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# Virial–potential-energy correlation and its relation to density scaling for 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, we examine the virial- and the potential-energy correlation for quasireal model systems. This correlation constitutes the framework of the theory of the isomorph in the liquid phase diagram commonly examined using simple liquids. Interestingly, our results show that for the systems characterized by structural anisotropy and flexible bonds, the instantaneous values of total virial and total potential energy are entirely uncorrelated. It is due to the presence of the intramolecular interactions because the contributions to the virial and potential energy resulting from the intermolecular interactions still exhibit strong linear dependence. Interestingly, in contrast to the results reported for simple liquids, the slope of the mentioned linear dependence is different than the values of the density scaling exponent. However, our findings show that for quasireal materials, the slope of dependence between the virial and potential energy (resulting from the intermolecular interactions) strongly depends on the interval of intermolecular distances that are taken into account. Consequently, the value of the slope of the discussed relationship, which enables satisfactory density scaling, can be obtained. Interestingly, this conclusion is supported by the results obtained for analogous systems without intermolecular attraction, for which the value the slope of the virial–potential-energy correlation is independent of considered intermolecular distances, directly corresponds to the exponent of the intermolecular repulsion, and finally leads to accurate density scaling.

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## I. INTRODUCTION

The first report on the density scaling of a real material [1,2], which had been published at the turn of the century, significantly stimulated studies on this property of supercooled liquids. The main reason for researchers' continuing fascination with phenomenon is the fact that it straightforwardly links the thermodynamics and dynamics of liquid based on the simple relationship,

$$X = \mathcal{F}(T\upsilon^{\gamma}), \tag{1}$$

where $X$ is a dynamic quantity characterizing the system (e.g., structural relaxation time, viscosity, or diffusion constant), $T$ is the temperature, $\upsilon$ denotes specific volume, and $\gamma$ is material-dependent constant. Extensive experimental works confirm that the presented form of the scaling is successfully fulfilled for more than 100 materials [3]. It must also be noted that despite remarkable universality, the form of scaling has another great virtue. The density scaling gives insight into the nature of intermolecular interactions occurring within the system because the scaling exponent, $\gamma$, is directly related to the repulsive part of intermolecular potential [4–8]. The latter implies that the density scaling is reflected in liquid properties such as reported virial- and potential-energy correlation [9,10], pressure densification [11], as well as in the physical aging of the glasses [12].

Among the aforementioned features of supercooled liquids, the virial- and potential-energy correlation deserves particular attention because it constitutes the framework of the isomorphs concept and relates it to the R-simple (Roskilde-simple) liquids [13]. Moreover, it finally led to the proposition of the redefinition of the classical term of the simple liquids [14]. R-simple systems exhibit strong correlation between fluctuations of virial and potential energy, where the $\gamma$ is a proportionality constant [10,15–18]. These liquids possess curves in their phase diagram linking isomorphic states at which several dynamic and statistic properties are identical. Consequently, the commonly examined particle distribution functions, normalized time-autocorrelation functions, as well as the transport coefficients, are invariant along the isomorphs, when they are expressed in so-called reduced units. Since the difference between scaling employing unreduced and reduced units is negligible in the supercooled regime, the density scaling rule, given by Eq. (1), is commonly fulfilled for the model as well as real liquids. Therefore, it is not surprising that a huge scientific effort has been made to examine the virial-$W$ and potential-energy $U$ correlation. The computational experiments on model systems revealed that in general $\gamma$ varies with the thermodynamic conditions [6,19]. However, given that many real liquids accurately fulfill the density scaling rule with a constant value of $\gamma$ even for a very wide temperature-pressure range [20,21], a passionate debate on the constancy of $\gamma$ is permanently ongoing in the literature [8,22–25].

Although the exact definition of R-simple liquids is introduced in Ref. [13], their initial name, i.e., "strongly correlating liquids," is used in the series of five papers devoted to the

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[*] kajetan.koperwas@us.edu.pl

pressure-energy correlations in liquids [10,15–18]. In the first paper, the authors introduced strongly correlated liquids as those exhibiting strong correlation between fluctuations of virial $\Delta W$ and potential-energy $\Delta U$. The correlation is suggested to be quantified by the Pearson coefficient $R$ of the equilibrium fluctuations

$$R = \frac{\langle \Delta W \Delta U \rangle}{\sqrt{\langle (\Delta W)^2 \rangle \langle (\Delta U)^2 \rangle}}, \tag{2}$$

