On the thermodynamic stability and structural transition of clathrate hydrates

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Gas mixtures of methane and ethane form structure II clathrate hydrates despite the fact that each of pure methane and pure ethane gases forms the structure I hydrate. Optimization of the interaction potential parameters for methane and ethane is attempted so as to reproduce the dissociation pressures of each simple hydrate containing either methane or ethane alone. An account for the structural transitions between type I and type II hydrates upon changing the mole fraction of the gas mixture is given on the basis of the van der Waals and Platteeuw theory with these optimized potentials. Cage occupancies of the two kinds of hydrates are also calculated as functions of the mole fraction at the dissociation pressure and at a fixed pressure well above the dissociation pressure. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1850904]

I. INTRODUCTION

A gas hydrate consists of guest molecules and host water molecules forming a hydrogen bonded network whose constituents are planar pentagonal and hexagonal rings only. Two common forms of clathrate hydrates are called structure I and structure II.[1,2] Another crystalline form called structure H, which was found more recently, falls into a category of *mixed hydrates*, which contain more than one guest species.[3] The clathrate hydrate is thermodynamically stable only when guest molecules are encapsulated in the host cages. The guest-host interactions, though much weaker than the hydrogen bonds of the host lattice, play a crucial role for clathrate hydrates to be stabilized. The thermodynamic stability of the clathrate hydrates has long been explained by the van der Waals and Platteeuw (vdWP) theory.[4] This has been the only rigorous statistical mechanical theory to account for the stability of clathrate hydrates and has been widely used to predict phase behavior of many hydrates. However, the theory requires some empirical parameters for all practical purposes.[1,2] When applied directly, with a simple free energy evaluation method, to estimation of clathrate hydrate stability for large guest species, it leads to an incorrect phase diagram due to its built-in assumptions that are invalid for host lattices occupied with large guests.

We proposed a method to calculate the free energy of clathrate hydrates encaging molecules comparable in size to the vacant space of the larger cages[5] and of hydrates in which both larger and smaller cages are occupied by a single guest species.[6] The fixed lattice approximation, the most serious shortcoming in the original vdWP theory, was removed by introducing the modulation of the phonon frequencies of the host molecules. Thus, more accurate evaluation of the dissociation pressure was made possible, which requires only intermolecular interactions but no other empirical parameters. It was revealed that the modulation of the frequencies lifts the free energy and thereby destabilizes the clathrate hydrates encaging large guest molecules such as propane.[5,6] The free energy calculation was further sophisticated in order to treat clathrate hydrates encaging nonspherical guest such as propane and ethane.[7] The free energy associated with the rotational degrees of freedom of the guest molecules was evaluated as a perturbation from the spherical guest. However, evaluation of the anharmonic free energy by the thermodynamic integration demands a large amount of CPU time. It is therefore desirable for the free energy calculation, whenever possible, to employ an *effective spherical potential* for a nonspherical guest that incorporates all the contributions from the anisotropy of the guest.

It is well known that both pure methane and pure ethane form the clathrate hydrate structure I, i.e., the each *simple hydrate*, which contains only one guest species, is type I. However it was found that temperature dependence of the dissociation pressure of a mixed hydrate formed by methane mixed with a small amount of ethane did not fit well to the prediction assuming structure I,[8] which naturally suggested a transition from structure I to II.[9] Convincing evidences have been reported recently that the gas mixture of methane and ethane stabilizes structure II rather than structure I.[10,11] The transition has been accounted for by minimizing the relevant Gibbs free energy of model systems with parameters optimized to reproduce thermodynamic properties of clathrate hydrates.[12,13] Here, we show that the structural transition can be accounted for on the basis of the vdWP theory with the free energy of cage occupancy evaluated from intermolecular interactions only. Our method treats a clathrate hydrate of a gas mixture as an open system with respect to the guest species and therefore is a more advantageous way to examine its thermodynamic stability and cage occupancy.

We first obtain sets of the potential parameters for methane and those for ethane, each optimized for reproducing the observed dissociation pressure of each simple hydrate. It is essential that these optimized potential parameters, when

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employed for the free energy calculation based on the vdWP theory, always give rise to structure I being more stable than structure II for each simple hydrate. Second, we examine whether or not structure II becomes more stable than structure I in some range of the mole fraction of ethane when they are in equilibrium with a methane+ethane gas mixture. Third, the cage occupancies are calculated with the sets of the potential parameters at dissociation pressure and at higher constant pressure.

