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## Liquid Crystals

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## Branchings of the fully symmetrical solution of the molecular field equation in liquid crystals

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A general scheme has been constructed to study the branching of the fully symmetrical solution of the molecular field equation in the case when the molecular coordinates parametrise a certain group  $Q$ . A relationship is established between these branchings and the phase transitions. Branchings corresponding to the formation of orientationally ordered and spatially modulated structures are studied explicitly. Special attention is paid to phase transitions from the isotropic liquid to nematic and cholesteric phases. Characteristics of these transitions (for example Curie temperature, order of transition, and symmetry of the phase formed) have been related to the intermolecular potential energy and the pair correlation function.

### 1. Introduction

Application of equilibrium statistical mechanics to molecular systems results in non-linear equations for the distribution functions or order parameters. As a rule, these equations are solved numerically, and it is necessary to specify the form of the intermolecular interaction potential. Thus, the results obtained do not possess sufficient generality. At the same time there are a number of papers where the corresponding equations have been studied by analytical methods. Several papers [1-9] have considered systems which consist of particles having three dimensional real space  $\mathfrak{R}^3$  or two dimensional sphere  $S^2$  as its single particle configurational space. Orientational ordering of molecules due to their multipole-multipole interaction has been considered [10-12]. In [13] the coordinates of molecules were parametrized by  $SO_3$ ; it was assumed, however, that the molecule possessed  $D_2$  symmetry. A general feature of all of these studies was the application of the branching theory of non-linear equations for description of phase transitions in the molecular systems.

A real molecule has as its configurational space not less than the euclidean group  $SO_3 \wedge T_3$ . This led us to consider the general case, when the molecular coordinates parameterize a certain group  $Q$ . In §2, the corresponding molecular field equations are derived and a relationship is obtained, which determines the bifurcation points of this equation. A scheme is presented for the construction of infinitesimal non-zero solutions emerging at these points. In §3 this scheme is applied to the case  $Q=SO_3$ . In particular, the nematic-isotropic transition is considered. Section 4 is dedicated to the case  $Q=SO_3 \wedge T_3$ . Infinitesimal solutions of the molecular field equation are constructed and studied, which correspond to one dimensional spatially modulated structures. In §5 a relationship is established between the bifurcational approach to the description of phase transitions proposed in the previous sections and

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the Landau–Ginsburg phenomenological theory. Factors are discussed which are responsible for the differences between the results of the present work and the results presented in [14].

## 2. Bifurcations of the molecular field equation

### 2.1. The molecular field equation

Let molecules with coordinates  $q_1$  and  $q_2$  interact with the potential energy  $U(q_1^{-1}q_2)$ . Such a form of the potential energy follows from the assumption of the two particle interaction energy being invariant with respect to the left handed shift of both particles upon the group  $Q$ .

In the space of complex-valued quadratically integrable functions upon the group  $Q$  we define the scalar product:

$$\langle \psi, \psi \rangle = \int dq \overline{\psi(q)} \psi(q).$$

Here  $\int dq \dots$  denotes invariant integration. In the case when the particle movement is restricted, integration is carried out only over the region accessible to the particle. Thus, for  $Q = \text{SO}_3$   $\langle 1, 1 \rangle = 8\pi^2$ , and for  $Q = \text{SO}_3 \wedge T_3$   $\langle 1, 1 \rangle = 8\pi^2 \cdot V$ , where  $V$  is the physical volume of the system. We now introduce a single particle distribution function  $f(q)$ ,

$$\langle 1, f \rangle = 1. \quad (2.1.1)$$

The fully symmetrical state of the system is described by the single particle function  $f = f_0 = 1/\langle 1, 1 \rangle$  and the pair correlation function  $g = g(q_1^{-1}q_2)$ , which is invariant with respect to the left handed shift of both molecules upon the group  $Q$ . Restricting ourselves to the mean field approximation, we neglect the dependence of the pair correlation function on the single particle function  $f$  and the temperature. In other words, it is assumed that in the temperature region of interest the pair correlation function does not differ significantly from the pair correlation function of the fully symmetric state. We define the operator  $\hat{K}$  by

$$\hat{K}\varphi(q) = \int dq' K(q'^{-1}q)\varphi(q'), \quad (2.1.2)$$

where

$$K(q'^{-1}q) = g(q'^{-1}q)u(q'^{-1}q). \quad (2.1.3)$$

We assume that the molecules are identical, i.e. the operator  $\hat{K}$  is hermitian. The free energy of the system is expressed as

$$F(f) = N^2/2 \langle f, \hat{K}f \rangle + NT \langle f, \ln f \rangle + F_0(T), \quad (2.1.4)$$

where  $N$  is the number of the particles. Differentiating the functional (2.1.4) under the condition of (2.1.1), we find the mean field equation

$$f = \frac{\exp(-\beta \hat{K}f)}{\langle 1, \exp(-\beta \hat{K}f) \rangle},$$

where  $\beta = N/T$ . It is convenient to transform to the function  $\psi = f - 1/\langle 1, 1 \rangle$ ; then

$$\psi = \hat{A}(\beta, \psi), \quad (2.1.5)$$

where

$$\hat{A}(\beta, \psi) = \frac{\exp(-\beta \hat{K}\psi)}{\langle 1, \exp(-\beta \hat{K}\psi) \rangle} - 1/\langle 1, 1 \rangle.$$

The non-linear operator  $\hat{A}$  acts in the space of functions  $\varphi(q)$ , satisfying the relationship  $\langle 1, \varphi \rangle = 0$ , which is a consequence of the relationship (2.1.1). The fully symmetrical state is described by the function  $\psi = 0$ . Such a solution exists for all values of  $\beta$ .

2.2. Bifurcation points and infinitesimal solutions of the molecular field equation

According to the implicit function theorem [15] a necessary condition for the point  $\beta = \beta^*$  to be the bifurcation point of equation (2.1.5) is the existence of unit eigenvalues of the operator  $\hat{A}'(\beta, 0)$  (the Fresche derivative of the operator  $\hat{A}$  at the point  $\psi = 0$ ). If the corresponding eigenvalue has an odd multiplicity, the point  $\beta = \beta^*$  is the true bifurcation point. In the opposite case additional study is necessary. The Fresche derivative of the operator  $\hat{A}$  at the point  $\psi = 0$  is a linear operator  $\hat{A}'(\beta, 0)$

$$\hat{A}'(\beta, 0)h(q) = -\beta \langle 1, 1 \rangle \hat{K}h(q).$$

We look for the solution emerging at the point  $\beta = \beta^*$  in the parametrical form

$$\beta = \beta^* + \beta_1 \varepsilon + \beta_2 \varepsilon^2 \dots, \quad \psi = \psi_1 \varepsilon + \psi_2 \varepsilon^2 + \dots, \quad \varepsilon > 0. \tag{2.2.1}$$

Substituting these expansions into equation (2.1.6), we find

$$\psi_1 = \frac{1}{\lambda^*} \hat{K} \omega_1, \tag{2.2.2}$$

$$\psi_p = \frac{1}{\lambda^*} \hat{K} \psi_p + G_p(\psi_1, \dots, \psi_{p-1}; \beta_1, \dots, \beta_{p-1}), \tag{2.2.3}$$

where  $\lambda^* = -\beta^* \langle 1, 1 \rangle$ ,  $p = 2, 3, 4, \dots$ ,  $G_p$  is the function on the group  $Q$ , depending upon  $q$  via the functions  $\psi_1(q), \dots, \psi_n(q) \dots$ . In particular,

$$G_2 = \frac{\beta_1}{\beta^*} \psi_1 + \frac{\langle 1, 1 \rangle}{2} \psi_1^2 - \frac{1}{2} \langle 1, \psi_1^2 \rangle, \tag{2.2.4}$$

$$\begin{aligned} G_3 = & -\frac{1}{\langle 1, 1 \rangle} \beta_1 \hat{K} \psi_2 - \frac{\beta_2}{\beta^*} \psi_1 + \frac{\beta_1}{\beta^*} \langle 1, 1 \rangle \psi_1^2 - \beta^* \psi_1 \hat{K} \psi_2 \\ & + \frac{\langle 1, 1 \rangle^2}{6} \psi_1^3 - \frac{\langle 1, 1 \rangle}{6} \langle 1, \psi_1^3 \rangle - \frac{\beta_1}{\beta^*} \langle 1, \psi_1^2 \rangle \\ & - \frac{1}{2} \langle 1, 1 \rangle \psi_1 \langle 1, \psi_1^2 \rangle + \frac{1}{\langle 1, 1 \rangle} \beta^* \langle 1, \psi_1 \hat{K} \psi_2 \rangle. \end{aligned} \tag{2.2.5}$$

Let  $\{e_1(q), \dots, e_n(q)\}$  be the complete orthogonal set of eigenfunctions of the operator  $\hat{K}$ , corresponding to the eigenvalue  $\lambda^*$ . We normalize them by the condition  $\langle e_i, e_j \rangle = \|e\| \delta_{ij}$ .

Equation (2.2.2) has the function

$$\psi_1(q) = \sum_i a_i e_i(q) \tag{2.2.6}$$

as its solution. Equation (2.2.3) may be considered as a linear equation on the function  $\psi_p$ . The condition for its solubility is

$$\langle e_i, G_p \rangle = 0, \quad p = 1, \dots, n. \tag{2.2.7}$$

Let us introduce a projection operator  $\hat{P}_i$ .

$$\hat{P}_i h(q) = \frac{1}{\|e\|} \langle e_i, h \rangle e_i(q). \tag{2.2.8}$$

The solution of equation (2.2.3) may be expressed as

$$\psi_p = \hat{R}G_p + \sum_i c_i^{(p)} e_i(q), \quad (2.2.9)$$

where

$$\hat{R} = \left( 1 - \frac{1}{\lambda^*} \hat{K} + \sum_i \hat{P}_i \right)^{-1}. \quad (2.2.10)$$

Factors  $a_i$  and  $c_i^{(p)}$  are determined by substitution of equations (2.2.6) and (2.2.9) into the condition (2.2.7). In particular, assuming  $p=3$ , we find

$$\beta_1 a_i \|e\| + \frac{1}{2} \beta^* \langle 1, 1 \rangle \sum_{k,j} a_k a_j \langle e_i, e_k e_j \rangle = 0. \quad (2.2.11)$$

If  $\langle e_i, e_j, e_k \rangle = 0$  for all sets  $(i, j, k)$  this equation is not sufficient to determine the infinitesimal non-zero solution. In fact, in this case

$$\psi_1 = 0, \quad (2.2.12)$$

or

$$\beta_1 = 0. \quad (2.2.13)$$

Let us consider the case (2.2.12) in detail. Assuming that  $\psi_1 = \dots = \psi_{p-1} = 0$  and using the expansions (2.2.1), we find from equation (2.1.5)

$$\psi_p = \frac{1}{\lambda^*} \hat{K} \psi_p, \quad (2.2.14)$$

$$\psi_{p+1} = \frac{1}{\lambda^*} \hat{K} \psi_{p+1} - \beta_1 \hat{K} \psi_p. \quad (2.2.15)$$

The compatibility condition of equations (2.2.14) and (2.2.15) is  $\psi_p = 0$ . Thus, under the assumption (2.2.12), we find by induction  $\psi_p = 0$  for any  $p$ . Now we consider the case (2.2.13). Substituting in equation (2.2.7)  $p=3$  and accounting for (2.2.13), we find equations, determining the factors  $a_i$  in this case

$$\left( \frac{\langle 1, 1 \rangle}{2} \|e\| \beta^* \sum_i |a_i|^2 - \beta_2 \right) \|e\| a_i + \beta^{*2} \langle e_1, \psi_1 \hat{K} \psi_2 \rangle - \frac{\langle 1, 1 \rangle^2}{6} \beta^* \sum_{i,j,k} a_i a_j a_k \langle e_i, e_j e_k \rangle = 0. \quad (2.2.16)$$

