

Analytical description for the chiral nematic state in terms of molecular parameters

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An analytical description for helical twisting in chiral liquid crystals is derived, which explores the correlation between the macroscopic properties of a liquid crystal and the parameters of single molecules. This theory is based on a simple model of a spiral-like rigid molecules that possess a limited number of parameters, each having transparent geometrical meaning. Expressions for the macroscopic helical pitch in the chiral nematic phase and the nematic order parameters were obtained in terms of molecular parameters. The theory explains the experimentally observed helical sense inversions induced by a change of temperature or mutual concentration of components in mixtures. It is also shown that the helical sense inversion may be observed in the process of denaturation of polypeptides. Different reasons for helical sense inversions were identified, such as competition between the dispersion attraction and the steric repulsion, distinct mechanisms of the steric packing for different kinds of molecules, and biaxiality of molecules.

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I. INTRODUCTION

Principles of the molecular organization in chiral mesophases are of the great interest since they throw light on the macroscopic properties of the liquid crystals. Different liquid crystals under similar conditions may behave in different ways. For example, variation of temperature, concentration, and other external parameters may lead to the change in the optical activity in one sample and may not in the other one. The question arises: what is the correlation between the macroscopic parameters of the liquid crystal (such as the nematic order parameter and the twisting power) and the microscopic features of single molecules (such as their shape and interaction)?

In an earlier paper [1] we derived the mean-field theory of the chiral nematic state, based on the principles of the statistical physics and the continuum theory. It allowed us to estimate numerically the value of the helical twisting power for the liquid crystal consisting of the molecules from our previous model. Nevertheless, that model was difficult to use, and the analytical expression for the helical pitch in terms of molecular parameters was not obtained.

In this paper we suggest a method that explores the correlation between the molecular parameters and the macroscopic properties of a liquid crystal. We use a model of the biaxial spiral-like molecule with a small set of parameters having transparent geometrical meaning. Any pair of molecules possesses dispersion attraction as well as steric repulsion. The resulting expressions predict the conditions for the helical sense inversion in an arbitrary liquid crystal. Vice versa, using these expressions one may estimate the molecular parameters needed for the helical sense inversion in the appropriate conditions.

In our theoretical studies we focus on the three situations that are investigated experimentally by many authors. First

we consider the pure liquid crystal, consisting of identical chiral molecules. In correspondence with the experiment [2–6], the helical sense inversion with the temperature variation may take place in a chiral nematic even in the case of the stable molecules, having the same handedness. We concentrate on the two reasons for the helical sense inversion: the competition of the steric repulsion with the dispersion attraction and the biaxiality of the molecules. These two factors were noticed by many authors to be responsible for various helical sense inversions in different classes of the chiral nematics. The detailed review of these investigations is presented, for example, in Ref. [7]. To combine the dispersion attraction together with the steric repulsion, many authors [8–11] used a special effective potential that took into account both effects. Thus, the resulting expression for the helical wave number contained both the dispersion and steric contributions. The signs of these contributions, however, remained undetermined since the effective potential was not accurately associated with the parameters of a molecular model. Recently the importance of a molecular biaxiality was recognized by several authors [12,13]. In this paper we present a quantitative scheme that allows one to estimate the effect of the molecular biaxiality.

The second experimentally observed situation is the helical sense inversion in binary mixtures with a change in the mutual concentration of the components. It was established that inversion may take place even in the case when one component is achiral [14–17]. In this paper, we notice and prove analytically that the identical molecules and the unlike molecules have different mechanisms of steric packing. This situation, as we suppose, is responsible for the helical sense inversion in mixtures of chiral and achiral molecules.

Finally, we consider the possibility of the helical sense inversion in polypeptides which may happen during the process of denaturation. Since our analytical expressions for the helical wave number contain molecular parameters explicitly, one can simply change some of them to obtain the helical sense inversion. Molecular length is one of these parameters. On the other hand, it is well known [18] that the long spiral molecules of protein melt into small pieces during de-

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naturation. Therefore, the possibility of the helical sense inversion exists. This situation is briefly discussed in the present paper where we suggest a simple scheme of denaturation.

The paper is arranged as follows. In Sec. II we introduce the alternative effective molecular interaction and derive analytical expressions for the nematic order parameters and helical wave number. In Sec. III we suggest our models of chiral and achiral molecules and define the effective interaction between similar and dissimilar molecules. In Sec. IV we analyze different situations, such as variations of temperature, concentration, or molecular length which may cause the helical sense inversions. Finally, in Sec. V we present the main results of the paper.

II. EFFECTIVE INTERACTION OF CHIRAL MOLECULES AND THE CHOLESTERIC STATE

In this section, we suggest a description for the interaction between anisotropic chiral molecules, which determines macroscopic properties of the liquid crystal: the nematic order parameters and the helical twisting power. In the common case of a multicomponent system, the prime nematic order parameter S_μ and the biaxiality order parameter D_μ of the component μ obey the generalized Maier-Saupe theory [1]:

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

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

where I_μ are the normalizing integrals,

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

parameters $t \equiv \cos \theta$ and ψ describe the orientation of a molecule with respect to the director, and the mean-field energy U_{MF}^μ of the component μ is interpolated as follows:

$$U_{MF}^\mu(t, \psi) \approx \frac{\rho}{k_B T} \sum_{\nu=1}^{\tau} \eta_\nu \{ [J_{0(\mu\nu)}^{202} S_\nu + M_{0(\mu\nu)}^{202} D_\nu] P_2(t) + [M_{0(\nu\mu)}^{202} S_\nu + Q_{0(\nu\mu)}^{202} D_\nu] \frac{3}{2} (1-t^2) \cos(2\psi) \}, \quad (3)$$

where τ is the total number of components in the system. If at least one of the components is chiral, then cholesteric distortion of the nematic state takes place. This is usually described [19–21] in terms of elastic constants. Then the helical wave number is determined by the following expression:

$$q = \frac{k_2}{K_2}, \quad (4)$$

where K_2 is the twist elastic constant and k_2 is a pseudo-scalar parameter, which is sensitive to molecular chirality. The gradient expansion of the director results in the following interpolations for the parameters k_2 and K_2 [1]:

$$k_2 \approx \frac{1}{6} \rho^2 \sum_{\mu, \nu=1}^{\tau} \eta_\mu \eta_\nu [J_{1(\mu\nu)}^{212} S_\mu S_\nu + M_{1(\mu\nu)}^{212} S_\mu D_\nu + M_{1(\nu\mu)}^{212} S_\nu D_\mu + Q_{1(\mu\nu)}^{212} D_\mu D_\nu], \quad (5)$$

$$K_2 \approx \frac{1}{2} \rho^2 \sum_{\mu, \nu=1}^{\tau} \eta_\mu \eta_\nu [J_{2(\mu\nu)}^{202} S_\mu S_\nu + M_{2(\mu\nu)}^{202} S_\mu D_\nu + M_{2(\nu\mu)}^{202} S_\nu D_\mu + Q_{2(\mu\nu)}^{202} D_\mu D_\nu]. \quad (6)$$

The coefficients $J_{n(\mu\nu)}^{l\lambda}$, $M_{n(\mu\nu)}^{l\lambda}$, and $Q_{n(\mu\nu)}^{l\lambda}$ in Eqs. (3), (5), and (6) are the moments of the corresponding coupling constants:

$$J_{n(\mu\nu)}^{l\lambda} = \int_0^\infty dr_{12} r_{12}^{n+2} J_{\mu\nu}^{l\lambda}(r_{12}),$$

$$M_{n(\mu\nu)}^{l\lambda} = \int_0^\infty dr_{12} r_{12}^{n+2} M_{\mu\nu}^{l\lambda}(r_{12}), \quad (7)$$

$$Q_{n(\mu\nu)}^{l\lambda} = \int_0^\infty dr_{12} r_{12}^{n+2} Q_{\mu\nu}^{l\lambda}(r_{12}).$$

The coupling constants $J_{\mu\nu}^{l\lambda}(r_{12})$, $M_{\mu\nu}^{l\lambda}(r_{12})$, and $Q_{\mu\nu}^{l\lambda}(r_{12})$ in Eq. (7) are the coefficients of the expansion of the effective intermolecular potential $V_{ef}^{\mu\nu}$ in a complete set of spherical invariants [1,22–25]. The effective interaction $V_{ef}^{\mu\nu}$ of a molecule of type μ with a molecule of type ν is an even function with the respect to the orientation of both molecules (since the phase observed is nonpolar), but it is not even with respect to the orientation of intermolecular vector \mathbf{r}_{12} (since the cholesteric distortion is observed). One can split the effective interaction $V_{ef}^{\mu\nu}$ into a large homogeneous part $V_0^{\mu\nu}$ (which is even with respect to the orientation of the intermolecular vector) and a small energy of distortion $V_d^{\mu\nu}$ (which is odd with respect to the orientation of the intermolecular vector):

$$V_{ef}^{\mu\nu}(1,2) = V_0^{\mu\nu}(1,2) + V_d^{\mu\nu}(1,2). \quad (8)$$

Then the homogeneous part $V_0^{\mu\nu}(1,2)$ expands in spherical invariants as

$$\begin{aligned}
V_0^{\mu\nu}(1,2) = & J_{\mu\nu}^{000} + J_{\mu\nu}^{202} P_2(\mathbf{a}_1 \cdot \mathbf{a}_2) + J_{\nu\mu}^{220} P_2(\mathbf{a}_1 \cdot \mathbf{u}_{12}) + J_{\mu\nu}^{022} P_2(\mathbf{a}_2 \cdot \mathbf{u}_{12}) + M_{\mu\nu}^{202} \{P_2(\mathbf{a}_1 \cdot \mathbf{b}_2) - P_2(\mathbf{a}_1 \cdot \mathbf{c}_2)\} + M_{\nu\mu}^{202} \{P_2(\mathbf{a}_2 \cdot \mathbf{b}_1) \\
& - P_2(\mathbf{a}_2 \cdot \mathbf{c}_1)\} + M_{\mu\nu}^{220} \{P_2(\mathbf{b}_1 \cdot \mathbf{u}_{12}) - P_2(\mathbf{c}_1 \cdot \mathbf{u}_{12})\} + M_{\nu\mu}^{022} \{P_2(\mathbf{b}_2 \cdot \mathbf{u}_{21}) - P_2(\mathbf{c}_2 \cdot \mathbf{u}_{21})\} + Q_{\mu\nu}^{202} \{P_2(\mathbf{b}_1 \cdot \mathbf{b}_2) \\
& - P_2(\mathbf{b}_1 \cdot \mathbf{c}_2) - P_2(\mathbf{b}_2 \cdot \mathbf{c}_1) + P_2(\mathbf{c}_2 \cdot \mathbf{c}_1)\} + \dots, \tag{9}
\end{aligned}$$

and the energy of distortion $V_d^{\mu\nu}(1,2)$ has the following expansion:

$$\begin{aligned}
V_d^{\mu\nu}(1,2) = & J_{\mu\nu}^{212} (\mathbf{a}_1 \cdot \mathbf{a}_2) ([\mathbf{a}_1 \times \mathbf{a}_2] \cdot \mathbf{u}_{12}) + M_{\mu\nu}^{212} \{(\mathbf{a}_1 \cdot \mathbf{b}_2) ([\mathbf{a}_1 \times \mathbf{b}_2] \cdot \mathbf{u}_{12}) - (\mathbf{a}_1 \cdot \mathbf{c}_2) ([\mathbf{a}_1 \times \mathbf{c}_2] \cdot \mathbf{u}_{12})\} + M_{\nu\mu}^{212} \{(\mathbf{a}_2 \cdot \mathbf{b}_1) \\
& \times ([\mathbf{a}_2 \times \mathbf{b}_1] \cdot \mathbf{u}_{21}) - (\mathbf{a}_2 \cdot \mathbf{c}_1) ([\mathbf{a}_2 \times \mathbf{c}_1] \cdot \mathbf{u}_{21})\} + Q_{\mu\nu}^{212} \{(\mathbf{b}_1 \cdot \mathbf{b}_2) ([\mathbf{b}_1 \times \mathbf{b}_2] \cdot \mathbf{u}_{12}) - (\mathbf{b}_1 \cdot \mathbf{c}_2) ([\mathbf{b}_1 \times \mathbf{c}_2] \cdot \mathbf{u}_{12}) \\
& + (\mathbf{c}_2 \cdot \mathbf{c}_1) ([\mathbf{c}_2 \times \mathbf{c}_1] \cdot \mathbf{u}_{21}) - (\mathbf{b}_2 \cdot \mathbf{c}_1) ([\mathbf{b}_2 \times \mathbf{c}_1] \cdot \mathbf{u}_{21})\} + \dots, \tag{10}
\end{aligned}$$

where the orientation of the first molecule is determined by the set of the orthogonal unit vectors $(\mathbf{a}_1, \mathbf{b}_1, \mathbf{c}_1)$, the orientation of the second molecule is determined by the vectors $(\mathbf{a}_2, \mathbf{b}_2, \mathbf{c}_2)$, and the direction of the intermolecular vector \mathbf{r}_{12} is determined by the unit vector $\mathbf{u}_{12} = -\mathbf{u}_{21}$. We assume that the axes $\mathbf{a}_1, \mathbf{a}_2$ correspond to the principal elongation of the molecules and call them ‘‘long axes.’’ The pairs $(\mathbf{b}_1, \mathbf{c}_1)$ and $(\mathbf{b}_2, \mathbf{c}_2)$ are called ‘‘short axes.’’ Taking into account that in Eqs. (9) and (10) the only coefficients with equal indices l and λ are used, it is enough to estimate for each pair of components μ and ν the three achiral coupling constants $J_{\mu\nu}^{202}(r_{12})$, $M_{\mu\nu}^{202}(r_{12})$, $Q_{\mu\nu}^{202}(r_{12})$ and the three chiral coupling constants $J_{\mu\nu}^{212}(r_{12})$, $M_{\mu\nu}^{212}(r_{12})$, $Q_{\mu\nu}^{212}(r_{12})$. One notes that the constants $J_{\mu\nu}^{lll}(r_{12})$ and $Q_{\mu\nu}^{lll}(r_{12})$ are also symmetrical with respect to the commutation of the indices μ and ν :

$$J_{\mu\nu}^{lll}(r_{12}) = J_{\nu\mu}^{lll}(r_{12}), \tag{11}$$

$$Q_{\mu\nu}^{lll}(r_{12}) = Q_{\nu\mu}^{lll}(r_{12}), \tag{12}$$

since they describe the correlation between the same axes: the long axis of the first molecule with the long axis of the second molecule, or the short axes of the first molecule with the short axes of the second molecule. At the same time the constant $M_{\mu\nu}^{lll}(r_{12})$ is not symmetrical with respect to the same commutation:

$$M_{\mu\nu}^{lll}(r_{12}) \neq M_{\nu\mu}^{lll}(r_{12}), \tag{13}$$

since it describes the correlation between different axes: the long axis of the first molecule with the short axes of the second molecule. Let us estimate the coupling constants us-

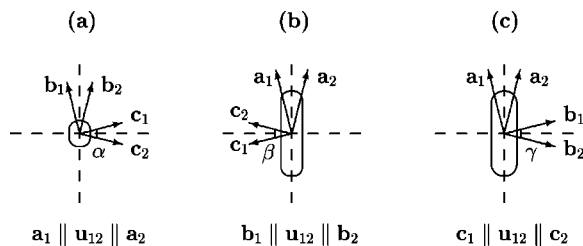


FIG. 1. Three mutual orientations of biaxial molecules ‘‘1’’ and ‘‘2’’ which are used for calculation of the coupling constants.

ing Fig. 1, where the three mutual orientations of the interacting molecules are presented. In Fig. 1(a) the long axis of the first molecule \mathbf{a}_1 is parallel to the long axis of the second molecule \mathbf{a}_2 and is parallel to the intermolecular vector \mathbf{u}_{12} . The angle between the corresponding short axes is equal to α . Figure 1(b) is obtained from Fig. 1(a) by the change $(\mathbf{a}_i, \mathbf{b}_i, \mathbf{c}_i) \rightarrow (\mathbf{b}_i, \mathbf{c}_i, \mathbf{a}_i)$, $\alpha \rightarrow \beta$, $(i=1,2)$ and Fig. 1(c) is obtained by the following change: $(\mathbf{b}_i, \mathbf{c}_i, \mathbf{a}_i) \rightarrow (\mathbf{c}_i, \mathbf{a}_i, \mathbf{b}_i)$, $\beta \rightarrow \gamma$. Rewriting Eq. (10) in the cases presented in Fig. 1(a)–1(c), then differentiating it with respect to the corresponding variable angle (α , β or γ) and solving the resulting equations for the chiral coupling constants $J_{\mu\nu}^{212}$, $M_{\mu\nu}^{212}$ and $Q_{\mu\nu}^{212}$, one obtains

$$\begin{aligned}
J_{\mu\nu}^{212} = & \frac{1}{2} \left(\left. \frac{\partial V_{ef}^{\mu\nu}}{\partial \gamma} \right|_{\gamma=0} + \left. \frac{\partial V_{ef}^{\mu\nu}}{\partial \beta} \right|_{\beta=0} \right) - \frac{1}{4} \left. \frac{\partial V_{ef}^{\mu\nu}}{\partial \alpha} \right|_{\alpha=0} \\
M_{\mu\nu}^{212} + M_{\nu\mu}^{212} = & \frac{1}{2} \left(\left. \frac{\partial V_{ef}^{\mu\nu}}{\partial \gamma} \right|_{\gamma=0} - \left. \frac{\partial V_{ef}^{\mu\nu}}{\partial \beta} \right|_{\beta=0} \right), \tag{14} \\
Q_{\mu\nu}^{212} = & \frac{1}{4} \left. \frac{\partial V_{ef}^{\mu\nu}}{\partial \alpha} \right|_{\alpha=0}.
\end{aligned}$$

Rewriting Eq. (9) in the cases presented in Figs. 1(a)–1(c), then differentiating it twice with respect to the corresponding variable angle (α , β or γ) and solving the resulting equations for the achiral coupling constants $J_{\mu\nu}^{202}$, $M_{\mu\nu}^{202}$, and $Q_{\mu\nu}^{202}$, one obtains

$$\begin{aligned}
J_{\mu\nu}^{202} = & -\frac{1}{6} \left(\left. \frac{\partial^2 V_{ef}^{\mu\nu}}{\partial \gamma^2} \right|_{\gamma=0} + \left. \frac{\partial^2 V_{ef}^{\mu\nu}}{\partial \beta^2} \right|_{\beta=0} \right) + \frac{1}{12} \left. \frac{\partial^2 V_{ef}^{\mu\nu}}{\partial \alpha^2} \right|_{\alpha=0}, \\
M_{\mu\nu}^{202} + M_{\nu\mu}^{202} = & -\frac{1}{6} \left(\left. \frac{\partial^2 V_{ef}^{\mu\nu}}{\partial \gamma^2} \right|_{\gamma=0} - \left. \frac{\partial^2 V_{ef}^{\mu\nu}}{\partial \beta^2} \right|_{\beta=0} \right), \tag{15} \\
Q_{\mu\nu}^{202} = & -\frac{1}{12} \left. \frac{\partial^2 V_{ef}^{\mu\nu}}{\partial \alpha^2} \right|_{\alpha=0}.
\end{aligned}$$

Thus, the chiral coupling constants $J_{\mu\nu}^{212}$, $M_{\mu\nu}^{212}$, and $Q_{\mu\nu}^{212}$ appear to depend on the first derivatives of the effective po-

