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published in

NIC Symposium 2010
G. Münster, D. Wolf, M. Kremer (Editors)

Forschungszentrum Jülich GmbH,
Jülich Supercomputing Centre (JSC),
John von Neumann Institute for Computing (NIC),
Schriften des Forschungszentrums Jülich, IAS Series, Vol. 3,
ISBN 978-3-89336-606-4, pp. 105-110.

Atomistic Simulations on Polymeric Nitrogen

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Single-bonded polymeric form of nitrogen, formed under high pressures, has been considered as a promising candidate for environmentally safe high energy density material. However, synthesis of this material has proven to be exteremely difficult due to the complex enthalpy landscape. We have conducted density functional theory calculations on the way towards drawing the full phase diagram to assist the experimentalists on this quest. First, we compared the most promising candidates for metastable or stable structures, and then set out to find new stable high pressure phases after we noticed that the previously considered structure was dynamically unstable. We also developed an analytical interaction model for classical molecular dynamics which can be used to study the synthesis process at atomistic precision and to explain the pitfalls while releasing the pressure from the synthesis conditions.

1 Introduction

Molecular nitrogen can be transformed under high compression into a variety of chemically bonded solid phases. This transformation to non-molecular phases is of fundamental interest for understanding the physics of both molecular solids and the chemistry of nitrogen. It may also have applications in energy technology, since non-molecular nitrogen can potentially be used as high energy density material (more than 140 kJ/mol or 2.0 MJ/g *i.e.* roughly 500 times larger value than for TNT). During the recent years, after the experimental realization[1] of non-molecular crystalline nitrogen structure, *cubic gauche*, *cg* (see Figure 1) – proposed in 1992 based on creative thinking and density functional theory (DFT) calculations[2] – several possible new non-molecular phases have been suggested by theorists[3–13]. The multitude of proposed phases calls for a consistent comparison of their thermodynamical stability allowing to draw the phase diagram of materials under a wide pressure and temperature range. This would be of vital importance for the experimentalists working in the field. Moreover, as the high pressure experiments are extremely difficult, simulations can also assist in designing experiments which would maximize the probability for a successful synthesis.

2 Method

In order to fully understand the behaviour of nitrogen under various conditions, the free energies of the various phases must be calculated under different pressures and temperatures. From these energies, we can then deduce the phase diagram of the material. The first step in such calculations is to compare the zero temperature enthalpies of the phases for the complete pressure range. While the proposed structures have been compared using a wide variety of different methods, we carried out an extensive comparison[14] regarding their thermodynamical stability using plane-wave basis set DFT code VASP[15] with the general

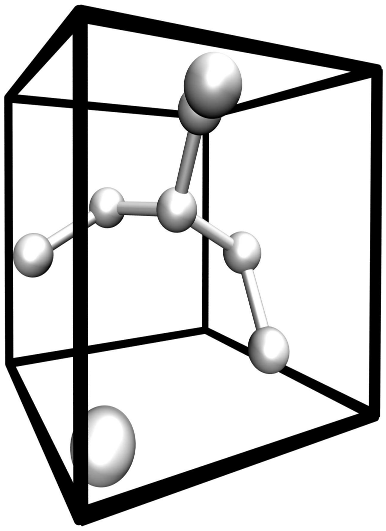

Figure 1. Cubic unit cell (twice the primitive cell) of the *cg* structure.

gradient approximation (GGA) exchange-correlation functional by Perdew *et al.*[16] . The core ($1s^2$) electrons were described with a projector augmented wave pseudopotential[17, 18]. A high kinetic energy cutoff (1200 eV) was used due to the lack of p or d states in the core. Brillouin zone sampling was performed using the scheme of Monhorst-Pack[19] (including the Γ-point). For consistency, a $13 \times 13 \times 13$ k-point mesh was used for all the relaxation simulations.

To estimate the dynamical stability of the different nitrogen phases, we also calculated the phonon dispersion relation following the scheme proposed by Kunc and Martin[20]. Within this method, a supercell of sufficient size to limit the forces inside the cell is first created, and all irreducible directions within the cell are searched for. After this, each plane of atoms perpendicular to each direction is displaced along the 3 degrees of freedom to calculate the forces exerted on all atoms by the displacement. The force constant matrix is then constructed and used to calculate the dynamical matrix Ψ_k for the primitive cell for different $\mathbf{k}$ vectors along the high symmetry axes. The square roots of the eigenvalues, $\omega_i(\mathbf{k})$, of $\Psi_\mathbf{k}$ give the frequencies of the phonon modes for each k. Imaginary frequencies correspond to directions of barrierless phase transitions indicating dynamical instability of the phase.

