Liquid carbon quenching on a cold diamond layer:  
Multiparticle molecular dynamics simulation

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Abstract. In the present paper, in order to create the model structure of amorphous carbon, we have performed classical molecular-dynamic calculations of liquid carbon quenching on a cold diamond substrate. For this purpose a double-layer simulation cell diamond–liquid carbon containing 90,000 atoms of carbon at a pressure of 1.2 GPa has been used. We have exploited a classical potential ReaxFF$_{C-2013}$. Characteristic quenching rates versus the distance from the diamond substrate and the velocity of thermal front of quenching have been obtained. The influence of the number of particles in a simulation cell on the results has been investigated as well.

1. Introduction
To investigate phase transformations in metastable diamond and liquid carbon we carried out a number of experiments on the cooling of a thin liquid carbon layer on a cold diamond surface. The experimental unit is described in [1]. We pressed manually an island of highly-oriented pyrolytic graphite flakes cca 40 $\mu$m in diameter and 1 $\mu$m height on the natural diamond face (111) of crystal about 1 mm thick and with a side length of 3 mm. The sample obtained was mounted in a hot isostatic press with the quartz window so that the diamond crystal face was oriented vertically, and the island faced the window. The graphite is known to melt only above the pressure in the liquid–graphite–vapor triple point (11 MPa [2]); at a lower pressure it sublimates to a gaseous state. That is why, a helium pressure of cca 25 MPa was maintained in the hot isostatic press. The island surface was subjected to a single Nd solid-state laser emission pulse having a wavelength of 1.06 $\mu$m, duration about 1 ms and energy of 5 J. The focus spot was cca 1 mm of diameter. This resulted in remelting of flakes, and the melt obtained was quenched on the diamond surface, forming various solid structures of carbon. The melting of such an island is equivalent to the fall of a melt drop on the cold substrate. A special role in this process plays an extremely high diamond thermal conductivity exceeding 2000 W/(mK) for natural diamond samples at the room temperature [3].

After the cooling of the melt we cut out a slice from the sample using the focused ion beam milling technique [4]. The slice obtained was investigated in the high-resolution transmission electron microscope TITAN 200/300. The slices were cut out in the direction perpendicular to the substrate. The signs of amorphous carbon presence were detected on a slice of the solidified drop.
The thickness of amorphous area obtained in the experiments is tens of nanometers only. This makes extremely difficult the investigation of mechanisms of the amorphous carbon formation directly during liquid carbon quenching. That is why, to study liquid carbon quenching and amorphous carbon structure we carried out molecular-dynamic (MD) calculations [5] and estimated the liquid carbon quenching rate as $10^{15}$ K/s [6]. As shown in [7], quenching rate is one of the determinative parameters for the amorphous carbon formation. In [6] it was also investigated the structure of a model amorphous carbon.

Despite the very important results obtained, there were an essential limitation of classical MD calculations in [6] which did not allow a comprehensive investigation of this problem. First of all, it is caused by the fact that the simulation cell in [6] contained 20,328 atoms of carbon, and, hence, the liquid layer thickness was only 40 Å. This did not allow us to study the quenching thermal front velocity inside the liquid carbon layer. The fact is that the cooling (quenching) of liquid carbon layers remote from the boundary with the diamond starts when the quenching thermal front reaches such a layer. And only thereafter an intensive decreasing of temperature in this layer begins. To estimate this thermal front velocity, similar MD calculations are required, but the simulation cell must have an essentially greater thickness of a liquid carbon layer and, respectively, much more atoms of carbon, than in [6]. Additionally, it was shown in [6] that the quenching rate of liquid carbon layers remote from the boundary with cold substrate does not depend on the distance to the latter. This conclusion should be verified for MD simulation with a greater number of particles. In [6] MD simulation of liquid carbon quenching was performed at a pressure of 7.25 GPa, what was related to the peculiarities of the complicated double-layer system model. But the pressure of 7.25 GPa is essentially higher than that in the hot isostatic press during the experiments. To understand actual processes taking place in the experiments, the pressure in MD simulation should be decreased at least to 1.0 GPa. This paper is aimed to overcome the limitations of earlier MD calculations of [6] and obtain more reliable data of liquid carbon quenching mechanisms.

