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Exploring the connection between the density-scaling exponent and the intermolecular potential for liquids on the basis of computer simulations of quasireal model systems

K. Koperwas[*], A. Grzybowski, and M. Paluch
University of Silesia in Katowice, Institute of Physics, 75 Pułku Piechoty 1, 41-500 Chorzów, Poland
and Silesian Center for Education and Interdisciplinary Research (SMCEBI), 75 Pułku Piechoty 1a, 41-500 Chorzów, Poland

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In this paper, based on the molecular dynamics simulations of quasireal model systems, we propose a method for determination of the effective intermolecular potential for real materials. We show that in contrast to the simple liquids, the effective intermolecular potential for the studied systems depends on the thermodynamic conditions. Nevertheless, the previously established relationship for simple liquids between the exponent of the inverse power law approximation of intermolecular potential and the density-scaling exponent is still preserved when small enough intermolecular distances are considered. However, our studies show that molecules approach each other at these very short distances relatively rarely. Consequently, only sparse interactions between extremely close molecules determine the value of the scaling exponent and then strongly influence the connection between dynamics and thermodynamics of the whole system.

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I. INTRODUCTION

The complex nature of fluids has been a subject of scientific interest since the latter half of the past century. One of the main reasons for the unceasing fascination with the liquid state is the appearance of a new and breakthrough method for its investigation: computer simulations of the molecular dynamics [1–3]. The most significant advantage of this computational technique is that it provides information unavailable until that time about the exact positions and velocities of every atom in the system as well as about interactions occurring between them. Consequently, the entirely new possibility of investigations of the liquid state has appeared. However, the initial limitation of computing power has been that most computational experiments were devoted to the so-called simple liquids, i.e., systems composed of many particles interacting via a radially symmetric pair potential. Interestingly, these simulated systems exhibit many properties similar to those of real liquids. Nevertheless, the simplicity of their molecular architecture, as well as the assumed intermolecular interactions, ensures that the natural and fundamental question of how well these model systems can capture the intricate thermodynamic and dynamic properties of real liquids is still a real one. One of the methods to answer this problem is to understand how the results obtained for simple liquids could be applied to the real systems.

Since the latter part of the last century, numerous computational studies of various systems have been performed. Among them, the most prevalent are those in which the Lennard-Jones (LJ) potential (or its approximation valid for short distances by the soft-sphere potential) describes intermolecular interactions. The reason for the scientific interest in those systems is the theoretical explanation of the origins of the repulsive and attractive parts of the LJ potential [4], making use of the fact that the LJ or soft-sphere potentials enable analytical modeling of the physical interactions between molecules of real van der Waals liquids. Among many obtained results, performed investigations revealed one exceedingly fascinating feature of examined systems, which is quasiuniversality of their properties [5–10]. The uniqueness of quasiuniversality of the simple liquids comes from the fact that it connects the micro- and macroproperties of the system. According to it, all (macroscopic) structural, dynamic, and transport properties at equilibrium are a function of the only single variable, $TV^{m/3}$, where T is the temperature, V is the volume of the system, and m is a (microscopic) parameter describing intermolecular interactions [11–14]. Theoretical analysis delivers the exact explanation of the origin of the m parameter. According to it, for the soft-sphere systems, an effective intermolecular potential could be dominated by the inverse power law (IPL),

$$U_{\mathrm{IPL}}(r) = \varepsilon(\sigma/r)^m + A, \tag{1}$$

where m is the exponent of repulsive term of intermolecular potential, A is a constant representing the attractive background, and ε and σ are potential parameters [15–19]. Additionally, the form of the scaling argument, $TV^{m/3}$, implies that the microscopic information about character of intermolecular interactions can be obtained from the analysis of only macroscopic properties, which is a remarkable result in the context of real materials for which knowledge of the intermolecular potential or its parameters is unknown from the real experiments. Interestingly, despite the fact that the discussed scaling is valid only for soft-sphere systems, it was shown that it works for LJ systems at low temperatures and hence at high densities [20–24] and also even for real van der Waals liquids. The latter was initially demonstrated by Tölle

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[*] Corresponding author: kajetan.koperwas@us.edu.pl

at the turn of century [25,26], who analyzed the quasielastic neutron scattering data for canonical van der Walls liquid ortho-terphenyl (OTP). Tölle pointed out that the observed dynamic crossover could be characterized by an effective constant value $T\upsilon^4$ (υ denotes the specific volume). The exponent 4 was immediately related via $m/3$ to the exponent 12 of the LJ repulsive core. This first experimental observation of quasiuniversality in real liquids not only maintained the fascination of researchers with this subject but also made it one of the most frequently studied issues of condensed matter physics over the last 20 years [27–31].

Next, Dreyfus successfully scaled rotational relaxation times, obtained from light-scattering data for different isotherms of OTP, onto a single master curve as a function of $T\upsilon^4$ [32]. However, other, numerous attempts to scale dynamic properties of various glass formers revealed that the exponent of 4 could not be treated as a universal value for all systems [33–36]. Nevertheless, it was reported that the use of the scaling exponent, which usually varies between 2 and 7, enables density scaling of more than 100 glass formers [37]. Consequently, the general form of the density scaling has been established [33–36,38–41],

$$X = \mathcal{F}(T\upsilon^{\gamma}), \tag{2}$$

where X is the dynamic quantity, e.g., the structural relaxation time, τ, viscosity, η, or diffusion constant, D, and the density-scaling exponent, γ, is a material constant. The deviation between γ and its expected value of 4 (a result of the LJ potential) has been rationalized by theoretical studies which showed that the IPL potential with $m = 12$ is much softer than the repulsive core of the LJ potential. In fact, the repulsive core of the LJ potential is similar to IPL potential with $m = 18$ [42]. It is due to the fact that the LJ potential is a combination of repulsive and attractive terms. Hence, even at short distances, the repulsive core of the LJ potential is modified by the attractive term, which leads to $m > 12$. Additionally, repulsive and attractive terms are expected to be different for different materials, and therefore one cannot expect that γ is identical for all materials. Nevertheless, the material dependence of γ does not influence its fundamental relation with the intermolecular potential,

$$\gamma = m/3, \tag{3}$$

which is still preserved. Hence, this relationship can be freely used to conclude on the intermolecular interactions occurring between molecules.

