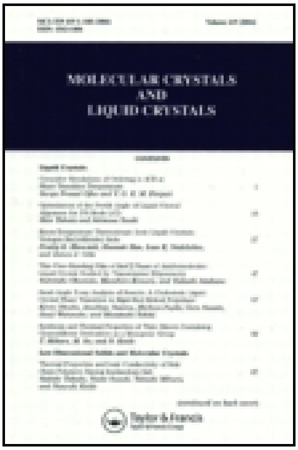

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On Theory of Order Parameters in (Nematic) Liquid Crystals Beyond Homogeneous Molecular Field Approximation†

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In this work there is presented a general theory of order parameters in liquid crystals beyond the homogeneous molecular field approximation, inclusive a new formula for C_V, and discussed in relation with Monte-Carlo based theories. There is shown that those two theoretical schemes are to some extend complementary. Numerical results for the temperature dependences of the average order parameter, "local order parameters" of individual molecules and C_V of a nematic with several different degrees of disorder are also deliberated.

The theory is then applied to the case of molecules of dyes in a nematic host in which the order parameter of the dye differs considerably relative to the order parameters of the host. Numerical results are given for several arrangements of the liquid crystal structure and discussed in relations with published experimental data. It is shown that by such an analysis there can be gained new information about the interatomic potentials.

Keywords: disorder, average and local order parameters, specific heat, anthraquinone dyes

I. INTRODUCTION

The problem of the determination of the order parameters in liquid crystals is related to a larger group of theoretical problems connected with the investigation of the behaviour of the order parameters in cooperative systems, in general. Among those belong, besides the order parameters in liquid crystals, also, for example, the magnetization in magnetic systems, the density parameter in liquid-vapour transitions, etc.

All those systems can be characterized by the Hamiltonian

$$H = \sum_{i\mu} H_{i\mu} a^{+}_{i\mu} a_{i\mu} + \sum_{ij\mu\nu} H_{i\mu j\nu} a^{+}_{i\mu} a_{j\nu} \tag{1}$$

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where $H_{i\mu}$ is the Hamiltonian of an isolated member of the system, for example a molecule or a spin (in an isolated molecule), at the site i in the state μ, $a_{i\mu}^{+}$ is the creation and $a_{i\mu}$ the annihilation operators of such a member, $H_{i\mu j\nu}$ is the Hamiltonian of the interaction between the molecule at the site i and its state μ with the molecule at the site j and the state ν.

Because the similarity of the general formulation of all those tasks there is possible to transfer modified treatments from one systems to another. In this work there were utilized, as explained below, some results of the works in the theory of amorphous magnetic materials.[1,2]

The problem of the order parameters in liquid crystals has been tackled mostly within the homogeneous molecular field approximation, applied either to a single lattice, or to several coupled lattices like in the case of the determination of the order parameters of binary mixtures of liquid crystals.[3,4] The latter problem is analogous to two lattice model in the theory of the magnetic crystalline materials.[5] There both the interactions within the same lattice and all the interlattice interactions are also assumed to be homogeneous.

However, the liquid crystals by their nature are not strictly crystalline because the centra of the molecules of which they constitute do not form a period lattice and the interactions between the molecules are subject to variations which need not to be small.[6] It is of an interest to investigate how much this feature effects the temperature behaviour of the order parameter in the liquid crystals.

That situation is similar, as pointed above to the task of the determination of the magnetization in amorphous magnetic materials.[1,2] There was shown that in such a case there should be employed a treatment which goes beyond the homogeneous molecular field approximation. One of the results of that investigation was that in the case of the inhomogeneous interactions among spins the temperature dependence of the magnitude of the projection of each spin into the direction of the total magnetization can differ strongly from spin to spin. When that result is projected back onto the problem of the ordered parameters in the liquid crystal it can provide, as shown below, an alternative qualitative explanation of the behaviour of the order parameters of a dye in a nematic liquid crystals relative to the order parameter of the host.[1,8]

The main problem to resolve is the size of the effect.

It can be provided by a modification of the quantitative treatment of the problem solved within the amorphous system of spins[1,2] to the investigation of the orientational properties of the molecules in the liquid crystals. Results of such a study is presented in this paper.

At first there is given a generalization of the Maier-Saupe equations for the nonhomogeneous task. Then there are presented numerical results of the solutions of those equations, and given analysis of some experimental data by the new theoretical scheme.

II. THEORY

Let us consider in detail a part of a liquid crystal–Figure 1.

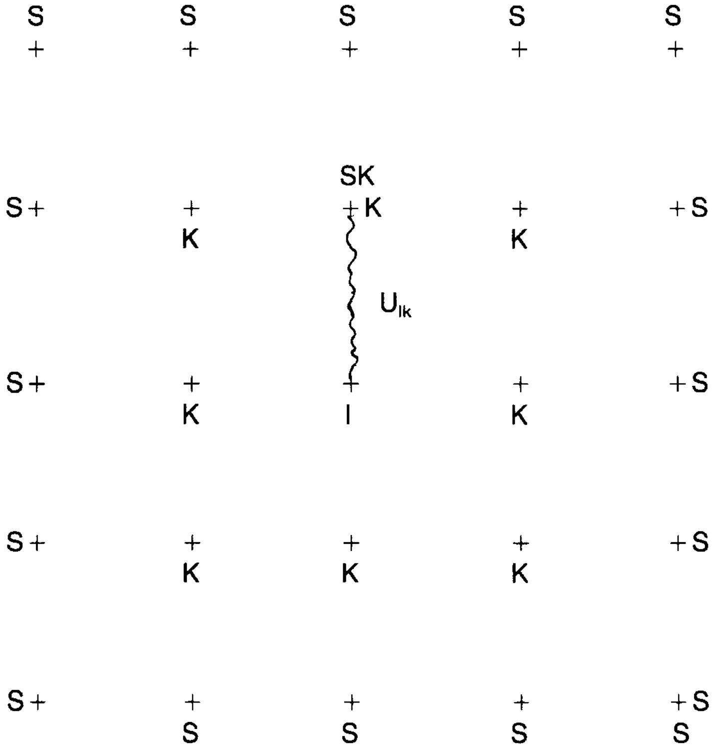

FIGURE 1 A schematic situation in the cluster in focus with its centre molecule l and its typical nearest neighbour k which has its local order parameter S_k. The regularity of the grid as depicted is not important. Any deformed grid topologically "congruent" with it, that is which preserves "to be a neighbour of", would do. S is the average-macro order parameter;

There is depicted a cluster of molecules of a liquid crystal. The topology of the distribution of the molecules in the picture is not essential. What there really matters physically, primarily, are the strengths of the intermolecular potentials (for an illustration see Figure 5 below), even when those are related, of course, through the potential function of the intermolecular interactions, to the spatial coordinates.

In the case of amorphous solids, or liquid crystals, the interactions of a molecule with its nearest neighbours can differ considerably from molecule to molecule. For that reason also the angles Θ_i of the director of a molecule at the site i relative to z-axis depends upon i; so the quantity[9]

$$S_i = 1 - \tfrac{3}{2}{*}\sin \Theta_i \tag{1}$$

which will be called the "local order parameter" of the molecule at the place i, or just "i-local order parameter".

