

CO₂ Clathrate Hydrate Structure: A Monte Carlo Approach

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ABSTRACT. Monte Carlo simulations have been carried out for the structure of CO₂ hydrate in the NPT ensemble using SPC intermolecular potential model of water. A mixture of water and CO₂ placed arbitrarily in a cubic cell has been used as a model system to simulate the CO₂ clathrate hydrate at a temperature 260 [K] and pressure 4 [MPa]. The comparison of the radial distribution functions between MC and MD are also presented. The present work is also directed to the study of structure with TIP4P potential model of water.

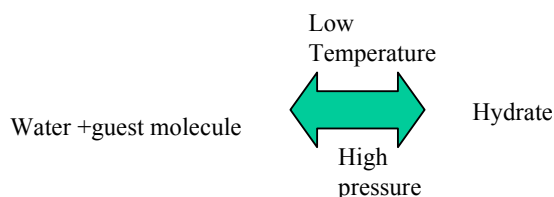
KEYWORDS: Clathrate hydrates; hydrate structure; radial distribution function; Monte Carlo method.

1. Introduction

Gas hydrates are a solid compound formed if a mixture of gas and water is exposed to high pressure and low temperature. The British scientist Sir Humphrey Davy first documented gas hydrates as early as 1810. However, hydrates did not receive much attention before the 1930s, when the oil and gas industry found out that unexpected formation of gas hydrates clogged pipelines, frequently at temperatures above the ice point [1]. The natural gas components like as CH₄, CO₂, C₂H₆ etc. are known to make gas hydrates. Hydrates have been suggested as a natural gas storage medium because of their high storage efficiency [2]. More recently, hydrate formation has been in focus in the production of hydrates for storage and transport of natural gas, gas separation, exploitation of gas hydrate deposits and depositing of CO₂ hydrates on the sea

floor. Gas hydrates have been increasingly involved in the development of various energy and environment-related technologies. It is estimated that the amount of energy stored in seafloor methane hydrates is more than twice of all other forms of fossil fuels. Hydrates can also be used for energy storage and transportation of gas, and for sequestering green house gases (i.e. CO₂). [3].

Three different structural types have been characterized so far. These types are the two well-known classical cubic structural types denoted as structural-I, structural-II and structure H and Sloan [3] summarized the property and diagram of these types of hydrate. The structure I consists of 46 water molecules and 8 guest molecules at most per unit cell and forms two smaller cages of pentagonal dodecahedron (5¹²) and six larger cages of tetrakaidodecahedron (6²5¹²). The formation process of clathrate hydrate is given below by the physical phenomena



The natural gas hydrates belong to a class of true clathrates where guest and host lattices interact only through weak, nonspecific van der Waals interactions. They have been known to scientists for over a century but attracted their attention primarily due to the problems that must be overcome when hydrates are found to be responsible for blocking the natural gas pipelines even at temperatures above the normal freezing point of water as determined by Hammerschmidt [4]. For the hydrate-I, the single unit cell of the CO₂ hydrates is a cubic box of length 12 Angstrom in which there are 46 water molecules and 8 CO₂ molecule at most.

Then the system is extended to 8-unit cells so, the total number of water molecules 368 and CO₂ molecules 64 at most correspondingly. A simulation system of 368 water molecules and 64,48,32, 16,8 guest molecules (CO₂ molecules and CH₄ molecules) has been studied by Molecular dynamics method for the clathrate hydrate [5] with SPC, SPC/E and TIP5P water potential model. Recently we have studied CO₂ hydrate using TIP4P potential by Monte Carlo simulation [6].

In this study, from the molecular point of view we focused the structure of CO₂ hydrate formation with (N, P, T) ensemble and SPC water model by using Monte Carlo computer simulation.

