Carbon nanotubes (CNTs) have been one of the most studied materials in the last years. Their nanosize and diameter have been exploited as a basis for a large variety of applications \[1\]. They exhibit very interesting electrical and mechanical properties. Among these properties, the ability of encapsulating atoms and molecules [2, 3] can be used to engineer one or quasi-one-dimensional systems.

For instance, the encapsulation of fullerene molecules into CNTs lead to self-assembled structures varying from linear chain (generically named peapods) [2, 3] to very complex ones such as multi-helices [4, 5, 6]. In general, there is not a strong electronic coupling between the fullerenes and the CNTs due to their weak interactions, mainly van der Waals (vdW) ones [7, 8]. When fullerenes are replaced with structures containing metallic atoms more complex structures can be formed with potential significant electronic interactions between molecules and CNTs [9, 10]. Diameter selective effect for the encapsulation of cobaltocene molecules into CNT has been experimentally reported [11].

More recently, García-Suárez and collaborators (GFL) [12, 13, 14] suggested that systems composed of cobaltocene (CNT@(7,7) or CNT@((8,8)) could be the basis for new spintronics devices. Cobaltocenes are molecules composed of two aromatic pentagonal rings (C5H5) sandwiching one cobalt atom. The authors based their conclusions on DFT (density functional theory) calculations using the SIESTA [15, 16] code. No temperature or dynamical effects were considered. Also, it must be considered that it is a well-known fact [17, 18] that DFT methods do not describe well the vdW interactions, especially in the GGA (generalized gradient approximation) used by GFL [12, 13]. In general, LDA (local density approximation) underestimates the bond-length values while GGA tends to overestimate them. In this sense in problems where the vdW interactions are very important, as in the case of cobaltocene encapsulated into CNTs, LDA would be the best choice, because it underestimates the bond-lengths, it overestimating the covalent aspects and, consequently, captures part of the missing vdW interactions.

Recent classical molecular dynamics simulations [5, 6] of the encapsulation of fullerenes into CNTs have shown that dynamical aspects and vdW interactions are of fundamental importance. In order to determine whether this is also the case for the encapsulation of cobaltocenes into CNTs we have carried out extensive molecular dynamics simulations and DFT ab initio calculations for those systems. We have investigated the CNT@((7,7), CNT@((8,8), CNT@((13,0), and CNT@((14,0). We have considered cases of frozen and free to relax CNTs. Our results show that when the dynamical aspects are explicitly taken into account, the cobaltocene encapsulation into CNT@((7,7) does not occur, in disagreement with GFL [12, 13] results. For the others investigated CNTs the encapsulation was observed. Initially we will discuss the results from MD simulations. We carried out a systematic study of impulse MD calculations, where the cobaltocene molecules, at different relative orientations and initial velocities (1.0, 5.0, and 10 Å/ps) are directed toward the CNTs, as schematically shown in Figure 1. The MD simulations were carried out using the UFF (universal force field), implemented in Cerius2 package [19]. UFF contains bond stretch, bond angle bending, inversion, torsion, rotational, and vdW terms. It has been shown to produce accurate results for organ-
FIG. 1: Different initial configurations for the molecular dynamics simulations. We have considered cobaltocene configurations at parallel (a), 45° tilted (b), and perpendicular (c) orientations in relation to the nanotube axial axis.

FIG. 2: Representative snapshots from molecular dynamics simulations for the CC encapsulation processes of a) CNT@(7,7); b) CNT@(8,8); c) CNT@(13,0); d) CNT@(14,0), respectively. For all the cases considered here (different velocities and initial cobaltocene orientations) we did not observe the cobaltocene encapsulation into CNT@(7,7) (a), while for all the other nanotubes considered it was observed (b-d).

In Figure 2 we present representative snapshots from MD simulations for the different nanotubes considered here. A better view of the process can be obtained from the movies in the supplementary materials [26].

