Simple approach to estimating the van der Waals interaction between carbon nanotubes

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The van der Waals (vdW) interactions between carbon nanotubes (CNTs) were studied based on the continuum Lennard-Jones model. It was found that all the vdW potentials between two arbitrary CNTs fall on the same curve when plotted in terms of certain reduced parameters, the well depth, and the equilibrium vdW gap. Based on this observation, an approximate approach is developed to obtain the vdW potential between two CNTs without time-consuming computations. The vdW potential estimated by this approach is close to that obtained from complex integrations. Therefore, the developed approach can greatly simplify the calculation of vdW interactions between CNTs.

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I. INTRODUCTION

It is widely recognized that the van der Waals (vdW) interaction between two carbon structures, including graphite,[1,2] buckyballs,[3–6] and carbon nanotubes (CNTs),[7–15] is fundamentally important. A wide range of topics for these structures, such as the growth mechanism of fullerene clusters[5,6] and CNTs,[12] the geometry,[7] stability,[9] and vibration modes[13,14] of CNTs, the mechanical performance of single-walled carbon nanotube (SWNT) ropes,[8] and the thermal expansion of solid fullerenes,[3] have been discussed based on the understanding of vdW interactions. Therefore, the subject of the vdW interaction is of great scientific and practical significance.

Although there have been extensive investigations on vdW interactions in graphitic structures, it is desirable to find a universal description for vdW interactions between any two graphitic structures since the structures of graphite, fullerenes, SWNTs, and multiwalled carbon nanotubes (MWNTs) are essentially similar to each other. Initially, Girifalco *et al.*[10] addressed this question using the continuum Lennard-Jones (LJ) model, which has been widely used in the graphitic system.[1,3–6,10,11,15,16] It was found that, when the potential energy is expressed in units of the well depth $|\phi_0|$ and the equilibrium vdW gap g_0, all the potentials between C_{60}-SWNT, C_{60}-C_{60}, SWNT-SWNT, graphene-graphene, and C_{60}-graphene potentials fall on the same curve.[10] Recently, Sun *et al.* confirmed that the conclusion suggested by Girifalco *et al.* was also applicable to SWNTs with different diameters.[15] So far, the vdW interactions between C_{60}-SWNT, C_{60}-C_{60}, SWNT-SWNT, graphene-graphene, and C_{60}-graphene can be described by a universal curve. However, the vdW interactions between MWNTs have not been quantitatively studied yet due to the structural complexity of MWNTs and integrations of hypergeometric functions involved in the expression of the potential. In fact, the complex integration has been met in the study of SWNTs (Refs. 10 and 15) and fullerenes.[16] Even using numeral integrations and simplified expressions,[10,15] the calculation involved of vdW interactions in graphitic structures is quite complex and time consuming.

Is it possible to find an effective, universal, and simple approach of obtaining the vdW interaction between CNTs without time-consuming integrations? In the present work, such an approach has been developed through three steps: (i) the vdW interaction between any two CNTs (labeled as *A* and *B*) has been calculated and found to fall on a universal curve when plotted in terms of certain reduced parameters, the well depth (ϕ_0^{AB}) and the equilibrium vdW gap (g_0^{AB}); (ii) ϕ_0^{AB} and g_0^{AB} are approximately estimated; (iii) using estimated ϕ_0^{AB} and g_0^{AB}, the vdW potential between *A* and *B* is reproduced based on the universal potential and compared with that obtained by numeral integrations.

II. MODELING AND CALCULATION APPROACHES

In the present work, double-walled carbon nanotube (DWNT) and MWNT are treated as the nesting of a series of concentric SWNTs. So the vdW interactions involving DWNT and MWNT are calculated by summing all potential terms contributed by isolated SWNTs. The interaction between two parallel SWNTs has been studied previously.[15] To compare with Girifalco's results and to keep consistent with our previous work, the same LJ parameters were used with $\epsilon=2.39$ meV and $\sigma=3.415$ Å, respectively.[10,15]

Figure 1 illustrates the schematic image of two three-layered MWNTs. With the assumption that the interlayer spacing is a constant, $c=3.39$ Å,[17] a tube can be uniquely expressed by an index $[R_{inner},n]$ under the continuum medium model, here R_{inner} and n indicate the inner radius and the number of layers, respectively. In this work, R_{inner} is in units of Å. Thus, the interaction between tubes *A* and *B* can be expressed by the combination of their indexes, $[R^A_{inner},n_A]$-$[R^B_{inner},n_B]$. For example, [5,1]-[10,20] labels the interaction between a SWNT with a radius of 5 Å and a 20-layered MWNT with an inner radius of 10 Å.

