Effect of Water on the Methane Adsorption on the Na-Montmorillonite Surface: Molecular Dynamics Study

Olga Solovyeva[1] , Vasily Pisarev[2], Grigory Smirnov[2]
[1]OmSTU University, Omsk, Russia, [2]HSE University, Moscow, Russia

Introduction

In this study, we investigated the effect of the surface coverage of H_2O molecules on CH_4 adsorption on Na-Montmorillonite surface. We performed molecular dynamics (MD) simulations for CH_4/ H_2O/clay systems with various amounts of H_2O molecules on the surface.

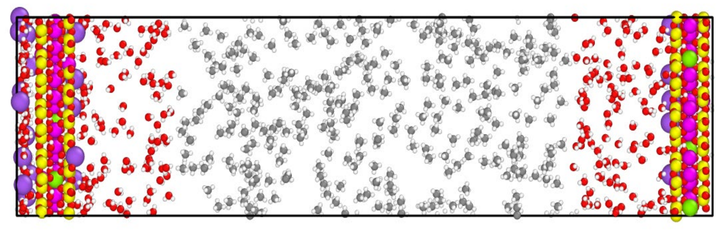
Models & Methods:

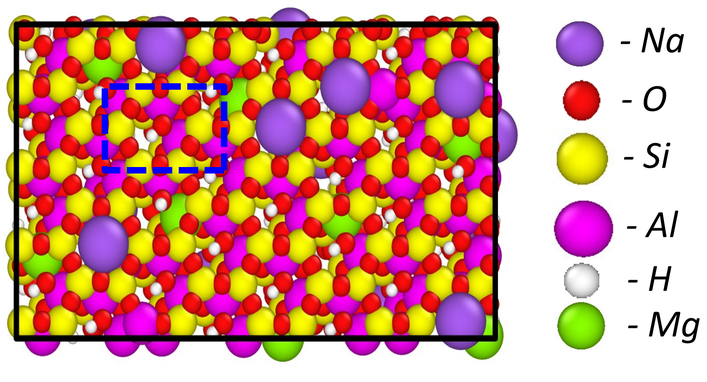
Structural model:

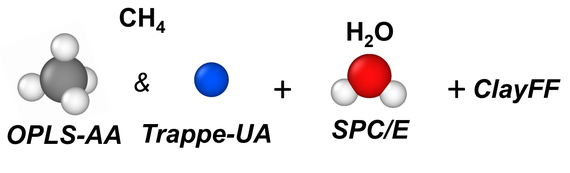
- Na-montmorillonite (RanTO model): $Na_{0.75}(Al_{3.75}Mg_{0.25})(Si_{7.75}Al_{0.25})O_{20}(OH)_4 \cdot 6H_2O$
- 300 methane molecules (OPLS-AA & Trappe-UA)
- 4x4x2 unit cells of Na-mont (ClayFF)
- SPC/E water (θ_w=0.0, 0.25, 0.5, 1.1)

