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INVITED ARTICLE

The theory of elastic constants

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The elastic theory of liquid crystals can be traced back to the early 1930s, but the origin of the molecular theory of elastic constants must be postponed to more than 30 years later, when Alfred Saupe wrote his famous papers on this subject. At approximately the same time, the seminal works by Priest and Straley also appeared. Since then, several theories have been developed to connect intermolecular interactions to curvature deformations, on a quite different length-scale, in liquid crystals. This field was particularly alive between the end of the 1970s and the beginning of the 1980s, in parallel with experimental investigations. In more recent times, a renewed interest was aroused by the controversy about the second-order splay-bend contribution, which appears in the Nehring–Saupe expression for the deformation energy density. In the first part of the present contribution the molecular theory of elastic constants is briefly reviewed. This paper focuses on the effects of molecular structure on the elastic constants of thermotropic nematics and the ability of different models to account for them. A few classical examples are discussed to illustrate these issues. The second part of this paper is dedicated to our recent 'Surface Interaction' model, a molecular field approach based on the Maier–Saupe theory, implemented into a framework allowing for atomistic molecular modelling. The theoretical background is outlined, then some new results are reported and the insights derived from a realistic molecular representation are discussed. We conclude that, after about 40 years of theoretical investigations, there is a general consensus on the importance of the molecular shape in determining the elastic constants of nematics: for fairly rigid compounds these can be simply related to the length-to-width ratio, but for the general case of non-rigid mesogens the molecular flexibility and shape curvature have to be taken into account.

Keywords: elasticity; molecular field theory; liquid crystals

1. Introduction

Long-range orientational order in liquid crystals (LCs) entails the definition of a mesoscale variable (the *director*) which can be controlled by external fields and is characterised by an elastic response. The latter property can be described by the continuum theory: herein an elastic energy is defined as a function of the *curvature strains*, with the assumption that the LC sample is incompressible. The constraints imposed by the LC symmetry lead to the identification of a small number of fundamental torsional modes. For long-wavelength deformations, the expansion of the elastic energy density as a function of the curvature strains can be truncated at quadratic terms, with coefficients that play the role of *elastic moduli*. The foundations of the elastic theory of LCs were laid by Oseen [1] and Zocher [2] in the 1930s and later re-examined by Frank [3]. The continuum theory forms the basis of our present understanding of LCs; in particular, it provides the framework for explaining the behaviour of LC samples under perturbing fields, which underlies most LC applications.

In the context of the continuum theory, the elastic constants are material parameters, whose number and kind are defined by the phase symmetry. The conditions for stability of the LC phase impose boundaries on their values: an example is provided by the so-called Ericksen inequalities for the elastic constants of nematics [4]. Several experimental data are available for nematics which, along with some general trends, also show a specific dependence upon the chemical constitution. The availability of LC materials with suitable elastic properties is important for LC applications [5], hence the interest in understanding their origin. The investigation of the relationship between the molecular structure and the elastic constants is also motivated by fundamental reasons, since the elastic parameters reflect the underlying intermolecular interactions responsible for the existence of LC phases: due to the anisotropic averaging, some features emerge in LCs that are completely washed out by the isotropic distribution in ordinary liquids.

A fundamental contribution to our present molecular-level understanding of the elasticity of thermotropic LCs is due to Alfred Saupe. He predicted the dependence of elastic constants on the orientational order parameter, $K \sim S^2$ [6], which he could then test experimentally [7]. Moreover, he derived an expression

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for the elastic free energy, hence denoted as the 'Nehring–Saupe' form [8, 9]; this contains the second-order *splay-bend* contribution, which has been the object of intense debate in subsequent years [10–13].

This paper is dedicated to the theory of elastic constants of LCs. In the next section an overview of molecular models will be presented, ranging from the early Saupe theory to recent developments. Exhaustive reviews of the elastic theory of LCs have already appeared [14, 15]; here we shall focus on issues which are more closely related to Saupe's work. So, despite their interest, elastic theories for LC polymers [16–22] will not be addressed; we shall rather deal with theories for the nematic phase of low molar mass thermotropic LCs and examine their ability to account for the molecular structure. Under this perspective, we shall describe in some detail a molecular field theory that we have recently proposed, known as the Surface Interaction (SI) model, which has the distinguishing feature of using a realistic representation of the mesogenic molecules [23]. A few classical examples will be presented, to illustrate the success and failure of the molecular theories in explaining the experimental findings. Finally, in the Conclusion, the main achievements of the theory of elastic constants will be summarised and open questions will be recalled.

2. Molecular theories for the elastic constants of nematics

For nematic LCs, three bulk (*splay, twist, bend*) and two surface-like (*saddle-splay, splay-bend*) deformation modes are defined; the corresponding elastic constants exhibit an intriguing dependence on the molecular structure. Particularly interesting in this respect is the relative stiffness for different deformations, the so-called *elastic anisotropy* which, besides being important as an amplification of the anisotropy of intermolecular interactions, is also relevant for the control of director configurations in devices [5] and in other LC applications [24, 25]. Molecular theories for elastic constants must deal with contrasting requirements: on the one hand, they should retain enough molecular detail to allow a comparison with experimental data but, on the other hand, approximations have to be made to connect the molecular scale with that of the director deformations. A compromise must be found; a variety of molecular theories have been developed, which differ in the form of the underlying intermolecular interactions and in the approximations used for the micro–macro connection. Some of these theories try to introduce a more realistic representation of the intermolecular interactions at the cost of even crude assumptions in the statistical description, whereas other approaches emphasise methodological aspects related to a statistical derivation appropriate for the LC phase but are forced to use basic molecular models. Particularly relevant in the latter respect are approaches based on the Density Functional Theory (DFT), which provides a systematic route to connect free energy and intermolecular interactions [14]. In the following, molecular theories for the elasticity of nematics will be briefly reviewed, under the perspective of featuring their ability to shed light on the relation between the molecular structure and the elastic constants.

