Modulated nematic structures induced by chirality and steric polarization

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What kind of one-dimensional modulated nematic structures (ODMNS) can form nonchiral and chiral bent-core and dimeric materials? Here, using the Landau–de Gennes theory of nematics, extended to account for molecular steric polarization, we study a possibility of formation of ODMNS, both in nonchiral and intrinsically chiral liquid crystalline materials. Besides nematic and cholesteric phases, we find four bulk ODMNS for nonchiral materials, two of which, to the best of our knowledge, have not been reported so far. These two structures are longitudinal (N_{LP}) and transverse (N_{TP}) periodic waves where the polarization field being periodic in one dimension stays parallel and perpendicular, respectively, to the wave vector. The other two phases are the twist-bend nematic phase (N_{TB}) and the splay-bend nematic phase (N_{SB}), but their fine structure appears more complex than that considered so far. The presence of molecular chirality converts nonchiral N_{TP} and N_{SB} into new N_{TB} phases. Surprisingly, the nonchiral N_{LP} phase can stay stable even in the presence of intrinsic chirality.

Until very recently only four classes of nematics were recognized: (i) uniaxial and (ii) biaxial nematics for nonchiral liquid crystalline materials and (iii) cholesteric and (iv) blue phases for chiral liquid crystals [1]. The most surprising recent discovery is the identification of the fifth. In this phase, found in liquid crystalline systems of chemically *achiral* dimers [2–5], bent-core mesogens [6,7], and their hybrids [8], the molecules are arranged to form a helical superstructure with nanoscale periodicity. This periodicity is about two orders of magnitude shorter than typically found in cholesteric and blue phases of ordinary chiral materials. With the molecular centers of mass distributed randomly in space the structure belongs to the nematic class. It coined the name twist-bend nematic phase (N_{TB}). Contrary to cholesterics, the director in N_{TB} is not perpendicular to the helix axis, but precesses on a cone, with the helical axis parallel to the cone's axis. Since molecules forming N_{TB} are chemically achiral experimentally coexisting domains of opposite chirality are observed. The N_{TB} phase is stabilized below uniaxial nematic phase (N) as a result of first order N-N_{TB} phase transition on the temperature scale. Hence, we observe a fundamentally new phenomenon, namely, the *spontaneous chiral symmetry breaking* within the nematic class of materials.

Very recently the N_{TB} phase has also been reported for chemically chiral asymmetric dimers [9,10]. Interestingly, when this intrinsic molecular chirality is added, up to seven distinct nematic phases can be stabilized in one system. They involve the cholesteric phase (N^*), a blue phase, and variants of N_{TB}, all with pitch which is larger than that found for N_{TB} of achiral dimers [10].

The issue of stable N_{TB} structure has been addressed at the theoretical level in three important papers [11–13]. With the aid of elasticity theory of the director field, Meyer [11,12] and Dozov [13] have analyzed some consequences of spontaneous local bend or splay deformations of the nematic director on the polar organization of the molecules—the so-called

flexoelectric effect. While the cholesterics can fill the space with homogeneous twist it appears that the corresponding bend state should always be associated either with some twist or splay. Consequently, in the presence of spontaneous bend, the uniform nematic phase would become unstable to the formation of a modulated phase, which could be either chiral N_{TB} or nonchiral N_{SB} [13]. A prerequisite to such behavior would be the sign change of the (effective) bend Frank elastic constant, K_3. Indeed, K_3 determined experimentally in N [4,14] is anomalously small as the transition to N_{TB} is approached.

Recently, Shamid *et al.* [15] have developed Landau theory and lattice simulations of polar order and director bend deformations, correlating flexoelectricity, negative K_3, and stability of the N_{TB} and N_{SB} phases. They predicted a second-order phase transition from N to N_{TB} or N_{SB}. At the transition, the effective K_3 changes sign and the corresponding structure develops modulated polar order, averaging to zero globally. All phases are uniaxial and described using director and polarization fields.

The purpose of this Rapid Communication is to investigate how nematics can self-organize into one-dimensional modulated structures (ODMNS) for nonchiral and intrinsically chiral V-shaped molecules, using generalized Landau–de Gennes–Ginzburg (LdeG) theory. We assume that the second-rank 3×3 traceless and symmetric alignment tensor field, $\mathbf{Q}(\mathbf{r})$, is the primary order parameter accounting for nematic order [1]. It permits that locally a system is described by a tripod of orthonormal directors $\{\hat{\mathbf{n}},\hat{\mathbf{l}},\hat{\mathbf{m}}\}$ and corresponding eigenvectors $\{\lambda_n,\lambda_l,\lambda_m\}$. Identifying the full biaxial field $\mathbf{Q}$ with primary order parameter of nematics, rather than its $\hat{\mathbf{n}}$ part only [13], should also clarify whether biaxiality ($\lambda_n \neq \lambda_l \neq \lambda_m$) is relevant for N_{TB}, for we know that chiral nematic phases of at least intrinsically chiral mesogens are all biaxial [16].

For the modeling of spontaneous chiral symmetry breaking as observed in N_{TB} the $\mathbf{Q}$ tensor alone is not sufficient. In the lowest-order scenario we need, in addition, at least one secondary order parameter, which can be either a first-rank (polar) field, $\mathbf{P}(\mathbf{r})$ [17], or a third-rank tensor field $\mathbf{T}(\mathbf{r})$, invariant with respect to tetrahedral point group symmetry

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[18–24]. The difference between these scenarios would be the polar order for **Q** and **P** couplings [17] and lack of polarity but the presence of nonlinear dielectric tensor for **Q** and **T**. Here we focus on the **Q** and **P** fields. We look systematically into extended LdeG free energy expansion and identify ordering mechanisms towards one-dimensional modulated structures using bifurcation and numerical analyses.

Before we proceed further it is important to realize that the polar field, **P**, does not need to be of electrostatic or magnetic origin. Bend-core molecules are primarily polar due to their "V" shape, while bimesogens acquire steric polarization in their conformational states. Such *steric dipoles* are present even in the absence of electrostatic dipoles. In a densely packed environment, we expect that these entropic, excluded volume interactions, rather than charge moments, define the local order, such as **P**. Recently, Greco and Ferrarini have provided strong support for the entropy-driven N-N_{TB} transition [25].