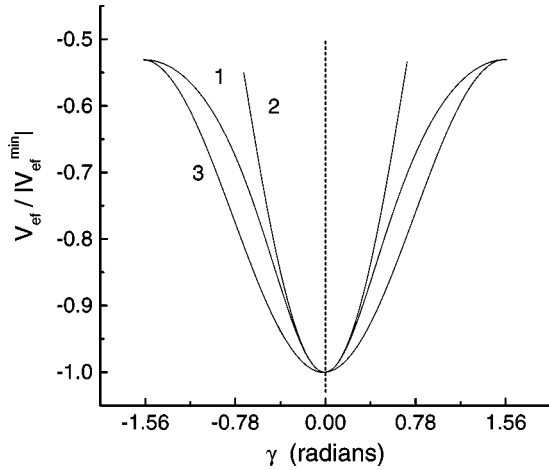


FIG. 2. Dependence of the effective potential V_{ef} on the angle γ between the long molecular axes \mathbf{a}_1 and \mathbf{a}_2 : (1) “real” site-site potential; (2) new model potential [achiral coupling constants J^{202} and J^{000} are determined by Eqs. (18) and (19)]; (3) standard model potential [the same constants are determined by Eqs. (20) and (21)].

tential $V_{ef}^{\mu\nu}$ with respect to the principal rotation angles, whereas the achiral coupling constants $J_{\mu\nu}^{202}$, $M_{\mu\nu}^{202}$, and $Q_{\mu\nu}^{202}$ appear to depend on the second derivatives of the effective potential with respect to same angles. To demonstrate the accuracy of this interpolation, let us fix two equivalent quasiuniaxial [37] chiral molecules some distance apart. To simplify the expression for the effective intermolecular potential V_{ef} , let each molecule rotate only in the plane perpendicular to the intermolecular vector \mathbf{r}_{12} . Then one obtains instead of Eqs. (8)–(10) the following expression for the effective potential:

$$V_{ef}(\gamma) = J^{000} + J^{202}P_2(\cos\gamma) + J^{212}\cos\gamma\sin\gamma + \dots, \quad (16)$$

where γ is the angle between the principal molecular axes \mathbf{a}_1 and \mathbf{a}_2 . The first and the second terms in Eq. (16) describe the large homogeneous part of the potential, whereas the third term is a small chiral addition, which is responsible for the helicity. The coupling constants J^{202} and J^{212} are interpolated then by the following simple expressions:

$$J^{212} \approx \left. \frac{\partial V_{ef}}{\partial \gamma} \right|_{\gamma=0}, \quad (17)$$

$$J^{202} \approx -\frac{1}{3} \left. \frac{\partial^2 V_{ef}}{\partial \gamma^2} \right|_{\gamma=0}, \quad (18)$$

which are analogous to Eqs. (14) and (15). The dependence of the effective potential V_{ef} on angle γ is presented in Fig. 2. Curve 1 corresponds to the site-site interaction [26,27] between chiral molecules. Let us call it “real” potential. Curve 2 in Fig. 2 corresponds to the model potential (16) with constants J^{212} and J^{202} determined by Eqs. (17) and (18), respectively, and the isotropic constant J^{000} determined by the following expression:

$$J^{000} \approx \left(V_{ef} + \frac{1}{3} \frac{\partial^2 V_{ef}}{\partial \gamma^2} \right) \Big|_{\gamma=0}. \quad (19)$$

One notes that curve 2 fits curve 1 in the vicinity of the most probable point $\gamma=0$ and the largest divergence of curves 1 and 2 arises in the least probable points $\gamma = \pm \pi/2$. However, the isotropic constant J^{000} is never used in the study of the cholesteric ordering. In other words, the absolute value of the effective potential makes no sense. On the contrary, the anisotropic constant J^{202} determines the width of the peak in curve 2 and the chiral constant J^{212} determines its declension from point $\gamma=0$. Therefore, the effective potential (16) with constants J^{212} , J^{202} , and J^{000} , determined by Eqs. (17), (18) and, (19) respectively, demonstrates the “true” position and width of the peak. This approach essentially differs from the standard interpolation [1] that “cares” about the depth of the effective potential instead of its width:

$$J^{202} \approx \frac{2}{3} (V_{ef}^{\parallel} - V_{ef}^{\perp}), \quad (20)$$

$$J^{000} \approx \frac{1}{3} (V_{ef}^{\parallel} + 2V_{ef}^{\perp}). \quad (21)$$

Here V_{ef}^{\parallel} and V_{ef}^{\perp} are the values of the effective potential in the orientation with parallel and perpendicular principal axes, respectively. The effective potential (16) with constants J^{212} , J^{202} , and J^{000} , determined by Eqs. (17), (20) and (21), respectively, fits the “real” potential in points $\gamma=0$ and $\gamma = \pm \pi/2$ (see curve 3 in Fig. 2). Nevertheless, the peak in curve 3 appears to be unsupportably wide. This leads to the mistake in the vicinity of the most probable orientation of molecules, which corresponds to $\gamma=0$. Therefore, interpolation (20) for the anisotropic constant J^{202} is less preferable than interpolation (18).

In the general case of biaxial molecules the anisotropic coupling constants are determined by Eqs. (14) and (15). Substituting Eqs. (14) and (15) into Eqs. (10) and (9), respectively, one obtains the model potential (8) fitting the “real” potential in the vicinity of the orientation with parallel corresponding axes ($\mathbf{a}_1 \parallel \mathbf{a}_2$, $\mathbf{b}_1 \parallel \mathbf{b}_2$, $\mathbf{c}_1 \parallel \mathbf{c}_2$) in the three cases presented in Fig. 1, which differ in the direction of the intermolecular vector \mathbf{r}_{12} . Since the relative orientation of the two molecules with parallel corresponding axes is the most probable in the nematic state, interpolations (14) and (15) demonstrate fitting in the most important area. In the chiral nematic state, the most probable angles between corresponding axes of the two molecules may be equal to a small non-zero values. Nevertheless, one may assume that the orientation with parallel corresponding axes belongs to the “vicinity” of the most probable orientation, since the cholesteric distortion usually accounts for only a few thousandths of the molecular dimension.

Let us determine the effective intermolecular potential in the same manner as in Refs. [28–31]. The two factors that are known to influence the behavior of chiral nematic are the steric repulsion and the dispersion attraction of molecules:

$$V_{ef}^{\mu\nu}(1,2) \equiv \langle -\partial k_B T \Theta_{\mu\nu}(\mathbf{r}_{12} - \xi_{12}) - [1 - \Theta_{\mu\nu}(\mathbf{r}_{12} - \xi_{12})] U_{\mu\nu}(1,2) \rangle. \quad (22)$$

In Eq. (22) the step function $\Theta_{\mu\nu}(\mathbf{r}_{12}-\xi_{12})$ represents the excluded volume effects, $U_{\mu\nu}(1,2)$ is dispersion interaction between the molecules 1 and 2, k_B is the Boltzmann constant, T is the temperature, and the factor ϑ depends on the packing fraction Φ . It has the following expression in the Parsons approach [32,33]:

$$\vartheta = \frac{|\ln(1-\Phi)|}{\Phi}. \quad (23)$$

In the case of low density one obtains $\vartheta \approx 1$, as in Onsager's theory [34]. The angular brackets in Eq. (22) denote the part of the corresponding expression which is even with respect to the rotation of any molecule $i=1,2$ by the angle π around any of its axes \mathbf{a}_i , \mathbf{b}_i or \mathbf{c}_i . The coefficients $J_{0(\mu\nu)}^{202}$, $M_{0(\mu\nu)}^{202}$, and $Q_{0(\mu\nu)}^{202}$, which are used in Eq. (3) for the mean-field energy U_{MF}^μ , the coefficients $J_{1(\mu\nu)}^{212}$, $M_{1(\mu\nu)}^{212}$, and $Q_{1(\mu\nu)}^{212}$, which are used in Eq. (5) for the pseudoscalar k_2 , and the coefficients $J_{2(\mu\nu)}^{202}$, $M_{2(\mu\nu)}^{202}$, and $Q_{2(\mu\nu)}^{202}$, which are used in Eq. (6) for the twist elastic constant K_2 , may be obtained after the corresponding integration of the coupling constants in Eq. (7). Substituting Eqs. (14) and (15) into Eq. (7) and taking into account Eq. (22) for the effective potential, one obtains the expressions for the coefficients $J_{n(\mu\nu)}^{LL\lambda}$, $M_{n(\mu\nu)}^{LL\lambda}$, and $Q_{n(\mu\nu)}^{LL\lambda}$ that appear to contain the integrals of the following two types:

$$\int_0^\infty dr_{12} r_{12}^n [V_{ef}^{\mu\nu}(r_{12})]' \\ = -\vartheta k_B T \langle \xi_{\mu\nu}^n \xi'_{\mu\nu} \rangle - \left\langle \int_{\xi_{\mu\nu}}^\infty dr_{12} r_{12}^n U'_{\mu\nu}(r_{12}) \right\rangle, \quad (24)$$

$$\int_0^\infty dr_{12} r_{12}^n [V_{ef}^{\mu\nu}(r_{12})]'' \\ = -\vartheta k_B T \langle \xi_{\mu\nu}^n \xi''_{\mu\nu} \rangle + 2 \langle \xi_{\mu\nu}^n \xi'_{\mu\nu} U'_{\mu\nu}(\xi_{\mu\nu}) \rangle \\ - n \vartheta k_B T \langle \xi_{\mu\nu}^{n-1} (\xi'_{\mu\nu})^2 \rangle - \left\langle \int_{\xi_{\mu\nu}}^\infty dr_{12} r_{12}^n U''_{\mu\nu}(r_{12}) \right\rangle, \quad (25)$$

where $\xi_{\mu\nu}$ is the minimal distance between a molecule of type μ and a molecule of type ν , which obviously depends on the orientation of both molecules. The first and second derivatives of the minimal distance $\xi_{\mu\nu}$ and the first and second derivatives of the dispersion attraction $U_{\mu\nu}(r_{12})$ in Eqs. (24) and (25) are considered with respect to the variable angles α , β , or γ in correspondence with Fig. 1.

III. MODEL OF A CHIRAL MOLECULE AND THE MOMENTS OF COUPLING CONSTANTS

To determine the minimal distance between molecules and to define their dispersion interaction, let us consider the universal molecular model presented in Fig. 3. A molecule consists of a rigid spiral-like tube with diameter d . In the common case, this helix has unequal semiaxes σ_b and σ_c ,

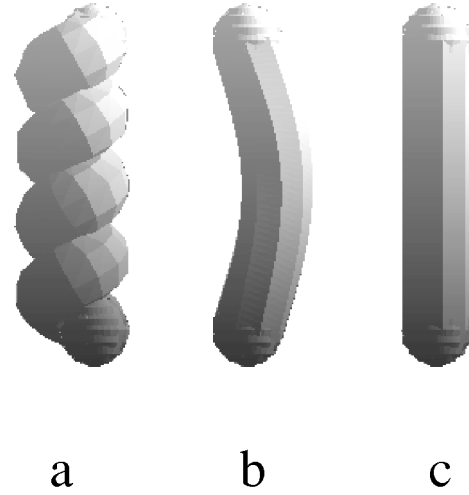


FIG. 3. Molecular model: (a) intensively twisted; (b) weakly twisted; (c) achiral.

which define the direction of the corresponding short axes \mathbf{b} and \mathbf{c} . One notes that the main section of the tube is not parallel to the plane of short axes \mathbf{b} and \mathbf{c} . Its inclination depends on the helical wave number k , semiaxes σ_b , σ_c and, in the biaxial case $\sigma_b \neq \sigma_c$, position t along the principal molecular axis \mathbf{a} . Let us fix parameter $t=0$ for the center of molecule. Then the parameter t ranges from $-\ell/2$ to $\ell/2$, where ℓ is the length of the molecule. Each end of the tube is capped by the hemisphere of the same diameter d . Any layer t of such a molecule has the following coordinates (the coordinate axes x , y , and z are parallel to the molecular axes \mathbf{b} , \mathbf{c} , and \mathbf{a} , respectively):

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \sigma_b \cos(kt + \varphi) \\ \sigma_c \sin(kt + \varphi) \\ t \end{pmatrix}. \quad (26)$$

Here φ is the structural parameter corresponding to the turn of the molecular center $t=0$ around the principal molecular axis \mathbf{a} with respect to the short axis \mathbf{b} . For simplicity of the following expressions, let us suppose that

$$\ell \gg d, \quad kd \geq 1, \quad \sigma_b \ll d, \quad \sigma_c \ll d. \quad (27)$$

Most of the chiral molecules are known to satisfy this constraint. The dispersion interaction of real molecules consists of the atomic dispersion contributions. If the dispersion interaction of the separate atoms with each other is isotropic, the only reason for the nematic ordering and helicity is the anisotropic and chiral composition of these atoms inside the molecules. The aggregate interaction of the two molecules is called ‘‘site-site’’ potential [26,27]. It cannot be expressed analytically in terms of the relative position and orientation of molecules. Nevertheless, in the simple case of identical atoms (or atomic groups) constituting the same molecule, one can change over from the summation by atoms to the

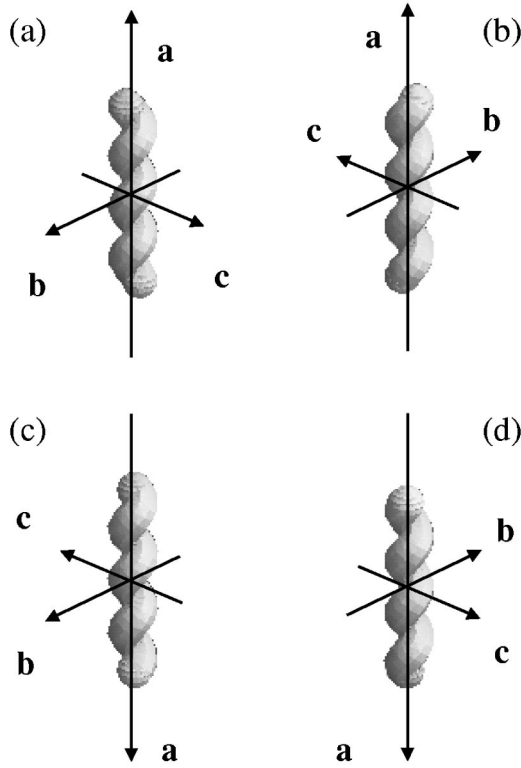


FIG. 4. Four odd orientations of a molecule which have equal probabilities.

integration along the molecular bodies. This can be done if the distance between the neighboring atoms (or atomic groups) is much less than the molecular length ℓ . Suppose that an arbitrary layer t_1 of the first molecule attracts an arbitrary layer t_2 of the second molecule via standard dispersion potential:

$$\Delta U(t_1, t_2) \sim - \frac{1}{\Delta r_{12}^6(t_1, t_2)}, \quad (28)$$

where $\Delta r_{12}(t_1, t_2)$ is the distance between the corresponding layers. If both molecules satisfy constraint (27), one can change over with the unity Jacobian from integrating along the helical molecular bodies to integrating along their principal axes, and the aggregate dispersion interaction may be approximated by the following double integral:

$$U_{12} = \int_{-\ell/2}^{\ell/2} dt_1 \int_{-\ell/2}^{\ell/2} dt_2 \Delta U(t_1, t_2). \quad (29)$$

Potential (29) obviously depends on the relative position and orientation of the interacting molecules. Let us consider two chiral molecules having parallel (or antiparallel) corresponding axes in the three cases presented in Figs. 1(a)–1(c). One notes that a biaxial chiral molecule is asymmetric with respect to its molecular axes \mathbf{a} , \mathbf{b} , and \mathbf{c} . Any molecule in the pair is therefore assumed to have one of the four odd orientations as presented in Fig. 4. Let the parameter φ in Eq. (26) describing the structure of a molecule correspond to Fig. 4(a). The orientation presented in Fig. 4(b) is obtained from

TABLE I. Set of the parameters φ^\mp for two molecules having parallel or antiparallel axes \mathbf{a} , \mathbf{b} , or \mathbf{c} . For example, the orientation with parallel long axes and antiparallel short axes is symbolized as $\{\mathbf{a}, -\mathbf{b}, -\mathbf{c}\}$.

Orientation	φ^-	φ^+
$\mathbf{a}, \mathbf{b}, \mathbf{c}$	0	φ
$\mathbf{a}, -\mathbf{b}, -\mathbf{c}$	$\pi/2$	$\varphi + \pi/2$
$-\mathbf{a}, \mathbf{b}, -\mathbf{c}$	$-\varphi$	0
$-\mathbf{a}, -\mathbf{b}, \mathbf{c}$	$-\varphi + \pi/2$	$\pi/2$

the orientation presented in Fig. 4(a) after the rotation of the whole molecule around its long axis \mathbf{a} by the angle π . This orientation is described by the same Eq. (26) with the substitution $\varphi \rightarrow \varphi + \pi$. The orientations presented in Figs. 4(c) and 4(d) are obtained from the orientation presented in Fig. 4(a) after the rotation of the molecule around its short axis \mathbf{b} or \mathbf{c} respectively, by angle π . These orientations are described by the same Eq. (26) with the substitution $\{\varphi \rightarrow -\varphi, t \rightarrow -t\}$ or $\{\varphi \rightarrow -\varphi + \pi, t \rightarrow -t\}$. One can see that only four different orientations of the two molecules having parallel or antiparallel axes are possible.

