# First-Principle Molecular Dynamics Study of Methane Hydrate

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# First-Principle Molecular Dynamics Study of Methane Hydrate

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**Abstract.** Currently, much attention of the scientific community and the gas industry is focused on the structural, physical and thermodynamic properties of gas hydrates. This interest is explained by the fact that there is a prospect of using natural gas hydrates as a new fuel source. This article presents the results obtained during the first-principle molecular dynamic study of the thermal and electronic properties of hydrates. For hydrates of methane with cubic sI and hexagonal sH configurations, the average heat capacity $C_V$ was computed. The densities of electronic states are studied for filled and unfilled configurations of sI and sH hydrates. The spectra of electron energy were calculated for sI hydrate, which has unfilled molecular cages. Also, for methane and ethane hydrates, the binding energies between the framework and the gas molecule are calculated.

## 1. Introduction

Great interest to the energy industry are crystalline compounds called hydrates. These are substances of variable composition, the clathrate lattice of which is formed by water molecules. Molecules of low-molecular gases can be enclosed in lattice cavities. Gas hydrates are compounds of variable composition and are described by the formula M*nH2O (M is a hydrate-forming molecule, n is a hydrate number, the average number of $H_2O$ molecules per guest molecule). The hydrate framework is formed by water molecules that are connected by a hydrogen bond. The crystal lattice of water has cavities in which low molecular weight compounds, including methane and ethane, can be enclosed. Hydrates containing natural gases are mainly formed in permafrost zones and on oceanic shelves. Vander-Waals interactions between the framework and the guest molecule ensure the energy stability of hydrates [1-3]. Gas hydrate stability  is insured by repelling the water frame from the internal guest molecules. The configuration stability and electronic features of various gas hydrates were investigated in Ref. [4] by quantum mechanical modeling in the framework of a generalized gradient approximation. The authors have shown that the inclusion of gases ($CO_2$, $CO$, $CH_4$, $H_2$) in molecular cells stabilizes the structure of hydrate. Also, the authors in Ref. [4] calculated the binding energies between the gas molecule and surrounding molecular cavity. For carbon dioxide, the binding energy in the hydrate was −2.36 eV, for carbon monoxide hydrate −1.57 eV, for methane hydrate −0.58 eV, for hydrogen hydrate −0.36 eV.

The type of hydrate structure depends on several factors: temperature, pressure, type of gas molecule, etc. The cubic configuration sI is the most common structure in nature, next in popularity is sII (cubic) and sH (hexagonal) [2]. The most common molecule of gas in hydrates is methane. It predominantly crystallizes into a cubic sI configuration, which has both large molecular water cells

($d$=58.6 $nm$) and small water cells ($d$=51 $nm$). These clusters can contain $CH_4$ molecules with a diameter of 43.6 $nm$ [1, 2]. Such a system usually forms when methane and water come into contact at pressure $p$~6.0 $atm$ and temperature $T$=300 K [3].

At present, much attention of the scientific community and the gas industry is focused on the structural, physical and thermal properties of gas hydrates. This interest is explained, firstly, by the fact there is a prospect of using natural gas hydrates as a new fuel source. Presumably, there is ~ $10^{16}$ $m^3$ of gas in the form of gas hydrates, and it is much larger than the reserves of usual natural gas [1-3]. Secondly, this interest is due to the fact that the hydrate formation problem is acute in the gas industry. Passing through wellbores and gas pipelines, natural gas is deposited on the walls in the form of hydrate and reduces the throughput of pipes.

## 2. Simulation details

To study hydrates, quantum-mechanical molecular dynamics simulations were performed using density functional theory. All simulation was performed using the VASP software package [5, 6]. Using the data obtained by X-ray diffraction, the algorithm for optimizing the positions of hydrogen atoms, and considering that total dipole moment is equal to zero, the sI and sH crystal structures were reconstructed [7-10]. Models of methane and ethane hydrates were obtained by including $CH_4$ and $C_2H_6$ molecules in free molecular cages.

