On the thermodynamic stability of hydrogen clathrate hydrates

Keisuke Katsumasa, Kenichiro Koga, and Hideki Tanaka[a)]
Department of Chemistry, Faculty of Science, Okayama University, 3-1-1 Tsushima, Okayama 700-8530, Japan

The cage occupancy of hydrogen clathrate hydrate has been examined by grand canonical Monte Carlo (GCMC) simulations for wide ranges of temperature and pressure. The simulations are carried out with a fixed number of water molecules and a fixed chemical potential of the guest species so that hydrogen molecules can be created or annihilated in the clathrate. Two types of the GCMC simulations are performed; in one the volume of the clathrate is fixed and in the other it is allowed to adjust itself under a preset pressure so as to take account of compression by a hydrostatic pressure and expansion due to multiple cage occupancy. It is found that the smaller cage in structure II is practically incapable of accommodating more than a single guest molecule even at pressures as high as 500 MPa, which agrees with the recent experimental investigations. The larger cage is found to encapsulate at most 4 hydrogen molecules, but its occupancy is dependent significantly on the pressure of hydrogen. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2751168]

I. INTRODUCTION

Clathrate hydrates are nonstoichiometric compounds made from water and guest molecules. The clathrate hydrate is stable only when guest molecules exist in its cages. It has long been believed that each cage accommodates only one guest molecule. Based on this assumption, the thermodynamic stability of the clathrate hydrates has been accounted for by van der Waals and Platteeuw (vdWP).[1] Phase behaviors of many hydrates have been successfully predicted by the vdWP theory.[2,3] It is assumed that host motions are independent of occupancy by guest molecules, i.e., a guest molecule moves in a cage of host water molecules *fixed* at the lattice sites. This is reasonable unless a guest molecule is large enough to alter the host vibrational motions. In that case, more sophisticated treatments lead to better agreement with experimental phase behaviors.[4–6] Furthermore, multiple occupancy of a single cage can be handled in the framework of the vdWP theory.[7]

Since their discovery by Mao *et al.*,[8] hydrogen clathrates have attracted considerable attention as a possible candidate for hydrogen storage. A hydrogen clathrate is identified with structure II, which is made by both 12- and 16-hedra.[8] It is formed at pressures around 200 MPa. The high pressure suggests a possibility of multiple occupancy of a single cage. In fact, it was pointed out that a larger cage can accommodate 4 hydrogen molecules and even a smaller cage might contain 2. However, occupancy of hydrogen molecule in a smaller cage is still controversial.[9–11] Also interesting is that the dissociation pressure can be fairly reduced by accommodating tetrahydrofuran (THF).[12,13] This is advantageous to its use for hydrogen storage because a moderate pressure such as 10 MPa suffices for its stabilization; a major disadvantage is its lower efficiency due to the fact that a fairly large portion of larger cages is occupied by THF in this binary clathrate.

Then, double occupancy in a smaller cage becomes more crucial for its application. Recently, however, experimental studies indicate that only a single molecule is contained in a smaller cage in binary clathrate hydrate.[14,15] Molecular dynamics simulation studies support the observations,[11,16] revealing that accommodation of two molecules in a smaller cage leads to a severe strain. This gives rise to a high free energy of cage occupation and thus casts doubt on a double occupancy.

In order to clarify the issue as to the smaller cage occupancy, it is desirable to evaluate more directly the cage occupancies as a function of pressure and temperature. Here, we consider clathrate hydrate which is in equilibrium with gas (fluid) hydrogen at a given temperature and is under hydrostatic pressure equivalent to the pressure on hydrogen gas. This condition seemingly corresponds to a grand canonical (GC) ensemble where the number of guest molecules is variable under the constant chemical potential. However, the number of water molecules is fixed to be consistent with the given crystalline structure. In fact, this is close to the condition that we set up the partition function according to the vdWP theory.[1] Thus, our simulation follows the protocols based on this hybrid (GC/NVT) ensemble. (A slightly different ensemble, GC/NPT, will be discussed below.) In addition to the number of water molecules N_w and temperature T, we may choose the pressure P (or chemical potential μ of guest hydrogen) as an independent intensive property instead of the density of water, N_w/V (or equivalently volume, V) under an unknown pressure. When P is increased, two opposite factors may lead to unpredictable pressure dependence of volume: the simple hydrostatic pressure reduces the volume, whereas the high chemical potential gives rise to higher occupancy of the cages, which in turn expands the volume. Thus, it seems more desirable to choose P rather than N_w/V as an independent variable because hydrogen clathrates are formed under high pressure and that pressure should be the same as the gas pressure of hydrogen. This is achieved by

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a)Electronic mail: htanakaa@cc.okayama-u.ac.jp

TABLE I. Potential parameters for hydrogen molecules. The LJ interaction exerts between two centers of mass for hydrogen molecule while the positive charges are located on each atom and the negative charge is on the center of mass. The two hydrogen atoms are separated by 0.074 14 nm.

Site	q (e)	σ (0.1 nm)	ε (kJ mol^{-1})
H	+0.4932		
C	−0.9864	3.038	0.2852

switching from the GC/*NVT* ensemble to the GC/*NPT* ensemble, which allows volume change under a fixed pressure. The GC/*NPT* Monte Carlo (MC) simulation gives both the cage occupancy and the equilibrium volume, which are the main concerns in the present study.

The present paper is organized as follows. Models and simulation methods used in the present study are described in Sec. II. The cage occupancies and the volume for hydrogen clathrate at various temperatures and pressures are shown and a relation between the vdWP theory and the GCMC/*NPT* (*NVT*) hybrid ensemble simulation is discussed in Sec. III. The conclusion is given in Sec. IV.

