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Molecular-field-theory approach to the Landau theory of liquid crystals: Uniaxial and biaxial nematics

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Nematic liquid crystal phase diagrams in temperature-biaxiality space are usually complex. We construct a Landau theory based on the analogous molecular-field theory for orthorhombic biaxial nematic fluids. A formal procedure yields coefficients (some of which, unusually, can be tensorial) in this Landau expansion, correctly predicts the complete set of invariants formed from the ordering tensors, and avoids *ad hoc* parametrization of the molecular biaxiality. By regularizing the Landau expansion to avoid unwanted order parameter divergences at low temperatures, we predict phase behavior over the whole range of biaxiality. The resulting phase diagrams have the same topology as those of molecular-field theory.

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I. INTRODUCTION

Idealized textbook models of liquid crystals usually start with the assumption that the constituent molecules are rigid and cylindrically symmetric. Neither of these assumptions is completely true especially for modern materials. Nevertheless the hope has been that at least the key features of the most common liquid crystal phases (in particular the nematic and smectic *A* phases) can be understood in terms of models that start with these assumptions. These key features would then be robust with respect to weak changes in the molecular structure. Much theoretical effort has then been expended over the years in an attempt to construct perturbation-theory-like approaches which consider more realistic molecular models [1–3].

In this paper we address the second of these assumptions, that of molecular cylindrical symmetry. In addition, we only discuss nematic phases, in which long-range positional order is absent, although a number of types of orientational order may be present. Traditionally basic theoretical approaches to the statistical mechanics of the nematic phase are either bottom-up or top-down. In a bottom-up (or *molecular*) approach we seek to make predictions about the phase behavior of a material constructed out of a particular type of molecule, using information about the molecular structure and intermolecular interactions. The paradigm for such theories in the context of liquid crystals is the celebrated molecular-field theory due to Maier and Saupe [4] in 1957 (and which, to some extent, was anticipated by Grandjean [5] forty years earlier). Nowadays, of course, if accurate results are required for a specific model system (rather than just a qualitative overview), a detailed computer simulation would be expected to yield more accurate results [6].

A top-down (or *phenomenological*) theory, by contrast, seeks to classify phases and phase transitions using as little molecular input as possible, concentrating more on the phase symmetry, but perhaps also allowing the input of information about molecular symmetry. The idea here is that the statistical mechanics (and hence the phase behavior) can be described by expressions for the free energy in terms of invariants constructed from the key order parameters. The original paradigm is due to Landau [7] in the 1930s, although it was modified in the 1970s by Wilson and Fisher [8,9] once it became clear that fluctuations play a key role in understanding critical exponents at phase transitions. The liquid crystal version of this theory was introduced by de Gennes in 1970 [10], and has come to be known as the Landau–de Gennes theory. However, we shall refer to this and the more generic theory as Landau theories in this paper.

In general, it is far from easy to make a reliable quantitative link between molecular and phenomenological theories. The phenomenological theory usually requires a small number of input parameters, which are often determined from experiment, from the macroscopic properties of the material, rather than calculated *ab initio*. Also it focuses explicitly on the vector or tensor nature of the relevant order parameters. The Ehrenfest classification of any particular phase transition depends on the existence or otherwise of third-order (and other) invariants of the order parameter in the free energy expansion.

The molecular-field theory, on the other hand, calculates a scalar order parameter, and sometimes appears to miss the more complex details of the order parameter symmetry. Nevertheless, it is an interesting fact that the molecular-field theories usually predict phase transitions with the same order as that predicted by the relevant Landau theory. Thus necessary inputs to the Landau theory should exist, as it were, in hidden recesses of the molecular-field theory. The hidden links between the two types of theory should also enable a quantitative connection to be made between the two types of theory. Indeed, some time ago, two of us (G.R.L. and T.J.S.) together with other co-authors, introduced an approach which performed precisely this task for uniaxial (i.e., cylindrically symmetric or $D_{\infty h}$) molecules in a uniaxial phase [11]. This approach, which we refer to as KKLS (Katriel, Kventsel, Luckhurst, Sluckin) in this paper, forms the basis for an analysis of phases constituted of more complicated molecules.

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Thus the traditional view of the nematic phase, as exemplified in the Landau theory proposed by de Gennes, is of a uniaxial phase, made up of uniaxial molecules. It is of some interest to note that the term *uniaxial* is borrowed from optics, and goes back to Hamilton in the 19th century. A phase with a single special axis will, in principle, exhibit double refraction, with the light velocity in any given direction depending on the light polarization. But along the special axis, and only along that axis, the light velocity is independent of polarization. It is the single special axis which is the symmetry axis of the phase and gives rise to the term "uniaxial." A related feature is that two of the principal axes of properties such as the electric or magnetic susceptibility tensors in such a liquid crystal are degenerate, and perpendicular to the special axis.

In optics, uniaxial materials traditionally stand in contrast to *biaxial* materials, in which there is not one, but two axes along which the velocity of light is impervious to polarization. Tensor fields reflecting the properties of such materials can also be diagonalized to give the symmetry axes of the phase, but now the principal axes are not simply related to the two special optical axes, and the degeneracy existing in the uniaxial materials is lifted. All real liquid crystal materials are in fact made from biaxial (here we take this term to mean not cylindrically symmetric) molecules, although computer models do, of course, enable the statistical mechanics of fluids of strictly uniaxial particles to be studied.

Some common liquid crystals must, as a result of other symmetry properties, necessarily be biaxial. Thus, for example, the chiral nematic (cholesteric) phase in its usual uniform twist texture must be locally biaxial, because the two axes perpendicular to the director—the twist axis and the third axis perpendicular to the director and the twist axis—can be distinguished from each other. However, in the limit that the cholesteric pitch goes to infinity, the degeneracy between these two axes returns and the resulting nematic is uniaxial. Likewise, in the smectic C phase, in which the director lies at an angle to the normal to the smectic layers, the two axes perpendicular to the director are not identical. Indeed, the recognition of this fact was crucial for the identification of the molecular structure of the phase by Taylor *et al.* [12]. Both of these systems are biaxial, but the biaxiality is not the principal distinguishing feature of either phase. Nor is the molecular biaxiality alone the driving feature to which the existence of either phase can be attributed. Rather the phase biaxiality is a derived feature following from other more profound properties of each phase.

On the other hand, given the biaxial structure of mesogenic molecules, there has long been theoretical speculation about the possible existence of purely orientational biaxial phases. As long ago as 1970 Freiser [13] constructed a molecular-field theory for a fluid of biaxial liquid crystal molecules, generalizing the Maier-Saupe theory. He predicted that the usual first order isotropic (uniaxial) nematic phase transition would be followed at lower temperatures by a second-order uniaxial-biaxial nematic phase transition. In 1973 Alben [14] constructed a Landau theory, which addressed some of the issues raised by Freiser. He was the first to predict the existence of a point at which the isotropic-nematic phase transition became continuous. At this point the uniaxial-biaxial and isotropic-uniaxial nematic transitions collide, at what Alben called an "accidental" second-order transition when the biaxial nematic yields the isotropic phase. This Landau point, at which the biaxial nematic phase undergoes a second-order transition to the isotropic phase, has been the focus of much subsequent study [15].

Then in 1974 Straley [16] constructed a Maier-Saupe-like theory for a fluid of hard biaxial particles with D_{2h} symmetry using a parametrization based on their excluded volume. His theory reproduced the phase sequence isotropic-uniaxial nematic-biaxial nematic predicted by Freiser and by Alben. An important advance made by Straley was the realization that a full description of the statistical mechanics required more order parameters than had hitherto been used. The minimum set introduced by Straley (in his language S,T,U,V, and for which we use S,P,D,C [17,18]) also took account of the orientational ordering of the minor molecular axes.

But what exactly constitutes a minor axis? We can say *ex post facto* that an axis is minor, in that there is some energetic parameter associated with this axis which is small in comparison with that for the major axis. Often the terms major and minor relate to the magnitude of the ordering tensor so by convention we define $S_{zz} > S_{xx} > S_{yy}$. But as soon as a distinction can be made, from an entropic point of view, it does not matter whether an axis is minor or major, it is simply different. Equivalently, Straley's quantities are not uniquely defined. There is a group theoretical structure connecting them [19], associated with rotations in a laboratory or molecular frame of reference. A full Landau theory for phase biaxiality requires an expansion of the free energy in rotational invariants. But the problem is, as a number of workers have found [20–22], that there are rather a large number of such invariants. Indeed there are probably too many for useful systematic studies to be carried out, without further guidance, either from experiment or from molecular theory as to the values of the associated proportionality constants. There is also another more fundamental problem for, having constructed the invariants from the ordering tensors, it is assumed that in the free energy expansion the proportionality constants for the invariants are scalars. As we shall see this need not be the case and so the invariants that occur in the Landau theory need to be constructed not only from the ordering tensors but also the proportionality tensors.

When the molecular-field theory is applied to noncylindrically symmetric molecules, it provides a free energy that may fail to attain a minimum at the equilibrium [23]. The physical significance of the saddle points is usually justified by appealing to the Bogoliubov minimax principle [24,25], whose status in this context is not entirely clear. By contrast, in Landau theories and density functional theories the strategy is always to construct a sensible expression for the free energy on heuristic grounds and then minimize it. It is interesting to notice that the KKLS protocol always seems to produce a free energy density with a global minimum, despite the fact that it borrows the internal energy from the MF theory.

Meanwhile, in recent years there has been a renaissance of interest in biaxial liquid crystal systems, partly (though not only) because of the prospect of a dramatic reduction in reorientation times in liquid crystal devices [26–28]. Although experimental demonstration of the existence of a lyotropic biaxial phase was achieved in 1980 [29], confirmation of a thermotropic biaxial phase has been slow in coming. Some well-publicized relatively recent experimental observations of thermotropic biaxial phases [30–32] remain controversial, but have stimulated considerable theoretical work.

This paper builds on KKLS, in that we seek to make a direct and quantitative connection between molecular and Landau theories of biaxial liquid crystals. Specifically we concentrate on molecules and phases with $D_{\infty h}$ symmetry (i.e., cylindrically symmetric), and those with D_{2h} symmetry (i.e., three orthogonal C_2 rotation axes). Accordingly we will be able to examine plausible free energy expansions, consistent with our understanding of molecular theories, rather than address the full invariant structure, which as we have noted is a wholly impractical undertaking. A particular advantage of the approach we adopt is that, by contrast with a wholly phenomenological theory, it is now possible to understand how the molecular symmetry can drive phase transitions in the biaxial-uniaxial-isotropic phase map and elsewhere.

It is of some interest to note that, in fact, the original goal of KKLS in the mid 1980s was to address just the biaxial problem we deal with in this paper. At that stage, however, computational problems restricted the scope of possible calculations, and we were limited to considering only the uniaxial case. Advances in computer algebra, and a deeper understanding of the invariant structure of the theory, now enable us to make further progress. Indeed a preliminary account of our early calculations has been presented [33].

The structure of paper is as follows. In Sec. II we give a general overview of the structure of molecular-field theory in liquid crystals. Then in Sec. III we summarize the KKLS theory. The development presented here is more general than the presentation in Ref. [11], in principle allowing for the presence of many order parameters. This allows us to construct the formal theory in algorithmic form using the molecular-field theory, via KKLS, to inform the structure of the Landau expansion. The rest of the paper then presents results which follow from the program articulated in Sec. III.

In Sec. IV we revisit and rederive the original KKLS model, in which both the molecules and the phase have $D_{\infty h}$ symmetry. We also make some important mathematical points concerned with the convergence of the series and of the order parameter in the limit of zero temperature. Although it is expected that Landau theory should be true close to a weak phase transition, it is desirable to be able to use it away from this region. In Sec. IV we suggest a kind of mathematical regularization which enables our KKLS-generated Landau theory, which we shall refer to as Landau-KKLS theory, to be used in this way without catastrophic divergences. We use this regularization in subsequent sections of the paper.

We then pass to a discussion of biaxial phases generated, as might reasonably be expected, by biaxial molecules taken to have D_{2h} point group symmetry. In Sec. V we discuss the higher temperature uniaxial phases which are expected to occur in this case. We also discuss the consequences of the physically appealing geometric mean approximation, widely used elsewhere in the literature [34,35], which reduces the number of parameters required to define the magnitude of the molecular biaxiality from 2 to 1. This approximation allows us to look at Alben's accidental second-order isotropic-nematic transition (also known as a Landau point) in a new light. Looked at within our framework, this transition loses its accidental nature. Then in Sec. VI we consider the most general case, in which biaxial molecules give rise to a biaxial phase. This section connects our work not only with the Landau points, but also with recent work by Virga and co-workers [19,36]. Finally, in Sec. VII, we make some concluding remarks.

II. OVERVIEW OF MOLECULAR FIELD THEORY

The earliest form of the Maier-Saupe molecular-field theory [4,5] for liquid crystals uses a single-particle orientational partition function for a rodlike particle in a uniaxial mean field. By enforcing self-consistency, the theory is able to derive a formula for the temperature dependence of an orientational order parameter as a function of a single scalar interparticle quantity related to an orientational energy parameter u. However, in this form the deeper theoretical status of the theory is lacking.

A more profound route to liquid crystal molecular-field theory is the variational approach outlined by de Gennes [10]. This begins with the thermodynamic internal energy U, which is written in terms of the dominant order parameters, collectively denoted by a vector $\langle \mathbf{Q} \rangle$, defining the phase involved. In its more general form [34,35], the internal energy is now written as a sum of invariants involving the order parameter $\langle \mathbf{Q} \rangle$, and a *supertensor* quantity $\mathbf{u}$, which is related in some way to the molecular interactions:

$$U = -\tfrac{1}{2}\,\mathbf{u} \cdot \langle \mathbf{Q} \rangle \otimes \langle \mathbf{Q} \rangle, \tag{1}$$

where the dot product signifies a full contraction of indexes in such a way that the energy itself is a scalar. In principle, an infinite number of order parameters is necessary to fully characterize the orientational distribution function. However, a standard simplifying assumption is to truncate the potential of mean torque, $U(\Omega)$, at the second-rank level. Indeed, experiment shows that second-rank order parameters are dominant, at least near the nematic-isotropic transition temperature. Hence they represent a useful surrogate for the distribution function and are then used to construct the molecular-field internal energy.