As described above, the interaction between tubes *A* and *B* was calculated by two steps, (i) calculate the interaction between the i layer of tube *A* and the j layer of tube *B* and label it as ϕ^{ij} with $i=1,2,\ldots,n_A$ and $j=1,2,\ldots,n_B$; (ii) sum

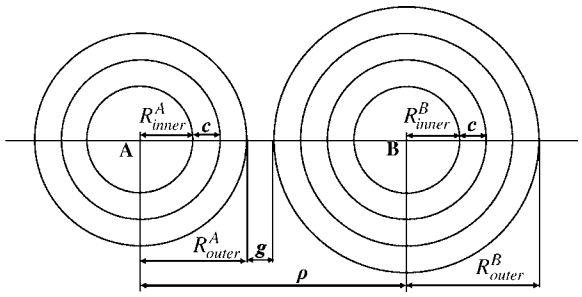

FIG. 1. Schematic drawing of two MWNTs, A and B, with center-to-center distance ρ, inner radii R^A_{inner} and R^B_{inner}, van der Waals gap g, and a constant interlayer spacing c. The value of the outer radius is determined by $R_{outer}=R_{inner}+(n-1)\times c$.

up ϕ^{ij}. Thus, the potential energy for $[R^A_{inner},n_A]$-$[R^B_{inner},n_B]$ was calculated by

$$\phi^{AB}=\sum_{i=1}^{n_A}\sum_{j=1}^{n_B}\phi^{ij}. \tag{1}$$

So far, the calculation of ϕ^{AB} is transformed to calculate the interaction between two SWNTs with the radii of $R_i=R^A_{inner}+(i-1)\times c$ and $R_j=R^B_{inner}+(j-1)\times c$. On the basis of our previous work,[15]

$$\phi_{ij}=\int_0^{2\pi}\theta R_j V(\sqrt{R_j^2+\rho^2-2\rho R_j cos\ \alpha},R_i)d\alpha, \tag{2}$$

where θ is the surface density of carbon atoms, $\theta=4/(\sqrt{3}a^2)$, $a=2.49$ Å is the lattice constant of CNTs;[18] ρ indicates the distance between the centers of two interacting tubes. Here, $\rho=R^A_{inner}+R^B_{inner}+g+(n_A+n_B-2)\times c$, and g is the vdW gap between A and B, as indicated in Fig. 1. And the function V is defined by[19,20]

$$V(r,R)=3\pi\theta\varepsilon\sigma^2\left[\frac{21}{32}\left(\frac{\sigma}{R}\right)^{10}\left(\frac{R}{r}\right)^{11}M_{11}\left(\frac{R}{r}\right)-\left(\frac{\sigma}{R}\right)^4\left(\frac{R}{r}\right)^5 M_5\left(\frac{R}{r}\right)\right] \tag{3}$$

with $r>R$ and M_{11} and M_5 are two elliptic integrals,

$$M_n(z)=\int_0^{\pi}d\beta\frac{1}{(1+z^2-2z\cos\beta)^{n/2}}, \tag{4}$$

where n is a positive integer. The integrals involving the elliptic function were evaluated numerically. Obviously, the effects due to helicity, length, and defects of CNTs are not taken into account in this calculation.

