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Molecular theory of helical sense inversions in chiral nematic liquid crystals

A. V. Emelyanenko,[1] M. A. Osipov,[2,3] and D. A. Dunmur[4]
[1]Department of Physics, Moscow State University, Moscow 119899, Russia
[2]School of Physics, University of Exeter, Exeter EX4 4QL, United Kingdom
[3]Institute of Crystallography, Russian Academy of Sciences, Leninski prospekt 59, Moscow 117333, Russia
[4]Department of Chemistry, University of Southampton, Southampton SO17 1BJ, United Kingdom

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A molecular theory of the helical twisting in chiral liquid crystals is developed, which provides an explanation for the experimentally observed helical sense inversion induced by a change of concentration in binary mixtures of chiral and nonchiral nematic liquid crystals. The theory also describes the sense inversion induced by a change of temperature observed in some single component nematics. The theory present is based on a simple model of a chiral rigid molecule, composed of several equivalent nonchiral sites, which are arranged in the molecule to form a chiral configuration. The macroscopic helical pitch in the chiral nematic phase, twist elastic constant, and nematic order parameters are calculated using the same molecular model. It is shown that the helical sense inversion can be determined by a large biaxiality of chiral molecules. It is also demonstrated that the biaxiality is important in determining the variation of the helical pitch with temperature and concentration.

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I. INTRODUCTION

Liquid-crystalline phases formed from chiral (i.e., handed) molecules exhibit a number of physical properties that derive from the reduced symmetry of the chiral mesophases. Thus chiral nematic phases can develop long-range helical structures with pitches ranging from a few tenths of microns to tens of microns or more, in which the local alignment axis of the molecules (the director) describes a helix, the handedness of which depends on a number of factors including the absolute configuration of the chiral molecules. The magnitude and sign of the helical pitch in chiral nematics can be measured by a variety of techniques; for example aligned films of chiral liquid crystals reflect electromagnetic radiation for particular wavelengths and circular polarization. Having a value for the helicity of a chiral nematic phase then raises the question: ‘‘what relation is there between the measured chirality of the phase (sign and magnitude), and the chirality of the constituent molecules [1,2]?’’ It has been possible to identify a number of qualitative correlations between the structure of mesogenic chiral molecules and the pitch of their corresponding chiral nematic phases [3], but the establishment of reliable quantitative correlations between molecular structure and the chiral properties of liquid-crystal phases has proved to be much more difficult. In fact there are a number of theoretical aspects to this problem. Firstly some representation for the molecular chirality must be adopted, secondly the nature of the chiral and, of course, nonchiral interactions between the molecules must be specified, and thirdly any theory of the chiral properties of mesophases must be able to explain their change with external variables, such as temperature, pressure, and composition for mixtures. The latter is especially important in the context of chiral nematic phases, since it has been found that chiral dopants that do not themselves form liquid-crystal phases will induce chiral mesophases when dissolved in nonchiral liquid-crystal hosts. This induction of chirality has been extensively studied experimentally [4,5], and it has been found that the sign of the induced pitch may be different for the same dopant in different host liquid crystals.

If the chiral dopant itself is mesogenic, then the helical pitch can be measured through the whole concentration range, including the pure chiral nematic phase of the dopant. It has been found that some chiral mesogens (in particular, cholesterol derivatives) may induce in a nonchiral nematic a helical structure of opposite sense to that observed in the corresponding pure chiral nematic phase. Such mixtures of chiral and nonchiral liquid crystals exhibit a helical sense inversion at some intermediate concentration of the two components. Examples of such behavior have been reported, for example, in Refs. [6–9]. This kind of helical sense inversion is not easily explained because the molecular chirality and all chiral intermolecular interactions appear to remain the same. Thus at present there is no consistent theoretical explanation of this phenomenon, although several semiphenomenological models, which rely on various additional assumptions, have been proposed [7,10,11]. Another interesting phenomenon is the helical sense inversion induced by change of temperature, which has been observed in few one-component chiral nematic phases [12–15]. Such inversion can, in principle, be explained by assuming that the particular chiral nematic is a mixture of two (or more) conformers of different handedness [13]. The relative populations of the conformational states may be strongly temperature dependent, and thus the helix inversion may be observed at some temperature within the nematic range. However, it should be noted that this explanation cannot always be valid, since for some chiral nematics showing temperature-induced pitch inversion, the chirality is located only in the rigid core. The experimental observations discussed above, indicate that a more detailed molecular theory of chiral nematics is needed, based on more realistic molecular models.

The first task of a theory of chiral nematic phases is to explain the formation of a helical distribution for the director, and a number of successful theories have been developed. All require that there is some form of chiral interaction between the molecules, but different models have been adopted for the origin of the chiral interaction. The packing of elongated hard particles having a chiral geometry can result [16,17] in the formation of helical nematic phases, and this is believed to be the predominant factor in lyotropic liquid crystals [18]. Similarly the chiral nematic phase can be modeled classically in terms of chiral dispersion forces [19,20], and recently a more general quantum-mechanical formulation of chiral interactions between fluctuating charge distributions has been given [21]. In formulating a theory of helical mesophases, the orientational order is modulated by chiral interactions having a particular handedness. Most treatments so far assume that the interacting molecules are effectively uniaxial, and so local ordering of the short axes of mesogens (molecular biaxiality) is neglected. A consequence is that important aspects of the molecular structure, i.e., biaxial shape are missing from the models. Furthermore, the theories do not deal with the chiral induction observed in mixtures, and are not able to explain significant experimental results, such as the change in sign of the pitch with temperature in pure mesogens [22], or with concentration and solvent in the case of mixtures [23]. Recently the importance of molecular biaxiality has been recognized by several authors [24,25].

In order to understand the subtle effects of changes of molecular structure and chirality on observed macroscopic chiral properties, many authors have considered ways of quantifying molecular chirality. Various approaches to the quantification of molecular chirality have been explored [26–29] which attempt to represent a chiral distribution of atoms in a molecule in terms of a parameter, or tensor which depends on the molecular structure. A simple measure that has been introduced is a function of minimal distances between atoms of a chiral molecule superimposed on its enantiomer [26]. We have developed [28] a general approach based on the Born-Boys theory of optical activity which allows a family of chirality tensors to be defined for a particular molecular geometry. Ferrarini *et al.* [25,27] have defined a helicity tensor which characterizes the chirality of the surface of a molecule, and Harris *et al.* [24] have defined a pseudoscalar molecular chirality index in terms of a coupling between higher-order mass distribution tensors. It is evident that there can be no single measure of molecular chirality, and the molecular parameter or index chosen will depend on the physical manifestation of chirality that is being examined.

The particular property of interest for chiral nematic phases is the pitch of the director helix which spontaneously forms in the mesophase. In order to discuss both single component and binary mixtures, it is convenient to introduce the helical twisting power h, which is the ratio of the helical wave number q to concentration of chiral molecules c at low $c \ll 1$:

$$h = \left. \frac{\partial q}{\partial c} \right|_{c=0},$$

where $q = 2\pi/p$ and where p is the helical pitch. At low concentrations the helical twisting power h is independent of concentration, and in appropriate units can be expressed as an area per molecule. Ferrarini *et al.* [29,30] have developed a semiphenomenological theory of twisting power for chiral solutes in nematic solvents. Their theory takes specific account of the molecular structure by considering the interaction of surface elements of the chiral dopant with the average nematic environment, and it also allows for local biaxial ordering of the solute molecules. Results for a number of different chiral molecules [25,31] are in reasonable agreement with experimental results, and the theory is able to explain the change in sign of helical pitch for consecutive odd and even homologues of alkyl cyanobiphenyls [25].

In this paper we develop a mean-field theory of chiral nematics in which chiral interactions in nematic mesophases are taken into account using a model mesogen, the structural chirality of which is a parameter of the theory. Single component and binary mixtures are considered, and we are able to derive the phenomenological result used by Ferrarini *et al.* [25,29,30] in the context of the mean-field molecular theory. From the theory we are able to calculate the chiral and nonchiral contributions to the free energy, and hence the uniaxial and biaxial order parameters and twisting power of the chiral molecules, using the same molecular model. The model for molecular chirality allows the effect of molecular shape to be determined, and it is shown that changes in temperature and/or concentration for binary mixtures can result in changes of sign for the measured pitch in chiral nematic phases. In Sec. II we develop expressions for the mean-field potential and free energy in terms of local biaxial and uniaxial order parameters and chiral and nonchiral coupling constants which describe the molecular interactions. The theory is developed for two-component systems in Sec. III, so that it can be applied to chiral induction in mesogenic mixtures. Details of our molecular model for chirality are given in Sec. IV, and some specimen results are presented in Sec. V. Here it is shown that the experimentally observed phenomena of pitch inversion with temperature, concentration, and change of nonchiral solvent can be quantitatively explained by the theory.

II. FREE ENERGY OF THE CHIRAL NEMATIC PHASE AND AN EXPRESSION FOR THE HELICAL PITCH

Let us consider a chiral nematic liquid crystal composed of biaxial molecules. The orientation of such a molecule can be specified by the two unit vectors **a** and **b** in the direction of the long and short molecular axes, respectively $(\mathbf{a}\cdot\mathbf{b}) = 0$. One notes that for a fixed long axis **a** the short axis **b** can only rotate about **a**. This rotation can also be specified by the Euler angle ψ. In a statistical theory such a system is characterized by the orientational distribution function $f([\mathbf{a}\cdot\mathbf{n}(\mathbf{r})],[\mathbf{b}\cdot\mathbf{n}(\mathbf{r})])$, which depends on the orientation of the molecular axes **a** and **b** with respect to the local director $\mathbf{n}(\mathbf{r})$ that may depend on the position **r**. For example, in the equilibrium chiral nematic state the director describes a helix along the z axis.

In the context of continuum theory the chiral nematic state is described by the following distortion-free energy density:

$$F_d = \frac{1}{2} K_2 (\mathbf{n}\cdot \mathrm{rot}\, \mathbf{n})^2 + k_2 \, (\mathbf{n}\cdot \mathrm{rot}\, \mathbf{n}), \tag{1}$$

where K_2 is the twist elastic constant and k_2 is a pseudoscalar parameter which is sensitive to molecular chirality.

