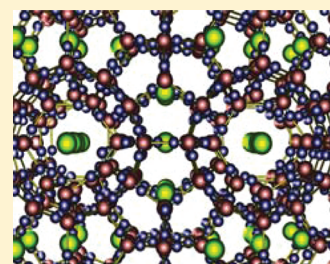


On the Thermodynamic Stability of Clathrate Hydrates V: Phase Behaviors Accommodating Large Guest Molecules with New Reference States

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ABSTRACT: We present a method that brings prediction of phase behaviors of various clathrate hydrates with firm statistical mechanical ground adopting a different reference state from the usual one. Accommodation of a large guest molecule makes the frequencies of the lattice vibrational motions higher, which is one of the breakdowns of the assumptions in the original van der Waals and Platteeuw theory. The frequency modulations are incorporated in the free energy of cage occupation in the present method. Moreover, the reference state, which is originally the corresponding empty clathrate structure, is alternated to a state where cages of at least one sort are fully occupied. This meets the stability condition of clathrate hydrates that most of the cages should be accommodated. Owing to this new reference state, the thermodynamic stability is evaluated with reasonable accuracy from the free energy of cage occupation especially by a large guest molecule without considering its dependence on the cage occupancy. This conversion is also beneficial to establish a relation between the chemical potential of water and the cage occupancy from grandcanonical Monte Carlo simulation. We show a new method indeed works well in predicting the dissociation pressures of clathrate hydrates containing isobutane, propane, ethane, Xe, and CF₄.



I. INTRODUCTION

Clathrate hydrates are nonstoichiometric compounds made of guest and water molecules.^{1,2} All the water molecules are tetrahedrally coordinated in a way similar to those in ice at low pressure, but the arrangement of water molecules beyond the second neighbors is different from that of ice, forming cages of 12-, 14-, and 16-hedra. Two sorts of crystalline forms have been known as structure I (CS-I) and structure II (CS-II) at low pressure, which can be made from only a single guest species. The total amount of methane hydrate in offshore and permafrost is expected to be huge and thus can be one of the future energy resources.² It is of great importance to predict the phase behaviors of clathrate hydrates by only intermolecular interactions for water and guest molecules since the thermodynamic condition for a clathrate hydrate to be stable is sometimes difficult to be attained compared with usual laboratory experiments.

Thermodynamic properties of clathrate hydrates have been calculated by the van der Waals and Platteeuw (vdWP) theory.³ It has been applied to predict the dissociation pressure of clathrate hydrates successfully with the intermolecular interactions appropriate to describe liquid water and aqueous solutions. The theory relies on a few assumptions: first each cage contains at most one guest molecule, second there is no spatial correlation among the encaged guest molecules, and finally accommodation of the guest molecules affects neither static nor dynamic properties pertinent to the host lattice. Owing to these assumptions, each accommodation of a guest molecule is treated independently, and the relevant partition function becomes much simpler. The free energy of cage occupation is calculated from the interaction of the guest with the surrounding water molecules

and is independent of occupation of the other cages. The assumptions have been removed by consideration of the host–guest coupling in the vibrational motions.^{4–6} Further generalizations to a multiple occupation and to a constant pressure system treating a clathrate hydrate at high pressures have been proposed.^{7–9}

A correlation of the occupied cages is handled by a mean field-like approximation.^{10,11} Another important advance is made by incorporating the effect on the host lattice with the existence of guest molecules. This is achieved by calculating the free energy of cage occupation arising from the difference in vibrational frequency of the host lattice between the empty and the occupied clathrate hydrate, where account is taken of the change in the Hessian matrix elements due to the host–guest interactions.^{4,12} The revised free energy of cage occupation is higher, and the revision is effective in the case that the guest molecule is large. Such a large guest species is capable of stabilizing the clathrate hydrate (especially CS-II) even when only its larger cages are occupied, where the cage occupancy should be almost unity. It is, therefore, highly desirable to describe the phase equilibrium with a reference state of the fully occupied clathrate hydrate instead of the commonly used empty state. Moreover, such a reference state is preferable for a case where a phase equilibrium is estimated in terms of the cage occupancy by numerical simulations such as grandcanonical Monte Carlo (GCMC).^{7–9,13–15}

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II. THEORY AND METHOD

A. vdWP Theory. Let us first derive the essential part of the vdWP theory^{1–3} for the purpose of a better understanding of consequences by breakdown of the assumptions in the original theory. That is, important elements missing in the original theory can be taken into consideration in the framework of the vdWP formalism by incorporating the frequency modulation in the host lattice, introducing the occupancy-dependent free energy, extending to multiple occupation, converting to a constant pressure system, and changing the reference state from the empty clathrate hydrate to the filled one.^{5–11}