Let us discuss the significance of the symbol  $\langle e_i, \psi_1 \hat{K} \psi_2 \rangle$ . According to equation (2.2.9)

$$\psi_2 = \hat{R}G_2 + \sum_i c_i^{(2)} e_i(q).$$

For  $\psi_1$  there is an expression (2.2.6). Earlier we had assumed that  $\langle e_i, e_j e_k \rangle = 0$  for all sets  $(i, j, k)$ . Consequently

$$\langle e_i, \psi_1 \hat{K} \psi_2 \rangle = \sum_i a_i \langle e_i, e_i \hat{K} \hat{R} G_2(\psi_1, 0) \rangle. \quad (2.2.17)$$

Substituting this equation into equation (2.1.16), we find an equation to determine  $\{a_i\}$

$$\begin{aligned} & \left[ \frac{1}{2} \beta^* \|e\| \sum_i |a_i|^2 \left( \langle 1, 1 \rangle - \frac{1}{\langle 1, 1 \rangle} \beta^* \langle 1, \hat{K} \hat{R} 1 \rangle \right) - \beta_2 \right] \|e\| a_i \\ & + \frac{\langle 1, 1 \rangle}{2} \beta^{*2} \sum_{i,j,k} \langle e_i, e_i \hat{K} \hat{R}(e_j e_k) \rangle a_i a_j a_k \\ & - \frac{\langle 1, 1 \rangle^2}{6} \beta^* \sum_{i,j,k} \langle e_i, e_i e_j e_k \rangle a_i a_j a_k = 0. \end{aligned} \quad (2.2.18)$$

In the same way we could consider the case  $\beta_1 = \beta_2 = 0$ , etc. It would correspond to some additional conditions laid upon the functions  $e_i(q)$  and, consequently, upon the intermolecular potential.

At high temperatures the global minimum of the functional (2.1.4) is realized by the function  $f = f_0 = 1/\langle 1, 1 \rangle$ , which corresponds to  $\psi = 0$ . At small  $\psi$

$$F = F(f_0) + \frac{N^2}{2} \left\langle \psi, \left( \frac{\langle 1, 1 \rangle}{N} T + \hat{K} \right) \psi \right\rangle + O(\langle \psi, \psi \rangle).$$

Let  $T^* = N/\beta^* = -\lambda^* N/\langle 1, 1 \rangle$ , where  $\lambda^*$  is the minimal eigenvalue of the operator  $\hat{K}$ . Then at  $T = T^*$  the fully symmetrical phase becomes absolutely unstable. The order parameter describing the corresponding phase transition is a linear functional  $S(\psi)$ . We have considered two essentially different cases of branching:  $\beta_1 = 0$  and  $\beta_1 \neq 0$ . The signs of  $\beta_1$  and  $\beta_2$  determine the sign of the temperature change on the corresponding branch. It is clear, that the case  $\beta_1 < 0$  and the case  $\beta_1 = 0, \beta_2 < 0$  should be associated with a first order phase transition. The case  $\beta_1 = 0, \beta_2 > 0$  corresponds to a second order phase transition.

Strictly speaking, we should compare the free energies on different branches at an arbitrary distance from the branching point. In this case the branch on which the global free energy minimum is realized may be found to contain no small solution appearing at the point  $\beta = \beta^*$ .

### 3. Orientational ordering

#### 3.1. General consideration

Let  $Q = SO_3$ . The problem of this kind arises in the description of the orientational ordering after averaging over translational degrees of freedom using a spherically symmetrical correlation function. With that,  $q = \Omega$  is a rotation transforming the laboratory system of coordinates into the molecular frame. We specify this rotation, measuring Euler angles  $(\alpha, \beta, \gamma)$  to the scheme A of [16]. In this case the kernel (2.1.3) of the integral transformation (2.1.2) is the function

$$\hat{K}(\Omega_1^{-1} \Omega_2) = \sum_{l, m, m'} K_{m, m'}^l \sum_n \overline{\mathcal{D}_{nm}^l(\Omega_1)} \mathcal{D}_{nm}^l(\Omega_2), \quad (3.1.1)$$

with  $K_{mm'}^l = K_{m'm}^l$ . Here and elsewhere the summation limits over  $l$  are from zero to infinity, and over  $n, m, m'$  (and other indexes having the sense of orbital momentum projections) from  $-l$  to  $+l$ . All indexes are integer. In a similar way we expand  $\psi(\Omega)$

$$\psi(\Omega) = \sum_{l, m, m'} \psi_{mm'}^l \mathcal{D}_{mm'}^l(\Omega), \quad (3.1.2)$$

with  $\psi_{00}^0 = 0$ . Using the orthogonality of the Wigner rotation matrices, we find

$$\hat{K}\psi(\Omega) = 8\pi^2/(2l+1) \sum_{l, m, m'} K_{m'm}^l \sum_n \psi_{nm'}^l \mathcal{D}_{nm}^l(\Omega). \quad (3.1.3)$$

Thus, the operator  $\hat{K}$  has invariant subspaces  $H^{(l, n)}$  from vectors of the form

$$h_n^l(\Omega) = \sum_m h_{nm}^l \mathcal{D}_{nm}^l(\Omega).$$

Study of the operator  $\hat{K}$  spectral properties reduces to the study of spectral properties of the hermitian matrices  $K^l$  with dimensions  $(2l+1) \times (2l+1)$  and matrix elements  $8\pi^2/(2l+1)K_{mm'}^l$ . Denoting the minimum characteristic value of this matrix by  $\lambda^*$ , we

assume it to be simple. (This assumption is not satisfied under some special restrictions upon the matrix elements  $K_{nm}^l$ .) According to equation (3.1.3),  $\lambda^*$  is a  $(2l + 1)$  times degenerate eigenvalue of the operator  $\hat{K}$ . The corresponding eigenvectors  $e_n^l(\Omega)$ ,  $|n| \leq l$ , have the form

$$e_n^l(\Omega) = \sum_m e_{0m}^l \mathcal{D}_{nm}^l(\Omega). \tag{3.1.4}$$

The normalization condition allows the phase of the  $e_n^l(\Omega)$  to be chosen arbitrarily. To eliminate this we demand

$$e_0^l(\Omega) = \overline{e_0^l(\Omega)}, \quad e_{00}^l \geq 0. \tag{3.1.5}$$

Using these relationships and the properties of the Wigner functions we find

$$e_n^l(\Omega) = (-1)^n \overline{e_n^l(\Omega)}. \tag{3.1.6}$$

Let us represent the function  $\psi_1$  in the form (2.2.6). Then equation (2.2.11) assumes the form

$$\frac{\beta_1}{\beta^*} a_i + B_l \sum_{k,j} C_{iklj}^i a_k a_j = 0, \tag{3.1.7}$$

where

$$B_l = \frac{1}{2l+1} (8\pi^2)^2 \sum_{i,j,k} \overline{e_{0i}^l} e_{0k}^l e_{0j}^l C_{iklj}^i,$$

and  $C_{iklj}^i$  is the Clebsch–Gordan coefficient, [16]. Equation (2.2.18) assumes the form

$$\sum_L E^L \sum_{j,k,p} C_{ijL(k+p)}^i C_{iklp}^{L(k+p)} a_j a_k a_p + T_k \left( \sum |a_k|^2 \right) a_i = \beta_2 \|e\| a_i, \tag{3.1.8}$$

where

$$\begin{aligned} T &= 4\pi^2 \|e\|^2 \beta^* (1 + \beta^* K_{00}^0)^{-1}, \quad E^L = E_2^L - E_1^L, \\ E_1^L &= (8\pi^2)^3 \frac{1}{6(2l+1)} \beta^* \sum_{k,p,i,j} e_{0k}^l e_{0p}^l C_{iklp}^{L(k+p)} C_{ijL(k+p)}^i e_{0j}^l \overline{e_{0i}^l} \\ E_2^L &= 4\pi^2 \frac{1}{(2l+1)} \beta^* \sum_{k,p,i,j} e_{0k}^l e_{0p}^l C_{iklp}^{L(k+p)} \langle \mathcal{D}_{0(k+p)}^L, \hat{K} \hat{R} \mathcal{D}_{0(i-j)}^L \rangle \\ &\quad \times C_{ijL(i-j)}^i e_{0j}^l e_{0i}^l. \end{aligned}$$

The values  $E^L$  and  $T$  are functionals of the function  $K$ . The function  $\psi_1$  being real, certain conditions are imposed on the factors  $a_i$ . Using equation (3.1.6), we find  $\overline{a_i} = (-1)^i a_{-i}$ . Let a set  $\{a_i\}$  be a solution of equation (3.1.7) or equation (3.1.8). The mean field equation being invariant with respect to the left hand shift over the group  $SO_3$  implies that the set  $\{a_i\}$  defined as

$$a_i = \sum_k \mathcal{D}_{ki}^l(c) a_k, \tag{3.1.9}$$

where  $c$  is an arbitrary element of the group  $SO_3$ , is also a solution.

Now we consider the case  $l=2$  in detail. This case corresponds to nematic ordering. Five constants  $a_n$  ( $n=0, \pm 1, \pm 2$ ) form an irreducible spherical tensor of the second rank. By rotating the laboratory frame, i.e. using transformation (3.1.9), two of its

components  $a_1$  and  $a_{-1}$  may be reduced to zero. This well-known fact was used for example in [17]. In Appendix A its simple proof is presented, based on the relationship between irreducible spherical tensors and cartesian tensors. Thus, in a certain laboratory frame

$$a_{-2} = \overline{a_2}, \quad a_{-1} = a_1 = 0, \quad a_0 = \overline{a_0}. \tag{3.1.10}$$

Substituting this result into equation (3.1.7) with  $B_2 \neq 0$ , we find the only non-zero solution

$$a_i = a_0^{(z)} \delta_{i0}, \quad a_0^{(z)} = \sqrt{7/\sqrt{2} B_2^{-1} \beta_1 / \beta^*}. \tag{3.1.11}$$

Using transformation (3.2.9), it is possible to obtain, starting from the solution (3.1.11), the two parameter family of solutions. All of the solutions of this family are uniaxial, i.e. they possess symmetry axes of infinite order. Thus, at  $B_2 = 0$  near  $T = T^*$  a first order nematic-isotropic phase transition takes place. If  $B_2 = 0$ , from equations (3.1.7) and (2.1.10) we find  $\beta_1 = 0$ . In this case coefficients  $a_i$  are determined from equation (3.1.8). Substituting equation (3.1.10) into (3.1.8), we find

$$\left. \begin{aligned} X a_0^3 + Y |a_2|^2 a_0 &= \beta_2 a_0, \\ X' a_0^2 a_2 + Y' |a_2|^2 a_2 &= \beta_2 a_2 \end{aligned} \right\} \tag{3.1.12}$$

where

$$\begin{aligned} X &= \frac{1}{\|e\|} \left( \sum_L E^L C_{20\ 20}^{L0} C_{20\ 20}^{L0} + T \right), \\ Y &= \frac{1}{\|e\|} \left( \sum_L E^L [C_{22\ L-2}^{L0} C_{20\ 2-2}^{L-2} + C_{2-2L\ 2}^{L0} C_{20\ 22}^{L2} + C_{20\ L0}^{L0} C_{2-2\ 22}^{L0}] + T \right), \\ X' &= \frac{1}{\|e\|} \left( \sum_L E^L [C_{22\ L0}^{L2} C_{20\ 20}^{L0} + 2C_{20\ L2}^{L2} C_{22\ 20}^{L2}] + T \right), \\ Y' &= \frac{1}{\|e\|} \left( \sum_L E^L [2C_{22\ L0}^{L2} C_{2-2\ 22}^{L0} + C_{2-2\ L4}^{L2} C_{22\ 22}^{L4}] + 2T \right). \end{aligned}$$

In these sums  $L$  runs over the values 0, 1, 2, 3, 4. To calculate  $X, Y, X', Y'$  we need to know the matrices  $K^L$  ( $L=0, 1, 2, 3, 4$ ).