III. RESULTS AND DISCUSSION

The numerical integrations for the potential energy of interactions between two infinitely long CNTs are plotted as $\phi'^{AB}=\phi^{AB}/|\phi_0^{AB}|$ against $\xi\equiv g/g_0^{AB}$, as shown in Fig. 2. Here ϕ_0^{AB} and g_0^{AB} are the minimal value of ϕ^{AB} and the equilibrium vdW gap, respectively. Figure 2(a) shows the results for ten pairs of identical CNTs labeled as $[5,n]$-$[5,n]$. The outer radius R_{outer} ranged from 5 to 197 Å, which were determined by $R_{outer}=R_{inner}+(n-1)\times c$ with $n=1,2,3,6,11,21,31,41,51$, and 61. Figure 2(b) showed the results for six pairs of CNTs labeled as $[5,n_A]$-$[5,n_B]$, and Fig. 2(c) for 12 pairs of different CNTs: $[5,1]$-$[10,1]$, $[5,1]$-$[10,2]$, $[5,2]$-$[10,5]$, $[5,5]$-$[10,10]$, $[10,1]$-$[20,1]$, $[10,1]$-$[20,2]$, $[10,2]$-$[20,5]$, $[10,5]$-$[20,10]$, $[20,1]$-$[50,1]$, $[20,1]$-$[50,2]$, $[20,2]$-$[50,5]$, and $[20,5]$-$[50,10]$. The unreduced potentials near the equilibrium position are also illustrated as the insets in Figs. 2(a)–2(c) for different interacting pairs. As can be seen, all possible combinations (SWNT-SWNT, SWNT-DWNT, SWNT-MWNT, DWNT-DWNT, DWNT-MWNT, and MWNT-MWNT) are included in Figs. 2(a)–2(c). Based on the results illustrated in Figs. 2(a)–2(c), it can be concluded that all potential energies between two infinitely long CNTs fall on the same curve when plotted in terms of certain reduced parameters suggested by Girifalco *et al.*[10] Consequently, the potentials can be represented by a simple analytical form as suggested by Girifalco *et al.*[10] and Sun *et al.*,[15] thereby all computations of vdW interactions in graphitic systems are simplified. Moreover, the unreduced potential energy of any two interacting CNTs can be generated from a universal function of $\phi'-\xi$ if the well depth ϕ_0^{AB} and the equilibrium vdW gap g_0^{AB} are known. The point is how to obtain the values of ϕ_0^{AB} and g_0^{AB}.

First, the value of g_0^{AB} for arbitrary pairs of CNT-CNT is considered. From the insets of Figs. 2(a)–2(c), it is found that g_0^{AB} is almost a constant (as indicated by the dash lines), $g_0^{AB}=3.10\pm0.07$ Å, which is pretty close to the previous numerical calculations for SWNT-SWNT.[10,15] For instance, Girifalco *et al.* suggested a value of 3.13 Å,[10] while the numerical integrations for the potential energy of interactions between two SWNTs with arbitrary radii produced a value of g_0 from 3.107 to 3.169 Å.[15] These results are consistent with the experimental observation.[21] Thus, $g_0^{AB}=3.15$ Å is a good approximation for both SWNTs (Ref. 22) and MWNTs.

Second, the value of ϕ_0^{AB} for arbitrary pairs of CNT-CNT was estimated. Previously, the calculation of the vdW potentials relied on the numeral integration,[10,15] which was time consuming. Considering that the potential between two CNTs can be described by a universal potential, is it possible to get the value of ϕ_0^{AB} without integration? Here a positive answer is given based on the universal potential function suggested by Girifalco *et al.*[10] The universal potential function of $\phi'-\xi$ is described by a series of points (ϕ'_i,ξ_i), which was obtained by the numeral integration of the potential between two identical SWNTs (10,10), as shown in Fig. 3. On the basis of Fig. 3, ϕ^{ij} with $i<(n_A-3)$ or $j<(n_B-3)$ can be neglected. Thereby, ϕ_0^{AB} is approximately estimated by

$$\phi_0^{AB}=\sum_{i=n_A-3}^{i=n_A}\sum_{j=n_B-3}^{j=n_B}\phi^{ij}. \tag{5a}$$

On the right-hand side, the terms of ϕ^{ij} indicate the interaction between i and j layers when A and B are at the equilibrium distance, that is, $g=g_0^{AB}$, as illustrated in Fig. 1. To further simplify Eq. (5a) and get the values of ϕ^{ij} without

