

Additive anisotropic interactions in molecular liquids and liquid crystals

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Formulae for a SO(3)-invariant expansion of the pair-molecular interaction-energy are derived. Two different cases, of exponential potential and of inverse-power potential, are considered for molecules of arbitrary shape. Methods for the determination of the generalized multipole components for molecules are developed on the base of transformation formulae for rotation and translation of a coordinate system. The importance of accounting the difference between the general expansion and that of a conventional multipole type is illustrated on the base of simulation data for mesogen substance PCH-5.

1. Introduction

Structure and physical properties of molecular systems are determined by molecular interactions (MI). In general, these interactions are non-central, i.e. are dependent on the relative orientation of molecules. It is usual for different computational schemes to account for this effect by expanding the pair-potential into a set of rotational invariants [1]:

$$E(1, 2) \equiv E(\mathbf{R}_{12}, \Omega_1, \Omega_2) = \sum U_{m_1 m_2}^{l_1 l_2 l_3}(\mathbf{R}_{12}) \Theta_{m_1 m_2}^{l_1 l_2 l_3}(\Omega_1, \Omega_2, \Omega_{12}), \quad (1.1)$$

where \mathbf{R}_{12} is the vector connecting the origins of the molecule-fixed coordinate

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systems; $\Omega_{1(2)}$ is the set of Euler angles, which determines the orientation of the 1 (2) molecule in the laboratory reference coordinate system;

$$\Theta_{m_1 m_2}^{l_1 l_2 l_3}(\Omega_1 \Omega_2 \Omega_{12}) = \sum_{|n_i| \leq l_i} \begin{pmatrix} l_1 & l_2 & l_3 \\ n_1 & n_2 & n_3 \end{pmatrix} D_{n_1 m_1}^{l_1}(\Omega_1) D_{n_2 m_2}^{l_2}(\Omega_2) D_{n_3 0}^{l_3}(\Omega_{12}); \quad (1.2)$$

$\begin{pmatrix} l_1 & l_2 & l_3 \\ n_1 & n_2 & n_3 \end{pmatrix}$ stands for a Wigner 3j-symbol; $D_{nm}^l(\Omega)$ is a Wigner D -function.

The properties of rotational invariants (1.2) are well known while comprehensive calculation of the $U_{m_1 m_2}^{l_1 l_2 l_3}(R_{12})$ -functions, taking into account all interactions between the particles constituting the molecules, are connected with substantial computational difficulties, even for the most simple molecules.

Almost all existing methods for the MI calculations, both quantum mechanical and semi-empirical, are based on the representation of the energy of the system as a sum of effective pair potentials which, in general, are not similar to the interaction potentials of pairs of isolated particles. In such cases some model of the molecular structure is used, depending on the computational methods and on the available experimental methods for determination of the MI parameters [2–9]. For example, the atom–atom potential method [3] corresponds to the representation of the molecule as the arrangement of sites (atoms). As a generalization of this method to the case of a continuous distribution of interacting sites, there exists the method of effective pair interactions (EPI) [9–14]. In the EPI method the MI energy is written as

$$E(1, 2) = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \rho_1(\mathbf{r}_1) \rho_2(\mathbf{r}_2) U(\mathbf{r}_{12}); \quad (1.3)$$

here $\mathbf{r}_{1(2)}$ is the radius-vector of the interacting site in the molecule 1 (2), $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1 + \mathbf{R}_{12}$ is the distance between the interacting sites, \mathbf{R}_{12} connects molecular reference systems, $\rho_i(\mathbf{r}_i)$ is the spatial distribution function of the interacting sites in the molecule i and $U(\mathbf{r}_{12})$ stands for the EPI of sites in molecules 1 and 2.

The representation of the energy in the system by formula (1.3) gives a possibility to obtain an analytical expression for $U_{m_1 m_2}^{l_1 l_2 l_3}(R_{12})$ in (1.1). For discrete models these functions have been evaluated in [9–11,15]; for a continuous distribution of the interacting sites in the ellipsoidal molecule, such formulae have been obtained in [13] in the multipole approximation for EPI (see also [14, refs.]). But in order to use the results of these papers, while treating microscopic models of molecular liquids and liquid crystals, one has to solve several problems.

In the second part of this work we derive asymptotical sets for the EPI potential, both of exponential and of inverse power type, generalizing the results of [10,11,15] to the case of arbitrary distribution $\rho_i(\mathbf{r}_i)$. It should be

realized that for the description of the interaction between extended bodies the multipole expansion in general is not applicable, except for the case of a Coulomb potential. Formally, it is due to the incompleteness of the set of multipole moments; a well-known fact in the theory of scattering [16].

Here we derive the expansion into the set of generalized moments $\overline{R_{lm}^{2r}}$, defined also in [17,18], giving a complete parameterization for the MI calculation.

In the third part, the transformation formulae for rotation and translation of generalized multipole moments are derived. These enable one to build up molecular tensors from atomic or fragment ones and in this way to take into consideration molecular configuration in MI calculations. This possibility is also interesting from the point of view of simplicity to treat the effect of substitution on different mesomorphic properties. On the other hand, by neglecting transformational properties of molecular tensors and MI asymptotics one can come (as in [19]) to false conclusions about the connection between the molecular structure and macroscopic properties.

In the fourth part, our algorithm for the MI computation in the case of a discrete-interacting-centers distribution is described and some results based on molecular dynamics simulation data for mesogenic PCH-5 are presented.

