

*Physics*  
*Physics fields*

---

Okayama University

Year 2007

---

On the thermodynamic stability of  
clathrate hydrates IV: Double occupancy  
of cages

Hideki Tanaka\*      Takeharu Nakatsuka<sup>†</sup>  
Kenichiro Koga<sup>‡</sup>

\*Okayama University

<sup>†</sup>Okayama University

<sup>‡</sup>Okayama University, koga@cc.okayama-u.ac.jp

This paper is posted at eScholarship@OUDIR : Okayama University Digital Information Repository.

[http://escholarship.lib.okayama-u.ac.jp/physics\\_general/23](http://escholarship.lib.okayama-u.ac.jp/physics_general/23)

# On the thermodynamic stability of clathrate hydrates IV: Double occupancy of cages

Hideki Tanaka,<sup>a)</sup> Takeharu Nakatsuka, and Kenichiro Koga

*Department of Chemistry, Faculty of Science, Okayama University, 3-1-1 Tsushima, Okayama 700-8530, Japan*

(Received 3 May 2004; accepted 22 June 2004)

We have extended the van der Waals and Platteeuw theory to treat multiple occupancy of a single cage of clathrate hydrates, which has not been taken into account in the original theory but has been experimentally confirmed as a real entity. We propose a simple way to calculate the free energy of multiple cage occupancy and apply it to argon clathrate structure II in which a larger cage can be occupied by two argon atoms. The chemical potential of argon is calculated treating it as an imperfect gas, which is crucial to predict accurate pressure dependence of double occupancy expected at high pressure. It is found that double occupancy dominates over single occupancy when the guest pressure in equilibrium with the clathrate hydrate exceeds 270 MPa. © 2004 American Institute of Physics. [DOI: 10.1063/1.1782471]

## 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. The guest species has some restriction on its size. This arises from the fact that there are limited number of cage types which encapsulate guest molecules without deviating the hydrogen bond angle from the ideal one. It has long been believed that each cage accommodates only one guest molecule.

The thermodynamic stability of the clathrate hydrates has been accounted for by van der Waals and Platteeuw (vdWP).<sup>1</sup> This is based on an ideal solid-solution theory and has been widely used to predict phase behavior of many hydrates. Some empirical parameters are always required in its application.<sup>2,3</sup> We first refer to the assumptions in the original vdWP theory. It is assumed that first, the cage structure is not distorted by the incorporation of guest molecules, second, the partition function of cage occupancy is independent of the occupation of other cages, and third, 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. These are reasonable unless a guest molecule is too large compared to a cage to be encapsulated or the pressure is too high.

Some of the assumptions in the original theory are no longer required with some elaborated treatments: The cage structure is allowed to deviate from the molecular arrangement of the ideal empty hydrate when guest molecules are encaged and the fixed lattice approximation is removed for the clathrate hydrate encaging a comparable size of a molecule with the cage to accommodate it, thereby introducing some coupling between host water and guest.<sup>4–6</sup> Thus, a more accurate evaluation could be made. It was revealed that the free energy term arising from the coupling of the host

with the guest molecules is significantly important for large guest molecules such as propane.

It was experimentally shown that small molecules such as argon and nitrogen stabilize not structure I but structure II.<sup>7</sup> Moreover, experimental investigation suggests that the larger cages in structure II hydrate can accommodate at most two small molecules such as nitrogen in the intermediate pressure range (lower than 400 MPa).<sup>8</sup> At the higher pressure, different morphologies (hexagonal and tetragonal) are more stable than the low pressure phase, structure II.<sup>9–12</sup> A recent Raman scattering study also revealed the multiple occupancy by nitrogen (at most five) molecules at high pressure.<sup>13</sup> A molecular dynamics simulation has recently been carried out to examine coupled guest motions in a cage.<sup>14</sup> Therefore, it is an urgent task to treat this multiple occupancy from a firm theoretical ground.

The present paper is organized as follows. The theory and methods developed in the present study are described in Sec. II. The thermodynamic stability for argon hydrates is evaluated and the obtained results are compared with experiments in Sec. III. The conclusion is given in Sec. IV.