where $\Delta$ denotes instantaneous value of given quantity minus its average value and $\langle \rangle$ means constant-volume canonical averages [10]. Liquids which exhibit $R \geqslant 0.9$ are recognized as strongly corelated and for them $\Delta W$ is a linear function of $\Delta U$ with the slope equal to $\gamma$. The latter can be directly calculated from [17]

$$\gamma = \frac{\langle \Delta \mathrm{W} \Delta \mathrm{U} \rangle}{\langle (\Delta U)^2 \rangle}, \tag{3}$$

which simultaneously gives the least squared of linear regression best-fit slope of $W(U)$. However, at this point, we would like to recall that the perfect correlation between virial- and potential-energy fluctuations is a case for the system with pure inverse power-law (IPL) pair potential [14], for which pair potential is proportional to $r_{ij}^{-n}$ ($r_{ij}$ is a distance between two molecules, $n$ is a potential parameter). This fact results directly from internal virial definition,

$$W = -\frac{1}{3} \sum_{i=1}^{N} \boldsymbol{r}_i \nabla_i \boldsymbol{U}, \tag{4}$$

where $r_i$ is a position of the $i$th particle and $U$ is a total potential energy [26,27]. Nevertheless, considering more realistic models, e.g., system described by the Lennard-Jones potential, a standard potential for liquids, one should take into account that the vast majority of $\Delta W$ and $\Delta U$ comes from molecules separated by the relatively short distances, i.e., distances at which Lennard-Jones potential can be accurately approximated by IPL. Hence, systems with an attractive part of intermolecular potential may also exhibit strong correlation [10]; e.g., density scaling is observed for the van der Waals liquids or ionic liquids [3,28]. A different scenario might be observed in the case of associated liquids. The presence of the hydrogen interactions essentially modifies intermolecular potential leading to the breakdown of the discussed correlation [29,30]. However, in the case of the real materials one crucial problem must be noted. The direct experimental examination of the correlation between $\Delta W$ and $\Delta U$ is not accessible, and therefore its existence can be concluded only on the basis of its consequences, e.g., validation of the density scaling [defined by Eq. (1)].

In this paper, we unify the results of computational studies made on simple-model systems with those obtained by examinations of the real materials. Based on computer simulations of quasireal molecules, which exhibit the simplicity of the common model systems but simultaneously mimic the crucial features of the real molecules, we examine in details the correlation between instantaneous $W$ and $U$. Our findings show that, in general, $\Delta W$ and $\Delta U$ are entirely uncorrelated if one considers “realistic” molecules. However, instantaneous contributions to $W$ and $U$ originating from intermolecular interactions might still exhibit strong mutual dependence. Interestingly, the value of the slope of this linear relationship is different than the density scaling exponent. Hence, the presented herein observations not only change the general understanding of $WU$ correlation, but they also question its direct relation to the density scaling.

The existence of isomorphs naturally is connected with the form of the intermolecular potential of simple liquids [26,31–33]. Nevertheless, the reasons for the existence of a strong $WU$ correlation for real materials are not evident. It is mainly because the real molecules possess anisotropic shape, which means that IPL cannot describe their (anisotropic) intermolecular potential. Taking this fact into account we would like to briefly recall that the correlation between $\Delta W$ and $\Delta U$ has been previously examined for a few model systems comprising molecules of nonspherical shape. Performed research revealed that the asymmetric and symmetric dumbbell-shaped molecules [34,35], Lewis and Wahnström model of *ortho*-terphenyl (OTP) [36,37], and freely joined chain of atoms [11,38], exhibit the strong $\Delta W$ and $\Delta U$ correlation and they obey the density scaling law [5,11,38]. However, at this point, we have to note that all of those systems possess rigid bonds, which is crucial for $WU$ correlation because bond interactions contribute to the virial as well as to the potential energy of the system. The problem is indirectly taken up in Ref. [35], where contribution to $W$ resulting from the constraint of bonds is estimated for rigid dumbbells and an entirely rigid model of OTP. The exclusion of contribution resulting from constraints decreases $\gamma$ values and increases $R$ value. Hence, it improves $\Delta W$ and $\Delta U$ correlation. Interestingly, through the last decades, the direct examination of $WU$ correlation for the system with the flexible bonds has been shown only for two model systems [39,40]. The authors pointed out that the existence of the flexible bonds destroys the correlation between $\Delta W$ and $\Delta U$ for the 10-bead chain of Lennard-Jones (LJ) particles and the asymmetric dumbbell molecules. However, both systems obey the density scaling law, and therefore the existence of the pseudoisomorphs in liquids with the intramolecular degrees of freedom has been suggested [40]. Then, the dynamics of liquid with lack of the $WU$ correlation remains unchanged along pseudoisomorph, which can be determined from a single equilibration configuration. The thermodynamic states characterized by the same dynamics are characterized by the identical low-frequency vibrational spectra of the inherent structure expressed in the reduced units. However, finding thermodynamic states of interest using the suggested method is complex, and requires determination of the inherent structure spectra for many states, which are subsequently compared to the reference one. Moreover, the form of the connection between intermolecular potential, $WU$ correlation, and density scaling exponent remains unclear.

