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Elastic Constants of a Disc-Like Nematic Liquid Crystal: Pseudo-Molecular Approach

P. S. Simonário¹ · T. M. de Andrade¹ · F. C. M. Freire¹

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Abstract The pseudo-molecular method is employed to obtain analytical expressions for the elastic constants of an ensemble of anisotropic particles, in both disc-like and rod-like geometries. These particles interact via a phenomenological pair potential constructed from the non-spherical correction to the dispersion forces between two identical molecules. The molecular shape appears in the calculations of the elastic constants in two different cases. The first case considers a molecular volume of ellipsoidal shape continuously deformed from a positive (prolate spheroid, rod-like molecule) to large negative (oblate spheroid, disc-like molecule) values of a parameter describing some kind of eccentricity. The second one considers a molecular volume shape continuously deformed from a cylinder (calamitic molecule) to a plane disc by changing the ratio between the diameter of the cylinder and its long axis. The particular cases of Maier-Saupe and Nehring-Saupe interactions are obtained as simple limiting cases of the general pair potential interaction. These general results may be helpful to understand the limits of the pseudo-molecular method, and to understand the origin of elastic constants in discotic liquid crystals from a molecular perspective.

Keywords Elastic constants · Liquid crystals · Lattice models · Pseudo-molecular method

1 Introduction

The pseudo-molecular method [1–6] has been successfully applied to determine the elastic constants of nematic liquid crystal (NLC) for the Maier-Saupe [7, 8], Nehring-Saupe [9, 10], and quadrupolar [11, 12] interaction energies, among others. The method is very simple and has some limitations [6], but it brings a direct way to connect the elastic constants with the intermolecular interaction responsible for the NLC phase. In a recent paper [13], the method was employed to obtain analytical expressions for the elastic constants of NLC whose intermolecular interaction is given by an “elastic model,” constructed from the non-spherical correction to the dispersion forces between two identical diatomic molecules [14–19]. This kind of interaction permits us to appreciate the dependence of the pair potential on the molecular orientation with respect to the intermolecular vector in a simple lattice model [18, 19]. When faced in a phenomenological way, this pair interaction embodies as particular cases of some important intermolecular interactions responsible for the nematic ordering, such as the Maier- (MS) and Nehring-Saupe (NS) interactions [1].

In this work, we use the method to obtain analytical expressions for the elastic constants of a disc-like NLC system interacting by means of this lattice interaction. The calculations are done in two distinct scenarios: one considers the molecular volume has an ellipsoidal shape, deformed to a oblate spheroid, whereas the other considers this volume represented by long cylinders, deformed to a disc. This procedure allows us to explore the behavior of the elastic constants by promoting a continuous change in the geometry of the molecule.

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The present approach is an extension of ref. [13], having in mind a detailed investigation of the elastic properties of the discotic phase obtained as a limiting procedure. Although we are willing to explore both cases as a continuous transition from calamitic to discotic shape, this is not what is assumed as true for the NLC phases. Indeed, both phases are well defined and distinct [20]. Our procedure has to be faced just as a geometrical tool to obtain, analytically, the expressions for the elastic constants of a discotic phase either in spheroidal or cylindrical geometries. Also, we are not stating that the method and/or the procedure to deform the molecular shape to a disc-like form is the definitive one. It is only an attempt to choose candidates to describe the discotic and the calamitic regimes from a pseudo-molecular perspective.

The paper is organized as follows. The next section is dedicated to a simple discussion about the pseudo-molecular method. In Section 3, we present the pair potential, depending on the relative anisotropy of the polarizability. This anisotropy enters in the potential by means of quadratic functions g_i ($i = 1, 2, 3, 4, 5$). For some particular values of g_i , we can recover the MS and NS interaction potentials. In Section 4, we discuss the two different approaches for the molecular volume shape, namely the spheroidal and the cylindrical ones, and how to obtain representations of the calamitic and discotic regimes. Section 5 is devoted to establish the analytical expressions for the elastic constants, valid for the two approaches already mentioned, by showing, explicitly, a formal way to introduce the geometry in the calculations. For specific values of the parameters is possible to obtain the elastic constants for the discotic and calamitic cases. In Section 6, we present some illustrative results, including remarkable non-monotonic behavior of the elastic constants, and even negative values of them, that will be discussed in a way to interpret it. Some concluding remarks are drawn in Section 7.

2 A Brief Discussion on the Pseudo-Molecular Method

Pseudo-molecular method is a tool to obtain macroscopic parameters—the elastic constants—using microscopic ones, such as the pair potential among the molecules. We assume that the scalar order parameter $S = 1$, which implies that the molecular axis of two different molecules, namely, \mathbf{a} and \mathbf{a}' , located in \mathbf{R} and \mathbf{R}' , with $\mathbf{R}' = \mathbf{R} + \mathbf{r}$, coincide with the directors \mathbf{n} and \mathbf{n}' , respectively. Another assumption is about the pair potential: let us admit that the potential is nonzero only in a region where $r_0 \leq r \leq r_N$, for r_0 being of the order of the molecular volume and r_N being the actual range of interaction.