A clathrate hydrate is made of N_w water molecules at temperature T (or β ; the inverse of T times the Boltzmann constant, k_B) and volume V . A specific guest species is engaged in a type j cage, where j runs over the possible types. We consider that a fixed number of molecules are engaged where only a single component of guest species, say i , is considered for simplicity. An extension to multiple-component of guest species is straightforward and is given later. According to the assumptions in the original vdWP theory, the canonical partition function for a clathrate hydrate accommodating n_{ij} guest molecules out of its N_j cages of type j is written by the product of the host and guest parts as

$$Z = \exp(-\beta A_c^0) \prod_j \binom{N_j}{n_{ij}} \exp(-\beta n_{ij} f_{ij}) \quad (1)$$

where A_c^0 stands for the free energy of the hypothetical empty clathrate hydrate and f_{ij} indicates the free energy of the cage occupation by the guest species i . The latter quantity is given in the framework of the vdWP theory as

$$\begin{aligned} & \exp(-\beta f_{ij}) \\ &= \left(\frac{2\pi m_i k_B T}{h^2} \right)^{3/2} \frac{1}{\sigma_i} \prod_l \left(\frac{2\pi I_l k_B T}{h^2} \right)^{1/2} \iint \exp[-\beta w(\mathbf{r}, \boldsymbol{\Omega})] d\mathbf{r} d\boldsymbol{\Omega} \end{aligned} \quad (2)$$

for a nonlinear rigid molecule and

$$\begin{aligned} & \exp(-\beta f_{ij}) \\ &= \left(\frac{2\pi m_i k_B T}{h^2} \right)^{3/2} \frac{2\pi I k_B T}{\sigma_i h^2} \iint \exp[-\beta w(\mathbf{r}, \boldsymbol{\Omega})] d\mathbf{r} d\boldsymbol{\Omega} \end{aligned} \quad (3)$$

for a linear molecule where the mass and the moment of inertia are expressed by m_i and I_l (or I) and the interaction of the guest molecule with the surrounding water molecules is described by $w(\mathbf{r}, \boldsymbol{\Omega})$ with the symmetry number of the guest molecule σ_i and the Planck constant h . The integration is performed over the position \mathbf{r} inside the given cage and all the orientation $\boldsymbol{\Omega}$.

The canonical partition function is converted to the grand-canonical one by multiplying $\exp(\beta n_{ij} \mu_i)$, and the summation is carried out over the possible occupations, which results in

$$\begin{aligned} \Xi &= \exp(-\beta A_c^0) \prod_j \sum_{n_{ij}=0}^{N_j} \exp(\beta n_{ij} \mu_i) \binom{N_j}{n_{ij}} \exp(-\beta n_{ij} f_{ij}) \\ &= \exp(-\beta A_c^0) \prod_j (\exp[\beta(\mu_i - f_{ij})] + 1)^{N_j} \end{aligned} \quad (4)$$

The above formulation implies that the clathrate hydrate thus described is an open system with respect to the guest species.

Therefore, the mean occupancy $\langle x_i \rangle$ is derived from the partition function as

$$\langle x_i \rangle = \frac{\partial \ln \Xi}{N_w \partial(\beta \mu_i)} = \sum_j \alpha_j \frac{\exp[\beta(\mu_i - f_{ij})]}{1 + \exp[\beta(\mu_i - f_{ij})]} = \sum_j \alpha_j x_{ij} \quad (5)$$

where the ratio of the number of j -type cages to water is denoted by $\alpha_j (= N_j/N_w)$ and x_{ij} is its occupancy (the filling ratio) by guest i . The chemical potential of water calculated from the free energy of the clathrate hydrate, $\Phi (= -k_B T \ln \Xi)$, is expressed by the two contributions: the chemical potential of water in the empty clathrate hydrate, $\mu_c^0 = (\partial A_c^0)/(\partial N_w)$, and the extra term from the cage occupation as

$$\begin{aligned} \mu_c &= \frac{\partial \Phi}{\partial N_w} = \mu_c^0 - k_B T \sum_j \alpha_j \ln \{ 1 + \exp[\beta(\mu_i - f_{ij})] \} \\ &= \mu_c^0 + k_B T \sum_{jl} \alpha_j \ln \left(1 - \frac{\exp[\beta(\mu_i - f_{ij})]}{1 + \exp[\beta(\mu_i - f_{ij})]} \right) \\ &= \mu_c^0 + k_B T \sum_j \alpha_j \ln(1 - x_{ij}) \end{aligned} \quad (6)$$

