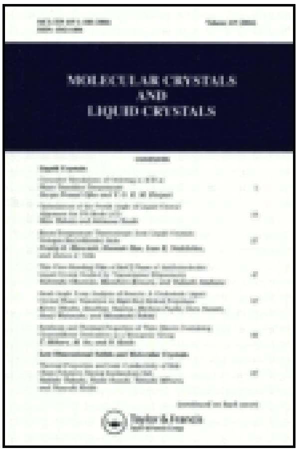

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Mesogen Molecules Orientation on Crystal Surfaces

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Version of record first published: 30 Jun 2011

To cite this article: A. K. Dadivanyan, Y. M. Pashinina, D. N. Chausov, V. V. Belyaev & A. S. Solomatin (2011): Mesogen Molecules Orientation on Crystal Surfaces, Molecular Crystals and Liquid Crystals, 545:1, 159/[1383]-167/[1391]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.571998

Mol. Cryst. Liq. Cryst., Vol. 545: pp. 159/[1383]–167/[1391], 2011
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.571998

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The goal of the work is a simulation of LC and their fragments orientation by calculating an interaction energy between atoms of different molecules with atoms of a substrate's surface with regular structure (graphite, polyethylene) vs *angles which characterize their orientation towards the surface. A model of a contacting surface is proposed to explain type of LC alignment.*

Keywords Crystal; graphite; orientation; polyethylene; simulation; surface

1. Introduction

Molecules of mesogens, some anisodiametric compounds and glass-like polymers are oriented towards the interfacial surfaces [1–6]. A lot of materials are known to align liquid crystals (LC) [7–9]. Empirical alignment parameters like pretilt angle, polar and azimuthal components of the LC anchoring energy have been measured for them [8–10]. In some cases an empirical link between molecular structure of both LC and orientant substance and alignment parameters has been found [8,9]. Only a few papers have been published on a theory of such interaction [11,12]. In [12] calculations of the 8CB (4-octyl-4′-cyanobiphenyl) on graphite surface is made by using of atom-atomic potential and Monte-Carlo methods. More promising are molecular dynamics simulations [13,14] allowing good accuracy calculations of many physical properties of both calamitic and discotic LC.

An urgent task is to develop a theoretical model for both qualitative and quantitative description of probability of some LC orientation type on surfaces with different structure. The goal of the work is a simulation of LC and their fragments orientation by calculating an interaction energy between atoms of different molecules with atoms of a substrate's surface with regular structure.

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2. Simulation Method

At initial modeling stage the surfaces of graphite and polyethylene with well-known structure [15] have been chosen. Cyanobiphenyl derivatives have been chosen as the LC molecules. Besides the interaction energy of alkanes, diphenyl, alkyldiphenyl molecules which can be imagined as mesogenic molecules fragments with the crystal surface has been estimated.

We have investigated the interaction of molecules of hexane (C_6H_{14}), decane ($C_{10}H_{22}$), dodecane ($C_{12}H_{26}$), heptadecane $C_{17}H_{34}$, diphenyl (C_6H_5-C_6H_5), pentyldiphenyl (C_6H_5-C_6H_4-C_5H_{11}) and 8CB (C_8H_{17}-C_6H_4-C_6H_4-CN) with the surfaces of both graphite and polyethylene.

The molecular models have been constructed on their atoms coordinates. In calculations the groups CH, CH_2, CH_3 have been replaced by model atoms. Their interaction energy well corresponds to the interaction of these groups [5,16]. Such replacement smoothes a dependence of the interaction energy on some parameters defined by molecules' mutual position and simplifies the calculation. The rotation angle between both phenyl rings has been taken initially as zero. Then a more realistic value equal to 30° has been taken which was confirmed by quantum chemistry calculation [17–18].

Model of the surface of the graphite crystal lattice is a set of the carbon atoms situated in the vertices of equilateral hexagons at a distance of 1.42 Å (Fig. 1). The distance between planes built on the atoms centers is equal to 3.35 Å.

An elementary cell of the polyethylene crystal is shown in Figure 2. The macromolecule's carbon atoms form a zigzag-like chain. The C-C distance in the chain is equal to 1.54 Å. The C-C-C valent angle is equal to 109.5°. The elementary cell dimensions are as high as $a = 7.40$ Å, $b = 4.93$ Å, $c = 2.534$ Å.

