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

1.1 Pressure: how to obtain a high-temperature solid of weakly interacting molecules

In everyday life, a large number of substances appear in the solid state. The plastic keyboard on which this thesis is written, or a metal hammer with which a computer can be smashed in case of frustration, are both made of solid material. As a common-or-garden definition of solids, one may speak of ‘those substances that can be transported without containers’. However, although both hammer and keyboard are solid materials, there are significant differences between metals and plastics. Usually, solid metals contain long range order, whereas solid plastics do not: solid metals belong to the class of solids that are crystalline. The nature of the crystallinity of a substance may, however, also need further specification. For instance, liquid crystals are crystalline in the sense that the long range orientational order of the building blocks (the molecules) is preserved, while there is only short range positional order. On the other hand, plastic crystals have long range positional order, but the orientations of the building blocks are disordered. The solid phases discussed in this thesis all involve a plastic crystal type, in the sense that they all have (partly) orientational disorder.

For mixtures, the situation becomes more complicated. For instance, molecules of a substance B may dissolve in the crystal lattice of substance A. In such a solid solution, the B molecules may either be located between the A lattice sites, i.e. dissolve interstitially, or the B molecules may occupy A lattice sites, i.e. dissolve substitutionally. In particular for the latter case, the underlying lattice still exhibits positional long range order, but this does not mean that it is a priori known whether a crystalline position contains molecule A or B. For instance, A and B may form a pattern (a superlattice) or the molecules may be completely randomly distributed over the lattice sites. If it is possible to change the composition of the mixture without altering the crystal structure, such a random distribution directly leads to an increase in configurational disorder. Of course, it is also possible that the two molecular species do not mix at all; in that case, phase separation occurs. Finally, the mixed solid may form a new structure that is not present in either of the pure substances A or B. Such a crystal is called a compound. In most cases, the composition of such a compound is fixed and determined by the intermolecular
interactions.

The properties of a (mixed) solid, e.g. whether they are plastic crystals or not, or whether there is configurational disorder or not, are determined by the interactions between the atoms or molecules that constitute the solid. Therefore, crystals can be characterized by the type of interaction of its constituting building blocks. Roughly, the interactions can be divided into four categories, although the boundaries between them are not strict. These categories are: metallic crystals, covalent crystals, ionic crystals and van der Waals crystals. Moreover, in mixed crystals, there is a competition between the strength of the unlike forces and the communal entropy. In van der Waals crystals, or molecular crystals, the bond between the molecules results from the van der Waals interaction. This is a very weak interaction compared to those of the other crystal types. As a result, the melting point of many molecular crystals is very low: the intermolecular bond is too weak to preserve the crystal at room temperatures and ambient pressures. However, the molecular crystalline state can be produced at room temperature by applying pressure, or, in an alternative view, increasing the density. When the pressure becomes high enough, crystallization occurs due to the reduction of the degrees of freedom. The solids studied in this work indeed are molecular solids. For example, let us consider the substance that plays the main role in all chapters of this thesis: nitrogen.

1.2 The role of nitrogen

Nitrogen molecules mainly interact via the van der Waals interaction, resulting in a melting temperature as low as 63 K at ambient pressure [Man97]. However, the solid state can be obtained at room temperature by pressurizing up to about 2.1 GPa (24,000 bar). Although nitrogen molecules consist of only two atoms (it is diatomic), and are chemically inert (due to the strong intramolecular bond) the pressure–temperature phase diagram of these molecules is very rich: up to 20 GPa, it consists of five recognized crystalline phases [Man97]. For all pressures there is a temperature range in which a plastic crystal phase occurs.

It is expected that at extremely high pressures only the repulsive forces play a role; in first approximation, monoatomic molecules (such as argon) behave much as hard spheres at very high pressures. Thus, in principle, high pressure studies of monoatomic van der Waals systems may be performed to obtain fundamental insight into solid mixtures [Sch99]. Complications related to the nonsphericity (i.e. non-isotropic interactions) of the molecules are then avoided.

However, from an experimental point of view, much more information about for instance the phase behaviour may be obtained if polyatomic molecules are used, as (Raman) spectroscopic methods can be applied. Then, the excitation of the intramolecular modes provides information of a molecule’s surroundings: Raman spectroscopy acts as a probe for the molecular environment. For example, for the same mode, a different intramolecular vibrational frequency will be measured in a fluid or solid phase, even at the same density. Alternatively, a change in vibrational frequency may be an indication for a phase transition. Thus, by using a slightly more complex molecule instead of a monoatomic one, it is possible to obtain (additional) information on the phase behaviour of substances if the
molecule is Raman active. On the other hand, one should try to keep matters as simple as possible, and only the smallest departure from monoatomics should be made. Diatomics are the obvious alternative, and the choice for nitrogen is based on the above-mentioned chemical inertness and its relatively small non-sphericity (see Fig. 1.1). Even though the non-sphericity is only small, the orientational behaviour of the molecules plays a large role, especially at higher pressures [Sch98, Mul98, Sch93]. To maintain contact with the experimental studies performed in our laboratory, the simulations described in this thesis also include nitrogen molecules as one of the basic molecular ingredients.

