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The calculation of the elastic constants of nematics

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A molecular model for nematics is proposed. Its elastic constants are calculated and the attendant approximations are discussed. The results are compared with those of existing models.

1. Introduction

The molecular statistical theory of the elastic constants of nematic liquid crystals has been the subject of several studies. Because of the unknown form of the intermolecular interaction these studies concentrate on model systems stressing one or some of the characteristic features of the intermolecular interaction that attend the underlying molecular structure. Priest [1], Poniewierski and Stecki [2] and Straley [3] derived expressions for the elastic constants of a system of hard rods thus stressing the repulsive part of the intermolecular interactions. On the other hand Nehring and Saupe [4] paid attention solely to the attractive part of the intermolecular interaction by considering the influence of the induced dipole–dipole interaction. The combined influence of anisotropic repulsive and attractive interactions was analysed by Stecki and Poniewierski [5] and Gelbart and Ben-Shaul [6] by adding an attractive term to the hard core model, and by Dunmur and Miller [7] using a procedure analogous to that given in [4]. Finally a pragmatic approach of van der Meer *et al.* [8] should be mentioned; this is based on a model consisting of harmonic intermolecular forces.

The purpose of this paper is to discuss the elastic constants of a model that can be conceived as a Lennard-Jones interaction between rods. Compared with existing models the present model takes into account the softness of the repulsive part of the intermolecular interaction as well as the connection between the extensiveness of the molecule and the orientation dependence of the attractive part. As a consequence of the introduction of these new features great calculational problems appear as soon as the thermodynamic properties, for example, the temperature dependence of the order parameter, are considered. For that reason we shall concentrate on the fully ordered state, i.e. the present calculation can only be related to the elastic constants and their mutual ratios in the highly ordered nematic state.

The organisation of this paper is as follows. In §2 the new model is introduced and the expressions for its elastic constants are derived. The behaviour of the elastic constants as a function of the different parameters is analysed numerically in §3, and the results are compared with experiment as far as possible. Finally, in §4, the results are discussed, among other things in comparison with the existing models.

2. Lennard-Jones rods

The starting point of our model is the Lennard-Jones interaction between spheres. A number of spheres can be linked together such that the resulting chain can be

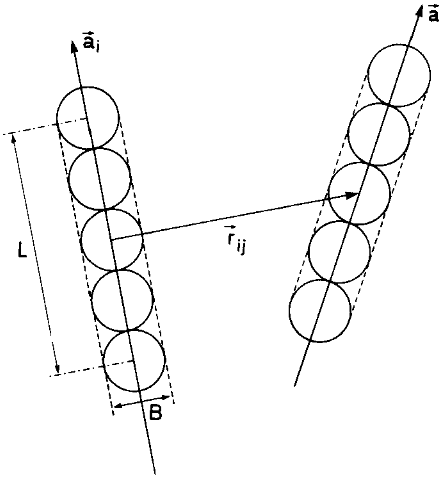

Figure 1. Schematic representation of two Lennard-Jones rods, each with length $L + B$ and width B. The unit vector **a** denotes the orientation of a rod, and the vector $\mathbf{r}_{ij}$ gives the mutual position of the rods i and j.

conceived approximately as a spherocylinder. Next a system of such spherocylinders, shown in figure 1, is considered. The spheres of a given chain interact with the spheres of a second chain according to the Lennard-Jones interaction

$$u_{ij} = -4\varepsilon'\left[\frac{\sigma^6}{r_{ij}^6} - \frac{\sigma^{12}}{r_{ij}^{12}}\right], \tag{1}$$

where ε' is the interaction strength and σ is related to the radius of the spheres. Further we assume that the interactions between the spheres of a given chain do not influence the resulting intermolecular interactions. Then, the total interaction between two spherocylinders i and j is

$$V_{ij} = -\varepsilon \int_{-\frac{1}{2}L}^{\frac{1}{2}L} da \int_{-\frac{1}{2}L}^{\frac{1}{2}L} db \left[\frac{2B^6}{[r_{ij}(a,b)]^6} - \frac{B^{12}}{[r_{ij}(a,b)]^{12}}\right], \tag{2}$$

with

$$r_{ij}(a,b) = |\mathbf{r}_{ij} + b\mathbf{a}_j - a\mathbf{a}_i|,$$

where $\mathbf{r}_{ij}$ is the vector connecting the centres of mass of the rods, the unit vector $\mathbf{a}_i$ gives the orientation of rod i and $\varepsilon = \varepsilon'\varrho^2$ with ϱ denoting the number of spheres per unit length of the rod. Here B denotes the width of the rods and is described by the distance r_{min} that minimizes u_{ij} in equation (1), giving $B^6 = 2\sigma^6$. The length of the rods is $L + B$.

