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Generalizing thermodynamic properties of bulk single-walled carbon nanotubes

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The enthalpy and Gibbs free energy thermodynamical potentials of single walled carbon nanotubes were studied of all types (armchairs, zig-zags, chirals (n>m), and chiral (n<m)). Bulk values of these thermodynamic potentials were obtained using a previously demonstrated robust method based on semi-empirical PM3 calculations and an extrapolated cluster approach. Those values were used to study the relationship between the thermodynamic potentials and the diameter of the nanotube. Results of this study led to the proposal of a single equation for the thermodynamical potential of $\Delta H_{AB}^{298 K}$ or $\Delta G_{AB}^{298 K}$ (assembly of nanotubes from atoms) versus the chiral vector indexes *n* and *m* for any given nanotube. The equations show a good level of accuracy in predicting thermodynamic potentials for practical applications. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4905263]

INTRODUCTION

The main goal of this paper is to perform an extensive study of important thermochemical properties for single-walled carbon nanotubes (SWCNT). This work determines the bulk thermodynamic potentials enthalpy (ΔH_{AB}) and Gibbs free energy (ΔG_{AB}) for assembly of nanotubes from carbon atoms. These potentials are directly related the more commonly reported values of molecular enthalpy and free energy of formation ($\Delta H_f^{298 K}$ and $\Delta G_f^{298 K}$) by well-known experimental values. The latter quantity is harder to obtain, but provides crucial information about the viability of a process. This is the first such study on SWCNT's ΔG_{AB} , to the best of our knowledge.

The amount of experimental and theoretical work done on carbon nanotubes during the last two decades has increased at an uncharacteristically fast pace. This is due to the wide variety of applications that have been discovered for these structures and also to their unique physicochemical properties.^{1–3} The amount and quality of the existent literature on nanotubes^{4–6} makes it almost superfluous to include a general description of these structures in this introduction. However, in order to establish common ground with readers, the next paragraph relates some important characteristics of SWCNTs.

A SWCNT can be described as a graphene sheet rolled into a cylindrical shape with axial symmetry that can be classified as achiral or chiral, based on whether or not there is mirror image symmetry. The structures are characterized in terms of the chiral vector which is constructed by a linear combination of the real space vectors of the hexagonal lattice in terms of the indexes *n* and *m*: $C_h = (n,m)$. There are two types of achiral nanotubes: armchair which occurs when n = m and zigzag which occurs when the index m = 0. All other (n,m) combinations correspond to chiral nanotubes and switching the indexes result in different handedness.⁵ Applications of SWCNTs are many and varied, including production of nanowires,⁷ whether metallic or semiconducting,³

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which are prime candidates for use in electrical conduction due to their range of electronic properties.¹ Another application of some forms of SWCNTs have been identified in effective catalytic processes.⁸ Other applications include nanotubes as field emitters,⁹ quantum conductance of carbon nanotubes,¹⁰ carbon nanotubes as single-molecule biosensors,¹¹ hydrogen fuel storage in nanotubes,¹² integration of carbon nanotubes for logic circuits,¹³ ultralong single-wall carbon nanotubes,¹⁴ and transistors with carbon nanotubes.^{2–5}

The bulk properties of nanotubes have been of interest to researchers in the recent past.^{15,16} However, their study has often been hindered by the fact that the computational methods commonly accepted to produce the best thermochemical results demand too much in the way of computer resources. Much work on the (5,5) armchair and (9,0) zig-zag SWCNT has been done¹⁶⁻²¹ but little has been done on other armchair, zig-zag, or chiral SWCNTs. Consequently, the situation calls for an effective but less computationally demanding strategy. In a previous study,¹⁶ reliable thermochemistry was presented for infinite stretches of pure carbon materials including acetylenic and cumulenic carbon chains, graphene sheet, and one single-walled carbon nanotube (5,5). That study was done by connecting the properties of finite size molecules that grow into infinitely long systems (cluster approach). In particular, thermochemical calculations were performed on finite polygne and polygne chains as a function of chain length using ab initio G3 theory (a composite of well-defined *ab* initio electronic structure calculations providing agreement with experimental thermochemistry) and calibrated against the less rigorous PM3 semi-empirical method (Stewart's semi-empirical PM3²² method-third parameterization of MNDO) yielding surprisingly good energetics. Those results validated the use of the less computationally demanding PM3 method to study more complex systems.

