

## Molecular Modeling of Thermodynamic and Transport Properties for CO<sub>2</sub> and Aqueous Brines

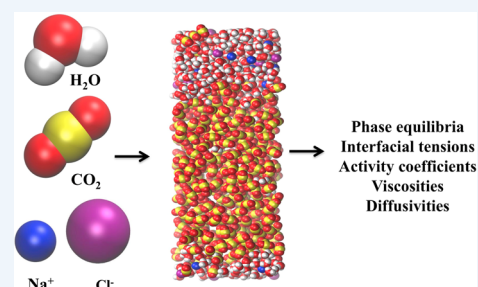
Published as part of the Accounts of Chemical Research special issue "Chemistry of Geologic Carbon Storage".

Hao Jiang,<sup>†</sup> Ioannis G. Economou,<sup>‡</sup> and Athanassios Z. Panagiotopoulos<sup>\*†</sup>

<sup>†</sup>Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08544, United States

<sup>‡</sup>Chemical Engineering Program, Texas A&M University at Qatar, P.O. Box 23874, Doha, Qatar

**CONSPECTUS:** Molecular simulation techniques using classical force-fields occupy the space between ab initio quantum mechanical methods and phenomenological correlations. In particular, Monte Carlo and molecular dynamics algorithms can be used to provide quantitative predictions of thermodynamic and transport properties of fluids relevant for geologic carbon sequestration at conditions for which experimental data are uncertain or not available. These methods can cover time and length scales far exceeding those of quantum chemical methods, while maintaining transferability and predictive power lacking from phenomenological correlations. The accuracy of predictions depends sensitively on the quality of the molecular models used. Many existing fixed-point-charge models for water and aqueous mixtures fail to represent accurately these fluid properties, especially when descriptions covering broad ranges of thermodynamic conditions are needed. Recent work on development of accurate models for water, CO<sub>2</sub>, and dissolved salts, as well as their mixtures, is summarized in this Account. Polarizable models that can respond to the different dielectric environments in aqueous versus nonaqueous phases are necessary for predictions of properties over extended ranges of temperatures and pressures. Phase compositions and densities, activity coefficients of the dissolved salts, interfacial tensions, viscosities and diffusivities can be obtained in near-quantitative agreement to available experimental data, using relatively modest computational resources. In some cases, for example, for the composition of the CO<sub>2</sub>-rich phase in coexistence with an aqueous phase, recent results from molecular simulations have helped discriminate among conflicting experimental data sets. The sensitivity of properties on the quality of the intermolecular interaction model varies significantly. Properties such as the phase compositions or electrolyte activity coefficients are much more sensitive than phase densities, viscosities, or component diffusivities. Strong confinement effects on physical properties in nanoscale media can also be directly obtained from molecular simulations. Future work on molecular modeling for CO<sub>2</sub> and aqueous brines is likely to be focused on more systematic generation of interaction models by utilizing quantum chemical as well as direct experimental measurements. New ion models need to be developed for use with the current generation of polarizable water models, including ion–ion interactions that will allow for accurate description of dense, mixed brines. Methods will need to be devised that go beyond the use of effective potentials for incorporation of quantum effects known to be important for water, and reactive force fields developed that can handle bond creation and breaking in systems with carbonate and silicate minerals. Another area of potential future work is the integration of molecular simulation methods in multiscale models for the chemical reactions leading to mineral dissolution and flow within the porous media in underground formations.



### 1. INTRODUCTION

As stated several times in this special issue, burning of fossil fuels transfers carbon from geologic storage to the atmosphere and oceans, causing global climate change and ocean acidification. A potential countermeasure is to capture carbon and return it underground.<sup>1,2</sup> In order to be able to design such geologic carbon storage (GCS) processes that sequester CO<sub>2</sub> in subsurface rock formations for sufficiently long periods of time, many different kinds of properties are needed. Other papers in this volume deal with CO<sub>2</sub>–water–mineral wetting and mineral reaction kinetics; in this Account, we focus on thermodynamic and transport properties of the fluid phases, specifically CO<sub>2</sub> and aqueous electrolyte solutions.

The main properties of interest are pressure–volume–temperature relationships,<sup>3,4</sup> number and composition of phases present, interfacial tensions, and transport properties such as viscosities and diffusivities. Volumetric properties and solubilities determine the storage capacities within the pore space of geologic formations. Interfacial tensions influence capillary phenomena and lead to preferential wetting of solid substrates. Viscosities determine the rate of flow through narrow constrictions for a given pressure drop, while diffusivities control the migration of CO<sub>2</sub> to different locations within a formation.

Received: December 16, 2016

Published: February 24, 2017

Experimental data exist for many of these properties,<sup>5</sup> but cover only a limited number of temperatures, pressures, and compositions. Molecular modeling methods aim to provide reliable methods for filling-in gaps in experimental measurements. In many cases, conflicting experimental results have been reported for important properties—a well-known example relevant for GCS is the discrepancies in phase composition for the CO<sub>2</sub>/H<sub>2</sub>O system between 423 and 523 K.<sup>3</sup> While simulations are not usually thought of as capable of discriminating among conflicting experimental data sets, there are cases (e.g., for critical parameters of long alkanes,<sup>6</sup> or for solubilities of long hydrocarbons in water<sup>7</sup>) for which they have been used in this way because they are immune to experimental artifacts (e.g., decomposition of long alkanes at high temperatures, presence of impurities for solubility measurements).

In the present Account, we briefly review current molecular models for water, CO<sub>2</sub>, and electrolytes that are used for quantitative modeling of thermodynamic and transport properties of the fluid phases relevant to GCS processes. Despite the large amount of prior work, we find that existing models have significant limitations in terms of accuracy or range of applicability. However, we are optimistic that a new generation of models with improved physical characteristics, specifically taking into account polarizability and hydrogen bonding in the systems of interest, can soon achieve a comprehensive description of the relevant systems. Extensions of the models to include surface interactions should be high priority for future work.

