Density and phase equilibrium for ice and structure I hydrates using the Gibbs–Helmholtz constrained equation of state

Heath Henley, Edward Thomas, Angelo Lucia

Department of Chemical Engineering, University of Rhode Island, Kingston, RI 02881, United States

Abstract

A new, rigorous framework centered around the multi-scale GHC equation of state is presented for predicting bulk density and phase equilibrium for light gas–water mixtures at conditions where hexagonal ice and structure I hydrate phases can exist. The novel aspects of this new framework include (1) the use of internal energies of departure for ice and empty hydrate respectively to determine densities, (2) contributions to the standard state fugacity of water in ice and empty hydrate from lattice structure, (3) computation of these structural contributions to standard state fugacity from compressibility factors and EOS parameters alone, and (4) the direct calculation of gas occupancy from phase equilibrium. Numerical results for densities and equilibrium for systems involving ice and/or gas hydrates predicted by this GHC-based framework are compared to predictions of other equations of state, density correlations, and experimental data where available. Results show that this new GHC-based EOS framework accurately predicts the densities of hexagonal water ice and structure I gas hydrates as well as phase equilibrium for methane–water and CO2–water mixtures.

Keywords: Hexagonal ice; Methane gas clathrate hydrates; Multi-scale Gibbs–Helmholtz Constrained equation; Lattice structure contributions to standard state fugacity of water; Gas hydrate occupancy; Structure 1 clathrate hydrates

1. Introduction

The general warming of land and oceans around the world has spawned interest in understanding long term environmental impacts associated with the melting of ice sheets and thawing of permafrost regions. Permafrost, which accounts for approximately 25% of the land mass in the Northern Hemisphere, is the general term used to describe land that remains below 0 °C for two or more years at depths that can range from less than a meter to around 1000 m. While temperatures and pressures in permafrost regions vary, typical ranges are −20 °C to 5 °C and 0.1 to ~10 MPa, respectively.

Phase behavior in permafrost regions is quite complicated and can involve light gases (e.g., methane and carbon dioxide), liquid water, brines, hexagonal ice, and gas hydrates – depending on conditions. Understanding physical property and phase behavior in permafrost regions is important for several competing reasons:

(1) The large amount of methane sequestered in permafrost is a potential source of low carbon fuel if it can be captured. According to Kvenvolden (1998) there is an estimated $2.1 \times 10^{18}$ standard cubic meters (SCM) of methane contained in hydrates on the ocean bottom, which is twice the energy sum of all other fossil fuels on Earth. There is also an estimated $7.4 \times 10^{14}$ SCM in permafrost regions (see, MacDonald, 1990).

(2) Thawing of permafrost increases microbial activity, which in turn has the potential to release large amounts of greenhouse gases (CO2 and methane).

(3) Deeper locations in permafrost have been suggested as potential sites for carbon storage.
nitrogen, hydrogen, ethane, etc.). The empty hydrate lattice is not stable on its own. There are three naturally occurring hydrate structures found on Earth – type I (SI), type II (S2) and type H (SH), where the structure is determined by conditions of temperature and pressure and the guest molecule(s).

Structure 1 hydrates are composed of two 5\(^1\) cages, six 5\(^2\) cages and from 6 water molecules. Structure 2 hydrates are composed of sixteen 5\(^2\) cages, eight 5\(^2\) cages, and 136 water molecules. Finally, structure H hydrates consist of three 5\(^2\) cages, two 4\(^5\)6\(^2\) cages, and one 5\(^2\)6\(^2\) cage and have 34 water molecules. Here the general notation \( \text{e}^n \) describes a polygon such that has \( e \) edges and \( n \) faces.

The focus of this work is the modeling of physical properties, specifically density, and phase behavior of mixtures of light gas and water at conditions typically found in permafrost regions (i.e., temperatures ranging from 250 to 280 K and pressures from 0.1 to \( \sim 10 \text{MPa} \)) using an equation of state. We show that the multi-scale Gibbs–Helmholtz Constrained (GHC) equation (Lucia, 2010; Lucia et al., 2012; Lucia and Bonk, 2012), can be used to predict thermo-physical properties and phase equilibrium in systems involving gas, liquid, hexagonal (1h) ice and gas hydrate. Accordingly, the remainder of this paper is organized in the following way. Section 2 gives a brief survey of relevant literature while Section 3 provides some general background information for the multi-scale Gibbs–Helmholtz Constrained (GHC) equation of state. In Section 4, lattice structure considerations in defining the standard state fugacity of water in an ice phase, NTP Monte Carlo simulations of liquid water, and the Clapeyron equation are used to extend the multi-scale GHC equation to calculate densities and phase equilibrium for hexagonal (1h) ice. A similar extension of the GHC equation that exploits structure in defining the standard state of water in a gas hydrate phase is described in Section 5. In Section 6, several numerical examples that illustrate the accuracy of multi-scale GHC equation predictions of physical properties and phase behavior of 1h ice and gas hydrates. Finally, conclusions of this work are described in Section 7 as well as future work in extending our approach to modeling ice and gas hydrates in the presence of brines.

2. A brief review of relevant literature

Many traditional equations of state (EOS) have been used to model various thermo-physical properties and phase equilibrium involving mixtures of light gases and water including the Soave–Redlich–Kwong (SRK) equation (Soave, 1972), the Peng–Robinson volume translation (Peneloux et al., 1982) of the SRK equation (SRK+), the Peng–Robinson (PR) equation (Peng and Robinson, 1976), the volume translated PR or VTPR equation (Ahlers and Gmehling, 2001), and various forms of the Statistical Associating Fluid Theory (SAFT) equation (see Chapman et al., 1986, 1988, 1989; Kontogeorgis and Folas, 2010). Other equations of state such as the cubic plus association (CPA) equation (Kontogeorgis et al., 1996; Voutsas et al., 2000) and the Elliott–Suresh–Donahue (ESD) equation (Elliott et al., 1990) have also been used. There are also specialized equations of state for water such as the International Association for the Properties of Water and Steam (or IAPWS-95) equation of Wagner and Pruß (2002), which is formulated in terms of the Helmholtz free energy function. Within the family of cubic equations, only the volume translated equations, SRK+ and VTPR, are capable of predicting reasonably accurate

\[
\text{Nomenclature}
\]

\[
\begin{align*}
a, a_m & \quad \text{pure component energy parameter, energy parameter for liquid mixture} \\
A & \quad \text{dimensionless energy parameter} \\
b, b_i, b_M & \quad \text{molecular co-volume, pure component molecular co-volume, mixture molecular co-volume} \\
B & \quad \text{dimensionless molecular co-volume} \\
f, f_i & \quad \text{fugacity, partial fugacity for component } i \\
G & \quad \text{Gibbs free energy} \\
H & \quad \text{enthalpy} \\
k_B & \quad \text{Boltzmann constant} \\
p, p_c & \quad \text{pressure, critical pressure} \\
q & \quad \text{electrostatic charge parameter} \\
R & \quad \text{universal gas constant} \\
S & \quad \text{structure parameter} \\
T, T_c & \quad \text{absolute temperature, critical temperature} \\
U, U_i, U_M & \quad \text{internal energy of departure for liquid, internal energy of departure for component } i, \text{ mixture internal energy of departure} \\
V & \quad \text{molar volume} \\
\chi_i & \quad \text{ith component liquid mole fraction} \\
z & \quad \text{compressibility factor} \\
\end{align*}
\]

\[
\text{Greek symbols}
\]

\[
\begin{align*}
\Delta & \quad \text{structure parameter, change in variable} \\
\varepsilon & \quad \text{well potential energy} \\
\varphi, \varphi_i & \quad \text{fugacity coefficient, ith component partial fugacity coefficient} \\
\rho & \quad \text{molar density} \\
\omega & \quad \text{acentric factor} \\
\end{align*}
\]

\[
\text{Superscripts}
\]

\[
\begin{align*}
cal & \quad \text{calculated} \\
D & \quad \text{departure function} \\
exp & \quad \text{exponential function, experimental} \\
fus & \quad \text{fusion} \\
hyd & \quad \text{hydrate} \\
\text{ice} & \quad \text{hexagonal ice} \\
ig & \quad \text{ideal gas} \\
L & \quad \text{liquid} \\
MT & \quad \text{empty hydrate} \\
0 & \quad \text{standard state} \\
\end{align*}
\]

\[
\text{Subscripts}
\]

\[
\begin{align*}
c & \quad \text{critical property} \\
i & \quad \text{component index} \\
M & \quad \text{mixture} \\
w & \quad \text{water} \\
\end{align*}
\]
densities (i.e., AAD% error ≈ 3–4%). See Table 2 in Frey et al. (2009) and Table 2 in Ahlers & Gmeingh (2001) respectively. The CPA, ESD, and SAFT models are much better at approximating properties and phase equilibrium of water and mixtures such as methane–water and CO₂–water, etc. because they explicitly incorporate association (i.e., hydrogen bonding) in the residual Helmholtz free energy. Finally, the IAPWS-95 equation is the most accurate (~AAD% error < 0.1%, see the abstract in Wagner and Prüß, 2002) for water because it involves a large number of parameters that have been regressed to a wide range of experimental data; however it cannot be used for mixtures.