II. MODEL AND METHOD

A. Intermolecular interaction

The water-water intermolecular interaction is described by the TIP4P potential.[14] This is one of the most frequently used potentials for water because of its ability to reproduce many important properties of pure water within the framework of pair potential. The TIP4P model consists of four interaction sites: a positive charge q_{H} on each of two hydrogen atoms, a negative charge $(-2q_{\mathrm{H}})$ on the bisector of two OH bonds, and a soft core interaction between oxygen atoms. The methane-methane and the ethane-ethane interactions are both described by the Lennard–Jones (LJ) potential, which is spherical. For each species, we determine its LJ energy and size parameters that give the observed dissociation pressure of the simple hydrate of that species at 263.15 K. The set of such two parameters is not unique, i.e., it is not a single point but forms a curve in the parameter space. The range of the LJ size parameter thus determined is from 0.37 to 0.39 nm for methane and from 0.44 to 0.46 nm for ethane. Adoption of the LJ potential for methane and ethane means that rotational motions of the two guest species are not considered. In general, this is a reasonable approximation for methane, for its anisotropy is very small. For ethane, however, the LJ potential with an optimized set of parameters should be regarded as an effective potential for the simple and mixed hydrates of ethane. Some remarks will be given on this effective potential. The water-guest intermolecular interaction is taken to be the LJ potential between the oxygen site of the TIP4P water and the center of each guest molecule, with the parameter set given by the Lorentz–Berthelot mixing rule from that of the oxygen site ($\epsilon_{\mathrm{OO}}=0.6487$ kJ mol^{-1} and $\sigma_{\mathrm{OO}}=0.3154$ nm) and that of the guest. The interaction potentials for all pairs of molecules are truncated smoothly at 0.8655 nm as was done in the previous calculation.[5]

B. The vdWP theory

The vdWP theory is applicable to any sort of hydrate, either type I or II and either simple or mixed. It is assumed in the vdWP theory that first the cage structure is not distorted by the incorporation of guest molecules, second a guest molecule inside a cage moves in the force field of water molecules fixed at lattice sites and there is no coupling between host and guest molecular motions. Here, we describe only an essential part of it for convenience of the later discussion. Let us consider a clathrate hydrate which contains N_w water molecules, N_l larger cages, and N_s smaller cages. (Once N_w and the structure are given, N_l and N_s are determined automatically for each structure.) The corresponding grand partition function Ξ is written as

$$\Xi = \exp(-\beta A_w^0)\left[1+\sum_j \exp\{\beta(\mu_j - f_j^s)\}\right]^{N_s} \times \left[1+\sum_j \exp\{\beta(\mu_j - f_j^l)\}\right]^{N_l}, \quad (1)$$

where μ_j stands for the chemical potential of guest species j, f_j is its free energy of cage occupancy with respect to either a larger cage (l) or a smaller cage (s) at temperature T, A_w^0 is the free energy of the empty hydrate, and β is $1/k_BT$ with Boltzmann's constant k_B. The free energy of cage occupancy has mostly been treated as input parameters. One of us showed that the free energy of cage occupancy f_j can be calculated for hydrates encaging smaller guests such as argon and methane with an assumption that all the host vibrational modes are independent of the presence of guest molecules. This assumption leads to the following expression of f_j:

$$\exp(-\beta f_j) = (2\pi m_j k_B T/h^2)^{3/2}\int_{v_{\mathrm{cage}}} \exp[-\beta w(\mathbf{r})]d\mathbf{r}, \quad (2)$$

where h is Planck's constant, m_j is molecular mass of guest j, $w(\mathbf{r})$ is the interaction potential between the guest molecule at $\mathbf{r}$ and all the water molecules with fixed configuration, and the integration spans the entire volume of the single cage v_{cage}.

