Molecular and Macroscopic Modeling of CO_2-Hydrate Formation and Dissolution

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Abstract

As a first step in developing a consistent macroscopic approach to accurately predict the dispersion of CO_2 in the ocean, we describe a methodology to calculate the rate of nucleation of CO_2 hydrate at the CO_2/H_2O interface, using classical molecular simulations. We find the lower and upper bound to the critical size of the CO_2 hydrate nucleus, that leads to the spontaneous growth of the hydrate phase at the interface. Based on our preliminary calculation of the free-energy of the system, it appears that the labile cluster hypothesis [D. Sloan, Clathrate Hydrates, (Marcel Dekker, NY, 1998) Ch. 3] is unlikely to be the mechanism for nucleation. Instead, we propose a local structuring mechanism wherein the formation of the critical nucleus is preceeded by a local geometrical arrangement of CO_2 molecules which is stabilized by the presence of the surrounding water molecules. It is proposed that the hydrate grows spontaneously if the cluster size of this arrangement of molecules exceeds the critical cluster size.

I. INTRODUCTION

The viability of ocean storage as a green house gas mitigation option is a topic of ongoing research and debate. Ocean represents the largest potential sink for anthropogenic CO_2. Environmental impacts and economics are the driving factors in determining the acceptability of ocean sequestration of CO_2. In order to accurately predict and asses the ecological ramifications due to the proposed scheme, a multi-scale modeling and understanding of the CO_2 sequestration process is necessary: (a) Physical-chemical interactions of CO_2 and sea-water-The hydrate formation at the CO_2/H_2O interface, and its effect on the diffusion and mass transfer between CO_2 and sea water. (b) The fluid dynamics of CO_2 droplets and plumes. (c) Fate of the CO_2 hydrate and the CO_2 dissolved in sea water.

Several theoretical and experimental approaches have been undertaken in the past in order to address these issues ([1] and refs. therein, [2–6]). Inspite of these efforts there does not exist a quantative and predictive model that accurately estimates the dispersion of CO_2 in the ocean under varying conditions (e.g., T, P, flow conditions). The main draw back of the existing macroscopic models [1], has been the lack of understanding of the physico-chemical interactions in the sequestration process at a molecular level; in order to circumvent this difficulty, the models assumed hypothetical constructs that were not carefully validated using experiments. Further, it was impossible to relate the model parameters to experimental measurements nor to thermo-physical and transport data.

Our primary objective is to construct a macroscopic model for estimating the dispersion of CO_2 in the ocean, that is consistent with the molecular level picture. Our approach is as follows: we begin with a molecular model for CO_2 and H_2O. The first goal is to develop a methodology wherein we calculate the physical-chemical properties (nucleation rate, diffusion rate etc.) for the assumed molecular model. The calculated physical-chemical properties, along with experimental measurements, will be the input to our macroscopic model. Since the molecular model parameters will be chosen to reproduce the experimentally measured thermo-physical and transport properties, the resulting macroscopic model will be (a) consistent with the molecular picture, (b) consistent with experiments, (c) self-consistent, and more importantly, (d) retain a predictive ability. In this paper, we focus on relating the molecular model parameters to the nucleation rate of CO_2 hydrate at the CO_2/H_2O interface. In section II we describe our molecular model and methodology to calculate the desired properties, our results are described in section III and we give our conclusions along with a description of ongoing and future work in section IV.

