

MOLECULAR DYNAMICS SIMULATION OF PHASE TRANSITIONS IN LIQUID CARBON

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Thermodynamic properties and phase transformations in amorphous carbon and in supercooled liquid carbon are studied by the method of molecular dynamics (MD). The dependence of the diamond melting temperature on pressure is found. The percolation properties of structures of liquid carbon with embedded diamond nanocrystals are studied. It is shown that sp^3 atoms form a percolation cluster in the simulation volume when their total concentration reaches the value close to 0.38. At temperatures less than 5000 K the stability of diamond nanocrystals correlates with the existence of percolation cluster of sp^3 atoms. We propose the following topological criterion: amorphous carbon is diamond-like if the percolation cluster exists and the embedded diamond nanocrystals are stable.

PACS: 81.05.Uw, 61.43.Bn, 64.70.Ja, 61.46.+w, 64.60.Ak

1. INTRODUCTION

The multiplicity of structural forms of carbon originates from the structure of its electron shells. Depending on the hybridization of electron shells carbon may form 2, 3 or 4 covalent bonds. Amorphous carbon (aC), in which sp^3 bonds dominate, exhibit diamond-like properties; in a graphite-like amorphous carbon the majority of atomic bonds are sp^2 [1,2].

Along with experiments the MD computer simulation helps to determine the nature of amorphous carbon and the origin of its unusual properties. In MD simulations described in [3] the phase transformation between the graphite-like aC and the diamond-like aC has been observed. Besides the glass transition temperature T_g was identified and its pressure dependence was determined. Using these results the phase diagram of aC has been constructed. However, thermodynamic and structural properties of both liquid and amorphous carbon were not studied in detail. In particular, the question of existence of correlation between the topology of clusters of 4-fold coordinated atoms in structures of glass and liquid with the phase transition was not studied systematically.

In this communication we continue the MD investigation of liquid and amorphous carbon. The form of aC with high concentration of sp^3 atoms is called tetrahedral amorphous carbon ($ta-C$). Raman scattering experiments with $ta-C$ revealed a peak which has been attributed to the diamond nanocrystals present in $ta-C$ [4-8]. The idea of diamond nanocrystals has been proposed by McKenzie [1]. It was used recently in [9] to define the $ta-C$ as the form of $a-C$ in which the embedded diamond nanocrystals are stable. In [9] the authors studied the stability of diamond nanocrystals embedded in amorphous carbon; however they observe neither growth nor melting of these nanocrystals. This effect could be due to slow atomic dynamics in amorphous state. Here we study the stability of diamond nanocrystals embedded in supercooled liquid carbon and propose the topological criterion for their stability at low temperatures.

2. SIMULATION METHOD

The computer studies of amorphous carbon are restricted to its highly non-equilibrium forms, because of extremely slow dynamics in glassy state, which requires enormous computational time (i) to simulate annealing similar to that in real experiments and (ii) to obtain well relaxed samples.

Below we perform the constant pressure MD simulation. The periodic boundary conditions were applied to the simulation volume that contained 13824 carbon atoms. The Newton equations for the classic motion of atoms were solved using the Verlet algorithm [10] with the time step ranging from 0.4 fs to 0.7 fs. To calculate the interaction forces between atoms the empirical potential proposed by Tersoff [11] was used. The Tersoff potential proved to be successful for modelling covalently bonded materials and amorphous carbon in particular [9, 12, 13]. The simulation results obtained with the Tersoff potential agree qualitatively with the behaviour of real materials. In the literature the calculation of cohesive energy with *ab initio* [14] or tight-binding methods [15] is considered to be more accurate than MD simulation with the Tersoff potential, but these methods are unsuitable for our problem since they are at least several orders of magnitude more slow.