Let $g(\mathbf{n}, \mathbf{n}'; \mathbf{r})$ be the potential when $\mathbf{a} = \mathbf{n}$, and $\mathbf{a}' = \mathbf{n}'$, i.e., the perfect molecular order of the nematic sample. For a small variation of the director, $|\mathbf{n}' - \mathbf{n}| = |\delta\mathbf{n}| \ll 1$, we can expand the potential as follows:

$$g(\mathbf{n}, \mathbf{n} + \delta\mathbf{n}; \mathbf{r}) = g_0 + q_i n_{i,k} x_k + \frac{1}{2} (q_i n_{i,kl} + q_{ij} n_{i,k} n_{j,l}) x_k x_l + \dots, \quad (1)$$

where the summation convention for repeated indices was applied. In (1), $g_0 := g(\mathbf{n}, \mathbf{n}; \mathbf{r})$ represents the reference state, and the other relevant quantities are

$$q_i := \left(\frac{\partial g}{\partial n'_i} \right)_{\mathbf{n}'=\mathbf{n}}; \quad q_{ij} := \left(\frac{\partial^2 g}{\partial n'_i \partial n'_j} \right)_{\mathbf{n}'=\mathbf{n}};$$

and

$$n_{i,k} = \frac{\partial n_i}{\partial x_k}; \quad n_{i,kl} = \frac{\partial^2 n_i}{\partial x_k \partial x_l}.$$

The elastic energy and the density energy are defined, respectively, as

$$F := \int_{v'} f dv'; \quad \text{and} \quad f := \int_{v'} g(\mathbf{n}, \mathbf{n}'; \mathbf{r}) dv', \quad (2)$$

where v' represents the region where the molecular interaction is comprehended. Replacing (1) in f given in (2), one has

$$f = f_0 + L_{ik} n_{i,k} + M_{ikl} n_{i,kl} + N_{ijkl} n_{i,k} n_{j,l}, \quad (3)$$

for which f_0 is the energy density of the undeformed state, and the tensor components of \mathbf{L} , \mathbf{M} , and \mathbf{N} are also given by the volume integrals as (2).

The symmetry of the problem permits us to write the energy density in terms of the elastic constants:

$$f = f_0 + \frac{1}{2} \left\{ K_{11} (\text{div } \mathbf{n})^2 + K_{22} (\mathbf{n} \cdot \text{curl } \mathbf{n})^2 + K_{33} (\mathbf{n} \times \text{curl } \mathbf{n})^2 \right\} + K_{13} [\text{div } (\mathbf{n} \text{ div } \mathbf{n})] - (K_{22} + K_{24}) [\text{div } (\mathbf{n} \text{ div } \mathbf{n} + \mathbf{n} \text{ curl } \mathbf{n})], \quad (4)$$

where the elastic constants are directly linked to the relevant parts of \mathbf{M} and \mathbf{N} .¹ Using tensor properties, we write

$$N_{ikl} = A_{ikl} + n_i B_{kl}; \\ M_{ijkl} = C_{ijkl} + n_i D_{jkl} + n_j E_{ikl} + n_i n_j F_{kl},$$

¹It is assumed $\mathbf{L} = 0$ in the nematic phase. In this case, there is no deformation in the ground state. \mathbf{L} would be nonzero only in the cholesteric phase [1].

and the only nonzero terms are the ones connected to A_{ikl} , B_{kl} , and C_{ijkl} . They can be decomposed as

$$\begin{aligned} A_{ikl} &= A_1 n_i n_k n_l + A_2 (n_i \delta_{kl} + n_k \delta_{il} + n_l \delta_{ik}); \\ B_{kl} &= B_1 n_k n_l + B_2 \delta_{kl}; \\ C_{ijkl} &= C_1 n_i n_j n_k n_l + C_2 (\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \\ &\quad + C_3 (n_i n_j \delta_{kl} + n_i n_k \delta_{jl} + n_i n_l \delta_{jk} \\ &\quad + n_j n_k \delta_{il} + n_j n_l \delta_{ik} + n_k n_l \delta_{ij}), \end{aligned}$$

and the unknown parameters A_1 , A_2 , B_1 , B_2 , C_1 , C_2 , and C_3 , are given by²

$$\begin{aligned} A_1 &= \frac{1}{2} (5n_i n_k n_l A_{ikl} - 3n_i A_{ikk}); \\ A_2 &= \frac{1}{2} (n_i A_{ikk} - n_i n_k n_l A_{ikl}); \\ B_1 &= \frac{1}{2} (3n_k n_l B_{kl} - B_{kk}); \\ B_2 &= \frac{1}{2} (B_{kk} - n_k n_l B_{kl}); \\ C_2 &= \frac{1}{8} (-5n_i n_j n_k n_l C_{ijkl} + 6n_i n_j C_{ijkk} - C_{iikk}); \\ C_3 &= \frac{1}{8} (n_i n_j n_k n_l C_{ijkl} - 2n_i n_j C_{ijkk} + C_{iikk}). \end{aligned}$$

