H_2O:CO:CO_2
C++ implementation of a force field set

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Introduction

This document gives a complete description of a set of pair potentials to model the interactions between H_2O, CO, and CO_2 molecules. These forcefields were used by L.J. Karssemeijer for the work during his Ph.D. project. A C++ implementation of the forcefield, with analytical implementation of all the forces, is available online, through the website of the theoretical chemistry group at the Radboud University Nijmegen (`http://www.theochem.ru.nl`).

All molecules are treated based on their atomic coordinates and are fully flexible within their own intramolecular potential, V^{intra}. Interactions between molecules are typically described as the sum of an electronic contribution from a set of charges on each molecule and a contribution accounting for the van der Waals forces.

Because the simulations use periodic boundary conditions, an interaction cutoff has to be introduced to avoid interaction between particles and their periodic images. All interactions are therefore smoothly truncated in a range $r_{\text{cut}} - d < |\boldsymbol{r}| < r_{\text{cut}}$ using a switching function:

$$S(x) = 2x^3 - 3x^2 + 1, \qquad \text{where} \qquad x = \frac{|\boldsymbol{r}| - r_{\text{cut}} + d}{d}. \tag{1}$$

The cutoff distance r_{cut} is set to 10 Å and the width of the switching window d is equal to 1 Å. To avoid the situation where molecules are partly inside the truncation range, the switching is based on the center of mass distance between the molecules. To avoid self-interactions between periodic images, this means that the dimensions of the simulation box needs to be at least $2(r_{\text{cut}} + L_{\text{mol}})$, where L_{mol} is the biggest atomic distance in the biggest molecule in the system.

In the following description, the molecules are numbered by Latin indices $i, j, \ldots$ and the atoms within each molecule with the Greek indices $\alpha, \beta, \ldots$. The position of atom α in molecule i is denoted by $\boldsymbol{r}_{i\alpha}$ and the shorthand $\boldsymbol{r}_{i\alpha-j\beta} \equiv\equiv \boldsymbol{r}_{i\alpha} - \boldsymbol{r}_{j\beta}$ is used to denote distance vectors. All the parameters of the model can be found in Table 1.

1 H_2O-H_2O

The TIP4P/2005f [1] potential is used to describe the interactions between water molecules. This potential is a flexible version of the rigid TIP4P/2005 potential [2], which was parametrized specifically to model the condensed phases of water.
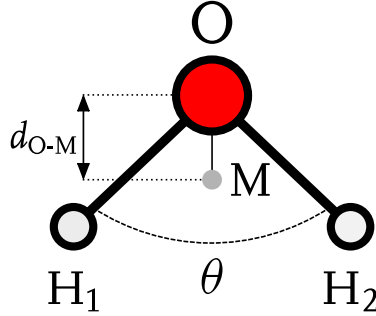
Figure 1: Schematic representation of the geometry of a water molecule in the TIP4P/2005f potential.

In the TIP4P/2005f model, every H_2O molecule is modeled with four interaction sites (see Fig 1). Three of these are situated on the the atomic sites (O,H_1, and H_2) and an additional interaction site, M, is located on the H-O-H bisector, at a distance $d_{\text{O-M}}$ from the oxygen atom, defined as

$$d_{\text{O-M}} = d_{\text{O-M}}^{\text{rel}} \left(|\boldsymbol{r}_{\text{O-H}_1}| + |\boldsymbol{r}_{\text{O-H}_2}| \right). \tag{2}$$

The full interaction potential is the sum of the intramolecular contributions, V^{intra}, and the intermolecular part: V^{inter}. The intramolecular part contains two Morse potentials to constrain the O-H bond lengths and an harmonic potential to allow the H-O-H angle θ to vary. The intramolecular part is, for each molecule, equal to

$$V^{\text{intra}} = V_{\text{O-H}_1}(\boldsymbol{r}_{\text{O-H}_1}) + V_{\text{O-H}_2}(\boldsymbol{r}_{\text{O-H}_1}) + V_{\text{H-O-H}}(\theta), \tag{3}$$

where

$$V_{\text{O-H}_i}(\boldsymbol{r}_{\text{O-H}_i}) = D_r \left\{ 1 - \exp\left[-\beta \left(|\boldsymbol{r}_{\text{O-H}_i}| - r_{\text{O-H}}^{\text{eq}} \right) \right] \right\}^2, \tag{4}$$

and

$$V_{\text{H-O-H}}(\theta) = \frac{1}{2} K_\theta \left(\theta - \theta^{\text{eq}} \right)^2. \tag{5}$$

