Structure of amorphous carbon quenched from liquid in the pressure range 1–40 GPa: Molecular dynamic modeling

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Abstract. It is well known, that quenching from the liquid state is the basis of many methods for creating new materials with unique properties. Liquid and amorphous carbon are a mixture of atoms with different states of hybridization (sp\textsuperscript{1}, sp\textsuperscript{2}, sp\textsuperscript{3}) owing to polymorphism. It is claimed that there is a tendency of growth of sp\textsuperscript{1} atoms in liquid and amorphous carbon at decreasing pressure. Great interest has been shown recently to carbyne and pseudocarbynes, consisting of sp\textsuperscript{1}-hybridizing atoms. These materials have unique optical and mechanical properties. In the present work a pressure dependence of the structure of amorphous carbon, quenched from liquid is studied by molecular dynamics simulation in the pressure range 1–40 GPa. The interaction between carbon atoms was determined by two bond-order potentials: Airebo and ReaxFF. These two potentials take into account the type of a chemical bond as well as breaking and formation of new chemical bonds during the modeling process. We study a bulk quenching from liquid carbon in the NPT ensemble at a constant pressure and determine the distribution of chemical bonds sp\textsuperscript{1}–sp\textsuperscript{2}–sp\textsuperscript{3} in amorphous carbon during the quenching. Quenched liquid structure modeling at a pressure of 1 GPa and the structure of an amorphous carbon sample obtained experimentally at a pressure of 25 MPa by Raman spectroscopy showed that the sp\textsuperscript{1} fraction of carbon was significant.

1. Introduction
Liquid and amorphous carbon are essentially disordered. Polymorphism generally typical for carbon results in the fact that these substances are a mixture of atoms with different states of hybridization sp\textsuperscript{1}, sp\textsuperscript{2}, sp\textsuperscript{3}. For this reason, one of the problems discussed in the literature [1–3] is the presence of a first-order phase transition between hexagonal-like and trigonal-like fluids.

Simulation of nucleation in a supercooled liquid carbon was executed by the group of authors [2]. They studied in detail a diamond carbon phase formation from the supercooled liquid at relatively high (higher than the pressure at the triple point of diamond–graphite–liquid, 10–11 GPa) pressures. In [4] an experimental study of the fluid near the triple point of graphite–liquid–vapor at pressures of about 0.01 GPa was done.

Recently, structures of disordered (amorphous) carbon have been obtained in a number of processes, including spallation in graphite targets under negative pressure upon nano- and picosecond laser irradiation [5, 6].

In this paper we study the changes in the structure of amorphous carbon, quenched from the liquid state, in the pressure range 1–40 GPa. Molecular dynamics (MD) simulation of structural
properties of amorphous carbon at pressures below the triple point diamond–graphite–liquid has a practical interest to determine the possibility of formation of nanodiamond structures from the supercooled liquid carbon at low pressure under quenching. This interest is caused by the fact that quenching from the liquid state is a promising method of obtaining new materials with unique properties. For testing the results of MD modeling additional experimental study of the carbon structures, quenched from liquid, is done by the Raman spectroscopy method. The obtained spectral data was compared with MD simulation results at a pressure of 1 GPa.

2. MD modeling

Software package for MD simulation LAMMPS (large-scale atomic/molecular massively parallel simulator) [7] is used for our research. An initial simulation cell is a cube with an edge of 42.9 Å with periodic boundary conditions containing 11 408 carbon atoms. The interaction between carbon atoms (both in the liquid and amorphous states) was determined by two empirical bond-order potentials. Such potentials take into account the type of a chemical bond as well as breaking and formation of new chemical bonds in the modeling process.

The first potential is an empirical bond-order potential Airebo (adaptive intermolecular reactive empirical bond-order potential) [8], which functional form is the sum of the Brenner Rebo [9] potential, the Lennard-Jones potential, and the torsion term. The Rebo potential considers only short-range interactions (less than 2 Å), depending on the coordination of each atom and the type of chemical bond between atoms. This potential describes the formation and breaking of chemical covalent bonds and different bonding configurations of each atom. The Lennard-Jones potential describes the long-range interaction between atoms at a distance of 2–10.2 Å. The torsion term is a 4-particle potential, considering the dihedral angle between the planes formed by each pair of atoms. Fitting of parameters of the Airebo potential was based on a large set of experimental data on properties of various carbon and hydrocarbon structures [8]. This potential has been successfully used to simulate different carbon and hydrocarbon materials [8–12]: diamond, graphite, amorphous carbon, liquid hydrocarbons, hydrocarbon polymers and films.

