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Computational study on the structure II clathrate hydrate of methane and large guest molecules

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Abstract Molecular dynamics (MD) simulations of structure II clathrate hydrates are performed under isobaric-isothermal (NPT) ensembles in a 2 × 2 × 2 structure II unit cell replica with 1,088 TIP4P water molecules to study two main aims: firstly, the effects of methane and large guest molecules (LGMs) on the stability of clathrate hydrate structure and secondly, to study the effects of LGMs on methane storage capacity. The studied LGMs are propane, *n*-butane, tetrahydrofuran (THF), 1,3-dioxane, 1,4-dioxane, allene, benzene, cyclohexane and neopentane. At the first part of this work, the dynamics of structure II clathrate hydrate is studied to clarify the effects of guest molecules on host lattice structure. The radial distribution functions (RDFs) analysis is used to understand the structure configuration. Then, MD simulations are performed to evaluate the effects of LGMs on methane-storage capacity of the structure II clathrate hydrates at temperature 278 K and as a function of pressures up to 1,000 MPa.

Keywords   Structure II clathrate hydrate · Molecular dynamics · Stability · Storage · Methane and large guest molecules · Radial distribution function

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Introduction

Clathrate hydrates (or gas hydrates) are non-stoichiometric inclusion compounds in which certain compounds stabilize the cages formed by hydrogen bonded water molecules. Hydrates formed by natural gases and water, either in nature or in industrial processes, are commonly known as gas hydrates. Gas hydrates naturally occur under conditions of high pressure and low temperature [1–5]. The clathrate hydrate stability is due to the interactions between the water molecules forming a host lattice and the gas molecules occupying the cavities of the lattice as a guest molecule [1, 3].

Gas hydrates importance is because of the large potential they possess as a future energy source. The other importance of gas hydrates is due to the problems they pose to the petroleum industry during the production, transportation, and processing of natural gas and oil [6]. Without proper precautions, hydrates can eventually block pipelines resulting in production losses [7]. The traditional response to this problem is to inject large volumes (up to 40%) of alcohols and/or glycols into production streams [8, 9].

There are three known hydrate structures, structure I, structure II and structure H depending principally on the molecular size of the guest molecules [1, 5]. Structure I is a cubic structure with a lattice parameter of 12.05 Å [10] and unit cell composition $2M_1 \cdot 6M_2 \cdot 46H_2O$, where M_1 and M_2 represent the 5^{12} (small) and $5^{12}6^2$ (large) cages. Structure II hydrate is also cubic, with lattice constant 17.3 Å and unit cell composition $16M_1 \cdot 8M_2 \cdot 136H_2O$ [11], where M_1 and M_2 are the 5^{12} (small) and $5^{12}6^4$ (large) cages [1, 12]. Structure H is a hexagonal structure [12, 13] with lattice parameters of $a = 12.2$ Å and $c = 10.1$ Å. The unit cell composition is $M_1 \cdot 2M_2 \cdot 3M_3 \cdot 34H_2O$, where M_1, M_2 and M_3 cages allocated to $5^{12}6^8$, $4^35^66^3$ and 5^{12} cages. Occupation

of both large and small cages by appropriately sized molecules appears to be necessary for stability of structure H hydrate.

As declared above, structure II has the two types of small (5^{12}) and large ($5^{12}6^4$) cages. The small cage is composed of 20 water molecules arranged to form twelve pentagonal faces where as the large cage of structure II is each formed by 28 water molecules [1, 5]. Some hydrates need a help gas filling the small cavities to stabilize the hydrate lattice. The stabilizing effect of a second encageable component is particularly evident for structure II clathrate hydrates, in which the help gas may occupy the otherwise empty cages. In many of these cases, the large guest molecule (LGMs) does not form a hydrate on its own and requires a help guest to stabilize the structure [1, 5]. In this work, some LGMs such as propane, *n*-butane, tetrahydrofuran (THF), 1,3-dioxane, 1,4-dioxane, allene, benzene, cyclohexane and neopentane are selected, in which methane molecule may occupy the empty cages as a help gas. The main important aim of this work is study on effects of LGMs on the capacity of fuel methane storage in structure II clathrate hydrates in addition to study on stability of clathrate structure in presence of guest molecules. On the other hand, we want to know in the presence of what LGMs and thermo-physical conditions the capacity of methane storage can be improved. Also we want to compare the effects of LGMs on structural properties and occupancy by methane in small cages. Therefore, we assumed that the large cages of structure II clathrate are occupied by LGM only; although, the theoretical and experimental results [1, 14] show that methane is partitioned over both small and large cages. Storage and transportation of natural gases as hydrates from remote gas fields is one of the most hopeful applications of gas hydrates [15–18]. This is an alternative technology to liquefied natural gas (LNG) at cryogenic temperatures or compressed natural gas (CNG) at high pressures [19]. However, hydrate technology is not conventional and thus further investigations are needed to determine the utility of these materials in a variety of pressure and temperature conditions. Recently, methane hydrate storage has been investigated as a major fuel. It is widely known that methane can be contained in structure I, II and H types of clathrate hydrates [1, 5]. Methane storage in structure II clathrate hydrates in presence of LGMs is expected to become one of the possible storage media of methane. This work aim is to find the methane storage in a hydrate and the stability conditions under which a hydrate can be formed, stored and transported.

Propane is one of the most common components of natural gases along with methane, ethane, and butane. Propane has the highest specific energy content of hydrocarbons [20]. Because natural gas contains propane and higher hydrocarbons, hydrates that form in gas producing pipelines are usually structure II [7]. In the structure of propane hydrate, only the large type of cavity is occupied by propane. The region of interest is primarily pressures from 0.1 to 1,500 MPa and temperatures from 235 to 334 K [20, 21]. Propane forms a structure II clathrate hydrate by occupying 8 large cavities. It is stable under normal conditions [21]. The details of propane hydrate structure along with methane and ethane has been reported by Udachin et al. [14]. They discussed all cases of small and large cages occupancy by methane, ethane and propane. Also, guest molecules lie off the geometrical center of the cage and form van der Waals contacts with water molecules [14].

Normal butane is generally regarded as a non-hydrate forming gas that will form a hydrate only when in a mixture with smaller molecules such as methane, ethane, CO_2, etc. [21, 22]. Normal butane together with methane and other small molecules occupying the small cages would be the point of interest for current research in oil and gas industries. This kind of arrangement of small molecules in *n*-butane hydrates may be useful to transport or storage of such molecules. This is the reason *n*-butane is considered for the present work. A normal gas mixture contains partial amounts of butane and high amounts of methane [22]. The detailed butane + methane hydrate system has been described by Luzi et al. [23]. They investigated the molecular characteristics of hydrates which were synthesized from gas mixtures containing the two isomers of butane in excess methane [23].

