

## Alignment of single-wall carbon nanotubes by inclusion of dipolar wires

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When a semiconducting single wall nanotube is filled by a dipolar, one-dimensional, molecular wire, its polarization is strongly enhanced leading to the occurrence of a large induced dipole. Upon exposure to an external electric field on the order of  $10^{-2}$  V Å<sup>-1</sup>, we show that the orientational energy of a tube with length equal to 30 Å filled by a set of 11 aligned dipolar molecules forming a wire can be 10 times (5 times) smaller than for a similar empty tube at 0 K (300 K). This factor increases to 60 (20) at 0 K (300 K) for a tube length that becomes infinite with an external field equal to  $10^{-4}$  V Å<sup>-1</sup>. The tube orientation is therefore largely stabilized by the wire inclusion. This energy gain is mainly due to the induced dipole which fully dominates the permanent dipole of the wire due to the screening of the nanotube. Extension of these results to two identical nearest neighbor tubes indicates that an assembly of filled nanotubes should be more stable in terms of orientational energy than a set of empty tubes.

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### I. INTRODUCTION

Because of their remarkable physicochemical properties, carbon nanotubes (NT) are at the origin of intense research since their discovery.<sup>1</sup> Aside from the control of their length and diameter, the spatial organization of NT's has become an important challenge in order to increase their potentiality in nanosciences components,<sup>2-5</sup> gas sensors,<sup>6-9</sup> etc. Most of the growth processes, using either laser ablation of carbon rods<sup>10</sup> or chemical vapor deposition with catalytic template,<sup>11-14</sup> result generally in the production of long, uniform single wall carbon nanotubes (SWNT). The precision of these methods is however very crucial and a small deviation in the fabrication process can result in a material constituted by an amorphous assembly of NT's, which are different in structure, order and size.

Large arrays of well-aligned NT's were first made possible by plasma enhanced chemical deposition without controlling the growth angle, the location and the spacing.<sup>15,16</sup> More recently, electron beam lithography has been used to accomplish these last properties.<sup>17,18</sup> Excellent aligned NT arrays have been grown using electrochemistry, although the control on location of each NT was initially lacking with this technique.<sup>19</sup> Recent successful growth of large arrays of NT's with diameter, length, location and spacing under control has finally been made using nanosphere lithography<sup>20</sup> or microwave plasma chemical deposition.<sup>14,21,22</sup> Very recently, it has been shown that water stimulated catalytic activity results in the growth of dense and vertically aligned SWNT forests with mm-scale height in a 10 min growth time.<sup>23</sup>

Assembling nanotubes on electrodes using an electric field is a practically attractive and efficient technique. A few efforts to align SWNT's using dc and ac fields have been done by applying voltages of several volts between two electrodes separated by a distance of a few micrometers.<sup>24-27</sup> and it was shown that these tubes orient nearly at right angle to the metal electrodes. In most of these experiments, the NT's were predominantly metallic. Grown nanotubes with diameter of about 20 Å and length of 10 μm having a semicon-

ducting behavior have nevertheless been aligned using an effective field of 1 V μm<sup>-1</sup>, suggesting that the high anisotropy of the NT polarizability could induce such an alignment.<sup>28</sup>

Another way to induce alignment of NT's would consist in exalting the dielectric properties of the carbon tubes. Indeed, while perfect NT's are generally apolar, they are extremely polarizable when submitted to an electric field created for instance by polar species adsorbed inside or outside their surface. Under these conditions, a relatively large dipole moment is induced in NT's, the orientation of which is very sensitive to an external static electric field, leading thus to a possible control of the NT orientation by this field. More particularly, filling NT's with molecular species has been reported<sup>29,30</sup> and one dimensional confined nanostructures with potentially remarkable properties have been discussed.<sup>31</sup> As an example, water molecular wires have been shown to be stable inside SWNT under ambient conditions in both experimental<sup>32</sup> and theoretical approaches,<sup>33,34</sup> and they could play in the future a key role in new devices for proton storage and transport applications. Although significantly dipolar, the water molecule is probably not a good candidate to produce strong polarization in the NT, due to its relatively free orientational motions. The H-bond duration has been shown to be very short (on the order of the picosecond) and thus inefficient to hinder the rotation of the molecules. We have chosen another simple diatomic molecule, namely HF, with a large dipole and a propensity to form zig-zag chains, i.e., structures which are close to one dimensional order. This will induce relatively large polarization effects on the NT.

In this paper, we present results obtained for the encapsulation of a one dimensional wire formed by a set of dipolar molecules in an ideal semiconducting SWNT, the internal size of which is consistent with that of the molecules. We then study the consequences of this encapsulation on the dielectric properties of the system in terms of the geometrical stability when an external static electric field is applied, by comparing the interaction energy with the field of the bare and wire filled NT. Section II is devoted to a rapid descrip-

TABLE I. Electrostatic description of the HF molecule. The interaction centers that bear the various electric poles  $M_n$  can be the atoms themselves (F or H) or the molecular center of mass (c.m.) or still the middle (M) of the bond depending on the description of the interaction potential. All data are given in atomic units. The Lennard-Jones parameters are also given depending on the HF-HF or the HF-C interaction.