II. METHODOLOGY

We perform Monte Carlo simulations in the isothermal, isobaric ensemble for the CO_2-H_2O system. The intermolecular potential for water is modelled using the TIP4P potential and that for CO_2 is modeled using the EPM model (see for e.g., [7]). The calculated thermo-physical properties using the respective models are in very close agreement with the experimental measurements for the pure phases as well as the liquid-mixture [7]. Our system size ranged from a $24\mathring{A}$ cubical box to a $48\mathring{A}$ cubical box and a rectilinear box of $192\mathring{A} \times 24\mathring{A} \times 24\mathring{A}$ for the interface calculation. The temperature and pressure in the simulations were maintained at 225 K and 4 MPa respectively. The TIP4P model water has a freezing temperature of about 220 K, thus the chosen temperature and pressure conditions correspond to 278 K and 4 MPa for real water, which is within the phase bounday of the real CO_2 clathrate. Under these conditions the number of H_2O and CO_2 molecules in the $24\mathring{A}$ box is 368 and 64 respectively. Periodic boundary conditions were applied in all three directions and the method of ewald summation was used to account for the long range electrostatic interactions due to the partial charges of water and CO_2. Typical production runs involved averaging the properties over a billion MC configurations. A Parallel version of the Monte Carlo program was used to simultaneously run on 8-16 processors.

Landau Free Energy method: The method to calculate the free energy relies on the calculation of the Landau free energy as a function of an effective order parameter, Φ, using NPT simulations. The Landau free energy is defined by [8],

$$\Lambda[\Phi] \; = \; -k_B T \; \ln(P[\Phi]) \; + \; \text{constant} \tag{1}$$

where $P[\Phi]$ is the probability of observing the system having an order parameter value between Φ and $\Phi + \delta\Phi$. The probability distribution function $P[\Phi]$ is calculated in a NPT simulation by collecting statistics of the number of occurrences of a particular value of Φ in the form of a histogram, with the help of umbrella sampling [9]. For a particular phase, for instance phase A, the grand free energy Ω_A is related to the Landau free energy by

$$\exp(-\beta\Omega_A) \; = \; \int_{\Phi_{min,A}}^{\Phi_{max,A}} d\Phi \; \exp(-\beta\Lambda[\Phi]) \tag{2}$$

The grand free energy at a particular temperature can be calculated by numerically integrating over the order parameter range ($\Phi_{min,A}$ to $\Phi_{max,A}$) that corresponds to the particular phase A in consideration. The Landau free energy method in conjunction with umbrella sampling is very effective is studying phenomena that occur over much larger timescales, that are otherwise inaccessible to conventional molecular simulations.

III. RESULTS

The CO_2/H_2O interface: It is known experimental fact that the CO_2 hydrate nucleates at the CO_2/H_2O interface. Thus, it is important to understand the nature of interface. The interface was equilibrated by sandwiching a CO_2 phase (saturated with water) between two H_2O phases (saturated with CO_2). The system size was chosen to be $192\mathring{A} \times 24\mathring{A} \times 24\mathring{A}$. The variation of the molefraction CO_2 across the interface was calculated and is shown in figure 1. Due to the hydrophobic nature of the CO_2 molecules, the interface is sharp, i.e., the variation of the mole fraction across the interface occurs in the range of $5\mathring{A}$. It is worthwhile to note that in such a narrow length scale, X_{CO_2} decreases from $\simeq 1.0$ to $\simeq 0.0$, passing through $X_{CO_2} = 0.14$ (the molefraction of CO_2 in a clathrate with all cages occupied).

Hydrate cluster implant and growth: In order to estimate the size of the critical nucleus of the CO_2 hydrate that leads to the spontaneous growth of the hydrate phase at the interface, we implanted clusters of different sizes in a CO_2+H_2O solution ($X_{CO_2} = 0.14$) and let the system equilibrate. We note that such a high concentration of CO_2 is only found near the interface as discussed previously. The interface between the implanted cluster and the liquid mixture was relaxed by energy minimization, prior to performing the Monte Carlo runs. A total of one billion MC steps were performed for each cluster size during which the size of the implanted cluster was monitored. The results for two different sizes of the implanted cluster are shown in figures 2 and 3. As the system evolved, the implanted cluster of dimension $24\mathring{A}$ grew in size, while an implanted cluster of $12\mathring{A}$ diminished in size and disintegrated into solution. From these results we conclude that the critical nucleus size for the formation of the CO_2 hydrate phase lies in between $12\mathring{A}$ and $24\mathring{A}$. This result is consistent with the estimate of the critical cluster size for methane hydrate previously reported by Baez and Clancy [10]. The significance of the bounds for the size of the critical nucleus is apparent when we compare the values to the critical cluster size of $\simeq 32\mathring{A}$ estimated by Larson and

Garside [11] using classical nucleation theory. The classical nucleation theory over-estimates the size of the critical nucleus for the CO_2 hydrate system.