Tetrahydrofuran (THF) is one of the most well-known guest molecules in the clathrate hydrate systems, mainly because THF as an additive to other gas hydrate systems is able to reduce the equilibrium pressure considerably. Therefore, it makes it possible to treat gas hydrates under mild pressure conditions [24]. THF hydrate in particular is a hopeful candidate for gas storage [25, 26]. The THF molecules are able to occupy the large cage only. The chemical formula for the ideal hydration is then given as THF·$17H_2O$ [27]. Pure THF hydrate forms at temperatures below 277.4 K under atmospheric pressure [24]. Recently, some authors [25, 28–30] reported the promoter effect of THF and 1,4-dioxane to form hydrate.

1,3-Dioxane and 1,4-dioxane are known to form structure II clathrate hydrates with methane as a help gas [1, 30]. Also, some researches show that the dioxanes are able to form hydrates by themselves (without help gas) [31, 32]. In this work, the binary hydrate systems of CH_4/1,4-dioxane and CH_4/1,3-dioxane [1] are investigated by computational simulations to get insight into the effect of dioxanes on structure stability and potential methane storage capacity.

Some other materials are known to form the structure II clathrate hydrate in the presence of small help guests.

Allene, benzene, cyclohexane and neopentane are formed structure II hydrate in presence of help guests like xenon and methane [1, 12]. So, they are also selected for our molecular dynamics (MD) study.

Molecular dynamics (MD) simulation is a powerful tool for studying thermodynamic properties of water and gas hydrates [33]. In MD simulation, the equations of motion are solved to study the behavior of atoms and molecules inside a simulation box. Atomic movements over small time steps are evaluated for a large number of steps to obtain macroscopic properties such as volume, energy, and temperature [34]. More recently, computational methods have been used to study gas hydrates and in many of these cases, methane hydrates receive the most attention to validate the published experimental data on thermodynamics of hydrate formation [35–43]. Most molecular simulation studies have focused on simple energy force fields, treating water molecules as rigid bodies and methane molecules as spherical particles [35–43].

The empty clathrate is unstable with respect to ice under standard temperature and pressure. It is useful as a reference system in discussing the thermodynamic stability [44]. In MD calculations, however, the empty structure was often found to be stable over the time period of the simulation about 10–100 ps [45]. Also, the metastability of the empty hydrate has been observed in several independent MD calculations [46, 47] employing different thermodynamic ensembles. The stability of the hydrate structure increases considerably when the guest molecules are included in the MD calculations [45].

Several molecular simulation studies on clathrate hydrates have been reported regarding the stability of clathrate hydrates. Rodger [48] applied the molecular simulation to investigate the van der Waals and Platteeuw (vdWP) [44] statistical mechanical theory. Their study discusses the importance of repulsive forces from the guest molecules on stabilizing the hydrate water lattice [1]. Tanaka et al. [49–52] investigated the thermodynamic stability of the structure I and structure II hydrates using molecular simulations. They proposed a generalized version of the vdWP theory, which was developed for each situation, and discussed the thermodynamic stability of clathrate hydrates only in terms of the intermolecular interactions. Their approach, however, requires an equation based on the statistical thermodynamics. Okano and Yasuoka [53] investigated the thermodynamic stability of the structure H hydrate.

Also, some authors [3, 17, 19, 28, 54–59] have been studied clathrate hydrates capability for storage and transportation of natural gases. As a result of their capacity to store large volumes of gas, hydrates have been considered as an alternative material for storing and transporting methane, hydrogen, and etc. [58]. The major advantages of hydrates as gas-storage materials, comparatively to other materials investigated for the same purpose, include reversibility, low cost, almost not any environmental hazards, and safety (in terms of toxicity and flammability). However, further research and development is required in order for these materials to achieve such a volumetric and gravimetric storage capacity that would render them suitable for practical applications [58]. However, gas storage phenomena has less mentioned by molecular simulation. These studies has restricted to Alavi et al. [59], Susilo et al. [19] and Papadimitriou et al. [58] and etc. works in which they studied the hydrogen storage in structures II and H and methane storage in structure H.

In this work, we use MD simulations to study binary methane + LGM structure II clathrate hydrates. Despite the fact that the propane + methane and THF + methane have been studied by MD simulation [19], to compare all LGMs + methane systems it should be necessary to repeat these simulations along with new materials. The main objective of this work is to apply the MD Simulation in order to study the stability of methane + LGM clathrate hydrate and then study the effects of LGMs on methane occupancy in small cages of structure II hydrates at temperature 278 K as a function of pressure (up to 1,000 MPa).

Computational methodology

The LAMMPS MD simulation code [60] is employed to study the stability and methane storage capacity of structure II clathrate hydrate. Therefore, the model system of methane and LGM as guest molecules along with water molecules as a host lattice is built for the study of the clathrate hydrate system. A $2 \times 2 \times 2$ replica of the structure II hydrate unit cell with $34.6 \times 34.6 \times 34.6$ Å^3 initial dimensions and periodic boundary conditions is used as the simulation cell. Fractional coordinates of oxygen and hydrogen atoms of the water molecules are obtained from the crystallography of structure II clathrate hydrate [11, 61, 62]. Guest molecules (methane and LGM molecules) are initially placed in the center of the appropriate cages and their positions are allowed to equilibrate during the simulation.

In the present study, water molecules are described with the transferable intermolecular potential 4 point (TIP4P) model [63], which is a four site water model with rigid atomic positions. This model presents the electrostatic energies between pairs of water molecules as the sum of interactions between sets of charges placed on the rigid monomers. The total interaction consists of a Lennard-Jones O–O potential plus the Coulomb interactions

between the charge sites which can be expressed in the following form

$$U(r_{O-O}) = \frac{A}{r_{O-O}^{12}} - \frac{C}{r_{O-O}^{6}} + \sum_{i,j} \frac{q_i q_j}{r_{ij}} \quad (1)$$

where i and j label the charge sites, r_{O-O} is the distance between two oxygen atoms, A and C are the potential parameters. Interaction parameters of the TIP4P model are obtained from Ref. [63].

