Landau–de Gennes model for nonuniform configurations in nematic liquid crystalline elastomers

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(Received 13 October 2003; published 2 June 2004)

Through a mean field theory, an elastic free energy describing the nonuniform elastic textures observed in nematic elastomers, is proposed. To construct it, an order parameter that describes the nematic-isotropic phase transition through the change of the elastic properties of the strain tensor at the transition point is introduced. The resulting elastic free energy can be written in a form that resembles the Frank free energy of the usual nematic liquid crystals, becoming equivalent to it when the size of the elastic nematic domains is a fixed constant along the whole sample. Using this approach, a model for nonhomogeneous deformations found by Godinho *et al.* [Macromolecules **33**, 7675 (2000)] in elastomeric thin films of urethane/urea is proposed.

I. INTRODUCTION

When de Gennes suggested [1,2] that the introduction of rigid and anisotropic molecules along the polymeric chain could induce a nematic character to a polymeric sample, the interest in nematic elastomers (NE) became widespread and many experimental and theoretical investigations have shed a new light on the physical behavior of these materials [3–5]. The model commonly used to study their thermodynamical behavior assumes that their macroscopic elastic properties are strongly determined by the entropy associated with the geometry of the long chain characterizing the polymeric molecules. For isotropic polymers, the interactions between different chains or between elements inside a chain are ignored, and the random walk shape assumed by the chain composing the macromolecules is taken as the main one responsible for their macroscopic elastic properties, conferring an entropic character to the corresponding statistical mechanics [6], whose probability distribution function becomes determined by the Gaussian form that describes the aleatoric end-to-end correlation function of the polymeric chain. For the case of NE this idea was generalized [3–5], being assumed that the probability distribution of an anisotropic cross-linked NE, in the limit of a long chain, is given by an anisotropic Gaussian form,

$$P_o(R^o) \sim (\text{Det}[l_{ij}^o])^{-1/2} \exp\left[-\frac{3}{2\mathcal{L}}R_i^o(l_{ij}^o)^{-1}R_j^o\right], \quad (1)$$

where $\vec{R}^o$ is the mean distance between the cross-linked points that, due to the anisotropy of the medium, satisfies the relation

$$\langle R_i^o R_j^o \rangle = \frac{1}{3}\mathcal{L}l_{ij}^o, \quad (2)$$

where $\mathcal{L}$ is the chain contour length, $\langle x \rangle$ is the statistical mean of x, and

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$$l_{ij}^o = l_\perp \delta_{ij} + (l_\parallel - l_\perp)n_i n_j \quad (3)$$

defines the chain shape parallel and perpendicular to the uniaxial director $\vec{n}$. The explicit values of $l_\perp$ and $l_\parallel$ determine the elastic anisotropy of the material. Equation (3) contains the essence of the anisotropic properties of the nematic elastomers, making explicit its uniaxial character and, at the same time that it reveals a privileged elastic direction given by the director direction $\vec{n}$, it also describes the amount of elastic anisotropy along the direction parallel and perpendicular to $\vec{n}$. Ahead, a generalization of this equation will be used to construct a unique order parameter that gathers these two aspects of the theory.

With a direct application of Eq. (1), considering all chain configurations as equiprobable and using a microcanonical ensemble, $S = -k \ln P_o(R^o)$, the corresponding free energy becomes

$$E_F = \frac{1}{2}N_c kT \ln P_o(R^o) + c, \quad (4)$$

where N_c is the number of cross-links per unit volume and c is a constant.

When the director is uniformly oriented, the thermodynamics resulting from these principles becomes analytically very simple and efficiently describes the observed phenomenology [3]. Nevertheless, when it is applied to nonuniform director configurations, it acquires unexpected and challenging aspects. For example, for nonuniform NE, the fundamental elastic constants (those corresponding to the splay, twist, and bend elastic constants of the usual nematic liquid crystals) would be negative, suggesting the nonexistence of a lower bound to the free energy [7]. However, this finding needs to be better investigated since, as mentioned above, the free energy from which it has been deduced disregarded the interactions between the different parts of the elastomer, being restricted to the description of entropic forces. So, when properly considered, these nonincluded interactions could modify the conclusions since, as it was pointed out by Terentjev, Warner, and Vervey [7], "one cannot forget that the basic uniform rubber elasticity and the underlying conventional Frank nematic elasticity were not taken into account"

in the assumptions that lead to Eq. (4). Thus, as nonuniform configurations are easily found in NE, being obtained, for example, through the simple application of an externally induced deformation [8], it is assumed that these structures can be described by some stable (or at least metastable) theory.

The aim of this paper is to fill this gap by constructing a mean field theory. It is important to emphasize that, as a rule, the results of a theory formulated from a microscopic point of view are more reliable than the ones coming from a mean field theory. But, as usual, the elaboration of a microscopic theory that takes into account all relevant physical aspects involved in a physical process can be extremely difficult, if not impossible. In the present case, we know that the microscopic arguments used to construct the probability distribution function given by Eq. (4) cannot take care of all aspects of the phenomenology involved in elastomeric physics. Essentially, Eq. (4) results from the resemblance of the polymeric chain with a random walk, and the entropic reasoning used to construct it cannot remain applicable when other contributions are taken into account. For example, the Frank free energy describing the aligning interaction between the nematic micelles is usually deduced from a Landau–de Gennes expansion of the free energy in terms of an order parameter [9], being therefore a mean field theory. Consequently, when such nematic contribution is added to Eq. (4) the theory will lose its microscopic character, becoming also a mean field theory.

As the nematic-isotropic phase transition involves a symmetry change, where a privileged direction for deformations arises at each point of the sample, it is usual to describe it through the construction of an order parameter expressing this change of order and, in terms of this order parameter, use the Landau–de Gennes prescription to find a free energy expression. Such an order parameter must be in accordance with the basic elastic properties, which must (a) express the anisotropic properties given in Eq. (3), (b) express the nematic interaction between the nematic domains, and (c) describe the basic elasticity of the elastomer. The construction of this order parameter is the aim of the first section of this paper. In the second section, the constructed order parameter will be used to postulate, through standard procedures, a Landau–de Gennes free energy that could be used to deduce the nonuniform elastic properties of the medium. In the last section, the resulting theory will be used to discuss some known results found in anisotropic elastomers [10].

