

A simple model for the stiffness constants of nematic liquid crystals based on distributed harmonic forces between the molecules

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The stiffness constants of a nematic liquid crystal are calculated for the situation of perfect orientational order with the aid of a model of distributed harmonic forces. Both attractive and repulsive forces are taken as distributed along the molecules, and thus are only important for the parts of two molecules that are in close proximity. For small deviations between the directors of two molecules the potential is assumed to vary quadratically in the deflection. In addition two models for the pair distribution function are considered. In the case of nematic-like pair correlation (molecular centres of neighbours distributed at random around the excluded volume due to the central molecule) K_3/K_1 is predicted to vary as L^2/W^2 , where L and W are the length and width of the molecule, respectively. This is in agreement with more sophisticated theories and explains the experimental trend observed for molecules without alkyl chains. The case of smectic-like pair correlation (the neighbours have some preference for their centres to be in the same plane) is simulated by taking a gaussian distribution. Increasing the sharpness of this distribution leads to a decrease of K_3/K_1 , which explains the experimental results for homologous series. In all cases $K_2/K_1 = 1/3$ is predicted, again in agreement with more elaborate theories and in reasonable agreement with the experimental results.

1. INTRODUCTION

In the nematic liquid-crystalline phase the elongated molecules are, on average, aligned with their long axes parallel to a preferred direction in space. This direction can be labelled by a unit vector \mathbf{n} , the director. The molecules translate freely, as in the isotropic phase, and the centres of mass of the molecules are distributed at random. In many practical circumstances constraints are imposed on the orientation of the nematic liquid by the walls of the container, which force \mathbf{n} to be non-uniform. The associated elastic properties are in the bulk determined by three elastic constants, or better, stiffness constants, corresponding to the restoring torques opposing splay (K_1), twist (K_2) and bend (K_3). The distortion free energy density is [1]

$$F_d = \frac{1}{2} [K_1(\nabla \cdot \mathbf{n})^2 + K_2(\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + K_3(\mathbf{n} \times \nabla \times \mathbf{n})^2].$$

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The stiffness constants are important for a number of reasons. In the first place they appear in the description of virtually all phenomena where the orientation of the director is manipulated by external fields (for example, in display devices). Secondly we might expect to learn something from the stiffness constants about the intermolecular interactions which are responsible for the orientational order in nematics. Finally we note that biomembranes and model membranes [2] are closely analogous to smectic liquid crystals and, as such, analogous to nematic liquid crystals. Though a continuum theory for the curvature elasticity of membranes has been developed [3], a molecular theory is not available as yet. In the present paper the concept of positional pair correlation (smectic-like correlation) is used such that it is in principle extendable to membranes.

When discussing the theory of the stiffness constants various authors have concentrated on the temperature dependence of K_1 , K_2 and K_3 , especially via the dependence on the degree of orientational order [4, 5]. Usually some form of an expansion of the intermolecular potential is required. In that case the calculation of the expansion coefficients, which contain the relevant molecular parameters, is prohibitively difficult. In this paper we take a much more pragmatic approach. Disregarding the temperature dependence of the stiffness constants we consider the special case of perfect orientational order. This situation allows the calculation of the distortion free energy for a relatively simple model for the intermolecular interaction. It is a variant on the ideas of Gelbart and coworkers [6] who studied the combined effect of attractive and repulsive forces. In their model attractive forces act between the molecular centres. This assumption would be acceptable for single atoms or small molecules, but not for large and elongated molecules. Therefore we assume instead that the attractive and repulsive forces are distributed along the molecules, and thus are only important for those parts of two molecules that are in close proximity. The interaction between two molecules being given, the stiffness constants still depend on the distribution of the centres of mass of the molecules with respect to one another. This is taken into account using the pair distribution function. In fact two cases are studied: nematic-like pair correlation, in which case the molecular centres of neighbours are distributed at random around the excluded volume of a central molecule, and smectic-like pair correlation, in which neighbours have some preference for their centres to be in the same plane. In this way the rather complicated trends in the stiffness constants observed so far can be understood at least qualitatively.

The plan of the paper is as follows. In the next section the experimental information on the stiffness constants and the present theoretical situation are summarized. In § 3 our model of distributed harmonic forces is introduced. Section 4 gives the calculations and the results for the stiffness constants, while § 5 contains a concluding discussion.

2. THE STIFFNESS CONSTANTS

From the experimental results available for the stiffness constants [7–11] we may draw the following conclusions [12]:

(i) The stiffness constants are of the order of 10^{-11} N. In all cases K_2 is the smallest of the three. For the nematogenic compounds studied up to now

we have

$$\begin{aligned} 0.5 < K_3/K_1 < 3.0, \\ 0.5 < K_2/K_1 < 0.8. \end{aligned}$$

(ii) To a first approximation we find that

$$K_i \sim S^2, \quad i = 1, 2, 3, \quad (1)$$

where $S \equiv \overline{P_2} = (3 \overline{\cos^2 \beta} - 1)/2$ is the usual orientational order parameter, β being the angle between the long molecular axis and the director. Looking more closely at the experimental results we observe that equation (1) holds only approximately, the more the better if K_1 and K_3 are about equal. If this is not the case then the temperature dependence of K_3/K_1 is such that with increasing temperature (decreasing orientational order) the values of K_1 and K_3 approach each other (see figure 1). For nematics that exhibit at lower temperatures a smectic phase there is a pre-smectic stiffening of K_2 and K_3 when the nematic-smectic phase transition is approached (see figure 1 for $m=6$ and $m=7$).

