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Abstract. — We develop a molecular model of non-uniform deformations within the framework of liquid crystal rubber elasticity. The result of this work is the general expression for the free energy of deformations which combines the effects of large non-symmetric affine strains in the rubbery network and gradients of curvature deformations of the director field, \( F \sim \lambda^T (\nabla \mathbf{n})^2 \lambda \). We derive the molecular expressions for the elastic constants governing non-uniform directors in the presence of elastic strains. These constants depend on the polymer step length anisotropy \( \ell_9/\ell_1 \) and - most strikingly - have an overall negative sense. We therefore predict that in some circumstances, especially at large elastic deformations \( \lambda \), these new terms may overpower the usual, positive Frank elastic moduli of the underlying nematic structure, and also in some cases the coupling of uniform relative rotations of the director to the elastic matrix. In this event highly distorted polydomain textures \( \mathbf{n}(\mathbf{r}) \) would be favoured.

1. Introduction

A large amount of experimental and theoretical work has been invested in recent years into studies of liquid crystalline elastomers and gels. Elastomers (as opposed to hard and brittle resins) are weakly crosslinked, percolating networks of polymers chains which retain a significant molecular mobility of their strands. Rubber, therefore, is a material with a very low shear modulus \( \mu \) (about \( 10^{-4} \) – \( 10^{-5} \) times that of conventional elastic solids) and thus deforms at practically constant volume. Its weakness is matched by its capacity to withstand very large deformations, commonly 100’s % and more, thus allowing large amounts of elastic energy to be stored in the material.

Nematic liquid crystals (and liquid crystal polymers) also represent an intermediate state between conventional liquids and solids. They flow under applied stress, but they have a long range orientational order and thereby a curvature elasticity associated with deformations of this order. When these two remarkable physical systems are combined in the same material, i.e. a weakly crosslinked network is formed of mesogenic polymer chains capable of spontaneous orientational ordering, a qualitatively new state of matter emerges. Elastomers, being marginal solids, display a high molecular mobility since connected crosslinks are distant from each other and the chains of mesogenic monomers have much freedom. The axis of orientational symmetry breaking (the nematic director \( \mathbf{n} \)) is mobile too and responds to imposed elastic strains. We

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have, therefore, a uniaxial solid where the preferred direction can be altered when the body is elastically deformed; $n$ becomes an independent elastic variable. Such systems resemble the so-called Cosserat medium, where internal torques are allowed and, therefore, elastic stress can be non-symmetric.

For most deformations $n$ is anchored in the elastic medium by the crosslinking. Its rotation requires the input of some external work, but at large strains it may jump in direction. For some deformations the director is (theoretically) freely mobile, although still intimately coupled to the network, and deformations occur without resistance, that is without applied stress. Thus nematic elastomers seem to exhibit a qualitatively different elasticity from other solids and, in the non-linear regime, display nematic and mechanical transitions hitherto unknown. Elastic non-linearity is an important motivation for developing a molecular theory of nematic elastomers: rubbery networks are capable of extremely large extensions and continuum elastic models are bound to break down well before elastomers do.

Another important motivation is that a specific picture of how the mesogenic chains spontaneously change their equilibrium shape on entering the nematic phase is unnecessary for a detailed description of most liquid crystal elastomer properties. This allows a universal description of nematic elastomers, a modest extension of the classical molecular theory of conventional rubbers, independent of molecular models of liquid crystal polymers where there is much less agreement.

Experimental studies of liquid crystal elastomers began more than a decade ago [1] and various side-chain [2–5] and main-chain [6–8] materials have been investigated. However, it was quickly discovered that if the mesogenic polymer is crosslinked in the isotropic phase, the nematic phase obtaining on cooling down through the clearing point $T_{ni}$ inevitably has a scattering, highly nonuniform equilibrium texture of the director. Although the question of quenched random disorder created by misoriented crosslinks has some fundamental interest, for most practical effects and applications a uniform monodomain birefringent elastomer was preferable. Several methods of obtaining such systems have been developed, notably crosslinking in a magnetic field [9] and two-step crosslinking with stress applied in the intermediate state [10]. Experiments then showed the effects of coupling of the mobile anisotropy axis to the elastic strain field in such monodomain nematic elastomers, for example the switching of the director by the perpendicular extension has been observed [11]. Interested readers can find more information in the recent review articles [12, 13].

There has been a substantial effort in developing both the continuum (applicable only for small deformations) and the full molecular theory of nematic elastomers, which are also reviewed in [13]. Much of this effort has been successful in describing the existing and predicting new physical effects. However, all these theoretical models addressed only the problem of uniform deformations and there has been no adequate theory describing the effect of director curvature. At the same time, there are many mechanisms of director deformation, for example due to surface anchoring, disclinations, stripe instabilities [14] or in other transient regimes. Therefore, it is important to know how director curvature is affected by elastic deformations of the rubber. The present paper is devoted to this particular point: after a brief overview of the basic concepts and results of the classical theory in the next Section, we derive the full non-uniform nematic rubber elastic free energy, which depends on the products of elastic strains tensors, chain step length tensors and on the second power of $\nabla n$ (only in chiral - cholesteric - systems can we expect linear gradients of $n$ [15]). In the last Section we examine the general free energy form via simple examples and compare its effect with that of standard Frank elasticity. The main conclusion of this paper is that some of the new non-uniform rubber elastic terms are negative and, in some circumstances, may favour equilibrium non-uniform textures $n(r)$. 
2. Basic Theory of Uniform Nematic Elastomers