In general, different SWCNTs, as characterized by their (n, m), have different energetic trends that vary significantly with length and diameter. The main purpose of this article is to study these thermodynamic properties for infinitely long (bulk) SWCNTs and a possible parameterization of them in terms of the SWCNT's chiral vector indexes n and m. In particular, an approach is proposed based on atomic binding energies to study the standard enthalpy change (ΔH_{AB}^{298K}) for the atomic binding reaction and the free energy (ΔG_{AB}^{298K}). These quantities are related to energies of formation and this approach is compared to previous studies found in the literature involving quantities such as strain energy^{18,19} or electronic energy.^{23,24} Specific details of our methods are given in the next section. This approach provides a useful tool in the characterization, preparation, and applications of these structures in the fast growing field of nanotechnology.

The remaining parts of this paper are organized as follows: the proposed method for this thermochemical study is briefly described in the methodology and procedure section, including the cluster approach to obtain thermochemical bulk values for an ample set of SWCNT. In the results section, our data analysis is presented as well as a parameterized expression that is proposed to predict the thermochemical properties of interest. Finally, results and conclusions are presented.

METHODOLGY AND PROCEDURE

The ever-increasing use of nanotube technology makes it imperative to establish the thermodynamic stability versus size with as much rigor as possible. The stability of a finite carbon cluster, changes significantly with molecular length and diameter. The connection of small molecule properties to infinite length can be established by mapping such properties versus length, yielding an essential basis for understanding properties in the nanosize regime. Computational chemistry is very effective at the absolute energetics of small gas phase molecules but it is more difficult to determine the bulk energy changes associated with infinite structures. The problem of computing reliable thermochemistry from optimizations and normal mode analyses is tackled by using a cluster technique consisting of determining the thermochemical properties of several finite size structures and extrapolating them to infinite length. In this way, bulk values are obtained for those properties. Once the bulk property is determined for a specific SWCNT with chiral vector indexes n and m, that property is compared to the same for another SWCNT with different indexes n and m. As a result, the thermodynamic potentials are studied in terms of the diameter at bulk. 127149-3 Rodriguez et al.

PM3 was developed on a training set of molecular properties including ΔH_f^{298K} hence its success in predicting these types of quantities for the structures of interest. Caution should be used however when using PM3 as a predictor of other molecular properties such as the geometry. The PM3 energetic results in our calculations will be divided by the number of carbons in order to turn these properties from extensive to intensive. The energetics in this work are eventually presented in terms of the incorporation of a gas phase carbon atom into the structure of interest, i.e. for the reaction $C(g) \rightarrow C$ (structure of interest).¹⁶ The details are summarized in the remaining paragraphs of this section.

Some semi-empirical methods commonly produce energetic results in terms of molecular enthalpy of formation. In particular, a carbon nanotube is formed from the elements in their standard state as

$$nC(graphite) \to C_n(g) \quad ; \quad \Delta H_f^{298K}[C_n].$$
 (1)

The ΔH_f^{298K} of Eq. (1) is related to the standard enthalpy change for the atomic binding reaction (denoted AB) by

$$\Delta H_{AB}^{298K} = \Delta H_f^{298K}[C_n] - \sum_{atoms} \Delta H_f^{298K}[atom(g)], \tag{2}$$

where ΔH_f^{298K} [*atom*(g)] corresponds to the enthalpy of formation of gas phase atoms whose accepted value is 171.29 *kcal/mol for* C atom.²⁵ The enthalpy change at 298 K for the atomic binding enthalpy reaction of Eq. (2) can be related to the corresponding change in electronic equilibrium energy (ΔE_{AB}^{eq}) by

$$\Delta E_{AB}^{eq} = \Delta H_{AB}^{298K} + \Delta H_{C_n}^{eq \to 298K} - \sum_{atoms} \Delta H_{atom}^{eq \to 298K},\tag{3}$$

where $\Delta H_{species}^{eq \rightarrow 298K}$ is the enthalpic correction for taking the species from equilibrium to 0 K (ZPE) and heating the species from 0 K to 298 K. Particularly, the values used for the atoms are $\Delta H^{eq \rightarrow 298K} = 1.48$ kcal/mol. The standard free energy change for the atomic binding energy reaction (ΔG_{AB}^{298K}) of these molecules can be obtained by using ΔE_{AB}^{eq} from Eq. (3) in

$$\Delta G_{AB}^{298K} = \Delta E_{AB}^{eq} + \Delta G_{C_n}^{eq \to 298K} - \sum_{atoms} \Delta G_{atom}^{eq \to 298K}.$$
(4)

The $\Delta H_{species}^{eq \rightarrow 298K}$, and $\Delta G_{species}^{eq \rightarrow 298K}$ quantities can be obtained using Gaussian 03^{26} by executing the vibrational normal mode analysis mentioned before.