The macroscopically measureable value of the order parameter of the whole liquid crystal—the "macro order parameter per a molecule" called further only the "average order parameter"—is then a statistical average of the local order parameters of all the molecules in the liquid crystal given by the formula

$$S = 1/N \sum_i S_i \tag{2}$$

where N is the number of the molecules in the liquid crystal (for a further theoretical discussion see the end of this section).

Within the nearest neighbours approximation each molecule is not exposed to any macroscopic molecular field acting upon it straight. It is subjected only to an ordering influence forced upon it through its interactions with its nearest neighbours, only. Because it is not subject to any direct interaction further than that the cooperative influence of the rest of the liquid crystal is communicated to it only through its nearest neighbours and, in an analogue with the works on amorphous magnetic systems,[1,2] that can be modelled by assuming that the "field" of the average order parameter S acts upon its next nearest neighbours (Figure 1).

In the nearest neighbour approximation the value of the local order parameter of an individual molecule is much more sensitive to the values of the local order parameters of its nearest neighbours than to the average-macro order parameter. For that reason such a situation is called a "soft core" model in contrast to the homogeneous molecular field approximation where the local order parameter is subject to the straight influence of the average-macro order parameter and equals it.[9,10] Such an approximation is strictly valid for a nearly perfect crystalline interactions only.

The average-macro order parameter is not much sensitive to the changes in the value of the local order parameter of any individual molecule.

Let us have the interaction between the molecules positioned at the sites l and k in the form of the Meier-Saupe potential given by the expression (for a discussion of the choice see below)[9,10]

$$\begin{aligned} U_{lk}(\Theta_l,\Theta_k) = \sum_{\mu,\nu} 1/(E_{oo}-E_{\mu\nu}) * (f_{o\mu} f_{o\nu} A(R_{lk})/R_{lk}^6 + (f_{o\mu}\delta_{o\nu} (1 - \tfrac{3}{2}\sin^2\Theta_l) \\ + f_{o\mu}\delta_{o\nu} (1 - \tfrac{3}{2}\sin^2\Theta_k)) B(R_{lk})/R_{lk}^6 \\ + \delta_{o\mu}\delta_{o\nu} (1 - \tfrac{3}{2}\sin^2\Theta_l)(1 - \tfrac{3}{2}\sin^2\Theta_k)) C(R_{lk})/R_{lk}^6) \end{aligned} \tag{3}$$

Here the axis z is chosen in the direction of the macro-director of the liquid crystal and Θ_k is the angle between the longest axes of the molecule at the site k with the z-axis, $E_{\mu\nu}$ is the energy difference between the state μ of the molecule at the site k and the state ν of the molecule at the site l, $f_{\mu\nu}$ is the oscillator strength of the transition $\mu \rightarrow \nu$, R_{lk} is the distance between the centre of mass of those two molecules. The quantities A,B,C are, in general, functions of that distance. Within this work, however, these functions have been taken to be constants.

Let us assume that we already know the solution of the nonhomogeneous case.

Then, because the relation (1) for S_i the potential can be written in the form

$$U_{lk}(S_l, S_k) = \sum_{\mu,\nu} 1/(E_{oo}-E_{\mu\nu})\,(f_{o\mu}f_{o\nu}A(R_{lk})/R_{lk}^6 + (f_{o\mu}\delta_{o\nu}\,S_l + f_{o\nu}\delta_{o\mu}S_k)\,B(R_{lk})/R_{lk}^6 + \delta_{o\mu}\delta_{o\nu}\,S_kS_l\,C(R_{lk})/R_{lk}^6). \quad (4)$$

For to be able to determine the values of S_i for all i of the molecules in the cluster in consideration there is necessary to supplement the scheme with the prescription of how to determine $\overline{S}_l$ which is given by the statistical average of the orientations of the molecule at the site l exposed to the nonhomogeneous interactions with its nearest neighbours. That is done by employing this iterative procedure.

Let any one of the positions of the nearest neighbours of the molecule at the site l is denoted by the letter k—see Figure 1.

For any fixed values of $\overline{S}_k$, known for example from the preceding step of the iterative relaxation of the whole system, the value of S_l can be calculated in the consecutive step by the formula

$$\overline{S}_l = (\langle S_l\rangle)_z = \frac{\int_\partial^{\pi/2} (1 - \tfrac{3}{2}\sin^2\Theta_l)e^{-\sum_{k\neq l} U_{lk}(\Theta_l,\overline{S}_k)/k_oT}\sin\Theta_l d\Theta_l}{\int_\partial^{\pi/2} \sin\Theta_l e^{-\sum_{k\neq l} U_{lk}(\Theta_l,\overline{S}_k)/k_oT} d\Theta_l} \quad (5)$$

where the interaction between the molecule at the site l and the molecule at the site k is given by the formula

$$U_{lk}(\Theta_l, S_k) = \sum_{\mu,\nu} 1/(E_{oo}-E_{\mu\nu})\,(f_{o\mu}f_{o\nu}\,A(R_{lk})/R_{lk}^6 + (f_{o\mu}\delta_{o\nu}\,(1 - \tfrac{3}{2}\sin^2\Theta_l) + f_{o\mu}\delta_{o\nu}\,\overline{S}_k)\,B(R_{lk})/R_{lk}^6 + \delta_{o\mu}\delta_{o\nu}\,\overline{S}_k\,(1 - \tfrac{3}{2}\sin^2\Theta_l)\,C(R_{lk})/R_{lk}^6) \quad (6)$$

Such a procedure can be now applied to any molecule of the "soft core cluster" of the liquid crystal, for example to one of the k-molecules above having now the l-molecule in the position of one of its nearest neighbours. When the position k is a site at the boundary, see Figure 1, instead of $\overline{S}_k$ there is substituted S given by the formula (2) calculated from $\overline{S}_i$ of the preceding iterative step. That makes the procedure self-consistent.

It results into a system of N simultaneous nonlinear integro-algebraic equations where N is the number of the molecules in the "soft-core cluster". Their solution provides us with the set of $\overline{S}_i$ for the given value of T and the form of the intermolecular potential–in this case (6). In the limit $N \rightarrow \infty$, the procedure is equivalent to an infinite site cluster approximation.

In the case of crystalline interactions there is obtained solution equivalent to that in one of the first works on this topic[10] for any value of N and thus there is sufficient to take $N=1$.

It is interesting to point out here that in the case of the homogeneous (crystalline) interactions the free energy of the ordering of the system is higher than when the condition of the homogeneous molecular field is released—amorphous system (liquid crystal).[11] It is because the condition of homogenity of the molecular field binds a part of the free energy to maintain the "totality" of matching the values of S_i to that field in the localities where it is not correct.

In principle the procedure is valid for any form of the potential function.

In the case of the homogeneous molecular field theories, there have been used, so far nearly exclusively, intermolecular potentials which are not r-dependent.