To construct the Helmholtz free energy, the entropy S is also required. Within the molecular-field theory this is related to the singlet orientational distribution function $f(\Omega)$ by the Gibbs entropy formula [7]

$$S = -k_B \int f(\Omega)\, \ln f(\Omega)\, d\Omega, \tag{2}$$

where Ω collectively describes the three Euler angles α, β, and γ, which give the molecular orientation in a laboratory frame of reference, and k_B is the Boltzmann constant. The free energy is then

$$A = -\frac{1}{2}\,\mathbf{u} \cdot \langle \mathbf{Q} \rangle \otimes \langle \mathbf{Q} \rangle + k_B\, T \int f(\Omega)\, \ln f(\Omega)\, d\Omega. \tag{3}$$

The equilibrium distribution function is as yet unknown, but can be obtained by a functional minimization of the free energy. This minimization is, however, subject to the following constraints. These are that the distribution function (a) be normalized, and (b) be related to the order parameters by

$$\int \mathbf{Q}(\Omega)\, f(\Omega)\, d\Omega = \langle \mathbf{Q} \rangle. \tag{4}$$

Equation (4) reflects the fact that the order parameters are defined as equilibrium averages of suitable angular functions, $\mathbf{Q}(\Omega)$. These are usually constructed as linear combinations of the Wigner rotation matrices [37].

The resulting distribution function is used to determine the potential of mean torque, $U(\Omega)$, via [35]

$$f(\Omega) = Z^{-1} \exp\left\{-\frac{U(\Omega)}{k_B T}\right\}, \tag{5}$$

where the orientational partition function is

$$Z = \int \exp\left\{-\frac{U(\Omega)}{k_B T}\right\} d\Omega \tag{6}$$

and the potential of mean torque is

$$U(\Omega) = -\mathbf{u} \cdot \langle \mathbf{Q} \rangle \otimes \mathbf{Q}(\Omega). \tag{7}$$

The *equilibrium* free energy is given by the formula

$$A = \tfrac{1}{2}\, \mathbf{u} \cdot \langle \mathbf{Q} \rangle \otimes \langle \mathbf{Q} \rangle - k_B T \, \ln Z, \tag{8}$$

and the order parameters $\langle \mathbf{Q} \rangle$ can be determined as the values which minimize it. Alternatively, they can be calculated by solving the consistency equations for the order parameters, namely,

$$\langle \mathbf{Q} \rangle = Z^{-1} \int \mathbf{Q}(\Omega) \exp\left\{\frac{\mathbf{u} \cdot \langle \mathbf{Q} \rangle \otimes \mathbf{Q}(\Omega)}{k_B T}\right\} d\Omega. \tag{9}$$

In principle, we can also define other order parameters which do not enter the potential of mean torque. The molecular-field theory can also be employed to calculate these quantities, via a Boltzmann average:

$$\langle X \rangle = Z^{-1} \int X(\Omega) \exp\left\{\frac{\mathbf{u} \cdot \langle \mathbf{Q} \rangle \otimes \mathbf{Q}(\Omega)}{k_B T}\right\} d\Omega. \tag{10}$$

Since one of the main interests in the present paper is that of a biaxial nematic liquid crystal composed of rigid molecules with D_{2h} point group symmetry, we explicitly recall the definition of the order parameters [18,37,38]. The orientation of the molecular frame $(\mathbf{m}_1, \mathbf{m}_2, \mathbf{m}_3)$ (dictated by molecular symmetry) with respect to the laboratory frame $(\mathbf{l}_1, \mathbf{l}_2, \mathbf{l}_3)$ (identified by the phase symmetry of the either $D_{\infty h}$ or D_{2h}) will be given by the three Euler angles α, β, γ $(\equiv \Omega)$. The functions $\mathbf{Q}(\Omega)$, whose averages define the order parameters $\langle \mathbf{Q} \rangle$, are conveniently expressed as the symmetry-adapted Wigner matrices [18,39,40]

$$R_{00}(\Omega) = D^{(2)}_{00}(\Omega) = \frac{1}{2}(3\cos^2\beta - 1), \tag{11a}$$

$$R_{02}(\Omega) = \mathrm{Re}\{D^{(2)}_{02}(\Omega)\} = \sqrt{\frac{3}{8}} \cos 2\gamma \, \sin^2\beta, \tag{11b}$$

$$R_{20}(\Omega) = \mathrm{Re}\{D^{(2)}_{20}(\Omega)\} = \sqrt{\frac{3}{8}} \cos 2\alpha \, \sin^2\beta, \tag{11c}$$

$$\begin{aligned} R_{22}(\Omega) &= \frac{1}{2}\mathrm{Re}\{D^{(2)}_{22}(\Omega) + D^{(2)}_{2-2}(\Omega)\} \\ &= \frac{1}{4}(1+\cos^2\beta)\cos 2\alpha \, \cos 2\gamma \\ &\quad - \frac{1}{2}\cos\beta \, \sin 2\alpha \, \sin 2\gamma. \end{aligned} \tag{11d}$$

We will also use the following alternative definition of the order parameters, which comes from a Cartesian representation of the ordering supertensor [38,41],

$$S^{AB}_{ab} = \tfrac{1}{2}\langle 3(\mathbf{m}_a \cdot \mathbf{l}_A)(\mathbf{m}_b \cdot \mathbf{l}_B) - \delta_{ab}\delta_{AB}\rangle. \tag{12}$$

We note in passing that the Cartesian definition in Eq. (12) comprises both rank-1 and rank-2 spherical tensors. Rank-1 spherical components are associated with the antisymmetric part of S^{AB}_{ab} and define *polar* order parameters. Nonpolar, rank-2 order parameters are given by the symmetric part $(S^{AB}_{ab} + S^{AB}_{ba})/2$ [42,43]. When D_{2h} point group symmetry is assumed for both the molecule and the phase, the four nonvanishing order parameters, S, P, D, and C, are [18]

$$S = S^{ZZ}_{zz}, \tag{13a}$$

$$D = S^{ZZ}_{xx} - S^{ZZ}_{yy}, \tag{13b}$$

$$P = S^{XX}_{zz} - S^{YY}_{zz}, \tag{13c}$$

$$C = \left(S^{XX}_{xx} - S^{XX}_{yy}\right) - \left(S^{YY}_{xx} - S^{YY}_{yy}\right). \tag{13d}$$

Following the usual convention, we have used the same symbol S for the entropy but also for one of the orientational order parameters. The correct meaning will be made clear by the context. The connection with the spherical tensor definition is

$$S = \langle R_{00}\rangle, \quad D = \sqrt{6}\,\langle R_{02}\rangle, \tag{14a}$$

$$P = \sqrt{6}\,\langle R_{20}\rangle, \quad C = 6\,\langle R_{22}\rangle. \tag{14b}$$

We note that, in the limit of perfect ordering, i.e., $\alpha,\beta,\gamma \to 0$, it follows from the definitions in Eqs. (11a)–(11d) that $S \to 1$, $P \to 0$, $D \to 0$, and $C \to 3$. Therefore we expect the order parameters P and D to vanish at sufficiently low temperatures, while S and C have to be interpreted as the main order parameters. We have chosen to use second-rank order parameters because for nematics in the vicinity of the transition to the isotropic phase these are found to be dominant [44].

III. KKLS METHODOLOGY

A central part of this paper will be to calculate the entropy contribution to the nonequilibrium free energy coming from a general set of second-rank anisotropic order parameters, associated with anisotropic molecular interactions. As such, the paper generalizes the procedure first used by Katriel *et al.* [11] connecting the Maier-Saupe theory to the Landau–de Gennes expansion. Here we briefly review the method. Rather than following the original treatment, however, we rewrite the formalism so as to emphasize its capacity to deal with a multiorder parameter problem.

We concentrate on *orientational* probability distributions. Although the method itself is, in principle, more general, all of the examples in the present paper are of this nature. In particular, we are interested in the free energy expansion for biaxial nematic liquid crystals.

In a homogeneous liquid crystal (i.e., where the director field is uniform), the molecular orientation with respect to the laboratory frame is described by Euler angles Ω, and in molecular-field theory the most important details of the statistical mechanics are determined by the single particle probability density function $f(\Omega)$, usually known as the singlet orientational distribution function. The probability of finding a molecule oriented within an infinitesimal solid angle $d\Omega = \sin\beta\, d\alpha d\beta d\gamma$ centered at Ω, is given by the product $f(\Omega)\, d\Omega$. Above a critical temperature, the system is isotropic and the probability distribution is uniform. When the temperature decreases below this critical value, $f(\Omega)$ is no longer uniform and its moments indicate the preferred molecular orientation.

Usually the nonequilibrium $f(\Omega)$ is not known; all we know is the mean value of some functions of the Euler angles. The idea is first to use the maximum entropy principle to find $f(\Omega)$, given our knowledge of the system. Then, we can use this distribution to write the nonequilibrium free energy. More specifically, the Gibbs entropy formula, for probability distributions $f(\Omega)$ defined for all possible molecular orientations, reduces to

$$S = -k_B \int_{\mathrm{SO(3)}} f(\Omega)\, \ln f(\Omega)\, d\Omega, \tag{15}$$

where SO(3) is the group of proper rotations of three dimensional space. We want to find the $f(\Omega)$ which maximizes S subject to constraints of the type

$$\int_{\mathrm{SO(3)}} Q_i(\Omega)\, f(\Omega)\, d\Omega = \langle Q_i \rangle, \quad i = 1 \dots n \tag{16}$$

and the normalization condition

$$\int_{\mathrm{SO(3)}} f(\Omega)\, d\Omega = 1. \tag{17}$$

In our specific case, $Q_i(\Omega)$ are angular functions whose averages define the orientational order parameters, and $\langle Q_i \rangle$ are the order parameters. When the problem is expressed in its discrete form (i.e., a discrete probability distribution), a direct connection with information theory can be made [45]. In this context, the entropy quantifies the amount of information which is missing in order to be able to describe the system microscopically. Since our knowledge of the system is given only by the order parameters, the most unbiased guess for the probability distribution is provided by maximizing Eq. (15) subject to the constraints in Eqs. (16) and (17).

To make the notation more compact, we define the three vectors: $\mathbf{Q}(\Omega) = [Q_1(\Omega), \dots, Q_n(\Omega)]$, $\boldsymbol{\eta} = (\eta_1, \dots, \eta_n)$, and $\langle \mathbf{Q} \rangle = (\langle Q_1 \rangle, \dots, \langle Q_n \rangle)$. The constants $\boldsymbol{\eta}$ are Lagrangian multipliers. They are introduced to satisfy the constraints in Eq. (16) and play an important role in the practical development of the method. An additional Lagrangian multiplier is used to satisfy the normalization constraint in Eq. (17).

The maximization of Eq. (15) subject to the constraints in Eqs. (16) and (17) can be performed formally and leads to a Maxwell-Boltzmann form for the probability distribution function

$$f(\Omega) = \frac{e^{\boldsymbol{\eta}\cdot\mathbf{Q}(\Omega)}}{8\pi^2\, Z(\boldsymbol{\eta})}, \tag{18}$$

where Z is the orientational partition function

$$Z(\boldsymbol{\eta}) = \frac{1}{8\pi^2} \int_{SO(3)} \exp[\boldsymbol{\eta} \cdot \mathbf{Q}(\Omega)]\, d\Omega. \tag{19}$$

The Lagrangian multipliers $\boldsymbol{\eta}$ are determined by inverting the series expansion of $\ln Z(\boldsymbol{\eta})$ as we shall describe later.

Using Eq. (19) the entropy difference ΔS between the orientationally ordered and isotropic phase is given by

$$\begin{aligned} \Delta S &= -k_B \int f(\Omega)\, \ln[8\pi^2 f(\Omega)]\, d\Omega \\ &= -k_B \int f(\Omega)\, \ln\left(\frac{e^{\boldsymbol{\eta}\cdot\mathbf{Q}(\Omega)}}{Z(\boldsymbol{\eta})}\right) d\Omega \\ &= k_B \int f(\Omega)\, [\ln Z(\boldsymbol{\eta}) - \boldsymbol{\eta} \cdot \mathbf{Q}(\Omega)]\, d\Omega \\ &= k_B\, [\ln Z(\boldsymbol{\eta}) - \langle \mathbf{Q} \rangle \cdot \boldsymbol{\eta}]\,. \end{aligned} \tag{20}$$

We can now sketch the KKLS protocol, presented in Ref. [11], in an algorithmic form.

(i) *Partition function and its expansion in terms of* $\boldsymbol{\eta}$. Expand the Boltzmann factor in Eq. (19) with respect to $\boldsymbol{\eta}$ up to the desired order. The coefficient of each term in the expansion is an integral. In the original KKLS examples, these integrals were trivial. For the examples considered in this paper, however, although it is always possible to evaluate these integrals, they can be extremely cumbersome. The underlying assumption is that it is possible to exchange the integral and the series so that the series can be integrated term by term. The final expression is a polynomial expansion of Z in $\boldsymbol{\eta}$ with real coefficients.

(ii) *Order parameters as series expansions in the Lagrangian multipliers*. The scalar order parameters can be obtained once we know the partition function. Specifically, it follows from Eq. (19) that

$$\langle \mathbf{Q} \rangle = \nabla_{\eta} \ln Z(\boldsymbol{\eta}) = W(\boldsymbol{\eta}). \tag{21}$$

This relation links the order parameters $\langle \mathbf{Q} \rangle$ with the Lagrangian multipliers $\boldsymbol{\eta}$. Because we already have $Z(\boldsymbol{\eta})$ as a series expansion in $\boldsymbol{\eta}$, we can now rewrite Eq. (21) as a series expansion. This provides n series of the type

$$\langle Q_h \rangle = \sum_{k=1}^{\infty} \sum_{i=1}^{n} a_{i,k}^{(h)}\, \eta_i^k, \quad a_{i,k}^{(h)} \in \mathbb{R}, \tag{22}$$

where n is the number of order parameters.

(iii) *Inversion of the series and determination of the Lagrangian multipliers*. The series (22) can be inverted [46] to give the series representation of $\boldsymbol{\eta}$ in terms of $\langle \mathbf{Q} \rangle$. These values of η_i are the Lagrangian multipliers which satisfy the constraints (16). We have thus obtained a series representation of the inverse function $G = W^{-1}$,

$$\begin{aligned} \eta_h &= G_h(\langle \mathbf{Q} \rangle) = W_h^{-1}(\langle \mathbf{Q} \rangle) \\ &= \sum_{k=1}^{\infty} \sum_{i=1}^{n} b_{i,k}^{(h)}\, \langle Q_i \rangle^k, \quad b_{i,k}^{(h)} \in \mathbb{R}. \end{aligned} \tag{23}$$

The function $G(\langle \mathbf{Q} \rangle)$ is well defined, as explained in Ref. [11].