We start by introducing the minimal coupling, LdeG free energy per volume, constructed as a power-series expansion in **Q** and **P**, and their derivatives [17,26]. It can be decomposed as

$$F = \sum_{i=2}^{4} F_i = \frac{1}{V} \sum_{i=2}^{4} \int_V (f_{iQ} + f_{iP} + f_{iQP}) d^3\mathbf{r}, \quad (1)$$

where f_{iX} are the free energy densities constructed out of the order parameters $\{X\}$ and contributing to F_i in ith order. By taking suitable units, disregarding external fields and surface terms and assuming deformations to appear only in a quadratic part of the free energy, the general form of f_{iQ} up to fourth order in **Q** is

$$f_{2Q} = \frac{1}{4}[t_Q \operatorname{Tr}(\mathbf{Q}^2) + (\nabla \otimes \mathbf{Q}) \cdot (\nabla \otimes \mathbf{Q})$$
$$+ \rho(\nabla \cdot \mathbf{Q}) \cdot (\nabla \cdot \mathbf{Q}) - 2\kappa \, \mathbf{Q} \cdot (\nabla \times \mathbf{Q})], \quad (2)$$

$$f_{3Q} + f_{4Q} = -\sqrt{6} \, B \operatorname{Tr}(\mathbf{Q}^3) + \operatorname{Tr}(\mathbf{Q}^2)^2, \quad (3)$$

where t_Q is the reduced temperature associated with **Q**; κ is the reduced chirality, proportional to the wave vector of the cholesteric phase; and ρ is the relative elastic constant. Likewise, the polar parts f_{iP} are

$$f_{2P} + f_{3P} + f_{4P} = \frac{1}{4}[t_P\mathbf{P}^2 + (\nabla \otimes \mathbf{P}) \cdot (\nabla \otimes \mathbf{P}) + a_c(\nabla \cdot \mathbf{P})^2$$
$$- 2\kappa_P\mathbf{P} \cdot (\nabla \times \mathbf{P})] + a_4(\mathbf{P}^2)^2. \quad (4)$$

Finally, the lowest-order cross-coupling terms f_{iQP} read

$$f_{2QP} = -\frac{1}{4}[e_P\mathbf{P} \cdot (\nabla \cdot \mathbf{Q}) + 2\kappa_{QP}(\nabla \cdot \mathbf{Q}) \cdot (\nabla \times \mathbf{Q})], \quad (5)$$

$$f_{3QP} = -\lambda P_\alpha Q_{\alpha\beta} P_\beta, \quad (6)$$

$$f_{4QP} = \lambda_1 P_\alpha Q_{\alpha\beta}^2 P_\beta + \lambda_2 \mathbf{P}^2 \operatorname{Tr}(\mathbf{Q}^2). \quad (7)$$

Clearly, for *electric dipoles* $\nabla \times \mathbf{P}$ would vanish in (4) and (5), while the a_c term should be replaced by direct interactions between charge distributions. However, for purely steric dipoles, associated with excluded volume interactions [25] these terms are all present. In particular, for intrinsically chiral materials that develop *steric* polar order the chiral parameters κ, κ_P, and κ_{QP} are all nonzero.

The LdeG expansion (2)–(7) is the minimal coupling theory for systems described in terms of **P** and **Q**, where **P** is chiefly of steric origin. Our objective in this Rapid Communication is to identify possible ODMNS that minimize $F([\mathbf{Q}(\mathbf{r}), \mathbf{P}(\mathbf{r})])$ for arbitrary t_Q and $t_P > 0$. A brief account of what to expect from such theory has already been presented long ago in [17], where we indicated a possibility of flexopolarization-induced periodic structures. Some of nematic structures that can be stabilized by (flexo-)polarization are found in [27–29]. In their theory Alexander and Yeomans [27] showed that applying an electric field to a sample with a large flexoelectric response can be a driving force for the formation of N_{SB} and a flexoelectric blue phase. Shamid *et al.* [28], on the other hand, have taken a simpler version of the expansion [17] and showed that polar two-dimensional hexagonal and three-dimensional bcc lattice phases can be stabilized in nonchiral materials.

In this Rapid Communication we study inhomogeneous nematics with inhomogeneity propagating in one spatial direction, both for nonchiral and intrinsically chiral materials. We show that stable modulated phases, identified so far as a result of polar coupling, do not exhaust all possibilities that the theory (1)–(7) allows for. Our ultimate goal will be to look into fine structure of these phases and clarify the role played by biaxiality. In order to address these issues we explore the bifurcation theory supplemented by numerical minimization and identify global minima of F, Eq. (1), within the ODMNS family. We leave a question of stable polar blue phases to our future studies.

The above program is realized in practice by expanding $\mathbf{Q}(\mathbf{r})$ and $\mathbf{P}(\mathbf{r})$ into plane waves of definite helicity [17]: $\mathbf{Q}(\mathbf{r}) = \sum_{\mathbf{k}} \sum_{m=-2}^{2} Q_m(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}) \mathbf{e}_{m,\hat{\mathbf{k}}}^{[2]}$, $\mathbf{P}(\mathbf{r}) = \sum_{\mathbf{k}} \sum_{m=-1}^{1} P_m(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}) \mathbf{e}_{m,\hat{\mathbf{k}}}^{[1]}$. Here **k** are the wave vectors, $P_m(\mathbf{k})$ and $Q_m(\mathbf{k})$ are the variational parameters in the free energy expansion, and $\mathbf{e}_{m,\hat{\mathbf{k}}}^{[L]}$, $m = 0, \pm 1, \pm L$ are the spin $L = 1, 2$ spherical tensors represented in a local coordinate system with $\hat{\mathbf{k}} = \mathbf{k}/|k|$ as quantization axis. The selection of **k**, $Q_m(\mathbf{k})$, and $P_m(\mathbf{k})$ is fixed by the bifurcation analysis [30,31] while their numerical values are found by the subsequent minimization of F. The theoretical analysis is outlined in the Supplemental Material [32], and only the salient points are highlighted here.

In the vicinity of the isotropic phase the dominant contribution, F_2, from the ODMNS structures is

$$F_2 = \sum_n \sum_{m=-2}^{2} [A_m(|n|k)|Q_m(n)|^2 + (1 - \delta_{m^2,4})$$
$$\times \{B_m(|n|k)|P_m(n)|^2 + iC_m(|n|k)[Q_m(n) P_m^*(n)$$
$$- Q_m^*(n) P_m(n)]/2 \}], \quad (8)$$

where

$$A_m(|n|k) = [t_Q + n^2k^2 + \rho(4 - m^2)n^2k^2/6 - \kappa m|n|k]/4,$$

$$B_m(|n|k) = [t_P + n^2k^2 + a_c(1 - m^2)n^2k^2$$
$$- 2\kappa_P m|n|k]/4, \quad (9)$$

$$C_m(|n|k) = -[e_P\sqrt{(4 - m^2)/6}|n|k + \sqrt{2}\kappa_{QP}mn^2k^2]/4.$$

Here **k** is replaced by nk, $n = 0, \pm 1, \ldots$, $P_m(\mathbf{k})$ by $P_m(n)$, and $Q_m(\mathbf{k})$ by $Q_m(n)$; $\delta_{i,j}$ is the Kronecker delta. Setting $\partial F / \partial Q_m(n) = \partial F / \partial P_m(n) = \partial F / \partial k = 0$ determines

the equilibrium value of the amplitudes and k vector for given material parameters. As it turns out, new classes of ODMNS can already be identified by taking $\kappa_P = \kappa_{QP} = \lambda_1 = \lambda_2 = 0$ and $\kappa \geqslant 0$. For thermodynamic stability it is also mandatory that $\rho > -\frac{3}{2}$ and $1 + a_c > 0$. Additionally, a_4 must be positive if $\lambda \neq 0$.