Let us consider, for an example, the expression for the potential U'_{Lkk} of the form

$$U^2_{Lkk}{}' = \rho \int dR_{12} 4\pi R^2_{12} U^{KK'}_{LLo}\,(R_{12}) g(R_{12})\,(2L+1)^{-1/2} \tag{7}$$

where $U^{KK'}_{LLo}\,(R_{12})$ is the true R_{12}-dependent intermolecular potential between the molecules at the positions 1 and 2, or rather between the molecules the center of gravity of which is at the positions 1 and 2, $g(R_{12})$ is the pair correlation function of the mutual positions of those molecules, ρ is the number density of the ordered phase and L an integer.

The function $g(R_{12})$ of a nematic liquid crystal has got a true liquid character especially along the director of the liquid crystal in question and so the positions of its molecules are highly irregular, as schematically sketched in Figure 1.[6,12] Thus there is of interest to investigate a scheme beyond the homogeneous molecular field approximation as presented above, and with it also to consider a kind of intermolecular potential which is R_{12}-dependent.

Such a R_{12}-dependency of the intermolecular potential comes from encounters of various chemical radicals of the long molecules of a liquid crystal as they contact each other with various distances of their centra of gravity. The "wiggly" and "spicky" character of those molecules[6,12] helps to maintain the inhomogenity of intermolecular interactions at a molecular scale, though at a macroscopic scale the results of those inhomogenities are averaged out, as expressed in equation (7).

However, so far there have not been published many different r-dependent potentials of liquid crystals.

In this work the Maier-Saupe potential was chosen for historical reasons, its straight physical relation to the quantum mechanical parameters of the molecules, and the fact that, unlike in the case of most of the pseudopotentials which have their r-dependences averaged out,[13-18] except in one case where the r-dependence is a simple s-like only,[19] it contains an explicit dependence upon the distance R_{lk} of the molecules at the sites l and k.

The fixed pinning of the director used in this work is not a disadvantage for even when that condition is released the macrodirector returns back into the laboratory z-director in the end of the calculation involved. Thus the lack of a full invariance of the Maier-Saupe potential is not a disadvantage.

The procedure is neither restricted to the nearest neighbours approximation, only. That approximation was chosen for its easy transparency, however, its assumption has not been essential anywhere. The scheme is valid for any short range interaction between the molecules of the liquid crystal. Only the span of the minimal "soft core" should be always larger than the range of the interaction.

It is important to solve the system (5) for a minimal size of the "soft core" cluster as possible, or necessary. In that respect there is substantial to remind here the results in the works on systems of spins.[1,2]

In those works there was shown, for the case of the clusters of spins in amorphous material that, when the fluctuations of the intermolecular interactions within the cluster in focus is equal to the fluctuactions of the intermolecular interactions within the whole material in question (such disorders will be called further "(mutually) equivalent disorder") the sufficient size of such a cluster for to produce an average order parameter (2) representative for the order parameter of the whole material in consideration is 9–16 spins for 2-D and 9–27 spins for 3-D, independent of the particular detailed configuration of the cluster (see below some illustrations).

It means that when there is computed the average order parameter of a cluster of 9 spins any enlargement of such a cluster to 25 spins, in 2-D, or 27, in 3-D, does not produce significant changes in the numerical results for the value of the average order parameter.

That is a very important correspondence between the average characteristics of the clusters of a finite size obtained from such a computation and the bulk properties of the material in consideration (with mutually equivalent disorder).

It makes possible to apply the statistical mechanics to an ensemble of clusters containing a given number N ($N > 9$–16 in 2D, or $N > 9$–27 in 3D) of spins and mutually equivalent disorder in a similar way as that is done for the individual spins in the case of the homogeneous molecular field approximation.[5]

Then:

1) the average value of the local order parameters in each such a cluster has its value and temperature behaviour same as in any other cluster of that group and equal to the value and temperature dependence of the average order parameter of the whole bulk—each of them, regardless its detailed spacial structure, represents the average property of the bulk;[1,2]

2) each special configuration of the given cluster of N spins will occur as often in the bulk as that is given by the N-particle correlation function related to the configuration of the cluster and that makes possible to justify the introduction of the local order parameters, and define their statistical meaning, as it has been done above (equation (1)). Each of such clusters can be taken for a representative cluster of all the group of such clusters in the bulk.

Because the system of equation (5) is in its mathematical structure similar to the system of equations analysed in the works on systems of spins[1,2] that result originally found for those systems holds also for the liquid crystals.

Here notice in Figure 1 that the number of the molecules within the "soft core" used in this calculation was, as in those works,[1,2] effectively 25 and thus the numerical results presented below are well representative for a bulk nematic liquid crystal with the same size of the fluctuations of the intermolecular potential in it as in the core cluster.

Even when one has to solve the systems (5) for higher number of atoms than 5 or 4 as in some works published earlier[13,20] the size of the core cluster in the "soft core" model is manageable.

The self-consistent condition (2) guarantees that for the "soft-core clusters" of any size, however small, the surface effects[17] do not change the character of this study which is concerned with the influence of the positional disorder for the bulk properties of the order parameter(s) of liquid crystals, only.

Here there is interesting to put into a relation the present work with works which used the Monte-Carlo method.[21-24] It is to point out here that the Monte-Carlo method gives fluctuations of *i*-local order parameters even for the crystalline interactions. These fluctuations monitor the effect of the thermal noise upon the uniformity of the homogeneous molecular field. Within the heuristic approach the solution of the Maier-Saupe equation,[10] or the Weiss equation in the case of the magnetic materials,[25,26] do not provide for those fluctuations and they have to be determined separately by using the fluctuation-dissipative theorem.[26]

In the case of the positional disorder the Monte-Carlo method does not give qualitatively different results for the fluctuations of the *i*-local order parameter to those for the crystalline case. These fluctuations are likely to be bigger and less homogeneous than in the crystalline case with the same temperature. However, they contain simultaneously the fluctuations due to both the thermal noise and the disorder in interactions. The Monte-Carlo methods cannot discern, then, these two kinds of the cause of those fluctuations.

On the contrary, the kind of the theory presented here, the generalized molecular field, provides, in an analogy with the simpler case, only the fluctuations of the *i*-local order parameters caused by the randomness in the intermolecular potentials. Thus when those are determined, as shown below, and subtracted from the total fluctuations of the *i*-local order parameters found out by the Monte-Carlo method for the same temperature and size of the fluctuations of the intermolecular potentials there can be obtained the size of the thermal fluctuations in the case of the disorder, unaccessible otherwise.

III. NUMERICAL RESULTS

It was reasoned above that the approximation of the homogeneous molecular field is equivalent to a situation within a kind of an abstract crystal in which the interaction of every molecule or atom with all its nearest neighbours is same and equal to the average value of the intermolecular interactions.

For that reason to be able to express simply the impact of the disorder upon the order parameters, both local and the average (macro) ones, of a nematic beyond the homogeneous molecular field relative to the situation within a homogeneous molecular field, the distribution of the molecules within the liquid crystal was constructed upon the background of a regular (here cubic) reference grid, of its lattice constant R_{av}, off which the real distribution of the molecules in a cluster of the liquid crystals was obtained by a simulated "tossing" via a generator of random numbers from the intervals $({}^{\alpha}R_i - dr,\ {}^{\alpha}R_i + dr)$, for all i, where ${}^{\alpha}R_i$ is the α-component of the coordinate of an *i*-node of the grid and *dr* is the maximal linear deviation of a molecule from the node.