An NVT-ensemble was chosen as the simulated system. The temperature was varied in the range T= [180; 260] K in 20K increments. The Nose–Hoover thermostat was used to establish the state of thermodynamic equilibrium. As mentioned above, the density functional theory was used for calculations. This method uses the electron density as a key quantity instead of the wave function. Interelectronic interaction is calculated using the generalized gradient approximation GGA [5,6] . The PBE functional [7] is used to take into account the exchange-correlation corrections. The interaction of electrons with ions is described using smoothed pseudopotentials (PAW potential). The basis set consisted of plane waves, and a cutoff energy of 245 eV was used. Since the initial configuration of the system was optimized for energy and dipole moment, a small number of ion steps were required for complete relaxation. The duration of the ion step was 1 fs. Within one ion step, at least 5 electronic optimization steps are calculated, with a convergence energy of $10^{-4}$ eV.



|  sI  |  sI+$CH_4$  |  sH  |  sH+$CH_4$  |
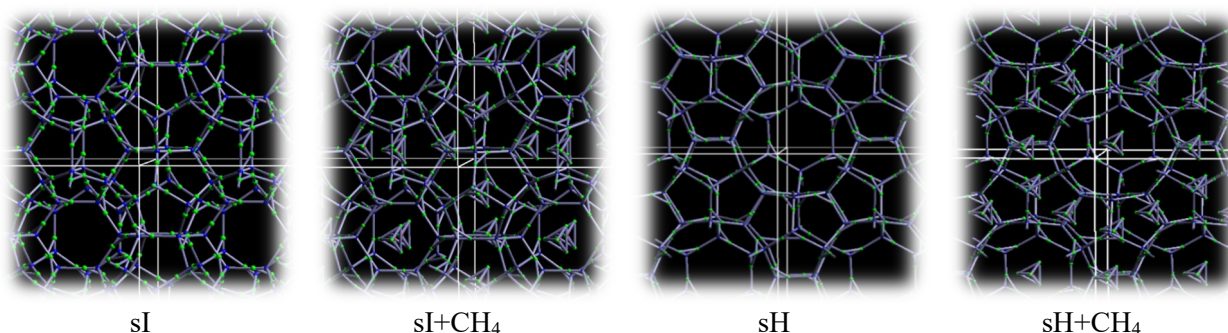
**Figure 1:** Empty and methane-filled hydrate molecular cavities with sI and sH configurations.

## 3. Results and discussion

First, the average heat capacity of empty clathrate frameworks and methane hydrates was calculated at a constant volume in the temperature range T = [180; 260] K (see table 1). For this, we used an sI cubic cell with $a$ = 12 Å with 8 methane molecules in the cavities (178 ions in total) and an sI cubic cell with empty molecular cavities (138 ions in total). For the hexagonal configuration sH, a rectangular cell was created with parameters a = 12 Å, b = 21 Å, c = 10 Å. For sH, two cases were also studied: the case with the inclusion of 12 methane molecules in the cavity (264 ions in total) and the case of empty molecular cavities (204 ions in total). Also, based on the equilibrium lattice parameters,

the methane hydrate densities sI (912 kg/m³) and sH (898 kg/m³) were estimated. A good agreement was reached with the known data [8-10].

**Table 1:** Calculated and experimental values of heat capacity.

| | $C_V$ (J/kg·K) | | $C_{V,\,EXP}$ (J/kg·K) |
|---|---|---|---|
| | sI | sH | |
| empty cages | 3007±152 | 3093±12 | 3300 [21] |
| CH$_4$ | 2362 | 2569±77 | 2160±100 [18], 2306 [19] |

