

LIQUID CRYSTALS

Molecular Dynamics Investigation of the Helical Structure of Smectic C*

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Abstract—The numerical simulation of the behavior of the molecules of the DOBAMBC liquid crystal by the molecular dynamics method allowed us to find the change of the the conformation of molecules as a function of temperature and to reveal the helical structures with various pitches in the smectic phase C*. These results explained the anomalous temperature dependences of the order parameter at the molecular level, as well as the optical second harmonic generation in the region of smectic A.

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1. INTRODUCTION

The response time of smectic liquid crystals during varying the external field is shorter than that for nematic liquid crystals. Therefore, they are used in high-performance optical modulators, controlled phase plates, converters into higher harmonics, etc. [1–4]. Smectics possess unique crystal-optical properties. In contrast to nematic liquid crystals, they have a layered structure with spatial periodicity, which manifests itself in the helical structure of smectic C*, the period of which depends on the structure of molecules and their tilt in the layers. The translational order is absent in the layer plane, and similarly to nematics, the orientational order is observed [5].

The structure of smectics can change with variations in external parameters, particularly temperature, both due to the variation in configuration of molecules and due to the orientational order parameter, the tilt angle of the molecules in the layer, and the translational period. For these reasons, they are characterized by a large number of structural transitions [1–5].

Various approaches allow us to interpret the behavior of smectics under specific temperature variations [1–15]. The molecular dynamics method allows us to describe the variation in properties at the molecular level in a broad temperature range [16].

The most studied liquid crystal among the ferroelectric ones is *p*'-decyloxybenzylidene *p*'-amino 2-methylbutylcinnamate (DOBAMBC) [17]. In connection with this, it is reasonable to calculate the main characteristics of this crystal at the molecular level.

2. CALCULATION

The molecular dynamics method allows us to investigate the structure of the liquid crystal at a level of the motion of individual molecules. It is described in details in some studies [16, 18–21]. The main task in this method is the calculation of forces that are found from the potential. Its selection is determining for the final result.

Molecules of the liquid crystal are extended and can be distorted, which should be taken into account in calculations. These distortions are taken into account using the molecular mechanics method [22]. The interaction potential is represented in the form

$$U = U_s + U_b + U_t + U_{\text{vdW}} + U_e,$$

where U_s is the potential energy of valence bonds, U_b —of valence angles, U_t —of torsion angles, U_{vdW} —of van der Waals forces, and U_e —of Coulomb forces.

Coefficients in potentials U_s , U_b , U_t , and U_e are taken from [16, 23, 24]. To describe the intermolecular interaction, we used the method of atom–atom potentials [25]. Interaction potential U_{vdW} was used in the form

$$U_{\text{vdW}} = \sum_{i,j} \left(\frac{A_{ij}}{r_{ij}^6} - B_{ij} \exp(-C_{ij} r_{ij}) \right),$$

where A_{ij} , B_{ij} , and C_{ij} are the interaction coefficients obtained previously [26–28] and r_{ij} is the interatomic distance.

When determining the interatomic interaction, we can find the forces, which are calculated as the derivatives of the potential energy. Knowing the forces and specifying the initial distribution of the molecules and

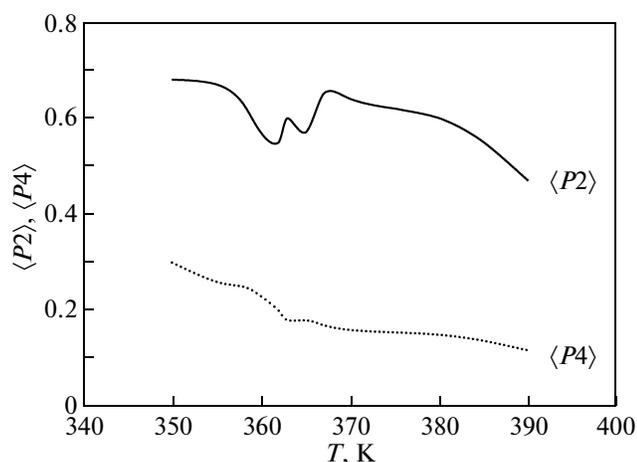


Fig. 1. Order parameters $\langle P2 \rangle$ and $\langle P4 \rangle$ as functions of the temperature for DOBAMBC.

atomic velocities in them, we can find the variation in atomic velocities and coordinates with time using the Verlet algorithm in the velocity form. The step in time was 2 fs. The number of molecules was no larger than 2000.

