Congrui Jin · Gianluca Cusatis Editors

New Frontiers in Oil and Gas Exploration



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Editors Congrui Jin Department of Mechanical Engineering Binghamton University State University of New York Binghamton, NY, USA

Gianluca Cusatis Department of Civil and Environmental Engineering Northwestern University Evanston, IL, USA

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Preface

The United States has seen a resurgence in petroleum production, especially when new discoveries of unconventional oil and gas sources have dramatically reshaped both the energy outlook and the future of chemicals production in this country. They have the potential to positively influence our overall trade balance and future economic growth rate for decades to come. Gas shale production sites throughout the United States are replacing coal power plant operations with environmental benefits associated with lower levels of life-cycle carbon dioxide emissions. However, production of gas from low permeability shale involves hydraulic fracturing of shale into a sufficiently dense system of cracks, and thus establishing fracture/ joint connectivity to facilitate fluid and gas flow. Unfortunately, these procedures are not without adverse environmental consequences, such as potential contamination of fresh water resources, seismic activities resulting from the stimulation of the rock formation (induced seismicity), and the disposal of flow-back and production water (triggered seismicity). It is clear that mitigation of the environmental impact of unconventional resource development needs to be pursued by a variety of technological innovations aiming at optimizing hydraulic fracturing protocols to increase recovery efficiency above the current level and to reduce water usage, which, however, requires the fundamental understanding of the failure and flow phenomena occurring in the heterogeneous shale formations, deeply buried under the earth surface, which cannot be investigated easily through experimental or field observations. This book will highlight how this new domestic energy source may be utilized and managed and the projection for the long-lasting economic impact if the United States is to take full advantage of this new unique opportunity. With the technologies simply changing too fast, this book will provide the latest research works and findings in this field, with a focus on key practical issues, such as computational characterization of shale at multiple length scales, mechanical interactions of proppant and hydraulic fractures, and production analysis of a multi-fractured horizontal well, etc. This book will bring unique perspectives of knowledge and experience in dealing with many of the issues about oil and gas exploration. It contains both cutting-edge original research and comprehensive reviews addressing both theory and practice. This book focuses on key practical issues, and it is a practical reference for geoscientists and engineers in the petroleum and geothermal industries, and for research scientists interested in reservoir modeling and their application to the improvement of current design of hydraulic fractures.

Binghamton, NY, USA Evanston, IL, USA Congrui Jin Gianluca Cusatis

Contents

1	Understanding Asphaltene Aggregation and Precipitation Through Theoretical and Computational Studies	1
2	Advancement in Numerical Simulations of Gas Hydrate Dissociation in Porous Media Zhen Liu and Xiong Yu	49
3	Discrete Element Modeling of the Role of In Situ Stress on the Interactions Between Hydraulic and Natural Fractures	113
4	Rock Physics Modeling in Conventional Reservoirs Dario Grana	137
5	Geomechanics and Elastic Anisotropy of Shale Formations Mehdi Ostadhassan	165
6	Nano-Scale Characterization of Organic-Rich Shale via Indentation Methods	209
7	On the Production Analysis of a Multi-Fractured Horizontal Well	235
8	Interfacial Engineering for Oil and Gas Applications: Role of Modeling and Simulation	257

9	Petroleum Geomechanics: A Computational Perspective Maurice B. Dusseault, Robert Gracie, Dipanjan Basu, Leo Rothenburg, and Shunde Yin	285
10	Insights on the REV of Source Shale from Nano- and Micromechanics	335
11	Experimental and Numerical Investigation of Mechanical Interactions of Proppant and Hydraulic Fractures Congrui Jin	367
12	Integrated Experimental and Computational Characterization of Shale at Multiple Length Scales	389
13	Recent Advances in Global Fracture Mechanics of Growthof Large Hydraulic Crack Systems in Gas or Oil Shale:A ReviewZdeněk P. Bažant and Viet T. Chau	435
14	Fundamentals of the Hydromechanical Behavior of Multiphase Granular Materials Francesca Casini	461
15	Beyond Hydrocarbon Extraction: EnhancedGeothermal SystemsMasami Nakagawa, Kamran Jahan Bakhsh,and Mahmood Arshad	487
16	Some Economic Issues in the Exploration for Oil and Gas Charles F. Mason	507
Err	atum	E1
Ind	ex	519

Chapter 2 Advancement in Numerical Simulations of Gas Hydrate Dissociation in Porous Media

Zhen Liu and Xiong Yu

Abstract The amount of research on gas hydrates has been rising dramatically due to the significant role gas hydrates play as a persistent trouble for gas industry, a promising energy source, and a potential threat to environment. In the energy exploration perspective, numerical simulations play a major role in improving our understanding of the fundamentals gas hydrate dissociation as well as hydrate reservoir behaviors. This chapter presents an integrative review on the computer simulation models of gas hydrate dissociation, which have boomed since their first appearance in 1980s. Necessary background knowledge for gas hydrates and the existing investigations on this topic are firstly summarized. A unified framework is then developed for the purpose of integrating and classifying the existing models. The major mechanisms involved in the phase change process are illustrated and explained on the level of governing equations. The similarities and discrepancies among the models are demonstrated and discussed using this framework. Discussions continue on the auxiliary relationships for describing the material properties based on their categories. The various auxiliary relationships employed in the existing computational models are summarized and compared. Finally, the results obtained by previous simulations as well as other laboratory or field data are discussed. Noteworthy trends in the numerical simulations of gas hydrates behaviors are also unveiled. Recommendations are provided for future research. By providing an overview of the topic area, this chapter intends to provide scientific basis to understand the existing gas hydrate simulation models as well as serve as a guide for future research on advanced gas hydrate simulations.

Z. Liu

X. Yu (🖂)

Department of Civil and Environmental Engineering, Michigan Technological University, 1400 Townsend Drive, Houghton, MI 49931, USA

Department of Civil Engineering, Case Western Reserve University, 2104 Adelbert Road, Bingham 206, Cleveland, OH 44106-7201, USA e-mail: xxy21@case.edu

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2.1 Introduction

This chapter intends to provide a systematic review on the theoretical basis of numerical simulation models for gas hydrates in porous media. The progresses in gas hydrate exploration have advanced to the stage that requires holistic computational simulations of reservoir behaviors. Examination of the existing literature sees a clear trend in developing advanced computational simulation models. The primary goal of this review chapter is to lay down a unified framework for mathematical models for the numerical simulations of gas hydrate dissociation as well as to integrate existing studies. Only models based on continuum mechanics are reviewed due to the fact that this type of model is more popular than alternative models such as the discrete element method and molecular dynamics. The chapter firstly reviews the history of gas hydrates research to lay down the corner stone for the subsequent introduction to numerical simulations. Existing gas hydrate simulation models are reviewed, categorized, compared, and discussed. Both analytical and numerical models are reviewed because analytical methods share a similar theoretical background with numerical ones. A new framework is proposed where the discrepancies among existing models are reconciled. Besides, auxiliary relationships needed for implementing computational simulations are summarized, compared and evaluated. The solution techniques are not included in this review due to the scope of this review as well as length limitation. Furthermore, the emphasis is placed on the dissociation process rather than the formation process considering the relevance to gas recoveries.

This chapter is composed of six sections, i.e., introduction, background, governing equation system, auxiliary relationships, discussion, and conclusion. The Introduction provides a brief technical and historical overview on gas hydrate related activities. The Background section firstly reviews the basic knowledge about gas hydrate including the definitions, physics, practical values, reserves and explorations as well as different recovery methods. This is followed by the introduction to previous research based on application types in chronological order. Then, common simulation methods for gas hydrates are described. The Governing Equation section reviews the various aspects about the governing equation system. It first discusses the basic mechanisms that might be involved in a recovery process of gas hydrates. This is followed by the establishment of a unified framework for the computer simulation models of gas hydrates. The existing models are then reviewed, categorized, and compared within this unified framework. Finally, discussions are made with respect to the chemical models and the recovery schemes that these models are associated with. In the Auxiliary Relationship section, different auxiliary relationships are discussed and categorized in the order of physical fields that they are related to. The differences and relationships among functions in the existing models are demonstrated. In the Discussion section, the performance of the existing models is evaluated. Comments are made on current simulations and disputes. Several trends which may indicate a direction for future research are revealed. The Conclusion section briefly summarizes the results of this review.

2.2 Background

2.2.1 Introduction to Gas Hydrates

Gas hydrates, or clathrate hydrates, exist in a solid, ice-like form that consists of a host lattice of water molecules enclosing cavities occupied by molecules of guest gases [1]. Common guest gases in gas hydrates include CH₄, C₂H₆, C₃H₈, i-C₄H₁₀, CO₂, and H₂S; they also include other gases such as Ne, Ar, Kr, Xe, N₂, O₂, and hydrocarbons such as cyclopropane [2, 3]. Gas hydrates can be categorized into Structure I, II, and H according to the type of cavity in the host lattice. Each cubic meter of gas hydrates can hold approximately 160 m³ of natural gas at standard temperature and pressure [4]. Gas hydrates stay stable under certain thermodynamic conditions, i.e., low temperatures and high pressures [5, 6]. Such a condition can be provided by geologic formations such as permafrost and suboceanic sediments [7-11]. Most marine gas hydrates are formed of microbially generated gas [12]. In general, gas hydrates can contain different guest molecules in different cages, depending on their sizes and the availability of guest molecules under given thermodynamics conditions. But methane is the prevalent gas in natural gas hydrates [13]. Therefore, many studies under the name of gas hydrates are actually directed to methane hydrate.

Gas hydrates are important energy sources mainly due to the huge amount of hydrocarbons in concentrated forms they contain [12, 14]. Of primary interest are the hydrates that contain combustible low molecular weight hydrocarbons such as methane, ethane, and propane [1, 15, 16]. According to Makogon [11], there are tremendous amounts of natural gas trapped in hydrates in the permafrost and the continental shell in the ocean around the globe [7, 11]. Worldwide, gas hydrate was estimated to hold about 10^{16} kg of organic carbon in the form of methane [17]. The surveys by the US Geological Survey (USGS) have estimated that reserves of methane in hydrate form exceed all the other fossil fuel forms of organic carbon [11, 17–20]. Therefore, naturally occurring gas hydrates on the earth, containing mostly methane, have the potential to become a major source of energy in the second half of the 21st century [21]. Gas hydrates have aroused great interest in disciplines such as chemical engineering, chemistry, earth sciences, and environmental sciences [3, 22]. But in fact, gas hydrates were initially regarded as a source of problems in the energy industry because the conditions under which oil and gas are produced, transported, and processed are frequently conducive to gas hydrates formation [2, 5, 14, 23–25]. Recently, considerable concern over the potential threat of gas hydrates to the global environment has been raised because of the great green house effect of methane. It was argued that release of the large volumes of greenhouse gas stored in hydrates into the ocean and atmosphere may have played a role in the past climate change [26, 27]. Besides, rapid hydrate dissociation may lead to landslides along continental margins as well as other geohazards [3, 28, 29].

Natural hydrate deposits can be divided into four classes [30–32]. Class 1 deposits are composed of two layers: an underlying two-phase fluid zone with

mobile (free) gas, and an overlying hydrate-bearing layer (HBL) containing water and hydrate (Class 1 W) or gas and hydrate (Class 1G). In Class 1 deposits, the bottom of the hydrate stability zone (HSZ) coincides with the bottom of the HBL. Class 2 deposits comprise two zones: the HBL overlying a mobile water zone. Class 3 deposits are composed of a single zone, the HBL. And this type of deposit is characterized by the absence of an underlying zone of mobile fluids. In Class 2 and 3 deposits, the entire hydrate interval may be at or within the HSZ. Class 4 deposits involve disperse, low-saturation accumulations in marine geologic media that are not bounded by confining strata and can extend over large areas. Within these four classes, Class 1 reservoirs are thought to be the easiest and probably the first type of hydrate reservoir to be produced [33]. Although most of the seafloor lies within the low-temperature and high-pressure conditions necessary for hydrate formation, hydrates are generally found in sediments along continental margins, where adequate supplies of biogenic gases are available [34, 35].

Technologies for recovering methane (CH₄) from gas hydrates reservoirs are very challenging and still under development [36]. The general concept of producing natural gas from geologic deposits of gas hydrates is to alter the reservoir environment (i.e., temperature or pressure) so that the gas hydrates transit from being thermodynamically stable to unstable [37]. The thermodynamic stability of gas hydrates is dependent upon the temperature and pressure of guest molecules as well as aqueous solute concentrations [35, 37]. Accordingly, the three most practical methods for gas hydrates harvesting are: (1) depressurization, in which the pressure of an adjacent gas phase or water phase is reduced to trigger gas hydrates decomposition; (2) thermal stimulation, in which an external source of energy is provided to increase the temperature; and (3) inhibitor injection, in which methanol or a combination of inhibitors is used to de-equilibrate the system by raising the aqueous solute concentration [8, 15, 20, 38, 39]. An alternative approach is to reduce the partial pressure of the guest molecule by introducing a substitute guest molecule, such as carbon dioxide [40]. For example, introducing carbon dioxide into geologic media filled with methane hydrate results in the displacement of methane with carbon dioxide as a guest molecule without dissociating the hydrate [41, 42]. Among these methods, thermal stimulation models are produced from laboratories [5, 39, 43, 44]. Depressurization, on the other hand, has been the method used in the field production such as in the Messoyakha field, USSR [45].

2.2.2 Existing Research on Gas Hydrates

The research on gas hydrates can be categorized based on the research subjects of the efforts and application types. In terms of the types of research subjects, the categories include: (1) basic research, which focuses on the physical properties, phase equilibrium and kinetics of gas hydrate and so on; (2) geologic explorations of natural gas hydrate resources, which focus on the geological setting, bottom simulating reflectors, geochemical anomalies around gas hydrate reservoirs and so on; (3) simulation techniques for the formation and dissociation processes, which include analytical, numerical and experimental methods; (4) hydrate-based new technologies, such as thermal energy storage, separation of gas mixtures, storage of natural gas [46]. Alternatively, previous studies on gas hydrates can be grouped based on their application types where the advances in this topic can be followed in chronological order, i.e., (1) flow assurance; (2) energy recovery; (3) hydrate-based new technologies (gas storage/transportation); and (4) environmental applications (safety and climate change) [47]. The following context is based on the second classification method.

Interest in gas hydrates was firstly sparked in the early 19th century by chemists when making hydrates of different gases, mostly as a curiosity in the laboratory [48]. In 1778, gas hydrates were first obtained by Priestley by means of bubbling SO₂ through 2 °C water at atmosphere pressure. In 1810, Sir Humphry Davy observed that a solid could be formed when an aqueous solution of chlorine was cooled to a temperature below 9 °C [49]. Faraday [50] confirmed the existence of this solid compound, the composition of which was believed to be 1 part of chlorine and 10 parts of water. It is now recognized that more than 100 species of gases can be combined with water to form nonstoichiometric solid compounds, to which the term "gas hydrates" has been applied [51]. During the first 100 years after the discovery of gas hydrates, most interest in these compounds was pure academic [3]. And the primary efforts were to understand (1) what species can form hydrates and (2) what are the thermodynamic conditions for the gas hydrates formation.

Industrial interest in gas hydrates began in the 1930s, accompanying the booming of gas and oil industry, due to the discovery that hydrate formation could plug natural gas pipelines. In 1934, Hammerschmidt noted that blockage observed in some gas-transmission pipelines was gas hydrates rather than ice [48]. Thereafter much research including extensive thermodynamic studies was carried out to understand the conditions of hydrate formation [2]. As commented by Phale et al. [14], until recently, the natural gas industry considered methane hydrates only as a nuisance, which occasionally plugs up pipelines or causes wellbores to collapse. However, this promoted intense research efforts on natural gas hydrates by industry, government, and academia. More information about these research efforts can be found in the monograph of Deaton and Frost [52].

