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Peculiar features and applicability of asymptotic expansions of additive intermolecular interactions in anisotropic media. II. The role of anisometry in formation of supramolecular structures in mesogenic systems

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Long-range components of coefficients of SO(3)-invariant expansions of intermolecular forces (U-coefficients) have been studied for Lennard-Jones interactions between force centers (atoms). In a simple geometrical model, a new effect has been discovered, consisting in inversion of the U-coefficient dependences upon intermolecular distances as function of molecular anisometry. Possible manifestations of this effect in experimentally observed properties of complex liquid and liquid crystalline systems are discussed, as well as its role in formation of microheterostructures.

Проведено исследование дальнодействующей составляющей коэффициентов SO(3)-инвариантных разложений анизотропных межмолекулярных взаимодействий (U-коэффициентов) для леннард-джонсовских взаимодействий между силовыми центрами (атомами). Для простой геометрической модели обнаружен эффект инверсии зависимостей U-коэффициентов от межмолекулярных расстояний как функции молекулярной анизометрии. Обсуждаются возможные проявления этого эффекта в экспериментально наблюдаемых свойствах сложных жидких и жидкокристаллических систем и его роль в образовании микрогетероструктур.

This paper is a continuation of a series of works that was initiated in our previous publication [1]. The sense and meaning of specific terms and notation introduced there has been preserved.

In microscopic models, substantial interest is aroused by analytical properties of intermolecular interactions (IMI) and peculiar features of their asymptotics. The latter are determined by the long-range component of IMI and largely determine physical properties of a substance in the vicinity of critical points and at the phase boundaries, solvatation phenomena on colloid systems, and many others [2]. The existence of a relationship between molecular shape and mesomorphic properties in liquid crystals has been intuitively clear since long ago (see [3] and literature therein). Possibly this was the reason why the first successful model of mesomorphism was the theory of Onsager [4] based on the concept of excluded volume. Later, Maier and Saupe proposed a simple mean field model in spherical approximation [5], based on anisotropy of molecular polarizability. This model was further developed by Luckhurst e.a. [6] (the use of cylindrical approximation, account for molecular biaxiality, etc.). The "language barrier" that had emerged was

largely overcome in numerous approaches combining the mean field and the excluded volume concept (see, e.g., [7, 8]). Among important theoretical results, one should note power dependences of the Frank elasticity moduli on molecular length (anisometry) [9, 10], which is in qualitative agreement with experimental data (in particular, for one-component system). However, in practical applications the most commonly used are multi-component liquid crystals (LC). Numerous experiments and numerical calculations involving LC mixtures show more complex dependences of their properties upon the shapes of constituent molecules [11, 12]. In particular, as it seems from analysis of a number of experimental data [12, 13], the difference in length between the constituent molecules of a LC mixture is a factor not less important than anisometry. Onsager-type theories were successfully applied to lyotropic and polymer LC [14, 15]. In colloids, mesomorphic transitions I-N, I-N-N were reported [16]. Theoretical description of broadening of the phase separation region, as well as of other effects, was proposed in [17–20], using a generalized Onsager theory and a model of polydisperse systems with partitioning over molecular lengths. It should be noted here that construction of such models is generally based on the choice of distribution statistics over molecular lengths in the system, with peculiar features of the involved IMI being largely neglected. In other words, an assumption is made that packing factors play a decisive role in formation of structural properties of the systems considered.

Recent developments in computer technologies have opened new possibilities for modeling of anisotropic media [21]. In this relationship, new advanced models of IMI accounting for real molecular structure would be welcome. In this paper, we propose a simple model of anisotropic IMI, considering first of all their long-range components.

The symmetry properties of coefficients of SO(3)-invariant expansions of anisotropic intermolecular interactions (IMI) were discussed in [25–31]. Here we pay our main attention to those properties that result from using additive (scalar) potentials (in particular, atom-atom potentials) in their general form for arbitrary distances.

Anisotropic IMI can be presented in the following form [1]:

$$E(i,j) = E(\Omega_i,\Omega_j,R_{ij}) = \sum_{\left\{\begin{smallmatrix} l_1, l_2, l_3 \\ m_1, m_2 \end{smallmatrix}\right\}} U^{l_1 l_2 l_3}_{m_1 m_2}(R_{ij})\Theta^{l_1 l_2 l_3}_{m_1 m_2}(\Omega_i,\Omega_j,\hat{R}_{ij}), \quad (1)$$

Here: $\mathbf{R}_{ij}$ — radius-vector connecting the centers of molecular system of coordinates (MSC) of molecules i and j; $R_{ij} = \mathbf{R}_{ij}/R_{ij}$; $R_{ij} = |\mathbf{R}_{ij}|$; $\Omega_{i(j)}$ is a set of Euler angles parametrizing the orientation of the coordinate system of the i-th (j-th) molecule; the rotational invariants $\Theta^{l_1 l_2 l_3}_{m_1 m_2}(\Omega_i,\Omega_j,\hat{R}_{ij})$ have been defined in [32].