In the papers co-authored with Nehring in the early 1970s [8, 9], Saupe presented a theory for the elastic constants of nematic LCs, considering dispersion forces between spherical molecules in a dipole–dipole approximation. Starting from the interaction energy between two volume elements, an expression for the elastic energy density was derived, using the molecular field approximation, together with the assumption of perfect orientational order. A second-order expansion of the free energy density, f_{el}, was taken, as a function of the director, $\mathbf{n}$, and its first and second gradients; for nematic and cholesteric LCs, of $D_{\infty h}$ and D_{∞} symmetry, respectively, the following expression was obtained:

$$
\begin{aligned}
f_{el} = {} & k_2 \mathbf{n} \cdot (\nabla \times \mathbf{n}) + \frac{1}{2} K_{11} (\nabla \cdot \mathbf{n})^2 + \frac{1}{2} K_{22} [\mathbf{n} \cdot (\nabla \times \mathbf{n})]^2 \\
& + \frac{1}{2} K_{33} |\mathbf{n} \times (\nabla \times \mathbf{n})|^2 + k_{13} \nabla \cdot (\nabla \cdot \mathbf{n}) \mathbf{n} \\
& + \frac{1}{2} (K_{22} + k_{24}) \nabla \cdot [(\mathbf{n} \cdot \nabla) \mathbf{n} - (\nabla \cdot \mathbf{n}) \mathbf{n}], \qquad (1)
\end{aligned}
$$

where k_2 is the *chiral strength*, which vanishes in the achiral nematic phase, and K_{11}, K_{22} and K_{33} are the elastic constants for *splay*, *twist* and *bend*, respectively, whereas k_{24} is the *saddle-splay* and k_{13} the *splay-bend* elastic constant. Equation (1) coincides with Frank's expression [3], except for the presence of the latter term and the redefinition of the splay and bend constants as $K_{11} = K^F{}_{11} - 2k_{13}$ and $K_{33} = K^F{}_{33} + 2k_{13}$, where the superscript is used for Frank's constants. These differences result from the inclusion of the second gradient of the director field in the free energy expansion. The splay-bend and the saddle-splay terms have the form of a divergence and their volume integrals over the nematic sample can be reduced to surface integrals over the boundary, using the Gauss theorem (hence the denomination *surface-like* to distinguish these from the other *bulk* contributions). Thus, these terms are often neglected when surface effects are not important. Surface-like terms have been the object of intense research activity, encompassing both theoretical and experimental issues [13]. The saddle-splay contribution has been shown to be responsible for the induction of spontaneous deformation and pattern formation in nematic layers [26, 27]. The role of the splay-bend contribution is more controversial, owing to problems related to the minimisation of the free energy when it is present [10–12].

In the Nehring–Saupe theory, the following form is assumed for the interaction energy dU between the volume elements dv at the position $\mathbf{R}$ and dv' at the position $\mathbf{R}'$:

$$dU(\mathbf{n},\mathbf{n}',\mathbf{r}) = g(\mathbf{n},\mathbf{n}',\mathbf{r})\,dv\,dv', \tag{2}$$

where $\mathbf{n}$ and $\mathbf{n}'$ are the directors in $\mathbf{R}$ and in $\mathbf{R}'$, respectively, $\mathbf{r} = \mathbf{R}'\text{–}\mathbf{R}$ and

$$g(\mathbf{n},\mathbf{n}',\mathbf{r}) = -\frac{C^2}{r^6}[\mathbf{n}\cdot\mathbf{n}' - 3(\mathbf{n}\cdot\mathbf{u} - \mathbf{n}'\cdot\mathbf{u})], \tag{3}$$

with $\mathbf{u} = \mathbf{r}/\mathrm{r}$. The strength of the interaction is taken as $C = \alpha\rho S$, where $S = \langle P_2\rangle$ is the second-rank orientational order parameter, ρ is the number density and α is a molecular property [28]. Thus, $K_{\mathrm{ii}} \propto S^2$ is obtained, together with the ratios K_{11}: K_{22}: K_{33}: k_{24}: k_{13} = 5: 11: 5: –9: –6, irrespective of the mesogen and the temperature; the contribution of the second-order derivatives (k_{13}) is essential for K_{11} to be positive. The predicted elastic ratios are in clear disagreement with experiment, since in general $K_{22} < K_{11} < K_{33}$ is found for calamitics. The difference from the experimental findings was ascribed by the authors to the neglect of short-range order effects.

Another reason for this discrepancy could be the interaction law given in Equation (3). The influence of the form of the interaction law, along with that of the deviation from spherical symmetry of the interaction volume, within the same molecular field approach proposed by Nehring and Saupe, were investigated by Evangelista, Barbero and co-workers [29–31]. Using simple parameterisations of $g(\mathbf{n}, \mathbf{n}', \mathbf{r})$, easily tractable expressions for the bulk and surface-like elastic constants are obtained, which allow a systematic analysis of the effects of the interaction law. These studies reveal that different choices can have dramatic effects, which encompass even negative values of the bulk elastic constants, a result deemed interesting in relation to the onset of instabilities in the nematic phase. As for the surface-like elastic constants, an even larger variety of behaviour is found, depending on the interaction model. These investigations highlight effects and show trends, but the connection with experimental data remains loose, because the relation between the model parameters and the structure of real mesogens is not straightforward.

The restriction to second-rank order parameters was relaxed by other approaches including, from the beginning, the partial degree of order in the nematic phase and considering with more care the angular dependence resulting from the intermolecular interactions. Priest, in the early 1970s [32], derived expressions for Frank's elastic constants under the molecular field approximation; taking as a reference the isotropic phase, the Helmholtz free energy of the nematic phase is decomposed into its internal energy ($\Delta\boldsymbol{U}$) and entropy (ΔS) contributions:

$$\Delta F = \Delta\boldsymbol{U} - T\Delta S. \tag{4}$$

Both terms are expressed as averages over the single-molecule orientational distribution function, $p(\Omega)$, with Ω denoting the Euler angles specifying the molecular orientation. $\Delta\boldsymbol{U}$ corresponds to the average of the intermolecular pair potential over all relative molecular positions and orientations; in the entropy difference, a translational (ΔS_{tr}) and an orientational contribution (ΔS_{or}) are distinguished. The latter is neglected when calculating the Helmholtz free energy in the presence of director deformation, with the assumption that the orientational distribution function with respect to the local director is the same in deformed and undeformed nematics. Simple expressions for Frank's elastic constants are obtained, where the role of the order parameters and the molecular properties can be easily disentangled:

$$\begin{aligned} K_{11}/\overline{K} &= 1 + \Delta - 3\Delta'\langle P_4\rangle/\langle P_2\rangle + \ldots, \\ K_{22}/\overline{K} &= 1 - 2\Delta - \Delta'\langle P_4\rangle/\langle P_2\rangle + \ldots, \\ K_{33}/\overline{K} &= 1 + \Delta + 4\Delta'\langle P_4\rangle/\langle P_2\rangle + \ldots, \end{aligned} \tag{5}$$

