Lattice Relaxation in Type I Gas Hydrates

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Computer simulations have been used to examine the approximations upon which the van der Waals-Platteeuw theory of hydrate stability is based, and in particular, the extent to which the water lattice relaxes about the guest molecules. It is found that the behavior of the water lattice depends significantly on both the nature and number of guest molecules present—an effect that is neglected in the van der Waals-Platteeuw theory. The simulations also indicate an important role for the repulsive guest-host interactions in generating the mechanical stability of gas hydrates in the bulk. On the basis of these simulations, it is conjectured that surface interactions (particularly at a water/guest interface) are fundamental to the phase behavior of gas hydrates.

Introduction

The van der Waals-Platteeuw (VDWP) theory of gas hydrate stability (van der Waals and Platteeuw, 1959) has proved to be very successful. It has been found to be particularly good for describing the phase behavior of simple hydrates (that is, clathrate hydrates involving a single guest species), but has also performed creditably when more than one guest species are involved (mixed hydrates), and one can now hope to reproduce the pressures at which mixed hydrates will begin to form, over a range of compositions, to within about 10% (Sloan, 1989a). Indeed, the VDWP theory is now the standard way of interpreting and interpolating between experimental data about conditions for gas hydrate formation.

For all its success, however, there are still some important indications that the VDWP theory needs further improvement. For example, while many of the mixed hydrates can be described quite well, there are some mixed hydrates for which the VDWP theory is not entirely satisfactory (Anderson and Prausnitz, 1986; Holder et al., 1980), and it is perhaps unfortunate that the predictions are least accurate with high mole fractions of methane (Holder and Hand, 1982). There are also inconsistencies in the parameterization of the model, with the potential parameters appearing to depend on the conditions and gas composition studied. As an example of this, Table 1 lists four different parameterizations of the ethane potential that have been suggested. The net effect of these problems is that the calculated properties are still less accurate than good experimental data, and prominent practitioners of VDWP calculations caution against using the method to extrapolate beyond the available experimental data (Sloan, 1989a).

Some further comment on the uniqueness of the parameterization is warranted. It may be thought that since the parameters are found empirically, it should not be surprising that there are variations between different sets of work. However, there are two important consequences of this. Firstly, it implies that the parameters so derived are not completely transferable. In particular, one should not simply add the potential parameters for a new guest species to existing data set without re-optimizing the entire set of parameters. This also means that parameters obtained from different sets of work should not be mixed without again re-optimizing the combined set.

The second consequence is more fundamental. The parameters within this approach have well defined physical meanings and hence should also have well defined values. If these values are not well defined, it suggests that the problem has been oversimplified in some way, and the parameters are being adjusted from their "true" values to compensate for more basic errors. Of course, some of the simplifications are easy to locate, such as the use of a spherically averaged Kihara potential to model the cavity potential; indeed, the use of empirical parameters arises precisely, because much of the

Table 1. Suggested Kihara potential parameters for ethane

Reference	ϵ/k (K)	σ (Å)	a (Å)	r_m (Å)[a]
Ng & Robinson (1977)	174.04	3.392	0.390	4.587
Holder & Hand (1982)	174.77	3.155	0.558	4.657
Anderson & Prausnitz (1986)	175.94	3.438	0.400	4.659
Sloan (1989a)	176.40	3.264	0.565	4.794

[a] r_m is the minimum energy separation for the dimer, and is equal to $2^{1/6}\sigma + 2a$

input needed by the VDWP theory (cavity potential, free energy of the empty hydrate lattice, and so on) is either unknown or too complicated to describe precisely. The risk in this approach is that discrepancies between calculated and experimental properties are put down to these known inadequacies in the parameterization, and more fundamental problems that might exist with the theory itself are not considered.

Recent simulations have indicated that there are some fundamental problems with the VDWP theory (Rodger, 1989, 1990a). In particular, these simulations found that the water lattice relaxed significantly when the number of guest molecules present was changed and that the energy associated with this relaxation was comparable with that needed to stabilize the hydrate water lattice; such relaxation of the water lattice is explicitly ignored in the VDWP theory. However, these simulations looked at extreme variations in occupancy (100%, 12.5% or 0% of cavities being occupied), whereas for real hydrates one usually finds that 80–100% of the cavities are occupied; as such the question of whether the lattice relaxation is significant for the physically important range of occupancies still needs to be addressed.