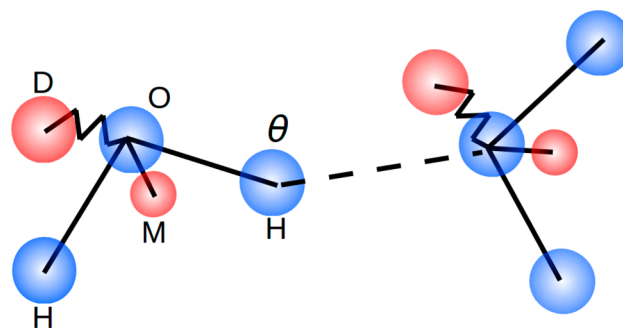
## 2. MOLECULAR MODELS

The accuracy of molecular simulations depends on the underlying molecular models, specifically the description of intra- and intermolecular interactions for the systems of interest. In this review, we focus on classical atomistic molecular models, which use interaction sites and functional forms of interaction potentials to represent the effective interactions, since the properties of interest require sampling at length and time scales inaccessible for *ab initio* methods that explicitly include electronic degrees of freedom. Complex water and CO<sub>2</sub> models<sup>8,9</sup> that give an accurate representation of pair interactions are also too demanding computationally for the routine calculation of the properties of interest here. Intramolecular degrees of freedom (e.g., bond vibrations and bending) are usually not included in simple models since their effects on the properties of interest is small. Molecular models reviewed here cannot represent the effects of pH on thermophysical properties of CO<sub>2</sub>/brine system.

Water has received much attention in the simulation community for several decades now. For most simple water models interactions are represented by the Lennard–Jones (LJ) potential, while the exponential term of the Buckingham potential is more realistic for the short-ranged repulsions at small intermolecular separations.<sup>10</sup> The properties of water models are strongly affected by their dipoles and any induced dipoles, since electrostatic interactions are essential to the proper description of real water. The dipole moment of an isolated water molecule is 1.85 D; however, this value increases to 2.2–2.9 D in the liquid phase, and to 3.1 D in hexagonal ice. Widely used rigid, fixed-point-charge water models, such as SPC/E<sup>11</sup> and TIP4P/2005<sup>12</sup> have dipole moments around 2.35 D because they were parametrized to properties of condensed phases. Thus, these models do not respond to changes of the dielectric environment and have significant limitations when

modeling properties of water and aqueous systems over a wide range of conditions.<sup>13</sup> Both SPC/E and TIP4P/2005 significantly underestimate the second virial coefficient and vapor pressure of pure water.

An important piece of physics that is omitted in many common water models is polarizability, a many-body electrostatic interaction, primarily because of its computational cost and complexity. Polarizability in simulations is often handled by Drude oscillators or induced dipoles/multipoles (which may also be effectively replaced with Drude oscillators<sup>14</sup>). In Drude oscillator models, a massless charge site (shell) is attached to the polarizable atom (core) using a harmonic spring with zero equilibrium length, and the trajectory of shell charges during a simulation is obtained by finding positions where electrostatic forces on shell charges are balanced by the spring forces. There are several polarizable models for water; two models, namely, BK3<sup>15</sup> and GCPM,<sup>16</sup> are of particular interest to GCS because of their good representation of vapor–liquid equilibria and other thermophysical properties, including the dielectric constant, interfacial tension and viscosity. Although polarizable models generally yield better properties, some intermolecular interactions in water and aqueous mixtures, such as charge transfer and hydrogen bonding, may still not be described properly. Recently, we proposed a hydrogen bonding polarizable potential model (HBP)<sup>17</sup> for water containing a short-ranged directional hydrogen bonding term to account explicitly for the effect of charge transfer during hydrogen bonding. A schematic representation of the HBP model is given in Figure 1. The model predicts satisfactorily several water properties



**Figure 1.** Schematic representation of the HBP water model.<sup>17</sup> “O”, “M”, “H”, and “D” stand for oxygen, dummy, hydrogen atoms, and Drude charge, respectively. The angle between the oxygen accepting the hydrogen bond, the hydrogen, and the oxygen donating to the hydrogen bond is  $\theta$ . The dashed line indicates the hydrogen bonding interaction and the zigzag line the harmonic spring. Reproduced with permission from ref 17. Copyright 2016 American Chemical Society.

over a wide range of temperatures and pressures, including vapor–liquid equilibrium, dielectric constant, density of supercritical water, viscosity and self-diffusion coefficient. It is less satisfactory for the second virial coefficient and minimum energy of gas phase water dimer, possibly due to its neglect of quantum effects at low temperature. The models reviewed here cannot represent accurately isobaric heat capacity also due to the neglect of quantum effects.

Molecular models of ions are usually developed in conjunction with one or more specific water models. Examples of commonly used ion models include those of Joung and Cheatham (JC)<sup>18</sup> for aqueous alkali halides, modeled as LJ spheres plus point charges, for use in conjunction with several nonpolarizable water models. Kiss and Baranyai<sup>19</sup> developed a

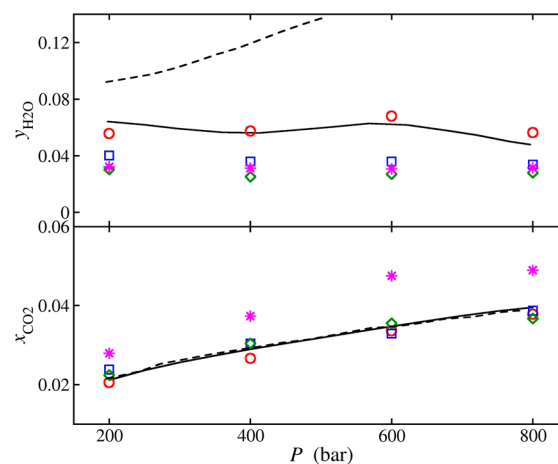
set of polarizable molecular models (AH/BK3) for alkali halide ions in conjunction with the polarizable BK3 water model. Even for the most commonly studied salt, NaCl, the performance of existing models with respect to prediction of thermodynamic properties of electrolyte solutions is not entirely satisfactory. For example, nonpolarizable ion models generally fail to represent the mean ionic activity coefficient of NaCl solutions at room temperature, with the exception of the model by Gee et al.<sup>20</sup> Introducing polarizability into ion models improves the representation of properties for aqueous solutions.<sup>21</sup> The polarizable BK3-AH/BK3 models are accurate for activity coefficient of NaCl at 298.15 K, but not at elevated temperatures. Solubility of salts in water is of great interest for geothermal applications. To the best of our knowledge, current ion models do not predict the solubility accurately, even when polarizability is included. Nezbeda et al.<sup>10</sup> has provided a comprehensive review of recent progress in development of molecular models for aqueous electrolytes.