Cage occupancy y_i for guest i is given by

$$\begin{aligned} y_i &\equiv \frac{\langle N_i\rangle}{(N_l+N_s)} = (N_l+N_s)^{-1}\,\partial\,\ln\Xi/\partial(\beta\mu_i) \\ &= \frac{N_s}{(N_l+N_s)}\exp[\beta(\mu_i - f_i^s)] \\ &\quad\times\left[1+\sum_j \exp\{\beta(\mu_j - f_j^s)\}\right]^{-1} + \frac{N_l}{(N_l+N_s)} \\ &\quad\times\exp[\beta(\mu_i - f_i^l)]\left[1+\sum_j \exp\{\beta(\mu_j - f_j^l)\}\right]^{-1}, \end{aligned} \quad (3)$$

where $\langle N_i\rangle$ is the mean number of cages occupied by guest species i. The chemical potential μ_c of water in the hydrate is given by

$$\mu_c = -k_BT\,\partial\,\ln\Xi/\partial N_w = \mu_c^0 - k_BT\left(\alpha_s\ln\left\{1+\sum_j \exp[\beta(\mu_j - f_j^s)]\right\} + \alpha_l\ln\left\{1+\sum_j \times\exp[\beta(\mu_j - f_j^l)]\right\}\right), \quad (4)$$

where μ_c^0 is the chemical potential of water in the hypothetical empty hydrate and α_l and α_s are the ratios of the numbers of the larger and smaller cages to the number of water molecules, respectively. Equations (1)–(4) describe the essential part of the vdWP theory.

TABLE I. Chemical potential μ_c^0 of empty hydrate and chemical potential difference $\Delta\mu$ between ice and empty hydrate for structures I and II at 263.15 K, where the anharmonic free energy and the residual entropy terms are omitted.

kJ mol^{-1}	Structure I	Structure II
μ_c^0	−47.93	−48.03
$\Delta\mu$	−0.834	−0.732

C. Free energies of ice and empty clathrate hydrates

The equilibrium condition between ice and clathrate hydrate is given by

$$\mu_i = \mu_c, \tag{5}$$

where μ_i and μ_c denote the chemical potentials of ice and clathrate hydrate. By subtracting the chemical potential μ_c^0 of the corresponding hypothetical empty clathrate hydrate from both sides of Eq. (5),

$$\mu_i - \mu_c^0 = \mu_c - \mu_c^0. \tag{6}$$

The left-hand side of the above equation is calculated assuming that the free energy is expressed by the sum of the potential energy of a given system at mechanically equilibrium positions of molecules, the harmonic vibrational free energy, the anharmonic vibrational free energy, and the residual entropy term, the last of which is common to all the proton-disordered ice forms. It is advantageous to calculate the chemical potentials relative to that of the empty hydrate [Eq. (6)] instead of the absolute chemical potentials [Eq. (5)] because, on both sides of Eq. (6), the residual entropy terms cancel out exactly and the difference in the anharmonic vibrational free energy terms is expected to be negligible, although each contribution may not be so small. We generate 100 proton-disordered structures for each of clathrate hydrate I and II and for ice Ih. The chemical potentials of clathrate hydrate I and II and that of ice Ih are calculated according to the above mentioned way and the differences $\Delta\mu$'s between ice and empty hydrate are tabulated in Table I. The chemical potential of empty hydrate II is always lower than that of empty hydrate I, which is expected from the preferential formation of structure II for argon and other smaller molecules.

III. INFERENCES FROM EXPERIMENTAL OBSERVATIONS

It would be worthwhile here to summarize the experimental facts that are relevant to the structural transition of the methane+ethane system and what we can learn from them.

(1) The structure II is more stable than the structure I when the guests are very small molecules such as argon, krypton, and nitrogen.[15]

(2) A methane molecule is encaged in both larger and smaller cages of the structure I.[2]

(3) An ethane molecule is encapsulated in only larger cages of the structure I except for a small amount in smaller cages near the dissociation pressure.[16]

The individual observations lead naturally to the following inferences.

