Molecular theory of elastic constants of liquid crystals. II. Application to the biaxial nematic phase

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The expression of distortion free energy derived in our earlier paper [Phys. Rev. A **45**, 974 (1992)] is used to derive expressions for the 12 elastic constants of a biaxial nematic phase. These expressions are written in terms of order parameters characterizing the nature and amount of ordering in the phase and the structural parameters which involve the generalized spherical-harmonic coefficients of the direct pair correlation function of an effective isotropic liquid, the density of which is determined using a criterion of the weighted density-functional formalism. Using a reasonable guess for the values of the order and structural parameters we estimate the relative magnitudes of these constants. The values of three constants, which are associated with the deformations confined to a plane perpendicular to the principal director $\hat{\mathbf{N}}$, are (three or four) orders of magnitude smaller than the other constants. Two of the three mixed modes which arise because of biaxial ordering and vanish in the uniaxial phase are also about one order of magnitude smaller than other constants. In going from the uniaxial to the biaxial phase each constant associated with splay, twist, and bend splits into two and a mixed mode which in the uniaxial phase is just equal to the difference of splay and twist becomes a new constant. It is shown that the contributions to elastic constants arising from biaxial ordering and the departure from the axial molecular symmetry are small.

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I. INTRODUCTION

In a previous paper [1] of this series (hereafter referred to as I) we developed a theory based on the density-functional formalism [2] for the elastic constants of ordered phases of molecular systems (liquid crystals, plastic crystals, and crystalline solids) in terms of order parameters characterizing the nature and amount of ordering, and in terms of molecular correlations which characterize the structure of the system. The theory was applied to the uniaxial phases of liquid crystals; uniaxial nematic (N_u) and smectic-A (Sm-A) phases [1,3]. The purpose of this paper is to apply the theory to the biaxial nematic (N_b) phase in which the molecular asymmetry becomes manifest.

Predicted on a theoretical basis by Freiser [4] and Alben [5], the occurrence of the N_b phase was first observed by Yu and Saupe [6] in an amphiphilic system (potassium laurate–1-decanol–D_2O mixture). A few thermotropic materials have recently been prepared [7,8] which indicate the possibility of the N_b phase. These compounds combine the features of rods and disks [4,9]. Field-induced biaxiality has been observed [10,11] in the nematic phase. Computer simulation of Allen [12] on hard biaxial ellipsoids indicate that the transition from the isotropic to the biaxial phase occurs over a very narrow range of particle shapes and possibly just in the neighborhood of the so-called self-dual point (which occurs when one axis length is the geometric mean of the other two). Evidence of biaxiality has also been reported in certain nematic polymers [13,14].

Usually uniaxial nematic liquid crystals are visualized as a system consisting of rotationally symmetric ellipsoids, the orientational order of which is denoted by a unit-vector field $\hat{\mathbf{N}}$, commonly known as a director. The biaxiality of the nematic system can be thought of as a breaking of rotational symmetry of the ellipsoid around $\hat{\mathbf{N}}$. Thus the biaxial nematic phase can be visualized as a system that breaks all three rotational symmetries but none of the translational ones and consists of oriented ellipsoids with three different axes, or equivalently, of oriented bricks. Depending on the discrete symmetries these systems can vary widely. In principle, all familiar symmetry groups, orthorhombic, triclinic, hexagonal, cubic or even more exotic one, are admissible. The description of such a system requires two directors, denoted by $\hat{\mathbf{N}}(r)$, the principal director corresponding to the director of the N_u phase, and $\hat{\mathbf{M}}(r)$, the transverse director describing the rotation of the biaxial ellipsoids around the principal director. There exists interesting differences between the two nematic phases N_u and N_b. The uniaxial nematic—isotropic liquid transition is of first order whereas the N_u-N_b transition is second order. The theoretical prediction [15] that the critical behavior of the N_u-N_b transition should follow the XY model has recently been confirmed experimentally [16,17]. There are three basic types of line defects [18] in a N_b phase as compared to only one basic type in the N_u phase.

A number of continuum theories [19–27] has been developed to describe the elastic and hydrodynamic properties of a biaxial nematic phase. According to the one given by Saupe [19], the hydrodynamics of a compressible biaxial nematic phase with local orthorhombic symmetry can be expressed in terms of 12 elastic constants (excluding three constants contributing only to the surface energy) and 12 viscosity coefficients. Saupe theory was rederived [25] by adopting the Ericksen-Leslie approach [28–30] developed for the uniaxial nematic phase. Kini and Chandrasekhar [31] discussed the feasibility of determining some of the 12 elastic constants of an orthorhombic nematic phase by studying the elastic and viscous responses of the system under the action of external magnetic and electric fields. Using the formalism of tensor analysis Govers and Vertogen [26] derived the expression for the distortion free-energy density involving 12 elastic constants.

In Sec. II we summarize, for the sake of fixing the notations and completeness, the result of continuum theory. In Sec. III we use the expression of excess Helmholtz free energy of the deformed state derived in I using the density-functional approach and derive expressions for the elastic constants of the N_b phase from the second-order term in the expansion of the free energy around the free energy of the equilibrium (undeformed) state in the ascending powers of a parameter which measure the deformation. The first term of this expansion is balanced by the equilibrium "stresses" of the undeformed state. The elastic constants found in this way are expressed in terms of the order parameters which measure the nature and amount of ordering in the system and the direct pair correlation function (DPCF) of an *effective* isotropic liquid the density of which is obtained by weighting the physical density over a physically relevant range about the given point using a suitable weight factor [2,32]. In Sec. IV, we discuss the relative magnitude of these constants using a reasonable guess for the values of order parameters and structural parameters (which involve harmonic expansion coefficients of DPCF). Most of the mathematical details of our derivations are summarized in five appendixes.

In writing this paper we have assumed that the reader is familiar with previous papers of this series [1–3] and, therefore, we assume that the reader is also familiar with the density-functional expansion.

II. RESULT OF CONTINUUM THEORY

Let us consider only small deformations and assume that the preferred direction of orientation of molecules in an orthorhombic nematic phase (N_b) is described by an orthonormal triad of director vector fields $\hat{\mathbf{N}}$, $\hat{\mathbf{M}}$, and $\hat{\mathbf{L}}$. Let the orientation of the director triad at a point 1 be

$$\hat{\mathbf{L}}_0=(1,0,0);\ \hat{\mathbf{M}}_0=(0,1,0);\ \hat{\mathbf{N}}_0=(0,0,1) \tag{2.1}$$

and the orientation of director triad at a neighboring point $\mathbf{R}$ be

$$\hat{\mathbf{L}}=(1,L_y,L_z);\ \hat{\mathbf{M}}=(M_x,1,M_z);\ \hat{\mathbf{N}}=(N_x,N_y,1)\ . \tag{2.2}$$

It is important to mention that although the N_b phase is essentially described by two-order parameters, for convenience, we use [19,31] three vectors and express all the relevant quantities in terms of the three vectors. We refer to the (x,y) plane as the $(\hat{\mathbf{L}}_0,\hat{\mathbf{M}}_0)$ plane, etc. As $\hat{\mathbf{L}}$, $\hat{\mathbf{M}}$, $\hat{\mathbf{N}}$ are orthonormal, we get

$$M_x=-L_y;\ N_y=-M_z,\ \ L_z=-N_x\ . \tag{2.3}$$

Here it should be noted that only three out of the six perturbations are independent. If we rotate the director triad about $\hat{\mathbf{L}}$ by a small angle then $\hat{\mathbf{M}}$ and $\hat{\mathbf{N}}$ should both rotate about $\hat{\mathbf{L}}$ by the same angle.

To second order in director gradients, the elastic free energy is written as

$$\begin{aligned}\Delta A_e=\int dR\,[&\tfrac{1}{2}K_{LL}(M_{z,x})^2+\tfrac{1}{2}K_{MM}(N_{x,y})^2+\tfrac{1}{2}K_{NN}(L_{y,z})^2+\tfrac{1}{2}K_{LM}(L_{y,x})^2+\tfrac{1}{2}K_{MN}(M_{z,y})^2\\&+\tfrac{1}{2}K_{NL}(N_{x,z})^2+\tfrac{1}{2}K_{ML}(L_{y,y})^2+\tfrac{1}{2}K_{NM}(M_{z,z})^2+\tfrac{1}{2}K_{LN}(N_{x,x})^2-C_{LM}N_{x,x}M_{z,y}\\&-C_{MN}L_{y,y}N_{x,z}-C_{NL}M_{z,z}L_{y,x}+K_{0L}(L_{y,y}N_{x,z}-L_{y,z}N_{x,y})+K_{0M}(M_{z,z}L_{y,x}-M_{z,x}L_{y,z})\\&+K_{0N}(N_{x,x}M_{z,y}-N_{x,y}M_{z,x})]\ .\end{aligned} \tag{2.4}$$

Here a subscribed comma denotes partial differentiation with respect to the subscript (e.g., $M_{z,x}=\partial M_z/\partial x$). There is complete symmetry in Eq. (2.4) with respect to both $(\hat{\mathbf{L}},\hat{\mathbf{M}},\hat{\mathbf{N}})$ and (x,y,z). In Eq. (2.4) the twelve K's, and the three C's are curvature elastic constants. Three K's constants, K_{0L}, K_{0M}, and K_{0N} contribute only to the surface torque so that elastic equilibrium is determined by the nine K's and three C's constants.

