Computational Studies of Small Carbon and Iron-Carbon Systems Relevant to Carbon Nanotube Growth

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Density functional theory (DFT) calculations show that dimers and longer carbon strings are more stable than individual atoms on Fe(111) surfaces. It is therefore necessary to consider the formation of these species on the metal surfaces and their effect on the mechanism of single-walled nanotube (SWNT) growth. The good agreement between the trends (energies and structures) obtained using DFT and those based on the Brenner and AIREBO models indicate that these analytic models provide adequate descriptions of the supported carbon systems needed for valid molecular dynamics simulations of SWNT growth. In contrast, the AIREBO model provides a better description of the relative energies for isolated carbon species, and this model is preferred over the Brenner potential when simulating SWNT growth in the absence of metal particles. However, the PM3 semiempirical model appears to provide an even better description for these systems and, given sufficient computer resources, direct dynamics methods based on this model may be preferred.

Keywords: Carbon Nanotubes, Growth, Computational Studies.

1. INTRODUCTION

A huge amount of research has focused on the growth and applications of single-walled carbon nanotubes (SWNTs) since their discovery in 1993.\textsuperscript{1,2} Although SWNTs could have a variety of uses, ranging from additives in composites to hydrogen storage, one of the most challenging applications is in electronics.\textsuperscript{3} SWNT-based electronics, where both the metallic and semi-conducting properties of the SWNTs are exploited, requires separation or selective growth of SWNTs based on their electronic properties. Although significant advances have been made in this area,\textsuperscript{4,5} there are still no efficient methods for SWNT separation, and all production methods yield a mixture of metallic and semiconducting nanotubes.

A deeper understanding of the SWNT growth mechanism is expected to assist in identifying improved and controlled production methods. Computational studies complement experiments, since they allow for easy manipulation and analysis at the atomic level during SWNT growth. For example, the molecular dynamics (MD) method is widely used to study the dynamics of chemical systems, and has been used to study SWNT growth.\textsuperscript{6-12} Although one can obtain the MD forces directly from electronic structure theory during trajectory propagation, the computational expense limits these studies to short time simulations of small systems.\textsuperscript{11,12} In contrast, analytic potential models offer the computational efficiency required to simulate ensembles of long-time trajectories required for statistically well converged results, which are needed for comparison with experiments. One model that is widely used to simulate carbon systems such as SWNTs\textsuperscript{3,10} is the Brenner potential.\textsuperscript{13,14} However, as for all models of complex systems, this potential has limitations. For example, defects in SWNTs have smaller formation energies in the Brenner framework than in the PM3 semiempirical or DFT formalisms.\textsuperscript{15} Several MD studies of SWNT growth have yielded nanotubes that contain high concentrations of defects\textsuperscript{6-10} which may be due, in part, to these deficiencies of the Brenner potential.

The Brenner potential has been extended to the reactive empirical bond order (REBO)\textsuperscript{16} and adaptive...
intermolecular reactive empirical bond order (AIREBO)\textsuperscript{17} models to reduce some of these limitations and include parameters for carbon–carbon intermolecular and hydrocarbon interactions. These modifications may also improve the description of other systems, such as SWNTs and graphene sheets, and the AIREBO model (which includes the modifications in the REBO model) is thus also included in the studies presented here.

The aim of this study is two-fold. First, we use the Brenner, AIREBO, PM3 and DFT methods to compare energies and structures of carbon and iron-carbon systems that are expected to be important in the initial stages of SWNT growth. This will be used to determine the suitability of using these models to simulate SWNT growth, focusing on the first two potentials since they allow for the long-time simulations required for growing defect-free SWNTs. Second, comparison of the energies of different carbon structures, either free or on catalytic iron surfaces, yields information on the structures that are likely to be most prevalent during the initial stages of SWNT growth. This analysis is primarily based on the DFT data, which is expected to be most accurate, especially for the combined metal-carbon systems.