Nucleation mechanism: The formation of the CO_2 hydrate at the interface is governed by the nucleation time and the rate of growth. The rate of growth can be precisely estimated by monitoring the growth of a cluster that is larger than the critical nucleus, as discussed above. The pre-requisite for claculating the nucleation time (or the rate of nucleation), however, is knowing the correct nucleation mechanism.

Labile Cluster Hypothesis: Sloan [12] proposed "the labile cluster hypothesis" as a viable pathway for nucleation, according to which "labile clusters" (a labile cluster being one CO_2 molecule encaged by 20 or 24 water molecules) move around in the liquid phase. The critical nucleus is formed by the agglomeration of the labile clusters. Although this hypothesis has been proposed more than a decade ago, there have been no theoretical attempts to validate the proposed mechanism. Further, the experiments show evidence of the presence of labile clusters only for very dilute concentrations of the hydrophobic solute. In order to test the labile cluster hypothesis, we define two classes order parameters: the first being the coordination number of a randomly chosen CO_2 molecule (defined as the number of H_2O molecules that are less than a distance r_{nn}, the nearest neighbor distance [1]). A labile cluster is identified as a CO_2 molecule along with the water molecules in its first coordination shell, if the coordination number is greater than or equal to twenty. The second class of order parameters are chosen to be the distance between labile clusters. Some examples of these order parameters are given in figure 5b. In figure 5b, each hexagon filled with the pattern represents a labile cluster. For example, the distance between an agglomerate of four labile clusters and an isolated labile cluster is denoted by L1,2,3,4-L5. Having defined the two classes of order parameters, we calculated the free energy change as a function of these order-parameters by using the Landau free energy method outlined in section II. If the labile cluster hypothesis were to provide the correct nucleation mechanism, then

(a) the formation of the labile cluster would have be either spontaneous, or an activated process **and** the labile cluster would exist as a metastable state (defined as a local minimum in the free energy along the order-parameter coordinate).

(b) Agglomeration of labile clusters would have to be spontaneous, **or** an activated process with a free energy barrier less than that of the stabilization energy of the metastable labile cluster.

Yet, the free energy functions in figure 4 and figure 5a indicate that both of the above criteria are violated. We also note that the the violation of the two criteria are more pronounced as the size of the agglomerate increases and as the concentration of CO_2 in water increases. Therefore we conclude that it is highly unlikely that the CO_2 hydrate nucleation occurs via the labile cluster hypothesis.

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[1]r_{nn} is calculated based on the position of the first peak in the radial distribution function $g_{H_2O\text{-}CO_2}(r)$ for the clathrate

Local Structuring Hypothesis: We propose an alternate hypothesis to describe the mechanism of nucleation. According to the local structuring hypothesis, the formation of the critical nucleus is preceeded by a local geometrical arrangement of CO_2 molecules whose symmetry is the same as that existing in the clathrate. The force field of the water mocules around the local geometry of CO_2 molecules have a stabilizing effect on the local geometry. This stabilization leads to the metastability of the geometrical arrangement. The metastable minimum in the free energy surface associated with the local geometrical arrangement is a function of the size of the geometrical arrangement; the larger the size, the more stable the local arrangement. There is a critical size associated with the the local arrangement of CO_2 molecules for which the system is trapped in the meta-stable state long enough for the clathrate to grow from the cluster. In order to validate this hypothesis, we define a set of geometrical order-parameters to describe the symmetry of the spatial distribution of CO_2 molecules in the clathrate. Among the CO_2 (guest) molecules, nearest neighbors are identified as those molecules that are less than a cutoff distance r_{nn}^{gg} away, from a given guest molecule. We used a cutoff distance based on the position of the first peak of $g_{gg}(r)$ in the clathrate. We then define the order parameter $\overline{Q}_{lm}$,