Various molecular models have been developed for CO<sub>2</sub>. One of the most successful is the EMP2 model of Harris and Yung,<sup>22</sup> which treats CO<sub>2</sub> as a linear molecule with 3 LJ sites and point charges. The TRAPPE model,<sup>23</sup> which is also widely used, can be viewed as a reparameterization of EPM2. Merker et al.<sup>24</sup> used LJ sites plus point quadrupole to model CO<sub>2</sub>, and the model shows excellent agreement with experiments for vapor–liquid equilibrium. Polarizable models have also been proposed, even though CO<sub>2</sub> does not have a net dipole moment. Polarizability effects are more pronounced when CO<sub>2</sub> is mixed with polar components, such as water. We have proposed a polarizable model that uses a Buckingham potential, Gaussian charges, and Drude oscillators to represent the intermolecular interactions of CO<sub>2</sub>.<sup>25</sup> The model gives satisfactory prediction of thermodynamic and transport properties, while the second virial coefficient of CO<sub>2</sub> is overestimated at low temperatures due to the inadequate handling of three-body interactions.<sup>26</sup>

### 3. THERMODYNAMIC PROPERTIES

Thermodynamic properties of water–CO<sub>2</sub>–electrolyte systems including phase equilibria, volumetric properties, and interfacial tensions are crucial factors that affect GCS processes. It is challenging to measure the phase compositions at elevated temperatures and pressures, and experimental data show significant discrepancies for the content of water in the CO<sub>2</sub>-rich fluid. Simulations have been conducted to evaluate various molecular models and to discriminate among conflicting experimental data sets. Liu et al.<sup>27</sup> studied the phase compositions for the water–CO<sub>2</sub> system using grand canonical Monte Carlo simulations with histogram reweighting and concluded that nonpolarizable water and CO<sub>2</sub> models are inadequate to represent simultaneously both water- and CO<sub>2</sub>-rich phases with conventional combining rules. Vlcek et al.<sup>28</sup> optimized the cross interactions between SPC/E water and EPM2 CO<sub>2</sub> models in order to account for the overpolarization of SPC/E model in CO<sub>2</sub>-rich phase; the representation of CO<sub>2</sub> solubility in water was improved, while the calculated composition for the CO<sub>2</sub> rich phase deviates from experimental data at 348.15 K. Orozco et al.<sup>29</sup> performed Gibbs ensemble Monte Carlo simulations to investigate the phase behavior of water–CO<sub>2</sub> mixtures and concluded that nonpolarizable models, with the exception of an Exponential-6 (exp-6) model, are inadequate for the binary mixture even with cross interactions optimized to the phase compositions. We have recently studied

this mixture using polarizable BK3<sup>15</sup> and GCPM<sup>16</sup> models for water, and the Gaussian charge polarizable model for CO<sub>2</sub>.<sup>25</sup> As shown in Figure 2, even with cross interactions optimized to



**Figure 2.** Phase composition of water–CO<sub>2</sub> at 423 K.<sup>34</sup> Solid and dashed lines are experimental data from Tödheide and Franck<sup>30</sup> and Takenouchi and Kennedy,<sup>35</sup> respectively. Cycles, squares, and diamonds are from the HBP, BK3, and GCP models combined with Gaussian charge CO<sub>2</sub> model, respectively. Stars are results from nonpolarizable SPC/E water and TraPPE CO<sub>2</sub> models.

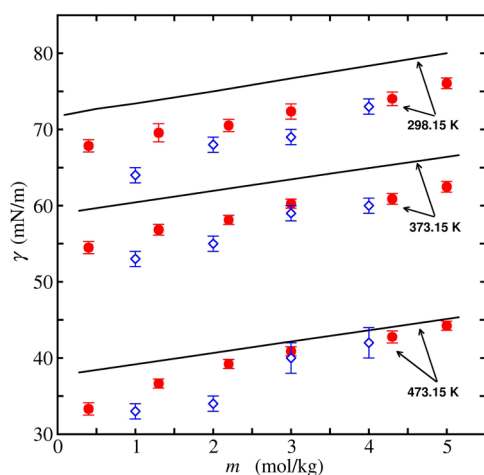
the phase compositions, most models fail to represent properly the composition of the CO<sub>2</sub>-rich phase. For the HBP water model,<sup>17</sup> we considered a hydrogen bonding interaction between water and CO<sub>2</sub>, and the strength of the hydrogen bond was optimized to the cross second virial coefficients of water–CO<sub>2</sub> dimer (but *not* the phase compositions) without considering quantum effects in the second virial coefficient. Phase equilibria predicted from the HBP water and Gaussian charge CO<sub>2</sub> models are in excellent agreement with the data from Tödheide and Franck<sup>30</sup> for both water and CO<sub>2</sub>-rich phases. The validity of the Tödheide and Franck data has also been confirmed by the experimental studies of Mather and Franck.<sup>31</sup>

For the ternary water–CO<sub>2</sub>–NaCl system, Liu et al.<sup>32</sup> conducted molecular dynamics (MD) simulations to investigate different models with respect to their prediction of CO<sub>2</sub> solubility in aqueous NaCl solutions. It was found that predictions are more sensitive to the choice of water and CO<sub>2</sub> models, rather than the ion models. A more detailed analysis of the effect of ion models on the prediction of CO<sub>2</sub> solubility in brine would involve calculation of the Setchenov constant.<sup>33</sup>

Interfacial tensions are key factors for CO<sub>2</sub> residual trapping, which refers to the storage of CO<sub>2</sub> by capillary pressure. It is highly desirable to have an accurate model representing available experimental data at multiple temperatures.<sup>36</sup> As shown in Figure 3, nonpolarizable SPC/E + Smith–Dang models systematically underpredict experimental data by up to 10%.<sup>37</sup> The polarizable AH/BK3 model reduces deviations to ~5% at low salt concentrations.<sup>38</sup> For the ternary water–CO<sub>2</sub>–NaCl, trends for interfacial tensions with respect to temperature, pressure and salt concentration are also in broad agreement with experimental data.<sup>32</sup>

For volumetric (*PVTx*) properties, numerous experimental data exist. Bodnar et al.<sup>3</sup> summarized such data for water–CO<sub>2</sub>–salt at conditions relevant to GCS. Although these





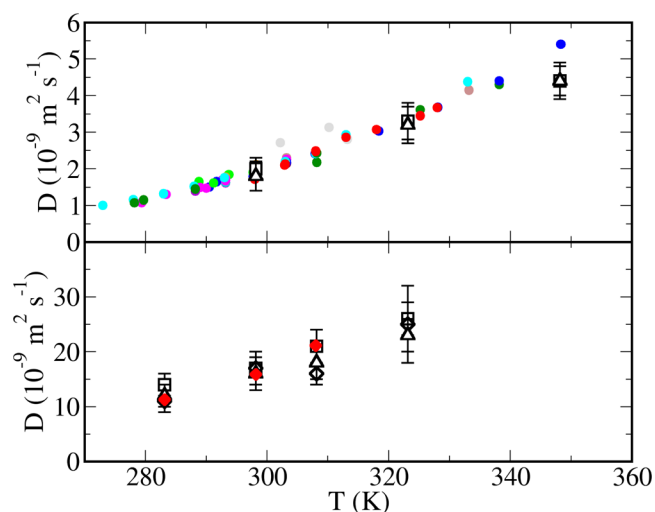
**Figure 3.** Interfacial tension of water–NaCl mixture from 298.15 to 473.15 K. Circles and diamonds are for the polarizable AH/BK3 and nonpolarizable SPC/E + Smith-Dang models, respectively. Solid lines are experimental data.<sup>36</sup>

