Computer simulations of nitrogen-containing molecular systems at very high density
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Doubly occupied $N_2$ clathrate hydrates and their properties

6.1 Introduction

Clathrate hydrates are crystalline inclusion compounds consisting of water molecules, that form an ice-like hydrogen-bonded network composed of cavities [Slo90, Atw91]. In these cavities, or cages, guest molecules are located. Not all of the cages need to be occupied to form a stable lattice.

It has been demonstrated that $N_2$ clathrate hydrates form clathrate structure II [Dav84, Dav86]. The unit cell contains 136 water molecules, forming 16 small and 8 large cavities, having radii of about 3.9 and 4.7 Å, respectively.

A number of experimental results [vH93, vH94, Cha97, Kuh97, Pau99, Pau97, Cha98] imply the possibility of double occupancy to occur in $N_2$ clathrate hydrates. In such doubly occupied clathrates, a non-negligible number of large cages contain two molecules each. This is a rather unexpected phenomenon, considering the size of the $N_2$ molecule.

In the previous chapter we have presented results of molecular dynamics (MD) simulations of doubly occupied $N_2$ clathrate hydrates [vK01]. It was demonstrated that a doubly occupied structure II $N_2$ clathrate is stable for all the pressures, temperatures and compositions at which the simulations had been performed. The structure of the host lattice is indistinguishable from that of a singly occupied clathrate hydrate. For the three ‘types’ of filling (i.e. an empty host lattice with only the small cages occupied in single occupation, with only the large cages occupied in single occupation and with only the large cages occupied in double occupation), the volumes and energies are linearly dependent on the filling fraction. The range of values for the volume and energy is the same for both the singly and the doubly occupied clathrates. In the doubly occupied cages, the O–$N_2$ radial distribution function, and therefore the structure in the vicinity of the $N_2$ molecule, is similar to that of the mixed fluid. An extensive investigation of the distances in the cages showed a large similarity between singly and doubly occupied clathrates. All these results indicate that, upon filling the large cages with pairs of molecules, the stresses on the host lattice are comparable to those in single occupation. Small changes in the intermolecular interactions did not affect the results. The clathrate hydrate destabilizes upon increasing
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the size of the guest molecules by more than about 10%.

In this chapter we wish to present results on the properties of the doubly occupied N₂ clathrate obtained via MD simulations. First, we have calculated neutron diffraction patterns for various fillings. In chapter 5 we have investigated the short range order via the radial distribution functions (RDFs). The long range order is determined via structure factor calculations. Although the long range order is of interest in itself, additional motivation for investigating it is that the results allows for a direct comparison with the experiments by Kuhs et al. [Kuh97]. Second, Raman frequencies are calculated for the three types of filling, and the results are compared with experiments. Third, we investigate the behavior of the clathrate hydrate under relatively high pressures and low temperatures, where a phase transition to an amorphous phase occurs.

6.2 Simulation details and potential models

Details of the applied simulation techniques and methods can be found in chapter 5, Refs. [Ali86, Fre96, DLP98] and references therein. Classical molecular dynamics (N, V, T) and (N, p, T) simulations were performed with the DL_POLY package [DLP98]. In addition, a number of analysis programs were written. The simulated system consisted of 8 unit cells, corresponding with 128 small and 64 large cages. Three dimensional periodic boundary conditions were preserved. 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. Internal degrees of freedom for the N₂ and H₂O molecules were not taken into account. A potential cutoff was set at 8.5 Å. For obtaining the initial configuration, the initial positions of the O atoms were taken from x-ray diffraction experiments [Mak64] and the positions of the H atoms, in compliance with the Bernal–Fowler ice rules [Ber33], were generated using a random number generator. The cages to be filled, being either in single or double (large cages only) occupation were selected at random. The distance between the mass centers of the guest molecules in the doubly occupied cages was initially set at 3 Å, each N₂ molecule being 1.5 Å displaced from the cage center. The initial N₂ orientations were taken to be random in all cases. We have performed calculations at different temperatures, pressures and compositions (i.e. the filling fractions).

For the H₂O–H₂O interaction we have taken the extended simple point charge (SPC/E) potential model [Ber87]. The Etters site–site potential [Ett86] was used for the N₂–N₂ Van der Waals interaction. For the H₂O–N₂ interaction we employed the (N-site)-(O-site) model as used by Lynden-Bell and co-workers [ihP98, Som99b, Som99a]. In chapter 5, it was demonstrated that this model shows a large resemblance with various ab initio calculations and gives good agreement with experimental results.