The van der Waals interactions between guest–guest and host–guest molecules are based on the Lennard-Jones (12-6) potential with a cutoff distance of 15 Å. Coulombic interactions between point charges q_i and q_j located on the atomic nuclei i and j are used to model the electrostatic intermolecular interactions. The standard Lorentz–Berthelot combination rules [64], $\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}$ and $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$ are used to derive the Lennard-Jones potential parameters between unlike atom-type force centers i and j from the values of the parameters between similar atom types. The intermolecular potential is expressed by

$$U(r) = \sum_{i=1}^{N-1} \sum_{j>i}^{N} \left\{ 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6} \right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right\} \quad (2)$$

The geometry of the LGMs are characterized by energy optimization using density functional theory at the B3LYP/6-311G level [65] with the GAUSSIAN 98 software [66] where the partial charges of the guest atoms are calculated with the QEq charge equilibration approach [67] as implemented in the GAUSSIAN 98 software. In addition to our DFT calculations, some of these data are available in Refs. [59, 68, 69].

The equations of motion are solved by using the Verlet algorithm [70], and rigid water molecule constraints are implemented with the SHAKE algorithm [71]. The temperature and pressure are controlled by a Nose–Hoover [72, 73] and Berendsen methods [74], respectively.

The trajectories are generated in the NPT ensembles with the integration time step of 1 fs, and the periodic boundary conditions are applied in all directions. The temperatures and pressures are set at $T = 273$ and 278 K and $P = 5$ and 10 MPa to simulate the thermodynamically stable hydrates. Also, to study the methane occupancy in small cages of structure II clathrate hydrate temperature and pressures are set into 278 K and up to 1,000 MPa, respectively. The simulations for stability study are performed at a total time of 300 ps. This simulation time is found to be sufficient for obtaining converged simulation energies and volumes. The simulations for methane storage study are performed at a total time of 5 ns. This simulation time is adequate to filling small cages by methane molecules. Long-range Coulomb interactions are calculated with the Ewald summation method [75] with a precision of 1×10^{-6} and all intermolecular interactions in the simulation box are calculated within a cutoff distance of 15.0 Å.

The model used in the present MD calculations contains 1,088 water molecules for a structure II clathrate hydrate with cubic $Fd3m$ cell dimensions $a = b = c = 34.6$ Å ($2 \times 2 \times 2$ unit cells). The methane molecules as a help gas and LGMs are filled in small and large cages in all the simulations and we obtain the thermodynamical properties and radial distribution functions (RDFs).

Results and discussions

In the first part of this work, the LGMs + methane hydrate system are simulated under isobaric-isothermal (NPT-ensemble) conditions to study the stability of structure II clathrate hydrate. An isobaric-isothermal simulation gives the equilibrium cell volume resulting from the enclathrated guest molecules. By changing the LGMs, the new cell constant can be directly obtained. The aim of the first part of the work is to study the effect of guest molecules and their size and also pressure and temperature on host lattice structure. The simulated cell volumes (and lattice constants) with different LGMs can demonstrate the effect of guest molecules, pressures and temperatures on host lattice structure. In NPT ensemble, the simulation box is kept in contact with a constant pressure bath. The volume of the box is periodically scaled to keep the pressure constant. The simulation box shape is fixed and only isotropic expansion is allowed. Therefore, the structure II LGMs + methane hydrate are simulated at constant pressure and temperature with different LGMs, pressure and temperature. Therefore, in Table 1, the equilibrium volumes and energies of systems are calculated by MD simulation at different pressures and temperatures for each case. These MD calculations are performed for various LGMs; since the equilibrium hydrate structure is sensitive to the LGMs and their size. The equilibrium in the simulations is reached when the total energy and the volume become constant. At the equilibrium state the structure of gas hydrate is visualized to see if it is in the stable form. For example, Figs. 1a and 2a are the network of H_2O before simulation at the time of 0 ps and Figs. 1b and 2b are the hydrate structure at the end of simulation ($t = 300$ ps) for THF + methane and 1,4-dioxane + methane, respectively. These figures are shown for whole calculation cell where a unit cell has methane and LGM. From these figures we can see that the systems are in stable condition.

To investigate the effect of LGMs, pressures and temperature on the host lattice structure, the equilibrium volumes as well as lattice constants are listed in Table 1. The

Table 1 Thermodynamic properties of structure II clathrate hydrate of methane and large guest molecules (LGMs) under NPT ensemble conditions

Guest molecules	Pressure (MPa)	Temperature (K)	E_{vdW} (kJ/mol)	E_{elect} (kJ/mol)	E_{config} (kJ/mol)	E_{kin} (kJ/mol)	E_{pot} (kJ/mol)	E_{tot} (kJ/mol)	Volume (nm^3)	Lattice constant (Å)
Propane + Methane	5	278	2.4800	−17.7630	−15.2830	2.3469	−70.8957	−68.5488	41.314	17.2850
	10	273	2.4968	−17.8271	−15.3303	2.3132	−70.9432	−68.6300	41.239	17.2745
	10	278	2.4897	−17.7745	−15.2848	2.3472	−70.8975	−68.5503	41.282	17.2806
n-Butane + Methane	5	278	2.3237	−18.0524	−15.7287	2.2958	−70.3472	−68.0515	41.895	17.3657
	10	273	2.3438	−18.1852	−15.8414	2.2532	−70.4615	−68.2083	41.734	17.3433
	10	278	2.3277	−18.0796	−15.7519	2.2939	−70.3708	−68.0769	41.855	17.3602
Tetrahydrofuran (THF) + Methane	5	278	2.0989	−16.0833	−13.9844	2.0006	−61.9061	−59.9055	41.312	17.2847
	10	273	2.1085	−16.1007	−13.9922	1.9984	−61.9143	−59.9158	41.274	17.2794
	10	278	2.0877	−5.9825	−13.9922	2.0311	−61.8154	−59.7843	41.295	17.2823
1,3-Dioxane + Methane	5	278	1.9081	−15.7504	−13.8423	2.2172	−67.9988	−65.7816	45.324	17.827
	10	273	1.9476	−15.9332	−13.9856	2.1704	−68.1439	−65.9735	44.850	17.7646
	10	278	1.9124	−15.7757	−13.8633	2.2112	−68.0205	−65.8093	45.102	17.7979
1,4-Dioxane + Methane	5	278	1.7234	−14.0187	−12.2953	1.9468	−59.4412	−57.4944	45.353	17.8308
	10	273	1.7352	−14.1326	−12.3974	1.9090	−59.5458	−57.6368	44.793	17.7572
	10	278	1.7144	−14.0144	−12.3000	1.9417	−59.4469	−57.5052	45.135	17.8023
Allene + Methane	5	278	2.8802	−18.8712	−15.9910	2.3453	−71.6035	−69.2581	41.264	17.2781
	10	273	2.9142	−18.9635	−16.0493	2.3039	−71.6622	−69.3583	41.177	17.2659
	10	278	2.8926	−18.8893	−15.9967	2.3415	−71.6092	−69.2678	41.240	17.2746
Cyclohexane + Methane	5	278	1.9188	−17.3374	−15.4186	2.2385	−68.1596	−65.9211	42.831	17.4941
	10	273	1.9441	−17.4236	−15.4795	2.2020	−68.2209	−66.0189	42.723	17.4793
	10	278	1.9282	−17.3524	−15.4242	2.2382	−68.1652	−65.9270	42.796	17.4892
Benzene + Methane	5	278	2.1949	−17.2626	−15.0677	2.2400	−67.8085	−65.5686	42.955	17.5108
	10	273	2.2226	−17.3532	−15.1306	2.2020	−67.8719	−65.6699	42.849	17.4964
	10	278	2.2048	−17.2782	−15.0734	2.2389	−67.8143	−65.5754	42.929	17.5074
Neopentane + Methane	5	278	2.0940	−17.7689	−15.6749	2.2810	−69.3396	−67.0587	42.465	17.4441
	10	273	2.1243	−17.8712	−15.7469	2.2333	−69.4121	−67.1788	42.345	17.4276
	10	278	2.1041	−17.7814	−15.6773	2.2782	−69.3420	−67.0638	42.440	17.4407