systems have been extensively studied in the laboratory, important ranges of conditions (especially at high pressures and/or salt concentrations) are still sparsely covered; molecular simulations provide results for these properties to use in interpolations and extrapolations of experimental measurements. For water–CO<sub>2</sub>, data for the density of water saturated with CO<sub>2</sub> are limited despite some recent measurements.<sup>39</sup> With accurate prediction of phase equilibria, molar volumes may be extracted from the HBP water<sup>17</sup> and Gaussian charge CO<sub>2</sub> models.<sup>25</sup> For CO<sub>2</sub> in aqueous NaCl solutions, *PVTx* data are rare at temperatures below 423 K and pressures above 300 bar, typical conditions for CO<sub>2</sub> storage. In addition, experimental studies of the *PVTx* properties are sparse for mixed NaCl–CaCl<sub>2</sub> solutions and synthetic formation brines.<sup>40</sup> The performance of molecular ion models with respect to the representation of *PVTx* properties for CO<sub>2</sub> bearing electrolyte solutions has not yet been fully evaluated.

In addition to molecular simulations, macroscopic thermodynamic models, especially equations of state (EoS), are useful to calculate thermophysical properties of water, CO<sub>2</sub> and brines without the computational cost of molecular simulations. Li et al. used the Soave–Redlich–Kwong equation of state to obtain gas solubilities in brines.<sup>41</sup> Equations of state rooted in statistical mechanics, such as the statistical associating fluid theory (SAFT), were also applied to calculate phase equilibria and volumetric properties of CO<sub>2</sub>–brine mixtures,<sup>42,43</sup> and the recently proposed SAFT2-KMSA model<sup>42</sup> provides accurate prediction for CO<sub>2</sub> solubility in synthetic formation brines.

#### 4. TRANSPORT PROPERTIES

The self-diffusion coefficients,  $D^{\text{self}}$ , for the binary H<sub>2</sub>O + CO<sub>2</sub> mixture were extensively investigated using combinations of nonpolarizable force fields, including SPC, SPC/E and TIP4P/2005 for H<sub>2</sub>O, and EPM2 and TraPPE for CO<sub>2</sub>.<sup>44,45</sup> A comparison of experimental data and MD simulations is presented in Figure 4. The combination TIP4P/2005 for H<sub>2</sub>O with EPM2 for CO<sub>2</sub> provides the best agreement with available experimental data for CO<sub>2</sub>  $D^{\text{self}}$  at temperatures lower than 323.15 K, while SPC/E – TraPPE is more accurate at higher temperatures.<sup>44</sup> For H<sub>2</sub>O  $D^{\text{self}}$ , the TIP4P/2005 with either EPM2 or TraPPE and the exp-6 model are the most accurate.<sup>45</sup>



**Figure 4.** Self-diffusion coefficients at infinite dilution of (top) CO<sub>2</sub> in H<sub>2</sub>O at 0.1 MPa and (bottom) H<sub>2</sub>O in CO<sub>2</sub> at 20 MPa. Filled points are experimental data<sup>48</sup> and open points are MD simulations using TIP4P/2005-EPM2 (squares), TIP4P/2005-TraPPE (triangles), and exp-6 for both H<sub>2</sub>O and CO<sub>2</sub> (diamonds).

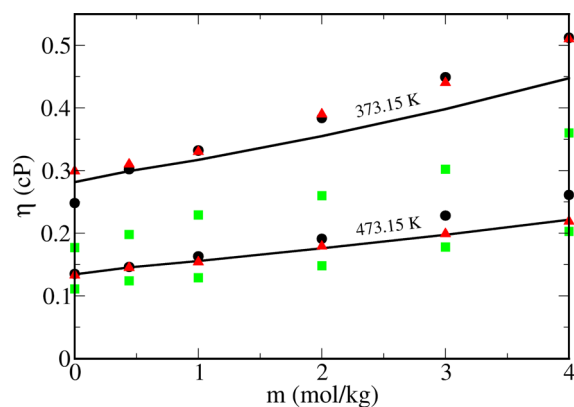
Experimental data are available in the temperature range 273–373 K for the CO<sub>2</sub> diffusivity in H<sub>2</sub>O and 283–308 K for the H<sub>2</sub>O diffusivity in CO<sub>2</sub>. Most measurements are at ambient pressures, with the exception of recent high pressure data by Trusler and co-workers.<sup>46</sup> The pressure effect on self-diffusion coefficient is relatively small for conditions well below the critical point of the solvent. However, near the critical temperature, pressure becomes important. The TIP4P/2005-EPM2 force field was used to predict self-diffusion coefficient data up to 1000 K and 1000 MPa, which are conditions of interest to geological and carbon sequestration applications.<sup>47</sup> Agreement with limited experimental data at 1000 MPa was excellent, in contrast to results from empirical correlations.<sup>47</sup>

Self-diffusion coefficient refers to single molecule diffusion, while Maxwell–Stefan diffusion coefficient,  $D_{\text{MS}}$ , refers to the collective motion of molecules and becomes important at finite solute concentrations. MD simulations for H<sub>2</sub>O in CO<sub>2</sub> revealed a weak composition dependence for  $D_{\text{MS}}$  at various temperatures and pressures.<sup>45</sup>

Addition of NaCl increases the viscosity of H<sub>2</sub>O, as can be seen in Figure 5. Various combinations of nonpolarizable models for H<sub>2</sub>O (SPC, SPC/E and exp-6) and for NaCl (Smith–Dang (SD), JC, and Tosi–Fumi) were examined. It was found that the SPC/E + SD is the most accurate for molalities less than 1 mol/kg, but at higher molalities all models deviate from experiments.<sup>37</sup> Calculations with polarizable models, namely BK3 for H<sub>2</sub>O and AH/BK3 for NaCl, provide accurate predictions for the viscosity at 473.15 K over the entire composition range, up to the solubility limit. As temperature decreases, the model becomes less accurate.<sup>38</sup> The new polarizable force field (HBP) for H<sub>2</sub>O that accounts explicitly for hydrogen bonding interactions<sup>17</sup> is expected to alleviate some of the limitations described above.

