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EXCLUDED VOLUME INTERACTION
IN A LENNARD-JONES FLUID

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ЛЬВІВ

Взаємодія виключеного об'єму в флюїді Леннард-Джонса

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Анотація. Обговорено розщеплення леннард-джонсівського потенціалу парної взаємодії на дві окремі взаємодії, а саме: взаємодію виключеного об'єму і когезійну взаємодію. Запропонований вибір взаємодії виключеного об'єму в флюїді Леннард-Джонса обґрунтовано за допомогою результатів, отриманих комп'ютерним моделюванням співіснування пари й рідини в системі з виключеним об'ємом, а також результатів для ван-дер-ваальсового параметру когезійної взаємодії.

Excluded volume interaction in a Lennard-Jones fluid

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Abstract. Split of the Lennard-Jones pair interaction potential into two distinct interactions, namely, excluded volume interaction and cohesion interaction, is discussed. The proposed choice of excluded volume interaction in Lennard-Jones fluid is justified by the results obtained from computer simulation studies of the vapor-liquid coexistence in excluded volume system as well as by the results for van der Waals cohesion interaction parameter.

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1. Introduction

Excluded volume in its modern understanding was introduced more than one century ago by van der Waals in his doctoral thesis [1] and concerns the hard-core molecules. More precisely, van der Waals pointed out that around each hard-sphere molecule there is a virtual spherical shell, of the thickness of molecule hard-core radii, that is unaccessible for the centers of all other molecules in the system. Despite the fact that original definition of excluded volume is valid only for low density gas, the van der Waals (vdW) theory captures many of the qualitative features of the gas-liquid phase transition.

It also was van der Waals who has realized that upon increasing number of molecules, the amount by which accessible volume of the system must be reduced, is variable depending on the density of system [2]. Indeed, when due to density increase the average distance between species in the system becomes less than two hard-core diameters, the virtual exclusion shells of the neighboring molecules are overlapping and excluded volume is not anymore the sum over molecules of the system. However, the law governing change of the excluded volume with density was not obvious and left unknown to van der Waals. The problem was answered by solving the Percus-Yevick approximation for hard-sphere system [3]. Nevertheless, even rather accurate description of the excluded volume within the hard-sphere model (by using accurate Carnahan-Starling expression [4], for example) does not help to improve the prediction of vdW theory against computer simulations [5,6].

Recently [7,8] it has been shown that vapour-liquid equilibrium as well as more generally the thermodynamics of the Lennard-Jones-like hard-core attractive Yukawa fluid in a wide range of density and temperature parameters can be rather accurately described within the van der Waals theory supposing that interparticle interaction instead of being divided into repulsion and attraction contribution is properly divided into excluded volume and cohesion interaction.

The goal of this paper is to discus the definition of excluded volume in the case of Lennard-Jones fluid in the way how it was done for the Lennard-Jones-like hard-core attractive Yukawa fluid model. To proceed, in Section 2 we describe the definition of the short-range excluded volume interaction in the hard-core interactiong model. Then in Section 3 we define the short-range excluded volume interaction potential for Lennard-Jones model. The results and comparison with computer simulation data for the vapor-liquid phase diagram of the system with short-range excluded volume interaction and Lennard-Jones interaction

are presented in Section 4. Finally, in Section 5 our conclusions are summarized.

2. Definition of excluded volume interaction for hard-core fluids

"Excluded volume interaction" is a term that usually is referred to the hard-core fluid models. It originates from the fact that composing hard-core particles are experiencing an emergent effective attraction induced by an overlap of their excluded volume shells upon increasing the density. One of the manifestation of such an interaction, e.g., in the hard sphere system, is significantly larger value of the first maximum of the radial distribution function, the so-called contact value. Since overlap of excluded volume shells is associated with an increase of entropy, excluded volume interaction very often is referred to as entropic interaction.

