Equilibrium and morphology studies of clathrate hydrates

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Abstract

Phase equilibria and morphology of clathrates or gas hydrates were investigated. Four-phase equilibrium conditions (hydrate-liquid$_{aq}$-liquid-vapor) and three-phase equilibrium conditions (hydrate-liquid$_{aq}$-vapor) were determined for the systems methane + carbon dioxide + neohexane + water and methane + carbon dioxide + water, respectively. It was found that the equilibrium mole fraction of carbon dioxide in the vapor phase follows opposite trends in both systems, with respect to equilibrium pressure, at rather constant temperature. Structure H equilibrium occurred at lower pressures and temperatures than structure I when the equilibrium vapor phase was methane rich. This phenomenon appeared to be reversed as the equilibrium vapor phase became richer in carbon dioxide.

A novel reactor was designed in order to acquire high-resolution images of clathrate phenomena occurring at high pressures. Methane clathrate formation on water films without previous hydrate formation history was studied and it was found that hydrates formed in three layers, each with a clearly distinct morphology. This difference in morphology disappeared as the clathrate aged. Higher driving forces produced smaller hydrate grains and smoother surfaces than lower driving forces within the water film. The converse was true for the periphery. Dissociation started on the perimeter of the hydrate layer and proceeded until numerous gas bubbles were observed within the film. As hydrate dissociation spread throughout the film, water receded until it regained its original shape. Moreover, images revealed that an extremely thin hydrate film grew outside of the water boundary. It was found that this growing, thin film could induce nucleation in neighboring water droplets.

Finally, the formation and decomposition of methane clathrate in water films containing silica gel particles were examined. It was observed that the hydrate front engulfed the particles as it advanced at a relatively constant velocity and that the growing clathrate could push a methane bubble. Grain boundary healing could
also be seen after the hydrate contacted a silica particle. Dissociation proceeded through two different mechanisms: the first gradual; the second however, began catastrophically through a sudden fracture in the clathrate.
Résumé

L’équilibre de phases et la morphologie des hydrates de gaz ont été étudiés. Les conditions d’équilibre à quatre phases (hydrates-liquide_{aq}-liquide-vapeur) et à trois phases (hydrates-liquide_{aq}-vapeur) ont été déterminées pour les systèmes méthane + dioxyde de carbone + neohexane + eau et méthane + dioxyde de carbone + eau, respectivement. On a constaté que la fraction molaire du dioxyde de carbone dans la phase vapeur suivait des tendances contraires dans les deux systèmes, quand à la pression d’équilibre, pour une température relativement constante. Il fut aussi observé que l’équilibre des hydrates de structure H se produisait à plus basses pressions et températures que celui des hydrates de structure I quand la phase vapeur est riche en méthane ; ce phénomène étant contraire quand la phase vapeur devient riche en dioxyde de carbone à l’équilibre.

Un réacteur a été conçu pour acquérir des images à haute résolution de phénomènes relatifs à la formation des hydrates à haute pression. La formation des clathrates de méthane sur des pellicules vierges a été étudiée et il a été établi que les hydrates se formaient en trois couches, chacune d’elles avec une morphologie unique. Cette différence de morphologie s’estompait à mesure que le clathrate vieillissait.

Des petits grains et des surfaces lisses ont été observés dans la pellicule pour de plus grandes forces d’entraînement, alors qu’à plus basses forces d’entraînement les grains étaient grands et les surfaces rugueuses ; le contraire s’est produit en périphérie de la pellicule. La dissociation a commencé dans le périmètre de la pellicule d’hydrates et a progressé jusqu’à l’apparition de nombreuses bulles gazeuses ; à mesure que la dissociation devenait omniprésente, la pellicule d’eau reculait pour retrouver sa forme originale. Il a aussi été possible de déceler qu’une pellicule extrêmement fine, capable de progresser au-delà de la limite d’une bulle d’eau, peut induire la nucléation dans des bulles d’eau voisines.

Finalement, la formation ainsi que la décomposition des hydrates de méthane dans des pellicules d’eau contenant des particules de gel de silice ont été étudiées. Tandis
que le front des hydrates avançait à une vélocité relativement constante, on a observé l’enveloppement des particules, de même que le déplacement d’une bulle de méthane. La fusion de deux grains d’hydrate a été aussi constatée après que le front ait touché une particule de silice. La dissociation a procédé selon deux mécanismes : le premier graduel ; le deuxième par contre, a commencé de façon catastrophique avec la fracture soudaine du clathrate.
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Chapter 1

Introduction

Clathrate hydrates are crystalline solids composed of a volatile guest trapped in a host water lattice (Van Der Waals and Platteeuw, 1959). Discovered in the early part of the nineteenth century (Davy, 1811), clathrate hydrates remained an academic curiosity until the 1930s when it was corroborated that hydrates plugged natural gas pipelines (Hammerschmidt, 1934). Renewed interest in clathrates came with the discovery of naturally occurring hydrates in the 1960s (Makogon, 1965). It is estimated that natural clathrates store as much as double the amount of energy of all fossil fuels combined (Suess et al., 1999). In addition, trapping carbon dioxide as a hydrate in the bottom of the ocean has been proposed as an alternative to reduce increasing atmospheric carbon dioxide concentration (Harrison et al., 1995). Moreover, concerns have been raised regarding the role that natural hydrates could play in global climate change; these compounds constitute a considerable carbon sink and are thus an important part of the organic carbon cycle (Kvenvolden, 2002). The possibility of using hydrates for gas storage and transportation has also been put forward (Chatti et al., 2005).

In summary, gas hydrates have been studied for two centuries, but only until recently have we realized the enormous implications that clathrates have on our environment and our secure supply of clean energy. Research in this field is not only necessary in order to safely pursue hydrates as an energy source or carrier, but
also to further understand the impact that such a vast resource has on nature and on our future.

The focus of this work was to provide experimental information relevant to thermodynamics and morphology of clathrates. Traditionally, the study of hydrate equilibrium was important in order to avoid undesirable formation in gas and oil pipelines; however, the need for thermodynamic data has been revived with the possibility of using hydrates beneficially. On the other hand, morphology studies are valuable for they increase our understanding of hydrate nucleation, growth and dissociation mechanisms.

This dissertation is based on three manuscripts presented in Chapters 3 to 5. Other manuscripts, product of collaborative work during the course of my studies, but not included in the thesis are listed in the “Other Related Work” section. A global introduction to clathrate phenomena relevant to this thesis is presented in Chapter 2. Chapter 3 addresses phase equilibria of clathrate forming systems with two degrees of freedom and has been published in the *Journal of Chemical Engineering Data, 53*: pp. 1745-1749. Based on visual evidence, Chapter 4 discusses the formation of methane clathrates from thin water films, and it is to be submitted to the *AICHE Journal*. In turn, Chapter 5 describes the response of the methane + water system upon addition of silica particles, and it is to be submitted to the *Journal of Crystal Growth*. Finally, an overall conclusion and some suggestions for future work are presented in Chapter 6.

**Contributions of Authors**

I am the first author for the three manuscripts included in this thesis and have performed the experimental work, as well as the analysis described therein. The morphology crystallizer was designed by myself with machining done at the chemical engineering shop at McGill University. Several modifications to the phase equilibrium reactor together with the construction of sampling devices was also undertaken by me. Professor Phillip Servio, co-author in all the papers, was in charge of the
overall supervision of the project.
Chapter 2

Background

A clathrate (from the Latin clathratus, meaning enclosed or protected by crossbars) is a substance in which one component, the host molecule, crystallizes with a structure that contains polyhedral cavities in which atoms or small molecules of a second component, the guest molecule, can be trapped (Cotton et al., 1995). The clathrate compounds are divided into two categories: aqueous clathrates or clathrate hydrates and non aqueous clathrates (Englezos, 1993). This work is concerned with the former, commonly known as gas hydrates.

Clathrate hydrates are non-stoichiometric compounds that form when small, volatile molecules (< 0.9 nm) come in contact with water at appropriate temperatures and pressures (typically $T < 300$ K and $p > 0.6$ MPa) (Sloan, 2003). Hydrates were described early in the nineteenth century (Davy, 1811), yet they remained an academic curiosity until the observation of clathrates in natural gas pipelines (Hammerschmidt, 1934). As a result, intense research has been aimed at understanding gas hydrates and also at finding ways of preventing their formation.

Interest in clathrate hydrates was further increased with the discovery of in situ gas hydrates by Makogon (1965). Since then, hydrates are being looked at as a probable energy source for the future, methane being the main component of clathrate hydrates found in nature. Most of the natural gas hydrates are found in the ocean bottom; however, there is a considerable amount of hydrates found in permafrost.
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regions (Sloan, 2003). Conservative estimates suggest that the amount of energy stored in hydrates is at least twice that of all other fossil fuels combined (Suess et al., 1999). In addition, trapping carbon dioxide as a hydrate in the bottom of the oceans, has been proposed as an alternative to reduce increasing atmospheric CO$_2$ concentration (Harrison et al., 1995; Sloan, 2000). Recently, concerns have been raised regarding the role that natural hydrates could play in global climate change (Brewer, 2000; Kvenvolden, 2000, 2002). Hydrates constitute a considerable carbon sink, making them an important part of the global, organic carbon cycle (Kvenvolden, 2002). Sizable releases of methane due to oceanic hydrate destabilization could exert a significant effect in enhancing global warming (Brewer, 2000). On a more short term basis, oceanic hydrate destabilization could also pose a submarine geological hazard, as industry moves to exploit resources in the seabed at greater and greater depths (Kvenvolden, 2000).

The possibility of using hydrates for gas storage and transportation has also been considered (Chatti et al., 2005; Wang et al., 2008). Hydrate energy density is comparable to that of compressed natural gas, but less than that of liquefied natural gas (Thomas and Dawe, 2003). Clathrate storage and production conditions being much milder than that of compressed and liquefied natural gas, it has been suggested that it would be economical to transport stranded gas as a hydrate (Thomas and Dawe, 2003; Sloan, 2003).

2.1 Clathrate Hydrates

Clathrate hydrates are solid solutions of a volatile solute (guest) in a host lattice. The empty hydrate lattice is thermodynamically unstable, yet stabilization may occur through the inclusion of a second component (Van Der Waals and Platteeuw, 1959). The lattice holds together due to hydrogen bonds among water molecules forming polyhedra (cages). The cavities of these polyhedra can be filled with molecules that do not interfere with the hydrogen bonding of water, as long as the guest diameter is of appropriate size (Englezos, 1993). Under suitable pressure
and temperature conditions, the inclusion of a guest forms a stable gas hydrate structure (Englezos, 1993). Guest-molecule repulsions cause water cages, to open and combine to form well defined crystals (Sloan, 2003). All common natural gas hydrates belong to three crystal structures: cubic structure I, cubic structure II, or hexagonal structure H (Sloan and Koh, 2008). Structure I predominates in nature, structure II occurs mostly in man-made environments, and structure H may arise in either artificial or natural environments (Sloan, 2003).

The basic building block for clathrate hydrate crystals is a polyhedron with twelve pentagonal faces ($5^{12}$) (Figure 2.1). Structure I is formed when $5^{12}$ cavities arrange themselves in space by linking through their vertices, a larger second type of cavity is then formed with twelve pentagonal and two hexagonal faces ($5^{12}6^2$) (Englezos, 1993). The resulting unit cell consists of six large $5^{12}6^2$ and two small $5^{12}$ cavities, formed by forty-six water molecules (Sloan, 2003) (Figure 2.2). Molecules with diameters 0.4 to 0.55 nm can form structure I hydrates. Common structure I guest molecules are methane, ethane and carbon dioxide (Sloan, 2003).

Figure 2.1: The basic building block of the clathrate hydrate crystal structure: a dodecahedron with twelve pentagonal faces and water molecules in each of its vertices. A methane molecule is shown inside the water cage. (Courtesy of A. Golsztajn. Personal communication, February 2009)
Figure 2.2: The three most common clathrate-hydrate crystalline structures. $5^{12}6^8$ represents a water cage made of twelve pentagonal faces and eight hexagonal faces. As an example the structure H unit cell is composed of three $5^{12}$ cages, two $4^{3}5^{6}6^3$ cages and one $5^{12}6^8$ cage.
Structure II forms when the $5^{12}$ cavities link through their faces (Sloan and Koh, 2008). The resulting arrangement creates a large cavity with twelve pentagonal and four hexagonal faces ($5^{12}6^4$). The large cavity in structure II is bigger than the large cavity in structure I; the converse is true for the small cavity. The unit cell contains 136 water molecules forming sixteen $5^{12}$ cavities and eight $5^{12}6^4$ cavities (Sloan, 2003) (Figure 2.2). Molecules with diameters of less than 0.4 nm or greater than 0.6 nm form structure II hydrates (Sloan, 2003). Common structure II guest molecules are propane and iso-butane (Sloan, 2003).