Let us first consider a pair of identical molecules. The relative odd orientations of such a pair may be described in terms of two parameters $\varphi^\mp \equiv (\varphi_2 \mp \varphi_1)/2$, where both parameters φ_1 and φ_2 may be equal to φ , $\varphi + \pi$, $-\varphi$ or $-\varphi + \pi$, depending on the choice of the odd orientation of molecules 1 and 2. The total set of parameters φ^\mp is presented in Table I, where the short symbolization of the corresponding odd orientation is given in the first column. For example, the orientation with parallel long axes and antiparallel short axes is symbolized as $\{\mathbf{a}, -\mathbf{b}, -\mathbf{c}\}$. The odd orientations have equal probabilities, since the phase observed is nonpolar. Thus, the angular brackets in Eqs. (24) and (25) assume simply an arithmetic mean over the four orientations defined in Table I. Let us enumerate them by index $i = 1, \dots, 4$ increasing with the growing minimal distance between molecules. One notes that enumeration will be different in the cases presented in Figs. 1(a)–1(c). Accordingly to the scheme used in Sec. II [see Eqs. (14) and (15)], the “end-to-end” orientation presented in Fig. 1(a) determines only the coefficients $Q_{0,2(\mu\nu)}^{202}$ and $Q_{1(\mu\nu)}^{212}$ describing, respectively, the achiral and chiral interactions between the short molecular axes. It is proved in Appendix B that

$$Q_{0(\mu\nu)}^{202} \sim Q_{2(\mu\nu)}^{202} \sim Q_{1(\mu\nu)}^{212} \sim (\sigma/d)^4, \quad (30)$$

where σ is the geometric mean of the parameters σ_b and σ_c . Thus, all the coefficients $Q_{0(\mu\nu)}^{202}$, $Q_{2(\mu\nu)}^{202}$ and $Q_{1(\mu\nu)}^{212}$ may be neglected with an error $\sim (\sigma/d)^4$ which becomes insufficient even for $\sigma/d \sim 0.5$. It may be proved that Eq. (30) is also valid in the case of two dissimilar molecules, in supposition that σ is an arithmetic mean of the corresponding parameters for two molecules. Performing calculations presented in Appendix A, one obtains the following expressions for the minimal distance between two identical chiral molecules in the “side-by-side” orientations presented in Figs. 1(b), 1(c) and

the first derivative of the minimal distance with respect to the corresponding rotational angle (β or γ) in the case $\beta=0$ or $\gamma=0$:

$$\xi_{\mathbf{b},\mathbf{c}} = \sqrt{d^2 - (2t^-)^2} + 2\sigma_{\mathbf{b},\mathbf{c}} |\sin(kt^- + \varphi^-)|, \quad (31)$$

$$\xi'_{\mathbf{b},\mathbf{c}} = -k\sigma_{\mathbf{b}}\sigma_{\mathbf{c}}\cos^2(kt^- + \varphi^-). \quad (32)$$

Here the parameter t^- (φ^-) is the root of the following equation:

$$k\sigma_{\mathbf{b},\mathbf{c}}\cos(kt^- + \varphi^-)\sqrt{d^2 - (2t^-)^2} = \pm 2t^-, \quad (33)$$

where the “ $-$ ” sign corresponds to the case $-\pi < \varphi^- + 2\pi n \leq 0$ (n is integer), the “ $+$ ” sign corresponds to the case $0 < \varphi^- + 2\pi n \leq \pi$, and the φ^- parameter is equal to one of the four values presented in Table I. Performing calculations presented in Appendix B and taking into account Eq. (24), one obtains in supposition (27) the following expressions for the chiral coefficients $J_{1(\mu\mu)}^{212}$ and $M_{1(\mu\mu)}^{212}$:

$$\begin{aligned} J_{1(\mu\mu)}^{212}/d^4 = & -\frac{1}{8}\vartheta k_B T \sum_{i=1}^4 [\xi'_c(i)\xi_c^3(i) + \xi'_b(i)\xi_b^3(i)]/d^4 \\ & -\frac{1}{128}J_0\frac{\sigma_{\mathbf{b}}\sigma_{\mathbf{c}}}{d^2}(kd)^3\frac{\ell}{d}([S_{4,1}^{5+}(1,4) \\ & + S_{4,1}^{5-}(2,3)\cos(2\varphi)] - \{C_{4,0}^{5+}(2,3) + [C_{4,0}^{5-}(1,4) \\ & - B^-]\cos(2\varphi)\}\cos(k\ell) - [S_{4,0}^{5+}(2,3) \\ & + S_{4,0}^{5-}(1,4)\cos(2\varphi)]\sin(k\ell)), \quad (34) \end{aligned}$$

$$\begin{aligned} M_{1(\mu\mu)}^{212}/d^4 = & -\frac{1}{16}\vartheta k_B T \sum_{i=1}^4 [\xi'_c(i)\xi_c^3(i) - \xi'_b(i)\xi_b^3(i)]/d^4 \\ & -\frac{1}{256}J_0\frac{\sigma_{\mathbf{b}}\sigma_{\mathbf{c}}}{d^2}(kd)^3\frac{\ell}{d}([S_{4,1}^{5-}(1,4) \\ & + S_{4,1}^{5+}(2,3)\cos(2\varphi)] - \{C_{4,0}^{5-}(2,3) + [C_{4,0}^{5+}(1,4) \\ & - B^+]\cos(2\varphi)\}\cos(k\ell) - [S_{4,0}^{5-}(2,3) \\ & + S_{4,0}^{5+}(1,4)\cos(2\varphi)]\sin(k\ell)), \quad (35) \end{aligned}$$

where J_0 is the constant having the dimension of energy and index i denotes the number of the odd orientation from Table I, increasing with the growing minimal distance. The parameters B^\pm , $C_{m,n}^{k\pm}(i,j)$ and $S_{m,n}^{k\pm}(i,j)$ in Eqs. (34) and (35) are determined, respectively, by the following expressions:

$$B^\pm \equiv \frac{105\pi}{8}k^{-4}\sum_{i=1}^4 [\xi_c^{-4}(i) \pm \xi_b^{-4}(i)], \quad (36)$$

$$\begin{aligned} C_{m,n}^{k\pm}(i,j) & \equiv C_{m,n}^{k\pm}(i) - C_{m,n}^{k\pm}(j), \\ S_{m,n}^{k\pm}(i,j) & \equiv S_{m,n}^{k\pm}(i) - S_{m,n}^{k\pm}(j), \quad (37) \end{aligned}$$

where

$$\begin{aligned} C_{m,n}^{k\pm}(i) & \equiv C_{m,n}^k(k\xi_c(i)) \pm C_{m,n}^k(k\xi_b(i)), \\ S_{m,n}^{k\pm}(i) & \equiv S_{m,n}^k(k\xi_c(i)) \pm S_{m,n}^k(k\xi_b(i)), \quad (38) \end{aligned}$$

and where the functions $C_{m,n}^k(x)$ and $S_{m,n}^k(x)$ are determined by Eqs. (E1) and (E2) (see Appendix E), respectively. Here we present the analytical expressions for functions $S_{4,1}^5(x)$, $C_{4,0}^5(x)$ and $S_{4,0}^5(x)$ which are used in Eqs. (34) and (35):

$$\begin{aligned} S_{4,1}^5(x) & \equiv 768 \int_0^\infty dt \int_x^\infty dr \frac{r^4 t \sin t}{[r^2 + t^2]^5} \\ & = \left(\frac{2}{3} + 5x^{-1} + 5x^{-2}\right) \frac{3\pi}{2} \\ & \quad \times \exp(-x) + \frac{3\pi}{2}\text{Ei}(-x), \quad (39) \end{aligned}$$

$$\begin{aligned} C_{4,0}^5(x) & \equiv 768 \int_0^\infty dt \int_x^\infty dr \frac{r^4 \cos t}{[r^2 + t^2]^5} \\ & = \left(\frac{1}{3}x^{-1} + 5x^{-2} + 14x^{-3} + 14x^{-4}\right) \frac{15\pi}{8} \\ & \quad \times \exp(-x) - \frac{3\pi}{8}\text{Ei}(-x), \quad (40) \end{aligned}$$

$$\begin{aligned} S_{4,0}^5(x) & \equiv 768 \int_0^\infty dt \int_x^\infty dr \frac{r^4 \sin t}{[r^2 + t^2]^5} \\ & = (5x^{-2} + 14x^{-4}) \frac{15}{8}E^-(x) \\ & \quad + \left(\frac{1}{3}x^{-1} + 14x^{-3}\right) \frac{15}{8}E^+(x) \\ & \quad - \frac{3}{4}x^{-1} - \frac{41}{2}x^{-3} + \frac{3}{4}Q(x), \quad (41) \end{aligned}$$

where

$$E^\mp(x) \equiv \exp(-x)\text{Ei}(x) \mp \exp(x)\text{Ei}(-x), \quad (42)$$

$$Q(x) \equiv \int_0^\infty \frac{1}{t} \left[\frac{\pi}{2} - \arctan\left(\frac{x}{t}\right) \right] \sin(t) dt. \quad (43)$$

The first term in Eqs. (34) and (35) corresponds to chirality of the steric repulsion, and the second term corresponds to chirality of the dispersion attraction. One notes that in the case $\sigma_{\mathbf{b}} \neq \sigma_{\mathbf{c}}$ both chiral coefficients $J_{1(\mu\mu)}^{212}$ and $M_{1(\mu\mu)}^{212}$ strongly depend on the molecular structural parameter φ . The corresponding dependences are presented in Fig. 5 for $J_0/k_B = 1300$ K, $T = 300$ K and the volume fraction $\Phi = 0.6$. Curves (1)–(3) in Fig. 5 correspond to the variations of the coefficient $J_{1(\mu\mu)}^{212}$ in the cases $\sigma_{\mathbf{b}}/\sigma_{\mathbf{c}} = 1, 1.4$ and 2 , respectively. Curves (4)–(6) correspond to the variations of the coefficient $M_{1(\mu\mu)}^{212}$ in the same three cases. One notes that the behavior of the coefficient $M_{1(\mu\mu)}^{212}$ is almost independent on the relation $\sigma_{\mathbf{b}}/\sigma_{\mathbf{c}}$, whereas the behavior of the coefficient $J_{1(\mu\mu)}^{212}$ strongly depends on this relation.

Taking into account Eq. (25) and using calculations presented in Appendix B, one obtains in supposition (27) the

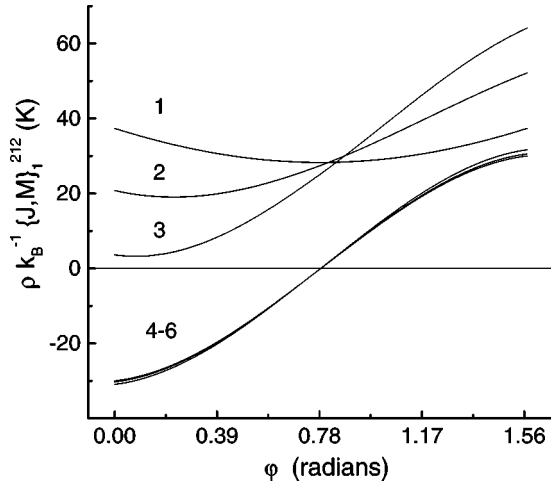


FIG. 5. Interaction coupling constants as functions of the molecular parameter φ : (1)–(3) $J_{1(\mu\mu)}^{212}$; (4)–(6) $M_{1(\mu\mu)}^{212}$; (1),(4) $\sigma_{\mathbf{b}} = \sigma_{\mathbf{c}} = 0.3d$; (2),(5) $\sigma_{\mathbf{b}} = 0.35d$, $\sigma_{\mathbf{c}} = 0.25d$; (3),(6) $\sigma_{\mathbf{b}} = 0.4d$, $\sigma_{\mathbf{c}} = 0.2d$.

following expressions for the achiral coefficients $J_{0(\mu\mu)}^{202}$, $M_{0(\mu\mu)}^{202}$, $J_{2(\mu\mu)}^{202}$, and $M_{2(\mu\mu)}^{202}$:

$$J_{0(\mu\mu)}^{202}/d^3 = \frac{5\pi}{3072} J_0 \left(\frac{\ell}{d}\right)^3 d^4 \sum_{i=1}^4 [\xi_{\mathbf{c}}^{-4}(i) + \xi_{\mathbf{b}}^{-4}(i)], \quad (44)$$

$$M_{0(\mu\mu)}^{202}/d^3 = \frac{5\pi}{6144} J_0 \left(\frac{\ell}{d}\right)^3 d^4 \sum_{i=1}^4 [\xi_{\mathbf{c}}^{-4}(i) - \xi_{\mathbf{b}}^{-4}(i)], \quad (45)$$

$$J_{2(\mu\mu)}^{202}/d^5 = \frac{5\pi}{1536} J_0 \left(\frac{\ell}{d}\right)^3 d^2 \sum_{i=1}^4 [\xi_{\mathbf{c}}^{-2}(i) + \xi_{\mathbf{b}}^{-2}(i)], \quad (46)$$

$$M_{2(\mu\mu)}^{202}/d^5 = \frac{5\pi}{3072} J_0 \left(\frac{\ell}{d}\right)^3 d^2 \sum_{i=1}^4 [\xi_{\mathbf{c}}^{-2}(i) - \xi_{\mathbf{b}}^{-2}(i)]. \quad (47)$$

Using Eqs. (44) and (45) one can estimate the relation $M_{0(\mu\mu)}^{202}/J_{0(\mu\mu)}^{202}$ for different values $\sigma_{\mathbf{b}}/d$, $\sigma_{\mathbf{c}}/d$, and kd , since the minimal distance between identical chiral molecules essentially depends only on these parameters and is almost independent on the parameter φ . Substituting the relation $M_{0(\mu\mu)}^{202}/J_{0(\mu\mu)}^{202}$ into the system of equations (1), one obtains the temperature variation of the primary order parameter S_{μ} and the ratio of the order parameters D_{μ}/S_{μ} which are presented respectively in Figs. 6(a), 6(b) for the cases $\sigma_{\mathbf{b}}/\sigma_{\mathbf{c}} = 1, 1.4$, and 2. One can see that the relation D_{μ}/S_{μ} is essentially nonzero in the case $\sigma_{\mathbf{b}} \neq \sigma_{\mathbf{c}}$ and grows with the increasing temperature.

The situation becomes more complicated when the interacting molecules are dissimilar. One can see from Eq. (31) that the minimal side-by-side distance between two identical molecules is independent on the molecular length ℓ . Indeed, when the molecules are identical, the loops of the first one penetrate deep into the alcoves of the second one, and the molecules may contact irrespective of the position of the molecular “ends.” At the same time, dissimilar molecules do not dock very well, and the minimal distance between them may depend on the length of each molecule. Then the fol-

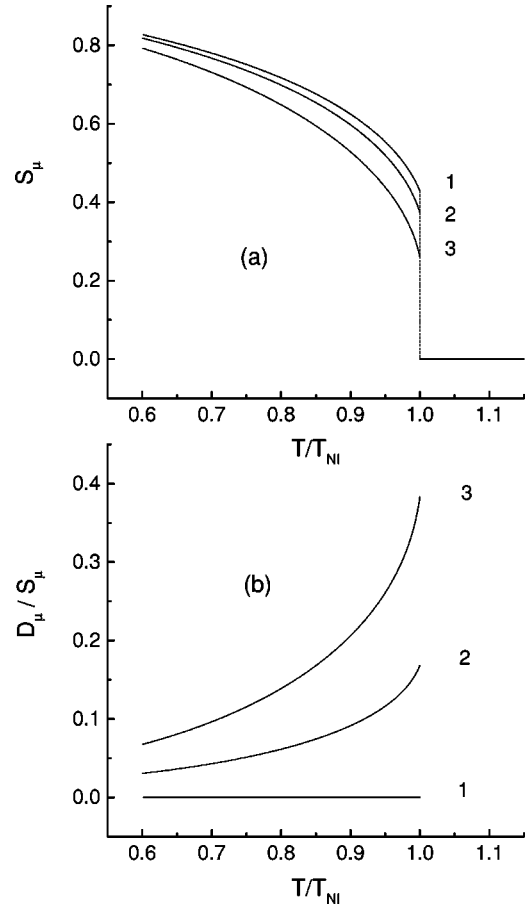


FIG. 6. Primary order parameter S_{μ} (a) and relation of the order parameters D_{μ}/S_{μ} (b) as functions of the temperature: (1) $\sigma_{\mathbf{b}} = \sigma_{\mathbf{c}} = 0.3d$; (2) $\sigma_{\mathbf{b}} = 0.35d$, $\sigma_{\mathbf{c}} = 0.25d$; (3) $\sigma_{\mathbf{b}} = 0.4d$, $\sigma_{\mathbf{c}} = 0.2d$.

lowing problem arises with the determination of the principal short directions of the interacting molecules. One notes that the principal directions \mathbf{a} , \mathbf{b} , and \mathbf{c} of the same molecule may be chosen in different ways depending on the molecular pair. The correct choice of the molecular axes should give the correct extrema of the effective potential which are mainly determined by the minimal distance between interacting molecules. Restricting imagination with the molecular model presented in Fig. 3, one can unambiguously define the main direction \mathbf{a} for each molecule. Nevertheless, the short directions \mathbf{b} and \mathbf{c} still depend on the molecular pair. One can ignore this dependence if both molecules are intensively twisted [$k_{\mu}\ell_{\mu} \gg 2\pi$, $\mu = 1, 2$, see Fig. 3(a)], because in this case the biaxiality of both molecules is mainly determined by inequality of their helical semiaxes ($\sigma_{\mathbf{b}}^{\mu} \neq \sigma_{\mathbf{c}}^{\mu}$, $\mu = 1, 2$). In the opposite case, when both interacting molecules are weakly twisted ($k_{\mu}\ell_{\mu} \lesssim 2\pi$, $\mu = 1, 2$), the direction of the short axes strongly depends on different parameters of both molecules, such as molecular length ℓ_{μ} .

Let us consider the practically important case of the binary mixture ($\tau = 2$), where the first component is a weakly twisted cholesteric [see Fig. 3(b)] having length ℓ_c , diameter of the tube d_c , equal semiaxes $\sigma_{\mathbf{b}} = \sigma_{\mathbf{c}} \equiv \sigma$, and helicity k satisfying the following constraint:

$$\pi/\ell_c < k < 2\pi/\ell_c \quad (48)$$

and the second component is an achiral nematic [see Fig. 3(c)], having length ℓ_n , diameter of the tube d_n , and zero semiaxes $\sigma_b = \sigma_c = 0$. One notes that in the case $\sigma_b = \sigma_c$, the φ parameter [see Eq. (26)] does not characterize the molecular shape and describes only the turn of the whole molecule around its principal axis **a**. Therefore, it happens to be the only parameter that determines the direction of the short axes **b** and **c** of a chiral molecule. Whether a chiral molecule satisfying Eq. (48) couples with a similar chiral molecule or with an achiral one, the correct choice of its short axes corresponds to the value $\varphi = \pi/2$. Then the minimal side-by-side distance between a chiral molecule and an achiral one is achieved when the axis **c** of a chiral molecule is collinear to the \mathbf{r}_{nc} vector connecting molecular centers. This situation corresponds to Fig. 1(c). Performing calculations presented in Appendix C, one obtains the following expressions for the minimal distance and its first derivative with respect to the rotational angle γ in the case $\gamma=0$:

$$\xi_{\min} = \sqrt{d^2 - \sigma^2 \sin^2\left(\frac{k\ell}{2}\right) + \sigma \left| \cos\left(\frac{k\ell}{2}\right) \right|}, \quad (49)$$

$$\xi'_{\min} = \sigma \frac{\ell}{2} \left| \sin\left(\frac{k\ell}{2}\right) \right| / \sqrt{d^2 - \sigma^2 \sin^2\left(\frac{k\ell}{2}\right)}, \quad (50)$$

where the parameter ℓ is the minimal length (ℓ_c or ℓ_n) and $d \equiv (d_c + d_n)/2$ is the average diameter. Performing calculations presented in Appendix D and taking into account Eq. (24), one obtains in supposition (27) the following expressions for the chiral coefficients $J_{1(nc)}^{212}$ and $M_{1(nc)}^{212}$, which describe the chiral coupling of chiral and achiral molecules having the same length ($\ell_c = \ell_n = \ell$):

$$\begin{aligned} J_{1(nc)}^{212}/d^4 &= -\frac{1}{4} \vartheta k_B T \xi'_{\min} \xi_{\min}^3 / d^4 \\ &\quad - \frac{105\pi}{1024} J_0 \left(\frac{\sigma}{d}\right)^2 (kd)^{-1} \frac{\ell}{d} \left[\left(\frac{d}{\xi_{\min}}\right)^4 \right. \\ &\quad \left. - \left(\frac{d}{d+\sigma}\right)^4 \right] \cos(k\ell), \end{aligned} \quad (51)$$

$$\begin{aligned} M_{1(nc)}^{212}/d^4 &= -\frac{1}{8} \vartheta k_B T \xi'_{\min} \xi_{\min}^3 / d^4 \\ &\quad - \frac{105\pi}{2048} J_0 \left(\frac{\sigma}{d}\right)^2 (kd)^{-1} \frac{\ell}{d} \left[\left(\frac{d}{\xi_{\min}}\right)^4 \right. \\ &\quad \left. + 3 \left(\frac{d}{d+\sigma}\right)^4 \right] \cos(k\ell), \end{aligned} \quad (52)$$

where first terms describe the steric part of the chiral interaction and the second terms describe the dispersion part. One can see that Eqs. (51) and (52) describing chiral interaction of chiral and achiral molecules are analogous to the corresponding expressions (34) and (35) for two identical chiral molecules. Nevertheless, the sign of the steric part in Eqs.

