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# Some current challenges in clathrate hydrate science: Nucleation, decomposition and the memory effect

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#### ABSTRACT

Among outstanding issues still to be understood regarding the clathrate hydrates are the mechanism of the processes involved in the formation and decomposition of clathrates: nucleation, decomposition, and the memory effect during reformation. The latter involves the shorter induction times required for solutions of decomposed hydrate to nucleate as compared to those for freshly prepared solutions. The formation of the clathrate hydrate phases of insoluble gases in water is accompanied by a ~6000 fold concentration of the gas content in the solid phase compared to the aqueous phase from which it forms. The nucleation mechanism for the solid hydrate which allows the delivery of such high concentration of gas and water in one location has been the subject of much experimental and computational study. While these studies have improved our understanding of the nucleation process, many unknown aspects remain. These developments are described in this Opinion.

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#### 1. Introduction

Clathrate hydrates are crystalline solid inclusion compounds where guest molecules are trapped in cages of hydrogen bonded water molecules. Various combinations of cage topology are required to fill three-dimensional space. There are three main families of hydrates with the crystal structure of each determined mainly by the largest guest molecules in the structure. Guest sizes (largest van der Waals diameter) cover a range from  $\sim$ 0.4 to 0.9 nm and include just about all chemical functionalities. When the guests are small gaseous molecules, the corresponding hydrates require application of some pressure for stability at 273 K, although some of the larger, guests only require temperatures near 273 K and ambient pressure. The stability of the clathrates is attributed mainly to short-range attractive interactions between the (paradoxically sufficiently hydrophobic) guest molecules and the hydrate cages. Since lattice stability depends on the collective guest-host interactions, hydrogen bonding and other interactions can also be present, thus modifying structural and dynamic properties.

The science of clathrate hydrates goes back to the time when the very foundations of chemistry were being explored around the year 1800. Among early hydrate researchers, well-known

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http://dx.doi.org/10.1016/j.cossms.2016.03.005 1359-0286/© 2016 Published by Elsevier Ltd. scientists such as Priestley, Davy and Faraday made significant contributions to "gas hydrate" studies. By the end of the 19th century some 40 guest materials had been identified, and hydrate science was seen as an emerging discipline focused especially on thermodynamic studies. Unusual properties led to hydrates being recognized as a distinct class of materials, e.g., with regards to non-stoichiometry and weakness of interactions between water and guest molecules. The structures remained a puzzle until the 1930s when a hydrogen-bonded water lattice with cages for the guests was proposed with van der Waals interactions between guest and host. These ideas were confirmed in 1951-1952 when two hydrate structures, the cubic structure I and structure II clathrate hydrates shown in Fig. 1, were identified by modeling and X-ray crystallography [1–3]. The hydrates were recognized as "clathrates", following Powell's nomenclature for inclusion compounds with guests trapped in cages of a host lattice [4]. With the structural and thermodynamic information at hand, van der Waals and Platteeuw [5] and Barrer and Stuart [6] developed a statistical mechanical model that accounted for the stability of hydrate lattices and a number of the unique hydrate properties such as non-stoichiometry. After 1970, application of physical methods allowed the measurement of a variety of hydrate properties of which the ability to measure guest distribution over the hydrate cages and hydrate compositions were of considerable importance. As well, a third hydrate family with larger guest molecules, known as hexagonal structure H (Fig. 1) was identified [7]. Further details

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**Fig. 1.** The unit cells (boundaries marked by outline) of the structure I, structure II, and structure H clathrate hydrate phase. In the phases, the 5<sup>12</sup> cages are blue, 5<sup>12</sup>6<sup>2</sup> cages are green, 5<sup>12</sup>6<sup>4</sup> cages are magenta, the 4<sup>3</sup>5<sup>6</sup>6<sup>3</sup> cages are red, and the 5<sup>12</sup>6<sup>8</sup> cages are gray. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

on the structures and properties of clathrate hydrates can be found in Refs. [8,9].

In 1934, gas hydrates first attracted interest from the engineering/technical community. Natural gas pipelines were known to form solid plugs during cold weather and this was attributed to ice formation. Hammerschmidt became aware of the existence of solid methane hydrate, discovered some 40 years earlier, and suggested that the solid pipeline plugs were gas hydrates rather than ice [10]. This sparked a line of intense investigation, both experimental and modeling, for predicting when hydrate plugs might form in gas and oil pipelines and how to prevent them [11]. Since all-encompassing solutions to the hydrate plug problem are still not available, activities in this area continue, in many instances as part of the discipline of flow assurance as practiced by the resource industry and service companies, and as investigated by chemical and petroleum engineering laboratories in academia.