An extension to clathrate hydrate in equilibrium with multiple-component gas is straightforward under the condition that each cage accommodates only one molecule of either guest species. The grand partition function is written as

$$\begin{aligned} \Xi &= \exp(-\beta A_c^0) \prod_j \left(\sum_{n_k=0}^{N_j} \frac{N_j!}{n_0!} \prod_{k=1}^n \frac{1}{n_k!} \exp[\beta n_k(\mu_k - f_{kj})] \right) \\ &= \exp(-\beta A_c^0) \prod_j \{ \sum_{k=1}^N \exp[\beta(\mu_k - f_{kj})] + 1 \}^{N_j} \end{aligned} \quad (7)$$

where the index k runs over all the guest species. The occupancy of the specific guest i is given by

$$\begin{aligned} \langle x_i \rangle &= \frac{\partial \ln \Xi}{N_w \partial(\beta \mu_i)} = \sum_j \alpha_j \frac{\exp[\beta(\mu_i - f_{ij})]}{1 + \sum_k \exp[\beta(\mu_k - f_{kj})]} \\ &= \sum_j \alpha_j x_{ij} \end{aligned} \quad (8)$$

The chemical potential of water in the clathrate hydrate is calculated from the free energy as

$$\begin{aligned} \mu_c &= \frac{\partial \Phi}{\partial N_w} = \mu_c^0 - k_B T \sum_j \alpha_j \ln \{ 1 + \sum_k \exp[\beta(\mu_k - f_{kj})] \} \\ &= \mu_c^0 + k_B T \sum_{jl} \alpha_j \ln \left(1 - \frac{\sum_i \exp[\beta(\mu_i - f_{ij})]}{1 + \sum_k \exp[\beta(\mu_k - f_{kj})]} \right) \\ &= \mu_c^0 + k_B T \sum_j \alpha_j \ln(1 - \sum_i x_{ij}) \end{aligned} \quad (9)$$

As is mentioned above, the free energy of cage occupation is calculated by the integration of the Boltzmann factor of the

interaction energy for the guest where the surrounding water molecules are all fixed to the equilibrium positions. That is, it is assumed in the original theory that the host lattice is not affected by the existence of guest molecules and that a guest molecule in a specific position does not induce occupation of the nearby cages (i.e., the occupation of one cage is independent of others). Under those assumptions, the grand partition function is given by the product of the host lattice and the guest partition functions. Furthermore, the guest partition function is expressed by a simple product of those for the individual guest. The applicability of the theory is conditional on that the host lattice is least perturbed by the existence of the guest molecule.

B. vdWP Theory with a Reference State of the Fully Occupied Cages. It has been recognized that the vdWP theory is of great use in predicting phase behaviors of clathrate hydrates.² In fact, this theory works well when the guest molecule is small enough not to alter the host lattice vibrations. However, a large guest molecule changes the frequencies of the host vibrational motions due to the coupling with the guest vibrations. The frequency generally shifts to higher value.¹² This shift is accounted for by suppression of the large amplitude motions of the host lattice with the existence of the large guest molecules. This gives rise to a higher dissociation pressure than that expected from the original vdWP theory.

It was indeed revealed that the modulation of the lattice vibrational motions raises the dissociation pressure.⁴ Then, the chemical potentials of water in both the empty and the occupied clathrate hydrate are rather accurately calculated from the free energy of harmonic vibrations (or anharmonic free energy may be included), where modulation of the lattice vibrations can be taken into account. Instead of the empty reference state where the effect by the guests is not included, we adopt the composite state where the available cages are all filled with the guest molecules. The clathrate hydrate with superscript 1 stands for that filled fully with guests. An equilibrium gives rise to removal of some guests from it. Suppose n_j cages, among N_j of type j , are occupied by the antiguest molecules of type i (yielding empty cages). The relevant canonical partition function is given by

$$Z = \exp(-\beta A_c^1) \prod_j \binom{N_j}{n_j} \exp(\beta n_j f_{ij}) \quad (10)$$

According to the above definition, A_c^1 is the free energy of the fully occupied clathrate hydrate by guest type of i . The free energy f_{ij} is calculated in the presence of the guest molecules including the host vibrational frequency modulation. In practice, it is given as

$$f_{ij} = \frac{A_c^1 - A_c^0}{N_j} \quad (11)$$

for a case in which cages of only type j are to be occupied or guests of the other sorts than i are small enough not to alter the vibrational frequencies of the host lattice. There is no unique method to calculate the free energies of cage occupation for the number of cage types l affecting the host lattice. A simple way is to accumulate the

free energy differences by filling cages stepwise as follows

$$\begin{aligned} f_{i1} &= \frac{A_c^1(N_1, 0, \dots, 0) - A_c^0(0, 0, \dots, 0)}{N_1}, \\ f_{i2} &= \frac{A_c^1(N_1, N_2, 0, \dots, 0) - A_c^1(N_1, 0, 0, \dots, 0)}{N_2}, \\ &\dots\dots\dots, \\ f_{il} &= \frac{A_c^1(N_1, N_2, \dots, N_{l-1}, N_l, 0, \dots, 0) - A_c^1(N_1, N_2, \dots, N_{l-1}, 0, 0, \dots, 0)}{N_l} \end{aligned} \quad (12)$$

