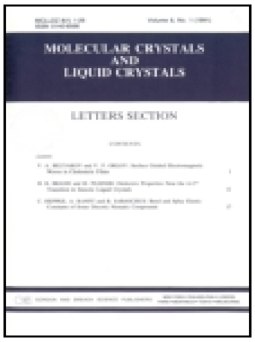

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: D. N. Chausov, A. K. Dadivanyan, O. V. Noah & V. V. Belyaev (2015) Dependence of Mesogen Molecules Interaction Energy on their Mutual Orientation, Molecular Crystals and Liquid Crystals, 611:1, 21-26, DOI: 10.1080/15421406.2015.1027991

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1027991

Mol. Cryst. Liq. Cryst., Vol. 611: pp. 21–26, 2015
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1027991

Dependence of Mesogen Molecules Interaction Energy on their Mutual Orientation

D. N. CHAUSOV,[1,2,*] A. K. DADIVANYAN,[1] O. V. NOAH,[3]
AND V. V. BELYAEV[1,4]

[1]Moscow Region State University, Moscow, Russia
[2]Moscow Academy of Market Labor and information Technologies, Moscow, Russia
[3]Moscow State University, Moscow, Russia
[4]People's Friendship University of Russia

For interaction energy of mesogenic model rod-like molecules an analytical expression is obtained. Interaction energy of dipole moments interaction is much less than the total interaction energy. The empirical Rapini-Papoulard potential for the free surface energy of liquid crystals corresponds well with a limiting case of the expression obtained for small orientation angles.

Keywords interaction energy; mesogenic molecules; modeling; atom-atom potential; dipole moments

I. Introduction

Liquid crystal (LC) orientation in relation to the interface surface is an important problem of both theory and technology [1–9]. There are interesting tasks of intermolecular interaction in different substances that are in different phases. The orientation process is also important in production technology of displays, electrooptic and organic electronics devices [10].

In our previous publications [11–15] a method of atom-atom potentials was used to investigate alkanes and mesogens interaction with different crystals surface. Dependence of molecules' interaction energy on their orientation angles in relation to the crystal surface of graphite, polyethylene, polyorganosiloxanes was determined and type of the LC alignment in relation to the surfaces investigated was explained. In [11–13, 16] a model was proposed to explain experimental temperature and order parameter dependences of both polar and azimuthal anchoring energy as well as these parameters values [17].

Mutual orientation of the mesogen molecules is considered in different molecular statistical theories [18–21]. Their detailed narration is presented in [21–23]. Nevertheless till present there was no analytical formula for the mutual orientation angle dependence of the mesogen molecules interaction energy.

The goal of the work is to find a dependence of the interaction energy of the rod-like molecules on their mutual orientation and their orientation in relation to a flat surface.

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[*] Address correspondence to D. N. Chausov, Moscow Region State University, Moscow, Russia. Email: d.chausov@yandex.ru

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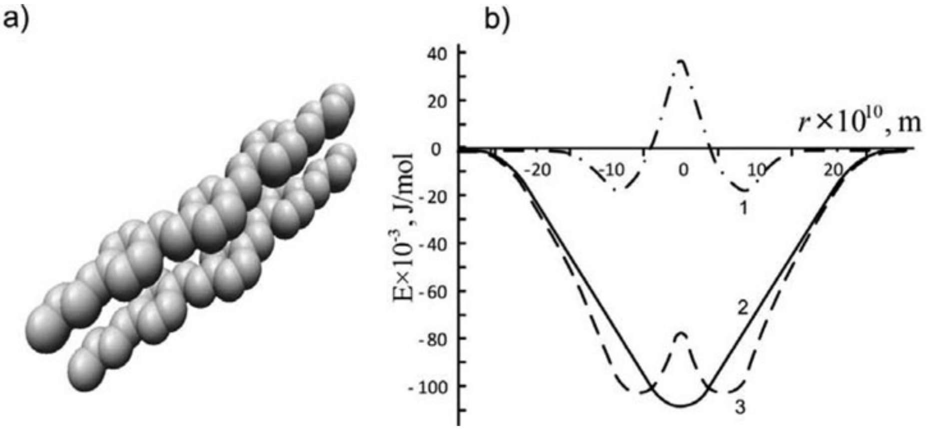

Figure 1. a) Mutual position of the TBBA molecules relative to each other. b) Dependences of the intermolecular interaction energy of the TBBA molecules moved relative to each other. 1 – dipole-dipole interaction, 2 – interaction calculated by using atom-atom potentials, 3 – total interaction energy.