## II. RESULTS

Taking the above into account, we use our recently proposed model of rhombuslike molecules (RMs) [7,8,41] and we study the $WU$ correlation in order to propose an alternative approach to the relation between $W$, $U$, $\gamma$, and the intermolecular potential. At this point, it is worth mentioning that the difference between a typical model system and the quasireal system used here is that the parameters of the intra- and intermolecular potentials of quasireal molecules are defined on the basis of the real atoms. Consequently, the relation between intra- and intermolecular forces has a practical justification. The difference between the real and quasireal molecules is the kind of atoms used and the modeled structure of the molecule. For example, RM is constructed of four identical atoms arranged in the rhombus shape, which is characterized by the ratio between diagonals equal to two. This scenario cannot be realized in reality. However, since the created molecule possesses only one type of atom, which implies only one type of interatomic interaction, it is much more convenient for examination than the real molecule of a similar structure; see Supplemental Material [42] for the scheme of the RM. The interactions between nonbonded and bonded atoms are set using the parameters of the OPLSAA force field defined for carbon atoms in aromatic ring [43]. Based on our previous results [7,8], we chose three isochoric conditions, i.e., conditions at which molecular volume $\upsilon_m = V/N$ ($N$ is a number of molecules, $V$ is the volume of the system) equals 0.075, 0.085, and 0.095 $\text{nm}^3$. Subsequently, we simulated RM at conditions of constant temperature and volume using Nosé-Hoover thermostat implemented in GROMACS software [44–49]. Data are collected from the half of a total simulation time, which is 10 ns (time step equals 0.001 ps). The applied cutoff for intermolecular interactions is set to distance $r_c = 1.065$ nm, which is 3 times longer than the $\sigma$ parameter of LJ potential describing nonbonded interactions. The chosen temperatures vary from 50 to 200 K, which results in a pressure range of 1.2 GPa (see Supplemental Material [42] for the temperature dependence of the pressure).

In order to confirm the density scaling for RM, the diffusion constants, $D$ (determined from mean-square displacement), and relaxation times, $\tau$ (estimated on the base of incoherent intermediate scattering function of molecules' centers of mass) expressed in the reduced units, which are denoted by * and defined as $D^* = (\upsilon_m^{-1/3}\sqrt{m/k_BT})D$ and $\tau^* = \tau/(\sqrt{m/k_BT}\,\upsilon_m^{1/3})$ (where $m$ is the molecule mass and $k_B$ is the Boltzmann constant) are plotted as a function of $T\upsilon_m^\gamma$ in Fig. 1. As one can see, being consistent with the isomorph theory [17], $D^*$ and $\tau^*$ accurately scale with the same $\gamma = 6.173$. The value of the density scaling exponent has been estimated using the linear dependence of $\log_{10}(T)$ on $\log_{10}(\upsilon_m)$ resulting from Eq. (1) at a constant value of $D^*$; see Refs. [7,8] for details. The error of $\gamma$ value is equal to 0.163.

Since the RM satisfies the density scaling and the value of the density scaling exponent is known, we can examine the correlation between instantaneous $W$ and $U$. However, the total potential energy $U_{\text{total}}$ of RM consists of the term related to the interaction between nonbonded and bonded atoms. Hence, the potentials of intermolecular, bond, bond-angle, and dihedral-angle interactions must be taken into account. At this point, we have to stress that the contribution of purely angle-dependent terms to the virial is zero [50]. Hence, $U_{\text{total}} = U_{\text{LJ}} + U_{\text{bond}} + U_{\text{angle}} + U_{\text{dihedral}}$, whereas $W_{\text{total}} = W_{\text{LJ}} + W_{\text{bond}}$.