#### 5. PROPERTIES UNDER CONFINEMENT

Molecular simulations can provide significant insights and quantitative predictions regarding the structure and properties of fluids in confinement, which are relevant for geologic storage of CO<sub>2</sub>. Calculation of these properties requires special



**Figure 5.** Viscosity of NaCl solutions as a function of molality  $m$  (mol NaCl/kg H<sub>2</sub>O) at 373.15 and 473.15 K. Solid lines are experimental data,<sup>49</sup> and points are MD simulations using SPC/E-SD (solid circles), exp-6 for both H<sub>2</sub>O and NaCl (squares), and BK3-AH/BK3 (triangles).

computational methodologies different from those for bulk fluids. Confinement affects the physical properties (such as critical point, normal boiling point, etc.) of pure fluids and mixtures considerably. Duffy et al.<sup>50</sup> applied positronium annihilation to investigate phase transitions of CO<sub>2</sub> in nanopores. They found that the confined fluid exhibits a triple point at a temperature and a pressure below the bulk triple point. Rivera et al.<sup>51</sup> studied phase equilibria of H<sub>2</sub>O and H<sub>2</sub>O + CO<sub>2</sub> mixtures confined within carbon nanotubes via MD simulations, confirming the lowering of critical temperature and density relative to the bulk. Using MD simulations, Chaban and Prezhdo<sup>52</sup> showed that the boiling temperature of H<sub>2</sub>O confined within carbon nanotubes increases substantially. Billefont et al.<sup>53</sup> studied the adsorption of CO<sub>2</sub> and CH<sub>4</sub> in the presence of H<sub>2</sub>O in carbon nanopores using both experiments and molecular simulations, obtaining fair agreement between the two. Solveyra et al.<sup>54</sup> studied capillary condensation of SPC/E H<sub>2</sub>O and Economou and co-workers studied the structure and dynamic properties of H<sub>2</sub>O–*n*-octacosane mixtures in TiO<sub>2</sub> nanopores using MD simulations.<sup>55</sup> H<sub>2</sub>O adsorbs strongly on TiO<sub>2</sub> and its mobility decreases substantially. Cygan et al.<sup>56</sup> studied CO<sub>2</sub> and H<sub>2</sub>O in the interlayer of montmorillonite clay. Bai et al.<sup>57</sup> have performed simulations of several gases and liquids in silica zeolites. Their force field was parametrized using experimental adsorption isotherms. Brandani and Ruthven<sup>58</sup> have shown that the addition of H<sub>2</sub>O strongly decreases the loading of CO<sub>2</sub> in type X zeolites.

For the transport properties, Hoang and Galliero<sup>59</sup> proposed a scheme to calculate viscosity of a fluid in a narrow pore using a combination of MD and nonequilibrium MD simulations that allows calculation of the configurational viscosity and translational viscosity based on the local average density. Franco et al.<sup>60</sup> proposed an efficient method to calculate the diffusion coefficient for either homogeneous or inhomogeneous fluids using MD simulations, by solving analytically the Smoluchowski equation. It was shown that near the confining wall, the diffusion coefficient of the fluid is anisotropic not only with respect to the perpendicular to the wall component,  $D_{zz}$ , but also for the two components parallel to the wall,  $D_{xx}$  and  $D_{yy}$ .<sup>60,61</sup> For the case of a calcite wall, it was shown that  $D_{yy} > D_{xx}$  for CH<sub>4</sub> and N<sub>2</sub>, because of more free space in the  $y$ -direction of the calcite plane. The opposite holds for CO<sub>2</sub>; the

difference was attributed to the electrostatic interactions between oxygen atoms of CO<sub>2</sub> and Ca<sup>+</sup> ions in calcite.<sup>61</sup> As a result, a CH<sub>4</sub> + CO<sub>2</sub> mixture confined between calcite planes shows significant compositional variation with distance from the planes, with CO<sub>2</sub> concentration being higher closer to the wall. At distances longer than ~10 nm from the wall, the diffusion coefficient becomes isotropic and approaches the bulk value.

Confinement affects also fluid-hydrate phase equilibria. Using molecular simulations, Seo et al.<sup>62</sup> observed that for CO<sub>2</sub> within silica nanopores, the hydrate-liquid–vapor equilibrium lines are shifted to higher pressures compared to the bulk equilibrium conditions, depending on the pore size. Anderson et al.<sup>63</sup> experimentally determined the ice melting and CO<sub>2</sub> clathrate dissociation conditions for nanoporous silica glass, showing that such conditions strongly depend on the pore size.

Macroscopic models in the form of EoS have been used to model the effect of fluid–solid interactions, size of confinement, etc., on the properties of the fluid. Castier and co-workers extended cubic EoS and predicted that under confinement fluids exhibit dual bubble points.<sup>64</sup> Their predictions were verified by recent experimental measurements for *n*-octane and *n*-decane in nanopores.<sup>65</sup> Recently, the approach was generalized to account for different types of external fields applied to fluids.<sup>66</sup>

## 6. SUMMARY AND FUTURE OUTLOOK

The present Account has presented a collection of molecular models developed in recent years that show promise in representing accurately phase compositions and densities, interfacial tensions, and transport properties of fluid mixtures relevant for GCS processes. Newer, polarizable models are able to represent properties over broad ranges of temperature and pressure, and are even capable of discriminating among conflicting experimental data sets. The new models are also likely to be able to be used in the near future for reliable calculation of wetting characteristics in fluid–mineral systems. The CO<sub>2</sub>-induced alterations in the wettability of mineral surfaces can significantly influence residual CO<sub>2</sub> saturation of geological reservoirs.<sup>67</sup>

There are several areas where it is clear that significant additional future research needs to be performed. There is a need for improving the ion models to be used with the new generation of polarizable water models, including ion–ion interactions that will allow for accurate description of dense, mixed brines. Another such area is the systematic generation of force-field parameters (including component cross-interaction and surface-fluid parameters) by utilizing both quantum chemical as well as direct experimental measurements. It will also be important to integrate molecular simulation methods in multiscale packages incorporating quantum chemical calculations for the chemical reactions leading to mineral dissolution, molecular-level calculations of thermodynamic and transport properties as described in the present Account, and large scale reservoir dynamics for the relevant flows within the porous media in the relevant underground formations. In the area of quantum effects, known to be important for water, methods for their explicit incorporation that go beyond the use of effective parameters need to be explored. Finally, the development of reactive force fields that can handle bond creation and breaking in systems with carbonate and silicate minerals would allow calculations over longer time and length scales than is possible with quantum chemical methods.

## ■ AUTHOR INFORMATION

## Corresponding Author

\*E-mail: [azp@princeton.edu](mailto:azp@princeton.edu).

ORCID 

Hao Jiang: 0000-0002-5596-0055

Ioannis G. Economou: 0000-0002-2409-6831

Athanassios Z. Panagiotopoulos: 0000-0002-8152-6615

## Author Contributions

The manuscript was written through contributions of all authors, who also have given approval to the final version of the manuscript.