TABLE II. Potential energy u at structures of minimum potential energy and free energy f of cage occupancy at 273.15 K (Ref. 6). Those free energy and the potential energy are calculated for larger and smaller cage occupancies, denoted by superscripts l and s, respectively.

kJ mol^{-1}	Methane in hydrate I	Methane in hydrate II
u^s	−22.13	−27.72
u^l	−20.26	−16.67
f^s	−27.83	−28.13
f^l	−30.30	−31.19
	Argon in hydrate I	Argon in hydrate II
u^s	−17.01	−17.61
u^l	−14.25	−11.43
f^s	−28.73	−28.97
f^l	−29.77	−30.48

(1) The free energy of cage occupancy for smaller guest molecules is rather insensitive to the type of the cage. In the previous work, we calculated the free energy for argon using the most reliable intermolecular interaction, which is listed in Table II.[6] Even if we choose a different intermolecular interaction, we obtain a similar tendency. This fact together with the preferential formation of the structure II hydrate necessarily indicates that the chemical potential of the empty structure II hydrate is lower than that of the empty structure I hydrate at an ambient pressure and temperature. Although there are some exceptions,[2] this view is supported by experiments tabulated in Ref. 2.

(2) The free energy difference, $f^s - f^l$ becomes larger with increasing guest size. A methane molecule is small enough to be accommodated in any type of cage but large enough to have fairly different free energy values for different types of cages as shown in Table II for each structure. The free energy of cage occupancy in the larger cage is lower than that in the smaller cage for both structure I and structure II. However, α_l (ratio of the number of larger cages to the number of water molecules) for structure I (6/46) is much larger than α_l for structure II (8/136). Thus, structure I is more stabilized by accommodating a large number of the larger cages. The free energies of cage occupancy for structure II are lower than the corresponding those for structure I. The preferential formation of structure I may occur under the subtle balance between the larger α_l and the less stable empty hydrate of structure I as realized in methane hydrate.

(3) Only larger cages can accommodate very large guest molecules such as ethane. Such guests prefer structure I to structure II since α_l for structure I is much larger than that for structure II.

The above inferences conduct to the following speculation on the mixed hydrate. If a small amount of ethane is mixed with a methane gas, ethane molecules occupy the larger cages exclusively while methane molecules can occupy both the smaller and larger cages. That is, both types of cages can be potentially occupied unlike in the case of the simple hydrate of ethane. The free energy of such hydrates would be lower than that of the simple hydrate of ethane. Under the methane-rich condition, structure II is more favorable because the chemical potential of empty structure II

TABLE III. Free energy f of cage occupancy at 263.15 K calculated by optimized LJ parameters σ and ϵ which can reproduce dissociation pressure p_d (σ, ϵ, and p_d are also listed here). Superscripts s and l stand for smaller and larger cages, and subscripts, I and II, stand for hydrate I and hydrate II. Linear ethane molecule means a rigid rotor composed two LJ interaction site.

	Methane	Ethane	Ethane (linear)
p_d (MPa)	1.84	0.306	…
σ (nm)	0.3850	0.4520	0.3775
ϵ (kJ mol^{-1})	1.277	1.736	1.720
f_{I}^{s} (kJ mol^{-1})	−27.38	…	…
f_{I}^{l} (kJ mol^{-1})	−30.47	−37.48	−37.62
f_{II}^{s} (kJ mol^{-1})	−27.43	…	…
f_{II}^{l} (kJ mol^{-1})	−31.34	−41.76	…

hydrate is lower than that of empty structure I hydrate. This is also supported by our direct calculation of the chemical potential of the empty hydrates relative to that of ice as shown in Table I. Under ethane-rich condition, on the contrary, structure I becomes more favorable. This is because the proportion of larger cages, which are available for ethane molecules, is much larger in structure I than in structure II.

IV. RESULTS AND DISCUSSION

We determine the LJ parameters for each guest species that reproduce the dissociation pressure of simple clathrate hydrate of that species. Ref. 2 accumulates a huge number of data on dissociation pressure. A simple interpolation provides a way to estimate the dissociation pressure at a given temperature. Conversely, once the dissociation pressure p_d is given as listed in Table III, the LJ parameters of a guest is determined. Since there are two parameters ϵ and σ to be fitted and a single datum p_d to fit, the optimized LJ parameters are not determined uniquely but their relation is determined, e.g., ϵ is determined as a function of σ. For both ethane and methane, the LJ parameters are fitted to the dissociation pressure of structure I hydrate at $T=263.15$ K. The free energy of cage occupancy in structure II is calculated using the parameter set thus obtained. It is revealed that, for both methane and ethane, structure I simple hydrate is always more stable than structure II within the parameter space we have examined.