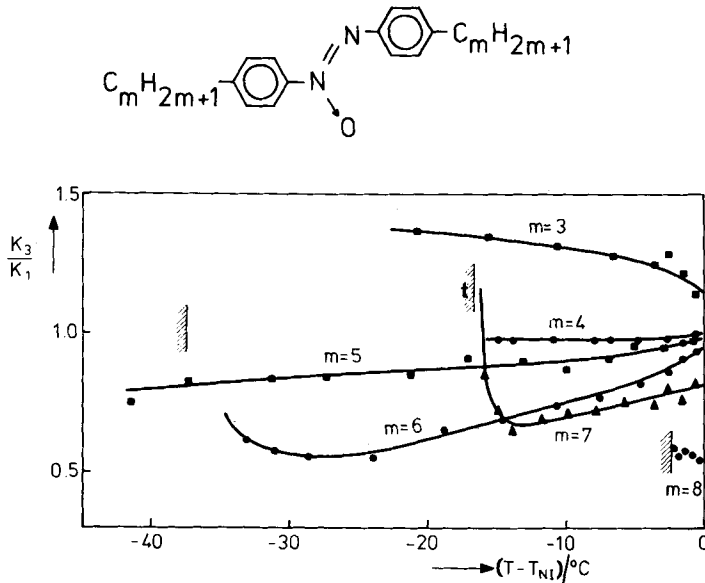


Figure 1. Ratio K_3/K_1 for the nematic phases of the series of 4,4'-di-n-alkylazoxybenzenes. The shaded regions indicate a smectic A phase [8].

(iii) No evidence has been found so far of a noticeable influence of differences in polarizability and dipole moment on the elastic behaviour. Rather, it seems that the stiffness constants are related to the molecular dimensions, especially the molecular length-to-width ratio L/W . However, this dependence is rather different for molecules with and without alkyl chains. In the latter case, introduction of relatively rigid end or side groups changes K_3/K_1 in the same direction as L/W (see figure 2). On the other hand, if the length of alkyl chains is increased, for example in a homologous series, K_3/K_1 is found to decrease (see figure 1). In all cases the variations of K_2 are small.

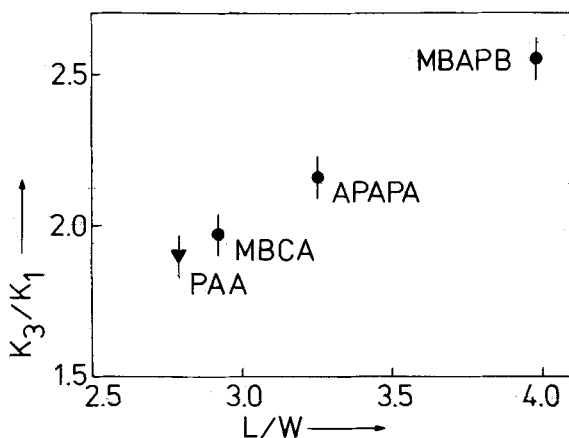
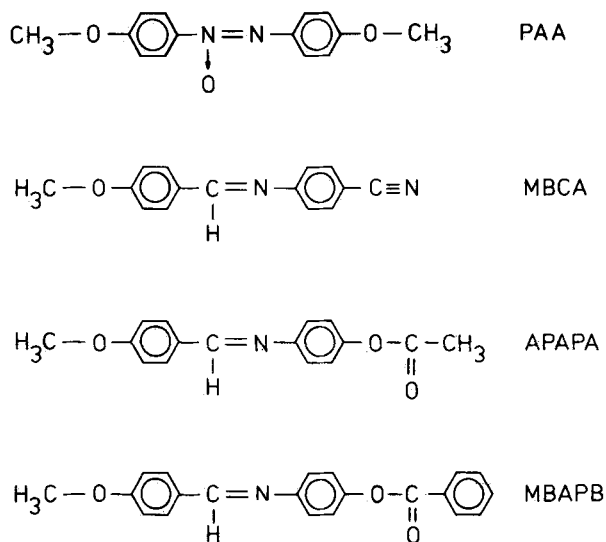


Figure 2. Variation of K_3/K_1 with L/W for some molecules without alkyl chains [11].

The theoretical situation concerning the stiffness constants may be summarized as follows :

(i) The main temperature dependence is attributed to the variation in orientational order. This is most easily seen by considering the Landau theory of the nematic-isotropic phase transition. Restricting ourselves to axially symmetric molecules we find by expanding the free energy density up to second order in the order parameter S that [13]

$$\left. \begin{aligned} K_1 = K_3 &= (2L_1 + L_2)S^2, \\ K_2 &= 2L_1S^2, \end{aligned} \right\} \quad (2)$$

where L_1 and L_2 are phenomenological constants appearing in the Landau free energy density. Thus, to order S^2 , $K_1 = K_3$ and all three elastic constants

vary with temperature as S^2 . Priest [4] also arrived at this result but from a mean-field theory by expanding the intermolecular potential and the pair distribution function in spherical harmonics. An alternative derivation of Priest's results can be found in [14]. Though these results have been disputed [5], they are in good agreement with the experiment. According to Priest [4], deviations from (1) are related in a simple way to \bar{P}_4/\bar{P}_2 , where $\bar{P}_4 = (35 \cos^4 \beta - 30 \cos^2 \beta + 3)/8$ is the fourth rank order parameter. With $\bar{K} = (K_1 + K_2 + K_3)/3$ the result is

$$\left. \begin{aligned} K_1/\bar{K} &= 1 + C - 3C'\bar{P}_4/\bar{P}_2, \\ K_2/\bar{K} &= 1 - 2C - C'\bar{P}_4/\bar{P}_2, \\ K_3/\bar{K} &= 1 + C + 4C'\bar{P}_4/\bar{P}_2. \end{aligned} \right\} \quad (3)$$

The quantities C and C' are constants depending on molecular properties; in order to calculate them, further assumptions have to be made.