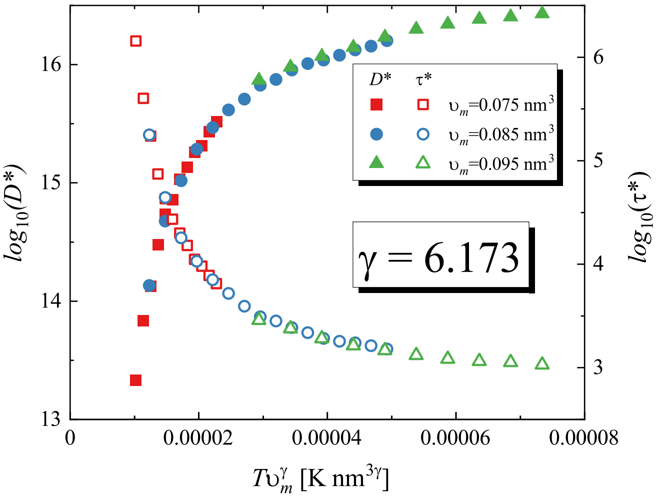

FIG. 1. The density scaling for RM with constant value of $\gamma$ determined as a slope of linear dependence of $\log_{10}(T)$ on $\log_{10}(\upsilon_m)$ at constant value of $D^*$.

The $WU$ correlation is examined on the example of the following thermodynamic conditions, $T = 200$ K and $\upsilon_m = 0.0075\,\text{nm}^3$. In the panel Fig. 2(a) one can clearly see that there is not any correlation between instantaneous $U_{\text{total}}$ and $W_{\text{total}}$. On the other hand, instantaneous values of $W_{\text{LJ}}$ and $U_{\text{LJ}}$ resulting from nonbonded interactions are almost perfectly correlated, $R = 0.993$; see Fig. 2(b). Hence, we can suspect that $W_{\text{LJ}}U_{\text{LJ}}$ correlation is broken by the contributions originating from intramolecular interactions, similarly to results presented in Refs. [39,40]. It is because the intramolecular interactions are described by harmonic potentials, which cannot be approximated by an IPL. It has to be noted that the harmonic form of intramolecular potentials is not only a matter of choice but it has a theoretical basis. Consequently,

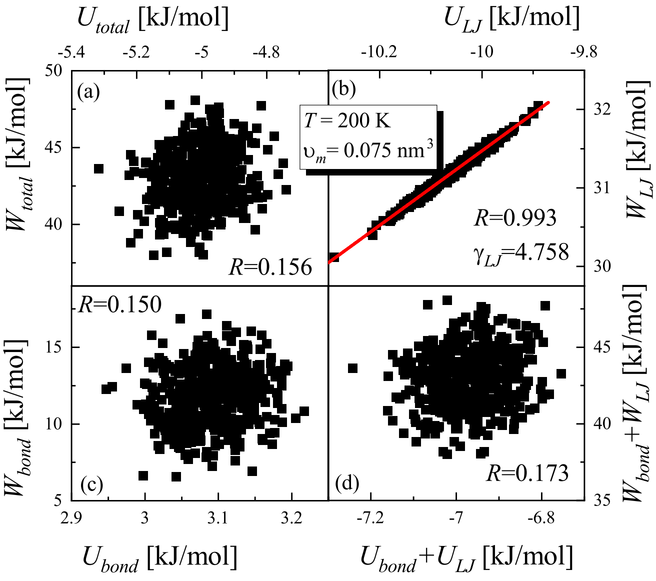

FIG. 2. The dependence of the instantaneous values of total virial on total potential energy is presented in (a). The contributions to $W_{\text{total}}$ and $U_{\text{total}}$ resulted from intermolecular interactions and from bond interactions are shown in (b) and (c), respectively. The red line in (b) represents the fit linear function. In (d) the sums of contributions shown in (b) and (c) are depicted.

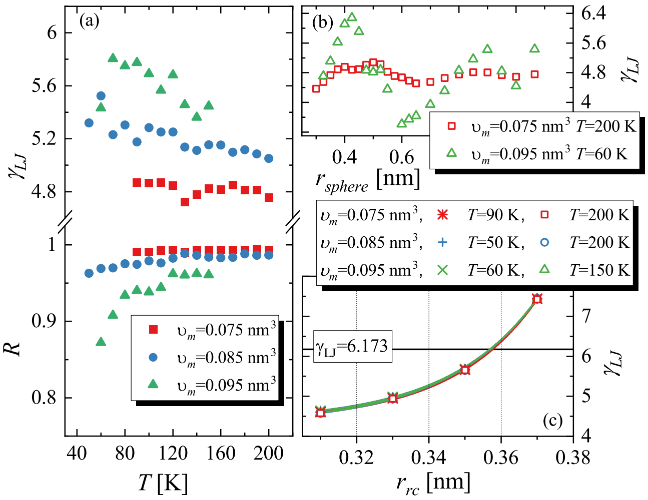

FIG. 3. The values of $\gamma_{\rm LJ}$ (top) and corresponding to them $R$ (bottom) calculated at various thermodynamic conditions are shown in (a). In (b) the dependence of $\gamma_{\rm LJ}$ on the radius of the sphere embracing interacted atoms are presented. In (c) the values of the $\gamma_{\rm LJ}$ obtained for the interatomic distance located within the interval of width equals 0.02 nm is plotted as a function of the positions of the interval centers. The vertical dotted lines represent the borders between subsequent intervals. Solid lines are fits to the exponential function of the obtained results.