Another important area of interest involving clathrate hydrates concerns the natural gas hydrates (NGH), first reported in reservoirs in Siberia in the 1960s by Makogon [12]. The discovery that natural gas hydrates are ubiquitous in offshore marine environments as well led to estimates of a vast natural gas resource potential. Over the last two decades research involving NGH has ramped up tremendously especially to improve resource estimation and to develop methods of natural gas recovery [13]. Other areas of importance include identification of possible geohazards related to NGH [14], as well as the possible impacts of NGH decomposition on global climate change [15]. Thus, gas hydrate research includes the fields of earth and ocean sciences as well as various engineering disciplines and the fundamental sciences. Researchers deal with hydrates on a scale from the molecular (nanometer) to that of gas hydrate reservoirs (meters to kilometers).

Since the outstanding physical property of clathrate hydrates is the efficient storage of gases, interest continues in applications where this property can be of use. Typically, a volume of gas hydrate, in its characteristic pressure–temperature stability region can hold ~160 volumes of gas at STP, thus, gas storage, especially of energy gases such as methane and hydrogen, continues to be actively pursued [16]. Since hydrate cages of each type have a preference for guests based on their dimensions, the separation of gas mixtures according to molecular size is also an active area of research, for instance, for separating  $CO_2$  from nitrogen in flue gas or  $CO_2$  from H<sub>2</sub> in fuel gas [17].

We note that the last three paragraphs deal with physiochemical processes related to hydrate formation – those that occur in pipelines and in nature, or those that are necessary for the application of hydrates as materials for storage and separation. As with almost all cases where there is the need to control physiochemical processes, a knowledge base is required, e.g., of thermodynamic and kinetic information, as well as of the properties of the starting materials and the products. Optimization of parameters for engineering processes often tends to proceed at least in part by trial and error, although complex processes eventually tend to demand an examination of fundamentals that may well reach down to the molecular scale.

Hydrate formation from water and essentially insoluble guest materials such as methane has some unique challenges and several aspects of the modeling of this process have reached the point where fundamentals need to be addressed. Methane hydrate formation, both in nature and in the laboratory, requires an increase of concentration of methane from that in a saturated aqueous solution (2.55  $\times$  10<sup>-5</sup> M) at STP to that of the solid CH<sub>4</sub>·6H<sub>2</sub>O, (0.167 M) thus by a factor of  $\sim$ 6500. Since the formation of the solid hydrate from the gas and liquid is exothermic, there is considerable heat that must be dispersed, in addition to the mass transfer of methane that needs to be optimized. What is more, hydrate nucleation is a stochastic process which, when it occurs in a stirred solution, tends to give a sudden, catastrophic appearance of the hydrate phase, thus making detailed experimental studies and measurements very difficult [18]. One parameter that has been used consistently to study hydrate nucleation is the macroscopic induction time, that is, the time interval between the nucleation event and when the experiment first enters the pressure/temperature region of hydrate stability. Usually induction times are highly scattered, although the mean value will depend on the driving force, which can be either sub-cooling  $(T_{svs} < T_{eq})$  and/or over-pressurizing  $(P_{svs} > P_{eq})$  the system with respect to the equilibrium conditions. It is also observed that the purer the initial aqueous solution, the greater the scatter in induction times, suggesting that nucleation is a heterogeneous process that depends on surfaces, impurities and other external factors such the volume of the aqueous solution.

Another feature of hydrate science with a long history is the observation of a memory effect, that is, when a hydrate is decomposed, the resulting solution forms a hydrate more readily, i.e., with a shorter induction time, that when a fresh solution is used to make hydrate. This observation goes back  $\sim$ 130 years, although acceptance of the phenomenon and its explanation(s) are far from equivocal.

