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Determination of the elastic constants of nematic liquid crystals by means of the affine transformation model

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In this paper the affine connection approach will be used to calculate the elastic constants of nematic liquid crystals. Following this approach, which was originally conceived to compute the nematic viscosity coefficients, an expression for the elastic constants, without adjustable free parameters, will be formulated in terms of a temperature dependent metric, whose non-isotropic part is proportional to the tensorial order parameter of the nematic phase. The dependence of the elastic constants on the scalar order parameter, in the geometry of the nematic molecules, and in the anisotropic part of the molecular interaction, will be determined.

1. Introduction

The determination of the thermal behaviour of elastic constants of nematic liquid crystals (NLC) [1–3] is a long-standing problem for which experimental [4–8], computational [9, 10] and analytical methods [11–17] have been applied and, for each of these approaches, new sets of results have been found. Nevertheless, despite such developments, the understanding of the elastic constants is not complete; only the leading terms of their dependence on the scalar order parameters are firmly established [18] and, even now, the nature of the anchoring of the molecules of these materials at the surface of the sample has been the theme of intense research [19–22]. The main aim of this paper is the proposition of a geometrical method for the determination of the dependence of the elastic constants on some important physical variables like the scalar order parameter, the geometry of the nematic grains (molecules or micelles) and on the anisotropic interaction between them. The geometrical affine transformation model [23–27] will be combined with the fundamentals of the pseudo-molecular approach [28–31] to produce an expression free of phenomenological adjustable parameters that, to our knowledge, for the first time blends these two approaches to obtain the nematic elastic constants.

In order to establish a firm starting point for the combined application of these two approaches, a study of the fundamentals of the affine connection approach

will be presented. In contrast to the usual procedure, we will not assume perfect ordering on the director alignment during our calculations and, in this way, the dependence on the scalar order parameter will appear naturally in our calculations. Afterwards, invariants that contain the Maier–Saupe [32–34] and Nehring–Saupe [11, 12] interactions, formerly used [28] in the computation of pseudo-molecular elastic constants [28], will be submitted to the affine transformation approach. As a consequence, the dependence of the elastic constants on the scalar order parameter, molecular geometry and monopolar and quadrupolar terms of the molecular interaction will appear naturally.

2. Fundamentals

There are, in the literature on liquid crystals, many works dealing with the dependence of the elastic constants on the order parameter. All of them agrees that in the case of small deformations the elastic energy would be expressed as a series in the scalar order parameter [35]. Nevertheless, usually, the coefficients of this power expansion would be determined by comparison with the experimental data [18, 29–31], and only through explicit models for the interaction between the grains constituting the nematic material could the physical nature of such coefficients be determined. The so-called pseudo-molecular models can accomplish this task [28–31]. Below, we recall some results previously obtained by them to be compared, ahead, with our forthcoming results. Firstly, we recall that a

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pure Maier–Saupe [32–34] term,

$$E_{MS} = A(\vec{m} \cdot \vec{n})^2, \quad (1)$$

where A is a constant and \vec{m} and \vec{n} represent two directors separated by a distance \vec{r} , cannot explain the three different values experimentally found in the bulk elastic constants; if the interaction between two neighbour molecules is restricted to a Maier–Saupe term, the elastic constants K_{11} and K_{22} would become identical [18, 28]. In order to obtain a distinction between them, two new hypotheses have been introduced. Firstly, a Nehring–Saupe [11, 12] term

$$E_{NS} = A[\vec{m} \cdot \vec{n} - 3\varepsilon(\vec{n} \cdot \vec{r})(\vec{m} \cdot \vec{r})]^2 \quad (2)$$

has been added, where the mixing parameter ε was arbitrarily fixed in the interval $0 < \varepsilon < 1$. Secondly, it was also assumed that around a molecule the volume of integration cannot be spherical, but must be ellipsoidal. That is, a macroscopic nematic domain does not interact equally along spherical symmetric surfaces with the origin in their centres, but along surfaces having ellipsoidal symmetry, producing a volume of interaction with such symmetry. With the combined application of these ideas, in a perfectly aligned condition, an analytic expression for the bulk contribution to the five elastic constants of a nematic material was obtained [28]. The motivation of this work arises from the perception that the way in which these results were found strongly resembles the approach used by Hess and co-workers in the calculation of the viscosity coefficients of a nematic compound [23–27]. Even formalized in a different manner and applied to different rheological phenomena, both approaches seem to have the same physical grounds; in the physics of nematic materials not only are the molecules non-spherical, but so also are the symmetries of their interaction. That is, the potential governing their interactions has the same symmetry of the nematic domains; it is not spherical but ellipsoidal.

In this work, a combination of the affine connection method and the pseudo-molecular approach will be applied to the computation of the elastic constants. In isolation, the Hess approach has already been used for the computation of the elastic constants in a sequence of papers by Osipov and Hess [10, 16, 17]. The essential improvement of our approach is that a metric description of the nematic phase will be obtained, which, being dependent on the tensorial order parameter, engenders a temperature dependent geometry. Pragmatically, our final expression will reveal the dependence of the elastic constants in the scalar order parameter, in the geometry of the nematic cell and in the monopolar and quadrupolar momenta of the interaction between the nematic grains.

