



# Test of athermal terms of activity coefficients by large scale molecular dynamics simulation for vapor–liquid equilibria



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## ABSTRACT

The vapor–liquid equilibria for Ar (1) + Ar<sub>dimer</sub> (2) system were calculated by molecular dynamics simulation to test the athermal terms of activity coefficient models. The calculations were carried out at 141 K. The interatomic distance between two atoms in Ar<sub>dimer</sub> molecule was fixed to the distance of the first peak of the radial distribution function of pure Ar at 141 K. Lennard-Jones potential was adopted for the interatomic potentials between Ar–Ar, Ar–atom in Ar<sub>dimer</sub>, and atom in Ar<sub>dimer</sub>–atom in Ar<sub>dimer</sub>. The number of atoms used for the calculations were from 3000 to 4200. The calculated results of activity coefficients for Ar (1) + Ar<sub>dimer</sub> (2) system at 141 K are smaller than unity, and are between the calculated results by Flory–Huggins equation based on hard-core volume and that based on volume.

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## 1. Introduction

The measurements and calculations of phase equilibria are essential for the design of separation equipment. Activity coefficient equations are widely used for the calculations of phase equilibria. Activity coefficient equations are usually expressed by interactional terms and athermal terms. Wilson [1] and NRTL [2] equations contain only interactional terms. UNIQUAC [3] equation contains interactional term and athermal term. Flory–Huggins [4,5], Staverman–Guggenheim [6], and Elbro-FV [7] equations are used for athermal terms.

Many researchers tested and improved the athermal terms by using the experimental data of activity coefficients for paraffin mixtures [8–11]. However, the paraffin mixtures are not exactly athermal solutions, and the solutions have a limitation of the variation of molecular shapes.

The most popular method to calculate phase equilibria by molecular simulation is Gibbs Ensemble Monte Carlo method [12]. Widom test particle insertion method [13] can be applied to calculate the chemical potential of a test particle in a solution, and calculate phase equilibria. However, as mentioned by Gelb and Muller [14], Monte Carlo methods have well-known deficiencies. When Monte Carlo methods are applied for dense phases, typical of strongly interacting liquids and solids, equilibration is difficult to

achieve because of the poor statistics associated with the insertion/deletion steps. Monte Carlo methods are also difficult to apply to the systems containing very complex molecules without substantial system-specific modification.

Sheng et al. [15] calculated the athermal contributions by Monte Carlo simulation with a Lennard-Jones bead model, and compared with several activity coefficient equations. Kontogeorgis et al. [10] and Radfarnia et al. [11] used the results of Sheng et al. to test the athermal terms. Sheng et al. mentioned that the calculation condition was  $T^* = kT/\epsilon = 1.15$  and near-atmospheric pressure ( $p^* = p\sigma^3/\epsilon = 0$ ). The calculated density of monomer was  $\rho^* = \rho\sigma^3 = 0.578$ . However, the properties of Lennard-Jones fluid have been well studied. Koutras et al. [16] collected the calculated results of vapor–liquid equilibria for pure Lennard-Jones fluid from several literature. From the review, the saturated density in vapor  $\rho^{*,V}$  is from 0.072 to 0.083, the saturated density in liquid  $\rho^{*,L}$  is from 0.601 to 0.612, and the saturated pressure  $p^{*,0}$  is from 0.056 to 0.064 at  $T^* = 1.15$ . The calculated condition for monomer of Sheng et al. ( $T^* = 1.15$  and  $\rho^* = 0.578$ ) was in a two phase region. From the phase diagram of Lennard-Jones fluid (Fig. 3 in the literature [17]), the calculated condition of Sheng et al. is in a metastable condition. Further, if the Lennard-Jones parameters of Ar ( $\epsilon = 0.9786$  kJ/mol and  $\sigma = 3.401$  Å) are used to calculate the saturated pressure at  $T^* = 1.15$ , the value becomes about 2.5 MPa, which is not near-atmospheric pressure.

Molecular dynamics simulation has been applied to directory calculate the phase equilibria with large number of molecules [14,18–20]. Vapor, liquid, and vapor–liquid interface exist in a

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computer cell by the method. The advantage of the method is that the chemical potentials of components are not necessary to calculate during the simulation.

In this work, the vapor–liquid equilibria for Ar (1) + Ar<sub>dimer</sub> (2) system at 141 K were calculated by molecular dynamics simulation. The calculated results of activity coefficients were compared with those of several equations.

## 2. Activity coefficient equations

Flory–Huggins and Elbro-FV equations can be expressed by the following general form:

$$\ln \gamma_i = \ln \frac{\varphi_i}{x_i} + 1 - \frac{\varphi_i}{x_i} \quad (1)$$

where  $\gamma_i$  is the activity coefficient,  $x_i$  is the mole fraction,  $\varphi_i$  is the fraction calculated by the following equation.

$$\varphi_i = \frac{x_i S_i}{\sum_j x_j S_j} \quad (2)$$

where  $S_i$  is the volume  $V_i$ , the hard-core volume  $V_i^*$ , and  $V_i - V_i^*$  for Flory–Huggins equation based on volume (Flory–Huggins (V)), Flory–Huggins equation based on hard-core volume (Flory–Huggins (V<sup>\*</sup>)), and Elbro-FV equations, respectively.