2. Asymptotical behavior of SO(3)-invariant expansions for molecular interactions

Following [11,13,15] we write down the energy (1.2) as a function of the Fourier transform of the EPI potential $U(\mathbf{r}_{12})$:

$$E(1, 2) = \int d\mathbf{r}_1 \rho_1(\mathbf{r}_1) \int d\mathbf{r}_2 \rho_2(\mathbf{r}_2) \int d\mathbf{k} \exp[i\mathbf{k} \cdot (\mathbf{r}_2 - \mathbf{r}_1 + \mathbf{R}_{12})] U(\mathbf{k}), \quad (2.1)$$

where $U(\mathbf{k}) = (2\pi)^{-3} \int d\mathbf{r} \exp(-i\mathbf{k} \cdot \mathbf{r}) U(\mathbf{r})$.

Expanding the exponent in (2.1) into a set in spherical functions [20], after integrating in \mathbf{k} -space and some transformations, we obtain an expansion similar to (1.1) in which $U_{m_1 m_2}^{l_1 l_2 l_3}(R_{12})$ functions are defined as

$$U_{m_1 m_2}^{l_1 l_2 l_3}(R_{12}) = \frac{\pi^3 (-1)^{l_1 l_3} (2l_1 + 1)(2l_2 + 1)(2l_3 + 1)}{2^{l_1 + l_2 - 6} \Gamma(l_1 + \frac{3}{2}) \Gamma(l_2 + \frac{3}{2})} \begin{pmatrix} l_1 l_2 l_3 \\ 0 0 0 \end{pmatrix} \times \int_0^\infty dk k^{l_1 + l_2 + 2} U(k) Q_{l_1 m_1}(k^2) Q_{l_2 m_2}(k^2) j_{l_3}(kR_{12}). \quad (2.2)$$

Here $j_i(z)$ is a spherical Bessel function, $\Gamma(z)$ is the Euler function and

$$\begin{aligned} Q_{LM}(k^2) &= \frac{\pi^{3/2}(-2)^L \Gamma(L + \frac{3}{2})}{k^L \sqrt{2L + 1}} \rho_{LM}(k), \\ \rho_{LM}(k) &= \frac{(-i)^L}{2\pi^2} \int_0^\infty dr r^2 j_L(kr) \rho_{LM}(r), \\ \rho_{LM}(r) &= \int d\hat{r} \rho(\mathbf{r}) Y_{LM}^*(\hat{r}), \end{aligned} \tag{2.3}$$

where \hat{r} shows the orientation of vector \mathbf{r} and $Y_{LM}(\hat{r})$ are spherical harmonics.

For further calculations let us outline the properties of $\rho(\mathbf{r})$. Because of the fact that molecules have definite shape and dimensions, $\rho_i(\mathbf{r}_i)$ can be considered as generalized functions with compact cores [21]. Therefore, their Fourier transforms are decreasing functions with $k \rightarrow \infty$ and in the upper semi-plane of complex k they decrease exponentially.

We shall consider, at first, the inverse power potentials of EPI:

$$U(r_{12}) = C_{2n} r^{-2n}, \quad U(k) = \frac{C_{2n} (-1)^{n-1}}{4\pi(2n-2)!} k^{2n-3}. \tag{2.4}$$

Because of the aforementioned asymptotical properties of $\rho_i(\mathbf{k})$, integrals in (2.1) and (2.2) are convergent if there is no interacting sites overlap, i.e. if $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1 + \mathbf{R}_{12} \neq 0$. Taking into account asymptotical properties of the integral in (2.2) (see appendix A) we have, after performing all transformations,

$$U_{m_1 m_2(n)}^{l_1 l_2 l_3}(R_{12}) = \sum_{p=0}^\infty \frac{A_{p(n)}^{l_1 l_2 l_3} C_{2n}}{R_{12}^{2n+l_1+l_2+2p}} \sum_{s_1+s_2} B_{0 s_1 s_2}^{0 l_1 l_2} \overline{R_{l_1 m_1}^{2s_1}}(1) \overline{R_{l_2 m_2}^{2s_2}}(2). \tag{2.5}$$

Here

$$\begin{aligned} A_{p(n)}^{l_1 l_2 l_3} &= (-1)^{l_3} \sqrt{\pi} \frac{2^{2n-2}}{(2n-2)!} (2l_3 + 1) \Gamma\left(\frac{l_1 + l_2 - l_3 - 1}{2} + n + p\right) \\ &\quad \times \Gamma\left(\frac{l_1 + l_2 + l_3}{2} + n + p\right) \begin{pmatrix} l_1 l_2 l_3 \\ 0 0 0 \end{pmatrix}, \\ B_{0 s_1 s_2}^{0 l_1 l_2} &= \frac{(-1)^{l_1} \pi (2l_1 + 1)(2l_2 + 1)}{2s_1! s_2! \Gamma(s_1 + l_1 + \frac{3}{2}) \Gamma(s_2 + l_2 + \frac{3}{2})}, \end{aligned}$$

and generalized moments (so-called 2s-power radii [17]) are defined by the

following expression:

$$\overline{R_{lm}^{2s}}(i) = \left(\frac{4\pi}{2l+1} \right)^{1/2} \int d\mathbf{r} r^{l+2s} Y_{lm}^*(\hat{r}) \rho_i(\hat{r}), \quad (2.6)$$

and give complete parameterization for $\rho_i(\mathbf{r}_i)$.

If in (2.5) $s_1 = s_2 = p = 0$, this expansion reduces to a multipole one (cf. [13]). The discrepancy between the multipole expansion and total dispersion interaction energy for the case of dumbbell molecules has been visualized in [11,14]. It is shown there that these deviations are increasing with decreasing intermolecular distance. One can suppose, based on these estimates, that for liquid crystals those terms in (2.5) that are neglected in multipole expansion, can be two orders of magnitude larger than those which are taken into account. It should be noted that influence of dispersion interactions on thermodynamic potentials and other parameters of orientationally ordered systems can also be underestimated on the base of multipole expansion [19]. In a general case one should either make the summation of the whole infinite set (2.5), or evaluate the integral over k in (2.2) for the given molecular parameters. But if it is possible to neglect the terms of order higher than l then the summation in (2.5) should be done not only for $l_1 + l_2 \leq l$, but also for $2p = l - l_1 - l_2$.