Equations of state for ice are also available. Within the van der Waals family of cubic equations, there is the translated Trebble–Bishnoi–Salim (TBS) equation of state (Salim and Trebble, 1994), which is a six-constant EOS for solids that suffers from the same difficulties that many traditional cubic equations suffer from: (1) excessive use of empirical relationships to correct deficiencies in the basic theory, (2) poor density predictions without the use of volume translation, and (3) the need to regress parameters to experimental data. The four primary parameters (a, b, c and d) in the TBS equation must be matched to experimental solid density, saturation pressure, and solid and vapor fugacities at the triple point. The other two parameters, m and p, are part of the α-functional for predicting vapor pressure. In addition, temperature and pressure-dependent binary interaction parameters are needed for reliable phase equilibrium computation. The IAPWS-95 model for water has been extended to 1 h ice by Feistel and Wagner (2006) and uses a Gibbs potential equation of state. Like the model for liquid water (Wagner and Prüß, 2002), the extended IAPWS-95 equation for 1 h ice has been fit to a large amount of experimental data (i.e., 14 independent parameters fit to 522 data points from 32 separate categories of experimental data). This experimental data includes specific Gibbs free energy data, specific entropy data, (ip/it) data along the ice melting curve, heat capacity data, volumetric and volume-temperature derivative data, isentropic compressibility data, and isentropic compressibility-temperature derivative data. See Table 5 on page 1027 in Feistel and Wagner (2006). As a result, the extended IAPWS-95 equation provides excellent agreement with experimental values of thermophysical properties of hexagonal ice. Other approaches for modeling ice (e.g., Yoon et al., 2002) use a more traditional solid–liquid equilibrium formulation in which the fugacity of ice is expressed in terms of the fugacity of sub-cooled water and an exponential correction based on enthalpy and volumetric differences due to fusion.

The most commonly used models for predicting the properties of gas hydrates are based on the cell theory model developed by van der Waals and Platteeuw (1959) and given the acronym vdWP. A detailed derivation of the model from statistical mechanics as well as a very good survey of the relevant hydrate literature can be found in the textbook by Sloan and Koh (2007). Here a brief overview of the modifications of the vdWP model is given starting with the work of Parrish and Prausnitz (1972) who extended the model to allow for the practical calculation of hydrate dissociation pressures for mixtures of guest molecules. Klauda and Sandler (2000) presented a fugacity-based model that removed the need for reference energy parameters for the empty hydrate lattice and relaxed the incorrect vdWP assumption that the volume of the crystal lattice is independent of guest molecule type. A similar model was developed by Ballard and Sloan (2002) and Jager et al. (2003). More recently, Bandyopadhyay and Klauda (2011) presented an updated fugacity model that uses the PRSK equation to represent the fluid phases in equilibrium with the hydrate. Other modifications include models that account for multiple cage occupancy (see, Klauda and Sandler, 2003; Martin, 2010), those that correct for contributions to the Helmholtz free energy due to guest-guest interactions (Zhdanov et al., 2012), and others (e.g., Jäger et al., 2013) that adapt the model originally developed by Ballard and Sloan (2002) so that highly accurate reference EOS can be used. This last approach has also been tested against a large data set for CO₂ hydrate. The vdWP model with all of its recent adaptations has enjoyed great success and is used heavily in industry because of its accuracy and relative simplicity. However, it is a semi-empirical model that requires adjustable parameters to be regressed to experimental data. For this reason it is difficult to make predictions about the phase behavior and properties of potentially hydrate-forming systems outside the ranges of experimental data.

### 3. The multi-scale Gibbs–Helmholtz Constrained (GHC) equation

The multi-scale Gibbs–Helmholtz Constrained (GHC) equation (Lucia, 2010; Lucia et al., 2012; Lucia and Bonk, 2012), which is a modification of the Soave form of the Redlich–Kwong (RK) equation (see Soave, 1972), is given by

\[
p = \frac{R T}{V - b} - \frac{a(T,p)}{V + b}
\]  

(1)

where \(p\) is pressure, \(T\) is temperature in Kelvins, \(V\) is the molar volume, \(R\) is the universal gas constant and \(a\) and \(b\) are the energy and molecular co-volume parameters respectively.

#### 3.1. Pure components

The multi-scale GHC equation is a radically different approach to EOS modeling that is based on three simple ideas:

1. The molecular co-volume for the liquid, \(b^l\), is set equal to the molar volume of the pure solid or high density (glassy) liquid.
2. The liquid phase energy parameter, \(a^l(T, p)\), is constrained to satisfy the Gibbs–Helmholtz equation, which results in the following expression for pure liquid components

\[
a^l(T, p) = \left[ \frac{a(T, p)}{T_c} + \frac{b^{l\text{UPL}}}{T_c \ln^2} + \frac{2b^l R \ln T_c}{\ln^2} \right] T - \frac{b^{l\text{UPL}}}{\ln^2}
\]  

(2)

where \(T_c\) is the critical temperature, \(p_c\) is the critical pressure, \(a(T, p_c) = 0.42748R^2T_c^2/p_c\), and \(U^{l\text{PL}}\) is the internal energy of departure for the liquid phase given by \(U^{l\text{PL}} = U^{l\text{PL}}(T, p) = U^l(T, p) - U^l(T, 0)\), where \(U^l(T, 0)\) is the ideal gas internal energy. Note that \(U^{l\text{PL}}\) serves as a natural bridge between the molecular and bulk fluid length scales.

3. The internal energy of departure, \(U^{l\text{PL}}\), is evaluated using NTP Monte Carlo simulations, where it is important to note that MC simulations are performed a priori and that the results are stored in pure component look-up tables for use in density and fugacity coefficient calculations.
Molecular scale information in Eq. (2) is what makes the GHC equation a multi-scale equation of state.

3.2. Non-electrolyte mixtures

For non-electrolyte liquid mixtures, the multi-scale GHC equation is

$$\alpha^i_p(T, p, x) = \left[ \frac{a(T, p, x)}{b^i_p T_{CM} \ln 2} + \frac{b^i_{UL} T_{CM}}{b^i_p \ln 2} \right] T + \frac{b^i_{UL} M_{CM}}{b^i_p \ln 2} \left( 2 b^i_p M_{CM} \ln 2 \right) T \ln T$$

where $b^i_p = \sum x_i b^i_p$ and $U^i_p = \sum x_i U^i_p$, $x_i$ is the mole fraction of component $i$, and $b^i_p$ and $U^i_p$ are the molecular co-volume and internal energy of departure for the $i$th pure liquid component. Again, a detailed derivation can be found in the literature (Lucia, 2010; Lucia et al., 2012). Mixture critical properties are calculated using Kay’s rules

$$M_{CM} = \sum x_i M_i \quad \text{for} \quad i = 1 \ldots C$$

where $M$ is either critical temperature or critical pressure.

More detailed information associated with the GHC equation, its derivation, expressions for pure component and partial fugacity coefficients, and density and phase equilibrium predictions for a number of systems including pure liquid water, water-light gas mixtures, n-alkanes of varying chain length, and electrolyte solutions can be found in Refs. Lucia (2010) and Lucia et al. (2012).

More recently, Lucia and Henley (2013) have shown that the GHC equation is thermodynamically consistent by demonstrating that it satisfies the relationship given by $RT(\partial \ln f/\partial p)_{T} = V$.

4. Modeling hexagonal ice using the GHC equation

To model hexagonal ice in the GHC framework, values for $b^{\text{ice}}$ and $U^{\text{D,ice}}$ are needed along with a means of calculating the pure component fugacity of ice.

4.1. The molecular co-volume and internal energy of departure for ice

Two straightforward but important physical interpretations are required to apply the multi-scale GHC equation (i.e., Eqs. (1) and (2)) with appropriate values of $b$ and $U^{\text{D}}$ to 1 h ice:

(a) Using the expression

$$U^{\text{D,ice}} = U^{\text{D}} + U^{\text{D,fus}}$$

where $U^{\text{D}}$ is the internal energy of departure for liquid water (already available from NTP Monte Carlo simulation) and $U^{\text{D,fus}}$ is the internal energy of departure associated with the fusion of water.

(b) By direct NTP Monte Carlo simulations of 1 h ice using an appropriate potential model (e.g., TIP4P-Ew, TIP4P/Ice, etc.).

These two methods for determining $U^{\text{D,ice}}$ are described and compared in considerable detail in Appendix A.

4.2. A reference state for ice

The fugacity coefficient of 1 h ice must be different from that of liquid water at phase equilibrium. Appendix B shows that the natural log of the fugacity coefficient for hexagonal ice can be rigorously expressed in the form

$$\ln \phi^{\text{ice}} = \ln \phi^{\text{water}} - \Delta^{\text{ice}}$$

where $\phi^{\text{water}}$ and $\phi^{\text{ice}}$ are the fugacity coefficients of 1 h ice and liquid water respectively and $\Delta^{\text{ice}}$ is a measure of the impact of long-range structure on the fugacity coefficient of ice and is assumed to be constant. This leads to the following expression for the standard state fugacity of ice

$$f^{\text{ice}} = S^{\text{ice}} p$$

where $S^{\text{ice}} = \exp(\Delta^{\text{ice}})$. We also refer to $S^{\text{ice}}$ as a lattice structure contribution.

We adopt this approach because liquid water and 1 h ice both have tetrahedral kernels but ice has long-range hexagonal structure. Furthermore, since ice is a condensed phase, it is not unreasonable to assume that the impact of long-range structure to be constant (see Fig. A1). Taking the temperature derivative of Eq. (6) at constant pressure gives

$$\left( \frac{\partial \ln \phi^{\text{water}}}{\partial T} \right)_p = \left( \frac{\partial \ln \phi^{\text{ice}}}{\partial T} \right)_p$$

Thus Eq. (2) is directly applicable for determining the energy parameter for 1 h ice. See Appendix B for a discussion of the fundamental basis for Eqs. (6) and (8).

