

Crystal growth simulations of methane hydrates in the presence of silica surfaces

Shuai Liang, Dmitri Rozmanov, and Peter G. Kusalik*

*Department of Chemistry, University of Calgary, 2500 University Drive NW,
Calgary, Alberta, Canada*

*Corresponding author. Email: peter.kusalik@ucalgary.ca

Potential parameters for molecular interactions

Throughout this work water was represented by the TIP4P/2005 potential model^{S1}, methane was modeled as a single Lennard-Jones interaction site^{S2}, and the silica-water interaction was taken from the previous work by Rossky et al.^{S3,4}. To avoid the (artificial) introduction of a frozen silica crystal into the system, we developed an “interaction matrix” methodology to describe the Lennard-Jones interactions within the silica crystal. We decomposed the hydroxylated silica crystal into two rigid units (see Figure S1) which can otherwise move freely through their interaction with other molecules (units). The crystal structure of this silica is constrained by relatively strong Lennard-Jones interactions (comparable to Si-O covalent bond interactions in the CHARMM force field^{S5}) between the two rigid units, while other cross terms for the Lennard-Jones interactions are determined using Lorentz-Berthelot mixing rules^{S6}. A detailed description of the molecular interaction parameters can be found in Table S1 and S2, with the sites labeled in Figure S1.

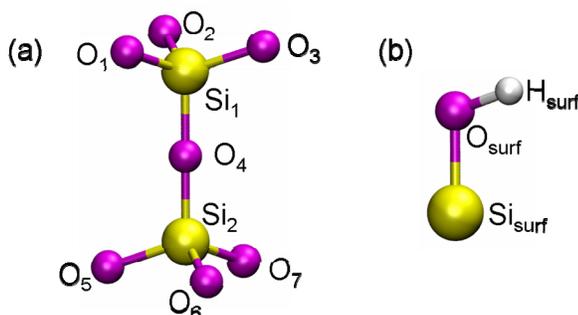


Figure S1. Molecular configurations of the two rigid (a) interior and (b) surface units used to build the hydroxylated silica crystal surface (see main manuscript). All the sites are denoted and utilized in Tables S1 and S2.

Table S1. Lennard-Jones parameters (ϵ) for interactions between silica surface, water and methane species. The sites in the silica surface are denoted in Figure S1. The interactions between silica – water, silica – methane, and water – methane are determined using Lorentz-Berthelot mixing rules^{S6}. The crystal structure of the silica surface is maintained by the (artificially) strong Lennard-Jones interactions (comparable to Si-O covalent bond interactions in a CHARMM force field^{S5}) between the sites of the two rigid units (shaded).

ϵ /(KJ/mol)	O_{H_2O}	C	O_{Surf}	Si_{Surf}	O_1	O_2	O_3	O_4	O_5	O_6	O_7	Si_1	Si_2
O_{H_2O}	0.7749	0.9760	0.7090	0.6430	0.7090	0.7090	0.7090	0.7090	0.7090	0.7090	0.7090	0.6430	0.6430
C	0.9760	1.22927	0.8930	0.8099	0.8930	0.8930	0.8930	0.8930	0.8930	0.8930	0.8930	0.8099	0.8099
O_{Surf}	0.7090	0.8930	0	0	80	80	80	0	80	80	80	60	60
Si_{Surf}	0.6430	0.8099	0	0	80	80	80	60	80	80	80	0	0
O_1	0.7090	0.8930	80	80	80	80	80	0	80	80	80	0	0
O_2	0.7090	0.8930	80	80	80	80	80	0	80	80	80	0	0
O_3	0.7090	0.8930	80	80	80	80	80	0	80	80	80	0	0
O_4	0.7090	0.8930	0	60	0	0	0	60	0	0	0	0	0
O_5	0.7090	0.8930	80	80	80	80	80	0	80	80	80	0	0
O_6	0.7090	0.8930	80	80	80	80	80	0	80	80	80	0	0
O_7	0.7090	0.8930	80	80	80	80	80	0	80	80	80	0	0
Si_1	0.6430	0.8099	60	0	0	0	0	0	0	0	0	0	0
Si_2	0.6430	0.8099	60	0	0	0	0	0	0	0	0	0	0

Table S2. Lennard-Jones parameters (σ) for interactions between silica surface, water and methane species. The sites in the silica surface are denoted in Figure S1. The cross terms were determined using Lorentz-Berthelot mixing rules^{S6}.

