Preferred orientations of encapsulated C_{60} molecules inside single wall carbon nanotubes*

Yao Zhen(姚 震), Liu Ran(刘 然), Ma Feng-Xian(马凤仙), Lu Shuang-Chen(路双臣), Tian Fu-Bo(田夫波), Duan De-Fang(段德芳), Cui Tian(崔 田), and Liu Bing-Bing(刘冰冰)†

State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, *China*

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A systematical study of the orientational behavior of C_{60} molecules in single wall carbon nanotubes (SWCNTs) with different chirality and diameter has been performed by using a model of an infinite long nanotube filled with two C_{60} (denoted as C_{60}-1 and C_{60}-2) molecules. We studied the preferred orientation of the C_{60}-1 molecule when the neighboring C_{60}-2 molecule was fixed at the pentagon, double-bond, and hexagon orientations respectively. Our results showed that the C_{60}-1 molecule prefers the pentagon (hexagon) orientation when the tube diameter is smaller (larger) than 1.31 nm (1.36 nm). For the tube diameter in between, the preferred molecular orientation of C_{60}-1 changes from pentagon to hexagon with the increasing tube diameter when the neighboring C_{60}-2 molecule is fixed at the pentagon or double-bond orientation. A novel vertex orientation for the C_{60}-1 molecule has been found when the C_{60}-2 molecule is fixed at the hexagon orientation.

Keywords: peapod, C_{60}, nanotube, orientation

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1. Introduction

The ideal one-dimension (1D) nano-channel of single wall carbon nanotubes (SWCNTs)[1] can be utilized for many potential applications, such as biohazard material carriers, anaerobic sealants, and one-dimensional array elements.[2] The incorporation of atoms or molecules into the inner space of SWCNTs is an important way to modify the properties of both the host and the guest materials.[3–12] Liu *et al*. found that the impurity doping in-tube is dependent on the SWCNT's diameter and chirality.[13] The so-called nanopeapod, a self-assembled chain of C_{60} molecules inserted into SWCNT,[14–16] is an ideal model system for studying the properties of dimensionally constrained crystal structures. It provides a unique opportunity to investigate the structures and properties of 1D host–guest hybrid materials.[17–23] The intermolecular interactions in these self-assembled carbon nanostructures and the dynamic behavior of the encapsulated molecules[24] are different from those in solid fullerenes.[25–27] Thus studying the rotation dynamics of C_{60} molecules under the 1D confined condition has attracted considerable interest recently.

Experimental studies on peapods by inelastic neutron scattering (INS)[28,29] and nuclear magnetic resonance (NMR)[30] suggest that the linear arrays of C_{60} molecules still rotate inside SWCNTs at room temperature, either showing quasi-free rotation or being dynamically disordered with high orientation mobility. Very recently, we have demonstrated using the high pressure Raman method that C_{60} molecules in nanotubes exhibit an unusual type of ratcheted rotation hindered at the hexagon orientation at very low temperatures.[31] To further understand the experimental results, we have theoretically studied the low-energy orientation of C_{60} molecules inside the nanotube. The results showed that well-regulated arranged C_{60} molecules in three armchair nanotubes ($n = m = 9$, 10, 11) have a preferred hexagon orientation with the lowest energy. This preferred orientation supports our experimental observations. In fact, more detailed theoretical studies on the low-energy orientation have already been conducted by Michel and Verberck[32–34] for armchair nanotubes as well as zigzag- and chiral-nanotubes. They suggested that there are three different lowest potential energy states with the pentagon, double-bond, and hexagon orientations (i.e., the five-, two-, and three-fold axes coincide with the tube axis, respectively) for the trapped C_{60}. In their studies, the most stable pentagon and double-bond orientations have been obtained in ($n = m = 9$, 10) and ($n = m = 11$) armchair nanotubes, respectively, which are different from our theoretical results of hexagon orientation.[31] We have carefully compared our theoretical model with the one constructed by Michel *et al*. It was noted that only one single C_{60} was filled into an infinite nanotube in their work, while a peapod system with C_{60} molecules periodically arranged into a nanotube was constructed in our simulation. We called it the one-dimension periodic model, which included not only the interaction between the C_{60} molecule and the tube wall, but also the in-

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†Corresponding author. E-mail: liubb@jlu.edu.cn

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teraction between adjacent C_{60} molecules. It is obvious that the intermolecular interaction can influence the preferred orientation of encapsulated C_{60} molecules significantly. In our previous work,[31] we only simulated the orientational behaviors of C_{60} encapsulated in three armchair-type nanotubes. In addition, only one axis rotation has been performed to search for the low-energy molecular orientation with the periodic arranged molecules in the same orientation. Thus, further studies with the rotary path covering all the molecular orientations and changing neighboring C_{60} molecule orientations are necessary.

In this work, we systematically study the orientational behaviors of C_{60} molecules in different nanotubes with the diameter ranging from 1.31 nm to 1.76 nm. In order to study the influence of the intermolecular interaction on the molecular preferred orientation, we construct a model with two C_{60} (C_{60}-1 and C_{60}-2) molecules filled in a tube. A comparative study on C_{60}–tube interaction energy, C_{60}–C_{60} interaction energy, and the total interaction energy is performed by using the van der Waals interaction potential calculation. The results show that the C_{60}-1 molecule exhibits three preferred orientations when we only consider the interaction between the C_{60}-1 molecule and the tube. If considering only the inner intermolecular interaction, we find that the C_{60}-1 molecule always prefers the hexagon orientation independent of the orientation of the neighboring C_{60}-2. The results obtained in the total interaction potential calculation show that the preferred orientation of the C_{60}-1 molecule is dependent on the tube confinement effect for the diameter smaller than 1.31 nm and the intermolecular interaction for the diameter larger than 1.36 nm. For the intermediate tubes, both the tube confinement effect and the intermolecular interaction affect the molecular preferred orientation. These results show that the intermolecular interaction of adjacent C_{60} molecules as well as the interaction between C_{60} and the tube wall plays an important role on the orientational behavior of C_{60} in tubes.