5. Modeling gas hydrates using the GHC equation

Although the approach for modeling gas hydrates using the GHC equation is similar to that of ice, it involves considerably more detail. This is because

(a) Gas hydrates are unusual heterogeneous structures so it is not at all clear that the usual mixing rules apply – since there is really no mixing taking place.

(b) Empty hydrate cages are not stable.

(c) Standard states only apply to pure components.

We start with the idea of estimating the bulk density of an empty hydrate. Why? The reason is that we need some physically sensible way of estimating the fugacity (or Gibbs free
energy) of pure or empty hydrate in order for our framework for addressing phase equilibrium to be consistent with classical theory. In order to predict empty hydrate density using the GHC equation values of the internal energy of departure for an empty hydrate, $U_{w}^{D,MT}$, and molecular co-volume, $b_{w}^{hyd}$, are required.

5.1. The molecular co-volume and internal energy of departure for hydrate

The value of the empty hydrate molecular co-volume is taken to be the same as that of a completely filled hydrate and given by

$$b_{w}^{hyd} = \frac{0.148148 \times 29.614 + 0.851852}{\rho_{w}^{x}}.$$  \hspace{1cm} (9)

where $b_{CH_{4}} = 29.614 \text{ cm}^{3}/\text{mol}$ and where the subscript $w$ denotes water and the superscript $hyd$ represents hydrate. Eq. (9) is derived using simple physics by considering the number of guest and water molecules in a completely filled structure 1 hydrate. Using Avogadro’s number and the number of guest and water molecules, one gets the coefficients (or mole fractions) shown in Eq. (9). Note also that Eq. (9) can be used for any guest molecule in a structure 1 hydrate, including CO$_{2}$.

While it appears that Eq. (9) is the same as the usual linear mixing rule for $b_{w}$, it is not. We interpret Eq. (9) as the high pressure limit of separable gas and solid phases in a hydrate. Additionally, within the GHC approach to hydrates, Eq. (9) is used for both empty and filled gas hydrates regardless of the gas occupancy in the cages. Thus there is no mole fraction weighted average of molecular co-volume for hydrate phases; it is held fixed at the value given in Eq. (9).

Because empty hydrates are not stable, considerable care must be taken to get estimates of internal energies of departure $U_{w}^{D,MT}$. To do this, we did the following:

1. Placed guest molecules in the hydrate cages.
2. Equilibrated the simulations with the guest molecules present.
3. Removed the guest molecules.
4. Ran production cycles with restricted volume moves so that the empty cages would not collapse.

We performed NTP Monte Carlo simulations for empty hydrate using the aforementioned procedure over relevant ranges of temperatures (250–280 K) and pressures (1–100 bar). Values of $U_{w}^{D,MT}$ ranged from $-4.65 \times 10^{5}$ to $-4.58 \times 10^{5}$ cm$^{3}$ bar/mol.

Note that the same general approach for estimating $b_{w}^{hyd}$ and $U_{w}^{D,MT}$ can be used for structure II and structure H gas hydrates by (1) modifying Eq. (9) using the correct molecular co-volume for the guest molecule, (2) using the appropriate mole fractions for a filled structure II or structure H gas hydrate, and (3) performing NTP Monte Carlo simulations for empty structure II and structure H gas hydrates.

5.2. Gas hydrate density

Next we developed theory for predicting density for physically meaningful gas hydrates, which have gas molecules occupying the cavities or cages. Because gas hydrates are heterogeneous structures, we calculate the density of an S1 gas hydrate using the expression

$$\rho_{w}^{hyd} = \frac{(5.75 + \theta)\rho_{MT}}{5.75}.$$  \hspace{1cm} (10)

where $\theta$ is the fractional occupancy of gas in the hydrate cages and ranges from 0 to 1, $\rho_{MT}$ is the empty hydrate density computed from the GHC equation (i.e., Eq. (2)), and the quantity 5.75 is simply the ratio of water molecules to guest molecules (46/8) in a structure 1 hydrate. Note that Eq. (10) is still an application of the multi-scale GHC equation to gas hydrates and, in our opinion, provides a straightforward, yet physically meaningful, way of computing hydrate density. Moreover, Eq. (10) covers the full range of gas occupancy, thus the more gas there is in the cages, the denser the hydrate. At the same time, it avoids many of the complications associated with composition dependence in determining hydrate properties like fugacity coefficients.

Eq. (10) can also be used to estimate the density of structure II and structure H hydrates by simply replacing the value 5.75 with 5.67, which is the ratio of water molecules to guest molecules per unit cell for both structure II and structure H hydrates.

5.3. A reference state for pure water in gas hydrate

To calculate a standard state for pure water in a hydrate phase we let $x_{w}^{hyd} = 1$ and use a procedure identical to that in Appendix B for ice. This leads to the expression

$$f_{w}^{D,hyd} = S^{co}S^{MT},$$  \hspace{1cm} (11)

where $S^{co} = \exp(\Delta^{co})$ and $S^{MT} = \exp(\Delta^{MT})$. The quantity $\Delta^{MT} = \ln \frac{\rho_{w}^{x}}{\rho_{w}^{MT}}$ represents the difference in long range structure between 1 h ice and empty hydrate and can be interpreted as a second structural contribution. Appendix C gives all of the details of the derivation of Eq. (11).

6. Numerical results

In this section, numerical results are presented for density and phase equilibrium for light gas–water mixtures in regions where ice and gas hydrate can form. All numerical results presented in this section use the GHC equation of state (except for comparisons) and were performed in double precision arithmetic on a Dell Inspiron laptop using the Lahey-Fujitsu LF95 FORTRAN compiler. Critical property and other relevant data are summarized in Appendix D.

6.1. Methane–water mixtures

Methane and water can exhibit a number of different phase equilibrium – gas–liquid, gas–ice, gas–ice-hydrate, and gas–liquid-hydrate at conditions typical of permafrost.

6.1.1. Methane–water in gas–liquid equilibrium

Numerical results for methane–water have been reported by Servio and Henley (2015), compared to experimental data of Servio and Englezos (2002), and are reproduced here for the reader’s convenience in Table 1, which shows that the GHC equation provides reasonable predictions of the solubility of methane in water at the conditions studied by Servio and Englezos (2002). Additional density and phase equilibrium
predictions for the GHC equation are compared to experimental data and shown in Figs. 1 and 2. Specifically, GHC EOS density predictions are compared to the 169 experimental density measurements in Joffrin and Eubank in Fig. 1 and range from 398.15 to 498.15 K and approximately 1 to 120 bar. The comparison in Fig. 1 clearly shows a very good match of the experimental data with statistics of an AAD% error of 1.45% and standard deviation of 2.6%. Fig. 2, on the other hand, shows a comparison of GHC-predicted methane solubility in water in the VLE region with the experimental data of Servio and Englezos (2002) and Chapoy et al. (2004). The temperatures and pressures for the data sets in Fig. 2 are 275–313 K and 10–180 bar while the GHC-predicted values are shown as unfilled triangles and the dot-dot-dash curves. Note the agreement is quite reasonable. Remember the GHC EOS does not use binary interaction parameters at all while the modeling results for the Valderrama–Patel–Teja (VPT) EOS used in Chapoy et al. require binary interaction parameters.

### Table 1 – Methane solubility in water predicted by the GHC equation.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>p (bar)</th>
<th>XCH4</th>
<th>XCH4</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>278.65</td>
<td>35</td>
<td>0.001190</td>
<td>0.001104</td>
<td>7.20</td>
</tr>
<tr>
<td>280.45</td>
<td>35</td>
<td>0.001102</td>
<td>0.001098</td>
<td>0.36</td>
</tr>
<tr>
<td>281.55</td>
<td>50</td>
<td>0.001524</td>
<td>0.001379</td>
<td>9.51</td>
</tr>
<tr>
<td>282.65</td>
<td>50</td>
<td>0.001357</td>
<td>0.001374</td>
<td>1.25</td>
</tr>
<tr>
<td>283.25</td>
<td>65</td>
<td>0.001720</td>
<td>0.001660</td>
<td>3.49</td>
</tr>
<tr>
<td>284.35</td>
<td>65</td>
<td>0.001681</td>
<td>0.001653</td>
<td>1.67</td>
</tr>
<tr>
<td>AAD%</td>
<td></td>
<td></td>
<td></td>
<td>3.91</td>
</tr>
</tbody>
</table>


Fig. 1 – Comparison of GHC-predicted density for methane–water mixtures with experimental data.

**Fig. 2 – GHC-predicted methane solubility in water.**

6.1.2. Hexagonal ice density and the ice-water melting curve

Before studying gas-ice equilibrium and to validate the theory developed in Sections 4.1 and 4.2 and Appendix B, we present results for the density and ice-water melting curve as predicted by the GHC framework.

Table 2 compares the densities of 1h ice predicted by the multi-scale GHC equation with those given in Feistel and Wagner (p. 1040. Table 11, Feistel and Wagner, 2006) for the extended IAPWS-95 equation over the range of interest in permafrost phase behavior. In the comparisons in Table 2, the % error is given by %error = 100|ρIAPWS-95 − ρGHC|/ρIAPWS-95, which clearly shows that the GHC equation captures the increase in 1h ice density with decreasing temperature and that there is reasonably good agreement between the two EOS models. However, the GHC equation does not show the same sensitivity of ice density to temperature and pressure as the extended IAPWS-95 equation.

