Clathrate Hydrates: Recent Advances on CH$_4$ and CO$_2$ Hydrates, and Possible New Frontiers

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Abstract

Gas hydrates continue to attract enormous attention throughout the energy industry, as both a hindrance in conventional production and a substantial unconventional resource. Scientists continue to be fascinated by hydrates because of their peculiar properties, including the ability of sequestering large amounts of hydrophobic gases, unusual thermal transport properties, and unique molecular structures. From a technological point of view, clathrate hydrates offer potential advantages in applications as diverse as natural gas production, carbon sequestration, water desalination and natural gas storage. The communities interested in hydrates span traditional academic disciplines, including earth science, physical chemistry, and petroleum engineering. The studies on this field are equally diverse, including field expeditions to attempt the production of natural gas from hydrate deposits accumulated naturally on the seafloor, to lab-scale studies to attempt to exchange CO$_2$ for the CH$_4$ present in hydrate deposits; from the scale up of water desalination plants to the testing of compounds used to prevent the formation of large hydrate plugs in pipelines; from theoretical studies to understand the stability of hydrates depending on the guest molecules, to molecular simulations to probe nucleation mechanisms. This review highlights a few fundamental questions faced by the research community, with focus on knowledge gaps representing some of the barriers that must be addressed to enable growth in the practical applications of hydrate technology, including natural gas storage, water desalination, CO$_2$ – CH$_4$ exchange in hydrate deposits, and prevention of hydrate plugs in conventional energy transportation.

## 1. Introduction: Fundamental Features of Clathrate Hydrates

Sir Humphrey Davy identified water clathrate hydrates (also known as gas hydrates) in 1811.[1] In clathrate hydrates, guest gas molecules (e.g., methane and CO_2) stabilize crystalline hydrogen-bonded water cages, the most common of which are sI, sII, and sH.[2] Other, less common, structures have also been reported, e.g., a trigonal structure in the presence of dimethyl ether.[2,3] Gas hydrates exhibit many unique thermophysical and transport properties. In liquid water, CH_4 solubility is approximately 1 molecule for every 4,000 waters, while in hydrates the same amount of water holds more than 600 CH_4 molecules. The thermal conductivity of hydrates is five to twenty times lower than that of ice,[4] and it depends on temperature in a way that resembles glasses above 100 K[5,6] and crystals below 100 K.[7,8] Many hydrate phase diagrams have been reported in the literature, depending on the guest gas species.[9,10] Under limited conditions, theoretical models enable reasonable predictions of the hydrate phase boundary.[11-18] Molecular simulations have contributed to understanding some of these unique hydrate properties,[19] including the enhanced stability of CO_2 hydrates relative to CH_4 ones.[20] However, several of the fundamental properties of clathrate hydrates remain elusive, including their formation mechanism.[21]

In this short review we first provide an overview of recent advancements along four main technological areas in which clathrate hydrates promise great advantages, focusing primarily on experimental observations. We then summarise selected advancements accomplished via the implementation of molecular simulations. The combined overview of experimental and simulation studies allows us to identify a few key fundamental questions that we believe remain open. We conclude by suggesting possible research activities that could be implemented to tackle such questions.

## 2. Selected Promising Technological Applications of Gas Hydrates
2.1. Producing CH_4 and sequestering CO_2 in hydrates

It has been estimated that the energy dormant in natural gas hydrates worldwide is at least twice that of all conventional fossil fuels combined.[9,22-24] However, reviewing approximately 40 years of research, Boswell and Collett,[25] pointed out that technical and economical limitations inhibit the transformation of hydrate deposits into reserves. To probe whether the large deposits can become resources, approximately 25 major field explorations have been initiated since 1995 worldwide,[26] including those in Japan,[27] Gulf of Mexico,[28] Alaska,[29] the Barents Sea,[30] and Hong Kong.[31] However, Boswell and Collett[25] pointed out that current technology is not ready for safe industrial-scale economic production of natural gas from hydrates. The 'mature' technologies include depressurization, thermal stimulation, and inhibitor injection, while CO_2/CH_4 gas exchange and microwave are being developed.[32-36]
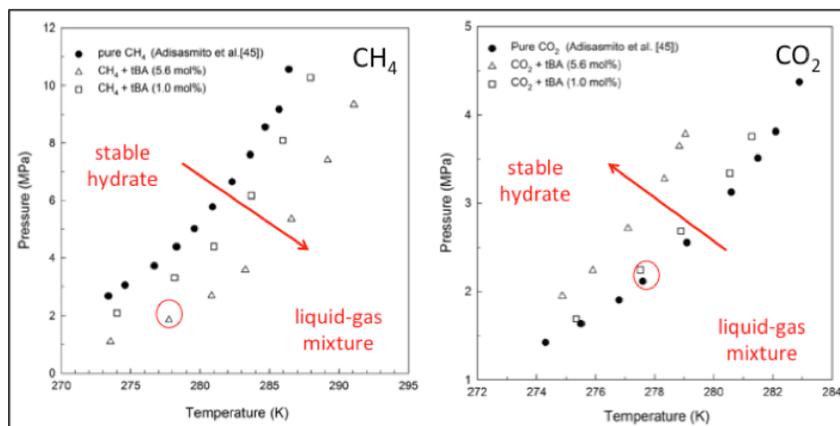
Figure 1. Phase boundaries for methane (left) and CO_2 (right) hydrates. The red circle indicates similar P&T conditions in the two diagrams: CO_2 hydrates are stable, while CH_4 ones are not at these conditions. The red arrows indicate the effect of adding tert-butyl alcohol (TBA) to the systems: the CH_4 hydrates increase their stability while the CO_2 ones become less stable. Figure adapted with permission from Kim *et al*.[41] Copyright (2016) Elsevier.

