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Nano-Substrate Influence on Liquid Crystals Behavior

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In this work the results of the behavior modeling of several nematic liquid crystals layers located on the flat carbon substrate in the absence of boundary conditions are presented.

Keywords Arylpropargyl ethers of phenols; modeling with free boundaries; nano-carbon substrate; nematic liquid crystal

1. Introduction

The understanding of the processes, that proceeds in systems with participation of liquid crystals (LC) and nano-formations, is an important condition of their effective application in practice. In this sense, the modeling of processes using molecular dynamics allows to find out such features. For example in [1] it was found that presence of nano-tubes limits mobility of molecules 5CB in the monolayer in comparison with the case of nano-tubes absence. What behavior of several layers of the LC will be on the nano formations surface?

It is known [2] that modeling at atomistic level requires large computing resources. Therefore, the researched systems are usually limited in sizes. In that case the boundary conditions are usually considered, which are inconsistent with the liquid state of the LC. In [3,4] it is shown that at the big times of modeling the LC system, where all modeling molecules were located in one cell, lost its ordering in the crystal state. At the same time, the results [5] show good compliance of the results of modeling with the experimental data at small times.

2. Experimental Methods

In the given work, the results of the behavior modeling of several NLC layers located on the flat carbon substrate in the liquid state are presented. As the research objects the arylpropargyl ethers of phenols–phenylpropargyl ether of p-chlourine of phenol

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Table 1. Basic information about substrates and clusters size (m and l – number of rings along the substrate width and length; x, y, z – distance between the neighboring molecules in corresponding directions, dy – displacement of gravity centers of neighboring molecules relative to each other)

Types of molecules	Substrates			Cluster				
	m	L	Gross formula	Size of molecule	X [nm]	Y [nm]	dy [nm]	Z [nm]
PEC	46	54	C10044 H308	$14 \times 14 \times 15$	0.8	1.6	0.7	0.4
PEF	46	54	C10044 H308	$14 \times 14 \times 15$	0.8	1.6	0.7	0.4
PEK	32	52	C6760 H272	$13 \times 13 \times 16$	0.6	1.6	0.7	0.5
MBBA	42	52	C8840 H292	$13 \times 13 \times 13$	0.8	1.6	0.7	0.4

(PEC), phenylpropargyl ether of p-fluorine of phenol (PEF), phenylpropargyl ether of p-cresolphenol (PEK) and 4-metoksibenziliden-4-butilanilin (MBBA) have been used.

The substrate was consisted of benzene rings with the angle of 120° and distances between atoms of: C-C = 1.4210 Å, C-H = 1.1005 Å. It had a zigzag structure. The substrate has been "frozen". So, it has not been under simulation during temperature and electric field influence. The substrate was introduced as the bottom side of initial cluster in XOY plane. The sizes of initial simulated clusters on OX and OY axes were corresponded to the width and length of the substrate (Table 1). The neighboring molecules of the cluster were located anti-parallel to each other on the distance of 4 angstrom. The director has been directed along the OY axis. In the initial cluster the layers with molecules were located planar in OXY plane.

Three kinds of the substrate, which differs from each other by energy of formation, have been considered. The substrate with the maximum energy (5022553 kJ/mol) had been obtained by assigning the OPLSAA (I) force field; with transitory energy (94792 kJ/mol) – by assigning the gm×2 force field, with use of the additional data [6] (II), with minimum energy (Table 2) – by assigning the gm×2 force field without dihedraltypes angles (III). In all cases the substrate with size of 46×54 were used. The geometry of the substrates was identical in all considered cases. The charges of atoms were set as in [6].

During the modeling the NPT assembly was used. The modeling time at the given temperature was 10 ps, the intensity of electric field was 1, 0×107 V/m. The cutoff radiuses of the dispersing and coulomb interactions were 2 nanometers. The charges

Table 2. Dependence of energy of nano-substrate on its size

Size of the substrate, the number of the benzene rings	Energy, kJ/mol
3×3	68,10985
5×3	55,35481
20×20	−2390,6
32×52	−12460,4
42×52	−17110,8
46×54	−19797,4

had the same values as in case of [4,5]. At the regime of heating the coherent annealing was done [4,5].

