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Xie Yu-Zhang (YÜ-Chang Hsieh) [a], Ou-Yang Zhong-can [a] & Lin Lei [b]

[a] Liquid Crystal Physics Research Group, Physics Department, Tsinghua University, Beijing, 100084, China

[b] Institute of Physics, Chinese Academy of Sciences, Beijing, 100080, China

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Electric Field Effects on the Elastic Constants of Nematics. I†

XIE YU-ZHANG (YÜ-CHANG HSIEH) and OU-YANG ZHONG-CAN

Liquid Crystal Physics Research Group, Physics Department, Tsinghua University, Beijing 100084, China

and

LIN LEI

Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

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The free energy density expression for nematics in an external electric field is derived both from a quasi-molecular approach similar to that used by Nehring and Saupe and a macroscopic approach based entirely on the symmetry properties of nematics. Under the special model assumed in the quasi-molecular theory the expressions of the elastic constants obtained from the two different methods agree with each other when one makes a proper choice of the material parameters introduced in the macroscopic theory.

1. INTRODUCTION

The theory of electric field induced elastic deformation in nematic liquid crystals was first given by Gruler and Meier.[1] A theory which takes the nonuniformity of the electric field into consideration was given later by Gruler, Scheffer and Meier[2] and by Deuling.[3]

The present work is to investigate the effect of electric field on the elastic constants of nematic liquid crystals. Two methods are used in the calculations. One is a quasi-molecular approach similar to that

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used by Nehring and Saupe.[4] In this approach the internal electric field is assumed as being the dipole field produced by molecular polarization satisfying the well known classical electrodynamic dipole field equation.[5] The other method is a macroscopic approach based purely on the symmetry properties of nematics. It is found that the two methods give the same result when one makes a proper choice of the material parameters introduced in the macroscopic theory.

2. QUASI-MOLECULAR THEORY

In the presence of an electric field $\mathbf{E}$, the free energy density g of nematic liquid crystal may be written as

$$\begin{aligned} g &= g_{el} + g_e, \\ g_{el} &= \tfrac{1}{2}\left[k_{11}(\nabla \cdot \mathbf{n})^2 + k_{22}(\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + k_{33}(\mathbf{n} \times \nabla \times \mathbf{n})^2\right], \\ g_e &= -(1/8\pi)\mathbf{D} \cdot \mathbf{E}. \end{aligned} \tag{1}$$

g_{el} is the Frank free energy density with k_{11}, k_{22} and k_{33} as the splay, twist and bend constants, respectively. g_e is the free energy density of the electric field. The director $\mathbf{n}$ satisfies the equation

$$\mathbf{n} \cdot \mathbf{n} = n_i n_i = 1, \qquad i = 1,2,3, \tag{2}$$

where the summation convention is used throughout this paper. The electric displacement $\mathbf{D}$ is related to $\mathbf{E}$ by

$$\mathbf{D} = \epsilon \cdot \mathbf{E}, \tag{3}$$

where the dielectric constant tensor ϵ_{ij} and the dielectric anisotropy ϵ_a are given by

$$\begin{aligned} \epsilon_{ij} &= \epsilon_\perp \delta_{ij} + \epsilon_a n_i n_j, \qquad i, j = 1,2,3 \\ \epsilon_a &\equiv \epsilon_\parallel - \epsilon_\perp . \end{aligned} \tag{4}$$

Let $\mathbf{E}_e$ and $\mathbf{E}_i$ be the external electric field and the internal field respectively, then the field $\mathbf{E}$ inside the nematic is given by

$$\mathbf{E} = \mathbf{E}_e + \mathbf{E}_i. \tag{5}$$

Substituting (5) into (3) and (1) one gets

$$\begin{aligned} g_e &= g_{ee} + \Delta g, \\ g_{ee} &\equiv -(1/8\pi)\mathbf{E}_e \cdot \boldsymbol{\epsilon} \cdot \mathbf{E}_e, \\ \Delta g &\equiv -(1/4\pi)\mathbf{E}_e \cdot \boldsymbol{\epsilon} \cdot \mathbf{E}_i, \end{aligned} \tag{6}$$

where the term $\mathbf{E}_i \cdot \boldsymbol{\epsilon} \cdot \mathbf{E}_i$ has been neglected on account of the fact that $\mathbf{E}_i$ is a small quantity.

From (3) the polarization $d\mathbf{p}'$ of a volume element $d\tau'$ around a point P' in the nematic is given by

$$d\mathbf{p}' = (1/4\pi)(\boldsymbol{\epsilon}' - \mathbf{I}) \cdot (\mathbf{E}_e' + \mathbf{E}_i')\, d\tau', \tag{7}$$

where $\mathbf{I}$ is the idemfactor. Neglecting the $\mathbf{E}_i'$ term and assuming that the internal electric field is the molecular dipole field, one finds that at the point P in the sample $\mathbf{E}_i$ is given by[5]

$$\begin{aligned} \mathbf{E}_i &= \int (1/r'^5)\left[3\, d\mathbf{p}' \cdot (-\mathbf{r}')(-\mathbf{r}') - r'^2\, d\mathbf{p}'\right] \\ &= \int (1/4\pi r'^5)(3\mathbf{r}'\mathbf{r}' - r'^2\mathbf{I}) \cdot (\boldsymbol{\epsilon}' - \mathbf{I}) \cdot \mathbf{E}_e'\, d\tau', \end{aligned} \tag{8}$$

where $\mathbf{r}'$ is the vector $\overrightarrow{PP'}$.