equilibrium volume of the cubic box resulting from these simulations is plotted against the LGMs occupying the cavities. Figure 3 shows the effect of LGMs and pressure on the simulated cell volume which is the cube of lattice parameter. As seen from this figure, the volume of system increases substantially with guest size and decreases with pressure. A similar conclusion can be applied for lattice constant variation with composition of guest molecules and pressure. Figure 4 shows the simulation lattice constants for structure II hydrate obtained in this work. The average unit cell constant resulting from smaller guest molecules is smaller than the unit cell length resulting from the larger guest molecules. Also, the temperature effects on the host lattice structure are shown in Figs. 5 and 6. These figures show an increase in volume and lattice constant with increment in temperature.

As we know, in the process of MD simulation achieving equilibrium of the studied system was recognized by stability in calculated pressure for NVT ensemble and volume

for NPT ensemble [75, 76]. Therefore, for the accuracy of MD calculations, the obtained equilibrium volumes in NPT ensemble should be compatible with experimental data. The correct equilibrium volumes indicate the correct intermolecular parameters and force field. As a result, the accurate force field leads to the truthful molecular simulation results. Therefore, the obtained results such as positions of particles, their distance, energy, etc. will be reliable. As a result, the structure II lattice parameters, which are obtained from equilibrium volumes (in structure II hydrate, volume is cube of lattice parameter), are compared with experimental data [1, 77, 78]. These comparisons are shown in Table 2. The lattice parameter of structure II hydrate (without guest molecule) is almost 17.3 Å [1]. Also, the lattice parameter of structure II hydrate including guest molecules is around this value due to weak interactions of guest molecules with host lattice. This fact is shown in Table 2. Therefore, the results of experimental data and MD calculations are compatible.
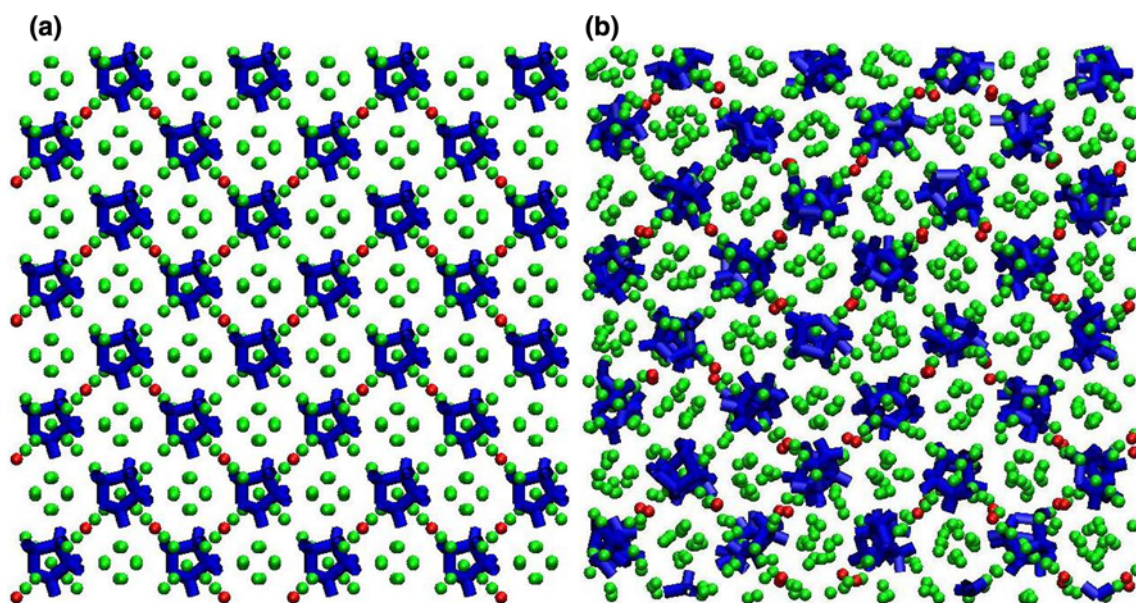
Fig. 1 Time variation of network of water at the time of **a** 0 ps (initial condition) and **b** 300 ps (end of simulation) for THF + CH$_4$ hydrate at P = 5 MPa and T = 278 K where O atoms of water, THF molecules and C atoms of methane are shown
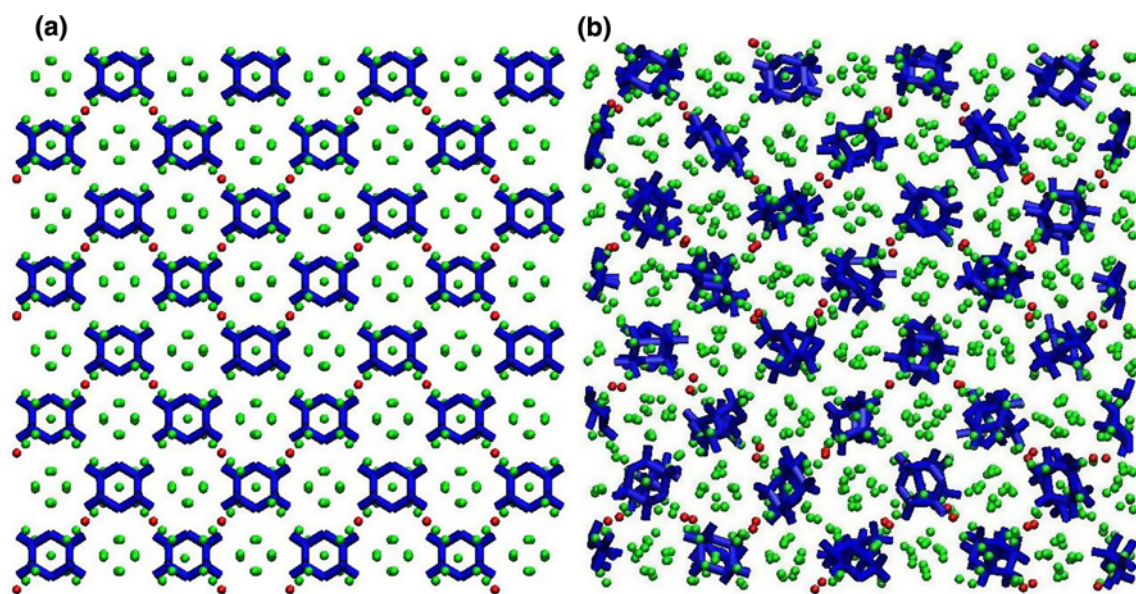