Finally, the elastic constants are related to these parameters as

$$\begin{aligned} K_{11} &= 2(-3A_2 - B_2 + 3C_3); \\ K_{22} &= 2(-A_2 - B_2 + C_3); \\ K_{33} &= 2(-A_1 - A_2 - B_1 - B_2 + C_2 + C_3); \\ K_{13} &= 2A_2; \\ K_{22} + K_{24} &= -(A_2 + B_2 - 2C_3). \end{aligned}$$

The relation between the elastic constants and the elastic tensors—consequently, the interaction potential—was extensively discussed in many other works, see, e.g., refs. [1, 9–13]. For a different approach, the reader can also see [1, 4–6]. Here, we are only interested in showing how the procedure works.

3 The Pair Potential

In ref. [13], the pseudo-molecular method was applied to determine the elastic constants of an ensemble of molecules interacting via a potential in the form:

$$\begin{aligned} g(\mathbf{n}, \mathbf{n}'; \mathbf{r}) &= \frac{\varepsilon}{r^6} \left\{ g_1 [(\mathbf{n} \cdot \mathbf{u})^2 + (\mathbf{n}' \cdot \mathbf{u})^2] \right. \\ &\quad + g_2 (\mathbf{n} \cdot \mathbf{u})^2 (\mathbf{n}' \cdot \mathbf{u})^2 + g_3 (\mathbf{n} \cdot \mathbf{n}')^2 \\ &\quad \left. + g_4 (\mathbf{n} \cdot \mathbf{u})(\mathbf{n}' \cdot \mathbf{u})(\mathbf{n} \cdot \mathbf{n}') + g_5 \right\}, \end{aligned} \quad (5)$$

²The value of C_1 will not be shown here, because when it is replaced in C_{ijkl} , it yields a vanishing contribution. In the following, we show that the elastic constants do not depend on C_1 .

where g_i ($i = 1, 2, 3, 4, 5$) are expressed in terms of the relative anisotropy in the polarizability α as

$$\gamma = \frac{\alpha_{\parallel} - \alpha_{\perp}}{\alpha_{\parallel} + 2\alpha_{\perp}}. \quad (6)$$

The subscripts \parallel and \perp refer to the nematic director \mathbf{n} , and ε is the scalar component of the dispersion interaction [19]. The parameters g_i are

$$g_1 = 6\gamma^2 - \frac{3}{2}\gamma, \quad g_2 = -\frac{27}{2}\gamma^2, \quad g_3 = -\frac{3}{2}\gamma^2 \quad (7)$$

$$g_4 = 9\gamma^2, \quad g_5 = -3\gamma^2 + \gamma. \quad (8)$$

This potential represents the dipolar contribution to the dispersion energy between two identical, neutral, and centrosymmetric linear molecules, according to the quantum theory of intermolecular forces [21].

Since $-1/2 \leq \gamma \leq 1$, g_i are also limited. However, if we disregard these limiting values and consider g_i as free phenomenological parameters, we can explore how these elements enter in the intermolecular interaction. Some particular cases may be obtained for a specific set of values of g_i . For instance, taking $g_3 = -g$, with $g > 0$ a new parameter, and $g_i = 0$ (for $i \neq 3$), the interaction energy reduces to the simple form

$$g(\mathbf{n}, \mathbf{n}'; \mathbf{r}) = -\frac{C_{\text{MS}}}{r^6} (\mathbf{n} \cdot \mathbf{n}')^2, \quad (9)$$

which corresponds to the MS intermolecular interaction whose strength is $C_{\text{MS}} = g\varepsilon$ [9]. Likewise, if we consider $g_3 = -g$, $g_2 = -9g$, and $g_4 = 6g$, with $g_1 = g_5 = 0$, the interaction energy reduces to

$$g(\mathbf{n}, \mathbf{n}'; \mathbf{r}) = -\frac{C_{\text{NS}}}{r^6} [(\mathbf{n} \cdot \mathbf{n}') - 3(\mathbf{n} \cdot \mathbf{u})(\mathbf{n}' \cdot \mathbf{u})]^2, \quad (10)$$

which corresponds to the NS intermolecular interaction with $C_{\text{NS}} = g\varepsilon$ [9]. The same limit may be obtained if we consider also that $g_1 = g_5 = 0$, with $\gamma = 1$ [22, 23].