Following the molecular approach used by Nehring and Saupe[4] in calculating the elastic constants of nematics under no external field we assume that the interaction between the molecules exists only within a distance "a" of an order not much greater than the molecular dimension. Since a is small, one may consider $\mathbf{E}_e'$ as being uniform and being equal to $\mathbf{E}_e$ throughout the sample. In this way one has

$$\begin{aligned} \Delta g &= \int (1/16\pi^2 r'^5)\mathbf{E}_e \cdot \boldsymbol{\epsilon} \cdot \left[(r'^2\mathbf{I} - 3\mathbf{r}'\mathbf{r}') \cdot (\boldsymbol{\epsilon}' - \mathbf{I}) \cdot \mathbf{E}_e\right] d\tau' \\ &\equiv \frac{1}{2}\int f_e\, d\tau'. \end{aligned} \tag{9}$$

f_e is now an additional function that should be added to the function f introduced by Nehring and Saupe.[4] We now choose a local coordinate system such that P is the origin and the director $\mathbf{n}$ coincides with the x_3-axis at P. The director $\mathbf{n}'$ at the neighboring point P' is given by $\mathbf{n}' = \mathbf{n} + \Delta\mathbf{n}$. Besides being a function of $\Delta\mathbf{n}$, f_e should now be a function of all the three cylindrical coordinates (ρ', θ', x_3') of the point

P' instead of just a function of $(\rho', x_3', \Delta\mathbf{n})$ as function f does, viz.

$$f_e = f_e(\rho', \theta', x_3', \Delta\mathbf{n}). \tag{10}$$

Following Ref. [4] one first expands f_e in terms of the cylindrical components of $\Delta\mathbf{n}$ and then expands the components of $\Delta\mathbf{n}$ in terms of the relative coordinates of P and P'. Then, to second order in the deformation,

$$\begin{aligned} g'(P) &\equiv g_{el}(P) + \Delta g(P) \\ &= c'_{im} n_{i,m} + c'_{ijmn} n_{i,m} n_{j,n} + c'_{imn} n_{i,mn}, \\ &\quad i, j = 1,2, \qquad m, n = 1,2,3, \end{aligned} \tag{11}$$

where

$$n_{i,m} = \partial n_i / \partial x_m, \qquad n_{i,mn} = \partial^2 n_i / \partial x_m \, \partial x_n. \tag{12}$$

The constants c'_{im}, c'_{imn} and c'_{ijmn} are the elastic constants. With no applied electric field ($\mathbf{E}_e = 0$), (11) reduces to the results given by Nehring and Saupe, i.e.

$$\begin{aligned} g'(P) &= g_{el}(P), \\ c'_{1111} &= c'_{2222} = c_{1111} = c_{2222} = \tfrac{1}{2}k_{11}, \\ c'_{1122} &= c'_{2211} = c_{1122} = c_{2211} = \tfrac{1}{2}k_{22}, \\ c'_{1133} + 2c'_{113} &= c'_{2233} + 2c'_{223} = c'_{1133} + 2c'_{223} = c_{1133} + 2c_{113} \\ &= c_{2233} + 2c_{223} = c_{1133} + 2c_{223} = \tfrac{1}{2}k_{33}. \end{aligned} \tag{13}$$

In an applied electric field,

$$g(P) = g'(P) + g_{ee}(P) = g_{el}(P) + \Delta g(P) + g_{ee}(P), \tag{14}$$

where $g_{ee}(P)$ is independent of curvature deformation. $g'(P)$ is still given by (11) with the nonvanishing c' coefficients given in (13) but now

$$\begin{aligned} c'_{im} &= c_{im} + \Delta c_{im}, \\ c'_{imn} &= c_{imn} + \Delta c_{imn}, \\ c'_{ijmn} &= c_{ijmn} + \Delta c_{ijmn}, \end{aligned} \tag{15}$$

where the c coefficients are those introduced by Nehring and Saupe (see Eq. (10) of Ref. [4]). It can be shown easily that the various Δc

coefficients are given by

$$\Delta c_{im} = \frac{1}{2}\int \sum_{\mu=\rho,\theta} \left[\partial f_e/\partial(\Delta n_\mu)\right]_{\Delta \mathbf{n}=0} a_{\mu i} x'_m \, d\tau',$$

$$\Delta c_{imn} = \frac{1}{4}\int \sum_{\mu=\rho,\theta} \left[\partial f_e/\partial(\Delta n_\mu)\right]_{\Delta \mathbf{n}=0} a_{\mu i} x'_m x'_n \, d\tau',$$

$$\Delta c_{ijmn} = \frac{1}{4}\int \sum_{\mu,\nu=\rho,\theta} \left[\partial^2 f_e/\partial(\Delta n_\mu)\,\partial(\Delta n_\nu)\right]_{\Delta \mathbf{n}=0} \cdot a_{\mu i} a_{\nu j} x'_m x'_n \, d\tau', \tag{16}$$

with $a_{\mu i}$ given by

$$a_{\rho 1} = \cos\theta, \qquad a_{\rho 2} = \sin\theta,$$
$$a_{\theta 1} = -\sin\theta, \qquad a_{\theta 2} = \cos\theta. \tag{17}$$