## II. THEORY AND METHOD

### A. Intermolecular interaction

The thermodynamic stability of the clathrate hydrates is evaluated with intermolecular potentials which are currently the most reliable. In the present study, all interactions are assumed to be pairwise additive. The water-water intermolecular interaction is described by the TIP4P potential.<sup>15</sup> 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 of not only pure water but also ice. 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. Argon atoms interact with each other via Lennard-Jones (LJ)

<sup>a)</sup>Electronic mail: htanaka@cc.okayama-u.ac.jp

potential. 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.<sup>16</sup> The correction term arising from the truncation of all the LJ interactions is taken into account in free energy calculation.

## B. Structure of the unit cell

A hundred of clathrate hydrate II structures are generated. The unit cell of the hydrate II is cubic and experimental lattice parameters are used in the following calculation;  $a = b = c = 1.731$  nm for hydrate II with  $\alpha = \beta = \gamma = \pi/2$ .<sup>2,3</sup> These structures are of proton-disordered form and have zero net dipole moment. The method for generating those structures is given elsewhere.<sup>4</sup> The same number of ice Ih (hexagonal) structures generated previously are used.<sup>17</sup> The basic cell is composed of a single unit cell of clathrate hydrate II, in which 136 water molecules are placed on the lattice sites. In the case of ice Ih, the basic cell consists of 72 unit cells, containing 288 water molecules. There exist eight larger and 16 smaller cages in the unit cell of clathrate hydrate II. Both larger and smaller cages accommodate guest argon atoms. The potential energy of the system is minimized to obtain the exact local minimum structure by the steepest descent method.

## C. vdWP theory and its extension to double occupancy

Here we consider the case where argon atoms are encapsulated in clathrate structure II, which is in equilibrium with low pressure ice and the fluid phase of argon. The ice structure is ice Ih, which is the stable form in the low pressure region below 200 MPa. It has been assumed that formation of clathrate hydrate is made at fairly low pressure, say, below 10 MPa where the gas can be treated as an ideal one or an imperfect one by considering only the second virial coefficient. However, this restriction should be removed so that the guest gas pressure in equilibrium with clathrate hydrate can be significantly high.

Let us first review the classical vdWP theory for a simple clathrate hydrate, where each cage accommodates one guest molecule. The canonical partition function for a Hamiltonian  $\mathcal{H}$  is given for spherical  $N_g$  guest atoms with  $N_w$  rigid rotor water molecules as

$$Z = \frac{1}{\sigma^{N_w} N_w! N_g! h^{6N_w + 3N_g}} \int_V d\mathbf{r}_w^{N_w} \int d\mathbf{p}_w^{N_w} \int_V d\mathbf{r}_g^{N_g} \int d\mathbf{p}_g^{N_g} \exp(-\beta\mathcal{H}), \quad (1)$$

where the integration in coordinates  $\mathbf{r}$  spans the whole volume denoted by  $V$  (the coordinates and the conjugate momenta for water include those associated with the orientational parameters) and the symmetry number  $\sigma$  is 2 for a water molecule. In Eq. (1),  $\beta$  stands for  $1/k_B T$  with the Boltzmann constant  $k_B$  and temperature  $T$  and  $h$  is the Planck constant. With the third assumption,  $Z$  can be separated into two terms arising from the empty hydrate and the guests encaged in it as

$$Z = h^{-6N_w} \sigma^{-N_w} \int_V d\mathbf{r}_w^{N_w} \int d\mathbf{p}_w^{N_w} \times \exp[-\beta\mathcal{H}_w(\mathbf{p}_w, \mathbf{r}_w)] \sum h^{-3N_g} \int_V d\mathbf{r}_g^{N_g} \int d\mathbf{p}_g^{N_g} \times \exp[-\beta\mathcal{H}_g(\mathbf{p}_g, \mathbf{r}_g; \mathbf{r}_w^0)], \quad (2)$$

where  $\mathcal{H}_w$  stands for the Hamiltonian of host water and the Hamiltonian  $\mathcal{H}_g$  includes both water and guest coordinates. The key in Eq. (2) is that the integration for guest coordinates is made for the fixed coordinates of water molecules denoted by  $\mathbf{r}_w^0$ , the local energy minimum configuration. The integration in the coordinate spans the smaller volume  $v$ , where each molecule is allowed to vibrate. Its size depends on molecular species to be encaged. The sum in Eq. (2) is taken over all possible assignment of the guests to each cage. The integral on guest is individually evaluated under the second assumption to give the free energy term for single occupancy of larger or smaller cage,  $\exp(-\beta f_l)$  or  $\exp(-\beta f_s)$ . The number of ways to choose  $n_l$  single occupancies of larger cages and  $n_s$  single occupancies of smaller cages out of  $N_l$  larger and  $N_s$  smaller cages is