To first order in the director gradients these elastic constants have the following significance: K_{LL}, K_{MM}, and K_{NN} represent, respectively, twists about $\hat{\mathbf{L}}$, $\hat{\mathbf{M}}$, and $\hat{\mathbf{N}}$. K_{ML}, K_{NM}, and K_{LN} represent splays of $\hat{\mathbf{L}}$ in the $(\hat{\mathbf{L}}_0,\hat{\mathbf{M}}_0)$ plane, of $\hat{\mathbf{M}}$ in the $(\hat{\mathbf{M}}_0,\hat{\mathbf{N}}_0)$ plane, and of $\hat{\mathbf{N}}$ in the $(\hat{\mathbf{N}}_0,\hat{\mathbf{L}}_0)$ plane, respectively. K_{LM}, K_{MN}, and K_{NL} represent, respectively, bends of $\hat{\mathbf{L}}$ in the $(\hat{\mathbf{L}}_0,\hat{\mathbf{M}}_0)$ plane, of $\hat{\mathbf{M}}$ in the $(\hat{\mathbf{M}}_0,\hat{\mathbf{N}}_0)$ plane, and of $\hat{\mathbf{N}}$ in the $(\hat{\mathbf{N}}_0,\hat{\mathbf{L}}_0)$ plane. All the three C's coefficients have similar interpretation. C_{LM} represents a simultaneous splay of $\hat{\mathbf{N}}$ in the $(\hat{\mathbf{L}}_0,\hat{\mathbf{N}}_0)$ plane and a bend of $\hat{\mathbf{M}}$ in the $(\hat{\mathbf{M}}_0,\hat{\mathbf{N}}_0)$ plane.

It must be noted that when we refer to "twist about $\hat{\mathbf{L}}$" we mean that $\hat{\mathbf{L}}$ remains unaltered but the director triad is rotated by a small angle about $\hat{\mathbf{L}}$ such that M_z and N_y appear ($N_y=-M_z$) and these are functions of $\mathbf{R}$.

For the N_u phase with uniaxial molecular order, an expression for the elastic energy in terms of the elastic constants was derived by Osean [33] and Frank [34]. Assuming that the director $\hat{\mathbf{N}}$ in the undistorted state is along the space-fixed (SF) z axis, one finds

$$\Delta A_{e,u}=\tfrac{1}{2}\int dR\,[K_1(N_{x,x}+N_{y,y})^2+K_2(N_{x,y}-N_{y,x})^2+K_3(N_{x,z}^2+N_{y,z}^2)-2(K_{22}+K_{24})(N_{x,x}N_{y,y}-N_{y,x}N_{x,y})]\ . \tag{2.5}$$

Here K_1, K_2, and K_3 denote, respectively, the splay, twist and bend Frank elastic constants. The last term of Eq. (2.5) reduces to a surface term. Comparing Eqs. (2.4) and (2.5) we note that in the uniaxial phase $M_x=-L_y=0$,

$$\begin{aligned} K_1&=K_{MN}=K_{LN} \ ,\\ K_2&=K_{LL}=K_{MM} \ ,\\ K_3&=K_{NL}=K_{NM} \ ,\\ K_1-K_2&=C_{LM} \ , \end{aligned} \tag{2.6}$$

and

$$K_{NN}=K_{LM}=K_{ML}=C_{MN}=C_{LN}=0 \ .$$

Thus, in going from uniaxial to biaxial phase the deformation modes of splay, twist, and bend split each into two modes. In addition, six new modes are developed.

III. ELASTIC CONSTANTS OF BIAXIAL NEMATIC PHASE

The expression found in I for the distortion free-energy density in the limit of long-wavelength distortion is written as

$$\frac{\beta\Delta A_e[\rho]}{V}=-\tfrac{1}{2}\rho_0^2\sum_{l_1,l_2,l}\ \sum_{m_1,m_2,m,m'}\ \sum_{n_1,n_2}\ \sum_{G}[(2l_1+1)(2l_2+1)]^{-1}C_g(l_1l_2l;m_1mm')Q_{l_1m_1n_1}(G)$$
$$\times Q_{l_2m_2n_2}(-G)\int d\mathbf{r}_{12}[\exp(i\mathbf{G}_e\cdot\mathbf{r}_{12})D^{l_2}_{mm_2}(\Delta\chi(\mathbf{r}_{12}))-\exp(i\mathbf{G}\cdot\mathbf{r}_{12})]y^{*}_{lm'}(\hat{\mathbf{r}}_{12})$$
$$\times C(l_1l_2l;n_1n_2;\mathbf{r}_{12}) \ . \tag{3.1}$$

Here $C_g(l_1l_2l;m_1mm')$ are Clebsch-Gordan coefficients, $D^l_{m,n}(\Omega)$ are the generalized spherical harmonics, and G is the reciprocal-lattice vectors of crystalline structure that might be present in the ordered phase. ρ_0 is the mean number density of the system and the subscript e stands for the quantity which corresponds to the distorted state of the system. $\Delta\chi(r_{12})$ represents the angle between the principal directors at R_1 and R_2. The order parameters which measure the nature and amount of ordering are defined in terms of the single-particle distribution $\rho(r,\Omega)$, i.e., [2]

$$Q_{lmn}(G)=\frac{2l+1}{N}\int d\mathbf{r}\int d\Omega\,\rho(\mathbf{r},\Omega)\exp[i\mathbf{G}\cdot\mathbf{r}]D^{l*}_{m,n}(\Omega) \ . \tag{3.2}$$

Since in a nematic liquid the centers of mass of the molecules move freely relative to one another as in the isotropic liquid, Eq. (3.2) reduces to

$$\begin{aligned} Q_{lmn}(0)&=(2l+1)\int d\Omega\,f(\Omega)D^{l*}_{m,n}(\Omega)\\ &=(2l+1)\bar{D}^l_{m,n} \ , \end{aligned}$$

where $\rho(r,\Omega)=\rho_n f(\Omega)$. Here ρ_n is the number density of the nematic liquid and $f(\Omega)$ is the orientational singlet distribution normalized to unity

$$\int d\Omega\, f(\Omega)=1 \ .$$

In Eq. (3.1), $C(l_1l_2l;\ n_1n_2;\ \mathbf{r}_{12})$ represents the harmonic expansion coefficient of the DPCF of an isotropic liquid in terms of the generalized spherical harmonics. In a SF frame this expansion is written as

$$C(r_{12},\Omega_1,\Omega_2)=\sum_{l_1,l_2,l}\ \sum_{m_1,m_2,m'}\ \sum_{n_1,n_2} C(l_1l_2l;n_1n_2;r_{12})C_g(l_1l_2l;m_1m_2m')D^{l_1*}_{m_1n_1}(\Omega_1)D^{l_2*}_{m_2n_2}(\Omega_2)y^{*}_{lm'}(\hat{\mathbf{r}}_{12}) \ . \tag{3.3}$$

In Eqs. (2.1) and (2.3) $\hat{\mathbf{r}}_{12}=\mathbf{r}_{12}/|\mathbf{r}_{12}|$ is a unit vector along the intermolecular axis.

The DPCF which appear in Eq. (3.1) is that of an effective isotropic reference fluid. The density of the effective fluid is found by any version of the weighted density-functional formalism [2]. In I and elsewhere [3] we generalized the formulation of Denton and Ashcroft [32] developed for the atomic fluids to the molecular systems. According to this scheme the density of the effective fluid is given as

$$\bar{\rho}[\rho]=\frac{1}{\rho_0 V}\int d\mathbf{x}_1\int d\mathbf{x}_2\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)\omega(\mathbf{x}_1,\mathbf{x}_2;\bar{\rho}) \ ,$$

where ω is a weight factor,

$$\omega(\mathbf{x}_1,\mathbf{x}_2,\bar{\rho})=-\frac{1}{2\Delta a'(\bar{\rho})}\left\{\beta^{-1}C(\mathbf{x}_1,\mathbf{x}_2;\bar{\rho})+\frac{1}{V}\bar{\rho}\Delta a''(\bar{\rho})\right\} \ .$$

Here $\Delta a(\bar{\rho})$ is the excess free energy per particle and the primes denote derivatives with respect to the density. $\bar{\rho}[\rho]$ is viewed here as a functional of $\rho(\mathbf{x})$.

As in a nematic phase there exists no positional ordering; the distortion free-energy density of Eq. (3.1) can be expressed as

$$\frac{1}{V}\beta\Delta A_e[\rho]=-\tfrac{1}{2}\rho_n^2 \sum_{l_1,l_2,l} \sum_{m_1,m_2m,m'} \sum_{n_1,n_2} [(2l_1+1)(2l_2+1)]^{-1}C_g(l_1l_2l,m_1mm') \times Q_{l_1m_1n_1}(0)Q_{l_2m_2n_2}(0)\int d\mathbf{r}_{12}[D^{l_2}_{mm_2}(\Delta\chi(\mathbf{r}_{12}))-1]y^*_{lm'}(\hat{\mathbf{r}}_{12})C(l_1l_2l,n_1n_2;\mathbf{r}_{12}) . \tag{3.4}$$

As noted in Sec. II, the main task is to compare the orientation of director triad $(\hat{\mathbf{L}},\hat{\mathbf{M}},\hat{\mathbf{N}})$ at a point $\mathbf{R}$ from the origin with its orientation at some neighboring point $\mathbf{R}+\mathbf{r}$ (Fig. 1). This helps us in extracting the relevant gradients of the director fields. Since the orientation of the director triad can be uniquely specified by three angles, we express the director components in terms of three Eulerian angles (Appendixes A and C).

