**Buckling Dynamics in Crystalline Membranes**

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Abstract. We study the dynamics of a flexible crystalline membrane with hexagonal pattern. The relaxational dynamics towards equilibrium is described through a Brazovskii-Helfrich-Canham Hamiltonian model. The coupled dynamics between the hexagonal structure and the deformation modifies the elastic properties of the membrane. In this paper, we explore the properties of this coupling by analyzing the structure factor of the deformation out of the plane of the considered membrane system.

1. Introduction
In recent years, there has been an increasing interest in the study of two-dimensional (2D) [1-6] textures on curved surfaces. This is motivated by the new properties that these systems present due to the coupling between the crystalline structure and the deformation metric. A clear example is observed in the dynamics of annihilation and buckling generated by the defect annihilation in graphene. The dynamics of defects is clearly modified by the interaction between said defects and the deformation of the system [7].

This study is focused on the description of the time evolution of a membrane with internal degrees of freedom that, below a critical temperature, undergoes a symmetry-breaking phase transition.

2. The Model
To describe the dynamics of a crystalline membrane, we use a Brazovskii Hamiltonian model geometrically coupled to the topography of the membrane.

The evolution of the crystalline structure occurs by means of the dynamics dictated by the Brazovskii Hamiltonian model, which evolves coupled to the membrane deformation through the dynamics imposed by the Helfrich-Canham Hamiltonian model.

2.1. Fluid Membrane
Fluid membranes occur in a wide variety of systems, from biological ones to condensed matter ones, such as surfactant films, vesicles, and lipid bilayer membranes [8–10].

During the last few years, the equilibrium phases and structures have been investigated intensively through different methods, including molecular dynamics [11], Monte Carlo [12] and phase-field [10] models.

We employ a phase-field approach to describe the morphology of the membrane during a symmetry-breaking phase transition.

In the Monge gauge, the deformation of a membrane can be described by \( \mathbf{r}(x, y) = [x, h(x, y)] \), where \( x = [x, y] \) represents a set of Cartesian coordinates in the plane, and \( z = h(x, y) \) is the out-of-plane deformation over the reference plane \( x \) (see Fig. 1). The equilibrium properties of the fluid membrane are described by the Helfrich-Canham Hamiltonian model \( F_{HC} \) [13-17]:

\[
F_{HC} = \int [F_1 + F_2 + F_3] \sqrt{g} \, dx \, dy
\]
Here, $g$ is the metric tensor [16]. The first term $F_1 = \frac{k_B}{2} (K - C_0)^2$ accounts for the bending elastic energy [16,17]. Where $k_B$ is the bending modulus, $K$ is the mean curvature, and $C_0$ is the homogeneous spontaneous curvature [18]. The second term $F_2 = \sigma$ is an isotropic contribution; therefore, the membrane area is characterized by a surface tension $\sigma$. The third contribution $F_3 = \frac{k_B}{2} R$ is a topological invariant that only depends on the genus of the surface. In this term, $k_B$ is the Gaussian rigidity and $R$ is the Gaussian curvature [19].

Figure 1. Monge gauge. The Monge gauge describes a surface by a single function $z = h(x, y)$, the height over a reference plane $(x, y)$.

2.2 Crystalline Phase.

The dynamics of buckling is studied through a continuous phase field model. The dynamics of buckling on membranes has been studied using many different approaches, such as molecular dynamics or Monte Carlo methods. However, these approaches have a great computational complexity and the results are limited as regards simulation time and length scale of the represented system. The phase field model naturally incorporates the elasticity properties of the hexagonal phase and also provides an efficient approach over long periods of system evolution, in diffusive time scales. This approach has been used in order to describe a wide range of systems on both atomic and mesoscopic length scales. For instance, pattern formation [20], grain boundary melting [21], defect dynamics [22], symmetry-breaking phase transitions [23], block copolymers [24], Langmuir films [25], and liquid crystals [26].

In the critical temperature surrounding, the order-disorder transition is phenomenologically described by a Brazovskii Hamiltonian [27] modified to account for the geometry of the membrane:

$$ F_\phi = \int \left( 2(\nabla L^2) - 2\nabla_i \phi \nabla^i \phi + \frac{\tau}{2} \phi^2 + \frac{1}{4} \phi^4 \right) dA \tag{2} $$

Here we use the equation $\phi(r) = \psi(r) - \bar{\psi}$, where $\psi(r)$ is the local composition, and $\bar{\psi}$ is the average composition. The reduced temperature is represented by $\tau = \frac{T_c - T}{T_c}$ and the critical temperature by $T_c$. The expression of energy above is a modified version of the Ginzburg-Landau expansion. To incorporate the contribution of the surface geometry, the expression has been conveniently modified by using the differential operators. $\nabla L^2$ is the Laplace-Beltrami operator [28,29]. The standard convention of index summation has been used, where subscripts and superscripts indicate contravariant and covariant vectors, respectively. Below the critical temperature, the free-energy functional contributes to the formation of structures with hexagonal symmetry with a wavelength of $k_0 = \frac{1}{\sqrt{2}}$ [1].

2.3 Crystalline Membrane Dynamics.

The total Hamiltonian that represents the dynamics of the membrane consists of the sum of the energies mentioned above, $F = F_{HC} + F_\phi$. A dissipative model [30] is used to obtain the time evolution of the membrane deformation, $h$ parameter, and composition, $\phi$. The dynamics of both order parameters is coupled through the membrane metric. The time evolution corresponds to the following equations:
3. Numerical Simulation
The equations (3) and (4) have been numerically solved using a semi-implicit pseudospectral algorithm with periodic boundary conditions. The time and spatial steps have been selected to provide numerical stability and precise resolution [32].