Though for a small *dr* the disordered distribution is very close to a crystalline grid, slightly "dishevelled" only, for a large *dr* the distribution is near to a purely random, or amorphous distribution, which lost the information of its relation to the original grid. In this calculation, however, there was checked so that even the most randomized distribution of the molecules used in the calculation did not lose the topological properties of the original grid—that is so that the property of a molecule to be a nearest neighbour to an another molecule was not changed.

When r_i is the actual position of an *i*-molecule of the cluster then the relative square deviation of the distance of the nearest neighbours from the average lattice spacing R_{av} which actually characterized the size of the disorder in the liquid crystal is given by

$$\Delta r = \left(\sum_{i=j\pm 1} (r_i - r_j)^2 - R_{av})^2 \right)^{1/2} / R_{av} \tag{8}$$

As further characteristics of various properties of the clusters there were used, similarily to the clusters of spins,[1,2] these quantities:

a) the average interaction

$$U_{av} = 1/N_I \sum_{l,k} U_{lk}(\Theta_l, \bar{S}_k) \tag{9}$$

here N_I is the number of the pair exchange interactions within the cluster;

b) the relative square deviation of the fluctuation of U_{lk} from U_{av}:

$$dU = \left(\sum_{l,k} (U_{lk} - U_{av})^2 \right)^{1/2} / U_{av} \tag{10}$$

The nearest neighbours approximation was imposed by the condition

$$U_{ij} = 0 \quad \text{for} \quad i \neq j \pm 1 \tag{11}$$

(a cut-off of the Maier-Saupe potential for longer distances than that of the nearest neighbours).

Firstly, in Figures 2–4, there are presented typical results of the temperature dependences of the average (macro) order parameter and the local order parameters in the middle plane of 3-D clusters for three values of *dr*. However here, for the sake of presentation there was applied the full relaxation according to the scheme described above to the order parameters of the presented plane, only. The rest of the "distorted cube" had been exposed straight to the overall order parameter. Such a system is symmetrical relative to the plane of interest.

By that simplification there was obtained a planar sample for presentation here (Figure 1), yet, there was retained the 3-D character of the system and the related solution for the local order parameters within it. For nematics such a simplification is not uncharacteristic.

In Figure 5 there are given the distributions of the pair interactions within the plain of the interest for two different choices of the constants A, B, C in the Maier-Saupe potential (6)–one such a choice as used in the figures 2–4, the second one as used in the Figures 8&9–and two values of dr. There is there also given the numbering of the molecules within the core cluster.

There is important to realize here that the local order parameters appear explicitely in the potential (6), unlike in the case of potentials within a systems of spins, which gives more "liquid" character to the Maier-Saupe potential relative to the exchange potential between spins.[1,2] For that reason the numerical values of those interactions given in Figure 5 change with T. Their values provided in Figure 5 are for $T=0$.

The rest of the interactions (in the direction orthogonal to the plane) were put to be equal U_{av}.

In the caption of Figure 5 there are given also the values of dU and Δr. From them there may be noticed that relatively small values of Δr cause much bigger values of dU as the potential U_{ik} is strongly R_{ik} dependent. Thus, a rather small disorder in positions of the molecules, not easily detectable by the scattering ex-

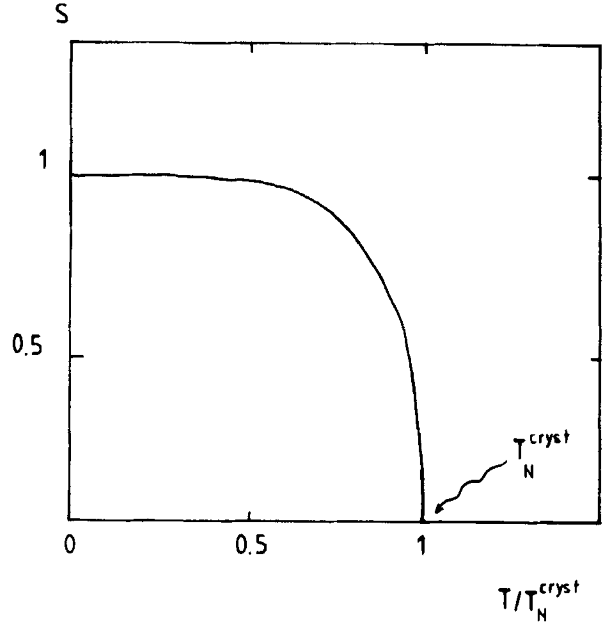

FIGURE 2 The temperature dependence of the average-macro order parameter S for the regular grid—related to both the clusters in Figures 5a and 5b—their crystal-like case; T_N^{cryst} denotes the crystalline nematic transition temperature T_N.

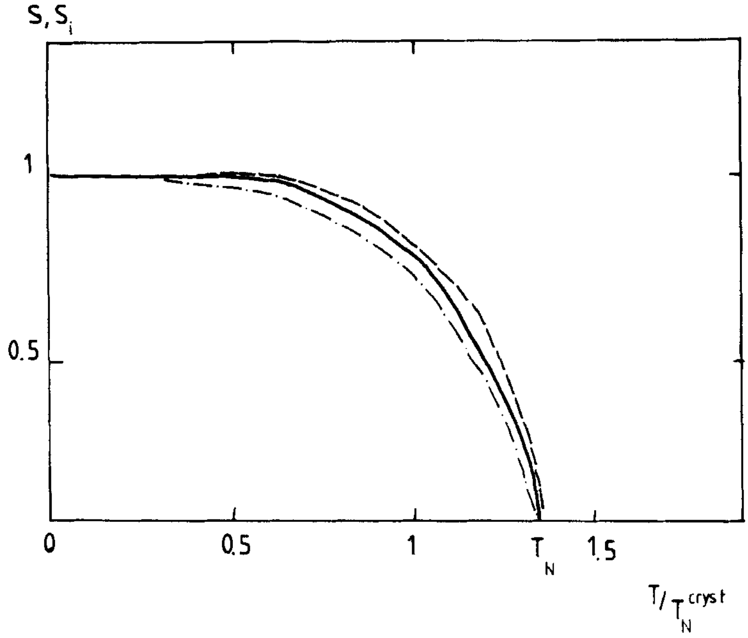

FIGURE 3 The temperature dependence of the local order parameters S_i and the average-macro order parameter S (thick line) of the molecules in the cluster depicted in Figure 5a ($dr = 0.1$) for A = $T_N^{cryst}/16$, B = $T_N^{cryst}/2$ and C = $15 * T_N^{cryst}/2$, $f_l = f_2 = 1$ (same as in figure 4)—the numbering of the molecules is as in Figure 5c; T_N^{cryst} is the related crystalline T_N to the Figure 2; the broken line is $S_i(T)$ of the molecules 8,9, the chain line of the molecule 2. The thick line represents also $S_i(T)$ of the molecules 1,3,4,5,6 and 7.

periments, causes much larger fluctuactions of the intermolecular interactions. Because in the Hamiltonian of the liquid crystal there appear straight only the quantities U_{ij} and not the positions R_i and R_j then dU and not Δr are those which effect most of the physical properties of the liquid crystals, the order parameters inclusive.

