

AN ANTI-NEMATIC PHASE OF LIQUID CRYSTALS

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Received 1 November 1983

Using a Corner-type potential for the interaction between two monoaxial molecules, a simple equation has been derived for the angular dependence of the single particle distribution function. We investigate this equation for values of the molecular parameters not considered before. The usual nematic–isotropic phase transition is found. It turns out, however, that below the transition temperature the distribution function describing the orientation of the molecules with respect to the director now has two maxima. The first maximum, which defines the director, corresponds to a preferred parallel orientation of the molecules. The second, maximum shows that orientations perpendicular to the director also occur with high probability. This effect is so strong that of the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ the latter is dominant while the first is an order of magnitude smaller.

1. Introduction

In a previous publication¹), to be referred to as I, order parameters and elastic constants for nematic liquid crystals were calculated on the basis of a mean field theory with a special form for the interaction $U(r, \mathbf{\Delta}, \mathbf{n}_1, \mathbf{n}_2)$ between two uni-axial molecules. The long axes of the molecules are parallel to the unit vectors \mathbf{n}_1 and \mathbf{n}_2 . The centres of the two molecules are separated by the vector \mathbf{r} , with a length denoted by r and a direction given by the unit vector $\mathbf{\Delta}$. For U we took a so called Corner²) potential $U = U(r/\sigma)$, in which σ was chosen to be of the following special form

$$\sigma = \sigma_0 [1 + S_1(\mathbf{n}_1 \cdot \mathbf{\Delta})^2 + S_1(\mathbf{n}_2 \cdot \mathbf{\Delta})^2 - S_2(\mathbf{n}_1 \cdot \mathbf{n}_2)^2]. \quad (1)$$

The parameter σ_0 with the dimension of a length, is a measure for the size of the molecules, while the dimensionless parameters S_1 and S_2 determine their shape. For instance for a Lennard-Jones interaction

$$U = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

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the equipotential surface $U = 0$ is given by

$$r = \sigma_0[1 + S_1(\mathbf{n}_1 \cdot \Delta)^2 + S_1(\mathbf{n}_2 \cdot \Delta)^2 - S_2(\mathbf{n}_1 \cdot \mathbf{n}_2)^2].$$

For $\mathbf{n}_1 \parallel \mathbf{n}_2$ and for $\mathbf{n}_1 \perp \mathbf{n}_2$ this surface is shown in fig. 1 (for $S_1 = 0.5$ and $S_2 = -1.0$) and in fig. 2 (for $S_1 = 1.2$ and $S_2 = 0.8$). While in I we concentrated on molecules described by the form as shown in fig. 1, we will now restrict ourselves to the case where both S_1 and S_2 are positive (fig. 2).

By using a mean field theory and by minimizing the free energy with respect to the distribution function $f_1(\cos \theta)$, which is normalised as

$$\int_0^1 f(x) dx = 1, \tag{2}$$

we derived the following equation[†] for $f(x)$:

$$\log f(x) - \lambda \int_0^1 K(x, y)f(y) dy = \text{const.} \tag{3}$$

The kernel of this integral equation is given by

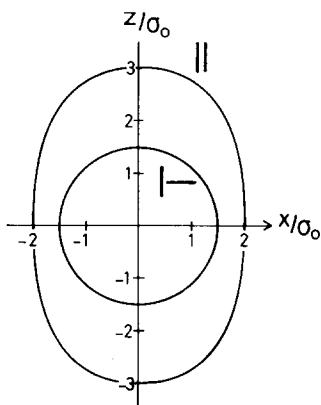


Fig. 1. Equipotential surfaces for $S_1 = 0.5$ and $S_2 = -1.0$.

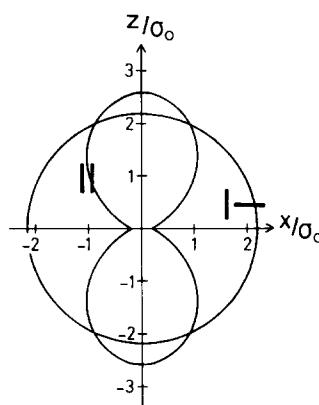


Fig. 2. Equipotential surfaces for $S_1 = 1.2$ and $S_2 = 0.8$.

