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Free-energy power expansion for orientationally ordered phases: Energy and entropy

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We propose an approach to the description of orientational phase transitions that utilizes the specific features of orientational energy and entropy. The approach is applied to building a model for nematic phases in materials with nonpolar parallelepiped-type molecules with symmetry D_{2h}. The model operates with complex order parameters, generalizes the Landau–de Gennes theory, and predicts the existence of a biaxial nematic phase for the fourth-order expansion of free energy.

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Introduction. An orientational order of anisometric molecules provides a rich variety of phases and phase transitions in liquid crystals, polymers, and other soft matter systems [1–3]. Recently, orientational transitions in materials with molecules of complex nonsymmetric shapes have attracted strong interest because of the possibility of biaxial nematic phase, see, e.g., review [4]. However, there is no commonly accepted view on the existence and observation of the biaxial nematic phase in thermotropic liquid crystals yet [5–11]. Theoretical studies of the liquid crystal phases are usually performed via three approaches: (1) microscopic models where the specific intermolecular interaction is averaged over orientations of neighboring molecules to produce the mean potential [12–14], (2) the Landau phenomenological power expansion of free energy in terms of the corresponding order parameters (OPs) [1,2,15–17], and (3) computer simulations [18]. Orientationally ordered phases are often characterized by the multicomponent OPs, thus even the lowest fourth-order Landau expansion contains many terms, e.g., 14 terms for nematic phases [19].

In this Rapid Communication, we propose an approach to the description of orientational phase transitions that utilizes the following specific features of the orientational energy E and entropy S: (a) S possesses an additional symmetry in comparison with E, being invariant under rotation of the molecular frame; and (b) E contributes only to the second-order terms because the pair molecular interaction is dominant. The approach is based on minimization of the scaled orientational free energy $\bar{F} = F/T = E/T - S$ instead of F because $\bar{F}$ obeys the standard assumption of the Landau theory that only the second-order terms are temperature dependent. We apply the approach to building a model for nematic phases in materials with nonpolar parallelepiped-type molecules with symmetry D_{2h}. The presented model introduces complex OPs, generalizes the Landau–de Gennes (LdeG) theory and predicts the existence of a biaxial nematic phase for the fourth-order expansion of $\bar{F}$.

General approach. We derive $\bar{F}$ per molecule considering $\bar{F}$ of the isotropic state as the zero reference point and using the same units for energy and temperature with the Boltzmann constant $k_B = 1$. The orientational order is described either by symmetric traceless tensor OPs [1,15–17] or by the averaged Wigner D functions $\langle D^L_{mk}\rangle$ [13,20–22]. We chose the latter because $D^L_{mk}(\boldsymbol{\Omega})$ form a complete set of orthogonal functions of the Euler angles $\boldsymbol{\Omega} = \{\omega_1,\omega_2,\omega_3\}$ [23]; $\boldsymbol{\Omega}$ define the molecular orientation through rotation $\mathbb{L} \xrightarrow{\boldsymbol{\Omega}} \mathbb{M}$ from the laboratory frame $\mathbb{L}$ to the molecular frame $\mathbb{M}$. A set of OPs $\langle D^L_{mk}\rangle$ obtained by averaging with the single-molecule orientational distribution function $f(\boldsymbol{\Omega})$ is complete and is equivalent to $f(\boldsymbol{\Omega})$

$$f(\boldsymbol{\Omega}) = \sum_{L=0}^{\infty} \frac{2L+1}{8\pi^2} \sum_{m,k=-L}^{L} \langle D^L_{mk}\rangle D^{L*}_{mk}(\boldsymbol{\Omega}), \qquad (1)$$

where $D^{L*}_{mk}(\boldsymbol{\Omega}) = (-1)^{m-k} D^L_{-m-k}(\boldsymbol{\Omega})$. OPs $\langle D^L_{mk}\rangle$ provide a unified description of orientationally ordered phases: polar, nematic, and tetrahedral phases correspond to $L = 1,2,3$, respectively.