2. MD simulation

To perform MD calculations, we used a well-known software LAMMPS [8]. A basic simulation cell with periodic boundary conditions is shown in figure 1. It has the form of a parallelepiped extended along the Y-axis. The cell dimensions along the axes X, Y, Z are 64.3, 180, 64.3 Å. Inside the simulation cell there are 90,852 atoms of carbon, among them 32,704 atoms of liquid carbon and 58,148 atoms of the diamond structure. The liquid layer thickness is 100 Å. The initial simulation parameters at the moment $t = 0$ are the following: the pressure in the cell is 1.2 GPa, the diamond layer temperature is 300 K, the liquid carbon layer temperature is 6500 K.

We used the classical coordination potential ReaxFF, proposed by the authors of [9] for the first time. The functional form of ReaxFF used in LAMMPS is rather complicated and described in addenda (supporting information) [10]. Technical details of the ReaxFF implementation in LAMMPS are given in [11]. ReaxFF describes a wide range of interactions between atoms of a substance. Formation and rupture of chemical bonds, torsion interactions, long-range Van der Waals forces, Coulomb forces, coupling of chemical bonds, influence of the atoms coordination numbers are taken into account. The ReaxFF functional parameters (coefficients) are generally found based upon the comparison with quantum-mechanical calculations. In [12] it is shown that the ReaxFF potential is applicable at the conditions different from the states where the potential parameters were found. Thus, the ReaxFF potential has the transferability property.

Here we use the potential ReaxFF$_{C-2013}$ [13] with parameters taken from a supporting information [14]. The authors of [13] redefined the parameters of the potential ReaxFF/cho from [15] for a more accurate description of condensed phases of carbon. The parameterization of ReaxFF$_{C-2013}$ is based upon the density functional theory calculations of graphite and diamond equation of state, formation energy of various defects in graphene, formation energy of fullerenes.
Figure 1. Initial simulation cell.

molecules, formation energy of various amorphous phases of carbon. We used a very low time step (0.05 fs) which allows us to correctly take into consideration the formation and rupture of chemical bonds, Coulomb forces and oscillations of atoms during the MD simulation [16, 17].

MD simulation of liquid carbon quenching was carried out within the NPH ensemble to maintain the contact with the cold diamond layer at a constant average pressure in the cell of 1.2 GPa. In real experimental conditions liquid carbon has a contact with cold diamond at one side only. Therefore, in the simulation on the boundary surface of the cell, perpendicular to the Y-axis and having coordinate 180 Å (see figure 1) special adiabatic conditions were created. In fact, it is the periodic boundary conditions along the Y-axis that make it possible to prevent for the heat outflow from the liquid carbon layer through the upper boundary of the cell (see figure 1). For this purpose, a thin region of thickness 5 Å, adjacent to the lower boundary and having coordinates from 0 to 5 Å along the Y-axis, is allocated at the bottom of the diamond substrate. Carbon atoms in this region remain fixed during the simulation. Due to the periodic boundary conditions along the Y-axis, the upper boundary of the liquid carbon layer adjoins the layer of fixed atoms in the image of the simulation cell located at the top. This thin layer of fixed diamond atoms blocks the energy flux through the upper boundary of the simulation cell, thus creating an adiabatic boundary. Above this layer of fixed atoms there is a second thin layer of carbon atoms, having coordinates from 5 to 10 Å along the Y-axis. The
temperature of atoms located in the second layer is close to 300 K due to the scaling of velocities according to the algorithm of the Berendsen thermostat [18]. This second layer of carbon atoms in the diamond substrate transmits thermal energy to the thermostat from the layer of liquid carbon at a temperature of 6000 K through the diamond substrate layer. The second layer was introduced to simulate a large thickness of the diamond substrate in the experiment. The described technique allowed an approximation to the experimental conditions where the volume of the diamond substrate is significantly greater than that of liquid carbon, and at the end of quenching the average equilibrium temperature is close to the room one. In addition, a thin layer of diamond substrate, where temperature is controlled by the Berendsen thermostat can be considered simply as a model boundary condition $T = \text{const}$ for the rest of the simulation cell.