2. Monte Carlo (MC) Method [7,8]

Monte Carlo method is a stochastic method using random number for arrangement of molecules under a law of probability. To simulate fluids, transitions between different states or configurations are achieved by (a) generating a random trial configuration, (b) evaluating an acceptance criterion by calculating the change in energy and other properties in the trial configuration and (c) comparing the acceptance criterion to a random number and either accepting or rejecting in the trial configuration. It is important to realize that not all states will make a significant contribution to the configurational properties of the system. To accurately determine the properties of the system in the finite time available for the simulation, it is important to sample those states that make the most significant contributions. This is achieved by generating a Markov chain.

A Markov chain is a sequence of trials in which the outcome of successive trials depends only on the immediate predecessor. In a Markov chain, a new state will only be accepted if it is more favorable than the existing state. In the context of a simulation using an ensemble, this usually means that the new trial state is lower in energy.

The pressure group is a statistical mass providing the particle number: N, the pressure: P and the temperature: T and called NPT ensemble. This statistical mass is suit to operate the system that volume change and pressure is constant. In the case of pressure group, the probability density $\rho(\vec{r}, \vec{p}, V)$ that is the density appearing the microscopic state is shown

$$\rho(\vec{r}, \vec{p}, V) = \frac{\exp\left(-\frac{H(\vec{r}, \vec{p}) + PV}{kT}\right)}{N!h^{3N}Y} \quad (1)$$

Here Y is the amount corresponding to the partition function, and shown

$$Y = \sum_N \frac{1}{N!h^{3N}} \iiint \exp\left(-\frac{H(\vec{r}, \vec{p}) + PV}{kT}\right) d\vec{r} d\vec{p} dV$$

$$= \int \exp\left(-\frac{PV}{kT}\right) Z dV \quad (2)$$

[In canonical ensemble, the partition function is defined as, $Z = \frac{1}{N!h^{3N}} \iint \exp\left(-\frac{H(\vec{r}, \vec{p})}{kT}\right) d\vec{r} d\vec{p}$; Here h is Planck's constant, $H(\vec{r}, \vec{p})$ is Hamiltonian and it can be defined as the sum of kinetic energy and potential energy i.e. $H(\vec{r}, \vec{p}) = K(\vec{p}) + U(\vec{r})$]

Using Hamiltonian equation (2) implies,

$$Y = \sum_N \frac{1}{N! \Lambda^{3N}} \iint \exp\left(-\frac{U(\vec{r})}{kT}\right) \exp\left(-\frac{PV}{kT}\right) d\vec{r} dV \quad (3)$$

Where, $\Lambda = \left(\frac{h^2}{2\pi mkT}\right)^{1/2}$ is called the thermal de Broglie wavelength.

The group average can be expressed as follows.

The probability that i will appear is expressed with the following equation,

$$\begin{aligned} \langle A \rangle &= \iiint A(\vec{r}) \rho(\vec{r}, \vec{p}, V) d\vec{r} d\vec{p} dV \\ &= \frac{1}{Y} \iint A(\vec{r}) V^N \exp\left(-\frac{U}{kT}\right) \exp\left(-\frac{PV}{kT}\right) d\vec{r} dV \end{aligned} \quad (4)$$

Therefore, the required can be expressed as

$$\begin{aligned} \rho_i(r_i, V) &= \frac{V^N \exp\left(-\frac{U_i}{kT}\right) \exp\left(-\frac{PV}{kT}\right)}{Y} \\ &= \frac{\exp\left(\frac{-U_i - PV + NkT \ln(V)}{kT}\right)}{Y} \end{aligned} \quad (5)$$

Required ρ_j/ρ_i can be expressed as follows,

$$\frac{\rho_j}{\rho_i} = \exp\left\{\frac{-(U_j - U_i) - P(V_j - V_i) + NkT \ln(V_j / V_i)}{kT}\right\} \quad (6)$$

The algorithm of the volume change in the NPT ensemble using this equation is as follows

