Computer simulations of nitrogen-containing molecular systems at very high density
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Orientational and Structural Properties of \( \text{N}_2 \) and \( \text{N}_2-\text{Ar} \) at High Pressure

4.1 Introduction

In many studies the mixed solid \( \text{N}_2-\text{Ar} \) is used as a model system for investigating the influence of isotropic impurities on the various solid phases of anisotropic molecules. Despite the simplicity of the molecular species, the many body effects complicate the physics in these mixtures notably. Moreover, considerable effort is needed to model the \( \text{N}_2-\text{N}_2 \) interactions in such a way that an acceptable agreement with experiments is obtained [Mul97a].

At both low and high pressures, the Ar atoms dissolve substitutionally in the \( \text{N}_2 \) lattice [Bar65, Kle90, Wes96a, Koo98]. Various interesting experimental results have been obtained at low pressures, such as quadrupolar glasses (see e.g. Refs. [Ham95, Hoc90] and references therein), and a number of simulations were reported [Kle88, Rau97].

The high pressure phases of pure \( \text{N}_2 \) are rather complex [Man97]. Therefore a study of the mixed solid \( \text{N}_2-\text{Ar} \) at higher pressures is expected to be even more interesting. Such interesting features have been found in experiments [Wes96a, Koo98]. In pure \( \text{N}_2 \) at high pressure, the low temperature \( \varepsilon \) phase is orientationally ordered, and the crystal has a trigonal (rhombohedral) lattice structure, space group \( \text{R}3\text{c} \). The high temperature \( \delta \) phase is a plastic crystal with space group \( \text{P}m\text{3}n \). The cubic unit cell consists of eight lattice sites. The molecules at the centers and the corners of the cell, the \( a \) sites, exhibit nearly complete orientational disorder, and hence are called ‘spheres’. The molecules in the faces of the unit cell, the \( c \) sites, exhibit orientational disorder in a plane normal to these faces. Since these molecules behave as planar rotors, they are referred to as ‘disks’. We will make a distinction between the \( c \) sites in the three different faces of the unit cell, and therefore speak of three different ‘types’ of disks.

In pure \( \delta \) \( \text{N}_2 \), an anomalous break in the slope of the vibrational Raman shift as a function of temperature has been detected experimentally [Sch93], which was interpreted as a second order phase transition. Monte Carlo (MC) calculations, explained this change in vibrational frequency of the sphere molecules as being due to the change in orientational behavior of the disk molecules [Mul98]. At the transition, an orientationally more localized phase \( \delta_{\text{loc}} \) transforms into the \( \delta_{\text{rot}} \) phase, with more or less complete disorder. In contrast,
model calculations suggest an increase in orientational degrees of freedom of the molecules at the a sites [Wes96a].