The stiffness constants for twist (K_2) and bend (K_3) are predicted to diverge at the nematic-smectic transition temperature or slightly below that temperature [15], in agreement with experiment.

(ii) The molecular quantities C and C' can be calculated by representing the molecules by spherocylinders, interacting via hard core repulsions. The result is with $R = L/W - 1$ [4, 16, 17]

$$\left. \begin{aligned} C &= (2R^2 - 3)/(7R^2 + 21), \\ C' &= \frac{2}{3}(3R^2 - 8)/(7R^2 + 21). \end{aligned} \right\} \quad (4)$$

For infinitely long rods this leads to $K_2/K_1 = 1/3$. Equations (3) and (4) predict that K_3/K_1 is a weakly increasing function of L/W , qualitatively in agreement with the experimental trend observed for molecules without alkyl chains. To reproduce the experimental results quantitatively we need values for \bar{P}_4/\bar{P}_2 that are too high.

(iii) For the special case of anisotropic dispersion forces between spherical molecules Nehring and Saupe [18] found up to order S^2

$$K_1 : K_2 : K_3 = 5 : 11 : 5. \quad (5)$$

This is not in agreement with the experimental finding that K_2 is the smallest of the three stiffness constants. The combined effect of repulsive and attractive forces has been considered by Poniewierski and Stecki [17]. They also find that K_3/K_1 is an increasing function of L/W . However, this ratio is reduced due to the presence of attractive forces.

The general result that $K_1 = K_3$ to order S^2 contrasts with some conclusions from more empirical models [19-21], that give $K_3/K_1 > 1$ and still $K_i \sim S^2$. This inconsistency arises from the *ad hoc* introduction of a pair distribution function that is independent of the orientational order.

3. DISTRIBUTED HARMONIC FORCES

In our model we assume complete orientational order, i.e. $\bar{P}_2 = \bar{P}_4 = 1$. The implications of this approximation are discussed in § 5. As the long axis

of a molecule and the local director now coincide the free energy density can be written as

$$F = \frac{1}{2}\sigma^2 \int d\mathbf{r} V[\mathbf{r}, \mathbf{n}(0), \mathbf{n}(\mathbf{r})] g[\mathbf{r}, \mathbf{n}(0), \mathbf{n}(\mathbf{r})], \quad (6)$$

where σ is the number density, V the pair potential, and g the pair distribution function. Furthermore \mathbf{r} is the vector between the centre of a molecule at the origin with local director $\mathbf{n}(0)$ and that of a molecule at position \mathbf{r} with director $\mathbf{n}(\mathbf{r})$. It is easily verified that with (6) various results quoted in the previous section can be reproduced. For example, taking for V the full dispersion interaction and in addition an isotropic pair distribution function $g = g(r)$ we obtain the Nehring-Saupe result $K_1 : K_2 : K_3 = 5 : 11 : 5$.

Theories of the nematic phase that take both attractive and repulsive forces into account usually assume attractive forces between the molecular centres and local repulsive forces where molecules touch. In the case of elongated molecules it seems more realistic to think of distributed forces between parts of two molecules in close proximity, both attractive and repulsive. Referring to figure 3 the molecules are represented by simple cylinders. The interaction is taken into account only for parts of the molecules that are opposite to each other in the state of parallel alignment. The lines drawn between the molecules are fictitious elastic threads of interaction. The threads are parallel if the molecular axes are in the same plane as the intermolecular vector \mathbf{r} . If the molecules are vertically displaced there are thus less interaction threads. In the situation of figure 3 (a) the interaction energy is, assuming a continuous uniform distribution of interaction threads :

$$V = V_0(1 - \alpha), \quad 0 \leq \alpha \leq 1, \quad (7)$$

where V_0 is the (negative) energy of the ground state ($\alpha = 0$). For $\alpha > 1$ we take $V = 0$. Such a potential would in principle promote smectic behaviour (minimum at $\alpha = 0$). However, in practice for $\alpha \neq 0$ the threads of interaction can be expected to go to a third molecule, above or below the central one, thus restoring a nematic-like distribution.

As we are interested in the elastic properties of the nematic, we consider now the interaction between molecules that have a slightly different director. The three elementary deformations are obtained by rotating the director of the second molecule over an angle θ around an axis perpendicular to \mathbf{n} . In figure 3 (b) such a deformation is shown with the rotation axis perpendicular to \mathbf{r} . It is a mixture of splay and bend, which deformations are obtained in their pure form for $\alpha = 0$ and $\alpha = 1$, respectively. The interaction energy is easily calculated as

$$\begin{aligned} V &= V_0(1 - \alpha) + \frac{1}{2}f \int_{-L/2}^{L/2 - \alpha L} (l\theta)^2 dl + O(\theta^4), \\ &= V_0(1 - \alpha) + \frac{1}{24}fL^3 \left[\frac{1}{2} + 4\left(\frac{1}{2} - \alpha\right)^3 \right] \theta^2 + O(\theta^4), \end{aligned} \quad (8)$$

where $l\theta$ is the deflection at a distance l from the centre of the molecule, and f a force constant. In figure 3 (c) the rotation axis is parallel to \mathbf{r} . Now the deflection is proportional to θ^2 , and the interaction is therefore