The first linear continuum picture of the local anchoring of the director with respect to the elastic matrix is due to de Gennes [16], the energy density being (phenomenologically)

\[ E_{\text{rot}} = \frac{1}{2} b_1 [(\Omega - \omega) \times \mathbf{n}]^2 + b_2 \mathbf{n} \cdot \mathbf{e} \cdot [(\Omega - \omega) \times \mathbf{n}]. \]  

(1)

The local rotation of the elastic medium, \( \Omega \), is given by the antisymmetric part of the infinitesimal deformation tensor, \( e_{ij}^\Omega \): \( \Omega_i = e_{ijk} e_{jk} \). \( \omega \) is the rotation of the director \( \mathbf{n} \) about an axis parallel to \( \omega \), the change in the director being for small rotations \( \delta \mathbf{n} = [\omega \times \mathbf{n}] \). The first term in equation (1) expresses the penalty for the relative director-matrix rotations. It is quite unlike usual nematic Frank elasticity, which depends on gradients of director rotation. In nematic solids uniform rotations are also penalised and the degeneracy of the local direction of orientational order is removed. The \( b_2 \) term is the first hint that it is not only rotations of the anchoring matrix that can rotate the director, but that the symmetric component of shear strain is coupled to the director as well.

More recently, molecular models of nematic elastomers have been constructed [17,18], which led to an understanding of mechanical critical points, memory of crosslinking, shifts in phase equilibria and stress-strain relations. The essential anisotropy of polymer chains leads to a straightforward modification of the conventional Gaussian rubber elasticity theory. The theory can be further developed, as in conventional networks, to account for junction point fluctuations [18] and other effects, but to understand the startling new effects visible in nematic elastomers these elaborations are not necessary. The theory is based on a single parameter, the anisotropy of the polymer strand shape, i.e. on the ratio of the mesogenic chain persistence lengths along and perpendicular to the nematic director, \( \ell_{\|} / \ell_{\perp} \). One should note that this ratio strongly depends on the molecular nature of the polymer (\( \ell_{\|} / \ell_{\perp} \sim 1.5 \) in side-chain liquid crystal polymers [14,19,20], while in a main-chain system one can find \( \ell_{\|} / \ell_{\perp} \sim 10 \) or more [21]) and that different values are predicted by the different theoretical approaches (which include freely-jointed chains, worm-like persistent chains, rotationally-isomeric chains, etc.). The happy situation in the theory of liquid crystal elastomers is that this single parameter \( \ell_{\|} / \ell_{\perp} \) is directly related to the macroscopic sample shape and can be easily measured simply by changing temperature through the nematic-isotropic transition [5] and observing the spontaneous sample shape change. After such a measurement the theory does not have any free parameters and should make accurate predictions.

The basic theory assumes that in a nematic monodomain with director \( \mathbf{n}^0 \), a given polymer chain span between connected crosslinking points, at the moment of crosslinking, is \( \mathbf{R}^0 \). If this chain is long enough (so that we obtain an elastomer, not a resin), this end-to-end distance has a Gaussian distribution:

\[ P_0(\mathbf{R}^0) \sim \text{Det}[^{ij}_k]^{-1/2} \exp \left( -\frac{3}{2\mathcal{L}} R^0_1 (R^0_1)^{-1} R^0_2 \right) \]  

(2)

(summation over repeated indices has been assumed). The matrix \( R^0_{ij} \) of effective step lengths defines the chain shape parallel and perpendicular to the director \( \mathbf{n}^0 \) for a uniaxial phase, that is

\[ \langle R^0_{ij} R^0_{ij} \rangle = \frac{1}{3} \mathcal{L} R^0_{ij} \]  

(3)

where \( \mathcal{L} \) is the chain contour length. The effective step lengths of the random walk, and thus the overall average shape, are functions of the nematic order parameter. For a uniaxial nematic one can write:

\[ \ell_{ij} = \ell_{\perp} \delta_{ij} + (\ell_{\|} - \ell_{\perp}) n_i n_j \]  

(4)
where the explicit functional form $\ell_{\parallel}(Q)$ and $\ell_{\perp}(Q)$ is dependent on the particular model of the liquid crystal polymer chain. We shall not need this information to describe the rubber-elastic effects.

Next comes the affine deformation assumption, an assumption that pervades network theory. Junction point fluctuations are damped by connectivity and in the case of very high crosslink functionality compel crosslinking points to move exactly in geometric proportion to the whole sample. We use the simplifying but unnecessary affine deformation assumption and define the current network span to be $R_s = \lambda_s R^0_s$ with $\lambda_s$ the macroscopic (Cauchy) strain tensor of the whole block of rubber. The polymer strand end-to-end vector probability is given by a distribution, $P(R)$, differing from $P_b(R^0)$ in equation (2) in that the $(\ell_{ij})^{-1}$ tensor, describing the current chain shape, depends on the current state of the nematic order after the deformation has taken place. Taking the usual quenched average for each network strand $F_{el} = -\langle k_B T \ln P(R) \rangle_{P_b(R^0)}$, one obtains the elastic free energy density describing uniform deformations of liquid crystal elastomers [22]:

$$F_{el} = \frac{1}{2} N_x k_B T \text{ Tr} [\ell^0 \times \lambda^{-1} \times \lambda],$$

(5)

where $N_x$ is the number of crosslinks per unit volume (see [18] for the insignificant corrections due to the junction point fluctuations) and we have used $\langle R^0_s R^0_{s'} \rangle = \frac{1}{3} \sigma \ell^0_{ij}$, equation (3).