(iv) *Entropy and free energy expansions.* It is now easy to express the nonequilibrium entropy as a function of the order parameters $\langle \mathbf{Q} \rangle$. Substitution of Eq. (23) in Eq. (20) yields

$$\Delta S = k_B(\ln Z(G(\langle \mathbf{Q} \rangle)) - \langle \mathbf{Q} \rangle \cdot G(\langle \mathbf{Q} \rangle)). \tag{24}$$

Finally, the Helmholtz free energy difference between the liquid crystal and the isotropic phases is

$$\Delta A = U - T\,\Delta S. \tag{25}$$

The internal energy per particle, U, will be given by a molecular-field approximation [35] in terms of the order parameters. Its form is detailed for each specific example in the following sections.

We should also note that given the free energies in any individual case, the phase transitions occur either when free energy branches cross (in the case of a first-order transition), or when the turning points are degenerate (in the case of a continuous transition). In either case, the relevant transition temperature can be found by solving a system of polynomial equations. These equations can be solved using the methods of elimination theory in algebra, specifically methods employing Gröbner basis calculations or repeated evaluation of polynomial resultants. We refer to the specific literature for details (see, for example, [47,48], and references therein). Most symbolic manipulation software, such as MAPLE® or MATHEMATICA®, already contain built-in functions for performing these algebraic operations.

A final comment is in order. The transcription of a molecular theory into a Landau expansion is well known from standard textbooks on liquid crystals and statistical mechanics [38,49]. This approach was first introduced in the liquid crystal literature by Palffy-Muhoray and Dunmur [50]. However, we regard this approach not as standard, but indeed rather as formally incorrect. A large portion of the KKLS paper [11] was devoted to a critical discussion of just this point. The key issue is that the higher-order terms in the Landau expansion are entropic and must (in a molecular-field context in which correlations are ignored) be proportional to the absolute temperature T. The expansions given in the textbook examples break this iron rule. An alternative approach, which follows from more elaborate DFT models, can also be found in the literature (see, for example, [51,52]). By contrast, we regard the approach in Refs. [51,52] (albeit on the Landau theory of the Onsager, rather than the Maier-Saupe, transition) as correct, and inconsistent with that of Refs. [38,49]. In our view the mathematical approach adopted in Refs. [51,52] is consistent with the KKLS protocol; the differences between [51] and [11] are a consequence of the physical differences between the systems under consideration.

IV. UNIAXIAL ($D_{\infty h}$) NEMATIC OF $D_{\infty h}$ MOLECULES

As a first example, we study the case of a uniaxial ($D_{\infty h}$) molecule in a uniaxial ($D_{\infty h}$) nematic phase. This was the standard example used by KKLS [11]. We first follow the standard KKLS argument in detail. The second subsection then points out some undesirable mathematical pathologies which result from the procedure. We examine the origin of these problems, and construct an empirical procedure which cures the worst of the difficulties. We thus introduce a pathology-free modified KKLS procedure. The philosophy behind this new procedure will guide our work in subsequent sections on biaxial liquid crystals.

A. Standard KKLS argument

The free energy is found following steps (i)–(iv) described in the previous section. The starting point is to obtain a polynomial expression for the partition function by expanding

$$Z(\eta) = \frac{1}{2\pi}\int_0^{\pi} \exp\left[\eta\,\frac{1}{2}(3\cos^2\beta - 1)\right]\sin\beta\, d\beta \tag{26}$$

in a Taylor series with respect to η and integrating term by term. We have assumed that the orientational probability distribution is given by the maximum entropy principle. The angular dependence of the exponent in Eq. (26) reflects the fact that we are using the dominant order parameter, which is the second-rank quantity function [44]

$$S = \langle P_2 \rangle = \tfrac{1}{2}\langle 3\cos^2\beta - 1\rangle, \tag{27}$$

where β is the angle between the molecular symmetry axis and the director, and $P_2(\cos\beta)$ is the second Legendre polynomial. We also recall that η is the Lagrangian multiplier associated with the constraint in Eq. (27) for fixed S.

A further expansion in powers of η of the right-hand side of

$$S = \frac{\partial \ln Z(\eta)}{\partial \eta} \tag{28}$$

leads to a series which can be inverted to give η in terms of a power series in the order parameter S. The entropy and the free energy can then be readily obtained from Eqs. (24) and (25).

The final expression for the Landau-KKLS scaled free energy expansion is then [11] given by

$$\Delta A/u_{200} = \tfrac{5}{2}\left(\widetilde{T} - \tfrac{1}{5}\right)S^2 - \tfrac{25}{21}\widetilde{T}S^3 + \tfrac{425}{196}\widetilde{T}S^4 + \cdots, \tag{29}$$

where $\widetilde{T} = k_B T/u_{200}$ is the scaled temperature, T is the absolute temperature, and u_{200} is a component of the second-rank supertensor $\mathbf{u}$. In deriving Eq. (29), we have used the following internal energy per particle:

$$U = -\frac{u_{200}}{2}S^2. \tag{30}$$

Equation (30) is consistent at equilibrium with the classic Maier-Saupe expression [4], which is used to construct the equilibrium free energy in a molecular-field approximation.

Solving the algebraic equation $\partial\Delta A/\partial S = 0$ yields three solutions. One solution is the absolute minimum, and this solution yields the value of the equilibrium order parameter $S = S_0$. Sufficiently close to T_{NI} there are two further solutions; one of these, at $S = 0$, corresponds to the metastable isotropic phase, while the third solution is a local maximum.

B. Some mathematical and physical remarks

We first point out the attractive features of the KKLS protocol.

(i) The temperature $\widetilde{T}^* = 1/5$ at which the isotropic phase becomes unstable agrees *exactly* (and indeed, by construction) with the underlying molecular-field theory.

(ii) The transition temperature $\widetilde{T}_{NI}$ for the first-order transition isotropic-uniaxial nematic phase occurs when the free energies of the isotropic and nematic phase are equal. From the extra condition that $\Delta A(S_0) = 0$, we find

$$\widetilde{T}_{NI} = \tfrac{153}{715} \approx 0.214, \tag{31}$$

in good agreement with Maier-Saupe result for $\widetilde{T}_{NI}$ of approximately 0.220.

(iii) The predicted order parameter jump at $\widetilde{T}_{NI}$, $S(T_{NI}) \approx 0.274$, is also in relatively good agreement with the underlying molecular-field theory, which gives 0.429 (and, indeed, experiment [35] where the value is approximately 0.3).

However, the expansion in Eq. (29) does differ from a standard Landau expansion in several important features. Thus we note the following:

(i) No previous knowledge of the invariants is required to construct the expansion. The correct invariants appear naturally in the expansion as a consequence of the calculations. Here, with just one order parameter, this feature may not appear important. But when dealing with D_{2h} molecules in a biaxial nematic phase which itself possesses D_{2h} symmetry, this question becomes much more urgent. We discuss this particular point in more detail below in Sec. VI.

(ii) The expansion coefficients are not phenomenological, but have precise numerical values determined by a molecular-field energy. Therefore the number of phenomenological parameters is reduced. This feature becomes extremely important in systems with a larger number of relevant order parameters. In particular, such complex systems involve a free energy which would otherwise contain terms with specific symmetry but arbitrary coefficients. This procedure possesses the obvious advantage of evaluating specifically the otherwise arbitrary terms in the free energy.

(iii) However, all terms, including those of higher order, depend linearly on temperature. Indeed apart from the second-rank terms, all terms are specifically *proportional* to temperature. This fact, coupled with a minor freedom in selecting the coefficients, has a somewhat undesirable consequence, as we discuss later in rather more detail.

The predicted dependence of the order parameter on the temperature is shown by the dashed line in Fig. 1. We notice how, using Eq. (29), S diverges to infinity as $\widetilde{T} \to 0$. This is, of course, unphysical. It is particularly undesirable if we wish to construct a theory which can be consistently extrapolated into the low temperature region. For comparison, we also show in Fig. 1 the behavior of the Maier-Saupe order parameter. This does not diverge at $T = 0$, but rather (as it should) approaches complete order, i.e., $S = 1$.

We show in Appendix A that this divergence can be specifically ascribed to the presence of $\widetilde{T}$ in the coefficient of the highest-order term retained in this expansion (in this case, the S^4 term). This feature is, by construction, absent in a standard Landau expansion where only the coefficients of the quadratic terms are assumed to depend on temperature. This indicates that keeping more terms in the expansion does provide a better approximation. But, for every finite n, there will continue to be a divergence in the order parameter at low temperatures.

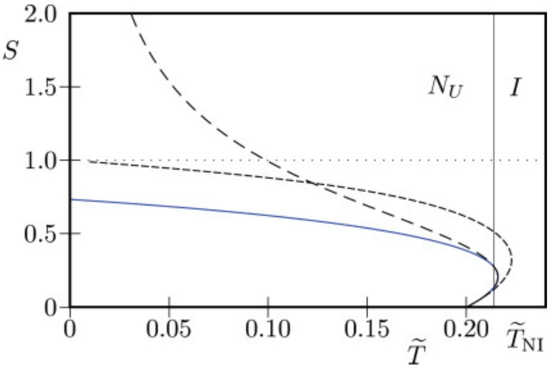

FIG. 1. (Color online) Temperature dependence of the uniaxial order parameter S in the uniaxial nematic phase from the Landau-KKLS theory. $\widetilde{T} = k_B T/u_{200}$ is the scaled temperature. Dashed line: original KKLS theory derived by minimizing Eq. (29). Solid line: regularized Landau-KKLS theory, minimizing Eq. (32) with $\theta = \widetilde{T}_{NI} \approx 0.214$. Short dashed line: prediction of the Maier-Saupe theory [35], with the same value of $\widetilde{T}^*$. Note the divergence of $S\,(\widetilde{T} \to 0)$ for the original KKLS theory, and the similarity between the regularized Landau-KKLS theory and the Maier-Saupe results.

A summary of the foregoing argument is as follows. We have constructed a polynomial approximation of the free energy by truncating the Taylor expansion of the molecular-field free energy about the isotropic phase. The KKLS protocol implies that the expansion coefficients of the terms of cubic order and higher should depend linearly on temperature. This conclusion is robust, so long as we use molecular-field theory (as seems sensible) to generate the expansion. However, a polynomial truncated at any *given* finite order n cannot be valid at all temperatures $T > 0$.

The full Maier-Saupe theory, by contrast, does not exhibit a pathological temperature dependence of the order parameter. The usual evaluation of the nonlinear self-consistent equation within the Maier-Saupe theory does not involve any series expansions, of course. But in principle, if the expansion in Eq. (29) were continued to all orders, it would presumably be *guaranteed* to provide identical answers, provided that the order parameter is less than the radius of convergence of the series. Is is shown elsewhere [53,54] that the series is logarithmically divergent, with radius of convergence $S = 1$. It is the factor of T, coming from the molecular-field derivation, which causes the problem. By contrast, there is no order parameter divergence when the coefficients are constant, as they are in the standard Landau approach.

We now discuss, briefly, strategies for avoiding the pathological divergence of $S(T \to 0)$. The straightforward strategy is to retain more terms in the expansion. The series then converges (eventually) to the original molecular-field potential. In practice, however, this is not feasible. The divergence itself can only be avoided by summing to all terms. In principle, for any given $T \neq 0$ there is a critical number of terms $n(T)$ required so that practical convergence can be established, but $n(T \to 0) \to \infty$. The degree of analytic power required seems prohibitive. Worse than that, it seems contrary to the spirit of Landau theories. The main simplification of the Landau formalism is thought to be precisely that the topological features of the phase diagram are given by an expansion which has been truncated at some low order.

A more fruitful strategy, and the one which we shall adopt, is to take the expansion coefficient of the highest degree term in Eq. (29) to be temperature independent. This requires the coefficient of temperature T in the dominant terms to be replaced by a constant, θ.[1] Another adjustable parameter has been introduced into the Landau-KKLS expansion, albeit in an *ad hoc* manner.

In this way we have followed a least disruption principle by introducing the minimum possible number of phenomenological parameters to avoid the divergence. We shall see in more complex cases that, in order to preserve the invariance of the free energy, θ has to multiply an invariant instead of a single term. We note from Fig. 1 that in this case the minimal disruption assumption does have the required effects. Thus close to the phase transition the behavior of the order parameter and associated thermodynamic quantities are quantitatively close to the molecular-field theory predictions. Close to $T = 0$, the order parameter divergence is cured, and indeed even the quantitative disagreement with molecular-field theory is not serious. We postpone further discussion of the merits of this procedure to the last section of the paper.

The free energy Eq. (29) now becomes

$$\Delta A/u_{200} = \tfrac{5}{2}\left(\widetilde{T} - \tfrac{1}{5}\right) S^2 - \tfrac{25}{21}\widetilde{T}\, S^3 + \tfrac{425}{196}\,\theta\, S^4. \qquad (32)$$

In Fig. 1 the constant θ is chosen to be 0.214, so that the free energies in Eqs. (29) and (32) coincide at $\widetilde{T} = \widetilde{T}_{NI} \approx 0.214$. This choice of θ yields for Eq. (32) the same nematic-isotropic transition temperature $\widetilde{T}_{NI} \approx 0.214$. In fact, the good accord between Eqs. (29) and (32) for the order parameter S is readily seen in Fig. 1.

We stress, however, that the parameter θ has to be regarded as an additional degree of freedom and its choice must be driven by physical considerations. There is no unique choice. In general, different criteria lead to different values of θ. For instance, one possible obvious strategy is to choose θ such that $S = 1$ at $\widetilde{T} = 0$. A second possibility is to set $\theta = \widetilde{T}^*$. However, we have found these values of θ lead to incorrect phase diagrams in the more complicated cases studied in Sec. VI. In particular, they fail to reproduce, even qualitatively, the phase diagram of Sonnet *et al.* [19].

Hence we preferred to set θ in order to match the phase map, rather than the order parameters and we decided to fix θ at 0.45, one value which seemed to provide, for all the cases considered here, phase maps which are in reasonably good agreement with those obtained using more complex methods. This is to be contrasted with conventional Landau theories, where all of the expansion coefficients are unknown; these are found by comparison with experiment.

In Appendix B we examine the KKLS theory, when we suppose that the molecules possess $D_{\infty h}$ symmetry but a phase may possess D_{2h} symmetry. The existence of such phases is a physically counterintuitive but robust prediction of the theory, which has also been predicted elsewhere [38,55]. We examine the prediction in some detail, comparing it with the contrasting predictions of molecular-field theory [13], before coming down on the side of the molecular-field theory.

