Quenching of liquid carbon under intensive heat transfer to the cold diamond substrate: Molecular-dynamic simulation

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Abstract. Quenching of liquid carbon \(T = 6600\) K on a cold diamond substrate at \(T = 300\) K in conditions close to the experimental laser melting of dispersed graphite on the substrate of natural diamond is investigated using molecular dynamics (MD) simulations. Quenching was carried out for two types of boundary conditions on the side opposite to the diamond substrate. The simulations confirmed the experimental result of the formation of amorphous carbon under such conditions. The calculations showed that the destruction of the diamond substrate did not take place because of its very high thermal conductivity. The estimation of the cooling rate of liquid carbon was done, the result is \(10^{15}\) K/s. Temperature profiles in different layers of liquid carbon were restored to reproduce the detailed picture of the quenching process. We evaluated the radial distribution functions (RDF), the distribution of carbon atom bond fractions \(sp^1–sp^2–sp^3\), the average bond length and the azimuthal angles distributions for amorphous carbon atoms. This analysis confirmed that the amorphous carbon obtained by quenching in MD-simulations had a graphite-like structure.

1. Introduction

Liquid carbon quenching on a cold diamond substrate was carried out as part of the experimental study of phase transitions in liquid carbon films. A highly oriented pyrolytic graphite (HOPG) was melted by a laser pulse (3 J, 1 ms) directly at the \((111)\) surface of initially cold natural diamond in a helium atmosphere at a pressure of 30 MPa, which is higher than the pressure at the triple point graphite-liquid-vapor. After that, the liquid carbon was quenched (by the direct contact with cold diamond) into different carbon solid forms, including amorphous. A high-resolution transmission electron microscope TITAN 200/300 was used to study a structure of different carbon solid forms obtained by quenching. To do this, ultra-thin layers were cut perpendicular to diamond substrate. Then the layers were welded by gallium ions to the electron microscope copper mesh and then thinned by the focused ion beam technology in a dual electron-ion scanning microscope Helios.

Using the microscopic images with the atomic resolution, we have found regions with an amorphous structure near the diamond–liquid interface, and the diamond substrate was not graphitized. This conclusion can be drawn by the presence of characteristic point reflections...
corresponding to the diamond lattice in the diffraction pattern of electrons from the substrate; in remelting carbon instead of the point reflections, we observed the blurred halo.

Experimental in-situ diagnostics have fundamental limitations related to the spatial resolution of the experimental equipment, since the thickness of the experimentally obtained amorphous region is only a few tens of nanometers. Determining the structure of a short-range order of matter is a very difficult task, due to the smallness of the substance volume. Therefore, to study the mechanism of formation of the amorphous carbon from the quenching of liquid carbon under conditions close to experimental ones and to study the structure of the liquid and amorphous carbon it was decided to use the molecular dynamics (MD) methods.

One of the defining parameters of the formation of amorphous carbon during quenching is its velocity [1]. This is because the amorphous state is not an equilibrium state, so the formation of the amorphous phase strongly depends on the kinetics of the process. There are many journal papers, where authors studied the formation of amorphous structures at liquid carbon quenching by MD methods [2–6] and compared the obtained structure to samples of the amorphous carbon produced by industrial methods [2, 3, 5, 6]. In contrast to amorphous metals and alloys which have a typical quenching rate about 10^6–10^10 K/s, to obtain amorphous carbon, these velocities should be significantly higher: 10^{14}–10^{16} K/s [4, 5]. Approximately at such high cooling rates the structure of the amorphous samples obtained by MD-simulations, agrees quite well with the structure of industrial amorphous films produced, for example, by magnetron sputtering.

The purpose of our MD calculations was to 1) evaluate the quenching rate of liquid carbon layers at different distances from the boundary with the diamond substrate and compare them with available literature data and to 2) study the structure of the solid forms of carbon formed from the quenching of liquid carbon on the cold diamond substrate. If the quenching rate of carbon layers decreases with increasing distance from the boundary, it would lead to the formation of various allotropic modifications of carbon. Perhaps this is one of the effects, those lead to formation of various forms of solid carbon, which were found experimentally.