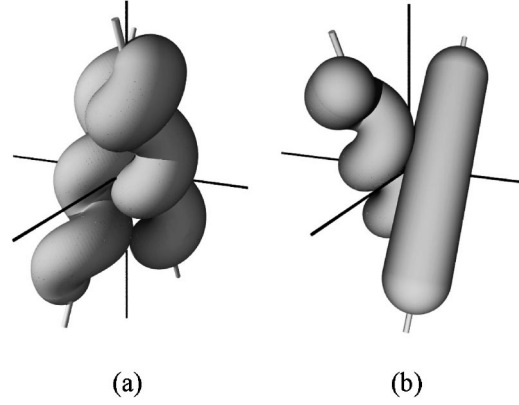


FIG. 7. Two identical right-handed molecules (a) penetrate deeper into each other having right-handed turn between their long axes, whereas an achiral molecule penetrates deeper into the same chiral molecule (b) having left-handed turn.

(51) and (52) is opposite to the sign of the steric part in Eqs. (34) and (35). Indeed, the first derivative of the minimal side-by-side distance between chiral and achiral molecules with respect to the rotational angle γ is positive [see Eq. (50)], whereas the first derivative of the minimal side-by-side distance between two identical chiral molecules with respect to the same angle is negative [see Eq. (32)]. Thus, for example, two identical right-handed molecules [Fig. 7(a)] penetrate deeper into each other having a right-handed turn between their long axes, whereas an achiral molecule penetrates deeper into the same chiral molecule [Fig. 7(b)] having a left-handed turn. This geometrical fact may lead to the helical sense inversion, which is discussed in the following section.

Taking into account Eq. (25) and using calculations presented in Appendix D, one obtains in supposition (27) the following expressions for the achiral coefficients $J_{0(nc)}^{202}$, $M_{0(nc)}^{202}$, $J_{2(nc)}^{202}$, and $M_{2(nc)}^{202}$ in the case $\ell_n = \ell_c$:

$$J_{0(nc)}^{202}/d^3 = \frac{5\pi}{1536} J_0 \left(\frac{\ell}{d}\right)^3 \left[\left(\frac{d}{\xi_{\min}}\right)^4 + 3 \left(\frac{d}{d+\sigma}\right)^4 \right], \quad (53)$$

$$M_{0(nc)}^{202}/d^3 = \frac{5\pi}{3072} J_0 \left(\frac{\ell}{d}\right)^3 \left[\left(\frac{d}{\xi_{\min}}\right)^4 - \left(\frac{d}{d+\sigma}\right)^4 \right], \quad (54)$$

$$J_{2(nc)}^{202}/d^5 = \frac{5\pi}{768} J_0 \left(\frac{\ell}{d}\right)^3 \left[\left(\frac{d}{\xi_{\min}}\right)^2 + 3 \left(\frac{d}{d+\sigma}\right)^2 \right], \quad (55)$$

$$M_{2(nc)}^{202}/d^5 = \frac{5\pi}{1536} J_0 \left(\frac{\ell}{d}\right)^3 \left[\left(\frac{d}{\xi_{\min}}\right)^2 - \left(\frac{d}{d+\sigma}\right)^2 \right], \quad (56)$$

which are analogous to the corresponding expressions (44)–(47) for two identical chiral molecules.

IV. HELICAL TWISTING POWER AND HELICAL SENSE INVERSIONS

A. Helical sense inversion with temperature variation

For simplicity, let us consider the case of pure one-component cholesteric ($\tau=1$). One can distinguish at least two reasons for the helical sense inversion with the temperature variation. The first reason is the competition between the dispersion interaction and the steric effects. For simplicity, let us first consider the system of similar quasiuniaxial molecules ($\sigma_b=\sigma_c$). As it was already noticed in Sec. III, the correct choice of the molecular short directions in the case $\sigma_b=\sigma_c$ corresponds to the parameter $\varphi=\pi/2$. The coefficients M_0^{202} and M_2^{202} [see Eqs. (45) and (47)] are equal to zero [38], and Eqs. (34), (35) for the chiral coefficients J_1^{212} and M_1^{212} do not contain the terms with the index “-.” Substituting $M_0^{202}=0$ into Eq. (3) and solving Eq. (1), one obtains for the biaxial order parameter $D\equiv 0$. Therefore the coefficient M_1^{212} [see Eq. (5)] does not influence the pseudoscalar k_2 . Substituting Eq. (34) for the resting coefficient J_1^{212} into Eq. (5) for the pseudoscalar k_2 and Eq. (46) for the coefficient J_2^{202} into Eq. (6) for the twist elastic constant K_2 , one obtains from Eq. (4) the following expression for the helical wave number q in the case of quasiuniaxial molecules ($\sigma_b=\sigma_c$):

$$q = q_{ster} + q_{disp}, \quad (57)$$

where q_{ster} and q_{disp} are the steric and dispersion contributions to the helical wave number, respectively,

$$q_{ster} \equiv -\frac{64}{5\pi} \frac{\partial k_B T}{J_0} \left(\frac{d}{\ell}\right)^3 \frac{\xi'(1)\xi^3(1) + \xi'(2)\xi^3(2)}{d^7 \{\xi^{-2}(1) + \xi^{-2}(2)\}}, \quad (58)$$

$$q_{disp} \equiv q_0 [1 - \Delta \sin(k\ell + \chi)], \quad (59)$$

where

$$q_0 \equiv -\frac{2}{5\pi} \left(\frac{\sigma}{\ell}\right)^2 (kd)^3 \frac{S_{4,1}^5(1,2)}{d^3 \{\xi^{-2}(1) + \xi^{-2}(2)\}}, \quad (60)$$

$$\Delta \equiv \frac{\sqrt{\{C_{4,0}^5(1,2)\}^2 + \{S_{4,0}^5(1,2)\}^2}}{S_{4,1}^5(1,2)}. \quad (61)$$

The parameters χ , $C_{m,n}^k(1,2)$, and $S_{m,n}^k(1,2)$ are determined, respectively by the following expressions:

$$\chi \equiv \arctan \frac{C_{4,0}^5(1,2)}{S_{4,0}^5(1,2)}, \quad (62)$$

$$C_{m,n}^k(1,2) \equiv C_{m,n}^k(k\xi(1)) - C_{m,n}^k(k\xi(2)),$$

$$S_{m,n}^k(1,2) \equiv S_{m,n}^k(k\xi(1)) - S_{m,n}^k(k\xi(2)), \quad (63)$$

and where the functions $S_{4,1}^5(x)$, $C_{4,0}^5(x)$, and $S_{4,0}^5(x)$ are determined by Eqs. (39), (40), and (41) respectively. The

minimal distance $\xi(i) \equiv \xi(k, \sigma, \varphi_i^-)$ between two identical quasiuniaxial molecules in the parallel side-by-side orientation number i (see Table I) and its derivative $\xi'(i) \equiv \xi'(k, \sigma, \varphi_i^-)$ with respect to the angle γ between the long molecular axes are determined by Eqs. (31) and (32), respectively, where $\sigma_b = \sigma_c \equiv \sigma$. Substituting $\varphi = \pi/2$ into Table I, one obtains the only two independent odd orientations for two identical quasiuniaxial molecules: $\varphi_1^- = 0$ and $\varphi_2^- = \pi/2$. The steric contribution q_{ster} derives from the packing entropy. The constant $\partial k_B / J_0$ in Eq. (58) may be approximated in the Parsons approach [32,33] by the following expression:

$$\frac{\partial k_B}{J_0} \approx 0.00574 \frac{|\ln(1-\Phi)|}{T_{NI}} \left(\frac{\ell}{d}\right)^2 [\xi^{-4}(1) + \xi^{-4}(2)], \quad (64)$$

which follows from Eq. (44), where the constant J_0^{202} is approximately equal to $4.54k_B T_{NI} / \rho$ according to the standard Maier-Saupe theory [35], and where the density $\rho \approx 4\Phi / (d^2\ell)$ is determined by the volume fraction Φ and molecular dimensions ℓ and d .

One notes from Eq. (58) that the steric contribution q_{ster} to the helical wave number is positive (since ξ' is negative). Thus, the steric effects lead to the same handedness of the liquid crystal as its molecules. At the same time, the dispersion term q_{disp} [see Eq. (59)] oscillates with the increasing molecular length ℓ about the negative value q_0 . The relative amplitude of these oscillations Δ depends on the molecular chirality, which is determined by parameters k and σ . From Eqs. (39)–(41) for the functions $S_{4,1}^5(x)$, $C_{4,0}^5(x)$, and $S_{4,0}^5(x)$, it follows that the value q_0 is finite for $k=0$, whereas the relative amplitude of oscillations Δ diverges for $k=0$. Strictly speaking, Eq. (59) for the dispersion contribution to the helical wave number q_{disp} is incorrect for $k=0$, since we used the assumption (27). Nevertheless, one can see from Eq. (61) the tendency of the amplitude Δ to arise for small k . This tendency is obliged to the dominant effect of the molecular ends on the dispersion interaction of the weakly twisted molecules ($k\ell \sim 2\pi$). In this case, the relative amplitude of oscillations Δ essentially exceeds unity. On the contrary, for intensively twisted molecules ($kd \sim 2\pi$) the effect of the molecular ends is comparable to the effect of the total molecular chirality, and the amplitude Δ has an order of unity. This situation is demonstrated in Fig. 8, where the dispersion contribution to the helical wave number q_{disp} is presented as a function of the parameter kd in the case $\ell/d = 5$ and $\sigma/d = 0.1, 0.2$. One can separate two limit regimes in Fig. 8. The first one (left side of Fig. 8) realizes for weakly twisted molecules. In this case the oscillations of the dispersion term are much larger than the average value, and the dispersion contribution to the helical wave number q_{disp} may be positive or negative, depending on values k and ℓ . The second regime (right side of Fig. 8) realizes for intensively twisted molecules. In this case the oscillations are of the same order as the average value, and the dispersion term has the dominant negative sign with small positive “islands.” These two regimes will be considered separately in Secs.

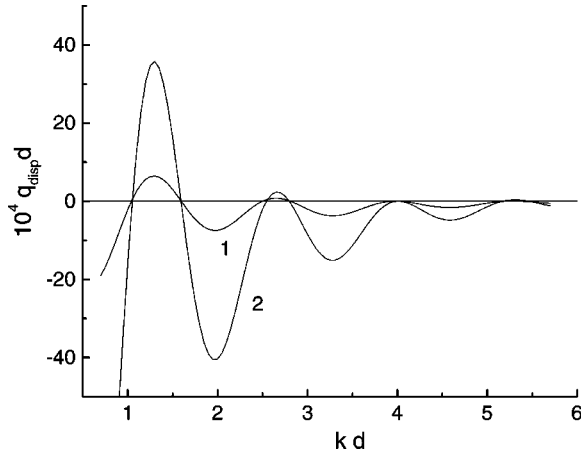


FIG. 8. Dispersion contribution to the helical wave number q_{disp} as a function of the molecular parameter kd in the case $\ell/d=5$, $\sigma_b=\sigma_c\equiv\sigma$: (1) $\sigma/d=0.1$; (2) $\sigma/d=0.2$. The behavior is different for small and large values of kd .

IV B and IV C. Here we stress that the dispersion contribution to the helical wave number q_{disp} may be negative irrespective of the regime. Thus, the steric and dispersion contributions may have opposite signs. Since the steric contribution q_{ster} is proportional to temperature T , and the dispersion contribution q_{disp} is independent on temperature T , the helical sense inversion with the temperature variation happens, when the dispersion and the steric contributions equal each other. The corresponding temperature dependence of the helical wave number q is presented in Fig. 9 for $\Phi=0.6$, $J_0/k_B=1000$ K, $\ell/d=5$, $\sigma/d=0.3$, and four different values of the parameter kd . One obtains the following relation from Eqs. (57)–(59):

$$\frac{T}{T_{inv}} = \frac{q_{ster}}{q_{disp}}, \quad (65)$$

where T_{inv} is the temperature of the helical sense inversion in the system of identical quasiuniaxial molecules. Knowing the temperature of the helical sense inversion T_{inv} and using

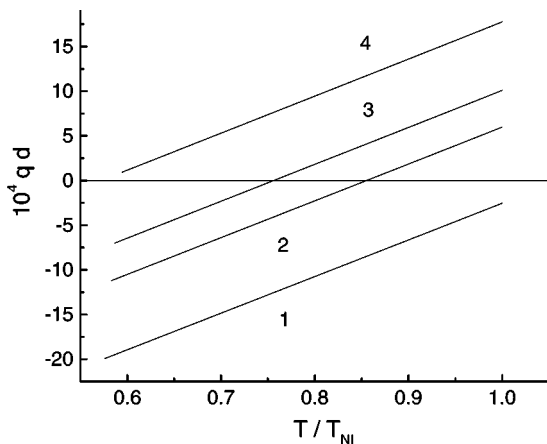


FIG. 9. Helical wave number q as a function of the temperature in the case $\Phi=0.6$, $J_0/k_B=1000$ K, $\ell/d=5$, $\sigma_b/d=\sigma_c/d=0.3$ and (1) $kd=2.3$; (2) $kd=2.34$; (3) $kd=2.36$; (4) $kd=2.4$.

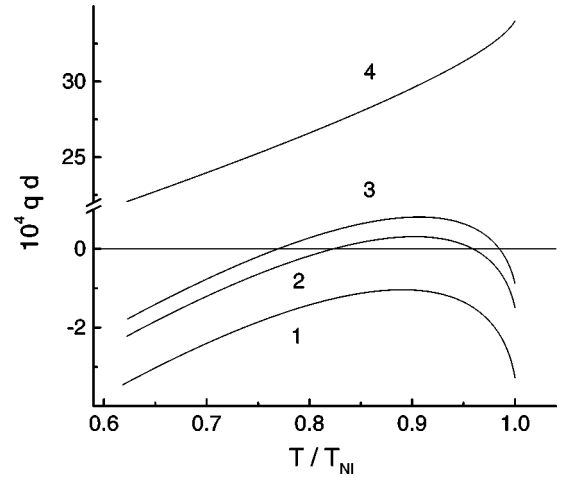


FIG. 10. Helical wave number q as a function of the temperature in the case $\Phi=0.6$, $J_0/k_B=1300$ K, $\ell/d=5$, $\sigma_b/d=0.4$, $\sigma_c/d=0.2$, $kd=5$ and (1) $\varphi=0.33$; (2) $\varphi=0.39$; (3) $\varphi=0.41$; (4) $\varphi=1.18$.

Eqs. (58), (59), and (65) one can estimate the energetic constant J_0 for the investigated molecules. Substituting the constant J_0 into Eq. (64), one can estimate the temperature of the nematic-isotropic phase transition T_{NI} . Similarly, knowing the temperature of the nematic-isotropic phase transition T_{NI} one can estimate the temperature of the helical sense inversion T_{inv} (in the case $T_{NI}>T_{inv}$).

In the case of biaxial molecules ($\sigma_b \neq \sigma_c$), the other possibility exists for the helical sense inversion. Indeed, as it follows from Fig. 5, the coefficient J_1^{212} describing chiral interaction between the long molecular axes, and the coefficient M_1^{212} describing chiral interaction between the long axis of the first molecule and the short axes of the second molecule, may have opposite signs. Since the relation of the order parameters D/S is usually small, but grows with the increasing temperature [see Fig. 6(b)], the helical sense inversion with the temperature variation is possible [see Eqs. (4) and (5)], when the coefficients J_1^{212} and M_1^{212} have opposite signs, and the absolute value of the coefficient J_1^{212} is essentially smaller than the absolute value of the coefficient M_1^{212} . Therefore, a good possibility of the helical sense inversion occurs when the parameters σ_b and σ_c of the chiral molecule are essentially unequal (see curves 3 and 6 in Fig. 5). The corresponding temperature dependence of the helical wave number q , calculated using Eqs. (4)–(6), is presented in Fig. 10 for $\Phi=0.6$, $J_0/k_B=1300$ K, $\ell/d=5$, $\sigma_b/d=0.4$, $\sigma_c/d=0.2$, $kd=5$, and four different values of parameter φ . Instead of Eq. (65), one obtains the following constraint for the helical sense inversion in the case of biaxial molecules:

$$J_1^{212}(T_{inv}) = -D/S(T_{inv})M_1^{212}(T_{inv}), \quad (66)$$

where the coefficients J_1^{212} and M_1^{212} are linear functions of temperature T [see Eqs. (34) and (35)], and the function $D/S(T)$ is determined by the recurrent Eq. (1). One notes from Fig. 10 that the temperature dependence of the helical wave number q always has the increasing branch. As in the

case of quasiuniaxial molecules, it corresponds to the growing positive steric contribution to the coefficient J_1^{212} . If the dispersion contribution to the coefficient J_1^{212} (which is independent on temperature T) is negative, the helical sense inversion from negative to positive sign may happen (curves 2, 3). At the same time, dependence $q(T)$ may also have the decreasing high-temperature branch, if the coefficient M_1^{212} is negative (curves 1–3). Indeed, the growing relation $D/S(T)$ may overbear the steric contribution to coefficient J_1^{212} . Then the helical sense inversion from positive to negative sign may happen (curves 2, 3). If the absolute value of the coefficient M_1^{212} is essentially larger than the absolute value of the coefficient J_1^{212} , the whole curve $q(T)$ appears to be below zero (curve 1). If the coefficient M_1^{212} is positive, the dependence $q(T)$ has the only increasing branch (curve 4), and the helical sense inversion from positive to negative sign is impossible. Finally, one notes that one or both hypothetical points of inversion may appear beyond the range of the nematic phase.

B. Helical sense inversion with variation of molecular length

Many biologically important polymers, such as polypeptides, are known to suffer the spiral-coil transition that is usually called the process of denaturation [18]. The native molecule of polypeptide is usually a long ($\ell/d \sim 100$) rod-like and highly intensive helix ($kd \sim 2\pi$). For simplicity let us consider the case of pure one-component polypeptide ($\tau = 1$) consisting of quasiuniaxial molecules ($\sigma_b = \sigma_c$). According to Eqs. (58)–(61), the dispersion contribution to the helical wave number, which is proportional to $(d/\ell)^2$, dominates for long molecules over the steric contribution which is proportional to $(d/\ell)^3$. On the other hand, molecules with highly intensive helix obey the regime that is presented in the right side of Fig. 8, when the dispersion contribution to the helical wave number is negative almost for any molecular length (excluding the small “islands”). In the process of denaturation, molecules of polypeptides are known to split into small ($\ell/d < 5$) spiral pieces, which are interrupted by coiled (achiral and flexible) fragments. When the spiral pieces become small enough, the steric contribution to the helical wave number may dominate. Since the steric contribution is positive, helical sense inversion may occur.

