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THE BEHAVIOUR OF THE SMECTIC LIQUID CRYSTALL AT THE APPROACH TO THE LIQUID STATE

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In this work results of computer modelling of a new kind liquid crystal on the basis of derivatives of ferrocene were presented. Features of the processes proceeding in such system were studied.

Keywords: computer modelling, liquid crystal, ferrocene, molecules geometry, conformer.

The presence of the ferrocene fragment in structure compound promotes development of the steady mesomorphism in many cases [1]. In particular 1, 1'-encore ferrocenes lead to the possibilities of development of the S- from structure with the big geometrical anisotropy [2]. Small potential barriers of rotation in ferrocene fragment [3-4] promote occurrence of the additional molecule conditions change mechanisms by the structure change. In the work [5] one kind of such compound with asymmetrical replacement has been synthesised and investigated. The results of these researches show the difficult picture of phase transitions in the obtained compound and variety of the observable mesomorphism kinds.

For the purpose of finding-out of character of the processes proceeding at phase transitions in case of heating of such compound, experiments on computer modelling of their behaviour have been made.

Gross-formula connection looked like $C_{63}H_{79}F_2FeNO$, consisting of 147 atoms. Considering that in [5] was not accurate data on geometry, we had been conducted researches of prospective structure in some stages. It has been connected with possibilities of the quantum-chemical methods limited in sizes of counted molecules. The fragment with participation of atom of iron and attached to it cycles has been investigated with the help of non empirical method GAMESS version 6.4. Molecule chains were optimised by half empirical method MNDO. Final optimisation of geometry of all connection with the account of charging conditions on atoms has been carried out by means of Gromacs software package. The initial structural data was set by results of the abovementioned calculations. The modelling time at last stage of definition of molecule geometry was equal to 5 nanoseconds (300K). It is established that the total energy of the investigated molecule was equal to 1327.7 kJ/mol, where the contribution of the potential energy - 781.1 kJ/mol and kinetic energy- 546.6 kJ/mol. The final geometry of a molecule is presented on fig. 1.

Methods of cluster formation and its researches were described in [6-8].

In subsequent of the received molecules cluster has been constructed, where they settled down in parallel each other in conformity with the data of experimental researches [5].

At carrying out of computer modelling consecutive annealing has been done [6-8]. The size of the initial cluster had the following sizes – 10x6x11 molecules and included 660 molecules or 97020 atoms. At the construction of the initial cluster the long axis of a molecule has been directed along Y axis (direction of the director). Planes, in which molecules settled down, were parallel to OXZ plane.

Packing of the initial cluster had following parameters:

X=1,3 nm (distance on x from the beginning of one molecule prior to the beginning of following)

Y=3,4 nm (distance on at from the beginning of one molecule prior to the beginning of following)

Z=0,8 nm (distance on z from the beginning of one molecule prior to the beginning of following)

$\Delta X = \Delta Y = 0$ (without displacement)

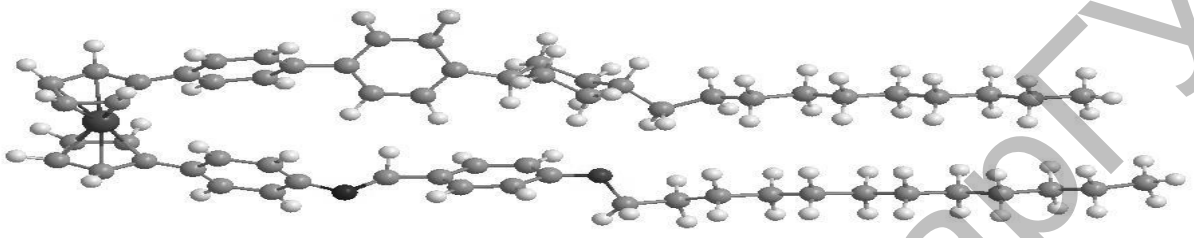

Fig. 1. The geometry of the compound

The first layer of molecules (60 molecules=8820 atoms) was considered motionless (substrate) and did not participate in modelling. Molecules have been focused planar and homeotropically in relation to the substrate.

As it has been established in [5], at heating phase transitions had the following order –

Cr1 **365K** Cr2 **476K** Sm **489K** N **545K** I,

where Cr1 and. Cr2 correspond to a crystalline state with presence of three and sets of layers accordingly, Sm – a smectic C phase [9], N – a nematic phase, I – an isotropic liquid.