On the flow assurance side, the longstanding solution for pipeline plug control is the addition of thermodynamic antifreezes such as methanol and glycol, often at concentrations of 20–50% of the water present in the produced fluids. For some twenty years there has been an interest in developing low-dosage kinetic inhibitors

and anti-agglomerants to avoid the costly and environmentally risky procedure of using toxic thermodynamic inhibitors. The kinetic inhibitors used tend to be synthetic polymers such as polyvinylpyrrolidone (PVP) and polyvinylcaprolactam (PVCap) in various formulations [19], with much research effort being expended in finding other inhibitors, e.g., biological materials such as anti-freeze proteins. The low dosages of the kinetic inhibitors tend to be concentrations of 0.1–0.5 wt% with respect to the water in the system under consideration. Even though the action of these inhibitors affects the kinetics of hydrate formation, that is, the nucleation and growth of gas hydrates, there are quite pronounced effects that apparently have thermodynamic implications as well, e.g., product distribution and decomposition properties.

In this contribution we examine some of recent scientific research relevant to these difficult and somewhat puzzling hydrate properties that are of importance for unraveling the details of both natural and industrial processes.

#### 2. Hydrate processes

#### 2.1. Nucleation

Because of the difficulties in obtaining direct experimental evidence on this topic, hydrate nucleation has become a favorite topic for study by molecular simulation. In addition to our discussion below, English and MacElroy have recently summarized molecular dynamics simulations of clathrate hydrate nucleation [20]. The direct molecular level simulation of the physical processes involved in methane hydrate formation from a gas–water system, which can take from minutes to hours, would be prohibitively long and additionally the mass transfer of the methane gas into the liquid phase and the dissipation of heat from the hydrate formation process are relatively slow processes.

In order to avoid problems of simulation timescale [21], simulation studies of hydrate nucleation and growth tend to be carried out at an unrealistically high driving force with the aqueous phase (homogeneously) supersaturated with the gas [22–25]. Simulations have also been performed with a flat liquid layer in contact with gaseous methane [26,27], or other gas species [28,29] but more recently, simulations of hydrate formation in the vicinity of curved water-gas surfaces have also been performed [30]. The simulations are carried out under the operation of a molecular dynamics thermostat which dissipates the heat released from the hydrate formation process in a non-directional manner, not necessarily consistent with heat transfer in the physical system (but in a manner which restores proper thermal equilibrium to the system). Under these supersaturated or "overdriven" conditions of the simulations, researchers were able to observe the formation of hydrate cages and the assembly of amorphous hydrate-like clusters which relax over time to more stable uniform (or mixtures of) hydrate phases. The mechanisms of hydrate formation in these simulations involves the juxtaposition of clusters of gas molecules in the aqueous phase and the arrangement of water molecules between and around these gas molecules in ordered cage-like structures. The cage structures coalesce to form the initial amorphous hydratelike structures, which can either decompose or relax to more stable clathrate hydrate structures. The cage formation and growth and been characterized by a variety of order parameters which consider both water structure and water-guest juxtapositions [31-33]. The cages formed first in these simulations were the  $5^{12}$  cages. Upon merging of these cages, waters could be sequentially inserted into the  $5^{12}$  cages to form the larger  $5^{12}6^2$  and  $5^{12}6^4$  cages, among other cage types. The transient coexistence of sI and sII domains of the methane and carbon dioxide clathrate hydrate phases have been observed following nucleation both experimentally and in simulations [34,35]. A sample of a simulation showing the nucleation of and growth of the methane hydrate phase from supersaturate solutions in shown in Fig. 2 [35]. Recent work demonstrated that the stable sI clathrate hydrate structure can be obtained from some trajectories of the homogeneous nucleation simulation [36,37]. Increased curvature of the water–gas interface was shown to increase the rate of clathrate hydrate nucleation [30].

While the details discovered in the simulations of homogeneous nucleation contribute to our understanding of the hydrate nucleation process, Knott et al. [38] demonstrated that under realistic conditions of methane hydrate formation, homogeneous nucleation cannot occur.

Somewhat more recently, a number of simulations of heterogeneous nucleation of hydrate formation in the presence of a solid surface have been performed [39,40] where a hydroxylated silica surface was put in contact with a supersaturated CO<sub>2</sub> aqueous phase. These studies showed that the heterogeneous nucleation of the hydrate phase occurs on a layer of water adjacent to the silica surface. Although the authors concluded that the layer was ice-like, experimental work sees this layer as non-freezable water that turns into a frozen glassy layer upon cooling; hence the dynamic properties are intermediate between those of ice and liquid water. A hydrate phase of "intermediate" structure forms on top of the water layer and this transitions to the sI CO<sub>2</sub> clathrate hydrate structure [39]. A second set of simulations was performed with a hydroxylated silica surface in contract with a water phase and a liquid CO<sub>2</sub> phase. In these simulations, the nucleation of hydrate formation occurs at the three phase silica-water-liquid  $CO_2$  contact lines. The 5<sup>12</sup> cages were found to form earlier in the nucleation stage than the  $5^{12}6^2$  and  $5^{12}6^4$  cages.