II. SIMULATION METHOD

A. Intermolecular interactions and structure of clathrate hydrate II

The thermodynamic stability and the cage occupancy of clathrate hydrate are evaluated with intermolecular potentials which are reliable but as simple as possible. In the present study, all interactions are assumed to be pairwise additive. The water-water intermolecular interaction is described by the TIP4P potential.[17] This potential has often been used in the study of water. It is believed to be the most reliable within the framework of pair potential, at least in reproducing important properties not only of pure water but also of ice.[18] The TIP4P model consists of four interaction sites: a positive charge, q_H, on the hydrogen atom, a negative charge ($-2q_H$) on the bisector of two OH bonds, and a soft-core interaction between oxygen atoms. It should also be noted that choice of the water-water interaction does not make a serious difference in cage occupancy under moderate compression which does not lead to collapse of the original hydrate structure or to significant hydrogen bond cleavage. A hydrogen molecule is modeled by a single site interacting via Lennard-Jones (LJ) potential. In addition, each atom has a positive charge separated from another atom by 0.074 14 nm and the corresponding negative charge sits on the midpoint of the chemical bond as given in Table I.[19,20] For the water-guest interaction, the Lorentz-Berthelot rule is assumed. The interaction potentials for all pairs of molecules are truncated smoothly at 0.8655 nm.[21] The correction term arising from the truncation of all the LJ interactions is taken into account in calculating the free energy of hydrogen fluid and the occupancy in clathrate hydrate.

A clathrate hydrate II structure was generated elsewhere.[4] The unit cell of the hydrate II is cubic and experimental lattice parameters are used in the following calculation: $a=b=c=1.7047$ nm with $\alpha=\beta=\gamma=\pi/2$.[2,3,8] The

structure is of proton-disordered form and has zero net dipole moment. The basic cell in the present MC simulations is composed of 8 unit cells of clathrate hydrate II, in each of which 136 water molecules are placed on the lattice sites.

B. GC/*NVT* and GC/*NPT* Monte Carlo simulations

The accommodation of the guest molecules can be regarded as an adsorption of the guest in the cavity. Thus, the number of guest molecules at a given pressure (at a given chemical potential of guest species in the gas phase) can be evaluated in the same fashion as usual adsorption process by GCMC simulation. This simulation is carried out with the fixed parameters of the temperature, the volume of the clathrate hydrate, and the chemical potential of the guest species, μ. The chemical potential of the guest molecule is calculated from the equation of state as shown below.

We proposed a GCMC method to facilitate the creation and annihilation of the guest molecule by a kind of preferential sampling, choosing a cavity center with a higher probability so that an interaction energy of a guest with surrounding host water molecules is favorable for insertion.[6] A simple weighting function was prescribed. However, this sampling makes the accept-reject scheme complicated.[6] The method does not seem to work efficiently for the multiple occupancy of cage unless a further revision of the weighting function is made. Moreover, a rather small hydrogen molecule may stay somewhere close to a center of a face shared by two cages. Therefore, it seems that a simple GCMC method is a better choice than a sophisticated one with a complicated weighting function.

In the following simulations, a standard GCMC simulation method is applied, which is commonly used for studying a phase equilibrium of fluids. The method is briefly outlined below. A usual MC technique is applied to water, that is, a system is treated as a canonical ensemble with respect to water. Thus, our simulation is a hybrid one, called GC/*NVT* MC simulation. The volume is fixed to the experimentally observed value 21.94 cm^3 around 200 MPa.[8] A guest hydrogen molecule is inserted or deleted according to the standard technique of GCMC simulation. A trial insertion is made at an arbitrary position with a random orientation. Such an insertion accompanied by the interaction energy w with all other molecules including N_g hydrogen molecules is accepted with a probability

$$p_i = \exp[\beta(\mu' - w)](2\pi m k_B T/h^2)^{3/2} V/(N_g + 1), \quad (1)$$

where h is the Planck constant and μ' stands for the chemical potential of hydrogen that excludes the contribution from the free-rotational motion. Here, β is $1/k_B T$ with Boltzmann constant k_B. A deletion of an arbitrarily chosen molecule out of N_g guests in the system is attempted. The trial is accepted with a probability

$$p_d = N_g(2\pi m k_B T/h^2)^{-3/2}\exp[\beta(-\mu' + w')]/V, \quad (2)$$

where w' is the interaction energy of the chosen guest with all other molecules. The intermolecular interaction is truncated smoothly as in GCMC simulations but its correction to the pressure is taken into consideration with an assumption

that molecular arrangement is uniform beyond the trunca-
tion.

We assume that the hydrostatic pressure on the hydrate is
equal to that of the hydrogen fluid. The pressure covered in
this study ranges from 100 to 500 MPa, which can lead to
alternation of the cell dimension. Then, there is a more ap-
propriate way to calculate the cage occupancy at a given
temperature and pressure, which is set equal to the pressure
of hydrogen being in equilibrium with the hydrate. The vol-
ume change is attempted according to the usual *NPT* MC
simulation in addition to the GC/*NVT* procedures, referred
to hereafter as GC/*NPT* MC simulation. In the present
GC/*NPT* (*NVT*)MC simulations, a single MC step consists
of either a trial creation or annihilation (with the same prob-
ability) followed by five trial moves of molecule, and a sub-
sequent volume change (in GC/*NPT*). Each MC simulation
at given temperature and pressure includes 4×10^7 steps.

