KINETICS OF 2D-3D TRANSFORMATIONS OF CARBON NANOSTRUCTURES

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In this work we consider the gas-phase formation of carbon nanostructures from graphite sheets under high-energy processing, such as arc discharge or laser evaporation [1]. Though there are quite a few of papers that examined fullerene and nanotube formation, the folding of a single plane sheet into a three-dimensional structure has not been investigated. Thus, here we discuss this process. Elementary processes resulting in both the folding and relaxation of the imperfect structure formed are also examined. A simple evaluation of the elastic energies of nanotubes indicates that the folding of a perfect graphite sheet requires overcoming a huge energy barrier (about 15 eV for square sheets) and, therefore, it can not be observed at an arc discharge temperature. In order to obtain kinetic characteristics of the process and to examine its mechanism we carried out molecular dynamics simulations [2].

Although the energy barrier is very high, our simulations showed that the folding of a graphite sheet proceeds in about 1 ns at 3500 K (Fig. 1). This is explained by the formation of numerous defects, which increase the system entropy and, hence, substantially reduce its free energy at high temperatures. Furthermore, the folding begins not simultaneously on both sides of the sheet but only at one corner having the highest density of defects. The defects are mostly localized at the edges and their density rapidly decreases towards the sheet interior. Consequently, defects should be mainly formed in surface reactions. The folding occurs when the density of defects at one of the corners reaches its critical value.

The graphite sheets of different size and shape were considered. The energy barrier of the process is 20–25 eV, being only slightly dependent on the sheet size. As the sheet size increases, the folding time and the energy change in the overall process rise. A hexagonal sheet takes somewhat more time for folding than a rectangular one, because it has more obtuse corners. In a long and thin sheet many atoms are close to the edges and the critical density of defects can be reached in any area of the sheet. All these facts correspond to the suggested mechanism.

During the simulation, the main reactions of defects were detected and then their kinetic characteristics were evaluated for a plane graphite sheet. The simulation showed that the most important reactions of defect transformation proceed with the breaking of only one bond and thus have a barrier of about 3 eV. The reactions that require two bonds to be broken, such as the modified Stone-Wales rearrangement [3], take a negligible part in the folding. The process of defect formation can be kinetically limited at low temperatures. Furthermore, the mechanism of defect penetration into the interior of the graphite sheet is most likely associated with the formation of small defects adjacent to a ten or more-membered ring. The curvature of the sheet only slightly affects the characteristics of the reactions if its radius is more than 10 Å.

Based on the elementary processes examined, we suggested a simple scheme of defect formation at sheet edges and used it for determining the equilibrium densities of defects. According to this scheme, the minimal temperature at which the folding of graphite sheets can be observed experimentally (proceeds in about 1 s) is 2500 K.

In addition to the processes that take place before the folding, the transformation of the formed structure to more perfect one containing a less number of defects was considered. After the folding process is completed the further relaxation of the structure proceeds via the Stone–Wales rearrangements [4] and the modified Stone–Wales rearrangements of defects [3]. Nevertheless, these reactions involve many steps rather than one (Fig. 2). First a big ring forms, then two small defects adjacent to it transform into two different rings and ultimately a bond forms inside the big one, dividing it into two smaller rings. Although the structures of

the transition states of the one-step reaction and the rate-limiting step of the multistep process are almost the same, their reaction coordinates are different. We suggest that in the latter case it corresponds to vibrational modes with higher frequencies and the multistep process proceeds faster.

We also examined the possibility that the number of defects in the imperfect structure can be reduced through the addition of carbon atoms and dimers [5]. The process of the addition was shown to proceed in two steps (Fig. 3). First, an atom or a dimer is attached to an atom of the fullerene to make it four-coordinated almost without an energy barrier. Then, this new atom or dimer is built into a neighboring bond. The barrier of this step is lower than the energy released in the first one. If the first step has proceeded, the overall process will definitely result in the product formation. Moreover, atoms and dimers are eventually built into a bond to form new defects. Therefore, the addition of carbon atoms and dimers to defects is not more favorable than their addition to hexagons and should not be considered as a way of reducing the number of defects.

References:

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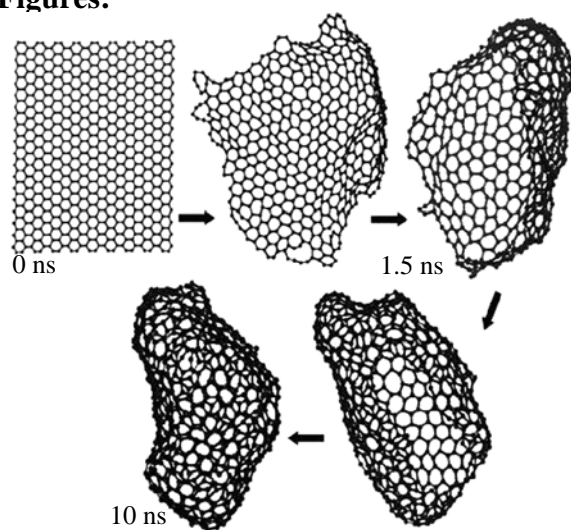[5] J. Xiaodun, J.R. Chelikowsky, Phys. Rev.B, **46** (1992-II) 5028.

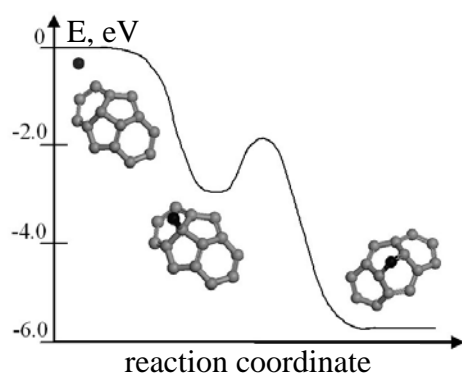**Figures:**

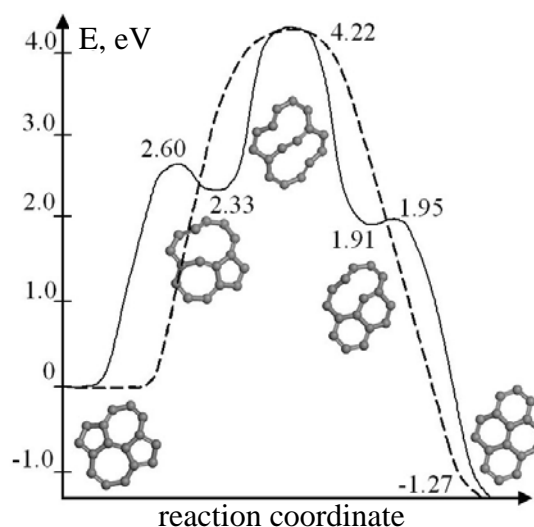Fig.1. Evolution of a graphite sheet at 3500K.

Fig 2.The modified Stone-Wales rearrangement of defects [3]. The solid line corresponds to the one-step process. The dashed line corresponds to the multistep process.

Fig. 3. The addition of a carbon atom to a common bond of two adjacent pentagons.