Investigation into stability and interfacial properties of CO₂ hydrate–aqueous fluid system

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ARTICLE INFO

Keywords:
Carbon dioxide hydrate
Carbon dioxide
Water
Molecular modeling

ABSTRACT

We applied the techniques of Molecular Dynamics (MD) to study the structural and dynamic properties of a stable interface between CO₂ hydrate and aqueous solution. The steady-state interface thickness was evaluated from a set of criteria, with the decay of hydrogen signature being the leading one. Applying the criteria has yielded an interface width of about 10 Å.

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1. Introduction

Clathrate hydrates of natural gases are ice-like structures composed of water molecules encaging guest gas molecules. The list of gas molecules capable of forming clathrate hydrates is extensive and includes a number of abundant compounds, from light hydrocarbons to refrigerants to sour gases like carbon dioxide and hydrogen sulfide. Under conditions typical for oil and gas production and transport in colder climates, clathrate hydrates can easily form in pipelines and production equipment.

2. Simulation protocol—Details

2.1. Molecular Dynamics

Our MD routine used the MDynaMix package of Lyubartsev and Laaksonen [1] with an explicit reversible integrator for NPT-dynamics of Martyna et al. [2], modified by us to implement implicit quaternion treatment of rigid molecules with the Nosé–Hoover thermostat for temperature and pressure [3–5]. Time step was set to 1 fs. The system was kept at a constant temperature of 240 K and a pressure of 20 MPa by means of the Nosé–Hoover thermostat and barostat, with the MD box allowed to fluctuate in all three directions. Our particular choice of temperature was dictated by a desire to obtain a hydrate–liquid system reproducing the real-life conditions characteristic of CO₂ storage hydrate on the ocean floor, given the specifics of the water model. Bryk and Haymet [6] found that the stable ice–water interface of SPC/E water lies in the vicinity of 225 ± 10 K. Thus the chosen value of 240 K represented a temperature of about 5° above the model-specific freezing point, and should ensure the liquidity of water. On the other hand, the point of +5 °C and 20 MPa is known to fall within the stability limits of the CO₂ hydrate [7], and we expected the simulations to yield a relatively stable hydrate–liquid interface.

Both experimental and modeling data indicate a substantial surface tension in the hydrate–liquid system. Therefore, only tangential components of pressure tensor were used to evaluate and control the pressure. Electrostatic interactions were handled by Ewald summation techniques with a variable number of reciprocal vectors, while a spherical cutoff of

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doi:10.1016/j.mcm.2009.08.007
11.0 Å was utilized for the short-range forces. Linux-based Message Passing Interface (MPI) was used to implement parallel computation on a cluster of dual-processor machines.

2.2. Simulation system setup, equilibration, and forcefields

The hydrate part of our system comprised a block of structure I [8,9] carbon dioxide hydrate made of $2 \times 2 \times 11$ unit hydrate cells (2024 SPC/E water [10] and 264 three-site CO$_2$ [11] molecules). Despite being a fairly simple fixed-charge model, SPC/E water model has proven to reproduce both structural and thermodynamic properties of liquid water with a notable degree of success and perform on the par with much more sophisticated (and computationally expensive) polarizable models [12,13]. Moreover, it works well in conjunction with the Harris and Yung carbon dioxide model we chose [14].

The hydrate structure was generated as a perfect equilibrated periodic hydrate crystal arbitrary broken in two (to facilitate possible melting) and brought into contact with a pre-equilibrated 40-Å long slab of 795 SPC/E water molecules. The resulting interfacial system ranged about 170 Å in length. Periodic Boundary Conditions were applied in all three directions. After being stacked together, the translational degrees of motion were switched off for all the molecules to overcome perturbations due to possible overlaps at the interface. The molecules were then allowed to move freely. The total simulation time comprised a 1 ns-long NPT equilibration at desired temperature and pressure followed by 4 million steps (4 ns) of production run at constant temperature and pressure.

3. Results and discussion

3.1. Density profiles and hydrate stability

The density profiles of $x$–$y$ averaged quantities of interest were generated by partitioning the simulation box into discrete bins in the $z$ direction. The atomic density profile for atom of type $i$ was thus obtained by

$$\rho_i(z) = \frac{\langle m_i N_i(z) \rangle}{A \Delta z},$$

where $N_i$ is the number of $i$-type atoms in a slab located between $z$ and $z + \Delta z$, $A$ is the cross-section area, $A = L_x L_y$, $m_i$ is the atom's mass, $\Delta z$, the slab's width. Varying the binning width in 0.095–0.475 Å range did not affect the profiles in any significant way. On the other hand, results obtained using coarser grids show a rather dramatic binning dependence. For instance, a definite additional long-range “hydrate” structure starts to emerge in case of 0.634 Å spacing (270 bins) and wider ones. This structure becomes quite obvious in case of 90 bins (1.9 Å-wide bin). The “sine” behavior of the envelopes was persistent but definitely not stationary.