Methods

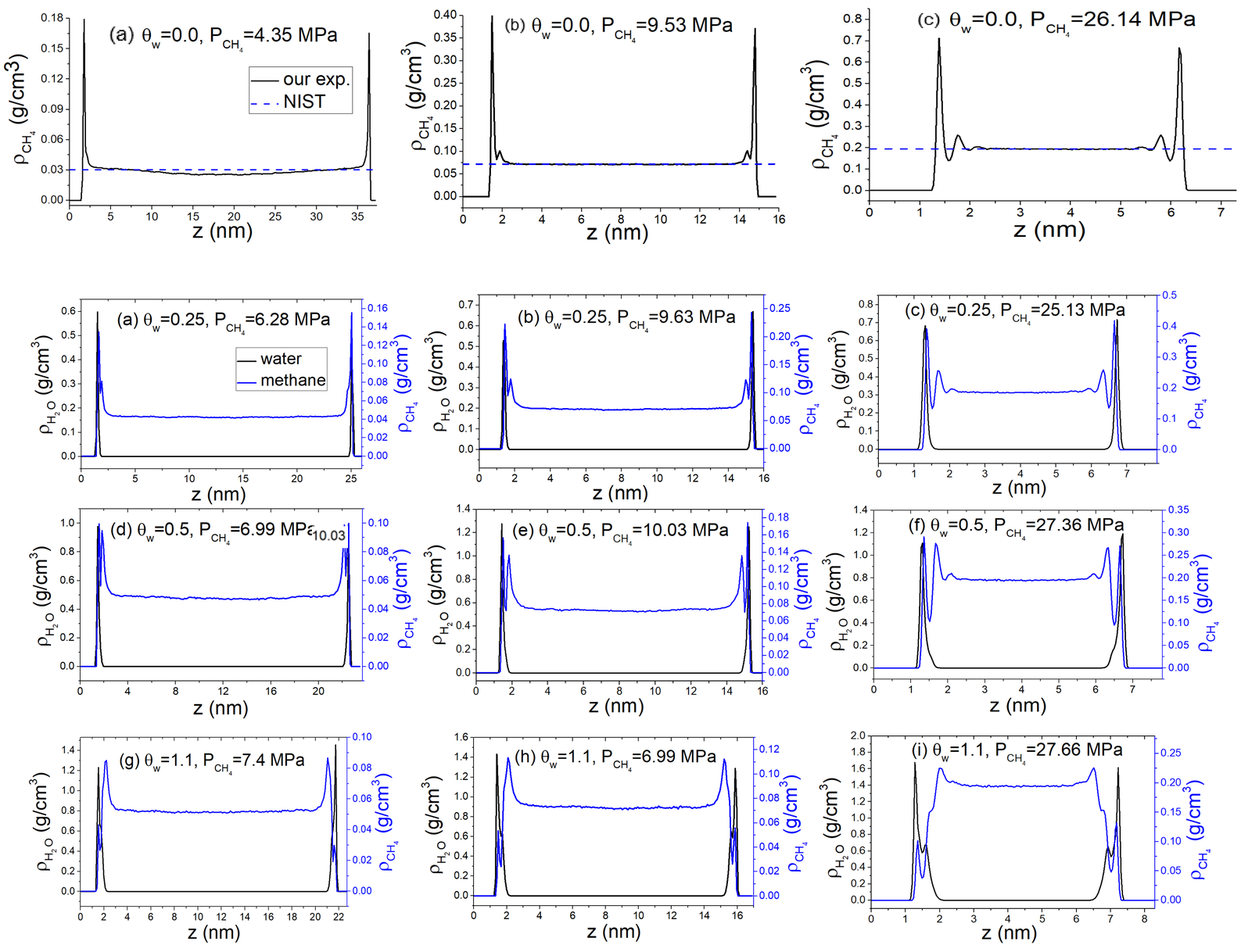
- Classical MD (LAMMPS)
  - 1ns NPT(relaxation)
    - T=298.15 K; P=4, 8, 20 MPa
  - 10 ns NVT (statistics)
  - LogMFD (PLUMED) for the adsorption free energy



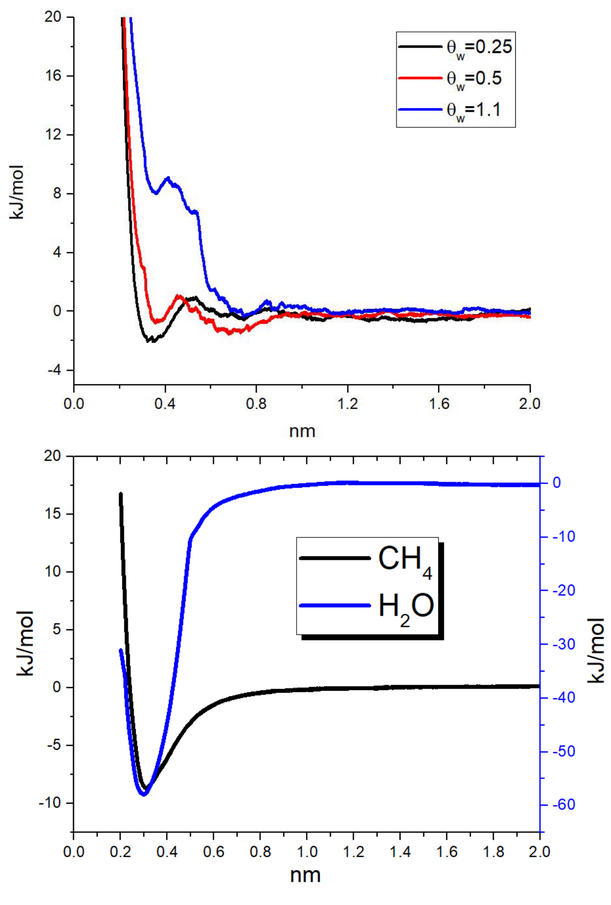




CH_4 and H_2O density inside the pore



Adsorption energy of CH_4



Conclusions

- Trappe-UA and OPLS-AA potentials are qualitatively the same
- Methane molecules are adsorbed on the centers of free siloxane rings.
- Water molecules do not change adsorption centers
- Sodium cations block part of the surface for methane.
- Sodium cations form intrasphere hydrate complexes at θ_w<0.5, outer sphere complexes at θ_w>0.5
- At higher pressures (> 6 MPa), there are two adsorption layers
- The first layer is always ordered
- The second layer is always disordered without water
- The structure of the second layer depends on P and θ_w
- The adsorption energy of methane is less than -4 kJ /mol.

2D density maps of CH_4