3. Essentials of the Hess approach

3.1. Transformation rules

According to Hess, the ellipsoidal interaction potential Φ_E between nematic molecules can be transformed into a spherical interaction potential Φ_S , once the vector \vec{r} connecting two particles is submitted to an affine transformation, in which the distance between the particles is expressed in terms of a metric determined by the non-spherical geometry of the equipotential surfaces of Φ_E . In mathematical terms,

$$\Phi_E(r^S) = \Phi_S(r^E), \quad (3)$$

where the indexes E and S stand for ellipsoidal and spherical symmetries, respectively. Namely, the non-spherical potential, Φ_E , can be replaced by a spherical potential, Φ_S , if the distance between two points is given by a metric in which two points on an equipotential surface are equidistant from the potential centre. In order to give a specific rule to this prescription, it was assumed that the distance between the different points in the nematic sample measured in spherical and non-spherical metrics are connected by the rule,

$$r_i^E r_j^E = E_{ij} r_i^S r_j^S, \quad (4)$$

where E_{ij} gives the metric induced by the non-spherical potential and the sum rule over repeated indexes is being assumed hereafter. An important aspect of the Hess approach is the knowledge of how the metric determines the rules connecting the different coordinate systems. To obtain these rules a matrix A_{ij} satisfying the relation,

$$A_{ik} A_{kj} = E_{ij}, \quad (5)$$

must be obtained because the rule transforming coordinates becomes,

$$r_i^E = A_{ik} r_k^S, \quad (6)$$

as can be seen by a direct substitution in equation (4). Furthermore, as the physical laws frequently involve variations, rules connecting derivatives between the two systems are also necessary. To obtain this rule, we observe that equation (6) implies that $dr_i^E = A_{ik} dr_k^S$. Consequently,

$$\frac{dr_k^S}{dr_i^E} = \chi_{ki}, \quad (7)$$

where χ_{ik} is the inverse of A_{kj} , i.e.,

$$\chi_{ik} A_{kj} = \delta_{ij}, \quad (8)$$

So,

$$\frac{d}{dr_j^E} = \frac{dr_i^S}{dr_j^E} \frac{d}{dr_i^S} = \chi_{ij} \frac{d}{dr_i^S}. \quad (9)$$

These rules formalize the affine transformation method; once a physical quantity is known in a spherically symmetric system, its expression in the non-spherical system can be obtained through the application of these rules. Thus, to begin the application of the Hess approach to the calculation of the nematic elasticity, all that remains to be done is the determination of the matrices E_{ij} , A_{ij} and χ_{ij} . The derivation of explicit expressions for these matrices in terms of nematic parameters is the aim of the next section.

3.2. Ellipsoidal metric

It will be assumed here that the metric E is determined by the same matrix \bar{E} that transforms a sphere into an ellipsoid, that is, $E = \bar{E}$. For this reason, no notational distinction between them will be used in this paper. Therefore, given a uniaxial ellipsoid there is always a local coordinate system in which it assumes the form,

$$\frac{x_1^2}{a^2} + \frac{x_2^2}{b^2} + \frac{x_3^2}{b^2} = 1, \quad (10)$$

where its three main axis lengths are given, respectively, by $\{a, b, b\}$, each of them pointing in the directions given, respectively, by the three orthonormal vectors, $\{\bar{p}_d, \bar{q}_d, \bar{r}_d\}$, where

$$\bar{p}_d = (1, 0, 0), \quad \bar{q}_d = (0, 1, 0), \quad \bar{r}_d = (0, 0, 1), \quad (11)$$

with x_1 , x_2 and x_3 the coordinates along them. In compact form, this ellipsoid can be written as $E_{ij}^d x_i x_j = 1$, where,

$$E_{ij}^d = \begin{pmatrix} \frac{1}{a^2} & 0 & 0 \\ 0 & \frac{1}{b^2} & 0 \\ 0 & 0 & \frac{1}{b^2} \end{pmatrix}, \quad (12)$$

being completely characterized by the eigenvalues

$$\left\{ \frac{1}{a^2}, \frac{1}{b^2}, \frac{1}{b^2} \right\}, \quad (13)$$

and eigenvectors given by equation (11). The indexes d in E_{ij}^d and $\{\bar{p}_d, \bar{q}_d, \bar{r}_d\}$ are used to recall that the corresponding characteristic matrix E_{ij}^d is diagonal. In this way, the matrix E_{ij} is the matrix E_{ij}^d , submitted to an arbitrary rotation in which its three orthonormal main axes are now given by a new set of orthonormal vectors $\{\bar{p}, \bar{q}, \bar{r}\}$.