C. MC simulations and chemical potential for hydrogen fluid

The equation of state for hydrogen fluid interacting via
the prescribed potential is not known. Thus, it is essential to
obtain the pressure at various densities for each temperature
from simulation. The number of molecules used in the simu-
lation is taken to be in a range between 128 and 512, depen-
dent on the density, so that the volume falls into a certain
range. The density ranges from 0.2 to 64 mol ℓ^{-1}, which is
enough for the present purpose. The chemical potential of the
imperfect gas (fluid) for a linear rigid rotor is calculated as
follows. At a given temperature, we perform *NVT* MC simu-
lations of pure hydrogen with various volumes (number den-
sities, ρ). The long-range interaction is again taken into ac-
count in the calculation of the pressure. Thus, we obtain an
isotherm of the pressure.

The free energy (per molecule), a, at T and ρ for hydro-
gen with the mass, m, and the moment of inertia, I, is given
by sum of the ideal and the nonideal parts as

$$a = k_B T[\ln \rho(h^2/2\pi m k_B T)^{3/2} - 1 + \ln\{h^2/(4\pi^2 I k_B T)\}]$$

$$+ \int_0^\rho (P - \rho k_B T)/\rho^2 d\rho. \qquad (3)$$

Since we deal with a one-component system, the chemical
potential, μ, is simply given by

$$\mu(T,P) = a + P/\rho, \qquad (4)$$

where ρ at a given pressure P is calculated from the interpo-
lation of the isotherm.

III. RESULTS AND DISCUSSION

We obtain the pressures of pure fluid hydrogen at various
densities, which are sufficient for numerical integration to
calculate the corresponding free energy. We calculate the
chemical potential of hydrogen fluid from these isotherms as
a function of pressure and temperature. Contrary to argon,
the chemical potential of the real hydrogen fluid in the inter-
mediate pressure range (10–100 MPa) is practically equiva-
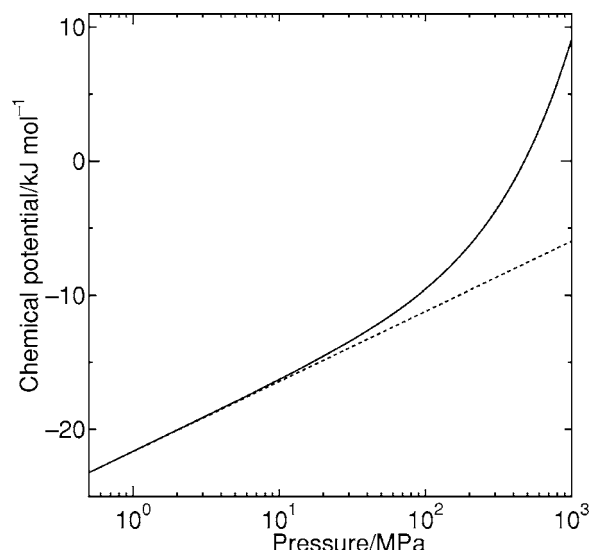lent to that treated as an ideal gas with rigid rotors as shown

FIG. 1. Pressure dependence of chemical potential for hydrogen gas and
hypothetical ideal gas at 273 K.

in Fig. 1. This is due to the negligibly small attractive inter-
action. It becomes higher than that of the corresponding ideal
gas in the high-pressure range 200–500 MPa, where multiple
occupancy is expected to dominate.

The potential energy curve of a guest hydrogen inside a
smaller cage is examined: it is the potential energy of a guest
molecule interacting with all the water molecules fixed to the
lattice sites. It is calculated as a function of radial distance, r,
from the center of the cage averaged over all orientations of
molecular positions relative to the unit cell and also over
orientations of hydrogen molecule. It is plotted in Fig. 2
along with the minimum energy at a given r. The potential
energy curve in a smaller cage is a monotonically increasing
function with the distance, r. A hydrogen molecule can move
in a sphere of radius of 0.13 nm.[10]

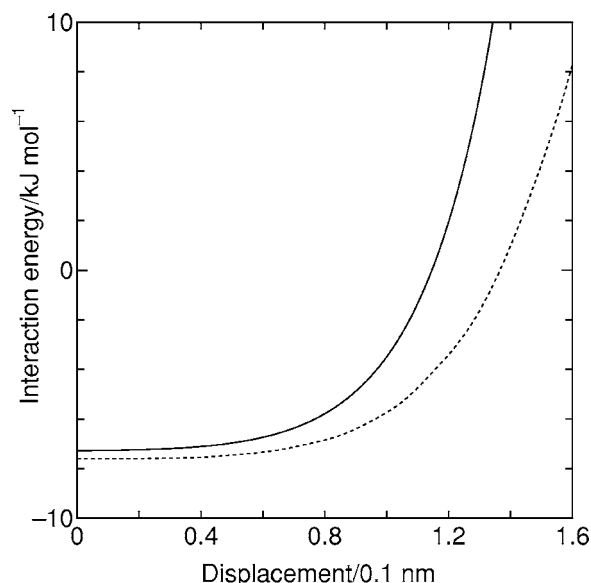Both GC/*NVT* and GC/*NPT* MC simulations are carried