Structure I and structure II hydrates can be stabilized by trapping one type of guest or by accepting a gas mixture (Sloan and Koh, 2008). In simple hydrates, single guests are sometimes too large for the smaller cage: while occupying the larger cage only, large guests leave the smaller cage empty. This is not the case for smaller molecules, which may fill up both cages (Sloan, 2003).

Contrary to structures I and II, structure H requires two types of guests to form (Sloan and Koh, 2008). The unit cell is formed by thirty-four water molecules forming three small $5^{12}$ cavities, two medium $4^35^66^3$ cavities, and one large $5^{12}6^8$ cavity (Figure 2.2). Examples of structure H guests are mixtures of methane and neohexane or methane and cycloheptane (Sloan, 2003).

2.2 Phase Equilibrium

Guest and host are not chemically bonded in clathrates, but rather interact through weak van der Waals forces. Temperature and pressure will dictate whether host and guest will exist as gas, liquid, solid or hydrate (Holder et al., 1988). A representative partial phase diagram for a sub critical gas is shown in Figure 2.3.

If a reactor containing an aqueous liquid phase and a hydrate forming gas in excess, is compressed, while the temperature is kept below the upper quadruple point (dotted arrow in Figure 2.3), the pressure will eventually reach a value where hydrates will appear. At this point hydrates, liquid water, and gas coexist. Further compression will result in more hydrates forming until only two phases will remain
Figure 2.3: Representative partial phase diagram for a binary clathrate-forming system. I = ice; W = liquid rich in water; V = vapor; H = hydrate; L = liquid rich in hydrate former. Two-phase and three-phase regions are represented by areas, and lines respectively. The arrow points to the first quadruple point (IWHV) and dotted arrow the second (VWLH).
The same principle applies to temperatures below the ice point, except ice replaces liquid water (Holder et al., 1988).

It is important to note that pressure-temperature diagrams for gases for which the vapor-liquid critical point is lower than the first quadruple point (solid arrow in Figure 2.3) are somewhat different to Figure 2.3. Due to the low critical temperatures, the VHL, VWL, and WLH lines in Figure 2.3 disappear, resulting in no upper quadruple point. Examples of such gases are nitrogen and methane (Sloan, 1998).

Traditionally, hydrate phase equilibrium data have been gathered using a pressured reactor equipped with windows, thus allowing the visual detection of the onset of hydrate formation (Holder et al., 1988). Such reactors could be operated in isothermal, isobaric or isochoric modes (Sloan and Koh, 2008). In addition to visual methods, on line pressure measurements can be used to detect the onset of hydrate formation through the significant pressure drop associated with hydrate formation (Holder et al., 1988). In a typical test the hydrates are formed by increasing the cell pressure (isothermal) or decreasing the cell temperature (isobaric and isochoric), beyond the hydrate equilibrium point. The hydrates are then dissociated by reducing the cell pressure (isothermal) or increasing the cell temperature (isobaric and isochoric). Continuous or stepwise heating can be used to increase the cell temperature and dissociate gas hydrates so as to measure the clathrate dissociation point (Tohidi et al., 2000).

The most widely used model for the calculation of hydrate phase equilibrium was developed by Van Der Waals and Platteeuw (1959). Based on statistical mechanics, the van der Waals model calculates the chemical potential of water in the hydrate phase and equates it to the chemical potential of water in the liquid phase. The model requires fugacities of the species in question, Langmuir constants for the hydrate former, and the difference in chemical potential of the empty hydrate lattice and pure liquid water. A robust equation of state such as the Trebble-Bishnoi equation of state (Trebble and Bishnoi, 1987; 1988b) can be used to calculate fugacities. The Langmuir constants can be calculated as suggested by Parrish and
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Prausnitz (1972) and finally the difference in chemical potential of the empty hydrate lattice and pure liquid water can be computed according to the model of Holder et al. (1988, 1980).

2.3 Kinetics of Hydrate Formation

The formation of gas hydrates is a phase transformation which requires a supersaturated environment in order to occur (Englezos et al., 1987a). Hydrate formation resembles a crystallization process, and as such it can be divided into nucleation and growth phases (Natarajan et al., 1994; Mullin, 1997). Hydrate nucleation is the process, during which small hydrate crystals (nuclei) form and disappear in an attempt to achieve critical size for continued growth (Sloan and Koh, 2008; Mullin, 1997). The beginning of hydrate growth is usually associated with the appearance of turbidity in the liquid phase and it is often referred to as the turbidity point (Englezos et al., 1987a).

2.3.1 Nucleation

The nucleation period is characterized by the formation and decomposition of small aggregates of molecules of the dissolved substance in an aqueous solution. For each supersaturated solution, there is a critical size cluster (or critical nucleus) that is in equilibrium with the surrounding medium, and may with the same probability grow or disintegrate (Natarajan et al., 1994; Mullin, 1997). Clusters that are smaller than the critical size will most likely decompose, while clusters larger than the critical size will grow spontaneously. The critical size represents a limit which the growing clusters must attain before spontaneous growth as solid crystal begins (Natarajan et al., 1994; Mullin, 1997).

The duration of the nucleation period or induction time (sometimes lag time) is believed to be stochastic (Sloan and Koh, 2008). There have been several attempts to identify the factors that affect induction times in addition to temperature and
pressure. The history of water has been pointed out as having an influence on nucleation times: hydrates prepared from thawed ice or dissociated hydrates having shorter lag times than hydrates prepared from distilled water \cite{Vysniauskas1983}. It has also been found that higher stirring rates reduce the nucleation periods, possibly due to reductions in mass transfer resistances \cite{Englezos1987,Skovborg1993}. Jensen \textit{et al.} \cite{Jensen2008} have suggested that the gas dissolution rate rather than the induction time of propane hydrate is influenced by a change in agitation. In addition, Sloan and co-workers \cite{Sloan1990,Sloan1991} have postulated that differences in the guest to cavity size ratio may determine whether a hydrate former exhibits a nucleation period or not. Finally, hydrate nucleation may also be affected by surface heterogeneities inside reactors, making it difficult to compare nucleation data from one laboratory to another one \cite{Natarajan1994}. The effect of temperature and pressure on hydrate nucleation has been assessed previously by quantifying the magnitude of the nucleation driving force. In general, high driving forces imply shorter induction times whereas the contrary is true for low driving forces \cite{Englezos1987,Skovborg1993}.

Several driving forces for nucleation have been defined in the past. Based on crystallization theory \cite{Vysniauskas1983} defined the nucleation driving force as the degree of subcooling, or the difference between the three-phase equilibrium temperature at the experimental pressure and the experimental temperature.

Natarajan \cite{Natarajan1994} noted that the minimum fugacity at which a gas can form a hydrate corresponds to the three-phase equilibrium fugacity, and defined the driving force for hydrate nucleation as the difference between the fugacity of the dissolved gas in the liquid at the systems temperature and pressure, and that corresponding to the three-phase equilibrium at the experimental temperature.

Skovborg \textit{et al.} \cite{Skovborg1993} expressed the nucleation driving force as the difference in the chemical potential of water in the hydrate phase and that of water in the liquid phase; both chemical potentials calculated at the system temperature and pressure.

A more general expression for the nucleation driving has been proposed by Sloan
CHAPTER 2. BACKGROUND

and co-workers (1995) as the difference in the Gibbs free energy of the forming hydrate and that of the reacting water and gas. Other general expressions based on the change in Gibbs free energy include those of [Kashchiev and Firoozabadi (2002)] and [Anklam and Firoozabadi (2004)].

2.3.2 Growth

The hydrate crystal growth period begins once hydrate nuclei reach the critical size. The growth period is characterized by the incorporation of significant amounts of gas into the hydrate phase. Gas content in hydrates is at least two orders of magnitude greater than the gas solubility in water (Sloan and Koh, 2008). Thus, mass and heat transfer effects become important during hydrate growth, in addition to the factors that affect nucleation (§2.3.1). An exception to this is water history, which contrary to its effect on nucleation (§2.3.1), has been reported to not have an influence on hydrate growth (Vysniauskas and Bishnoi, 1983).

Based on crystallization theory and their own definition of the nucleation driving force Vysniauskas and Bishnoi (1983) put forward a semi-empirical model for hydrate growth. They obtained an expression for the overall rate of gas consumption dependent on the degree of sub cooling, pressure and several empirical parameters (Vysniauskas and Bishnoi, 1983).

Englezos et al. (1987a,b) derived a model for hydrate growth founded on homogeneous crystallization theory. The model also incorporated mass transfer effects. The overall driving force for hydrate growth was defined as the difference between the fugacity of the gas dissolved in the liquid, at the experimental temperature and pressure, and the fugacity at the three-phase equilibrium pressure at the experimental temperature.

A simplification of the Englezos et al. (1987a,b) model, based on mass transfer limitations and neglecting crystallization kinetics was proposed by Skovborg and Rasmussen (1994). A new driving force for hydrate growth was defined as the difference between the gas concentration at the water-gas interface, at the experimental temperature and pressure, and the gas concentration in the bulk liquid phase at the
experimental temperature and pressure.

The Englezos model (1987a, 1987b) was recently reformulated using a concentration gradient, based on two-phase equilibria rather than three-phase equilibria (Hashemi et al., 2007). A further simplification has been put forward by Bergeron and Servio (2008) where the hydrate-growth driving force was defined as the difference between the experimentally measured bulk gas concentration in the liquid and the two-phase hydrate-water equilibrium concentration.

2.4 Morphology

Pioneering morphology work was done by Maini and Bishnoi (1981) and by Makogon and co-workers (1997). Maini and Bishnoi (1981) captured images of hydrate formation in natural gas bubbles as they ascended through a high-pressure water tunnel kept at 3°C and reported that a thin hydrate layer formed over the entire surface of the gas bubble above 4.8 MPa. Makogon (1997) found that crystal shape and growth was determined by the hydrate formation conditions. Other early observational studies include that of Mori and Mori (1989b,a) on refrigerants, that of Hwang et al. (1990) on methane hydrate formed from ice supported on stainless-steel discs and that of Long and Sloan (1996) on methane and CO₂ hydrate grown inside a sapphire tube.

Sugaya and Mori (1996) presented one of the first studies on hydrates formed from bubbles of a fluorocarbon immersed in water; it was found that the surface morphology of the hydrate layer formed at the interface depends strongly on the degree of saturation of the water phase with the guest component. Ohmura and Mori (1999) expanded the study of Sugaya and Mori (1996) to include a different type of refrigerant; in addition, it was hypothesized that a concentration driving force could explain the differences in morphology observed at high and low driving forces. The crystal-growth behavior of structure I, structure II and structure H was described by Smelik and King (1997); it was proposed that the characteristic crystal morphology of each structure could be used to identify hydrate types in situ.
CHAPTER 2. BACKGROUND

Uchida and co-workers have published a number of articles on the morphology of CO$_2$ hydrate (1996; 1999; 2000b; 2002). The first focused on determining the interfacial tension between liquid CO$_2$, water and hydrate, yet illustrations of their observations were also provided (Uchida and Kawabata, 1996). Later on, still frames of video recordings of hydrate formation on water droplets suspended in liquid CO$_2$ were presented (Uchida et al., 1999). It was concluded that hydrates formed initially at the interface between the two fluids and proceeded until complete coverage of the water bubble; on some occasions secondary nucleation was also observed inside the water bubble (Uchida et al., 1999). Uchida et al. (2002) measured the lateral growth rates of CO$_2$ hydrate films on water bubbles to range from 6 to 15 mm/s, and concluded that sub cooling was the parameter that highly determined the growth rate of the crystal.

Servio and Englezos (2003) studied the morphology of methane and carbon dioxide hydrates formed on nearly spherical water droplets. It was found that the type of hydrate guest did not have an effect on the crystal morphology. Furthermore, when hydrates were formed at high driving forces water droplets were observed to become jagged, and numerous needle-like crystals were seen to extend away from the water surface into the gas phase. This was not the case at low driving force, where the hydrate surface was observed to be smooth and shiny (Servio and Englezos, 2003). Servio and Englezos (2003) also observed that adjacent water droplets would nucleate almost simultaneously and hypothesized that this could be attributed to a bridge formed by minute water droplets between the water bubbles.

A unique study has been put forward by Schicks and Ripmeester (2004) where micrographs suggesting the formation of structure II methane hydrate were shown. This observation was corroborated with Raman spectroscopy, and it was concluded that the thermodynamically unstable, structure II methane hydrate eventually converts to structure I methane hydrate (Schicks and Ripmeester, 2004).

