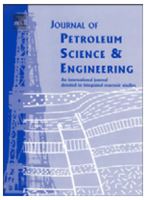
Journal of Petroleum Science and Engineering 76 (2011) 148–154

Contents lists available at ScienceDirect

Journal of Petroleum Science and Engineering

journal homepage: www.elsevier.com/locate/petrol



Effect of potential energy on the formation of methane hydrate

Junfang Zhang [a,*], Zhejun Pan [b]

[a] CSIRO, Earth Science and Resource Engineering P.O. Box 1130, Bentley, Western Australia, 6102, Australia
[b] CSIRO, Earth Science and Resource Engineering, Private Bag 10, South Clayton, Victoria, 3169, Australia

ARTICLE INFO

Article history:
Received 19 June 2009
Accepted 10 January 2011
Available online 21 January 2011

Keywords:
Methane hydrate formation
Molecular dynamics simulation
Hydrogen bond number

ABSTRACT

Molecular dynamics (MD) simulations were performed on the system of methane and water using the SPC/TSE (TSE) and the optimised SPCE/OPLS-UA potentials to decide how the structural and dynamical properties of the methane hydrate are affected when adopting different potential energy models. Our simulations were carried out at a temperature range from 230 to 260 K and a pressure of 300 bar under NPT condition. The results that compare the two models were discussed in terms of the potential energy, hydrogen bond number, mean square displacement, diffusivity, radial distribution function and number density profile for the two models. Investigation over a timescale of 85 ns demonstrated that the methane–water interaction potential energy does have an effect on the structural and dynamical properties and consequently on the hydrate formation. For the optimised SPCE/OPLS-UA potential no methane hydrate was formed over a temperature range of 230–260 K, while for the TSE model the formation of methane hydrate was observed at 230 and 240 K. The hydrate formation is not favoured by the optimised SPCE/OPLS-UA model where the methane–water interaction potential energy becomes more attractive. However, the TSE model, the more repulsive methane–water potential, stabilizes the hydrate structure. Our results for the structural and dynamical properties are self-consistent.

1. Introduction

Gas hydrates are complexes in which gas molecules (guest molecules) are encaged within the hydrogen-bonded lattice network formed by the water molecule (host molecules) (Baez and Clancy, 1994; Berendsen et al., 1984). The different guest molecules, depending principally on their sizes, typically form three types of gas hydrate, type I, II and H which differ in the crystal structure of the host lattice and hence in the number and size of the cages found in the lattice. In the case of methane, type I structure is formed (Berendsen et al., 1995; Cao et al., 2001). Gas hydrates have attracted a lot of interest in the past decade due to the flow assurance and safety considerations of hydrate plugs and the major risks they pose to oil and gas drilling and production operations (Chau and Mancera, 1999; Christiansen and Sloan, 1994). Many years of research has been devoted to the studies on hydrate formation and dissociation because the industrial and environmental applications of gas hydrates require a fundamental understanding of the mechanism of the hydrate formation which involves nucleation, growth and the inhibition.