To obtain the constraint for helical sense inversion during denaturation, let us estimate the average axial ratio ℓ/d of spiral pieces. Let the free energy of the system depend on three internal parameters: the density of the spiral pieces ρ (with the respect to the total density of the spiral and coiled pieces), the average elongation of the spiral pieces ℓ/d , and the orientational distribution function of the spiral pieces $f(\cos \theta)$. The equilibrium values of all the internal parameters can be obtained by independent minimization of the free energy F with respect to these parameters. A schematic illustration of the hypothetical free energy F as a function of the average axial ratio ℓ/d is presented in Fig. 11. For any set of external parameters, it has the global minimum corresponding to the equilibrium value ℓ/d . The spiral pieces split into smaller ones or combine into bigger ones with the variation of the external parameters. Suppose that, in addition to

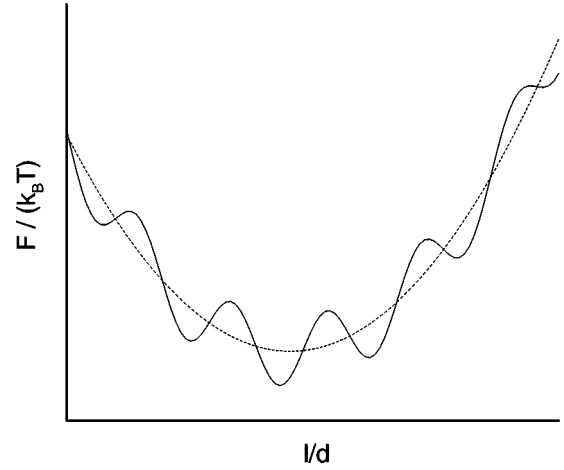


FIG. 11. Schematic illustration of the free energy F as a function of the average axial ratio ℓ/d of spiral pieces.

the global minimum, the free energy of the system has a set of the local minima with respect to the axial ratio ℓ/d . Then the process of denaturation (or renaturation) may be interpreted as a sequence of phase transitions, when the free energy of the system changes by little steps corresponding to the discrete change in the average axial ratio ℓ/d . Let us expand the hypothetical free energy $F(\ell, d, k, \sigma)$ in Taylor series with respect to the small parameter σ/d and collect the terms with the same power of the small parameter d/ℓ :

$$F(\ell, d, k, \sigma) = \sum_{\alpha} \sum_{\gamma} F_{\alpha\gamma}(k\ell, kd) (\sigma/d)^{\alpha} (d/\ell)^{\gamma}. \quad (67)$$

Let the first few coefficients $F_{\alpha\gamma}(k\ell, kd)$ in the sum (67) be independent of the parameter $(k\ell)$ till the coefficient $F_{mn}(k\ell, kd)$, which is a finite periodical function of the parameter $(k\ell)$. Then in the supposition $\sigma/d \ll 1$, $d/\ell \ll 1$ one obtains the following approximate constraint for the global minimum of the function $F(\ell, d, k, \sigma)$ with respect to the axial ratio of a spiral piece ℓ/d [for the constant parameters (kd) and σ/d]:

$$\sum_{\alpha=0}^m (\sigma/d)^{\alpha} \sum_{\gamma=\gamma_0}^n \gamma F_{\alpha\gamma}(d/\ell)^{\gamma+1} = 0. \quad (68)$$

Likewise, one obtains the following constraint for the local minima in the vicinity of the global one:

$$\frac{\partial}{\partial(k\ell)} F_{mn}(k\ell) = 0. \quad (69)$$

In addition to the standard internal energy F_{int} and orientational entropy F_{or} , the free energy of the system F contains also the energy of the hydrogen bonds F_H [18] that stabilize the molecular spiral and various forcing fields F_{ext} provided by the external actions (temperature, chemical, etc.) which, on the contrary, denature the hydrogen bonds:

$$F \equiv F_{int} + F_{or} + F_H + F_{ext}. \quad (70)$$

It is clear that the energy of the hydrogen bonds F_H and external action F_{ext} do not depend explicitly on the parameter σ/d . Indeed, they are simply proportional to the number of screws in a spiral piece ($\sim \ell/d$) and the number of spiral pieces ($\sim \rho$):

$$F_H + F_{ext} \sim \rho \ell / d. \quad (71)$$

The orientational entropy F_{or} is also independent explicitly of the parameter σ/d , since it does not contain any molecular parameters. Then the only term in the free energy F depending explicitly on the parameter σ/d is the internal energy F_{int} :

$$F_{int} \equiv -\frac{1}{2} \rho^2 J_0^{202}(\ell, d, k, \sigma) S^2. \quad (72)$$

Expanding the moment of the coupling constant $J_0^{202}(\ell, d, k, \sigma)$ in the Taylor series with respect to the small parameter σ/d and collecting the terms with the same power of the small parameter d/ℓ , as is presented in Appendix B, one obtains the following expression for the largest oscillating term in the sum (67):

$$F_{osc}(\ell, d, k, \sigma) \approx F_{2,-2}(k\ell, kd)(\sigma/d)^2(\ell/d)^2, \quad (73)$$

where

$$F_{2,-2} \sim -(kd)^3 \{C_{2,0}^5(1,2) \sin(k\ell) - S_{2,0}^5(1,2) \cos(k\ell)\}, \quad (74)$$

where parameters $C_{2,0}^5(1,2)$ and $S_{2,0}^5(1,2)$ are determined by Eqs. (63). Here we present the explicit expressions for the functions $C_{2,0}^5(x)$ and $S_{2,0}^5(x)$ which are calculated in Appendix E:

$$\begin{aligned} C_{2,0}^5(x) &\equiv 768 \int_0^\infty dt \int_x^\infty dr \frac{r^2 \cos t}{[r^2 + t^2]^5} \\ &= \left(\frac{1}{60} x^{-1} - \frac{1}{60} x^{-2} + \frac{5}{6} x^{-3} + \frac{11}{2} x^{-4} \right. \\ &\quad \left. + 14x^{-5} + 14x^{-6} \right) \frac{5\pi}{4} \exp(-x) + \frac{\pi}{48} \text{Ei}(-x), \end{aligned} \quad (75)$$

$$\begin{aligned} S_{2,0}^5(x) &\equiv 768 \int_0^\infty dt \int_x^\infty dr \frac{r^2 \sin t}{[r^2 + t^2]^5} \\ &= \left(-\frac{1}{60} x^{-2} + \frac{11}{2} x^{-4} + 14x^{-6} \right) \frac{5}{4} E^-(x) \\ &\quad + \left(\frac{1}{60} x^{-1} + \frac{5}{6} x^{-3} + 14x^{-5} \right) \frac{5}{4} E^+(x) + \frac{1}{24} x^{-1} \\ &\quad + \frac{1}{36} x^{-3} - \frac{79}{5} x^{-5} - \frac{1}{24} Q(x), \end{aligned} \quad (76)$$

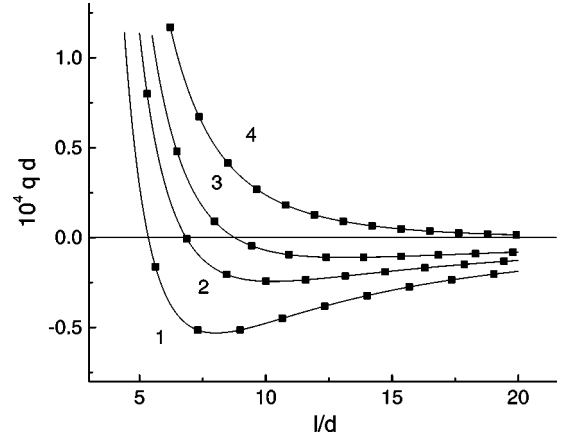


FIG. 12. Helical wave number q as a function of the average axial ratio ℓ/d of spiral pieces in the case $\vartheta=1$, $J_0/k_B=6000$ K, $T=300$ K, $\sigma/d=0.3$ and (1) $kd=3.75$; (2) $kd=4$; (3) $kd=4.25$; (4) $kd=5.5$. During denaturation it changes by steps denoted by square bars.

where functions $E^\mp(x)$ and $Q(x)$ are determined by Eqs. (42) and (43), respectively. Differentiating Eq. (74) with respect to parameter $(k\ell)$, one obtains from Eq. (69) the following constraint for the local minima of the free energy F in the vicinity of the global one:

$$k\ell_n = \pi - \psi(k, \sigma) + 2\pi n, \quad n=0,1,2, \dots \quad (77)$$

Here function $\psi(k, \sigma)$ is determined by the following expression:

$$\psi(k, \sigma) \equiv \arctan \frac{C_{2,0}^5(1,2)}{S_{2,0}^5(1,2)}. \quad (78)$$

The function $\psi(k, \sigma)$ is equal to $\pi/2$ in the case $k=0$, monotonically decreases with the increasing parameter k and tends to zero with the parameter k tending to infinity. In the case of intensively twisted molecules ($kd \sim 2\pi$) the function $\psi(k, \sigma)$ in Eq. (77) may be neglected, and the average length of the spiral pieces ℓ satisfies the constraint $k\ell = \pi + 2\pi n$. This result may also be obtained from the common sense. Indeed, the molecules, consisting of the integer number of loops, have in the nearest orientation $\{\mathbf{a}, \mathbf{b}, \mathbf{c}\}$ (see Table I) the maximal number of contacts per unity of their length. Substituting Eq. (77) into Eq. (59), one obtains the following expression for the dispersion contribution to the helical wave number:

$$q_{disp} = q_0 \left[1 - \frac{C_{2,0}^5(1,2) S_{4,0}^5(1,2) - C_{4,0}^5(1,2) S_{2,0}^5(1,2)}{S_{4,1}^5(1,2) \sqrt{\{S_{2,0}^5(1,2)\}^2 + \{C_{2,0}^5(1,2)\}^2}} \right], \quad (79)$$

which is negative for the intensively twisted molecules. Thus, the steric and dispersion contributions to the helical wave number have opposite signs. Helical sense inversion may be observed in the process of denaturation, since the dispersion contribution dominates for the long spiral pieces, and the steric contribution dominates for the short ones. Substituting Eqs. (58) and (79) into Eq. (57), one obtains the

total helical wave number q , which is presented in Fig. 12 as a function of the axial ratio ℓ/d in the case $\vartheta=1$ [39], $J_0/k_B=6000$ K, $T=300$ K, $\sigma/d=0.3$ and four different values of the parameter kd . The points corresponding to the constraint (77) are presented in Fig. 12 by the square bars. One should, however, stress, that the constraint (77) was obtained in the supposition that the molecule may be broken into pieces in an arbitrary place. The real places of the tear may only correspond to the positions of the hydrogen bonds which repeat 3.6 times a loop as the average [18]. Thus, the real places of the tear lie in the vicinity $\Delta\ell_n \approx \pm 0.14/k$ of the places denoted by Eq. (77). Since functions $C_{m,n}^k(x)$ and $S_{m,n}^k(x)$ rapidly decrease with the increasing variable x [see Eqs. (39)–(41) and (75) and (76)], the dispersion contribution to the helical wave number q_{disp} also decreases with the increasing parameter kd [see Eqs. (79) and (60)]. Therefore, the point of helical sense inversion moves in Fig. 12 towards the larger axial ratio ℓ/d with the increasing parameter kd (see curves 1–3). Beginning with some critical value kd , the dispersion contribution to the helical wave number q_{disp} does not overbear the steric contribution q_{ster} for any ratio ℓ/d , and helical sense inversion is not observed during denaturation of such molecules (see curve 4 in Fig. 12). The decrease of the absolute value of the helical wave number q with the molecular elongation ℓ/d has a simple explanation. Indeed, chirality of the nematic phase arises from chirality of the effective intermolecular potential. It is clear that the long molecular “ends” attract each other. This makes the cholesteric distortion less preferable.

C. Helical sense inversion in nematic-cholesteric mixtures with variation of mutual concentration of components

Let us consider the case of the binary mixture ($\tau=2$), where the first component is a weakly twisted cholesteric [see Fig. 3(b)] having equal semiaxes ($\sigma_b=\sigma_c\equiv\sigma$) and satisfying the constraint (48), and the second component is an achiral nematic [see Fig. 3(c)]. As it was discussed in Sec. III, the steric contribution to the chiral interaction of a chiral molecule with an achiral one, and the steric contribution to the chiral interaction of two identical chiral molecules have opposite signs (see Fig. 7). On the other hand, choosing a special set of molecular parameters, one can minimize the influence of the dispersion interaction on the helical wave number. Indeed, weakly twisted molecules constituting the pure one-component cholesteric obey the regime in the left side of Fig. 8, when the dispersion contribution may have different signs depending on the choice of molecular parameters. Choosing the intermediate parameters, one obtains zero dispersion contribution to the helical wave number. The same situation may be achieved in the case of binary nematic-cholesteric mixture. Then only the steric effects may be responsible for helical sense inversion with the variation of the mutual concentration of components. Substituting Eqs. (44) and (45) for the coefficients $J_{0(\mu\mu)}^{202}$ and $M_{0(\mu\mu)}^{202}$ ($\mu=n,c$)—describing the achiral interaction of identical molecules (an achiral molecule with an achiral one or a chiral molecule with a chiral one)—and Eqs. (53) and (54) for the coefficients $J_{0(nc)}^{202}$ and $M_{0(nc)}^{202}$ —describing the achiral inter-

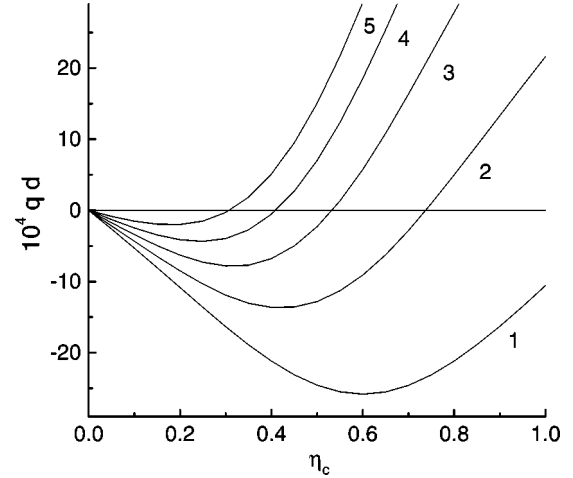


FIG. 13. Helical wave number q as a function of the concentration of the chiral component in the mixture of chiral and achiral molecules in the case $\Phi=0.6$, $J_0/k_B=800$ K, $T=T_{NI}-5$ K, $\ell_c/d_c=5$, $\sigma/d_c=0.3$, $d_n/d_c=1.2$ and $k\ell_c=5.1$ (1); 5.3 (2); 5.5 (3); 5.7 (4); 5.9 (5).

action of an achiral molecule with a chiral one—into Eq. (3) for the mean-field energy U_{MF}^μ , one obtains from the recurrent Eqs. (1) the values of the order parameters S_μ and D_μ . Next, substituting Eqs. (34) and (35) for the coefficients $J_{1(cc)}^{212}$ and $M_{1(cc)}^{212}$ —describing the chiral interaction of identical chiral molecules—and Eqs. (51) and (52) for the coefficients $J_{1(nc)}^{212}$ and $M_{1(nc)}^{212}$ —describing the chiral interaction of an achiral molecule with a chiral one—into Eq. (5), one obtains the value of the pseudoscalar k_2 . Finally, substituting Eqs. (46) and (47) for the coefficients $J_{2(\mu\mu)}^{202}$ and $M_{2(\mu\mu)}^{202}$ ($\mu=n,c$) and Eqs. (55) and (56) for the coefficients $J_{2(nc)}^{202}$ and $M_{2(nc)}^{202}$ into Eq. (6), one obtains the value of the twist elastic constant K_2 . The helical wave number q of the binary nematic-cholesteric mixture, calculated using Eq. (4), is presented in Fig. 13 as a function of the mutual concentration of the components in the case $\Phi=0.6$, $J_0/k_B=800$ K, $T=T_{NI}-5$ K, $\ell_c/d_c=5$, $\sigma/d_c=0.3$, and $d_n/d_c=1.2$. Different curves in Fig. 13 correspond to different values of the parameter $k\ell_c$, describing helicity of chiral molecules. Changing the value of the parameter $k\ell_c$, one obtains negative or positive shift of the previous dependence, either the chiral part of the dispersion interaction is negative or positive. Variations of the helical wave number with the concentration of components in the common case $\sigma_b \neq \sigma_c$ are rather complicated. Nevertheless, the helical sense inversions are still possible due to the steric effects.

V. CONCLUSION

In this paper we presented a simple description for the correlation between molecules constituting a chiral nematic (cholesteric) phase. We suggested a model of chiral molecule that involves only five parameters having transparent geometrical meaning: the axial ratio ℓ/d , the intensity of the helix kd , semiaxes of the helix σ_b/d , σ_c/d and the parameter φ that determines the turn of the molecular center around the long axis \mathbf{a} with respect to the short axis \mathbf{b} . In the

case of quasiuniaxial molecule (when $\sigma_b = \sigma_c \equiv \sigma$) we have only three independent parameters of the molecule: ℓ/d , kd , and σ/d . In addition to these geometrical parameters, we use only the following variable values: the volume fraction of the molecules Φ , temperature T , and (in the case of the τ -component mixture) the relative concentration of its components η_μ ($\mu = 1, \dots, \tau - 1$).

We obtained the analytical expression for the helical wave number q in terms of these parameters. As it was predicted in Refs. [7–11], this expression appeared to consist of two contributions [in the case of the pure quasiuniaxial cholesteric see Eq. (57)], which derive from the steric repulsion and the dispersion attraction.

The steric contribution to the helical wave number q_{ster} [see Eq. (58)] is mostly managed by the minimal distance ξ_{12} between molecules. If both interacting molecules were achiral, the minimal distance between them would correspond to the parallel side-by-side orientation. At the same time, if at least one of the molecules is chiral, the minimal distance between them is achieved when the angle γ between their long axes is equal to a nonzero value. To analyze which turn (left or right) corresponds to the decreasing minimal distance ξ_{12} , we calculated its derivative ξ'_{12} with respect to the angle γ in the parallel side-by-side orientation [see Eqs. (32) and (50)]. It was established that, for example, two identical right-handed molecules dock better in the right-handed orientation [see Fig. 7(a)], whereas a right-handed molecule and an achiral one dock better in the left-handed orientation [see Fig. 7(b)]. We demonstrate in Sec. IV C that the difference between steric packing of identical and dissimilar molecules may be responsible for helical sense inversions in nematic-cholesteric mixtures with the change in the mutual concentration of the components (see Fig. 13). This result is confirmed by numerous experimental data [14–17].

The dispersion contribution to the helical wave number q_{disp} [see Eqs. (59)–(61)] is provided by the attractive forces between molecules. The dispersion attraction of the two achiral molecules U_{12} is known to be maximal in the parallel side-by-side orientation. At the same time, if at least one of the molecules is chiral, the maximal dispersion attraction may correspond to the small deviation from the parallel side-by-side orientation. This deviation may be opposite to the turn providing the minimal distance between molecules. We demonstrated that competition between the dispersion forces and the steric effects may lead to helical sense inversion with the change of the temperature. Indeed, according to Eq. (58) the steric contribution to the helical wave number q_{ster} is proportional to temperature T , whereas the dispersion contribution q_{disp} is independent on temperature T [see Eqs (59)–(61)]. If these contributions have opposite signs, helical sense inversion may happen at some temperature (see Figs. 9 and 10).

The other possibility for helical sense inversion exists if the molecules are essentially biaxial. According to the standard scheme [see Eq. (1)], the relation D/S between the biaxial and primary order parameters increases with the increasing temperature T [see Fig. 6(b)]. If the optimal packing of the short molecular axes corresponds to the rotation of the

nematic phase that is opposite to the rotation providing the optimal packing of the primary molecular axes, the other helical sense inversion may happen at some temperature (see Fig. 10).

Helical sense inversions with the variation of temperature were observed experimentally by different authors [2–6]. Using our analytical scheme presented in Sec. IV A, one can, in particular, estimate whether the molecules of the investigated liquid crystal are biaxial or uniaxial. Indeed, if the dependence $q(T)$ is linear (see Fig. 9), the molecules are uniaxial according to our scheme. Otherwise (see Fig. 10) the molecules possess essential shape biaxiality.