2. METHODS

Minimum energy geometries are determined for isolated carbon structures, as well as carbon structures supported on a BCC Fe(111) surface. The former structures are relevant, for example, to carbon nanotube growth in the absence of catalyst particles (e.g., arc-discharged production) and the latter structures for the iron-catalyzed growth of carbon nanotubes. Iron (Fe) is chosen since it is commonly used to catalyze SWNT growth.\textsuperscript{10}

The initial structures were the same for all models (analytic, semiempirical and DFT) and were approximated as perfectly linear or cyclic \( C_N \) structures, either in isolation or on the Fe(111) surface. In addition, calculations of the Fe supported \( C_N \) structures also considered zigzag chain structures that can be stabilized by lattice matching with the surface. Perfect ‘cyclic’ structures for small \( N \) are triangular \( (C_3) \), square \( (C_4) \), pentagonal \( (C_5) \), hexagonal \( (C_6) \) and heptagonal \( (C_7) \). For larger \( N \) they are circular. Optimization of other structures (e.g., Stone-Wales type structures discussed below) is also begun from their ideal geometries. The calculations of the supported carbon structures were performed with a single Fe layer since this is expected to give the correct trends in the system geometries and energies.\textsuperscript{18} All calculations were performed at zero temperature and without zero-point motion.

The Brenner and AIREBO potentials, used to study the isolated carbon systems, have been described previously.\textsuperscript{15,17} The Brenner potential has previously been incorporated into a model that describes Fe catalyzed SWNT growth, and this model\textsuperscript{10} is used to obtain the minimum energy structure of the Fe–C systems presented below. The development of this model, and its use in studying SWNT growth, has been detailed elsewhere.\textsuperscript{10} Briefly, the potential energy surface PES is a summation of \( \text{Fe}–\text{Fe}, \text{C}–\text{C} \) and \( \text{Fe}–\text{C} \) interactions. The \( \text{Fe}–\text{Fe} \) interactions are described by many-body potentials which are based on the second moment approximation of the tight binding model, and which are suitable for studying the thermal properties of pure and alloy transition metal systems. The \( \text{C}–\text{C} \) interaction strengths depend on whether the C atom is precipitated or dissolved. The Brenner potential is used to describe the interaction between precipitated C atoms, and a weak Lennard-Jones (12–6) potential is used for the interactions between dissolved C atoms, and between dissolved and precipitated C atoms. These Lennard-Jones interactions were added merely to prevent the distance between the dissolved and precipitated carbon atoms from becoming too short. The interaction between the dissolved C and the solvent Fe atoms is described by the Johnson’s potential, which provides a valid description for carbon in \( \alpha \)-Fe, martensite and cementite, and has been used to simulate C dissolved in liquid iron. The interaction between the precipitated C atoms and Fe atoms depends on whether the precipitated atom is bond-saturated (i.e., it is in the center of a graphite island or SWNT) or if it is bond-unsaturated (i.e., if it is at the edge of an island or at the nanotube end). DFT calculations show that bond-saturated atoms have far stronger bonding to iron clusters than bond-unsaturated atoms. In our PES the interaction between the precipitated carbon atoms and iron atoms are represented by the Johnson’s potential, with the well depth fitted to these DFT results. The major limitation of this force field for the present calculations is that precipitated \( \text{C}–\text{C} \) bond strengths do not depend on the length or structure of the supported carbon structure, or the interaction strength of the C atoms with the Fe cluster or surface. This is discussed in more detail later when comparing the energies obtained from this force field with those obtained from DFT theory. Results for the Fe–C systems, but using the AIREBO potential, were obtained using the same model but where the Brenner potential is replaced by the AIREBO potential.

