Thermodynamic properties of hydrate phases immersed in ice phase

V. R. Belosludov\textsuperscript{1,4*}, O. S. Subbotin\textsuperscript{1}, D. S. Krupskii\textsuperscript{1}, T. Ikeshoji\textsuperscript{2}, R. V. Belosludov\textsuperscript{3}, Y. Kawazoe\textsuperscript{3} and J. Kudoh\textsuperscript{4}

\textsuperscript{1} Nikolaev Institute of Inorganic Chemistry, Lavretyeva avenue 3, Novosibirsk 630090, Russia
\textsuperscript{2} Research Institute for Computational Sciences, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan
\textsuperscript{3} Institute for Materials Research, Tohoku University, Sendai, Japan
\textsuperscript{4} Center for Northeast Asia Studies of Tohoku University, Sendai, Japan

E-mail: bel@che.nsk.su

Abstract. Thermodynamic properties and the pressure of hydrate phases immersed in the ice phase with the aim to understand the nature of self-preservation effect of methane hydrate in the framework of macroscopic and microscopic molecular models was studied. It was show that increasing of pressure is happen inside methane hydrate phases immersed in the ice phase under increasing temperature and if the ice structure does not destroy, the methane hydrate will have larger pressure than ice phase. This is because of the thermal expansion of methane hydrate in a few times larger than ice one. The thermal expansion of the hydrate is constrained by the thermal expansion of ice because it can remain in a region of stability within the methane hydrate phase diagram. The utter lack of preservation behavior in CS-II methane–ethane hydrate can be explain that the thermal expansion of ethane-methane hydrate coincide with than ice one it do not pent up by thermal expansion of ice. The pressure and density during the crossing of interface between ice and hydrate was found and dynamical and thermodynamic stability of this system are studied in accordance with relation between ice phase and hydrate phase.

1. Introduction

Natural gas hydrates generate great attention as globally distributed deposits harboring potential hydrocarbon reserves on Earth, which are considered as a potential energy resource in the future. Natural gas hydrates are being studied worldwide as transport manufactured materials so there are more suitable for large-scale transport of natural gas over long distances than liquefied natural gas. A main component of hydrate deposits is methane hydrate formed from water and methane molecules so the hydrocarbon gas mixture contain >99% methane \cite{1, 2}. Many experimental researches were focused on the considerable delayed dissociation of gas hydrate at 1 atm. (the so-called self-preservation effect) above equilibrium temperature for hydrate breakdown, but below the H\textsubscript{2}O ice point \cite{3-17}. The anomalous preservation of methane hydrate observed below melting point of ice at 242–271K \cite{11, 15} has potential application for temporary low-pressure transport and storage of

\textsuperscript{*}Corresponding author Tel: ++7 3833 3308057, Fax: ++7 3833 3309489 E-mail adress: bel@che.nsk.su

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natural gas and developing safe and dependable technologies to produce natural gas from methane hydrates. The formation of ice film on the surface of decomposing hydrate as the main reaction mechanism responsible for incomplete dissociation of gas hydrate at temperatures below the ice point was suggested in [3-5], [7], [14]. The two-stage dissociation process of CH₄ hydrate crystals at <1 kPa methane pressure, at very low temperatures (168–189 K) was observed using time-resolved X-ray diffraction techniques [12]. There are two regimes: an initially fast regime of the dissociation of CH₄ and the slower regime. The authors have used an ice-shielding mechanism for the interpretation their observations. Recently 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 sII methane–ethane hydrate [11], [15]. The dissociation behavior of methane hydrate depends on dissociation procedures.

