Computer simulations of nitrogen-containing molecular systems at very high density

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5

The stability of doubly occupied \( \text{N}_2 \) clathrate hydrates

5.1 Introduction

Clathrate hydrates are non stoichiometric, crystalline inclusion compounds consisting of guest molecules and water molecules \([\text{Slo90}, \text{Atw91}]\). The latter form an ice like hydrogen-bonded network composed of cavities. The guest molecules occupy the voids inside these cages. A minimum number of guest molecules is needed to stabilize the host framework.

At low pressures, \( \text{N}_2 \) clathrates are known to form structure II \([\text{Dav84}, \text{Dav86}]\). In the structure II clathrates, the unit cell contains 136 water molecules, forming 16 small and 8 large cavities: if all cavities contain one guest molecule, 24 guests can be en-caged in the unit cell. The small and large cages consist of 20 and 28 water molecules, and have a radius of about 3.9 and 4.7 Å, respectively.

Raman measurements of the \( \text{N}_2 \) vibron stretch in natural or synthetic clathrate hydrates have been performed by several authors \([\text{Pau99}, \text{Pau97}, \text{Pau96}, \text{Pau95}, \text{Cha97}, \text{Nak88}]\). A Raman investigation of the high pressure behavior of the \( \text{N}_2 \) clathrate has been performed by van Hinsberg et al. \([\text{vH93}, \text{vH94}]\). At a temperature of 273 K, the \( \text{N}_2 \) vibron shows a splitting of the vibron peak at around 8.5 kbar. In addition, the coupled \( \nu_1 \) symmetric \( \text{H}_2\text{O} \) stretch shows a jump in the frequency-pressure behavior. The authors suggested a number of possible explanations, one of them being a sudden increase for the possibility of double occupancy. Champagnon et al. \([\text{Cha97}]\) used polarized Raman scattering techniques which revealed that the unpolarized Raman lines have two components, separated by 0.4 cm\(^{-1}\). The authors proposed two explanations, one being that the two components reflect the two types of cages in which the \( \text{N}_2 \) molecules should be hosted. However, since the difference in wavenumbers is only small, the authors consider it more likely that the two components reflect a partial double occupancy, with a coupling of the intramolecular vibrational modes of two guest molecules in a large cage.

A high resolution neutron diffraction study on \( \text{N}_2 \) clathrates has been performed \([\text{Kuh97}, \text{Pau99}, \text{Pau97}, \text{Cha98}]\). In this study, the filling fractions of the small and large cages could be obtained by the refinement and screening of several compatible structural models, using convergence behavior and crystallographic agreement factors as selection
criteria. The filling of the cages roughly follows Langmuir isotherms with different Langmuir constants for the various types of filling. For the large cages, a significant deviation of the data with a one-parameter Langmuir curve occurs for higher fillings, at higher pressures. By the refinements of the structure, the authors find that, for all but the lowest pressures, the large cages are partly doubly occupied. In the best model for the small cages, the guests were located at the center of the cage and oriented along the cubic main axes. For the large cages, the best agreement was obtained with the N\textsubscript{2} molecules shifted off the cage-center by 0.8 Å and oriented along the unit cell diagonals. Other models produced only marginal changes in the cage occupancies.

A large number of interesting papers on simulations of clathrate hydrates have appeared in literature, with only a few papers on simulations of N\textsubscript{2} clathrates: In a MD study of the dynamic behavior of N\textsubscript{2} and O\textsubscript{2} molecules [Hor97b], the positions and orientations of the guest molecules were explained in terms of cage size and cage distortion. In addition, vibrational stretching spectra were calculated. No significant difference in behavior of the two guest species was found. In another study, the filling fractions and sorption energies of N\textsubscript{2} and CO\textsubscript{2} were calculated using Monte Carlo calculations [Kha98].

To our knowledge, there is only one very limited simulation study on doubly occupied clathrates [Hor97a], however, the work was not published. To obtain insight into the experimental results described above, and in particular to investigate the possibility of doubly occupied N\textsubscript{2} clathrates, we have performed a series of MD simulations.