## Notes

The authors declare no competing financial interest.

## Biographies

**Hao Jiang** received an undergraduate degree in Oil & Gas Transportation and Storage Engineering from China University of Petroleum in 2010 and a Ph.D. in Chemical Engineering from University of Wyoming in 2014. He joined Princeton University as a postdoctoral research associate in 2014.

**Ioannis G. Economou** received an undergraduate degree from the National Technical University of Athens, Greece in 1987 and a Ph.D. from Johns Hopkins University in 1992, both in Chemical Engineering. He held postdoctoral positions in Delft University of Technology and Exxon Research and Engineering. Since 1995, he is a researcher in the National Center for Scientific Research “Demokritos”, in Greece. From 2009 to 2012, he was the Associate Provost at the Petroleum Institute, Abu Dhabi, and since 2013 he is Professor of Chemical Engineering at Texas A&M University at Qatar. He has coauthored more than 160 peer-reviewed publications and 7 book chapters.

**Athanassios Z. Panagiotopoulos** received an undergraduate degree from the National Technical University of Athens in 1982 and a Ph.D. from MIT in 1986, both in Chemical Engineering. After a postdoctoral in Physical Chemistry at Oxford, he held faculty positions at Cornell and the University of Maryland; he is currently the Susan Dod Brown Professor and Department Chair of Chemical and Biological Engineering at Princeton University. He is a member of the U.S. National Academy of Engineering and the American Academy of Arts and Sciences. He is the author of more than 250 technical articles and of the undergraduate textbook “Essential Thermodynamics.”

## ■ ACKNOWLEDGMENTS

This publication was made possible by NPRP Grant Number 6-1157-2-471 from the Qatar National Research Fund (a member of Qatar Foundation). The statements made herein are solely the responsibility of the authors. Additional support was provided by the Office of Basic Energy Sciences, U.S. Department of Energy, under Award DE-SC0002128, and by the Carbon Mitigation Initiative at Princeton University. We would like to thank Othonas A. Moulτος and Luis F.M. Franco for providing input to the manuscript.

## ■ REFERENCES

(1) IPCC. *Special Report on Carbon Dioxide Capture and Storage*; Metz, B., Davidson, O., et al., Eds.; Cambridge University Press: New York, 2005.

(2) Jenkins, C. R.; Cook, P. J.; et al. Safe storage and effective monitoring of CO<sub>2</sub> in depleted gas fields. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, E35–E41.

(3) Bodnar, R. J.; Steele-MacInnis, M.; Capobianco, R. M.; et al. PVTX Properties of H<sub>2</sub>O-CO<sub>2</sub>-“salt” at PTX Conditions Applicable to Carbon Sequestration in Saline Formations. *Rev. Mineral. Geochem.* **2013**, *77*, 123–152.

(4) Steele-MacInnis, M.; Capobianco, R. M.; Dilmore, R.; et al. Volumetrics of CO<sub>2</sub> Storage in Deep Saline Formations. *Environ. Sci. Technol.* **2013**, *47*, 79–86.

(5) Hu, J.; Duan, Z.; Zhu, C.; Chou, I. M. PVTx Properties of the CO<sub>2</sub>-H<sub>2</sub>O and CO<sub>2</sub>-H<sub>2</sub>O-NaCl Systems below 647 K: Assessment of Experimental Data and Thermodynamic Models. *Chem. Geol.* **2007**, *238*, 249.

(6) Siepmann, J. I.; Karaborni, S.; Smit, B. Simulating the Critical Behaviour of Complex Fluids. *Nature* **1993**, *365*, 330–332.

(7) Ferguson, A. L.; Debenedetti, P. G.; Panagiotopoulos, A. Z. Solubility and Molecular Conformations of n-Alkane Chains in Water. *J. Phys. Chem. B* **2009**, *113*, 6405–6414.

(8) Wheatley, R. J.; Harvey, A. H. Intermolecular Potential Energy Surface and Second Virial Coefficients for the Water-CO<sub>2</sub> Dimer. *J. Chem. Phys.* **2011**, *134*, 134309.

(9) Szalewicz, K.; Leforestier, C.; van der Avoird, A. Towards the Complete Understanding of Water by a First-Principles Computational Approach. *Chem. Phys. Lett.* **2009**, *482*, 1–14.

(10) Nezbeda, I.; Moucka, F.; Smith, W. R. Recent Progress in Molecular Simulation of Aqueous Electrolytes: Force Fields, Chemical Potentials and Solubility. *Mol. Phys.* **2016**, *114*, 1665.

(11) Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. The Missing Term in Effective Pair Potentials. *J. Phys. Chem.* **1987**, *91*, 6269–6271.

(12) Abascal, J. L. F.; Vega, C. A General Purpose Model for the Condensed Phases of Water: TIP4P/2005. *J. Chem. Phys.* **2005**, *123*, 234505.

(13) Vega, C.; Abascal, J. L. F. Simulating water with rigid non-polarizable models: a general perspective. *Phys. Chem. Chem. Phys.* **2011**, *13*, 19663–19688.

(14) Chialvo, A. A.; Moucka, F.; Vlcek, L.; Nezbeda, I. Vapor–Liquid Equilibrium and Polarization Behavior of the GCP Water Model: Gaussian Charge-on-Spring versus Dipole Self-Consistent Field Approaches to Induced Polarization. *J. Phys. Chem. B* **2015**, *119*, 5010–5019.

(15) Kiss, P. T.; Baranyai, A. A Systematic Development of a Polarizable Potential of Water. *J. Chem. Phys.* **2013**, *138*, 204507.

(16) Paricaud, P.; Predota, M.; Chialvo, A. A.; Cummings, P. T. From Dimer to Condensed Phases at Extreme Conditions: Accurate Predictions of the Properties of Water by a Gaussian Charge Polarizable Model. *J. Chem. Phys.* **2005**, *122*, 244511.

(17) Jiang, H.; Moulτος, O. A.; Economou, I. G.; Panagiotopoulos, A. Z. Hydrogen-Bonding Polarizable Intermolecular Potential Model for Water. *J. Phys. Chem. B* **2016**, *120*, 12358–12370.

(18) Joung, I. S.; Cheatham, T. E. Determination of Alkali and Halide Monovalent Ion Parameters for Use in Explicitly Solvated Biomolecular Simulations. *J. Phys. Chem. B* **2008**, *112*, 9020–9041.

(19) Kiss, P. T.; Baranyai, A. A New Polarizable Force Field for Alkali and Halide Ions. *J. Chem. Phys.* **2014**, *141*, 114501.