$$\overline{Q}_{lm} = \frac{1}{N_b} \sum_{i=1}^{N_b} Y_{lm}(\theta_i, \phi_i) \tag{3}$$

where the index i runs over the total number of nearest neighbor bonds N_b and the Y_{lm}'s denote the spherical harmonics. In order that the order parameter does not depend on the overall orientation of the crystal in the simulation cell, rotationally isotropic combinations of the $\overline{Q}_{lm}$'s are defined as,

$$Q_l \equiv \left(\frac{4\pi}{2l+1} \sum_{m=-l}^{+l} \left| \overline{Q}_{lm} \right|^2 \right)^{1/2} \tag{4}$$

and,

$$W_l = \frac{1}{\left(\sum_m \left| \overline{Q}_{lm} \right|^2 \right)^{3/2}} \sum_{m_1, m_2} \begin{pmatrix} l & l & l \\ m_1 & m_2 & -m_1-m_2 \end{pmatrix} \overline{Q}_{lm_1} \overline{Q}_{lm_2} \overline{Q}_{l(-m_1-m_2)} \tag{5}$$

The matrix in equation (5) is a representation of the Wigner $3J$ symbols defined in ref. [13]. The value of these order parameters for the clathrate and the liquid are given in table I.

The Q_i and W_i for $i = 4, 6, 8$ determine the symmetry of the spatial distribution of the guest molecules in the clathrate uniquely. The necessary conditions for the local structuring hypothesis to hold is that the free energy surface must display a local minimum for the set of order parameters $Q_i(n)$ and $W_i(n)$ for $i = 4, 6, 8$ (now the Q's and W's are calculated only for the cluster of n molecules) equal to the value in the clathrate (see table I). The free energy functions shown in figure 6, indeed display such a behavior for a cluster of size 12Å ($n = 8$), thereby giving strong evidence in support of the local structuring hypothesis. The least stable coordinate to thermal fluctuations for this cluster size is the W_4 coordinate for which the metastable well depth is $3k_BT$. It remains to be shown that the metastable state is further stabilized as the size of the cluster increases. Such a result will validate the local structuring hypothesis.

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IV. CONCLUSIONS AND FUTURE WORK

Based on the free energy calculations, our preliminary results indicate that the mechanism of hydrate nucleation is in accord with the local structuring hypothesis. A quantative estimation of the free-energy barrier to nucleation is then be obtained using a path integral method, that samples the six-dimensional guest-guest order-parameter space. The precise free-energy difference between the liquid-phase and the transition state, and the transition state and the hydrate phase can be calculated. Ongoing work in our group involves investigation of a mechanism of diffusion of CO_2 through the clathrate. The nucleation and diffusion rates diffusion will ultimately be used as an input for the macroscopic model for the dispersion of CO_2.

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TABLE I. Guest-Guest Order Parameters in Clathrate

