PORE-SCALE MODELING OF OVERPRESSURE CAUSED BY HYDRATE DISSOCIATION

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ABSTRACT

It has been suggested that volume expansion caused by hydrate dissociation in sediment pores can result in large overpressure, which in turn may destabilize the sediment and trigger massive submarine landslides. Here, we investigate the pressure evolution during thermally-induced dissociation, by means of a pore-scale model that couples dissociation kinetics, multiphase flow and geomechanics. Dissociation is controlled by a self-preservation mechanism: increasing pore pressure reduces the driving force for dissociation. Hence, the overpressure is constrained by the phase equilibrium pressure, regardless of the kinetic rate of dissociation, heat supply, and sediment permeability. Furthermore, we find that the timescale for buildup of pressure by dissociation is typically much larger than that for its dissipation by drainage. Consequently, the overpressure is controlled by the capillary entry thresholds, which depend on the mode of gas invasion. In tight systems, fracturing is the preferred mechanism, occurring at capillary pressures lower than the entry thresholds in the undeformed sediment. Our results suggest that while the large overpressures evaluated in the literature cannot be sustained by rapid dissociation, dissociation can induce important geomechanical effects. Gas migration by fracturing provides a possible link between dissociation, sediment deformation and methane venting.

Keywords: hydrate-bearing sediments, hydrate dissociation, overpressure, multiphase flow, fracturing

NOMENCLATURE

\( a \) characteristic length scale of a pore [m]
\( A \) pore throat area \([m^2]\)
\( A_h \) surface area for hydration reaction \([m^2]\)
\( A_p \) grain area upon which pressure acts \([m^2]\)
\( c_t \) effective fluid compressibility \([Pa^{-1}]\)
\( E \) hydration activation energy \([J mol^{-1}]\)
\( E^* \) constrained Young modulus \([Pa]\)
\( f \) fugacity \([Pa]\)
\( f_c \) interparticle contact forces \([N]\)
\( f_p \) pressure force \([N]\)
\( f_{eq} \) equilibrium fugacity \([Pa]\)
\( F_A \) (hydration) area adjustment factor [-]
\( h \) spring contraction \([m]\)
\( h_0 \) initial spring contraction \([m]\)
\( \Delta h \) change in spring contraction \([m]\)
\( j \) index of adjacent pore [-]

\( k \) pore-scale permeability \([m^2]\)
\( K \) spring stiffness \([N/m]\)
\( K_h \) hydration reaction constant \([kg m^{-2} Pa^{-1} s^{-1}]\)
\( l \) pore-scale length for pressure drop \([m]\)
\( L_p \) pressure dissipation length scale \([m]\)
\( \Delta m_h \) dissociated hydrate mass \([kg]\)
\( M_i \) molar mass of phase \( i \) \([kg]\)
\( n_q \) number of gas moles in a cluster [-]
\( N_h \) hydration number [-]
\( p \) pore fluid pressure \([Pa]\)
\( p_0 \) initial water pressure (hydrostatic) \([Pa]\)
\( p_c^e \) capillary entry pressure \([Pa]\)
\( p_{eq} \) three-phase equilibrium pressure \([Pa]\)
\( p_{ex} \) mean gas overpressure \([Pa]\)
\( p_g \) mean cluster (gas) pressure \([Pa]\)
\( p_j \) fluid pressure in pore \( j \) \([Pa]\)
\( p_w \) water pressure \([Pa]\)
\( q_j \) pore-scale volumetric flow rate \([m^3/s]\)
\( r \) pore throat aperture \([m]\)
\( \Delta r \) change in throat aperture \([m]\)

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Methane hydrate is a solid compound that forms by crystallization of water and methane upon cooling and/or pressurization. Accumulations of methane hydrate in hydrate-bearing sediments (HBS) have gained much attention for their potential as an energy resource [1] and their role as a greenhouse gas in future global warming [2]. Heating or depressurization cause hydrate to dissociate into free gas and water. Dissociation of hydrate within the pore space of sediments has often been invoked as a mechanism that may lead to significant overpressures (up to tens of MPa), in view of the multiple-fold volume increase that occurs upon dissociation [3–5]. Overpressure induced by dissociation has been suggested as a trigger for sediment failure, including submarine landslides [3, 6, 7], soft-sediment deformation [8], pingo-like features [9], mud volcanoes [10] and wellbore damage [4]. Warming of ocean waters and consequent dissociation of extensive HBS layers, leading to sediment failure and massive release of methane gas, has been proposed as the cause of the Paleocene-Eocene Thermal Maximum [11], and as a potential key player in the current carbon cycle [12, 13].

