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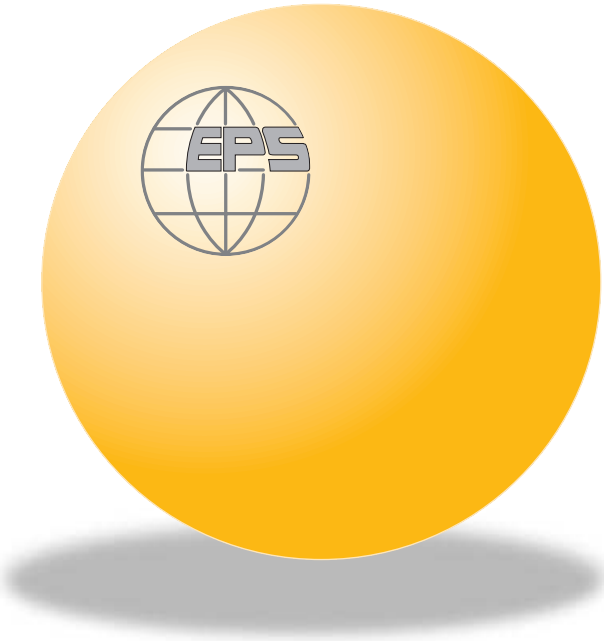
K. Nordlund, A. Krasheninnikov, N. Juslin, J. Nord and K. Albe



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Structure and stability of non-molecular nitrogen at ambient pressure

K. Nordlund[1](*), A. Krasheninnikov[1], N. Juslin[1], J. Nord[1] and K. Albe[2]
[1] *Accelerator Laboratory, University of Helsinki - P.O. Box 43, FIN-00014, Finland*
[2] *Institut für Materialwissenschaft, TU Darmstadt*
Petersenstr. 23, D-64287 Darmstadt, Germany

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Abstract. – Non-molecular solid nitrogen, metastable even at zero pressure and low temperature, was recently manufactured by Eremets *et al.* (*Nature*, **411** (2001) 173) and investigated with respect to its pressure stability. In this study we present analytical potential molecular-dynamics simulations that allow reproducing all the stages of the experiment. The bonding structure and energetics of the N polymeric state obtained from the dynamical simulations are verified to be reasonable using a plane-wave *ab initio* method. We predict that the metastable low-pressure phase has predominantly 3-folded bonded atoms in a disordered configuration. The energy accumulated in the metastable phase is about 1 eV/atom.

Introduction. – Recent high-pressure experiments [1–3] demonstrated the existence of a non-molecular solid phase of nitrogen which was metastable at ambient pressure and temperatures of 100 K and below. This breakthrough confirmed theoretical predictions [4–11] that non-molecular nitrogen could exist and potentially be used for energy storage, thus opening new routes to the development of ecologically clean high-energy density materials. However, it is not clear yet what the detailed atomic structures of the phases observed are. Besides this, knowing the amount of energy stored and understanding the phase transition mechanisms are indispensable for further progress in this field.

Density-functional theory (DFT) calculations [4–8] have outlined the most probable nitrogen solid-state structures which should appear under high pressure. They have also predicted a considerable hysteresis effect [4] upon removing pressure and explained the existence of the potential barriers along paths to dimerization at atmospheric pressure [6]. However, these methods are too computationally expensive for dynamic simulations of the system behavior. Thus, they cannot be used for studying the time scales and pathways of phase transitions, *e.g.*, the mechanisms of energy release from the system upon local heating and shock waves or behavior at the gas-solid interface.

At the same time, an analytical molecular-dynamics (MD) model, parametrized from the results of the DFT calculations on many different phases of nitrogen, can retain the essential characteristics of the DFT description of the phases, yet also describe phase transitions by dynamical simulation of the atom behavior in a wide range of temperatures and pressures. Since MD models enable one to simulate systems composed of thousands of atoms, an analytical potential model would be a powerful tool to study realistic systems with defects, both in and out of equilibrium.

(*) E-mail: kai.nordlund@helsinki.fi

In this letter, we first describe the parametrization of such a potential and then present molecular-dynamics simulations that reproduce all the essential stages of the experiment [1]: the formation of a high-pressure solid phase, its stability at zero pressure and 100 K, and its subsequent decomposition on heating. Based on the simulations, we describe what the atomic structure is in each phase, and how the bonding states evolve during all the phase transitions involved. In particular, we show that the phase which is stable at zero pressure is a disordered, polymer-like phase with predominantly 3-fold bonded atoms. We also use plane-wave DFT calculations of the final polymeric phase obtained from the MD calculations to verify its stability and calculate a more accurate estimate on the accumulated energy.