The total number of guest molecules in the small cages is indicated with Nₚₛ (single occupancy only: Nₚₛ ≤ 128 for 8 unit cells). Likewise, the number of guest molecules in the large cages are Nₖₛ and Nₖ_d for single and double occupancy, respectively (Nₖₛ ≤ 64, Nₖ_d ≤ 128).
6.3 Results

6.3.1 Neutron diffraction patterns

A neutron diffraction pattern is directly related to the neutron-weighted structure factor

\[ S(k) = \left| \sum_i b_i e^{-i\mathbf{k} \cdot \mathbf{r}_i} \right|^2, \tag{6.1} \]

with \( b_i \) the coherent scattering length of atom \( i \) [Han86, Squ78]. That is, the scattering intensity at a certain wave-vector \( \mathbf{k} \) is proportional to \( S(k) \). This quantity can be calculated in a simulation; we have determined it for subsequent configurations with a fixed time-interval. The result corresponds with an ensemble averaged neutron scattering powder pattern. One can determine which density correlations contribute to a certain Bragg peak by calculating the partial structure factor of a selected pair of atomic species [End80, Fab64]. Since in neutron diffraction experiments deuterated water is used (the undesirable incoherent cross section of H is much larger than that of D), the D scattering length is attributed to the H atoms in the calculation of \( S(k) \). Performing a simulation with D atoms and the D scattering length will most probably lead to the same result.

First, we have calculated the diffraction pattern at conditions close to those of the published spectrum in Ref. [Kuh97]. The result is shown in Fig. 6.1(a) and agrees well with experiment. In our comparison with the experimental spectrum, we will focus on the most intense peaks (calculated intensity \( > 0.1 \)), although the weaker features also show a large degree of agreement. A prominent feature of the spectrum is the two pairs of peaks at 26.2 with 27.8 and 30.4 with 31.8° (the latter with a wing), the intensities at 26.2 and 30.4° being roughly 50% smaller than those at 27.8 and 31.8°, respectively. This feature is also observed in the experimental spectrum, although there are differences in relative intensities. Although the lower angle peaks, 9.3, 15.0, 17.5, 18.5, 21.3, and 23.3°, are also found in the experimental spectrum, in our calculation the relative intensities are generally overestimated. Exceptions are the intensities of the peaks at 17.5 and 23.3°, which show the best quantitative agreement with experiment. At larger scattering angles, there is one prominent peak at 57° with weaker features at smaller and higher angles; this is also the case in the experimental spectrum. For the calculated neutron scattering spectra, the widths of the peaks are larger than the experimental ones, this property becomes more evident at larger diffraction angles. Since all peak positions and, to a large extent, the intensities are well reproduced in our calculations, we find the agreement with experiments good.

Having established agreement with experiment, we investigate the influence of the presence of double occupation on the calculated diffraction pattern for this particular case (i.e. close to experimental conditions). This is done by performing an additional simulation in which the 5 pairs of molecules in the doubly occupied large cages were replaced with 5 single molecules. An analysis of the simulation results gives the pattern shown in Fig. 6.1(b). It is clear that it is very similar to that of a partial doubly occupied clathrate hydrate (Fig. 6.1(a)); in particular there are no changes in the peak positions. Of the four prominent peaks (see above), only the peak at 30.4 shows a difference: it has
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Figure 6.1: Calculated diffraction patterns as a function of the wavenumber $k$ (corresponding with the momentum transfer in experiments, upper horizontal axis) and the scattering angle $2\theta$ (lower horizontal axis) at the experimental wavelength 1.59 Å. The intensities are normalized with respect to the maximum intensity. The simulation conditions are $p = 0.06$ GPa, $T = 273$ K. The occupation numbers are $N_{S,S} = 120, N_{L,S} = 58$ and $N_{L,D} = 5$ (a) and $N_{S,S} = 120, N_{L,S} = 63$ and $N_{L,D} = 0$ (b). Only the forward scattering angles are shown, since at larger angles, all intensities (calculated in this work as well as experimentally [Kuh97]) are very small.

A somewhat stronger intensity (of about 10%) in the case of a partial doubly occupied clathrate hydrate. This also holds for the peak at 21.3°. The peaks at the lowest diffraction angles have a weaker intensity in the case of partial double occupation: although the intensity difference at 17.5° is very small, it is at least 15% for the three other low angle peaks (comparison with experiments will be given in the discussion).

A clearer picture of the contributions from the types of occupancies may be obtained when the host lattice is fully occupied with one of the three specified types of filling only. Thus, to obtain unambiguous results while maximizing statistics, we calculated $S(k)$ by analyses of simulations at 273 K and 0.1 GPa (close to experimental conditions) for three
hypothetical extreme cases: complete filling of the small cages only (i.e. in an otherwise empty host lattice: \( N_{L,S} = N_{L,D} = 0, N_{S,S} = 128 \): case I), complete single filling of the large cages only \( (N_{S,S} = N_{L,D} = 0, N_{L,S} = 64 \): case II) and complete double filling of the large cages only \( (N_{S,S} = N_{L,S} = 0, N_{L,D} = 128 \): case III). These fillings are purely academic and we do not expect such occupancies to be found in nature. For comparison, we also calculated the neutron scattering spectra for an empty host lattice at the same conditions.