FIG. 2. Interaction energy curve of a hydrogen molecule in smaller cage as
a function of displacement from its center: averaged energy over orientation,
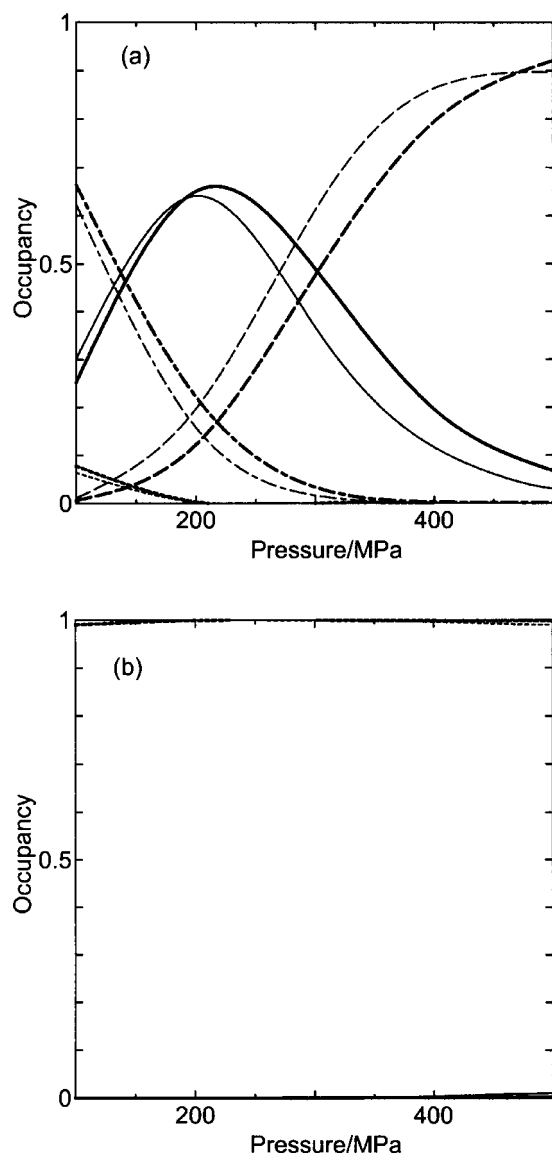solid line; minimum energy, dotted line.

FIG. 3. Occupancy of (a) larger cage (dotted, single; dotted-dashed, double; solid, triple; dashed, quadruple occupancy) and (b) smaller cage (solid, single; dotted, double occupancy) obtained from GC/*NPT* and GC/*NVT* MC simulations at 170 K (heavy lines, GC/*NPT*; thin lines, GC/*NVT*).
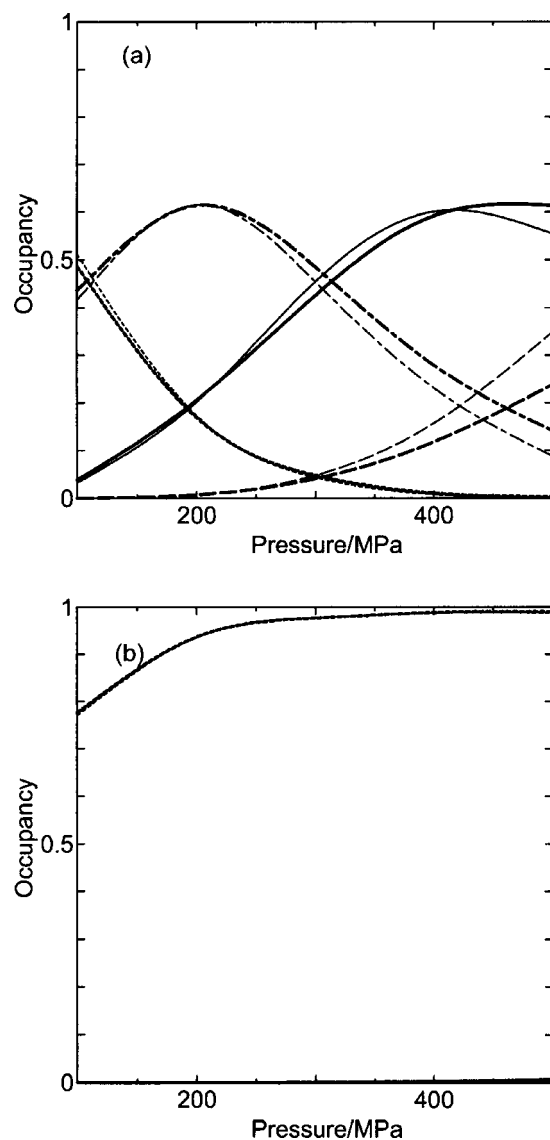

FIG. 4. Occupancy of (a) larger cage (dotted, single; dotted-dashed, double; solid, triple; dashed, quadruple occupancy) and (b) smaller cage (solid, single; dotted, double occupancy) obtained from GC/*NPT* and GC/*NVT* MC simulations at 273 K (heavy lines, GC/*NPT*; thin lines, GC/*NVT*).

out at $T=170$, 210, 250, and 273 K and at pressure ranging from 100 to 500 MPa. Pressure dependence of the cage occupancies at 170 K are plotted in Fig. 3 for both larger and smaller cages. For the larger cage, the occupancies depend significantly on the pressure of hydrogen fluid. Single occupancy makes minor contribution even at 100 MPa. Double occupancy prevails in a low-pressure range. It decreases with increasing pressure. Then, triple occupancy becomes dominant. At higher pressure, it is replaced finally by quadruple occupancy. No further incorporation of hydrogen molecule is observed at 500 MPa. On the other hand, a small cage contains only a single hydrogen molecule in the pressure range we have examined. Only 0.2% of smaller cage encapsulates two hydrogen molecules at 500 MPa. At temperature 273 K, single occupancy of smaller cage decreases and double occupancy is slightly increased but is still hardly observed (only 0.7%), even at 500 MPa as shown in Fig. 4. For a

larger cage, multiple occupancy is not so distinct compared with that at 170 K but it becomes dominant at higher pressure.

