Soft Elasticity in Nematic Liquid-Crystal Networks.

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Liquid-crystal networks consist of weakly crosslinked polymers that are coupled to liquid-crystal molecules. The resultant hybrid system has rich elastic properties. We develop a phase field model to describe mechanical properties of a hexagonal liquid-crystal network. The hexagonal liquid-crystal network is found to have soft shear deformations. The elastic properties are predicted analytically and confirmed with numerical simulations. In addition the model naturally incorporates non-linear elasticity and dislocations or disclinations.

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Soft elasticity is an exotic elastic phenomenon found in liquid-crystal networks which incorporates liquid-crystalline order and rubber elasticity [1]. The simplest liquid-crystal network (LCN) consists of weakly crosslinked polymers with the constituent rodlike liquid-crystal molecules in the nematic phase. A nematic LCN can relieve a shear stress via the additional deformation of crosslinked polymers with the constituent rodlike liquid-crystal molecules in a liquid-crystalline environment into an ordered network. Our model could be tested experimentally in a block copolymer system that can self-assemble nematic molecules. Our system is distinct from the actuator [3], and tunable mirror-less lasers [4].

Ideally, the nematic molecules are free to wiggle about their anisotropic axes. As a consequence, when a shear deformation is applied to a nematic LCN in a plane that involves the nematic director, the nematic molecules can tilt locally such that the system retains its equilibrium configuration. This phenomena is referred to as soft elasticity [1] and is in the same spirit as the prediction of Golubovic-Lubensky that an anisotropic glass breaks spontaneously a continuous symmetry must have a vanishing shear modulus [3].

In this article we show that the phenomenon of soft elasticity is not limited to nematic gels [3] and smectic gels [1] but can also be realized in networks with more translational order. Our system is distinct from the “soft crystal” phases of a liquid crystal fluid [8] due to the topological constraints offered by the network. Our hybrid system thus shrinks or elongates spontaneously depending on the orientational distribution of the nematic molecules. Our model could be tested experimentally in a block copolymer system that can self-assemble in a liquid-crystalline environment into an ordered network. For example, a ABA triblock copolymer solution has been shown to physically crosslink when the A-type monomers are phobic to the liquid crystal solvent [3].

To capture the properties of a LCN we couple the network molecular shape to the orientational order of the background nematic molecules. The coupling is such that in the nematic phase, the network is elongated in a direction determined by the average orientation of the nematic molecules. In this state the network density field \( \psi(\mathbf{r}) \) is anisotropic. We assume that the network molecular lengths as obtained from its characteristic wavenumber \( q_0 \) is much larger than the dimension of the nematic molecules \( a \). This assumption holds in the case of the ABA triblock network system where the radius of gyration of the polymers \( R_g \approx 1/q_0 >> a \). This allows us to utilise the nematic director field \( \theta(\mathbf{r}) \) to describe the nematic molecules.

Under these conditions we propose the phenomenological free energy functional

\[
F = \int d^2r \left\{ K (\nabla \theta)^2/2 + \tau \psi^2/2 + \lambda_\psi^3/3 + \psi^4/4 + \left[ q_0^2 \psi + A\partial_{xx} \psi + B\partial_{yy} \psi + C\partial_{xy} \psi \right]_r^{2}/2 \right\},
\]

where \( A(\theta) = \cos^2 \theta + \kappa^2 \sin^2 \theta \), \( B(\theta) = \sin^2 \theta + \kappa^2 \cos^2 \theta \), and \( C(\theta) = (\kappa^2 - 1) \sin 2\theta \) and where \( K \) is the Frank elastic constant for liquid crystals, \( \kappa \) is the anisotropy ratio of the density fluctuations in the nematic state, \( \tau \) is a control parameter and \( \lambda < 0 \) is a phenomenological constant. In the limit \( \kappa = 1 \), the network fluctuations are isotropic regardless of the nematic order and thus the two fields are uncoupled.

The dynamics of the model are driven by the minimization of the free energy, i.e.,

\[
\begin{align*}
\partial \psi(\mathbf{r},t)/\partial t &= \nabla^2 [\delta F/\delta \psi(\mathbf{r})], \\
\partial \theta(\mathbf{r},t)/\partial t &= -[\delta F/\delta \theta(\mathbf{r})] + \mu \eta(\mathbf{r},t),
\end{align*}
\]

where \( \eta(\mathbf{r},t) \) is a noise field and \( \mu \) is the intensity of the noise. For simplicity, the thermal fluctuations are only incorporated in the orientational field such that \( \eta \) is assumed to be a Gaussian random function, with a mean variance \( \langle \eta(\mathbf{r},t), \eta(\mathbf{r}',t') \rangle = \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \). The square of the intensity of the noise is linearly proportional to temperature.

