



# Direct calculation of mutual diffusion coefficients of binary system using non-equilibrium molecular dynamics simulation



Hidenori Higashi\*, Kazuhiro Tamura, Takafumi Seto, Yoshio Otani

School of Natural System, College of Science and Engineering, Kanazawa University, Kakuma-machi, Kanazawa, 920-1192 Ishikawa, Japan

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## ABSTRACT

Molecular dynamics (MD) simulation is widely used to calculate transport properties of fluids. In this study, non-equilibrium molecular dynamics (NEMD) simulation was applied to calculate mutual diffusion coefficients from the molecular flux at a given concentration gradient. First, the applicability of spherical molecular model was investigated by calculating self- and tracer diffusion coefficients of methane and *n*-decane mixture by an equilibrium MD simulation. The simulated self- and tracer diffusion coefficients of both components were in good agreement with literature data except in the case that methane molar fraction was nearly equal to zero. Further, the NEMD simulation was adopted to calculate mutual diffusion coefficients of binary system of methane and *n*-decane. This binary system exhibits anomalous concentration dependence of mutual diffusion coefficients in the vicinity of critical molar fraction according to the previously reported experimental data. The NEMD simulation well reproduced such concentration dependence of mutual diffusion coefficients. The simulation also gave a fairly good agreement with the calculated results by the Darken equation using tracer diffusion coefficients with a thermodynamic factor.

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## 1. Introduction

Mutual diffusion coefficient is one of the most fundamental transport properties which are essential to design extractors, separators and reactors. Many data of mutual diffusion coefficients for binary system have been reported in the single phase region. The mutual diffusion coefficients are known to have anomalous concentration dependence in the vicinity of critical point of vapor-liquid equilibria (VLE) and at supercritical conditions [1–8]. Such anomalous behavior may appear by the chemical potential (activity and fugacity) gradient which can be represented by a thermodynamic factor [9–12]. In general, the thermodynamic factor was coupled with self- or tracer diffusion coefficients in order to calculate the mutual diffusion coefficient by theoretical methods such as the Darken equation [13]. Therefore, in order to predict the complex concentration-dependent behavior of mutual diffusion coefficients, the calculation methods of thermodynamic factor and self- or tracer diffusion coefficients have to be established as a function of concentration.

Molecular dynamics simulation may be helpful in obtaining the thermodynamic data for mixtures at a high pressure. In our

previous works [14–16], NVT ensemble molecular dynamics simulation using spherical molecular model was successfully applied to calculate the self-diffusion coefficients of pure carbon dioxide and the tracer diffusion coefficients in carbon dioxide + aromatic compound systems. We showed that the spherical molecular model was applicable to calculate the self- and tracer diffusion coefficients for the given system by using parameters adjusted to the solubility. However, the equilibrium MD simulation cannot be applied to the direct calculation of mutual diffusion coefficients because creation of a non-equilibrium condition is required for the direct calculation of mutual diffusion coefficients. In order to calculate the mutual diffusion coefficients by the equilibrium MD simulation, theoretical approaches should be employed [17–20]. One of the other approaches is a direct calculation of mutual diffusion coefficients using non-equilibrium molecular dynamics (NEMD) simulation.

NEMD simulation is a powerful tool to calculate transport properties directly from the fluxes and it may be useful to explain the anomalous decrease in mutual diffusion coefficient near the critical point. Wang and Cummings [21] were firstly proposed the NEMD simulation to calculate the transport properties including the diffusion coefficient of carbon dioxide. They showed that the NEMD simulation could be applicable to calculate the transport properties and the thermal conductivity and diffusion coefficients obtained through the simulation quantitatively agreed with the

\* Corresponding author. Tel.: +81 76 264 6260; fax: +81 76 234 4829.

E-mail address: [hhigashi@mail.kanazawa-u.ac.jp](mailto:hhigashi@mail.kanazawa-u.ac.jp) (H. Higashi).

experimental data. They applied forced fluxes to generate non-equilibrium conditions in the general method of NEMD and they showed the possibility of calculating transport properties. In our previous work [22], we proposed new NEMD method with the given natural concentration gradient similar to the experimental condition. The calculation results for pseudo binary system of carbon dioxide showed good agreement with the experimental results of self-diffusion coefficients for carbon dioxide. However, the applicability of the NEMD simulation to calculate transport properties of real binary system composed of complex components have not examined yet. In particular, this method may possess a potential to predict detail behavior of binary components such as mutual diffusion coefficients in the wide range of concentration, especially at the vicinity of critical condition. The purposes of this work are to investigate the applicability of the new NEMD method to real binary system and to examine the limit of the spherical molecular model. In this work, the same procedure was applied to calculate the mutual diffusion coefficients for more complex binary system of methane and *n*-decane. Although *n*-decane is a chain-like molecule, we examined the spherical approximation for *n*-decane to simplify the NEMD calculation. In our previous works [14–17], we applied the spherical molecule model assumption to aromatic compounds and the spherical model was applicable to estimate solubility and diffusion coefficient of aromatic compounds in supercritical carbon dioxide. The mutual diffusion coefficients of the system were directly simulated by the NEMD simulation. The simulated results were compared with literature data and those calculated by a thermodynamic model using tracer diffusion coefficients with a thermodynamic factor.