Being scalars, E and S are invariant under the rotation $\mathbb{L} \xrightarrow{\boldsymbol{\Phi}} \mathbb{L}'$ from one laboratory frame $\mathbb{L}$ to another $\mathbb{L}'$ with the Euler angles $\boldsymbol{\Phi}$. If we neglect the intermolecular correlations, E contains only the second-order terms with the same L [22]

$$E = -\frac{1}{2}\sum_{L=1}^{\infty}\sum_{m,k=-L}^{L} U_L(k_1k_2)\langle D^L_{mk_1}\rangle\langle D^L_{-mk_2}\rangle, \qquad (2)$$

where $U_L(k_1k_2)$ are the parameters of intermolecular interactions.

We assume that S possesses an additional symmetry: the expression for S does not depend on the choice of the molecular frame and thus is invariant under the rotation $\mathbb{M} \xrightarrow{\Psi} \mathbb{M}'$ from one molecular frame $\mathbb{M}$ to another $\mathbb{M}'$. The reason for this "molecular isotropy" is that S is expressed through the invariant integral of the orientational distribution function $f_\nu(\boldsymbol{\Omega}^\nu)$ over the orientational space $\boldsymbol{\Omega}^\nu$ of the ν molecules' system

$$S = -\nu^{-1}\int f_\nu(\boldsymbol{\Omega}^\nu)\log[(8\pi^2)^\nu f_\nu(\boldsymbol{\Omega}^\nu)]\mathbf{d}\boldsymbol{\Omega}^\nu. \qquad (3)$$

We can directly prove this assumption if we neglect the orientational correlations and $f_\nu(\boldsymbol{\Omega}^\nu) = \prod_{n=1}^{\nu} f(\boldsymbol{\Omega}_n)$, where $\boldsymbol{\Omega}_n$ is a set of the Euler angles of the nth molecule. Then

$$S = -\int f(\boldsymbol{\Omega})\log[8\pi^2 f(\boldsymbol{\Omega})]\mathbf{d}\boldsymbol{\Omega}, \qquad (4)$$

and we construct S as an invariant power series in $\langle D^L_{mk}\rangle$ using the power expansion for $\log(1+x)$ in Eq. (4), where 1 stems from the term $L = 0$ in Eq. (1); expressions (4) and (1) remain the same in different $\mathbb{M}$ and therefore the power series does not depend on $\mathbb{M}$ either.

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In the standard models, the energy [Eq. (2)] usually contains OPs with one or a few values of L, $L \in \{\bar{L}_i\}$. In this case, we can *a priori* maximize S with respect to all $\langle D^L_{mk}\rangle$ with $L \notin \{\bar{L}_i\}$. Then the maximized entropy $\bar{S}$ remains invariant and contains only terms with $L \in \{\bar{L}_i\}$ which can be derived using their transformational properties.

Thus the proposed approach contains the following steps: (a) selection of the orientational OPs $\langle D^L_{mk}\rangle$ that describe the phases of interest and determine the expression for orientational energy E, (b) derivation of the invariant terms of $\bar{S}$ that contain $\langle D^L_{mk}\rangle$, (c) determination of the phase diagram by minimization of scaled free energy $\bar{F} = E/T - S$.

Free energy for nematics with molecular symmetry D_{2h}. To illustrate our approach and demonstrate how the invariant form of $\bar{S}$ is derived, we present a model for nematic phases in materials with molecular symmetry D_{2h}. The nematic phases are described by the OPs $R_{mk} = \langle D^2_{mk}\rangle$ and by energy [Eq. (2)] with $L = 2$. D_{2h} molecules in nematic phases have four independent OPs, which have the simplest representation R_{00}, $R_{20} = R_{\pm 20}$, $R_{02} = R_{0\pm 2}$, and $R_{22} = R_{\pm 2\pm 2}$ in the molecular frame defined by the symmetry axes and planes and in the laboratory frame along the directors [20,21]. R_{00} and R_{20} describe, respectively, the uniaxial and biaxial orientational orderings of the long molecular axis $\hat{\mathbf{e}}_3$ and are related to the traceless tensor order parameter $\mathbf{Q} = \langle \hat{\mathbf{e}}_3 \otimes \hat{\mathbf{e}}_3\rangle - \boldsymbol{I}/3$ [1–3]. R_{02} and R_{22} describe, respectively, the uniaxial and biaxial orderings of the short axes $\hat{\mathbf{e}}_{1,2}$ and are equivalent to the tensor $\mathbf{B} = \langle \hat{\mathbf{e}}_1 \otimes \hat{\mathbf{e}}_1 - \hat{\mathbf{e}}_2 \otimes \hat{\mathbf{e}}_2\rangle$ [14]. The scaled orientational energy $\bar{E} = E/T$ is defined as [22]