$$V = V_0(1 - \alpha) + O(\theta^4). \quad (9)$$

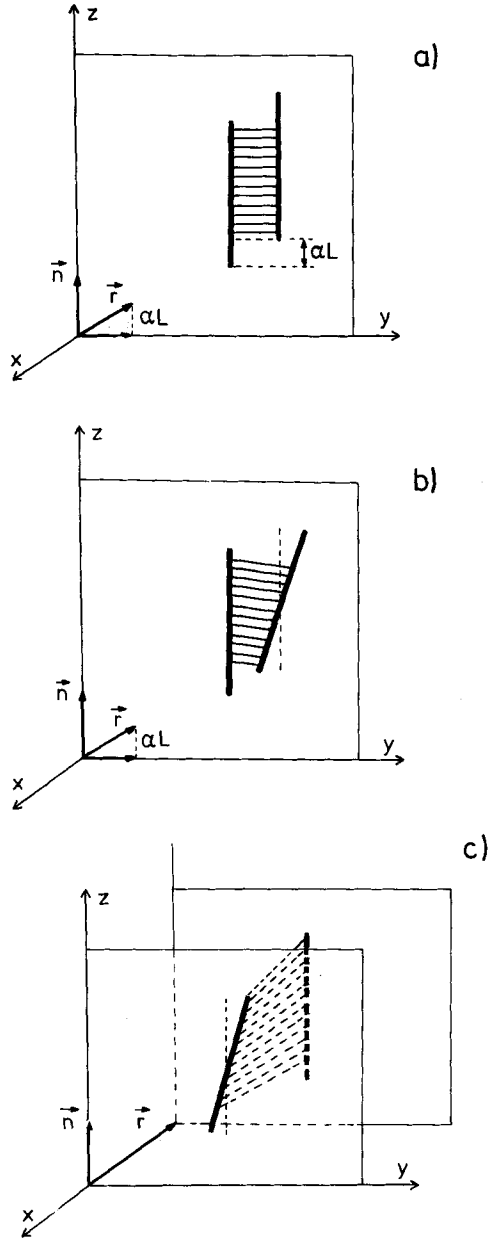


Figure 3. Introduction of the distributed harmonic forces ; the heavy lines indicate the axes of the molecules, the separation as drawn is approximately equal to W (see text).

The general case (not shown) is obtained by combining the results of figures 3 (b) and (c). Introducing the angle ψ between the component of \mathbf{r} in the xy plane and the rotation axis, we find for the interaction energy

$$\begin{aligned}
 V &= V_0(1 - \alpha) + \frac{1}{2}f \int_{-L/2}^{L/2 - \alpha L} (l\theta \sin \psi)^2 dl + O(\theta^4), \\
 &= V_0(1 - \alpha) + \frac{1}{24}fL^3 \left[\frac{1}{2} + 4\left(\frac{1}{2} - \alpha\right)^3 \right] \theta^2 \sin^2 \psi + O(\theta^4). \tag{10}
 \end{aligned}$$

To construct the distortion we have rotated the second molecule around its centre, which thus remains fixed at a distance W . For $\alpha \neq 0$ we could alternatively choose the middle of the overlapping part as centre of the rotation. In this way the molecular centre would move away from the first molecule for $\alpha > 0$, and move in the opposite direction for $\alpha < 0$. As we want to mimic with our interaction the effect in an ensemble of molecules of a real nematic, we have chosen to leave the molecular centre fixed during the distortion. In that case also no terms with odd powers of θ appear in (8), (9) and (10). For the other choice the term between square brackets in (10) would read $(1 - \alpha)^3$.

Equations (6) and (10) form the basis of our calculations. Of course, (10) can be expected to apply only for values of $l\theta$ small in comparison to W , in which case the quadratic term is dominant. This means that θ must be small, and in addition that L/W must be restricted to values that are not too large. The choice of a specific pair distribution function in (6) influences the way in which the various values of α in (10) are weighted. An evenly distributed scale of α -values represents a pure nematic phase, while it is possible to mimic the effect of smectic-like correlations by emphasizing the value $\alpha = 0$.

4. RESULTS

In order to calculate the stiffness constants we construct the three different distortions of the director field corresponding to splay, twist and bend, respectively. With \mathbf{n} along the z -axis and taking the x -axis as the rotation axis the following representation for the director can be used

$$\mathbf{n} = \begin{pmatrix} 0 \\ \sin \theta \\ \cos \theta \end{pmatrix}, \quad (11)$$

where $\theta = \theta(\mathbf{r})$ is a function of the position \mathbf{r} in the sample. With our choice of the x -axis as rotation axis, a splay, twist or bend deformation can be constructed as $\partial n_y / \partial y$, $\partial n_y / \partial x$, and $\partial n_y / \partial z$, respectively. Thus the variation of ∂n_y must be along the y -axis, x -axis or z -axis, respectively, and we find

$$\left. \begin{array}{l} \text{splay : } \sin \theta = qy/[q^2 y^2 + (1 + qz)^2]^{1/2}, \\ \text{twist : } \quad \theta = -qx, \\ \text{bend : } \sin \theta = qz/[q^2 z^2 + (1 - qy)^2]^{1/2}. \end{array} \right\} \quad (12)$$

Here q , which serves to normalize the argument, is the inverse of a typical distance over which the deformation takes place. In the spirit of the continuum theory the distances over which significant variations of the director occur are much larger than the molecular dimensions. Thus the condition $\theta L \ll W$ given at the end of the previous section can also be interpreted as $q \ll L^{-1}$. A central molecule is situated in the origin and the interactions with its neighbours are considered. Then the free energy density of the system can be

expanded in powers of qx , qy and qz ; terms higher than quadratic in q are disregarded. Thus we can write from (12)

$$\sin^2 \theta \approx \theta^2 = \begin{cases} q^2 y^2, & \text{splay,} \\ q^2 x^2, & \text{twist,} \\ q^2 z^2, & \text{bend.} \end{cases} \quad (13)$$

The distortion free energy density (1) is now calculated to be

$$F_d = \frac{1}{2} K_i q^2, \quad i = 1, 2, 3. \quad (14)$$

By equating this expression to the change in the interaction energy due to a deformation (6) expressions for K_1 , K_2 and K_3 are obtained.