In the homogeneous chiral nematic state the director distribution is a pure twist, $\mathbf{n}=\{\cos(qz),\sin(qz),0\}$, where q is the macroscopic helical wave number. The equilibrium value of the wave number q which corresponds to the minimum of the distortion free energy (1) is given by

$$q=\frac{k_2}{K_2}. \tag{2}$$

The coefficients k_2 and K_2 can be evaluated using a molecular-statistical theory.

In the molecular-statistical approach the free energy of a chiral nematic liquid crystal can be written explicitly in the mean-field approximation

$$F=k_BT\rho\int d\mathbf{x}_1 f(\mathbf{x}_1)\ln[16\pi^2 f(\mathbf{x}_1)] + \frac{1}{2}\rho^2\int d\mathbf{x}_1 d\mathbf{x}_2 f(\mathbf{x}_1)f(\mathbf{x}_2)\Theta(\mathbf{r}_{12}-\boldsymbol{\xi}_{12})U(1,2), \tag{3}$$

where $\mathbf{x}_i\equiv\{\mathbf{a}_i,\mathbf{b}_i,\mathbf{r}_i\}$, $d\mathbf{x}_i\equiv d^2\mathbf{a}_i d^2\mathbf{b}_i d\mathbf{r}_i$, $i=1,2$, and where $U(1,2)$ is the intermolecular interaction potential; here $\mathbf{r}_{12}\equiv|\mathbf{r}_2-\mathbf{r}_1|$ is the intermolecular vector. The step function $\Theta(\mathbf{r}_{12}-\boldsymbol{\xi}_{12})$ represents the excluded volume effects. The function $\Theta(\mathbf{r}_{12}-\boldsymbol{\xi}_{12})=0$ if the two molecules penetrate each other and $\Theta(\mathbf{r}_{12}-\boldsymbol{\xi}_{12})=1$ otherwise. The first term in Eq. (3) represents the orientational entropy while the second term is the internal energy of the nematic state.

The chiral nematic phase is nonpolar and therefore only the nonpolar part of the effective intermolecular potential $\Theta(\mathbf{r}_{12}-\boldsymbol{\xi}_{12})U(1,2)$ (i.e., the part which is even both in the long axes $\mathbf{a}_1,\mathbf{a}_2$ and the short axes $\mathbf{b}_1,\mathbf{b}_2,\mathbf{c}_1,\mathbf{c}_2$ of the two interacting molecules) will contribute to the value of the pitch. This part of the interaction potential can be expanded in the set of the spherical invariants in the following way:

$$\begin{aligned}\{\Theta(\mathbf{r}_{12}-\boldsymbol{\xi}_{12})U(1,2)\}_e &= -\sum_{lL\lambda} J^{lL\lambda}T^{lL\lambda}(\mathbf{a}_1,\mathbf{u},\mathbf{a}_2)\\ &\quad -\sum_{lL\lambda} M^{lL\lambda}[T^{lL\lambda}(\mathbf{a}_1,\mathbf{u},\mathbf{b}_2)-T^{lL\lambda}(\mathbf{a}_1,\mathbf{u},\mathbf{c}_2)]\\ &\quad -\sum_{lL\lambda} M^{lL\lambda}[T^{lL\lambda}(\mathbf{b}_1,\mathbf{u},\mathbf{a}_2)-T^{lL\lambda}(\mathbf{c}_1,\mathbf{u},\mathbf{a}_2)],\end{aligned} \tag{4}$$

where $\mathbf{u}=\mathbf{r}_{12}/|r_{12}|$, and the coupling constants $J^{lL\lambda}$ and $M^{lL\lambda}$ depend on the intermolecular separation r_{12}. The functions $T^{lL\lambda}(\mathbf{x},\mathbf{u},\mathbf{y})$ are the so-called spherical invariants [32] which depend on the relative orientation of the two molecules (see Fig. 1). The function $T^{lL\lambda}(\mathbf{x},\mathbf{u},\mathbf{y})$ depends on the three unit vectors $\mathbf{x},\mathbf{u}$ and $\mathbf{y}$ and contains $\mathbf{x}$ to the power l, $\mathbf{u}$ to the power L, and $\mathbf{y}$ to the power λ. The summation in Eq. (4) runs over all integers l,L, and λ with $l,\lambda\geqslant 0$ and $|l-\lambda|\leqslant L\leqslant l+\lambda$. In nonpolar liquid-crystal phases the terms odd in l and λ do not contribute and thus $J^{lL\lambda}=J^{\lambda Ll}$ and $M^{lL\lambda}=M^{\lambda Ll}$.

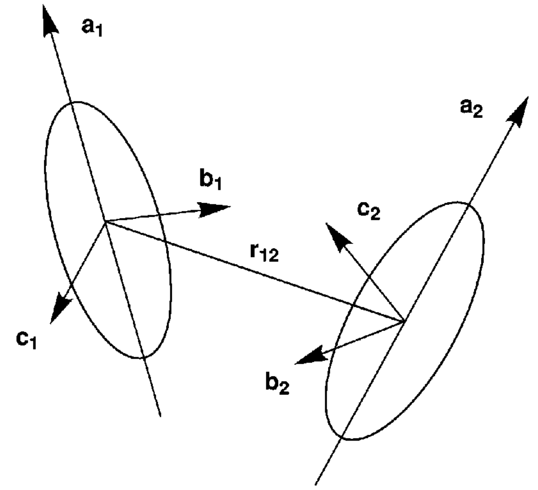

FIG. 1. Mutual orientation of the biaxial molecules ''1'' and ''2.'' The unit vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are in the direction of the primary molecular axes and the vectors $\mathbf{b}_1$ and $\mathbf{b}_2$ are in the direction of short molecular axes.

Spherical invariants make a complete set of orthogonal functions and can be defined in terms of spherical harmonics [32–34]. In some cases an expansion in spherical invariants is more convenient then the expansion in spherical harmonics because in the former expansion each term is invariant under rotation of the laboratory frame. Thus, spherical invariants are the natural basic functions for an expansion of various two-body functions like the pair potential or pair correlation functions, which do not depend on the absolute frame. Moreover, the order parameters of the nematic phase $\langle P_l\rangle$ are directly obtained by orientational averaging of the spherical invariants in the mean-field approximation [10]. Some useful properties of these functions are described in Appendix C and several low-order invariants are presented, for example, in [35]. One notes that the invariants with one zero index appear as the Legendre polynomials, i.e., $T^{l0l}(\mathbf{x},\mathbf{y})=P_l(\mathbf{x}\cdot\mathbf{y})$.

The first term in Eq. (4) describes the coupling between the long molecular axes of the two molecules; the second term is the interaction energy which depends on the orientation of the long axis of one molecule and of the short axis of another molecule. The coupling between the two short molecular axes is neglected.

Substituting Eq. (4) into Eq. (3) and using the properties of the spherical functions $T^{lL\lambda}$ one obtains

$$\begin{aligned}F &= k_BT\rho\int d\mathbf{x}_1 f(\mathbf{x}_1)\ln[16\pi^2 f(\mathbf{x}_1)]\\ &\quad -\frac{1}{2}\rho^2\sum_{lL\lambda} S_lS_\lambda\int d\mathbf{r}_1 d\mathbf{r}_2 J^{lL\lambda}T^{lL\lambda}(\mathbf{n}_1,\mathbf{u},\mathbf{n}_2)\\ &\quad -\rho^2\sum_{lL\lambda} S_lD_\lambda\int d\mathbf{r}_1 d\mathbf{r}_2 M^{lL\lambda}T^{lL\lambda}(\mathbf{n}_1,\mathbf{u},\mathbf{n}_2),\end{aligned} \tag{5}$$

where the order parameters S_l, which characterize the nematic ordering of the long molecular axes, are given by

$$S_l=\int d^2\mathbf{a}d^2\mathbf{b}P_l(\mathbf{a}\cdot\mathbf{n})f((\mathbf{a}\cdot\mathbf{n}),(\mathbf{b}\cdot\mathbf{n})). \tag{6}$$

The order parameters D_l which specify the ordering of the short axes of biaxial molecules in the uniaxial nematic phase are expressed as

$$D_l = \int d^2\mathbf{a} d^2\mathbf{b} \{P_l(\mathbf{b}\cdot\mathbf{n}) - P_l(\mathbf{c}\cdot\mathbf{n})\} f((\mathbf{a}\cdot\mathbf{n}),(\mathbf{b}\cdot\mathbf{n})). \quad (7)$$

Here $P_l(x)$ are the Legendre polynomials.

One notes that Eq. (5) presents an expression for the free energy of an inhomogeneous liquid crystal. This total free energy includes the free energy of the homogeneous nematic state F_0 and the free energy of the director distortion F_d,

$$F = F_0 + \int F_d(\mathbf{r}) d\mathbf{r}. \quad (8)$$

The distortion-free energy of the chiral nematic state is given by Eq. (1).

