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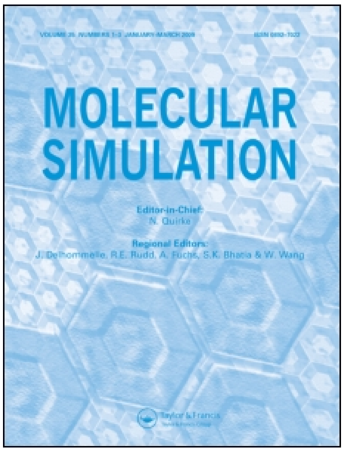

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Molecular dynamics simulations of structure-H hydrates formed with methane and 3,3-dimethylpentane or 2,2-dimethylpentane

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Molecular dynamics simulations of structure-H hydrates formed with methane and 3,3-dimethylpentane or 2,2-dimethylpentane

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Molecular dynamics (MD) simulations of structure-H hydrates formed with methane +2,2-dimethylpentane and methane +3,3-dimethylpentane were performed in the *NPT* ensemble. We obtained the trajectories and the distribution profile of the sites of the dimethylpentane molecules. The results revealed the distinct molecular motions of the two dimethylpentanes in the cages of the hydrates. The dimethylbutane molecules mainly exhibited translational motion, but rotational motions were also observed. Despite the similar molecular structure of the two dimethylpentanes, distinct molecular motions were observed; a greater spacial range of molecular motions was observed with 2,2-dimethylpentane. The difference in the unit cell sizes of the hydrates, which were relevant to the different molecular motions, was also observed.

Keywords: Hydrates; Structure-H; Molecular dynamics; Water; Methane; Dimethylpentane

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1. Introduction

Structure-H hydrates are crystalline solids composed of three types of the cages, 5^{12}, $4^{3}5^{6}6^{3}$ and $5^{12}6^{8}$ cages that are formed with hydrogen-bonded water molecules and the guest molecules enclosed in the cages [1]. Guest molecules with a relatively smaller molecular size such as methane are enclosed in the 5^{12} and $4^{3}5^{6}6^{3}$ cages, whereas large molecule guest substances (LMGS) are such as methylcyclohexane in the $5^{12}6^{8}$ cages. Guest molecules in hydrate structures are expected to behave unlike themselves in the liquid and vapor states and their motions are expected to affect the thermodynamic properties of the hydrates. The molecular dynamics (MD) simulation could be a significant tool for better understanding the molecular motion as well as the thermodynamic properties of the structure-H hydrates.

Okayno and Yasuoka very recently performed MD simulations on the structure-H hydrates formed with methane and various LMGSs using the spherical one-site Lenard-Johnes potential model for the guest substances [2]. The use of the one-site model for the LMGSs may be beneficial as one can readily test various chemical species of LMGSs by changing the parameter set in the potential model. However, it is reported that the shape of the LMGS molecules is an important factor for determining the thermodynamics properties of the hydrates [3]. Thus, the rather complex shape of the LMGS molecules should be considered in the MD simulations. As an example of MD simulation studies considering the molecular shape of LMGS molecules, we have performed MD simulations for the two different structure-H hydrates; one being a hydrate formed with methane and 2,2-dimethylpentane and the other being with methane and 3,3-dimethylpentane, using the multi-site OPLS-UA model [4] for the two dimethylpentanes. It was experimentally known that the equilibrium pressures for the two hydrates are significantly different despite the apparent similarity in the two LMGSs; 4.56 MPa for the 2,2-dimethylpentane system whereas 3.01 MPa for the 3,3-dimethylpentane system at the same temperature of 279.2 K [5]. This paper describes the difference of the molecular motions in the two LMGSs in the hydrate that were determined from the analysis of the MD simulation data.

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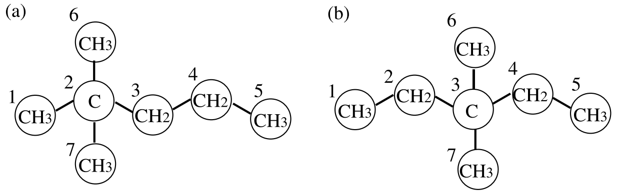

Figure 1. Structures of the computational model of (a) 2,2-dimethylpentane and (b) 3,3-dimethylpentane. The numbers indicate the site number.