For a specified distribution density of the force centers $\rho(\mathbf{r}, i)$ over the volume of molecule i and potential of their interaction $u(\mathbf{r}_{ij})$ (e.g., atom-atom interaction), the expression for U-coefficients has the form [29, 1]:

$$U^{l_1 l_2 l_3}_{m_1 m_2}(R_{ij}) = (2p)^6(-1)^{l_2} i^{l_3} [l_1 l_2 l_3^2] \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \times \int_0^\infty dk k^2 j_{l_3}(kR_{ij}) u(k) \overline{\rho_{l_1 m_1}}(k;i) \overline{\rho_{l_2 m_2}}(k;j) \quad (2)$$

where

$$\overline{\rho_{lm}}(k;i) = \frac{(-i)^l}{2\pi^2} \int_0^\infty dr r^2 j_l(kr)\rho_{lm}(r;i),$$
$$\rho_{lm}(r;i) = \frac{[l]}{\sqrt{4\pi}} \int d\hat{r} D^l_{m0}(\hat{r})\rho(\mathbf{r},i), \quad (2a)$$

$j_l(z)$ — spherical Bessel function, $u(k) = (2\pi)^{-3}\int u(r)e^{-i(k\cdot r)}dr$.

Coefficients $U^{l_1 l_2 l_3}_{m_1 m_2}(R_{ij})$ of the expansion (1) possess the following general properties that follow from (2):

I. *Translational invariance* — IMI energy depends only on the difference $R_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$, which is reflected in (2);

II. *IMI energy is a scalar* with respect to rotation of the laboratory system of coordinates. This corresponds to the existence of expansion (1) and the property of $3j$ — symbols under rotation of the coordinate system [33]:

$$\sum_{(\mu,\nu,\lambda)} \begin{pmatrix} m & n & l \\ \mu & \nu & \lambda \end{pmatrix} D^m_{\mu\mu'}(\Omega) D_{\nu\nu'}(\Omega) D^l_{\lambda\lambda'}(\Omega) = \begin{pmatrix} m & n & l \\ \mu' & \nu' & \lambda' \end{pmatrix}. \quad (3)$$

III. *Real character of IMI*, i.e., the imaginary part is equal to zero. Accounting for the fact that the $3j$ — symbol in (2) is

not equal to zero only if $l_1 + l_2 + l_3 = 0$ (mod 2), we obtain:

$$\left(U^{l_1 l_2 l_3}_{m_1 m_2}(R_{ij})\right)^* = (-1)^{m_1+m_2} U^{l_1 l_2 l_3}_{-m_1 -m_2}(R_{ij}). \quad (4)$$

It should be noted that this relationship implies that U-coefficients are Hermitian when used as operators in quantum-mechanical problems, e.g., in calculation of Coulomb forces.

IV. *Permutation symmetry*. Transposing ($\Omega_1 \rightleftarrows \Omega_2$, $\hat{R}_{ij} \to \hat{R}_{ji}$), permutations ($l_1 \rightleftarrows l_2$) should also be made in (2). Then, accounting for the condition $l_1 + l_2 + l_3 = 0$ (mod 2), we obtain:

$$U^{l_2 l_1 l_3}_{m_2 m_1}(R_{ij}) = (-1)^{l_1+l_2} U^{l_1 l_2 l_3}_{m_1 m_2}(R_{ij}). \quad (5)$$

There is a peculiar feature in application of this relationship — it expresses invariance of the interaction energy with respect to permutation of the particles and has sense only together with the said permutations, i.e., they should be also made in the expansion (1):

$$\Theta^{l_1 l_2 l_3}_{m_1 m_2}(\Omega_i,\Omega_j,\hat{R}_{ij}) \leftarrow \Theta^{l_1 l_2 l_3}_{m_2 m_1}(\Omega_j,\Omega_i,\hat{R}_{ji}).$$

It is not quite correct to consider (5) as an identity relationship for the array of U-coefficients — first of all, it is a description of the result of permutation of the arguments in E_{ij}. The meaning of this property would be evident in macroscopic models of anisotropic solutions, where a symmetrized Hamiltonian should be constructed.