In an arbitrarily rotated coordinate system, this ellipsoid can be written as,

$$E_{ij} y_i y_j = 1, \quad (14)$$

where [24],

$$E_{ij} = \frac{1}{b^2} \{ \delta_{ij} - e p_i p_j \}, \quad (15)$$

is the rotated characteristic matrix of the ellipsoid, and

$$e = 1 - \frac{b^2}{a^2}, \quad (16)$$

is the ellipsoid eccentricity and \bar{p} corresponds to the symmetric axis of the uniaxial ellipsoid.

As the condition $e=0$ reduces the ellipsoid to a sphere, the anisotropy found in the rheological parameters can be interpreted as the deformation induced on the nematic medium by the non-spherical equipotential surfaces. Consequently, this anisotropy can be quantified by measuring how much this ellipsoid differs from an equivalent sphere. To obtain such a sphere we remember that, according to equation (12), the tensor characterizing an ellipsoid is a linear function of the inverse of the square of its axes and, furthermore, it would be reduced to a sphere if these axes become equal. Accordingly, the equivalent sphere can be defined as that for which the radius r satisfies the relation,

$$\frac{1}{r^2} = \frac{1}{3} \text{Tr}(E) = \frac{1}{b^2} \left(1 - \frac{e}{3} \right). \quad (17)$$

Therefore, if E is the characteristic matrix of an ellipsoid, the elements of the characteristic matrix of the equivalent sphere would be given by $S_{ij} = \delta_{ij} \text{Tr}(E)/3$ and, consequently, the ellipsoidal deformation ΔE could be defined by the difference between the ellipsoid and its equivalent sphere,

$$\Delta E_{ij} = E_{ij} - S_{ij} = E_{ij} - \frac{1}{3} \delta_{ij} \text{Tr}(E), \quad (18)$$

which, with the use of equations (15) and (17), becomes

$$\Delta E_{ij} = \frac{e}{b^2} \left\{ \frac{1}{3} \delta_{ij} - p_i p_j \right\}. \quad (19)$$

That is, the ellipsoidal deformation ΔE is determined by the product of two distinct terms, e/b^2 and

$$Q_{ij} = \frac{1}{3} \delta_{ij} - p_i p_j. \quad (20)$$

This last term is the tensorial component of the ellipsoidal deformation; formally it coincides with the quadrupolar momentum [38], having a structure similar to the tensorial order parameter of a nematic liquid

crystal [35]. Otherwise, the eccentricity term, e , furnishes the magnitude of the ellipsoidal anisotropy; different eccentricities correspond to different molecular shapes; when $e < 0$, we have that $b > a$, corresponding to a discotic phase and, when $e > 0$, we have that $a > b$, corresponding to a calamitic phase.

Summarizing, the ellipsoidal matrix can be written as

$$E_{ij} = S_{ij} + \frac{e}{b^2} Q_{ij} \\ = \frac{1}{3} \text{Tr}(E) \delta_{ij} + \frac{e}{b^2} Q_{ij}, \quad (21)$$

which will be taken as the metric to be used in equation (4).

3.3. Order parameter in the metric

As the metric induced by the equipotential surfaces can be written in terms of a tensorial term which is structurally similar to the order parameter tensor, it will be shown that such a similarity can be taken as a microscopic order parameter that will induce a macroscopic temperature-dependent metric. This remarkable result is the essence of the Hess approach. We will begin this study by remembering some standard considerations about the meaning of the order parameter and its construction using microscopic considerations.

The anisotropy of liquid crystal materials can be observed at two levels, macroscopically and microscopically. On thermodynamic measurements it appears macroscopically. But, it has a microscopic origin: the LC domains have an intrinsic anisotropy that, when averaged, induces the observed macroscopic anisotropy. This distinct range of anisotropy scales has important consequences in our next developments; as the metric is a function of a tensor similar to the order parameter it will also be subject to such a distinction; its essential microscopic anisotropy will lead to a metric that depends on the order parameter. To be precise, let us distinguish between the microscopic and the macroscopic nature of Q_{ij} by putting a hat over its vectorial parameter \vec{n} when it denotes a microscopic unitary vector. So, $Q_{ij}(\hat{n})$ means that \hat{n} is a microscopic random variable and the associated quantity coincides with what de Gennes named the microscopic order parameter. Likewise, $Q_{ij}(n)$ means that \vec{n} is a macroscopic variable, the director, and the corresponding order parameter is a macroscopic order parameter. The connection between these two quantities is made by assuming that the microscopic random variable \hat{n} oscillates so rapidly that when $Q_{ij}(\hat{n})$ is averaged, over time and in the neighbourhood of a point, it determines the macroscopic order parameter $Q_{ij}(n)$, from which the uniaxial macroscopic anisotropy can be measured. In mathematical

terms,

$$\langle Q_{ij}(\hat{n}) \rangle = S Q_{ij}(n), \quad (22)$$

where $\langle x \rangle$ stands for the statistical average of the random variable x . As anticipated above, S gives the intensity by which the random oscillations make the microscopic anisotropy be observed on a macroscopic scale. It is enough to multiply the left side of the above expression by the macroscopic order parameter, $Q_{kl}(n)$, and calculate the trace of the resulting expression,

$$\langle Q_{ji}(n) Q_{ij}(\hat{n}) \rangle = S Q_{ji}(n) Q_{ij}(n), \quad (23)$$

to obtain,

$$S = \frac{3}{2} \left(-\frac{1}{3} + \langle (\hat{n} \cdot \vec{n})^2 \rangle \right). \quad (24)$$