II. Model

Let us consider interaction of two terephtal-*bis*-(*n*-butylaniline) (TBBA) molecules moved relative to each other (Fig. 1a). Two types of interaction were calculated: intermolecular interaction energy by using atom-atom potentials (curve 2 in Fig. 1b) and interaction of molecular dipole moments (curve 1 in Fig. 1b). In calculation with using atom-atom potentials relations as follows were used:

$$E = \sum_{i,j} E_{i,j}, \tag{1}$$

$$E_{i,j} = \frac{\mathrm{A}}{R_{i,j}^{12}} - \frac{\mathrm{B}}{R_{i,j}^{6}} \tag{2}$$

A relation as follows was used for the dipole-dipole interaction:

$$E_{i,j} = [\vec{p}_i\vec{p}_j r_{i,j}^2 - 3(\vec{r}_{i,j}\vec{p}_i)(\vec{r}_{i,j}\vec{p}_j)]/r_{i,j}^5 \tag{3}$$

where A and B values are taken from [24], p_i, p_j are dipole moments of molecules i and j positioned in points with coordinates r_i, r_j.

The dipole-dipole interaction energy is by one order of magnitude lower than the total interaction energy (curve 3 in Fig. 1b). Therefore the dipole-dipole interaction is not considered in the model developed. In the model all atoms C and groups CH, CH_2, CH_3 were replaced with model atoms C′. The validity of such replacement is proven in [17, 24]. The distance between the atoms is chosen so that the model molecule length would be equal to the mesogen molecule length and the number of atoms and groups in both real and model mesogen molecules would be the same too.

The molecules' orientation is defined by both polar θ and azimuthal φ angles (Fig. 2).

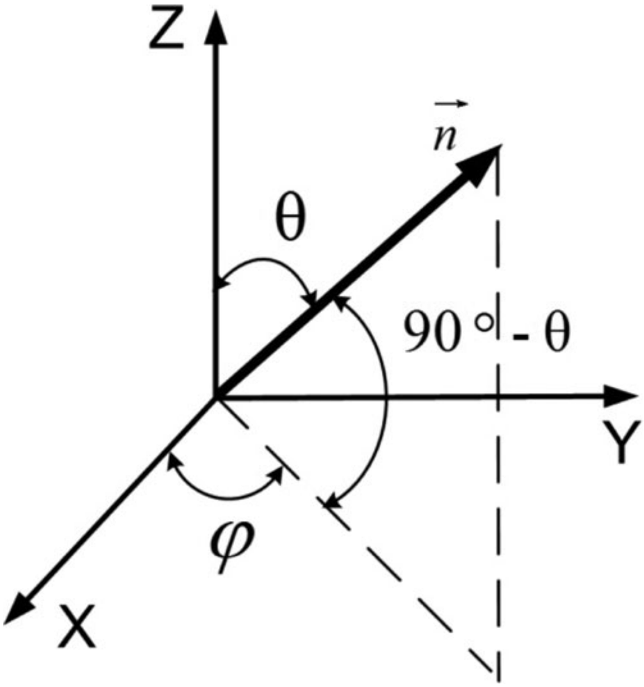

Figure 2. The coordinates system for a description of the mesogen molecules interaction.

In the model the molecule is presented as a rigid rod with the atoms beaded on it. The intermolecular interaction energy E was calculated by the method of atom-atom potentials (2), it was presented in a view of sum of the interaction energy of separate atoms of the molecule (1) (Fig. 2).

