Structural evolution of amorphous polymeric nitrogen from \textit{ab initio} molecular dynamics simulations and evolutionary search

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Polymeric nitrogen with single bonds can be created from the molecular form at high pressure and due to large energy difference between triple and single bonds it is interesting as energetic material. Its structure and properties are, however, still not well understood. We studied amorphous nitrogen by \textit{ab initio} simulations, employing molecular dynamics and evolutionary algorithms. Amorphous nitrogen was prepared at pressure of 120 GPa by quenching from hot liquid, by pressure-induced amorphization of molecular crystal and by evolutionary search. All three amorphous forms were found to be structurally similar. We studied in detail the structural evolution of the system upon decompression from 120 GPa to zero pressure at 100 K. At pressures above 100 GPa, system consists mainly of 3-coordinated atoms (80\%) connected by single bonds while some short chains made of 2-coordinated atoms are also present. Upon decompression, the number of 3-coordinated atoms rapidly decreases below 60 GPa and longer chains are created. At 20 GPa the system starts to create also N\textsubscript{2} molecules and the ultimate structure at \( p = 0 \) contains molecules inside a polymeric network consisting dominantly of longer chains made of 2-coordinated atoms. Besides structure, we also study vibrational and electronic properties of the system and estimate the amount of energy that could be stored in amorphous nitrogen at ambient pressure.

I. INTRODUCTION

Nitrogen is one of the most important elements, abundant in the Earth’s atmosphere as well as in the Solar System. Its phase diagram is complex and contains a number of molecular phases (for review see Ref. \cite{1}). The diatomic molecule N≡N has a unique property of large binding energy of 4.88 eV/atom due to the presence of a very strong triple bond \cite{2,3}. Long ago it was suggested that this triple bond can be destabilized at high pressure where molecular crystal would be replaced by polymeric phase with each atom having three single bonds \cite{4}. As possible crystal structure for such phase the cubic-gauche (cg-N) structure was proposed which represents, in a sense, an analogue of diamond structure for trivalent atoms \cite{5}. The large energy difference between single bond polymeric cg-N and triple bond molecular N\textsubscript{2} crystal, estimated at zero pressure to about 1.4 eV/atom \cite{2}, makes polymeric nitrogen interesting as potential energetic material. According to theoretical prediction cg-N at \( T = 0 \) should become thermodynamically more stable than molecular crystal at pressure above 50 GPa \cite{5}. The experimental preparation of cg-N is, however, not easy, due to large kinetic barriers. The predicted phase was finally experimentally confirmed in Refs. \cite{6,7} where it was synthesized by considerable overpressurization of the molecular phase to about 110 GPa at high temperature over 2000 K. It was also shown that this phase cannot be decompressed to ambient pressure since at room temperature it converts at 42 GPa back to the molecular phase \cite{8}. The mechanism of creation of cg-N from molecular phase was theoretically studied by \textit{ab initio} metadynamics in Ref. \cite{8}. Several recent works investigated the possibility of creating and stabilizing single N-N bonds in systems other than pure nitrogen \cite{9,11}.

Besides the cg-N phase, also amorphous polymeric N (a-N) called \( \eta \)-phase was observed in experiments starting from molecular crystal upon compression to about \( p = 150 \) GPa at room temperature \cite{15–17}. A possibly different amorphous form with reddish colour was observed by direct laser heating of molecular form to 1400 K at 120-130 GPa in Ref. \cite{18}. Importantly, a-N at low temperature below 100 K was shown to be quenchable to ambient pressure \cite{16}. Since the property of main interest here is the stored energy, which is not related to crystallinity but rather to the number of single bonds, the amorphous version of polymeric nitrogen is certainly worth study, not only for fundamental but also practical reasons. In fact, it is not obvious that the structure of a-N represents a plain disordered analogue of the cg-N phase and it might include some structural motifs from low-lying metastable phases as well. In Ref. \cite{15} it was shown, based on optical measurements and analysis of the Urbach tail that at \( p = 160 \) GPa a-N has a coordination number of about 2.5 suggesting that it might consist of mixture of 2- and 3-coordinated atoms. In Ref. \cite{19} it was suggested that there might be a connection between the negative slope of liquid-solid phase boundary in nitrogen (in pressure range of 66–87 GPa) and existence of a-N, similar to the existence of amorphous water ice \cite{20}. According to this interpretation the amorphous phase represents a product of mechanical melting of the parent crystalline phase occurring upon crossing the metastable extension of the melting line.