To apply these formulae to our model we introduce cylindrical coordinates with $x = \rho \cos \psi$, $y = \rho \sin \psi$, where $\rho = (x^2 + y^2)^{1/2}$. Then (6) can be written as

$$F = \frac{1}{2} \sigma^2 \int_{-\infty}^{\infty} dz \int_0^{\infty} d\rho \rho g(z, \rho) \int_0^{2\pi} d\psi V(z, \rho, \psi). \quad (15)$$

Before inserting V from (10) we note that in the model

$$\left. \begin{aligned} V &= 0 && \text{if } |z| > L, \\ V(z, \rho, \psi) &= V(-z, \rho, \psi), \\ g(z, \rho) &= g(-z, \rho). \end{aligned} \right\} \quad (16)$$

Consequently the integration over z can be replaced by an integration over αL with $0 \leq \alpha \leq 1$. This is illustrated in figure 4 for nearest neighbours. Thus

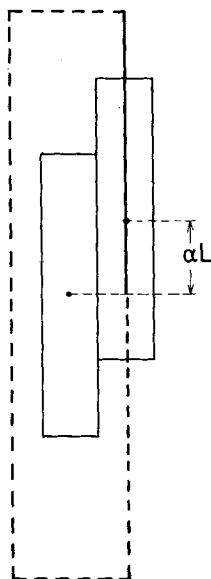


Figure 4. Integration contour for the nearest neighbours of a central molecule. The full line is the part of the full contour over which the integration is carried out.

we can write

$$F = \frac{1}{2}\sigma^2 \left\langle (2\pi)^{-1} \int_0^{2\pi} d\psi V(\alpha, \rho, \psi) \right\rangle, \tag{17}$$

where the average is defined as

$$\langle A \rangle = 4\pi L \int_0^1 d\alpha \int_0^\infty d\rho g(\alpha, \rho) A. \tag{18}$$

Substituting (10) for V and using (13) we can carry out the integration over ψ using the cylindrical symmetry of the nematic phase. The resulting expressions for the three types of director deformations are

$$\left. \begin{aligned} \text{splay : } F &= \frac{1}{2}\sigma^2 \{ \langle V_0 \rangle (1 - \alpha) + \frac{1}{2}fL^3 \frac{3}{8} \langle [\frac{1}{2} + 4(\frac{1}{2} - \alpha)^3] \rho^2 \rangle q^2 \}, \\ \text{twist : } F &= \frac{1}{2}\sigma^2 \{ \langle V_0 \rangle (1 - \alpha) + \frac{1}{2}fL^3 \frac{1}{8} \langle [\frac{1}{2} + 4(\frac{1}{2} - \alpha)^3] \rho^2 \rangle q^2 \}, \\ \text{bend : } F &= \frac{1}{2}\sigma^2 \{ \langle V_0 \rangle (1 - \alpha) + \frac{1}{2}fL^5 \frac{1}{2} \langle [\frac{1}{2} + 4(\frac{1}{2} - \alpha)^3] \alpha^2 \rangle q^2 \}. \end{aligned} \right\} \tag{19}$$

The stiffness constants for this model are then

$$\left. \begin{aligned} \text{splay : } K_1 &= \frac{1}{2}fL^3 \sigma^2 \frac{3}{8} \langle \text{st}(\alpha) \rho^2 \rangle, \\ \text{twist : } K_2 &= \frac{1}{2}fL^3 \sigma^2 \frac{1}{8} \langle \text{st}(\alpha) \rho^2 \rangle, \\ \text{bend : } K_3 &= \frac{1}{2}fL^5 \sigma^2 \frac{1}{2} \langle \text{be}(\alpha) \rangle, \end{aligned} \right\} \tag{20}$$

with

$$\left. \begin{aligned} \text{st}(\alpha) &= \frac{1}{2} + 4(\frac{1}{2} - \alpha)^3, \\ \text{and} \\ \text{be}(\alpha) &= \alpha^2 \text{st}(\alpha). \end{aligned} \right\} \tag{21}$$

The functions $\text{st}(\alpha)$ and $\text{be}(\alpha)$ are shown in figure 5. For the ratios of the stiffness constants we obtain

$$K_1 : K_2 : K_3 = 3 : 1 : 4L^2 \langle \text{be}(\alpha) \rangle / \langle \text{st}(\alpha) \rho^2 \rangle. \tag{22}$$

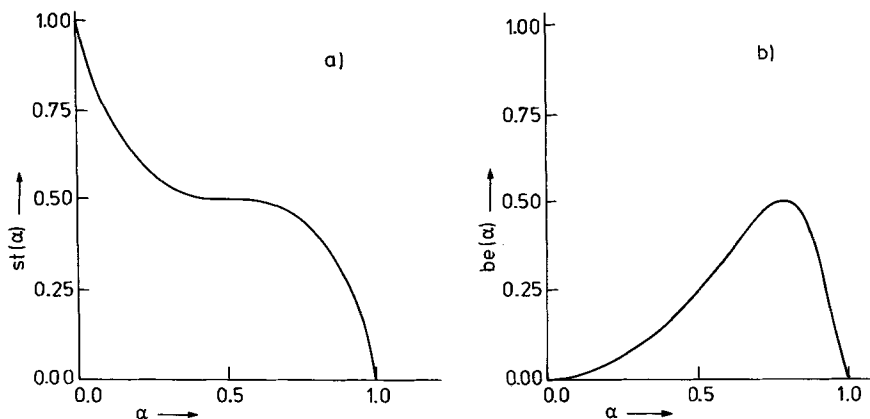


Figure 5. Variation of the functions $\text{st}(\alpha)$ and $\text{be}(\alpha)$ defined in (21).