The anomalous preservation up to 93 % of methane hydrate was observed after slowly depressurizing the sample to several MPa above the equilibrium curve The subsequent rapidly depressurizing of the sample to 0.1 MPa leads to immediately destabilize the hydrate (“rapid depressurization” method) [11]. SEM imaging showed that the ice-rind development was not observed around individual hydrate grains of the as-grown material (30% porous). The formation uniformly dense material with distinct textural changes along cavity walls was observed. The monitoring of the thermal state of samples has shown short-lived (several minutes) temperature gradient (2K) between sample interiors and surroundings in rapid depressurization method [15]. The low preservation (<8%) of methane hydrate was observed after slowly cooled and depressurized to T < 193 K and P = 0.1 MPa, then slowly heated above the dissociation curve (“temperature-ramping” method) only [11]. The large temperature differences (up to 30K) between sample interiors and surroundings were observed in the time of methane hydrate rapid (endothermic) dissociation [15].

The experiment research showed the formation ice phase during dissociation of gas hydrate and existent thermal gradients between sample interiors and surroundings. Does the ice phase form uniformly dense material including individual hydrate grains? This question is important to understand the mechanism of the anomalous preservation behavior of gas hydrate. As it was shown in [11], [13], [15] the macroscopic ice-shielding model does not explain anomalous preservation up to 93 % of methane hydrate but it can be used for description the preservation of the small amounts of hydrate observed in “temperature-ramping” method. The mechanism of the anomalous preservation behavior of gas hydrate is not clear and needed further investigation.

Without antagonisms with experiment we will suggest that at first stage of dissociation of gas hydrate the ice phase including gas hydrate phase with temperature lower that surroundings temperature with subsequent establishment of temperature balance. Increasing of pressure is happening inside methane hydrate under increasing temperature and if the ice structure does not destroy, the methane hydrate may have larger pressure than ice phase. This is because of the thermal expansion of methane hydrate is a few times larger than ice one. Large attention was focused on the thermal expansion of clathrate hydrates because it was found to be considerably larger than for the hexagonal ice. [1]. Molecular dynamics (MD) calculations of the thermal expansion of ice and structure I ethylene oxide hydrate [18] and structure II krypton hydrate [19] have shown that the linear expansion coefficients of hydrates are greater than in the hexagonal ice. The lattice dynamic (LD) calculations also give larger values of thermal expansion of gas hydrates than that of the ice [20-22].

In this work we study the structure, thermodynamic properties and pressure of hydrate phases immersed in the ice phase with the aim to understand the nature of self-preservation effect of methane hydrate in the framework of molecular model.

2. Theory

The free energy $F_{qh}$ of crystal can be calculated within the framework of lattice dynamics approach in the quasiharmonic approximation as

$$F_{qh} = U + F_{vib},$$

where $U$ is the potential energy, $F_{vib}$ is the vibrational contribution,
\[ F_{vb} = \frac{1}{2} \sum_{j} \hbar \omega_{j}(\mathbf{q}) + k_{B} T \sum_{j} \ln(1 - e^{-\hbar \omega_{j}(\mathbf{q})/k_{B} T}) \]  

(2)

where \( \omega_{j}(\mathbf{q}) \) is the \( j \)-th frequency of crystal vibration and \( \mathbf{q} \) is the wave vector. For determination of eigenfrequencies \( \omega_{j}(\mathbf{q}) \) of molecular crystal vibrations one need to solve numerically the following system of equations

\[
m_{\alpha} \omega^{2}(\mathbf{q}) U_{\alpha}^{j}(k,q) = \sum_{\alpha',\beta} \left[ D_{\alpha\beta}^{\nu}(q,k,k') U_{\alpha'}^{j}(k',q) + D_{\alpha\beta}^{\nu}(q,k,k') U_{\alpha'}^{j}(k',q) \right]
\]

\[
\sum_{\alpha} l_{\alpha}(k) \omega^{2}(\mathbf{q}) U_{\alpha}^{j}(k,q) = \sum_{\alpha',\beta} \left[ D_{\alpha\beta}^{\nu}(q,k,k') U_{\alpha'}^{j}(k',q) + D_{\alpha\beta}^{\nu}(q,k,k') U_{\alpha'}^{j}(k',q) \right]
\]

(3)

where \( D_{\alpha\beta}^{\nu}(\mathbf{q},kk') \), \((\alpha, \beta=x,y,z)\) are translational \((i, i=t)\), rotational \((i, i=r)\) and mixed \((i=t, i=r \) or \( i=r, i=t \)) elements of the molecular crystal’s dynamical matrix, the expressions for which are presented elsewhere [23-24] \( U_{\alpha}^{j}(k,q) \), \((\alpha, \beta=x,y,z)\) is the amplitude of vibration, \( m_{\alpha} \) and \( I_{\alpha\beta}^{(k)} \) are the mass and inertia tensor of \( k \)-th molecule in the unit cell.