There is also an additional term which arises from the normalization of $P(R)$ (see [18,23]). This term depends on the magnitude, $Q$, of the nematic order parameter which could, in principle, also be affected by elastic strains. At sufficiently low temperatures, away from the clearing point $T_{ni}$, the degree of the nematic order, and hence the polymer chains anisotropy $\ell_{\parallel}/\ell_{\perp}$ is strongly constrained by thermodynamic forces. Nematic energies are large and little perturbed by elastic distortions. It is quite safe to assume $Q = \text{ const}$. The order parameter of a nematic elastomer undergoing drastic director distortions has been measured [11,14] and indeed found unchanged. If one considers only uniform rotations of the nematic director $n$ in response to elastic strains in equation (5), the matrix $\ell_{ij}$ would be just a rotated version of $\ell_{ij}'$. We are in effect asserting that rubber elasticity is a minor perturbation on top of the nematic processes in the fluid. Indeed, all rubber effects are per polymer strand rather than per monomer. Thus (5) is weighted by the number density of strands, $N_x \sim 1/N$, where $N$ is the number of monomers on this strand, while the nematic interactions are affecting each of these monomers. Rubber elasticity arises from a restriction in the set of all possible random walks, in this case anisotropic. The separation of the rubber elasticity from the magnitude of the nematic order also suggests that the component monomers have Frank and other nematic phenomena much as they would in the uncrosslinked state. Here we are calculating rubber-elastic additions to the underlying Frank curvature energy, these additions being determined by the strand entropy rather than due to the details of nematic rod ordering at the local level. There is a corresponding separation of length scales. The director and its distortions are defined at a point. The idea of a nematic continuum will break down if the distortions are significant over molecular dimensions, in this case those of the mesogenic rods that create the nematic order. Continuum rubber elasticity will only be meaningful on length scales greater than the separation of crosslinks, a scale of order $\sqrt{N}$ greater than that for the nematic order (see the review article [13] for a detailed discussion).

The elastic free energy (5) shows a rich behaviour, based on the fact that the elastic strain tensor enters this expression in a generally non-symmetric form, unlike in any other solid material (or isotropic rubber), where one always has $F_{el} \sim \{\lambda^T \lambda\}$. Antisymmetric components of strain couple to the director rotation away from $n_0$ (given by $\ell^0$) to $n$ (the principal axis of the current step length tensor $\ell$). In particular, after implementing the limit of infinitesimal
deformations $\lambda = 1 + \epsilon$, one obtains molecular expressions for de Gennes' coupling terms in equation (1):

$$b_1 = N_x k_B T \frac{(\ell_{\|} - \ell_{\perp})^2}{\ell_{\|} \ell_{\perp}}; \quad b_2 = N_x k_B T \frac{\ell_{\|}^2 - \ell_{\perp}^2}{\ell_{\|} \ell_{\perp}}$$

(6)

(a positive coupling $b_2$ corresponds to prolate polymers, those with mesogenic units in or aligned parallel to the backbone and thus with $\ell_{\|} > \ell_{\perp}$). Several new physical effects have been predicted with the help of equation (5), notably discontinuous nematic transitions driven by an imposed elastic strain (also observed experimentally [11]), reorientation by external electric or magnetic fields and the so-called ‘soft elasticity’. However, the above arguments are applicable only in the case of uniform director rotations and uniform elastic strains. There is now firm evidence [14] that in some cases the new transitions are to states with a modulated director field.

It is the purpose of this paper to derive the non-uniform elastic free energy, by a modification of equation (5), that describes the coupling between curvature deformations and elastic strains in nematic elastomers.

3. Non-Uniform Director Field

We shall assume, as a simplifying starting point, that the director distribution before deformation, $n_0$, which is implicitly present in the initial chain step length tensor $\ell_{ij}^0$, is uniform. In other words, the polymer network has been formed in a uniform monodomain nematic state, or brought to its present state in a sufficiently strong external field. Another simplifying assumption will be that the present temperature is sufficiently below the clearing point $T_{\text{ni}}$, so that the magnitude of the nematic order (and the related chain step length anisotropy $\ell_{\|}/\ell_{\perp}$) is not changed during the deformation and only director rotation takes place. Both these assumptions are not crucial for the arguments below and a straightforward generalization to account to these effects is possible. However, these two factors, $\nabla n_0$ and $\ell_{ij}(Q)$, bring additional degrees of freedom and geometric constraints, which make the resulting elastic free energy very difficult to read. We prefer to present the main line of derivation in a more clear, albeit slightly less general form and, therefore, consider $n_0 = \text{const}$ and $\ell_{\|}/\ell_{\perp} = \text{const}$.