Figure 6.2 shows the results. In general, for the empty host lattice and the above mentioned cases, the peaks appear at the same positions. There are two main exceptions. The largest difference is in the reflection at 9°, which has zero intensity in the case of double occupancy (case III). Its intensity is also very small for case II. Also, the intensity of the reflection near 23.3° is nearly zero for case I. In addition to these observations, the overall differences in relative intensities are obvious. For case III, the peaks are still present, suggesting that a degree of long range order is preserved during the simulation run (30 ps). However, the Bragg peaks are widened and there is broad background as compared to the other two cases. On the basis of an analysis of the RDFs, in chapter 5 we concluded that even in this academic case, the structure remained stable. The structure factors probe density correlations and are sensitive to the long range order. They are therefore a better indication of the crystallinity and thus the stability of the system. We must conclude that in this case, the structure is slightly less stable than for the other cases. On the other hand, the peaks are still evident and a broad background can also be observed for the case of mixed single fillings (Fig. 6.1(b)), for which the structure is clearly stable.

We now discuss the results in more detail by comparing the results for the three cases with the diffraction pattern of the empty host lattice. Since all peaks are already present for the latter case, we note that the diffraction pattern essentially is generated by the host lattice. The fact that the host lattice plays a dominant role in the diffraction patterns is to be expected from the multitude of H atoms (with the relatively large D scattering length). For case I, roughly all intensities are increased in relation to the peak of maximum intensity for the empty host lattice, at 18.5°. For case II, the intensities at scattering angles larger than 20° have increased, for smaller angles the intensities have decreased. This structure shows the largest agreement with that of an empty host lattice. For case III, these two trends are even stronger.

The peak positions for cases I, II and III (Fig. 6.2) are essentially the same as those in Fig. 6.1, the relative intensities are different. For instance, for the three hypothetical cases the maximum intensity does not occur at a scattering angle of 27.8°, and it depends on the type of filling. Keeping in mind the results of the three hypothetical cases in relation to the empty host lattice (Fig. 6.2), we note the following. Going from single (Fig. 6.1(b)) to double occupancies (Fig. 6.1(a)), the existing intensity differences between the peaks are characterized by an increase for scattering angles larger than 20°, and a decrease for smaller angles.
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Figure 6.2: Calculated diffraction patterns as a function of the wavenumber $k$ (upper horizontal axis) and scattering angle $2\theta$ at wavelength 1.59 Å (lower horizontal axis). Shown are the four individual cases (from bottom to top): an empty host lattice (a) and case I (b), II (c) and III (d): see text for explanation. The intensities are normalized with respect to the maximum intensity. Only the forward scattering angles are shown, since hardly any features appear at larger angles.

6.3.2 Vibrational frequencies

Since the current investigation has partly been initiated by Raman measurements [vH93, Cha97, Pau96, Pau95, Nak88], we have calculated the Raman frequencies of the N$_2$ molecules. The determination of these frequencies is based on a perturbation calculation [Buc68, Oxt79].

For completeness, we summarize the method of calculation. The energy of a vibrating molecule in a solvent (being either a liquid or a solid) can be expressed as the sum of
the intermolecular and intramolecular interactions. Both contributions are expandable in terms of the normal coordinate. The intramolecular interaction consists of a harmonic and anharmonic part. When taking the intermolecular interactions as well as the anharmonic part of the intramolecular interaction as perturbations to the energy levels of the harmonic oscillator, one can calculate the transitions between the perturbed energy levels. Consequently, the shift with respect to the (anharmonic) vibration of the molecule in the gas phase may be calculated, i.e. the shift that occurs as a result of the intermolecular interactions. For the transition of a diatomic molecule from the ground state to the first excited state, the result is that the shift in vibrational excitation frequency with respect to the non-rotating, isolated (gas phase) molecule is directly proportional to the axial forces, i.e. the forces along the bond axis due to all intermolecular interactions. A principally important ingredient is neglected in this calculation: upon excitation, a molecule changes its polarizability and therefore its intermolecular interaction with the surrounding medium (see e.g. Refs. [Mic95, Mic, Fra99] and references therein). By neglecting this contribution for fluid N₂, a blue shift will be calculated for all pressures, even where red shifts have been observed [Mic95]. Similar discrepancies are found for many other molecular systems [Fra99]. We are interested only in the differences in frequency for the three types of filling, and omitting this contribution will not change these differences essentially. Note that the distributions we present are static distributions. The line shape will be affected by the dynamics.