We perform GC/*NPT* MC simulations where the cell size is variable subject to a condition that the same magnitude of pressure is applied to clathrate hydrate as imposed on hydrogen fluid. Our qualitative argument on occupancy in larger cage does not change, although some quantitative differences are observed as shown in Fig. 3. This difference arises mainly from the fact that the input volume is fixed to 21.94 cm^3 over the entire series of GC/*NVT* simulations. In fact, the difference is negligibly small when we adopt the volume obtained in GC/*NPT* MC simulation. Considering this, GC/*NPT* MC simulation is more preferable since it provides the same information as experiments, the cage occupancy and the volume (density).

Here, let us examine a relation between the vdWP theory and the GCMC/*NPT* (*NVT*) hybrid ensemble simulation in

more detail. In both the vdWP theory and the GCMC/NVT MC simulation, we fix the temperature T, the volume V, the number of water molecules N_w, and the chemical potential μ of hydrogen molecules. This meets the phase rule; there are three intensive properties, $\rho_w = N_w/V$, T, and μ other than one extensive property of clathrate hydrate, say N_w or V. That is, f (number of independent intensive properties) $= c$(number of components)$+2-p$(number of phases) $=3$ with $p=2$ leads to $c=3$. It is assumed under this circumstance that there is an extra molecular species, which cannot be encaged in the clathrate hydrate and serves to increase the pressure. Then, the pressure on the clathrate hydrate can be different from the partial pressure of hydrogen gas of the given chemical potential μ. For simplicity, we consider only single occupancy for this comparison. The grand canonical partition function for the clathrate with N_l larger and N_s smaller cages is given by

$$
\begin{aligned}
\Xi = &\exp(-\beta A_w^0) \sum_{n_l=0}^{N_l} \binom{N_l}{n_l} \exp[\beta n_l(\mu - f_l)] \\
&\times \sum_{n_s=0}^{N_s} \binom{N_s}{n_s} \exp[\beta n_s(\mu - f_s)] \\
= &\exp(-\beta A_w^0)\{1 + \exp[\beta(\mu - f_l)]\}^{N_l} \\
&\times \{1 + \exp[\beta(\mu - f_s)]\}^{N_s},
\end{aligned}
\tag{5}
$$

where A_w^0 is the Helmholtz free energy of the empty clathrate hydrate and both f_l and f_s indicate the free energies of the larger and smaller cage occupation, respectively. The pressure is derived by

$$
P = \partial \ln \Xi / \partial(\beta V),
\tag{6}
$$

which is necessarily different from the pressure of the guest with the chemical potential, μ. Instead, we may consider a system of two components. Then, $f = c + 2 - p = 2 + 2 - 2 = 2$ and the independent intensive properties may be T and μ, or T and P. The volume (or ρ_w) is not an independent variable but is rather so determined that $\Xi \exp(-\beta PV)$ takes it maximum value.

In the GC/NPT MC simulation, the relevant partition function is given by

$$
\Upsilon = \frac{1}{v_0} \int_0^\infty dV \exp(-\beta PV) \Xi,
\tag{7}
$$

where v_0 is a unit volume, which is introduced to make the partition function dimensionless. The volume (and ρ_w) is not an independent property but is calculated as

$$
V = -\partial \ln \Upsilon / \partial(\beta P) = \frac{1}{v_0 \Upsilon} \int_0^\infty dV V \Xi \exp(-\beta PV).
\tag{8}
$$

The second equality holds since the chemical potential is irrelevant to the pressure, P. Thus, the same argument as in GC/NVT MC simulation holds for the system composed of three components. If we do not introduce an extra species, $f = 2 + 2 - 2 = 2$, which means that ρ_w (or V) is no longer an independent property. Then, the Laplace transform is not required to change to GC/NPT ensemble as in Eq. (7), but Ξ

in Eq. (5) $\times \exp(-\beta PV)$ should be maximized with respect to variation of the volume, giving the equilibrium volume $\langle V \rangle$ at given P, which corresponds to GC/NPT ensemble. In any case, Υ is expressed as

$$
\begin{aligned}
\Upsilon \simeq &\exp(-\beta G_w^0)\{1 + \exp[\beta(\mu - f_l)]\}^{N_l} \\
&\times \{1 + \exp[\beta(\mu - f_s)]\}^{N_s},
\end{aligned}
\tag{9}
$$

where G_w^0 indicates the Gibbs free energy of empty clathrate $(A_w^0 + PV)$ and both f_l and f_s are the free energies at the equilibrium volume $\langle V \rangle$ filled with the equilibrium number of guest molecules.

