

# Phase field theory modeling of CH<sub>4</sub>/CO<sub>2</sub> gas hydrates in gravity fields

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**Abstract**—Natural gas hydrates in reservoirs are thermodynamically unstable due to the interactions with surrounding fluids (aqueous, gas) and mineral surfaces. Depending on the local flow hydrate will dissociate as well as reform. If the dissociation rate is faster than the capacity of the surrounding fluids to dissolve the released gas, the gas will form bubbles. Depending on the rate of released gas and possible fracture patterns this may lead to venting of gas. The proper implementation of hydrodynamics will provide a deeper insight of the hydrate kinetics involved during dissociation and formation processes which involve hydrate former phase as smaller or larger bubbles or even continuous gas phase. In this work the phase field theory coupled with hydrodynamics model is implemented with variable density using the relative composition, phase field parameter and flow, which is an extension of our previous work which considers a constant density.

**Keywords**—Phase field theory, Natural gas hydrate, Hydrodynamics, Dissociation, Hydrate.

## I. INTRODUCTION

Gas hydrates are ice-like substances of water molecules encaging gas molecules (mostly methane) that form under specific pressure and temperature conditions within the upper hundred meters of the sub-seabed sediments. They occur worldwide and are a potential energy resource for the near future [1].

Natural gas hydrates are widely distributed in sediments along continental margins, and harbor enormous amounts of energy. Massive hydrates that outcrop the sea floor have been reported in the Gulf of Mexico [2]. Hydrate accumulations have also been found in the upper sediment layers of Hydrate ridge, off the coast of Oregon and a fishing trawler off Vancouver Island recently recovered a bulk of hydrate of approximately 1000kg [3]. Håkon Mosby Mud Volcano of Bear Island in the Barents Sea with hydrates are openly exposed at the sea bottom [4]. These are only few examples of the worldwide evidences of unstable hydrate occurrences that

leaks methane to the oceans and eventually may be a source of methane increase in the atmosphere.

Hydrates of methane are not thermodynamically stable at mineral surfaces. From a thermodynamic point of view the reason is simply that water structure on hydrate surfaces are not able to obtain optimal interactions with surfaces of calcite, quarts and other reservoir minerals. The impact of this is that hydrates are separated from the mineral surfaces by fluid channels. The sizes of these fluid channels are not known and are basically not even unique in the sense that it depends on the local fluxes of all fluids in addition to the surface thermodynamics. Stability of natural gas hydrate reservoirs therefore depends on sealing or trapping mechanisms similar to ordinary oil and gas reservoirs. Many hydrate reservoirs are in a dynamic state where hydrate is leaking from top by contact with groundwater/seawater which is under saturated with respect to methane. Dissociating hydrate degasses as bubbles if dissociation rate is faster than dilution in surrounding fluids and/or surrounding fluid is supersaturated. The kinetic rate depends on mass transport dynamics as well as thermodynamic driving force. Phase field theory will be a power full tool to quantify this balance and provide basis for development of simplified models for reservoir modeling tools.

The primary focus in this work is to incorporate the density of all phases based on relative compositions and calculation of free gas exist in form of bubbles which can escape through empty channels and hence will be useful in calculation of an accurate natural gas flux.

## II. PHASE FIELD THEORY

Phase field model follows the formulation of Wheeler et al. [5], which historically has been mostly applied to descriptions of the isothermal phase transition between ideal binary-alloy liquid and solid phases of limited density differences. The hydrodynamics effects were incorporated in a three components phase field theory by Kvamme et al. [6] through implicit integration of Navier stokes equation. The phase field  $\phi$  is an order parameter describing the phase of the system as a function of spatial and time coordinates. The field  $\phi$  is allowed to vary continuously on the range from solid to liquid.