The order of the cage type is chosen to be in accordance with the significance of the host vibrational motions and/or the preference of each cage type for accommodation of guest species. The practical method for calculation of A_c is given below.^{16,17} It is noted that some sorts of cages may not encage any type of guest species and that the free energy for a small guest can be calculated from the simple integration by eq 2 or 3 rather than from the normal modes. It is also typical that only the larger cages are occupied, while the smaller ones are left empty. We exemplify the above procedure by ethane clathrate hydrate. The free energy by the integration (Table II) suggests that the smaller cages hardly contain ethane molecules. The harmonic approximation is first applied to the calculation of the free energy of occupation of the larger cage leaving the smaller cages empty. Then, the free energy of occupation of the smaller cage is obtained under the full occupancy.

The canonical ensemble is converted to the grandcanonical ensemble in a way similar to the original vdWP theory as

$$\begin{aligned} \Xi &= \exp(-\beta A_c^1) \prod_j \sum_{n_j=0}^{N_j} \exp(-\beta n_j \mu_i) \binom{N_j}{n_j} \exp(\beta n_j f_{ij}) \\ &= \exp(-\beta A_c^1) \prod_j (\exp[\beta(f_{ij} - \mu_i)] + 1)^{N_j} \end{aligned} \quad (13)$$

The number of the empty cages is given by

$$\langle n_e \rangle = \frac{\partial \ln \Xi}{\partial(-\beta \mu_i)} = \sum_j N_j \frac{\exp[-\beta(\mu_i - f_{ij})]}{1 + \exp[-\beta(\mu_i - f_{ij})]} \quad (14)$$

This gives the same occupancy as that from the original vdWP theory, that is

$$\begin{aligned} \langle x_i \rangle &= \frac{1}{N_w} \sum_j N_j \left\{ 1 - \frac{\exp[-\beta(\mu_i - f_{ij})]}{1 + \exp[-\beta(\mu_i - f_{ij})]} \right\} \\ &= \sum_j \frac{N_j}{N_w} \frac{\exp[\beta(\mu_i - f_{ij})]}{1 + \exp[\beta(\mu_i - f_{ij})]} \end{aligned} \quad (15)$$

The free energy and the chemical potential of water are also calculated likewise

$$\Phi = A_c^1 - k_B T \sum_j N_j \ln \{ 1 + \exp[-\beta(\mu_i - f_{ij})] \} \quad (16)$$

$$\begin{aligned}
 \mu_c' &= \frac{\partial \Phi}{\partial N_w'} = \mu_c' - k_B T \sum_j \alpha_j \ln \{1 + \exp[-\beta(\mu_i - f_{ij})]\} \\
 &= \mu_c' + k_B T \sum_j \alpha_j \ln \frac{\exp[\beta(\mu_i - f_{ij})]}{1 + \exp[\beta(\mu_i - f_{ij})]} \\
 &= \mu_c' + k_B T \sum_j \alpha_j \ln x_{ij}
 \end{aligned} \quad (17)$$

where the number of the composite molecules, each made of a water molecule and fractional ($\sum_j \alpha_j$) guest, is identical to the number of water molecules ($N_w' = N_w$). It is further written as

$$\mu_c' = \mu_c + \mu_i \sum_j \alpha_j \quad (18)$$

in view of the fact that the total chemical potential is an additive property. The reference state is so chosen that its chemical potential is the sum of the chemical potential of water and the free energy of the cage occupation as given by

$$\mu_c' = \mu_c^0 + \sum_j \alpha_j f_{ij} \quad (19)$$

Thus, we obtain

$$\begin{aligned}
 \mu_c &= [\mu_c^0 + \sum_j \alpha_j (f_{ij} - \mu_i)] + k_B T \sum_j \alpha_j \ln x_{ij} \\
 &= \mu_c^0 + k_B T \sum_j \alpha_j \ln x_{ij}
 \end{aligned} \quad (20)$$

The first term $\mu_c^0 + \sum_j \alpha_j (f_{ij} - \mu_i)$ in the above eq 20 can be regarded as a chemical potential of water in another reference state. The full occupancy is attained in the limit of $\mu_i \rightarrow \infty$ in eq 6. The same is true in eq 17. The advantage of eq 17 is 2-fold: (1) it gives a clearer physical insight into the chemical potential of water in a clathrate hydrate which is not stable until its occupancy becomes almost unity and (2) a comparison with simulation is rather easily made taking little account of the statistical errors in the simulation.