If  $(X' - X)/(Y - Y') > 0$ , the system of equations (3.1.12) has three non-zero solutions

- (a)  $a_0^2 = \beta_2 \left[ X + Y \left( \frac{X' - X}{Y - Y'} \right) \right]^{-1}, \quad |a_2|^2 = \frac{X' - X}{Y - Y'} a_0^2;$
- (b)  $a_0 = 0, \quad |a_2|^2 = \beta_2 / Y';$
- (c)  $|a_0|^2 = \beta_2 / X, \quad a_2 = 0.$

In the case when  $(X' - X)/(Y - Y') < 0$ , there are only two solutions (b) and (c). Solutions (a) and (b) generate three parameter families of solutions, while solution (c) gives a two parameter family. Thus, there always exist both uniaxial (c) and biaxial solutions. To find out which of the three branches corresponds to the actual orientational ordering, we have to analyse equations (2.2.7) with  $p > 3$ , and to calculate values of the functional (2.1.4) on all three branches, finding its global minimum. Each of the solutions (a), (b), (c) depends in an intricate way upon the function  $K$ , more precisely, upon the  $K^l$  matrices with  $l=0, 1, 2, 3, 4$ . The order of the corresponding phase transition is determined by the sign of  $\beta_2$ , which, in turn, is determined from the condition that  $a_0^2$  and  $|a_2|^2$  are



positive. This implies, that the question, concerning the symmetry of the phase formed at a given point on the phase diagram (i.e. at  $B_2=0$ ) and the order of the transition should be solved for each specific molecular system.

Based upon the results of our study, we can assume the shape of the phase diagram in the  $B_2$ - $T$  plane. Two variants are possible, shown in the figures 1 (a) and (b). We distinguish two phases  $N^+$  and  $N^-$ , which are phenomenologically indiscernible and are determined within the choice of the molecular coordinate system. Both of these phases are uniaxial. In the phase  $N^+$  the  $Z$  axis of the molecular frame is at the average angle of  $0 \leq \beta \leq \arccos(1/\sqrt{3})$  to the  $z$  axis of the laboratory frame. For the phase  $N^-$  this angle is in the limit  $\pi \geq \beta \geq \arccos(1/\sqrt{3})$ . The diagram presented in the figure 1 (a), has been widely discussed [13, 14, 17, 18]. The possibility reflected in figure 1 (b) was noted in [18]. In our approach, this corresponds to the solution and analysis of the equations (2.2.7) and (2.2.9) up to  $p=6$  in the same way as was done for  $p=3$ . In addition to this, a special situation is possible for some molecular systems when  $X' = X$ , and solution (a) vanishes, i.e. the topology of the phase diagram is described by figure 1 (b). As we have already noted by the isolated point  $B_2 = 0$  it is possible to realize both continuous and first order phase transitions, depending upon the constituent molecules and external conditions. We have not found, however, any discussion of the second possibility in the literature.

The isotropic liquid-nematic phase transition has been related to the bifurcation of the molecular field equation, taking place at the maximum temperature  $T = T^* = \beta^*/N$ . There also exist bifurcations occurring at a lower temperature. The corresponding non-zero solutions also possess the symmetry of a nematic. Thus, on decreasing temperature a first order phase transition is possible between the two nematic phases without symmetry changes. The theoretical study of such a situation requires calculation of the free energy functional on all the nematic solutions far enough from the bifurcation points.

Studying matrices  $K^l$  with  $l > 2$ , it is possible to construct small solutions of the mean field equation, which correspond to other orientationally ordered structures. In particular, putting  $l=4$ , we obtain a so-called hedgehog ordering, [19]. The corresponding phase is of cubic symmetry. It is usually assumed that in real molecular systems orientational ordering is described by the case with  $l=2$ . We should note that

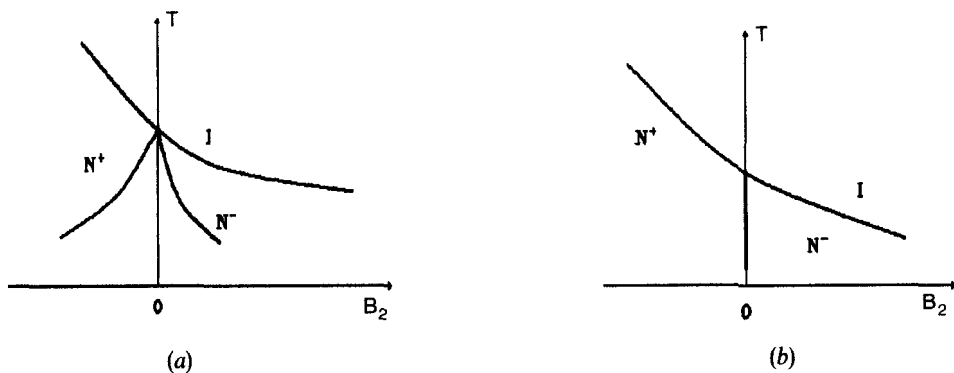


Figure 1. The phase diagram in the  $B_2$ - $T$  plane. I, isotropic liquid,  $N^+$ ;  $N^-$ , uniaxial nematic; B, biaxial nematic. In the  $N^+$  phase the  $z$  axis of the molecular frame is at the average angle of  $0 \leq \beta \leq \arccos(1/\sqrt{3})$  to the  $z$  axis of the laboratory frame. For the phase  $N^-$  this angle has the limits  $\pi \geq \beta \geq \arccos(1/\sqrt{3})$ .

in this situation the existence of the solution with  $l=4$  is also important because there is the possibility of a first order phase transition, corresponding to a jump from the branch  $l=2$  to the branch  $l=4$ . It is natural to expect the optical properties of the cubic phase ( $l=4$ ) to be similar to those of the isotropic liquid. Consequently, such a phase transition could be easily mistaken experimentally for reentrant polymorphism.

3.2. *Orientational ordering of molecules possessing point group symmetry*

According to the general scheme described in §3.1, the study of the orientational ordering in a system of mesogenic molecules requires knowledge of the spectral properties of the matrix  $K^l$ . In particular, putting  $l=2$ , we obtain a  $5 \times 5$  matrix. However, if the molecule possesses a point group symmetry  $H$ , the problem is simplified. Let us consider the case when  $H$  is the intrinsic group of the symmetry, i.e.  $H \subset SO_3$ . In other words

$$K(\Omega_1^{-1}\Omega_2) = K((\Omega_1 h_1)^{-1}\Omega_2 h_2), \quad \psi(\Omega) = \psi(\Omega h),$$

when  $h, h_1, h_2 \in H; \quad \Omega, \Omega_1, \Omega_2 \in SO_3$ . Thus,

$$\left. \begin{aligned} \psi(\Omega) &= \int_H dh \psi(\Omega h) / \int_H dh, \\ K(\Omega) &= \int_H dh K(\Omega h) / \int_H dh = \int_H dh K(h\Omega) / \int_H dh, \dots \end{aligned} \right\} \quad (3.2.1)$$

in the case, when  $H$  is a finite group, integration should be substituted by summation. Using equation (3.1.2), we obtain from equation (3.2.1)

$$\psi(\Omega) = \sum_{l, m, m'} \psi_{mm'}^l \Delta_{mm'}^l(\Omega; H),$$

where

$$\Delta_{mm'}^l(\Omega; H) = \sum_{m''} \mathcal{D}_{mm''}^l(\Omega) \int_H dh \mathcal{D}_{m''m}^l(h) / \int_H dh. \quad (3.2.2)$$

In a similar way

$$K(\Omega_1^{-1}\Omega_2) = \sum_{l, m, m'} K_{mm'}^l \sum_n \overline{\Delta_{nm'}^l(\Omega_1)} \Delta_{nm}^l(\Omega_2).$$

Among the functions  $\Delta_{mm'}^l$ , may be linearly dependent ones (in particular, some of these functions may be reduced to zero). A molecule (considered as a classical object) can possess one of the following intrinsic symmetry groups  $C_\infty, C_n, D_n, T, O, Y$  (see for example [20]). We choose the  $z$  axis of the molecular frame along the symmetry axis of the highest order. According to equation (3.2.2) we find

$$\left. \begin{aligned} \Delta_{mm'}^l(\Omega, C_\infty) &= \mathcal{D}_{m0}^l(\Omega) \delta_{m'0}, \\ \Delta_{mm'}^l(\Omega, C) &= \mathcal{D}_{m, np}^l(\Omega) \delta_{m' np}, \quad p = 0, \pm 1, \dots \end{aligned} \right\} \quad (3.2.3)$$

we are interested in the case  $l=2$ . From these equations it is seen that at  $n \geq 3$  the matrix has only one non-multiple non-zero eigenvalue,  $8\pi^2/5K_{00}^2$ . The corresponding eigenvectors of the operator  $\hat{K}$  are  $e_n^2(\Omega) = \mathcal{D}_{n0}^2(\Omega), n=0, \pm 1, \pm 2$ . We recall that  $C_3 \subset T, C_n \subset D_n, C_4 \subset O, C_5 \subset Y$  and so, in the approximation considered molecules possessing symmetry groups  $H = T, O, Y, C_n, D_n (n \geq 3)$  behave as uniaxial objects. Turning to

equation (3.1.7), we find:  $B_2 = -(8\pi^2)^2 \sqrt{2/10}/\sqrt{7}$  and so in these cases the uniaxial nematic phase  $N^+$  is formed as a result of orientational ordering. The case  $H = C_2$  or  $H = D_2$  appears to be non-trivial; if  $H = C_2$ , we have to deal with the matrix

$$\begin{bmatrix} K_{-2-2}^2 & K_{-20}^2 & K_{-22}^2 \\ K_{0-2}^2 & K_{00}^2 & K_{02}^2 \\ K_{2-2}^2 & K_{20}^2 & K_{22}^2 \end{bmatrix},$$

with  $K_{mm'}^2 = K_{m'm}^2 = K_{-m'-m}^2$ . The study of its spectral properties in general form is rather a difficult problem.

After the necessary computations we obtain, for the case  $H = D_2$ , the relationships presented in [13]. In particular, the minimum characteristic value of the matrix  $K^l$  is

$$\lambda^* = 4\pi^2/5(K_{00}^2 + 2K_{22}^2 - \sqrt{[(K_{00}^2 - 2K_{22}^2)^2 + 8(K_{02}^2)^2]}). \quad (3.2.4)$$

The corresponding eigenvectors of the operator  $\hat{K}$  are

$$\begin{aligned} e_n^2(\Omega) = & \sqrt{2K_{02}^2} \mathcal{D}_{n0}^2(\Omega) + 1/2/\sqrt{2(2K_{22}^2 - K_{00}^2)} \\ & - \sqrt{(K_{00}^2 - 2K_{22}^2)^2 + 8(K_{02}^2)^2} (\mathcal{D}_{n2}^2(\Omega) + \mathcal{D}_{n-2}^2(\Omega)). \end{aligned} \quad (3.2.5)$$

This expression may not be used when  $K_{mm}^2 = K_{00}^2 \delta_{m0} \delta_{m'0}$ ; this case has already been considered.

