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Modeling the Self-Preservation Effect in Gas Hydrate/Ice Systems

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Molecular dynamics simulations were performed to investigate the possible role of ice shielding in the anomalous preservation of gas hydrates. Two cases of ice shielding were considered: immersion of hydrate particles into bulk ice *Ih* and wrapping of similar particles in a thin ice shell. For a microscopic-level model of methane hydrate clusters immersed in bulk ice the excess pressure in the hydrate phase at 250 K was found to be sufficient to shift the gas hydrate into the region of thermodynamic stability on the phase diagram. For the second model the temperature dependence of various properties of the hydrate/ice nanocluster was studied. The surface tension estimates based on the Laplace equation show non-monotonic dependence on temperature, which might indicate the possible involvement of hydrate/ice interfacial phenomena in the self-preservation of gas hydrates. [doi:10.2320/matertrans.N-MRA2007866]

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1. Introduction

About 40 years have passed since the discovery of natural gas hydrates. Now the gas hydrates are recognized as one of the most significant energy resources and are likely to play a very important role in the future. The total amount of gas stored in hydrate form is roughly estimated as at least 10^{14} m^3 ,^{1,2)} which is approximately equal to all explored reserves of other fossil fuels. On the other hand, gas hydrates were found to exist in nature predominantly near their thermodynamic stability limit. Changes in the environmental conditions due to global warming might cause the dissociation of gas hydrates, which will result in the release of methane into the atmosphere with a drastic increase of the greenhouse effect. Such predictions lead to great interest focused on investigations of the physical, chemical and geological properties of gas hydrates.

One of the key features of methane hydrate is the so called “self”-preservation effect.³⁾ This term describes the ability of methane hydrate to resist dissociation at temperatures higher than the equilibrium temperature of decomposition. The effect of incomplete dissociation of methane hydrate has been the subject of many experimental studies in the last years (see, for example⁴⁻¹³⁾). The experiments show the anomalous preservation of methane hydrate at temperatures below 273 K (ice *Ih* melting point) under ambient pressure with simultaneous formation of ice phase at temperatures above 242 K (beginning of methane hydrate dissociation). The experiment shown the preservation effect is affected by the nature of the gas hydrate and the dissociation rate of hydrate is strongly dependent on the heating rate of samples. When the pressure on the sample of methane hydrate was rapidly decreased below the equilibrium value, preservation of up to 93% of methane was observed (“anomalous preservation”).⁹⁾ The interest in anomalous preservation is caused by the possible application of this effect for production, storage and transportation of natural gas.

The research of the preservation in pure methane and methane-ethane hydrates have shown extremely nonlinear temperature-dependence of methane hydrate dissociation behavior and the utter lack of comparable preservation behavior in CS-II methane-ethane hydrate.^{9,12)}

The most popular explanation of the self-preservation effect assumes a kinetic barrier for methane diffusion through the ice film of the surface of gas hydrate particles.^{4,5,10,13)} Large-scale nanosecond classical molecular dynamics (MD) calculations support this assumption (the formation of an ice layer inhibits the decomposition of gas hydrate).¹⁴⁾ However, as mention about, similar self-preservation effect was never observed in the experimental studies of the mixed methane-ethane hydrate,¹²⁾ which does not support the “kinetic” approach of self-preservation effect. Moreover, as it was shown in^{9,12,15)} the macroscopic ice-shielding model does not explain anomalous preservation up to 93% of methane hydrate. A mechanism of the anomalous preservation behavior of gas hydrate is not clear and needed further investigation.

The experimental research showed that the anomalous preservation of methane hydrate depends on a warm-temperature regime of the decomposition of gas hydrate. A large temperature differences (up to 30 K) between sample interiors and surroundings were observed^{5,9,11,12)} and the ice phase formation and existent thermal gradients between sample interiors and surroundings¹²⁾ in the time of methane hydrate rapid (endothermic) dissociation.

To explain the self-preservation effect we assume that upon heating of methane hydrate, which is immersed in ice phase, the differences in thermal expansion coefficients lead to an increase of the excess pressure in the hydrate phase, and, consequently, the hydrate phase appears to be stable.