In each integration step the stress tensor S was calculated. The pressure is derived as $P = 2(E_k - \Xi)/3V$, where $\Xi = Tr(S)/2$ is the virial and $E_k = 1.5k_B T$ is the mean kinetic energy of atoms in the structure. The Berendsen algorithm [16] was used to control the pressure and the temperature. To generate the structure with embedded crystallites the method of Berendsen was modified to keep the density of crystallites constant when the simulation volume changes. The atomic volume in crystallites was calculated as the mean volume of Voronoi polyhedrons constructed around internal atoms of crystallites. The coordination number of each atom was found by counting neighboring atoms within the distance of 0.18 nm, i.e. in the first coordination sphere. The mean atomic coordination \bar{Z} in the structure was

found by averaging the coordination numbers over all atoms of the structure including 4-fold coordinated atoms of diamond crystallites.

3. RESULTS AND DISCUSSION

3.1. GENERATION OF STRUCTURES WITH EMBEDDED DIAMOND CRYSTALLITES

The structures with embedded diamond crystallites were formed by melting and subsequent quenching the diamond crystal at a various values of pressure. Atoms of diamond structure where crystallite had to be formed were fixed in the initial position. Depending on size and number of embedded crystallites, three types of structure were considered: (i) 8 crystallites, 216 atoms in each, (ii) 27 crystallites, 64 atoms in each, (iii) 8 crystallites, 64 atoms in each. In all three cases crystallites formed cubic lattice. Stability of several crystallites were studied in order to reduce the statistical error of simulation.

After quenching the structures with embedded crystals were equilibrated at a temperature T_L chosen in the interval between glass transition temperature T_g and diamond melting temperature. The equilibration was done in order to equilibrate the liquid around crystals, equilibrate the density of crystals and to obtain the boundaries between crystals and liquid that correspond to the minimum of free energy of the structure. The equilibration was made in two stages. In the first stage the structure was annealed for 30 ps keeping fixed the positions of atoms in crystallites. In the second stage the atoms in crystals were allowed to move and the structure were subsequently annealed at 10 K for 0.05 ps, then at 1000 K (much less than T_g) for 0.5 ps and then at T_L for 5...10 ps. We checked if the applied procedure is sufficient for structure equilibration. 8 crystallites with 216 atoms in each were embedded in structures. In the first case the specific volume was $5.6 \text{ \AA}^3/\text{atom}$, what approximately correspond to the density of diamond at value of temperature and pressure used, in the second case the specific volume was $5.2 \text{ \AA}^3/\text{atom}$, what corresponds to the density of atoms at much higher pressure, about 80 GPa. The pressure dependence of the specific volume of crystals after equilibration at $T_L = 4500 \text{ K}$ is shown in Fig. 1.

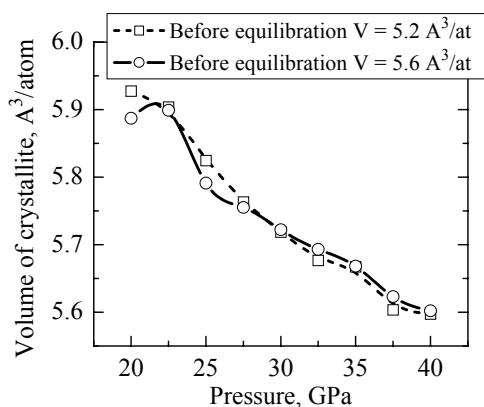


Fig. 1. Specific volume of atoms of diamond crystallites in equilibrated structures as a function of pressure at 4500 K

3.2. STABILITY OF CRYSTALLITES

The stability of diamond crystallites embedded in supercooled liquid was checked in an ordinary way, i.e. by annealing the equilibrated structures with crystallites. Three types of MD experiments were done depending on size and number of embedded crystallites (see above). The results of annealing at 4500 K are presented in Fig. 2.