where $\overline{K} = (K_{11} + K_{22} + K_{33})/3$ and $\langle P_2\rangle, \langle P_4\rangle$ are average values of the second and fourth rank Legendre polynomials, respectively; Δ, Δ' are constants which depend on the molecular structure. The presence of the fourth rank order parameter introduces a difference between the splay and bend elastic constant; for $\langle P_4\rangle \ll \langle P_2\rangle$, the Nehring–Saupe equality, $K_{11} = K_{33}$ is recovered. Explicit results were obtained for hard spherocylinders, using the second virial approximation for the translational entropy, according to Onsager theory [33]; in this case the molecular parameters Δ and Δ' can be simply expressed in terms of the length-to-width ratio. The correct sequence, $K_{22} < K_{11} < K_{33}$, is predicted, with K_{33}/K_{11} being an increasing function of this ratio and $K_{11} = K_{22}$ for infinitely long rods. Analogous results were obtained at approximately the same time by Straley, who calculated the elastic constants for hard-rod LCs in a different way, but under essentially the same assumptions [34]. Poniewierski and Stecki used a DFT approach and derived expressions for the Frank elastic constants of hard spherocylinders in terms of the direct correlation function and the single-particle orientational distribution function [35]. The numerical results are similar to those obtained by Priest, even though the form of the parameters Δ and Δ' in Equation (5) is different. Again within the density functional formalism, more general expressions for the elastic constants were derived by Somoza and Tarazona by relaxing the assumption that the orientational distribution function in the presence of a deformation is locally the same as in the undeformed nematic phase [36]. It was found that this effect may lower the elastic energy, so reducing the value of the elastic constants. Hard particle models, although unable to describe the temperature dependence of the elastic constants in thermotropic nematics, have played an important role for elucidating the relevant physics behind the elastic behaviour of LCs, showing the importance of molecular shape. However, simple models of ellipsoids or spherocylinders may not be sufficient to capture more subtle effects which come from the molecular structure.

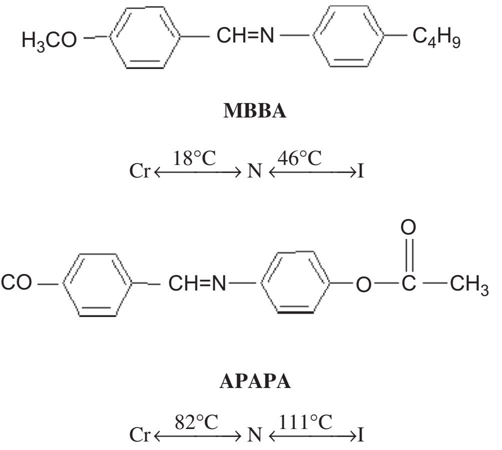
Important progress towards a more realistic description of molecular interactions in thermotropic LCs was made by models including both short-range repulsions and dispersion attractions. Gelbart and Ben-Shaul developed a generalised van der Waals theory, wherein excluded volume interactions between spherocylinders are superimposed on angle-dependent pair attractions, introduced at the molecular field level [37]. The bulk elastic constants were found to be very sensitive to the four input parameters of the model: the length and width of the spherocylinders, and the strength and anisotropy of the attractive potential. Quantitative predictions are made difficult by the uncertainty in the values specific to the real nematogens; however, with reasonable choices, elastic constants close to the experimental results could be obtained for *para*-azoxyanisole (PAA or 4,4′-dimethoxyazoxybenzene). The Nehring–Saupe results [8, 9] and purely entropic theories [32] are obtained as special cases, for the vanishing anisotropy of hard core repulsions and for vanishing intermolecular attractions, respectively. To emphasise the importance of the molecular shape for intermolecular interactions in LCs, van der Meer and co-workers proposed a model of distributed harmonic forces between those parts of the molecules that are in close proximity [38]. Moreover, they introduced the possibility of short-range smectic-like correlations between the relative positions of pairs of molecules. Assuming complete orientational order for molecules represented as simple cylinders, they found that the increase in the degree of correlation leads to a decrease of the ratio K_{33}/K_{11}, without affecting K_{11}/K_{22}. Intermolecular attractions, of dispersive or electrostatic nature, superimposed on hard core repulsions between ellipsoids, were also introduced into DFT treatments [39, 40]; the results were found to be very sensitive to the model parameters and, with suitable choices, satisfactory agreement with experiment could be achieved. Interestingly, Osipov and Hess, using the DFT approach for a system of perfectly aligned ellipsoids, showed that, with the assumption of ellipsoidal equipotential surfaces, the elastic constant anisotropy can be expressed simply in terms of the molecular axial ratio, irrespective of the specific form of the intermolecular attraction interaction potential [41]. The DFT formalism was also used to evaluate the full set of bulk and surface-like elastic constants of a Gay–Berne fluid, with a perturbative treatment of the attractive and repulsive (hard core) contributions to the pair potential [42]. The surface-like elastic constants k_{13} and k_{24} were found to be of the same order of magnitude as the bulk moduli, with k_{13} taking positive or negative values, depending on the details of the long-range intermolecular potential.

All of the theories mentioned so far use crude representations of molecules, mostly as ellipsoids or spherocylinders. Given the role played by the molecular shape in modulating the intermolecular interactions in thermotropic LCs, this choice, which is essentially dictated by reasons of simplicity, may be a limit for the elastic constant theories. In fact, the possibility that deviations from a rod-like shape can produce significant effects was proposed early on; however, such deviations were considered by phenomenological models, rather than introduced into statistical mechanics theories. In particular, the reduction of the cost for splay and bend deformations was predicted for wedge- and banana-shaped molecules, respectively; estimates of these effects were provided by Helfrich and Gruler, under the assumption of different mechanisms: the former ascribed the reduction of elastic constants to the flexoelectric effect [43], whereas steric bend and splay were invoked by Gruler [44]. More recently, Dozov discussed the possibility of spontaneous bend deformations for bent-core mesogens [45]. Using a modified Maier–Saupe potential, with the point-like intermolecular interactions replaced by a distribution of point-like interaction centres inside V-shaped molecules, he estimated the bend elastic constant as a function of the length-to-curvature ratio; for high enough values, he predicted a negative K_{33} modulus and so a spontaneous director bend.

Even more difficult is the inclusion of molecular flexibility in the theory of elastic constants. In this respect, an important and probably overlooked contribution is due to Terentjev and Petscheck, who developed a molecular field theory for the nematic phase of semiflexible bimesogens, taking into account short-range repulsions and attractions between monomers [46]. Within this model the spacer between mesogens is responsible for an intrinsic angle between mesogens and for the molecular flexibility, which is described in terms of a bare stiffness parameter. All the elastic constants are predicted to decrease as the average angle between the mesogens deviates from 180° and as the spacer rigidity decreases, with particularly strong effects for K_{33}.