In our previous work,¹⁶⁾ we have suggested a macroscopic model of self-preservation effect. We have shown that the pressure of methane hydrate immersed in ice phase is somewhat greater than the pressure of ice and that excess

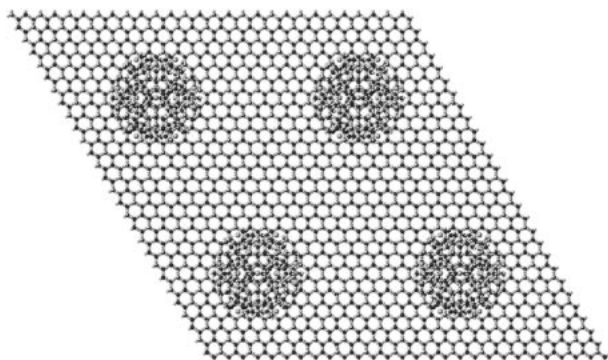


Fig. 1 Structure of methane hydrate sphere immersed in ice *Ih* phase. The structure (model 1) was made within periodically boundary conditions approximation.

pressure may be large enough to relocate the methane hydrate phase into its stability region. The investigation of methane hydrate – ice *Ih* interface in nanoclusters carried out by Brodskaya *et al.* confirms the stability of the hydrate core up to the melting point of water, at least when the SPC/E water model is used.¹⁷⁾ However, it is not yet clear if a thin ice shell can build up sufficient excess pressure to insure the stability of methane hydrate above the melting point of water.

2. Computation Details

In order to investigate different cases of ice shielding two models of hydrate/ice systems were considered. The first model consisted of a methane hydrate sphere, surrounded by bulk ice *Ih*. Methane hydrate was modeled as a supercell containing 63 molecules of methane and about 370 water molecules; ice *Ih* contained more than 5000 water molecules (to a total of 6287 molecules). The average radius of the hydrate sphere was about 1.25 nm. Periodic boundary conditions were applied to emulate an infinite ice matrix with immersed hydrate clusters (Fig. 1).

At the beginning, the sphere of methane hydrate was cut off and then pasted in ice *Ih* shell with the same radii of cut sphere. The structure of the resulting system was initially optimized using the conjugate gradient method. After that, molecular dynamics (MD) simulations were performed using the TINKER software package.¹⁸⁾ The MD simulations were carried out for 300 ps with 1 fs time step at $T = 195$ K. Then, the temperature was increased up to 250 K, i.e. above the temperature of methane hydrate dissociation at atmospheric pressure. After the temperature increasing the structure was once more optimized within conjugate gradient method. The MD simulations were carried out in the NVT-ensemble using the Berendsen thermostat. We used an SPC/E-based water model with modified parameters ($\epsilon = 0.6506$ kJ/mol, $\sigma = 0.3156$ nm) and OPLS-UA model of methane ($\epsilon = 1.2314$ kJ/mol, $\sigma = 0.373$ nm). Though the simple one-center Lennard-Jones representation of methane tends to exaggerate the hydrophobic nature of the hydrate-former, it is widely used in simulations of gas/water systems, unless a detailed description of the intramolecular structure becomes a vital necessity.

The molecular-level scheme which was suggested and

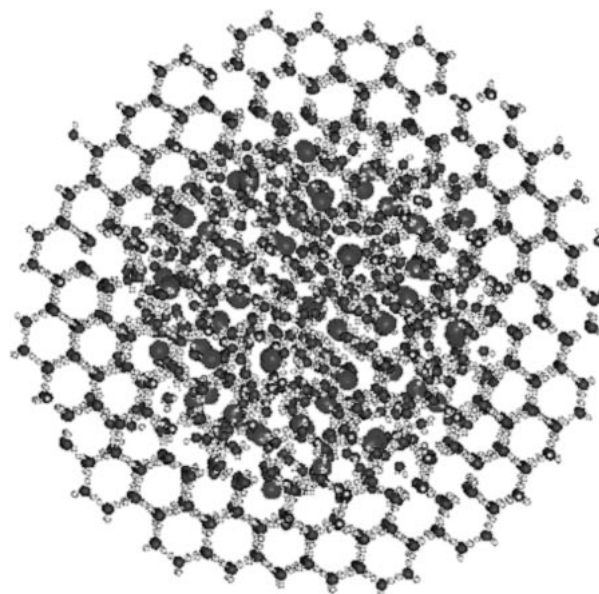


Fig. 2 The initial configuration of the isolated nanocluster with the methane hydrate core in an ice shell.

