Local pressure and density distribution in methane hydrate – ice I\text{h} system

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Abstract. Effect of self-preservation of gas hydrates was explored over many years but there is no complete understanding how can hydrates exist in their thermodynamic instability region. We are suggesting the microscopic-level model of methane hydrate clusters immersed in ice matrix. Due to differences in thermal expansion of methane hydrate and Ice I\text{h} the additional pressure appears in the hydrate phase and this moves it into its stability field. MD simulations were performed to find local pressure and density profiles. Results are well confirming our assumption.

1. Introduction

The unusual behavior of some gas hydrate at heating i.e. delayed dissociation of gas hydrate (the so-called self-preservation effect) at temperatures above equilibrium for hydrate decomposition, but below the H\textsubscript{2}O melting point was the subject of many experimental researches in the last years (see, for example [1-10]). Such interest is caused by possible application of this effect for production, storage and transportation of natural gas. The experiments show the anomalous preservation of methane hydrate at temperatures below 273K (ice I\text{h} melting point) at ambient pressure with simultaneous formation of ice phase at temperatures above 242K (beginning of methane hydrate dissociation). When the pressure on sample of methane hydrate was rapidly decreased under the equilibrium curve the preservation up to 93\% of methane was observed [6]. It was shown [6,8,9] that the model of ice shield can not explain anomalous preservation of big amounts of methane hydrate. Most popular explanation of the self-preservation now is kinetic handicapping of methane diffusion through ice film [10], but exact mechanism of the self-preservation effect in gas hydrate is not clear yet.

To explain this effect we assume that at thermal expansion of methane hydrate, which is immersed in ice phase, differences of coefficients of thermal expansion lead to arising of the additional pressure in the hydrate phase, consequently hydrate phase appears in its stability area, and it is the main reason of the self-preservation effect.

In our earlier work [14] we have offered the macroscopic model of self-preservation effect. We have shown that the density of methane hydrate immersed in ice phase is somewhat greater than the density of ice and that addition pressure may be big enough to place the methane hydrate phase in its stability area. The investigations of methane hydrate – ice I\text{h} interface in nanoclusters performed by Brodskaya \textit{et al.} [13] shows the stability of hydrate core up to melting point of water, at least in the SPC/E model. But the question arises: Is such model stable? Would not the ice, rounding the hydrate phase, be destroyed under pressure?

The goal of this work was to investigate the local pressure and stability of structure of crystalline ice I\text{h} and methane hydrate immersed in the ice phase on molecular level.
2. Simulation details

The molecular-level scheme for calculation local pressure was offered and applied to inhomogeneous systems by Ikeshoji et al. [11,12]. It is based on the Irving-Kirkwood definition of the pressure tensor and is most convenient for systems consisting of pair-wise interacting particles. We have used this scheme to calculate local pressure in spherical layers in methane hydrate – ice Ih system.

Our model consisted of methane hydrate sphere, surrounded by Ice Ih. Methane hydrate is modeled as supercell containing 63 molecules of methane and about 1100 water molecules; ice Ih contained more than 5000 water molecules (full model contained 6287 molecules). Water molecules with distance O-O less than 2 angstrom were rejected. Radius of hydrate sphere on the average was about 12.5 angstrom. Periodic boundary conditions have been imposed on this structure that corresponds to infinite ice matrix with hydrate clusters included.

Initially the structure of model was optimized within the conjugated gradient method. Then the long-time Molecular Dynamic simulations were performed. For these calculations we have used software package TINKER (http://dasher.wustl.edu/tinker). MD simulation was run 300 ps with 1 fs timestep at T = 195K. Then the temperature was elevated up to 250K, i.e. above the temperature of methane hydrate dissociation at atmospheric pressure. SPC/E modified potential for water molecules with the parameters $\varepsilon = 2.6025$ kJ/mol, $\sigma = 3.1556$ Å and OPLS model for methane with parameters $\varepsilon = 4.922$, $\sigma=3.73$ have been chosen. For calculations we have used Berendsen thermostat and microcanonical ensemble. Structure which was obtained after MD simulation is presented in Fig.1.

![Figure 1. Structure of methane hydrate sphere immersed in ice Ih phase.](image)

3. Results and discussion

The resulting structure characteristics are presented on Fig.2 (angle distribution of O-O-O angles) and Fig.3 (Radial Distribution function O-H). As one can see, in both hydrate and ice phases O-O-O angles remain near tetrahedral values. Moreover, most molecules within ice-hydrate interphase keep O-O-O angle values close to tetrahedral. Taken together with O-H length distribution, which shows that O-H distances change in very restricted range, we can conclude that in all volume of model almost all water molecules are bonded with hydrogen bonds. At the interface gas hydrate – ice Ih at initial decomposition of hydrate water molecules work for take up position which allows save the network of hydrogen bonds.

The local and average densities calculated within the model are presented on Fig.4. The averaging was performed during last 1 picosecond instantaneous configurations. It was found that the density in hydrate phase is larger than in ice phase that is in agreement with experimental data. At the methane hydrate – ice Ih interphase anomalously high local density was observed. The anomalous behavior of local density at interface apparently is connected with increased pressure there.
On Fig. 5 and Fig. 6 the profiles of radial and transversal components of local pressure are presented. Local pressures include the static part connected with forces between interacting molecules and kinetic part of pressure connected with molecular movements.

Figure 2. Distribution of O-O-O angles for ice Ih, methane hydrate and ice-hydrate interphase.

Figure 3. Radial distribution function O-H methane hydrate – ice system.

Figure 4. Radial distribution of local density. Dashed line shows average density in ice Ih and methane hydrate phase. On Ice-hydrate interphase one can see anomalous behavior of local density.

On Fig. 5 and Fig. 6 the profiles of radial and transversal components of local pressure are presented. Local pressures include the static part connected with forces between interacting molecules and kinetic part of pressure connected with molecular movements.

Figure 5. Radial part of local pressure profile

Figure 6. Transversal part of local pressure profile
The anomalous high pressure, which is observed on boundary of hydrate phase, well correlates with high density area. Our calculations show that it can reach 60 bar. On average the radial component of pressure in methane hydrate is about 40 bar larger then the same component in ice Ih, but in some positions local pressure reach 120 bar. For transversal component of pressure exceeding of pressure in hydrate phase reach 25 bar and local pressure reach 120 bar respectively. Experimental pressure of methane hydrate decomposition is about 13 bar at 250K. Thus calculated redundancy pressure in hydrate phase at still lower temperatures found to be enough to prevent dissociation of hydrate phase.

4. Conclusion

The molecular-level model of self-preservation effect was developed. Within combined approach the components of local pressure and local density profiles were found. It was shown that ice matrix with immersed methane hydrate can be stable at ambient pressure and temperatures higher than temperature of methane hydrate dissociation. The calculations show that the pressure in methane hydrate sphere immersed in ice matrix is notably higher than pressure of ice phase, but this does not lead to system distortion.

Acknowledgments

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