2.1 Theory and experiments: Schiff's bases and thiadiazole derivative

The early development of molecular theories for elastic constants was accompanied by systematic experimental investigations, aimed at discovering the differences and analogies between the elastic properties of mesogens and checking the ability of theories to explain them. A classical series of compounds is represented by the LC Schiff bases, which were thoroughly investigated, mostly by Leenhouts and co-workers [47–50]. Here we shall take two derivatives, 4-methoxybenzylidene-4′-butylaniline (MBBA) and 4-methoxybenzylidene-4′-acetoxybenzene (APAPA), whose structures are shown in Figure 1. These compounds have the same rigid core and differ only in the end group attached to the aniline ring: a relatively rigid acetate substituent in APAPA and the highly flexible *n*-butyl chain in MBBA. Figure 2 shows the bulk elastic constants measured in the nematic phase of these mesogens [47–50] as a function of the square of the major second-rank orientational order parameter, S_{zz}. For this purpose, the experimental temperature dependence of the order parameter was used (see [51] for APAPA and [52] for MBBA). We can see in the figure some discrepancies between the elastic constants of MBBA obtained from different measurements; in fact, the experimental determination of the elastic moduli is not easy and values of the elastic ratios K_{33}/K_{11} and K_{22}/K_{11} are generally more reliable than those of the individual terms.


MBBA

$\mathrm{Cr} \xleftrightarrow{18°\mathrm{C}} \mathrm{N} \xleftrightarrow{46°\mathrm{C}} \mathrm{I}$

APAPA

$\mathrm{Cr} \xleftrightarrow{82°\mathrm{C}} \mathrm{N} \xleftrightarrow{111°\mathrm{C}} \mathrm{I}$

Figure 1. Chemical structure of the Schiff's bases MBBA (top) and APAPA (bottom), with the corresponding transition temperatures [47].

The main differences between APAPA and MBBA concern the bending stiffness: not only is K_{33} of the former roughly twice as large as that of the latter, but also the ratio K_{33}/K_{11} is significantly higher for APAPA. Moreover, the dependence of the bend elastic constant of this mesogen on the square of the order parameter exhibits pronounced deviations from linearity. As a rule, it has been found that fairly rigid mesogens, such as PAA, exhibit elastic properties similar to those shown for APAPA [47]. For these systems K_{33}/K_{11} increases with the length-to-width ratio, in qualitative agreement with the prediction of theories for hard uniaxial particles [32, 34–36]. Theoretical predictions tend to overestimate K_{33}/K_{11}; closer agreement with experiment could be obtained with the additional inclusion of electrostatic and dispersion intermolecular interactions [40]. In general, the results obtained for fairly rigid mesogens indicate that the molecular shape, and thus the steric repulsions and short-range dispersion interactions, which are

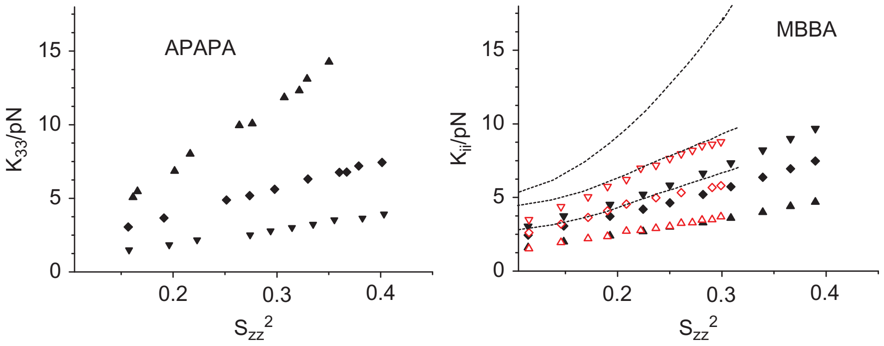


Figure 2. Experimental values of the elastic constants for the nematic phases of APAPA (left, [47, 48]) and MBBA (right, closed symbols [49], open symbols [50]). The dashed lines represent theoretical predictions from [40]. The elastic constants are shown as a function of the square of the second-rank order parameter, S_{zz}; the relation between temperature and S_{zz} was derived from [51] for APAPA and from [52] for MBBA. From bottom to top: K_{22}, K_{11}, K_{33}.

modulated by the molecular shape, are the main determinants of the elastic properties of nematics.

In contrast, theories for hard uniaxial particles cannot explain the changes in the elastic constants when going from APAPA to MBBA. Even considering that the flexibility of the alkyl chain contributes to a decrease in the average length and an increase of the average width, in comparison to the all-*trans* conformer, the length-to-width ratio of MBBA is greater than that of APAPA [47]. Therefore, an increase of K_{33}/K_{11} would be predicted by theories for hard uniaxial particles, which is exactly the opposite of what is found experimentally. Actually, the differences between the elastic properties of APAPA and MBBA are an example of a quite general behaviour: the bend modulus K_{33} and the ratio K_{33}/K_{11} usually decrease with the increasing length of the alkyl chains along homologous series [48, 53–55]. Numerical calculations of the bulk elastic constants of MBBA were performed, based on a weighted density functional formalism, for a system of hard ellipsoids of revolution with superimposed quadrupolar and dispersion interactions [40]. It was found that inclusion of the latter has the effect of reducing the elastic constant ratios. The theoretical results are also shown in Figure 2; we can see that even so the calculated elastic constants remain too high, especially K_{33}, which is also too steep a function of the order parameter in comparison to the experimental results. The reduction of the elastic ratios with increasing chain length was also ascribed to short-range smectic-like correlations, which would be promoted by chain flexibility. This interpretation was substantiated by the results of the van der Meer model based on distributed harmonic forces with smectic-like short-range correlations, assuming that the latter are enhanced by the alkyl chains and increase with the chain length within homologous series [38].

Another possible reason for the decrease of the K_{33}/K_{11} ratio with increasing chain length along homologous series was suggested: the presence of bent conformers in very flexible molecules [50]. Namely, according to the predictions of Helfrich [43] and Gruler [44], director bending should be easier for bent-shaped molecules. To test such predictions, the elastic constants were measured for the nematic phase of the thiadiazole derivative shown in Figure 3, which was deemed as a particularly good example because of its structure and its rigidity [56]. However, no special effects were detected; the elastic ratios, which are also shown in the figure, are in keeping with those of similar, rigid and non-curved mesogens. Thus, a weak effect of the shape bending was inferred. However, some years later the opposite conclusion was reached from measurements of the elastic constants for mesogenic dimers, separated by an odd or an even number of units in the spacer [57]. In these systems, a small chemical difference has significant steric consequences, since odd dimers are characterised by an intrinsic bend, whereas the even homologues are nearly straight. It was found that, whereas the ratio K_{22}/K_{11} is similar for the two kinds of dimers, the ratio K_{33}/K_{11} is considerably smaller for odd members than for even members. Such a behaviour could be explained by the model developed by Terentjev and Petscheck [46].