The time step used is \( \Delta t \sim 10^{-4} \), and the spatial discretization is \( \Delta x \sim 10^{-2} \), both of which are typical values used in these numerical schemes. The size of the simulated system is \( L \times L = 512 \times 512 \).

Figure (2) illustrates the time evolution of both order parameters. The parameters used are the following: \( \psi_0 = 0.4, \tau = \alpha = 1.1, k_h = 0.1 \) and \( \zeta_h = 0 \).

4. Buckling Dynamics
At the mesoscopic level, the order within the hexagonal phase alters or modifies the stiffness constant of the membrane. As a result, the dynamics towards the equilibrium of the membrane is modified. A linear analysis of the bending energy predicts an exponential decay of the modes that constitute the initial condition of the membrane [33]. The amplitude of the different \( q \) modes is translated into the general form of the structure factor of the \( h \) parameter. Note that we have used the \( q \) notation to describe Fourier modes to avoid any confusion with the \( k \) value of the bending stiffness. The structure factor can be expressed as:

\[
S_h(q) = \langle |h_q|^2 \rangle \sim \frac{1}{kq^4}
\]  
(5)

Where \( h_q \) represents the Fourier Transform of \( h \), and \( \langle \ldots \rangle \) represents the radial average over the wave vectors with equal \( q \) modulus.

The dynamics of a membrane with crystalline structure is different from that of a liquid membrane [34], in which the \( k \) stiffness is an isotropic variable. In membranes with crystalline order, the crystalline structure produces a modification in the typical dynamics of the \( q \) modes, presented in equation (5). In the literature, it has been shown that the stiffness of the membrane can be renormalized to write a membrane with crystalline order according to the expression [35]:

\[
\langle |h_q|^2 \rangle \sim q^{4-\eta}
\]  
(6)

Where \( \eta = 2 \), according to the theory of partially polymerized membranes [35]. Experimental work shows that the value changes with respect to the theoretical value between (2-3.1) for different degrees of polymerization [34]. The structure factor of the \( h \) parameter allows the analysis of the dynamics of the membrane and the study of the influence of the crystalline structure on it.
Figure 2. The images on the left correspond to the time evolution of the \( h \) order parameter associated with the deformation height. The images on the right correspond to the time evolution of the order parameter \( \phi \), i.e. the composition.

Figure c corresponds to the critical time \( t_c \), where the coupling between deformation and composition that evolves in a coupled manner from that moment on begins to be observed.

Times: (a) \( t=0 \), (b) \( t=50 \) (c) \( t=100 \) (d) \( t=10000 \)

Figure 3. Time evolution of the membrane. Only the hexagonal pattern is illustrated in the last figure for clarity purposes and to better appreciate the evolution of the deformation, which corresponds to the time evolution shown in figure (2).

5. Results and Discussion

The time evolution of the order parameter \( \phi \) and the \( h \) height are illustrated in Figure (3). When \( \phi \) reaches a critical value, the coupling between both parameters \( \phi \) and \( h \) occurs (Image c, Figure 3).

The time when the coupling between both parameters occurs is identified as critical time \( t_c \).

In this model, the elastic constants of the membrane are determined through the value of the order of composition parameter. For an hexagonal configuration, we get \( \lambda = 30 |A_k| k_0^2 \mu = 6 |A_k| k_0^2 \) and \( K_0 = \frac{\mu (\mu + \lambda)}{2 \mu + \lambda} \) \cite{[36]}. Where \( \lambda, \mu \) are the Lamé constants and \( K_0 \) represents the Young modulus. In all cases, the parameters depend on the amplitude of the composition \( A_k \), which results for an hexagonal configuration.

\( A_k = \frac{1}{15} \left( -3 \psi_0 + \sqrt{3} \sqrt{20 k_0^2 - 20 k_0^2 - 5 \tau - 12 \psi_0^2} \right) \) It is interesting to analyze the time evolution of the membrane deformation by calculating the structure factor of the \( h \) parameter.
The structure deformation factor of the membrane for different simulation times is illustrated in the figure. Note the change of exponent in the power law of the structure factor with respect to the wave vector, which indicates a liquid membrane behavior at short times ($t < t_c$) and a crystalline membrane one at long times ($t \gg t_c$).

Figure (5) shows the structure factor for different simulation time values of an hexagonal-phase membrane. At short times, during the structure formation stage by spinodal decomposition, the dynamics between the parameters $\phi$ and $h$ is completely uncorrelated. At this stage, the structure factor shows a clear power law relation between the amplitudes of the $q$ modes and the wave vector. In this time scale, we observe that the exponent $(\langle |h|^{2}\rangle) \sim q^{-4.3 \pm 0.3}$ follows a similar law to the one predicted for a liquid membrane $(\langle |h|^{2}\rangle) \sim q^{-4}$ [37].

When the value of the order parameter reaches a critical value, the coupling between the composition or crystal structure and the deformation of the membrane occurs. In this time, which we call critical time, it occurs in our simulation in $t_c = 80$. Note in Figure (5) the change in the exponent at subsequent times to the critical time. The exponent value varies from $-4.3 \pm 0.3$ to $-1.8 \pm 0.2$. The change in the exponent characterizes the dynamics of the hexagonal-phase copolymer membrane. Note that the long time exponent is comparable to the value observed in polymer membranes with different degrees of polymerization [34].

6. Conclusions
In summary, the evolution of an hexagonal membrane is analyzed by means of numerical simulation. The evolution towards the equilibrium of the order parameter that represents the hexagonal phase modifies the deformation dynamics of the membrane shape, which results in the variation of the elastic constants of the membrane.

7. References
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