We shall now proceed by analyzing the case of $\lambda = a_4 = 0$ and later discuss the effect of $\lambda \neq 0$. For the first-mentioned case the condition $\partial F / \partial P_m(n) = 0$ can be solved for $P_m(n)$ given fixed $Q_m(n)$. It yields

$$P_m(n) = -i \frac{C_m(|n|k)}{2B_m(|n|k)} Q_m(n), \quad m = 0, \pm 1. \quad (10)$$

Substituting (10) back to F we obtain the effective free energy that still has to be minimized with respect to $Q_m(n)$. Only F_2 is modified by this substitution. It becomes

$$F_{2,\text{eff}} = \sum_n \sum_{m=-2}^{2} \left[A_m(|n|k) - \frac{C_m(|n|k)^2}{4B_m(|n|k)}(1 - \delta_{m^2,4}) \right]$$

$$\times |Q_m(n)|^2 = \frac{1}{V} \int_V f_{\text{eff}}(\mathbf{Q}, \partial \mathbf{Q}) d^3 \mathbf{r}. \quad (11)$$

Note that the leading elastic part of f_{eff} can again be cast in form (2), but with ρ being replaced by $\rho - \frac{e_P^2}{4t_P}$. Since $(\nabla \cdot \mathbf{Q})^2$ vanishes for twist deformations [26] the flexopolarization must induce an instability towards ODMNS for $\rho - \frac{e_P^2}{4t_P} \leqslant -\frac{3}{2}$. However, generally, the e_P term alone *cannot* bring about spontaneous chiral symmetry breaking. For that, as it turns out, we need either nonzero chirality or sufficiently large $|\lambda|$, or both.

We shall now seek for ODMNS that can be stabilized as result of a phase transition from the isotropic phase (I). The general method is to analyze the nonlinear equations $\partial F / \partial Q_m(n) = \partial F / \partial P_m(n) = 0$ for $Q_m(n)$ and $P_m(n)$ using the bifurcation analysis (BA) [30,31]. We applied this method to identify the leading amplitudes in the expansion of $\mathbf{Q}$ and $\mathbf{P}$ [32]. In the zeroth order of BA each single amplitude $Q_m(1)$ can bifurcate from I to a modulated structure at $t_Q = t_m$ at which the coefficient in front of $|Q_m(1)|^2$ in Eq. (11) vanishes. Maximum of t_m's represents a potential transition temperature for a continuous phase transition, or spinodal for a first-order phase transition.

To identify trial ODMNS, consistent with standard approximations for the N^* phase ($|n| \leqslant 1$) [16], we need to proceed with BA to higher orders. A subsequent minimization of F either with respect to so identified trial states or with respect to all 21 amplitudes of $|n| \leqslant 1$ gives (consistently) six different ODMNS: (i) $N_{\text{LP}}\{Q_0(1), P_0(1), \text{Re}\, Q_0(0)\}$, (ii) $N_{\text{TP}}\{\text{Re}\, Q_{\pm 1}(1), \text{Re}\, Q_0(0), \text{Re}\, Q_2(0), \text{Im}\, P_{\pm 1}(1)\}$, (iii) N_{TB} {as in N_{TP}}, (iv) N_{SB} {as in N_{TP}, $\text{Im}\, Q_{\pm 2}(1)$, $\text{Im}\, Q_0(1)$}, (v) N_{SB}^* {as in N_{SB}}, and (vi) N^* {$\text{Im}\, Q_{\pm 2}(1)$, $\text{Re}\, Q_0(0)$}, where the leading nonzero amplitudes are given in braces. The structures are pictured in Fig. 1 with the exemplary phase diagrams shown in Figs. 2(a)–2(d). All phase transitions found are first order although with increasing t_Q and decreasing t_P the difference between the bifurcation and transition temperatures becomes numerically negligible.

Figures 2(a) and 2(b) show new ODMNS structures as predicted by the model for $\kappa = 0$. These flexopolarization-
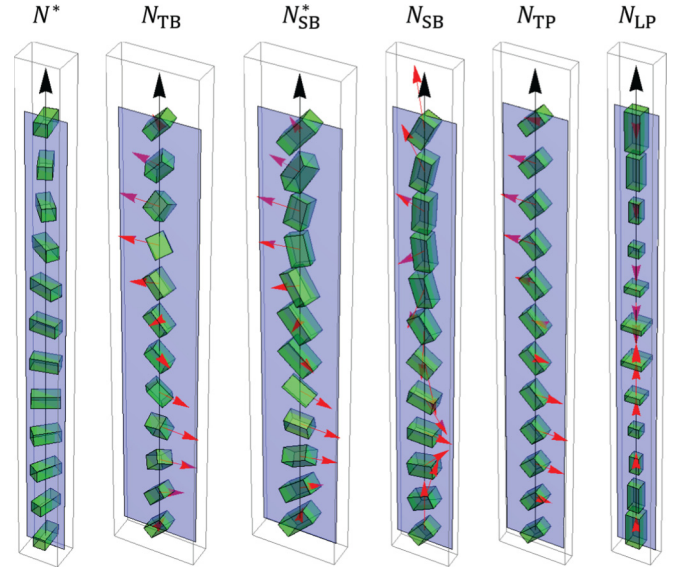

FIG. 1. ODMNS predicted by the theory. Lengths of cuboid edges are proportional to the eigenvalues of $\mathbf{Q} + c\mathbf{I}$, where $\mathbf{I}$ is the unit matrix and c is a constant, such that the isotropic state is represented by a cube. Red arrows represent $\mathbf{P}$ and the black arrow is the direction of $\mathbf{k}$.

induced nonchiral phases are referred to as the transverse periodic nematic (N_{TP}) and the longitudinal periodic nematic (N_{LP}) phases. In N_{TP} the polarization vector, marked by red arrows in Fig. 1, is always perpendicular to $\mathbf{k}$ and to the third director $\hat{\mathbf{m}}$. It is given by a linear combination of $\hat{\mathbf{n}}$ and $\hat{\mathbf{l}}$. In addition, we have $|\text{Re}\, Q_{+1}(1)| = |\text{Re}\, Q_{-1}(1)|$. As a result of nonvanishing homogeneous nematic background [$\text{Re}\, Q_0(0) \neq 0$, $\text{Re}\, Q_2(0) \neq 0$] the N_{TP} structure is locally biaxial with biaxiality modulated along $\mathbf{k}$.