Table 3 shows melting temperatures of ice predicted by the extended IAPWS-95 and GHC equations as a function of

### Table 2 – Density of sub-cooled hexagonal ice.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Pressure (MPa)</th>
<th>IAPWS-95&lt;sup&gt;a&lt;/sup&gt;</th>
<th>GHC&lt;sup&gt;b&lt;/sup&gt;</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>0.1013</td>
<td>918.61</td>
<td>931.31</td>
<td>1.38</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>923.84</td>
<td>931.77</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>928.96</td>
<td>931.93</td>
<td>0.32</td>
</tr>
<tr>
<td>270</td>
<td>0.1013</td>
<td>917.18</td>
<td>927.48</td>
<td>1.12</td>
</tr>
<tr>
<td>273</td>
<td>0.1013</td>
<td>916.74</td>
<td>926.25</td>
<td>1.04</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reproduced from Table 11 in Feistel and Wagner (2006).

<sup>b</sup> GHC equation with T<sub>0</sub>,he calculated using Eqs. (5) and (A1).
Table 3 – Melting temperatures of 1 h ice predicted by the extended IAPWS-95 & GHC equations.

<table>
<thead>
<tr>
<th>Pressure (MPa)</th>
<th>IAPWS-95a</th>
<th>GHC</th>
<th>(\Delta T_m) (K)</th>
<th>% Error in (T_m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1013</td>
<td>273.159</td>
<td>273.151</td>
<td>0.048</td>
<td>0.0154</td>
</tr>
<tr>
<td>2.1453</td>
<td>273</td>
<td>273.042</td>
<td>0.042</td>
<td>0.0154</td>
</tr>
<tr>
<td>15.135</td>
<td>272</td>
<td>272.041</td>
<td>0.041</td>
<td>0.0151</td>
</tr>
<tr>
<td>27.4942</td>
<td>271</td>
<td>271.093</td>
<td>0.093</td>
<td>0.0343</td>
</tr>
<tr>
<td>39.3133</td>
<td>270</td>
<td>270.189</td>
<td>0.189</td>
<td>0.0700</td>
</tr>
<tr>
<td>50.6633</td>
<td>269</td>
<td>269.320</td>
<td>0.320</td>
<td>0.1190</td>
</tr>
<tr>
<td>61.5996</td>
<td>268</td>
<td>268.493</td>
<td>0.493</td>
<td>0.1840</td>
</tr>
</tbody>
</table>

* Reproduced from Table 19 in Feistel and Wagner, p. 1045, 2006.

6.1.3. Methane gas–ice equilibrium

At low enough temperature and pressure, methane and water will exhibit gas–solid equilibrium with essentially pure phases. However, it is important for the reader to understand that other equilibrium solutions (e.g., gas–liquid equilibrium) that satisfy the equality of chemical potential but have a higher Gibbs free energy can be found for the same specifications of feed composition, temperature, and pressure. Table 4 presents results for the phase equilibrium of a mixture of 10 mol% methane and 90 mol% water at 272 K and 1 bar.

At the given temperature, the pressure is too low for methane hydrate to form so this example represents a reasonable test of the capability of the multi-scale GHC EOS to find gas–solid equilibrium. Also note that the correct global minimum Gibbs free energy solution is methane gas with a very small amount of water vapor in equilibrium with 1 h ice (GSE). However, there is also a gas–liquid equilibrium (GLE) solution with a value of G/RT that is only slightly higher than the gas–ice equilibrium solution. It is also possible to find a gas–liquid–ice (GLSE) equilibrium at these conditions with a value of G/RT between that of the GS and GL equilibria and a very small amount of solid (\(~3.5 \text{ mol/mol} \text{ feed}\)).

6.1.4. Methane hydrate density

The next example gives numerical results for GHC-predicted density of empty and filled hydrate and, in doing so, tests the validity of the theoretical material presented in Sections 5.2 and 5.3 and Appendix C. Empty and filled methane hydrate densities are shown in Table 5 along with a comparison of the GHC-predicted filled methane hydrate density with the analytical expression given in Sloan and Koh (2007) with and without the temperature and pressure dependence of empty cell volume given by Klauda and Sandler (2000). Note that there is reasonably good agreement among all three methods.

Table 4 – Phase equilibria for 10 mol% methane–90 mol% water at –1.15 C and 0.1 MPa.

<table>
<thead>
<tr>
<th>Type of equilibrium</th>
<th>G/RT</th>
<th>GLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>G/RT</td>
<td>–7.885069</td>
<td>–7.880715</td>
</tr>
<tr>
<td>Phase 1</td>
<td>1h ice</td>
<td>Liquid</td>
</tr>
<tr>
<td>Phase 1 fraction</td>
<td>0.899987</td>
<td>0.900014</td>
</tr>
<tr>
<td>Phase 1 composition</td>
<td>(0, 1)</td>
<td>(3.28 \times 10^{-4}, 0.999967)</td>
</tr>
<tr>
<td>Phase 1 density (kg/m^3)</td>
<td>926.67</td>
<td>1015.041</td>
</tr>
<tr>
<td>Phase 2</td>
<td>Gas</td>
<td>Gas</td>
</tr>
<tr>
<td>Phase 2 fraction</td>
<td>0.000013</td>
<td>0.009986</td>
</tr>
<tr>
<td>Phase 2 composition</td>
<td>(0.999841, 1.59 \times 10^{-4})</td>
<td>(0.999840, 1.60 \times 10^{-4})</td>
</tr>
<tr>
<td>Phase 2 density (kg/m^3)</td>
<td>1.95</td>
<td>1.95</td>
</tr>
</tbody>
</table>
Table 5 – Methane hydrate density from Eq. (10) for \( \theta = 1 \).

<table>
<thead>
<tr>
<th>T (K)</th>
<th>p (bar)</th>
<th>( \rho_{MT} ) (kg/m(^3))</th>
<th>( \rho_{h\ell} ) (kg/m(^3))</th>
<th>( \rho_{h\vartheta} ) (kg/m(^3))</th>
<th>( \rho_{h\ell} ) (kg/m(^3))(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>50</td>
<td>795.43</td>
<td>918.61</td>
<td>913.79</td>
<td>926.46</td>
</tr>
<tr>
<td>100</td>
<td>795.74</td>
<td>918.78</td>
<td>913.79</td>
<td>926.60</td>
<td></td>
</tr>
<tr>
<td>270</td>
<td>50</td>
<td>788.48</td>
<td>910.59</td>
<td>913.79</td>
<td>924.05</td>
</tr>
<tr>
<td>100</td>
<td>788.96</td>
<td>911.14</td>
<td>913.79</td>
<td>924.19</td>
<td></td>
</tr>
<tr>
<td>280</td>
<td>50</td>
<td>781.51</td>
<td>902.54</td>
<td>913.79</td>
<td>921.55</td>
</tr>
<tr>
<td>100</td>
<td>781.99</td>
<td>903.09</td>
<td>913.79</td>
<td>921.69</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Analytical expression from Sloan and Koh (2007).

\(^b\) Sloan & Koh with expression from Klauda and Sandler (2000) temperature and pressure dependent empty cell volume.

Table 6 – Phase equilibria at approximate quadruple point (272.751 K, 25.624 bar) for GHC equation.

<table>
<thead>
<tr>
<th>Type of equilibrium</th>
<th>G/RT</th>
<th>GSE</th>
<th>HSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase 1 fraction</td>
<td>Liquid</td>
<td>Ice</td>
<td>Ice</td>
</tr>
<tr>
<td>Phase 1 composition</td>
<td>(0.000804, 0.999196)</td>
<td>(0, 1)</td>
<td>(0, 1)</td>
</tr>
<tr>
<td>Phase 1 density (kg/m(^3))</td>
<td>1014.05</td>
<td>926.39</td>
<td>926.39</td>
</tr>
<tr>
<td>Phase 2 fraction</td>
<td>Gas</td>
<td>Gas</td>
<td>Hydrate</td>
</tr>
<tr>
<td>Phase 2 composition</td>
<td>(0.999899, 1.09 \times 10^{-5})</td>
<td>(0.999899, 1.09 \times 10^{-5})</td>
<td>(0.140978, 0.859022)</td>
</tr>
<tr>
<td>Phase 2 density (kg/m(^3))</td>
<td>19.19</td>
<td>19.19</td>
<td>901.31</td>
</tr>
<tr>
<td>Occupancy</td>
<td></td>
<td></td>
<td>0.9437</td>
</tr>
</tbody>
</table>

6.1.5. The quadruple point for methane–water equilibrium

Below the melting point of ice, the phase equilibrium that exists is either methane gas–ice or methane hydrate–gas/ice equilibrium. That is, at low pressure, below pressures for which hydrate can form, methane gas is in equilibrium with 1 h ice. See Table 4 for an example of low pressure GSE. As one raises the pressure at fixed temperature, methane hydrate will form and gas hydrate will be in equilibrium with gas and/or ice – depending on the overall amounts of methane and water in the system. Above the melting point of ice the equilibrium changes from gas–liquid to methane hydrate–gas/liquid as a function of increasing pressure. One of the more challenging tasks in the neighborhood of the ice melting point is predicting the quadruple point – the temperature and pressure at which four phases (ice, methane hydrate, liquid water, and gas) co-exist. Anderson (2004) reports a quadruple point of 272.9 K and 25.63 bar. Table 6 gives calculated results for the GHC equation prediction of the quadruple point, which is approximately 272.751 K and 25.624 bar.