One notes from Eqs. (58) and (59)–(61) that the steric contribution to the helical wave number q_{ster} is inversely proportional to the third power of the molecular axial ratio ℓ/d , whereas the dispersion contribution q_{disp} is inversely proportional to the second power of this ratio. Thus, the steric contribution may dominate for the short molecules, whereas the dispersion contribution may dominate for the long ones. Taking this into account, one may suppose helical sense inversion in the process of denaturation of some polypeptides, if the steric and dispersion contributions have opposite signs. Indeed, the long native molecules are known to split into small chiral pieces in the process of denaturation [18]. In Sec. IV B we suggested a simple analytical scheme of denaturation, which resulted in the diagram presented in Fig. 12.

Finally, one should stress that very long molecules ($\ell/d \gg 1$), such as tobacco mosaic virus [36], usually constitute the achiral nematic phase because the long “ends” of one molecule attract the “ends” of the other one and the parallel side-by-side orientation of such molecules appears to be the most probable. This effect is confirmed by Fig. 12, where the absolute value of the helical wave number q rapidly decreases with the increasing molecular length ℓ/d .

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APPENDIX A: MINIMAL DISTANCE BETWEEN TWO IDENTICAL CHIRAL MOLECULES

1. Minimal distance between two identical chiral molecules in side-by-side orientation

Let us first consider the two identical chiral molecules in the side-by-side orientation presented in Fig. 1(c). A schematic illustration of the contacting identical molecules in the case $\mathbf{a}_1 \uparrow \uparrow \mathbf{a}_2$, $\mathbf{b}_1 \uparrow \uparrow \mathbf{b}_2$, $\mathbf{c}_1 \uparrow \uparrow \mathbf{c}_2 \uparrow \uparrow \mathbf{u}_{12}$, $\varphi = \pi/2$ is presented in Fig. 14. In correspondence with the molecular model presented in Sec. III, the coordinates (x_1, y_1, z_1) of an arbitrary layer t_1 of the first molecule and the coordinates (x_2, y_2, z_2)

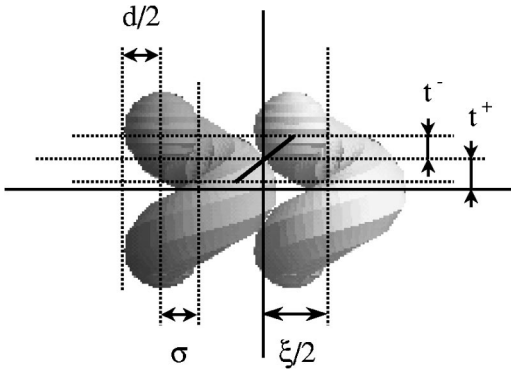


FIG. 14. Schematic illustration of the contacting identical chiral molecules in side-by-side orientation: $\mathbf{a}_1 \uparrow \uparrow \mathbf{a}_2$, $\mathbf{b}_1 \uparrow \uparrow \mathbf{b}_2$, $\mathbf{c}_1 \uparrow \uparrow \mathbf{c}_2 \uparrow \uparrow \mathbf{u}_{12}$, $\varphi = \pi/2$.

of an arbitrary layer t_2 of the second molecule in this orientation are, respectively, equal to

$$\begin{pmatrix} x_1(\gamma, t_1) \\ y_1(\gamma, t_1) \\ z_1(\gamma, t_1) \end{pmatrix} = \begin{pmatrix} \sigma_b \cos(kt_1 + \varphi_1) \cos(\gamma/2) - t_1 \sin(\gamma/2) \\ \sigma_c \sin(kt_1 + \varphi_1) \\ \sigma_b \cos(kt_1 + \varphi_1) \sin(\gamma/2) + t_1 \cos(\gamma/2) \end{pmatrix}, \quad (\text{A1})$$

$$\begin{pmatrix} x_2(\gamma, t_2) \\ y_2(\gamma, t_2) \\ z_2(\gamma, t_2) \end{pmatrix} = \begin{pmatrix} \sigma_b \cos(kt_2 + \varphi_2) \cos(\gamma/2) + t_2 \sin(\gamma/2) \\ r_{12} + \sigma_c \sin(kt_2 + \varphi_2) \\ -\sigma_b \cos(kt_2 + \varphi_2) \sin(\gamma/2) + t_2 \cos(\gamma/2) \end{pmatrix}, \quad (\text{A2})$$

where both parameters t_1 and t_2 range from $-\ell/2$ to $\ell/2$ and both parameters φ_1 and φ_2 may be equal to φ , $\varphi + \pi$, $-\varphi$ or $-\varphi + \pi$ depending on the choice of the odd orientation of molecules 1 and 2 (see Fig. 4). Penetration of a layer t_1 of the first molecule into a layer t_2 of the second molecule is forbidden. The minimal distance between layers is the diameter of the tube d . According to Eqs. (A1) and (A2), the corresponding distance between the molecular centers $\xi_c(\gamma, t_1, t_2)$ satisfies the following constraint:

$$\begin{aligned} d^2 = & [\xi_c(\gamma, t^-, t^+) + 2\sigma_c \sin(kt^- + \varphi^-) \cos(kt^+ + \varphi^+)]^2 \\ & + [2\sigma_b \sin(kt^- + \varphi^-) \sin(kt^+ + \varphi^+) \cos(\gamma/2) \\ & - 2t^+ \sin(\gamma/2)]^2 + [2\sigma_b \cos(kt^- + \varphi^-) \cos(kt^+ + \varphi^+) \\ & \times \sin(\gamma/2) - 2t^- \cos(\gamma/2)]^2, \end{aligned} \quad (\text{A3})$$

where $t^\mp \equiv (t_2 \mp t_1)/2$, $\varphi^\mp \equiv (\varphi_2 \mp \varphi_1)/2$. The total set of the parameters φ^\pm is presented in Table I. The minimal distance between molecules $\xi_c(\gamma)$ corresponds to the maximal value $\xi_c(\gamma, t^-, t^+)$. Maximizing $\xi_c(\gamma, t^-, t^+)$ in Eq. (A3) separately by t^- and t^+ in the case $\gamma=0$, one obtains

$$\cos(kt^+ + \varphi^+) = \mp 1, \quad (\text{A4})$$

$$k\sigma_c \cos(kt^- + \varphi^-) \sqrt{d^2 - (2t^-)^2} = \pm 2t^-, \quad (\text{A5})$$

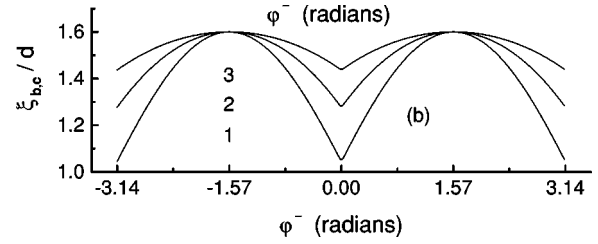


FIG. 15. Functions $t^-/d(\varphi^-)$ (a) and $\xi_{b,c}/d(\varphi^-)$ (b) in the case $\sigma/d \equiv \sigma_b/d = \sigma_c/d = 0.3$ and $kd=1$ (1), $kd=3$ (2), $kd=5$ (3).

where the down sign corresponds to the case $-\pi < \varphi^- + 2\pi n < 0$ (n is integer), the upper sign corresponds to the case $0 < \varphi^- + 2\pi n < \pi$, and in the case $\varphi^- = \pi n$ the sign in Eqs. (A4) and (A5) is determined by the parameter φ^+ : the down sign corresponds to the case $-\pi/2 \leq \varphi^+ + 2\pi n < \pi/2$ and the upper sign corresponds to the case $\pi/2 \leq \varphi^+ + 2\pi n < 3\pi/2$. The corresponding minimal distance between two molecules and its first and second derivatives with respect to the angle γ in the case $\gamma=0$ are determined then by the following expressions:

$$\xi_c(0) = \sqrt{d^2 - (2t^-)^2} + 2\sigma_c |\sin(kt^- + \varphi^-)|, \quad (\text{A6})$$

$$\xi_c'(0) = -k\sigma_b \sigma_c \cos^2(kt^- + \varphi^-), \quad (\text{A7})$$

$$\begin{aligned} \xi_c''(0) = & -[\xi_c'^2(0) + (t^+)^2 - (t^-)^2 + \sigma_b^2 \cos^2 \\ & \times (kt^- + \varphi^-)] / \sqrt{d^2 - (2t^-)^2}, \end{aligned} \quad (\text{A8})$$

where t^- is the root of Eq. (A5) [see Figs. 15(a) and 16(a)], and t^+ is the minimum in the absolute value root of Eq.

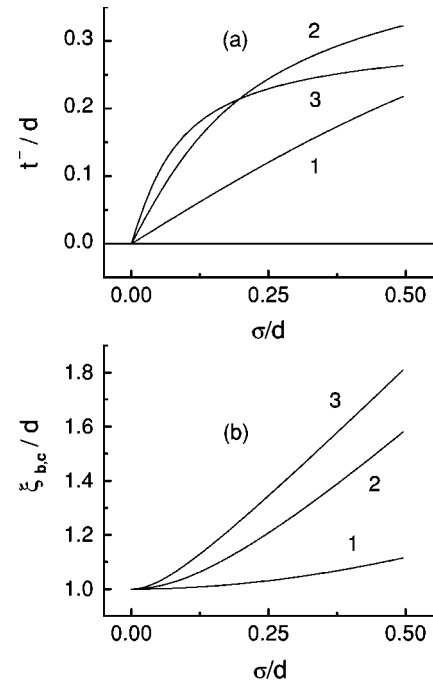


FIG. 16. Functions $t^-/d(\sigma/d)$ (a) and $\xi_{b,c}/d(\sigma/d)$ (b) in the case $\varphi^- = 0$ and $kd=1$ (1), $kd=3$ (2), $kd=5$ (3).

(A4). One notes that the function t^- and consequently the functions ξ_c and ξ'_c depend only on parameter φ^- , whereas the function ξ''_c depends on both parameters φ^- and φ^+ . One notes that the same expressions (A4)–(A8) with the change $\sigma_b \rightarrow \sigma_c$, $\sigma_c \rightarrow \sigma_b$ and $\varphi \rightarrow \varphi + \pi/2$ determine the minimum distance ξ_b and its derivatives ξ'_b , ξ''_b in the case presented in Fig. 1(b). The reduced functions $\xi_{b,c}/d(\varphi^-)$ and $\xi_{b,c}/d(\sigma/d)$ are presented in Figs. 15(b) and 16(b), respectively.

$$\begin{pmatrix} x_1(\alpha, t_1) \\ y_1(\alpha, t_1) \\ z_1(\alpha, t_1) \end{pmatrix} = \begin{pmatrix} \sigma_b \cos(kt_1 + \varphi_1) \cos(\alpha/2) + \sigma_c \sin(kt_1 + \varphi_1) \sin(\alpha/2) \\ -\sigma_b \cos(kt_1 + \varphi_1) \sin(\alpha/2) + \sigma_c \sin(kt_1 + \varphi_1) \cos(\alpha/2) \\ t_1 \end{pmatrix}, \quad (\text{A9})$$

$$\begin{pmatrix} x_2(\alpha, t_2) \\ y_2(\alpha, t_2) \\ z_2(\alpha, t_2) \end{pmatrix} = \begin{pmatrix} \sigma_b \cos(kt_2 + \varphi_2) \cos(\alpha/2) - \sigma_c \sin(kt_2 + \varphi_2) \sin(\alpha/2) \\ \sigma_b \cos(kt_2 + \varphi_2) \sin(\alpha/2) + \sigma_c \sin(kt_2 + \varphi_2) \cos(\alpha/2) \\ r_{12} + t_2 \end{pmatrix}, \quad (\text{A10})$$

where both parameters t_1 and t_2 range from $-\ell/2$ to $\ell/2$ and both parameters φ_1 and φ_2 may be equal to φ , $\varphi + \pi$, $-\varphi$ or $-\varphi + \pi$ depending on the choice of the odd orientation of molecules 1 and 2 (see Fig. 4). Penetration of a layer t_1 of the first molecule into a layer t_2 of the second molecule is forbidden. The minimum distance between layers is the diameter of the tube d . According to Eqs. (A9) and (A10), the corresponding distance between the molecular centers $\xi_a(\alpha, t_1, t_2)$ satisfies the following constraint:

$$\begin{aligned} d^2 = & [\xi_a(\alpha, t^-, t^+) + 2t^-]^2 + [2\sigma_b \sin(kt^- + \varphi^-) \\ & \times \sin(kt^+ + \varphi^+) \cos(\alpha/2) + 2\sigma_c \cos(kt^- + \varphi^-) \\ & \times \sin(kt^+ + \varphi^+) \sin(\alpha/2)]^2 + [2\sigma_b \cos(kt^- + \varphi^-) \\ & \times \cos(kt^+ + \varphi^+) \sin(\alpha/2) + 2\sigma_c \sin(kt^- + \varphi^-) \\ & \times \cos(kt^+ + \varphi^+) \cos(\alpha/2)]^2, \end{aligned} \quad (\text{A11})$$

where $t^\pm \equiv (t_2 \mp t_1)/2$, $\varphi^\pm \equiv (\varphi_2 \mp \varphi_1)/2$. The total set of the parameters φ^\pm is presented in Table I. It follows from

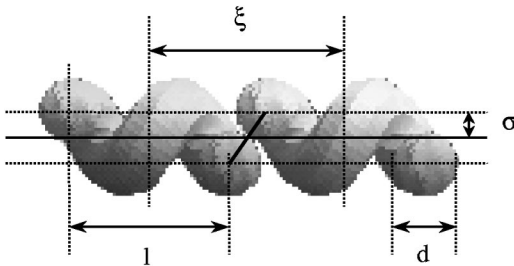


FIG. 17. Schematic illustration of the contacting identical chiral molecules in end-to-end orientation: $\mathbf{a}_1 \uparrow \uparrow \mathbf{a}_2 \uparrow \uparrow \mathbf{u}_{12}$, $\mathbf{b}_1 \uparrow \uparrow \mathbf{b}_2$, $\mathbf{c}_1 \uparrow \uparrow \mathbf{c}_2$, $\varphi = 0$.

2. Minimum distance between two identical chiral molecules in end-to-end orientation

Next let us consider the two identical chiral molecules in the end-to-end orientation presented in Fig. 1(a). A schematic illustration of the contacting molecules in the case $\mathbf{a}_1 \uparrow \uparrow \mathbf{a}_2 \uparrow \uparrow \mathbf{u}_{12}$, $\mathbf{b}_1 \uparrow \uparrow \mathbf{b}_2$, $\mathbf{c}_1 \uparrow \uparrow \mathbf{c}_2$, $\varphi = 0$ is presented in Fig. 17. The coordinates (x_1, y_1, z_1) of an arbitrary layer t_1 of the first molecule and the coordinates (x_2, y_2, z_2) of an arbitrary layer t_2 of the second molecule in this orientation are, respectively, equal to

Eq. (A11) that the function $\xi_a(\alpha, t^-, t^+)$ increases with the decreasing variable t^- . On the other hand, the minimum possible value $t^- = -\ell/2$. Thus, maximization of the function $\xi_a(\alpha, t^-, t^+)$ with the respect to the variable t^- gives

$$t^- = -\ell/2. \quad (\text{A12})$$

The following maximization of the function $\xi_a(\alpha, t^-, t^+)$ in Eq. (A11) with respect to the variable t^+ (in supposition $\sigma_b \geq \sigma_c$) gives

$$\sin(kt^+ + \varphi^+) = 0. \quad (\text{A13})$$

The corresponding minimum distance between two molecules and its first and second derivatives with respect to the angle α in the case $\alpha = 0$ are determined then by the following expressions:

$$\xi_a(0) = \ell + \sqrt{d^2 - 4\sigma_c^2 \sin^2(k\ell/2 - \varphi^-)}, \quad (\text{A14})$$

$$\xi'_a(0) = -\sigma_b \sigma_c \sin(k\ell - 2\varphi^-) / [\xi_a(0) - \ell], \quad (\text{A15})$$

$$\begin{aligned} \xi''_a(0) = & [-\xi_a'^2(0) + \frac{1}{2}(\sigma_b^2 - \sigma_c^2) + \frac{1}{2}(\sigma_b^2 + \sigma_c^2) \\ & \times \cos(k\ell - 2\varphi^-)] / [\xi_a(0) - \ell]. \end{aligned} \quad (\text{A16})$$

APPENDIX B: DISPERSION INTERACTION OF TWO IDENTICAL CHIRAL MOLECULES

1. Dispersion interaction of two identical chiral molecules in side-by-side orientation

Let us first estimate the dispersion interaction of the two identical chiral molecules in the side-by-side orientation, presented in Fig. 1(c). According to Eq. (28), the dispersion

interaction of an arbitrary layer t_1 of the first molecule with an arbitrary layer t_2 of the second molecule in this orientation is determined by the following expression:

$$\Delta U_c(r_{12}, t^-, t^+) = - \frac{J_0 d^4}{[(r_{12} + \Delta y_c)^2 + \Delta x_c^2 + \Delta z_c^2]^3}, \quad (\text{B1})$$

where J_0 is the constant having the dimension of energy. In correspondence with Eqs. (A1) and (A2), the parameters Δx_c , Δy_c , and Δz_c satisfy the following expressions:

$$\begin{aligned} \Delta x_c &= -2\sigma_b \sin(kt^- + \varphi^-) \sin(kt^+ + \varphi^+) \cos(\gamma/2) \\ &\quad + 2t^+ \sin(\gamma/2), \\ \Delta y_c &= 2\sigma_c \sin(kt^- + \varphi^-) \cos(kt^+ + \varphi^+), \quad (\text{B2}) \\ \Delta z_c &= -2\sigma_b \cos(kt^- + \varphi^-) \cos(kt^+ + \varphi^+) \sin(\gamma/2) \\ &\quad + 2t^- \cos(\gamma/2). \end{aligned}$$

It follows from Eq. (B2) that the parameter Δy_c is independent on the angle γ between the long molecular axes. One obtains, therefore, the following expressions for the first and second derivatives of the interaction between layers with the respect to the angle γ :

$$\Delta U'_c(r_{12}, t^-, t^+) = \frac{3J_0 d^4 [\Delta x_c^2 + \Delta z_c^2]'}{[(r_{12} + \Delta y_c)^2 + \Delta x_c^2 + \Delta z_c^2]^4}, \quad (\text{B3})$$

$$\begin{aligned} \Delta U''_c(r_{12}, t^-, t^+) &= \{\Delta U''_c(r_{12}, t^-, t^+)\}_{\text{mon}} \\ &\quad + \{\Delta U''_c(r_{12}, t^-, t^+)\}_{\text{osc}}, \quad (\text{B4}) \end{aligned}$$

where the second derivative $\Delta U''_c(r_{12}, t^-, t^+)$ consists of the two parts that we conditionally call ‘‘monotonic’’ and ‘‘oscillating’’ parts,

$$\{\Delta U''_c(r_{12}, t^-, t^+)\}_{\text{mon}} \equiv \frac{3J_0 d^4 [\Delta x_c^2 + \Delta z_c^2]''}{[(r_{12} + \Delta y_c)^2 + \Delta x_c^2 + \Delta z_c^2]^4}, \quad (\text{B5})$$

$$\{\Delta U''_c(r_{12}, t^-, t^+)\}_{\text{osc}} \equiv - \frac{12J_0 d^4 \{[\Delta x_c^2 + \Delta z_c^2]'\}^2}{[(r_{12} + \Delta y_c)^2 + \Delta x_c^2 + \Delta z_c^2]^5}. \quad (\text{B6})$$