Perhaps the most successful systematic approaches to correlate the observed clathrate morphology with the corresponding driving force have been put forward by Ohmura and co-workers (1999; 2004; 2005; 2009). Based on hypothesized concen-
tration differentials between the liquid phase near the newly formed hydrate and the liquid bulk concentration, they were able to match images to their proposed driving force (Ohmura and Mori, 1999; Ohmura et al., 2004, 2005). Very recently, the same group used sub cooling as an index for the driving force of the system; through this index it was then possible to correlate the driving force with the observed hydrate morphology (Tanaka et al., 2009). As a general trend it was observed that sub coolings $\geq 3$ K produced sword-like crystals whereas at smaller sub cooling polygonal faces appeared, the size of the latter increasing with decreasing sub cooling (Tanaka et al., 2009).

Ohmura and Mori (1999) worked with liquid droplets of refrigerant R-141b (CH$_3$CCl$_2$F) in water and distinguished two stages of hydrate-crystal growth, which were very different from each other. The primary stage was characterized by lateral growth of a thin, fine-grained polycrystalline layer along the surface of each R-141b drop; the secondary stage began typically after 10 min and lasted for several hours: it was characterized by radial growth of plate-like crystals growing from the outer surface of the hydrate shell formed in the primary stage (Ohmura and Mori, 1999). The second stage was never observable with pure water (not presaturated) and/or at a small sub cooling. Ohmura and Mori (1999) also observed that the hydrate surface formed in non-presaturated water smoothed over time. In subsequent work Ohmura extended the study done on presaturated water to other hydrate formers including carbon dioxide (2004) and methane (2005). With carbon dioxide it was observed that when sub cooling was greater than 3 K, a hydrate film first grew along the carbon dioxidewater interface; then hydrate crystals with dendritic morphology grew into the liquid-water phase from that hydrate film (Ohmura et al., 2004). With sub cooling levels lower than 2 K it was found that dendritic crystals were replaced by skeletal or polyhedral crystals (Ohmura et al., 2004). Similar conclusions were presented for the methane-water system (Ohmura et al., 2005).

Using laser interferometry, Ohmura et al. (2000) measured the thickness of a

Sub cooling is defined as the temperature difference between the experimental temperature and the guest-rich phase-hydrate-water equilibrium temperature at the experimental pressure.
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17

R-134a (CH$_2$FCF$_3$) hydrate film and concluded that initially the film could be as thick as 80 $\mu$m. Hirai et al. (2000), Kobayashi et al. (2001) and Freer et al. (2001) have studied growth of hydrate films. The former (Hirai et al., 2000) and the latter (Freer et al., 2001) measured velocities of the advancing hydrate film for CO$_2$ and methane respectively by successively recording images. Hirai et al. (2000) reported that lateral growth rates could vary from 0.044 mm/s at 284.2 K and 39.2 MPa to 6.5 mm/s at 278.7 K and 39.2 MPa for CO$_2$ hydrate. Freer et al. (2001) determined methane hydrate growth rates varying from 20 $\mu$m/s at 3.55 MPa and 1$^\circ$C to 690 $\mu$m/s at 9.06 MPa and 1$^\circ$C.

Morphology of hydrates prepared from melting ice has been studied with an optical microscope by Stern et al. (1998), and with magnetic resonance imaging by Moudrakovski and co-workers (1999; 2004). Stern et al. (1998) concluded that fine-grained ice can persist to temperatures well above its ordinary melting point while slowly reacting to form methane hydrate under elevated methane gas pressure. Moudrakovski et al. (2004) saw evidence for inhomogeneous hydrate conversion throughout their experiments, as well as for secondary nucleation taking place well away from the hydrate film that covered their samples initially. Using electron microscopy, Kuhs’s group has analyzed hydrates forming on ice and have concluded that clathrate surfaces have a sub micron porous structure (Kuhs et al., 2000; Staykova et al., 2003). Using a similar approach, Stern et al. (2004) and Stern and Kirby (2008) have shown that porous hydrate develops initially and that growth textures of clathrate made from ice eventually anneal, producing dense clusters of grains with prominent crystal face development.

2.4.1 Particles and Restricted Geometries

The formation of clathrates in deep ocean water has been studied for methane hydrate (Brewer et al., 1997) and for CO$_2$ hydrate (Brewer et al., 2008) with the aid of a remotely operated vehicle. Brewer et al. (1997) observed that in a coarse sand matrix methane hydrate filled the pore spaces and turned the sand column into a solidified block that was eventually lifted and ruptured by methane gas. For
methane hydrate formation in fine grained black mud it was found that gas flow
carved out channels, clathrates then formed on the channel walls and subsequently
filled the channels until forming large, discrete masses. Carbon dioxide behaved
differently: liquid CO$_2$ that was spilled onto the sea floor did not penetrate or
appear to react with the sediment in any way, eventually being washed away by
passing eddies (Brewer et al., 2008).

Tohidi et al. (2001) studied tetrahydrofuran, methane and CO$_2$ hydrate forming
inside an asymmetric porous network etched into glass micro models. Clathrates
were observed to form within the centers of the pore space, rather that on grain
surfaces. A thin film of free water persisted on grain surfaces even at high driving
forces and it was proposed that limited cementation occurred in regions of small
grain size or where a large proportion of the pore space was filled with hydrate. The
idea of using glass micro models was further pursued by Katsuki and co-workers
using a symmetric network of straight microchannels to study both CO$_2$ (Katsuki
et al., 2006) and methane hydrates (Katsuki et al., 2007, 2008). It was found that
higher driving forces induced the formation of dendrites that quickly changed into
particulate crystals. Lower driving forces induced faceted hydrate growth; this
morphology changed very little over time (Katsuki et al., 2006, 2007). Faceted
 crystals filled the individual channels and extended onto others; furthermore, the
presence of liquid water layers was not observable (Katsuki et al., 2006, 2007). As
for methane clathrate dissociation, it was found that methane gas produced upon
hydrate decomposition formed “slugs” that completely occupied the pore space
(Katsuki et al., 2008).

Mork et al. (2000) conducted nuclear magnetic resonance imaging studies on
tetrahydrofuran hydrate formed in the presence of sand and found that lumpy vol-
umes of solidified sand and hydrate formed and that in between them a three-
dimensional network of channels made of a highly mobile phase existed. Based
on the way sand particles appeared suspended in the hydrate, Mork et al. (2000)
suggested that it was likely that the growing clathrate was able to push the sand par-
ticles apart upon formation. Nagashima et al. (2008) also worked with tetrahydro-
CHAPTER 2. BACKGROUND

furan hydrates using a directional growth apparatus, and observed that clathrates formed a layered pattern in solutions containing glass beads 2 µm in diameter, but that the layered pattern was not present in solutions containing glass beads 50 µm in diameter. The observed layered pattern was attributed to pushing of the glass beads by the growing hydrate layer (Nagashima et al., 2008).

The formation of hydrates from CO$_2$ and N$_2$ mixtures and water dispersed in silica gel has been monitored with nuclear resonance micro imaging by Seo et al. (2005); it was found that the reaction proceeded to almost complete conversion of water to hydrate in one hour. Kvamme et al. (2007) and Ersland et al. (2008) have used magnetic resonance imaging as a tool to visualize methane hydrate conversion into CO$_2$ hydrate in sandstone core plugs and concluded that CO$_2$ transport probably occurs through aqueous channels that separate the hydrate from the mineral surface.

Uchida et al. (2000a) were able to characterize macroscopic forms of natural gas hydrates recovered from the Canadian permafrost using a modified medical computed tomography scanner. Later on, Jin et al. (2004) improved on the spatial resolution with a micro focus X-ray computed tomography scanner, and were able to calculate porosities of artificial samples containing ice, hydrate, free gas and quartz sand. Also with a modified medical computed tomography scanner, Kneafsey et al. (2007) monitored methane hydrate behavior while forming in the presence of moist silica sand 100 to 200 µm grain size, and found that water could migrate throughout the sample. The formation of a hydrate rind between the sample and the vessel wall was also observed (Kneafsey et al., 2007). Using synchrotron radiation-based computer tomography (Jones et al., 2007) presented a preliminary study on THF hydrate formation in oceanic sediment samples, and concluded that there was no evidence for the existence of free-floating hydrate at the micrometer scale.

Stern et al. (2004) used cryogenic scanning electron microscopy to compare artificial methane hydrate + quartz aggregates synthesized from melting ice to natural gas hydrates in nodules recovered from the Mallik drill site in Canada, and found that there was a striking similarity in phase distribution, grain contacts and tex-
tured between the natural and the lab-synthesized sample that had been subject to compaction. Later, the same group studied natural hydrate samples from various locations around the world and concluded that gas hydrate often occurs as a dense substrate with typical grain size of 30 to 200 \( \mu \text{m} \). In addition, it was reported that the hydrate often contains a significant fraction of isolated macropores that can be 5 to 10 \( \mu \text{m} \) in diameter and occupy 10 to 30\% of the domain (Stern and Kirby, 2008).
Chapter 3

Equilibrium Studies for the System Methane + Carbon Dioxide + Neohexane + Water

3.1 Preface

Phase equilibrium is perhaps the most studied subject pertaining to clathrates. As a consequence, many of the high-pressure experimental techniques often required for its study are well known. In addition, without knowledge of the conditions at which hydrates are stable it would be impossible to undertake the kind of morphology studies described in the ensuing chapters. For these reasons, studying phase equilibrium is frequently used as an initiation to hydrate phenomena. Pure methane clathrate, which concerns the rest of the chapters of this thesis, would have been the natural choice; however, this system has been studied extensively in the past. Thus, a system where a significative contribution to the field could be made was chosen instead: in particular, the system methane + carbon dioxide + neohexane.

+ water. This system was found interesting because important theoretical inconsistencies regarding the data analysis from previous investigations were found. The study described below completed the equilibrium data set for the system in question and clarified some common misconceptions found in the literature.

3.2 Abstract

Four-phase equilibrium conditions (hydrate-liquid-liquid\textsubscript{aq}-vapor) were studied for the system methane + carbon dioxide + neohexane + water by the pressure search method. In addition, three-phase equilibrium conditions (hydrate-liquid-vapor) were determined for the same system in the absence of neohexane. Experimental conditions were varied in the temperature range of (275 to 285) K and the pressure range of (1.3 to 7.5) MPa. Equilibrium temperature and pressure values were found to agree, within the uncertainties herein reported, with existing literature values for both systems. The data was used to produce experimental contour plots that summarize the equilibrium temperature, pressure, and vapor composition on the same graph. It was observed that the equilibrium mole fraction of carbon dioxide in the vapor phase follows opposite trends in both systems, with respect to equilibrium pressure, at rather constant temperature. The data also suggest that hexagonal structure H equilibrium occurs at lower pressures and temperatures than cubic structure I when the vapor phase is methane rich; however, this phenomenon appears to be reversed as the equilibrium vapor phase becomes richer in carbon dioxide.

3.3 Introduction

Clathrate hydrates are nonstoichiometric, crystalline compounds that form when small molecules come in contact with water at appropriate temperatures and pressures. The terms “gas hydrates” and “clathrate hydrates” are now used interchangeably to designate this kind of compound (Englezos [1993]). Clathrates of natural gas were first observed in pipelines in 1934 (Hammerschmidt [1934]) and have since then been considered a nuisance to the gas and oil industry. Natural-gas hydrates are
CHAPTER 3. EQUILIBRIUM

abundantly found in the ocean bottom and to a lesser extent in permafrost regions (Sloan, 2000). Conservative estimates suggest that the amount of energy stored in natural hydrates is at least twice that of all other fossil fuels combined (Kvenvolden, 2002). In addition, trapping carbon dioxide as a hydrate in the bottom of the ocean has been proposed as an alternative to reduce increasing atmospheric CO$_2$ concentration (Brewer, 2000).