Because the quadruple point is a singular point, it is very difficult to compute accurately. However, note that the GHC prediction of the quadruple point gives all three two-phase equilibria that have dimensionless Gibbs free energies that are quite close (i.e., differing by \(<10^{-3}\)). Note also the predicted fractional occupancy of the gas in the hydrate phase is 0.9437, which is quite close to the value of occupancy of 0.9461 predicted by the correlation in Parrish and Prausnitz (1972) but less close to the value of occupancy of 0.90 \pm 0.01 predicted by Gibbs ensemble Monte Carlo simulation (GEMC).

6.1.6. Sub-cooled methane hydrate–ice equilibrium

This last methane–water example in this article is used to illustrate that phase equilibrium and gas occupancy for conditions away from phase boundaries can be determined using the theoretical framework described in Sections 3–5 and Appendices A–C. Consider permafrost conditions for a mixture of 13 mol\% methane and 87 mol\% water at 272 K and 27 bar. For the given problem (1) there is an excess amount of water, (2) methane hydrate should be in equilibrium with pure ice, and (3) the resulting phase equilibrium solution is away from the phase boundary. Numerical results for this example are shown in Table 7.

Table 7 – Phase equilibria for 13 mol\% methane–87 mol\% water at –1.15 \degree C and 2.7 MPa.

<table>
<thead>
<tr>
<th>Type of equilibrium</th>
<th>G/RT</th>
<th>GSE</th>
<th>HSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase 1 fraction</td>
<td>Liquid</td>
<td>Ice</td>
<td>Ice</td>
</tr>
<tr>
<td>Phase 1 composition</td>
<td>(0.000850, 0.999150)</td>
<td>(0, 1)</td>
<td>(0, 1)</td>
</tr>
<tr>
<td>Phase 1 density (kg/m(^3))</td>
<td>1014.37</td>
<td>926.70</td>
<td>926.70</td>
</tr>
<tr>
<td>Phase 2</td>
<td>Gas</td>
<td>Gas</td>
<td>Hydrate</td>
</tr>
<tr>
<td>Phase 2 composition</td>
<td>(0.999990, 9.87 \times 10^{-4})</td>
<td>(0.999990, 9.81 \times 10^{-4})</td>
<td>(0.132198, 0.867802)</td>
</tr>
<tr>
<td>Phase 2 density (kg/m(^3))</td>
<td>20.35</td>
<td>20.35</td>
<td>893.66</td>
</tr>
<tr>
<td>Occupancy</td>
<td></td>
<td></td>
<td>0.8759</td>
</tr>
</tbody>
</table>
It is important to describe the phase equilibrium computations for this ice–gas hydrate equilibrium flash solution in a bit more detail. The water-to-methane ratio in the feed is equal to 6.6923, well in excess of the value of 5.75 for a completely filled methane hydrate. Therefore, if methane hydrate is one of the equilibrium phases, there should also be excess water and this implies that either liquid water or ice will also exist. In addition, from Table 7 it is clear that ice should be the phase in equilibrium with methane hydrate at the given conditions. This is true because the GSE solution has a lower value of G/RT than that for the VLE solution. Moreover, in any ice–methane hydrate equilibrium, methane is confined to the hydrate phase. Thus, defining equilibrium becomes a bit more challenging since, in theory, there is only a single chemical potential to use to define conditions of phase equilibrium. This is where the use of structural contributions to the ice and empty hydrate standard state fugacities for water become important. To define equilibrium we use the condition that

$$\mu_{w}^{eq} - \mu_{w}^{MT} = 0 \quad (12)$$

It is also important to understand that Eq. (12) is singular unless trace amounts of methane are permitted in the ice and empty hydrate phases. However, even if trace amounts of methane are present in these phases to avoid singularity, the problem is still so nearly singular that quadratic acceleration (see, Eq. (A2), p. 2562 in Lucia and Yang, 2003) is required to get convergence to a reasonable tolerance.

To give the reader some appreciation for this last point, we have shown the calculated equilibrium solution to Eq. (12) in the presence of trace amounts of methane at 272 K and 27 bar in Table 8. Using quadratic acceleration, these computations converge to the solution shown in Table 8 in 20 iterations. However, note how very close in composition both phases in Table 8 are; both contain less than 0.1 mol% methane. The two critical pieces of information that come from solving Eq. (12) in this regard are the ice and hydrate phase fractions. From these phase fractions, it is straightforward to determine the methane occupancy, gas hydrate density (i.e., using Eq. (10)), and corresponding value of G/RT for the hydrate phase – as well as G/RT for the ice–methane hydrate equilibrium solution.

For this particular example, we also calculated the fractional occupancy of methane in the hydrate phase using Gibbs–ensemble Monte Carlo simulations for the purpose of comparison. The value obtained from GEMC was 0.89 ± 0.01. Table 7, on the other hand, shows that the calculated fractional occupancy using the GHE-based framework developed in the work is 0.8759, whereas the occupancy determined using the correlation in Parrish and Prausnitz (1972) is 0.9497. Thus it is clear that the proposed GHE-based framework for gas hydrates gives reliable values of gas occupancy directly from phase equilibrium.

### 6.2. Carbon dioxide–water mixture

Like methane–water mixtures, carbon dioxide–water mixtures can exhibit a number of different types of phase equilibria – gas–liquid, liquid–liquid, gas–ice, hydrate–ice, etc.

#### 6.2.1. Gas–liquid equilibrium

In previous work, Lucia et al. (2012) have compared phase equilibrium results for CO$_2$–water predicted by the GHE EOS with those of the Predictive Soave–Redlich–Kwong (PSRK) equation and the experimental data from Coan and King (1971). See example 6.6 and Fig. 14 in Lucia et al. (2012). In general, both equations of state are in good agreement with experimental data with the GHE equation performing better overall.

#### 6.2.2. Carbon dioxide gas–ice equilibrium

CO$_2$–ice equilibrium is straightforward to compute using the GHE-based framework developed in this work. However, depending on conditions, there can be many other equilibria with values of G/RT that are close to the global minimum value of G/RT, as illustrated in Table 9. The presence of many equilibria makes the prediction of the correct solution quite challenging.

### 6.2.3. Carbon dioxide hydrate density

The density of CO$_2$ hydrate is considerably higher than that of methane hydrate due to the fact that CO$_2$ is much heavier than methane. However, because CO$_2$ hydrate is also a structure 1 hydrate, Eq. (10) can be used to calculate hydrate density. Table 10 compares GHE-predicted CO$_2$ hydrate densities with densities calculated using the analytical expression given in Sloan and Koh (2007) with and without the Klauda and Sandler (2000) correction for empty hydrate cell volume.
Brewer et al. (1999) report a value of 1100 kg/m³ for the bulk density of CO₂ hydrate at –4 °C and depths from 1100 to 1300 m (pressures ranging from ~110 to 130 bar). From Note 17 in Brewer et al., we can deduce that the fractional gas occupancy is 0.9583. For the same conditions of temperature and pressure, the empty hydrate density predicted by the GHC equation is 0.0442967 mol/cm³. Using the gas occupancy from Brewer et al. (1999), the molecular weight of CO₂ hydrate is 21.59 g/mol. From Eq. (10), the actual hydrate density for a fractional CO₂ occupancy of 0.9583 is 0.051679 mol/cm³, which when multiplied by the molecular weight of the CO₂ hydrate gives a mass density of 1115.57 kg/m³. This GHC-predicted value of CO₂ hydrate density represents an error of 1.43%. For the exact same conditions, the analytical expression in Sloan and Koh (2007) gives a density of 1101.02 kg/m³ while the expression in Sloan and Koh with the Klauda and Sandler (2000) correction for empty hydrate cell volume results in a mass density of 1162.25 kg/m³. In our opinion, the 1.43% error in CO₂ hydrate density predicted by the multi-scale GHC equation, which is neither a correlation nor a fit to experimental data, is quite accurate.

6.2.4. Phase equilibrium in regions where CO₂ hydrates can exist

One of the interesting differences between methane hydrates and CO₂ hydrates is the presence of liquid CO₂ at high pressure so we consider an example that would potentially result in storage of CO₂ in a hydrate phase. Let the temperature and pressure be 269.15 K and 130 bar respectively. At this pressure, CO₂ is a liquid and the temperature and pressure are such that hydrate can form. Moreover, Brewer et al. (1999) provide clear experimental evidence that a hydrate phase can form from liquid CO₂ at high pressures. See Fig. 3 and the associated discussion in Brewer et al. (1999). Finally, for hydrate in equilibrium with fluid phases (and not 1 h ice), the conditions defining equilibrium are the equality of chemical potentials for CO₂ and water in all phases. Numerical results are shown in Table 11, which are consistent with the experimental observations of Brewer et al. (1999), where the authors report the presence of a mass of floculent CO₂ hydrate along with liquid CO₂ and, in their case, seawater. The GHC-estimated freezing point depression of water with CO₂ solute mole fractions of 0.018762 or 0.018782 at an elevated pressure is approximately –3.8 °C. Thus the estimated freezing point of the water phase at 130 bar pressure is 269.32 K, which is very close to 269.15 K. This, in our opinion, explains why the values of G/RT for the LLE and SLE flash solutions in Table 11 are so close. In addition, Brewer et al. state that after some time (17 days), they observed no hydrate present in their experiment – either because the hydrate phase dissolved or because it sank into the surrounding seawater. The GHC-predicted hydrate density shown in Table 11 is consistent with the hydrate phase sinking in water. Finally, the GHC-predicted density and fractional occupancy agree quite well with the density of 1100 kg/m³ and occupancy of 0.9583 reported in Brewer et al. (1999). The fractional occupancy predicted by Parrish and Prausnitz (1972) correlation was 0.9680.