In order to determine the elastic response of a random polymer network to a non-uniform deformation field one has to find the statistical weight $P(R)$ of configurations of a given polymer strand in the presence of such a field. This statistical weight for a chain with a fixed contour length, $L$, is determined by the general tensor of chain persistent lengths $\ell_{ij}$, see equations (2, 5). Then the quenched averaging should be performed, exactly as in equation (5), with respect to the initial state $P(R^0)$, which is characterized by the corresponding initial $\ell_{ij}^0$ and which we assumed to be uniform. Therefore, we need to describe the configurations $\ell_{ij}(n, \nabla n)$ of a liquid crystal polymer chain in the presence of director curvature deformations. After expansion in powers of small gradients (long-wavelength limit) we should then have in a uniaxial non-chiral nematic:

$$\ell_{ij} \approx \ell_{ij}^{[u]} + \kappa_{ijkl}^{abcd}(n) \nabla_a n_b \nabla_c n_d + \ldots$$

(7)

which tells us that the shape of the polymer coil is slightly altered when the mesogenic units of this chain are subjected to a spatially non-uniform nematic mean field potential ($\ell_{ij}^{[u]}$ represents the uniaxial step length tensor of the uniform system). The statistical weight of such a chain with its end-to-end vector $R$ affected by the affine elastic deformation of the network is, as before,

$$P(R) \sim \exp \left( -\frac{3}{2L} \lambda \cdot R^0 \cdot \ell_{ij}^{-1}(n, \nabla n) \{ \lambda \cdot R^0 \}^T \right)$$

(8)
Performing the quenched averaging with the (uniform) initial probability distribution $P(R^0)$, equation (2), one obtains

$$F_{el} = \frac{1}{2} N_x k_B T \text{Tr}[\ell^0 \lambda^T \ell^{-1} \lambda] - \frac{1}{2} \ln \text{Det} [\ell^0 \ell^{-1}]$$

$$\approx F_{el}^{[u]} - \frac{1}{2} N_x k_B T \text{Tr}[\ell^0 \lambda^T \{\ldots \nabla n \nabla n \ldots\} : \lambda],$$

(9)

where the “ln Det”-term, due to the normalization of distributions $P(R)$ and $P_0(R^0)$, also makes a non-trivial contribution to the elastic energy due to the change in the persistence length matrix $\ell$. $F_{el}^{[u]}$ is the uniform liquid crystal elastomer elastic energy equation (5). Note the minus sign at the non-uniform part of $F_{el}$, which is due to the inversion $\ell^{-1}$ of equation (7) and which will appear to represent a genuinely negative free energy contribution.

How can one find $\ell_{ij}(n, \nabla n)$? Obviously a specific model of the liquid crystal polymer chain must be employed and the result could be very different for highly ordered main-chain mesogenic polymers (best modelled by a persistent worm-like chain) and for side-chain materials (their backbone configuration is adequately described by the much simpler freely-jointed rod model). Since the majority of existing liquid crystal elastomers are made of side-chain polymers, we shall concentrate on this case. We present a calculation of the average end-to-end distance ($R_e R_e$) of the uniaxial nematic polymer in a non-uniformly distorted director field $n(r)$, within a freely-jointed chain model. Later we shall also briefly outline the similar calculation for the main-chain worm-like nematic polymer.

Let us choose the starting point of the chain trajectory as the origin of coordinate system, then the position of the $\alpha$th monomer on the chain is given by $r^{(\alpha)} = a \sum_{\nu=1}^{\alpha} u^{(\nu)}$, where $a$ is the physical length of the monomer and $u_{\nu}$ is the tangent vector of monomer number $\nu$ on this chain. The direct product of end-to-end vectors is, therefore, $R \cdot R = a^2 \sum_{\nu, \nu'=1}^{N} u^{(\nu)} u^{(\nu')}$, where $N = L/a$ is the number of monomers on the chain. For the freely-jointed chain there is no correlation between orientations of different monomers, $u^{(\nu)}$ and $u^{(\nu')}$ for $\nu \neq \nu'$, and the shape of the polymer coil is determined by

$$\langle R_i R_j \rangle = a^2 \sum_{\nu=1}^{N} \langle u_i^{(\nu)} u_j^{(\nu)} \rangle$$

$$= \frac{1}{3} a N \sum_{\nu=1}^{N} \left[ \ell_\perp \delta_{ij} + [\ell_\parallel - \ell_\perp] a_\nu(r^{(\nu)}) n_i^{(\nu)}(r^{(\nu)}) \right]$$

(10)

(we take Latin indices to represent the vector components, $i, j = 1, 2, 3$, while Greek indices number monomers along the chain, $\alpha, \nu = 1, \ldots, N$). For the freely-jointed chain there is a trivial relation between the monomer length, step lengths and the backbone order parameter $Q$: $a = \frac{1}{3} (\ell_\parallel + 2 \ell_\perp)$; $Q = \frac{1}{3} (\ell_\parallel - \ell_\perp)/a$. In the second expression in equation (10) we explicitly expose the fact that the orientation of the principal axis of the uniaxial average $\langle uu \rangle$ depends on the position of the corresponding monomer, numbered $\nu$. This is the crux of the problem since $r^{(\nu)}$ itself depends on all the preceding monomers orientations and hence on the nematic director $n(r)$ on all these locations. The formerly simple problem of a freely-jointed random walk has become a higher order Markov process, the $\nu$th step depending on all the previous steps. This problem can be solved systematically in powers of $(\nabla n)^2$.