(20) Mester, Z.; Panagiotopoulos, A. Z. Temperature-Dependent Solubilities and Mean Ionic Activity Coefficients of Alkali Halides in Water from Molecular Dynamics Simulations. *J. Chem. Phys.* **2015**, *143*, 044505.

(21) Jiang, H.; Mester, Z.; Moulτος, O. A.; Economou, I. G.; Panagiotopoulos, A. Z. Thermodynamic and Transport Properties of H<sub>2</sub>O + NaCl from Polarizable Force Fields. *J. Chem. Theory Comput.* **2015**, *11*, 3802.

(22) Harris, J. G.; Yung, K. H. Carbon Dioxide’s Liquid-Vapor Coexistence Curve And Critical Properties as Predicted by a Simple Molecular Model. *J. Phys. Chem.* **1995**, *99*, 12021–12024.

(23) Potoff, J. J.; Siepmann, J. I. Vapor–liquid Equilibria of Mixtures Containing Alkanes, Carbon Dioxide, and Nitrogen. *AIChE J.* **2001**, *47*, 1676–1682.

(24) Merker, T.; Engin, C.; Vrabec, J.; Hasse, H. Molecular Model for Carbon Dioxide Optimized to Vapor-Liquid Equilibria. *J. Chem. Phys.* **2010**, *132*, 234512.