1. Initial volume and initial state are given and the state is made into state i
2. The potential energy U_i is calculated.
3. A random number R_1 is taken out from the uniform random number sequence distributed over the range of 0 and 1.

$$V_j = V_i + (2R_1 - 1)\delta V_{\max}$$

Here, δV_{\max} is the maximum amount of change

4. The potential energy U_j is calculated.
5. $\Delta H' = \{P(V_j - V_i) + U_j - U_i - NkT \ln(V_j / V_i)\}$
6. $\Delta H' \leq 0$, If it becomes, it will consider that state j is one state, which constitutes the Markov chain, and therefore, do again step 3.
7. $\Delta H' > 0$, If it becomes, a random number R_2 will be further taken out from the above-mentioned random number sequence.
 - 7.1 $\exp(-\Delta H' / kT) > R_2$, state j is put at one state which constitutes the Markov chain. It makes and repeats from step 3.
 - 7.2 $\exp(-\Delta H' / kT) \leq R_2$, the state before changing the volume is the Markov chain and do again step 3.

In calculation of the NPT ensemble in the Monte Carlo method as usually shown in Fig.1. After volume change performed the NVT ensemble process about all particles.

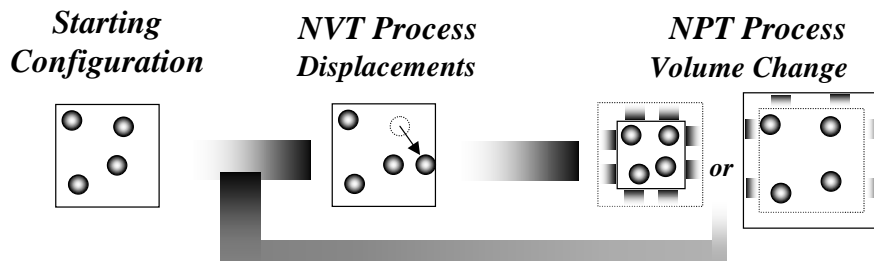


Fig.1 General flowchart of NPT ensemble

Outline of the Monte Carlo method is shown in chart.1.

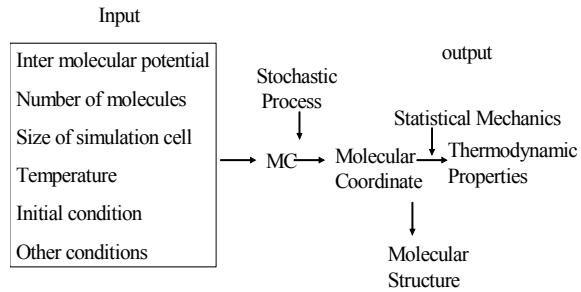


Chart.1: Outline flowchart of Monte Carlo method

3. Physical Model

In this work, physical model for the intermolecular interactions in CO₂ hydrates is supposed to be consisting of three parts: (1) The interactions between water-water molecules, (2) The interactions between water- CO₂ molecules, and (3) The interactions between CO₂ - CO₂ molecules. The interactions between the molecules are shown in Fig.2.

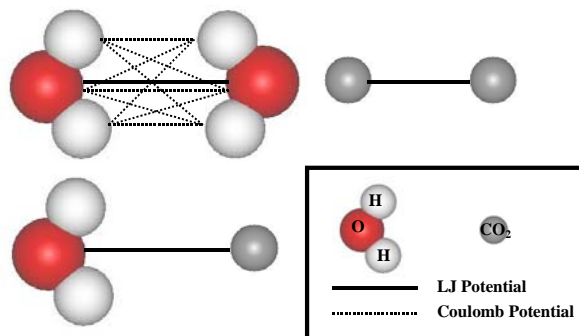


Fig.2 Interaction between molecules.