While developing hydrate deposits is not yet attractive, the economic landscape depends on local market forces. Environmental motivations are also important and often justify field studies. Because CO_2 hydrates are more stable than CH_4 hydrates, one could extract CH_4 from naturally occurring hydrates, and simultaneously store industrially emitted CO_2.[29] CO_2 and CH_4, as well as their mixtures, form sI hydrates.[37,38] Lee et al.[39] used ^{13}C NMR to assess the equilibrium composition of mixed CO_2-CH_4 hydrates and the kinetics of conversion. They found that (a) for gas compositions between 10 and 70% CO_2, hydrates show significant enrichment in CO_2, and (b) the kinetics of CO_2/CH_4 replacement when a CH_4 hydrate is exposed to CO_2 is ~ 6 times faster than the kinetics of both CO_2 and CH_4 hydrate formation from ice. Several approaches could be attempted to enable the CO_2-CH_4 swap in hydrates. For example, laboratory investigations on a 60 L reactor quantified advantages and disadvantages of heating the system while CO_2/CH_4 swap occurs.[40] The results show that the efficiency of the process strongly depends on factors such as hydrate saturation and heating rate. An analysis of the carbon balance at moderate heating rates suggested "*a substantially negative carbon footprint*". The Alaska field study[29] seeks to assess the feasibility of exchanging CO_2 for CH_4 in naturally occurring hydrate reservoirs. The results are promising, although it has been reported that "*the nature, extent, and efficiency of the exchange reaction [is] uncertain*". Laboratory studies have been able to explain why CO_2 can replace CH_4 (**Figure 1**),[35,41] identify some of the rate-limiting steps for hydrates growth,[42] and quantify the conversion rate dependence on hydrate surface area, nucleation and diffusion barriers.[43] Many studies, including field campaigns, continue to be conducted to determine the optimal operation conditions (T, P, addition of liquid vs. gaseous CO_2) to enhance CH_4 removal from hydrates.[44-50] Because it is a very aggressive hydrate former, H_2S is proposed as an additive for this application,[48,51] and it could help improving the kinetics of the CO_2/CH_4 swap process.
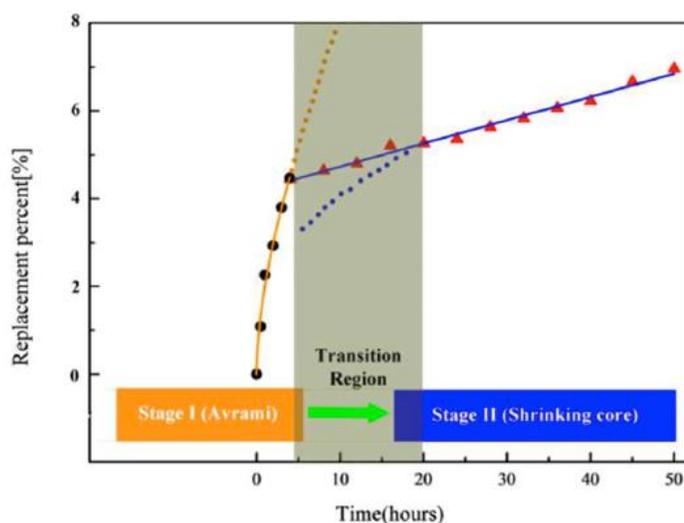

Figure 2. Experimental amount of CH_4 gas replaced by CO_2 during CO_2/CH_4 swap. The transition from fast replacement to slow, diffusion-limited process is identified by the dark band. Figure reproduced with permission from Zhao et al.[52] Copyright 2015 American Chemical Society.

Although analysis of experimental studies often reveals unexpected phenomena, kinetics barriers have been shown to be very important in the exploitation of natural hydrate deposits. For example, Zhao et al.[52] showed that CH_4 production from hydrates is fast when the experiment starts; however, after 5 hours, the production rate decreases (**Figure 2**). The initial production of CH_4, and its slow decay at short times, can be described by models,[53-55] which are able to account for the reduction in driving force (i.e., CO_2 pressure) as CH_4 hydrates are destabilised and CO_2 hydrates are formed. The following slow CH_4 production is thought to be due to strong barriers to diffusion that appear because of the formation of CO_2 hydrates on the surface of a particle. Among models developed to describe such observations, the shrinking-core one seems able to account for the observed slow CH_4 production because it can account for barriers to diffusion.[56] Salamatin et al.[42] developed a phenomenological model to describe the shrinking-core stage achieving predictions that are semi-quantitative with respect to experiments. Because hydrate formation is exothermic, the formation of CO_2 hydrate releases heat that could melt CH_4 hydrates. Baig et al.[57] developed a model based on non-equilibrium thermodynamics, which highlighted the effect of heat-transport on the kinetics of CO_2/CH_4

