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CHEMPHYSCHEM

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Molecular Simulations of Methane Hydrate Nucleation

John A. Ripmeester^{*[a]} and Saman Alavi^[a, b]

Gas hydrates have been known for 200 years or more and the nature of these interesting solids remained hidden until crystallographic studies some 140 years later revealed that they were crystalline guest-host materials classified as clathrates.^[1] The discovery of vast quantities of natural gas hydrate in sediment offshore on the continental margins and under the permafrost has brought these materials into the public eye once again as there are implications concerning the global energy supply and the environment. Although natural gas hydrates come in three distinct structural forms, depending on the guest molecules present, herein we will be concerned with methane hydrate-by far the most extensively occurring of the three. Hydrate formation in nature requires the presence of methane, either of biogenic or thermogenic origin, and it will form hydrate under appropriate thermodynamic conditions (p, T) where there is a trapping mechanism as, for example, in sediment.

So, how do natural gas hydrates form? The thermodynamic conditions under which methane hydrate can form in nature have been discussed and summarized. Under appropriate temperatures and pressures, hydrates can form at gas-liquid interfaces, as well as in methane-saturated bulk aqueous phases of characteristic salinity, perhaps mediated by solid interfaces.^[2] Because of the low mutual solubility of small hydrophobic guests such as methane in water, the concentration of methane must suddenly increase by a factor of \approx 670 upon solid hydrate formation from a saturated solution. Due to the small size of the hydrate nuclei formed upon nucleation, gaining direct experimental information about the mechanism of hydrate formation is difficult, although some progress in this area has been made.^[3] A major effort has been put into molecular dynamics simulations of hydrate formation from aqueous solutions to elucidate the mechanism and the recent work of Sum, Wu and co-workers in this area,^[4] is the subject of this Highlight.

From laboratory studies it is known that the initial formation of solid hydrate is delayed from the time when the thermodynamic conditions for hydrate formation are met initially. The delay period, known as the induction time, may range from seconds to days or longer. Therefore, simulations of hydrate

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[b] Dr. S. Alavi Department of Chemistry, University of Ottawa Ottawa, Ontario K1N 6N5 (Canada) formation tend to introduce a number of factors to shorten the induction time so that nucleation can be seen on accessible simulation time scales (usually tens of ns to a few μ s). These include using higher thermodynamic driving forces for nucleation (for example, higher pressure at constant temperature), the presence of a methane gas phase adjacent to the solution, supersaturation of the water solution by methane, or the presence of curved interfaces such as at gas bubblesolution interfaces.

Rodger and co-workers^[5] have performed a series of molecular dynamics simulations and have recently published a comprehensive study and review of hydrate nucleation mechanisms for the methane/water system. They describe mechanisms for hydrate nucleation as being driven by either 1) water ordering around individual methane guests to form hydrate cages which then agglomerate into other cages to form the bulk hydrate phase (the 'labile cluster hypothesis'), or 2) random collective guest ordering in the water phase which induces the water molecules in their vicinity to rearrange to form hydrate-like networks of water molecules around and between the guests (the "local-structuring hypothesis"). This network then expands to form the bulk hydrate phase.

Rodger and co-workers started their simulation from the methane hydrate structure I (sl) phase and decomposed it for 45 ns at 250 K (or 25 ns at 300 K in a different simulation). After hydrate decomposition and partial separation of the methane gas and solution phases, they added more methane molecules to the gas phase to give a simulation with a total of 1089 methane molecules and 1656 water molecules. The initial setup of the simulation is a flat slab of aqueous methane solution bounded on the top and bottom by methane gas. The resulting aqueous solutions in the simulations were supersaturated with a methane content between 0.32–0.47 of the hydrate phase (which has a methane mole fraction of 0.143).

In these simulations, after induction times of up to 15 ns, hydrate cage formation events were observed. In all cases of cage formation, collective gathering of a number of methane molecules and the subsequent formation of dodecahedral (5^{12}) water cages in between the methane guests was observed, that is, the dodecahedral water cages did not form in isolation around individually solvated methane molecules. Indeed, in two cases in the simulations, every one of the 12 faces of the hydrate cage had an adjacent methane molecule. Thus, a high degree of methane coordination appears to be necessary for cage formation, which favours the local-structuring hypothesis. The cages and their adjacent methane molecules then agglomerate by face sharing and after a further induction period of 5 to 10 ns after initial hydrate cage formation, 14-sided $5^{12}6^4$ cages required for the formation of complete sl

and structure II (sII) hydrate phases, respectively, were seen to form.

