JASMAC
Conference of the Japan Society of Microgravity Appllication

PS29

ソーレ係数算出に向けた水/エタノール系の分子動力学計算

Molecular Dynamics Simulation of Water/Ethanol System for Calculating the Soret Coefficient

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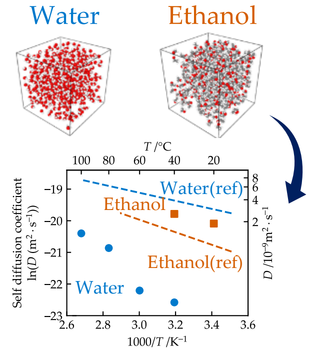

Abstract: This study evaluates the applicability of the machine learning potential PFP for calculating the Soret coefficient by analyzing molecular diffusion and structural properties. Molecular dynamics simulations were conducted using PFP version 6.0.0 for pure water (600 molecules) and pure ethanol (400 molecules) on Matlantis. The results were compared with classical force fields (TIP4P/2005 for water, OPLS-AA for ethanol). Initial configurations were generated using Packmol, followed by equilibration for 50 ps in the NPT ensemble and a 10 ps production run in the NVT ensemble with a 1 fs time step. Self-diffusion coefficients D and partial pair distribution functions $g_{ij}(r)$ were calculated from production trajectories. PFP reproduced molecular structures similar to those obtained from classical models, with peak positions in $g_{ij}(r)$ largely consistent. D for ethanol agreed well with experimental values, whereas D for water was about an order of magnitude lower, which can be attributed to overestimated hydrogen bonding inherited from its Perdew-Burke-Ernzerhof functional training data. Based on a water/ethanol mixture, the time required for water molecules to diffuse across half the simulation box was estimated to be approximately 13 ns, indicating that at least this simulation duration is necessary to achieve steady-state concentration profiles under the Soret effect.

Keywords: Soret effect, Molecular dynamics, Water/ethanol, Self-diffusion coefficient, Partial pair distribution function, Machine learning potential

1. Introduction

The Soret effect is a mass transport phenomenon induced by a temperature gradient in a multi-component system. The Soret coefficient S_T, which quantifies this effect, has been measured in microgravity environments[1)] to achieve high accuracy, making a more convenient method desirable. Molecular dynamics (MD) simulation offers a promising solution. Recently, machine learning potentials, such as PreFerred Potential (PFP)[2)], that can be versatile, have become available. However, unlike classical force fields that are meticulously parameterized for specific systems, these versatile potentials must be validated for the target system in terms of dynamics and structures of molecules. The objective of this research is to evaluate diffusion and the structures of molecules of PFP for calculating S_T.

2. Computational Procedures

MD simulations were carried out with 600 molecules for pure water and 400 molecules for pure ethanol using PFP version 6.0.0 on Matlantis3), an atomic-level AI simulator. For comparison, a 1000-molecule water system with the TIP4P/2005 model4) and a 1000-molecule ethanol system with the OPLS-AA model5) were also simulated. Initial configurations were generated by randomly placing molecules with Packmol6). Each system was equilibrated for 50 ps in the NPT ensemble, followed by 10 ps production run in the NVT ensemble with a 1 fs time step. From the production run trajectories, the self-diffusion coefficient D and partial pair distribution function $g_{ij}(r)$ were calculated.

3. Results

Figure 1 shows the self-diffusion coefficient calculated by PFP. The result for ethanol was close to the experimental value7), but D for water was an order of magnitude lower than its experimental value8).

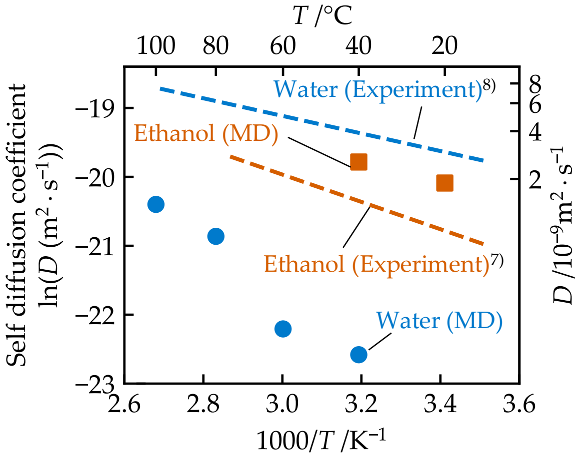

Figure 1. Self-diffusion coefficients of water and ethanol. The plots and lines show the results of PFP in this study and reference data obtained from experiments7, 8).