swap, and suggested that it might be beneficial to have a layer of free water around the hydrate particle. This appears somewhat surprising, as the water layer implies some distance between the growing CO_2-CH_4 hydrate and the dissolving CH_4 hydrate, which could delay heat transfer. The CO_2/CH_4 swap could lead to structural reorganisations, which could be monitored using Raman spectroscopy.[58] For example, Lee et al.[59] studied the structural transition from hydrate sH to sI as CO_2 replaces CH_4. The results suggested that in CO_2-rich conditions, CO_2 functions as a co-guest in sH hydrates. Approximately 88% of CH_4 was recovered during those experiments. The dissociation of sH hydrates, followed by the formation of sI hydrates was confirmed by calorimetry.

To directly observe the kinetics of hydrate formation, Daniel-David et al.[60] reported a simple, yet insightful set of data, summarised in **Figure 3**. They studied hydrate growth, seeded by a hydrate fragment, on a sessile water droplet
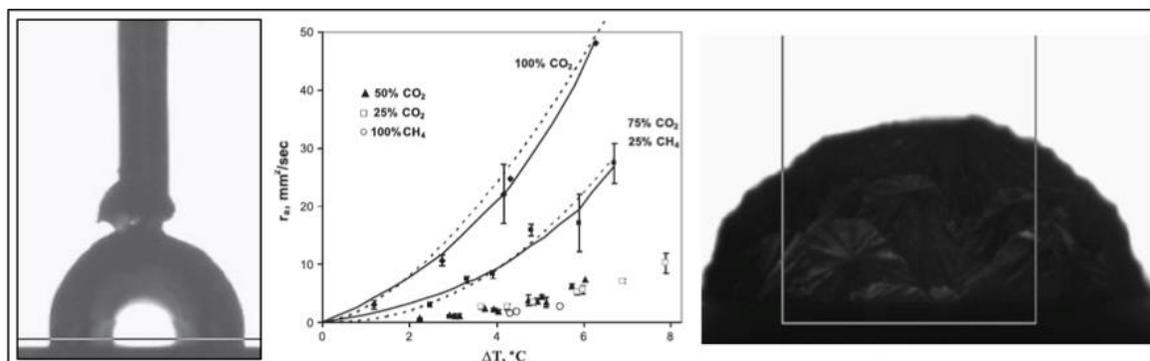

Figure 3. Hydrate growth on a sessile water droplet. The experimental set up is shown on the left panel, where a hydrate fragment is on top of the droplet as seed. In the middle panel, the growth rate is shown as a function of the difference between experimental and equilibrium temperature of formation. Fastest growth rates were observed for 100% CO_2. On the right panel, the morphology of one droplet is shown once all the water has been transformed in hydrate. Figure reproduced with permission from Daniel-David et al.[60] Copyright (2015) Elsevier.

exposed to CH_4 and/or CO_2. The authors observed rapid hydrate growth on the surface of the droplet. When the droplet surface was covered by hydrate, the growth decreased significantly. Hydrate growth was much faster when at least 75% of the gas was CO_2. When the gas was CO_2-rich, adding surfactants had a negligible effect on the growth rate; conversely, hydrate growth in a CH_4-rich gas system was enhanced by ionic surfactants (e.g., SDS and AOT), while non-ionic surfactants (e.g., Tweens and Pluronics) had no effect on the growth rate.

Ionic surfactants also affect the morphology of the resultant hydrate particle, suggesting that a capillary-driven pattern occurs during hydrate growth when the gas is CH_4 and SDS or AOT are present, while a rapid growth of a non-permeable hydrate 'skin' grows in the other cases. The results summarised are consistent with previous observations, [61 - 63] including those reported by Dicharry et al.,[64] who studied hydrate formation triggered by tetrahydrofuran (THF), where the effect of the alkyl chain length of sodium alkyl sulfates (from 8 to 18 carbon atoms) was studied explicitly. It has been argued that surfactants are not effective in CO_2-rich systems because of a competitive adsorption between CO_2 and the surfactants at the water-gas interface.[63] Alberti et al.[65] suggested a different explanation. Using MD simulations, they found that CO_2 dissolved in water orients neighbouring water molecules in a hydrate-like structure. When SDS is present, CO_2 preferentially interacts with SDS, thus reducing its effect on re-structuring water molecules. The simulations were however too short to observe nucleation.