- (25) Jiang, H.; Moultois, O. A.; Economou, I. G.; Panagiotopoulos, A. Z. Gaussian-Charge Polarizable and Nonpolarizable Models for CO<sub>2</sub>. *J. Phys. Chem. B* **2016**, *120*, 984–994.
- (26) Yu, K.; Schmidt, J. R. Many-Body Effects Are Essential in a Physically Motivated CO<sub>2</sub> Force Field. *J. Chem. Phys.* **2012**, *136*, 034503.
- (27) Liu, Y.; Panagiotopoulos, A. Z.; Debenedetti, P. G. Monte Carlo Simulations of High-Pressure Phase Equilibria of CO<sub>2</sub>-H<sub>2</sub>O mixtures. *J. Phys. Chem. B* **2011**, *115*, 6629.
- (28) Vlcek, L.; Chialvo, A. A.; Cole, D. R. Optimized Unlike-Pair Interactions for Water–Carbon Dioxide Mixtures Described by the SPC/E and EPM2 Models. *J. Phys. Chem. B* **2011**, *115*, 8775–8784.
- (29) Orozco, G. A.; Economou, I. G.; Panagiotopoulos, A. Z. Optimization of Intermolecular Potential Parameters for the CO<sub>2</sub>/H<sub>2</sub>O Mixture. *J. Phys. Chem. B* **2014**, *118*, 11504–11504.
- (30) Tödheide, K.; Franck, E. U. Das Zweiphasengebie Und Die Kritische Kurve Im System Kohlenoxid-Wasser Bis Zu Drucken Von 3500 bar. *Z. Phys. Chem.* **1963**, *37*, 387–401.
- (31) Mather, A. E.; Franck, E. U. Phase Equilibria in the System Carbon Dioxide-Water at Elevated Pressures. *J. Phys. Chem.* **1992**, *96*, 6.
- (32) Liu, Y.; Lafitte, T.; Panagiotopoulos, A. Z.; Debenedetti, P. G. Simulations of vapor-liquid phase equilibrium and interfacial tension in the CO<sub>2</sub>-H<sub>2</sub>O-NaCl system. *AIChE J.* **2013**, *59*, 3514–3522.
- (33) Pawlikowski, E. M.; Prausnitz, J. M. Estimation of Setchenow Constants for Nonpolar Gases in Aqueous Solutions of Common Salts at Moderate Temperatures. *Ind. Eng. Chem. Fundam.* **1983**, *22*, 86–90.
- (34) Jiang, H.; Economou, I. G.; Panagiotopoulos, A. Z. Phase Equilibria of Water/CO<sub>2</sub> and Water/*n*-Alkane Mixtures from Polarizable Models. *J. Phys. Chem. B* **2017**, *121*, 1386.
- (35) Takenouchi, S.; Kennedy, G. C. The Binary System H<sub>2</sub>O-CO<sub>2</sub> at High Temperatures and Pressures. *Am. J. Sci.* **1964**, *262*, 1055–1074.
- (36) Abramzon, A. A.; Gaubert, R. D. Surface-Tension of Salt-Solutions. *Russ. J. Appl. Chem.* **1993**, *66*, 1473–1480.
- (37) Orozco, G. A.; Moultois, O. A.; Jiang, H.; Economou, I. G.; Panagiotopoulos, A. Z. Molecular Simulation of Thermodynamic and Transport Properties for the H<sub>2</sub>O + NaCl System. *J. Chem. Phys.* **2014**, *141*, 234507.
- (38) Jiang, H.; Mester, Z.; Moultois, O. A.; Economou, I. G.; Panagiotopoulos, A. Z. Thermodynamic and Transport Properties of H<sub>2</sub>O + NaCl from Polarizable Force Fields. *J. Chem. Theory Comput.* **2015**, *11*, 3802–3810.
- (39) Hu, Q. C.; Guo, H. R.; Lu, X. B.; Lu, W. J.; Chen, Y.; Zhu, Y.; Geng, L. T. Determination of P-V-T-x Properties of the CO<sub>2</sub>-H<sub>2</sub>O System up to 573.15 K and 120 MPa-Experiments and Model. *Chem. Geol.* **2016**, *424*, 60–72.
- (40) Zhao, H.; Dilmore, R.; Allen, D. E.; Hedges, S. W.; Soong, Y.; Lvov, S. N. Measurement and Modeling of CO<sub>2</sub> Solubility in Natural and Synthetic Formation Brines for CO<sub>2</sub> Sequestration. *Environ. Sci. Technol.* **2015**, *49*, 1972–1980.
- (41) Li, J.; Toppoff, M.; Fischer, K.; Gmehling, J. Prediction of Gas Solubilities in Aqueous Electrolyte Systems Using the Predictive Soave-Redlich-Kwong Model. *Ind. Eng. Chem. Res.* **2001**, *40*, 3703–3710.
- (42) Jiang, H.; Panagiotopoulos, A. Z.; Economou, I. G. Modeling of CO<sub>2</sub> Solubility in Single and Mixed Electrolyte Solutions using Statistical Associating Fluid Theory. *Geochim. Cosmochim. Acta* **2016**, *176*, 185–197.
- (43) Sun, R.; Dubessy, J. Prediction of Vapor-Liquid Equilibrium and PVTx Properties of Geological Fluid System with SAFT-LJ EOS Including Multi-Polar Contribution. Part I: Application to H<sub>2</sub>O-CO<sub>2</sub> System. *Geochim. Cosmochim. Acta* **2010**, *74*, 1982–1998.
- (44) Moultois, O. A.; Tsimpanogiannis, I. N.; Panagiotopoulos, A. Z.; Economou, I. G. Atomistic Molecular Dynamics Simulations for CO<sub>2</sub> Diffusivity in H<sub>2</sub>O for a Wide Range of Temperatures and Pressures. *J. Phys. Chem. B* **2014**, *118*, 5532–5541.
- (45) Moultois, O. A.; Orozco, G. A.; et al. Atomistic Molecular Dynamics Simulations for H<sub>2</sub>O Diffusivity in Liquid and Supercritical CO<sub>2</sub>. *Mol. Phys.* **2015**, *113*, 2805–2814.
- (46) Cadogan, S. P.; Maitland, G. C.; Trusler, J. P. M. Diffusion Coefficients of CO<sub>2</sub> and N<sub>2</sub> in Water at Temperatures between 298.15 and 423.15 K at Pressures up to 45 MPa. *J. Chem. Eng. Data* **2014**, *59*, 519–525.
- (47) Moultois, O. A.; Tsimpanogiannis, I. N.; Panagiotopoulos, A. Z.; Economou, I. G. Self-Diffusion Coefficients of the Binary (H<sub>2</sub>O + CO<sub>2</sub>) Mixture at High Temperatures and Pressures. *J. Chem. Thermodyn.* **2016**, *93*, 424–429.
- (48) Cadogan, S. P. Diffusion of CO<sub>2</sub> in Fluids Relevant to Carbon Capture, Utilisation and Storage. Ph.D. Thesis, Imperial College London, 2015.
- (49) Phillips, S. L.; Igbene, A.; Fair, J. A.; Ozbek, H.; Tavana, M. A. *Technical Databook for Geothermal Energy Utilization*; Lawrence Berkeley Laboratory, UC Berkeley: Berkeley, CA, 1981.
- (50) Duffy, J. A.; Wilkinson, N. J.; Fretwell, H. M.; Alam, M. A.; Evans, R. Phase Transitions of CO<sub>2</sub> Confined in Nanometer Pores as Revealed by Positronium Annihilation. *J. Phys.: Condens. Matter* **1995**, *7*, L713–L717.
- (51) Rivera, J. L.; McCabe, C.; Cummings, P. T. Layering Behavior and Axial Phase Equilibria of Pure Water and Water + Carbon Dioxide inside Single Wall Carbon Nanotubes. *Nano Lett.* **2002**, *2*, 1427–1431.
- (52) Chaban, V. V.; Prezhdo, O. V. Water Boiling Inside Carbon Nanotubes: Toward Efficient Drug Release. *ACS Nano* **2011**, *5*, 5647–5655.
- (53) Billemont, P.; Coasne, B.; De Weireld, G. An Experimental and Molecular Simulation Study of the Adsorption of Carbon Dioxide and Methane in Nanoporous Carbons in the Presence of Water. *Langmuir* **2011**, *27*, 1015–1024.
- (54) Solveyra, E. G.; Llave, E. D. L.; et al. Structure, Dynamics, and Phase Behavior of Water in TiO<sub>2</sub> Nanopores. *J. Phys. Chem. C* **2013**, *117*, 3330–3342.
- (55) Papavasileiou, K. D.; Makrodimitri, Z. A.; et al. Molecular Simulation of n-Octacosane-Water Mixture in Titania Nanopores at Elevated Temperature and Pressure. *J. Phys. Chem. C* **2016**, *120*, 24743–24753.
- (56) Cygan, R. T.; Romanov, V. N.; Myshakin, E. M. Molecular Simulation of Carbon Dioxide Capture by Montmorillonite Using an Accurate and Flexible Force Field. *J. Phys. Chem. C* **2012**, *116*, 13079–13091.
- (57) Bai, P.; Tsapatsis, M.; Siepmann, J. I. TraPPE-zeo: Transferable Potentials for Phase Equilibria Force Field for All-Silica Zeolites. *J. Phys. Chem. C* **2013**, *117*, 24375–24387.
- (58) Brandani, F.; Ruthven, D. M. The Effect of Water on the Adsorption of CO<sub>2</sub> and C<sub>3</sub>H<sub>8</sub> on Type X Zeolites. *Ind. Eng. Chem. Res.* **2004**, *43*, 8339–8344.
- (59) Hoang, H.; Galliero, G. Local Viscosity of a Fluid Confined in a Narrow Pore. *Phys. Rev. E* **2012**, *86*, 021202.
- (60) Franco, L. F. M.; Castier, M.; Economou, I. G. Diffusion in Homogeneous and in Inhomogeneous Media: A New Unified Approach. *J. Chem. Theory Comput.* **2016**, *12*, 5247–5255.
- (61) Franco, L. F. M.; Castier, M.; Economou, I. G. Anisotropic Parallel Self-Diffusion Coefficients Near the Calcite Surface: A Molecular Dynamics Study. *J. Chem. Phys.* **2016**, *145*, 084702.
- (62) Seo, Y.; Lee, H.; Uchida, T. Methane and Carbon Dioxide Hydrate Phase Behavior in Small Porous Silica Gels: Three-Phase Equilibrium Determination and Thermodynamic modelling. *Langmuir* **2002**, *18*, 9164–9170.
- (63) Anderson, R.; Llamedo, M.; Tohidi, B.; Burgass, R. W. Experimental Measurement of Methane and Carbon Dioxide Clathrate Hydrate Equilibria in Mesoporous Silica. *J. Phys. Chem. B* **2003**, *107*, 3507–3514.
- (64) Travalloni, L.; Castier, M.; Tavares, F. W.; Sandler, S. I. Thermodynamic Modeling of Confined Fluids Using an Extension of the Generalized van der Waals Theory. *Chem. Eng. Sci.* **2010**, *65*, 3088–3099.
- (65) Luo, S.; Nasrabadi, H.; Lutkenhaus, J. L. Effect of Confinement on the Bubble Points of Hydrocarbons in Nanoporous Media. *AIChE J.* **2016**, *62*, 1772–1780.

(66) Dawass, N.; D'Lima, M. L.; Economou, I. G.; Castier, M. Phase Equilibrium with External Fields: Application to Confined Fluids. *J. Chem. Eng. Data* **2016**, *61*, 2873–2885.

(67) Bourg, I. C.; Beckingham, L. E.; DePaolo, D. J. The Nanoscale Basis of CO<sub>2</sub> Trapping for Geologic Storage. *Environ. Sci. Technol.* **2015**, *49*, 10265–10284.