The second potential is an empirical bond-order potential ReaxFF (reactive force field for hydrocarbons), describing a chemically reacting complex systems [13]. The ReaxFF functional form, used in LAMMPS, is very complicated and is described in detail in [14,15]. The potential differs from the other bond-order potentials by very detailed consideration of all kinds of interactions between the atoms in the material. It describes not only formation and breaking of chemical bonds, the influence of an atom hybridization and torsion interactions, but also the long-range van der Waals forces, Coulomb forces [16, 17], the chemical bond-order and the influence of atomic coordination numbers. Such a complete description of the interaction energy allows us to simulate sophisticated and complex interaction between the atoms, but there are also serious drawbacks. The main disadvantage of this potential is not only the increasing demands of computing power, but the complexity of its parameterization (fitting of coefficients) for specific substances. Typically, the functional coefficients are determined on the basis of quantum mechanical calculations. In the present study, we used the parameters of the ReaxFF potential from [18], where the correction term that takes into account the London dispersion forces was added to the main functional form.

One of the most important parameters of quenching is the cooling rate. As shown in [19, 20], structural properties of the amorphous carbon, quenched from the liquid carbon in MD simulation can greatly depend on the quenching rate. According to our estimates [21] from MD experiments, the cooling rate of liquid carbon quenching on a cold face of the diamond substrate is $10^{15}$ K/s. This value was used in this work.

To obtain the necessary structure of amorphous carbon by MD the bulk quenching from the liquid carbon in the $NVT$ ensemble is performed at a constant density chosen from experimental
data. To verify the correctness of MD simulation the structure of the obtained amorphous carbon compared with the corresponding experimental structure.

In our calculations, we study the bulk quenching from the liquid carbon in the NPT ensemble at constant pressure to determine the influence of pressure on the structure of the obtained amorphous carbon. First of all, we are interested in the distribution of chemical bonds, $sp^1$–$sp^2$–$sp^3$ in the amorphous carbon. In the first stage of simulation the equilibrium cells with liquid carbon were prepared in the NPT ensemble at a temperature $T = 6000$ K and pressures $P = 1, 5, 10, 25, 40$ GPa. Then, these cells were quenched at a speed of $10^{15}$ K/s (1 K/fs) from 6000 K to 300 K in the NPT ensemble. The change in temperature during the quenching was maintained by a direct scaling of velocities of the atoms. This simple approach was used because we are not interested in thermodynamic properties during the quenching process. Thus a number of amorphous carbon structures at different pressures were prepared.

3. Simulation results
The analysis of coordination fractions ($sp^1$–$sp^2$–$sp^3$) for atoms in the simulation cell was performed by calculating the nearest-neighbor coordination number $Z$. This is the number of the nearest neighbors to a given atom within the coordination sphere of a radius equal to the first minimum of the radial distribution functions (RDF). If an atom has 4 neighbors ($Z = 4$), it is believed that all these atoms have $sp^3$ hybridization, if $Z = 3$–$sp^2$ hybridization, and finally, for $Z = 2$–$sp^1$ hybridization. Obviously, this approach (nearest-neighbor analysis) contains many uncertainties, since the RDF shape can be quite complicated and often the determination of the first RDF minimum is not an easy task. However, in classical simulation this method of determination of the type of chemical bonds is quite reasonable.

Results of our simulation are presented in a graphical form in figure 1 for the Airebo and ReaxFF potentials.

The analysis of figure 1 shows that the quantitative data obtained for the Airebo and ReaxFF potentials differ significantly. It is well known that quantitative MD simulation results may depend not only on the type of the potential, but also on the fitting parameters of a given potential. On the other hand, the qualitative results for the selected potentials are quite the same. With increasing pressure the number of atoms of $sp^3$ hybridization increases while the number of $sp^1$ atoms decreases, and vice versa. This leads to the fact (assuming fraction $sp^1$ + fraction $sp^2$ + fraction $sp^3 = 100\%$) that in the range of pressure 10–12 GPa (close to the pressure at the triple point graphite–diamond–liquid) the curve of $sp^2$ atoms fraction has a maximum for both potentials. This result is consistent with the behavior of carbon in its phase diagram [22, 23]. In fact at pressures below the pressure at the triple point graphite–diamond–liquid liquid carbon has more atoms with $sp^2$ hybridization than with $sp^3$ one; on the contrary, at pressures above the pressure at the triple point graphite–diamond–liquid liquid carbon has more atoms with $sp^3$ hybridization than with $sp^2$ one.

The obtained data shows significant difference between the amorphization and crystallization processes. At pressures below the triple point graphite–diamond–liquid, the liquid carbon completely crystallizes to graphite with the $sp^2$ hybridization. At pressures above the triple point, the liquid carbon completely crystallizes into diamond with the $sp^3$ hybridization. The amorphous carbon, however, as well as the liquid carbon, is a mixture of atoms with the $sp^1$, $sp^2$ and the $sp^3$ hybridization in a wide pressure range.