This equation is the standard expression for the scalar order parameter. From it, a simplification frequently used in liquid crystal physics can be used: the mean field approximation. According to this, save for the critical points and self-interaction terms, the correlation between microscopic order parameters is given by,

$$\langle Q_{ik}(\hat{m}) Q_{kj}(\hat{n}) \rangle \simeq \langle Q_{ik}(\hat{m}) \rangle \langle Q_{kj}(\hat{n}) \rangle \\ = S^2 Q_{ik}(m) Q_{kj}(n). \quad (25)$$

Equations (23) and (25) give the thermal basis of our subsequent development. They justify the hypothesis assumed in this work that the metric can be made temperature dependent. Nevertheless, it is important to observe that our further development is subject to the restrictions of validity of the approximation made in equation (25); it cannot be applied for coincident points of space and, consequently, for molecular self-interaction.

So, let us begin by showing how the metric can become dependent on the order parameter, and consequently also on the temperature. If we take the mean over the ellipsoidal matrix E_{ij} around the neighbourhood of a point we obtain,

$$\langle E_{ij} \rangle = \frac{1}{3} \text{Tr}(E) \delta_{ij} + \frac{e}{b^2} \langle Q_{ij}(\hat{n}) \rangle \\ = \frac{1}{b^2} \left(1 - \frac{e}{3} \right) \delta_{ij} + \frac{e}{b^2} S Q_{ij}(n). \quad (26)$$

This equation reveals that the metric induced by the ellipsoidal anisotropy is macroscopically observed to be dependent on the scalar order parameter and, therefore, it is determined by the nematic temperature; at the isotropic phase ($S=0$) the metric is spherical and no

anisotropy would be observed on macroscopic scales. As the temperature is reduced, the nematic-isotropic phase transition creates a non-null S , which induces a macroscopic anisotropy.

Finally, with this explicit form of E_{ij} the computation of the tensors A_{ij} and χ_{ij} is a straightforward exercise. If it is assumed that

$$r = 1 - \frac{b}{a} \text{ and } x = 1 - \frac{a}{b}, \quad (27)$$

it can be easily demonstrated that

$$\begin{aligned} A_{ij} &= a_0 \delta_{ij} + a_1 Q_{ij}(\hat{n}), \\ \chi_{ij} &= x_0 \delta_{ij} + x_1 Q_{ij}(\hat{n}). \end{aligned} \quad (28)$$

It follows that,

$$\begin{aligned} \langle A_{ij} \rangle &= a_0 \delta_{ij} + a_1 S Q_{ij}(n), \\ \langle \chi_{ij} \rangle &= x_0 \delta_{ij} + x_1 S Q_{ij}(n), \end{aligned} \quad (29)$$

where $a_0 = (1-r/3)/3$, $a_1 = r/b$, $x_0 = (1-x/3)/3$, and $x_1 = bx$. To complete the definitions that will be used later, we also define the tensor H_{ij} as the contraction of A_{ik} and χ_{kj} , i.e.

$$H_{ij} = A_{ik} \chi_{kj} = h_0 \delta_{ij} + h_1 Q_{ij}(\hat{n}) + h_2 Q_{ik}(\hat{n}) Q_{kj}(\hat{n}), \quad (30)$$

and

$$\langle H_{ij} \rangle = h_0 \delta_{ij} + h_1 S Q_{ij}(n) + h_2 S^2 Q_{ik}(n) Q_{kj}(n), \quad (31)$$

where

$$\begin{aligned} h_0 &= \frac{1}{9} \left(1 - \frac{r}{3}\right) \left(1 - \frac{x}{3}\right), \\ h_1 &= \frac{1}{3} \left(bx \left(1 - \frac{r}{3}\right) + \frac{r}{b} \left(1 - \frac{x}{3}\right)\right), \\ h_2 &= rx. \end{aligned} \quad (32)$$

Observe that it is exactly on $\langle H_{ij} \rangle$ that the restrictions of validity quoted above must be considered.