Method. – To simulate phase transitions in a material with atomic-scale computer simulations, one needs an interatomic potential that describes variations of the local atomic environment and therefore allows to reproduce energy and structure of different phases correctly. Developing such a potential for nitrogen is a challenging task, because at ambient pressure the lowest-energy configuration for nitrogen is the dimer. The bond-order concept and a Tersoff-Brenner functional form [12–14] have proved to be well suited for developing interatomic potentials capable of describing a wide range of bonding structures correctly [12,15]. We have developed an interatomic bond-order potential for N [16]. The potential was fit to the dimer, diamond, simple cubic, body-centered cubic (bcc), and face-centered cubic (fcc) phases of nitrogen, giving a reasonable description of all of these phases, and care was taken to ensure that the potential truly gives the dimer as the ground state. A detailed discussion of the potential fit and its transferability are given in ref. [16].

To test the potential on systems intermediate between the gaseous and bulk phases, we now checked the energetics of the putative nitrogen cluster cubane N_8, which is one of the most studied small N clusters [9–11]. Our simulations indicate that the cluster is metastable with an accumulated energy of 1.8 eV/atom, which is in good agreement with the results of *ab initio* calculations [9–11] (from 1.5 to 2.6 eV, depending on the method used).

To simulate phase transitions on an atomic scale, we used a molecular-dynamics [17] simulation code designed by us for efficient simulation of large-scale systems [18, 19]. Unless otherwise mentioned, periodic boundary conditions were used in all dimensions to model a system without free surfaces. The Berendsen method [20] was used for the temperature and orthogonal cell pressure control [21]. To ensure that the time constants used in this method do not affect the qualitative results obtained, we repeated all central simulation stages with time constants varying by more than one order of magnitude.

A bonding analysis was employed to characterize the system state. In our bonding analysis, a bond was counted as 1 if it was inside the lower cutoff distance $R_{\mathrm{cut}} - D_{\mathrm{cut}}$ defined by the potential cutoff function [15] and as a fractional bond with a value ranging from 1 $R_{\mathrm{cut}} - D_{\mathrm{cut}}$ to 0 at $R_{\mathrm{cut}} + D_{\mathrm{cut}}$, as given by the cutoff sine function of the potential (eq. (3) in ref. [22]).

When during any given processing stage the bonding statistics did not change any more, the system was judged to have reached equilibrium.

Results and discussion. – We first created a high-pressure phase of solid nitrogen by raising our simulation cell with 1024 atoms (arranged as a gas with 512 nitrogen dimers with random positions and random velocities) under different high pressures and equilibrating it until the bonding structure stabilized. Below 600 GPa, the system remained in molecular dimers. At 700 GPa the sample transformed into a high-coordinated structure, both at 300 and 450 K, although a small number of dimers remained over the limited time scale of the simulation. At higher pressures, $\sim$ 1000 GPa, the transition became complete in the time frame used (up to 3 nanoseconds). There was no significant difference between the 300 and 450 K states. The average coordination in these structures is about 11. The pressure at which

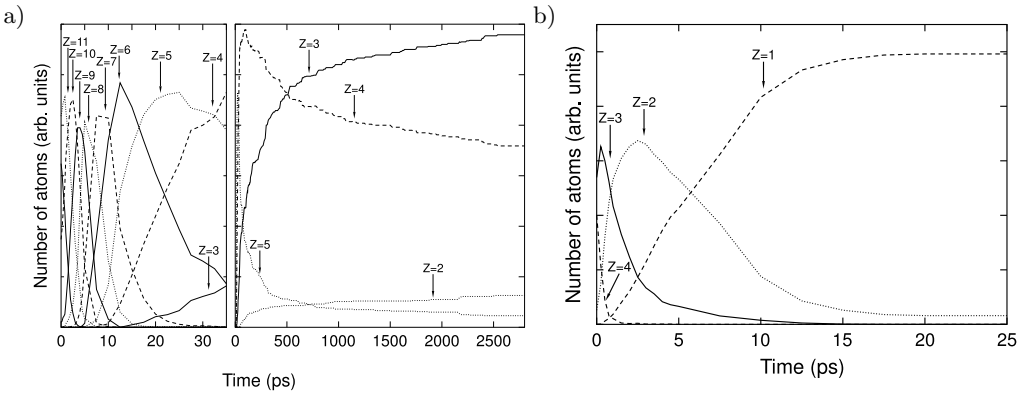

Fig. 1 – a) Evolution of coordination states during relaxation and heating of non-molecular nitrogen. "Z" denotes the coordination number of atoms as defined by the potential energy function. a) Evolution of bonding states during relaxation of pressure from 1100 GPa to 0 GPa. b) Evolution of bonding states when the metastable low-coordinated nitrogen state is heated up to 1500 K with no free surfaces.