The equilibrium states for Eq. (11) can be determined in mean field theory by considering the minima of \( F \). We can assume that the average molecular orientation is
along the y-axis [i.e., \( \langle \theta(r) \rangle = 0 \)]. In this instance the free energy functional simplifies to

\[
F^m \approx \int d^2r \left\{ r_\perp^2 \partial_{xx} \psi + r_\parallel^2 \partial_{yy} \psi + \rho^2 \psi^2 / 2 + \tau \psi^2 / 2 + \lambda \psi^4 / 3 + \psi^4 / 4 \right\},
\]

where \( r_\parallel^2 \equiv \langle B(\theta) \rangle \), \( r_\perp^2 \equiv \langle A(\theta) \rangle \) and the brackets imply an average over the liquid crystal orientational distribution. Since the nematic director is assumed to be along the \( y \)-coordinate, from Eq. (3) we obtain that \( r_\parallel \) and \( r_\perp \) define the periodicity of the network parallel and perpendicular to the nematic director respectively.

The averaged free energy \( F^m \) is in the form of the Landau-Brazovskii (LB) phenomenological theory [10] that describes phase transitions of a uniform system to a periodic state. The only difference is the scaling factor between the two coordinates. The mean field phase diagram of this model is well known [11][12]. The approximate equilibrium solutions of the density fluctuations are then similar to the crystalline solutions of the LB theory. For example the hexagonal phase is described by

\[
\psi(x, y) = A_1 \left\{ \cos \left[ \sqrt{3} \eta_0 x / (2r_\perp) \right] \cos \left[ \eta_0 y / (2r_\parallel) \right] + \cos \left[ \eta_0 y / r_\parallel \right] / 2 \right\},
\]

where \( A_1 = 4(-\lambda + \sqrt{-15\lambda^2 + \lambda^2}) / 15 \) is the amplitude of the local density fluctuations. The sinusoidal solution Eq. (4) is the leading term approximation of a Fourier series and is only valid for \( 0 > \tau >> -1 \).

At low temperatures, the nematic molecules have a preferred direction \( \theta(r) = 0 \), in our case and thus we have \( r_\parallel^{\text{nem}} = \kappa \) and \( r_\perp^{\text{nem}} = 1 \). In the high-temperature isotropic phase, the nematic molecules have no preferred direction, i.e., \( \theta(r) \) is a random field. Thus we have \( r_\parallel^{\text{iso}} = r_\perp^{\text{iso}} = \sqrt{(\kappa^2 + 1) / 2} \). The change of \( r_\parallel \) and \( r_\perp \) with temperature highlights elongations of the network lattice due to nematic ordering. An example of the network lattice distortion is presented in Fig. 1. Spontaneous elongation of the network during an isotropic-nematic transition is a hallmark of LCNs [3].

The continuum elastic free energy of our elongated hexagonal LCN is constructed from the lattice symmetry of the network and the coupling of its rotational deformation to the nematic director orientation. It is given by

\[
E_{el} = \left\{ C_{11}(u_{xx}^2 + u_{yy}^2) + 2C_{12}u_{xx}u_{yy} + 4C_{66}u_{xy}^2 \right\} / 2 + D_1 (\theta - \omega_{xy})^2 / 2 + D_2 (\theta - \omega_{xy}) u_{xy} + K (\nabla \theta)^2 / 2,
\]

where \( u_{\alpha\beta} = (\partial_\beta u_\alpha + \partial_\alpha u_\beta) / 2 \) is the symmetric strain tensor and \( \omega_{\alpha\beta} = (\partial_\beta u_\alpha - \partial_\alpha u_\beta) / 2 \) is the antisymmetric strain tensor. \( u_{\alpha\beta} \) and \( \omega_{\alpha\beta} \) describe respectively the relative translations and rotations of the network due to an applied deformation. The first line in Eq. (5) is the elastic free energy of a two dimensional hexagonal crystal [12] and the second line is the de Gennes elastic energy [14], which describes the coupling of the nematic molecules to local fluctuations of the network strands.

