Full Length Article

# Nucleation curves of methane hydrate from constant cooling ramp methods

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## ABSTRACT

A High Pressure Automated Lag Time Apparatus (HP-ALTA) was used to measure the nucleation curves of Structure I (sI) – forming methane hydrate. The instrument applied a large number of constant cooling ramps to a quiescent water sample contained in a glass sample cell under isobaric conditions and recorded maximum achievable subcooling distributions. Survival curves were constructed from the measured data and nucleation curves were derived from the survival curves using the model-independent method we had recently devised. The convergence of nucleation rates with the number of experimental runs was observed after approximately 400 runs which suggests that sampling of 400 nucleation events is sufficient for the unambiguous determination of the nucleation curves. The impact of the experimental cooling rates and the approximations used in the derivation of the nucleation curves was also assessed in details. Importantly, the derived nucleation curves continuously covered over a range of 15 K. The obtained nucleation curves were then compared to the nucleation rates of methane hydrate measured at several subcoolings by Makogon and analyzed by Kashchiev and Firoozabadi. Our nucleation curves yielded nucleation rates that were broadly similar to but somewhat lower than those of Makogon and Kashchiev and Firoozabadi at the relevant subcoolings.

## 1. Introduction

Gas hydrates are ice-like crystalline solids that contain high concentrations of small gas molecules as guests. They can be viewed as solid solutions of gas in water [1]. The much greater gas concentrations in the hydrate form than the solubility of the same gas in liquid water renders the gas hydrate stable at higher temperatures than ice. Gas hydrates have potential applications in gas storage, carbon dioxide sequestration, gas separation and desalination [2]. On the other hand, gas hydrates pose risks of blockage in oil and natural gas pipelines [3].

Nucleation is the first step of gas hydrate formation. Nucleation of gas hydrates is desirable for some applications such as gas storage, carbon dioxide sequestration, gas separation and desalination, but undesirable for the flow assurance of oil and natural gas pipelines. When gas hydrate formation is desirable, there are a few methods that can promote nucleation such as the use of a microbubble generator [4], dry water [5] or ice seeding [6–9]. The heterogeneous nucleation probability of gas hydrates at the relevant interfaces characterize the efficacy of each of these promotion methods. When gas hydrate formation is undesirable, knowledge about the nucleation probability of gas hydrates in subcooled systems is very useful in assessing the associated risks in flow assurance.

The stochastic nature of nucleation events means that each

nucleation event is not repeatable even under the same set of conditions. Since the nucleation probability of a given system depends on the size of the system and the time over which the system is observed, the nucleation probability of a given system needs to be normalized to the unit size and to the unit time for meaningful comparison. Here the relevant system "size" is volume for homogeneous nucleation and interfacial area for heterogeneous nucleation. In either case, this nucleation probability per unit size and per unit time is the definition of the *nucleation rate* and the most important quantity that defines the nucleation characteristics of a given system. Since the nucleation rate is a function of system subcooling, our goal is to find a nucleation curve – a curve that relates the nucleation rate to the system subcooling.

Nucleation rates of methane hydrates have been investigated theoretically and by molecular dynamics simulations [10–16]. However, despite its critical importance, nucleation curves of gas hydrate systems were rarely measured and – for the few systems for which there are reports – their values vary wildly [6,17–26]. The main reason for this lack of data is the time consuming nature of the measurements and lack of reproducibility (repeatability) of such measurements. The conventional method for measurements of nucleation rates of gas hydrates has been to measure the so-called induction time at a given subcooling [6,17–26]. Induction time is the time that a system has spent at a given constant subcooling temperature, and the survival probability is

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expected to have an exponential distribution as a function of induction time [21,27,28]. Once the exponential distribution is known then the nucleation rate can be calculated from the inverse of the most probable induction time. However, the stochastic nature of nucleation requires a large number of repeat measurements at a given subcooling to obtain a reasonable shape of the exponential distribution and its decay constant. Svartaas and co-workers recently improved the analysis method to shorten such data collection procedure at a given subcooling by limiting the number of repeat measurements to about 20 or 25 at each subcooling temperature [21]. Still, each induction time measurement can take a very long time, especially at small subcoolings, and consequently the extent of stochastic behavior ("stochasticity") also worsens at small subcoolings [22].

For gas hydrates, the multi-component nature of the system further complicates the challenging situation by mass-transfer limitations of the guest molecules in the aqueous phase. An additional factor that further complicates the study on nucleation of gas hydrates is that stirring action was often present in the past studies but it was not clear how the stirring action influenced the heterogeneous nucleation probability of gas hydrates. A number of effects that stirring action could potentially cause – accelerated guest gas diffusion, increased heat transfer rate, increased guest–aqueous interfacial area, the presence of the solid walls of a stirrer, etc. – are all expected to increase the nucleation rate but have neither been characterized nor decoupled from the intrinsic heterogeneous nucleation rates in the past studies. We previously discussed the experimental challenges associated with the measurements of nucleation curves of gas hydrate systems [29] which could explain why the relevant experimental data are scarce.

Recent advent of automated instruments such as a High Pressure Automated Lag Time Apparatus (HP-ALTA) [30,31] rendered time-consuming measurements of nucleation curves over a wide range of system subcooling practical. HP-ALTA can apply a large number of linear cooling ramps at a constant cooling rate to a quiescent sample under isobaric conditions and record the temperature at which gas hydrate formation takes place. The resulting ensemble of maximum achievable subcooling distributions can be systematically converted to survival curves and then to nucleation curves [28]. HP-ALTA also has a well-defined sample cell geometry and a quiescent water surface for which the surface area of the guest gas–aqueous interface is known (approximately 132 mm² for the first generation of HP-ALTA MkI).