The purpose of this work is to extend the previous study to intermediate occupancies and show that the lattice relaxation is significant over the entire range of occupancies. The implications for the VDWP theory will be discussed in the Conclusions Section. As a background to this discussion, we give a brief, heuristic description of the VDWP theory in the next section; a more complete discussion of this theory can be found elsewhere (van der Waals and Platteeuw, 1959; Sloan, 1989a).

Theoretical Background

The VDWP theory of gas hydrate stability is entirely analogous to Langmuir's theory of adsorption. It embodies a picture in which the energetic advantage of surrounding a guest molecule with water molecules is used to offset both the entropic loss in caging the guest molecule and the energetic penalty of forming the hydrate water lattice. By calculating the gain in free energy made by caging a guest molecule in water and by comparing this with the increase in free energy associated with arranging the water molecules into the hydrate lattice, it is possible to estimate both the composition and pressure at which the gas hydrate is expected to become thermodynamically stable.

To achieve such a calculation it is useful to note that water-water interactions are much stronger than typical water-guest interactions. As such, one might expect the properties of the water lattice to be determined by the water-water interactions and to be unaffected by the much weaker forces that the guest molecules will exert on it. Thus, the water molecules merely provide the environment in which the encaged guest molecules exist, and it is the way in which the guest molecules interact with this environment that determines the hydrate's properties.

The VDWP theory proceeds precisely in this manner. The free energy of the water lattice is assumed to be independent of the nature or number of guest molecules present. The environment created by the water lattice is then described in terms of a potential energy surface within the cavities (termed the cavity potential), so that implementing the VDWP theory involves calculating the free energy of a guest molecule within a cavity potential. Thus, the VDWP theory focuses attention on the behavior of the guest molecules and away from that of the water lattice. In this work we shall reverse this emphasis and examine explicitly the extent to which guest molecules can induce lattice relaxation.

Simulation Details

The simulation method has been described in detail elsewhere (Rodger, 1989, 1990a), and so only a brief outline will be given here. Isothermal-isochoral molecular dynamics simulations were used to model the properties of a type I gas hydrate. A single unit cell was considered, with the initial positions for the water molecules being taken from neutron scattering experiments (Hollander and Jeffrey, 1977), and periodic boundary conditions were used to mimic an infinite lattice; a unit cell length of 12.03 Å was used throughout. Up to eight guest molecules were included in the unit cell. To check that this system was large enough to provide a realistic model, two simulations were performed using eight crystallographic cells and with (i) 100% and (ii) 75% of the cavities occupied by methane molecules. The larger simulations did reveal some differences from their smaller counterparts, due to the inclusion of longer wave length phonon modes and to a longer truncation length for the dispersion interactions; however, the *differences* between the two larger simulations were in quantitative agreement with those observed between the smaller simulations, implying that the trends observed were not artifacts of the size of the simulations.

Intermolecular potentials were the same as those used in previous studies (Rodger, 1990b): a simple point charge model (SPC) (Berendsen et al., 1981) was used for the water-water interactions, and the guest was modeled by a single Lennard-Jones site with the parameters being chosen to describe methane. Long-range electrostatic interactions were evaluated with a EWALD summation, while all other interactions were truncated when the site-site separation exceeded half the unit cell length.

All simulations were equilibrated for 10 ps (2,000 time steps) before accumulating a further 30 ps for analysis. Two independent trajectories were run for some of the systems, but these revealed no significant differences, indicating that a single trajectory was sufficient to calculate equilibrium properties.

We note that the conditions used in these simulations (constant volume and only 40 ps runs) are not conducive to observing phase transitions. Rather, they are likely to sample equilibrium within a metastable state, and it is this "equilibrium" that was tested by duplicating the simulations. However, our aim in this work is to examine the approximations behind the VDWP theory. Since the VDWP theory compares the free energy of various possible metastable states to see which one of them is actually thermodynamically stable, we conclude that our simulation conditions are the most appropriate ones for this study.

Results

In many ways, it is the assumption that guest molecules do not induce any relaxation in the host lattice that gives the VDWP theory its form, as it serves to focus attention on the behavior of the guest molecules instead of the host. The purpose of this section is to examine explicitly the extent of lattice relaxation induced by changes in either the number or nature of guest molecules present. Strictly speaking, this assumption relates only to changes in the free energy of the host lattice; however, it is to be expected that variations in the free energy of the host lattice will coincide with relaxation of other lattice properties. Since free energies for crystalline phases are very difficult to evaluate in simulations, we have used other related properties such as the internal energy and lattice dynamics of the host to probe lattice relaxation.