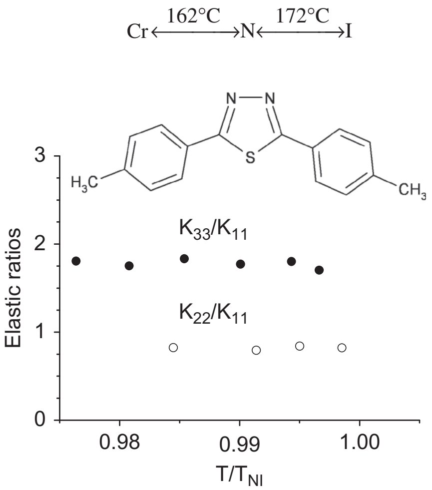


Figure 3. Elastic constant ratios measured in the nematic phase of the thiadiazole derivative shown at the top as a function of the reduced temperature, T/T_{NI} [56].

3. The Surface Interaction model

3.1 Theoretical background

The 'Surface Interaction' model can be seen as a generalisation of the Maier–Saupe theory [28], to enable a detailed account of the molecular structure. The starting point for the derivation of the deformation free energy in nematics is the change in the single-molecule orientational distribution function, $p(\Omega)$, due to the director distortion; a phenomenological form of $p(\Omega)$ in terms of the director field, $\mathbf{n}(\mathbf{R})$, is used. This is a major difference from other theories, which generally start from the pair-wise interactions between molecules located at positions where the director has different orientations, under the assumption that the single-molecule orientational distribution function with respect to the local director is not affected by director deformations. Some analogy can be found with the approach proposed some years ago by Marrucci and Greco, who also tried to introduce features of the mesogen shape into a Maier–Saupe-like molecular field theory [58].

A distinguishing feature of the SI model is the possibility of taking into account the conformational freedom, which characterises most thermotropic mesogens. The molecular structure is introduced into the single-molecule orientational distribution function, $p(\Omega)$, through the concept of the *molecular surface*. This can be easily constructed on the basis of the atomic coordinates [59]; nowadays, these can be accurately obtained by modern computational techniques, such as molecular mechanics and quantum chemical methods. Indeed, the possibility of being integrated with such techniques, so as to exploit their capability, is a valuable feature of the SI method.

The full derivation of the expressions for the elastic constants of the nematics according to the SI model is presented in [23], to which interested readers are referred; only the main features of the approach will be outlined here, to help the understanding of the results which we report later. The basic feature of the SI model is the parameterisation of the orientational molecular field in the nematic phase according to the anisotropy of the molecular surface. This is done by assuming a Maier–Saupe form for the angular dependence of the orientational molecular field experienced by each element of the molecular surface:

$$\mathrm{d}U = k_{\mathrm{B}}T\varepsilon\, P_2(\mathbf{n}\cdot\mathbf{s})\,\mathrm{d}S, \tag{6}$$

where $\mathbf{s}$ and $\mathbf{n}$ are unit vectors normal to the surface element $\mathrm{d}S$ and parallel to the director, respectively, and P_2 is the second Legendre polynomial. The parameter ε, which has dimensions of inverse square length, specifies the orienting strength of the medium. Equation (6) can be simply seen as the truncation to the lowest-order term, allowed by phase symmetry, of a Taylor series expansion of the angular dependence of the molecular field.

The orientational molecular field experienced by a molecule in the uniaxial nematic phase, $U(\Omega)$, is then obtained by integrating Equation (6) over the molecular surface [60, 61]:

$$U(\Omega) = k_{\mathrm{B}}T\varepsilon\int_S dS\; P_2(\mathbf{n}\cdot\mathbf{s}), \tag{7}$$

where Ω denotes the Euler angles specifying the molecular orientation in a laboratory frame and S is the molecular surface. Given the orientational molecular field, the single-molecule orientational distribution function, $p(\Omega)$, is defined as

$$p(\Omega) = \frac{\exp[-U(\Omega)/k_{\mathrm{B}}T]}{Q}, \tag{8}$$

where Q is the orientational partition function:

$$Q = \int \mathrm{d}\Omega\, \exp[-U(\Omega)/k_{\mathrm{B}}T]. \tag{9}$$

The model can be easily generalised to the case of flexible molecules; if these can exist in a set of different conformational states [62], the orientational distribution function, in Equation (8), should be replaced by the conformational-orientational distribution function

$$p_m(\Omega) = \frac{\exp\left[-\left(V_m + U_m(\Omega)\right)/k_{\mathrm{B}}T\right]}{Q}, \tag{10}$$

where the index m denotes the mth conformer, characterised by the torsion potential V_m and the orienting potential U_m. Then, the conformational-orientational partition function reads

$$Q = \sum_m \exp\left[-V_m/k_{\mathrm{B}}T\right] Q_m, \tag{11}$$

where the sum is over all molecular conformers and Q_m is the orientational partition function for the mth conformer:

$$Q_m = \int \mathrm{d}\Omega\, \exp\left[-U_m(\Omega)/k_{\mathrm{B}}T\right]. \tag{12}$$

The average value of any arbitrary function, g, can be expressed as

$$\langle g\rangle = \sum_m w_m\overline{g_m}, \tag{13}$$

where w_m is the statistical weight of the mth conformer,

$$w_m = \frac{\exp\left[-\mathrm{V}_m/k_{\mathrm{B}}T\right] Q_m}{Q}, \tag{14}$$

and $\overline{g_m}$ is the orientational average of the function, calculated for the mth conformer,

$$\overline{g_m} = \frac{\int \mathrm{d}\Omega\, \exp\left[-U_m(\Omega)/k_{\mathrm{B}}T\right] g_m(\Omega)}{Q_m}. \tag{15}$$

In the nematic phase the statistical weights of conformers will be different from those in the isotropic phase and will depend on the degree of order. Namely, depending on their shape, conformers will be more or less well accommodated in the nematic phase; in general, elongated conformers are expected to be stabilised over the bent ones.

The orienting strength ε appearing in Equation (6) is assumed to take the form [60, 63]

$$\varepsilon = -\frac{\xi^2}{vk_{\mathrm{B}}T}\langle a\rangle, \tag{16}$$

where v is the volume per molecule, ε is a constant and $\langle a\rangle$ is the average value of the surface integral appearing in Equation (7). We can write for the *m*th conformer

$$a_m = \int_{S_m} dS\, P_2(\mathbf{n}\cdot\mathbf{s}), \tag{17}$$

with S_m being the molecular surface of the conformer. The average value $\langle a\rangle$ can be seen as an order parameter, which vanishes in the isotropic phase and measures the degree of molecular order in the nematic phase.