The function  $B_2$  for a system of molecules possessing symmetry  $D_2$  assumes the form

$$B_2 = (8\pi^2)^2 \sqrt{2/10}/\sqrt{7} e_{00}^2 (6(e_{02}^2)^2 - (e_{00}^2)^2). \quad (3.2.6)$$

Mulder [13] considered the orientational ordering of molecules possessing three mutually orthogonal planes of symmetry. From the presence of this symmetry, conditions on the elements  $K_{mm}^l$  were derived, and it was assumed that inversion of the molecular frame led to the multiplication of  $K_{mm}^l$  by  $(-1)^l$ . This seems, however, not quite correct. These remarks do not raise any doubt about the concrete results of [13], because to obtain them it is sufficient to assume that the molecules have an intrinsic symmetry group  $\mathcal{D}_2$ . Assuming the molecule to possess three mutually orthogonal planes of symmetry implies that all the elements of symmetry belong to  $\mathcal{D}_2$ .

### 3.3. Orientational ordering in the system of quadrupole moments possessing symmetry $\mathcal{D}_2$

The method of bifurcation analysis of the mean field equation is oriented towards using the pseudo-potential  $U(\Omega_1^{-1} \Omega_2)$ , which reflects the structure of the constituent molecules in detail. Thus, the question of adequate parametrization of the intermolecular interaction becomes very important. As a basis for this parametrization we take the method of effective pair interactions (see [21, 22]). A molecule is represented by a distribution  $\rho(\mathbf{r})$  of the force centres, interacting with the force centres of other molecules according to a  $\varphi(\mathbf{r})$  law. The function  $\rho(\mathbf{r})$  is defined in the molecular frame. The potential energy of interaction between the  $i$ th and  $j$ th molecule is calculated using the additive scheme

$$E(i, j) = \int d\mathbf{r}_i \rho(\mathbf{r}_i) \int d\mathbf{r}_j \rho(\mathbf{r}_j) \varphi(\mathbf{r}_{ij});$$

the sense of this definition is clear from figure 2. Let us consider a system of molecules possessing the symmetry  $\mathcal{D}_2$ . Assuming the mean intermolecular distance to be

sufficiently large and putting  $\varphi(\mathbf{r}) = c_6/r^6$ ,  $c_6 < 0$  (which corresponds to a dispersion attraction), it is possible to express the coefficients  $K_{nm}^2$ , using the quadrupole moments of density

$$\left. \begin{aligned} K_{mm'}^2 &= \gamma(-1)^m R_{2-m} R_{2m'}, \\ R_{21} &= R_{2-1} = 0, \quad R_{22} = R_{2-2}, \end{aligned} \right\} \quad (3.3.1)$$

where the quadrupole moment is defined by the relationship (3.3.4), and the effective interaction constant  $\gamma < 0$ . The calculations are presented explicitly in Appendix B. A similar parametrization of the intermolecular interaction potential energy was used in [23].

Assuming  $R_{20} \neq 0$ , we can introduce parameters  $\omega = R_{20}$  and  $\alpha = R_{22}/R_{20}$ ; the parameter  $\alpha$  characterises the biaxiality of the molecule. Using equations (3.2.4) and (3.2.5), we find

$$\lambda^* = -\frac{8}{3}\pi^2|\gamma|\omega^2(1 + 2\alpha^2), \quad (3.3.2)$$

$$e_n^2(\Omega) = -\sqrt{2}|\gamma|\omega^2\alpha\mathcal{D}_{n0}^l(\Omega) - \sqrt{2}|\gamma|\omega^2\alpha^2(\mathcal{D}_{n2}^l(\Omega) + \mathcal{D}_{n-2}^l(\Omega)). \quad (3.3.3)$$

When  $\alpha = 0$ , the system consists of uniaxial molecules, and equations (3.2.5) and (3.3.3) are not applicable in this case. The eigenvectors  $e$  are defined to a constant factor and so in place of equation (3.3.3) we may assume

$$e_n^2 = \mathcal{D}_{n0}^l(\Omega) + \alpha(\mathcal{D}_{n2}^l(\Omega) + \mathcal{D}_{n-2}^l(\Omega)). \quad (3.3.4)$$

This expression may also be used when  $\alpha = 0$ . The eigenvector from equation (3.3.4) satisfies the condition (3.1.5). Using equations (3.2.5) and (3.3.4), we find

$$B_2 = \sqrt{2/\sqrt{7/10(8\pi^2)^2(6\alpha^2 - 1)}}. \quad (3.3.5)$$

In figures 3(a)–(d) possible variants of phase diagrams in the plane  $\alpha - T/(\omega^2|\gamma|)$  are shown. The parabola  $T/(\omega^2|\gamma|) = 0.2(1 + \alpha^2)$ , drawn as a dash-dotted line, defines existence limits of the supercooled liquid. The line of equilibrium nematic–isotropic phase transition is not shown.

We will model the molecule possessing symmetry  $D_2$  by a parallelepiped uniformly filled by force centres. Let us put the origin of the molecular frame at the centre of the parallelepiped; the axes are directed along the edges:  $x$  along  $a$ ,  $y$  along  $b$ ,  $z$  along  $c$ . As a result of calculations presented in Appendix B, we find

$$R_{20} = \frac{abc}{96}\sqrt{6}\sqrt{2/\sqrt{3(2c^2 - a^2 - b^2)}},$$

$$R_{22} = \frac{abc}{96}\sqrt{6(a^2 - b^2)}.$$

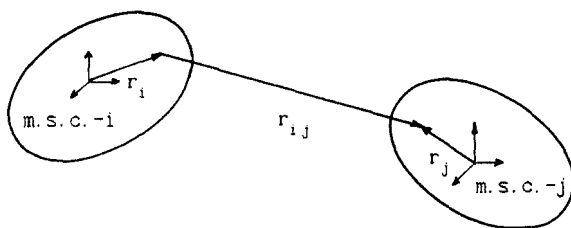


Figure 2. Model arrangement for the interacting molecules. The molecular frame is denoted by m.s.c.

The relationship  $B_2=0$  implies that at least one of the following three relationships should be fulfilled

$$a^2 + b^2 = 2c^2, \quad b^2 + c^2 = 2a^2, \quad c^2 + a^2 = 2b^2.$$

The phase diagram is presented in figure 4, using  $\xi = (b/c)^2$  and  $\eta = (a/c)^2$  as variables (for  $T < T^*$ ); the solid dense lines describe the set of points  $(\eta, \xi)$  for which  $B_2=0$ .

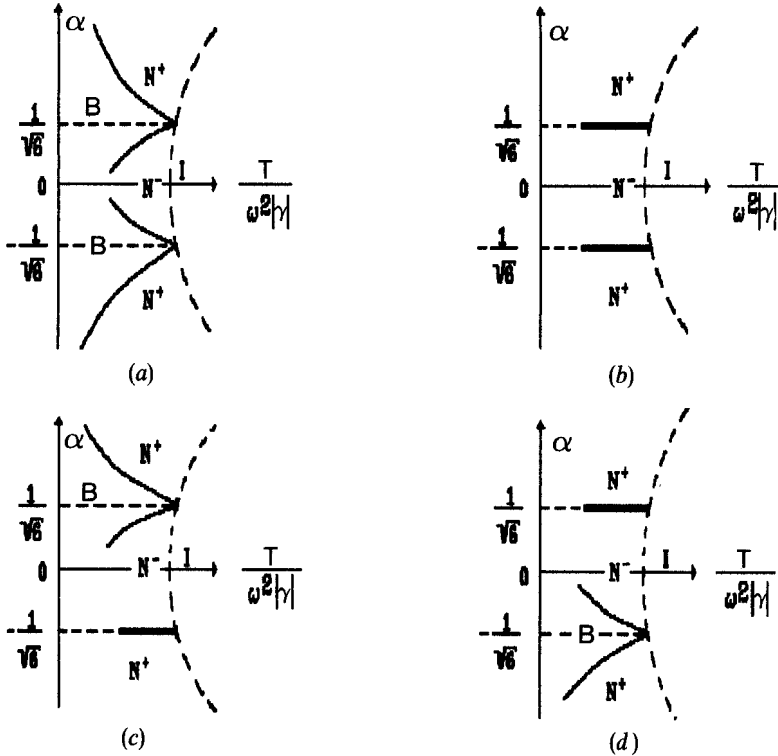


Figure 3. The phase diagrams in the plane  $\alpha-T/(\omega^2|\gamma|)$ . The parabola  $T/(\omega^2|\gamma|)=0.2(1+2\alpha^2)$ , drawn as a dash-dotted line, defines the existence limits of the supercooled liquid. The line of the equilibrium nematic-isotropic phase transition is not shown.

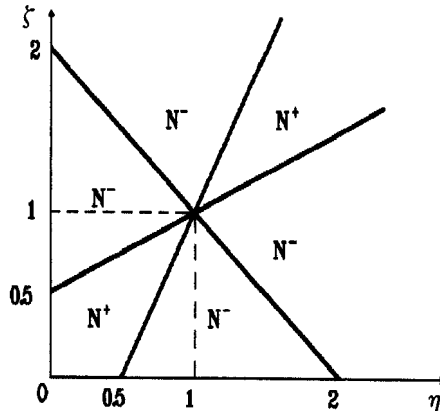


Figure 4. The phase diagram, using  $\xi = (b/c)^2$  and  $\eta = (a/c)^2$  as variables (for  $T < T^*$ ). The solid dense lines describe the set of points  $(\eta, \xi)$  for which  $B_2=0$ .

4. Perturbation theory and modulated structures

4.1. General consideration

Let  $Q = SO_3AT_3$ ; the elements of this group are  $(\mathbf{r}, \Omega)$ , where  $\mathbf{r} \in T_3, \Omega \in SO_3$ . The operator  $\hat{K}$  is now determined by the relationship

$$\hat{K}\psi(\mathbf{r}_2, \Omega_2) = \int d\mathbf{r}_1 d\Omega_1 K(\mathbf{r}_{12}, \Omega_1, \Omega_2)\psi(\mathbf{r}_1, \Omega_1),$$

$$K(\mathbf{r}_{12}, \Omega_1, \Omega_2) = \sum_{l, l', L} \sum_{m, m'} K_{mm'}^{ll'L}(\mathbf{r}_{12}) \Theta_{mm'}^{ll'L}(\Omega_1, \Omega_2, \hat{\mathbf{r}}_{12}),$$

$$\Theta_{mm'}^{ll'L} = \sum_{n, n', N} \binom{ll'L}{nn'N} \mathcal{D}_{nm}^l(\Omega_1) \mathcal{D}_{n'm'}^{l'}(\Omega_2) \mathcal{D}_{N0}^L(\hat{\mathbf{r}}_{12}), \tag{4.1.1}$$

where  $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$ ; here and subsequently we denote by the symbol  $\hat{r}$  the angular coordinates  $(\theta, \varphi)$  of the vector  $\mathbf{r}$ ; we assume by definition  $\mathcal{D}_{n0}^l(\hat{r}) = \mathcal{D}_{n0}^l(\theta, \varphi, 0)$ . Such a form of the function  $K$  is a result of the invariance of the product  $q_1^{-1}q_2$  with respect to the left hand shift of the elements  $q_1$  and  $q_2$  on a euclidean group, reflecting the choice of the laboratory frame being arbitrary. Expansions of the form (4.1.1) are usually used in molecular physics to present the pair interaction of asymmetric molecules (see, for example [23]). Under the assumption made in § 2.1, the symmetry of the function  $K$  is the same as the symmetry of the pair potential. The operator  $\hat{K}$  may be presented in the form  $\hat{K} = \hat{K}(0) + \hat{K}_1$ , with the operator  $\hat{K}(0)$  being an integral transformation with the kernel  $K(0) = \int d\mathbf{r} K(\mathbf{r}, \Omega_1, \Omega_2)$ . In § 3 we introduced eigenfunctions of such an operator, defined on  $SO_3$ . Each eigenvalue  $\lambda^l$  is  $(2l + 1)$  times degenerate in the space of these functions. Now the operator  $\hat{K}(0)$  is considered effective in the space of functions defined on all the euclidean group, with degeneration multiplicity of the eigenvalue  $\lambda^l$  turning to be infinite; the corresponding eigenvector is

$$e(\mathbf{r}, \Omega) = \sum_n \varphi_n^l(\mathbf{r}) e_n^l(\Omega), \tag{4.1.2}$$

where  $\varphi_n^l(\mathbf{r})$  is an arbitrary function. Splitting of the eigenvalue  $\lambda^l$  in a first approximation will be defined by the secular equation (see, for example [24]). In other words, we should look for eigenvectors corresponding to the minimum eigenvalue of the operator  $\hat{K}$  in the form (4.1.2), minimizing the form  $\langle e, \hat{K}e \rangle$  at a fixed value of  $\langle e, e \rangle$ .

