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

Direct Calculation of Mutual Diffusion Coefficients of Binary System using Non-Equilibrium Molecular Dynamics Simulation

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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 a 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.

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 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.

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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.

METHOD

1. Intermolecular Potential Function

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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.

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

where i and j represent particle i and j, respectively. ϕ is the intermolecular potential, ε is the energy parameter, σ 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.

$$\varepsilon_{12} = \left(\varepsilon_{11} \times \varepsilon_{22} \right)^{0.5} \tag{2}$$

$$\sigma_{12} = \left(\sigma_{11} + \sigma_{22} \right)/2 \tag{3}$$

2. Determination of Potential Parameters

The potential parameters ε and σ 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.

$$\rho^{r} = n\sigma^{3}/V, \quad T^{r} = kT/\varepsilon, \quad P^{r} = \sigma^{3}P/\varepsilon \tag{4}$$

where ρ is the number density. Nicolas *et al.* proposed the reduced value at the critical point ρ_{C}^{r}, T_{C}^{r} and P_{C}^{r} as follows.

$$\rho_C{}^r = 0.35, \quad T_C{}^r = 1.35, \quad P_C{}^r = 0.1418 \tag{5}$$

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

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.

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i - \zeta \, m_i \mathbf{v}_i \tag{6}$$

where m_i is the mass of particle i, $\mathbf{r}_i$ the position, and $\mathbf{v}_i$ the velocity. $\mathbf{F}_i$ is the force acting on the particle i and ζ 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 2×10^3 equilibration steps (10 ps), 2×10^6

production steps (1 ns) were performed. The self- and tracer diffusion coefficients for

methane and n-decace can be calculated by the Einstein equation as

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

where t is the elapsed time and $\mathbf{r}$ is the position of a particle of each component.

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_I and C_{II} 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 region A and B was controlled by using the replacing method. The

concentration of the region A and B was controlled by replacing the corresponding molecules.

For example, when the methane molecules diffuse into the region B, the concentration of

n-decane in the region B was compared with the target concentration (=average concentration

+/- 0.01 to 0.05). If the concentration of n-decane is lower than the target value, the methane

molecule was replaced with *n*-decane molecule. We also apply this procedure for *n*-decane

molecules diffusing into the region A. It should be noted that pressure in the regions A and B

did not change significantly (less than 10%) in this procedures.

The equations of motion were solved with the leap-frog algorithm with the damped force

method proposed by Brown and Clarke [25] to achieve constant mean temperature of mixture.

The potential was truncated at a cut off length of the half-length of the small box and long

range correction was applied. The time step of the calculation was 5 fs. After repeating more

than 1×10^5 steps (500 ps) for the equilibration, 2×10^6 steps (1 ns) and 1×10^7 steps (5 ns) for

the production were performed. The temperatures were set at 303 and 333 K, and the

calculated pressures of simulation were about 40 MPa at 303 K and about 30 MPa at 333 K.

5. Calculation of Mutual Diffusion Coefficients

The fluxes of each component were calculated at the center of mass for the components in

the regions C_I and C_{II}. The diffusion coefficients were determined as the average of diffusion

coefficients in the regions C_I and C_{II} which were calculated by the fluxes and the

concentration gradients. The calculation procedure for the region C_I is as follows.

The fluxes relative to those for a fixed plane N_1 and N_2 in the region C_I were calculated by

the following equations.

$$N_1^{C_I} = \frac{m_1}{V^{C_I}} \sum_{i=1}^{n_1^{C_I}} v_{xi} \tag{8}$$

$$N_2^{C_I} = \frac{m_2}{V^{C_I}} \sum_{i=1}^{n_2^{C_I}} v_{xi} \tag{9}$$

where m_1 and m_2 are the mass of molecules, and n_1 and n_2 are the number of molecules of methane(1) and decane(2). V^{C_I} is the volume of the region C_I. v_{xi} is the x-component of velocity vector of molecule i. The fluxes relative to the plane of no net mass flow J_1 and J_2 in the region C_I were given by the following equations.

$$J_1^{C_I} = N_1^{C_I} - y_1^{C_I} \left(N_1^{C_I} + N_2^{C_I} \right) \tag{10}$$

$$J_2^{C_I} = N_2^{C_I} - y_2^{C_I} \left(N_1^{C_I} + N_2^{C_I} \right) \tag{11}$$

