



# Hydrate phase transition kinetics from Phase Field Theory with implicit hydrodynamics and heat transport



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## ARTICLE INFO

### Article history:

Received 23 August 2013

Received in revised form 6 May 2014

Accepted 6 August 2014

### Keywords:

Hydrate

Thermodynamics

Non-equilibrium

Supersaturation

Kinetics

Carbon dioxide

## ABSTRACT

Most hydrate that forms or dissociates are in situations of constant non-equilibrium. This is due to the boundary conditions and Gibbs Phase rule. At a minimum this leaves a hydrate with two adsorbed phases in addition to hydrate and fluids. One adsorbed phase is governed by the mineral surfaces and the other by the hydrate surface. With pressure and temperature defined by local conditions, hydrate formation will never be able to reach any state of equilibrium. The kinetics of hydrate formation and dissociation are a complex function of competing phase transitions. This requires kinetic theories that include minimization of free energy under constraints of mass and energy transport. Since phase transitions also change density, further constraints are given by fluid dynamics. In this work, we describe a new approach for non-equilibrium theory of hydrates together with a Phase Field Theory for simulation of phase transition kinetics. We choose a three component system of water, methane and carbon dioxide for illustration. Conversion of methane hydrate into carbon dioxide hydrate is a win–win situation of energy production combined with safe long term storage of carbon dioxide. Carbon dioxide is able to induce and proceed with a solid–state exchange, but is slow due to mass transport limitations. A faster process is the formation of new hydrate from injected carbon dioxide and residual pore water. This formation releases substantial heat. This assists in dissociating in situ methane hydrate, making the conversion progress substantially faster, because heat transport is very rapid in these systems. But conversion of liquid water into carbon dioxide hydrate, in the vicinity of the hydrate core will increase temperatures to some portions of the surface. The dissociating regions of the methane hydrate core will show a local decrease in temperature, due to extraction of heat for methane hydrate dissociation from surroundings. Another reason for heat transport implementation is that regions of the system that contains non-polar gas phase will have low heat conductivity and low heat convection. At this stage we apply a simplified heat transport model in which “lumped” efficient heat conductivity is used. We illustrate the theory on the conversion of methane hydrate to mix methane–carbon dioxide hydrate using three initial hydrate sizes:  $150 \text{ \AA} \times 150 \text{ \AA}$ ,  $500 \text{ \AA} \times 500 \text{ \AA}$  and  $5000 \text{ \AA} \times 5000 \text{ \AA}$ . The hydrate cores used are spherical because it makes it easier to illustrate the impact of curvature. Symmetrical aspects simplifies the dependency to a two dimensional problem – although there are no such limitations in theory. The mineral surfaces are considered to be water wetting in these examples. It was observed that the smaller sizes convert to a more unstable mix hydrate for some periods of the simulation time, during which there were significant losses of the initial methane hydrate core. These instabilities are caused by local under saturated fluid phases around the hydrate core. Eventually a steady state progress was observed. The largest size system appeared to reach a steady state situation comparable faster than the two smaller systems.

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## 1. Introduction

Natural gas hydrates are icelike crystalline compounds in which water serves as a host for different small non polar, or slightly polar,

guest molecules. Industrial hydrate problems are mostly related to two of these structures, structure I and II, that forms hydrates with hydrocarbons up to butanes. In this work, we focus on hydrates of methane, carbon dioxide and mixtures of these. These components form structure I hydrates. The lowest symmetrical unit of this is a cubic cell with almost constant (Kvamme and Tanaka, 1995; Shpakov et al., 1997, 1998) average side lengths  $12.01 \text{ \AA}$  for the region of industrial interest (above  $-70 \text{ }^\circ\text{C}$ ) and natural

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conditions on earth. Inside this unit crystal there are 46 water molecules constituting 6 large cavities and 2 small cavities. The large cavities are made from 24 water molecules arranged into the formation of 2 hexagonal faces and the rest as pentagonal faces. The small cavities are made from 20 water molecules forming pentagonal faces. Macroscopically, hydrates both look similar to ice and share some important properties of. An important distinction, however, is that hydrates can form also at temperatures above 0 °C depending on pressure. Another distinction from ice is the multi-component nature of the hydrate and its interaction with other phases. Hydrate formation from methane and water can happen in a number of ways. The most commonly discussed hydrate formation is on the interface between hydrate former phase and water (Kvamme and Tanaka, 1995), for which numerous experimental data are available (see for instance Koh and Sloan for a compilation (Koh and Sloan, 2008)). But hydrate can also form dissolved hydrate formers in water (Kvamme, 2002, 2003). Theoretically, hydrate can also form water dissolved in hydrate former phase (Kvamme et al., 2013a). Although more complete studies are needed to reveal whether that is realistic in view of mass transport limitations. Phase Field Theory is one theoretical method for investigating this (Qasim et al., 2011; Kvamme et al., 2004a, 2007, 2009, 2012a,b; Svandal, 2006; Tegze and Gránásy, 2005; Tegze et al., 2007). In addition, mineral surfaces will serve as adsorption sites for water as well as hydrate formers (Kvamme et al., 2012b; Cuong et al., 2012a,b). For the simplest case of one hydrate former this can give rise to at least three different hydrate formation cases: (1) water and hydrate former, both from adsorbed phase, form hydrate, (2) adsorbed water and hydrate fluid forms hydrate and (3) adsorbed hydrate former and water from fluid phase forms hydrate. It should be mentioned that the first layers of adsorbed water might have too low chemical potential to form hydrate, but few (2–4) water molecules outside will have chemical potentials suitable for hydrate formation (Kvamme et al., 2012b). If we sum up all phases for distribution of the two components methane and water it is easy to verify that these systems can generally not reach equilibrium (Gibbs's phase rule) in industrial situations or in nature, where pressure and temperature are normally given locally. Going even a step further in the analysis, it is also apparent that hydrates formed from different phases will result in different free energies. This can be visualized through Eq. (A.29) in the next section, in which the canonical partition function for the each cavity contains the chemical potential of the molecule inside that cavity (Kvamme and Tanaka, 1995), which at equilibrium would have to be equal to the chemical potential of the same molecule in the coexisting phase it came from. So even if the total system cannot reach equilibrium, the equality of chemical potentials at the (unreachable) asymptotic limit of equilibrium, are still driving forces during a process of hydrate formation. This will have impact on the hydrate filling and corresponding hydrate free energy.