The intermolecular part of the interactions are the sum of the electrostatic interactions, V^{el}, between the charges of the hydrogen and the M sites, and a Lennard-Jones interaction, V^{vdW}, between the oxygen atoms. We thus have

$$V^{\text{inter}} = V^{\text{el}} + V^{\text{vdW}} \tag{6}$$

$$= \sum_{\substack{i,j=0 \\ i<j}}^{N_{H_2O}} \sum_{\substack{\alpha=H_1,H_2,M \\ \beta=H_1,H_2,M}} \frac{1}{4\pi\epsilon_0} \frac{q_\alpha q_\beta}{|\boldsymbol{r}_{i\alpha} - \boldsymbol{r}_{j\beta}|}$$

$$+ \sum_{\substack{i,j=0 \\ i<j}}^{N_{H_2O}} 4\epsilon_{OO} \left(\left(\frac{\sigma_{OO}}{|\boldsymbol{r}_{iO} - \boldsymbol{r}_{jO}|} \right)^{12} - \left(\frac{\sigma_{OO}}{|\boldsymbol{r}_{iO} - \boldsymbol{r}_{jO}|} \right)^{6} \right) \tag{7}$$

2   CO-CO

Every CO molecule is modeled with three sites: one on each atom and an additional site on the center of mass (X). The complete potential contains a Morse interaction with each molecule to constrain the C-O bond lengths and an intermolecular part

Table 1: Potential parameters of the pair interaction models.

		Intramolecular parameters	

H$_2$O		CO		CO$_2$	
q_{H}	0.5564 e	$q_{\mathrm{C}}^{\mathrm{eq}}$	-0.47 e	q_{C}	0.6645 e
$r_{\mathrm{O\text{-}H}}^{\mathrm{eq}}$	0.9419 Å	$q_{\mathrm{O}}^{\mathrm{eq}}$	-0.615 e	$r_{\mathrm{C\text{-}O}}^{\mathrm{eq}}$	1.161 Å
$d_{\mathrm{O\text{-}M}}^{\mathrm{rel}}$	0.13194 Å	$r_{\mathrm{C\text{-}O}}^{\mathrm{eq}}$	1.1282 Å	θ^{eq}	180 deg
θ^{eq}	107.4°	D	11.2301 eV	K_θ	1.46×10^{-3} eV deg^{-2}
D	4.48339 eV	a	2.3281 Å^{-1}	K_1	96.7 eV Å^{-2}
a	2.287 Å^{-1}	γ_{C}	3.844 Å^{-1}	K_2	8.11 eV Å^{-2}
K_θ	1.16123×10^{-3} eV deg^{-2}	γ_{O}	2.132 Å^{-1}		

		Intermolecular parameters	

H$_2$O-H$_2$O		CO-CO		CO$_2$-CO$_2$	
ϵ_{OO}	8.03×10^{-3} eV	A_{CO}	1517 eV	ϵ_{CO}	4.2277×10^{-3} eV
σ_{OO}	3.1644 Å	A_{OO}	6370 eV	ϵ_{OO}	7.1521×10^{-3} eV
		A_{CC}	361.4 eV	ϵ_{CC}	2.4989×10^{-3} eV
		B_{CO}	3.543 Å^{-1}	σ_{CO}	2.921 Å
		B_{OO}	4.252 Å^{-1}	σ_{OO}	3.064 Å
		B_{CC}	2.835 Å^{-1}	σ_{CC}	2.785 Å
		C_{CO}	15.19 eV Å^6		
		C_{OO}	10.55 eV Å^6		
		C_{CC}	33.45 eV Å^6		