4. Simulation Method

Monte Carlo simulation was performed for a system of 368 water molecules and 64 CO₂ molecules with constant pressure and constant temperature. A conventional NPT ensemble algorithm used in the simulation is described in detail elsewhere [9]. MC technique is used to simulate CO₂ hydrate as the process of formation of the hydrate structure from a random initial configuration. The number of step is 600,000. In each MC run we can confirm that the system sufficiently got to the equilibrium state in the initial 100000 steps. After this the subsequent period of 500000 steps was carried out to calculate the statistical thermodynamic property and structure of CO₂ hydrate. As a first step of study, a single unit cell length of 12 Angstrom is considered and periodic boundary conditions are used to mimic an infinite lattice. Regarding intermolecular potentials, we used the effective SPC model [10] for the water-water interactions and the water- CO₂ and CO₂ - CO₂ interactions are modeled by a single LJ site model. The conceptual figure of water potential is shown in Fig.3. The parameters of the LJ potential and water potential are shown in table 1 and table 2 respectively. Here the parameters for the water-CO₂ interactions are estimated by Lorentz-Berthelot rules shown in equation (2) and (3). The intermolecular potential function is

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (7)$$

$$\epsilon = \sqrt{\epsilon_i \times \epsilon_j} \quad (8)$$

$$\sigma = \frac{\sigma_i + \sigma_j}{2} \quad (9)$$

Table 1. Parameter of LJ Potential.

	Water -water	CO ₂ - CO ₂	CO ₂ -water
σ [Å]	3.16	3.94	3.55
ϵ [J]	1.080×10^{-21}	3.10×10^{-2}	1.83×10^{-21}

Table 2. Parameters of SPC Potential model.

Nature	Parameter	SPC
Coulomb parameters	q[e]	0.41
Geometric parameters	r[Å]	1
	HOH	109.47
Lennard-Jones parameters	σ [Å]	3.16
	ϵ [J]	1.080×10^{-21}

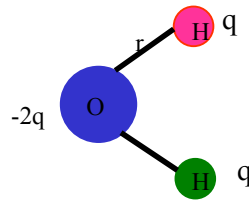


Fig.3 Potential model of water

5. Mathematical Equation

The radial distribution function [8] is defined with the equation

$$g_{ij}(r) = \frac{1}{N_i n_j} \left\langle \sum_1^{N_i} \frac{\Delta N_j}{(4\pi r_{ij}^2 \Delta r)} \right\rangle \quad (10)$$

Where, ΔN_j is the number of all the pairs of i and j atoms (molecules) in a cell of width Δr at distance r_{ij} . N_i and n_j are the number of atoms (molecules) i and atoms (molecules) j in the cell respectively. $g_{ij}(r)$ is the radial distribution function.

Running coordination numbers are calculated as

$$N = 4\pi\rho \int_0^r g_{ij}(r) r^2 dr \quad (11)$$

Clearly $g(r) \rightarrow 0$ as $r \rightarrow 0$; $g(r) \rightarrow 1$ as $r \rightarrow \infty$

Equation (10) is as shown in Fig.4, formed that density $n_j(r_{ij})$ of numbers of atoms j which locate on where radius is r_{ij} from atoms i is divided by medium

density \bar{n}_j . Thus when it is equal to medium density, $g(r)$ will be 1. Also when $n_j(r_{ij})$ is bigger than \bar{n}_j that means more atoms exist where radius is r_{ij} rather than medium. Otherwise fewer atoms exist on r_{ij} rather than medium.

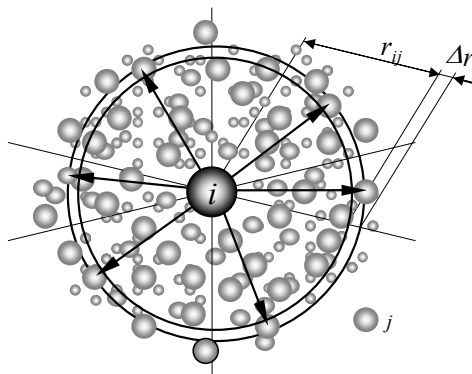


Fig.4 Image of Distribution Function

We next take Fig.5 as an example, and show radial distribution function of liquid circumstance of LJ fluid. It is obvious from the figure that it converges to 1 with increment of radius r through some local minimum point and local maximum point. Existence of extreme number indicates to constitutive property in short distance area, also converges to 1 indicates that as distance becomes shorter, the constitutive property becomes less or weaker. Gases generally do not have constitutive property, so $g(r)$ converges to 1 immediately through the liquid line seen characteristically in substances.