The first experimental results obtained in the high pressure region for $N_2$–Ar mixtures were obtained with a Raman investigation at room temperature [Wes96a]. The results indicate that the Ar atoms are positioned at the sphere-like disordered a sites, which is supported by model calculations [Wes96a]. The $e^*$ phase was not found (a ‘*’ denotes the mixed phase). In Ref. [Koo98] it was concluded that the preference for the a sites is temperature and pressure dependent. Moreover, a transition similar to the second order transition in pure $N_2$ was found in the mixed solid for Ar mole fractions $x < 0.25$, with a transition temperature independent of $x$ within the experimental accuracy [Koo98]. Recently, the break in the Raman slope in pure $N_2$ is believed to be due to a weak first order transition [Han97]. Upon the transition, the space group changes from $Pm3n$ to $P4_{2}2_{1}2_{1}$. Preliminary results of the calculations of the $N_2$–Ar mixture at high pressure have been reported [vK98]. The simulations show that the Ar atoms have an enthalpic preference for the a sites. The $e^*$–$\delta^*$ transition was found to shift to lower temperature. In chapter 3, we presented the calculated phase diagram for compositions up to $x = 0.25$, with the temperature $T \geq 50$ K. There, we investigated the influence of the Ar atoms on the phase behavior and the shift of the vibron frequency. The simulation results showed that the effect of substituting Ar atoms in the $N_2$ lattice has a threefold influence on the phase transitions in the mixture. First, the $e^*$–$\delta^*$ transition shifts rapidly to lower temperatures with increasing $x$. The $e^*$ phase has vanished for $x \geq 0.05$. Second, as in pure $N_2$, the $\delta^*_{\text{loc}}$ and $\delta^*_{\text{rot}}$ phases were observed in the mixture. The onset as well as the completion of the cascade process that corresponds to the $\delta^*_{\text{loc}}$–$\delta^*_{\text{rot}}$ transition in pure $N_2$ is independent of composition. Third, for $0.12 \leq x \leq 0.25$ and low temperatures, a cubic phase appears which exhibits more orientational order for the disk molecules than in the $\delta^*_{\text{loc}}$ phase. Neglecting the orientational disorder of the spheres, this phase is labeled an orientationally ordered $\delta^*$ phase, $\delta^*_{\text{oo}}$. The transition from this phase to the $\delta^*_{\text{loc}}$ and the $\delta^*_{\text{rot}}$ phases shifts to higher temperatures with increasing $x$.

The vibron frequency behavior of the sphere molecules of the $\delta^*_{\text{oo}}$–$\delta^*_{\text{rot}}$ transition is very similar to that of the $\delta^*_{\text{loc}}$–$\delta^*_{\text{rot}}$ transition. However, the temperature range in which the decrease of the sphere frequencies takes place is much smaller in the first case. The simulations predict an asymmetry on the high frequency side, probably due to a tetragonal modification of the $\delta^*_{\text{loc}}$ phase. Both Refs. [Wes96a] and [Koo98] report an asymmetry on the high frequency side of the disk peak.

In this chapter, we will focus on the correlation between the orientational behavior and the lattice positions of the molecules. As in Ref. [vK99a], the results have been obtained at a pressure of 7 GPa and $T \geq 50$ K.

### 4.2 Method and potential model

The Monte Carlo calculations have been performed in the constant stress $(N, p, T)$ ensemble [Par80, Par81], with periodic boundary conditions. The total number of molecules was 512. One MC cycle consists of trial moves in position and orientation of the molecules,
and a trial move in the dimensions and angles of the simulation cell. In the constant-stress technique used, a symmetric transformation matrix $h_{a3}$ maps the molecules from a scaled cubic simulation cell to the (in general) triclinic simulation cell. In the simulations, consisting of runs in the order of $10^4$ MC cycles, an acceptance of 50% is maintained. Occasionally, e.g. near phase transitions, longer runs are performed.

Since in the experiments as well as in the simulations [Koo98, vK98, Wes96a] the Ar atoms turned out to prefer the a sites, the Ar atoms are distributed statistically over the a sites in all simulations. Both heating and cooling runs are performed for all compositions. For the initial configuration at $T + \Delta T$, the final configuration of a run at $T$ was taken. The structure of the $\varepsilon^*$ phase was taken as the primary configuration in all runs. However, at high temperatures, the $\varepsilon^*$ structure immediately transformed to the $\delta_{rot}$ structure for all values of $x$ investigated.

The basis for the N$_2$–N$_2$ interaction was the Etters site–site potential [Ett86]. A correction accounted for the fact that the site–site interaction is anisotropic [Mul98]. The Ar–Ar and the Ar–N ‘atom’ interaction were modeled by Buckingham potentials, for which the used parameters are given in Ref. [vK99a]. A linear quadrupole represented the Coulomb interaction between the N$_2$ molecules. A cutoff range for the potentials was taken at 9 Å.