The annealing time at one temperature was 10 picoseconds, but at that condition cluster was settled down in one cell, so the liquid modular condition of the system has been realised [10-11]. The vector of intensity of electric field has been directed perpendicularly to the substrate, and its value was equal to $1,0 * 10^7$ V/m.

The analysis of the modelling results has been done for two cases, when as directing molecules atomic pairs on both chains were chosen (fig. 1). The qualitative picture of the received data has completely coincided. Therefore further results of the analysis will be shown for only one of the chosen directing.

The analysis of molecules distribution depending on the values of heat formation for detailed elaboration of the processes occurring at phase transitions has been carried out. The special program has been created for this purpose. Distribution of molecules according to heat formation from distance to the centre of cluster was corresponded to the total energy of all molecules which were in the given segment. The given distance corresponds to the large radius of the segment relative to the certain centre that was defined before. Also dependences of the average value of heat formation of one molecule in the given cluster segment have been defined. The centre of the cluster was defined by finding coordinates of the molecules that have maximum and minimum values.

The uniform energy distribution all along cluster, not including small deviations on border, has been established. It allows considering the condition of molecules in cluster close to equilibrium. The average values of heat formation of one molecule at the concrete temperature value in the basic part of cluster remain almost constant.

The results of experiments on computer modelling are presented in Figures 2-7.

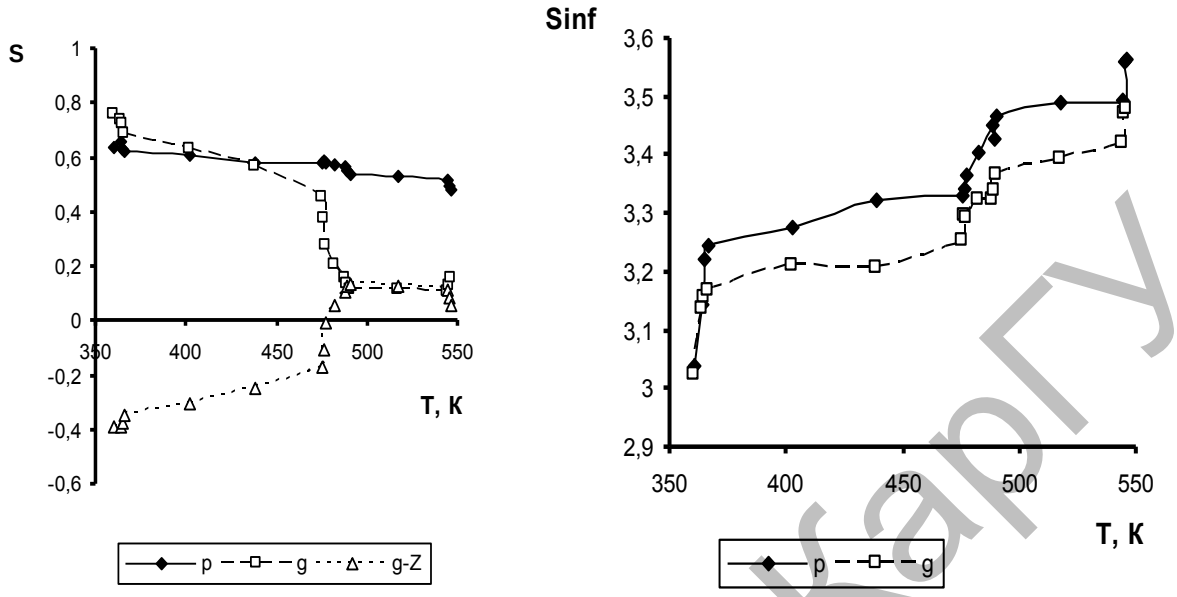

Fig. 2. Temperature dependences of the degree of order S(T) and the information entropy Sinf at planar (p) and homeotropical (g) subtract orientations