4 The Molecular Shape

In previous works [1, 6, 9], the NLC molecule was considered as an ellipsoid of revolution around the director \mathbf{n} , and the parameter which gives the exact shape of this ellipsoid was an eccentricity e , given by

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

where a and b represent the short and long axes of this ellipsoid, respectively, and $0 \leq e < 1$. One can also imagine an ellipsoid of revolution around the short axis, which implies that the parameter $e < 0$. By rotating the ellipse around

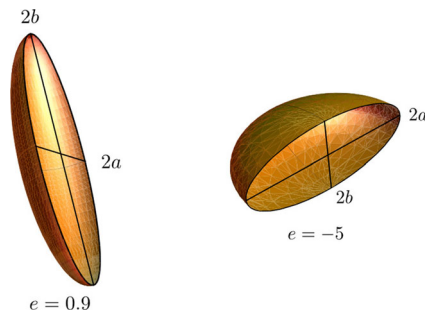


Fig. 1 Cross sections of prolate ($e = 0.9$) and oblate ($e = -5$) spheroids, intended as representing calamitic and disc-like molecular volume shape for an NLC molecule

its long axis, one obtains the prolate spheroid, also known as ellipsoid; by rotating it around its short axis, one obtains the oblate spheroid [24]. The illustration depicted in Fig. 1 shows both prolate and oblate spheroids.

Figure 1 also shows that the oblate spheroid is obtained for very large values of e , while the prolate one is found within the limits $0 \leq e < 1$. Another values of e and the respective spheroids are shown in Fig. 2. A discotic shape occurs when $e = -10$. To cover the calamitic and discotic approaches, the eccentricity e will be used in a range $-10 \leq e < 1$.

On the other hand, we define a similar procedure in a cylindrical perspective. Let us use a cylindrical coordinates system, and define a cylinder with radius a and length h . The analogous to an eccentricity e for the spheroids is here the parameter R , defined as

$$R = \frac{2a}{h}.$$

This parameter is a measure of the anisotropy in the molecular shape and has been employed to investigate the micellar shape anisotropy behavior from the elastic point of view in a lyotropic system [10]. In this assumption, h may represent the bilayer thickness, supposed to remain essentially independent of the temperature [25]. Here, however,

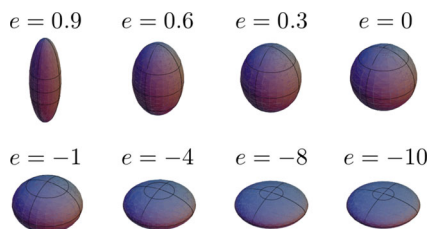


Fig. 2 Spheroids with different values of e . The sphere appears for $e = 0$

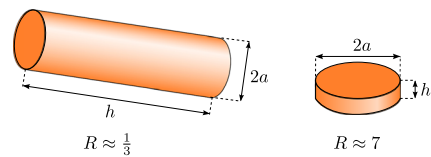


Fig. 3 Cylinders defined for two different values of the shape anisotropy R

we consider that h may assume any value. Figure 3 exhibits two different cylinders for very different values of R .

According to Fig. 3, the calamitic phase is found when $0 < R < 1$, and the discotic phase for $1 < R < \infty$. For $R \approx 1$, we have a “cylindric pillbox” which represents an intermediate region between calamitic and discotic phases, more alike, eventually, with biaxial objects [20]. In Fig. 4, a few cylindrical shapes are illustrated.

5 The Elastic Constants

The procedure to connect the elastic constants with the molecular interaction was discussed in Section 2. Here, we will only present the elastic constants, determined in a general form in ref. [13]. Thus,

$$\begin{aligned} K_{11} &= \left[\frac{3g_1}{8}(I_0 - 6I_2 + 5I_4) + \frac{3g_2}{8}(I_2 - 6I_4 + 5I_6) \right. \\ &\quad \left. + \frac{g_3}{2}(-I_0 + I_2) + g_4(-I_2 + I_4) \right] \varepsilon; \\ K_{22} &= \left[\frac{g_1}{8}(I_0 - 6I_2 + 5I_4) + \frac{g_2}{8}(I_2 - 6I_4 + 5I_6) \right. \\ &\quad \left. + \frac{g_3}{2}(-I_0 + I_2) + \frac{g_4}{2}(-I_2 + I_4) \right] \varepsilon; \\ K_{33} &= \left[\frac{g_1}{2}(3I_2 - 5I_4) + \frac{g_2}{2}(3I_4 - 5I_6) \right. \\ &\quad \left. - g_3(I_2) + \frac{g_4}{2}(I_2 - 3I_4) \right] \varepsilon, \end{aligned} \quad (11)$$