The third period in the history of gas hydrates studies was initiated by the discovery of naturally occurring gas hydrates under different geological formations [11, 24]. In the 1960s, it was realized that clathrate hydrates of natural gas exist in vast quantities in the earth's crust [9, 53, 54]. For example, gas production from naturally occurring hydrate deposits was reported in the Messoyakha field in western Siberia where an interval saturated with gas hydrates overlaid a gas-saturated formation [48]. The discovery of naturally occurring gas hydrates coincided with the peak of a global energy crisis, which pushed forward the study of gas hydrates in the 1970s [24]. Starting in the 1970s, the search for oil and gas extended into regions which were more difficult to explore, but where geological temperatures and pressures were suitable for the formation of natural gas hydrates [6]. Natural gas hydrates, once considered merely as a nuisance in gas pipelines,

were then examined as a long-term energy resource [5]. A bottom simulating reflector was commonly employed to mark the base of gas hydrates in marine sediments [55, 56]. The large amounts of gas in hydrate form justified efforts to find economic recovery schemes [57]. The need to understand gas hydrates together with other technological considerations motivated most of these research efforts [3].

Along with the investigations in gas hydrates as an energy resource, more concern regarding the influence of gas hydrates recovery or naturally dissociation on the climate change, ecosystems, and stability of gas hydrate reservoirs including wellbore safety has been expressed [26–29, 35, 48, 58–65]. For example, studies on the processes of formation and dissociation of gas hydrates in many recent studies are focused on the problems of hydrate formation in the face zones of boreholes, inside boreholes, and in pipelines [25]. Despite the concern with the potentially detrimental effects, there have also been efforts in developing innovative technologies based on the characteristics of gas hydrates for various purposes, such as natural gas storage [66–69], hydrogen storage [70, 71], thermal energy storage ([72]; McCormack, 1990; [73]), and separation of gas mixtures [74].

By reviewing the research on gas hydrates, the state of the art and the key challenges for the future advances in gas hydrates research can be summarized as follows. (1) In flow assurance research, a new approach, known as risk management is being developed to take the place of conventional methods such as thermodynamic chemical inhibitor injection due to economic and ecological concerns [61]. (2) Various aspects for gas recovery from hydrate-bearing formation are being investigated for commercial recovery due to the huge potentials. (3) The environmental impact of naturally occurring hydrates is still mostly unknown, but has been arousing increasing interest. (4) The use of hydrates to store fuel is an exciting prospect that has potential advantages over other storage materials. It should be noted that recovering gas hydrates from naturally occurring reservoirs serves as the major stimulus for various research on gas hydrates. And substantial computer simulations and laboratory experiments have been conducted while in situ explorations have just started. However, the behaviors of gas hydrate in porous media have not been completely understood. Permafrost hydrates are being considered for production tests in the USA, while efforts for marine gas hydrate are also being explored due to the huge amount of marine hydrates (by several orders of magnitude larger than that in the permafrost areas) [61].

2.2.3 Numerical Simulations of Gas Hydrates

Despite the vast reserves, gas hydrates have not been significantly exploited for energy. One of the reasons for this paradox is the limitation in our understanding of the hydrate reservoirs behaviors [75]. A large amount of literature exists on the fundamental behaviors of pure gas hydrates. However, the behaviors of hydrates in porous media, especially those during dissociation processes, are not yet

completely understood. Progress is needed to understand the behaviors of gas hydrate dissociation inside pore space, especially at the reservoir scale. This will help develop efficient and economic recovering methods. Theoretical studies including analytical and numerical models need to be coordinated with laboratory studies to address the knowledge gaps that are critical to the prediction of gas production [32].

Numerous analytical methods were proposed for predicting the dissociation rate of gas hydrates to understand the feasibility of recovering gas hydrates, especially in early times. As little was known about naturally occurring hydrates at that time, relatively simple models were used to yield good "ball park" numbers in many studies [76]. Examples of these models include those proposed by Selim et al. [44], Makogon [11], Goel et al. [77], Ji et al. [78], Hong and Pooladi-Darvish [8], Hong et al. [8], and Vasil'ev et al. [79]. In these models, hydrate dissociation was generally viewed as a moving boundary ablation process similar to solid melting [80, 81]. Accordingly, these analytical models usually assumed that decomposition happens at a sharp interface that divides the medium into two regions: the hydrate zone and the dissociated zone. The analytical solutions to these models were obtained based on the use of the governing equation linearization method [79, 82]. Geramiand and Pooladi-Darvish [83] provided a good review for analytical models for the dissociation of gas hydrates.

More detailed studies employ numerical simulation studies. Numerical studies give useful information for predicting the potential and technical viability of a gas recovery process. Modeling gas production from hydrate reservoirs involves solving the coupled equations of mass and energy balances [84]. Numerical models are developed based on similar mathematical equations to those used in analytical models. However, numerical models could be much more rigorous yet more computing resource demanding as they eliminate the simplifications which are necessary for analytical solutions. The theoretical bases of these numerical models are the mathematical model consists of a governing equation system and auxiliary relationships. Governing equations describe the basic mechanisms involved in the physical process of gas dissociation or formation, such as heat transfer (thermal field), mass transfer (extended hydraulic field), conservation of momentum (extended mechanical field), and the kinetics of chemical reactions (chemical field). One governing equation is used to formulate one basic mechanism for the whole system or for one phase/component within the system. Based on the types of basic mechanisms considered, the existing numerical models for gas hydrate recovery can be categorized as Thermo-Chemical models (TC), Hydro-Chemical models (HC), Thermo-Hydro-Chemical models (THC), and Thermo-Hydro-Mechano-Chemical models (THMC). Therefore, these models are in general of a multiphysics nature. On the other hand, various auxiliary relationships are necessary to mathematically close the equation system. These auxiliary relationships represent different material properties of gas hydrates and are affiliated with different physical fields. A mathematical equation system is usually solved with numerical methods such as the finite difference method or the finite element method.

Contribution of this Review: There have been numerous reviews conducted on the various aspects of gas hydrates research. However, a direct comprehensive review on the existing computational models is rare. Mandelcorn [85] reviewed the structure, molecular and thermodynamic properties, and uses of clathrates. The review of van der Waals and Platteeuw [86] included details regarding hydrate structures, a summary of the field and an application of thermodynamics. Byk and Fomina [87] summarized the known structures of hydrates, the thermodynamics of hydrate formation, and methods of determining the composition of hydrates and so on. Hand et al. [88] presented a general view of gas hydrates. Davidson [51] offered the most comprehensive review on the properties and structures. Jeffrey and McMullan [89] and Jeffrey [90] also reviewed the structures of gas hydrate. Holder et al. [91] offered a review on the gas hydrate equilibrium predictive methods. Makogon [92] summarized the work in the Soviet Union on the thermodynamics and kinetics of hydrate formation and the formation of hydrates in porous media. Berecz and Balla-Achs [93] reviewed the literature up to 1980 with emphasis on properties which are important to engineering applications of gas hydrates. The volume edited by Cox [94] contained eight peer-reviewed papers on the properties, phase equilibriums, kinetics, occurrence, and recovery of gas hydrates. Sloan [95] presented a comprehensive overview on the clathrate hydrates of natural gas. More recent advances could also be found in reviews conducted by Englezos [3], Makogon [11], Sloan [96], Buffett [97], Koh [98], Guo [46], Waite et al. [99]. Despite the numerous numerical models that have been developed, a critical review on the theoretical basis for numerical simulations of gas hydrate recovery is unfortunately absent at this time. Such a review paper could be extremely useful for researchers by offering a bird's view and laying down directions of future research. Research of Hong et al. and Sung et al. (i.e., [8, 100]) only very briefly summaries the previous simulation models in the introduction part of their research papers. This chapter contributes by providing an integrative review, which is conducted within a unified theoretical framework, to stress the similarities and differences among existing models and to highlight the underlying mechanisms. This will address an urgent need in advancing computational simulations for gas hydrate utilization.

Structure of Review: A mathematical model is essential in numerical simulations because such simulations involve the solutions of the mathematical model using numerical techniques. However, the reality is in spite of the large number of investigations on hydrate dissociation in reservoirs, there still has no complete, even qualitative picture of the physical processes accompanying hydrate dissociation [79]. One major reason is that gas hydrate dissociation is a multiphysical process. This process occurs in porous media system of multiphases and multicomponents. The properties of these porous materials are not completely understood, partly due to the fact that these materials were formed in remote environments under high pressures and low temperatures. Therefore, it is needed to thoroughly understand the individual process in order to construct a complete picture of the dissociation process [8, 79].

With this in mind, we firstly categorize the various mathematical descriptions involved in the dissociation process of gas hydrates into two components: (1) equations for the basic mechanisms, which determine the form of governing equation system (i.e., the number of equations needed, the dependent variables, and the terms in each equation). (2). equations describing the auxiliary relationships, which determine the form of individual terms in the governing equations and the relationships between different terms and dependent variables (i.e., how to formulate each term, the relationships between two terms, between a term and a dependent variables, or between two dependent variables). Section 2.3 focuses on the first component, i.e., equations for the basic mechanisms; while Sect. 2.4 focuses on the second component, i.e., equations describing the auxiliary relationships. The first part of Sect. 2.3 is a review on the primary mechanisms. Based on this, a unified framework for these models is proposed. The integration of existing models within the proposed framework is then discussed.

2.3 Basic Mechanisms in Hydrate Disassociation: Governing Equation System

2.3.1 Basic Mechanisms Involved in Gas Hydrate Dissociation

The term, *basic mechanism*, is used here to describe the fundamental processes involved in gas hydrate dissociation, which typically involves chemical, thermal, hydraulic, and mechanical fields.

The chemical field describes the dissociation reactions in gas hydrate. Chemical reactions, which describe the dissociation reaction of gas hydrates into gas and water, is the major driving force for the whole multiphysical process. These dissociation reactions can be triggered by breaking the thermodynamic equilibriums by means of lowering the pressure, raising the temperature or changing the concentrations. The chemical field is the dominant mechanism in most simulation models for gas hydrate dissociation in porous media. The mass and/or energy produced by the dissociation reactions can be established based on either an equilibrium model or a kinetic model. For equilibrium models, the computational domain is divided into an un-dissociated hydrate zone and a dissociated zone, which are separated by a boundary. Thermodynamic equilibrium is ensured on the boundary to provide one more equation for the equation system. The two zones are related by the use of conservation laws along the boundary. For kinetic models, chemical kinetics is used to predict the rate of dissociation, that is, the rate of dissociation reactions is determined by the relative positions of current state (a point) with regard to the equilibrium state (a line or a surface) in the phase diaphragm.

The thermal field (i.e., heat transfer) and hydraulic field (i.e., extended mass transfer) are two other important mechanisms frequently involved in modeling gas hydrate dissociations in the existing simulation models. For example, Sun et al. [12] proposed and implemented two different simulation schemes, i.e., the dissociation-controlled scheme (which corresponds to chemical field domination) and the flow-controlled scheme (which corresponds to hydraulic field domination). It was found that dissociation produced in the laboratory-scale experiments was often dissociation-controlled while that produced in the field-scale processes was typically flow-controlled. A few other studies claimed that the chemical field and thermal field dominated the dissociation process [1], but models established based on this viewpoint are rare.

Other than treating dissociation as a coupled chemo-thermal (TC) process or a coupled chemo-hydraulic (HC) process, researchers have also described the dissociation process of gas hydrates as a coupled chemo-thermo-hydraulic (THC) process. Maksimov [25] claimed that the process of dissociation (formation) of gas hydrates was linked to the change in the governing thermodynamic parameters (pressure and temperature) and was accompanied by transport of heat, gas, and water. Similarly, Hong et al. [8] reported that the heat transfer to the dissociation zone, intrinsic kinetics of hydrate decomposition, and gas-water two phase flow are the three primary mechanisms involved in the hydrate dissociation processes in porous media. Tonnet and Herri [101] commented that mass and heat transfers can be coupled in a complex way, firstly because of the permeability changes, and secondly due to material conduction changes.

All of the studies cited in the previous paragraphs treated the gas-bearing sediments as rigid porous media, i.e., a soil in which a hydrate is found is assumed to be non-deformable at all time [60]. While fluid flow, energy flow, and chemical kinetics were believed to be the major mechanisms governing the dissociation process of gas hydrates, the geomechanical effects could also be significant in some hydrate-bearing formations where the hydrates form parts of the solid matrix and contribute to the stiffness [48, 62, 63, 65, 102]. Kim et al. [59] reported that coupled flow and geomechanics processes play an important role in gas hydrate reservoirs because the stiffness of the rock skeleton, porosity and permeability are directly influenced by changes in fluid (water and gas) and solid (hydrate and ice) phase saturations, and in the deformation of the reservoir. The coexistence of fluid and solid phases yields a high nonlinearity for flow and mechanics, and consequently complicated the coupled problems for hydrates. The geomechanical field also needs to be involved for solving practical issues. For example, the stability of gas hydrate reservoir is related to coupled flow and geomechanics such as stability of borehole and surface facilities, hydraulic fracturing, reservoir compaction, heavy oil and oil sand production, CO₂ sequestration, and gas hydrate production [59, 103–109]. Besides, experimental observations also suggested to include the mechanical field. For example, in a series of experiments conducted by Kneafsey [4], the computerized tomography work showed significant shifting of mineral grains in response to hydrate formation and dissociation.

Based on the previous discussions, it can be concluded that energy transfer, mass transfer, geomechanical response, and dissociation reactions are the four major mechanisms which are needed to holistically describe the dissociation process of gas hydrates in porous media. Accordingly, a comprehensive Thermo-Hydro-Mechano-Chemical (THMC) model is needed in order to simulate the phenomena accompanying this type of dissociation process.

But it is also worthwhile to mention that most existing models only accounted for some of these four mechanisms, as the result of simplifications. Certain mechanisms are ignored due to focus of these research as well as their limited effects under given conditions. Besides, some mechanisms are unnecessary for a particular purpose. For example, the state-of-art simulators, such as TOUGH-Hydrate and STOMP, were developed for the simulations of gas recovery from gas hydrate reservoirs. Due to this reason, geomechanical responses were not a primary concern and thus assumed to have negligible effects on the recovery processes. Another important comment is that each individual mechanism mentioned is associated with several affiliated sub-mechanisms. For example, heat transfer typically involves conduction, convection, and radiation; mass transfer typically involves advection, diffusion, and dispersion; momentum transfer may or may not involve a convective part. For each of them, a source/sink term due to dissociation reactions may need to be included. These sub-mechanisms will be further discussed based on the mathematical equations.

2.3.2 A Unified Mathematical Framework for Different Mechanisms

In this part, we propose a unified mathematical framework. That is used to organize all the existing simulation models. All of the mechanisms mentioned in Sect. 2.3.1 can be expressed by mathematical equations. Mathematic equations for the heat transfer, mass transfer, and geomechanical responses boil down to the conservation of energy, mass, and momentum. They are all typical transport phenomena and can be formulated within the framework of continuum mechanics. The role of dissociation reactions is to determine the rate of energy/mass release or consumption in the chemical reactions, while the influence of these reactions on momentum balance is usually neglected. Therefore, the chemical field can be mathematically formulated as a source/sink term in the transport equations of heat and mass. A unified framework is introduced in this subsection to integrate the various mathematical descriptions of existing simulation models for gas hydrate dissociations. The derivation is started from global or integral balance laws as (Eq. 2.1).

$$\frac{d}{dt} \int_{\Omega} u d\mathbf{x} + \oint_{\partial \Omega} \mathbf{J} \cdot \mathbf{n} d\mathbf{x} = \int_{\Omega} Q d\mathbf{x}$$
(2.1)

where Ω corresponds to the Representative Element Volume (REV) in continuum mechanics, *u* is the generic conserved quantity defined by unit mass, **x** is the coordinate vector, **J** is the flux of this conserved quantity. Material points occupying $\Omega(0)$ may move under the influence of inertia and applied loads, so that at any time *t* they may occupy a volume $\Omega(t)$ which is different from $\Omega(0)$. The function $\Omega(t)$ is a material volume which is defined by a set of material points rather than by any explicit spatial coordinates.