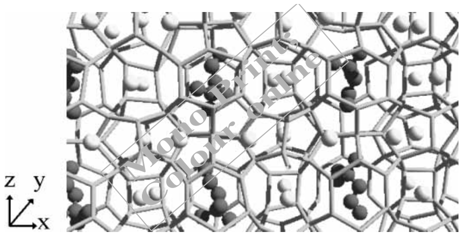

Figure 2. Snapshot of structure-H hydrates formed with methane and 2,2-dimethylpentane.

2. Methodology

2.1 Molecular model

MD simulations were performed for a 6120 water molecules + 900 methane molecules + 180 2,2-dimethylpentane molecules system (2,2-dimethylpentane hydrate) and a 6120 water molecules + 900 methane molecules +180 3,3-dimethylpentane molecules system (3,3-dimethylpentane hydrate). TIP4P [6] and OPLS-UA [4] were adopted for the models of the water and methane or LMGS, respectively. OPLS-UA regards an LMGS as a multi-site model as shown in figure 1. The multi-site model could provide more information from the MD simulations, e.g. intramolecular configuration and rotation. The coulombic interactions were exactly calculated by the Ewald method. The forces caused by the two-body interactions were calculated by the special purpose computer for MD simulations, MDGRAPE-2 [7].

2.2 Simulation method

Newton's laws of motion were integrated using the leapfrog algorithm [8]. The molecular structures were preserved by the SHAKE constraint algorithm [9]. All simulations were carried out under *NPT* constant conditions. The simulation condition, pressure and temperature, was chosen from those at which the structure-H hydrates are formed in the experiments [5]. The pressure was set at 20.0 MPa using the Andersen method [10]. The temperature was maintained at 280 K by the Berendsen thermostat [11]. The initial positions of the water molecules were quoted from the positions presented in a previous study [2]. In this study, the MD simulations of the 2,2-dimethylpentane hydrate and 3,3-dimethylpentane hydrate were performed for 40 ps, while the potential energies of both hydrates converged within a few ps. The MD simulations of 100 ps were then performed for sampling.

3. Results and discussion

Figure 2 shows the configuration of the molecules in the 2,2-dimethylpentane hydrate. It can be seen in this snapshot that each dimethylpentane molecule in each $5^{12}6^8$ cage is arranged in a configuration fitting into the inner space of the cage. This may be dominantly determined by the interactions between the sites in the 2,2-dimethylpentane and 3,3-dimethylpentane molecules and water molecules enclosing the guest molecules, which activate and confine the motion of the dimethylpentane molecules. The molecular motions of the dimethylpentanes were characterized by the trajectory of the positions of the sites in the dimethylpentane molecules. Figures 3 and 4 show the trajectories of the positions of the sites in the 2,2-dimethylpentane and 3,3-dimethlypentane molecules which were observed during the 3000 steps (= 6.0 ps). Figure 3 shows the most frequently-observed trajectories of the positions of the sites in the 2,2-dimethylpentane and 3,3-dimethlypentane molecules. The trajectories in figure 3 represent the translational motion of the dimethylpentane molecules. In figure 3, the trajectory of every site tends to remain around a certain position. Every site has a stable position in the $5^{12}6^8$ cage.

As described above, the translational motions of the dimethylpentane molecules were most frequently observed. In addition to the translational motions, rotational motions of the molecules were sometimes observed. The trajectory of this category of molecular motions are shown in figure 4. In figure 4 (a) and (c), the trajectory of every site is like a circle with its center at the center of the cage, that is, every site rotates around the center of the cage in the $x-y$ plane. In figure 4 (b) and (d), the trajectory of every atom site is like an ellipse. The longest diameter of the ellipse runs parallel to the x-axis. Therefore, these trajectories indicate the rotational motions of the LMGS molecules along the z-axis. The results indicated in figures 3 and 4 are the first to show such rotational and translational motions of the guest molecules with relatively large molecular sizes like the methylpentanes, which are known from the MD simulations using the multi-site molecular models for the guest molecules. The differences in the motions of the 2,2-dimethylpentane and 3,3-dimethylpentane molecules, illustrated in figures 3 and 4, are discussed in more detail below.