2. Model and simulation method

In the theoretical study of this hybrid system, we construct a model with two rigid C_{60} molecules filled in a nanotube. As shown in Fig. 1, we fix the nanotube on a Cartesian coordinate system (X, Y, Z) with the center of mass in the origin O, the Z axis coincides with the tube's long axis. As the length (~ 40 Å) of the nanotube is long enough compared to the diameter of the encapsulated C_{60} molecule, the edge effect can be ignored. Two C_{60} molecules (C_{60}-1 and C_{60}-2) are put on the tube axis position with the centers of mass on origins o_1 and o_2 of coordinate systems (x_1, y_1, z_1) and (x_2, y_2, z_2). Origins o_1 and o_2 respectively locate at (0, 0, 4.85 Å) and (0, 0, −4.85 Å) in the (X, Y, Z) coordinate system. Thus, the center-to-center distance of the two C_{60} molecules is 9.7 Å, which is consistent with the previous report in experiment[35] and the theory value.[21] We describe the molecular orientation by using two Euler angles β and γ, which correspond to the x_1 (x_2) and z_1 (z_2) axis rotation angles, respectively. The starting orientations (with $\beta = \gamma = 0$) of the two C_{60} molecules have been defined as the five-fold axis coinciding with the tube axis. As shown in Fig. 2, we define the molecular pentagon, double-bond, and hexagon orientations as the five-, two-, and three-fold axes coinciding with the tube axis, respectively. In addition, we introduce a new molecular orientation in Fig. 2(d), in which the tube axis crosses two opposite vertex atoms. Within the model of Fig. 1, we rotate the C_{60}-1 molecule around the z_1 and the x_1 axes with angles of $\gamma_1 = 360^\circ$ and $\beta_1 = 180^\circ$, respectively. The rotary path covers all the molecular orientations. For the C_{60}-2 molecule, the pentagon, double-bond, and hexagon orientations have also been considered in this work, which correspond to the Euler angles ($\beta_2 = 0$, $\gamma_2 = 0$), ($\beta_2 = 148$, $\gamma_2 = 0$), and ($\beta_2 = 37.37$, $\gamma_2 = 0$), respectively. Thus, we can calculate the systematic van der Waals interaction potential V between C_{60} and the nanotube, as well as that between C_{60}-1 and C_{60}-2 with varying molecular orientations, which can be written as V(C_{60}-1, tube), V(C_{60}-2, tube), and V(C_{60}-1, C_{60}-2), respectively. For the V(C_{60}-1, C_{60}-2) calculation, all the C_{60}-1 molecular orientations have been considered with the C_{60}-2 molecule fixed on the pentagon, double-bond, or hexagon orientation. Here, we define the total interaction potential V_{total} as the summation of V(C_{60}-1, tube), V(C_{60}-2, tube), and V(C_{60}-1, C_{60}-2). The interaction potential $v(\boldsymbol{r};\beta,\gamma) = v|\boldsymbol{r}_{\text{C60}}\text{-}\boldsymbol{r}_{\text{tube}}|$ or $v|\boldsymbol{r}_{\text{C60}}\text{-}\boldsymbol{r}_{\text{C60}}|$ for given Euler angles β and γ arises from a pair of atoms from C_{60} (C_{60}-1 or C_{60}-2) and the nanotube or C_{60}-1 and C_{60}-2, respectively. The total interaction potential $V(R_{\text{T}};\beta,\gamma)$ for a given tube diameter R_{T} can be obtained by summing over all pair interactions

$$V(\text{C}_{60}\text{−}1,\text{tube}) = \sum_{N_\tau}\sum_{N_\lambda} v(|\boldsymbol{r}_\tau - \boldsymbol{r}_\lambda|), \tag{1}$$

$$V(\text{C}_{60}\text{−}2,\text{tube}) = \sum_{N_\tau}\sum_{N_{\lambda^*}} v(|\boldsymbol{r}_\tau - \boldsymbol{r}_{\lambda^*}|), \tag{2}$$

$$V(\text{C}_{60}\text{−}1,\text{C}_{60}\text{−}2) = \sum_{N_\lambda}\sum_{N_{\lambda^*}} v(|\boldsymbol{r}_\lambda - \boldsymbol{r}_{\lambda^*}|), \tag{3}$$

where τ, λ, and λ^* index the atoms of the nanotube, C_{60}-1, and C_{60}-2, respectively; $\boldsymbol{r}_i$ and N_i ($i = \tau, \lambda, \lambda^*$) stand for the coordinate and the resulting number of corresponding atoms, respectively. The total interaction potential V_{total} can be written as

$$\begin{aligned} V_{\text{total}} = {} & V(\text{C}_{60}\text{−}1,\text{tube}) + V(\text{C}_{60}\text{−}2,\text{tube}) \\ & + V(\text{C}_{60}\text{−}1,\text{C}_{60}\text{−}2). \end{aligned} \tag{4}$$

The Lennard–Jones 6–12 potential has been applied to describe the van der Waals interaction between atoms separated

by a distance r

$$v(r) = D_0 \left(-2 \left(\frac{R_0}{r} \right)^6 + \left(\frac{R_0}{r} \right)^{12} \right), \quad (5)$$

with $D_0 = 0.0951$ kcal/mol and $R_0 = 3.8983$ Å.[36] Such an interaction potential has been successfully used in describing the C_n-peapod system.[37–40]

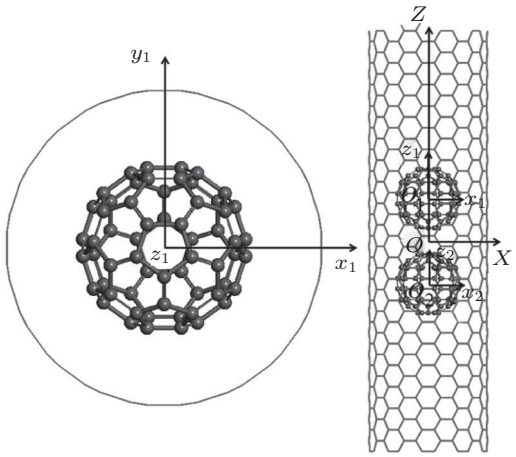


Fig. 1. The constructed model with two C_{60} molecules (C_{60}-1 and C_{60}-2) encapsulated in an SWCNT with a center–center distance of 9.7 Å. The left and right images are the projections in the (X, Y) and (X, Z) planes, respectively.

