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# SHORT NANOTUBES OR BIG MOLECULES? THE CONCEPT OF MINIMAL LENGTH.

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**ABSTRACT**

We have studied the problem of what must be the minimal length of a nanotube with a given diameter to reasonably assert that its electronic properties can be extrapolated to longer structures. For this purpose the variation of the electronic chemical potential (ECP) was plotted against the number of units composing the nanotube for three systems: (5,5) armchair, (9,0) zigzag and (10,0) zigzag nanotubes. We found that the ECP curve defines a different minimal length for each system. This minimal length corresponds to the boundary between large molecules (short nanotubes) and nanotubes properly speaking. We suggest that this minimal length exists for at least all armchair and zigzag nanotubes.

## INTRODUCTION

Nanotubes (NTs), discovered in 1991, have emerged as premier building blocks for the coming age of nanotechnology (1-3). Pure and perfectly cylindrical defect-free carbon nanotubes (NTs) are viewed as a conformal mapping of the two-dimensional honeycomb lattice of a single sheet of graphite onto the surface of a cylinder. The helical symmetry of the carbon atoms around the axis of the cylinder is denoted by two integers (m,n) that indicate the number of lattice vectors in the graphite plane used to make the tubule (see Ref. 4 for pictorial details). For certain values of (m,n) two sub-families of NTs are obtained. For the case m=n the so called armchair nanotubes are generated. At their ends, one side of the benzene rings is exposed. For the case (m,0), the zigzag family of NTs is obtained. At the ends of the zigzag NTs one vertex of the benzene rings is exposed It is accepted that a relationship exists between the values of (m,n) and the conductivity properties of perfectly cylindrical defect-free carbon NTs. If m-n=3t (with t=0,1,2,…) the tube will display a metallic behaviour. Otherwise the NT will have semiconducting properties. This relationship indicates

that all the zigzag and one third of the armchair NTs will be metallic.

When we notice that for any NT with constant diameter there is an infinite number of structures differing only in their length, the following question arises: What must be the minimal length (ML) of a given nanotube to reasonably assert that the main features of the electronic structure can be extrapolated to longer ones?

## METHODS, MODELS AND CALCULATIONS

As the physical criterion to determinate the ML we have chosen the invariance of the electronic chemical potential (ECP, or Fermi level) upon addition of units to build the nanotube. The ECP is related to the work function, a physical observable (5). When the ECP reaches a constant or an almost constant value for a certain number of units, we have got an answer to this problem. The ECP invariance criterion was employed (6-8) to generate minimal models to describe other molecular systems. The ECP, μ, was approximated by (8):

$$\mu \cong \frac{E_H + E_L}{2} \qquad (1)$$

where EH is the one-electron orbital energy of the highest occupied molecular orbital (HOMO) and EL is the one-electron energy of the lowest unoccupied molecular orbital (LUMO).

The following kinds of nanotubes were selected for the study: an armchair (5,5) set of NTs with metallic properties, a set of metallic (9,0) zigzag NTs, and a set of semiconducting (10,0) zigzag NTs. Because some studies eliminated the free valences existing at the ends of the NTs by saturating them with hydrogen atoms, we also analyzed the hydrogenated systems (H-NTs).

The procedure to construct the elements of each set is the following. The first member of the family is a NT composed by only one rod (called unit) of benzene rings rolled in the appropriate way. The second member is a NT composed by two fused rods of benzene rings and so on. Figure 1 shows the numbering of units for armchair and zigzag NTs.