However, in the case of real liquids, any consideration of the relationship between γ and the exponent of the IPL approximation of the intermolecular potential, m, has to begin with the answer to the fundamental question about the origin of the effective intermolecular interaction potential (EIIP), which could be described by IPL. The most evident crucial aspect is the shape anisotropy of real materials, which results in intermolecular interactions generated by the one molecule not having a spherical character. Therefore, this paper aims to add to knowledge about the problem of the definition of EIIP for real systems. We propose a method for estimating the discussed potential and show that the determined exponent of the approximation of EIIP by the IPL is close to the density-scaling exponent (for two model systems). As a consequence, the applied method for the determination of the EIIP helps in understanding the origin of the effective intermolecular interactions. Thus our findings contribute significantly to discussion of the quasiuniversality of the real systems.

II. METHOD

The most evident difference between simple liquids and the real liquids is the shape of the molecules, which for the majority of real liquids drastically departs from the sphere. Therefore, over the last few decades, many approaches to the problem of the influence of the molecular anisotropy on the thermodynamics and dynamics of the system have been proposed. The proposed model systems can be divided into two main groups. The first group treats molecules as hard objects with a given shape, in which anisotropy results from short-range repulsive forces resulting from impenetrability of hard cores [43]. Performed studies show that the molecular shape may be crucial in determining the phase behavior as a function of the density. One of the examples is hard dumbbells, i.e., two hard spheres connected by the rigid-bond, phase diagram, which strongly depends on the bond length [44–47]. At low elongations, the liquid freezes into a closely packed plastic crystal where the centers of mass of the molecules form an ordered lattice, but they can rotate. The FCC plastic crystal is stable at low elongations, although it becomes metastable concerning the HCP when elongation (and pressure) increases [47,48]. The transformation of the plastic crystal to the orientationally ordered solid is observed when one further increases the bond length. Another example is hard rods, which exhibit five different phases depending on the density and the shape anisotropy estimate by the ratio of length and width [49]. Summarizing, the complexity of the phase diagram of the hard molecules strongly depends on the molecular shape. However, it must be stressed that for this type of the systems the density is a crucial factor influencing the phase behavior, whereas the temperature enters the thermodynamics in only a trivial way [50]. In contrast to hard molecules, the second group of model systems considers the molecular anisotropy by modeling intermolecular interactions occurring between nonspherical molecules. The most popular are systems governing by the Kihara potential [51], the Gaussian overlap model [52], and the Gay-Bern potential [53]. This approach enables one to include a short-range repulsion as well as a long-range attraction as a function of the distance between molecules and their mutual orientations. Consequently, the temperature is also an important thermodynamic variable affecting the physical properties of the system.

However, from the experimental point of view, the most natural is a phenomenological description of the intermolecular interaction, which includes all atom-atom interactions, i.e., the atom-atom (or site-site) model potential. In that way, the structure of real molecules is reflected, and then closer agreement with the experiments may be expected. Extensive studies of those types of molecules proved that they provide a fairly good description of dynamical [54–58] and structural [59–62] properties of slightly nonspherical molecules [63]. Moreover, this way to model interactions between the real molecules possesses a huge advantage, which is the possibility of applying the charge distribution and then creating an electric dipole (or quadrupole) moments—the inherent feature of real molecules, whose impact on the density-scaling exponent has been recently demonstrated [64].

Taking the above into account, we decided to apply the atom-atom model to reflect the interactions between systems studied herein. In that way the potential resulting from a single molecule at the given point within the space is a sum of the interactions induced by all atoms which form that molecule. Hence, not only the distance from the molecule but also the orientation of the molecule plays a role in the estimation of the EIIP. At this point, we would like to recall our recent paper, where EIIP was determined [65] (see discussion there). In the mentioned studies, the three main directions in respect to the molecular shape have been taken into account. Estimated along these lines, EIIPs had been averaged and described with very good accuracy by the IPL, with the exponent equal to 3γ. A natural generalization of this approach, which makes it become independent of the molecular shape, is consideration of all spherical angles for determination of the average EIIP. However, we have to mention some limitations of this method. First, for systems exhibiting some molecular ordering, i.e., liquid crystals for which dependence on the scaling exponent on the phase has been reported [66], not all spherical angles would be equally relevant. As a consequence, one should predict which spherical angles should be neglected for estimation of EIIP for different phases. Second, the discussed approach leads to a striking conclusion. The two hypothetical molecules, which differ only in the flexibility of the bonds and angles between them (but not in their value at equilibrium), possess the same EIIP. Consequently, two different systems would be characterized by the same physical properties, which seems to be contestable. Naturally, the presence of the other molecules in the system implies bending of the bonds as well as change of their length. It yields to a temporary modification of molecular shape and influence on EIIP, which is more prominent for more flexible molecules. Variations in EIIP result in the different physical properties of two hypothetical systems, as may be expected. The solution is the calculation of the EIIP based on the temporary shape of the molecule within the system. However, the shape of the molecule changes with time because it depends on the positions and orientations of the neighboring molecules, which are constantly in motion. It constitutes a challenging problem for an analytical solution, which should consider modifications of molecular shape resulting from possible mutual orientations of molecules. However, as we previously mentioned, not all of the latter are relevant. Therefore, an analytical solution of the discussed issue faces the problem of eliminating the mutual arrangement (positions and orientations) of molecules, which does not (frequently) occur within a real system. Nevertheless, the use of the computer simulations of the molecular dynamics enables elimination of this problem. This method provides the exact positions of all atoms during the time evolution of the system. Hence, in the natural way irrelevant mutual orientations and positions of molecules, which do not occur, are not registered. Consequently, in the most general way, the EIIP could be estimated by calculation of the interaction taking place between all atoms of both interacting molecules considering their temporary positions and presenting this as a function of the distance between the centers of the molecules' masses or geometries.

To analyze the behavior of the EIIP at various thermodynamic conditions calculated according to the method described in the previous paragraph as well as its correspondence to the density-scaling exponent, we examined two model systems. The first is conceptually based on simple liquids, whose interaction potential depends solely on the intermolecular distance. Since, as we already mentioned, the spherical potential cannot be ideally imitated by the real molecules, we employed the structure of the methane molecule to create the model molecule of the tetrahedron shape; see the scheme in Fig. 1(a). The advantage of that choice is not only the fact that the tetrahedronlike molecule (TLM) has representatives within real liquids, but also the fact that it approximates the sphere, and simultaneously it comprises a tiny number of atoms, which facilitates computational studies. To eliminate influences of different factors we simplify the molecule as much as possible. We set all its atoms to be identical; i.e., they are characterized by the same masses and the intermolecular potential parameters, which are defined for the carbon atoms of the benzene ring by an OPLS all-atom force field [67]. Consequently, the bonds lengths and their stiffness as well as the stiffness of the angles they create are set to correspond to those of the benzene ring. The second examined model of a quasireal molecule has been recently introduced by us [65]. Its molecules are made up of four identical atoms (of carbon atom mass) arranged in a rhombus shape; see the scheme in Fig. 1(b). The shape of the rhombuslike molecules (RLMs) implies that they possess short and long molecular axis, whereas bonds lengths are constant. We set the bond lengths to be equal to 0.14982 nm (0.14 nm is the length of a bond for carbon atoms in a benzene ring and then in TLMs), whereas angles between bonds are established to make one diagonal two times longer than the other. Similarly, to the first model system the stiffness of bonds, angles, and dihedrals, as well as the nonbonded interaction between atoms of different molecules, have been defined by OPLS all-atom force field parameters provided for carbon atoms of the benzene ring.