Molecule	Site	Position (Å)	$M_0$ (e)	$M_1$ (e Å)	$M_2$ (e Å <sup>2</sup> )	$\alpha_{\perp}$ (Å <sup>3</sup> )	$\alpha_{\parallel}$ (Å <sup>3</sup> )
HF	F	-0.046	-0.07	0.164	0.168		
	M	0.412	-0.54	-0.079	0.011		
	H	0.870	0.61	0.05	0.017		
Molecular electric pole	c.m.	0	0	0.400	0.491	0.7756	0.5690
Lennard-Jones parameters	atom-atom	$\sigma$ (Å)	$\epsilon$ (meV)				
HF-C	C-H	2.10	2.79				
	C-F	2.65	3.61				
HF-HF	c.m.-c.m.	2.57	39.1				

tion of the model and to the expression of the interaction potential between the tube and the wire depending whether the external field is switched off or on. We give in Sec. III the geometry of the confined wire in the NT and calculate the orientational energy due to the external electric field for the empty and wire filled NT. The behavior of the mutual orientation of two tubes under application of the field is studied, depending on the NT's are empty or filled by the dipolar wire. Then the influence of the tube length and the temperature on the orientational effect of a filled tube is discussed. A conclusion on the efficiency of doping NT's by dipolar molecule encapsulation to control their orientation by an external electric field is presented.

## II. THEORETICAL BACKGROUNDS

### A. The system

In order to optimize the linear geometry of the molecular wire trapped inside a NT, we consider a simple diatomic molecule bearing a large dipolar moment. The HF molecule has been selected for (i) its relatively strong dipole, (ii) its ability to form zig-zag chains in solid phase, and (iii) its ability to diffuse inside nanotubes, as discussed in a previous paper.<sup>35</sup> Once the molecular parameters are known, we have to decide what NT radius size is the most appropriate to allow for a quasilinear spatial arrangement of the HF molecules and to avoid their free rotation inside this tube. Semiconducting tubes of the type  $(n,0)$  have been considered and the tube radius which will lead to the most stable energy with the HF molecule(s) will be retained for the calculations of the orientational energy between the NT, the HF wire, and the electric field. The determination of the stable energy requires the knowledge of the interaction potential between the NT and the HF molecules. Note that the tube length considered here corresponds to a reasonable compromise, which allows us to fill the tube with a molecular wire containing a sufficient number of HF molecules and to preserve relatively short computational times. Thus a maximum number of 11 HF molecules will be considered for the wire description in a SWNT with length equal to 30 Å because the calculation of the polarization effect within a nonlocal approach is very

time consuming. Extension to a periodic NT will be discussed in Sec. III C.

### B. Interaction energy

The nanotube is described by a set of  $N$  carbon atoms. Each atom is characterized by the Lennard-Jones parameters  $\epsilon_C$  and  $\sigma_C$  defining the quantum interactions (dispersion and repulsion terms) and by a static anisotropic polarizability tensor  $\vec{\alpha}_C$ .  $\alpha_{C\perp}$  is taken for the component of the polarizability perpendicular to the hexagonal plane of the curved graphite sheet while  $\alpha_{C\parallel}$  defines the polarizability along the direction parallel to this plane. The values of  $\alpha_{C\perp} = 0.86 \text{ Å}^3$  and  $\alpha_{C\parallel} = 2.47 \text{ Å}^3$  have been fitted in order to recover the measured polarizability for the  $C_{60}$  and  $C_{70}$  molecules and the results issued from the tight-binding study of Benedict *et al.*<sup>36</sup> for the SWNT polarizability. It can be noted that this polarizability is based on a localization of the electrons (atomic description) and it is therefore valid only for semiconducting tubes and not for metallic tubes.

The electric properties of the molecular species are described by the Lennard-Jones parameters  $\epsilon_M$  and  $\sigma_M$  which are taken at the molecular center of mass for the molecule-molecule interaction and at three dispersion centers (H, F, and M centers) for the molecule-carbon interaction.<sup>35</sup> In addition, the first two permanent multipolar moments (dipole and quadrupole) and the static anisotropic polarizability tensors of the molecules are also given in Table I.

The local electric field  $\vec{E}_l(\vec{r}_i)$  at the position  $\vec{r}_i$  (index  $i$  characterizes either any carbon atom of the tube or any HF molecule which is confined inside the tube) can be written as

$$\vec{E}_l(\vec{r}_i) = \vec{E}_0 + \sum_{j \neq i}^{N_d} \left[ \vec{T}_R^3(\vec{r}_i, \vec{r}_j) \vec{\mu}(\vec{r}_j) - \frac{1}{3} \vec{T}_R^3(\vec{r}_i, \vec{r}_j) \vec{Q}(\vec{r}_j) \right] + \sum_{j \neq i}^{N+N_d} \vec{T}_R^3(\vec{r}_i, \vec{r}_j) \vec{\alpha}(\vec{r}_j) \vec{E}_l(\vec{r}_j), \quad (1)$$

where  $\vec{E}_0$  describes the external static, homogeneous, electric field created on the system formed by the tube and the HF molecules of the wire. Since the tube orientation is random

