Virial based equations of state with account of three-body interaction for noble gases and their mixtures

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Abstract. Within the frame of molecular dynamics the equations of state of noble gases and their mixtures have been obtained by means of time averaging procedure for virial based equation with account of three-body interaction. It has been shown, that equations of state can be extrapolated by van-der-Waals-type equations. The corresponding parameters have been calculated. A visible foliation of Xe and Kr components of Kob–Andersen mixture has been found.

Binary mixtures of Lennard-Jones (LJ) particles are of interest for a long time [1, 2]. An extensive set of isobaric–isothermal molecular dynamics (MD) simulations of binary mixtures of LJ particles have been performed by the large scale atomic/molecular massively parallel simulator (LAMMPS) package in [3], where different segregation regimes of constituent components was analyzed. Properties of binary mixtures may differ significantly from those of pure substances. It has been found, for example, that the crystallization of a binary mixture occurs with a considerably smaller rate than the crystallization of a pure LJ fluid [4].

The pair correlation function for krypton, beyond the critical isotherm, by using the two–and three-body contributions to the interatomic potential have been calculated in [5]. It has been emphasized, that three-body interaction cannot be ignored and that their effects become more significant for intermediate densities. The good agreement was found between semianalytic calculations and simulation or experimental results of the structural and thermodynamic properties by the use of integral equation method conjugated with an effective pair potential consisting of the Aziz–Slaman two–body potential plus the Axilrod–Teller three-body triple–dipole potential to describe the interactions between Xe atoms [6] (see also a review article [7]).

The purpose of the present research is to test a new method, based on time averaging of the virial equations of state for noble gases and their mixtures within the frame of MD with account of three-body interactions. The basic equation is in agreement with that expressed through correlation functions, the direct calculation of which is not indispensable within the present approach.

We have developed a modification of MD method with no fitting parameters involved, based on consideration of three-body interactions for those molecules which enter the first coordination sphere, whereas for all other molecules a pair potential is used. Three-body interaction energy
Table 1. Axilrod–Teller three-body potential constant $C$ for krypton and xenon atoms.

| Interacted atoms | $10^{-6} C$, K Å$^9$ |
|------------------|-----------------------|
| Kr–Kr–Kr        | 2.32                  |
| Xe–Xe–Xe        | 9.06                  |
| Kr–Kr–Xe        | 3.67                  |
| Kr–Xe–Xe        | 5.77                  |

is calculated on the base of one of six algebraically independent polynomials which are invariant under the $O(3) \times S_3$ transformation group [8] and which are composed of components of particle’s radii vectors

$$I_3 = r_{ij}^2 r_{jk}^2 r_{ki}^2,$$  \hspace{1cm} (1)

where $r_{ij} = | r_i - r_j |$ is a distance between $i$–th and $j$–th particles.

A three-body potential of van der Waals type has been obtained by Axilrod and Teller [9] and is expressed through the invariant $I_3$ (1) and cosines of angles which define atomic directions

$$\Phi^{(3)}_{ijk} = \frac{C}{I_3^{3/2}} \left( 1 + \frac{3(r_{ij}r_{jk})(r_{ik}r_{jk})(r_{ij}r_{ik})}{I_3} \right),$$ \hspace{1cm} (2)

where $C = I_0\alpha^3$, $I_0$ is an ionization potential of an isolated atom, $\alpha$ is the atom polarizability. For the case of gas mixtures the coefficient $C$ is proportional to the product of polarizabilities of interacted atoms.

The values of $C$ for three krypton, three xenon atoms and their combinations are given in table 1.

Two–body potential for noble gases and their mixtures is described well by Lennard-Jones potential

$$\Phi^{(2)}_{AB}(r) = 4\varepsilon_{AB} \left[ \left( \frac{\sigma_{AB}}{r} \right)^{12} - \left( \frac{\sigma_{AB}}{r} \right)^6 \right],$$ \hspace{1cm} (3)

where subscripts $AB$ correspond to the types of interacted atoms, $\varepsilon_{AB}$ is a depth of the potential well. Lorentz–Berthelot mixing rules are used for pair potential in our calculations [10]

$$\sigma_{AB} = \frac{\sigma_{AA} + \sigma_{BB}}{2},$$ \hspace{1cm} (4)
$$\varepsilon_{AB} = \left( \varepsilon_{AA} \varepsilon_{BB} \right)^{1/2}.$$ \hspace{1cm} (5)

I can be concluded from [11, 12] that these relations are accurate enough for the purpose of the present study. The three–parameter LJ potential function has been empirically modified by introducing a temperature–correction parameter to the reduced temperature for the calculation of the thermodynamic property and dilute transport properties of noble gases (He, Ne, Ar, Kr, and Xe) and their binary mixtures in [12]. Parameters of LJ potential which we have used in this paper are presented in table 2.