Now we shall proceed with the determination of the so-called radial factor $U_{m_1 m_2}^{l_1 l_2 l_3}(R_{12})$ in expansion (1.1) for the EPI potentials of exponential (repulsive) type:

$$U(r_{12}) = A \exp(-ar_{12}), \quad U(k) = \frac{A}{\pi^2} \frac{1}{(k^2 + a^2)^2}. \quad (2.7)$$

The radial factor, corresponding to it, can be written as

$$U_{m_1 m_2}^{l_1 l_2 l_3}(\infty)(R_{12}) = 4A(2\pi)^4 (-1)^{l_1 l_3} [(2l_1 + 1)(2l_2 + 1)(2l_3 + 1)]^{1/2} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \\ \times \int_0^\infty dk \frac{k^2}{(k^2 + a^2)^2} j_{l_3}(kR_{12}) \rho_{l_1 m_1}(k; 1) \rho_{l_2 m_2}(k; 2), \quad (2.8)$$

where $\rho_{l_i m_i}(k; i)$ are defined by (2.3).

First of all it should be noted that $l_1 + l_2 + l \pmod{2} = 0$, because in the other cases the $3j$ -symbols are vanishing. Thus, integration in (2.8) can be extended over the whole real axis. Accounting the known property of Bessel functions [22]

$$j_l(z) = (-1)^l j_l(-z) = \frac{1}{2} [h_l^{(1)}(z) + (-1)^{l+1} h_l^{(1)}(-z)], \quad (2.9)$$

(2.8) can be transformed to

$$\begin{aligned}
 U_{m_1 m_2}^{l_1 l_2 l_3}(\mathbf{R}_{12}) &= 2A(2\pi)^4 (-1)^{l_2+l_3} [(2l_1+1)(2l_2+1)(2l_3+1)]^{1/2} \begin{pmatrix} l_1 l_2 l_3 \\ 0 0 0 \end{pmatrix} \\
 &\times \int_{-\infty}^{\infty} dk \frac{k^2}{(k^2+a^2)^2} h_{l_3}^{(1)}(kR_{12}) \rho_{l_1 m_1}(k; 1) \rho_{l_2 m_2}(k; 2).
 \end{aligned} \tag{2.10}$$

Reminding the aforementioned properties of $\rho_i(\mathbf{k})$, the integral in (2.10) can be easily evaluated in the complex plane. Finally, after all transformations, we have

$$\begin{aligned}
 U_{m_1 m_2}^{l_1 l_2 l_3}(\mathbf{R}_{12}) &= -A\pi^3 i^{l_1-l_2} [(2l_1+1)(2l_2+1)(2l_3+1)]^{1/2} \begin{pmatrix} l_1 l_2 l_3 \\ 0 0 0 \end{pmatrix} \\
 &\times \left(k_{l_3}(aR_{12}) \frac{d\bar{\Psi}(a)}{da} + [(l_3+1)k_{l_3}(aR_{12}) - aR_{12}k_{l_3+1}(aR_{12})] \frac{\bar{\Psi}(a)}{a} \right).
 \end{aligned} \tag{2.11}$$

Here

$$\begin{aligned}
 \bar{\Psi}(a) &= [i^{l_1+l_2} \rho_{l_1 m_1}(k; 1) \rho_{l_2 m_2}(k; 2)]_{k=ia}, \\
 k_l(z) &= (-z)^l \left(\frac{d}{z dz} \right)^l \frac{e^{-z}}{z}.
 \end{aligned}$$

For discrete molecular models, corresponding to the method of atom-atom potential,

$$\bar{\Psi}(a) = i_{l_1}(ar_{\xi 1}) i_{l_2}(ar_{\eta 2}),$$

where $i_l(z)$ are modified spherical Bessel functions. Using the identity relation $(d/dz) i_l(z) = (1/z) i_l(z) + i_{l+1}(z)$ for this case, we obtain

$$\begin{aligned}
 U_{m_1 m_2}^{l_1 l_2 l_3}(\xi, \eta, R_{12}) &= -A\pi^3 i^{l_1-l_2} [(2l_1+1)(2l_2+1)(2l_3+1)]^{1/2} \begin{pmatrix} l_1 l_2 l_3 \\ 0 0 0 \end{pmatrix} \\
 &\times \left[k_{l_3}(aR_{12}) \left(\frac{l_1-l_2+l_3+1}{a} i_{l_1}(ar_{\xi 1}) i_{l_2}(ar_{\eta 2}) + r_{\xi 1} i_{l_1+1}(ar_{\xi 1}) i_{l_2}(ar_{\eta 2}) \right. \right. \\
 &\left. \left. + r_{\eta 2} i_{l_1}(ar_{\xi 1}) i_{l_2+1}(ar_{\eta 2}) \right) - R_{12} i_{l_1}(ar_{\xi 1}) i_{l_3+1}(aR_{12}) \right].
 \end{aligned} \tag{2.12}$$

Formula (2.12) is the particular case of (2.11) for the interaction of atom ξ in the molecular 1 with atom η in the molecule 2, and it coincides with the similar one obtained in [15]. Asymptotic properties of (2.11) and (2.12) with R_{12} variation follow in a trivial way from the asymptotic properties of Bessel functions.