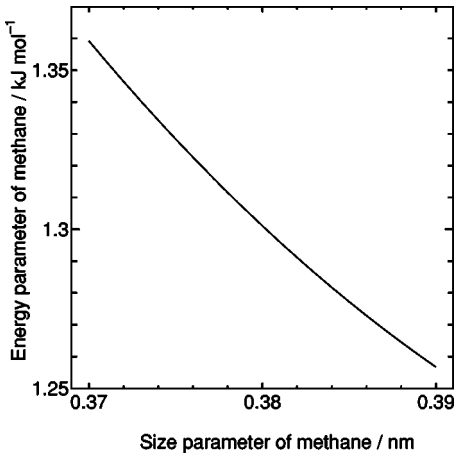

FIG. 1. Appropriate energy parameter for methane against size parameter at 263.15 K.

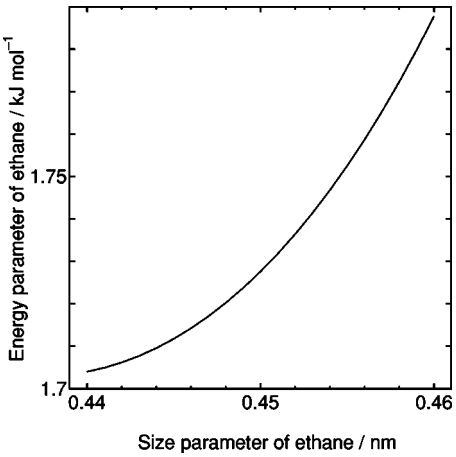

FIG. 2. Appropriate energy parameter for ethane against size parameter at 263.15 K.

The energy parameter thus obtained is plotted against the size parameter in Fig. 1 for methane and Fig. 2 for ethane. Note that the region above the curve of the optimized parameter set in Fig. 1 and that in Fig. 2 give rise to the free energy lower than the value to fit. The energy parameter decreases with increasing the size parameter for methane whereas the reverse holds for ethane. The figure contrasts the role of vacant volume in the larger cage for the two guest species. To account for the difference, the potential energy $w(r)$ of a guest molecule in a larger cage (interacting with surrounding water molecules fixed to the lattice sites) is calculated as a function of radial distance r from the center of the cage, which is the average over all the directions. Figure 3 shows the potential energy curve (solid line) for each guest species obtained from an optimized parameter set ($\sigma=0.38$ nm and $\epsilon=1.3$ kJ mol^{-1} for methane and $\sigma=0.45$ nm and ϵ

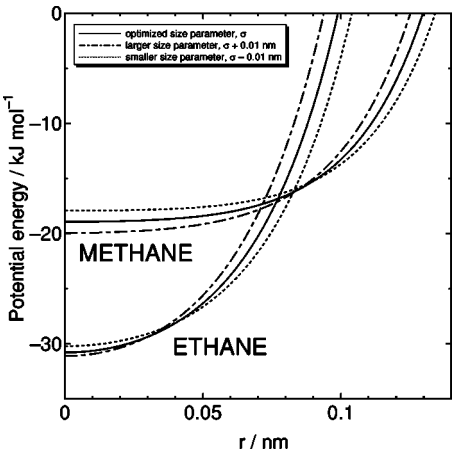

FIG. 3. Potential energy curves of methane and ethane molecules for the optimized size parameter ($\sigma=0.38$ nm for methane, $\sigma=0.45$ nm for ethane) as a function of radial distance r from the center of the larger cage (solid line). The dotted and dot-dashed lines are corresponding to those for larger and smaller size parameters ($\sigma\pm0.01$ nm), respectively. The three potential energy curves are calculated with the same energy parameter ($\epsilon=1.3$ kJ mol^{-1} for methane, $\epsilon=1.7$ kJ mol^{-1} for ethane).