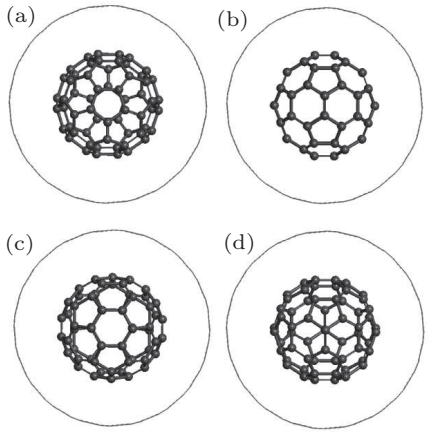


Fig. 2. (a) Pentagon, (b) double–bond, (c) hexagon, and (d) vertex orientations for the encapsulated C_{60} molecule inside the tube obsevered in the parallel tube axis orientation. The circle is the tube wall.

3. Result and discussion

The calculated results of interaction potential V(C_{60}-1, tube) is shown in Fig. 3; only the interaction between C_{60}-1 and the nanotube has been considered. We can see that the C_{60}-1 molecule inside the (10,10) nanotube prefers the pentagon orientation, corresponding to twelve low-energy states. For the (12,12) nanotube, the thirty low-energy states indicate that the C_{60}-1 molecule prefers the double-bond orientation. With the tube diameter increased, the preferred double-bond and hexagon molecular orientations are found for the (16,8) achiral nanotube. Further increasing the tube diameter to a (13,13) nanotube, the obtained twenty low-energy states suggest that the C_{60}-1 molecule prefers the hexagon orientation. More results on the preferred orientations of C_{60}-1 in nanotubes with various diameters are listed in Table 1. It can be seen that the C_{60}-1 molecule prefers the pentagon orientation in the tubes with a diameter smaller than 1.46 nm and the hexagon orientation in the tubes with a diameter larger than 1.66 nm. The double-bond orientation is preferred in the tubes with intermediate diameters. The critical diameters for the variations from pentagon to double-bond and to hexagon orientation are slightly larger than those calculated in Ref. [33], in which the corresponding critical diameters are 1.4 nm and 1.58 nm, respectively. We believe that this small difference is owing to the different simulation equation and potential parameters.

Secondly, we study the preferred orientation of the C_{60}-1 molecule when only considering the C_{60}-1 and C_{60}-2 intermolecular interaction without the tube confinement by using Eq. (3). As shown in Fig. 4, the van der Waals interaction potential as a function of rotation angles β_1 and γ_1 of the C_{60}-1 molecule has been calculated when the C_{60}-2 molecule adopts the pentagon, double-bond, and hexagon orientations respectively. We compare the stability of the different relative orientations between C_{60}-1 and C_{60}-2 molecules. We use 1, 2, and 3 to denote the pentagon, double-bond, and hexagon orientations, respectively. Thus, the interaction potential for two molecules with different relative orientations can be written as V_{ij} ($i, j = 1, 2, 3$;, subscripts i and j stand for the orientations of C_{60}-1 and C_{60}-2 molecules, respectively). When the C_{60}-2 molecule is fixed at the pentagon orientation (see Fig. 4(a)), we can see that the interaction potential V_{11} is larger than V_{13}, but smaller than V_{12}, i.e., $V_{12} > V_{11} > V_{13}$. The obtained minimum interaction potential V_{13} indicates that the C_{60}-1 molecule prefers the hexagon orientation, and the maximum value of V_{12} suggests that the double-bond orientation is not stable. The intermediate value of V_{11} indicates that the pentagon orientation is the metastable state. In the case of the C_{60}-2 molecule fixed at the double-bond orientation (Fig. 4(b)), the obtained relationship of interaction potential is $V_{22} > V_{21} > V_{23}$. It is clear that the C_{60}-1 molecule still exhibits a preferred hexagon orientation, a metastable pentagon orientation, and an unstable double-bond orientation. When the C_{60}-2 molecule is fixed at the hexagon orientation (Fig. 4(c)), the relationship of interaction potential is found to be $V_{31} > V_{32} > V_{33}$. In this case, the hexagon orientation is still the preferred orientation of the C_{60}-1 molecule, and the double-bond orientation is more stable than the pentagon orientation. Since the interaction potentials V_{12}, V_{13}, V_{23} are equal to V_{21}, V_{31}, V_{32}, respectively,

we can obtain the total relationship of interaction potential as $V_{22} > V_{12}(V_{21}) > V_{11} > V_{13}(V_{31}) > V_{23}(V_{32}) > V_{33}$. According to the above analysis, we know that the C_{60}-1 molecule always prefers the hexagon orientation independent of the orientation of C_{60}-2. In addition, we find that the maximum positive interaction potential is V_{22} (0.03 eV), suggesting the existence of a strong repulsion between the double-bond of two C_{60} molecules when facing each other. The minimum V_{33} (-0.3904 eV) indicates the maximum gravitational interaction between the hexagons of the two C_{60} molecules when facing each other. Thus, the two cases correspond to the most unstable and the most stable molecular orientations, respectively.