a-N was studied theoretically in Refs. \cite{21,26}. In an early study Ref. \cite{21} a-N was studied by \textit{ab initio} molecular dynamics (MD) simulations employing supercell with 64 atoms and simulation time about 10 ps. It was suggested that the average coordination of a-N is between 2.2
and 2.4, slightly less than in experiment [15]. In Ref. [22] a simulation study was performed using a classical potential, finding that a-N at ambient pressure consists mainly of 3-coordinated atoms. This study, however, compressed the system to a pressure of 1100 GPa and the applicability of a classical force field at such extremely high pressures might not be justified. In a more recent ab initio MD study Ref. [23] a-N was prepared by cooling from liquid and a mixture of 2 and 3-coordinated atoms was found. The analysis of a-N focused mainly at the Peierls distortion of the polymeric chains and electronic DOS in the range of pressures from 90 to 330 GPa. To our knowledge, a comprehensive analysis of structural evolution upon decompression from pressures of order of 100 GPa down to ambient pressure based on state-of-the-art ab initio simulations has not been performed for a-N. We mention that ab initio MD studies of structural evolution of amorphous phases of sulphur and CO$_2$ were performed by some of us in Refs. [27] and [28].

In order to fill this gap we study here the structure and properties of a-N by ab initio MD simulations and evolutionary algorithms. The paper is organized as follows. In section II we describe several approaches to preparation of amorphous structures by computer simulations, focusing on the applicability of evolutionary algorithms. In section III we present the details of ab initio calculations and describe the protocols employed to create amorphous nitrogen. Section IV is devoted to analysis of the properties of amorphous structures and their evolution upon decompression to ambient pressure and subsequent molecularization. In the final section V we summarize the results and draw conclusions.

II. PREPARATION OF AMORPHOUS STRUCTURES

The preparation of amorphous structures via ab initio simulations represents a non-trivial task for several reasons. First of all, periodic boundary conditions that are routinely used impose on the disordered system an unphysical periodicity and this effect can only be mitigated by making the simulation supercell sufficiently large. Second, the short time scale available in ab initio simulations necessarily implies that any structural transformation simulated has to be extremely fast compared to experimental time scales. As discussed in Ref. [29], the standard method of quenching the liquid suffers from the drawback of dependence of the final structure on the cooling rate - if the latter is too fast, the resulting amorphous structure is likely to "remember too much" of the structure of the hot liquid. Similar problem arises in case of pressure-induced amorphization, where the amorphous structure prepared by rapid amorphization might "remember" too much of the parent crystalline structure. In principle, one might attempt also to simulate the heating of compressed molecular form similar to experimental procedure in Ref. [15]. In order to avoid computational artefacts it would be highly desirable to have an independent method allowing to prepare amorphous structures "from scratch", without relying on a particular initial liquid or crystalline phase, such as e.g. the Monte Carlo bond-switching method [30].

In this work we approached the problem of finding the high-pressure structure of amorphous polymeric nitrogen by three independent simulation methods. Two of them - formation of amorphous form by melt quenching (glass) (1) and by pressure-induced amorphization (2) represent real physical experiments and in our work were simulated by means of ab initio MD at constant pressure. The new one is evolutionary structure searching method (3) in combination with ab initio total-energy calculations that aims at finding a structure with minimal enthalpy. We prepared and analyzed three amorphous states of nitrogen at $p = 120$ GPa employing the above methods and compared them to each other and to available experimental data.

The application of evolutionary algorithms (EA) to crystal structure prediction [31, 32] was shown to be highly successful in numerous cases [14, 31, 33-36]. For systems with not too large unit cells, counting up to 20 - 40 atoms it is now a routine task to determine the lowest energy or enthalpy structure, employing evolutionary algorithms in combination with ab initio total-energy calculations. With increasing cell size, however, finding the crystalline structure becomes a problem because of too large dimensionality of the search space and necessity to generate an astronomical number of structures to reach the crystalline ground state. This can also be interpreted as failure of the search to reach the ground state due to excessive computational complexity of the problem. Intuitively, in such case the evolutionary algorithm is still likely to produce low-energy (or enthalpy) structures, which, however, do not exhibit a long-range crystalline order. Such structures are likely to represent good disordered or amorphous structures and it is therefore plausible to expect that an efficient evolutionary algorithm applied to large unit cell can be employed to search for such structures. In good glass formers the system is protected from crystallization by the time scale gap between experimental cooling time and much longer time required for crystallization. Similarly, even if in EA there is no concept of time, a sufficiently large system is protected from crystallization by excessively large number of structures necessary to find the crystalline ground state. We note that while in search for crystal structures the space group symmetries are commonly used we do not make use of these symmetries in our search as it would contradict our aim of finding non-crystalline amorphous phases.

