

# VISUALIZATION OF MOLECULAR DYNAMICS BY SIMULATION

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The formation mechanism of methane hydrate is investigated at a molecular level using a molecular dynamics method. The key to whether or not methane hydrates can be formed is the stability of the hydrate structure. Computer simulation results show that very stable methane hydrates type I can be formed below 275K. The stability of the hydrates increasingly degrades logarithmically as a power function above 275K up to 300K.

## INTRODUCTION

The extensive accumulations of natural gas hydrates in permafrost regions and in sediments on deep ocean floors have recently been explored. Sloan<sup>1)</sup> suggests that the total resource may surpass the energy content of the total fossil fuel reserves by a factor of two. Since methane gas (main constituent of natural gas) could be recovered by the dissolution of methane hydrates, natural gas hydrates are a potential future energy supply. On the other hand, hydrates have been suggested as a natural gas storage medium<sup>2)3)</sup> because of their high storage efficiency. Compared to liquid natural gas (LNG), hydrates have been proven to have the advantages of lower storage pressure and temperature at a lower cost<sup>4)</sup>. More detailed knowledge of the thermodynamic, kinetic, and mechanical parameters that affect the formation and dissolution of hydrates is required<sup>5)6)</sup>. An attempt is made here to form methane hydrate type I under the conditions allowing all the molecules to move freely at a series of temperatures, and to gain detailed information on the crystal structure in order to compare it to the experimental data.

## SIMULATION PROCEDURE

The computer simulation using a molecular dynamics method requires a model to specify initial and boundary conditions, an equation of motion and its solution method, and a most important interaction potential between particles. For a crystal solid, a single unit cell is selected as the model system. For methane hydrate type I, it is a cube of length 12.0 Å containing 46 water molecules and 8 methane molecules. In general, hydrate formation simulation should be started from the initial condition of a random configuration. The equations of motion are solved by the 'leap-frog' algorithm. The constant-NVT method is used, in which the number of molecules, the volume size and the temperature remains constant throughout the simulation. The total system potential energy  $\Phi$  is a sum of pair-wise potential energies over all the pairs of particles, where  $i$  and  $j$  denote the interaction sites.

$\Phi = \sum \phi_{ij}$  (1). For the interactions between water molecules, the analytical potential model of Matsuoka, Clementi, and Yoshimine (MCY)<sup>7)</sup> is used. (It consistently gives more accurate predictions of the ice crystal structures than do other potentials such as those of ST2, BNS, Rowlinson,

RSL, RSL2, Watts, LS, TI4P, and SPC<sup>8)</sup>). For a long-range electrostatic interaction, Ewald's method is used<sup>9)</sup>. For a short-range interaction such as the exponential terms in MCY and the terms in L-J, the potential calculation is truncated with a spherical cutoff distance of half the length of the cube edge.

## RESULTS & DISCUSSION

According to the previous study<sup>8)</sup>, The O-O atomic pair distance<sup>8)</sup> predicted by the MCY potential is about 7% too large. However, the geometry of the crystal lattice is not influenced by that error. To resolve this problem, the O-O atomic pair distance is scaled here by the factor of 1.07 only for the MCY potential energy calculation between water molecules. As a result, the practical O-O pair distance in the simulation equals the normal value. .

**Crystal structure:** The system potential at 0K is nearly minimum and stable during the latter part of the simulation, i.e., the system is in an equilibrium state. The structure obtained at this time is defined as the static structure and is shown in Fig.1. It is the structure of hydrate type I. The drawings are made using RasMac v2.6. Figure 1 shows the hydrogen-bonded network of water molecules. Fig. 2 shows the trajectories of molecule motion at 350K in two dimensions, monitored every 100 steps over the last 5000 steps. In these figures, the trajectories of 46 water molecules and 8 methane molecules in the cell are shown as the projections on the YZ plane. As is shown the hydrate structure is completely destroyed at 350K and it is concluded that it is impossible to form methane hydrate type I at 350K. Another point of interest is that the range of motion of a methane molecule in a large cage is greater than that in a small cage. This implies that a methane molecule in a large cage more easily escapes from the hydrates than that in a small cage. The quantitative descriptions of the hydrate structure will be given below.

**Pair distribution function:** Fig. 3 exhibits the simulated  $g_{HH}(R)$ , the pair distribution function of hydrogen at different temperatures, where the bin width is 0.1 Å. Each curve is obtained as the average of data collected over the last 1000 steps. At 0K, the first peak position in  $g_{HH}(R)$  is at around 2.4 Å. This means the distance between the two nearest hydrogen atoms belonging to the two nearest water molecules, is 2.4 Å. Up to 300K, the changes in  $g_{HH}(R)$  are confined to the reductions in the peak heights and the increases in peak widths as the temperature increases. According to the present simulation studies, this is a distinct feature in the hydrate structure stability.

