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# Order electricity reconsidered

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# Order electricity reconsidered

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We have considered the Landau–de Gennes expansion of the distortion free energy to examine a possible connection between the electric polarization in terms of a gradient of the order parameter and the electric polarization resulting from splay and bend distortions of the director. In addition we have considered the electric polarization connected with the electric quadrupole density, which is not contained in the Landau–de Gennes expansion.

## 1. Introduction

Long ago Meyer [1] argued that distortions of the director field **n**(**r**) may induce a macroscopic polarization. Considering $n_{i,j} = \partial n_i/\partial r_j$ and the electric field $E_i$, $i, j = x, y, z$, as the independent variables in the differential of the thermodynamic potential he expanded the conjugate variable $D_i$ as

$$D_i = \varepsilon_{ij}E_j + 4\pi e_{ijk}n_{j,k}. \tag{1}$$

Employing the local symmetry with respect to $\mathbf{n} = (0, 0, n_z)$ he showed that the flexoelectric polarization $(P_f)_i = e_{ijk}n_{j,k}$ is determined by the independent tensor elements $e_{zxx} = e_{zyy} = e_1$, and $e_{xxz} = e_{yyz} = e_3$ leading to

$$\mathbf{P}_f = e_1\mathbf{n}(\nabla \cdot \mathbf{n}) + e_3(\mathbf{n} \cdot \nabla)\mathbf{n}. \tag{2}$$

Recently Barbero *et al.* [2] have extended equation (1) by considering the gradient of the order parameter $S$ as an additional independent variable, that is $D_i$ is expanded as

$$D_i = \varepsilon_{ij}E_j + 4\pi e_{ijk}n_{j,k} + 4\pi R_{ij}S_{,j}. \tag{3}$$

The order electric polarization $(P_0)_i = R_{ij}S_{,j}$ was written as

$$\mathbf{P}_0 = r_1\mathbf{n}(\mathbf{n} \cdot \nabla)S + r_2\nabla S. \tag{4}$$

In order to relate the unknown coefficients $r_1$ and $r_2$ to the well-known coefficients $e_1$ and $e_3$ they then considered the free energy as a function of the independent variables $E_i$ and $Q_{ij,k}$, where $Q_{ij} = S(n_in_j - \delta_{ij}/3)$, leading to

$$D_i = \varepsilon_{ij}E_j + 4\pi G_{ijkl}Q_{jk,l}. \tag{5}$$

Using,

$$(P_d)_i = G_{ijkl}Q_{jk,l} \tag{6}$$

they produced some relations up to second order in $S$ between the coefficients $r_1$ and $r_2$ in equation (4) and the coefficients $e_1$ and $e_3$ in equation (2). As the derivation of these relations cannot be found and the problem itself is intriguing we recalculate in §2 $(P_d)_i$ from equation (6). Moreover we introduce in the expansion of $D_i$ in terms of

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$Q_{jk,l}$, given by equation (5), the next higher order term proportional to $Q_{ij}Q_{kl,m}$, giving rise to additional terms for $(P_{\mathrm{d}})_i$ in equation (6), second order in $S$. As it turns out that the relations given in [2] between the coefficients $r_1$ and $r_2$ and the coefficients $e_1$ and $e_3$ cannot be verified, equation (4) is just a formal expression without a physical meaning. Therefore we consider in §3 the possible existence of order electric polarization in connection with flexo-electric polarization on the basis of the interaction between the electric quadrupole density and the gradient of the electric field. The inhomogenity of the field is described in terms of the anisotropy of the dielectric tensor, which indeed is a different procedure than used in [3]. The discussion of the results is given in section 4 together with a consideration of the Landau–de Gennes expansion of the distortion free energy [4, 5] and its extension to the elastic free energy [6, 7].

## 2. The Landau–de Gennes expansion of the distortion polarization

In the Landau–de Gennes description of liquid crystals the free energy is expanded in powers of the tensor elements $Q_{ij} = S(n_in_j - \delta_{ij}/3)$ and the derivatives $Q_{ij,k} = \partial Q_{ij}/\partial r_k$. The distortion free energy in lowest order of the independent variables $Q_{ij}$ and $Q_{ij,k}$, originally introduced as [4, 5]:

$$f_{\mathrm{d}} = \tfrac{1}{2}L_1 Q_{ij,k}Q_{ij,k} + \tfrac{1}{2}L_2 Q_{ij,j}Q_{ik,k}, \tag{7}$$

where $L_1$ and $L_2$ are temperature independent material parameters, is, in its general form, given by

$$f_{\mathrm{d}} = \tfrac{1}{2}B_{ijklmn}Q_{ij,k}Q_{lm,n}. \tag{8}$$

The connection between the coefficients $L_1$ and $L_2$ and the tensor elements $B_{ijklmn}$ is derived in the Appendix and discussed in §4.

In an electric field there is a contribution to the free energy which, with the electric field $\mathbf{E}$ as the independent variable, is given by

$$f_{\mathrm{E}} = -\frac{1}{8\pi}\varepsilon_{ij}E_iE_j. \tag{9}$$

The elements $\varepsilon_{ij}$ of the dielectric tensor can be written as

$$\varepsilon_{ij} = \varepsilon_{\perp}\delta_{ij} + (\varepsilon_{\parallel} - \varepsilon_{\perp})n_in_j, \tag{10}$$

where $\varepsilon_{\perp}$ and $\varepsilon_{\parallel}$ are the dielectric constants perpendicular and parallel to the director, respectively.

In addition to the pure distortion and dielectric free energy, quadratic in the independent variables $Q_{ij,k}$ and $E_i$, respectively, we may also consider an additional contribution $\Delta f$ to $f$ due to a coupling between the distortion $Q_{ij,k}$ and the electric field $E_i$. In lowest order of the independent variables $\Delta f$ is written as [2]

$$\Delta f = -E_iG_{ijkl}Q_{jk,l}. \tag{11}$$

Minimizing the free energy

$$f = f_{\mathrm{d}} + f_{\mathrm{E}} + \Delta f \tag{12}$$

with respect to $E_i$ we find for the conjugate variable $D_i = -4\pi\partial f/\partial E_i$

$$D_i = \varepsilon_{ij}E_j + 4\pi(P_{\mathrm{d}})_i, \tag{13}$$

where the distortion polarization $(P_{\mathrm{d}})_i$ is given by

$$(P_{\mathrm{d}})_i = -\frac{\partial(\Delta f)}{\partial E_i} = G_{ijkl}Q_{jk,l}. \tag{14}$$

The independent non-zero elements of the fourth-order $G$ tensor can be found in the standard way by employing the local symmetry with respect to the director. In a local coordinate system $x$, $y$, $z$ where the director at the origin is along the $x$, $y$ or $z$ axis, these axes are two-fold rotational symmetry axes. Symmetry then demands that $G_{ijkl}$ is pairwise even in the indices $i, j, k, l = x, y, z$ that is

$$(P_\mathrm{d})_i = G_{ijji}Q_{jj,i} + (G_{iijj} + G_{ijij})Q_{ij,j}. \tag{15}$$

Considering an infinitesimal rotation of $\mathbf{n}$ in this coordinate system, i.e. $\mathbf{n}(\mathbf{r}) = \mathbf{n}(0) + \delta\mathbf{n}(\mathbf{r})$, and taking into account the constraint $\mathbf{n}^2(\mathbf{r}) = \mathbf{n}^2(0) = 1$, we have in equation (15)

$$Q_{jj,i} = (n_j^2 - 1/3)S_{,i} \tag{16}$$

$$Q_{ij,j} = S(n_in_j)_{,j}, \tag{17}$$

leading to

$$(P_\mathrm{d})_i = (3G_{iiii}(n_i^2 - \tfrac{1}{3}) + G_{ijji}(n_j^2 - \tfrac{1}{3}))S_{,i} + (G_{iijj} + G_{ijij})S(n_in_j)_{,j}, \tag{18}$$

where $i, j = x, y, z$ with the proviso that in equation (18) $i \neq j$. In view of the equivalence of the $x$, $y$ and $z$ coordinates, we may introduce the independent coefficients

$$r^{(0)} = 3G_{iiii} - G_{ijji}, \quad e^{(0)} = G_{iijj} + G_{ijij}, \quad i \neq j, \tag{19}$$

to write equation (18) in the form

$$(P_\mathrm{d})_i = (P_\mathrm{d}^{(0)})_i = r^{(0)}(n_in_j - \delta_{ij}/3)S_{,j} + e^{(0)}S(n_in_{j,j} + n_jn_{i,j}), \tag{20}$$

valid for any direction of $\mathbf{n}$. These equations show that in first order of $S$ there is no relation between the polarization due to a gradient of $S$ and the polarizations due to a splay and a bend distortion both proportional to $e^{(0)}S$. As the splay and bend polarizations described in [1] and considered in [2] are independent modes, second order in $S$, we therefore introduce in equation (11) the next higher order term in the expansion of $\Delta f$ linear in $Q_{ij,k}$ that is,

$$\Delta f = -E_iG_{ijkl}Q_{jk,l} - E_iG_{ijklmn}Q_{jk}Q_{lm,n} \tag{21}$$

leading to

$$(P_\mathrm{d})_i = (G_{ijkl} + G_{imnjkl}Q_{mn})Q_{jk,l} = (P_\mathrm{d}^{(0)})_i + (P_\mathrm{d}^{(1)})_i \tag{22}$$