To our knowledge, the only application of this approach so far is Ref. [37] where amorphous forms of silicon and indium gallium zinc oxide (IGZO) have been found by using relatively small supercells with 64 and 84 atoms, respectively. The generated disordered structures were compared to the ones found from ab initio MD melt...
quenching and from experiment focusing on local quantities such as coordination, bond lengths and bond angles. This reveals information about local order but not about medium-range order since e.g. the bond length represents a stiff degree of freedom and it is by necessity very similar in both crystalline and amorphous state. In order to assess the applicability of the EA-based computational methodology it is necessary to perform a detailed comparison of amorphous structures created by EA and those prepared by cooling a liquid or by pressure-induced amorphization. In our study we address this question in case of a-N at Mbar pressure and compare the structure of three amorphous forms prepared in three completely independent manners.

III. SIMULATION PROTOCOLS

A. Ab initio calculations

For all DFT calculations we used the VASP\textsuperscript{38–40} software package along with the PAW\textsuperscript{41} method. The exchange-correlation energy was described by the PBE\textsuperscript{42} functional. All MD simulations were performed with hard pseudopotential PAW PBE\textsubscript{h} using cutoff 700 eV and with Γ point only, except for the MD in the liquid cooling protocol at high temperatures where softer pseudopotential PAW PBE\textsubscript{N} with cutoff 520 eV was employed (decompression of this structure and subsequent heating was performed with the former settings). Both pseudopotentials have 5 valence electrons. To calculate final enthalpies in Table I we chose hard pseudopotential with cutoff 900 eV and with Γ centered k-point grid with density of 20\textsuperscript{1}. Bulk moduli were calculated by inducing a small volume change (0.03 %) and calculating the finite difference of pressure. For this calculation we used the hard pseudopotential with cutoff 900 eV and Γ centered k-point grid with density of 30.

B. a-N obtained as glass:

The first method we used to obtain a-N was the simulation of standard process of glass formation by quenching of liquid. Similar method was used in Ref.\textsuperscript{23}. We started from a 512 atoms sample of the cg-N phase structurally relaxed at 120 GPa and gradually heated the system in NPT MD simulations until the crystal melted at 4500 K. Afterwards we cooled the system down to 1500 K where the liquid froze and an amorphous state a-N was created. The simulation protocol is shown in Fig. 1.

For better comparison with other methods used to prepare a-N which employ smaller supercells we also applied a very similar liquid-cooling protocol to a smaller 256-atom system (see Table I).

The principal structural information is contained in N-atoms coordinations, where single-coordinated N atoms are associated with molecules (1m) or free chain endings (1\textsuperscript{c}), two-coordinated (2\textsuperscript{c}) atoms with internal chain segments and the 3\textsuperscript{c} ones act as nodes of the network (mainly cross-links for 2\textsuperscript{c} chains). The radial limit for coordination was taken as first minimum of radial distribution functions and it turned out that it could be kept at 1.8 Å throughout the calculations.

The corresponding evolution of N atoms coordinations and the change in density and enthalpy are shown in Fig. 2. The liquid at high temperature above 4000 K has about 60 % of 2\textsuperscript{c} atoms and 30 % of 3\textsuperscript{c} atoms. This ratio, however, changes dramatically upon cooling and below 3000 K the number of 3\textsuperscript{c} atoms increases substantially. Below 1500 K the number of atoms with different coordinations stabilizes with about 70 % atoms being 3\textsuperscript{c} and 30 % being 2\textsuperscript{c}, resulting in average coordination of 2.7, well comparable to the experimentally estimated value of 2.5\textsuperscript{15}. The structure of this form can be characterized by very short segments of 2\textsuperscript{c} chains connecting the 3\textsuperscript{c} sites which dominate the system. The density drops upon melting by about 6 % but upon cooling down to 500 K approaches the density of cg-N and remains only about 1 % below the latter. Concerning enthalpy, a-N below 1500 K stays about 0.4 eV/atom above the cg-N form.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{The simulation protocol in which a-N was obtained as glass. First, the cg-N phase (blue points) was melted into a high-pressure polymeric liquid (green) at 120 GPa and a-N was obtained upon cooling down to 500 K (red points). This glassy amorphous form was cooled down to 100 K at 120 GPa, after which it was decompressed to 0 GPa. Finally, the decompressed form was heated in order to observe the molecularization process when energy is released (see section IV_C).}
\end{figure}

