Molecular Dynamics Simulations of the Formation of Ethane Clathrate Hydrates

Daniel T. Wilson,^a Brian C. Barnes,^{a,b} David T. Wu,^{c*} and Amadeu K. Sum^{a*}

^a Chemical & Biological Engineering Department, Colorado School of Mines, 1500 Illinois St.,
Golden, CO 80401, USA

^b Energetic Materials Science Branch, RDRL-WML-B, US Army Research Laboratory,
Aberdeen Proving Ground, MD 21005, USA

^c Chemistry Department, Colorado School of Mines, 1500 Illinois St., Golden, CO 80401, USA

* Corresponding authors: asum@mines.edu, dwu@mines.edu

Abstract

This study details molecular dynamics simulations for the formation of ethane clathrate hydrates. Ethane hydrate nucleation shares with methane hydrate nucleation the formation of coordinated guest clusters in water, resulting in structures such as guest-saturated pentagonal and hexagonal faces. Ethane hydrate also forms structure I, which consists of two 5^{12} and six $5^{12}6^2$ cages in its unit cell. Observations from the simulations reveal differences between methane and ethane in the nucleation process, including the types and occupancies of cages. While the formation of occupied 5^{12} cages dominates methane hydrate nucleation, nucleation of ethane hydrates predominately exhibits the $4^15^{10}6^2$ cage as both the first and most common early cage type. These $4^15^{10}6^2$ cages do not occur in the crystal structure, and due to their oblong shape, restrict the ori-

entation of the coordinated guest ethane molecule. The initial kinetically favored $4^{12}5^{10}6^2$ cages are observed to undergo transformation into different cage types, such as, the thermodynamically favored $5^{12}6^2$ cage.

Keywords: molecular simulation, hydrates, ethane, nucleation, formation

Introduction

Gas hydrates are crystalline, inclusion compound formed by the coordination of hydrogen bonded water molecules (host) around a gas molecule (guest), such as, methane, ethane, propane, carbon dioxide [1]. The two most common hydrate structures are denoted as sI (structure I) and sII (structure II). These are cubic structures that form from the combination of polyhedral cages hosting the guest molecules. The sI unit cell is composed of two 5^{12} cages (water polyhedron with 12 pentagonal faces) and six $5^{12}6^2$ cages (polyhedron with 12 pentagonal and 2 hexagonal faces), while sII has sixteen 5^{12} cages and eight $5^{12}6^4$ cages (polyhedron with 12 pentagonal and 4 hexagonal faces). The stable hydrate structure formed depends on the temperature, pressure, and largely on the guest molecules present [2].

One of the major applications for gas hydrates is their occurrence as a flow assurance issue in the production and transportation of oil and gas, causing severe operational issues, production inefficiencies, and safety concerns [3]. The conditions in oil and gas pipelines are typically conducive to the formation of gas hydrates, and their accumulation in pipelines can lead to eventual blockages, jeopardizing production and equipment. Typical methods to prevent hydrate formation in pipelines include injection of so-called thermodynamic hydrate inhibitors (e.g., alcohols, glycols). Due to the large volumes of thermodynamic hydrate inhibitors usually required, their con-

tinued usage has significant challenges and concerns. Alternatively, low dosage hydrate inhibitors, such as the kinetic inhibitors, act by delaying the hydrate formation. Fundamentally, the ideal hydrate inhibitor would target the nucleation of hydrate, that is, keep the system in a metastable state by significantly increasing the activation energy to overcome the free energy barrier for nucleation. To understand the process of hydrate nucleation, it is imperative to have access to phenomena occurring at the nanometer and nanosecond scales, which remains a challenge with current experimental approaches. On the other hand, molecular simulations conveniently probe molecular processes in the length (nanometer) and time (nanosecond) scales of interest for hydrate nucleation.

In the past several years, there have been a significant number of studies probing the nucleation and growth of hydrates by means of molecular simulations. Most of these simulation studies on hydrate nucleation have primarily focused on systems containing methane as the guest molecule. As such, significant advances have broadened our understanding of how methane hydrate nucleation occurs. Walsh et al. [4] were able to provide a first look into the process of methane hydrate nucleation through molecular dynamics (MD) simulations by performing simulations into the microsecond time scale. Their studies revealed the initial cage preferences exhibited by methane, and how many different water cages were also formed in the incipient hydrate nucleation [5]. Other MD studies have provided data to demonstrate the impacts of methane concentration, interfacial curvature, and system size on the rate of methane hydrate nucleation [6-7]. These results showed that guest concentration plays a critical role in the driving force for nucleation.