we observe the transition, $P_{\mathrm{T}} \sim 600$ Gpa, is higher than the transition pressure observed experimentally. This is because analytical bond-order potentials of the type used here tend to overestimate transition barriers because of the shape and short range of the cutoff function [23]. In this particular case, we examined broadening of the cutoff and found that *e.g.* when the cutoff range is increased from ± 0.2 Å to ± 0.4 Å the transition pressure is lowered from about 700 GPa to 300 Gpa. Because the transition involves atoms moving over barriers at elevated temperatures, however, this does not reflect a problem in the description of the equilibrium configuration reached when the transition is complete. Indeed, even with the different cutoffs the structure of the high-pressure phase was similar as with the original one.

We analyzed one of the high-pressure structures (the one produced at 300 K and with 1100 Gpa) in greater detail. The average coordination (counting only nearest-neighbour bonds) was 11, but the bonding states varied between 9 and 12. The angles between the bonds showed peaks at about 60°, 90°, 110° and 145° which are fairly close to the angles between bonds in perfect bcc and fcc, but not in the simple cubic structure. Hence the state appears to be a disordered phase near a close-packed state, but one which cannot clearly be identified as either fcc or bcc. This result originates from the fact that, although the bcc phase is lower in energy than fcc in our model, the difference is small, only about 0.2 eV. Thus it is not surprising that the system remains disordered and that the average coordination approaches that of fcc (12) under the high pressures used. Notice that the optical data [2] provide evidence that the experimentally observed high-pressure nitrogen phase is indeed amorphous.

We then relaxed this high-pressure phase carefully to low temperatures and zero pressure, as done in the experiments of Eremets *et al.* [1]. The temperature was first cooled to 100 K, and subsequently the pressure relaxed over times up to several nanoseconds to zero pressure, keeping the temperature constant. The evolution of the system during the relaxation is illustrated in fig. 1a), which shows the number of atoms with coordination Z as a function of time. We see that the system first relaxes through a large number of intermediate bonding configurations from $Z \approx 11$ down to $Z = 6$. After this, when the pressure was about 20 GPa, a transition to a predominantly 3-fold coordinated structure begins, which then remained stable for the remainder of the runs, over several nanoseconds. We observed the same transition path in several different pressure relaxation runs. The final structure consisted of atoms with coordinations 2–5 [24].

The fact that the progression to lower bonding states goes steadily in our simulation also

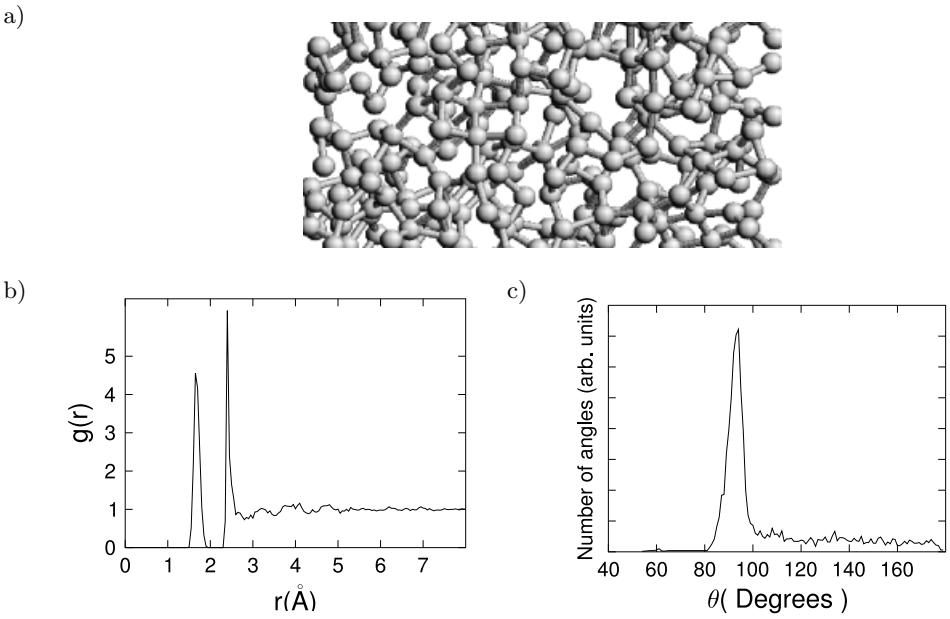

Fig. 2 – Structure of low-coordinated (Z = 3–4) nitrogen at ambient pressure at 100 K produced by our simulations. a) Ball-and-stick image showing atom positions and bonds between them. The figure shows a slice with about half the thickness and height of the entire cell of 1024 atoms. Bonds connecting to atoms outside the drawing area or over the periodic boundary on the left and right sides are not shown. b) Pair correlation function $g(r)$. c) Angles between bonds shorter than 2.3 Å.

indicates that there are no strong transition barriers between the high-coordinated phases, at least when the system is disordered.