no correlation can be expected between instantaneous contributions to $W$ and $U$ from intramolecular interactions; see Fig. 2(c), where results for bond interactions are presented. Moreover, it can be seen in Fig. 2(d) that the addition of even one intramolecular interaction to $W$ and $U$ completely destroys the correlation between them. Summarizing, from Fig. 2 it is evident that $W_{\rm total}U_{\rm total}$ correlation cannot hold for real liquid. Hence, only intermolecular interaction would be responsible for the density scaling, if its relation with $WU$ correlation is valid for the real materials.

## III. DISCUSSION

In Fig. 3(a) we present $R$ and $\gamma_{\rm LJ}$ values estimated on the base of $W_{\rm LJ}U_{\rm LJ}$ correlation for all studied thermodynamic conditions. It is worth noting that only at $T = 60$ K and $\upsilon_m = 0.0095\,{\rm nm}^3$ is $R$ less than 0.9 and hence it does not satisfy the proposed definition of R-simple liquids. Nevertheless, as we present in Fig. 1, $\tau^*$ and $D^*$ determined at mentioned thermodynamic conditions can be accurately scaled together with all remaining data. However, the most puzzling observation which can be drawn from Fig. 3(a) is that although $V_{\rm LJ}$ and $U_{\rm LJ}$ are almost perfectly correlated, none of $\gamma_{\rm LJ}$ values calculated from Eq. (3) exceeds 6.0. It implies that the average $\gamma_{\rm LJ}$ cannot be equal (or even close) to the expected 6.173. Consequently, density scaling using values shown in Fig. 3(a) is not valid; see Supplemental Material [42] for the density scalings with a state-dependent $\gamma_{\rm LJ}$, the average for each isochrone, and the average over all studied thermodynamic conditions. The key finding is that none of those scalings can be recognized as valid. Hence, one can suspect that despite the correlation between $V_{\rm LJ}$ and $U_{\rm LJ}$ occurring for the quasireal liquids it is not directly responsible for its density scaling. On the other hand, all the progress which has been achieved due to the studies on the simple liquids leading to constitution that $W = \gamma U + {\rm const.}$ cannot be simply ignored. Therefore, we would like to again point out the cardinal difference between typical simple liquids and the real materials, which is the shape and then the interaction anisotropy. Since simple liquids comprise monatomic molecules their intermolecular potential is entirely spherically symmetrical. Then, it does not vary when relative orientation of molecules changes. This means that it can be approximated by an inverse power law with constant parameters independent of the relative orientation of molecules and distance between them. As a consequence, atoms occupy positions determined solely by the atom-atom intermolecular potential. This situation does not take place for real molecular systems and for the quasireals system considered herein. In these cases, interactions between molecules result from the many atom-atom interactions. It means that the intermolecular potential depends on mutual orientations of molecules. The latter implies that at given distances some mutual orientations of the molecules are more probable. Taking the above into account, we test the dependence of $\gamma_{\rm LJ}$ values on the interatomic distance. For this purpose, we determine $\gamma_{\rm LJ}$ considering only interactions occurring within the sphere of radius $r_{\rm sphere}$ starting from a given atom. Importantly, the described analysis implies that the number of atoms giving rise to the $V_{\rm LJ}U_{\rm LJ}$ correlation is not identical for each $r_{\rm sphere}$. Therefore, we divided the obtained $V_{\rm LJ}$ and $U_{\rm LJ}$ by a number of considered interactions. The results are presented in Fig. 3(b), where notable oscillations of $\gamma_{\rm LJ}$ during increasing of $r_{\rm sphere}$ can be observed. However, it is worth noting that for $v_m = 0.075\,{\rm nm}^3$ (red points) even the highest value of $\gamma_{\rm LJ}$ is considerably smaller than 6.173. Nevertheless, for all presented isochrones $\gamma_{\rm LJ}$ initially increases up to its maximal value (a small minimum can be observed but it does not occur for all studied thermodynamic conditions), which suggests that omitting the shortest interatomic distances would lead to higher values of $\gamma_{\rm LJ}$. Consequently, we decided to consider subsequent intervals of distances characterized by width 0.02 nm. Then $\gamma_{\rm LJ}$ can be expressed as a function of the position of the interval center, $r_{rc}$; see Fig. 3(c). Consistently, with the results shown in Fig. 3(b), at short intermolecular distances the increase in interatomic distance causes a gain in $\gamma_{\rm LJ}$ values. It is worth mentioning that for consecutive intervals the obtained values are even a few times higher than 6.173 (results not presented).