The numerical aspects associated with computing the HLLÉ flash solution in Table 11 are somewhat complicated. Because there are two components and three phases, the

<table>
<thead>
<tr>
<th>T (K)</th>
<th>p (bar)</th>
<th>( \rho^{MT} ) (kg/m³)</th>
<th>( \rho^{HYD} ) (kg/m³)</th>
<th>( \rho^{HYD} ) (kg/m³)</th>
<th>( \rho^{HYD} ) (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>20</td>
<td>803.28</td>
<td>1144.57</td>
<td>114.89</td>
<td>1182.83</td>
</tr>
<tr>
<td>270</td>
<td>20</td>
<td>796.57</td>
<td>1135.00</td>
<td>114.89</td>
<td>1182.86</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>797.90</td>
<td>1135.31</td>
<td>114.89</td>
<td>1181.72</td>
</tr>
<tr>
<td>280</td>
<td>50</td>
<td>789.73</td>
<td>1125.25</td>
<td>114.89</td>
<td>1181.75</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>789.92</td>
<td>1125.52</td>
<td>114.89</td>
<td>1180.53</td>
</tr>
</tbody>
</table>

a Analytical expression from Sloan and Koh (2007).

b Sloan & Koh expression with Klauda and Sandler (2000) temperature and pressure dependent empty cell volume.

<table>
<thead>
<tr>
<th>Type of equilibrium</th>
<th>LLE</th>
<th>SLE</th>
<th>HLLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>G/RT</td>
<td>–7.341224</td>
<td>–7.337202</td>
<td>–7.365097</td>
</tr>
<tr>
<td>Phase 1</td>
<td>Liquid</td>
<td>Ice</td>
<td>Liquid</td>
</tr>
<tr>
<td>Phase 1 fraction</td>
<td>0.886538</td>
<td>0.870542</td>
<td>0.873997</td>
</tr>
<tr>
<td>Phase 1 composition</td>
<td>(0.018762, 0.981238)</td>
<td>(0, 1)</td>
<td>(0.018782, 0.981218)</td>
</tr>
<tr>
<td>Phase 1 density (kg/m³)</td>
<td>1029.03</td>
<td>927.92</td>
<td>1029.03</td>
</tr>
<tr>
<td>Phase 2</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Liquid</td>
</tr>
<tr>
<td>Phase 2 fraction</td>
<td>0.113462</td>
<td>0.129458</td>
<td>0.111677</td>
</tr>
<tr>
<td>Phase 2 composition</td>
<td>(0.999161, 8.39 \times 10^{-4})</td>
<td>(0.999157, 8.43 \times 10^{-4})</td>
<td>(0.999156, 8.44 \times 10^{-4})</td>
</tr>
<tr>
<td>Phase 2 density (kg/m³)</td>
<td>995.77</td>
<td>995.77</td>
<td>995.77</td>
</tr>
<tr>
<td>Phase 3</td>
<td>Hydrate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phase 3 fraction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phase 3 composition</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phase 3 density (kg/m³)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Occupancy</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 10 – Carbon dioxide hydrate density from Eq. (10) for \( \theta = 1 \).

Table 11 – Phase equilibria for 13 mol% CO₂–87 mol% water at –4 °C and 13 MPa.
solution is near singular and quadratic acceleration is required for reliable convergence. In this example, the HLLE flash computations converge to an accuracy of $10^{-6}$ in the 2-norm of the equality of chemical potentials in 9 iterations.

7. Conclusions

The multi-scale Gibbs–Helmholtz Constrained (GHC) equation of state-based framework has been extended for determining densities and phase equilibrium in light gas–water mixtures at conditions where ice and/or hydrates can exist. This extended framework is built around the use of the multi-scale GHC EOS, and the novel ideas that (1) make use of the GHC equation to determine densities of ice and empty hydrate, (2) derive and employ structural contributions to the standard state fugacities of ice and empty hydrate in phase equilibrium, (3) use of only densities and EOS parameters to determine these structural contributions, and (4) determine gas occupancy directly from phase equilibrium. A novel theoretical framework was developed and a number of examples for mixtures of methane–water and carbon dioxide–water at conditions relevant to hydrate formation were presented to show the efficacy of the proposed new approach. Numerical results clearly show that this extended multi-scale, GHC-based framework is rigorous and provides accurate predictions of densities, phase equilibrium, and gas occupancy for light gas–water mixtures for conditions where ice and/or gas hydrates exist.

7.1. Extensions of ice and gas hydrate modeling to include brines

As noted in Section 1, permafrost and other regions containing gas hydrates can also contain brines. However, the presence of brines further complicates fluid modeling in many ways. Brines

1. Increase the internal energy of departure and molecular co-volume of an aqueous electrolyte solution in comparison to pure water and thus increase the density of the aqueous liquid phase.
2. Directly affect the fugacity of gases in the aqueous phase, generally lowering their solubility by a process known as salting out.
3. Affect the fugacity of water in the aqueous phase.
4. Result in freezing point depression, generally causing a shift in phase boundaries.
5. Generally lower the heat of fusion of water.

Moreover, these factors are all strongly interrelated, effect the formation/dissociation of gas hydrates, and require very careful study. In future work, we show how to extend the multi-scale GHC EOS framework for systems that exhibit ice and gas hydrates presented in this article to include brines.

Appendix A. Internal energies of departure for ice

Internal energies of departure for hexagonal ice can be determined either from $U^D$ for liquid water plus energies of fusion or by direct Monte Carlo simulation.

Internal energies of departure for hexagonal ice from energies of fusion

Along the melting curve, internal energies of departure associated with fusion, $U_{w}^{D, fus}$, needed in Eq. (5) can be calculated as follows:

i. A reference value of the internal energy of departure associated with fusion, $U_{w}^{D, fus}$, can be estimated from data for the heat of fusion for water, which is abundantly available (at 273.15 K and 0.1013 MPa; $U_{w}^{D, fus} = −600890325 \times 10^{-5}$ cm$^3$ bar/mol).

ii. The effect of temperature and pressure on $U_{w}^{D, fus}$ along the melting curve can be included by using the Clapeyron equation (see Smith et al., 2004) in the form

\[
U_{w}^{D, fus} = U_{w}^{D, fus} + \Delta V \left( \frac{\partial p}{\partial T} \right) \Delta T + p
\]

where $\Delta V = V_{w}^{fus} - V_{w}^{i}$, $(\partial p/\partial T)$ is the derivative of pressure with respect to temperature along the melting curve, and $\Delta T = T - 273.15$.

iii. It is straightforward to calculate a very good estimate of the volume difference between 1 h ice and liquid water, $\Delta V$, needed in Eq. (A1) using the multi-scale GHC equation. To do this,

(a) First calculate the density of liquid water at 273.15 K and 0.1013 MPa using the GHC equation with values of $b_{w}' = 16.363$ cm$^3$/mol and $U_{w}^{D, fus} = −8.420981356 \times 10^{-5}$ cm$^3$ bar/mol, which is the value of $U_{w}^{D}$ for liquid water from NTP Monte Carlo simulations. The calculated molar density of liquid water is $\rho_{w} = 0.0563139$ mol/cm$^3$, which corresponds to a mass density of 1014.49 kg/m$^3$.

(b) Next set $U_{w}^{D, fus} = U_{w}^{D, fus}$ and calculate $U_{w}^{D, fus}$ at 273.15 K and 0.1013 MPa. This gives a value of $U_{w}^{D, fus} = −5.4218889 \times 10^{-5}$ cm$^3$ bar/mol.

(c) Calculate the density of 1 h ice at 273.15 K and 0.1013 MPa using the GHC equation (i.e., Eqs. (1) and (2)) with $b_{w}' = 18.015$ cm$^3$/mol and $U_{w}^{D, fus} = −5.4218889 \times 10^{-5}$ cm$^3$ bar/mol, which gives a molar density of $\rho_{i}^{D, fus} = 0.0514144$ mol/cm$^3$ or a mass density of 926.19 kg/m$^3$.

(d) Finally, use the results from (a) and (c) to calculate a value of $\Delta V = V_{w}^{fus} - V_{w}^{i} = (1/\rho_{w}^{D, fus}) - (1/\rho_{i}^{D, fus}) = 1.69311$ cm$^3$/mol.

iv. Given the reference internal energy of fusion, $U_{w}^{D, fus}$, and the change in volume, $\Delta V$, it is straightforward to use the Clapeyron equation to estimate the derivative, $(\partial p/\partial T)$, along the melting curve at the reference temperature and pressure. By direct application of the Clapeyron equation we have

\[
(\frac{\partial p}{\partial T}) = \frac{U_{w}^{D, fus}}{T \Delta V} = \frac{U_{w}^{D, fus}}{T \Delta V}
\]

which holds since the term $p \Delta V$ is negligible compared to $U_{w}^{D, fus}$. From Eq. (A2), we find that $(\partial p/\partial T) = (0.0600890325 \times 10^{-5}$ cm$^3$ bar/mol)/(273.15 K) 

(1.6931 cm$^3$/mol) = −129.902 bar/K, which is close to the published experimental value of −134.58 bar/K found in the open literature. See, for example, Table IV in Abascal et al. (2005) or p. 1034 in Feistel and Wagner (2006).
The minimum energy structure is shown at 272 K.