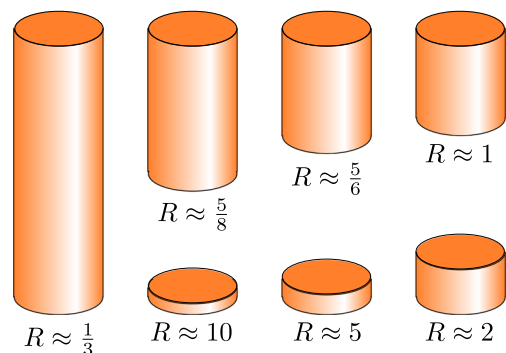


Fig. 4 A short sequence of cylinders illustrating the continuous limiting process leading to the discotic shape, as the values of R is changed. The discotic shape is supposed to occur for $1 < R < \infty$

are the bulk elastic constants, and the surface-like constants are

$$K_{13} = \left[\frac{g_1}{2}(I_2 - I_4) + \frac{g_2}{2}(I_4 - I_6) + \frac{g_4}{4}(I_2 - I_4) \right] \varepsilon;$$

$$K_{22} + K_{24} = \left[\frac{g_1}{4}(I_0 - 4I_2 + 3I_4) + \frac{g_2}{4}(I_2 - 4I_4 + 3I_6) + \frac{g_3}{4}(-2I_0 + 2I_2) + \frac{g_4}{4}(-2I_2 + 2I_4) \right] \varepsilon, \quad (12)$$

where I_n ($n = 0, 2, 4, 6$) are integrals that take into account the shape of the molecular and interaction volumes and will be discussed further.

In Section 3, we show how to find the elastic constants for the MS and NS potentials. For the MS potential, using $g_3 = -g$, with $g > 0$, $g_i = 0$ (for $i \neq 3$), and $g\varepsilon = C_{MS}$ in (11) and (12), we have

$$K_{11} = K_{22} = \frac{C_{MS}}{2}(I_0 - I_2) = -2K_{24};$$

$$K_{33} = C_{MS}I_2; \quad K_{13} = 0. \quad (13)$$

On the other hand, for $g_3 = -g$, $g_2 = -9g$, $g_4 = 6g$, and $g\varepsilon = C_{NS}$, we have the constants of the NS potential:

$$K_{11} = \frac{C_{NS}}{8}(4I_0 - 79I_2 + 210I_4 - 135I_6);$$

$$K_{22} = \frac{C_{NS}}{8}(4I_0 - 37I_2 + 78I_4 - 45I_6);$$

$$K_{33} = \frac{C_{NS}}{2}(8I_2 - 45I_4 + 45I_6);$$

$$K_{13} = \frac{C_{NS}}{2}(3I_2 - 12I_4 + 9I_6);$$

$$K_{24} = \frac{C_{NS}}{4}(-I_0 + 7I_2 - 15I_4 + 9I_6). \quad (14)$$

5.1 Ellipsoidal System

In this approach, both molecular and interaction volumes are assumed as being of ellipsoidal shape, with the director \mathbf{n} aligned with the z -axis of the system in spherical coordinates, such that $\mathbf{n} \cdot \mathbf{u} = \cos \theta$, where $u_1 = \sin \theta \cos \phi$,

$u_2 = \sin \theta \sin \phi$, and $u_3 = \sin \theta$. The intermolecular interaction is assumed as different from zero only in a region limited by these two similar ellipsoids. The inner part corresponds to the molecular volume, while the outer one is connected with the long-range part of the intermolecular interaction. The equations representing the ellipsoids may be expressed as

$$r_0(\theta) = \frac{a}{\sqrt{1 - e \cos^2 \theta}}; \quad r_N(\theta) = \frac{A}{\sqrt{1 - e \cos^2 \theta}},$$

where a and A refer to the inner (molecular) and outer (interaction) volumes. The integrations I_n , comparing in (11) and (12), now become $I_n^{(s)}$, which the superscript (s) stands for spheroid, and are given by [13]:

$$I_n^{(s)} = \left(\frac{2\pi}{a} \right) \frac{1 + (-1)^n}{1 + n} \times {}_2F_1 \left(-\frac{1}{2}, \frac{n+1}{2}; \frac{n+3}{2}; e \right), \quad (15)$$

where ${}_2F_1(a, b; c; x)$ is the hypergeometric function [26]. It was stressed in ref. [1] that the elastic constants do not depend on the outer volume, and the limit $A \rightarrow \infty$ ($r_N \rightarrow \infty$) may be taken. For simplicity, we will also take $a = 1$, that is, the lengths will be measured in units of the molecular dimensions.

5.2 Cylindrical System

Now, we determine the integrals I_n related to the cylindrical symmetry. Again, we choose the z -axis of the coordinate system along \mathbf{n} . In cylindrical coordinates,

$$x = \rho \cos \theta, \quad y = \rho \sin \theta, \quad \text{and} \quad z.$$

We also have

$$u_1 = \frac{x}{r} = \frac{\rho \cos \theta}{r}, \quad u_2 = \frac{y}{r} = \frac{\rho \sin \theta}{r}, \quad \text{and} \quad u_3 = \frac{z}{r},$$

and $\mathbf{n} \cdot \mathbf{u} = z/r$, where $r = \sqrt{\rho^2 + z^2}$. In the calculations, we need to deal with integrals as

$$J_n = \int_v f_n(\rho, \theta, z) \rho d\rho d\theta dz,$$

with

$$f_n(\rho, \theta, z) = \frac{z^n}{(\rho^2 + z^2)^{(n+4)/2}}$$

Fig. 5 Elastic constants for the Maier-Saupe potential. In (a), the spheroidal symmetry; (b) the cylindrical symmetry