At this point, we would like to draw readers' attention to the following important issue. The invariance of the estimated dependences for all considered thermodynamic conditions [Fig. 3(c)] is a consequence of the interval width, which is relatively narrow in this case. For wider intervals, the evident $\gamma_{\rm LJ}$ dependence on the thermodynamic conditions is observed; see Fig. 3(b) where the interval from 0 to $r_{\rm sphere}$ is considered. The latter is a consequence of the fact that the local density is not constant within the system. Hence, we have to stress that the proposed herein width of the intervals is not binding. Even more, we might suspect that the interval width should not be identical for all types of molecules, but more probably, it would seem to be an inherent feature of the molecular structure (further works are required).

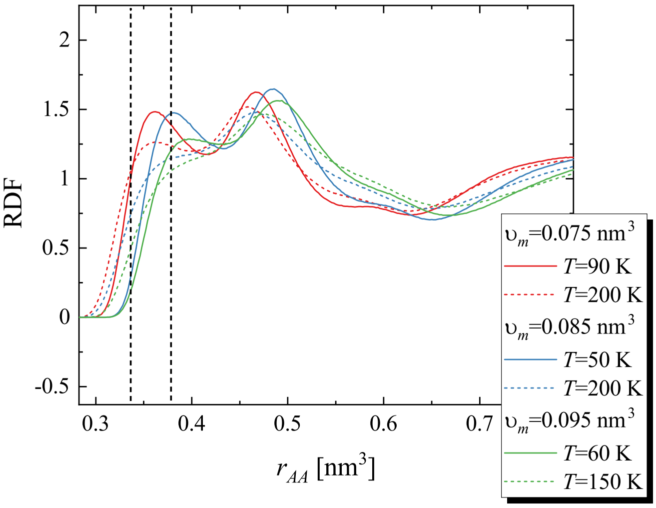

FIG. 4. The radial distribution functions for atoms calculated for the thermodynamic conditions analyzed in Fig. 3(c). The vertical dotted lines correspond to the intermolecular distance interval within which analysis of $W_{\mathrm{LJ}}U_{\mathrm{LJ}}$ correlation results in the $\gamma_{rc}$ value close to 6.173.

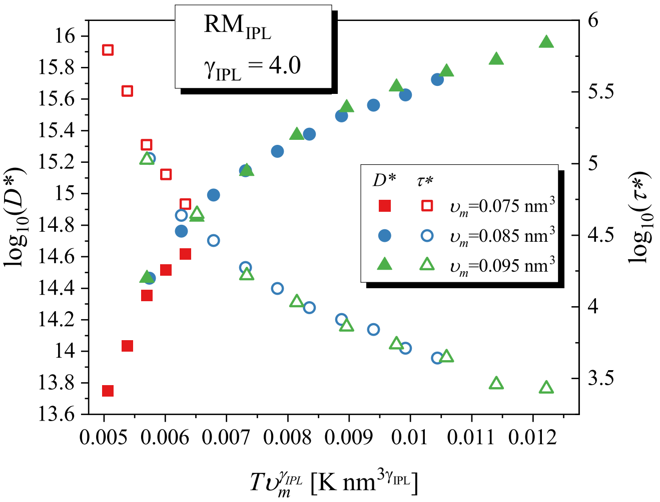

FIG. 5. The density scaling for RM$_{\mathrm{IPL}}$ with a constant value of $\gamma_{\mathrm{IPL}} = 4$.