We write the rotation matrix $D^{l_2}_{mm_2}(\Delta\chi(\mathbf{r}))$, which describe the rotation of the director triad at $\mathbf{R}+\mathbf{r}$ with respect to the director triad at $\mathbf{R}$ as

$$D^{l_2}_{mm_2}(\Delta\chi(\mathbf{r}))=e^{im\alpha'}d^{l_2}_{mm_2}(\beta')e^{im_2\gamma'} , \tag{3.5}$$

where α', β', γ' are the Euler angles. Assuming that (see Appendix C)

$$\xi'=\alpha'+\gamma'$$

and using the result of Appendix C [Eqs. (C9) and (C10)],

$$\alpha'=0_1;\ \beta'=0_s;\ \gamma'=-(\alpha'-\xi')=0_1$$

we write

$$D^{l_2}_{mm_2}(\Delta\chi(r))=e^{i(m-m_2)\alpha'}d^{l_2}_{mm_2}(\beta')e^{im_2\xi'} . \tag{3.6}$$

Since β' is small (weak deformation), we expand $d^{l_2}_{mm_2}$ in terms of the powers of β',

$$d^{l_2}_{mm_2}(\beta')=d^{l_2}_{mm_2}(0)+d'\beta'+\tfrac{1}{2}d''\beta'^2+\cdots , \tag{3.7}$$

where

$$d^{l_2}_{mm_2}(0)=\delta_{m,m_2} , \tag{3.8}$$

$$d'\equiv\left.\frac{\partial d^{l_2}_{mm_2}(\beta')}{\partial\beta'}\right|_{\beta'=0} =-\tfrac{1}{2}\{[(l_2+m)(l_2-m_2)]^{1/2}\delta_{m'm_2+1} -[(l_2-m)(l_2+m_2)]^{1/2}\delta_{m,m_2-1}\} , \tag{3.9}$$

and

$$d''\equiv\left.\frac{\partial^2 d^{l_2}_{mm_2}(\beta')}{\partial\beta'^2}\right|_{\beta'=0} =\tfrac{1}{4}\{[(l_2+m)(l_2-m+1)(l_2+m_2+1)(l_2-m_2)]^{1/2}\delta_{m,m_2+2}-[(l_2+m)(l_2-m+1)(l_2-m_2+1)(l_2+m_2)]^{1/2}\delta_{m,m_2} -[(l_2-m)(l_2+m+1)(l_2+m_2+1)(l_2-m_2)]^{1/2}\delta_{m,m_2} +[(l_2-m)(l_2+m+1)(l_2-m_2+1)(l_2+m_2)]^{1/2}\delta_{m,m_2-2}\} . \tag{3.10}$$

Expanding $e^{im_2\xi'}$ terms in Eq. (3.7) and retaining the terms up to the second order, we get

$$D^{l_2}_{mm_2}(\Delta\chi(\mathbf{r}))=e^{i(m-m_2)\alpha'}\delta_{m,m_2}+d'\beta'e^{i(m-m_2)\alpha'}+\tfrac{1}{2}d''\beta'^2e^{i(m-m_2)\alpha'}+im_2\xi'\delta_{m,m_2}e^{i(m-m_2)\alpha'} -\tfrac{1}{2}m_2^2\xi'^2\delta_{m,m_2}e^{i(m-m_2)\alpha'}+d'\beta'e^{i(m-m_2)\alpha'}im_2\xi' . \tag{3.11}$$

Substituting Eq. (3.11) into Eq. (3.4) and using the results of Appendix C, i.e., Eqs. (C11) and (C12), we write the distortion free-energy density in terms of the director components.

$$\frac{1}{V}\beta\Delta A_e[\rho]=-\tfrac{1}{2}\rho_n^2 \sum_{l_1,l_2,l} \sum_{m_1,m_2m,m'} \sum_{n_1,n_2} [(2l_1+1)(2l_2+1)]^{-1}Q_{l_1m_1n_1}(0)Q_{l_2m_2n_2}(0) \times\int d\mathbf{r}[(a_{11}+a_{12})\underline{\sigma}_1^{(3)'}+i(a_{11}-a_{12})\underline{\sigma}_2^{(3)'}+ib_2\underline{\sigma}_2^{(1)'} +(a_{21}+a_{22}+a_{23})(\underline{\sigma}_1^{(3)'})^2+(a_{23}-a_{22}-a_{21})(\underline{\sigma}_2^{(3)'})^2 -\tfrac{1}{2}b_2^2(\underline{\sigma}_2^{(1)'})^2+i(2a_{21}-2a_{22}+\tfrac{1}{2}b_2)\underline{\sigma}_1^{(3)'}\underline{\sigma}_2^{(3)'} +im_2(a_{11}+a_{12})\underline{\sigma}_1^{(3)'}\underline{\sigma}_2^{(1)'}+m_2(a_{12}-a_{11})\underline{\sigma}_2^{(3)'}\underline{\sigma}_2^{1'}] \times C(l_1l_2l;n_1n_2;r_{12})y^*_{lm'}(\hat{\mathbf{r}}) , \tag{3.12}$$

where

$$\underline{\alpha}_1^{(3)'}=\beta'\cos\alpha' \qquad (3.13a)$$

$$\underline{\alpha}_2^{(3)'}=\beta'\sin\alpha' \qquad (3.13b)$$

$$\underline{\alpha}_2^{(1)'}=\xi'-\tfrac{1}{2}\beta'^2\sin\alpha'\cos\alpha' , \qquad (3.13c)$$

$$a_{11}=-\tfrac{1}{2}\{(l_2+m_2+1)(l_2-m_2)\}^{1/2} \times C_g(l_1l_2l,m_1m_2+1,m') , \qquad (3.13d)$$

$$a_{12}=\tfrac{1}{2}\{(l_2-m_2+1)(l_2+m_2)\}^{1/2} \times C_g(l_1l_2l,m_1m_2-1,m') , \qquad (3.13e)$$

$$a_{21}=\tfrac{1}{8}\{(l_2+m_2+2)(l_2-m_2-1) \times(l_2+m_2+1)(l_2-m_2)\}^{1/2} \times C_g(l_1l_2l,m_1m_2+2,m') \qquad (3.13f)$$

$$a_{22}=\tfrac{1}{8}\{(l_2+m_2+2)(l_2+m_2-1) \times(l_2-m_2+1)(l_2+m_2)\}^{1/2} \times C_g(l_1l_2l,m_1m_2-2,m') , \qquad (3.13g)$$

$$a_{23}=-\tfrac{1}{8}\{(l_2+m_2)(l_2-m_2+1) +(l_2-m_2)(l_2+m_2+1)\} \times C_g(l_1l_2l,m_1m_2m') , \qquad (3.13h)$$

$$b_2=C_g(l_1l_2l,m_1m_2m')m_2 , \qquad (3.13i)$$

$$b_2^2=C_g(l_1l_2l,m_1m_2m')m_2^2 . \qquad (3.13j)$$

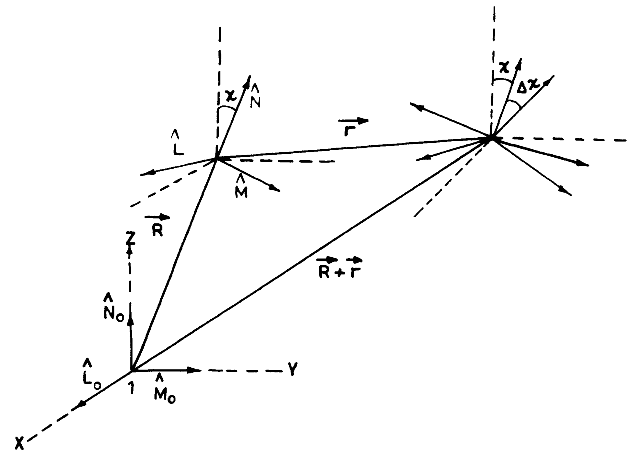

FIG. 1. Deviation angle for director triad at **R**+**r** with respect to director triad at **R**.

In Appendixes B and C [Eqs. (B9) and (C4)] we express each basic deformation variable in terms of coordinates of intermolecular separation r_{12}. The expressions for elastic constants are derived by comparing free-energy density relation with the continuum relation. We write the continuum relation (1.4) in terms of the director components in Appendix D. Retaining only those terms which appear in the continuum relation [Eq. (D4)], we write Eq. (2.12) as

$$\begin{aligned}
\frac{\beta\Delta A_e[\rho]}{V}=&-\tfrac{1}{2}\rho_n^2\sum_{l_1,l_2,l}\sum_{m_1,m_2,m'}\sum_{n_1,n_2}[(2l_1+1)(2l_2+1)]^{-1}Q_{l_1m_1n_1}(0)Q_{l_2m_2n_2}(0)\\
&\times\int r^2dr\int d\hat{\mathbf{r}}(\tfrac{1}{2}B_1^{(3)^2}\{(q_1^2+q_3^2)(\hat{\mathbf{r}}\cdot\hat{\mathbf{x}})(\hat{\mathbf{r}}\cdot\hat{\mathbf{y}})(a_{11}+a_{12})+(a_{21}+a_{22}+a_{23})[q_1^2(\hat{\mathbf{r}}\cdot\hat{\mathbf{x}})^2+q_2^2(\hat{\mathbf{r}}\cdot\hat{\mathbf{y}})^2+q_3^2(\hat{\mathbf{r}}\cdot\hat{\mathbf{z}})^2]\}\\
&+\tfrac{1}{2}B_2^{(3)^2}\{i(a_{11}-a_{12})(-q_2^2+q_3^2)(\hat{\mathbf{r}}\cdot\hat{\mathbf{y}})(\hat{\mathbf{r}}\cdot\hat{\mathbf{z}})+(a_{23}-a_{22}-a_{21})[+q_1^2(\hat{\mathbf{r}}\cdot\hat{\mathbf{x}})^2+q_2^2(\hat{\mathbf{r}}\cdot\hat{\mathbf{y}})^2+q_3^2(\hat{\mathbf{r}}\cdot\hat{\mathbf{z}})^2]\}\\
&+\tfrac{1}{2}B_2^{(1)^2}\{ib_2(-q_2^2+q_1^2)(\hat{\mathbf{r}}\cdot\hat{\mathbf{x}})(\hat{\mathbf{r}}\cdot\hat{\mathbf{y}})-\tfrac{1}{4}b_2^2[q_1^2(\hat{\mathbf{r}}\cdot\hat{\mathbf{x}})^2+q_2^2(\hat{\mathbf{r}}\cdot\hat{\mathbf{y}})^2+q_3^2(\hat{\mathbf{r}}\cdot\hat{\mathbf{z}})^2]\}\\
&+\{2i(a_{21}-a_{22})(\hat{\mathbf{r}}\cdot\hat{\mathbf{x}})(\hat{\mathbf{r}}\cdot\hat{\mathbf{y}})-\tfrac{1}{2}(a_{11}+a_{12})(\hat{\mathbf{r}}\cdot\hat{\mathbf{x}})(\hat{\mathbf{r}}\cdot\hat{\mathbf{z}})-\tfrac{1}{2}i(a_{11}-a_{12})(\hat{\mathbf{r}}\cdot\hat{\mathbf{y}})(\hat{\mathbf{r}}\cdot\hat{\mathbf{z}})\}\\
&\times q_1q_2B_1^{(3)}B_2^{(3)}+\{\tfrac{1}{2}ib_2(\hat{\mathbf{r}}\cdot\hat{\mathbf{x}})(\hat{\mathbf{r}}\cdot\hat{\mathbf{y}})-\tfrac{1}{2}(a_{11}+a_{12})(\hat{\mathbf{r}}\cdot\hat{\mathbf{x}})(\hat{\mathbf{r}}\cdot\hat{\mathbf{z}})\\
&\qquad+i[\tfrac{1}{2}(a_{11}-a_{12})+m_2(a_{11}+a_{12})](\hat{\mathbf{r}}\cdot\hat{\mathbf{y}})(\hat{\mathbf{r}}\cdot\hat{\mathbf{z}})\}q_2q_3B_1^{(3)}B_2^{(1)}\\
&+\{\tfrac{1}{2}ib_2(\hat{\mathbf{r}}\cdot\hat{\mathbf{x}})(\hat{\mathbf{r}}\cdot\hat{\mathbf{y}})+[m_2(a_{12}-a_{11})-\tfrac{1}{2}(a_{11}+a_{12})](\hat{\mathbf{r}}\cdot\hat{\mathbf{x}})(\hat{\mathbf{r}}\cdot\hat{\mathbf{z}})\\
&-\tfrac{1}{2}i(a_{11}-a_{12})(\hat{\mathbf{r}}\cdot\hat{\mathbf{y}})(\hat{\mathbf{r}}\cdot\hat{\mathbf{z}})\}q_1q_3B_2^{(3)}B_2^{(1)})y_{lm'}^*(\hat{\mathbf{r}})C(l_1l_2l,n_1n_2,r) . \qquad (3.14)
\end{aligned}$$