After applying the Gauss theorem, Reynolds transport theorem, and du Bois-Reymond Lemma theorem [110], we can obtain the local balance equations as (Eq. 2.2).

$$\frac{\partial u}{\partial t} + \nabla \cdot (u\mathbf{v}) + \nabla \cdot \mathbf{J} = Q \tag{2.2}$$

where the flux, J, can be induced by different mechanisms such as diffusion, dispersion, electromagnetic field and so on. This flux term can be formulated as (Eq. 2.3).

$$\mathbf{J} = f(t, \mathbf{x}, u, \nabla u) = -K\nabla u - D\nabla u + \dots$$
(2.3)

By substituting this flux term into the local balance equation, we then obtain the general conservation equation for transport phenomena (Eq. 2.4). More mechanisms responsible for flux across the boundary can be added by extending the flux term.

$$\underbrace{\frac{\partial u}{\partial t}}_{\text{Accumulation}} \underbrace{+\nabla \cdot (u\mathbf{v})}_{\text{Advection}} \underbrace{-\nabla \cdot (K\nabla u)}_{\text{Diffusion (Conduction)}} \underbrace{-\nabla \cdot (D\nabla u)}_{\text{Dispersion}} = \underbrace{Q}_{\text{Source}}$$
(2.4)

The conservation equation states that the accumulation of conserved quantity is balanced with the conserved quantity advected into the control volume via mobile phases, diffused into the control volume via the aqueous and gas phases, plus the component mass associated with sources [14, 22]. For the conservation of mass, momentum and energy, the conserved quantities are ρ ($\rho = m/V$, mass per unit volume (density)), $\rho \mathbf{v}$ ($\rho \mathbf{v} = m \mathbf{v}/V$, momentum per unit volume) and *e* (internal energy per unit volume), respectively. The corresponding conservation equations are formulated as (Eqs. 2.5–2.7).

2 Advancement in Numerical Simulations of Gas Hydrate Dissociation in Porous Media 61

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) + \nabla \cdot \mathbf{J}_{\mathrm{H}} = Q_{\mathrm{H}}$$
(2.5)

$$\frac{\partial(\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}_i) + \nabla \cdot \mathbf{J}_{\mathbf{M}} = Q_{\mathbf{M}}$$
(2.6)

$$\frac{\partial e}{\partial t} + \nabla \cdot (e\mathbf{v}) + \nabla \cdot \mathbf{J}_{\mathrm{T}} = Q_{\mathrm{T}}$$
(2.7)

where the subscripts, H, M, and T, denote the conservation of mass, momentum and energy, which are extended definitions of hydraulic, mechanical and thermal fields, respectively. The conservation of quantities and the corresponding physical fields are used interchangeably throughout this chapter. It is seen that the dependent variable for momentum conservation equation, $\rho \mathbf{v}$, is a vector. Therefore, the flux term, \mathbf{J}_{M} , is a second order tensor and $\mathbf{J}_{M} = -\boldsymbol{\sigma}$, in which $\boldsymbol{\sigma}$ is the stress tensor.

A composite such as methane hydrate, can be conceptualized as a mixture of several phases, such as gas (g), water (w), hydrate (h) and solid matrix (m). Under such conditions, the conservation equations for each phase are (i = g, w, h, and m):

$$\frac{\partial(\rho_i\theta_i)}{\partial t} + \nabla \cdot (\rho_i\theta_i \mathbf{v}_i) + \nabla \cdot \mathbf{J}_{\mathrm{H},i} = Q_{\mathrm{H},i}$$
(2.8)

$$\frac{\partial(\rho_i \theta_i \mathbf{v}_i)}{\partial t} + \nabla \cdot (\rho_i \theta_i \mathbf{v}_i \mathbf{v}_i) + \nabla \cdot \mathbf{J}_{\mathrm{M},i} = Q_{\mathrm{M},i}$$
(2.9)

$$\frac{\partial(e_i\theta_i)}{\partial t} + \nabla \cdot (e_i\theta_i \mathbf{v}_i) + \nabla \cdot \mathbf{J}_{\mathrm{T},i} = Q_{\mathrm{T},i}$$
(2.10)

where $\theta_i \mathbf{v}_i$ is written as $\overline{\mathbf{v}}_i$ in some cases, in which $\overline{\mathbf{v}}_i$ represents the superficial velocity or Darcy's velocity. One thing needs to be pointed out is that the multiphase nature is usually solely considered for mass balance. For momentum balance, most of the existing THMC models only account for the momentum balance of the solid phase(s). If a solid phase is believed to be immobile, then the governing equation, which is in fact a Navier–Stokes equation, degenerates into a Navier's equation. Energy balance is mostly considered for the whole system instead of individual phases. This treatment is based on the assumption that thermodynamic equilibrium is maintained between different phases. In some petroleum engineering studies, the consideration of mass balance can be even more complicated. For example, the transformation between different phases is possibly considered. In such cases, a composite is a mixture of several components existing in different phases. For each component, a phase change may happen between any two phases that a component is possibly in, depending on the underlying assumptions. Accordingly, mass balance equations are usually established with respect to individual components as the following equation.

$$\frac{\partial \left(\sum_{i} \rho_{i} \theta_{i} \chi_{i}^{\alpha}\right)}{\partial t} + \nabla \cdot \left(\sum_{i} \rho_{i} \theta_{i} \chi_{i}^{\alpha} \mathbf{v}_{i}\right) + \nabla \cdot \left(\sum_{i} \chi_{i}^{\alpha} \mathbf{J}_{\mathrm{H},i}\right) = \sum_{i} \chi_{i}^{\alpha} \mathcal{Q}_{\mathrm{H},i}$$
(2.11)

where χ_i^{α} is the mass fraction of component α in phase *i*. It is possible that in the future the coexistence of components in different phases and concomitant phase changes will also be considered in the thermal and mechanical fields as a result of increasing computational capacities and emerging application needs.

2.3.3 Classification of Existing Methods

The total number of numerical models for simulating gas hydrate dissociation in porous media or related phenomena is unclear but this number has been increasing in a nonlinear way since 1970s. Hundreds of models can be found by a quick internet search. It can be rather confusing when one is exposed to such a great pool of models with seemingly large discrepancies. However, great similarities can be identified between different models with a careful comparison of their theoretical bases. *Therefore, it is of great value to summary, classify and compare the existing models to elucidate how they represent the basic mechanisms and what assumptions they make*. In such a way the similarities and differences would be identified. Furthermore, uncovering the fundamental mechanisms underlying those similarities and differences will also help deepen our understanding of gas hydrate dissociation. This chapter reviews representative types of simulation models for gas hydrate dissociation currently available. These selected models are classified and compared with reference to the unified framework introduced in the previous subsection.

In existing studies, the simulation models for gas hydrate dissociation have been classified according to the solution method (analytical or numerical), application (production by depressurization, or thermal stimulation, etc.), and chemical reaction description (equilibrium or kinetic). Classifications based on these criteria helped researchers to categorize and differentiate different models. However, they are far from enough in clarifying the different mechanisms of hydrate disassociation described by the mathematical equation systems. This study proposes new criteria to classify computer simulation models for gas hydrate simulations. These criteria are established based on the unified framework described in the previous section. The key idea for establishing the criteria is to allow classify the selected models based on the simplifications employed in the models. This is based on the fact that different models are derived from the general framework using different

simplifications. The four classification criteria we propose in this study are listed as follows.

- 1. *Types of the governing equations*. This criterion is based on the number of independent variables used in the governing equations, or equivalently, the types of physical phenomena simulated by the model. By reviewing existing literature, it is found that most models fall into categories such as Hydro-Chemical (HC), Thermo-Chemical (TC), Thermo-Hydro-Chemical (THC), and Hydro-Thermo-Mechano-Chemical (THMC).
- 2. *Number of phases and components*. Generally speaking, more phases or components require more governing equations for each field. Taking mass transfer for example, the hydraulic field can be described as single phase flow, two-phase flow, and multiple (more than two) phase flow. If phase exchange happens, the components (species) in different phases may need to be considered. Hydrate, methane, and water are usually the phases formulated in the hydraulic field. When there are more gases than just methane, or when there are other components such as inhibitors, carbon dioxide, and other hydrocarbons, or when mass exchanges between phases occur, the compositional model frequently employed in petroleum engineering has to be used for mass transfer.
- 3. *Sub-mechanisms considered*. Each term in a governing equation has a specific physical meaning. The accumulation term is necessary for any transient process while the source term is reserved for chemical reactions. All other terms represent the contribution of affiliated sub-mechanisms (such as convection, diffusion (conduction), and dispersion) in different physical fields. The inclusion of these sub-mechanisms is dependent on the relative contribution of individual item and the purpose of the simulation model. Therefore the existing models can also be differentiated by the number and type of sub-mechanisms considered.
- 4. *Method for the source term*. The treatment of the source/sink generated by dissociation reactions determines whether the model is an equilibrium model or a kinetic model. This criterion was frequently adopted in existing studies. However, its physical meaning with respect to the mathematical equations has seldom been clarified.

The existing methods were also frequently classified based on their applications. This criterion is also somewhat meaningful as the recovery schemes that a model was designed for may imply certain features of that model. This is because there is, to some extent, a relationship between the recovery method and the thermodynamic conditions for the applications of that model. Simplifications may thus be made accordingly to obtain the model. For example, some models used for depressurization neglected the heat transfer process as it was assumed to be insignificant. However, this does not mean that heat transfer is not included in every simulator for depressurization. In fact, many new simulation models for gas recovery from gas hydrate dissociation are all-purpose. Hence this criterion is not as physics-based as the four criteria introduced above. In the following classification process, the recovery scheme will be marked only if it was clearly stated in the original paper.

The selected model will be classified using the proposed criteria with the following expression.

$$X|imjn...\cdot Y|...\cdot C|\gamma$$

where,

Classification criterion 1: X, Y = T, H, M (T = Thermal, H = Hydraulic, M = Mechanical, C = Chemical);

Classification criterion 2: i, j = w, g, h, s, i, c, b, a (w = water, g = gas (or methane); h = hydrate; s = salt; i = ice; c = carbon dioxide; b = inhibitor; a = all components);

Classification criterion 3: m, n = 1, 2, 3, 4 (1 = advection; 2 = diffusion/conduction; 3 = dispersion; 4 = radiation);

Classification criterion 4: $\gamma = \varepsilon$, κ (ε = equilibrium; k = kinetic).

Based on these classification criteria and the notation convention, the selected models between 1980 to 2011 for gas hydrate simulations are summarized and categorized in Table 2.1.

2.3.4 Comparison and Integration

The classifications presented in the last subsection grouped and marked the representative models that are currently available. However, the classifications are not to indicate that one group of models are superior to others. The judgments will be saved for readers based on their experience. One fact is that a comprehensive reservoir model without many simplifying assumptions would be extremely complex and difficult to solve numerically especially in the early stage. Sometimes simplifications could be made without significantly compromising the integrity of the model for the purposes intended [15]. Also, the uncertainty about major hydrate variables significantly limited the practice usefulness of sophisticated multidimensional multicomponent reservoir models [76]. But these factors will not put the brakes on the trend that more complicated and powerful simulators are being developed due to the growing needs and the increasing computational capacity.

2.3.4.1 Classifications Based on Criteria 1, 2, and 3

The classification based on criterion 1 divides the existing models into different categories from a viewpoint of multiphysics. Thus, the classification determines what types of physical phenomena are taken into account. As shown in Table 2.1, different types of multiphysics models have been proposed for the dissociation of gas hydrates. The major reason is that although a dissociation/formation process is a THMC or an even more complicated process, the influences of different physical

Table 2.1 Summary of	the sele	scted models between 1980 to 2011 for gas hydrate si	simulations
Model	Year	Classification	Additional information
Verigin et al.	1980	$ H g1 \cdot C \varepsilon$	Depressurization, Analytical
Holder and Angert	1982	$ T a2 \cdot H g1 \cdot C \varepsilon$	Depressurization, H for gas layer only
Selim and Sloan	1985	$ T a2 \cdot C \varepsilon$	Thermal, Analytical, Undissociated zone
Burshears et al.	1986	$ T a2\cdot H g1w1\cdot C \epsilon$	Depressurization, 3D, Penetrating well
Selim and Sloan	1990	$ T a2\cdot H g1\cdot C \epsilon$	Thermal, Analytical, H for dissociated zone only
Yousif et al.	1991	$ H g1w1h \cdot C \kappa$	Depressurization, 1D
Maksimov	1992	$ T a2 \cdot H g1w1 \cdot C \epsilon$	Analytical, Dissociated and undissociated zones
Tsypkin	1993	$ T a2 \cdot H g1w1 \cdot C \epsilon$	Analytical, phase change, three zones
Rempel and Buffett	1997	$ T a12 \cdot H g123 \cdot C \epsilon\kappa$	Analytical with ε ; Numerical with κ , Formation and dissociation
Tsypkin	1998	$ T a12 \cdot H g1w1 \cdot C \varepsilon$	Analytical, phase change, three zones
Sung et al.	2000	$H g1w1h \cdot C \kappa$	Depressurization, 1D, Gas dissolves in water
Goel et al.	2001	$ H g1\cdot C \kappa$	Analytical, Dissociated and undissociated zones, Axisymmetric,
			Depressurization
Masuda et al.	2002	$ T a12 \cdot H g12w12h \cdot C k$	The three conventional recovery schemes were tested
Jeannin et al.	2002	$ T a2 \cdot H g12w12 \cdot C \kappa$	3D, Formation and dissociation
Sung et al.	2002	$H g1w1b1h \cdot C \kappa$	Depressurization and inhibitor injection, Gas and inhibitor dissolve in
			water
Hong et al.	2003	Tla2, Hla1, Clk	Analytical, solutions to 3 regimes
Ahmadi et al.	2004	$ T a12 \cdot H g1 \cdot C \varepsilon$	TH for two zones and linked by C
Chen et al.	2005	$ T a12 \cdot H g1s1 \cdot C \varepsilon$	Salt is considered
Li et al.	2005	$ H g1w1h \cdot C \kappa$	Depressurization, Compared with Yousif et al. [45], parametric study
Klar and Soga	2005	$ H g1w1h \cdot M m1 \cdot C \kappa$	Bishop's model used for unsaturated mechanics
Pawar and Zyvoloski	2005	$ T a12 \cdot H g1w1h \cdot C \kappa$	Hot water injection and depressurization
Hong and Pooladi- Darvish	2005	$T a12\cdot H g1w1h\cdot C \kappa$	2D cylindrical simulator, penetrating well though two layers
Sun et al.	2005	$T a12\cdot H g1w1h\cdot C \kappa$	Depressurization, 1D
			(continued)

Table 2.1 (continued)			
Model	Year	Classification	Additional information
Phale et al.	2006	T a123 · H g123w123c123s123 · C ?	Injection of CO ₂ Microemulsion, STOMP-HYD, 6 phases 4 components, Phase change
Scott et al.	2006	$ T a12 \cdot H g1w1 \cdot C \varepsilon $	Hot water injection, FEM
Sun and Mohanty	2006	$T a12\cdot H g12w12s12h\cdot C \kappa$	PVSM for ice melting, 4 component 5 phases
Vasil'ev et al.	2006	$T a12\cdot H g1w1\cdot C \epsilon$	Gas-hydrate (g) and gas-water regions (g, w), analytical and
			numerical
Sean et al.	2007	$ T w12h2 \cdot H g12w \cdot M w1 \cdot C k$	Dissociation under water flow, for testing a proposed kinetic model
Ahmadi et al.	2007	$ T a12 \cdot H g1w1 \cdot C \varepsilon $	Depressurization, axisymmetric, Tla1 for gas zone, Tla12 for hydrate
			zone
Du et al.	2007	$ T a12 \cdot H g1w1h \cdot C \kappa$	Thermal stimulation
Kimoto et al.	2007	$\left T a2 \cdot H g1 w1 hm \cdot M g1 w1 m1 \cdot C \kappa \right.$	Viscoplastic
Liu and Flemings	2007	$ T a12 \cdot H g12w12s12 \cdot C \epsilon$	Switch primary variables (ε)
Nazridoust and Ahmadi	2007	$T a12 \cdot H g1w1h \cdot C k$	Depressurization, FLUENT, axisymmetric
Tsypkin	2007	$T a2 \cdot H g1w1 \cdot C \varepsilon$	Isothermal and nonisothermal, developed for reservoir with high pressure gradients
Tsimpanogiannis and Lichtner	2007	$T a2\cdot H g1\cdot C \epsilon$	H is only for dissociated zone, parametric study
Bai et al.	2008	$ T a12 \cdot H g1w1h \cdot C \kappa$	Ice was considered as a part of water
Esmaeilzadeh et al.	2008	$ T a12 \cdot H g1w1h \cdot C \kappa$	Depressurization and thermal stimulation
Garg et al.	2008	$T a12\cdot H g1w1s1m\cdot M (hm)1\cdot C \epsilon$	Organic carbon is considered in H, kinetics for organic carbon dis- sociation, formation and dissociation
Liu et al.	2008	$T a12 \cdot H g1w1 \cdot C e$	Depressurization, No water in hydrate zone, Class III hydrate
Ma and Plan	0000	The 10 III at 11.1 III at 11.1	
Ng and Klar	2008	al2+H glwlh+M ml+C κ	Use FLAC, based on Klar and Soga [60]
Uddin et al.	2008	$T a12 \cdot H g1w1c1h \cdot C k$	CO_2 sequestration. Formation and dissociation, Phase change, h includes CH_4 hydrate and CO_2 hydrate