During the MD simulation of quenching the temperature profile was calculated along the Y-axis of the simulation cell. To this end, the cell was divided into 50 parallel layers along the Y-axis, each 3.6 Å height. In each layer an average temperature was calculated versus the time of quenching. This made it possible not only to calculate the temperature profile variation during the quenching along the Y-axis of the simulation cell, but also to estimation the quenching rate for each liquid carbon layer.

3. Results
The temperature profile variation along the Y-axis during the liquid carbon quenching versus the layer number $N_Y$ is shown in figure 2. Layers 1 and 2 are excluded from figure 2, since in these layers there are immovable atoms. The kinetic temperatures of layers 1 and 2 are zero.
Figure 3. Temperature profiles along the $Y$-axis at the initial stage of liquid carbon quenching.

by convention. At the initial moment ($t = 0$ ps) the profile has a stepwise shape, the average temperature of the diamond substrate is 300 K and that of liquid carbon is, respectively, 6500 K. In layer number 23, there are atoms both of the diamond substrate and the liquid carbon layer. The temperature of the 23rd layer was calculated as the average over all atoms in this layer, therefore the initial temperature of the layer is equal to 4500 K. Then the process of active heat interchange begins between the layers of the cold diamond and liquid carbon in accordance with the heat conductance mechanism. Due to the very high diamond thermal conductivity—2000 W/(m K) [3] and its significantly greater mass as compared with liquid carbon, there is a sufficiently fast cooling rate (quenching) of the liquid carbon layer. In this quenching process the diamond substrate is not destroyed, and its maximal temperature at the boundary with the melt reaches cca 1500 K. At $t = 250$ ps the average temperature of the cell becomes equal to 300 K.

The temperature profile variation along the $Y$-axis of the simulation cell at the initial stage of quenching is shown in figure 3. Layers 1 and 2 are excluded from figure 3, as in figure 2. The motion of the thermal front of quenching along the $Y$-axis is observed very well. At the start of quenching the temperature of liquid carbon layers remote from the diamond boundary remains at the level of 6500 K. With the development of this process, the thermal front of quenching moves, and the growing volume of liquid carbon takes part in the heat transfer. Our estimations show that after 20 ps after the start of quenching, the thermal front reaches the upper boundary layers of liquid carbon, and then the quenching of the whole liquid carbon layer begins. Taking into account that the liquid layer thickness is 100 Å, we obtain the velocity of the thermal front of quenching to be equal to 5 Å/ps or in SI units 500 m/s. This value allows
to estimate a characteristic time of quenching in actual experiments. This is very important for the reproduction of quenching in laser heating experiments.

The results of MD calculations help us in obtaining the liquid carbon quenching rate versus the layer position towards the boundary with the diamond substrate. In figure 4 shown is the temperature evolution in five liquid carbon layers. Layer \(N_Y = 24\) is adjacent to the boundary with the diamond substrate and layer \(N_Y = 49\) is at a maximum distance from it.

The curves in figure 4 show very obviously the quenching process at different distances from the boundary with the diamond substrate. The closer to the substrate, the higher the cooling rate at the initial stage and, respectively, the more is the curvature of the temperature dependence.

For liquid carbon, it is conventional to calculate quenching rate versus time of cooling at temperatures higher than 3000 K [19]. In our simulation the quenching was assumed to start when the temperature in a layer reached 6000 K. In table 1 we summarize the results of quenching rate calculations versus the distance from the boundary with the diamond substrate.