Functions $U_{m_1 m_2}^{l_1 l_2 l_3}(R_{12})$, obtained here, possess several obvious symmetry properties, as it is clear from their definition. First of all, MI energy is scalar and that is why there are constraints on the variation of indices: $l_i \leq l_j + l_k$ $\{i, j, k\} = 1, 2, 3$. Secondly, this energy is invariant during the inversion of space-coordinates and this fact is provided by the vanishing of $3j$ -symbols if $l_1 + l_2 + l_3 \pmod{2} \neq 0$. And thirdly, the MI Hamiltonian is a hermitian operator. This fact can be directly checked with the help of (2.5) and (2.11) and corresponds to the following relation:

$$[U_{m_1 m_2}^{l_1 l_2 l_3}(R_{12})]^* = (-1)^{m_1 + m_2} U_{-m_1 -m_2}^{l_1 l_2 l_3}(R_{12}).$$

And besides of this, for identical molecules the following relation is valid: $U_{m_1 m_2}^{l_1 l_2 l_3}(R_{12}) = U_{m_1 m_2}^{l_2 l_1 l_3}(R_{12})$. It should be mentioned that if interacting molecules possess some symmetry then additional constraints exist for summation indices in (1.1).

Further computational simplifications can be achieved while considering systems of rigid organic molecules. In this case, it is convenient to divide each molecule in subsets of identical atoms and to evaluate $\overline{R_{LM}^{2N}}(i, x)$ in the coordinate system of the i th molecule, not for one interacting site, but for the whole subset of identical atoms x . If the interaction constant between the atoms of the x th and y th type is C_{2n}^{xy} , then (2.5) can be rewritten as

$$U_{m_1 m_2(n)}^{l_1 l_2 l_3}(R_{12}) = \sum_{x=1}^{z_1} \sum_{y=1}^{z_2} C_{2n}^{xy} \sum_{p=0}^{\infty} \frac{A_{p(n)}^{l_1 l_2 l_3}}{R_{12}^{2n+l_1+l_2+2p}} \sum_{s_1+s_2} B_{0 s_1 s_2}^{0 l_1 l_2} \overline{R_{l_1 m_1}^{2s_1}}(1, x) \overline{R_{l_2 m_2}^{2s_2}}(2, y). \quad (2.13)$$

Here z_i is the number of different types of atoms in molecule i .

Thus, expressions (2.11), (2.12) and (2.5) or (2.13) give the solution of the problem of asymptotical expansion for MI in the method of EPI. The convergence of these expansions depends on the ratio of $\overline{R_{LM}^{2N}}(i, x)$ to R_{12} and consequently, as is clear from formulae (2.5) and (2.6), on the relation between molecular dimensions and intermolecular distances. Being written in the form (2.5), this expansion is convergent only when R_{12} is larger than molecular dimensions and we shall deal with only this case in what follows.

Normally, only a finite number of terms in (2.5) or (2.13) is taken into

account. Because of the fact that these sets are of the Taylor type, it is natural to keep, after truncation, the terms not of similar rank l , but up to some power $k = 2n + l_1 + l_2 + 2p$ of intermolecular distance. For example, for dispersive attractive forces, when the interaction between the sites is proportional to r_{12}^{-6} , we have

$$U_{m_1 m_2(3)}^{l_1 l_2 l_3}(R_{12}) = \sum_{p=0}^{(k-l_1-l_2-6)/2} \frac{W_{m_1 m_2(3)}^{l_1 l_2 l_3(p)}}{R_{12}^{6+l_1+l_2+2p}} + O(R_{12}^{-k}), \tag{2.14}$$

where explicitly

$$W_{m_1 m_2(3)}^{l_1 l_2 l_3(p)} = A_{p(n)}^{l_1 l_2 l_3} \sum_{s_1=0}^p \sum_{s_2=0}^{p-s_1} B_{0 s_1 s_2}^{0 l_1 l_2} \sum_{x=1}^{z_1} \sum_{y=1}^{z_2} C_{2n}^{xy} \overline{R_{l_1 m_1}^{2s_1}}(1, x) \overline{R_{l_2 m_2}^{2s_2}}(2, y), \tag{2.15}$$

and $|l_1 - l_2| \leq l_3 \leq l_1 + l_2$. For Lennard–Jones repulsive forces the summation in p to the same order of accuracy should be performed up to $\frac{1}{2}(k - l_1 - l_2 - 12)$.

3. Transformational properties of molecular tensors

Contribution of any interacting site into MI potential depends on its position and orientation in the molecule reference system. Various aspects of tensor transformations have been treated already by many authors. In classic papers [23,24] transformational formulae for Cartesian components of multipole moments during translation are presented. In [25–27] similar formulae are derived for one-particle wave functions. In molecular options it is of common practice to use relations, connecting tensorial components of a special kind in coordinate systems with different orientation [28]. In this part we shall derive SO(3)-invariant relations connecting the components of generalized multipoles in the coordinate systems, different both in orientation and position.

An arbitrary function $\rho(\mathbf{r})$, satisfying the relation

$$\int d\mathbf{r} |\rho(\mathbf{r})|^2 < \infty$$

can be expanded into a set in spherical harmonics:

$$\rho(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{|m| \leq l} \rho_{lm}(\mathbf{r}) Y_{lm}(\hat{\mathbf{r}}), \tag{3.1}$$

where $\rho(\mathbf{r})$ are defined in (2.3). On the other hand, for its Fourier transform we have

$$\rho(\mathbf{k}) = \sum_{l,m} \rho_{lm}(\mathbf{k}) Y_{lm}(\hat{\mathbf{k}}) = \frac{1}{2\pi^2} \sum_{l,m} (-i)^l \int d\mathbf{r} j_l(kr) \rho_{lm}(\mathbf{k}) Y_{lm}(\hat{\mathbf{k}}). \quad (3.2)$$

