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Unusual Crystalline and Polycrystalline Structures in Methane Hydrates

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Methane hydrates (MH) are crystals made from cages of water molecules that accommodate methane molecules.[1,2] These compounds are of great importance to a wide range of fields,[3−5] and hence there has been a dramatic increase in experimental and theoretical research[6] related to these compounds. Although it is apparently surprising that two molecules with such low affinity can actually form a well-defined crystal, the stability of these crystals can be easily understood from some intuitive steric and energetic considerations. In these compounds the methane molecules provide, by their size, the right steric template for water molecules to organize in cages around the methane. On the other hand, the interaction energy between water molecules making up the cages is ∼40 kJ/mol, while the interaction between methane and the surrounding water is much smaller, ∼5 kJ/mol, and too weak to interfere with the strong hydrogen bonds of the water in the cages.

Although there are at least five known methane hydrate structures,[7−12] the most common are the so-called structures sI (MH-sI) and sII (MH-sII). These two types of hydrates differ by the kind of water cages they contain and their relative arrangement (see Supporting Information). The unit cell of a gas hydrate sI consists on small dodecahedra (5^{12}) water cages and bigger tetradecahedra ($5^{12}6^2$) cages. The gas hydrate structure sII contains slightly distorted 5^{12} cages and much bigger cages of hexadecahedra ($5^{12}6^4$).[1,2,7,8] As well, transitions between various methane-hydrate structures with applied pressure have been extensively studied experimentally, with some polymorphs and unknown structures being identified at relatively high pressures.[12,14,16]

In this Communication we will present previously unreported crystalline and polycrystalline structures for methane hydrates obtained by atomistic simulations at relatively low pressures. Specifically, we will show that during the crystal growth of MH-sI, an unexpected kind of structural defect, consisting of layers containing cages with 12 pentagonal faces and 3 hexagonal faces ($5^{12}6^3$), can form. These $5^{12}6^3$ cages have a significant impact on the structure of the resulting crystal and could provide a possible explanation for several experimental observations regarding in-situ transformations from MH-sI to MH-sII.[13−15] We have identified a new possible structure of methane hydrates which we propose to call structure sK (MH-sK). In addition, we predict an unusual polycrystalline structure consisting of this new hydrate and MH-sI and suggest a mechanism for the formation of a polycrystalline structure consisting of sequences of MH-sI and MH-sII.

The molecular simulations performed in this work utilize two methodologies recently developed[17,18] and successfully employed in several other studies[19,20] to investigate steady-state heterogeneous crystal growth. The main difference between the two methods can be viewed as that in one approach Newtonian dynamics is used to evolve the growing interface while in the second method a canonical sampling of the fluctuations is achieved. The observed kinetics of growth and interfacial properties are essentially identical from the two methodologies confirming that heterogeneous crystal growth is a stochastic process that is independent of the details of the
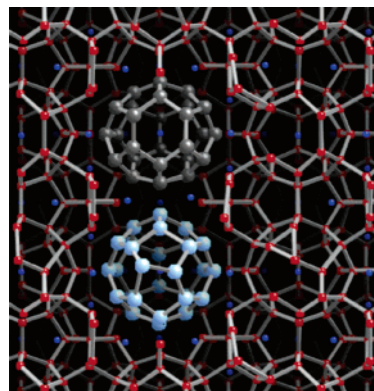

Figure 1. An averaged configuration from the growing [001] surface of the MH-sII. Both intermediate $5^{12}6^3$ and $5^{12}6^4$ cages tend to form during the growth, but only one kind of cage will survive the ordering−disordering fluctuations of the growing layer. The $5^{12}6^3$ cage has its water molecules appear as gray spheres, while the $5^{12}6^4$ cage has its water molecules in light blue.

underlining dynamics. (For further details of the methodologies and setup employed see the Supporting Information and refs 17, 18, and 20.)

In a recent publication[20] we have reported seeing the formation of a [001] MH-sII structure on the template provided by the [001] face of MH-sI. However, the rather striking question of how a [001] MH-sI face could actually accommodate the [001] face of MH-sII (since these two faces are sterically incompatible) was raised by this result. A subsequent careful inspection of the layer connecting the MH-sI and MH-sII structures revealed an interesting fact: a new kind of cage made from 3 hexagonal faces and 12 pentagonal faces provided the required steric template to connect the two structures. Although a $5^{12}6^3$ cage has been reported in several tertiary-amine inclusion compounds,[21] to our knowledge it has not been considered as a possible structural component of methane hydrates (or gas hydrates in general). In MH-sI, the larger $5^{12}6^2$ cages have a cubic arrangement in space and are connected via their hexagonal faces. In MH-sII, its $5^{12}6^4$ cages are connected into a tetrahedral arrangement via their hexagonal faces. These two different kinds of crystal can be linked structurally through an intermediate layer of $5^{12}6^3$ cages, where one hexagonal face is shared with a hexagon of a $5^{12}6^2$ cage of MH-sI and the two other hexagonal faces are shared with two hexagonal faces of the larger cages of MH-sII (see Supporting Information).