### 5.2 Simulation details

This section describes the simulation techniques and methods used. The details of these techniques can be found in Refs. [All86, Fre96, DLP98] and references therein. Classical molecular dynamics (N\textsubscript{V}T) and (N\textsubscript{p}T) simulations were performed with the DL\_POLY package [DLP98]. In addition, a number of analysis programs were written. We have used 8 unit cells as a compromise between computational cost and the ability of the simulation cell to allow for deformations in the clathrate hydrate structure. This corresponds with 1088 water molecules, which constitute 128 small and 64 large cages. To mimic an infinite crystal, three dimensional periodic boundary conditions were preserved. Long range Coulomb interactions were treated with the Ewald summation method. The temperature was controlled with a single Nosé–Hoover thermostat. The Hoover barostat in the Melchionna modification controlled the pressure. The equations of motion were integrated using the Verlet leapfrog integration scheme. The simulation time step was 1 fs. the length of the simulation went up to 300 ps, while up to 50% of its length was used for equilibration. Correlation times and errors were checked. For the H\textsubscript{2}O molecules we have used constrained bonds using the SHAKE algorithm. For the N\textsubscript{2} molecules, we have used rigid bonds using Fincham’s implicit quaternion algorithm. To save time, we have used a cutoff at 8.5 Å for the van der Waals interactions. A long range correction was added to the pressure and energy. We have performed calculations at different temperatures and pressures. In addition, we have changed the composition of the mixture (i.e. the filling fraction of N\textsubscript{2} guest the molecules).

The initial positions of the O atoms were taken from x-ray diffraction experiments.
5.3 Potential models

5.3.1 Description

For the H$_2$O–H$_2$O interaction we have taken the extended simple point charge (SPC/E) potential model [Ber87]. It is computationally very cost-effective, while it has been shown in the literature that the model allows one to simulate many features of water and water mixtures under various conditions. Similar empirical models result only in differences in details, as has been demonstrated e.g. in Refs. [Han91] and [Jor83]. The van der Waals part of the SPC/E water model consists of one Lennard-Jones site, located at the position of the oxygen atom. The electrostatic interactions are represented by three point charges, located at the oxygen and two hydrogen sites, embodying the water dipole moment. The features of the potential models are given in Table 5.1.

For the N$_2$–N$_2$ van der Waals interaction we used the Etters site–site potential [Ett86]. The repulsive part of this potential model is based on *ab initio* calculations and the authors took considerable effort to accurately describe the condensed phases of N$_2$ via a re-fitting of the parameters. The Etters potential leads to very good agreement with experimental results for the dense fluid and the solid high pressure phases [Bel88, Bel90]. Also based on our own work in which we used this potential (see e.g. Refs. [Mul98, Mic98] and [vK00]), we trusted it to be an excellent model of the N$_2$–N$_2$ interaction. A model of high excellence is important for this work, since the local number density within a doubly occupied cage is high, and therefore the repulsive part of the N$_2$–N$_2$ potential may play an important role in the interactions. The electrostatic interaction is discussed below, as it is the same for the N$_2$–N$_2$ as for the N$_2$–H$_2$O interactions.

The non-sphericity of the N$_2$ molecules is also reflected in the H$_2$O–N$_2$ van der Waals interaction. The (N-site)–(O-site) model as used by Lynden-Bell and co-workers [ihP98,
5. The stability of doubly occupied N\textsubscript{2} clathrate hydrates

<table>
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<th>van der Waals (LJ) parameters</th>
<th>bond properties</th>
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<tr>
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</tr>
<tr>
<td>( q_{CM_{N_2}} )</td>
<td>0.9908</td>
</tr>
</tbody>
</table>

Table 5.1: Potential parameters used for the interactions. Note that for the N–N van der Waals interaction, the bracketed Lennard-Jones parameters are only an indication of the interaction curve: we have used the Etters potential, a parametrization of this potential is found in Ref. [Ett86].

Som99b, Som99a], is the only model we have found in the literature that featured this non-spherical van der Waals interaction. As will be shown later (section 5.3.2), this potential shows a large resemblance with various \textit{ab initio} calculations and gives a good agreement with experimental results. We have modified the charges of the N\textsubscript{2} molecule slightly to be closer to the experimentally observed value of the quadrupole moment \( (-4.7 \cdot 10^{-40} \text{ Cm}^2 \) [Buc68]).

5.3.2 \textit{N}_2–\textit{H}_2\textit{O} potential examination

The \textit{N}_2–\textit{H}_2\textit{O} potential model was used previously [ihP98, Som99b, Som99a] to investigate the structure and mobility of dilute solutions of \textit{N}_2 in water as well as the passage of these molecules through the liquid–vapor interface. With the potential, the authors found satisfactory agreement with experiments. By varying the potential parameters, it was found that the diffusion constant and the radial distribution functions (RDFs) were roughly independent of molecular size and quadrupole moment. The Lennard-Jones part dominated the friction coefficient. The orientational behavior was slightly dependent on the quadrupole moment.

