Thermal expansion of ice based gas hydrates

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Abstract. This work aims at studying thermal expansion of ice Ih based gas hydrates that play important role in self-preservation effect of classical gas hydrates. Linear thermal expansion of ice Ih based hydrogen hydrates are calculated using a very effective statistical thermodynamic model of gas hydrates developed by the authors of this work. Molecular structures of all studied systems are obtained by MD simulations, and all parameters required by the model are obtained by using Quasiharmonic Lattice Dynamic approach. In accordance with our calculations, introduction of hydrogen into the system not only significantly affect the unit cell parameter of ice, but also increases linear thermal expansion and makes it comparable to the classical gas hydrates such as CH₄, CO₂, etc.

1. Introduction
Gas hydrates are inclusion compounds formed by guest molecules entrapped in cavities of crystalline framework composed from water molecules (hosts). These compounds are well known from 18th century after their discovery by Priestley in 1780 [1], and still have been intensely studied by theoretical and experimental methods. Hydrogen molecules despite their size can form gas hydrates of cubic structure II (sII) with multiple occupation of large cavities of the structure [2,3]. Namiot’s works demonstrated that hydrogen molecules can fill up voids in ice Ih structure with forming the so-called ice Ih based hydrogen hydrate [4]. With pressure increase ice Ih based hydrogen hydrate transforms into classic sII hydrogen hydrate [3], then into ice II based gas hydrate [5], and, finally, at a very high pressure it transforms into ice Ic based hydrogen hydrate [5,6].

During experimental research of clathrate hydrates it has been found that hydrates formed by some guest molecules display very slow (few orders of magnitude lesser that expected) dissociation speed having been removed from the zone of their thermodynamical stability. This phenomenon was called “self-preservation effect” [7]; its use can significantly improve application of hydrogen gas hydrates in industry, especially, in terms of environmentally safe energy demands.

In our previous work [8] we studied sII hydrogen hydrates self-preservation effect assuming that its key factor is the difference of thermal expansion coefficient of hydrate and ice that covers hydrate surface right after removing the hydrate from thermodynamic stability zone. It is this difference that causes arising additional pressure for hydrate and effectively returns hydrate back to the zone of its stability. In work [8] we did not consider the possibility of filling of the surface ice by hydrogen, that may play significant role.

In this work we theoretically study the effect of hydrogen filling of ice Ih on thermodynamic properties of ice based hydrate. We mainly focus on thermal expansion coefficient as a main factor
responsible for the existence of self-preservation effect in hydrogen hydrates. Quasiharmonic Lattice Dynamic approach and Molecular Dynamic simulation methods are used to produce all necessary data for applying the theoretical model of inclusion compounds [8].

2. Calculation details
In the introduction section we have mentioned that the key factor responsible for self-preservation effect is the difference of thermal expansions of the ice, covering the bulk hydrate phase and the hydrate phase itself immersed in the ice phase. Using this assumption we have successfully calculated the hydrate systems formed from different gases [8-10]. For the present work we use the same approach for calculating the thermal expansion coefficient for hydrogen ice based hydrate: combination of Molecular Dynamic calculation for obtaining equilibrated and minimized structures with different volumes, Quasiharmonic Lattice Dynamic approach for calculating Free energy of these systems, with further processing of all the data using the statistical thermodynamic theory of inclusion compounds developed in our laboratory [8].

The used system of ice Ih consists of $4 \times 4 \times 2$ unit cells of ice Ih that gives 128 water molecules in total. Unlike the only one unit cell that we typically use for classical hydrates calculation, in this case we construct this super-cell in order to make the total dipole moment of the systems equal to zero, which is important for proper calculation of electrostatic interaction.

Water molecules are described by modified SPC/E rigid model [11]. Hydrogen molecules are considered as spherical symmetric particles with only van-der-Waals interaction described by 6-12 Lennard-Jones potentials [12].

3. Results and Discussion
Thermal expansion coefficient of ice based hydrates as well as of classical clathrate hydrates strongly depends on the hydrate cavities occupation ratio. Therefore, this parameter should be carefully taken into account, fortunately in the most cases this influence is linear. For the hydrogen ice based hydrates, we have only one “cavity” type and it is required only to calculate a hydrate with maximum fraction of hydrogen. All intermediate values can be interpolated from empty and fully occupied structures of ice Ih.

Usually self-preservation effect is studied at atmospheric pressure, because pressure removing is the most convenient method to move hydrate outside of its stability zone. Therefore, we calculated the system volume, and then the thermal expansion coefficient at ambient pressure.

Fig. 1 presents the calculated data of the linear thermal expansion of ice Ih based hydrogen hydrate, methane sI hydrate, and hydrogen sII hydrate, and empty ice Ih, sI, sII lattices depending on temperature. According to our results the thermal expansion of ice based hydrate is significantly greater than that for empty ice Ih structure. Moreover, the absolute value of the coefficient is comparable to the thermal expansion of the methane sI hydrate at a temperature below ~200 K; at higher temperature the ice based hydrogen hydrate thermal expansion exceeds the one of methane hydrate.

Because of hydrogen hydrate melting it is reasonable to suggest that the hydrogen sII hydrate is covered by ice Ih based hydrate with decreasing hydrogen content, but not just by ice Ih as we suggested in our previous work [8]. Hydrogen sII hydrate has lesser thermal expansion than ice based hydrate of hydrogen. In other words additional interlayer of ice based hydrate does not create additional pressure due to the thermal expansion coefficient difference. But this interlayer could reduce effectiveness of the self-preservation, since in this case, the fraction of hydrogen to be melted to form ice layer with quite low thermal expansion seems to be larger than in case when gas trapped in the hydrate has no opportunity to occupy channels in ice Ih structure.

The most striking feature of large thermal expansion coefficient of ice based hydrogen hydrates is self-preservation. The first of all these hydrate types requires much lesser pressure than sII hydrate [13]. Additionally the hydrogen storage capacity in ice Ih is about the same as in sII hydrates. These two factors could make hydrogen storage in ice based hydrates very promising.
Figure 1. Temperature dependence of the coefficient of thermal expansion for ice Ih based hydrogen hydrate, methane sI hydrate, hydrogen sII hydrates, empty ice Ih structure, empty sI hydrate lattice, and empty sII hydrate lattice.

Conclusions
In the presented work we have calculated linear thermal expansion coefficient for ice Ih based hydrogen hydrates and compared the obtained values with previous data for different hydrate types. In accordance with our calculations the thermal expansion of ice Ih based hydrogen hydrates is greater than for sII hydrogen hydrates and even greater than for methane hydrates at temperature over ~200 K. Therefore, formation of ice based hydrate atop of sII hydrogen hydrate does not affect the self-preservation possibility of the latter. In addition, the self-preservation of ice based hydrogen hydrate itself makes it more suitable for a hydrogen storage container compared with classical sII hydrate.

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