Heterogeneous growth of hydrate on the CO_2/aqueous solution interface

BJØRN KVAMME, TRYGVE BUANES, TATYANA KUZNETSOVA,
Department of Physics,
University of Bergen
Allègt. 55, 5007 Bergen,
NORWAY
http://web.ift.uib.no/php/php/bkvamme.html

Abstract: - Phase Field Theory is applied to the modelling of heterogeneous hydrate formation on the aqueous solution CO2 interface. Interface properties needed in the parameterisation of the theory was estimated using NPT molecular simulations. Different initial hydrate hydrate crystals on the interface have been applied in order to investigate the mechanism for hydrate growth and hydrate film penetration. On the basis of these simulations it is concluded that rearrangement of hydrate at the aqueous/CO_2 interface is likely to be one of the reason for the penetration of the hydrate film and the transition over to massive hydrate growth.

Key-Words: - kinetics; methane; water; hydrate; molecular modeling

1 Introduction

Hydrate induction time is the time lag before onset of massive hydrate growth in heterogeneous hydrate formation. In a stirred batch system it is typically seen as an initial limited consumption of hydrate formers [1, 2] followed by a variable time lag which depends on the sub-cooling, density of hydrate former and contact area. The contact area is typically manipulated through the stirring rate. Interpretation of unstirred experimental systems [3] shows that hydrate particles on methane/water interface rearrange so that some particles disappear in favour of larger and more stable particles. A recent study using Magnetic Resonance Imaging (MRI) also confirmed induction time in the order of 100 hours for the system methane/water at 83 bar and 3 C [4]. In this work we use Phase Field Theory to study how the free energy in the systems directs heterogeneous hydrate growth patterns and the consequences this might have on the possible mechanisms for the onset of macroscopic hydrate growth.

2 Numerical simulations

Heterogeneous hydrate formation from a single hydrate former on the interface between the hydrate former phase and aqueous solution involves the coexistence of three phases that contain only two components, and thus only a single degree of freedom. The presence of solid walls will further reduce the number of degrees of freedom by one, since the density and the component distribution in the adsorbed layer close to the solid surface will differ from those of the surrounding phases and must be treated as a separate phase. This means that there are no degrees of freedom in this system and the combined first and second laws of thermodynamics will direct the dynamic paths of changes in the systems towards local and global minimum free energy. In this work we use a version of phase field theory which includes three fields; the phase ϕ, molar CO_2 concentration c, and microscopic orientation, θ. Note that for historical reasons $\phi = 0$ corresponds to solid and $\phi = 1$ to liquid in the scope of PFT. From the free energy functional [5 – 11]:

$$F = \int d^3r \left\{ \tfrac{1}{2}\varepsilon_\phi^2 T\left(\nabla\phi\right)^2 + \tfrac{1}{2}\varepsilon_c^2 T\left(\nabla c\right)^2 + f_{ori}(|\nabla\phi|) + f(\phi,c) \right\} \quad (1)$$

$$f(\phi,c) = wTg(\phi) + f_L p(\phi) + f_S\left[(1-p(\phi)\right] \quad (2)$$

The thermodynamic properties of the hydrate, f_H, and fluid phase, f_L, are derived from molecular simulations as described by Svandal et.al. [12 - 14]. The functions $g(\phi)$ and $p(\phi)$ are not uniquely defined but constrained by the requirements of thermodynamic consistency. The following forms [5 – 8] have been adopted: $g(\phi) = {}^1\!/_4\, \phi^2(1-\phi)^2$ and $p(\phi) = \phi^3(10 - 15\phi + 6\phi^2)$ throughout this work. If ε_c is set equal to zero or equal to ε_φ then there are two unknown parameters in addition to the orientation dependency of the free energy. These two parameters can be estimated from the interface properties [12].

$$d = \left(\frac{\varepsilon^2 T}{2}\right)^{1/2} \int_{0.1}^{0.9} d\xi \left\{\Delta f[\xi, c(\xi)]\right\}^{-1/2} \quad (3)$$

where d is the 10 – 90 interface thickness for a 10% - 90% confidence interval. Parameters ε and w appear in Δf (see equation (2) and equation (5) below) in adition to the appearance of ε in the prefactor. Manipulations of Eq. (3) [12] gives a corresponding expression for the

interface free energy of the solid-liquid interface:

$$\gamma_\infty = (\varepsilon^2 T)^{1/2} \int_0^1 d\xi \{\Delta f[\xi, c(\xi)]\}^{1/2} \quad (4)$$

where $\Delta f = f - f_0$, and

$$f_0 = f_L(c_L^{eq}) + (\frac{\partial f_L}{\partial c})\Big|_{c_L^{eq}} (c - c_L^{eq}) = f_S(c_S^{eq}) + (\frac{\partial f_S}{\partial c})\Big|_{c_S^{eq}} (c - c_S^{eq}) \quad (5)$$