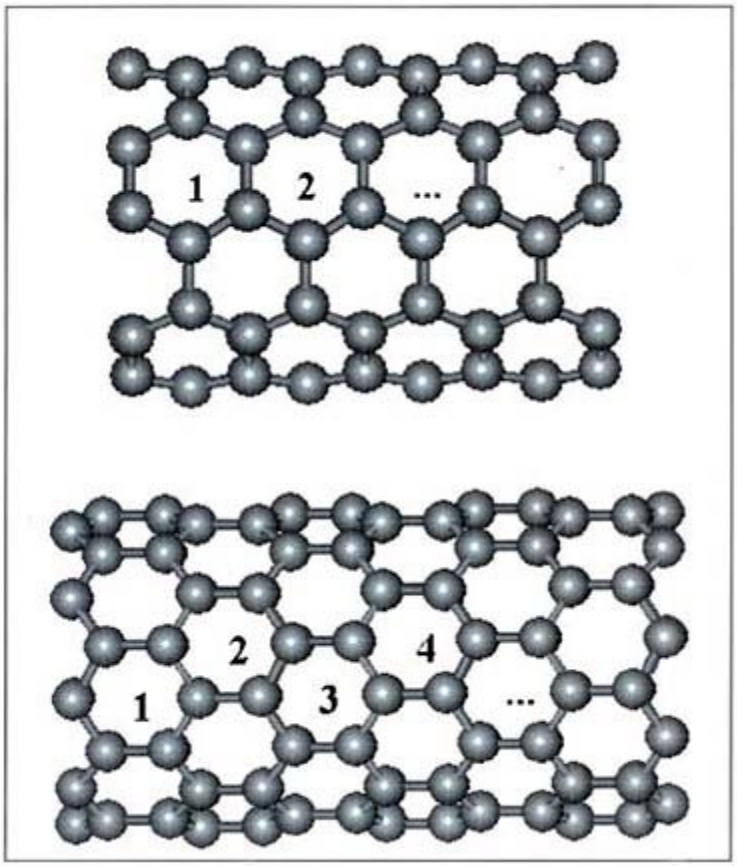


**Figure 1**. Numbering of units for armchair and zigzag nanotubes.

The geometries of all systems were fully optimized with Molecular Mechanics and the wavefunctions and associated eigenvalues were obtained with the Extended Hückel Method (EHT) (9). This choice is based on the size of the molecular systems and on the good results we obtained for fullerenes with the EHT method (10).

## RESULTS AND DISCUSSION

Figure 2 shows the ECP curves for the family of (5,5) armchair metallic NTs in their hydrogenated and unhydrogenated forms. For the case of unhydrogenated NTs (C-NTs hereafter) we may observe that after some abrupt changes the ECP value begins to stabilize at the level of 13 units (280 atoms). This point is the minimal length associated to the (5,5) armchair nanotube. In the case of the H-NT only when it is composed by 16 units (360 atoms) a tendency to reach a constant value begins to appear. At the level of 860 atoms the ECP is still slowly raising its value. As the ECP value cannot rise indefinitely for physical reasons it is probable that a constant value will be reached after adding some 5 to 10 more units. Apart from the fact that using hydrogenated NTs to study phenomena involving pure carbon nanotubes is not licit because of the changes of the electronic structure, our results clearly indicate that if we want to use as model an hydrogenated (5,5) armchair NT, it must be one composed by about 600 carbon atoms or more. Finally, we note that the ECP curves for the H-NT family do not intersect in the interval studied here.

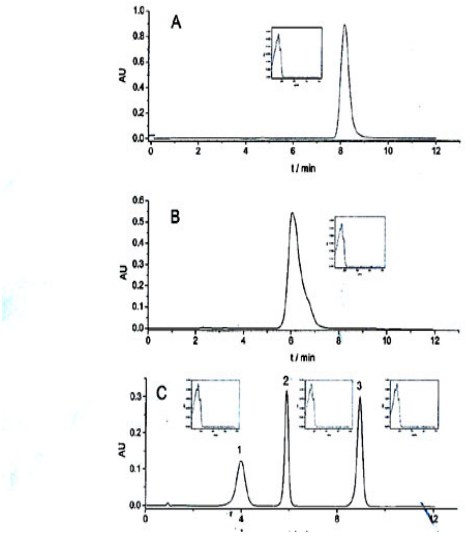


**Figure 2**. ECP curve for the family of metallic (5,5) armchair nanotubes.
□ holds for the pure carbon NTs and ∗ for the hydrogenated forms.

Figure 3 shows the ECP curves for the (9,0) C-NT and H-NT zigzag NTs. The ECP curve for C-NT shows, between 7 and about 22 units (414 atoms), an almost linear increase. The ML lies about 31 units (576 atoms) and the electronic chemical potential seems to be constant up to 47 units (864 atoms). For the case of the H-NT family, the ECP curve begins an almost linear increase, starting at 20 units (396 atoms). At the level of the longest H-NT studied (47 units with 882 atoms) the ECP curve does not seem to behave constant. Therefore, the ML length for H-NT (9,0) remains undetermined. Also, contrary to the (5,5) case both curves intersect at the level of 13 units, and the situation at 47 units is not clear.