The PM3 model was used for the isolated carbon systems only, since there are no PM3 parameters for transition metal clusters in MOPAC 7.0,\textsuperscript{19} which was used for the semiempirical calculations in this work. Only spin non-polarization was considered in this work, since this is expected to give the correct trends for the carbon systems studied here (and this is confirmed by the similar trends seen for the DFT spin polarized and non-polarized results discussed below). The geometry relaxations, which were done using the eigenvector following method, were terminated once the gradient norm was below 0.01 kcal/molÅ. This is recommended for accurate energy and force calculations.\textsuperscript{19}

The DFT calculations were performed using the Vienna Ab Initio Simulation Program (VASP).\textsuperscript{20–22} Calculations
were performed with ultrasoft pseudopotentials\textsuperscript{23} and within the GGA-PW91\textsuperscript{24} formalism. Thirty Fe atoms were included in a 5 × 6 atom unit cell (the Fe–Fe nearest neighbor distance is 2.48 Å). The cell dimensions in the surface perpendicular direction were chosen to avoid interaction between adjacent cells. We used an energy cutoff of 290 eV and a 4 × 4 × 1 k-point Monkhorst-Pack mesh.\textsuperscript{25} Test calculations on smaller cells but using 7 × 7 × 1 and 9 × 9 × 1 meshes showed that the trends presented here are converged using the 4 × 4 × 1 mesh. The energy tolerance for structural relaxation was 0.005 eV. This method has recently been used to obtain adhesion energies for various SWNT structures on Fe, Ni and Co clusters, where the results were in good agreement with those calculated for structural relaxation was 0.005 eV. This method has recently been used to obtain adhesion energies for various SWNT structures on Fe, Ni and Co clusters, where the results were in good agreement with those calculated using TURBOMOLE\textsuperscript{26} with atom centered Gaussian basis sets and the PBE\textsuperscript{27} functional. This indicates that energetic and structural trends in Fe–C systems, such as those reported here, are not sensitive to the program, functional or basis set that is used. For the isolated carbon systems the DFT calculations were done within the LDA and GGA approximations for comparison, and with spin polarization and non-polarization. The spins that give the lowest energies in the spin polarized calculations are tabulated below. Since the results of the isolated carbon systems are insensitive to the functional and spin treatment used, and since the calculations of the Fe-supported systems are computationally expensive, only GGA-PW91 with spin non-polarization is used for the Fe–C systems.

The stability and geometry of carbon structures on Fe surfaces is affected by the relative strengths of the C–C and Fe–C bonds. These were calculated for the analytic (Brenner and AIREBO) and DFT potentials to allow for their comparison. Obtaining the C–C and Fe–C contributions is trivial for the analytic potentials, but only the total energies are obtained from the DFT calculations. To estimate the energetic contributions from the C–C and Fe–C bonds, the optimized system was separated into the carbon structure and iron surface, and the energies of these two separated systems was obtained without further optimization. The energy of the separated carbon structure gives an estimate of the C–C contribution, and the difference between the total energy and the sum of the energies of the separated carbon structure and iron surface yields an estimate of the Fe–C contribution.

3. RESULTS AND DISCUSSION

Previous direct dynamics simulations have shown that non-catalyzed growth of fullerene occurs from carbon chains, and not individual atoms.\textsuperscript{23} The stability of carbon chains relative to the atoms has also been observed in tight-binding based Monte Carlo simulations of carbon on Ni surfaces.\textsuperscript{29} It is important that (analytic) models used for MD simulations yield the correct energetic ordering of these—and other—carbon species to ensure that the correct growth mechanism is revealed. For example, pentagons, hexagons and heptagons are important for the growth of the SWNT cap, and the potential model must correctly describe the stability of these structures relative to other 5, 6 and 7 carbon atom structures. Correct descriptions are also needed for smaller structures (from dimers to tetramers) that are involved in the formation of carbon strings, islands and nanotubes. This work focuses on these structures, but also includes structures with 10 and 16 carbon atoms (the latter structure can include Stone-Wales type defects that are common defects in SWNT structures).

This work presents data obtained for minimum energy (optimized) carbon structures of relevance to CNT growth, and not the activation barriers that are required to produce these structures. Identifying these barriers is extremely complex, especially in the presence of catalyst particles, and is left for future work. The results are thus most relevant when there is slow addition of carbon species to the growing CNT system (where the system has time to relax to its minimum energy structures). This provides a good complement to the data that has been obtained from MD simulations, where carbon atoms are added more that 10\textsuperscript{4} times faster than in experiments,\textsuperscript{10} and the growing CNT contains many defects associated with high energy structures.