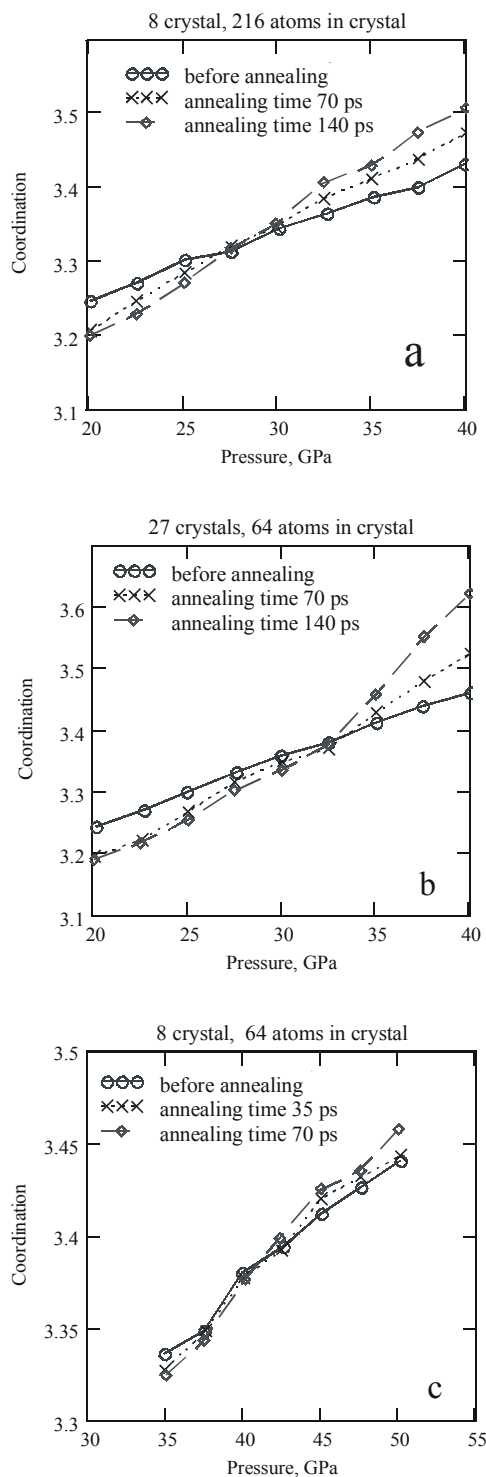


Fig. 2. The pressure dependence of the mean atomic coordination in structures before and after annealing at $T = 4500 \text{ K}$. The numbers of embedded crystallites are indicated in figures (a), (b) and (c)

It is seen that a critical pressure exists. After annealing at pressures below this critical pressure the atomic coordination in the structure decreases. At pressures higher than the critical one the coordination increases. In the first two types of experiments the critical pressure is about 30 GPa (Figs. 2,a and 2,b), and in the third type of structures the critical pressure is about 40 GPa (Fig. 2,c).

The embedded crystals are the nucleation centers for crystallization. At low pressure the embedded crystals are melting and coordination decreases. Small crystals melt faster and the coordination of structures reaches the value of coordination of liquid after 70 ps already. The volume of structures decreases when the coordination increases and vice-versa.

In accordance with the classical theory of nucleation, when the nucleus of a new phase is formed the free energy of the system increases by

$$\Delta G_{total} = n\Delta G_{phase} + \eta n^{2/3}\gamma,$$

where γ is the interface energy, ΔG_{phase} is the difference of chemical potentials of two phases (in our case these are diamond and supercooled liquid), η is the factor that depends on the shape of the nucleus, and n is the number of atoms in nucleus. In the supercooled liquid $\Delta G_{phase} < 0$, hence $\Delta G_{total} < 0$ for large n .

There exists the critical nucleus size that corresponds to $\Delta G_{total} = 0$. The critical nucleus is in unstable equilibrium with the liquid, it either melts or grows if the pressure or temperature changes. The point in which the annealing curves intersect (see Fig. 2), corresponds to the unstable equilibrium of the crystallites. From Fig. 2,a and 2,b one can see that critical pressure depends weakly on the size of crystallite. One can conclude that the size of the critical nucleus changes rapidly with a small change of pressure. However when the number of embedded crystallites of the same size is decreased, the critical pressure increases considerably (Fig. 2,c). In all three cases at the critical pressure the mean coordination has the same value close to 3.37.