The end-to-end vector $R$ of a chain with $N$ monomers can also be written in a recurrent form, $R = r^{(N-1)} + a u^{(N)}$ and thus the average required in equation (10) is

$$\langle R_i R_j \rangle = \langle r_i^{(N-1)} r_j^{(N-1)} \rangle + a^2 \langle u_i^{(N)} u_j^{(N)} \rangle$$

(11)
(cross terms \( \langle r^{(N-1)} u^{(N)} \rangle \) vanish in a non-chiral system for obvious symmetry reasons). The last term in (11) is equal to \( \frac{1}{3} a(\delta_{ij} \ell_{\perp} + [\ell_{\perp} - \ell_{\perp}] n_i (r^{(N-1)} n_j (r^{(N-1)})) \) where it is explicitly noted that the directions of the \( N \)th link are biased according to the director \( n(r^{(N-1)}) \) at its starting point \( r^{(N-1)} \). Recognizing that in the long-wavelength limit the difference between \( n(r^{(1)}) \) and \( n(r^{(N)}) \) is small (which implies the upper cut-off for the curvature wave vectors, \( |q| \ll |r^{(1)}|^{-1} \), the inverted network mesh size), we perform the gradient expansion: \( n_i (r^{(N-1)}) \rightarrow n_i (r^{(1)}) + \langle (r^{(N-1)} \cdot \nabla) n_i (r^{(1)}) \rangle + \frac{1}{2} \langle (r^{(N-1)} \cdot \nabla \nabla) n_i (r^{(1)}) \rangle \) ... , where one should treat \( n_i (r^{(1)}) \) as the local current director \( n \). Substituting this into equation (11) we obtain

\[
\langle R_i R_j \rangle = \langle r^{(N-1)} r^{(N-1)} \rangle + \frac{1}{3} a(\ell_{\perp} 
_i + [\ell_{\perp} - \ell_{\perp}] n_i n_j) + \frac{1}{2} a[\ell_{\perp} n_i \nabla n_j + \nabla n_i \nabla n_j]
\]

(we have eliminated cross terms like \( \langle n_i (r^{(N-1)} \cdot \nabla n_j) \rangle \) which vanish for a non-chiral system).

So far equation (12) is exact at \( O(\nabla n)^2 \) and the problem of correlations has been set back to \( \langle r^{(N-1)} r^{(N-1)} \rangle \). This equation can now be iterated to give \( \langle r^{(N-1)} r^{(N-1)} \rangle \) in terms of \( \langle r^{(N-2)} r^{(N-2)} \rangle \) and gradients of \( n \), and so on. Each step of such iteration generates successively higher powers of \( \langle \ell_{\perp} \rangle \) \((\nabla n)^2 \) and always involves all linear terms, ignoring all powers greater than \( (\nabla n)^2 \) is equivalent to taking the uniform-\( n \) value for \( \langle r^{(N-1)} r^{(N-1)} \rangle \) (see Eq. (10) with \( N = \nu \)). In this way we obtain

\[
\ell_{ij} \equiv \frac{3}{4N} \langle R_i R_j \rangle = \ell_{\perp} \delta_{ij} + [\ell_{\perp} - \ell_{\perp}] n_i n_j + \frac{1}{6} a N [\ell_{\perp} - \ell_{\perp}] \left( (\ell_{\perp} - \ell_{\perp})(n \cdot \nabla) n_i (n \cdot \nabla) n_j + \ell_{\perp} (\nabla n_i \nabla n_j) \right) + \frac{1}{2} (\ell_{\perp} - \ell_{\perp}) [n_i (n_i : \nabla \nabla n_j + n_j (n_i : \nabla \nabla) n_i) + \frac{1}{2} \ell_{\perp} n_i \nabla^2 n_j + n_j \nabla^2 n_i]
\]

where the extra power of \( N \) has appeared due to the summation \( \sum_{\nu=1}^{N} \nu = \frac{1}{2} N(N + 1) \) of all \( \langle r^{(N-1)} r^{(N-1)} \rangle \) terms in the iterated equation (12). Inverting the matrix (13) is trivial because we should only keep the lowest (second in this case) powers of \( \nabla n \); in this limit of small gradients we obtain

\[
\ell_{ij}^{-1} \approx \ell_{ij}^{[u]} - \frac{1}{6} a N (\ell_{\perp} - \ell_{\perp}) \ell_{ij}^{[um]} - 1 \left[ \right]_{\nu} \ell_{ij}^{[u]^{-1}},
\]

where \( \ell_{ij}^{[u]} \) is the local "uniform" step length tensor depending on \( n \), and the expression in square brackets should be directly taken from equation (13).

All that remains is to substitute this inverse of the non-uniform step length tensor in the general local rubber-elastic free energy density equation (9) and integrate by parts in order to convert the result to the form consistent with \( (\nabla n)^2 \) only (instead of having the second-derivative terms, suggested by Eq. (13)). This integration by parts is quite tedious and strictly speaking, since the elastic strain tensor is in general a function of coordinates, will generate derivatives of \( \lambda \) too. However, it is common in elasticity theories to neglect the gradients of strains (which correspond to second derivatives of displacement in infinitesimal models). We, accordingly, shall ignore the terms of the form \( \{ \lambda^2 (\nabla n)^2 \} \) in favour of the coupling to the uniform part of strains \( \{ \lambda^2 (\nabla n)^2 \} \), which bears a superficial similarity with the nematic Frank free energy and rubber-elastic energy (5). In this case the algebra is straightforward and
we obtain the main result of this paper, the elastic free energy density of non-uniform director deformations in nematic elastomers (compare with Eq. (9)):

$$\Delta F_{el} = -\frac{1}{2} \kappa_1 \text{Tr} \left[ \epsilon^{0T} \lambda \{ (n \cdot \nabla) n_z (n \cdot \nabla) n_j \} \cdot \lambda \right]$$

$$- \frac{1}{2} \kappa_2 \text{Tr} \left[ \epsilon^{0T} \lambda \{ \nabla_k n_z \nabla_k n_j \} \cdot \lambda \right]$$