The solid state is represented by the hydrate and the liquid state represents fluid and aqueous phase. The solidification of hydrate is described in terms of the scalar phase field  $\phi(x_1, x_2, x_3)$  where  $x_1, x_2, x_3$  represents the molar fractions of CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub>O respectively with obvious constraint on

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conservation of mass  $\sum_{i=1}^3 x_i = 1$ . The field  $\phi$  is a structural order parameter assuming the values  $\phi = 0$  in the solid and  $\phi = 1$  in the liquid [7]. Intermediate values correspond to the interface between the two phases. The starting point of the three component phase field model is a free energy functional [6],

$$F = \int d\mathbf{r} \left( \frac{\epsilon_\phi^2}{2} T(\nabla\phi)^2 + \sum_{i,j=1}^3 \frac{\epsilon_{x_i,j}^2}{4} T\rho(x_i \nabla x_j - x_j \nabla x_i)^2 + f_{bulk}(\phi, x_1, x_2, x_3, T) \right), \quad (1)$$

which is an integration over the system volume, while the subscripts  $i, j$  represents the three components,  $\rho$  is molar density depends on relative compositions, phase and flow. The bulk free energy density described as

$$f_{bulk} = WTg(\phi) + (1 - p(\phi))f_S(x_1, x_2, x_3, T) + p(\phi)f_L(x_1, x_2, x_3, T). \quad (2)$$

The phase field switches on and off the solid and liquid contributions  $f_S$  and  $f_L$  through the function  $p(\phi) = \phi^3(10 - 15\phi + 6\phi^2)$ , and note that  $p(\phi) = 0$  and  $p(1) = 1$ . This function was derived from density functional theory studies of binary alloys and has been adopted also for our system of hydrate phase transitions. The binary alloys are normally treated as ideal solutions. The free energy densities of solid and liquid is given by

$$f_S = G_S \rho_m^{hyd}, \quad (3)$$

$$f_L = G_L \rho_m^L. \quad (4)$$

The thermodynamics for the hydrate system is treated more rigorously and the free energy  $G_S$  and  $G_L$  are presented in thermodynamics section. Hydrate density  $\rho_m^{Hyd}$  is calculated using the formulation by Sloan et al. [8]

The liquid density  $\rho_m^L$  for fluid phase is calculated as

$$\bar{V}_L^{Fluid} = \sum_{i=1}^3 x_i \bar{V}_i \quad (5)$$

$$\rho_m^{L,Fluid} = \frac{1}{\bar{V}_L^{Fluid}},$$

where  $\bar{V}_i$  represents the molar volume of  $i$ th component. The molar volume is calculated using gas law

$$\bar{V}_i = \frac{ZRT}{p} + \frac{nRT}{p} \left( \frac{\partial Z}{\partial n_i} \right)_{p,T,n_{i \neq j}}, \quad (6)$$

where  $p$  represents the pressure and  $Z$  is compressibility factor calculated using SRK equation of state. For simplicity to avoid partial molar volume at infinite dilution the density of liquid in aqueous phase is calculated as

$$V_L^{aqueous} = \sum_{i=1}^2 x_i \bar{V}_i + x_3 \bar{V}_3^0 \quad (7)$$

$$\rho_m^{L,aqueous} = \frac{1}{V_L^{aqueous}},$$

where  $\bar{V}_3^0$  is the average molar volume of pure water. The function  $g(\phi) = \phi^2(1 - \phi^2)/4$  ensures a double well form of the  $f_{bulk}$  with a free energy scale  $W = \left(1 - \frac{x_i}{v_m}\right)W_A + \frac{x_i}{v_m}W_B$  with  $g(0) = g(1) = 0$ , where  $v_m$  is the average molar volume of water. In order to derive a kinetic model we assume that the system evolves in time so that its total free energy decreases monotonically [7]. The usual equations of motion are supplemented with appropriate convection terms as explained by Tegze et al [9]. Given that the phase field is not a conserved quantity, the simplest form for the time evolution that ensures a minimization of the free energy is

$$\frac{\partial \phi}{\partial t} + (\vec{v} \cdot \nabla)\phi = -M_\phi(\phi, x_1, x_2, x_3) \frac{\delta F}{\delta \phi}, \quad (8)$$