3.1. Carbon Species in Vacuum

Table I presents data for the two lowest energy structures for each \(C_N\) system, \(2 \leq N \leq 16\). Two additional structures for \(C_{16}\) are shown, since these are associated with a perfect graphene sp\textsuperscript{2} geometry and a Stone-Wales defect. Other structures that have been calculated, but that are not shown in the table, include a carbon atom joined to a pentagon ring \((C_5)\), a carbon atom joined to a hexagon ring \((C_6)\) and two fused hexagons \((C_{10})\). These structures have energies that are higher than those of the linear and cyclic structures shown in the table.

It is evident from the table that:

1. All methods yield increasing stability of the isolated carbon systems with increasing number of carbon atoms. For example, the minimum \(C_{N+1}\) structure is energetically preferred to the \(C_N + C\) system (since the reference energy of C is zero) and the \(C_{10}\) energies are less than twice the \(C_5\) energies.
2. All models capture the trend that chain structures are more stable than ring structures for systems that contain at most four carbon atoms, and that ring structures are more stable than linear chains for carbon structures with at least 10 atoms.
3. The Brenner potential incorrectly predicts that the pentagon is more stable than the \(C_5\) chain, whereas the other models predict that the chain is 3–4 eV more stable.
4. The Brenner potential predicts that the hexagon is a lot (≈3 eV) more stable than the \(C_6\) chain, whereas
Structures and energies of isolated C\textsubscript{N} carbon systems, 2 \leq N \leq 16. Potential energies are given for Brenner and AIREBO potentials, total energies for the PM3 Hamiltonian and total free energies for DFT models. Energies are given in eV and magnetic moments of the minimum energy spin-polarized DFT structures are given in parentheses. All energies are relative to the separated atomic energies, and the lowest energies are highlighted in bold.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Brenner</th>
<th>AIREBO</th>
<th>PM3</th>
<th>LDA Non-polarized</th>
<th>LDA Polarized (\mu_\text{L})</th>
<th>GGA Non-polarized</th>
<th>GGA Polarized (\mu_\text{L})</th>
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<tr>
<td>Chain</td>
<td>−5.79</td>
<td>−6.21</td>
<td>−8.88</td>
<td>−9.20</td>
<td>−7.39 (2)</td>
<td>−8.55</td>
<td>−6.69 (2)</td>
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<tr>
<td>Hexagon</td>
<td>−11.58</td>
<td>−12.90</td>
<td>−21.16</td>
<td>−19.25</td>
<td>−15.97 (0)</td>
<td>−18.17</td>
<td>−14.68 (0)</td>
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<tr>
<td>Unstable</td>
<td>−8.83</td>
<td>−9.29</td>
<td>Unstable</td>
<td>−18.36</td>
<td>−15.59 (2)</td>
<td>−16.95</td>
<td>−14.02 (2)</td>
</tr>
<tr>
<td>Chain</td>
<td>−17.48</td>
<td>−19.03</td>
<td>−28.01</td>
<td>−26.49</td>
<td>−22.41 (2)</td>
<td>−24.76</td>
<td>−20.53 (2)</td>
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<tr>
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<td>−16.46</td>
<td>−14.35</td>
<td>−25.72</td>
<td>−24.13</td>
<td>−20.05 (2)</td>
<td>−22.20</td>
<td>−17.94 (2)</td>
</tr>
<tr>
<td>Hexagon</td>
<td>−23.39</td>
<td>−25.14</td>
<td>−38.66</td>
<td>−36.58</td>
<td>−31.11 (0)</td>
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<td>−22.89</td>
<td>−29.97</td>
<td>−30.97</td>
<td>−26.80 (6)</td>
<td>−27.68</td>
<td>−23.94 (6)</td>
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<tr>
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<td>−46.03</td>
<td>−44.21</td>
<td>−37.79 (2)</td>
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<td>−34.41 (2)</td>
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<tr>
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<td>−30.74</td>
<td>−44.95</td>
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<td>−38.68 (0)</td>
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<td>−54.03</td>
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<td>−93.35</td>
<td>−139.50</td>
<td>−134.30</td>
<td>−116.80 (3)</td>
<td>−123.59</td>
<td>−105.04 (3)</td>
</tr>
<tr>
<td>Hexagon</td>
<td>−92.22</td>
<td>−94.61</td>
<td>−132.38</td>
<td>−132.76</td>
<td>−115.56 (2)</td>
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<td>−102.91 (2)</td>
</tr>
<tr>
<td>Hexagon</td>
<td>−91.96</td>
<td>−93.04</td>
<td>−131.72</td>
<td>−131.99</td>
<td>−114.42 (0)</td>
<td>−120.31</td>
<td>−101.45 (2)</td>
</tr>
</tbody>
</table>