The diffusion coefficients relative to the plane of no net mass flow were calculated by the following equations.

$$D_{12}^J = J_1^{C_I} \frac{v^{C_I}}{m_1} \frac{\Delta x}{n_1^{E_I} - n_1^{E_{II}}} \tag{12}$$

$$D_{21}^J = J_2^{C_I} \frac{v^{C_I}}{m_2} \frac{\Delta x}{n_2^{E_I} - n_2^{E_{II}}} \tag{13}$$

where Δx is the width of the flux calculation regions shown in **Fig.1**, and $n_1^{E_I}$, $n_2^{E_I}$, $n_1^{E_{II}}$ and $n_2^{E_{II}}$ are the number of molecules of each component in zones E_I and E_{II}.

The diffusion coefficients relative to the plane of no net volume flow D_{12}^V and D_{21}^V, which are the mutual diffusion coefficients and essentially D_{12}^V equals D_{21}^V, were calculated by the following equations.

$$D_{12}{}^{\mathrm{V}} = \frac{\bar{v}_2}{v} D_{12}{}^{\mathrm{J}} \tag{14}$$

$$D_{21}{}^{\mathrm{V}} = \frac{\bar{v}_1}{v} D_{21}{}^{\mathrm{J}} \tag{15}$$

where v is the molar volume of this system. $\bar{v}_1$ and $\bar{v}_2$ are the partial molar volume of each component. The partial molar volumes were calculated by:

$$\bar{v}_1 = \frac{V^{\mathrm{E}}\left\{\left(n_2^{\mathrm{E_{II}}} \middle/ n_2^{\mathrm{E_I}}\right) - 1\right\}}{n_1^{\mathrm{E_I}}\left(n_2^{\mathrm{E_{II}}} \middle/ n_2^{\mathrm{E_I}}\right) - n_1^{\mathrm{E_{II}}}} N_{\mathrm{AV}} \tag{16}$$

$$\bar{v}_2 = \frac{V^{\mathrm{E}}\left\{\left(n_1^{\mathrm{E_I}} \middle/ n_1^{\mathrm{E_{II}}}\right) - 1\right\}}{n_2^{\mathrm{E_{II}}}\left(n_1^{\mathrm{E_I}} \middle/ n_1^{\mathrm{E_{II}}}\right) - n_2^{\mathrm{E_I}}} N_{\mathrm{AV}} \tag{17}$$

where V^{E} is the volume of the region $\mathrm{E_I} \sim \mathrm{E_{IV}}$ and N_{AV} is the Avogadro number.

6. Thermodynamic model

The mutual diffusion coefficient is correlated by a thermodynamic model such as Darken equation [13] using tracer diffusion coefficient with a thermodynamic factor.

$$D_{21} = \left(y_2 D_1 * + y_1 D_2 *\right)\left(\frac{\partial \ln f_2}{\partial \ln y_2}\right) \tag{18}$$

where f_2 is the fugacity of solute and D^* is the tracer diffusion coefficient. In this work, the simulated results of the mutual diffusion coefficients were compared with those calculated by the Darken equation. The tracer diffusion coefficients were smoothed by applying cubic

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functions of molar fraction. The SRK equation of state (EOS) [26] was adopted to calculate

the fugacity of solute. The critical constants and acentric factor which were used to determine

the parameters of SRK-EOS are given in **Table 1**.

RESULTS AND DISCUSSION

1. Self- and Tracer Diffusion Coefficients

The simulated results of self- and tracer diffusion coefficients of methane and *n*-decane by

the equilibrium MD simulation at 303 and 333 K were shown in **Figs.2(a)** and **(b)** as a

function of methane molar fraction. The experimental data measured by Helbæk *et al.* [27] at

the temperature from 294.7 to 302.7 K and from 331.0 to 333.7 K are also plotted in the

figures. The simulated results of tracer diffusion coefficients showed similar

concentration-dependency of experimental results but not in agreement with the experimental

data at high *n*-decane concentration (x<0.4). It may be the limit of the spherical molecular

assumption.