For multiple guest species, the cages of type j are filled with the guest species i_j ; however, all the cage types need not to be filled, and some of the smaller cages may be left unoccupied. The grand partition function is obtained from replacement of the occupying guest by other guest species (including removal of it) as

$$\begin{aligned}
 \Xi &= \exp(-\beta A_c^1) \prod_j \sum_{\substack{n_k=0 \\ (\sum n_k = N_j)}} \frac{N_j!}{n_0!} \\
 &\exp[\beta n_0 (f_{ij} - \mu_i)] \prod_{k=1} \frac{1}{n_k!} \exp[\beta n_k (\mu_k - f_{kj} - \mu_{i_j} + f_{ij})] \\
 &= \exp(-\beta A_c^1) \prod_j \{ \exp[\beta (f_{ij} - \mu_i)] \\
 &\quad + \sum_{k=1} \exp[\beta (\mu_k - f_{kj} - \mu_{i_j} + f_{ij})] \}^{N_j}
 \end{aligned} \quad (21)$$

where the free energy A_c^1 is calculated for the fully occupied clathrate hydrate by the appropriate guest species i_j in at least one of the available cage types. The chemical potential of the

composite molecule is written as

$$\begin{aligned}
 \mu_c' &= \frac{\partial \Phi}{\partial N_w'} \\
 &= \mu_c' - k_B T \sum_j \alpha_j \ln \{ \exp[\beta (f_{ij} - \mu_i)] \\
 &\quad + \sum_{k=1} \exp[\beta (\mu_k - f_{kj} - \mu_{i_j} + f_{ij})] \} \\
 &= \mu_c' + k_B T \sum_j \alpha_j \ln \frac{\exp[\beta (\mu_{i_j} - f_{ij})]}{1 + \sum_{k=1} \exp[\beta (\mu_k - f_{kj})]} \\
 &= \mu_c' + k_B T \sum_j \alpha_j \ln x_{ij}
 \end{aligned} \quad (22)$$

with $\mu_c' = \mu_c^0 + \sum_j \alpha_j f_{ij}$.

The chemical potential of water is given by

$$\mu_c = \mu_c^0 + \sum_j \alpha_j [(f_{ij} - \mu_i) + k_B T \ln x_{ij}] = \mu_c^0 + k_B T \sum_j \alpha_j \ln x_{ij} \quad (23)$$

The free energy f_{ij} should be obtained for each component i in the gas mixture separately. That is, we must consider all the combinations of the possible guest species and the cage types accommodating them.

C. Evaluation of the Free Energy for Clathrate Hydrates.

The free energy of a whole clathrate hydrate, which is either empty or containing spherical guest molecules, is calculated as the sum of the interaction energy at 0 K, the harmonic vibrational free energy, and the residual entropy neglecting the anharmonic term as

$$A = U_q + k_B T \sum_k \ln \frac{h \nu_k}{k_B T} - N_w k_B T \ln(3/2) \quad (24)$$

where U_q is the potential energy at the local minimum structure, and individual vibrational frequency of the clathrate hydrate with or without guest molecules is denoted by ν_k . The last term arises from the residual entropy of the proton disordering.¹⁸ This approximation is justified since the anharmonic contribution to the free energy is rather small compared with the other term; its difference between ice and empty clathrate hydrate is one order of magnitude smaller than the other terms.¹⁴

A further manipulation is necessary for nonspherical guest species since the potential surface on the rotational motion of such a guest is described by neither free rotation nor harmonic vibration. In other words, an approximate method for calculation of the rotational free energy is required. To this end, we first calculate the free energies of cage occupation for the spherical and nonspherical guest whose interactions with fixed host water molecules are denoted by $w'(\mathbf{r})$ and $w(\mathbf{r}, \Omega)$, respectively. For example, the difference between them is given for a nonlinear guest molecule by

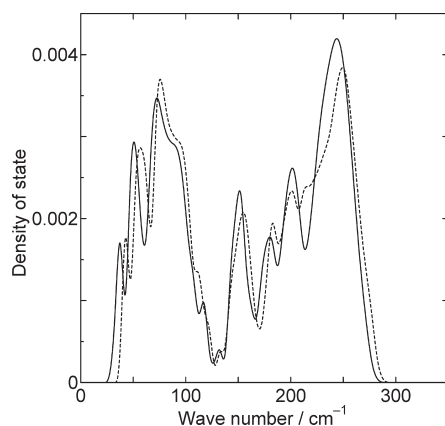
$$\begin{aligned}
 \Delta f_{ij} &= k_B T \ln \left[\int \exp[-\beta w'(\mathbf{r})] d\mathbf{r} - \right. \\
 &\quad \left. k_B T \ln \left[\frac{1}{\sigma_i} \prod_l \left(\frac{2\pi I_l k_B T}{h^2} \right)^{1/2} \iint \exp[-\beta w(\mathbf{r}, \Omega)] d\mathbf{r} d\Omega \right] \right]
 \end{aligned} \quad (25)$$

