Self-preservation effect modelling in hydrate systems using Lattice Dynamic methods

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Abstract. The thermodynamic properties of the carbon dioxide clathrate hydrate as well as hexagonal ice Ih have been calculated using Quasiharmonic Lattice Dynamic framework in connection with Molecular Dynamic methods in order to show the existence of the self-preservation effect in the carbon dioxide hydrates. The statistical thermodynamics theory has been applied to calculate the thermal expansion coefficients for hydrate and ice systems. The calculations clearly show that because the thermal expansion of the hydrate phase is limited by the thermal expansion of ice it is possible to keep the hydrate in a stable region within the phase diagram. The differences in thermal expansion should lead to the self-preservation effect with the application of additional pressure on the hydrate phase. This effect allows using the self-preservation effect for the storage and transportation of gas in the hydrate form.

1. Introduction
Clathrate hydrates are also known that gas hydrates are host-guest inclusion compounds, being crystalline materials consisting of water molecules that incorporate guest molecules inside hydrogen-bonded water cages [1]. Yakushev and Istomin in their study [2] reported about the unsuspected stability of some gas hydrates at temperatures below the ice melting point outside their thermodynamic stability region; and this phenomenon was called as “self-preservation” effect or “anomalous preservation” [3]. Recently the preservation of CO2 clathrate hydrate under thermodynamically stable condition is studied often due to ecological problems that modern society has been facing in the recent decades [4]. The “anomalous preservation” has been observed for carbon dioxide hydrates [5-9] and many other gases such as methane, ethane, etc. The relative volume ratios for various clathrate hydrates were measured by PXRD and were analyzed as a function of temperature [9].

In this work we aimed at explaining the self-preservation effect in carbon dioxide hydrates from thermodynamic point of view. For this purpose we have studied the thermodynamic properties of the carbon dioxide hydrate and hexagonal ice Ih with the main focus on thermal expansion coefficient using Quasiharmonic Lattice Dynamic (QLD) approach [10,11] in connection with Molecular Dynamic methods.

2. Model description
We have suggested that the process of hydrate dissociation starts on the hydrate surface that causes formation of an ice layer. Since the resulting “hydrate – ice” system is continuous it is possible to
suggest a similar relative thermal expansion of the ice shell and the hydrate immersed inside the ice. Hydrates and ice in general have different thermal expansion coefficients, therefore, this difference causes creation of an additional pressure in order to equilibrate thermal expansion of the immersed hydrate and the ice shell. The equality of relative changes in ice I_h and hydrate volume can be written in the following form:

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

where \( P_0 \) and \( T_0 \) are the initial pressure and temperature and \( P, T \) are the ambient pressure and temperature. Full description of the used model can be found in the work [12].

Equation of states \( P(V,T) \) for carbon dioxide hydrate and ice I_h are found numerically as partial derivatives of the free energy \( F \):

\[
P = -\frac{\partial F(V,T)}{\partial V}.
\]

The free energy \( F \) of each phase is found using the QLD method [10,11]. Free energy is derived as a sum of the potential energy \( U \) and the vibrational component \( F_{\text{vib}} \):

\[
F_{\text{vib}} = \frac{1}{2} \sum_{j \neq} \hbar \omega_j(q) + kT \sum_{j \neq} \ln \left( 1 - e^{-\frac{\hbar \omega_j(q)}{kT}} \right),
\]

where \( \omega_j(q) \) is the \( j \)th frequency of crystal vibration and \( q \) is the wave vector.

The H\(_2\)O molecule in our calculation is described by a modified Simple Point Charge Extended (SPC/E) potential with parameters presented in our previous study [13]. This potential has been modified for better description of the thermal expansion of H\(_2\)O solid phases and proved its applicability for calculation of physical parameters and composition of gas hydrates.

CO\(_2\) molecule was considered as a spherical particle with only van der Waals interaction described by Lennard-Jones potential with parameters from work [14].

The complete simulation method description and details can be found in the Belosludov et. al work [12].

3. Results and discussion

The main parameters connected with the presence or absence of the self-preservation effect are a difference of thermal expansion of covering ice and immersed hydrate phase. Figure 1 presents calculated the thermal expansion (ratio between the volume at temperature \( T \) and pressure \( P_0 \) and the volume at \( T_0, P_0 \)) in dependence on temperature for empty CS-I hydrate, Ice I_h, carbon dioxide and methane hydrates, and the experimental data for thermal expansion of CO\(_2\) hydrate [15]. The thermal expansion of Ice I_h is found to be in agreement with experimental data [16] as well as the one for CO\(_2\) hydrate, moreover, the expansion of Ice I_h and empty CS-I hydrate are similar. According to our calculations the relative thermal expansion of CH\(_4\) hydrate and of CO\(_2\) hydrate are comparable by magnitude and both of them are found to be larger than the relative thermal expansion of Ice I_h. Since the self-preservation effect for CH4 hydrate is experimentally observed we can reasonable assume that the difference of the relative thermal expansion between CO\(_2\) hydrate and Ice I_h phase is large enough for self-preservation effect too.
Figure 1. Dependence of the relative thermal expansion (V/V₀) on temperature for empty CS-I hydrate, ice Ih, CH₄ and CO₂ hydrates, and experimental data for CO₂ hydrate [15].

Figure 2. The dependence of surplus pressure on temperature for CO₂ hydrate in relation to Ice Ih.

Using the dependence of relative thermal expansion of the hydrate V(P,T)/V(P₀,T₀) at certain pressures P = 5, 10, 20, 50, 75, 100 MPa it is possible to find the temperature of equal relative thermal expansion for Ice Ih phase with that hydrate; and this dependence is presented in Figure 2. In other words this dependence shows the additional pressure that appeared in the carbon dioxide hydrate phase; exactly this additional pressure governs the self-preservation effect in the suggested model. Therefore the hydrate can be preserved by the covering ice shell. From thermodynamic point of view in this system it is more energetically favorably to keep CO₂ molecules in the hydrate cavities that causes an expansion of the hydrate lattice. The presence of carbon dioxide molecules in the hydrate phase creates conditions for the process of self-preservation effect.
4. Conclusions
In this work we propose a macroscopic thermodynamic model for the description of the self-preservation effect in carbon dioxide hydrates. The thermal expansion of the CO$_2$ hydrate and Ice Ih has been calculated and is found to be in good agreement with the experimental data. Based on the thermal expansion coefficient it has been shown that an increase in pressure occurs in the hydrate phase immersed in ice caused by increasing systems’ temperature. Therefore, the hydrate phase remains thermodynamically stable under heating because of that additional pressure.

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