The Brenner and AIREBO potentials predict that these structures have similar energies (within \(\approx 1\) eV of each other).

The other models predict that these structures have similar energies (within \(\approx 1\) eV of each other).

The Brenner and AIREBO potentials predict that the heptagon is more stable than the C\textsubscript{6} chain (\(\approx 4\) eV and 0.1 eV, respectively), whereas the DFT models predict that the chain is more stable by \(\approx 1\)–3 eV. The AIREBO model is thus in better agreement with DFT than the Brenner potential.

All DFT methods show the same trends, except for C\textsubscript{6}, where there are slight differences between LDA and GGA results. LDA predicts that the closed hexagon structure is \(\approx 1\) eV more stable than chain structure, whereas GGA...
(7) Except for the AIREBO model, all methods show that the fused-ring \( C_N \) structures (the final two structures in Table I) are not as stable as the cyclic structure. However, the Brenner potential predicts that both of the fused-ring structures are more stable than the linear structure, spin non-polarized DFT GGA predicts that only the most stable fused-ring structure is lower in energy than the chain structure, whereas PM3, spin-polarized DFT LDA and DFT GGA predict that both fused-ring structures are less stable than the chain structure. The AIREBO model predicts that the energy of the most stable fused-ring structure is lower than the cyclic structure.

(8) The structures and energies obtained from PM3 follow the same trends as those calculated using GGA with no spin-polarization.

In summary, the Brenner model generally yields ring structures that are too stable compared to the chain structure. Except for \( C_6 \), this is not the case for the AIREBO model where, in agreement with DFT, the chain structures are more stable than the rings for small systems. The PM3 model yields the same trends in energies and structures as the DFT GGA predictions. Hence, in the absence of metal catalysts, dynamics based on PM3 forces should yield correct structures during the growth of SWNTs. In addition, dynamics based on the AIREBO force field should give structures that are more reliable than those obtained from the Brenner force field.

The largest difference between the energetic trends predicted for the isolated carbon structures is found for the \( 5 \leq N \leq 7 \) structures. In particular, the Brenner potential predicts pentagons and heptagons that are too stable compared to the \( C_6 \) and \( C_7 \) linear chains. This is significant for the formation of a SWNT cap since the preferential formation of pentagons, as predicted by the Brenner model, may well hinder the formation of the hexagons needed to construct the SWNT graphitic structure. That is, it is expected that a carbon atom can be added more easily to an open \( C_5 \) chain (to produce a hexagon) than to a pentagon—where all \( C-C \) bonds must be ruptured.

### 3.2. Carbon Species on Fe(111) Surfaces

The energetic trends observed above for the isolated carbon species may well be affected by the presence of the metal catalyst, where the formation of carbon-metal bonds competes with carbon–carbon bond formation. For example, whereas the dimer is more stable than the isolated atoms in vacuum (see Table I), it is possible that this stability is greatly decreased on metal surfaces. In fact, carbon atoms are believed to be the stable species in dilute metal carbides. Inclusion of the metal dramatically increases the computational expense of the calculations, and they are therefore limited to carbon monomers, dimers and pentamers (due to the importance of the \( C_5 \) system described above).

