Phase field modeling of the conversion from methane hydrate to carbon dioxide hydrate

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Abstract: - A ternary phase field theory has been developed to study kinetics of transformation of methane hydrate into CO_2 hydrate is investigated in the presence of fluid CO_2 under conditions characteristic to underwater reservoirs. We present illustrative simulations.

Key-Words: - methane hydrate; CO_2 hydrate; transformation kinetics; phase field modelling

1 Introduction

Natural gas hydrates are crystalline solids built of water cages containing gas molecules (mostly methane). These substances can be found in abundance in the Arctic regions and in marine sediments. The methane hydrate is stable at water depths larger than 300 m, and forms sediment layers of hundreds of meters thick. According to conservative estimates, the worldwide amount of carbon in gas hydrates is more twice of the carbon in fossil fuels [1-5]. Gas hydrates are regarded as a new abundant energy source, whose exploitation may become economic with increasing oil prices and after developing the appropriate technologies [3-5]. Under conditions typical to underwater reservoirs the CO_2 hydrate is more stable than the methane hydrate. This raises the possibility that via pumping industrial CO_2 into hydrate fields one can gain methane, a process that can make CO_2 deposition economic. It is, however, worth mentioning that methane is about 20 times more efficient green house gas than CO_2. Therefore, technologies that handle the released methane safely need to be developed. The methane stored in underwater hydrate reservoirs represents itself a natural climatic hazard: if released even a small fraction could cause serious climatic changes [3-5]. Therefore, it is a basic interest of humanity to understand details of methane balance of Earth including the formation and dissolution of gas hydrates [3-5]. Summarizing, gas hydrate reactions (formation and dissolution) are interesting for the following reasons [4]:

(1) Gas hydrates contain methane in abundance that could serve in the future as a new energy source provided that its economic exploitation is solved.

(2) Gas hydrate reservoirs, as methane source and sink, represent an essential part of the methane balance of the Earth, and may play an essential role in climatic changes.

In accordance with these, we have investigated the kinetics of gas hydrate reactions since years. Our research team has recently developed a phase field model of polycrystalline solidification [6-9] and adapted it for gas hydrate reactions. The kinetic data evaluated from molecular dynamics calculations are used in phase field simulation describing the time and spatial evolution of gas hydrate reactions [10-14]. These extremely computation intensive simulations have been performed on computer clusters consisting of 60 and 120 processors, respectively. In this work present a ternary phase field theory and address the transformation of methane hydrate into CO_2 hydrate in the presence of fluid CO_2.

2 Phase Field Model for Hydrate Conversion

The local state of matter is characterized by four fields: the phase field $\phi(\mathbf{r})$ that monitors the solid liquid transition, and three concentrations fields $\{c_1(\mathbf{r}),\ c_2(\mathbf{r}),\ c_3(\mathbf{r})\}$ that specify the local composition. The free energy of the inhomogeneous system is given by the integral

$$F = \int d^3r \left\{ \begin{array}{l} \dfrac{\varepsilon_\phi^{\ 2} T}{2} \left|\nabla\phi\right|^2 + wTg(\phi) + \\ {[1-p(\phi)]}\, f_S(c_1,c_2,c_3,T) + \\ p(\phi)\, f_L(c_1,c_2,c_3,T) \end{array} \right\}$$

where $c_3 = 1 - c_1 - c_2$, and the coefficient of the square gradient term ε_ϕ^2 and the free energy scale w can be related to the free energy and thickness of the hydrate-fluid interface in equilibrium, while the double-well, interpolation and anisotropy functions have the form shown below

$$g(\phi) = \tfrac{1}{4}\phi^2(1-\phi)^2, \quad p(\phi) = \phi^3(10 - 15\phi + 6\phi^2)\,.$$

Assuming relaxation dynamics, the respective equations of motions are as follows:

$$\dot{\phi} = -M_\phi \frac{\delta F}{\delta\phi} = M_\phi \left\{ \nabla\left(\frac{\partial f}{\partial\nabla\phi}\right) - \frac{\partial f}{\partial\phi} \right\}$$

$$\dot{c}_1 = \nabla M_{c,1} \nabla \frac{\delta F}{\delta c_1} = \nabla\left\{ M_{c,1}(c_1,c_2)\nabla\left[\left(\frac{\partial f}{\partial c_1}\right) - \nabla\left(\frac{\partial f}{\partial\nabla c_1}\right)\right]\right\}$$

$$\dot{c}_2 = \nabla M_{c,2} \nabla \frac{\delta F}{\delta c_2} = \nabla\left\{ M_{c,2}(c_1,c_2)\nabla\left[\left(\frac{\partial f}{\partial c_2}\right) - \nabla\left(\frac{\partial f}{\partial\nabla c_2}\right)\right]\right\}$$

where M_ϕ and $M_{c,j}$ are the respective mobilities determining the time scale of the evolution of the system. These equations are solved simultaneously in a dimensionless form using an explicit finite difference scheme and periodic boundary conditions. Here the same $M_{c,j} = D$, where D is the diffusion coefficient has been used for all the concentration fields.

