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MICROSCOPIC ORDER PARAMETERS IN LIQUID CRYSTALS

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Microscopic order parameters based on the pair molecular interaction are introduced. They are defined as the expansion coefficients of the Mayer function f_{ij} to the series of the Wigner rotation functions. The temperature behaviour of microscopic order parameters offers a new qualitative view on phase transitions and on pretransitional effects in condensed phases. The order parameters offer a unified view of the translational, directional and orientational microscopic structure of phases. A preliminary analysis of various aspects of an orientational microscopic structure of nematics is presented. Distinguishing between directional and purely translational microscopic ordering, the work gives also a new insight into the origin of the translational structure in smectic and columnar liquid crystals.

I. INTRODUCTION

Order parameters characterize the structural order and the physical properties of liquid crystals. They have been introduced to quantify the degree of the ordering of "intermediate", i.e. liquid crystal phases in comparison with the perfect order of ideal crystals [1].

The known number of different types of liquid crystal structures continuously increases. To describe them adequately it is necessary to introduce new order parameters [2].

The greater number of conceptions and definitions of orientational and translational order parameters and their mathematical description is known [1—3]. Due to the flexibility of molecules [4], and due to the existence of fluctuations and averaged mean fields in liquid crystals [5] the definition of the order parameters is the subject of a continuous discussion.

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A general analysis of the order parameters in terms of the Wigner rotation functions (WRF) has been given by Zannoni [6]. For any condensed state the singlet distribution function can be written in the form of expansion

$$P^{(1)}(\boldsymbol{r},\Omega)=\sum P_{Lmn}(\boldsymbol{k})\exp(i\boldsymbol{k}.\boldsymbol{r})D^{L}_{m,n}(\Omega) \tag{1}$$

where $(\boldsymbol{r},\Omega)$ describe the position and orientation of a molecule in the ensemble, $\boldsymbol{k}$ is the lattice vector of the phase in reciprocal space and $D^{L}_{m,n}(\Omega)$ are the Wigner rotation functions (WRF). From the inverse transformation of eq. (1) it is clear that the expansion coefficients $P_{Lmn}(\boldsymbol{k})$ represent the order parameters of the system [6]

$$P_{Lmn}(\boldsymbol{k})=K\langle\cos(\boldsymbol{k}.\boldsymbol{r})D^{L}_{m,n}(\Omega)\rangle \tag{2}$$

(K is the normalization constant). In particular the coefficients $P_{000}(\boldsymbol{k})$ and $P_{Lmn}(0)$ represent positional and orientational order parameters respectively.

The expansion (1) represents an infinite orthogonal series. The number of considered order parameters is usually reduced on the basis of the known symmetry properties of the mesophase and of its constituent molecules [6]. The present paper shows that the *a priori* unknown symmetry properties of the phase can be deduced from the properties of pair interaction. For these reasons the microscopic order parameters are introduced.

II. MICROSCOPIC ORDER PARAMETERS

II.1. Definition

The configuration partition function Q_N of the ensemble of N interacting molecules can be written in the form [7]

$$Q_N=(N!)^{-1}\int \mathrm{d}X^N\exp\{-\beta U(X^N)\}, \tag{3}$$

where $U(X^N)$ is the interaction energy of the whole ensemble. X^N and $\mathrm{d}X^N$ represent the set of the configuration coordinates $(\boldsymbol{R}_i,\Omega_i)$ and their corresponding differentials to each individual molecule of the ensemble. In the approximation of pair-wise additive interactions between molecules of the ensemble, the partition function has the form [7]

$$\begin{aligned}Q_N&=(N!)^{-1}\int \mathrm{d}X^N\exp\left\{-\beta\sum_{i,j}U(X_i,X_j)\right\}\\&=(N!)^{-1}\int \mathrm{d}X^N\prod_{i,j}\exp\{-\beta U(X_i,X_j)\}.\end{aligned} \tag{4}$$

The ensemble partition function can be rewritten in terms of the so-called Mayer functions [7]

$$f_{ij}=(\exp\{-\beta U(X_i,X_j)\}-1). \tag{5}$$

Then the partition function has the form of the sum of integrals [7]

$$Q_N=(N!)^{-1}\int\prod_{i,j}(f_{ij}+1)\mathrm{d}X^N=(N!)^{-1}\int\left[1+\sum f_{ij}+\sum\sum f_{ij}f_{kl}+\cdots\right]\mathrm{d}X^N.$$

As long as the pair interaction function of liquid crystal molecules depends on their mutual orientation, the Mayer functions will depend on the space orientation-translational configuration of molecules, too.