The interaction energy is presented as a sum of the interaction energies between the molecule's atoms and the crystal surface's atoms in accordance with an equation (Lennard-Jones potential):

$$E = \sum_{i,j} E_{ij}, \quad E_{ij} = \frac{A}{r_{ij}^{12}} + \frac{B}{r_{ij}^{6}},$$

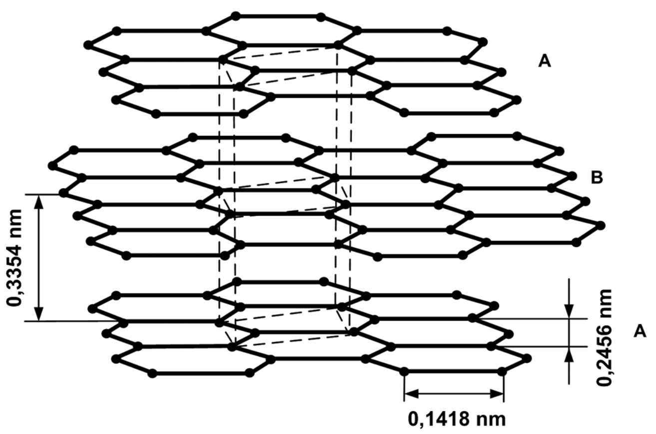

Figure 1. Graphite crystal lattice.

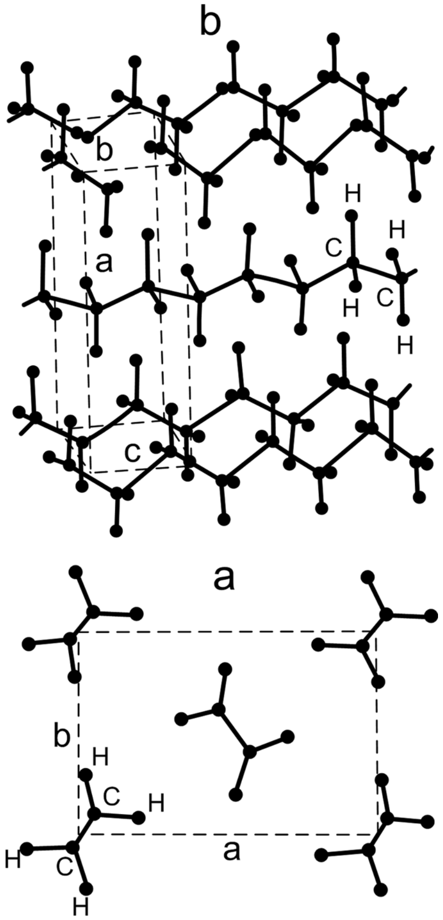

Figure 2. The polyethylene elementary cell. (a) view from *ac* plane; (b) view from *ab* plane.

where $A = 1.15 \cdot 10^{10}\,\mathrm{J \cdot mole^{-1}\,Å^{12}}$; $B = -5.3 \cdot 10^{6}\,\mathrm{J \cdot mole^{-1}\,Å^{6}}$; R_{ij} – distance between the surface's atom i and molecule's atom j.

Recently by using such method of atom-atom potential the short-range orientational order in polymer-solvent system has been investigated and good agreement of both theoretical results and experimental data has been obtained [19].

The molecule's orientation towards the crystal surface is defined by angles θ, φ and ψ which vary from 0 to 90° with pitch 10° (Fig. 3). The initial distance r from the inertia center of the molecule to the plane formed by the inertia centers of the surface carbon atoms was taken to be equal to 3 Å. Then the energy was minimized on r.

3. Results

Dependences of the interaction energy for systems diphenyl – graphite surface and diphenyl – polyethylene surface are presented in Figures 4 and 5, respectively. For the system diphenyl – graphite surface the interaction energy depends strongly on the angles θ, ψ, and does not depend on φ. For the system diphenyl – polyethylene

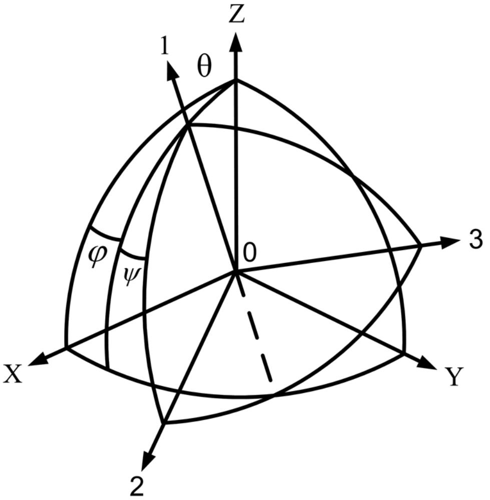

Figure 3. Molecule (1, 2, 3) and surface (x, y, z) coordinate systems.

surface the interaction energy depends on all three angles. There is a well-expressed *E* minimum (E_{min}) in a restricted range of the angles.