The expressions for the stiffness constants can be evaluated further if the pair distribution function is known. However, we see that independently of $g(\alpha, \rho)$ the model always predicts $K_2/K_1 = 1/3$.

First we consider a nematic phase without smectic-like short-range correlation. In that case the molecules slide rather freely along each other and the pair distribution function is independent of α : $g = g(\rho)$. Furthermore, for $|z| < L$, $g(\rho)$ will be strongly peaked at $\rho \approx W$ [22]. Consequently we obtain

$$\left. \begin{aligned} \langle \text{st}(\alpha)\rho^2 \rangle &= W^2 \zeta \int_0^1 d\alpha \text{st}(\alpha) = \frac{1}{2} W^2 \zeta, \\ L^2 \langle \text{be}(\alpha) \rangle &= L^2 \zeta \int_0^1 d\alpha \text{be}(\alpha) = \frac{7}{60} L^2 \zeta, \end{aligned} \right\} \quad (23)$$

where ζ is the coordination number. The ratio of the stiffness constants thus becomes

$$K_1 : K_2 : K_3 = 3 : 1 : \frac{14}{15} \frac{L^2}{W^2}. \quad (24)$$

When smectic-like short-range correlation is present the molecules will have some preference for the situation $\alpha = 0$, and the pair distribution function will depend on α : $g = g(\alpha, \rho)$. We assume that the α -dependence and the ρ -dependence are separable, i.e.

$$g(\alpha, \rho) = g_v(\alpha)g_h(\rho). \quad (25)$$

For $g_v(\alpha)$ we take a gaussian distribution

$$g_v(\alpha) = \exp(-\kappa^2 \alpha^2) \int_0^1 \exp(-\kappa^2 \alpha^2) d\alpha, \quad (26)$$

Table 1. Some results for a gaussian distribution for $g_v(\alpha)$ for different values of κ .

κ	$\langle \text{st}(\alpha) \rangle$	$\langle \text{be}(\alpha) \rangle$	$K_1 : K_2 : K_3$	$\langle \alpha^2 \rangle^{1/2}$
0	0.5	0.116	3 : 1 : 0.933 L^2/W^2	0.58
1	0.54493	0.09845	3 : 1 : 0.723 L^2/W^2	0.50
2	0.62267	0.05728	3 : 1 : 0.368 L^2/W^2	0.34
3	0.68541	0.02989	3 : 1 : 0.174 L^2/W^2	0.24

where κ^{-1} is a measure for the width of the distribution. Further we assume that $g_h(\rho)$ is still the same function as used for the pure nematic. The results for the averages of $\text{st}(\alpha)$ and $\text{be}(\alpha)$ and for the ratio $K_1 : K_2 : K_3$ are given in table 1 for a few choices of κ . With increasing value of κ the ratio K_3/K_1 decreases.

5. DISCUSSION

Before discussing the model in more detail, we shall compare its predictions with the experimental results now available. Independent of the pair distribution function $K_2/K_1 = 1/3$ is predicted. As we have seen in § 2, experimentally

indeed this ratio does not vary much, while moreover $K_2 < K_1$. Though it is gratifying that, in contrast to other simple models, $K_2 < K_1$ is found, the value of this ratio is a factor of about 2 too small. Interestingly a value of $1/3$ is also predicted by some much more elaborate theories [16, 17] [see also following (4)]. In our model it results in a very simple way from the difference between integrating $\sin^2 \psi \cos^2 \psi$ and $\sin^4 \psi$ in going from (17) to (19). Intuitively we should expect K_2/K_1 to be somehow related to the degree of flatness of the molecules. However attempts to find such a relation experimentally have failed [8 b].

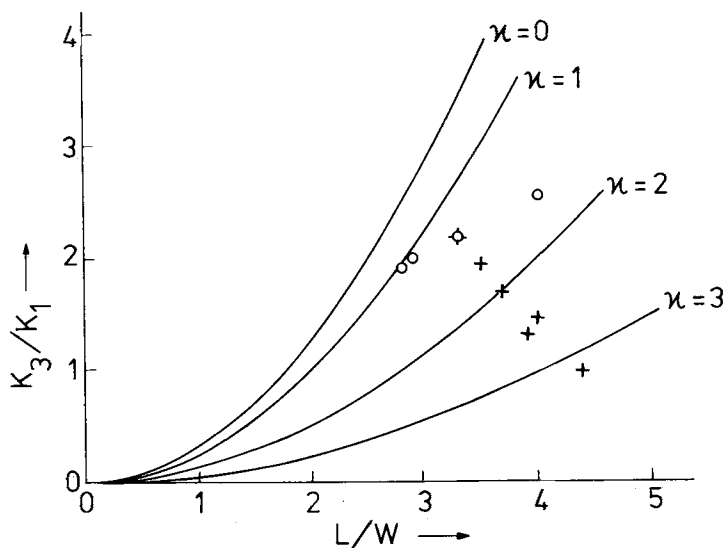
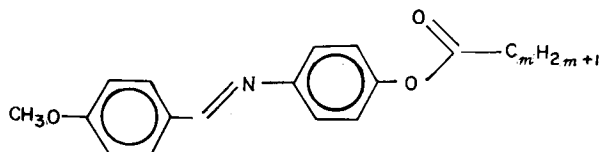


Figure 6. Results for K_3/K_1 as a function of L/W for various degrees of smectic-like correlation (indicated by κ); \circ experimental results for molecules without alkyl chains (figure 2), \times experimental results for the homologous series APAPAm [11].