To evaluate the various Δc coefficients one may take at P the three unit vectors of the Cartesian coordinates and the cylindrical coordinates as $(\mathbf{i}, \mathbf{j}, \mathbf{k} \equiv \mathbf{n})$ and $(\mathbf{e}_\rho, \mathbf{e}_\theta, \mathbf{e}_3 = \mathbf{k})$ respectively, with

$$\mathbf{e} = \mathbf{i}\cos\theta + \mathbf{j}\sin\theta,$$
$$\mathbf{e}_\theta = -\mathbf{i}\sin\theta + \mathbf{j}\cos\theta. \tag{18}$$

The dielectric constant tensor ϵ_{ij} at P can then be written in the following two forms:

$$\boldsymbol{\epsilon} = \epsilon_\perp(\mathbf{ii} + \mathbf{jj}) + \epsilon_\parallel \mathbf{kk}$$
$$= \epsilon_\perp(\mathbf{e}_\rho\mathbf{e}_\rho + \mathbf{e}_\theta\mathbf{e}_\theta) + \epsilon_\parallel \mathbf{kk}. \tag{19}$$

At P', in terms of the local coordinates, the dielectric constant tensor ϵ'_{ij} is given by

$$\boldsymbol{\epsilon}' = \epsilon_\perp(\mathbf{e}_1\mathbf{e}_1 + \mathbf{e}_2\mathbf{e}_2) + \epsilon_\parallel \mathbf{n}'\mathbf{n}'. \tag{20}$$

$\mathbf{e}_1$, $\mathbf{e}_2$ and $\mathbf{n}'$ are three mutually perpendicular unit vectors which can be chosen as

$$\mathbf{e}_1 = \left(1 - \Delta n_\theta^2\right)^{-1/2}\left[\left(1 - \Delta n_\rho^2 - \Delta n_\theta^2\right)^{1/2}\mathbf{e}_\rho - \Delta n_\rho \mathbf{k}\right],$$
$$\mathbf{e}_2 = \left(1 - \Delta n_\theta^2\right)^{-1/2}\left[-\Delta n_\rho \Delta n_\theta \mathbf{e}_\rho + \left(1 - \Delta n_\theta^2\right)\mathbf{e}_\theta - \left(1 - \Delta n_\rho^2 - \Delta n_\theta^2\right)^{1/2}\Delta n_\theta \mathbf{k}\right],$$
$$\mathbf{n}' = \Delta n_\rho \mathbf{e}_\rho + \Delta n_\theta \mathbf{e}_\theta + \left(1 - \Delta n_\rho^2 - \Delta n_\theta^2\right)^{1/2}\mathbf{k}. \tag{21}$$

TABLE I

Expressions of Δc_{imn} in quasi-molecular theory $K \equiv \epsilon_a a^2/120\pi$

m	n	$\Delta c_{1mn}/K$	$\Delta c_{2mn}/K$
1	1	$(\epsilon_{\parallel} - 2\epsilon_{\perp}) E_1 E_3$	$(\epsilon_{\parallel} + \epsilon_{\perp}) E_2 E_3$
1	2	$-\frac{3}{2}\epsilon_{\perp} E_2 E_3$	$-\frac{3}{2}\epsilon_{\perp} E_1 E_3$
1	3	$-\frac{3}{2}(\epsilon_{\perp} E_1^2 + \epsilon_{\parallel} E_3^2)$	$-\frac{3}{2}\epsilon_{\perp} E_1 E_2$
2	2	$(\epsilon_{\parallel} + \epsilon_{\perp}) E_1 E_3$	$(\epsilon_{\parallel} - 2\epsilon_{\perp}) E_2 E_3$
2	3	$-\frac{3}{2}\epsilon_{\perp} E_1 E_2$	$-\frac{3}{2}(\epsilon_{\perp} E_2^2 + \epsilon_{\parallel} E_3^2)$
3	3	$-(2\epsilon_{\parallel} - \epsilon_{\perp}) E_1 E_3$	$-(2\epsilon_{\parallel} - \epsilon_{\perp}) E_2 E_3$

To second orders,

$$\begin{aligned}\boldsymbol{\epsilon}' = &\left[\epsilon_{\perp}(\mathbf{e}_\rho\mathbf{e}_\rho + \mathbf{e}_\theta\mathbf{e}_\theta) + \epsilon_{\parallel}\mathbf{kk}\right] \\ &+\epsilon_a\left[\Delta n_\rho(\mathbf{e}_\rho\mathbf{k} + \mathbf{ke}_\rho) + \Delta n_\theta(\mathbf{e}_\theta\mathbf{k} + \mathbf{ke}_\theta)\right] \\ &+\epsilon_a\left[\Delta n_\rho^2\mathbf{e}_\rho\mathbf{e}_\rho + \Delta n_\theta^2\mathbf{e}_\theta\mathbf{e}_\theta - (\Delta n_\rho^2 + \Delta n_\theta^2)\mathbf{kk}\right. \\ &\left.+\Delta n_\rho\Delta n_\theta(\mathbf{e}_\rho\mathbf{e}_\theta + \mathbf{e}_\theta\mathbf{e}_\rho)\right]. \qquad (22)\end{aligned}$$

Substituting (9) and (22) into (16) and integrating over a spherical volume of radius a around the point P one gets by taking into account the evenness or oddness of the integrand the following results:

(i) $$\Delta c_{im} = 0. \qquad (23)$$

(ii) The various Δc_{imn} are given in Table I. Besides, one has

$$\Delta c_{imn} = \Delta c_{inm}. \qquad (24)$$

(iii) The various Δc_{ijmn} are given in Table II. One has also

$$\Delta c_{ijmn} = \Delta c_{jimn} = \Delta c_{ijnm} = \Delta c_{jinm}. \qquad (25)$$