66

White and McGrail	2008	$T a123 \cdot H g123w123c123i123 \cdot C \varepsilon\kappa$	STOMP, Equilibrium or kinetic
Bai et al.	2009	$T a12 \cdot H g1w1h \cdot C \kappa$	ice formation (switching primary variables), depressurization
Rutqvist et al.	2009	$T a123\cdot H g123w123c123i123\cdot M g1w1m1\cdot C \epsilon\kappa $	depressurization, TOUGH-Hydrate + FLAC3D
Salehabadi et al.	2008	$\left T a12 \cdot H w1 \cdot M m1 \cdot C \epsilon \right.$	T is coupled to HM, but the coupling is weak
Tonnet and Herri	2009	$T a12\cdot H g1w1h\cdot C \kappa$	Depressurization, Gas dissolves in water
White et al.	2009	T a123 · H g123w123c123i123 · C εκ	CO ₂ sequestration, Class 1 gas hydrate
Bai and Li	2010	$T a12\cdot H g1w1h\cdot C \kappa$	Ice was considered as a part of water, Combination of warm water
			flooding and depressurization
Gamwo and Liu	2010	$T a124\cdot H g12w12h\cdot C \epsilon\kappa$	Three phases three components, Consider phase change,
			HydrateResSim
Konno et al.	2010	$T a12\cdot H g1w1s1i1n1\cdot C \kappa$	MH21-HRATES, 4 phases 5 components
Kwon et al.	2010	$T a2\cdot H w1\cdot M m1\cdot C \epsilon$	FLAC2D, one-way coupling
Peszynska et al.	2010	$T a12 \cdot H g12w12s12 \cdot C \varepsilon$	Adaptive modeling
Phirani and Mohanty	2010	$T a12\cdot H g1w1c1h\cdot C \kappa$	CO ₂ sequestration, UH-hydrate, 5 phases 6 components, h include
			CO ₂ and CH ₄ hydrates, Phase change
Janicki	2011	$T g12w12h12m12\cdot H g1w1c1h1\cdot C \kappa$	UMSICHT HyReS, h includes CO2 and CH4 hydrates, consider mass
			balance of 4 phases 2 components
Kim et al.	2011	$T a123 \cdot H g123w123c123i123 \cdot M m1 \cdot C \varepsilon \kappa$	TOUGH-Hydrate + FLAC3D, Coussy's theory for M, "two way" but
			not fully coupled, depressurization, thermal stimulation, and
			plasticity
Kimoto et al.	2011	$T a2\cdot H g1w1hm\cdot M g1w1m1\cdot C \kappa$	Very close to Kimoto et al. [111]
Li et al.	2011	$ T a12\cdot H g1w1h\cdot M m1\cdot C \kappa$	m is fully coupled into H, effective stress and Drucker-Prager elasto-
			plastic
Schnurle and Liu	2011	$T a12\cdot H g1w1h\cdot C \kappa$	Simulate gas hydrate and free gas accumulation in marine sediments
Chin et al.	2011	$T a123 \cdot H g123w123c123i123 \cdot M m1 \cdot C \epsilon\kappa$	Depressurization, Developed M one way coupled with TH (TOUGH-
			Hydrate), effective stress theory for M
Ruan et al.	2012	$T a12\cdot H g1w1h\cdot C \kappa$	2D axisymmetric



mechanisms differ under various conditions. As a result, the effects of some physical fields on the multiphysical process as well as the strength of their coupling to other physical fields are insignificant. Under such conditions, these physical fields can be excluded without significantly affecting the analysis results. Such models within which less physical mechanisms were considered might have certain advantages for specific problems.

Figure 2.1 shows the percentage of each common types of model based on the multiphysics fields involved. As can be seen from this figure, the majority of existing models belong to THC, while THMC and HC models also take a considerable share. Models at least include two physical fields. The chemical field is an essential component for all the models.

The classification based on Criterion 2 classifies the existing models based on the number of phases or components simulated. Because multiple phases or components are to some extent unavoidable due to the composite nature of gas hydrates, especially for mass balance, a rigorous analysis requires considering at least gas and water. It is impossible to consider the composite as an ensemble because the mass transfers of different phases and components are not coordinated. For heat transfer, under the assumption of the thermodynamic equilibrium between different phases and components, analyses can be conducted with respect to the whole system [112]. For momentum balance, the inclusion of geomechanical responses, in which only the momentums of solids are considered, is still in a preliminary stage. Thus the treatment of gas hydrates as a multiphase multicomponent composite has not been discussed extensively in momentum balance analyses of gas hydrate dissociation.

Due to the aforementioned reasons, the classification based on criterion 2 is only summarized for the hydraulic field in this study. As shown in Fig. 2.2, the majority of the existing models (around 60%) are two-phase (gas and water) flow model. Immobile phases such as solid matrix and hydrates might or might not be included in these models. Around 18% of existing models are single phase models. Around 22% of existing models are "Multi" models, which represents models with more complicated considerations for mass transfer. Examples of these comprehensive models are those simulators (TOUGH-Hydrate, from LBNL; STOMP-Hyd, from PNNL; MH-21, from Japan Oil Engineering Company; CMG-STARS, from University Calgary and University Alaska at Fairbanks; UH-hydrate, from University of Houston) that have been developed for methane hydrate reservoirs [113]. These simulators are the state of the art within the framework of THC.





The classification based on Criterion 3 categorizes the existing models based on the number of sub-mechanisms (i.e., convection, diffusion (conduction), and dispersion) considered. The governing equations of the thermal, hydraulic and mechanical fields can be derived from the same form of local balance equation. This implies that these three types of transport phenomena share certain similarities. All of them might include terms representing advection, diffusion, dispersion, and so on. These terms might be called differently when describing different physical phenomena. For example, diffusion term in the governing equation of the thermal field is conventionally called conduction. In addition, some terms are only associated with specific phenomena, for example, radiation occurs in the thermal field only. Inclusion of a certain term in a physical field is dependent upon the nature of this field (as can be seen in Table 2.1). Specially, the conduction term is included in the thermal field and the advection term is included in the hydraulic field for almost every simulation model. Besides, the advection term is always included for the momentum balance of solid phases. Taking the advection term in the hydraulic field as an example, it is usually implemented with Darcy's law which relates the superficial velocity of a phase to the phase pressure. In fact, momentum balance is satisfied implicitly because Darcy's law can be derived from the momentum balance of the fluid at low velocity. That is, Darcy's law is just a special case of the momentum balance equations of fluids. However, in this chapter we treat Darcy's law as an auxiliary relationship for momentum balance of fluids rather than a governing equation describing the mechanical field.

2.3.4.2 Classifications Based on Criteria 4

The classification with Criteria 4, which is based on the chemical model, divides the simulation models into equilibrium models and kinetic models. However, some recent simulators include both modules. The statistical review of published models is plotted in Fig. 2.3, which shows that more than one half of the models are kinetic models. The equilibrium model is used by more than one third of the existing models. By comparison with Table 2.1, it is interesting to find that all analytical models reviewed used equilibrium models [114], except the study conducted by Goel et al. [77]. It is worthwhile to mention that only one type of chemical model, either equilibrium or kinetic, can be used for a single simulation though a simulator can include both.





In the equilibrium model, the relationships between thermodynamic variables (pressure, temperature, concentration) follow the equilibrium curve (phase) in the reaction sites. These reaction sites are usually distributed on a moving boundary (thin layer) between dissociated and undissociated zones. Therefore, the system stays at equilibrium all the time. The production of the various phases and the amount of phase transitions are determined by the availability and relative distribution of heat and reactants [35]. In the kinetic model, thermodynamic equilibrium does not necessarily coincide with any boundary. Instead, dissociation reactions occur at any locations where the local thermodynamic state falls in the unstable region of the phase diagram. And the hydrate is not treated as a thermodynamic state of methane and water but as a third distinct compound. Rates of phase changes are decided by the kinetic rate of dissociation or formation, which depends on the relative position between the current thermodynamic status and the equilibrium curve.

Hong et al. [8] suggested to differentiate the two approaches, i.e., equilibrium and nonequilibrium (kinetic), with respect to conditions at the decomposition zone. The underlying assumption of the models using the equilibrium approach is that the intrinsic rate of hydrate dissociation is fast enough so that the overall rate of hydrate dissociation is controlled by other mechanisms, i.e., fluid flow or heat transfer [84]. In kinetic models, however, the condition at the hydrate-gas-water interface was kinetically approaching equilibrium. Kowalsky and Moridis [35] reported that for large-scale systems undergoing thermal stimulation and depressurization, the calculated responses for both reaction models were remarkably similar, though some differences were observed at early times. However, for modeling short-term processes, such as the rapid recovery of a hydrate-bearing core, the kinetic characteristic could be important, and neglecting them may lead to significant underprediction of recoverable hydrate. The systematic parametric study of the kinetic reaction constants conducted by Liu and Gamwo [114] argued that the equilibrium model was only a limiting case of the kinetic model for both constant temperature and adiabatic thermal boundary conditions. Their study clearly showed that results obtained the kinetic model approached that by the equilibrium model when the intrinsic mole dissociation constant far exceeded the common range found in the literature. Additionally, the equilibrium model exhibited a moving front pattern for hydrate dissociation while the kinetic model showed a moving zone pattern under adiabatic boundary conditions. For the constant temperature boundary condition, the hydrate dissociated by shrinking in all dimensions for the

equilibrium model; while for the kinetic model, it dissociated with no specific pattern throughout the entire reservoir.

The use of equilibrium model often appears to be justified and preferred for simulating the behavior of gas hydrates, given that the computational demand for the kinetic reaction model far exceeds that for the equilibrium reaction model [35]. Evidence in favor of the use of equilibrium model has also been presented for the marine environment. This is because hydrate formation and dissociation in the marine environment occur over an extended period (thousands to millions of years). It is thus permissible to assume local thermodynamic equilibrium and to neglect any chemical kinetic effects [112]. On the other hand, Dendy and Sloan [47] used the Raman spectra to show that the hydrate formation was a rate-dependent process to transform methane into methane hydrate. And the rate-dependent hydrate dissociation process predicted by the kinetic model is similar to the experimental observations. This indicated that kinetic model more realistically describe the natural gas hydrate dissociation process. As commented by Koh and Sloan [61], the paradigm has shifted from thermodynamics (time-independent properties) to hydrate formation and dissociation kinetics in all the gas hydrate technological applications.

2.4 Materials Properties for Gas Hydrate Modeling: Auxiliary Relationships

This section discusses the auxiliary relationships that describe material properties required for gas hydrate simulation. These relationships are needed to mathematically close the equation system for simulating the dissociation process of gas hydrates in porous media. For example, an accurate simulation of hydrate depressurization requires accurate petro-physical and thermophysical data [12]. Typical information needed for reliably predicting the feasibility of natural gas production from hydrates includes but is not limited to: the abundance of the hydrates in the selected reservoir; lithologic and geologic structure of the reservoir; presence or absence of a free gas zone; arrangement of hydrate within the porous medium; permeability, relative permeability-saturation relationships; capillary pressure-saturation relationships; thermal conductivity of the hydrate-bearing and hydrate free medium; energy required to dissociate the hydrate (how close the hydrate to equilibrium); and kinetics of dissociation [4]. Some information is reservoir specific, while the others such as dissociation kinetics, thermal conductivity, and relative permeability can be evaluated in the laboratory [4]. For both types of information, a mathematical representation is required to incorporate the information into a computer simulator. Additionally, natural hydrate samples are not widely available and can be compromised by collection, recovery, transport, and handling [4]. Also, improvements in sampling and remote sensing of hydrate deposits as well as laboratory technologies to study both natural and artificial gas hydrate samples are in crucial demand to determine these relationships [12]. Therefore, more reliable and accurate mathematical expressions for formulating these relationships are especially helpful. Generally, these relationships can be expressed by constants, functions (for continuous relationship), or matrices (for discrete relationship). In the subsections of this section, the various auxiliary relationships used by different simulation models are categorized and discussed based on their roles in the different governing equations (fields). A few mathematical equations for the auxiliary relationships that have not been adopted by the existing models are also introduced.

2.4.1 Material Properties Related to Heat Transfer

The governing equation for heat transfer in Sect. 2.3.2 can be further transformed to obtain the solution. Generally, terms such as energy density, heat flux, and source can be formulated as functions of the dependent variables and material properties. In such a way, only the dependent variables, materials properties depending on the dependent variables, and constants will appear in the equation. One governing equation may contain multiple dependent variables, but the total numbers of dependent variables and that of the governing equations should be equal in the equation system to guarantee a unique solution. Auxiliary relationships necessary for the internal energy and heat flux mainly refer to the heat capacity and thermal conductivity, which are discussed in this subsection. The auxiliary relationships for the source term will be considered in the subsection for chemical reactions. Let us start from the formation of the energy density term as (Eq. 2.12).

$$e = \underbrace{\left(\int_{T_0}^{T} \rho C_{\mathbf{v}} T + U_0\right)}_{\text{Internal Energy}} + \underbrace{\left(\frac{1}{2}\rho \mathbf{v} \cdot \mathbf{v}\right)}_{\text{Kinetic Energy}} + \underbrace{\left(\rho g z\right)}_{\text{Potential Energy}}$$
(2.12)

where C_v is the gravimetric heat capacity at constant volume, U_0 is the internal energy per unit volume at the reference temperature T_0 , C_p is the heat capacity at a constant pressure.

The internal energy is a part of the accumulation term in addition to the kinetic energy and potential energy. But for gas hydrate dissociation, in general, the internal energy is dominant over the other energy types. As a result, the energy density is frequently represented by the internal energy density only as (Eq. 2.13) [115], in which the pressure term will vanish for solids [112, 116].

2 Advancement in Numerical Simulations of Gas Hydrate Dissociation in Porous Media 73

$$e = \int_{T_0}^{T} \rho C_{\mathbf{v}} T + U_0 = \int_{T_0}^{T} \rho C_{\mathbf{p}} T - \int p dV + U_0$$
(2.13)

Secondly, the flux term is linked to temperature by Fourier's law of heat conduction as

$$\mathbf{J}_{\mathrm{T}} = -\lambda \nabla T \tag{2.14}$$

where λ is the thermal conductivity. Substituting the above equations for energy density and thermal conductivity into the energy balance equation, we can obtain the heat equation including advection and source terms as (Eq. 2.15).

$$\frac{\partial(\rho C_{\mathbf{v}}T)}{\partial t} + \nabla \cdot (\rho C_{\mathbf{v}}T\mathbf{v}) - \nabla \cdot (\lambda \nabla T) = Q_{\mathrm{T}}$$
(2.15)

As introduced before, most existing models of gas hydrate dissociation employed one governing equation for gas transfer for the whole system. Governing equations are established for individual phases/components only in a few cases [13]. The general form of the governing equation for heat transfer of the whole system is as the following.

$$\frac{\partial \left(\sum \rho_i \theta_i C_{\mathbf{v},i} T\right)}{\partial t} + \sum \nabla \cdot \left(\rho_i \theta_i C_{\mathbf{v},i} T \mathbf{v}_i\right) - \nabla \cdot \left(\lambda \nabla T\right) = Q_{\mathrm{T}}$$
(2.16)

2.4.1.1 Heat Capacity

Heat capacities of individual components are mostly used to directly construct the accumulation term in (Eq. 2.16) based on the formulation of the internal energy (Eq. 2.13) [21, 22, 33, 63, 84, 101, 112, 117–121]. This formulation, which is the weighted average of the thermal conductivities of the components with respect to mass, has long been used for soils [122, 123]. This mass weighted average method was also used in many simulation methods [16, 25, 79–81, 111, 124–127].

$$C_{\rm v} = \sum \left(\rho_i \theta_i C_{\rm v,i}\right) / \sum \left(\rho_i \theta_i\right) \tag{2.17}$$

This physics-based treatment is based on the definition of the thermal energy and can be derived from thermodynamics.