The frequency distributions are shown in Fig. 6.3 for a partial doubly occupied clathrate hydrate in an \((N, V, T)\) calculation with lattice constant 17 Å and \(T = 273\) K, while \(N_{s,s} = 128, N_{l,s} = 32\) and \(N_{l,d} = 64\). Results for the pure N₂ fluid are also shown for comparison. We find that, for the same volume, differences in filling fraction and temperature only have minor effects on the results. Moreover, there are no significant differences with \((N, p, T)\) results.

The N₂ guest molecules in the singly occupied large cages on average have the lowest frequency, with a maximum around 2330 cm\(^{-1}\) and a narrow peak. The guests in the small cages have the highest frequencies, with a maximum near 2335 cm\(^{-1}\), and a broad distribution. The latter is also the case for the guests in the doubly occupied cages, of which the distribution resembles that in the liquid. With a maximum around 2332.5 cm\(^{-1}\), these guest molecules have a frequency larger than in the singly filled large cages, but smaller than in the small cages.

### 6.3.3 Pressure-induced amorphous phase

As in many substances, by an extremely rapid cooling of the liquid water phase, a (low-density) amorphous (LDA) phase is obtained. In contrast, a high-density amorphous phase (HDA) was discovered by the compression of ice \(I_I\) below 150 K [Mis84]. The amorphous phase is recovered upon the release of pressure. By changes in \(p\) and \(T\) LDA–HDA transitions can be obtained [Mis85]. The transition between the metastable amorphous phases appears to be first order.

Similar transitions have been observed in both structure I and II clathrate hydrates [Han91]: in piston-cylinder experiments, a pressure-induced phase transition was found. Molecular dynamics calculations suggested [Han91] that the external pressure applied to
the clathrate hydrate is beyond the limit of mechanical stability: the open structure of the clathrate framework collapses around the guest molecules and forms an amorphous, high density phase. In the simulations, an empty lattice shows such a transition at much lower pressures than a fully (singly) occupied clathrate. The repulsive guest–host forces were found to be mainly responsible for the reversibility of the transition: a fully (singly) occupied clathrate hydrate reverts back to the original clathrate structure upon the release of pressure. Further experiments on clathrasils confirmed this [Tse94]. By compression and subsequent decompression of an empty clathrate, the host lattice remains amorphous, similar to the ice case.

Performing simulations of the compression of doubly occupied N$_2$ clathrates can provide simultaneously insight into the clathrate–amorphous transition and into the properties of the doubly occupied clathrate hydrates. Therefore, we have performed a series of $(N, p, T)$ calculations in which the N$_2$ clathrate hydrate is compressed at 80 K for two different fillings: complete single occupancy (case A, $N_{S,S} = 128$, $N_{L,S} = 64$, $N_{L,D} = 0$) and partly double occupancy (case B, $N_{S,S} = 128$, $N_{L,S} = 32$, $N_{L,D} = 64$).

Let us first focus on the results for complete single filling. Figure 6.4(a) shows that below roughly 2 GPa, the compressibility is constant. Between 2 and 4 GPa, there is a transition to a high density phase with a small densification, as the system shows a relatively abrupt compression. After the transition, the compressibility again is constant but it is smaller than at lower pressures: the clathrate is more readily compressed than the amorphous mixture. A plot of the O–O RDF (Fig. 6.5(a)) shows that the O–O distances slightly decrease as a function of pressure while all peaks but the first broaden to such
Figure 6.4: Properties of the pressurized simulation cell at 80 K. Open symbols represent the singly occupied clathrates (case A), closed symbols represent the partly doubly occupied clathrates (case B). The enlarged symbols (circles) are the results after releasing the 7 GPa pressure. For details about the simulation conditions, see text. (a) The average box dimensions versus pressure, the line represents the Kr results, Ref. [Han91]. (b) The system energy versus pressure.

an extent that they vanish. Since at these temperatures there is hardly any translational diffusion, we conclude that the structure has become amorphous. While the clathrate remains stable, there is only a small increase in energy (Fig. 6.4(b)) with increasing pressure up to 2 GPa. At the break-down of the host lattice, the decrease in volume corresponds with an increase in energy. The small and large energy change with increasing pressure are consistent with the large and small compressibility in the clathrate and amorphous phases, respectively. The box-angles (not shown) reveal that also in the amorphous phase the system remains cubic. After having released the pressure on the amorphous structure, the structure as well as the density are close to the results of the original zero pressure calculation: the amorphous phase transforms back to its original structure; the transition to the amorphous phase is reversible. However, not all of the damage done to the clathrate structure is repaired after releasing the pressure, as shown by the top and bottom curves in Fig. 6.5. In conclusion, the behavior is similar to that of the simulated Kr clathrate hydrate, as investigated by Handa et al. [Han91].