It is essential to choose an appropriate spherical model for accurate evaluation of the free energy. Next, the free energy is

Table I. LJ Size (σ) and Energy (ϵ) Parameters and Bond Length and Angle for Guest Molecules^a

guest	σ /0.1 nm	ϵ /kJ mol ⁻¹	bond length /0.1 nm	bond angle /degree
isobutane				
spherical	5.341	2.611		
propane			1.540	114.0
methyl	3.930	0.950		
methylene	3.930	0.389		
spherical	5.061	2.112		
ethane			1.540	
methyl	3.930	0.950		
spherical	4.180	1.720		
Xe	4.047	1.921		
CF ₄	4.700	1.267		

^aThe Lorentz–Berthelot rule is applied to all the unlike interactions including guest–water (oxygen atom).

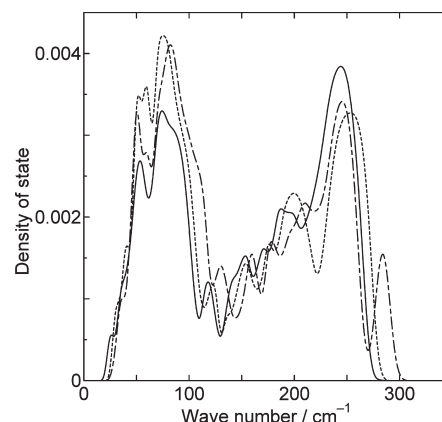
**Figure 1.** Densities of state for intermolecular vibrational motions for clathrate hydrate structure II, empty (solid line) and with isobutane contained in the larger cages (dotted line), where only V_{ww} is diagonalized.

calculated for the clathrate hydrate encaging a spherical guest according to eq 24. The free energy containing nonspherical molecules is calculated by adding the contribution from eq 25 as

$$A_c^1 = U_q + k_B T \sum_k \ln \frac{h\nu_k}{k_B T} - N_w k_B T \ln(3/2) + \sum_j N_j \Delta f_{ij} \quad (26)$$

The free energy of cage occupation including the hindered rotation calculated here is viewed from a different perspective as a sum of the free energy of cage occupation for the realistic guest model under the fixed lattice and the host vibrational free energy difference between empty and occupied clathrate hydrates.

D. Generation of Structure and Intermolecular Interactions. A set of clathrate hydrate structures (CS-I and CS-II) are so generated that each water molecule has four hydrogen bonded neighbors and the net polarization has a vanishing value. The unit cells of both structures are cubic. CS-I and CS-II contain 46 and 136 water molecules, respectively.^{1,2} In the present calculation, the number of water molecules (N_w) is 368 in CS-I, while that in

**Figure 2.** Densities of state for intermolecular vibrational motions for clathrate hydrate structure I, empty (solid line), with spherical ethane contained in the larger cages (dotted line), and with spherical ethane contained in all the cages (dash-dot line).**Table II.** Free Energies (kJ mol⁻¹) of Cage Occupation for Isobutene and Propane in CS-II, Ethane, Xe, and CF₄ in CS-I, Which Are Calculated from the Integration of the Boltzmann Factor for the Guest Interaction (Integration) or from the Free Energy of the Vibrational Motions (Vibrational Frequency)^a

guest/cage type	integration		vibrational frequency	
	large	small	large	small
iso-pentane				
spherical	-50.73		-47.47	
propane				
nonlinear	-44.87			
spherical	-52.18		-51.59	
ethane				
linear	-38.29	-15.55		
spherical	-38.63	-19.70	-37.86	-15.95
Xe	-43.81	-38.59	-45.26	-37.50
CF ₄	-36.50	-11.66	-34.43	-6.97

^aThe free energy of the rotational part, which is cancelled by the chemical potential of the guest gas, is removed for comparison between the spherical and nonspherical model.

Table III. Chemical Potential of Water μ_c^0 for Empty Clathrate Structure I and II (CS-I, CS-II) at 273.15 K along with That of Hexagonal Ice (ice Ih) μ_i in kJ mol^{-1a}

type	$\mu_c^0(\mu_i)$	$\Delta\mu_c^0$
ice Ih	-48.88	
CS-I	-48.12	0.76
CS-II	-48.30	0.58

^aThe common residual entropy term is omitted.