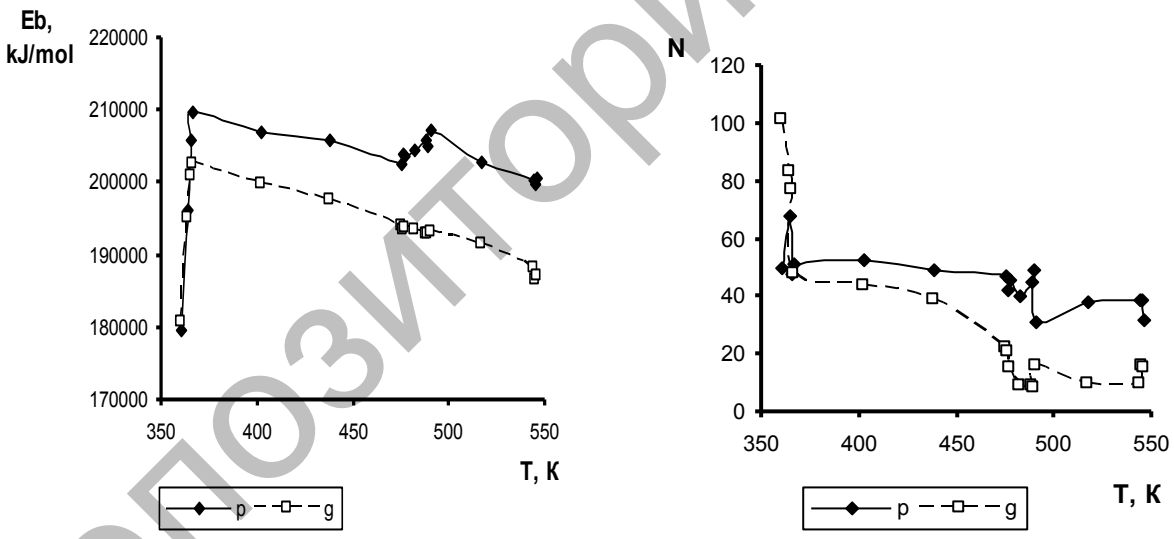

Fig. 3. Temperature dependences of energy of the compound Eb and number of molecules N at planar (p) and homeotropical (g) subtract orientations

The received results show good correspondence to the experimental data that is defined by inflection in the region of temperatures of phase transitions on curves of dependences of degree of order S(T) (fig. 2), information entropy Sinf (T) (fig. 2), volume of cell V (T) (fig. 4), energy of the compound Eb (T) (fig. 3), number of molecules N (T) which longitudinal axes make an angle of 10^0 relative to the direction of the director (OY axis) (fig. 3), functions of distribution D (T) of the molecules pairs which are located under a certain angle(fig. 5). The D (T) plot is presented in polar

coordinates, in the right part the axis of angle counting (from 0 to 900) is the vertical axis, and in the left part – a horizontal axis (from 90^0 to 180^0). The angle counting is made clockwise.

It can be seen from Fig. 2 that degree of order in case of planar orientation keep high value (see the case **p**). At the homeotropical orientation after melting temperature that value start sharp decrease. It is caused by the turn of whole cluster relative to the substrate that proves by the r-Z, curve i.e. change of direction of the director.

As the Sinf (T) curves show (fig. 2) the greatest order is observed at the homeotropical orientation. In many respects it is caused by possibility of the cluster expansion at the temperature influence along OZ axis.

Apparently, for the same reason at planar orientation higher values of compound energy Eb and N number are observed (see fig. 3). In this case at the region of the smectic phase bond energy with temperature rise starts to increase. That is associated with the restrictions in displacement of molecules because of presence of the substrate perpendicular to the OZ axis. It leads to growth of heat formation of separate molecules. The absence of restriction at homeotropical orientation leads to increase in volume of cell V with the cluster in it (fig. 4). The conservation of the high order causes the rise of the general cluster of dipole d molecules (fig. 4).

The conservation of high order in many respects is caused by strong intermolecular interaction. The reason of it is the big sizes of investigated compound. Therefore, at temperature influences the mobility of such compounds will be small. The changes of self-diffusion coefficients k confirm observable tendencies for molecules next to the substrate and in the centre of cluster (fig. 4 see).