$$\frac{\partial x_i}{\partial t} + (\vec{v} \cdot \nabla)x_i = \nabla \cdot \left( M_{x_i}(\phi, x_1, x_2, x_3) \nabla \frac{\delta F}{\delta x_i} \right), \quad (9)$$

where  $\vec{v}$  is the velocity,  $M_{x_i} = x_i(1 - x_i) \frac{1}{RT} D$  and  $M_\phi = \left(1 - \frac{x_i}{v_m}\right)M^A + \frac{x_i}{v_m}M^B$  are the mobilities associated with coarse-grained equation of motion which in turn are related to their microscopic counter parts. Where  $D = D_S + (D_L - D_S)p(\phi)$  is the diffusion coefficient. The detail may found elsewhere [6].

An extended phase field model is formed to account for the effect of fluid flow, density change and gravity. This is achieved by coupling the time evolution with the Navier Stokes Equations. An incompressible and viscous fluid is considered. The phase and concentration fields associates hydrodynamic equation as described by conti [10]-[12]

$$\frac{\partial \rho}{\partial t} = -\rho_m \nabla \cdot \vec{v}, \quad (10)$$

$$\rho \frac{\partial \vec{v}}{\partial t} + \rho(\vec{v} \cdot \nabla)\vec{v} = \rho \vec{g} + \nabla \cdot P.$$

Where  $\vec{g}$  is the gravitational acceleration.  $\rho_m$  is the density of the system in hydrate ( $\rho_m^{Hyd}$ ) and liquid ( $\rho_m^L$ ). Further

$$P = \mathfrak{z} + \Pi. \quad (11)$$

is the generalization of stress tensor [10]-[13],  $\mathfrak{z}$  represents non-dissipative part and  $\Pi$  represents the dissipative part of the stress tensor.

### III. THERMODYNAMICS

The expression for chemical potential of water in hydrate is

$$\mu_3^H = \mu_3^{0,H} - \sum_i RT\theta_i \ln\left(1 + \sum_j h_{ij}\right), \quad (12)$$

This equation is derived from the macro canonical ensemble under the constraints of constant amount of water, corresponding to an empty lattice of the actual structure. Details of the derivation are given elsewhere [14] and will not be repeated here.  $\mu_3^{0,H}$  is the chemical potential for water in an empty hydrate structure and  $h_{ij}$  is the cavity partition function of component  $j$  in cavity type  $i$ . The first sum is over cavity types, and the second sum is over components  $j$  going into cavity type  $i$ . Here  $\theta_i$  is the number of type  $i$  cavities per water molecule.

#### A. Fluid Thermodynamics

The free energy of the fluid phase is assumed to have

$$G_L = \sum_{i=1}^3 x_i \mu_i^{Fluid}, \quad (13)$$

where  $\mu_i^{Fluid}$  is the chemical potential of the  $i$ th component. The solubility of water is assumed to follow the Raoult's law. The lower concentration of water in the fluid phase and its corresponding minor importance for the thermodynamics results in the following form of water chemical potential with some approximation of fugacity and activity coefficient:

$$\mu_3^{Fluid} = \mu_3^\infty + RT\ln(y_3), \quad (14)$$

where  $\mu_3^\infty$  chemical potential of water at infinite dilution and  $y_3$  is the mole fraction of water in the fluid phase. The chemical potential for the mixed fluid states considered as

$$\mu_i^{Fluid} = \mu_i^{SRK,pure} + RT\ln(y_3), \quad (15)$$

where  $i$  represents  $\text{CH}_4$  or  $\text{CO}_2$ . The details are available in Svandal et al. [15].