The N_{LP} phase is constructed out of $m = 0$ modes, with $\hat{\mathbf{n}}$ and $\mathbf{P}$ being parallel to $\mathbf{k}$. Hence its name longitudinal wave. The phase is uniaxial and periodically changes from prolate to oblate through the isotropic point. The transition from I to N_{LP} is controlled by the a_c term, which gives nonzero contribution only for the $m = 0$ mode, Eq. (8).

In the N_{SB} phase the polarization $\mathbf{P}$ is periodically modulated in the $\{\hat{\mathbf{n}}, \hat{\mathbf{l}}\}$ plane. The primary modes of $m = 0$ and $m = \pm 1$, which characterize N_{SB}, emerge at the same bifurcating temperature [32]. Through a coupling to the nematic background and the $m = \pm 2$ modes in higher orders of BA, the structure shows an inhomogeneous biaxial modulation.

The phase diagrams in Figs. 2(c)–2(d) illustrate changes induced by intrinsic molecular chirality for $\lambda = 0$. Clearly, $\kappa \neq 0$ results in replacing N by N^*, where $\mathbf{P} = 0$ and $\hat{\mathbf{n}} \perp \mathbf{k}$ rotates about $\mathbf{k}$. Changes also concern N_{TP} and N_{SB} phases. N_{TP} transforms into biaxial N_{TB} (see Fig. 1), with $\hat{\mathbf{n}}$ precessing on the right elliptic cone about $\mathbf{k}$, and with $\mathbf{P}$ perpendicular to $\mathbf{k}$. For $\kappa > 0$ the periodicity of N_{TB} is lower than that of N_{TP}.

The N_{SB} phase turns into its chiral, biaxial analog N_{SB}^*, which is another variant of N_{TB}. Here, two out of the three directors generate twist deformations, similar to the ones modeled in [29], with $\mathbf{P}$ being a linear combination of all three directors.
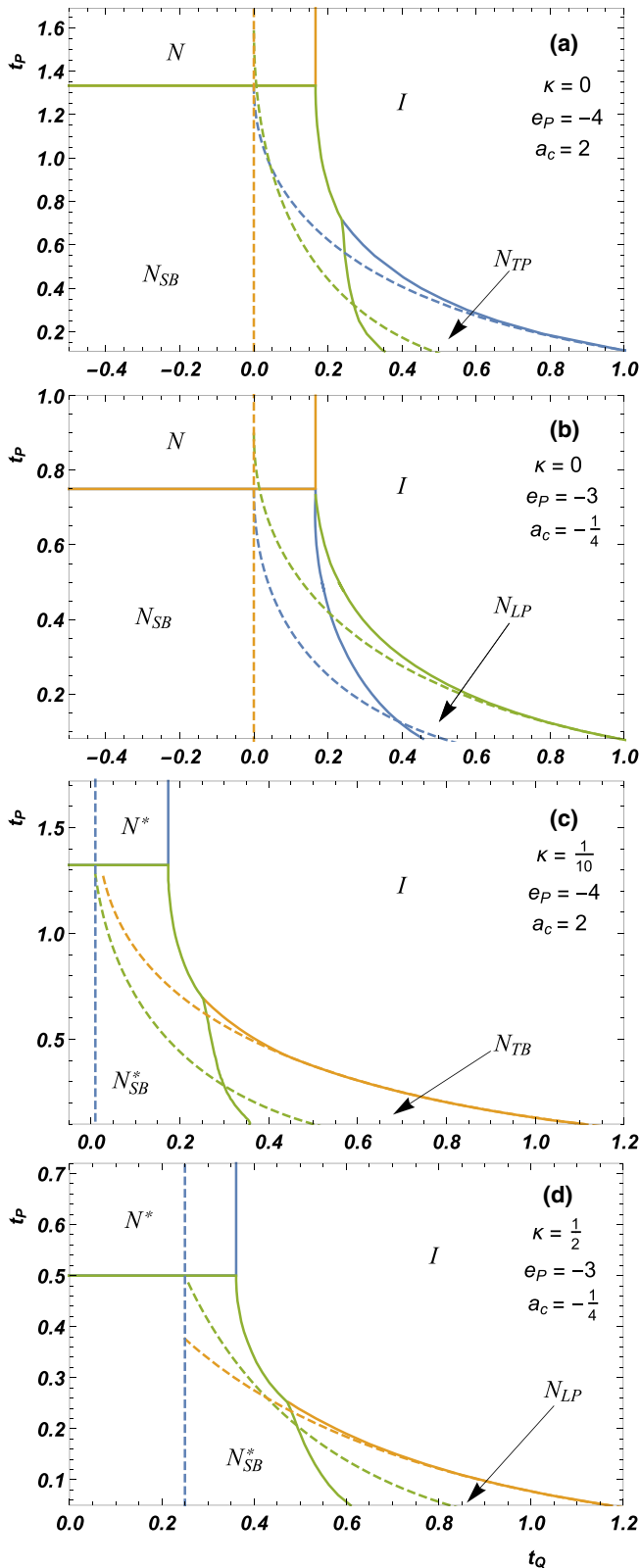
FIG. 2. Phase diagrams for $\rho = 1$ and $B = 1/\sqrt{6}$. Other coupling constants are indicated in each panel. Solid lines are obtained from numerical minimization while dashed curves are bifurcation temperatures from the isotropic phase. In panels (a) and (b) all phases are nonchiral, while in panel (c) all modulated phases are chiral. Despite nonzero intrinsic chirality in panel (d) there is a stable region of achiral modulated N_{LP} structure.

The most striking, however, is the prediction of the nonchiral and uniaxial N_{LP} phase. A remarkable property of this structure is that it stays nonchiral even for intrinsically chiral systems. The phase can become absolutely stable within the ODMNS class [Fig. 2(d)] given the free energy of the $m = 0$ mode is sufficiently lowered by the a_c term.