The orientationally dependent pair interaction of molecules can be expanded to the general series of the Wigner rotation functions [8, 9, 10]

$$U_{AB}=\sum_{k,l}K^{k,l}(R)^{t}D^{k}(\Phi)D^{l}(\Omega). \tag{7}$$

In eq. (7) a laboratory axis system referring to the axes of molecule A is used. R together with the spherical angles $\Phi=(\Theta,\varphi)$ describe the mutual configuration of the centres of the mass of molecules A, B. The Euler angles $\Omega=(\alpha,\ \beta,\ \gamma)$ describe the mutual orientation of their molecular axes. We have used a shortened notation [10], where ${}^{t}D^{k}$ and D^{l} represent the Wigner rotation function ${}^{t}D^{k}_{0\zeta}$ and $D^{l}_{\mu\xi}$, respectively, with $k,\ l=0,\ 2,\ 4$ and $\zeta=0,\ 2,\ldots,k$; $\mu\xi=0,\ 2,\ldots.l$. The form of the expansion coefficients $K^{k,l}(R)$ (in [8] denoted as $u^{kk'}_{LL'j}$) was derived in the previous work [10]. In contradiction to the usual approach, where $u^{kk'}_{LL'j}$ are the products of multipole moments of interacting molecules, the coefficients $K^{k,l}(R)$ originate in the non-multipole expansion of the pair interaction [10].

The Mayer function f_{ij} for molecules A,B can formally be expanded to the same general basis of WRF (compare with [6])

$$\exp\{-\beta U_{AB}\}-1=\sum_{k,l}c_{k,l}(R,T)^{t}D^{k}(\Phi)D^{l}(\Omega)-1, \tag{8}$$

where $c_{k,l}$ is the short notation of $c^{0\zeta,\mu\xi}_{k,l}$. The values of the coefficients of expansion to the space of WRF can be obtained from the inverse transformation

$$c_{k,l}(R,T)=\int{}^{t}D^{k}(\Phi)d^{l}(\Omega)\exp\{-\beta U_{AB}\}\mathrm{d}\Phi\mathrm{d}\Omega. \tag{9}$$

Since the term $\exp\{-\beta U_{AB}\}$ is the Boltzmann weight function, the expansion coefficients $c_{k,l}$ represent some kind of averaged values

$$c_{k,l}(R,T)=\langle{}^{t}D^{k}(\Phi)D^{l}(\Omega)\rangle \tag{10}$$

of the given basis function ${}^{t}D^{k}D^{l}$ by the distance R and the temperature T. They will be therefore called microscopic order parameters.

II.2. Finite basis of microscopic order parameters

Analyse now the relation between the expansion coefficients of the pair interaction $K^{k,l}$ eq. (7), and the expansion coefficients $c_{k,l}$. The function $\exp\{-U_{AB}(kT)^{-1}\}$ can be expanded to the Taylor series

$$\exp\{-U_{AB}(kT)^{-1}\} = 1 - U_{AB}(kT)^{-1} + (2!)^{-1}\left[U_{AB}(kT)^{-1}\right]^{-2} - \cdots \qquad (11)$$

In the first approximation we can limit ourselves to the linear term of the expansion. Due to the orthogonality of WRF the substitution of (11) into eq. (9) leads to

$$c_{k,l}(R,T) = \delta_{k0}\delta_{l0} - K^{k,l}(R)(kT)^{-1}. \qquad (12)$$

The shape and the value of $c_{k,l}$ with given k,l are thus primarily determined by the corresponding coefficient $K^{k,l}$ of the expansion of the pair interaction (7).

Using the multipole expansion of the interaction which is divergent for liquid crystal molecules, the series (7) is in principle infinite. On the other hand it has been shown [10] from the convergence of the non-multipole expansion that one can use a limited part of the expansion (7) for the correct description of the intermolecular forces. The finite part of the infinite orthogonal basis of WRF in which the translation-orientational properties of the pair interaction can be described is, on the basis of eq. (12) suitable for the expansion of the Mayer functions. Thus it can be said without any knowledge of the symmetry properties of the mesophase, that there is a finite number of microscopic order parameters for any ensemble of molecules. Which from this set of order parameters are responsible for the formation and which is the mechanism of the formation (at least qualitative) of the liquid crystal phases will be briefly analysed in the following section.