As a result of that the temperature dependence of the average order parameter does not depend upon the actual positions of the molecules but only upon the magnitude of dU generated by Δr (upon the magnitude of the "equivalent disorder" related to it). Thus precise real setting of the molecules is not necessary for the kind of study presented in this work. Any randomly generated cluster which has an equivalent disorder (the same size of dU) to the quenched disorder will do.

For that reason the positions of the molecules were not relaxed to fulfil exactly the conditions for the quenched disorder of a real liquid crystal. Besides, it is a task of a higher numerical order of complexity to that presented here.

From Figures 2–4 there is interesting to notice these points:

a) that the temperature T_N, the lowest temperature at which the overall order parameter acquires zero value, increases with the degree of disorder, similarly to the case of amorphous systems of spins.[1,2]

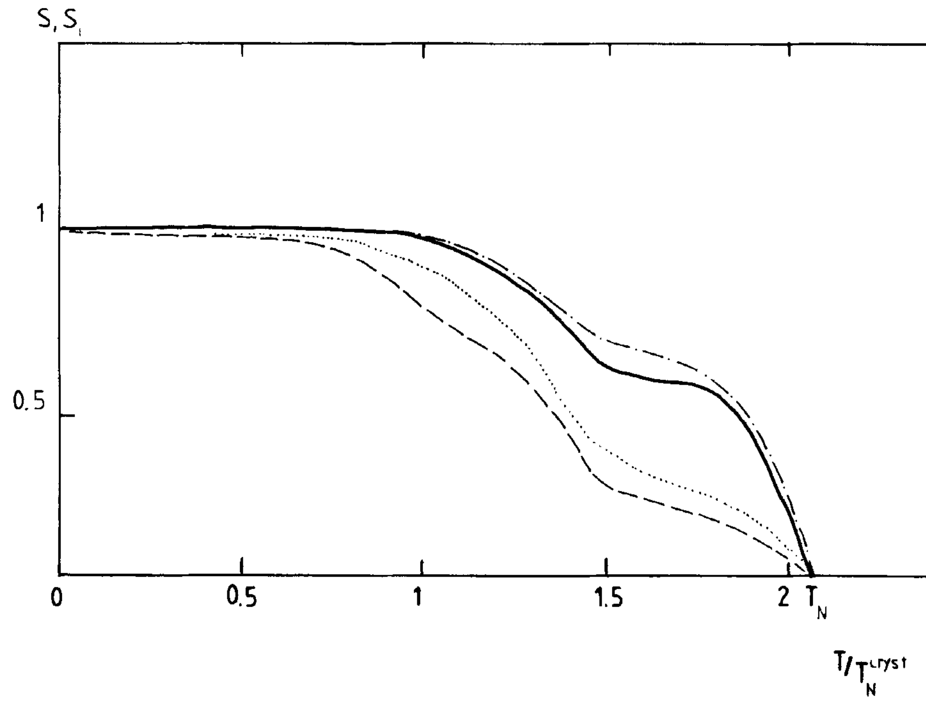

FIGURE 4 The temperature dependence of the local order parameter S_i and the average-macro order parameter S (thick line) of the molecules in the cluster with its $dr=0.2$ and $A=T_N^{cryst}/16$, $B=T_N^{cryst}/2$ and $C=15*T_N^{cryst}/2$, $f_i=f_2=1$ (same as in Figure 3)—the numbering of the molecules is as in figure 5c; T_N^{cryst} the related crystalline T_N—see figure 2; the chain line is $S_i(T)$ of the molecules 3,6,8,9, the broken line of the molecule 2 and the dot line of the molecule 1. The thick line represents also $S_i(T)$ of the molecules 4,5 and 7.

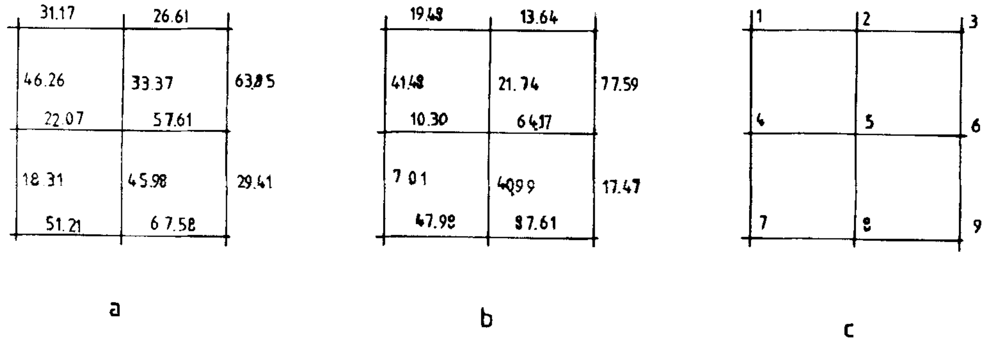

FIGURE 5 Distribution of the pair nearest neighbour interactions in 2-D clusters of nine molecules: a) with $dr=0.1$ and $A=T_N^{cryst}/16$, $B=T_N^{cryst}/2$ and $C=15*T_N^{cryst}/2$, $f_i=f_2=1$ for which $dU=0.386$ and $r=0.068$; b) with $dr=0.2$ and $A=0.09*T_N^{cryst}/26$, $B=2.1*T_N^{cryst}/26$, $C=41.7*T_N^{cryst}/26$, $f_i=f_2=1$ for which $dU=0.712$ and $r=0.131$. Here T_N^{cryst} is the related crystalline T_N of the particular sample (see the figure 2).

It is because the molecules for which $S_i > S$ cause the molecules with $S_i < S$, for example the molecule no. 2 in Figure 4, to have the values of their S_i nonzero even when the strength of their local interactions U_{ij} with their nearest neighbours, measured by the average value $\overline{U}_i$ of those U_{ij}, would not support those values outside the liquid crystal, for example within a crystalline grid in which the intermolecular interactions is set to be equal to $\overline{U}_i$.

b) due to that aspect the slope of the curve of the temperature dependence of $S(T)$ decreases with increasing disorder thus indicating that the alignment of the molecules, while the liquid crystal approaches the phase transition from the low temperature direction, loses its coherency and, in an analogy with the systems of amorphous spins,[1,2] the phase transition becomes more "smeared".

In detail, from the point of view of some recent works on binary mixtures[3,4] which belong all within the homogeneous molecular field concept which does not take into the account the fluctuations in the clustering of the mixture[27,28] and/or the off-diagonal randomness,[28,29] one can view the strongly disordered liquid crystals as if consisting of several distinct groups of "components": one main one, here "dishevelled", represented by the molecules 4,5,7 in Figure 4, which just happen to have their $S_i = S$ and several minor ones, with their members (molecules) having both their $S_i < S$, for example the molecules 1,2 in Figure 4, and their $S_i > S$, for example the molecules 3,6,8,9, there.

These "component" are only an abstract grouping of the molecules with a similar temperature behaviour of S_i. They do not need to have more than one nearest neighbour, if any at all, of the same group. However, they are all "nimbly" interconnected by nonzero interactions, see in Figure 5a, so they cannot be considered for mutually free (noninteracting) domains. The whole cluster forms an entirely interconnected entity organized relative to the same main director.