After performing the angular integrations over $\hat{\mathbf{r}}$, we compare Eq. (3.10) with Eq. (D4) and obtain relations for the elastic constants.

$$\begin{aligned}
\beta K_{LL}=&-\rho_n^2\sum_{l_1,l_2}\sum_{m_1,m_2}\sum_{n_1,n_2}\bar{D}_{m_1n_1}^{l_1*}\bar{D}_{m_2n_2}^{l_2*}J_{l_1l_2l}^{n_1n_2}\\
&\times\left[(a_{23}-a_{22}-a_{21})\left\{\frac{1}{3}(4\pi)^{1/2}\delta_{l0}\delta_{m'0}-\left[\frac{4\pi}{45}\right]^{1/2}\delta_{l2}\delta_{m'0}+\left[\frac{2\pi}{15}\right]^{1/2}\delta_{l2}\delta_{m'2}\right.\right.\\
&\left.\left.+\left[\frac{2\pi}{15}\right]^{1/2}\delta_{l2}\delta_{m'\underline{2}}\right\}\right] , \qquad (3.15)
\end{aligned}$$

$$\beta K_{MM} = -\rho_n^2 \sum_{l_1,l_2} \sum_{m_1,m_2} \sum_{n_1,n_2} \bar{D}^{l_1 *}_{m_1 n_1} \bar{D}^{l_2 *}_{m_2 n_2} J^{n_1 n_2}_{l_1 l_2 l} \left[(a_{21}+a_{22}+a_{23}) \left\{ \frac{1}{3}(4\pi)^{1/2}\delta_{l0}\delta_{m'0} - \left(\frac{4\pi}{45} \right)^{1/2} \delta_{l2}\delta_{m'0} - \left(\frac{2\pi}{15} \right)^{1/2} \delta_{l2}\delta_{m'2} - \left(\frac{2\pi}{15} \right)^{1/2} \delta_{l2}\delta_{m'\underline{2}} \right\} \right] , \tag{3.16}$$

$$\beta K_{NN} = -\rho_n^2 \sum_{l_1,l_2} \sum_{m_1,m_2} \sum_{n_1,n_2} \bar{D}^{l_1 *}_{m_1 n_1} \bar{D}^{l_2 *}_{m_2 n_2} J^{n_1 n_2}_{l_1 l_2 l} (-\tfrac{1}{2} b_2^2) \left\{ \frac{1}{3}(4\pi)^{1/2}\delta_{l0}\delta_{m'0} + \left(\frac{16\pi}{45} \right)^{1/2} \delta_{l2}\delta_{m'0} \right\} , \tag{3.17}$$

$$\beta K_{LM} = -\rho_n^2 \sum_{l_1,l_2} \sum_{m_1,m_2} \sum_{n_1,n_2} \bar{D}^{l_1 *}_{m_1 n_1} \bar{D}^{l_2 *}_{m_2 n_2} J^{n_1 n_2}_{l_1 l_2 l} \left[b_2 \left(\frac{32\pi}{15} \right)^{1/2} (\delta_{l2}\delta_{m'2} - \delta_{l2}\delta_{m'\underline{2}}) - \tfrac{1}{2} b_2^2 \left\{ \frac{1}{3}(4\pi)^{1/2}\delta_{l0}\delta_{m'0} - \left(\frac{4\pi}{45} \right)^{1/2} \delta_{l2}\delta_{m'0} + \left(\frac{2\pi}{15} \right)^{1/2} \delta_{l2}\delta_{m'2} + \left(\frac{2\pi}{15} \right)^{1/2} \delta_{l2}\delta_{m'\underline{2}} \right\} \right] , \tag{3.18}$$

$$\beta K_{MN} = -\rho_n^2 \sum_{l_1,l_2} \sum_{m_1,m_2} \sum_{n_1,n_2} \bar{D}^{l_1 *}_{m_1 n_1} \bar{D}^{l_2 *}_{m_2 n_2} J^{n_1 n_2}_{l_1 l_2 l} \left[\frac{1}{2} \left(\frac{8\pi}{15} \right)^{1/2} (a_{11}-a_{12}) \{ \delta_{l2}\delta_{m'1} + \delta_{l2}\delta_{m'\underline{1}} \} + (a_{23}-a_{22}-a_{21}) \times \left\{ \frac{1}{3}(4\pi)^{1/2}\delta_{l0}\delta_{m'0} - \left(\frac{4\pi}{45} \right)^{1/2} \delta_{l2}\delta_{m'0} - \left(\frac{2\pi}{15} \right)^{1/2} \delta_{l2}\delta_{m'2} - \left(\frac{2\pi}{15} \right)^{1/2} \delta_{l2}\delta_{m'\underline{2}} \right\} \right] , \tag{3.19}$$

$$\beta K_{NL} = -\rho_n^2 \sum_{l_1,l_2} \sum_{m_1,m_2} \sum_{n_1,n_2} \bar{D}^{l_1 *}_{m_1 n_1} \bar{D}^{l_2 *}_{m_2 n_2} J^{n_1 n_2}_{l_1 l_2 l} \left[\frac{1}{2} \left(\frac{8\pi}{15} \right)^{1/2} (a_{11}+a_{12}) \{ \delta_{l2}\delta_{m'\underline{1}} - \delta_{l2}\delta_{m'1} \} + (a_{21}+a_{22}+a_{23}) \left\{ \frac{1}{3}(4\pi)^{1/2}\delta_{l0}\delta_{m'0} + \left(\frac{16\pi}{45} \right)^{1/2} \delta_{l2}\delta_{m'0} \right\} \right] , \tag{3.20}$$

$$\beta K_{ML} = -\rho_n^2 \sum_{l_1,l_2} \sum_{m_1,m_2} \sum_{n_1,n_2} \bar{D}^{l_1 *}_{m_1 n_1} \bar{D}^{l_2 *}_{m_2 n_2} J^{n_1 n_2}_{l_1 l_2 l} \left[b_2 \left(\frac{32\pi}{15} \right)^{1/2} \{ \delta_{l2}\delta_{m'\underline{2}} - \delta_{l2}\delta_{m'2} \} - \tfrac{1}{2} b_2^2 \left\{ \frac{1}{3}(4\pi)^{1/2}\delta_{l0}\delta_{m'0} - \left(\frac{4\pi}{45} \right)^{1/2} \delta_{l2}\delta_{m'0} - \left(\frac{2\pi}{15} \right)^{1/2} \delta_{l2}\delta_{m'2} - \left(\frac{2\pi}{15} \right)^{1/2} \delta_{l2}\delta_{m'\underline{2}} \right\} \right] , \tag{3.21}$$

$$\beta K_{NM} = -\rho_n^2 \sum_{l_1,l_2} \sum_{m_1,m_2} \sum_{n_1,n_2} \bar{D}^{l_1 *}_{m_1 n_1} \bar{D}^{l_2 *}_{m_2 n_2} J^{n_1 n_2}_{l_1 l_2 l} \left[\frac{1}{2} \left(\frac{8\pi}{15} \right)^{1/2} (a_{11}-a_{12}) \{ \delta_{l2}\delta_{m'\underline{1}} - \delta_{l2}\delta_{m'1} \} + (a_{23}-a_{22}-a_{21}) \left\{ \tfrac{1}{3}(4\pi)^{1/2}\delta_{l0}\delta_{m'0} + \left(\frac{16\pi}{45} \right)^{1/2} \delta_{l2}\delta_{m'0} \right\} \right] , \tag{3.22}$$