A constant value was also used for the average heat capacity of a gas hydrate composite for simplicity [8, 128]. There are also more complex relationships that allow more effects on the heat capacity to be considered. For example, the capacity of gas can be described as a function of temperature [44].

$$C_{g} = C_{0} + C_{1} \cdot T + C_{2} \cdot T^{2} + C_{3} \cdot T^{3}$$
(2.18)

where C₀ is 1238.79, C₁ is 3.1303, C₂ is 7.905×10^{-4} , C₃ is -6.858×10^{-7} and C_i is employed to denote fitting constants throughout this section. Similar considerations were also taken by Schnurle and Liu [120]. When the phase changes of water occur, especially for freezing and thawing, the latent heat is typically dealt with the concept of apparent heat capacity [121]. This term was introduced by Williams [129] and later used by Anderson and Morgenstern [130]) to ensure the computational stability. In this treatment, the released or absorbed energy was incorporated into the heat capacity term using (Eq. 2.19).

$$C_{\rm a} = C + L_{\rm f} \frac{d\theta_{\rm i}}{dT} \tag{2.19}$$

where C_a is the apparent gravimetric heat capacity, L_f is the latent heat of phase transition.

2.4.1.2 Thermal Conductivity

The formulation of thermal conductivity is not as straightforward as that of the heat capacity. The average thermal conductivity of a composite is usually used. In several simulation models, this average thermal conductivity was assumed to be a constant [8, 44, 75, 119, 128]. This treatment was adopted to reduce the non-linearities of the models to allow the solution of the analytical models. However, a volume weighted value of thermal conductivities was more frequently employed in the existing models [13, 21, 22, 25, 33, 63, 79–81, 84, 111, 115, 117, 127, 131]. The mathematical formulation of this volume weighted average value is as follows:

$$\lambda = \sum \theta_i \lambda_i / \sum \theta_i \tag{2.20}$$

The formulation in (Eq. 2.20), which has been extensively used, is essentially an empirical equation. There are still other ways for the calculation of the average thermal conductivity, such as the one used by Tonnet and Herri [101], which was originally used by Henninges et al. [132]. This method used a geometric average as the following.

$$\lambda = \left(\prod \lambda_i^{\theta_i}\right)^{1/\sum \theta_i} \tag{2.21}$$

Russell's equation [133] has also been applied to the formulation of thermal conductivity by Scott et al. [121].

2 Advancement in Numerical Simulations of Gas Hydrate Dissociation in Porous Media 75

$$\lambda = \lambda_{\rm m} \sum \frac{\left[\theta_i / (1 - \theta_{\rm m})\right] \left[(1 - \theta_{\rm m})^{2/3} (\lambda_i / \lambda_{\rm m} - 1) + 1 \right]}{\left[(1 - \theta_{\rm m})^{2/3} - (1 - \theta_{\rm m}) \right] (\lambda_i / \lambda_{\rm m} - 1) + 1}$$
(2.22)

where m indicates solid matrix, and *i* denotes the phases other than the solid matrix.

Thermal conductivity can also be calculated using a nested Revil-type mixing rule according to Waite et al. [134] in the following form [120]

$$\lambda = \lambda_{\rm m} + \frac{(\lambda_{\rm f} - \lambda_{\rm m})(1 - \theta_{\rm m})^2}{2\left\{1 - \lambda_{\rm m}/\lambda_{\rm f} + \left[(1 - \lambda_{\rm m}/\lambda_{\rm f})^2 + 4\lambda_{\rm m}/\lambda_{\rm f}/(1 - \theta_{\rm m})^2\right]^{0.5}\right\}}$$
(2.23)
$$\lambda_{\rm f} = \lambda_{\rm h}$$

$$+\frac{\left(\lambda_{\rm wg}-\lambda_{\rm h}\right)\left[1-\theta_{\rm h}/(1-\theta_{\rm m})\right]^{2}}{2\left\{1-\lambda_{\rm h}/\lambda_{\rm wg}+\left[\left(1-\lambda_{\rm h}/\lambda_{\rm wg}\right)^{2}+4\lambda_{\rm h}/\lambda_{\rm wg}/\left[1-\theta_{\rm h}/(1-\theta_{\rm m})\right]^{2}\right]^{0.5}\right\}}$$
(2.24)

where $\lambda_{\rm f}$ is the fluid thermal conductivity, and $\lambda_{\rm wg} = \lambda_{\rm w} \theta_{\rm w} + \lambda_{\rm g} \theta_{\rm g}$.

There are also other approaches that are popular yet have not been used in the existing models for gas hydrate simulations. These models also deserve attention. One example is the physics-based models proposed by de Vries [123] [135]. Another example is the empirical relationship proposed by Johansen [136], which was later modified by Cote and Konrad [137] and Lu et al. [138]. The key concept in the latter one is the unique relationship between the normalized thermal conductivity and normalized saturation. The basic relations in these models are expressed by (Eqs. 2.25–2.26).

$$\lambda_{\rm r} = \frac{\lambda - \lambda_{\rm dry}}{\lambda_{\rm sat} - \lambda_{\rm dry}} \tag{2.25}$$

$$\lambda_{\rm r} = f(\Theta) \tag{2.26}$$

where λ_r is the normalized thermal conductivity; and λ , λ_{dry} and λ_{sat} are the actual thermal conductivity and the thermal conductivity of dry and saturated soils, respectively. Θ is the normalized saturation. The relationship between normalized thermal conductivity and the normalized saturation (function *f*) can be different for different materials. A simplified version of this relationship was once used in the USGS/NETL code comparison project with *f* assumed as a linear function [139].

The thermal conductivities of individual phases are mostly assumed to be a constant. But in some cases, the thermal conductivities of some phases are considered to be a function of temperature. For example, Schnurle and Liu [120] used the following relations to represent the thermal conductivities of water and hydrate

[134], with a table of 201 precomputed values for the Web Book of Chemistry at NIST (http://webbook.nist.gov).

$$\lambda_i = C_{1,i} + C_{2,i} \cdot (T - 273) \tag{2.27}$$

where $C_{1,w}$ is 0.562, $C_{2,w}$ is 1.75×10^3 , $C_{1,h}$ is 0.624, $C_{2,h}$ is -2.78×10^3 .

Another example is the equation suggested by Sean et al. [140] for the thermal conductivity of aqueous phase.

$$\lambda_{\rm w} = \mathcal{C}_1 \ln T - \mathcal{C}_2 \tag{2.28}$$

where C₁ is 487.85 and C₂ is 2173.8.

2.4.1.3 Thermal Diffusivity

Thermal diffusivity has also been used in a few early simulation models [1, 15, 44]. As thermal diffusivity is the combination of heat capacity and thermal conductivity, the purpose for using this term is to simplify the governing equation and solution process. So in these methods, a constant value of thermal diffusivity was usually employed. Later researchers such as Rempel and Buffett [16] claimed that the effective thermal diffusivity should include dispersive effects.

2.4.2 Material Properties Related to Mass Transfer

Relationships between phase pressures and phase saturations as well as the relationship between the phase saturations and relative phase permeabilities are generally necessary to compute the transport properties of the system [37]. Relations that are additionally required include the relationship between absolute permeability and porosity, and that between permeability and hydrate saturation. Also, coefficients for diffusion and dispersion have to be determined if these two transport mechanisms need to be taken into account. In this subsection, permeability is discussed first because convection is the primary mass transport mechanism in the dissociation processes of gas hydrates. Methods for formulating the influences of porosity, hydrate saturation, and fluids saturations are summarized. Then, auxiliary relationships related to diffusion, dispersion, and mass transfer between phases (phase change) as well as other correlations are reviewed successively.

2.4.2.1 Absolute Permeability and Permeability Considering Hydrate Saturation

Absolute permeability is the permeability when the solid matrix serves as the only component (no fluids and no hydrates). A constant value is frequently assigned for this parameter. However, it can also be calculated with porosity by assuming a unique relationship between absolute permeability and porosity, such as the function used by Garg et al. [112].

$$\kappa_0 = \kappa_1 \cdot (\phi/\phi_1)^{C_1} \cdot [(1-\phi_1)/(1-\phi)]^{C_2} \cdot \exp[C_3(\phi-\phi_1)]$$
(2.29)

where κ_0 is the absolute permeability corresponding to any porosity, ϕ ; κ_1 is the permeability at the original porosity, ϕ_1 . Garg et al. [112] commented that this equation was a rather general expression. With a suitable choice of material constants C₁, C₂, and C₃, the equation could reproduce virtually any measured variation of absolute permeability with porosity.

In addition to porosity, the presence of hydrates in pores can also alter the permeability significantly. There are at least seven methods, in which the influence of porosity is also included, for quantifying this influence of hydrates. The first method (Eq. 2.30) was firstly used by Masuda et al. [119] and later adopted by other simulation models [21, 75, 116, 125, 141, 142].

$$\kappa = \kappa_0 \cdot \left[1 - \theta_{\rm h}/\phi\right]^{\rm C_1} \tag{2.30}$$

Kleinberg et al. obtained two functions for the variation of the permeability with respect to hydrate saturation according to the way in which hydrates form in pores. If the porous medium is approximated as a bundle of capillaries and hydrates form in the center of each capillary (pore-filling), the (Eq. 2.31) can be obtained.

$$\kappa = \kappa_0 \cdot \left[1 - \left(\frac{\theta_{\rm h}}{\phi}\right)^2 + \frac{2(1 - \theta_{\rm h}/\phi)^2}{\log(\theta_{\rm h}/\phi)} \right]$$
(2.31)

This method was used by Liu and Flemings [117], Garg et al. [112], and Schnurle and Liu [120]. However, if the formation of hydrate starts by coating the walls of pores (pore-coating), a function similar to Masuda's method is obtained.

$$\kappa = \kappa_0 \cdot \left[1 - \theta_{\rm h}/\phi\right]^2 \tag{2.32}$$

Garg et al. [112] believed that a large value for the exponent in (Eq. 2.32) corresponds to a faster reduction in permeability with the hydrate saturation, which in fact makes the model the same as Masuda's model. It is noted that the first hydrate formation behavior was supported by experimental evidence with Nuclear Magnetic Resonance.

The fourth method is the power-law model proposed by Civan [143],

$$\kappa = \kappa_0 \cdot (\phi_e/\phi_0) \cdot [(\phi_e/\phi_0) \cdot (1 - \phi_0)/(1 - \phi_e)]^{C_1}$$
(2.33)

where $\phi_{\rm e} = (\phi - \theta_{\rm h})$.

This method was used in the simulation models of Tonnet and Herri [101], Bai et al. [80, 81], and Bai et al. [124]. Jeannin et al. [144] linked the permeability to the porosity and hydrate saturation through a logarithmic law.

$$\log(\kappa) = C_1 \phi_e - C_2 \tag{2.34}$$

Similar relationships were used by Uddin et al. [36], Janicki et al. [13], and STARS. For instance, the Carmen–Kozeny formula used by Uddin et al. [36] is as following.

$$\kappa = \kappa_0 \cdot (\phi_e/\phi_0)^{C_1} \cdot \left[(1 - \phi_0) / (1 - \phi_e) \right]^2$$
(2.35)

2.4.2.2 Relative Permeability

Relative permeability describes the reduction in permeability because of the presence of fluids. Except for a few simulation models which assumed constant permeability [8, 16, 25], relative permeability is generally considered as long as fluids are involved. Some simulation models used the concepts of relative permeability and matric suction without specifying their relationships [15, 115, 127]. In other cases, the following methods have been proposed to formulate this parameter. The first method is to directly import the relationship between relative permeabilities and fluid saturations from experimental data [45, 100, 112, 128, 145]. The second method is to use an adaptation of the equation suggested by van Genuchten [146] and later extended to multiphase flow by Parker et al. [147].

$$\kappa_{\rm rw} = \kappa_{\rm rw0} \overline{S}_w^{1/2} \left[1 - \left(1 - \overline{S}_w^{1/C_1} \right)^{C_1} \right]^2 \tag{2.36}$$

$$\kappa_{\rm rg} = \kappa_{\rm rg0} \overline{S}_{\rm g}^{1/2} \left(1 - \overline{S}_{\rm w}^{1/C_1} \right)^{2C_1} \tag{2.37}$$

where $\overline{S}_{w} = \frac{S'_{w} - S_{wr}}{1 - S_{wr} - S_{gr}}$, $\overline{S}_{g} = \frac{S'_{g} - S_{gr}}{1 - S_{wr} - S_{gr}}$, and the effective water and gas saturations [117] are $S'_{w} = \frac{S_{w}}{S_{w} + S_{g}}$, $S'_{g} = \frac{S_{g}}{S_{w} + S_{g}}$.

Klar and Soga [60] used the original form in which κ_{rw0} and κ_{rg0} are equal to 1. Hong and Pooladi-Darvish [84], [36, 125] assumed that κ_{rw0} equals 0.5, and κ_{rg0} equals 1.

The third method includes those variants of the Brooks and Corey model [148–150]. The general form of this model for a system containing two or three fluid phases is

2 Advancement in Numerical Simulations of Gas Hydrate Dissociation in Porous Media 79

$$\kappa_{\rm rw} = \kappa_{\rm rw0} \overline{S}_{\rm w}^{\rm C_1} \tag{2.38}$$

$$\kappa_{\rm rg} = \kappa_{\rm rg0} \overline{S}_{\rm g}^{\rm C_2} \tag{2.39}$$

This type of method seems to be the most popular one in existing simulation models. Different values of constants have been used. For example, C_1 and C_2 were assumed to be equal to 4 and 2, and κ_{rw0} and κ_{rg0} to be 1 in some models [21, 33, 101, 116, 117, 120]. Sun and Mohanty [22] assumed C_1 equals 4, C_2 equals 2.5, and κ_{rw0} equals 0.2, κ_{rg0} equals 1. Bai et al. [80, 81], [124]) assigned C_1 to be 4 and C_2 to be 1.5. In the model proposed by Jackini et al. [13] C_1 was 4 and C_2 was 1.75. Both C_1 and C_2 were assumed to be 3 in the simulation models of White et al. [37] and Gamwo and Liu [151]. There are still some other methods such as the empirical equations used by Verigin et al. [152] and the power law correlations [153] used in the model proposed by Scott et al. [121].

2.4.2.3 Capillary Pressure–Saturation Relationship

The relationship between capillary pressures and phase saturations in porous media (multiphase) is an extension of the soil water characteristic curve in soils (two phase). The soil water characteristic curve (water retention curve or soil moisture characteristic curve) is the relationship between water content (volumetric or gravimetric, or saturation) and soil water potential (or suction, [154]). In the past decades, numerous empirical equations have been proposed for SWCCs [146, 149, 155–157]. In terms of thermodynamics, the SWCC is attributable to the chemical thermodynamics of interfacial phenomena [158–160].