Interacting Lennard-Jones rods are now used as a model for a nematic liquid crystal. For the sake of simplicity the system is assumed to possess perfect order, i.e. $\mathbf{a}_j$ can be identified with the director at position $\mathbf{r}_j$. Without loss of generality $\mathbf{r}_i$ may be chosen as the origin. The vector $\mathbf{r}_j - \mathbf{r}_i$ is abbreviated to $\mathbf{r}$; because its deviation is small the director at the position $\mathbf{r}$ may be expanded with respect to the director at the origin in the following way:

$$\mathbf{n}(\mathbf{r}) = \mathbf{n}(0) + r_\beta \partial_\beta \mathbf{n}(0) + \tfrac{1}{2} r_\beta r_\gamma \partial_\beta \partial_\gamma \mathbf{n}(0). \tag{3}$$

Then substitution of equation (3) into equation (2) and expansion of the denominators to second order in **n**, gives

$$\begin{aligned} V(\mathbf{r}) \;=\; & -\varepsilon \int_{-\frac{1}{2}L}^{\frac{1}{2}L} da \int_{-\frac{1}{2}L}^{\frac{1}{2}L} db \left[\left[\frac{2B^6}{|\mathbf{r}+(b-a)\mathbf{n}(0)|^6} - \frac{B^{12}}{|\mathbf{r}+(b-a)\mathbf{n}(0)|^{12}}\right]\right. \\ & - 6(br_\alpha r_\beta r_\gamma \partial_\alpha \partial_\beta n_\gamma(0) - abn_\gamma(0)\, r_\alpha r_\beta \partial_\alpha \partial_\beta n_\gamma(0)) \\ & \times \left[\frac{B^6}{|\mathbf{r}+(b-a)\mathbf{n}(0)|^8} - \frac{B^{12}}{|\mathbf{r}+(b-a)\mathbf{n}(0)|^{14}}\right] \\ & + 12b^2 r_\alpha r_\beta r_\gamma r_\delta \partial_\alpha n_\beta(0)\, \partial_\gamma n_\delta(0) \\ & \left.\times \left[\frac{4B^6}{|\mathbf{r}+(b-a)\mathbf{n}(0)|^{10}} - \frac{7B^{12}}{|\mathbf{r}+(b-a)\mathbf{n}(0)|^{16}}\right]\right]; \end{aligned} \tag{4}$$

where summation over repeated indices is implied. The coordinate system may be chosen such that **n**(0) is parallel to the z axis ($\theta(0) = \phi(0) = 0$). An arbitrary **n**(**r**) can be written in terms of eulerian angles $\theta(\mathbf{r})$ and $\phi(\mathbf{r})$ as

$$\mathbf{n}(\mathbf{r}) = (\sin\theta(\mathbf{r})\cos\phi(\mathbf{r}), \sin\theta(\mathbf{r})\sin\phi(\mathbf{r}), \cos\theta(\mathbf{r})). \tag{5}$$

Differentiation of **n** with respect to **r** gives

$$\partial_\alpha \mathbf{n}(0) = (\partial_\alpha\theta, 0, 0) \tag{6a}$$

and

$$\partial_\alpha\partial_\beta \mathbf{n}(0) = (\partial_\alpha\partial_\beta\theta, \partial_\alpha\theta\partial_\beta\phi + \partial_\alpha\phi\partial_\beta\theta, -\partial_\alpha\theta\partial_\beta\theta); \tag{6b}$$

further

$$\partial_x\partial_z\theta + \partial_z\theta\partial_y\phi + \partial_z\phi\partial_y\theta = (\partial_z\theta)^2 - (\partial_x\theta)^2, \tag{7}$$