A recent study by Barnes et al. has established a validated nucleation mechanism for methane hydrate, by using the mutually coordinated guest (MCG) order parameter [8] as a reaction coordinate for the nucleation process. This study identified the critical nucleus size for nucleation as well as the free energy curve. However, the pathway for methane nucleation may not be universal to all hydrate-forming guest molecules. Ethane, for example, like methane also forms sI hydrates as the thermodynamically stable structure; however, ethane can only fit in the $5^{12}6^2$ cages of sI, leaving all the 5^{12} cages empty. As such, it is likely that the nucleation mechanism for ethane hydrates differs from that for methane hydrates while still retaining some similarities. This study is an initial effort to investigate the process for ethane hydrate nucleation, so that we can develop a greater understanding of the underlying nucleation mechanisms for hydrates in general. Our approach for this study is similar to what has been done for methane hydrate nucleation, focusing initially on the description of the molecular processes observed from MD simulations. This paper reports the findings of the simulations for ethane hydrate nucleation, with emphasis on the initial cages and structures formed leading to growth of the hydrate phase.

Simulation Methodology

All MD simulations were performed using GROMACS 4.5 [9]. The systems consisted of 2,944 TIP4P/Ice water molecules [10] and 384 OPLS-UA ethane molecules [11]. Each simulation was run for 2 μ s using the leap-frog integration algorithm employing 2-fs time steps. The initial configurations were phase-separated fluids consisting of ethane and water in a spherical interfacial geometry (ethane phase as a gas bubble). These configurations were obtained by melting a sI crystal in two stages: a short (1-ns) NVT simulation at 400 K followed by an 8-ns NVT simula-

tion at 300 K. The smooth particle mesh Ewald (PME) summation algorithm was used to compute long-range electrostatics (0.12 as the Fourier spacing value) for the NPT ensemble [12].

The production simulations were performed in the NPT ensemble with the Nosé-Hoover thermostat (time constant of 2 ps) set at a temperature of 260 K [13], and the isotropic Parrinello-Rahman barostat (time constant of 4 ps) set at a pressure of 1,300 bar [14]. These values for temperature and pressure used in the simulations were established through successive trials to observe nucleation. By fixing the temperature (between 250 and 260 K), a number of different pressures were tested, ranging from 100 to 1,500 bar. The appropriate pressure was selected such that the observed system displayed metastability before nucleation and growth occurred. The presence of a metastable period and consequently nucleation and growth was determined by the potential energy of the system. If hydrates did not nucleate at given temperature and pressure values, then these parameters were adjusted in successive simulations. Appropriate hydrate formation temperatures and pressures generally ranged from 250-260 K and 500-1500 bar, respectively. A total of 10 simulations were performed under the selected conditions of 260 K and 1,300 bar (each with different initial velocities). Hydrate nucleation was observed in 8 out of the 10 simulations with times to nucleation ranging from 400-800 ns.

Visual analyses of the simulation trajectories were completed with VMD (version 1.9.1) [15]. Observations indicated that the initial structuring leading to the nucleation of ethane hydrates, i.e., the duration of the initial structuring during nucleation leading up to the growth phase occurred over about a 100 ns time period. The analysis of hydrate nucleation over this period was performed at a frame resolution of 100 ps. Trajectory smoothing by averaging over a running

window of 30 frames (3 ns), a timescale that has been found appropriate to suppress noise generated by the thermal motion of molecules not participating in stable cage formation [5]. Note that we thus define a hydrate cage by the instance of its formation using this trajectory smoothing, which is different from when the cage might form without smoothing. A cage is then considered persistent should it last for longer than a few tens of nanoseconds, though such cages often last until the end of the simulation. Figure 1 shows the beginning, middle, and end of a typical ethane hydrate simulation as well as the representations used for analyzing the hydrate structure. An animation depicting the hydrate formation and growth events in detail is presented as Supplementary information.