As it was expected from the qualitative analysis of results in figure 4 and table 1, the maximum quenching rates are reached in liquid carbon layers, close to the boundary with the diamond substrate (\(N_Y = 24, 30\)). The data obtained in this work for these layers coincide with those of [6]. With the growing distance from the boundary the quenching rate decreases. Analyzing the data shown in table 1, we can notice that the rate of quenching almost does not change beginning with layer number 40. It is quite natural to assume that with a further increase in the thickness of liquid carbon, the cooling rate will reach a constant value and the order of this quantity \(10^{13}\) K/s is obtained in our calculations. Therefore, in real experiments with liquid carbon layers 1 \(\mu\)m thick the average quenching rate is expected not to exceed \(10^{13}\) K/s.

**Figure 4.** Local temperatures versus time in 5 liquid carbon layers.
Table 1. Quenching rate of liquid carbon.

| The number of liquid carbon layer $N_Y$ | Quenching rate $V$, K/s |
|----------------------------------------|-------------------------|
| 24                                     | $1.0 \times 10^{15}$    |
| 30                                     | $1.4 \times 10^{14}$    |
| 35                                     | $6.8 \times 10^{13}$    |
| 40                                     | $5.7 \times 10^{13}$    |
| 49                                     | $5.4 \times 10^{13}$    |

Based upon the temperature profiles along the $Y$-axis of the cell we can estimate the thermal conductivity coefficient for liquid carbon. Taking into account a stationary cooling regime for the liquid carbon layer, the thermal flux $Q_Y$ in the diamond substrate and in the liquid carbon layer will be the same along the $Y$-axis. Then, on the basis of the thermal conductivity theory, we can write the expression:

$$Q_Y = -\lambda_d \left( \frac{dT}{dY} \right)_d = -\lambda_l \left( \frac{dT}{dY} \right)_l.$$

Here $\lambda_d$ and $\lambda_l$ are the thermal conductivity coefficients for diamond and liquid carbon, $(dT/dY)_d$ and $(dT/dY)_l$ are the corresponding temperature derivatives along the $Y$-axis. Based on this expression, we can estimate the thermal conductivity for liquid carbon using the formula:

$$\lambda_l = \lambda_d \frac{(dT/dY)_d}{(dT/dY)_l}.$$

From the temperature profiles obtained in our calculations (see figures 2 and 3), one can find the ratio of the derivatives, and at given $\lambda_d$, one can calculate the thermal conductivity coefficient for liquid carbon. Our estimations show that the thermal conductivity coefficient for liquid carbon at a temperature cca 5000 K is 10 times lower than that of diamond at 700 K:

$$\frac{(dT/dY)_d}{(dT/dY)_l} = 0.1.$$  

According to papers [3, 20], the thermal conductivity for diamond at 700 K is approximately 900 W/(m K). Therefore, the thermal conductivity coefficient for liquid carbon at a temperature of 5000 K should be of the order of 90 W/(m K). Data on the coefficient of thermal conductivity for liquid carbon in the literature are practically absent. The available data have a wide spread: from 5 [21] to 290 W/(m K) [22]. Our estimation falls into this range. To obtain a more reliable value further investigation is required.

4. Conclusions

Our deductions are as follows:

- With the aid of multiparticle MD simulation we have obtained the velocity of the thermal front of quenching of 5 Å/ps. This parameter is necessary for correct interpretation of laser heating experiments.
- It has been shown that in real experiments that the quenching rate of a liquid carbon layer cca 1 μm thick is not exceed $10^{13}$ K/s. This result is very important for further modeling of carbon structures obtained at liquid carbon quenching on a cold diamond substrate.
On the one hand, multiparticle MD simulation confirmed the conservation of the diamond substrate during quenching [6]. On the other hand it allowed obtaining new more accurate results as compared with those of [6].

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