in space, this field will be applied along the three Cartesian directions, i.e., along the tube axis ( $E_{0z}$ ) and perpendicular to the tube axis (along  $E_{0x}$  and  $E_{0y}$ ). The second term in the right-hand side of Eq. (1) defines the molecular field due to the permanent dipole  $\vec{\mu}$  and quadrupole  $\vec{Q}$  moments on the  $j_{th}$  HF molecule inside the tube.  $N_d$  (equal to 11 for the complete wire) is the number of HF molecules. The tensors  $\vec{T}_R^2$  and  $\vec{T}_R^3$  are the double and triple gradients of the renormalized Green function for the Laplace equation. These tensors are properly renormalized using a Gaussian distribution of charges to avoid divergences in the close neighboring of the carbon atoms and to account for the screening effect on the electric field by the electronic cloud of carbon atoms.<sup>37</sup>

The interaction between  $N_d$  confined HF molecules and the SWNT is written as

$$V = \sum_{i=1}^{N_d} \left[ -\vec{\mu}(\vec{r}_i) \cdot \vec{E}_l(\vec{r}_i) + \frac{1}{3} \vec{Q}(\vec{r}_i) \cdot \vec{\nabla} \vec{E}_l(\vec{r}_i) \right] - \sum_{i=1}^{N+N_d} \frac{1}{2} \vec{\alpha}(\vec{r}_i) \vec{E}_l(\vec{r}_i)^2 + \sum_{i=1}^N \sum_{j=1}^{N_d} V_{DR}^C(\vec{r}_i, \vec{r}_j) + \sum_{i,j>i}^{N_d} V_{DR}(\vec{r}_i, \vec{r}_j). \quad (2)$$

The first three terms in the right-hand side of Eq. (2) describe the electrostatic and induction contributions between the nanotube and the molecules and between the molecules themselves including the effect of their permanent dipole and quadrupole moments. The fourth term is the sum over the  $N$  carbon atoms and the  $N_d$  molecules of the dispersion-repulsion contributions, each of them being described by a pairwise Lennard-Jones potential, and the fifth term is the same contribution for the dispersion-repulsion between the HF molecules. Higher order, nonadditive, contributions have been disregarded for these quantum interactions.

### C. Binding and orientational energies

Several energies will be calculated. First, we determine the optimized size (radius) of the NT consistent with the HF inclusion. The interaction energy between the encapsulated wire and the NT is minimized at 0 K according to a sequential procedure. We consider first a single HF molecule inside the NT and calculate the minimum energy  $E_{NT-HF}(1)$ , with the corresponding orientation of the molecular axis. Once determined, we confine a second HF molecule, by releasing the constraint on the first HF molecule and minimize the energy  $E_{NT-HF}(2)$ , and then we proceed accordingly up to  $E_{NT-HF}(11)$ . Any energy  $E_{NT-HF}(n')$  is thus obtained by the minimization of the interaction energy  $V$  [Eq. (2)] including the influence of  $N_D=n'$  trapped HF molecules. This can be written as

$$E_{NT-HF}(n') = \min[V(E_0 = 0, N_D = n')]. \quad (3)$$

For  $n'=1$ , we can find the adequate radius for the NT leading to a minimum energy  $E_{NT-HF}(1)$  and use this result to build the optimized quasilinear structure of the HF wire. Note that the external field could in principle change the

energy. In practice, we have verified that the values of the external field are sufficiently weak to keep the results unchanged without and with the field  $\vec{E}_0$ . Therefore, we have considered that  $E_0=0$  in Eq. (3).

In a second step, we define the polarization energy  $E_P(\vec{E}_0)$  due to the presence of the polar wire when the filled NT is submitted to the external field. It is written as

$$E_P(\vec{E}_0) = V_{NT+W}(\vec{E}_0) - (V_W(\vec{E}_0) + V_{NT}(\vec{E}_0)). \quad (4)$$

The first contribution in the right-hand side of Eq. (4) is the potential  $V$  defined in Eq. (2) determined for the total wire ( $n'=N_D=11$ ) and the nanotube, which is minimized with respect to the positions and orientations of the 11 confined HF molecules. The second term characterizes the potential energy for the wire alone minimized with respect to the orientations and positions of the HF molecules aligned to form a one dimensional structure. The third term in Eq. (4) represents the polarization interaction due to the external field  $\vec{E}_0$  on the carbon atoms of the NT, only. All these contributions are minimized in the presence of the field  $\vec{E}_0$ . When  $E_0=0$ , the contribution  $V_{NT+W}(0)$  is equal to  $E_{NT+HF}(11)$  defined in Eq. (3), while  $V_{NT}(0)$  vanishes (no NT polarization when  $E_0=0$ ).

The central quantity for this paper is the energy  $E_G$  gained by the filled nanotube with respect to the empty one when the electric field  $\vec{E}_0$  is switched on. It is defined as

$$E_G = E_P(\vec{E}_0) - E_P(0). \quad (5)$$

$E_G$  characterizes the stabilization gain supplied to a dipolar wire filled nanotube when compared to the empty nanotube, and it describes therefore the possibility for an electric field to act on the orientation of a single NT.