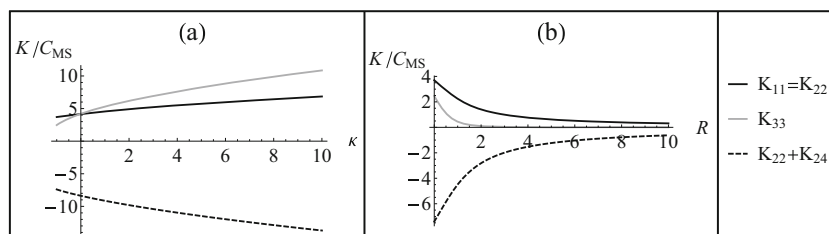
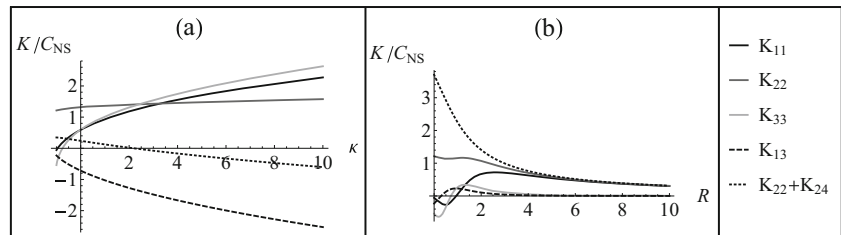


Fig. 6 Elastic constants for the Nehring-Saupe potential: **a** the elastic constants are represented in the spheroidal case; **b** elastic constants as function of R , in the cylindrical case



being a continuous function of the variables. The relevant integrations can be written as

$$J_n = \int_0^{2\pi} d\theta \left[\int_{-H/2}^{H/2} dz \int_0^A f_n(\rho, \theta, z) \rho d\rho - \int_{-h/2}^{h/2} dz \int_0^a f_n(\rho, \theta, z) \rho d\rho \right],$$

which represents the integral over the interaction volume, of a cylinder whose height is H and radius is A , minus the integral over the molecular one of the function $f_n(\rho, \theta, z)$ [10]. As in the spheroidal case, the intermolecular interaction was supposed to be different from zero only in the region between these two similar cylinders. The limits $H \rightarrow \infty$ and $A \rightarrow \infty$ were performed, and then, the integrals I_n ($n = 0, 2, 4, 6$) become

$$I_n^{(c)} = \frac{2\pi}{(1+n)(2+n)R} \left[\left(-\frac{1}{R} \right)^n + \left(\frac{1}{R} \right)^n \right] \times {}_2F_1 \left[\frac{1+n}{2}, \frac{2+n}{2}, \frac{3+n}{2}, -\frac{1}{R^2} \right], \quad (16)$$

with ${}_2F_1(a, b; c; x)$ being the hypergeometric function introduced above. The superscript (c) stands for the cylindrical symmetry.

6 Results

Let us analyze the behavior of the elastic constants as a function of the eccentricity e for the spheroidal case, and the parameter R for the cylindrical one. In Section 4, we show that the discotic shape for the spheroidal symmetry happens

for $e < 0$, so the geometrical transition discotic \rightarrow sphere \rightarrow calamitic occurs for e crescent; on the other hand, the similar geometrical transition in the cylindrical symmetry occurs for R decrescent. To follow the same order for both cases, let us introduce a different parameter. Now, the elastic constants in the spheroidal case vary when $\kappa = -e$ varies, and then, the elastic constants will be plotted as a function of $-1 \leq \kappa \leq 10$.

Figure 5 presents the elastic constants (13) for MS potential, in both spheroidal and cylindrical geometry.

For $\kappa < 0$ in Fig. 5a, we have an approximation for calamitic molecules, and this case obeys the order relation $K_{11} = K_{22} > K_{33}$, which was observed before, for instance, in ref. [1]. Also, as expected, when the molecular shape is a sphere, $\kappa = 0$, the bulk elastic constants are equal. The new feature here is in the discotic approximation ($\kappa > 0$). There is an inversion in the elastic constants, and $K_{11} = K_{22} < K_{33}$, which is not what is observed in experiments with usual discotic nematics. Moreover, the theoretical work in ref. [27] shows $K_{33} < K_{11} < K_{22}$.

Figure 5b shows the elastic constants in the cylindrical geometry. In this case, the order relation of the bulk elastic constants is the same for both scenarios, and we obtain $K_{11} = K_{22} < K_{33}$. When $R \approx 1$, the volume is neither a rod or a disc, we do not have an equal value for the bulk elastic constants. While R increases, the elastic constants tend to zero, which means that the elastic energy density tends to the undeformed state.