The free energy of the homogeneous state F_0 is given by the same Eq. (5) but with $\mathbf{n}_2 = \mathbf{n}_1 = \mathbf{n}$. The distortion energy can be extracted using the gradient expansion of the director $\mathbf{n}(\mathbf{r}_2)$,

$$\mathbf{n}(\mathbf{r}_2) = \mathbf{n}(\mathbf{r}_1) + (\mathbf{r}_{12}\cdot\boldsymbol{\nabla})\mathbf{n}(\mathbf{r}_1) + \frac{1}{2}(\mathbf{r}_{12}\cdot\boldsymbol{\nabla})^2\mathbf{n}(\mathbf{r}_1) + \cdots. \quad (9)$$

Explicit expressions for the constants k_2 and K_2 (and thus for the helical wave number q) can be obtained after the substitution of Eq. (9) into Eq. (5) and the truncation of the sum over l, L, λ. The simplest truncation of the expression (5) is achieved by neglecting all the terms with $l, \lambda > 2, L > 1$. The calculations presented in Appendix A result in the following expressions for the free energy F_0, pseudoscalar k_2, and the twist elastic constant K_2:

$$F_0 = k_B T \rho \int d\mathbf{x} f(\mathbf{x}) \ln[16\pi^2 f(\mathbf{x})] - \frac{1}{2}\rho^2 J_0^{202} S_2^2 - \rho^2 M_0^{202} S_2 D_2, \quad (10)$$

$$k_2 = \frac{1}{6}\rho^2 J_1^{212} S_2^2 + \frac{1}{3}\rho^2 M_1^{212} S_2 D_2, \quad (11)$$

$$K_2 = \frac{1}{2}\rho^2 J_2^{202} S_2^2 + \rho^2 M_2^{202} S_2 D_2, \quad (12)$$

where

$$J_n^{lL\lambda} = 4\pi \int_0^\infty dr_{12} r_{12}^{n+2} J^{lL\lambda}(r_{12}),$$

$$M_n^{lL\lambda} = 4\pi \int_0^\infty dr_{12} r_{12}^{n+2} M^{lL\lambda}(r_{12}). \quad (13)$$

The order parameters S_2 and D_2 in Eqs. (11) and (12) can be determined by minimization of the free energy F_0 (10), subjected to the constraint

$$\int d\mathbf{x} f(\mathbf{x}) = V, \quad (14)$$

where V is the volume of the system. One obtains

$$S_2 = \frac{1}{I}\int_{-1}^{1} dt \int_0^{2\pi} d\psi P_2(t) \exp[U_{MF}(t,\psi)],$$

$$D_2 = \frac{1}{I}\int_{-1}^{1} dt \int_0^{2\pi} d\psi \frac{3}{2}(1-t^2)\cos(2\psi)\exp[U_{MF}(t,\psi)], \quad (15)$$

with

$$I = \int_{-1}^{1} dt \int_0^{2\pi} d\psi \exp[U_{MF}(t,\psi)] \quad (16)$$

and

$$U_{MF}(t,\psi) = \frac{\rho}{k_B T}\left[J_0^{202} S_2 P_2(t) + M_0^{202} S_2 \frac{3}{2}(1-t^2)\cos(2\psi) + M_0^{202} D_2 P_2(t) \right], \quad (17)$$

where $t \equiv (\mathbf{a}\cdot\mathbf{n})$. The numerical solution of Eqs. (15) gives the temperature dependence of the order parameters S_2 and D_2.

One notes that in the nematic or chiral nematic phase composed of biaxial molecules the mean-field potential (17) depends on the two order parameters S and D. In this simple derivation, however, we have neglected the term proportional to D^2 because we did not take into account a coupling between short molecular axes. This term does not change the qualitative behavior of the system because usually the parameter D is much smaller then S. The complete expression for the mean-field potential of the biaxial nematic phase (which takes into account both long- and short-range biaxial order) has been presented by Bergersen *et al.* [36]. For uniaxial molecules the coupling constant M_0^{202} in Eq. (17) vanishes and the mean-field potential is reduced to the Maier-Saupe form.

III. NEMATIC-CHOLESTERIC BINARY MIXTURES

In this section we consider a more general case of the nematic uniaxial liquid crystal doped with biaxial chiral molecules. This system is characterized by the number density of the two components η_α and the corresponding orientational distribution functions $f_\alpha([\mathbf{a}\cdot\mathbf{n}(\mathbf{r})],[\mathbf{b}\cdot\mathbf{n}(\mathbf{r})])$ for nonchiral and chiral molecules, $\alpha = N, C$. Here the director $\mathbf{n}$ depends on the position of a molecule $\mathbf{r}$. Similar to Eq. (4) the nonpolar part of the effective interaction potential between the molecules of the components α and γ can be expressed as

$$\begin{aligned}\{\Theta_{\alpha\gamma}(\mathbf{r}_{12}-\boldsymbol{\xi}_{12})U_{\alpha\gamma}(1,2)\}_e &= -\sum_{lL\lambda} J_{\alpha\gamma}^{lL\lambda} T^{lL\lambda}(\mathbf{a}_1,\mathbf{u},\mathbf{a}_2) \\ &\quad - \sum_{lL\lambda} M_{\alpha\gamma}^{lL\lambda}[T^{lL\lambda}(\mathbf{a}_1,\mathbf{u},\mathbf{b}_2) - T^{lL\lambda}(\mathbf{a}_1,\mathbf{u},\mathbf{c}_2)] \\ &\quad - \sum_{lL\lambda} M_{\gamma\alpha}^{lL\lambda}[T^{lL\lambda}(\mathbf{a}_2,\mathbf{u},\mathbf{b}_1) - T^{lL\lambda}(\mathbf{a}_2,\mathbf{u},\mathbf{c}_1)], \\ &\quad (\alpha,\gamma = N, C). \end{aligned} \quad (18)$$

Now the expressions for the free energy F_0 and the elastic constants k_2 and K_2 for the mixture can be obtained as a straightforward generalization of Eqs. (10)–(12),

$$F_0=k_BT\rho\sum_{\alpha=N,C}\eta_\alpha\int d\mathbf{x}f_\alpha(\mathbf{x})\ln[16\pi^2 f_\alpha(\mathbf{x})]$$

$$-\tfrac{1}{2}\rho^2\sum_{\alpha,\gamma=N,C}\eta_\alpha\eta_\gamma[J^{202}_{0(\alpha\gamma)}S_\alpha S_\gamma$$

$$+M^{202}_{0(\alpha\gamma)}S_\alpha D_\gamma+M^{202}_{0(\gamma\alpha)}S_\gamma D_\alpha], \tag{19}$$

$$k_2=\tfrac{1}{6}\rho^2\sum_{\alpha,\gamma=N,C}\eta_\alpha\,\eta_\gamma[J^{212}_{1(\alpha\,\gamma)}S_\alpha\,S_\gamma$$

$$+M^{212}_{1(\alpha\gamma)}S_\alpha\,D_\gamma+M^{212}_{1(\gamma\alpha)}S_\gamma\,D_\alpha], \tag{20}$$

$$K_2=\tfrac{1}{2}\rho^2\sum_{\alpha,\ \gamma=N,C}\eta_\alpha\,\eta_\gamma[J^{202}_{2(\alpha\gamma)}S_\alpha S_\gamma$$

$$+M^{202}_{2(\alpha\gamma)}S_\alpha D_\gamma+M^{202}_{2(\gamma\alpha)}S_\gamma D_\alpha]. \tag{21}$$

Here the definitions of the constants $J^{lL\lambda}_{n(\alpha\gamma)}$ and $M^{lL\lambda}_{n(\alpha\gamma)}$ are analogous to those for $J^{lL\lambda}_n$ and $M^{lL\lambda}_n$, given by Eqs. (13), where the index n denotes the power of the distance r_{12} under the integral.

In Eqs. (19)–(21) S_N, S_C are the nematic order parameters of the nonchiral and chiral components of the mixture. The parameter D_C is the additional order parameter which characterizes the ordering of a biaxial molecule in the uniaxial nematic phase. One notes that $D_N=0$ because the nonchiral compound is assumed to be uniaxial.

In Eq. (20) the pseudoscalar coefficients $J^{212}_{1(\alpha\gamma)}$ and $M^{212}_{1(\alpha\gamma)}$ are different from zero only if at least one of the interacting molecules is chiral. Therefore, for two nonchiral molecules the coefficients $J^{212}_{1(NN)}=M^{212}_{1(NN)}=0$. As a result Eq. (20) can be rewritten as

$$k_2=\frac{1}{6}\eta_C[2\,\eta_N S_N(J^{212}_{1(NC)}S_C+M^{212}_{1(NC)}D_C).$$

$$+\eta_C S_C(J^{212}_{1(CC)}S_C+2M^{212}_{1(CC)}D_C)]. \tag{22}$$

The order parameters S_N, S_C, and D_C can be obtained by minimization of the free energy (19):

$$S_\alpha=\frac{1}{I_\alpha}\int_{-1}^{1}dt\int_0^{2\pi}d\psi P_2(t)\exp[U^\alpha_{MF}(t,\psi)],$$

$$D_C=\frac{1}{I_C}\int_{-1}^{1}dt\int_0^{2\pi}d\psi\frac{3}{2}(1-t^2)\cos(2\psi)\exp[U^C_{MF}(t,\psi)], \tag{23}$$

with

$$I_\alpha=\int_{-1}^{1}dt\int_0^{2\pi}d\psi\exp[U^\alpha_{MF}(t,\psi)],$$

where $\alpha=N,C$ and

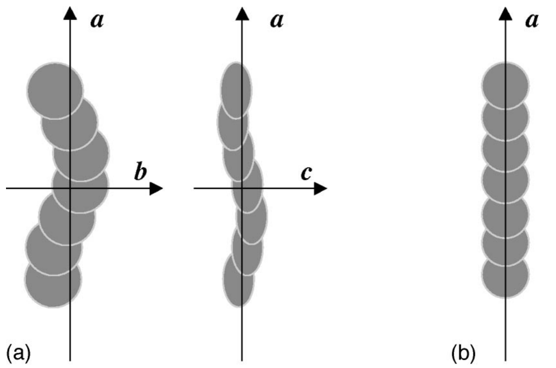

FIG. 2. Molecular model for a biaxial chiral mesogenic molecule (a) and nonchiral uniaxial mesogenic molecule (b).

$$U^\alpha_{MF}(t,\psi)=\frac{\rho}{k_BT}\sum_{\gamma=N,C}\eta_\gamma\Big[J^{202}_{0(\alpha\gamma)}S_\gamma P_2(t)+M^{202}_{0(\alpha\gamma)}D_\gamma P_2(t)$$

$$+M^{202}_{0(\gamma\alpha)}S_\gamma\frac{3}{2}(1-t^2)\cos(2\psi)\Big]. \tag{24}$$

The order parameters S_N, S_C, and D_C can be determined by numerically solving Eqs. (23) provided the coefficients $J^{202}_{0(\alpha\gamma)}$, $M^{202}_{0(\alpha\gamma)}(\alpha,\gamma=N,C)$ are known. These coefficients depend only on molecular structure and can be evaluated using an appropriate molecular model. In this paper we use a simple site-site interaction model, which is described in detail in the following section. The calculation of the coefficients in Eqs. (19)–(21) is performed in Appendix B.