Fig. 2 Time variation of network of water at the time of **a** 0 ps (initial condition) and **b** 300 ps (end of simulation) for 1,4-dioxane + CH$_4$ hydrate at P = 5 MPa and T = 278 K where O atoms of water, 1,4-dioxane molecules and C atoms of methane are shown

To understand the characteristic configurations of the structure of particle fluids, a set of distribution functions are used; the simplest of them is the RDF $g(r)$. The pair RDFs, $g_{ij}(r)$ give the probability of finding a pair of particles i and j with distance r apart, relative to the probability expected for a completely random distribution of particles at the same density [79, 80]. Therefore, the microstructure of the hydrate is described by the host–host RDFs $g_{OO}(r)$, $g_{OH}(r)$, and $g_{HH}(r)$ (Fig. 7a–c) and the host–guest and guest–guest RDFs $g_{OG}(r)$, $g_{OM}(r)$, $g_{HG}(r)$, $g_{HM}(r)$, $g_{GG}(r)$,

$g_{GM}(r)$ and $g_{MM}(r)$ (Fig. 7d–j) for clathrate hydrate including methane (M) and LGM as a guest molecules in NPT ensemble, where G denote the LGMs such as allene, benzene, cyclohexane, 1,3-dioxane, neopentane and THF. The obtained RDFs are at pressure 5 MPa and temperature 278 K. These RDFs have been calculated to the length of $r = 15$ Å for the clathrate hydrates.

It may be seen that the host lattice structure possesses similar structural characteristics and is reasonably similar to previous computer simulation results [81, 82]. The

Fig. 3 Volume variation of simulated systems with pressure and guest molecules for structure II clathrate hydrate
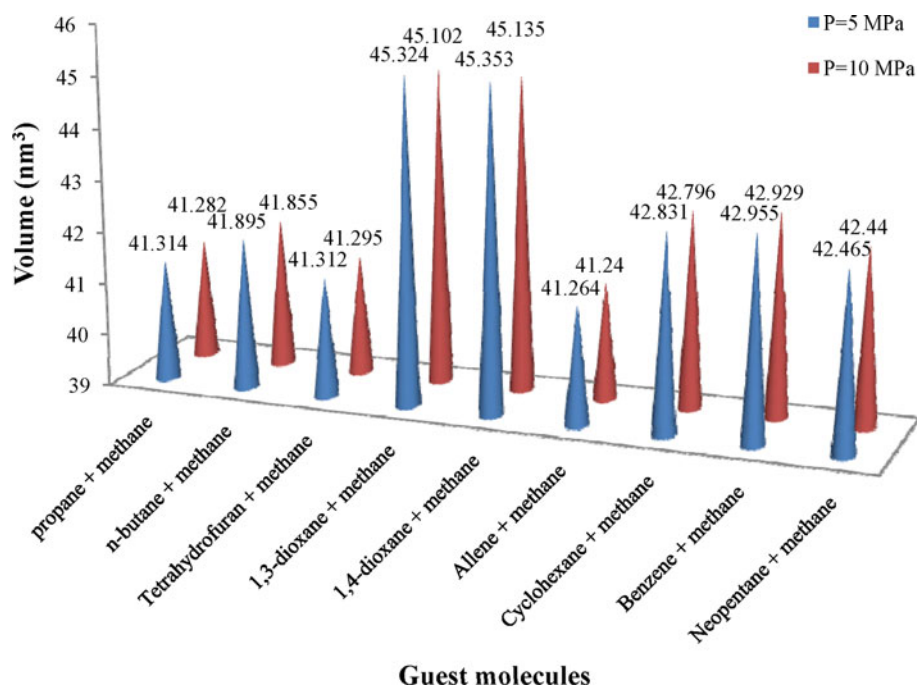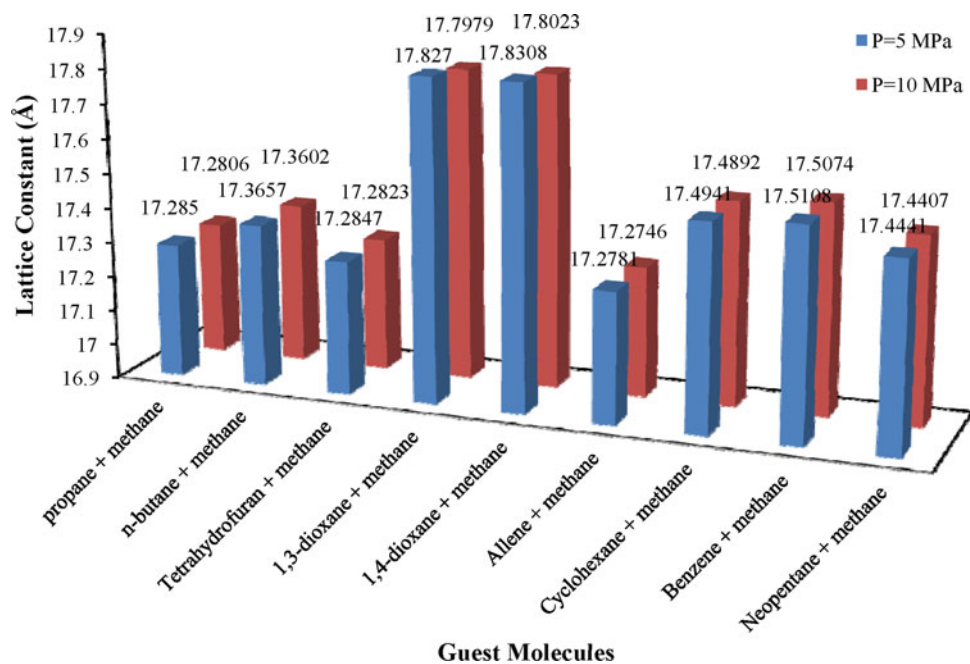

Fig. 4 Lattice constant variation of simulated systems with pressure and guest molecules for structure II clathrate hydrate

$g_{OO}(r)$ function shown in Fig. 7a 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 RDFs in the water and clathrate hydrates. At short distances (less than atomic diameter) $g(r)$ is zero. The first peak location of oxygen–oxygen atoms of water molecules is at 2.775 Å for allene + methane, benzene + methane, cyclohexane + methane, 1,3-dioxane + methane, neopentane + methane and THF + methane hydrates; and this means that all the neighboring oxygen atoms are at the obtained distances. Therefore, the polyhedrons composed of oxygen atoms have the equal edges in the hydrate structure [79, 80]. The second and third peak located at 4.575 and 6.525 Å, respectively for all six cases.