The route from the orientational distribution function to the elastic constants goes through the Helmholtz free energy and its dependence on the director orientation. The internal energy and entropy contributions to the free energy density, indicated as Δu and Δs, respectively, are expressed in terms of the molecular field potential and the orientational distribution function in the nematic phase [63], as

$$\Delta u = \frac{1}{2v}\langle U\rangle + \frac{1}{v}\langle \Delta V\rangle, \tag{18a}$$

and

$$\Delta s = -\frac{k_B}{v}\langle \ln p\rangle, \tag{18b}$$

where $\Delta V = V - <V>_{\text{iso}}$, with $<V>_{\text{iso}}$ being the average value of the torsional potential in the isotropic phase. Then, the Helmholtz free energy density takes the form

$$f = f_{\text{iso}} + \frac{\xi^2}{2v^2}\langle a\rangle^2 - \frac{k_B T}{v}\ln Q + \frac{1}{v}\langle \Delta V\rangle, \tag{19}$$

where f_{iso} is the density of Helmholtz free energy in the isotropic phase.

The key point for the derivation of expressions for the elastic constants is the recognition that the free energy defined by Equation (19) is an implicit function of the director distortions. These affect the orienting potential, Equation (7), since in a non-uniform nematic phase the vector **n** becomes a function of the position on the molecular surface. For small deformations, characterised by a length scale much longer than the molecular dimensions, the Taylor series expansion of the free energy density (see Equation (19)) with respect to deformations, can be truncated at the quadratic contributions and the elastic constants are identified with the coefficients of these terms. The following molecular expressions are obtained for the elastic constants appearing in Equation (1):

$$k'_2 = c_{XYZ}, \tag{20a}$$

$$k'_{13} = c_{XZXZ}, \tag{20b}$$

$$\begin{aligned} K'_{ii} = {} & c_{IIXX} - c_{IIZZ} - 2c_{XZXZ}(\delta_{i1} - \delta_{i3}) \\ & - 3\varepsilon\big(c_{IXZ,IXZ} - c_{IXZ^2}\delta_{i2}\big), \\ & I = \mathrm{X} \text{ for } i = 1,\ I = \mathrm{Y} \text{ for } i = 2,\ I = \mathrm{Z} \text{ for } i = 3, \end{aligned} \tag{20c}$$

$$\begin{aligned} K'_{22} + k'_{24} = {} & \frac{1}{2}\{c_{XXXX} + c_{XXYY} - c_{XXZZ} \\ & - 6\varepsilon\big(c_{XXZ,XXZ} - c_{XXZ,YYZ}\big)\}, \end{aligned} \tag{20d}$$

where $K'_{ii} = (v/3\varepsilon k_B T)K_{ii}$, $k'_i = (v/3\varepsilon k_B T)k_i$. The terms c_{JKL}, c_{JKLM}, $c_{JKL,JKL}$, b_{JKL} appearing in these expressions are the average values, calculated over the orientational distribution for undeformed nematics, of elements of Cartesian tensors, defined as integrals over the molecular surface; they have cumbersome forms, which are reported in [23]. The indices X,Y,Z refer to the axes of a laboratory frame. In these equations ε denotes the orienting strength, $\varepsilon = -\xi^2\langle a\rangle_0/vk_B T$. The elastic constants can be calculated using Equations (20) for any mesogen, without free parameters, only on the basis of the geometry and the relative torsional energy of the conformers.

3.2 Predictions for Schiff's bases and thiadiazole derivative

The elastic constants of MBBA, APAPA and the thiadiazole derivative shown in Figure 3 were obtained according to the same procedure outlined in [23, 64]. For each mesogen all conformers were generated and for each conformer: (1) the geometry was optimised – for the cases reported in this work, DFT calculations at the B3LYP/6-31G** level were performed [65]; (2) the solvent-excluded molecular surface was constructed according to the Sanner algorithm, as implemented in the MSMS package [66] (the solvent-excluded molecular surface was calculated assuming the following van der Waals radii [67]: $r_C = 0.185$ nm, $r_O = 0.15$ nm, $r_N = 0.155$ nm, $r_H = 0.1$ nm, $r_S = 0.18$ nm and a rolling sphere radius equal to 0.3 nm); (3) the conformer contribution to the order parameters and the elastic constants was evaluated. Calculations were performed in the same molecular frame for all conformers and the average values then evaluated according to Equation (13), with the orientational distribution function of the undeformed nematic phase. The Saupe ordering matrix of a mesogen was also obtained in this way and then diagonalised.

For the Schiff's bases shown in Figure 1 several conformers were found. These have the same aromatic core, which is not fully planar because the C(Phe)-C(Phe)-NCH dihedral angle takes values around 37–38°. For MBBA, 28 conformers were included, differing in the orientation of the methoxy group (in

Table 1. Torsional energy of MBBA conformers with different alkyl chain conformations, as obtained from DFT calculations at the B3LY/6-31G** level [65]; the all-*trans* conformation is taken as a reference. The symbol g_i+(-) denotes a *gauche*+(-) state in the *i*th CH_2–CH_2 chain bond. A given conformer is identified by the sequence of its *gauche* states (e.g., g_1+ g_2+ denotes a conformer having the first and the second chain bond in *gauche*+ states).

Alkyl chain conformation	V_m/kJ mol^{-1}
all-*trans*	0
g_1+, g_1−	2.1
g_2+, g_2−	3.4
g_1+ g_2+, g_1− g_2−	5.5

the plane of the attached aromatic ring, on both sides), in that of the alkyl chain (approximately perpendicular to the adjacent benzene plane, above and below) and in the alkyl chain conformation. All conformers with the same alkyl chain conformation were assumed to have the same energy; in Table 1 the chain conformations considered in our calculations are reported, together with the corresponding torsional energies. For APAPA, which has a limited flexibility, only eight conformers were included, with the methoxy group on both sides of the coplanar phenyl ring and four possible orientation of the O–CO–C plane, forming dihedral angles of about ±45° and ±135° with the linked aromatic plane; the same energy was assumed for all these conformers. For the thiadiazole derivative shown in Figure 3, a single structure was taken; this has the three aromatic rings in the same plane and an angle of about 20° between the *para* axes of the two benzene rings, which is close to the value of 18° derived from electron diffraction measurements on the unsubstituted central ring system [56].

The elastic constants for a given compound were calculated as averages over all conformers, according to Equation (20). The molecular volume, in Equation (20), was given the value 0.27 nm^3 for APAPA, 0.29 nm^3 for MBBA and 0.26 nm^3 for the thiazole derivative, as obtained from the molecular surface calculation [66].

Figure 4 shows the calculated elastic constants of APAPA and MBBA as a function of the square of the major principal value of the Saupe ordering matrix, S_{zz}. We can see that the theoretical results are well in line with the experimental data, as shown in Figure 2. The magnitude, anisotropy and order parameter dependence of the elastic constants of APAPA and MBBA are correctly predicted. In agreement with experiment, all the bulk elastic coefficients of APAPA are higher than those for MBBA, but the most impressive difference is exhibited by K_{33}. The main reason behind this behaviour is molecular flexibility: for MBBA several more conformers than those for APAPA can be found and, more importantly, they can have quite different shapes. We have found similar results when comparing other mesogens with increasing flexibility, namely PAA, 4-*n*-pentyl-4′-cyanobiphenyl (5CB) and 4-*n*-octyl-4′cyanobiphenyl (8CB) [64].