V. UNIAXIAL NEMATIC OF D_{2h} MOLECULES

A. General considerations

We now generalize the analysis of the previous section. Specifically we move from $D_{\infty h}$ molecular symmetry to D_{2h} molecular symmetry. This molecular symmetry is generally regarded as being a minimal precondition for the existence of a biaxial liquid crystal phase. In this section we confine our interest to the N_U (uniaxial nematic) phase with $D_{\infty h}$ point group symmetry. The more general case, which includes the D_{2h} nematic phase, will be presented in Sec. VI.

In order to apply the KKLS protocol, we have to identify the relevant and dominant order parameters and their angular functional form. Now, in addition to the second-rank order parameter S, given by Eq. (27), we also have to consider the molecular biaxiality D [defined by Eq. (14a)] and given by

$$D = \tfrac{3}{2}\langle \cos 2\gamma\ \sin^2\beta\rangle. \qquad (33)$$

The orientational partition function, shown in general vector form in Eq. (19), requires two auxiliary Lagrangian multipliers. The parameter η_1 is conjugate to the order parameter S. The new parameter η_3 is conjugate to the molecular biaxiality order parameter D. The explicit form of $Z(\eta_1,\eta_3)$ is now

$$Z(\eta_1,\eta_3) = \frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{\pi} \exp\left[\eta_1\,\frac{1}{2}(3\cos^2\beta - 1) + \eta_3\,\frac{3}{2}(\cos 2\gamma\ \sin^2\beta)\right]\sin\beta\, d\beta\, d\gamma. \qquad (34)$$

In order to derive the free energy expression, we expand $Z(\eta_1,\eta_3)$ in Eq. (34) in powers of η_1,η_3 and follow the KKLS protocol. The coefficients of this expansion can be expressed explicitly in terms of angular integrals. The result, as we shall see, bears a considerable formal resemblance to the biaxial phase free energy expression in Eq. (B8) as a function of the order parameters S and P. We consider the entropy and energy contributions separately.

We start with the entropy contribution. The partition function $Z(\eta_1,\eta_3)$ in Eq. (34) possesses the same functional form as $Z(\eta_1,\eta_2)$ in Eq. (B7). This is a consequence of the symmetry between the Euler angles α and γ in the probability distribution function. Specifically, the quantities D and P defined in Eqs. (11b) and (11c) are related by the transformation $\alpha \leftrightarrow \gamma$; furthermore the probability measure has the same functional dependence on α and γ. The necessary consequence is that (for simplicity suppressing a common dependence on S) the functional dependence of the two relevant *entropy* contributions to the nonequilibrium free energy $\Delta S(P)$ and $\Delta S(D)$ are identical.

By contrast, the average internal energy contributions will, in general, be different. The D_{2h} molecular symmetry imposes some restrictions on the coefficients $u_{2kk'}$ [35,56]. There are only three independent coefficients, which in the molecular symmetry frame of reference can be expressed as u_{200}, u_{220},

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[1] The symbol θ is sometimes used for the absolute temperature in thermodynamics, but it does not have this meaning here.

and u_{222}. In this reference frame, the molecular-field theory expression for the internal energy yields [34,35]

$$U = -\frac{1}{2}\{u_{200}\langle R_{00}\rangle^2 + 4u_{220}\langle R_{00}\rangle\langle R_{02}\rangle + 4u_{222}\langle R_{02}\rangle^2\}$$
$$= -\frac{1}{2}\left\{u_{200}S^2 + u_{220}\sqrt{\frac{8}{3}}SD + u_{222}\frac{2}{3}D^2\right\}. \quad (35)$$

The presence of the three nonzero parameters, u_{200}, u_{220}, and u_{222}, signals molecular anisotropy. If u_{200} is the only nonzero coefficient, the molecules possess $D_{\infty h}$ symmetry (i.e., are uniaxial). In general, if either u_{220} or u_{222} are nonzero the molecules are biaxial and only possess D_{2h} symmetry, which requires the equalities $u_{220} = u_{2-20}$, $u_{222} = u_{22-2} = u_{2-22} = u_{2-2-2}$.

We can now substitute Eq. (35) into Eq. (25). We then combine this with the entropy difference expansion to obtain the following nonequilibrium Landau-KKLS free energy expansion:

$$\Delta A/u_{200} = \frac{5}{2}S^2\left(\tilde{T} - \frac{1}{5}\right) + \frac{5}{6}D^2\left(\tilde{T} - \frac{2\lambda^2}{5}\right)$$
$$- \sqrt{\frac{2}{3}}\gamma SD - \frac{25}{21}\tilde{T}S(S^2 - D^2)$$
$$+ \frac{425}{196}\theta\left(S^2 + \frac{1}{3}D^2\right)^2 + \cdots. \quad (36)$$

The degree of molecular biaxiality is parametrized by the two quantities $\gamma = u_{220}/u_{200}$ and $\lambda^2 = u_{222}/u_{200}$; we refer to these as the relative molecular biaxialities. We note that in the literature there are a number of different conventions for these parameters. We follow the definition of Luckhurst [44], rather than that of Sonnet *et al.* [19]. Here we have truncated the expansion at fourth order, although we note that, in principle, it is possible to calculate further terms. We also observe that (subject to the replacement of P by D), as discussed previously, Eqs. (36) and (B8) differ in the quadratic terms, but are the same in higher-order terms.

The terms in the expansion Eq. (36) correspond to invariants of the symmetry-adapted Wigner functions $\langle R_{0j}\rangle$. A discussion of the free energy invariants is postponed to the general case, which is considered in Sec. VI. Following the discussion in Sec. II, a constant factor θ has replaced the temperature in front of the highest-order invariant retained in the expansion. We do not study the detailed thermodynamic consequences of Eq. (36) as a function of both γ and λ. The calculations are rather cumbersome and not particularly relevant for understanding the physical problem. In the next subsection, however, we consider a particular case of special interest.

B. Geometric mean approximation

Within the geometric mean version of the molecular-field theory for the uniaxial nematic composed of D_{2h} molecules [34,35], the coefficient u_{220} is replaced by the geometric mean $\sqrt{u_{200}\,u_{222}}$. The theory is now defined by a single measure of the relative molecular biaxiality, with

$$\gamma = \frac{u_{220}}{u_{200}} = \sqrt{\frac{u_{222}}{u_{200}}} = \lambda. \quad (37)$$

It has been noted that the geometric mean approximation is consistent with the molecular interactions originating from London dispersion forces [32,38,55]. However, we also note that the approximation is more general than this requiring only that the expansion coefficient u_{2mn} can be separated into the product $u_{2m}u_{2n}$ of molecular properties so that λ is given by the molecular ratio u_{22}/u_{20}. Furthermore, it carries an extra advantage over and above that of relating the two measures of molecular biaxiality. It is now possible to define the orientational order in the theory in terms of a single composite order parameter $\langle J_1\rangle$. This is a well-defined combination of the two order parameters S and D occurring within the theory, and which are, in general, independent.

The composite order parameter is

$$\langle J_1\rangle = \langle R_{00}\rangle + 2\lambda\langle R_{02}\rangle = S + \sqrt{\frac{2}{3}}\lambda D, \quad (38)$$

with the associated

$$J_1(\Omega) = R_{00}(\Omega) + 2\lambda R_{02}(\Omega). \quad (39)$$

With this composite quantity, the potential of mean torque in the uniaxial nematic phase simplifies to

$$U(\Omega) = -u_{200}\,\langle J_1\rangle J_1(\Omega). \quad (40)$$

We now use this composite order parameter to develop a Landau-like expansion of the free energy using the KKLS protocol. This is particularly interesting since, as we shall see, the relative molecular biaxiality λ now appears in *all* terms of the expansion, in contrast to the standard phenomenological approach, in which molecular information is restricted to terms of quadratic order. This conclusion is unexpected because all higher-order terms are derived from the entropy. They should *not* depend therefore in any way on details of the molecular interactions, except insofar as they affect the molecular symmetry.

Under the geometric mean assumption the partition function turns out to be a function only of $J_1(\beta,\gamma)$. The whole molecular-field theory can thus be applied with only one order parameter as appreciated by Luckhurst *et al.* [32]. Likewise, the KKLS method only requires a single order parameter. From Eq. (35) and also Eq. (40), the molecular internal energy is given by

$$U = -\frac{u_{200}}{2}\,\langle J_1\rangle^2, \quad (41)$$

and the partition function is

$$Z(\eta) = \frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{\pi}\exp[\eta J_1(\beta,\gamma)]\,\sin\beta\,d\beta\,d\gamma. \quad (42)$$

Using Eq. (41) and the expansion of the entropy difference, we obtain the scaled free energy difference

$$\frac{2\lambda^2+1}{u_{200}}\Delta A = \frac{5}{2}\left(\tilde{T} - \frac{2\lambda^2+1}{5}\right)\langle J_1\rangle^2$$
$$- \frac{25}{21}\tilde{T}\frac{1-6\lambda^2}{(2\lambda^2+1)^2}\langle J_1\rangle^3$$
$$+ \frac{25}{196}\theta\frac{56\lambda^6+444\lambda^4-78\lambda^2+17}{(2\lambda^2+1)^4}\langle J_1\rangle^4. \quad (43)$$

Now, this result for ΔA involves only a single order parameter $\langle J_1 \rangle$. We can then use standard methods to locate the $N_U - I$ phase transition [38], and determine its properties. The first-order $N_U - I$ transition line is given by the equation

$$50(1-6\lambda^2)^2\widetilde{T}^2 + 9\,\theta\,(56\lambda^6 + 444\lambda^4 - 78\lambda^2 + 17) \times (1 + 2\lambda^2 - 5\widetilde{T}) = 0. \tag{44}$$

The nematic supercooling temperature (below which the isotropic phase becomes unstable) is given by

$$1 + 2\lambda^2 - 5\widetilde{T} = 0. \tag{45}$$

We observe that the molecular-field theory for this system, necessarily, also gives the same prediction for $\widetilde{T}$.

A particularly interesting feature of the expansion in Eq. (43) is that the cubic term *vanishes* for $6\lambda^2 - 1 = 0$. This implies immediately that the $N_U - I$ phase transition becomes continuous at this special value of $\lambda = \frac{1}{\sqrt{6}}$. This value is consistent with that found in the literature by solving the molecular-field theory numerically [41]. We further observe that the condition $\lambda = \frac{1}{\sqrt{6}}$ implies that the conditions in Eq. (44) for T_{NI}, and in Eq. (45) for T^*, coincide, as indeed is expected at a continuous phase transition. In fact it is known that $\lambda = \frac{1}{\sqrt{6}}$ also corresponds to a Landau point at which there is a direct continuous transition to a biaxial phase, although this possibility is not included in the restricted expansion used in this section.

The structural feature of note in Eq. (43) is that the relative molecular biaxiality λ is embedded in the entropy terms as well as in the purely energetic terms. The seemingly unnatural appearance of λ in the entropic part of the free energy can be understood by a closer inspection of the derivation of the entropy for the ordered phase [see Eq. (20)]. This is obtained from the singlet orientational distribution function with its dependence on the Boltzmann factor [see Eq. (18)]. This involves the conjugate functions $\mathbf{Q}(\Omega)$, whose averages are the order parameters $\langle \mathbf{Q} \rangle$. Normally these functions are simple combinations of Wigner rotation matrices. However, occasionally approximations introduced into the molecular-field theory, such as the geometric mean approximation [see Eq. (37)], result in the energy being a function of a reduced number of independent order parameters [see, e.g., Eq. (41)]. These order parameters are combinations of pure order parameters, but with the weighting factors related to the relative molecular interactions [see, e.g., Eq. (38)]. The occurrence of these composite order parameters means that the conjugate functions will also depend on the relative molecular interactions [see, e.g., Eq. (39)]. This introduces the relative molecular interactions into the Boltzmann factor and then eventually into the expansion for the entropy.

The jump in the composite order parameter at the nematic-isotropic transition as a function of the relative molecular biaxiality λ is shown in Fig. 2. The phase map, including also the biaxial phase, is shown in Fig. 5.

The cubic term vanishes [and also the quintic, as we will see in Eq. (76)] when λ is $1/\sqrt{6}$ and so the transition to the isotropic phase is predicted to be second order as given by the numerical results of molecular-field theory, which also predicts that the phase formed is a biaxial nematic, i.e., this is a Landau point. When the biaxial nematic is excluded from the phase behavior the Landau expansion predicts that the uniaxial nematic-isotropic transition will be second order when λ is $1/\sqrt{6}$ in agreement with the numerical analysis of the molecular-field theory.

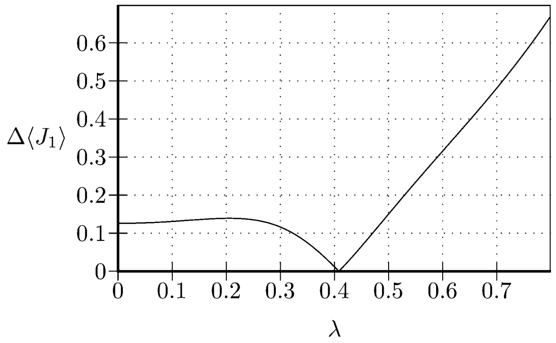


FIG. 2. The dependence of the order parameter jump $\Delta\langle J_1\rangle$ at the nematic-isotropic phase transition on the relative molecular biaxiality λ calculated from Eq. (43) with $\theta = 0.45$. Note that the jump goes to zero at $\lambda = 1/\sqrt{6} \approx 0.4082$.