2. Mutual Diffusion Coefficients

The mutual diffusion coefficients at $x_1 = 0.5$ and 303 K were calculated by changing the

concentration profiles according to the method described in METHOD section. They were

plotted in **Fig.3** as a function of difference between the average molar fractions (Δx_1) in the

regions A and B. The plots are the averaged mutual diffusion coefficients of regions C_I and

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C_II and the error bar shows the difference between two regions. By extrapolating the data shown in Fig.3 to $\Delta x_1 = 0$ we determined the mutual diffusion coefficients. The mutual diffusion coefficient obtained with 324 particles (upper figure) is close to the one obtained with 768 particles (lower figure) and the deviation is about 5 %. The deviation is smaller than the calculated errors of simulations for each Δx_1 shown by the error bar in Fig.3. Thus, we conducted the simulation with 324 particles to obtain the mutual diffusion coefficients at various molar fractions.

Fig.4(a) shows the mutual diffusion coefficients of the binary system as a function of methane molar fraction at 303 K. Anomalous behavior of mutual diffusion coefficients measured by Dysthe and Hafskjold [1] is shown by hollow symbols in **Fig.4(a)**. They reported the critical molar fraction of methane was 0.899 for methane + *n*-decane system at 303 K. The anomalous phenomena would be observed near the critical molar fraction. The broken lines in Fig.4 are the mutual diffusion coefficients calculated by the Darken equation using the tracer diffusion coefficients and thermodynamic factor. The decreases in mutual diffusion coefficients near the critical molar fraction observed in the experimental data are well described by the Darken equation. However, it should be noted that we need the tracer diffusion coefficients and the thermodynamic factor to calculate the mutual diffusion coefficient. The simulated results shown by solid symbols well expresses the anomalous decrease of the experimental mutual diffusion coefficient. The NEMD simulation could

directly calculate the mutual diffusion coefficients of the system without using adjustable parameters.

The mutual diffusion coefficients by the NEMD simulation at 333 K are compared with the calculated results by the Darken equation in **Fig.4(b)**. The simulated results are lower than the calculated results except for x_1=0.5. It is because that the temperature effect to thermodynamic factor of each molar fraction could not be represented exactly by the spherical molecular model with the combining rules, considering the small temperature dependence of self- and tracer diffusion coefficients. Since the results could not be compared to the experimental values at this temperature, we could not show which one is able to reproduce the experimental behavior. However, the trend of concentration dependence of simulated results well represents the complex concentration dependence calculated by the Darken equation. Although there are no the experimental mutual diffusion coefficients available at this temperature, we may conclude that the NEMD simulation proposed in this work would be a useful tool to predict the mutual diffusion coefficients of the system at various temperatures.

The calculated results of vapor liquid equilibria (VLE) for methane + *n*-decane system by the SRK-EOS are also shown in **Fig.5**. The simulated and experimental conditions (about 40 MPa) at 303 K would be single phase region above the critical pressure of VLE for the binary system. However the conditions (about 30 MPa) at 333 K might be in the two phase region at the vicinity of x_1=0.9. Hence, the mutual diffusion coefficients calculated by the Darken equation show a discontinuity at this region.

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The simulated mutual diffusion coefficients by the NEMD simulation without the thermodynamic factor well describe the experimental data, predicting the anomalous decrease in mutual diffusion coefficients as calculated by the Darken equation near the critical molar fraction. Consequently, the NEMD simulation presented in this work is applicable to calculate directly the mutual diffusion coefficients of the system without adjustable parameters.

CONCLUSIONS

The NEMD simulation with natural concentration gradient was adopted to calculate the mutual diffusion coefficients of methane + n-decane binary system. The applicability of spherical molecular model to the system was investigated by calculating the self- and tracer diffusion coefficients. The behavior of tracer diffusion coefficients as a function of methane mole fraction are well correlated by the results of equilibrium MD simulation. The simulated results of mutual diffusion coefficients by the NEMD simulation are quantitatively in agreement with the experimental data. The simulated results showed the same trend with the experimental data as well as the calculated results by the Darken equation using tracer diffusion coefficients with the thermodynamic factor. Although the spherical molecular model is one of the simplest models, the anomalous behavior of mutual diffusion coefficients near the critical mole fraction could be presented quantitatively by the present NEMD simulation without considering the thermodynamic factor. The direct estimation method of mutual diffusion coefficients by the NEMD simulation proposed in the present work would be

effective to calculate the complex behavior of mutual diffusion coefficients of binary mixtures.