because surface terms may be neglected. In view of symmetry the interaction in equation (4) must be invariant to inversion. Substitution of equations (6) and (7) into equation (4), using the symmetry argument of the invariance of the expression for the direction of **r** and changing to cylindrical coordinates

$$x = \varrho\cos\psi, y = \varrho\sin\psi, \tag{8}$$

leads to

$$V = V_0 + V_1, \tag{9}$$

where V_0 is the contribution to V of the undistorted system

$$V_0(\varrho, z, \psi) = -\varepsilon \int_{-\frac{1}{2}L}^{\frac{1}{2}L} da \int_{-\frac{1}{2}L}^{\frac{1}{2}L} db \left[\frac{2B^6}{[\varrho^2 + (b-a+z)^2]^3} - \frac{B^{12}}{[\varrho^2 + (b-a+z)^2]^6}\right], \tag{9a}$$

and V_1 is the extra contribution due to the distortion

$$\begin{aligned} V_1(\varrho, z, \psi) \;=\; & 6\varepsilon \int_{-\frac{1}{2}L}^{\frac{1}{2}L} da \int_{-\frac{1}{2}L}^{\frac{1}{2}L} db \left[b[2z\varrho^2\cos^2\psi[(\partial_z\theta)^2 - (\partial_x\theta)^2]\right. \\ & + (a-z)[\varrho^2\cos^2\psi(\partial_x\theta)^2 + \varrho^2\sin^2\psi(\partial_y\theta)^2 + z^2(\partial_z\theta)^2]] \\ & \times \left[\frac{B^6}{[\varrho^2 + (b-a+z)^2]^4} - \frac{B^{12}}{[\varrho^2 + (b-a+z)^2]^7}\right] \\ & - 2b^2\varrho^2\cos^2\psi[\varrho^2\cos^2\psi(\partial_x\theta)^2 + \varrho^2\sin^2\psi(\partial_y\theta)^2 + z^2(\partial_z\theta)^2] \\ & \left.\times \left[\frac{4B^6}{[\varrho^2 + (b-a+z)^2]^5} - \frac{7B^{12}}{[\varrho^2 + (b-a+z)^2]^8}\right]\right]. \end{aligned} \tag{9b}$$

V_1 results in an increase of the free energy. Using the standard procedure of linear response the so-called distortion free energy can be written as [9]

$$F_d = \tfrac{1}{2}d \int d^3r\, g(\mathbf{r}, \mathbf{n}(0))\, V_1, \tag{10}$$

where $g(\mathbf{r}, \mathbf{n}(0))$ denotes the pair distribution function in the undistorted system and d is the density of the system. Because of symmetry $g(\mathbf{r}, \mathbf{n}(0))$ does not depend on the angle ψ, introduced in equation (8). Therefore the integration over ψ in equation (10) can be performed immediately. When the distortion interaction of equation (9 *b*) is substituted into equation (10), the expression for the free energy may be compared with that due to Frank [10], which in terms of the derivatives of the eulerian angle θ is

$$F_d = \frac{1}{2}\int d^3r[K_1(\partial_x\theta)^2 + K_2(\partial_y\theta)^2 + K_3(\partial_z\theta)^2]. \tag{11}$$

The expression appears to be independent of the derivatives of the angle ϕ. Such a comparison gives the elastic constants of the system of Lennard-Jones rods as

$$\begin{aligned}\begin{bmatrix} K_1 \\ K_2 \\ K_3 \end{bmatrix} = {} & 6d\varepsilon\pi \int_0^\infty d\varrho \int_{-\infty}^{\infty} dz\, \varrho g(\varrho, z) \int_{-\frac{1}{2}L}^{\frac{1}{2}L} da \int_{-\frac{1}{2}L}^{\frac{1}{2}L} db \\ & \times\; b\left[\frac{B^6}{[\varrho^2 + (b - a + z)^2]^4} - \frac{B^{12}}{[\varrho^2 + (b - a + z)^2]^7}\right] \\ & \times \begin{bmatrix} \varrho^2(a - 3z) \\ \varrho^2(a - z) \\ 2z(\varrho^2 - z^2 + 2az) \end{bmatrix} \\ & - \tfrac{1}{2}b^2\varrho^2\left[\frac{4B^6}{[\varrho^2 + (b - a + z)^2]^5} - \frac{7B^{12}}{[\varrho^2 + (b - a + z)^2]^8}\right]\begin{bmatrix} 3\varrho^2 \\ \varrho^2 \\ 4z^2 \end{bmatrix}.\end{aligned} \tag{12}$$