$$\bar{E} = -\frac{u}{2}\big[R_{00}^2 + 2R_{20}^2 + 4\gamma(R_{00}R_{02} + 2R_{20}R_{22}) + 4\lambda\big(R_{02}^2 + 2R_{22}^2\big)\big], \tag{5}$$

where $u = U_2(00)/T$ is proportional to the inverse temperature and $\gamma = U_2(\pm 20)/U_2(00)$ and $\lambda = U_2(\pm 2,\pm 2)/U_2(00)$ are dimensionless parameters that describe the anisotropy of intermolecular interaction [24].

The general expression of the power expansion of $\bar{S}$ in R_{mk}

$$\bar{S} = -\sum_{N,m_n,k_n} H_N(m_1,k_1,\ldots,m_N,k_N)\prod_{n=1}^{N} R_{m_n k_n} \tag{6}$$

is invariant with respect to the rotations of the laboratory $\mathbb{L} \xrightarrow{\Phi} \mathbb{L}'$ and molecular $\mathbb{M} \xrightarrow{\Psi} \mathbb{M}'$ frames. Because of the independence of the rotations with $\boldsymbol{\Phi}$ and $\boldsymbol{\Psi}$, we present H_N as

$$\begin{aligned} &H_N(m_1,k_1,\ldots,m_N,k_N) \\ &\quad = \sum_{\alpha\beta} H_N^{\alpha\beta} h_N^{\alpha}(m_1,\ldots,m_N) h_N^{\beta *}(k_1,\ldots,k_N). \end{aligned} \tag{7}$$

Here $H_N^{\alpha\beta}$ is an arbitrary numeric coefficient for an invariant term and $h_N^{\alpha}(m_1,\ldots,m_n,\ldots,m_N)$ is the αth solution of the equation

$$\sum_{m_n} h_N^{\alpha}(m_1,\ldots,m_N)\prod_{n=1}^{N} D^2_{m_n l_n}(\boldsymbol{\Phi}) = h_N^{\alpha}(l_1,\ldots,l_N) \tag{8}$$

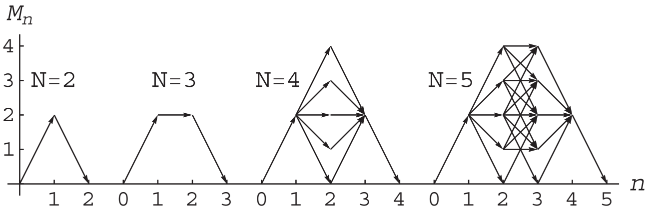

FIG. 1. Chains of arrows represent the solutions [Eq. (9)]; each arrow $\{M_{n-1},M_n\}$ corresponds to $\langle M_{n-1}\bar{m}_{n-1}2m_n|M_n\bar{m}_n\rangle$.

for an arbitrary $\boldsymbol{\Phi}$. Using the standard expressions for the products of D functions [23], we obtain the solutions of Eq. (8)

$$h_N^{\alpha}(m_1,\ldots,m_N) = \prod_{n=1}^{N}\langle M_{n-1}\bar{m}_{n-1}2m_n|M_n\bar{m}_n\rangle, \tag{9}$$

where $\bar{m}_n = \bar{m}_{n-1}+m_n$, $M_0 = \bar{m}_0 = M_N = \bar{m}_N = 0$, and α runs over α_N possible sets $\{M_1\ldots M_{N-1}\}$ that provide nonzero products of Clebsch-Gordan coefficients $\langle M_{n-1}\bar{m}_{n-1}2m_n|M_n\bar{m}_n\rangle$ in Eq. (9), see Fig. 1. There is no solution for $N = 1$, and there are single solutions for $N = 2$ and for $N = 3$. For higher orders $N \geqslant 4$, the number of solutions of Eq. (9) α_N drastically increases: $\alpha_4 = 5, \alpha_5 = 16$, $\alpha_6 = 65$, etc. Thus expressions (6), (7), and (9) contain α_N^2 invariant Nth-order terms; however, these α_N^2 terms may contain the same combinations of R_{mk} and the actual number of independent invariants is substantially smaller.