Starting from an ice phase, Małolepsza and Keyes [41] show by molecular dynamics simulations using a replica exchange algorithm that the formation of methane hydrate is nucleated by the incorporation of methane molecules into the ice phase which catalyzes the transformation of ice to a metastable  $\beta$ -phase which then transforms to a methane hydrate. This work describes a route to hydrate formation at low temperatures. Experimentally, hydrate formation from ice is a two-stage process with a relatively fast conversion of the ice surface [42–44,34] and a much slower process for bulk ice. Catalysts that interrupt surface hydrogen bonding can speed up this process by orders of magnitude [45].

It is evident that there is a large gap in time and length scales between simulation studies and the usual experimental techniques applied to hydrate problems. Also, there are likely to be sensitivity problems as the early stages of nucleation may well involve very few precursor species, which also are likely to be transient.

However, several observations still may be useful in giving some additional insight/confirmation for comparison with simulation studies. For instance, in simulations it is quite commonly observed that in addition to the thermodynamically stable phase that is observed during synthetic procedures other metastable hydrate phases are formed [46,47,36], in agreement to the appearance of mixed phases in modeling studies. In other experiments where nucleation and growth takes place rather slowly (min/h), cage populations can be measured as a function of time. In the case of the preparation of a sI xenon hydrate as a surface layer on ice with hyperpolarized xenon gas, it is shown that the cage occupancy ratio for large and small cages,  $n_1/n_s$  is much less than 1 before massive growth takes place. When massive growth starts, the ratio reaches a value of  $\sim$ 4, as expected for the hydrate with an equilibrium distribution [42]. Thus, there is a preponderance of small cages before a hydrate with the equilibrium composition appears. Recently a Raman study of the formation of sII hydrogen hydrate also showed evidence of hydrogen-filled small cages before evidence of larger hydrogen-filled cages appeared during early times of hydrate growth [48]. In these studies there appears



**Fig. 2.** Snapshots of a simulation of the nucleation and growth of methane hydrate at 285 K and 50 MPa. The formation of 5<sup>12</sup> and 5<sup>12</sup>6<sup>2</sup> cages are seen in this figure. Reproduced from Ref. [35] with permission from the American Chemical Society.

to be little evidence for the filling of any cages that do not appear in the final products.

#### 2.2. Hydrate decomposition and memory effects

The observation that a solution obtained from decomposed hydrate nucleates hydrate more easily than a freshly made solution goes back to the early history of clathrate hydrate science as such effects were discussed by Bakhuis Roozeboom, Cailletet and Wroblewski in 1884 [49]. The former closes the discussion in his paper by asking "Can one not assume: that a little time after dissociation of the solid hydrate, some aggregates of liquid molecules again present a favorable arrangement for the reformation but which they lose later?" thus postulating a structural memory effect. These early observations appear to have been forgotten, but in more recent times memory effects have been observed quite regularly as discussed by Sloan [50], who also promoted the residual structure hypothesis discussed below. Many other researchers have contributed results and suggestions for mechanisms as recently reported by Sowa and Maeda [51]. We think that one can safely conclude that the memory phenomenon has been well documented and supported by many trained observers over a period of more than 100 years. On the other hand, a number of studies designed specifically to test for memory effects have failed to observe it [52]. We can therefore conclude that memory effects do not occur for all hydrate systems all of the time and that the responsible mechanism(s) are still at large.

#### Table 1

Mean induction time for the methane–ethane–propane gas mixture nucleation from gas uptake experiments from fresh solution ( $t_{\rm fresh}$ ) or from melted hydrate solution ( $t_{\rm repeat}$ ).

| t <sub>repeat</sub> (S) |
|-------------------------|
| 65                      |
| 95                      |
| 100                     |
| 140                     |
|                         |

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Fig. 3. The growth of the hydrate phase at 280 K after 50 ns. On the left side, the hydrate phase is adjacent to methane saturated aqueous solution and a further places methane gas reservoir. On the right hand side, the growing hydrate face is exposed to an aqueous solution and a nanobubble of methane hydrate.