For all pressures, the simulation cell dimensions for case B are practically the same as for case A. In addition, the scatter of the points of the doubly occupied clathrate is of the same order of magnitude in both cases. This illustrates that also in this respect double occupation is quite possible. Figures 6.4 and 6.5(a) show that just as in the case of single occupancies the clathrate–amorphous transition occurs, and that it takes place
Figure 6.5: Several RDFs for the pressures (from bottom to top) 0, 2, 3, 5 and 7 GPa; the uppermost plot corresponds to the system after having released the 7 GPa pressure. (a) The O-O RDFs for case A (solid) and case B (dashed). The O-N₂ RDFs are shown for case B only: small cages (b), doubly occupied large cages (c) and singly occupied large cages (d).
Results

in about the same pressure range as that of a singly occupied clathrate. The volume in
the clathrate phase is the same for both systems, although the densification is smaller.

The O-O RDFs show a behavior very similar to that in the singly occupied case. However, there are two minor differences. First, a peak around 3 Å appears for higher
densities. This peak is higher in case A than in case B. Second, the peaks of the clathrate
phase, after depressurizing the amorphous phase, are higher for case B: the resemblance
with the original crystalline structure is better. Both differences are due to the smaller
amount of void space available in the doubly occupied clathrate hydrate. This is obvious
for the latter observation. A small peak near 3 Å was found for pressurized structure I
clathrates [Han91], and for ice Ih [Tse90]. For the ice case, its presence was found to be
consistent with the collapse of the hexagonal water framework, and a filling of the voids.
Less void space therefore leads to a smaller peak near 3 Å.

For the O-H and H-H RDFs, the differences between the results for single and double
occupation are similar to those for the O-O RDF.

Let us now focus on the O-N₂ RDFs of case B at various pressures. (Note that, for the
N₂ guest molecules in the small cages as well as in the (singly occupied) large cages, there
is hardly any difference between the O-N₂ RDFs of case A and case B.) As the pressure
increases, the shape of the O-N₂ RDF gradually changes for the doubly occupied cages
(Fig. 6.5(c)); the peaks broaden and shift to smaller distances. For the singly occupied
large cages (Fig. 6.5(d)), the situation is different. At pressures up to 2 GPa, there is also
a gradual decrease to smaller distances of the first peak position. However, between 2 and
3 GPa, the first peak jumps to relatively much smaller distances. Above 3 GPa, again a
gradual decrease follows. Roughly speaking, with respect to the behavior of the RDFs as a
function of pressure, three ranges can be distinguished. These ranges correspond with the
three ranges observed in Fig. 6.4. Also for the small cages (Fig. 6.5(b)), we can indicate
three ranges, which roughly correspond with those of the singly occupied large cages. The
branches also correspond with the presence and disappearance of all but the first peak in
the O-O RDF (Fig. 6.5(a)).

In the higher pressure region, the three RDFs increasingly resemble. Above 6 GPa,
there is essentially no difference. When the pressure is released at 7 GPa, the RDF of
the doubly occupied cages is quite similar to its original zero pressure shape. Again, the
situation is quite different for the other cages: the RDF is somewhat in-between that of
their original shape and that of the doubly occupied cages. This illustrates that the struc-
tural changes, caused by pressurization, are not completely eliminated after the release of
pressure. For the small cages and especially for the singly occupied large cages, the O-N₂
distance has decreased compared to the original zero pressure calculation. Together with
the remaining changes in the host structure, this is reflected in the differences in energy
and simulation cell shape as compared to the original zero pressure calculations.

In an attempt to make a connection with experimental results [vH93], we have also
compressed the clathrate at 273 K. We obtain results very similar to those at 80 K: the
clathrate hydrate becomes amorphous (or possibly liquid), the transition shifting to a
somewhat smaller pressure. This means that, in the higher pressure region, also at 273 K
the RDFs as well as the Raman vibrational frequency distributions of the guest molecules
for the three types of fillings become very similar, and that the distributions resemble
those in the liquid.
6.4 Discussion

6.4.1 Neutron diffraction pattern

Comparing the neutron diffraction pattern of the fully singly and partial doubly occupied clathrates, no new reflections appear when going from single to double occupancies, and none of the peaks is extinguished. Therefore, it seems cumbersome to follow the inverse route, i.e. to determine the existence of double occupancy from these neutron scattering spectra. However, this has been done [Kuh97]: in fitting the neutron diffraction data with crystallographic models, it was found that only the intensities are affected [Kuh]. Although not large, the differences were found to be significant [Kuh]. Our calculations are in agreement with this. Moreover, these intensity changes are present mainly for lower diffraction angles and they are of the order of 10 to 15\(^\circ\). Also, from x-ray diffraction experiments on type I methane clathrates, an indication of the cage occupancies as a function of pressure could be obtained by comparing the (dis)appearance of reflections in the experimental and theoretical diffraction spectrum [Hir00].