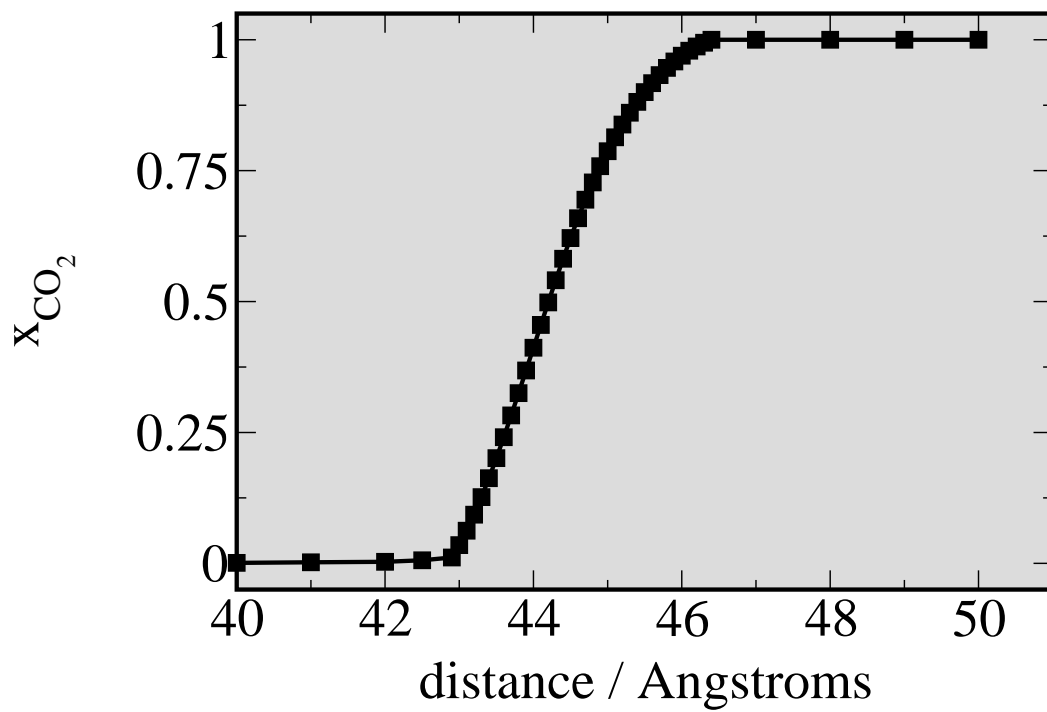| Order Parameter	Clathrate	liquid
Q_4	0.17	0.33
Q_6	0.15	0.33
Q_8	0.17	0.33
W_4	0.13	0.0
W_6	0.0	0.0
W_8	0.0	0.0

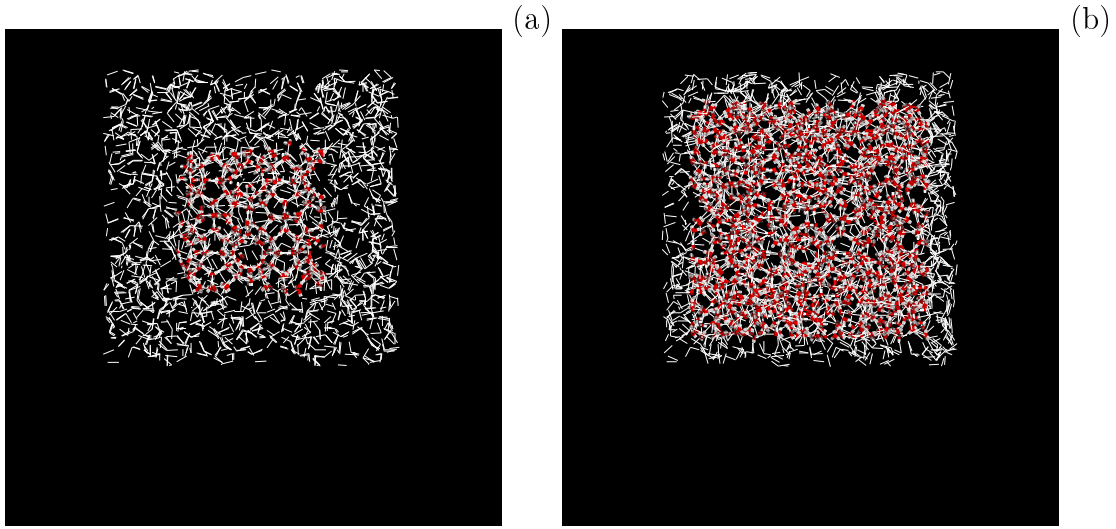FIG. 1. The equilibrium distribution of the mole fraction of CO_2 across the interface. The interface width is of the order of $5\mathring{A}$.