Mixtures of carbon dioxide and methane form cubic structure I (sI) hydrates (Uchida et al., 2005), but in the presence of a larger molecule, like neohexane, the hexagonal structure H (sH) is also stable (Servio et al., 1999; Uchida et al., 2006). Structure H differs from other hydrate structures for it requires at least two guests to form a stable lattice; in addition, sH will form at lower pressures than its corresponding sI hydrate, at the same temperature. Structure H hydrates were discovered in 1987 by Ripmeester and co-workers (Ripmeester et al., 1987). Since then, the study of structure H hydrates has gone beyond a laboratory curiosity: naturally occurring sH hydrates were found by Sassen and Macdonald (1994) and schemes to transport gas and sequester gas as a solid, in sH form, have been proposed in the past (Khokar et al., 1998; Susilo et al., 2007). In particular, it has been shown that sH hydrates from methane and neohexane exhibit fast overall formation kinetics and almost 100% enclathration of methane (Susilo et al., 2007). Servio et al. (1999) have studied equilibria of methane-carbon dioxide mixtures in the presence and absence of neohexane and suggested that above a certain temperature structure H equilibrium moved into a structure I equilibrium regime. This suggestion was later confirmed by Uchida and co-workers (Uchida et al., 2006), who in addition to equilibrium measurements used Raman spectroscopy and X-ray diffraction to confirm the presence of sH hydrates. Both Servio et al. (1999) and Uchida et al. (2006) showed partial phase diagrams where equilibrium pressure and temperature of methane + carbon dioxide gas mixtures in the presence of neohexane were compared to mixtures in the absence of neohexane. Comparisons were based on initial gas compositions and not equilibrium, vapor-phase compositions. Servio et al. (1999) used only two gas mixtures obtaining limited amounts of data, and Uchida et al. (2006) did not
port equilibrium vapor-phase compositions. In contrast, methane + carbon dioxide mixtures in contact with water have been studied extensively \cite{Unruh1949, Berecz1983, Adisasmito1991, Ohgaki1996, Dholabhai1994, Seo2001}.

In this paper, we report equilibrium pressure, temperature, and vapor-phase composition for the system methane + carbon dioxide + neohexane + water and the same in the absence of neohexane. In addition to completing the equilibrium data set for the system with neohexane, we present experimental contour plots that allow direct comparison of the equilibria of methane + carbon dioxide hydrates with methane + carbon dioxide + neohexane hydrates.

### 3.4 Experimental Apparatus

Experiments were carried out in a Jefri-DBR phase behavior system (Oilphase-DBR- Schlumberger) (Figure \ref{fig:3.1}). The heart of the system was a high-pressure PVT cell consisting of a glass cylinder (20 cm in height and total void volume 150 cm$^3$), secured between two full-length sight glass windows, inside a stainless steel frame. This design allowed for unimpaired visibility of the entire contents of the cell. Pressure was regulated through an automated, high-pressure, positive displacement pump (Oilphase-DBR-Schlumberger). Fluid inside the pump was connected to a floating isolation piston which exerted pressure on the mixture of interest, and prevented contact with the hydraulic fluid inside the glass cylinder. The PVT cell was mounted inside a temperature controlled air bath by means of a bracket, attached to a horizontal shaft. An electric motor powered the shaft, which oscillated through sixty degrees about its center of gravity at forty cycles per minute. Temperature and pressure inside the PVT cell were monitored with a platinum RTD probe, and a pressure transducer (both supplied with the Phase Behavior system). Using a coverage factor of $k = 2$ and assuming the corresponding standard uncertainty had a normal distribution, each expanded uncertainty was estimated to be $U_T = 0.2 \text{ K}$ and $U_P = 14 \text{ kPa}$, for temperature and pressure, re-
spectively. Vapor-phase samples were taken using a previously evacuated sample bomb and analyzed with a gas chromatograph (Varian CP3800) equipped with a gas sampling, injection valve. After injection, separation of the gas mixture was achieved by passing the sample through an arrangement consisting of a 0.5 m × 1/8” precolumn, packed with 80 to 100 mesh Hayesep T (Varian Inc.), and a 2.6 m × 1/8” column, packed with 80 to 100 mesh Hayesep R (Varian Inc.). The effluent was monitored with a thermal conductivity detector.

Figure 3.1: Experimental Apparatus
3.5 Experimental Procedure

Gas mixtures containing a mole fraction of 80 %, 70 %, 60 %, and 50 % methane, respectively, the balance being carbon dioxide, were supplied by MEGS Specialty Gases. The PVT cell was filled with 30 cm$^3$ of distilled water and 15 cm$^3$ of neohexane (2,2-dimethylbutane). These liquids were then brought into contact with the gaseous mixture under study. For the three-phase equilibrium experiments neohexane was not added. Agitation was commenced once all the necessary chemicals were loaded into the PVT cell. Temperature control of the bath was then started, and temperature inside the PVT cell was let to equilibrate over night, while pressure was kept constant to a value just below the expected equilibrium pressure. Hydrates were formed by increasing the pressure above the equilibrium point for pure methane hydrate. When a considerable amount of hydrate crystals was observed in the PVT cell, pressure was reduced in steps of 30 kPa, allowing for temperature in the cell to equilibrate between each decrement. Pressure reduction was achieved by retracting the floating isolation piston inside the PVT cell with the help of the positive displacement pump, and care was taken to ensure the temperature in the cell was constant within 0.5 K for at least 30 min before proceeding with the next pressure decrease. The procedure was repeated until visual confirmation of hydrate-phase disappearance. The equilibrium temperature and pressure values were taken as the average between the conditions at which the last hydrate crystal was observed and the conditions at which the last hydrate crystal disappeared. A vapor phase sample was taken immediately after complete hydrate decomposition and analyzed by gas chromatography. Using the method described above to determine the equilibrium point for both the system with neohexane and that without, it was estimated that the standard uncertainties were as follows: for temperature $u_T = 0.5$ K, for pressure $u_P = 0.03$ MPa, and for vapor-phase mole fraction $u_{y_1} = 0.02$. With a coverage factor of $k = 2$ and assuming the corresponding standard uncertainty had a normal distribution, each expanded uncertainty was estimated to be $U_T = 1.0$ K, $U_P = 0.06$ MPa, and $U_{y_1} = 0.04$. 
3.6 Results and Discussion

Table 3.1 and Table 3.2 present the complete three-phase and four-phase equilibrium data for the systems methane + carbon dioxide + water and methane + carbon dioxide + neohexane + water, respectively. Figure 3.2 and Figure 3.3 show three-phase (hydrate-liquid-vapor) and four phase (hydrate-liquid-liquid_{aq}-vapor) equilibrium temperature and pressure, respectively, for gas mixtures initially containing a mole fraction of 80 %, 70 %, and 50 % methane, the balance being carbon dioxide. These figures are shown to offer a comparison against the data available in the literature where analysis of the results was made based on the feed vapor-phase composition and not on the equilibrium vapor-phase composition. To increase readability, data from mixtures used in this work but not available in the literature are not presented in Figure 3.2 and Figure 3.3, but rather incorporated into Figure 3.5, Figure 3.6 and Figure 3.7. Equilibrium pressure and temperature values for gas mixtures in contact with water only (Figure 3.2) and with water and neohexane (Figure 3.3) agree with previously reported values within our estimated expanded uncertainties. (Servio et al., 1999; Uchida et al., 2006; Dholabhai and Bishnoi, 1994).

As can be seen from Figure 3.2, equilibrium pressure at constant temperature decreases with increasing initial carbon dioxide concentration. This trend is expected since pure carbon dioxide hydrate forms at lower pressures than pure methane hydrate (Sloan and Koh, 2008). Figure 3.3 shows how the presence of neohexane inverts the trend: mixtures with higher initial carbon dioxide concentration form hydrates at higher pressures at constant temperature. Uchida et al. (2006) explained this effect by postulating that sH stability is controlled by methane occupancy of the 5^{12} cage, and thus increasing carbon dioxide concentrations tend to destabilize structure H (Uchida et al., 2006).

It is important to reiterate that previous analyses of the phase equilibrium of the system methane + carbon dioxide + neohexane + water were done based on initial vapor phase compositions and not equilibrium vapor phase compositions, which is incorrect. According to the Gibbs phase rule a four-phase, quaternary system at equilibrium has two degrees of freedom. Thus, by fixing two intensive variables
Table 3.1: Hydrate-liquid-vapor equilibrium Temperature $T$, Pressure $p$, and vapor-phase mole fraction of carbon dioxide $y_1$, for the system methane + carbon dioxide + water.

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<th>$p$/MPa</th>
<th>$10^2y_1$</th>
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Table 3.2: Hydrate-liquid,liquid$_{aq}$-vapor equilibrium Temperature $T$, Pressure $p$, and vapor-phase mole fraction of carbon dioxide $y_1$, for the system methane + carbon dioxide + neohexane + water.

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<th>$p$/MPa</th>
<th>$10^2y_1$</th>
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</table>
Figure 3.2: Hydrate-liquid-vapor equilibrium conditions for the system methane + carbon dioxide + water. Black, solid markers represent gas mixtures initially containing a mole fraction of 80 % CH$_4$ and 20 % CO$_2$; empty markers represent gas mixtures initially containing a mole fraction of 50 % CH$_4$ and 50 % CO$_2$. Triangles, this work; squares, Dholabhai and Bishnoi (1994); circles, Servio et al. (1999).
Figure 3.3: Hydrate-liquid-liquid_{aq}-vapor equilibrium conditions for the system methane + carbon dioxide + neohexane + water. Black, solid markers represent gas mixtures initially containing a mole fraction of 80 % CH\textsubscript{4} and 20 % CO\textsubscript{2}; grey, solid markers represent gas mixtures initially containing a mole fraction of 70 % CH\textsubscript{4} and 30 % CO\textsubscript{2}; empty markers represent gas mixtures initially containing a mole fraction of 50 % CH\textsubscript{4} and 50 % CO\textsubscript{2}. triangles, this work; circles Servio et al. (1999); dashes, Uchida et al. (2006).
such as temperature and pressure, the system is uniquely determined irrespective of initial compositions. This is more clearly seen in Figure 3.4 which is shown for illustrative purposes only.

Figure 3.4: Equilibrium surface for the system methane + carbon dioxide + neo-hexane + water constructed numerically from the experimental data in this work. The black ‘x’, ‘circle’ and ‘square’ are shown for illustrative purposes only and do not represent actual data. At a fixed temperature and pressure, the black ‘x’ represents an equilibrium four-phase point. At the same temperature and pressure the ‘circle’ and ‘square’ represent two possible initial, CO$_2$ vapor-phase mole fractions. The arrows pointed at the ‘x’ illustrate how the four-phase equilibrium point at a fixed temperature and pressure is unique and independent of the initial vapor phase composition.

In order to present the data in a theoretically sound, and easy to read format, experimental isotherms are presented below. Figure 3.5 shows equilibrium isotherms for the system methane + carbon dioxide + water. Since experimental isotherms are presented in this work, comparison with the literature was made with the only available experimental isotherm (Ohgaki et al., 1996) and with data points at the
same temperature as Ohgaki et al. (1996) from other researchers Servio et al. (1999; Adisasmito et al. 1991; Seo and Lee, 2001). The four data sets are in agreement within the estimated expanded uncertainties from this work. At constant temperature, increasing equilibrium concentrations of carbon dioxide in the vapor phase occur at lower equilibrium pressures. Figure 3.6 displays equilibrium isotherms for methane + carbon dioxide mixtures in the presence of water and neohexane. Comparison with Servio et al. (1999) work is done at the same temperature as in Figure 3.5. Agreement between both studies is observed within the estimated expanded uncertainties from this work.

The isotherms in Figure 3.6 show a trend opposite to those in Figure 3.5: at constant temperature, increasing equilibrium concentrations of carbon dioxide in the vapor phase occur at higher equilibrium pressures. This is more clearly seen by superimposing both sets of data (Figure 3.7). From Figure 3.7, it can be inferred that structure H equilibrium occurs at lower pressures and temperatures than sI when the vapor phase is methane rich; however, this phenomenon appears to be reversed as the equilibrium vapor phase becomes richer in carbon dioxide. The latter might explain why Uchida et al. (2006) observed structure I formation for a gas mixture initially containing a mole fraction of 70 % methane, the balance being carbon dioxide, in the presence of water and neohexane, at conditions below the expected equilibrium pressure and temperature for the same gas mixture in the presence of water only.