## 2. Method

### 2.1. Intermolecular potential function

A spherical molecular model was employed for all molecules in the present study and the Lennard-Jones(12-6) potential function was used to calculate the molecular interaction.

$$\phi_{ij} = 4\epsilon_{ij} \left\{ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\} \quad (1)$$

where *i* and *j* represent particle *i* and *j*, respectively.  $\phi$  is the intermolecular potential,  $\epsilon$  is the energy parameter,  $\sigma$  is the size parameter, and *r* is the molecular distance.

The interaction parameters between component 1 and 2 are given using the combining rules as follows.

$$\epsilon_{12} = (\epsilon_{11} \times \epsilon_{22})^{0.5} \quad (2)$$

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})/2 \quad (3)$$

### 2.2. Determination of potential parameters

The potential parameters  $\epsilon$  and  $\sigma$  of each component were determined from the data of the critical point of each component by Nicolas method [23]. According to the corresponding state principle, the reduced properties, such as pressure *P*, volume *V* and absolute temperature *T*, of the Lennard–Jones fluid of a pure substance is given by the following equations.

$$\rho^r = \frac{n\sigma^3}{V}, T^r = \frac{kT}{\epsilon}, P^r = \frac{\sigma^3 P}{\epsilon} \quad (4)$$

where  $\rho$  is the number density. Nicolas et al. proposed the reduced value at the critical point  $\rho_c^r$ ,  $T_c^r$  and  $P_c^r$  as follows.

$$\rho_c^r = 0.35, T_c^r = 1.35, P_c^r = 0.1418 \quad (5)$$

The parameters for methane and *n*-decane determined by the critical temperatures and pressures are listed in Table 1.

### 2.3. Equilibrium molecular dynamics simulation

As first step, validity of spherical molecular model was investigated by calculating the self- and tracer diffusion coefficients of methane and *n*-decane in the mixture by equilibrium MD simulation. NVT ensemble equilibrium MD simulation using the leap-frog algorithm with a damped force method for constant mean temperature proposed by Brown and Clarke [25] was applied to calculate the self-diffusion coefficients of methane and *n*-decane and tracer diffusion coefficients of both components in the mixture. The equation of motion with the damped force method is given by the following equation.

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i - \zeta m_i \mathbf{v}_i \quad (6)$$

where  $m_i$  is the mass of particle *i*,  $r_i$  the position, and  $v_i$  the velocity.  $F_i$  is the force acting on the particle *i* and  $\zeta$  is the restriction factor to keep the temperature constant. The simulations were performed at 303 and 333 K. The calculated pressures were about 40 MPa at 303 K and 30 MPa at 333 K. The number of molecules was 256 and the simulation conditions were determined from our previous works [14–17]. The potential was truncated at a cut off length of the half-length of simulation cell and long range correction was applied. The time step of calculation was 5 fs. After repeating more than  $2 \times 10^3$  equilibration steps (10 ps),  $2 \times 10^6$  production steps (1 ns) were performed. The self- and tracer diffusion coefficients for methane and *n*-decane can be calculated by the Einstein equation as

$$D_i^* = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle \quad (7)$$

where *t* is the elapsed time and *r* is the position of a particle of each component.

### 2.4. Non-equilibrium molecular dynamics simulation

A snapshot of simulation for binary system of spherical molecules mixture is shown in Fig. 1(a). The simulation cell consisted of four regions, as shown in Fig. 1(b). The concentration in regions A and B was controlled and flux calculation regions C<sub>I</sub> and C<sub>II</sub> were placed. The simulated systems consisted of 324 particles (108 particles  $\times$  3 boxes). In the case of simulation for the pseudo binary system of single component, the particles were colored with white and black, and the conditions of each concentration control regions A and B were assigned as those pure components. The molar fractions of component 2 in the concentration control regions,  $y_2^A$  and  $y_2^B$ , were set to the molar fraction of  $y_{20}^A$  and  $y_{20}^B$  for binary system. The concentration of the

**Table 1**  
Physical properties and potential parameters.

	$T_c$ [K]	$P_c$ [MPa]	$\omega$ [–]	$\sigma$ [nm]	$\epsilon/k$ [K]
Methane (1)	190.6 <sup>a</sup>	4.599 <sup>a</sup>	0.011 <sup>a</sup>	0.392 <sup>b</sup>	141.2 <sup>b</sup>
<i>n</i> -Decane (2)	617.7 <sup>a</sup>	21.1 <sup>a</sup>	0.490 <sup>a</sup>	0.751 <sup>b</sup>	457.6 <sup>b</sup>

<sup>a</sup> Poling et al. [24].

<sup>b</sup> The potential parameters were determined by the corresponding method of Nicolas et al. [23] using critical temperature and pressure.

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