In view of the above hydrate formation or dissociation, kinetics are very complex and not constantly going in one direction. Even if free energy change is negative and sufficiently negative to overcome the work involved in pushing the surrounding to give space for the growing hydrate, there could be gradients in free energy that involves positive free energy change. As an example consider formation of hydrate on a methane/pure water interface. After the hydrate has reached some thickness, the transport limitations through the hydrate film become substantial. If the initial water is pure, then hydrate will dissociate (Kvamme, 2002, 2003; Kvamme and Kuznetsova, 2004) again until a concentration of methane is in quasi equilibrium with the hydrate film. Similarly, on the methane side of the interface, in which the water content of the gas will be controlled by the chemical potential of water in hydrate (Kvamme et al., 2013a).

Injection of carbon dioxide into methane hydrate will lead to conversion of the in situ methane hydrate into a mixed hydrate in which carbon dioxide dominates occupation of the large cavities and methane fills some of the small cavities. The conversion is governed by two main mechanisms. Formation of new carbon dioxide from residual liquid water in the porous media releases heat that contributes to dissociation of surrounding methane hydrate. A second mechanism is direct solid-state exchange, which is substantially slower (Lee et al., 2003; Kuznetsova et al., 2012). This hydrate exchange is also feasible with injection of carbon dioxide and nitrogen mixtures as also demonstrated in a field pilot in Prudhoe Bay in the winter of 2012. Not all the result from this pilot has been published yet; although press release from Department of Energy states that the test was successful. The NETL web-page is continuously updated (National Energy Technology Laboratory, 2013).

In this work we discuss extension of the Phase Field Theory (Qasim et al., 2011; Kvamme et al., 2004a, 2007, 2009, 2012a,b; Svandal, 2006; Tegze and Gránásy, 2005; Tegze et al., 2007) to include hydrodynamics and heat transport. The first is needed if the dissociation of hydrate is more rapid than the solution of released methane into the surrounding water, so that methane bubbles form and affect the phase transition kinetics. Heat transport by hydrate dissociation is normally 2–3 orders of magnitude faster than mass transport in liquid water/hydrate system (Qasim et al., 2011; Kvamme et al., 2004a, 2007, 2009, 2012a,b; Svandal, 2006; Tegze and Gránásy, 2005; Tegze et al., 2007). Heat transport will, however, be slow through gas layers or gas bubbles. Implicit heat transport is obviously needed is the case where formation of new hydrate contributed to dissociation of original methane hydrate. For the fluid phases extensions to regions outside of equilibrium is quite trivial and the equations are given in Appendix 1 along with the equilibrium description for hydrate. The reason that these equations are included here are the use of chemical potentials and absolute thermodynamics (ideal gas as reference for all components in all phases). This is the most convenient choice since it will avoid any need for shifting reference state during the free energy minimization which implicit in the Phase Field Theory (PFT) (Section 2). The extension of hydrate thermodynamics to outside equilibrium in all independent variable are accomplished using first order Taylor expansions as explained in Appendix 2. The reason these equations are included here is that the mole-fraction conservation is implicit in the PFT model and that gradients in all mole-fractions are treated as independent in the thermodynamic description. The PFT theory is described in Section 2 and examples of conversion of methane hydrate into carbon dioxide is used to illustrate the theory.

## 2. Phase Field Theory model

Generally the phase transition in a system follows two well defined physical processes, nucleation and growth. In addition some hydrate phase transitions shows a delay in the onset of massive growth, which is normally denoted as induction time. Nucleation is the unstable stage in which there is a competition of the free energy gain by the phase transition and the penalty of pushing old phases away in order to give room for the new phase. In this stage nuclei grow and decay as a function of different processes which induces some randomness to the system, like for instance diffusional transport of mass which by nature contain randomness element in direction versus location and orientations of growing nuclei. Within PFT modeling this is handled by subtracting the thermodynamic limits of the initial and final phase(s) from the free energy and adding a voice term which incorporates the impact on the system from the outside boundaries. See Gránásy

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