There is an inconsistency in the surface-like elastic constants in the spheroidal case. Notice that when $\kappa < 1$, $K_{22} + K_{24}$ becomes negative; the odd behavior in the cylindrical regime is that this surface-like elastic constant is

Fig. 7 Elastic constants for the HLR potential, in the spheroidal approximation, as function of γ , for κ fixed. **a** For $\kappa = -0.9$, the discotic case; **b** for $\kappa = 10$, the calamitic regime

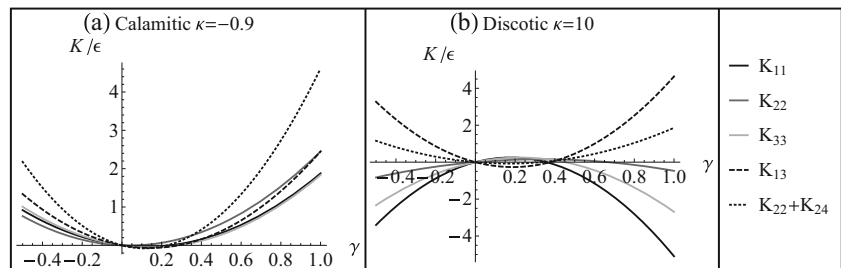
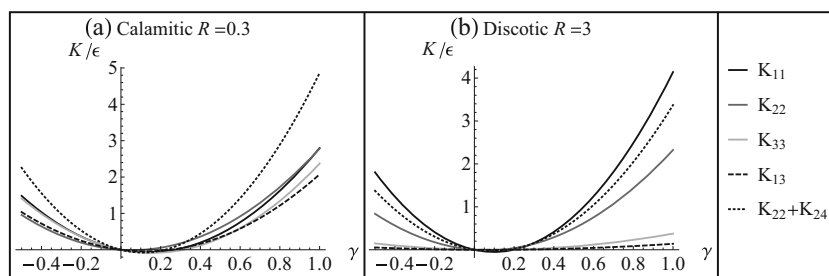


Fig. 8 Elastic constants for the HLR potential, in cylindrical approximation. In both cases, R is fixed and the elastic constants are plotted as function of γ . In (a), $R = 0.3$ is the calamitic case, and in (b), $R = 3$ represents the discotic case



bigger than K_{11} and K_{22} . For the MS potential, the elastic constant K_{13} is zero.

Now, let us consider the elastic constants of the NS potential, given by (14). Figure 6 shows their behavior in both spheroidal and cylindrical geometries.

In the spheroidal regime, K_{11} and K_{33} are negative when κ tends to -1 (or $e \rightarrow 1$), i.e., close to the calamitic shape, and when $\kappa < -7/9$, it cannot describe a nematic phase any more. Another unusual behavior is that $K_{13} < 0$ in the whole interval observed. In the discotic shape region, there are three inversions among the order relation of the bulk elastic constants, namely for $0 < \kappa < 2.4$, the order is $K_{22} > K_{33} > K_{11}$; where $2.4 < \kappa < 3.3$, $K_{33} > K_{22} < K_{11}$; and finally, for $\kappa > 3.3$, we observe $K_{22} < K_{11} < K_{33}$.

Figure 6b shows how the elastic constants behave as a function of R . When $R \lesssim 1$, K_{11} , K_{33} , and K_{13} are negative. In the discotic shape, all the constants are positive, but some of them tend to zero as R increases. Among the bulk elastic constants, the order relation is $K_{11} \approx K_{22} > K_{33}$, which is in agreement with the literature.

Let us consider now the potential (5), with g_i ($i = 1, 2, 3, 4, 5$) given by (7) and (8). From now on, (5) will be called HLR potential, named after Humphries, Luckhurst and Romano³ [18]. The constants of HLR potential have a quadratic dependence on γ . Instead of plotting 3D graphs of this double dependence, as in [13], let us vary γ for fixed values of κ and R .

In Fig. 7a, K_{13} is mostly the largest of the elastic constants. When $\gamma < 0$, we found $K_{33} \lesssim K_{11} \lesssim K_{22}$, which is acceptable for calamitic liquid crystals; when $\gamma > 0$, the order relation is $K_{11} \approx K_{33} < K_{22}$, more alike to a discotic liquid crystal behavior. Figure 7b shows that the bulk elastic constants in the discotic case cannot describe the nematic phase, because they are negative for all γ .

Figure 8 shows the elastic constants in the cylindrical approximation. All the bulk elastic constants are positive

in both cases. Roughly speaking, an order for the elastic constants may be found for $\gamma < 0$, i.e., $K_{22} < K_{33} \approx K_{11}$.