The experimental procedure was similar for two systems. After construction of the perfect FCC lattice crystal, in which the 2048 RLM or TLM was inserted in place of atoms, we heated the systems from a starting temperature equal to 10 K (at isobaric conditions of 40 MPa for TLMs and 100 MPa for RLMs) to determine the melting of the crystal structure and then the conditions corresponding to the liquid phase. The molecular dynamics simulations have been performed using GROMACS software [68–71] at conditions controlled by a Nose-Hoover thermostat and Martyna-Tuckerman-Tobias-Klein barostat. Each simulation run lasts for a relatively long time, 1 billion time steps ($dt = 0.001$ ps), whereas the change of the temperature is equal to 5 K ($\Delta T = 5$ K). The cutoff of the intermolecular interaction occurs at a distance equal to 1.065 nm, which is three times larger than the distance of the minimum of the LJ potential describing the nonbonded interaction between atoms. After appropriate melting of the structure, which has been done at a temperature 50 K higher than the temperature of the observed sudden increase in volume, we cooled the systems at isobaric conditions to the

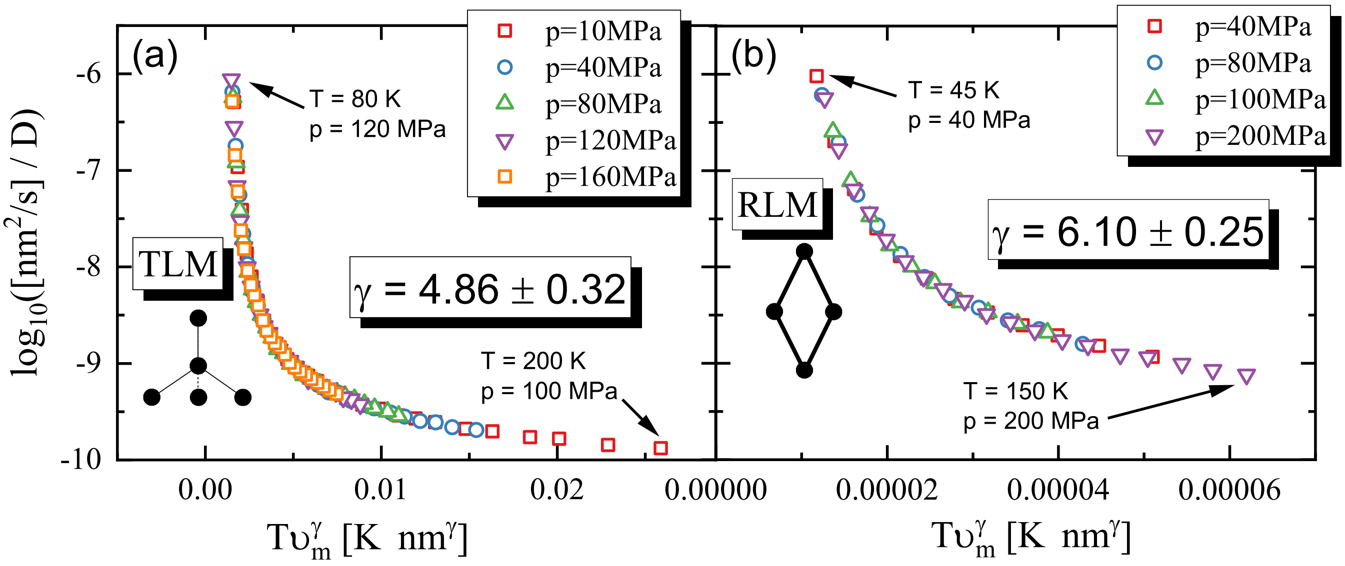

FIG. 1. Density scaling for two model systems, TLM and RLM, in panels (a) and (b), respectively. The schemes of the molecular structures are presented as well as the values of the density-scaling exponent, γ. The arrows denote the two boundary thermodynamic conditions corresponding to the highest and lowest values of diffusion constant.

starting temperature. This procedure was performed for TLMs at pressures equal to 10, 40, 80, 120, and 160 MPa, and at 40, 80, 100, and 200 MPa for RLMs. The temperature dependences of volume per molecule, υ_m, have been described with a very good accuracy by the quadratic equation. Additionally, at each thermodynamic condition, using GROMACS software, we determined the diffusion constants, where the temperature dependences have been approximated with the well-known Vogel-Fulcher-Tammann equation. Next we determined the scaling exponent using Eq. (2), according to which $\log T|_{D=\text{const}}$ is a linear function of $\log \upsilon_m|_{D=\text{const}}$ with the slope equal to γ. At this point, it should be recalled that this equation is valid only for soft-sphere systems. Consequently, this form of the scaling function for real systems is a hypothesis. Nevertheless, it works perfectly for numerous materials and therefore from the experimental point of view can be used for further analysis. Employing the Vogel-Fulcher-Tammann equation for each isobar we calculated the temperature corresponding to the given value of the diffusion constant [$\log([\text{nm}^2/\text{s}]/D) = -9$ for TLMs and $\log([\text{nm}^2/\text{s}]/D) = -8$ for RLMs]. Subsequently, exploiting the aforementioned cubic approximation of the dependence of υ_m on T we got the appropriate for a given temperature value of the molecular volume. Fitting established dependences of $\log T|_{D=\text{const}}$ on $\log \upsilon_m|_{D=\text{const}}$ we easily estimated the γ value. As is presented in Figs. 1(a) and 1(b) for TLMs and RLMs, respectively, the obtained values of γ lead to the satisfying density scaling of diffusion constants. We refer interested readers to our recent article [65], where the discussed procedure is described in great detail for the RLM system.