$=1.7$ kJ mol^{-1} for ethane). The others show the potential energy curves for the optimized $\sigma \pm 0.01$ nm with the common energy parameter. Both the potential energy curves are monotonically increasing functions of r. The potential curve for methane is fairly flat around the center, indicating that a methane molecule can move around a wide space. This relatively large region of lower energy seems to contribute to lowering the free energy of cage occupancy. The curves obtained from three size parameters (0.37–0.39 nm) show that the potential energy becomes lower as the size parameter increases in the region from the center to $r=0.09$ nm. Because this region is wide for methane, the free energy is lowered with increasing the size parameter if the energy parameter is fixed. This explains why the curve of the optimized parameter set has a negative slope as shown in Fig. 1. On the other hand, the potential energy of ethane exhibits a quadratic character that confines an ethane molecule in a relatively small space. It is shown by the curves obtained from three size parameters (0.44, 0.45, 0.46 nm) that the potential energy near the center of the cage is lowered as the size parameter increases as found for methane. However, this tendency is limited to a very small region from the center to $r=0.04$ nm, where the energy is still low, and the reverse holds for the outer region. The difference in the energy is intensified with increasing the distance from the crossover point. This character of the potential energy curve for ethane gives rise to increase in free energy with increasing the size parameter if the energy parameter is fixed, and therefore explains why the slope of the optimized parameter curve is positive as shown in Fig. 2. This completes the explanation of the difference between Figs. 1 and 2.

Table III lists a set of the free energies of cage occupancy calculated from the optimized LJ parameters for structure I and II at 263.15 K (these are optimized not only for the simple hydrates but also for the mixed hydrates as shown below). The size parameter for ethane is fairly large compared to that given in a classical textbook.[17] This is justified by considering oblate shape of the larger cage in clathrate structure I and anisotropic nature of an ethane molecule. If a two-site model of ethane is adopted,[18] a reasonable value for the free energy as that in Table III would be obtained without invoking the fitting. Figure 4 shows to what extent structure I hydrate encaging methane is stabilized compared to structure II by plotting both sides of Eq. (6) against gas pressure. The left-hand side of Eq. (6) is constant with a good approximation while the right-hand side is heavily dependent on the gas pressure. The intersection gives a dissociation pressure. Although the difference, $\mu_i - \mu_c^0$ is not preferable to formation of structure I compared to structure II, the slope of $\mu_c - \mu_c^0$ for structure I is steeper than that for structure II, which gives rise to the lower dissociation pressure of structure I. This is true for the methane hydrate with the parameters examined here.

With those LJ parameters, we examine whether or not structural transitions take place at 263.15 K. Now we consider a three-component system (water+ethane+methane) at four-phase equilibrium where an ice phase, a methane +ethane gas mixture, and the two types of clathrate hydrates coexist. As Gibbs's phase rule tells us ($F=2+C-P$, where

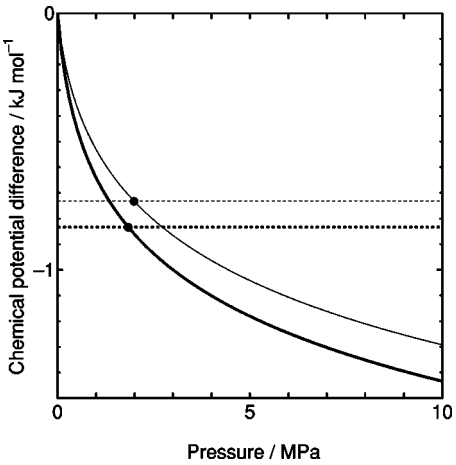

FIG. 4. The chemical potential changes due to the incorporation of methane molecules for hydrate I (thick line) and II (thin line) as a function of the coexistence pressure at 263.15 K. The dotted line shows the chemical potential difference between ice and empty hydrate I (below, thick) and II (above, thin).