However, we do not restrict ourselves to the high-pressure behaviour of nitrogen molecules only. In conjunction with the experimental studies, we have investigated systems of nitrogen-containing molecular systems at very high density, these systems very often involve a solid, crystalline phase. The motivations for studying these systems are related to exciting experimental results in this field. The studies in this thesis are performed to obtain insight in the macroscopic behaviour, found in experiments, via microscopic computer simulations.

1.3 This thesis

Roughly speaking, the systems under study are weakly bound crystalline high-pressure mixtures of nitrogen with a second component. The extra degree of freedom, the composition, may lead to shifts in phase transitions and to drastic changes in properties compared to the pure components: the second component always plays a role in the behaviour of the nitrogen molecules (and vice versa). This is obvious for mixtures in which the \( \text{N}_2 \) molecules are a minority. Three nitrogen-containing systems have been studied.

1.3.1 \( \text{N}_2 \)-noble gas van der Waals crystals

In the first system, the nitrogen molecules form a bulk high pressure phase. In this crystal a second component (a noble gas, we have in particular studied the case of argon) may be dissolved [Kle90, Hoc90] thus forming a van der Waals mixed solid. The phase behaviour
and orientational properties under the influence of argon are examined: order-disorder transitions of various kinds are investigated in detail by Monte Carlo (MC) simulations.

Solid nitrogen appears as a natural substance in the low lying geological levels as, over the ages, air is encapsulated and transported downwards due to shifts in the earth’s crust. In high pressure N$_2$, the high temperature phase (the $\delta$ phase) is a plastic crystal [Man97]. The crystal consists of two lattice sites, the $a$ and the $c$ cites, each lattice site exhibiting an orientational disorder that corresponds with the point group symmetry: the $a$ sites have three-dimensional orientational freedom, whereas the $c$ sites exhibit two-dimensional orientational freedom (see Fig. 1.2). The two lattice sites have their corresponding counterparts in the low temperature, orientationally ordered $\varepsilon$ phase. As in the low pressure phases, at high pressures, the N$_2$–Ar mixtures form mixed solids in which the Ar molecules dissolve substitutionally in the N$_2$ lattice [Wes96a, Koo98]. However, since at high pressures there are two types of lattice sites, one may predict that the molecules are not distributed randomly over these sites. Indeed, it has been found experimentally that Ar dissolves substitutionally in the N$_2$ matrix, thereby having a preference for the $a$ sites.

In chapter 2, the distribution of noble gas atoms, in particular Ar atoms, over the two types of lattice sites in the nitrogen crystal at high pressure, and its consequences for the phase behavior, has been investigated with Monte Carlo simulations as a function of $p$, $T$, and $x_{Ar}$ ($x_{Ar} \leq 0.25$). In particular, the experimentally detected redistribution of Ar atoms over the lattice sites [Koo98], as the conditions change, will be studied since this redistribution suggests that despite the high pressures, a relatively fast diffusion occurs within the system.

With the knowledge from experiments that the Ar atoms prefer the $a$ sites, a series
of calculations has been performed in which the orientational response of the N$_2$ atoms under the influence of increasing Ar content is investigated (chapter 3). We studied three order-disorder transitions in the mixture, the $\varepsilon^*-\delta^*$ transition being one of them.

The orientational order is correlated with the positions of the molecules. Therefore, in the third part of this topic, orientational order parameters and displacements of the molecules with respect to the positions of the space group are investigated in more detail in chapter 4.

### 1.3.2 N$_2$ clathrate hydrates

In this system the second component is water. Here, the situation is quite different: only a small amount of nitrogen molecules is dissolved in an ice-like lattice of water molecules. This lattice can be considered to be built of cages (Fig. 1.3(a-c)). These cages consist of polyhedra, formed by the water molecules [Rip94, Slo90, Atw91]. The voids, or cavities, inside these cages, may be occupied by guest molecules such as N$_2$. In fact, these structures are not stable without the presence of a minimum amount of guest molecules: it is a compound. In contrast to the previously mentioned compounds, the composition for these compounds is not fixed. By the inclusion of the guest molecules, these so-called clathrate hydrates are mixtures that belong to the class of inclusion compounds. This distinguishes the clathrate hydrates from the solid solutions in which guest molecules dissolve interstitially in ice phases that may exist for pure water. Although the hydrogen bond obviously is the dominant interaction as far as the host lattice is concerned, the interaction between the guest and host molecules is predominantly of the van der Waals type.