3.7 Conclusion

Four-phase equilibrium conditions (hydrate-liquid-liquid\textsubscript{aq}-vapor) and three-phase equilibrium conditions (hydrate-liquid-vapor) were determined for the systems: methane + carbon dioxide + neohexane + water and methane + carbon dioxide + water, respectively. The data presented here were found to agree with the available literature data within the uncertainties herein reported. Experimental isotherms were presented. It was observed that the equilibrium mole fraction of carbon diox-
Figure 3.5: Hydrate-liquid-vapor equilibrium isotherms for the system methane + carbon dioxide + water. Equilibrium, vapor-phase mole fraction of CO$_2$, $y_1$. Empty triangles, this work; stars, Ohgaki et al. (1996) at 280.3 K; black solid squares, Adisasmito et al. (1991) at 280.2 K; black solid circles Servio et al. (1999) at 280.1 K; Crosses, Seo and Lee (2001) at 280.2 K. The curves connecting the experimental data were drawn to increase the readability of the graph; curve fitting should not be inferred.
Figure 3.6: Hydrate-liquid-liquid$_{aq}$-vapor equilibrium isotherms for the system methane + carbon dioxide + neohexane + water. Equilibrium, vapor-phase mole fraction of CO$_2$, $y_1$. Triangles, this work; circles, Servio et al. (1999) at 280.6 K. The curves connecting the experimental data were drawn to increase the readability of the graph; curve fitting should not be inferred.
Figure 3.7: Black triangles, Hydrate-liquid-liquid\textsubscript{aq}-vapor equilibrium isotherms for the system methane + carbon dioxide + neohexane + water. Empty triangles, hydrate-liquid-vapor equilibrium isotherms for the system methane + carbon dioxide + water. Equilibrium, vapor-phase mole fraction of CO\textsubscript{2}, $y_1$. The curves connecting the experimental data were drawn to increase the readability of the graph; curve fitting should not be inferred.
ide in the vapor phase follows opposite trends in both systems, with respect to equilibrium pressure, at constant temperature. The data also suggest that structure H equilibrium occurs at lower pressures and temperatures than sI when the vapor phase is methane rich; however, this phenomenon appears to be reversed as the equilibrium vapor phase becomes richer in carbon dioxide.

3.8 Supporting Information Available

Representative raw data plot (Figure 3.8), showing temperature and pressure readings leading to the determination of a three-phase or a four-phase equilibrium point.
Figure 3.8: Representative, raw data leading to the determination of one of the equilibrium points for three-phase hydrate-liquid-vapor equilibrium of the system methane + carbon dioxide + water, for a gas mixture initially containing a mole fraction of 80 % CH\textsubscript{4} and 20 % CO\textsubscript{2}. Crosses, Pressure; triangles, Temperature; \( t \), elapsed time since the beginning of the experiment (the first pressure and temperature readings corresponding to \( t = 0 \) min, were intentionally shifted by 5 minutes to increase the readability of the graph). The equilibrium point corresponds to the average of the last two temperature and pressure readings, in this case leading to: \( T_{\text{avg}} = 283.38 \) K and \( p_{\text{avg}} = 6.16 \) MPa. The same type of plot could be prepared for any other of the three-phase conditions studied or for the determination of any of the equilibrium points for the four-phase hydrate-liquid-liquid\textsubscript{aq}-vapor equilibrium for the system methane + carbon dioxide + neo-hexane + water.
Chapter 4

Three-Layered Methane Clathrate and Implications for Hydrate Propagation

4.1 Preface

After having acquired experience with clathrate systems and high-pressure equipment (Chapter 3), the design of a custom-made reactor that would allow for direct observation of hydrate phenomena in water films was undertaken. A technical drawing of the high-pressure crystallizer is presented in Appendix A. Together with the novel experimental setup, a unique technique was developed in order to observe methane clathrates as they form on water films. The application of this viewing technique revealed several features of hydrate morphology that were previously unknown.

\footnote{To be submitted to the \textit{AIChE Journal}.}
4.2 Abstract

Methane clathrate formation on water films without previous hydrate formation history was studied with the aid of high resolution video microscopy. It was found that hydrates form in two layers, each with a clearly distinct morphology. As the clathrate aged this difference in morphology tended to disappear giving way to a rough surface, uniform throughout the hydrate film. Higher driving forces produced smaller hydrate grains and smoother surfaces than lower driving forces within the water film. The converse was true for hydrate formed on the periphery. A third hydrate layer growing outside of the original water boundary was also observed. It was shown for the first time that this growing front could create a “bridge” between segregated water droplets and thus induce nucleation. Hydrate reformation was also studied and it was found that it proceeded in a different manner than that of a system without previous clathrate formation history. For reformation, nucleation occurred within the film and a circular hydrate front(s) with uniform morphology advanced towards the periphery of the water film. Dissociation started at the perimeter of the hydrate layer and proceeded until gas bubbles were observed within the film; moreover, as hydrate decomposition became ubiquitous water was seen to recede until it regained its original shape.

4.3 Introduction

Clathrate hydrates are non-stoichiometric, crystalline compounds that form when small molecules come in contact with water at appropriate temperatures and pressures. The terms “gas hydrates” and “clathrate hydrates” are now used interchangeably to designate this kind of compounds (Englezos 1993). Natural-gas hydrates are abundantly found in the ocean bottom, and to a lesser extent in permafrost regions (Sloan 2003). Conservative estimates suggest that the amount of energy stored in natural hydrates is at least twice that of all other fossil fuels combined (Kvenvolden 2002). In addition, trapping carbon dioxide as a hydrate in the bottom of the ocean has been proposed as an alternative to reduce increasing atmospheric CO\textsubscript{2} concentration (Brewer 2000). Hydrates may also play a key role in the global carbon cycle (Kvenvolden 2002) and could constitute an alternative mean to transport natural
Morphology studies increase our understanding of hydrate nucleation, growth and dissociation mechanisms, thus allowing us to develop appropriate models for these processes. Pioneering morphology work was done by Makogon and co-workers (1997) and by Maini and Bishnoi (1981). Other early observational studies include that of Mori and Mori (1989b,a) on refrigerants, that of Hwang et al. (1990) on methane hydrate formed from ice supported on stainless-steel discs and that of Long and Sloan (1996) on methane and CO\textsubscript{2} hydrate grown inside a sapphire tube.

Sugaya and Mori (1996) presented one of the first studies on hydrates formed from bubbles of a fluorocarbon immersed in water; it was found that the surface morphology of the hydrate layer formed at the interface depends strongly on the degree of saturation of the water phase with the guest component. Ohmura and Mori (1999) expanded the study of Sugaya and Mori (1996) to include a different type of refrigerant; in addition, it was hypothesized that a concentration driving force could explain the differences in morphology observed at high and low driving forces. The crystal-growth behavior of structure I, structure II and structure H was described by Smelik and King (1997); it was proposed that the characteristic crystal morphology of each structure could be used to identify hydrate types \textit{in situ}.

Uchida and co-workers have published a number of articles on the morphology of CO\textsubscript{2} hydrate (1996; 1999; 2000b; 2002). The first paper focused on determining the interfacial tension between liquid CO\textsubscript{2}, water and hydrate, yet illustrations of their observations were also provided (Uchida and Kawabata, 1996). Later on, still frames of video recordings of hydrate formation on water droplets suspended in liquid CO\textsubscript{2} were presented (Uchida et al., 1999). It was concluded that hydrates formed initially at the interface between the two fluids and proceeded until complete coverage of the water droplet; on some occasions secondary nucleation was also observed inside the water droplet (Uchida et al., 1999). Uchida et al. (2002) measured the lateral growth rates of CO\textsubscript{2} hydrate films on water bubbles to range from 6 to 15 mm/s, and concluded that sub cooling was the parameter that highly determined the growth rate of the crystal.
Servio and Englezos (2003) studied the morphology of methane and carbon dioxide hydrates formed on nearly spherical, adjacent water droplets. It was found that the type of hydrate guest did not have an effect on the crystal morphology. It was also reported that hydrate nucleation would occur almost instantaneously in all droplets after one of them had nucleated, and it was suggested that an imperceptible water “bridge” between the droplets was the plausible explanation for this phenomenon (Servio and Englezos, 2003). Furthermore, when hydrates were formed at high driving forces water droplets were observed to become jagged, and numerous needle-like crystals were seen to extend away from the water surface into the gas phase. This was not the case at low driving force, where the hydrate surface was observed to be smooth and shiny (Servio and Englezos, 2003).

Perhaps the most successful systematic approaches to correlate the observed clathrate morphology with the corresponding driving force have been put forward by Ohmura and co-workers (1999; 2004; 2005; 2009). Based on hypothesized concentration differentials between the liquid phase near the newly formed hydrate and the liquid bulk concentration, they were able to match images to their proposed driving force (Ohmura and Mori, 1999; Ohmura et al., 2004, 2005). Very recently, the same group used sub cooling as an indicator for the driving force of the system; through this index it was then possible to correlate the driving force with the observed hydrate morphology (Tanaka et al., 2009). As a general trend it was observed that sub coolings $\geq 3$ K produced sword-like crystals whereas at smaller sub cooling, polygonal faces appeared, the size of the latter increasing with decreasing sub cooling (Tanaka et al., 2009).

Ohmura and Mori (1999) worked with liquid droplets of refrigerant R-141b ($\text{CH}_3\text{CCl}_2\text{F}$) in water and distinguished two stages of hydrate-crystal growth, which were very different from each other. The primary stage was characterized by lateral growth of a thin, fine-grained polycrystalline layer along the surface of each R-141b drop; the secondary stage began typically after 10 min and lasted for several hours: it was characterized by radial growth of plate-like crystals growing from the outer surface of the hydrate shell formed in the primary stage (Ohmura and Mori, 1999).
The second stage was never observable with pure water (not presaturated) and/or at a small sub cooling. Ohmura and Mori (1999) also observed that the hydrate surface formed in non-presaturated water smoothed over time. In subsequent work Ohmura et al. extended the study done on presaturated water to other hydrate formers including carbon dioxide (2004) and methane (2005). With carbon dioxide it was observed that when sub cooling was greater than 3 K, a hydrate film first grew along the carbon dioxide-water interface; then hydrate crystals with dendritic morphology grew into the liquid-water phase from that hydrate film (Ohmura et al., 2004). With sub coolings less than 2 K it was found that dendritic crystals were replaced by skeletal or polyhedral crystals (Ohmura et al., 2004). Similar conclusions were presented for the methane-water system (Ohmura et al., 2005).

Using laser interferometry Ohmura et al. (2000) measured the thickness of a R-134a (CH₂FCF₃) hydrate film and concluded that initially the film could be as thick as 80 μm. Hirai et al. (2000), Kobayashi et al. (2001) and Freer et al. (2001) have studied growth of hydrate films. The former (Hirai et al., 2000) and the latter (Freer et al., 2001) measured velocities of the advancing hydrate film for CO₂ and methane respectively by successively recording images. Hirai et al. (2000) reported that lateral growth rates could vary from 0.044 mm/s at 284.2 K and 39.2 MPa to 6.5 mm/s at 278.7 K and 39.2 MPa for CO₂ hydrate. Freer et al. (2001) determined methane hydrate growth rates varying from 20 μm/s at 3.55 MPa and 1°C to 690 μm/s at 9.06 MPa and 1°C.

The objective of this work was to provide new insights on the mechanism of gas hydrate formation in unstirred systems. The novel experimental design coupled with high-resolution video microscopy allowed for detailed morphological observation of the initial stages of clathrate formation, as well as aging and dissociation of hydrates in water films. Furthermore, the observed layered structure of hydrates formed on water films was found to have interesting implications for hydrate propagation.
4.4 Experimental Procedure

The experimental design enabled the observation, with the aid of a microscope, of a nearly planar water film resting on a glass slide, immersed in a methane atmosphere under controlled temperature and pressure. The heart of the setup was a 316 stainless steel cell, fitted with two sapphire windows on the top and bottom (Figure 4.1). The cell had several ports used as follows: to feed gas, to purge gas out of the cell, to insert a thermocouple, and to communicate pressure to a pressure transducer. Temperature was measured with a type K mini thermocouple probe (± 1 K), (Omega Engineering, QC Canada). Pressure was monitored with a Rosemount 3051S pressure transducer (Rosemount, MN USA) with an accuracy of ± 0.1 % of the span. A copper coil, wound around the high pressure cell, and connected to a Neslab RTE740 refrigerated bath (Fisher Scientific, Canada) was used to circulate a mixture of ethylene glycol and water (50/50, V/V) to provide the cooling necessary to reach hydrate forming conditions. A Schott KL 2500 (Optikon Corporation, ON Canada) cold light source fitted with an articulated light pipe illuminated the interior of the reactor through the bottom window. Images were acquired with a PCO.2000 (Optikon Corporation, ON Canada) high-resolution video camera fitted to a configuration of KC Infinity lenses (Optikon Corp, ON Canada) that allowed an optical magnification of up to 5×. The video camera, the temperature signal, and the pressure signal were connected to a personal computer in order to acquire and analyze the data. The high pressure cell, the video camera and the light source were mounted on an optical table in order to minimize the effect of environmental vibration.