We will determine the elastic moduli from our molecular free energy. We will assume that the distortions are small, so changes of the density amplitude \( \psi(x, y) \) are negligible. We will choose the molecular axis and nematic director to be along the \( y \)-axis, where \( \theta(r) = 0 \), and thus employ Eq. (3) as the effective free energy density. A pure shear distortion is described by the density \( \psi = \psi(x + \zeta y, y + \zeta x) \), where \( \zeta \) is the elastic strain. In this state the shear free elastic energy per unit area \( f_{\text{shear}} \equiv \left[ F^m(\zeta) - F^m(\zeta = 0) \right] / \text{area} \) can be calculated by substituting a one mode approximation for \( \psi \) [i.e., Eq. (4)] into Eq. (3) to obtain

\[
f_{\text{shear}} = 3 \frac{C_{66}}{32} \left( \frac{r_\parallel}{r_\perp} + \frac{r_\perp}{r_\parallel} \right)^2 \frac{u_{xy}^4}{A_0^4} + O(\zeta^4).
\]

Eq. (5) can now be used to calculate \( C_{66} \) recalling that for a pure shear \( u_{\alpha\beta} = 0 \), except for \( u_{xy} = \zeta \). This gives

\[
C_{66} = 1 \frac{\partial^2 f_{\text{shear}}}{\partial \zeta^2} = 3 \frac{3}{64} \left( \frac{r_\parallel}{r_\perp} + \frac{r_\perp}{r_\parallel} \right)^2 \frac{u_{xy}^4}{A_0^4}.
\]

At low temperatures we have \( r_\parallel^{\text{nem}} / r_\perp^{\text{nem}} = \kappa \), which means the shear modulus is strongly dependent on the network molecular anisotropy. Under a similar procedure, other physical elastic moduli such as the bulk modulus \( B_u = 3A_0^2 q_0^4 / 32 \) and the deviatoric modulus \( C_d = 3A_0^2 q_0^4 / 16 \) are obtained. These do not depend on the molecular aspect ratio [12] and note that when \( r_\parallel = r_\perp \) then \( C_d = C_{66} \) as expected for a hexagonal lattice.

A pure rotational deformation is described by the strain tensor \( \omega_{xy} = \zeta \) and \( u_{\alpha\beta} = 0 \). The elastic energy terms in Eq. (5) all vanish except the term with coefficient \( D_1 \). In this state, \( \psi = \psi(x + \zeta y, y - \zeta x) \).
FIG. 2: The free-energy density evolution after commencement of a shear flow with a shear rate $\gamma = 0.002$. The system is shown at noise strengths: $\mu = 1.0, \mu = 2.0,$ and $\mu = 5.0$ for (a)-(c) respectively. The molecular ratio is $\kappa = 2$.

evaluated free-energy density of the deformed state gives

$$D_1 = \frac{3}{16} \left( \frac{r_{\parallel}}{r_{\perp}} - \frac{r_{\perp}}{r_{\parallel}} \right)^2 \lambda_0^4 A_t^2. \tag{8}$$

From the difference between two simple shears along each coordinate we can determine $D_2$:

$$D_2 = \frac{\partial^2 f_{\text{shear}}}{\partial \zeta^2} - \frac{\partial^2 f_{\text{shear}}}{\partial \zeta^2} = \frac{3}{16} \left( \frac{r_{\parallel}^2}{r_{\parallel}^2} - \frac{r_{\perp}^2}{r_{\perp}^2} \right) \lambda_0^4 A_t^2. \tag{9}$$

The coupling moduli $D_1$ and $D_2$ vanish when the network density fluctuations are isotropic (where $r_{\perp} = r_{\parallel}$), i.e., in the isotropic liquid-crystal phase or when $\kappa = 1$. It is interesting to note that these calculations for the molecular moduli $C_{66}$, $D_1$ and $D_2$ are consistent with the theoretical result of Warner and Terentjev [1] for nematic elastomers derived from classical rubber elasticity.

When the nematic director is allowed to relax to an optimum state, then $\partial E_{el}/\partial \theta = 0$ and thus Eq. (5) reduces to

$$E_{el}^{\parallel} = C_{11} \left( u_{xx}^2 + u_{yy}^2 \right) / 2 + C_{12} u_{xx} u_{yy} + 2 C_{66} u_{xy}^2 + K D_2^2 \left( \nabla u_{xy} \right)^2 / (2 D_1^2) + K \left( \nabla \omega_{xy} \right)^2 / 2, \tag{10}$$

where $\tilde{C}_{66} = C_{66} - D_2^2 / (4 D_1)$ is the renormalized shear modulus.