Excluded volume itself is a pairwise-additive quantity that is uniquely defined only for the fluid system of hard-sphere molecules upon the distance between pair of the nearest-neighboring molecules (part a in Fig. 1). Initially, van der Waals has assumed that excluded volume per molecule does not depend on the distance between molecules, i.e., is a constant and equals fourfold the volume of molecule, i.e., $v_0 = b \equiv (2/3)\pi\sigma^3$, where σ is a hard-core diameter. This corresponds to the case of a dilute gaseous phase (see part b in Fig. 1) when the distance between centers of the pair of neighboring molecules is larger than 2σ. However, in the dense gaseous phase and, especially, in the liquid phase the distance between neighboring molecules decreases and becomes shorter than 2σ. Consequently, then excluded volume shells overlap, indicating that amount of excluded volume per molecule is a function of the distance between pair of particles. While for a fluid system composed of pure
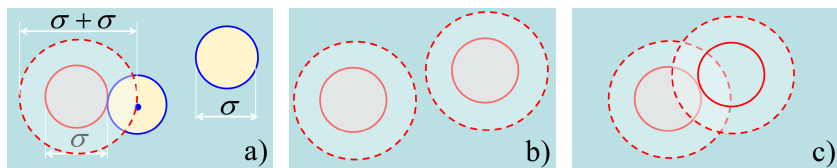

Figure 1. Definition of the excluded volume in a fluid composed of hard-core molecules with diameter σ (part a) and its qualitative dependence on the distance between pair of neighbouring molecules in a gaseous phase (part b) and in a liquid phase (part c).

hard spheres the distance between particles depends exclusively on the density, in the case of fluid composed of interacting hard spheres,

$$u(r) = u_{\text{hs}}(r) + u_{\text{attr}}(r), \quad (2.1)$$

i.e., the hard-sphere system with an extra attractive interaction $u_{\text{attr}}(r)$, the distance between particles depends on the temperature as well by means of the forces due to extra attraction. However, not all extra forces between hard-core particles are affecting the excluded volume in the system. Such exemption is only for those forces that are acting on the distances associated with the overlap of excluded volume shells, i.e., on the distances shorter than 2σ. In what follows such forces, and corresponding interaction, are referred to as short-range.

By following above arguments, the pair interactions $u(r)$ in the case of fluid system composed of interacting hard spheres can be seen to consist of three terms,

$$u(r) = u^{\text{hs}}(r) + u_{\text{attr}}^{\text{sr}}(r) + u_{\text{attr}}^{\text{lr}}(r). \quad (2.2)$$

Since hard-sphere repulsion is of short-range too, then it seems quite naturally to split the pair interaction energy $u(r)$ into two parts, namely, the short-range part $u_{\text{tot}}^{\text{sr}}(r)$ and long-range part $u_{\text{attr}}^{\text{lr}}(r)$ in the form [7, 8],

$$u(r) = u_{\text{tot}}^{\text{sr}}(r) + u_{\text{attr}}^{\text{lr}}(r) = u_{\text{excl}}(r) + u_{\text{coh}}(r), \quad (2.3)$$

The subscript "tot" in the short-range part of interaction energy in Eq. (2.3) stands for the total (repulsive plus attractive) short-range interaction energy of a target molecule and its nearest neighboring counterpart. In what follows this interaction will be referred to as excluded volume interaction $u_{\text{excl}}(r)$, while long-range attraction energy of a target molecule and any molecule outside of the first coordination shell will be referred to as cohesion interaction $u_{\text{coh}}(r)$.

The nearest neighboring molecules as well as corresponding short-range excluded volume interaction energy $u_{\text{tot}}^{\text{sr}}(r) \equiv u_{\text{excl}}(r)$ both are defined by means of the distance (range) criterion. According to this criterion, the excluded volume interaction energy, incorporates the full repulsion energy $u_{\text{rep}}(r)$ and the short-range part $u_{\text{attr}}^{\text{sr}}(r)$ of the full attraction energy, and can be presented in the form,

$$u_{\text{excl}}(r) \equiv u^{\text{hs}}(r) + u_{\text{attr}}^{\text{sr}}(r) = \begin{cases} u(r), & r \leq \sigma \\ u_{\text{attr}}^{\text{sr}}(r), & r > \sigma \end{cases}. \quad (2.4)$$

with hard-core diameter σ being the location of a potential well in the total pair interaction potential $u(r)$.

How to model the short-range attraction $u_{\text{attr}}^{\text{sr}}(r)$? In the case of fluid system composed of interacting hard spheres, the short-range attraction has been modeled by Yukava function,

$$u_{\text{attr}}^{\text{sr}}(r) = -\epsilon \frac{\sigma}{r} \exp\left[-\kappa(r - \sigma)\right], \tag{2.5}$$

where κ determines the decay of attraction.