6. Results and Discussion

The structure of particle fluids is characterized by a set of distribution functions for the particle positions, the simplest of which is the radial distribution function

$g_{ij}(r)$. The atom-to-atom radial distribution functions, $g_{ij}(r)$ give the probability of finding a pair of atoms i and j with distance r apart, relative to the probability expected for a completely random distribution of atoms at the same density. The atom-to-atom radial distribution functions, $g_{oo}(r)$, $g_{hh}(r)$, $g_{co}(r)$ and $g_{cc}(r)$ are shown in figures (Fig.6(a) and Fig.6 (b), Fig.7, Fig.8 and Fig.9).

The $g_{oo}(r)$ function shown in Fig.6 (a) is defined with respect to the oxygen-oxygen distance between two water molecules. The $g_{oo}(r)$ is the most informative, since it invites comparison with the known pair occurrences have regularly spaced oxygen's radial distribution functions in the water and clathrate hydrates. It can be seen that the first peak in $g_{oo}(r)$ is a sharp peak with summit at 2.8 [Å] and this means that all the neighboring oxygen atoms are at the distance of 2.8 Angstrom. Therefore, the polyhedrons composed of oxygen atoms have the equal edges in the hydrate structure.

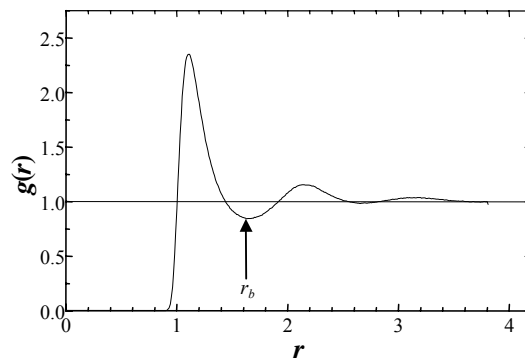


Fig.5 Distribution Function $g(r)$

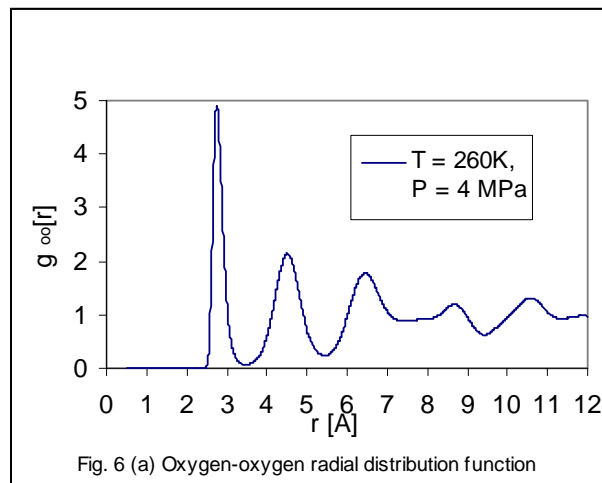
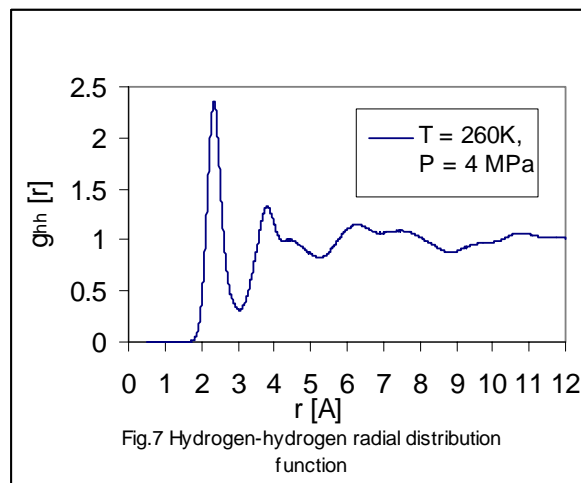
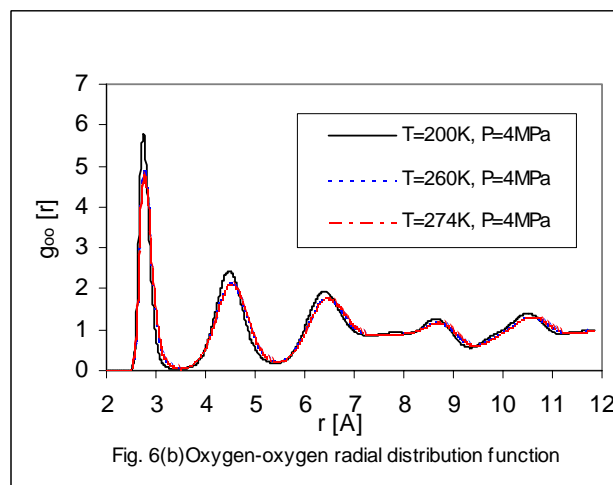


Fig. 6 (a) Oxygen-oxygen radial distribution function

In order to investigate the influence of temperature change on the structure nature of CO₂ hydrate [The way between water-water radial distribution functions], we conducted the simulations at pressure 4 [MPa] and temperatures ranging from 200 to 274 [K]. The comparisons are shown in the Fig.6 (b). We observe that up to 274 [K], the change of water-water radial distribution functions, the amplitude of the CO₂ molecules is almost invariant corresponding concave upward of temperature.



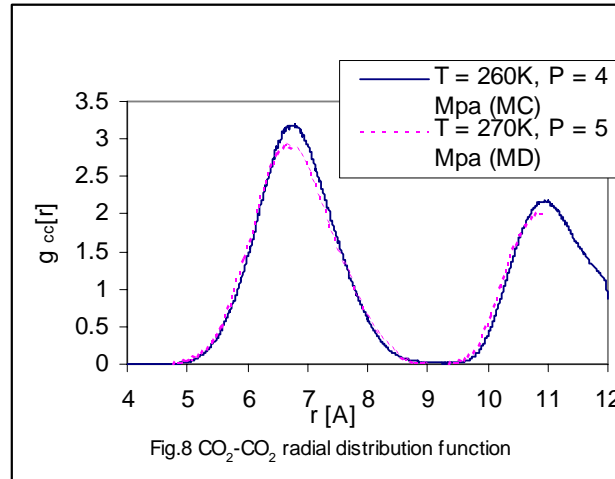
In Fig.7, the radial distribution function of $g_{hh}(r)$ is shown. The first peak is appeared at 2.5 [Å], which indicates that the distance between two nearest hydrogen atoms is 2.5 [Å].

According to the MD simulations [5] the O-O distance are mostly at 2.78[Å], the H-H distances are at 2.3 [Å]. Comparing the MC simulation results at 260 [K] with MD simulation results at 270 [K] as shown in table 3. MC simulation result is in good correspondence with MD simulations.

