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Graphitization of single-wall nanotube bundles at extreme conditions: Collapse or coalescence route

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We determine the reaction phase diagram and the transformation mechanism of (5,5) and (10,10) single-walled carbon nanotube bundles up to 20 GPa and 4000 K. We use Monte Carlo simulations, based on the state-of-the-art reactive potential LCBOPII, that incorporates both covalent and van der Waals interactions among the tubes. At low temperature, upon increasing pressure, large (10,10) nanotubes first collapse and then coalesce, yielding almost perfect graphitic structures. In contrast, small (5,5) nanotubes do not collapse, but coalesce and transform to graphite via a mixed graphite-tube structure. At high temperature (above ~ 2000 K), for both (10,10) and (5,5) nanotubes, coalescence dominates the transformation to graphitic structures. We argue that the sp^3 -interlinking defects appearing at coalescence can act as seed and facilitate the transformation to diamond structures.

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I. INTRODUCTION

The transformation of carbon nanotubes under extreme conditions is of importance as it can lead to new routes for the synthesis of diamond and novel superhard, polymerized, or porous carbon structures. Single-walled and multiwalled carbon nanotubes are often produced in aligned bundles, held together by weak van der Waals interactions. These bundles of aligned nanotubes can be produced with different procedures, like arc-discharge (ARC), laser ablation, and chemical vapor deposition (CVD).^{1,2} The resulting bundles vary significantly in their size, purity (i.e., absence of catalysts), and monodispersity, as well as in the amount of defects.

In the past decade there have been several experimental^{3–10} and theoretical^{11–23} investigations focusing on the effects of pressure on bundles of single-walled carbon nanotubes (SWCNT) at room temperature. Most experimental studies indicate that the bundles undergo a structural phase transition upon increasing the pressure to a few GPa. To identify the nature of the transition, simulations and analytical models^{11–23} have been used. The nanotubes appear to deform into an oval or polygonal shape first, then to collapse into a peanutlike shape, when a critical pressure is reached. The critical pressure and some geometrical details of the structural transition depend on the radius of the nanotubes, but not on their chirality or their length. For the (10,10) SWCNT bundle, most experimental and theoretical studies locate the critical pressure at room temperature between 1.5 and 2.5 GPa.^{3,5} It is suggested²⁴ that, being stiffer, nanotubes of small radii may polymerize under a pressure of several GPa, due to the formation of covalent bonds between neighboring tubes. At ambient pressure, SWCNT bundles rearrange upon increasing temperature into multiwalled carbon nanotubes (MWCNT) or more complex graphitic structures called graphitic nanoribbons (GNR).^{6,25} Upon imposing high pressure it is possible to convert the bundle into graphite, and possibly diamond crystallites and novel polymerized or jammed structures.²⁴ The understanding of the possible transformation mechanism is still at a speculative stage, although some insight is provided by the simulations of Refs. 26–28.

In this work we address the stability of small and large radii SWCNT bundles at high pressure and high temperature by performing Monte Carlo simulations of pure (5,5) and (10,10) bulk SWCNT bundles. We employ a state-of-the-art reactive interaction potential (LCBOPII)²⁹ that accounts accurately for bonding interactions, but also incorporates long-range nonbonded interactions among the tubes. We determine the reaction phase diagram and obtain a detailed picture of the transformation pathways that are found to depend strongly on the tube size and on temperature.

II. COMPUTATIONAL SETUP

We perform Monte Carlo (MC) simulations in the isobaric (NpT) ensemble with a rectangular, periodically replicated, supercell with independent variations of the box size in the directions parallel and perpendicular to the tubes. The supercell contains eight SWCNT with five unit cells along the tube axis (z axis, 12.3 Å at ambient conditions), which is compatible with the long range tail of LCBOPII. The total number of particles is $N = 800$ and $N = 1600$ for the (5,5) and (10,10) nanotubes, respectively. At ambient conditions the radii of the tubes are 3.44 Å and 6.88 Å for the (5,5) and (10,10) nanotubes, respectively. The corresponding volume per particle are 10.77 Å³ and 15.01 Å³, to be compared to 8.91 Å³ for graphite. Simulations of a state point consist of typically 10^5 MC cycles, which follow an equilibration of 2×10^4 MC cycles, where a MC cycle consists of N attempted particle moves. The volume moves were performed randomly, with an average of one for every five MC cycles. Our computational setup is validated against the low-temperature properties.