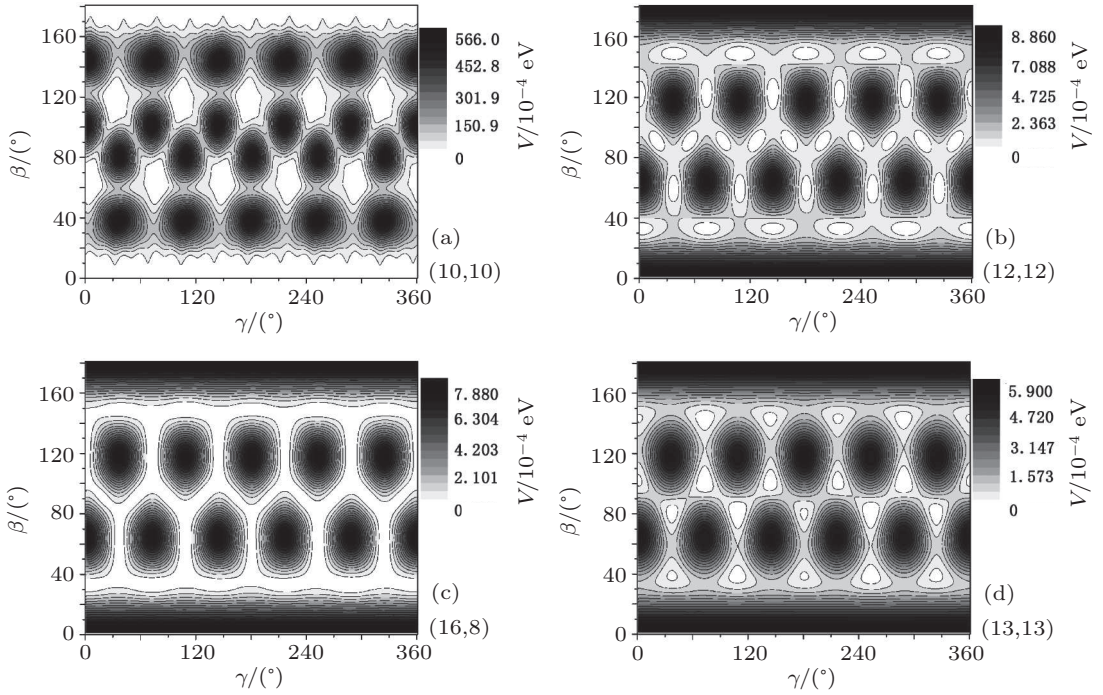


Fig. 3. Contour maps of the systematic van der Waals interaction potential $V(C_{60}\text{-}1(\beta, \gamma)$, tube) for (a) (10,10), (b) (12,12), (c) (16,8), and (d) (13,13) nanotubes. The minimum value has been subtracted.

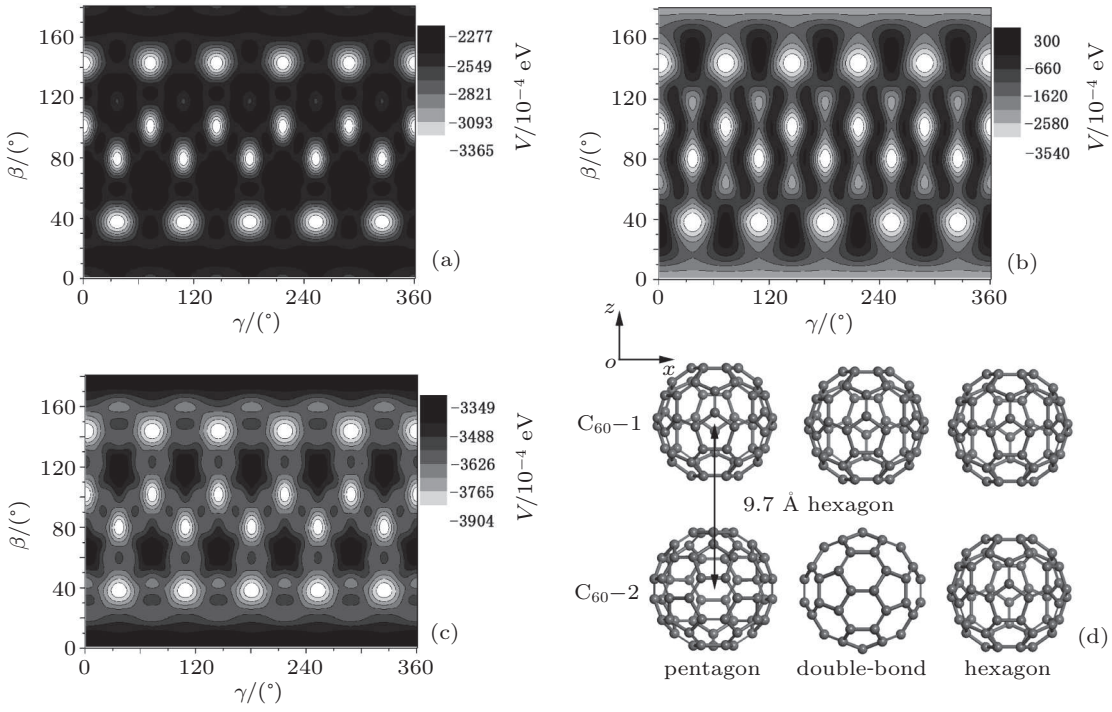


Fig. 4. Contour maps of the systematic van der Waals interaction potential $V(C_{60}\text{-}1(\beta,\gamma),C_{60}\text{-}2)$ with the C_{60}-2 adopted (a) pentagon, (b) double-bond, and (c) hexagon orientations respectively. (d) The preferred orientations of the C_{60}-1 molecule and the fixed orientations of the C_{60}-2 molecule are presented on the (x, z) plane.