The initial velocities were specified by the Maxwell distribution. The temperature of the system was maintained by means of correction of velocity of the particles. The Berendsen thermostat was used for this purpose [30]. Computations were performed using the program written in the FORTRAN language with the CUDA technology [31, 32]. This made it possible to use graphic processors when solving the problems and perform the parallel computations, which considerably increased the computation rate.

As a result of computations, we found the distribution of the DOBAMBC molecules from the orientation of their long axes (the axes passing along the molecule through benzene rings) and their conformation in the bulk of the liquid crystal under study for various temperatures. This allowed us to compute the order parameters $\langle P2 \rangle$ and $\langle P4 \rangle$ as functions of the temperature (Fig. 1).

It is seen from Fig. 1 that an anomalous behavior of the order parameter is observed in the phase transition region from smectic C^* into smectic A at about 363 K. Based on the computations, we obtained the arrangement of the molecules in the existence region of smectic C^* ; the coexistence of some helical modes with various periods is observed in the structure. The short-period modes are mainly formed by distorted molecules. Therefore, we can construct the temperature dependence of the number of the molecules of a certain conformation, which will apparently reflect the ratio of helical modes with specific pitches at a given temperature (Fig. 2). Region 1 in Fig. 2 is occupied by molecules with the undistorted conformation. Distorted molecules are arranged in region 4. Regions of

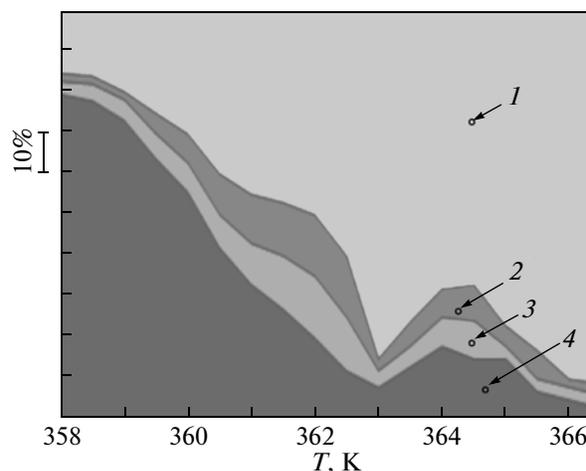


Fig. 2. Relative number of molecules in the unit volume of the liquid crystal of smectic phase C^* of DOBAMBC as a function of the conformation temperature (regions 1 and 2 contain undistorted molecules, and regions 3 and 4 contain distorted molecules) and mutual orientation (regions 1 and 4 contain the molecules with the deviation angle of long axes from the director less than 30° and regions 2 and 3—with this angle larger than 30°).

orientation-disordered molecules with the deviation angle of their long axes from the director more than 30° can be distinguished in the structure at the same temperature. These regions are formed both by undistorted (Fig. 2, region 2) and distorted molecules (Fig. 2, region 3).

The computations showed that the number of disordered molecules increases in the region from 358.0 to ~ 362.5 K, and the interlayer distance increases. With the further increase in temperature in the vicinity of 363 K, the most of molecules inside the layers become undistorted thereby decreasing the distance between the centers of gravity. As the temperature increases, fluctuations inside the layers that do not lead to the destruction of the global structure appear in the vicinity of ~ 364 K. With the further increase in temperature, the distance between the layers increases, which is accompanied by an increase in molecular ordering inside the layer. Figure 2 reflects the variation in the structure of the liquid crystal, which agrees with the behavior of the order parameter in Fig. 1.

A similar plot for the ratio of the molecules of various configurations was constructed for the existence region of smectic A (Fig. 3). No helical modes are observed in smectic A in this case, but an increase in the fluctuation of orientation of the molecules in the vicinity of 377 K is revealed.