The problem still remains of finding a suitable distribution function. An exact calculation of this function is prohibitively difficult, and therefore it must be approximated. The following approximation is used here [9]:

$$g(\varrho, z) = \frac{\exp[-\beta V_0(\varrho, z)]}{\int_0^\infty d\varrho \int_{-\infty}^{\infty} dz \int_0^{2\pi} d\psi\, \varrho \exp[-\beta V_0(\varrho, z)]}, \tag{13}$$

where $V_0(\varrho, z)$ is given by equation (9 *a*), $\beta = [kT]^{-1}$, and k is the Boltzmann constant. It should be noted that the main effect of this distribution function is that two molecules can hardly overlap.

The elastic constants can now be calculated and this must be done numerically. An important quantity is the length-to-width ratio $R = (L + B)/B$. The results of the calculations will be presented in the following section.

3. Results

In order to determine the dependence of the elastic constants on, for example, the length-to-width ratio of the molecules or the temperature it is important to give an acceptable value to the interaction strength ε. Because it is very difficult to calculate the transition temperature of the present model, it is not possible to estimate the right value of ε in that way. A second method is to choose ε such that one of the elastic constants has the experimentally measured value; this method is used here. Further the molecules are assumed to be perfectly aligned, i.e. an elastic constant of a perfectly ordered nematic must be used as reference. The experimental quantities K_i^0 obtained by Leenhouts *et al.* [11] seem to represent this situation. It should be remarked here that the choice of K_1^0, K_2^0 or K_3^0 as reference is totally free; here K_1^0 is chosen. Out of the variety of available K_1^0 data, which are all of the same order of magnitude, we choose the K_1^0 value of 4-methoxybenzylidene-4′-cyanoaniline (MBCA). The temperature dependence is chosen such that the material described is in the nematic state, for example, $\beta = 2 \times 10^{20}\,\mathrm{J}^{-1}$. The density d is selected to be of the right order of magnitude [12], i.e. $d = 2{\cdot}5 \times 10^{27}\,\mathrm{m}^{-3}$.

Table 1. Variation of the interaction strength ε in order to give it a reasonable value; the length-to-width ratio R is 3. In the last column the experimental K_1^0 value is given for MBCA, whose length-to-width ratio is also about 3.

$\varepsilon/\mathrm{J\,m^{-2}}$	$K_1/10^{-12}\,\mathrm{N}$	$K_2/10^{-12}\,\mathrm{N}$	$K_3/10^{-12}\,\mathrm{N}$	$\frac{K_2}{K_1}$	$\frac{K_3}{K_1}$	$K_1^0\,(\mathrm{MBCA})/10^{-12}\,\mathrm{N}$
$0{\cdot}63 \times 10^{-5}$	4·59	1·56	6·67	0·340	1·454	18·2
$1{\cdot}25 \times 10^{-5}$	17·1	5·79	17·4	0·337	1·012	18·2
$1{\cdot}88 \times 10^{-5}$	51·5	17·2	36·7	0·333	0·714	18·2
$2{\cdot}50 \times 10^{-5}$	126	41·6	65·7	0·330	0·523	18·2

Table 2. Influence of the length-to-width ratio, R, on the values of the elastic constants and their ratios for $\varepsilon = 1{\cdot}25 \times 10^{-5}\,\mathrm{J\,m^{-2}}$.