Figure 1: Images from ethane/water simulation. The initial configuration of the system has the ethane bulk phase as a bubble surrounded by water (left image). Over the course of the simulation, ethane hydrate nucleation occurs (middle image). As the simulation progresses into the growth of the hydrate, nearly all the simulation box is filled with hydrate (right image).

Results and Discussion

Figure 2 presents the potential energy curve for each of the eight simulation runs analyzed in this study. The time at which nucleation occurs, approximately indicated by the start of the descending section in each curve, is stochastic and can be observed to vary considerably between simulations. Before nucleation, the potential energy fluctuates about a plateau, consistent with nucleation occurring from a metastable state. The potential energy continues to fall as the nucleus grows until the solid nearly fills the cell, at which point the potential energy is seen to level off.

Figure 2: Potential energy plot of the eight simulation runs used in this study. The plateau in the energy prior to the drop at nucleation is indicative of a metastable system.

First Cage Types Formed

Since the specific sequence of events during nucleation varied between trajectories, each trajectory was analyzed to identify and characterize the first five cages formed. Figure 3 gives an example of the first fully formed cage in a trajectory. The first five cages recorded were those per-

sistent over time in accordance with our definition above of a stable cage. We collected statistics on both the initial cage types that formed as well as any that underwent subsequent cage type transformation. Figure 4 catalogues the first five cages formed, in order that they are formed, during the simulations among the eight simulation trajectories analyzed. Table 1 summarizes the numbers of each cage type formed for each trajectory, both initially and after any transformations. Figure 4 shows that the first cage to form is predominantly the $4^15^{10}6^2$ cage type, and it remains prevalent in subsequent cage formation. Another significant observation is the tendency for $4^15^{10}6^2$ cages to transform into $5^{12}6^2$ cages, as reflected in the changing frequencies of these cage types in Table 1 and Figure 4. Initial formation among the first five cages favors $4^15^{10}6^2$ cages over $5^{12}6^2$ cages by a factor of three, but after transformations, their numbers are roughly equal (aside from the first cage formed).

Figure 3: Example of the first complete cage (the $4^15^{10}6^2$ cage highlighted in blue) formed in a simulation. The square face of this cage type can be better seen in the rotated image of this same cage (right).

Figure 4: Frequency histogram of cage types, for each of the first five cages formed. Top panel shows cage types as initially formed, and bottom panel shows types after any cage transformations. The y-axis has been normalized by dividing the count by 8, the total number of trajectories.

The average time to form the first cage, counting from the formation of the first MCG cluster of coordinated ethane and water molecules, was 29 ± 10 ns. In comparison, the average time between the formation of the first and second cages was 11 ± 9 ns. The large error bars (standard deviations) reflect the wide range in time intervals over the trajectories. The time to form the first cage is 2 to 3 times longer than the time interval to form the second cage. This might be due to the relative difficulty in forming the first cage, particularly a $4^15^{10}6^2$ cage, or to the relative speed in forming an additional cage, once the scaffold of the first (or partial) cage is already in place--indeed both cages may be forming at the same time. While the statistics are noisy, there

is a slight anticorrelation between the first and second time intervals, consistent with simultaneous cage formation; the anticorrelation is only partial, consistent with some dependence on the first cage to form for the second cage to form. We should note that the second cage always form adjacent to the first one with sharing of one face.

Table 1: Numbers of each cage type among the first five cages formed (after transformation) for each trajectory. The numbers for each cage type correspond to initial formation and after any transformation.

Trajectory	5^{12}	$4^1 5^{10} 6^2$	$5^{12} 6^2$	$4^1 5^{10} 6^3$	$5^{12} 6^3$
1	0/0	4/4	1/1	0/0	0/0
2	0/0	3/3	2/2	0/0	0/0
3	0/0	3/3	1/1	0/0	1/1
4	0/0	2/2	2/1	0/0	0/0
5	1/1	1/1	2/2	0/0	1/1
6	1/1	2/1	0/2	1/1	0/0
7	2/2	2/1	0/0	0/0	1/2
8	2/2	0/1	0/0	1/1	1/1