Then, the long-range cohesion attraction $u_{\text{attr}}^{\text{lr}}(r) \equiv u_{\text{coh}}(r)$ in Eqs. (2.2) and (2.3) is determined as the difference, $u(r) - u_{\text{tot}}^{\text{sr}}(r)$, in the form

$$u_{\text{coh}}(r) = \begin{cases} 0, & r \leq \sigma \\ \\ u(r) - u_{\text{attr}}^{\text{sr}}(r), & r > \sigma. \end{cases} \tag{2.6}$$

Since by definition $u_{\text{coh}}(r)$ does not include short-range interaction and equals zero at the potential well, it excludes the interaction with its neighbors and stands for the interaction energy of target molecule with molecules from outside of the first coordination shell only.

Concluding this Section, we can summarize as follows: (i) excluded volume interaction is the short-range part of the total pair interaction energy and incorporates full repulsion and only short-range part of the full attraction energy; (ii) short-range attraction $u_{\text{attr}}^{\text{sr}}(r)$ represents the attraction energy between a target molecule with each of the molecules that are on the distance within the first coordination shell; (iii) following a definition (2.4), the short-range attraction $u_{\text{attr}}^{\text{sr}}(r)$ incorporates the full interaction energy $u(r)$ at the distances of potential minimum, $r = r_{\text{m}} \equiv \sigma$, between two molecules, but decays faster than the full attraction energy $u_{\text{attr}}(r)$ for the distances $r > r_{\text{m}} \equiv \sigma$, aiming does not exceed the radii of the first coordination shell; (iv) short-range attraction $u_{\text{attr}}^{\text{sr}}(r)$ can be modeled by Yukawa function (2.5); (v) range of the short-range attraction $u_{\text{attr}}^{\text{sr}}(r)$ is around of one hard-core diameter σ and is controlled by parameter κ.

3. Excluded volume interaction in Lennard-Jones fluid

Let us now consider the fluid system composed of molecules interacting through Lennard-Jones (LJ) potential

$$u(r) = 4\epsilon \left[\left(\frac{\sigma_{\text{LJ}}}{r} \right)^{12} - \left(\frac{\sigma_{\text{LJ}}}{r} \right)^{6} \right], \tag{3.1}$$

where ϵ is the depth of potential well and σ_{LJ} is the Lennard-Jones diameter of the molecules.

The main difference of the LJ fluid from the case considered in Section 2 concerns the absence in LJ potential of the hard-core repulsion. Therefore, one could think that there does not make sense to discuss the excluded volume interaction at all. The van der Waals theory, and even more sophisticated WCA theory, are not strong enough arguments since neither of them is applicable in the whole range of the system parameters such as density and temperature. However, results for the LJ-like attractive Yukawa model as well as for Sutherland model are convincing.

Following the definition (2.4), excluded volume interaction in any fluid system, including LJ fluid, consists of full repulsion energy and short-range attraction energy, that is described by Yukawa potential function (2.5). Since repulsion in the LJ fluid is soft, to keep the excluded volume potential function continuous, the modeling of short-range attraction $u_{\text{attr}}^{\text{sr}}(r)$ involves two Yukawa terms in the form,

$$u_{\text{attr}}^{\text{sr}}(r) =$$

$$\epsilon \frac{r_{\text{m}}}{r} \left[e^{-\alpha(r - r_{\text{m}})} - 2e^{-\beta(r - r_{\text{m}})} \right], \quad r > r_{\text{m}}. \tag{3.2}$$

The decay parameters α and β are determined from two conditions: (1) the distance derivative of the function $u_{\text{attr}}^{\text{sr}}(r)$ should equals zero at $r = r_{\text{m}}$ and (2) short-range attraction $u_{\text{attr}}^{\text{sr}}(r)$ should decays in such way that at distance $r = r_{\text{c}}$, associated with the radii of the first coordination shell, its energy will be equal $\delta k_{\text{B}} T$, where δ is a small enough quantity. Proceeding in this way we obtained $\alpha \sigma_{\text{LJ}} = 24.17$ and $\beta \sigma_{\text{LJ}} = 11.63$.