We used MATHEMATICA to analyze terms in $\bar{S}$, Eq. (6), and found that the fourth-order entropy $\bar{S}_4$ has four independent invariants:

$$\bar{S}_4 = -\left(\frac{a}{2}I_2 - \frac{b}{3}I_3 + \frac{c_1}{4}I_2^2 + \frac{c_2}{4}I_4\right), \tag{10}$$

where $I_2 = R_{00}^2 + 2(R_{20}^2 + R_{02}^2) + 4R_{22}^2$, $I_3 = R_{00}^3 + 24R_{20}R_{02}R_{22} + 6R_{00}(2R_{22}^2 - R_{20}^2 - R_{02}^2)$, and $I_4 = J_2^2$. $J_2 = 4(R_{00}R_{22} - R_{20}R_{02})$ is the second-order so-called pseudoinvariant because it changes its sign under $\pi/2$ rotation around the long molecular axis or the long director.

The sixth-order expansion has an additional seven terms:

$$\bar{S}_6 = \bar{S}_4 - \left(\frac{d_1}{5}I_2I_3 + \frac{d_2}{5}I_5 + \frac{e_1}{6}I_2^3 + \frac{e_2}{6}I_3^2 + \frac{e_3}{6}I_2I_4 + \frac{e_4}{6}I_{6s} + \frac{e_5}{6}I_{6a}\right), \tag{11}$$

where $I_5 = J_2J_3$, $I_{s6} = J_3^2$, $J_3 = 6R_{00}R_{20}R_{02} + 3R_{22}(R_{00}^2 - 2R_{20}^2 - 2R_{02}^2) + 4R_{22}^3$ is the third-order pseudoinvariant, and $I_{a6} = 4(R_{02}^2 - R_{22}^2)^3 + 3[(R_{00}^2 + 2R_{20}^2)^2(R_{02}^2 + 2R_{22}^2) + 2(R_{00}R_{02} + 2R_{20}R_{22})^2(R_{00}^2 + 2R_{20}^2 - 2R_{02}^2 - 4R_{22}^2)]$. The obtained invariants are similar to the terms in Refs. [25,26].

Expressions (6), (7), and (9) provide a general explicit form for the power expansion of the maximized entropy $\bar{S}$ for nematic OPs ($L = 2$). This form is further simplified by extracting independent combinations of OPs taking into account the molecular symmetry D_{2h} [Eqs. (10) and (11)]. The method is straightforward and can be easily applied to phases with other orientational OPs.

Complex order parameters. To simplify the analysis of nematic phases we introduce uniaxial $\tilde{s} = R_{00} + i\sqrt{2}R_{02} = se^{i\alpha}$ and biaxial $\tilde{p} = \sqrt{2}R_{20} + 2iR_{22} = pe^{i\beta}$ complex OPs, where their phases α and β determine the ratios between the short and long molecular axis orderings. $\tilde{s}$ and $\tilde{p}$ are equivalent to any set of four order parameters, systematized in [27], e.g., $\tilde{s} = S + iU$, $\tilde{p} = P + iF$. They also allow us to build the complex tensor OP $\mathbf{C} = \mathbf{Q} + \frac{i}{\sqrt{3}}\mathbf{B}$ with the diagonal form $\{-(\tilde{s} - \sqrt{3}\tilde{p})/3, -(\tilde{s} + \sqrt{3}\tilde{p})/3, 2\tilde{s}/3\}$ in the laboratory frame along the directors.