It is of an utmost interest to link the temperature dependences of $S_i(T)$ of the molecules of the core cluster, described above, with the temperature dependence of C_V which is an quantity accessible experimentally.

C_V can be calculated from the equation (4) according to the formula

$$\begin{aligned} C_V = (\partial E/\partial T)_V = \sum_{l,k} \sum_{\mu,\nu} 1/(E_{oo} - E_{\mu\nu})* \\ ((f_{o\mu} f_{o\nu} \delta_{o\nu} \partial S_l/\partial T + f_{o\nu} \delta_{o\mu} \partial S_k/\partial T)B \\ + \delta_{o\mu}\delta_{o\nu} (S_k \partial S_l/\partial T + S_l \partial S_k/\partial T)C)/R_{lk}^6 \end{aligned} \tag{12}$$

where there was taken $E = \sum_{l,k} U_{lk}$.

When one compares that formula with the one for C_V of the systems of amorphous spins[11] the main difference is that in the equation (12), just above, there are additional linear terms in $\partial S_i/\partial T$, to that quadratic ones which are present in both the cases.

In Figures 6 and 7 there are given the temperature dependences of C_V according to the equation (11) for the cases depicted in Figures 2–4. In Figure 6 for the

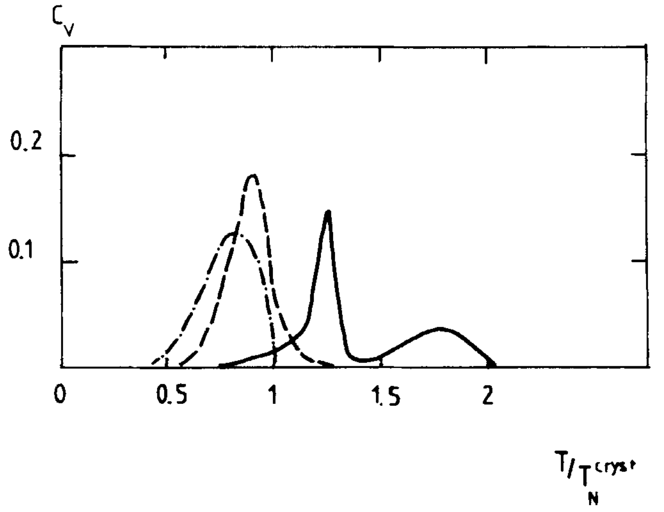

FIGURE 6 The temperature dependence of $C_V(T)$ of the clusters the $S_i(T)$ are presented in figures 2–4. The chain line is for $dr = 0$ (figure 2), the broken line for $dr = 0.1$ (Figure 3) and the full line for $dr = 0.2$ (figure 4). All the curve were normalised to 1 so the C_V is given in dimensionless units. The unit of temperature is T_N; to show the absolute positions of the peaks in C_V in that units.

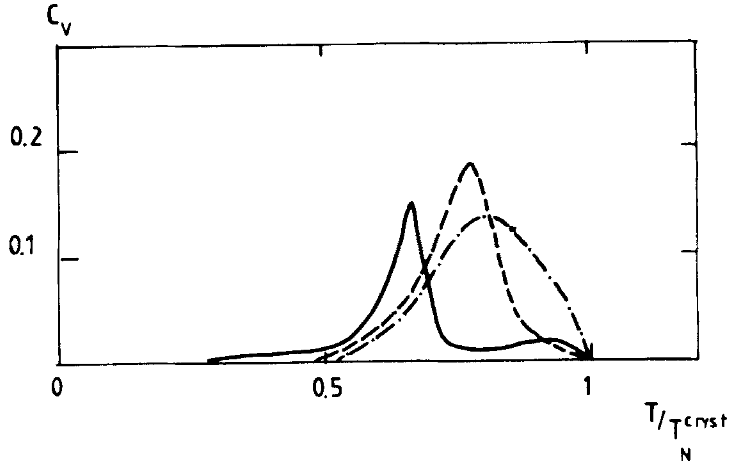

FIGURE 7 A temperature dependence of $C_V(T)$ related to that depicted in Figure 6. The only difference is that in all cases the $T_N = 1$; to show positions of the peaks of C_V relative to their own T_N. All the other features are same as in the Figure 6.

temperature unit was chosen T_N; in Figure 7 there are set T_Ns of all the case to be equal to 1 (see their captions).

From these figures there are of an importance these points to be noticed here:

1) in the case of the lower disorder, $dr=0$ and $dr=0.1$, there is only one peak in the temperature dependence of C_V;

2) in the case of a higher disorder, here for $dr=0.2$, there appear two peaks–one principle one which is higher and corresponds to that single peak ad 1), and one secondary one, which is much lower and more difused than the main peak. The side peak occurs closer to T_N than the principle one. In a comparison with the temperature dependence of C_V of the amorphous systems of spins the peaks of C_V of the liquid crystals are sharper. It is due to the linear terms in $\partial S_i/\partial T$ in the formula (12). They are chiefly responsible for those peaks. In the quadratic terms the factor $S_i<1$ "blunts" the factor $\partial S_i/\partial T$.

3) Not even in the crystalline case, Figure 2, there occurs anything close to the λ-type transitions observed in the case of crystalline systems of spins.[25,26] It is because for the liquid crystals not even in this case there holds $\lim_{T\to TN-} dS/dT = -\infty$; like for the systems of spins. In the nematic liquid crystals $\lim_{T\to TN-} dS/dT$ is known to be finite.

4) $C_V(T)$ is a smooth function of T in all the cases and thus in neither of those cases there was found any real phase transition of the second order;[31]

5) as seen from Figure 7 the stronger disorder is the more distant from T_N, in the relative units same for all the cases, the principle peak is; and becomes narrower.

6) when the temperature $T_P<T_N$ at which there occurs the maximum of a peak in $C_V(T)$, especially of the principle peak, is taken for an indication of the phase transition, as that is in the case of bulk measurements, like those of C_V,[11] and not T_N which is more difficult to indicate experimentally, than there can be found the long distance order even above thus experimentally defined transition temperature T_P.[32] In that there is a way of an explanation of why some of the "components" with their S_i higher than S may be observable even for $T > T_P$. The present theory provides a more natural explanation of so called "metastable phases".

The properties of the order parameters of liquid crystals summarized in the point above had been extracted from the numerical investigation of a large number of similar clusters of same dr as those depicted and they are rather of a general holding.

For an additional illustration of the summarized points in Figures 8 and 9 there is presented an another example of $S_i(T)$ of such clusters for a different choice of parameters A,B,C of the Maier-Saupe potential given in their captions.

Here, although the ratio T_N/T_N^{cryst} is approximately same for $dr=0.2$, Figure 9, as in the previous case, Figure 4, and related to the size of the constant C, which is the dominant one from those three constants in the equation (4), for $dr=0.1$, figure 8, it is smaller than in Figure 3. That indicates that the size of the constants A,B influence the sensitivity of the average-macro order parameter upon the deviation of the disordered (amorphous) grid from the regular one.