(cf. equation (14)). Proceeding as before it is easily found that $(P_\mathrm{d}^{(1)})_i$, determined by

$$(P_\mathrm{d}^{(1)})_i = G_{ijkjki}Q_{jk}Q_{jk,i} + G_{iikjjk}Q_{ik}Q_{jj,k} + G_{ijkijk}Q_{jk}Q_{ij,k} + G_{iikjkj}Q_{ik}Q_{jk,j}, \tag{23}$$

yielding

$$(P_\mathrm{d}^{(1)})_i = (G_{ijjjji}Q_{jj} + G_{iiijji}Q_{ii})Q_{jj,i} + (G_{ijjijj}Q_{jj} + G_{iiiijj}Q_{ii})Q_{ij,j}, \tag{24}$$

can be written as

$$(P_\mathrm{d}^{(1)})_i = 4G_{iiiiii}Q_{ii}Q_{ii,i} + (G_{ijjjji}Q_{jj} + G_{iiijji}Q_{ii})Q_{jj,i} + (G_{ijjijj}Q_{jj} + G_{iiiijj}Q_{ii})Q_{ij,j}, \tag{25}$$

where $i, j = x, y, z$ with the proviso that in equation (25) $i \neq j$. In view of the equivalence of the $x$, $y$ and $z$ coordinates we may use the following notation for the independent non-zero elements of the sixth order $G$ tensor

$$g_1 = G_{iiiiii}, \quad g_2 = G_{ijjjji}, \quad g_3 = G_{iiijji}, \quad g_4 = G_{ijjijj}, \quad g_5 = G_{iiiijj}, \tag{26}$$

to write equation (25) in a coordinate free form

$$(P_{\mathrm{d}}^{(1)})_i = (r_1^{(1)} n_i n_j + r_2^{(1)} \delta_{ij}) S S_{,j} + (e_1^{(1)} n_i n_{j,j} + e_2^{(1)} n_j n_{i,j}) S^2, \tag{27}$$

where

$$\left.\begin{array}{llll} r_1^{(1)} = (4g_1 - g_2 - g_3)/3, & r_2^{(1)} = (r_1^{(1)} + 2g_3)/3, \\ e_1^{(1)} = (2g_5 - g_4)/3, & e_2^{(1)} = (2g_4 - g_5)/3, \end{array}\right\} \tag{28}$$

are in general four independent coefficients. Accordingly there is also, in second order of $S$, no relation between a possible polarization due to a gradient of $S$ and the now mutually independent splay and bend polarizations.

To compare these results with those of [2] it should be noted that the Landau expansion of the free energy in powers of $Q_{ij}$ and $Q_{ij,k}$ was introduced by de Gennes to describe the nematic-isotropic phase transition [4]. The free energy connected with the spatial variation $Q_{ij,k}$ of the order parameter $Q_{ij}$ was for that purpose written in terms of two rotational invariants shown in equation (7); this implies that the tensor $B_{ijklmn}$ in equation (8) is constrained to the form

$$B_{ijklmn} = L_1 \delta_{il} \delta_{jm} \delta_{kn} + L_2 \delta_{il} \delta_{jk} \delta_{mn},$$

appropriate indeed for the isotropic phase [4]. As such an expansion is inadequate to describe the distortion free energy of the ordered phase, it was not meant for that, the expansion of $f_{\mathrm{d}}$ in equation (7) has been extended with all possible third order rotational invariants of the form $Q_{ij} Q_{hl,i} Q_{hl,j}$, $Q_{ij} Q_{ik,l} Q_{jk,l}$, etc., with arbitrary temperature independent coefficients [6, 7]. This extension of the original Landau-de Gennes expansion in equation (7) is equivalent to the statement that the tensor $B_{ijklmn}$ in equation (8) should be written as

$$L_1 \delta_{il} \delta_{jm} \delta_{kn} + L_2 \delta_{il} \delta_{jk} \delta_{mn} + \mathscr{L}_1 \delta_{il} \delta_{jm} Q_{kn} + \mathscr{L}_2 \delta_{il} Q_{jm} \delta_{kn} + \cdots .$$

This indeed is the essence of the procedure in [8], albeit in a slightly different way, to account for the possible symmetries of the ordered phase, also discussed in [9]. Considering now the expansion of $\Delta f$ in equation (21), linear in $Q_{ij,k}$, as an expansion in terms of rotational invariants with temperature independent coefficients $G_i$, similar to the extended expansion of $f_{\mathrm{d}}$, we find

$$\Delta f = -G_1 Q_{ij,j} E_i - (G_2 Q_{jk} Q_{jk,i} + G_3 Q_{ik} Q_{jj,k} + G_4 Q_{jk} Q_{ij,k} + G_5 Q_{ik} Q_{kj,j}) E_i, \tag{29}$$

valid for any direction of **n**. This expansion immediately shows that all tensor elements $G_{ijkl}$ in equation (11) are replaced by one coefficient $G_1$, making both $r^{(0)}$ and $e^{(0)}$ in equation (20) equal to $2G_1$. Further inspection of equation (25), cf. equation (24), shows that both tensor elements $G_{iiiiii} = g_1$ and $G_{ijjjji} = g_2$ in equation (25) are represented in equation (29), $\Delta f = -(P_{\mathrm{d}})_i E_i$, by one coefficient, i.e. $G_2$, that is $g_1 = g_2 = G_2$. The same applies to the couples $G_{iiiiii}$ and $G_{iiijji} = g_3$, $G_{iiiiii}$ and $G_{ijjijj} = g_4$ and $G_{iiiiii}$ and $G_{iiiijj} = g_5$, that is $g_1 = g_2 = g_3 = g_4 = g_5$, yielding the following, special form of equation (28)

$$r_1^{(1)} = 2g_1/3, \quad r_2^{(1)} = 8g_1/9, \quad e_1^{(1)} = e_2^{(1)} = g_1/3. \tag{30}$$

The only way to retain in the Landau–de Gennes expansion of $\Delta f$ the splay and bend polarizations as independent modes, is to make in the last two terms of equation (24), cf. (29), the restriction $i \neq j$; then indeed $G_{ijjijj} = G_4 = g_4$ and $G_{iiiijj} = G_5 = g_5$

remain independent of $G_{iiiiii} = G_2 = g_1 = g_2 = g_3$ and of each other, yielding

$$\left.\begin{array}{llll} r_1^{(1)} = (2g_1 - g_1 - g_1)/3 = 0, & r_2^{(1)} = 2g_1/3, \\ e_1^{(1)} = (2g_5 - g_4)/3, & e_2^{(1)} = (2g_4 - g_5)/3, \end{array}\right\} \qquad (31)$$

which are discussed in §4.