The finite cluster method that is used in this work to obtain energetics at infinite length by extrapolation has been described in detail in the literature.^{16,27} This method is based on fitting the data of a thermochemical property per carbon atom vs. the reciprocal of the number of carbon atoms in order to extrapolate to the value of the property in an infinite structure of pure carbon. The general fit of an intensive property X (e.g. $\Delta H_{AB}^{298K}/n_c$, $\Delta G_{AB}^{298K}/n_c$, $\Delta E_{AB}^{0K}/n_c$, $\Delta E_{AB}^{eq}/n_c$) vs. the number of carbons n_c has the form:

$$X = \sum_{i=0}^{n_{\max}} \alpha_i (n_c^{-k})^i,$$
 (5)

where the parameter k is the dimension of the growth (k is 1 for chains, 2 for sheets, and 3 for clusters) and the parameter α_0 represents the value at infinite length. The $\Delta H_{AB}^{298K}/n_c$ and $\Delta G_{AB}^{298K}/n_c$ values that we use are given vs n_c^{-1} ; i >1 is not needed in our calculations. These intensive quantities will be referred to simply as ΔH_{AB}^* and ΔG_{AB}^* in the remainder of this paper.

The specific procedure starts by using a program that was designed to construct any (n,m) single-walled carbon nanotube in a previous work.²⁸ The variables n, m, and the length of nanotube in Angstrom serve as input to the program that generates a file containing the connectivity of the molecule in a Gaussian (.gjf) format, which is used as input for GaussView.²⁶ The GaussView visualization application is used to perform some manual "trimming" in order to obtain the final

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nanotube. Once a nanotube of a given length is built, an optimization calculation is carried-out at the semi-empirical PM3 level to obtain a stable configuration. This process is repeated to acquire enough data for different lengths of the same type of nanotube. The length of a finite nanotube is increased each time by merging two previously optimized structures and rerunning the job at the same level of theory. The enthalpy of formation for the nanotube molecules was acquired from the files generated by Gaussian. It is important to note that the energy contribution to the bulk values deriving from the endings of the SWCNT becomes negligible as the SWCNT's length increases.^{16,17} In this paper uncapped SWCNTs are used.

After each finite nanotube calculation has been optimized, a vibrational normal mode analysis is performed on the already optimized geometry [simply by replacing "opt" with "freq=numer" in the command line]. The frequency command calculates the zero point energy and thermochemical corrections from Equilibrium \rightarrow 0K and Equilibrium \rightarrow 298K for enthalpy and free energy. The theory behind normal mode analysis is based on an ideal gas partition function, as discussed in previous work.¹⁶ These data together with the enthalpy of a carbon atom at 298K (170.9 kcal/mol) and enthalpy correction from 0 to 298K (1.48 kcal/mol), is all that is needed to use Eqs. (2) to (4) for the calculation of those thermochemical quantities on a per carbon basis. The data points obtained for each nanotube are then fitted using a linear least square routine of Eq. (5) extrapolating to the infinite thermochemical quantity on a per carbon atom basis (α_0 is the bulk value at infinite length). This procedure was implemented to obtain the bulk thermodynamic potential value for a large set of different SWCNT (different *n*, *m* indexes)

Once the bulk value for a thermodynamic potential was determined for each SWCNT, then they were fit versus the inverse of the SWCNT's squared diameter. This relationship characterizes the SWCNTs in terms of their diameter and therefore addresses the issue of strain energy for the different types of SWCNT.