If the rotation angle between both phenyl rings is equal to 34° the *E* value reduces, it does not depend on φ like for parallel rings.

For the hydrocarbons the angular dependences of the intermolecular interaction energy of the alkanes with the crystal surfaces are similar. The absolute E_{min} value increases with the growing elongation of the molecular chain (Fig. 6). For the system with polyethylene the absolute E_{min} value is 1.5–2 times lower than for another system investigated.

We have studied the interaction of different molecules with single crystal layer as well as two layers of both graphite and polyethylene surfaces. The second layer contribution into the interaction energy is ~10% that insufficiently influences the molecule's orientation on the crystal surface. Therefore the interaction can be calculated

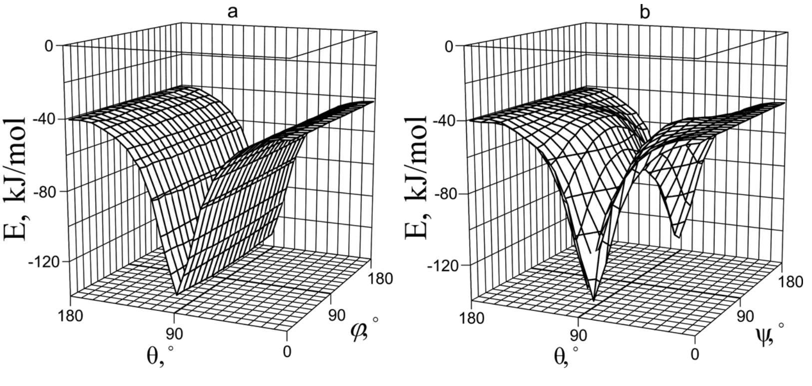

Figure 4. Dependence of the interaction energy *E* for the system diphenyl – graphite surface *vs* orientation angles θ, φ (a) and θ, ψ (b).

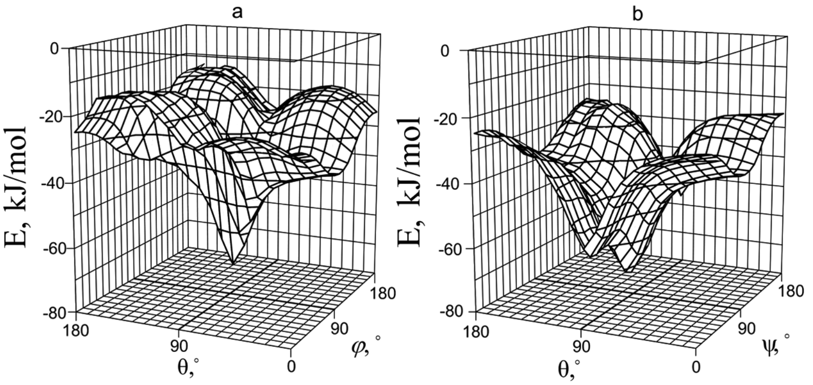

Figure 5. Dependence of the interaction energy E for the system diphenyl – polyethylene surface *vs* orientation angles θ, φ (a) and θ, ψ (b).

using only one layer on the crystal surface. The same conclusion has been obtained earlier in [12].

Dependences of the interaction energy for systems pentyldiphenyl – graphite surface and pentyldiphenyl – polyethylene surface are presented in Figures 7 and 8, respectively. In general these dependences calculated for the systems with pentyldiphenyl and diphenyl are similar. The absolute E_{min} value reduces in the case of the molecule with longer substituent – a similar effect has been obtained for both dodecane and heptadecane (Fig. 6). The absolute E_{max} value increases at addition of the pentyl fragment to the diphenyl core while in the case of alcanes it remains constant at different N. Main difference of both systems with pentyldiphenyl and diphenyl is another value of the ψ angle at which the energy E has its minimum.

In Table 1 the calculated values of the interaction energy minimums E_{min} are shown for the orientation states described by the angles θ_0, ψ_0, φ_0. The values of the interaction energy maximums E_{max} are also shown for the comparison. The $E(\theta, \psi, \varphi)$ dependence reaches its maximum at $\theta = 90°$ at any φ and ψ.