The equation proposed by van Genuchten [146] and later extended to multiphase flow by Parker et al. [147] and the one suggested by Brooks and Corey [149] have gained popularity in simulation models for gas hydrate dissociation in porous media. The van Genuchten equation (Eq. 2.40) has been applied in several simulations [13, 33, 36, 60, 84, 111, 120].

$$\psi = \psi_0 \left(\overline{S}_w^{1/C_1} - 1 \right)^{1-C_1} \tag{2.40}$$

This general form of the model of Brooks and Corey [149] is expressed by the following equation.

$$\psi = \psi_0 \left(\overline{S}\right)^{C_1} \tag{2.41}$$

Typical applications of this method include the simulations of Sun and Mohanty [22], Bai et al. [124], and Janicki et al. [13]. It is worthwhile to point out that the dependence of relative permeability on fluids saturations is capable of being derived from the relationship between capillary pressure and fluid saturations due to their common basis on internal structure morphology and interface physical

chemistry [156, 161, 162]. So it is not surprised that the models used for these two types of auxiliary relationships are to some extent related.

2.4.2.4 Diffusion Coefficients

Diffusion is usually incorporated by those state-of-the-art simulators for THC modeling of gas hydrate dissociation in porous media. The reason may be that its effects on the mass transport could be considerable in a composite with multiphases and multicomponents, especially for the species transported in the fluids. Dispersion could also be considerable due to the same reason, though mechanical dispersion is not as significant as advection. These two phenomena of different natures: dispersion is caused by nonideal flow patterns (i.e., deviations from plug flow) and is a macroscopic phenomenon; while diffusion is caused by random molecular motions (i.e., Brownian motion) and is a microscopic phenomenon. But both of them describe the spread of particles from regions of higher concentration to regions of lower concentration. As the result, both of them can be described using Fick's first law. For example, in the reservoir simulator, STOMP, a combined diffusion–dispersion coefficient replaces the classical Fickian diffusion coefficient.

$$\mathbf{J}^{\alpha} = -D_i^{\alpha} \nabla \chi_i^{\alpha} \tag{2.42}$$

where *D* are is the coefficient for diffusion or dispersion depending on the transport mechanisms considered. Taking the model of Sun and Mohanty [22] for instance, the advective-dispersive model (ADM) used by Webb [163] was employed to consider the diffusion in gas phase. Based on Fick's law, the molecular diffusions of methane, salt, and water are calculated by (Eqs. 2.43-2.45), respectively.

$$\mathbf{J}^{\mathrm{m}} = -D_{\mathrm{g}}^{\mathrm{m}} \chi_{\mathrm{g}}^{\mathrm{m}} - D_{\mathrm{w}}^{\mathrm{m}} \chi_{\mathrm{w}}^{\mathrm{m}}$$
(2.43)

$$\mathbf{J}^{\mathrm{s}} = -D^{\mathrm{s}}_{\mathrm{w}} \boldsymbol{\chi}^{\mathrm{s}}_{\mathrm{w}} \tag{2.44}$$

$$\mathbf{J}^{\mathrm{w}} = -\mathbf{J}^{\mathrm{m}} - \mathbf{J}^{\mathrm{s}} \tag{2.45}$$

where the effective diffusion coefficient of component α in phase *i*, D_i^{α} , is determined with the model proposed by Pruess and Moridis [164]:

$$D_i^{\alpha} = \rho_i \phi^{4/3} S_i^{10/3} D_{i,B}^{\alpha}$$
(2.46)

where $D_{j,B}^{i}$ is the diffusion coefficient of component α in phase *i* in bulk phase system. For the gas phase composed of methane and water vapor, the diffusion is a binary diffusion. Then the binary diffusion coefficient, $D_{g,B}^{m}$, can be calculated as a function of pressure and temperature as

$$D_{\rm g,B}^{m} = 1.89 \times 10^{-5} \left(\frac{101325}{p_{\rm G}}\right) \left(\frac{T}{273.2}\right)^{3/2}$$
 (2.47)

For aqueous-phase composed of methane, salt, and water, $D_{w,B}^m$ can be evaluated with the following equation [165]. The diffusivity of salt in aqueous phase which is dependent on salt type was set to be a constant.

$$D_{\rm w,B}^m = 10^{-1.6865 - 920.576/T} \times 10^{-4}$$
(2.48)

The diffusion coefficient of methane in the aqueous phase can be calculated using the second-order polynomial function [140]

$$D_{w,B}^{m} = C_0 + +C_1 \cdot T + C_2 \cdot T^2$$
(2.49)

In the simulation conducted by Janicki et al. [13], diffusion coefficients were calculated from the IFM-GEOMAR data functions [166].

2.4.2.5 Hydraulic Diffusivity

Similar to thermal diffusivity, hydraulic diffusivity is also used in a few models [7, 77, 167]. The employment of this concept makes the mass balance equation appear similar to the heat equation. Hydraulic diffusivity could be linked to permeability via the following correlation.

$$\alpha = \frac{\kappa}{\mu} \left| \frac{dp}{d\theta} \right| \tag{2.50}$$

2.4.2.6 Mass Transfer Between Phases

Mass transfer between phases could be significant in some cases, e.g., in a system containing highly volatile soils and thus was considered in complex simulation models [168]. For example, Henry's law was used to quantify the solubility of gases in solvents while partial pressure rule could be used to define the molecular fraction of water in the gas phase [151]. Mass transfer of gaseous components to liquids and vice versa were also modeled by a two-film theory linear approach [13]. Other simple functions are also available, such as the one used in the model proposed by Sean et al. [140] for methane solubility in water.

$$\chi = C_1 [C_1 p + C_2 \cdot \exp(C_3 T)]$$
(2.51)

2.4.3 Material Properties Related to Chemical Reactions

2.4.3.1 Thermodynamic State

A thermodynamic state is a set of values of properties of a thermodynamic system that must be specified to reproduce the system. Thermodynamic state variables include entropy, pressure, temperature, density, and so on. Some variables such as pressure and temperature are the dependent variables of the hydraulic and thermal fields, respectively. Therefore no auxiliary relationships are necessary for their calculations when no phase transition occurs. However, an auxiliary relationship is required to specify the relationship between these variables to close the system when dissociation reactions occur. This relationship is called phase diagram and is discussed later. Other variables such as the densities of phase components are also important parts in the governing equations for thermal, hydraulic, and mechanical fields. Similar observations apply to the enthalpy of gas hydrate dissociation. In the following paragraphs the auxiliary relationships on density and enthalpy of gas hydrate dissociation will be summarized successively.

While the density of solid matrix typically does not need complicated treatments, the densities of other phases such as water, gas, and hydrates are frequently considered as functions of other state variables. For example, water is regarded to be slightly compressive, and its density can be given by (Eq. 2.52) [124].

$$\rho_{\rm w} = \rho_{\rm w0} [1 - C_1 (\rho_{\rm w} - \rho_{\rm w0})] \tag{2.52}$$

In the model of Schnurle and Liu [120], the density of pore-water is related to the temperature as follows [134, 169],

$$\rho_{\rm w} = 999.9 + 5.33 \times 10^{-2} (T - 273) - 6.834 \times 10^{-3} (T - 273)^2 \tag{2.53}$$

The variation of density of hydrate with temperature is described in Waite et al. [134] after Shpakov et al. [170]):

$$\rho_{\rm h} = 926.45 - 0.239(T - 273) - 3.73 \times 10^{-4}(T - 273)^2 \tag{2.54}$$

The ideal gas law was commonly used for the densities of gas components [115, 171]. In more accurate considerations, property data of gas phase components were taken from NIST Standard Reference Database and are molar-weighted; for the gas phase density, the Peng–Robinson equation was used. Data for the density of common liquid phase were typically taken from NIST and other available sources; special corrections were applied on the density of saline seawater (UNESCO Standard Reference Equation) [13].

Although the enthalpy of gas hydrate dissociation could be approximated by a constant [144], its variation with temperature has been considered in many simulation models. According to Sloan [172], the enthalpy of hydrate dissociation can be computed using the Clapeyron equation as follows,

2 Advancement in Numerical Simulations of Gas Hydrate Dissociation in Porous Media 83

$$\Delta H = T \Delta V \frac{dp}{dT} \tag{2.55}$$

where $\frac{dp}{dT}$ is the slope of the phase line, ΔV is the volume change during the phase transition. This equation can be further transformed into the Clausius–Clapeyron equation if the volume of hydrate approximates that of water trapped in hydrates.

$$\Delta H = n_h Z R T^2 \frac{d \ln p}{dT} \tag{2.56}$$

where n_h is the number of moles of hydrate per kilogram.

Moridis [173] obtained a graph for ΔH based on (Eqs. 2.55–2.56) and found that ΔH increased by a factor of 3 to 4 over the temperature range 0 °C to 40 °C [112]. The following function was usually adopted for ΔH as a function of *T* in simulation models for gas hydrate dissociation [7, 15, 33, 63, 80, 81, 116, 119, 124, 140, 167].

$$\Delta H = C_1 \cdot T + C_2 \tag{2.57}$$

A piecewise function for ranges on the two sides of the freezing point of bulk water was also suggested [44]

$$\Delta H = C_1 \cdot T + C_2, T < 273 \text{ K}; \Delta H = C_3 \cdot T + C_4, T > 273 \text{ K}$$
(2.58)

When the hydrates contain different species of gases, the influence of composition on the dissociation of enthalpy may be considerable. Under such a condition, ΔH could be calculated as the following equation [15],

$$\ln\left(\frac{\Delta H}{\Delta H_0}\right) = \sum \left(C_{1,i} \cdot \chi_i + C_{2,i} \cdot \chi_i^2\right)$$
(2.59)

where χ_i is the mole fractions of the guest gas, and $C_{1,i}$ and $C_{2,i}$ are the binary coefficients which depend on the gas type and temperature range.

2.4.3.2 Equilibrium: Phase Diagram

A phase diagram is usually used to show conditions at which thermodynamically distinct phases can occur at equilibrium, which could possibly involve pressure, temperature, specific volume, specific enthalpy, or specific entropy. But for gas hydrate dissociation simulations in porous media, a 2D diagram with pressure and temperature as the ordinate and abscissa, respectively, is usually used. Common components of a phase diagram are lines of equilibrium or phase boundaries, which refer to the lines that mark the conditions under which multiple phases can coexist at equilibrium. Among these boundaries, the one indicating the coexistence of

methane hydrate, methane, and water is the one most frequently adopted in the simulations. Several empirical equations have been used to represent this boundary. The first type of equation is as follows

$$p = C_1 \cdot \exp(C_2 + C_3/T)$$
 (2.60)

where C_1 was assumed to be 1 in some studies [15, 33, 171] as well as other values in other simulation models [111, 115, 116]. Values assigned to the other two constants were close in these models, in which C_3 was usually a negative value. A similar equation to the above one was used by Maksimov [25] ($p = C_1 \cdot \exp(C_2 + C_3 \cdot T)$).

The second type of equation for the line of phase boundary was in the polynomial form, i.e.,

$$\log p = C_0 + C_1 \cdot (T - T_0) + C_2 \cdot (T - T_0)^2$$
(2.61)

This type of phase equilibrium condition was used by Verigin et al. [152], Admadi et al. [167], Ahmadi et al. [7], Nazridoust and Ahmadi [21], and Liu et al. [118].

A similar empirical fit for the hydrate melting pressure as a function of temperature was proposed by Bakker [174] and later included in the simulation model of Garg et al. [112].

$$\log p = C_0 + C_1 \cdot T + C_2 \cdot T^2 + C_3 \cdot T^3$$
(2.62)

The third type of mathematical expression for the phase equilibrium was developed from the work of Adisasmito et al. [175] [36]. The experimental data summarized in the form of average curves were expressed by a three-parameter K value correlation as (Eq. 2.63),

$$K = \frac{C_1}{p} \exp\left(\frac{C_2}{T - C_3}\right) \tag{2.63}$$

where C_1 is in kPa and C_2 and C_3 are in °C.

In addition, a detailed piecewise function obtained by Moridis [176] based on experimental data [172] was also used in several models (TOUGH-Hydrate/TX; [113, 124]).

The above equations are designated for single substance under simple conditions. Tishchenko et al. [177] proposed empirical algorithms for hydrate dissociation pressures and methane concentrations, in seawater and pore water equilibrated with methane hydrate, as functions of chlorinity Cl (in ppt), temperature, and hydrostatic pressure. The algorithms described pore-water dissociation pressure for a temperature range of 273–293 K and chlorinity range of 0–70 ppt [120]. More advanced methods consider the influence of composition. For example, the one proposed by Burshears et al. [15] considered this influence by using the equation proposed by Holder and John [178]:

$$\ln(p/p_0) = \sum \left(C_{1,i} \cdot \chi_i + C_{2,i} \cdot \chi_i^2 \right)$$
(2.64)

where χ_i is the mole fractions of the guest gases, and $C_{1,i}$ and $C_{2,i}$ are the binary coefficients which depend on the gas type and temperature range.

2.4.3.3 Kinetic: Dissociation Kinetics

Different from phase boundaries, which are required for every simulation model, the chemical kinetics is only necessary for models using chemical kinetics for reactions (dissociation and formation). However, this term is critical due to the high nonlinearity it could result in. And the fact is that, in contrast to the advances made in the thermodynamics of hydrates, the kinetics are less understood [2]. Most of the kinetic models used in simulation models for gas hydrate dissociation are related to or in a similar form to the Kim and Bishnoi model [179]. This model assumed that the hydrate decomposition rate is proportional to a driving force defined by the difference between the fugacities of gas molecules at the three-phase equilibrium pressure and that in the bulk state [36]. The general form of the model could be expressed as

$$\frac{dn_{\rm g}}{dt} = k \cdot A \cdot (f_{\rm e} - f) \tag{2.65}$$

$$k = k_0 \exp\left(\frac{\Delta E}{RT}\right) \tag{2.66}$$

where n_g is the moles of gas, A is the total surface area of hydrates per unit volume, ΔE is the activation energy, f and f_e are the gas fugacity and equilibrium gas fugacity, respectively. It is noticed that the assumption of ideal gas was not adopted in the studies of Masuda et al. [119] and Esmaeilzadeh et al. [33]; and accordingly, the gas fugacities were calculated using the Peng–Robinson equation of state [180] or modified equations [33].

To relate the rate of generated gas to the source term, the following equation should be used, which considers the fact that only a fraction of total volume is occupied by gas hydrates.

$$\frac{dm_{\rm g}}{dt} = M_{\rm g}\phi \frac{dn_{\rm g}}{dt} = M_{\rm g} \cdot \phi \cdot k \cdot \Gamma \cdot A \cdot (f_{\rm e} - f)$$
(2.67)

where M_g is the molecular weight of gas, Γ is the effective ratio of particle area or active fraction coefficient. A simple approach to implement the above model was presented by Yousif [45] and later used by Sung et al. [145], Jeannin et al. [144], Du et al. [125], and Bai et al. [124]. In this approach, $M_g \cdot \phi \cdot k$ was simplified to be a constant k_d (kinetic constant), whose value was assigned to be 4.4×10^{-13} (mol/ (m² · Pa · s))) in the above-mentioned studies (2 × 10⁻⁹ was used by Du et al. [125]). A was calculated using the parallel-cylinder model proposed by Amyx et al. [181] as follows:

$$A = \left[\frac{\left(\theta_{\rm w} + \theta_{\rm g}\right)}{2\kappa_{\rm a}}\right]^{1/2} \tag{2.68}$$

Γ was usually not considered and the fugacities were replaced by the gas pressures under the assumption of ideal gas [8]. In the simulation studies of Sun and Mohanty [22] and Phirani and Mohanty [113], the kinetic constant was assumed to be 0.5875×10^{-11} (mol/(m² · Pa · s)), which is the average of the results measured by Englezos et al. [182]; or 0.35×10^{-10} (mol/(m² · Pa · s)) for carbon dioxide hydrate in the latter study. The method adopted by Sun and Mohanty [22] and Phirani and Mohanty [113] is a little complicated than Yousif's. In this method, $M_g \cdot \phi \cdot k$ was calculated with $k_d = k_{d0} \exp(\Delta E/RT)$; and an active fraction coefficient, Γ, equal to S_h , was used to allow for the fact that only a portion of hydrates get involved in the reaction.