Complex OPs provide several advantages. First, $\mathbf{C}$ determines any second-rank susceptibility tensor $\bar{\chi}$ that is an orientational average of molecular tensor χ

$$\bar{\chi} = \chi_{\rm iso}\mathbf{I} + {\rm Re}[\tilde{\chi}\mathbf{C}], \qquad (12)$$

where $\mathbf{I}$ is a unit tensor and $\tilde{\chi} = \chi_u - i\sqrt{3}\chi_b/2$. Here $\chi_{\rm iso} = (\chi_1 + \chi_2 + \chi_3)/3$, $\chi_u = \chi_3 - (\chi_1 + \chi_2)/2$, and $\chi_b = \chi_1 - \chi_2$ are, respectively, isotropic, uniaxial, and biaxial combinations of the diagonal components χ_i of the molecular tensor that is diagonal in the molecular frame $\chi_{ij} = \chi_i \delta_{ij}$.

Second, the energy of Eq. (5) and invariants I_n in Eqs. (10) and (11) are even functions of the amplitude p; e.g., $\bar{E}$ contains the above-defined $I_2 = \frac{3}{2}\,{\rm Tr}(\mathbf{C}\mathbf{C}^*) = s^2 + p^2$ and the complex invariant $\tilde{I}_2 = \frac{3}{2}\,{\rm Tr}(\mathbf{C}^2) = \tilde{s}^2 + \tilde{p}^2$:

$$\begin{aligned}\bar{E} &= -\frac{u}{2}[(1 - \tilde{v} - \tilde{v}^*)I_2 + \tilde{v}\tilde{I}_2 + \tilde{v}^*\tilde{I}_2^*]\\ &= -\frac{u}{2}\{s^2 + p^2 - 2v[s^2 \sin\alpha \sin(\alpha - \theta)\\ &\quad + p^2 \sin\beta \sin(\beta - \theta)]\},\end{aligned} \qquad (13)$$

where $\tilde{v} = \frac{1}{2} - \lambda - i\sqrt{2}\gamma = ve^{-i\theta}$ is the complex parameter that describes the anisotropy of intermolecular interaction, $0 \leqslant \theta \leqslant \pi/2$.

Third, the complex OP representation demonstrates that the presented model is a generalization of the LdeG theory [1,15,16], because the sixth-order expansion $\bar{F}_6 = \bar{E} - \bar{S}_6$ reduces to the LdeG theory under the assumption $\alpha = \beta = 0$, which corresponds to the free molecular rotation around the long axis. However, this assumption is not valid (does not correspond to the absolute minimum) if $\gamma \neq 0$ or $\lambda \neq 0$, see below.

Phase diagram for uniaxial and biaxial nematics. The LdeG theory forbids N_b phase in the fourth-order expansion, allowing its existence only with the sixth-order terms [1,15,16]. However, in our model the N_b phase already appears in the fourth-order expansion $\bar{F}_4 = \bar{E} - \bar{S}_4$, which we analyze using $\tilde{s} = se^{i\alpha}$ and $\tilde{p} = pe^{i\beta}$ representation

$$\bar{F}_4 = \bar{F}_{\rm uni} + \frac{1}{2}[g_0 - g_2\cos(2\beta - \psi)]p^2 + \frac{c_1}{4}p^4, \qquad (14)$$

where

$$\begin{aligned}\bar{F}_{\rm uni} = \frac{s^2}{12}\{&6[a - u + uv\cos\theta - uv\cos(2\alpha - \theta)]\\ &- 4bs\cos 3\alpha + 3s^2c_1\},\end{aligned} \qquad (15)$$

and $g_0 = a - u + uv\cos\theta + (c_1 + c_2)s^2$; g_2 and ψ are, respectively, the amplitude and phase of the complex term $g_2e^{i\psi} = uv\cos\theta + c_2s^2 - 2bs\cos\alpha + i\,[uv\sin\theta + 2s\,(b + c_1s\cos\alpha)\sin\alpha]$.