The memory effect can be illustrated by Table 1 where mean induction times for methane–ethane–propane hydrate nucleation are given in gas uptake experiments [53]. Hydrate formation experiments were performed from gas in contact with water and gas in contact with aqueous solutions of hydrate inhibitors. Induction times were measured from "fresh" liquid/solutions and from solutions of melted hydrate. An order of magnitude (or higher) decrease in mean induction time is observed for the hydrate recrystallization from the melt solution compared to the fresh solutions.

In 1996, Bishnoi offered this cautious opinion on his observation of hydrate nucleation and re-nucleation under a variety of conditions, "Such a process (nucleation) would then be accurately defined as a regular stochastic process that is influenced by deterministic variables which are at present ill-defined" [54]. In 2015, Sowa and Maeda offered "Even though the nucleation phenomena were intrinsically stochastic, a clear bias was observed which supported the existence of the memory effect" [51]. This suggests very modest progress in explaining the memory phenomenon, however, they did suggest three leading candidates for explaining the memory effect, and categorized, the by now better defined, deterministic variables suggested by Parent and Bishnoi [54].

#### 2.2.1. Residual structure hypothesis

As pointed out, the oldest and likely still most popular model for the memory effect is the residual structure hypothesis. According to this hypothesis, dissociation of gas hydrates leads to formation of some "hydrate melt"; residual structures that retain structural features of the hydrate phase (e.g., guests molecules with associated pentagonal rings of hydrogen-bonded water molecules). These residual structures would need to persist in the liquid water phase for a long time after dissociation in order provide nucleation sites for gas hydrate formation when cooled again. However, molecular dynamics simulations of methane hydrate decomposition do not show any residual structure in the melt [55], in keeping with the fact that the lifetime of a hydrogen bond in water is of the order of a picoseconds. We can assume then that, similar to the freezing of bulk water [56], the freezing of a bulk hydrate-forming solution occurs upon heterogeneous nucleation and that homogeneous nucleation is rarely if ever observed in bulk solution. This automatically eliminates the "residual structure"

hypothesis, as residual structure in solution is an intrinsic property and hence it should affect homogeneous as well as heterogeneous nucleation. As shown later on, there appears to be no effect of memory on the homogeneous nucleation of THF hydrate.

#### 2.2.2. Guest supersaturation hypothesis

Supersaturation is ubiquitous both during formation and decomposition of hydrate. It is known that gas diffusion in a quiescent decomposing hydrate system is slow and that this can lead to significant concentration gradients. Recent computer simulations of methane hydrate decomposition [23,57,58] show that when methane is injected from the melting solid hydrate into the aqueous phase, the solution does indeed become supersaturated in methane. Does supersaturation imply the presence of only a high concentration of dissolved molecules or is there more to it? If it is the former, then again, if nucleation occurs, it will be a homogeneous process and therefore quite unlikely. However, simulation suggests that supersaturation results in the spontaneous formation of methane nanobubbles, which in the simulation have a finite lifetime [59], see Fig. 3, although in many actual observations of nanobubbles they persist for long periods of time (days). Nanobubbles still provide regions of high concentration of gas (thus solving the mass transfer process during hydrate formation) and, by the formation of gas-solution interfaces they also will have an effect on the thermodynamic state of the solution. Interestingly, nanobubbles have also been observed to act as nucleation centers for crystal formation in various experiments [60,61] and simulations [59] as presumably, the gas-liquid interfaces can act as surfaces for heterogeneous nucleation. This is shown in Fig. 3 where a hydrate growth simulation shows the faster growth of the hydrate side near the nanobubble compared to the side adjacent to aqueous solution of methane in contact with a gas reservoir. If this is so, then the memory effect should be observable until the supersaturated state disappears and the gas-solution interfaces have shrunk significantly.