The thermodynamic data for the $CO_2 - H_2O - CH_4$ ternary molecular system have been taken from Svandal et.al.[15, 16, 17]. Typical free energy surfaces for the hydrate and fluid phases are displayed in Figure 1. The model parameters ε_ϕ^2 and w have been chosen so that they correspond to an interfacial free energy of $\gamma = 30$ mJ/m^2 and an interface thickness of $d = 0.85$ nm. The spatial step was taken as $\Delta x = 0.1$ nm, and the time step as $\Delta t = 5 \times 10^{-12}$ s. The diffusion coefficient has been assumed to be $D = 10^{-9}$ m^2/s in the liquid phase, and about 1000 times smaller in the solid hydrate. The size of the rectangular simulation grid has been 500 × 250. Two slabs of CO_2 hydrate have been placed into the simulation window: One to the left, and another to the right. The gap in between has been filled in by a dominantly CO_2 fluid.

3 Discussion and conclusions

The conversion of methane hydrate into CO_2 hydrate in the presence of CO_2 solution is shown in Figure 2. The left side of the simulation window is displayed. In the first 0.1 ns the inititally sharp concentration and phase field profiles relax towards the diffuse interfaces analogous to those seen in modelcular dynamics and phase field simulations in binary systems [14]. This leads to a "softening" of the interface layer and a fractional melting of the methane hydrate at its surface. The CO_2 molecules diffuse into hydrate, and replace the methane molecules, which move into the fluid, accumulating in the blue peak on the right hand side. Note that the methane concentration in the methane hydrate is larger (~0.14) than the CO_2 concentration in the CO_2 hydrate (~0.11). As time proceeds, the CO_2 hydrate layer thickens, albeit with a continuously decreasing rate. The average thickening rate, taken for the duration of the simulation, is rather high ~ 0.1 m/s. This and the observation that the conversion rate decelerates are consistent with the diffusion controlled process assumed here. Molecular dynamics simulations might, however, be necessary to verify that indeed this is the dominant transformation mechanism. Work is underway to explore how the present results depend on the materials properties and the model parameters.

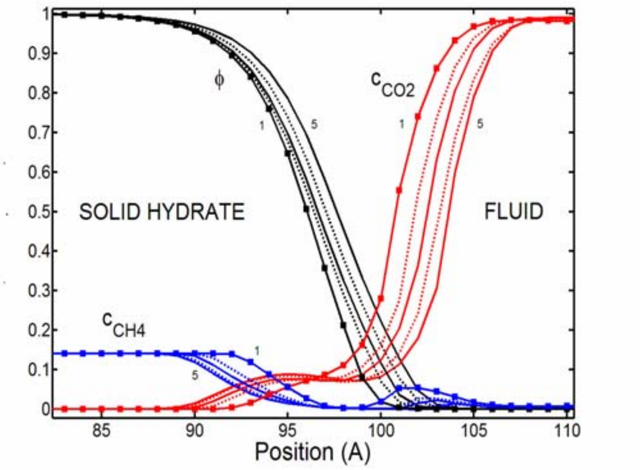

Figure 1. Conversion of methane-hydrate to CO_2-hydrate at 1 C and 6.2 GPa pressure. Time evolution of the phase field (black) is shown together with that of the CO_2 concentration (red), and the CH_4 concentration (blue). On the vertical axis, a common scale applies for the phase field and the two concentrations. The five curves correspond to times t = 0.1, 0.5, 1, 1.5 and 2.7 ns, respectively. Numbers 1 and 5 denote the curves corresponding to the first and last instances.

4 Summary

We have developed a phase field model for methane hydrate conversion into CO_2 hydrate in the presence of CO_2 fluid, and presented illustrative simulations under conditions typical to underwater reservoirs. Systematic investigation of the transformation kinetics is underway.

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