$$\binom{N_l}{n_l} \binom{N_s}{n_s}, \quad (3)$$

with  $N_g = n_l + n_s$ . Thus, the canonical partition function is given by

$$Z = \binom{N_l}{n_l} \binom{N_s}{n_s} \exp(-\beta A_w^0) \exp(-\beta n_l f_l) \exp(-\beta n_s f_s), \quad (4)$$

where  $A_w^0$  is the Helmholtz free energy of the empty clathrate hydrate arising from the integral on host water in Eq. (2). The grandcanonical partition function, where the number of guest molecules is variable with a given chemical potential of the guest  $\mu$  is obtained by multiplying  $\exp(n_l \beta \mu + n_s \beta \mu)$  and taking sum over  $n_l$  and  $n_s$  as

$$\Xi = \exp(-\beta A_w^0) \sum_{n_l=0}^{N_l} \binom{N_l}{n_l} \exp[\beta n_l (\mu - f_l)] \sum_{n_s=0}^{N_s} \binom{N_s}{n_s} \times \exp[\beta n_s (\mu - f_s)] \\ = \exp(-\beta A_w^0) \{1 + \exp[\beta(\mu - f_l)]\}^{N_l} \times \{1 + \exp[\beta(\mu - f_s)]\}^{N_s}. \quad (5)$$

Hence, the average number of guest molecules is calculated as

$$\langle N_g \rangle = \frac{\partial \ln \Xi}{\partial (\beta \mu)} = \frac{N_l \exp[\beta(\mu - f_l)]}{\{1 + \exp[\beta(\mu - f_l)]\}} + \frac{N_s \exp[\beta(\mu - f_s)]}{\{1 + \exp[\beta(\mu - f_s)]\}}. \quad (6)$$

Extension to double occupancy of the larger cage is made as follows. The number of ways to choose  $n_l$  singly occupied and  $n_d$  doubly occupied larger cages and  $n_s$  singly occupied smaller cages is

$$\binom{N_l}{n_d} \binom{N_l - n_d}{n_l} \binom{N_s}{n_s}. \quad (7)$$

Thus, the canonical partition function is given by

$$Z = \binom{N_l}{n_d} \binom{N_l - n_d}{n_l} \binom{N_s}{n_s} \exp(-\beta A_w^0) \exp(-\beta n_d f_d) \\ \times \exp(-\beta n_l f_l) \exp(-\beta n_s f_s). \quad (8)$$

The grandcanonical partition function is again obtained by multiplying  $\exp(2n_d\beta\mu + n_l\beta\mu + n_s\beta\mu)$  and taking sum over  $n_d$ ,  $n_l$ , and  $n_s$  as

$$\Xi = \exp(-\beta A_w^0) \sum_{n_d=0}^{N_l} \sum_{n_l=0}^{N_l - n_d} \binom{N_l}{n_d} \binom{N_l - n_d}{n_l} \\ \times \exp[\beta n_d(2\mu - f_d)] \exp[\beta n_l(\mu - f_l)] \sum_{n_s=0}^{N_s} \binom{N_s}{n_s} \\ \times \exp[\beta n_s(\mu - f_s)] \\ = \exp(-\beta A_w^0) \{1 + \exp[\beta(2\mu - f_d)] \\ + \exp[\beta(\mu - f_l)]\}^N \{1 + \exp[\beta(\mu - f_s)]\}^{N_s}. \quad (9)$$

Hence, the average number of guest molecules is calculated as

$$\langle N_g \rangle = \frac{\partial \ln \Xi}{\partial (\beta\mu)} \\ = \frac{N_l \{2 \exp[\beta(2\mu - f_d)] + \exp[\beta(\mu - f_l)]\}}{\{1 + \exp[\beta(2\mu - f_d)] + \exp[\beta(\mu - f_l)]\}} \\ + \frac{N_s \exp[\beta(\mu - f_s)]}{\{1 + \exp[\beta(\mu - f_s)]\}}. \quad (10)$$