When the system reaches the lower-coordinated structures, diamond-like states with $Z = 4$ and the many polymeric configurations with $Z = 3$ [6], it finds a disordered state with 3 as the predominant coordination. This is not surprising in comparison with other group-V elements, phosphorus and arsenic, which are known to have several low-coordinated configurations close in energy [25]. Since the DFT calculations show that there are many possible low-coordinated structures close in energy for N as well [5–7], it is quite reasonable that the nitrogen structures tend to be in disordered states.

The final zero-pressure structures had potential energies of about −2.7 eV/atom (to be compared with the dimer ground-state energy of −4.9 eV/atom) and densities of about 0.12 atoms/Å^3. But here we have to raise a note of caution. Different test parametrizations of our potential gave quite different energies for the polymeric nitrogen phase, even though they gave similar polymeric structures and densities. Hence our analytical model can be considered to be reliable in predicting the structure of the polymeric phase, but not in predicting the exact accumulated energy. Our DFT calculations (see below) give a more reliable estimate of the accumulated energy. The atomic structure is illustrated in fig. 2a). The pair correlation function shows a distinct first-nearest-neighbour peak between 1.5 and 1.9 Å, with no bonds with lengths between 1.95–2.3 Å (fig. 2b). The height of the second-nearest-neighbour peak is enhanced by the tendency of the potential formalism to shun bonds in the cutoff range, 2.0–2.4 Å. Hence the true second-nearest peak can be expected to be broader and extend more into the range below 2.3 Å.

The angles between the bonds (analyzed by counting the nearest-neighbour bonds shorter than 1.95 Å only) had one distinct peak between 85° and 100°. The three-fold coordinated

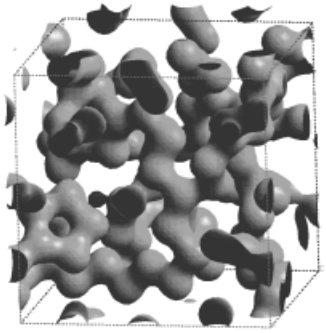

Fig. 3 – Isometric plot of the electron density of the polymeric nitrogen state obtained using the CASTEP [27, 28] plane-wave basis set DFT code.

structures which are found to be low in energy in the DFT calculations of ref. [6] have bond angles between 95° and 105°, which is well in line with our result (note that our potential is not fitted to any of the polymerlike structures, so this indeed is a true prediction). Hence we find that the polymeric nitrogen does have clear short-range order, but is missing long-range order.

We also performed a ring analysis [26] on the topological network formed by the bonds between the atoms in the polymeric nitrogen. In a structure with 1024 atoms we found 7 3-membered rings, 220 4-membered rings, 122 5-membered rings, 111 6-membered rings and 101 7-membered rings. The fact that 4-membered rings clearly dominate is of course related with the observation that many bonds have angles around 90°. It is also well in line with the DFT prediction that the cubic structure cubane (see above) is relatively stable.

In order to check the stability and energetics of the zero-pressure empirical-potential structures, we carried out *ab initio* calculations for a small system composed of 100 nitrogen atoms. This cell was first manufactured with the analytical potential starting from a 50 dimer gas using the same pressure and thermal treatment as for the larger 1024 atom system. We checked that the 100 atom cell had similar bonding structure as the larger one. We then employed the plane-wave basis set code CASTEP [27, 28] implementing DFT and the Generalized Gradient Approximation (GGA) for exchange and correlation as developed by Perdew and Wang [29]. Standard ultrasoft pseudopotentials (USP) were used, since they require much lower-energy cutoff for first-row elements than norm-conserving pseudopotentials. A kinetic energy cutoff of 300 eV was found to converge the total energy of the system to at least 0.05 eV. Even better accuracy was achieved with respect to the $\boldsymbol{k}$-point sampling of the Brillouin zone. We did not perform simulations with a higher accuracy because this accuracy was sufficient for estimating the energy difference between the phases and calculating the system geometry. Calculations of the nitrogen dimer energy with the above-mentioned parameters gave 10.1 eV (with account for spin-polarization energy of single N atoms [30]) which is in good agreement with the experimental value of 9.9 eV.