Second, for the empty configuration sI, the DOS was obtained (see Fig. 2). The obtained DOS spectra agree well with the data given in Ref. [4]. Also at present work, the band structure was obtained (see Fig. 3). The energy band structure gives information about how the energy of an electron will change when moving along a certain direction in the space of k-vectors. As a rule, lines connecting points of high symmetry are considered as distinguished directions of the k-vector. The sI configuration has a cubic lattice, and the cubic Brillouin zone was chosen for it. As can be seen from Fig. 3, electrons with energy –20 ÷ 0 eV (lower energy levels and valence band) have a direct form relationship $E(\mathbf{k})$. The conduction band spectra (energy range 0 ÷ 5 eV) has extremums at the different points. The upper bound of the band gap has a maximum at point R and a minimum at point W. The calculated band gap in the sI crystal is about 5.0 eV. This suggests that hydrates have strong dielectric properties.
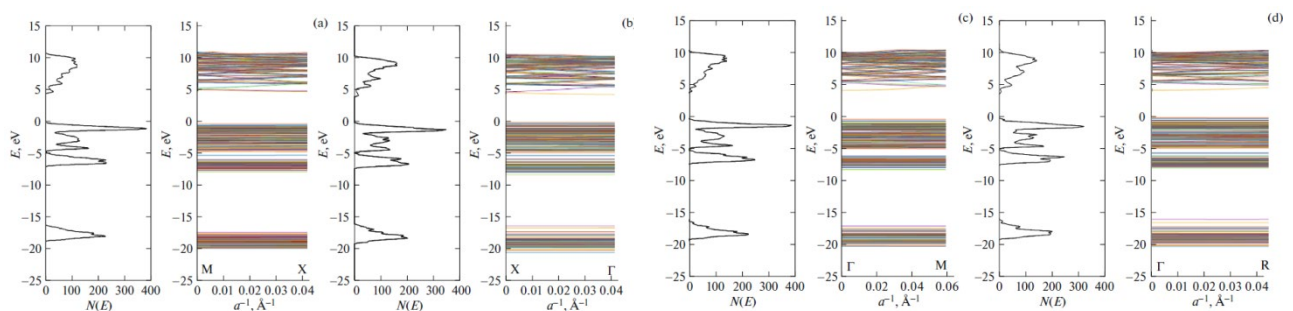


**Figure 2:** Density of states $N(E)$ and the band structure $E(\mathbf{k})$ of sI unfilled configuration.
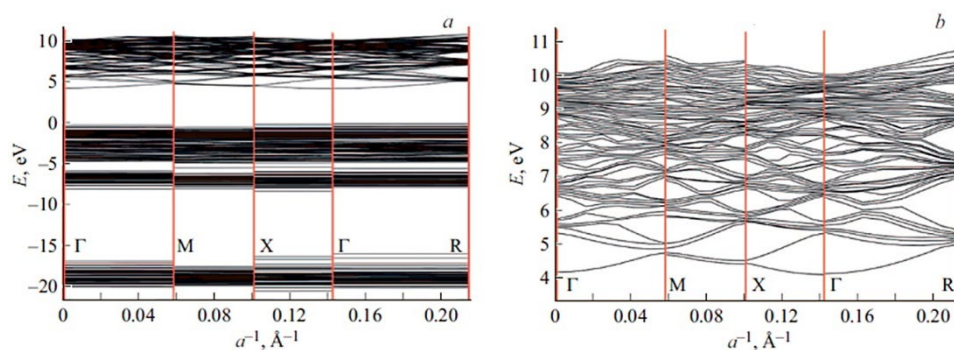


**Figure 3:** Complete energy band structure of sI crystal (a) and band structure in the energy range 4÷11eV (conduction band) in different directions.