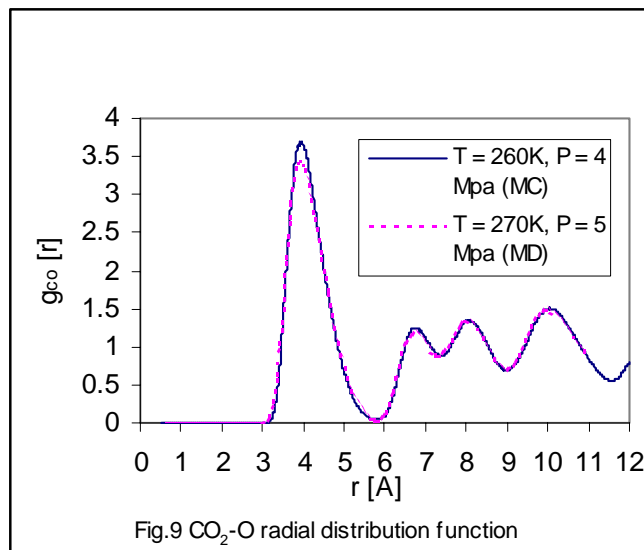
Table 3. MC and MD Comparison of the hydrate structure.

Pair	MC	MD
O-O	2.8	2.78 (Ref.5)
H-H	2.5	2.3 (Ref.5)

In Fig.8, the MC simulated radial distribution function between CO₂ and CO₂ molecules are shown. As for CO₂·5.75H₂O a peak about 6.8 [Å] which is a distance for CO₂ molecule of hydrate is kept and a definite peak comes around 11 [Å] as well. The function drops to zero after the main peak at about 9 Angstrom. This means that there is a distance range at which no pair separation occurs. So, CO₂ molecules are rather well structured. The second peak appears at about 11 [Å], this is the favored distance of the neighbors of the second shell. This favored distance is considerably smaller than the double of the first shell radius of 6.8 [Å], indicating that the second neighbors are located at spatial directions different from that of the first neighbors.



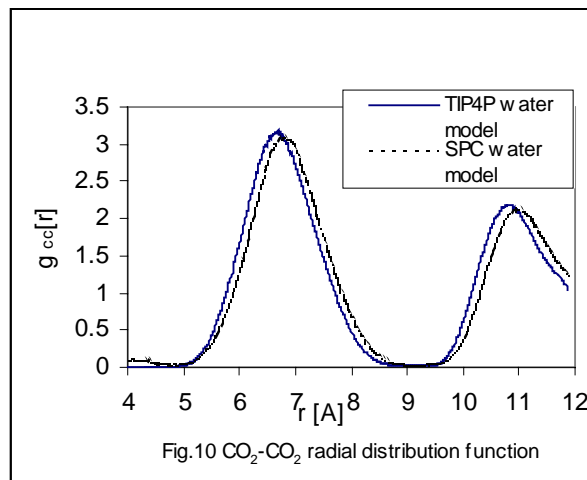
In Fig.9, we simulated the CO₂-water distribution functions. From this figure the first peak happens summit at 3.9 [Å], this means that the molecules are separated at 3.9 [Å].



In Fig.8 and Fig.9, we compare our $g_{cc}[r]$ and $g_{co}[r]$ with MD simulated $g_{cc}[r]$ and $g_{co}[r]$ [5]. We compare our results with the results investigated by molecular dynamics method. Seeing the radial distribution function it is understood that our results is apparently higher than MD simulation results in the first and second peak. This means that our MC simulation of CO₂ hydrate is more stable than MD simulations.

From the above discussions we conclude that hydrate structures are maintainable in all of the cases.

To verify the independence of MC the simulation result on the potential model, we carry out the simulations at Temperature 280 [K] and Pressure 4 [MPa] by using TIP4P [11] potential model of water. The calculated CO₂- CO₂ radial distribution functions are depicted in Fig.10.



The results show that there are some differences on the hydrate structure between SPC and TIP4P potential model.

7. Conclusion

The Monte Carlo simulations conducted at 260 [K] and 4 [MPa] reveal the structure of CO₂ hydrate in the NPT ensemble based on SPC effective intermolecular potential model of water. In order to evaluate the structure of a system, we introduced the radial distribution functions and our results indicated that the distribution functions are showed striking evidence for hydrate formation.

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