Acknowledgment

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Table 1   Physical properties and potential parameters

	T_C	P_C	ω	σ	ε/k
	[K]	[MPa]	[-]	[nm]	[K]
methane (1)	190.6[*1]	4.599[*1]	0.011[*1]	0.392[*2]	141.2[*2]
n-decane (2)	617.7[*1]	21.1[*1]	0.490[*1]	0.751[*2]	457.6[*2]

*1   Poling *et al*. [24].

*2   The potential parameters were determined by the corresponding method of Nicolas *et al.* [23] using critical temperature and pressure.

Figure Captions

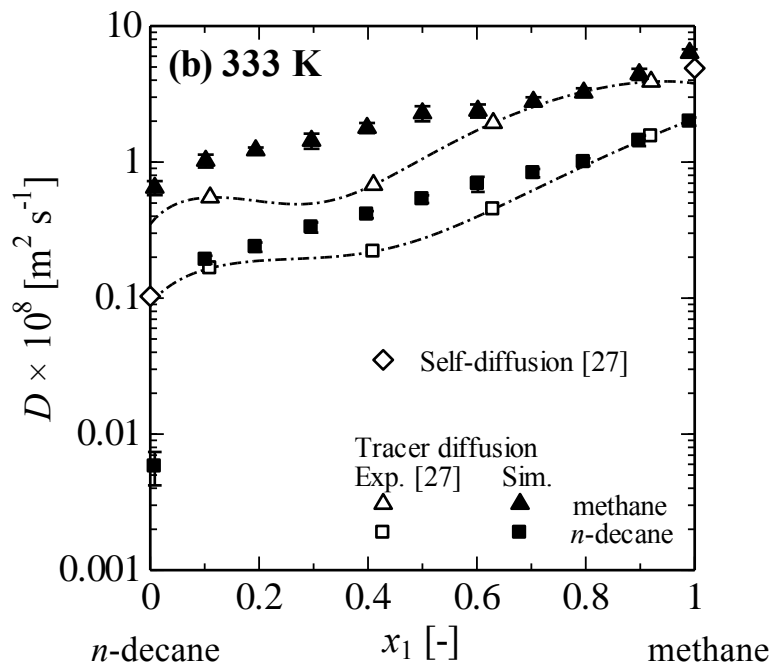**Figure 1   Snap shot and simulation cell.**

Figure 2   Simulated results and experimental data of self- and tracer diffusion

coefficients at 303 K (a) and 333 K (b).

Figure 3   Detarmination method of mutual diffusion coefficient at x_1=0.5 and 303 K.

Figure 4   Simulated results and experimental data of mutual diffusion coefficients at

303 K (a) and 333 K (b).

Figure 5   Vapor-liquid equilibria of methane + n-decane system.

methane   *n*-decane

(a) Snap shot

E_I E_{II} E_{III} E_{IV}

A C_I B C_{II} A

Δx Δx
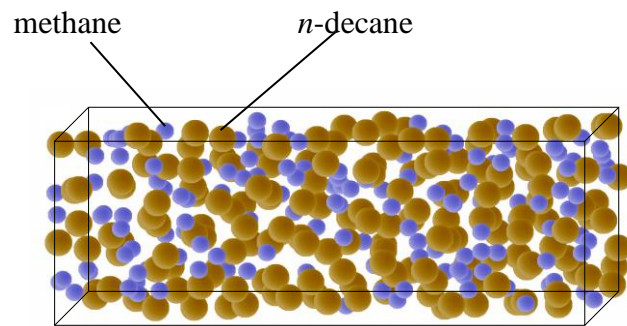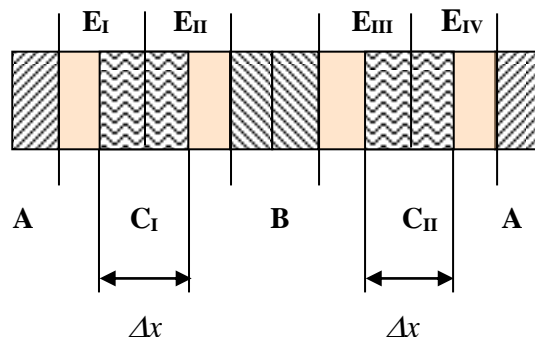
Concentration control region, A