The N_{TB} phase can be stabilized not only for $\kappa \neq 0$, but primarily for $\lambda < 0$ ($a_4 > 0$). In order to obtain this phase for nonchiral materials $|\lambda|$ must exceed a threshold value, where N_{TB} bifurcates from N_{TP}. For example, if we take parameters of Fig. 2(a) and $a_4 = 1$, then N_{TB} becomes stable for $\lambda \lesssim -0.4$. Exemplary calculations carried out for $\lambda = -1/2$ show this scenario with a rich sequence of accompanied phase transitions: $I \leftrightarrow (N_{TP}, N_{SB}, N) \leftrightarrow N_{TB}$ (phases in parentheses are optional). Although the N_{TB} phases obtained for (a) $\{\kappa \gg 0, \lambda = 0\}$ and (b) $\{\kappa = 0, \lambda \neq 0\}$ have the same symmetry with **P** being an eigenvector of **Q**, in the first case the structure of single helicity $m = \text{sgn}(\kappa)$ minimizes F, while for the case (b) structures of opposite helicities $m = \pm 1$ are of the same free energy. The cases *(a)* and *(b)* also differ quantitatively, that is in their periodicities and biaxialities [16].

In conclusion, the LdeG theory of nematics, extended to account for molecular steric polarization, can stabilize five different ODMNS as a result of first-order phase transition from the isotropic phase. Three of these, N^*, N_{SB}, and N_{TB}, are standard ODMNS, but the two achiral ones, N_{LP} and N_{TP}, have not been reported so far. The most surprising observation is that the nonchiral N_{LP} phase can stay stable even in the presence of intrinsic molecular chirality.

Although great experimental strides have been made recently towards an understanding of the structural properties of the chiral N_{TB} phase, there is no consensus as to what mechanism is responsible for chiral symmetry breaking. Our analysis shows that correlating steric dipoles, flexopolarization, and molecular chirality at mesoscopic scale can bring a fundamental understanding of this issue. Indeed, except for N^*, a prerequisite for the existence of the aforementioned structures is nonzero flexopolarization. But, in order to obtain a stable chiral N_{TB} an additional factor is necessary. This can be either sufficiently strong **PQP** coupling, governed by the parameter λ, or the presence of intrinsic molecular chirality ($\kappa \neq 0$), or both.

So far, only two of the ODMNS, namely, N_{TB} and N_{SB}, have been reported by experimental groups. But the N_{LP} phase, being purely uniaxial, might have already been observed in chiral materials as well, as there are a few unidentified structures with a uniaxial low temperature phase [9]. Generally, the predicted ODMNS can be looked for in nonchiral and intrinsically chiral materials such as recently investigated dimers and stabilized trimers [33] (even oligomers), all exhibiting nematiclike bend modulated phases. Conventionally, the N_{TB} phase is formed from the nematic phase. The presented theory also permits a direct I-N_{TB} phase transition. Very recently, this novel possibility has been confirmed experimentally [34,35].

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SUPPLEMENTAL MATERIAL

Modulated nematic structures induced by chirality and steric polarization

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Abstract

The first section presents an outline of the helicity mode expansion as applied to the generalized Landau-deGennes free energy with polarization field. In the second section details on how to identify stable one-dimensional structures using bifurcation analysis is given.

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THEORY

Minimal coupling free energy expansion for alignment tensor and polarization field

The $SO(3)$-symmetric Landau-deGennes free energy (LdeG) of nematics is an expansion about the isotropic phase in a second rank, symmetric and traceless tensor order parameter, $\mathbf{Q}(\mathbf{r})$, with Cartesian components $Q_{\alpha\beta}(\mathbf{r})$, $(\alpha, \beta = x, y, z)$ and its derivatives $\partial_\gamma Q_{\alpha\beta}$. The original expression for F, complete up to fourth order can be found in [1]. General theory that involves an extension containing lowest order couplings with the polarization field $\mathbf{P}(\mathbf{r})$ has been developed in [2, 3]. It reads

$$F = \sum_{i=2}^{4} F_i = \frac{1}{V} \int_V f \, \mathrm{d}^3\mathbf{r} = \frac{1}{V} \sum_{i=2}^{4} \int_V (f_{iQ} + f_{iP} + f_{iQP}) \, \mathrm{d}^3\mathbf{r}, \tag{1}$$

where f_{iX} are the free energy densities in $i-$th order. The successive contributions to f are

$$\begin{aligned}
f_{2Q} &= \frac{1}{4} \left[t_Q \operatorname{Tr}(\mathbf{Q}^2) + (\nabla \otimes \mathbf{Q}) \cdot (\nabla \otimes \mathbf{Q}) \right. \\
&\qquad \left. + \rho(\nabla \cdot \mathbf{Q}) \cdot (\nabla \cdot \mathbf{Q}) - 2\kappa \, \mathbf{Q} \cdot (\nabla \times \mathbf{Q}) \right],
\end{aligned} \tag{2}$$

$$f_{3Q} + f_{4Q} = -\sqrt{6} \, B \operatorname{Tr}(\mathbf{Q}^3) + \operatorname{Tr}(\mathbf{Q}^2)^2, \tag{3}$$

$$\begin{aligned}
f_{2P} + f_{3P} + f_{4P} = \frac{1}{4} \left[t_P \mathbf{P}^2 + (\nabla \otimes \mathbf{P}) \cdot (\nabla \otimes \mathbf{P}) \right. \\
\left. + a_c (\nabla \cdot \mathbf{P})^2 - 2\kappa_P \, \mathbf{P} \cdot (\nabla \times \mathbf{P}) \right] + a_4 (\mathbf{P}^2)^2,
\end{aligned} \tag{4}$$

$$f_{2QP} = -\frac{1}{4} \left[e_P \mathbf{P} \cdot (\nabla \cdot \mathbf{Q}) + 2\kappa_{QP} (\nabla \cdot \mathbf{Q}) \cdot (\nabla \times \mathbf{P}) \right], \tag{5}$$

$$f_{3QP} = -\lambda P_\alpha Q_{\alpha\beta} P_\beta, \tag{6}$$

$$f_{4QP} = \lambda_1 P_\alpha Q_{\alpha\beta}^2 P_\beta + \lambda_2 \mathbf{P}^2 Tr(\mathbf{Q}^2), \tag{7}$$

where the number of the constitutive parameters has been reduced by taking suitable units [4]. Also summation over repeated Greek indices is to be understood if not stated otherwise. Out of 13 phenomenological parameters left, t_Q is the reduced temperature, κ is the reduced intrinsic chirality in the absence of $\mathbf{P}$, ρ is the relative elastic constant and e_P is the flexopolarization coefficient. Taking $t_P > 0$ eliminates spontaneous polar order $(\mathbf{P} \neq 0)$ in the absence of $\mathbf{Q}$.