Equation (5) is the common tangent equation for the equilibrium condition. With appropriate values for d and γ_∞ from experiments or theoretical studies/molecular simulations then equations (3) and (4) can be solved iteratively for ε and w For details see Kvamme et.al. [15] and references therein. The orientational free energy contributions require typically 1 or 2 empirical parameters, depending on the complexity of the crystal morphology. Throughout this work we adopt the form:

$$\varepsilon_\phi = \varepsilon_{\phi_0} \left[1 + \frac{s_0}{2} \cos\left(n\vartheta - 2\pi\theta \right) \right] \quad (6)$$

$\vartheta = arctan[(\nabla\phi)_y/(\nabla\phi)_x]$, which results in dendritic growth of hydrate from aqueous CO_2 solution [9 - 11]. Subject to conservation of mass the equations of motion are derived [5 - 11]. In the examples used in this work we set the mobility [5 - 11] of phase field and concentration field as identical and equal to an interpolation between liquid and solid diffusivity coefficients of CO_2 according to the local phase field. The latter value is not accurately known but is likely to be smaller than 10^{-12} m^2/s [15], which is the value we have used. For liquid CO2 we have used $1.56 \cdot 10^{-9}$ m^2/s.

$$\dot{\phi} = M_\phi \frac{\delta F}{\delta \phi} + \varsigma_\phi \quad (7)$$

$$\dot{c} = \nabla \bullet \left(M_c \nabla \frac{\delta F}{\delta c} \right) + \varsigma_c , \quad (8)$$

$$M_c = \frac{D_S + (D_L - D_S) p(\phi)}{RT} \quad (9)$$

$$\dot{\theta} = M_\theta \frac{\delta F}{\delta \theta} + \varsigma_\theta \quad (10)$$

The PFT approach is a mean field theory and the noice terms ζ_c and ζ_φ are added so as to mimic some of the effects of the dynamics across the boundary between the limits of the simulation cell and the infinite surroundings while at the same time normalized so that the total average net effect on the system should be zero.