In [3] the authors predicted the peculiarities in behavior of physical properties of amorphous carbon at the value of mean coordination, at which neighboring 4-fold coordinated atoms form a large cluster that penetrates the whole structure, i.e. when concentration c_4 of atoms in sp^3 configuration reaches the percolation threshold. It was found in this work that the diamond crystallites embedded in supercooled carbon liquid are stable if they are parts of percolation cluster. From the percolation theory it is known that in an infinitely large random mixture of percolating and nonpercolating sites the fraction of sites that belong to the largest cluster tends to zero as $(p - p_c)^\beta$, where p_c is the percolation threshold, p is the fraction of percolation sites in the structure, $\beta \approx 0.41$ in 3D systems [17]. In our case the percolation of sp^3 atoms is studied, $p \equiv c_4$, the cluster of neighboring sp^3 atoms are considered. The fraction of atoms in the largest cluster formed in structures equi-

brated at 4500 K (before annealing and crystallite stability examination) is shown in Fig. 3.

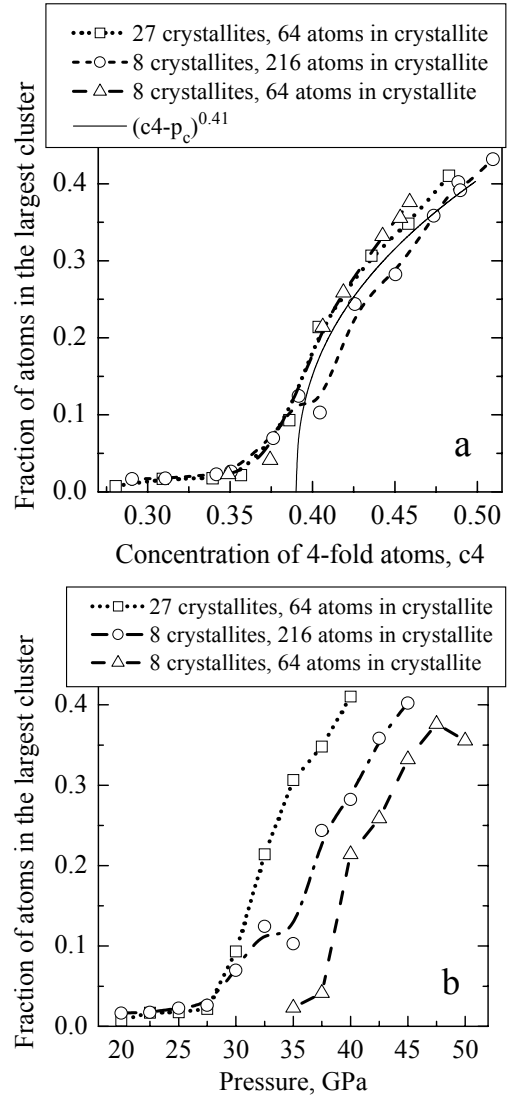


Fig. 3. Percolation properties of structures with embedded crystallites. Fraction of atoms in the largest cluster of 4-fold coordinated atoms is shown versus (a) mean concentration of 4-fold coordinated atoms in the structure and (b) pressure

One can see that in the first two experiments the percolation cluster forms at the pressure close to 30 GPa; and in the third experiment it forms at 40 GPa, that is at pressure values above which crystallites are stable. In all three simulation experiments the percolation threshold p_c is in the interval from 0.38 to 0.4. Note that the approximate value of percolation threshold on diamond lattice is 0.43. It seems that for the random 3D mixture the concentration dependence of the fraction of atoms in the largest cluster can be described by the function $(p - p_c)^{0.41}$ (Fig. 3,a). Thus the correlation of percolation effects and crystallites stability is well seen in computer experiments.

By modeling coexistence of diamond and liquid phases [18] we have found the diamond melting temperature (Fig. 4). For comparison the diamond melting line obtained in [19] using a recent empirical potential of atomic interaction is also shown in Fig. 4.