RESULTS

Thermodynamics of Zig-zag, Armchair, and Chiral SWCNTs

This work focused on the standard enthalpy change (ΔH_{AB}^*) and free energy change (ΔG_{AB}^*) for assembly of atoms into nanotubes (the atomic binding reaction) which required a normal mode vibrational. analysis Semi-empirical PM3 optimizations and normal mode analyses were performed on 48 different nanotubes of the four different types (armchair, zig-zag, chiral (n>m) and chiral (n < m)).¹⁶ In particular, we studied eleven different armchair nanotubes [(3,3), (4,4), (5,5), (6,6), (7,7), (8,8), (9,9), (10,10), (11,11), (12,12), and (15,15)], eleven different zig-zag nanotubes [(3,0), (4,0), (5,0), (6,0), (9,0), (10,0), (11,0), (12,0), (13,0), (15,0), and (17,0)], eight different chiral (n < m) nanotubes [(2,4), (3,9), (4,5), (5,6), (7,9), (8,9), (8,10), and (10,11)], and eighteen different chiral (n>m) nanotubes out of which seven were near the armchair line [(5,4), (6,5), (7,5), (7,6), (8,6), (9,8), and (11,10) and the rest were not near the armchair line [(3,2), (4,1), (4,2), (7,(8,2), (9,1), (9,4), (10,3), (12,3), (11,6), and (12,8)]. In order to apply the cluster approach to obtain bulk values (infinite length), PM3 calculations were performed on 196 finite structures: 48 finite armchair structures, 43 zig-zag structures, 33 finite chiral structures with n < m handedness, and 72 finite chiral structures with n > m handedness. The calculations on the chiral nanotubes are especially important since methods involving periodic boundary conditions are difficult to implement with these nanotubes. The raw data obtained for all of the 196 finite structures optimized and the normal mode analysis can be found in S- 1.3^{0} See the supplemental materials for all thermodynamic data tables for all SWCNTs.³⁰

Fig. 1(a)-1(b) shows a plot of a linear fit of the 6 finite structures built for the (7,7) armchair nanotube. This exemplifies how the cluster method was implemented to obtain the bulk values for the thermodynamic potentials^{16,17} of all the 48 different nanotubes that were studied (see S-1³⁰ for these data). Analysis focused on atomic binding energies (see the Methodology and Procedure section of this paper), the practicality and usefulness of focusing on the atomic binding approach will be addressed in the discussion and conclusion section of this paper.



FIG. 1. (a.) The enthalpic atomic binding energy per carbon atom and (b.) the free energy per carbon atom. plotted against the inverse carbon atom for the finite size (7,7) armchair extrapolated to bulk applying cluster method approach.

Given the fact that nanotubes have been synthesized in which their length is hundreds of million times longer than their diameter,¹⁴ it is important to study the relationship between the thermodynamic potentials and the diameter (d) for these bulk size nanotubes. Therefore, the bulk values that were obtained for each of the two thermodynamic potentials were further used to study their dependency on the diameter of the SWCNT. In other words, ΔH_{AB}^* and ΔG_{AB}^* vs $1/d^2$ were studied for each of our 48 different (n,m) nanotubes.

For ΔH_{AB}^* vs $1/d^2$, a separate linear fit was constructed for each one of the four different types of nanotubes that we are studying (i.e. a linear fit for armchair, another for zig-zag, another for chiral (n>m) and another for chiral (n<m)). The result is a very good fit for each type, as presented in Fig. 2(a)–2(d). These results led to the following relationships for ΔH_{AB}^* vs $1/d^2$ where the units for enthalpies are kcal/mol and those for diameters are Å:

Armchair:
$$\Delta H_{AB}^* = 193.01(\pm 1.50)\frac{1}{d^2} - 168.25(\pm 0.03),$$

Zig-zag: $\Delta H_{AB}^* = 190.56(\pm 1.85)\frac{1}{d^2} - 168.22(\pm 0.05),$

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FIG. 2. The enthalpy atomic binding energy per carbon atom plotted against the inverse squared diameter of various finite nanotubes for (a). Zig-Zag SWCNTs, (b). Armchair SWCNTs, (c). Chiral (n>m) SWCNT's, and (d). Chiral (n<m) SWCNT's extrapolated using the cluster method.

Chiral(n>m):
$$\Delta H_{AB}^* = 192.85(\pm 1.14) \frac{1}{d^2} - 168.29(\pm 0.02),$$

Chiral(n\Delta H_{AB}^* = 192.67(\pm 0.73) \frac{1}{d^2} - 168.23(\pm 0.02). (6)

The intercept for all of these fits corresponds to a nanotube with an infinite diameter. In other words, it corresponds to an open sheet of graphene. The reported ΔH_{AB}^* for graphene in the literature is -169.3 ± 0.2 kcal/mol,²⁵ which matches the values we obtain within 1 kcal/mol.