II. THE ORDER PARAMETER

To describe the elastic properties of the NE, it will be assumed that an infinite number of microscopic elastic domains produces the observed macroscopic collective behavior. Initially, only one of these elastic domains will be studied. Afterwards, through the introduction of an order parameter and the consequent construction of an elastic mean field free energy, the thermodynamics resulting from their interacting collective behavior will be proposed [9]. As usual, the construction of such order parameter will be done through the choice of a physical property that expresses the symmetry change at the nematic-isotropic phase-transition point. To accomplish this task, the elastic anisotropy acquired by the system at the nematic phase will be the chosen property. The reason for this choice follows from the physical meaning of Eq. (3); where different amounts of deformations are observed when forces with the same intensity act along perpendicular directions. This observation is the essence of the difference between the NE order parameter that will be constructed here and that usually defined for the nematic liquid crystals. To be precise, for NE the knowledge of the direction that characterizes, at each point, the uniaxial deformation—the director direction — is not enough to fully characterize the elasticity of the material. It is also necessary to know the position dependent intensity of deformations or elongations along different directions when, for example, externally induced deformations are imposed along these directions. The realization of this task is the aim of this work.

A. Strain tensor as an order parameter

The strain tensor is the mathematical object that completely depicts the elasticity of a material undergoing deformations. Elastic properties like symmetries, inhomogeneties, anisotropies, or the behavior of the material under externally induced stress are described by it. Consequently, it is usual to expect that an order parameter describing those phase transitions presenting changes in the elasticity of a material could be expressed by the strain tensor. In order to see how this can be done, one should consider two infinitely close points A and B of an undeformed body, whose squared distance is given by [12]

$$(ds)^2 = (dx_1)^2 + (dx_2)^2 + (dx_3)^2. \tag{5}$$

When the body is deformed, these points are led to new positions given by A^* and B^* and, if the deformation does not cause ruptures, the new squared distance becomes

$$(ds^*)^2 = [d(x_1 + \mu_1)]^2 + [d(x_2 + \mu_2)]^2 + [d(x_3 + \mu_3)]^2 = (\delta_{ij} + 2\mu_{ij})dx_i\, dx_j, \tag{6}$$

where μ_1, μ_2, and μ_3 are the components of the deformation vector $\vec{\mu}$, which is assumed as a continuous function of the position, being infinitely differentiable, and μ_{ij} is the strain tensor, given by [11,12]

$$\mu_{ij} = \frac{1}{2}\left(\frac{\partial \mu_i}{dx_j} + \frac{\partial \mu_j}{dx_i} + \frac{\partial u_k}{\partial x_i}\frac{\partial u_k}{\partial x_j} \right). \tag{7}$$

As it stands, the rules that lead Eq. (5) to Eq. (6) are not restricted to describe deformations, it considers a larger set of transformations that conduct the points A and B to the points A^* and B^*. That is, these equations can also be used to describe, for example, uniform translations and uniform rotations, which are not deformations. So, when using Eq. (6), we must be sure that we are really describing deformations. Thus we remember that, locally, the distance between two neighbor points cannot remain the same after the action of a deformation. Consequently, the difference

$$\delta\varepsilon^2 = (ds^*)^2 - (ds)^2 = 2\mu_{ij}\, dx_i\, dx_j, \qquad (8)$$

which measures the local deformations of the elastic domain, must be non-null. From now on, $\delta\varepsilon$ will be called local deformation, or simple deformation, and, as mentioned above, all elastic properties of a material submitted to deformations must be described by the strain tensor, μ_{ij}. For example, the transition from an isotropic to a uniaxial elastomer creates a privileged direction for deformations leading to a change in the behavior of μ_{ij} when the transition point is crossed. Moreover, it follows from Eq. (8) that the points undergoing an equal amount of deformation ($\delta\varepsilon = $const) stay along a conic curve, whose geometrical forms (spherical, elliptical, hyperbolical) are determined by the eigenvalues of the strain tensor. So, from the point of view of the symmetries by rotation, three possibilities can be considered: three equal eigenvalues, which correspond to isotropic deformations; one different and two equal eigenvalues, which correspond to uniaxial deformations; and three different eigenvalues, which correspond to biaxial deformations. In this paper we will restrict our study to the transition that happens when a system with three distinct eigenvalues changes to a system with only two distinct eigenvalues; from an isotropic to a uniaxial phase. Of course, there are other possibilities for changing symmetries, but they will not be studied here.

To show how an order parameter can be constructed from the strain tensor, we consider the de Gennes argument which supports that if a generic tensor χ_{ij} represents some physical property, which being isotropy, becomes uniaxial through a phase-transition, then [9]

$$Q_{ij} = G\left(\chi_{ij} - \frac{1}{3}\delta_{ij}\sum_{\nu}\chi_{\nu\nu}\right) \qquad (9)$$

will be taken as an order parameter describing the corresponding nematic-isotropic phase transition, where G is an arbitrary constant. To see that Q_{ij} is really an order parameter, consider, at each point of the sample, a system of coordinates where χ_{ij} is diagonal. In the isotropic phase all eigenvalues of χ_{ij} are equal and, therefore, Q_{ij} is null. However, in a nonisotropic phase, at least one eigenvalue becomes different from the other two and, consequently, Q_{ij} becomes non-null. As the nullity of a tensor does not depend on the system of coordinates, this property is maintained in all coordinate systems. Consequently, as Q_{ij} becomes non-null when the system passes through the isotropic-nematic phase-transition point, it satisfies the requirements to be taken as an order parameter.

Now, we use the fact that at the nematic-isotropic phase transition, the symmetries described by the strain tensor μ_{ij} must change dramatically; at the isotropic phase it describes isotropic deformations, while at the nematic phase it must describe the uniaxial elasticity acquired by the system. So, as μ_{ij} has three equal eigenvalues at the isotropic phase, and at least one different at the uniaxial phase, it can be used as the property χ_{ij} that included in Eq. (9) leads to the construction of an order parameter. Consequently,

$$Q_{ij} = G\left(\mu_{ij} - \frac{1}{3}\delta_{ij}\sum_{\nu}\mu_{\nu\nu}\right) \qquad (10)$$

is an order parameter, which is written in terms of the strain tensor, and describes the nematic-isotropic phase transition.