The LdeG expansion (2-7) offers the minimal coupling, mesoscopic level description of the systems whose orientational properties depend on $\mathbf{Q}$ (primary order parameter) and $\mathbf{P}$

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(secondary order parameter). Our objective is to identify possible ODMNS that minimize $F([\mathbf{Q}(\mathbf{r}), \mathbf{P}(\mathbf{r})])$ for arbitrary t_Q and $t_P > 0$.

The problem of finding global minima of the free energy functional, Eq. (1), is extremely difficult since the bending and bulk energies favour different forms of the order parameters $\mathbf{Q}$ and $\mathbf{P}$. Usually the order, for which the free energy becomes locally minimal, cannot be extended globally (frustration), which causes liquid crystalline phases of complex orientational order to emerge [5–9]. Below we show how to identify some of these. We sketch a variant of the general procedure [10, 11] that allows to identify the absolute minimizers of F close to the isotropic phase within the class of one-dimensional modulated nematic structures (ODMNS).

Helicity mode expansion

To identify (quasi-)periodic structures in the LdeG theory, Eq. (1), the order parameter fields $\mathbf{Q}$ and $\mathbf{P}$ usually are expanded into plane waves with helicity [3]

$$\mathbf{Q}(\mathbf{r}) = \sum_{\mathbf{k}} \sum_{m=-2}^{2} Q_m(\mathbf{k}) \exp(\mathrm{i}\,\mathbf{k} \cdot \mathbf{r})\, \mathbf{e}^{[2]}_{m,\hat{\mathbf{k}}}, \tag{8}$$

$$\mathbf{P}(\mathbf{r}) = \sum_{\mathbf{k}} \sum_{m=-1}^{1} P_m(\mathbf{k}) \exp(\mathrm{i}\,\mathbf{k} \cdot \mathbf{r})\, \mathbf{e}^{[1]}_{m,\hat{\mathbf{k}}}, \tag{9}$$

where $\mathbf{e}^{[L]}_{m,\hat{\mathbf{k}}}$, $m = 0, \pm 1, \pm L$ are the spin $L = 1, 2$ spherical tensors represented in an orthonormal, right handed local coordinate system $\{\hat{\boldsymbol{\xi}}, \hat{\boldsymbol{\eta}}, \hat{\mathbf{k}}\}$ with $\hat{\mathbf{k}} = \mathbf{k}/|\mathbf{k}|$ as quantization axis. They read [3]

$$\begin{aligned}
\mathbf{e}^{[1]}_{\pm 1,\hat{\mathbf{k}}} &= \mp \frac{1}{\sqrt{2}} (\hat{\boldsymbol{\xi}} \pm \mathrm{i}\hat{\boldsymbol{\eta}}), \\
\mathbf{e}^{[1]}_{0,\hat{\mathbf{k}}} &= \hat{\mathbf{k}}, \\
\mathbf{e}^{[2]}_{\pm 2,\hat{\mathbf{k}}} &= \frac{1}{2} (\hat{\boldsymbol{\xi}} \pm \mathrm{i}\hat{\boldsymbol{\eta}}) \otimes (\hat{\boldsymbol{\xi}} \pm \mathrm{i}\hat{\boldsymbol{\eta}}), \\
\mathbf{e}^{[2]}_{\pm 1,\hat{\mathbf{k}}} &= \mp \frac{1}{2} \left[(\hat{\boldsymbol{\xi}} \pm \mathrm{i}\hat{\boldsymbol{\eta}}) \otimes \hat{\mathbf{k}} + \hat{\mathbf{k}} \otimes (\hat{\boldsymbol{\xi}} \pm \mathrm{i}\hat{\boldsymbol{\eta}}) \right], \\
\mathbf{e}^{[2]}_{0,\hat{\mathbf{k}}} &= \frac{1}{\sqrt{6}} (3\hat{\mathbf{k}} \otimes \hat{\mathbf{k}} - \mathbf{1}).
\end{aligned} \tag{10}$$

The reality condition: $\{\mathbf{Q}(\mathbf{r}) = \mathbf{Q}(\mathbf{r})^*, \mathbf{P}(\mathbf{r}) = \mathbf{P}(\mathbf{r})^*\}$ implies that $Q_m(-\mathbf{k}) = (-1)^m Q_m(\mathbf{k})^*$ and $P_m(-\mathbf{k}) = (-1)^{m+1} P_m(\mathbf{k})^*$. Substitution of the expansions (8,9) into the free energy,

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Eq. (1), gives

$$
\begin{aligned}
F_2 &= \frac{1}{4}\sum_{\mathbf{k}}\sum_{m=-2}^{2}\left\{t_Q+\left[1+\frac{1}{6}\rho(4-m^2)\right]k^2-\kappa mk\right\}|Q_m(\mathbf{k})|^2 \\
&+ \frac{1}{4}\sum_{\mathbf{k}}\sum_{m=-1}^{1}\left\{t_P+\left[1+a_c(1-m^2)\right]k^2-2\kappa_P mk\right\}|P_m(\mathbf{k})|^2 \\
&+ \sum_{\mathbf{k}}\sum_{m=-1}^{1}\left(\frac{e_P\sqrt{4-m^2}}{4\sqrt{6}}k+\frac{\kappa_{QP}}{2\sqrt{2}}mk^2\right)\left[\frac{P_m(\mathbf{k})^*Q_m(\mathbf{k})-P_m(\mathbf{k})Q_m(\mathbf{k})^*}{2i}\right], \\
F_3 &= -\sqrt{6}B\sum_{\mathbf{k},\mathbf{k}',\mathbf{k}''}\sum_{m,m',m''}Q_m(\mathbf{k})\,Q_{m'}(\mathbf{k}')\,Q_{m''}(\mathbf{k}'')Tr\left[\mathbf{e}^{[2]}_{m,\hat{\mathbf{k}}}\mathbf{e}^{[2]}_{m',\hat{\mathbf{k}}'}\mathbf{e}^{[2]}_{m'',\hat{\mathbf{k}}''}\right]\delta_{\mathbf{k}+\mathbf{k}'+\mathbf{k}'',\,\mathbf{0}} \\
&- \lambda\sum_{\mathbf{k},\mathbf{k}',\mathbf{k}''}\sum_{m,m',m''}P_m(\mathbf{k})\,Q_{m'}(\mathbf{k}')\,P_{m''}(\mathbf{k}'')\,\mathbf{e}^{[1]}_{m,\hat{\mathbf{k}}}\cdot\mathbf{e}^{[2]}_{m',\hat{\mathbf{k}}'}\cdot\mathbf{e}^{[1]}_{m'',\hat{\mathbf{k}}''}\delta_{\mathbf{k}+\mathbf{k}'+\mathbf{k}'',\,\mathbf{0}}, \\
F_4 &= \;....\; .
\end{aligned}
\tag{11}
$$

The calculations above are carried out subject to the condition that

$$
\frac{1}{V}\int_V e^{i\mathbf{k}\cdot\mathbf{r}}\mathrm{d}^3\mathbf{r}=\delta_{\mathbf{k},\,\mathbf{0}},
\tag{12}
$$

where $\delta_{i,j}$ is the Kronecker delta. Two amplitudes of opposite helicity out of $\{Q_m(\mathbf{k}),\,P_m(\mathbf{k})\}$ can be taken real due to invariance of $\mathbf{P}$ and $\mathbf{Q}$ with respect to uniform translations in 3D and global rotations about $\mathbf{k}$. We choose $\mathfrak{Im}Q_{\pm 1}=0$.