## III. RESULTS

### A. The optimized system

Various semiconducting SWNT's of the type  $(n,0)$  have been considered with a length around 30 Å, consistent with reasonable computing times. The inclusion of one HF molecule inside these  $(n,0)$  NT's shows an interaction energy  $E_{NT-HF}(1)$  which is minimum for  $n=10$  and equal to -307 meV. The stable position for the molecule center of mass is located on the tube axis and the molecular dipole is perpendicular to this axis with the hydrogen atom pointing toward the NT wall. The corresponding energies for the neighbor tubes with  $n=8$  and 11 ( $n=9$  corresponds to a metallic species) are clearly much larger with a sharp well for  $n=8$  while the stable position of the molecule center of mass moves away from the tube axis (Fig. 1) when  $n \geq 11$ .

When a second HF molecule is introduced in the  $(10,0)$  SWNT, the two molecules tend to move closer in order to minimize their lateral interactions while their centers of mass remain located in the close neighborhood of the tube axis. The main influence of the lateral interaction is to orient the two dipoles along the tube axis, leading to a total interaction energy  $E_{NT-HF}(2) = -0.840$  eV. Note that the mutual orienta-

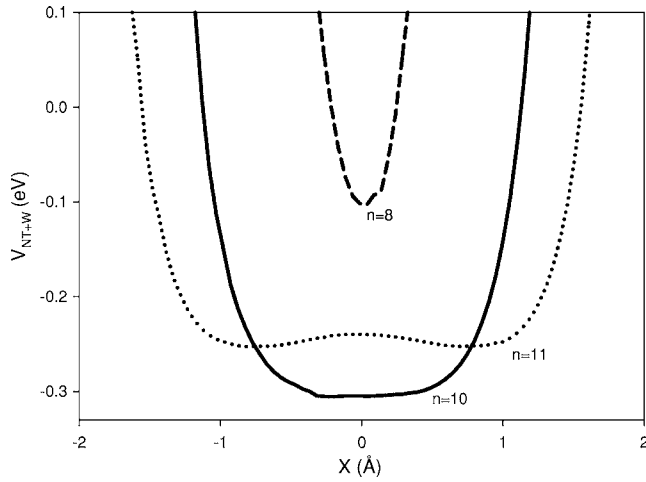


FIG. 1. Behavior of  $V_{NT-HF}(1)$  for the inclusion of one HF molecule inside (8,0) (dashed curve), (10,0) (full curve), and (11,0) (broken curve) SWNT's.

tion of two HF molecules in a floating dimer is equal to  $120^\circ$  showing that the NT confinement influences strongly the molecule orientation, while the energy loss remains very small. Indeed, adding to the energy of two HF monomers ( $-307 \text{ meV} \times 2$ ), the minimized interaction of the floating dimer ( $-240 \text{ meV}$ ) would result in a total energy equal to  $-0.854 \text{ eV}$  instead of  $-0.840 \text{ eV}$ .

Encapsulating additional HF molecules in the (10,0) tube does not produce significant changes in the orientation of the dipole moments. Figure 2 shows the behavior of  $E_{NT-HF}(n')$  vs the number  $n'$  of HF molecules up to the maximum filling of the tube. The energy  $E_{NT-HF}(11)$  at zero external electric field is equal to  $-5.952 \text{ eV}$ . The side effects are totally negligible on the position and orientation of the molecules which thus display a one dimensional structure due to the NT confinement (Fig. 3). Moreover, it has been verified that switching on the electric field  $E_0$  up to about  $0.1 \text{ V \AA}^{-1}$  does not modify the HF orientations and positions.

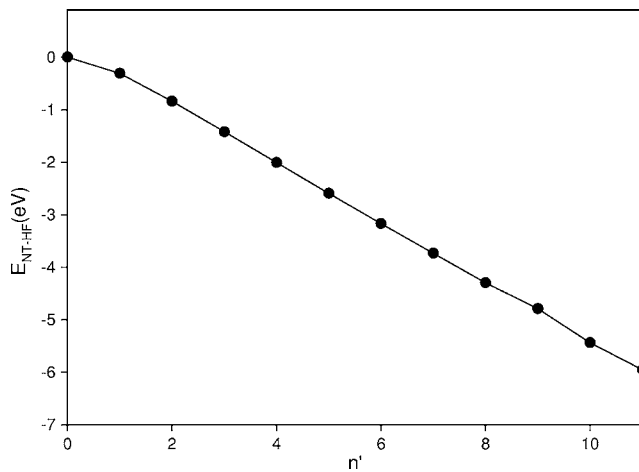


FIG. 2. Behavior of  $E_{NT-HF}$  as a function of the number  $n$  of HF molecules included in the tube.