Figure 1 shows the structures of the Fe(111) supported monomer and dimer systems that were studied, and Table II their energies. All models show that the monomer in site ‘3’ (Fig. 1) on the Fe(111) surface is favored. Also, the Brenner and AIREBO favor the formation of trimers from monomers, since the magnitude of the energy of the dimer is more than twice that of the monomers (Table II). This is expected since the \( Fe-C \) energy in these analytic potentials does not depend on the length of the chain, and hence longer chains are stabilized from each new \( C-C \) bond that is formed (this is consistent with the data shown in Table III for pentamers where, for the most stable structures, the average \( Fe-C \) energy is \( \approx 4 \) eV and the average \( C-C \) energy \( \approx 6 \) eV in agreement with the data in Table II). The stability of carbon dimers and longer chains on metal surfaces has also been seen in previous semiempirical studies.29, 30

This trend is not as clear in the DFT results. Table II shows that, in agreement with the analytic potentials, the dimer is favored over two monomers if they are on sites 1 or 2, but not when they are both in site 3. In fact, the energy of two monomers in site 1 (2 \( \times \) −9.09 eV = −18.18 eV) is 0.32 eV more stable than the dimer, showing that the gain in stability due to the formation of the dimer \( C-C \) bond is slightly less than the loss in stability by the weakening \( Fe-C \) bonds (the similarity between the gain in stability from forming \( C-C \) bonds and the loss
in stability in the weakening Fe—C bonds is also seen for the pentamers—Table III—where the total energy for 5 monomers of \( \approx -45 \text{ eV} \) is the same as the total C—C and Fe—C energy of the more stable structures shown in Table III.

Figure 2 shows the initial geometries of the nine supported pentamer systems studied here, as well as the numbering of the structures that is used in Figure 3, Table III and the discussion. Figure 3 shows the energies of structures 1–9 obtained from the different models. Differences in total energies obtained from the analytic and DFT models are larger than they were for the isolated carbon structures, primarily due to the large differences in Fe—Fe bond strengths. However, of relevance to this work is that all models show similar trends with the zigzag topology of structure 1 (Zigzag-1) being the most stable (largest negative energy) and the linear chain structures being the least stable. Hence, the Fe—C interaction has brought the trends obtained from the Brenner model into agreement with the DFT results and, in the presence of the iron surface, this analytic model is expected to predict the correct structures of this system.

Figure 3 shows that the energies predicted by the AIREBO model for structure 3 (Ring-2), and to a lesser extent structures 4 (Ring-3), 7 (Zigzag-2) and 8 (Chain-2), are far larger than that obtained from the Brenner model.
and diverges from the trend of a gradual increase in energy from structure 1 to structure 9 shown by the Brenner and DFT models. This occurs in spite of the small differences in optimized structures obtained from the Brenner (Fig. 4(a)) and AIREBO (Fig. 4(b)) models, and is due to the fact that these models define a C=C bond as being formed when the C−C distance is at most 2 Å. The Brenner optimized structure (Fig. 4(a)) has five C=C bonds linking the five sp carbon atoms. Since these atoms are not sp² (saturated) they have strong interactions with the Fe surface, giving a total Fe−C energy of −18.36 eV. In contrast, the AIREBO optimized structure (Fig. 4(b)) is slightly compressed, leading to seven C=C bonds (between the 5 atoms). Hence, three of these atoms are modeled as sp² atoms and thus have weaker interactions with the Fe surface, leading to a total Fe−C energy of −3.78 eV (according to the analytic models the Fe−C energy for saturated carbon atoms is approximately one tenth of that of the unsaturated carbon atoms). The difference in energies obtained from the Brenner and AIREBO models for structures 4, 7 and 8 are due to difference in both C−C and Fe−C contributions (as shown in Table III). The energies obtained from the AIREBO model for all four structures are in closer agreement with the results obtained from the Brenner model when the optimization (with the AIREBO model) is initialized from the optimized Brenner structures.