IV. SITE-SITE INTERACTION MODEL FOR CHIRAL AND NONCHIRAL MOLECULES

Let us consider the following molecular model presented in Fig. 2. A chiral molecule [see Fig. 2(a)] is composed of seven identical ellipsoidal sites. Such flattened ellipsoids may be considered as simple images of aromatic rings. The symmetry axes of all the sites of a molecule are parallel to each other and to the short molecular axis **c**. At the same time the centers of ellipsoidal sites are twisted about the principal molecular axis **a**. This twist determines the molecular chirality in the framework of the present model. The center of the site i is determined by the position vector

$$\mathbf{s}_i=\begin{pmatrix} s_\perp\cos\{i\kappa\,h+\varphi\}\\ s_\parallel\sin\{i\kappa\,h+\varphi\}\\ i\,h\end{pmatrix}, \tag{25a}$$

where h is the distance between neighboring sites along the principal molecular axis, κ is the wave number of the molecular twist, and the phase φ determines the turn of the central site with respect to the the short molecular axis **b** ($i=0$ for the central site).

The model of a nonchiral molecule is presented in Fig. 2(b). A nonchiral molecule is composed of seven sites, which lie on the principal molecular axis **a**. Their positions are determined by the following vectors:

$$\mathbf{s}_i = \begin{pmatrix} 0 \\ 0 \\ i\,h \end{pmatrix}. \tag{25b}$$

In both cases (of chiral and nonchiral molecules) we take the distance between the neighboring sites $h = 2d/3$, where d is the average diameter of a site. For a chiral molecule we take the step of the molecular helix $\kappa h = 0.8$. The phase φ is considered as a model parameter, which specifies the particular structure of the chiral molecule. It should be noted, however, that a change of the parameter φ does not change the molecular handedness because all sites remain to be located on the same helix with the constant wave number κ [see Eq. (25a)] for all values of φ. At the same time we show in this paper that both value and sign of the macroscopic helical pitch in the chiral nematic phase strongly depend on the parameter φ.

We assume that each site of a molecule interacts with each site of another molecule via the standard Gay-Berne potential [37]:

$$U_{ij}^{\alpha\gamma}(\mathbf{u}_i,\mathbf{r},\mathbf{u}_j) = \varepsilon_{\alpha\gamma}(\mathbf{u}_i,\mathbf{r},\mathbf{u}_j)\left[\left(\frac{d}{r-\sigma_{\alpha\gamma}(\mathbf{u}_i,\mathbf{r},\mathbf{u}_j)+1}\right)^{12} - \left(\frac{d}{r-\sigma_{\alpha\gamma}(\mathbf{u}_i,\mathbf{r},\mathbf{u}_j)+1}\right)^{6}\right], \tag{26}$$

where $\mathbf{u}_i$ and $\mathbf{u}_j$ are the symmetry axes of the interacting sites, and $\mathbf{r}$ is the vector connecting these sites.

The functions $\varepsilon_{\alpha\gamma}$ and $\sigma_{\alpha\gamma}$ are defined in Ref. [37]. These functions contain three model parameters: ε which mainly determines the nematic-isotropic transition temperature, $\sigma_\parallel/\sigma_\perp$ which is the axial ratio of the molecular site, and $\varepsilon_s/\varepsilon_e$ which determines the ratio of the interaction energies for side-by-side and end-to-end configurations of two sites. These parameters, however, should be different for different pairs of interacting sites reflecting their different symmetry. In this paper we assume that the nonchiral molecules are uniaxial while the chiral ones are strongly biaxial. Therefore, in our model the nonchiral molecule is assumed to be composed of simple spherical sites with the diameter d, while the chiral molecule is composed of flattened sites. Thus, for any two sites of interacting nonchiral molecules we should take $(\sigma_\parallel/\sigma_\perp)_{NN} = 1$ and $(\varepsilon_s/\varepsilon_e)_{NN} = 1$. Taking the short (principal) dimension of the flattened site of a chiral molecule equal to $0.6\,d$ and its long (secondary) dimension equal to $1.2\,d$, one obtains for two sites of chiral molecules $(\sigma_\parallel/\sigma_\perp)_{CC} = 0.5$ and for a site of nonchiral molecule and a site of chiral molecule: $(\sigma_\parallel/\sigma_\perp)_{NC} = 0.73$. We take $(\varepsilon_s/\varepsilon_e)_{CC} = 0.7$ and $(\varepsilon_s/\varepsilon_e)_{NC} = 0.9$ to have a good agreement with the experimental values of the biaxiality order parameter D_C in pure cholesterics and in nematic-cholesteric mixtures. Finally, parameters ε in each case have been chosen in order to account for the transition temperatures of para-azoxyanisole (N), cholesteryl chloride (C), and their mixture [7]. All parameters are presented in Table I. The total interaction potential between the two molecules is calculated as a sum over all site-site interactions,

TABLE I. Model parameters for the Gay-Berne potential.

	N-N	N-C	C-C
$\varepsilon/k_B(10^3\ \mathrm{K})$	1.60	1.28	1.03
$\sigma_\parallel/\sigma_\perp$	1	0.73	0.5
$\varepsilon_s/\varepsilon_e$	1	0.9	0.7

$$U_{\alpha\gamma}(1,2) = \sum_{i=1}^{m_\alpha}\sum_{j=1}^{m_\gamma} U_{ij}^{\alpha\gamma}(\mathbf{u}_i,\mathbf{r},\mathbf{u}_j), \tag{27}$$

where the number of sites in both cases (of chiral and nonchiral molecules) have been chosen equal to $m_N = m_C = 7$.

The chiral coefficients $J_{1(\alpha\gamma)}^{212}$, $M_{1(\alpha\gamma)}^{212}$, which are used in Eq. (22) for the pseudoscalar constant k_2, and the two sets of nonchiral coefficients, $J_{0(\alpha\gamma)}^{202}, M_{0(\alpha\gamma)}^{202}$ and $J_{2(\alpha\gamma)}^{202}, M_{2(\alpha\gamma)}^{202}$ [used in Eqs. (21) and (24)], are calculated in Appendix B in the framework of this molecular model. The results are discussed in the following section.

V. RESULTS AND DISCUSSION

The nonchiral (scalar) coupling constants $J_{0(NN)}^{202}, J_{0(NC)}^{202}, J_{0(CC)}^{202}, M_{0(NC)}^{202}, M_{0(CC)}^{202}, J_{2(NN)}^{202}, J_{2(NC)}^{202}, J_{2(CC)}^{202}, M_{2(NC)}^{202}, M_{2(CC)}^{202}$, and chiral (pseudoscalar) coupling constants $J_{1(NC)}^{212}, J_{1(CC)}^{212}, M_{1(NC)}^{212}, M_{1(CC)}^{212}$, which determine the cholesteric pitch and the order parameters, are presented in Fig. 3 as functions of the molecular model parameter φ. One notes that the nonchiral interaction constants depend only weakly on φ [see Figs. 3(b) and 3(c)] while the chiral coefficients strongly depend on φ and may even change sign. This difference is related to the fact that in the present model the parameter φ mainly effects the molecular chirality while the averaged molecular shape remains to be intact. Using these coupling constants one can calculate numerically the order parameters S_N, S_C, and D_C from Eqs. (23) and then substitute them into Eqs. (22), (21), (2) for the helical wave number. As a result one obtains the helical wave number q as a function of the concentration of chiral molecules in the binary mixture. The results are presented in Fig. 4 for different values of the parameter φ. (We take five values of the parameter φ, which are shown in Fig. 3(a) by the dashed lines.) One can readily see that in all cases the concentration dependence of the helical wave number of a mixture appears to be strongly nonlinear. At low values of the structural model parameter φ the helical wave number q changes sign at some concentration (see curves 1 and 2 in Fig. 4). Thus, the present model describes a helical sense inversion in a mixture of chiral and nonchiral nematics with the increasing concentration of the chiral compound. As discussed in the Introduction, this kind of helical sense inversion in binary mixtures has been observed by several authors [6–9] and one notes that the curves 1 and 2 in Fig. 4 are very similar to the experimental ones which have been obtained for various nematic-cholesteric mixtures.

For higher values of the model parameter φ (see curves 3 and 4 in Fig. 4) the helix inversion is becoming less pronounced and finally disappears (see curve 5). One notes that the concentration dependence of the helical pitch in real binary mixtures of liquid crystals is very sensitive to the mo-