3 Phase Comparison

In this study, we included two molecular structures (α-N_2 and ϵ-N_2), one chain-like structure (coordination $N_c = 2$) and seven of the most likely structures proposed before the time of the study ($N_c = 3$). Our results agree well with the previous calculations[2], although for the layered phases we obtained qualitative agreement only with a fixed simulation cell. When the lattice vectors were relaxed, we observed that – similar to graphite – it is energetically favoured to separate the layers rather than to expand the structure in all three

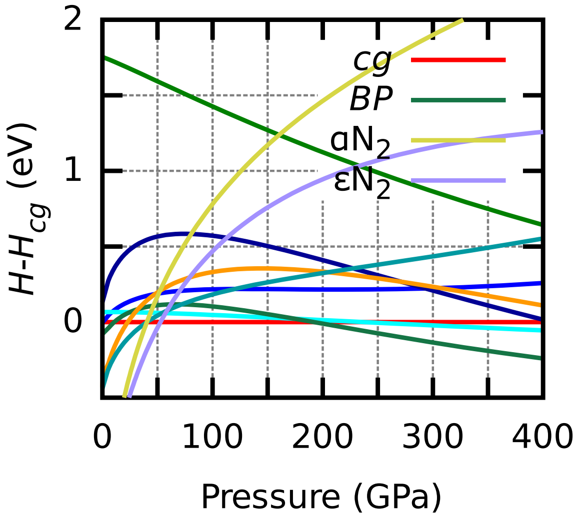

Figure 2. Enthalpy comparison of the relevant phases. Only molecular phases with *cg* and *bp* are labeled.

dimensions, leading to a flat tail in the equation of state curve (energy as a function of the atomic volume). Also the properties calculated for *cg* agree well with the results published by others[2, 1, 21]. The enthalpies of the various structures as compared to that of *cg* is plotted in Figure 2 as a function of the pressure.

The next step towards calculating the complete phase diagram would be to include the temperature into the equation via phonon density of states calculations for all phases under the complete range of pressures. This work has partly been already carried out[14]. However, while many new phases have been proposed[7, 10–13] since the last comparison was made, the previously made calculations must be extended.

3.1 High Pressure Phases

One of the curious features we noticed while calculating the phonon spectra for some of the structures, was that the phase with the lowest enthalpy at pressures above 200 GPa (*black phosphorus, BP*), is dynamically unstable at pressures close to 200 GPa[14]. The obvious conclusion from this fact is that there must exist another structure with lower enthalpy, perhaps not previously observed because of a large number of atoms in the primitive unit cell. Keeping this in mind, we started to look for new high-pressure structures for nitrogen using an evolutionary search method with DFT as the method for total energy calculation[13]. We were able to identify four new structures. Still, after including these in the enthalpy comparison, the *cg* remains most stable up to pressure of 188 GPa. One new structure – an orthorhombic $Pba2$ is stable at the pressure range of $188 - 320$ GPa, and above 320 GPa the $P2_12_12_1$ is the ground state. All four described structures displayed real phonon modes (no dynamical instabilites) throughout the interesting pressure ranges.

The optimized lattice parameters at 250 GPa for the $Pba2$ structure are $a = 4.17$ Å, $b = 4.15$ Å and $c = 3.95$ Å with N atoms occypying four inequivalent Wyckoff $4c$ positions: (0.2933, 0.2172, 0.6608), (0.7852, 0.2167, 0.3403), (0.0209, 0.3363, 0.177) and