For realization of modeling of these compounds behavior the set of programs under the general name GROMACS [7] version 3.3.1 has been used.

Methods of cluster formation and its researches were described in [4,5].

3. Results and Discussion

As could be seen from the Figure 1, the reduction of the substrate energy leads to increase of ordering of the PEC cluster molecules. The temperature dependences prove it. The bond energy shows that it happens by means of bond energy increase in the cluster. In such case on the curves of the ordering degree and information entropy there are typical bends in the field of the mesophase, caused by the disintegration of dimers [8]. The analysis of temperature dependences of cell volumes, in which researched systems are located, shows the difference between these cases: in I – increase, in II – decrease.

The reason of such difference is the distinctions in molecules dynamics. As can be seen from the Figure 2, in case II at the bleaching temperature (390 K) there is a flowing stream of multilayered cluster, while in case I, there is not. Consequently, the reduction of substrate formation energy leads to the appearance of flow and to the increase of orderliness.

Considering that atoms of the substrate are in the " frozen" condition, it is interesting to examine the situation of the substrate with even less energy. For this purpose, the substrate, in which dihedral types angles have not been set, was used. This led to significant reduction of energy (Table 2). In that case the energy value decreased with an increase of the substrate size.

The research of the single-layered clusters behavior has shown that in general the cluster molecules move along the substrate surface. As could be seen from the

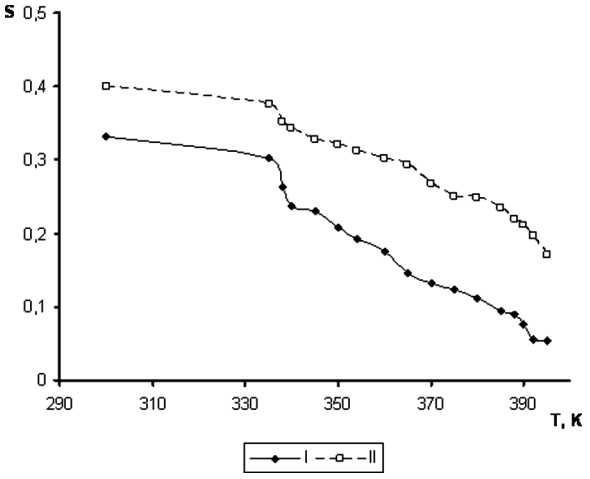

Figure 1. Temperature dependence of the ordering degree of clusters with PEC in I and II cases.

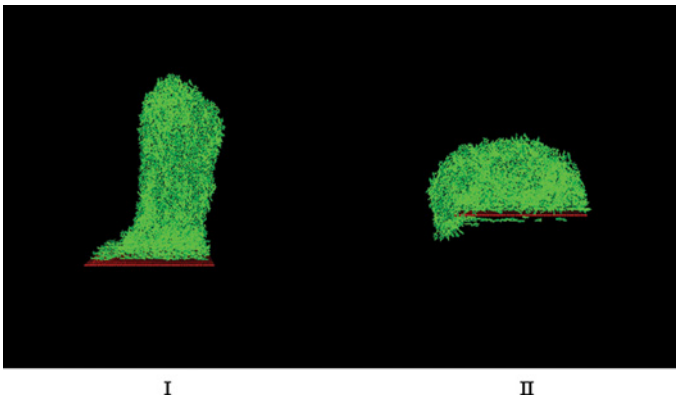

Figure 2. Pictures of clusters with PEC in XOZ plane at T = 390 K in I and II cases. (Figure appears in color online.)

Figure 3, the ordering degree in various directions varies differently, depending on the molecules polarity and structure.