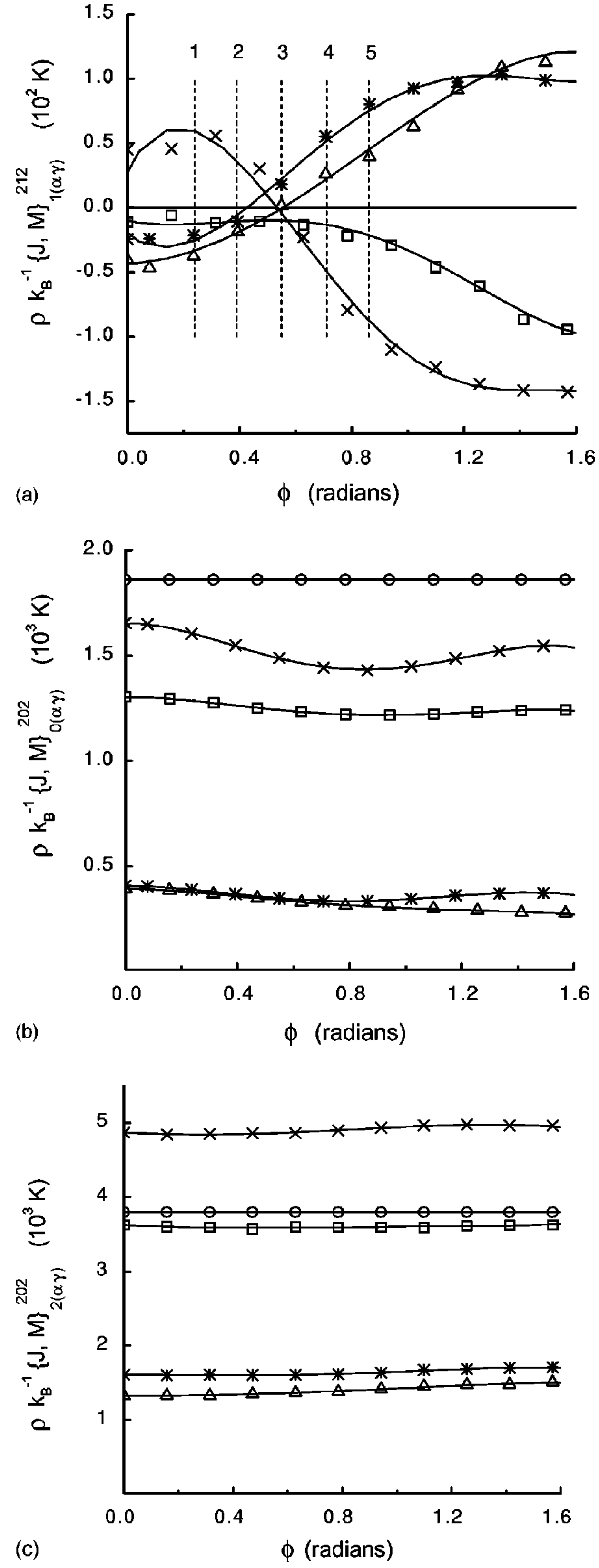

FIG. 3. Interaction coupling constants as functions of the structural factor φ. (a) Chiral coefficients in Eq. (22): rectangles, $J^{212}_{1(NC)}$; triangles, $M^{212}_{1(NC)}$; crosses, $J^{212}_{1(CC)}$; stars, $M^{212}_{1(CC)}$. (b) Nonchiral coefficients in Eq. (19): circles, $J^{202}_{0(NN)}$; rectangles, $J^{202}_{0(NC)}$; triangles, $M^{202}_{0(NC)}$; crosses, $J^{202}_{0(CC)}$; stars, $M^{202}_{0(CC)}$. (c) Nonchiral coefficients in Eq. (21): circles, $J^{202}_{2(NN)}$; rectangles, $J^{202}_{2(NC)}$; triangles, $M^{202}_{2(NC)}$; crosses, $J^{202}_{2(CC)}$; stars, $M^{202}_{2(CC)}$.

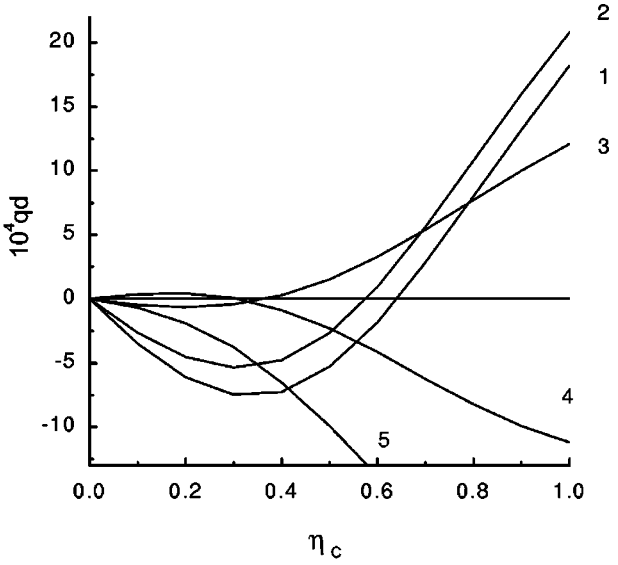

FIG. 4. Dimensionless helical wave number as a function of the molar fraction of chiral molecules in the binary mixture for four different values of the model parameter φ: (1) $\varphi=0.24$ rad; (2) $\varphi=0.39$ rad; (3) $\varphi=0.55$ rad; (4) $\varphi=0.71$ rad; (5) $\varphi=0.86$ rad.

lecular structure. A small change in the structure of chiral molecules may result in the disappearance of the helical sense inversion. This effect has been observed, for example, in the series of cholesterol derivatives with different structure of the 3β chain [38].

There have been several attempts to explain the behavior of nematic-chiral nematic mixtures in the context of a molecular theory [11,35,39]. As shown by Hanson *et al.* [39], an experimentally observed concentration dependence of the helical wave number of a nematic-cholesteric mixture can be described by Eq. (2) where the pseudoscalar coefficient k_2 and the twist elastic constant K_2 are quadratic functions of the concentration of chiral and nonchiral molecules in the mixture. In this case [compare with Eq. (22)] the coefficient k_2 is expressed as $k_2=k_{CC}\eta_C^2+2k_{NC}\eta_N\eta_C$. However, the helical sense inversion can be described only if the coefficients k_{CC} and k_{NC} possess opposite signs. The latter requirement appears to be the most challenging one for a molecular theory. Simple models, based on chiral dispersion interactions [35], yield the same sign for both coefficients k_{CC} and k_{NC}. In this case both coefficients are proportional to the same pseudoscalar parameter that characterizes the molecular chirality.

The model presented in this paper enables one to explain the helical sense inversion in nematic-cholesteric mixtures in a consistent way, without using any additional assumptions. One can readily see from Fig. 3(a) that the chiral interaction constants in Eq. (22) may possess either equal or opposite signs depending on the parameter φ. Thus in the context of one and the same model for a rigid molecule with a simple chiral distortion one can qualitatively explain different types of concentration dependence of the helical pitch in nematic-chiral nematic mixtures, including the ones with or without helical sense inversion. Similar to real binary mixtures of liquid crystals, in the context of the present model, different types of the concentration dependence of the helical pitch are obtained by changing the structure of chiral molecules (by changing the model parameter φ).

The microscopic mechanism of the helical sense inversion in the present model can be understood in more detail if one considers the behavior of the helical pitch at very low and very high concentrations of chiral molecules in the mixture. At low concentrations of chiral molecules ($\eta_C \ll 1$) the helical wave number is expressed as

$$q \sim 2\eta_N \eta_C S_N [J^{212}_{1(NC)} S_C + M^{212}_{1(NC)} D_C]. \tag{28}$$

In the opposite limit, i.e., in the pure one-component cholesteric phase ($\eta_C = 1, \eta_N = 0$) one obtains

$$q \sim \eta_C^2 S_C [J^{212}_{1(CC)} S_C + 2M^{212}_{1(CC)} D_C], \tag{29}$$

where the four pseudoscalar coefficients $J^{212}_{1(NC)}, J^{212}_{1(CC)}, M^{212}_{1(NC)}, M^{212}_{1(CC)}$ are presented in Fig. 3(a) as functions of the model parameter φ.

In Eqs. (28) and (29) the second terms in the square brackets, which are proportional to the secondary order parameter D_C, are determined by molecular biaxiality. Generally these terms are smaller then the leading contribution proportional to the primary nematic order parameter S_C. Now it is possible to ask how important are the biaxiality contributions for the qualitative behavior of the pitch. One notes that for each curve in Fig. 4 the helical wave number q possesses opposite signs for $\eta_C \ll 1$ and $\eta_C = 1$. This means that the terms $J^{212}_{1(NC)} S_C + M^{212}_{1(NC)} D_C$ and $J^{212}_{1(CC)} S_C + 2M^{212}_{1(CC)} D_C$ must have opposite signs. One can see from Fig. 3(a) that for the first two values of φ(φ_1 and φ_2), which correspond to the curves 1 and 2 in Fig. 4, the coefficients $J^{212}_{1(NC)}$ and $J^{212}_{1(CC)}$ possess opposite signs. In these cases the helical sense inversion is preserved, even if one neglects the order parameter D_C determined by the molecular biaxiality. For $\varphi = \varphi_3$ and $\varphi = \varphi_4$ [see Fig. 3(a)] the coefficients $J^{212}_{1(NC)}$ and $J^{212}_{1(CC)}$ have equal signs. In these cases the helical sense inversion (see curves 3 and 4 in Fig. 4) takes place because the coefficients $M^{212}_{1(NC)}$ and $M^{212}_{1(CC)}$ have large positive values, and in the third case $M^{212}_{1(CC)}$ dominates over $J^{212}_{1(CC)}$, whereas in the fourth case $M^{212}_{1(NC)}$ dominates over $J^{212}_{1(NC)}$. Therefore, in case 3 the helical wave number is positive when the cholesteric is pure ($\eta_C = 1$), and in case 4 the helical wave number is positive when the cholesteric is a small dopant ($\eta_C \ll 1$). In both cases 3 and 4 the helical sense inversion takes place due to biaxiality of chiral molecules. Thus the biaxiality contribution to the helical pitch is very important and can even be responsible for the helical sense inversion in some cases. Finally, the helical wave number q has no inversion in case 5 in Fig. 4 [correspondent to $\varphi = \varphi_5$ in Fig 3(a)]. Such a behavior of the helical pitch is also confirmed by experiment with some nematic-cholesteric mixtures.

The helical pitch of a nematic-chiral nematic mixture also depends on the orientational order parameters of chiral and nonchiral molecules. Typical values of the nematic order parameters S_N and S_C, calculated in the framework of the present model, are depicted in Fig. 5(a) as functions of the temperature and in Fig. 6(a) as functions of the concentration of chiral molecules. One notes that both parameters S_N and S_C strongly depend on concentration. At the same time the relative importance of the biaxiality contribution is determined by the ratio D_C/S_C [see Eqs. (28) and (29)]. This ratio is depicted in Figs. 5(b) and Fig. 6(b) as a function of temperature and concentration, respectively, for one particular value of the parameter φ. It is interesting to note that the ratio D_C/S_C increases with the decreasing concentration of chiral molecules in binary mixture. This means that at least in the present model the order parameter D_C for a chiral dopant in a nematic host is higher than D_C for a pure cholesteric phase composed of the same chiral molecules. This result is expected to be more general and intuitively should correspond to any biaxial dopant in a uniaxial (or less biaxial) host. Indeed, rather high values of the parameter $D \approx 0.2 \div 0.3$ have been measured for various nonchiral dopant molecules in nematic hosts [40].