2. MD simulation details

For our MD simulations we used a well-known software package LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) [7].

The simulation cell (as shown in figure 1) is a rectangular parallelepiped with periodic boundary conditions, consisting of 20328 carbon atoms. Cell sizes are: 39 × 90.0 × 39 Å (X × Y × Z). The computational cell is conventionally divided into two parts along the Y-axis. In the lower part (Y < 49.7 Å) there is the diamond substrate (13704 atoms) at a temperature 300 K, and in the upper (Y > 49.7 Å)—the liquid carbon stratum (6624 atoms) at a temperature 6600 K. The initial cell pressure is \( P = 7.25 \) GPa.

We use the constant-pressure, constant-enthalpy ensemble NPH \( (P = 7.25 \text{ GPa}) \) for the numerical time integration of the Nose–Hoover-type non-Hamiltonian equations of motion without any temperature control and with periodic boundary conditions.

To describe the potential energy and interaction between the atoms, we use the adaptive intermolecular reactive empirical bond-order (AIREBO) potential [8], which takes into account the covalent bonding interactions as well as non-bonded interactions between carbon atoms in our simulation cell:

\[
E = \frac{1}{2} \sum_i \sum_{j \neq i} \left[ E_{ij}^{\text{REBO}} + E_{ij}^{LJ} + \sum_{k \neq i} \sum_{l \neq i,j,k} E_{ijkl}^{\text{tors}} \right],
\]

\[
E_{ij}^{\text{REBO}} = V_{ij}^{R} + b_{ij} V_{ij}^{A},
\]

where \( E_{ij}^{\text{REBO}} \) is the so-called 2-nd generation REBO potential [9] which describes the short-ranged reactive C-C interactions \((r < 2 \text{ Å})\), \( E_{ij}^{LJ} \)—the longer-ranged non-bonded interactions...
Figure 1. The simulation cell.

Figure 2. MSD of carbon atoms in the upper part of the simulation cell at $T = 6600$ K, $P = 7.25$ GPa.

$(2 \, \text{Å} < r < 10.2 \, \text{Å})$ in a form similar to the standard Lennard–Jones potential, $E_{kijl}^{\text{tors}}$—4-body potential that describes the torsion interaction various dihedral angle preferences in carbon configurations between pairs of atoms $(k, i)$ and $(j, l)$, $V_{ij}^R$ and $V_{ij}^A$ are the repulsive and attractive pairwise potentials, $b_{ij}$—the bond-order term.

In a real experiment liquid carbon is quenching due to the contact with the surface of the diamond substrate at room temperature. Boundary conditions of quenching on the side opposite to the diamond substrate in experiment are generally unknown. Therefore, during the molecular dynamic simulations we used 2 types of boundary conditions in the simulation cell:

(i) The boundary conditions of type A. The liquid carbon is quenching between two identical slabs of cold diamond;
(ii) The boundary conditions of type B. The lower boundary of the liquid carbon stratum is the cold diamond substrate. The upper boundary is the adiabatic wall, preventing the exchange of energy.

Most likely, that the real boundary conditions will should correspond to some intermediate situation be between types A and B.

In the experiment, after liquid carbon quenching, equilibrium temperature in the end of process is close to the room temperature, since the volume of the diamond substrate significantly exceeds the volume of liquid carbon. To create such conditions in the modeling process we organized the special heat sink in the diamond substrate: the temperature of a small flat layer of the diamond substrate was controlled using the Berendsen thermostat at value of 300 K. In the case of type A boundary conditions this layer is located in the middle of the diamond substrate. In the case of type B this layer is located at the bottom of the diamond substrate at the maximal distance from the interface to of the quenching liquid carbon.

The statistical ensemble NPH used in the modeling fixes the pressure inside the cell (in this case at the level of 7.25 GPa) and provides adiabatic conditions. Thus, the process of heat transfer within the cell is determined only by the initial conditions (temperatures of the diamond
substrate and liquid carbon), the quenching boundary conditions in the MD simulation (in this case, the boundary conditions of the type A or B) and the thermophysical properties of carbon (thermal conductivity and heat capacity of diamond and liquid carbon).