3. DISCUSSION

The following transitions are experimentally observed in DOBAMBC [17]: from the crystalline

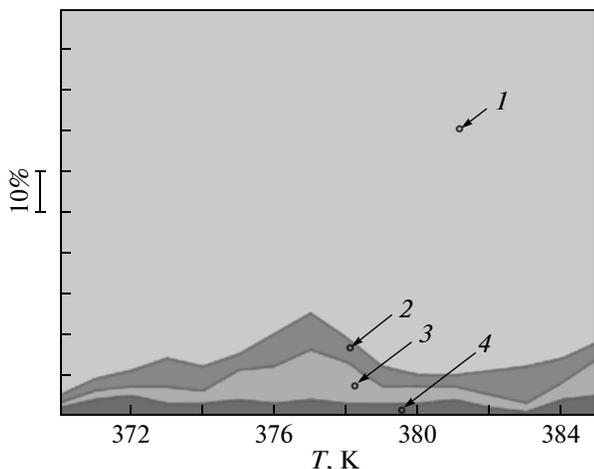


Fig. 3. Relative number of molecules in the unit volume of the liquid crystal of smectic phase *A* of DOBAMBC as a function of the conformation temperature and mutual orientation. Notation of the regions is the same as in Fig. 2.

state into smectic C^* at 349 K, from smectic C^* into smectic *A* at 367 K, and from smectic *A* into the isotropic state at 388 K.

Smectic C^* phase has the layered structure, where the preferential direction of long axes of molecules forms angle θ with the normal to smectic layers. In each layer of phase C^* , there is the only element of symmetry, namely, the second-order axis.

Because of chiral properties of molecules, they rotate from layer to layer in space relative to the axis perpendicular to smectic layers, which is accompanied by the formation of the helical structure (helicoid) with a specific pitch. Molecules in the layers of smectic phase *A* are more mobile than in layers of phase C^* . In phase *A* (angle $\theta = 0$), the layers also slide relative to each other.

An interesting feature in the behavior of the order parameter is observed in the region of smectic C^* –smectic *A* transition. When experimentally studying the behavior of the ratio of polarization to the tilt angle [33] in the range with the beginning distanced for 2 K from the phase transition temperature smectic C^* –smectic *A*, the anomalous behavior was found. In another work, the anomalous behavior was found at a temperature by 0.5 K below the phase transition point [6]. However, no anomalies are observed in this region in the NMR spectra [7], although the NMR method is one of the most sensitive to the variation in local parameters, for example, such as the tilt angle. When investigating the crystal with a shorter chain (C_7 instead of C_{10}) *S*-2-methylbutyl 4-*n*-heptyloxybiphenyl-4'-carboxylate (C_7), no anomalies are observed for the phase transition from smectic C^* into smectic *A*. Therefore, it was of interest to calculate the variation in order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ by the molecular dynamics method and to compare with similar data

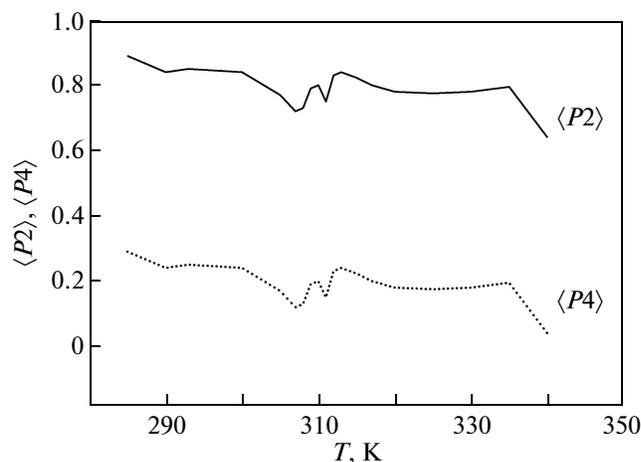


Fig. 4. Order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ as functions of the temperature for C_7 .

for DOBAMBC. The computed temperature dependences of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ for DOBAMBC are presented in Fig. 1, while those for C_7 are presented in Fig. 4. It is seen from the comparison of Figs. 1 and 4 that the variation in $\langle P_4 \rangle$ for C_7 is more clearly pronounced than for DOBAMBC, i.e., the fluctuations in the orientation of the molecules and the amplitude of the tilt for DOBAMBC are smaller.