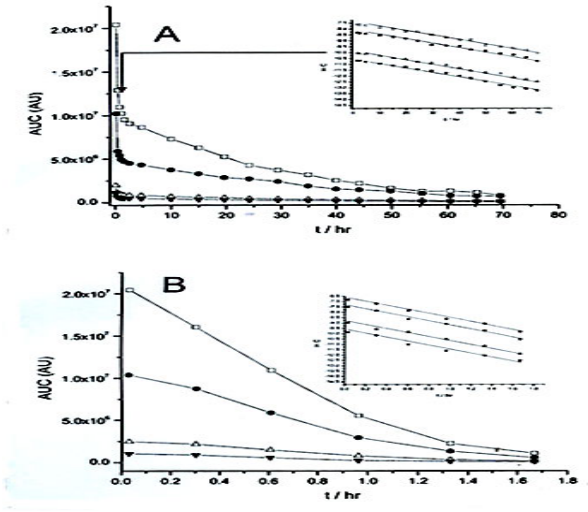


**Figure 3**. ECP curve for the family of metallic (9,0) zigzag nanotubes.
□ holds for the pure carbon NTs and ∗ for the hydrogenated forms.

Figure 4 shows the ECP curves for the semiconducting (10,0) C-NT and H-NT zigzag NTs. The ECP for both systems begins to stabilize at the level of 17 units (360 atoms for C-NT and 380 atoms for H-NT) (11). As in the case of the (9,0) family, here both curves also intersect at 4

units. We have not arrived to an explanation of this fact but we note that curve intersection occurs only in zigzag nanotubes.

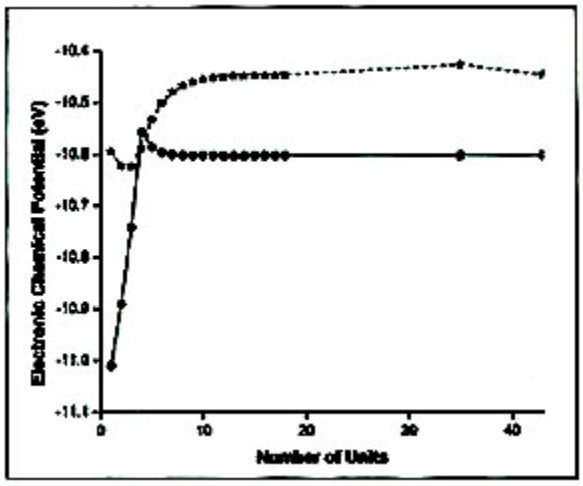


**Figure 4**. ECP curve for the family of semiconducting (10,0) zigzag nanotubes. □ holds for pure carbon NTs and * for the hydrogenated forms.

Our main result can be generalized as a conjecture stating that all pure carbon armchair and zigzag NTs have a minimal length defining the boundary between large molecules (short NTs) and nanotubes. The corollary is that any NT with a length falling below ML should be treated only as a big molecule and not as a nanotube whose electronic properties are similar to the ones of longer NTs. Finally, we found that the minimal length for a given hydrogenated NT seems to be greater than the ML for the pure carbon analogue

We must stress that the concept of minimal length introduced here is valid only for the electronic properties (mainly for the frontier molecular orbitals and molecular orbitals closer to them in energy and the associated eigenvalues). There are other properties that not necessarily converge to a definite value with an increase in tube length. This is, for example, the case of the thermal conductivity of the (5,5) armchair NT which seems to obey a power law relation (12).

Within these results, we suggest that calculations made on systems lying below the minimal length are not representative of the kind of NT they use. This is the case of the results reported for short fragments of (5,5) and (10,0) NTs (13). Also, the diffusion barriers for a Li atom inside a short (5,5) hydrogenated armchair nanotube should be re-examined using a longer (5,5) hydrogenated fragment (14).

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11. In the case of the H-NT we could not reach complete geometry optimization for the 35 unit (740 atoms) NT. We decided to include in the plot the corresponding ECP value because it is an upper bound giving a qualitative idea of the error when full geometry optimization is not achieved.

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