Figure 2 shows the total LJ interaction energy $u(r)$, the excluded volume interaction energy $u_{\text{tot}}^{\text{sr}}(r)$, and the long-range attractive interaction energy $u_{\text{attr}}^{\text{lr}}(r)$, all according to their definitions by Eq. (3.1), Eqs. (2.4) and (3.2), and Eq. (2.6), respectively.

It worth to mention that outlined in Section 2 scheme, being applied to LJ potential in fact represents the separation of pair interaction energy $u(r)$ into two parts (2.3) that is in contrast to the common practice [6, 13,14]. The latter suggests that pair interaction energy $u(r)$ be split off into repulsion and attraction energy contributions,

$$u(r) = u_{\text{rep}}(r) + u_{\text{attr}}(r). \tag{3.3}$$

To illustrate distinction, Fig. 2 shows the similar results according to the
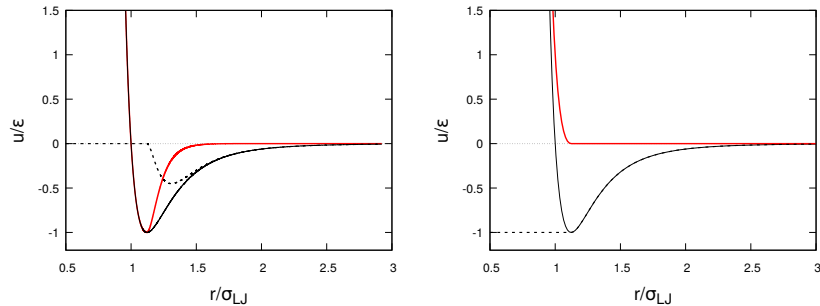
Figure 2. Lennard-Jones potential $u(r)$ (the thin solid line) and two choices of its decomposition. Top: The one suggested in the present study – into the short-range excluded volume interaction $u_{\text{tot}}^{\text{sr}}(r)$ (the thick solid line) and the long-range attraction $u_{\text{attr}}^{\text{lr}}(r)$ (the thin dashed line). Bottom: The one suggested within the WCA approach – into the repulsive interaction (the thick solid line) and the attractive interaction (the thin dashed line).

WCA approach [14] with repulsion energy,

$$
u_{\text{rep}}(r) = \begin{cases} u(r) + \epsilon, & r \leq r_{\text{m}} \\ \\ 0, & r > r_{\text{m}} \end{cases}.
\tag{3.4}
$$

and attraction energy being the difference $u_{\text{attr}}(r) = u(r) - u_{\text{rep}}(r)$.

In following Section 4 we will discuss the consequences that result from two approaches (2.3) and (3.3) to splitting the pair interaction energy into two parts in the light of van der Waals theory of liquid state of matter.

4. Results and discussions

The idea to split LJ pair interaction energy into the short-range and long-range part is not new. It originates from statistical mechanics treatment of the vdW theory in the framework of various realization of perturbation theory by Zwanzig [13], Barker and Henderson [6], Week, Chandler and Anderson [14]. However, in all these cases the short-range forces in LJ fluid always were associated exclusively with the repulsive forces. The reason for that was two-fold. First of all, because of van der Waals and the vdW theory of phase transition, and secondly, because of existence

and success of the Percus-Yevick theory of a hard-sphere system that were applied to describe the contribution of a soft repulsion in the LJ fluid.

Completely different philosophy and approach to separate the pair interaction energy and/or forces into the short-range and long-range contributions were implemented in the computer simulations of the LJ fluid. The main reasons to do so in this case were dictated by taking into account the long-range forces when using the finite size of the simulation box and/or by increasing the computing time when increasing the system size. As the result, majority of reported data for LJ fluid are performed with pair potential energy (3.1) cut off at $r_{\text{cut}} = 2.5\ \sigma_{\text{LJ}}$. To take into account the contribution of a remaining long-range tail the various techniques were suggested; another possibility is to neglecting this contribution.