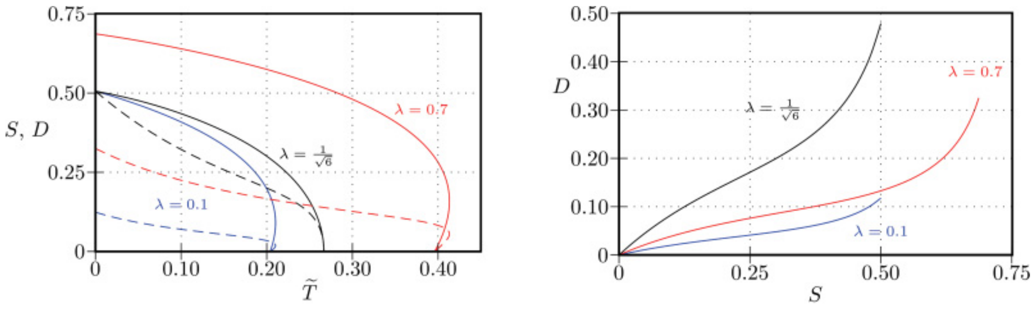
It is worth noticing that Eq. (36), with the geometric mean approximation $\gamma = \lambda$ imposed, does not reduce analytically to Eq. (43). The two expressions are different approximations for a uniaxial nematic composed of D_{2h} molecules and in fact, as expected, they provide two phase maps which are numerically very similar, but not identical. The expansion in Eq. (36) is more complicated but can directly provide information on both S and D separately. The dependence of S and D on the scaled temperature $\widetilde{T}$ for three different values of λ and within the geometric mean approximation, is reported in Fig. 3. For a given value of λ the two order parameters vanish at the same temperature as expected because of the coupling between them. We see that the constraint $D \to 0$ in the high order limit ($S \to 1$), which follows from the definition in Eq. (11b) and obtained from molecular-field theory, is not respected by the expansion although the other limit $D \to 0$ as $S \to 0$ is.

By contrast, Eq. (43) is easier to handle, but yields only the combined order parameter. Individual order parameters must be calculated using the explicit expression of $f(\Omega)$ as obtained by Eq. (18), with the substitution of Eq. (23), and then averaging their functional dependence. As long as we are only interested in the phase, however, Eq. (43) is clearly more convenient.

VI. BIAXIAL NEMATIC OF D_{2h} MOLECULES

We now proceed to the most general case, in which the molecules possess D_{2h} symmetry so that the nematic phase may also possess this symmetry. The molecular-field energy now has additional terms coming from the orientational order in the N_B phase.

As in Sec. V, the D_{2h} molecular symmetry enforces restrictions on the intermolecular coefficients u_{2mn}, [35,56]. As we have seen, the three independent coefficients can be written as u_{200}, u_{220}, and u_{222}. The molecular-field internal



(a) (b)

FIG. 3. (Color online) (a) The dependence of the order parameters, S (solid line) and D (dashed line), on the scaled temperature, $\widetilde{T} = k_B T/u_{200}$, and (b) the dependence of the order parameter D on S. The graphs are calculated from Eq. (36) with $\theta = 0.45$ and $\gamma = \lambda = 0.1, \frac{1}{\sqrt{6}}, 0.7$ (i.e., the geometric mean approximation).

energy is [44]

$$\begin{aligned} U &= -\{u_{200}(\langle R_{00}\rangle^2 + 2\langle R_{20}\rangle^2) + 4u_{220}(\langle R_{00}\rangle\langle R_{02}\rangle + 2\langle R_{20}\rangle\langle R_{22}\rangle) + 4u_{222}(\langle R_{02}\rangle^2 + 2\langle R_{22}\rangle^2)\} \\ &= -\frac{1}{2}\left\{u_{200}\left(S^2 + \frac{1}{3}P^2\right) + u_{220}\sqrt{\frac{8}{3}}\left(SD + \frac{1}{3}PC\right) + u_{222}\frac{2}{3}\left(D^2 + \frac{1}{3}C^2\right)\right\}. \end{aligned} \tag{46}$$

The KKLS partition function is then

$$Z(\eta_1,\eta_2,\eta_3,\eta_4) = \frac{1}{8\pi^2}\int_{SO(3)} \exp\left[\eta_1 R^2_{00}(\Omega) + \eta_2\sqrt{6}R^2_{20}(\Omega) + \eta_3\sqrt{6}R^2_{02}(\Omega) + \eta_4 6R^2_{22}(\Omega)\right] d\Omega, \tag{47}$$

where the factors $\sqrt{6}$ and 6 in front of $R^2_{20}(\Omega)$, $R^2_{02}(\Omega)$, and $R^2_{22}(\Omega)$ have been introduced for consistency with the definitions in Eqs. (14a) and (14b) of the order parameters S, P, D, and C.

Following the KKLS protocol outlined in Sec. III leads to the unregularized free energy expansion, where we have taken terms up to fourth order:

$$\begin{aligned} \Delta A/u_{200} = {} & \frac{5}{2}\left(\widetilde{T} - \frac{1}{5}\right)\left(S^2 + \frac{1}{3}P^2\right) + \frac{5}{6}\left(\widetilde{T} - \frac{2}{5}\lambda^2\right)\left(D^2 + \frac{1}{3}C^2\right) - \sqrt{\frac{2}{3}}\gamma\left(SD + \frac{1}{3}PC\right) - \frac{25}{21}\widetilde{T}S(S^2 - P^2) \\ & + \frac{25}{21}\widetilde{T}\left(SD^2 - \frac{1}{3}SC^2 - \frac{2}{3}PDC\right) + \frac{425}{196}\widetilde{T}\left[\left(S^2 + \frac{1}{3}P^2\right)^2 + \frac{1}{9}\left(D^2 + \frac{1}{3}C^2\right)^2 + \frac{2}{3}\left(SD + \frac{1}{3}PC\right)^2\right] \\ & + \frac{325}{588}\widetilde{T}(SC - PD)^2. \end{aligned} \tag{48}$$

As in previous sections, the two relative molecular biaxialities are given by $\gamma = u_{220}/u_{200}$ and $\lambda^2 = u_{222}/u_{200}$.

We now make a few remarks on the group of transformations G of the order parameter set, and on invariants of these quantities which occur in Eq. (48). The full symmetry group G is the direct product of two subgroups, H_L and H_M. Each of these is isomorphic to the dihedral group D_3 of reflection and rotation symmetries of an equilateral triangle with labeled vertices [57]. Conventionally the vertices are labeled x, y, and z. The elements of the subgroups correspond to the following six permutation operations on the axis labels: (1) identity, (2) exchange x and y, (3) exchange y and z, (4) exchange z and x, (5) $(x,y,z) \mapsto (y,z,x)$, and (6) $(x,y,z) \mapsto (z,x,y)$. H_L is the subgroup obtained when the transformation is applied to the laboratory axes and H_M is the subgroup acting on the molecular axes. The product group $G = H_L \times H_M$ of all the admissible transformations is thus of order 36. We recall that a group G is a direct product of two subgroups, i.e., $G = H_L \times H_M$, if the elements of different subgroups commute and every element $g \in G$ can be uniquely decomposed into the product $g = h_L \circ h_M$ of two elements $h_L \in H_L$ and $h_M \in H_M$.

Using a Cartesian tensor definition of the order parameters [18], it is easy to find the action of the group transformations on the order parameters. Apart from the identity, the elements of H_L are

$$(S,P,D,C) \mapsto (S,-P,D,-C), \tag{49}$$

$$\begin{aligned} &(S,P,D,C) \\ &\mapsto \left(-\frac{S}{2} \pm \frac{P}{2}, \frac{P}{2} \pm \frac{3S}{2}, -\frac{D}{2} \pm \frac{C}{2}, \frac{C}{2} \pm \frac{3D}{2}\right), \end{aligned} \tag{50}$$

$$\begin{aligned} &(S,P,D,C) \\ &\mapsto \left(-\frac{S}{2} \mp \frac{P}{2}, -\frac{P}{2} \pm \frac{3S}{2}, -\frac{D}{2} \mp \frac{C}{2}, -\frac{C}{2} \pm \frac{3D}{2}\right). \end{aligned} \tag{51}$$

The transformations given by H_M are the identity plus the following:

$$(S,P,D,C) \mapsto (S,P,-D,-C), \tag{52}$$

$$(S,P,D,C) \mapsto \left(-\frac{S}{2} \pm \frac{D}{2}, -\frac{P}{2} \pm \frac{C}{2}, \frac{D}{2} \pm \frac{3S}{2}, \frac{C}{2} \pm \frac{3P}{2}\right), \tag{53}$$

$$(S,P,D,C) \mapsto \left(-\frac{S}{2} \mp \frac{D}{2}, -\frac{P}{2} \mp \frac{C}{2}, -\frac{D}{2} \pm \frac{3S}{2}, -\frac{C}{2} \pm \frac{3P}{2}\right). \tag{54}$$

In Eq. (48) we have grouped together in round brackets the homogeneous terms which are invariant under H_L. When we further consider the subgroup H_M, we see that there is only one third-order invariant and two fourth-order invariants. We now specifically consider the fourth-order invariants. These are

$$I_{41} = \left(S^2 + \tfrac{1}{3} P^2\right)^2 + \tfrac{1}{9} \left(D^2 + \tfrac{1}{3} C^2\right)^2 + \tfrac{2}{3} \left(S\,D + \tfrac{1}{3} P\,C\right)^2, \tag{55}$$

$$I_{42} = (S\,C - P\,D)^2. \tag{56}$$

Following our general rule, we now replace the coefficient $\widetilde{T}$ of I_{41} in Eq. (48) by a constant θ. However, we retain $\widetilde{T}$ in the coefficient of I_{42}. This choice of regularization is necessary and sufficient to avoid divergence of the order parameters S and C in the limit $\widetilde{T} \to 0$. We finish therefore with the following regularized Landau-KKLS free energy:

$$\begin{aligned}
\Delta A/u_{200} = {} & \frac{5}{2}\left(\widetilde{T} - \frac{1}{5}\right)\left(S^2 + \frac{1}{3} P^2\right) + \frac{5}{6}\left(\widetilde{T} - \frac{2}{5}\lambda^2\right)\left(D^2 + \frac{1}{3} C^2\right) \\
& - \sqrt{\frac{2}{3}}\,\gamma\left(S\,D + \frac{1}{3} P\,C\right) - \frac{25}{21}\,\widetilde{T}\,S\,(S^2 - P^2) + \frac{25}{21}\,\widetilde{T}\left(S\,D^2 - \frac{1}{3} S\,C^2 - \frac{2}{3} P\,D\,C\right) \\
& + \frac{425}{196}\,\theta\left[\left(S^2 + \frac{1}{3} P^2\right)^2 + \frac{1}{9}\left(D^2 + \frac{1}{3} C^2\right)^2 + \frac{2}{3}\left(S\,D + \frac{1}{3} P\,C\right)^2\right] + \frac{325}{588}\,\widetilde{T}\,(S\,C - P\,D)^2 .
\end{aligned} \tag{57}$$

A further particularly important observation is that the molecular interaction coefficients u_{2mn} are affected by H_M (change of molecular frame), but remain invariant under the transformations in H_L (change in laboratory frame). This follows from the requirement that the internal energy in Eq. (46) be independent of the choice of molecular and laboratory axes. Therefore we can require that the internal energy be invariant under the action of Eqs. (52)–(54) to obtain the following transformations for the intermolecular coefficients (apart from the identity):

$$(u_{200}, u_{220}, u_{222}) \mapsto (u_{200}, -u_{220}, u_{222}), \tag{58}$$

$$(u_{200}, u_{220}, u_{222}) \mapsto \left(\frac{u_{200}}{4} \mp \sqrt{\frac{3}{2}} u_{220} + \frac{3u_{222}}{2}, \mp\sqrt{\frac{3}{32}} u_{200} + \frac{u_{220}}{2} \pm \sqrt{\frac{3}{8}} u_{222}, \frac{3u_{200}}{8} \pm \sqrt{\frac{3}{8}} u_{220} + \frac{u_{222}}{4}\right), \tag{59}$$

$$(u_{200}, u_{220}, u_{222}) \mapsto \left(\frac{u_{200}}{4} \pm \sqrt{\frac{3}{2}} u_{220} + \frac{3u_{222}}{2}, \mp\sqrt{\frac{3}{32}} u_{200} - \frac{u_{220}}{2} \pm \sqrt{\frac{3}{8}} u_{222}, \frac{3u_{200}}{8} \mp \sqrt{\frac{3}{8}} u_{220} + \frac{u_{222}}{4}\right). \tag{60}$$

The key conclusion is that for quadratic terms the construction of the invariants depends not only on the order parameters (as is the case for third-order and higher invariants) but also on the interaction coefficients u_{2mn}. In Appendix C we relate the spherical quantities u_{200}, u_{220}, and u_{222} to their Cartesian counterparts. In Appendix D we show how it possible to use Eqs. (49)–(54) to construct the free energy invariants or to collect the terms coming from the Landau-KKLS expansion.

In all the cases that we have checked, the KKLS procedure generates, automatically, the correct invariants for the free energy expansion. In particular, for special restricted manifolds in the biaxial phase space (e.g., Landau points), where the molecular-field theory predicts a nongeneric continuous phase transition, the KKLS procedure automatically renders the coefficients of the relevant odd-order invariants zero. We conjecture that this is true in all cases, and that a formal proof of this conjecture exists, but we have not been able to construct it.

In addition, by construction, the KKLS procedure takes account of the tensorial nature of the interaction coefficients, u_{2mn}. By contrast, a classical phenomenological approach fails to include these tensorial interactions, and as a consequence omits some possible invariants. An example of this approach where such omissions occur is that of Allender and Lee [20,21] (AL). The approach adopted in these papers presents a number of difficulties as follows:

(a) Certain combinations of order parameters are ignored. In fact, classic Landau theory assumes that the expansion coefficients multiplying the invariants are scalars and hence not affected by axes transformations. Therefore AL neglect the tensorial nature of the coefficients. Specifically, they delete the term $(S\,D + \frac{1}{3}\,P\,C)$ because it is not itself invariant under the exchange of the x and y molecular axes [see Eq. (52)]. In our Eq. (57), by contrast, this term is multiplied by γ, which also changes sign under exchange of the x and y molecular axes. Thus symmetry considerations do not cause this term to cancel, as might naively be expected. A more careful study shows that, as it has to be, the whole quadratic term in Eq. (57) is invariant. In general, it is possible that all terms in a Landau expansion, not just second order, might have coefficients which are tensorial.

(b) The parameters have no obvious relationship to the molecular biaxiality.

(c) There is only a single divergence temperature.

(d) There is a very large number of adjustable or unknown expansion coefficients in the theory.

By contrast, the KKLS approach does not suffer from these problems. Specifically for the Landau-KKLS free energy we find the following:

(a) The quadratic expansion coefficients are tensorial and so allow the terms neglected by Allender and Lee and others [22] to be included.

(b) These unknown expansion coefficients are directly related to the molecular biaxiality and anisotropy.

(c) The quadratic terms also include two divergence temperatures clearly related to the molecular biaxiality.

(d) The expansion for the free energy contains just four unknown parameters, namely λ, γ, $\widetilde{T}$, and θ.

In the following two subsections we compare the predictions obtained by our expansion with those found in the literature using other methods.