Here we have used Rayleigh expansion for the plane waves. For the second part of eq. (3.2) we have

$$\rho_{lm}(\mathbf{k}) = \frac{(-i)^l}{2\pi^2} \int_0^\infty dr r^2 j_l(kr) \rho_{lm}(r), \quad (3.3a)$$

and the inverse relation obtained in the same manner is

$$\rho_{lm}(r) = 4\pi i^l \int_0^\infty dk k^2 j_l(kr) \rho_{lm}(k). \quad (3.3b)$$

As is known, translation in r -space results in the following transformation in k -space:

$$\rho^{(n)}(\mathbf{k}) = \exp(i\mathbf{k}\mathbf{a}) \rho^{(o)}(\mathbf{k}). \quad (3.4)$$

Here vector \mathbf{a} is a shift of the new 'n' coordinate system relatively to the old 'o' one. Superposition of (3.4) and (3.2) with using Rayleigh expansion leads to

$$\begin{aligned} \rho^{(n)}(\mathbf{k}) &= \sum_{l,l_a} \sum_{m,m_a,m'} \sqrt{4\pi} i^{l_a} [l_{l_a} L^{-1}] j_{l_a}(k\mathbf{a}) \rho_{lm}^{(o)}(\mathbf{k}) \\ &\times C_{l_0 l_a 0}^{L0} C_{l m l_a m_a}^{LM} Y_{l_a m_a}^*(\hat{\mathbf{k}}) D_{mm'}^l(\Omega). \end{aligned} \quad (3.5)$$

Here $C_{l m l_a m_a}^{LM}$ are Clebsh–Gordan coefficients [20]. During the derivation of (3.5) the relation between functions $\rho_{lm}(\mathbf{k})$ in different coordinate systems has been used,

$$\rho_{lm}(\mathbf{k}) = \sum_{|m'| \leq l} \rho_{lm'}(\mathbf{k}) D_{mm'}^l(\Omega). \quad (3.6)$$

In (3.5) we introduced the short-hand notation

$$[l_1^{b_1} l_2^{b_2} \dots l_n^{b_n}] = (2l_1 + 1)^{b_1/2} (2l_2 + 1)^{b_2/2} \dots (2l_n + 1)^{b_n/2}, \quad (3.7)$$

and Ω stands for the set of Euler angles parameterizing the relative orientation

of the old and new systems. Superposition of (3.3b) and (3.5) leads to the result in r -space. Thus, in a straightforward way we obtain a generalization of formulae used in [23–29].

Further, for tensorial fields $Q_{LM}(k^2)$, defined by the first formula (2.3), we obtain, inserting it in (3.5),

$$Q_{LM}^{(n)}(k^2) = \sum_{l, l_a} \sum_{m, m_a, m'} \frac{i^{l_a} [l^2 l_a^2] (-1)^{l+L}}{\sqrt{4\pi} [L^2] \Gamma(l + \frac{3}{2})} \left(\frac{2}{k}\right)^{L-l} j_{l_a}(ka) Q_{lm'}^{(o)}(k^2) \\ \times C_{l0l_a0}^{L0} C_{lm_l m_a}^{LM} D_{m_a0}^{l_a}(\hat{a}) D_{mm'}^l(\Omega). \quad (3.8)$$

After using a power set in (3.3a) as representation of the Bessel function we obtain

$$\rho_{LM}(k) = \sum_{s=0}^{\infty} \frac{i^L [L] (-1)^{s+L}}{8\pi^2 s! \Gamma(s + L + \frac{3}{2})} \left(\frac{k}{2}\right)^{2s+L} \overline{R_{LM}^{2s}}. \quad (3.9)$$

Inserting (3.5) into (3.9) and comparing factors at similar powers of k we obtain transformation relation for generalized moments:

$$\overline{R_{LM}^{2N}}^{(n)} = \sum_{n_1, n_2=0} \sum_{l, l_a} \sum_{m, m_a, m'} B_{Nn_1 n_2}^{Ll_a} \delta_{l+l_a, 2(N-n_1-n_2)+L} a^{l_a+2n_2} \\ \times \overline{R_{lm'}^{2n_1}}^{(o)} C_{l0l_a0}^{L0} C_{lm_l m_a}^{LM} D_{m_a0}^{l_a}(\hat{a}) D_{mm'}^l(\Omega). \quad (3.10)$$

Here

$$B_{Nn_1 n_2}^{Ll_a} = \frac{(-1)^{l+L} \sqrt{\pi} [l^2 l_a^2] N! \Gamma(N + L + \frac{3}{2})}{2 [L^2] n_1! n_2! \Gamma(n_1 + l + \frac{3}{2}) \Gamma(n_2 + l_a + \frac{3}{2})}. \quad (3.10a)$$

It is worth to remind here that $-l \leq m, m' \leq l$, $-l_a \leq m_a \leq l_a$, and all other indices are natural numbers. Because of the fact that $C_{lm_l m_a}^{LM}$ is non-vanishing only when $|l - l_a| \leq L \leq l + l_a$, the sums in (3.10) contain a *finite* number of terms and this means that $\overline{R_{LM}^{2N}}^{(n)}$ can be determined with absolute accuracy.