The decrease of the bending stiffness on going from APAPA to MBBA is not a generic effect, associated with the decrease of order for the more flexible mesogen; neither can it be related to the difference in biaxiality between the two mesogens. We have calculated the biaxiality ratio $(S_{xx} - S_{yy})/S_{zz}$, where S_{ii} are the principal values of the Saupe ordering matrix ($S_{zz} > S_{xx} > S_{yy}$), and we have found very close values for the two compounds. Even the fourth rank order parameters $<P_4>$ which, according to Equations (5), would be the main reason for the difference between K_{33} and the other elastic constants, is similar for APAPA and MBBA. In contrast, as we have already shown in [64], the bending stiffness seems to be sensitive to a specific molecular property, that is, the curvature of the molecular shape. APAPA conformers are elongated and similar in shape, whereas the conformers of MBBA exhibit more significant differences, as a consequence of rotation of the alkyl chain bonds, and some of them are really curved. We show in Figure 5 two MBBA conformers, both having a single *gauche* in the alkyl chain, one in the first and

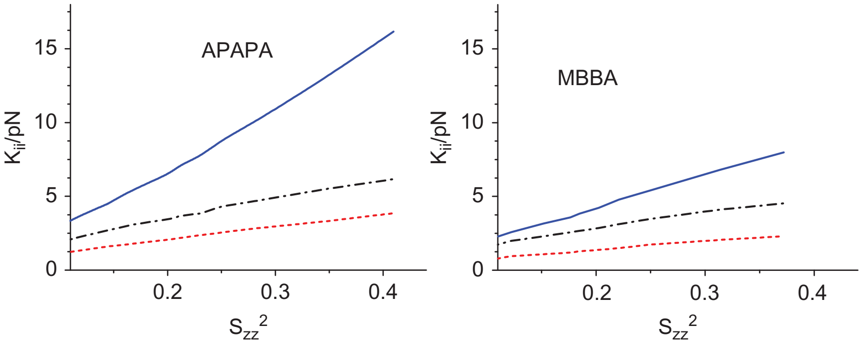


Figure 4. Bulk elastic constants calculated with the SI model for the nematic phase of APAPA (left) and MBBA (right), as a function of the square of S_{zz}, the major principal component of the Saupe ordering matrix. From bottom to top: K_{22}, K_{11}, K_{33}.

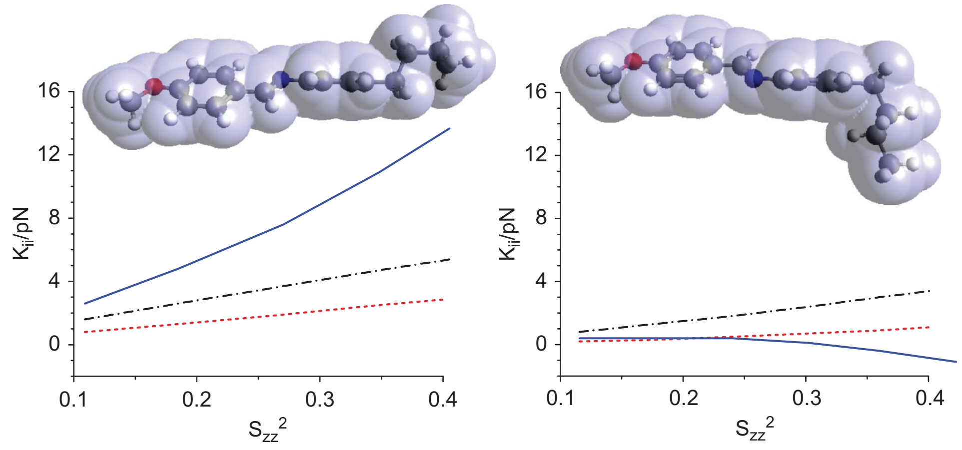


Figure 5. The bulk elastic constant calculated with the SI model for the hypothetical nematic phase formed by two different conformers of MBBA, as a function of the square of S_{zz}, the major principal component of the Saupe ordering matrix. The two conformers have a *gauche* state in the second (left) and in the first (right) CH_2–CH_2 bond of the alkyl chain. The molecular structures obtained from the geometry optimisation are shown at the top. Left, from bottom to top: K_{22}, K_{11}, K_{33}; right, from bottom to top: K_{33}, K_{22}, K_{11}.

the other in the second CH_2–CH_2 bond. In the same figure we also show the bulk elastic constants calculated for these conformers as a function of $S_{zz}{}^2$, the square of the major principal value of the Saupe ordering matrix. These results highlight two important issues. First, the significant differences between the elastic constants calculated for the single conformers, which are even larger than those generally found in experiments between different mesogens, clearly show that the conformational distribution cannot be neglected when connecting elastic constants and molecular structure. Secondly, the peculiar behaviour of K_{33} and its special sensitivity to molecular bending clearly appears from the results in Figure 5. Whereas K_{11} and K_{22} simply exhibit a decrease on going from the elongated to the bent conformer, the bend elastic constant K_{33} exhibits a large change: K_{33} is comparable to that predicted for APAPA, for the elongated conformer, whereas for the bent conformer it is very small and even negative at high ordering. We can also see in Figure 5 that for both conformers, in contrast to K_{11} and K_{22}, the bend elastic constant K_{33} displays a non-linear dependence on the square order parameter. It might be worth noticing that a negative K_{33} contribution by some conformers can be compatible with the stability of the uniform nematic phase, because the physical property of the LC corresponds to an average over all conformers [64].

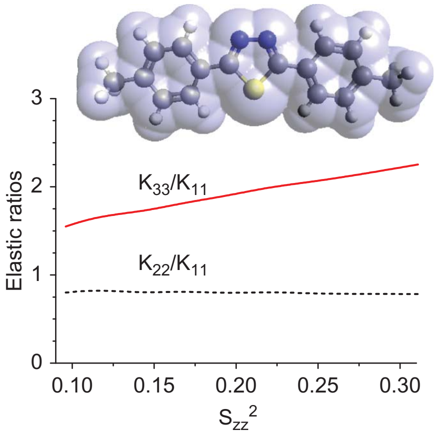


Figure 6. Elastic constant ratios calculated with the SI model for the nematic phase of the compound shown in Figure 3, as a function of the square of S_{zz}, the major principal value of the Saupe matrix. The molecular structure obtained from geometry optimisation is shown at the top.