For example when A is much bigger than the other two constants there is effectively eliminated all the angular dependence in the potential (6). On the other hand, when A is small the angular dependence is not dwarfed by that constant

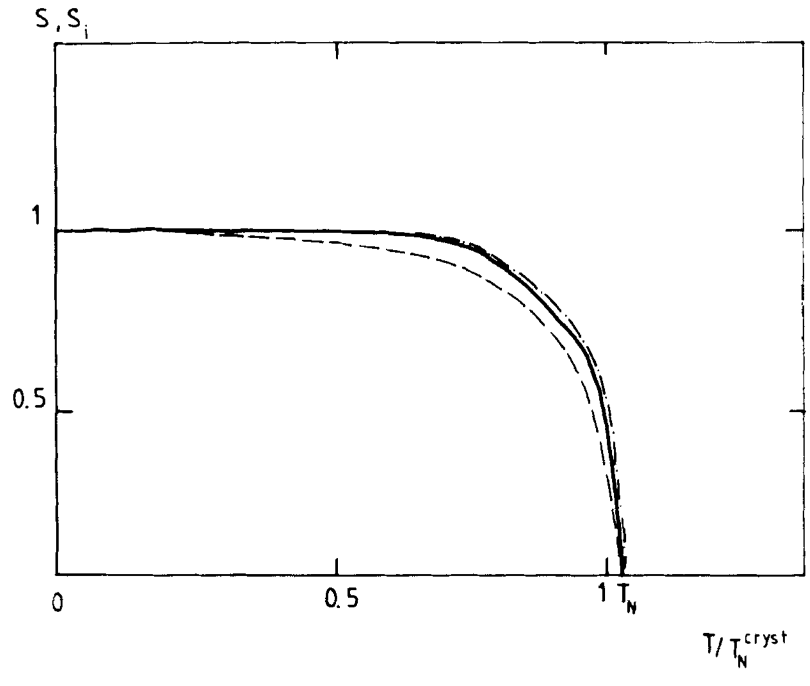

FIGURE 8 The temperature dependence of the local order parameters S_i and the average-macro order parameter S (thick line) of the molecules in the cluster with its $dr = 0.1$ and $A = 0.09 * T_N^{\text{cryst}}/26$, $B = 2.1 * T_N^{\text{cryst}}/26$, $C = 41.7 * T_N^{\text{cryst}}/26$, $f_l = f_2 = 1$ (same as in the figure 7)—the numbering of the molecules is as in the figure 5c; T_N^{cryst} is equal to the related crystalline T_N—see figure 2; the chain line is $S_i(T)$ of the molecules 8,9, the broken line of the molecule 2. The thick line represents also $S_i(T)$ of the molecules 1,3,4,5,6 and 7.

like in the previous case. Generally the angular roots of the equation $U_{lk}(\Theta_l(\overline{S}_k), \overline{S}_k) = 0$ depends upon the balance of those three constants. Because of that the relative sizes of the constants A, B and C have an impact upon the angular dependence of the potential (6). That property shows stronger, through the inhomogeneous values of $\overline{S}_l$ in the equation (6), when a stronger positional disorder is present.

An another example of demonstration of the influence of the mutual balance of the constants A, B, C upon the shape of $S(T)$ there is the appearance of the "plateau" near T_N in $S(T)$, in some cases, like in Figure 9.

Thus, in principle, a study of the dependence of T_N, T_N/T_N^{cryst} and the temperature dependences of the order parameters of a given liquid crystal upon dr could help to provide data for determination of its constant A, B, C, and to gain more detailed information about its intermolecular interactions, approximated by the Maier-Saupe potential (6).

Because most of the experiments are set in such a way that the average order parameter of the whole sample, in our case the direction of the director against which the orientations of the molecules of the cluster in consideration are defined, is oriented along one of the axis of the Cartezian laboratory coordinate system[33]

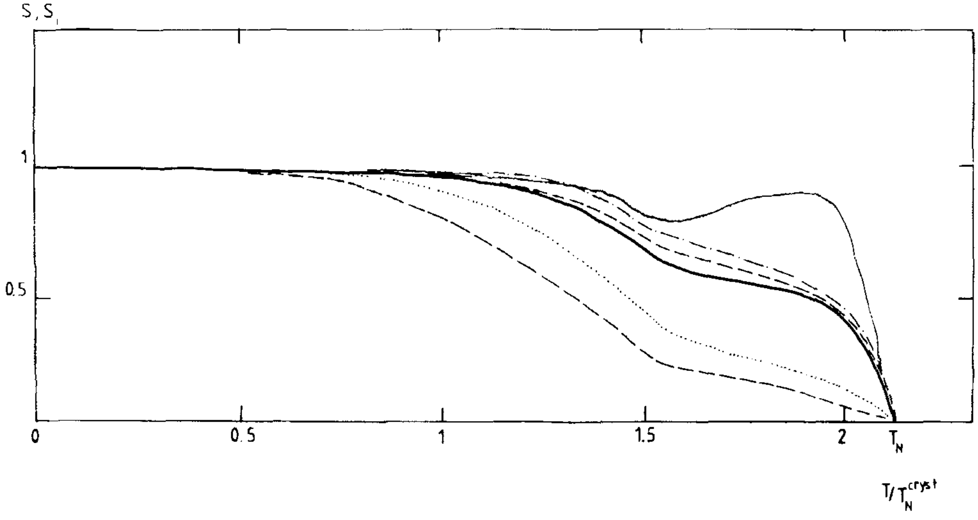

FIGURE 9 The temperature dependence of the local order parameters S_i and the average-macro order parameter S (thick line) of the molecules in the cluster with depicted in Figure 5b ($dr=0.2$) and $A=0.09*T_N^{cryst}/26$, $B=2.1*T_N^{cryst}/26$, $C=41.7*T_N^{cryst}/26$, $f_l=f_2=1$ (same as in the Figure 6)—the numbering of the molecules is as in the Figure 5c; T_N^{cryst} is equal to the crystalline T_N—see Figure 2; the chain line is $S_i(T)$ of the molecules 3,8 and 9, the broken line above the thick line of the molecule 5,7, the broken line below the thick line for the molecule 2, the dot line for the molecule 1 and the thin full line of the molecules 6. The thick line represents also $S_i(T)$ of the molecules 4.

the fact that the Maier-Saupe potential (6) is not invariant to a general transformation of the coordinate system is not here a sever disadvantage. Such a setting will be assumed in the application of the general theory presented above to the analysis of some experimental data below.

As pointed earlier the features summarized above are representative for any cluster in focus of the materials in question which has the same U_{av}, dU and A,B,C as the clusters discussed here. The only difference could be in the location of those molecules with the extreme behaviours of their local order parameters, like molecule Nos. 1,2,3,6,8,9 in Figure 4 and all the molecules but No. 4 in Figure 9, in that cluster in focus.