Cage Preference and Occupancy

A structural motif common to both methane and ethane nucleation is the MCG structure [16], formed by coordination of two guest molecules on either side of hydrogen-bonded water clusters. These clusters, illustrated for both methane and ethane in Figure 5, each represent the first struc-

ture identified preceding the nucleation process. After the first MCG cluster is formed, however, methane and ethane nucleation then begin to show differences due to the different sizes and shapes of the guest molecules. These differences are evident in the subsequent prevalence and occupancy of cage types formed. Methane is known to preferentially form the 5^{12} cage (containing 20 water molecules) as both the first and most prevalent full hydrate cage in the initial stages of nucleation, demonstrating almost total occupancy of such cages. Ethane forms the larger $4^15^{10}6^2$ cage (containing 22 water molecules) first and most frequently, for the same initial period of cage formation in nucleation. As the $4^15^{10}6^2$ cage is not part of the stable hydrate crystal structure, this cage does not represent a thermodynamically stable configuration for ethane hydrate nucleation. Methane and ethane differ strongly also in the observed frequency and occupancy of 5^{12} cages. In comparison to other cages formed by ethane molecules, Table 2 shows that the 5^{12} cage is a minority compared to the prevalence of larger water cages, particularly the $4^15^{10}6^2$ and $5^{12}6^2$ cages. The $5^{12}6^3$ cage is also present, but as is the case of both 5^{12} and $4^15^{10}6^3$ cages, their number is relatively low compared to the $4^15^{10}6^2$ cage.

Figure 5: Mutually coordinated guest clusters for methane and ethane. Green/blue spheres represent (united) methane/ethane carbon atoms, red spheres represent oxygen atoms, white spheres are hydrogen atoms, and dashed red lines are hydrogen bonds. Left: methane pentagonal water cluster. Right: ethane pentagonal water cluster.

Table 2: Number of cages of various cages types formed. "Total Formed" is defined as the total number of cages formed, regardless of cage lifespan. "Total Remaining" counts only those cages that exist at the end of the simulation, and did not dissociate or transform.

Water molecules	Cage	Total Formed	Total Remaining
20	5^{12}	5	4
22	$4^15^{10}6^2$	22	16
24	$5^{12}6^2$	11	11
24	$4^15^{10}6^3$	3	3
26	$5^{12}6^3$	5	4

The 5^{12} cages formed in the ethane simulations were occupied infrequently, as shown in Figure 6. In the simulations for methane nucleation, the 5^{12} cages were rarely found empty. Table 3 shows the geometrical differences between empty and occupied 5^{12} cages with ethane. The volume and surface area for the 5^{12} cages were calculated based on the geometry of a dodecahedron with vertices at the oxygen atoms averaged over 1 ns. (This averaging is different from the standardized averaging we have defined previously for smoothing in that it is an average over 10 smoothed frames.) Occupied 5^{12} cages, on average, are clearly larger by size, surface area, and volume than their empty counterparts. Although the 5^{12} cages form with coordinated guest ethane molecules, these cages are likely too small to comfortably enclose ethane molecules. As such, the larger $4^15^{10}6^2$ cage, being the next largest common cage [5], might represent the most feasible cage for ethane molecules to form during nucleation, as consistent with their observed prevalence. These findings underline the influence of molecular size on hydrate cage preference and

occupancy during nucleation. We should add that these observations in the prevalence of empty 5^{12} cages is consistent with experimental observations, where only a small fraction of the 5^{12} cages in sI are occupied by ethane.

Figure 6: An empty 5^{12} cage (highlighted blue cage), frequently seen in ethane nucleation. Cyan spheres represent ethane carbon atoms and red lines represent hydrogen bonds.

Table 3: Average size metrics of occupied and empty 5^{12} cages formed.

Cage	Height (Å)	Width (Å)	Depth (Å)	Edge length (Å)	Surface area (Å ²)	Volume (Å ³)
5^{12} (empty)	6.11	7.25	7.51	2.79	160.7	166.4
5^{12} (occupied)	6.39	7.53	7.84	2.84	166.0	174.7