However, the consistent change of ordering degree along directions of OY (director) and OX axes was observed in all of them. This corresponds to our earlier concepts about the ''herringbone'' arrangement of the neighboring rows of molecules

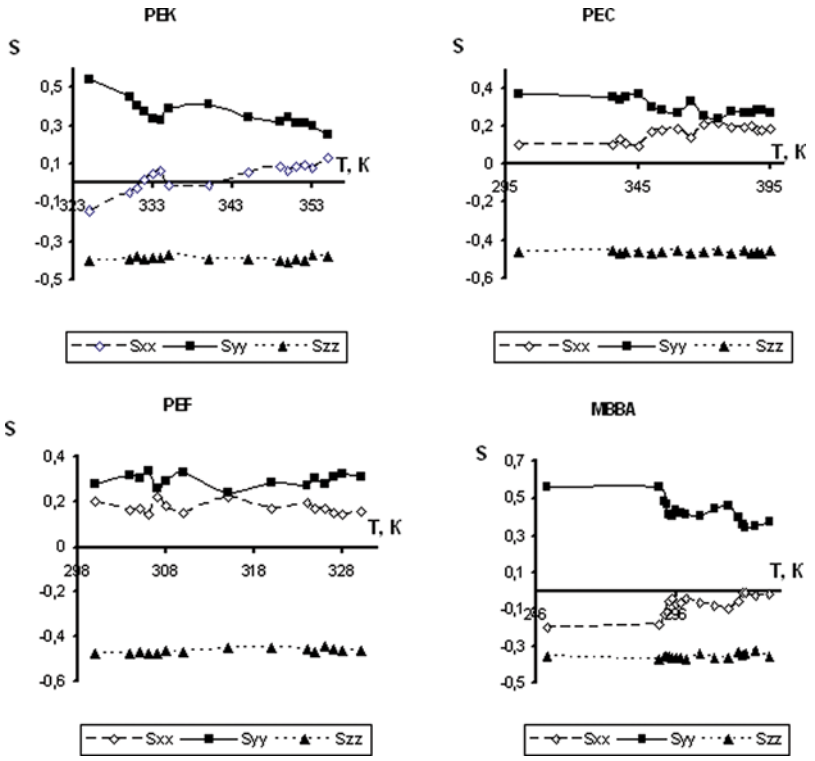

Figure 3. Temperature dependences of the ordering degree in single-layered clusters. (Figure appears in color online.)

[4,5,8]. The increase of degree along one direction leads to the reduction along another one. At that case the character of compliance is expressed more in case of polar PEC and PEF molecules, where in the field of the mesophase the adjacency of values of this size along two directions are observed. Apparently, it is connected with melting, disintegration of dimers and bleaching, when additional levels of freedom appear.

The other picture was observed at the modeling of multilayered clusters (Table 1). As could be seen from the Figure 4, the change of the ordering degree is very similar to the changes of this value in typical substrates – the presence of the significant bend in the area of melting temperature and the essential reduction in the area of bleaching temperature. At the same time there is a slight increase of the ordering degree in the carbon nano-substrate in all compounds, especially in PEK and MBBA.

During the process of molecule temperature rise the ordering along other directions also varied. That can be caused by the consistent movement of the neighboring rows of atoms that is located in the "herringbone" position relatively to each other.