Both the theory presented in the section II, and the experimental results presented in this section, are valid for any kind of liquid crystals with disorder equivalent to that used within this section. That included also binary mixtures which are not crystalline,[3,4] but a kind of binary substitutional alloys.[28,29,34]

IV. ORDER PARAMETERS OF DYE MOLECULES IN A HOST (ANALYSIS OF EXPERIMENTAL DATA)

There is interesting to notice that the values of the local order parameters of some of the molecules, those with considerably different interactions with their nearest neighbours from U_{av}, differ substantially from the values of the average-macro

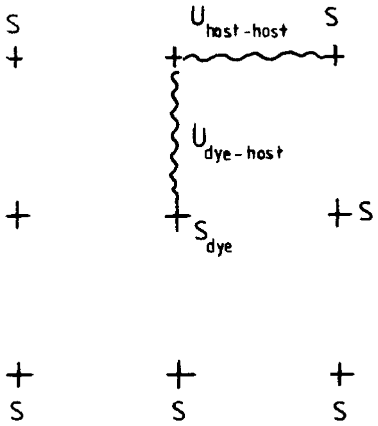

FIGURE 10 A cluster consisting of one molecule of a dye surrounded by its nearest molecules of the host which have their order parameter equal to S. For the rest of the notation see the text.

order parameter. That can provide a quantitative explanation of the anomalous behaviour of the order parameter of a molecule of a dye in a nematic host.[7]

In that work there were studied the dependence of the temperature behaviour of the order parameters of two anthraquinone dyes upon their interaction with various cyano and noncyano two ring nematic hosts. It was found there that the order parameters of those dyes can be both greater or lesser to those of their host. Within the pseudopotential treatment when the molecules are considered for rigid bodies those differences were explained qualitatively,[7] is to be caused by the differences in shapes and sizes of the molecules of those dyes relative to the shapes and sizes of the molecules of their host.

However, to prove that mathematically one cannot stay, in principle, within the homogeneous molecular field concept. Because the shapes and sizes of the molecules are different the positions of the centre of gravity of those dye molecules become disordered relative to the crystalline grid of the pure host and the philosophy of this work should be employed.

When the concentration of the dye is very small, below 1%,[7] its molecules cannot form a physical grid because their mutual distances are too large for them to interacts mutually and so for to explain the anomalous behaviour of the order parameter of a dye in a host[7] there cannot be used a two grid model.[3 4] Each molecule of the dye is effectively on its own and there can be used the following scheme which is a special case of the general theory presented above:

Let us consider in detail the situation when there is placed a single molecule of a dye into a liquid crystal host. Let $I_{\text{dye-host}}$ is the interaction of the molecules of the dye and the host which is, generally, much different to the interaction $I_{\text{host-host}}$ of the molecules of the host mutually (Figure 10).

For such a situation there is produced, at first, the best least square fit of the average-macro order parameter of the host by varying the constant A, B and C in U_{lk}—the expression (6).

Then, a molecule of a dye is substituted into the central position of the cluster in focus (Figure 10) and the interaction $I_{\text{dye-host}}$ is varied to reach the least square fit of its local order parameter to the order parameter of the dye.

By that procedure there can be determined the ratio $I_{\text{dye-host}}/I_{\text{dye-dye}}$.

In such a procedure there is convenient to take a slightly different form of the potential (6). Namely

$$U_{lk}(\Theta_l,S_k) = \sum_{\mu,\nu}{}' 1/(E_{oo}-E_{\mu\nu}) * A_1(R_{lk})/R^6_{lk} + B_1\,\delta_{o\mu}\,(1 - \tfrac{3}{2}\sin^2\Theta_l)/R^6_{lk}$$
$$+ r_f B_1 \overline{S}_k\,\delta_{o\nu}/R^6_{lk} + \delta_{o\nu}\delta_{o\mu}\,\overline{S}_k(1 - \tfrac{3}{2}\sin^2\Theta_l)C/R^6_{lk}) \quad (13)$$

with $A_1=Af_{o\mu}f_{o\nu}$, $B_1=Bf_{o\mu}$ and $r_f=f_{o\mu}/f_{o\nu}$. The parameters of the variation within the least square fit are A_1, B_1 and C. Their values give us information about the intermolecular potential (6).

When the intermolecular distance is given in terms of the average lattice constant R_{av} then, instead of A_1,B_1 and C, there are to be taken the quantities $A_a=R_{av}A_1$, $B_a=R_{av}B_1$ and $C_a=R_{av}C$ to safeguard so that the expression (13) has the dimension of energy.

The results of a schematical application of that scheme to the order parameters of the antraquinone dyes in a nematic host are given in Figure 11.

From them one can estimate that the dyes with higher values of its local order parameter than those of the order parameter of the host[7] have their ratios $r_d=I_{\text{dye-host}}/I_{\text{host-host}} = 1.3$. The case of the low behaviour of the local order parameter, there, corresponds to the value $r_d=0.8$.

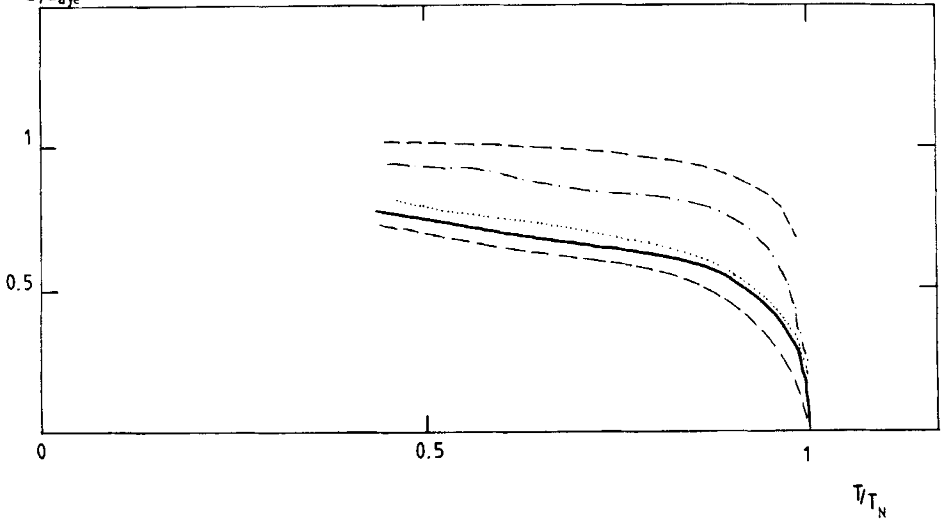

FIGURE 11 The temperature dependence of the order parameters of the host and the molecule of the dye for the situation depicted in figure 9 for $A_1=1$, $B_1=20$ and $C=125$, $dr=0.2$ and various values of r_d;

The fit of those data[7] by the scheme described above could not been achieved close enough to gain more than the values of the relative characteristics of the interactions within the liquid crystal guesting a sparse amount of dye molecules, such as the values of r_d, and not the absolute values of the constants A_1, B_1 and C. Nevertheless even such a limited gain is usefull and not easily accessible by other methods.

V. CONCLUSION

In this work there was outlined a theory of the order parameters in nematic liquid crystals beyond the homogeneous molecular field approximation and shown that it provides a framework of how to learn more about the nature of the intermolecular interactions in them.

Though it was primarily designed for to deal with the case of anthraquinone dyes in a nematic host,[7,8] see the paragraph 4, its general results have implications of a wider interest of a "forward" character.

The present calculation could be modified also for the smectic phase. It means, however, also relaxation of the positions of the molecules and recalculation of the intermolecular potential, a task which has been beyond the scale of the present work.

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