V. If (and only if) the molecules are identical, i.e., when $\overline{\rho_{lm}}(k;i) = \overline{\rho_{lm}}(k;j)$, then (again using the condition $l_1 + l_2 + l_3 = 0$ (mod 2)), we find:

$$\left(U^{l_2 l_1 l_3}_{m_2 m_1}(R_{ij})\right) = (-1)^{l_1+l_2} U^{l_1 l_2 l_3}_{m_1 m_2}(R_{ij}). \quad (6)$$

VI. The molecular symmetry also leads to constraints upon indexes of U-coefficients, i.e., reduces the number of independent U-coefficients. But more important is the possibility of direct determination of the relationship between molecular properties and macroscopic parameters of the medium (in the mean field approximation). Among the possible molecular symmetry groups, the best studied are point groups (finite subgroups of the rotation and reflection group O(3)). Using methods of group representation theory, conditions can be obtained for indexes required for non-zero U-coefficients [25–30]. E.g., if both interacting molecules are of $D_{\infty v}$ symmetry, it is easy to obtain from (2a)

$$U^{l_1 l_2 l_3}_{m_1 m_2}(R_{ij}) = \delta_{m_1 0}\delta_{m_2 0} U^{l_1 l_2 l_3}_{m_1 m_2}(R_{ij}). \quad (7)$$

This assumption on the mesogen symmetry is used in nearly all molecular models of nematics and smectics A. Other cases of point symmetry were discussed in this relationship in [25, 28, 30].

In calculations of different properties (electric, magnetic, etc.) represented by the respective molecular tensors, it is often necessary to use different reference systems [45]. But molecular symmetry can be different with respect to different properties. This is important to keep in mind for correct interpretation of experimental results (see., e.g., Chapter 7 in [33]). In other words, for calculations of different structural, physical and chemical molecular properties several different reference systems may be required. The corresponding transformation rules are given by the relationships (15) in [1].

VII. Effects of chirality are not apparent in additive anisotropic IMI (at least for rigid molecules). I.e., pseudoinvariants due to $\begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix}$ factor are absent among the U-coefficients. This also follows from their construction, since the initial system of atom-atom potentials is scalar. Psevdoinvariants in pair IMI cannot be also obtained by any partition of the molecules into fragments. To show this, it is sufficient to consider the long-range part of IMI. Really, in this case the use of the expression (3.10) from [29] gives the total molecular tensor of a molecule $\overline{r^{2N}_{LM}(1)}$ defined by the sum over fragment tensors $\overline{r^{2n_1}_{1m'}}$ centered at points with radius-vectors $\mathbf{d}_i$ with orientation ω_i with respect to the relative molecular coordinate system.

$$\overline{r^{2N}_{LM}(I)} = \quad (8)$$

$$= \sum_i \sum_{(n_1 n_2)>0} \sum_{\substack{l,l_d,m' \\ m,m_d}} \delta_{l+l_d+2(n_1+n_2),\,2N+L} B^{Lll}_{Nn_1 n_2} d_i^{l_d+2n_2} \times$$

$$\times \overline{r^{2n_1}_{1m'}(i)} C^{L0}_{l0l_d0} C^{LM}_{lml_d m_d} D^{l_d}_{m_d 0}(\hat{d}_i) D^{l}_{mm'}(\omega_i).$$

Here the index **i** numbers the fragments.

It is clear that the use of (8) in $U^{l_1 l_2 l_3}_{m_1 m_2}(R_{ij})$ for power potentials [1] allows us to expand our method to tensor interactions

and more complex molecular structures. However, the presence of the above-noted factor (the 3*j*-symbol with zero moment projections) excludes the presence of pseudoinvariants. This also applies, in particular, to electrostatic forces (regardless of the molecular shape and/or charge distribution over the molecule). Still, chiral interactions can be (and probably should be) purposely introduced into the additive models by many ways, when three- or many-particle distribution functions are used in one or another form as a result of recomputation of pair IMI in the field of a third molecule [34], or when restrictions are imposed (e.g., steric) upon molecular degrees of freedom [35], etc. Our assertion that pseudoinvariants are excluded in anisotropic IMI is also in agreement with considerations of Lubensky e.a. [36]: molecular chirality does not always imply chirality of the corresponding interactions, and the presence of chiral interactions is not unambiguously related to observed properties, e.g., helical twisting (cholesteric pitch).