The methods used by some other researchers [21, 33, 63, 75, 116, 119] took the form of the general formulation, but the value of intrinsic kinetic constant varies from model to model. In the models of Masuda et al. [119], Ruan et al. [116], Nazridoust and Ahmadi [21], and Esmaeilzadeh et al. [33], *A* was calculated using a different equation as follows.

$$A = \theta_{\rm h} \cdot A_{\rm s} \tag{2.69}$$

where A_s is the surface area of the spherical particles.

Other forms of the Kim–Bishnoi model also exist. For example, Kimoto et al. [111] used an equation which was suggested in the original paper of Kim et al. [179] as following:

$$\frac{dn_{\rm g}}{dt} = 0.585 \times 10^7 \cdot \exp(-9400/T) \cdot (f_{\rm e} - f) \cdot n_{\rm h0}^{1/3} \cdot n_{\rm h}^{2/3}$$
(2.70)

where $\frac{dn_e}{dt}$ is in mol/s, n_h is the moles of hydrates, and gas fugacities are represented by the average fluid pressure. Uddin et al. [36] extended the Kim–Bishnoi model used by Hong and Pooladi-Darvish [8] to allow for both formation and dissociation reactions and also the influence of water saturation on the reaction area. Other kinetic models have also been developed, which were in a similar form to that of the Kim–Bishnoi model. For example, the model proposed by Rempel and Buffett [16] assumed the driving force for formation/dissociation reactions was proportional to the difference between mass fraction and equilibrium mass fraction; while Sean et al. [140] believed the driving force for dissociation was proportional to the difference in volumetric molar concentrations of methane under current and equilibrium conditions. In general, the Kim–Bishnoi model for chemical kinetics is used as a chemical kinetic model. However, Goel et al. [77] extended the Kim–Bishnoi model and incorporated it into an equilibrium model.

2.4.4 Material Parameters for Momentum Balance

The incorporation of momentum balance module into the simulation of gas hydrate dissociation in porous media is still in a very preliminary stage. This is mainly due to the limited understanding of the mechanical properties of solid and fluid phases during the dissociation process and of the interactions between phases. However, problems relevant to the momentum balance, such as the geomechanical behaviors, have started to attract attention recently.

2.4.4.1 Solid: Geomechanical Properties, Solid–Fluid Coupling, Constitutive Relations

Gas hydrates are typically found in unconsolidated or weakly consolidated sands in shallow marine floors and permafrost areas [183, 184]. In such sediments, gas hydrate crystals work as cementing materials for bonding solid grains and increasing the stiffness of sediments.

The microscopic distribution of hydrates in sediments was described using three modes, i.e., pore-filling, load-bearing, and cementation [37, 185, 186]. Macroscopic gas hydrate structures inside geologic formation were categorized as massive hydrate blocks on the seabed, massive or thin streak, pore-filling in sand, and vein or fracture filling in clay and so on. In the pore space scale, gas hydrates have different forms such as floating, frame building, coating, and cementation [65]. Under a specific condition, i.e., high pressure and low temperature, methane hydrate is stable, and is a relatively strong and ductile material [187]. However, once the hydrate dissociates, due to the decrease in pressure or increase in temperature, the bonded structure disappears and the soils may behave as unconsolidated materials, leading to some geotechnical engineering problems. Of particular interest are submarine geo-hazards, such as initiation of marine landslides due to hydrate dissociation [28, 188, 189] and wellbore instability during methane gas production from the hydrates [60, 64, 126]. Besides, understanding of the physical and mechanical properties of hydrate-bearing sediments is important for interpreting geophysical data, borehole and slope stability analyses, and reservoir simulations and for developing production models [190].

Current knowledge on the accurate constitutive behaviors of the soil-hydrate structure, e.g., knowledge about how hydrate pattern influences the intermediate and large strain behavior and the failure condition, are limited. The current knowledge of geophysical and geotechnical properties of hydrate-bearing sediments has been largely derived from laboratory experiments conducted on disparate soils at different confining pressures, water saturations, and hydrate concentrations [37, 186, 190]. This is because the mechanical properties of methane hydrate bearing sediments are highly dependent on factors such as the saturation of methane hydrate, pressure, temperature, and hydrate structure in pore spaces [65].

The mechanical properties influence various scales of geological formation stabilities. Taking Young's modulus for example, Ng et al. [126] used the following relationship for the Young's modulus of gas hydrates:

$$E = 125 + 1000S_{\rm h} \tag{2.71}$$

where E is Young's modulus in MPa, S_h is the degree of gas hydrate saturation.

The mechanical stability of methane hydrate is a function of temperature and pressure. Besides, its mechanical properties are coupled to fluid dynamics and heat transfer phenomena [65]. To evaluate the mechanical properties of sediment samples, Ran et al. [191] simulated loading of a disordered pack of spherical grains by incremental displacements of its boundaries. A series of possible scenarios was simulated, showing the degradation of sediment strength as a reduction in the macroscopic elastic moduli. This trend agreed qualitatively with the published results of experimental and numerical studies. It was concluded that dissociation might lead to a loss of solid support of the skeleton, causing seafloor instabilities such as landslides and subsidence.

The underlying mechanisms for geomechanical responses of gas hydrate dissociation have been investigated. Soga et al. [186] reviewed the mechanical properties of methane hydrate bearing soils and highlighted the following major characteristics. (1) The strength of the gas hydrate bearing soil is dependent on the hydrate saturation; and the contribution to the strength by hydrate is of a cohesive nature rather than frictional nature. (2) The dilation angle is a function of hydrate saturation. (3) The Young's modulus of soil-hydrate formation is higher than that of the soil without hydrates, but the Poisson's ratio was found to be independent of hydrate saturation. Yamamoto [65] summarized the following major effects of the hydrate dissociation on the mechanical behavior of the geological formation [65]: (1) reduction of the bonding between grains; (2) the change of the water content and gas saturation, and hence change in the consistency and capillary suction force; (3) change in the capillary force due to production of water and gas; (4) reduction in the effective stress and shear strength due to increase in the pore pressure in low permeability soils; (5) increase in the permeability and advection fluid transfer due to increases in the effective porosity; (6) decrease in the pore space compressibility, decrease in shear wave velocity, and increase in Poisson's ratio; (7) thermal stress due to decrease in the temperature; (8) change of the dilatancy character from positive to negative because of the change in sand character from dense to loose. The shear strength of artificial hydrate-bearing sediments was found to be similar to that of natural hydrate-bearing sediments [192, 193]. Their strength varies with the content of hydrate, sediment properties and experimental conditions [194–196]. Furthermore, during hydrate dissociation without axial loading, the volumetric strain has dilative tendency regardless whether there is a change in the effective confining pressure [197].

2.4.4.2 Liquid: Darcy's Law, Viscosity

The primary auxiliary relationship for the fluid phases in the mechanical field is Darcy's law. The employment of Darcy's law predominates in the simulations of gas hydrate dissociation in porous media. Thus, the non-Darcy's effects [198] for non-Newtonian fluids, e.g., very low pressure (slip phenomenon) or high velocity range (turbulence, inertia, and other high velocity effects) behaviors, are not discussed in this chapter. The Darcy's law is formulated as the following:

$$\overline{\mathbf{v}}_i = \theta_i \mathbf{v}_i = \frac{k}{\mu} (\nabla p - \rho \mathbf{g} \mathbf{i})$$
(2.72)

where $\overline{\mathbf{v}}_i$ is the superficial (or Darcy) velocity, and \mathbf{i} is the unit vector along the gravitational direction.

Darcy's law is extended to multiphase flow by postulating that the same phase pressures are involved in causing each fluid to flow [168]. However, each phase interferes with the flow of the other due to the simultaneous flow of the multiple phases. That is why relative permeability is introduced in most of the existing models.

$$k_i = k_0 k_{\mathrm{r},i} \tag{2.73}$$

where k_i and $k_{r,i}$ is the permeability and relative permeability of phase *i*, k_0 is the intrinsic permeability of the porous material.

Since all the terms in the Darcy's law except viscosity have been discussed in previous parts of the text, only typical mathematical formulations for viscosity are summarized in the current subsection. Viscosity is usually formulated as a function of some state variables, such as temperature and density. For gas phase, one typical function is that proposed by Selim and Sloan [44], which was later used by Schnurle and Liu [120].

$$\mu = C_0 + C_1 T + C_2 T^2 + C_3 T^3 + C_4 T^4 + C_5 \rho + C_6 \rho^2 + C_7 \rho^3 + C_8 \rho \qquad (2.74)$$

where μ is the viscosity. For aqueous phase, Sean et al. [140] used the following equation in their simulation model.

$$\mu = C_0 + C_1 T + C_2 T^2 \tag{2.75}$$

For the overall viscosity of one phase consisting of several components, Janicki et al. [13] suggested to use the following molar-weighted functions:

$$\mu = \sum_{\alpha} \chi_i^{\alpha} \mu_i \tag{2.76}$$

where μ_i is the viscosity of phase *i*.

2.4.4.3 Solid–Liquid Interaction: Stress Formulation

The solid–liquid interaction, which describes the couplings between the solid matrix and pore liquids, has received very limited attention in gas hydrate simulations. This is because the momentum balance of fluids has hardly been considered except in very few works [111, 141], although the geotechnical responses, i.e., the momentum balance of solid phases, have started to attract increasing attention. But the topic is not new to relevant disciplines, i.e., Geomechanics (e.g., consolidation), Hydrogeology (e.g., groundwater storage), and Petroleum Engineering (subsidence, stress around boreholes). For single phase flow, Tezarghi's consolidation theory lent us a good practical approach. For this two-way coupling problem, the coupling from the pore liquid (water) to solid (soil grains) was dealt with the stress formulation (effective stress) while the coupling from solid to pore liquid was tackled with experimental relations. The later consolidation theory presented by Biot [199] provided a fully theoretical explanation to the single phase (saturated with compressible water) solid–fluid coupling problem. Biot's theory, as the departure point of poroelasticity, could be formulated by the following equations [200]:

$$\varepsilon_{\rm v} = \frac{1}{K}\sigma + \frac{1}{H}p \tag{2.77}$$

$$\Delta \phi = \frac{1}{H}\sigma + \frac{1}{R}p \tag{2.78}$$

where ε_v is the volumetric strain (positive in expansion), σ is the isotropic applied stress (positive if tensile), p is the fluid pressure (greater than atmosphere is positive), $\Delta \phi$ is the increment of water content (positive as fluid is added to the volume), K is the drained bulk modulus, 1/H is the poroelastic expansion coefficient, 1/R is the specific storage coefficient.

It is seen that the first equation describes the liquid-to-solid coupling: a change in fluid pressure or fluid mass produces a change in volume of the porous skeleton (solid matrix), while the second equation represents the solid-to-fluid coupling: a change in applied stress produces a change in fluid pressure or mass. The first equation could be reformulated as:

$$\sigma = K\varepsilon_{\rm v} - Bp \tag{2.79}$$

where B = K/H is the Biot–Willis coefficient, which can be calculated with the classical micro–macro relations of poroelasticity as

$$B = 1 - \frac{K_{\text{hom}}}{K_{\text{s}}} \tag{2.80}$$

where K_{hom} is the homogenized bulk modulus and K_{s} is the bulk modulus of solid grains.

By employing the assumption used in Terzaghi's theory, that is, solid grain is incompressible, the above equation degenerates into the formulation of effective stress. On the other hand, Biot's theory for one liquid was extended to two liquid condition (water and air) by Bishop [201], Fredlund and Morgenstern [202], and Lu and Likos [203] in the framework of unsaturated soil mechanics as well as Coussy [204] in the framework of poromechanics. When more liquids get involved, the mixture theory needs to be employed [205]. It is noted that these solid–fluid coupling theories for multiple phases have not been explicitly validated by experiments.

For geomechanical responses, Li et al. [63] developed the stress equilibrium equation based on the effective stress law. However, the definition of pore fluid pressure is unclear for the two-phase flow. In the study of Rutqvist et al. [64], the basic couplings between hydraulic and mechanical processes in the deformable porous media were considered through constitutive laws that define how changes in pressure, temperature, and hydrate saturation affect deformation and stresses, and how changes in stress and strain affect fluid flow. And the numerical simulation involved linking the TOUGH+Hydrate simulator to the FLAC3D commercial geomechanical code. Kim et al. [59] computed the geomechanical responses by connecting a continuum theory in coupled flow to geomechanics. The governing equations of fluid and heat flow were based on Moridis [176] (TOUGH + Hydrate). The constitutive relationships were extended from Coussy's model [204]. A similar study was conducted by Chin et al. [206]. In the work of Klar and Soga [60] and Ng et al. [126], the mechanical behaviors of hydrate soils which depend on effective stresses formulated with the pore pressure (including gas and water) were formulated by Bishop's theory [201] for unsaturated soils. Of great importance is the work of Kimoto et al. [111], which considered the momentum balance of both solids and fluids. And the liquid-to-solid couplings were considered with the mixture theory [205]. In addition, empirical models for solid-fluid interactions have also been used. For example, pore fluid pressure generation was postulated to be proportional to the initial hydrate fraction and the sediment bulk stiffness [62]. Garg et al. [112] calculated the intrinsic sediment stress with the equation proposed by Morland et al. [207], in which a relationship between the sediment porosity and effective stress was assumed.

2.5 Discussions

This section presents discussions on several critical aspects of gas hydrate dissociation simulations including validations, applications, recovery schemes, critical factors in recovery, governing mechanisms, research trends, and needs for future research. All the discussions are made on basis of published simulation results, or direct analyses of existing data, or other solid facts. In such a way, this review study lays down a solid foundation for future research.

2.5.1 Validation of the Performance of Existing Models

As shown in Sect. 2.3, a number of simulation models have been developed for predicting gas hydrate dissociation in porous media. In addition to their common features and differences, the functions and potential applications also need to be evaluated. Strategies for the performance validation include: validation by experiments, validation by comparisons between models, and validation by field production applications. The ultimate success of a given model, i.e., the usefulness and applicability of the model, can only be more effectively demonstrated based on their applications to real-world problems.

2.5.1.1 Validations by Experiments

Commercial attempts in gas recovery from gas hydrate reservoirs are limited at the current stage. Besides, the natural samples are not readily available because of the remote locations of the accumulations and the difficulties in collecting and transporting samples without compromising them. Consequently, only a few models have been validated against results from laboratory experiments. Listed below are a few of these studies, for which details can be found in the cited references. The predictions yielded by the model of Yousif et al. [45] closely matched their experimental data of gas and water productions, the progress of the dissociation front, and the pressure and saturation profiles. The simulation results of Bai et al. [80, 81] were well validated by their laboratory experiments. Laboratory scale experiments were conducted at the Pacific Northwest National Laboratory (PNNL) to analyze the feasibility of the simulation method of Phale et al. [14]. Mass and heat transfers have been studied both experimentally and numerically by Tonnet and Herri [101]. And their numerical model was validated by the experiments. The model-predicted performance by Goel et al. [77], i.e., production rate, compared well with the published experimental studies on the hydrate dissociation in porous media [45, 208, 209]. The predicted vertical distribution of hydrate in the study of Rempel and Buffett [16] was consistent with geophysical inferences from observed hydrate occurrences along the Cascadia margin. The simulation results of Garg et al. [112] applied at the Blake Ridge (site 997) and Hydrate Ridge (site 1249) were compared with the chlorinity, sulfate, and hydrate distribution data. However, field validations of gas hydrate simulation models are still rare at this moment. With global wise interest in gas hydrate pilot production, it is anticipated that there will be more opportunities for direct field validations of simulation models.

2.5.1.2 Mutual Validation Between Models

In addition to direct validations of simulation models with in situ or laboratory data, mutual validations between different models have also been carried out frequently. Li et al. [210] validated the model proposed by Yousif et al. [45]. A close agreement was achieved between the results reported by Hong and Pooladi-Darvish [8] and that of Uddin et al. [36]. The numerical solution obtained by Gamwo and Liu [151] was verified against the state-of-the-art simulator TOUGH-Hydrate. For comparisons between analytical and numerical models, Admadi et al. [7, 167] compared their numerical simulation results with that of the linearization approach. Similarly, Hong [8] compared the analytical solution with the numerical solution to the original equation system. The code comparison project conducted by USGS/ NETL is of great importance for evaluating the existing large-scale simulators for THC modeling of gas hydrate dissociation.