For conventional multipoles in particular, we have with $n_1 = n_2 = N$

$$\overline{R_{LM}^0}^{(n)} \equiv Q_{LM}^{(n)} = \sum_{l+l_a=L} \sum_{m, m_a, m'} (-1)^{l_a} \left(\frac{(2L)!}{(2l)!(2l_a)!}\right)^{1/2} a^{l_a} \\ \times Q_{lm'}^{(o)} C_{lm_l m_a}^{LM} D_{m_a0}^{l_a}(\hat{a}) D_{mm'}^l(\Omega). \quad (3.11)$$

Transformation of interacting sites densities which possess spherical symmetry, is of particular interest because they are very closely related to the

atom–atom interaction potentials. In this case $l = m' = 0$ in (3.10) and thus $L = l_a$, $M = m_a$ and $N = n_1 + n_2$. Therefore, when the molecules are constituted from the ‘balls’ we have

$$\overline{R_{LM}^{2N}}^{(n)} = a^L D_{M0}^L(\hat{a}) \sum_{n_1+n_2=N} B_{Nn_1n_2}^{L0L} a^{2n_2} \overline{R_{00}^{2n_1}}^{(o)}. \quad (3.10b)$$

And for molecules which consist of interacting points, that is usual for atom–atom potential interaction, we have $\overline{R_{00}^{2n_1}}^{(o)} = \delta_{n_1,0} \rho_0$ and consequently

$$\overline{R_{LM}^{2N}}^{(n)} = (-1)^L a^{L+2N} D_{M0}^L(\hat{a}) \rho_0, \quad \text{where } \rho_0 = \int_0^\infty dr r^2 \rho_{00}(r). \quad (3.10c)$$

Formulae (3.5), (3.8)–(3.11) are basic ones for MI computation within the EPI method. For many classes of organic molecules additivity of their properties, i.e. the possibility to represent them by the sum of the properties of their fragments, is characteristic behavior [8]. This makes it possible to extract from experimental data the components of fragment tensors [6–8,28–30] for subsequent MI computations with the help of (3.5), (3.8)–(3.11). In [19,28,29] only (3.6) has been taken into account during such computations, which is obviously not correct when one deals with interactions. As a result, quantitative and even qualitative contradictions can be observed in the comparison of experimental results concerning molecular structure and arrangement with theoretical predictions [31,32]. This can be illustrated by the helicoidal molecule model (see appendix B). Calculations in accordance with the usual optical additive scheme (3.6) give only the isotropic part, which corresponds to the spherically symmetric distribution of interacting sites and, consequently, to the absence of orientational correlations between such molecules in condensed matter.

4. Numerical results

To illustrate the method developed in this paper and to compare the results of different approximations, we could take some model molecules and follow the dependence of intermolecular forces on their separation and relative orientation. This would lead us to an enormously detailed multi-dimensional picture. But keeping in mind our main goal, that this approach is especially effective for treating interactions between large anisotropic molecules, we accepted another procedure. We have taken the typical mesogen p-n-pentyl-(p'-cyanophenyl)cyclohexane (PCH-5) and evaluated different contributions to

the interaction energy, based on the simulation data [33] of this substance under normal conditions.

Simulation data were obtained by a molecular dynamics method with 50 molecules in a box and periodic boundary conditions using the general simulation programme GROMOS [34]. Integration of the equations of motion has been performed with time steps of 2 fs. After 90 000 steps every 100th configuration has been stored and 49 such configurations were taken for energy computations. For the simulation, the molecules were divided into 18 fragments ('pseudoatoms') CH_n ($n = 0, 1, 2, 3$) and the N atom. The simulation has been performed under conditions corresponding to an isotropic state at 333 K, just above the liquid crystalline nematic phase. The density of the resulting ensemble (972 kg m^{-3}) agrees well with the experimental value of 938 kg m^{-3} [35]. The simulated molecular ensemble possesses a relatively high order parameter 0.264, which may not be surprising for such a small volume. For macroscopic samples the nematic-to-isotropic phase transition occurs at higher values of the order parameter. Keeping this fact in mind and the negligibly small value of $P_1 = 0.075$ (which characterizes spontaneous polarization) we believe that this ensemble is sufficiently orientationally disordered.

In order to make our results and conclusions more transparent, we performed all subsequent energy computations not with the interaction parameters used in GROMOS, but with the London approximation for dispersion interactions. So we adopted for atoms

$$U(r_{12}) = \alpha_1 \alpha_2 r_{12}^{-6}, \quad (4.1)$$

and computed the total energy in the system

$$E = \frac{1}{2} \sum_i \sum_{j \neq i} E(i, j), \quad (4.2)$$

where $E(i, j)$ are given by (1.3).

Fragment ('pseudoatom') polarizabilities were taken according to the Vogel system for molar refraction R (see fig. 1):

$$\alpha = \frac{3R}{4\pi N_a}. \quad (4.3)$$

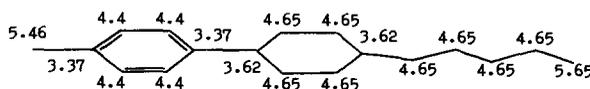


Fig. 1. Molar refractions for the fragments of PCH-5 according to the Vogel system.

It should be noted that in this case the energy in (4.1) is a dimensionless variable. For the benzene ring fragments we have taken the sixth part of the whole benzene ring polarizability and in the positions of substitution we subtracted the polarizability of the hydrogen atoms. The total molar refraction, obtained in the approximation of polarizability additivity is equal to 79.9, in good agreement with the experimental value 81.35 [35].

Because of the fact that we neglected the anisotropy of the fragment polarizability, it is implied in our model that fragments possess spherical symmetry and, consequently, only R_{00}^0 is non-vanishing in the coordinate system which is centered in a fragment. Taking this into account, for the determination of the components of generalized multipole moments in the molecular reference system, formulae (3.10) can be taken in the form (3.10c). Putting $\rho(r) \equiv \alpha(r)$ we can determine $\overline{R_{LM}^{2N}}$ for the whole set of atoms in the molecule. Another advantage of the representation of interaction in the form of (4.1) is that, after identifying $\rho(r)$ with $\alpha(r)$, in our case $C_{2n}^{xy} = 1$, and the computation of molecular interactions (formula (2.14)) is substantially simplified. The center of the molecular reference system was fixed in the center of the molecular polarizability and due to this, only moments with even L are non-vanishing. Several lowest rank components are presented in table I. It should be noted that $\overline{R_{LM}^{2N}}$ are defined such that R_{00}^0 coincides with the molecular polarizability. The $\overline{R_{00}^2}$ component in our case is comparable in magnitude with R_{20}^0 and, consequently, one can suppose that their contribution to the molecular interaction energy is also comparable. So we can conclude that for strongly elongated molecules the effect of both these terms should be taken into account, while $\overline{R_{LM}^0}$ with $M \neq 0$ contributes to a much smaller extent.