The actual integration for a guest atom located at  $\mathbf{r}_1$  with the mass  $m$  spans inside a cage and the free energy  $f_l$  is given (and  $f_s$  as well) by

$$\exp(-\beta f_l) = \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \int_v d\mathbf{r}_1 \exp[-\beta w(\mathbf{r}_1)], \quad (11)$$

where  $w$  is the interaction of a given guest with all the surrounding water molecules. The integration for two guest atomic coordinates  $\mathbf{r}_1$  and  $\mathbf{r}_2$  in a single cage is performed to give the free energy  $f_d$  as

$$\exp(-\beta f_d) = \frac{1}{2!} \left( \frac{2\pi m k_B T}{h^2} \right)^3 \int_v d\mathbf{r}_1 \int_v d\mathbf{r}_2 \\ \times \exp\{-\beta[w(\mathbf{r}_1) + w(\mathbf{r}_2) + \phi(\mathbf{r}_1, \mathbf{r}_2)]\}, \quad (12)$$

where  $\phi$  is the LJ interaction between two guest atoms. Because of the symmetry, the task may be reduced by a factor of 1/2.

The chemical potential of the imperfect gas (fluid) is calculated as follows. The equation of state for LJ fluids (pressure,  $p$ ) has been well established as  $p(T, \rho)$  (number density,  $\rho$ ).<sup>18</sup> The free energy (per molecule)  $f$  at  $T$  and  $\rho$  is given by separating the nonideal and the ideal parts as

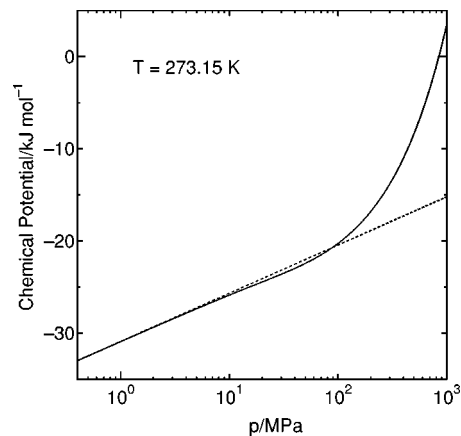


FIG. 1. Pressure dependence of chemical potential for realistic argon fluid (solid line) and hypothetical ideal gas (dotted line) at 273.15 K.

$$f = \int_0^p (p - \rho k_B T) / \rho^2 d\rho + k_B T [\ln \rho (h^2 / 2\pi m k_B T)^{3/2} - 1]. \quad (13)$$

Since we are dealing with one-component system, the chemical potential  $\mu$  is simply given by

$$\mu(T, p) = f + p/\rho, \quad (14)$$

after inversion of the equation of the state as a function of  $p$ .

### III. RESULTS AND DISCUSSION

We calculate the chemical potential of argon fluid as a function of pressure and temperature. This is made based on the numerical integration of the equation of state, which has been obtained as an analytical function of both temperature and number density.<sup>18</sup> The equation of state is common to fluids interacting via LJ potential with the LJ reduced units. To calculate the pressure and chemical potential for argon, assignment of the LJ size and energy parameters is required along with the mass; those are set to 0.3405 nm, 1.096 kJ mol<sup>-1</sup>, and 40.0 g mol<sup>-1</sup>.<sup>19</sup> As shown in Fig. 1, the chemical potential of the real argon fluid in the intermediate pressure range (10–100 MPa) is lower by about a few percent than that treated as an ideal gas, which is due to the weak but attractive interaction. In this pressure range, the chemical potential of argon gas is also calculated taking account of only the second virial coefficient and is in almost complete agreement with that calculated by the method described above (not shown here). However, it becomes higher than that of the corresponding ideal gas in the high pressure range, 200 MPa–1 GPa, where double occupancy is expected to dominate.

The potential energy curve of a guest inside a given cage is examined; a guest with water molecules which are fixed to lattice sites. The potential energy of a guest molecule interacting with surrounding water molecules is calculated as a function of radial distance  $r$  from the center of the cage averaged over all orientations, which is denoted by  $\langle w \rangle_\Omega$ . Those for larger and smaller cages,  $\langle w(r) \rangle_\Omega$ , are plotted in Fig. 2. The potential energy curve in a smaller cage is a monotonically increasing function with the distance  $r$ . The