Constraints upon indexes (l_1, m_1, l_2, m_2) in the U-coefficients are due to symmetry properties of the interacting molecules. These indexes correspond to orientational ordering in liquid and molecular crystals. E.g., $l_1 = l_2 = 0$ correspond to molecular ordering models in isotropic liquids, and $l_1 = l_2 = 2$ — in nematics. The index l_3 in the expansion (1) characterizes the symmetry (if present) of distribution of MCS centers. E.g., the value $l_3 = 0$ corresponds to models describing ordering of these centers in isotropic liquids and nematics. For description of smectics, coefficients with $l_3 > 0$ are required. In this relation, one should remember that multipole expansions of electrostatic forces can be directly related to the orientational ordering in molecular field models only in systems with violations of translational symmetry (see references in [37]), e.g., in smectics, colloids, in the vicinity of interfaces and phase boundaries, and, naturally, in molecular crystals. E.g., $l_3 = 2$ corresponds to the quadrupole-type ordering of molecular centers.

In this work, we limit ourselves to studying the role of molecular shape in mesogenic systems. For our problem, the most appropriate seem to be "standard" models of molecules used in computer modeling (see, e.g., [21]) with real geometry, real values of atomic mass (hence, calculated moments of inertia), but with one difference. Namely: we assume that similar atoms of all molecules create similar force fields, i.e., the energy parameters characterizing atom-atom (non-valence) interactions are the same. As MCS, we chose the systems of principal moments of inertia. Such a model was also used in [22–25], reflecting the ideas and perceptions of interaction of uniform ("homogeneous") molecules [38, 39]. The atom coordinates for each molecule were taken from AM-1 molecular dynamics calculations. As initial atom- atom potentials, we have chosen Lennard-Jones potentials (for non-valence interactions) with the energy constants $C_6 = 2.987 \cdot 10^3$ (kcal mol^{-1} A^{-6}), $C_{12} = 1.715 \cdot 10^7$ (kcal mol^{-1} A^{-12}) for aliphatic carbon atoms [40]). From the expressions (13) and (18) of [1], using the gamma-function property $\Gamma(z+1) = z\Gamma(z)$, for U-coefficients of the long-range part of anisotropic IMI we obtain:

$$U^{l_1 l_2 l_3}_{m_1 m_2}(R_{12}) = (-1)^{l_3} \frac{2[l_3^2]}{3\sqrt{\pi}} C_6 \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \times \quad (9)$$

$$\times R^{-(12+l_1+l_2)} \sum_{p=0}^{p_{\max}} \frac{\Gamma(3+p+\frac{l_1+l_2+l_3}{2})}{R_{12}^{2p}} \times$$

$$\times \Gamma(3+p+\frac{l_1+l_2-l_3-1}{2}) F^{l_1 l_2 l_3}(p, R_{12}) \times$$

$$\times \sum_{s_1+s_2=p} B^{0 l_1 l_2}_{0 s_1 s_2} \{r^{2s_1}_{l_1 m_1}(1) \{r^{2s_2}_{l_2 m_2}(2).$$

Here $F^{l_1 l_2 l_3}(p,R)$ functions have the form:

$$F^{l_1 l_2 l_3}(p,R) = R^6 - \frac{C_{12}}{C_6} \cdot \frac{3 \cdot 2^9}{(10)!} \times \quad (9a)$$

$$\times \prod_{s=1}^{3} [4+p+\frac{1}{2}(l_1+l_2+l_3)+s] \cdot \prod_{t=1}^{3} \frac{[4+p+1}{2}(l_1+l_2-l_3-l)+t].$$

As a result of multiple trial calculations, we have found that for our molecules the value $p_{max} = 135$ gives the accuracy of about 0.5 %.

For model calculations, we chose typical mesogenic molecules - cholesteryl acetate and MBBA, as well as molecules of O_2 и H_2O. Three possible conformational states of the MBBA molecule were considered, differing in their anisometry. Such choice of molecular structures, alongside with approbation of our method, was aimed at understanding anisotropic IMI as function of the molecular shape (first of all, of anisometry) and, in this sense, of conformations. The three conformations of MBBA are schemati-

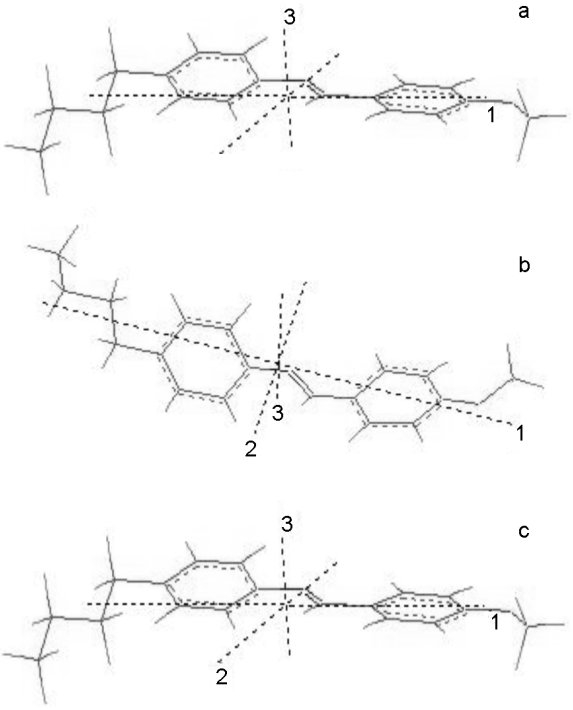

Fig. 1. Three conformational states of the MBBA molecule: a) the most stable (basic) state; b) an excited state [41]. c) another possible excited state, which differs from the case (b) by the alkyl chain conformation, resulting in lower molecular anisometry.