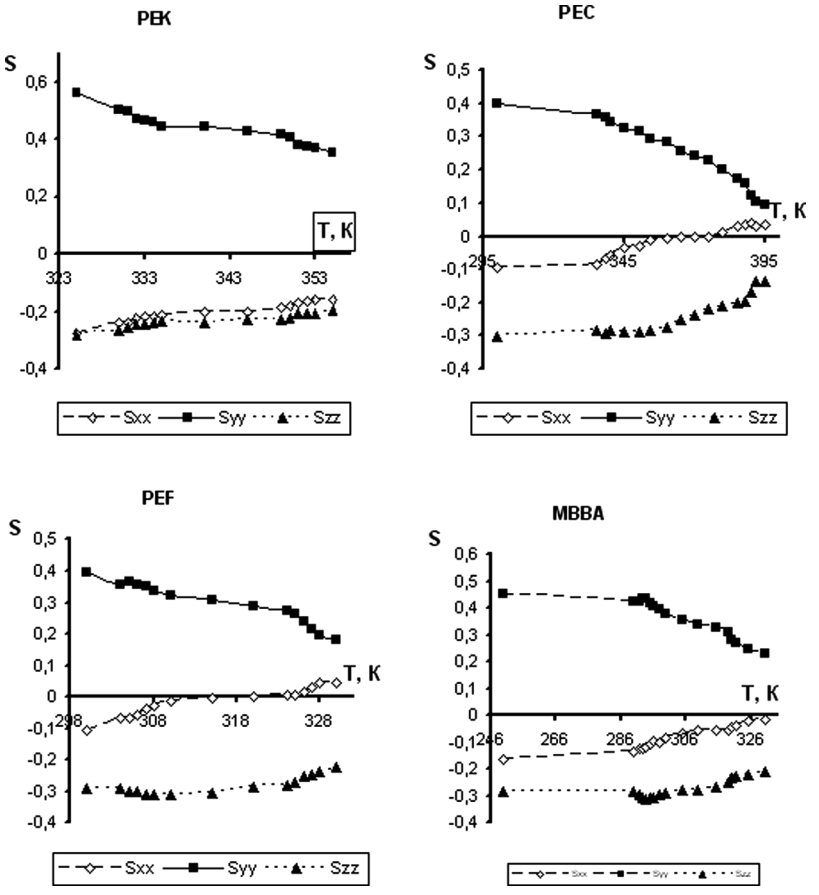

Figure 4. Temperature dependence of the ordering degree in the multilayer clusters.

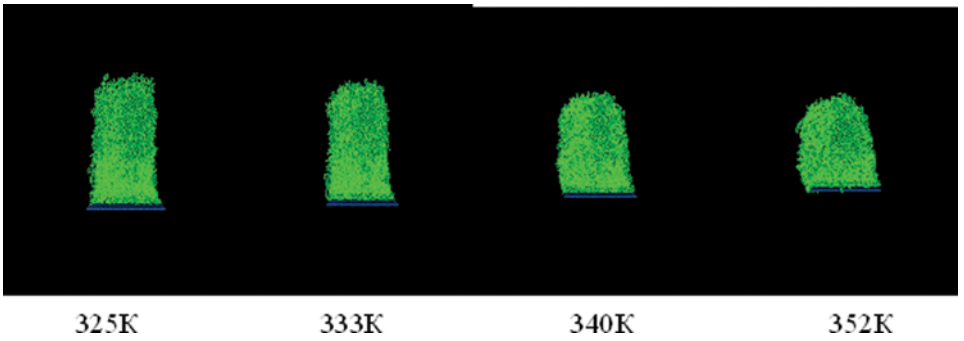

Figure 5. Pictures of cluster with PEK in XOZ plane at crystal condition, melting, mesophase and bleaching. (Figure appears in color online.)

The greatest values of self-diffusion coefficient are observed for the molecule, which is placed on the edge of XOZ plane in all researched clusters.

The temperature dependences of cells volume represent the curves, which show the reduction of these values with the temperature rise, and which has characteristic bends in the phase of transitions regions of these compounds [4,5,8]. It can be connected to the ⟨⟨flowing⟩⟩ of cluster with the temperature rise.

The visualization of the condition had confirmed this assumption. As could be seen in the Figures 5–8, the form of clusters varies, passing evolution from the crystalline state, melting, and mesophases and bleaching.

In this case, the original ''stream'' at which molecules crawl over the long side of the substrate (OY axis) is observed. Considering the fact that ordering monotonously changes with the temperature rise, it can be stated that movement of the molecules occurs in the direction that is perpendicular to longitudinal axis of the molecule. It less appear in case of the PEK, which can be connected with 'slowing down' of molecules by means of CH3 branched group.

The discovered stream of the molecules, which are placed on the flat carbon nano – substrate, at the temperature influence, is the reason of higher values of the ordering in clusters with PEK, which is less floating. There was no stream at usual substrates. The ordering degree on this compound was lower than in others.