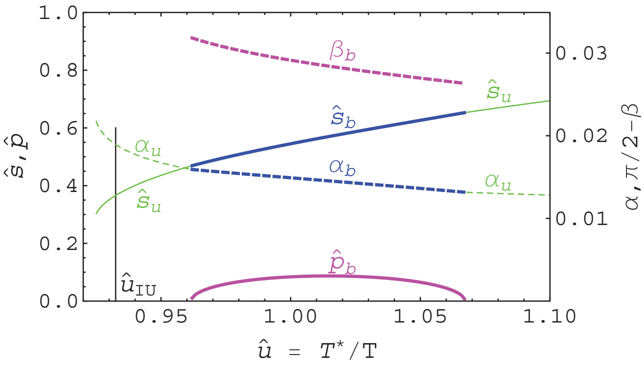

FIG. 2. (Color online) Temperature dependencies of normalized OP amplitudes $\hat{s}, \hat{p}$ (solid) and OP phases α, β (dashed) in N_u (thin) and N_b (thick) phases for $\hat{b} = 0.5, \hat{c}_2 = 0.2, v = 0.09$, and $\theta = \pi/18$. The vertical line at $\hat{u}_{iu} = T^*/T_{iu}$ corresponds to the phase transition between isotropic and N_u phases at the temperature T_{iu}. Note that $\hat{s} = 0.37$ at $\hat{u}_{iu}$, thus the normalization factor for $\hat{s}$ and $\hat{p}$ is close to unity.

The uniaxial phase is described by s_u and α_u, obtained by minimization of $\bar{F}_{\rm uni}$, Eq. (15). The two α-dependent terms in $\bar{F}_{\rm uni}$ create twofold and threefold radial valleys in polar coordinates (s,α) with minima at $\alpha = \pi n + \theta/2$ and $\alpha = 2\pi n/3$, respectively. Thus the absolute minimum corresponds either to the calamitic phase, $0 < \alpha < \theta/2$, if $0 \leqslant \theta \leqslant \pi/3$, or to the discotic phase, $\pi + \theta/2 < \alpha < 2\pi/3$ if $\pi/3 \leqslant \theta \leqslant \pi/2$. The phase transition between calamitic and discotic phases is impossible because the balance between them is not affected by the temperature factor u. Below we consider the case when $0 \leqslant \theta \leqslant \pi/3$ and the uniaxial phase is calamitic with $0 < \alpha < \theta/2 \leqslant \pi/6$.

To simplify the analysis of Eqs. (14) and (15), we set $a = c_1 = 1$ without losing generality, because Eqs. (14) and (15) transform into the normalized free energies $(\hat{F}_4, \hat{F}_{\rm uni}) = (\bar{F}, \bar{F}_{\rm uni})a^2/c_1$, with normalized OP amplitudes $(\hat{s}, \hat{p}) = (s,p)\sqrt{c_1/a}$ and parameters $\hat{b} = b/\sqrt{c_1 a}$, $\hat{c}_2 = c_2/c_1$, and $\hat{u} = u/a = T^*/T$, where T^* is the low temperature limit of the metastable isotropic phase; parameter $\tilde{v} = ve^{-i\theta}$, and phases α, β, ψ remain unchanged. The normalization also allows us to analyze the nematic phases only when $\hat{u} < 1.6$, because the temperature range of nematic phases rarely exceeds 150°.

For small v, both N_u and N_b phases occur; typical temperature dependencies of OPs are shown in Fig. 2. The N_b phase is enclosed by two N_u phases with second-order phase transitions between them, $N_u \overset{2}{\leftrightarrow} N_b$, Fig. 2.

When $\theta < \pi/4$, the effect of θ on the phase diagram is rather small, because $\alpha \lessapprox \theta/8$ and $\beta = \psi/2 \approx \pi/2$, Fig. 2. Figure 3 presents phase diagrams in $\{v,\hat{u}\}$ coordinates for several sets of $\{\hat{b},\hat{c}_2\}$ parameters, when $\theta = 0$ and $\hat{F}_4$ reaches the minimum at $\alpha = 0$ and $\beta = \pi/2$. The N_b phase occurs if $v < v_b = (\hat{b}^2 - 4\hat{c}_2 + 2\sqrt{\hat{b}^2 - 2\hat{b}^2\hat{c}_2 + 4\hat{c}_2})/(8 - 2\hat{b}^2)$. The N_b phase appears under the cooling ($\hat{u}$ increasing) through the $N_u \overset{2}{\leftrightarrow} N_b$ transition when $v_b > v > v_t = \hat{b}^2(3 - 2\hat{c}_2)/(9 - 2\hat{b}^2)$, or through the $I \overset{1}{\leftrightarrow} N_b$ transition when $v < v_t$; $\{v_t, \hat{u}_t = 1 - 2\hat{b}^2/9\}$ is the triple point. If $\hat{c}_2 > 0$, the further cooling can result in the second low-temperature N_u phase