We have also calculated the diffraction patterns for three hypothetical cases. From Fig. 6.2(b), we conclude that the quality of the long range order is highest in the case of a filling of the small cages only. This was also concluded from the O–O RDF analysis presented in chapter 5. It is not surprising that the pattern of an empty host lattice resembles that of the case where only the large cages are filled in single occupation: the void space is very large in both cases, allowing for an increase in the available phase space for the molecules in the host lattice as compared to the other cases.

6.4.2 Pressure induced amorphous phase

Upon compressing either the singly or the partial doubly occupied clathrate at low temperatures results in the appearance of an amorphous phase. Previous MD results on the clathrate–amorphous transition [Han91], suggested that a more open structure would result in a sharper transformation at a lower pressure. Comparing our results for single and double occupation, we find that an increased filling indeed decreases the densification, making the transition less pronounced. However, within statistical uncertainty, the transition pressures are the same for both systems. From the large difference between the transition pressures of an empty host lattice and a fully (singly) occupied clathrate [Han91] one may predict that for doubly occupied clathrates, the transition to the amorphous phase is postponed to higher pressure. However, we find no difference in the transition-pressure range, nor with that of the Kr clathrate hydrates. In this respect, the partial double occupation does not affect the properties of the clathrate hydrate but an empty lattice does: the host lattice is hardly affected by the double occupancy.

Despite the similar pressure range, the jump in density is affected by the difference in occupancy. In the amorphous phase, the volume is obviously larger in the case of double occupation, as the volume scales with the number of molecules. In contrast, this volume effect is not reflected in the clathrates. The main consequence in the clathrate is a reduction of the void space, and we again note that the clathrate hardly notices the presence of double occupation. Figure 6.4(a) also illustrates that the pressure volume
behavior of the singly occupied Kr clathrate resembles that of the double rather than that of the single N$_2$ occupation. The same holds for the shape of the O–O RDFs. Moreover, for the Kr clathrate, the above mentioned peak around 3 Å is of about the same height as for the doubly occupied N$_2$ clathrates. These observations suggest that the void space in the Kr clathrates would be closer to that in the doubly rather than that in the singly occupied N$_2$ clathrates, and can be explained by differences in the potential models of the N$_2$–H$_2$O and the Kr–H$_2$O interaction. The compressibilities before and after the transitions are the same for the three above mentioned systems. This is obvious for the amorphous phase, as there is no void space anymore, and we simply have a mixture of molecules. For the clathrate phase, this is in agreement with our interpretation that the host is not affected by the double occupancy.

It is possible that the occupancy of the small cages plays the major role in the behaviour under pressure. The guests in the small cages provide support the host lattice to prevent it from collapsing, as was also suggested from previous results [Rod90, Ino96, Tan93b]. Possibly, the presence of guest molecules in the large cages, either in single or double occupancy, provide no substantial additional support. Then, properties such as the compressibility are determined by the rigidity of the host lattice plus the occupancy of the small cages.

In the high pressure amorphous mixture, the RDFs for the three ‘types’ of cages are similar. This is not a big surprise. On forehand, one would expect the amorphous system to be similar to the water mixture. We already showed that the O–N$_2$ RDF of the fluid mixture (see chapter 5) resembles that of the doubly occupied cages. Therefore, in an amorphous mixture, the differences between the three RDFs should disappear, and become similar to the one in water, and thus to the O–N$_2$ RDF of the doubly occupied cages.

The observation that the host lattice is hardly affected by the double occupation is an important conclusion, since it endorses that the doubly occupied clathrate hydrate is stable (chapter 5).