$$\beta K_{LN} = -\rho_n^2 \sum_{l_1,l_2} \sum_{m_1,m_2} \sum_{n_1,n_2} \bar{D}^{l_1 *}_{m_1 n_1} \bar{D}^{l_2 *}_{m_2 n_2} J^{n_1 n_2}_{l_1 l_2 l} \left[\frac{1}{2} \left(\frac{8\pi}{15} \right)^{1/2} (a_{11}+a_{12}) \{ \delta_{l2}\delta_{m'1} - \delta_{l2}\delta_{m'\underline{1}} \} + (a_{21}+a_{22}+a_{23}) \left\{ \frac{1}{3}(4\pi)^{1/2}\delta_{l0}\delta_{m'0} - \left(\frac{4\pi}{45} \right)^{1/2} \delta_{l2}\delta_{m'0} + \left(\frac{2\pi}{15} \right)^{1/2} \delta_{l2}\delta_{m'2} + \left(\frac{2\pi}{15} \right)^{1/2} \delta_{l2}\delta_{m'\underline{2}} \right\} \right] , \tag{3.23}$$

$$\beta C_{LM} = -\rho_n^2 \bar{D}^{l_1 *}_{m_1 n_1} \bar{D}^{l_2 *}_{m_2 n_2} J^{n_1 n_2}_{l_1 l_2 l} \times \left[\frac{1}{2} \left[\frac{32\pi}{15} \right]^{1/2} (a_{21} - a_{22}) \{ \delta_{l2}\delta_{m'2} - \delta_{l2}\delta_{m'\underline{2}} \} + \frac{1}{4} \left[\frac{8\pi}{15} \right]^{1/2} (a_{11} + a_{12}) \{ \delta_{l2}\delta_{m'1} - \delta_{l2}\delta_{m'\underline{1}} \} + \frac{1}{4} \left[\frac{8\pi}{15} \right]^{1/2} (a_{11} - a_{12}) \{ \delta_{l2}\delta_{m'\underline{1}} + \delta_{l2}\delta_{m'1} \} \right], \tag{3.24}$$

$$\beta C_{MN} = \rho_n^2 \bar{D}^{l_1 *}_{m_1 n_1} \bar{D}^{l_2 *}_{m_2 n_2} J^{n_1 n_2}_{l_1 l_2 l} \left[\frac{1}{8} b_2 \left[\frac{32\pi}{15} \right]^{1/2} \{ \delta_{l2}\delta_{m'2} - \delta_{l2}\delta_{m'\underline{2}} \} + \frac{1}{4} (a_{11} + a_{12}) \left[\frac{8\pi}{15} \right]^{1/2} \{ \delta_{l2}\delta_{m'1} - \delta_{l2}\delta_{m'\underline{1}} \} + \frac{1}{2} \{ \tfrac{1}{2}(a_{11} - a_{12}) + m_2(a_{11} + a_{12}) \} \left[\frac{8\pi}{15} \right]^{1/2} \{ \delta_{l2}\delta_{m'\underline{1}} + \delta_{l2}\delta_{m'1} \} \right], \tag{3.25}$$

$$\beta C_{NL} = -\rho_n^2 \bar{D}^{l_1 *}_{m_1 n_1} \bar{D}^{l_2 *}_{m_2 n_2} J^{n_1 n_2}_{l_1 l_2 l} \left[\frac{1}{8} b_2 \left[\frac{32\pi}{15} \right]^{1/2} \{ \delta_{l2}\delta_{m'2} - \delta_{l2}\delta_{m'\underline{2}} \} - \frac{1}{2} \left[\frac{8\pi}{15} \right]^{1/2} \{ m_2(a_{12} - a_{11}) - \tfrac{1}{2}(a_{11} + a_{12}) \} \{ \delta_{l2}\delta_{m'1} - \delta_{l2}\delta_{m'\underline{1}} \} - \tfrac{1}{4}(a_{11} - a_{12}) \left[\frac{8\pi}{15} \right]^{1/2} \{ \delta_{l2}\delta_{m'\underline{1}} + \delta_{l2}\delta_{m'1} \} \right], \tag{3.26}$$

where

$$J^{n_1 n_2}_{l_1 l_2 l} = \int r^4 dr\, C(l_1 l_2 l, n_1 n_2, r) \tag{3.27}$$

are the structural parameters. A line under a numerical subscript denotes a negative quantity.

Equations (3.15)–(3.26) give general expressions for the 12 elastic constants in the long-wavelength limit of a biaxial nematic liquid crystal. From these equations we derive expressions for the elastic constants of the uniaxial phase of nonaxial molecules by putting all terms involving order parameters $\bar{D}^l_{m,n}$ with $m \neq 0$ equal to zero. The results found this way satisfy Eq. (2.6). As is shown below, however, the contribution due to the breaking of the axial molecular symmetry to the elastic constants is small which is in agreement with the experimentally observed results [35]. If in the above expressions we retain only terms involving order parameters $\bar{D}^l_{00}$ and put all other terms equal to zero we get expressions given in I for the uniaxial nematic phase.

IV. DISCUSSION

In order to calculate the values of elastic constants given above one needs the values of the order parameters, generalized harmonic coefficients of the DPCF of an effective fluid as a function of the temperature and density and the information about the constituent molecules, viz., electric multipole moments, geometry of the repulsive core, length-to-width ratio, etc. as input parameters. In the limit of long-wavelength distortion, it is assumed that the magnitude of the order parameters is not affected due to the distortion; it is only the direction of the directors which becomes position dependent. Thus, one may use the value of the order parameters either determined experimentally or calculated from theory. The c harmonics for a given system can, in principle, be found either by solving the Ornstein-Zernike equation with suitable closure relations [36] or by adopting a perturbation scheme which is based on the fact that the fluid structure at high densities is primarily controlled by the repulsive part of the interactions. However, such calculations for nonaxial molecules are very complicated and may need enormous computational efforts to generate reliable data for c harmonics [37].

In what follows, we therefore restrict our attempts to a system of rigid molecules possessing three mutually orthogonal mirror planes with inversion symmetry through their intersection, e.g., ellipsoids with three different axes or spheroplatelets. Ordered phase (here it refers to N_b) is also assumed to have the same symmetry as the constituent molecules. Thus, to characterize the system, we choose four order parameters [38] $\bar{P}$, $\bar{\eta}$, $\bar{\mu}$, and $\bar{\tau}$. The order parameter $\bar{P} = \bar{D}^2_{0,0} = \langle \tfrac{1}{2}(3\cos^2\theta - 1) \rangle$ measures the alignment of the molecular e_z axis along the SF z axis (or the director $\hat{\mathbf{N}}$). The order parameter $\bar{\eta} = \bar{D}^2_{0,2} = \langle \tfrac{1}{2}\sqrt{3}\sin^2\theta\cos 2\psi \rangle$ is an indicator of the difference in alignment of the molecular e_x and e_y axes along the director. If the molecules are axially symmetric, the molecular e_x and e_y axes are indistinguishable and $\bar{\eta}$ vanishes. The other two order parameters $\bar{\mu} = \bar{D}^2_{2,0} = \langle \tfrac{1}{2}\sqrt{3}\sin^2\theta\cos 2\phi \rangle$ and $\bar{\tau} = \bar{D}^2_{2,2} = \langle \tfrac{1}{2}(1 + \cos^2\theta)\cos 2\phi\cos 2\psi - \cos\theta\sin^2\phi\sin 2\psi \rangle$ are the measure of the biaxial ordering in the system. If the phase is uniaxial, $\bar{\mu}$ and $\bar{\tau}$ vanish. Introduction of biaxiality in the molecular shape and/or in the intermolecular interaction has been found [37,39] to have pronounced effects on the isotropic-uniaxial nematic (I-N_u) transition; both the order parameters and the first orderedness of the I-N_u transition are greatly reduced from that of the comparable uniaxial bodies.

In Appendix E we give explicit results for all 12 constants in terms of these order parameters. To have an order-of-magnitude estimate of the contributions arising due to different ordering to elastic constants, we assume that

$$\bar{\eta}/\bar{P} \simeq \bar{\mu}/\bar{P} \sim 0.1, \quad \bar{\tau}/\bar{P} \sim 0.01$$

$$J^{22}_{22i}/J^{00}_{22i} \sim 0.2 \ ,$$

and

$$J^{02}_{22i}/J^{00}_{22i} \sim (J^{22}_{22i}/J^{00}_{22i})^{1/2} \sim 0.45 \ ,$$

where $i=0$ or 2. Although it is difficult to prove the correctness of these values, they are believed [37,39] to provide a reasonable estimate for any real system.

We note that the first terms in K_{LL} and K_{MM} [see Eqs. (E1) and (E2)] are equal to $K_2(2,2)$ of I (see Eq. (A7) of [1] and note that $J^{00}_{22i}=(5/4\pi)J_{22i}$). The next two terms in their expressions are due to the breaking of axial symmetry of molecules. The contribution of these terms is of the order of 5% of that of the first term. The remaining three terms of Eqs. (E1) and (E2) are due to the ordering that makes the system biaxial. The combined contribution of these terms is of the order of 5% or less. Thus, while the elastic constants associated with twists about $\hat{\mathbf{L}}$ and $\hat{\mathbf{M}}$ axes have magnitudes nearly equal to that of K_2 ($\sim 10^{-6}$ dyn), the twist elastic constant of the uniaxial phase, the magnitude of K_{NN} which represents the twist about the $\hat{\mathbf{N}}$ axis [i.e., the twist is confined in the $(\hat{\mathbf{L}}_0,\hat{\mathbf{M}}_0)$ plane] is about 3 or 4 orders of magnitude smaller than K_2. Similarly, we find that K_{LM} and K_{ML} [see Eqs. (E3) and (E4)], which represent, respectively, the splay and bend of L in the $(\hat{\mathbf{L}}_0,\hat{\mathbf{M}}_0)$ plane, are very small compared to K_1 or K_3.

As is noted in I, in a N_u phase, $K_1(2,2)=K_3(2,2)$. This equality may be seen from Eqs. (E5)–(E9) by $\bar{\mu}$ and $\bar{\tau}$ equal to zero. The first term in these equations is equal to expression $K_1(2,2)$ or $K_3(2,2)$ given in Appendix A of [1]. The terms that involve $\bar{\eta}$ are due to a departure from axial symmetry in the molecular shape. As noted in the case of the twist constant, their contribution to elastic constants is small. The contribution of terms arising due to ordering giving rise to biaxiality in the phase is also small. Among the three C constants associated with mixed modes of deformation, we find that one, i.e., C_{LM}, is about ten times larger than the other two. It may also be noted that only this constant survives in the uniaxial phase where it becomes equal to K_1-K_2 [see Eq. (2.6)], and the other two, which at this level of approximation are equal in magnitude, vanish in uniaxial phase.