The positions of 180 molecules of 2,2-dimethylpentane and 3,3-dimethylpentane were sampled for 100 ps to determine the distribution along the x- and z-axes as shown in figure 5. Because symmetrical distribution profiles were observed, the horizontal axis of figure 5 is the distance from the center of the $5^{12}6^8$ cage. Figure 5 clearly indicates that there are stable positions for the sites

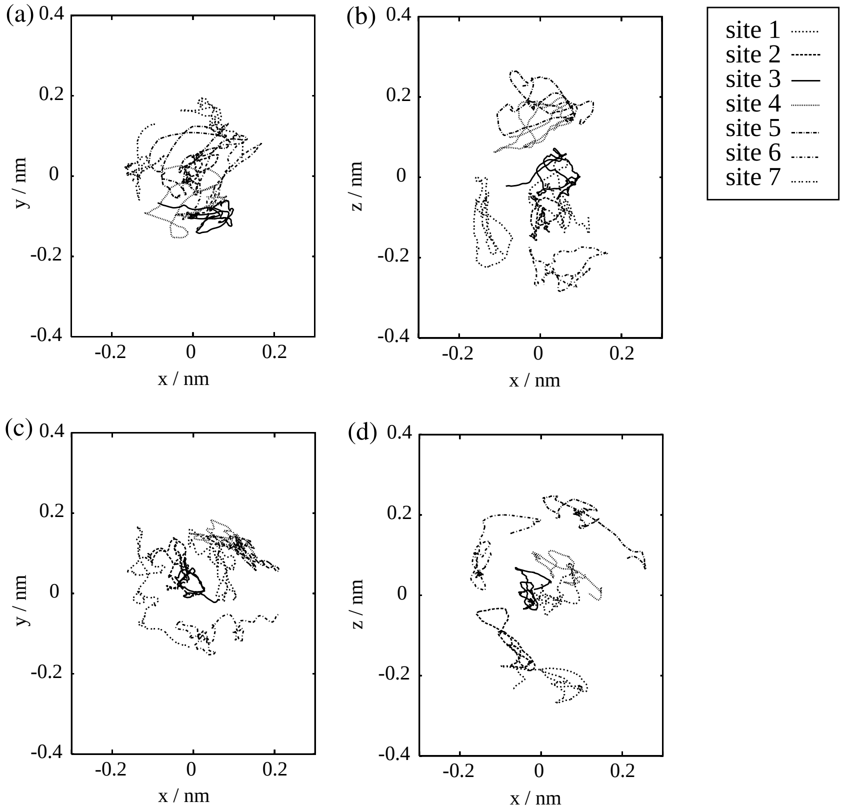

Figure 3. The trajectory of the sites of (a) and (b) 2,2-dimethylpentane and (c) and (d) 3,3-dimethylpentane in a $5^{12}6^{8}$ cage of structure-H hydrates, which represents the translational motions of the dimethylpentane molecules. The origin of *x*, *y* and *z* was set at the center of the $5^{12}6^{8}$ cage.