3. Results
To make sure that in the upper part of the cell, the carbon before modeling was in the liquid state, the mean square displacement (MSD) of the particles was calculated. It is well known that the MSD of liquid is linearly dependent on the time and the slope of this line is proportional to the self-diffusion coefficient:

$$MSD = \langle (\Delta r)^2 \rangle = 6Dt + a,$$

where \(D\) — the self-diffusion coefficient, \(t\) — time, \(a\) is a constant.

Figure 2 shows the graph of the MSD time dependence. The linear approximation of this dependence allows us to calculate the self-diffusion coefficient of liquid carbon \(D = 25 \times 10^{-5} \text{ cm}^2/\text{s}\), which have the order of \(10^{-5}\) — typical for liquids.

During the MD-quenching we measure the temperature profile along the axis Y. The cell is divided into 25 equal layers along the Y-axis with the layer height of 3.6 Å (the layer volume is 5475.6 Å³). In each diamond layer there are approximately 1000 atoms, and each liquid carbon layer contains about 600 atoms. We measured the average local temperature in each of the 25 layers as a function of quenching time.

Figures 3 and 4 show the time history of temperature profiles along the Y-axis in the liquid carbon quenching process for the boundary conditions of type A (quenching time is 15 ps) and type B (quenching time is 30 ps).

![Figure 3. Temperature profiles along the Y-axis at type A boundary conditions.](image1)

![Figure 4. Temperature profiles along the Y-axis at type B boundary conditions.](image2)

At the beginning of MD modeling \((t = 0 \text{ ps})\) we can see the temperature profile in the initial state (shown as black squares), average temperatures of the diamond and liquid carbon are respectively equal to 300 K and 6600 K. Active heat exchange between the cold substrate and molten carbon begins with the quenching process starting. It is clearly seen that after 1 ps (red circles in the figures), the temperature near the boundary between the substrate and the liquid carbon at \(Y = 49.7 \text{ Å}\) is set about 1500 K for both types of boundary conditions. Due to the very high thermal conductivity of diamond [10] there is a sharp cooling of the liquid carbon (quenching), while the substrate itself is also heated, but not enough to melt the diamond. This is clearly seen when rendering the dynamics of quenching. Probably the upper layers of
the diamond can be destroyed at the beginning of the simulation, when there is a contact of the molten carbon with temperature 6600 K with the diamond substrate. The study of this hypothesis will require additional MD calculations.

The shape of the temperature profiles is determined primarily by the type of boundary conditions, as it can be clearly seen from figures 3 and 4. As the boundary conditions of type A are symmetric, the temperature profiles inside the stratum of liquid carbon are also symmetric about the center of the stratum (approximately at \(Y = 70 \text{ Å}\)), where the temperature is maximal. The heat flux through the adiabatic wall for the boundary conditions of type B is zero and, consequently, the tangent to the temperature profile is perpendicular to the boundary. With boundary conditions A the heat flows away from the liquid carbon stratum through both borders and, as can be seen from figure 3, already after 15 ps, the temperature in the center of the stratum is lowered to 700 K. With boundary conditions B the heat outflows from the liquid carbon stratum through only one border and, as can be seen from figure 4, even after 30 ps, the temperature near the adiabatic wall is lowered only to 1800 K. The temperature curves in figures 3 and 4 allow us to analyze mainly the change in the shape of the curves during quenching. To study the quenching rate it is necessary to present these graphs in other coordinates.

In figures 5 and 6 shown is the local temperature along the Y-axis in the layers of liquid carbon depending on the quenching time for the boundary conditions of type A and B.

**Figure 5.** Local temperatures in the layers of liquid carbon depending on the time of quenching for type A boundary conditions at different distances from the diamond substrate boundary.

**Figure 6.** Local temperatures in the layers of liquid carbon depending on the time of quenching for type B boundary conditions at different distances from the diamond boundary.