Occupancy

To examine the effect of occupancy (that is, the percentage of cavities occupied) on the host lattice we have performed a series of simulations, in which the number of cavities occupied by a guest molecule was varied. These simulations will be denoted *Mi*, if the large cavities were occupied in preference to the small cavities and *MiS* otherwise, where *i* is the number of cavities that were occupied. Note that *M*8 has all of the cavities occupied, and *M*6 has all of the large cavities occupied. Some of the properties of *M*0 showed considerable variations between different trajectories, and in one of the *M*0 simulations there was clear evidence of the host lattice melting (Rodger, 1990c); all of the other systems were well behaved on the timescale of the simulations.

Potential energies arising purely from the water-water interactions were calculated for all systems and are listed in Table 2; note that these energies include electrostatic interactions to infinite separation, but the Lennard-Jones interactions were truncated at about 6 Å. The results show a consistent trend for the lattice energy to increase as the number of guest molecules decreases, with the most rapid changes being in the physically important region (80–100%). The magnitude of these variations may seem quite small, with the difference between *M*8 and *M*6 being only 0.27 kJ/mol, but we note that the current estimate of the difference in chemical potential between ice and an empty hydrate lattice at 273 K is only 1.3 kJ/mol (Tse et al., 1986); although these two quantities are not directly comparable, this does suggest that changes in the water lattice due to variations in guest occupancy could provide as much as 20% of the energy needed to stabilize the hydrate. It would seem, therefore, that the energy of the water-water interactions does depend significantly on the number of guest molecules present.

Occupancy also affects the structural properties of the water lattice. In previous work, it was found that the radial distribution of water molecules about the centers of the cavities (CRD) is very sensitive to changes in the structure of the host lattice (Rodger, 1990a) and so should be a good probe of lattice relaxation. Accordingly, we have calculated the CRD's arising at different occupancies, and representative examples are depicted in Figure 1. The general features of these curves are as expected: there is a void that defines the cavity, and this is bounded by a region of very high density that corresponds to the cavity wall. The spread of water molecules in each distribution arises from vibrations of the water lattice. As was found with the lattice energies there is again a consistent trend, with the cavity wall spreading out more as the occupancy decreases. This indicates that the amplitude of the host lattice vibrations increases when guest molecules are removed. Although the differences among *M*6, *M*2 and *M*0 are small in this case, there is a considerable difference between *M*6 and *M*8, with the spreading of the cavity wall from *M*8 to *M*6 being comparable with an increase in the temperature of 70 K (Rodger, 1991). Remember that typical occupancies found in real hydrates are in-between those of *M*6 and *M*8.

Table 2. Average properties obtained from simulations

Simulation	T (K)	$-U_{ww}$[a] (kJ·mol^{-1})	R_{inner}[b] (Å) Small	Large	x_{∞}^{2}[c] (Å^2)
*M*8	270	47.58	3.447	3.689	0.295 (4)
*M*7	270	47.39	3.416	3.678	0.303 (5)
*M*6	270	47.31	3.388	3.675	0.337 (5)
*M*5	270	47.23	3.390	3.682	0.337 (5)
*M*4	270	47.14	3.381	3.680	0.340 (6)
*M*2	270	47.00	3.368	3.673	0.350 (5)
*M*2*S*	270	47.10	3.437	3.654	0.356 (6)
*M*0	270	46.71	3.367	3.644	0.408 (7)
*R*8	270	47.53	3.452	3.686	0.308 (4)
*R*6	270	47.29	3.376	3.679	0.341 (4)
*A*8	272	46.86	3.351	3.601	0.498 (28)
*A*6	273	46.77	3.340	3.631	0.466 (26)

[a] Potential energy due to water-water interactions. Statistical uncertainties are ±0.04 kJ·mol^{-1}

[b] Inner radii of cavities (see text). Statistical uncertainties are ±0.005 Å

[c] Average mean square displacement of oxygen atoms at long times. Calculated from values of the MSD for $1.5 < t < 5$ ps. Uncertainties in final digits are given in parentheses.

The CRD's emphasize the fact the water molecules adopt a distribution of positions and show quite graphically that the cavity walls have a finite thickness. As such, the size of the cavities should not be obtained from the crystallographic position of the water molecules (which is associated with the peak in the CRD), but rather with the location of the inner wall. Although this is not uniquely defined, it seems reasonable to locate the inner wall of the cavity at the edge of the region that is deficient in water molecules, that is, the radius at which the CRD equals 1. In this way, it is possible to quantify the changes in the "thickness" of the cavity wall. Values for these inner radii have been included in Table 2.