A. Sonnet-Virga-Durand limit

In this approximation the number of molecular interaction coefficients is reduced by assuming $u_{220}/u_{200} = \gamma = 0$. Virga and co-workers have shown [19,36] that, apart from removing one of the coupling coefficients, the order parameters P and D essentially vanish for all temperatures and relative molecular biaxiality. In view of this simplification in the molecular-field theory, we follow the approach used in Ref. [36] and further simplify Eq. (57) assuming that $P = D = 0$. We note that this assumption is consistent with the equilibrium points of Eq. (57). Hence we write the free energy difference as

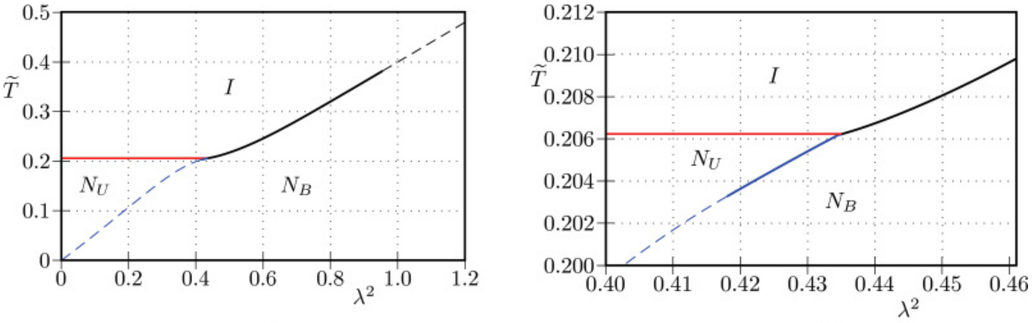
$$\begin{aligned}\Delta A/u_{200} = {} & \frac{5}{2}S^2\left(\widetilde{T} - \frac{1}{5}\right) + \frac{5}{18}\left(\widetilde{T} - \frac{2\lambda^2}{5}\right)C^2 \\ & - \frac{25}{21}\widetilde{T}S^3 - \frac{25}{63}\widetilde{T}SC^2 + \frac{325}{588}\widetilde{T}S^2C^2 \\ & + \frac{425}{196}\theta\left(S^4 + \frac{1}{81}C^4\right). \end{aligned} \tag{61}$$

We recall that $\lambda^2 = u_{222}/u_{200}$, is the relative biaxiality, and $\widetilde{T} = k_B\,T/u_{200}$ is the scaled temperature. The phase diagram, obtained from this free energy with θ set to 0.45, is shown in Fig. 4. It has been calculated by solving systems of polynomial equations as sketched at the end of Sec. III. We observe that the value of θ has been chosen in order to obtain a good general qualitatively agreement with the phase diagrams reported in Refs. [19,36]. The topology of the phase diagram does not change for values of θ within the approximate range $0.25 - 0.60$.

It is worth noticing that the second-order transition line from the N_B to the N_U phase passes through the origin $(\lambda,\widetilde{T}) = (0,0)$. Therefore no biaxial phase is predicted for $D_{\infty h}$ molecules in the Sonnet-Virga-Durand approximation. This is in marked contrast with the predictions of Landau theory which are reported in Appendix B and in Sec. VI B, where there appears to be a biaxial phase also for a vanishing relative molecular biaxiality. This feature is independent of the value chosen for θ. In fact, the second-order transition line from the N_B to the N_U phase is given by

$$\left.\frac{\partial^2 \Delta A}{\partial C^2}\right|_{\substack{S = S_0 \\ C = 0}} = \frac{5}{9}\left(\widetilde{T} - \frac{2\lambda^2}{5}\right) - \frac{50}{63}\widetilde{T}S_0 + \frac{325}{294}\widetilde{T}S_0^2 = 0, \tag{62}$$

where S_0 is the equilibrium value of the uniaxial order parameter S. When λ is set equal to zero, the only possible solution to Eq. (62) is $\widetilde{T} = 0$ (we recall that, by construction, S_0 is always finite for finite $\widetilde{T}$), which shows that the transition line has to pass through the origin.



(a) (b)

FIG. 4. (Color online) The phase diagram for the biaxial nematic calculated from the Landau-KKLS expansion [see Eq. (61)] in the Sonnet-Virga-Durand limit as a function of the relative molecular biaxiality with $\theta = 0.45$. The dashed lines indicate second-order transitions and the solid lines first-order transitions. The phase diagram in (b) shows an enlargement of that given in (a) in the vicinity of the triple point.

We can use the method described in Refs. [36,58,59] to locate the tricritical points. This entails the numerical solution of the equations in the three unknowns S, λ, and $\widetilde{T}$, namely

$$\left.\frac{\partial \Delta A}{\partial S}\right|_{C=0} = 0, \tag{63}$$

$$\left.\frac{\partial^2 \Delta A}{\partial C^2}\right|_{C=0} = 0, \tag{64}$$

$$\left.\frac{\partial^2 \Delta A}{\partial S^2}\frac{\partial^4 \Delta A}{\partial C^4} - 3\left(\frac{\partial^3 \Delta A}{\partial S \partial C^2}\right)^2\right|_{C=0} = 0. \tag{65}$$

The first equation is the equilibrium condition for the uniaxial order parameter S, the second equation expresses the bifurcation condition valid for a second-order transition to the N_B phase, and the third equation identifies the tricritical point. The numerical solutions of Eqs. (63)–(65) yield

$$TC_1 : (\lambda^2, \widetilde{T}) \approx (0.418, 0.203), \tag{66}$$

$$TC_2 : (\lambda^2, \widetilde{T}) \approx (0.956, 0.383). \tag{67}$$

The triple point is found, numerically, to be

$$TP : (\lambda^2, \widetilde{T}) \approx (0.435, 0.206). \tag{68}$$

The qualitative similarity of the phase diagram in Fig. 4 with that reported in Ref. [19], obtained by solving self-consistency equations for the order parameters in the molecular-field theory, is remarkable. For comparison, we show the numerical values for the tricritical points TC_1 and TC_2 and the triple point TP obtained in Refs. [19,36], suitably converted to match our convention for λ:

$$TC_1 : (\lambda^2, \widetilde{T}) \approx (0.30, 0.212), \tag{69}$$

$$TC_2 : (\lambda^2, \widetilde{T}) \approx (1.21, 0.485), \tag{70}$$

$$TP : (\lambda^2, \widetilde{T}) \approx (0.33, 0.220). \tag{71}$$

The numerical agreement between the results is moderate, but it is still acceptable in view of the fact that numerical predictions are usually poor for standard Landau theories, whose main aim is to provide a qualitative description of the transitions. Moreover, they depend on the value of θ and so we could change θ to match a region better, but at the cost of decreasing the accuracy in another.

B. Geometric mean approximation

When the geometric mean approximation is employed, which also reduces the number of molecular biaxiality parameters from 2 to 1 ($\gamma = u_{220}/u_{200} = \sqrt{u_{222}/u_{200}} = \lambda$), an additional combined order parameter can be defined,

$$\langle J_2 \rangle = \langle R_{20} \rangle + 2\lambda \langle R_{22} \rangle, \tag{72}$$

with the obvious associated function

$$J_2(\Omega) = R_{20}(\Omega) + 2\lambda R_{22}(\Omega). \tag{73}$$

The order parameter $\langle J_1 \rangle$ [see Eq. (38)] is then nonzero in both N_U and N_B phases, while $\langle J_2 \rangle$ is nonzero only in the N_B phase.

With these definitions, the molecular internal energy and the partition function are

$$U = -\frac{u_{200}}{2}\left(\langle J_1 \rangle + 2\langle J_2 \rangle^2\right), \tag{74}$$

and

$$Z(\eta_1, \eta_2) = \frac{1}{8\pi^2}\int_{SO(3)} \exp[\eta_1 J_1(\Omega) + \eta_2 J_2(\Omega)]\, d\Omega, \tag{75}$$

respectively. Application of the KKLS protocol yields the Landau-KKLS order parameter expansion of the free energy difference as

$$\begin{aligned}
\Delta A \frac{2\lambda^2+1}{u_{200}} =\ & \frac{5}{2}\left(\widetilde{T} - \frac{2\lambda^2+1}{5}\right)\left(\langle J_1 \rangle^2 + 2\langle J_2 \rangle^2\right) - \widetilde{T}\,\frac{25}{21}\frac{1-6\lambda^2}{(2\lambda^2+1)^2}\left(\langle J_1 \rangle^3 - 6\langle J_1 \rangle \langle J_2 \rangle^2\right) \\
& + \widetilde{T}\,\frac{25}{196}\frac{56\lambda^6 + 444\lambda^4 - 78\lambda^2 + 17}{(2\lambda^2+1)^4}\left(\langle J_1 \rangle^2 + 2\langle J_2 \rangle^2\right)^2 \\
& - \widetilde{T}\,\frac{125(1-6\lambda^2)(224\lambda^6 + 2316\lambda^4 - 492\lambda^2 + 83)}{3773(2\lambda^2+1)^6}\left(\langle J_1 \rangle^2 + 2\langle J_2 \rangle^2\right)\left(\langle J_1 \rangle^3 - 6\langle J_1 \rangle \langle J_2 \rangle^2\right) \\
& + \theta\,\frac{125(1\,851\,808\lambda^{12} + 22\,121\,904\lambda^{10} + 165\,267\,840\lambda^8 - 83\,432\,680\lambda^6 + 23\,521\,530\lambda^4 - 2\,571\,921\lambda^2 + 193\,707)}{6\,180\,174(2\lambda^2+1)^8} \\
& \times \left(\langle J_1 \rangle^2 + 2\langle J_2 \rangle^2\right)^3 \\
& + \theta\,\frac{625(54\,880\lambda^{12} + 26\,544\lambda^{10} + 11\,164\,368\lambda^8 - 7\,314\,280\lambda^6 + 1\,916\,238\lambda^4 - 192\,753\lambda^2 + 8958)}{6\,180\,174(2\lambda^2+1)^8} \\
& \times \left(\langle J_1 \rangle^3 - 6\langle J_1 \rangle \langle J_2 \rangle^2\right)^2.
\end{aligned} \tag{76}$$

The sixth-order terms in Eq. (76) are necessary to obtain a phase diagram which shows a biaxial phase. In fact, it can be shown that when the free energy expansion is truncated at the fourth-order term, the N_B region vanishes shrinking to a single vertical line placed at $\lambda = 1/\sqrt{6}$.

It is possible to derive analytically the implicit expressions for the transition lines, using the algebraic methods outlined at the end of Sec. III. These are, however, rather cumbersome and will not be reported here. A picture of the phase diagram is more effective and it is shown in Fig. 5 (to be compared

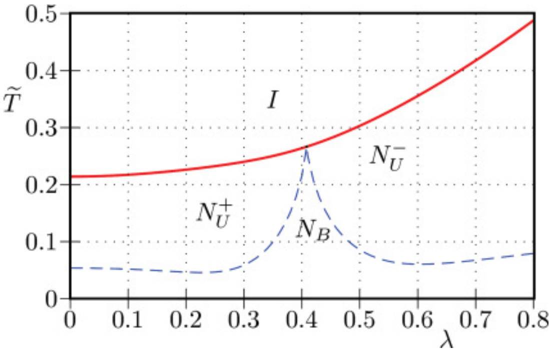


FIG. 5. (Color online) The phase map for the biaxial nematic with the expansion coefficients related by the geometric mean approximation [see Eq. (37)] with θ, multiplying the sixth-order invariants, set equal to 0.45.

with the molecular-field prediction in Ref. [15], see also [40]). In Fig. 6 we also show the dependence of the order parameters on temperature, for three values of the relative molecular biaxiality. We recall that, in the geometric mean approximation, the relative molecular biaxiality vanishes when $\lambda = 0$ or $\lambda = \sqrt{3/2} \approx 1.2247$ and hence the theory describes a system of uniaxial ($D_{\infty h}$) molecules. By contrast, the maximum molecular biaxiality is obtained when $\lambda = 1/\sqrt{6}$.

We notice how the cubic and quintic invariants vanish when λ is $1/\sqrt{6}$. However, this fact is of no immediate help in deriving the nature of the phase transition, as, in principle, a free energy given by an even sixth-order polynomial could describe both first- and second-order transitions. The free energy expansion in Eq. (76) correctly predicts a Landau point at $\lambda = 1/\sqrt{6}$, where the transition is second order and direct from the N_B to the isotropic phase. As we approach this point the transition from the N_U to the isotropic phase is still first order, but becomes weaker and weaker. However, the expansion fails to predict the correct phase map at low $\widetilde{T}$ as it allows at $\lambda = 0$ (where the theory reduces to that of Appendix B for $D_{\infty h}$ molecules) (1) a biaxial ground state and (2) nonvanishing values for the biaxial order parameters $\langle J_2 \rangle$ in the high-order limit [contrary to the bounds given in Eq. (B9)]. These predictions are physically unsound and also contrast with molecular-field theory, which gives the correct physical behavior as shown in Ref. [15].

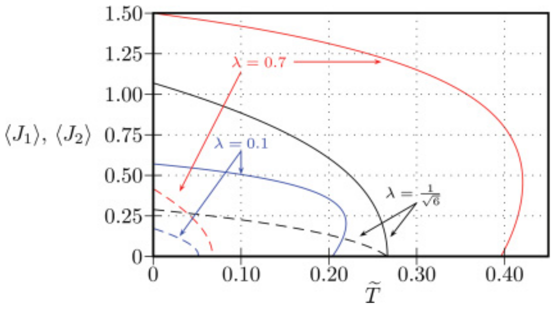


FIG. 6. (Color online) The dependence of the composite order parameters $\langle J_1 \rangle$ (solid line) and $\langle J_2 \rangle$ (dashed line) on the scaled temperature $\widetilde{T} = k_B T/u_{200}$, as calculated from Eq. (76) with $\theta = 0.45$. The molecular biaxiality λ is set equal to 0.1, $1/\sqrt{6}$, and 0.7.

C. Macroscopic order parameter

It is appropriate at this point to discuss an alternative definition of the order tensor, which we refer to as the macroscopic definition, discussed by de Gennes [10]. At a macroscopic level for some general symmetric second-rank tensorial property **G**, such as the magnetic susceptibility tensor, there are three principal components, G_{XX}, G_{YY}, and G_{XX}, where X, Y, and Z are the principal axes for **G** which, if the phase had, say, D_{2h} symmetry, would correspond to the symmetry axes and hence the three directors. For convenience we define **G** to be traceless so that the components necessarily vanish in the isotropic phase, then there are just two independent macroscopic order parameters. These can be taken to be the major order parameter, G_{ZZ}, and the biaxial order parameter, $(G_{XX} - G_{YY})$. These are both nonzero in the N_B phase but in the N_U phase G_{ZZ} is nonzero and $(G_{XX} - G_{YY})$ is zero. The relative phase biaxiality is defined as $\eta = (G_{XX} - G_{YY})/G_{ZZ}$.