2.2. Preventing hydrate plugs formation in pipelines

Since 1934, gas hydrates have been regarded as a hindrance in oil and gas pipelines, as they can result in blockages that fully occlude flow.[66] These plugs can (1) decrease the mechanical integrity of the pipeline during remediation, increasing the risk of pipeline rupture with the connected environmental consequences; (2) negatively affect the safety of operators; or (3) interrupt production, with economic losses due to reduced productivity and compromised well integrity. The conceptual model for hydrate blockage formation in gas-water pipelines is presented in **Figure 4**.[67] Most attention concerns CH_4 hydrates because in oil and gas pipelines, water and methane are at contact, sometimes at high pressure and low temperature conditions. CO_2 hydrates in pipelines have received attention as a pure species due to their sequestration potential,[68] but it could also be important to quantify how polar species (CO_2 and H_2S) affect mixed hydrate phase boundary and growth kinetics. In fact, both quantifying accurately the thermodynamic conditions at which hydrates could form, and the kinetics of their growth are important for ensuring pipelines integrity, which is the goal of the industrial sector known as 'flow assurance'.
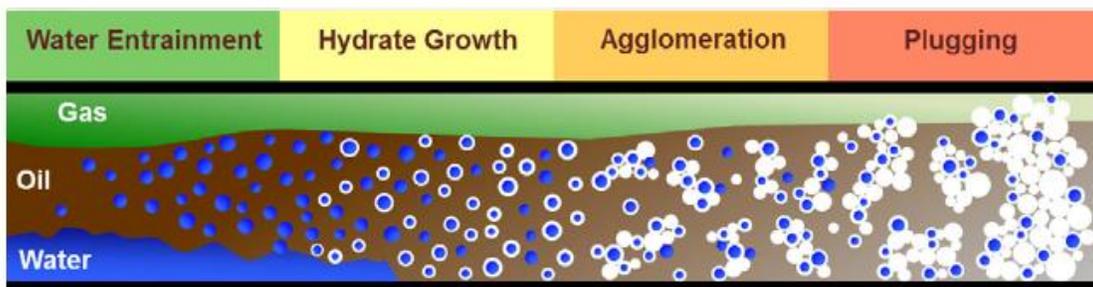
Figure 4. Conceptual model of hydrate plug formation in a pipeline. Figure reproduced with permission from Joshi et al.[67] Copyright (2013) Elsevier.

Conventional flow assurance approaches includes the addition of thermodynamic hydrate inhibitors (THIs), such as methanol, to fully suppress the hydrate equilibrium condition.[69] Unfortunately, for this approach to be effective, some fields may require methanol dosages in excess of 50 wt% with respect to the aqueous phase, which causes severe limitations both in terms of economics and environmental footprint. Alternatives are needed to reduce costs and carbon emissions, including the development of low dosage hydrate inhibitors (LDHIs), which are injected at concentrations as low at 0.5 wt% with respect to the aqueous phase.[2,70]

Current LDHI classes include both kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs).[70] KHIs are thought to inhibit hydrate nucleation and growth, perhaps by perturbing the water structure or interfering with the formation of a critical hydrate nucleus. Nature inspired the development of KHIs, as some aquatic species (e.g., the winter flounder) survive in sub-zero waters via specialised proteins.[71] KHIs are usually polymers, such as poly(N-vynil pyrrolidone), PVP; polyvinyl-caprolactam, PVCap; polydiethylacrylamide; or co-polymers of DEAMA or PVCap that exhibit improved biodegradability. The presence of caprolactam or pyrrolidone rings has been shown to significantly enhance KHI performance. Pendant alkyl groups should interact with cavities on the hydrate surface, and carbonyl groups form hydrogen bonds with water. Kelland[72] showed that PVP, PVCap, PolyNIPMAM, and Polyesteramide are equally effective in preventing cyclopentane hydrates at 100 ppm; note that cyclopentane hydrates form at atmospheric pressures and temperatures below 7.7°C, and they can be easily formed in the laboratory at conditions where ice is not stable while maintaining the same hydrate structure (sII) that is found in most industrial pipelines.

The other common class of LDHIs are AAs, which are typically ionic surfactants.[70] The best performing AAs are based on quaternary ammonium salts. The leading hypothesis for their active mechanisms involves the generation of stable water-in-oil emulsions, whereby the AA can adsorb to the hydrate-oil surface following crystallisation of the water droplets into hydrates. Aman et al.[73] developed the micromechanical force (MMF) apparatus to quantify the adhesion between hydrate particles, demonstrating that both ionic and non-ionic surfactants can adsorb to the hydrate-oil interface reducing adhesion forces and, by extension, particle aggregation potential. At present, the

standard characterisation test for AAs involves trial-and-error methods, such as rocking cells,[74-76] although it is often preferred to assess the AAs performance on flow loops, which are expensive to operate and maintain.

Several phenomena are important and should be considered to completely understand how hydrate plugs form in pipelines. Such phenomena include, but are probably not limited to, the adhesion between two hydrate particles and that between hydrates and the pipe, the diffusion of gases across the interface between water and hydrocarbons, the adhesion between water droplets covered by anti-agglomerants, the effect of impurities on both the nucleation and growth of hydrate particles, etc. Aman and Koh recently studied the formation of hydrates from either pure methane gas, or a ternary gas mixture containing CH_4, CO_2 and C_3H_8.[77] They found that CO_2 hydrates adhere to the vessel surfaces much more strongly than CH_4 ones. Sojoudi et al.[78] considered the adhesion of cyclopentane hydrates on polymeric coatings. A clear understanding of the adhesion mechanisms in hydrates is needed for securing progress in this field. Along these lines, Aman et al.[73, 79] employed the MMF to measure adhesion, both between two cyclopentane hydrate particles, and between one hydrate and a surface. Among the adhesion mechanisms proposed is the formation of a capillary bridge followed by sintering.