F, C, and P stand for the number of degree of freedom, the number of components, and the number of phases in the system), we are left with $F=2+3-4=1$. Since the temperature is fixed, the composition of the gas mixture is determined uniquely. Thus, once the temperature is given, the four phases can coexist only at a unique composition of the system, not in a finite range of composition. This equilibrium condition is derived from the vdWP theory alone. The two sets of the LJ parameters shown in Figs. 1 and 2 are subject to further optimization in order to reproduce the structural transitions. Since the optimized LJ parameter set for each guest species has one degree of freedom, the two sets of such parameters have two degrees of freedom. So we first calculate the dissociation pressures of structure I and II mixed hydrates over the two-dimensional optimized parameter space, varying the methane mole fraction of the gas mixture. The structure with lower dissociation pressure is more stable at a given condition. For each given LJ parameter set, the structural transition (i.e., the four-phase equilibrium) is observed if the two dissociation pressures of structures I and II become equal at some mole fraction of methane. Such mole fraction is found for a wide range of the two-dimensional optimized parameter space. In Fig. 5, we show the methane mole fraction at which the structural transition occurs at 263.15 K (or the mole fraction at four-phase equilibrium) as a function of the size parameters of methane and ethane. There are two surfaces in the three-dimensional space, which indicates the structural transition occurs twice as the methane mole fraction is increased from 0 to 1. The structure II clathrate hydrate is the stable phase in the space between the two surfaces and the structure I is more stable elsewhere. Now we can further optimize the LJ parameter sets for the two guest species such that they give the experimentally observed composition range, 78%–98%, in which structure II forms at 263.2 K.[13] Given in Table III are the free energies obtained from those doubly optimized LJ parameters. The free energy of larger cage occupancy for structure II is lower than that for structure I for both guest species. But the difference is more prominent in the case of ethane, which is the

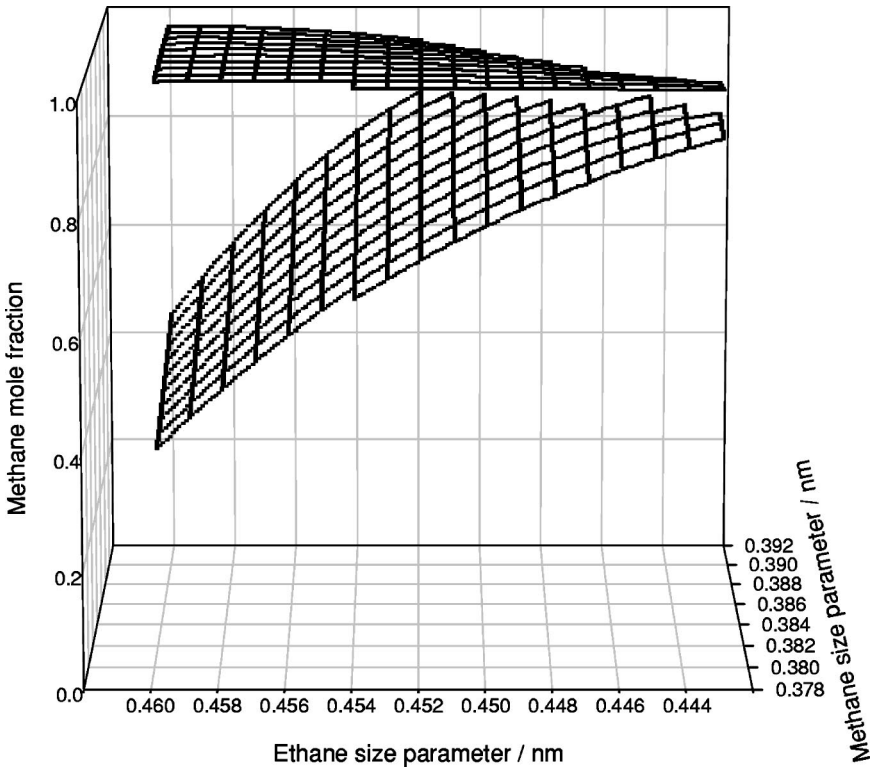

FIG. 5. Methane mole fraction for the occurrence of structural transition against both methane and ethane size parameters at 263.15 K.

dominant factor for inducing the transition from structure I to structure II together with the difference in relative number of the larger cages to the smaller cages. Figure 6 shows occupancy of methane and ethane along the dissociation pressure at 263.15 K. Two discontinuities in each occupancy are caused by the structural transition. The figure also shows that each guest does not fully occupy the cages of clathrate hydrate at any mole fraction of methane. The mean cage occupancies averaged over the mole fraction for structures I and II are about 76% and 71%, respectively. The transition to structure II does not necessarily gives rise to larger cage occupancy. Thus, the most dominant contribution to the stability of structure II is higher stability in its empty state (Table I). We also show cage occupancy in Fig. 7 at a fixed pressure, 10 MPa, which is far higher than the dissociation pressure. Under this high pressure, the chemical potential of water μ_c given by Eq. (4) determines which is the more stable structure of clathrate hydrate. As seen from Fig. 7, a methane+ethane gas mixture almost fully occupies the cages of either structure I or II; the mean cage occupancies of structure I and II are about 95%. The structural transition from I to II occurs in higher methane mole fraction at 10 MPa compared with the case around the dissociation pressure although this feature is slightly different from the previous work.[19] Comparing the results at 10 MPa (Fig. 7) with those at the dissociation pressure (Fig. 6), we note that cage occupancy of each guest increases with increasing gas pressure except for that of ethane in the structure II hydrate, which hardly increases with increasing pressure because almost all the available cages are already occupied by ethane