For the energy computations we have a truncated expansion (2.5) (or more precisely (2.14)) at terms proportional to R_{12}^{-8} . Thus, in our case, taking into account the identity of molecular scalar parameters

$$E(1, 2) = A_{0(3)}^{000} B_{000}^{000} \frac{1}{R_{12}^6} \overline{R_{00}^0}(1) \overline{R_{00}^0}(2) + A_{1(3)}^{000} B_{001}^{000} \frac{1}{R_{12}^8} \overline{R_{00}^0}(1) \sum_{i=1}^2 \overline{R_{00}^2}(i) + A_{0(3)}^{022} B_{000}^{002} \frac{1}{R_{12}^8} \overline{R_{00}^0}(1) \sum_{i=1}^2 \sum_{m=-2}^2 \overline{R_{2m}^0}(i) D_{m0}^2(\hat{r}_{12}), \quad (4.4)$$

Table I

Components of the generalized multipole moments for PCH-5 with $R_{00}^0 = 31.7 \times 10^{-3} \text{ nm}^3$ and $\overline{R_{00}^2} = 6.05 \times 10^{-3} \text{ nm}^5$.

M	-2	-1	0	1	2
$\text{Re}(\overline{R_{2M}^0}) (10^{-3} \text{ nm}^5)$	-0.05	-0.04	4.82	0.04	-0.05
$\text{Im}(\overline{R_{2M}^0}) (10^{-3} \text{ nm}^5)$	-0.01	0.01	0.00	0.01	0.01

where the $\overline{R_{2m}^0}(i)$ are taken in the laboratory fixed coordinate system and are different for different molecules, due to variations of their orientation and conformational flexibility. As it is clear from (4.4), we can distinguish three types of contributions to the total energy: isotropic molecular interaction (the first term), quadrupole interaction, arising from the elongation of our molecules (the third term), and a correction to the quadrupole interaction originating from generalized multipole moments, which takes into account the fact that the interacting molecules have finite dimensions (the second term). Coupling between these three types of interaction appears only in the higher order terms. The results of the computation of the total energy in the system according to (4.2) and (4.4) are represented in table II.

The data in table II are divided into 3 columns with different intermolecular separation. For example, in the first column contributions to the interaction energy from all the molecules separated not more than 2 nm are collected (molecular length is approximately 2 nm). As it is clear a priori, for small separations an expansion in the form (2.5) can not give agreement with the result obtained by direct summation of atom–atom interactions (last line). In this case it is even better to treat the molecules as isotropic points (first line) than to take into account non-central interactions. It is obvious that even the first anisotropic terms in this diverging set of multipole corrections lead to gross errors. This conclusion is especially important for anisotropic fluids, where the mesophase existence is caused by the anisotropic part of the molecular interactions. For densities usual for such substances, the multipole expansion gives errors of an order of magnitude larger than the estimated energy.

With increasing molecular separations (second and third columns) the difference between multipole expansion and the precise result is decreasing. The conventional multipole expansion is sign-alternating and therefore the result given by it is strongly dependent on the order of truncation. Nevertheless, some conclusions can be made, even from the distance dependence of the first term. It is seen, for example, that its contribution is decreasing more quickly

Table II
Contributions to the molecular interaction energy for PCH-5 arising from different terms in (4.4). In different columns we gathered contributions from the molecules with different intermolecular separation.

Separation (nm)	<2	>2	>4
I term	2.4917	0.0852	0.0278
II term	6.9256	0.0255	0.0042
III term	-12.2115	0.0011	0.0001
Pseudoatom–pseudoatom interaction	3.9319	0.3555	0.0408

than that of the generalized multipoles. For isotropic surroundings it vanishes completely, in contrast to the generalized multipoles. Even the scalar part of the latter ones contribution into the total energy is of the order of twenty or thirty per cent and of course they should be taken into account. It is evident that this contribution partly covers the difference between interaction energies for the cases where molecules and atoms are treated as interacting sites. This shows that the anisotropic part of interactions is rather small even for typical mesogens.

5. Conclusions

The analysis of the numerical results for the multipole expansion of the molecular interaction energy has shown that the difference between the conventional multipole expansion and a more complete one, obtained in this paper, is sufficiently large for liquid densities. The neglect of this difference can lead to large quantitative and even qualitative errors. While the results for large intermolecular separations are encouraging, much should be done for re-summing this expansion in order to ensure its convergence for the nearest neighbors interactions in liquids consisting of anisotropic molecules.

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Appendix A. Asymptotics of the Fourier–Bessel transformation

An asymptotical expansion of

$$J = \int_0^{\infty} dk k^a j_l(kr) \phi(k) \quad (\text{A.1})$$

at $r \rightarrow \infty$ should be found. After the substitution of an integral representation for Bessel functions [22]

$$j_l(z) = \frac{(\frac{1}{2}z)^l}{2l!} \int_{-1}^1 dt \cos(zt) (1-t^2)^l \quad (z = kr), \quad (\text{A.2})$$

into (A.1) (we suppose that the conditions of Fubini's theorem are fulfilled) and changing the order of integration we have

$$J = \int_{-1}^1 dt \frac{1}{2l!} (1-t^2)^l \left(\frac{1}{2}r\right)^l \int_0^\infty dk k^{a+l} \exp(ikrt) \phi(k). \quad (\text{A.3})$$