A molecular configuration of the interface during the crystal growth of the [001] face of MH-sII is shown in Figure 1. We can see that at this point in its growth, the interface contains both kinds of cages, the larger $5^{12}6^4$ cage of MH-sII and the "intermediate" $5^{12}6^3$ cage. Depending on which cage will survive the ordering−disordering fluctuations taking place at the interface, the next layer of crystal to form will be either sII or sI; if the $5^{12}6^3$ survives, the next layer will be MH-sI, otherwise the MH-sII will continue to grow. We suggest that through this mechanism it may be possible
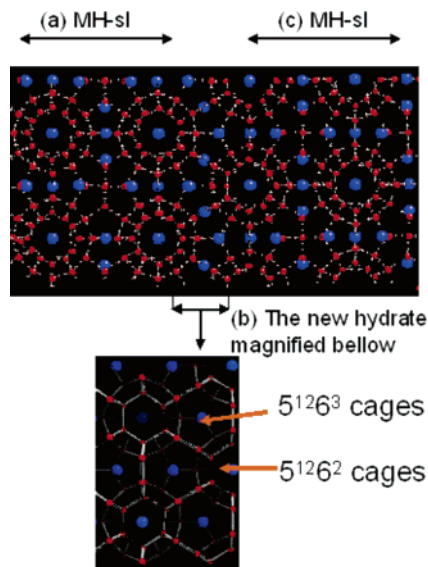
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Figure 2. The structure of the crystal formed during the heterogeneous growth of methane hydrate (a) two layers of MH-sI, (b) a layer of MH-sK, and (c) two more layers of MH-sI misaligned with respect to the MH-sI crystal in part a. The $5^{12}6^2$ and $5^{12}6^3$ water cages of the newly identified MH-sK are indicated by arrows in the figure.

to obtain (under specific conditions of temperature and pressure) a polycrystalline methane hydrate solid formed by sequences of hydrate MH-sI and MH-sII connected via layers with the intermediate $5^{12}6^3$ cages. Additionally, we postulate that on the [001] MH-sI surface, the [001] MH-sII can be heterogeneously nucleated via intermediate layers of $5^{12}6,^3$ thereby allowing a system to transform between the two structures. This could provide a mechanism for the in-situ transformations of MH-sI to MH-sII observed experimentally.[12,14]

In some of our simulations of the MH-sI growth, we have obtained a sequence of two intermediate layers containing $5^{12}6^3$ cages with subsequent growth of MH-sI crystal, but now misaligned with respect to the initial crystal (see Figure 2). A closer inspection of the hydrate structure composing these two layers reveals it is a new kind of methane hydrate structure (which we label sK). MH-sK consists of six 5^{12} cages, four $5^{12}6^3$ cages, and four $5^{12}6^2$ cages per repeating unit, where 80 molecules of water and 14 molecules of methane are contained in a 12.118 Å × 12.118 Å × 20.824 Å orthorhombic box. The Cartesian coordinates of the water and methane molecules of the MH-sK crystal are given in the Supporting Information.

This hydrate structure, with its $80H_2O14CH_4$ stoichiometry and apparent hexagonal symmetry (see Supporting Information), appears consistent with one of the three structures under hydrate structure IV from the Jeffrey's Table (see pages 148 and 150 of ref 1). This $80H_2O14X$ structure in Jeffrey's Table has only been theoretically extrapolated from a less symmetric tertiary-amine hydrate structure III,[21] and we are aware of no report of its experimental existence. We suggest that it may be possible for methane hydrates (or gas hydrates in general) to adopt this sK structure under appropriate conditions. To provide further insight when it might be possible to observe sK hydrates, we have compared the energies of sI, sII, and sK hydrate crystals as a function of the size (spherical) of the

guest molecule, at a pressure of 100 atm and a temperature of 245 K (see Supporting Information). Although sI has the lowest energy (as expected) above a certain molecular diameter, the sK does become more stable than the sII, suggesting that it might be possible to identify sK for certain guest compounds (gases) at certain conditions. Additionally, a polycrystal of MH-sI and MH-sK, as well as an in-situ transformation of MH-sI to MH-sK could be possible at appropriate conditions.

Finally, it is important to note that, even if the percentage of $5^{12}6^3$ cages (as defects) in a MH-sI structure is small (and therefore difficult to detect experimentally) it could nonetheless have significant consequences in the stacking structure of the crystal (see Figure 2) as well as in its morphology. Further studies focused on understanding the implications of $5^{12}6^3$ cages on MH-sI are under way.

Supporting Information Available: Figures describing hydrate structure, the simulation setup, how $5^{12}6^3$ cages link MH-sI and MH-sII, relative energies of sI, sII, and sK, molecular coordinates of a repeating unit of MH-sK, and the structure of MH-sK. This material is available free of charge via the Internet at http://pubs.acs.org.

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