TABLE II

Expressions of Δc_{ijmn} in quasi-molecular theory $K \equiv \epsilon_a a^2/120\pi$

m	n	$\Delta c_{11mn}/K$	$\Delta c_{12mn}/K$	$\Delta c_{22mn}/K$
1	1	$-2(2\epsilon_{\perp} E_1^2 + \epsilon_{\parallel} E_3^2)$	$-\epsilon_{\perp} E_1 E_2$	$2(\epsilon_{\perp} E_2^2 - \epsilon_{\parallel} E_3^2)$
1	2	$-3\epsilon_{\perp} E_1 E_2$	$-\frac{3}{2}\epsilon_{\perp}(E_1^2 + E_2^2)$	$-3\epsilon_{\perp} E_1 E_2$
1	3	$-3\epsilon_a E_1 E_3$	$-\frac{3}{2}\epsilon_{\parallel} E_2 E_3$	$3\epsilon_{\perp} E_1 E_3$
2	2	$2(\epsilon_{\perp} E_1^2 - \epsilon_{\parallel} E_3^2)$	$-\epsilon_{\perp} E_1 E_2$	$-2(2\epsilon_{\perp} E_2^2 + \epsilon_{\parallel} E_3^2)$
2	3	$3\epsilon_{\perp} E_2 E_3$	$-\frac{3}{2}\epsilon_{\parallel} E_1 E_3$	$-3\epsilon_a E_2 E_3$
3	3	$2(\epsilon_{\perp} E_1^2 + 2\epsilon_{\parallel} E_3^2)$	$2\epsilon_{\perp} E_1 E_2$	$2(\epsilon_{\perp} E_2^2 + 2\epsilon_{\parallel} E_3^2)$

In Tables I and II, E_1, E_2 and E_3 are the three local Cartesian components of the applied electric field.

3. MACROSCOPIC THEORY

In the presence of a homogeneous electric field $\mathbf{E}_e$ the free energy density g of the liquid crystal may be written as a sum of three terms as stated before:

$$g = g_{el} + g_{ee} + \Delta' g. \tag{14}$$

If one retains up to the second order deformation terms, g_{el} corresponds simply to the Frank free energy density. g_{ee} is the free energy density of the applied electric field and is independent of the curvature deformation. The term $\Delta' g(n_i, n_{i,m}, n_{i,mn}, \ldots, E_i)$ is that part of the free energy density which is associated with the correlations between the curvature deformation and the applied electric field. If one expands $\Delta' g$ into a power series each term of the expansion would be a product of E_i, $E_i E_j, \ldots$ and n_i, $n_{i,m}$, $n_{i,mn}, \ldots$. For liquid crystals $\mathbf{n}$ and $-\mathbf{n}$ are equivalent. Therefore each term in the expansion of $\Delta' g$ must contain an even number of n_i, $n_{i,m}$, $n_{i,mn}, \ldots$. Up to the second order of deformation and of the field strength there are only three types of terms in the expansion of $\Delta' g$, namely,

$$n_i n_{j,k} E_l, \qquad n_i n_{j,mn} E_k E_l, \qquad n_{i,m} n_{j,n} E_k E_l.$$

Those terms linear in E_l correspond to Meyer's flexoelectric effect[7] and will not be discussed here.

One may choose a local Cartesian coordinate system (x_1, x_2, x_3) at the point P in the nematic with x_3-axis coincides with the director at P. Let the components of the electric field in this coordinate system be (E_1, E_2, E_3). Up to the second order, the most general form of $\Delta' g$ is given by

$$\Delta' g = c_{3imnjk} n_3 n_{i,mn} E_j E_k + d_{imjnkl} n_{i,m} n_{j,n} E_k E_l, \tag{26}$$

where the coefficients c_{3imnjk} and d_{imjnkl} are material parameters. Under a complex transformation

$$\xi = x_1 + i x_2, \qquad \eta = x_1 - i x_2, \qquad x_3 = x_3, \tag{27}$$

all the indices in (26) will take their proper values of (ξ, η, x_3). It has been pointed out by Lin[6] that:

(i) Since nematics have C_∞ symmetry around the x_3-axis and $\Delta' g$ is invariant under rotations around the x_3-axis, every coefficient in (26)

should have equal number of ξ's and η's in its indices. Those coefficients with indices containing unequal number of ξ's and η's vanish.

(ii) For nematics any plane parallel to the director is a plane of symmetry. Thus any two c coefficients (or d coefficients) with mutually transposed ξ indices and η indices equal to each other. Consequently, only the real part of the two coefficients needs to be considered. With these requirements the number of nonvanishing coefficients in (26) are restricted.

(iii) Since any plane perpendicular to the director is a plane of symmetry of the nematics, there must be an even number of 3's in the indices of any coefficient.