\textsuperscript{1} For more information about k-point density option see the VASP manual https://cms.mpi.univie.ac.at/vasp/vasp/Automatic_k_mesh_generation.html
C. a-N obtained from pressure-induced amorphization:

Another way to create a-N was the simulation of pressure-induced amorphization (PIA) process, which is the actual experimental method how \(\eta\)-N was obtained\[15–17\]. We started from a 192-atom sample of the molecular phase \(\epsilon\)-N\[43\] at 60 GPa and 600 K and gradually increased pressure to 190 GPa. Then the system was further compressed to 200 GPa and heated to 1000 K. In this step the PIA occurred and right after the polymeric a-N was created the density dropped by 12 %. In order to speed up the kinetics and allow atoms to relax we heated the system to 2000 K where it was decompressed to 120 GPa during 120 ps. Afterwards the system was cooled down to 500 K and finally to 100 K. This path is shown in Fig. 3.

D. a-N obtained by the evolutionary search:

We employed the code Xtalopt\[32\] to search for low-enthalpy structures in a supercell with 256 atoms at pressure of 120 GPa. In order to keep simulation cell cubic-like, we imposed the following constraints: the cell vectors were chosen from interval 10 Å to 16 Å, angles between cell vectors from interval 80° to 100° and finally the density from interval 4.11 g/cm\(^3\) to 4.58 g/cm\(^3\). Since we are dealing with element we have excluded atom-exchange type operators (permustain). We also observed that structure-mixing type operator (crossover) hardly generated better structures than random search and therefore we mainly used the stripple operator consisting of strain and wave-like displacement of atoms. We generated total of 4600 structures within 39 generations and no crystalline structure was found (not even with local crystalline order).
IV. RESULTS

A. Comparison and properties of amorphous structures at high pressure

It is interesting to compare the samples of a-N prepared independently in three entirely different ways. In Table I one can see that the enthalpies, densities and the number of atoms with different coordinations and length of various kinds of chains are rather similar which is reassuring. We note that each protocol was applied only once and more detailed comparison would require averaging over a larger number of samples prepared by each protocol. In Fig. 4 (top) we see that the radial distribution functions (RDF) in all four samples are also very similar. For comparison we included in the figure also RDF of cg-N and other two theoretically proposed metastable polymeric crystalline structures Pccn [44] and Pba2 [45] calculated from MD runs at temperature of 100 K. We can see that polymeric a-N retains the positions of the first two RDF peaks of cg-N, however, the position of the small third peak at 3.3 Å in a-N is different from that in the cg-N crystal which is caused by different geometry of the rings. Beyond that distance, a-N is essentially structureless, apart from a small and broad peak around 4.3 Å. More detailed discussion of RDF can be found in Supp. Mat. (Fig.1).

|                | LC512  | LC256  | PIA   | XTO   |
|----------------|--------|--------|-------|-------|
| enthalpy H/atom [eV] | -2.067 | -2.069 | -2.097 | -2.067 |
| density [g/cm³]    | 4.361  | 4.375  | 4.388 | 4.441 |
| bulk modulus [GPa] | 241.1  | 235.1  | 249.9 | 258.8 |
| ratio of 1m atoms [%] | 1.19  | 0.78  | 0.00 | 0.00 |
| ratio of 1c atoms [%] | 0.20  | 0.00  | 0.52 | 0.00 |
| ratio of 2c atoms [%] | 26.17 | 25.78 | 16.67 | 14.06 |
| ratio of 3c atoms [%] | 71.68 | 73.44 | 82.81 | 85.94 |
| aver. coord. number| 2.70  | 2.75  | 2.82 | 2.86 |
| aver. chain length 3c × 3c | 1.52 | 1.56 | 1.5 | 1.35 |
| aver. chain length 1c × 3c | 1.00 | absent | 1.0 | absent |
| aver. chain length 1c × 1c | absent | absent | absent | absent |