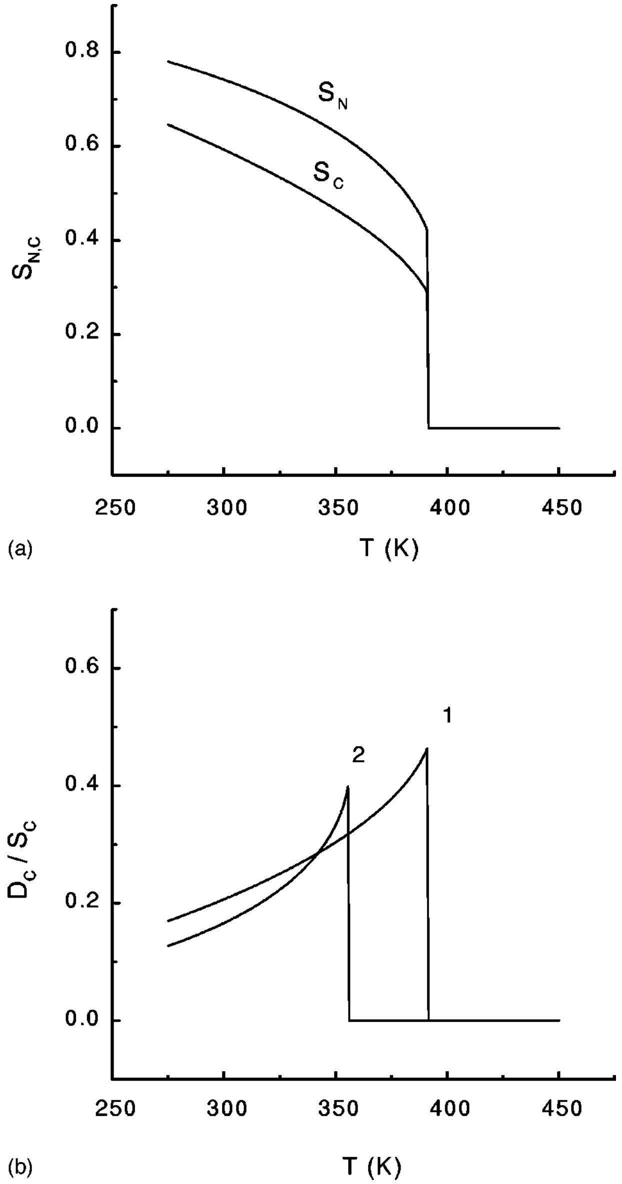

FIG. 5. Temperature variation of the order parameters of chiral and nonchiral molecules in the binary nematic mixture ($\varphi = 0.39$ rad): (a) primary nematic order parameters S_N and S_C for $\eta_C = 0.1$; (b) ratio of the two order parameters D_C/S_C for $\eta_C = 0.1$ (curve 1) and $\eta_C = 0.9$ (curve 2), where D_C is the biaxiality order parameter for chiral molecules.

Finally we note that a strong temperature variation of the

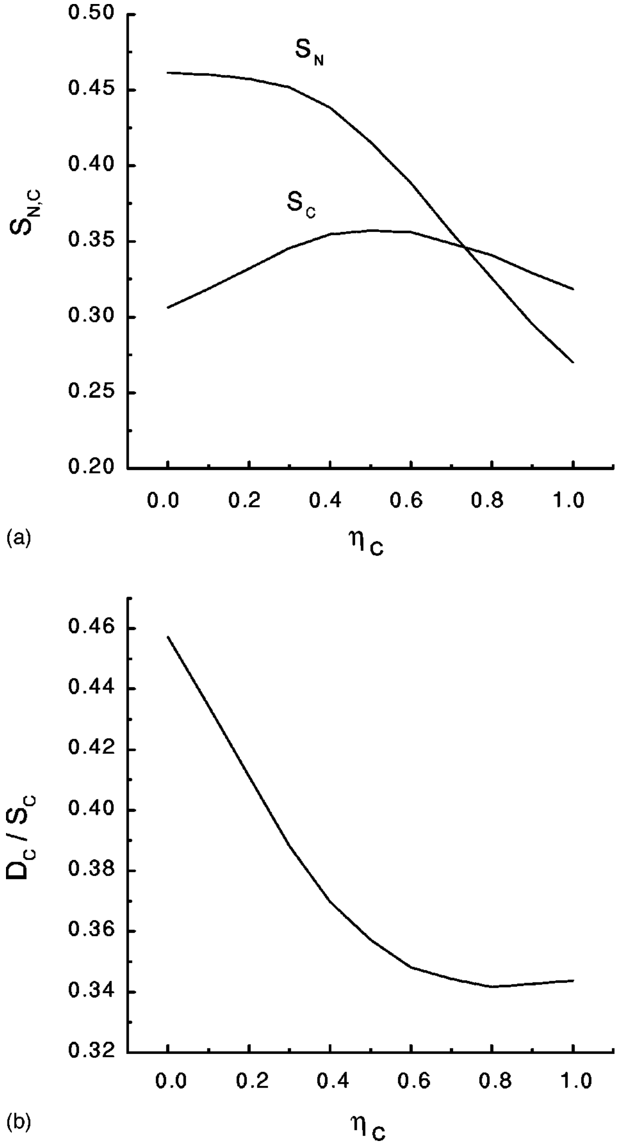

FIG. 6. Order parameters as functions of the molar fraction of chiral molecules in the binary mixture for $\varphi = 0.39$ rad and $T = T_c - 4$ K: (a) primary order parameters S_N and S_C; (b) ratio of the two order parameters for chiral molecules D_C / S_C.

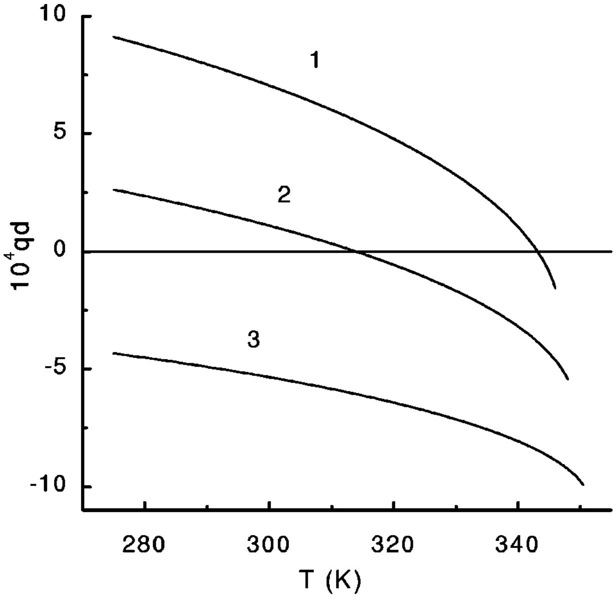

FIG. 7. Temperature variation of the dimensionless helical wave number for pure chiral nematic liquid crystal plotted for four different values of the model parameter φ: (1) $\varphi = 0.63$ rad.; (2) $\varphi = 0.60$ rad; and (3) $\varphi = 0.57$ rad.

ratio D_C / S_C [see Fig. 5(b)] may cause the helical sense inversion induced by a change of temperature. Such inversion may take place both in mixtures and in pure chiral nematics, and for simplicity we consider only the latter case. The helical pitch of the chiral nematic is given by Eq. (29) which can be rewritten as

$$q = \frac{2\pi}{p} \sim J_1^{212} + 2 M_1^{212} \frac{D(T)}{S(T)}, \tag{30}$$

where we have dropped the index C everywhere.

The expression in the right-hand side of Eq. (30) may change sign only if the coefficients J_1^{212} and M_1^{212} possess opposite signs and if, in addition, $|2 M_1^{212}| > |J_1^{212}|$. One can readily see from Fig. 3(a) that these conditions are satisfied for values of the parameter φ slightly larger then 0.5. The temperature variation of the helical pitch in a pure chiral nematic, obtained in the context of the present model, is depicted in Fig. 7 for three values of the model parameter φ between $\varphi = 0.55$ and $\varphi = 0.65$. Two of these curves demonstrate a helical sense inversion with the decreasing temperature.

Thus one concludes that in the context of the present model it is possible also to explain the helix inversion in chiral nematics induced by a change of temperature. As discussed in the Introduction, such inversion has recently been observed experimentally by different authors [12–15]. It should be noted that in the present model the molecules are assumed to be completely rigid and thus the inversion is not related to any conformational changes. By contrast, in the present theory the inversion is related to molecular biaxiality and among other factors is determined by different temperature variation of the order parameters $D(T)$ and $S(T)$. One notes also that the temperature-induced sense inversion takes place only in the narrow range of the values of the parameter φ. On the other hand, this enables one to understand why the temperature-induced helical sense inversion has been observed only for few one-component chiral nematics.

Recently the influence of the real molecular shape (including the molecular biaxiality) on the helical twisting power of a chiral dopant in the nematic solvent has been studied by Ferrarini, Moro, and Nordio using a simple surface interaction model [25,29,30]. In this model the surface of a chiral dopant molecule is assumed to be directly coupled to the director of the nematic solvent via the local mean-field potential $\varepsilon P_2(\mathbf{e} \cdot \mathbf{n})$ where $\mathbf{e} = \mathbf{e}(\mathbf{R})$ is the surface normal at point $\mathbf{R}$. Here the vector $\mathbf{R}$ points from the center of mass to some point at the molecular surface. The total interaction of a dopant molecule with the nematic solvent is then determined by the corresponding surface integral. This interaction is sensitive to a molecular shape including the chirality of the molecular surface. It is interesting to note that the final equation for the helical twisting power of the chiral dopant, obtained by Ferrarini *et al.*, can be written in the form which is mathematically equivalent to Eq. (28) of this paper,

$$h \sim \varepsilon S_N(\Delta Q S_C + \Delta Q_\perp D_C). \tag{31}$$

Similar to the results obtained in this paper, the helical twisting power (31) is proportional to the sum of two terms. The first term in brackets in Eq. (31) is proportional to the nematic order parameter of the chiral dopant molecule S_C while the second term is proportional to the biaxiality order parameter D_C. Similar terms are also present in our Eq. (28) although the meaning of the coefficients is different.

In the model of Ferrarini, Moro, and Nordio the chirality of the molecular surface is characterized by the so-called helicity tensor $Q_{\alpha\beta}$ which is represented as the following surface integral:

$$Q_{\alpha\beta} = \int d\sigma\, e_\alpha [\mathbf{R} \times \mathbf{e}]_\beta . \tag{32}$$

Then the coefficients ΔQ and ΔQ in Eq. (31) can be expressed as

$$\Delta Q = \tilde{Q}_{zz} - \frac{1}{2}(\tilde{Q}_{xx} + \tilde{Q}_{yy}), \tag{33}$$

$$\Delta Q_\perp = \frac{1}{2}(\tilde{Q}_{xx} - \tilde{Q}_{yy}), \tag{34}$$

where

$$\begin{aligned} \tilde{Q}_{zz} &= (\mathbf{a} \cdot \mathbf{Q} \cdot \mathbf{a}), \\ \tilde{Q}_{xx} &= (\mathbf{b} \cdot \mathbf{Q} \cdot \mathbf{b}), \\ \tilde{Q}_{yy} &= (\mathbf{c} \cdot \mathbf{Q} \cdot \mathbf{c}), \end{aligned} \tag{35}$$

and the unit vector **a** is in the direction of the primary axis of the dopant molecule and the unit vectors **b** and **c** are in the directions of the two short molecular axes.