There are 12 nonvanishing c_{3imnjk} terms. Out of these 12 terms 6 of them have the factor $n_{3,mn}$. They are called the ψ' functions (see (30)). Since $n_i n_i = 1$ and $\mathbf{n} \equiv (0, 0, 1)$, it follows that:

$$\begin{aligned} &n_i n_{i,m} = n_{3,m} = 0, \qquad m = 1,2,3; \\ &n_i n_{i,mn} = -n_{i,m} n_{i,n} = n_{3,mn} = -(n_{1,m} n_{1,n} + n_{2,m} n_{2,n}), \\ &\qquad\qquad m, n = 1,2,3. \end{aligned} \tag{28}$$

Thus the 6 terms with the factor $n_{3,mn}$ can be grouped into the d_{imjnkl} terms. Only 6 independent nonvanishing $n_3 n_{i,mn} E_j E_k$ terms are left behind. They are called the ψ functions (see (29)). It can be shown easily that after transforming from the (ξ, η, x_3) coordinate system back to the (x_1, x_2, x_3) coordinate system, the 12 terms are respectively:

$$\begin{aligned} \psi_1 &= n_3 E_3 \mathrm{Re}\left[E_\xi n_{\eta,\xi\eta}\right] = E_3 E_1 (n_{1,11} + n_{1,22}) + E_3 E_2 (n_{2,11} + n_{2,22}), \\ \psi_2 &= n_3 E_3 \mathrm{Re}\left[E_\xi n_{\xi,\eta\eta}\right] = E_3 E_1 (n_{1,11} - n_{1,22} + n_{2,12} + n_{2,21}) \\ &\qquad + E_3 E_2 (n_{2,22} - n_{2,11} + n_{1,12} + n_{1,21}), \\ \psi_3 &= n_3 E_\xi E_\eta \mathrm{Re}[n_{\xi,\eta 3}] = \tfrac{1}{2}(E_1^2 + E_2^2)(n_{1,13} + n_{1,31} + n_{2,23} + n_{2,32}), \\ \psi_4 &= n_3 \mathrm{Re}\left[E_\xi^2 n_{\eta,\eta 3}\right] = (E_1^2 - E_2^2)(n_{1,13} - n_{2,23}) \\ &\qquad + 2E_1 E_2 (n_{1,23} + n_{2,13}), \\ \psi_5 &= n_3 E_3^2 \mathrm{Re}[n_{\xi,\eta 3}] = E_3^2 (n_{1,13} + n_{2,23}), \\ \psi_6 &= n_3 E_3 \mathrm{Re}\left[E_\xi n_{\eta,33}\right] = E_1 E_3 n_{1,33} + E_2 E_3 n_{2,33}; \end{aligned} \tag{29}$$

$$\psi_1' = n_3 E_\xi E_\eta n_{3,\xi\eta} = (E_1^2 + E_2^2)(n_{3,11} + n_{3,22})$$
$$= -(E_1^2 + E_2^2)(n_{1,1}^2 + n_{2,1}^2 + n_{1,2}^2 + n_{2,2}^2),$$
$$\psi_2' = n_3 \mathrm{Re}[E_\xi^2 n_{3,\eta\eta}] = (E_1^2 - E_2^2)(n_{3,11} - n_{3,22}) + 4E_1E_2n_{3,12}$$
$$= (E_2^2 - E_1^2)(n_{1,1}^2 + n_{2,1}^2 - n_{1,2}^2 - n_{2,2}^2)$$
$$-4E_1E_2(n_{1,1}n_{1,2} + n_{2,1}n_{2,2}),$$
$$\psi_3' = n_3 E_3^2 n_{3,\xi\eta} = E_3^2(n_{3,11} + n_{3,22})$$
$$= -E_3^2(n_{1,1}^2 + n_{2,1}^2 + n_{1,2}^2 + n_{2,2}^2),$$
$$\psi_4' = n_3 E_3 \mathrm{Re}[E_\xi n_{3,3\eta}] = E_3E_1n_{3,13} + E_3E_2n_{3,23}$$
$$= -E_3E_1(n_{1,1}n_{1,3} + n_{2,1}n_{2,3}) - E_3E_2(n_{1,2}n_{1,3} + n_{2,2}n_{2,3}),$$
$$\psi_5' = n_3 E_\xi E_\eta n_{3,33} = (E_1^2 + E_2^2)n_{3,33}$$
$$= -(E_1^2 + E_2^2)(n_{1,3}^2 + n_{2,3}^2),$$
$$\psi_6' = n_3 E_3^2 n_{3,33} = -E_3^2(n_{1,3}^2 + n_{2,3}^2); \tag{30}$$

where Re[$\cdots$] means the real part of the function [$\cdots$].

The contribution Δg_1 of the ψ functions to $\Delta' g$ is

$$\Delta g_1 = KA_i\psi_i, \qquad i = 1,2,\ldots,6, \qquad K \equiv \epsilon_a a^2/120\pi, \tag{31}$$

where the A_i's are material parameters. The factor K is introduced for the convenience of comparison with the quasi-molecular theory. The equivalent expression in the quasi-molecular theory is

$$\Delta g_1 = \Delta c_{imn} n_{i,mn}, \qquad i = 1,2, \qquad m,n = 1,2,3. \tag{32}$$

TABLE III

Expressions of Δc_{imn} in macroscopic theory
$K \equiv \epsilon_a a^2/120\pi$

m	n	$\Delta c_{1mn}/K$	$\Delta c_{2mn}/K$
1	1	$(A_1 + A_2)E_1E_3$	$(A_1 - A_2)E_2E_3$
1	2	$A_2E_2E_3$	$A_2E_1E_3$
1	3	$\frac{1}{2}[A_3(E_1^2 + E_2^2) + A_4(E_1^2 - E_2^2) + A_5E_3^2]$	$A_4E_1E_2$
2	2	$(A_1 - A_2)E_1E_3$	$(A_1 + A_2)E_2E_3$
2	3	$A_4E_1E_2$	$\frac{1}{2}[A_3(E_1^2 + E_2^2) + A_4(E_2^2 - E_1^2) + A_5E_3^2]$
3	3	$A_6E_1E_3$	$A_6E_2E_3$

Substituting (29) into (31) and comparing with (32) one finds the various Δc_{imn} as given in Table III.