## 3. Distortion polarization in connection with the electric quadrupole density

Apart from the formally introduced contribution $\Delta f$, equation (21), to the free energy we now consider the additional energy

$$\Delta f_q = -\boldsymbol{q}\colon \nabla \mathbf{E} = -q_{jk}E_{k,j}, \qquad (32)$$

due to the interaction of a given electric quadrupole density with the gradient of an applied field [10]. The electric quadrupole density is defined in terms of a second order tensor $q_{jk}$, which for uniaxial orientational order can be written as [3, 11]:

$$q_{jk} = q_a^* S(n_j n_k - \delta_{jk}/3) = q_a^* Q_{jk}. \qquad (33)$$

Here $q_a^* S = q_\parallel - q_\perp$ is the anisotropy of the electric quadrupole density with respect to the director. For later use we note that equation (32) is based on the interaction energy of a molecular quadrupole $\boldsymbol{q}_m = \frac{1}{2}\Sigma_\nu e_{m\nu}\mathbf{r}_{m\nu}\mathbf{r}_{m\nu}$ with the gradient of a local electric field, averaged with an appropriate single particle orientational distribution function $f(\cos\vartheta)$. The local field can be written as $\mathbf{E}_{\mathrm{loc.}} = \boldsymbol{K}\cdot\mathbf{E}$ where $\mathbf{E}$ is the Maxwell field and $\boldsymbol{K}$ a molecular tensor which is independent of the dielectric anisotropy $\varepsilon_\parallel - \varepsilon_\perp$ and accordingly independent of the molecular orientation with respect to the director [12, 13]. Hence the orientationally averaged interaction energy density $\langle \boldsymbol{q}_{\mathrm{m}} \colon \nabla(\boldsymbol{K}\cdot\mathbf{E})\rangle$ defined by

$$\langle \boldsymbol{q}_{\mathrm{m}} \colon \nabla(\boldsymbol{K}\cdot\mathbf{E})\rangle = \varrho \int_0^1 d(\cos\vartheta)\cdot f(\cos\vartheta)\boldsymbol{q}_{\mathrm{m}} \colon \nabla(\boldsymbol{K}\cdot\mathbf{E}) \qquad (34)$$

can be written as

$$\langle \boldsymbol{q}_{\mathrm{m}}\cdot\boldsymbol{K}\rangle \colon \nabla\mathbf{E} = q_a^*\boldsymbol{Q}\colon\nabla\mathbf{E}, \quad q_a^* = \varrho q_a,$$

where $q_a = q_l K_l - q_t K_t$ is an effective anisotropy of the molecular quadrupole tensor and $\varrho$ is the number density; l(ongitudinal) and t(ransverse) respectively refer to parallel and perpendicular to the long molecular axis.

The condition div $\mathbf{D} = 0$, appropriate to the case of an insulating medium, can be written as, cf. equation (13),

$$D_{j,j} = \frac{\partial}{\partial r_j}(\varepsilon_{jk}E_k + 4\pi P_j) = \varepsilon_{jk,j}E_k + \varepsilon_{jk}E_{k,j} + 4\pi P_{j,j} = 0 \qquad (35)$$

which, in view of the condition rot $\mathbf{E} = 0$, yields

$$E_{k,j} = -\frac{\delta_{jk}}{\varepsilon_{jj}}(\varepsilon_{ij,j}E_i + 4\pi P_{j,j}), \qquad (36)$$

where $\varepsilon_{ij}$, defined in equation (10), can also be written as

$$\varepsilon_{ij} = \varepsilon\delta_{ij} + \varepsilon_a^* Q_{ij}, \quad \varepsilon_a^* S = \varepsilon_\parallel - \varepsilon_\perp, \quad \varepsilon = (2\varepsilon_\perp + \varepsilon_\parallel)/3. \qquad (37)$$

Substitution of equation (36) in equation (32) yields

$$\Delta f_q = q_{jj}(\varepsilon_{ij,j}E_i + 4\pi P_{j,j})/\varepsilon_{jj} \tag{38}$$

giving rise to an electric polarization $(P_q)_i$ given by

$$(P_q)_i = -\frac{\partial(\Delta f_q)}{\partial E_i} = -q_{jj}\varepsilon_{ij,j}/\varepsilon_{jj} \tag{39}$$

which in view of equations (33) and (37) can likewise be written as

$$(P_q)_i = -q_{\mathrm{a}}^*\varepsilon_{\mathrm{a}}^*Q_{jj}Q_{ij,i}/\varepsilon_{jj}. \tag{40}$$

Writing $(P_q)_i = (P_0)_i + (P_f)_i$ we then have

$$(P_0)_i = -q_{\mathrm{a}}^*\varepsilon_{\mathrm{a}}^*(n_j^2 - 1/3)(n_in_j - \delta_{ij}/3)SS_{,j}/\varepsilon_{jj}, \tag{41}$$

$$(P_f)_i = -q_{\mathrm{a}}^*\varepsilon_{\mathrm{a}}^*(n_j^2 - 1/3)(n_in_j)_{,j}S^2/\varepsilon_{jj}, \tag{42}$$

valid for any direction of **n**. Equation (42) shows the flexoelectric polarization resulting from a distortion of the quadrupole density does not discriminate between splay and bend distortions; it is only when the director is along the $x$, $y$ or $z$ axis that these can be separated, that is with **n** along the $z$ axis,

$$(P_f)_z = \frac{+q_{\mathrm{a}}^*\varepsilon_{\mathrm{a}}^*S^2}{3\varepsilon - \varepsilon_{\mathrm{a}}^*S}\cdot n_zn_{i,i}, \quad (P_f)_i = \frac{-2q_{\mathrm{a}}^*\varepsilon_{\mathrm{a}}^*S^2}{3\varepsilon + 2\varepsilon_{\mathrm{a}}^*S}n_zn_{i,z}; \quad i = x, y. \tag{43}$$

Here we also note that equation (42) for $(P_f)_i$ is quite different from the equation

$$(P_f)_i = -L_{ii}q_{\mathrm{a}}^*S(n_in_j)_{,j} \tag{44}$$

derived in [3] (the quadrupole tensor $\Theta_{ij}$ in this is defined so that $\Theta_{ij} = 3q_{ij}$ and $\Theta_{\mathrm{a}} = 3q_{\mathrm{a}}^*S$) with $L_{ii} = L + L_{\mathrm{a}}/3$ and reconsidered in [14] with $L_{ii} = L_{zz}$ for splay and $L_{ii} = L_{xx}$ for bend polarization respectively; $L$ is a Lorentz local field tensor written in terms of a macroscopic anisotropy $L_{\mathrm{a}} = L_{\parallel} - L_{\perp}$ that is

$$L_{ij} = L\delta_{ij} + L_{\mathrm{a}}(n_in_j - \delta_{ij}/3). \tag{45}$$

The basis for the derivation of equation (44) is the introduction of a polarization $P_i$, cf. equations (2.4), (2.5) and (2.8) l.c., given by

$$P_i = (g_{ij} - \delta_{ij})q_{jk,k} = g_{ij}q_{jk,k} - q_{ik,k} \tag{46}$$

in terms of the gradient of the quadrupole density and the unknown tensor $g_{ij}$. Compatibility of equation (46) with the free energy of a quadrupole density in a field gradient, written as

$$F = \int d\mathbf{r}f_q = -\int d\mathbf{r}q_{ij}\frac{\partial}{\partial r_j}(L_{ik}E_k) = -\int d\mathbf{r}q_{ij}L_{ik}E_{k,j} \tag{47}$$

apparently requires, l.c.,

$$g_{ij} = (1 + L_{ij})\delta_{ij}, \tag{48}$$

which is conceivable only when equation (47) is integrated by parts to yield

$$F = +\int d\mathbf{r}E_iL_{ii}q_{ij,j} = +\int d\mathbf{r}E_iL_{ii}q_{\mathrm{a}}^*S(n_in_j)_{,j}. \tag{49}$$

Here it should be noted that equations (47) and (49) together are only meaningful together i.e. non-zero, when $n_in_j - \delta_{ij}/3$ and $(n_in_j)_{,j}$ are simultaneously non-zero; this indeed requires that the director is not along the $x$, $y$ or $z$ axis. In that respect equation (49) cannot be interpreted in terms of independent splay and bend polarizations; the definition of a Lorentz local field tensor in terms of a macroscopic anistropy, cf. equation (45), being at the same time independent of position, cf. equation (47) is also noteworthy.