For the 8CB our data ($E_{min} = 205.8$ kJ/mole) correspond well to the data obtained in [12] by using an atom-atomic potential for a single 8CB molecule on

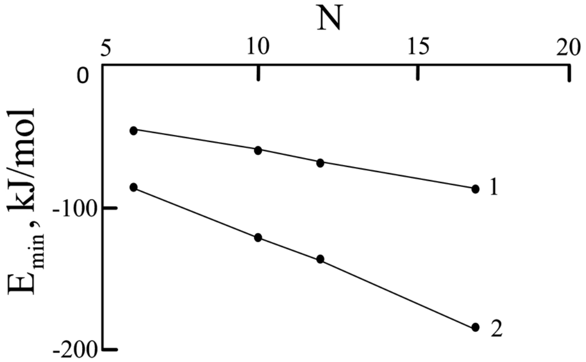

Figure 6. Dependence of the interaction energy E_{min} minimum for the systems alcane – graphite surface (1) and alcane – polyethylene surface (2) on the alcane length (N – number of the carbon atoms in the molecule).

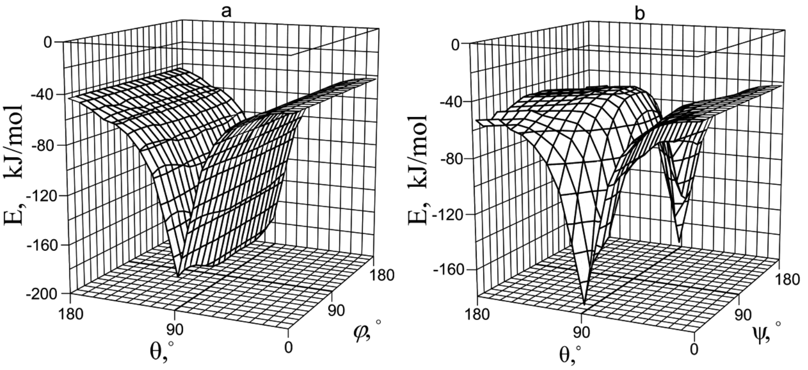

Figure 7. Dependence of the interaction energy E for the system pentyldiphenyl – graphite surface *vs* orientation angles θ, φ (a) and θ, ψ (b).

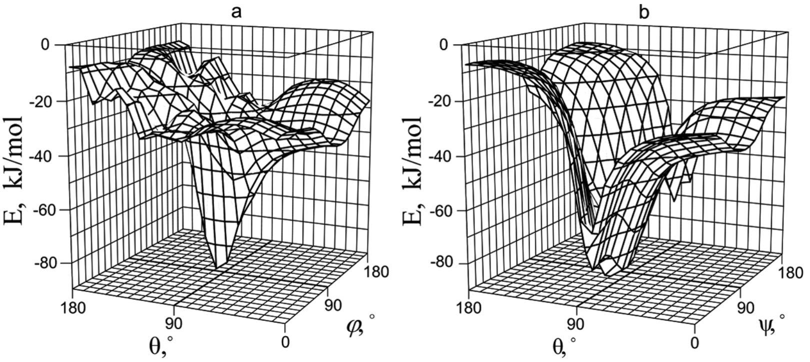

Figure 8. Dependence of the interaction energy E for the system pentyldiphenyl – polyethylene surface *vs* orientation angles θ, φ (a) and θ, ψ (b).

Table 1. Energy of interaction between the molecule and surface of both graphite and polyethylene

	Graphite surface					Polyethylene surface				
Substance	E_{min} kJ/mol	θ_0	φ_0	ψ_0	E_{max} kJ/mol	E_{min} kJ/mol	θ_0	φ_0	ψ_0	E_{max} kJ/mol
Hexane (C_6H_{14})	−68.6	90	30	0	−19.5	−47.1	90	80	60	−6.6
Decan ($C_{10}H_{22}$)	−113.8	90	30	0	−19.9	−60.1	90	90	60	−6.2
Dodecan ($C_{12}H_{26}$)	−136.5	90	30	0	−20.0	−69.04	80	80	60	−6.7
Diphenyl ($C_{12}H_{10}$)	−121.2	90	0	0	−40.6	−68.2	90	90	90	−12.5
Pentyldiphenyl (C_6H_5–C_6H_4–C_5H_{11})	−174	90	0	0	−21.3	−88.6	90	90	70	−6.6
8CB (C_8H_{17}–C_6H_4–C_6H_4–CN)	−205.8	90	0	0	−28.0	−104.6	60	90	90	−7.4
8CB (C_8H_{17}–C_6H_4–C_6H_4–CN)	−235				−5.0			[12]		

the crystalline graphite surface ($E_{min} = 235$ kJ/mole). A small discrepancy can be owing to using another potential with other interaction constants [20,21].