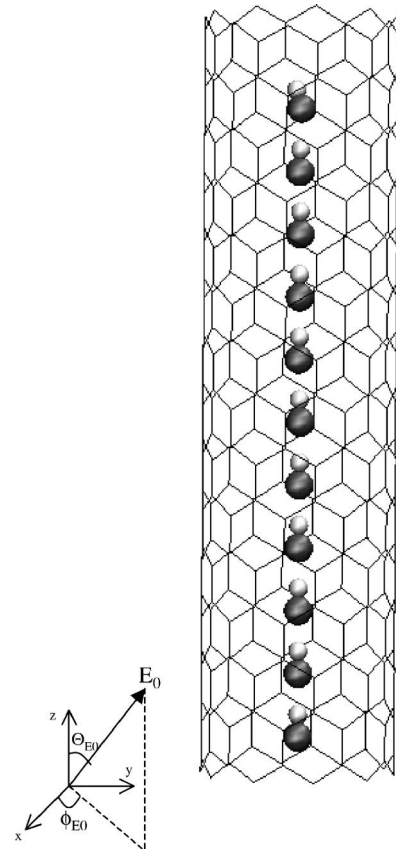


FIG. 3. Geometry of the (10,0) SWNT with the molecular wire adsorbed inside. 11 HF molecules oriented in a quasicollinear configuration with the (10,0) tube axis are forming a one-dimensional wire. The components of the external electric field  $\vec{E}_0$  are also given.

## B. Influence of the external field on the wire filled NT

To see whether a (10,0) SWNT filled by a polar molecular wire is more or less sensitive to the orientational influence of an external electric field than the SWNT alone, the external electric field  $\vec{E}_0$  has been independently applied to the two systems and their total energy has been minimized with respect to the geometry of the wire.

### 1. Orientation of the tube by the external electric field

The isoenergy map  $E_P(\vec{E}_0)$  as a function of the field direction described by two angles  $\Theta_{\vec{E}_0}$  (representing the angle between the  $z$  axis of the tube and the field direction) and  $\phi_{\vec{E}_0}$  [standing for the azimuthal angle in the  $(x, y)$  plane] is relatively flat and shows two extrema. The maximum is located at  $\Theta_{\vec{E}_0} = 0$  where  $\vec{E}_0$  is aligned with the tube axis and the dipole moments of the HF molecules, while the minimum at  $\Theta_{\vec{E}_0} = \pi$  is more pronounced and corresponds to an anticolinear orientation of  $\vec{E}_0$  with respect to the molecular dipoles. The  $\phi_{\vec{E}_0}$  dependence of  $\vec{E}_0$  remains very small. The asymmetry of the map  $E_P(\vec{E}_0)$  as a function of  $\Theta_{\vec{E}_0}$  can be explained by the polarization effects on the C atoms. The permanent dipole moments of the HF molecules induce isoelectric field

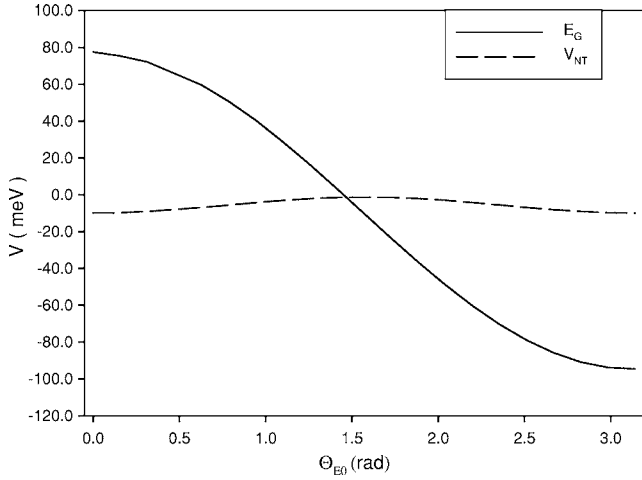


FIG. 4. Difference in the behavior of  $E_G$  (full curve) and  $V_{NT}$  (broken curve) as functions of  $\Theta_{\vec{E}_0}$  for  $\vec{E}_0=0.01 \text{ V/\AA}$  and  $\Phi_{\vec{E}_0}=0$ .

curves responsible for the polarization of the C atoms along the opposite direction. As a matter of course, a lot of induced dipoles beared by the carbon atoms are created by the molecular field on the tube. When  $\vec{E}_0$  is applied, there is a competition between the permanent dipoles which tend to be oriented along the field  $\vec{E}_0$  and the induced dipoles on the NT which tend to be oriented along the opposite direction. But, due to the cage effect created by the SWNT which drastically decreases the interaction (until 50%) between the screened permanent dipoles and  $\vec{E}_0$ , the interaction between the induced dipoles and the field becomes dominant and leads to a preferential orientation for  $\vec{E}_0$  along the induced dipoles ( $\Theta_{\vec{E}_0}=\pi$ ).