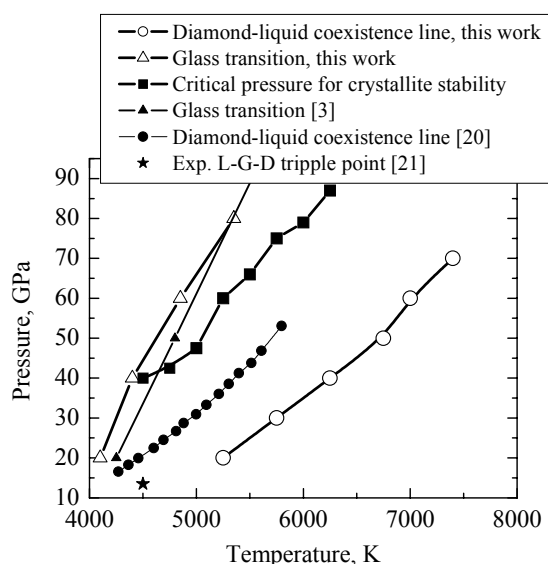


Fig. 4. State diagram of carbon. \circ - \circ - temperature dependence of the pressure, at which diamond melts, on the left of this curve the liquid is in supercooled state; \bullet - \bullet - diamond-liquid coexistence line [19]; \blacksquare - stability limit for diamond crystallites embedded into the liquid carbon; \blacktriangle - glass transition temperature from [3]; \triangle - glass transition temperature (this work). The star shows the experimental estimate of liquid-graphite-diamond triple point [20]

The stability of diamond crystallites in the structure with 8 crystallites (64 atoms in each) was examined at different temperatures. The temperature dependence of the critical pressure for crystallites stability is shown in Fig. 4. In the high temperature range this curve is parallel to diamond-liquid coexistence line.

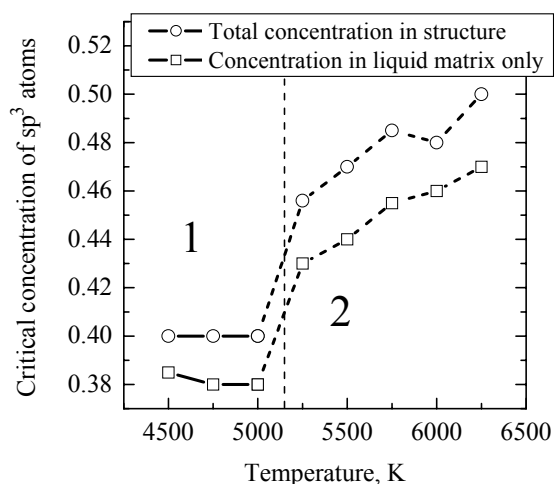


Fig. 5. Concentration of 4-fold coordinated atoms in structures with embedded diamond crystallites on the crystallites stability curve (Fig. 4). In region 1 this concentration coincides with the percolation threshold for sp^3 atoms

The mean concentration of 4-fold coordinated atoms in the structure and the concentration of 4-fold coordinated atoms in the liquid at the critical pressure are shown in Fig. 5 as a function of temperature. At 5250 K a jump is seen in these plots (Fig. 4 and Fig. 5).

At lower temperatures (region 1 in Fig. 5) the percolation phenomenon correlates with the crystallite stability. No correlation is observed at higher temperatures (region 2 in Fig. 5).

Evidently at temperatures below 5250 K the percolation cluster keeps the crystallites from melting. This result could be explained if crystallites would touch each other at the critical pressure. However crystallites are situated at a rather large distance from each other. In the case of 8 embedded crystallites with 64 atoms this distance exceeds 8 interatomic spacings.

We explain the correlation of diamond crystallites stability with the percolation phenomenon as follows: it is thermodynamically favorable for 4-fold coordinated atoms to form large clusters; hence, the percolation cluster of neighboring 4-fold coordinated atoms joins the diamond crystallites into one stable nucleus. In terms of the classical nucleation theory the correlation of the crystallite stability with the percolation may be explained by a sharp reduction of the interface energy γ when the large percolation cluster forms. Thus the low temperature part of the temperature dependence of the critical pressure (solid line in Fig. 4) corresponds to the transition from the liquid with large γ (when $\Delta G_{total} > 0$) to the liquid with small γ (when $\Delta G_{total} < 0$). The high temperature part of this dependence (the dashed line in Fig. 4) corresponds to the condition of nucleus stability ($\Delta G_{total} = 0$) in the liquid with small γ .