4. The elastic energy

Since the free energy is a scalar function, it can be assumed that it can be constructed from the simplest unitary invariants of the theory. Therefore, tensorial products of the order parameter, as for example,

$$I_{ij}(p, q) = Q_{ik}(p) Q_{kj}(q), \quad (33)$$

has been considered as the basic tool for the construction of invariants [39]. To find the first invariant, consider the thermal average of the trace of the tensor $\langle I_{ij}(\hat{n}, n) \rangle$, where \hat{n} and n are, respectively, microscopic and macroscopic random variables. It is easily found

that

$$S = \frac{3}{2} I_{ii}(\hat{n}, n) = \frac{3}{2} \left(-\frac{1}{3} + \langle (\vec{\hat{n}} \cdot \vec{n})^2 \rangle \right). \quad (34)$$

As the trace of an operator is invariant by unitary transformations, it follows that all observers connected by unitary transformations should measure the same S . Nevertheless, this is not the unique invariant that can be formed with the tensor $I_{ij}(p, q)$; another one occurs when both of its variables, p and q , are taken as random variables, $I_{ij}(\hat{m}, \hat{n}) = Q_{ik}(\hat{m}) Q_{kj}(\hat{n})$. As this is a function of random variables, only its mean value has thermodynamic meaning. By supposing that the connected part of the two-point function $\langle Q_{ik}(\hat{m}) Q_{kj}(\hat{n}) \rangle$ can be neglected and, consequently, it implies that we are not on a critical point and that each random variable describes different points of space, we can write $\langle I_{ij}(\hat{m}, \hat{n}) \rangle = \langle Q_{ik}(\hat{m}) \rangle \langle Q_{kj}(\hat{n}) \rangle$ [40]. So, using equation (12) we arrive at

$$\begin{aligned} \langle I_{ij}(\hat{m}, \hat{n}) \rangle &= S^2 Q_{ik}(m) Q_{kj}(n) \\ &= S^2 I_{ij}(m, n). \end{aligned} \quad (35)$$

To obtain a scalar invariant with this expression it is enough to form its trace,

$$\begin{aligned} i_1 &= \langle I_{ii}(\hat{m}, \hat{n}) \rangle = S^2 I_{ii}(m, n) \\ &= S^2 \left(-\frac{1}{3} + (\vec{m} \cdot \vec{n})^2 \right). \end{aligned} \quad (36)$$

In this equation i_1 express an angular interaction, the Maier-Saupe interaction. That is, two directors, \vec{m} and \vec{n} , localized at different points of the sample, only are elastically coupled when $S \neq 0$, otherwise, in the isotropic phase ($S=0$), they are uncoupled. However, as its dependence on the relative position of the directors is not explicit, it would be a poor generator of energy expressions where an explicit dependence on the relative distance between the directors is necessary. This fact can be used to inspire the construction of a unitary invariant that explicitly contains a dependence on the radius vector between two nematic molecules. If we take $\vec{r} = \vec{r}_1 - \vec{r}_2$, $r_1 \neq r_2$, as the distance between two nematic domains we observe that the object

$$i_2 = \langle r_i r_j I_{ij}(\hat{m}, \hat{n}) \rangle = S^2 r_i r_j I_{ij}(m, n) \quad (37)$$

is also invariant by unitary transformations. The full expression of i_2 :

$$i_2 = \frac{S^2}{9} \left(\vec{r}^2 - 3 \left((\vec{m} \cdot \vec{r})^2 + (\vec{n} \cdot \vec{r})^2 \right) + 9 (\vec{m} \cdot \vec{r})(\vec{n} \cdot \vec{r})(\vec{m} \cdot \vec{n}) \right), \quad (38)$$

reveals that once \vec{r}^2 is a fixed invariant, i_2 becomes a

function of the variables, $\vec{m}, \vec{r}, \vec{n}, \vec{r}$ and \vec{m}, \vec{n} , that correlates orientational order with positional order, exactly what would be expected from this kind of invariant. In the remainder of this work, due to that fact that $\vec{m} = \vec{m}(\vec{r}_2)$ and $\vec{n} = \vec{n}(\vec{r}_1)$, both notations, $i_1(\hat{m}, \hat{n})$ and $i_1(\vec{r}_1, \vec{r}_2)$, will be used according to convenience (analogously for $i_2(\hat{m}, \hat{n})$ and $i_2(\vec{r}_1, \vec{r}_2)$).

5. Elastic constants

5.1. The Maier–Saupe approximation

Here, all the formalism developed above will be gathered to compute the elastic constants. This task will be divided in two parts. Firstly, the contribution of equation (36), the Maier–Saupe interacting term,

$$F_1 = \int d^3 r_1 d^3 r_2 a_1(\vec{r}_2 - \vec{r}_1) \langle I_{ii}(\vec{r}_1, \vec{r}_2) \rangle, \quad (39)$$

to the elastic energy will be computed, where, $a_1 = a_1(\vec{r}_1, \vec{r}_2) = a_1(\vec{r}_1 - \vec{r}_2)$, $r_1 \neq r_2$ is the expansion coefficient of the energy in terms of $\langle I_{ii}(\vec{r}_1, \vec{r}_2) \rangle$. The contribution of the other term, equation (38), will be considered later. In the above equation the notation used so far has been shortened; when microscopic variables appear inside brackets the duplicity of notation is avoided and, for example, $\langle I_{ij}(\vec{r}_1, \vec{r}_2) \rangle$ is to be understood as

$$\langle I_{ij}(\vec{r}_1, \vec{r}_2) \rangle = \langle Q_{ik}(\hat{n}) Q_{kj}(\hat{m}) \rangle \equiv \langle Q_{ik}(\vec{r}_1) Q_{kj}(\vec{r}_2) \rangle, \quad (40)$$

where $\hat{m} \equiv \hat{m}(\vec{r}_2)$ and $\hat{n} \equiv \hat{n}(\vec{r}_1)$. Observe that in equation (39), the condition $r_1 \neq r_2$ can be fully justified by the fact that we are computing an elastic energy and, therefore, considering the interaction between different points of the sample; self-energy terms have no contribution to the elastic energy. Previously, this hypothesis was taken as a restriction to the applicability of our formulas. Now, it becomes a natural constraint.