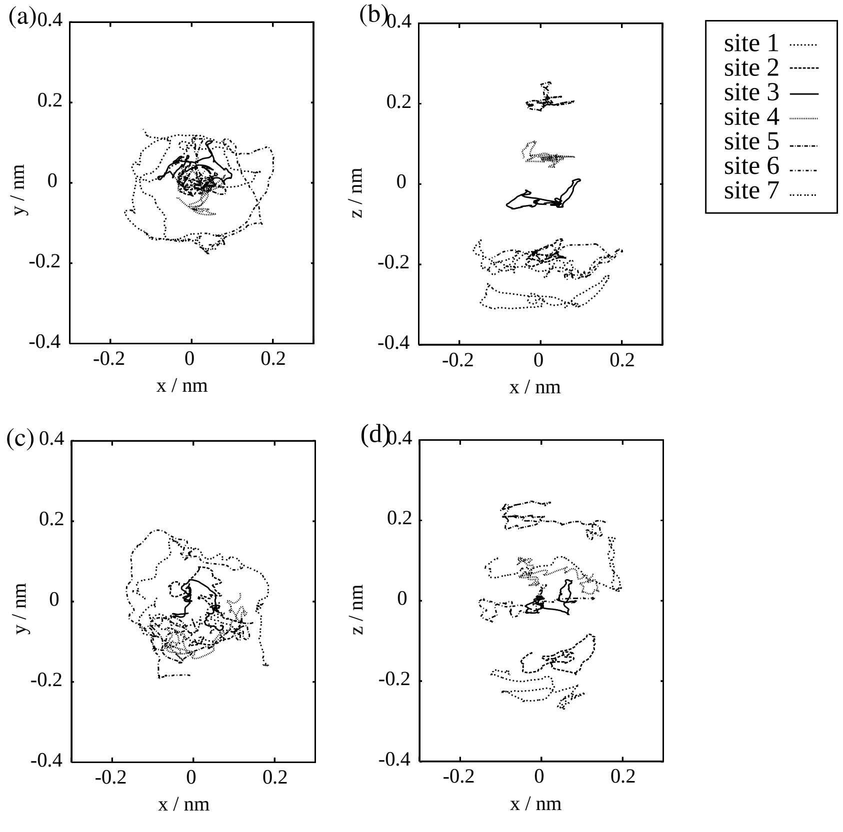

Figure 4. The trajectory of the sites of (a) and (b) 2,2-dimethylpentane and (c) and (d) 3,3-dimethylpentane in a $5^{12}6^{8}$ cage of structure-H hydrates, which represents the translational and rotational motions of the dimethylpentane molecules. The origin of *x*, *y* and *z* was set at the center of the $5^{12}6^{8}$ cage.

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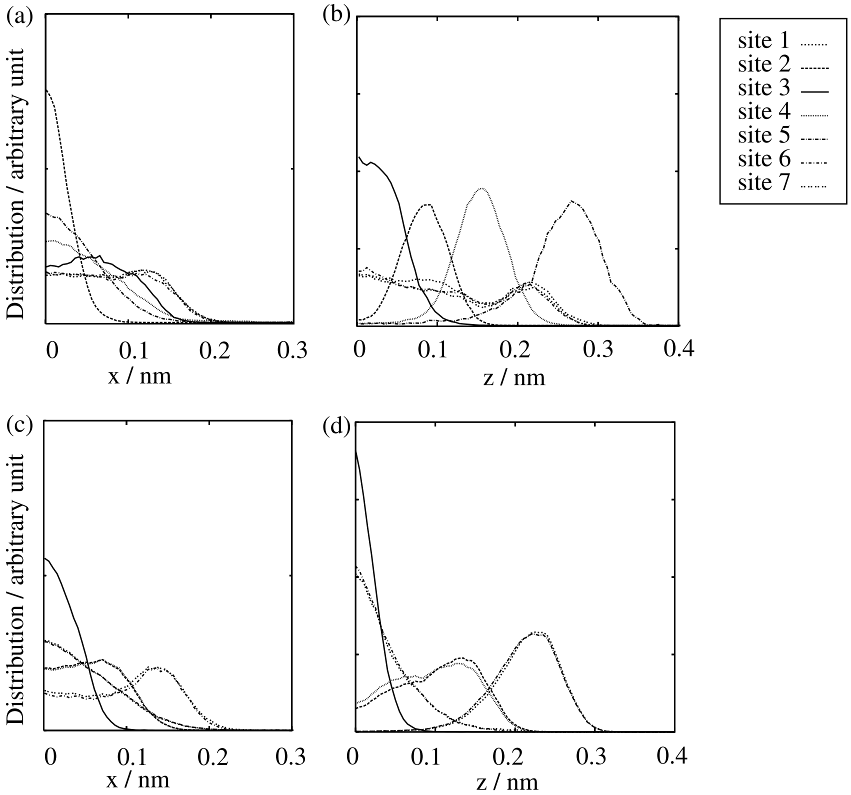

Figure 5. The distribution of positions of the sites of (a) and (b) 2,2-dimethylpentane and (c) and (d) 3,3-dimethylpentane in a $5^{12}6^8$ cage of structure-H hydrates during 6 ps. *X*, *y* and *z* shows the distance from the center of the $5^{12}6^8$ cage along the *x*, *y* and *z*, respectively, which represents the rotational motions of the molecules.

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and different stable positions are observed depending on the chemical species of the dimethylbutanes.

In the distribution along x, site 2 of 2,2-dimethylpentane and site 3 of 3,3-dimethylpentane have a sharp peak at $x = 0$, indicating the molecules tend to stay at the center of the x-axis. Both species of the LMGSs may be viewed as n-pentanes with branched methyl groups and hence one might expect that site 3 in both LMGSs would be the most stable at the center considering the interactions with water molecules along the z-axis. However, site 2 of 2,2-dimethylpentane tends to stay at the center of the x–y plane. This may be mainly due to the interactions of site 2 and the branched sites with water molecules in the x–y plane. The branched sites make site 2 stably located at the center of x–y plane. As for the 2,2-dimethylpentane, the peaks of sites 1, 6 and 7 are almost the same, $x = 0.12$ nm due to the molecular geometry; sites 1, 6 and 7 are all branched sites connected to site 2. Sites 4 and 5 have a peak at $x = 0$, whereas site 3 peaks at $x = 0.06$ nm. The distribution profiles differ depending on the sites. The existence of these several peak positions of the sites may be ascribed to the complex structure of the 2,2-dimethylpentane molecule. As for the 3,3-dimethylpentane, the distribution peak positions of sites 1 and 5, sites 2 and 4 and sites 6 and 7 are almost the same, as expected from the symmetrical structure of the molecule.