It is interesting to add some comments on the amorphization results. There is an ongoing debate about whether the pressure-induced amorphization is a one-phase melting (mechanical transition due to a collapse of the solid) or a conventional two-phase melting (thermodynamic transition) [Mis98, Tse99, Tse92]. HDA forms at a pressure close to the experimental melting curve of ice I$_h$. suggesting that HDA has a structure similar to that of the high-density liquid (HDL) as it should be its glassy manifestation. Thermodynamically connecting water and the amorphous ices by the extrapolation of the HDA–LDA coexistence line into the liquid region has led to the hypothesis that there might exist a second critical point for water and to the speculation that liquid water consists of a mixture of the HDA and LDA structures. However, experimentally a glass transition between HDL and HDA can not be observed directly [Mis98]. Moreover, the extrapolation of the LDA–HDA transition line to higher temperatures has been shown to be invalid [Wha89]. In addition, recent theoretical calculations suggested that the ice I$_h$–HDA transformation is not due to a thermodynamic melting process, but is the result of a mechanical instability [Tse99]. As a consequence, this proposal casts doubt on the assumption that HDA is connected with a liquid state, and therefore on the proposed two-structure liquid water model.
The nature of the clathrate–amorphous transition may also provide indirect hints on the existence of the two-structure model for liquid water. In this study, we find that although the compression is smaller in the case of (partly) doubly occupied large cages, the \( p-V \) curve, and in particular the transition pressure, is very similar for singly and doubly occupied large cages, and it is similar to the case of the MD results for Kr. Although the van der Waals diameter of Kr is about the same as that for \( \text{N}_2 \), the potential energy surface is more shallow for the latter. Thus, the interactions are different for Kr and for \( \text{N}_2 \) clathrate hydrates. Moreover, we have used atom–atom interactions for the \( \text{N}_2 \) molecules. Experimentally, the difference between the two guest molecules is reflected in the difference in the decomposition curves of the two different clathrates: the decomposition curve of the \( \text{N}_2 \) clathrate is shifted a few kbar (at least 50\%) above the decomposition line of Kr. Since for the clathrate–amorphous transition the pressure is about the same for the three cases this indicates that the details of the guest–host interaction are hardly important for that transition. This suggests that the instability of the clathrate upon compression is due to a collapse of the host framework, which would support the suggestion that the transition is due to mechanical instabilities. On the other hand, the interactions do influence the densification.

In an attempt to compare our results with those found experimentally at 273 K, we have compressed the \( \text{N}_2 \) clathrate hydrate at this temperature. The results are very similar to those at 80 K have been obtained, and the structures resemble those in the mixed liquid. For ice, the hydrogen bonding interactions have been found to differ significantly for the cases of HDA ice, LDA ice and rapid-cooled water [Klu99]. There may also be small but significant differences between the structures of the compressed clathrates at low and high temperatures, and the liquid mixture. Such differences are probably too subtle to be found in the simulations.

### 6.4.3 Raman frequencies

This compression of the clathrate at 273 K has been performed for comparison with experimental results [vH93]. However, a splitting of a Raman peak, as has been experimentally detected at 0.85 GPa [vH93] has not been found. It has been found recently that the compression of the structure I methane hydrate up to 10 GPa shows to two structural phase transitions [Lov01]. One of the transitions occurs near 1.1 GPa. This may suggest that the observed splitting of the vibron peak near 0.85 GPa for structure II nitrogen is related to a similar structural transition. We do not find such a transition in the simulations. This is not surprising as most crystal-crystal transitions are suppressed due to the small simulation cell. Also, for our simulations, the occupancies can not fluctuate spontaneously upon compression.

In the clathrate we find that the molecules in the doubly occupied large cages have an average frequency larger than for single fillings, but smaller than in the small cages. This is an unexpected result, since the RDFs (discussed below and in chapter 5) illustrate that the \( \text{N}_2-O \) distances are smallest for the doubly occupied clathrate. Consequently, one might expect that the mutual average \( \text{N}_2-H_2O \) forces are highest in the last case, thus leading to higher frequencies. To have an intuitive understanding of these results, we distinguished [Koo99a] two contributions to the \( \text{N}_2-H_2O \) RDF, depending on the
Figure 6.6: The parallel (solid) and perpendicular (dashed) contributions to the $N_2$-$O$ radial distribution function (for explanation and simulation conditions, see text) for the large cages in double occupation (a), large cages in single occupation (b) and small cages (in single occupation, c). Note the different vertical scale in panel (c).

A position of the O atom with respect to the $N_2$ bond axis. If the vector connecting the center of mass of a $N_2$ molecule and an O atom makes an angle of less than 60° with the $N_2$ bond axis, it contributes to the 'parallel RDF', otherwise to the 'perpendicular RDF'. The results are shown in Fig. 6.6. The differences between the perpendicular and parallel RDF are small in the small cages and the singly occupied large cages. Still, for the smallest intermolecular $N_2$-$O$ distances, it is more probable that the molecules are in a perpendicular configuration, as expected. For the doubly occupied cages, the differences between the two contributions are much larger. By the mutual repulsion between the two $N_2$ guest molecules, they push each other against the wall of the cage, their bond axes being roughly tangential to the cage wall. The results suggest that the O-bonded configuration (explained in chapter 5) occurs most frequently at short intermolecular distances.

Now let us try to explain the calculated Raman frequencies in terms of these RDFs. At small intermolecular distances, the water molecules that contribute to the parallel O-
N\textsubscript{2} RDF would lead to a compression of the N\textsubscript{2} bond length, resulting in an increase in frequency. Likewise, water molecules contributing to the perpendicular RDF would lead to a stretch of the N\textsubscript{2} bond axis, resulting in a decrease in frequency.