#### 2.2.3. Impurity imprinting hypothesis

The third hypothesis regarding impurity imprinting was suggested by Zeng et al., who studied the nucleation of THF hydrate [62] and methane hydrate [63]. They measured the homogeneous nucleation temperature of  $\sim 1 \,\mu m$  droplets of THF-water solution

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Fig. 4. Hydrate melting curves formed during ramping runs in (a) pure water, (b) solution of a type III antifreeze protein, (c) solution of polyvinylpyrrolidone (PVP), and (d) solution of a commercial low dosage hydrate inhibitor (H1W85281). Ref. [67].

to be 243 K, a value rather similar to the homogeneous nucleation temperature of water. For the THF-water system, additives such as anti-freeze protein (AFP) inhibitors, proteins, had no effect on the homogeneous temperatures. Just-melted THF hydrate crystals in micron sized droplets affected the homogeneous nucleation temperature by no more than a fraction of a degree, whereas significantly larger effects were noted on nucleation in bulk solutions of melted THF hydrate. This was taken as evidence that both hydrate inhibition by kinetic inhibitors and the memory effect operated strictly by affecting heterogeneous nucleation, thus leading to the imprinted impurity hypothesis. This hypothesis has the benefit of explaining a number of features, including memory effects on surfaces that have been activated by imprinting and the poisoning of such sites by materials that likely are also strong absorbers on hydrates. The latter property has been attributed to a variety of inhibitors. In this case, any soft water-solid interface has the potential for acting like a catalyst for nucleation with oxides (iron, silicon, calcium) with hydroxylated surfaces as good candidates. Formation of a hydrate crystal at the surface then imprints the surface, likely through a soft interface of surface hydroxyl - surface water-hydrate surface, thus making it a stronger nucleator on a cycle of hydrate decomposition – reformation. Strong absorption by hydrate inhibitors on the surface of such solid particles then could eliminate the memory effect ("poison" the nucleation catalyst sites), as well as inhibiting hydrate formation in the initial cycle of the hydrate formation experiment. Once the hydrate crystal decomposes, the imprinted surface can retain some order until the surface hydroxyls – surface water interface is randomized with time, thus giving the memory effect a certain lifetime which depends on temperature. However, it would be difficult to distinguish supersaturation (with nanobubbles) from solid impurities as agents of nucleation without additional research.

We can add to these considerations the observations that the history of the water used to make hydrate also affects induction times [54]. The important agents for heterogeneous hydrate nucleation likely are dissolved gas, gas bubbles, or solid impurities, as discussed above. Such solutions respond to stimuli like freezing or boiling in a characteristic (yet often unknown) way, possibly with a relaxation time during which the solution returns to a steady state (or equilibrium?) depending on conditions (presence of air, impurities, nature of container surface). Clearly, very careful experiments are required to follow some of these different paths.

Other recent observations of hydrate nucleation–decomposition and hydrate re-nucleation after decomposition in the presence of inhibitors offer additional hints of the complexity of these processes and show possible mechanisms by blocking certain routes of nucleation. Whereas hydrates made in a stirred reactor can be expected to be reasonably homogeneous solids, it has become apparent that in the presence of at least some kinetic inhibitors the hydrate products appear to become quite heterogeneous [64,65]. This is quite apparent upon examination of pressure–time plots [66] or gas evolution versus time plots [64] for decomposing hydrates with or without inhibitors present. In the presence of inhibitors, pressure does not return to its former value at the

expected temperature point and the hydrate must be heated to a higher temperature [66]. In some cases, hydrate decomposition for samples made in the presence of an inhibitor appears to be a two-step process with regions of faster and slower decomposition as compared to the sample of hydrate made in the absence of inhibitor [64]. This complexity is even more apparent on experiments carried out on a high pressure calorimeter, where hydrates made in the presence of inhibitor show complex decomposition behavior with multiple melting peaks [64,65]. Fig. 4 shows the hydrate decomposition behavior for a methane/ethane/propane hydrate on successive formation/decomposition cycles with and without a number of low dosage inhibitors. There are significant changes in both product distribution as well as notable differences upon successive cycles indicating an apparent memory effect.

#### 3. Conclusions

A large body of work on the nucleation of clathrate hydrate phases and the memory effects of gas hydrates point to molecule level understanding of these phenomena, however, unequivocal understanding which allows the explanation of these phenomena are still not available. As further computational and experimental studies are being designed, it would be a good chance to look at the fundamental molecular level understanding of these phenomena we have obtained so far. Heterogeneous nucleation with fast mass transfer seem to be involved in the nucleation and growth processes of hydrates and more simulation studies which explicitly consider these factors would be advantageous. The role of nanobubbles in hydrate nucleation and describing memory effects is a further intriguing aspect that merits specific consideration. With new physical factors being proposed to explain these phenomena, the time is ready to explicitly address them.

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