**(Fig. A1 – Comparison of minimized and simulated structures of hexagonal.**

(ip/RT) remain constant at values of \(\Delta V = 1.69311 \text{ cm}^3/\text{mol}\) and (ip/RT) = −129.902 bar/K respectively.

**Internal energies of departure for hexagonal ice from direct Monte Carlo simulation**

We have also calculated internal energies of departure for 1 h ice using the TIP4P-Ew force field model initialized from a hexagonal structure. The optimized force field parameters for liquid water used in the MC simulations of ice were taken from Horn et al. (2004) and are given in Appendix D. Fig. A1 gives a snapshot of the crystal structure predicted by Monte Carlo simulation for \(N = 96\) water molecules, \(T = 272\) K and \(p = 10\) MPa during the sampling (or production) phase. For these simulations, 50,000 equilibration cycles and 200,000 production cycles were used. The minimum energy structure for hexagonal ice at 0 K is also shown in Fig. A1 for comparison.

Note that the minimum energy structure (at 0 K) is perfectly hexagonal while NTP Monte Carlo simulation using TIP4P-Ew gives a structure that shows some lattice distortion at the elevated temperature of 272 K. Similar results were obtained using the TIP4P/Ice force field model (Abascal et al., 2004). The important point here is that NTP Monte Carlo simulations account for the effects of lattice distortion and this lattice distortion is correctly reflected in values of \(U_w^{B,\text{ice}}\).

It is also important to note that the estimation of \(U_w^f\) for hexagonal ice from direct NTP Monte Carlo simulation is not restricted to the melting curve but can be used for any temperature and pressure. However, it is unclear if this distinction matters in practice since Table A1, which gives a comparison of \(U_w^{B,\text{ice}}\) calculated using energies of fusion and the Clapeyron equation (i.e., Eqs. (A1) and (A2)) with values of \(U_w^{B,\text{ice}}\) calculated from direct NTP Monte Carlo simulations, shows only relatively small differences in \(U_w^{B,\text{ice}}\) between the two methods over reasonable ranges of temperature and pressure.

The results in Table A1 show that there is strong agreement between the two methods for determining internal energies of departure for hexagonal ice. Specifically, the % error, which is defined as \(100 \times \frac{|U_w^{B,\text{ice}}(\text{MC}) - (U_w^{\text{MC}} + U_w^{\text{fusion}})|}{U_w^{\text{MC}} + U_w^{\text{fusion}}} \), is less than 3% and the standard deviation, \(\sigma_N\), is small – despite the fact that estimations of \(U_w^{\text{ice}}\) using the Clapeyron equation are really not strictly applicable at conditions that are not on the melting curve. Note that Table A1 also shows that the pressure effect on \(U_w^{B,\text{ice}}\) is small. We use \(U_w^{B,\text{ice}} = U_w^{\text{MC}} + U_w^{\text{fusion}}\) because (1) we already have an extensive database of \(U_w^{\text{MC}}\) using TIP4P-Ew and (2) \(U_w^{\text{ice}} = U_w^{\text{MC}} + U_w^{\text{fusion}}\) provides internal energies of departure that are in good agreement with those computed using TIP4P/Ice.

### Appendix B. A reference state for water in a hexagonal ice phase

The expression for \(\ln \phi\) in the multi-scale GHC framework for a pure component is

\[
\ln \phi = z - 1 - \ln(z - \frac{A}{B}) \left(1 + \frac{B}{z}\right)
\]

where \(A = ap/RT^2\) and \(B = bp/RT\). Application of Eq. (B1) to 1 h ice and liquid water gives

\[
\ln \phi_w^{\text{ice}} = z_w^{\text{ice}} - 1 - \ln(z_w^{\text{ice}} - B_w^{\text{ice}}) = \left(\frac{A_w^{\text{ice}}}{B_w^{\text{ice}}}\right) \ln \left(1 + \frac{B_w^{\text{ice}}}{z_w^{\text{ice}}}\right) + \ln \left(1 + \frac{B_w^{\text{ice}}}{z_w^{\text{ice}}}\right)
\]

\[
\ln \phi_w^{\text{fus}} = z_w^{\text{fus}} - 1 - \ln(z_w^{\text{fus}} - B_w^{\text{fus}}) = \left(\frac{A_w^{\text{fus}}}{B_w^{\text{fus}}}\right) \ln \left(1 + \frac{B_w^{\text{fus}}}{z_w^{\text{fus}}}\right)
\]

Subtracting Eq. (B2) from Eq. (B3) and some algebra gives

\[
\Delta^{\text{ice}} = \ln \frac{\phi_w^{\text{ice}}}{\phi_w^{\text{fus}}} = z_w^{\text{ice}} - z_w^{\text{fus}} - \ln(z_w^{\text{ice}} - B_w^{\text{ice}}) + \ln(z_w^{\text{fus}} - B_w^{\text{fus}}) - \left(\frac{A_w^{\text{ice}}}{B_w^{\text{ice}}}\right) \ln \left(1 + \frac{B_w^{\text{ice}}}{z_w^{\text{ice}}}\right) + \left(\frac{A_w^{\text{fus}}}{B_w^{\text{fus}}}\right) \ln \left(1 + \frac{B_w^{\text{fus}}}{z_w^{\text{fus}}}\right)
\]

where \(\Delta^{\text{ice}}\) denotes the difference between the natural log of the fugacity coefficients for water and 1 h ice due to long-range structural differences between water and ice. Note that Eq. (B4) is a rigorous relationship between \(\ln \phi_w^{\text{ice}}\) and \(\ln \phi_w^{\text{fus}}\) and permits the calculation of the difference between the two fugacity coefficients from information that is readily available.

### Table A1 – Internal energies of departure for hexagonal ice.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>p (MPa)</th>
<th>(U_w^{\text{MC}} + U_w^{\text{fusion}}) (10^5 cm^3 bar/mol)</th>
<th>NTP MC(^a)</th>
<th>(2\sigma_N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>0.1</td>
<td>−5.45437</td>
<td>−5.60955</td>
<td>203.7649</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>−5.48108</td>
<td>−5.61205</td>
<td>536.3299</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>−5.47443</td>
<td>−5.61080</td>
<td>224.7205</td>
</tr>
<tr>
<td>270</td>
<td>0.1</td>
<td>−5.43590</td>
<td>−5.57666</td>
<td>207.6345</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>−5.42835</td>
<td>−5.57490</td>
<td>359.8061</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>−5.42557</td>
<td>−5.59308</td>
<td>335.1859</td>
</tr>
<tr>
<td>280</td>
<td>0.1</td>
<td>−5.39142</td>
<td>−5.53664</td>
<td>430.5228</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>−5.38874</td>
<td>−5.54026</td>
<td>362.6037</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>−5.38620</td>
<td>−5.54201</td>
<td>150.2200</td>
</tr>
</tbody>
</table>

\(^a\) Force field model = TIP4P-Ew.
from density calculations for 1 h ice and water. At conditions of ice-water phase equilibrium,

\[ G^\text{ice} = \frac{G^\text{ice}}{w} \]  

(B5)

where \( G \) denotes the Gibbs free energy, the subscript \( w \) denotes water and the superscripts \( \text{ice} \) and \( \text{l} \) represent hexagonal ice and liquid respectively. Eq. (B5) can be expanded in the form

\[ G^\text{ice} = G^\text{ice} + RT \ln x^\text{ice} + RT \ln \frac{\phi^\text{ice}}{\phi^\text{h}} - RT \ln p = G^\text{l} + \]  

(B6)

where \( R \) is the universal gas constant. Because \( x^\text{ice} = x^\text{h} = 1, \) Eq. (B6) reduces to

\[ G^\text{ice} = G^\text{ice} + RT \ln \frac{\phi^\text{ice}}{\phi^\text{h}} \]  

(B7)

However, Eq. (B7) implies

\[ G^\text{ice} = G^\text{ice} + RT(\ln \frac{\phi^\text{ice}}{\phi^\text{h}} - \ln \frac{\phi^\text{h}}{\phi^\text{l}}) \]  

(B8)

Use of Eq. (B4) in Eq. (B8) gives

\[ G^\text{ice} = G^\text{ice} + RT[\ln x^\text{ice} - \ln(\phi^\text{ice} - \ln(\phi^\text{h} - \phi^\text{h}) + \ln(\phi^\text{ice} - \phi^\text{h}) - \ln(\phi^\text{h} - \phi^\text{h})] + \ln(\phi^\text{ice} - \phi^\text{h})]  

(B9)

As is usual in equation of state calculations, we choose the standard state fugacity of liquid water to be equal to the pressure. Using this fact and the definition of \( \Delta^\text{ice} \) from Eq. (B4) in Eq. (B9) gives

\[ G^\text{ice} = G^\text{ice} + RT \ln p + RT \Delta^\text{ice} \]  

(B10)

Defining \( S^\text{ice} = \exp(\Delta^\text{ice}) \) implies \( \Delta^\text{ice} = \ln S^\text{ice} \) and Eq. (B10) becomes

\[ G^\text{ice} = G^\text{ice} + RT \ln p + RT \ln S^\text{ice} \]  

(B11)

All that remains is to evaluate \( S^\text{ice} \) at some reference state, say \( T_\text{ref} = 273.15 \, \text{K} \) and \( p_\text{ref} = 0.1013 \, \text{MPa} \), which is easily accomplished using information from density calculations at reference state conditions. Table B1 shows the values of the quantities needed in Eq. (B4) evaluated at \( T_\text{ref} \) and \( p_\text{ref} \). Using Eq. (B4) and the data in Table B1 in Eq. (B10) gives \( \Delta^\text{ice} = 1.15855 \) and \( S^\text{ice} = 3.18531 \).