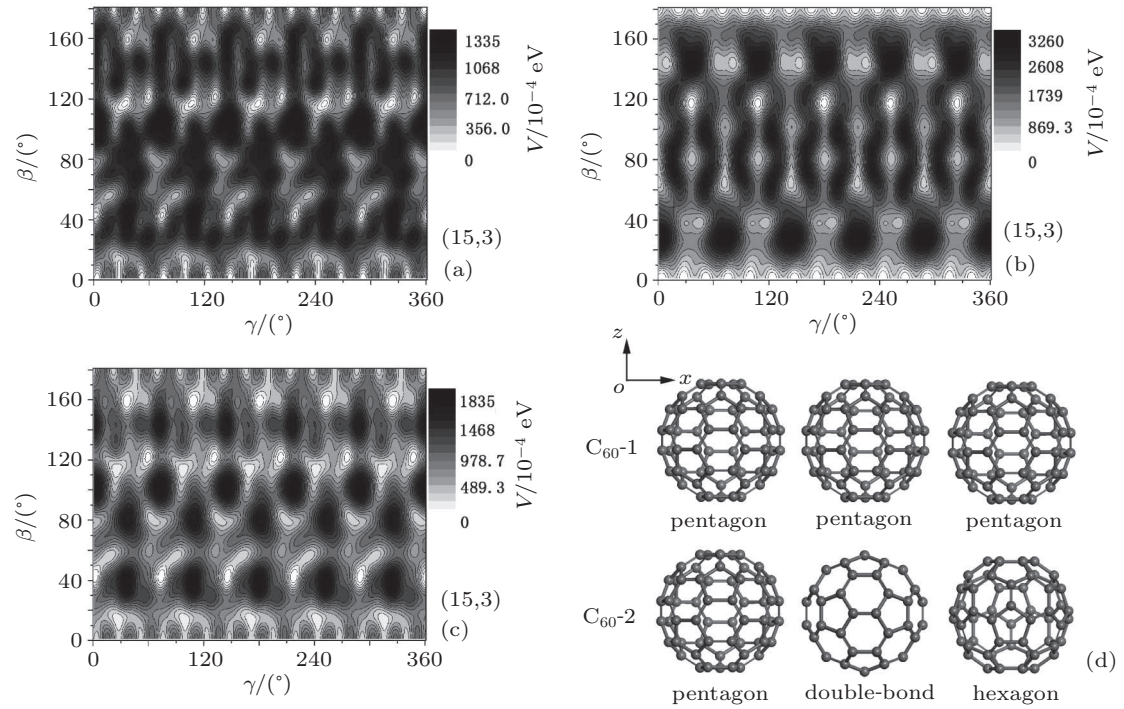


Fig. 5. Contour maps of the systematic total van der Waals interaction potential V_{total} for the (15,3) nanotube with the C_{60}-2 adopted (a) pentagon, (b) double-bond, and (c) hexagon orientations respectively. The minimum value has been subtracted. (d) The preferred orientations of the C_{60}-1 molecule and the fixed orientations of the C_{60}-2 molecule are presented on the (x, z) plane.

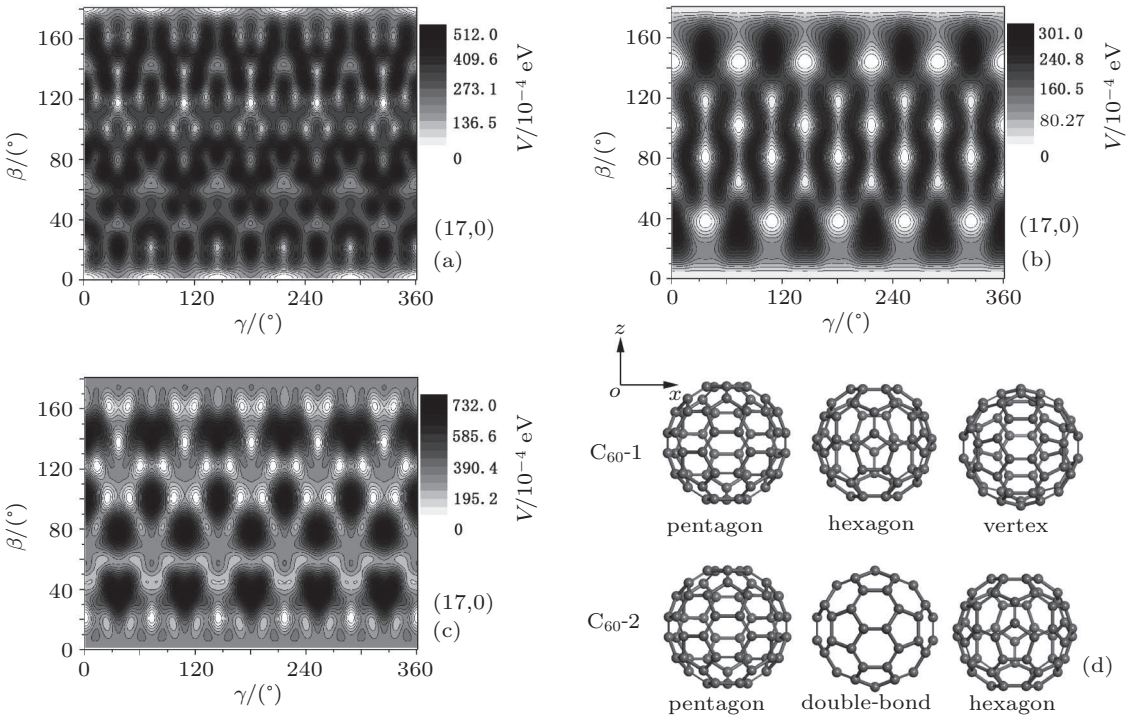


Fig. 6. Contour maps of the systematic total van der Waals interaction potential V_{total} for the (17,0) nanotube with the C_{60}-2 adopted (a) pentagon, (b) double-bond, and (c) hexagon orientations respectively. The minimum value has been subtracted. (d) The preferable orientations of the C_{60}-1 molecule and the fixed orientations of the C_{60}-2 molecule are presented on the (x, z) plane. The image of preferable pentagon orientation of the C_{60}-1 molecule when the C_{60}-2 molecule is fixed on the double-bond orientation can be found in Fig. 5.

We further study the total interaction potential V_{total} by considering the interaction between the two C_{60} molecules and the nanotube, as well as the intermolecular interaction, to search for the preferred molecular orientation. As shown in Figs. 5–8, the total interaction potential as a function of rotation angles β_1 and γ_1 of C_{60}-1 has been calculated with the C_{60}-2 molecule adopted the pentagon, double-bond, and hexagon orientations respectively. For the (15,3) nanotube in Fig. 5, it can be seen that the C_{60}-1 molecule prefers the pentagon orientation, which is independent of the orientation