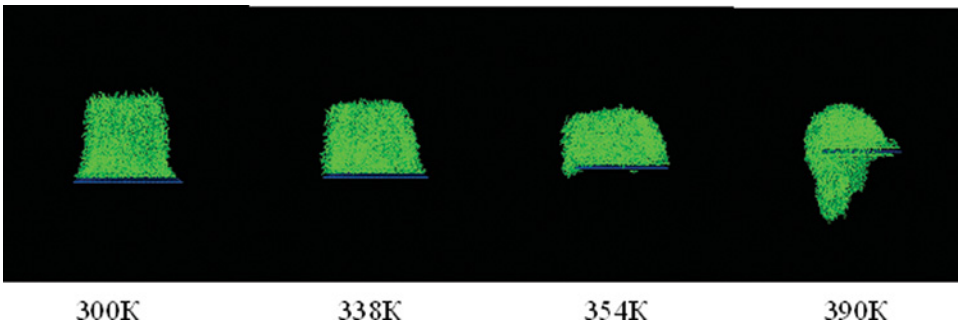

Figure 6. Pictures of cluster with PEC in XOZ plane at crystal condition, melting, mesophase and bleaching. (Figure appears in color online.)

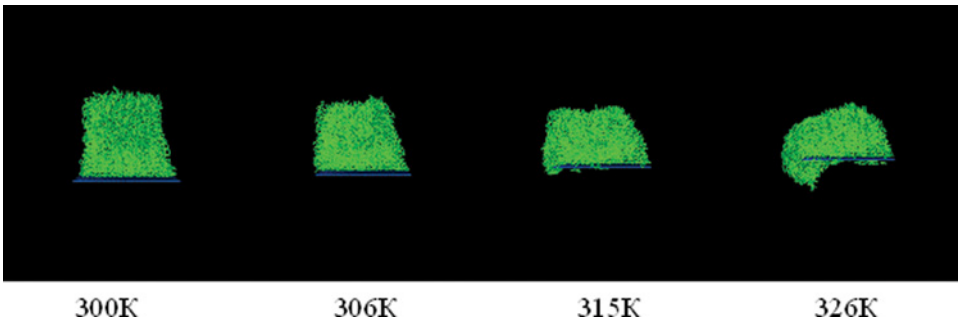

Figure 7. Pictures of cluster with PEF in XOZ plane at crystal condition, melting, mesophase and bleaching. (Figure appears in color online.)

The temperature dependences of the information entropy of cluster show that processes of disorder proceeds slowly with temperature increase, which might be connected to the orienting role of nano-substrate.

4. Conclusions and Perspectives

The discovered effects show a considerable role of the substrate and its influence on the dynamic of the researched nematic liquid crystals.

As dependence of substrate energy on its sizes shows (Table 2) it has negative values that absolute values of which increase with growth of its sizes. Apparently, the symmetry of the substrate itself explains negative values. This leads to mutual compensation of forces of interaction inside the substrate. Non-compensated forces represent forces of attraction, defined by the atoms on border of the substrate. Obviously, the forces of the greatest attraction should be generated along the normal to the long side of substrate. In our experiment the stream goes by the exact way.

The presence of flow was observed in II and III cases. The discovered effect explains the experimental fact of change of polarizing pictures at the application of such substrate into work [9].

So, the undertaken researches have allowed establishing the effect of the stream of various nematic liquid crystals along nano- substrate and the influence of their structure on the processes of disorder.

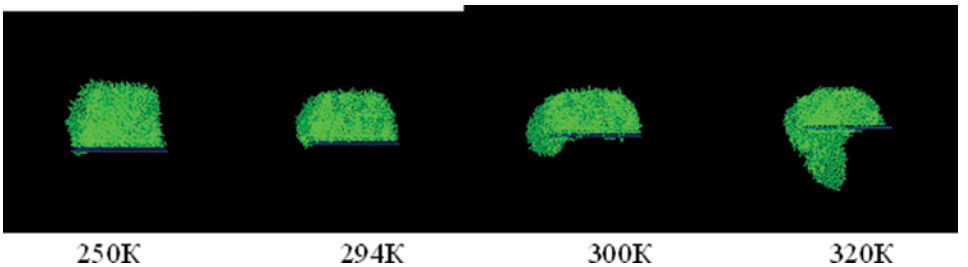

Figure 8. Pictures of cluster with MBBA in XOZ plane at crystal condition, melting, mesophase and bleaching. (Figure appears in color online.)

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