$$- \frac{1}{2} \kappa_3 \text{Tr} \left[ \epsilon^{0T} \lambda \{ n_z n_j \} \cdot \lambda \right] [(n \cdot \nabla) n]^2$$

$$- \frac{1}{2} \kappa_4 \text{Tr} \left[ \epsilon^{0T} \lambda \{ n_z n_j \} \cdot \lambda \right] (\nabla_k n_i)(\nabla_k n_l)$$

$$+ \frac{1}{2} \kappa_5 \left( \text{Tr} \left[ \epsilon^{0T} \lambda \{ n_z (n \cdot \nabla) n_k \nabla_k n_z + n_j (n \cdot \nabla) n_k \nabla_k n_z \} \cdot \lambda \right] \right)$$

$$+ \text{Tr} \left[ \epsilon^{0T} \lambda \{ n_z n_z + n_j (n \cdot \nabla) n_z \} \cdot \lambda \right] \text{div} n$$

$$+ \frac{1}{2} \kappa \left( (\ell_{||} - \ell_{\perp}) [(n \cdot \nabla) n]^2 + \ell_{\perp} (\nabla_k n_i)(\nabla_k n_l) \right),$$

where the elastic constants have the form

$$\kappa_1 = \frac{1}{6} \rho k_B T a \frac{(\ell_{||} - \ell_{\perp})^3}{\ell_{||} \ell_{\perp}^2}; \quad \kappa_2 = \frac{1}{6} \rho k_B T a \frac{(\ell_{||} - \ell_{\perp})^2}{\ell_{||} \ell_{\perp}};$$

$$\kappa_3 = \frac{1}{6} \rho k_B T a \frac{(\ell_{||} - \ell_{\perp})^2}{\ell_{||} \ell_{\perp}}; \quad \kappa_4 = \frac{1}{6} \rho k_B T a \frac{(\ell_{||} - \ell_{\perp})^2}{\ell_{||} \ell_{\perp}};$$

$$\kappa_5 = \frac{1}{12} \rho k_B T a \frac{(\ell_{||} - \ell_{\perp})^2}{\ell_{||} \ell_{\perp}}; \quad \kappa = \frac{1}{6} \rho k_B T a \frac{(\ell_{||} - \ell_{\perp})^2}{\ell_{||} \ell_{\perp}},$$

and where \( \rho = N_x N \) is the total number density of monomers in the system. The last term in equation (15), which does not depend on the elastic strain \( \lambda \), is the effect of the “\( \ln \text{Det} \)”-term due to the normalization in (9).

There can be different representations of the elastic constants, using chain step lengths, or the physical monomer length along with the backbone order parameter. Experimentally, perhaps the most easily accessible parameters of the material are the monomer size \( a \) (simply from its chemical structure) and the aspect ratio of the nematic polymer chain \( r = \ell_{||}/\ell_{\perp} \) (from neutron scattering or from the sample shape change on isotropization), which is also the single parameter of the “uniform” theory [22] and determines all elastic instabilities. In these variables, the five non-uniform nematic rubber-elastic constants take the form:

$$\tilde{\kappa}_1 = \frac{1}{2} \rho k_B T a^2 \frac{(r - 1)^3}{r(r + 2)}; \quad \tilde{\kappa}_2 = \frac{1}{2} \rho k_B T a^2 \frac{(r - 1)^2}{r(r + 2)};$$

$$\tilde{\kappa}_3 = \frac{1}{2} \rho k_B T a^2 \frac{(r - 1)^2}{r^2(r + 2)}; \quad \tilde{\kappa}_4 = \frac{1}{2} \rho k_B T a^2 \frac{(r - 1)^2}{r^2(r + 2)};$$

$$\tilde{\kappa}_5 = \frac{1}{4} \rho k_B T a^2 \frac{(r - 1)^2}{r(r + 2)}.$$

In order to complete these equations, an additional factor of \( \ell_{\perp} \) has been pulled out of the tensor \( \ell^0 \) in the traces in equation (15), so that the initial step length tensor \( \ell_{ij}^0 \) there should now be regarded as dimensionless, \( \ell_{ij}^0 = \delta_{ij} + (r - 1)n_i^0 n_j^0 \). For freely jointed rod polymers
\[ \ell_\perp = \frac{3\alpha}{r + 2}. \] One can immediately notice that the dimensions of the elastic constants \( \kappa \) is energy per length, the same as the Frank constants of a nematic.

The reader should be reminded that the above derivation is performed explicitly within the framework of the freely jointed rod model for the polymer chain. In the most general case there could be two more non-uniform nematic rubber elastic terms, arising from the persistent correlations along the chain.

\[ \frac{-1}{2 \kappa_8} \text{Tr} \left[ \ell^0 \lambda^T \{ \delta_{ij} \} \cdot \lambda \right] [\nabla n] \right) + \frac{-1}{2 \kappa_7} \text{Tr} \left[ \ell^0 \lambda^T \{ \delta_{ij} \} \cdot \lambda \right] (\nabla_k n_i)(\nabla_k n_i) \right) \] (18)

The effect of these two terms is not qualitatively different from the terms \( \kappa_3 \) and \( \kappa_4 \) of the main equation (15) and, since they depend only on the symmetric product of strains \( \lambda^T \lambda \), no new nematic effects should be expected from these particular terms. We did not specifically endeavor to obtain the molecular expressions for the corresponding constants and, for all practical purposes, we should adopt the approximate equations for the elastic constants (17) of the general non-uniform nematic rubber-elastic free energy (15).