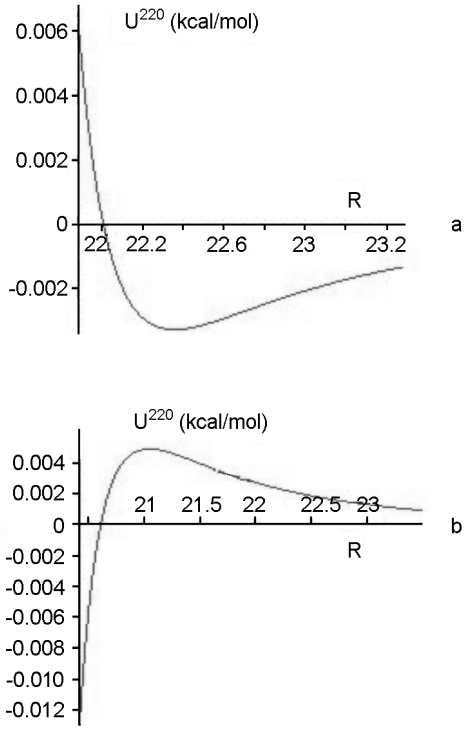

Fig. 2. Calculated $U^{220} = U_{00}^{220}(R)$ plots for two pairs of molecules: a) cholesteryl acetate + MBBA (in the basic state), b) cholesteryl acetate + MBBA-2 (in the excited state).

cally shown in Fig. 1 in their respective MSC (directions of axes shown by dotted lines). The stable state of MBBA molecule in the liquid crystalline phase is shown in Fig. 1a. The excited states are shown in Figs. 1b and 1c (we denote these states as MBBA-2 and MBBA-3). Peculiar properties and physical effects that are related to different conformations of MBBA molecules were studied in в [41–43]. It should be noted that MBBA-3 differs from MBBA-2 only by conformation of its alkyl tail. This conformation can exist in the same conditions as MBBA-2, since the energy of conformational transitions in alkyl chains is small as compared with thermal energy [44].

Our calculated plots for U-coefficients as function of the distance R between the molecule centers are of a characteristic form with a local maximum (or minimum). At large R, they are approaching zero, remaining positive or negative, respectively. At small intermolecular distances, the U-coefficients tend, respectively, to plus or minus infinity at $R = R_S = 0.5(L_1 + L_2)$, where L_1 и L_2 are maximum dimensions of the interacting molecules [1]. In our following discussions, we will consider a sphere of

Table. Values of U-coefficients at the local extremum points

$l_1 l_2 l_3$	Chol-Chol	Chol-MBBA	Chol-MBBA-2	Chol-MBBA-3	Chol-2atom	Chol-H_2O	MBBA-MBBA	MBBA-MBBA-3
0 0 0	−0.08	−0.08	−0.07	−0.08	−0.11	−0.22	−0.044	−0.2
2 2 0	−0.0032	−0.0032	0.0048	0.009	0.0007	0.0005	−0.012	0.008
2 0 2	−0.05	−0.050	−0.044	−0.06	−0.15	−0.23	0.085	0.31
0 2 2	−0.05	−0.052	0.068	0.14	0.006	0.012	0.085	−0.09
4 4 0	−0.0024	−0.0028	−0.0004	0.002	3·10−6	2·10−6	−0.0009	0.00051
4 0 4		0.08	0.076	0.12	0.4	0.44	−0.04	−0.11
0 4 4		0.08	0.012	−0.052	−0.00004	−0.00012	0.04	0.06

radius R_s centered at the MSC origin; we will call it a "singular sphere". As an example, $U_{00}^{220}(R)$ dependences are shown in Fig. 2 for two pairs of molecules: cholesteryl acetate — MBBA (Fig. 2a) and cholesteryl acetate — MBBA-2 (Fig. 2b).

We have limited ourselves to calculations of U-coefficients with lower indexes equal to zero; for brevity, we omit them in expressions below. For different indexes and molecular pairs, these plots are different in scale. Knowing qualitatively the general form of the plots, we can relate to each of them just one number — the U-coefficient value at the local extremum. Results of our calculations are presented in Table 1. The three figures in the first column denote a U-coefficient with these indexes, and the first line indicates the pair of interacting molecules.