Sum, Wu and co-workers used a methane clathrate with 512 methane and 2944 water molecules as the starting point of their simulation. Their total simulation times were as long as 5 µs. They decompose this phase by a 3.5 ns simulation at high temperature 425 K and 10 MPa until a two-phase gasliquid system is formed. The two-phase system is next quenchequilibrated at 250 K and 50 MPa (conditions of hydrate formation). The quenching of the two-phase system increases the methane mole fraction in the water phase to between 0.016 and 0.039, so the degree of methane supersaturation under hydrate formation conditions is less than that of the simulations of Rodger and co-workers. The smaller supersaturation in the simulations of Walsh et al. leads to longer induction times $(\approx 1 \,\mu s)$ before the hydrate formation stage. A complication of these simulations, however, is the relative excess of water in the two-phase system, which allows the water to minimize its exposed liquid-gas surface by enclosing the existing methane gas as a bubble. The curved surface at the methane-water interface increases the effective pressure on the methane gas phase above that of the nominal value of the NpT simulation. The presence of the methane bubble in the water phase in the simulation will also make it more difficult to discern methane diffusion into the liquid phase and its effect on the nucleation and hydrate formation process and rate.

The strength of the work of Sum, Wu, and co-workers lies in the long simulation times employed, which allows a more detailed study of the process of bulk hydrate phase formation from the individual hydrate cages. Within \approx 1.1 µs they observe the collective arrangement of methane molecules (similar to Rodger and co-workers) which induce ordering of water molecules to form pentagonal hydrate faces and 5¹² cages. Within 100 ns of the formation of the minimal nucleus of methane molecules, water molecules rearrange into pentagonal faces, additional methane molecules are trapped in the hydrogen bonding network of the hydrate nucleus (preferentially ordered across the faces of the cages) and further cage formation occurs. The cages then agglomerate by sharing pentagonal faces. Since three-dimensional space is incommensurate with tessellation by 5¹² cages, the cages (including the initial nucleus) can decompose and reform again elsewhere.

Rodger and co-workers observed the independent formation of $5^{12}6^2$ cages at the sites of agglomeration of the 5^{12} rings. However, Sum, Wu, and co-workers make the interesting observation that new water molecules may be inserted into the faces of the central cages in an agglomeration that have no adsorbed methane molecule. The resulting new hexagonal faces on the cage facilitate the space filling of the hydrate cages and this has an autocatalytic effect on the subsequent hydrate growth which occurs relatively quickly within a timescale of about 400 ns. The same process of water insertion into pentagonal faces leads to the formation of 15-sided $5^{12}6^3$ cages which were previously shown to allow for the transition between sl and sll methane hydrate phases.^[6] Single large $5^{12}6^4$ cages with a trapped methane molecule are known to be unstable, but are seen to form at even later times in the simulation. They enhance space-filling by the hydrate cages and relieve some of the strain in the dodecahedral cage agglomerates. The end result of the simulations after 2 μ s is an aperiodic solid hydrate phase which accommodates 5^{12} , $5^{12}6^2$, $5^{12}6^3$, and $5^{12}6^4$ cages encapsulating methane molecules. Presumably, given more time, the phase would relax to the thermodynamically stable sl clathrate hydrate phase, although both sl and sll methane hydrate have been observed experimentally during methane hydrate synthesis under moderate methane pressure conditions.^[7]

The simulations of Sum, Wu, and co-workers illustrate the need for long-time simulations to observe some of the phenomena and processes that lead to hydrate nucleation with hydrophobic gas-phase guests and bulk hydrate phase formation. In previous simulations, the use of higher methane superstaturation in the aqueous phase has led to a decrease in the induction time needed to observe hydrate nucleus formation. The simulations by Sum, Wu and co-workers have smaller methane content in the aqueous phase and should give a more realistic estimate of the time scale of the processes leading to bulk hydrate formation.