4. Discussion

From the outset, the non-uniform elastic energy of a nematic rubber attracts attention by its negatively determined structure; the qualitative form \( -\kappa \lambda^2 (\nabla n)^2 \) apparently demands an elastic distortion of the sample accompanied by a curvature deformation of the director. One, however, should be careful with conclusions because the elastic free energy (15) contains several matrix products and its overall scalar magnitude depends on the mutual orientation of several independent objects: the initial director \( n_0 \) before deformation, the elastic strain tensor, the local director \( n \) and its gradient. In addition, the effect of \( \Delta F_{el}^n \) must be considered together with two other relevant contributions, the "uniform" nematic rubber elasticity \( F_{el}^u \), equation (5), which penalizes any deviations of the director with respect to initial \( n_0 \), and the underlying, conventional Frank nematic elasticity [24], which is the response to any non-uniform deformation \( \nabla n \). In order to examine the implications of this new elastic energy we should consider some simple particular cases.

In the simplest imaginable situation one clamps the sample, thus prohibiting all uniform deformations. (There would still be a possibility for the soft material to deform in a non-uniform fashion with, say, \( \int [\lambda(z) - 1] dz = 0 \), but such an effect could be neglected in the first approximation as being of higher order in small deformations). Taking \( \lambda_{ij} = \delta_{ij} \) and collecting the similar terms, we arrive at the following expression

\[ \Delta F_{el} = \frac{1}{12 \rho k_B T a} \left( \ell_\parallel - \ell_\perp \right)^2 \left[ \frac{-\ell_\parallel - \ell_\perp}{\ell_\parallel} \left( 1 + \frac{\ell_\parallel - \ell_\perp}{\ell_\perp} (n \cdot n^0)^2 \right) \right] [\nabla n] \right) \] (19)

Here, in contrast to simple nematics, the difference between \( n^0 \) and \( n \) is a director rotation that is penalised even for uniform distortions. The energetic cost is substantial, of the order of \( \mu \approx 3 \rho k_B T / N \) per unit volume and it is thus very unlikely that such a rotation can be easily
achieved, for example the influence of external electric or magnetic fields is shown [25] to be quite insufficient to create a significant deviation of \( \mathbf{n} \) from \( \mathbf{n}^0 \). If we then take \( \mathbf{n} = \mathbf{n}^0 + \delta \mathbf{n}(\mathbf{r}) \) and retain, as usual, only the leading terms in small non-uniform deviations \( \delta \mathbf{n} \), the elastic energy simplifies dramatically to:

\[
\Delta F_{\text{el}} = -\frac{1}{12} \rho k_B T a \frac{(\ell_\parallel - \ell_\perp)^2}{\ell_\parallel} (\text{div} \mathbf{n})^2 - \frac{1}{12} \rho k_B T a \frac{(\ell_\parallel - \ell_\perp)^2}{\ell_\perp} (\mathbf{n} \cdot \nabla \times \mathbf{n})^2
\]

\[
-\frac{1}{12} \rho k_B T a \frac{(\ell_\parallel - \ell_\perp)^2}{\ell_\perp} [\mathbf{n} \times \nabla \times \mathbf{n}]^2,
\]

which has the exact form of the Frank elasticity of regular nematic liquid crystals. This is an expected conclusion, since we have eliminated all independent vector and tensor variables from our simplified, clamped system leaving only gradients of \( \mathbf{n} \). What can be considered unexpected is that the remaining combinations of elastic constants yield negative square gradient contributions to the free energy!

For completeness we also present another simplified version of the general non-uniform elastic energy (15), with infinitesimal deformations of the rubbery matrix. We define such a deformation tensor, \( e_{ij} \), as \( \lambda = 1 + \epsilon \) and obtain

\[
\Delta F_{\text{el}} = \frac{1}{6} \rho k_B T a \frac{(\ell_\parallel - \ell_\perp)^2}{\ell_\parallel} \left[ -\frac{\ell_\parallel - \ell_\perp}{\ell_\perp} (\mathbf{n} \cdot \nabla) n_i e^{S}_{ij} (\mathbf{n} \cdot \nabla) n_j - \nabla k n_i e^{S}_{ij} \nabla k n_j - n_i e^{S}_{ij} n_j \left( \frac{\ell_\parallel - \ell_\perp}{\ell_\perp} (\nabla \mathbf{n}) n_i + (\nabla k n_i) (\nabla k n_i) \right) \right. \\
+ \frac{\ell_\parallel n_i e^{S}_{ij} (\mathbf{n} \cdot \nabla) n_j \text{div} \mathbf{n} + (\nabla k n_i) (\mathbf{n} \cdot \nabla) n_j \right],
\]

where \( e^{S}_{ij} \) is the symmetric part of the infinitesimal elastic deformation tensor. At linear order in \( \epsilon \ll 1 \) there is no contribution of antisymmetric part. The effect of the linear coupling \( \sim e^{S}(\nabla \mathbf{n})^2 \), given by the equation (21), turns out to be entirely trivial: a small imposed director modulation, \( \delta \mathbf{n} \sim \theta_0 \cos qx \), induces a corresponding wave of compression-extension \( e_{zz} \sim e_{xx} \sim 1/4 Na [(\ell_\parallel - \ell_\perp)^2/\ell_\parallel] \theta_0^2 q^2 \sin^2 qx \). All effects due to the balance of angular momenta, involving antisymmetric part of strain, appear only in higher orders of expansion of the elastic energy in powers of \( \epsilon \) (the same as in the case of uniform nematic rubber elasticity, equation (5), where qualitatively new effects of strain-director coupling required substantial elastic distortions [22]).