Various theoretical approaches are used to interpret the behavior of chiral smectic liquid crystals [1–15] since we cannot describe them in the context of a unique model. However, when accounting the nonlinear interaction, Lykakh and Syrkin [15] obtained a unique description of the behavior of the chain of molecules for a broad range of energies enveloping the regions of ordering, orientation melting, and rotational motion of the molecules in the chain. In this case, the simultaneous existence of several subsystems with various periods is mentioned. The solutions are found for the nonlinear subsystem both in the form of single waves and in the form of periodic excitations. The model, in which the features of physical and structural properties of chiral smectic liquid crystals are described in the context of the theory of helical modes with a small pitch, seems to be the most interesting among the models describing the behavior of smectic liquid crystals [11–13]. This model agrees well with the X-ray structural data. Incommensurability of the lattice, which depends on chirality, is a small parameter in this model. Along with the length of smectic correlations, these characteristics allow us to interpret the structure of various phases in the semi-phenomenological model.

Our results confirm the existence of a fine structure at a molecular level by the example of DOBAMBC and determine the temperature boundaries of their existence. It is seen from Fig. 2 that the behavior of the ratio of helical modes in the region of smectic phase

C^* correlates with the behavior of the order parameter in Fig. 1. This behavior also agrees with the temperature dependence of intensity of the second harmonics [8–10] including the occurrence of the peak of second harmonic generation (SHG) in the paraelectric phase of smectic A .

When applying the orienting field in parallel to smectic layers, molecules in the layer rotate so that their dipole moments are parallel to this field, which leads to the appearance of macroscopic polarization. In this case, vectors of spontaneous polarization in all the smectic layers are oriented identically along the direction of the electric field. The symmetry of such a group is described by the point group 2 with the second-order axis. For this point group, the tensor of the nonlinear permittivity has eight nonzero components describing the intensity of the SHG of the laser radiation [9], which agrees with results [11]. However, we also found the SHG for components that should be equal to zero according to symmetry. This means physically that the second-order tensor of nonlinear susceptibility changed due to random deviations of the molecules from the average site. Fluctuations of the molecules in this temperature region are also confirmed by other methods [6]. The dependence of the SHG intensity on the orienting field is complex [9]. As the field rises, the SHG intensity initially increases and then decreases.

It is seen from calculations [10] that the helical structure destructs at large fields of the external effect, which decreases the synchronization length and, consequently, the SHG intensity.

It is seen from Fig. 3 that the anomaly associated with an increase in disorder in the arrangement of molecules is observed in the vicinity of 377 K, which manifests itself in the appearance of the low-intense SHG peak during the experimental investigation of the second harmonics [10].

4. CONCLUSIONS

Thus, the numerical simulation of the behavior of the molecules of the DOBAMBC liquid crystal by the molecular dynamics method explained anomalous temperature dependences of the order parameter and the optical second harmonic generation at the molecular level. Calculations showed that the ordered region of arrangement of molecules is observed in the temperature region with the onset 2 K below the transition temperature from phase C^* into smectic phase A , which explains the previously found anomaly in the behavior of the ratio of the polarization to the tilt angle in this temperature region. It is found that the conformation of molecules changes as the temperature varies. The presence of helical modes in the structure (molecular ensembles helically twisted along one coordinate) is noted in the existence region of smectic phase C^* . The pitch of helix depends on the confor-

mation of molecules in the ensemble. The pitch of helix is longer for undistorted molecules and shorter for distorted molecules. Calculations showed the possibility of existence of ensembles of molecules with various pitches of helices in the structure of smectic C^* , which agrees with the data [11–13]. The region of the enhanced conformation fluctuation of molecules is found by 10 K above the phase transition temperature from phase C^* into phase A , which can lead to the formation of defects initiating the second harmonic generation. This generation is experimentally observed in the region of smectic phase A , which had not been explained previously.

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