2.3. High-tech applications: Natural gas storage and water desalination

From a different technological perspective, the controlled formation of gas hydrates promises to boost high-tech applications such as natural gas storage[80-82] ("*solidified natural gas offers the safest, cleanest and the most compact mode of storage*")[83,84] and seawater desalination,[85,86] among others.[87-89] The success of these applications depends strongly on our ability to control hydrates nucleation and growth.

The experimental investigation of hydrates nucleation is extremely difficult because of the need to probe nucleation events, which are stochastic by nature.[90,91] Neutron diffraction data suggest that the structure of water around methane does not change substantially during hydrate formation, but it is dramatically different once the hydrate has formed.[91] NMR data suggested that 20 water molecules are present in the methane hydration shell during hydrate formation.[92] Because additives often promote the formation of hydrates,[83,84,86] it becomes of fundamental and practical interest to quantify how they affect hydrates. Among interesting results available in the literature, Luo et al.[93] showed that although dimethyl sulfoxide (DMSO) increases the solubility of CO_2 in water,[94,95] it reduces the range of stability of CO_2 hydrates. On the other hand, tetra-n-butyl ammonium bromide (TBAB, an environmentally friendly additive often used to apply hydrates in gas storage applications because its hydrates form at atmospheric pressures[96,97]) increases the stability of the CO_2 hydrate. Kim et al.[41] employed ^{13}C NMR, Raman spectroscopy, and X ray diffraction to investigate the effect of tert-butyl alcohol, TBA, in CO_2, CH_4 and N_2 hydrates. For CH_4 and N_2 hydrates, TBA increases the range of thermodynamic stability (lower P and constant T, or higher T at constant P), while it destabilised CO_2 hydrates (see **Figure 1**). This is in part surprising, because in both CH_4 and CO_2 hydrates, TBA causes a transition from sI hydrate (the stable form for the pure hydrates) to sII, and it preferentially occupies the large cage in the sII hydrate. These observations are consistent with others suggesting that large guests stabilise hydrates,[98-101] unless hydrogen bonds or other preferential interactions between guest and water molecules perturb the cages.[10] Tetramethylammonium hydroxide, e.g., reduces the stability region of both CH_4 and CO_2 hydrates due to its strong electronegative interactions with water.[102]

THF is a widely studied promoter of hydrate nucleation.[103-105] Because THF hydrates are stable at near-ambient conditions,[106] mixed THF-CH_4 hydrates could be useful for long-term energy storage. Linga and his group showed that THF has both a thermodynamic and a kinetic effect on CH_4 hydrates.[84,107,108] It would be helpful to develop a quantifiable molecular mechanism that explains these observations.

When hydrates are used for desalination, it becomes important to understand and control the effect of salt on the properties of hydrates. Linga and his group studied formation and dissociation of CO_2 hydrates in the presence of NaCl, up to seawater concentration:[109] NaCl has a thermodynamic inhibition effect during hydrate formation, as expected,[110] but not a kinetic one. Not much effect was observed on the dissociation. Yagasaki et al.[111] conducted molecular dynamics (MD) simulations for CH_4 hydrate dissociation in the presence of NaCl. They found two competing phenomena: NaCl slightly slows the early stage of hydrate dissociation, before the formation of a methane bubble, but it decreases CH_4 solubility in water, which causes the formation of methane bubbles. It could be that experimental

data see little effect of NaCl on hydrate dissociation because these two effects cancel each other out. It remains to be tested whether the effect of NaCl on CH_4 hydrate dissociation is different than that on CO_2 hydrates.

3. Some advancements in the understanding of clathrate hydrates enabled by molecular simulations

Among the pioneers in the use of molecular simulations for better understanding the fundamental properties of hydrates a note of tribute goes to the late Prof. Rodger. He and his group studied hydrate formation at water-methane interfaces,[112,113] the phase transition between structures sI and sII, hydrate melting, among other fundamental topics related to the subject.[114-116]