#### B. Aqueous Thermodynamics

The free energy of the aqueous phase assumed as

$$G_L = \sum_{i=1}^3 x_i \mu_i^{aqueous}, \quad (16)$$

the chemical potential  $\mu_i^{aqueous}$  of aqueous phase has the general form derived from excess thermodynamics

$$\mu_i^H = \mu_i^\infty + RT\ln(x_i \gamma_i^\infty) + v_i(P - P_0). \quad (17)$$

$\mu_i^\infty$  is the chemical potential of component  $i$  in water at infinite dilution,  $\gamma_i^\infty$  is the activity coefficient of component  $i$  in the aqueous solution in the asymmetric convention ( $\gamma_i^\infty$  approaches unity in the limit of  $x$  becoming infinitely small). The chemical potentials at infinite dilution as a function of temperature are found by assuming equilibrium between fluid and aqueous phases ( $\mu_3^{Fluid} = \mu_3^{aqueous}$ ). This is done at low pressures where the solubility is very low, using experimental values for the solubility and extrapolating the chemical

potential down to a corresponding value for zero concentration. The activity coefficient can be regressed by using the model for equilibrium to fit experimental solubility data. The chemical potential of water can be written as:

$$\mu_3 = \mu_3^p + RT\ln(1 - x)\gamma_3 + v_3(P - P_0), \quad (18)$$

where  $\mu_3^p$  is pure water chemical potential. The strategy for calculating activity coefficient is given in [15].

## IV. RESULTS

The phase field model is implemented on a 2D geometry. This structure is used to dissociate circle of hydrate placed in the center surrounded by pure liquid water. The size of system is (500×500) grids with diameter of 200 grids for circular hydrate placed in the center as shown in Fig.1. One grid is equal to one angstrom (Å) and temperature (273.21 K) and pressure (63.90 bar) remain constant in the system. The values for temperature and pressure are taken at Nyegga cold seeps located on the edge of the Norwegian continental slope and the northern flank of the Storegga slide, on the border between two large oil/gas prone sedimentary basin – the Møre basin to the south and the Vøring basin to the north[16]-[17]. The temperature and pressure condition is well inside the stability region of  $\text{CH}_4$ . The standard value of  $9.8 \text{ m/s}^2$  is assumed for gravity along the Y-axis of 2D geometry.

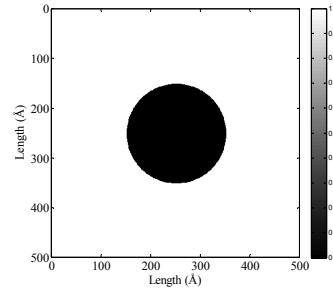


Fig. 1 Simulation at time zero, showing the initial picture of hydrate in black circle and liquid water in white with 500x500 Å and hydrate diameter of 200 Å.

The simulation is run to  $3.6\text{E}+06$  total time steps this corresponds to the time of 3.6 ns (Table.I).

Table. I The properties used to setup the simulations.

Total number of grid points	500×500
Corresponding area in $\text{m}^2$	$2.5\text{E}-15$
No. of time steps	$3.6\text{E}+06$
Total time in seconds	$3.6\text{E}-09$
$\text{CH}_4$ mole fraction in hydrate	0.14
Water mole fraction in liquid phase	1.0

The ratio between solid and liquid was taken as 1:2.5. This ratio is adjusted to achieve the stability.

The  $\text{CH}_4$  concentration initially was adjusted to 0.14 in the hydrate assuming that all the cavities were filled with  $\text{CH}_4$ . The Fig.2(a) shows that the mole fraction is equal to the initial value which means that  $\text{CH}_4$  has not yet diffused at time

zero. If the concentration of methane drops below the hydrate stability limit for the given temperature and pressure, a chemical potential driving force towards dissociation will arise as shown in Fig. 2(b) – 2(d). Also, these figures clearly indicate a non uniform dissociation of hydrate due to the effect of different velocities in different directions, which is a direct consequence of gravity.

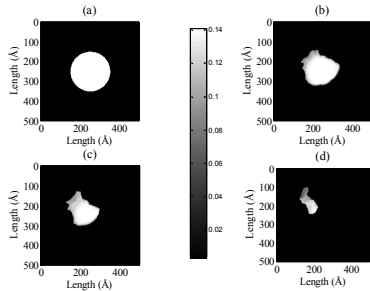


Fig. 2 The concentration profile, where a, b, c & d are 0, 1.225, 2.401 & 3.6 ns respectively.