of the C_{60}-2 molecule. With the diameter increased to a (17,0) nanotube, the C_{60}-1 molecule still prefers the pentagon orientation when the C_{60}-2 molecule is fixed at the pentagon orientation (Fig. 6(a)). When the C_{60}-2 molecule adopts the double-bond orientation, we find that both the pentagon and the hexagon orientations become the preferred arrangements of C_{60}-1 (Fig. 6(b)). Interestingly, a new preferred orientation of the C_{60}-1 molecule has been found when the C_{60}-2 molecule is fixed at the hexagon orientation (Fig. 6(c)), which corresponds to sixty low-energy states. We can see that the tube axis crosses two opposite carbon atoms of the C_{60}-1 molecule in this preferred orientation, and it has been defined as the vertex orientation (see Fig. 2(d)). For the (20, 0) and (13, 13) nanotubes with larger diameters (see Figs. 7 and 8), we can see that the C_{60}-1 molecule prefers the hexagon orientation independent of the orientation of the C_{60}-2 molecule. In order to determine the transition diameters for the preferred orientation variations, we list the preferred orientations of the C_{60}-1 molecule for all considered nanotubes in Table 1. It can be seen that the C_{60}-1 molecule prefers the pentagon orientation when the tube diameter is smaller than 1.31 nm. This preferred orientation is consistent with the interaction potential V(C_{60}-1,tube) calculation, we thus suggest that the tube confinement plays a leading role in such small diameter nanotubes. With the tube diameter increased, the preferred orientation becomes the hexagon orientation when the C_{60}-2 molecule is fixed at the pentagon or double-bond orientation. When the C_{60}-2 molecule adopts the hexagon orientation, the C_{60}-1 molecule prefers the vertex orientation in the tubes with a diameter in the range from 1.31 nm to 1.36 nm. Thus, we know that the preferred orientation of the C_{60}-1 molecule is dependent on not only the tube confinement but also the neighboring molecules interaction. With further increasing the tube diameter, the C_{60}-1 molecule prefers the hexagon orientation. This preferred orientation is the same as that only considering the C_{60}-1 and C_{60}-2 interaction, indicating that the intermolecular interaction plays a leading role in large diameter tubes. According to these studies, we know that the interactions of C_{60}-1–tube and C_{60}-1–C_{60}-2 compete to determine the molecular preferred orientation. The preferred molecular orientation is dependent on the tube confinement effect when the tube diameter is smaller than 1.31 nm, and it is dependent on the intermolecular interaction when the tube diameter is larger than 1.36 nm. And both interactions play a very important role for the intermediate tubes. It should be mentioned that the double-bond orientation of the C_{60}-1 molecule with the lowest-energy state is absent when the intermolecular interaction is considered in this work. This can be explained by the fact that the hexagon orientation of the C_{60}-1 molecule is more suitable than the double-bond orientation when only considering the C_{60}-1 and C_{60}-2 interaction. The result clearly shows that the interaction between adjacent C_{60} molecules and that between C_{60} and the tube wall play important roles in determining the orientational behaviors of C_{60} molecules inside the nanotubes. It is important to note

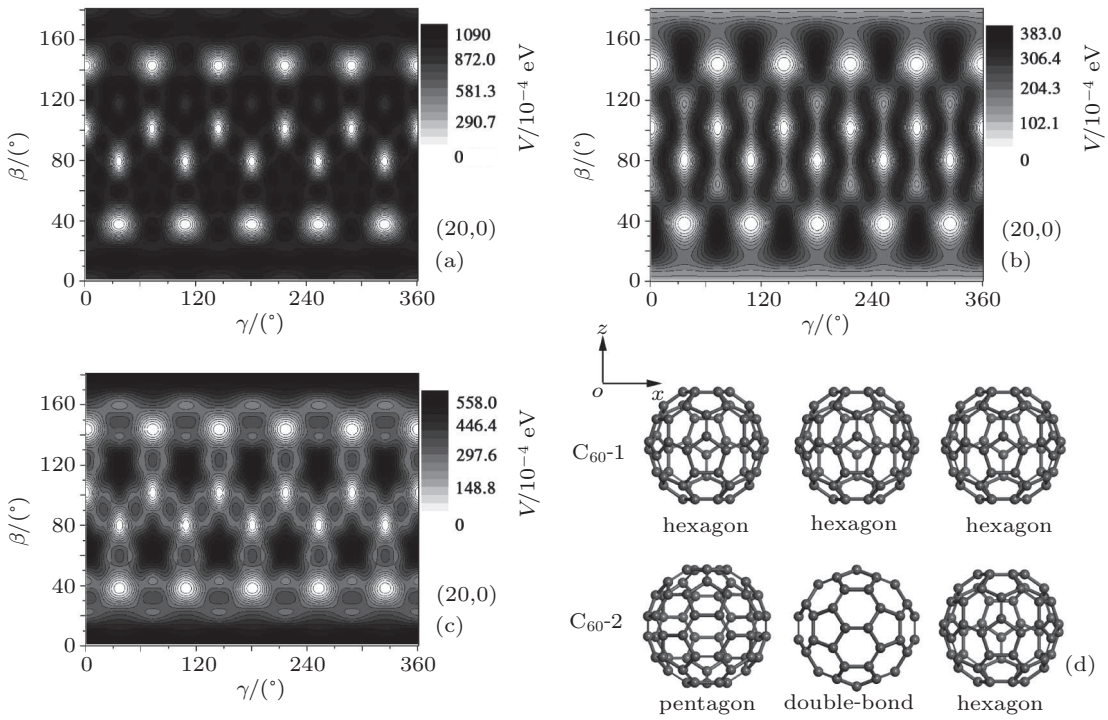


Fig. 7. Contour maps of the systematic total van der Waals interaction potential V_{total} for the (20,0) nanotube with the C_{60}-2 adopted (a) pentagon, (b) double-bond, and (c) hexagon orientations respectively. The minimum value has been subtracted. (d) The preferable orientations of the C_{60}-1 molecule and the fixed orientations of the C_{60}-2 molecule are presented on the (x, z) plane.