Table III shows the contributions of the C−C and Fe−C bonds to the total energies shown in Figure 3. It is evident that the Brenner potential yields C−C energies that are similar for all configurations. In addition, these are similar to the Fe−C energies, although the latter energies increase (become less negative) from structures 1 to 9. This causes the decrease in stability of structures from 1 to 9 shown in Figure 3. The large decrease in the Fe−C contribution for structure 9 is due to the lattice mismatching of the Fe(111) surface atoms with the carbon atoms when the chain structure has this placement on the surface (see Fig. 2).

Table III shows that, for the DFT model, the C−C energies are three times larger than the Fe−C contributions. The larger C−C energies compared to Fe−C energies have been seen in previous DFT calculations. This is different from the results of the two analytic models, where the Fe−C and C−C contributions are similar, and shows that the trends seen for the isolated carbon structures will be more important for the DFT model than for the analytic models even in the presence of the metal surface. The reason for the difference in the DFT and analytic models is seen when comparing the C−C and Fe−C energies for the carbon monomers and dimers (Table II) with the pentamer values. The analytic Fe−C interaction for all unsaturated carbon atoms (i.e., having less than 3 neighboring carbon atoms) was fit using previously determined DFT energies of single carbon atoms on iron surfaces. These are stronger than the bond-average Fe−C energy obtained from DFT for the pentamer, which results in the larger bond strengths calculated from the analytic models.

It can be noted that simple analytic models, such as those used here, cannot be expected to correctly describe detailed changes in C−C and Fe−C binding energies for different configurations. As seen from the data above, these energies depend on the positions of the carbon atoms and the number of neighboring carbon and metal atoms. In addition, the metal catalyst particles are expected to be liquid, or have liquid-like surfaces, under SWNT growth conditions, and this also leads to rapid and large amplitude changes in atom–atom distance and number of atomic neighbors. It is not reasonable (and probably not necessary) to include this detailed information in the analytic description, and one should probably resort to other methods, such as direct dynamics methods, when these details are required.

4. CONCLUSION

The DFT results presented here show that supported dimers and pentamer carbon strings have similar stabilities to the separated monomer atoms when these atoms are in the lowest energy Fe(111) site, and that they are more stable than individual atoms when they are in meta-stable sites. Since SWNT growth occurs from molten metal particles or solid particles with large surface diffusion, these meta-stable sites may be more relevant, and longer chains may be more stable than individual atoms. The analytic potentials used here predict that chain structures are always more stable than individual atoms, with the stability of the chain increasing with chain length. Hence, according to all models, chains will form, but according to DFT this may only occur under conditions when the metal surface has significant carbon coverage. It is therefore necessary to consider the formation of these chains on the metal surfaces and the effect on the mechanism on the growing SWNT.

However, formation of these species from individual atoms requires that there is sufficient time for them to interact which depends, among other things, on the rate of carbon feedstock addition to the SWNT system, the rate of feedstock decomposition, the rates of surface and bulk diffusion of carbon on and in the iron particle, the phase of
the particle and the activation barriers for bonding. This can be studied using MD simulations at temperatures relevant to experiment, and the results reported here indicate that both the Brenner and AIREBO models provide adequate descriptions of the supported carbon systems needed for valid reaction mechanisms.

In contrast, the AIREBO model provides a better description of the relative energies for isolated carbon species, and this model is preferred over the Brenner when simulating SWNT growth in the absence of metal particles. However, semi-empirical methods such as PM3 (1975) appear to be better descriptions for these systems and, given sufficient computer resources, direct dynamics methods based on these models may be preferred.

Due to the computational expense of DFT modeling of carbon-iron systems, the above studies were limited to the particle and the activation barriers for bonding. This will be revealed by MD or Monte Carlo simulations at these temperatures using analytic or semiempirical models which we have shown gives the correct energetic trends relative to DFT at zero Kelvin. This work is in progress.

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References and Notes


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