In the space of vectors  $e(\mathbf{r}, \Omega)$  we introduce a basis

$$e_{\mathbf{k}, n}^l(\mathbf{r}, \Omega) = \exp(i\mathbf{k}\mathbf{r}) e_n^l(\Omega) (\|e\|V)^{-1/2}, \tag{4.1.3}$$

where  $l$  is fixed,  $n = 0, \dots, \pm l$ ,  $\mathbf{k}$  is an arbitrary vector from  $\mathfrak{R}^3$ . Thus,  $\langle e_{\mathbf{k}, n}^l, e_{\mathbf{k}', n'}^l \rangle = \delta_{\mathbf{k}\mathbf{k}'} \delta_{nn'}$ . Using equations (4.1.1), (4.1.3), (3.1.4) and (3.1.6), we find

$$\langle e_{\mathbf{k}, n}^l, \hat{K} e_{\mathbf{k}', n'}^l \rangle = \delta_{\mathbf{k}, \mathbf{k}'} (-1)^{n'} \sum_{L, N} K_{mm'}^{ll'L}(k) \binom{ll'L}{nn'N} \mathcal{D}_{N0}^L(\hat{k}), \tag{4.1.4}$$

where

$$K_{mm'}^{ll'L}(k) = 4\pi i^L \int dr r^2 K_{mm'}^{ll'L}(r) j_L(kr),$$

$$K^{ll'L}(k) = (8\pi^2)^2 / (2l + 1) / \|e\| \sum_{m, m'} (-1)^{(m+m')} K_{mm'}^{ll'L}(k) e_0^l -_m e_0^l -_{m'}.$$

The matrix composed from the elements from equation (4.1.4), is subdivided into blocks located along the diagonal, which are labelled with the index  $\mathbf{k}$ ; the position of an element inside the block is defined by two indexes  $n_1, n_2 = 0, \pm 1, \dots, \pm l$ . The dimensions of the block are  $(2l+1) \times (2l+1)$ . Let the vector  $\mathbf{k}_0$  be parallel to the laboratory frame. The block where  $\mathbf{k} = \mathbf{k}_0$  is diagonal; it has  $(2l+1)$  eigenvalues

$$\lambda_n^l = (-1)^n \sum_{n,L} (2L+3)^{-1} C_{nl-n}^{L0} K^{ll}, \quad (4.1.5)$$

with eigenvectors  $e_{\mathbf{k}_0, n}^l(\mathbf{r}, \Omega)$ .

Using the properties of the Wigner rotation matrices and Clebsch–Gordan coefficients, we can show that blocks with  $\mathbf{k} = \mathbf{k}_0$  and  $\mathbf{k} = \mathbf{k}' = w\mathbf{k}_0$ ,  $w \in \text{SO}_3$ , are related by the unitary transformation representing rotation of the laboratory frame

$$\langle e_{\mathbf{k}_0, n}^l, \hat{K} e_{\mathbf{k}_0, m}^l \rangle = \sum_{n', m'} \mathcal{D}_{n'n}^l(w) \langle e_{\mathbf{k}', n'}^l, \hat{K} e_{\mathbf{k}', m'}^l \rangle \mathcal{D}_{mm'}^l(w^{-1}).$$

Hence their eigenvalues are the same. Eigenvectors of the block with  $\mathbf{k} = \mathbf{k}'$  have the form  $\exp(i\mathbf{k}'\mathbf{r})e_n^l(w^{-1}\Omega)$ .

We have to find the minimum  $\lambda_n^l(k)$  by variation of  $\mathbf{k}$  and  $n$ . Such a study should lead us to determine  $k^*$ ,  $n^*$ , corresponding to the minimum value  $\lambda^* = \lambda_{n^*}^l(k^*)$ . The temperature  $T^* = -\lambda^* N / 8\pi^2 / V$  determines the existence limit of the supercooled isotropic liquid. The case when the absolute minimum of the function  $\lambda_n^l(k)$  is at  $k=0$  corresponds to non-modulated, orientational ordering.

To go on with our study we have to specify the functions  $K(\mathbf{r}, \Omega_1, \Omega_2)$ . We assume that this function is such that the minimum in question is realized when the  $k$  are small. Expanding  $K^{ll}(k)$  in a series over powers of  $k_1$  we find

$$\lambda_n^l(k) = \lambda^l + \alpha_n^l k + \beta_n^l k^2, \quad (4.1.6)$$

where

$$\alpha_n^l = (-1)^n 1 / \sqrt{3} C_{nl-n}^{10} \left. \frac{dK^{ll}}{dk} \right|_{k=0},$$

$$\beta_n^l = \frac{(-1)^n}{2} \left( C_{nl-n}^{00} \left. \frac{d^2 K^{ll}}{dk^2} \right|_{k=0} + 1 / \sqrt{5} C_{nl-n}^{20} \left. \frac{dK^{ll}}{dk^2} \right|_{k=0} \right).$$

In particular

$$\left. \begin{aligned} \lambda_{\pm 1}^2 &= \lambda^2 \pm vk + (\mu + \eta)k^2, \\ \lambda_{\pm 1}^2 &= \lambda^2 \mp 2vk + \mu k^2, \\ \lambda_0^2 &= \lambda^2 + (\mu + \frac{4}{3}\eta)k^2, \end{aligned} \right\} \quad (4.1.7)$$

where

$$v = -\frac{1}{2\sqrt{30}} \left. \frac{dK^{ll}}{dk} \right|_{k=0},$$

$$\mu = \frac{1}{2\sqrt{5}} \left( \left. \frac{dK^{220}}{dk^2} \right|_{k=0} + \frac{\sqrt{2}}{\sqrt{7}} \left. \frac{dK^{222}}{dk^2} \right|_{k=0} \right),$$

$$\eta = -\frac{\sqrt{2}}{\sqrt{7}} \left. \frac{dK^{222}}{dk^2} \right|_{k=0}.$$

To use these formulae, we require that

$$(\mu + \eta) > 0, \quad \mu > 0, \quad (\mu + \frac{4}{3}\eta) > 0. \tag{4.1.8}$$

If these conditions are not fulfilled, one of the functions from equation (4.1.7) decreases unboundedly with increase of  $k$ .

If  $v > 0$ , the minimum eigenvalue of the operator  $\hat{K}$  to be found is

$$\lambda^* = \min \{ \lambda_{-1}^2(k_{-1}), \lambda_2^2(k_2) \}, \tag{4.1.9}$$

where

$$k_{-1} = \frac{1}{2(\mu + \eta)}v, \quad k_2 = v/\mu.$$

If  $v < 0$ , then

$$\lambda^* = \min \{ \lambda_1^2(k_1), \lambda_{-2}^2(k_{-2}) \}, \tag{4.1.10}$$

where

$$k_1 = -\frac{1}{2(\mu + \eta)}v, \quad k_{-2} = -v/\mu.$$

If  $v = 0$ , then  $\lambda^* = \lambda^1, k^* = 0$ . From equations (4.1.7), (4.1.9) and (4.1.10) we find

$$\left. \begin{aligned} \lambda_{\pm 1}^2(k_{\pm 1}) &= \lambda^2 - \frac{1}{4(\mu + \eta)}v^2, \\ \lambda_{\pm 2}^2(k_{\pm 2}) &= \lambda^2 - v^2/\mu. \end{aligned} \right\} \tag{4.1.11}$$

From this and equation (4.1.8) it can be seen that  $\lambda_{\pm 2}^2 < \lambda_{\pm 1}^2$ . Thus,

$$\lambda^* = \lambda^2 - v^2/\mu, \quad k^* = |v|/\mu, \quad n^* = 2 \operatorname{sgn}(v). \tag{4.1.12}$$

We recall that this result was obtained by assuming that the minimum of the functions  $\lambda_n^2(k)$  occurs at small  $k$ .

In agreement with what was said in §2, we should look for the infinitesimal solution  $\psi_1(\mathbf{r}, \Omega)$  in the form

$$\begin{aligned} \psi_1(\mathbf{r}, \Omega) &= \int d\hat{k} a_{n^*}^l(\hat{k}) \exp(i\mathbf{k}\mathbf{r}) e_{n^*}^l(w^{-1}\Omega), \\ |\mathbf{k}| &= k^*, \quad w\mathbf{k}_0 = \mathbf{k}, \quad w \in \text{SO}_3; \end{aligned}$$

the vector  $\mathbf{k}_0$  is directed along the laboratory  $z$  axis. Functions  $a_{n^*}^l(\hat{k})$  are defined from equation (2.2.7). Putting  $p=2$ , we can find a solution  $\psi_1$  possessing hexagonal symmetry. Putting  $\beta_1=0, p=3$ , from equation (2.2.7) we find a solution with cubic symmetry. It seems that the first solution corresponds to the hexagonal structure mentioned in [14], and the second to the blue phase. More than one solution is possible for each of these symmetries.