Since the \textit{N}_2–\textit{H}_2\textit{O} potential energy function plays a major role in this investigation (in particular, whether double occupancy leads to a stable structure or not is dependent on this potential energy function, as will be shown in the discussion), we have performed a small investigation in which the potential energy of the dimer has been compared to \textit{ab initio} calculations [Sad95, San94, Cou98, Mok92, Fra94, Fra93, Kit87, Cur84, Dem82] and a structural analysis from spectral data [Lue89].

The two most important bonding configurations, referred to as H-bonded and O-bonded, can already be rationalized on the basis of the charge distributions of the molecules. We have investigated the potential energy function by calculating the energy for different configurations of the dimer. The shape of the \textit{N}_2–\textit{H}_2\textit{O} potential energy surface is qualitatively the same as, and quantitatively similar to that of various \textit{ab initio} calculations [Sad95, San94, Cou98, Mok92, Fra94, Fra93, Kit87, Cur84, Dem82].
The global minimum energy configuration (Fig. 5.1a) is similar to those found in the \textit{ab initio} calculations and to the geometry found in microwave experiments \cite{Lue89}. The energy of this configuration is $-4.3$ kJ/mol. In addition, the $\text{N}_2$-$\text{H}_2\text{O}$ potential exhibits a local minimum of $-2.8$ kJ/mol. This minimum has been found in some of the theoretical works, but most investigators point out that it is a saddle point rather than a minimum. For our potential, the barrier separating the local and global minimum has an energy very close to the local minimum. For higher temperatures, this minimum may indeed behave as a saddle point.

When minimising the energy with respect to the molecular orientations at a fixed intermolecular distance, one finds that this minimum energy corresponds to a H-bonded configuration for distances larger than about $r_H = 3.6$ Å, while it corresponds to an O-bonded configuration for distances shorter than about $r_O = 3.4$ Å. Therefore, the type of bond and correspondingly the relative orientations of the $\text{N}_2$ guest and nearest $\text{H}_2\text{O}$ molecule may be completely different in the case of single and double occupancy, since a significant difference in intermolecular $\text{H}_2\text{O}$-$\text{N}_2$ distance is expected for the two cases.

In summary, the potential is shallow, and the potential energy surface as well as the minimum energy configuration is similar to those found in earlier investigations. Differences with the theoretical results may be explained with the unrealistic large $\text{H}_2\text{O}$ bond angle in the SPC/E molecule, and the fact that we employ an \textit{effective} pair potential. Note also that the \textit{ab initio} results themselves vary with the level of calculation to the same extent as our deviations from the \textit{ab initio} results.

### 5.4 Results

#### 5.4.1 Stability

An indication of the stability of the clathrate is the behavior of the simulation cell. When performing $(N, p, T)$ calculations the simulation cell may show large deviations from that of the clathrate phase (for which the structure should be cubic). In that case, it should be concluded that the clathrate is not stable. Figure 5.2(a) and (b) show the cell dimensions at $T = 273$ K and $p = 0.1$ GPa as a function of the number of guest molecules in the indicated cages only. This state point was chosen since it is close to the conditions at which double occupancy has been observed. Both the average cell length and the average cell angle are slightly dependent on the filling fraction, which is reflected in the behavior of the volume (discussed below). However, within statistical accuracy, there is only a small deviation from the average cell lengths and cell angles, and this deviation is hardly dependent on the filling fraction or type of filling.

Other indications of the stability of the clathrate hydrates are the RDFs. The RDFs that reflect the structure of the host lattice are the H–H, H–O and O–O RDFs. If the system is not stable, it is most likely that a liquid or liquid-like structure will appear, resulting in relatively flat RDFs at larger distances (Fig. 5.3(a)). Figure 5.2(c) shows the O–O RDFs for the various types of filling and filling fractions. Clearly, all RDFs are resemblant. Only the for the small cages, the peaks sharpen slightly with increasing number of $\text{N}_2$ guests. However, these changes are small. The H–H and O–H RDFs behave
5. The stability of doubly occupied N$_2$ clathrate hydrates

in a similar fashion. We therefore conclude that the RDFs are the same for all types of filling and for all filling fractions.