(a)   (b)

FIG. 2. (a) Implanted hydrate cluster of dimensions $24\mathring{A} \times 24\mathring{A} \times 24\mathring{A}$ in a CO_2+H_2O solution ($X_{CO_2} = 0.14$). The system size is $48\mathring{A} \times 48\mathring{A} \times 48\mathring{A}$. (b) Snapshot after 1×10^9 Monte Carlo steps. The Clathrate implant has grown to almost encompass the whole system.
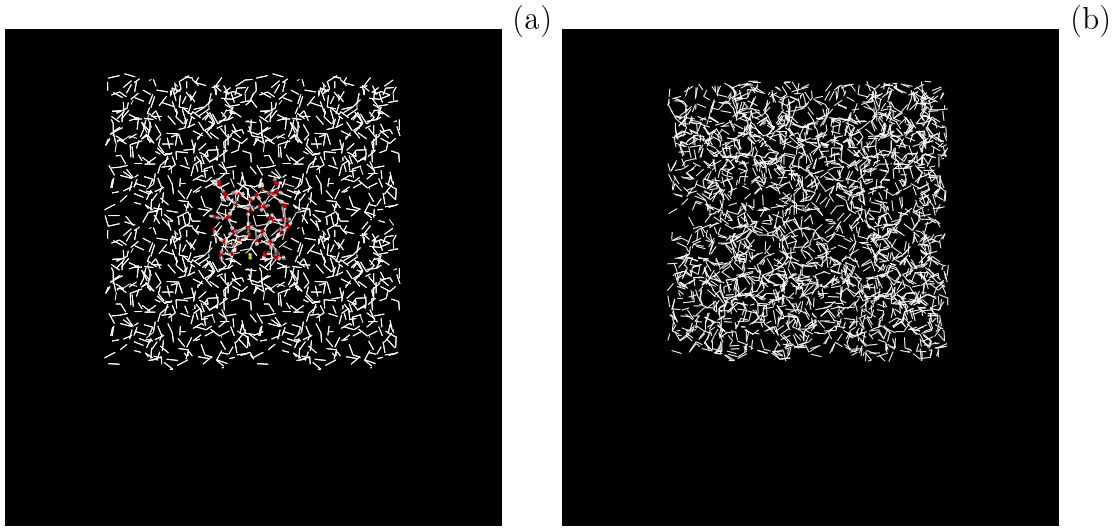
FIG. 3. (a) Implanted hydrate cluster of dimensions $12\overset{\circ}{A} \times 12\overset{\circ}{A} \times 12\overset{\circ}{A}$ in a $CO_2 + H_2O$ solution ($X_{CO_2} = 0.14$). The system size is $48\overset{\circ}{A} \times 48\overset{\circ}{A} \times 48\overset{\circ}{A}$. (b) Snapshot after 1×10^9 Monte Carlo steps. The Clathrate implant has diminished in size and disappeared into solution.
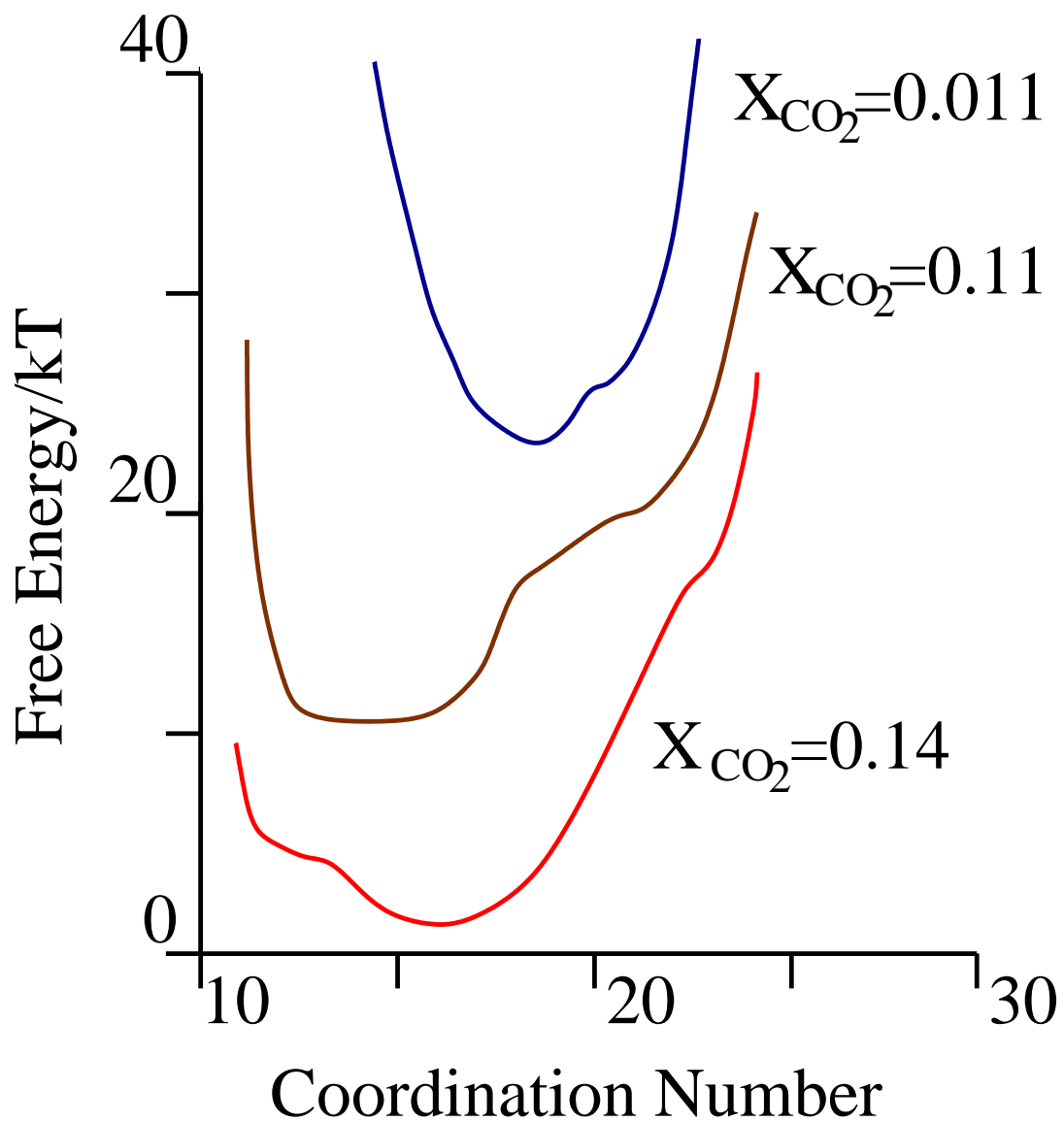
FIG. 4. Formation of a "labile cluster": Free energy verses coordination number of H_2O molecules around a CO_2 molecule at three different concentrations. The free energy functions clearly indicate that the labile cluster is not a metastable state.
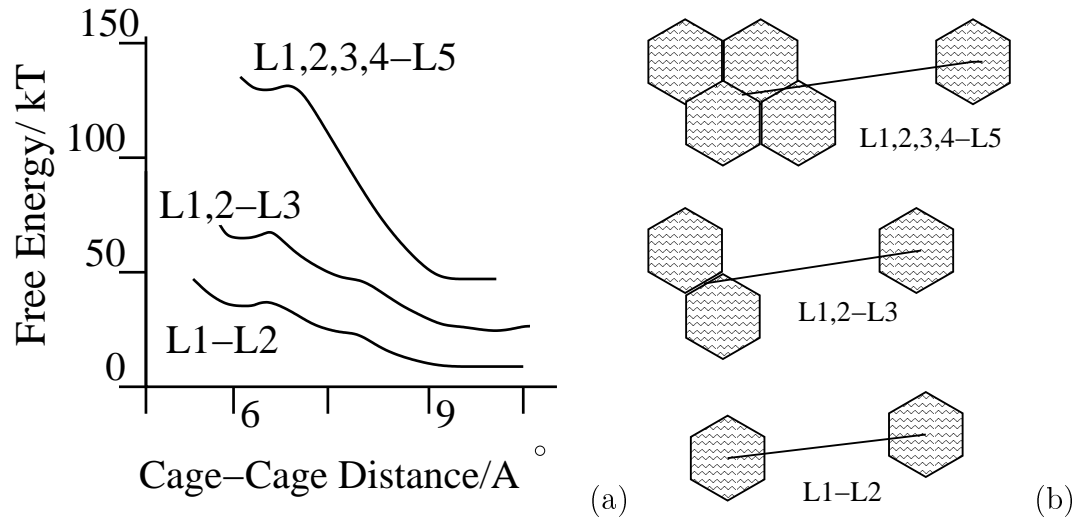