An extension of vdWP theory to multiple occupancy was given previously.[6] The corresponding GC/NPT partition function is given as

$$
\Upsilon = \exp(-\beta G_w^0) \prod_k \left\{ \sum_{n=0} \exp[\beta(n\mu - f_{kn})] \right\}^{N_k},
\tag{10}
$$

where f_{kn} is the free energy of occupancy of type-k cage by n guest molecules out of N_k cages in clathrate hydrate at the equilibrium volume $\langle V \rangle$. The average guest number is calculated as

$$
\langle N_g \rangle = \frac{\partial \ln \Upsilon}{\partial(\beta\mu)} = \sum_k \frac{N_k\{\sum_{n=1} n \exp[\beta(n\mu - f_{kn})]\}}{\{\sum_{n=0} \exp[\beta(n\mu - f_{kn})]\}}.
\tag{11}
$$

The integration for n hydrogen guest coordinates in a cage is performed with the interaction with water w and that between two guests ϕ to give the free energy, f_{kn} as

$$
\begin{aligned}
\exp(-\beta f_{kn}) = &\frac{1}{n!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3n/2} \left(\frac{2\pi I k_B T}{h^2} \right)^n \\
&\times \prod_i^n \int_v d\mathbf{r}_i \int_{2\pi} d\mathbf{\Omega}_i \\
&\times \exp\left\{ -\beta \left[\sum_i^n w(\mathbf{r}_i, \mathbf{\Omega}_j) \right. \right. \\
&\left. \left. + \sum_{i<j}^n \phi(\mathbf{r}_i, \mathbf{\Omega}_i, \mathbf{r}_i, \mathbf{\Omega}_j) \right] \right\},
\end{aligned}
\tag{12}
$$

where $\mathbf{r}$ and $\mathbf{\Omega}$ stand for the Cartesian coordinate and the orientational parameters. The integration is made in the available volume of the individual cage and in the orientational space of 2π for each molecule considering the symmetry of individual molecules. The above integration is hard to perform even for $n=2$ to examine the possibility of double occupancy in a smaller cage. However, we can evaluate the minimum interaction energy of two hydrogen molecules by a usual MC simulation, and thus, the upper limit of the double occupancy in a smaller cage as

$$
\eta'_{sd} = \frac{2 \exp[\beta(2\mu - f_{2\min})]}{1 + \exp[\beta(\mu - f_1)] + \exp[\beta(2\mu - f_{2\min})]}.
\tag{13}
$$

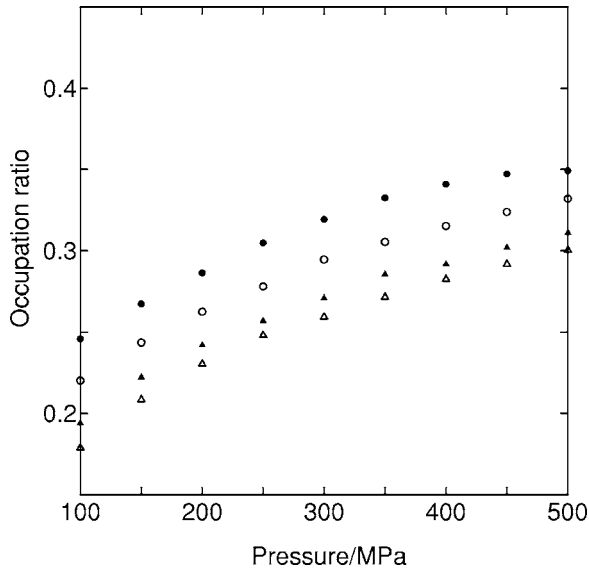The free energies f_1 and $f_{2\min}$ are calculated as

FIG. 5. Ratio of H_2/H_2O obtained from GC/NPT MC simulations at various pressures and temperatures (filled circle, $T=170$ K; open circle, $T=210$ K; filled triangle, $T=250$ K; open triangle, $T=273$ K).
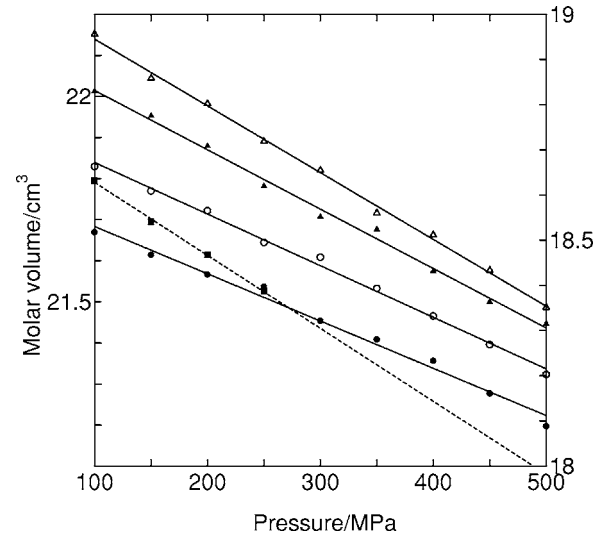

FIG. 6. Pressure dependence of (water) molar volume of clathrate hydrates obtained from GC/NPT MC simulations at various pressures and temperatures [filled circle, $T=170$ K; open circle, $T=210$ K; filled triangle, $T=250$ K; open triangle, $T=273$ K; together with that of cubic ice (with no guest molecule) at 170 K, dotted line and square (in the right vertical scale)].

