Molecular Dynamics Study of Gas Hydrate Formation

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The mechanisms for nucleation, growth, and melting in gas hydrates (also called clathrate hydrates) are of considerable current interest.[1] The past decade has seen a great deal of effort aimed at developing kinetic inhibitors that prevent methane and natural gas hydrates from forming in oil and gas pipelines. These are antifreeze agents, akin to antifreeze peptides, which are active in very low concentrations and work by delaying nucleation and slowing crystal growth. A better understanding of the nucleation process would facilitate the design of better inhibitors. Further, several green-house gas mitigation strategies involve CO_2 hydrate formation and thus require an adequate understanding of how CO_2 hydrate nucleates and grows in different environments.

Various mechanisms have been proposed for hydrate nucleation. The most popular, the labile cluster mechanism, postulates that guest molecules spontaneously induce a clathrate-cage-like structure in their solvation shell, and stochastic aggregation of these cages ultimately generates a critical nucleus for sustained growth.[2] An alternative postulate focuses on the development of order in the arrangement of guest molecules;[3] similar ideas were embodied in an earlier surface-driven model.[4] Unfortunately, the available experimental evidence does not differentiate between the different models.

Molecular dynamics (MD) simulations have had recent success in studying nucleation,[5] even in aqueous systems,[6] and thus provide a timely complement to experiments for elucidating the structural changes associated with clathrate hydrate nucleation. We present here multinanosecond MD simulations of a methane/water mixture under hydrate-forming conditions. Previous attempts to simulate hydrate nucleation have studied the bulk melt,[7] which uses unreasonably high methane concentrations and neglects the mass transport limitations that control hydrate formation with hydrophobic guests. In this work, we have simulated a methane/water interface to avoid these problems. The results show that moderate subcooling (ca. 20 K below freezing[8]) generates a rapid increase in hydrate-like order with clathrate clusters of 280 water molecules forming within 10 ns. Although full crystallization is not seen on this time scale, the clusters are comparable with the predicted size of the critical nucleus.[9]

Molecular dynamics simulations of the nucleation and growth of a type I methane hydrate were performed using DL_POLY.[10] Periodic boundary conditions were applied, and a time step of 1 fs used. Potentials were the same as those used in previous studies.[9] The smooth particle mesh Ewald (SPME) method was used for long-range electrostatics, and other forces truncated at 12 Å. Bond length and angle constraints for water were implemented with SHAKE.

The water/methane interface was constructed by embedding a melted film of methane hydrate in a methane atmosphere. A $3 \times 3 \times 4$ ($x \times y \times z$) array of type I methane hydrate crystal unit cells (1656 water and 288 methane molecules; $36 \times 36 \times 48$ Å) was simulated with *NPT* MD at 300 K, 0.03 kbar for 0.87 ns during which time it separated into two distinct regions: liquid water and
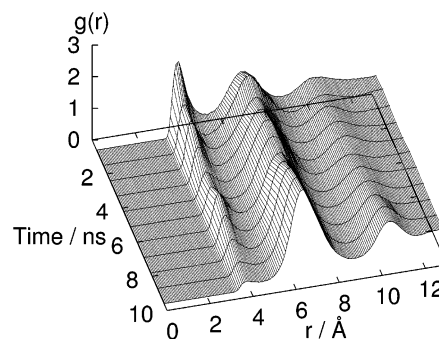

Figure 1. Methane−methane radial distribution functions, calculated from successive 0.9 ns portions of the simulation.

methane gas. By 0.87 ns, no evidence of clathrate structure was apparent from either radial distribution functions or an order parameter analysis (see below). The final configuration was then embedded in a methane gas configuration (801 methane molecules, $T = 300$ K, $P = 0.03$ kbar), and the merged system was simulated with *NPT* MD for 25 ps at 300 K, 0.03 kbar. This gave a planar water film across the *xy* plane. The methane shows a concentration gradient across the film with $[CH_4]$ in the central 40 Å being ca. 50% of that for methane hydrate. While this does not represent equilibrium at 300 K, subsequent simulations at 250 K, 0.3 kbar gave a net dissolution of methane and thus indicated that the water film was undersaturated in methane at the target conditions. We note that methane hydrate forms preferentially near the water/methane interface where there will be a concentration gradient.

The system was crash-cooled to 250 K and simulated for 5 ps at 0.3 kbar (a subcooling of about 20 K). We report here an analysis of the subsequent 9.6 ns of trajectory, calculated using *NPT* MD at 250 K and 0.3 kbar. To analyze for hydrate nucleation, we have used the local phase assignment method.[11] The method is based on a set of three local order parameters, that are designed to differentiate between ice, hydrate, and liquid water structures, and can identify individual water molecules as having a local environment that matches one of these phases (the "local phase").