Minimization scheme for periodic one-dimensional structures

Usually, the phases of the complex amplitudes $Q_m(\mathbf{k})$ and $P_m(\mathbf{k})$ are fixed by symmetry of the structure considered [4, 5, 12], while the real parts of the amplitudes and $\mathbf{k}$-vectors are found by minimizing the free energy, F. Here, we show how to find stable ODMNS.

Modulated, one-dimensional minimizers of F composed of (11) are determined by one type of wave vector set. Hence $|\mathbf{k}|$ can be replaced by nk, $n=0,\pm 1,...$, $P_m(\mathbf{k})$ by $P_m(n)$ and $Q_m(\mathbf{k})$ by $Q_m(n)$; the direction of $\mathbf{k}$ being arbitrarily oriented in space can be fixed

parallel to z-axis of a laboratory system of frame. The equations (11) now become

$$
\begin{aligned}
F_2 &= \sum_n \sum_{m=-2}^{2} \left\{ A_m(|n|k)|Q_m(n)|^2 + (1 - \delta_{m^2,4}) \left[B_m(|n|k)|P_m(n)|^2 \right. \right. \\
&\qquad\qquad \left. \left. + \frac{\mathrm{i}}{2} C_m(|n|k) \left(Q_m(n) P_m^*(n) - Q_m^*(n) P_m(n) \right) \right] \right\}, \tag{13} \\
F_3 &= -\sqrt{6} B \sum_{n,n',n''} \sum_{m,m',m''} Q_m(n) Q_{m'}(n') Q_{m''}(n'') Tr \left[\mathbf{e}_{m,\hat{\mathbf{k}}}^{[2]} \mathbf{e}_{m',\hat{\mathbf{k}}}^{[2]} \mathbf{e}_{m'',\hat{\mathbf{k}}}^{[2]} \right] \delta_{n+n'+n'',0} \\
&\qquad - \lambda \sum_{n,n',n''} \sum_{m,m',m''} P_m(n) Q_{m'}(n') P_{m''}(n'') \mathbf{e}_{m,\hat{\mathbf{k}}}^{[1]} \cdot \mathbf{e}_{m',\hat{\mathbf{k}}}^{[2]} \cdot \mathbf{e}_{m'',\hat{\mathbf{k}}}^{[1]} \delta_{n+n'+n'',0} \\
F_4 &= ....,
\end{aligned}
$$

where

$$
\begin{aligned}
A_m(|n|k) &= \frac{1}{4} \left[t_Q + n^2 k^2 + \frac{\rho(4 - m^2)}{6} n^2 k^2 - \kappa m |n| k \right], \\
B_m(|n|k) &= \frac{1}{4} \left[t_P + n^2 k^2 + a_c(1 - m^2) n^2 k^2 - 2\kappa_P m |n| k \right], \\
C_m(|n|k) &= -\frac{1}{4} \left(e_P \sqrt{\frac{4 - m^2}{6}} |n| k + \sqrt{2} \kappa_{QP} m n^2 k^2 \right). \tag{14}
\end{aligned}
$$

The equilibrium length of the **k**-vector is easily found from the solution of linear equation in k:

$$
\partial F / \partial k = \partial F_2 / \partial k = 0. \tag{15}
$$

Setting

$$
\partial F / \partial Q_m(n) = 0, \tag{16}
$$
$$
\partial F / \partial P_m(n) = 0 \tag{17}
$$

determines the equilibrium value of the amplitudes for given material parameters. Now there are three steps to identify relevant $Q_m(n)$ and $P_m(n)$ for ODMNS. We illustrate the procedure for

$$
\kappa_P = \kappa_{QP} = \lambda = \lambda_1 = \lambda_2 = a_4 = 0. \tag{18}
$$

Extension to the general case is straightforward.

1. Diagonalization of F_2, Eq. (13).

This step is particularly simple for (18) since $P_m(n)$ appears only in (13). By solving the condition (17) for $P_m(n)$ (given fixed $Q_m(n)$):

$$P_m(n) = -\mathrm{i}\frac{C(m,|n|k)}{2B(m,|n|k)} Q_m(n), \quad m = 0, \pm 1. \tag{19}$$

and substituting (19) back to (13) we obtain F_2 in the diagonal form (due to global translational and rotational symmetries of the expansion)

$$F_{2,eff} = \sum_n \sum_{m=-2}^{2} \left[A(m,|n|k) - \frac{C(m,|n|k)^2}{4B(m,|n|k)}(1 - \delta_{m^2,4}) \right] |Q_m(n)|^2. \tag{20}$$

$F = F_{2,eff} + F_3 + F_4$ still has to be minimized with respect to $Q_m(n)$.

2. Identification of ODMNS through bifurcation analysis.

General form of the Eqs. (16) for F_2 given by (20) is

$$\Lambda_i x_i = f(\{x_\alpha\}), \qquad i = 1, 2, ... \tag{21}$$

where $f(...)$ is the third-rank polynomial in $\{\mathfrak{Re}Q_m(n), \mathfrak{Im}Q_m(n)\} \equiv \{x_\alpha\}$ and where the set $\{\Lambda_i\}$ denotes the corresponding coefficients in front of $|Q_m(n)|^2$, Eq. (20). The isotropic phase (I), where $x_i = 0$ ($\forall i$), always solves (21). Decreasing t_Q (or t_P) we expect that for $t_Q \leq t_Q^c$ the isotropic phase is no longer a local minimum of F. We now employ a bifurcation analysis to Eqs (21) to determine the stability limit t_Q^c of I as well as the ODMNS structures that become stable below t_Q^c (see [11] and references therein). For this purpose we expand Λ_i and x_i in an arbitrary parameter ϵ,

$$\begin{aligned} \Lambda_i &= \Lambda_{i,0} + \epsilon\Lambda_{i,1} + \epsilon^2\Lambda_{i,2} + ..., \\ x_i &= \epsilon\, x_{i,1} + \epsilon^2\, x_{i,2} + ... \ . \end{aligned} \tag{22}$$

By substituting Eqs. (22) into Eqs. (21) and comparing terms of the same order in ϵ, we find equations for $x_{\alpha,i}$ and $\Lambda_{\alpha,i}$ of which the ones up to first order in ϵ are obvious for Landau expansion:

$$\begin{aligned} (\epsilon^0): \quad &\Lambda_{i,0} = \Lambda_i(t_Q = t_i) = 0 \\ (\epsilon^1): \quad &x_i = x_{i,1} \neq 0, \qquad \text{for} \quad t_Q < t_i. \end{aligned} \tag{23}$$

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They give the critical (or spinodal) temperatures for each independent mode i and the wavelength, Eq. (15), of the bifurcating solution i.