One of the fundamental properties of gas hydrates that remain highly debated concerns their nucleation. Because molecular dynamics simulations (MD) follow the trajectory of individual molecules, they have been used to address this topic.[112,117-123] Walsh et al.[124] were the first to report microsecond-long simulations successful in observing hydrates nucleation: the critical step for homogeneous nucleation was found to be the arrangement of methane molecules in a bowl-like structure interspersed by water. Both hydrate sI and sII formed, stabilised by uncommon $5^{12}6^3$ cages that prevented energetically unfavourable interfaces. This group quantified effects due to methane concentration, system size, and simulation ensembles.[125,126] Sarupria and Debenedetti also conducted microsecond-long MD simulations.[127] Their results show the formation of subcritical clusters of water and methane structures, dynamic in nature, that undergo continuous rearrangements, until they aggregate yielding the critical nucleus. These two results summarise the two mechanisms proposed for hydrate nucleation: (i) the 'labile cluster hypothesis',[128,129] consistent with the results reported by Sarupria and Debenedetti[127] and with the coarse-grained simulations of Molinero et al.,[130] according to which isolated hydrate cages form independently and agglomerate to yield the critical nucleus; and (ii) the 'local structure hypothesis',[118] consistent with the results reported by Walsh et al.,[124] according to which the guest molecules pre-arrange in a structure to yield a very small hydrate critical nucleus. Knott et al.[131] also simulated hydrate nucleation. This contribution is important because the Authors extracted from the simulations parameters to be applied to the classical nucleation theory. They obtained a nucleation rate of ~ 10^{-111} nuclei $cm^{-3}s^{-1}$ at 273 K and 900 atm. He et al. simulated the nucleation of CO_2/CH_4 mixed hydrates.[132] The results show that the difference in hydrophobicity between CH_4 and CO_2 affects the stability of gas nano-bubbles, that high CO_2 content accelerates hydrate formation, and that CH_4 and CO_2 preferentially adsorb in cages that are consistent with their sizes, and that multiple pathways lead to hydrate formation. These simulations are important because in many practical conditions gas mixtures are present, rather than pure gases.

Concerning the nucleation of hydrates, an important question that is being addressed by the community concerns the effect on the nucleation rate due to the proximity of mineral surfaces and the presence of impurities. Recently, Cox et al.[133] combined atomistic MD simulations with neutron scattering experiments to address this question and reported no effect on hydrate nucleation due to the presence of a wide variety of nanoparticles. These results seem to be consistent with coarse-grained simulations by DeFever and Sarupria,[134] who showed that even in proximity of an interface nucleation follows a bulk-like mechanism. However, DeFever and Sarupria also suggested that an interface could lead to enhanced concentrations of the hydrate-forming solute, which could affect nucleation rates, and therefore it is possible that confinement yields a measurable effect on hydrates nucleation. For example, Phan et al.[135] reported evidence of short-lived hydrates when water-methane systems were confined in narrow slit-shaped pores carved out of silica. It is likely that these effects are strongly dependent on the chemical nature of the solid surface, as well as on pressure-temperature-composition conditions. Borchardt et al.[136] recently reviewed experimental, theoretical and simulations studies conducted on the topic of hydrates formation in confined spaces.

Molecular simulations were used to study hydrate dissociation. English et al.[137] found that the diffusion of methane away from the dissolving hydrate is the rate-limiting step in this process. These simulations were consistent with those of Baez and Clancy,[119] who showed that even hydrate dissociation, not only hydrate nucleation, is stochastic, and those of others confirming the importance of the transport of guest gases away from the hydrate.[111,138] The occupancy of the hydrate affects the rate of dissociation,[137,139] as well as the size of the guest molecules and their interactions with the water molecules in the cage.[140] Adiabatic MD simulations showed that, because the hydrate dissociation is endothermic, it is possible that the local temperature decreases upon dissociation, regenerating hydrate cages from the melt.[139,141,142] Thermodynamic inhibitors such as NaCl and CH_3OH promote the formation of nano-bubbles, which deplete the surrounding water of gas molecules, enhancing hydrate dissociation. NaCl reduces CH_4 solubility in water,

while CH_3OH reduces the gas-liquid interfacial tension.[143] The presence of CO_2 in the large cages stabilises CO_2-CH_4 mixed hydrates, and hydrate dissociation does not follow a regular layer-by-layer process.[144]

Simulations attempted to address how a CH_4 hydrate transforms into a CO_2 one. It is crucial for the stability of the mixed hydrate that CH_4 occupies the small cages, and that CO_2 occupies the large ones.[145,146] Liu et al.[147,148] considered the stable structures of CO_2, N_2, CH_4 and mixed hydrates and computed structural and thermal fluctuations. Their results suggest that to recover most CH_4 from methane hydrates, CO_2 should occupy the larger cages and N_2 the smaller ones. While useful, these results stop short at revealing the mechanism of CO_2/CH_4 swapping. Muromachi et al.[149] studied the occupancy of CO_2 and CH_4 within the cages of mixed hydrates to interpret experimental XRD data: TBAB generated an elongated distorted cage within the hydrate structure. While CO_2 preferentially adsorbed within this elongated cage, CH_4 did not.