To allow for a good comparison with the results in pure N$_2$, the same orientational order parameters were calculated as used in Ref. [Mul98], see Table 4.1. The definitions of the angles are as follows: for the three disk types, situated in the faces of the unit cell, $\theta = 90^\circ$ is the plane normal to the particular face of the unit cell. For $\theta = 90^\circ$ and $\phi = 0^\circ$, the molecular principle axis is normal to the faces of the unit cell. In addition, the local orientational correlation of the N$_2$ molecules was investigated. For this purpose, we calculated the second order Legendre polynomial of the dot product of the orientations of the nearest neighbors. A distinction was made between the orientational correlations of the different types of molecules. The order parameters are given in Table 4.2.

<table>
<thead>
<tr>
<th>$O_{0}^c$</th>
<th>$\cos(4(\phi - 45^\circ))$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_{0}^e$</td>
<td>$\cos(\sqrt{3}\pi \cos(\theta - \frac{1}{3} \sqrt{3})$</td>
</tr>
<tr>
<td>$O_{0}^p$</td>
<td>$\cos(4\phi)$</td>
</tr>
<tr>
<td>$O_{0}^d$</td>
<td>$\cos(\pi \cos(\theta))$</td>
</tr>
</tbody>
</table>

Table 4.1: The order parameters used to quantify the orientational behavior of the molecules. The first two measure the orientational preference of the spheres for the unit cell diagonals. The third measures the preference for $\phi = 0$ and $90^\circ$ for the disks. The fourth measures the degree of confinement to planar rotation of the N$_2$ molecules on the c sites.
The properties of high-pressure $N_2$ and $N_2$–Ar

<table>
<thead>
<tr>
<th>order parameter</th>
<th>type of molecules</th>
<th># nearest neighbors</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mathcal{O}_{SS}$</td>
<td>S:S</td>
<td>8</td>
</tr>
<tr>
<td>$\mathcal{O}_{SD}$</td>
<td>S:D</td>
<td>4</td>
</tr>
<tr>
<td>$\mathcal{O}_{D_D}^D$</td>
<td>D$_i$D$_i$ (coplanar)</td>
<td>2</td>
</tr>
<tr>
<td>$\mathcal{O}_{D_D}^F$</td>
<td>D$_i$D$_j$ (non-coplanar)</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 4.2: The order parameters probing the local orientational correlation and their meaning. $D$ and $S$ denote the molecules at the $c$ (disk) and $a$ (sphere) sites respectively. An index refers to one of the three types of disks. For all correlations, $\mathcal{O} = \langle P_2(\cos(\theta_{nm})) \rangle = \frac{3}{2}(\cos^2(\theta_{nm})) - \frac{1}{2}$, where $\theta_{nm}$ is the angle between molecules $n$ and $m$. The brackets denote statistical averages (i.e. also over combinations $nm$).

real distances with the transformation matrix $h_{\alpha,\beta}$. A correction was applied for the shift of the center of mass of the complete system.

### 4.3 Results

For low temperature and $0 \leq x \leq 0.05$, the $\varepsilon^*$ phase remains stable. With respect to the trigonal (rhombohedral) reference frame, the threefold symmetry axis of the $R3c$ space group is preserved with a displacement $\Delta$ of the molecular centers of mass to the position $(\Delta, \frac{1}{4}, \frac{1}{2} - \Delta)$, and likewise for the other 6e sites. All simulations started with the 6e sites at coordinates with $\Delta = 0$, but at 7 GPa the equilibrium value for $\Delta$ is 0.05 Å, in pure $N_2$ as well as in the mixture.