Global Fitting

It is important to notice that the slopes of these linear fits in Eq. (6) present a standard deviation of only 0.996 Å² kcal/mol with an average value of 192.27 kcal Å² kcal/mol. Also, the intercepts show a standard deviation of 0.027 kcal/mol, with an average value of -168.25 kcal/mol. Alternatively, the values for the slopes and intercepts in those linear fits have percent relative standard deviations of 0.68% and 0.02% respectively. The slope of these linear fits can be related to the strain energy of the nanotube, as it will be discussed later. This leads to the assumption that for practical purposes, such as possible bulk engineering applications, all the different types of nanotubes could be fitted together in a single linear fit without a significant margin of error (thermo parameters in kcal/mol, diameters in Å):

All nanotubes:
$$\Delta H_{AB}^* = 192.23(\pm 0.70)\frac{1}{d^2} - 168.25(\pm 0.02).$$
 (7)

This global linear fit is also excellent and shows a σ =0.075 kcal/mol and R²=0.9994 as can be seen in Fig. 3.

In a similar fashion, the data for the bulk values of ΔG_{AB}^* vs $1/d^2$ were analyzed and these data are plotted and presented in Fig. 4(a)-4(d). From those fits, we obtained the following relations



FIG. 3. The extrapolated bulk enthalpic atomic binding energy on a per carbon versus the inverse squared diameter for all carbon nanotubes constructed.

(thermo parameters in kcal/mol, diameters in Å):

Armchair:
$$\Delta G_{AB}^* = 193.36(\pm 1.33) \frac{1}{d^2} - 158.02(\pm 0.03),$$

Zig-zag: $\Delta G_{AB}^* = 190.60(\pm 1.48) \frac{1}{d^2} - 158.00(\pm 0.04),$
Chiral(n>m): $\Delta G_{AB}^* = 195.99(\pm 1.37) \frac{1}{d^2} - 158.28(\pm 0.02),$
Chiral(n\Delta G_{AB}^* = 196.79(\pm 0.85) \frac{1}{d^2} - 158.25(\pm 0.02). (8)

The ΔG_{AB}^* standard deviation of the slopes for the four types of SWCNT is only 2.43 kcal/mol, with an average value of 194.19 Å² kcal/mol. Also, the intercepts show a standard deviation of 0.128, with an average value of -158.14 kcal/mol. A linear fit of all our data, both achiral and chiral together, for the ΔG_{AB}^* vs $1/d^2$ was performed discovering an excellent match as attested to in Fig. 5. This again leads to the assumption that, for practical purposes, they all could be fitted together without a significant margin of error:

All nanotubes:
$$\Delta G_{AB}^* = 193.99(\pm 1.14) \frac{1}{d^2} - 158.15(\pm 0.03).$$
 (9)

This global linear fit is also excellent and shows a $\sigma = 0.12$ kcal/mol and R²=0.9995 as can be seen in Fig. 5.

The existence of what seems to be a good approximation to a unique fit for ΔH_{AB}^* vs $1/d^2$ as well as another unique fit for ΔG_{AB}^* vs $1/d^2$, has led to the parameterization of these thermodynamic potentials in terms of the nanotube vector indexes (n,m). Based on the successful linear fit of the bulk energy value versus the inverse of the square of the diameter, the following equation is obtained for the bulk energy:

$$\Delta X_{AB}^* = \frac{a}{(m^2 + nm + n^2)} + \Delta X_{graphene}^{298K}.$$
 (10)

Where $\Delta X_{AB}^* = \Delta H_{AB}^*$ or ΔG_{AB}^* and $a = (\beta_1 \pi^2)/(3c^2)$ with c being the carbon-carbon distance (1.42 Å) and β_1 is the slope from the global fit of the thermodynamic potential X vs $1/d^2$. Therefore, from the data (Fig. 3) and using Eq. (10), the best fit equation that best describes ΔH_{AB}^* (in kcal/mol)





FIG. 4. The free energy atomic binding energy per carbon atom plotted against the inverse squared diameter of various finite nanotubes for (a). Zig-Zag SWCNTs, (b). Armchair SWCNTs, (c). Chiral (n>m) SWCNT's, and (d). Chiral (n<m) SWCNT's extrapolated using the cluster method.

in terms of a SWCNT's indexes n and m is:

$$\Delta H_{AB}^* = \frac{313.63}{(m^2 + nm + n^2)} - 168.25(\pm 0.02). \tag{11}$$

Fig. 6 shows a plot of ΔH_{AB}^* vs the indexes *n* and *m* together with the data points for all the SWCNT studied in this project.