As a final probe of the lattice behavior we have examined

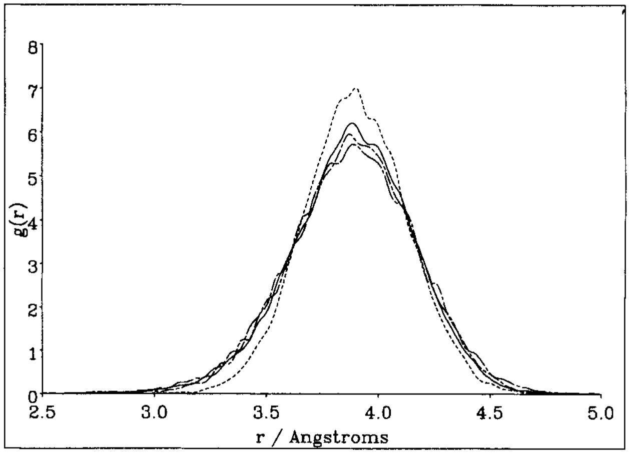

Figure 1. Radial distribution of oxygen atoms about the center of cavities in a type I hydrate at 270 K and various occupancies.

___, *M*8; ______, *M*6; _ _ _ _ _ _ _, *M*2; ________ _, *M*0.

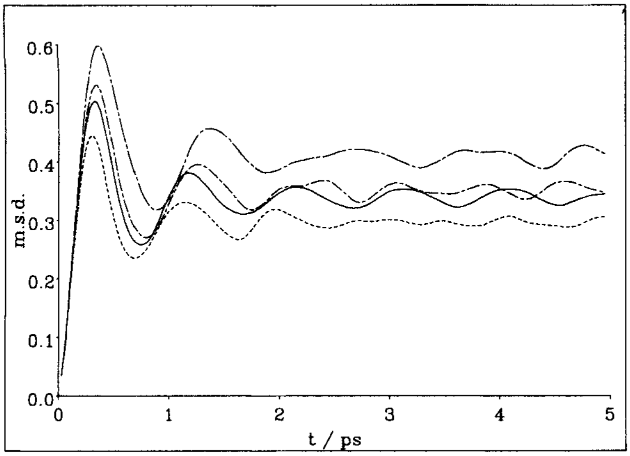

Figure 2. Mean square displacement of oxygen atoms in the hydrate lattice at 270 K and using various occupancies.

– – –, *M*8; ———, *M*6; ——– ——– –, *M*2; ———– ———– –, *M*0.

the mean square displacement (MSD) of water molecules in the host lattice, and the results are depicted in Figure 2. In all cases the mean square displacement reaches a long time plateau that characterizes the amplitude of the lattice vibrations; heights for these plateaus are listed in Table 2. As the occupancy decreases the plateau gets higher, thus confirming that the amplitude of vibrations in the host lattice has increased.

The conclusion to be drawn from this section is that the behavior of the water lattice is affected by the number of guest molecules present. In particular, when the occupancy was decreased, the water molecules appeared to vibrate further from their lattice sites and intruded further into the cavities; this leads to a significant rise in the internal energy of the host lattice. Note that this represents a relaxation, rather than a distortion, of the lattice since the average positions of the host molecules are not changed.

It is instructive to restate these conclusions in a different way: if removing guest molecules from the hydrate increases mobility within the host lattice, then we may also say that adding guest molecules will restrict the mobility of the host lattice. Since real hydrates are usually found to have most of their cavities occupied, this suggests that limiting the amplitude of the host lattice vibrations is an important step in stabilizing gas hydrates. In other words, the guest molecules are not only trapped within a water cage, they also act to confine the water molecules, and thus add to the mechanical stability of the crystal. This picture is consistent with the very low diffusion coefficients for water in clathrate hydrates (Sloan, 1989b).

Type of guest

If, as suggested above, confining the water molecules to their lattice sites is important in stabilizing gas hydrates, then there are some interesting implications about the guest-host interactions that need to be considered. In particular, it suggests a much more important role for the repulsive guest-host interactions than was previously thought. The VDWP theory is concerned primarily with the attractive guest-host interactions which are thought to lower the hydrate's energy sufficiently to make it thermodynamically stable. However, the observations of the last section result largely from an excluded volume: the guest molecules occupy a finite volume and hence obstruct large amplitude vibrations in the water lattice. This is confirmed by the way smaller guest molecules allow greater flexibility in the water lattice (Rodger, 1990a).