TABLE I. High pressure properties of amorphous structures prepared in different ways. LC512 denotes the structure prepared by liquid cooling with 512 atoms in unit cell, LC256 the structure prepared by similar protocol with 256 atoms in unit cell. PIA stands for pressure induced amorphization and XTO refers to the structure prepared by evolutionary algorithm. Chain type 3c × 3c means that two 3c atoms are connected to each other via chain of 2c atoms, similarly 1c × 3c represents chain with one 1c and one 3c atom on its ends and finally 1c × 1c represents open chain with only 1c atoms on its ends. We note that we calculated the length of chain by counting only 2c atoms while 3c or 1c atoms at the ends were excluded. All statistics are at 120 GPa and 100 K, except for the bulk moduli and enthalpies which was calculated at 0 K.

In Fig. 4 (bottom) we see that the angular distribution function (ADF) of all three versions of a-N is very similar as well. In particular the glassy a-N and the a-N from evolutionary search are very close while the angular distribution of a-N prepared by PIA is slightly shifted to higher angles. In all three versions the distribution spans the region from 95° to 130° and can be regarded as broadened version of the distribution in cg-N and Pccn phases where the bond angle is close to the ideal tetrahedral angle of 109° (the ADF of crystalline structures were also calculated from MD at 100 K).

An important quantity in polymeric nitrogen is the lp-N-N-lp dihedral angle. In Ref. [46] it was shown that the N-N single bond has minimal energy for the dihedral angle close to 90°, i.e. in the gauche conformation, while the trans and cis conformations were shown to be energetically higher and much higher, respectively (see Fig.3 in Ref.[46]). Subsequently, this result was used in Ref.[5] to identify the cg-N structure as one satisfying the condi-
FIG. 5. Dihedral angles (lp-N-N-lp) for 3c atoms connected by single bond in a-N prepared by liquid cooling (LC), pressure-induced amorphization (PIA) and evolutionary search (XTO).

The distribution of dihedral angles in polymeric a-N is shown in Fig. 5. It can be seen that polymeric a-N has a broad distribution of dihedral angles spanning the whole interval from 0 to 180° with a broad maximum around the gauche angle of 90°. The relative population of cis, gauche and trans states is in qualitative agreement with the energy curve calculated in Ref. [46].

The broad character of the distribution of dihedral angles suggests that polymeric a-N does not represent a simple disordered version of cg-N. We also note that in the cg-N structure the bond and dihedral angles are strictly connected by a geometrical relation (Eq. (11), [5]) which prevents both angles from independently adopting their optimal values. This is probably the reason why the dihedral angle in cg-N is not so close to the optimal value of 90° but has instead a distinctly higher value of about 104° in the experimental structure (106.8° in the LDA calculation in Ref. [5]).

We also calculated the bulk modulus of the a-N prepared by the three protocols at 120 GPa. We employed the formula $B = -V \frac{\partial P}{\partial V}$ and numerically calculated the derivative by introducing small isotropic deformation. The results are included in Tab. I. For comparison the bulk modulus of cg-N at the same pressure of 120 GPa is 300-340 GPa [6]. Our results show that similarly to cg-N also a-N is a very hard material.

An important information about disordered structure is provided by the vibrational density of states. We calculated this quantity for a-N prepared by liquid cooling and cg-N in standard way from Fourier transform of the velocity autocorrelation function from a 10 ps MD run at temperature 100 K and pressure of 120 GPa. The comparison is shown in Fig. 6 where one can see that there is some similarity between cg-N and a-N. The amorphous version of polymeric nitrogen has some fraction of double bonds which are likely to be responsible for nonzero density in the region beyond 1500 cm$^{-1}$ where VDOS of cg-N already drops to zero.

A specific quantity characterizing medium-range order in amorphous system is the ring statistics. While in cg-N all rings consist of 10 atoms, in disordered a-N one may expect also other ring sizes. We employed the R.I.N.G.S software [47] and found that a-N has a broad distribution of ring sizes (see Fig. 2 in Supp. Mat.) roughly centered around the ring size of 10.