4. Discussion

The data obtained allow a determination of the type of the molecule's orientation towards the interfacial surface. For this purpose the specific surface interaction energy should be found which can be calculated by division of the interaction energy of the molecule by the interface contact area of the single molecule $\varepsilon = E_{min}/S_i$. The method of ε evaluation is illustrated in Figure 9. For the diphenyl in the case of $\theta = 90°$ the molecule's contact area is equal to $S_p = 1 \cdot w$ ($8.0 \cdot 10^{-17}\,m^2$) and to $S_h = w \cdot t$ ($2.8 \cdot 10^{-17}\,m^2$) in the case of $\theta = 0°$. In the case of random orientation of the molecules in the plane parallel to the interface area per one molecule is equal to $\pi w^2/4$ ($3.7 \cdot 10^{-17}\,m^2$).

The specific surface interaction energy of the diphenyl molecule with the graphite surface is equal to $-0.28\,J/m^2$ in the case of planar orientation ($\theta = 90°$) and $-0.24\,J/m^2$ (dense packing) or $-0.18\,J/m^2$ (random packing) in the case of homeotropic orientation ($\theta = 0°$). Hence the interaction energy values are rather close for both planar and homeotropic orientation of the diphenyl on the graphite surface. The type of the mesogen orientation can be determined by the substituents. For the 8CB the specific surface interaction energy is equal to $-0.28\,J/m^2$ in the case of planar orientation and $-0.15\,J/m^2$ in the case of homeotropic orientation on the graphite surface (Table 2). On the polyethylene surface these values are equal to $-0.14\,J/m^2$ (planar orientation) and $-0.04\,J/m^2$ (homeotropic orientation),

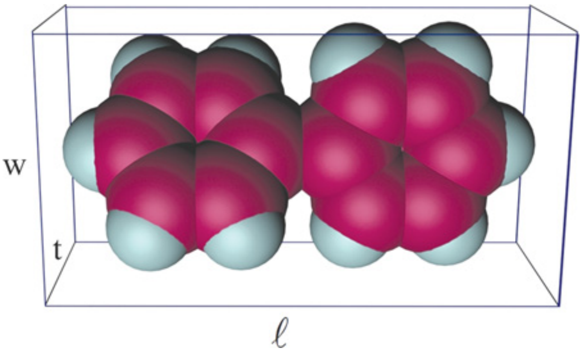

Figure 9. A model of the diphenyl molecule for an evaluation of the specific surface interaction energy ε, *l*, *w* and *t* are respectively length, width and thickness of the model parallelepiped comprising the molecule. (Figure appears in color online.)

Table 2. Specific surface interaction energy

System	$\varepsilon J/m^2$, $\theta = 90°$	$\varepsilon J/m^2$, $\theta = 0°$	$\varepsilon J/m^2$, $\theta = 90°$ $0° < \psi < 90°$
Graphite – diphenyl	−0.285	−0.242	−0.182
Graphite – 8CB	−0.284	−0.15	−0.113
Polyethylene −8CB	−0.138	−0.04	−0.03

respectively. Therefore the 8CB should have the planar orientation on both types of the surfaces that corresponds well to experimental data and other calculations. Typical surface interaction energy for mesogens is as high as 30–40 mJ/m^2 [7–9].

5. Conclusions

- A method of atom-atom potential has been used to calculate a dependence of interaction energy of molecules of mesogens, aromatic and aliphatic hydrocarbons with graphite and polyethylene surface *vs* angles of their orientation. A calculation of the 8CB-graphite interaction energy corresponds to literature data by V. Palermo, F. Biscarini, C. Zannoni [12].
- Absolute value of the interaction energy of alcanes molecules with both graphite and polyethylene surfaces increases with the increase of the molecule length in the case of planar orientation and remains constant in the case of homeotropic orientation.
- A model has been proposed to evaluate the specific surface energy of a single molecule. An evaluation made for liquid crystals molecules allows an explanation of both planar and homeotropic alignment, while diphenyl and 8CB molecules have the planar orientation towards the surface.

Acknowledgment

The authors thank Professor C. Zannoni for helpful discussion of the work and Dr. T. Ichinose, Prof. G. Derfel, Prof. A. Vajda, Prof. I. Janossy for their attention to the work.

The work is supported by Russian Foundation for Basic Researches, grants ##10-07-00385-a, 10-03-90028-Bel_a and Ministry of Education and Science of Russian Federation, State Contract #02.740.11.5218.

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