Although the interest in clathrate hydrates has increased significantly during the 1950s, the idea of double occupancy—the occurrence of two guest molecules inside one cage—has hardly been considered seriously. Considering the sizes of the smallest guest molecules (of which N$_2$ is an example) for which stable clathrates exist, a double occupation of the cages is not expected (Fig. 1.3(d,e)). However, a number of other experimental results [vH93, Cha97] on N$_2$ clathrates could be explained by the phenomenon of double occupancy. Moreover, recent experimental results have led to the suggestion of a partly double occupation of the large cages of a structure II clathrate hydrate, with N$_2$ as guest molecules [Kuh97]. The occurrence of double occupancy of similar molecules, such as CO$_2$ and CH$_4$, may be important from the viewpoint of applications: natural gas hydrate deposits present across the sea floor are a potential energy resource, while ideas about the storage of CO$_2$ into such clathrates have been put forward.

Although the occurrence of double occupancy was suggested but not proven, we have investigated whether the occurrence of double occupancy is possible from a theoretical point of view. Using Molecular Dynamics (MD) simulations, we have systematically studied the effect of double occupancy on the mechanical stability of the clathrate. Moreover, we have investigated thermodynamic (chapter 5), structural (chapters 5 and 6) and dynamic properties (chapter 7) of such clathrates, and compared them with known experimental results. We have also investigated the influence of double occupancy on the occurrence of a pressure-induced amorphous phase [Han91] (chapter 6).
Figure 1.3: (a) The unit cell of a structure II clathrate hydrate, consisting of 136 water molecules that form 8 large and 16 small cages. Only the small cages are visible, these form a tetrahedral structure (note the tetrahedral arrangement along the diagonals of the faces of the unit cell). The large cages form a diamond lattice. (b) the large and (c) the small cages. The O atoms of the water molecules are denoted by the dots at the vertices of the lines. The either covalently or hydrogen bonded H atoms are located inbetween neighbouring O atoms, as illustrated by the large (O atom) and small (H atom) shaded circles in (c). (d) and (e) illustrate the free space diameters of the large and small cages (roughly 6.2 Å and 4.6 Å, respectively); a dotted circle denotes a nitrogen molecule, as given by its molecular van der Waals radius (roughly 3.6 Å).

1.3.3 $N_2$ in cylindrical nanopores

In the last study (chapter 8), the second component is a rigid cylindrical wall, in which nitrogen is confined. Speaking in terms of mixtures, in this case there is complete phase separation, the second component being the pore material. However, since the confining geometry is of the same scale as the molecular dimensions, the (phase) behaviour of the confined substance is strongly influenced by the confinement [Chr01]. If the dimension of the pore is small enough, the structure at one side of the pore is influenced by the structure at the other side of the pore. One may think of this in terms of interference of the density oscillations induced by each wall [Zwa01].

In porous materials, the change in phase behaviour is partly due to the sheer confinement. The nature of the interactions between the molecules and the walls of the porous material also plays a role [Gel99]. In general, for higher pressures, the attractive part of the intermolecular potential becomes less important as the molecules are ‘forced’ up to short intermolecular distances, corresponding with the repulsive part of the potential. This also holds for the molecule-wall interaction. It is therefore expected that, at higher pressures, since the (attractive) nature of the molecule-wall interaction becomes less important, the sheer geometrical confinement dominates the (phase) behaviour.

Raman measurements of geometrically confined $N_2$ molecules in cylindrical nanopores suggest the occurrence of a phase transformation in the layers near the wall upon the increase of pressure [Lot01]. These so-called adsorbate layers consist of stacked monolayers
with a two-dimensional amorphous-like structure. This is reflected in the very broad peaks in the experimentally obtained Raman spectra. For small pore sizes (smaller than about 40 Å), the pore is completely filled with such an adsorbate state, leading to the most evident phase transition. For larger pore sizes, the adsorbate layers coexist with bulk-like solid phases.

In chapter 8, we have made an effort to obtain microscopic insight into the behaviour of cylindrically confined N₂ molecules as a function of density by means of MD simulations. In particular, we are interested in the above-mentioned phase transition in the adsorbate layers. The simulations are therefore performed with a cylindrical pore of the same dimension.

### 1.4 Computational methods

In this study, we have used classical Monte Carlo (MC) and Molecular Dynamics (MD) simulations [Fre96, Ali86]. Such techniques are now standard, although more efficient techniques to simulate an increasing number of degrees of freedom are continuously devised. With both methods it is possible to calculate any static ensemble average, but the two techniques have their own advantages. In addition to the ensemble averages, MD simulations provide information about the dynamics of the system under investigation. The main advantage of MC techniques is that unphysical moves can be carried out. The benefits of both techniques have been exploited in this thesis. We put little emphasis on the computational techniques; we mainly focus on the physics involved. However, occasionally we will explain the approach we have followed.