More relevant however is to examine the origin and meaning of equation (46). Consider therefore the microscopic field equation [15, 16]

$$\nabla \cdot \mathbf{e} = 4\pi \sum_m \sum_\nu e_{m\nu}\delta(\mathbf{R}_{m\nu} - \mathbf{R}), \tag{50}$$

where $\mathbf{e}$ is the electric field in vacuum in the presence of point charges $e_{m\nu}$ with radius vectors $\mathbf{R}_{m\nu}$; the indices $\nu$ and $m$ refer to the $\nu$th charge of the $m$th molecule, considered as a stable cluster of charges. The radius vector $\mathbf{R}_{m\nu}$ is written as $\mathbf{R}_m + \mathbf{r}_{m\nu}$ where $\mathbf{r}_{m\nu}$ is the radius vector of the charge $e_{m\nu}$ with respect to the $m$th centre of mass with the radius vector $\mathbf{R}_m$. The development of the right hand side of equation (50) in a Taylor series up to second order in $\mathbf{r}_{m\nu}$ yields

$$\nabla \cdot \mathbf{e} = 4\pi(e_R - \nabla \cdot \mathbf{p}_R + \nabla\nabla : \boldsymbol{q}_R), \tag{51}$$

where

$$e_R = \sum_m e_m\delta(\mathbf{R}_m - \mathbf{R}), \quad e_m = \sum_\nu e_{m\nu}, \tag{52}$$

$$\mathbf{p}_R = \sum_m \mathbf{p}_m\delta(\mathbf{R}_m - \mathbf{R}), \quad \mathbf{p}_m = \sum_\nu e_{m\nu}\mathbf{r}_{m\nu}, \tag{53}$$

$$\boldsymbol{q}_R = \sum_m \boldsymbol{q}_m\delta(\mathbf{R}_m - \mathbf{R}), \quad \boldsymbol{q}_m = \tfrac{1}{2}\sum_\nu e_{m\nu}\mathbf{r}_{m\nu}\mathbf{r}_{m\nu}, \tag{54}$$

are the densities of the discretely distributed molecular moments $e_m$, $\mathbf{p}_m$ and $\boldsymbol{q}_m$ respectively. The corresponding macroscopic densities, considered as continuous, slowly variable functions of the space coordinates are defined as the statistical averages of the fluctuating densities taken over a volume element $\Delta V$, large on a molecular scale and yet small on a macroscopic scale. These averages can be written as

$$\langle m_R \rangle = \int d\Gamma\, m_R(\Gamma)\exp(-U(\Gamma)/kT)\Big/\int d\Gamma \exp(-U(\Gamma)/kT), \tag{55}$$

where $\Gamma$ denotes the set of translational and orientational variables of all molecules in the volume $\Delta V$ around $\mathbf{R}$; $U(\Gamma)$ is the total energy as a function of the variables $\Gamma$. The Maxwell field $\mathbf{E}$ inside the system is the macroscopic field generated by the internal and external sources, i.e. $\mathbf{E} = \langle \mathbf{e} \rangle + \mathbf{E}_{\text{ext.}}$. As $\nabla \cdot \mathbf{E}_{\text{ext.}} = 0$ inside the system, equation (66) may be written after averaging as

$$\nabla \cdot \mathbf{E} = 4\pi(\langle e_R \rangle - \nabla \cdot (\langle \mathbf{p}_R \rangle - \nabla \cdot \langle \boldsymbol{q}_R \rangle)) \tag{56}$$

or

$$\nabla \cdot \mathbf{D} = 4\pi\langle e_R \rangle = 4\pi e \tag{57}$$

which defines the displacement vector $\mathbf{D}$, i.e.

$$\mathbf{D} = \mathbf{E} + 4\pi\mathscr{P} = \mathbf{E} + 4\pi(\langle \mathbf{p}_R \rangle - \nabla \cdot \langle \boldsymbol{q}_R \rangle). \tag{58}$$

Up to now the origin of the polarization $\mathscr{P}$ has not been specified, which indeed is not necessary to arrive at equation (58). However by extracting that part of $\mathscr{P}$ due to the molecular interaction with **E** and usually linear in **E**, i.e. $\mathscr{P}(\mathbf{E}) = \boldsymbol{\chi}\cdot\mathbf{E}$, equation (58) can be written in the general form

$$\mathbf{D} = \mathbf{E} + 4\pi\boldsymbol{\chi}\cdot\mathbf{E} + 4\pi(\langle\mathbf{p}_R\rangle - \boldsymbol{\nabla}\cdot\langle\boldsymbol{q}_R\rangle) = \boldsymbol{\varepsilon}\cdot\mathbf{E} + 4\pi\mathscr{P}, \tag{59}$$

in which a possible non-zero $\mathscr{P}$ is due to intermolecular interactions. Up to the order written equation (59) is complete. The addition of a term $g_{ij}q_{jk,k}$ to this equation to describe the specific polarization in liquid crystals leading to equation (46) is redundant and ambiguous, no distinction being made between $\langle\boldsymbol{q}_R\rangle$ defined according to equation (55) and the averaged value $\langle\boldsymbol{q}_m\rangle = q_{\mathrm{a}}^*\boldsymbol{Q}$ in equations (33) and (34). Therefore, it is difficult to appreciate the meaning of equations (46) and (48). We end this section by considering the case that $\mathbf{n} = (n_x(z), 0, n_z(z))$ and $S = S(z)$, relevant indeed when a voltage $V = \int_0^d dzE(z)$ is applied across the sample. From equations (41) and (42) we easily find

$$(P_0)_x = -\frac{q_{\mathrm{a}}^*\varepsilon_{\mathrm{a}}^*(n_z^2 - 1/3)n_xn_zSS_{,z}}{\varepsilon + \varepsilon_{\mathrm{a}}^*S(n_z^2 - 1/3)}, \tag{60}$$

$$(P_0)_z = -\frac{q_{\mathrm{a}}^*\varepsilon_{\mathrm{a}}^*(n_z^2 - 1/3)^2SS_{,z}}{\varepsilon + \varepsilon_{\mathrm{a}}^*S(n_z^2 - 1/3)}, \tag{61}$$

$$(P_f)_x = -\frac{q_{\mathrm{a}}^*\varepsilon_{\mathrm{a}}^*S^2(n_z^2 - 1/3)(n_xn_z)_{,z}}{\varepsilon + \varepsilon_{\mathrm{a}}^*S(n_z^2 - 1/3)}, \tag{62}$$

$$(P_f)_z = -\frac{q_{\mathrm{a}}^*\varepsilon_{\mathrm{a}}{}^*S^2(n_z^2 - 1/3)(n_z^2)_{,z}}{\varepsilon + \varepsilon_{\mathrm{a}}^*S(n_z^2 - 1/3)}, \tag{63}$$

whereas equation (32) can be written as

$$\begin{aligned}\Delta f_q &= -q_{zz}E_{z,z} = \frac{q_{zz}}{E_{zz}}(\varepsilon_{zz,z}E_z + \varepsilon_{zx,z}E_x + 4\pi P_{z,z})\\ &= \frac{q_{zz}}{\varepsilon_{zz}}\left(\varepsilon_{zx,z}E_x + \frac{\varepsilon_{zz,z}}{\varepsilon_\parallel\varepsilon_\perp}(\varepsilon_{xx}[D_z - 4\pi P_z] + 4\pi\varepsilon_{zx}P_x) + 4\pi P_{z,z}\right)\end{aligned} \tag{64}$$

yielding with

$$E_x = -\frac{\varepsilon_{xz}}{\varepsilon_\parallel\varepsilon_\perp}[D_z - 4\pi P_z] - \frac{\varepsilon_{zz}}{\varepsilon_\parallel\varepsilon_\perp}4\pi P_x = \text{constant}$$

$$\Delta f_q = -\left(\frac{\varepsilon_{xx}D_z}{\varepsilon_\parallel\varepsilon_\perp} + \frac{4\pi(\varepsilon_\parallel + \varepsilon_\perp)P_z}{2\varepsilon_\parallel\varepsilon_\perp}\right)q_{zz,z} + \frac{\partial}{\partial z}\left[\left(\frac{\varepsilon_{xx}D_z}{\varepsilon_\parallel\varepsilon_\perp} + \frac{4\pi(\varepsilon_\parallel + \varepsilon_\perp)P_z}{2\varepsilon_\parallel\varepsilon_\perp}\right)q_{zz}\right]. \tag{65}$$

The last term gives rise to a surface energy

$$F_{\text{surf.}} = \frac{4\pi(\varepsilon_\parallel + \varepsilon_\perp)}{2\varepsilon_\parallel\varepsilon_\perp}P_zq_{zz} = \frac{4\pi(\varepsilon_\parallel + \varepsilon_\perp)}{2\varepsilon_\parallel\varepsilon_\perp}\frac{\varepsilon_{\mathrm{a}}^*(q_{\mathrm{a}}^*S)^2(n_z^2 - 1/3)^2}{\varepsilon + \varepsilon_{\mathrm{a}}^*S(n_z^2 - 1/3)}\frac{\partial}{\partial z}(S(n_z^2 - 1/3)) \tag{66}$$

in the absence of the external field which couples the director at the surface with the gradient of the order parameter at the surface.