For all the cases we investigated (different velocities and orientations) we did not observe the cobaltocene encapsulation into CNT@(7,7). The cobaltocene molecules, even at the most favorable situations, are “trapped” at the nanotube borders (see videos 01 e 02). Although the configuration of the cobaltocene inside the nanotube is energetically favorable, there is a dynamic barrier, mainly due to vdW interactions, that prevents the cobaltocene encapsulation into CNT@(7,7). We have also carried non-impulse dynamics placing CC near CNT ends and we obtained similar results, no encapsulation was observed for CNT@(7,7).

For the other investigated tubes (CNT@(8,8), CNT@(13,0), and CNT@(14,0)) we observed the cobaltocene encapsulation. For the cases CNT@(8,8) and CNT@(14,0), there is enough free space so the barrier for cobaltocene rotation is small. They can move almost freely. But, as well pointed out by GFL [12, 13] this rotation freedom will render the nanodevices useless at
FIG. 3: Snapshots from rigid-body molecular mechanics simulations of the encapsulation processes of a cobaltocene into CNT @(7,7). Even at favorable initial configurations (a-c) the molecule never crosses the CNT border (c).

room temperature, since the potentially magnetic ordering would be destroyed by the available thermal energies.

On the other hand for the CNT @(13,0), there is enough axial space to allow an easy encapsulation, but not enough to allow freely rotations (see video 03). Thus, from a structural point of view our results suggest that CNT @(13,0), and not CNT @(7,7) as proposed by GFL [12, 13], would be a feasible candidate for these kind of applications.

As mentioned before our conclusions are in clear disagreement with GFL [12, 13] ones and the origin of these discrepancies needs to be addressed. One obvious possibility it is that this is just the consequence of different geometrical results, and in this case the reliability of our molecular force field results against the ab initio DFT ones needs to be established.

In order to do this we carried out a comparative study of the geometries of the cobaltocene molecules, the nanotubes, and some selected configurations involving cobaltocene and nanotubes. We contrasted the results from UFF with the ones obtained using DMol3 [27, 28] and SIESTA [16] code. DMol3 is state of art \textit{ab initio} DFT methodology. In all our DMol3 simulations we have used relativistic all-electron DFT total energy approach in LDA (Wang-Perdew [29]) and generalized gradient approximation (GGA - PBE) [30] for CC molecule and CNTs. All atoms position were set free and the structure was relaxed for forces below to 0.04 eV/Å using a conjugate gradient algorithm. The pseudopotential was constructed according to Troulier Martins scheme.

In Tables I and II we present a summary of the main geometrical features obtained with the different methods. As we can see there is an excellent agreement between the geometrical data obtained with the classical force field and the ab initio DFT ones. In particular, although the cobaltocene’s H(high) dimension using UFF is a little off in relation to the DMol3 ones the relevant magnitude determining the encapsulation is L, and in this case it is in very good agreement with DMol3 results. It should be stressed from the experimental point of view it is difficult to determine the chirality of CNT based on the diameter estimations. Experimental diameter estimatives from transmission electron microscopy(TEM) measurements contain errors as large as 30% for CNT with diameters less than 1.0 nm and about 10% for CNT of large diameters [35]. Considering these error bars it is not possible to discriminate (7,7) from (13,0) CNTs.

In Table III we present the differences of the “free space” (not considering the excluded volume due to the van der Waals repulsions) for the different methods for the magnitudes indicated in Table I.

|          | (7,7) | (8,8) | (13,0) | (14,0) | L    | H    |
|----------|-------|-------|--------|--------|------|------|
| GGA(Dmol3) | 0.036 | 0.024 | 0.080  | 0.001  | 0.006| 0.126|
| LDA(Dmol3)/UFF| 0.019 | 0.013 | 0.058  | 0.089  | 0.061| 0.236|
| GGA(Siesta)/UFF| 0.019 | 0.013 | 0.058  | 0.089  | -0.093| 0.428|
| LDA(Siesta)/UFF| 0.070 | 0.128 | 0.066  | 0.075  | -0.083| 0.319|
| GGA(Dmol3/Siesta | -0.106 | -0.192 | -0.031 | -0.087 | 0.160 | -0.066|
| LDA(Dmol3/Siesta | -0.051 | -0.115 | -0.008 | 0.014  | 0.144 | -0.083|