applied to inhomogeneous systems by Ikeshoji *et al.*^{19,20)} was used for calculations of local pressure. This scheme is based on the Irving-Kirkwood definition of the pressure tensor, and is most convenient for systems consisting of particles with pairwise interactions.

We used the model of ice/hydrate system described above to validate the hypothesis that the immersion of gas hydrate particle into bulk ice might lead to a significant increase of pressure in the hydrate phase. The conditions implied by this model (i.e. the bulk nature of the ice surrounding the hydrate particle) resemble those actually found at the initial stage of hydrate decomposition. However, as the decomposition proceeds further, the bulk system tends to disintegrate into nanoparticles, composed of small fragments of hydrate covered by an ice shell. Since the nature of the system of interest is likely to undergo significant changes in the process of decomposition, the role of the ice shell should be investigated separately for the bulk-like and nanocluster-like states. While the former task can be accomplished using the model described above, the second part of this study is carried out for a different model.

The second simulated system consisted of CS-I methane hydrate core (95 CH₄ and 550 H₂O molecules) embedded in ca. 1 nm thick ice *Ih* shell (1705 H₂O molecules). The resulting cluster (Fig. 2) was surrounded by a repulsive spherical boundary with 3.3 nm radius to limit the space available to the gas phase outside the cluster. A similar system with CS-II krypton hydrate core (94 Kr and 3042 H₂O molecules) was also considered. The SPC/E model was used for water molecules, while methane and krypton were described by a one-center Lennard-Jones potential ($\epsilon = 1.2314$ kJ/mol, $\sigma = 0.373$ nm for methane and $\epsilon = 0.1403$ kJ/mol and $\sigma = 0.368$ nm for krypton). Following the initial equilibration of the nanocluster at 50 K the temperature in the system was gradually increased up to 250 K. For every temperature value the length of MD runs exceeded 2 ns with 1 fs time step. It should be noticed that free external surface

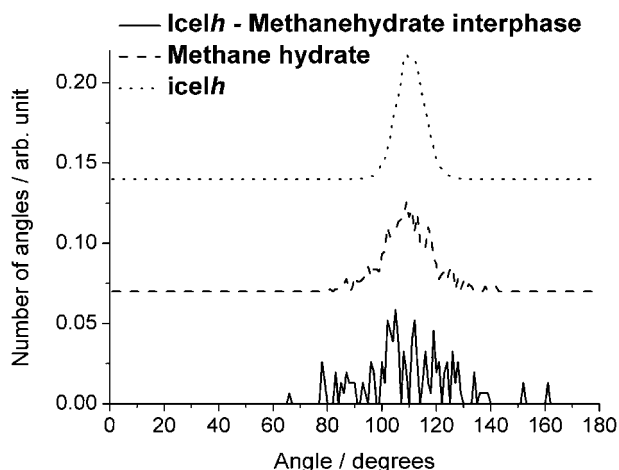


Fig. 3 Distribution of O-O-O angles for ice *Ih*, methane hydrate and ice-hydrate interface.

of the shell contributes to the disordering of ice and promotes the process of surface melting at the temperatures below the melting point of bulk crystal. The available estimations of the melting point for the SPC/E water model lie between 215 K and 240 K, the lower values being obtained from free energy calculations and generally believe to be more precise. This explains the fact that at relatively low temperature (200 K) the aqueous shell of the isolated nanocluster is either strongly distorted ice or supercooled water instead of the ideal *Ih* ice. This point distinguishes the second model from the first one.

The data on the properties of the ice/hydrate interface were obtained from the local pressure calculated as the normal component (P_N) of Irving-Kirkwood tensor. The surface tension γ was estimated by averaging the pressure over both coexisting phases and applying the Laplace formula for the spherical boundary $\gamma = 0.5R\Delta P$, where R is the boundary radius (1.75 nm) and ΔP is the pressure difference between hydrate and ice.