## 4. Discussion

The Landau–de Gennes expansion of the distortion free energy in terms of the gradients of the tensor order parameter is a simultaneous expansion in terms of the gradients of the order parameter $S$ and of the gradients of the director field $(n_i n_j)$. In such an expansion the coefficients determining the contributions in terms of $S_{,i}$ and $(n_i n_j)_{,i}$, are directly connected; cf. equation (A 2). Therefore a connection could be sought between the coefficients $r_1$ and $r_2$ in equation (4) and the coefficients $e_1$ and $e_3$ in equation (2) by making a similar expansion of the electric distortion free energy. Indeed considering the relevant expression of the distortion free energy in equation (11) it may be noted that equation (18) yields two contributions to the distortion polarization which on account of symmetry are unrelated; the tensor elements $G_{iiii}$, $G_{ijji}$ and $G_{iijj} = G_{ijij}$ are independent. Considering however equation (11) as a Landau–de Gennes expansion, i.e. writing $\Delta f = G_1 E_i Q_{ij,j}$, the various tensor elements $G_{ijkl}$ are replaced by the coefficient $G$, connected with the one invariant $E_i Q_{ij,j}$. Then the coefficients $r^{(0)}$ and $e^{(0)}$ in equation (20) are equal, i.e. $r^{(0)} = e^{(0)} = 2G_1$. Equations (27) and (28) show that in second order of $S$ also there is, on account of symmetry, no relation between order electricity and the now mutually independent splay and bend polarizations. When however equation (21) is considered as a Landau–de Gennes expansion, then all contributions to $(P_{\mathrm{d}}^{(1)})_i$ in equation (27) are determined by one common coefficient. Indeed the four coefficients connected with the four invariants $Q_{jk} Q_{jk,i} E_i \cdot Q_{ik} Q_{jj,k} E_i$, $Q_{jk} Q_{ijmk} E_i$ and $Q_{ik} Q_{jk,j} E_i$ in equation (29) which replace the second term in the right hand side of equation (21) are all equal, due to the presence of the common tensor element $G_{iiiiii}$ in equation (24), cf. equation (25) leading to equation (30).

At this stage we note that the coefficients $e_1$ and $e_3$ in equation (2) describing splay and bend polarization as independent modes are in lowest order quadratic in $S$ and in principle different coefficients. Indeed according to the physical model [1, 17] the splay and bend polarizations are due to a coupling between the geometrical asymmetry of conical and bow like molecules respectively, and the macroscopic splay and bend distortions respectively. In the simple model of [17] $e_1 = K_{11} S_c p_l / kT$ and $e_3 = K_{33} b_c p_t / kT$, where $K_{11}$ and $K_{33}$ are the elastic constants for splay and bend respectively, in lowest order proportional to $S^2$; $p_l$ and $p_t$ are the longitudinal and transverse components of the permanent molecular dipole and $S_c$ and $b_c$ are a characteristic splay and bend, respectively in terms of the geometrical asymmetry of the molecular anisotropy. The essence of this description of the splay and bend polarizations comes also to the fore in the refined and elaborate theories in [18, 19]. Then indeed it may be concluded that the polarization linear in $S$ given by equation (20) has no relation with the splay and bend polarization in equation (2), where $e_1$ and $e_3$ are proportional to $S^2$. Without a physical model equation (20) is just a formal expression. In order that the second part of equation (27) can be identified with equation (2), in which $e_1 \neq e_3$, it is necessary to retain the independence of the tensor elements $g_4$ and $g_5$ that is $g_4$, $g_5 \neq g_1$. Then the splay and bend polarizations in equation (27) are also in a Landau–de Gennes expansion independent of each other and of the order polarization, the latter being undetermined and independent of $\mathbf{n}$; $r_1^{(1)} = 0$, cf. equation (31). In this respect it is difficult to appreciate the meaning of the relations between the coefficients $r_1$, $r_2$, $e_1$ and $e_3$, given in [2], which relate the order electric polarization with the mutually independent splay and bend polarizations in second order of $S$. Indeed as shown in equation (30) the order, splay and bend polarizations in equation (27) are all determined by one unspecified coefficient $g_1 = g_4 = g_5$ or they are, according equation (31), mutually independent, i.e. $g_1 \neq g_4 \neq g_5$, where $(2g_5 - g_4)S^2/3 = e_1$ and $(2g_4 - g_5)S^2/3 = e_3$. The same result for the coefficients $e_1$ and $e_3$ in terms of the expansion coefficients in a Landau–de Gennes expansion has been obtained in [20], where $A_1^{(3)} \equiv G_5 = g_5$ and $A_3^{(3)} \equiv G_4 = g_4$.

In view of the consequences of the Landau–de Gennes expansion of the distortion free energy in terms of scalar invariant combinations of $Q_{ij}$ and $Q_{ij,k}$ for the description of the distortion polarization linear in $Q_{ij,k}$, we have considered in the Appendix the usual Landau–de Gennes expansion of the distortion free energy quadratic in $Q_{ij,k}$ [4, 5] and the extension of it in terms of scalar invariant combinations quadratic in $Q_{ij,k}$ and linear in $Q_{ij}$ [6, 7, 9]. There it is shown that the expansion in equation (A 2), cf. equation (7), in terms of two invariants with arbitrary coefficients $L_1$ and $L_2$ give rise to four relations between the six coefficients, introduced as independent tensor elements, which occur in the expansion of equation (A 4); cf. equation (A 16). The addition of a third invariant to equation (A 2) give rise to additional relations between the tensor elements in equation (A 18); cf. equation (A 20). The relations in equations (A 16) and (A 20) are compatible only if all of the coefficients $b_i$ are equal, that is $L_1 = L_2 = L_3 = b_i$.

This restriction is the consequence of the fact that the invariants are introduced as scalar contractions of the tensor elements $Q_{ij}$ and their derivatives, independent of the choice the coordinate system. This is also the case in equation (A 21) where as a consequence of equation (A 28) all coefficients $C_i^{(3)}$ are equal, leading to equation (A 33). These equalities resolve the arbitrariness of the relations between the various tensor elements in equations (A 16), (A 20) and (A 31), which indeed have no conceivable relations to the symmetry of the director field $(n_i n_j)$ and its derivatives; they do not interfere, however, with the independence of the four elastic modes $V_i$ defined in equation (A 24).

The existence of an electric polarization due to a gradient of a quadrupole tensor is not surprising; the equivalence of both, explicitly shown in equations (58) and (59) is well known and needs no elucidation [15, 16]. The proper relation between the macroscopic polarization and the orientational averaged quadrupole density, shown in equation (40), is on the contrary not trivial; the statistical averaged value of the molecular quadrupole density defined in equation (55) is not the same as the orientational averaged value of the molecular quadrupole density in equation (34) cf. equation (33). It is satisfactory in that the required anisotropy of the quadrupole density is consistent with that of the molecular shape and polarizability, which indeed determine the orientational order [11]. Equation (42) shows that the polarization due to the quadrupole density in terms of $(n_i n_j)_{,i}$, does not discriminate between splay polarization and bend polarization introduced in [1] as independent modes; cf. equation (2). Indeed the quadrupole polarization has no relation with the flexoelectric polarization in terms of the geometrical asymmetry of the molecular anisotropy. We may also note that the free energy $\Delta f_q = -(P_q)_i E_i$ due to the quadrupole polarization $(P_q)_i$ defined in equation (40) is not contained in the Landau–de Gennes expansion of the free energy $\Delta f = -(P_d)_i E_i$ in equation (29). Comparison of equation (40) with equation (29) shows that only the invariant $E_i Q_{jk} Q_{ij,k} = E_i Q_{jj} Q_{ij,j} + E_i (Q_{jk} Q_{ij,k})_{i \neq j}$ in equation (29) contains a term which resembles the energy $(P_q)_i E_i$; in view of the denominator $\varepsilon_{jj} = \varepsilon + \varepsilon_a^* Q_{jj}$ in equation (40) they are however not identical. So we may conclude that a Landau–de Gennes expansion of the distortion free-energy is not very useful for the discussion of order, splay, bend and quadrupole polarization. Finally the consequence of the coupling between the director and the gradient of the order parameter at the surface, described by equation (66), for the director orientation at the surface will be discussed in the near future.