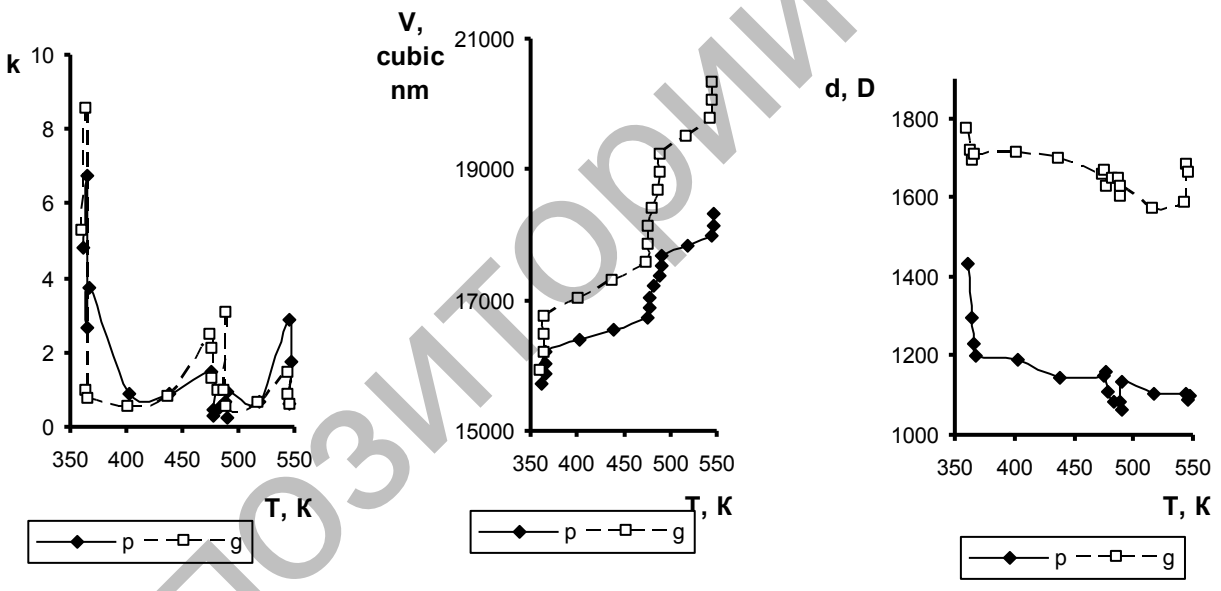

Fig. 4. Temperature dependences of self-diffusion factor k, volume of cell V and dipole moment of d cluster molecules at planar (p) and homeotropical (g) substrate orientations

The carried out analysis of the coordinates of the adjacent molecules, located in the centre of cluster, shows that with temperature rise the displacement Δ of the molecules relative to each other increase along all directions. Maximum displacement occurs along OZ axis. The displacement on the OY axis strongly increases especially at the transition from smectic phase to the nematic phase (fig. 5).

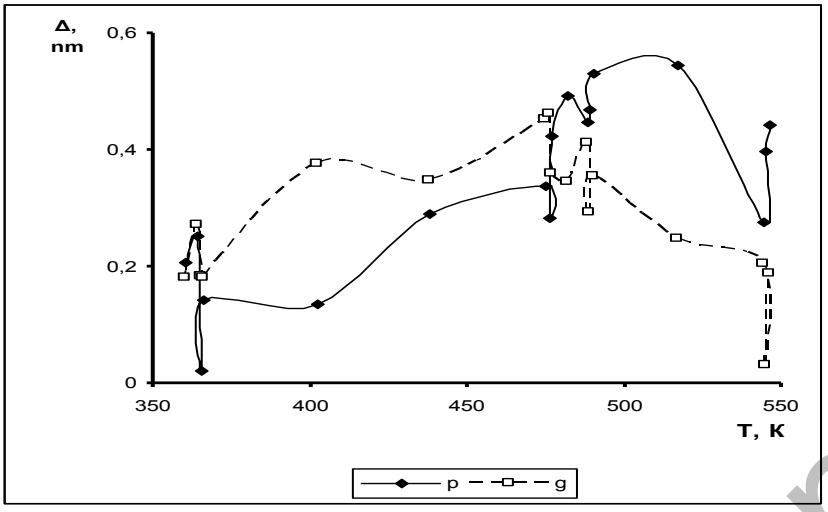

Fig. 5. Temperature dependence of the displacement of adjacent molecules relative to each other, located at the centre of cluster

It is matched with [9], that smectic phase is more ordered in comparison with nematic and the centres of gravity of molecules in it lie in one plane. The difference in the displacement change at hometropical orientation, most probably, is caused by strong movement at high temperatures of whole cluster relative to the substrate.