For the distribution along the z, every atom has a shaper peak than along the x, indicating that the LMGS molecules tend to be more ordered along the z-axis than along the x-axis. In both species of the LMGSs, site 3 has the sharpest peak. As for the 2,2-dimethylpentane, the sharp peak appeared at $z = 0$ nm for site 3, $z = 0.08$ nm for site 2, $z = 0.15$ nm for site 4, $z = 0.21$ nm for sites 1, 6 and 7 and $z = 0.27$ nm for site 5 whereas a loose peak appeared at $z = 0$ for sites 1, 6 and 7. As for 3,3-dimethylpentane, the peaks are located at $z = 0$ nm for sites 3, 6 and 7, at $z = 0.13$ nm for sites 2 and 4, at $z = 0.23$ nm for sites 1 and 5.

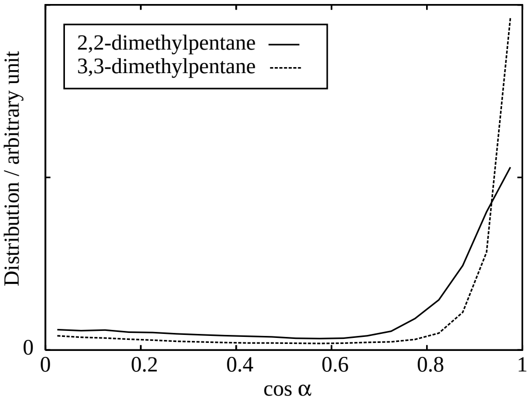

Figure 6. The distributions of cos α which is the angle between z-axis and the vector from site 2 to site 4 of 2,2-dimethylpentane and 3,3-dimethylpentane.

We focused on the values of z for the outermost-site peaks; 0.27 nm for 2,2-dimethylpentane and 0.23 nm for 3,3-dimethylpentane. These peak positions have a correlation with the size of the cages of the water molecules or with the size of the unit cell of the hydrate. The volume and lengths along the x-axis and along the z-axis of the unit cell of the hydrates were deduced from the MD-simulation data to be 1.328 nm^3, 1.231 and 1.013 nm for the 2,2-dimethylpentane hydrate and 1.317 nm^3, 1.234 and 1.004 nm for the 3,3-dimethylpentane hydrate. The spacial range of the motions of the LMGS molecules may be related to the lengths of the cages. The differences in the molecular motions and the resultant change in the configuration of the water-molecule cage may, affect the thermodynamic stability of the hydrates. However, the factors such as the molecular motions and the unit cell volume cannot be directly related to the thermodynamic stability. To exactly evaluate the thermodynamic stabilities, the quantities directly relevant to the stabilities, e.g. the free energy, should therefore be investigated in future studies.

Furthermore, the inclinations of the LMGS molecules were evaluated by the angle α which is the angle between the z-axis and the vector from site 2 to site 4. In figure 6, the distributions of the angle show that the 2,2-dimethylpentanes tend to have a larger α than that of 3,3-dimethylpentane although both species of the LMGSs tend to stay at $\cos \alpha = 1$. This may affect the z-range of the motions of the LMGS molecules.

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4. Conclusions

MD simulations were performed for the structure-H hydrates each formed with methane and 2,2-dimethylpentane or 3,3-diemthylpentane. Different motions for the two different dimethylpentane molecules were observed in the simulation. Although translational or simultaneous translational and rotational motions around the center of the $5^{12}6^8$ cage along z-axis were commonly observed for the two dimethlypentane molecules, site 2 of the 2,2-dimethylpentane molecule and site 3 of the 3,3-dimethylpentane molecule were located at the center along the z-axis. This difference is caused by the change in the interaction of the dimethylpentane molecules with water molecules forming cages. The different water–dimethlypentane interactions are relevant to the different molecular motions and configurations of the two different dimethylpentanes. The different motions of the two different dimethylpentane molecules are relevant to the difference in the unit cell volume of the hydrates and therefore, may affect the thermodynamic stability of the hydrates.

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