There are 14 nonvanishing d_{imjnkl} terms. They are respectively:

$$\begin{aligned}
\phi_1 &= E_\xi E_\eta \mathrm{Re}\left[n_{\xi,\eta}^2\right] = \left(E_1^2 + E_2^2\right)\left[(n_{1,1} + n_{2,2})^2 - (n_{2,1} - n_{1,2})^2\right],\\
\phi_2 &= E_\xi E_\eta n_{\eta,\eta} n_{\xi,\xi} = \left(E_1^2 + E_2^2\right)\left(n_{1,1}^2 + n_{2,2}^2 - 2n_{1,1}n_{2,2} + n_{2,1}^2\right.\\
&\qquad \left. + n_{1,2}^2 + 2n_{1,2}n_{2,1}\right),\\
\phi_3 &= \mathrm{Re}\left[E_\xi^2 n_{\eta,\eta} n_{\xi,\eta}\right] = \left(E_1^2 - E_2^2\right)\left(n_{1,1}^2 + n_{2,1}^2 - n_{2,2}^2 - n_{1,2}^2\right)\\
&\quad + 4E_1E_2(n_{2,1}n_{2,2} + n_{1,2}n_{1,1}),\\
\phi_4 &= \mathrm{Re}\left[E_\xi^2 n_{\eta,\eta} n_{\eta,\xi}\right] = \left(E_1^2 - E_2^2\right)\left(n_{1,1}^2 - n_{2,2}^2 - n_{2,1}^2 + n_{1,2}^2\right)\\
&\quad + 4E_1E_2(n_{1,1}n_{2,1} + n_{2,2}n_{1,2}),\\
\phi_5 &= E_3^2 n_{\xi,\eta} n_{\eta,\xi} = E_3^2\left[(n_{1,1} + n_{2,2})^2 + (n_{2,1} - n_{1,2})^2\right],\\
\phi_6 &= E_3^2 \mathrm{Re}\left[n_{\xi,\eta}^2\right] = E_3^2\left[(n_{1,1} + n_{2,2})^2 - (n_{2,1} - n_{1,2})^2\right],\\
\phi_7 &= E_3 \mathrm{Re}\left[E_\xi n_{\eta,3} n_{\xi,\eta}\right] = E_1E_3(n_{1,1}n_{1,3} + n_{1,3}n_{2,2} - n_{2,3}n_{1,2}\\
&\qquad + n_{2,3}n_{2,1}) + E_2E_3(n_{2,2}n_{2,3}\\
&\qquad + n_{1,1}n_{2,3} - n_{1,3}n_{2,1} + n_{1,3}n_{1,2}),\\
\phi_8 &= E_\xi E_\eta n_{\xi,3} n_{\eta,3} = \left(E_1^2 + E_2^2\right)\left(n_{1,3}^2 + n_{2,3}^2\right),\\
\phi_9 &= \mathrm{Re}\left[E_\xi^2 n_{\eta,3}^2\right] = \left(E_1^2 - E_2^2\right)\left(n_{1,3}^2 - n_{2,3}^2\right) + 4E_1E_2n_{1,3}n_{2,3},\\
\phi_{10} &= E_3^2 n_{\xi,3}\eta_{\eta,3} = E_3^2\left(n_{1,3}^2 + n_{2,3}^2\right),\\
\phi_{11} &= E_\xi E_\eta n_{\xi,\eta} n_{\eta,\xi} = \left(E_1^2 + E_2^2\right)\left[(n_{1,1} + n_{2,2})^2 + (n_{2,1} - n_{1,2})^2\right],\\
\phi_{12} &= E_3^2 n_{\xi,\xi} n_{\eta,\eta} = E_3^2\left(n_{1,1}^2 + n_{2,2}^2 - 2n_{1,1}n_{2,2} + n_{2,1}^2 + n_{1,2}^2\right.\\
&\qquad \left. + 2n_{1,2}n_{2,1}\right),\\
\phi_{13} &= E_3 \mathrm{Re}\left[E_\xi n_{\eta,3} n_{\eta,\xi}\right] = E_3E_1(n_{1,1}n_{1,3} + n_{1,3}n_{2,2} + n_{2,3}n_{1,2}\\
&\qquad - n_{2,3}n_{2,1}) + E_3E_2(n_{2,2}n_{2,3}\\
&\qquad + n_{2,3}n_{1,1} + n_{1,3}n_{2,1} - n_{1,3}n_{1,2}),\\
\phi_{14} &= E_3 \mathrm{Re}\left[E_\xi n_{\xi,3} n_{\eta,\eta}\right] = E_3E_1(n_{1,1}n_{1,3} - n_{1,3}n_{2,2} + n_{2,3}n_{1,2}\\
&\qquad + n_{2,3}n_{2,1}) + E_3E_2(n_{2,2}n_{2,3}\\
&\qquad - n_{2,3}n_{1,1} + n_{1,3}n_{2,1} + n_{1,3}n_{1,2}).
\end{aligned} \tag{33}$$