Since for a realistic potential model J^{00}_{222} is negative (see Fig. 4 of [1]) we conclude from Eqs. (E10)–(E12) that while $C_{LM}(2,2)$ and $C_{MN}(2,2)$ are positive, $C_{NL}(2,2)$ is negative. In general, as argued by Kini and Chandrasekhar [31], the determination of the signs of the C's is experimentally difficult. When a symmetric initial orientation is subjected to a destabilizing field in some arbitrary direction, deformation can set in without a threshold. In this case, the elastic response will also involve the C's. A study of the deformation for different fields should yield an estimate of the magnitudes of the C's. The sign of the C constants can, however, be determined by the conoscopic observations [31].

From the above results, one therefore concludes that the three constants, viz., K_{NN}, K_{LM}, and K_{ML}, which are associated with deformation in the $(\hat{\mathbf{L}}_0, \hat{\mathbf{M}}_0)$ plane (the principal director $\hat{\mathbf{N}}$ is perpendicular to this plane in the undeformed state), are of the order of 10^{-9} or 10^{-10} dyn, which is three or four orders of magnitude smaller than the value of the constants found in the N_u phase. The constant C_{MN}, associated with the mode of deformation representing simultaneous splay of $\hat{\mathbf{L}}$ in the $(\hat{\mathbf{M}}_0,\hat{\mathbf{L}}_0)$ plane and a bend of $\hat{\mathbf{N}}$ in the $(\hat{\mathbf{N}}_0,\hat{\mathbf{L}}_0)$ plane, and the constant C_{NL}, which is associated with the simultaneous splay of $\hat{\mathbf{M}}$ in the $(\hat{\mathbf{N}}_0,\hat{\mathbf{M}}_0)$ plane and a bend of $\hat{\mathbf{L}}$ in the $(\hat{\mathbf{L}}_0,\hat{\mathbf{M}}_0)$ plane, are about one order of magnitude smaller than C_{LM} which is associated with simultaneous splay of $\hat{\mathbf{N}}$ in the $(\hat{\mathbf{L}}_0,\hat{\mathbf{N}}_0)$ plane and a bend of $\hat{\mathbf{M}}$ in the $(\hat{\mathbf{M}}_0,\hat{\mathbf{N}}_0)$ plane. The seven constants, viz., K_{LL}, K_{MM}, K_{LN}, K_{NM}, K_{MN}, K_{NL}, and C_{LM} have nearly equal value and are of the order of the values found in the uniaxial phase. We have already noted in Sec. II the relationship of these constants with the Frank's constants of the uniaxial nematic phase. We thus conclude that the effect of biaxial ordering and, also, the effect of departure from axial molecular symmetry on the value of the elastic constants are small (almost negligible in view of the large experimental error bars). However, these orderings give rise to several modes of deformation. By studying the effects of the external magnetic and electric fields applied in different sample geometries, Kini and Chandrasekhar [31] have examined the feasibility of determining some of these 12 curvature elastic constants.

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APPENDIX A: DIRECTOR TRIAD AT A GENERAL POINT $\mathbf{R}=\mathbf{R}_1$

Suppose $\mathbf{R}=\mathbf{R}_1$ is the position vector of a chosen molecule (Fig. 1) referred to a laboratory-fixed Cartesian frame with unit vectors $\hat{\mathbf{e}}^{(j)}$ $(j=1,2,3)$. At the point $\mathbf{R}$, let S^0 be the unperturbed director frame described by the unit vector $\hat{\mathbf{N}}_0^{(1)}=\hat{\mathbf{L}}_0=\hat{\mathbf{e}}^{(1)}$, $\hat{\mathbf{N}}_0^{(2)}=\hat{\mathbf{M}}_0=\hat{\mathbf{e}}^{(2)}$, $\hat{\mathbf{N}}_0^{(3)}=\hat{\mathbf{N}}_0=\hat{\mathbf{e}}^{(3)}$; let S be the perturbed director frame described by the unit vectors $\hat{\mathbf{N}}^{(1)}=\hat{\mathbf{L}}=\hat{\mathbf{N}}_0^{(1)}+\boldsymbol{\sigma}^{(1)}$, $\hat{\mathbf{N}}^{(2)}=\hat{\mathbf{M}}=\hat{\mathbf{N}}_0^{(2)}+\boldsymbol{\sigma}^{(2)}$, $\hat{\mathbf{N}}^{(3)}=\hat{\mathbf{N}}=\hat{\mathbf{N}}_0^{(3)}+\boldsymbol{\sigma}^{(3)}$, where $\boldsymbol{\sigma}^{(j)}$ may be regarded as the distortion vectors; and let $N_k^{(j)}=\hat{\mathbf{N}}^{(j)}\cdot\hat{\mathbf{N}}_0^{(k)}=\delta_{jk}+\sigma_k^{(j)}$ be the components of the perturbed directors with respect to the S^0 frame.

The transformation from S^0 to S is effected by a 3×3 orthogonal matrix T with elements $T_{jk}=N_k^{(j)}=\delta_{jk}+\sigma_k^{(j)}$ such that

$$\hat{\mathbf{N}}^{(j)}=T_{jk}\hat{\mathbf{N}}^{(k)}=\hat{\mathbf{N}}_0^{(j)}+\sigma_k^{(j)}\hat{\mathbf{N}}_0^{(k)} \ , \tag{A1}$$

where the sum over the repeated index k is understood. The orthogonality condition

$$T_{lj}T_{lk}=\delta_{jk}$$

implies

$$\sigma_k^{(j)}+\sigma_j^{(k)}+\sigma_l^{(j)}\sigma_l^{(k)}=0 . \tag{A2}$$

At this stage suppose that the deformation components $\sigma_k^{(j)}$ are infinitesimal. Taking first the nondiagonal $(j\neq k)$ terms in (A2), we find that

$$\sigma_j^{(k)}=-\sigma_k^{(j)}-\sigma_l^{(j)}\sigma_l^{(k)}=O_s+O_s^2 \quad (j\neq k) , \tag{A3}$$

where O_s means a first-order small quantity. Next, taking the diagonal $(j=k)$ terms in (A2), we notice that

$$\sigma_j^{(j)}=-\frac{1}{2}\sum_l\{\sigma_l^{(j)}\}^2=O_s^2 \quad (\text{no sum over } j) . \tag{A4}$$

It follows that $\sigma_2^{(1)}$, $\sigma_1^{(3)}$, and $\sigma_2^{(3)}$ can be regarded as the basic independent distortion variables (all as functions of $\mathbf{R}$). Every other component can be constructed with the help of (A3) and (A4).

APPENDIX B: DIRECTOR TRIAD AT NEIGHBORING POINT $\underline{\mathbf{R}}=\mathbf{R}_2=\mathbf{R}_1+\mathbf{r}_{12}$

Next, we consider a neighboring molecule at the point $\underline{\mathbf{R}}=\mathbf{R}_2=\mathbf{R}_1+\mathbf{r}_{12}$ (Fig. 1) at which the perturbed director frame is called $\underline{\mathbf{S}}$. The corresponding unit vectors $\hat{\underline{\mathbf{N}}}^{(j)}$ have components $\underline{\mathbf{N}}_k^{(j)}=\delta_{jk}+\underline{\sigma}_k^{(j)}$ with respect to the S^0 frame. By definition,

$$\underline{\sigma}_k^{(j)}=\underline{\mathbf{N}}_k^{(j)}(\mathbf{R}+\mathbf{r})-\delta_{jk}$$

$$=\left[1+\frac{\mathbf{r}\cdot\nabla_R}{1!}+\frac{(\mathbf{r}\cdot\nabla_R)(\mathbf{r}\cdot\nabla_R)}{2!}+\cdots\right]N_k^{(j)}(\mathbf{R})-\delta_{jk} , \tag{B1}$$

where a second-order Taylor expansion in powers of the intermolecular separation vector $\mathbf{r}$ has been performed. In terms of the laboratory Cartesian components (X_1,X_2,X_3) of $\mathbf{R}$ and (x_1^0,x_2^0,x_3^0) of $\mathbf{r}$ we can rewrite (B1) more compactly as

$$\underline{\sigma}_k^{(j)}=\sigma_k^{(j)}+\left[x_a^0\frac{\partial\sigma_k^{(j)}}{\partial X_a}+\frac{x_a^0x_b^0}{2}\frac{\partial^2\sigma_k^{(j)}}{\partial X_a\partial X_b}\right] . \tag{B2}$$

At this juncture, it is convenient to express the components x_a^0 of $\mathbf{r}$ (with respect to the S^0 frame) in terms of its components x_a (with respect to the S frame). The relevant transformation equations, in close analogy with (A1) are

$$x_a^0=x_a+\sigma_a^{(m)}x_m . \tag{B3}$$

Substituting (B2), we get

$$\underline{\sigma}_k^{(j)}=\sigma_k^{(j)}+\{x_a+\sigma_a^{(m)}x_m\}\frac{\partial\sigma_k^{(j)}}{\partial X_a}$$

$$+\tfrac{1}{2}\{x_a+\sigma_a^{(m)}x_m\}\{x_b+\sigma_b^{(n)}x_n\}\frac{\partial^2\sigma_k^{(j)}}{\partial X_a\partial X_b} . \tag{B4}$$

Retaining terms up to second order in the σ's, we obtain

$$\underline{\sigma}_k^{(j)}=\sigma_k^{(j)}+t_k^{(j)}, \tag{B5}$$

where

$$t_k^{(j)}=\{x_a+x_m\sigma_a^{(m)}\}\frac{\partial\sigma_k^{(j)}}{\partial X_a}$$

$$+\{\tfrac{1}{2}x_ax_b+x_ax_n\sigma_b^{(n)}+\cdots\}\frac{\partial^2\sigma_k^{(j)}}{\partial X_a\partial X_b} , \tag{B6}$$