The simulations show a steady growth of clathrate clusters right from the start of the long trajectory. This is seen clearly in the radial distribution functions (RDFs) calculated for methane located within the water film (Figure 1). Initially there is a strong peak at about 4 Å due to methane−methane close contacts within the water. As time progresses, this peak disappears, while a strong symmetric peak appears at 6.5 Å: this is precisely the nearest intermethane distance in methane hydrate and corresponds to two methane molecules separated by a planar water ring. A third peak at 10.5 Å also grows throughout the simulation. Increases in structure are also seen in water RDFs, with five peaks evident by the end of the simulation in the RDF for hydrate-like waters (Supporting Information). This is strong evidence for the onset of long-range order in the arrangement of these solvent-separated methane molecules.
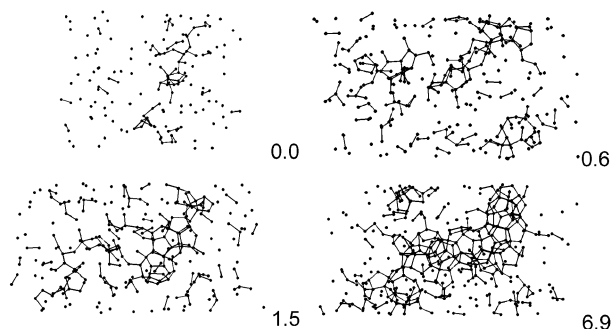
Figure 2. Snapshots of clathrate clusters at given times (ns). Only hydrate-like waters are shown; lines indicate the hydrogen bond network.

Figure 3. A stable face-sharing dimer of 5^{12} cages, formed by 6 ns.

Corresponding changes were observed in other structural descriptors. The configurational energy of the system decreased steadily throughout the simulation − by about 1 kJ mol^{-1} water over 10 ns − consistent with a crystallization process. There was also a net absorption of methane into the water film, amounting to about a 6% increase in the number of dissolved methane molecules over the duration of the simulation; experimentally, the onset of hydrate formation is often identified from such uptake of gaseous methane into the water (clathrate) phase.

The local phase assignment also showed a substantial increase in hydrate-like order during the simulation. Initially 14% of the water molecules were classified with hydrate local phase (as compared with 6% for pure SPC water at 270 K, 1 atm), increasing to 24% by 10 ns. These hydrate-water molecules were found to aggregate into clusters with clathrate-like features. Snapshots of specific configurations are given in Figure 2. Initially there is no evidence of clustering. As early as 0.6 ns, there has been some aggregation to form a two-dimensional sheetlike structure. By 7 ns, this has progressed to form a structured chain of clathrate-like cages that spans the width of the simulation box.

The trajectory was further analyzed for clathrate-cage formation. Cages were defined by locating the set of hydrate-water molecules solvating a given methane molecule and then checking whether the hydrogen-bonding network within this set conformed to one of the known clathrate cages; no attempt has been made to analyze for unoccupied cages at this stage. The first complete clathrate cage (a pentagonal dodecahedron, or 5^{12}) formed by 0.8 ns, with numerous incomplete cages evident even earlier. By the end of the simulation, there were at least six stable complete cages − all 5^{12} − and another 20 incomplete or fluxional cages. These occurred in a single cluster of more than 30 methane and 280 hydrate-like water molecules; the critical nucleus is estimated to involve 600 water molecules at a lesser degree of subcooling.[9]

The packing of these 5^{12} cages differentiates between the type I and type II clathrate hydrate crystal structures. 5^{12} cages are face-sharing in type II hydrates, but they are bridged by additional water molecules in the type I hydrate; methane forms the type I hydrate. The cage analysis shows the existence of a face-sharing doublet of 5^{12} cages (see Figure 3), which formed around 6 ns and remained stable for the remainder of the simulation. No evidence of bridged 5^{12} cages was found. This is in pleasing agreement with diffraction and NMR studies of other type I hydrate-forming guests, which showed initial formation of the type II structure prior to the more stable type I structure forming.[12]
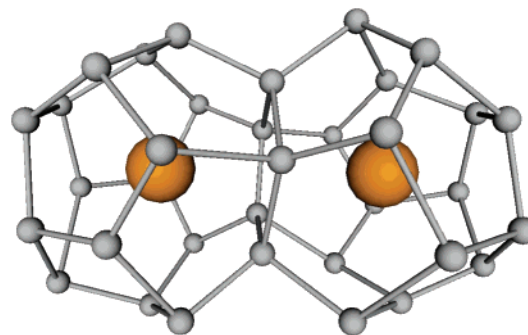
The simulations show an immediate and steady growth of clathrate order within a water film under a methane atmosphere, and this occurs at a moderate subcooling (ca. 20 K). While the simulations are not sufficiently long to observe complete crystallization, the formation of substantive methane hydrate clusters with a size comparable to the predicted critical cluster size is clearly demonstrated. Longer simulations are now in progress, but the present 10 ns simulations contain important information about the nucleation mechanism. In particular, there is no evidence that the solvation shell around the dissolved methane molecules resembles a clathrate cage. Indeed the initial stages of aggregation lead to a convoluted two-dimensional hydrogen bonded surface and thus cannot result from an aggregation of cagelike water structures. Long-range structure is seen in the arrangement of methane molecules within the cluster, with up to five peaks but no close-contact peak apparent in the RDFs for methane in the water. We conclude that our simulations are consistent with the local order model of nucleation, but they do not support the labile cluster model.

Supporting Information Available: Concentration profile for methane and water; radial distribution functions for hydrate-water (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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