In a certain sense, the glass is a frozen liquid. Therefore the proposed percolation criterion may be also used to determine the stability of diamond nanocrystals embedded into the carbon glass. Thus, the definition of *ta-C* as a form of amorphous carbon in which embedded diamond nanocrystals are stable [1,9] has to be redefined as follows: amorphous carbon is tetrahedral if the percolation cluster of neighboring 4-fold coordinated atoms is present in its structure.

4. CONCLUSIONS

The results of MD study of the liquid carbon are summarized as follows:

1. The pressure dependence of diamond melting temperature has been determined.
2. The percolation properties of structures formed by carbon liquid with embedded diamond nanocrystals have been considered. It is shown that independently of the number of embedded nanocrystals the percolation cluster of neighboring 4-fold coordinated atoms forms when the total concentration of 4-fold coordinated atoms in the structure reaches the value close to 0.38.
3. It has been shown that the stability of diamond crystallites embedded into the supercooled carbon liquid depends on the presence of the percolation cluster of 4-fold coordinated atoms. The correlation of stability of diamond crystallites with the percolation phenomenon disappears at temperatures above 5000 K.
4. The topological criterion for the definition of tetrahedral amorphous carbon is proposed: amorphous carbon is tetrahedral if its structure contains the percola-

tion cluster and the embedded diamond nanocrystals are stable.

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МОЛЕКУЛЯРНО-ДИНАМИЧЕСКОЕ МОДЕЛИРОВАНИЕ ФАЗОВЫХ ПРЕВРАЩЕНИЙ В ЖИДКОМ УГЛЕРОДЕ

М.С. Бышкін, А.С. Бакай, А.А. Туркин

Методом молекулярно-динамического моделирования изучены термодинамические свойства и фазовые превращения в переохлажденной жидкости углерода. Найдена зависимость температуры плавления алмаза от давления. Изучены перколяционные свойства структур sp^3 (4-координированных) атомов, образующихся в жидком углероде с различным количеством внедренных кристаллитов алмаза. Показано, что независимо от количества внедренных кристаллитов алмаза, протекающий кластер 4-координированных атомов возникает, когда их суммарная концентрация в структуре достигает величины близкой к 0.38. Оказывается, что устойчивость кристаллитов алмаза, внедренных в переохлажденную жидкость, коррелирует с наличием протекающего кластера sp^3 атомов. Связь устойчивости кристаллитов с протеканием исчезает при температуре более 5000 К. Предложен топологический критерий для определения тетрагонального (алмазоподобного) углерода: аморфный углерод является алмазоподобным, если в нем существует протекающий кластер и внедренные кристаллиты алмаза устойчивы.

МОЛЕКУЛЯРНО-ДИНАМІЧНЕ МОДЕЛЮВАННЯ ФАЗОВИХ ПЕРЕТВОРЕНЬ У РІДКОМУ ВУГЛЕЦЮ

М.С. Бишкін, А.С. Бакай, А.А. Туркін

Методом молекулярно-динамічного моделювання вивчені термодинамічні властивості і фазові перетворення в переохлажденній рідині вуглецю. Знайдено залежність температури плавлення алмаза від тиску. Вивчені перколяційні властивості структур sp^3 (4-координованих) атомів, що утворюються у рідкому вуглецю з різною кількістю впроваджених кристалітів алмаза. Показано, що незалежно від кількості вбудованих кристалітів алмаза, кластер 4-координованих атомів, що протікає, виникає, коли їхня сумарна концентрація в структурі досягає величини близької до 0.38. Виявляється, що стійкість кристалітів алмаза, впроваджених у переохлажденну рідину, корелює з наявністю кластера sp^3 атомів, що протікає. Зв'язок стійкості кристалітів із протіканням зникає при температурі більш 5000 К. Запропоновано топологічний критерій для визначення тетрагонального (алмазоподібного) вуглецю: аморфний вуглець є алмазоподібним, якщо в ньому існує кластер що протікає, і вбудовані кристаліти алмаза стійкі.