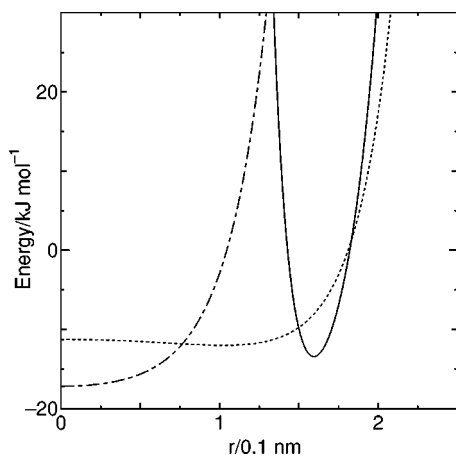


FIG. 2. Potential energy curves of argon atom(s). Solid line, double occupancy in larger cage; dotted line, single occupancy in larger cage; dash-dot line, single occupancy in smaller cage. See text.

potential energy curve in a larger cage is fairly different and a minimum energy position locates not at the center of the cage but on the periphery of it. A similar plot defined by  $\langle w_1(\mathbf{r}) + w_2(-\mathbf{r}) + \phi(2r) \rangle_{\Omega_1, \Omega_2}$  with vector  $\mathbf{r}$  from the center of a larger cage to a guest and  $r = |\mathbf{r}|$  is also given in Fig. 2, where two guest atoms are located symmetrically against the center of the cage. There are other arrangements of two guest atoms but those have much higher energy in general. Thus, the function defined above is enough to understand a general feature of the potential surface for a doubly occupied cage. The curve shows that two guests are confined in a (radially) limited region, which arises from mismatch between minimum locations in  $w$  and  $\phi$ . However, there is some room accommodating a pair of argon atoms with low potential energy comparable to a single occupancy.

We have examined the dissociation pressure and the pressure dependences of the cage occupancies at several temperatures, 213.15–273.15 K with an increment of 10 K. The free energies of cage occupancy  $f_l$  and  $f_s$  were calculated previously.<sup>20</sup> The free energy of double occupancy is obtained in the same way. For efficient evaluation of it, care is taken of the fact that the six-dimensional character in the integrand appears only in the guest-guest interaction  $\phi$  which is evaluated much faster than  $w$ . The free energies of cage occupancy,  $f_l$ ,  $f_s$  and  $f_d$  are given in Table I. It is easily anticipated from the Table that double occupancy is not expected to dominate under the condition that  $f_d - f_l = \mu > -15 \text{ kJ mol}^{-1}$  at 273.15 K.

The equilibrium condition between ice and clathrate hydrate is given by

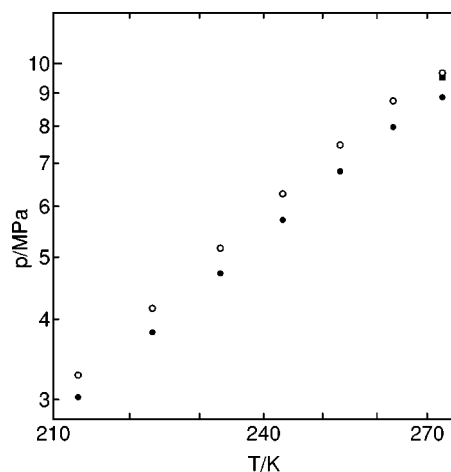


FIG. 3. Calculated temperature dependence of dissociation pressure for argon clathrate hydrate together with experimental dissociation pressure (filled square). Clathrate hydrate is in equilibrium with realistic argon fluid (open circle) and hypothetical ideal gas (filled circle).

$$\mu_i = \mu_c, \quad (15)$$

where  $\mu_i$  and  $\mu_c$  denote the chemical potential of ice and clathrate hydrate. By subtracting the chemical potential of hypothetical empty clathrate hydrate  $\mu_c^0$

$$\mu_i - \mu_c^0 = \mu_c - \mu_c^0. \quad (16)$$

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, and the residual entropy term. Each chemical potential is a function of pressure and temperature but its pressure dependence is insignificant unless the pressure is high. Therefore, we may neglect the pressure dependence (up to about 10 MPa) and it is listed in Table I. The right-hand side is calculated to give

$$\begin{aligned} \mu_c - \mu_c^0 = & -k_B T [\alpha_l \ln\{1 + \exp[\beta(\mu - f_l)] \\ & + \exp[\beta(2\mu - f_d)]\} \\ & + \alpha_s \ln\{1 + \exp[\beta(\mu - f_s)]\}], \end{aligned} \quad (17)$$

where  $\alpha_l$  and  $\alpha_s$  are the ratios of the numbers of the larger and smaller cages to the number of water molecules, respectively. This includes the chemical potential of the gas, which is heavily dependent on pressure. Thus, we obtain temperature dependency of the dissociation pressure, which is plotted in Fig. 3, which is almost the same as the previous calculation neglecting double occupancy.<sup>20</sup> Agreement with

TABLE I. Free energy for double occupancy of the larger cage ( $f_d$ ), single occupancy of the larger cage ( $f_l$ ), and single occupancy of the smaller cage ( $f_s$ ) together with chemical potential difference between ice and empty hydrate ( $\Delta\mu$ ) at temperature  $T$  (K).