We analyzed also electronic properties and bonding pattern of a-N at 120 GPa. We calculated the electron localization function (ELF) [48] which is shown in Fig. 7 where one can see the bonds as well as the lone pairs. In experiment [16] it was found that polymeric a-N is semiconducting in the broad range of pressures from below 100 GPa up to beyond 240 GPa. We calculated the electronic density of states (e-DOS) of three a-N samples (except for the LC512) prepared at 120 GPa employing the recent meta-GGA SCAN functional [49]. It turned out, however, that the e-DOS has a semimetallic character which might be due to some underestimating of the band gap by the SCAN functional.

B. Decompression of a-N to $p = 0$ at 100 K

After characterizing the local structure of polymeric a-N at high pressure we studied its structural evolution upon low-temperature decompression, motivated by the experiment of Eremets et al. [16], where a-N was in one case successfully decompressed to ambient pressure at temperature below 100 K. We chose to take the glassy 512-atoms sample of a-N as the representative one and brought it down to $p = 0$ at $T = 100$ K in steps of ...
\( \Delta p = 20 \text{ GPa} \) (see also Fig. 1). Evolution of nitrogen coordinations along the process is shown in Fig. 8. Throughout the decompression, we observed two rather sharp changes in coordinations upon change of pressure from 60 to 40 and from 20 to 0 GPa. We believe that the apparent sharp character of these changes is related to the fast decompression in the simulation and it is likely that if we could decompress the system more slowly and with much smaller pressure steps \( \Delta p \) the evolution would be more gradual. The first change is related to the dramatic drop of the number of 3c atoms and increase of the number of 2c atoms. This correlates with the change of slope of the density and energy (Fig. 9) curves revealing a major structural change in the system. This structural transformation can also be seen in Fig. 10 where the presence of longer chains made of 2c atoms is well visible at 40 GPa. Starting at 20 GPa we also observe the onset of partial molecularization of the system (Fig. 8) that becomes even more pronounced at 0 GPa. The number of 3c atoms continues to decrease while number of 1c atoms increases by roughly the same amount. Interestingly, during this process the number of 2c atoms does not change much. This, however, does not imply that 2c atoms do not change coordination. Instead, two transformation processes proceed at the same time and roughly at the same rate: 3c atoms turn into 2c atoms and 2c atoms turn into 1c atoms. As can be seen in Fig. 10, the final amorphous form of nitrogen decompressed to ambient pressure (a'-N) is significantly less dense and structurally very different from the high-pressure forms.

The decompressed a'-N form contains around 20% of 1c atoms, some of which represent \( N_2 \) molecules that are stable inside the voids of polymeric network made up of 2c and 3c atoms. The structure of the network is based on the presence of 3c atoms which act as nodes connected by substantially longer (compared to a-N at 120 GPa) chain segments made of 2c atoms (see Fig. 10). We note that the decompressed a'-N can be regarded as non-equilibrium amorphous structure, similarly to high-density-amorphous (HDA) water ice decompressed to \( p=0 \) at liquid nitrogen temperature [51]. It is in fact doubly metastable structure - with respect to equilibrium amorphous structure at \( p=0 \), which is molecular disordered and also with respect to crystallization. Even though the energy difference between the fully 3c single-bonded cg-N and molecular \( N_2 \) form at \( p=0 \) is predicted to be as high as 1.4 eV/atom [2], this value can hardly be expected in experiment since cg-N has not been successfully decompressed to ambient pressure. In decompressed a'-N a lower value should be expected due to the existence of large amount of 2c and 1c atoms resulting in much smaller fraction of single bonds. We calculated the energy difference between our a'-N form and
FIG. 10. Atomic configurations from the decompression of glassy a-N with 512 atoms at $T = 100$ K at different pressures: in the top figure is the structure at 120 GPa with density 4.361 g/cm$^3$, the middle one represents the structure at 40 GPa with density 3.376 g/cm$^3$ and in the bottom figure is the structure decompressed to $p = 0$ with density 1.149 g/cm$^3$ (a’-N). The different colours represent different coordinations of N atoms. The blue color represents the 3-coordinated atoms, yellow the 2-coordinated and orange the 1-coordinated. Red color represents the 1-coordinated atoms within a molecule. Visualization was made by VESTA package\[50]\.