III. RESULTS

At the beginning of our results we would like to consider the two boundary dynamic conditions, ($T = 200$ K, $p = 100$ MPa) and ($T = 80$ K, $p = 120$ MPa) for TLMs and ($T = 150$ K, $p = 200$ MPa) and ($T = 45$ K, $p = 40$ MPa) for RLMs, which are characterized by the highest and the smallest values of D, respectively. Given the aforementioned discussion of EIIP, we examined the final configuration obtained from the molecular dynamics simulations. For each pair of molecules we determined the distance between their centers of masses, r_{CM}. Subsequently for every atom of one molecule we calculated the potential energy resulting from all atoms of the other molecule. The sum of these potential energies, U_E, was assigned to r_{CM}. Additionally, to obtain better statistics at short distances the periodic boundary conditions have been applied. The estimation of the base of one configuration $U_E(r_{CM})$ for all molecular pairs is presented in Fig. 2 (filled circles). We can see that thermodynamic conditions corresponding to the lower value of the diffusion constant exhibit smaller distribution of U_E. It is a result of the insufficient values of the kinetic energies of the molecules, which make impossible exploration of the less energetically optimal orientations of molecules. Observed for the state of fast dynamics, high values of U_E correspond to the pairs of molecules whose potential energy significantly exceeds the energy needed for its separation. As a consequence, those molecules probably change their environments, contributing to quickening the diffusion process. Interestingly, we can also observe that for both studied thermodynamic conditions the lowest calculated values of U_E lie in one curve exhibiting a typical shape of the LJ potential cure. It suggests that the liquid systems could be described by some boundary potential. Since the minimum of the boundary potential is characterized by the smallest value, the discussed potential described the interactions between the molecules, whose mutual orientations make separation of those molecules as difficult as is possible. This ensures that analysis of the boundary potential would be an interesting topic for further studies. Nevertheless, in this paper we focus on an EIIP, which describes mean (not extreme)

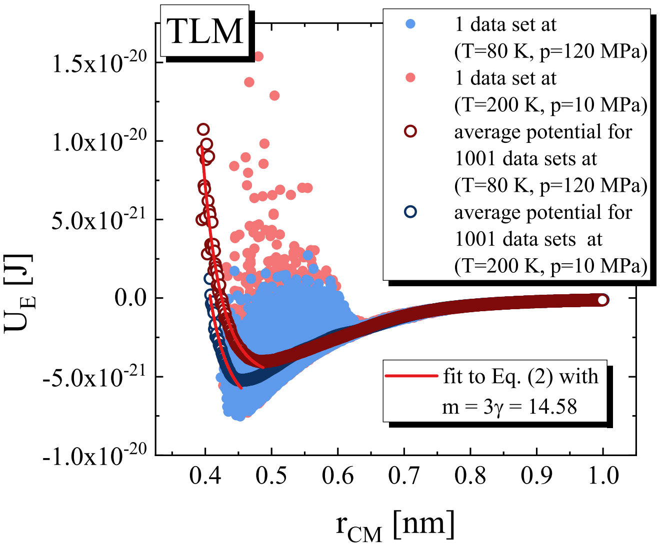

FIG. 2. The effective intermolecular potential as a function of the distance between centers of molecule mass is presented for two dynamic boundary conditions (filled symbols consider only one configuration without any averaging). The open symbols represent the average at each intermolecular distance for all collected configurations at given thermodynamic conditions. The straight lines denote the approximation by the IPL with the constant value of exponent m equal to 3γ.

intermolecular interactions. Hence the natural way to estimate EIIP is averaging of determined $U_E(r_{CM})$. To provide better statistics we take into account all configurations registered during each simulation run (1001 data sets). Results are presented in Fig. 2 (open symbols). Here we can clearly notice that at both dynamic conditions the average U_E is arranged in a manner which is similar to the shape of the LJ potential. One can also observe that the average U_E determined at conditions of slower dynamics reaches lower values and that its minimum is registered at shorter intermolecular distances. The shift of the potential minimum to the smaller distances is probably connected with the lowering of the temperature [see also Fig. 3(a). Thermal motions lead to U_E differing from the aforementioned boundary potential, i.e., the potential which describes the most energetically optimal angular positions and their mutual orientations. At given r_{CM} one molecule can surround another, but some angular positions and orientations are more energetically preferable. The higher the temperature, the more (and more frequently) energetically nonoptimal configurations are achieved. As a consequence, the minimum of U_E moves farther from the minimum of the boundary potential. Interestingly, the lowering of U_E observed in Fig. 2 suggests indirectly some ordering of the structure. Lower values of U_E at given r_{CM} implies that the average energy which must be overcome to separate two molecules of system becomes higher. Since we consider a constant value of r_{CM} it is a result of mutual positions and orientation of molecules. The latter are less diverse and more similar to the most energetically optimal ones at a condition of a smaller value of D. Additionally, we would like to call readers' attention to the fact that the smaller values of r_{CM} are detected for the system characterized by the higher value of D. It can be a result of the higher kinetic energy of the molecules, which facilitates overcoming the repulsive intermolecular interactions and makes molecules be temporarily closer to each other.

Since $U_E(r_{CM})$ determined in the proposed way changes when the thermodynamic conditions differ, a natural consequence of performed research is a detailed examination of U_E variations. We choose the condition of constant temperature, volume, and diffusivity, since these quantities occur in Eq. (2). The results are presented in Fig. 3 for the TLM system. Interestingly, we can observe that at isothermal conditions [Fig. 3(a)] the position of the U_E minimum remains unchanged and that variation of U_E, when pressure (and thereby volume) changes, is much less than in the case of constant volume and diffusion; see Figs. 3(b) and 3(c), respectively. This fact supports our previous claim that the shift of the EIIP minimum is mainly due to the temperature changes. Interestingly, the almost identical shapes of U_E means that changes occurring within the system are similar to those observed in simple liquids, for which mutual orientations and angular positions of molecules do not play any role in the shape of EIIP (according to the definition of EIIP introduced herein). Hence, we can suspect two possible scenarios. The molecules exclusively move closer to each other, keeping their mutual orientations and angular positions unchanged, or the (average) orientation and angular positions of molecules are directly connected with the distance between them; i.e., when one molecule is approaching another (r_{CM} decreases), their mutual orientations and angular positions change but not in the unrestricted way. The constant temperature results in that