II.3. Space dependence and temperature behaviour of microscopic order parameters

Similarly as the coefficients $K^{k,l}$ [12], the microscopic order parameters (miOP-s) $c_{k,l}(R,T)$ can be divided into four groups:

i) the angle independent order parameter $c_{0,0}(R,T)$ which represents the main radial part of f_{AB}.

ii) the orientational miOP-s, $c_{0,1}({}^tD^0 = 1)$, representing the terms which depend only on the relative orientation of the molecules A and B and on their mutual distance, irrespectively of the space configuration of their centres of mass described by the angles Φ.

iii) the directional miOP-s, $c_{k,0}(D^0 = 1)$, which make it probable to find the center of the mass of the molecule B in the given direction of the vector R, irrespectively of the orientation of the molecular frames.

iv) the combined direction-orientational miOP-s, $c_{k,l}$, $k,l \neq 0$, which correlate the orientational and the directional ordering.

It is complicated to formulate mathematically the criterion of anisotropy of pair molecular interactions within the Wigner rotation functions [10]. An explicit criterion of anisotropy has been formulated only recently [11]. In fact this criterion is defined on the basis of the consequent physical properties (phase diagram) of the statistical ensemble of the interacting molecules, i.e. indirectly. Now the behaviour of the microscopic order parameters in the case of the anisotropic pair interaction will be analysed.

To understand qualitatively the mechanism of the phase transitions in terms of the microscopic order parameters let us analyse the simplest system consisting of spherical molecules. The pair interaction of the exactly spherical molecules is angle independent, i.e. all coefficients $K^{k,l}(R)$ with $k \neq 0 \neq l$ are equal to zero. The temperature dependence of the value of the order parameter $c_{0,0}(R,T)$ in its maximum $c_{0,0}^{max.}(T)$ (minimum of the angle independent part of U_{AB} in dependence on the intermolecular distance R) is a smooth exponential function. With decreasing temperature it continuously increases. The continuous increase of $c_{0,0}^{max.}(T)$ should, however, result in the phase transitions to the solid state by some critical value of temperature. This critical point should be in the region of temperatures where the function increases steeply. At this stage, for the purposes of the present paper a qualitative understanding of the phase transition mechanism is satisfactory. We do not find it necessary to characterize the critical temperature point more precisely.

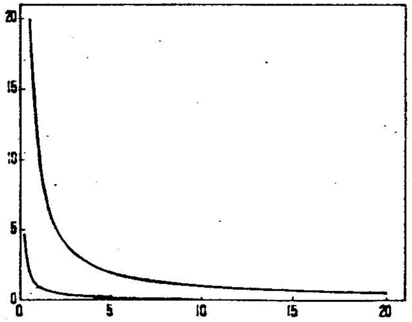

Fig. 1. The dependence of the exponential part of the Mayer function $f_{AB} = \exp\{-(kT)^{-1}U_{ab}\}$ in the system with two local minima $U_{AB} = u_1 = -u_1 = -u_0$ and $U_{AB} = u_2 = -10\ u_0$ on the temperature.

To comprehend the behaviour of the ensemble consisting of real non-spherical molecules consider first the idealized pair interaction function with two energy minima $u_1 = -u_0$ and $u_2 = -10\ u_0$ in dependence on R. The temperature dependence of f_{AB} in these two minima can be divided three intervals, fig. 1 of the scaled temperature $T^* = kT/u_0$; i) $T^* < 3$; ii) $3 < T^* < 10$ and iii) $T^* > 10$.

In the point $T^* = 10$, the maximum value of $f_{AB}(u_2)$ begins to grow rapidly with decreasing temperature. For the function $f_{AB}(u_1)$ a comparatively great increase of the maximum (estimated from the value of the first derivation) begins at temperatures below the value $T^* \cong 3$.

In the interval of high temperatures $T^* > 10$, the values of the Mayer functions in both energy minima are small. They asymptotically approach zero as the temperature tends to infinity $T^* \Rightarrow \infty$. From this it can be deduced that this interval of temperatures is clearly above the possible appearance of critical temperatures of the phase transition from the isotropic liquid phase.

In the interval of intermediate temperatures $3 < T^* < 10$ the shapes of $f_{AB}(u_1)$ and $f_{AB}(u_2)$ are different. The function f_{AB} corresponding to the energy u_1 changes still slowly in dependence on T^*, although the function f_{AB} of the energy u_2 steeply increases with decreasing temperature. Hence in this interval of temperatures the value of the function $f_{AB}(u_2)$ can increase above the critical value necessary for the phase transition. It means that by a slow cooling of the system below the critical temperature $T^*_{crit}(u_2)$ the system will form a phase whose structure is determined by the energy minimum u_2.