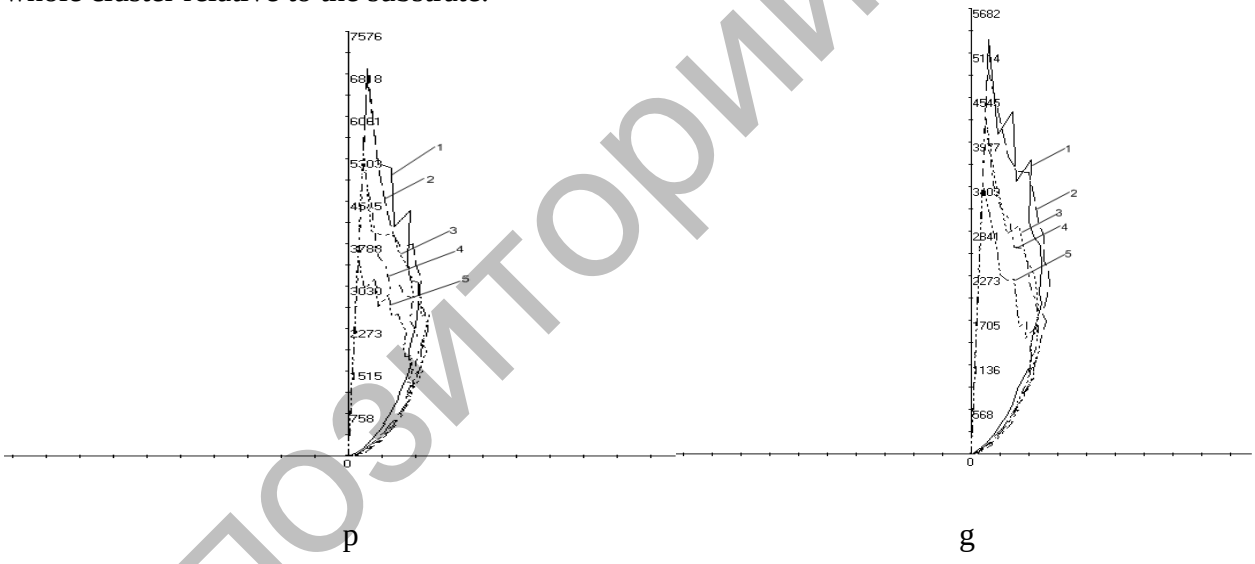

Fig. 6. Functions of distribution D of pairs molecules in a crystalline state (1, 360K), at temperatures of transition Cr1-Cr2 (2, 365K), melting (3, 476K), transition Sm-N (4, 489K) and enlightenments (5, 545K) in case of planar (p) and homeotropical (g) orientations

High asymmetric property of curves of the distribution function of pairs molecules D (α), located under defined angle to each other (fig. 6), shows that in process of the annealing molecules are not developed strongly, keeping the direction of the director almost invariable. It is enough to compare situation with nematic liquid crystals [6-8], where there are always pairs with angles, bigger then 90^0. The shown curves correspond to the temperatures, which conform to the various phase conditions.

Two crystalline states differ by different packing of molecules [5]. For Cr1 condition 3 layers with big sizes, for Cr2 with set of small sizes are typical. The visual analysis of the cluster type at temperatures of existence of these conditions has allowed finding out in the region of Cr1 existence

accurate stratification on pile of clusters' molecules and from the moment of transition Cr1 – Cr2 the beginning of the processes of their associations. It can be seen from fig. 6 that the maximum quantity of pair molecules in these conditions almost does not vary.

The significant reduction of D (α) occurs at the further rise of temperature. At both orientations of the substrate features on curves are found out in the form of the peaks, that is located in the regions close to the values of angles– 2 (maximum), ~5, ~9, ~14, ~22 degrees. The analysis of D (α) function values (on fig. 6, curves 1 for a case п and г) give following values – 6812 (п) and 5284 (г) at 2^0, 5153 and 4388 at 5-6^0, 4429 and 3797 at 9^0, 3184 and 2746 at 14^0, 1863 и1264 at 22-28^0 accordingly. It is easy to see that with increase of angle of the subsequent peak there is a reduction of quantity of pairs somewhere on a quarter from the previous value. Presence of peaks on all curves says that their nature is caused by the nature of the compound.

The most sensitive to external influences fragment of a molecule is ferrocene, where there is a rotation of both chains relative to the atom of iron at the expense of mobility of five member cycles. In fact, the angle between molecule chains varies in limits from 9^0 to 22^0 at both orientations of the substrate (fig. 7).