We first relaxed the system to the ground state while keeping the box size fixed, then relaxed the system again with the box size optimization. The amorphous nitrogen network proved to be stable at zero pressure, although the linear box size increased by 10%. Of course, a different interaction model gave slightly different bond lengths and angles, but the overall root-mean-square atom displacement was less than 0.08 Å, which means that the geometry remained essentially the same after the relaxation and that the analytical potential indeed gives a reliable structure, as argued above. We also calculated the energy difference between the polymeric and dimer phases. The accumulated energy proved to be 1.1 eV/atom.

Figure 3 shows an isometric plot of the electron density. It is evident that the zero-pressure

system is a random network of polymeric chains of nitrogen atoms, not just a collection of weakly interacting dimers. Thus, *ab initio* simulations confirm that the structures predicted by our empirical-potential simulations are metastable.

Having found a low-coordinated metastable state, we proceeded to examine its stability on heating. Experimentally, it was observed that the phase produced at 10 GPa decomposed on heating above 175 K (ref. [1]). We first heated the phase using periodic boundaries in all directions to prevent surface effects, and monitored the evolution of bonding states. The system decomposed by successive progression into lower bonding states, until finally ending up in dimers. This is illustrated in fig. 1b) for 1500 K. After $\sim$ 10 ps, the breakup rate of atoms with coordination $Z > 1$ decreases because some remain in free molecules with more than 2 atoms. Unless the internal energy of these is enough to cause dissociation, they can only break up after collisions with other molecules. This process will occur over much longer time scales than those used here. The behaviour at other temperatures is similar, but the time scale is of course different.

Although we found before that there is some uncertainty in the energy scale of the analytical model, it is not computationally feasible to calculate the breakup time from the electronic-structure calculations. Since the structure is disordered, it is not practical to do a static calculation of the transition barrier, and a dynamic MD calculation over long time scales is not tractable in the electronic-structure calculation. Hence to obtain at least a rough estimate of the transition barrier, we used our analytical MD modeling. We repeated the heating simulations in the temperature range 900–2000 K, measuring the decomposition as the time t from the beginning of the simulation until 80% of the atoms were in dimers at each temperature. We obtained a very good fit of the function $t = t_0 \exp[E_A/k_\mathrm{B}T]$ into the data, with $t_0 = 71$ fs and $E_A = 0.63$ eV. Here k_B is Boltzmann's constant and T the temperature.

We also examined how the presence of a free surface affects the breakup of the metastable state. To this end, we first constructed a polymer phase as described above with no free surfaces, then opened up 1 or 6 free surfaces. We constructed one cell with 4096 atoms and one free surface (with atoms at the opposite end held fixed), and another with 8192 atom in a cubic cluster which had free surfaces in all 6 directions. At low temperatures ($T \ll 1000$ K) the structures were stable over nanosecond time scales. Both systems decomposed at high temperatures rapidly by formation of dimers both on the surfaces and in bubbles inside, which eventually made the system explode. The evolution of bonding states was qualitatively similar to that in fig. 1b), *i.e.* the dissociation occurred via triply and doubly bonded states. But the rate of decomposition was roughly two orders of magnitude faster than in those with no free surfaces.

Since the dissociation of the N polymeric state occurs by the breaking of chemical bonds with a well-defined energy, it is justifiable to extrapolate the breakup time to lower temperatures. Thus, we obtain for the decomposition time of the system with no free surfaces a lifetime of the order of 1 ms at room temperature, and 1 day at 175 K. In an experimental system, however, it is possible that surfaces where the N can outgas more easily are present. As indicated in our simulations with a free surface, the decomposition could then occur orders of magnitude faster. Since we do not know what kinds of surfaces or interfaces are present in the experimental setup, the values given for the lifetime in a system with no free surfaces should be regarded as an upper limit. Still, our decomposition simulations clearly show that the metastable, low-coordinated nitrogen we observe in our simulations can (at least under suitable containment) be stable over macroscopic time scales at low temperatures, in agreement with the experimental observations [1].

Conclusions. – Using an analytical simulation model parametrized on density-functional theory calculations of different bonding states of nitrogen, we have described the atom-level

structure of non-molecular solid nitrogen. We find that this phase has predominantly 3-folded bonding, no long-range order but some short-range order in the form of preferred bonding angles around 90°. The energy accumulated in the metastable phase is about 1 eV/atom.

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