III. VALIDATION AND LOW-TEMPERATURE PROPERTIES

Figure 1 shows the volume per particle of the (5,5) and (10,10) SWCNT bundles at $T = 300$ K, obtained by gradually compressing the bundle in a series of successive runs. The volume drops are associated with structural changes of the

FIG. 1. (Color online) Lower panel: volume per particle for the (5,5) and (10,10) SWCNT bundles at $T = 300$ K, indicated by (blue) circles and (red) diamonds, respectively. Solid and dashed lines are a guide to the eye. Statistical errors are comparable to the size of the symbols. Upper panel: typical configurations for the indicated pressures show the change in shape of the cross section of the SWCNT. For clarity, the periodic cell is replicated twice in both the x and y direction, orthogonal to the tube axis.

SWCNTs. The (10,10) SWCNT ovalize around $p = 3$ GPa [Fig. 1(a)], and at $p = 4$ GPa collapse in a peanutlike shape [Fig. 1(b)], where the tubes are arranged in the herringbone structure predicted in Ref. 15. Upon further increase of pressure, the (10,10) SWCNT further flattens [$p = 7.5$ GPa in Fig. 1(c)], and finally show some cross linking [Fig. 1(d) at $p = 15$ GPa], yielding a density close to that of graphite. The collapse pressure obtained from the simulations depends slightly on the pathway: if instead of successive compression, we perform a simulated annealing from 500 to 1 K at fixed pressure in the range 0–3.5 GPa, we find a collapse pressure of 2.5 GPa, which is in the range of the values obtained experimentally.^{3,5} Note that in our simulations the collapse is reversible, although a small hysteresis up to 1 GPa is present.

Compared to the (10,10) SWCNT, the (5,5) SWCNT collapse at higher pressures, around 12 GPa, yielding a structure of flattened tubes with some cross linking [Fig. 1(e)]. The increase in collapse pressure with decreasing tube diameter is consistent with the experimental values of 7 GPa for the (6,6) SWCNT and 12 GPa for the (7,0) SWCNT.¹⁵

IV. HIGH-TEMPERATURE HIGH-PRESSURE TRANSFORMATIONS

We now examine the transformations taking place at high pressure and high temperature. Figure 2 shows the pressure dependence of the volume per particle of the (5,5) and (10,10) bundles at different temperatures compared to the LCBOPII equation of state of graphite.³⁰ For the (10,10) SWCNT bundles a volume drop occurs at a well defined pressure that is associated with the transformation to graphite. The large magnitude of the volume drop reflects the relative large difference in density between graphite and the (10,10) SWCNT

FIG. 2. (Color online) Volume per particle of SWCNT bundles as a function of pressure for several temperatures, compared to the LCBOPII equation of state for graphite.³⁰ Upper panel: (5,5) SWCNT. Lower panel: (10,10) SWCNT.

bundles. As will be discussed below, the transformation mechanism shows a strong dependence on temperature.

Conversely, we find that the (5,5) SWCNT bundles at temperatures below ~ 1500 K do not show full graphitization and exhibit history-dependent transformations. At 500 K, the tubes cross link above 7.5–10.0 GPa, but the sample does not evolve to graphite. At 1000 K we observe a partial graphitization at 3 GPa, with graphitic sheets appearing together with coalesced tubes. Beyond 4 GPa a layered graphitic structure appears, with numerous diamondlike covalent bonds linking the sheets.

