



# An efficient fully atomistic potential model for dense fluid methane



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## ARTICLE INFO

### Article history:

Received 28 January 2016

Received in revised form

25 March 2016

Accepted 28 March 2016

Available online 30 March 2016

### Keywords:

OPLS

Radial distribution function

Diffusion coefficient

Molecular dynamics

## ABSTRACT

A fully atomistic model aimed to obtain a general purpose model for the dense fluid methane is presented. The new optimized potential for liquid simulation (OPLS) model is a rigid five site model which consists of five fixed point charges and five Lennard-Jones centers. The parameters in the potential model are determined by a fit of the experimental data of dense fluid methane using molecular dynamics simulation. The radial distribution function and the diffusion coefficient are successfully calculated for dense fluid methane at various state points. The simulated results are in good agreement with the available experimental data shown in literature. Moreover, the distribution of mean number hydrogen bonds and the distribution of pair-energy are analyzed, which are obtained from the new model and other five reference potential models. Furthermore, the space–time correlation functions for dense fluid methane are also discussed. All the numerical results demonstrate that the new OPLS model could be well utilized to investigate the dense fluid methane.

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## 1. Introduction

Methane is considered as a key fuel with environmental advantages and industrial importance because it releases less sulfur oxides, hydrocarbons, and carbon monoxide when combusted. Due to its general importance and common appearance, methane has been widely studied by researchers using experiment and computer simulation [1–4]. However, it is still not completely understood, especially at low temperature domain [5–7]. Although the molecular dynamics (MD) and Monte Carlo (MC) simulations based on statistical mechanics have played a critical role in investigating the various properties of different methane systems [8–20], the simulation result and computational efficiency are mainly determined by the intermolecular potential model [15]. Therefore, developing a credible and highly efficient intermolecular potential model is an interesting work for methane molecule system.

Over the past three decades, many classical potential models have been developed, which allow capturing different aspects of methane [2,6,12,21,22]. The site–site potential model (SITE–SITE) was reported by Williams [23,24], and employed to study the static properties of methane [7]. Elijah Johnson introduced the reference interaction site model (RISM) which had been successfully utilized to investigate the structural properties of molecular liquids [7,25].

Meantime, RISM was firstly applied to discuss the carbon–carbon distribution function of the dense liquid methane by Anton Habenschuss [5]. However, all of these potential functions adopted the exp-functions, which makes the calculations of the long range interaction more complex and costs much more the computational time in numerical simulations.

Williams and co-workers have developed the highly efficient Lennard-Jones (12-6) (LJ (12-6)) potential for the fluid methane since 1984 [26–29], which has been applied to study the water and methane binary mixture system [29]. And later it was successfully used in studying the methane molecular adsorbed on a graphite surface by Serevin et al. [27,30]. A short-range LJ potential interaction and a long-range electrostatic potential for exploring the phase transitions of liquid methane under high pressure were given by S.M. El-Sheikh et al. [8]. Liu D. and Yang Q. applied it to investigate the adsorption of methane in heterometallic metal-organic frameworks with anions [13]. Meantime, Williams and co-workers have employed the optimized potential for liquid simulation (OPLS) model for studying the methane ensemble [23,24]. It has also been applied to study the thermodynamics, transport and structural properties by M. Abbaspour [6]. Nevertheless, these highly efficient all-atom potential of methane cannot exactly predict the structural property and diffusion coefficient for dense fluid methane at low temperature domain.

To obtain a reasonable, credible and highly efficient OPLS model for accurately investigating the dense fluid methane, in this paper, we propose a modification of OPLS (MOPLS) model based on the

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experimental data of dense fluid methane using MD simulation. The main difference between the MOPLS model and Williams' OPLS model includes the following two points: (1)  $l_{\text{CH}} = 1.026 \text{ \AA}$  was used in the Williams' OPLS model [10]. However,  $l_{\text{CH}} = 1.087 \text{ \AA}$  is employed in this work, since the bond length of methane is about  $1.087 \text{ \AA}$  obtained by the experiment [4,31]. (2) The parameters of Williams' OPLS model were determined using the numerous MC simulations, while we employ a fit of the experimental data of dense fluid methane to obtain the parameters of LJ potential using MD simulation, and use the same charges as Williams' OPLS model. To check the validity of the MOPLS model, the structural and dynamical properties of dense fluid methane are obtained from the MOPLS model using MD simulation at the various state points.

The remainder of the paper is organized as follows: In Section 2, we give the MOPLS model for dense fluid methane and describe other five different potential models for comparison. Some of the details of the computer MD calculations are given in Section 3. The structural and dynamical properties of dense fluid methane are discussed and analyzed in Section 4. Finally, we summarize the current work, and illustrate several newly developed aspects.