The interaction potential for the whole system with $N$ particles can be expressed as a sum of two–body, tree–body etc. contributions

$$U(r_1, r_2, \ldots, r_N) = \sum_{\{ij\}} \Phi^{(2)}_{ij} + \sum_{\{ijk\}} \Phi^{(3)}_{ijk} + \ldots,$$ \hspace{1cm} (6)
### Table 2. Parameters of Lennard-Jones potential ($k_B$ is Boltzmann constant).

|         | $T_0 = \varepsilon/k_B$, K | $\sigma$, Å |
|---------|----------------------------|-------------|
| Kr–Kr   | 164.56                     | 3.601       |
| Xe–Xe   | 218.18                     | 4.055       |
| Kr–Xe   | 189.48                     | 3.828       |

where $\Phi_{ij}^{(2)} \equiv \Phi^{(2)}(r_i, r_j)$ is a two body potential, $\Phi_{ijk}^{(3)} \equiv \Phi^{(3)}(r_i, r_j, r_k)$. Summations in equation (6) are extended to those values of $n$–particle potentials which prevent doubling, i.e. two–body term contains $N(N - 1)/2$ terms, three-body term contains $N(N - 1)(N - 2)/6$ terms etc. This fact is shown in equation (6) by figured brackets under the sum: $\{ij\}$, $\{ijk\}$, etc.

For further we introduce $n$-body correlation function $g^{(n)}(r_1, r_2, \ldots, r_n)$, which is normalized as

$$
\int g^{(n)}(r_1, r_2, \ldots, r_n) d^{(n)}r = \left(\frac{V}{N}\right)^n \frac{N!}{(N-n)!} \approx V^n,
$$

(7)

where $d^{(n)}r \equiv dr_1 dr_2 \ldots dr_n$. Particularly for $n = 2$ and if spherical symmetry of interaction potential is assumed, than function $g^{(2)}(r_1, r_2) = g(r_{12})$ coincides with the radial distribution function normalized as

$$
\int_0^\infty g(r) 4\pi r^2 dr = V.
$$

(8)

The latter relation in equation (7) assumes that $N \gg 1$ and $N \gg n$.

Following the well known procedure (see, for example, [13], §29) one can express the equation of state of the system through the correlation functions

$$
PV = k_B TN - \frac{1}{3} \sum_{n=2}^\infty \frac{N!}{V^n(N-n)!n!} \times
$$

$$
\times \int g^{(n)}(r_1, \ldots, r_n) \left( \sum_{m=1}^n \frac{\partial \Phi^{(n)}(r_1, \ldots, r_n)}{\partial r_m} r_m \right) d^{(n)}r,
$$

(9)

where $P$ is the pressure.

In the particular case of three-body interaction we obtain

$$
PV = k_B TN - \frac{1}{6v^2} \int dr_1 dr_2 g^{(2)}(r_1, r_2) \left( \frac{\partial \Phi^{(2)}(r_1, r_2)}{\partial r_1} r_1 + \frac{\partial \Phi^{(2)}(r_1, r_2)}{\partial r_2} r_2 \right) -
$$

$$
- \frac{1}{18v^3} \int dr_1 dr_2 dr_3 g^{(3)}(r_1, r_2, r_3) \left( \sum_{m=1}^3 \frac{\partial \Phi^{(3)}(r_1, r_2, r_3)}{\partial r_m} r_m \right),
$$

(10)

where $v = V/N$ is the volume per particle (specific volume). It is assumed in (10) that $N \gg 1$ and no spherical symmetry takes place. If the latter happens we obtain for two–body interaction system a familiar formula for equation of state expressed through the radial distribution function (see equation (30.20) in [13])

$$
Pv = k_B T - \frac{1}{6v} \int_0^\infty \frac{d\Phi^{(2)}(r)}{dr} g(r) 4\pi r^3 dr.
$$

(11)
Three-body equation of state (10) for spherically symmetric interaction potential is well known and has been utilized by many authors (see, for example, Eqn. (2.19.3) in [1]).

On the other hand the equation of state can be expressed by means of time averaging of the system’s virial [14]

\[ W_P = k_B T - \frac{2}{3N} \langle W(r_1, r_2, \ldots, r_N) \rangle, \]

where \( \langle \ldots \rangle \) does mean averaging over time. The virial in equation (12) is

\[ W(r_1, r_2, \ldots, r_N) = \frac{1}{2} \sum_{i=1}^{N} r_i \frac{\partial U}{\partial r_i}. \]

Making use the system potential in the form of equation (6), we obtain the equation of state of the system

\[ P v = k_B T - \frac{1}{3N} \left( \sum_{(ij)} r_i \frac{\partial \Phi^{(2)}}{\partial r_i} + \sum_{\{ijk\}} r_i \frac{\partial \Phi^{(3)}}{\partial r_i} \right). \]