H$_2$O-CO		H$_2$O-CO$_2$			
A_{CH}	677.23 eV	A_{CH}	80.711 eV		
A_{OH}	537.70 eV	A_{OH}	40.450 eV		
A_{CO}	427.92 eV	A_{CO}	47.974 eV		
A_{OO}	6.8674×10^7 eV	A_{OO}	5469.6 eV		
B_{CH}	4.5056 Å^{-1}	B_{CH}	3.00581 Å^{-1}		
B_{OH}	4.5505 Å^{-1}	B_{OH}	3.52071 Å^{-1}		
B_{CO}	2.7252 Å^{-1}	B_{CO}	2.47961 Å^{-1}		
B_{OO}	8.0222 Å^{-1}	B_{OO}	3.92658 Å^{-1}		
C_{CH}	1.9421 eV Å^6	C_{CH}	7.3953 eV Å^6		
C_{OH}	1.2903×10^{-3} eV Å^6	C_{OH}	0.0854 eV Å^6		
C_{CO}	70.378 eV Å^6	C_{CO}	19.872 eV Å^6		
C_{OO}	1.8897 eV Å^6	C_{OO}	30.983 eV Å^6		

consisting of electrostatic and Buckingham interactions between each pair of sites:

$$V_{\text{CO-CO}} = V^{\text{intra}} + V^{\text{es}} + V^{\text{vdW}} \tag{8}$$

$$= \sum_{i=\text{O}}^{N_{\text{CO}}} D\left[1 - \exp\left\{-a(|\boldsymbol{r}_{i\text{C-}i\text{O}}| - r_{\text{C-O}}^{\text{eq}})\right\}\right]^2$$

$$+ \sum_{\substack{i,j=\text{O} \\ i<j}}^{N_{\text{CO}}} \sum_{\substack{\alpha=\text{C,O,X} \\ \beta=\text{C,O,X}}} \frac{1}{4\pi\epsilon_\text{O}} \frac{q_{i\alpha}q_{j\beta}}{|\boldsymbol{r}_{i\alpha\text{-}j\beta}|}$$

$$+ \sum_{\substack{i,j=\text{O} \\ i<j}}^{N_{\text{CO}}} \sum_{\substack{\alpha=\text{C,O} \\ \beta=\text{C,O}}} \left[A_{\alpha\beta}\exp\left\{-B_{\alpha\beta}|\boldsymbol{r}_{i\alpha\text{-}j\beta}|\right\} - \frac{C_{\alpha\beta}}{|\boldsymbol{r}_{i\alpha\text{-}j\beta}|^6}\right], \tag{9}$$

where the charges depend on the following way on the atomic coordinates:

$$q_{i\text{C}} = q_{\text{C}}^{\text{eq}}\exp\left\{-\gamma_{\text{C}}\left(|\boldsymbol{r}_{i\text{C-}i\text{O}}| - r_{\text{C-O}}^{\text{eq}}\right)\right\},$$
$$q_{i\text{O}} = q_{\text{O}}^{\text{eq}}\exp\left\{-\gamma_{\text{O}}\left(|\boldsymbol{r}_{i\text{C-}i\text{O}}| - r_{\text{C-O}}^{\text{eq}}\right)\right\},$$
$$q_{i\text{X}} = -q_{i\text{C}} - q_{i\text{O}}.$$

3 CO_2-CO_2

The CO_2-CO_2 interactions are modeled in a pairwise manner between the atomic sites. For the intermolecular part, the EPM model by Harris and Yungh [3] is used. The intramolecular interactions are modeled according to the model by Zhu and Robinson [4]. The full interaction potential is the following:

$$V_{\text{CO}_2\text{-CO}_2} = V^{\text{intra}} + V^{\text{es}} + V^{\text{vdW}} \tag{10}$$

$$\sum_{i=\text{O}}^{N_{\text{CO}_2}} \sum_{i=1}^{N_{\text{CO}_2}} \frac{K_1}{2}\left(\Delta r_{i1}^2 + \Delta r_{i2}^2\right) + K_2 \Delta r_{i1} \Delta r_{i2} + \frac{K_\theta}{2}\Delta\theta_i^2$$