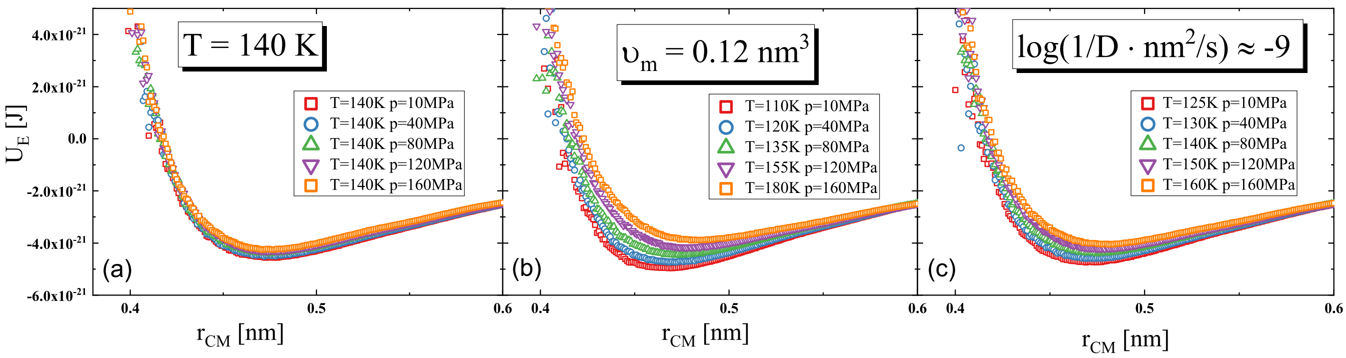

FIG. 3. The evolutions on the EIIP when conditions of constant temperature (a), volume (b), and diffusion (c) are maintained.

at given r_{CM}, independent of the system density, the same mutual orientations and angular positions can be achieved by molecules. In other words, the kinetic energy of molecules is too small to enable the arrangement of molecules in more nonenergetically efficient configurations. It results in the same (or very similar) shapes of the EIIP at isothermal conditions, and we believe that this scenario is more probable than the first one.

The highest variation of U_E is observed for isochoric conditions; see Fig. 3(b). Moreover, one can note that the position of the U_E minimum shifts toward the longer intermolecular distances when temperature increases. In this case the average distances between molecules are maintained. Hence the changes in U_E are caused by the different orientations and angular positions between molecules. At low temperatures kinetic energies of molecules do not enable one to obtain configurations that are not energetically optimal. Hence, the energy needed for separation of the two molecules is high, and the potential curve exhibits a pronounced minimum. An increase in the temperature guarantees that configurations that are not energetically optimal are registered more frequently, which causes a gain in U_E. Hence, simplifying, different potential curves obtained for various temperatures at isochoric conditions correspond to EIIP curves determined for different mutual orientations and angular positions of molecules.

The fulfillment of the last studied conditions, $D = \text{const}$, requires a modification of both temperature and volume. However, the discussed thermodynamic quantities influence similarly the diffusion process (an increase in T and υ_m implies a gain in the diffusion constant). Therefore, to keep the conditions of constant diffusion, one of them must decrease when the other increases. Consequently, in Fig. 3(c) we can see that an increase in the temperature makes U_E varies, which is similar to results presented in Fig. 3(b). However, its alternations are less prominent because the variation of the temperature is smaller [this is presented in Fig. 3(b)], whereas a decrease in volume slightly influences the U_E [see Fig. 3(a)].

Concluding, on the basis of the results presented in Fig. 3 we can state that the temperature plays the most important role in the evolution of the EIIP. Discussed changes are due to the changes in mutual orientations and angular positions of molecules, which lead to the ordering of the structure. In this context, we would like to call readers' attention to the conclusion noticed from Fig. 3(a). The decrease in the volume at isothermal conditions results in the increase of the EIIP, which means that the structure becomes easier to perturb. Consequently, at higher densities, one can expect that the system is less ordered. To confirm this finding we calculated the global bond-orientational order parameters [72], Q_6. The local structure around atom i could be quantified by a set of numbers $\bar{q}_{lm}(i) \equiv \frac{1}{N(i)}\sum_{j=1}^{N(i)} \Upsilon_{lm}(\hat{r}_{ij})$, where $l = 6$ for q_6, $\hat{r}_{ij}$ is a unit vector in the direction between atom i and atom j, $N(i)$ is a total number of considered i atoms, and $\Upsilon_{lm}(\hat{r}_{ij})$ is a spherical harmonics. Then the average of $\bar{q}_{lm}$ over all particles gives $\bar{Q}_{lm}$, and the rotational invariant takes the form $Q_l \equiv (\frac{4\pi}{2l+1}\sum_{m=-l}^{l}|\bar{Q}_{lm}|^2)^{1/2}$. The latter is recognized as a global order parameter (Q_6 for $l = 6$). In Fig. 4 we present evolution of Q_6 (calculated for atoms separated by a distance smaller than 0.6 nm) when the pressure increases (along the three thermodynamic paths considered in Fig. 3). Consistent with the result presented in Fig. 3(a), a decrease in the density at isothermal conditions results in the ordering of the structure and Q_6 decreases. The same behaviors are observed for thermodynamic conditions of constant volume and diffusivity, which correspond to the shift of EIIP curves towards higher values; see Figs. 3(b) and 3(c), respectively. Hence, the structural ordering concluded from Fig. 3 finds confirmation in the changes of Q_6. However, despite that a good qualitative agreement between results presented in Figs. 3 and 4 is achieved, the quantitative changes registered at the discussed schemes are not consistent. The evolution of EIIP at isothermal conditions is tiny, whereas respective changes in Q_6 are highest. Similarly, differences in Q_6 are smallest for isochoric conditions, while EIIP significantly varies when the volume is constant. The lack of quantitative agreement could be a result of the way used to the parameterization of the structural order. In this context, establishing the general connection between EIIP and the structure seems to be an interesting topic for further studies. Nevertheless, based on the presented analysis of Q_6 we can state that the EIIP can be used for qualitative examination of the structure evolution.

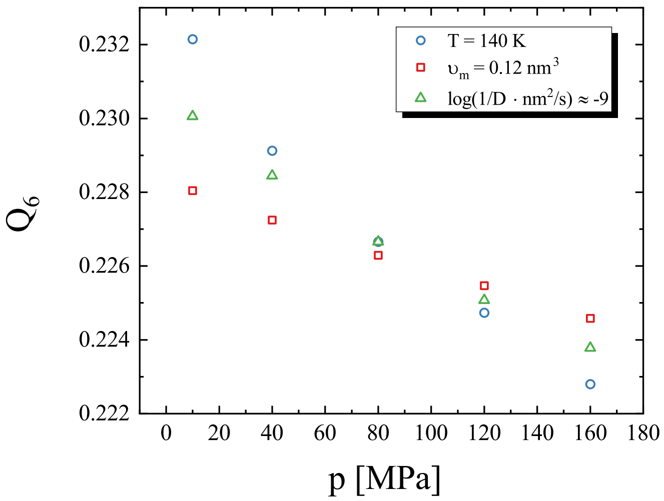

FIG. 4. The global bond-orientational order parameters calculated at thermodynamic conditions considered in Fig. 3.