The possible implications of dissociation raise the need for understanding the relevant mechanisms, in particular the interplay between dissociation and pressure evolution. Existing models predict large overpressures in fine-grained sediments, where the low permeability would prevent rapid pressure dissipation [3, 5, 14]. [3] evaluate overpressures as high as 50 MPa for undrained (no-flow) conditions and 7 MPa for low permeability sediment, assuming a constant dissociation rate which is independent of the pore pressure. The end-member scenario of no flow and restricted volumetric expansion was investigated by [5], who correctly point out that since rising pressure stalls further dissociation, additional heat is required to continue the dissociation process. This self-preservation mechanism leads to pressure-temperature (p-T) conditions which follow the three-phase (hydrate-gas-brine) equilibrium curve during dissociation. Therefore, a large overpressure (hereafter defined as the gas pressure above the initial water pressure $p_0$ prior to dissociation) implies a large temperature increase; for example, an increase of ~9 MPa is accompanied by a temperature rise of over 9°C (Fig. 1). A pressure increase of tens of MPa requires heating by tens of degrees, an unrealistic scenario in natural systems. Smaller pressures (less than 3 MPa) were predicted by [14] in simulating dissociation due to a wellbore (~20°C warmer than its surrounding) in a low-permeability clay. While the authors honor self-preservation by constraining the pressure by the equilibrium pressure, they do not account for dissociation kinetics, and assume that hydrate saturation is sufficiently low to neglect gas flow. However, we will show that gas flow and percolation can occur at hydrate saturations as low as 5%, in agreement with [15].

A crucial mechanism which is missing from the models cited above is the coupling among disso-
vation kinetics, flow of gas and water, and sediment deformation, including the formation of preferential flow paths and fractures. Consideration of this mechanism requires description of the pore-scale physics. [15] investigated the flow patterns of methane gas produced by heating an HBS, demonstrating that larger pore apertures or wider aperture distribution allow larger gas quantities to percolate through a sample, hence increasing the gas productivity. The authors used a pore-network model based on invasion percolation, assuming instantaneous dissociation and fixed network properties (no geometric effects).

In this paper we study the pressure evolution during thermally-induced dissociation. We present a mechanistic, pore-scale model that couples dissociation kinetics, multiphase flow and sediment mechanics. We explore the range of behaviors between the two end-members: (a) no-flow (undrained) conditions; and (b) instantaneous pressure dissipation (fully drained). We demonstrate that rapid pressure buildup is not possible because of the negative feedback between dissociation rate and fluid pressure. Our results suggests that while self-preservation restricts the pore pressure below the equilibrium value, rapid pressure dissipation by drainage further limits the overpressure by the characteristic capillary entry pressures. In compliant, fine-grained sediments in which invasion occurs by fracture opening, the fracturing pressure becomes the limiting value.

We simulate a low-permeability sample saturated with water and dispersed hydrate crystals, subjected to a sudden temperature increase which brings hydrate out of thermodynamic equilibrium. We assume that heat dissipates much faster than pressure, and therefore we model isothermal dissociation at a fixed, uniform temperature. We evaluate the temporal and spatial evolution of the mass, volume and pressure of hydrate, water and gas, and their impact on the sediment’s mechanical and flow properties. At each time step we compute: (1) the dissociated hydrate mass for every crystal, given the surrounding fluid pressures; (2) pore pressure variations caused by the conversion of hydrate into water and gas; (3) flow of gas and water induced by the rising pore pressure; and (4) changes in hydraulic properties by deformation of the solid matrix (microstructural rearrangements). We emphasize the role of drainage by assuming that the driving force for flow is the rise in gas pressure. Once gas pressure overcomes the local capillary thresholds, gas expands by invading into nearby water-filled pores.