Since the deviations in simulation cell angles and lengths are small and hardly depend on the type of filling or on the filling fraction, and since the RDFs that reflect the host lattice do not depend on the type of filling or on the filling fraction, we conclude that the clathrate hydrate in double occupancy is stable (or at least as stable as for single occupancy). The stability of the clathrate is not only preserved at the conditions given above, but at all conditions at which we have performed simulations (at 80 and 273 K,
Results

Figure 5.2: The simulation cell angles (a) and lengths (b) as a function of occupation number for various fillings: empty host lattice (X), double occupancy of large cages only (□), single occupancy of large cages only (○) and (single) occupancy of small cages only (○). The calculated statistical errors are about 0.5 and 0.2 for the angles and lengths, respectively. (c) The O-O RDFs for various fillings. The types of filling are (from top to bottom): empty host lattice, double occupancy of large cages only, single occupancy of large cages only, (single) occupancy of small cages only. Where appropriate, the occupation numbers are 16, 32, 64 and 128 (indicated by solid, dashed, dotted and dot-dashed lines, respectively).

pressures below 0.25 GPa, and various fillings). Unless stated otherwise.

For instance, the stability is also preserved for a partial doubly ($N_{S,S} + N_{L,S} + N_{L,D} = 128 + 32 + 64$) occupied clathrate at 273 K, of which the O-O RDF is given in Fig. 5.3(a). These results were obtained with (N.V.T) calculations with a lattice parameter of 17 Å. Now let us compare several RDFs in the clathrate with those in the fluid. Figure 5.3 shows RDFs in the liquid phase and in the clathrate hydrate. In the liquid, the same total number of $N_2$ molecules was taken, thus giving the same mole fraction as in the clathrate phase.

The O-O RDFs show that there is a clear difference in structure for the clathrate host lattice and the water molecules in the fluid. There is long range positional order in the clathrate hydrate: it is crystalline. As expected, the most probable $N_2$–O distance (the maximum in the first peak) is smallest and largest for the doubly and singly occupied large cages, respectively.

Now let us compare the $N_2$–O RDF in the doubly occupied large cage with the one in the fluid phase. The onset as well as the maximum of the first peak occur at the same distance. From this we conclude that the mutual average $N_2$–H$_2$O forces in the clathrate (the forces the $N_2$ guest molecules exert on the wall of the cage) are of the same order of
Figure 5.3: Radial distribution functions for a \( \text{N}_2 \) clathrate hydrate and a mixed liquid at the same conditions (see text). (a) \( \text{O-O} \) RDF for the liquid (solid line) and clathrate (dashed line) phases. (b) \( \text{O-N}_2 \) RDF for the liquid (solid line), small cages (dashed line), singly occupied large cages (dotted line) and doubly occupied large cages (dash-dotted line). The vertical bars indicate the radii of the small and large cages [Slo90]. For simulation conditions, see text.

magnitude as in the fluid. Thus, although the \( \text{N}_2-\text{H}_2\text{O} \) distances are shorter compared to the single fillings, the cage-wall is not exposed to excessively large forces.

Similar to the ices, clathrate hydrates have an open molecular structure, leading to a lower density than in the fluid phase. In the \( (N,V,T) \) calculations this is reflected in a higher pressure (4.5 kbar) and lower energy (\( -7.3 \cdot 10^6 \) K) for the clathrate compared to the liquid mixture (4.0 kbar and \( -6.5 \cdot 10^6 \) K, respectively). The overall shape of the RDFs for the liquid mixture and doubly occupied cages is similar. Therefore, the structure in
Figure 5.4: The energy (a) and volume (b) as a function of occupation number for various types of fillings. The simulation conditions and symbols are the same as for Fig. 5.2. The calculated statistical errors are about $3 \cdot 10^3$ K and $2 \cdot 10^2$ Å$^3$ for the energy and volume, respectively.

the vicinity of the $N_2$ molecule must be similar for both systems. We also expect that the local density in the doubly occupied large cage is similar to that in the mixed fluid.

Apart from the structure of the mixture, the stability of the system can be investigated by calculating the system energy and volume. We have calculated these quantities for the conditions corresponding to Fig. 5.2, the results are shown in Fig. 5.4. In all three cases the system energy decreases as a function of the number of guests. The behavior of the energy is the same for the small and the singly occupied large cages. The decrease in energy with increasing occupation number is smaller for doubly occupied large cages. As a result, the energy of the doubly occupied cage is larger at the same occupation number. However, the energy as a function of occupied cages is roughly the same for the three types of filling. Since the pressures are low, the enthalpy behaves similar to the energy.

For the singly occupied large cages, there is hardly any dependence of the volume of the system on the occupation number within statistical uncertainty. In contrast, addition of $N_2$ molecules in the small and in the doubly occupied large cages leads to an increase in volume. Again within statistical uncertainty, at the same occupation number the volume
of the small cages is slightly higher than that of the doubly occupied large cages. As all curves should intersect at zero filling, the slope of volume versus filling is slightly higher for the small cages, but the behavior of the volume is roughly the same in both cases.

