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 LCBOPPII, 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 \(\sim 2000\) K), for both (10,10) and (5,5) nanotubes, coalescence dominates the transformation to graphitic structures. We argue that the \(sp^2\)-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 experimental3–10 and theoretical11–23 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 models11–23 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 (LCBOPPII)23 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 LCBOPPII. 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 \(2 \times 10^4\) 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.

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 for graphite. As 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. 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

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. After 4 GPa a layered graphitic structure appears, with numerous diamondlike covalent bonds linking the sheets.
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 LCBOPI potential, except the graphite-diamond coexistence that has been obtained with LCBOPIi by Ghiringhelli et al.\textsuperscript{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 coalescence\textsuperscript{33} 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 occurs after, or simultaneously, with the collapse of the nanotubes, while, at high temperatures, the formation of bonds between tubes occurs 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.

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,\textsuperscript{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. 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).

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).
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 suggestions 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. Indeed, the $sp^3$ defects could act as seed facilitating the transformation of graphite into diamond, which takes place on a longer time scale that the one needed to obtain graphite from nanotubes.

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