In the interval of low temperatures $T^* < 3$ the shape of the function $f_{AB}(u_1)$ is similar to the form of $f_{AB}(u_2)$ in the intermediate temperature interval. It means that in this interval the function $f_{AB}(u_1)$ increases above its critical value necessary for the phase transition. By the slow cooling rate of the system, however, the possibility of this phase transition depends on the type of the previous phase transition at $T^*_{crit}(u_2)$ and on the structural and dynamic properties of the phase formed by it. In our presented case of two energy minima u_1 and u_2 the phase transition caused by the energy minimum u_1 could not be even visible by slow cooling of the system. However, if the témperature T^* rapidly decreases from the values $T^* > 10$ up to temperature $T^* < T^*_{crit}(u_1)$ the resulting solid phase will have a combined structure determined by both energy minima. In a more complicated system with a greater number of local energy minima this mechanism can qualitatively explain the formation of an amorphous structure.

The analysis of the temperature behaviour of the system with two local minima can be generalized to an arbitrary system described by the function U_{AB}. In the introduced expansion (8) only the coefficients $c_{k,l}(R,T)$ depend on temperature. Let u_{max} and u_{min} be the maximal and minimal absolute values of the local minima of the pair molecular interaction U_{AB}. The temperature interval $T^* = kT/u_{min}$ can again be divided into three parts:

i) low temperatures $T^* < 1$
ii) intermediate temperatures $1 < T^* < (u_{max}/u_{min})$

iii) high temperatures $T^* > (u_{max}/u_{min})$.

As will be shown in the next section, the coefficients $c_{k,l}$ (with the exception of $c_{0.0}$) need not have an extreme in dependence on the intermolecular distance R. Therefore, on the basis of WRF the temperature dependence of the value of the expansion coefficients at the mean intermolecular distance $\bar{R}$ will be considered. Then one obtains the dependence of the functions $c_{k,l}(\bar{R},T)$ similar to the previous simple example with two unequal minima, u_1, u_2.

In the interval of high temperatures of condensed phases the value of all terms $c_{k,l}(\bar{R},T)$ is approximately equal, approaching zero. Thus the Mayer function changes very slightly in dependence on the angles and has no sharp maximum in dependence on the distance R. At high temperatures the dispersion of the function f_{AB} is great. The molecules can quite freely move from one configuration to another. The ensemble of so freely pair-wise connected molecules forms the structure known as the isotropic liquid.

The width of the intermediate temperature interval T^* can be different for different molecules and depends on the anisotropy of interaction (i.e. on the difference between u_{max} and u_{min}). In the case when the interaction is isotropic, i.e. $u_{max} = u_{min}$, the interval of intermediate temperatures does not exist. The angle independent microscopic order parameter $c_{0.0}$ has the greatest value of all the parameters in the whole interval of temperatures $(0,\infty)$.

With increasing u_{max}/u_{min} the interval $\Delta T^* = kT(u_{max}/u_{min} - 1)$ becomes broader. In this case, according to the criterion of anisotropy, the values of several coefficients $K^{k,l}(R)$ are comparable with the angle independent interaction $K^{0.0}(R)$ [10,11]. It means, in analogy with the previous simple example, that the value of several coefficients $c_{k,l}(\bar{R})$ in this temperature interval begins to grow rapidly. Some of them can reach their critical values (i.e. the point of the phase transition) at a higher temperature than the angle independent order parameter $c_{0,0}(\bar{R})$ does. As far as the angle dependent order parameters need not have the maximum in dependence on the distance, the formed phase has not the character of the solid state. This is according to our opinion a microscopic reason for the appearance of all intermediate phases in the ensembles of molecules. It also explains the form of the criterion of pair molecular anisotropy which was recently introduced [11].

As far there are many possible combinations which of the order parameters grow rapidly, there are many possible structures of the resulting phases. The character of the observed phase transition can also differ from the phase transitions observed in the usual ensembles where the interval of the intermediate temperatures does not exist or is very narrow.

Now consider some general properties of the space dependence of the Mayer functions.