Before starting an experiment a new, pre-cleaned, microscope glass slide was cut to fit inside the high pressure cell (Figure 4.1). A drop (35 µL) of distilled, deionized water was deposited on the glass slide. Methane gas, 99.99 % purity (MEGS, QC Canada), was then fed to the reactor and the cell content was purged several times to remove any air inside the reactor. After purging, the pressure in the reactor was increased well above the hydrate-liquid-vapor equilibrium line for methane until hydrate nucleation was observed. The experimental conditions for
Figure 4.1: Simplified schematic of the experimental apparatus.
Table 4.1: Experimental conditions for hydrate formation on water films without previous hydrate formation history.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>T/K</th>
<th>p/MPa</th>
<th>Growth beyond water boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>274</td>
<td>8.2</td>
<td>Yes</td>
</tr>
<tr>
<td>2</td>
<td>274</td>
<td>8.2</td>
<td>Yes</td>
</tr>
<tr>
<td>3</td>
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<td>Yes</td>
</tr>
<tr>
<td>4</td>
<td>275</td>
<td>4.0</td>
<td>Yes</td>
</tr>
</tbody>
</table>

hydrate formation are summarized in tables 4.1 and 4.2. A hydrate formation experiment was terminated when it became apparent that no liquid water was left on the microscope slide. At this point, a dissociation experiment was initiated by slowly decreasing the pressure inside the reactor through the purge port down to a preset value, and maintained constant thereafter. A dissociation experiment was terminated after having left the reactor for several hours at a pressure well below the gas hydrate stability region. An aging experiment consisted in observing the evolution of formed hydrates while keeping the system well within the hydrate stability region at constant temperature and pressure.

### 4.5 Results and Discussion

#### 4.5.1 Nucleation and Growth

Figure 4.2 presents a sequence of still frames of hydrate nucleation and growth ($T = 275$ K, $p = 3.6$ MPa) on a water film with no previous hydrate formation history. The intact water surface, prior to nucleation, can be seen in figure 4.2a. Nucleation occurred on the periphery of the water film first; hydrate appeared as a whiskery structure that grew towards the center of the water film (figure 4.2b). While clathrate growth proceeded from the edge towards the center, keeping a whiskered appearance, new nucleation sites became visible as white spots within
Table 4.2: Experimental conditions for hydrate reformation on water films.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$T$/K</th>
<th>$p$/MPa</th>
<th>Growth beyond water boundary</th>
</tr>
</thead>
<tbody>
<tr>
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<td>8.2</td>
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</tr>
<tr>
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<td>Yes</td>
</tr>
<tr>
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<td>8.3</td>
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</tr>
<tr>
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<td>275</td>
<td>8.3</td>
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</tr>
<tr>
<td>5</td>
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</tr>
<tr>
<td>10</td>
<td>276</td>
<td>8.3</td>
<td>Yes</td>
</tr>
</tbody>
</table>

the water film (figure 4.2c). Hydrate propagation continued from the periphery and from the center (figure 4.2d), eventually covering the whole water film (about 3 cm$^2$) in less than fifteen seconds (figure 4.2e). Following complete hydrate coverage of the water surface, a considerably slower process was observed: the growth of a hydrate layer outside of the original water boundary (figure 4.2f). The growth of this layer was observed both at low driving forces and high driving forces (figure 4.3).

A detailed view of this layer can also be seen to the right of figure 4.4. Although morphologically different, a similarly slow phenomenon was reported previously where dendrites protruded out of bubbles that had been covered with a hydrate layer (Ohmura and Mori (1999); Servio and Englezos (2003); Uchida et al. (1999)). The observed whiskery structures seem to agree well with the results of Uchida et al. (1999), where hydrate was first detected as crystal facets growing from the edge of a pendant water bubble in contact with a hydrophilic surface. Although Uchida et al. (1999) also reported growth of a secondary hydrate film on a water bubble, their findings contrast with the morphology of the secondary nucleation observed in this work which proceeded in a spotted pattern (figure 4.2c to figure 4.2d). Fur-
Figure 4.2: Hydrate formation and growth on a water film with no previous hydrate formation history. $T = 275$ K, $p = 3.6$ MPa. (a) Water film before hydrate formation. (b) $t = 0$ s, nucleation occurs at the periphery of the film; newly formed clathrate appears as a white whiskered layer. (c) $t = 2.5$ s, growth of the hydrate from the edges towards the center of the water film. New nucleation sites appear in the center of the water film as white spots. (d) $t = 6$ s, the spotted hydrate and the whiskered hydrate continue to grow. (e) $t = 14.5$ s, clathrate propagates until covering the water film completely. (f) $t = 42.5$ s, bottom right, hydrate extends outside of the original water boundary.
Figure 4.3: Water films completely covered by hydrate at low driving force (left) and high driving force (right). Three clearly different regions are appreciable: interior of the film, periphery of the same and clathrate extending outside of the original water boundary. (a) Nucleation and growth occurred at $T = 275$ K, $p = 3.6$ MPa. (b) Nucleation and growth occurred at $T = 274$ K, $p = 8.2$ MPa.
Figure 4.4: Detail of the original water boundary after hydrate formation at low driving force (left) and high driving force (right). Three layers can be clearly distinguished (only two shown in (a)). Translucent layer: hydrate growing outside of the original water boundary. Light gray: hydrate formed in the periphery. Darker gray: hydrate formed within the water film. (a) Hydrate formed at $T = 275$ K, $p = 3.6$ MPa. (b) Hydrate formed at $T = 274$ K, $p = 8.2$ MPa.
thermore, the possibility of having two clearly different types of morphology during clathrate formation contrasts with previous reports, where a unique morphology was attributed to a fixed driving force (Ohmura et al. 2005; Tanaka et al. 2009).

Figure 4.3 shows water films covered completely by hydrate. In figure 4.3b nucleation and hydrate growth occurred at a much higher driving force \( (T = 274 \text{ K}, p = 8.2 \text{ MPa}) \) than in figure 4.3a \( (T = 275 \text{ K}, p = 3.6 \text{ MPa}) \). Hydrate growth proceeded in a similar fashion at high and low driving forces, however the process was much faster at high driving force where complete water film coverage was achieved in less than 3 s (figure 4.3b).

Comparison of figure 4.3a and figure 4.3b reveals three common features. First, the water boundary has a clear effect on the morphology of newly formed hydrates. Second, two types of morphology can be clearly seen in the water films covered with hydrate: one within the film and another one in the periphery of the same. Third, the clathrate extends beyond the original water boundary. Two clear differences can also be appreciated. First, the high driving force nucleation shows a rather smooth surface (figure 4.3b) whereas a striated pattern is observed at low driving force (figure 4.3a). Second, the hydrate annulus on the periphery is about twice the width at high driving force (figure 4.3b) than that at low driving force (figure 4.3a). Enlarged views of the periphery of the formed hydrate (figure 4.4a and figure 4.4b) reveal further details of the morphology of high and low driving force formation.

Figure 4.4 presents a detailed view of the layers that can be observed after hydrate formation at high and low driving force. In figure 4.4b the translucent structure corresponds to the hydrate layer that grew outside of the original water boundary, the somewhat darker formation corresponds to the clathrate that crystallized in the periphery of the water film and the black granular morphology is characteristic of the hydrate that formed within the water film. Figure 4.4a shows two of the three observed hydrate layers (figure 4.3a) at low driving force (layer growing outside of the hydrate boundary not shown). The morphology of the newly formed hydrate layer growing outside of the water boundary was very similar both at high and low driving force, being rather smooth and translucent (right of figure 4.4b).
There was a clear effect of the water boundary both at high and low driving force, producing a particular morphology on the film periphery; however, at low driving force (figure 4.4a) this annulus was smoother and narrower than at higher driving force (figure 4.4b). The contrary seemed to be true for the inside of the hydrate film where coarse grains were observed at low driving force (figure 4.4a) and finer grains at high driving force (figure 4.4b). The larger width of the edge morphology as well as the smaller grain size at high driving force are indicative of the higher speed at which hydrate growth occurred. Furthermore, coarser grains suggest fewer nucleation points within the film at lower than at higher driving force. At lower driving force grains are allowed to grow to a certain extent before meeting each other (figure 4.2c to figure 4.2e and figure 4.4a). At high driving forces nucleation sites can be numerous (Mullin, 1997) which would explain the smaller grain size observed at high driving force (figure 4.4a).

The effect of the driving force on the morphology of the clathrate formed at the edge of the water film (figure 4.4a and figure 4.4b) seems to agree with the results of Servio and Englezos (2003) where the high driving force produced a rougher hydrate surface. However, the images acquired in this study showed the effect was reversed for the morphology of the interior of the water film: lower driving forces resulted on a rougher surface (figure 4.4a and figure 4.4b). The latter is more in accord with the results of Tanaka et al. (2009).

4.5.2 Aging

By focusing on a particular region near the edge of the water surface, it was possible to observe the evolution of the formed hydrate over a period of three days (Figure 4.5). Figure 4.5a shows both the interior and the edge of the formed hydrate 20 min after complete coverage of the water surface. Two different morphologies are clearly appreciated: a smooth shiny hydrate formed at the edge, while coarse darker grains were observable away from the original water boundary (figure 4.5a). After 20 h the grain boundaries and the difference between the interior and the periphery of the formed hydrate was less evident; grain boundaries were also less pronounced
Figure 4.5: Aging effect on hydrate formed on a water film with no previous hydrate formation. $T$ and $p$ were kept at 275 K and 8.0 MPa. $t$ refers to the elapsed time after nucleation was observed. (a) $t = 20$ min, hydrate that forms near the film edge appears smooth and shiny; towards the interior grain boundaries are evident. (b) $t = 20$ h, grain boundaries and the edge effect observed in (b) become less evident. (c) $t = 51$ h, the edge and interior morphologies become almost indiscernible, slight depressions appear on the surface. (d) $t = 76$ h, only one morphology shows on the hydrate film, grain boundaries have disappeared and small depressions cover the entire surface.
A comparable smoothing phenomenon has been reported previously by Sugaya and Mori (1996) for fluorocarbons, by Uchida et al. (1999) for CO$_2$ and by Ohmura and Mori (1999) for CH$_3$CCl$_2$F. Figure 4.5b shows how edge and interior morphologies were almost indiscernible 51 h past hydrate formation, in addition grain boundaries were hardly noticeable and slight depressions appeared on the whole surface. After 76 h, small depressions covered the whole hydrate surface and a uniform morphology was seen throughout; grain boundaries were not perceptible (figure 4.5d).

### 4.5.3 Reformation

Hydrate reformation (i.e. clathrate formation on films with previous hydrate formation history) proceeded in an entirely different manner than that of clathrates formed from water with no previous history of hydrate formation. Methane bubbles were always present prior to reformation, product of the preceding dissociation (top left, figures 4.6b and 4.6c). Reformation commenced from a localized point or...
points within the water film (Figure 4.6a), and advanced as a circular front(s) until reaching the edge of the water surface (Figures 4.6b and 4.6c). The type of morphology shown in figure 4.6 seems alike to the one previously shown by Freer et al. (2001). As was the case with hydrate formation from water films with no previous hydrate formation history, a translucent hydrate layer grew out of the original water boundary (bottom right 4.6c), although at a much slower rate than that within the water surface. Only one type of morphology was evident from reformation experiments inside the original water boundary, in contrast to the results of formation experiments performed on water with no previous hydrate formation history.

4.5.4 The “Bridge Effect”

As mentioned in the introduction, Servio and Englezos (2003) observed almost simultaneous hydrate nucleation in adjacent water droplets, and attributed this phenomenon to an imperceptible water “bridge” that allowed communication across the polytetrafluoroethylene surface on which their water droplets were placed. Here, the growth beyond the original water boundary observed for both formation with and without previous hydrate formation history (Figures 4.3, 4.4b and 4.6c) suggests that this “bridge effect” is probably due to growth of the clathrate on a foreign surface free from water (glass in this case). The “bridge effect” was clearly observed by examining the nucleation and propagation of methane hydrate in segregated water droplets. Figure 4.7a shows newly formed hydrate (black) on the broadest, water-covered region that appears in the micrograph’s field of view; an almost imperceptible halo (figure 4.7a and figure 4.8a), corresponding to an advancing hydrate front, surrounds the black hydrate boundary. As the hydrate halo grows outside of the water boundary, it induces nucleation in a water bubble (figure 4.7b). Clathrate propagation within a water droplet that has just nucleated can be seen from figure 4.7c to 4.7d. Hydrate halos that grow outside of nucleated water-boundaries induce nucleation in other water droplets (figure 4.7e, 4.7f, and 4.7g and enlarged view in figure 4.8b).

Figure 4.7 and Figure 4.8 show a representative example of similar experiments
conducted several times. For this experiment in particular, hydrate nucleation and growth was conducted at 8.2 MPa and 276 K. For all runs, it was observed that clathrate nucleation occurred first on the most extensive water region, and then it spread as hydrate halos formed “bridges” between nucleated and un-nucleated water droplets as described above.