3. Results and Discussion

The resulting structure characteristics of the first model (i.e., the one with periodic boundary conditions) are presented in Fig. 3 (angle distribution of O-O-O angles) and Fig. 4 (the radial distribution (O...H) function for methane hydrate- ice *Ih* interface shown 1.18–1.47 nanometers from the center of methane hydrate bubbles). As one can see, the O-O-O angles remain close to tetrahedral both in hydrate and ice phases. Moreover, the majority of molecules in the ice-hydrate interface also have O-O-O angle values close to tetrahedral. Considering the O...H length distribution, which shows that O...H distances change only in a very restricted range, one can conclude that almost all water molecules in the system are linked by hydrogen bonds. The O...H hydrogen bonds distribution in this case was in limits of 0.17–0.2 nm. During the initial stage of gas hydrate dissociation the arrangement of water molecules at the methane hydrate – ice *Ih* interface allows the network of hydrogen bonds to be preserved.

The calculated local and average densities for the first model are presented in Fig. 5. The averaging was performed

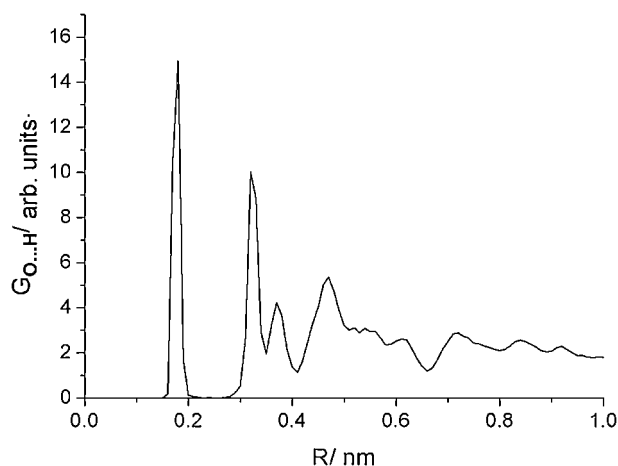


Fig. 4 The radial distribution (O...H) function for methane hydrate- ice *Ih* interface shown 1.18–1.47 nm from the center of methane hydrate bubbles.

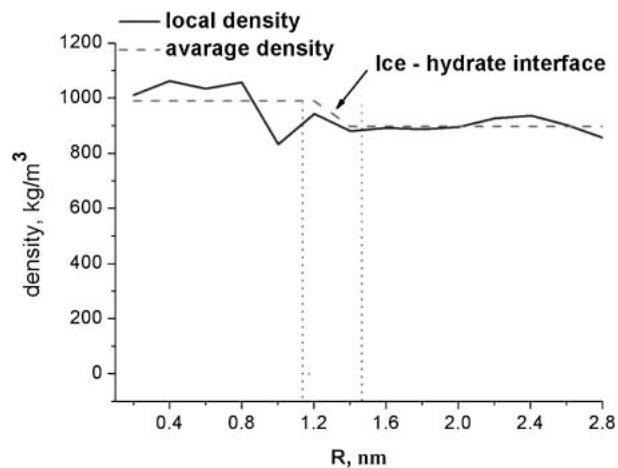


Fig. 5 Local and average density profiles of modeling system.

over the last 1 ps of the MD simulation run. It was found that the density in the hydrate phase is larger than in the ice phase, which is in agreement with experimental data. At the methane hydrate – ice *Ih* interface an anomalously high local density was observed, and this behavior is caused by the increased pressure in the interface region (Fig. 6, 7).

The region of the high pressure anomaly (up to 6 MPa) at the boundary of the hydrate phase, coincides with the high density region. On the average, the radial component of pressure in methane hydrate is about 4 MPa higher than the same component in ice *Ih*, though at certain positions the local pressure reaches 12 MPa. For the transversal component the average pressure in the hydrate phase is ca. 2.5 MPa higher than in the ice phase, while the local pressure values may reach 12 MPa. The experimental decomposition pressure for methane hydrate is about 1.3 MPa at 250 K. Thus, the calculated excess pressure in hydrate phase at lower temperatures was found to be sufficient to prevent dissociation of hydrate phase.