It will be proved below that the term $\{\Delta U''_c(r_{12}, t^-, t^+)\}_{\text{mon}}$ contains the largest monotonic function of the molecular elongation ℓ/d , whereas the term $\{\Delta U''_c(r_{12}, t^-, t^+)\}_{\text{osc}}$ contains the largest oscillating function of the same parameter. Substituting Eq. (B2) into Eqs. (B1), (B3), (B5), (B6), then expanding them in the small parameter $\sigma/d \equiv \sqrt{\sigma_b \sigma_c}/d$ and taking into account the only first nonzero term (which at the same time is not odd with respect to the change $\varphi \rightarrow \varphi + \pi$ corresponding to the rotation of both molecules around their long axes \mathbf{a}_1 and \mathbf{a}_2 by the angle π), one obtains the follow-

ing expressions for the dispersion interaction of the layers and its first and second derivatives with respect to the angle γ in the case $\gamma=0$:

$$\Delta U_c(r_{12}, t^-, t^+) \approx - \frac{J_0 d^4}{[r_{12}^2 + (2t^-)^2]^3}, \quad (\text{B7})$$

$$\Delta U'_c(r_{12}, t^-, t^+) \approx 96 \frac{\sigma_b \sigma_c}{d^2} J_0 d^6 \frac{r_{12} W_1(t^-, t^+)}{[r_{12}^2 + (2t^-)^2]^5}, \quad (\text{B8})$$

$$\{\Delta U''_c(r_{12}, t^-, t^+)\}_{\text{mon}} \approx 6J_0 d^4 \frac{(t^+)^2 - (t^-)^2}{[r_{12}^2 + (2t^-)^2]^4}, \quad (\text{B9})$$

$$\{\Delta U''_c(r_{12}, t^-, t^+)\}_{\text{osc}} \approx -48 \frac{\sigma_b \sigma_c}{d^2} J_0 d^6 \frac{W_2(t^-, t^+)}{[r_{12}^2 + (2t^-)^2]^5}, \quad (\text{B10})$$

where

$$\begin{aligned} W_1(t^-, t^+) &\equiv t^+ \sin^2(kt^- + \varphi^-) \sin(2kt^+ + 2\varphi^+) \\ &\quad + t^- \cos^2(kt^+ + \varphi^+) \sin(2kt^- + 2\varphi^-), \quad (\text{B11}) \end{aligned}$$

$$\begin{aligned} W_2(t^-, t^+) &\equiv [(t^+)^2 + (t^-)^2] \{1 + \cos(2kt^- + 2\varphi^-) \cos(2kt^+ \\ &\quad + 2\varphi^+)\} - [(t^+)^2 - (t^-)^2] \{\cos(2kt^- + 2\varphi^-) \\ &\quad + \cos(2kt^+ + 2\varphi^+)\} + t^- t^+ \sin(2kt^- \\ &\quad + 2\varphi^-) \sin(2kt^+ + 2\varphi^+). \quad (\text{B12}) \end{aligned}$$

One notes from Eqs. (B7) and (B9) that the dispersion interaction $\Delta U_c(r_{12}, t^-, t^+)$ of the layers and the monotonic part of its second derivative $\{\Delta U''_c(r_{12}, t^-, t^+)\}_{\text{mon}}$ with respect to the angle γ do not depend on the parameter σ/d at zeroth approximation and have exactly the same expressions as for achiral molecules. The total dispersion interaction of the two molecules is determined by Eq. (29). In the case of the two identical molecules one can rewrite Eq. (29) in the following form:

$$U_{12}(r_{12}) = 8 \int_0^{\ell/2} dt^- \int_0^{\ell/2 - t^-} dt^+ \langle \Delta U(r_{12}, t^-, t^+) \rangle, \quad (\text{B13})$$

where the angular brackets denote the even part of the corresponding expression with respect to both parameters t^+ and t^- . Substituting Eqs. (B7) and (B9) into Eq. (B13), taking into account the constraint (27) and generalizing all the expressions for both cases presented in Figs. 1(b), 1(c), one obtains the following expressions for the total dispersion interaction between two identical chiral molecules in the side-by-side orientation and the monotonic part of its second derivative with respect to the corresponding rotational angle (β or γ) in the case $\beta=0$ or $\gamma=0$:

$$U_{\mathbf{b},\mathbf{c}} \approx - \frac{3\pi}{8} J_0 \left(\frac{d}{r_{12}} \right)^5 \frac{\ell}{d}, \quad (\text{B14})$$

$$\{U''_{\mathbf{b},\mathbf{c}}\}_{\text{mon}} \approx \frac{5\pi}{32} J_0 \left(\frac{d}{r_{12}}\right)^7 \left(\frac{\ell}{d}\right)^3. \quad (\text{B15})$$

If the molecules satisfy constraint (27), the first three terms in integral (25) may be neglected with the respect to the fourth one. Indeed, according to Eqs. (A6)–(A8) and (B15), the fourth term in Eq. (25) contains the maximal (third) power of the large parameter ℓ/d and the minimal (zeroth) power of the small parameter σ/d . Substituting Eq. (B15) into the fourth term of Eq. (25) and taking into account Eqs. (7), (15), and (30), one obtains Eqs. (44)–(47) for the coefficients $J_{0(\mu,\mu)}^{202}$, $M_{0(\mu,\mu)}^{202}$, $J_{2(\mu,\mu)}^{202}$ and $M_{2(\mu,\mu)}^{202}$.

At the same time, the first nonzero terms in functions $\Delta U'_c(r_{12}, t^-, t^+)$ and $\{\Delta U''_c(r_{12}, t^-, t^+)\}_{\text{osc}}$ are proportional to $(\sigma/d)^2$ [see Eqs. (B8) and (B10)], as well as the function ξ'_c/d [see Eq. (A7)]. Thus, both terms in the integral (24), as well as the largest oscillating term in Eq. (25), are proportional to $(\sigma/d)^2$. Substituting Eqs. (B8) and (B10) into Eq. (B13), one obtains functions $U'_c(r_{12})$ and $\{U''_c(r_{12})\}_{\text{osc}}$. Defining the parameters $r \equiv kr_{12}$, $t \equiv 2kt^-$, and $x \equiv k\xi_c$, integrating the functions $r_{12}^3 U'_c(r_{12})$ and $r_{12}^2 \{U''_c(r_{12})\}_{\text{osc}}$ with respect to the variable r_{12} and taking into account constraint (27), one obtains [40]

$$\begin{aligned} d^{-4} \int_{\xi_c}^{\infty} r_{12}^3 U'_c(r_{12}) dr_{12} &\approx \frac{1}{16} J_0 \frac{\sigma_{\mathbf{b}} \sigma_{\mathbf{c}}}{d^2} (kd)^3 \frac{\ell}{d} \left\{ S_{4,1}^5(k\xi_c) \cos(2\varphi^-) \right. \\ &\quad - \left[C_{4,0}^5(k\xi_c) \right. \\ &\quad \left. \left. - \frac{105}{8} (k\xi_c)^{-4} \cos(2\varphi^-) \right] \cos(2\varphi^+) \cos(k\ell) \right. \\ &\quad \left. - S_{4,0}^5(k\xi_c) \cos(2\varphi^+) \sin(k\ell) \right\}, \quad (\text{B16}) \end{aligned}$$

$$\begin{aligned} d^{-3} \int_{\xi_c}^{\infty} r_{12}^2 \{U''_c(r_{12})\}_{\text{osc}} dr_{12} &\approx \frac{1}{32} J_0 \frac{\sigma_{\mathbf{b}} \sigma_{\mathbf{c}}}{d^2} (kd)^5 \left(\frac{\ell}{d}\right)^2 \cos(2\varphi^+) \{ C_{2,0}^5(k\xi_c) \sin(k\ell) \\ &\quad - S_{2,0}^5(k\xi_c) \cos(k\ell) \}, \quad (\text{B17}) \end{aligned}$$

where functions $S_{4,1}^5(x)$, $C_{4,0}^5(x)$, $S_{4,0}^5(x)$ are determined by Eqs. (39), (40), and (41), respectively, and functions $C_{2,0}^5(x)$ and $S_{2,0}^5(x)$ are determined by Eqs. (75) and (76), respectively. Substituting $\varphi^+ \rightarrow \varphi^+ + \pi/2$, one obtains the analogous expressions for the other side-by-side orientation presented in Fig. 1(b):

$$\begin{aligned} d^{-4} \int_{\xi_b}^{\infty} r_{12}^3 U'_b(r_{12}) dr_{12} &\approx \frac{1}{16} J_0 \frac{\sigma_{\mathbf{b}} \sigma_{\mathbf{c}}}{d^2} (kd)^3 \frac{\ell}{d} \left\{ S_{4,1}^5(k\xi_b) \cos(2\varphi^-) \right. \\ &\quad + \left[C_{4,0}^5(k\xi_b) \right. \\ &\quad \left. \left. - \frac{105}{8} (k\xi_b)^{-4} \cos(2\varphi^-) \right] \cos(2\varphi^+) \cos(k\ell) \right. \\ &\quad \left. + S_{4,0}^5(k\xi_b) \cos(2\varphi^+) \sin(k\ell) \right\}, \quad (\text{B18}) \end{aligned}$$

$$\begin{aligned} d^{-3} \int_{\xi_b}^{\infty} r_{12}^2 \{U''_b(r_{12})\}_{\text{osc}} dr_{12} &\approx -\frac{1}{32} J_0 \frac{\sigma_{\mathbf{b}} \sigma_{\mathbf{c}}}{d^2} (kd)^5 \left(\frac{\ell}{d}\right)^2 \cos(2\varphi^+) \\ &\quad \times \{ C_{2,0}^5(k\xi_b) \sin(k\ell) - S_{2,0}^5(k\xi_b) \cos(k\ell) \}. \quad (\text{B19}) \end{aligned}$$

Substituting Eqs. (B16) and (B18) into Eq. (24) and taking into account Eqs. (7), (14), and (30), one obtains Eqs. (34) and (35) for the coefficients $J_{1(\mu,\mu)}^{212}$ and $M_{1(\mu,\mu)}^{212}$. Substituting Eqs. (B17) and (B19) into the fourth term of Eq. (25), neglecting the other terms in Eq. (25), substituting Eqs. (15) and (25) into Eq. (7) and, finally, substituting the first line of Eq. (7) into Eq. (72), one obtains Eq. (73) for the largest oscillating term in the free energy.

2. Dispersion interaction of two identical chiral molecules in end-to-end orientation

Next let us estimate the dispersion interaction of the two identical chiral molecules in the end-to-end orientation, presented in Fig. 1(a). Accordingly to Eq. (28), the dispersion interaction of an arbitrary layer t_1 of the first molecule with an arbitrary layer t_2 of the second molecule in this orientation is determined by the following expression:

$$\Delta U_{\mathbf{a}}(r_{12}, t^-, t^+) = -\frac{J_0 d^4}{[(r_{12} + \Delta z_{\mathbf{a}})^2 + \Delta x_{\mathbf{a}}^2 + \Delta y_{\mathbf{a}}^2]^3}, \quad (\text{B20})$$

where J_0 is the constant having the dimension of energy. In correspondence with Eqs. (A9) and (A10), the parameters $\Delta x_{\mathbf{a}}$, $\Delta y_{\mathbf{a}}$, $\Delta z_{\mathbf{a}}$ are determined by the following expressions:

$$\begin{aligned} \Delta x_{\mathbf{a}} &= -2\sigma_{\mathbf{b}} \sin(kt^- + \varphi^-) \sin(kt^+ + \varphi^+) \cos(\alpha/2) \\ &\quad - 2\sigma_{\mathbf{c}} \cos(kt^- + \varphi^-) \sin(kt^+ + \varphi^+) \sin(\alpha/2), \end{aligned}$$

$$\begin{aligned} \Delta y_{\mathbf{a}} &= 2\sigma_{\mathbf{b}}\cos(kt^- + \varphi^-)\cos(kt^+ + \varphi^+)\sin(\alpha/2) \\ &+ 2\sigma_{\mathbf{c}}\sin(kt^- + \varphi^-)\cos(kt^+ + \varphi^+)\cos(\alpha/2), \end{aligned} \quad (\text{B21})$$

$$\Delta z_{\mathbf{a}} = 2t^-.$$

Expanding expression (B20) in the small parameter $\sigma/d \equiv \sqrt{\sigma_{\mathbf{b}}\sigma_{\mathbf{c}}}/d$ and taking into account the only first nonzero term, one obtains the following expressions for the disper-

$$\Delta U''_{\mathbf{a}}(r_{12}, t^-, t^+) \approx 3J_0 d^4 \frac{(\sigma_{\mathbf{b}}^2 + \sigma_{\mathbf{c}}^2)\cos(2kt^- + 2\varphi^-) + (\sigma_{\mathbf{b}}^2 - \sigma_{\mathbf{c}}^2)\cos(2kt^+ + 2\varphi^+)}{[r_{12} + 2t^-]^8}. \quad (\text{B24})$$

One notes from Eq. (B22) that at zeroth approximation the interaction of an arbitrary layer in the case $\alpha=0$ is independent of the rotation of molecules around their principal axes \mathbf{a}_1 and \mathbf{a}_2 . At the same time, its first and second derivatives with respect to the angle α [see Eqs. (B23) and (B24)] change their signs after the rotation of any molecule by the angle π around its principle axis. Therefore, the total interaction of molecules in the end-to-end orientation $U_{\mathbf{a}}$ is also independent of the rotation of the molecules around their principal axes, and its first and second derivatives $U'_{\mathbf{a}}$ and $U''_{\mathbf{a}}$ with the respect to the angle α in the case $\alpha=0$ change their signs after the rotation of any molecule by the angle π around its principle axis. Expanding expression (A14) for the minimal distance $\xi_{\mathbf{a}}(0)$ between the two molecules in the small parameter σ/d , one obtains

$$\xi_{\mathbf{a}}(0) \approx \ell + d[1 - 2(\sigma_{\mathbf{c}}/d)^2 + \dots], \quad (\text{B25})$$

$$[\xi_{\mathbf{a}}(0) - \ell]^{-1} \approx d^{-1}[1 + 2(\sigma_{\mathbf{c}}/d)^2 + \dots]. \quad (\text{B26})$$

Therefore, after the rotation of any molecule by the angle π , expressions (A15) and (A16) for the derivatives $\xi'_{\mathbf{a}}(0)$ and $\xi''_{\mathbf{a}}(0)$ also change their signs, keeping approximately the same absolute values [with an error $\sim(\sigma/d)^4$]. Thus, the integrals (24) and (25) appear to be approximately equal to zero in the end-to-end orientation with the same error $\sim(\sigma/d)^4$. Substituting Eqs. (24) and (25) together with the third line of Eqs. (14) and (15) into the third line of Eq. (7), one obtains Eq. (30). In other words, one may neglect the interaction of short molecular axes with each other.

APPENDIX C: MINIMAL DISTANCE BETWEEN ACHIRAL AND CHIRAL MOLECULES IN SIDE-BY-SIDE ORIENTATION

Let us determine the minimal distance between an achiral molecule [see Fig. 3(c)] and a weakly twisted quasiuniaxial chiral molecule [see Fig. 3(b)] in the parallel side-by-side orientation presented in Fig. 1(c). A schematic illustration of the contacting achiral and chiral molecules in the case

of side-by-side interaction of the layers and its first and second derivatives with respect to the angle α in the case $\alpha=0$:

$$\Delta U_{\mathbf{a}}(r_{12}, t^-, t^+) \approx -\frac{J_0 d^4}{[r_{12} + 2t^-]^6}, \quad (\text{B22})$$

$$\Delta U'_{\mathbf{a}}(r_{12}, t^-, t^+) \approx 6\frac{\sigma_{\mathbf{b}}\sigma_{\mathbf{c}}}{d^2}J_0 d^6 \frac{\sin(2kt^- + 2\varphi^-)}{[r_{12} + 2t^-]^8}, \quad (\text{B23})$$

of side-by-side interaction of the layers and its first and second derivatives with respect to the angle α in the case $\alpha=0$ is presented in Fig. 18. In correspondence with the molecular model presented in Sec. III, the coordinates (x_n, y_n, z_n) of an arbitrary layer t_n of the achiral molecule and the coordinates (x_c, y_c, z_c) of an arbitrary layer t_c of the chiral molecule in this orientation are equal to

$$\begin{pmatrix} x_n(\gamma, t_n) \\ y_n(\gamma, t_n) \\ z_n(\gamma, t_n) \end{pmatrix} = \begin{pmatrix} -t_n \sin(\gamma/2) \\ 0 \\ t_n \cos(\gamma/2) \end{pmatrix}, \quad (\text{C1})$$

$$\begin{pmatrix} x_c(\gamma, t_c) \\ y_c(\gamma, t_c) \\ z_c(\gamma, t_c) \end{pmatrix} = \begin{pmatrix} -\sigma \sin(kt_c) \cos(\gamma/2) + t_c \sin(\gamma/2) \\ r_{nc} + \sigma \cos(kt_c) \\ \sigma \sin(kt_c) \sin(\gamma/2) + t_c \cos(\gamma/2) \end{pmatrix}, \quad (\text{C2})$$

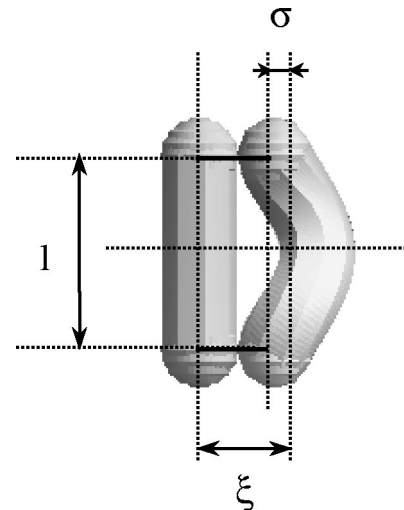


FIG. 18. Schematic illustration of the contacting achiral and chiral molecules in side-by-side orientation: $\mathbf{a}_1 \uparrow \uparrow \mathbf{a}_2$, $\mathbf{b}_1 \uparrow \uparrow \mathbf{b}_2$, $\mathbf{c}_1 \uparrow \uparrow \mathbf{c}_2 \uparrow \uparrow \mathbf{u}_{12}$, $\varphi = \pi/2$.

where the parameter t_n ranges from $-\ell_n/2$ to $\ell_n/2$, the parameter t_c ranges from $-\ell_c/2$ to $\ell_c/2$, and the parameters σ and k define the twist of the chiral molecule. Penetration of a layer t_n of the achiral molecule into a layer t_c of the chiral molecule is forbidden. The minimal distance between layers is the average diameter $d \equiv (d_n + d_c)/2$. Accordingly to Eqs. (C1) and (C2), the corresponding distance between the molecular centers $\xi_{nc}(\gamma, t_n, t_c)$ satisfies the following constraint:

$$d^2 = [\xi_{nc}(\gamma, t_n, t_c) + \sigma \cos(kt_c)]^2 + \sigma^2 \sin^2(kt_c) + t_n^2 - 2t_n t_c \cos \gamma + t_c^2 - 2\sigma t_n \sin(kt_c) \sin \gamma. \quad (\text{C3})$$

The minimal distance between two molecules $\xi_{\min}(\gamma)$ corresponds to the maximal value $\xi_{nc}(\gamma, t_n, t_c)$. Maximizing $\xi_{nc}(\gamma, t_n, t_c)$ in Eq. (C3) separately by the parameters t_c and $t^- \equiv (t_c - t_n)/2$ in the case $\gamma=0$, one obtains

$$t_n = t_c = \pm \frac{\ell}{2}, \quad (\text{C4})$$

where the parameter ℓ is the minimal length (ℓ_n or ℓ_c). Substituting Eq. (C4) into Eq. (C3), one obtains Eq. (49) for the minimal distance between molecules and Eq. (50) for the derivative of the minimal distance with the respect to the angle γ in the case $\gamma=0$.