**Tetrahedral angle:** As mentioned above, every water molecule is hydrogen-bonded to 4 others in a tetrahedral structure. According to Uttormark et al.<sup>9)</sup>, an angular order parameter, F, can be used to evaluate the deviation from perfect tetrahedral bonding: 
$$F = \sum_{i=1}^6 (|\cos X_i| |\cos X_{i+1}| + 0.11)^2$$

where  $X_i$  is the bond angle formed by the "test" oxygen atom with pairs of oxygen atoms from among its nearest-neighboring water molecules and  $6=4(4-1)/2$  is the number of independent angles. The nearest-neighboring molecules are considered to be those within a distance less than the position of the first minimum in the oxygen-oxygen pair distribution function. F has a value of zero for the perfect tetrahedral structure, and positive nonzero values for all other structures. The calculated results for the distribution of the angular order parameter, where the bin width is 0.006, are shown in Fig.4. For the static structure at 0K, the first sharp peak position is 0. This means that the hydrate structure is hydrogen-bonded by means of a nearly perfect tetrahedron. With increasing temperature, the peak positions shift to larger values, and

the curves become flatter. For comparison, the distribution of F for the hydrates at 240K from Baez and Clancy<sup>10)</sup> are also presented in Fig.4. The slight differences in the peak height may be due to the different methods of collecting data. It is shown that at 350K, the curve is almost horizontal, so that the feature of the tetrahedral structure has disappeared completely.

### CONCLUSION

The molecular dynamics simulations conducted at different temperatures under the constant-NVT conditions reveals the molecular mechanism of hydrate formation. Methane Hydrate type I can be formed more stably below 275K, although it can also be formed up to 300K, but not at 350K.

### REFERENCES

1) Sloan, E. D., Jr., 1994, "conference Overview," *Annals of the New York Academy of Sciences*, vol.715, pp.18-19. 2) Ota, M., Komatsu, H., Murakami K., Sakamoto M., 1997, *Int Conf On Fluid and Thermal Energy Conversion*, Yogyakarta, Indonesia, pp. 413~417. 3)Wagatsuma, Y., Ota, M., Qi, Y. X., et al, 1998, *Nat Thermal Eng Conf*, No. 98-7, JSME, pp. 151~152.(in Japanese). 4) Gudmundsson, J. S., Borrehaug A., 1996, *The Second Inter Conf on Natural Gas Hydrates*, Toulouse, France. pp. 415-422. 5) Ota M. and Yingxia Qi, *JSME Int J*, B,43-4,2000,pp.719-726. 6) Qi Y. and Ota, M., *Proc NHTC'00, 34 th National Heat Transfer Conf*, Pittsburgh, August 2000, p.1-8. 7) Matsuoka, O., Clementi, E., Yoshimine, M., 1976, *J. Chem. Phys.*, Vol. 64, No. 4, pp. 1351-1361. 8) Morse, M. D., Rice, S. A., 1981, "Tests of Effective Pair Potentials for Water: Predicted Ice Structures", *J. Chem. Phys.*, Vol.76, pp. 650-660. 9) Uttormark, M. J., 1992, *Ph.D. dissertation*, Cornell Univ, Ithaca, NY. 10)Baez, L. A., and Clancy, P., *Ann New York Acad Sci*, vol.715, 1994, pp. 177-186.

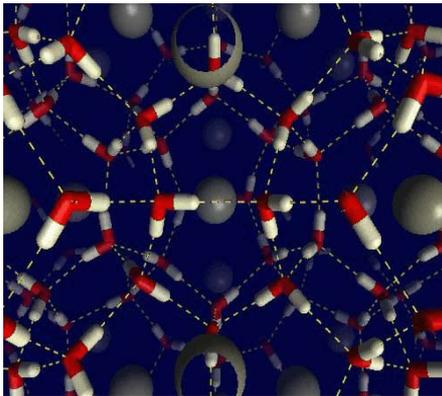


Fig. 1 Hydrate lattice structure shown in three-dimensions  
The gray represent methane molecules and the red - white water molecules.

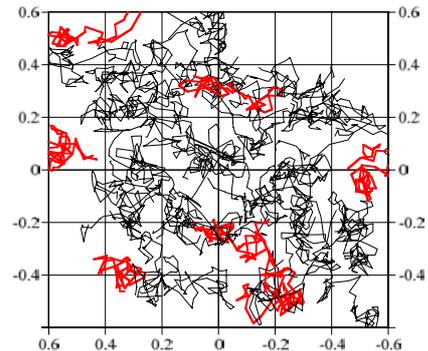


Fig. 2 Trajectories of motion of the molecular centre-of-mass at 350K

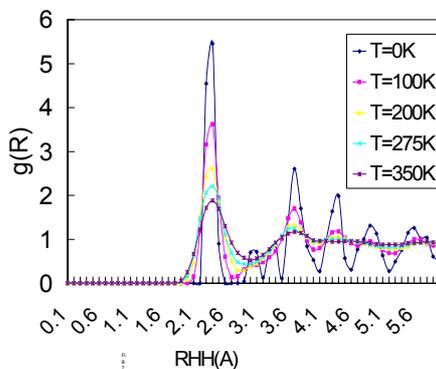


Fig.3 Hydrogen-hydrogen pair distribution functions at 0K,100K,200K,275K and 350K

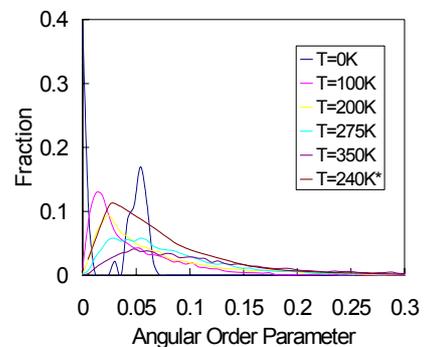


Fig.4 Distribution of angular order parameter in methane (10)