## Appendix

The Landau–de Gennes expansion of the distortion free energy is given by [4]

$$f_{\mathrm{dist.}} = \tfrac{1}{2}L_1 Q_{ij,k}Q_{ij,k} + \tfrac{1}{2}L_2 Q_{ij,j}Q_{ik,k}, \tag{A 1}$$

yielding [5]

$$\begin{aligned}
f_{\mathrm{dist.}} &= L_1(\tfrac{1}{3}(\nabla S)^2 + (\nabla\mathbf{n})^2S^2 + (\mathbf{n}\cdot\operatorname{rot}\mathbf{n})^2S^2 + ((\mathbf{n}\cdot\nabla)\mathbf{n})^2S^2) \\
&\quad + L_1(n_{i,j}n_{j,i} - n_{i,i}n_{j,j})S^2 \\
&\quad + \tfrac{1}{2}L_2\left(\tfrac{1}{9}(\nabla S)^2 + \tfrac{1}{3}((\mathbf{n}\nabla)S)^2 + \frac{2S}{3}(2(\nabla\cdot\mathbf{n})(\mathbf{n}\cdot\nabla) - ((\mathbf{n}\cdot\nabla)\mathbf{n})\cdot\nabla))S\right) \\
&\quad + \tfrac{1}{2}L_2((\nabla\mathbf{n})^2S^2 + ((\mathbf{n}\nabla)\mathbf{n})^2S^2) \\
&= \tfrac{1}{3}(L_1 + \tfrac{1}{6}L_2)(\nabla S)^2 + \tfrac{1}{6}L_2((\mathbf{n}\cdot\nabla)S)^2 \\
&\quad + \tfrac{1}{3}L_2S(2(\nabla\cdot\mathbf{n})(\mathbf{n}\cdot\nabla) - ((\mathbf{n}\nabla)\mathbf{n})\cdot\nabla)S \\
&\quad + \tfrac{1}{2}(2L_1 + L_2)((\nabla\cdot\mathbf{n})^2 + ((\mathbf{n}\cdot\nabla)\mathbf{n})^2)S^2 + L_1(\mathbf{n}\cdot\operatorname{rot}\mathbf{n})^2S^2 \\
&\quad + L_1(n_{i,j}n_{j,i} - n_{i,i}n_{j,j}),
\end{aligned} \tag{A 2}$$

where the last term can be written as

$$n_{i,j}n_{j,i} - n_{i,i}n_{j,j} = \nabla\cdot((\mathbf{n}\cdot\nabla)\mathbf{n} - \mathbf{n}(\nabla\cdot\mathbf{n})). \tag{A 3}$$

The distortion free energy can also be written in the general form

$$f_{\mathrm{dist.}} = \tfrac{1}{2}B_{ijklmn}Q_{ij,k}Q_{lm,n}, \tag{A 4}$$

where the $B_{ijklmn}$ are the elements of a sixth order tensor. In order to employ the symmetry with respect to the local director, we consider a local coordinate system $x$, $y$, $z$ in which the director at the origin is along the $x$, $y$ or $z$ axis. Symmetry then demands that the indices $i$, $j$, $k$, $l$, $m$, $n$ are pairwise equal, yielding

$$f_{\mathrm{dist.}} = \tfrac{1}{2}B_{ijkijk}Q_{ij,k}Q_{ij,k} + \tfrac{1}{2}B_{ijjikk}Q_{ij,j}Q_{ik,k}. \tag{A 5}$$

Considering an infinitesimal rotation of the director, i.e.

$$\mathbf{n}(\mathbf{r}) = \mathbf{n}(0) + \delta\mathbf{n}(\mathbf{r})$$

where $\mathbf{n}(0) = \mathbf{n}(\mathbf{r}) = 1$, we have

$$Q_{ii,j} = (n_i^2 - 1/3)S_{,j}; \quad i,j = x,y,z, \tag{A 6}$$

$$(Q_{ij,k})_{i\neq j} = S(n_in_j)_{,k}; \quad i,j,k = x,y,z. \tag{A 7}$$

The expression $B_{ijkijk}Q_{ij,k}Q_{ij,k}$ in the right hand side of equation (A 5) can consequently be written as the sum of four separate terms i.e.

$$\left.\begin{aligned}
&(1) \quad B_{iiiiii}Q_{ii,i}^2 = B_{iiiiii}(n_i^2 - 1/3)^2S_{,i}^2 \\
&(2) \quad B_{iijiij}Q_{ii,j}^2 = B_{iijiij}(n_i^2 - 1/3)^2S_{,j}^2; \quad i\neq j \\
&(3) \quad 2B_{ijjijj}Q_{ij,j}^2 = 2B_{ijjijj}(n_in_j)_{,j}^2S^2; \quad i\neq j \\
&(4) \quad 2B_{ijkijk}Q_{ij,k}^2 = 2B_{ijkijk}(n_in_j)_{,k}^2S^2; \quad i\neq j\neq k\neq i,
\end{aligned}\right\} \tag{A 8}$$

where, in view of the equivalence of the $x$, $y$ and $z$ coordinates, the four distinct elements of the sixth order $B$ tensor can be written as

$$b_1 = B_{iiiiii}, \quad b_2 = B_{iijiij}, \quad b_3 = B_{ijjijj}, \quad b_4 = B_{ijkijk}; \tag{A 9}$$

here $i \neq j \neq k \neq i$, $i, jk = x, y, z$.

With the director along the $z$ axis we find

$$\left.\begin{array}{lrcl}
(1) & b_1(n_i^2 - 1/3)^2 S_{,i}^2 & = & \frac{1}{9}b_1(S_{,x}^2 + S_{,y}^2 + 4S_{,z}^2) \\
(2) & b_2(n_i^2 - 1/3)^2 S_{,j}^2 & = & \frac{1}{9}b_2(5(S_{,x}^2 + S_{,y}^2) + 2S_{,z}^2) \\
(3) & 2b_3(n_i n_j)_{,j}^2 S^2 & = & 2b_3(n_z^2(n_{x,x}^2 + n_{y,y}^2) + n_z^2(n_{x,z}^2 + n_{y,z}^2))S^2 \\
(4) & 2b_4(n_i n_j)_{,k}^2 S^2 & = & 2b_4(n_z^2(n_{x,y}^2 + n_{y,x}^2)S^2
\end{array}\right\} \tag{A 10}$$

which can be written in the general form

$$\begin{aligned}
B_{ijkijk} Q_{ij,k} Q_{ij,k} = {} & \tfrac{1}{9}(b_1 + 5b_2)(\nabla S)^2 + \tfrac{1}{3}(b_1 - b_2)((\mathbf{n}\cdot\nabla)S)^2 \\
& + 2b_3((\nabla\cdot\mathbf{n})^2 + ((\mathbf{n}\cdot\nabla)\mathbf{n})^2)S^2 + 2b_4(\mathbf{n}\cdot\operatorname{rot}\mathbf{n})^2 S^2 \\
& - 2b_3 n_{i,i} n_{j,j} S^2 + 2b_4 n_{i,j} n_{j,i} S^2; \quad i \neq j.
\end{aligned} \tag{A 11}$$