The $g_{OH}(r)$ function is presented in Fig. 7b at pressure 5 MPa and temperature 278 K. The position of the first peak of $g_{OH}(r)$ appears at about 1.725 Å for all six cases of LGM + methane hydrates; the obtained distance shows the hydrogen bonding length.

In Fig. 7c, the RDF of $g_{HH}(r)$ is presented. The first peak is appeared at 2.325 Å, which is also same for all six cases

Fig. 5 Volume variation of simulated systems with temperature and guest molecules for structure II clathrate hydrate
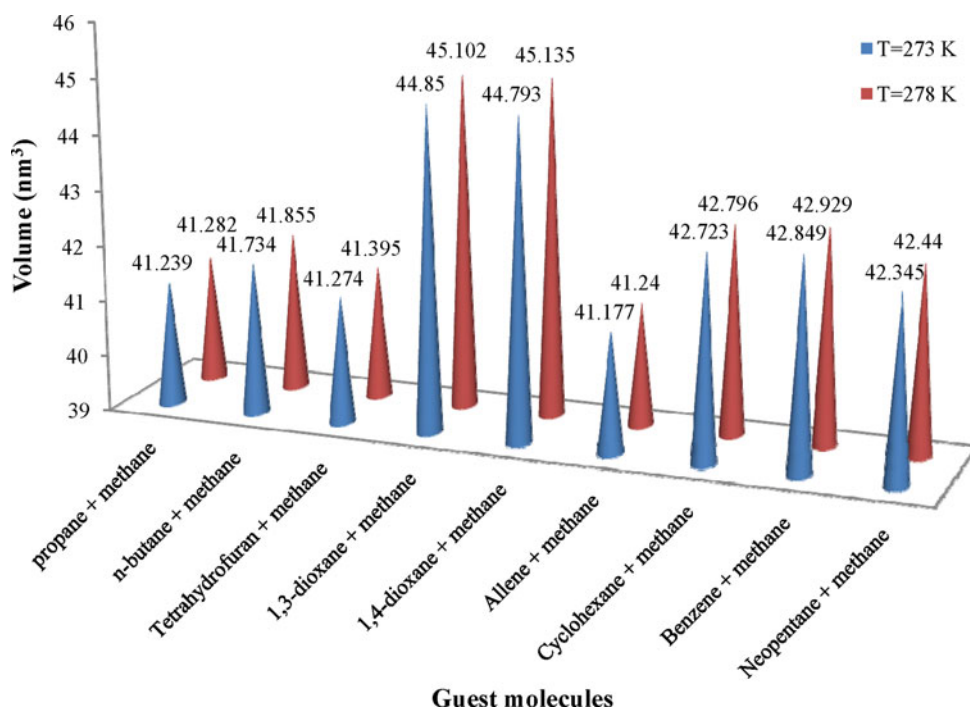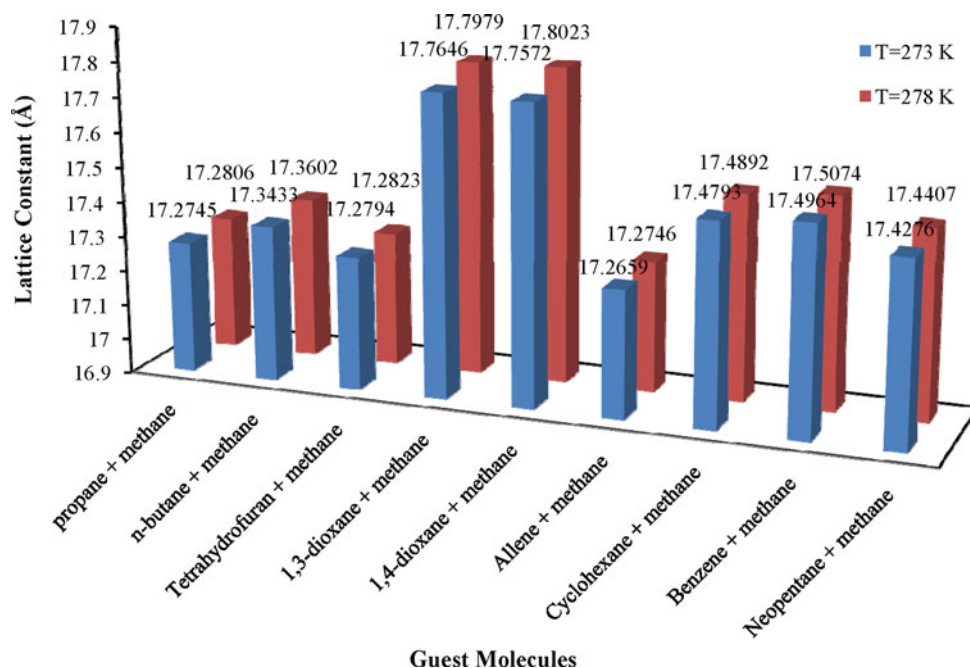

Fig. 6 Lattice constant variation of simulated systems with temperature and guest molecules for structure II clathrate hydrate

of LGM + methane hydrate; this indicates the distance between two nearest hydrogen atoms.

The host–host RDFs give us useful information about host lattice structure. As we know, in a crystal which referred as a long-range order system, RDF has an infinite number of sharp peaks whose heights and separations are characteristic the lattice structure [83]. This state cannot be seen in a gas or liquids which have disordered or short-range order system. In liquids, molecules are in an approximately close packed arrangement in which first two or three shells around given molecule are identified but well-defined positional relationships disappear gradually over longer range [84]. In real gases, molecules are essentially in random relative positioning and there is a single peak in $g(r)$ at the point which potential energy has a minimum [85]. It is concluded from these points that the host lattice structure preserves its crystalline stability during the simulation time.