4.5.5 Dissociation

Dissociation proceeded in a similar manner in spite of the history of the hydrate film: formed from water with or without previous hydrate formation or aged. Figure 4.9 presents a representative sequence, The intact hydrate surface is shown on figure 4.9a; the layered structure clearly appreciable. The lighter shade corresponds to the original water boundary. To the right of the latter the hydrate film that extended out of the same boundary can be seen. On the top left dark granular hydrate formed within the original water film is observed. Hydrate dissociation did not become evident until several seconds after decreasing the pressure from \( p = 8.2 \) MPa and \( T = 274 \) K to \( p = 2.0 \) MPa and \( T = 273 \) K. Crystal decomposition started at the periphery and spread towards the center (figure 4.9b). Widespread dissociation led to the appearance of a hydrate water-slurry; (figure 4.9c). As the slurry thinned down individual clathrate crystals were observable and retraction of the water film became apparent (figure 4.9d). As massive amounts of bubbles appeared the water film continued to retract (figure 4.9e). The water film retraction ceased after about a minute of having reduced the pressure, regaining its original shape. Finally methane bubble migration and agglomeration near the center of the water film were also apparent (figures 4.9f).

4.6 Conclusion

For methane clathrates formed from water films without previous hydrate formation history it was found that hydrate nucleation occurred on the periphery of a film first; secondary nucleation occurred within the water film, and the crystals thus formed
Figure 4.7: Still frames of a hydrate propagation video sequence. (a) $t = 0$ s, hydrate appears dark after forming in a water film. The almost imperceptible halo observed around the dark hydrate corresponds to a growing clathrate film outside of the water boundary. (b) $t = 3$ s, as soon as the growing hydrate halo touched a new water bubble nucleation occurred. (c) $t = 4$ s, halo from the bubble that nucleated in (b) induces nucleation in another bubble. (d) $t = 8$ s, Hydrate growth within the water film that nucleated in (c). (e) $t = 9$ s, nucleation induced in two new water bubbles. (f) $t = 11$ s, Newly induced nucleation.
had a completely different morphology than that of the ones formed on the water edge. This difference in morphology tended to disappear over time, giving way to a rough surface uniform throughout the hydrate film. Higher driving forces produced smaller hydrate grains and smoother surfaces than lower driving forces within the water film; the converse was true for hydrate formed on the periphery. Furthermore, a third layer that grew outside of the original water boundary displaying yet another morphology was observed. Images suggested that this third layer could grow on water-free glass, and thus was capable of communicating nucleation from one water covered region to another. Hydrate reformation proceeded in a different manner than that of clathrates formed from water without previous hydrate formation history: nucleation occurred within the film and a circular hydrate front(s) with uniform morphology advanced towards the periphery of the water film. Dissociation progressed in a similar manner in spite of whether the hydrate was formed from water with or without previous clathrate formation: decomposition started on the periphery and proceeded until gas bubbles were observed within the film;

Figure 4.8: Detail of hydrate propagation by the bridge effect. Hydrate appears dark after forming in a water film. (a) A clathrate halo that grew out of the water boundary is about to touch two water bubbles. (b) After one second, the hydrate halo reaches the two water bubbles and induces nucleation.
Figure 4.9: Dissociation of a layered hydrate film. (a) Intact layered hydrate structure \((T = 274 \text{ K}, p = 8.2 \text{ MPa})\). The bottom right of the figure corresponds to the original water boundary; directly opposed, black granular hydrate can be observed. (b) Hydrate dissociation became evident 22 s after reducing the pressure to \(p = 2.0 \text{ MPa}, T = 273 \text{ K}\). (c) Widespread hydrate dissociation led to the appearance of a hydrate-water slurry 26 s after reducing \(p\). (d) The water-hydrate slurry thinned down until individual hydrate crystals were observable 30 s after reducing \(p\). Retraction of the water film boundary became apparent. (e) 64 s after reducing \(p\) massive amounts of methane bubbles appeared and retraction of the water film boundary continued. (f) \(t = 100 \text{ s}\), water retraction completed and agglomeration of methane bubbles; no hydrate crystals were observable at this point.
moreover, as dissociation became ubiquitous within the film, water receded until the water film regained its original shape and gas bubbles agglomerated in the center of the water film.
Chapter 5

Engulfing of Silica Gel Particles by an Advancing Methane Clathrate Front\textsuperscript{1}

5.1 Preface

Having studied methane clathrates formed from thin water films (Chapter 4) introducing particles into the system seemed like a reasonable next step considering hydrates interact with particulate matter in nature (\textsuperscript{2}2.4.1). The results of such study follow.

5.2 Abstract

The formation and decomposition of methane clathrate in water films containing randomly dispersed particles of silica gel were studied. It was observed that the hydrate front engulfed the silica particles as it advanced at a relatively constant velocity of approximately 300 $\mu$m/s compared to 700 $\mu$m/s for a silica-free, methane + water system under the same conditions. In ad-

\textsuperscript{1}To be submitted to the \textit{Journal of Crystal Growth}. 
dition, it was found that the growing clathrate could push a methane bubble and that grain boundary healing could occur after the clathrate contacted a silica particle. Dissociation was found to proceed through two different mechanisms. In the first, decomposition developed gradually until a hydrate-water slurry was observable, subsequently the slurry thinned down until very few crystallites remained visible in the bulk liquid phase. The second type of dissociation began catastrophically by a sudden fracture in the clathrate. However, the ensuing decomposition occurred as in the first mechanism.

5.3 Introduction

Clathrate hydrates are non-stoichiometric, crystalline compounds that form when small molecules come in contact with water at appropriate temperatures and pressures. The terms “gas hydrates” and “clathrate hydrates” are now used interchangeably to designate this kind of compounds (Englezos, 1993). Natural-gas hydrates are abundantly found in close interaction with marine sediments, and to a lesser extent in permafrost regions. Conservative estimates suggest that the amount of energy stored in natural hydrates is at least twice that of all other fossil fuels combined (Kvenvolden, 2002). In addition, trapping carbon dioxide as a hydrate in the bottom of the ocean has been proposed as an alternative to reduce increasing atmospheric CO$_2$ concentration (Brewer, 2000). Our ability to exploit the immense potential of hydrates, whether it be as an energy source or as way to sequester CO$_2$, depends greatly on our understanding of clathrates in natural settings, and an important part of this corpus of knowledge is the behavior of these crystals in the presence of particles. While the hydrate phenomenon at the hydrate-liquid interface has been investigated extensively, the interaction between such an interface and foreign particles present in the melt, as a separate phase, has not received as much attention. Yet observational studies of this kind are of paramount importance in order to obtain information about mechanisms of hydrate formation and dissociation.

With the aid of an optical microscope, glass micro models have been used to study tetrahydrofuran, methane and CO$_2$ hydrate forming inside an asymmetric
porous network etched into glass micro models (Tohidi et al., 2001). The idea was further pursued using a symmetric network of straight micro channels to study both CO_2 (Katsuki et al., 2006) and methane hydrates (Katsuki et al., 2007, 2008). Cryogenic scanning electron microscopy has also been used to compare artificial methane hydrate + quartz aggregates synthesized from melting ice to natural gas hydrates (Stern et al., 2004; Stern and Kirby, 2008). Other imaging techniques such as nuclear magnetic imaging (Mork et al., 2000; Seo et al., 2005; Kvanne et al., 2007; Ersland et al., 2008) and X-ray computed tomography (Uchida et al., 2000a; Jin et al., 2004; Kneafsey et al., 2007; Jones et al., 2007) have been utilized as well.

Of particular concern here was whether growing methane hydrate would push or engulf particles. The importance of this phenomenon in soil mechanics and permafrost behavior has been recognized for ice (Jackson and Chalmers, 1958; Corte, 1962). Engulfment of a particle is predicted when the free energy for the process of inclusion is less than zero (Omenyi and Neumann, 1976). When the contrary is true, rejection or pushing of the particle by the advancing solid front is expected. However, there is a kinetic limit for this thermodynamic consideration, a critical velocity above which an advancing front will engulf particles independent of the thermodynamic prediction (Uhlmann and Chalmers, 1964). Mork et al. (2000) speculated that growing tetrahydrofuran clathrate could push sand particles apart upon formation and Nagashima et al. (2008) observed both pushing and engulfing of particles in contact with THF hydrates.

This paper reports on a first attempt to observe methane hydrate formation and decomposition while in close interaction with granular material with the aid of high resolution video microscopy.

5.4 Experimental Apparatus and Procedure

The heart of the setup was a 316 stainless-steel cell, fitted with two sapphire windows on the top and bottom (Figure 5.1). The cell had several ports used as follows: to feed gas, to purge gas out of the cell, to insert a thermocouple, and to communicate
pressure to a pressure transducer. Temperature was measured with a type K mini

thermocouple probe (± 1 K), (Omega Engineering, QC Canada). Pressure was monitored with a Rosemount 3051S pressure transducer (Rosemount, MN USA) with an accuracy of ± 0.1% of the span. A copper coil, wound around the high pressure cell, and connected to a Neslab RTE740 refrigerated bath (Fisher Scientific, Canada) was used to circulate a mixture of ethylene glycol and water (50/50, V/V) to provide the cooling necessary to reach hydrate forming conditions. A Schott KL 2500 (Optikon Corporation, ON Canada) cold light source fitted with an articulated light pipe illuminated the interior of the reactor through the bottom window. Images were acquired with a PCO.2000 (Optikon Corporation, ON Canada) high-resolution

Figure 5.1: Simplified schematic of the experimental apparatus.
video camera fitted to a configuration of KC Infinity lenses (Optikon Corp, ON Canada) that allowed an optical magnification of up to $5 \times$. The video camera, the temperature signal, and the pressure signal were connected to a personal computer in order to acquire and analyze the data. The high pressure cell, the video camera and the light source were mounted on an optical table in order to minimize the effect of environmental vibration.

Before starting an experiment, a new pre-cleaned microscope slide was cut to fit inside the high pressure cell (Figure 5.1). A very small amount (2 mg) of silica gel (Davisil 636 from Sigma-Aldrich), 250 to 500 µm in diameter and with an average pore size of 6 nm (as quoted from the manufacturer), was then put on the microscope slide and randomly dispersed as evenly as possible to form a loosely packed layer. Subsequently, enough water (35 µL) to cover the silica particles completely was deposited on the glass slide. Methane gas, 99.99% purity (MEGS, QC Canada), was then fed to the reactor and the cell content was purged several times to remove any air inside the reactor. After purging, the pressure in the reactor was increased well above the hydrate-liquid-vapor equilibrium line for methane until hydrate nucleation was observed. In order to attenuate for the memory effect on the system, clathrates were reformed at least once before starting to record data. A hydrate formation experiment was terminated when it became apparent that no liquid water was left on the microscope slide. At this point, a dissociation experiment was begun by slowly decreasing the pressure inside the reactor through the purge port down to a preset value, and maintained constant thereafter. A dissociation experiment was terminated after having left the reactor for several hours above the freezing point of water, and at a pressure well below the gas hydrate stability region.