5.4.2 Positions

We have investigated the distances of the molecules with respect to the cage centers. CC (the cage centers are the same as the positions of the guest molecules according to crystallographic data [Mak64]), by determining the distribution \( f(r) \) of these distances \( r \). This function gives the probability that a particle is in a spherical shell at distance \( r \) from another particle (the particles being either real or fictitious, such as the cage center), and will be referred to as the radial distribution probability (RDP). This is not the usual RDF \( g(r) \): the RDF will lead to statistical problems at small distances.

For the determination of the RDP, only the first coordination shell is considered, such as the cage surrounding its cage center. For example, \( f_{CC,O}(r) \) gives the probability that a CC O distance (O being in the cage corresponding to the particular cage center) occurs at \( r \). Its integral over \( r \) equals 1. We have also calculated these RDPs while considering only the O atom closest to the \( N_2 \) molecule or cage center (referred to as \( O^1 \)). For example, only the shortest CC-O distances contribute to \( f_{CC,O}(r) \). Thus, for each small cage (containing 20 O atoms) at each time-step all CC-O distances are calculated: all 20 distances contribute to \( f_{CC,O}(r) \), but only the shortest distance contributes to \( f_{CC,O}(r) \).

Clearly, for an \( (N,p,T) \) calculation it is very likely that the centers of the cages move continuously. To simplify matters, \( (N,V,T) \) calculations were performed with a lattice constant of 17 Å. For a fully occupied clathrate hydrate with 50% double occupation \( (N_{SS} = 128, N_{LS} = 32, N_{L,D} = 64) \), at a temperature of 80 K, this resulted in a pressure of \(-0.132 \pm 0.008 \text{ GPa}\). We calculated at a lower temperature since it leads to smaller peak widths. Figure 5.5 shows the RDPs for the CC-O, CC-N\(_2\), N\(_2\) O as well as the CC-O\(^1\) and N\(_2\)-O\(^1\) distances for the three types of cages.

In the small cage (Fig. 5.5(a)), the most probable \( N_2 \) CC distance is about 0.22 Å. The distributions of both the \( N_2-O^1 \) and CC-\( O^1 \) distances are the same, with a maximum around 3.5 Å. Although one might expect \( d_{CC-O} = d_{CC-N_2} + d_{N_2-O} \) for the distances \( d \), this condition is not fulfilled. However, the result can be understood if one assumes that the cage is non-spherical and that the displacement of the \( N_2 \) guest molecules from the cage center is in a direction perpendicular to the CC O\(^1\) direction.

In the singly occupied large cage, the \( N_2 \) molecules show a larger displacement from the cage center: it is about 0.85 Å. These molecules may be considered to be adsorbed to the wall of the large cage. This results in a most probable \( N_2-O^1 \) (adsorption) distance of 3.7 Å. This distance corresponds to the minimum energy configuration. Fig 5.1(a). Of course, for the doubly occupied cages, the guest molecules show the largest shift with respect to the cage center (1.6 Å).

The distributions of CC-O\(^1\) and CC O distances are the same for the singly and doubly occupied large cages, which supports the conclusion that the doubly occupied clathrate is stable. Although the shape of the \( N_2-O \) distributions is quite different for the cases of single and double occupation, they have about the same average value. Going from the singly occupied large cages to the small cages to the doubly occupied large cages
Figure 5.5: The radial distribution probabilities (RDPs) for the small (a), singly occupied large (b), and doubly occupied large (c) cages. See text for simulation conditions. Shown are the CC-N$_2$ (solid), N$_2$–O (dashed), CC–O (dotted) distributions. The corresponding N$_2$–O$_1$ (dashed) and CC–O$_1$ (dotted) distributions are indicated with small arrows.

the average N$_2$–O$_1$ distance gradually decreases.

5.4.3 Orientational distributions and sensitivity to force field

We have determined the orientational correlations of the two nearest N$_2$ molecules in the clathrate hydrate using the (pair) distribution of cos(θ), θ being the angle between two N$_2$ guest molecules. For the small and singly occupied large cages it corresponds with the orientational correlations between the N$_2$ guest molecules in neighboring cages. It turns out that these correlations are negligible.

For the doubly occupied large cages, this distribution indicates the orientational correlation between the two N$_2$ guest molecules within the same cage. Figure 5.6 gives the
Figure 5.6: The distributions of $|\cos(\theta)|$, $\theta$ being the angle between two $N_2$ molecules within the doubly occupied large cages. For simulation conditions, see text. The lines show the results for different point charges at the respective $N_2$ sites. The original charges are multiplied by 1 (solid line, original calculation), 0 (dashed line, $N_2$ charges omitted) and 2 (dotted line).