TABLE I: Summary of the main geometrical features for the investigated CNTs. The lateral (L) and vertical (H) cobaltocene dimensions are also displayed. Results in Angstroms.

standard double zeta plus polarization(DZP) basis with an energy shift of 0.27 eV to represent the pseudostatic confinement for all atoms. A cutoff of 180 Ry for the grid integration was utilized to represent the electronic charge density for both (LDA - CA) [33] and generalized gradient approximation (GGA - PBE) [30] for CC molecule and CNTs. All atoms position were set free and the structure was relaxed for forces below to 0.04 eV/Å using a conjugate gradient algorithm. The pseudopotential was constructed according to Troulier Martins scheme.

In Tables I and II we present a summary of the main geometrical features obtained with the different methods. As we can see there is an excellent agreement between the geometrical data obtained with the classical force field and the \textit{ab initio} DFT ones. In particular, although the cobaltocene’s H(high) dimension using UFF is a little off in relation to the DMol3 ones the relevant magnitude determining the encapsulation is L, and in this case it is in very good agreement with DMol3 results. It should be stressed from the experimental point of view it is difficult to determine the chirality of CNT based on the diameter estimations. Experimental diameter estimatives from transmission electron microscopy(TEM) measurements contain errors as large as 30% for CNT with diameters less than 1.0 nm and about 10% for CNT of large diameters [35]. Considering these error bars it is not possible to discriminate (7,7) from (13,0) CNTs.

In Table III we present the differences of the “free space” (not considering the excluded volume due to the van der Waals repulsions) for the different methods. Although the differences are very small it could be argued that if we are in the limit cases these differences could be decisive determining whether a molecule would be encaps-
sulated or not. In order to rule out this possibility we run a final test where we used the SIESTA-GGA geometries for the tube and cobaltocene molecules in a simulation of rigid body (the geometries are keep fixed during the process of energy minimization). Even in this limit case using the SIESTA geometries the cobaltocene molecule is prevented to be encapsulated by the vdW interactions (not well described in DFT approaches) (Figure 3). It should stressed that for CNT diameters considered here no significant charge transfer was observed from SIESTA calculations [9]. These results strongly indicate that the encapsulation of cobaltocene into CNT@(7,7) is not possible, in contrast with GFL results [12].

In summary, we have investigate using impact classical molecular dynamics and ab initio DFT methods the encapsulation processes of cobaltocene molecules (CC) into carbon nanotubes. In contrast with previous DFT studies [12,13] our results show that, the CC encapsulation into CNT@(7,7) it is not possible when dynamical effects are explicit taken into account. Our results also show that CNT@(13,0) would be a better candidate for spintronic applications. These results also point out that conclusions based on DFT results of geometrical configurations where van der Waals are of central importance should be take with caution.

TABLE III: Difference (in Angstroms) between the tube diameter value and the lateral (L) cobaltocene dimension, for the different methods considered here. In parenthesis are displayed the differences relative to the LDA ones.

| Method        | (7,7) | (8,8) | (13,0) | (14,0) |
|---------------|-------|-------|--------|--------|
| LDA(Dmol3)    | 4.895 | 6.159 | 5.624  | 6.429  |
| GGA(Dmol3)    | 4.923 (0.028) | 6.175 (0.016) | 5.696 (0.072) | 6.422 (-0.007) |
| UFF(Cerius)   | 4.935 (0.040) | 6.205 (0.046) | 5.625 (-0.082) | 6.399 (-0.030) |
| LDA(Siesta)   | 5.088 (0.193) | 6.416 (0.257) | 5.774 (0.150) | 6.557 (0.128) |
| GGA(Siesta)   | 5.189 (0.294) | 6.527 (0.368) | 5.887 (0.263) | 6.669 (0.240) |

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