With the help of the Riemann–Lebesgue lemma for the first integral in (A.3) we have

$$\begin{aligned} \int_0^\infty dk k^{a+l} \exp(ikrt) \phi(k) &= \sum_{s=0}^\infty \left(\frac{i}{rt}\right)^{s+1} \frac{d^s}{dk^s} [k^{a+l} \phi(k)]|_{k=0} \\ &= \sum_{p=l+a}^\infty \left(\frac{i}{rt}\right)^{p+a+l+1} \frac{\Gamma(p+a+l+1)}{p!} \phi^{(p)}(0) \quad (r \rightarrow \infty). \end{aligned} \quad (\text{A.4})$$

After this, in the complex t plane following Cauchy's theorem we deform the contour of the integration in (A.3). For the integral

$$J' = \oint_c \frac{(1-t^2)^l}{t^{p+a+l+1}} dt$$

using Jordan's lemma in the limit of infinite radius of integration contour we have

$$J' = \begin{cases} 0, & p+a+l+1 = 1 \pmod{2}, \\ (-1)^l \frac{\Gamma(\frac{1}{2}(p+a+l+1))}{l! \Gamma(\frac{1}{2}(p+a-l+1))}, & p+a+l+1 = 0 \pmod{2}. \end{cases} \quad (\text{A.5})$$

Substituting (A.5) and (A.4) into (A.3) we finally obtain

$$\begin{aligned} J &= \sum_{p=0}^\infty A_p r^{-p-a-1} \quad (r \rightarrow \infty), \\ \text{where } A_p &= \frac{\Gamma(\frac{1}{2}(p+1-l+1)) 2^{p+a-1} \sqrt{\pi}}{p! \Gamma(\frac{1}{2}(l-p-a+2))} \phi^{(p)}(0). \end{aligned}$$

Appendix B. Helical molecular model

Let us consider as a model molecule a set of balls placed in a helix. In

principle, such model can be further modified using the results of section 3 of the paper in order to treat interactions between bio-molecules. So we define h as a helix pitch and R as its radius, b is a ball radius and λ is the distance between them, $\hbar = h/2\pi$, ϕ is an azimuthal angle and L is the length of the helix along its axis. In these notations the positions of the balls in the coordinate system fixed in the center of symmetry of the helix are given by

$$x = R \cos \phi, \quad y = R \sin \phi, \quad z = \hbar \phi.$$

In the coordinate system fixed in the ball center only $\rho_{00}(k)$ differs from zero and if the ball is homogeneous, straightforward calculations give

$$\rho_{00}(k) = \frac{b^2}{\sqrt{\pi}^3 k} j_1(kb). \quad (\text{B.1})$$

After applying (3.5) twice, first for radial translation and then for translation along the helix axis, we have

$$\begin{aligned} \rho_{lm}(k) = 4\pi \sum_{l_1, l_2=0}^{\infty} i^{l_1+l_2} \rho_{00}(k) j_{l_1}(kR) \frac{[l_1^2 l_2^2]}{[1]} \delta_{l_1+m, 2s} \\ \times C_{l_1 0 l_2 0}^{l 0} C_{l_1 m l_2 0}^{l m} D_{m 0}^{l 1} (0, \frac{1}{2}\pi, 0) S. \end{aligned} \quad (\text{B.2})$$

Here

$$S = \sum_{n=-N}^N \exp(-im\phi_n) j_{l_2}(k|a_{z_n}|) [\text{sgn}(\phi_n)]^{l_2},$$

$2N + 1$ is the number of balls in the helix (it is assumed that one of them is placed in the plane $z = 0$), s is a natural number, $|a_{z_n}| \equiv |n\alpha\hbar| = |n|\lambda\hbar / (R^2 + h^2)^{1/2}$ is the distance of the translation along the z axis for the n th ball and ϕ_n is its azimuthal angle; $\phi_n = n\alpha$, where $\alpha = \lambda / (R^2 + h^2)^{1/2}$ is the azimuthal angle between neighboring balls. Taking into account these notations we can rewrite

$$S = \sum_{n=-N}^N \exp(-imn\alpha) j_{l_2}(k|n|\alpha\hbar) [\text{sgn}(n)]^{l_2}. \quad (\text{B.3})$$

The limit of large N , i.e. when $\lambda \ll (R^2 + h^2)^{1/2}$, is of the most interest. In this case one can change the sum in (B.3) into an integral, i.e. to keep only the first term of the Euler–MacLaurin formula. Then we have

$$\begin{aligned}
S &\approx 2i \left(\delta_{l_2, 2p+1} \int_0^\infty dx \sin(\alpha mx) j_{l_2}(k\alpha\hbar x) + \delta_{l_2, 2p} \int_0^\infty dx \cos(\alpha mx) j_{l_2}(k\alpha\hbar x) \right) \\
&= \frac{\pi}{\sqrt{\alpha k\hbar}} i^{l_2+1} P_{l_2} \left(\frac{m}{k\hbar} \right), \tag{B.4}
\end{aligned}$$

where P_l is a Legendre polynomial. The inequality $0 < |m\alpha| < k\alpha\hbar$ should be fulfilled. Finally, in the limit of infinitely large N we have

$$\begin{aligned}
\rho_{lm}(k) &= \frac{4\lambda b^2}{\sqrt{\hbar k^3(R^2 + \hbar^2)}} \sum_{l_1, l_2=0}^{\infty} i^{l_1+1} (-1)^{l_2} \frac{[l_1^2 l_2^2]}{[l]} j_{l_1}(kR) \\
&\quad \times j_{l_1}(kb) P_{l_2} \left(\frac{m}{k\hbar} \right) C_{l_1 0 l_2 0}^{l 0} C_{l_1 m l_2 0}^{l m} D_{m 0}^{l_1} \left(0, \frac{1}{2} \pi, 0 \right). \tag{B.5}
\end{aligned}$$

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