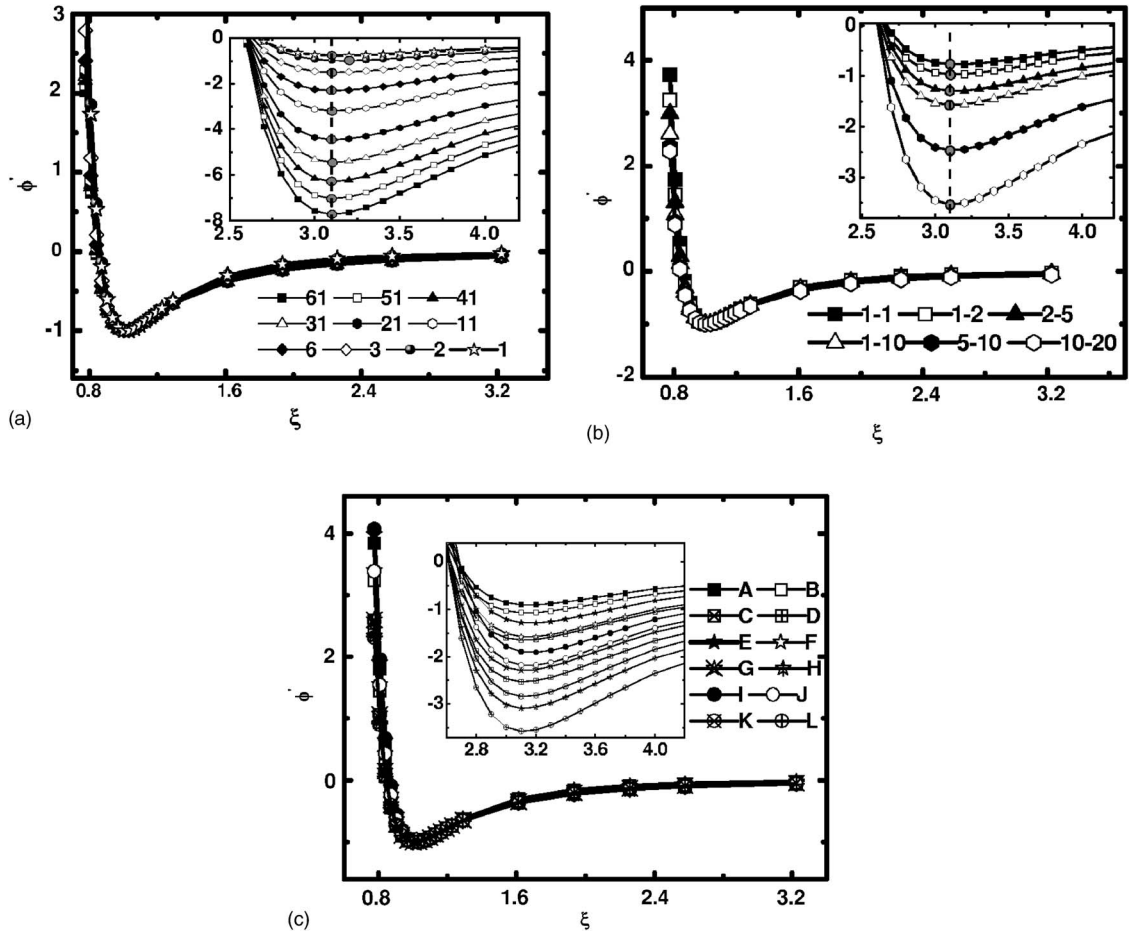

FIG. 2. The tube potential energy of an interaction between two CNTs $[R^A_{inner},n_A]$-$[R^B_{inner},n_B,n_B]$. (a) $[5,n]$-$[5,n]$ with n=61, 51, 41, 31, 21, 11, 6, 3, 2, and 1; (b) $[5,n_A]$-$[5,n_B]$ with six pairs of n_A-n_B (1-1, 1-2, 2-5, 1-10, 5-10, and 10-20); (c) $[R^A_{inner},n_A]$-$[R^B_{inner},n_B]$ for 12 pairs of different CNTs marked as $A,B,\ldots$, and L, sequentially corresponding to $[5,1]$-$[10,1]$, $[5,1]$-$[10,2]$,…, and $[20,5]$-$[50,10]$, as listed in the text.

integration, it is assumed that $g_0^{AB}\approx 3.15$ Å as illustrated above, which to $\xi_1=1$, $\xi_2=2.02$, $\xi_3=3.03$, and $\xi_4=4.05$, with $\phi_1'=-1$, $\phi_2'=-0.13$, $\phi_3'=-0.03$, and $\phi_4'=-0.01$ from the potential function, as shown in Fig. 3. Thereby, Eq. (5a) was expanded as