CS-II is set to 136, imposing a periodic boundary condition. The unit cell size is fixed to 1.203 nm in CS-I and 1.731 nm in CS-II.^{1,2}

The interaction between two water molecules is described by the TIP4P water with smooth tapering.^{17,19} The intermolecular

Table IV. Dissociation Pressures in Bar and Cage Occupancies Obtained from the Free Energies of Cage Occupation at 273.15 K According to the Present and the Original vdWP Theory^a

guest	theoretical (present)	theoretical (original)	experimental	occupancy (large)	occupancy (small)
isobutane (spherical)	0.91	0.22	1.0	0.99	---
propane (nonlinear)	2.2	1.9	1.7	0.99	---
propane (spherical)	0.1	0.08	1.7	0.99	---
ethane (linear)	4.2	3.0	5.3	0.92	0.00
ethane (spherical)	3.6	2.6	5.3	0.98	0.00
Xe	2.0	1.9	1.5	0.91	0.38
Xe(ref 28)				0.98	0.72
CF ₄	81.8	32.9	42.0	0.92	0.00

^aThe listed occupancies are calculated according to the present theory.

interaction for guest ethane and the propane molecule either linear or nonlinear is given by the sum of the site–site interactions; methyl and methylene groups are treated as united atoms each interacting with Lennard-Jones (LJ) potential.^{20,21} Xe, CF₄, and isobutane molecules are described by a single LJ interaction site.^{22,23} The Lorentz–Berthelot rule is applied to all the unlike LJ interactions. All the interaction parameters for guests are tabulated in Table I. Ethane and propane are approximated to spherical ones in the intermediate stage of free energy evaluation. The potential parameters for (hypothetical) spherical molecules adopted here were estimated from experimental observations.^{22,23}

III. RESULTS AND DISCUSSION

A. Local Energy Minimum Structures and Normal-Mode Analyses. Each 100 structures of hexagonal ice, empty, and occupied clathrate hydrates are subject to quenching by the steepest descent method.²⁴ The mean potential energy of the local energy minimum is a component of the free energy in eq 24. The Hessian is calculated for each local energy minimum structure, and a set of the lattice frequencies are obtained. The free energy of the vibrational motions is given as the sum of the free energy of the individual harmonic oscillator in the second term of eq 24. The density of state for isobutane clathrate hydrate is shown in Figure 1 along with that for the empty one. It clearly shows a shift to higher frequency for modes below 300 cm⁻¹, which are associated with the translational motions of individual water molecules. The density only for the lower frequency region is plotted since no remarkable difference is observed in the higher frequency region between 500 and 1000 cm⁻¹, which corresponds to the rotational motions. A similar plot for ethane clathrate hydrate is given in Figure 2. It is shown that occupation of the larger cages gives rise to an increase in the population of the lower frequency region as well as a shift to higher frequency. Ethane in smaller cages brings high frequency vibration around 300 cm⁻¹. Therefore, accommodation of ethane in a smaller cage is unlikely to occur due to the increase in the vibrational free energy of the host lattice.

B. Free Energies of Cage Occupation. The free energy of cage occupation for the isobutane guest is calculated simply from the normal modes of the CS-II hydrate, the larger cages of which are fully occupied by the guest molecule. The long-range interaction is taken into account assuming a uniform distribution of the guest and host molecules. That for propane is obtained from the sum of the two components: (1) the free energy of cage occupation of a spherical guest propane by the normal-mode analysis and (2) the free energy difference between a realistic

(three site) and the spherical model, Δf_{ij} , in eq 26. The free energies thus calculated are listed in Table II. A large guest molecule such as isobutane gives rise to a higher free energy than that from the integration of the corresponding Boltzmann factor.

Ethane, Xe, and CF₄ guests are accommodated in CS-I. Both the smaller and larger cages are examined whether they encage those guest species. The free energy of occupation of the larger cage is first calculated under the full occupancy of the larger cage, while the smaller cages are left empty. The free energy of occupation of the smaller cage is then obtained with two sorts of cages fully occupied. A further process is required for ethane to incorporate its rotational motion as in propane guest.

C. Dissociation Pressure. In evaluation of the chemical potential of water in ice and empty clathrate hydrate, the small pV (pressure times volume) term is neglected in a low pressure region below 1 MPa. The chemical potentials of ice Ih and empty clathrate hydrates at 273.15 K are tabulated in Table III, where the common residual entropy term is removed.¹⁸ It is of interest to compare these values with the experimental ones.²⁵ Both experiment and theoretical calculation show that empty CS-II is more stable than empty CS-I. The present values of the chemical potential difference between ice Ih and empty clathrate hydrate for CS-I and CS-II are rather smaller compared with the experimental ones. Even if we generate each 1000 structures of different proton ordering, no deviations in the chemical potential difference are found. These values depend solely on the potential function, the TIP4P,¹⁹ which is designed in a subtle balance between the Coulombic and LJ interactions. The smaller values in the present model potential seem to be compensated by the free energies of cage occupation.