By applying a pressure between 1 and 2 GPa to an uncoalesced (5,5) bundle at 1500 K or above, we always observe the formation of a perfect graphitic structure, with the transition pressure slightly decreasing with increasing temperature.

These results allow us to draw the reaction phase diagram of Fig. 3, where we report the graphitization pressure for the (5,5) and (10,10) bundles at different temperatures. As SWCNT are metastable, Fig. 3 has to be interpreted as a reaction phase diagram, with the plotted (T, p) points indicating the conditions where graphitization happens on the time scale of our simulations, that is estimated to be on the nanosecond time scale.³² Note that in this range of temperatures the (5,5) bundles evolve to graphite at pressures lower than that of the (10,10) bundles. This is contrary to the expectation²⁴ that,

FIG. 3. (Color online) Reaction diagram for the (5,5) and (10,10) bundles, indicated by (blue) squares and (red) circles, respectively. The stars indicated state points where only partial graphitization ($T = 1500, 1000$ K) or interlinking ($T = 500$ K) is observed. Solid lines are guides to the eye. The graphite coexistence lines with graphite and diamond are indicated with (dark green) triangles connected by dashed lines. All results were obtained with the LCBOP2 potential, except the graphite-diamond coexistence that has been obtained with LCBOP1 by Ghiringhelli *et al.*³¹

being more rigid, the (5,5) would remain stable, with some minor interlinking, up to high T and P .

V. GRAPHITIZATION MECHANISM

Atomistic simulations are ideally suited to examine the detailed mechanism of transformation and discriminate between several proposed routes. Our simulations show that the pressure induced structural transformations of SWCNT bundles show a strong temperature dependence and occur via different routes involving coalescence³³ or collapse.

We begin by examining the (10,10) bundles. Figure 4 and Fig. 5 show a series of snapshots from our simulations at $T = 1500$ K and $T = 3000$ K, showing that graphitization occurs through successive coalescence of nearby tubes. Despite the similarity, there is a significant difference between the transition at the higher and lower temperatures. Below 2000 K the coalescence happens after, or simultaneously, with the collapse of the nanotubes, while, at high temperatures, the formation of bonds between tubes happens first and seems to trigger the collapse. The difference is further clarified by Fig. 4 and Fig. 5, that show how the volume drop is correlated to the formation of interlinking sp^3 bonds. Since the initial (SWCNT) and final (graphite) structures are fully sp^2 coordinated, the presence of sp^3 bonds signals coalescence of the SWCNT. In the top panels of Fig. 4 and Fig. 5 we plot the evolution of the volume per particle and of the fraction of carbon atom with a sp^3 environment. At $T = 1500$ K (Fig. 4, lower panel) the increase of sp^3 atoms begins with the onset of the volume drop associated to the graphitization process. The coalescence process is completed after the tubes have collapsed and the volume has dropped. At 3000 K (Fig. 5, lower panel), instead, the formation of interlinking sp^3 bonds seems to trigger the coalescence. In fact, the peak of sp^3 coordination clearly precedes the volume drop and an almost completely sp^2 structure is formed before the volume reaches its stable value.

FIG. 4. (Color online) Graphitization path of the (10-10) SWCNT bundle at $T = 1500$ and $p = 3$ GPa. Upper panel: a series of typical snapshots of the transformation process is reported. Lower panel: the (blue) dotted line is the volume per particle during the simulations (left y axis), while the red solid line represents the fraction of fourfold (sp^3) coordinated atoms in the sample (right y axes).

Hence, at lower temperature (below ~ 2000 K) coalescence happens after or simultaneously with the collapse of the SWCNT, while, at higher temperatures, the formation of bonds between tubes seems to happen first and to trigger the collapse. The behavior at high temperature is an important observation. It shows that, contrary to expectations,²⁴ the collapse of the tubes is not a necessary step in the graphitization process. When the thermal energy is high enough, intratube bonds can break and rearrange into intertube bonds without collapse.