$$\exp(-\beta f_1) = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{2\pi I k_B T}{h^2} \int_v d\mathbf{r} \int_{2\pi} d\mathbf{\Omega}$$
$$\times \exp\{-\beta[w(\mathbf{r},\mathbf{\Omega})]\}, \tag{14}$$

and as

$$\exp(-\beta f_{2\min})$$
$$= \frac{1}{2!}\left(\frac{2\pi m k_B T}{h^2}\right)^3 \left(\frac{4\pi^2 I k_B T}{h^2}\right)^2 (4\pi r_0^3/3)^2$$
$$\times \exp\{-\beta[w(\mathbf{r},\mathbf{\Omega}) + w(\mathbf{r}',\mathbf{\Omega}')$$
$$+ \phi(\mathbf{r},\mathbf{r}',\mathbf{\Omega},\mathbf{\Omega}')]_{\min}\}$$
$$> \frac{1}{2!}\left(\frac{2\pi m k_B T}{h^2}\right)^3 \left(\frac{2\pi I k_B T}{h^2}\right)^2 \int_v d\mathbf{r} \int_{2\pi} d\mathbf{\Omega} \int_v d\mathbf{r}'$$
$$\times \int_{2\pi} d\mathbf{\Omega}' \exp\{-\beta[w(\mathbf{r},\mathbf{\Omega})$$
$$+ w(\mathbf{r}',\mathbf{\Omega}') + \phi(\mathbf{r},\mathbf{r}',\mathbf{\Omega},\mathbf{\Omega}')]\}, \tag{15}$$

where the last term gives the free energy of double occupancy, f_2. The integration is performed within a sphere of volume v of radius $r_0 = 0.13$ nm. The minimum free energy for double occupancy, $f_{2\min}$ in a smaller cage is -1.9 kJ mol^{-1} and the free energy for single occupancy is -7.7 kJ mol^{-1}, which lead to $\exp[\beta(2\mu - f_{2\min})] \simeq 5.6$ and $\exp[\beta(\mu - f_1)] \simeq 46$ at 273.15 K with $\mu = 1$ kJ mol^{-1} at $P = 500$ MPa. This implies that a pair of hydrogen molecules hardly occupies a smaller cage, considering the fact that $\exp[\beta(2\mu - f_{2\min})] > \exp[\beta(2\mu - f_2)]$.[22]

The mean occupation ratio, η, at various temperatures are shown in Fig. 5, in which η is defined here as a ratio of the number of hydrogen molecules to that of water; note that η is different from η' in Eq. (13). If all the smaller and larger cages are double and quadruple occupied, the occupancy ratio is $(16\times2 + 8\times4)/136 \simeq 0.47$. It is about 0.35 by the

present GC/NVT MC simulation at 170 K and 500 MPa. This is also supported from MD simulation by Alavi et al.[11] Recent experimental studies also indicate that a smaller cage encapsulates only a single hydrogen molecule.[14,15]

The equilibrium (water) molar volume is obtained from GC/NPT MC simulations. Pressure dependences of the molar volume are plotted at various temperatures in Fig. 6. Both pressure and temperature dependence seem to be normal. However, the clathrate hydrate contains more guest hydrogen molecules with increasing pressure on hydrogen fluid. This gives rise to sluggish pressure dependence compared with ice, which does not encage guest molecules. We perform a similar simulation of cubic ice (ice I_c) at constant pressure up to 250 MPa and at 170 K. The molar volume of ice I_c is also shown in Fig. 6. The compressibility of the clathrate hydrate is clearly smaller than that of ice I_c. This observation is accounted for by the pressure arising from accommodation of guests molecules. The volume in Eq. (10) is so optimized as

$$\frac{\partial A_w^0}{\partial V} + P - k_B T \frac{\partial \Sigma_k N_k \ln\{\Sigma_{n=0} \exp[\beta(n\mu - f_{kn})]\}}{\partial V} = 0. \tag{16}$$

This gives the pressure P, which should coincide with the pressure conducted from the chemical potential as

$$P = -\frac{\partial A_w^0}{\partial V} - \sum_k \frac{\{\Sigma_{n=1}(\partial f_{kn}/\partial v_k)\exp[\beta(n\mu - f_{kn})]\}}{\{\Sigma_{n=0}\exp[\beta(n\mu - f_{kn})]\}}$$
$$= -\frac{\partial A_w^0}{\partial V} - \sum_k \sum_{n=1}(\partial f_{kn}/\partial v_k)\eta_{kn}, \tag{17}$$

where v_k is defined by V/N_k and η_{kn} is the n-fold occupancy in the cage. The second term in Eq. (17) arises from accommodation of guests and is usually positive. The compressibility κ_T is given by

TABLE II. Cage occupancies (%) of hydrogen molecules at $T=170$ K and $P=500$ MPa with various Lennard-Jones energy parameter of hydrogen, ε'. The energy parameter for the original potential is ε as in Table I. L and S mean the larger and smaller cages.

ε'	$\varepsilon/2$	ε	2ε
L/triple	5.7	6.8	4.1
L/quadruple	81.3	92.2	95.9
S/single	95.9	99.8	100.0
S/double	4.1	0.02	0.0

$$\kappa_T^{-1} = -\frac{\partial P}{\partial \ln V} = V\frac{\partial^2 A_w^0}{\partial V^2} + \sum_k \sum_{n=1} v_k[(\partial^2 f_{kn}/\partial v_k^2)\eta_{kn}$$
$$+ (\partial f_{kn}/\partial v_k)(\partial \eta_{kn}/\partial v_k)]. \qquad (18)$$

The first term is similar to that of ice and the second term is usually positive and contributes to increase κ_T^{-1}. The third term is negative as $(\partial f_{kn}/\partial v_k)$ is negative, but $(\partial \eta_{kn}/\partial v_k)$ is positive in the volume range where the clathrate is stable. The latter, however, seems to be insignificant since the volume change does not cause substantial increase in occupancy. Thus, the third contribution seems to be smaller compared with the second, which leads to the sluggish pressure dependence of volume in the clathrate hydrate compared with ice I_c.