APPENDIX D: DISPERSION INTERACTION OF ACHIRAL AND CHIRAL MOLECULES IN SIDE-BY-SIDE ORIENTATION

Let us estimate the dispersion interaction of the achiral molecule with the chiral one in the side-by-side orientation presented in Fig. 1(c) (see also Fig. 18). Performing the same calculations as in Appendix B, one obtains that the interaction $\Delta U_{nc}(r_{nc}, t_n, t_c)$ between a layer of the achiral molecule and a layer of the chiral one and its second derivative $\Delta U''_{nc}(r_{nc}, t_n, t_c)$ with respect to the angle γ in the case $\gamma=0$ are determined by the same Eqs. (B7) and (B9), respectively, where $t^\mp = (t_c \mp t_n)/2$. Indeed, at zeroth approximation these expressions are the same even for two achiral molecules. Substituting Eqs. (B7) and (B9) into Eq. (29), one obtains in the supposition $\ell_n \gg d$ and $\ell_c \gg d$ the following expressions for the total interaction between an achiral molecule and a chiral one and its second derivative with respect to the angle between the long molecular axes:

$$U_{nc} \approx -\frac{3\pi}{8} J_0 \left(\frac{d}{r_{nc}} \right)^5 \frac{\ell_n}{d} + 2J_0 \frac{\Delta \ell}{d} d^5 \int_{\Delta \ell/2}^{\infty} \frac{dt}{[r_{nc}^2 + (2t^-)^2]^3}, \quad (\text{D1})$$

$$U''_{nc} \approx \frac{5\pi}{32} J_0 \left(\frac{d}{r_{nc}} \right)^7 \left(\frac{\ell_n}{d} \right)^3 + J_0 \frac{\ell_c^3 - \ell_n^3}{d^3} d^7 \int_{\Delta \ell/2}^{\infty} \frac{dt}{[r_{nc}^2 + (2t^-)^2]^4}, \quad (\text{D2})$$

where $\Delta \ell \equiv \ell_c - \ell_n$. One notes that Eqs. (D1) and (D2) fit Eqs. (B14) and (B15), respectively, in the two limit cases: $\Delta \ell/d=0$ and $|\Delta \ell/d| \gg 1$, where the parameter ℓ equal the minimal length (ℓ_n or ℓ_c). The intermediate case ranges really from $\Delta \ell/2=0$ to $|\Delta \ell/2| \sim r^*$ with r^* is the distance, where the dispersion potential vanishes. Since the dispersion potential vanishes very quickly, the intermediate range is very small. Therefore, one can restrict his consideration to the case $\Delta \ell=0$ without losing any homogeneous features of the potential. Substituting Eq. (D2) into the fourth term of Eq. (25) and taking into account Eqs. (7), (15), and (30), one obtains in the case $\Delta \ell=0$ Eqs. (53)–(56) for the coefficients $J_{0(nc)}^{202}$, $M_{0(nc)}^{202}$, $J_{2(nc)}^{202}$, and $M_{2(nc)}^{202}$.

At the same time, the expression for the first derivative $\Delta U'_{nc}(t_n, t_c, r_{nc})$ of the interaction between a layer of the achiral molecule and a layer of the chiral one with respect to the angle γ in the case $\gamma=0$ differs from its analog (B8) for two identical chiral molecules. Substituting Eqs. (C1) and (C2) into Eq. (B3), where it is assumed $\Delta x_c \equiv x_c - x_n$, $\Delta y_c \equiv y_c - y_n$, $\Delta z_c \equiv z_c - z_n$, expanding the resulting expression in the small parameter σ/d and taking into account the only first nonzero term, one obtains

$$\Delta U'_{nc}(t_n, t_c, r_{nc}) \approx -24(\sigma/d)^2 J_0 d^6 \frac{r_{nc} t_n \sin(2kt_c)}{[r_{nc}^2 + (2t^-)^2]^5}. \quad (\text{D3})$$

Substituting Eq. (D3) into Eq. (29), one obtains the function $U'_{nc}(r_{nc})$. Defining the parameters $r \equiv kr_{nc}$ and $t \equiv 2kt^-$, integrating the function $r_{12}^3 U'_{nc}(r_{nc})$ with respect to the variable r_{nc} and using a constraint (27), one obtains

$$d^{-4} \int_{\xi_{\min}}^{\infty} r_{nc}^3 U'_{nc}(r_{nc}) dr_{nc} \approx -12J_0 \left(\frac{\sigma}{d} \right)^2 (kd)^3 \frac{\ell_c}{d} \cos(k\ell_c) \times \int_{k\xi_{\min}}^{\infty} dr \int_{k\Delta \ell}^{\infty} dt \frac{r^4}{(r^2 + t^2)^5}. \quad (\text{D4})$$

Equation (D4) has a simple extrapolation in the three limit cases

$$d^{-4} \int_{\xi_{\min}}^{\infty} r_{nc}^3 U'_{nc}(r_{nc}) dr_{nc} \approx \begin{cases} 0, & \ell_n \ll \ell_c \\ -\frac{105\pi}{256} J_0 \left(\frac{\sigma}{d} \right)^2 (kd)^{-1} \left(\frac{d}{\xi_{\min}} \right)^4 \frac{\ell_c}{d} \cos(k\ell_c), & \ell_n = \ell_c \\ -\frac{105\pi}{128} J_0 \left(\frac{\sigma}{d} \right)^2 (kd)^{-1} \left(\frac{d}{\xi_{\min}} \right)^4 \frac{\ell_c}{d} \cos(k\ell_c), & \ell_n \gg \ell_c. \end{cases} \quad (\text{D5})$$

As was already discussed, the intermediate case corresponds to the very small range of the parameters ℓ_n and ℓ_c due to the shortrange of the dispersion potential. The difference between the limit cases in Eq. (D5) has a simple explanation. Indeed, the chiral part of the dispersion interaction is associated with the position of the ends of the chiral molecule.

Thus, the small achiral molecule does not “feel” the ends of the large chiral molecule, and the expression (D5) is therefore equal to zero. Conversely, the long body of the achiral molecule suffers the double effect from the ends of the short chiral molecule, with respect to the case of the equal molecular lengths ($\ell_n = \ell_c$). In any case, the sign of the chiral interaction does not depend on the respective length of both molecules and depends only on the length of the chiral molecule. Therefore one can restrict his consideration to the case $\Delta\ell = 0$ without losing any chiral properties of the potential, as well as homogeneous ones. Substituting Eqs. (D5) into Eq. (24) and taking into account Eqs. (7), (14), and (30), one obtains in the case $\Delta\ell = 0$ Eqs. (51) and (52) for the coefficients $J_{1(nc)}^{212}$ and $M_{1(nc)}^{212}$.

APPENDIX E: INTEGRALS $C_{m,n}^K(x)$ AND $S_{m,n}^K(x)$

Let us determine the integrals $C_{m,n}^k(x)$ and $S_{m,n}^k(x)$ as follows:

$$\begin{aligned} C_{m,n}^k(x) &\equiv 2^k(k-1)! \int_x^\infty dr \int_0^\infty dt \frac{r^m t^n \cos t}{[r^2 + t^2]^k} \\ &= \int_x^\infty C_n^k(r) r^m dr, \end{aligned} \quad (E1)$$

$$\begin{aligned} S_{m,n}^k(x) &\equiv 2^k(k-1)! \int_x^\infty dr \int_0^\infty dt \frac{r^m t^n \sin t}{[r^2 + t^2]^k} \\ &= \int_x^\infty S_n^k(r) r^m dr, \end{aligned} \quad (E2)$$

where the integrals $C_n^k(r)$ and $S_n^k(r)$ are determined by the following expressions:

$$C_n^k(r) \equiv 2^k(k-1)! \int_0^\infty \frac{t^n \cos t dt}{[r^2 + t^2]^k}, \quad (E3)$$

$$S_n^k(r) \equiv 2^k(k-1)! \int_0^\infty \frac{t^n \sin t dt}{[r^2 + t^2]^k}. \quad (E4)$$

Using the obvious recurrent relations

$$C_n^{k+1}(r) = -\frac{\partial C_n^k(r)}{\partial r}, \quad (E5)$$

$$S_n^{k+1}(r) = -\frac{\partial S_n^k(r)}{\partial r}, \quad (E6)$$

and the recurrent relations

$$C_{n+1}^k(r) = \frac{\partial}{\partial \alpha} \Big|_{\alpha=1} \{ \alpha^{2k-n-1} S_n^k(\alpha r) \}, \quad (E7)$$

$$S_{n+1}^k(r) = -\frac{\partial}{\partial \alpha} \Big|_{\alpha=1} \{ \alpha^{2k-n-1} C_n^k(\alpha r) \}, \quad (E8)$$

one obtains the following expressions for the integrals $C_n^k(r)$ and $S_n^k(r)$:

$$C_{2n}^k(r) = (-1)^{n+k-1} \left(\frac{1}{r} \frac{\partial}{\partial r} \right)^{k-1} \{ \pi r^{2n-1} \exp(-r) \}, \quad (E9)$$

$$\begin{aligned} C_{2n+1}^k(r) &= (-1)^{n+k-1} \left(\frac{1}{r} \frac{\partial}{\partial r} \right)^{k-1} \left\{ -r^{2n} E^+(r) \right. \\ &\quad \left. + 2 \sum_{i=0}^{n-1} (2i+1)! r^{2n-2i-2} \right\}, \end{aligned} \quad (E10)$$

$$\begin{aligned} S_{2n}^k(r) &= (-1)^{n+k-1} \left(\frac{1}{r} \frac{\partial}{\partial r} \right)^{k-1} \left\{ r^{2n-1} E^-(r) \right. \\ &\quad \left. - 2 \sum_{i=0}^{n-1} (2i)! r^{2n-2i-2} \right\}, \end{aligned} \quad (E11)$$

$$S_{2n+1}^k(r) = (-1)^{n+k-1} \left(\frac{1}{r} \frac{\partial}{\partial r} \right)^{k-1} \{ \pi r^{2n} \exp(-r) \}, \quad (E12)$$

where $E^\pm(r)$ is determined by Eq. (42). For example, performing differentiation in Eqs. (E9) and (E11) in the case $n = 0$, one obtains the following expressions for the integrals $C_0^k(r)$ and $S_0^k(r)$:

$$C_0^k(r) = \exp(-r) \sum_{i=k}^{2k-1} \frac{W_i^k}{r^i}, \quad (E13)$$

$$\begin{aligned} S_0^k(r) &= E^-(r) \sum_{i=[k/2]}^{k-1} \frac{X_i^k}{r^{2i+1}} + E^+(r) \sum_{i=[(k+1)/2]}^{k-1} \frac{Y_i^k}{r^{2i}} \\ &\quad - \sum_{i=[k/2]+1}^{k-1} \frac{Z_i^k}{r^{2i}}, \end{aligned} \quad (E14)$$

where the square brackets denote the integer part of the corresponding value and the coefficients W_i^k , X_i^k , Y_i^k , and Z_i^k are determined by the following expressions:

$$W_i^k \equiv \frac{\pi(i-1)!}{(2k-i-1)!(2i-2k)!!}, \quad (E15)$$

$$X_i^k \equiv \frac{(2i)!}{(2k-2i-2)!(4i-2k+2)!!}, \quad (E16)$$

$$Y_i^k \equiv \frac{(2i-1)!}{(2k-2i-1)!(4i-2k)!!}, \quad (\text{E17})$$

$$Z_i^k \equiv \frac{(2i-2)!!}{(2k-2i-1)!} \sum_{j=k}^{2i-1} \frac{(2j-2i-1)!!}{(j-i)(2j-2k)!!}. \quad (\text{E18})$$

Substituting Eq. (E13) into Eq. (E1) and using the relation

$$\int \frac{\exp(-r)}{r^i} dr = \frac{\exp(-r)}{(i-1)!} \sum_{j=1}^{i-1} \frac{(-1)^{i-j}(j-1)!}{r^j} + \frac{\text{Ei}(-r)}{(i-1)!} (-1)^{i-1}, \quad (\text{E19})$$

one obtains the following expression for the integral $C_{m,0}^k(x)$ in the case $k-m \geq 1$:

$$C_{m,0}^k(x) = \exp(-x) \sum_{j=1}^{2k-m-2} \frac{W_{m,j}^k}{x^j} + \text{Ei}(-x) V_m^k(k-m), \quad (\text{E20})$$

where the function $V_m^k(\alpha)$ and the coefficient $W_{m,j}^k$ are determined, respectively, by the following expressions:

$$V_m^k(\alpha) \equiv \sum_{i=\alpha}^{2k-m-1} \frac{W_{m,i}^k}{(i-1)!} (-1)^i, \quad (\text{E21})$$

$$W_{m,j}^k \equiv (-1)^{j-1} (j-1)! V_m^k(p), \quad (\text{E22})$$

where $p \equiv k-m$ if $j=1, \dots, (k-m-1)$, or $p \equiv j+1$ if $j=(k-m), \dots, (2k-m-2)$, and where the coefficients W_i^k are determined by Eq. (E15). For example, substituting $k=5$, $m=4$ into Eq. (E20), one obtains Eq. (40) for the integral $C_{4,0}^5$. Substituting $k=5$, $m=2$ into Eq. (E20), one obtains Eq. (75) for the integral $C_{2,0}^5$.

Substituting Eq. (E14) into Eq. (E2) and using the relations

$$\int \frac{E^-(r)}{r^{2i+1}} dr = -\frac{E^-(r)}{(2i)!} \sum_{j=0}^{i-1} \frac{(2j+1)!}{r^{2j+2}} + \frac{E^+(r)}{(2i)!} \sum_{j=0}^{i-1} \frac{(2j)!}{r^{2j+1}} + \frac{2}{(2i)!} \sum_{j=0}^{i-1} \frac{(2j)!}{(2j+1)r^{2j+1}} + \frac{2Q(r)}{(2i)!}, \quad (\text{E23})$$

$$\int \frac{E^+(r)}{r^{2i}} dr = -\frac{E^-(r)}{(2i-1)!} \sum_{j=0}^{i-2} \frac{(2j+1)!}{r^{2j+2}} + \frac{E^+(r)}{(2i-1)!} \sum_{j=0}^{i-1} \frac{(2j)!}{r^{2j+1}} + \frac{2}{(2i-1)!} \sum_{j=0}^{i-1} \frac{(2j)!}{(2j+1)r^{2j+1}} + \frac{2Q(r)}{(2i-1)!}, \quad (\text{E24})$$

where the function $Q(r)$ is determined by Eq. (43), one obtains the following expression for the integral $S_{2m,0}^{2k+1}(x)$ in the case $k-m \geq 0$:

$$S_{2m,0}^{2k+1}(x) = E^-(x) \sum_{j=0}^{2k-m-1} \frac{X_{m,j}^k}{x^{2j+2}} - E^+(x) \sum_{j=0}^{2k-m-1} \frac{Y_{m,j}^k}{x^{2j+1}} - \sum_{j=0}^{2k-m-1} \frac{Z_{m,j}^k}{x^{2j+1}} + 2Q(x) R_m^k(k-m, k-m+1), \quad (\text{E25})$$

where the function $R_m^k(\alpha, \beta)$ and the coefficients $X_{m,j}^k$, $Y_{m,j}^k$, $Z_{m,j}^k$ are determined, respectively, by the following expressions:

$$R_m^k(\alpha, \beta) \equiv \sum_{i=\alpha}^{2k-m} \frac{X_{m+i}^{2k+1}}{(2i)!} - \sum_{i=\beta}^{2k-m} \frac{Y_{m+i}^{2k+1}}{(2i-1)!}, \quad (\text{E26})$$

$$X_{m,j}^k \equiv (2j+1)! R_m^k(p, p+1), \quad (\text{E27})$$

$$Y_{m,j}^k \equiv (2j)! R_m^k(p, q), \quad (\text{E28})$$

$$Z_{m,j}^k \equiv \frac{1}{2j+1} [2(2j)! R_m^k(p, q) + \delta_{pq} Z_{m+j}^{2k+1}], \quad (\text{E29})$$

where $p \equiv k-m$, $q \equiv p+1$ and $\delta_{pq} \equiv 1$ if $j=0, \dots, (k-m-1)$, or $p \equiv j+1$, $q \equiv p$ and $\delta_{pq} \equiv 0$ if $j=(k-m), \dots, (2k-m-1)$, and where the coefficients X_i^k , Y_i^k , and Z_i^k are determined by Eqs. (E16)–(E18) respectively. For example, substituting $k=2$, $m=2$ into Eq. (E25), one obtains Eq. (41) for the integral $S_{4,0}^5$. Substituting $k=2$, $m=1$ into Eq. (E25), one obtains Eq. (76) for the integral $S_{2,0}^5$.

Performing differentiation in Eq. (E12) in the case $n=0$, one obtains the following expression for the integral $S_1^k(r)$:

$$S_1^k(r) = \exp(-r) \sum_{i=k-1}^{2k-3} \frac{F_i^k}{r^i}, \quad (\text{E30})$$

where

$$F_i^k \equiv \frac{\pi(i-1)!}{(2k-i-3)!(2i-2k+3)!!}. \quad (\text{E31})$$

Substituting Eq. (E30) into Eq. (E2) and using relation (E19), one obtains the following expression for the integral $S_{m,1}^k(x)$ in the case $k-m \leq 1$:

$$S_{m,1}^k(x) = \exp(-x) \sum_{j=k-m-1}^{2k-m-4} \frac{F_{m,j}^k}{x^j} + \text{Ei}(-x) G_m^k(1), \quad (\text{E32})$$

where the function $G_m^k(\alpha)$ and the coefficient $F_{m,j}^k$ are determined, respectively, by the following expressions:

$$G_m^k(\alpha) \equiv \sum_{i=\alpha}^{2k-m-3} \frac{F_{i+m}^k}{(i-1)!} (-1)^i, \quad (\text{E33})$$

$$F_{m,j}^k \equiv \begin{cases} \sum_{i=k-m-1}^j \frac{(-i)!}{(-j)!} F_{m+i}^k & \text{if } j = (k-m-1), \dots, 0 \\ (-1)^{j-1} (j-1)! G_m^k(j+1) & \text{if } j = 1, \dots, (2k-m-4), \end{cases} \quad (\text{E34})$$

where the coefficients F_i^k are determined by Eq. (E31). For example, substituting $k=5$, $m=4$ into Eq. (E32), one obtains Eq. (39) for the integral $S_{4,1}^5$.

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- [37] Chirality of geometrical objects assumes their biaxiality. Nevertheless, one can imagine a chiral object (for instance, a long intensive circle helix) that has negligible biaxiality. We call

such objects “quasiuniaxial.”

- [38] We omit the only number of the component $\mu=1$ in the case of the one-component liquid crystal.
- [39] One may apply the Parsons approach to the dilute solution of the minor spiral pieces in the coiled system.
- [40] In Eq. (B17) we keep only the terms oscillating with the mo-

lecular length ℓ , because the resting monotonic terms, being much larger than the oscillating ones, nevertheless are much smaller than the main monotonic term (B15). At the same time, it may be proved that all the oscillating terms that have been missed in Eq. (B15) are much smaller than any oscillating term in Eq. (B17).