Our studies clearly show that an effective intermolecular potential depends on the thermodynamic conditions. It is due to structural anisotropy of the molecules because the discussed effect is not observed in the case of isotropic simple liquids. For the latter EIIP is identical to the intermolecular potential describing interactions between two molecules independently of the thermodynamic conditions. As a consequence, the dependence of the shape of U_E on thermodynamic conditions suggests that single IPL with constant value of the parameters cannot describe all U_E for anisotropic molecules, even when constant dynamics of the system is maintained. Thus, we should expect different m values, which leads to the conclusion that the density-scaling exponent depends on the thermodynamic conditions. Interestingly, this scenario is consistent with the few reports on van der Waals liquids [73,74] and metals [74,75]. They show that γ depends on the

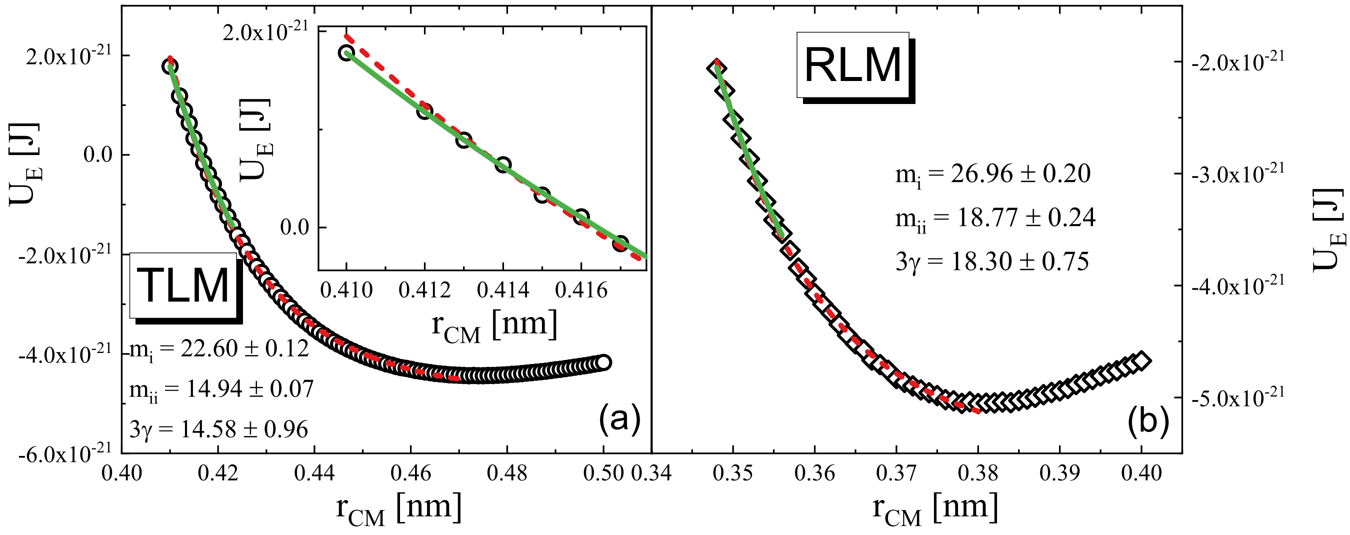

FIG. 5. The EIIP average for all studied thermodynamic conditions is represented by the open symbols for TLM and RLM systems in panels (a) and (b), respectively. Lines are the EIIP approximation by the IPL, Eq. (1), for two considered ranges of intermolecular distances. The vertical arrows indicate the first range of r_{CM}, which is limited by the minimum of EIIP, whereas horizontal arrows point to the intermolecular distance corresponding to the middle of the EIIP repulsive slope (second range of distances). We also present the obtained values of the IPL exponent, m, and their comparison to the value of the scaling exponent γ. In the inset of panel (a) the accuracy of the IPL fit at shortest r_{CM} is shown.

temperature and/or density, which at present is a subject of extremally hot debate [76–79].

IV. DISCUSSION

At the beginning of this section, we would like to note two technical issues related to the relationship between U_E and m. Intuitively, a steeper slope of U_E should be characterized by a higher value of m. However, the shape of the IPL potential, and then its steepness, does not depend exclusively on m values but also on the values of other parameters, i.e., ε and σ [Eq. (1)]. Hence, to study changes of the m parameter at different thermodynamic conditions, we cannot base our work only on visual examination of potential curves but also on the detailed description of U_E by IPL. It immediately leads to a second problem. The approximation of U_E by IPL is valid only at short distances; i.e., the maximum value of r_{CM} considered should not exceed the distance at which U_E reaches a minimum. Consequently, to compare a different parameter of IPL, a precise definition of considered r_{CM} range is required. The most natural way is to use the maximal accessible range of intermolecular distances, i.e., the range between shortest registered r_{CM} and r_{CM} corresponding to the minimum of U_E. In Fig. 2 $U_E(r_{CM})$ are described by an IPL with a constant value of $m = 3\gamma$ for two boundary dynamic conditions. The accuracy of the fit parameterized with the R^2 parameter equals 0.94 and 0.97 for ($T = 200$ K, $p = 10$ MPa) and ($T = 80$ K, $p = 120$ MPa), respectively. We observe in Fig. 2 that fairly good agreement is reached at short r_{CM}, while during the approach of r_{CM} corresponding to the minimum of U_E, fit curves underestimate the curvature of $U_E(r_{CM})$. Nevertheless, we can state that for both extreme dynamic conditions the constant value of $m = 3\gamma$ yields a satisfactory description of EIIP by IPL at short distances. It possesses important consequences for estimating U_E at all thermodynamic conditions. If N different potentials are described by IPL with the same m value, their average is s $U_{\mathrm{IPL}}^{\mathrm{avg}} = \frac{1}{N}\sum_{i=1}^{N}[\varepsilon_i(\frac{\sigma_i}{r})^m + A_i]$. This can be rewritten in the form $\frac{1}{N}\sum_{i=1}^{N}[\varepsilon_i(\frac{\sigma_i}{\sigma_{\mathrm{eff}}})^m(\frac{\sigma_{\mathrm{eff}}}{r})^m + A_i]$, in which $(\frac{\sigma_{\mathrm{eff}}}{r})^m$ does not depend on N. Hence, we get the formula $U_{\mathrm{IPL}}^{\mathrm{avg}} = (\frac{\sigma_{\mathrm{eff}}}{r})^m\sum_{i=1}^{N}\frac{\varepsilon_i}{N}(\frac{\sigma_i}{\sigma_{\mathrm{eff}}})^m + \sum_{i=1}^{N}\frac{A_i}{N}$, which immediately leads to the final expression

$$U_{\mathrm{IPL}}^{\mathrm{avg}} = \varepsilon_{\mathrm{eff}}\left(\frac{\sigma_{\mathrm{eff}}}{r}\right)^m + A_{\mathrm{eff}}. \tag{4}$$