The color of each curve is determined by the Y coordinate of the middle of each liquid carbon layer relative to the boundary of the diamond substrate. The distance from the center of each layer to the boundary with diamond is also indicated. From figures 5 and 6 it can be clearly seen the process of quenching of liquid carbon. The cooling of layers, closest to the boundary with diamond (at distances 1.9, 5.5, 9.1 Å) does not practically depend on the type of boundary conditions. It is obvious that the quenching of these layers begin immediately with respect to the beginning of the process of MD simulations, and that the closer to the diamond substrate surface, the sharper the initial temperature drop. After about 2–3 ps the cooling rate decreases, and all three temperature curves (1.9, 5.5, 9.1 Å) are likely transferred into the exponential decay mode.

As the distance from the boundary with diamond increases, the picture changes significantly—
there is a time delay between the beginning of the simulation and the beginning of quenching. The process for these layers begins when the quenching thermal wave that propagates from the cold substrate reaches a given layer. This situation is especially clearly seen for type B boundary conditions (see figure 6). To estimate the propagation speed of such waves it is necessary to carry out similar MD calculations for the simulation cell with much greater thickness of the molten carbon stratum. As soon as the quenching thermal wave reaches a layer of molten carbon, a significant temperature drop begins in it similar to the exponential decay.

The quenching velocity for liquid carbon is usually estimated as the cooling time from the initial temperature up to about 3000 K \[4\]. The results of calculations of quenching rates for the two types of boundary conditions are presented in table 1.

| Distance from the liquid carbon layer to the cold diamond boundary \(L\) [Å] | Type A boundary conditions, quenching rate \(V\) [K/s] | Type B boundary conditions, quenching rate \(V\) [K/s] |
|---|---|---|
| 1.9 | \(3.6 \times 10^{15}\) | \(3.6 \times 10^{15}\) |
| 5.5 | \(1.0 \times 10^{15}\) | \(1.0 \times 10^{15}\) |
| 9.1 | \(0.9 \times 10^{15}\) | \(0.5 \times 10^{15}\) |
| 12.6 | \(0.7 \times 10^{15}\) | \(0.3 \times 10^{15}\) |
| 16.1 | \(0.7 \times 10^{15}\) | — |
| 19.7 | \(0.7 \times 10^{15}\) | \(0.2 \times 10^{15}\) |
| 26.8 | — | \(0.2 \times 10^{15}\) |
| 37.5 | — | \(0.2 \times 10^{15}\) |

As expected from the previous analysis, the maximum quenching rates are achieved in the layers close to the diamond substrate (at 1.9, 5.5, 9.1 Å), and these rates are independent of the boundary conditions.

Starting with the layer 12.6 Å for type A boundary conditions the quenching rates are identical and equal to \(0.7 \times 10^{15}\) K/s. Since for these boundary conditions the temperature profiles along the axis \(Y\) are symmetric, it makes no sense to calculate the velocity at distances more than 19.7 Å. For type B boundary conditions we can see the same situation, when the quenching rates are independent on the distance to the diamond substrate beginning from the layer with distance 12.6 Å and equal to \((0.2–0.3) \times 10^{15}\) K/s.

Thus, our initial hypothesis that at a considerable distance from the diamond substrate the decrease of the quenching rate can lead to the formation of the experimentally observable crystalline spherolithic forms was not confirmed. Obtained quenching rates \((0.2–3.6) \times 10^{15}\) K/s are in good agreement with those used for “production” of amorphous carbon in atomistic modeling in the available literature [4, 5]. It is known that such quenching rates are typical for amorphous carbon formation in industrial processes [2, 3, 5, 6].

At the end of the MD-simulation we have got the simulation cell visually similar to the original one shown in figure 1, but in the upper part the liquid carbon had transferred to the solid state, presumably amorphous structure. To study this structure, we have done a topological analysis of the resulting solid disordered carbon (SDC). We calculated the density, the radial distribution function (RDF), the average distribution of carbon atom bond fractions: sp\(^1\)–sp\(^2\)–sp\(^3\), the average bond length between two carbon atoms C-C, and the average azimuthal angle distributions for triples of neighboring carbon atoms C-C-C.
Figure 7 shows the SDC RDF obtained at the end of the simulation (black color line) and the liquid carbon RDF before the MD simulation (magenta color line) for comparison.