The value of the function $(f_{AB} + 1)$ is always positive at arbitrary thermodynamic temperature in any point of the configurational space (R, Φ, Ω). Nevertheless, the individual base WRF ${}^{t}D^{k}D^{l}$ can, in dependence on the angles Φ and Ω reach positive as well as negative values [13]. Therefore the expansion coefficients can be negative or positive in dependence on R and T. Based on the conception that the microscopic order parameters are expansion coefficients of the Mayer function they can reach positive as well as negative values. It is no more surprising that also the ensemble averaged order parameter $\langle P_4 \rangle = (Q_N)^{-1} \int P_4 \prod (f_{ij} + 1) \mathrm{d}X^N$ can be negative for some nematic liquid crystals [13].

If the "orientational" expansion coefficients $K^{0,l}(R)$ are considerably greater than the rest of the expansion coefficients $K^{k,l}(R)$, $k \neq 0$ (i.e. the amplitude of the angle dependent interaction in dependence on the Euler angles $\Omega = (\alpha, \beta, \gamma)$ is comparable with the absolute value of the angle independent interaction $K^{0,0}(R)$), the macroscopic ensemble of such molecules will form an orientationally ordered but translationally disordered condensed phase in some interval of temperatures. A typical example of such a phase are the nematic liquid crystals. The orientational order in nematics is usually described by $\langle P_4 \rangle$ and $\langle P_2 \rangle$ [2–4], which corresponds to the distance averaged miOP-s $c_{0,4}^{00,00}$ and $c_{0,2}^{00,00}$. The introduced limited basis of functions [10] consists of further eleven orientational miOP-s: $c_{0,2}^{00,02}$, $c_{0,2}^{00,20}$, $c_{0,2}^{00,22}$, $c_{0,4}^{00,20}$, $c_{0,4}^{00,02}$, $c_{0,4}^{00,22}$, $c_{0,4}^{00,40}$, $c_{0,4}^{00,04}$, $c_{0,4}^{00,42}$, $c_{0,4}^{00,24}$, $c_{0,4}^{00,44}$. All these corresponding terms depend, apart from the angle β also on the angles α and γ. If some of them start to increase steeply in the intermediate temperature interval they can contribute to the so-called bi-axial ordering [14–17]. From the preliminary analysis of these order parameters it seems to us that there could exist at least two types of a bi-axial ordering in liquid crystals. A detailed analysis of the various properties of biaxiality [14–17] on the basis of microscopic order parameters will be given in some future paper.

In dependence on R the shape of the individual miOP-s $c_{k,l}$ follows the shape of the corresponding coefficients $K^{k,l}$. Generally three different types of dependence of $c_{k,l}$ on R are possible:

i) $c_{k,l}$ (negative or positive) has no extreme value in the considered interval and asymptotically approaches zero with increasing R; (From the preliminary analysis almost all microscopic order parameters $c_{k,l}(R,T) l \neq 0 \neq k$ belong to this type).

ii) $c_{k,l}$ has one or more extremes, but does not change the sign in the whole interval; (The angle independent order parameter $c_{0,0}(R,T)$ has always one maximum).

iii) $c_{k,l}$ has more extremes and changes the sign within the interval of R.

The translational dependence of the Mayer function by fixed values of the angles Φ nad Ω is given by the sum of $c_{k,l}(R)$ multiplied by the values of the corresponding functions ${}^{t}D^{k}(\Phi).D^{l}(\Omega)$. The function f_{AB}, in dependence on R can have a sharp extreme, which means that the molecules are "bonded" (solid state), or the Mayer function has only a broad extreme typical of the "free" molecules (liquid-like structure). This property is primarily determined by the angle independent order parameter $c_{0,0}(R,T)$. In dependence on the direction of the vector $\boldsymbol{R}$ (described by the angles Φ), the translational dependence of f_{AB} can be different. Microscopic order parameters are thus able to describe also the directional properties of distribution. Hence on the basis of microscopic order parameters it is possible to distinguish between directional and translational properties of distribution. Based on them we try to give a qualitatively new view on smectic and columnar liquid crystals.

In the ensemble which forms the smectic liquid crystal phase it is most probable to find the molecule B somewhere in the plane perpendicular to the long axis of the rod-like molecule A. The probability to find B in any other direction is considerably lower. In this plane the interaction energy U_{AB} is for rod-like molecules considerably greater than along the rod axis, which is schematically shown in fig. 2. (This is in contradiction to the opinion that the interaction is greater if the molecules interact via their chain ends [18]).