$T$	213.15	223.15	233.15	243.15	253.15	263.15	273.15
$f_d$	-37.490	-38.762	-40.054	-41.365	-42.694	-44.041	-45.402
$f_l$	-25.699	-26.490	-27.286	-28.090	-28.899	-29.715	-30.585
$f_s$	-25.290	-25.882	-26.481	-27.089	-27.705	-28.329	-29.070
$\Delta\mu$	-0.799	-0.785	-0.772	-0.759	-0.745	-0.732	-0.719



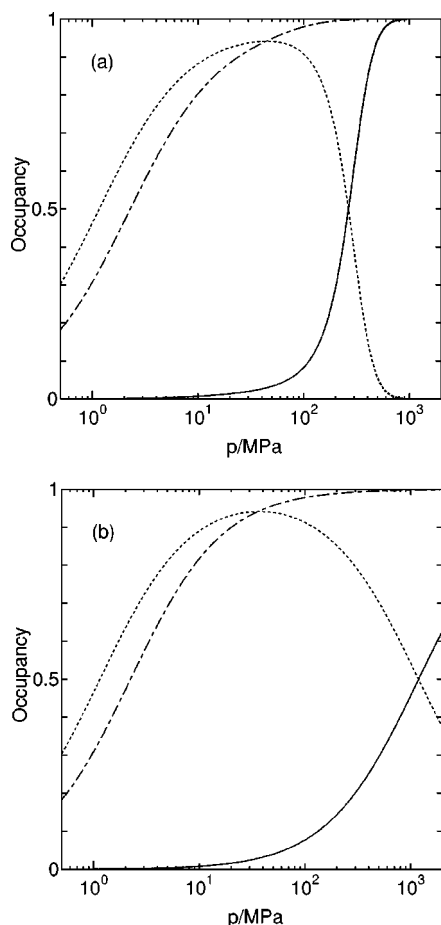


FIG. 4. Cage occupancy ratio of guest argon atoms in equilibrium with (a) realistic argon gas and (b) hypothetical ideal gas. Solid line, double occupancy in larger cage; dotted line, single occupancy in larger cage; dash-dot line, single occupancy in smaller cage.

experiment is excellent in view of the simple potential function and the conventional combining rule.<sup>21</sup> A more realistic treatment of argon gas gives rise to slightly better agreement with the experimental observation but difference in dissociation pressure from the ideal gas chemical potential is less than 0.08 MPa. Therefore, argon gas can be regarded as an ideal gas in this low pressure region below 10 MPa. There are some other factors that lead to better agreement such as introduction of the pressure dependence of the cell dimension. Here, we will not try make further improvement.

The cage occupancy is plotted in Fig. 4. In equilibrium with ice,  $\approx 80\%$  and  $90\%$  of smaller and larger cages are occupied. At any temperature, occurrence of double occupancy is less than 1% and thus only single occupancy is important as to estimation of the dissociation pressure. Double occupancy gradually increases with increasing the gas pressure up to 10 MPa. Then, a harsh increase is seen. The double occupancy dominates over the single occupancy of a larger cage as the gas pressure exceeds 270 MPa at 273.15 K. If the gas is treated as an ideal one, occupancy of smaller cages is almost the same but occupancy of larger cages is significantly different and the cross-over occurs at a pressure higher than 1 GPa, which is four times higher than the case of a real gas (fluid). Some experimental evidences

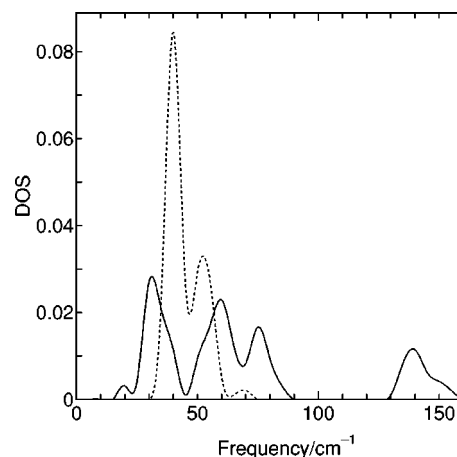


FIG. 5. Density of state for intermolecular vibrational modes. Solid line, double occupancy of argon atoms in larger cage; dotted line, single occupancy of argon atom in smaller cage.