At first, we carried out calculations for pairs cholesteryl acetate — MBBA (in different conformation states). We noticed an unusual behavior — inversion of the dependences for U^{220} и U^{440}. These dependences are of primary importance for molecular models of mesophases. E.g., U^{220} determines the transition remperature from isotropic liquid to nematic ([5–8]). Our data indicate that properties of mixtures can be qualitatively changed upon variations in anisometry of one of the constituent molecules. To check up the validity of this observation, we complemented the table by the results of similar calculations for interactions of cholesteryl acetate with water and a two-atom molecule (meaning, e.g., O_2). The results obtained can be expressed by the following relationship:

$$U_{00}^{\lambda\lambda 0}(R) \quad (L_2^{c\lambda} - L_1)^{t_{12}}, \qquad (10)$$

$$t_{12} = \begin{cases} 1(\mathrm{mod}\ 2), \text{ if molecules 1 and 2 are different}, \lambda \neq 0 \\ 0(\mathrm{mod}\ 2), \text{ if molecules 1 and 2 are identical} \end{cases}$$

where $L_2^{c\lambda}$ is the length of the second molecule at which $U_{00}^{\lambda\lambda 0}(R) = 0$, or by a similar relationship with lengths replaced by the corresponding anisometries: $\varepsilon_1 = L_1/a_1$, and $\varepsilon_2^{c\lambda}$. Here a_1 is the smallest molecular dimension (i.e., diameter, if the molecular shape is approximated by a cylinder).

The relationship (10) is also illustrated by Fig. 2. We shall call this behavior "inversion of the U-coefficient dependences" or just "U-inversion".

As we already noted in the previous part of this paper, IMI depend on the choice of the molecular system of coordinates (MSC).

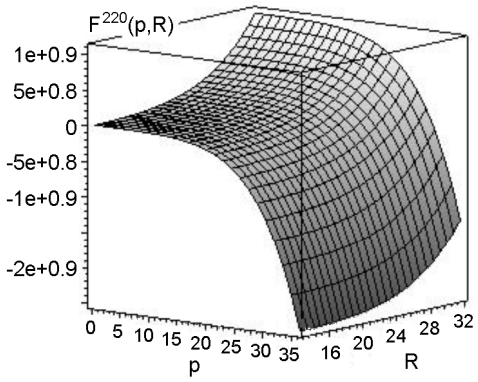

Fig. 3. Graphic representation of the F^{220}(p,R) surface.

In our case, there are three obvious MSC choices: the first one is obtained by diagonalization of the inertia moment tensor, and the others are obtained from the distribution of C_6 and C_{12} force constants over the molecule. Let us check up an assumption that the U-inversion is a certain consequence of a relative shift and/or rotation of these MSC. Putting all masses equal (as well as force constants), we superpose all three MCS. Then we carry out all the calculations again and obtain a similar table. The figures obtained are slightly different, but the qualitative picture remains the same. I.e., the phenomenon of U-inversion is invariant with respect to MSC choice.

The force constants of atom-atom potentials for different atoms are determined empirically. So, the values obtained have, in fact, absorbed effects of non-additivity and other physico-chemical properties of the medium formed by these atoms, as well as of the used measurement methods and assumed theoretical notions on IMI. For each class of substances, its own set of these parameters is developed [46]. Maybe our choice corresponds somehow to hydrophobic interactions as a specific type of IMI, thus making the U-inversion a predetermined fact? We again carried out similar calculations using atom-atom potentials for five more types of carbon atom, as well as for oxygen (which is obviously not hydrophobic) given in [40]. The obtained six more tables are also different in numerical values, but qualitatively are fully similar to Table 1. I.e., the U-inversion is determined by molecular geometry, and not by specific properties of the constituent atoms.

Let us determine is such behavior is possible for U-coefficient series. From analytical structure of the series (9) one can conclude that their qualitative features are es-

sentially determined by the properties of $F^{l_1 l_2 l_3}(p,R)$ functions. These are polynomials, if we consider the first (indexing) variable as continuous. In Fig. 3, one of these functions is plotted at $(l_1 l_2 l_3) = (220)$. For other indexes, the corresponding surfaces are similar.