Figure 2 shows the partial pair distribution functions $g_{ij}(r)$ at 40°C. These functions describe the probability of finding a j-type atom at a distance r from a reference i-type atom. Overall, the peak positions obtained using PFP corresponded well with those from classical force fields. Focusing on the details of $g_{OO}(r)$ of water, the height of the first peak of PFP was larger than that of TIP4P, as shown in **Figs. 2(a)** and **(b)**. Moreover, PFP produced an additional peak in $g_{OH}(r)$ of ethanol that was absent with OPLS-AA, see **Fig. 2(c)**.

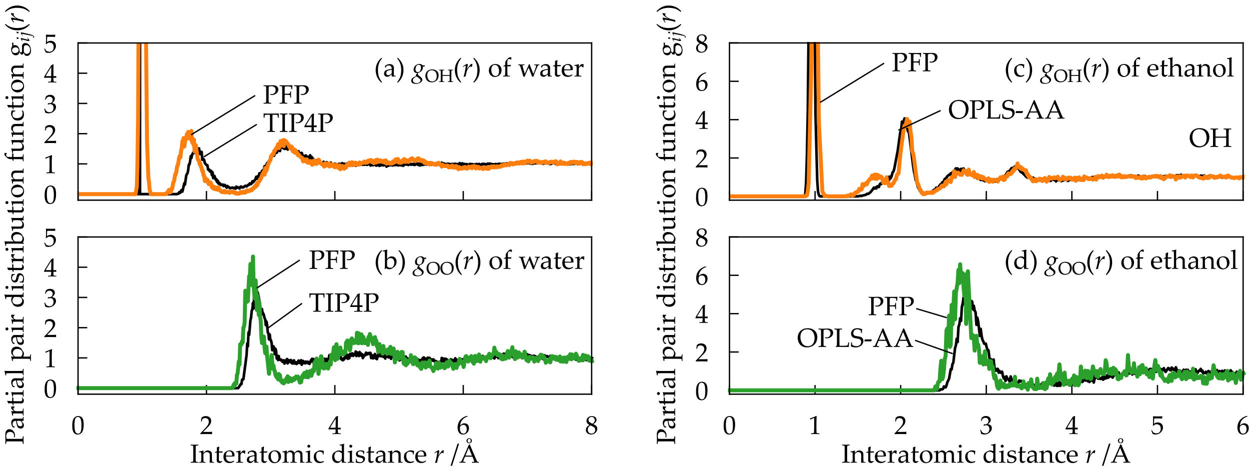

Figure 2. Partial pair distribution function $g_{ij}(r)$ calculated with PFP and classical potentials at 40°C: (a) $g_{OH}(r)$ of water; (b) $g_{OO}(r)$ of water; (c) $g_{OH}(r)$ of ethanol; (d) $g_{OO}(r)$ of water.

4. Discussion

The Perdew-Burke-Ernzerhof functional, which provides the training data for PFP2), is known to overestimate hydrogen bonding between water molecules, resulting in a small self-diffusion coefficient and a large first peak of $g_{OO}(r)$ for water9). It is suggested that PFP inherits these tendencies. Furthermore, to estimate the simulation time required to calculate the Soret effect in a water/ethanol mixture using MD, a water/ethanol mixture with 300 molecules of each component was considered. The system was placed in a rectangular box with an aspect ratio of 1:2. Assuming a density of 0.9 g/cm^3 (9×10^2 kg/m^3), the box width ($2w$) is calculated to be 52 Å (5.2×10^{-9} m). The time t needed for water molecules to diffuse across half the box width at 40°C can be estimated by the following equation10).

$$t = 3\tau_r = \frac{3w^2}{\pi^2 D} \tag{1}$$

resulting in approximately 13 ns. Here, τ_r is the relaxation time of water diffusion. Therefore, a simulation time of at least 13 ns is required for the concentration profile to reach a steady state under the Soret effect.

5. Conclusions

PFP reproduces the structures of molecules similar to those obtained from classical force fields. In addition, the self-diffusion coefficient of water calculated with PFP is approximately one order of magnitude lower than the experimental value, indicating that at least 13 ns of simulation time is required for calculating the Soret effect.

Acknowledgments

This research was supported by the "FY2024 Waseda University – ENEOS FS Research Grant", Kimura Foundry Co., Ltd., and the Embodiment Informatics Course of Waseda University. We are grateful to them.

Conflicts of Interest

The authors declare no conflict of interest.

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