R	$K_1/10^{-11}\,\mathrm{N}$	$K_2/10^{-11}\,\mathrm{N}$	$K_3/10^{-11}\,\mathrm{N}$	$\frac{K_2}{K_1}$	$\frac{K_3}{K_1}$
3	1·71	0·579	1·74	0·337	1·012
4	8·13	2·74	13·4	0·337	1·645
5	32·7	11·0	70·0	0·337	2·142
6	94·3	31·7	237	0·336	2·513

The results for ε are given in table 1, showing that $\varepsilon = 1{\cdot}25 \times 10^{-5}\,\mathrm{J\,m^{-2}}$ is an acceptable reference value; this value will be used in the following. Table 2 shows the influence of the length-to-width ratio on the magnitude of the elastic constants and their ratios; both the ratio K_3/K_1 and the elastic constants themselves increase with increasing R. This feature agrees with experiment, so far as the molecules can be conceived as rigid rods. The ratio K_2/K_1 does not depend on R. This is also in agreement with experiment, although the ratio is a factor of 2 too small. Finally, the temperature dependence of the elastic constants has been determined. The results are shown in table 3. The constants increase with decreasing temperature as expected. The ratio K_2/K_1 remains constant, whereas K_3/K_1 decreases with decreasing temperature. These last two features do not agree with experiment. This is certainly due largely to

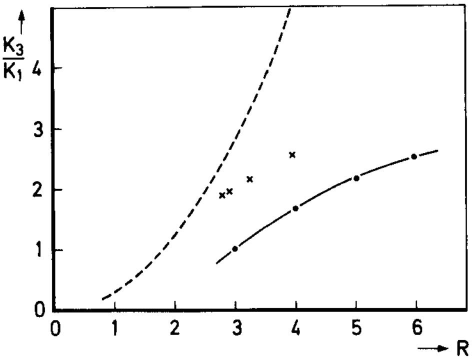

Figure 2. The relation between the ratio K_3/K_1 and the length-to-width ratio R; (1) the dashed line results from the harmonic model [8]; (2) the crosses are the experimental results of Leenhouts *et al.* [11]; (3) the full line is obtained from the present model.

Table 3. Influence of temperature on the values of the elastic constants and their ratios for $\varepsilon = 1{\cdot}25 \times 10^{-5}\,\mathrm{J\,m^{-2}}$ and $R = 3$.

T/K	$K_1/10^{-11}$ N	$K_2/10^{-11}$ N	$K_3/10^{-11}$ N	$\frac{K_2}{K_1}$	$\frac{K_3}{K_1}$
342	1·87	0·628	1·81	0·337	0·969
354	1·77	0·595	1·76	0·337	0·977
362	1·71	0·579	1·74	0·337	1·012
366	1·69	0·571	1·73	0·337	1·019

the fact that in reality, there exists also a temperature dependence in the order parameter. Presently, this quantity is assumed to be one and constant. Therefore, a comparison of the temperature dependence of the elastic constants with experiment is out of the question. The present calculation only indicates the effect of the correlation function.

4. Discussion

The results of the present model can be compared best with the theoretical results of the rather similar approach of van der Meer *et al.* [8]. Unfortunately, it is hard to compare them with other models because the order parameter is not taken into account in the present approach. The paper of van der Meer *et al.* stresses the relation between the length-to-width ratio and the behaviour of the ratio K_3/K_1. Their result, as well as the result for Lennard-Jones rods, is plotted in figure 2. The experimental results of supposed rigid rods, as measured by Leenhouts *et al.*, are also indicated in that figure. As can be seen, the shape of the curve resulting from the present model is in better agreement with experiment than that obtained from the harmonic model developed by van der Meer *et al.* [8]. Regarding the temperature dependence of the elastic constants, it should be remarked that a comparison with the harmonic forces model is not possible because in that model temperature is not included.

The ratio K_2/K_1 remains a problem theoretically. Although it varies a little in the present model, it still remains more or less equal to the value of $\frac{1}{3}$. That situation might be improved by making ε dependent on the variables a and b in the interaction given in equation (2), i.e. by making the interaction strength of the spheres in a given chain (cf. figure 1) dependent on their position in the chain. In such a way it would be possible to imitate real molecules and to distinguish different groups of atoms in a molecule. Another extension that might improve the results is the following. The spheres that are used to construct the molecules can be linked together to form disks first. Then these disks can be piled up to cylinders. The interactions between these cylinders can be considered as interactions between molecules in liquid crystals, where the direction perpendicular to the disk plane corresponds to the orientation of the molecules. Unfortunately, such a model leads to very complicated calculations.

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