## 3. Molecular dynamics simulation

### 3.1. Potential

#### 3.1.1. Argon

Lennard-Jones potential was adopted for the intermolecular interaction potential energy  $U$  between atoms.

$$U(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (3)$$

where,  $r$  is the interatomic distance,  $\varepsilon$  is the energy parameter, and  $\sigma$  is the size parameter. The values of the parameters adopted for Ar in this work were  $\varepsilon = 0.9786$  kJ/mol and  $\sigma = 3.401$  Å [21].

#### 3.1.2. Ar<sub>dimer</sub>

Ar<sub>dimer</sub> was made by bonding two Ar atoms as an artificial molecule. The interatomic distance was determined to the first peak distance of radial distribution function 3.71 Å in the liquid of pure Ar at 141 K which was calculated by molecular dynamics simulation. Ar<sub>dimer</sub> was treated as a rigid molecule. All the heterologous interatomic potential parameters were the same as those of pure Ar;  $\varepsilon = 0.9786$  kJ/mol and  $\sigma = 3.401$  Å.

### 3.2. Calculation conditions

Molecular dynamics simulation was performed by the software SCIGRESS ME 2.0 (Fujitsu Ltd, Japan). All simulations were carried out with the time step of 4 fs, and the NVT ensemble was adopted. The cell lengths were 34.01, 34.01, and 600 Å in  $x$ ,  $y$ , and  $z$  directions, respectively. Periodic boundary conditions were applied in all directions. The cut off distance was fixed to  $5\sigma$ , and any modifications for the potential were not applied near the cut off distance. Long-range corrections were not applied. Because the averaged number densities in vapor and liquid phases are very different each other, and the values of long-range corrections depend on the position from the vapor–liquid interface. When the cut off distance becomes longer, the values of long-range corrections become smaller

(the calculated results become more accurate), and the computation time becomes longer. The cut off distance was decided from the trade-off relation.

The temperature was brought to 141 K ( $T^* = kT/\varepsilon = 1.20$ ) by Nose's method. The number of steps before equilibrated state were  $6 \times 10^6$  for pure Ar,  $5 \times 10^6$  for pure Ar<sub>dimer</sub>, and  $3.1 \times 10^7$  for Ar (1) + Ar<sub>dimer</sub> (2) system. The number of steps to obtain the equilibrium values were  $4 \times 10^6$  for pure Ar,  $5 \times 10^6$  for pure Ar<sub>dimer</sub>, and  $9 \times 10^6$  for Ar (1) + Ar<sub>dimer</sub> (2) system. The number of molecules in the cells were 4200 and 3000 for pure Ar and pure Ar<sub>dimer</sub>, respectively. The number of molecules of Ar + 2 × the number of molecules of Ar<sub>dimer</sub> are 3500 for Ar (1) + Ar<sub>dimer</sub> (2) system.

### 3.3. Method to calculate vapor–liquid equilibria

The initial placement was made as follows. First, a liquid cell was produced by setting molecules at random positions. The structure of molecules in the liquid cell was relaxed for 10,000 time steps by Monte Carlo simulation. Furthermore, molecular dynamics simulation was carried out for 5000 time steps. Then, the liquid cell was combined with a vapor cell which was empty. Molecular dynamics simulation was carried out to calculate the vapor–liquid equilibria.

After reach the equilibrium conditions, the number of molecules in vapor and liquid phases were counted as follows. The cell was divided into 100 columns in  $z$  direction. The number of molecules in each column were averaged. Fig. 1 shows an example of the profile of number of molecules in  $z$  direction. The densities in vapor and liquid phases were determined by averaging the flat parts of the profile. The saturated vapor pressure was determined with the pressure  $p_z$  which is the tensor in vertical direction for the interface, because surface tension cases the anisotropy of pressure.

### 3.4. Calculation of activity coefficients

The activity coefficient of component  $i$ ,  $\gamma_i$ , is expressed by the following equation,

$$\phi_i^V p y_i = \gamma_i x_i p_i^o \phi_i^{o,V} \exp \left\{ \frac{V_{m,i}^{o,L} (p - p_i^o)}{RT} \right\} \quad (4)$$

where  $\phi$  is the fugacity coefficient,  $p$  is the pressure,  $y_i$  is the mole fraction in vapor phase,  $x_i$  is the mole fraction in liquid phase,  $V_m$  is the molar volume,  $R$  is the gas constant, and  $T$  is the temperature. The superscripts o, V, and L mean pure, vapor phase, and liquid phase, respectively.

In this work, non-ideality in vapor phase was correlated by the virial equation.

$$Z = \frac{pV_m}{RT} = 1 + \frac{B}{V_m} \quad (5)$$

where,  $Z$  is the compressibility factor and  $B$  is the second virial coefficient.

For Ar (1) + Ar<sub>dimer</sub> (2) system, the value of  $B_1$  for pure Ar at 141 K was cited from Eubank et al. [22]. The value of  $B_2$  for pure Ar<sub>dimer</sub> at 141 K was determined by the following method. First, 500 molecules were set in a cell. The cell volumes were fixed as  $V_m^V$  and  $1.5V_m^V$  where  $V_m^V$  is the molar volume in vapor phase at vapor–liquid equilibrium condition of Ar<sub>dimer</sub> at 141 K. The calculation of pressure for each cell volume was carried out with 10 million time steps before equilibrated state and 30 million time steps after equilibrated state. The value of  $B_2$  was determined by the slope of a linear line of Eq. (5).

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