In order to give further insight to the meaning of this order parameter, let us remember that it is usual to assume the existence of an "ideal" elastic deformation that preserves the volume of the elastomer. That is, extensions along one direction are accompanied by compensating contractions along the other directions, resulting in a global deformation that does not change the total volume of the material. This condition can be written in a local and differential form. Consider a differential volume element given by $dV = dx\, dy\, dz$ that, after a deformation, becomes given by $dV^* = (dx + d\mu_1)(dy + d\mu_2)(dz + d\mu_3) = (1 + \mu_{11})(1 + \mu_{22})(1 + \mu_{33})dx\, dy\, dz$. By neglecting terms of high order, we have $dV^* = dV(1 + \mu_{ii})$. So, the relative change of volume, Δv, is given by

$$\Delta v = \frac{(dV^* - dV)}{dV} = \mu_{ii}, \qquad (11)$$

the trace of the strain tensor μ_{ii}, which, for any tensor, is known as an invariant under coordinate transformations [12]. An immediate consequence of this result is that the usual assumption that the deformation does not cause changes in the volume of the elastomer can be put in the form

$$\mu_{ii} = 0, \qquad (12)$$

which from now on will be taken as the local condition for the volume invariance under deformations of the elastomer. Consequently, by imposing this condition in the order parameter given by Eq. (10) we found that Q_{ij} becomes

$$Q_{ij} = G\mu_{ij}, \qquad (13)$$

showing that, aside from the multiplicative constant G, the strain tensor coincides with the order parameter of the volume preserving the elastomeric nematic-isotropic phase transition.

B. Uniaxial strain tensor

Here, a detailed study of the forms that the uniaxial strain tensor μ_{ij} can assume will be discussed. Its explicit form, containing the symmetry changes determined by the elastomeric nematic-isotropic phase transition, will be postulated. As mentioned before, at the isotropic phase, the strain tensor must have three equal eigenvalues, while at the uniaxial phase, one of them must become distinct from the other two. To the different eigenvalue will correspond, at each point, an eigenvector whose direction gives the nematic director, being the relative amount of the elastic anisotropy measured by the ratio between the eigenvalue of this direction and any eigenvalue of any other degenerated direction. Furthermore, contrary to what happens with a molecule or micelle of a normal nematic liquid crystal, where this ratio is constant along the entire sample, in elastomeric materials, the corresponding ratio need not be constant; at differently deformed regions it

will assume different values and, as this is an elastic property acquired at the phase transition, the order parameter must also describe it. That is, such an order parameter must measure the order acquired with the introduction of a main direction for deformation as well as the respective amount of anisotropic elongation along that direction.

So, if a strain tensor with the form

$$\mu_{ij} = \frac{1}{2}\left(-\frac{g}{3}\delta_{ij} + \eta_i\eta_j\right) \tag{14}$$

is assumed, then it can describe a phase transition with the properties described above. Here, $\vec{\eta}$ is a non-normalized position dependent vector and g is a position dependent parameter whose meaning will be discussed later. To prove this assertion, one must consider those points that, through the application of this expression to Eq. (6), transforms an undeformed sphere into an equally deformed surface, $(ds^*)^2 = cte$. In addition, one must assume that the resulting surface will stay along the set of points $\vec{x} = (x, y, z)$. Then, according to Eq. (8), the resulting set of transformed points will satisfy the relation

$$(\delta_{ij} + \mu_{ij})x_ix_j = \left[\left(1 - \frac{g}{3}\right)\delta_{ij} + \eta_i\eta_j\right]x_ix_j = cte. \tag{15}$$

Consequently, when $\vec{\eta} = 0$ the equally deformed surface remains a sphere. Otherwise, when $\vec{\eta} \neq 0$, the corresponding surface becomes a conic curve. In order to verify whether it corresponds to a uniaxial ellipsoid, the matrix appearing in Eqs. (6) and (15), $\Delta_{ij} = (\delta_{ij} + 2\mu_{ij}) = (1 - g/3)\delta_{ij} + \eta_i\eta_j$, must be considered. It can take a diagonal form, and its set of eigenvectors, $\{V_i\}$, defines the directions of the principal strains (strain axes), while its set of eigenvalues, $\{E_i\}$, defines the corresponding principal extension. A straightforward calculation shows that the set of eigenvalues $\{E_i\}$ of the matrix Δ_{ij} is given by the set

$$E_1 = 1 - \frac{g}{3}, \quad E_2 = 1 - \frac{g}{3}, \quad E_3 = 2 - \frac{g}{3}, \tag{16}$$

showing that there are two degenerated eigenvalues, $E_1 = E_2$. Likewise, the corresponding eigenvectors, $\{V_i\}$, are given by

$$\vec{V}_1 = (-\eta_z, 0, \eta_x), \quad \vec{V}_2 = (-\eta_y, \eta_x, 0),$$

$$\vec{V}_3 = \vec{\eta} = (\eta_x, \eta_y, \eta_z) \equiv \vec{\eta}, \tag{17}$$

which reveals that the vector $\vec{\eta}$ effectively deforms a sphere into a uniaxial ellipsoid, where $\vec{V}_3 = \vec{\eta}$ gives the local direction of its long axis, while the degenerated directions perpendicular to it, $\vec{V}_1$ and $\vec{V}_2$, give the direction of the smallest axis of the ellipsoid.