In figure 6, where the predictions for K_3/K_1 are shown, the open circles represent the experimental results for molecules without alkyl chains from figure 2. The trend of increasing K_3/K_1 with increasing L/W is well reproduced. We associate this situation with a theoretical curve for $\kappa \approx 0$. The quantitative difference between theory and experiment can be attributed to the fact that the experiments do not refer to perfect orientational order. Moreover, the condition of small θ is less well fulfilled with increasing value of L/W . The crosses in figure 6 represent Leenhouts' results [11] for the homologous series APAPAm:



In agreement with the results shown in figure 1, for this series K_3/K_1 decreases with increasing m . This effect has been attributed qualitatively to short-range smectic-like correlation that increases with m [7, 8]. Our results substantiate this interpretation in a semi-quantitative way. Increasing the value of m has two effects. First L/W increases, though less than in case of addition of a rigid group because of the presence of *gauche-trans* conformations. For a fixed κ this would lead to an increase of K_3/K_1 . However, if the smectic-like pair correlation also increases, this would lead to a larger value of κ and thus to a decrease of K_3/K_1 . As we see from figure 6 the experimental trend can be well reproduced by assuming in the series APAPAm an increase of κ to a value of about 3. In the series of substituted azoxybenzenes shown in figure 1 even lower values of K_3/K_1 are observed, that require a slightly higher value of κ . This can be attributed to the fact that alkyl chains are now present at both sides of the molecules.

Experimentally in several nematic systems smectic-like correlation between the molecules has been observed by X-ray diffraction [23]. In the spirit of McMillan's theory of the smectic phase [24] it can be attributed to the larger polarizability of the central aromatic part of the mesogenic molecules as compared with the aliphatic end groups, which gives an enhanced preference for the aromatic parts to be close together. Furthermore, steric effects can also be expected to contribute [8 b], because the long axes of the alkyl chains and of the central part of the molecules are not collinear. As depicted in figure 7 in a two-dimensional way, this will hinder the free sliding of molecules along each other. We conclude that it is quite reasonable to expect an increase of smectic-like pair correlations in a homologous series. The peaking of the pair distribution function $g_v(\alpha)$ can be compared with the situation in a real smectic A phase having a smectic distribution function $f(z)$ in the range $z \in (-\frac{1}{2}L, \frac{1}{2}L)$.

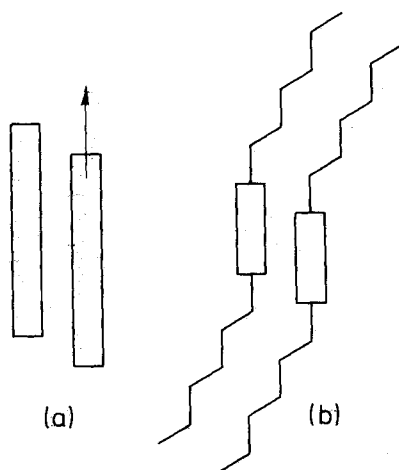


Figure 7. Sliding of two molecules along each other for a model of rods and for a model with alkyl chains.

Here $f(z)$ is the probability that the z -component of the position of a molecule is equal to z ; the layer normal is along the z -axis; the thickness of the smectic layers is d , which is approximately equal to L . The quantity

$$\langle z^2 \rangle^{1/2} = \left[\int_{L/2}^{L/2} z^2 f(z) dz \right]^{1/2} \quad (28)$$

can be measured with X-ray diffraction. Leadbetter *et al.* find for the smectic A phase of TBBA

$$\langle z^2 \rangle^{1/2}/L = 4/23 = 0.17.$$

This should be compared with

$$\langle \alpha^2 \rangle^{1/2} = \left[\int_0^1 \alpha^2 g_v(\alpha) d\alpha \right]^{1/2}, \quad (29)$$

which is given for various values of κ in the last column of table 1. As we see, the peaking of $g_v(\alpha)$ required to explain the experimental results for K_3/K_1 is still less than that found in a typical smectic phase.

The smectic-like pair correlation should not be confused with the smectic fluctuations that occur as a pre-transitional effect above a smectic-nematic phase transition. The smectic-like pair correlation is a *short-range* effect that is expected to occur as soon as alkyl chains are present in the mesogenic molecules. It is independent of the possible presence of a smectic phase at lower temperatures. (In fact in the series APAPAm no smectic phases are observed.) Pre-transitional smectic fluctuations are associated with large groups of molecules. As the smectic phase is approached the correlation length ξ increases, typically from a few hundred Å at a few degrees above the transition temperature to a few thousand Å at a few tenths of a degree [15]. It is the relatively *long-range* pseudo-layer structure within these fluctuating smectic droplets, that tends to inhibit a bend or twist distortion, because these deformations require compression and/or dilatation of the pseudo-layers. This causes an increase of K_3 and K_2 proportional to ξ . Our model is concerned with the short-range correlation in the z -coordinates of the molecular centres; the second effect is completely ignored. Thus, in the limit of complete smectic ordering, i.e. $\langle \alpha^2 \rangle = 0$, our results for K_3 and K_2 cannot be expected to be correct. Furthermore we have assumed that the short-range effect of smectic-like correlation and the relatively long-range pre-transitional tendency to form smectic layers are independent of each other. From the experiments this seems to be correct, as the last effect influences the value of the stiffness constants only close to the transition temperature to the smectic phase. This is nicely illustrated in figure 1. The increase in smectic-like correlation with m explains the decrease of K_3/K_1 with increasing m . Pre-smectic fluctuations explain the increase of K_3/K_1 for $m=6$ and $m=7$ at temperatures close to the nematic-smectic transition.