We evaluate the pressure of gas clusters as they expand and coalesce, in addition to the local increase in water pressure due to fluid redistribution along the gas-water interface [16].

We capture the interplay between pore pressure and dissociation by computing the decomposition rate in each hydrate crystal using a kinetic model. The dissociated hydrate mass at each time step, \( \Delta m_h \), is determined according to a driving force which is proportional to the difference between the phase equilibrium fugacity \( f_{eq} \) and the methane fugacity at the hydrate crystal surface \( f \) [17].

\[
\Delta m_h = -K_h \exp \left( \frac{-E}{RT} \right) F_A h \left( f_{eq} - f \right) \Delta t.
\]

where \( K_h \) is the hydration reaction constant, \( E \) is the hydration activation energy, \( A_h \) is the surface area for the reaction (computed from its volume assuming spherical crystal, with area adjustment factor of \( F_A = 1 \)), \( \Delta t \) is the time step, and \( R = 8.314 \text{ J mol}^{-1} \text{K}^{-1} \) is the universal gas constant. Negative \( \Delta m_h \) implies decreasing mass. We evaluate \( f_{eq} \) and \( f \) from the equilibrium pressure \( p_{eq} \) (for a given temperature \( T \)) and the pressure of gas surrounding the dissociating crystal, \( p_g \). The reverse process, hydrate reformation, can occur locally upon reversal of the driving force \( (p_{eq} > p_g) \) [18]; this process is excluded from the current model.

The gas pressure in each gas cluster, \( p_g \), is evaluated through the ideal-gas equation of state (EOS), where we compute the cluster volume \( V_g \) from mass balance. Each mole of dissociated hydrate (with volume of \( \Delta V_h = M_h/\rho_h \)) is converted to \( N_h \) moles of water, which occupies a volume of \( \Delta V_w = N_h M_w/\rho_w \). Here, \( \rho_h = 900 \text{ kg/m}^3 \), \( M_h = 0.119 \text{ kg/mol} \), \( \rho_w = 1000 \text{ kg/m}^3 \) and \( M_w = 0.018 \text{ kg/mol} \) are the density and molar mass of methane hydrate and water, respectively, and \( N_h = 5.75 \) is the hydration number [19]. To obtain the cluster volume \( V_g \) we note that \( \Delta V_w / \Delta V_h \approx 0.8 \), hence the remainder 20% of the dissociated hydrate volume \( \Delta V_h \) is replaced with gas. For simplicity, we use here the ideal gas law, \( p_g V_g = n_g RT \), where \( n_g \) is the number of gas moles in the cluster. We have confirmed that the use of a more accurate EOS does not alter our results substantially; for example, the difference between overpressures evaluated with the ideal gas law and with the EOS in [20] in several representative simulations is \( \sim 0.1\% \). The number of gas moles \( n_g \) is computed from the number of disso-
associated hydrate moles, $\Delta n_h = \Delta m_h / M_h$. Given the low solubility of methane in water [19], we consider only two methane phases, hydrate and gas, neglecting the small quantities that dissolve in water.

Our model incorporates the two-way coupling between fluid displacement and mechanical deformation: pore opening in response to pressure loading (direct coupling), and alteration of the flow properties by grain rearrangements (reverse coupling) [21]. A deformable porous material is represented by a 2-D square lattice of dented blocks (grains), connected mechanically by nonlinear springs [Fig. 2(a)]. The voids between the blocks define a pore network: the narrow openings at the contacts are the pore throats, which connect the larger openings (pore bodies). Variation in block shapes leads to variability in throat apertures, which is assumed to be uncorrelated in space. This provides two interacting networks, solid and fluid, whose nodes are the particles centers and the pore bodies, respectively. We solve for displacement of the particles and fluid pressures at the pore bodies.