C. Molecularization of a’-N after heating

Since one would like to preserve at ambient pressure as much of the polymeric structure as possible it is interesting to investigate the thermal stability of the decompressed a’-N sample and the mechanism of its molecularization. To this end we decompressed the LC256 sample down to $p = 40$ GPa during 60 ps in steps of 20 GPa. Further decompression to $p = 0$ was in this case performed more slowly during 62 ps in steps of 2 GPa resulting in an a’-N-sample. Since at low temperatures we cannot observe the molecularization process on its natural time scale which is too long for MD simulation, we chose to work at higher temperature and gradually heated the system from 100 K to 300 K during a 130 ps run. The structure in our simulation did not entirely convert into a molecular form, however, the fraction of molecules increased significantly from 6% to 14% (see Fig.11 A). Most of the atoms in the structure remained 2c (change from 70% to 66%), nevertheless the fraction of 3c atoms decreased from 18% to 10%, while that of 1-coordinated chain ends (excluding molecules) increased from 6% to 11%. To analyze the mechanism closer we show in Fig.11 the evolution of the number of different bond types (B) and the total number of broken/created bond types (C$^2$).

First we note that no 1c-3c bonds are present (Fig.11 B). The breaking of 1c-2c and 1c-1c bonds is not observed since it would result in non-bonded atoms which is highly unlikely in nitrogen at these temperatures (Fig.11 C). The largest change is seen for the 2c-3c bonds, mainly due to 2c-3c bond breaking (Fig.11 C). As we can see, all molecule creation events (increase of number of 1c-1c bonds, Fig.11 B) are accompanied by 2c-3c and 2c-2c bond breaking (Fig.11 C). First bonds that break are 2c-3c resulting in open chains. Later, after 40 ps, when the temperature reaches about 200 K also 2c-2c bonds start to break. This latter process appears to correlate better with the increase of number of 1c-1c bonds and therefore can be considered as the main mechanism for the formation of molecules. Our analysis suggests that molecules are created mainly from open chains and not by directly detaching from 3c atoms.

V. SUMMARY AND CONCLUSIONS

We prepared polymeric a-N at high pressure of 120 GPa in three different ways, including quenching from $\alpha$-N$_2$ molecular crystal at $p = 0$ and found it to be 0.87 eV/atom which represents about 60% of the ideal value of 1.4 eV/atom.

\footnote{We note that the creation or breaking of certain bond is not the only way how the bond type can enter or leave the statistics. For example, if a 2c-3c bond breaks it does not anymore count. However, the originally 2c atom becomes 1c atom and the originally 3c atom becomes 2c atom and therefore the number of bonds other than the broken 2c-3c is also affected.}
liquid, pressure-induced amorphization and evolutionary search. The structure of all three versions of a-N was found to be quite similar, consisting of mainly 3-coordinated atoms linked by a small amount of short chains. While the short range order of a-N is similar to that of polymeric cg-N, we found significant differences in the distribution of dihedral angles which is in a-N quite broad. For this reason a-N cannot be considered as a plain disordered version of cg-N. We managed to decompress a-N to ambient pressure at temperature of 100 K, in agreement with Ref. [16]. Upon decompression the structure undergoes substantial changes around 60 GPa where the fraction of 3c atoms and of single bonds decreases and the length of zig-zag chains (made of 2c atoms) connecting 3c atoms grows. Below 20 GPa molecules start to appear. The final a’-N structure at 100 K and p = 0 consists of small number of 3-coordinated atoms linked by longer polymeric chains and some number of molecules is also present. We calculated the energy stored in such decompressed amorphous phase (difference between a’-N and α-N2 molecular crystal at p = 0) to be about 0.87 eV/atom. This actually amounts to more than half of the ideal value calculated for the cg-N phase decompressed to p = 0 [2]. Finally, we analyze the process of molecularization of the decompressed amorphous phase by heating it to room temperature and show that its main mechanism is creation of molecules from open chains.

On the methodological side, the application of EA to search for amorphous structures may represent a promising new approach to generate amorphous materials that in principle can be applied to practically every system. It could open new possibilities for generating and studying amorphous form of e.g. poor glass formers for which it was not yet possible to avoid crystallization and experimentally prepare a disordered structure. At the same time it may allow to study the structural evolution under pressure by preparing the amorphous structure from scratch at different pressures. This would be of particular interest in connection with the phenomenon of polymorphism which is still incompletely understood even in important compounds such as, e.g., water. In comparison to commonly used approach to preparation of glassy structures based on cooling a liquid, evolutionary algorithm represents an athermal process where no physical temperature is involved and therefore it might in principle converge to some form of “ideal glass”, long before reaching the crystalline state.

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