[†] In I we incorrectly used $+\lambda$ in eq. (3) instead of $-\lambda$. We have repeated the calculations of I with the correct sign in front of λ and it turns out (miraculously) that the agreement with experiment even improves. The values of the parameters had to be changed, however. We thank Bela Mulder for drawing our attention to this error.

$$K(x, y) = \sum_{i,j=0}^3 \alpha_{ij} x^{2i} y^{2j}, \quad (4)$$

where the elements of the symmetric matrix α_{ij} are polynomials in S_1 and S_2 of a degree not higher than three. They are listed* in appendix B of I. The coefficient λ is defined by $\lambda = -(\pi/\sigma)n\sigma_0^3 B_2^*$, in which n is the number density and the reduced second virial coefficient is equal to

$$B_2^* = 3 \int_0^\infty [1 - e^{-\beta U(z)}] z^2 dz.$$

We assume that the temperature is in the range where B_2^* is negative³⁾ so that only positive values of λ will have to be considered. With increasing temperature λ is decreasing.

2. Solution of the equations

Since the kernel $K(x, y)$ (eq. (4)) is a polynomial in x^2 of third degree it follows from eq. (3) that the distribution function $f(x)$ necessarily is of the following form

$$f(x) = e^{c_0 + c_1 x^2 + c_2 x^4 + c_3 x^6}. \quad (5)$$

Introducing the parameter $\tau = \lambda e^{c_0}$ instead of λ , eq. (3) can be written as

$$c_i = \tau \sum_{j=0}^3 \alpha_{ij} Z_j \quad (i = 1, 2, 3) \quad (6)$$

with

$$Z_j = \int_0^1 y^{2j} e^{c_1 y^2 + c_2 y^4 + c_3 y^6} dy. \quad (7)$$

After solving these equations for c_1 , c_2 and c_3 , the fourth number c_0 is found from the normalization condition eq. (2), which now reads

$$e^{-c_0} = Z_0 = \int_0^1 e^{c_1 y^2 + c_2 y^4 + c_3 y^6} dy. \quad (8)$$

* The coefficient 112.3 occurring in α_{12} should read 112.5.

The uniform distribution $f(x) \equiv 1$, i.e., $c_0 = c_1 = c_2 = c_3 = 0$, is always a solution of eqs. (6), (7) and (8). This follows from the fact (see appendix B of I) that for the matrix M defined by

$$M_{il} = \sum_{j=0}^3 \frac{\alpha_{ij}}{2j + 2l + 1} \quad (i, l = 0, 1, 2, 3) \quad (9)$$

the following relation holds:

$$M_{i0} = 0 \quad \text{for } i \neq 0. \quad (10)$$

This is a special case of a more general formula

$$M_{il} = 0 \quad \text{for } i > l. \quad (11)$$

This equality was first found by numerical calculation for special values of S_1 and S_2 and afterwards proved by substituting in eq. (9) the expressions for α_{ij} taken from appendix B of I.

Not for every λ (or τ) is the uniform distribution the only solution, neither is it always the solution with lowest free energy. At certain bifurcation points $\lambda_b = \tau_b$ an additional solution will become possible. Since in the neighbourhood of such a bifurcation point the numbers c_i will still be small eqs. (6) and (7) can be linearized. This gives rise to the equations

$$c_i = \lambda_b \sum_{l=1}^3 M_{il} c_l \quad (i = 1, 2, 3). \quad (12)$$

This is an eigenvalue problem which, because of the special property eq. (11) of the matrix M , can be solved explicitly. There are three bifurcation points given by the expressions

$$\lambda_b^{(i)} = M_{ii}^{-1} \quad (i = 1, 2, 3). \quad (13)$$

The eigenvectors can also be given in closed form. They are not orthogonal and their lengths can of course only be determined from the nonlinear equations. The ratio of the components of the eigenvectors, however, are completely fixed. Exactly these ratios determine the possible values of $x = \cos \theta$ for which $f(x) = \exp(c_0 + c_1 x^2 + c_2 x^4 + c_3 x^6)$ has an extremum in the interval $0 < x < 1$. In fig. 3 we show the different parts into which the S_1 - S_2 parameter plane can be divided. The restriction to positive S_1 means that we only consider elongated molecules. Calculations for flat molecules were published previously⁴). The