Note however that  $E_P(\vec{E}_0)$  contains the dispersion-repulsion terms which are independent of  $\vec{E}_0$ . To study the influence of  $\vec{E}_0$  on the system and thus eliminate the influence of these terms, we must subtract to  $E_P(\vec{E}_0)$  the contribution at zero field  $E_P(0)$  and calculate  $E_G$ . The results are plotted in Fig. 4 as a function of  $\Theta_{\vec{E}_0}$  for  $\phi_{\vec{E}_0}=0$ , since  $\phi_{\vec{E}_0}$  does not significantly influence the values of  $E_G$ . The behavior of  $E_G$  represents the real impact of  $\vec{E}_0$  on the system and it can directly be compared to the electric response of the empty nanotube  $V_{NT}(\vec{E}_0)$  shown by the broken curve in Fig. 4. While  $V_{NT}(\vec{E}_0)$  is symmetric with respect to  $\Theta_{\vec{E}_0}$  due to the radial geometry of the tube,  $E_G$  displays a asymmetric shape due to the presence of the polar wire inside the tube, which polarizes the C atoms. Comparing the two minima obtained in Fig. 4, we see that the filled nanotube is much more stable than the empty one, by about a factor ten [ $E_G^{min}=-0.0947 \text{ eV}$  and  $V_{NT}^{min}(\vec{E}_0)=-0.0099 \text{ eV}$ ] for  $E_0=0.01 \text{ V \AA}^{-1}$ . Such an increase of the tube stability is the signature of the molecular wire which induces dipoles on the tube that are very sensitive to the external field. This demonstrates that a filled SWNT can be stabilized and preferentially oriented in a peculiar direction by an electric field.

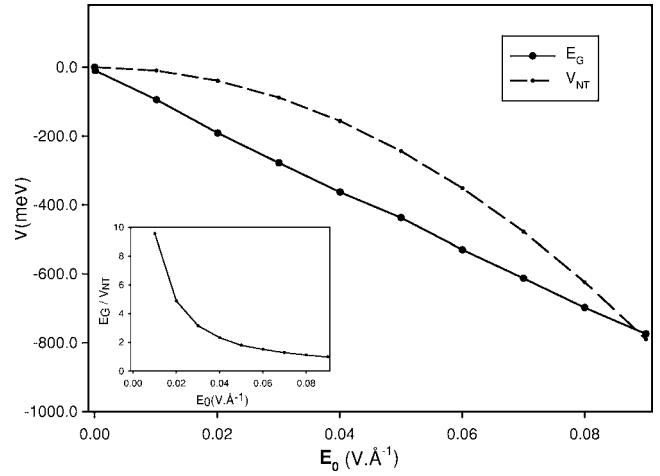


FIG. 5. The full curve represents  $E_G^{min}$  as a function of the intensity  $E_0$  of the electric field and the dashed curve the behavior of  $V_{NT}(\vec{E}_0)$ . The inset shows the increase factor between  $E_G^{min}$  and  $V_{NT}(\vec{E}_0)$  vs  $E_0$ .

## 2. Influence of the electric field intensity

For a particular value of the field intensity  $E_0=0.01 \text{ V \AA}^{-1}$ , we have demonstrated that  $E_G$  is minimum when  $\vec{E}_0$  is oriented in the opposite direction to the permanent dipolar molecules, with an increase factor of about 10. Figure 5 shows the behavior of  $E_G^{min}$  (full line) and  $V_{NT}^{min}(\vec{E}_0)$  (dashed line) as a function of the intensity  $E_0$  of the field. The inset displays the increase factor with  $E_0$ . We see that the curve  $E_G^{min}$  decreases linearly with  $E_0$  while the curve  $V_{NT}^{min}(\vec{E}_0)$  has a quadratic dependence with  $E_0$ . The two curves intersect when  $E_0=0.09 \text{ V \AA}^{-1}$ . The calculations have been stopped at this field value because other effects, not considered here, already occur, such as field emission<sup>22</sup> or still influence of the external electric field on the wire conformation (dipole orientation, etc.).

To interpret this different behavior with  $E_0$ , let us consider the dominant contributions in both energies  $V_{NT}$  and  $E_G$ . For an empty tube, the polarization of the carbon atoms by the external field is the main term in the potential  $V_{NT}$  (if we disregard the quantum dispersion-repulsion contribution which is not influenced by the field  $E_0$ ). This polarization term is quadratic with  $E_0$ , since it has the form  $-\alpha_C E_0^2/2$ . On the contrary, for the wire filled tube, the main contribution is due to the polarization of the carbon atoms by the internal electric field created by the HF dipole moments in the wire. As a result, the influence of the tube polarization by the external field, even if it exists, remains small with respect to the dipole effect. This latter contribution is rather proportional to  $-\mu E_0$ , i.e., linear with the external field where  $\mu$  is the resulting dipole due to the permanent dipole of HF and to the induced one. It is obvious that increasing the external field value beyond  $0.1 \text{ V \AA}^{-1}$  should modify both behaviors, adding specific field effects on the empty tube as already mentioned and acting on the one hand on the wire conformation and on the other hand on the relative importance of the linear and quadratic contributions.