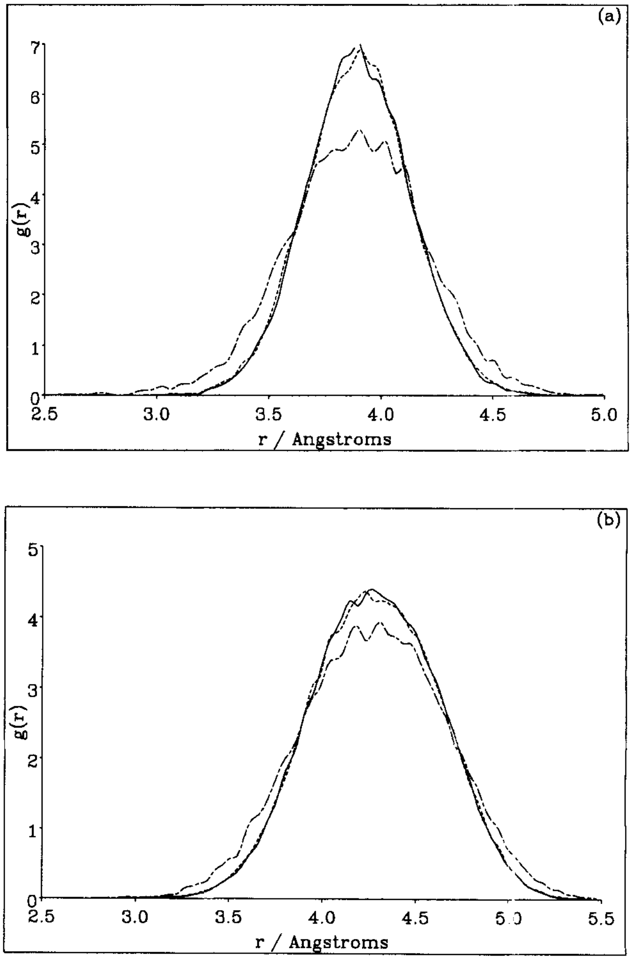

Figure 3. CRD's for (a) small cavities and (b) large cavities at 270 K.

100% of the cavities are occupied in all cases: ———, *M*8; – – –, *R*8; ——– ——– –, *A*8.

The easiest way to examine the relative importance of repulsive and attractive guest-host interactions is to look at them separately. Of course, in real systems this is not possible, since any guest molecule will feel both a long-range attraction and a short-range repulsion to the water lattice. It is, however, possible to simulate either a purely attractive or a purely repulsive guest molecule, and to examine the effect this has on the host lattice. Provided that the model of the host lattice is realistic (as appears to be the case for SPC water), the results of such "thought experiments" will give a reasonable indication of how the various guest-host interactions modify the water's behavior.

Accordingly, we have performed new simulations in which six or eight purely repulsive guests (*R*6 or *R*8) and six or eight purely attractive guests (*A*6 or *A*8) were placed in the cavities of a type I gas hydrate. The repulsive and attractive guest "molecules" were created by partitioning the methane potential into its attractive and repulsive branches (Weekes et al.,

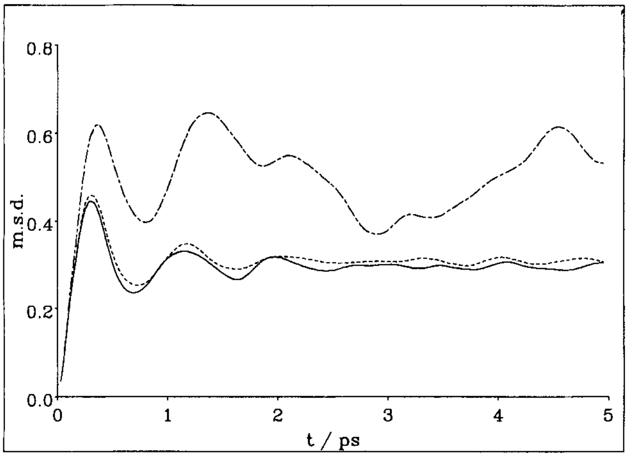

Figure 4. MSD's for oxygen atoms in the hydrate lattice at 270 K.

———, *M*8; – – –, *R*8; — — — —, *A*8.

1971). A harmonic binding force was also needed in the attractive-guest simulations to ensure that the guest did not escape from its cavity; in this case, the binding force acted only on the guest molecule, and the force constant was chosen to make the translational frequency of guest motion similar to that observed in the methane hydrate simulations.