Simulations quantified the diffusion of guest gas molecules, since experimental measurements are problematic.[150] Burnham et al.[151] considered diffusion of H_2 in sII hydrates. The lowest energy barrier was found to be the one between adjacent cages that share one hexagonal face. To quantify the free energy barriers they employed the umbrella sampling method,[152] and they calculated iso-surface energy profiles as a function of H_2 loading.[153] The results were presented for 50, 100 and 200 K. As T increases the energy barrier also increases, which is at odds with expectations and with the results by Trinh et al.,[154] perhaps because of entropic effects.[151] Peters et al.[155] studied CH_4 diffusion, and Demurov et al.[156] reported the rates of hopping events for CO_2 molecules. The approach by Peters et al.[155] is particularly instructive. They employed the equilibrium path sampling method[157] to compute the free energy landscape as CH_4 diffuses across neighbouring cages in a structure I hydrate. They then employed a kinetic Monte Carlo formalism[158] to estimate the self-diffusion coefficient of CH_4 within the hydrate. The estimated self-diffusion coefficient was found to be ~ 10^{-15} m^2/s, depending on the degree of occupancy. This data-point is a few orders of magnitude faster than CH_4 diffusion in ice, and a few orders of magnitude slower than that through polycrystalline ice and hydrate layers.[159-161] Thus methane diffusion in hydrates preferentially occurs along grain boundaries, which can be quantified using the technique proposed by Klapp et al.[162] Lo et al.[163] conducted equilibrium MD simulations in a periodic system within which they had introduced water vacancies. The estimated CO_2 diffusivities are 3.6 10^{-16} m^2/s at 273 K and 1.1 10^{-15} m^2/s at 288 K, while the water vacancy defect was found to diffuse with ~ 10^{-12} m^2/s. Futera et al.[164] combined experimental Raman spectroscopy and MD to determine the vibrational modes of hydrogen molecules confined in structure II hydrates.[165,166] The simulations agreed qualitatively with the experimental Raman spectra. The ability of reproducing vibrational spectra is key for predicting thermal conductivities in systems that show many interfaces.[167]

Simulations helped better understand the thermal conductivity of hydrates.[168-170] English et al.[171,172] employed classic MD to predict the thermal conductivity of methane hydrates (sI, sII and sH). Following others,[173-175] the thermal conductivity was extracted by the Green-Kubo linear response theory[176] via the heat flux auto-correlation function. The results are in good agreement with experiments not only with respect to the thermal conductivity, but also with respect to its changes with T. The thermal conductivity of the CH_4 sI hydrate at 30 K (~1.05 $Wm^{-1}K^{-1}$) is lower than that of ice at the same T (1.79 $Wm^{-1}K^{-1}$) but also that of the hydrate with no CH_4 (1.41 $Wm^{-1}K^{-1}$).[172]

Simulations shed light on the mechanism by which LDHIs function. Available studies report the strength of adsorption of a short polymer and a hydrate:[177] those compounds that adsorb more strongly and perturb the interfacial water more effectively are possible KHIs candidates.[177] Trout and his group recently reported similar simulations for single AAs.[178] Jimenez-Angeles and Firozaabadi, after studying hydrate nucleation and the hydrate-methane interface,[179-181] focused on the adsorption of individual AA molecules on a hydrate surface.[182] On a related footpath, some recent simulations attempted to quantify the collective features of AAs at hydrate-hydrocarbon interfaces. The importance of these contributions is predicated on the models of hydrate growth:[9] hydrates form in droplets dispersed within oil. Hydrates form on the droplet surface, and grow towards its centre. For the hydrate particle to complete, it is necessary that CH_4 diffuse from the oil to the droplet core. Bui et al.[183] simulated various AAs at the hydrate-hydrocarbon interface changing systematically the AAs concentration, their molecular features, and also the composition of the hydrocarbon phase. The MD results suggest that those AAs effective at preventing hydrate plugs yield ordered films, reminiscent of the 'interfacial freezing' phenomenon reported for surfactants at oil-water interfaces.[184] Some hydrocarbon chains were found to penetrate the AAs film, in qualitative agreement with experimental data by Tokiwa et al.[185] These results also provide a new hypothesis for the mechanism by which AAs function: when the AAs form an ordered film, they could prevent methane transport across the interface.[186]

4. Some Open Fundamental Multidisciplinary Questions

The overview provided above considers explicitly four multi-disciplinary advanced applications: (a) CH_4 production from hydrate deposits and simultaneously sequester CO_2, via swapping CO_2 for CH_4; (b) reduce the likelihood of hydrates formation in pipelines; and (c) control hydrate formation to advance gas storage and water desalination. While diverse, these applications share several fundamental principles, and their further development depends on the community ability to answer a few fundamental questions, such as: (1) Why are H_2S and tetrahydrofuran (THF) effective promoters of hydrates nucleation? (2) How do TBA, dimethylsulfoxide (DMSO) and tetra-n-butylammonium bromide (TBAB) affect hydrates stability, and why do they have different effects on different hydrates? (3) Can inclusions or co-adsorbents modulate the diffusion of guest molecules in hydrates? (4) Why is the growth of CO_2-rich hydrates faster than that of CH_4-rich hydrates? (5) Why do ionic surfactants such as sodium dodecyl sulphate (SDS) speed up the growth of CH_4 hydrates, but are ineffective for CO_2-rich hydrates? (6) What are the mechanisms by which LDHIs function? (7) Are the mitigation strategies effective for preventing CH_4 hydrate plugs effective for other hydrates? (8) Why do CO_2 hydrates adhere more strongly to surfaces than CH_4 ones?