The eigenvalues $\{E_i\}$ that measure the relative amount of anisotropy of the nematic domains are functions of the parameter g. This finding reveals the meaning of this parameter. For example, when $g = 0$ the system is isotropic and, as g becomes non-null, a uniaxial phase is found. Furthermore, as the trace of the strain tensor μ_{ii}, given in Eq. (11), measures the relative variation of volume of an elastic domain,

$$\mu_{ii} = \Delta v = \frac{1}{2}\left(-\frac{g}{3}\delta_{ii} + \eta_i\eta_i\right) = \frac{1}{2}(-g + \eta^2), \tag{18}$$

the parameter g can be expressed as

$$g = \eta^2 - 2\Delta v, \tag{19}$$

showing that g is fixed by the deformation of the elastic domain. Under these conditions the eigenvalues of the system become

$$E_1 = 1 - \frac{\eta^2 + 2\Delta v}{3}, \quad E_2 = 1 - \frac{\eta^2 + 2\Delta v}{3},$$

$$E_3 = 2 - \frac{\eta^2 + 2\Delta v}{3}, \tag{20}$$

which reveals a connection between the eigenvalues $\{E_i\}$ and the length of the eigenvector $\vec{\eta}$. Consequently, the length of η can be used to study the anisotropy of the system. That is, assuming that η^2 is position dependent, we can take on the assumption that the deformation of the elastic domains is not homogeneous.

As a further simplification, notice that when the deformation preserves volume, $\Delta v = 0$, it is found that

$$g = \eta^2,$$

implying that the strain tensor, which under this condition coincides with the order parameter [Eq. (13)], assumes the form

$$Q_{ij} = \mu_{ij} = \frac{1}{2}\left(-\frac{\eta^2}{3}\delta_{ij} + \eta_i\eta_j\right), \tag{21}$$

where the constant G has been fixed with the value $G = 1$.

This order parameter is similar to the order parameter which describes the nematic-isotropic phase transition of the usual nematic liquid crystals, as expected. But, contrary to what happens in that case, the order parameter here is not restricted to the description of the alignment of the system along the director direction; as η^2 need not be constant along the sample, the order parameter that we have constructed also describes the intensity of the domain deformation along the director direction. It is important to notice that the non-constancy of η^2, and its presence in the order parameter, arises naturally from the theory that we have developed. The origin of this result stays in the utilization of the strain tensor as the physical property utilized in the construction of the order parameter. Nevertheless, it is easy to obtain a normalized director direction ($\vec{N}$) from the theory; it is sufficient to make

$$N_i = \frac{\eta_i}{\sqrt{\eta^2}}, \tag{22}$$

which will lead to an order parameter restricted to the description of the uniaxial elastomer orientational properties. Hence the order parameter given by Eq. (21) encompasses in the same mathematical object, the main direction for defor-

mations, the director direction, and the relative amount of such deformation.

To complete the development of the tools usually utilized in the study of nematic materials, a scalar order parameter will be defined. Following the form given by Eq. (21), the scalar order parameter Q is defined through the usual relation

$$\left\langle \frac{1}{3}\eta^2 \delta_{\alpha\beta} - \eta_\alpha \eta_\beta \right\rangle = Q\left(\frac{1}{3}\delta_{\alpha\beta} - n_\alpha n_\beta \right) \qquad (23)$$

where $\vec{n}$ fixes a normalized direction at the point under consideration and $\langle x \rangle$ gives the statistical average of the random variable x. A straightforward calculation shows that

$$Q = \frac{3}{2}\left(\langle \vec{\eta} \cdot \vec{n} \rangle^2 - \frac{1}{3}\eta^2 \right). \qquad (24)$$

This scalar order parameter describes simultaneously the amount of "order" along the direction n and the intensity of the elongation of the domain along such direction, as expected. Furthermore, it reduces to the usual nematic order parameter when a fixed elongation of the elastic domain, i.e., $\eta^2 = 1$, is considered.

Concluding, as the vector $\vec{\eta}$ is not normalized and the deformation described by the strain tensor given at Eq. (14) is uniaxial, this tensor is apt to be used in an order parameter describing the elastic nematic-isotropic phase transition. Finally, Eq. (14) is similar to the expression used in Eq. (3) and, as demonstrated in this study, such resemblance is not accidental; in both cases they describe the affine transformation that changes spheres into ellipsoids.

III. MEAN FIELD ELASTIC ENERGY

The Landau–de Gennes approach will be utilized to get a mean field elastic free energy for the NE. It will be assumed that in the neighborhoods of the nematic-isotropic phase transition, the elastic free energy can be expressed through a polynomial expansion in terms of the order parameter and its derivatives, i.e.,

$$F_{el} = E_0 + a_{ij}\mu_i\mu_j + b_{ijkl}\mu_i\partial_j Q_{kl} + c_{ij}Q_{ij} + d_{ijkl}Q_{ij}Q_{kl}$$
$$+ L_{kij}\partial_k Q_{ij} + M_{ijklmn}(\partial_i Q_{jk})(\partial_l Q_{mn}) \qquad (25)$$

where the expansion coefficients a_{ij}, c_{ij}, L_{kij}, b_{ijkl}, d_{ijkl}, and M_{ijklmn} are tensors that depend on the parameters of the theory, E_0 is a constant, and μ_i is the deformation imposed to the sample along the direction i, which has already been defined by Eq. (6). This theory will be complete when an explicit form for all these tensorial coefficients is carried out using the symmetries of the theory. Hence it will be assumed that

(a) each one of these coefficients must be a function of η_i, δ_{ij}, and ϵ_{ijk}. As η_i is the unique natural vectorial object of the theory the necessity of its presence in these tensorial coefficients is immediate. Furthermore, the possible existence of symmetries undergoing changes of indexes in each of these coefficients relies on the assumption that they must also be a function of δ_{ij} and ϵ_{ijk}; and

(b) due to the nature of the elastic deformation, the

elongations η_i and $-\eta_i$ are indistinguishable, having the same energy.

There are in Eq. (25) tensorial coefficients of zero, second, third, fourth, and sixth orders to be determined. A simple explicit form for each of these tensors is exhibited below.

So, the simplest first order tensor is given by

$$T_i^1 = C_0 \eta_i; \qquad (26)$$

where the index n over the tensor $T_{ij\dots}^n$ gives the rank of the tensor and C_i, $i = 0, 1, 2, \dots$ is a generic notation for constants that will be used along the forthcoming developments. Similarly, the simplest second-order tensor that can be constructed from the natural objects mentioned above is given by

$$T_{ij}^2 = C_1 \eta_i \eta_j + C_2 \delta_{ij} + C_3 \eta_k \epsilon_{kij}. \qquad (27)$$

To construct this object, all linear combinations of tensors of second order, such as δ_{ij} and $\eta_k \epsilon_{kij}$, and the possibility that it can be the result of product of lower-order tensors, such as $\eta_i \eta_j$ have been considered.