$\sigma/\text{\AA}$	O_{H_2O}	C	O_{Surf}	Si_{Surf}	O_1	O_2	O_3	O_4	O_5	O_6	O_7	Si_1	Si_2
O_{H_2O}	3.1589	3.42945	3.1565	3.4770	3.1565	3.1565	3.1565	3.1565	3.1565	3.1565	3.1565	3.4770	3.4770
C	3.42945	3.7	3.4270	3.7475	3.4270	3.4270	3.4270	3.4270	3.4270	3.4270	3.4270	3.7475	3.7475
O_{Surf}	3.1565	3.4270	0	0	2.2005	2.2005	2.2005	0	2.2005	2.2005	2.2005	3.4700	3.4700
Si_{Surf}	3.4770	3.7475	0	0	1.3453	1.3453	1.3453	3.4700	1.3453	1.3453	1.3453	0	0
O_1	3.1565	3.4270	2.2005	1.3453	2.2005	2.2005	2.2005	0	2.2005	2.2005	2.2005	0	0
O_2	3.1565	3.4270	2.2005	1.3453	2.2005	2.2005	2.2005	0	2.2005	2.2005	2.2005	0	0
O_3	3.1565	3.4270	2.2005	1.3453	2.2005	2.2005	2.2005	0	2.2005	2.2005	2.2005	0	0
O_4	3.1565	3.4270	0	3.4700	0	0	0	4.7971	0	0	0	0	0
O_5	3.1565	3.4270	2.2005	1.3453	2.2005	2.2005	2.2005	0	2.2005	2.2005	2.2005	0	0
O_6	3.1565	3.4270	2.2005	1.3453	2.2005	2.2005	2.2005	0	2.2005	2.2005	2.2005	0	0
O_7	3.1565	3.4270	2.2005	1.3453	2.2005	2.2005	2.2005	0	2.2005	2.2005	2.2005	0	0
Si_1	3.4770	3.7475	3.4700	0	0	0	0	0	0	0	0	0	0
Si_2	3.4770	3.7475	3.4700	0	0	0	0	0	0	0	0	0	0

Density x-profiles of water and methane molecules in aqueous solution

Figure S2 shows the x-profiles of water and methane molecules in the aqueous solution. Although the density of methane molecules near the silica surface are much higher than that in bulk solution, the layer of molecules nearest to the silica surface is composed of water molecules.

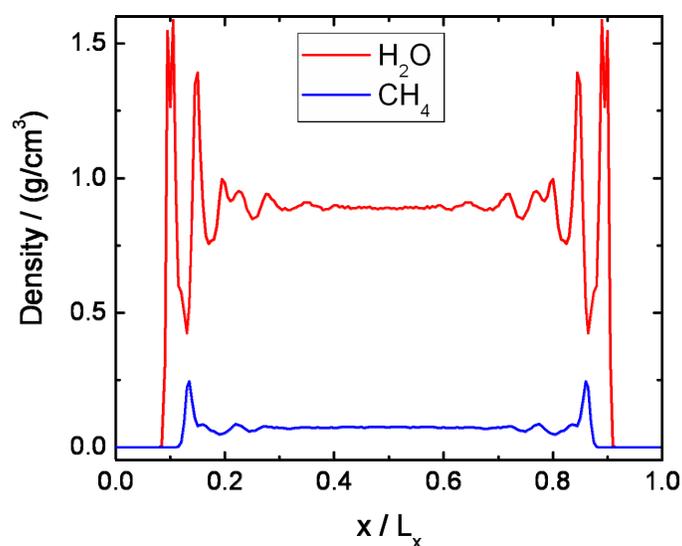


Figure S2. The density x-profiles for water and methane molecules in the liquid part of the system. The two curves for water and methane are presented in Figure 4(a) and Figure 5(a), respectively, in the main manuscript.

References:

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