In the quasiharmonic approximation the free energy of crystal has the same form as in the harmonic approximation but the structural parameters at fixed volume depend on the temperature. This dependence can be determined self-consistently at calculation of the system’s free energy. To obtain the equation of state \( P(V) \) at fixed temperature the expression:

\[
P = -\left( \frac{\partial F_{vb}}{\partial V} \right)_{0}
\]

(4)

has been used. For calculation of the free energy, the molecular coordinates (the centers of mass positions and orientations of molecules in the unit cell) have been determined by the Conjugate-gradient method. In this method new coordinates of molecules can be found from the minimum of potential energy of the expanded lattice.

3. Computation details

Considering ice Ih, methane hydrate phases and methane hydrate phases immersed in the ice Ih phase, we used modified SPC water–water interaction potential. The parameters describing short-range interaction between the oxygen atoms \( \sigma = 3.17 \text{ Å} \) and the energy parameter \( \varepsilon = 0.64977 \text{ kJ mol}^{-1} \) of Lennard-Jones potential of SPC water potential [27] were changed and was taken \( \sigma = 3.1556 \text{ Å}; \varepsilon = 0.65063 \text{ kJ mol}^{-1} \). The charges on hydrogen \((q_{H} = 0.4238 |e|)\) and on oxygen \((q_{O} = 0.8476 |e|)\) of SPC model were changed and remained the same. The modified SPC potential significantly improves the agreement between the calculated cell parameters for ice Ih and methane hydrate with the experimental values.

The protons have been placed according to the Bernal–Fowler rule and the water molecules have been oriented so that total dipole moments of the unit cells of ice Ih and hydrates were equal to zero. The long-range electrostatic interactions have been computed by the Ewald method.

3.1. Ice Ih phase

QLD calculations have been performed on a 64 water molecules supercell of ice Ih. The structure of this model has been obtained by optimizing with a conjugate-gradient method employing a modified SPC potential for water. The free energy and the derivatives of free energy have been calculated using 2x2x2 k-points inside the Brillouin zone.

3.2. Methane hydrate phase

For clathrate hydrate of CS-I, the initial configuration for QLD calculations was a single unit cell with 46 water molecules and 8 methane molecules in both large and small cavities. The initial positions of the oxygen atoms and the guests have been taken from the X-ray analysis of ethylene oxide hydrate of CS-I [25]. The orientations of water molecules and the positions of the oxygen atoms and guests have been determined by the conjugate-gradient method at each concerned lattice.
parameters of the unit cell. The guests are considered as spherically symmetric Lennard–Jones particles. The potential parameters for the methane–methane interaction $\sigma = 3.73\,\text{Å}; \varepsilon = 1.2305\,\text{kJ/mol}$ (OPLS potential) are taken from [26]. The guest–host interaction potential is also represented in the Lennard–Jones form with relevant parameters estimated from the usual combination rules.

3.3. Methane-Ethane hydrate phase

For clathrate hydrate of CS-II, the initial configuration for QLD calculations was a single unit cell with 136 water molecules and 16 methane molecules in small cavities and 8 ethane molecules in large cavities. The orientations of water molecules and the positions of the oxygen atoms and guests have been determined by the conjugate-gradient method at each concerned lattice parameters of the unit cell. The potential parameters for the methane–methane interaction are the same: $\sigma = 3.73\,\text{Å}; \varepsilon = 1.2305\,\text{kJ/mol}$ (OPLS potential). For ethane-ethane interactions potential parameters are $\sigma = 4.418\,\text{Å}; \varepsilon = 1.704$ (proposed by Tanaka). In the other case parameters was taken from OPLS potential, i.e. $\sigma = 3.954\,\text{Å}; \varepsilon = 2.01933$. The guest–host interaction potential is also represented in the Lennard–Jones form with relevant parameters estimated from the usual combination rules.