$(N, V, T)$ results for $N_{S,S} = 128$, $N_{L,S} = 32$ and $N_{L,D} = 64$ at 80 K with lattice parameter 17 Å (constant pressure calculations give similar results). It shows that there is some preference for the two molecules to be parallel. This is a rather unexpected result, since it leads to a peculiar charge distribution within the cage. If the $N_2$-$N_2$ interaction would have the major influence on the relative orientation, they would be in a X-configuration, since then the $N_2$-$N_2$ quadrupole–quadrupole interaction energy as well as the van der Waals interaction would be lowest. From this we conclude that the $N_2$–H$_2$O interaction causes the alignment of the two guest molecules.

To investigate this further, we have multiplied the charges on all $N_2$ molecules by a factor of 2, 1/2 and 0, respectively. These large changes are chosen to obtain unambiguous results (larger charges on the $N_2$ molecule, or similar changes in the H$_2$O charges lead to an unstable clathrate lattice). Neglecting changes in position, a multiplication of the $N_2$ charges by a factor of 2 increases the (water dipole)–(nitrogen quadrupole) interaction by a factor of 2, while it increases the $N_2$–$N_2$ quadrupole–quadrupole interaction by a factor of 4. As shown in Fig. 5.6, the increase of the $N_2$ charges indeed changes the preferred relative orientations drastically: there is now a small preference for a X-configuration. There is not much difference in the distribution function upon multiplication by 1/2 or 0: only the results with the $N_2$ charges omitted is shown in Fig. 5.6. In that case, the preference for alignment has increased compared to the original calculation. We conclude that the $N_2$–H$_2$O van der Waals interaction dictates the relative orientation of the two $N_2$ guest molecules.
Note that we also find that the above changes in the charges do not influence the RDFs: the van der Waals interaction is the dominating interaction with respect to positions as well as orientations of the guest molecules. In contrast, the Coulomb interaction plays a major role in the stability of the hydrogen bonded host lattice.

One may wonder what the maximum size of the guest molecules inside a doubly occupied large cage may be without destroying the host lattice. Therefore, in addition to changes in the Coulomb interaction, we have investigated the stability of a doubly occupied clathrate hydrate as a function of the van der Waals diameter \( \sigma_{NN} \) of the N-atoms. To simplify these calculations, we have used a Lennard-Jones site-site interaction for the \( N_2-N_2 \) interaction (the bracketed parameters given in Table 5.1 are used), and applied the Lorentz–Berthelot rule for the \( N_2-H_2O \) interaction. \( \sigma_{NN} \) was altered in steps of 10%. Considerably larger molecules cannot occupy the small cages. Therefore, we have performed these calculations for the extreme case that all large cages are doubly occupied while the small cages remain empty, the applied temperature and pressure being 273 K and 0.1 GPa, respectively. Occupation of the small cages and/or smaller filling fractions of the doubly occupied large cages will most likely enhance the stability: we will probably find a conservative estimate for the upper limit of \( \sigma_{NN} \).

Figure 5.7 shows the results. At about \( \sigma_{NN} = 4 \text{ Å} \), the energy shows a large jump. In addition, around and above this van der Waals radius, the box-lengths and box-angles show large deviations from a cubic simulation cell: the clathrate has become unstable.

For the first four \( \sigma_{NN} \) values, the O–O RDFs show close mutual resemblance (Fig. 5.8). They also are similar to the O–O RDFs of the empty host lattice and the singly occupied clathrate hydrate. For \( \sigma_{NN} \geq 4 \text{ Å} \), there is a considerable change. The only sharp peak is the first: the clathrate has become unstable, and instead a fluid-like behavior occurs. Naturally, for the \( N_2-N_2 \) RDF, the onset and the first peak shift to larger distances with increasing \( \sigma_{NN} \). This shift is gradual for the first four \( \sigma_{NN} \) values, but it shows a jump between \( \sigma_{NN} = 3.6 \) and 4 Å. From that value on, the shift again is gradual. Other RDFs, such as the \( N_2-O \) RDF (not shown), behave in a similar fashion. Therefore, with respect to the RDFs, the \( \sigma_{NN} \)-dependence can be divided into two branches. These two branches correspond with the two energy ranges discussed above. Therefore, we conclude that an increase of 10% (\( \sigma_{NN} \approx 3.6 \text{ Å} \)) in \( \sigma_{NN} \), and possibly for somewhat larger values, the doubly occupied clathrate remains stable.