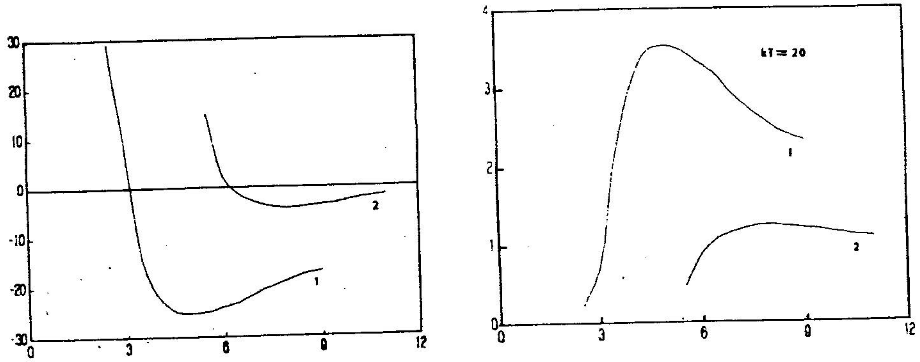

Fig. 2. The distance dependence of the interaction energy (a) and of the probability distribution (b) of two parallel rod-like molecules in two space configurations $\vartheta = 0°$ (1) and $\vartheta = 90°$ (2).

As shown in various direction (angle ϑ) the distribution can have at the same temperature a "liquid-like" and a "solid-like" character.

The distance dependence of f_{AB} in this plane determines whether the lamellae have isotropic liquid-like or quasi-periodic two-dimensional structures. If the coefficients describing the direction anisotropy of the Mayer function have no significant extreme in dependence on the distance R, the lamellae could have liquid-like structure (SmA). On the other hand if there are some distinctive maxima on the distance dependence of f_{AB} in the plane, the lamellae could have a two-dimensional structure (SmB). As far as the ensemble is in the intermediate temperature region relatively great fluctuations in f_{AB} hinder the formation of lamellar clusters with defined lateral dimensions. Only the thickness of all clusters is the same, and is equal to the conformationally averaged length of rod-like molecules. The ensemble of such lamellar clusters forms then the one-dimensional macroscopic structure typical for smectic liquid crystals.

A similar situation can be observed in columnar liquid crystals. For the disc-like molecules it is most probable to find the molecule B somewhere along the disc axis of the molecule A. The anisotropy of the pair distribution causes the formation of columnary shaped clusters of undefined length. The clusters can have a liquid-like nonperiodic or quasi-periodic one-dimensional structure which is determined by the distance dependence of f_{AB} in this direction. In dependence on the column's transection which is connected with the orientational ordering, the ensemble of such clusters can form different types of macroscopic periodic structures in two dimensions.

The partial translational ordering observed in the smectic and columnar liquid crystals is thus the result of the anisotropy in the directional characteristics of the microscopic Mayer function. Microscopic order parameters offer a physical insight into the confused understanding of the partial translational ordering of liquid crystals.

III. CONCLUSIONS

The defined microscopic order parameters offer a unified view on the directional, orientational and translational microscopic structure of condensed phases. (Especially useful seems to be the distinguishing between the directional and the translational ordering, which so far has not been performed.) They offer a new qualitative explanation of the appearance of intermediate phases in the phase diagrams of the ensembles of real molecules.

The anisotropy of the pair interaction and the appearance of the system in the interval of intermediate temperature below the critical T^*_{crit} are the inevitable and sufficient conditions for the formation of partially ordered condensed phases. The temperature behaviour of microscopic order parameters seems to us to be able to explain the pretransitional effects in mesophases (continuous growth of miOP-s) as well as the great variety of different types of phase transitions in liquid crystals.

In the present paper we have analysed only the general space and temperature properties of the miOP-s $c_{k,l}$. For a more detailed analysis of the ordering in liquid crystals and of the character of phase transitions the form and the temperature dependence of the pair distribution function f_{AB} for concrete molecules should be analysed.

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ПАРАМЕТРЫ МИКРОСКОПИЧЕСКОГО ПОРЯДКА В ЖИДКИХ КРИСТАЛЛАХ

Проводятся параметры микроскопического порядка парного молекулярного взаимодействия. Определены коеффициенты функции Майера $f_{i,j}$ в наборе ротационных функций Вигнера. Поведение микроскопических параметров порядка позволяет наблюдать новое качество в фазовых переходах и предпереходных еффектах фазовых переходов в конденсированой фазе. Параметры порядка позволяют получить единым образом сведения о трансляционной; направленной и ориентационной микроскопической структуре фаз. Приводится предварительный анализ разных аспектов ориентационной микроскопической структуры. Кроме возможности разделения направляющего и чисто трансляционного микроскопических порядков, работа также позволяет получить сведения о принципе трансляционной структуры в жидких кристаллах.