A similar analysis was performed for ΔG_{AB}^* . The data from Fig. 5, together with Eq. (10), yielded the following equation for the parameterization of ΔG_{AB}^* (in kcal/mol) in terms of the SWCNT indexes *n* and *m*:

$$\Delta G_{AB}^* = \frac{316.51}{(m^2 + nm + n^2)} - 158.15(\pm 0.03). \tag{12}$$

Fig. 7 shows this equation together with the data we collected for the free energy of SWCNTs in terms of its indexes, n and m.

The discussion of these results, the proposed generalizations and parameterizations, as well as comparison to other results reported in the literature is presented next.

DISCUSSION AND CONCLUSION

An important quantity to study for SWCNT is the strain energy, (E_s) which essentially corresponds to the amount of energy that is required to "roll up" a single carbon graphene sheet into a SWCNT. This can be calculated in different ways. The common approach to calculate the strain energy is by looking at the ΔH_f of the SWCNT in comparison to the ΔH_f for a single graphene sheet as shown in the following equation:

$$E_s = \Delta H_{f (SWCNT)} - \Delta H_{f (graphene)}.$$
(13)

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FIG. 5. The extrapolated bulk free energy atomic binding energy on a per carbon versus the inverse squared diameter for all carbon nanotubes constructed.

Another approach, which we follow in this paper, is to consider the binding energies for both the SWCNT and the graphene sheet. In this case, using $\Delta H_{f(SWCNT)} = \Delta H_{AB(SWCNT)} - \Delta H_{d(graphite)}$ and $\Delta H_{f(graphene)} = \Delta H_{AB(graphene)} - \Delta H_{d(graphite)}$, where ΔH_{AB} , ΔH_d correspond to binding and dissociation energies respectively. It follows from this two expressions that $\Delta H_{f(SWCNT)} - \Delta H_{f(graphene)}$ and $\Delta H_{AB(SWCNT)} - \Delta H_{d(graphite)}$. Using Eq. (13), then

$$E_s = \Delta H_{AB (SWCNT)} - \Delta H_{AB (graphene)}.$$
(14)

Based on general Eq. (7) and using Eq. (14), it is important to realize that $E_s = a/(n^2+nm+m^2)$ where *a* is a constant that depends on the thermodynamic potential to be used. It is also equally important to realize from this relationship that the strain energy is inversely proportional to the SWCNT's diameter: $E_s = k/d^2$.



FIG. 6. A 3-D contour fit of the enthalplic change per carbon atoms global plot of various n and m SWCNT.

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FIG. 7. A 3-D contour fit of the free energy change per carbon atoms global plot of various n and m SWCNT.

Strain energy has been studied previously in the literature^{18–20} and values for the proportionality constant k between the strain energy and the inverse of the square of the nanotube's diameter have been reported. In particular, Bettinger *et al.*,¹⁹ using an approach based on density function theory (Perkew Burke Ernzerhof (PBE)) and periodic boundary conditions on armchair fluoro-carbon nanotubes, obtained a value for k of 183.66 Å² kcal/mol. Also for armchair SWCNT Budyka *et al.*,²⁰ using a symmetry constrained PM3 method obtained a value for k of 203.0 Å² kcal/mol. The main goal of that paper was to find actual radii for armchair SWCNTs. However, the ΔH_f using the SWCNT diameter presented by Dresselhaus and Dresselhaus⁶ for ideal nanotubes versus the ΔH_f using Budyka *et al.* constrained diameters is about 1.8% different, according to equation 4 in their paper. It is important to clarify that in our calculations we used the standard Dresselhaus and Dresselhaus diameter equation in this work. Finally, only Hernandez *et al.*¹⁸ studied the strain energy for both armchairs and zig-zags single-walled carbon nanotubes based on a Young modulus study using a tight binding model. The values of k they reported were 186.8 Å² kcal/mol and 200.6 Å² kcal/mol for armchairs and zig-zags SWCNT respectively.

Hernandez's work differentiated the armchair from the zig-zag SWCNT by obtaining a different value for the strain energy for each one of these two types of SWCNT. Following their lead, four different types of SWCNT were separated for our study. The following proportionality constants (*k*) were obtained between strain energy and $1/d^2$: for armchairs 193.01(±1.50) Å² kcal/mol; for zig-zags 190.56(±1.85) Å² kcal/mol; for chiral (*n*>*m*) 192.85(±1.14) Å² kcal/mol; and for chiral (*n*<*m*) 192.67(±0.73) Å² kcal/mol.