From Eqs. (7), (8), and (9) we obtain the remarkable result that $\tilde{C}_{66} = 0$. This means the nematic director relaxes to cancel out the elastic energy cost for a shear deformation. In this limit, the nematic molecules “wiggle” until the deformed structure is compatible with the boundary conditions. The stability of the crystalline state at zero shear modulus requires higher orders terms, like $O(\mathcal{C}^4)$, in the elastic free energy.

To confirm these approximate analytic calculations, we numerically solve Eq (2). To examine soft elasticity, we impose a steady shear deformation by adding an advective term on the dynamics, i.e., $\partial \psi / \partial t \rightarrow \partial \psi / \partial t + V_x \partial_x \psi$, where the velocity, $V_x = \gamma y$, has a gradient in the y-axis. We set the initial nematic director orientation such that it is along the shear flow direction and we also shift our periodic boundaries to be consistent to the shear flow using the Lees-Edwards method [18]. We choose the following numerical parameters: $\tau = -0.03, \lambda = -0.9, \text{ and } K = 1$, such that the network forms a hexagonal lattice.

The influence of the shear on the total free energy density $F_s$ is displayed in Fig. 2 for three values of the thermal noise strength, $\mu$. At the lowest temperature the free energy is flat at small strains up to $\gamma t \approx 0.25$. Thus the system has the same free energy as the undeformed state at small strains. However at higher temperatures, $F_s$ increases for all shears as it is expected for a conventional network. These results are consistent with Eq. (11), since the coupling constants $D_1$ and $D_2$ vanish with increasing temperature. Thus soft elasticity vanishes with increasing temperature. We also examined the influence of the network anisotropy on the shear deformation and the results are displayed in Fig. 3 when $\kappa = 1$ the two fields are decoupled, and the elastic response is that of classical solid. When $\kappa = 1.7$ a soft regime is observed up to $\gamma t \approx 0.3$ as indicated by the flat free-energy density.

Finally it is interesting to consider the configuration of the network density $\psi(r)$ and the spatial average orien-
Evolution of the free-energy density $F$ and the nematic director orientation after commencement of a steady flow with shear a strain rate $\gamma = 0.0025$. The snapshots of the density configuration correspond to the data at the given strains. The dashed line corresponds to the linear elastic theory. ($\kappa = 2, \mu = 1.0$)

tation of the nematic molecules $\langle \theta(r) \rangle$ as the system is being sheared. The snapshots in Fig. 4 show that the network structure changes with increasing shear strain even in the elastic soft regime. A uniaxial hexagonal lattice has a continuous set of structures which within our mean field theory have the same free energy. The switching of $\langle \theta(r) \rangle$ is different from the rotational component of the shear which is given by $\omega_{xy} = \gamma t/2$. The initial dependence of $\langle \theta(r) \rangle$ on the shear can be calculated by minimizing the elastic energy $E_{el}$ for a simple shear deformation applied along the nematic director. This gives

$$\theta_{soft}(t) = (D_1 + D_2)\xi(t)/(2D_1) = \xi(t)/(1 - \kappa^2)$$  \hspace{1cm} (11)

in the long wavelength limit. As shown in Fig. 4, this prediction works quite well. After this soft regime the strain energy increases until a yield occurs, e.g., for $\kappa = 2$ at $\gamma t \approx 0.75$. Interestingly this first yield occurs without the nucleation of mobile dislocations as would occur in a normal crystalline material. Of course at higher shear dislocations do eventually appear as can be seen in Fig. 4.

We have also made numerical calculations in the case of a static strain. For small strains $\langle \theta(r) \rangle$ relaxes to the value determined by Eq. (11), and the total free energy decays to the value of the undeformed state in agreement with our mean field predictions. We tested our numerical computations for $-0.03 \leq \tau \leq -0.3$ where the hexagonal phase is stable, and these simulations indicate that the analytic results are exact as $\tau \to 0_-$, with small corrections at larger $|\tau|$. The limit $\tau \to 0_-$ is also where our sinusoidal density approximation is valid.

In summary, a model of liquid crystal networks was presented and shown by analytical and numerical methods to reproduce soft elasticity as a function of temperature and molecular shape. In addition the numerical simulations provide evidence of unusual non-linear yield mechanisms which provide avenues of future research.

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