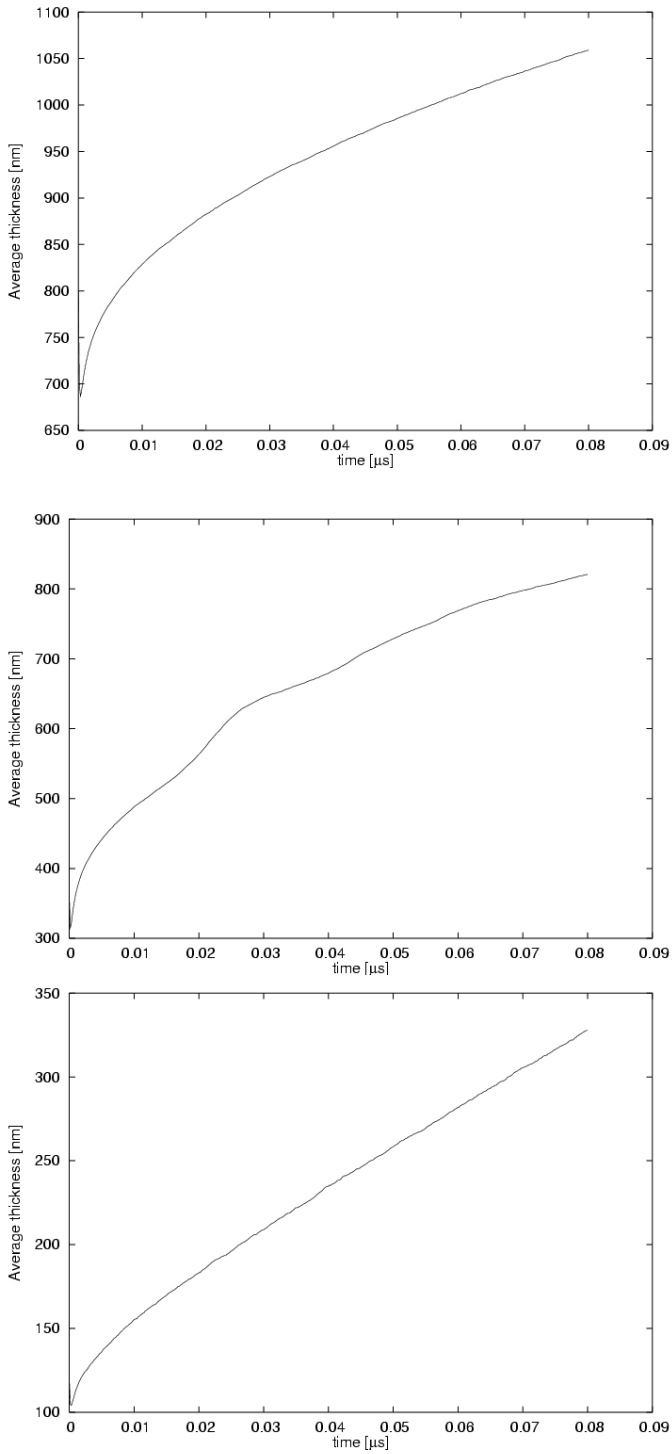

Figure 1. Average thickness of hydrate as function of time for systems I (top), II (middle) and III (bottom)

The interface width needed in equation (3) is estimated using molecular dynamics simulations of model hydrate-aqueous fluid system. The SPC/E [17] model for water and the CO_2 model of Harris & Yung [18] were used. The envelope of the density peaks, which may by loosely identified as the spatial variation of the amplitude of the dominant density wave (i.e., a constant times $\phi(z)$), was fitted to the following hyper tangential functional form:

$$X(z) = A + \tfrac{1}{2} B\{1 + \tanh[(z - z_0) / (2^{3/2}\delta)]\}, \qquad (11)$$

where the interface thickness δ is related to the 5% – 95% interface thickness d (the distance on which the phase field changes between 0.1 and 0.9) as $d = 2^{5/2}\text{atanh}(0.9)\ \delta$. The average value of d was estimated to be 0.85 ± 0.07 nm.