Using a similar reasoning, it can be seen that the third-order tensor has the form

$$T_{ijk}^3 = C_6 \epsilon_{ijk} + C_7 A_{ijk}^3 + C_8 A_{ikj}^3 + C_9 A_{jki}^3 + C_{10}A_{jik}^3 + C_{11}A_{kij}^3$$
$$+ C_{12}A_{kji}^3 \qquad (28)$$

where $A_{ijk}^3 = T_i^1 T_{jk}^2$.

Similarly, the tensors of fourth and sixth orders are given by

$$T_{ijkl}^4 = C_{13}T_i^1 A_{jkl}^3 + C_{14}T_j^1 A_{ikl}^3 + C_{15}T_k^1 A_{ijl}^3 + C_{16}T_l^1 A_{ijk}^3$$
$$+ C_{17}T_{ij}^2 T_{kl}^2 + C_{18}T_{ik}^2 T_{jl}^2 + C_{19}T_{il}^2 T_{jk}^2, \qquad (29)$$

and

$$T_{ijklmn}^6 = C_{21}A_{ijk}^3 A_{lmn}^3 + C_{22}A_{ijl}^3 A_{kmn}^3 + C_{23}A_{ijm}^3 A_{k\,ln}^3$$
$$+ C_{24}A_{ijn}^3 A_{klm}^3 + C_{25}A_{ikl}^3 A_{jmn}^3 + C_{26}A_{ikm}^3 A_{j\,ln}^3$$
$$+ C_{27}A_{ikn}^3 A_{jlm}^3 + C_{28}A_{ilm}^3 A_{jkn}^3 + C_{29}A_{i\,ln}^3 A_{jkm}^3$$
$$+ C_{30}A_{imn}^3 A_{jkl}^3 + C_{31}A_{ij}^2 A_{kl}^2 A_{mn}^2 + C_{32}A_{ij}^2 A_{km}^2 A_{ln}^2$$
$$+ C_{33}A_{ij}^2 A_{kn}^2 A_{lm}^2 + C_{34}A_{ik}^2 A_{jl}^2 A_{mn}^2 + C_{35}A_{ik}^2 A_{jm}^2 A_{ln}^2$$
$$+ C_{36}A_{ik}^2 A_{jn}^2 A_{lm}^2 + C_{37}A_{il}^2 A_{jk}^2 A_{mn}^2 + C_{38}A_{im}^2 A_{jk}^2 A_{ln}^2$$
$$+ C_{39}A_{in}^2 A_{jk}^2 A_{lm}^2 + C_{40}A_{il}^2 A_{jm}^2 A_{kn}^2 + C_{41}A_{il}^2 A_{jn}^2 A_{km}^2$$
$$+ C_{42}A_{im}^2 A_{jl}^2 A_{kn}^2 + C_{43}A_{in}^2 A_{jl}^2 A_{km}^2 + C_{44}A_{im}^2 A_{jn}^2 A_{kl}^2$$
$$+ C_{45}A_{in}^2 A_{jm}^2 A_{kl}^2. \qquad (30)$$

By putting together all the above expressions, through algebraic computation, it was found that

$$E_F = \frac{1}{2}K_{11}[\vec{\nabla}\cdot\vec{\eta} - K_{12}\vec{\eta}\cdot\vec{\nabla}(\eta^2)]^2 + \frac{1}{2}K_{13}(\vec{\eta}\cdot\vec{\nabla}(\eta^2))^2$$

$$+ \frac{1}{2}K_{33}[\vec{\eta}\times(\vec{\nabla}\times\vec{\eta}) - K_{31}\vec{\nabla}(\eta^2)]^2 + \frac{1}{2}K_{32}(\vec{\nabla}(\eta^2))^2$$

$$+ \frac{1}{2}K_{23}[\vec{\eta}\cdot(\vec{\nabla}\times\vec{\eta})]^2 + \frac{1}{2}K_{21}(\vec{\nabla}\times\vec{\eta})^2 + \frac{1}{2}\Omega_1\eta^2$$

$$+ \frac{1}{4}\Omega_2\eta^4 + \frac{1}{2}K_{41}(K_{42}-\eta^2)\vec{\nabla}\cdot\left(\frac{1}{2}\vec{\nabla}(\eta^2) - \vec{\eta}(\vec{\nabla}\cdot\vec{\eta}) - \vec{\eta}\right.$$

$$\left.\times(\vec{\nabla}\times\vec{\eta})\right) + \frac{1}{2}\epsilon_0(\vec{\mu}\cdot\vec{\eta})^2 + \frac{1}{2}\bar{\epsilon}_1(\vec{\mu}\times\vec{\eta})^2$$

$$+ p_1(\vec{\mu}\cdot\vec{\eta})\vec{\nabla}\cdot\vec{\eta} + p_2[(\vec{\mu}\cdot\vec{\nabla})\eta^2 - \Delta\vec{l}\cdot(\vec{\eta}\times(\vec{\nabla}\times\vec{\eta}))]$$

$$+ p_3(\vec{\mu}\cdot\vec{\eta})(\vec{\eta}\cdot\vec{\nabla}\eta^2) \tag{31}$$

where K_{ij} is the new elastic constants that are function of the C_i's, and ϵ_0, ϵ_1, p_1, and p_2 are the coefficients coupling the deformations imposed externally with the internal deformations of the elastic domains. A procedure similar to the one used in the development that goes from Eq. (26) or (30) to Eq. (31), and with the details of the calculations, can be found, for example, in [13] and [14].