In contrast with pure $N_2$, in the mixture the orientational distribution functions (ODF) of all disk molecules in the $\delta^*_{\alpha\beta}$ phase exhibit a slight preference for $\phi = 0$ and 90°, while the distributions are more or less uniform for the pure solid [Mull98]. This is demonstrated by $\mathcal{O}_{D}^\phi$. At 220 K this order parameter increases from about 0.04 to 0.13 when $x$ increases from 0 to 0.22. The gradual increase indicates that within the $\delta^*_{\alpha\beta}$ phase, the preference for the aforementioned angles indeed increases with $x$, even at high temperature. As can be expected, a sudden jump (to $\mathcal{O}_{D}^\phi = 0.30$) occurs at even larger $x$, since the $\delta^*_{\alpha\beta}$ phase becomes manifest at these mole fractions [vK99a]. A less pronounced increase is present in $\mathcal{O}_{D}^\theta$ as a function of $x$. The values are around 0.7, and have a small positive slope in the $\delta^*_{\alpha\beta}$ as well as in the $\delta^*_{\alpha\beta}$ phase as a function of $x$. The slope is larger in the $\delta^*_{\alpha\beta}$ region. This indicates that the orientational confinement to a plane of the $\delta^*_{\alpha\beta}$-$N_2$ molecules at the $c$ sites also increases as a function of $x$.

In the (tetragonal deformed) $\delta^*_{\alpha\beta}$ phase, two disk types show relatively large orientational disorder, while one disk type shows a pronounced preference for $\phi = 0$ and 90°. The latter disk molecules will be referred to as the orientationally ordered disks in the $\delta^*_{\alpha\beta}$ phase. These orientationally ordered disk molecules in the $\delta^*_{\alpha\beta}$ phase show a much larger value of $\mathcal{O}_{D}^\phi$ (Fig. 4.1). At the $\delta^*_{\alpha\beta}$-$\delta^*_{\alpha\beta}$ transition, the value of $\mathcal{O}_{D}^\phi$ for these disk molecules shows a slight jump to higher values, which implies that the orientational order for these specific molecules is larger than in the low temperature $\delta^*_{\alpha\beta}$ phase. Thus, indeed there is a
Figure 4.1: $\Omega_D^\phi$ as a function of $T$ in heating runs for the disk molecules. Open symbols correspond with the three different disks at $x = 0.16$ ($\delta_{\phi o}$, $\delta_{\phi c}$ and $\delta_{\phi r}$ phases upon increasing the temperature, respectively). The disk molecules with the highest value in the $\delta_{\phi c}$ phase show 1. a jump to higher values upon entering this phase ($T \approx 110$ K), and 2. a rapid decrease to lower values, which corresponds with the $\delta_{\phi c}^{\phi} - \delta_{\phi r}^{\phi}$ transition in pure $N_2$ ($T \approx 180$ K). Closed symbols correspond with $x = 0.23$ in the $\delta_{\phi o}^{\phi}$ and $\delta_{\phi r}^{\phi}$ phases (they are denoted by one symbol since the three values are the same). A sharp decrease occurs at $T \approx 230$ K. The errors are smaller than the symbol size.

strong orientational localization of these disk molecules in the $\delta_{\phi c}$ phase. The other two disk types, however, show only a very small orientational localization compared to the $\delta_{\phi o}$ phase, as reflected by their values of $\Omega_D^\phi$. In the simulations of pure $N_2$, the value of $\Omega_D^\phi$ of the orientationally ordered disk molecules in the $\delta_{\phi c}$ phase shows a rapid decrease as a function of temperature between 170 and 180 K [Mul98]. The temperature at which this decrease occurs in pure $N_2$ was identified as the $\delta_{\phi c}^{\phi} - \delta_{\phi r}^{\phi}$ transition temperature. In the mixture this effect is less clear, as shown in Fig. 4.1. For the mixtures in which the jump could be observed, all three values for $\Omega_D^\phi$ of the disk types become equal at about 20 K above the $\delta_{\phi c}^{\phi} - \delta_{\phi r}^{\phi}$ transition, as in pure $N_2$. Since this latter behavior was clearly observed for all mixtures, we identified the transition temperature with the temperature at which these three values become equal.

