wt: Molecular modeling of gas hydrate disassociation

by

Henrik Andersen Sveinsson

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Faculty of Mathematics and Natural Sciences
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Abstract

The most important things

Acknowledgements

I acknowledge...

Contents

Chapter 1

Introduction

Here, I introduce the introduction

1.1 Gas Hydrates

Part I

State of the science

Chapter 2

The Theory of Gas Hydrates

2.1 The Water Molecule

Table 2.1: Experimental data for the water molecule.

Description	Symbol	Value
H-O-H angle	θ	104.52°
Distance O-H	d_{OH}	0.9572 Å

2.2 The Methane Molecule

2.3 Gas Hydrates

Chapter 3

Existing Models

3.1 TIP4P-ICE water model

The TIP4P-ICE was developed by [1], and was used by [2] in the first successful simulation of spontaneous methane hydrate growth.

3.1.1 Overview

The TIP4P-ICE water model is a rigid water model with 4 sites for each water molecule: One O-site, two H-sites, and a site commonly referred to as the M-site. The M-site is supposed to slightly move the oxygen charge, and it is situated on the bisector of the H-O-H angle. The parameters for the arrangement as well as the masses of hydrogen and oxygen are taken from experimental observations, and were listed in table 2.1.

Table 3.1: Parameters for TIP4P-ICE model as in [1].

Description	Symbol	Value
Lennard-Jones energy	ε/k	100.5 K
Lennard-Jones characteristic distance	σ_{OO}	3.155 Å
Distance O-site to M-site along bisector	d_{OM}	0.157 Å
Hydrogen charge	q_H	0.5676 e

3.1.2 Interactions

There are two interaction potentials for TIP4P-ICE: electrostatic interactions and Lennard-Jones (LJ) interactions, with the following functional forms:

Table 3.2: Lennard-Jones parameters for united atom methane.

Description	Symbol	Value
Lennard-Jones energy	ε/k_B	147.9 K
Lennard-Jones characteristic distance	σ_{MM}	3.73 Å

$$U_{LJ} = 4\varepsilon \left[\left(\frac{\sigma}{r_{OO}} \right)^{12} - \left(\frac{\sigma}{r_{OO}} \right)^{6} \right] \tag{3.1}$$

$$U_e = \frac{e^2}{4\pi\varepsilon_0} \sum_{a,b} \frac{q_a q_b}{r_{ab}} \tag{3.2}$$

Since the molecules are treated as rigid, interactions are only between sites on different molecules.

3.2 United Atom Methane

United atom methane is the united atom model for methane, and is effectively a single Lennard-Jones interaction site for each methane molecule.

$$U_{LJ} = 4\varepsilon \left[\left(\frac{\sigma}{r_{MM}} \right)^{12} - \left(\frac{\sigma}{r_{MM}} \right)^{6} \right] \tag{3.3}$$

A parameter set for this methane representation can for example be taken from [3], and are listed in 3.2.

3.3 Combining particles of different species in a model

Having different potentials, for different aggregate particles (such as TIP4P/ICE), we want a way to combine them in a model containing both species. For electrostatic interactions, the combination rules are straightforward, as they follow from Coulombs law. For Lennard-Jones interactions, there is not such a simple combination law, and in principle, one has to fit parameters for each unique pair of particles. Luckily, it is possible to make rules that combine particles without going into an extensive parameter fitting exercise.

3.3.1 Lorentz-Berthelot combination rules

Perhaps the simplest way to combine two species Lennard-Jones particles, is to use the following rules from two sets of parameters (ε_{ii}, σ_{ii}) and (ε_{jj}, σ_{jj}) for interactions between two particles of the same species i or j, on to a set of parameters (ε_{ij}, σ_{ij}) for interactions between one particle of each species:

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \tag{3.4}$$

$$\sigma_{ij} = \frac{1}{2}\left(\sigma_{ii} + \sigma_{jj}\right) \tag{3.5}$$

Part II

Numerical models

Chapter 4

Verification of LAMMPS simulation setup

In this chapter, i verify that my LAMMPS setup reproduces known results from the literature. This is necessary to trust the model to go further with modifications.

4.1 TIP4P/ICE

4.2 United atom methane

4.3 Nucleation of methane hydrates

Chapter 5

Simulation tools

5.1 LAMMPS

5.1.1 Input files

Lammps input files are a set of commands to be executed. Some commands are only valid in the right order. The structure of such a file is:

1. **Initialization:** Units, processors, boundary conditions, atom_style, pair_style
2. **Atom definition:** Either from input file (restart/data) or making a lattice or region and create a box and atoms.
3. **Settings:**
4. **Run:**

Most properties are already set with a standard value, which means that only non-standard properties has to be set.

atom_style atom_style decides what kinds of interactions are possible to implement.

pair_style The pair_style interaction is somewhat misleading. What it actually means is that bonds and angles are not predefined.

All commands ar available from the LAMMPS documentation [4]. A very good beginners guide for LAMMPS [5]

Part III

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