Explicitly, the leading $m = \pm 2$ modes $Q_{\pm 2}(1)$ bifurcate from I when

$$t_Q = t_{\pm 2} = \kappa^2,$$

$$k_{\pm 2} = \pm \kappa > 0. \tag{24}$$

The condensation of the leading $m = \pm 1$ modes $Q_{\pm 1}(1)$ occurs when $t_{\pm 1}$ and $k_{\pm 1}$ satisfies the implicit relations

$$t_Q = t_{\pm 1} = \frac{k_{\pm 1}\left(e_P^2 k_{\pm 1} - 4\left(k_{\pm 1}^2 + t_P\right)\left(\mp 2\kappa + (\rho + 2)k_{\pm 1}\right)\right)}{8\left(k_{\pm 1}^2 + t_P\right)},$$

$$\kappa = \frac{k_{\pm 1}\left(\mp e_P^2 t_P \pm 4(\rho + 2)\left(k_{\pm 1}^2 + t_P\right)^2\right)}{4\left(k_{\pm 1}^2 + t_P\right)^2}, \tag{25}$$

which can be resolved for non-chiral materials $(\kappa = 0)$ giving

$$t_Q = t_{\pm 1} = \frac{1}{8}\left(e_P^2 - 4\sqrt{(\rho + 2)e_P^2 t_P} + 4(\rho + 2)t_P\right)$$

$$k_{\pm 1} = \sqrt{\sqrt{\frac{e_P^2 t_P}{4(\rho + 2)}} - t_P}, \quad \text{for} \quad 0 < t_P < \frac{e_P^2}{4(\rho + 2)}. \tag{26}$$

Similarly, for $m = 0$ $(Q_0(1)$ mode$)$ we get

$$t_Q = t_0 = \frac{e_P^2 - 2\sqrt{2(2\rho + 3)e_P^2 t_P} + 2(2\rho + 3)t_P}{6\left(a_c + 1\right)}, \tag{27}$$

$$k_0 = \sqrt{\frac{\sqrt{\frac{2e_P^2 t_P}{2\rho + 3}} - 2t_P}{2(a_c + 1)}}, \quad \text{for} \quad 0 < t_P < \frac{e_P^2}{2(2\rho + 3)}. \tag{28}$$

Finally, the bifurcation from I to N $(Q_0(0)$ $)$ takes place at $t_Q = t_{IN} = 0$.

The actual critical (spinodal) temperature t_Q^c is the largest of the above temperatures. The corresponding amplitude $Q_m(n)$ $(|n| \le 1)$, which we refer to as x_1, gives the leading contribution to $\mathbf{Q}$, Eq. (8). The next to leading contributions are found systematically by studying equations generated by higher order terms in ϵ. Up to ϵ^n we get a finite, small subset $X[\epsilon, n]$ of nonzero x_αs that couple to x_1 (*see example below*). Using $X[\epsilon, n]$, we can construct a perturbative expansion for $\mathbf{Q}$ and, subsequently, for F. A much better alternative is to carry out *full* minimization of F with respect to all variables $x_m \in X[\epsilon, n]$, while setting $x_p = 0$ for $x_p \notin X[\epsilon, n]$. Since the difference between $X[\epsilon, n]$ and $X[\epsilon, n-1]$

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is in variables that are of the order of x_1^n (ϵ^n) we can carry out the minimization starting from $n = 1$ and systematically improve the results by increasing n. Hence, the free energies of all ODMNS can be found to arbitrary accuracy.

An equivalent approach would be to construct the effective Landau expansion in the primary amplitude x_1 by systematically eliminating x_α, $\alpha > 1$ [10].

2. Example: Isotropic-Cholesteric bifurcation

Our analysis can be illustrated for the well known case of the Isotropic-Cholesteric phase transition [4]. We assume that $\kappa > 0$ and that $t_Q^c = t_2 = \kappa^2$, Eq. (24). The real and imaginary parts $\{x_1 = \mathfrak{Re}Q_2(1), x_2 = \mathfrak{Im}Q_2(1)\}$ of $Q_2(1)$ bifurcate at the same temperature; hence they are both nonzero for $t_Q < t_2$ with $\Lambda_1 = \Lambda_2 = t_Q - \kappa^2$.

Let $x_0^2 = x_1^2 + x_2^2$ and $x_3 = \mathfrak{Re}Q_0(0)$. Then

$$
\begin{aligned}
(\epsilon^1): \quad & \Lambda_{1,1} = \Lambda_{2,1} = x_{3,1} = 0 \\
(\epsilon^2): \quad & \kappa^2\Lambda_{1,2} = \kappa^2\Lambda_{2,2} = 16\left(9 - \kappa^2\right)x_{0,1}^2 \\
(\epsilon^2): \quad & \kappa^2 x_{3,2} = -12x_{0,1}^2 \\
(\epsilon^3): \quad & ... = ...,
\end{aligned}
\tag{29}
$$

where the relation $x_{0,1}x_{0,2} = x_{1,1}x_{1,2} + x_{2,1}x_{2,2}$ has been used. As can be seen from (29) the nonzero parameter x_0 generates nonzero x_3 in second order of ϵ. Hence x_0 and x_3 are coupled and nonzero value of the former one implies nonzero value of the latter.

If we limit to $|n| \leq 1$ no further nonzero $Q_m(n)$s are coupled by the procedure (29). Hence, up to $|n| \leq 1$ the cholesteric structure is characterized by $X[\epsilon, 2] = \{\mathfrak{Re}Q_2(1), \mathfrak{Im}Q_2(1), \mathfrak{Re}Q_0(0)\}$ amplitudes, which is commonly accepted parameterization of the cholesteric phase [4]. The ODMNS relevant for the competition with the N and N^* phases, are reported in the main text.

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