Nevertheless, the sought after value of $\gamma_{\mathrm{LJ}}$ ($= 6.173$) could be obtained if one considered a specific interval of intermolecular distances. For example, based on the result presented in Fig. 3(c), the centers of the intervals corresponding to $\gamma_{\mathrm{LJ}} = 6.173$ can be estimated describing $\gamma_{\mathrm{LJ}}(r_{rc})$ by the following function: $\gamma_{\mathrm{LJ}} = A\exp(r_{rc}/B) + C$, where $A, B, C$ are the fit parameters. The solid lines in Fig. 3(c) represent results. It is worth noting that the predicted centers of the sought after interval are obtained at practically the same $r_{rc}$. The estimated values of $r_{rc}$ vary from 0.3572 nm ($T = 50$ K and $\upsilon_m = 0.0085\,\mathrm{nm}^3$) to 0.3578 nm ($T = 200$ K and $\upsilon_m = 0.0075\,\mathrm{nm}^3$) and correspond to the interatomic distances shorter than or comparable to the position of the first peak of radial distribution function for atoms; see Fig. 4. Thus, the interactions between the very closest atoms seem to be responsible for the density scaling. Subsequently, the value of $\gamma_{rc}$ can be estimated taking into account interatomic distances within intervals characterized by 0.02 nm of width, the centers of which are placed in the predicted $r_{rc}$. Considering the $W_{\mathrm{LJ}}U_{\mathrm{LJ}}$ correlation within above distances, the smallest $\gamma_{rc} = 6.119 \pm 0.009$ is established for $T = 50$ K and $\upsilon_m = 0.0085\,\mathrm{nm}^3$, whereas the highest one is registered for $T = 90$ K and $\upsilon_m = 0.0075\,\mathrm{nm}^3$ and equals $6.160 \pm 0.009$. Naturally, all obtained values are very close to each other and are close to 6.173. Consequently, it is not surprising that all of them lead to the satisfactory density scaling of $\tau^*$ and $D^*$ (results not presented). Additionally, it is worth mentioning that $R > 0.999$ for all thermodynamic conditions considered in Fig. 3(c). Thus, within the examined intervals, instantaneous $W_{\mathrm{LJ}}$ and $U_{\mathrm{LJ}}$ are perfectly correlated.

Concluding, the analysis of the $W_{\mathrm{LJ}}U_{\mathrm{LJ}}$ correlation could still be a useful method to establish the density scaling exponent value. However, one has to remember that a specific interval of interatomic distances must be considered. Then, instead of performing complex studies, which lead to the determination of some effective intermolecular potential and subsequent approximate its part by the IPL (which is analogous to the method valid for simple liquid), one can directly consider the dependence of instantaneous values of $W_{\mathrm{LJ}}$ on $U_{\mathrm{LJ}}$ at only one thermodynamic condition. However, the above statement could be accepted only if a crucial test is passed. Namely, it must be noted that $W_{\mathrm{IPL}}$ is always a linear function of $U_{\mathrm{IPL}}$ with an identical value of the slope independently of the selected interval of intermolecular distances for the system with a single IPL intermolecular potential. As a consequence, for IPL systems, the choice of the intermolecular distances interval is not necessary, and those systems should obey the density scaling law with $\gamma_{\mathrm{IPL}} = n/3$, where $n$ is the exponent of IPL potential. To verify this scenario, we test RM with the intermolecular potential of single IPL form, i.e., RM$_{\mathrm{IPL}}$. The new system is obtained by omitting the attractive part of the LJ potential. All other characteristics of the molecule remain unchanged. Hence, taking into account that $n$ for RM$_{\mathrm{IPL}}$ is equal to 12, the studied system should scale with $\gamma_{\mathrm{IPL}} = 4$. The results are presented in Fig. 5. One can clearly see that $\gamma_{\mathrm{IPL}} = 4$ leads to the density scaling, with satisfactory accuracy within a range of pressure from 670 to 2733 MPa. Additionally, we estimate the value of $\gamma$ in the way corresponding to that applied for RM, i.e., we have analyzed the linear dependence of $\log_{10}(T)$ on $\log_{10}(\upsilon_m)$, which results from Eq. (1) The obtained value of the density scaling exponent is $\gamma = 4.044 \pm 0.071$. At this point, it is worth mentioning the work by Berthier and Tarjus [51], where the important role of the attractive forces in the quality of the density scaling is noted. Consequently, the tiny inaccuracies in the density scaling, which could be seen in Fig. 5, would be a result of the entire neglection of the intermolecular attraction.

However, at this point we have to draw the reader's attention to important consequence of $\gamma$ estimation on the basis of $W_{\mathrm{IPL}}U_{\mathrm{IPL}}$ correlation. Since the described above analysis does not consider structure of the molecules [the slope of $W_{\mathrm{IPL}}(U_{\mathrm{IPL}})$ is always the same if the identical form of single IPL is used], all quasireal molecules constructed from the same atoms should be scaled with the same $\gamma_{\mathrm{IPL}}$, independently of their structures. The latter conclusion seems to be abnormal; however, when molecules can freely rotate it would