To answer these, and other questions, and to quantify their effects at the large scale, it is necessary to implement comprehensive multi-scale quantitative models that link different molecular phenomena, sometimes synergistically and other times antagonistically, to macroscopic observables. To develop such understanding, advanced experiments, high-end simulations and theoretical approaches are required, and care should be placed in combining synergistically their results. Progress requires reconciling observations obtained from a variety of experiments (e.g., spectroscopy and micromechanical forces), perhaps using state-of-the-art molecular simulations. For example, the literature shows that chemical promoters and inhibitors can both facilitate and impede the formation of hydrates. The critical missing link is a comprehensive understanding of how these compounds work: do they affect the nucleation of hydrates, their growth, their agglomeration, are they synergistic or antagonistic? Practical progress will then require translating such understanding into macroscopic observables via the implementation of meso-scale approaches. At a minimum, three steps should be attempted:
1. Discover new molecular mechanisms;
2. Quantify how molecular mechanisms affect macroscopic observables;
3. Verify all theoretical predictions via experimental observations.

Within this over-arching framework, possible activities along these outlines include:

Discover new molecular mechanisms. Perhaps, massive molecular dynamics simulations and advanced experiments could be combined to address, for example: (a) growth of CO_2 & CH_4 hydrates, and effects of surfactants on the growth rate; (b) hydrates nucleation promoters, with emphasis on THF, H_2S and caprolactone rings (the latter, a critical component of LDHIs, is expected to delay nucleation, while THF and H_2S are very effective promoters); (c) guest diffusion in hydrates, with emphasis on the effect of chemical additives; (d) the effect of chemical additives on CO_2/CH_4 swap, with emphasis on TBAB, DMSO and TBA. These, and other studies will yield a detailed understanding of the underlying molecular mechanisms, which is essential to promote progress, but also to quantify time constants and parameters that could be used in meso-scale models (e.g., hydrates nucleation rate, growth kinetics, etc.)

Quantitative multi-scale considerations. Meso-scale models are needed to quantify the practical meaning of molecular discoveries such as those just listed. This proposition is complicated because multiple phenomena occur simultaneously and affect each other. For example, in the case of swapping CO_2 for CH_4 in hydrates, it will be critical to consider the kinetics of CH_4 hydrates dissociation, with the respective heat released, the CO_2 hydrate formation and the correspondent heat adsorbed, heat dissipations, and, perhaps more importantly, the transport of CH_4 out of, and that of CO_2 into the hydrate particle. Perhaps, stochastic approaches such as kinetic Monte Carlo (KMC) could be successful to identify the true rate-limiting steps, therefore allowing the community to design strategies to optimise various practical applications. KMC has been successfully applied to catalysis, where a number of chemical reactions can occur simultaneously to transform reactants and intermediates into a variety of products, to describe transport in porous networks, as well as in many other applications. [187-190]

Experimental validation. It is necessary to validate the quantitative understanding achieved via fundamental research. Relevant laboratory experiments include those conducted with an autoclave to study the kinetics of hydrates growth under various conditions, and with a rocking cell to quantify the effect of, e.g., AAs on the formation of hydrate plugs. Other experiments of relevance include micromechanical force measurements, kinetics of CH_4 production from hydrates, as well as calorimetric and spectroscopic measurements. It remains to be demonstrated that laboratory-scale experiments are representative of large-scale applications in the area of hydrates. For example, in flow assurance it is necessary to test models on flow loops, of which only few are available in academic laboratories, and to quantify the feasibility and sustainability of CO_2-CH_4 swaps in hydrate deposits field campaigns are essential.

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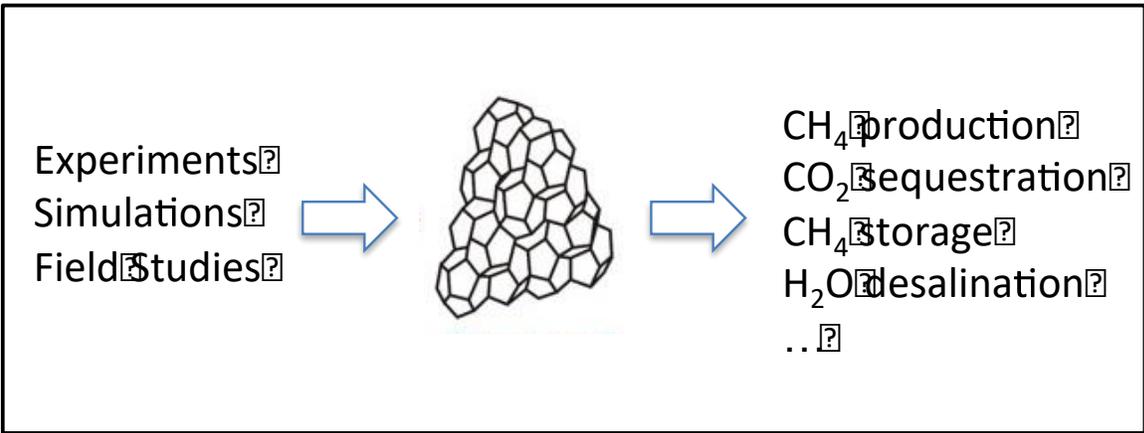
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Experiments
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Graphical Abstract.