A sequence of time-averaged liquid–hydratedensity profiles was obtained using 450 and 90 bins sectioning. Figs. 1 and 2 present unfiltered 450 bin density profiles taken throughout the production run. Each figure is an average over a hundred snapshots taken every 0.1 ps. The starting averaging points are 10 ps apart. The total production run used to evaluate hydrate–liquid system behavior amounted to 4.0-plus ns. Comparison between the 450 and 90 bin pictures shows some substantial differences even in the behavior of “envelopes” themselves. It underlines the fact that neither coarse-grain nor fine-grain profile envelope are capable of describing (or even defining) the interface on their own.

As noted, we wanted to study a steady-state interface between carbon dioxide hydrate and an aqueous solution. Our previous simulations led us to conclude that temperatures above 260 K lie outside the model-specific stability limit of CO$_2$ hydrate. As for the chosen temperature of 240 K, the analysis of hydrate interface dynamics (Figs. 1 and 2) has revealed a quick destruction of disrupted cages, followed by the dissolution of two high peaks belonging to the next hydrate layer. This process took roughly 700 ps of the simulation time (Fig. 1), and the remaining hydrate proved to be stable throughout the rest of the run (4 ns). This stable hydrate structure comprised 18 high and 18 low peaks of “hydrate-quality” and one each low and high interfacial peak. The interfacial peaks are characterized by significantly decreased amplitude and weakened hydrogen signature.

3.2. Interface width

Our estimate of the interface width was based on the analysis of all of the datasets. It is our belief that the density-profile envelopes are not completely reliable since they reflect not only the interfacial phenomena but long-range oscillations as well, thus causing a perceived broadening of the interface. We have used the structural differences between the liquid phase and the hydrate to isolate the transitional region where the crystal ordering makes way for the liquid disorder. And even though the analysis of plain density profiles is complicated by the CO$_2$ diffusing away from the interface and into the water bulk, applying a composite criteria allows to distinguish between features characteristic for water molecules encaging a CO$_2$ guest molecule and those of carbon dioxide molecule dissolved in water. Fig. 3 presents several of structural details specific to hydrates only. The hydrogen density proved to be an especially useful hydrate marker, since its hydrate profile features a distinctive triple-peak structure, with the central hydrogen peak coinciding with the lower carbon density peak.
Fig. 1. Density profiles. 0.73 ns elapsed after the start of the simulation. Full lines—fine-scale densities for individual atoms. Dashed lines—summed up fine-scale densities of water and CO$_2$ molecules. Blue—hydrogen in either liquid or hydrate. Cyan—water oxygen in either liquid or hydrate. Red—CO$_2$ oxygen. Magenta—CO$_2$ carbon. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. Density profiles. 3.73 ns elapsed after the start of the simulation. See Fig. 1 for conventions.

and hydrate oxygen valley. This hydrogen signature is totally absent in both liquid water and water–CO$_2$ mixtures, so one can define the interface as the transition length along which the triple-peak feature decays from the one characteristic for bulk to non-existent (in combination with other criteria).

Another hydrate-structure marker is supplied by the positioning of water-oxygen valleys relative to the carbon peaks. In general, we found that the density profiles of CO$_2$’s carbon provided the better idea of the guest behavior, therefore we will concentrate on carbon rather than oxygen guest profiles. The regular succession of alternating high and low peaks evident in Fig. 3 is a typical feature of Structure I carbon dioxide hydrate when it is projected on a given direction; the water-oxygen valleys flank the high peaks and coincide with the low ones. The latter valleys vary in depth throughout the whole of the hydrate crystal; these long-range envelope oscillations can be clearly seen in coarse-grain density profiles.

The steady-state interface thickness was evaluated from a set of criteria, with the decay of hydrogen signature being the leading one, so it is not a straightforward “10–90” value of the classical vapor–liquid interface evaluations. The other criteria included the correct alignment of the lower carbon peak and its corresponding hydrogen maximum, as well as the roughly equivalent depth of water-oxygen valleys that flank the higher carbon peak. A good example of these features as in their undisturbed hydrate crystal state are present as Items 1 to 3 in Fig. 3, while Items 4 and 5 show their deterioration in the interfacial area. Applying the criteria has yielded an interface width of about 10 Å. This estimate is close to the value deduced
Fig. 3. Items 1 to 5 point out hydrate structural markers (see text for further details and Fig. 1 for conventions).

from the envelopes of fine-scale density profiles; so even though the interface profiles (especially the coarse-grained ones) might look broader, our analysis of structural details points to a narrower interface.

References