FIG. 5. (Color online) Graphitization path of the (10-10) SWCNT bundle at $T = 3000$ and $p = 2$ GPa. Upper panel: a series of typical snapshots of the transformation process is reported. Lower panel: the (blue) dotted line is the volume per particle during the simulations (left y axis), while the red solid line represents the fraction of fourfold (sp^3) coordinated atoms in the sample (right y axes).

FIG. 6. Top row: SWCNT (5,5) transforming to a jammed graphitic structure, $T = 1500$ K, and $p = 2.0$ GPa. Middle row: SWCNT (5,5) transforming to graphite, $T = 2000$ K, and $p = 1.5$ GPa. Bottom row: SWCNT (5,5) transforming to (defected) graphite, $T = 3000$ K, and $p = 1.5$ GPa.

The structural changes of the (5,5) are more complex, in particular at temperatures below 2000 K. At a temperature of 500 K we observed partial graphitization and some coalescence for pressures around 10 GPa, but no evolution to graphitic structures. For 1000 K we observe either graphitization into an almost perfect graphitic structure at a pressure of 4 GPa, or the formation of jammed metastable structures. At 1500 K and above, the (5,5) bundles are thermally unstable and evolve towards graphitic structures in a manner that depends on temperature and pressure. At $T = 1500$ K and low pressures (below 2 GPa) the tubes interlinking and coalescence form a polydisperse sample with small and large tubes as observed experimentally.³³ At 2 GPa and above we observed the formation of a jammed graphitic structure containing both coalesced tubes and graphitic sheets, as shown in the top panels of Fig. 6. At 3 GPa we observed in part of our simulations a full conversion into graphite.

At temperatures of 2000 K and above, we always found a direct transformation path from the ideal bundle to graphite at pressures ranging from 1.5 GPa for 2000 K to 1 GPa for 4000 K. We stress that in these cases we applied the high pressure and the high temperature simultaneously, to avoid the low-pressure formation of coalesced or jammed structures

that could hinder the graphitization process. Examples of transformation pathways are shown in the middle and bottom row of Fig. 6. A common feature for all temperatures is that interlinking of the tubes precedes collapse.

VI. DISCUSSION AND CONCLUSIONS

In summary, we have studied the stability of SWCNT bundles at high pressure and temperature by means of state-of-the-art computer simulations.

We provide the first accurate reaction phase diagram of SWCNT bundles comparing the behavior of (5,5) and (10,10) bundles. Our simulations confirm earlier suggestions²⁴ that nanotube bundles transform into graphite at high temperature and pressure, and that, in the lower temperature range, bundles of large SWCNT are less stable than bundles of small SWCNT. We find, however, that at higher temperature this scenario is reversed and small SWCNT transform to graphite at lower pressure.

Careful analysis of our simulations reveals that the origin of the reversed stability is due to a change in the transformation mechanism. Above temperatures of $T = 1500$ K we observe that interlinking precedes collapse for both small and large nanotubes. This suggests that at these temperature the thermal energy is sufficient to break intratube bonds that convert into intertube bonds. Hence a high thermal energy provides a new pathway for pressure-induced transformation, making collapse not always necessary for graphitization. This implies that although stiffer, the (5,5) tubes at high temperature can graphitize at lower pressure than the (10,10) because the bonds in the smaller, more strongly curved, tubes are intrinsically less stable.

At low temperatures the conversion proceeds via a collapse mechanism. As smaller nanotubes are stiffer, a higher pressure is required for their transformation to graphite. Moreover, our simulations suggest that small radii nanotubes might form jammed graphitic structures for temperatures around 1500 K.

Finally, we note that the graphitic structures obtained by compression and heating of SWCNT often contain sp^3 -interlinking defects between sheets. We speculate that this could explain the fact that nanodiamond forms from nanotube bundles at pressures close to, but lower than, the ones needed to transform graphite itself.²⁴ Indeed, the sp^3 defects could act as seed facilitating the transformation of graphite into diamond, which takes place on a longer time scale than the one needed to obtain graphite from nanotubes.

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