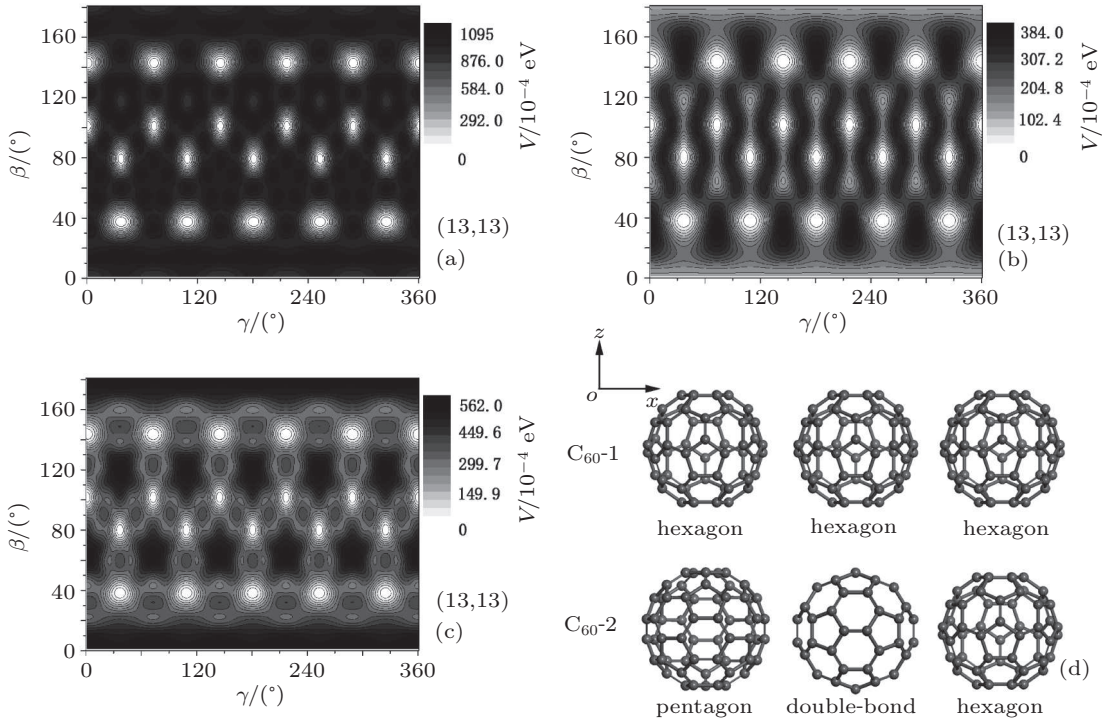


Fig. 8. Contour maps of the systematic total van der Waals interaction potential V_{total} for the (13,13) nanotube with the C_{60}-2 adopted (a) pentagon, (b) double-bond, and (c) hexagon orientations respectively. The minimum value has been subtracted. (d) The preferable orientations of the C_{60}-1 molecule and the fixed orientations of the C_{60}-2 molecule are presented on the (x, z) plane.

Table 1. All achiral (zigzag and armchair) and chiral SWCNTs with diameter ranging from 1.31 nm to 1.76 nm studied in this work. The obtained preferred orientations of C_{60}-1 according to the calculated interaction potentials V(C_{60}-1, tube) and V_{total} are presented.

SWCNT	Diameter/nm	Preferred orientation	Preferred orientation	Preferred orientation	Preferred orientation	Chirality
(n,m)		C_{60}-1, tube	C_{60}-2 (pentagon), C_{60}-1, tube	C_{60}-2 (double-bond), C_{60}-1, tube	C_{60}-2 (hexagon), C_{60}-1, tube,	
(15,3)	1.31	pentagon	pentagon	pentagon	pentagon	chiral
(17,0)	1.33	pentagon	pentagon	pentagon & hexagon	vertex	zigzag
(10,10)	1.35	pentagon	hexagon	hexagon	vertex	armchair
(15,4)	1.36	pentagon	hexagon	hexagon	vertex	chiral
(15,5)	1.41	pentagon	hexagon	hexagon	hexagon	chiral
(17,3)	1.46	double-bond	hexagon	hexagon	hexagon	chiral
(11,11)	1.49	double-bond	hexagon	hexagon	hexagon	armchair
(18,3)	1.54	double-bond	hexagon	hexagon	hexagon	chiral
(20,0)	1.57	double-bond	hexagon	hexagon	hexagon	zigzag
(12,12)	1.63	double-bond	hexagon	hexagon	hexagon	armchair
(16,8)	1.66	double-bond & hexagon	hexagon	hexagon	hexagon	chiral
(13,13)	1.76	hexagon	hexagon	hexagon	hexagon	armchair

that the centers of mass of the studied C_{60} molecules have been fixed on the tube axis position. As is well known, the encapsulated C_{60} molecule will deviate from the tube axis for large nanotubes.[41] Thus, further studies with the C_{60} molecule deviated from the tube axis position are necessary. We expect that our theoretical study on the preferred orientation of encapsulated C_{60} molecules can be employed to understand and guide experimental studies of nanopeapod structures.

4. Conclusion

In summary, we have presented a detailed orientational behavior study of C_{60} molecules inside armchair-, zigzag-, and chiral-type nanotubes with diameters ranging from 1.31 nm to 1.76 nm by using the van der Waals interaction calculation. Within the model of two C_{60}(C_{60}-1 and C_{60}-2) molecules filled in a tube, we studied the preferred orientation of the C_{60}-1 molecule by comparing the calculated interaction potentials V(C_{60}-1, tube), V(C_{60}-1, C_{60}-2), and V_{total}. For the total interaction potential calculation, it was found that the C_{60}-1

molecule prefers the pentagon orientation when the tube diameter is smaller than 1.31 nm due to the strong confinement effect from the tube. As the tube diameter increases, the preferred orientation of the C_{60}-1 molecule is dependent on the orientation of the C_{60}-2 molecule due to the synergistic role played by the tube confinement effect and the intermolecular interaction. When the tube diameter is larger than 1.36 nm, the C_{60}-1 molecule prefers the hexagon orientation, which is dependent on the intermolecular interaction. Taking into account both interactions in our calculations also results in the absence of the double-bond orientation as the lowest-energy state in the previous report, in which only the interaction between C_{60} and the tube wall was considered. The obtained results indicate that besides the expected interaction between C_{60} and the tube wall, the interaction between adjacent C_{60} molecules also plays an important role on the orientational behavior of C_{60} molecules inside the nanotubes. These results not only help us to understand the competition relationship between the tube confinement effect and the intermolecular interaction, but also show the importance of the utilization of peapods in molecule engineering at the nanoscale.