We note that the parameter ΔQ in Eq. (31) has the meaning of the ‘‘projection’’ of the helicity tensor $Q_{\alpha\beta}$ on the primary molecular axis **a** and therefore it represents the properties of a freely rotating (about the axis **a**) molecule. By contrast, the parameter $\Delta Q_\perp$ represents the biaxiality of the chiral dopant surface.

Parameters ΔQ and $\Delta Q_\perp$ as well as the order parameters S_C and D_C have been calculated by Ferrarini *et al.* for a number of different chiral dopants. Some of these results, taken from Refs. [25] and [31], are presented in Table II. One can readily see from the table that the results, obtained in the context of a completely different molecular model [28–30], confirm some important qualitative conclusions made in the present paper. Firstly, the two terms in the expression for the inverse helical pitch (31) (i.e., the ‘‘uniaxial’’ contribution $\Delta Q S_C$ and the ‘‘biaxiality’’ contribution $\Delta Q_\perp D_C$) may possess opposite signs depending on the molecular structure. Secondly, the biaxiality order parameter D_C of a chiral dopant molecule in the nematic solvent may be sufficiently large and substantially larger than typical values found in one-component nematic liquid crystals. As a result the biaxiality contribution is usually comparable with the uniaxial one and for some dopants the former is even predominant. Thus the biaxiality of a chiral dopant molecule appears to be a very important factor which strongly effects the value and sign of the helical twisting power.

TABLE II. Order parameters S_C and D_C for different chiral dopants, and contributions $S_C \Delta Q$ and $D_C \Delta Q_\perp$ to the helical twisting power calculated using the data presented in [25,31].

Chiral dopant	S_C	D_C	$S_C\Delta Q$	$D_C\Delta Q_\perp$
Biphenyl 45°	0.34	0.2	0.748	−5.04
Binaphthyl 45°	0.27	0.4	1.78	−20.24
Binaphthyl 135°	0.31	−0.37	−2.7	−18.43
Heptalene	0.24	0.14	8.38	−4.2
Heptalene 3	0.32	0.28	16	−3
Heptalene 4	0.17	0.37	13.5	−13.5
Heptalene 6	0.61	0.19	−55.8	22
CB-2	0.61	0.09	−9.2	3
CB-3	0.66	0.08	0	3.8
B0	0.22	0.4	3.3	−35.2
B1	0.18	0.47	1.62	−43.7
B2(A)	0.24	0.42	1.08	−39.7
B2(B)	0.21	0.45	−0.32	−43.9
B2(C)	0.17	0.49	−28.2	−24.3
B5(A)	0.42	0.31	−83.2	−16.4
B5(B)	0.28	0.28	−27.3	−29
B5(C)	0.42	0.32	13.2	−31.5
B6(A)	0.41	0.39	−110.3	−57
B6(B)	0.56	0.26	−92.4	18.2

Ferrarini *et al.* did not consider either the temperature or the concentration variation of the helical pitch in mixtures of liquid crystals. Nevertheless, the similarity of some existing results enables one to believe that the main qualitative conclusions of the present paper are not restricted to a particular model. We expect that the main effects, described in the present theory, including helical sense inversions induced by a change of concentration in a mixture or by a change of temperature, can be found in any realistic model that takes into consideration chiral interactions between biaxial molecules.

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APPENDIX A

Let us integrate Eq. (5). If we restrict the sums in Eq. (5) with the constraint $l, \lambda \leqslant 2, L \leqslant 1$, then we have only to consider the two integrals for the long-long axes interaction,

$$Z_0=\int d\mathbf{r}_{12}J^{202}(\mathbf{r}_{12})T^{202}(\mathbf{n}_1,\mathbf{u},\mathbf{n}_2)$$

$$=\int d\mathbf{r}_{12}J^{202}(\mathbf{r}_{12})P_2(\mathbf{n}_1\cdot\mathbf{n}_2), \tag{A1}$$

$$Z_1=\int d\mathbf{r}_{12}J^{212}(\mathbf{r}_{12})T^{212}(\mathbf{n}_1,\mathbf{u},\mathbf{n}_2)$$

$$=\int d\mathbf{r}_{12}J^{212}(\mathbf{r}_{12})(\mathbf{n}_1\cdot\mathbf{n}_2)([\mathbf{n}_1\times\mathbf{n}_2]\cdot\mathbf{u}) \tag{A2}$$

and their analogs for the short-long axes interaction. Using the gradient expansion (9) for the director $\mathbf{n}_2=\mathbf{n}(\mathbf{r}_2)$ and neglecting terms higher than quadratic in the gradients of $\mathbf{n}$ one obtains

$$Z_0\approx\int d\mathbf{r}_{12}J^{202}(\mathbf{r}_{12})\{1+\tfrac{3}{2}\mathbf{n}(\mathbf{r}_{12}\cdot\boldsymbol{\nabla})^2\mathbf{n}\}$$

$$=J_0^{202}+\tfrac{1}{2}J_2^{202}\sum_{\alpha\,\beta} n_\alpha\,\nabla_\beta^2 n_\alpha. \tag{A3}$$

Taking into account equation

$$\sum_\alpha (\nabla_\beta n_\alpha)^2+\sum_\alpha n_\alpha\nabla_\beta^2 n_\alpha=\sum_\alpha \nabla_\beta(n_\alpha\nabla_\beta n_\alpha)$$

$$=\tfrac{1}{2}\nabla_\beta^2\sum_\alpha n_\alpha^2=0, \tag{A4}$$

we have

$$Z_0=J_0^{202}-\tfrac{1}{2}J_2^{202}\sum_{\alpha\beta}(\nabla_\beta n_\alpha)^2. \tag{A5}$$

Adding the surface term $\boldsymbol{\nabla}\{\mathbf{n}(\boldsymbol{\nabla}\cdot\mathbf{n})\}-\boldsymbol{\nabla}\{(\boldsymbol{\nabla}\cdot\mathbf{n})\mathbf{n}\}$ to Eq. (A5) leads to the following expression for Z_0:

$$\begin{aligned}Z_0&=J_0^{202}-\tfrac{1}{2}J_2^{202}\sum_{\alpha\beta}\{(\nabla_\beta n_\alpha)^2+(\nabla_\beta n_\beta)(\nabla_\alpha n_\alpha)\\&\quad-(\nabla_\alpha n_\beta)(\nabla_\beta n_\alpha)\}\\&=J_0^{202}-\tfrac{1}{2}J_2^{202}\{(\boldsymbol{\nabla}\cdot\mathbf{n})^2+[\boldsymbol{\nabla}\times\mathbf{n}]^2\}\\&=J_0^{202}-\tfrac{1}{2}J_2^{202}\{(\operatorname{div}\mathbf{n})^2+(\mathbf{n}\cdot\operatorname{rot}\mathbf{n})^2+[\mathbf{n}\times\operatorname{rot}\mathbf{n}]^2\}.\end{aligned} \tag{A6}$$

The same procedure for the integral Z_1 gives

$$\begin{aligned}Z_1&\approx\int d\mathbf{r}_{12}J^{212}(\mathbf{r}_{12})\{[\mathbf{n}\times(\mathbf{r}_{12}\cdot\boldsymbol{\nabla})\mathbf{n}]\cdot\mathbf{u}\}\\&=\tfrac{1}{3}J_1^{212}\sum_{\alpha\,\beta\,\gamma}(n_\beta\nabla_\alpha n_\gamma-n_\gamma\nabla_\alpha n_\beta)\\&=-\tfrac{1}{3}J_1^{212}(\mathbf{n}\cdot\operatorname{rot}\mathbf{n}).\end{aligned}$$

Substituting expressions (A6) and (A7) for Z_0 and Z_1 and their analogs for the short-long axes interaction into Eq. (5), one obtains Eqs. (10)–(12) for F_0, k_2, and K_2.

APPENDIX B

To obtain the interaction coefficients $J_{n(\alpha\gamma)}^{lL\lambda}, M_{n(\alpha\gamma)}^{lL\lambda}$, let us return to expansion (18) for the even part of the effective pair interaction. If we retain the only terms with $l,\lambda\leqslant 2, L\leqslant 1$ in these series, the effective pair interaction approximates by the following expression:

$$\begin{aligned}-\{\Theta_{\alpha\gamma}(\mathbf{r}_{12}-\boldsymbol{\xi}_{12})U_{\alpha\gamma}(1,2)\}_e&=J_{\alpha\gamma}^{000}+M_{\alpha\gamma}^{000}+M_{\gamma\alpha}^{000}+J_{\alpha\gamma}^{202},P_2(\mathbf{a}_1\cdot\mathbf{a}_2)+J_{\alpha\gamma}^{220}P_2(\mathbf{a}_1\cdot\mathbf{u})+J_{\alpha\gamma}^{022}P_2(\mathbf{a}_2\cdot\mathbf{u})\\&\quad+M_{\alpha\gamma}^{202}\{P_2(\mathbf{a}_1\cdot\mathbf{b}_2)-P_2(\mathbf{a}_1\cdot\mathbf{c}_2)\}+M_{\gamma\alpha}^{202}\{P_2(\mathbf{a}_2\cdot\mathbf{b}_1)-P_2(\mathbf{a}_2\cdot\mathbf{c}_1)\}\\&\quad+M_{\alpha\gamma}^{022}\{P_2(\mathbf{b}_2\cdot\mathbf{u})-P_2(\mathbf{c}_2\cdot\mathbf{u})\}+M_{\gamma\alpha}^{220}\{P_2(\mathbf{b}_1\cdot\mathbf{u})-P_2(\mathbf{c}_1\cdot\mathbf{u})\}+J_{\alpha\gamma}^{212}(\mathbf{a}_1\cdot\mathbf{a}_2)([\mathbf{a}_1\times\mathbf{a}_2]\cdot\mathbf{u})\\&\quad+M_{\alpha\gamma}^{212}\{(\mathbf{a}_1\cdot\mathbf{b}_2)([\mathbf{a}_1\times\mathbf{b}_2]\cdot\mathbf{u})-(\mathbf{a}_1\cdot\mathbf{c}_2)([\mathbf{a}_1\times\mathbf{c}_2]\cdot\mathbf{u})\}\\&\quad+M_{\gamma\alpha}^{212}\{(\mathbf{a}_2\cdot\mathbf{b}_1)([\mathbf{a}_2\times\mathbf{b}_1]\cdot\mathbf{u})-(\mathbf{a}_2\cdot\mathbf{c}_1),([\mathbf{a}_2\times\mathbf{c}_1]\cdot\mathbf{u})\}.\end{aligned} \tag{B1}$$