#### 4.2. One dimensional modulated structures

We now consider the simplest case, i.e. the one dimensional solution

$$\psi_1(z, \Omega) = A \exp(ik^*z) e_{n^*}^l(\Omega) + \bar{A} \exp(-ik^*z) \overline{e_{n^*}^l(\Omega)}. \tag{4.2.1}$$



Substituting equation (2.1) into equation (2.2.7) with  $p=2, 3$ , we find

$$\beta_1 = 0, \quad |A|^2 = \beta_2 \|e\| (\beta^* 4\pi^2 VF)^{-1}, \tag{4.2.2}$$

where

$$\begin{aligned} F_i = & \|e\|^2 V \left( 1 + \frac{1}{V} \beta^* K_{00}^0(0) \right)^{-1} - 4\pi^2 V \int d\Omega |e_{n^*}^l(\Omega)|^4 \\ & + \beta^* \left( \int d\Omega |e_{n^*}^l(\Omega)|^2 \hat{K}(0) \hat{R}(0) |e_{n^*}^l(\Omega)|^2 \right) \\ & + 0.5 \left( \int d\Omega (e_{n^*}^l(\Omega))^2 K(2\mathbf{k}_0) \hat{R}(2\mathbf{k}_0) (e_{n^*}^l(\Omega))^2 \right), \quad |\mathbf{k}_0| = \mathbf{k}^*; \end{aligned}$$

the vector  $\mathbf{k}_0$  is directed along the laboratory  $z$  axis. The operator  $\hat{K}(\mathbf{k})$  is defined by the relationship

$$\hat{K}(\mathbf{k})\varphi(\Omega) = \int d\Omega' \varphi(\Omega') \int d\mathbf{r} K(\mathbf{r}, \Omega, \Omega') \exp(-i\mathbf{k}\mathbf{r}),$$

and the operator  $\hat{R}(\mathbf{k})$  by the relationship

$$\hat{R}(\mathbf{k}) = \left( 1 - \frac{1}{\lambda^*} \hat{K}(\mathbf{k}) + \frac{1}{\|e\|} \delta_{\mathbf{k}\mathbf{k}_0} \sum_m \hat{P}_m^l \right)^{-1},$$

where

$$\hat{P}_m^l \varphi(\Omega) = \frac{1}{\|e\|} \langle e_m^l, \varphi \rangle e_m^l(\Omega).$$

$|A|^2 > 0$ , hence we determine the sign of  $\beta_2$  and make assumptions about the order of the phase transition. When  $F_i > 0$ , the corresponding modulated structure may emerge as a result of the second order phase transition. If  $F_i < 0$ , we should expect the phase transition to be first order. Equation (4.2.2) cannot be used when  $F_i = 0$ . In this case, substituting equation (4.2.1) into equation (2.2.7) and putting  $p=3$ , we find that  $\beta_2 = 0$ . To find the coefficient  $A$ , we should put  $p=4$  in these equations. We note, that  $F_i$  turns out to be zero only under certain special restrictions upon the function  $K$ .

Let  $n^* \neq 0$ . Using the definition from equation (3.1.4) and the properties of the Wigner functions, equation (3.2.1) can be represented in the form

$$\psi_1(\mathbf{r}, \Omega) = A e_{n^*}^l(\omega^{-1}(z)\Omega) + \bar{A} e_{n^*}^l(\overline{\omega^{-1}(z)\Omega}), \tag{4.2.3}$$

where  $\omega(z) \in \text{SO}_3$  is defined by the Euler angles  $(k^*z/n^*, 0, 0)$ . We shall interpret  $\omega(z)$  as a rotation transforming the laboratory frame  $(x, y, z)$  into a local laboratory system of coordinates  $(x', y', z')$ . The orientation of the molecular frame relative to the local laboratory frame is defined by the matrix  $\Omega' = \omega^{-1}(z)\Omega$ . The rotation  $\omega(z)$  is realized around the laboratory  $z$  axis. Moving along this axis, unit vectors of the local laboratory frame  $x'$  and  $y'$  axes describe a helix with pitch  $h = 2\pi n^*/k^*$ . The right handed helix corresponds to  $m^* > 0$ , and the left handed to  $m^* < 0$ .

It follows directly from equation (4.2.1) that  $\psi_1(z, \Omega) = \psi_1(z + pd, \Omega)$ , where  $d = 2\pi/k^*$ ,  $p = 0, \pm 1, \pm 2, \dots$ . Thus, the spatial period  $d$  of the one dimensional solution from equation (4.2.1) is, generally speaking, not the same as the helical pitch  $h$ .

Let  $l=2$ . Putting  $n^* = 0$  in equation (4.2.1), we obtain a solution with the symmetry of a smectic A phase. However, for the smectic A phase a small additional term to the fully symmetrical distribution function should be of a different form. With  $n^* \neq 0$ , having performed the local coordinate transformation (see equation (4.2.3)), we see that

the solution describes helicoidal structures which look locally like the biaxial nematic. Following the tradition (see, for example, [14]), we call the structure with  $n^* = \pm 2$  cholesteric, and the structure with  $n^* = \pm 1$  the conic phase. We note, however, that, as both structures are locally biaxial, these names are but conventional.

To determine which of the five possible one dimensional structures ( $n^* = 0, \pm 1, \pm 2$ ) is realized, we have to find the minimum eigenvalue  $\lambda^* = \lambda_n^2(k^*)$ . Assuming the one dimensional structure formed to be one with a long period (small  $k^*$ ), we see from equation (4.1.11) that with  $\nu > 0$  near the point  $T^* = -\lambda^*N/(8\pi^2V)$  a right handed cholesteric helix is formed, and with  $\nu < 0$  a left handed helix. Breaking the liquid state symmetry is also possible by formation of structures with  $n^* = 0, \pm 1$ . These structures, however, should be ones with a short period, for which equation (4.1.12) is inapplicable. These conclusions about stability of the one dimensional structures are but tentative. The states corresponding to the one dimensional solution (equation (4.2.1)) may be not realized because of competition with structures of more than one dimension.

In this reasoning, we have identified the symmetry of the modulated structure with the symmetry of the corresponding infinitesimal solution  $\psi_1(\mathbf{r}, \Omega)$  of the molecular field equation. This identification is justified if the structure is formed as a result of a second order phase transition. In the case of a first order transition it is necessary, generally speaking, to study the symmetry of the function  $\psi = \varepsilon\psi_1 + \varepsilon^2\psi_2 + \dots$ . Using equations (2.2.9), (2.2.10) and (2.2.7) and assuming the expression (4.2.1) for  $\psi_1$ , it is possible to construct  $\psi_n (n \geq 2)$  and to show that its symmetry is the same as that of the function  $\psi_1$ . Putting  $k^* = 0$ , we can extend this to the case of orientational ordering considered in § 3.

### 5. Phenomenological description of phase transitions and bifurcation analysis of the molecular field equation

Phenomenological approaches to the isotropic liquid–spatially modulated structure phase transitions use the Landau–Ginzburg free energy expansion. In particular, Brazovski and Dmitriev [14], describing the isotropic liquid–cholesteric phase transition, used the expression

$$\left. \begin{aligned} F\{\hat{Q}\} &= F_0 + T(H_2\{\hat{Q}\} + H_3\{\hat{Q}\} + H_4\{\hat{Q}\}), \\ H_2\{\hat{Q}\} &= \frac{1}{2!} \int d\mathbf{r} [a(Q_{\alpha\beta})^2 + b(\partial_\alpha Q_{\gamma\delta})^2 + C(\partial_\alpha Q_{\alpha\gamma} \partial_\beta Q_{\beta\gamma} + 2de_{\alpha\beta\gamma} Q_{\alpha\delta} \partial_\gamma Q_{\beta\gamma}), \\ H_3\{Q\} &= \frac{1}{3!} M \int d\mathbf{r} Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\delta}, \quad H_4\{\hat{Q}\} = \frac{1}{4!} \Lambda \int d\mathbf{r} (Q_{\alpha\beta}^2)^2, \end{aligned} \right\} \quad (5.1)$$

where  $\partial_\alpha = \partial/\partial r_\alpha$ ,  $\alpha = x, y, z$ ,  $Q_{\alpha\beta}$  is a symmetrical real traceless second rank tensor. According to Appendix A, the tensor  $Q_{\alpha\beta}$  is linearly expressed using an irreducible second rank spherical tensor  $Q_n^2$ . With  $d=0$  the expansion (5.1) describes the free energy of the nematic liquid crystal. The term  $H_2(\hat{Q})$  can be expressed in the form

$$H_2\{\hat{Q}\} = \frac{1}{2} \sum_{\mathbf{q}} t_\alpha^\gamma(\mathbf{q}) \delta_{\beta\delta} Q_{\alpha\beta, \mathbf{q}} Q_{\alpha\delta, -\mathbf{q}} \quad (5.2)$$

where

$$t_\alpha^\gamma(\mathbf{q}) = (a + bq^2)\delta_{\alpha\gamma} + cq_\alpha q_\gamma + 2dqL_{\alpha\gamma}(\mathbf{q}),$$

$$\hat{Q}_\mathbf{q} = V^{-1/2} \int d\mathbf{r} \hat{Q}(\mathbf{r}) \exp(-i\mathbf{q}\mathbf{r}),$$

$$L_{\alpha\gamma}(\mathbf{q}) = ie_{\alpha\beta\gamma} q_\beta / q, \quad q = |\mathbf{q}|.$$

In §2.3 the phase transition from the fully symmetrical phase was associated with branching of the fully symmetrical solution of the molecular field equation, which is a necessary condition for the extremum of the free energy functional (2.1.4). Solutions of equation (2.1.5) were looked for in the form of equation (2.2.1). Substituting  $f=f_0 + \psi$  into equation (2.1.4) and assuming  $\psi$  to be small, we find

$$F = F(f_0) + \frac{N^2}{2} \left\langle \psi, \left( \hat{K} + \frac{T\langle 1, 1 \rangle}{N} \right) \psi \right\rangle - \frac{N}{6} T \langle 1, 1 \rangle^2 \langle \psi, \psi^2 \rangle + \frac{N}{12} T \langle 1, 1 \rangle^2 \langle \psi, \psi^3 \rangle + 0(\langle \psi, \psi \rangle^2). \tag{5.3}$$

The free energy of the ordered phase close to the bifurcation point  $\beta = \beta^*$  can be calculated by substituting the initial terms of the expansion (2.2.1) into equation (5.3). The parametrical dependence of the free energy on temperature is

$$F = F(f_0) + \frac{N^2}{2} \left\langle \psi_1, \left( \hat{K} + \frac{T\langle 1, 1 \rangle}{N} \right) \psi_1 \right\rangle \varepsilon^2 + N^2 \left\langle \psi_2, \left( \hat{K} + \frac{T\langle 1, 1 \rangle}{N} \right) \right\rangle \varepsilon^3 - \frac{N}{6} T \langle \psi_1, \psi_1^2 \rangle \varepsilon^3 + \frac{N^2}{2} \left\langle \psi_2, \left( K + \frac{T\langle 1, 1 \rangle}{N} \right) \psi_2 \right\rangle \varepsilon^4 - \frac{N}{2} T \langle 1, 1 \rangle^2 \langle \psi_2, \psi_1^2 \rangle \varepsilon^4 + \frac{N}{12} T \langle 1, 1 \rangle^2 \langle \psi_1 \cdot \psi_1^3 \rangle \varepsilon^4 + 0(\varepsilon^4), \tag{5.4}$$

$$\beta = \frac{N}{T} = \beta^* + \varepsilon \beta_1 + \varepsilon^2 \beta_2 + \dots$$

To describe a modulated structure, we have to assume

$$\psi_1 = \sum_n a_n^l(\mathbf{r}) e_n^l(\Omega), \quad \overline{a_n^l(\mathbf{r})} = (-1)^n a_n^l(\mathbf{r}). \tag{5.5}$$

Cholesteric phases correspond to the case with  $l=2$ . Thus, the expansion (5.4) contains invariants constructed from the tensor field  $a_n^2(\mathbf{r})$ . Expanding  $a_n^2(\mathbf{r})$  in a Taylor series, it is possible to obtain integro-differential invariants, which correspond to the invariants of the expansion (5.1). We note that in this way we will find, in addition, invariants containing derivatives of higher order, which are not present in equation (4.1). It is more convenient to carry out the corresponding expansion in Fourier space. Putting

$$a_n^2(\mathbf{k}) = V^{-1/2} \int d\mathbf{r} a_n^2(\mathbf{r}) \exp(-i\mathbf{k}\mathbf{r}),$$

and using equations (4.1.1), (4.1.4) and (5.5), we find

$$\langle \psi_1, K\psi_1 \rangle = \|e\| \sum_{\mathbf{k}} \sum_{n, n'} (-1)^{n'} \sum_{L, N} \binom{22L}{nn'N} \mathcal{D}_{N0}^L(\hat{k}) K^{22L}(k) a_n^2(\mathbf{k}) a_{n'}^2(\mathbf{k}). \tag{5.6}$$

The expression (5.6) is the analogue of equation (5.2). The irreducible second rank spherical tensor  $a_n^2(\mathbf{k})$  is an analogue of the tensor  $Q_{\alpha\beta, \mathbf{q}}$ .