TABLE IV

Expressions of Δc_{ijmn} in macroscopic theory $K \equiv \epsilon_a a^2/120\pi$

m	n	$\Delta c_{11mn}/K$	$\Delta c_{12mn}/K$	$\Delta c_{22mn}/K$
1	1	$(B_1 + 2B_2 + B_3 + B_4)E_1^2 + (B_1 + 2B_2 - B_3 - B_4)E_2^2 + (2B_5 + B_6)E_3^2$	$2B_4E_1E_2$	$(-B_1 + 2B_2 + B_3 - B_4)E_1^2 + (-B_1 + 2B_2 - B_3 + B_4)E_2^2 + (2B_5 - B_6)E_3^2$
1	2	$2B_3E_1E_2$	$B_1(E_1^2 + E_2^2) + B_6E_3^2$	$2B_3E_1E_2$
1	3	$\frac{1}{2}(2B_7 + B_{13})E_1E_3$	$\frac{1}{2}B_{13}E_2E_3$	$\frac{1}{2}(2B_7 - B_{13})E_1E_3$
2	2	$(-B_1 + 2B_2 - B_3 + B_4)E_1^2 + (-B_1 + 2B_2 + B_3 - B_4)E_2^2 + (2B_5 - B_6)E_3^2$	$2B_4E_1E_2$	$(B_1 + 2B_2 - B_3 - B_4)E_1^2 + (B_1 + 2B_2 + B_3 + B_4)E_2^2 + (2B_5 + B_6)E_3^2$
2	3	$\frac{1}{2}(2B_7 - B_{13})E_2E_3$	$\frac{1}{2}B_{13}E_1E_3$	$\frac{1}{2}(2B_7 + B_{13})E_2E_3$
3	3	$(B_8 + B_9)E_1^2 + (B_8 - B_9)E_2^2 + B_{10}E_3^2$	$2B_9E_1E_2$	$(B_8 - B_9)E_1^2 + (B_8 + B_9)E_2^2 + B_{10}E_3^2$

It can readily be shown that:

$$\begin{aligned}
\psi_1' &= -\tfrac{1}{2}(\phi_2 + \phi_{11}),\\
\psi_2' &= -\phi_3,\\
\psi_3' &= -\tfrac{1}{2}(\phi_5 + \phi_{12}),\\
\psi_4' &= -\tfrac{1}{2}(\phi_7 + \phi_{13}),\\
\psi_5' &= -\phi_8,\\
\psi_6' &= -\phi_{10}.
\end{aligned} \tag{34}$$

Thus the six ψ' functions are linear combinations of the ϕ functions. In the free energy density expression one may simply neglect the ψ' functions and take the ϕ functions instead.

The contribution Δg_2 of the ϕ functions to $\Delta' g$ may be written as

$$\Delta g_2 = KB_i\phi_i, \qquad i = 1,2,\ldots,14, \tag{35}$$

where again all the B_i's are material parameters. The equivalent expression in the quasi-molecular theory is

$$\Delta g_2 = \Delta c_{ijmn} n_{i,m} n_{j,n}, \qquad i, j = 1,2, \quad m, n = 1,2,3. \tag{36}$$

Substituting (33) into (35) and comparing with (36) while taking (25) into consideration one finds that there are three relations between the B_i's, viz.

$$B_{11} = B_2, \qquad B_{12} = B_5, \qquad B_{14} = B_7. \tag{37}$$

Thus there are only 11 independent B_i coefficients. The various Δc_{ijmn} are given in Table IV. Together with the six A_i's there are 17 independent coefficients in total. We note that the results in this section remain correct when the electric field $\mathbf{E}_e$ is replaced by an external magnetic field.

4. COMPARISON OF THE TWO THEORIES

In the quasi-molecular theory the expressions of the elastic constants are derived with the aid of certain model, i.e., assumptions about the molecular interaction and the internal field. The results show that the elastic constants depend not only upon the assumed effective radius of interaction a between the molecules and the dielectric constants $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ of the nematic, but also upon the electric field intensity $\mathbf{E}$ in which the nematic is placed. In other words, the elastic constants are

functions of the applied electric field instead of pure constants. On the other hand, the macroscopic theory uses only the symmetry properties of the nematics without referring to any specific model. The expressions of the elastic constants as obtained are quite general. However, the macroscopic theory introduces 17 independent material parameters which can only be determined experimentally. The theory gives no indications on what material constants these 17 parameters are related to, not to mention their specific form of dependence. It would certainly be very difficult to design 17 independent experiments to determine these parameters. For the present, the only thing one can do is to see if the quasi-molecular results are consistent with the macroscopic results.

If the two theoretical results agree with each other, each element of Δc_{imn} given in Table I should equal to its corresponding element in Table III and so does Table II and Table IV. Furthermore, since the applied electric field can be chosen arbitrarily, it is necessary that the coefficient of each $E_k E_l$ term in any element of Table I (Table II) should equal to the coefficient of the corresponding term in the corresponding element of Table III (Table IV). In this way, from Δc_{imn} one gets 16 equations for the A_i's. Out of these 16 equations only 6 of them are independent which are just enough to solve the 6 A_i's. The results are:

$$A_1 = \epsilon_{\parallel} - \tfrac{1}{2}\epsilon_{\perp}, \quad A_2 = -\tfrac{3}{2}\epsilon_{\perp}, \quad A_3 = -\tfrac{3}{2}\epsilon_{\perp},$$
$$A_4 = -\tfrac{3}{2}\epsilon_{\perp}, \quad A_5 = -3\epsilon_{\parallel}, \quad A_6 = \epsilon_{\perp} - 2\epsilon_{\parallel}. \tag{38}$$