At the first sight, the potentials can represent the nematic phases only for specific values of their parameters. The NS potential, for example, describes the discotic phase, having positive elastic constants and obeying the order relation. Unfortunately, the same potential and geometry cannot describe the calamitic phase, producing negative values of K_{11} and K_{33} . Although the NS potential is being largely used in the nematic phase for calamitic molecules, in the spheroidal approximation, it gives negative values for the bulk elastic constants.

Let us consider the HLR potential. In the spheroidal approximation, the nematic order occurs for both cases, but for the discotic one, the elastic constants are negative. For the calamitic one in spheroidal and cylindrical symmetries, the expected order appears only for a small interval of γ . The discotic case in the cylindrical approximation does not have the results usually accepted.

To summarize the results, let us introduce two prerequisites to help us in finding the candidates to describe the nematic phase. We use the following statements: (i) at least the bulk elastic constants must be positive; (ii) the order relation of the bulk elastic constants must be satisfied. Analyzing Figs. 5, 6, 7, and 8, we found the intervals that describe the nematic phase, and the results are in Table 1.

Notice that even with the order relation being satisfied, there is an inconsistency in the values. For the first two candidates, for example, the values of $K_{11} \approx K_{22}$ are ~ 10 times bigger than K_{33} . However, the other cases are in the same order of magnitude, and considering $K_{11} \approx K_{33}$, we find better candidates to describe the nematic phase.

Lastly, following the same steps as ref. [13], using the parameters given in ref. [19], we estimate the order of magnitude of K_{ii} ($i = 1, 2, 3$) for the HLR potential. Using the scale temperature $T^* = k_B T / \epsilon \gamma^2$, and admitting that $T^* \approx 1$, and $\gamma = 1$, we have that $\epsilon \sim 10^{-20}$ J; for simplicity, we stated before that $a_0 = 1$ in all the calculations – and we measure the elastic constants in molecular length units –, but if we use $a_0 \sim 10^{-9}$ m instead [13], we have $K_{ii} \sim 10^{-11}$ N ($i = 1, 2, 3$), which is in the order of magnitude experimentally found.

³In ref. [28], Bates calls HLR potential a similar potential to (5), used in computational simulations. As (5) appears in [18], and there is a reference to it in the paper from Humphries, Luckhurst and Romano [19], it is convenient to call (5) HLR potential, too.

Table 1 Approximated values of the elastic constants in each case better described via pseudo-molecular method in spheroidal and cylindrical approximations

K_{11}	K_{22}	K_{33}	Potl.; approximation; molecular shape	Parameters
0.62	0.62	0.01	MS; cylindrical; disc-like	$C_{MS} = 1; R = 5$
0.54	0.58	0.03	NS; cylindrical; disc-like	$C_{NS} = 1; R = 5$
0.92	0.76	1.01	HLR; spheroidal; rod-like	$\gamma = -0.5; \kappa = -0.9$
1.03	0.64	0.99	HLR; cylindrical; rod-like	$\gamma = -0.4; R = 0.3$

7 Conclusions

The elastic constants were found in closed form, via pseudo-molecular method, for both calamitic and discotic molecular approximations, by means of two different approaches: spheroidal geometry, deforming an ellipsoid to an oblate spheroid; and the cylindrical one, which deforms a long cylinder to a disc. Firstly, all the calculations were made independently of the symmetry or the molecular shape, and each different case can be found just by replacing the constituent parameters in the hypergeometric function. The pseudo-molecular method is applied in a interaction potential between two molecules. We choose a general potential, with its parameters depending on the anisotropy of the polarizability, but we took these parameters as phenomenological ones, then they were free to vary and leading to the classical Maier-Saupe and Nehring-Saupe potentials. By doing this, we may build different scenarios for the elastic constants, involving the interaction potentials, the geometry, and the molecular shape themselves. The new feature is the discotic molecules, and we were successful in finding the elastic constants by this particular kind of liquid crystal. To rank the results, we used two important prerequisites: the bulk elastic constants must be positive and respect the order relation among them. Surprisingly, the only candidate that had fully positive answers for the two statements was for the Nehring-Saupe potential, in the cylindrical approximation and discotic molecular shape. The other cases just fail at it or have partial results, for specific values of the parameters. Nevertheless, the best candidate elected by our statements had $K_{33} \rightarrow 0$ more rapidly than the other bulk constants, which gives one order of magnitude smaller than the others. Some other cases, the HLR potential, spheroidal approximation and calamitic molecular shape, for instance, choosing specific values of the parameters had better results than the case cited before. All the other cases had aberrations in the elastic constants, like negative values of them, which is not true for pure nematic liquid crystals—and it is even controversial for the new nematic twist-bend phase. The relevance in this work is in applying a tool to find the elastic constants for both calamitic and discotic molecules—mostly

for discotic ones, which are more difficult to find works in this sense about them—and link these quantities by an interaction model. We all know that the method has some problems and the results were not what expected, but we believe that the work can be useful for future improvements, applying new kinds of geometries, for example, or to test it in different interaction potentials.

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