Comparing the contributions to the RDFs for the small cages and the doubly occupied large cages, one sees that the onset as well as the first peak position of the parallel contributions occur at about the same distance. If only these contributions would be present, the bond-compressing forces would increase the vibrational frequency to about the same amount for both cages. However, the onset and first peak position of the perpendicular contributions to the RDFs occur at much smaller distances for case III. This suggests that the bond-stretching forces, that lower the frequency, are larger in that case. Therefore, the negative contributions to the frequency shift are larger for the guests in these cages, whereas the positive contributions are the same for both cages. Hence, the average frequency is smaller in the case of the doubly occupied large cages.

The peak positions of the first peak of both the parallel and perpendicular contribution for the singly occupied large cage are at relatively large distances compared to the other two cases; then, on average the N\textsubscript{2}-H\textsubscript{2}O interaction is attractive. The parallel forces are bond-stretching, while the perpendicular forces are bond-compressing. Also, at larger intermolecular distances, both contributions are relatively small. In addition, the axial component of the perpendicular contributions will be smaller at relatively large distances. This is not the case for the parallel contributions. The result is that the N\textsubscript{2} molecules in the singly occupied large cages have the lowest frequencies.

From a similar RDF-analysis, we find for case III that the neighboring N\textsubscript{2} molecule only has contributions to the perpendicular (N\textsubscript{2}) N\textsubscript{2} RDF. This also contributes to a frequency lowering.

Since the average frequencies are separated by a few wavenumbers, according to our calculations Raman spectroscopy should be a much better tool to detect double occupation than neutron diffraction. However, Kuhns et al. [Kuh97] found that for instance at 2 kbar, about 20\% of the large cages are doubly occupied. Thus, in this relatively low pressure region a new Raman peak should be observable, which has not been found in experiments [vH93]. On the other hand, it is possible that the spectrum of the pure N\textsubscript{2} fluid overlaps with that in the doubly occupied clathrate, similar to what we find in the simulations.

In a Raman spectroscopic investigation of structure I CH\textsubscript{4} clathrate hydrates, it was found that the band corresponding with the $\nu_1$ symmetric stretch in the clathrate shifts to lower frequencies with respect to the coexisting fluid [Sum97]. Based on the intensities of the peaks, the authors concluded that the frequency is smaller for the molecules in the large cages than for the molecules in the small cages. This is in qualitative agreement with our simulation results: the N\textsubscript{2} molecules in the large cages have a smaller frequency than those in the small cages. It is, however, not trivial to quantitatively compare the two different cases, especially when comparing the shifts with respect to the Raman frequency in the fluid phase. In principle, one may argue that the positions of the peaks are the result of differences in local density in the fluid or clathrate cages. However, it is important to note what is generally observed in Raman spectroscopic measurements of molecular fluids: at moderately low pressures, the frequencies show a red shift with respect to the gas phase value. After reaching a minimum frequency, at larger pressures a blue shift occurs, which
continues to extremely high pressures [Clo88]. This means that there is always a non-zero pressure at which the vibrational frequency equals the gas phase value. This complicates the interpretation of the density effect on the spectra in the clathrate cavities.

6.5 Conclusions

We have performed molecular dynamics calculations of structure II clathrate hydrates with varying N\textsubscript{2} cage occupancies and at different state conditions. Comparing the results for single and partial double occupancies at conditions close to those in experiments, we find small (10 to 15\%) differences in intensities for the neutron diffraction pattern, in agreement with experimental findings.

A marked difference for the three types of fillings is, however, found in the calculated Raman spectra. The N\textsubscript{2} molecules in the small cages have the highest frequency, those in the singly occupied large cages have the smallest frequency. The N\textsubscript{2} molecules in the doubly occupied large cages roughly have a vibrational frequency between the other two, this frequency being close to that in the fluid at roughly the same conditions. The results have been explained by investigating separately the RDFs of the O atoms perpendicular and parallel to the N\textsubscript{2} bond axis. It is demonstrated that the position of the water molecules with respect to the N\textsubscript{2} bond axis is important.

For low temperatures, by applying large pressures (up to 7 GPa) on the doubly occupied N\textsubscript{2} clathrate, the system transforms to an amorphous phase and it transforms back to the clathrate structure as the pressure is released. The clathrate–amorphous transition occurs roughly at the same pressure as for a singly occupied N\textsubscript{2} clathrate, but the densification is larger for the latter. The differences in behavior upon pressurization can be explained in terms of the smaller amount of void space present in the doubly occupied clathrate. The fact that the transition pressure is roughly the same suggests that the host lattice is hardly influenced by the presence of double occupancy and therefore endorses the results that a doubly occupied N\textsubscript{2} clathrate is stable. The results are very similar to the simulation results of the pressure induced amorphization of a Kr clathrate hydrate [Han91].