Thus in general the standard state for 1 h ice at any temperature can be calculated from Eq. (B11) with \( S^\text{ice} = 3.18531 \). Also note that \( G^\text{ice} \) defined by Eq. (B11) is a function of temperature and pressure as it should be.

Remark

It turns out that the value, \( G^\text{ice} = 3.18531 \), is very close to the second peak distance in the O-H partial radial distribution function for 1 h ice (see Fig. 1, p. 514 in Chau and Hardwick, 1998). However, it is unclear if there is a rigorous relationship between \( \Delta^\text{ice} \) and the O-H partial radial distribution function or if this is just a coincidence.

Appendix C. A reference state for pure water in a gas hydrate phase

At conditions of ice-hydrate phase equilibrium,

\[ G^\text{ice} = \frac{G^\text{ice}}{RT} \]  

(C1)

where the superscript \( \text{hyd} \) represents hydrate and all other quantities are defined as in Appendix B. Moreover,

\[ G^\text{ice} = \frac{G^\text{ice}}{RT} + \ln x^\text{ice} + \ln \frac{\phi^\text{ice}}{\phi^\text{h}} \]  

(C2)

and

\[ G^\text{ice} = \frac{G^\text{ice}}{RT} + \ln x^\text{ice} + \ln \frac{\phi^\text{ice}}{\phi^\text{h}} \]  

(C3)

From Eqs. (C2) and (C3) and the fact that \( x^\text{ice} = 1 \), since hexagonal ice is a pure phase, it follows that

\[ \frac{G^\text{ice}}{RT} + \ln x^\text{ice} + \ln \frac{\phi^\text{ice}}{\phi^\text{h}} = \frac{G^\text{ICE}}{RT} + \ln \phi^\text{ice} \]  

(C4)

Rearranging Eq. (C4) gives

\[ \frac{G^\text{ice}}{RT} = \frac{G^\text{ice}}{RT} + \ln x^\text{ice} - \ln x^\text{ice} - \ln \frac{\phi^\text{ice}}{\phi^\text{h}} \]  

(C5)

where \( \Delta^\text{ICE} = \ln \frac{\phi^\text{ice}}{\phi^\text{h}} - \ln \frac{\phi^\text{ice}}{\phi^\text{h}} \) is the structural component of \( G^\text{ice} \) that represents the long range hexagonal order of solid hexagonal ice as defined in Appendix B.

To calculate a standard state of pure water in the hydrate phase we let \( x^\text{ice} = 1 \) in Eq. (C5), which means the hydrate cage is empty. This gives

\[ \frac{G^\text{ice}}{RT} = \ln p + \Delta^\text{ICE} + \ln \frac{\phi^\text{ice}}{\phi^\text{h}} - \ln \frac{\phi^\text{ice}}{\phi^\text{h}} = \ln p + \Delta^\text{ICE} + \Delta^\text{MT} \]  

(C6)

where the quantity \( \Delta^\text{MT} = \ln \frac{\phi^\text{ice}}{\phi^\text{h}} - \ln \frac{\phi^\text{ice}}{\phi^\text{h}} \) represents a second structural component that captures the differences in long range structure between 1 h ice and empty hydrate.

To calculate this second structural component contribution to the standard state for pure water in the hydrate phase we use the same strategy that we used for determining the structural component for 1 h ice. That is, we apply Eq. (B3) to determine the natural log of the fugacity coefficients for ice and empty hydrate and simply subtract the latter from the

---

**Table B1 – Quantities for calculating \( S^\text{ice} \).**

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Liquid water</th>
<th>Hexagonal ice</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x )</td>
<td>0.000078191</td>
<td>0.00085646</td>
</tr>
<tr>
<td>( A )</td>
<td>0.01912947</td>
<td>0.02234875</td>
</tr>
<tr>
<td>( B )</td>
<td>0.00072050</td>
<td>0.00079325</td>
</tr>
<tr>
<td>( \ln(x-B) )</td>
<td>-9.6979892</td>
<td>-9.6689374</td>
</tr>
<tr>
<td>( (A/B)\ln(1+B/x) )</td>
<td>17.3395588</td>
<td>18.4691635</td>
</tr>
</tbody>
</table>

---

**Table C1 – Quantities for calculating \( S^\text{hyd} \).**

<table>
<thead>
<tr>
<th>Quantity</th>
<th>1 h ice</th>
<th>Empty hydrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x )</td>
<td>0.043254</td>
<td>0.0437682</td>
</tr>
<tr>
<td>( A )</td>
<td>1.148913</td>
<td>1.1568889</td>
</tr>
<tr>
<td>( B )</td>
<td>0.040150</td>
<td>0.0466179</td>
</tr>
<tr>
<td>( \ln(x-B) )</td>
<td>-5.766967</td>
<td>-5.455963</td>
</tr>
<tr>
<td>( (A/B)\ln(1+B/x) )</td>
<td>18.792192</td>
<td>16.137596</td>
</tr>
<tr>
<td>( \Delta^\text{IR} )</td>
<td>-2.3512243</td>
<td>0.0953</td>
</tr>
</tbody>
</table>

---


former to get $\Delta^{MT}$ in terms of compressibility and equation of state parameters, $A$ and $B$. The resulting expression for $\Delta^{MT}$ is

$$
\Delta^{MT} = \frac{z^{\text{ice}} - z^{MT} - \ln(z^{\text{ice}} - B^{\text{ice}}) + \ln(z^{MT} - B^{MT})}{\gamma^{\text{hyd}} a}
$$

which clearly shows that only EOS information is needed to determine $\Delta^{MT}$. Straightforward computations using the GHC equation of state shows that $\Delta^{MT}$ varies very little with temperature and pressure (i.e., values of between $-2.51$ and $-2.21$ over the temperature and pressure ranges shown in Table 1). Table C1 gives a sample calculation of $\Delta^{MT}$ at 270 K and 50 bar.

$$
G_w^{\text{hyd}} = RT \ln \left( p + \ln S^{\text{ice}} + \ln S^{MT} \right)
$$

where $S^{\text{ice}} = \exp(\Delta^{\text{ice}})$ and where $S^{MT} = \exp(\Delta^{MT})$ is allowed to vary with $\Delta^{MT}$ computed by Eq. (C7). However, it is important to note that the value of $S^{MT}$ is a very weak function of pressure in the range 250–280 K.

We also repeated the same derivation of the structural component for empty hydrate by using water as the reference condition. Specifically, we re-wrote Eq. (C5) as

$$
\frac{G_w^{\text{hyd}}}{R T} = C_{p}^{b} + \ln \left( \frac{p}{\phi_{W}} \right) - \ln \left( \frac{\phi_{W}}{\phi_{b}} \right)
$$

where $\Delta^{MT} = \ln \frac{\phi_{W}}{\phi_{b}} - \ln \frac{\phi_{W}}{\phi_{b}}$ now measures the structural contribution to the hydrate standard state with respect to pure liquid water. This, in turn, led to an expression very similar to Eq. (C7). That is,

$$
\Delta^{MT} = \frac{z^{\text{aq}} - z^{MT} - \ln(z^{\text{aq}} - B^{\text{aq}}) + \ln(z^{MT} - B^{MT})}{\gamma^{\text{hyd}} a}
$$

However, this choice for the expression for $\Delta^{MT}$ did not yield good results.

### Table D1 – Critical and other physical property data.

<table>
<thead>
<tr>
<th>Species</th>
<th>$T_c$ (K)</th>
<th>$p_c$ (MPa)</th>
<th>$\omega$</th>
<th>$b$ (cm$^3$/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>190.58</td>
<td>4.592</td>
<td>0.008</td>
<td>29.614</td>
</tr>
<tr>
<td>Water</td>
<td>647.37</td>
<td>22.120</td>
<td>0.345</td>
<td>16.363</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>304.20</td>
<td>73.80</td>
<td>0.224</td>
<td>28.169</td>
</tr>
</tbody>
</table>

### Table D2 – NTP Monte Carlo simulation parameters.

<table>
<thead>
<tr>
<th>$\nu/k_B$ (K)</th>
<th>$\sigma$ (Å)</th>
<th>$q$ (e)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>81.8989</td>
<td>3.1645</td>
<td>–1.0484</td>
</tr>
<tr>
<td>H</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5242</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>148.0</td>
<td>3.73</td>
<td>0.0</td>
</tr>
<tr>
<td>EPM</td>
<td>28.999</td>
<td>2.785</td>
<td>0.6645</td>
</tr>
<tr>
<td>O</td>
<td>82.997</td>
<td>3.064</td>
<td>–0.33225</td>
</tr>
</tbody>
</table>

### Appendix D. Critical and other relevant physical property data

Critical properties and Monte Carlo simulation parameters for the chemical species in this work are shown in Tables D1 and D2 respectively.

### References