Molecular computations on the structural and thermodynamic properties of gas hydrate and the factors influencing its stability have been performed (Cruickshank and Masutani, 1999; Darden et al., 1993; Duffy et al., 2004; English and Johnson, 2005; English and MacElroy, 2004; Essmann et al., 1995; Forrisdahl et al., 1996; Guissani and Guillot, 1993; Guo et al., 2008; Hammerschmidt, 1934; Hawtin and Rodger, 2006; Hermans et al., 1984; Huang and Bartell, 2002; Klapproth et al., 2003; Koh, 2002; Konrad and Lankau, 2005; Lee and Holder, 2000; Lee and Holder, 2002). A number of studies have also been performed that relate to the mechanisms by which hydrate growth commences. Several different models for hydrate nucleation (Forrisdahl et al., 1996; Guissani and Guillot, 1993; Hammerschmidt, 1934; Lindahl et al., 2001) have been proposed. The nucleation processes in a number of different systems have been investigated by the MD method (Mancera and Buckingham, 1995; Matsumoto et al., 2002; Moon et al., 2003a). More recently MD has been used to simulate water–methane–hydrate mixtures in their full dynamical complexity (Moon et al., 2003b; Paschek, 2004), hydrate nucleation and growth (Radhakrishnan and Trout, 2002; Rodger, 1990a; Rodger, 1990b; Ryckaert et al., 1977; Skipper, 207; Sloan, 2000; Storr et al., 2004). Tse et al. (Subramanian et al., 2000) have demonstrated that the simple point charge (SPC) model for the interaction of water molecules is able to describe many of the observed dynamical properties of ice IC and hydrates. Calculations using the optimised SPCE/OPLS-UA model (Thompson et al., 2006) predict a larger cavity for the methane molecule than the calculations using the Lorentz–Berthelot mixing rules. Although numerous MD simulations on methane/water have been conducted, very few focus on solvation energies (Forrisdahl et al., 1996; Guissani and Guillot, 1993; Thompson et al., 2006; Toxvaerd, 2001). Oliver and Timm (Thompson et al., 2006) have shown that the position and shape of the peak in the

---

* Corresponding author.
E-mail address: Junfang.Zhang@csiro.au (J. Zhang).

0920-4105/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.petrol.2011.01.004

radial distribution function of methane and water are controlled by water–water interactions and consequently by the structural effects of the chosen water potential; the structure of the cavity generated by the water–methane interaction potential seems to be more important than the structure of the liquid water. Paschek (Toxvaerd, 2001) has suggested that the result of MD simulations on the methane solvation depends critically on the chosen water potential.

The SPC model of water interactions and its extension, SPCE are widely used in the computer simulation of water and aqueous systems. Although simple in form, these potentials have predicted the liquid–vapour coexistence curve of water with good accuracy (Zhang et al., 2007) and reproduced a number of properties of methane in the liquid phase. In this paper we use these relatively simple water potentials to investigate the effect of the methane–water interaction potential energy on the structural and dynamical properties and consequently on the hydrate formation by comparing the results from the TSE model (Subramanian et al., 2000) and the optimised SPCE/OPLS-UA model (Thompson et al., 2006) over the temperature range from 230 to 260 K. The starting condition of 230 K was chosen by referring to the literature: Baez and Clancy observed the growth of methane hydrate at 220 K and 60 Mpa by means of a MD simulation using a system that involved a fixed methane hydrate structure (Tse et al., 1983) and the immediate and sustained growth of the hydrate phase was observed throughout the duration of the 30 ns simulation where the starting configuration contains a substantive cluster of methane hydrate and the temperature is under 240 K in our previous paper (Zhang, 2008). In order to avoid the memory effect on hydrate nucleation, we generate a disordered water film which contains no methane molecules and the water film is surrounded by the methane molecules. The reason to set the methane concentration within the water film as zero is that the high concentration of aqueous methane is expected to provide a large thermodynamic driving force for the formation of the methane hydrate phase in our previous paper (Zhang, 2008). In the current work, we run simulation for up to 85 ns to compare the structural and dynamical properties and hydrate formation for the two potential energy models.

The remainder of this paper is structured as follows. In Section 2 simulation details are explained. In Section 3 the results and discussions are presented and finally the analysis is summarized and concluded in Section 4.