References

[1] Iijima S 1991 *Nature* **354** 56

[2] Bandow S, Takizawa M, Hirahara K, Yudasaka M and Iijima S 2001 *Chem. Phys. Lett.* **337** 48

[3] Sloan J, Hammer J, Zwiefka-Sibley M and Green M L H 1998 *Chem. Commun.* **3** 347

[4] Sloan J, Wright D M, Woo H G, Bailey S, Brown G, York A P E, Coleman K S, Hutchison J L and Green M L H 1999 *Chem. Commun.* **8** 699

[5] Meyer R R, Sloan J, Dunin-Borkowski R E, Kirkl A I, Novotny M C, Bailey S R, Hutchinson J L and Green M L H 2000 *Science* **289** 1324

[6] Sloan J, Novotny M C, Bailey S R, Brown G, Xu C, Williams V C, Friedrichs S, Flahaut E, Callender R L, York A P E, Coleman K S, Green M L H, Dunin-Borkowski R E and Hutchison J L 2000 *Chem. Phys. Lett.* **329** 61

[7] Fan X, Dickey E C, Eklund P C, Williams K A, Grigorian L, Buczko R, Pantelides S T and Pennycook S J 2000 *Phys. Rev. Lett.* **84** 4621

[8] Sloan J, Terrones M, Nufer S, Friedrichs S, Bailey S R, Woo H G, Ruhle M, Hutchison J L and M L H Green 2002 *J. Am. Chem. Soc.* **124** 2116

[9] Sloan J, Grosvenor S J, Friedrichs S, Kirkland A I, Hutchison J L and Green M L H 2002 *Angew. Chem. Int. Ed.* **41** 1156

[10] Koga K, Gao G T, Tanaka H and Zeng X C 2001 *Nature* **412** 802

[11] Wang Y, Zhao Y J and Huang J P 2012 *Chin. Phys. B* **21** 076102

[12] Xie Y and Zhang J M 2011 *Chin. Phys. B* **20** 127302

[13] Liu H, Dong J M, Qian M C and Wan X G 2003 *Chin. Phys. Soc.* **12** 0542

[14] Smith B W, Monthioux M and Luzzi D E 1998 *Nature* **396** 323

[15] Smith B W, Russo R M, Chikkannanavar S B and Luzzi D E 2002 *J. Appl. Phys.* **91** 9333

[16] Burteaux B, Claye A, Smith B W, Monthioux M, Luzzi D E and Fischer J E 1999 *Chem. Phys. Lett.* **310** 21

[17] Okazaki T, Okubo S, Nakanishi T, Joung S K, Saito T, Otani M, Okada S, Bandow S and Iijima S 2008 *J. Am. Chem. Soc.* **130** 4122

[18] Hornbaker D J, Kahng S J, Misra S, Smith B W, Johnson A T, Mele E J, Luzzi D E and Yazdani A 2002 *Science* **295** 828

[19] Lee J, Kim H, Kahng S J, Kim G, Son Y W, Ihm J, Kato H, Wang Z W, Okazaki T, Shinohara H and Kuk Y 2002 *Nature* **415** 1005

[20] Okada S, Saito S and Oshiyama A 2001 *Phy. Rev. Lett.* **86** 3835

[21] Otani M, Okada S and Oshiyama A 2003 *Phys. Rev. B* **68** 125424

[22] Rochefort A 2003 *Phys. Rev. B* **67** 115401

[23] Okada S, Otani M and Oshiyama A 2003 *Phys. Rev. B* **67** 205411

[24] Abou-Hamad E, Kim Y, Wagberg T, Beosch D, Aloni S, Zettl A, Rubio A, Luzzi D E and Goze-Bac C 2009 *ACS Nano* **3** 3878

[25] David W I F, Ibberson R M, Matthewman J C, Prassides K, Dennis T J S, Hare J P, Kroto H W, Taylor R and Walton D R M 1991 *Nature* **353** 147

[26] Alemany M M G, Rey C, Dieguez O and Gallego L J 2000 *J. Chem. Phys.* **112** 10711

[27] Girifalco L A 1992 *J. Phys. Chem.* **96** 858

[28] Rols S, Cambedouzou J, Chorro M, Schober H, Agafonov V, Launois P, Davydov V, Rakhmanina A V, Katura H and Sauvajol J L 2008 *Phys. Rev. Lett.* **101** 065507

[29] Cambedouzou J, Rols S, Almairac R, Sauvajol J L, Kataura H and Schober H 2005 *Phys. Rev. B* **71** 041403

[30] Matsuda K, Maniwa Y and Kataura H 2008 *Phys. Rev. B* **77** 075421

[31] Zou Y G, Liu B B, Wang L C, Liu D D, Yu S D, Wang P, Wang T Y, Yao M G, Li Q J, Zou B, Cui T, Wagberg T, Sundqvist B and Mao H W 2009 *Proc. Natl. Acad. Sci. USA* **106** 22135

[32] Michel K H, Verberck B and Nikolaev A V 2005 *Phys. Rev. Lett.* **95** 185506

[33] Michel K H, Verberck B and Nikolaev A V 2005 *Eur. Phys. J. B* **48** 113

[34] Verberck B and Michel K H 2006 *Phys. Rev. B.* **74** 045421

[35] Zou Y G, Liu B B, Yao M G, Hou Y Y, Yu S D, Wang P, Li B, Zou B, Cui T and Zou G T 2007 *Phys. Rev. B* **76** 195417

[36] Rappe A K, Casewit C J, Colwell K S, Goddard III W A and Skiff W M 1992 *J. Am.Chem. Soc.* **114** 10024

[37] Hodak M and Girifalco L A 2001 *Chem. Phys. Lett.* **350** 405

[38] Troche K S, Coluci V R., Braga S F, Chinellato D D, Ssto F, Legoas S B, Rurali R and Galvao D S 2005 *Nano Lett.* **5** 349

[39] Girifalco L A, Hodak M and Lee R S 2000 *Phys. Rev. B* **62** 13104

[40] Song J and Cappelletti R L 1994 *Phys. Rev. B* **50** 14678

[41] Verberck B, Cambedouzou J, Vliegenthart G A, Gompper G and Launois P 2012 *Fullerence, Nanotubes, and Carbon Nanostructures* **20** 371