5.5 Results and Discussion

5.5.1 Formation

The experimental conditions for hydrate formation in the presence or absence of silica gel are summarized in table 5.1. Figures 5.2a and 5.2b show the starting
Figure 5.2: Advancing hydrate front with and without silica particles. (a) Starting point of a silica-free experiment. The water film appears light gray, methane bubbles can be seen in the top left. \( T \) and \( p \) were kept constant at 275 K and 8.4 MPa: (b) \( t = 0 \) s, hydrate grows in a circular fashion (c) \( t = 2 \) s, advancement of the clathrate front continues towards the water film boundary. (d) \( t = 4 \) s, eventually the whole water surface is covered with hydrate. (e) Starting point of an experiment with silica particles: silica gel grains covered with water before hydrate formation. Water appears light gray under the lighting conditions. \( T \) and \( p \) were kept constant at 275 K and 8.0 MPa: (f) Advance of thehydrate film 2 s after nucleation. (g) The hydrate film engulfs the silica particles as it grows, 6 s after nucleation. Surface coverage was completed 12 s after nucleation. (h) Silica grains completely engulfed by methane clathrate 26 s after nucleation.
Table 5.1: Experimental conditions for hydrate reformation in the presence and the absence of silica gel.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Silica Present</th>
<th>$T$/K</th>
<th>$p$/MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Yes</td>
<td>275</td>
<td>8.0</td>
</tr>
<tr>
<td>2</td>
<td>Yes</td>
<td>275</td>
<td>8.2</td>
</tr>
<tr>
<td>3</td>
<td>Yes</td>
<td>277</td>
<td>8.0</td>
</tr>
<tr>
<td>4</td>
<td>No</td>
<td>275</td>
<td>8.4</td>
</tr>
<tr>
<td>5</td>
<td>No</td>
<td>275</td>
<td>8.3</td>
</tr>
<tr>
<td>6</td>
<td>No</td>
<td>275</td>
<td>8.3</td>
</tr>
</tbody>
</table>

point of hydrate formation experiments in the absence and presence of silica gel, respectively. Under the lighting conditions water appears light gray. In both cases clathrate formation was first evinced by the appearance of a gray translucent film on the water surface (Figures 5.2b and 5.2f). The hydrate front advanced rapidly on the water film without silica particles at an estimated, relatively constant velocity of roughly 700 $\mu$m/s (Figure 5.2b to d) whereas the hydrate front in the presence of silica particles moved at a slower pace of approximately 300 $\mu$m/s (Figure 5.2f to h). The introduction of particles in the methane + water system did not induce morphological changes in the growing clathrate. Both crystal fronts grew in a circular fashion until complete coverage of the water surface (Figure 5.2), and particles were engulfed upon contact in the system with silica (Figure 5.2f to h). In one of the experiments, pushing of a methane bubble (Figure 5.3a), trapping of the same between the hydrate front and a silica particle (Figure 5.3b) and subsequent engulfment by the growing clathrate were observed (Figure 5.3c). There are three plausible reasons for this. First, pushing becomes more favorable as particle diameter decreases (Rempel and Worster 2001). Second, gas bubbles require a higher velocity for entrapment than solids particles of the same size (Asthana and Tewari 1993). Third, the bubble was placed right on the grain boundary which makes pushing more favorable (Bolling and Cisse 1971). It is conceivable then
Figure 5.3: Pushing, engulfing and healing during hydrate growth. (a) A grain boundary is evident in the growing clathrate (black) 2 s after nucleation. A methane bubble is being pushed at the hydrate front, precisely at the grain boundary. $T$ and $p$ were kept constant at 275 K and 8.2 MPa. (b) 4 s after nucleation the methane bubble can be seen between a silica grain and the advancing clathrate front. (c) Both the methane bubble and the silica grain have been engulfed by the hydrate, 6 s after nucleation. (d) The grain boundary is not observable past the point of contact of the hydrate front with a silica particle, 16 s after nucleation.
that configurations in which the methane clathrate will push, rather than engulf exist, perhaps with particles of smaller diameters or at much lower crystal growth velocities.

Also during clathrate formation, another interesting phenomenon was observed: the healing of a hydrate grain boundary upon contact of the growing clathrate front with a silica particle (Figure 5.3c to d). Similar phenomena have been previously recognized in non-clathrate, solidifying systems (Asthana and Tewari, 1993).

5.5.2 Dissociation

Several hydrate dissociation experiments were performed where gradual decomposition led to similar morphological patterns as the ones shown in Figure 5.4. In general, dissociation was first evinced by minute eruptions on the hydrate surface. This seemed to happen independent of whether the hydrate was in contact with a silica particle or not. The second step involved small rotations (on the order of 0.04 rad) of the silica grains within the hydrate matrix. These subtle signs of dissociation were hardly appreciable while analyzing the data on high-resolution video, and cannot be seen in the still frames of Figure 5.4. Decomposition became evident as partial dissociation of the clathrate allowed light to pass through the sample resulting in white hues observable in Figure 5.4b. As dissociation progressed to other regions until becoming widespread (Figure 5.4c) a hydrate-water slurry appeared (Figure 5.4d). As the slurry thinned down, due to the hydrate dissociation, few hydrate crystals remained visible on the water surface (Figure 5.4e). Complete clathrate dissociation occurred within 5 to 10 minutes and the system returned to the state observed before hydrate formation (Figure 5.4f). On one occasion dissociation started with a sudden fracture of the clathrate (Figure 5.5a and b) before proceeding with the mechanism described above. This was found particularly interesting as the dissociation conditions were very similar between different experiments (Table 5.2).
Figure 5.4: Gradual dissociation of methane clathrate in contact with silica gel particles. (a) Intact hydrate 22 s after decreasing the pressure below the hydrate stability region. $T$ and $p$ were kept constant at 275 K and 4.0 MPa. (b) Hydrate dissociation became evident 42 s after decreasing $p$. (c) Widespread hydrate dissociation 46 s after reducing $p$. (d) Clathrate decomposition led to the appearance of a hydrate-water slurry 50 s after reducing $p$. (e) The water-hydrate slurry thinned down until few hydrate crystals were observable 1 min after reducing $p$. Minimal or no methane bubble formation was observed. (f) The system returned to its original state 2 min after reducing $p$. 
Table 5.2: Experimental conditions for hydrate dissociation in the presence of silica gel particles.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$T$/K</th>
<th>$p$/MPa</th>
<th>Dissociation Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>275</td>
<td>4.0</td>
<td>gradual</td>
</tr>
<tr>
<td>2</td>
<td>276</td>
<td>4.0</td>
<td>fracture</td>
</tr>
<tr>
<td>3</td>
<td>275</td>
<td>4.0</td>
<td>gradual</td>
</tr>
</tbody>
</table>

Figure 5.5: (a) Sudden fracture of the clathrate 28 s after decreasing $p$ below the hydrate stability region (kept constant at $T = 276$ K and $p = 4.0$ MPa). (b) Hydrate dissociation becomes evident outside the crack region by the appearance of clear spots 1 min after decreasing $p$. As of this point decomposition proceeded in the same way as described in Figure 5.4.
5.6 Conclusion

Methane clathrate formation and decomposition while in contact with silica gel particles (250 to 500 µm in diameter) were studied with the aid of a novel setup equipped high resolution video microscopy. It was observed that the hydrate front engulfed the silica particles as it advanced at a relatively constant velocity of 300 µm/s compared to 700 µm/s for the methane-water system under the same conditions but without the presence of silica gel. Furthermore, it was found that the growing clathrate could push a methane bubble and it was suggested that this is indicative of the existence of methane hydrate configurations where pushing of solid particles by the growing crystal would be possible. In addition, hydrate grain boundary healing was seen after the clathrate contacted a silica particle. Finally, clathrate dissociation was found to proceed through two different mechanisms. In the first, decomposition developed gradually until a hydrate-water slurry was observable, subsequently the slurry thinned down until very few crystallites remained visible in the bulk liquid phase. As for the second mechanism, dissociation began catastrophically by a sudden fracture in the clathrate; however, the ensuing decomposition occurred as in the first mechanism.
Chapter 6

Comprehensive Conclusion

Phase equilibria and morphology of gas hydrates were the object of study in this dissertation. Chapter 3 addressed phase equilibria of clathrates while the rest of the document discussed several aspects of methane hydrate morphology.

Chapter 3 showed a data set that describes the four-phase equilibrium conditions (hydrate-liquid-liquid\textsubscript{aq}-vapor) for the system methane + carbon dioxide + neohexane + water. With this data set it was possible to present a theoretically sound graphical format that allows comparison of structure H and structure I clathrate equilibrium for systems with two degrees of freedom. The ensuing analysis allowed for clarification of a common mistake found in hydrate phase-equilibria literature whereby initial compositions and not the theoretically correct, equilibrium compositions are used as intensive variables with respect to Gibbs phase rule.

The morphology section started with Chapter 4 where growth of methane clathrates from water films was shown. For methane clathrates formed from water films without previous hydrate formation history it was found that hydrate nucleation occurred on the periphery of a film first. Secondary nucleation occurred within the water film, and crystals thus formed had a completely different morphology than that of the ones formed on the water edge. This difference in morphology tended to disappear over time, giving way to a rough surface uniform throughout the hydrate film. Higher driving forces produced smaller hydrate grains and smoother surfaces.
than lower driving forces within the water film. The converse was true for hydrate formed on the periphery. Furthermore, a third layer that grew outside of the original water boundary displaying yet another morphology was observed. Images suggested that this third layer could grow on water-free glass, and thus was capable of communicating nucleation from one water covered region to another. Hydrate reformation proceeded in a different manner than that of clathrates formed from water without previous hydrate formation history: nucleation occurred within the film and a circular hydrate front(s) with uniform morphology advanced towards the periphery of the water film. Dissociation progressed in a similar manner in spite of whether the hydrate was formed from water with or without previous clathrate formation. Decomposition started on the periphery and proceeded until gas bubbles were observed within the film. Moreover, as dissociation became ubiquitous within the film, water receded until the water film regained its original shape and gas bubbles agglomerated in the center of the water film.

Finally, silica particles were introduced into the methane + water system (Chapter 5) and it was observed that the hydrate front engulfed the silica particles as it advanced at a relatively constant velocity about half that of the methane-water system under the same conditions, but without the presence of silica gel. Furthermore, it was found that the growing clathrate could push a methane bubble and it was suggested that this was indicative of the existence of methane hydrate configurations where pushing of solid particles by the growing crystal would be possible. In addition, hydrate grain-boundary healing was seen after the clathrate contacted a silica particle. Clathrate dissociation was found to proceed through two different mechanisms. In the first, decomposition developed gradually until a hydrate-water slurry was observable, subsequently the slurry thinned down until very few crystallites remained visible in the bulk liquid phase. As for the second mechanism, dissociation began catastrophically by a sudden fracture in the clathrate; however, the ensuing decomposition occurred as in the first mechanism.
6.1 Recommendations for Future Work

Direct ramifications of the work described herein are presented below:

1. The graphical format and analysis of clathrate equilibrium shown in Chapter 3 is extensible to other systems with two degrees of freedom that might become of interest to the scientific community. An example may already be found in the literature (Bruusgaard et al., 2008).

2. The morphology crystallizer has much room for improvement. Perhaps the most important modification would be to make the methane chamber shorter, thus a flatter reactor. This is very important for imaging purposes; a closer focal distance would allow higher magnifications.

3. The high versus low driving force scheme presented in Chapter 4 calls for systematic work to be done at various levels of driving forces. This would allow for a generalized classification of morphological features of hydrates formed on systems without previous formation. Efforts to do this for reformed hydrates exist in the literature (Ohmura et al., 2004).

4. Studying heat dissipation as hydrates crystallize from water films would be advantageous before attempting to model the system. The same type of experimental setup used in this work could be used for that purpose, except an infrared camera would be required.

5. The “bridge effect” as shown in Chapter 4 opens many research doors. Among them we find: first, a methodical study, correlating front velocity to driving forces. Second, a comparison between hydrate “bridging” on hydrophilic and hydrophobic surfaces. Third, studying the effect of hydrate inhibitors or promoters on the “bridging” capabilities of a system would give valuable information regarding the effectiveness of such additives.

6. A first step in direct observation of clathrate interaction with particles at high pressure was presented in Chapter 5; however, a complete study requires work-
ing with different sizes and kinds of particles and introducing a temperature controlled stage with the aim to manipulate crystal growth velocity. Both of these approaches with the idea to find the limiting conditions at which pushing versus engulfing configurations occur.
Original Contributions

The main contributions to knowledge contained in this thesis are summarized below:

1. From Chapter 3, published in the *Journal of Chemical Engineering Data*, **53**: pp. 1745-1749:
   
   (a) A data set that describes the four-phase equilibrium conditions (hydrate-liquid-liquid<sub>aq</sub>-vapor) for the system methane + carbon dioxide + neo-hexane + water.

   (b) A theoretically sound graphical format to compare structure H and structure I equilibrium for hydrate forming systems with two degrees of freedom.

   (c) Clarification of a common mistake found in hydrate phase-equilibria literature whereby initial compositions and not the theoretically correct, equilibrium compositions are used as intensive variables with respect to Gibbs phase rule.

2. From Chapter 4, to be submitted to the *AICHE Journal*:

   (a) Finding that clathrates grown in films without previous formation history form in layers, each with a characteristic morphology that depends on both the location within the film and the driving force in the system.

   (b) Discovering that a hydrate layer can grow on a foreign surface, outside of a water boundary and communicate nucleation to other regions of the foreign surface covered with water.
3. From Chapter 5 to be submitted to the *Journal of Crystal Growth*:

(a) Observation of the engulfment of particles by an advancing methane clathrate front occurring at high-pressure.
Other Related Work

Collaboration with other members of Professor Servio’s research group during my doctoral studies resulted in the following additional manuscripts, not included in this thesis:


Appendix A

Technical Drawing for the Morphology Reactor
APPENDIX A. MORPHOLOGY REACTOR

Juan Beltrán
Morphology reactor
316L SS, dimensions in inches

McGill Chem Eng, Prof Servio's Group
April 11, 2007
Juan Beltrán

36L SS, dimensions in inches
April 11, 2007

McGill Chem Eng, Prof Servio's Group
Juan Beltrán

Morphology reactor


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