FIG. 5. Agglomeration of "labile clusters": (a) Free energy versus distance between labile clusters for three different sizes of agglomerates. The distance between the labile clusters are defined pictorially in (b).
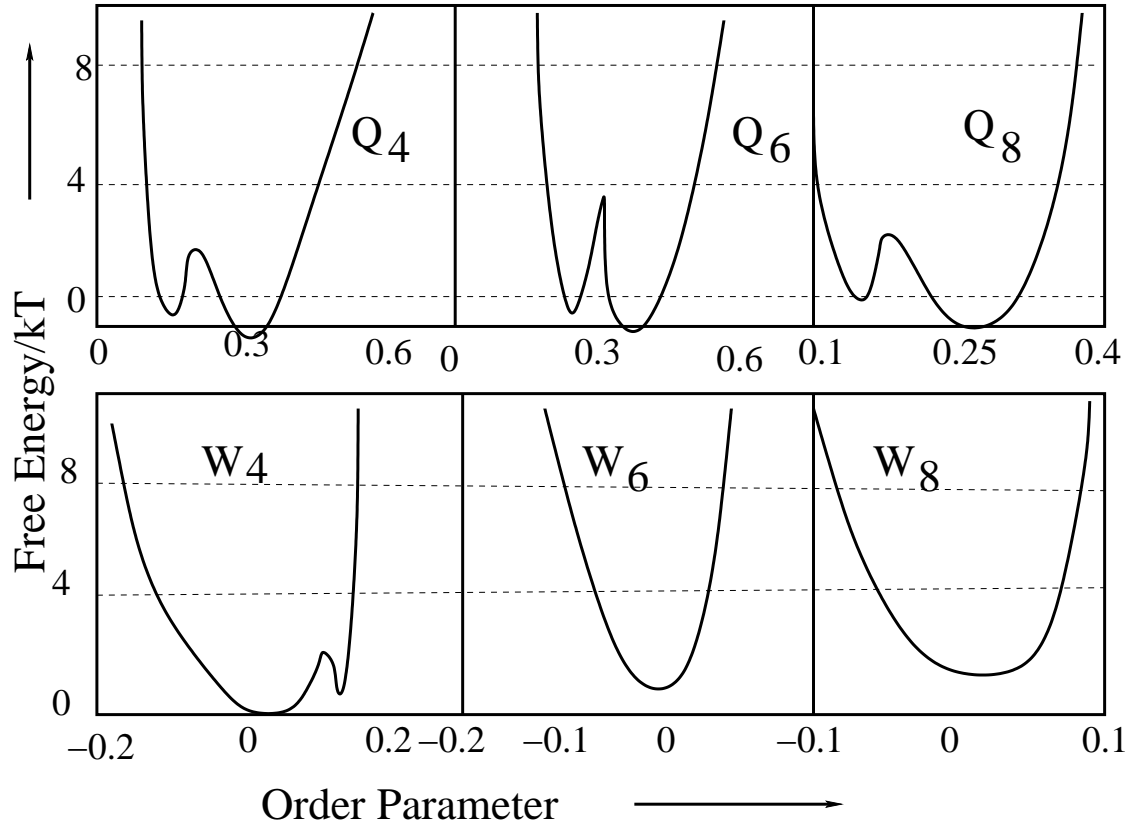
FIG. 6. Free Energy as a function of order-parameters, $Q_i, W_i, i = 4, 6, 8$, for a cluster of $12\mathring{A} \times 12\mathring{A} \times 12\mathring{A}$. The free-energy surface has a metastable minimum when the symmetry of the cluster is exactly the same as the symmetry of the clathrate.