Third, for hydrates with the sI configuration containing methane and ethane, the bond energies between the guest molecule and the surrounding molecular cavity were calculated. The methane molecule fills all 8 cavities in the sI structure, and the binding energy calculated for it was –0.25 eV. This value differs from the value obtained in Ref. [4], which is equal to –0.58 eV. The reason for the differences may be that different potentials and cutoff energies are used. And also in that different lattice parameters are used, in this work the value $a = 12.03$ Å is used, while in Ref. [4] the value $a = 11.62$ Å is used. The ethane molecule fills only 6 large cavities in the sI configuration, and the calculated binding energy for it was –0.27 eV. As mentioned earlier, the presence of gas molecules in the cavities stabilizes the frame, reducing the total energy of the cell. This is confirmed by the negative value of the binding energy of the gas molecule in the hydrate. When comparing the DOS $N(E)$ for the unfilled and filled hydrate frameworks (see Fig. 4), in the second case, an electron density peak is detected at an energy of -10 eV. The observed shift of the electron density to the low−energy region when gas molecules are included in the cavity indicates a decrease in the cell energy, which leads to the stabilization of the gas hydrate.
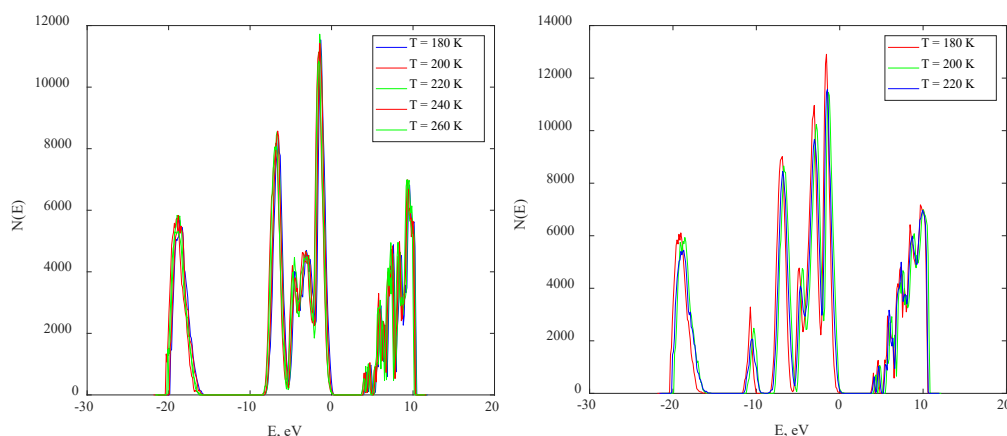


**Figure 4:** Density of electronic states *N(E)* of hydrates with empty cavities (left column) and cavities filled with methane (right column).

## 4. Conclusions

This paper presents the quantum-mechanical simulations results of the hydrates for a wide temperature range T=[180;260] K. This temperature range corresponds to the phase of the stable state of gas hydrates in nature. We have carried out detailed studies of the electronic and thermal properties of various crystalline forms of methane and ethane hydrates. First, for methane hydrates and empty configurations sI, sH, good agreement was found between the computed data for heat capacity $C_V$ and density and experimental data [4, 8-10]. Second, for the configuration sI with unfilled cages, the DOS and the energy band structure are calculated. Third, the binding energies of methane and ethane molecules with the hydrate lattice sI were calculated; the values were –0.25 eV and –0.27 eV, respectively. Based on a comparison of the density of electronic states of filled and unfilled hydrates of $CH_4$, it is confirmed that the inclusion of these molecules in the cavity leads to energy gain.

## References

[1] Sloan E D, Koh C A 2007 *Clathrate Hydrates of Natural Gases* (CRC Press, Taylor&Francis USA)

[2] Yunusov M B, Khusnutdinoff R M,  Mokshin A V 2021 *Phys. Solid State* **63** 372
[3] Khusnutdinoff  R M  2017 *Colloid J.* **79** 152
[4] Casco M E, Silvestre-Albero J, Ramirez-Cuesta A J 2015 *Nature Commun.* **6** 6432
[5] Kresse G, Hafner J 1994 *J. Phys.: Condens. Matt.* **6** 8245
[6] Kresse G, Joubert D 1999 *Phys. Rev.* **59** , 1758
[7] Perdew J P, Burke K, Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[8] Makogon Yu F 2010 *Geology And Mineral Resources Of World Ocean* №2 5
[9] Istomin V I, Yakushev V S 1992 *Natural gas hydrates* (Nedra. M.)
[10] Gabitto J F, Tsouris C 2010 *Journal of Thermodynamics* **2010** 12