In order to apply the affine transformation approach in equation (39), and calculate the resulting elastic constants, the change $\vec{r}_2 = \vec{r}_1 + \vec{r}$ will be made, giving

$$\begin{aligned} Q_{kj}(\vec{r}_2) &= Q_{kj}(\vec{r}_1 + \vec{r}) \\ &\approx Q_{kj}(\vec{r}_1) + r_r \partial_r Q_{kj}(\vec{r}_1) + \frac{1}{2} r_r r_s \partial_r \partial_s Q_{kj}(\vec{r}_1). \end{aligned} \quad (41)$$

Using the mean field approximation, as in equation (25), it is found that

$$\begin{aligned} \langle I_{ij}(\vec{r}_1, \vec{r}_2) \rangle &= \langle Q_{ik}(\vec{r}_1) Q_{kj}(\vec{r}_1 + \vec{r}) \rangle \\ &\approx \langle Q_{ik}(\vec{r}_1) Q_{kj}(\vec{r}_1) \rangle \\ &+ \langle Q_{ik}(\vec{r}_1) \rangle \langle r_r \partial_r Q_{kj}(\vec{r}_1) \rangle \\ &+ \frac{1}{2} \langle Q_{ik}(\vec{r}_1) \rangle \langle r_r r_s \partial_r \partial_s Q_{kj}(\vec{r}_1) \rangle \end{aligned} \quad (42)$$

In this equation the term $\langle Q_{ik}(\vec{r}_1) Q_{kj}(\vec{r}_1) \rangle$ corresponds to a self-energy term and, as explained above, can be disregarded. According to the above reasoning, the integrals given by equation (39) must be performed considering that the symmetry of the interacting potential is ellipsoidal. Nevertheless, through the Hess affine transformation its elliptical geometry is transformed to a spherical one. The following sequence of transformations synthesizes this procedure for each of these terms:

$$\begin{aligned} r_r \partial_r &\equiv r_r^E \frac{d}{dr^E} = A_{rk} \chi_{rp} r_k^S \frac{d}{dr^S_p} \rightarrow H_{kp} r_k \partial_p, \\ r_r r_s \partial_r \partial_s &\equiv r_r^E r_s^E \frac{d}{dr^E} \frac{d}{dr^E} \\ &= A_{rk} \chi_{rp} A_{sl} \chi_{sq} r_k^S r_l^S \frac{d}{dr^S_p} \frac{d}{dr^S_q} \rightarrow H_{kp} H_{lq} r_k r_l \partial_p \partial_q, \end{aligned} \quad (43)$$

where the definition given by equation (30) has been used.

In order not to lose the focus of this work, we remember that the second term of equation (42) is linear in the derivative; therefore, it is, at most, responsible for the cholesteric term. Since, in this work, the points of interest are the elastic constants, it will be assumed that our system is not cholesteric. As a result,

$$\langle I_{ij}(\vec{r}_1, \vec{r}_2) \rangle = \frac{1}{2} \langle r_m r_l \rangle \langle H_{mp} \rangle \langle H_{lq} \rangle \langle Q_{ik} \rangle \langle \partial_p \partial_q \langle Q_{kj} \rangle \rangle. \quad (44)$$

In equation (44) the mean field approximation, equation (25), has been used and the indication of the vectors, \vec{r} and \hat{n} , in $Q_{ik}(\vec{r}_1)$ and $Q_{kj}(\hat{n})$ has been suppressed to simplify the notation. Furthermore, as $r_m r_l$ is a second rank symmetric tensor, it could be written in terms of the natural second rank symmetric tensors of the theory [18, 28], Q_{ml} and δ_{ml} ,

$$r_m r_l = A Q_{ml} + B \delta_{ml}, \quad (45)$$

where, as can be easily shown, $A = 2r_r r_j Q_{ij} / 3$ and $B = r^2 / 3$. So,

$$\begin{aligned} \langle I_{ij}(\vec{r}_1, \vec{r}_2) \rangle &= \frac{1}{2} (A \langle Q_{ml} \rangle + B \delta_{ml}) \\ &\langle H_{mp} \rangle \langle H_{lq} \rangle \langle Q_{ik} \rangle \langle \partial_p \partial_q \langle Q_{kj} \rangle \rangle. \end{aligned} \quad (46)$$