Let us put forward some comments on the meaning of this free energy by examining the conditions for its stability and its form when the elongation of the elastic domains is uniformly frozen along the entire sample. The stability of the elastic deformations requires that

$$K_{11}\geqslant 0, \quad K_{13}\geqslant 0, \quad K_{33}\geqslant 0, \quad K_{32}\geqslant 0, \quad K_{23}\geqslant 0,$$

$$K_{21}\geqslant 0, \quad \Omega_2\geqslant 0.$$

Once $\Omega_2>0$, there are no constraints on Ω_1. So it can assume negative values. Later, an experiment which suggests that $\Omega_1<0$, implying that the corresponding structures are metastable, is discussed. Furthermore, when the elongation of the elastic domains becomes uniform, assuming the same value at all points of the sample, $\eta^2\rightarrow$const, or $\vec{\nabla}(\eta^2)=0$, the above elastic energy becomes formally identical to the Frank free energy of a nematic liquid crystal becoming, therefore, restricted to the description of an orientational interaction between neighboring elastic domains. As the difference between these two free energies is given by these local length variations of the elastic domains, we must conclude that Eq. (31) considers at least three kinds of contributions to the energy stored in the elastic domains; the energy stored in these local variations of elongations, the energy stored in the interaction between the elements giving the orientational order to the elastomer, and the interaction between them.

IV. PATTERN FORMATION

In this section, the theory developed above will be used to describe a nonhomogeneous pattern formation phenomenon found by Godinho *et al.* [10] in an elastomeric thin film of urethane/urea. It is important to observe that there are not concluding experimental evidences showing that this elas-
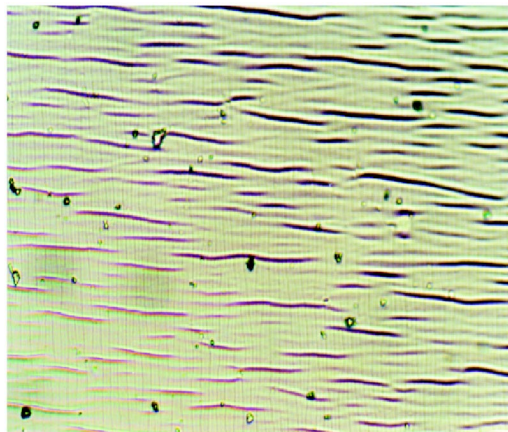

FIG. 1. Texture observed, under a polarizing microscope, when a stretching external force is applied on a membrane of urethane/urea along the direction indicated by the arrow; its length indicates 20 μm. The stripes are extended along the direction of the external force, having a well-defined periodicity along the perpendicular direction. (Courtesy of Professor Dr. M. H. Godinho.)

tomer has in fact a nematic character; however, there are some non-nematic systems that present periodic patterns when submitted to an externally induced tension [15]. Since the results that will be presented next have a strong agreement with the experimental observations, the results found in this section can be taken as an indication of the uniaxial nature of the elastic phase observed in the urethane or urea membrane. Although it recognizes that the nematic nature of the urethane or urea membrane may not be confirmed by forthcoming experimental research, this section remains as a nontrivial exercise of application of the theory developed above.

Godinho *et al.* [10] have observed that when a thin film of urethane/urea is submitted to an alternating sequence of deforming mechanical stresses, an unusual succession of structures is observed in the sample. Before the first application of an externally induced deformation, the elastomer seems to be isotropic and slightly translucent. But, once a mechanical stress is applied, the film becomes transparent with a set of textures observable by a polarizing microscope. A remarkable aspect of this process concerns the behavior and form assumed by these textures when the mechanical stress is switched on and off. As it is shown in Fig. 1, when the elastic film is stretched, a periodic structure (stripes) parallel to the axis of the extending direction and with a wave vector perpendicular to the stretching direction is observed. These stripes are similar to those observed by Kundler and Finkelmann in homogeneous aligned elastomers [8]. Nevertheless, a fundamental difference has been found. When the mechanical stress is removed, the elastomer does not return to its initial condition. Even with its undeformed dimensions apparently restored, a new set of structures (bands) arises in the sample, and a texture consisting of periodic, long, black, parallel, fine equidistant lines perpendicular to the direction of the axis of the previous applied mechanical stress is observed (see Fig. 2). Furthermore, this process is cyclic; when the membrane is elongated again, the bands perpendicular to
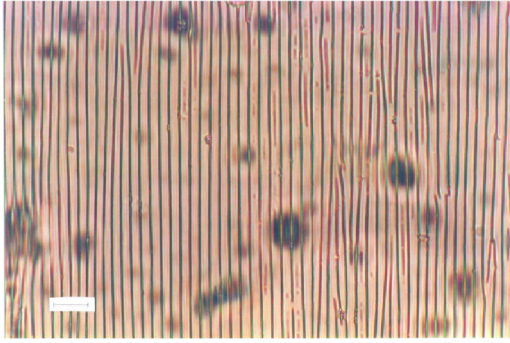
FIG. 2. Texture observed, under a polarizing microscope, when a stretching external force has been removed from the membrane that have had a texture like the one described in the Fig. 1. These new bands, observed in a situation where there is not an external force, are perpendicular to the old ones being also one-dimensional and periodic. The line indicates the direction of the preexisting force; its length indicates 20 μm. (Courtesy of Professor Dr. M. H. Godinho.)

the external force disappear, and the stripes parallel to the external force reappear. However, when the externally induced deformation is again reduced to zero, the process is inverted, the bands reemerge and the stripes disappear. It has also been observed that the presence of one of these structures does not prevent us from observing the other, Fig. 3, where an interval of external forces where they coexist can be seen. That is, as the induced extension is being reduced, and the stripes parallel to it are disappearing, the perpendicular bands begin to appear and, along a certain interval, they live together.

Next, the use of the elastic energy proposed in Eq. (29) to describe the textures found by Godinho *et al.* [10] is discussed. In this study, only the lower order terms of the theory
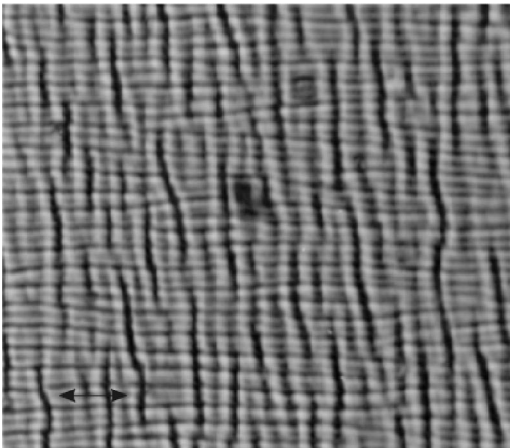