The expression $B_{ijjikk} Q_{ij,j} Q_{ik,k}$ on the right hand side of equation (A 5) can equally be given an explicit form, that is with the director along the $z$ axis, the four separate terms are

$$\left.\begin{array}{lrcl}
(1) & b_1(n_i^2 - 1/3)^2 S_{,i}^2 & = & \frac{1}{9}b_1(S_{,x}^2 + S_{,y}^2 + 4S_{,z}^2) \\
(2) & 2b_5(n_i^2 - 1/3)S_{,i}(n_i n_j)_{,j} S & = & \frac{4}{3}b_5 S(n_z(n_{x,x} + n_{y,y}))S_{,z} \\
 & & & - \frac{2}{3}b_5 S(n_z n_{x,z} S_{,x} + n_z n_{y,z} S_{,y}) \\
(3) & b_3(n_i n_j)_{,j}^2 S^2 & = & b_3(n_z^2(n_{x,x}^2 + n_{y,y}^2) + n_z^2(n_{x,z}^2 + n_{y,z}^2))S^2 \\
(4) & b_6(n_i n_j)_{,j}(n_i n_k)_{,k} S^2 & = & 2b_6 n_z^2 n_{x,x} n_{y,y} S^2,
\end{array}\right\} \tag{A 12}$$

where $b_3$ and $b_6$ denote the tensor elements

$$b_5 = B_{iiiijj}; \quad b_6 = B_{ijjikk}; \quad i \neq j \neq k \neq i. \tag{A 13}$$

Rewritten in a coordinate free form we find

$$\begin{aligned}
B_{ijjikk} Q_{ij,j} Q_{ik,k} = {} & \tfrac{1}{9}b_1((\nabla S)^2 + 3((\mathbf{n}\cdot\nabla)S)^2) \\
& + \tfrac{2}{3}b_5 S(2(\nabla\cdot\mathbf{n})(\mathbf{n}\cdot\nabla) - ((\mathbf{n}\cdot\nabla)\mathbf{n})\cdot\nabla)S + b_3((\nabla\cdot\mathbf{n})^2 + ((\mathbf{n}\cdot\nabla)\mathbf{n})^2)S^2 \\
& + (b_6 - b_3)n_{i,i} n_{j,j} S^2; \quad i \neq j
\end{aligned} \tag{A 14}$$

Substitution of equations (A 14) and (A 11) in equation (A 5) yields

$$\begin{aligned}
2f_{\mathrm{d}} = {} & \tfrac{1}{9}(2b_1 + 5b_2)(\nabla S)^2 + \tfrac{1}{3}(2b_1 - b_2)((\mathbf{n}\cdot\nabla)S)^2 \\
& + \tfrac{2}{3}b_5 S(2(\nabla\cdot\mathbf{n})(\mathbf{n}\cdot\nabla) - ((\mathbf{n}\cdot\nabla)\mathbf{n})\cdot\nabla)S + 3b_3((\nabla\mathbf{n})^2 + ((\mathbf{n}\nabla)\mathbf{n})^2)S^2 \\
& + 2b_4(\mathbf{n}\cdot\operatorname{rot}\mathbf{n})^2 S^2 + 2b_4 n_{i,j} n_{j,i} S^2 - (3b_3 - b_6)n_{i,i} n_{j,j} S^2; \quad i \neq j
\end{aligned} \tag{A 15}$$

Compatibility with equation (A 2) requires

$$2b_1 = L_i + L_2, \quad b_2 = b_4 = L_1, \quad 3b_3 = 2L_1 + L_2, \quad b_5 = b_6 = L_2. \tag{A 16}$$

According to [6 and 7], the expansion in equation (A 1) should be completed with the term $\frac{1}{2}L_3 Q_{ij,k}Q_{jk,i}$, where the invariant $Q_{ij,k}Q_{jk,i}$ can be evaluated as

$$\begin{aligned} Q_{ij,k}Q_{jk,i} &= \tfrac{1}{9}(\nabla S)^2 + \tfrac{1}{3}((\mathbf{n}\cdot\nabla)S)^2 + \tfrac{2}{3}S(2((\mathbf{n}\cdot\nabla)\mathbf{n})\cdot\nabla - (\nabla\cdot\mathbf{n})(\mathbf{n}\cdot\nabla))S \\ &\quad + ((\nabla\cdot\mathbf{n})^2 + ((\mathbf{n}\cdot\nabla)\mathbf{n})^2)S^2 + (n_{i,j}n_{j,i} - n_{i,i}n_{j,j})S^2 \end{aligned} \tag{A 17}$$

yielding

$$\begin{aligned} 2f_\mathrm{d} = {} & \tfrac{1}{9}(6L_1 + L_2 + L_3)(\nabla S)^2 + \tfrac{1}{3}(L_2 + L_3)((\mathbf{n}\cdot\nabla)S)^2 \\ & + \tfrac{1}{3}(L_2 + L_3)S((\nabla\cdot\mathbf{n})(\mathbf{n}\cdot\nabla) + ((\mathbf{n}\cdot\nabla)\mathbf{n})\cdot\nabla)S \\ & + (L_2 - L_3)S((\nabla\mathbf{n})(\mathbf{n}\nabla) - ((\mathbf{n}\nabla)\mathbf{n})\cdot\nabla)S \\ & + (2L_1 + L_2 + L_3)((\nabla\cdot\mathbf{n})^2 + ((\mathbf{n}\cdot\nabla)\mathbf{n})^2)S^2 + 2L_1(\mathbf{n}\cdot\mathrm{rot}\,\mathbf{n})^2S^2 \\ & + (2L_1 + L_3)(n_{i,j}n_{j,i} - n_{i,i}n_{j,j})S^2 = \tfrac{1}{9}(3b_1 + 5b_2)(\nabla S)^2 \\ & + \tfrac{1}{3}(3b_1 - b_2)((\mathbf{n}\cdot\nabla)S)^2 + \tfrac{1}{3}(b_5 + b_7)S((\nabla\cdot\mathbf{n})(\mathbf{n}\cdot\nabla) + ((\mathbf{n}\nabla)\mathbf{n})\cdot\nabla)S \\ & + (b_5 - b_7)S((\nabla\cdot\mathbf{n})(\mathbf{n}\cdot\nabla) - ((\mathbf{n}\cdot\nabla)\mathbf{n})\cdot\nabla)S + 4b_3((\nabla\cdot\mathbf{n})^2 + ((\mathbf{n}\cdot\nabla)\mathbf{n})^2)S^2 \\ & + (2b_4 + b_8)(n_{i,j}n_{j,i})S^2 - (4b_3 - b_6)n_{i,i}n_{j\cdot j}S^2 + 2b_4(\mathbf{n}\cdot\mathrm{rot}\,\mathbf{n})^2S^2, \end{aligned} \tag{A 18}$$

where

$$b_7 = B_{iijiji}, \quad b_8 = B_{ijkkji}. \tag{A 19}$$

Compatibility requires

$$\left.\begin{aligned} 3b_1 &= L_1 + L_2 + L_3, \quad b_2 = b_4 = L_1, \quad b_5 = b_6 = L_2, \\ 4b_3 &= 2L_1 + L_2 + L_3, \quad b_7 = b_8 = L_3. \end{aligned}\right\} \tag{A 20}$$

In order to lift the degeneracy of the elastic constants $K_{11}$ and $K_{33}$, cf. equation (A 15), we may introduce an additional distortion free-energy of third order in $S$ which, in [6 and 7] is written as

$$\Delta f_\mathrm{d} = \sum_{i=1}^{6} C_i^{(3)}G_i^{(3)}. \tag{A 21}$$

Here the $C_i^{(3)}$ are phenomenological coefficients and the $G_i^{(3)}$ the six invariants

$$\left.\begin{aligned} G_1^{(3)} &= Q_{ij}Q_{ik,j}Q_{ki,l}, \quad G_2^{(3)} = Q_{ij}Q_{ik,k}Q_{jl,l}, \\ G_3^{(3)} &= Q_{ij}Q_{ik,l}Q_{jk,l}, \quad G_4^{(3)} = Q_{ij}Q_{ik,l}Q_{jl,k}, \\ G_5^{(3)} &= Q_{ij}Q_{ik,l}Q_{kl,j}, \quad G_6^{(3)} = Q_{ij}Q_{kl,i}Q_{kl,j}. \end{aligned}\right\} \tag{A 22}$$