3.4. Methane hydrate phases immersed in the ice Ih phase

The description of thermodynamic properties of hydrate phase immersed in the ice phase was carried out within the framework of macroscopic and microscopic models.

In the macroscopic model hydrate phase having volume $V_{\text{hyd}}$ was located inside ice phase having volume $V_{\text{ice}}$ at temperature $T_0$ and pressure $P_0$. For calculation of pressure of hydrate phase immersed in the ice Ih phase the approximation of the coordinated compression was used, i.e. relative change of volume was considered identical to ice and hydrate. Pressure in hydrate at heating ice from $T_0$ up to some temperature $T$ at pressure $P$ was taken from a condition of equality of relative change of equilibrium volume of ice and hydrate:

$$
\frac{V_{\text{hyd}}(T, P)}{V_{\text{hyd}}(T_0, P_0)} = \frac{V_{\text{ice}}(T, P)}{V_{\text{ice}}(T_0, P_0)}
$$

(5)

Figure 1. The methane hydrate cluster immersed in the ice Ih phase.

The equations of state $V_{\text{ice}}(T, P_0)$ and $V_{\text{hyd}}(T, P)$ have been calculated using the equation (4) of the lattice dynamics approach within the quasiharmonic approximation.
In the microscopic model for the calculations we have started from the quasicrystal-like model with the supercell contains 8190 water molecules and 96 methane molecules (Figure 1). Ice-hydrate interface for a hydrate particle inside the ice phase was spherical shape. It has been considered the model at increasing temperatures from 195 K to melting point of ice at atmosphere pressure. The structure of this model has been obtained by optimizing with a conjugate-gradient method employing a modified SPCE potential for water and OPLS potential for methane. The final optimized structure has been used then for the long molecular dynamic (MD) calculations. MD equilibration over 10000 ps has been performed using Berendsen’s constant temperature - pressure (NPT) method with 1 ps time steps. Ewald summation was used for the electrostatic interactions.

A density of system hydrate of metane - ice depending on radius \( r \) \( (r_1<r<r_2) \) was taken as a density of spherical layer between two spheres of radius \( r_1 \) and \( r_2 \) (thickness of layer is 3.15 Å).

4. Results and discussion

Linked together by hydrogen bonds, the water molecules in clathrate hydrates form the host lattice with the cavities where the guest molecules can be encaged. Properties of clathrate hydrates depend on the structure of the host lattice and the kind of guest molecules in these cages. Short-range ordering of the host lattice is similar to that in the hexagonal ice and it may be assumed that properties of the hydrates depending on the short-range ordering of the host lattice are also similar to these in hexagonal ice. However, the thermal expansion of clathrate hydrates is considerably larger than for the hexagonal ice. The guest molecules influence on the host lattice significant.

![Figure 2. Relative change of volumes of ice Ih and methane hydrate V/V(195K). Experimental data for ice Ih was taken from [27].](image2)

![Figure 3. Relative change of volumes of ice Ih and ethane-methane hydrate V/V(195K).](image3)

The calculated temperature dependences of relative changes of volume \( V/V \) (195K) for Ice Ih and methane hydrate CS-I at pressure \( P=1\text{atm.} \) are displayed in Figure 2. For Ice Ih the relative change of volume at temperatures from 195 up to 270 K is compared with experimental results [27]. It was show in [21], [22] for methane hydrate the coincidence of the calculated results and experimental data is sufficiently good at temperatures below 200 K. At higher temperatures that 195 K the methane hydrate exist as a metastable phase and the calculated relative changes of the volume \( V/V \) (195K) become larger than relative changes of the volume \( V/V \) (195K) for Ice Ih.