Given the rotational properties of **g**, the molecular analog of **G**, then components of the molecular ordering tensor can be related to those of the macroscopic ordering tensor by [17]

$$G_{ZZ} = \frac{2}{3}\left[\frac{3g_{zz}}{2}S + \frac{g_{xx} - g_{yy}}{2}D\right], \tag{77}$$

$$G_{YY} = -\frac{1}{3}\left[\frac{3g_{zz}}{2}(S + P) + \frac{g_{xx} - g_{yy}}{2}(D + C)\right], \tag{78}$$

$$G_{XX} = -\frac{1}{3}\left[\frac{3g_{zz}}{2}(S - P) + \frac{g_{xx} - g_{yy}}{2}(D - C)\right]. \tag{79}$$

These results give the two independent macroscopic order parameters as

$$G_{ZZ} = g_{zz}(S + \mu D), \tag{80}$$

$$G_{XX} - G_{YY} = g_{zz}(P + \mu C), \tag{81}$$

and the relative biaxiality as

$$\eta = \frac{P + \mu C}{S + \mu D}, \tag{82}$$

where the combining parameter μ is $(g_{xx} - g_{yy})/3g_{zz}$, which is essentially the relative biaxiality of the molecular tensor **g**.

These results have a striking resemblance to the definitions of the two composite order parameters, $\langle J_1 \rangle$ and $\langle J_2 \rangle$ [see Eqs. (38) and (72)], suggested by the molecular-field theory based on the geometric mean approximation for the molecular interaction coefficients, u_{2mn}. In view of the apparently different origins of the two composite order parameters, their resemblance is quite remarkable. However, the reason for this resemblance is more mathematical than physical as the previous considerations of the molecular-field potential of mean torque followed by the introduction of the geometric mean approximation for u_{2nm} have shown.

There is also another important difference: since the combination of order parameters in $\langle J_1 \rangle$ and $\langle J_2 \rangle$ are related to the molecular interactions, it is not unreasonable that they should be employed in the Landau expansion for the free energy. In marked contrast, the macroscopic order parameter, G_{ZZ} and $(G_{XX} - G_{YY})$, is arbitrary in the sense that any symmetric second-rank molecular property can be used to construct them. In consequence, they will vary with the choice of **g**, which may or may not be related to the molecular interactions. In view of this variation it seems unrealistic that they should be employed to generate the Landau free energy expansion from which the transitional properties will be obtained.

VII. CONCLUSIONS

In this paper we have introduced a theory for the coefficients of a Landau expansion which can describe certain biaxial nematic liquid crystals. In doing so, we have followed a program first outlined by some of us almost 25 years ago, which we have labeled the KKLS protocol. The KKLS protocol describes a procedure and a philosophy which relate the coefficients of the Landau expansion describing the transition between a uniaxial nematic liquid crystal and an isotropic liquid to those in the corresponding molecular-field theory. We note that in recent years, other workers have independently rediscovered a similar approach [54].

The key idea has been to try to relate some terms quadratic in the order parameter to the molecular-field potential, while relating all other terms to the entropy associated with a symmetry-broken phase. In the case of the uniaxial nematic-isotropic phase transition, the number of independent invariants in the theory is small. The most important feature of the theory was simply to relate the magnitude of the terms which appeared in the Landau expansion to quantities occurring in molecular-field theories. These in turn enable contact with experiment to be made.

However, for biaxial liquid crystals the problem is more complicated because there are several order parameters, and even more invariants. In what we have called phenomenological (or standard) Landau theory [20–22], all such invariants could in principle enter the Landau expansion describing transitions involving biaxial phases. Our theory stands or falls in comparison with this approach.

The phenomenological Landau theory is attractive for its simplicity. However, in the context of a description of phase transitions in biaxial liquid crystals, it turns out that it faces serious drawbacks. We note that it seems likely that these difficulties will be compounded for more complex materials with phase transitions involving significant symmetry breaking.

We have discussed in this paper some serious disadvantages of the standard Landau theory, which we re-emphasize here. First, we mention points of principle. The classic Landau free energy does not make a clear distinction between energetic and entropic contributions. Partly as a consequence of this omission, the usual treatment of what might be interpreted as the energetic contribution ignores the fact that the molecular interaction is tensorial. Rather, all the expansion coefficients are taken to be scalars. This has the fundamental implication that the standard Landau expansion, by appearing to follow rigorously Landau'âs prescriptions, may in fact omit allowable and significant terms. In addition, there is an important practical point. In the most complex cases the standard Landau expansion generates a very large number of phenomenological coefficients. Moreover, these coefficients carry no connection whatever with the molecular properties which presumably are driving the phase transitions at a molecular level. We might think of this freedom as a key advantage of a Landau theory. But in practice, the freedom is excessive; it makes the search for realistic phase maps an almost impossible task, even when the correct topology of the phase map is prescribed. As de Gennes might have written, this is, in fact, an *embarrass de richesse*. By contrast with the difficulties associated with the classic Landau theory, natural molecular-field theories of biaxial liquid crystals yield phase maps in excellent agreement with experiment [60]. The drawback here, however, is that the molecular-field theories require numerical solutions of complicated self-consistency equations for the order parameters or minimization of the equilibrium free energy with respect to the order parameters.

In this paper, we have shown how the KKLS protocol, suitably extended and regularized, provides a good compromise between these two approaches. We have developed the necessary formal theory. Moreover, we have used the theory to explore the behavior of various model systems. The molecular-field theory had predicted that these model systems would form both uniaxial and biaxial nematic phases, and our theory serves as a bridge between the two philosophically contrasting approaches.

The KKLS protocol proves to have two main advantages. From a theoretical point of view, although retaining the simplicity of a Landau-like polynomial expansion, it includes all of the correct invariants and, importantly, drastically reduces the number of phenomenological coefficients. Furthermore, from a more practical point of view, it predicts phase maps which are consistent with those given by molecular-field theory, albeit occasionally for a limited range of temperatures. We have discussed at some length problems which have arisen, and explained why, these problems notwithstanding, the KKLS protocol provides a fruitful procedure within which to discuss free energies in biaxial fluids.

More specifically, we have studied a system of uniaxial molecules, in both a uniaxial (Sec. IV) and a biaxial nematic phase (Appendix B). The first example served to justify the introduction of a regularized KKLS expansion. At first sight, the regularization procedure seems arbitrary, in that it introduces a constant coefficient for an entropic term which should have a coefficient linear in temperature. However, this procedure is nevertheless necessary in order to avoid a divergence of certain order parameters at low temperatures. Mathematically, the problem arises because the Landau expansion is only valid within a given radius of convergence, and the existence of this limit is what ensures that the order parameter obeys some rigorous physical bounds. Equivalent bounds in a truncated series can only be restored by doing some violence to the dominant terms (i.e., those of largest order) in the series at low temperatures.

The consequence of the regularization is that an additional phenomenological parameter θ is introduced. In Appendix B we compare the prediction of the standard Landau theory with the predictions of the KKLS protocol. The standard theory predicts, anomalously and, of course, incorrectly, the existence of a biaxial nematic phase N_B in a fluid composed of uniaxial molecules. It turns out that, in agreement with Landau theory, the KKLS protocol also predicts the existence of a stable N_B phase. We have discussed at some length the reasons for this unphysical result. As hinted previously, the key problem remains that the order parameters predicted by this theory, as well as phenomenological Landau theory, do not always obey the constraints imposed by their definitions.

A further calculation in Sec. V contains a discussion of the phase transition from the uniaxial nematic N_U, to the isotropic phase for a system composed of D_{2h} molecules. This calculation adopts the so-called geometric mean or separability approximation [34]. This physically inspired approximation reduces the number of molecular biaxial coefficients. Then (and only then) a mathematical trick enables some molecular details to be built into all the expansion coefficients, and not merely, as shown elsewhere, into the quadratic terms. The nature of the phase transition is then demonstrated without having to make *ad hoc* assumptions about the expansion coefficients.

Finally, in Sec. VI we have discussed the general case of a fluid composed of D_{2h} molecules in a biaxial nematic phase N_B. Although this is not the most general case of a biaxial liquid crystal, it is the biaxial phase most commonly discussed in the literature. A necessary part of this calculation involved the group structure of the order parameter transformations. These transformations also affect the tensorial coefficients in the free energy expansion. Following this, we have studied two specific limits which have been treated in the literature. These are, first, the Sonnet-Virga-Durand limit (Sec. VI A) and second, the geometric mean approximation (Sec. VI B). Each of these limits correspond in some sense to physically opposite single-parameter parametrizations of molecular biaxiality and therefore serve as good tests of the applicability of our methods.

In both cases, the phase behavior predicted by the KKLS protocol agree with the general predictions of molecular-field theory, although there are some minor differences in detail. Moreover, in the Sonnet-Virga-Durand approximation, the predictions of the KKLS protocol are also correct in the limit of vanishing relative molecular biaxiality. For the Sonnet-Virga-Durand limit, the theory correctly predicts a vanishing N_B phase as the relevant molecular biaxiality parameter λ goes to zero. In the opposite geometric mean approximation limit, we are able to see how to build molecular information explicitly into the expansion coefficients of the free energy for the N_B phase.

We now look to applications and limitations of the present work. The theory could be exploited in understanding, in general terms, how changing molecular shape can generate complex phase maps in temperature-molecular biaxiality space (see, for instance, [61] for a detailed study of the phase map dependence on the molecular shape in a system composed of C_{2h} molecules, in the context of the MF theory). A particular point of interest might be the examination of the mean field bifurcation properties of complex multicritical points in such biaxial phase maps. The method can also be applied to uniaxial and biaxial smectic liquid crystals. It should also be possible to use the free energies which we generate in dynamical theories to examine relaxation channels. The theories which we have discussed only pertain to uniform systems, but in principle nonuniform systems could be examined using similar principles. As such, these ideas could also be used to draw connections between molecular parameters and elastic properties in biaxial liquid crystals; it is known that these materials have a rich menagerie of elastic constants [62,63]. A further possibility is the discussion of more complex biaxial liquid crystal phases than those considered here, involving further order parameters [64].

Finally, although we believe that the methods discussed here will have wide applicability, we caution that the methods all involve mapping between molecular-field theories and (mean field) Landau theories. These theories should not be used to examine critical exponents without a detailed analysis of the effects of fluctuations. We have made no attempt to include fluctuations which could be important close to critical points, nor even to examine the region of applicability of a Landau theory using a Ginzburg criterion. These points, as well as further applications, we postpone to future work.

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APPENDIX A: LOW TEMPERATURE DIVERGENCE

For the simple free energy density Eq. (29), we now use a standard asymptotic argument which shows that the divergence of the order parameters S at low temperature can be specifically ascribed to the presence of $\widetilde{T}$ in the coefficient of the highest-order term retained in this expansion (in this case, the S^4 term).

Let us assume, for the sake of concreteness, a free energy truncated at quartic terms and of the form

$$\Delta A = \tfrac{1}{2}a_2(\widetilde{T} - \widetilde{T}^*)S^2 + \tfrac{1}{3}a_3\widetilde{T}S^3 + \tfrac{1}{4}a_4\widetilde{T}S^4. \tag{A1}$$

In the nematic phase, the equilibrium value for the order parameter necessarily satisfies the equation

$$a_2(\widetilde{T} - \widetilde{T}^*) + a_3\widetilde{T}S + a_4\widetilde{T}S^2 = 0. \tag{A2}$$

Of course, this equation for S could be solved directly. However, we will follow a different path and apply a dominant balance argument which can be extended to any order in S. Let us assume that there exist two real constants, k and c, such that S behaves asymptotically as

$$S \sim c\,\widetilde{T}^k, \tag{A3}$$

when $\widetilde{T} \to 0$. Equation (A2) then becomes

$$a_2\widetilde{T} + a_3c\,\widetilde{T}^{k+1} + a_4c\,\widetilde{T}^{2k+1} \sim a_2\widetilde{T}^*. \tag{A4}$$

Now, since the right-hand term is finite as $\widetilde{T} \to 0$, at least one of the left-hand terms must balance $a_2\widetilde{T}^*$ to be able to solve the equation in the limit $\widetilde{T} \to 0$. The remaining terms must be of the same or lower order with respect to the dominant term. We can distinguish two cases:

(1) $a_3c\,\widetilde{T}^{k+1} \sim a_2\widetilde{T}^*$, then $k = -1$ but one of the remaining terms would be $\widetilde{T}^{2k+1} = \widetilde{T}^{-1}$ which is dominant for low $\widetilde{T}$. Therefore, we must discard this solution,

(2) $a_4 c\,\widetilde{T}^{2k+1} \sim a_2 \widetilde{T}^*$, then $k = -\frac{1}{2}$ and $\widetilde{T}^{k+1} = \widetilde{T}^{1/2}$, which is infinitesimal. This solution is acceptable.

Thus we have that for low temperatures the order parameter varies as

$$S \sim c\,\widetilde{T}^{-1/2}, \tag{A5}$$

which indeed diverges to infinity. It is now easy to extend this argument to any order and show that if we truncate the free energy expansion at S^n ($n > 2$), the solution diverges at $\widetilde{T} \to 0$ as $\widetilde{T}^{-1/(n-2)}$.