We had recently investigated the nucleation curves of 90 mol% methane–10 mol% propane (C1/C3) mixed gas hydrate which is an analog of natural gas [28,29,32]. However, we have not yet been able to measure the nucleation curves of Structure I (sI)-forming pure methane gas hydrate to date. The reason for this difficulty is that Structure II (sII)-forming C1/C3 mixed gas hydrate has much higher equilibrium dissociation temperature ($T_{eq}$) values at a given guest gas pressure than the sI-forming pure methane gas hydrate [3]. The high pressure windows of an HP-ALTA can withstand gas pressures of up to 15 MPa [31], which places an upper bound of a guest gas pressure that can be studied. In contrast, ice formation was found to occur below 267 K in a glass sample cell of HP-ALTA at these pressures [33] which could interfere with the measurements of the nucleation curves of gas hydrates. Since HP-ALTA is not capable of discerning the formation of ice from the formation of gas hydrates, the origin of the data below 267 K can be in doubt. In short, this potential ice formation cut-off considerably narrows the experimental window that can be accessed by HP-ALTA for the measurements of pure methane hydrate formation [34].

One way to access the nucleation curves of pure methane hydrate using the HP-ALTA technology, without a major and expensive upgrade of the instrument, is to use even slower cooling rates than in the past studies. The use of slow cooling rates effectively allows more sampling time, and hence chances for nucleation, before a cooling ramp reaches the temperatures at which ice formation becomes likely. Ideally we would wish to measure the nucleation curves of pure methane hydrates in the absence of a solid wall, as we did for C1/C3 mixed gas hydrates
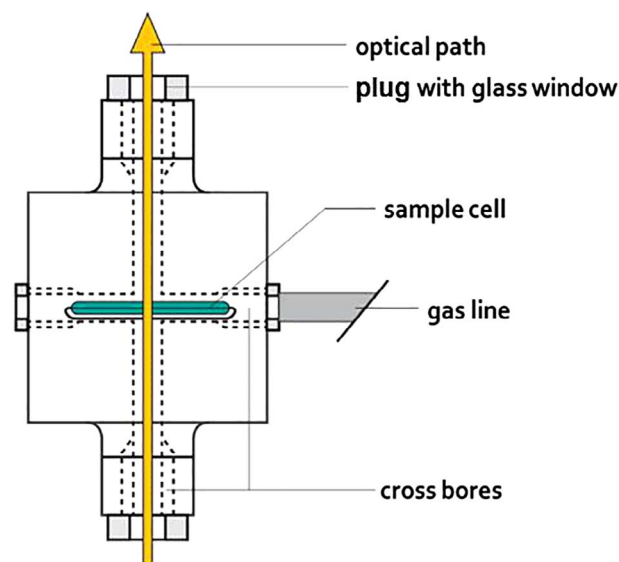


**Fig. 1.** A schematic illustration of HP-ALTA MkI. The sample water is obtained from a Milli-Q unit and contained in a custom-made glass sample cell ('boat'). The surface area of the sample water when contained in a boat is about 132 mm².

before [28]. Unfortunately, even with the use of the slowest cooling rates accessible by HP-ATLA, it was still impractical to measure the nucleation curves of pure methane hydrate on a quasi-free water droplet because of the deeper subcoolings required for nucleation in the absence of a solid wall [28,30,32].

In this study, we report the measurements of the nucleation curves of sI–forming pure methane hydrate using HP-ALTA MkI. The obtained results were then compared to the nucleation rates of methane hydrate measured by Makogon [6] and analyzed by Kashchiev and Firoozabadi [10].

## 2. Materials and methods

Fig. 1 shows the schematic illustration of HP-ALTA MkI. The descriptions of HP-ALTA MkI and its modes of operation, with all the instrumental and operational details, are described in our previous publications [31,35]. The instrument applied a large number of linear (constant cooling rate) cooling ramps to a sample at a selected cooling rate under isobaric conditions, and recorded the temperature at which gas hydrate formation took place, $T_f$, for each cooling ramp. The ensemble of $T_f$ was then used to construct a survival curve. A survival curve in $T_f$ can readily be converted to that in subcooling, $\Delta T$, via $\Delta T \equiv T_{eq} - T_f$, where $T_{eq}$ is the thermodynamic dissociation temperature of the guest gas hydrates at the experimental pressure. The values of $T_{eq}$ at the relevant experimental guest gas pressures were calculated using CSM Gem [3]. Survival probability of a sample at a given subcooling is denoted here as $F$ which is a function of the system subcooling.

HP-ALTA MkI then heated the sample to 300 K for 200 s after each cooling ramp for all the experiments presented in this study. This dissociation temperature corresponds to about 14 K above $T_{eq}$ (286 K at 10 MPa) of methane hydrate, which we assume to be sufficiently high to avoid the controversial memory effect [3,36].

Ultra-high purity methane gas (purity 99.995%) was obtained from BOC Ltd and used as received. The guest gas pressure range studied was 8.0–11.0 MPa with the vast majority of the measurements carried out at 10.0 MPa. The sample water was obtained from a Millipore unit (resistance > 18.2 MΩ) and contained in a custom-made glass sample cell which we may refer to as a 'boat' hereafter [31,37]. The long axis of a boat is 35 mm and the sample water contained in a boat has a surface area of about 132 mm². For each fresh sample, the sample was left at an