The properties of the water lattice calculated from these new simulations are listed in Table 2, while the CRD's and MSD's are depicted in Figures 3 and 4. It is interesting to note that there is a very strong similarity between the behavior of the water molecules in the methane and repulsive hydrates. In all cases, the internal energy of the water lattice, the inner radii of the cavities, and the limiting mean square displacement of water molecules agree to within the statistical uncertainty of the simulations. On the other hand, the attractive guests lead to markedly different water behavior, giving rise to a host lattice that is more flexible and higher in energy. Such results are consistent with the suggestion that the excluded volume of the guest molecules plays an important part in determining the properties of the host lattice in gas hydrates. Once the repulsive contribution is included, the attractive guest-host interactions do not appear to perturb the host lattice further. Thus the assumptions of the VDWP theory appear to be valid for the attractive guest-host interactions, but some means of describing relaxation of the water lattice due to the volume occupied by the guest molecules is still required.

Discussion and Conclusions

The simulations presented above were designed to test the assumptions that underlie the van der Waals-Platteeuw (VDWP) theory of clathrate hydrates; in particular, we were concerned with the way the VDWP theory describes the water lattice. Our simulations indicated that the percentage of cavities occupied does influence the behavior of the host lattice and results in systematic variations in both the internal energy of the water lattice and the amplitudes of lattice vibrations. It is interesting to note that changes in the energy of the water lattice due to variations in occupancy may be as large as 20% of the difference in chemical potential between the hydrate water lattice and ice at 273 K. Such variations could be significant in determining the conditions for thermodynamic stability; they are, however, explicitly neglected in the VDWP theory.

The mechanism of this interaction appears to involve the hard-core repulsions between the guest and host molecules, with the excluded volume generated by the guest molecules obstructing the motion of the water molecules, and so confining the water molecules to their lattice sites. The net effect of this is that the guest molecules are not only trapped in a water cage, but they also serve to entrap the water molecules. It is for this reason that translational diffusion of either water or guest molecules is negligible in clathrate hydrates (Sloan, 1989b).

The importance of the repulsive interactions in mutually trapping the water and guest molecules raises an important question. If the hydrate crystal is impervious to both water and guest molecules, then is it possible to form a true three-phase equilibrium—bulk water (*W*), bulk guest (*G*), and bulk hydrate (*H*)? Hydrate crystals tend to form at the *W*/*G* interface, since this is the only region where there is a sufficient concentration of both water and guest molecules to form a hydrate; however, once the hydrate nucleates, it immediately forms an impervious barrier between *W* and *G*, thus preventing a direct equilibration between these two phases. Transport of water and guest molecules between *W* and *G* must then take place through the *H* phase and so will not take place independently (that is, for every six water molecules that cross the *H* phase, roughly one guest molecule must be transferred in the same direction). If this is true, then the condition for stability of the bulk hydrate is that the net chemical potential of each of the three phases be equal, and not that the chemical potential of the individual components (water and guest molecules separately) be the same in each phase; this is a less restrictive condition. Note that the one situation in which water and guest molecules will move independently between the three phases is during the initial formation of the interfacial hydrate film. This suggests that it is the free energy of an interfacial hydrate film (rather than that of the bulk hydrate) relative to that of the bulk water and bulk guest phases that determines the conditions for hydrate formation.

In conclusion, the simulations presented in this work provide evidence that the contribution of water-water interactions to the free energy of the hydrate does depend on the number of guest molecules present. This effect is not accounted for by the VDWP theory. Further, the variation with occupancy highlights the role of the repulsive guest-host interactions, and thereby suggests that surface interactions may be more important than interactions in the bulk hydrate in determining the phase behavior of gas hydrates.

Acknowledgment

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Notation

a = hard-sphere parameter in Kihara potential
CRD = cavity radial distribution function
k = Boltzmann's constant
Mi = simulation with i cavities occupied with preference to large cavities (i = 0, 2, 4, 5, 6, 7, or 8)
MiS = as for Mi, but with small cavities filled first

MSD = mean square displacement
r_m = separation of minimum energy for a dimer
R_{inner} = inner radius of a cavity
T = temperature
U_{ww} = potential energy arising from water-water interactions
VDWP = van der Waals-Platteeuw theory of hydrate stability
x_∞^2 = long-time limit of the mean square displacement
ϵ = well-depth parameter in Kihara potential
σ = soft-sphere parameter in Kihara potential

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