The calculated temperature dependencies of relative changes of volume \( V/V \) (195K) for Ice Ih and ethane-methane hydrate CS-II at pressure \( P=1\text{atm.} \) are displayed in Figure 3. For ethane-methane hydrate CS-II the relative change of volume at temperatures from 195 up to 270 K is compared with experimental results for Ice Ih and the methane hydrate. As can see from the relative change of volume of ethane-methane hydrate CS-II coincide with the relative change of volume of Ice Ih at temperatures from 195 up to 225 K and is lower at higher temperature.
In Figure 4 the temperature dependences of relative volumes \( V(P, T=195 \text{ K})/V(P=1 \text{ atm.}, T=195 \text{ K}) \) for methane hydrate and Ice Ih at different pressure are presented. The temperature dependencies of pressure in hydrate phase immersed in the Ice Ih phase are defined from crossing of curves of relative volumes for methane hydrate at different pressures and ice Ih as shown in Figure 4.

The calculated temperature dependence of pressure in hydrate at heating ice from \( T=195 \text{ K} \) at pressure \( P=1 \text{ atm} \) are displayed in Figure 5. The calculation shows that with a rise of 1 K in temperature the pressure can be increased up to 13 - 20 bar in the center of cluster of hydrate depending on temperature. This leads to situation when the methane hydrate can be thermodynamically stable under heating (overheating of methane hydrate) because it can be stay in region of its stability on methane hydrate phase diagram.

![Figure 4](image4.png)

**Figure 4.** Calculated thermal expansion of methane hydrate at different values of pressure in comparison with thermal expansion of ice 1h at 1 bar. One unit cell of methane hydrate was taken into account.

![Figure 5](image5.png)

**Figure 5.** Calculated dependence of surplus pressure of temperature in methane hydrate cluster included in ice 1h.

In Figure 4 the temperature dependences of relative volumes \( V(P, T=195 \text{ K})/V(P=1 \text{ atm.}, T=195 \text{ K}) \) for methane hydrate and Ice Ih at different pressure are presented. The temperature dependencies of pressure in hydrate phase immersed in the Ice Ih phase are defined from crossing of curves of relative volumes for methane hydrate at different pressures and ice Ih as shown in Figure 4.

The calculated temperature dependence of pressure in hydrate at heating ice from \( T=195 \text{ K} \) at pressure \( P=1 \text{ atm} \) are displayed in Figure 5. The calculation shows that with a rise of 1 K in temperature the pressure can be increased up to 13 - 20 bar in the center of cluster of hydrate depending on temperature. This leads to situation when the methane hydrate can be thermodynamically stable under heating (overheating of methane hydrate) because it can be stay in region of its stability on methane hydrate phase diagram.

![Figure 6](image6.png)

**Figure 6.** Calculated density of cluster of methane hydrate included in ice 1h.

The calculated density of cluster of methane hydrate and ice 1h surrounding the cluster depending on radius after heating up to \( T=270 \text{ K} \) is show on Figure 6. The calculation show that ice phase with cluster of methane hydrate can be stable. The densities of methane hydrate and ice near methane...
hydrate – ice interface are greater than in the bulk phases. Density of state of ice far from interface approaches to density of bulk phase of ice.

5. Conclusion
Increasing of pressure appears inside methane hydrate phases immersed in the ice phase under increasing temperature and if the ice structure does not destroy, the methane hydrate will have larger pressure than ice phase. The methane hydrate remains thermodynamically stable under heating (overheating of methane hydrate). This is because of the thermal expansion of methane hydrate in a few times larger than ice one. Thermal expansion of hydrate pent up by thermal expansion of ice because it can be stay in region of its stability on methane hydrate phase diagram. The utter lack of preservation behavior in CS-II methane–ethane hydrate can be explain that the thermal expansion of ethane-methane hydrate coincide with than ice one it do not pent up by thermal expansion of ice.

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