Let us denote the internal sum in (9) as

$$M^{l_1 l_2}_{m_1 m_2} = \sum_{s_1+s_2=p} B^{0 l_1 l_2}_{0 s_1 s_2} \overline{r^{2s_1}_{l_1 m_1}}(1) \overline{r^{2s_2}_{l_2 m_2}}(2). \quad (11)$$

The expression (11) can be presented as function defined on the surface of Fig. 3, and the result of summation in (9) — as passing along a certain trajectory (with integer p). For the given set of indexes, this trajectory will be defined by properties of $M^{l_1 l_2}_{m_1 m_2}(p,1,2)$, i.e. finally, by the molecular structure. As one can see from Fig. 3, there can be a trajectory that corresponds to the U-coefficient inversion, i.e., when several first terms of a series (positive and large in magnitude) are not compensated for by subsequent negative terms; according to a theorem proven in [1], the series is convergent, so, the total sum of the series will be positive.

In addition to differences in molecular shape, another important factor is that a sufficiently large number of terms in the U-coefficient series should be accounted for. Most of the authors considering IMI limit themselves to the first (i.e., multipole) approximation, which can lead not to just quantitative, but also to qualitative errors.

One should note several peculiar features that characterize our plots obtained for U-coefficients. Since we consider the long-range IMI component, the local extremum points are located farther, and their values can be much lower (by several orders — depending upon anisometries of both interacting molecules) than those of the corresponding atoms. In fact, they already characterize ordering tendencies outside the first coordination sphere. According to (1), each U-coefficient describes a contribution to the total energy, which depends upon mutual orientation of the molecules:

$$\Delta E^{l_1 l_2 l_3}_{m_1 m_2}(i,j) = U^{l_1 l_2 l_3}_{m_1 m_2}(R_{ij}) \Theta^{l_1 l_2 l_3}_{m_1 m_2}(\Omega_i, \Omega_j, \hat{Rij}). \quad (12)$$

In approaching the singular sphere, U-coefficients are tending to $+_{-if}$ according to [1], which means, provided the orientation is mutually parallel, contributions to repulsion or attraction (respectively) at distances close to the radius of the singular sphere. Only the isotropic component always tends to $+\infty$ irrespective of the orientation. This singularity has a very simple physical sense — this is the largest distance between the molecular centers at which a direct contact between the molecules is possible under arbitrary rotations of molecules around their centers. We have proven a theorem under which asymptotics of the U-coefficients have the same signs when the intermolecular distance tends to the radius of the singular sphere from inside or from outside (this proof will be described elsewhere). In an obvious manner, from IMI properties one can get some information on the distribution functions (without calculating them). Thus, the internal energy of a system can be calculated by averaging pair interactions with a two-particle distribution function and has a finite value. Therefore, the above-discussed features of anisotropic IMI should be reflected in the pair distribution functions. Plots of their SO(3)-invariant expansions used in the theory of anisotropic liquids will show not only those features that are due to the phase microstrucrure, but also some peculiar features that are due to specific behavior of the corresponding U-coefficients (see, e.g., [47]); the features of both origins can partially coincide.

As noted above, IMI behavior is different for systems formed by molecules that are similar in their length (anisotropy) and molecules that are different in this respect. Thus, in the first case (as in Fig. 2a) U-coefficients responsible for purely orientational interactions — $U^{\lambda\lambda 0}_{00}(R)$ — are negative and tending to zero at large intermolecular distances, i.e., they contribute to attraction provided their mutual position is parallel. When the molecules are approaching each other, in the same configuration these terms correspond to repulsion. Such behavior of anisotropic IMI is, in fact, assumed in various molecular models of mesophases that account for repulsion forces (see., e.g., [3, 7, 8, 24, 49]). Theoretical results obtained in the molecular field approximation are in good agreement with experiment in the case when the molecules are similar in dimensions. In the other case, discrepancies between calculated and measured data may be quite substantial. For molecules of different anisometry, as it is clear from Table, relationship (10) and Fig. 2b, the behavior of $U^{\lambda\lambda 0}_{00}(R)$ is the opposite: for large intermolecular distances and parallel mutual orientation these coefficients are positive and are tending to zero, i.e.,

contribute to repulsion, while when the molecules are approaching each other in the same configuration, they correspond to attraction.

The sign of $\Delta E_{00}^{\lambda\lambda 0}(i,j)$ contribution to the total energy depends upon mutual orientation of the molecules. At $\lambda = 2$, the sign is inversed if the angle between their long axes is $\pi/2$; for $\lambda = 4$, this angle is equal to $\pi/4$. This can be verified by substituting the values of these angles into (12).

The results obtained provide us with better understanding of microscopic nature of some phenomena in anisotropic liquids related to violations of spatial uniformity, i.e., formation of clusters. In the approach proposed by Lev, Belotsky e.a. [50–53], this was shown to be possible in systems with short-range attraction and long-range repulsion. In anisotropic liquids (including classic LC) the situation with repulsion dominating over attraction is realized in the case of inversion of U-coefficients and can become apparent already at rather low concentration of dopant molecules. We turn our attention just to anisotropic IMI, since the isotropic component can change only in magnitude, remaining negative with increasing intermolecular distances (i.e., attraction is predominant).