suggest double occupancy takes place around 400 MPa prior to the transition from structure II to structure H.<sup>9–12</sup> Agreement with experiment is expected only when argon is treated as not an ideal gas but a more realistic LJ fluid.

Guest motions are represented conveniently by normal modes, which correspond to intermolecular vibrational modes at 0 K.<sup>22</sup> Only a part of the Hessian matrix associated with guests is diagonalized to extract the vibrational motions of guest atoms. Judging from the shape of the potential surface in single occupancy of larger cage, it is too large for normal mode analysis to work, and therefore their normal modes are not calculated. Only the density of state for vibrational modes of argon in doubly occupied larger cages and singly occupied smaller cages are shown in Fig. 5. General features are similar to those obtained elsewhere in which a different intermolecular potential was adopted and the density of state was calculated from Fourier transform of the time correlation functions.<sup>14</sup> In particular, a mode around  $145\text{ cm}^{-1}$ , which was assigned to a stretching motion of a pair of argon atoms in a larger cage, is observed in a slightly lower frequency region centered at  $140\text{ cm}^{-1}$  in our normal mode analysis. This was also seen around  $135\text{ cm}^{-1}$  in Raman spectra and is associated with the double occupancy of larger cages.<sup>12</sup>

Further extension to multiple occupancy is easily made by considering indistinguishability of the same kind of guest molecules in a single cage although numerical burden becomes increasingly heavier. The relevant grandcanonical partition function is given as

$$\Xi = \exp(-\beta A_w^0) \prod_k \left\{ \sum_{n=0}^{N_k} \exp[\beta(n\mu - f_{kn})] \right\}^{N_k}, \quad (18)$$

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. The average guest number is calculated as

$$\langle N_g \rangle = \frac{\partial \ln \Xi}{\partial (\beta \mu)} = \sum_k \frac{N_k \{ \sum_{n=1}^{N_k} n \exp[\beta(n\mu - f_{kn})] \}}{\{ \sum_{n=0}^{N_k} \exp[\beta(n\mu - f_{kn})] \}}. \quad (19)$$

The integration for  $n$  (atomic) guest coordinates in a single cage is performed to give the free energy  $f_{kn}$  as

$$\exp(-\beta f_{kn}) = \frac{1}{n!} \left( \frac{2\pi m k_B T}{h^2} \right)^{3n/2} \int_v \prod_i^n d\mathbf{r}_i \times \exp \left\{ -\beta \left[ \sum_i^n w_k(\mathbf{r}_i) + \sum_{i<j}^n \phi(\mathbf{r}_i, \mathbf{r}_j) \right] \right\}. \quad (20)$$

The above extension will be used in higher pressure clathrate hydrate, structure H whose larger cage can accommodate maximally five argon atoms.

#### IV. CONCLUDING REMARKS

We have examined thermodynamic stability of argon clathrate hydrate whose larger cages can be doubly occupied. A simple extension of the vdWP theory is given so that double occupancy of a cage can be treated. We have calculated the free energies of various types of cage occupancies, from which the dissociation pressure and the ratio of the double occupancy are estimated. As far as the dissociation pressure is concerned, double occupancy at a pressure of 10 MPa is negligibly small, less than 1%. However, its ratio gradually increases with increasing pressure. Finally, crossover is expected around 300 MPa of the guest pressure, above which double occupancy dominates over single occupancy. The Raman peak intensity, which is attributed to double occupancy in structure II by Shimizu *et al.*, increases with increasing pressure from 100 to 400 MPa.<sup>12</sup> This arises from increase in the number of cages occupied by two argon atoms. Quantitative comparison should await a more detailed experimental study in a pressure range between 100 and 400 MPa.