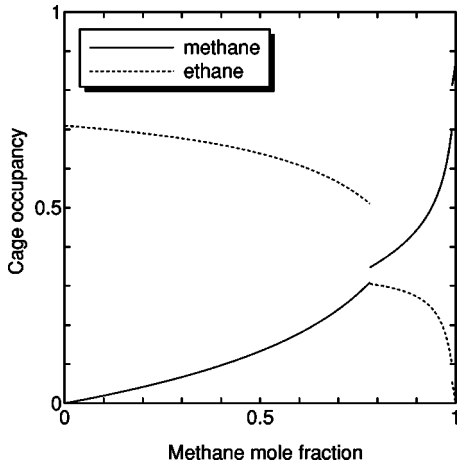

FIG. 6. Occupancy of cages for methane (solid line) and ethane (dotted line) as a function of methane mole fraction at dissociation pressure and at 263.15 K.

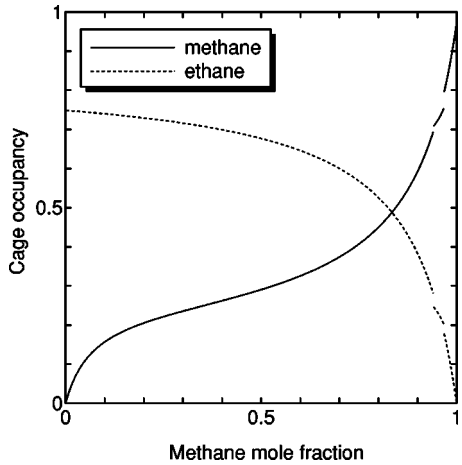

FIG. 7. Occupancy of cages for methane (solid line) and ethane (dotted line) as a function of methane mole fraction at constant pressure, 10 MPa and at 263.15 K.

molecules at the dissociation pressure. Hence it follows that the structure II hydrate cannot gain a significant amount of the extra (negative) free energy of larger cage occupancy with increasing ethane gas pressure. This explains why the lower limit of the methane mole fraction for structure II hydrate is much higher at 10 MPa than at the dissociation pressure.

V. CONCLUSIONS

The appropriate LJ parameters are so determined as to reproduce the dissociation pressure for simple clathrates, which contain only a single component of guest species, either methane or ethane. With those appropriately chosen LJ parameters, we examine stability of structure I and II hydrates over the entire range of the mole fraction. Many parameter sets reproduce the expected structural transitions in a certain range of methane and ethane composition. We choose among many the two parameter sets that reproduces the compositions of the phase transitions experimentally observed. In this way, the LJ parameter sets for methane and ethane are doubly optimized. The structural transition for the mixed clathrate hydrate is accounted for by only the intermolecular interactions, which are deduced from the simple clathrate hydrates of methane and ethane.

There are three important factors to explain which form, structure I or II, of the methane+ethane mixed hydrate is more stable. First empty structure II hydrate takes the lower chemical potential value than empty structure I hydrate, second the ratio of the number of larger cages to the number of water molecules for structure I is much larger than that for structure II, third the free energy of larger cage occupancy for structure II is lower than that for structure I in the both cases of methane and ethane. The first and third factors contribute to stabilizing structure II hydrate, while the second one contributes to stabilizing structure I hydrate. The preferential structure at a given condition is determined by competition among these three factors.

The seemingly gradual transformation from structure I to II with increasing the ethane mole fraction observed by experiments[12,13] needs to be examined carefully. Coexistence of four phases in a certain range of the mole fraction of the gas mixture should be due to a kinetic factor, because it violates the Gibbs phase rule and therefore cannot be a true equilibrium state. Such observation, however, may be helpful to provide some information on the role of guest species to stabilize cage structure.

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