It is worth noting that the last formula fulfills IPL as well (the exponent m is preserved, whereas $\varepsilon_{\mathrm{eff}}$, σ_{eff}, and A_{eff} are "effective" parameters). Taking this fact into account, we calculated EIIP for all performed simulations considering all registered configurations. Then we determined the average for all thermodynamic conditions U_E and approximated it by the IPL, but this time we treated m as a free fit parameter. Results are presented in Fig. 5. The dashed lines represent the fit of all r_{CM} shorter than the distance at which U_E exhibits a minimum. Since in this case m is a free fit parameter,, the shape of U_E close to minimum is much better reflected than is observed in Fig. 2. As a consequence the obtained m values are higher than 3γ. However, it simultaneously results in deviations of the fit from U_E at the shortest distances, which is presented in the inset of Fig. 4.

The possible explanation of $m > 3\gamma$ could be offered by the recent paper by Fragiadakis and Roland [80], where on the basis of molecular dynamics simulations of molecular liquid having rigid bonds and using the same intermolecular potential, a general form of the relationship between γ and m has been proposed, $\gamma = m/\delta$, where δ relates the intermolecular distance to the density along an isomorph (the line of approximately constant dynamics and structure). The authors pointed out that δ depends only on the structure of molecules and not on the intermolecular potential, and therefore δ plays the role of the dimensionality. The latter can be understood as the aspect ratio of the molecules; i.e., during compression of the system comprising long, rigid, rodlike molecules (simultaneously maintaining the same structure) each molecule compresses mainly in the two latter distances, $\delta \simeq 2$. Since the model molecules exploited in our studies do not have rigid bonds and they can be compressed alongside all dimensions, one can suspect that δ should be higher than 3. Using values of m obtained from the free fit in the range to the minimum of U_E, we immediately get $\delta_{\mathrm{TLM}} = 4.65$ and $\delta_{\mathrm{TLM}} = 4.42$. On the other hand, we would like to note that the studied molecules vary significantly in their structure, whereas the difference in δ values is slight. Nevetheless, the complete understanding of the connection between δ and the molecular architecture seems to be interesting topic for subsequent studies.

The alternative approach to solving the problem of inconsistency between m and 3γ is the limitation of the r_{CM} range, which naturally improves the fit accuracy. The narrower the range of r_{CM} the better the agreement achieved. A similar situation has been reported for single-component LJ systems; see Fig. 3 in Ref. [23], where the repulsive part of the intermolecular potential is approximated by IPL. Likewise, in Ref. [24] it has been pointed out that for a binary mixture of molecules interacting via LJ potentials the approximation of "effective" LJ potential by IPL is valid only at distances shorter than the position of potential minimum. Interestingly, as the authors pointed out, the range of intermolecular distances used for the approximation of potential by IPL corresponds to typical distances registered between closest particles. Summarizing, for LJ systems the intermolecular distances shorter than the minimum of the intermolecular potential are essential in the context of estimating m value. Hence, we can suspect that the range of r_{CM} applied in Figs. 2 and 5 is also too high, and the inconsistency between IPL fit curve and U_E value, which takes place close to the minimum of U_E, can be neglected.

Consequently, we performed another analysis during which we limited the r_{CM} to the value which corresponds to the half of the repulsive slope of U_E, i.e., to r_{CM} at which $U_E = \max(U_E) - [\max(U_E) - \min(U_E)]/2$. The fit is denoted by the solid lines; see Fig. 5. In this case estimated m values are in an excellent agreement with 3γ. This finding leads to the conclusion that for analyzed systems the value of the IPL exponent is sensitive to the range of r_{CM}. In order to conform our system to the result obtained for standard model systems, we approximate the standard LJ potential (expressed in the typical reduced units of simulation) by the IPL. The used ranges of intermolecular distances are identical to that applied for the TLMs in Fig. 5. For the fit in the range limited by the minimum of the LJ potential we obtain $m = 21.63 \pm 0.23$. Given that the maximal intermolecular distance, which is considered, corresponds to the middle of repulsive slope we get $m = 17.24 \pm 0.04$. Our analysis is consistent with Ref. [42]. Hence, even for a standard model system the variance of the IPL exponent in respect to intermolecular distances is noticeable. This situation (probably) takes place for any system in which the intermolecular potential consists of repulsive and attractive terms, which fulfill IPL with different exponents.

The consistency between m and 3γ when only short intermolecular distances are considered puts our main attention on the interactions occurring between very close molecules. As we previously mentioned, Coslovich and Roland [24] argue that that these very short intermolecular distances correspond to typical distances registered between closest particles for simple liquids studied by them. It is confirmed by the shape of the radial distribution function (RDF), which reaches half of its maximum at considered distances. This situation is natural for simple liquids for which the center of molecule mass is a source of isotropic intermolecular interactions. However, in our studies we consider (quasireal) molecules comprising many atoms. For this type of system distribution of distances between centers of molecule mass results from interactions between particular atoms. Consequently, we cannot expect that the similarity observed for simple liquids between the distance at which the RDF for centers of molecules masses possesses a maximum and a distance corresponding to the U_E minimum holds for these systems. In Fig. 6 we present $U_E(r_{CM})$ and the RDFs calculated for the centers of molecules masses as well as for atoms (at two extreme dynamic conditions). One can observe that the minimum of U_E occurs at distances notably shorter than the maximum of the RDF for the centers of molecules masses. This is clearly apparent for RLMs, for which values of the RDF at r_{CM} corresponding to the U_E minimums are much smaller than unity. Unity of the RDF denotes that the local density is equal to the average density estimated for the whole system. Hence, the U_E minimum occurs at distances corresponding to the length between nearest atoms. Indeed, as we can see in Fig. 6(b), for RLMs, characterized by the flat structure, the minimum of U_E is much closer to the first maximum of the RDF for atoms than for centers of molecules mass. It means that for this system the nearest atoms of the adjacent molecule are placed in the area of U_E minimum. In contrast to RLMs, for TLMs the U_E minimum is practically in the middle of the region, which corresponds to the atoms of neighboring molecule. It is a reasonable result since TLMs are projected to mimic the sphere and are characterized by the minimal structural anisotropy. Consequently, this system exhibits behavior more similar to simple liquids. We would like to call attention to the fact that the structure ordering, which was previously suggested by us, is also reflected in the behavior of the RDF functions. At thermodynamic conditions, which correspond to the small diffusivity, RDFs exhibit higher and narrower peaks. Additionally, at discussed conditions, RDFs for the centers of molecule masses start to separate, which indicates some organization of the molecules rather than the situation in which they can freely occupy a position within some range of mutual distances. The latter is described by the single and wide peak of the RDF, like as can be seen for the RDF calculated for the condition of high diffusivity.