The above considerations form a new standpoint from which some theoretical problems and interpretations of experimental results in the field of liquid crystals and complex liquids can be treated in a different way, supplementing the existing concepts.

Thus, in the Landau-de Gennes phenomenological theory of nematics a question arises on the nature of the cubic term in the free energy expansion over orientational order parameter. It has been generally accepted [3] that there should be no cubic term in this expansion, since the phases differing by the order parameter sign would correspond to different types of molecular arrangement (parallel and perpendicular), which are not related by symmetry operations, and their free energies are not equal. However, this is just the situation resulting from our calculations (e.g., the last column in Table), if we account for the presence of different conformers in the LC phase and pretransitional region of MBBA [41–43]. Inversion of the IMI dependences can be the main microscopical reason for cluster formation in such systems. In [54], it was assumed that a non-zero cubic term could result from fluctuations — either of alkyl chain conformations or short-range smectic order. This should probably lead to phase transitions from the isotropic liquid to the nematic phase (I-N) becoming closer to the second order, but experimental data are either contradictory or indicate a weakly first-order transition. Our results suggest that smectic fluctuations could be an important factor in nematics, which is demonstrated by the third and fourth lines of Table 1: the extremums of U_{00}^{202} and U_{00}^{022}, which characterize the coupling between translational and orientational ordering, are sufficiently large as compared with the "purely orientational" U_{00}^{220} for MBBA and its excited state, with this energy being much higher for the MBBA-MBBA-2 pair.

In [55], differences were noted in "dopant-solvent" interaction parameters, predicted in the uniform mixing model [56, 57], and it was assumed that a possible reason for this could be violations of translational order. In [58], numerous anomalies were found in binary mixtures (in order parameter, density, etc.) When the concentration of the nematogen with shorter molecular length is increased, irregular temperature dependences are observed, which cannot be described in terms of existing molecular field theories of LC. The authors of [58] explain this by the effects of alkyl tail fluctuations. Basing on our calculations, we think that violations of spatial uniformity can be a consequence of the inversion of U-coefficient dependences, and fluctuations of the alkyl chains can contribute to this by changing the molecular anisometry, thus inducing the U-coefficient inversion.

In experiments on light scattering [59], anomalous concentration dependences were observed in mixtures of water with glycerol and *tert*-butanol at relatively low alcohol concentrations (known also for other systems) [60]. The authors of [59] related this behavior with formation of clusters. Basing on our calculations, within the context of the models of [50–53] the following qualitative interpretation can be proposed. The cluster formation itself can be also due to the inversion of U-coefficient dependences. I.e., in the vicinity of the dopant molecule, at distances of the order of the singular sphere radius and less, the molecules of water show a tendency to orientational ordering (as an analogy, see Fig. 2b and the "Chol-2atom" column in Table), forming the first coordination sphere, outside which the situation is quite different — either the dopant tends to orient the water molecules

orthogonal to their long axes (at weaker ordering and/or higher temperature), or repulsion forces emerge between the cluster and water molecules (stronger ordering and/or lower temperatures). These assumptions are also supported by the low dopant concentration values and small (according to authors' estimates) number of molecules in the cluster.

In [12, 13], basing on numerous experimental data, a conclusion was made that good miscibility and high thermal stability of smectic mixtures required minimal differences in molecular lengths of the components. Our results fully agree with these facts. Of course, as noted in [13], this criterion is not the only one in composing the optimum mixtures. Contributions from other types of intermolecular forces, as well as other molecular parameters, should also be accounted for. In this relation, the most interesting would be effects of polar-type interactions. Another largely unsolved problem is the role of molecular biaxiality. Further studies are under way in these directions.

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Особливості та застосовність асимптотичних розкладів анізотропних адитивних міжмолекулярних взаємодій в анізотропних середовищах. II. Роль анізометрії в формуванні надмолекулярних структур в мезогенних системах

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Проведено дослідження далекодіючої компоненти коефіцієнтів SO(3)-інваріантних розкладів анізотропних міжмолекулярних взаємодій (U-коефіцієнтів) для леннард-джонсівських взаємодій між силовими центрами (атомами). Для простої геометричної моделі виявлено ефект інверсії залежностей U-коефіцієнтів від міжмолекулярних відстаней як функції молекулярної анізометрії. Обговорюються можливі прояви цього ефекту в експериментально спостережуваних властивостях складних рідких та рідкокристалічних систем та його роль в утворенні мікрогетероструктур.