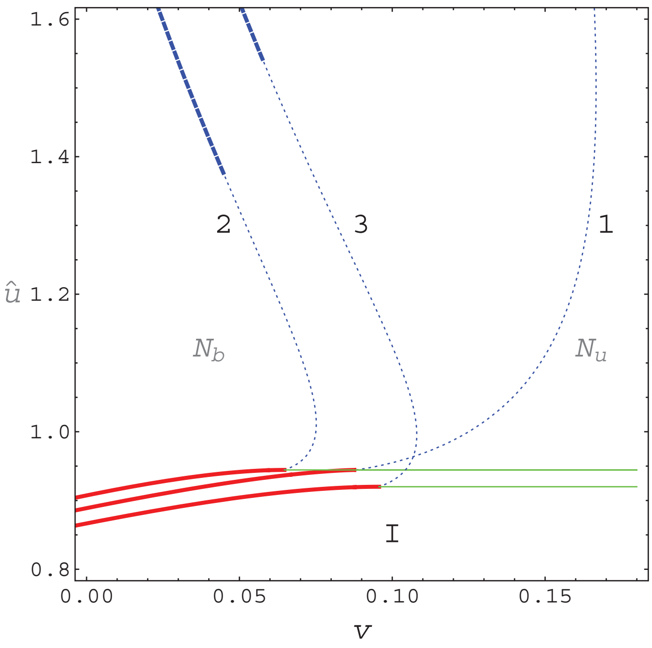

FIG. 3. (Color online) Phase diagrams in $\{\hat{u}, v\}$ plane for $\theta = 0$ and different sets of $\hat{b}$ and $\hat{c}_2$: (1) $\hat{b} = 0.5$, $\hat{c}_2 = 0.0$; (2) $\hat{b} = 0.5$, $\hat{c}_2 = 0.2$; (3) $\hat{b} = 0.6$, $\hat{c}_2 = 0.2$. Curves correspond to phase transitions: $I \overset{1}{\leftrightarrow} N_u$ (thin solid), $I \overset{1}{\leftrightarrow} N_b$ (thick solid), $N_u \overset{2}{\leftrightarrow} N_b$ (dotted), $N_u \overset{1}{\leftrightarrow} N_b$ (dashed).

either through the second-order transition $N_b \overset{2}{\leftrightarrow} N_u$ or through the first-order transition $N_b \overset{1}{\leftrightarrow} N_u$, Fig. 3. The temperature range of the N_b phase is enhanced by $\hat{b}$ and is suppressed by $\hat{c}_2$ and v. The shape of the phase diagrams in Fig. 3 is similar to that observed in lyotropic materials [28]. However, this similarity should not be overstated because both calamitic and discotic uniaxial phases are present and may be caused by micelle shape transformation, which effectively changes the interaction between micelles [28].

The obtained results clearly demonstrate why the LdeG theory shows no N_b phase for the fourth-order expansion. The LdeG theory corresponds to the assumption $\beta = 0$, whereas the minimum of $\bar{F}_4$ for the N_b phase occurs when $\beta = \psi/2 \approx \pi/2$.

Conclusions. We demonstrated an approach for describing orientational phase transitions. The approach provides a straightforward method for minimization of scaled free energy $\bar{F} = E/T - S$ in the space of selected orientational OPs that describe the phases of interest. We applied this approach to nematic phases with molecular symmetry D_{2h} building a model that generalizes the LdeG theory and predicts the biaxial N_b phase for the fourth-order expansion of $\bar{F}$. $\bar{F}$ has only the second-order temperature-dependent term in other theoretical models, e.g., Bragg-Williams theory, and may be useful for the description of various types of phase transitions.

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