It is important to compare the magnitude of the new elastic constants with the standard Frank constants \( K_{11}, K_{22} \) and \( K_{33} \), which work against the above destabilizing effect. The order of magnitude of our new constants is easy to estimate because they are determined by the usual entropic effects of polymers in rubber elasticity. Within orders of magnitude we have \( \kappa \sim \rho k_B T a^2 \) or, in dense thermotropic side-chain systems, \( \kappa \sim k_B T/a \sim 10^{-11} \text{J/m} \). This is comparable to values of typical Frank constants. If one considers a main-chain polymer liquid crystal, with an extremely large backbone anisotropy ratio \( r = \ell_\parallel/\ell_\perp \gg 1 \), forming a rubbery network, this comparison can become even more favourable to the new negative non-uniform nematic rubber elasticity.

As we have discussed above, this new elastic energy should be compared with the "uniform" nematic rubber elasticity, equation (5), which produces for the same clamped case

\[
F_{\text{el}}^{[u]} = \frac{1}{2} \rho e k_B T \frac{(r - 1)^2}{r} (\delta \mathbf{n})^2,
\]
i.e. the magnitude of the director rotation, whether uniform or non-uniform, is penalized by the anchoring to the clamped network [22, 25]. Let us assume that the destabilizing effect of equation (20) has won against the Frank elasticity and consider the overall orientational stability of the sample. For a qualitative analysis we take the angular deviation $\Delta \theta \sim \theta_0 \cos q x$ and write both the uniform and non-uniform parts of the elastic energy, pulling out common factors:

$$F_{el} \sim \frac{1}{2} N_x k_B T \theta_0^2 \left[ 1 - N a^2 q^2 \right]$$  \hspace{1cm} (23)

(we have neglected all other factors, like $r$, which we assume to contribute factors of order unity in a side-chain polymer system). Within equation (23), clearly, the orientational instability may occur only with very short wave lengths, $q^{-1} \sim \sqrt{\langle R^2 \rangle} \sim a N^{1/2}$ that is of the order of network mesh size. A more detailed analysis of higher order contributions, i.e. $(\nabla \mathbf{n})^4$, $(\nabla \mathbf{n})^6$, etc., would then be required. If such small textures, at the very limits of applicability of rubber and nematic network theory, were to be formed (in a typical experimental case $a N^{1/2} \sim 30 - 50 \, \text{Å}$), they would be impossible to detect by any optical method and the nematic elastomer would appear uniform. It is likely therefore that, in the equilibrium state of a nematic elastomer, spontaneous long wave-length deformations, which would be favoured by the new elastic energy $\Delta F_{el}$, are prohibited by the strong uniform anchoring of the director to the network.

This situation may be changed in three circumstances.

(i) In a mechanically unconstrained sample, or one with non-uniform distortions such that the sample is globally undistorted, there exists a possibility of having so-called "soft elastic deformations" [26, 27]. These do not give rise to the uniform part of elastic energy $F_{el}^{(u)}$, and happen when a special class of elastic strains is combined with certain director rotations in such a way that the network polymer strands are not forced to change their equilibrium shape. These strains therefore do not cause a drop in configurational entropy. One example of such a soft strain tensor could be $\lambda = \ell^{-1/2} \ell_0^{-1/2}$ (see [27] for details). Insertion of this $\lambda$ into the uniform part, $F_{el}^{(u)}$ of equation (9), that is equation (5) with uniform fields, shows trivially that this class of strains leaves the "uniform" elastic energy unchanged from the unstrained state. It can still allow a negative non-uniform contribution $\sim -\kappa (\nabla \mathbf{n})^2$. It is expected that networks crosslinked in isotropic state and then cooled down into the nematic phase should exhibit such "soft elasticity" due to their rotational invariance [28]. The destabilising negative gradient terms, restrained by the positive penalty for uniform rotation, may explain why all such elastomers in practice form scattering polydomain textures in thermodynamic equilibrium.

(ii) Another, perhaps more relevant case, when the destabilising effect of the new non-uniform elastic energy $\Delta F_{el}$ can be felt, is during the mechanically driven orientational transitions, for example the ones described in [11, 14, 22]. An imposed elastic strain overcomes the barrier to director rotation, given by the uniform energy $F_{el}^{(u)}$. The transitions predicted and observed were to a uniform, rotated state. But we now see that orientational modulations could occur in the strained state. This, of course should take place only when the new constants $\kappa$ are actually more relevant than the (stabilizing) Frank constants. We, therefore, predict that materials with higher backbone density $r = \ell_0 / \ell_1$ should be more likely to exhibit such spontaneous breaking into orientational domains during various director transitions.

(iii) It is possible, when there is sufficiently strong surface anchoring of the director in a direction in conflict with the principal axes of the imposed strain, that one can have a mechanical Fredericks transition to a non uniform state. Even if the new, negative constants do not outweigh the Frank constants in the limit equation (20), it is possible that for larger $\lambda$ and for $\mathbf{n}$ not close to $\mathbf{n}^0$, these effects help the nematic rubber elastic contributions overcome the
Frank penalty and tip the balance in favour of the distorted state with non-uniform nematic textures.

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