It is now interesting to check the predictions of the SI model for the thiadiazole derivative shown in Figure 3. The calculated elastic ratios are shown in Figure 6 as a function of the square order parameter, S_{zz}. We can see that the calculated ratio, K_{22}/K_{11}, is close to 0.8 and nearly independent of temperature, as found experimentally; the ratio, $K_{33}/K_{11,}$ ranges between 1.5 and 2, and is not far from the measured value, which is about 1.8 and scarcely dependent upon temperature. As observed when the experimental data were reported [56], the predicted behaviour is similar to that of other rather rigid and non-curved mesogens with similar aspect ratios. In fact, this result is not surprising in view of the molecular shape obtained by geometry optimisation, also shown in Figure 6, which does not exhibit any pronounced bend. In contrast to [56], we can conclude that the normal behaviour exhibited by the bend elasticity of this thiadiazole derivative is not in contrast to Gruler's predictions; because of the low bend angle, this

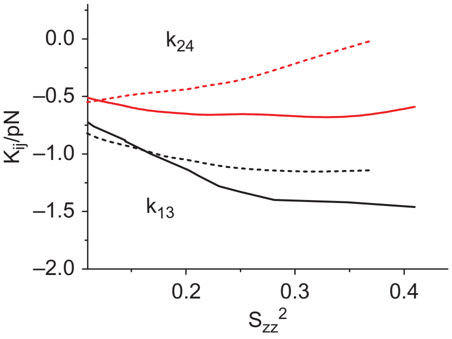


Figure 7. Surface-like elastic constants calculated with the SI model for the nematic phases of APAPA (solid lines) and MBBA (dashed lines), as a function of the square of S_{zz}, the major principal component of the Saupe ordering matrix.

compound does not appear to be a good choice with which to test the effect of a curved molecular shape on the bend stiffness of the nematic phase.

Finally, we show in Figure 7 the surface-like elastic constants, k_{13} and k_{24}, calculated for APAPA and MBBA, as a function of the square of the major principal component of the Saupe ordering matrix. We cannot compare these results with experiment, due to the scarcity of available data; only a comparison with a few theoretical predictions is possible. An analogy between the trends shown in Figure 7 and those reported in [64] for *n*-alkyl-cyanobyphenyls (*n*CBs) can be recognised, with k_{24} taking values close to zero, whereas k_{13} is negative and larger in magnitude, yet smaller than the bulk elastic constants. In all of these cases the saddle-splay elastic constant is in clear disagreement with the Nehring–Saupe prediction, according to which it should be negative and comparable in magnitude to the largest of the bulk elastic constants. In contrast, the Eriksen inequality [4], $K_{22} \geq |k_{24}|$, is satisfied.

4. Concluding remarks

Molecular models for the elasticity of nematic LCs have at least a 40-year history; the foundations were laid in the 1970s by the pioneering molecular field theory of Nehring and Saupe [8, 9] and the works of Priest [32] and Straley [34]. Subsequent developments, aimed at overcoming simplifying assumptions, such as the molecular field approximation or the existence of perfect orientational order, as well as exploring the role of different intermolecular interactions, have contributed to our present understanding. A powerful methodology is represented by the DFT, which provides a general framework to derive expressions for the free energy of deformed nematics, exploiting the theoretical tools developed in the context of liquid state theory. The theoretical expressions for the elastic constants are obtained in terms of the orientational order parameters and the structural parameters related to the direct correlation functions. Numerical estimates are feasible for simple model systems of uniaxial particles. It has been shown that the main features of the dependence of the elastic constants on temperature and on molecular structure can be simply explained in terms of the length-to-width ratio in the case of fairly rigid mesogens.

However, these models fail when dealing with flexible mesogens. This is not a minor issue, since flexibility is a basic characteristic of mesogens and the degree of molecular flexibility represents an important way of controlling the properties of LC materials. Different explanations have been proposed for the effects of flexibility, such as the presence of curved conformers [50], which would reduce the cost for bend director distortions [44, 46], or the enhancement of smectic-like short-range correlations by alkyl chains [38]. However, these proposals could not be adequately tested by theory and calculations, because of the difficulty of dealing with arbitrarily shaped particles. We have recently developed an approach, called the Surface Interaction, which can overcome some of these limitations and which has enabled us to investigate unexplored issues [23, 64]. The SI model can be seen as a reformulation of the Maier–Saupe theory, which is suitable for integration with modern computational tools for molecular structure determination, so as to enable a realistic account of the molecular features. Two main effects emerge from our calculations for typical mesogens:

(1) Flexibility plays an essential role and cannot be neglected when considering the elastic properties of nematics. Different conformers, by virtue of their different shape, can give quite different contributions to the elastic constants. Interestingly, geometrical changes deriving from rotation around alkyl chain bonds are sufficient to produce non-negligible effects.
(2) Special effects of a curved molecular shape emerge when considering the bending stiffness. These were suggested fairly early on by Gruler [44], but since then almost ignored, with a significant exception [45], in which the possible implications for the stability of the nematic phase, in particular for intrinsically bent mesogens, were pointed out.

It is worth mentioning that similar conclusions were reached in [46], where theoretical expressions for the elastic constants of semiflexible mesogenic dimers were derived. The investigation can now be extended to any kind of mesogen, using the SI model.

After about 40 years of theoretical investigations, we may say that there is a general consensus on the importance of the molecular shape in determining the elastic constants of nematics; this means that steric repulsions and short-range dispersion interactions, which are modulated by the molecular shape, must be the main factor responsible for the elastic response. Likewise, theoretical and experimental studies have shown that electrostatic interactions, although in some cases non-negligible, are not the main reason for the orientational order, which underlies the curvature elasticity in LCs [68].

In the future, there is room for improvement in the available theories in different respects, but inclusion of molecular features seems to be a major issue. Their importance has been shown by the SI model, which, however, is only a phenomenological approach; a sounder statistical theory should combine a realistic molecular representation with a suitable account of the structure of the fluid. We can envisage that in this respect an important contribution will be given by computer simulation techniques. These have contributed to our present understanding of LC elasticity [69–71], but still there are practical and theoretical difficulties, related on the one hand to the high computational cost and on the other to the connection between the structural LC properties and elastic response [72, 73]. A stronger impact is expected in the future, with the feasibility of large-scale atomistic studies [74].

A few final comments are deserved by the surface-like elastic constants of nematics, which remain an open problem. In the mid-1990s the following was stated [13]:

'The present situation with k_{13} and k_{24} is similar to that of the elastic constants K_{22} about thirty years ago when its value was not known. Over these years joint efforts of the theoretical macroscopic approach and experiment have made the twist elasticity a well-defined physical idea and K_{22} a reliable measured quantity. We believe that the same approach will allow us to comprehend the nature of the surface-like elasticity in LCs.'

After another 15 years, our knowledge in this field does not seem to have advanced significantly. A joint theoretical and experimental effort is probably needed to shed light on this problem, treating on the same footing the surface elasticity and anchoring.

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