Hence,

$$\begin{aligned} \langle I_{ij}(\vec{r}_1, \vec{r}_2) \rangle &= \frac{1}{2} \{ A \langle H_{pm} \rangle \langle Q_{ml} \rangle \langle H_{lq} \rangle + B \langle H_{pl} \rangle \langle H_{lq} \rangle \} \\ &\langle Q_{ik} \rangle \partial_p \partial_q \langle Q_{kj} \rangle. \end{aligned} \quad (47)$$

From this point until the final determination of the elastic constants the calculations are long, but simple. Using the definition of H_{lm} , given by equation (31), we have

$$\begin{aligned} \partial_q \partial_p \langle Q_{ij} \rangle &= -S \left((\partial_q \partial_p n_i) n_j + n_i (\partial_q \partial_p n_j) + (\partial_p n_i) (\partial_q n_j) \right. \\ &\quad \left. + (\partial_q n_i) (\partial_p n_j) \right), \\ (\partial_p n_i)^2 &= \left(\vec{n} \cdot \vec{\nabla} \times \vec{n} \right)^2 + \left(\vec{n} \times \vec{\nabla} \times \vec{n} \right)^2 + \left(\vec{\nabla} \cdot \vec{n} \right)^2 \\ &\quad + \vec{\nabla} \cdot \left(\vec{n} \vec{\nabla} \cdot \vec{n} + \vec{n} \times \vec{\nabla} \times \vec{n} \right) \end{aligned} \quad (48)$$

$$n_p n_q (\partial_p n_i) (\partial_q n_i) = \left(\vec{n} \times \vec{\nabla} \times \vec{n} \right)^2,$$

and comparing the resulting equations with the Frank free energy,

$$\begin{aligned} F = \frac{1}{2} \int_V d^3 r \left\{ K_{11} \left(\vec{\nabla} \cdot \vec{n} \right)^2 + K_{22} \left(\vec{n} \cdot \vec{\nabla} \times \vec{n} \right)^2 + K_{33} \left(\vec{n} \times \vec{\nabla} \times \vec{n} \right)^2 \right. \\ \left. + K_{13} \vec{\nabla} \cdot \left(\vec{n} \vec{\nabla} \cdot \vec{n} \right) - (K_{22} + K_{24}) \vec{\nabla} \cdot \left(\vec{n} \vec{\nabla} \cdot \vec{n} + \vec{n} \times \vec{\nabla} \times \vec{n} \right) \right\}, \end{aligned} \quad (49)$$

it is found that

$$\begin{aligned} K_{11} &= B h_o S^2 \left(1 + \frac{1}{3} \left(\frac{2h_1}{h_o} + \frac{A}{B} \right) S \right), \\ K_{22} &= B h_o S^2 \left(1 + \frac{1}{3} \left(\frac{2h_1}{h_o} + \frac{A}{B} \right) S \right) \\ K_{33} &= B h_o S^2 \left(1 - \frac{1}{3} \left(\frac{2h_1}{h_o} + \frac{A}{B} \right) S \right) \quad (50) \\ K_{13} &= 0, \\ K_{22} + K_{24} &= B h_o S^2 \left(1 + \frac{1}{3} \left(\frac{2h_1}{h_o} + \frac{A}{B} \right) S \right) \end{aligned}$$

where only the cubic terms in S have been retained, and A and B , being given by,

$$\begin{aligned} A &= \frac{2}{3} \int_V d^3 r a_1(\vec{r}) r_i r_j Q_{ij}, \\ B &= \frac{2}{3} \int_V d^3 r a_1(\vec{r}) r^2 \end{aligned} \quad (51)$$

represent the quadrupolar and monopolar contribution of the interacting potential to the elastic constants values.

As h_o and h_1 are functions of e (see equations 32 and 27), we see that according to this model the elastic constants are determined by the scalar order parameter, the eccentricity of the nematic molecule/micelle, and its monopolar and quadrupolar momenta. To our knowledge, an expression containing such elastic constants dependence has not been published before. Anyway, this result is inconsistent with the experimental results; it predicts that $K_{11} = K_{22}$, which disagrees with the

experimental data. Nevertheless, this disagreement is a known outcome of the Maier–Saupe interaction, which is not enough to take care of the diversity of the elastic constants [28]. In the next section, we will show that when the term i_2 of equation (38) is considered these inconsistencies are removed.