### 5.4.4 Simulations at experimental conditions

Up to this point, we have used rather academic occupancies. In particular, we have changed the three types of occupancies at the same temperature and pressure. This was necessary to systematically investigate the stability. To interrelate with the experimental results, in this section we take conditions that are much closer to those in the experiments.

The cage occupancy is related to the external pressure via the Langmuir equation. For single occupancy, this equation follows from the van der Waals–Platteeuw theory [vdW59]. In analogy with surface adsorption, it can be extended to double occupancy [Fog86]. Kuhs et al. [Kuh97] experimentally determined the Langmuir constants for the three types of filling in \( N_2 \) clathrates at 273 K using neutron diffraction.

We have performed \((N, p, T)\) calculations for a number of pressures at 273 K. At every
Figure 5.7: The energy (a), three simulation box-angles (b) and simulation box-lengths (c) as a function of van der Waals (LJ) radius with a complete double filling of the large cages only, and conditions as mentioned in the text. The small closed symbols are the results for an empty host lattice. The large closed symbols are the results for a clathrate hydrate with a complete single filling of the large cages only. The calculated statistical errors are about $2 \times 10^{-2}$, 0.5 and 0.8 for the energy, box-angles and box-lengths, respectively.

pressure, the cage occupancies that we have taken as input in the simulations (shown in Table 5.2) follow directly from the Langmuir curves, with the three Langmuir constants as determined by Kuins et al.

As in the above, to investigate the stability of the clathrates, the radial distribution functions (RDFs) and box dimensions were monitored. None of the RDFs showed any significant changes with pressure, indicating a stable clathrate hydrate upon compression up to about 2 kbar. Figure 5.9(a) shows that the system energy decreases as a function of pressure. The filling fractions are determined by the pressure via the Langmuir curves. In section 5.4.1 we have shown that, at constant pressure, the system energy decreases linearly with filling fraction. Although the current results are not obtained at constant pressure, the energy clearly reflects the Langmuir behavior. A plot of the molar energy versus pressure gives a similar curve, but with an opposite sign: the molar energy increases with filling fraction. This roughly means that the energy of the added $N_2$ molecule is higher.
Results

Figure 5.8: The O–O (a) and \( \text{N}_2–\text{N}_2 \) (b) RDFs for various values of the van der Waals diameter \( \sigma_{\text{NN}} \), with a complete double filling of the large cages only, and conditions as mentioned in the text. The solid lines denote the radii \( \sigma_{\text{NN}} = 1.986, 2.684, 3.31 \) and 3.641, with increasing line thickness (the stable branch). The dashed lines denote \( \sigma_{\text{NN}} = 3.972, 4.303, 4.634 \) and 4.965, with increasing line thickness (the unstable branch). In addition, the results for the empty host lattice (solid squares) and a clathrate with a complete single filling of the large cages only (solid diamonds) are shown.

(although negative) than the specific energy of the molecules that are already present: the molar energy gets closer to zero.

The simulation cell and angles lengths are shown in Fig. 5.9(b) and (c). The figure shows that at low pressures the rapid increase in number of guest molecules causes an increase in the cell volume, again in correspondence with Fig. 5.4. At higher pressures, the increase in filling fraction (slope of the Langmuir curve) is much smaller, resulting in a smaller expansion of the system. As a consequence, the effect of the increasing pressure prevails over the effect of the increasing filling fraction. The result is a decrease in volume.
Table 5.2: Occupation numbers of the three types of cages at several pressures. The filling fractions are calculated using the Langmuir constants as calculated by Kuhs et al. [Kuh97]. The pressures and occupation numbers are used as input for the \((N, p, T)\) results given in Fig. 5.9 \((T = 273 \text{ K})\).
5.5 Discussion

In section 5.4.1 it was found that the energy decreases linearly with increasing filling fractions. At the same time there is a linear increase in volume for the small and doubly occupied large cages. For the singly occupied large cages the volume remains more or less constant: the host lattice remains uninfluenced when these cages are filled.

Since the interaction between the guests in different cages is negligible, the dependence of the volume and energy for mixed fillings is expected to be a linear combination of the isolated cases. Then the energy and volume for double occupancies behave very similar to, and lie within the same range of values as those for single occupations. Since the volumes and energies do not show large differences for the 3 types of filling, the configurational entropy may be a driving force for the occurrence of double occupancy. If 1/3 of the large cages is empty, 1/3 is singly occupied and 1/3 is doubly occupied, the entropy is maximal. For the effects of double occupancy on thermal entropy, additional calculations need to be performed.