FIG. 3. Texture observed, under a polarizing microscope, showing a combination of both textures observed in Figs. 1 and 2. To produce this texture the elastomer has been initially stretched in such a way that the texture of Fig. 1 is obtained. Afterwards, the external force has been gradually reduced and, before it reaches at a null value, the two textures are found living together. The length of the arrow indicates 20 mm. (Published with authorization of Proof. Dr. M. H. Godinho.)

will be considered. Notice that in that equation $\vec{\eta}$ appears having various different orders. For example, the term coupled by K_{21}, $(\vec{\nabla} \times \vec{\eta})^2$, is of a second order in $\vec{\eta}$, while the term coupled by K_{13}, $(\vec{\eta} \cdot \vec{\nabla}(\eta^2))^2$, is of a sixth order. Our approximation restricts our study to the linear part of the differential equations describing the theory. The effect of the nonlinear terms will be considered in a forthcoming paper. So, considering the lowest order in $\vec{\eta}$, and ignoring the boundary effects described by the term coupled by K_{41}, we have

$$
\begin{aligned}
E_F \simeq {} & \frac{1}{2}K_{11}(\vec{\nabla} \cdot \vec{\eta})^2 + \frac{1}{2}K_{21}(\vec{\nabla} \times \vec{\eta})^2 + \frac{1}{2}\Omega_1\eta^2 + \frac{1}{2}\epsilon_0(\vec{\mu} \cdot \vec{\eta})^2 \\
& + \frac{1}{2}\bar{\epsilon}_1(\vec{\mu} \times \vec{\eta})^2 + p_1(\vec{\mu} \cdot \vec{\eta})\vec{\nabla} \cdot \vec{\eta} + 2p_2[(\vec{\mu} \cdot \vec{\nabla})\eta^2 \\
& - \Delta\vec{l} \cdot (\vec{\eta} \times (\vec{\nabla} \times \vec{\eta}))].
\end{aligned}
\tag{32}
$$

As the deformation externally imposed to the membrane is fixed along a constant direction, it can be assumed that $\vec{\mu} = (\mu_x, 0, 0)$. Minimizing the resulting equation with relation to $\vec{\eta}$ it can be shown that

$$
\begin{aligned}
& -K_{11}\frac{\partial^2 \eta_x}{\partial x^2} + (K_{21} - K_{11})\left(\frac{\partial^2 \eta_y}{\partial xy} + \frac{\partial^2 \eta_z}{\partial xz}\right) - K_{21}\left(\frac{\partial^2 \eta_x}{\partial y^2} + \frac{\partial^2 \eta_x}{\partial z^2}\right) \\
& + \mu_x(p_1 - 2p_2)\left(\frac{\partial \eta_y}{\partial y} + \frac{\partial \eta_z}{\partial z}\right) + \eta_x(\epsilon_0^2\mu_x^2 + \Omega_1) = 0, \quad (33)
\end{aligned}
$$

$$
\begin{aligned}
& -K_{11}\frac{\partial^2 \eta_y}{\partial y^2} + (K_{21} - K_{11})\left(\frac{\partial^2 \eta_x}{\partial xy} + \frac{\partial^2 \eta_z}{\partial yz}\right) - K_{21}\left(\frac{\partial^2 \eta_y}{\partial x^2} + \frac{\partial^2 \eta_y}{\partial z^2}\right) \\
& + \mu_x(p_1 - 2p_2)\frac{\partial \eta_x}{\partial y} + \eta_y(\bar{\epsilon}_1^2\mu_x^2 + \Omega_1) = 0,
\end{aligned}
\tag{34}
$$

$$
\begin{aligned}
& -K_{11}\frac{\partial^2 \eta_z}{\partial z^2} + (K_{21} + K_{11})\left(\frac{\partial^2 \eta_x}{\partial xz} + \frac{\partial^2 \eta_y}{\partial yz}\right) - K_{21}\left(\frac{\partial^2 \eta_z}{\partial x^2} + \frac{\partial^2 \eta_z}{\partial y^2}\right) \\
& + \mu_x(p_1 - 2p_2)\frac{\partial \eta_x}{\partial z} + \eta_z(\bar{\epsilon}_1\mu_x^2 + \Omega_1) = 0
\end{aligned}
\tag{35}
$$

give the solutions that minimize Eq. (32). This is a set of linear coupled second-order differential equations containing first-order derivatives that, independently of any boundary condition, damp all oscillations presented by the solutions of the system, eliminating any possibility of extended patterns. Consequently, to describe textures these first-order derivatives must be null, that is

$$
\frac{\partial \eta_y}{\partial y} + \frac{\partial \eta_z}{\partial z} = 0,
$$

$$
\frac{\partial \eta_x}{\partial y} = 0,
$$

$$
\frac{\partial \eta_x}{\partial z} = 0.
\tag{36}
$$

As all these terms depict polarizations of the NE, the imposition of these conditions is equivalent to affirm that, in the sample the geometry acquired by the induced textures assumes a configuration that prevents any local polarization. As shown further in this study, this is the origin of the one-dimensional regularity observed in these patterns. So, by substituting these conditions in the above-differential equations, that system of differential equations becomes

$$-K_{11}\frac{\partial^2 \eta_x}{\partial x^2} + \eta_x(\Omega_1 + \epsilon_0 v \mu_x^2) = 0, \tag{37}$$

$$-K_{21}\left(\frac{\partial^2 \eta_y}{\partial x^2} + \frac{\partial^2 \eta_y}{\partial y^2} + \frac{\partial^2 \eta_y}{\partial z^2}\right) + \eta_y(\Omega_1 + \epsilon_1 \mu_x^2) = 0, \tag{38}$$

$$-K_{21}\left(\frac{\partial^2 \eta_z}{\partial x^2} + \frac{\partial^2 \eta_z}{\partial y^2} + \frac{\partial^2 \eta_z}{\partial z^2}\right) + \eta_z(\Omega_1 + \epsilon_1 \mu_x^2) = 0. \tag{39}$$