Table 2 Comparison MD simulation results of the structure II lattice parameters with experimental data

Structure II guests	Experimental lattice parameter (Å) [1, 77, 78]	Structure II guests (this work)	MD calculation (at P = 5 MPa and T = 278 K)
Benzene (Xe as second guest)	17.363 (at −100 °C)	Benzene + methane	17.5108
Propane	17.40	Propane + methane	17.2850
Tetrahydrofuran (THF)	17.194 (at −100 °C)	THF + methane	17.2847
1,3-Dioxane	17.157 (at −100 °C)	1,3-Dioxane + methane	17.827
		n-Butane + methane	17.3657
		1,4-Dioxane + methane	17.8308
		Allene + methane	17.2781
		Cyclohexane + methane	17.4941
		Neopentane + methane	17.4441

The RDFs of oxygen atoms (water)–guest molecules are shown in Fig. 7d and e. Since the RDFs of oxygen atoms (water)–guest molecules are similar to those of hydrogen atoms (water)–guest molecules, Fig. 7f and g, we focus only the RDFs of oxygen atoms–guest molecules. The first peak position of oxygen–(large) guest (OG) molecules occurs at 3.825 Å for 1,3-dioxane + methane and benzene + methane hydrates, at 3.675 Å for THF + methane and cyclohexane + methane hydrates, at 4.575 Å for allene + methane hydrate, and at 4.725 Å for neopentane + methane hydrate. This peak is due to the water molecules that are composed of $5^{12}6^4$ cages (large cage) that contain LGMs. Also, the first peak in oxygen–methane RDF $g_{OM}(r)$ located at 3.825 Å for all six cases of LGM + methane hydrates, which is represented in Fig. 7e due to distance between oxygen and methane in the structure. This peak is due to the water molecules that are composed of 5^{12} cages (small cage) that contain small methane molecules.

The RDFs of guest–guest molecules (GG, GM and MM) are shown in Fig. 7h–j. The MD simulated RDF between two LGMs are shown in Fig. 7h. The first and large peak position happens at 7.425 Å for allene + methane, benzene + methane and cyclohexane + methane hydrates, at 7.125 Å for 1,3-dioxane + methane and THF + methane hydrates, and at 7.575 Å for neopentane + methane hydrate, due to two LGMs close contacts within the water molecules. The first peak position of LGM–methane (GM), Fig. 7i, is at approximately at 7.275 Å for 1,3-dioxane + methane and neopentane + methane hydrates, at 6.525 Å for cyclohexane + methane and benzene + methane hydrates, at 7.125 Å for allene + methane hydrate, and at 6.375 Å for THF + methane hydrate; due to nearest distance between LGM and methane in the small and large cages of structure II clathrate hydrate. In Fig. 7j, the similar MD simulated RDFs between methane and methane are shown. The first peak position in methane–methane

RDF $g_{MM}(r)$ occurs at approximately 6.375 Å for 1,3-dioxane + methane, and at 6.225 Å for benzene + methane hydrate, and at 6.075 Å for cyclohexane + methane, allene + methane, neopentane + methane and THF + methane hydrates; which is the average length between the small cages (5^{12} cages).

From the distribution functions we conclude that the selected LGM + methane structures for this study are indeed stable over the length of our MD simulations under suitable pressure and temperature conditions and that the presence of the methane and LGMs in the clathrate hydrate helps to more stability of overall structure.

In the next part of this work, the effects of LGMs on methane hydrate occupancy in small cages are studied as a function of pressure. MD simulations are performed for the binary LGM + CH$_4$ hydrate in order to determine its CH$_4$ uptake at 278 K in the pressure range up to 1,000 MPa. The LGMs such as THF, 1,4-dioxane, propane, allene, benzene, cyclohexane and neopentane are selected to accommodate in large cages of structure II clathrate hydrates. Then small cages of structure II are filled by methane molecules under temperature 278 K and pressures up to 1,000 MPa. The results are shown in Fig. 8a and b. These results correspond to the situation where all the small cages are occupied by one CH$_4$ molecule. It must be reminded that the large cages are explicitly set to contain one LGM molecule each. The obtained figures show that after 300 MPa the methane occupancy reach an equilibrium amount for 1,4-dioxane + methane and THF + methane while this value for other LGMs + methane is progressive. It seems that the highly methane occupancy in 1,4-dioxane + methane hydrate maybe due to its larger equilibrated volume than the volume of the other LGMs + methane hydrates (see Table 1). The comparison between these results shows the importance of organic promoters on amount of methane storage and its transportation. As it seen in Fig. 8a and b, THF and 1,4-dioxane are better LGMs in order to gas
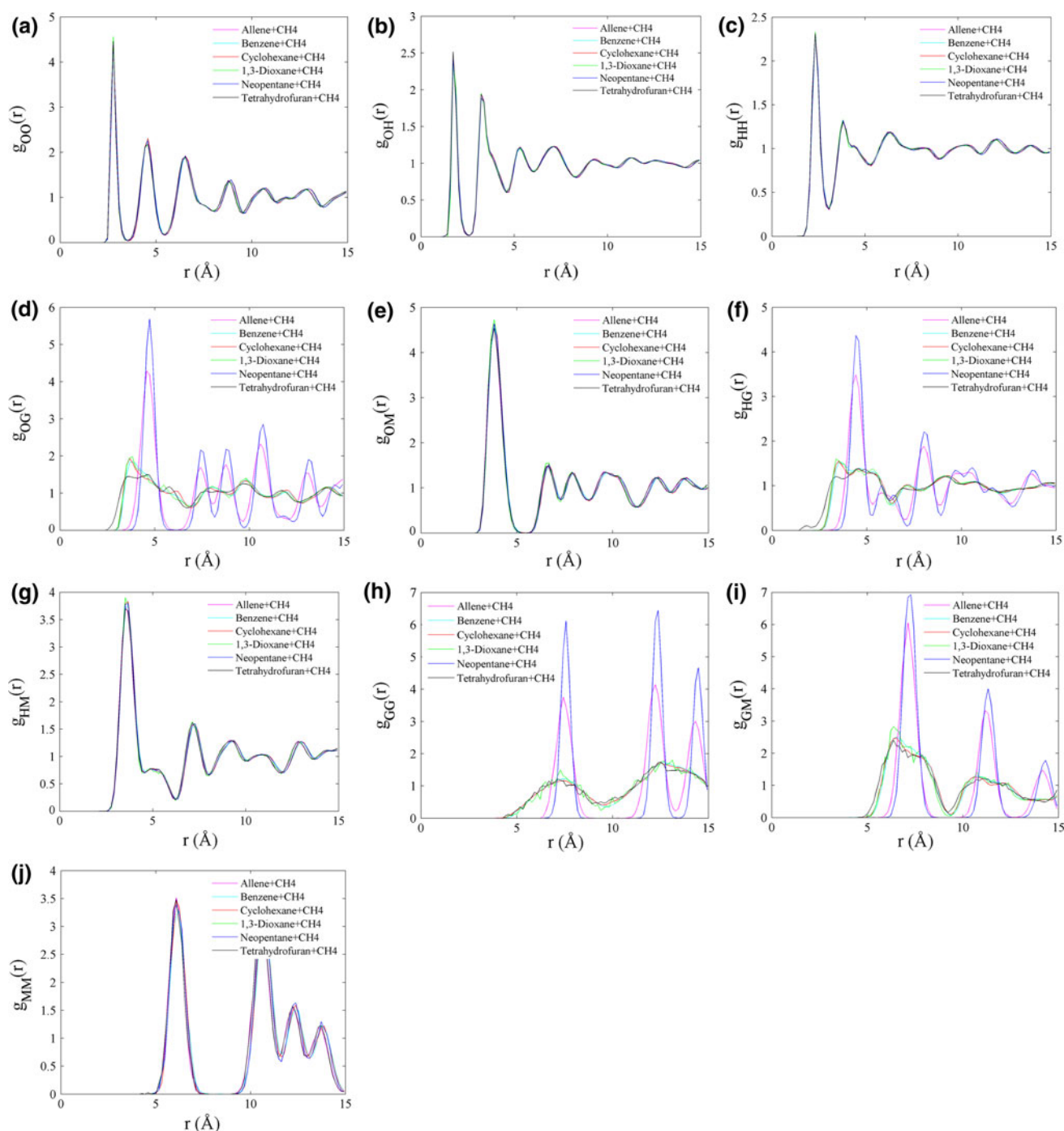
Fig. 7 Comparison of radial distribution functions of **a** $g_{OO}(r)$, **b** $g_{OH}(r)$, **c** $g_{HH}(r)$, **d** $g_{OG}(r)$, **e** $g_{OM}(r)$, **f** $g_{HG}(r)$, **g** $g_{HM}(r)$, **h** $g_{GG}(r)$, **i** $g_{GM}(r)$ and **j** $g_{MM}(r)$, where G is allene, benzene, cyclohexane, 1,3-dioxane, neopentane and tetrahydrofuran, respectively. The RDFs are obtained at $P = 5$ MPa and $T = 278$ K