At the end of this discussion of the relationship between the r_{CM} range and exponent of IPL we would like to call readers' attention to a very interesting observation. The vertical dashed line in Fig. 6 represents the r_{CM} corresponding to the distances at which the repulsive slope of U_E possesses a middle value. We recall that the approximation of this range by IPL leads to $m = 3\gamma$. As we can see, at discussed value of r_{CM} the RDF for centers of molecules masses starts to grow. This scenario is independent of the systems as well as of the thermodynamic conditions. The obtained result is extremally intriguing because U_E is a function of r_{CM}. Since the RDF for centers

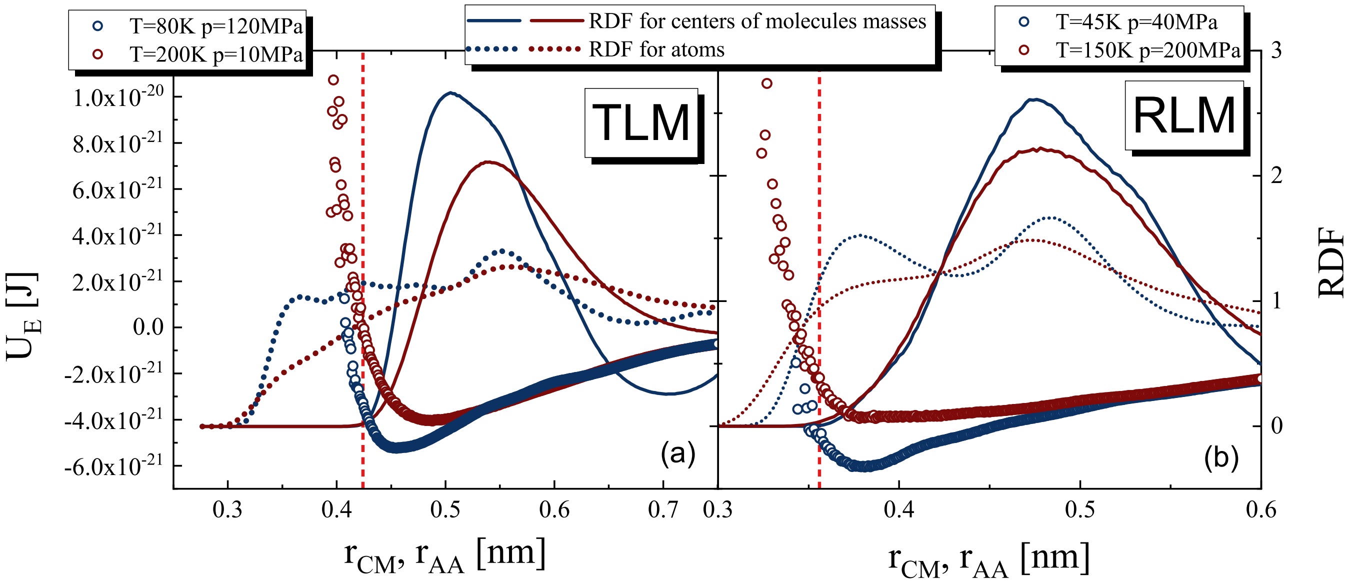

FIG. 6. The results for two boundary dynamic conditions are shown. Lines present the radial distribution functions calculated for centers of molecules' masses (solid line) and for atoms (dotted line) for TLMs and RLMs, respectively, in panels (a) and (b). r_{AA} is the distance between atoms. Open points indicate the EIIP as a function of the distance between centers of molecule mass. The red vertical lines denote the intermolecular distances at which repulsive slope of EIIP reach a middle value.

of molecules masses exhibits very low values the very small number of molecules are separated by the considered distance. As a consequence, the rare interactions between extremely close molecules determine the slope of U_E and then the value of γ. It implies that the connection between thermodynamics and dynamics of the whole system is governed by the sparse "molecular events."

V. CONCLUSIONS

In this paper, we propose a method for estimating the effective intermolecular potential for quasireal systems. The suggested approach is a natural consequence of our recent work because besides the molecular structure it considers the mutual orientations and positions of molecules within the system as well as temporary deformations of molecular shape caused by other molecules. Consequently, both intra- as well as intermolecular interactions contribute to the effective intermolecular interactions. Based on our analysis, we demonstrate that EIIP depends on the thermodynamic conditions, whereas the smallest changes are observed under isothermal conditions. The observed dependence of EIIP on the thermodynamic conditions is caused by the molecular anisotropy, which makes spatial orientation of the neighboring molecule play an essential role in the mutual interactions between molecules. Consequently, $U_E = U_E(T, V)$ puts into doubt the established relationship in the literature between the exponent of the intermolecular potential approximation by the IPL and the density-scaling exponent. However, we pointed out two crucial facts. First, the shape of EIIP is not determined solely by m, and therefore, identical values of m could be used to describe different potentials. Second, for the approximation of EIIP with the IPL, only the distances shorter than the position of the EIIP minimum are relevant. Taking the above into account as well as the fact that arithmetic average of IPL potential also fulfills IPL, Eq. (4), we calculate the average for all thermodynamic conditions U_E and describe it with the IPL. Obtained in that way, values of m are in very good agreement with the 3γ for studied quasireal systems. However, very short intermolecular distances must be considered. Interestingly, molecules extremally rarely approach each other at these distances. This finding implies that spare mutual positions of molecules have a significant influence on the value of the density-scaling exponent and then on the link between thermodynamics and dynamics of liquids.

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