In extension of vdWP theory to double occupancy, a gas (fluid) in equilibrium with clathrate hydrate must be treated as a realistic one. This is essential when the gas pressure exceeds 100 MPa. Otherwise, the predicted double occupancy is erroneously small. The chemical potential of any (pure) LJ fluid is easily calculated as a function of temperature and pressure from the equation of state.<sup>18</sup>

For further refinement, the pressure dependences of ice and occupied clathrate hydrate volumes should be taken into consideration. These are not so serious when considering an equilibrium between low pressure ice and clathrate hydrate

II. However, they are more important for an equilibrium between two clathrate hydrate structures such as II and H, which is anticipated around 400–500 MPa. Further extension to treat multiple occupancy other than double is useful in a theoretical study on pressure-induced phase transition from structure II to structure H, and finally to tetragonal structure.<sup>9–12</sup>

#### ACKNOWLEDGMENTS

This work was supported by grant-in-aid from JSPS and Ministry of Education in Japan, by Okayama Foundation for Science and Technology, and by NAREGI nanoscience project. The authors are grateful to I. Okabe for generating ice structures and to Professor H. Shimizu and Dr. H. Itoh for stimulating discussion.

- <sup>1</sup>J. H. van der Waals and J. C. Platteeuw, *Adv. Chem. Phys.* **2**, 1 (1959).
- <sup>2</sup>E. D. Sloan, *Clathrate Hydrates of Natural Gases*, 2nd ed. (Marcel Dekker, New York, 1998).
- <sup>3</sup>D. W. Davidson, *Water—A Comprehensive Treatise*, edited by F. Franks (Plenum, New York, 1973), Vol. 2.
- <sup>4</sup>H. Tanaka and K. Kiyohara, *J. Chem. Phys.* **98**, 4098 (1993).
- <sup>5</sup>H. Tanaka and K. Kiyohara, *J. Chem. Phys.* **98**, 8110 (1993).
- <sup>6</sup>H. Tanaka, *J. Chem. Phys.* **101**, 10833 (1994).
- <sup>7</sup>D. W. Davidson, Y. P. Handa, C. I. Ratcliffe, J. S. Tse, and B. M. Powell, *Nature (London)* **311**, 142 (1984).
- <sup>8</sup>W. F. Kuhs, B. Chazallon, P. G. Radaelli, and P. Pauer, *J. Inclusion Phenom. Mol. Recognit. Chem.* **29**, 65 (1997).
- <sup>9</sup>H. T. Lotz and J. A. Schouten, *J. Chem. Phys.* **111**, 10242 (1999).
- <sup>10</sup>A. Y. Manakov, V. I. Voromin, A. V. Kurnosov, A. E. Teplykh, E. G. Larionov, and Y. A. Dyadin, *Dokl. Phys. Chem.* **378**, 148 (2001).
- <sup>11</sup>A. V. Kurnosov, A. Y. Manakov, V. Y. Komarov, V. I. Voromin, A. E. Teplykh, and Y. A. Dyadin, *Dokl. Phys. Chem.* **381**, 303 (2001).
- <sup>12</sup>H. Shimizu, S. Hori, T. Kume, and S. Sasaki, *Chem. Phys. Lett.* **368**, 132 (2003).
- <sup>13</sup>S. Sasaki, S. Hori, T. Kume, and H. Shimizu, *J. Chem. Phys.* **118**, 7892 (2003).
- <sup>14</sup>H. Itoh, J. S. Tse, and K. Kawamura, *J. Chem. Phys.* **115**, 9414 (2001).
- <sup>15</sup>W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, and M. L. Klein, *J. Chem. Phys.* **79**, 926 (1983).
- <sup>16</sup>I. Ohmine, H. Tanaka, and P. G. Wolynes, *J. Chem. Phys.* **89**, 5852 (1988).
- <sup>17</sup>H. Tanaka, *J. Chem. Phys.* **108**, 4887 (1998).
- <sup>18</sup>J. J. Nicolas, K. E. Gubbins, W. B. Streett, and D. J. Tildesley, *Mol. Phys.* **37**, 1429 (1979).
- <sup>19</sup>J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, (Wiley, New York, 1954).
- <sup>20</sup>H. Tanaka and K. Nakanishi, *Mol. Simul.* **12**, 317 (1994).
- <sup>21</sup>R. M. Barrer and A. V. J. Edge, *Proc. R. Soc. London, Ser. A* **300**, 1 (1967).
- <sup>22</sup>A. Pohorille, L. R. Pratt, R. A. LaViolette, M. A. Wilson, and R. D. MacElroy, *J. Chem. Phys.* **87**, 6070 (1987).