The SDC RDF has a number of typical properties for amorphous carbon:

(i) A high and sharp first peak compared to the liquid carbon RDF;
(ii) The first minimum is equal to zero;
(iii) Rather high and sharp (compared to the liquid carbon RDF) second peak;
(iv) Tendency of the RDF to 1 at big distances, as for disordered structures (including amorphous).

The SDC RDF analysis shows, that the MD simulation of the quenching liquid carbon on the cold diamond substrate leads to the formation of amorphous carbon. This statement coincides with the experimental results for the laser melting of HOPG and subsequent quenching directly on the (111) surface of initially cold natural diamond.

From the amorphous carbon RDF the first coordination sphere radius was determined: $R_{cs} = 1.88–1.90 \, \text{Å}$ (its equal to the radius of the RDF first minimum). It helps us to analyze the average distribution of carbon atom covalent bond fractions: $\text{sp}^1–\text{sp}^2–\text{sp}^3$, presented in table 2. The same data for the liquid carbon before modeling are shown in the table for comparison.

| Bond Fraction | Liquid Carbon, $T = 6600 \, \text{K}, \rho = 2.15 \, \text{g/cm}^3$ | Amorphous Carbon, $T = 400 \, \text{K}, \rho = 2.40 \, \text{g/cm}^3$ |
|---------------|---------------------------------|---------------------------------|
| $\text{sp}^1$       | 11.6%                           | 5.3%                            |
| $\text{sp}^2$       | 79.4%                           | 86.5%                           |
| $\text{sp}^3$       | 9.0%                            | 6.2%                            |

As we can see from the table, amorphous and liquid carbon consist mainly of atoms with $\text{sp}^2$ covalent bonds; this can be explained by the fact that MD simulations were carried out at pressure $P = 7.25 \, \text{GPa}$—below the triple point of the diamond-graphite-liquid carbon. The number of $\text{sp}^2$-bonds slightly increased in amorphous carbon in comparison with the liquid.
carbon. This follows from the phase diagram of carbon [11], since at \( T = 3000 \text{ K} \) and \( P = 7.25 \text{ GPa} \) the equilibrium phase is graphite, having 100\% \( \text{sp}^2 \)-bonds.

The calculations of the average bond length between two carbon atoms and the average azimuthal angle distributions for triples of neighboring carbon atoms show that both distributions have maxima, the first is about 1.44 Å and second is about 120°. Quite well known, these values are typical for graphite-like structures.

Therefore, the results of our structural analysis clearly show that the amorphous carbon in the MD-simulations is a graphite-like material (i.e. most of atoms are connected by \( \text{sp}^2 \) covalent bonds), therefore, we expect that the same result should be in our experiment. This result is very important because neither an experimental in-situ diagnostics, nor a high resolution transmission electron microscope does not allow us to study the structure of amorphous carbon.

4. Conclusions
(i) The formation of amorphous structure in the quenching of liquid carbon at a temperature of 6600 K on the cold diamond substrate, as in the experiment with the pulsed laser heating, is confirmed by MD-simulations.

(ii) Due to the high thermal conductivity of diamond, the diamond substrate (at room temperature) was not destroyed during its contact with the liquid carbon at a temperature of 6600 K.

(iii) MD analysis shows that the quenching rates of the liquid carbon layers are independent of the distance to the diamond substrate (at a considerable distance from it) and equal to \((0.2–0.3) \times 10^{15} \text{ K/s}\).

(iv) Structural analysis of amorphous carbon obtained by MD-simulation at a pressure of 7.25 GPa showed that it has a graphite-like structure.

Acknowledgments
This work was supported by the Russian Foundation for Basic Research (grants No. 13-08-01098 and 13-08-12248).

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