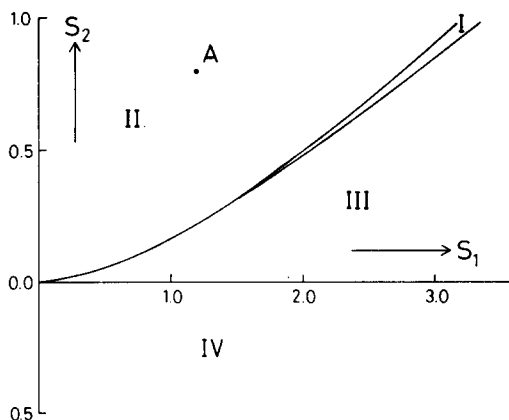


Fig. 3. The structure of the S_1 - S_2 parameter plane.

requirement that two molecules have a positive distance of closest approach (defined by $U = 0$) imposes the restriction $S_2 < 1$. In region I all $\lambda_b^{(i)}$ are negative. In region II only $\lambda_b^{(2)}$ is positive, the other two bifurcation points are negative. The distribution function $f(x)$ has one extremum in the interval $0 < x < 1$.

In region III only $\lambda_b^{(1)}$ is positive and $f(x)$ has no extrema between 0 and 1.

In region IV all $\lambda_b^{(i)}$ are positive and $f(x)$ can have up to three extrema between 0 and 1. It must be emphasized, however, that these statements about the number of extrema only hold for values of λ close to a bifurcation point and for distribution functions which have an infinitesimal difference with the uniform distribution. Other solutions can and do exist so that definite statements can only be made after all solutions of the nonlinear equations for a given λ have been found and their free energies have been compared. Therefore the above statements only serve as an indication of the kind of solutions that can be expected.

For the point A in fig. 3, i.e. $S_1 = 1.2$ and $S_2 = 0.8$, we have performed a detailed investigation of eqs. (6) and (7). For a range of values of τ we used a Newton-Raphson method to solve c_1 , c_2 and c_3 , after which e^{-c_0} was calculated with eq. (8). In this way the function $\lambda(\tau) = \tau e^{-c_0}$ was calculated. The result is shown in fig. 4. The stable part of the solution, indicated by the full curve, was found by a detailed calculation of the difference in free energy between the isotropic and the nematic solution. This is shown in fig. 5, where we only have drawn the branch connected with the smallest positive bifurcation point $\lambda_b^{(2)} = 2.68044$, the other points being given by $\lambda_b^{(1)} = -0.2380$ and $\lambda_b^{(3)} = -45.8221$. For the non-isotropic solution we have calculated the average values of the second and fourth Legendre functions $\langle P_2 \rangle$ and $\langle P_4 \rangle$, which are plotted in

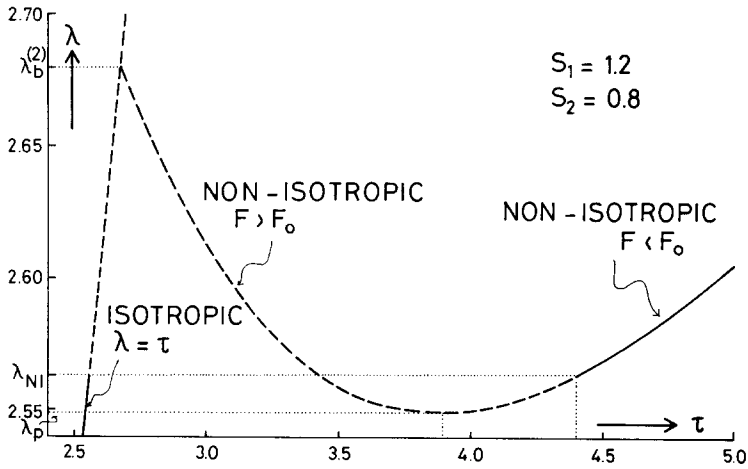


Fig. 4. λ as a function of τ . The stable solution is shown by the full curve.