Our conclusion on the occupancy depends on the choice of the hydrogen intermolecular potential used. A detailed study on quantum-mechanical calculation was made for isolated cages.[10] The result is somewhat different from our conclusion on the occupancy of the smaller cage. The hydrogen potential of Silvera and Goldman[19] is designed for reproducing the properties of bulk hydrogen and may not be appropriate for small hydrogen clusters. Since the stability of doubly occupied cage should arise solely from the dispersion interaction, a systematic change of it may be helpful to examine the validity of the present potential and the relation between the cage occupancy and the strength of dispersion interaction. Two GCMC/NPT simulations are carried out with the dispersion interaction parameters for hydrogen ε' set to 1/2 and 2× the original parameter at $T=170$ K and $P=500$ MPa, while the relation between chemical potential and pressure remain intact. The cage occupancies of both types are listed in Table II. For the lager cage, quadruple occupancy simply increases with increasing the attractive dispersion interaction, ε'. The reverse tendency holds for double occupancy of the smaller cage. This seems to arise from a less steep repulsive part of the interaction in the smaller ε'. The potential parameter ε' covers a fairly wide range of the dispersion interaction, from 1/2 to 2× the original potential parameter. However, the ratios of the double occupancy in the smaller cage remain smaller values. Therefore, it is not plausible that the smaller cage is occupied by two hydrogen molecules with a high probability.

IV. CONCLUDING REMARKS

The cage occupancy of hydrogen clathrate hydrate has been examined by GCMC simulations for wide ranges of temperature and hydrogen pressure. The simulations are carried out with a fixed number of water molecules and a fixed chemical potential of guest hydrogen molecules that can be created or annihilated. The method is extended to a clathrate hydrate under a constant guest pressure. We show that a hybrid MC is useful to estimate the occupancy of guests in clathrate hydrate. It is found that the smaller cage in structure II is capable of accommodating only a single guest molecule even at a high pressure such as 500 MPa, which agrees with the recent experimental observations. The larger cage is found to encapsulate at most 4 hydrogen molecules. This leads to the highest occupancy ratio of 0.35. The obtained result is reasonable in light of the size of a hydrogen molecule. Pressure dependence of the volume of hydrogen clathrate is also examined and a relation between the vdWP theory and the GCMC/NPT (NVT) hybrid ensemble simulation is discussed.

[1] J. H. van der Waals and J. C. Platteeuw, Adv. Chem. Phys. **2**, 1 (1959).
[2] E. D. Sloan, *Clathrate Hydrates of Natural Gases*, 2nd ed. (Marcel Dekker, New York, 1998).
[3] D. W. Davidson, in *Water—A Comprehensive Treatise*, edited by F. Franks (Plenum, New York, 1973), Vol. 2.
[4] H. Tanaka and K. Kiyohara, J. Chem. Phys. **98**, 4098 (1993).
[5] H. Tanaka and K. Kiyohara, J. Chem. Phys. **98**, 8110 (1993).
[6] H. Tanaka, J. Chem. Phys. **101**, 10833 (1994).
[7] H. Tanaka, T. Nakatsuka, and K. Koga, J. Chem. Phys. **121**, 5488 (2004).
[8] W. L. Mao, H.-K. Mao, A. F. Goncharov, V. V. Struzhkin, Q. Guo, J. Hu, J. Shu, R. J. Hemly, M. Somayazulu, and Y. Zhao, Science **297**, 2247 (2002).
[9] K. A. Lokshin, Y. Zhao, D. He, W. L. Mao, H.-K. Mao, R. J. Hemley, M. V. Lobanov, and M. Greenblatt, Phys. Rev. Lett. **93** 125503 (2004).
[10] S. Patchkovskii and J. S. Tse, Proc. Natl. Acad. Sci. U.S.A. **100**, 14645 (2003).
[11] S. Alavi, J. A. Ripmeester, and D. D. Klug, J. Chem. Phys. **123**, 024507 (2005).
[12] L. J. Florusse, C. J. Peters, J. Schhoonman, K. C. Hester, C. A. Koh, S. F. Dec, K. N. Marsh, and E. D. Sloan, Science **306**, 469 (2004).
[13] H. Lee, J.-W. Lee, D. Y. Kim, J. Park, Y.-T. Seo, H. Zeng, I. L. Moudrakovski, C. I. Ratcliffe, and J. A. Ripmeester, Nature **434**, 743 (2005).
[14] K. C. Hester, T. A. Strobel, E. D. Sloan, C. A. Koh, A. H. Huq, and A. J. Schultz, J. Phys. Chem. B **110**, 14024 (2006).
[15] T. A. Strobel, C. J. Taylor, K. C. Hester, S. F. Dec, C. A. Koh, K. T. Miller, and E. D. Sloan, J. Phys. Chem. B **110**, 17121 (2006).
[16] S. Alavi, J. A. Ripmeester, and D. D. Klug, J. Chem. Phys. **124**, 014704 (2006).
[17] W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, and M. L. Klein, J. Chem. Phys. **79**, 926 (1983).
[18] Y. Koyama, H. Tanaka, G. T. Gao, and X. C. Zeng, J. Chem. Phys. **121**, 7926 (2004).
[19] I. F. Silvera and V. Goldman, J. Chem. Phys. **69**, 4209 (1978).
[20] D. E. Stogryn and A. P. Stogryn, Mol. Phys. **11**, 371 (1966).
[21] I. Ohmine, H. Tanaka, and P. G. Wolynes, J. Chem. Phys. **89**, 5852 (1988).
[22] A rough estimation of f_2 at 273.15 K by simple Monte Carlo integration gives $f_2=15$ kJ mol^{-1}. Thus, the probability for two hydrogen molecules to be contained in a smaller cage is extremely low.