Concentration control region, B

Flux calculation regions, C_I, C_{II}

(b) Simulation cell

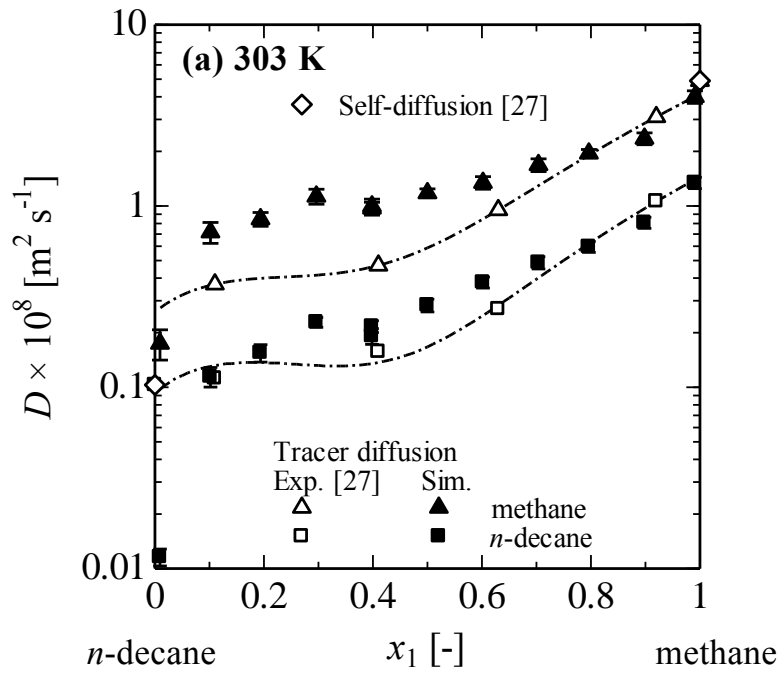