The value of k we obtained for armchair SWCNT was slightly higher than the one reported by Bettinger *et al.* (4.8% difference) and also by Budyka *et al.* (5.2%) but it was slightly lower than the one reported by Hernandez *et al.* (3.2%). Regarding the zig-zag SWCNT, the value we obtained for k was slightly lower than the only value reported in the literature by Hernandez *et al.* (5.3%). To the best of our knowledge, we are the first group to offer strain energy values for chiral nanotubes of both kind of handedness.

On the other hand, in terms of comparing the values of k that we obtained for all four types of SWCNT with each other, it is important to notice again that all those values are within an absolute percent relative standard deviation of 0.68%. A fit of all the 48 different SWCNT of all type of chiralities yielded an excellent fit with a $k = 192.23(\pm 0.70)$ Å² kcal/mol (Fig. 3). Additionally, our result for the enthalpic binding energy of graphene for all SWCNTs is -168.25(± 0.02) kcal/mol, yielding a percentage error of 0.62% when compared to the NIST Chemistry WebBook²⁵ which reports an experimental value for the enthalpy change of C(g) \rightarrow C(graphene sheet) is -169.3 ± 0.2 kcal/mol. All of this led us to propose a unique equation for all types of SWCNTs. Eq. (8) describes ΔH_{AB}^* for any SWCNT in terms of its vector indexes *n* and *m* as shown in Fig. 6. The data

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available for k in the literature were also compared to the one obtained for our global fit (192.23 $Å^2$ kcal/mol) and as a result, it seems that our thermodynamic predictions are within a maximum discrepancy of 5.6%.

Additionally, Kato *et al.* studied properties of armchairs, zig-zags, and chirals (n>m) SWCNTs using DFT with local density approximations (LDA).²³ They addressed the electronic energy versus $1/d^2$ dependency and they found a fit corresponding to a second order. We also fit all our ΔH_{AB}^* data (48 SWCNTs) to a second order

$$\Delta H_{AB}^* = -141.49(\pm 6.92) \left(\frac{1}{d^2}\right)^2 + 200.64(\pm 1.07) \frac{1}{d^2} - 168.32(\pm 0.02),\tag{15}$$

with $\sigma = 0.092$ kcal/mol and R² = 0.9998. The excellent quality of this fit can be seen in Fig. 8(a). When looking at the shapes of SWCNT, for those with diameters less than 4 Å, the bond angle reduction implies that the nanotube effectively loses it cylindrical character. This observation, prompted us to ignore nanotubes with diameters less than 4 Å in the analysis that led us to the linear dependency between the thermodynamic potentials versus $1/d^2$ which we proposed. It may also be the reason no other data on SWCNT with diameters less than 4 Å can be found in the literature. The same analysis was performed on our ΔG_{AR}^* data which led to similar results;

$$\Delta G_{AB}^* = -198.12(\pm 16.77) \left(\frac{1}{d^2}\right)^2 + 213.07(\pm 2.59) \frac{1}{d^2} - 158.34(\pm 0.05),\tag{16}$$

with $\sigma = 0.22$ kcal/mol and R² = 0.9987, as presented in Fig. 8(b).

Kato *et al.* mentioned an apparent extra stability for near-armchair SWCNTs. He related this observation to experimental results reported by Bachilo *et al.*²⁹ In particular, Bachilo *et al.*, using a technique based on measuring the intensity of light emission as a function of excitation and emission wavelengths found that the (6,5) was more abundant than the (9,1).²⁹ These two SWC-NTs have the same diameter but the (6,5) is considered a near-armchair nanotube. Based on this, we analyzed our bulk ΔH_{AB}^* results for near-armchairs against other chiral (*n*>*m*) SWCNTs. We did not observe a significant difference between these two groups of SWCNT at infinite lengths. Specifically, when the (6,5) and the (9,1) were compared, the difference in bulk ΔH_{AB}^* was only 0.05 kcal/mol in favor of the near-armchair (6,5). However, the difference becomes more significant between these two SWCNT when their lengths are finite and decreasing, as shown in Fig 9(a). This observation is in agreement with Bachilo *et al.* experimental work which must have been performed on finite size SWCNT. We cannot comment specifically on Kato's claim as their data was not shown. The same analysis for ΔG_{AB}^* was performed and once again similar results were found for this thermodynamical potential as shown in Figs. 8(b) and 9(b).