$$+ \sum_{\substack{i,j=\text{O} \\ i<j}}^{N_{\text{CO}_2}} \sum_{\substack{\alpha=\text{C,O}_1,\text{O}_2 \\ \beta=\text{C,O}_1,\text{O}_2}} \frac{1}{4\pi\epsilon_\text{O}} \frac{q_{i\alpha}q_{j\beta}}{|\boldsymbol{r}_{i\alpha-j\beta}|} + 4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{|\boldsymbol{r}_{i\alpha-j\beta}|}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{|\boldsymbol{r}_{i\alpha-j\beta}|}\right)^6\right],$$

$$\tag{11}$$

where θ_i is the O-C-O angle,

$$q_{\text{O}} = -0.5 q_{\text{C}}, \tag{12}$$

and

$$\Delta r_{i1} = |\boldsymbol{r}_{i\text{O}_1\text{-}i\text{C}}| - r_{\text{C-O}}^{\text{eq}}, \tag{13}$$
$$\Delta r_{i2} = |\boldsymbol{r}_{i\text{O}_2\text{-}i\text{C}}| - r_{\text{C-O}}^{\text{eq}}, \tag{14}$$
$$\Delta\theta_i = \theta_i - \theta^{\text{eq}}. \tag{15}$$

4 H$_2$O-CO

The interactions between the water and CO molecules are described in Karssemeijer *et al.* [5]. The potential contains an electrostatic part with the same charges on the molecules as in the H$_2$O-H$_2$O and CO-CO potentials complemented with Buckingham interactions between each intermolecular atom-atom pair to account for the van der Waals interactions:

$$V_{\text{H}_2\text{O-CO}} = V^{\text{es}} + V^{\text{vdW}} \tag{16}$$

$$\sum_{i=0}^{N_{\text{H}_2\text{O}}} \sum_{j=0}^{N_{\text{CO}}} \left\{ \sum_{\alpha=\text{H}_1,\text{H}_2,\text{M}} \sum_{\beta=\text{C,O}} \frac{1}{4\pi\epsilon_0} \frac{q_{i\alpha} q_{j\beta}}{|r_{i\alpha-j\beta}|} \right.$$

$$\left. + \sum_{\alpha=\text{H}_1,\text{H}_2,\text{O}} \sum_{\beta=\text{C,O}} A_{\alpha\beta} \exp\left\{-B_{\alpha\beta} |r_{i\alpha\text{-}j\beta}|\right\} - \frac{C_{\alpha\beta}}{|r_{i\alpha\text{-}j\beta}|^6} \right\}. \tag{17}$$

5 H$_2$O-CO$_2$

The H$_2$O-CO$_2$ interaction is introduced in Karssemeijer *et al.* [6] and is very similar in form to the H$_2$O-CO potential. Again, the charges are the same as in the H$_2$O-H$_2$O and CO$_2$-CO$_2$ potentials and the van der Waals interactions are described with a Buckingham potential:

$$V_{\text{H}_2\text{O-CO}_2} = V^{\text{es}} + V^{\text{vdW}} \tag{18}$$

$$\sum_{i=0}^{N_{\text{H}_2\text{O}}} \sum_{j=0}^{N_{\text{CO}_2}} \left\{ \sum_{\alpha=\text{H}_1,\text{H}_2,\text{M}} \sum_{\beta=\text{C,O}_1,\text{O}_2} \frac{1}{4\pi\epsilon_0} \frac{q_{i\alpha} q_{j\beta}}{|r_{i\alpha-j\beta}|} \right.$$

$$\left. + \sum_{\alpha=\text{H}_1,\text{H}_2,\text{O}} \sum_{\beta=\text{C,O}_1,\text{O}_2} A_{\alpha\beta} \exp\left\{-B_{\alpha\beta} |r_{i\alpha\text{-}j\beta}|\right\} - \frac{C_{\alpha\beta}}{|r_{i\alpha\text{-}j\beta}|^6} \right\}. \tag{19}$$

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