Energy of particles pair interaction is described by Lennard-Jones potential. Therefore

$$E = 2\sum_{i,j,k}\left(\mathrm{A}\left(\frac{1}{R_{i,j}^{12}} + \frac{1}{R_{j,k}^{12}}\right) - \mathrm{B}\left(\frac{1}{R_{i,j}^{6}} + \frac{1}{R_{j,k}^{6}}\right)\right). \tag{4}$$

Distances $R_{i,j}$ and $R_{j,k}$ (Fig. 3) have a view as follows

$$R_{i,j}^2 = r_i^2 + r_j^2 + D^2 - 2r_i r_j \cos\alpha = a_{i,j} - b_{i,j}\cos\alpha, \tag{5}$$

$$R_{j,k}^2 = r_j^2 + r_k^2 + D^2 + 2r_j r_k \cos\alpha = a_{j,k} + b_{j,k}\cos\alpha. \tag{6}$$

where $a_{i,j} = r_i^2 + r_j^2 + D^2$, $b_{i,j} = 2r_i r_j$, D is the atom's diameter, r_i and r_j are radii-vectors from the coordinates center to atoms i and j. The values of r_k and r_i can be chosen so that r_k = -r_i, then equalities $a_{i,j} = a_{j,k}$ and $b_{i,j} = b_{j,k}$ can be obtained.

Then the intermolecular interaction energy can be written in a view as follows:

$$E = 4\sum_{i,j}\left(2\mathrm{A}\left(\frac{a_{i,j}^3 + 3a_{i,j}b_{i,j}^2\cos^2\alpha}{\left(a_{i,j}^2 - b_{i,j}^2\cos^2\alpha\right)^3}\right)^2 - \mathrm{B}\left(\frac{a_{i,j}^3 + 3a_{i,j}b_{i,j}^2\cos^2\alpha}{\left(a_{i,j}^2 - b_{i,j}^2\cos^2\alpha\right)^3}\right)\right). \tag{7}$$

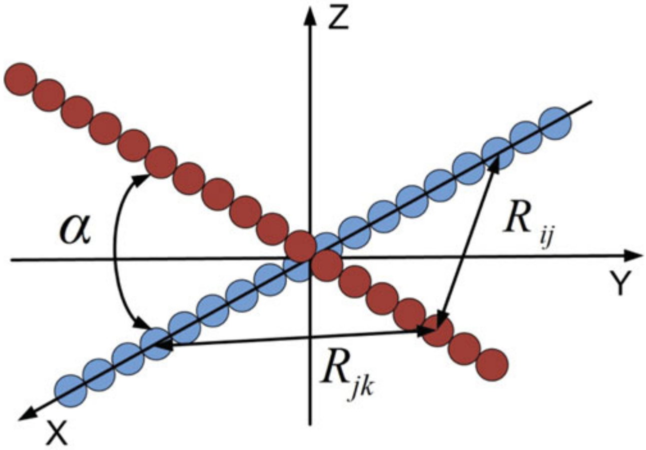

Figure 3. Mutual position of the mesogen molecules.

The formula (5) can be approximated at α close to 90° to an expression follows:

$$E = 4\sum_{i,j}\left(\frac{\mathrm{A}}{a_{i,j}^6}\left(1 + 12\frac{b_{i,j}^2}{a_{i,j}^2}\cos^2\alpha\right) - \frac{\mathrm{B}}{a_{i,j}^3}\left(1 + 6\frac{b_{i,j}^2}{a_{i,j}^2}\cos^2\alpha\right)\right) \tag{8}$$

After summation the expression (8) is transformed to $E = C_1 + C_2\cos^2\alpha$, where C_1, C_2 are constants.