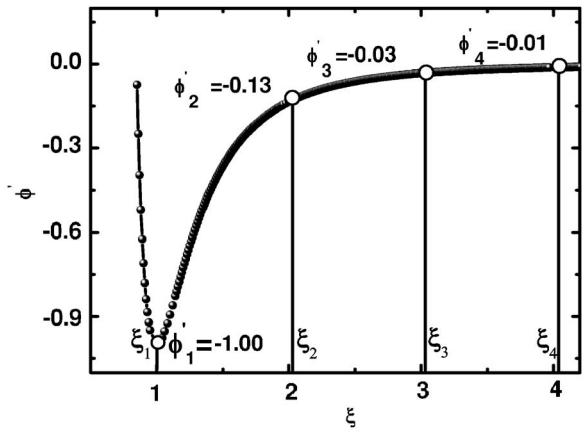

FIG. 3. The universal potential reproduced by numeral calculations of the potential between two isolated (10,10) SWNTs with the well depth ϕ_0=95.16 meV/Å and the equilibrium vdW gap g_0=3.15 Å (Ref. 10).

$$\phi_0^{AB} = \phi_0^{n_An_B} + 0.13(\phi_0^{(n_A-1)n_B} + \phi_0^{n_A(n_B-1)}) + 0.03(\phi_0^{(n_A-2)n_B} + \phi_0^{(n_A-1)(n_B-1)} + \phi_0^{n_A(n_B-2)}) + 0.01(\phi_0^{(n_A-3)n_B} + \phi_0^{(n_A-2)(n_B-1)} + \phi_0^{(n_A-1)(n_B-2)} + \phi_0^{n_A(n_B-3)}) \quad (5b)$$

with

$$\phi_0^{ij} = -\sqrt{(3.13-37.9\sqrt{R_i^A})\times(3.13-37.9\sqrt{R_j^B})} \quad (i=n_A,\ldots,n_A-3,\quad j=n_B,\ldots,n_B-3), \quad (5c)$$

$$R_i^t = R_{inner}^t + (i-1)\times c \quad (i=n_t,\ldots,n_t-3;t=A,B). \quad (5d)$$

Potential terms (ϕ_0^{AB} and ϕ_0^{ij}) and radii (R_i^t and R_{outer}^t) are in units of meV/Å and Å, respectively. In Eq. (5c), the well depth for the potential between *identical* SWNTs is based on the formula proposed by Girifalco *et al.*[10] with a slight

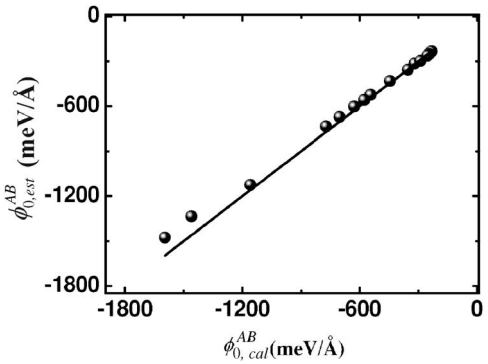

FIG. 4. ϕ_0^{AB} obtained by numeral integrations based on Eq. (1) and an approximate estimation according to Eqs. (5b)–(5d), labeled as $\phi_{0,cal}^{AB}$ and $\phi_{0,est}^{AB}$, respectively.

modification.[23] And the well depth of the potential between two different SWNTs is simply estimated by the geometric value, and this approximate treatment has been confirmed to be acceptable when the radius of the i layer is close to that of the j layer according to previous numeral calculations.[15] So far, based on Eqs. (5b)–(5d), the well depth of the potential between two CNTs can be obtained without any integration. Specially, when one CNT of A and B contains less than four layers, corresponding terms in Eq. (5a) can be expanded without further simplification.