To make further progress we need the quantities $\underline{\mathbf{N}}_k^{(j)\prime}=\delta_{jk}+\underline{\sigma}_k^{(j)\prime}$, which are the components of $\hat{\underline{\mathbf{N}}}^{(j)}$ referred to the S frame. Evaluation of the relevant dot product in terms of S^0 frame components yields

$$\underline{\mathbf{N}}_k^{(j)\prime}=\hat{\underline{\mathbf{N}}}^{(j)}\cdot\hat{\mathbf{N}}^{(k)}=\{\delta_{jl}+\underline{\sigma}_l^{(j)}\}\{\delta_{kl}+\sigma_l^{(k)}\} . \tag{B7}$$

Hence,

$$\underline{\sigma}_k^{(j)\prime}\equiv\hat{\underline{\mathbf{N}}}_k^{(j)\prime}-\delta_{jk}=\underline{\sigma}_k^{(j)}+\sigma_j^{(k)}+\underline{\sigma}_l^{(j)}\sigma_l^{(k)} . \tag{B8}$$

Substituting for $\underline{\sigma}_k^{(j)}$ from (B5) and using the orthogonality condition, we find the general expressions correct to O_s^2,

$$\underline{\sigma}_k^{(j)\prime}=t_k^{(j)}+t_l^{(j)}\sigma_l^{(k)}$$

$$=[\{x_a+x_m\sigma_a^{(m)}\}\delta_{kl}+x_a\sigma_l^{(k)}]\frac{\partial\sigma_l^{(j)}}{\partial X_a}$$

$$+[\{\tfrac{1}{2}x_ax_b+x_ax_n\sigma_b^{(n)}\}$$

$$+\tfrac{1}{2}x_ax_b\sigma_l^{(k)}]\frac{\partial^2\sigma_l^{(j)}}{\partial X_a\partial X_b}+\cdots , \tag{B9}$$

along with

$$\underline{\sigma}_k^{(j)\prime}\underline{\sigma}_n^{(m)\prime}=x_ax_b\frac{\partial\sigma_k^{(j)}}{\partial X_a}\frac{\partial\sigma_n^{(m)}}{\partial X_b}+O_s^3 . \tag{B10}$$

From the physical viewpoint, the quantities $\underline{\sigma}_k^{(j)\prime}$ are very important because they represent the change in the director frame at $\underline{\mathbf{R}}$ relative to that at $\mathbf{R}$.

APPENDIX C: SINUSOIDAL DEFORMATION AND EULER ANGLES

For practical applications of these results, it is very convenient to assume long-wavelength deformations given, in the space-fixed frame, by

$$\sigma_k^{(j)}=B_k^{(j)}\sin(\mathbf{q}\cdot\mathbf{R}) , \tag{C1}$$

where $B_k^{(j)}$ are small amplitudes and $\mathbf{q}$ is the wave vector. Substitution of (B11) into (B9) and (B10) yields rather complicated expressions for $\underline{\sigma}_k^{(j)\prime}$ and for $\underline{\sigma}_k^{(j)\prime}\underline{\sigma}_n^{(m)\prime}$ in terms of sines and cosines. However, considerable simplification occurs if we recall that, in statistical mechanical calculations, we shall always encounter these functions under $\int d\mathbf{R}$ integration. Since

$$\int d\mathbf{R}\sin^2(\mathbf{q}\cdot\mathbf{R})=\int d\mathbf{R}\cos^2(\mathbf{q}\cdot\mathbf{R})=V/2 , \tag{C2}$$

$$\int d\mathbf{R}\sin(\mathbf{q}\cdot\mathbf{R})\cos(\mathbf{q}\cdot\mathbf{R})=0 , \tag{C3}$$

we obtain, effectively,

$$\underline{\sigma}_k^{(j)\prime}=-\tfrac{1}{2}sx_mq_aB_a^{(m)}B_k^{(j)}-\tfrac{1}{4}s^2B_l^{(j)}B_l^{(k)} , \tag{C4}$$

$$\underline{\sigma}_k^{(j)\prime}\underline{\sigma}_n^{(m)\prime}=\frac{1}{2}s^2B_l^{(j)}B_n^{(m)} , \tag{C5}$$

where

$$s = x_c q_c \quad \text{(sum over } c \text{ implied)} . \tag{C6}$$

Note that the components x_c of $\mathbf{r}$ are measured in the S frame while the components q_c of $\mathbf{q}$ are measured in the laboratory frame S^0.

Finally, if the rotation of the director frame $\underline{\mathbf{S}}$ with respect to the director frame S is parametrized by the Euler angles (α',β',γ'), then some typical elements of the relevant transformation matrix are

$$\cos\alpha' \sin\beta' = \underline{\sigma}_1^{(3)'}, \quad \sin\alpha' \sin\beta' = \underline{\sigma}_2^{(3)'} , \tag{C7}$$

$$(\cos\beta' - 1)\sin\alpha' \cos\gamma' + \sin\xi' = \underline{\sigma}_2^{(1)'} , \tag{C8}$$

where $\xi' \equiv \alpha' + \gamma'$. Since, in general, each of the quantities $\underline{\sigma}_1^{(3)'}$, $\underline{\sigma}_2^{(3)'}$ and $\underline{\sigma}_2^{(1)'}$ should be O_s, we conclude that the Euler angles must have the orders of magnitude

$$\sigma' = O_1, \quad \beta' = O_s , \tag{C9}$$

$$\gamma' \equiv (\alpha' - \xi') = O_1, \quad \xi' = O_s , \tag{C10}$$

where O_1 means order unity. Thus, the Euler angles correct to O_s^2 are given by

$$\beta' \cos\alpha' = \underline{\sigma}_1^{(3)'}, \quad \beta' \sin\alpha' = \underline{\sigma}_2^{(3)'} , \tag{C11}$$

$$\xi' = \underline{\sigma}_2^{(1)'} + \tfrac{1}{2}\underline{\sigma}_1^{(3)'}\underline{\sigma}_2^{(3)'} , \tag{C12}$$

where the $\underline{\sigma}_k^{(j)}$ functions are read off from Eq. (C4).

APPENDIX D: BIAXIAL CONTINUUM RELATION IN TERMS OF DIRECTOR COMPONENTS

Let the orientation of the unperturbed director triad at point 1 be

$$\hat{\mathbf{L}}_0 = (1,0,0), \quad \hat{\mathbf{M}}_0 = (0,1,0), \quad \hat{\mathbf{N}}_0 = (0,0,1) ,$$

and orientation of the perturbed director triad at point $\mathbf{R}$ be

$$\hat{\mathbf{L}} = (1, L_y, L_z), \quad \hat{\mathbf{M}} = (M_x, 1, M_z), \quad \hat{\mathbf{N}} = (N_x, N_y, 1) .$$

In the small-distortion limit, when the director triad undergoes spatial distortion, the elastic free energy is given by Eq. (4). In this Appendix we intend to write the elastic free energy in terms of the deformation variable defined in Appendix A, viz.,

$$L_y = \sigma_2^{(1)}, \quad M_x = \sigma_1^{(2)}, \quad N_x = \sigma_1^{(3)} ,$$
$$L_z = \sigma_3^{(1)}, \quad M_z = \sigma_3^{(2)}, \quad N_y = \sigma_2^{(3)} . \tag{D1}$$

Now Eq. (2.4) reads

$$\begin{aligned} \Delta A_e = \int dR \Bigg[& \tfrac{1}{2}K_{LL}\left[\frac{\partial\sigma_3^{(2)}}{\partial x_1}\right]^2 + \tfrac{1}{2}K_{MM}\left[\frac{\partial\sigma_1^{(3)}}{\partial x_2}\right]^2 + \tfrac{1}{2}K_{NN}\left[\frac{\partial\sigma_2^{(1)}}{\partial x_3}\right]^2 + \tfrac{1}{2}K_{LM}\left[\frac{\partial\sigma_2^{(1)}}{\partial x_1}\right]^2 \\ & + \tfrac{1}{2}K_{MN}\left[\frac{\partial\sigma_3^{(2)}}{\partial x_2}\right]^2 + \tfrac{1}{2}K_{NL}\left[\frac{\partial\sigma_1^{(3)}}{\partial x_3}\right]^2 + \tfrac{1}{2}K_{ML}\left[\frac{\partial\sigma_2^{(1)}}{\partial x_2}\right]^2 + \tfrac{1}{2}K_{NM}\left[\frac{\partial\sigma_3^{(2)}}{\partial x_3}\right]^2 \\ & + \tfrac{1}{2}K_{LN}\left[\frac{\partial\sigma_1^{(3)}}{\partial x_1}\right]^2 - C_{LM}\left[\frac{\partial\sigma_1^{(3)}}{\partial x_1}\frac{\partial\sigma_3^{(2)}}{\partial x_2}\right] - C_{MN}\left[\frac{\partial\sigma_2^{(1)}}{\partial x_2}\frac{\partial\sigma_1^{(3)}}{\partial x_3}\right] - C_{NL}\left[\frac{\partial\sigma_3^{(2)}}{\partial x_3}\frac{\partial\sigma_2^{(1)}}{\partial x_1}\right]\Bigg] . \end{aligned} \tag{D2}$$

Equation (D2) does not contain the contribution due to surface terms.

