 0.33 for ϕ .

of the system exhibit emergent patterns that are similar to phenomena of domain coarsening the calcium dynamic. For intermediate noise level, emerging waves nucleate in the system (pattern with spiral structures). In the case of neuronal behavior, when noise is at an intermediate level, there is spiral wave nucleation, but at low noise level, the spatial patterning is that of domain coarsening. It also is a property of a chemical system like the chlorite dioxide-iodide-malonic acid (CDIMA) reaction [23]. The noise in this reaction, only enhances the phases difference of the pattern. It would be interesting to study the patterns emerging from a stochastic version of Eqs. (6), keeping the same parameter values as in Table 2 in order to compare with the deterministic case. For instance, can be addend to the deterministic Eqs. (6), an additive noise $\xi(\vec{r}, t)$ in the order parameter ϕ , and/or multiplicative noise $\eta(\vec{r}, t)$ for the parameter of control $\varepsilon \longrightarrow \varepsilon + \eta(\vec{r}, t)$ (or $\alpha \longrightarrow \alpha + \eta(\vec{r}, t)$) and/or $\gamma \longrightarrow \gamma + \eta(\vec{r}, t)$). The physical meaning of $\xi(\vec{r}, t)$ is for example the internal thermal fluctuations, and $\eta(\vec{r}, t)$ is associated to the external fluctuations in the parameter of control. Both terms would be given as in the Ref. [20].

Parameters	Fig. 1(a)	Fig. 1(b)	Fig. 1(c)	Fig. 1(d)	Fig. 1(e)
α	0.5	0.5	0.5	0.5	0.5
ε	0.0	0.0	0.0	0.0	0.0
γ	-0.2	-0.2	-0.1	-0.1	0.2
g	0.0	0.0	-1.0	1.0	1.0
λ	0.5	1.0	0.8	1.0	0.6
t	9000	5000	5000	5000	800
scalar field	ψ	ψ	ψ	ψ	ϕ

Table 1Values of parameters in Fig. 1.

Table 2

Values of parameters in Figs. 2-5.

Parameters	Figs. 2(a) and 3(b)	Figs. 2(b), 4(a) and (b)	Figs. 2(c) and 5(a)
α	0.5	0.5	0.5
ε	-0.6	-0.2	-2.4
γ	-0.5	1.0	-2.3
g	-1.0	-1.0	1.0
λ	0.8	1.0	0.5

Finally, it is important to mention that the loss of scaling in the correlation length for ψ or ϕ , in some cases previously presented, and the slow growth length that may take the form, $L(t) \sim \ln(t)$ has not been explained. This will be the scope of future studies.

6. Conclusions and summary

Patterns similar to the Gila monster's skin or to the CIMA reaction, are obtained by the model proposed here. The phase ordering dynamics of these patterns present a characteristic scaling length ($L(t) \sim t^z$ where z = 0.18) which is slower than those reported in Refs. [7,8,10,14–17,28] for binary and ternary systems. This dynamic is sluggish, or "glassy", with many metastable states.

The patterns obtained from Eqs. (13) with behavior similar to membranes with lipid bilayers, exhibit a characteristic length scales that grows with time as a power-law with exponent z = 0.5, which corresponds to the results reported in the literature [8,10], when the fields are not locally conserved. For a smaller coupling parameter ε , the exponent lowers to z = 0.3. This *z* value has not been obtained in models with nonconserved order parameters. Another important aspect related to these patterns, is the decrease of the superficial tension. Such results are in accordance with the experiments [34] and the results of numerically solved models, that have been published in Ref. [36].

A last experimental fact reproduced for the emergent patterns obtained from the proposed model, for other values of γ and ε , is the porous membranes formation. The pores growth obeys a growth length that takes the form $L(t) \sim t^z$ where $z = 0.29 \pm 0.01$, which has been published elsewhere [12], while in the present study it is found that $z = 0.3 \pm 0.03$.

The difference between the coupled Ginzburg–Landau and Swift–Hohenberg equation and the ternary mixture models of lattice gas type [34,36] or continuous models with two conserved order parameters [16,17], is that these do not produce patterns with greater complexity. Instead, depending on the parameters, modulated patterns emerge (for instance patterns with patterns similar to the skin of Gila monster's or porous membranes or CIMA reaction). The kinds of patterns obtained here, like in the Ginzburg–Landau and Swift–Hohenberg models, are independent of the initial conditions. A property of the phases analyzed here is that ψ acts on ϕ as an effective periodic potential, with important consequences on the dynamics of the system. This effect is difficult to obtain with more sophisticated models such as two coupled reaction–diffusion systems or diffusion-driven instability [4–6] or mechanochemical models [1,3,39].

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Appendix. Numerical simulation details

See Tables 1 and 2.

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