We account for pore-scale disorder by assigning different initial area $A$ and permeability $k$ to the pore throats. Both parameters scale with the square of the throat aperture $r$, that is, $A \sim r^2$, $k \sim r^2$. We characterize disorder through a scalar parameter, $\lambda \in (0,1)$, drawing values from a uniform distribution, $\lambda \in [1 - \lambda, 1 + \lambda] \bar{r}$, where $\bar{r} \sim a$. The characteristic length scale is the pore size $a$, which we take as half the distance between nodes in the lattice [Fig. 2(a)]. Partially-drained conditions are simulated through a decrease in permeability and throat area at the boundary (each by 3 orders of magnitude), equivalent to a reduction in throat aperture by a factor of $10^{3/2}$ relative to the sample’s interior. We enforce a constant hydrostatic pressure $p_0$ at the boundary pores.

In simulating flow we assume that gas is inviscid, such that its pressure adjusts instantaneously and is uniform within each cluster. The water pressure in an undrained pore is updated from mass conservation at a pore body: $p_w(t + \Delta t) = p_w(t) + \sum_j q_j^l \Delta t / (\epsilon_j V)$, where $V$ is the pore volume, and the summation is over all neighboring pores. The volumetric flow rate between the pore and its neighbor $j$ is given by Darcy’s law $q_j^l = (Ak/\mu)(p_j^l - p_w) / \ell_j^3$, where $\mu$ is the water dynamic viscosity and $\ell_j$ is the length over which the pressure drop $p_j^l - p_w$ occurs. For flow between two undrained pores, $\ell_j^3 = 2a$. If pore $j$ is drained, the meniscus between the two pores starts advancing once the cap-

![Figure 2](image.png)

Figure 2: (a) Schematic of the pore-scale model. The solid matrix is represented by a square lattice of dented blocks (grains), connected mechanically by springs. The narrow openings between grains are the pore throats, which connect the larger openings (pore bodies). Some pores are filled with hydrate crystals (brown), which decompose into water (white) and free gas (dark gray). (b) Pore pressure during simulation of dissociation. The grayscale intensity represents the pressure scaled to increase contrast: white corresponds to the ambient pressure $p_0$, black to high pressures in gas filled pores. The location of clusters of $3 \times 3$ pores originally occupied by hydrate crystals is marked in brown. The pressure halo that develops ahead of newly invaded pores reflects the finite timescale required for pressure dissipation. We use a network of $200 \times 200$ pores with $\lambda = 0.2$, $\epsilon_0 = 0.01$, $a = 1 \mu m$, $\mu = 10^{-5}$ Pa s and $\gamma = 0.07$ N/m. A system in equilibrium at $T_0 = 0.5^\circ C$ and $p_0 = 2.58$ MPa is subjected to $\Delta T = 10^\circ C$. 
illary pressure exceeds the capillary entry pressure, \( p^i - p_w > 2\gamma /r \), where \( \gamma \) is the gas-water interfacial tension. As the meniscus advances, the length is updated by \( \ell(t + \Delta t) = \ell(t) - (q^i / A)\Delta t \).

Readjustments of the gas-water interface associated with local rise in water pressures decrease the capillary pressures, therefore suppressing further invasion until the excess water pressure is dissipated [16]. The main effect of this mechanism is modeled here by assigning an effective fluid compressibility, \( c_t = a/\gamma \) [21]. The finite time required for pressure dissipation leads to the development of a pressure halo around the expanding gas clusters [Fig. 2(b)].