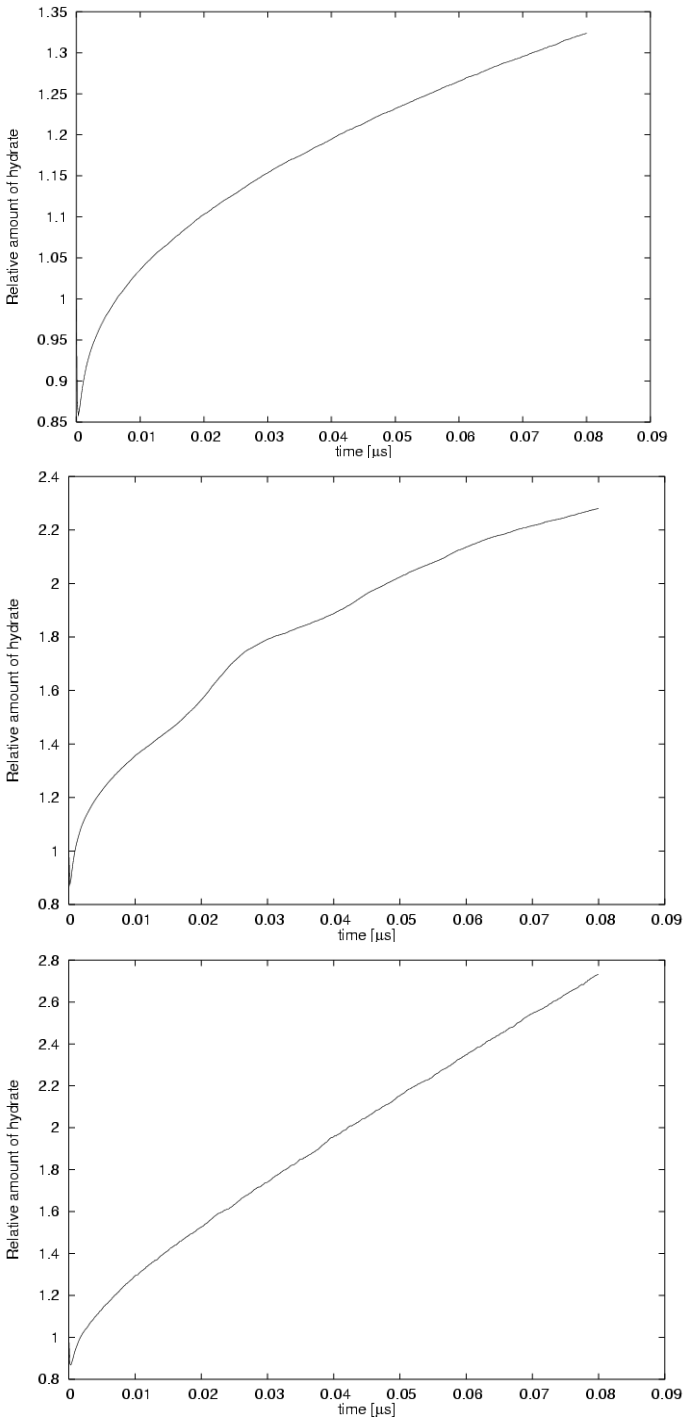

Figure 2. Amount of hydrate relative to initial hydrate amount as function of time for systems I (top), II (middle) and III (bottom).

Work is in progress on estimation of interface free energy by means of Molecular Dynamics simulations but for the present simulations we have use the liquid water/ice value of 29.1 mN/m [19].

We have conducted PFT simulations on systems consisting of a CO_2 slab surrounded saturated (mole-fraction CO_2 equal to 0.033) aqueous solution of CO_2 at 150 bar and 274 K. The simulation window consists of 200 x 500 gridpoints, i.e.: 100000 pixels in 2 dimensions. Each pixel represents an area of 4 Å x 4 Å. At start the initial region of separate CO_2 phase in the middle equals the total region of the initial aqueous solution region on both sides of the CO_2 slab.. Three different systems have been simulated. In system I an initial hydrate film is covering the entire CO_2/aquous interface. In system II a regular pattern of initial hydrate cores have been placed on the interface towards the aqueous phase and initially covering 3600 pixels of hydrate. System III consists of an initial single particle covering 1200 pixels.

In figure 1 we plot the growth of the three systems in terms of average hydrate thickness as function of time. In Figure 2 we plot the growth of hydrate relative to the initial amount of hydrate.

3 Discussion and conclusions

The initial complete film can only grow from the saturated solution. The systems have only one degree of freedom according to Gibb's phase rule and as such the lower free energy of the hydrate relative to the aqueous solution will define the thermodynamic driving force. The initial CO_2 solution concentration corresponds to a mole fraction of 0.033 while the equilibrium concentration with respect to hydrate is 0.016 [12, 13]. System I is essentially dominated by the diffusion of CO2 from solution to the growing hydrate front. System II has a more composite growth pattern since it is able to extract CO_2 from the pure CO_2 phase for the initial regions of the interface which were not covered by hydrate. After the closing of the hydrate film the growth pattern is similar to that of system I. Also note that merging of hydrate particles has a different kinetic behaviour and is responsible for the non smooth behaviour of this system relative to system I before the hydrate film is closing in. System III has free access to CO_2 from the pure CO_2 phase on both sides of the hydrate core in addition to access of CO_2 from the solution and exhibits the fastest growth relative to the initial hydrate. The practical implication of this is that hydrate regions of higher free energy may be consumed by hydrate regions of lower free energy, which eventually may lead to punctuation of the hydrate film and massive hydrate growth. Within the initial configurations of system II and the limited simulation

times this is not as distinct in these simulations compared to our previous results on similar systems [20 - 22]. The rearrangement process is fairly slow and may be partly responsible for the large induction times that can be observed for these types of systems [23]. It should, however, be pointed out that it is not possible at this stage to concluded that this is the dominant process responsible for the induction time delays. As pointed out by Kvamme et.al. [4], capillary transport of hydrate formers along the walls of the experimental container may be responsible for some of the transition over to massive hydrate growth. This has also been observed in pictures from macroscopic experiments [3]. Also note that equation (6) estimated growth of dendrites, which may be appropriate for methane hydrate [3] but may not be the most realistic growth morphology for carbon dioxide hydrate. More complex crystal growth morphologies can be simulated at the cost of an extra adjustable parameter [23-26]. The use of equal mobility for concentration field and phase field is also questionable. One possible approach for addressing this is to consider the changes in free energy associated with the change in structure across the interface. This can be accomplished using molecular simulations along the lines described by Kvamme & Tanaka [14].

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