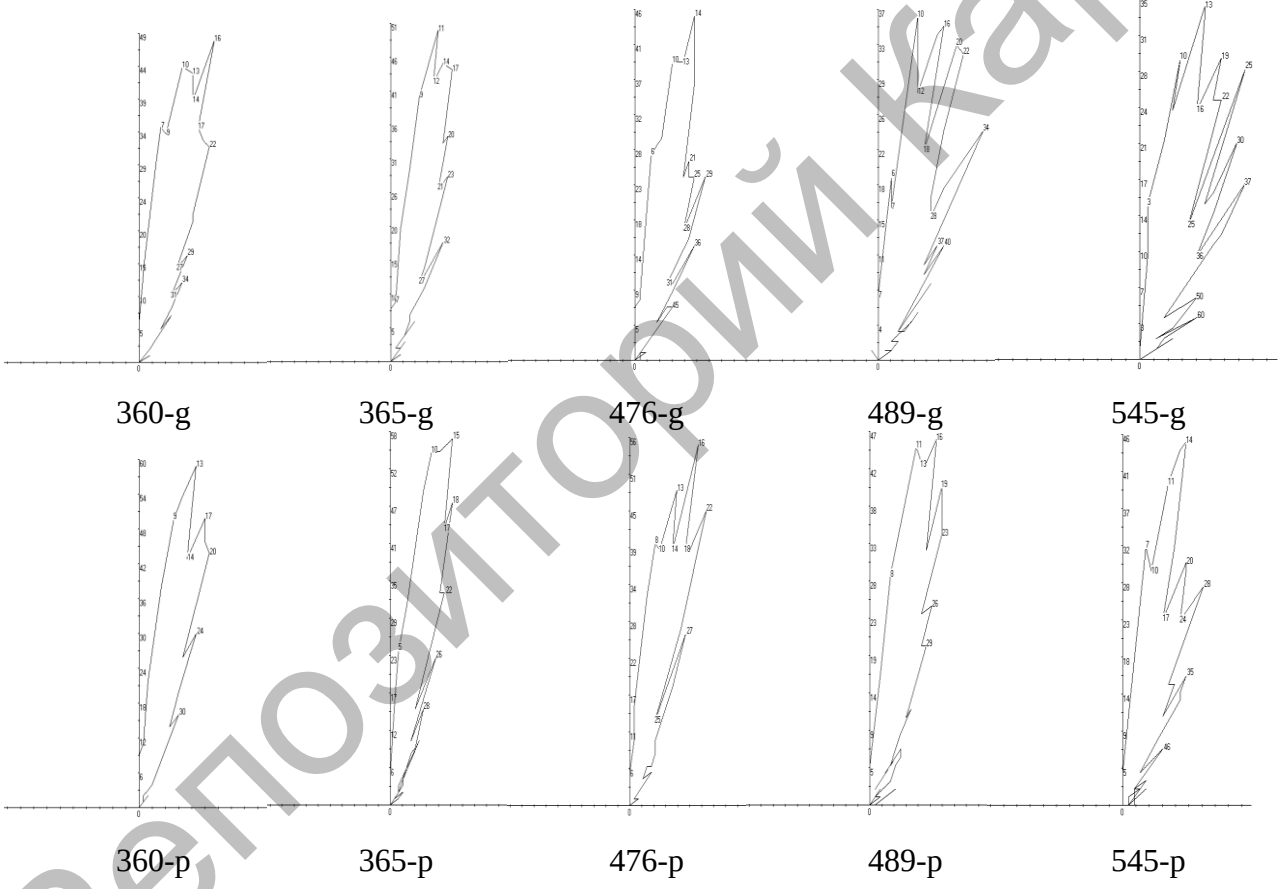

Fig. 7. Distribution of molecules on angle between chains at various temperatures and substrate orientations

Plots of distribution of molecules at the internal angle (fig. 7) between chains are constructed in polar coordinates, where the angle is counted from the vertical axis, and the length of radius corresponds to quantity of molecules. It is easy to see that with increase in temperature the value molecules with the exceeding the specified limit angles, starts to grow. However, generally the majority of molecules have angles between chains within 9-22^0.

The comparison of the results on this distribution and distribution of pairs molecules D (α) allows to assume the connection between peaks on fig. 6 and maxima on fig. 7. Considering that molecules have been constructed in parallel relative to each other in the initial cluster and at all

stages of temperature influence there was no pair with angle larger than 90^0, it is possible to assume a contiguity of angles projections on plane OXZ in the specified interval of $9\text{-}22^0$.

Thus, the experimental results from computer modelling show the difference of the molecules geometry, which are located in cluster, from the molecules geometry that was obtained from the optimisation of initial compound. It is established that molecules in cluster represent conformers with various values of angles in ferrocene fragment. It causes the variety of mesomorphism, which was observed experimentally. It is shown that transition from one crystalline phase in another is caused by strengthening the cooperativity of intermolecular interaction as a result of temperature rise.

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