For the Airebo potential the portion of atoms with the $sp^2$ hybridization in the whole range of pressure is sufficiently high: 75–90%. The part of atoms with the $sp^3$ hybridization even at a pressure of 40 GPa is only 15–17%. Such a relatively small value may be due to the fact that at high pressures for the given potential a kinetic mechanism of quenching significantly predominates in comparison with the equilibrium mechanism responsible for the formation of atoms with the $sp^3$ hybridization. Thus, for the Airebo potential there is a tendency of formation
Figure 1. Coordination fractions in the amorphous carbon at temperature 300 K as a function of pressure of the liquid quenching for Airebo and ReaxFF potentials.

of atoms with the sp$^2$ hybridization, and the number of sp$^2$ atoms changes only slightly with pressure.

Compared with the Airebo potential, changes in the fraction of atoms with the sp$^2$ hybridization for the ReaxFF potential are significantly greater. Almost linearly increasing part of sp$^3$ atoms with pressure is observed reaching 57% at 40 GPa. Surprisingly, for the ReaxFF potential at the pressure decrease below 10 GPa the fraction of sp$^3$ atoms begins to rise sharply, reaching 51% at 1 GPa. Such a high fraction of sp$^1$ atoms may probably indicate about significant reorganization of the structure and the transformation of the liquid and amorphous carbon in a polymeric state. To test this hypothesis, further studies are needed, especially because there are a number of ReaxFF potentials with different parametrizations. For this reason, we show the analysis of structure of liquid and amorphous carbon calculated by means of the Airebo potential. In figure 2 the RDFs at $P = 1$ GPa are presented.

The RDF for the liquid carbon has a classical look, typical for a disordered liquid state. The RDF for the amorphous carbon, quenched from liquid at a pressure of 1 GPa, has typical features for the amorphous state: the highest first peak, zero first minimum, a high enough and sharp second peak (compared to the liquid carbon RDF), at large distances the function tends to unity which is typical for disordered structures. The RDF results obtained in this paper qualitatively match with RDFs of the liquid and amorphous carbon, presented in [21] for numerical simulation of quenching of liquid carbon on a cold diamond substrate in NPH ensemble conditions at a pressure of 7.25 GPa for the same Airebo potential.

It is very interesting that the amorphous carbon RDF shown in figure 2, practically coincides with an amorphous carbon RDF presented in [24] for the Airebo potential, despite the fact that the conditions of quenching in [24] were different from the present work. In [24] a bulk quenching of liquid carbon with a density of 2 g/cm$^3$ was carried out in the NVT ensemble at a speed of $5 \times 10^{14}$ K/s during a temperature decrease from 5000 to 300 K. Thus, for simulations in
different ensembles (NPT and NVT) by quenching with different cooling rates similar structures of samples of amorphous carbon were obtained.

Figure 3 shows a simulation cell at the end of the quenching process for the Airebo potential at \( P = 1 \) GPa. The figure clearly indicates the fractions of carbon atoms in the linear (white \( sp^1 \) atoms), graphite-like (grey \( sp^2 \) atoms), or tetrahedral (black \( sp^3 \) atoms) configurations. The white atoms are 2-fold coordinated \((Z = 2)\), grey atoms are 3-fold coordinated \((Z = 3)\), and black atoms are 4-fold coordinated \((Z = 4)\). It is clearly seen that the biggest volume is occupied by the atoms with the \( sp^2 \) chemical bond. The fractions of \( sp^3 \) and \( sp^1 \) atoms are significantly less, and these atoms are randomly “scattered” by the volume of the cell.

4. Experimental study

Flakes of highly-oriented pyrolytic graphite (HOPG) with a characteristic size of 40 \( \mu m \) assembled into an islet were hand-pressed onto the face of a natural diamond having a thickness of 1 mm and a side length of 3 mm. The sample thus prepared was placed into a gasostat with helium pressure 25 MPa. The surface of the islet was illuminated through the window in the gasostat by a single laser pulse of about 1 ms duration [21]. Upon the irradiation the flakes first melted, and then the melt was quenched on the natural diamond having the highest thermal conductivity of about 2000 W/(m K). Quenching from liquid carbon at a pressure of 25 MPa resulted in the production of amorphous carbon and then an inverse replica was prepared to study amorphous carbon by Raman scattering (RS).

To do this, a bismuth film was pressed on the diamond surface with a force of 20 MPa and then the bismuth film was torn off with the island of the disordered carbon. The actual transfer of the whole island to the bismuth film controlled by an optical microscope. This method ensured that carbon is studied on the direct contact diamond–island at a depth of the skin layer, which is about 30 nm for opaque carbon.
Figure 3. MD computational cell with amorphous carbon at 300 K: white atoms—sp\(^1\) hybridization; grey atoms—sp\(^2\) hybridization; black atoms—sp\(^3\) hybridization.