One may wonder how the volume of the small and of the doubly occupied large cages can increase upon addition of N$_2$ molecules, while the energies decrease as a function of filling. It suggests that although the most dominant contributions to the energy arise from the repulsive range of the N$_2$-H$_2$O interaction, it must be in the negative part of the interaction potential. We have tested this by comparing the RDFs (similar to those in Fig. 5.3(b)) for the various fillings with the orientationally averaged potential energy curve (Fig. 5.1(b), solid line). The use of this curve can be justified by an investigation of the orientational distributions of the guest molecules: these are nearly flat under these conditions.

For the small cages, the N$_2$-O RDF has its first peak at 3.78 Å. Indeed, this is in the repulsive, but negative-energy part of the average potential curve. For singly occupied large cages, the first maximum in the RDF occurs at 4.35 Å. Thus, in the same line of reasoning, the energy should be about the same as for the small cages, as it is. However, this distance corresponds with attractive forces and thus could lead to a decrease in volume with increasing occupation number. On the other hand, since the slope in the potential is relatively small at this distance, while the RDF has a large width, one may argue that the decrease in volume will be only small. These handwaving arguments would be too speculative in the case of double occupancy. For a large part, the energy is determined by the N$_2$-N$_2$ interaction. Second, the RDF peak is broad and highly asymmetric. Third, orientational preferences do play a role for these cages. These orientational preferences may be the reason for the smaller volume compared to the small cages.

Although we do not have perfect intermolecular potential models, it is unlikely that our model is wrong by more than 10% in $\sigma_{NN}$, or a factor of 2 in N$_2$ point charges. Since we demonstrated that doubly occupied clathrates remain stable under these changes, it increases the confidence in the results with the original potential models, and with it the confidence in the existence of a doubly occupied N$_2$ clathrate hydrate in nature. From the fact that the doubly occupied clathrate remains stable even for somewhat larger molecules, it is tempting to speculate on the existence of these clathrate hydrates for other guest molecules than N$_2$. For instance, CO$_2$ and CH$_4$ are only about 5% larger in size compared to N$_2$. It would be interesting to have simulation results, and preferably experimental
results, that confirm or preclude the existence of double occupancy in these systems.

The compressibility calculated from the slope of the curve in the higher pressure region of Fig. 5.9 is the same as found in the experiments [Kuh97], and similar to calculations of other type II clathrates [Han91]. Unfortunately, no volume or lattice constants are given in the low pressure region in Ref [Kuh97]. Such data would be necessary in order to check the predicted competition between pressure and filling fraction. Additional experimental evidence on the existence of doubly occupied N₂ clathrate hydrates would also be desirable.

5.6 Conclusions

We have performed molecular dynamics calculations of structure II clathrate hydrates with varying N₂ cage occupancies and at different state conditions. The H₂O-N₂ model used in this study is a good representation of the interaction, as was concluded by comparing the model with *ab initio* studies and experimental results.

For all state points at which calculations were performed, the N₂ clathrate remained stable, even for the case of a full double occupation of the large cages in an otherwise empty host lattice. Upon filling the large cages in double occupation, the energies and volume behave very similar to, and lie within the same range of values as those for single occupations. The energy is negative and decreases as a function of occupation number for single (small as well as large cages) and double (large cages only) fillings, it is highest for double fillings. For the singly occupied large cages, the volume is independent of occupation number, for the other two fillings the volume increases with occupation number. In the case of occupations of the small cage only, the volume is even somewhat higher than for a double filling of the large cages. This suggests that for double fillings the stresses on the host lattice are at least not larger than in the case of single fillings.

There is a striking similarity between the N₂-H₂O RDF obtained from the doubly occupied large cages and from the mixed liquid. Although the intermolecular N₂-H₂O distances are much smaller for doubly occupied cages, this similarity suggests that the cage wall is not exposed to excessively large forces. For the doubly occupied large cages and the mixed liquid, the local density and the local structure around the N₂ molecule are similar.

For singly and doubly occupied large cages, the average N₂-H₂O distance, as well as the distance between the cage centers and the (nearest) H₂O molecules is the same. This again indicates that the cage, and therefore the host lattice, is not distorted by a double occupancy.

The two molecules in the doubly occupied large cages have a small but significant preference to be parallel. This is a consequence of the van der Waals interaction between the H₂O-N₂ molecules. Increasing the size of the guest molecules does not lead to an unstable clathrate hydrate, until the diameter is at least increased by more than 10%. This also leaves open the possibility for somewhat different molecules, such as methane and carbon dioxide.

When the experimentally obtained conditions by Kuhls *et al.* are closely followed, the clathrate hydrate remains stable. The compressibility found in the higher pressure region corresponds with experimental results [Kuh97] and previous simulations [Han91].