The methane hydrate density is  $5.089E+04$  moles/m<sup>3</sup> and water density is  $1000$  kg/m<sup>3</sup> at time zero. The water density on the interface is decreasing due to the diffusion of dissociated methane from hydrate Fig.3. The dissociated gas may contain a fraction of free gas depending on the saturation of surrounding water with methane. The free gas exists in the form of bubbles which may escape in the environment through the empty channels.

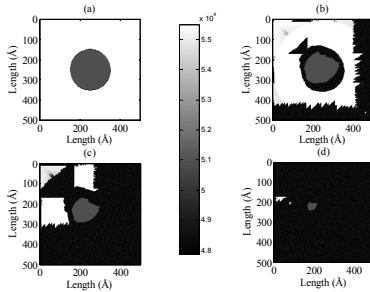


Fig. 3 Density of methane where a, b, c & d are 0, 1.225, 2.401 & 3.6 ns respectively.

The free gas is calculated by using the Raoult's law.

$$x_{CH_4} = \frac{y_{CH_4} f_{CH_4} P}{KH_{pc}} \quad (19)$$

Where  $f_{CH_4}$  is the fugacity of methane,  $KH_{pc}$  is the Henry's constant in atm units at current temperature,  $P$  is the pressure of the system,  $y_{CH_4}$  is the concentration of methane containing free gas and  $x_{CH_4}$  is free gas concentration. The Henry's constant calculated using the formulation from [18].

$$KH_{pc} = K_H^\theta \exp\left(\frac{-\Delta_{soln}H}{R}\left(\frac{1}{T} - \frac{1}{T^\theta}\right)\right) \quad (20)$$

Where  $K_H^\theta$  is the Henry's constant at temperature 298.15 K in M/atm,  $\Delta_{soln}H$  is the enthalpy of the solution. The temperature dependence term is calculated as

$$\frac{-d \ln K_H}{d(1/T)} = \frac{-\Delta_{soln}H}{R} \quad (21)$$

The free gas calculation after dissociation of the CH<sub>4</sub> hydrate is shown in the Fig.4 (b) at some time instant when some hydrate is dissociated. The difference between CH<sub>4</sub> containing free gas can be seen from the values shown in color bars.

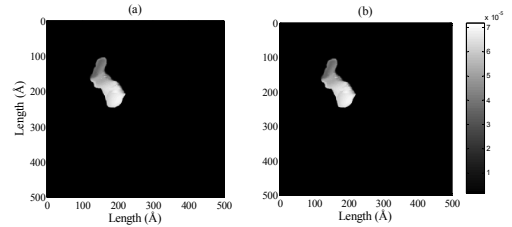


Fig. 4 Free gas profile, where (a) represents the methane concentration may contain free gas and (b) concentration of free gas.

The merging or deformation of bubbles depends on colliding force, elasticity and the interfacial energy of the bubbles. The criteria for potential merging or deformation may be found in literature. The thermo capillary and buoyancy forces drives the bubbles with velocity increasing with size and the square of the linear size respectively, thus large bubbles capture smaller bubbles [9]. Having the amount of free gas and velocity field, an improved and more realistic methane flux can be calculated than the previous work in Baig et al. [13].

## V. DISCUSSION

Previous phase field models used for hydrate phase transitions dynamics like in Baig et al. [13] have been extended with more appropriate description of density dependencies in the phase field part as well as in the hydrodynamic parts. For the fluid phases containing variable relative amounts of CO<sub>2</sub> and CH<sub>4</sub> this will be crucial for two important cases. One case is the dissociation of mixed hydrates of these two components and the potential of free gas formation. The other important application is for simulations of the exchange process between CH<sub>4</sub> and CO<sub>2</sub> during injection of CO<sub>2</sub> into natural gas hydrate. In this case a crucial question is to what extent the released methane will dissolve into CO<sub>2</sub> versus the extent of separate methane bubbles escaping due to buoyancy. Simulation studies of these cases will follow in a subsequent paper and then related to experimental studies of the exchange process in porous media.

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