The surface of the island contacting with the diamond, were heterogeneous and contained gray inclusions with a size of tens microns. The Raman scattering spectrum from one of these inclusions is shown in figure 4. It was recorded at an excitation wavelength of 532 nm with a resolution of 3 cm\(^{-1}\) and a spatial resolution of 1 µm on the Raman spectrometer “Senterra” (Bruker).

The spectrum contains greatly expanded D and G lines of a strongly disordered graphite. Normally the E\(_{2g}\) monocrystalline graphite line is located at the frequency of 1585 cm\(^{-1}\) and has a width less than 14 cm\(^{-1}\). In our case it has been shifted to the frequency of 1592 cm\(^{-1}\) and broadened to 93 cm\(^{-1}\). Along with this, the intensity of the D-line at the frequency of 1340 cm\(^{-1}\) is higher than the intensity of the G-line. According to the Ferrary classification [25], such a picture corresponds to amorphous sp\(^2\) graphite with a characteristic crystallite size of about 1 nm, and confirms the absence of sp\(^3\) carbon.

Also, the spectrum contains a very broad wing in the region of 2000 cm\(^{-1}\). Usually this area is associated with conjugated bonds C=C and C≡C in carbon. It is known [26] that the bonding energy and, respectively, double bond Raman scattering light frequency \(\omega_{C=C}\) depends on the number of atoms in a carbon chain sp\(^1\) as \(N = \omega_1/(\omega_{C=C} - \omega_2)\), where \(\omega_1 = 3980\) cm\(^{-1}\), \(\omega_2 = 1750\) cm\(^{-1}\). Accordingly, the broad line may be an indication of the existence of carbon chains with different length \(N\) in carbon quenched from liquid.

Although the Raman method is not a quantitative method of determining the structure, and fractions of atoms with different hybridizations cannot be determined from a spectral line intensity, nevertheless according to the obtained spectrum, we can say that the fraction of sp\(^1\) atoms is significant. This follows from the fact that the cross section of the Raman spectrum for
sp\textsuperscript{2} carbon is much higher than that for sp\textsuperscript{1} carbon. In addition, as shown in [27], the conjugated bonds in carbon are rapidly destroyed by oxygen in the air for several hours after the synthesis, and in our case a few days have passed to the moment of measurement.

5. Comparison of experimental data and simulation

Due to significant fluctuations of pressure in the simulation we could fix the pressure below 1 GPa. We can see that at the beginning of the pressure range, the fraction of sp\textsuperscript{1} atoms is significant for both of the applied potential: 19\% for the Airebo potential and 51\% for the ReaxFF potential. The structure of both liquid and amorphous carbon (for the Airebo potential) is determined mainly by sp\textsuperscript{2} atoms, and the fraction of sp\textsuperscript{3} atoms is negligible.

A similar picture was obtained from the analysis of the Raman scattering data for the amorphous carbon produced by quenching from liquid at a pressure of 0.025 GPa. We also see a significant fraction of the sp\textsuperscript{1} atoms and absence of sp\textsuperscript{3} atoms.

For further development of methods for determining the structure of amorphous carbon obtained experimentally, the use of x-ray technologies is required.

6. Conclusions

(i) Simulation of amorphous carbon quenched from the liquid state showed that close to a pressures of 10 GPa (near to the pressure at the triple point graphite–diamond–liquid) the fraction of sp\textsuperscript{2} atoms has a maximum for both potentials (Airebo and ReaxFF). At \( P < 10 \) GPa, the fraction of sp\textsuperscript{2} atoms is decreased due to the rise of the fraction of sp\textsuperscript{1} atoms (the part of sp\textsuperscript{3} atoms is small); at \( P > 10 \) GPa, the fraction of sp\textsuperscript{2} atoms decreases due to the increase of sp\textsuperscript{3} fraction (the part of sp\textsuperscript{1} atoms is small).
(ii) The results of the Raman spectroscopy study of amorphous carbon, quenched from liquid carbon at a pressure of 25 MPa confirm a significant fraction of sp\(^1\) atoms in amorphous carbon. The main contribution to the structure of the amorphous carbon is determined by sp\(^2\) atoms, and the fraction of sp\(^3\) atoms is negligible.

(iii) Analysis of the relationship between chemical bonds distribution and pressure showed that the structure of amorphous carbon quenched from liquid depends on the “equilibrium” phase transitions in carbon, even in a non-equilibrium process at very high quenching rate of 10\(^{15}\) K/s.

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