## 2. The potential model

### 2.1. MOPLS and OPLS models

The OPLS model reported by Jorgensen and Tirado-Rives is written as [10,11].

$$U_{\text{OPLS}}(r) = \sum_{\alpha,\beta} \sum_{i \in \alpha, j \in \beta} \left( 4\epsilon_{ab} \left( (\sigma_{ab}/r_{ij})^{12} - (\sigma_{ab}/r_{ij})^6 \right) + q_i q_j / 4\pi\epsilon_0 r_{ij} \right), \quad (1)$$

where  $\epsilon_0$  represents the permittivity of vacuum,  $\epsilon_{ab}$  governs the strength of the interaction and  $\sigma_{ab}$  defines a length scale,  $a$  and  $b$  are the types of carbon and hydrogen,  $\alpha$  and  $\beta$  denote different methane molecules,  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$  indicates the Cartesian distance between the site of atoms  $i$  and  $j$ ,  $\mathbf{r}_i$  and  $q_i$  stand for the site and charge of atom  $i$ . The parameters of OPLS model atom–atom interactions of methane were given by Williams using the numerous MC simulations [11]. However, the structural and dynamical properties of dense fluid methane predicted by the OPLS are in poor agreement with the experimental data at low temperature domain. In order to overcome the drawbacks of OPLS model, we modify the OPLS model based on a fit of the experimental data of dense fluid methane using numerous MD simulations, and the corresponding parameters are listed in Table 1.

### 2.2. RISM and SITE–SITE model

We introduce the RISM and SITE–SITE models because they are in good agreement with experimental data for dense fluid methane [5], and can be employed to compare with the properties obtained by MOPLS model. RISM is given by:

$$U_{\text{RISM}}(r) = \sum_{\alpha,\beta} \sum_{i \in \alpha, j \in \beta} \epsilon_{ab} \lambda_{ab} (\lambda_{ab} - 6)^{-1} \left( - \left( r_{ab}^0 / r_{ij} \right)^6 + (6/\lambda_{ab}) \exp \left( \lambda_{ab} \left( 1 - r_{ij} / r_{ab}^0 \right) \right) \right), \quad (2)$$

where  $r_{ab}^0$  indicates the equilibrium interatomic distance,  $\lambda$  denotes the steepness of the repulsion in the potential. The parameters  $r_{ab}^0$ ,  $\lambda$  and  $\epsilon$  are determined by SITE–SITE model. The SITE–SITE potential is defined as [7].

$$U_{\text{SITE-SITE}}(r) = \sum_{\alpha,\beta} \sum_{i \in \alpha, j \in \beta} \left( A_{ab} \exp(B_{ab} r_{ij}) + C_{ab} r_{ij}^{-6} \right), \quad (3)$$

where the parameters  $A_{ab}$ ,  $B_{ab}$  and  $C_{ab}$  have been determined from crystal lattice energies of hydrocarbons by Williams [24]. The details of two models are given in Table 2. The distance between the carbon C and hydrogen H sites on the same methane molecule is  $l_{\text{CH}} = 1.026 \text{ \AA}$  in the two models.

### 2.3. Lennard-Jones potential model

The LJ (12-6) atom–atom pair interaction is a highly efficient model for methane. It was given by Refs. [27,30].

$$U_{\text{LJ}}(r) = \sum_{\alpha,\beta} \sum_{i \in \alpha, j \in \beta} 4\epsilon_{ab} \left( (\sigma_{ab}/r_{ij})^{12} - (\sigma_{ab}/r_{ij})^6 \right), \quad (4)$$

the parameters of the LJ (12-6) of fluid methane are listed in Table 3, whereas it cannot exactly predict the structural properties and diffusion constants of dense fluid methane. In this work, because the Williams' and Severin' LJ (12-6) potential models are in poor agreement with experimental data, we make use of James M. Phillips' LJ (12-6) potential to discuss the properties of dense fluid methane.

## 3. Simulation method and details

In this paper, the five sites all-atom rigid tetrahedral molecule model is adopted. The carbon-hydrogen  $l_{\text{CH}} = 1.087 \text{ \AA}$  is used in the MOPLS model. However, the carbon-hydrogen  $l_{\text{CH}} = 1.026 \text{ \AA}$  is employed in other five potential models. All the MD simulations have been performed for the system of 1000 methane molecules in the cubic box and the periodic boundary condition [33] has been applied. The intermolecular interactions were spherically truncated at cutoff distances,  $r_{\text{cut}} = 3.0\sigma$  based on the atom of different

**Table 2**

The parameters of RISM and SITE–SITE potential models for fluid methane, were given by Anton Habenschuss [5].

Type	$A(\text{kcal/mol})$	$B(\text{\AA}^{-1})$	$C(\text{\AA}^6 \text{ kcal/mol})$	$\epsilon/k_B(\text{K})$	$\sigma(\text{\AA})$	$r^0(\text{\AA})$	$\lambda$
C-C	61900	3.60	505	48.8	3.25	3.78	13.60
C-H	11000	3.67	128	20.7	2.80	3.43	12.59
H-H	2629	3.74	32.3	6.83	2.42	3.26	12.21

**Table 1**

The parameters of different OPLS models for fluid methane, were given by Kaminski et al. (I) [32], and M. Abbaspour. (II) [6], modified in this work by using extensive MD simulations (III).

Type	$\epsilon/k_B(\text{K})^I$	$\sigma(\text{\AA})^I$	$\epsilon/k_B(\text{K})^{II}$	$\sigma(\text{\AA})^{II}$	$\epsilon/k_B(\text{K})^{III}$	$\sigma(\text{\AA})^{III}$
C-C	33.21	3.50	51.2	3.35	46.8	3.45
C-H	22.39	3.00	20.98	3.08	17.17	3.06
H-H	15.10	2.50	8.60	2.81	6.30	2.67
$q(e)$	$q_C = -0.24^I$ , $q_H =$	$0.06^I$ ; $q_C = -0.572^{II,III}$ , $q_H =$		$0.143^{III}$		

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