Perhaps the most important conclusion of this work, which verifies the results of Rodgers and co-workers, is that the methane hydrate formation predominantly occurs through a "local-structuring" mechanism. Water cage formation around isolated methane molecules in the liquid phase has not been observed during the us duration of the simulations. This was also verified by the simulations of Guo et al.^[8] Experiments also seem to show the absence of ordering in the liquid phases prior to hydrate formation.^[9] Therefore, perhaps somewhat counter intuitively, we can conclude that despite the similarities of the hydrate structure with ice, hydrate formation is primarily induced by the guest molecules forcing the water molecules to rearrange into cage structures. The hydrophobic islands formed by the clustering of the methane molecules forces the water molecules to rearrange into cage structures to avoid interacting with these hydrophobic molecules.

As is the case for any good study, this one raises many further questions for future work, some related to the mechanism of hydrate formation and others related to technical aspects of simulations of the hydrate formation process.

So far, despite the presence of the gas phase, hydrate formation in simulations proceeds by a homogenous nucleation mechanism. The hydrate formation in these simulations does not seem to be favoured at the gas-liquid interface. Experimentally, there is little information on homogeneous nucleation of methane hydrate as all experimental work has been done under conditions where heterogeneous nucleation will prevail and the mechanism for natural hydrate formation (which occurs in the absence of a methane gas reservoir), more than likely, is heterogeneous as well. It is not clear whether mechanistic details of hydrate formation under homogenous nucleation conditions of the simulations would transfer to the hydrate formation under conditions of near-saturation of methane in the presence of sand or other surfaces.

Secondly, the hydrate formation mechanisms presented are very specific to methane hydrate. Larger hydrophobic sI form-

ing guests such as ethane occupy the 5¹² cages only sparingly in the sl hydrate.^[10] So do large 5¹²6² cages form preferentially in the aqueous phase saturated with ethane? Furthermore, it is not clear how this mechanism will be extended to still larger hydrophobic guest molecules which form sll or sH hydrates, either alone or in binary hydrates with methane gas (necessary for sH hydrate formation). In binary hydrates such as the CH₄+ CO₂ sl hydrate, the smaller methane guests are found to fill the small cages preferentially when a hydrate is formed from a mixture of these gases.^[11] Can the present mechanism account for this?

Does the mechanism of hydrophobic hydrate formation depend on whether the guest is in the liquid or gas phase? The mechanism of formation of clathrate hydrates with guests with partial hydrophilic character such as tetrahydrofuran (THF) will likely be totally different from the one determined here for methane hydrate. There are also cases where the hydrate forms from ice exposed to high pressures of gases; what is the mechanism there?

A number of computational questions are also raised regarding hydrate formation simulations and these can also be addressed in future work. The first is that the equilibrium solubility of methane in aqueous solutions for the various models used in the simulations is unknown. Rodger et al. use the Tse, Klein, and McDonald united atom potential for methane^[12] and the SPC potential^[13] for water while Walsh et al. use the united atom methane potential of Goodbody et al.^[14] and the TIP4P-ICE potential for water.^[15] The degree of solubility of methane in these water phases will affect the driving force for hydrate formation at a specific value of supersaturation and need to be determined before the results of the simulations can be compared to experiment.

Another issue is the relative stability of the sl and sll methane hydrate phases for the force fields used in the simulation. In simulations performed so far, the 5¹² and 5¹²6² cages form at a faster rate during the simulation. However, notable numbers of $5^{12}6^4$ cages form by the end of the simulation. It is speculated that this is related to kinetic effects of cage formation in the simulations, but it may conceivably be an equilibrium feature of the force fields used that underestimates the stability of the sl phase relative to sll. Determining the relative free energy for the two sI and sII solid hydrate phases, however is not a straightforward calculation. It should also be noted that the force fields used in simulations do not have the same directionality of hydrogen bonding as observed experimentally. Experimentally, the relative stability of pentagonal water rings over hexagonal water rings in the hydrate and water phases are usually conjectured. The pentagonal rings can accommodate the natural hydrogen bonding angle of the water molecules without distortion. However, the relative stability of the pentagonal rings needs a more detailed study for force fields using the Lennard–Jones+electrostatic point charge models to describe the intermolecular interactions of water molecules.

Further questions may be raised about the effect of thermostats and barostats on *NpT* simulations on the hydrate formation mechanism. By thermostating the simulations, heat generated upon face or cage formation can be removed from the vicinity by the operation of the (Nosé-Hoover) thermostat, and not by natural thermal conductivity, and this may affect the rate of hydrate nucleus formation.

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