Formula (14) is in complete agreement with equation (10) if we assume that the averaging over correlation functions in (10) is equal to the averaging over time in (14). Formula (14) is convenient in MD calculations. In this approach tree–body interaction terms in (14) are taken into account inside the sphere of radius \( r_1 \) equal to several characteristic interaction lengths \( \sigma \) [15], whereas contribution to the equation of state of interactions with particles outside the sphere have been calculated in binary spherically symmetric approximation by adding to the right hand side of equation (14) the term similar to that in equation (11)

\[ -\frac{1}{6v} \int_{r_1}^{\infty} \frac{d\Phi^{(2)}(r)}{dr} g(r) 4\pi r^3 dr. \]

The three-body interaction contribution to potential energy per particle for equilateral triangle atomic configuration is shown in figure 1.

Equations of state obtained in our MD simulation have been approximated by the van der Waals equation

\[ P = \frac{k_B T}{\varepsilon (v - b)} - \frac{a}{v^2}, \]

as well as by the equation of state in the Vulcanovich–Novikov form [16]

\[ P = \frac{k_B T}{\varepsilon (v - b)} - \frac{a}{(c + v)^2(k_B T/\varepsilon)^m}, \]

where \( \varepsilon \) is a depth of Lennard-Jones potential well. Volume is measured in the units of \( \sigma^3 \), whereas time is given in the units \( t_0 = (M/\varepsilon)^{1/2} \sigma = 5.88 \times 10^{-12} \) s. Influence of three-body interaction on the equation of state is shown in figure 2 for two dimensional xenon gas. Evaluation of the equation of state for monolayer physical adsorption of krypton atoms on smooth surface was considered in [17].

We have also carried out MD simulation of the behavior of Kr and Xe gases mixture at temperatures close to the condensation temperature by means of LAMMPS parallel computer package. Effectiveness of LAMMPS package for multiprocessor computers have been analyzed in [18]. Molar concentrations in our simulations were taken as \( c_A = 0.8 \) for krypton and \( c_B = 0.2 \) for xenon, which correspond to Kob–Andersen mixture [2]. Similar calculations for pure noble gases [19] have been demonstrated the increase of difference of the calculated equation of state from that of standard Lennard-Jones gas with increase of atomic mass.
Figure 1. Potential energy per particle for xenon atoms localized in vertexes of an equilateral triangle. Solid lines: 1—binary approximation, 2—potential energy with three-body interaction contribution.

Figure 2. Equations of state for two dimensional xenon gas at temperature $T/T_0 = 1.15$. Solid line—binary approximation, dashed line—calculation with Axilrod–Teller three-body interaction potential (2).

Equations of state for Kob–Andersen Kr–Xe mixture for different temperatures are shown in figure 3. Temperature $T = 1.2T_0$ (see the curve shown by squares in figure 3) is close to the critical temperature for this system. These curves can be fairly approximated by Vulcanovich–
Figure 3. Equations of state of Kr–Xe Kob–Andersen mixture for different temperatures: squares—1.2$T_0$, bubbles—1.15$T_0$ and triangles—1.11$T_0$.

Figure 4. Spatial configuration of Kr–Xe mixture at temperature $T = 1.15T_0$ and time instant $t = 50t_0$. The volume of the system is normalized to unity.

Novikov equation of state (17) with parameters $a = 5.27$, $b = 1.05$, $c = 0.035$ and $m = 0.44$. Results of MD computer simulation provide values of van der Waals parameters $a$ and $b$ in (16) given in table 3 for different temperatures. As it follows from the table 3 values of van der Waals parameters calculated for different temperatures coincide within the accuracy of 5 percent. It does mean, that van der Waals approximation for equations of state is not a bad approximation. One can, for example, extract from figure 3 the binary phase regions by means of standard procedures with van der Waals equation.

Figure 4 demonstrates the time evolution of Kr–Xe Kob–Andersen mixture for time instant $t = 50t_0$. As it is seen from figure 4, a spatially uniform at initial time instant gases mixture
Table 3. Van der Waals parameters calculated for the Kob–Andersen Kr–Xe mixture at different temperatures.

| $T/T_0$ | $a$   | $b$   | $T_c/T_0$ | $T_c$, K |
|---------|-------|-------|-----------|----------|
| 1.11    | 4.60  | 1.12  | 1.22      | 266      |
| 1.15    | 4.44  | 1.11  | 1.19      | 259      |
| 1.20    | 4.35  | 1.105 | 1.17      | 254      |

suffers visible foliation at $t = 50t_0$. Dark (red) regions at this figure represent xenon. Different single–component volume regions coexist maintaining a thermodynamic equilibrium. Such picture looks like a Tsiklis–Bolshakov–Krichevsky gas–gas equilibrium [20, 21].

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