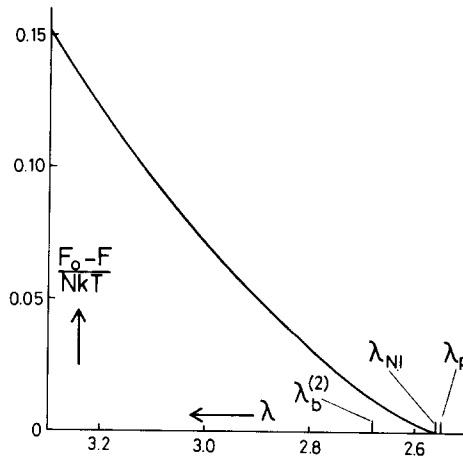


Fig. 5. The difference in free energy between the isotropic and the nematic phase.

fig. 6. We observe that $\langle P_2 \rangle$ is an order of magnitude smaller than $\langle P_4 \rangle$. This is caused by the fact that for all values of λ for which the non-isotropic solution exists the distribution function $f(\cos \theta)$ has a peak not only for $\theta = 0$, but also for $\theta = \pi/2$. In fig. 7 we have plotted this function for two values of λ , one of which is the point $\lambda_{NI} = 2.563$. . . at which the nematic-isotropic phase transition occurs. The existence of the two peaks means that the molecules have two preferred orientations, one parallel and the other orthogonal to the director. For the spatial distribution of the molecules we therefore expect something as shown in fig. 8. It must be emphasized, however, that in our calculations no

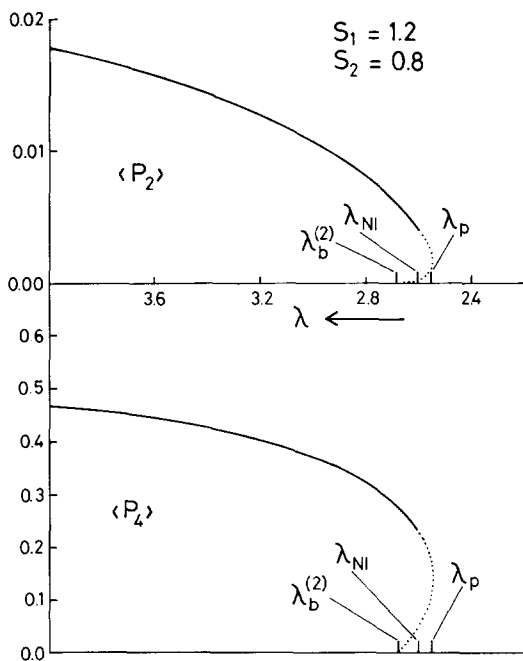


Fig. 6. The order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ as functions of λ . Note the difference in scale for the two curves.

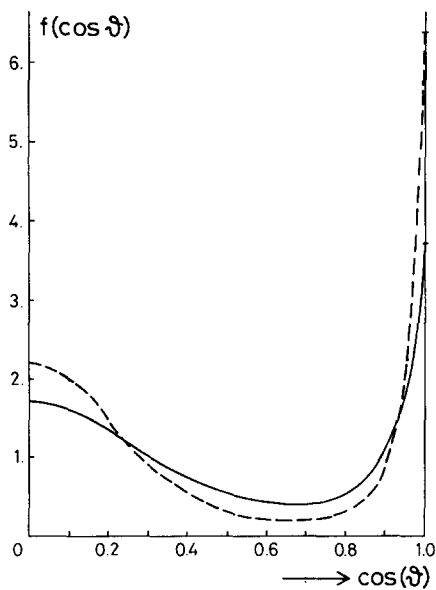


Fig. 7. $f(\cos \theta)$ for $S_1 = 1.2$ and $S_2 = 0.8$. Full curve: $\lambda = \lambda_{NI} = 2.563 \dots$; dashed curve: $\lambda = 2.71$.