Let us introduce the functions

$$X_{\alpha\gamma}^n(\mathbf{a}_\alpha,\mathbf{b}_\alpha,\mathbf{a}_\gamma,\mathbf{b}_\gamma)\equiv-\int_{-\infty}^{\infty}dr_{12}r_{12}^{n+2}\{\Theta_{\alpha\gamma}(\mathbf{r}_{12}-\boldsymbol{\xi}_{12})U_{\alpha\gamma}(1,2)\}_e. \tag{B2}$$

Substituting the expansion (B1) into (B2) and using the relative orientations of the two molecules, presented in Fig. 8(a), one obtains for the nonchiral coefficients ($n=0,2$):

$$J_{n(\alpha\gamma)}^{202}=\tfrac{1}{3}[X_{\alpha\gamma}^n(1)+X_{\alpha\gamma}^n(2)-X_{\alpha\gamma}^n(3)-X_{\alpha\gamma}^n(4)], \tag{B3}$$

$$M_{n(\alpha\gamma)}^{202}=\tfrac{1}{6}[X_{\alpha\gamma}^n(1)-X_{\alpha\gamma}^n(2)-X_{\alpha\gamma}^n(3)+X_{\alpha\gamma}^n(4)], \tag{B4}$$

and using the relative orientations, presented on Fig. 8(b), one obtains for the chiral coefficients ($n=1$):

$$J_{1(\alpha\gamma)}^{212}=\tfrac{1}{2}[X_{\alpha\gamma}^n(5)+X_{\alpha\gamma}^n(6)-X_{\alpha\gamma}^n(7)-X_{\alpha\gamma}^n(8)], \tag{B5}$$

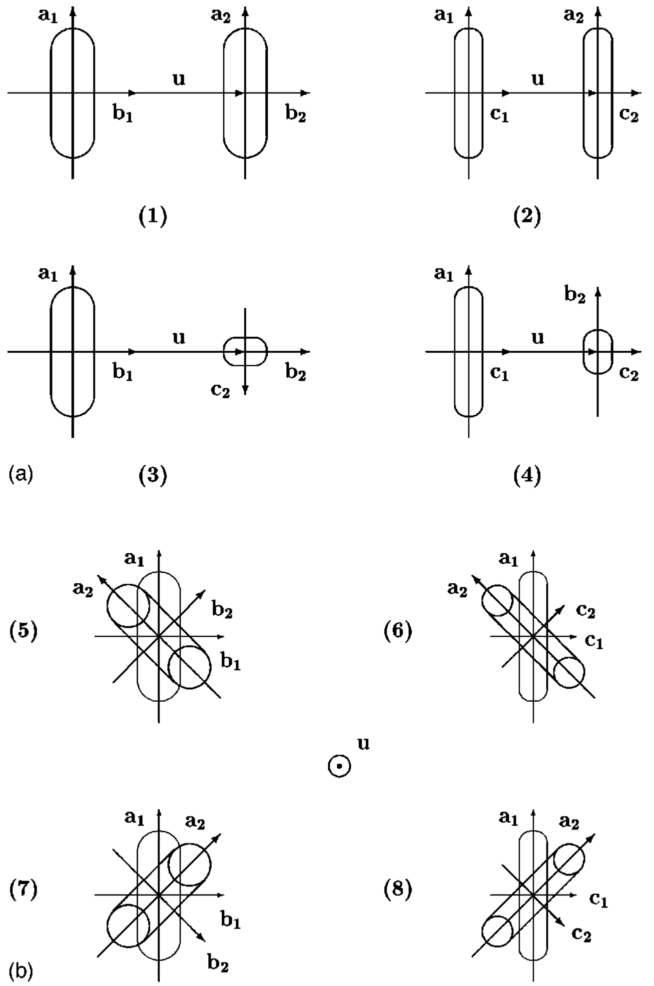

FIG. 8. Relative orientations of the interacting molecules used for calculation of the nonchiral coefficients (a) in Eqs. (B3) and (B4) and chiral coefficients (b) in Eqs. (B5) and (B6).

$$M^{212}_{1(\alpha\gamma)}=\tfrac{1}{4}\,[-X^{n}_{\alpha\gamma}(5)+X^{n}_{\alpha\gamma}(6)+X^{n}_{\alpha\gamma}(7)-X^{n}_{\alpha\gamma}(8)]. \tag{B6}$$

The values $X^{n}_{\alpha\gamma}(i), i=1\div 8$, were calculated numerically using the interaction model, described in Sec. IV. The corresponding coefficients obtained in Eqs. (B3)–(B6) are presented on Figs. 3(a)–3(c) as functions of the structural parameter φ.

APPENDIX C

Spherical invariants are a convenient complete orthogonal set of basis functions which are used in the expansion of a pair potential, pair correlation function and other two-body functions [32,33]. In this appendix we present a definition of these invariant functions for a simple case of two uniaxial molecules. The more general case is considered in [32].

Any function $V(r_{12},\mathbf{a}_1,\mathbf{u},\mathbf{a}_2)$, depending on the position and orientation of two uniaxial molecules ‘‘1’’ and ‘‘2’’, can be expanded in terms of spherical harmonics as

$$V(r_{12},\mathbf{a}_1,\mathbf{u},\mathbf{a}_2)=\sum_{lL\lambda}\sum_{mM\mu}J^{mM\mu}_{lL\lambda}Y_{lm}(\Theta_1,\phi_1)\times Y_{\lambda\mu}(\Theta_2,\phi_2)Y_{LM}(\Theta,\phi), \tag{C1}$$

where the summation runs through $-l<m<l, -\lambda<\mu<\lambda$, and $-L<M<L$, and where the coupling constants $J^{mM\mu}_{lL\lambda}$ depend on the intermolecular distance r_{12}. Here the angles $(\Theta_1,\phi_1),(\Theta_2,\phi_2)$, and (Θ,ϕ) specify the orientation of the unit vectors $\mathbf{a}_1,\mathbf{a}_2$, and $\mathbf{u}$, respectively.

One notes that the spherical harmonics in Eq. (C1) depend on the orientation of the laboratory frame. Since the function $V(r_{12},\mathbf{a}_1,\mathbf{u},\mathbf{a}_2)$ is invariant under rotation of the coordinate system, its coordinate free expansion can be performed by the integration of Eq. (C1) over all rotations of the coordinate system and employing the rotational properties of spherical harmonics. Then the expansion (C1) can be rewritten as

$$V(r_{12},\mathbf{a}_1,\mathbf{u},\mathbf{a}_2)=\sum_{lL\lambda}J^{lL\lambda}T^{lL\lambda}(\mathbf{a}_1,\mathbf{u},\mathbf{a}_2), \tag{C2}$$

where

$$J^{lL\lambda}=\sum_{mM\mu}J^{lL\lambda}_{mM\mu}\begin{pmatrix} l & L & \lambda \\ m & M & \mu \end{pmatrix}(C^{lL\lambda})^{-1} \tag{C3}$$

and

$$T^{lL\lambda}(\mathbf{a}_1,\mathbf{u},\mathbf{a}_2)=C^{lL\lambda}\sum_{mM\mu}\begin{pmatrix} l & L & \lambda \\ m & M & \mu \end{pmatrix}Y_{lm}(\Theta_1,\phi_1)\times Y_{\lambda\mu}(\Theta_2,\phi_2)Y_{LM}(\Theta,\phi). \tag{C4}$$

Here $C^{lL\lambda}$ is a numerical coefficient introduced for normalization and $\begin{pmatrix} l & L & \lambda \\ m & M & \mu \end{pmatrix}$ are the $3j$ symbols. The functions $T^{lL\lambda}(\mathbf{a}_1,\mathbf{u},\mathbf{a}_2)$ are rotational invariants, i.e., they do not depend on the choice of the coordinate system. These functions depend on all possible couplings between the three unit vectors $\mathbf{a}_1,\mathbf{a}_2$, and $\mathbf{u}$ and contain $\mathbf{a}_1$ to the power l,$\mathbf{u}$ to the power L, and $\mathbf{a}_2$ to the power λ with $|l-\lambda|\leqslant L\leqslant l+\lambda$.

The spherical invariants $T^{lL\lambda}$ are natural basis functions in the statistical theory of anisotropic fluids because the mean-field average of these functions directly yields the orientational order parameters $\langle P_l(\mathbf{a}\cdot\mathbf{n})\rangle$. This can be seen by employing the following useful mathematical properties of spherically invariant functions

$$\int d^2\mathbf{a}_1 d^2\mathbf{a}_2 T^{lL\lambda}(\mathbf{a}_1,\mathbf{u},\mathbf{a}_2)f(\mathbf{a}_1\cdot\mathbf{n}_1)f(\mathbf{a}_2\cdot\mathbf{n}_2) =T^{lL\lambda}(\mathbf{n}_1,\mathbf{u},\mathbf{n}_2)\int d^2\mathbf{a}_1 P_l(\mathbf{a}_1\cdot\mathbf{n}_1)\int d^2\mathbf{a}_2 P_\lambda(\mathbf{a}_2\cdot\mathbf{n}_2), \tag{C5}$$

where $f(\mathbf{a}\cdot\mathbf{n})$ is an arbitrary function and $\mathbf{n}$ is a unit vector. Equation (C5) has been used in the derivation of the results of Secs. II and III by setting f to be equal to the orientational distribution function.

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