That constitutes, in this approximation, a set of differential equations describing uncoupled elastic deformations. These deformations are coupled by a different set of elastic constants. The deformation η_x is coupled through K_{11}, which according to Eq. (31) describes a kind of splay deformations in the nematic elastomer. While η_y and η_z are coupled through K_{21}, which describes a kind of twist deformation, meaning that the deformations occurring in the sample have two different topologies. Likewise, the constants coupling the imposed global elastic deformation with the deformation vector, ϵ_0 and ϵ_1, also present the same difference, ϵ_0 being the susceptibility attributed for η_x and ϵ_1 the susceptibility attributed for η_y and η_z. In summary, the effects of the externally imposed deformation μ_x are determined by the relative values of Ω_1, ϵ_0, ϵ_1, K_{21}, and K_{11} and, as they come from different basic elastic deformations, different topologies for the corresponding patterns will be observed. Let us study the relative values of these constants by imposing that the resulting theory may describe the Godinho effect. First, it has been found that even when the external force vanishes, some textures are still observed on the bulk along the direction $\vec{e}_x$, that is $\eta_x \neq 0$ when $\mu_x^2 \rightarrow 0$. As, under these conditions, Eq. (42) becomes

$$-K_{11}\frac{\partial^2 \eta_x}{\partial x^2} + \Omega_1 \eta_x = 0,$$

and the stability of the system requires that $K_{11} > 0$, the unique way to admit the observation of the bands periodically distributed along the $\vec{e}_x$ direction when $\mu_x \rightarrow 0$ is to assume that $\Omega_1 < 0$. So, by making $\Omega_1 \rightarrow -K$, $K > 0$ we have that

$$-K_{11}\frac{\partial^2 \eta_x}{\partial x^2} - \eta_x(K - \epsilon_0 \mu_x^2) = 0.$$

Furthermore, to explain the disappearance of the periodicity of η_x along $\vec{e}_x$ as μ_x^2 increases, we must have $\epsilon_0 > 0$. So, once the elastomer is distended, the periodicity along the $\vec{e}_x$ direction will be given by
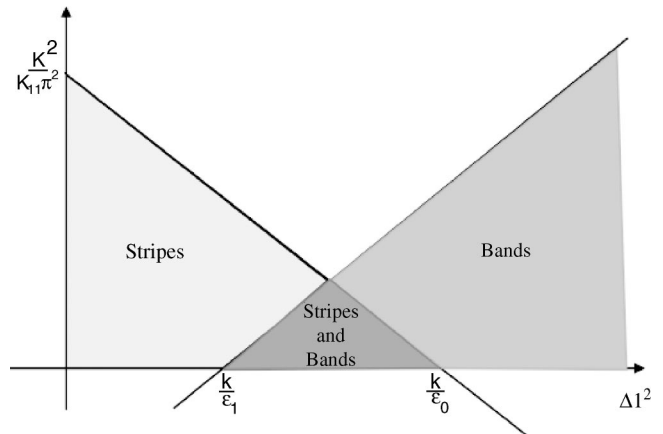

FIG. 4. Graphic representation of Eqs. (40) and (43) where the region where stripes and bands live together is detached.

$$k_x^2 = \frac{(K - \epsilon_0 \mu_x^2)}{K_{11}}. \tag{40}$$

As a result, as the externally induced deformation μ_x increases, the periodicity k_x diminishes in such a way that when it becomes greater than $\mu_x^2 > K/\epsilon_0$, the real solutions become hyperbolic and no periodicity along $\vec{e}_x$ will be observed; exactly what has been observed in the Godinho experiment.

In order to study the behavior of the deformations η_y and η_z, described by Eqs. (38) and (39) the boundary conditions acting on the system must be considered. A detailed study of the boundary conditions acting on the system on these conditions can be found in [8]. It will be assumed, due to the connection of the membrane to its x borders, $x=0$ and $x=L_x$, being not tied along its y and z borders we must have

$$\frac{\partial \eta_y}{\partial x} = \frac{\partial \eta_y}{\partial z} = 0 \tag{41}$$

leading to

$$K_{21}\frac{\partial^2 \eta_y}{\partial y^2} + \eta_y(K + \epsilon_1 \mu_x^2) = 0. \tag{42}$$

These equations show that, as the stability of the system requires that $K_{21} > 0$ the periodicities observed along the $\vec{e}_y$ direction, the stripes, can be explained if it is admitted that $\epsilon_1 < 0$. With these hypotheses, and making the changes $\Omega_1 \rightarrow -K$, with $K > 0$, $\epsilon_1 \rightarrow -\bar{\epsilon}_1$ with $\epsilon_1 > 0$, and $\epsilon_0 > 0$ it is found that Eq. (38) becomes

$$K_{21}\frac{\partial^2 \eta_y}{\partial y^2} + \eta_y(K - \bar{\epsilon}_1 \mu_x^2) = 0,$$

which has a non-null solution, with a periodicity given by

$$k_y^2 = \frac{\epsilon_1 \mu_x^2 - K}{\pi^2 K_{21}}. \tag{43}$$

In Fig. 4 a superposition of the graphs generated by Eqs.

(40) and (43) is shown. This figure shows that there is a range of values of the external force where stripes and bands can be found together, exactly what has been found experimentally.

V. FINAL REMARKS AND CONCLUSION

The main result of this paper has been the elaboration of a mean field elastic theory describing properties of a uniaxial nematic elastomer. The construction of an order parameter for the elastomeric nematic-isotropic phase transition has been essential to such an approach. This order parameter generalizes the corresponding order parameter of the usual nematic liquid crystals, which, besides the description of the degree of alignment of the nematic domain along a given direction, it also describes the elongation of the elastic domain when the sample is submitted to a deformation. At the end it has been assumed that the elastomeric sample of urethane/urea discovered by Godinho *et al.* presents an isotropic-uniaxial phase-transition being, therefore, described by the theory proposed above. Results show a good agreement between the theory and the experiment.

As a final conjecture, let us make a brief digression on the range of the theory that has been developed in this study. Notice that the theory here developed has a unique fundamental requirement: the existence of a phase transition presenting an isotropic-uniaxial symmetry change. Cited as an example, nowhere along the development of the theory has the nematic origin for the uniaxiality presented by one of the phases of the sample been used. Consequently, the theory may be applicable to every elastic material with an isotropic-uniaxial phase transition, not being restricted to isotropic-nematic phase transitions.

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