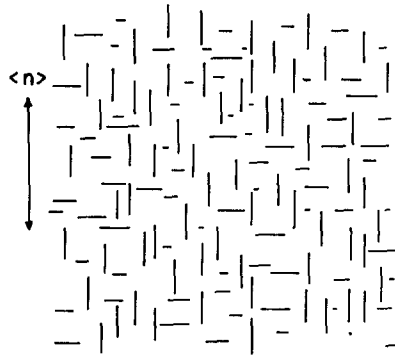


Fig. 8. Artist view of the anti-nematic phase.

spatial dependence of the distribution function was taken into account and that therefore fig. 8 must be considered as nothing more than the artist view of what the "anti-nematic" phase might look like. In order to substantiate our prediction of the existence of such a phase a more elaborate (lattice-) model should be investigated. For diatomic molecules on a lattice Monte Carlo and molecular dynamics calculations were performed and in some cases an orientational order-disorder phase transition was found indeed^{5,6}).

On the experimental side such a new phase could perhaps be discovered by looking for liquid crystals with small $\langle P_2 \rangle$ and a large $\langle P_4 \rangle$.

For $S_1 = 0.5$ and $S_2 = -1$, i.e. for a typical point taken from the region IV of fig. 3, there are three positive bifurcation points. The smallest one, which corresponds to the highest temperature, is equal to $\lambda_b^{(1)} = 0.09375$. In the neighbourhood of this point the function $\lambda(\tau) = \tau e^{-\alpha}$ was again calculated. The result, given in fig. 9, shows two branches, corresponding to the isotropic solution $c_0 = c_1 = c_2 = c_3 = 0$ and to a non-isotropic solution. The stable parts of this non-isotropic branch (with a lower free energy than the isotropic solution) are given by the full curve. The first part, extending from $\tau = 0$ to $\tau = 0.016$ has the lowest free energy and therefore describes the equilibrium state. The distribution function has only one peak at $\theta = 0$ and $\langle P_2 \rangle$ is larger than $\langle P_4 \rangle$. This is shown in fig. 10.

The second part for $\tau > \lambda_b^{(1)}$ corresponds to non-isotropic distribution functions with a peak only at $\theta = \pi/2$ and not at $\theta = 0$, so that $\langle P_2 \rangle$ is negative and $\langle P_4 \rangle$ is positive. In this very strange state the molecules have a tendency to lie in a plane perpendicular to a fixed vector, which can hardly be called the director.

Although for a given λ (temperature) the free energy is lower than for the isotropic distribution it is not as low as for the first part of the non-isotropic branch. This planar state is therefore at most metastable.

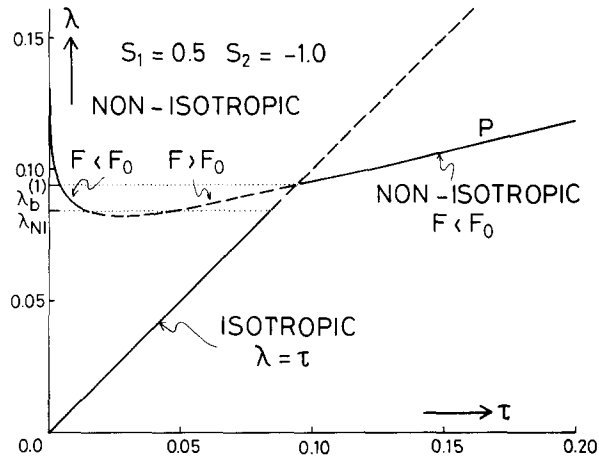


Fig. 9. λ as a function of τ . The planar nematic phase is indicated by P.

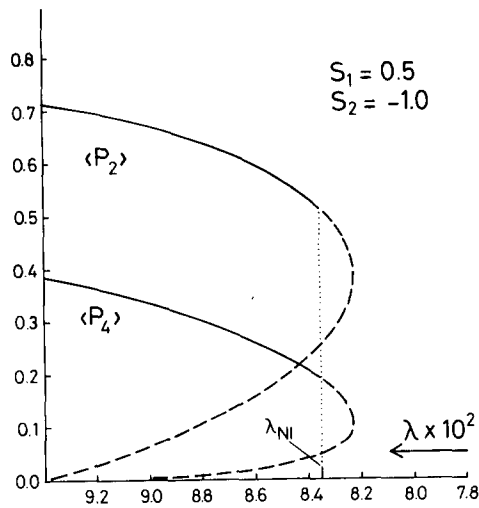


Fig. 10. The order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ as functions of λ for $S_1 = 0.5$ and $S_2 = -1.0$.

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