For the second model (the model of methane hydrate cluster immersed in ice cluster without periodically boundary conditions) the computed caloric curves indicate anomalous behavior around 200–205 K and 230 K. The former point is

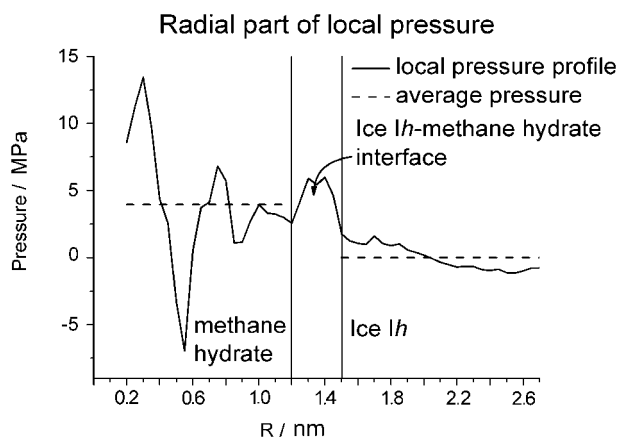


Fig. 6 Radial part of local pressure profile.

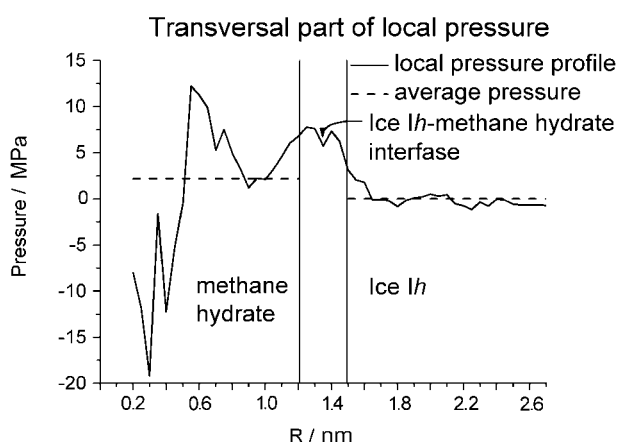


Fig. 7 Transversal part of local pressure profile.

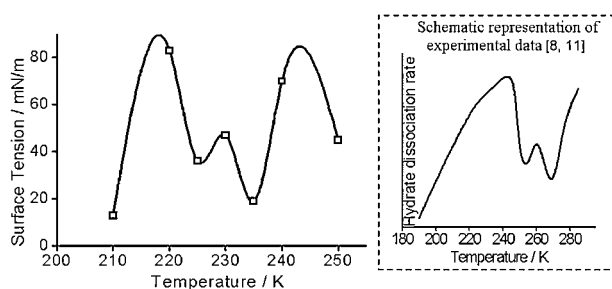


Fig. 8 Calculated surface tension for the non-planar ice/hydrate (CS-I) interface.

associated with the beginning of the deformations in the hydrate core, while the anomaly at 230 K is caused by the entire destruction of the hydrate. Lindemann criteria confirm the conclusions made from the analysis of caloric curves, pointing out the same temperature regions: 200 K and 230 K. At 230 K melting of the hydrate core is suspected. Anomalies in diffusion coefficients can be found at 200 K and 230 K; in both points the diffusivity of core water decreases slightly as the temperature increases. However, the most informative property is the temperature dependence of surface tension, which is presented in Fig. 8.