(methane or hydrogen) storage. The advantages of these organic compounds to gas storage have been proved by experimental and theoretical results [24–30]. Therefore, our MD calculations are proved the experimental and theoretical findings.

Conclusions

The application of MD simulation on the study of the structure II clathrate hydrate of LGM and methane has been reviewed. In the first part of the study, MD
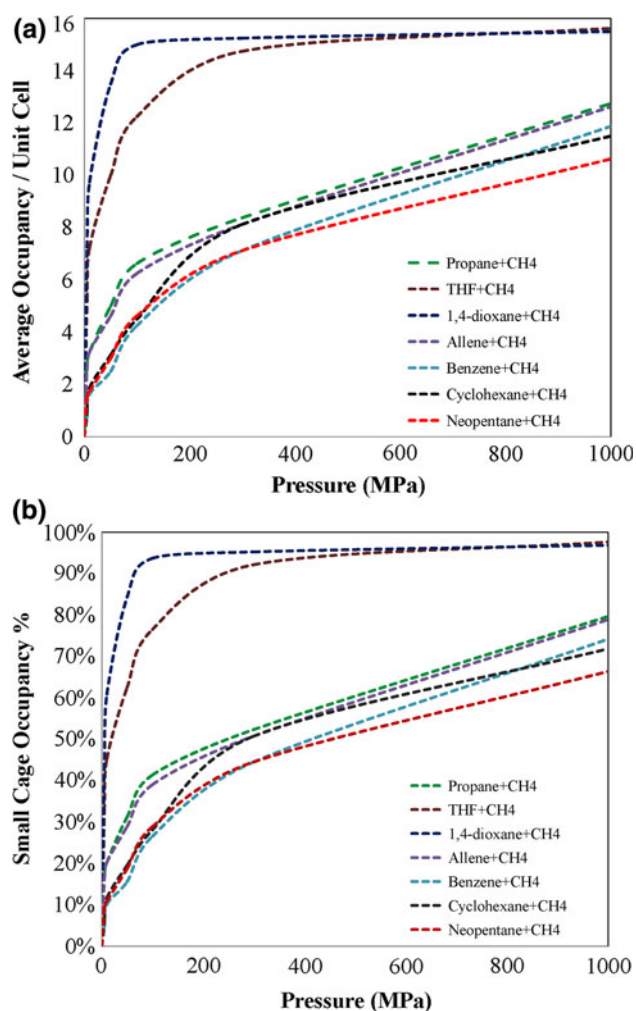
Fig. 8 a Average methane occupancy per unit cell for small cage of structure II clathrate hydrate obtained from MD simulations on the hypothetical methane + LGMs structure II hydrate as a function of pressure at 278 K. **b** Small cage occupancy fraction by methane molecules

indicate the accuracy of molecular simulation for crystal formation and its stability. Existence of an infinite number of sharp peaks in RDF diagrams proves the formation and stability of hydrate crystals during the simulation. Otherwise, in a dissociated system the amount of equilibrium volume and lattice parameter will increase and its diagram will behave as a disordered system. In the next part of the work, the effects of LGMs (located in large cages) on methane occupancy in small cages of structure II hydrate was studied at constant temperature (278 K) and as a function of pressure (up to 1,000 MPa). These results show that the small cages occupancy by methane molecules not only depends on the thermophysical conditions, but also depends on organic promoter type which accommodates in large cages. Our MD results proved that THF and 1,4-dioxane are appropriate compounds to gas storage which is compatible with experimental and theoretical results.

simulations were carried out at isobaric-isothermal (NPT) conditions to obtain equilibrium volume of system and consequently lattice constant. The lattice parameters at equilibrium of simulation were compared with experimental equilibrium data which indicated a good consistency between these data. These simulations showed that average volume of system (and the lattice constants) increases with guest size and temperature, and decreases with pressure. On the other hand, the effects of the binary guest molecules on the thermodynamic stability for the structure II clathrate hydrates have been clarified by evaluating the thermodynamic properties for the hydrates with various binary guest molecules. Also, the obtained RDFs by MD simulations and their analysis proved the stability of selected clathrate hydrates during the simulations under suitable pressures and temperatures. The obtained RDFs

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