2. Simulation details

In this study, the MD simulations were performed using GROMACS (Van der Waals and Plateeuw, 1959; Vatamanu and Kusalik, 2008). The system studied consists of CH_4 and H_2O. The initial configuration is composed of a disordered water film with the methane concentration being zero within the film and surrounding methane fluid. This configuration contained 1000 water and 600 methane molecules in an orthorhombic cell of initial dimensions $33 \times 29 \times 140$ Å^3. The water was contained in a film of 40 Å. The region surrounding this film contained methane fluid. The methane and water interface is perpendicular to the *z* direction. Fig. 1 shows the initial setup of the geometry of the simulation environment with the barostat (300 bar) applied. Two potential energy models were used. One is the potential energy model of Tse et al. (Subramanian et al., 2000) and the other one is the optimised SPCE/OPLS-UA model (Thompson et al., 2006). The former used the simple point charge (SPC) water potential model, a three-center one, (Westacott and Rodger, 1998) for water interaction. Point charges are placed on the atomic sites and the oxygen centers interact through a Lennard-Jones potential. For methane and water interaction, a potential energy model, here we called the TSE model (Subramanian et al., 2000) was used. The interaction parameters were listed in Table 1. The latter model, the optimised SPCE/OPLS-UA model, proposed by Oliver et al. (Thompson et al., 2006), used the SPCE potential for the description of the water–water interactions, because the SPCE potential produced the most reliable description of the density of pure water. The interaction parameters for the optimised SPCE/OPLS-UA models are summarized in Table 2. The comparison of the methane–water oxygen potential energy for the two models is shown in Fig. 2 where we can see that the methane–water oxygen interaction energy becomes more attractive for the optimised SPCE/OPLS-UA model. Force calculations were truncated at a distance of 1.2 nm. For the calculation of long-range electrostatic forces, the Particle-Mesh Ewald (PME) method proposed by Darden (Westacott and Rodger, 1996; Zhang and Choi, 2006) was used. All bond lengths were constrained using the Shake algorithm (Zhang et al., 2009). The temperature was fixed by using Berendsen thermostat (Zhang et al., 2008) over the temperature range from 230 to 260 K and the Berendsen pressure coupling algorithm was used to keep the pressure constant at 300 bar. Periodic boundary conditions were applied in three directions. The equations of motion were integrated with a 2 fs time step. Each MD run was done in two steps. The first step consisted of a 5 ps simulation with the steepest-descent method to perform energy minimization in order to reduce the thermal noise in the structures and potential energies which can prevent the crash of the simulation due to bad contact (extremely large force) between molecules. The second step consisted of an 85 ns production run. The general equilibrium molecular dynamics simulation consists of two parts. The first part of the simulation is performed to allow the system to relax to reach the equilibrium and then a production run starts

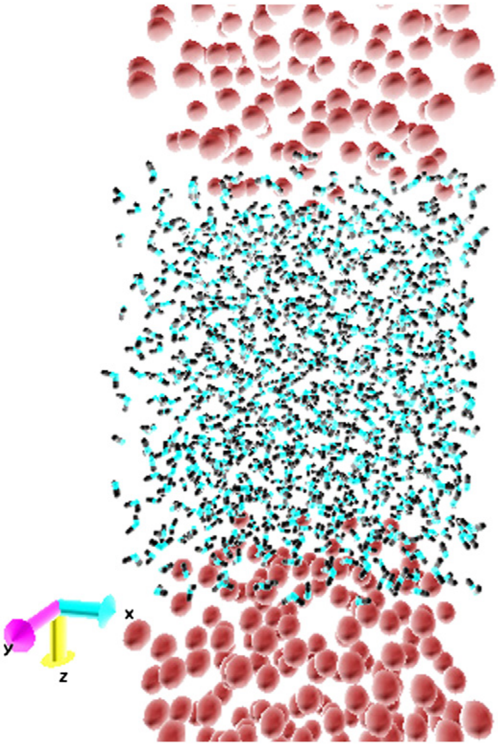


Fig. 1. Initial setup of the simulation environment showing the water film and part of the methane fluid. Much of the methane fluid region is not shown for clarity. The spheres are methane, while the small cylinders represent water molecules. The *Z*-direction is normal to the methane/water interface.

Table 1
Intermolecular potential parameters for the TSE model.

Interaction	σ(nm)	4ε(kJ/mol)
O–O	0.316	2.60
CH_4–O	0.333	3.05
CH_4–H	0.325	1.69
CH_4–CH_4	0.364	5.46