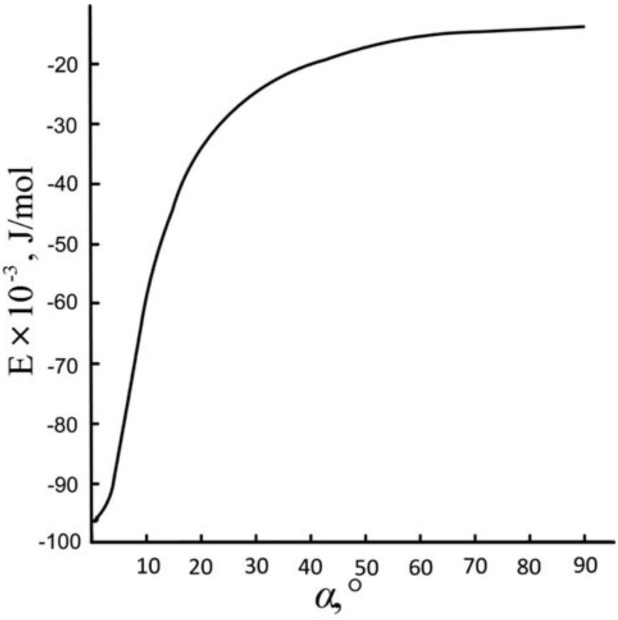

Figure 4. A dependence of the intermolecular interaction energy E on the angle between the mesogen molecule and a layer of mesogen molecules.

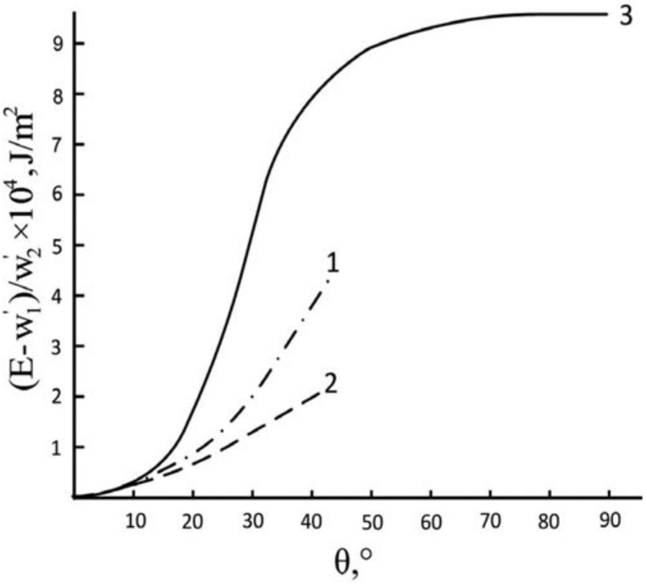

Figure 5. A dependence of the energy $(E - w'_1)/w'_2$ on the angle between the molecule and the normal to the surface. 1 – data from [25], 2 – data from [26], 3 – data of the model developed.

If the angle α is replaced for the angle θ between the molecule axis and a perpendicular to the *XOY* plane then the angular dependence of the energy is written as $E = w'_1 + w'_2 \sin^2 \theta$. It coincides with the expression of the surface energy proposed by Rapini and Papoulard [25].

In Fig. 4 a dependence of the intermolecular interaction energy *E* on the angle between the mesogen molecule and a layer of mesogen molecules is presented. The number of the atoms in the molecule is equal to 20 and the number of the molecules in the layer is equal to 10. In Fig. 5 a comparison of our modeling results and data presented in [25, 26] is shown. The energy per the unit surface is presented as a parameter $(E - w'_1)/w'_2$.

One can see that in Fig. 5 the curves 1, 2 and 3 almost coincide at small θ angles. In [25, 26] the calculations are made for the surface energy while in our model for the system internal energy. Therefore the surface energy change *vs.* the orientation angle is determined mainly by the internal energy.

Conclusions

1. A component of the interaction energy relating to the dipole moments interaction is much less than the total interaction energy.
2. Dependence for energy of interaction of isolated rod-like molecules on the angle between them is derived and calculated.
3. Well known empirical Rapini-Papoulard potential for the free surface energy of liquid crystals is in good agreement with an ultimate case of the expression obtained at $\alpha \sim 90^\circ$.

Funding

The work was supported by Russian Foundation for Basic Researches, grants №14-07-31327-mol_a and 14-07-00574-A and the President of the Russian Federation, grant of MK-2382.2014.9.

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