### 3. Extension to two identical SWNT's

When the external electric field is switched off, the mutually parallel stable configuration for two empty SWNT's close together is naturally imposed by the dispersion-repulsion interaction potential between carbon atoms.<sup>10</sup> The influence of  $E_0$  on the induction interaction between the two tubes remains nearly negligible when  $E_0$  does not exceed  $0.1 \text{ V \AA}^{-1}$ . This interaction is equal to  $-14 \text{ meV}$  when  $E_0 = 10^{-2} \text{ V \AA}^{-1}$ . Note however that this contribution, even if it remains very weak, favors a configuration for which the tubes move far away. An opposite behavior is obtained for the wire filled nanotubes which prefer to be close to each other. The interaction energy  $E_G$  due to the occurrence of dipoles induced by the field created by the permanent dipoles of the HF molecules is equal to  $-215 \text{ meV}$  while the value of  $E_G$  for two infinitely separated monomers is  $2 \times -95 \text{ meV} = -190 \text{ meV}$ . In this stable configuration, the filled tubes are mutually parallel and anticollinear with the external field, indicating that the permanent dipoles of HF are significantly screened by the tube wall (cage effect). Indeed, the orientation energy of the two tubes comes from a competition between the interaction of the permanent dipoles of the two wires which would tend to orient the filled tubes mutually anticollinear, and the interaction of the permanent dipoles of one tube with the induced dipoles in the other tube (and vice versa), which favors a collinear orientation for the two filled tubes. This latter contribution adds to the orientation energy of each filled tube by the field  $\vec{E}_0$ . As a result, the main contribution (disregarding once again the dispersion-repulsion terms) comes from the interaction between the induced dipole and the external field. It may be noted that changing the sense of all the dipoles of the wire in a tube with respect to the other leads to a very unstable configuration for the tube in terms of the polarization energy, with  $E_G = -15 \text{ meV}$  instead of  $-215 \text{ meV}$ . This result shows once again the role of the wire inclusion on the stabilization of two tubes.

## C. Influence of other parameters

### 1. SWNT length

A study of longer tubes using the same approach becomes very time consuming due to the increasing number of carbon atoms. For a (10,0) tube, doubling the tube length from  $30 \text{ \AA}$  to  $60 \text{ \AA}$  leads to an increase of the C atoms number from 300 to 600. It is nevertheless crucial to determine the side effects on the nanotube alignment with the external electric field, since most of the experimental data on NT's are given for tube lengths around  $3 \text{ \mu m}$ , i.e.,  $10^3$  larger than the situation considered in Sec. III B. The present approach is based on a self consistent calculation of the polarization experienced by the carbon atoms due to the external electric field and the dipolar field created by the HF wire. The fact that the dipolar field is slowly convergent with the tube length leads to a cut off of the orientational energy as a function of the tube length. As a consequence, no extrapolation of the results obtained for a short tube ( $30 \text{ \AA}$ ) can be done for a much longer one.

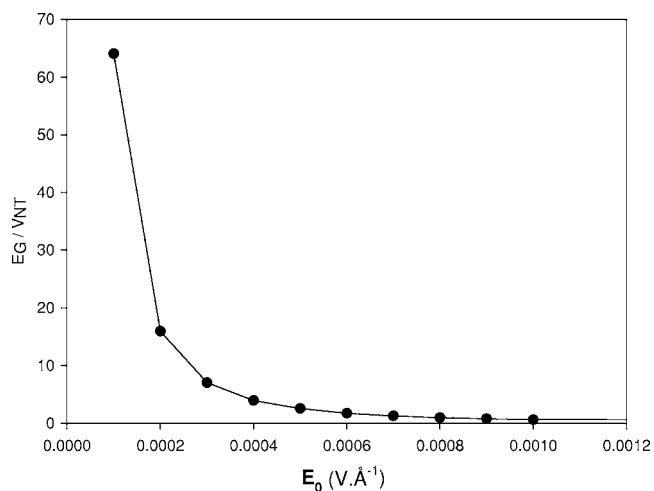


FIG. 6. Increase factor  $E_G^{min}/V_{NT}$  as a function of the intensity  $E_0$  for periodic infinite tube. The filling of the tube favors the tube growth for small external electric field.

An approximate method has thus been used by applying quasi-periodic conditions to the (10,0) SWNT and determining the values of  $E_G$  and  $V_{NT}$  for an infinite length of the empty and wire filled tubes. The mean distance between two nearest neighbor HF molecules in the wire is calculated to be  $2.56 \text{ \AA}$ , whereas the empty (10,0) tube period (i.e., the primitive vector along the tube axis) is  $4.32 \text{ \AA}$ . We can assume that 3 empty tube periods filled by 5 HF molecules reasonably represent the primitive cell of the wire filled tube with a mismatch less than 1.3%.

Figure 6 shows the ratio  $E_G/V_{NT}$  as a function of the external electric field for an infinite (10,0) tube. This curve is similar to the curve given in the inset of Fig. 5 for the  $30 \text{ \AA}$  long SWNT, but with a major difference regarding the scale of the field intensity. Indeed, we find an energy gain in the orientation energy due to the HF inclusion in the infinite case when  $E_0$  is smaller than  $8 \times 10^{-4} \text{ V \AA}^{-1}$ . The ratio can reach a value of 60 for  $E_0 = 10^{-4} \text{ V \AA}^{-1}$ , while it was only 10 for  $E_0 = 10^{-2} \text{ V \AA}^{-1}$  for the  $30 \text{ \AA}$  long SWNT. In the opposite situation, the  $E_G/V_{NT}$  ratio becomes equal to 1 (no gain due to HF inclusion) for  $E_0 = 8 \times 10^{-4} \text{ V \AA}^{-1}$  ( $10^{-1} \text{ V \AA}^{-1}$  for the  $30 \text{ \AA}$  long tube).