Transforming equation (5.6) to the diagonal form, we find equations (4.1.5), or (4.1.7) in the case of long period structures. An expression similar to (4.1.7) was found in

[14] by diagonalisation of equation (5.2). Five eigenvalues which have been found there are

$$\left. \begin{aligned} \tau^{1,2}(q) &= a + bq^2 \pm 2dq, \\ \tau^{3,4}(q) &= a + (b+c)q^2 \pm 2dq, \\ \tau^0(q) &= a + (b + \frac{4}{3}c)q^2. \end{aligned} \right\} \quad (5.7)$$

The correspondence with equation (4.1.7) is established, if we put

$$a = (\beta^* \lambda^2 - 8\pi^2 V)/N, \quad b = \mu, \quad d = \nu, \quad k = q.$$

With that,  $\tau^{1,2}$  is identified with  $(\beta^* \lambda_{\pm 2}^2 - 8\pi^2 V)/N$ ,  $\tau^0$  with  $(\beta^* \lambda_0^2 - 8\pi^2 V)/N$ ,  $\tau^{3,4}$  differs from  $(\beta^* \lambda_{\pm 1}^2 - 8\pi^2 V)/N$  by the factor in the term linear in  $q$ .

It seems that in [14] there is an error; the correct calculation yields

$$\tau^{3,4} = a + (b+c)q^2 \pm dq.$$

In [14] it was assumed that  $c > 0$ . The authors conclude, using equation (5.7), that the mode corresponding to  $\tau^1$  or  $\tau^2$  is of the lowest energy. The correction to the expression for  $\tau^{3,4}$  makes the requirement  $c > 0$  unnecessary (see equation (4.1.12)).

Expression (4.1.5) contains in itself a possibility of the existence of short period structures. In other words, its minimum can be reached in the region of large  $k$ , where the expansion (4.1.7) is not applicable. The phenomenological account for such a possibility would require the introduction of additional integro-differential invariants to equation (5.1), containing higher-order differential derivatives.

Thus correspondence is established between the second term in equation (5.4) and the term  $H_2$  in equation (5.1). Not all of the terms in equation (5.4) have their analogies in equation (5.1). In fact, it is clear from equations (2.2.4), (2.2.9) and (5.5) that  $\psi_2(\mathbf{r}, \Omega)$  can be represented in the form

$$\psi_2 = \sum_{l=0}^4 \psi_{(2)mm}^l(\mathbf{r}) \mathcal{D}_{mm}^l(\Omega),$$

where  $\psi_{(2)mm}^l(\mathbf{r})$  are certain functions. Thus, invariants appear in equation (5.4) which are constructed from variables transformed by rotation of the laboratory frame over irreducible representations  $\mathcal{D}^l$ ,  $l=0, 1, 2, 3, 4$ , of the group  $SO_3$ . An account of such terms in a phenomenological description of the nematic–isotropic phase transition has been partially carried out [25]. The presence of such terms can affect the order of the phase transition, because they are accounted for in the calculations of  $F_2$  (see equation 2.3)). According to § 3.1, these terms can influence significantly the characteristics of the phase transition at the isolated point  $B_2 = 0$ .

### 6. Summary

In this work we have studied the branchings of the fully symmetrical solutions of the molecular field equation. Relationships have been established between these branchings and phase transitions from the fully symmetrical phase. Infinitesimal solutions were constructed, describing the emergence of orientationally ordered structures from the isotropic liquid. Assumptions were made about the form of the corresponding phase diagrams. It is shown that a phase diagram does not necessarily contain a point where the direct transition biaxial nematic–isotropic is possible. If such a point does exist, the corresponding phase transition is not necessarily continuous, as it is commonly assumed. It should be noted, however, that all constructions of the present

work are based upon the mean field approximation and do not allow for fluctuations. Additional work is needed to establish microscopic criteria determining the order of the phase transition. Using perturbation theory, infinitesimal solutions were obtained, describing the emergence of spatially modulated structures. One dimensional structures were studied in detail. Solutions have been found corresponding to the cholesteric phase, the conic phase and a uniaxial modulated structure of the same symmetry as the smectic A phase. It is shown that for long period structures the most thermodynamically favourable are symmetry distortions of the isotropic liquid accounting for the formation of the cholesteric helix.

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### Appendix A

*Relationship between irreducible spherical second rank tensors and cartesian tensors*

An irreducible spherical tensor of second rank  $T_m^2$ , satisfying the condition  $T_m^2 = (-1)^m T_{-m}^2$ , can be represented in the form (see, for example [16])

$$T_0^2 = T_{zz}, \quad T_{\pm 1}^2 = \pm(-\sqrt{2}/\sqrt{3})(T_{zx} \pm iT_{zy}), \quad T_{\pm 2}^2 = 1/\sqrt{6}(T_{xx} - T_{yy} \pm i2T_{xy}),$$

where  $T_{ik}$  is a symmetrical second rank tensor with

$$\sum_i T_{ii} = 0.$$

As known from linear algebra, the tensor  $T_{ik}$  can be reduced to the diagonal form. Turning to equation (A 1), we see, that the diagonal form corresponds to

$$T_0^2 = T_{zz}, \quad T_{\pm 1}^2 = 0, \quad T_{\pm 2}^2 = (T_{xx} - T_{yy}).$$

### Appendix B

*Application of the effective pair interactions method to calculations of the intermolecular potential*

In [21, 22] the intermolecular potential energy is presented in the form

$$E(\mathbf{r}_{12}, \Omega, \Omega) = \sum_{l, l', L} \sum_{m, m'} U_{mm'}^{ll'L}(\mathbf{r}_{12}) U_{mm'}^{ll'L}(\Omega_1, \Omega_2, \hat{r}_{12}), \quad (\text{B } 1)$$

where  $\mathbf{r}_{12}$  is the radius vector connecting the molecular frame centres of molecules 1 and 2,  $\Omega_{1(2)}$  is the set of Euler angles describing the orientation of the molecule 1(2) in the laboratory frame; function  $\Theta_{mm'}^{ll'L}$  is defined by equation (4.1.1).

$$U_{mm'}^{ll'L}(\mathbf{r}_{12}) = \sum_{p=0}^{\infty} A_{p(n)}^{ll'L} \mathbf{r}_{12}^{-(2n+l+l'+2p)} \sum_{\substack{s, s' \\ s+s'=p}} B_{0s's'}^{0ll'} R_{lm}^{2s} R_{l'm'}^{2s'} \quad (\text{B } 2)$$

Here the molecule is considered as a set of force centres interacting with the force centres of other molecules according to the law  $\varphi(r) = C_{2n} r^{-2n}$ . The molecule is assumed to be rigid and its structure is defined by the distribution density of the force centres  $\rho(\mathbf{r})$ , specified in the molecular frame. The generalized moments

$$R_{lm}^{2s} = (4\pi/(2l+1))^{1/2} \int d\mathbf{r} r^{l+2s} Y_{lm}(\hat{\mathbf{r}}) \overline{\rho(\mathbf{r})} \quad (\text{B } 3)$$

assure the full parametrisation of this density. In particular, the Fourier image of density  $\rho(\mathbf{r})$ ,

$$\rho(\mathbf{k}) = (2\pi)^{-3} \int d\mathbf{r} \exp(-i\mathbf{k}\mathbf{r})\rho(\mathbf{r}), \tag{B 4}$$

is represented in the form

$$\rho(\mathbf{k}) = \sum \rho_{lm}(k) Y_{lm}(\hat{k}), \tag{B 5}$$

$$\rho_{lm}(k) = \sum_{s=0}^{\infty} \frac{(-1)^{s+l} i^l (2l+1)^{1/2}}{8\pi s! \Gamma(s+l+3/2)} \left(\frac{k}{2}\right)^{2s+1} R_{lm}^{2s}. \tag{B 6}$$

This can be easily proved by substituting the Rayleigh plane wave expansion,

$$\exp(-i\mathbf{k}\mathbf{r}) = 4\pi \sum (-i)^l j_l(kr) \overline{Y_{lm}(\hat{r})} Y_{lm}(\hat{\mathbf{k}}),$$

into equation (B 5) and expanding the spherical Bessel function  $j_l$  in the Taylor series. Explicit expressions for symbols  $B_{0ss'}^{0ll}$  and  $A_{p(n)}^{ll'L}$  are presented in [22].

The expansion (B 3) is, in fact, an expansion over the dimensionless parameter  $\Delta/R_{12}$ , where  $\Delta$  is a characteristic molecular dimension. Hence, it is valid only for  $\Delta < R_{12}$ . From now on it is assumed that in the system studied the average intermolecular distance  $\langle R_{12} \rangle > \Delta$ . Let interaction of the force centres of the model molecules be governed by the Lennard-Jones law  $\varphi(r) = C_6/r^6 + C_{12}/r^{12}$  ( $C_6 < 0, C_{12} > 0$ ).

$$U_{mm'}^{ll'L} = U_{mm'}^{ll'L(3)} + U_{mm'}^{ll'L(6)}$$

should be substituted into the expansion (B 1).

According to § 3.1, the pseudo-potential should be averaged with a spherically symmetric correlation function  $g(R_{12})$ . In this way the transition is realized by the model system having  $SO_3$  as its one particle configuration space. Particles forming such a system, interact with the potential

$$U(\Omega_1^{-1}, \Omega_2) = \int d\mathbf{r} g(r) E(\Omega_1, \Omega_2, \mathbf{r}_{12}). \tag{B 7}$$

Correlations in this system are not considered, and  $K(\Omega_1^{-1}\Omega_2) = U(\Omega_1^{-1}\Omega_2)$ . Substituting equations (B 1)–(B 3) into (B 8) and carrying out the integration, we obtain

$$U(\Omega_1^{-1}, \Omega_2) = \sum_{l,m,m'} U_{mm'}^l \sum_{m''} \mathcal{D}_{m''m'}^l(\Omega) \mathcal{D}_{m''m}^l(\Omega),$$

$$U_{mm'}^l = 4\pi / (2l+1)^{1/2} (-1)^{l+m} \sum_{n=3,6} \sum_{p=0}^{\infty} A_{p(n)}^{ll'0}$$

$$\times \left[ \int_0^{\infty} dr r^{-(2n+l+l'+2p-2)} g(r) \right] \sum_{\substack{s,s' \\ s+s'=p}} B_{0ss'}^{0ll} R_{l-m}^{2s} R_{lm'}^{2s'}.$$

When actual calculations are made, the series has to be truncated. To a first approximation we may account only for the dispersion interaction, caused by the multipole moments  $R_{lm} \equiv R_{lm}^0$ . In particular, in this approximation

$$U_{mm'}^2 = \gamma (-1)^m R_{2-m} R_{2m'}, \tag{B 8}$$

where the effective interaction constant  $\gamma < 0$ .