In a local coordinate system in which the director at the origin is along the $z$ axis, these invariants are easily evaluated, that is with $S$ constant and $Q_{ij} \propto \delta_{ij}$, $Q_{ij,k} \propto (1 - \delta_{ij})$, we find

$$\begin{aligned} G_1^{(3)} &= Q_{ii}Q_{ik,i}Q_{kl,l} = -\tfrac{1}{3}Q_{xz,x}(Q_{zx,x} + Q_{zy,y})S \\ &\quad - \tfrac{1}{3}Q_{yz,y}(Q_{zx,x} + Q_{zy,y})S + \tfrac{2}{3}(Q_{zx,x}Q_{xz,z} + Q_{zy,y}Q_{yz,z})S \\ &= -\tfrac{1}{3}((n_xn_z)_{,x} + (n_yn_z)_{,z})^2S^3 + \tfrac{2}{3}((n_xn_z)_{,z}^2 + (n_yn_z)_{,z}^2)S^3 \\ &= -\tfrac{1}{3}(\nabla\cdot\mathbf{n})^2S^2 + \tfrac{2}{3}((\mathbf{n}\cdot\nabla)\mathbf{n})^2\mathrm{S}^3. \end{aligned} \tag{A 23}$$

Proceeding in the same way and using the notation

$$\left.\begin{aligned} V_1 &:= (\nabla\cdot\mathbf{n})^2 S^3/3, \quad V_2 = (\mathbf{n}\cdot\operatorname{rot}\mathbf{n})^2 S^3/3, \quad V_3 = ((\mathbf{n}\cdot\nabla)\mathbf{n})^2 S^3/3, \\ V_4 &:= (n_{i,j}n_{j,i} - n_{i,i}n_{j,j})S^3/3, \end{aligned}\right\} \tag{A 24}$$

we obtain for the six contributions to equation (A 21)

$$\left.\begin{aligned} C_1^{(3)}G_1^{(3)} &= C_1^{(3)}(-V_1 + 2V_3), & C_2^{(3)}G_2^{(3)} &= C_2^{(3)}(2V_1 - V_3), \\ C_3^{(3)}G_3^{(3)} &= C_3^{(3)}(V_1 + V_2 + V_3 + V_4), & C_4^{(3)}G_4^{(3)} &= C_4^{(3)}(2V_1 - V_3 + 2V_4), \\ C_5^{(3)}G_5^{(3)} &= C_5^{(3)}(-V_1 + 2V_3 - V_4), & & \\ & & C_6^{(3)}G_6^{(3)} &= 2C_6^{(3)}(-V_1 - V_2 + 2V_3 - V_4). \end{aligned}\right\} \tag{A 25}$$

Equation (A 21) however, can by analogy with equations (A 4) and (A 5) be written in a more general form, that is with the director along the *x*, *y* or *z* axis, the coefficients $C^{(3)}_{i,i=1\ldots b}$, in equation (A 21) being replaced by a set of elements of an eighth order tensor, that is, cf. equation (A 22),

$$\left.\begin{aligned} C_1^{(3)} &\Rightarrow B_{iiikikll}, & C_2^{(3)} &\Rightarrow B_{iiikkill}, & C_3^{(3)} &\Rightarrow B_{iiiklikl}, \\ C_4^{(3)} &\Rightarrow B_{iiiklilk}, & C_5^{(3)} &\Rightarrow B_{iiiklkli}, & C_6^{(3)} &\Rightarrow B_{iiklikli}. \end{aligned}\right\} \tag{A 26}$$

The invariants in equation (A 21) and defined in equation (A 22) have now to be evaluated in combination with the tensor elements given in equation (A 26). Considering the first term with $S$ constant and $Q_{ij} \propto \delta_{ij}$, $Q_{ij,k} \propto (l - \delta_{ij})$ and $\mathbf{n}$ along the $z$ axis we obtain

$$\begin{aligned} & B_{iiikikll}Q_{ii}Q_{ik,i}Q_{kl,l} \\ &= +B_{iiikikii}S^3\left(-\tfrac{1}{3}((n_xn_z)^2_{,x} + (n_yn_z)^2_{,y}) + \tfrac{2}{3}((n_zn_x)^2_{,z} + (n_zn_y)^2_{,z})\right) \\ &\quad + B_{iiikikll}S^3\left(-\tfrac{1}{3}((n_xn_z)_{,x} + (n_yn_z)_{,y} + (n_yn_z)_{,y}(n_xn_z)_{,x})\right) \\ &= +B_{iiikikii}S^3\left(-\tfrac{1}{3}((n_xn_z)_{,x} + (n_yn_z)^2_{,y}) + \tfrac{2}{3}((n_zn_x)^2_{,z} + (n_zn_y)^2_{,z})\right) \\ &\quad + (B_{iiikikii} - B_{iiikikll})S^3\cdot\tfrac{2}{3}(n_xn_z)_{,x}(n_yn_z)_{,z} \\ &= B_{iiikikii}\frac{S^3}{3}(-(\nabla\mathbf{n})^2 + ((\mathbf{n}\nabla)\mathbf{n}^2)^2) + (B_{iiikikii} - B_{iiikikll})\frac{S^3}{3}n_{j\cdot j}n_{t,t}; \quad j \neq t. \end{aligned} \tag{A 27}$$

All other contributions can be evaluated in the same way. Collecting the results, the six contributions to $\Delta f_{\mathrm{d}}$ in terms of the six invariants from equation (A 22) in combination with the tensor elements of equation (A 26) come to the fore as

$$\begin{aligned} & c_1(-V_1 + 2V_3) + (c_1 - c_2)n_{i,i}n_{j,j} \\ & c_3(2V_1 - V_3) - 2(c_3 - c_4)n_{i,i}n_{j,j} \\ & c_1(-V_1 + 2V_3) + c_3(2V_1 - V_3) + c_5(V_2 + V_4) + (c_1 - 2c_3 + c_5)n_{i,i}n_{j,j} \\ & c_3(2V_1 - V_3) + 2c_6V_4 + 2(c_6 - c_3)n_{i,i}n_{j.j} \\ & c_1(-V_1 + 2V_3) - c_7V_4 + (c_1 - c_7)n_{i,i}n_{j,j} \\ & 2c_1(-V_1 + 2V_3) - 2c_8(V_2 + V_4) + 2(c_1 - c_8)n_{i,i}n_{j,j}; \quad i \neq j, \end{aligned} \tag{A 28}$$

where

$$\left.\begin{aligned} c_1 &= B_{iiikikii}, & c_2 &= B_{iiikikll}, \\ c_3 &= B_{iiikkikk}, & c_4 &= B_{iiikkill}, \\ c_5 &= B_{iiiklikl}, & c_6 &= B_{iiiklilk}, \\ c_7 &= B_{iiiklkli}, & c_7 &= B_{iiklikli} \end{aligned}\right\} \tag{A 29}$$

leading to

$$\begin{aligned} 2\Delta f &= (6c_3 - 5c_1)V_1 - (2c_8 - c_5)V_2 + (12c_1 - 3c_3)V_3 \\ &\quad + ((2c_6 - c_3) - (2c_8 - c_5))V_4. \end{aligned} \tag{A 30}$$

on the condition that

$$5c_1 - c_2 - 6c_3 + 2c_4 + (2c_6 - c_7) + (2c_8 - c_5) = 0. \tag{A 31}$$

As in [6 and 7] only one of the four terms of equation (A 25) is considered to contribute to $\Delta f_\mathrm{d}$ we may require that all of the separate terms in equation (A 28) are compatible with those of equation (A 25), that is instead of equation (A 31) we have

$$\left.\begin{aligned} &c_1 = c_2 = c_5 = c_7 = c_8 = C_1^{(3)} = C_3^{(3)} = C_5^{(3)} = C_6^{(3)}, \\ &c_3 = c_4 = c_5 = C_1^{(3)} = C_3^{(3)} = C_4^{(3)} = c_1, \text{etc.}, \end{aligned}\right\} \tag{A 32}$$

yielding

$$2\Delta f_\mathrm{d} = c(V_1 - V_2 + cV_3) = \frac{cS^3}{3}((\boldsymbol{\nabla} \cdot \mathbf{n})^2 - (\operatorname{rot} \mathbf{n})^2 + c(\mathbf{n} \cdot \boldsymbol{\nabla})\mathbf{n})^2), \tag{A 33}$$

where

$$c = c_i = C_i^{(3)}.$$

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