To the best of our knowledge there are neither theoretical nor computer simulations studies where the short-range interaction energy that includes both the repulsion and attraction terms, was identified with excluded volume contribution to the properties of LJ fluid. The closest are recent studies due to Toxvaerd and Dyre [9, 10] who were interested to find the shortest cut off distance r_{cut} for the pair potential energy (3.1) such that effect of the neglected forces to the properties of LJ fluid could be recovered as a mean contribution, calculated from the particle distribution of the system which ignores the long-range forces. These authors found that the shortest cutoff when properties of dense LJ fluid are still well reproduced corresponds to location of the first minimum of the radial distribution function that is $1.55\sigma_{\text{LJ}}$ at density $\rho\sigma_{\text{LJ}}^3 = 0.85$ and temperature $k_{\text{B}}T/\epsilon = 1$. This is very close to range of the excluded volume interaction $u_{\text{excl}}(r)$ in Fig. 2. Since our definition of the range of excluded volume interaction is associated with the distances of the first coordination shell, we are considering findings by Toxvaerd and Dyre [9–11] as one of the justifications of our approach.

In what follows we will discuss some results of the present study that concern: (i) the stability of the system with excluded volume interaction from point of view of vapor-liquid phase separation and (ii) the density dependence of the long-range contribution to the properties of LJ fluid.

4.1. Phase stability of system with excluded volume interaction

Simulations of phase equilibrium in the system composed of particles interacting via excluded volume interaction potential, Eqs. (2.4) and (3.2), were performed by means of NVT Gibbs ensemble Monte Carlo (MC) method.
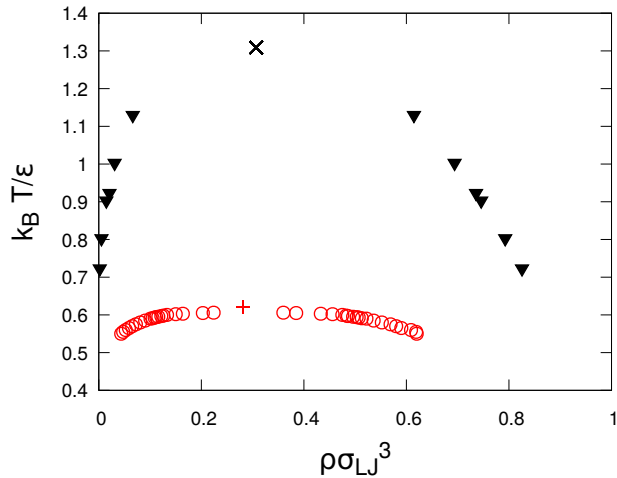
Figure 3. Vapor-liquid phase diagram of the system with short-range excluded volume interaction in comparison against the same for the Lennard-Jones fluid.

The simulated system consists of $N = 1000$ particles in initial configuration generated in one of the Gibbs ensemble MC boxes as *fcc* lattice with reduced number density $\rho\sigma_{\mathrm{LJ}}^3 = \rho^* = 0.3$. The simulation runs of 10^6 MC cycles for equilibration and another 10^6 cycles were used for production run. In each MC cycle was performed on average one attempt to move each particle in system, 10^3 attempts to exchange particles between boxes and one attempt to 10^6 the volume of boxes. In these simulation the total number of particles N and total volume V were kept constant. In simulations we used $\sigma_{\mathrm{LJ}} = 3.405$ Å, $\varepsilon = 119.8$ K, and short-range excluded volume potential (3.2) was formally cut off at $r_c = 12$ Å.

The results for coexisting densities at various temperatures are shown in Fig. 3. The parameters of the critical point – critical temperature and critical density were estimated from the density data using the law of rectilinear diameters [5]. The values of critical temperature is $k_{\mathrm{B}}T_{\mathrm{c}} = 0.621(2)$ and critical density $\rho_c \sigma \mathrm{LJ}^3 = 0.281(2)$. The most important observation from the data presented in Fig. 3 concerns the fact that critical point temperature of the system with short-range excluded volume interaction does not exceed the triple point temperature of the LJ fluid.

4.2. Long-range interaction contribution to the properties of LJ fluid

Within vdW theory the contribution of long-range interaction is associated with coefficient a, that in general case is given by

$$a = -2\pi \int_0^\infty g^{\mathrm{excl}}(r) u_{\mathrm{coh}}(r) r^2 dr \,. \tag{4.1}$$