A basic assumption in the model is that molecules interact pairwise. As a consequence the stiffness constants are determined completely if the pair potential, the pair distribution function and the density are specified. This is illustrated in table 2 where the ratios of the stiffness constants are given for various combinations. Formally, the pair distribution function g should be an output from the theory, resulting from an input pair potential V . Since such

Table 2. Summary of the results for $K_1 : K_2 : K_3$ of various models.

g	V independent of the relative position	V dependent upon the relative position	
		Dispersion forces	Distributed harmonic forces
Isotropic	1 : 1 : 1	5 : 11 : 5	—
Anisotropic	1 : 1 : $\frac{L^2}{W^2}$	5 : 11 : 5 $\frac{L^2}{W^2}$	45 : 15 : 14 $\frac{L^2}{W^2}$
Anisotropic + smectic-like correlation†	1 : 1 : $\mu \frac{L^2}{W^2}$	5 : 11 : 5 $\mu \frac{L^2}{W^2}$	45 : 15 : 14 $\mu \frac{L^2}{W^2}$

† μ is a function of κ as can be read from table 1.

an approach is quite difficult we have chosen a model not only for V but for g as well. For the pair potential distributed harmonic forces were introduced. Harmonic, because the pair potential is quadratic in the deflection. Distributed, because the interaction is not attributed to one centre of force per molecule, but to a uniform distribution of centres located along the molecular axes. Centres at a molecule opposite to centres at another neighbouring molecule attract or repel each other: they are connected by elastic interaction threads. When the intermolecular vector has a component parallel to the director, interaction threads suddenly disappear in the present model. In reality the potential will decay more continuously. Furthermore, all threads are assumed to be of equal strength. In spite of these obvious shortcomings we feel that the model has in its simplicity enough virtues to be used as basis for the calculation of the distortion free energy. The reader who wishes to judge differently may verify that any quadratic potential of the form

$$V = V_0 + \lambda(\delta r/r)^2, \quad (29)$$

where δr is the change in the distance r between interacting centres due to the distortion and λ a constant, gives results very similar to the treatment presented here. Equation (29) can be derived, for example, from an expansion of a Lennard-Jones potential around the equilibrium value.

Our pair potential is anisotropic with respect to the dependence upon the relative position. The anisotropy results from the elongated form of the molecules (shape anisotropy). In the case of interaction between mutually induced dipoles [18] the potential is anisotropic as well; however, this anisotropy has a different origin (polarizability anisotropy). As shown in table 2, polarizability anisotropy in combination with an isotropic pair distribution gives $K_2/K_1 = 11/5$, in the absence of coupling between position and orientation we have $K_2/K_1 = 1$, while shape anisotropy leads to $K_2/K_1 = 1/3$. Obviously, the result for K_2/K_1 depends strongly on the model used. By taking both shape and polarizability anisotropy into account agreement with the experimental range for K_2/K_1 can be obtained.

Finally, we have adopted the approximation that the orientational order is complete. This does not mean that we rely necessarily on (3). Any theory would do, provided that the factors depending on the properties of the molecules

and/or their mutual rearrangement are decoupled from the degree of orientational order. One could still object that if the true intermolecular potential were expanded in spherical harmonics almost certainly for $S=1$ components with large L would be more important than for practical values of S . Though this might change that ratio K_3/K_1 (as can also be seen from figure 1), it seems unlikely that this would change the trend in K_3/K_1 as discussed for relatively rigid compounds and for homologous series. Moreover in the spirit of our model of distributed forces we expect the convergence of such a series expansion not to be very good for elongated molecules. This view is supported by the observation that for some 4-n-alkyl-4'-cyanobiphenyls, that have $\bar{P}_4 \approx 0$ [26], we find nevertheless $K_3 > K_1$ [7]. Therefore we shall refrain from an attempt to calculate C and C' by inserting K_1 , K_2 and K_3 in (3). A further objection to (3) is that though the temperature dependence due to the orientational order is taken into account, the temperature dependence of the pair distribution function (e.g. that the peaks sharpen if the temperature is lowered) is ignored. This last effect can be estimated from our model for K_1 . Using (21) and (22) we can calculate K_1 for complete smectic order ($\kappa = \infty$), and compare the result with that for a nematic with $\kappa = 0$; we find

$$K_1(\text{smectic}) = 2K_1(\text{nematic}). \quad (30)$$

This effect is of the right order of magnitude to explain the observed increase of K_1 when the nematic-smectic phase transition is approached [8, 27]. For K_1 this cannot be due to a divergence of the stiffness constant, as for K_2 and K_3 .

We conclude that our model of distributed harmonic forces, in combination with reasonable assumptions for the pair distribution function, is remarkably successful in reproducing the rather complicated trends observed so far for the stiffness constants of nematic liquid crystals. For molecules without alkyl chains we find that K_3/K_1 varies as L^2/W^2 , in agreement with the experimental trend. Assuming that alkyl chains enhance the tendency towards smectic-like correlation and that this tendency is stronger for longer chains, the experimental trend of decreasing K_3/K_1 in a homologous series is reproduced. The observation that molecules with and without alkyl chains cannot be treated on the same basis could be important for molecular-statistical theories of the nematic-isotropic phase transition as well.

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