In the central part of the cluster occupied by hydrates the

local pressure is an actually complex function. It is known that in small spherical systems all the components of the pressure tensor are functions of the location and the surface tension depends on the choice of the dividing surface. In order to find the surface tension it is necessary to define the dividing surface and determine the values of the pressure in coexisting phases. According to Gibbs approach, in the absence of the bulk region the pressure inside a small system should be equal to the pressure of the corresponding bulk phase with the same values of the chemical potentials. In practical applications, however, it is sometimes very difficult to follow this approach even for binary systems. Therefore, the volume-averaged value of the normal component of the pressure tensor is taken as an approximation for the pressure inside the cluster. The estimated uncertainty of the proposed technique is around 20%. We believe that the significant result is the possible nonmonotonic temperature dependence of the surface tension but not the numerical values of it. In this respect our results show distinct correlation with the experimental data of Stern *et al.*^{9,12} for the temperature dependence of the methane hydrate dissociation rate. The non-monotonic behavior of this dependence for temperatures above 250 K is known as anomalous preservation or self-preservation (Fig. 8). However, simulation results suggest a temperature value of 220 K as the lower boundary of the self-preservation window. This 30 K difference between experiment and our simulation can be attributed to the very low melting point of ice described by the SPC/E water model (from 215 K²¹) to 225 K²²). Obviously, in the absence of external pressure the nanocluster model is unable to preserve the stable (or metastable) ice phase far beyond its melting point. The bulk-like model, in which periodic boundary conditions were used, is more successful in dealing with this problem.

Unlike CS-I methane hydrate, no anomalous preservation was observed experimentally for CS-II hydrates. In the case of krypton CS-II hydrate the structure of the nanocluster core appears to be destroyed already at 220 K that is why we are able to estimate the surface tension for the hydrate/water interface only at 210 K. The value of γ is approximately equal to 30 mNm⁻¹, which is in reasonable agreement with experimental data for the ice/water interface. This temperature (210 K) is only 5 degrees lower than the established value of the melting point for the SPC/E water model (215 K). Calculated thermal expansion of krypton hydrate as shown in Fig. 9 is close to ice Ih thermal expansion. This can mean that nature of self-preservation effect connected with difference of thermal expansions of ice and gas hydrates. While methane hydrate can be 'relocated' to a stable phase state due to the very large pressure difference (over 100 MPa) between the hydrate and surrounding ice, in krypton hydrate nanocluster the ice shell does not exert significant pressure on the CS-II hydrate core, thus failing to stabilize the hydrate near its melting point.

4. Conclusion

The components of local pressure and local density profiles were obtained from molecular dynamics simulations. It was shown that ice matrix with immersed methane hydrate

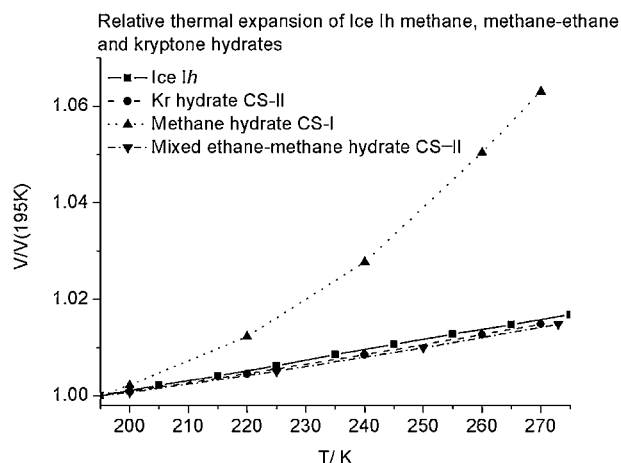


Fig. 9 Thermal expansions of ice *Ih*, methane hydrate CS-I, mixed methane-ethane and krypton hydrates CS-II at ambient pressure.

can be stable at ambient pressure and the temperatures higher than temperature of methane hydrate dissociation. The calculations show that the pressure in the methane hydrate clusters immersed in ice matrix is significantly higher than the pressure of ice phase, but this does not lead to structural distortions because of the formation of a network of hydrogen bonds between hydrate and ice phases.

The theoretical models presented here show the possibility of existence of a well-defined ice and hydrate interface and thermodynamically stable nanoclusters of methane hydrates included in the ice phase. These models describe only initial and final stages of the decomposition of hydrates with the formation of the thermodynamically equilibrium phases of hydrate in the phase of ice and do not intend to describe the rate of dissociation of methane hydrate measured in the experiment. The observed correlation between the calculated surface tension with the “measured” rate can be helpful for understanding the mechanism of the anomalous preservation behavior of gas hydrate

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