The function $g^{\mathrm{excl}}(r)$ in this equation stands for the radial distribution function of the system with short-range excluded volume interaction potential $u_{\mathrm{excl}}(r)$ given by Eqs. (2.4) and (3.2). This function was evaluated by means of molecular dynamics (MD) simulations with $N = 2000$ particles in a cubic box subject to periodic boundary conditions at temperature fixed at $180\ K$, and five densities $\rho\sigma_{\mathrm{LJ}}^3 = 0.2351$, 0.3571, 0.4465, 0.6352 and 0.8712. All the simulations were performed in microcanonical constant energy ensemble over the production runs of 200 000 time steps. With a purpose of comparison, the same MD simulations were
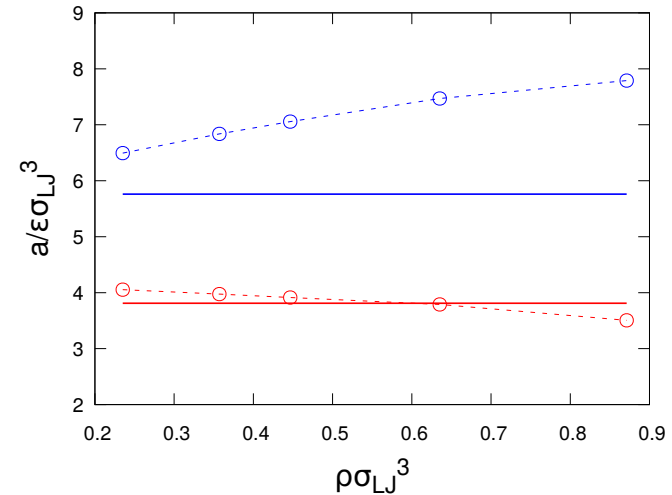
Figure 4. Density dependence of the van der Waals coefficient a for two different choices of excluded volume interactions: WCA (at the top) and of the present study (at the bottom). The symbols correspond to the results of Eq. (4.1), while solid lines – to Eq. (4.2). The temperature fixed at temperatures $T = 180$ K.

performed with short-range repulsion interaction $u_{\mathrm{rep}}(r)$ defined within the WCA theory by Eq. (3.4).

The results of calculations of coefficient a according to Eq. (4.1) are shown in Fig. 4 by symbols. The solid lines correspond to the case $g^{\mathrm{excl}}(r) = 1$ in Eq. (4.1). We can see, that only by using for excluded volume interaction energy $u_{\mathrm{tot}}^{\mathrm{sr}}(r)$ its definition according to Eqs. (2.4) and (3.2), it is possible to justify the assumption, $g^{\mathrm{o}}(r) = 1$, in Eq. (4.1) and obtain coefficient a that practically does not depend on the density. In the present case it results in the analytical expression,

$$a = -2\pi \int_0^\infty u_{\mathrm{coh}}(r)r^2 dr =$$

$$-2\pi\sigma^3\epsilon \left[\frac{4}{9}\left(\frac{\sigma_{\mathrm{LJ}}}{r_{\mathrm{m}}}\right)^9 - \frac{4}{3}\left(\frac{\sigma_{\mathrm{LJ}}}{r_{\mathrm{m}}}\right)^3 - \frac{r_{\mathrm{m}}}{\sigma_{\mathrm{LJ}}}\left(\frac{\alpha r_{\mathrm{m}}+1}{\alpha^2\sigma_{\mathrm{LJ}}^2} + 2\frac{\beta r_{\mathrm{m}}+1}{\beta^2\sigma_{\mathrm{LJ}}^2}\right) \right].$$

We can summarize, that proposed in this paper split of the LJ interaction interaction energy into short-range excluded volume interaction and long-range cohesion interaction results in mean-field that is formed by all molecules except those from the first coordination shell.

5. Conclusions

The original way to split Lennard-Jones (LJ) pair interaction energy into two parts, namely, the short-range excluded volume interaction and long-range cohesion interaction, is presented. The short-range excluded volume interaction is defined by the range that corresponds to the distances between neighboring particles within the first coordination shell. The long-range cohesion interaction is the difference between LJ interaction energy and excluded volume interaction energy.

It is shown that short-range excluded volume interaction still exhibit the vapor-liquid coexistence, but its critical temperature is below the triple point temperature of the LJ fluid. Therefore, excluded volume contributions to the properties of the LJ fluid are well defined in all thermodynamic states of the interest.

By calculating the van der Waals coefficient a it is shown that proposed definition of excluded volume interaction results in the contribution of long-range cohesion forces that is independent on the density as it was predicted by van der Waals [2].

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