For the sinusoidal deformation we write

$$\sigma_k^{(j)} = B_k^{(j)} \sin(\mathbf{q}\cdot\mathbf{R}) , \tag{D3}$$

where $B_k^{(j)}$ is the amplitude. Using Eqs. (B16) and (B17) (Appendix B), we write the elastic free-energy density as

$$\begin{aligned} \frac{1}{V}\Delta A_e = \tfrac{1}{2}[& \tfrac{1}{2}K_{LL}q_1^2 B_3^{(2)^2} + \tfrac{1}{2}K_{MM}q_2^2 B_1^{(3)^2} + \tfrac{1}{2}K_{NN}q_3^2 B_2^{(1)^2} + \tfrac{1}{2}K_{LM}q_1^2 B_2^{(1)^2} + \tfrac{1}{2}K_{MN}q_2^2 B_3^{(2)^2} \\ & + \tfrac{1}{2}K_{NL}q_3^2 B_1^{(3)^2} + \tfrac{1}{2}K_{ML}q_2^2 B_2^{(1)^2} + \tfrac{1}{2}K_{NM}q_3^2 B_3^{(2)^2} + \tfrac{1}{2}K_{LN}q_1^2 B_1^{(3)^2} - C_{LM}q_1 q_2 B_1^{(3)} B_3^{(2)} \\ & - C_{MN}q_2 q_3 B_2^{(1)} B_1^{(3)} - C_{NL}q_3 q_1 B_3^{(2)} B_2^{(1)}] . \end{aligned} \tag{D4}$$

APPENDIX E: EXPRESSION FOR ELASTIC CONSTANTS IN TERMS OF LEADING-ORDER PARAMETERS

In this appendix we evaluate the series of Eqs. (3.15)–(3.26) for $l_1 = l_2 = 2$.

$$\begin{aligned} \beta K_{LL}(2,2) = \left[\frac{4\pi}{5}\right]^{1/2} \rho_n^2 \Bigg\{ & \bar{P}^2 \left[\frac{1}{2}J_{220}^{00} + \left[\frac{2}{7}\right]^{1/2} J_{222}^{00}\right] + \bar{\eta}^2 \left[\frac{1}{2}J_{220}^{22} + \left[\frac{2}{7}\right]^{1/2} J_{222}^{22}\right] \\ & + \bar{P}\bar{\eta}\left[\frac{1}{2}J_{220}^{02} + \left[\frac{2}{7}\right]^{1/2} J_{222}^{02}\right] + \frac{1}{\sqrt{6}}\bar{P}\bar{\mu}\left[\frac{1}{2}J_{220}^{00} + \left[\frac{2}{7}\right]^{1/2} J_{222}^{00}\right] \\ & + \frac{1}{\sqrt{6}}\bar{P}\bar{\tau}\left[\frac{1}{2}J_{220}^{02} + \left[\frac{2}{7}\right]^{1/2} J_{222}^{02}\right] + \frac{1}{\sqrt{56}}[\bar{\mu}^2 J_{222}^{00} + \bar{\tau}^2 J_{222}^{22}] \Bigg\} , \end{aligned} \tag{E1}$$

$$\beta K_{MM}(2,2)=\left[\frac{4\pi}{5}\right]^{1/2}\rho_n^2\left\{\bar{P}^2\left[\frac{1}{2}J_{220}^{00}+\left[\frac{2}{7}\right]^{1/2}J_{222}^{00}\right]+\bar{\eta}^2\left[\frac{1}{2}J_{220}^{22}+\left[\frac{2}{7}\right]^{1/2}J_{222}^{22}\right]\right.$$
$$+\bar{P}\bar{\eta}\left[\frac{1}{2}J_{220}^{02}+\left[\frac{2}{7}\right]^{1/2}J_{222}^{02}\right]-\frac{1}{\sqrt{6}}\bar{P}\bar{\mu}\left[\frac{1}{2}J_{220}^{00}+\left[\frac{2}{7}\right]^{1/2}J_{222}^{00}\right]$$
$$\left.-\frac{1}{\sqrt{6}}\bar{P}\bar{\tau}\left[\frac{1}{2}J_{220}^{02}+\left[\frac{2}{7}\right]^{1/2}J_{222}^{02}\right]+\frac{1}{\sqrt{56}}[\bar{\mu}^2J_{222}^{00}+\bar{\tau}^2J_{222}^{22}]\right\}, \tag{E2}$$

$$\beta K_{NN}(2,2)=\frac{2}{3}\left[\frac{4\pi}{5}\right]^{1/2}\rho_n^2\bar{\tau}^2\left[J_{220}^{22}+\left[\frac{8}{7}\right]^{1/2}J_{222}^{22}\right], \tag{E3}$$

$$\beta K_{LM}(2,2)=\frac{2}{3}\left[\frac{4\pi}{5}\right]^{1/2}\rho_n^2\bar{\tau}^2\left[J_{220}^{22}-\left[\frac{2}{7}\right]^{1/2}J_{222}^{22}\right], \tag{E4}$$

$$\beta K_{ML}(2,2)=\frac{2}{3}\left[\frac{4\pi}{5}\right]^{1/2}\rho_n^2\bar{\tau}^2\left[J_{220}^{22}-\left[\frac{2}{7}\right]^{1/2}J_{222}^{22}\right], \tag{E5}$$

$$\beta K_{MN}(2,2)=\left[\frac{4\pi}{5}\right]^{1/2}\rho_n^2\left\{\bar{P}^2\left[\frac{1}{2}J_{220}^{00}-\frac{1}{\sqrt{14}}J_{222}^{00}\right]+\bar{\eta}^2\left[\frac{1}{2}J_{220}^{22}-\frac{1}{\sqrt{14}}J_{222}^{22}\right]\right.$$
$$\left.+\bar{P}\bar{\eta}\left[\frac{1}{2}J_{220}^{02}-\frac{1}{\sqrt{14}}J_{222}^{02}\right]+\frac{1}{\sqrt{6}}\bar{P}\bar{\mu}\left[\frac{1}{2}J_{220}^{00}-\frac{1}{\sqrt{14}}J_{222}^{00}\right]-\frac{1}{\sqrt{56}}[\bar{\mu}^2J_{222}^{00}+\bar{\tau}^2J_{222}^{22}]\right\}, \tag{E6}$$

$$\beta K_{NM}(2,2)=\left[\frac{4\pi}{5}\right]^{1/2}\rho_n^2\left\{\bar{P}^2\left[\frac{1}{2}J_{220}^{00}-\frac{1}{\sqrt{14}}J_{222}^{00}\right]+\bar{\eta}^2\left[\frac{1}{2}J_{220}^{22}-\frac{1}{\sqrt{14}}J_{222}^{22}\right]\right.$$
$$+\bar{P}\bar{\eta}\left[\frac{1}{2}J_{220}^{02}-\frac{1}{\sqrt{14}}J_{222}^{02}\right]+\frac{1}{\sqrt{6}}\bar{P}\bar{\mu}\left[\frac{1}{2}J_{220}^{00}-\frac{1}{\sqrt{14}}J_{222}^{00}\right]$$
$$\left.+\frac{1}{\sqrt{6}}\bar{P}\bar{\tau}\left[\frac{1}{2}J_{220}^{02}-\frac{1}{\sqrt{14}}J_{222}^{02}\right]\right\}, \tag{E7}$$

$$\beta K_{LN}(2,2)=\left[\frac{4\pi}{5}\right]^{1/2}\rho_n^2\left\{\bar{P}^2\left[\frac{1}{2}J_{220}^{00}-\frac{1}{\sqrt{14}}J_{222}^{00}\right]+\bar{\eta}^2\left[\frac{1}{2}J_{220}^{22}-\frac{1}{\sqrt{14}}J_{222}^{22}\right]\right.$$
$$+\bar{P}\bar{\eta}\left[\frac{1}{2}J_{220}^{02}-\frac{1}{\sqrt{14}}J_{222}^{02}\right]-\frac{1}{\sqrt{6}}\bar{P}\bar{\mu}\left[\frac{1}{2}J_{220}^{00}+\frac{1}{\sqrt{14}}J_{222}^{00}\right]$$
$$\left.-\frac{1}{\sqrt{6}}\bar{P}\bar{\tau}\left[\frac{1}{2}J_{220}^{02}+\frac{1}{\sqrt{14}}J_{222}^{02}\right]-\frac{1}{\sqrt{56}}[\bar{\mu}^2J_{222}^{00}+\bar{\tau}^2J_{222}^{22}]\right\}, \tag{E8}$$

$$BK_{NL}(2,2)=\left[\frac{4\pi}{5}\right]^{1/2}\rho_n^2\left\{\bar{P}^2\left[\frac{1}{2}J_{220}^{00}-\frac{1}{\sqrt{14}}J_{222}^{00}\right]+\bar{\eta}^2\left[\frac{1}{2}J_{220}^{22}-\frac{1}{\sqrt{14}}J_{222}^{22}\right]\right.$$
$$\left.+\bar{P}\bar{\eta}\left[\frac{1}{2}J_{220}^{02}-\frac{1}{\sqrt{14}}J_{222}^{02}\right]-\frac{1}{\sqrt{6}}\bar{P}\bar{\mu}\left[\frac{1}{2}J_{220}^{00}-\frac{1}{\sqrt{14}}J_{222}^{00}\right]-\frac{1}{\sqrt{6}}\bar{P}\bar{\tau}\left[\frac{1}{2}J_{220}^{02}-\frac{1}{\sqrt{14}}J_{222}^{02}\right]\right\}, \tag{E9}$$

$$\beta C_{LM}(2,2)=-\left[\frac{4\pi}{5}\right]^{1/2}\rho_n^2\left[\frac{3}{\sqrt{14}}\{\bar{P}^2J_{222}^{00}-\bar{\eta}^2J_{222}^{22}+\bar{P}\bar{\eta}J_{222}^{02}\}-\frac{2}{\sqrt{14}}\{\bar{\mu}^2J_{222}^{00}+\bar{\tau}^2J_{222}^{22}\}\right], \tag{E10}$$

$$\beta C_{MN}(2,2)=\frac{1}{2}\left[\frac{4\pi}{105}\right]^{1/2}\rho_n^2\{\bar{P}\bar{\mu}J_{222}^{00}+\bar{P}\bar{\tau}J_{222}^{02}\}, \tag{E11}$$

$$BC_{NL}(2,2)=-\beta C_{MN}(2,2). \tag{E12}$$

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