We examine the phase equilibrium between ice Ih and clathrate hydrate in the presence of a guest (ideal) gas at pressure p . The equilibrium is attained when $\mu_c = \mu_i$. Since the free energy of occupation by Xe from the simple integration is higher for the larger cage than that by the mode frequency, the former way seems to be more accurate and is actually used. The correction from the lattice vibration Δf_{ij} is added to the free energy of occupation by the spherical guest molecule. The dissociation pressures for isobutane, propane, ethane, Xe, and CF₄ are given in Table IV according to the present and the original vdWP theory. The agreement with experiment is fairly good but is not perfect.^{2,26,27} The original vdWP theory always gives the lower dissociation pressures than those from the present theory. Notable differences appear in isobutene and CF₄ clathrate hydrates. The smaller cage in CS-I contains neither ethane nor CF₄. To aim at further agreement with experiment, an anharmonic free energy neglected in the present method may be taken

into account. Computational cost in the present calculation is much smaller, despite its limitations, than that by the standard free energy calculation such as thermodynamic integration. The small to large cage occupancy ratio for Xe clathrate hydrate had been studied by Xe-129 NMR,²⁸ and its agreement with the present theoretical calculation is fairly good in the larger cage but is rather poor in the smaller cage as listed in Table IV. However, discrepancies of the mean occupancy among various experiments are also large.²⁸ The origin of the discrepancies must be addressed in future study.

IV. CONCLUDING REMARKS

We propose a novel method to evaluate thermodynamic stability of clathrate hydrates, in which some sorts of cages are *almost fully* occupied. It is considered that an equilibrium is attained by removing some of the guest molecules from the fully occupied clathrate hydrate, which is chosen to be a new reference state. One of the advantages to adopt this reference state is that it is closer to the real clathrate hydrate, and therefore a possible dependence of the free energy of cage occupation on the occupancy of the other cage can be eliminated. It also serves to evaluate accurately the thermodynamic stability from GCMC simulations. In fact, the last term in eq 20 is rather insignificant in the limit of the full occupancy. The present method is not computationally demanding except for calculation of the free energy for occupation of nonlinear guest molecules, and it is possible to cover a wide range of temperatures.

The situation mentioned above is realized in CS-II, the larger cages of which contain propane or isobutane molecules. The present method is preferable when guest molecules affect the lattice vibrations and thus the dissociation pressure becomes higher than that expected from the original vdWP theory. In particular, an isobutane molecule is large enough to shift the frequencies of the host vibrational motions, and the occupancy of the larger cage is almost unity (see Table IV). Then, the chemical potential of water is approximated to

$$\mu_c \approx \mu_c^0 + \frac{1}{17} (\mu_{\text{butane}} - \mu_{\text{butane}}^0) \quad (27)$$

by which the dissociation pressure is easily calculated. Therefore, isobutane clathrate hydrate is one of the most suitable targets to examine the effectiveness of the present theoretical treatment. Indeed, the present method reasonably predicts the dissociation pressure.

It should also be noted that the chemical potential of water in eq 23 is expressed only by the properties of the guest species filling the corresponding cages in the new reference state, which is preferable for experimental (and also GCMC) evaluation of the thermodynamic stability of clathrate hydrates in equilibrium with gas mixtures. That is, we may take advantage of the fact that only one of the free energies of cage occupation is required as revealed by eq 23. The present alternative reference state is also applicable to multiple cage occupation.

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$$V = \begin{pmatrix} V_{ww} & V_{wg} \\ V_{gw} & V_{gg} \end{pmatrix}$$
 where subscripts w and g indicate water and guest. The small submatrix V_{ww} is different from that for a corresponding empty clathrate hydrate since the block diagonal elements contain extra terms associated with the host–guest interaction, $\phi(\mathbf{r}_w, \mathbf{r}_g)$. When a guest molecule is large but causes no distortion, the extra terms are given by $(\partial^2 \phi(\mathbf{r}_w, \mathbf{r}_g))/(\partial \mathbf{r}_w \partial \mathbf{r}_w)$, whose diagonal elements are positive due to the dominated contribution from the repulsive interaction. Thus, the extra positive diagonal terms result in the high frequency of the host lattice. A more detailed explanation and an instance are given in ref 4.
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