We therefore see that the energy gain and the corresponding external field that must be applied to the tube drastically depend on the tube length  $L$ . This can be easily interpreted since the local field on the carbons behaves like the square of the tube length when  $L$  remains small (less than  $10^2 \text{ \AA}$ ) and it becomes linear with  $L$  for longer tubes. Since the variation of  $E_G$  is linear with the tube length, due to the predominant influence of the dipolar field over the external one, the ratio  $E_G/V_{NT}$  varies like  $L^{-2}$  and  $L^{-1}$  respectively for small and large  $L$  values.

Note incidentally that the ratio of the component along the tube axis of the mean dipole moment induced by the dipolar wire and by the external field follows approximately the same law as the ratio  $E_G/V_{NT}$ . It is equal to 1 for  $E_0 = 10^{-1} \text{ V \AA}^{-1}$  in a  $30 \text{ \AA}$  long (10,0) SWNT and for  $E_0 = 4 \times 10^{-4} \text{ V \AA}^{-1}$  in an infinitely long (10,0) SWNT.

TABLE II. Evolution of the ratio  $E_G/V_{NT}$  as a function of the temperature. The second column deals with finite 30 Å long tube for an external electric field  $E_0=10^{-2}$  V Å<sup>-1</sup>, whereas the third column is devoted to an infinite tube with  $E_0=10^{-4}$  V Å<sup>-1</sup>.

$T$ (K)	$E_G/V_{NT}$ (finite case)	$E_G/V_{NT}$ (periodic case)
0	10	64
100	7	27.3
1000	4.3	1.1

## 2. Influence of temperature

To estimate the sensitivity of the ratio  $E_G/V_{NT}$  with the temperature, we use a Monte Carlo algorithm in the phase space defined by the five degrees of freedom (translation and rotation) of the set of the HF molecules forming the wire alone or embedded inside the finite (10,0) SWNT. The values of this ratio determined for  $E_0=10^{-2}$  V Å<sup>-1</sup> and two extreme temperatures (10<sup>2</sup> and 10<sup>3</sup> K) are given in Table II. We see that this ratio remains significantly larger than 1, even for the higher temperature, indicating a significant orientational effect due to the wire inclusion. At 300 K, the ratio  $E_G/V_{NT}$  is still equal to 6. For an infinitely long tube (using the periodic conditions previously mentioned), with  $E_0=10^{-4}$  V Å<sup>-1</sup>, the law of  $E_G/V_{NT}$  vs  $T$  differs appreciably from the one obtained for the small tube (30 Å long). Indeed, we see a faster decrease of this ratio which is close to 20 at 300 K, while the energy gain nearly vanishes at 1000 K.

## IV. CONCLUSION

Due to their specific dielectric properties, single wall carbon nanotubes can be strongly polarized by permanent electric fields. Using a superimposition of two electric fields, an internal molecular field created by a set of dipolar molecules arranged in a one dimensional structure inside the tubes and an external directional field, we suggest that the orientation of the tubes in this latter field could be easily controlled. The internal molecular field polarizes the carbon atoms and in-

duces a relatively large dipole which dominates the permanent one screened by the tube. The resulting dipole interacts with the external field to orient the wire filled tube along a direction which is collinear to the induced dipole and thus anticollinear to the permanent moment of the wire. Two similar wire filled tubes located in a nearest neighbor position are identically oriented anticollinear to the external field and their mutual interaction energy stabilizes this configuration when compared to a set of infinitely separated tubes.

Our approach shows that the external field applied to a small (10,0) SWNT (length equal to 30 Å) should not be larger than 10<sup>-1</sup> V Å<sup>-1</sup> to prevent additional effects of this field on the tube and on the wire. A convenient value for this field within the model proposed here, i.e., a small wire formed by HF dipoles encapsulated in a (10,0) SWNT, could be around 10<sup>-2</sup> V Å<sup>-1</sup>. A temperature increase up to 10<sup>3</sup> K clearly reduces the orientational effect, but does not destroy it since the energy gain due to the tube filling is still equal to 4. When the tube length increases up to become infinite, ideal values for the external field which should favor the tube orientation filled with HF range between 10<sup>-4</sup> and 4 × 10<sup>-4</sup> V Å<sup>-1</sup> at 0 K. When  $T$  increases to 300 K orientational influence of the wire is still very significant (gain around 20), while this effect is totally annihilated at 1000 K.

As a consequence our calculations performed on filled or empty SWNT indicate that the orientational influence of the dipolar wire encapsulation depends strongly on the tube length. Quasi one dimensionality of the wire inside the tubes is also crucial regarding the influence of temperature. Indeed the strategy to obtain the strongest effect is to choose dipolar molecule sizes which are consistent with the tube diameter to reduce the molecule axis disorientation due to temperature and tube lengths which are sufficiently small to enhance the energy gain. In experiments, the tube length is about a few μm, and the corresponding external field that will produce the strongest effect on the orientation of the filled tube should be around 10<sup>-4</sup> V Å<sup>-1</sup>. It may be noticed that such values of the electric field are currently used in experiments on metallic NT's.<sup>26</sup>

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