Changes in pore pressure cause grain rearrangements, which are represented in our model through contraction of the springs over time, \( h(t) \). We highlight the effect of disorder in flow properties by assuming that initially all springs are contracted by the same amount, \( h_0 \), corresponding to a macroscopic strain \( \epsilon_0 = h_0 /2a \). The confinement \( \epsilon_0 \) is sufficiently large to prevent granular flow. Each grain is subject to two types of forces: pressure and contact forces. The force exerted by the fluid occupying an adjacent pore body is oriented at 45° and is of magnitude \( f_p = p A_p \), where \( A_p = a^2 \) is the area upon which the pressure \( p \) acts. The intergranular contact forces \( f_c \) are updated by \( f_c(t + \Delta t) = f_c(t) + K\Delta h \), where \( K \) is the spring stiffness and \( \Delta h = h(t + \Delta t) - h(t) \) is the change in spring contraction. Grain positions are determined at the new time step by imposing force balance at every grain, \( \sum (f_p + f_c) = 0 \), which leads to a linear system of equations in \( \Delta h \). Grain displacements impact fluid flow by modifying the throat apertures. We evaluate changes in apertures and in intergranular forces from the grain displacements in analogy with cubic packing of particles with frictionless, Hertzian contacts, such that \( \Delta r = -\Delta h(1 - \epsilon)/[2\sqrt{1 + (1 - \epsilon)^2}] \), where \( \epsilon = h(t)/2a \), and \( K = 2E^s\sqrt{R^s}h \), where \( R^s = a/2 \), and \( E^s \) is the constrained Young modulus of the grain material [21]. We model an unconsolidated sediment with negligible tensile strength. Therefore, a spring is removed when there is net elongation between blocks (\( h < 0 \)). A small cohesive force is applied as a regularization parameter.

Our simulations demonstrate that the pressure always remains below the equilibrium value, \( p_{eq}(T) \). Self-preservation, where increasing gas pressure diminishes the driving force for further dissociation [Eq. (1)], is evident from the decreasing rate of pressure buildup by dissociation between gas invasion (pore-filling) events. Furthermore, comparison of the gas and water pressure evolution indicates that the timescale for pressure buildup by dissociation, \( t_d \), is much larger than that of pressure dissipation following drainage of one or more pores and water flow ahead of the moving meniscus, \( t_p \) (Fig. 3). The contrast in timescales can be deduced by scaling: \( t_p \sim L_p^2 /D \), where \( D = (k/\mu) /c_t \) is the hydraulic diffusivity, and \( L_p \) is the characteristic distance over which pressure dissipation takes place. With \( k \sim a^2 \) and \( c_t \sim a/\gamma \) we obtain \( t_p \sim \mu L_p^2 / (\gamma a) \). The dissociation timescale can be obtained from Eq. (1), by using the EOS to relate the change in the number of gas moles (\(-\Delta m_H / M_M \)) to the change in gas pressure, \( \Delta p_g \), and assuming that the latter scales as the fugacity driving force, \( \Delta p_g \sim f_{eq} - f \). This provides \( t_d \sim M_b a /|RT K_a \exp(-E/RT)| \). Using published values of \( E = 8.1 \times 10^{-4} \text{J mol}^{-1} \) and \( K_a = 3.6 \times 10^4 \text{kg m}^{-2} \text{Pa}^{-1} \text{s}^{-1} \) [22] suggests that \( t_p \) is smaller than \( t_d \) by 4 to 8 orders of magnitude, depending on the value of \( L_p \); \( L_p \sim \alpha \) provides an upper bound of \( 10^3 \), whereas the contrast becomes smaller as \( L_p \) approaches the system size. Since \( L_p \) reflects the spacing between gas clusters, the timescale ratio will be between the two values.

The rapid dissipation of pressure by drainage relative to its buildup by dissociation implies that the pressure evolution is governed by capillary effects: once the gas pressure exceeds the sum of the water pressure \( p_w \) and entry pressure \( p_c^e \) in an adjacent undrained pore, gas expands by invasion and its pressure drops. For the scale of interest here, we can understand gas invasion driven by hydrate dissociation as a quasi-static process, where the water pressure relaxes quickly to a value close to \( p_h \) (Fig. 3). Thus, gas overpressure is controlled by the capillary entry thresholds for gas invasion.