From Δc_{ijmn} there are 31 equations for the B_i's to satisfy, but only 12 equations are independent. However there are only 11 independent B_i's in Table II. Whether there exists a set of solutions of the 12 equations becomes crucial. If no solution exists then the quasi-molecular theory is not in agreement with the macroscopic theory and at least one of the two theories is at fault. Calculation shows that there does exist a unique set of solutions of the B_i's. They are:

$$B_1 = -\tfrac{3}{2}\epsilon_{\perp}, \quad B_2 = B_{11} = -\tfrac{1}{4}\epsilon_{\perp}, \quad B_3 = -\tfrac{3}{2}\epsilon_{\perp},$$
$$B_4 = -\tfrac{1}{2}\epsilon_{\perp}, \quad B_5 = B_{12} = -\epsilon_{\parallel}, \quad B_6 = 0,$$
$$B_7 = B_{14} = -\tfrac{3}{2}\epsilon_{\parallel} + 3\epsilon_{\perp}, \quad B_8 = \epsilon_{\perp},$$
$$B_9 = \epsilon_{\perp}, \quad B_{10} = 4\epsilon_{\parallel}, \quad B_{11} = -3\epsilon_{\parallel}. \tag{39}$$

The 17 material parameters are now simple functions of the dielectric constants $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ of the sample.

When the 17 material parameters introduced in the macroscopic theory do satisfy (38) and (39), the macroscopic theory, up to the

second order, and the quasi-molecular theory lead to the same expressions of the elastic constants. This means that the quasi-molecular theory does satisfy the symmetry requirements of nematics and is indeed a particular solution of the macroscopic theory. The fact that the 17 material parameters given by (38) and (39) is a set of unique solutions of 18 equations seems to indicate that it is not merely a coincidence that the two theories yield the same result under the particular model. The quasi-molecular theory is likely to be correct.

5. DISCUSSION

Eq. (14) gives the expression for the free energy density of nematic liquid crystals in an external electric field. Besides the Frank free energy term (g_{el}) and the free energy term of the external electric field (g_{ee}) there is an additional term (Δg) which comes from the electric field effect on the elastic constants. The term Δg can be calculated from Eq. (11) or Eq. (26) with the expressions of Δc's given in Tables I and II. However, in Tables I and II, the Δc's are expressed in the local coordinate system. For calculation, it would be more desirable to express Δg in a form independent of the coordinate system chosen. When the external electric field intensity $\mathbf{E}$ is space independent, with careful manipulation, one can write the expression of Δg in the form:

$$\begin{aligned}\Delta g = K\epsilon_a\{&4(\mathbf{E}\cdot\mathbf{n})(\nabla\cdot\mathbf{n})[\mathbf{n}\cdot\nabla(\mathbf{E}\cdot\mathbf{n})]\\&+2(\mathbf{E}\cdot\mathbf{n})[(\mathbf{n}\cdot\nabla\mathbf{n})\cdot\nabla(\mathbf{E}\cdot\mathbf{n})]\\&+(\mathbf{E}\cdot\mathbf{n})^2[2(\nabla\cdot\mathbf{n})^2-(\mathbf{n}\cdot\nabla\times\mathbf{n})^2-(\mathbf{n}\cdot\nabla\mathbf{n})^2]\\&-[\nabla(\mathbf{E}\cdot\mathbf{n})]^2+3[\mathbf{n}\cdot\nabla(\mathbf{E}\cdot\mathbf{n})]^2\}\\&+6K\epsilon_\perp(\mathbf{E}\cdot\mathbf{n})\{(\nabla\cdot\mathbf{n})[\mathbf{n}\cdot\nabla(\mathbf{E}\cdot\mathbf{n})]\\&\qquad-[(\mathbf{n}\cdot\nabla\mathbf{n})\cdot\nabla(\mathbf{E}\cdot\mathbf{n})]\}\\&+K\nabla\cdot\mathbf{P},\end{aligned}\tag{40}$$

where

$$\begin{aligned}\mathbf{P} = {}&\epsilon_a(\mathbf{E}\cdot\mathbf{n})\{\nabla(\mathbf{E}\cdot\mathbf{n})-3[\mathbf{n}\cdot\nabla(\mathbf{E}\cdot\mathbf{n})]\mathbf{n}\}\\&-\epsilon_a(\mathbf{E}\cdot\mathbf{n})^2[2(\nabla\cdot\mathbf{n})\mathbf{n}+(\mathbf{n}\cdot\nabla\mathbf{n})]\\&+\epsilon_\perp\{(\mathbf{E}\cdot\mathbf{n})[2\nabla(\mathbf{E}\cdot\mathbf{n})-3(\nabla\cdot\mathbf{n})\mathbf{E}]-3[\mathbf{E}\cdot\nabla(\mathbf{E}\cdot\mathbf{n})]\mathbf{n}\\&-(3/2)[\mathbf{E}^2-(\mathbf{E}\cdot\mathbf{n})^2](\mathbf{n}\nabla\cdot\mathbf{n}-\mathbf{n}\cdot\nabla\mathbf{n})\}.\end{aligned}\tag{41}$$

Tables I and II show that the Δc's are functions of **E**. In other words the elastic constants are functions of the applied electric field. However all the Δc's has a factor a^2, where a is an effective radius of interaction of molecular dimension. Therefore, the Δc's and the effect of the electric field on the elastic constants are probably not very large.

Also, measurements on the elastic constants by the electric Freedericksz effects are not very simple. Gerber and Schadt[8] discussed some of the important sources of ambiguity and error that are often neglected in measurements and in the evaluation of the elastic constants. Further discussions on the relevance of the present theoretical results in connection with experiments will be presented separately.

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