APPENDIX B: BIAXIAL NEMATIC OF $D_{\infty h}$ MOLECULES

The dominant orientational order parameters for nematics are second rank, at least near $\widetilde{T}_{NI}$ [44]. These quantities can be written in the most general and convenient form as averages of the Wigner functions, $\langle D^2_{pm} \rangle$. For uniaxial molecules in a uniaxial nematic phase, the labels p and m are both zero and for a biaxial nematic p is ±2. For a biaxial nematic with D_{2h} symmetry, there are, however, just two independent order parameters for uniaxial molecules (see, for example, [35]). Using Eqs. (11a), (11c) and (14a), (14b), these are

$$S = \left\langle D^2_{00} \right\rangle = \langle R_{00} \rangle; \tag{B1a}$$

$$P = \left\langle D^2_{20} \right\rangle \equiv \left\langle D^2_{-20} \right\rangle = \langle R_{20} \rangle. \tag{B1b}$$

These order parameters can then be used to construct the molecular-field version of the thermodynamic internal energy [34,35]. This yields

$$\begin{aligned} U &= -\frac{u_{200}}{2}\left(\langle R_{00}\rangle^2 + 2\,\langle R_{20}\rangle^2\right) \\ &= -\frac{u_{200}}{2}\left(S^2 + \frac{1}{3}\,P^2\right). \end{aligned} \tag{B2}$$

In general, the values of the order parameters, S and P, depend on the specific choice of the axis labels for the laboratory frame. On the other hand, the internal energy must be independent of the chosen laboratory frame. In particular, U must be independent of all possible exchanges of axis labels. But each of these elementary exchanges produces different order parameters. U will thus be constructed from a set of homogeneous polynomials in the order parameters S and P, each of which is left invariant by an exchange of laboratory axis. We discuss the symmetry transformation of the order parameters more thoroughly in Sec. VI and Appendix D. However, it is worth noticing that in the present case $S^2 + \frac{1}{3}P^2$ is the only second-order invariant formed from the second-rank order parameter.

The variational strategy then gives the following expression for the potential of mean torque, $U(\Omega)$, with its single expansion coefficient:

$$U(\Omega) = -u_{200}\left(S\,P_2(\cos\beta) + \tfrac{1}{2}\,P\,\cos 2\alpha\,\sin^2\beta\right). \tag{B3}$$

This differs from the Maier-Saupe theory by the introduction of the term in the phase biaxiality order parameter P. The scaled molecular Helmholtz free energy difference is

$$\Delta A/u_{200} = \tfrac{1}{2}\left(S^2 + \tfrac{1}{3}\,P^2\right) - \widetilde{T}\,\ln Z, \tag{B4}$$

where the orientational partition function is

$$\begin{aligned} Z = \int \exp\Bigg[\frac{1}{\widetilde{T}}\Bigg(&S\,P_2(\cos\beta) \\ &+\frac{1}{2}\,P\,\cos 2\alpha\,\sin^2\beta\Bigg)\Bigg]\sin\beta\,d\beta\,d\alpha. \end{aligned} \tag{B5}$$

However, we show elsewhere [60] that numerical minimization of the free energy in Eq. (B4) with respect to the order parameters shows that there is only one stable nematic phase; this is uniaxial with $S \neq 0$ and $P = 0$. This result is consistent with the conjecture (see, for example, [44,64]) that the symmetry of a nematic liquid crystal phase should be equal to or higher than that of its constituent molecules.

The results for the molecular-field theory for uniaxial molecules have been included for, as we shall see, the Landau theory for this system does predict the existence of a biaxial nematic. Our derivation of the Landau-KKLS theory expansion starts with the relevant order parameters, which are the usual S and P. The phase biaxial order parameter P is defined in Eq. (14b); explicitly, it is

$$P = \tfrac{3}{2}\langle \cos 2\alpha\,\sin^2\beta \rangle. \tag{B6}$$

The partition function required in the KKLS protocol is then

$$\begin{aligned} Z(\eta_1,\eta_2) = \frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{\pi}\exp\Bigg[&\eta_1\,\frac{1}{2}(3\cos^2\beta - 1) \\ &+\eta_2\,\frac{3}{2}(\cos 2\alpha\,\sin^2\beta)\Bigg]\sin\beta\,d\beta\,d\alpha. \end{aligned} \tag{B7}$$

We now follow steps (i)–(iv) of Sec. III. We expand the exponential in Eq. (B7), and integrate term by term to arrive, finally, at an expansion of the entropy difference in terms of S and P. The average internal energy per particle is again given by Eq. (B2). Adding the two contributions yields the nonequilibrium free energy.

We shall retain terms up to the sixth order. The motivation is as follows. The usual Landau expansion for nematics capable of forming uniaxial and biaxial phases is truncated at fourth order, and it is not difficult to prove mathematically, that a biaxial phase cannot exist [38,55]. An expansion must be truncated at even order so that an absolute minimum exists. The next consistent point at which to truncate the expansion is then at sixth order. The authors of Refs. [38,55] work with expansions truncated at sixth order for a biaxial ordering tensor, and these calculations suggest the existence of a biaxial phase. It seems sensible therefore at least to include terms of order 6.

The scaled Landau-KKLS free energy up to the sixth order is found to be

$$\begin{aligned} \Delta A/u_{200} = {}&\tfrac{5}{2}\left(\widetilde{T} - \tfrac{1}{5}\right)\left(S^2 + \tfrac{1}{3}\,P^2\right) \\ &- \tfrac{25}{21}\,\widetilde{T}\,S(S^2 - P^2) + \tfrac{425}{196}\,\widetilde{T}\,\left(S^2 + \tfrac{1}{3}\,P^2\right)^2 \\ &- \tfrac{10375}{3773}\,\widetilde{T}\,S(S^2 - P^2)\left(S^2 + \tfrac{1}{3}\,P^2\right) \\ &+ \tfrac{2690375}{686686}\,\theta\,\left(S^2 + \tfrac{1}{3}\,P^2\right)^3 \\ &+ \tfrac{933125}{1030029}\,\theta\,S^2(S^2 - P^2)^2. \end{aligned} \tag{B8}$$

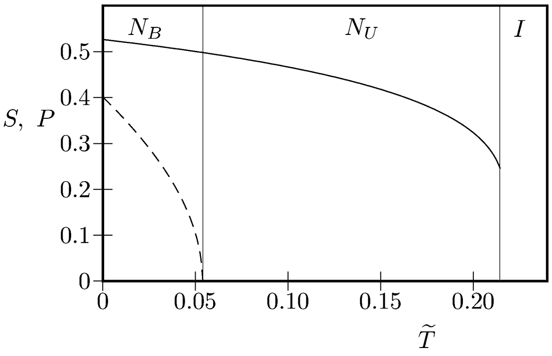

FIG. 7. The temperature dependence of the uniaxial order parameter S (solid line) and the biaxial order parameter P (dashed line) for a liquid crystal composed of $D_{\infty h}$ molecules. These results were obtained by minimizing the Landau-KKLS free energy [see Eq. (B8)] with the regularization parameter θ set equal to 0.45. Note the counterintuitive existence of the biaxial-uniaxial nematic phase transition at the scaled temperature $\widetilde{T} \approx 0.05$.

In agreement with the discussion following Eq. (B2), this expansion is uniquely formed by polynomial invariants.[2] We observe that these invariants exactly correspond to the terms that appear also in the classical Landau thermodynamic potential [38,55]. We also note that these theories were based on the symmetry of a second-rank tensorial property such as the magnetic susceptibility. This has two independent components: one the major, G_{zz}, and the other the biaxiality, $G_{xx} - G_{yy}$, which reflects the phase biaxiality. Their definition makes no assumptions about the molecular symmetry and so is valid for uniaxial as well as biaxial molecules.

We have carried out a numerical bifurcation study for the equilibrium points of the free energy in Eq. (B8) with $\theta = 0.45$. The results for the temperature dependence of the order parameters, S and P, are shown in Fig. 7. These reveal the existence of a stable biaxial phase, N_B, $\widetilde{T} \approx 0.05$. Our calculations show that the prediction of a biaxial phase is not sensitive to the choice of the regularization parameter θ over a wide range of values. The existence of the low temperature biaxial phase is consistent with other Landau-theory predictions [38,55]. However, in view of the absence of a stable N_B phase in the analogous molecular-field theory, the predicted existence of a stable N_B phase here is rather surprising.

In view of the appearance of the same form of invariants in both our calculations and those of Refs. [38,55] the prediction by both of a stable biaxial nematic phase may not be so surprising. However, we are skeptical about the conclusion. It would mean that a fluid of uniaxial molecules would sustain a low temperature biaxial phase, without there being any energetic advantage for such a broken symmetry phase. Further discussion of this can be found in Sec. VI A.

The key problem is that a completely uniaxially ordered phase, in which $S = 1$, *necessarily*, from the definition of the order parameters, requires that $P = 0$. Specifically, Sonnet, Virga, and Durand [19] have shown that, although S and P are independent quantities, their physical definition requires a constraint on the relationship between them. This constraint is

$$-(1 - S) \leqslant P \leqslant (1 - S). \tag{B9}$$

It is worth noting that an analogous inequality also applies when the order parameters are replaced by the major and biaxial components of a second-rank tensorial property as used by [38,55] [see Eqs. (80) and (81)].

Close to the onset of the N_U phase from the N_B phase the predicted order parameters, obtained from the minimization of the Landau-KKLS expansion, satisfy this constraint. However, at lower temperatures, where both order parameters can, in principle, become large, neither Landau theory nor the Landau-KKLS theory (at any given order) respect the constraint in Eq. (B9). But this is not predicted either by Eq. (B8) or by any classical Landau expansion. Thus in order to verify the prediction of a biaxial phase, it would be necessary to seek a different approximation of the free energy, which remains valid even close to $\widetilde{T} \approx 0$.

Finally, we should point out that when we set $\widetilde{T} = \widetilde{T}^*$ in all the $n > 2$ terms, the KKLS expansion yields a standard Landau expansion with expansion coefficients whose numerical values are taken from the molecular-field based KKLS approach. A bifurcation study of the phase diagram for this Landau-like free energy does not yield a stable biaxial nematic phase for uniaxial molecules. However, this strategy has been revealed not to be successful in general. In fact, the same procedure (i.e., setting $\widetilde{T} = \widetilde{T}^*$ in all terms with $n > 2$) does not lead to the qualitatively correct phase diagrams in the more complicated cases.

APPENDIX C: SPHERICAL TO CARTESIAN TRANSFORMATION

The second-rank approximation to the pair potential of two identical molecules (averaged over **r** the intermolecular vector) can be written, in terms of the Wigner rotation matrices, as

$$U(\Omega) = \sum_{k,k'=-2}^{+2} (-1)^k \, u_{2kk'} \, D^{(2)}_{-k\,k'}(\Omega), \tag{C1}$$

where Ω collects the Euler angles, which describe the rotation of the second molecule in the frame of reference of the first molecule. The intermolecular coefficients $u_{2kk'}$ are those of Sec. VI, where we encountered only three independent coefficients: u_{200}, u_{220}, and u_{222}, and with coefficients having odd components being equal to zero. In fact, the D_{2h} molecular symmetry imposes the constraints $u_{220} = u_{2-20} = u_{20-2} = u_{202}$ and $u_{222} = u_{2-22} = u_{22-2} = u_{2-2-2}$. We now want to find a Cartesian representation of Eq. (C1) of the form

$$U(R) = \sum_{\substack{i_1,i_2\\ j_1,j_2=1}}^{3} C_{i_1 i_2; j_1 j_2} R_{i_1 j_1} \, R_{i_2 j_2}, \tag{C2}$$

where $R \in \mathrm{SO}(3)$ is the rotation matrix associated with the Euler angles Ω. The coefficients $C_{i_1 i_2; j_1 j_2}$ can be determined by comparison of Eqs. (C2) and (C1) with the use of the orthogonality property of the Wigner rotation matrices. We

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[2] It is worth noting that the relationship of our invariants with those obtained from the classic $\boldsymbol{Q}$-tensor theory of nematics is $\mathrm{tr}(\boldsymbol{Q}^2) = \frac{2}{3}(S^2 + \frac{1}{3}P^2)$ and $\mathrm{tr}(\boldsymbol{Q}^3) = \frac{2}{9}S(S^2 - P^2)$.

say that the coefficients $C_{i_1 i_2; j_1 j_2}$ yield a *Cartesian* representation of the intermolecular coefficients, $u_{2kk'}$. The Cartesian representation is highly redundant and indeed the $C_{i_1 i_2; j_1 j_2}$ are subject to the following constraints:

$$C_{i_1 i_2; j_1 j_2} = C_{i_2 i_1; j_2 j_1} = C_{j_1 j_2; i_1 i_2}, \tag{C3}$$

$$\sum_{k=1}^{3} C_{i_1 i_2; kk} = \sum_{k=1}^{3} C_{kk; j_1 j_2} = 0. \tag{C4}$$

Furthermore, using the restrictions on $u_{2kk'}$ imposed by the D_{2h} molecular symmetry, the equivalence of Eqs. (C1) and (C2) finally yields

$$u_{200} = \frac{3}{2} C_{zz;zz} = \frac{3}{2}(C_{xx;xx} + 2\,C_{xx;yy} + C_{yy;yy}), \tag{C5}$$

$$u_{220} = \sqrt{\frac{3}{8}}(C_{yy;yy} - C_{xx;xx}), \tag{C6}$$

$$u_{222} = \frac{1}{4}(C_{xx;xx} - 2\,C_{xx;yy} + C_{yy;yy}). \tag{C7}$$

APPENDIX D: CALCULATION OF THE INVARIANTS

The polynomial invariants can be easily calculated from Eqs. (49)–(54) using the *Reynolds operator* [47]. Given a finite group G and a polynomial $p(\mathbf{x})$, $\mathbf{x} \in \mathbb{R}^n$, we associate to each element $g \in G$ a linear transformation of the variables, $O_g : \mathbb{R}^n \to \mathbb{R}^n$. Equations (49)–(54) are examples of such transformations. The Reynolds operator of G is defined as

$$R_G(p) = \frac{1}{|G|} \sum_{g \in G} p(O_g \mathbf{x}). \tag{D1}$$

We can think of $R_G(p)$ as averaging the effect of G on p. The Reynolds operator has the crucial property that it projects onto the ring of the invariants. In fact, a further application of O_g on the right-hand side of Eq. (D1) simply leads to a rearrangement of the terms in the sum: $O_g R_G(p) = R_G(p)$.

Therefore the evaluation of the Reynolds operator of H_L, H_M, or $H_L \times H_M$ for the set of all the monomials of homogeneous degree k generates all the invariants (with respect to H_L, H_M, or $H_L \times H_M$) that have to be included in the kth-order term of a Landau expansion. For example, the invariant with respect to the exchange of the laboratory axes, generated by S^3, is

$$\begin{aligned} R_{H_L}(S^3) &= \frac{1}{6}\left\{2S^3 + 2\left(-\frac{S}{2} + \frac{P}{2}\right)^3 + 2\left(-\frac{S}{2} - \frac{P}{2}\right)^3\right\} \\ &= \frac{S}{4}(S^2 - P^2). \end{aligned} \tag{D2}$$

Likewise, for a KKLS protocol this procedure is very useful to check the validity of the calculations and it provides valuable hints for collecting terms of the correct order.

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