The behavior of $\Omega_D^\phi$ for the orientationally ordered disk type in the $\delta_{\phi c}$ phase ($x = 0.16$) and the three ordered disk types in the $\delta_{\phi o}$ phase ($x = 0.23$) show a similar behavior (Fig. 4.1). However, the decrease in $\Omega_D^\phi$ occurs in a much smaller temperature range for $x = 0.23$. Moreover, the orientational correlations behave quite different for the ordered disk type in the $\delta_{\phi c}$ phase than for the three ordered disk types in the $\delta_{\phi o}$ phase, Fig. 4.2. In the $\delta_{\phi c}$ phase, the ordered disks have a smaller value for $\Omega_D^\phi$ (-0.15) than the disk types with larger orientational freedom (0.2). At the transition to the $\delta_{\phi o}^{\phi}$ phase, all three values jump to 0.55. Consequently, the alignment for the coplanar disks in the $\delta_{\phi o}$ phase
The orientational correlation parameter $O_{D,D}^\infty$ as a function of $x$ at a temperature of 170 K, for the sphere (□) and the disk (○, △, and ◊) molecules. For $x \leq 0.18$, the $\delta_{loc}$ phase is present, for $x \geq 0.18$ the $\delta_{oo}$ phase.

is much larger than in the $\delta_{loc}$ phase. At high $x$, the degree of alignment increases with increasing $x$.

When plotting $O_{S,S}$ as a function of $x$, its value remains constant in the $\varepsilon^*$ phase ($\simeq 0.8$) and in the $\delta_{loc}^*$ phase ($\simeq 0$). In the region where the $\delta_{oo}^*$ phase sets in, $O_{S,S}$ decreases to $-0.25$. Whereas the order parameters imply a large degree of orientational freedom, the sphere molecules have a preferential orientation relative to the other sphere molecules: the axes of the neighboring sphere molecules tend to be perpendicular. In addition to the changes in orientational behavior, there are changes in the equilibrium center of mass positions of the molecules. Furthermore, there is a correlation between these displacements and the orientational distributions of the various types of molecules. In the $\delta_{loc}^*$ phase, the $N_2$ molecules at the $c$ sites behave as planar rotors in a plane perpendicular to the faces of the unit cell. Equivalently, these planes are perpendicular to the lines of closest intermolecular contact. The orientationally ordered disk molecules, which have the largest value for $O_D^\varepsilon$ and the smallest value for $O_D^\infty$, are displaced along these lines over a distance of 0.15 Å, Fig. 4.3(a). A parallel neighboring line is displaced in the same direction over a distance of $-0.15$ Å. The third and fourth row behave as the first and second, respectively. This means that the orientationally ordered disk molecules in the $\delta_{loc}^*$ phase do not remain at the $c$ sites of the $Pm3n$ lattice. For the disk types exhibiting larger orientational freedom, no displacement was measured. With these displacements, the cubic unit cell contains 64 molecules in the $\delta_{loc}^*$ phase. The average nearest neighbor distance remains the same for all three disk types and the average displacements of these disk types remains zero. The appearance of a tetragonal modification[vK99a] of the $\delta_{loc}^*$ phase, found for $0.12 \leq x \leq 0.19$, has no influence on the behavior of the displacements and orientations. However, there is a correlation between the order parameters of the disk
Results

Figure 4.3: Schematic views of the displacements in the $\delta_{\text{oc}}$ phase (a) and the $\delta_{\text{oo}}$ phase (b,c). (a) shows the disk molecules in four unit cells in the $\delta_{\text{oc}}$ phase. In the plane of the paper and perpendicular to the paper, a disk is indicated by a line and a circle, respectively. The solid lines denote the 6c positions of the disk molecules, while the dashed lines give the position of the displaced disk molecules (not to scale). The sphere molecules have been omitted for clarity. (b) shows the directions of displacements of the sphere molecules in the $\delta_{\text{oo}}$ phase, denoted by dots. All molecules along the direction parallel to diagonal A that cross the points a are displaced in this direction parallel to diagonal A. Similarly, all molecules along the direction parallel to diagonal B that cross the points b are displaced in this direction parallel to diagonal B, and likewise for the other sphere molecules. These displacements are present for the N$_2$ as well as the Ar molecules. The disk molecules have been omitted for clarity. In (c), the arrows indicate the direction of the displacements of the disk molecules along the line of closest intermolecular contact in the $\delta_{\text{oo}}$ phase. A helical structure arises with a wavelength of four molecules.

molecules, and the direction of the c-axis: this axis is perpendicular to the disk plane of the orientationally ordered disk molecules. That is, the c-axis is parallel to the line of closest intermolecular contact for the displaced disk molecules.