As mentioned earlier in the manuscript, we believe that this work is the first to study Gibbs free energy properties of SWCNTs. In order to do this, a similar approach followed for the enthalpy study was used. The free energy work started by separating the four different types of SWCNTs with separate analysis. Excellent fits (Figs. 4(a)-4(d)) were obtained for the data of the Free energy vs $1/d^2$. The term in those fits involving $1/d^2$ can again be related to the process of "rolling up" the graphene sheet into a SWCNT. We have called it strain free energy (G_s) which is given by

$$G_s = \Delta G_{AB (SWCNT)} - \Delta G_{AB (graphene)}.$$
(17)

Once again, this strain free energy is inversely proportional to the square of the SWCNT's diameter: $G_s = k'/d^2$. We obtained the following values for the proportionality coefficient (k') between the free strain energy and $1/d^2$: for armchair 193.36±1.33 Å² kcal/mol, for zig-zag 190.60±1.48 Å² kcal/mol, for chiral (n>m) 195.99±1.37 Å² kcal/mol, and for chiral (n<m) 196.79±0.85 Å² kcal/mol. When comparing the values of k that we obtained for all four types of SWCNT, it is important to notice that all those values are within a percent relative standard deviation of ±0.02. A fit of all the 48 different SWCNT of all type of chiralities yielded an excellent fit with a $k' = 193.99\pm1.14$ kcal Å²/mol and an extrapolated value of $\Delta G^*_{AB(graphene)} = -158.15\pm0.03$ kcal/mol (see Fig. 3 and Eq. (12)). There does not seem to be a reported experimental value for the Gibbs free energy of



FIG. 8. (a). All 48 SWCNTs bulk ΔH_{AB}^* vs 1/d² plot and fitted to a 2nd order polynomial. (b). All 48 SWCNTs bulk ΔG_{AB}^* vs 1/d² plot and fitted to a 2nd order polynomial.

graphene. However, a theoretical value resulting from extrapolations on paralleluene PAH's, triagnulene PAH's, pure-carbon triangulene, and pure-carbon triangulene transitions states (constrained to be flat) growing into graphene sheet,¹⁶ yielded ΔG_{AB}^* is -158.30 ± 0.7 kcal/mol. This seems to be the only known reported value for free energy graphene and the value we obtained from our work is within a margin of difference of 0.095%. All this information led us to propose a unique Eq. (9) for the Gibbs energy of all types of SWCNTs. Fig. 7 shows a three dimensional plot of Eq. (9), where it can be seen that as the indexes increase (radius increases) the Gibbs energy turns more negative. The enthalpy does the same while the strain energy becomes smaller, reducing the entropic contribution to the Gibbs energy. The entropic contribution in kcal/mol, which from the global fits

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FIG. 9. (a.) The enthalpic atomic binding energy per carbon atom and (b.) the free energy per carbon atom plotted against the inverse carbon atom for the finite size near-armchair (6,5) and not near-armchair (9,1) extrapolated to bulk applying cluster method approach.

is $T\Delta S = -166\frac{1}{d^2} - 10.10$ (where diameter is in Å), becomes more relevant as the radius of the SWCNT decreases.

In conclusion, the computationally cost efficient Stewarts semi-empirical PM3 method²² was used to analyze 48 different SWCNTs (armchairs, zig-zag, chiral (n>m), and chiral (n<m)). The accuracy of the PM3 method for thermodynamic calculations combined with a cluster approach has yielded reliable data. Based on these results, a general equation for thermodynamic potentials was proposed in terms of the SWCNT's vector indexes (n,m) for diameter less than 4 Å. This led to a unique equation for all types of SWCNT for ΔH_{AB}^* and another equation for ΔG_{AB}^* . Our results compared well with previously reported results on armchairs and the limited results reported on zig-zags. The comparison with published results was based on strain energy values. Our proposed general unique equation for ΔH_{AB}^* also produces a ΔH_{AB}^* value for graphene which is in excellent 127149-14 Rodriguez et al.

agreement with the accepted experimental value reported in the literature. Finally, this work provides the first enthalpy information on both types of chiral nanotubes and this is a first study that provides Gibbs free energy information on SWCNT structures. All of this gives us the confidence to say that the proposed equations (Eqs. (11) and (12)) should be able to predict thermodynamic values that fall within a percent of error that is acceptable for most practical applications.

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