Let us place the origin of the molecular frame at the centre of a rectangular parallelepiped ( $a; b; c$ ). Let  $\rho(\mathbf{r})$  be equal to unity inside this parallelepiped and to zero

outside. We direct the molecular frame axes along the edges of the parallelepiped. The Fourier image of the distribution considered is

$$\rho(\mathbf{k}) = (2\pi)^{-3} \int d\mathbf{r} \exp(-i\mathbf{k}\mathbf{r}),$$

with integrating being carried out over the entire volume of the parallelepiped. Expanding  $\exp(-i\mathbf{k}\mathbf{r})$  in a Taylor series, we obtain

$$\rho(\mathbf{r}) = (2\pi)^{-3} \int d\mathbf{r} (\dots - \frac{1}{2}(\mathbf{k}\mathbf{r})^2 + \dots).$$

Here only the terms of order  $k^2$  are written down explicitly. Now we present the vectors  $\mathbf{k}$  and  $\mathbf{r}$  in the cyclic basis [16]. The covariant component of the vector  $\mathbf{k}$  is

$$k_\mu = (4\pi/3)^{1/2} k Y_{1\mu}(\hat{k}), \quad \mu = 0, \pm 1.$$

Contravariant cyclic components of the vector  $\mathbf{r}$  are expressed in terms of its cartesian components  $x, y, z$

$$\left. \begin{aligned} r^{+1} &= -(x - iy)/\sqrt{2}, \\ r^{-1} &= (x + iy)/\sqrt{2}, \\ r &= z. \end{aligned} \right\} \tag{B 9}$$

The scalar product  $(\mathbf{k}\mathbf{r})$  is a convolution  $k_\mu r^\mu$ . In this way,

$$\rho(\mathbf{k}) = \dots - \frac{1}{6\pi^2} \left(\frac{k}{2}\right)^2 \sum_{\mu, \mu'} Y_{1\mu}(\hat{k}) Y_{1\mu'}(\hat{k}) I^{\mu\mu'}, \tag{B 10}$$

where

$$I^{\mu\mu'} = \int_{a; b; c} d\mathbf{r} r^\mu r^{\mu'}. \tag{B 11}$$

The product of two spherical functions is expressed as [16]

$$Y_{1\mu}(\hat{k}) Y_{1\mu'}(\hat{k}) = \frac{3}{\sqrt{[4\pi(2l+1)]}} C_{1010}^{l0} \sum_{l, m} C_{1\mu 1\mu'}^{lm} Y_{lm}(\hat{k}). \tag{B 12}$$

Substituting equation (B 12) into (B 11), we find the function  $\rho_{2m}(k)$ , defined by the relationship (B 6)

$$\rho_{2m}(k) = -\frac{k^2}{16\pi^{5/2}\sqrt{5}} C_{1010}^{20} \sum_{\mu, \mu'} C_{1\mu 1\mu'}^{2m} I^{\mu\mu'}. \tag{B 13}$$

Using equation (B 10), we carry out the integration and obtain  $I^{\mu\mu'}$

$$\left. \begin{aligned} I^{11} &= I^{-1-1} = \frac{abc}{24} (a^2 - b^2), \\ I^{1-1} &= I^{-11} = -\frac{abc}{24} (a^2 + b^2), \\ I^{00} &= \frac{abc}{12} c^2, \\ I^{10} &= I^{01} = I^{0-1} = I^{-10} = 0. \end{aligned} \right\} \tag{B 14}$$

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Comparing equation (B 13) with (B 7), we find

$$R_{2m}^0 = \frac{\sqrt{6}}{4} \sum_{\mu, \mu'} C_{1\mu, 1\mu'}^{2m} l^{\mu\mu'}. \quad (\text{B } 15)$$

Substituting into this equation the expression (B 14) for  $l^{\mu\mu'}$  and the tabulated values of the Clebsch–Gordan coefficients, we find

$$R_{20}^0 = -\frac{1}{2} \frac{abc}{24} (a^2 + b^2 - 2c^2),$$

$$R_{22}^0 = \frac{\sqrt{6}}{4} \frac{abc}{24} (a^2 - b^2),$$

$$R_{21}^0 = R_{2-1}^0 = 0.$$

### Appendix C

#### *Parametrisation of the orientational degrees of freedom*

Neglecting spin degrees of freedom, we regard molecules forming the system as classical asymmetric tops. We introduce a laboratory system of coordinates and molecular system of coordinates frozen into the  $j$ th molecule. We denote the coordinate column of an arbitrary vector  $\mathbf{A}$  in the laboratory frame as  $(\mathbf{A})_L$ , and in the molecular frame as  $(\mathbf{A})_{M-j}$  for the  $j$ th molecule.

Let  $\mathbf{R}_i$  be a vector frozen into the  $i$ th molecule and rotating with it. When the molecular and laboratory frames coincide, the vector  $\mathbf{R}_i$  coincides with a certain stationary vector  $\mathbf{R}_0$ , with that,  $(\mathbf{R}_0)_L = (\mathbf{R}_i)_L$ . It is clear that always

$$(\mathbf{R}_i)_{M-i} = (\mathbf{R}_0)_L \quad (\text{C } 1)$$

Orientation of the  $i$ th molecule is defined by the matrix  $\Omega_i$

$$(\mathbf{R}_i)_L = \Omega_i (\mathbf{R}_0)_L. \quad (\text{C } 2)$$

For an arbitrary vector  $\mathbf{A}$  we have

$$(\mathbf{A})_{M-i} = \Omega_i^{-1} (\mathbf{A})_L. \quad (\text{C } 3)$$

The relative orientation of the  $i$ th and  $j$ th molecules is defined by the matrix  $\Omega_{ij}$  such that

$$(\mathbf{R}_i)_{M-j} = \Omega_{ij} (\mathbf{R}_i)_{M-i}. \quad (\text{C } 4)$$

Knowing the matrix  $\Omega_{ij}$ , it is possible for every vector  $\mathbf{R}_j$  of the  $j$ th molecule defined in its molecular frame to construct the corresponding vector  $\mathbf{R}_i$  of the  $i$ th molecule. From the relationships (C 1) and (C 2) it follows that

$$(\mathbf{R}_i)_L = \Omega_i^{-1} \Omega_j (\mathbf{R}_j)_{M-j};$$

thus,

$$\Omega_{ij} = \Omega_i^{-1} \Omega_j. \quad (\text{C } 5)$$

Let us consider how the results would change if we defined the orientation of the  $i$ th molecular frame relative to the new laboratory system of coordinates. Let unit vectors of the new laboratory frame be the result of matrix  $C$  acting upon the unit vectors of the



original laboratory frame. Then the coordinates of an arbitrary vector  $\mathbf{A}$  in these systems are related by

$$(\mathbf{A})_{L-n} = C^{-1}(\mathbf{A})_L. \quad (C6)$$

According to equation (C3), the orientation of the  $j$ th molecular frame relative to the new laboratory frame is defined by the matrix  $W_j$  such that  $(\mathbf{A})_{M-j} = W_j^{-1}(\mathbf{A})_{L-n}$ . It follows from equation (A3) that

$$(\mathbf{A})_{M-j} = \Omega_j^{-1}C(\mathbf{A})_{L-n}.$$

Thus

$$W_j = C^{-1}q_j. \quad (C7)$$

Expression (C5) is invariant under the substitution  $\Omega_i \rightarrow C^{-1}q_i$ ,  $\Omega_j \rightarrow C^{-1}q_j$ . Consequently, the value of  $\Omega_{ij}$  does, in fact, define the relative orientation of the molecules and does not depend upon the choice of the laboratory system of coordinates.

The kernel (C3) of the integral transformation (C2) has the form

$$K(\Omega_{ij}) = K(\Omega_i^{-1}\Omega_j). \quad (C8)$$

This function is expanded over matrix elements of irreducible unitary representations of the group  $SO_3$  [16]

$$\begin{aligned} K(\Omega_{ij}) &= \sum_{l,m,m'} K_{mm'}^l \mathcal{D}_{mm'}^l(\Omega_{ij}) \\ &= \sum_{l,m,m'} K_{mm'}^l \sum_n \overline{\mathcal{D}_{mn}^l(\Omega_i)} \mathcal{D}_{nm'}^l(\Omega_j). \end{aligned} \quad (C9)$$

It is assumed that the molecules in the system are identical, therefore  $K(\Omega_{ij}) = K(\Omega_{ji})$ . Using the relationship (C9), we obtain

$$K_{mm'}^l = K_{m'm}^l.$$

In the physics of liquid crystals it is conventional to define the molecular orientation by parametrisation of the rotation transforming the laboratory into the molecular frame using Euler angles  $(\alpha, \beta, \gamma)$ , counted according to the scheme A, i.e. presenting a set of successive rotations (see figure C1):

- (1) rotation about  $OZ$  by an angle  $\alpha$  ( $0 \leq \alpha \leq 2\pi$ );
- (2) rotation about  $Y_1$  axis by an angle  $\beta$  ( $0 \leq \beta \leq \pi$ );
- (3) rotation about the new  $Z_2 = Z'$  axis by an angle  $\gamma$  ( $0 \leq \gamma \leq 2\pi$ ).

The matrix element of the irreducible representation  $\mathcal{D}_{mm'}^l(\Omega)$  is the Wigner rotation matrix  $\mathcal{D}_{mm'}^l(\alpha, \beta, \gamma)$ .

Finally, let us consider how our construction will be changed under a transformation to a new molecular system of coordinates, related to the same molecule. Let us define the new molecular frame, defining the matrix  $h$  such that for an arbitrary vector  $\mathbf{A}$

$$(\mathbf{A})_{M-n} = h^{-1}(\mathbf{A})_M. \quad (C10)$$

This definition corresponds to Euler angles defining the orientation of the new molecular frame being counted from the molecular frame axes. Comparing equations (C10) and (C3), we find

$$(\mathbf{A})_{M-n} = (\Omega h)^{-1}(\mathbf{A})_L.$$

Thus, the matrix  $\Omega h$  defines the orientation of the new molecular frame relative to the laboratory frame.

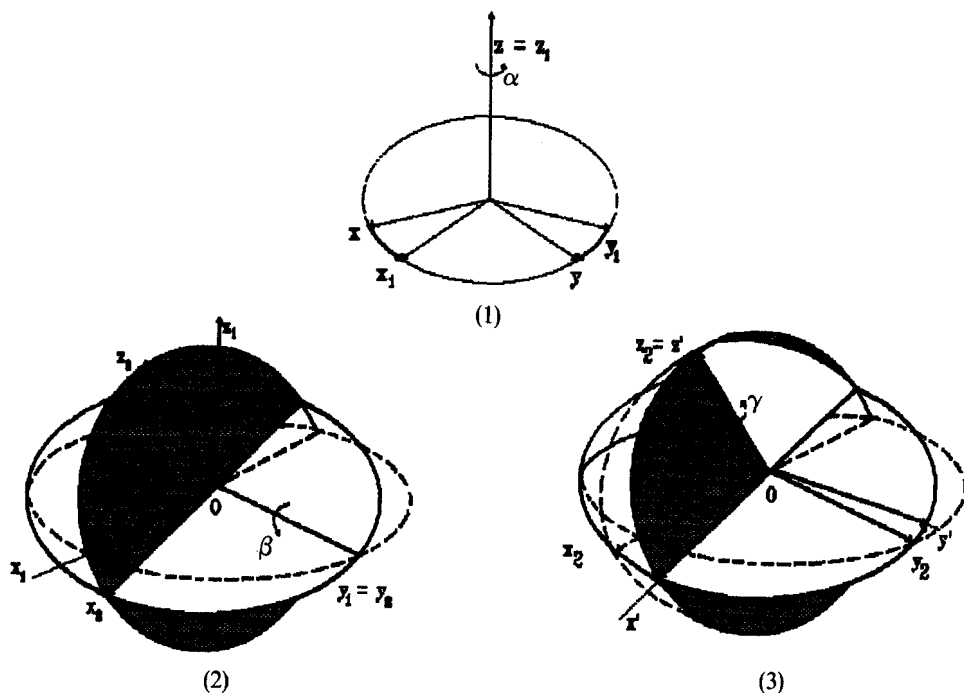


Figure C1. The notations defining the three Euler angle  $\alpha$ ,  $\beta$  and  $\gamma$ .

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