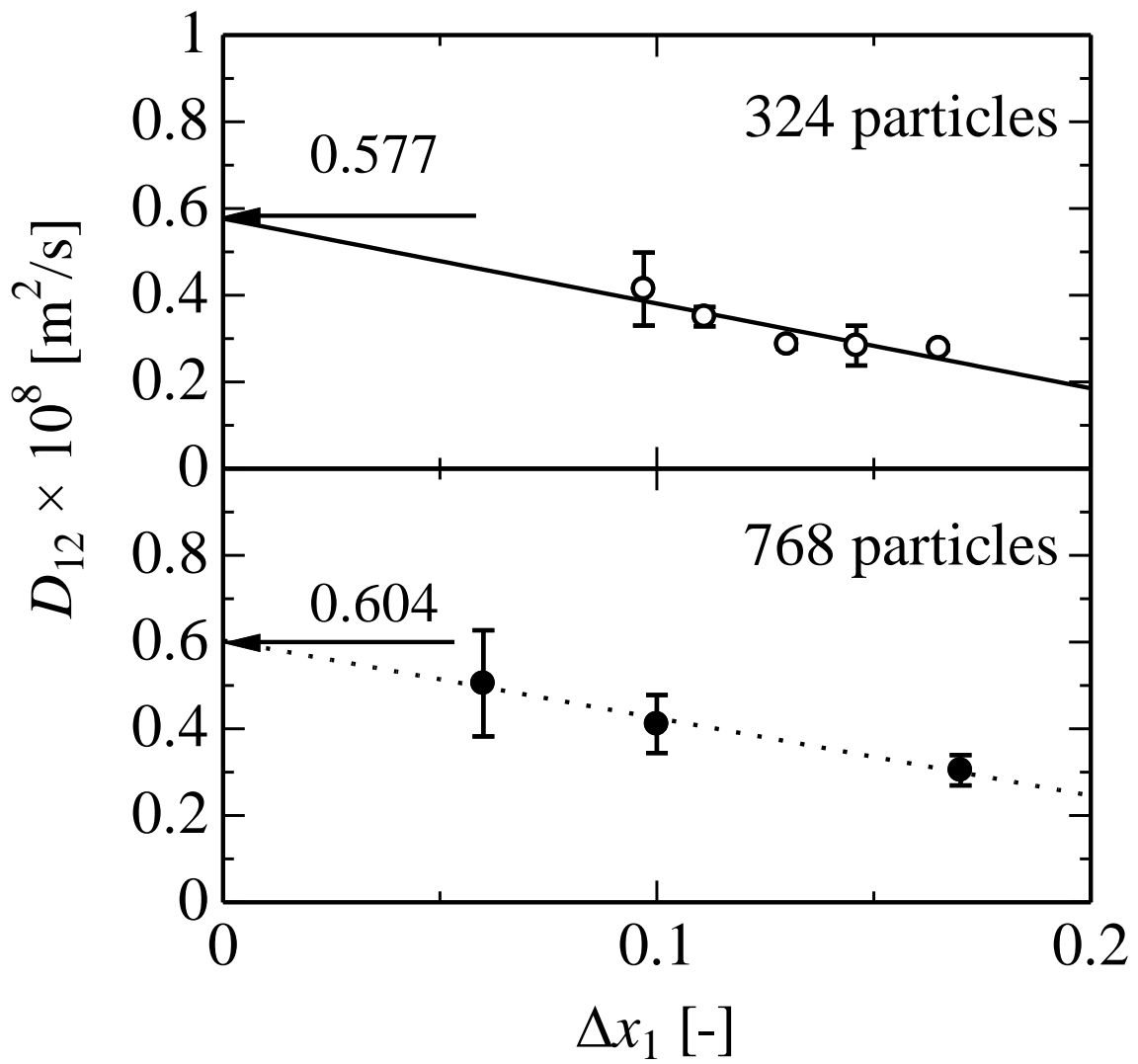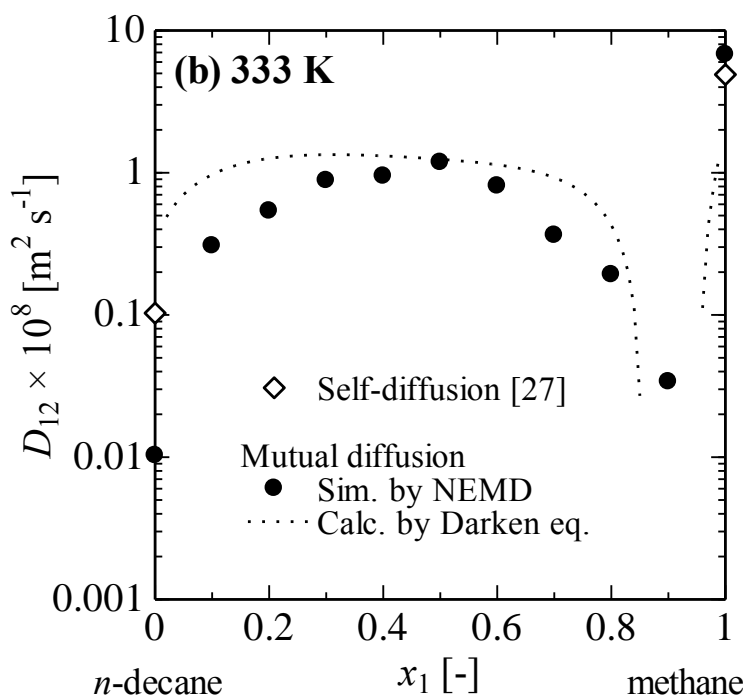**Figure 1   Snap shot and simulation cell.**