To illustrate the validity of the above approach, 15 pairs of CNT-CNT were selected and their potentials from numeral integrations and the above estimation were compared, as shown in Fig. 4. The diameters of MWNTs employed in Fig. 4 range from 4 to 200 nm. The solid line indicates the function of $\phi_{0,cal}^{AB}=\phi_{0,est}^{AB}$. Clearly, the estimated results indicated by solid spheres in Fig. 4 are quite close to those obtained from numeral integrations. The maximal relative error is 8.0%. As suggested by Eq. (5a) and the above approximate treatment of g_0^{AB}, the errors are mainly attributed to three factors, (i) ϕ^{ij} with $i<(n_A-3)$ or $j<(n_B-3)$ are neglected, while, the weight of these terms in ϕ_0^{AB} gradually increases with the increment in radius; (ii) the estimation of g_0^{AB} is too simple for CNTs with large radii; (iii) ϕ_0^{ij} estimated by Eq. (5c) is slightly lower than that from numeral integrations for large CNTs. According to the present calculation, to take more terms of ϕ^{ij} into account is an effective approach to improve the estimation quality of ϕ_0^{AB}, without any time-consuming calculation.

Using the above approach [Eqs. (5a)–(5d)], both ϕ_0^{AB} and g_0^{AB} can be easily estimated without any integration, thus, the vdW potential function for any two CNTs can be reproduced. As a confirmation, [5,20]-[10,40] was employed and its vdW potential function ($\phi-g$) was estimated on the basis of Eqs. (5a)–(5d) and compared with that obtained by numeral integrations, as shown in Fig. 5. Clearly, the estimated potential is quite close to that obtained by numeral integrations based on Eq. (1). In the range with $g^{AB}>4$ Å, the potential is underestimated due to the underestimation of ϕ_0^{AB}, as described above. However, in overwhelming cases, the range near the equilibrium position is of interest, and the estimated results in this range are quite good. Thereby, the vdW potential function for CNTs can be approximately reproduced just based on Eqs. (5a)–(5d) and the universal potential indicated by Girifalco *et al.*[10], without time-consuming integrations.

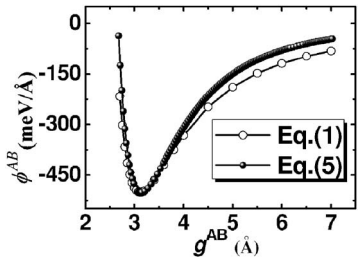

FIG. 5. The vdW potential functions of $\phi-g$ for [5,20]-[10,40]. Solid spheres and open circles are obtained by an approximate estimation based on Eq. (5) and numeral integrations based on Eq. (1), respectively.

The vdW interaction between CNTs is a basic subject for the research of CNTs and has a great effect on a lot of properties of CNTs, as demonstrated previously.[10,15] Here, it is especially important to point out that the universal potential shown in Fig. 3 is also suitable for other graphitic structures,[10] such as fullerenes and multiwalled hollow carbon nanoparticles (CNPs), thereby, the approach suggested in the present work is also applicable for these systems. As an example of its application, the vdW interaction between CNTs with a diameter of about 40 nm was calculated and compared with that between CNPs which were mixed with MWNTs. It was found that the vdW interaction between MWNTs was 1 order of magnitude higher than that for CNPs, indicating that MWNTs and CNPs can be separated from each other. As a result, a novel method through the polymer-induced steric stabilization has been developed to separate MWNTs and CNPs.[24]

IV. CONCLUSIONS

The potential energy of vdW interactions between two parallel, infinitely long and perfect CNTs labeled as A and B has been calculated based on the continuum LJ model. It is found that, (i) when the energy is expressed in units of the well depth ϕ_0^{AB} and the equilibrium vdW gap g_0^{AB}, all the potentials between two arbitrary CNTs fall on the universal curve suggested by Girifalco *et al.*; (ii) $g_0^{AB}\approx 3.15$ Å is a good approximation for both SWNTs and MWNTs; (iii) on the basis of Eqs. (5a)–(5d), the value of ϕ_0^{AB} can be approximately estimated without any integration. Based on the above results, the vdW potential function for any two CNTs can be reproduced without any integration, which greatly simplifies the computation of the vdW interaction between CNTs.

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[22] L.A. Girifalco *et al.* suggested a value of 3.13 Å based on the interaction between two identical SWNTs with a radius from several angstroms to nanometers. Based on our previous work (Ref. 15) and the present work, 3.15 Å seems better, especially for CNTs with large radii.
[23] As pointed in Ref. 15, the values calculated from Eq. (15) in Ref. 10 correspond to the potentials between two SWNTs *in a close-packing rope*. Hence, they should be divided out by 3 when they are employed to describe the interaction between two *isolated* SWNTs.
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