The $4^15^{10}6^2$ cage

Based on the cage count table, the $4^15^{10}6^2$ cage dominates as the most frequently formed cage type, in terms of the initial and total numbers formed and number remaining at the end of the simulation. The preference of an ethane molecule for the $4^15^{10}6^2$ cage type compared to the occupied 5^{12} cage type can be rationalized in terms of the larger size of the former. While the $4^15^{10}6^2$ cage is longer than the 5^{12} cage in two dimensions, one dimension is comparatively shorter. The smaller dimension appears to prevent the ethane molecule from freely rotating in all three dimensions. Within the $4^15^{10}6^2$ cage, the ethane molecule exhibits a preferred orientation with the molecular axis normal to the square face of the $4^15^{10}6^2$ cage (see Figure 3). The motion is that of a hindered rotation, where over time the molecule makes 180-degree flips. This orientational preference for the square face persists even when the location of the square face changes, as shown in Figure 7. The square face of one $4^15^{10}6^2$ cage underwent a relocation to a new side of the cage as a result of water hydrogen bonding reorganization, with the ethane molecular axis following the square face. An animation demonstrating this cage behavior in action is presented as Supplementary information.

Figure 7: The orientation of an ethane molecule prefers to be aligned toward the square face of a $4^15^{10}6^2$ cage, even as the square face moves to a new location. Cyan spheres represent ethane carbon atoms, while red lines are hydrogen bonds.

Cage Transformations

Previous studies performed by Walsh et al. have established the predominant methane clathrate hydrate cages that occur during hydrate formation, as well as the mechanisms for transformation between different cage structures [5]. These transformations occur through either the addition/removal of a pair of water molecules or the rotation of a water molecule pair such that the number of water molecules is conserved. These studies of incipient methane hydrate formation showed four common cage: 5^{12} , $4^15^{10}6^2$, $5^{12}6^2$, and $5^{12}6^3$. These structures all contain an even number of water molecules. We observed a similar set of cage transformations to occur in the ethane hydrate simulations. Most of the transformations observed are the addition of a pair of water molecules to a $4^15^{10}6^2$ cage to form a $5^{12}6^2$ cage, though the $4^15^{10}6^2$ cage has also been found to transform into a 5^{12} cage through the removal of water molecules. This suggests that the $4^15^{10}6^2$ cage is kinetically favored over a $5^{12}6^2$ cage, but it will likely eventually rearrange into the thermodynamically favored $5^{12}6^2$ cage. Figure 8 shows the near simultaneous transformation of two adjacent $4^15^{10}6^2$ cages, which occurred within 7 ns of each other over about 20 ns. Transformation of a $4^15^{10}6^2$ cage into a $5^{12}6^2$ cage, as observed with the left cage in Figure 8, involved the removal of a single bond in the square face of the initial cage. This bond breakage allowed for the addition of a pair of water molecules to form three additional pentagonal faces, consistent with the cage transformation rules established by Walsh [5]. The right cage in Figure 8 does not accept additional water molecules on the square face, and ultimately reforms a $4^15^{10}6^2$ cage. As previously noted by Walsh et al. [5], the rate and possible cage transformations are influenced by the surrounding cage or fluid environment. Transformations that occurred on the outer fringes of the hydrate core occurred faster and with greater success than internal transformations. An animation demonstrating both of these transformation events is presented as Supplementary information.

Figure 8: Simultaneous transformation of adjacent $4^15^{10}6^2$ cages. Order of transformation progresses from left to right.

Conclusions

This study elucidates the molecular process of ethane hydrate nucleation and highlights the similarities and differences with methane hydrate nucleation. Though both molecules can form structure I hydrates and coordinated guest water clusters, there are notable differences in cage preference and occupancy resulting from the differences in guest size and shape. From statistical analysis of multiple ethane hydrate nucleation simulations at the same thermodynamic conditions, the full cage most likely to form first is the $4^15^{10}6^2$ cage. The $5^{12}6^2$ cage represents the second-most prevalent cage type, and is observed to result from transformation of $4^15^{10}6^2$ hydrate cages. The $4^15^{10}6^2$ cage can also transform into the smaller 5^{12} cage, although this transformation is less frequent. This supports the concept of ethane hydrates forming kinetically preferred cages before transforming into more thermodynamically stable cages. In addition, the orientation of the guest ethane molecule displays a clear preference for an orientation along the axis of the square face, undergoing hindered rotation with 180-degree flips, and following the square face location

if it relocates due to cage reorganization. We have analyzed, for the first time, ethane hydrate nucleation at the molecular level, observed guest dynamics within hydrate cages, and evaluated both cage type distribution and occupancy along the nucleation process.

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Supporting Information

Video files showing the entire simulation for the ethane hydrate formation, cage transformation, cages face swapping are included as part of the supporting information.

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