Figure 2   Simulated results and experimental data of self- and tracer diffusion

coefficients at 303 K (a) and 333 K (b).

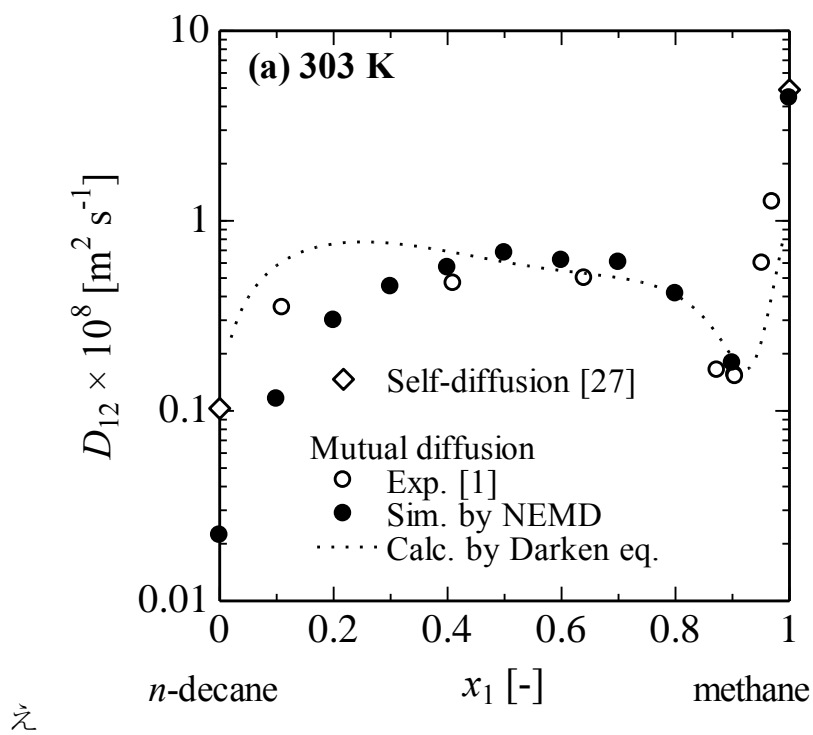**Figure 3**   Determination method of mutual diffusion coefficient at x_1=0.5 and 303 K.

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Figure 4 Simulated results and experimental data of mutual diffusion coefficients at
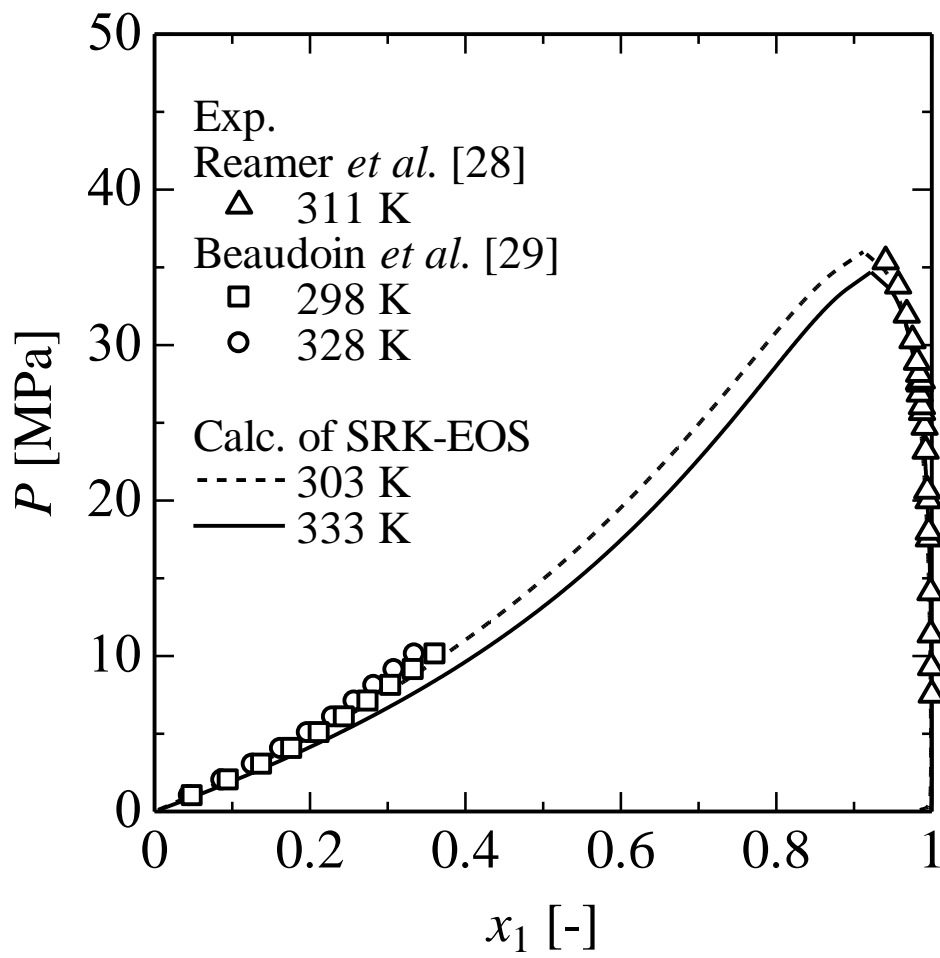
303 K (a) and 333 K (b).

Figure 5 **Vapor-liquid equilibria of methane + *n*-decane system.**