(0.8381, 0.0171, 0.8219). This is a layered structure, which consists of N_4 units (one central N atom being covalently bonded to three others, among which two of such N-N single bonds are equivalent). In contrast to the layered structure, the orthorhombic $P2_12_12_1$ adopt fully 3D packing consisting of helical tunnels connected to each other by covalent N-N bonds. At 350 GPa the optimized lattice parameters are $a = 4.01$ Å, $b = 3.31$ Å, $c = 2.39$ Å with atomic positions: N1 at $4a$ (0.8298, 0.261, 0.2384) and N2 $4a$ (0.5704, 0.3963, 0.5025). Again, each atom has three covalent bonds, but they are all nonequivalent. As the pressure increases, nitrogen tends to decrease local symmetry of nitrogen atoms *cg* $\rightarrow Pba2 \rightarrow P2_12_12_1$. Both of the stable high-pressure structures are insulators with band gaps of 5.2 eV and 2.64 eV, respectively, under above-mentioned pressures. The actual band gap can be expected to be twice as large, due to the typical underestimation of band gaps within DFT.

Due to the complex enthalpy landscape with very small differences between many structures under different pressures, experimental realization of also other non-molecular phases than *cg*, $Pba2$ and $P2_12_12_1$ is possible, at least in high temperatures (say, 2000 K). However, we suggest the experimentalists to especially look for these structures while synthesizing polymeric nitrogen.

3.2 Analytical Potential

Although DFT is most likely the best method for searching for new atomic structures, due to its computational requirements, it remains impossible to carry out dynamical simulations with large system sizes for modeling phase transitions or amorphous structures with DFT. To this end, we have developed a new analytical interaction model[22], similar to an earlier model[23], to be used in classical molecular dynamics simulations. Our preliminary studies indicate that the model can be used to study the transition from a molecular structure to the ordered polymeric phase. Since our model is constructed using *cg* phase as the main structure for fitting, our results can be expected to improve on the earlier synthesis calculations[24].

Further, it is somewhat surprising from the theoretical point of view that bringing the *cg* phase to ambient conditions has proven to be, if not impossible, at least extremely difficult. We use the recently developed interaction model also to attack this problem. So far, we have been able to show that both intrinsic vacancies – introduced into the structure during synthesis – and grain boundaries (see Figure 3) have a significant effect on serving as seeds for the collapse of the structure during pressure release.

4 Concluding Remarks

The enthalpy landscape of nitrogen under high pressures has proven out to be extremely complicated, well highlighted by the number of predicted structures which can exist under extreme conditions[2–13]. First determining the relevant structures from this pool, and then calculating their free energies for wide pressure and temperature ranges, will allow drawing the phase diagram for this material to assist experimental work on realizing its potential as an high energy density material. We have conducted the first two steps on this path by first comparing the different known structures (at the time of the study)[14] and then finding stable high pressure structures[13] after we realized that the previously considered

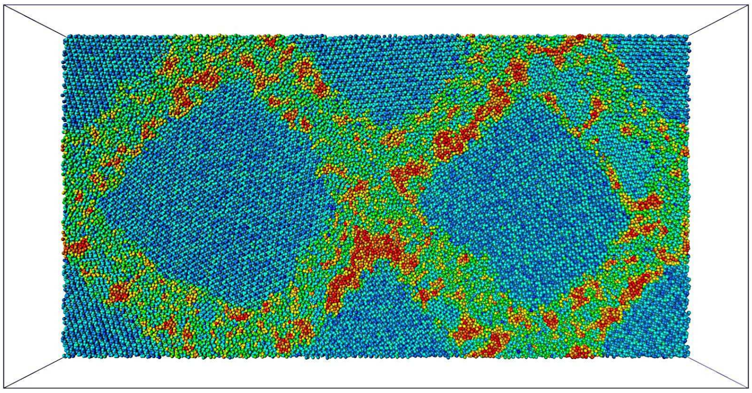

Figure 3. Polycrystalline *cg* as described by our analytical interaction model. The colouring is based on potential energy of each atom. The grain boundaries have clearly higher energy than the crystalline parts of the system.

high pressure structure is actually unstable. Also, we have developed a new interatomic interaction model for nitrogen[22] which can be used to study the synthesis process and to describe the problems and their solutions on the path towards ambient conditions after successful synthesis of the material.

Acknowledgements

Grants of computer time from the Jülich Supercomputing Centre in Jülich, Germany are gratefully acknowledged. This work has been supported by Deutsche Forschungsgemeinschaft through Project No. AL 578/3-1 and -2. We also acknowledge financial support through a program funded by the German foreign exchange server (DAAD) and the Academy of Finland.

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