In the $\delta_{\text{oo}}$ phase, the displacements are such, that a complicated structure arises. For the molecules at the a sites, which are mainly Ar atoms, all molecules connected by a line parallel to a body diagonal have an equal displacement along this line. Thus, the displacements are in the (111) directions, and the displacements are the same for the molecules along the (111) directions, see Fig. 4.3(b). The magnitude of the displacements along the diagonal is about 0.3 Å. The disk molecules only show an in-plane displacement of about 0.1 Å. The displacements are such that for these disks, along the line of closest intermolecular contact, a helical structure arises with a wavelength of four molecules, Fig. 4.3(c). Also for the $\delta_{\text{oo}}$ phase, the cubic unit cell contains 64 molecules. Again, the average displacement of the molecules at both the a sites and the c sites is zero.

In the $\delta_{\text{rot}}$ phase, no displacements have been found. The molecules remain at the 2a and 6c sites of the $Pm\bar{3}n$ space group.
4.4 Conclusions

The value of $\Delta = 0.05$ Å, found for the displacements of the molecules at the 6e sites of the $\varepsilon^*$ phase, is in agreement with the MC results of Etters et al. [Ett86], who performed zero-temperature calculations. However, a large difference with that work is that in their calculations only trial moves in $\Delta$ were performed, while we performed more realistic trial moves in all directions and for all molecules, independently.

The break of the symmetry in the orientational disorder of the disk molecules in the $\delta_{loc}^*$ phase is accompanied by a similar symmetry break in the positions of these molecules. In the $\delta_{loc}^*$ phase, the orientationally ordered disk molecules do not remain at the $c$ sites of the $Pm\bar{3}n$ structure. The displacements are $0.15$ Å along the line of closest intermolecular contact. The disk molecules in parallel neighboring lines have an equal but opposite shift. We did not verify whether this structure still has space group $Pm\bar{3}n$. The behavior is similar in pure $N_2$ as well as in the tetragonal modification of the $\delta_{loc}^*$ phase, for which $c/a > 1$. The $c$ axis of the tetragonal phase is always perpendicular to the orientationally ordered and displaced disks. Also, the space group of the tetragonal modification in the mixed solid was not determined. The experimentally found tetragonal phase in pure $N_2$ [Han98], with $c/a < 1$, has space group $P4_2/nmc$.

Also in the $\delta_{\infty}^*$ phase, the orientational order of the disk molecules is accompanied by a change in all molecular positions. The molecules at the $a$ sites are displaced over $0.3$ Å in the $\langle 111 \rangle$ directions, for all molecules along that direction. The three disks types show an in-plane displacement of $0.1$ Å. These displacements are such that, along the line of closest intermolecular contact, a helical structure arises with a wavelength of four molecules. Again, we did not verify whether such an arrangement has $Pm\bar{3}n$ space group symmetry, or belongs to another space group. Such space group analyses have to be performed in order to make contact with crystallographic experiments.

The order parameters used are appropriate tools to determine the phase transitions and to understand the orientational behavior in the mixture. Despite the large similarity of the orientational distributions, the orientationally ordered disk molecules in the $\delta_{loc}^*$ phase have a much smaller degree of alignment than the disk molecules in the $\delta_{\infty}^*$ phase. In that phase, the orientations of the nearest neighbor sphere molecules tend to be perpendicular. At the $\delta_{\infty}^*$--$\delta_{\infty}^{rot}$ transition, the order parameters show a sharp decrease, despite the fact that the distributions and preferential angles are similar in both phases for all three disk types. Small structural changes are present between the three $\delta^*$ phases found.