5.2. The Nehring–Saupe approximation

Here, the contribution of the term i_2 to the elastic constants will be considered. It is assumed that the energy can be written as

$$F_2 = \int d^3 r_1 d^3 r_2 a_2(\vec{r}) \langle r_i r_j I_{ij}(\vec{r}_1, \vec{r}_2) \rangle, \quad (52)$$

where $a_2 = a_1(\vec{r}_1, \vec{r}_2) = a_2(\vec{r}_1 - \vec{r}_2)$ is the expansion coefficient of the energy in terms of $\langle r_i r_j I_{ij}(\vec{r}_1, \vec{r}_2) \rangle$. As above, it will be assumed that $\vec{r}_2 = \vec{r}_1 + \vec{r}$, and the affine connection transformation would be applied to $r_i r_j I_{ij}(\vec{r}_1, \vec{r}_2)$. Hence,

$$\begin{aligned} \langle r_i r_j I_{ij} \rangle &\rightarrow \langle r_m r_l \rangle \langle E_{mi} \rangle \langle E_{lj} \rangle \langle Q_{ik} \rangle \langle Q_{kj} \rangle \\ &\quad + \frac{1}{2} \langle r_n r_l r_m r_o \rangle \langle E_{mi} \rangle \langle E_{lj} \rangle \langle H_{np} \rangle \\ &\quad \langle H_{oq} \rangle \langle Q_{ik} \rangle \langle \partial_p \partial_q \langle Q_{kj} \rangle \rangle, \end{aligned} \quad (53)$$

where, again, we have omitted the cholesteric term.

Now, the term $\langle r_n r_l r_m r_o \rangle$ is rewritten as

$$\begin{aligned} \langle r_n r_l r_m r_o \rangle &= \frac{1}{3} \{ \langle r_n r_l \rangle \langle r_m r_o \rangle + \langle r_n r_m \rangle \langle r_l r_o \rangle + \langle r_n r_o \rangle \langle r_l r_m \rangle \} \\ &= \frac{1}{3} \{ (A Q_{nl} + B \delta_{nl}) (A Q_{mo} + B \delta_{mo}) \\ &\quad + (A Q_{nm} + B \delta_{nm}) (A Q_{lo} + B \delta_{lo}) \\ &\quad + (A Q_{no} + B \delta_{no}) (A Q_{lm} + B \delta_{lm}) \}, \end{aligned} \quad (54)$$

where equation (45) was used. By putting this relation in equations (11) and (10), and considering only terms up to third order in S to avoid a useless and complicated expression, it is found that

$$\begin{aligned} K_{11} &= \frac{2}{3} c_o S^2 \left(1 - \frac{1}{6} c_1 S \right), \\ K_{22} &= \frac{1}{9} c_o S^2 \left(1 - \frac{2}{3} c_1 S \right), \\ K_{33} &= \frac{2}{3} c_o S^2 \left(1 - \frac{1}{6} c_2 S \right), \\ K_{13} &= \frac{1}{9} c_o S^2 \left(1 - \frac{1}{3} c_3 S \right), \\ K_{22} + K_{24} &= \frac{4}{9} c_o S^2 \left(1 + \frac{1}{6} c_4 S \right). \end{aligned} \quad (55)$$

where

$$\begin{aligned}c_o &= h_o^2 w_o^2 B^2, \\c_1 &= \frac{w_1}{w_o} - 3 \frac{h_1}{h_o} - \frac{A}{B}, \\c_2 &= 7 \frac{w_1}{w_o} + 9 \frac{h_1}{h_o} + 8 \frac{A}{B}, \\c_3 &= \frac{w_1}{w_o} + \frac{h_1}{h_o} + \frac{A}{B}, \\c_4 &= -2 \frac{w_1}{w_o} + 4 \frac{h_1}{h_o} + \frac{A}{B},\end{aligned}$$

h_o and h_1 have been defined in equation (32), A and B are defined in equation (51), but with the replacement $a_1 \rightarrow a_2$, and

$$\begin{aligned}w_1 &= \frac{e}{b^2}, \\w_2 &= \frac{1}{3} \left(1 - \frac{e}{3} \right).\end{aligned}$$

In contrast with the Maier–Saupe case, these equations present a clear distinction between all elastic constants; the invariant i_2 introduced a clear distinction between the five elastic constants and, furthermore, the bulk value of K_{13} is no longer null.

6. Final remarks and conclusion

In this work, we have used the affine connection model to make a pseudo-molecular study of the nematic elastic constants. Our final expressions have revealed their dependence on the scalar order parameter, the geometry of the nematic cell, and the first moments of the interaction between them. We have restricted our equation to the third-order terms of the scalar order parameter because the experimental data can hardly go beyond it. Furthermore, our expression is free of parameters to be adjusted by means of comparison with experimental data. Nevertheless, as the momentum constants, A and B , depend on a specific model for the interaction between the nematic molecules/micelles they can also be used as adjustable free parameters.

At this moment we are comparing known experimental data of elastic constants with the predictions given by equation (55). Part of our experimental results, some of them suggested by the above developments, have already been published [41]. At this moment we are preparing an experimental set of the above elastic constants values. Our results, which will be published soon, have revealed excellent agreement between the above expressions and experiment.

Finally, we would like mention that the use of the affine connection method in the computation of the elastic constants reveals the fertility of this approach, which has been applied here in a context different from that for which it was originally conceived. Furthermore, the richness of the obtained result is afforded by the possibility of taking care of the anisotropy of a nematic compound through a redefinition of the metric of the sample, which according to the developments of this work, becomes temperature dependent.

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