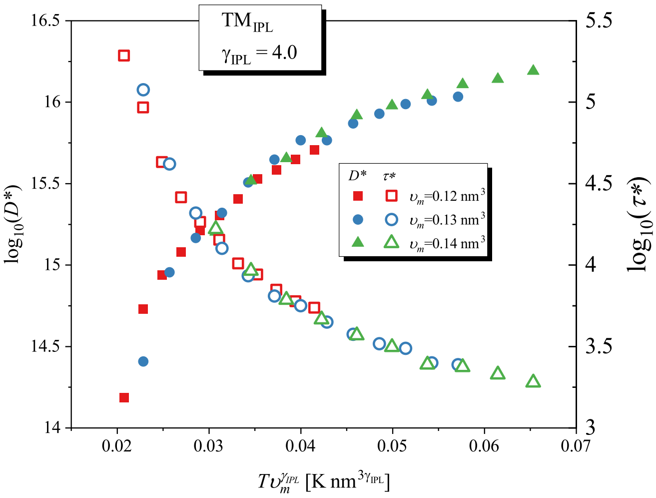

FIG. 6. The density scaling for $\mathrm{TM}_{\mathrm{IPL}}$ with a constant value of $\gamma_{\mathrm{IPL}} = 4$.

be justified. Therefore, we would like to mention that the discussed situation could not take place for big and complex molecules as well as in case of thermodynamic conditions close to the glass transition. Nevertheless, for simple and small molecules, we have to expect the accurate density scaling with the same $\gamma_{\mathrm{IPL}}$. To verify obtained conclusion, we use another quasireal system, i.e., tetrahedronlike molecules system with the intermolecular potential of the IPL form ($\mathrm{TM}_{\mathrm{IPL}}$). The tetrahedronlike molecules comprise five identical atoms, the same as for $\mathrm{RM}_{\mathrm{IPL}}$. The lengths of bonds and angles between them are identical. Similarly to RM they are defined by the parameters of OPLSAA force field defined for carbon atoms of aromatic ring [8]. We examined three isochoric conditions and the temperature from 80 to 200 K for $\mathrm{TM}_{\mathrm{IPL}}$, which result in the pressure range from 311 to 881 MPa. Interestingly, in Fig. 6, we show that indeed $\mathrm{TM}_{\mathrm{IPL}}$ can be accurately scaled with the $\gamma_{\mathrm{IPL}} = 4$. The independent analysis of the dependence of $\log_{10}(T)$ on $\log_{10}(\upsilon_m)$ leads to $\gamma = 3.959 \pm 0.095$. Thus, the results of the analysis described in the previous paragraph do not disprove our outcomes obtained for RM. The examination of the correlation between $W$ and $U$ resulting only from intermolecular interactions at a specific interval of the intermolecular distances enables us to estimate the density scaling exponent. However, the formulation of the exact prescription for the position of the interval center as well as its width requires further intensive investigations.

## IV. CONCLUSIONS

Summarizing, based on the results for RM, we have shown that for quasireal model systems, the $WU$ correlation is not observed. Consequently, a similar situation should be expected for the real liquids instead of that which is commonly suggested in the literature. However, contributions to the virial and potential energy resulting from intermolecular interactions ($W_{\mathrm{LJ}}$ and $U_{\mathrm{LJ}}$) still exhibit the strong mutual dependence. Through the wide range of examined thermodynamic conditions, the correlation coefficient only once falls below the requested value of 0.9. Unfortunately, in contrast to previously studied simple model systems, the evident linear $W_{\mathrm{LJ}}U_{\mathrm{LJ}}$ correlation does not correspond to the slope, which leads to satisfactory density scaling. The reason for mentioned difference would be the structural anisotropy of the quasireal molecules, which makes the effective intermolecular potential exhibit complex behavior. As a consequence, the effective intermolecular potential cannot be described by single IPL over a wide range of intermolecular distances. Consistent with this hypothesis, we found significant variations of $\gamma_{\mathrm{LJ}}$ when different intervals of intermolecular distances are considered. Then, the $\gamma_{\mathrm{LJ}} = 6.173$, which enables accurate density scaling, would be achieved at specific interval of intermolecular distances. This interval of intermolecular distances, i.e., its position and width, would be an inherent part of the molecular structure. However, for the examined model systems in which the IPL describes intermolecular potential, the density scaling is accurately realized with the identical value of the scaling exponent independently of the structure. This fact indicates the crucial role of the intermolecular attraction in the density scaling. Hence, our results suggest that the molecular structure would become crucial for the value of the density scaling exponent, and consequently, for the $W_{\mathrm{LJ}}U_{\mathrm{LJ}}$ correlation, but only in the presence of the intermolecular attraction. Then, the $W_{\mathrm{LJ}}U_{\mathrm{LJ}}$ correlation analysis could be a useful method for determining the density scaling exponent for real materials; however, the knowledge about the relevant intermolecular distances is required.

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