2.5.1.3 Applications

A number of simulation models have been designed for applications. For example, results from the solution of Selim and Sloan [1] were presented in graphs to estimate the amount of hydrate dissociated as a function of time. The model of Garg et al. [112] was applied to studying hydrate distributions and predicting chlorinity, sulfate, and hydrate distribution data at the Blake Ridge (site 997) and Hydrate Ridge (site 1249). The simulation study of Konno et al. [142] confirmed the advantage of employing depressurization as a gas production method with the hydrate sample in sandy turbidite sediments at the Eastern Nankai Trough. Their numerical analysis was proven to be effective in analyzing the dissociation behavior of hydrate-bearing cores obtained at natural hydrate reservoirs; and it enabled evaluation of gas productivity in those reservoirs. The code presented by Klar and Soga [60] was used for investigating the stability of a methane extraction well by depressurizing the well. The simulation by Janicki et al. [13] considered two scenarios: the depressurization of an area 1000 m in diameter and a one/two-well scenario with CO₂ injection. Realistic rates for injection and production were estimated. Their study also discussed the limitations of these processes. The production modeling conducted by Phale et al. [14] would help in deciding the critical operating factors such as pressure and temperature conditions of the injecting CO₂-slurry, the injecting flow rate the slurry, and the concentration of the slurry. The work of Rutqvist et al. [64] analyzed the geomechanical responses during the depressurization production from two known hydrate-bearing permafrost deposits: the Mallik (Northwest Territories, Canada) deposit and Mount Elbert (Alaska, USA) deposit. The simulation results showed that general thermodynamic and geomechanical responses for these two sites were similar.

2.5.2 Suggestion on Practice Production by Model Simulations

2.5.2.1 Recovery Schemes

For the conventional recovery schemes, depressurization received particular attention in the early stage of the development of simulation models for gas hydrate dissociation in porous media. This is possibly attributed to the application of this method in the Messovakha field, USSR [45]. Special interest was repeatedly expressed for a type of reservoir with a gas layer overlaid by a hydrate layer, which was later classified as Class 1 accumulation. Numerous simulations proved the feasibility and effectiveness of applying depressurization to this type of gas hydrate reservoir [8, 84] and indicated that the hydrate layer have a large impact on improving the productivity of the underlying gas reservoir [84]. For example, the simulation results of Burshears et al. [15] inferred that massive hydrate can be dissociated without external heat energy source, which would not be significantly affected by the water from gas hydrate dissociation. In addition, gas produced by hydrate dissociation contributed significantly to the total production [124], i.e., 20% to 30% of the total gas production [6]. Also, the computer simulation by Bai et al. [124] showed that overlying hydrate zone could evidently prolong the lifespan of the gas reservoir. The study of Konno et al. [142] confirmed the advantage of employing depressurization as a gas production method using the hydrate in sandy turbidite sediments at the Eastern Nankai Trough. With depletion of reservoir energy, methods such as thermal stimulation and inhibitor injection were suggested to replace depressurization (Bai et al. [80, 81]). For example, the simulation of Yang et al. [211] suggested to use the depressurization method in the initial stage and the thermal stimulation method in the later stage. On the contrary, the simulation of Masuda et al. [119] indicated that the production schemes of depressurization and heating well were not effective to economically obtain feasible gas production rates.

Computer models also provided important insights into other recovery methods. For example, for thermal stimulation, an energy efficiency value about 9% was found in the study of Selim and Sloam [44], which appeared encouraging for natural gas production from hydrates. The thermal stimulation using constant temperature at the reservoir with a single well was found to have a limited effect on gas production compared to gas production due to depressurization [118]. Within various techniques of thermal stimulation, hot water injection was proven to be able to remarkably improve gas productivity and a maximum production rate of 860 m³/day was obtained per unit length of well [119]. And the energy balance for this scheme was proven to be high enough to be a promising gas recovery method. Bai and Li [212] demonstrated that, under certain conditions, the combination of warm water flooding and depressurization has the advantage of longer stable period of high gas rate than single production method. The theoretical analysis presented by Kamath and Godbole [39] indicated that there was good potential in the brine

injection technique for thermally efficient production of gas from hydrate reservoirs if the hydrates exist in a pure state and the economics is favorable. From the results of numerical studies, Sung et al. [100] noticed that the effect of methanol injection only appeared near the well, rather than whole reservoir, possibly due to the extremely low permeability of hydrate reservoirs before dissociation occurred. From their parametric study, methanol content was identified as the most sensitive parameter in a sense of the time that a well block to be completely dissociated. Phirani and Mohanty [113] used computer model to study the gas hydrate production from CO_2 injection. It was found that to dissociate methane hydrate by CO_2 injection, the CO_2 mole fraction needs to be kept very high in the fluid phase or to be operated at a relative lower pressure. The results obtained by Phale et al. [14] indicated that the injection of CO_2 -microemulsion produced considerably larger amount of methane than warm water injection alone.

2.5.2.2 Critical Factors in Recovery

The recovery process is influenced by various factors ranging from material properties, environmental conditions to operating factors. Results obtained by Bayles et al. [5] indicated that increasing the hydrate-filled porosity or increasing the zone thickness contributed to better gas production and energy efficiency ratios for steam stimulation. And deeper reservoirs appeared to yield more favorable gas production and energy efficiency ratios, a result that was dependent on the natural geothermal gradient. Also for steam and hot water stimulation, the parametric study conducted by Selim and Sloan [44] showed that the dissociation rate was a strong function of the thermal properties of the system and the porosity of the porous medium for thermal stimulation. Pawar and Zyvoloski [75] reported that the gas production predictions were sensitive to operational parameters such as injection temperature, injection rate, and pumping well pressure. For depressurization, it was observed that numerical grid size has a significant impact on simulation results. Admadi et al. [7, 167] and Esmaeilzadeh et al. [33] showed that the gas production rate was a sensitive function of well pressure. The simulation results from the study of Ruan et al. [116] showed that the depressurizing range has a significant influence on the final gas production the in the depressurization process. In contrast, the depressurizing rate only affects the production lifetime. A greater amount of cumulative gas can be produced with a larger depressurization range or a lower depressurizing rate for a certain depressurizing range. For CO_2 sequestration, the simulation results of White et al. [37] inferred that low injection pressures can be used to reduce secondary hydrate formation, and that direct contact of injected CO2 with the methane hydrate in the formation was limited due to bypass through the higher permeability gas zone. The simulation of Phale et al. [14] indicated that a higher hydraulic conductivity resulted in much faster methane production for CO₂slurry injection. This lent supports to the use of fracturing the formation to improve injectivity. It was also concluded that moderate concentrations and higher temperatures might help in optimizing methane recovery. However, in general, Sun and

Mohanty [22] found that an increase in initial temperature, an introduction of salt component into system, a decrease in outlet pressure, or an increase in boundary heat transfer coefficient can lead to faster hydrate dissociation. Nazridoust and Ahmadi [21] illustrated that the rate of hydrate dissociation in a core was a sensitive function of the surrounding environment temperature, outlet pressure condition, and permeability. But in the study of Sun et al. [12], gas production was not very sensitive to the temperature boundary conditions of the well. It was also found that an increase in the reservoir and well pressures and a decrease in the permeability suppressed the formation of an extended hydrate dissociation region [79].

Several factors relevant to chemical models have been identified to be able to affect simulation results. The simulation conducted by Li et al. [210] reported that higher permeability led to a lower initial saturation, a lower production pressure, a higher production rate, and a faster moving dissociation front. Liu et al. [118] also concluded that the speed of the moving front and the gas production rate were strong functions of the well pressure and the absolute permeability of porous media. In addition, their simulations showed that the assumption of stationary water phase underpredicted gas production and overpredicted the speed of the moving front. The combustion of methane yielded 44% less CO₂ than coal, per unit energy release, and 29 % less CO₂ than oil. Similarly, Kwon et al. [62] demonstrated the speed of the moving front and the gas production rate were strong functions of the well pressure and the absolute permeability of the porous media. Gamwo and Liu [151] found that the hydrate dissociation patterns differed significantly when the thermal boundary condition was shifted from adiabatic to constant temperature. In their study, the surface area factor was found to have an important effect on the rate of hydrate dissociation for the kinetic model. The deviation between the kinetic and equilibrium models was found to increase with a decreasing surface area.

Various factors critical to geomechanical responses have also been identified. Results obtained by Ng et al. [126] showed that heat flows from the clay layer to the sand layer led to a faster hydrate dissociation rate in the hydrate region near the clay-sand boundary than that at the center of the hydrate-sand layer, which influenced the stress distribution around the wellbore. As the soil relaxed toward the wellbore, arching effect in the vertical plane can be seen in the sand layer in addition to the usual increase in the circumferential stress. This was due to the force transferred from the casing to the clay layer, which deformed greater than the sand layer during depressurization. The modeling results of Chin et al. [206] predicted the possible range of peak surface subsidence and the maximum downward displacement within the modeled formations. Li et al. [63] showed that mechanical properties of the formation became worse sharply with the thermal decomposition of hydrates, which easily resulted in the instability of the formation. It was demonstrated by Tsimpanogiannis and Lichtner [171] that, at low permeabilities of oceanic sediments, extremely high dissociation pressures developed at the hydrate dissociation front and would result in fracturing of the hydrate-sediments and led to break down of the model. In the study of Rutqvist et al. [64], depressurization resulted in an increasing shear stress within the body of the receding hydrate and caused a vertical compaction of the reservoir. The increasing shear stress might lead to shear failures in the hydrate-free zone bounded by the hydrate layer overburden and the downward-receding upper dissociation interface. The Poisson's ratio of the hydrate-bearing formation was a particularly important parameter that determined whether the evolution of the reservoir stresses will increase or decrease the likelihood of shear failure. Kim et al. [59] demonstrated that noticeable differences between one- and two-way couplings for several cases.

2.5.2.3 Governing Mechanisms for Hydrate Dissociation

The computer modeling also provided insights into the governing mechanisms of gas hydrate dissociation. There have been debates over questions such as if gas hydrate dissociation is localized or globalized or if the process is thermal conduction controlled, convection controlled, or diffusion controlled. Yang et al. [211] found that gas hydrate dissociation occurred throughout the hydrate zone, which was controlled by both mass transfer and heat transfer throughout the stages. But the sharp-interface was hardly found during the hydrate dissociation. And the ice arisen from hydrate dissociation slowed the hydrate dissociation rate below the ice point, which would affect gas production rate. The simulations and experiments of Tonnet and Herri [101] demonstrated that the dissociation limiting step switched from thermal transfer to mass transfer depending on the initial permeability and conductivity of the porous medium. In the study of Hong et al. [8], the analytical solutions for the rates of decomposition in a semi-infinite zone controlled by separate mechanisms were obtained by ignoring the other two mechanisms. For the case studied, the effect of two-phase flow was shown to be significantly smaller than heat transfer and intrinsic kinetics of hydrate decomposition. In the study of Sun et al. [12], the results showed that laboratory-scale experiments were often dissociation-controlled, but the field-scale processes were typically flow-controlled. Vasil'ev et al. [79] reported that for high-permeability rocks the convective heat transfer in the near-well space of the reservoir predominated over the conductive transfer. This indicated that the use of intra-well heaters was ineffective. Admadi et al. [7, 167] and Esmaeilzadeh et al. [33] showed that both heat conduction and convection in the hydrate zone were important during gas recovery from gas hydrates by depressurization method. Moreover, the study of Tonnet and Herri [101] established criteria for distinguishing dissociation governed by heat transfer and that governed by mass transfer. For high permeability sediments, the heat conductivity of the sediment was identified as a key parameter that controlled the dissociation kinetics; for low permeability sediment ($<5e^{-12} m^2$), the dissociation kinetics became dependent on the parameters that influence mass transfer, i.e., the initial hydrate saturation and the absolute permeability of the sediment.

2.5.3 Research Trends and Future Needs

2.5.3.1 Physical Fields

Shown in Fig. 2.4 is a summary on the development of simulation models with respect to physical field over the last three decades. It is seen that the importance of mass transfer has been more and more emphasized. This explains the fact that there were few efforts for TC modeling, while THC models achieved a sustained growth in numbers. On the other hand, THMC models which emerged just a few years ago have been increasing dramatically. It is thus estimated that, with the maturity of THC models representing by those state-of-the-art simulators, more and more attention will be directed to the incorporation of the momentum balance module, ranging from geotechnical responses to fluid momentum.

2.5.3.2 Phases and Components

Trends in the development of simulation models regarding the number of phases are summarized in Fig. 2.5, from which a few trends can be clearly observed. It is seen that the development of two-phase models, which dominate in the current models, is slowing down in recent years. The possible reason is that two phase models have became mature and possessed the ability to deal with the problems that they are designed for. On the other hand, the amount of models designed for more than two phases and those complicated behaviors between phases are increasing rapidly. This trend may imply that, with the settlement of simple issues with single phase or two phase models for gas hydrate dissociation is increasing. The increase in computer capacity also helps to promote and to support the births of these more powerful simulators.

2.5.3.3 Equilibrium Versus Kinetic Models

As discussed in Sect. 2.3, there are still some disputes over the difference between equilibrium and kinetic models. Figure 2.6 summarizes a quantitative evaluation of the numbers of different types of models developed at different times. As can be seen, equilibrium models received major attention in the early stage. This is possibly due to that chemical kinetics for dissociation reactions was not well known at that time. Equilibrium models are attractive because they are able to yield qualitatively reasonable results with limited computational resources. However, after 2000, the number of kinetic models started to increase in a greater and more stable rate. At the same time, the idea to include both chemical methods (or modules) into one simulator has also attracted considerable attention.



Fig. 2.4 Development of models with respect to physical fields



Fig. 2.5 Development of models with respect to phases in H

2.5.3.4 Environmental Effects

The detrimental effects of the naturally gas hydrate dissociation and the gas recovery from gas hydrates have been debated. As commented by Beauchamp [58], many researchers believed that, if released in the environment, the methane from hydrates would be a significant hazard to marine ecosystems, coastal populations and infrastructures, or worse, would dangerously contribute to global warming. But evidence indicated that the greatest threat to gas hydrate stability in oceanic settings does not come from minor environmental fluctuations, but rather from the buildup of free gas beneath the gas hydrate stability zone, which leads to overpressurizing and catastrophic release of gas through pockmarks expulsion,



Fig. 2.6 Development of models with respect to chemical model

volcanoes, or surface seepage [213]. A truth conflicting with the assumed threats of released gas during gas recovery processes is that methane has to bypass normal fermentation processes to be a warming agent and thus needs to be released very quickly and massively. However, that type of releasing process is impossible within a conventional recovery process. Therefore, while more and more research has been launched due to the possible detrimental effects of gas hydrate dissociation, attention may also be needed to identify solid evidence to support the original judgment.

2.6 Conclusion

Understanding and modeling the gas hydrate dissociation (formation) process have been stimulating a tremendous amount of research due to the potential role of gas hydrates as a major energy resource in the future. Various computational simulation models have been developed over the past three decades. But a systematical organization of the rich collection of the literature is currently lacking. Such an effort, however, will help researchers to build a broad picture on the research in this area. This chapter conducts an integrative review on the topic of computer simulations of gas hydrate simulation with emphasis on the theoretical basis for the simulation models. A unified framework is developed to classify and integrate the existing models. The intention is to provide not only an overview but also the specific angles for understanding the literature. The major mechanisms involved in the process are illustrated and explained on the level of governing equation. The discrepancies among models are demonstrated and discussed with reference to the governing equation system. To facilitate implementation, the auxiliary relationships, which are intended to describe material properties of gas hydrates, are discussed according to their categories. The auxiliary relationships used by existing models together with other possible useful information are summarized and compared. Finally, discussions are made based on the results obtained by existing models as well as other solid data. Specific trends are revealed and beneficial conclusions are reached to provide reference for future research.

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