To demonstrate the role of capillarity we compare the maximum pressure that develops during the simulations (until complete dissociation) in systems of different permeability. We vary the permeability by scaling a given aperture distribution (\( r_0 \), similar in all samples) by a pore-to-throat parameter \( \beta = r_0 /r \), keeping the pore size \( a \) fixed. The resulting gas overpressures in most simulations are bounded between the minimum and maximum capillary entry pressures, \( p_c^e,_{\text{min}} = 2\gamma /[(1 + \lambda) r] \) and \( p_c^e,_{\text{max}} = 2\gamma /[(1 - \lambda) r] \), with values closer to \( p_c^e,_{\text{min}} \) as the permeability increases and to \( p_c^e,_{\text{max}} \) as it gets smaller (Fig. 4). This behavior is caused by two mechanisms: heterogeneity and matrix deformation.
The higher capillary pressures that develop in low-permeability systems lead to smaller number of invaded pores (smaller gas volume, higher density), hence sampling of a smaller portion of the aperture distribution, with only the widest throats (lowest \(p_e^c\)) invaded. In addition, higher capillary pressures cause more pore opening through grain rearrangements, creating fractures [21, 23]. Fracturing allows gas invasion at capillary pressures lower than the original thresholds in the undeformed system, \(p_e^c\). For a given aperture distribution, the mode of invasion is determined by the grain stiffness and the external confinement: fracturing tends to occur in softer sediments under lower confinement [21].

Finally, the scaling of the characteristic time for dissociation \(t_d\) suggests that it can become comparable to that of pressure dissipation \(t_p\) if the kinetics were much faster, that is, for much larger reaction constant \(K_h\) or characteristic distance \(L_p\) values. We investigate this theoretical limit by simulating dissociation with \(K_h\) values up to \(10^4\) higher than published values [22]. While the resulting overpressures exceed the hydrodynamic limit imposed by capillarity, they always remain well below the thermodynamic equilibrium value \(p_{eq}\).

In conclusion, we have shown that the overpressure from hydrate dissociation in sediments is governed by the competition between thermodynamics (reaction rate) and hydrodynamics (pressure dissipation). Due to self-preservation, the overpressures cannot exceed the phase equilibrium pressure, regardless of the heat supply and sediment permeability. If the intrinsic kinetic rate was many orders of magnitude faster than its published value, the dissociation rate could be controlled by the ability of the medium to dissipate the pressure. Our results suggest, however, that the timescale for pressure buildup by dissociation is much larger than that of pressure dissipation following an invasion event, \(t_p \sim 10^{-5}\) s [between the peak and the plateau in inset (a)]. The effect of expansion and coalescence of different gas clusters is captured by the volume-averaged gas pressure, \(\bar{p}_g = \sum_j (p_j V_j) / \sum_j V_j\) (summation over all drained pores). During the entire simulation [inset (b)], the gas pressure is constrained by both thermodynamics (\(p_g < p_{eq}\)) and hydrodynamics (\(p_g < p_e^c + p_w\)). We use a network of 100×100 pores and \(\lambda = 0.1\). Here, we simulated a relative low temperature increase, \(\Delta T = 1.5^\circ C\), to emphasize the effect of self-preservation.
Figure 4: Mean overpressure $p_{ex} = \bar{p}_g - p_0$ and typical invasion pattern (insets) in systems of different permeability $k \sim \bar{r}^2$ (varied by scaling the aperture distribution by $\beta$). Because dissipation of pressure by drainage is much faster than its buildup by dissociation, the overpressure is governed by the capillary entry thresholds. In most simulations, $p_{c,min} < p_{ex} < p_{c,max}$. As the permeability becomes smaller, $p_{ex}$ approaches the lower bound $p_{c,min}$ due to the combined effect of heterogeneity and deformation. In low-permeability systems, the highly-pressurized gas occupies a smaller volume and hence samples a smaller portion of the aperture distribution, with only the widest throats (lowest $p_{c}^e$) invaded. In addition, the high capillary pressures can lead to fracture opening, which is the preferred mode of gas invasion in soft, fine-grained sediments. In the coarsest samples ($k > 0.02 \text{ mD}$), the overpressures slightly exceed $p_{c,max}$ (by $\sim 0.1 \text{ MPa}$) due to a similar increase in water pressure (Fig. 3) which elevates the gas pressure required for invasion. Such pressure increment is negligible relative to the high gas pressure that develops in lower-permeability systems. We use networks of $100 \times 100$ and $200 \times 200$ pores for the main plot and the insets, respectively, with $\lambda = 0.1$ and $E^* = 2 \text{ GPa}$.

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