# Can single-walled carbon nanotube diameter be defined by catalyst particle diameter?

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# ABSTRACT

The need of designing and controlling single-walled carbon nanotube (SWCNT) properties is a challenge in a growing nanomaterials-related industry. Recently, great progress has been made experimentally to selectively control SWCNT diameter and chirality. However, there is not yet a complete understanding of the synthesis process and there is a lack of mathematical models that explain nucleation and diameter selectivity of stable carbon allotropes. Here, in-situ analysis of chemical vapor deposition SWCNT synthesis confirms that the nanoparticle to nanotube diameter ratio varies with the catalyst particle size. It is found that the tube diameter is larger than that of the particle below a specific size ( $d_c \approx 2nm$ ) and above this value is smaller than particle diameters. To explain these observations, we develop a statistical mechanics based model that correlates possible energy states of a nascent tube with the catalyst particle size. This model incorporates the equilibrium distance between the nucleating SWCNT layer and the metal catalyst (e.g. Fe, Co, Ni) evaluated with density functional theory (DFT) calculations. The theoretical analysis explains and predicts the observed correlation between tube and solid particle diameters during growth of supported SWCNTs. This work also brings together previous observations related to the stability condition for SWCNT nucleation. Tests of the model against various published data sets and our own experimental results show good agreement, making it a promising tool for evaluating SWCNT synthesis processes.

## **INTRODUCTION**

Single-walled carbon nanotubes (SWCNTs) are among the most studied and promising carbon allotropes for flexible electronics and biomedical applications due to their mechanical stability and high electronic conductivity<sup>1–3</sup>. The design and controlled synthesis of carbon allotropes (e.g. nanotubes, fullerenes) and many other 2D polymorph materials have received increasing attention of several industries due to their wide range of applications<sup>1–5</sup>. Catalytic chemical vapor deposition (CVD) is currently the most widely used technique for growing carbon nanotubes<sup>6–9</sup>. This technology has been especially important in the mass production of SWCNTs and achieving a better selectivity in diameter and chirality. The structure of catalyst nanoparticles, including size, composition, morphology and their evolution during the CVD process (e.g. interaction with adsorbate gases and substrate) play a critical role in the growth of SWCNTs<sup>10</sup>.

There is some consensus among experimentalists about the diameter-controlled synthesis of SWCNTs grown using a supported nanocatalyst: A uniform distribution of supported small solid catalyst particles is suggested to produce a homogeneous narrow nanotube's diameter distribution<sup>11–14</sup>. These works show a strong relationship between the solid nanocatalysts size and the tube diameter profile. The phase of the catalyst (i.e. solid or liquid) has been suggested as an important factor for reducing the variability of possible chiral structures<sup>15,16</sup>, as well as that for diameter selectivity, with solid structures favoring such selectivity. Statistical analyses establishing the ratio between the diameters of catalyst particles and those of SWCNTs<sup>17–19</sup> together with observations regarding the growth mode, have given birth to additional understanding, such as the tangential vs. perpendicular growth classification<sup>20</sup>. However, a model that may quantitatively explain the link between SWCNTs and catalyst particle diameters has not been successfully established limiting the advances of targeted synthesis for selective nanotube production and chirality control.



**Figure 1.** Simulated structure of a nucleated cap system (green/orange) growing over a nanocatalyst (blue) supported on an oxygen-rich insulating substrate (*e. g.*  $SiO_2$ ,  $Al_2O_3$ ). [Top-Right] Nucleated semi-fullerene cap. [Bottom-Right] Curved tubular nanoribbon (orange) at the SWCNT open-end interacting with the catalyst.

Earlier studies have highlighted the thermodynamics-driven nature of the SWCNTs nucleation process<sup>21</sup> and its connection with chirality selectivity<sup>22</sup>. For all chiral angles  $\chi$ , the energy scale variability associated with the SWCNT caps is small, compared to that of the SWCNT to catalyst interface<sup>23</sup>. A high interfacial surface stress between metal and carbon tends to peel off the cap. This process creates an incipient nanotube nucleus that could be described as composed of a thin curved tubular nanoribbon interacting with the metal surface topped by a semi fullerene cap as shown in Figure 1. We postulate that the fact that the nascent tube has elastic properties, and therefore curvature energy, allows the SWCNT to reach a defined range of energetically stable states. We show that the probability of reaching these stable states may determine the diameter of the tube.

Here we have used high-resolution in-situ environmental transmission electron microscopy (ETEM) to determine the diameter relationship between Co metal catalyst particles and SWCNTs experimentally, and propose an innovative model based on the elastic energy of the rim nanostructure (orange region in Figure 1) at the open-end tube edge. Such model offers an understanding of the correlation between catalyst particle and nanotube diameter through the analysis of most probable energy states for the atoms in contact with the metal immediately after cap nucleation.

The statistical-mechanical based model is tested against our own data and that from the literature. The paper is structured as follows: First we introduce the basic concepts on which the model is developed, and then we provide a physical description and define the main equations, assumptions, and parameters. Finally, we apply the model and compare the prediction with experimental results.

# THEORETICAL BACKGROUND AND MODEL DEVELOPMENT

We model a system conformed by an infinitesimal section of the incipient SWCNT wall referred here as the tubular nanoribbon (Figure 2). The nanoribbon is described as the outer edge of the nascent tube in contact with the metal particle after the nucleation occurs. This tubular nanoribbon has a single degree of freedom, the radial position on a curved surface (i.e. tube diameter). According to the dislocation theory<sup>24</sup>, the presence of free radicals at the edge of the early sp<sup>2</sup> carbon structure allows the carbon atoms in contact with the surface to spread into new planes (edge dislocations) forming pentagons and hexagons until the complete cap is formed. This stepped spreading of the nascent cap<sup>25</sup> allows the system to find a local minimum in the carbon structure's curvature energy, and therefore a stable tube diameter ( $d_T$ ). The probability function  $f_d(d_T)$  of a tube having a certain diameter  $d_T$  can be evaluated with a statisticalmechanical model. We define the diameter distribution  $f_d$  as a probability function of generalized coordinates (p,q) such that the statistical equilibrium condition can be expressed mathematically using Equation 1.

$$\sum_{i} \left( \frac{df_d}{dp_i} \dot{p}_i + \frac{df_d}{dq_i} \dot{q}_i \right) = 0 \quad Eq. 1$$

This condition of statistical equilibrium dictates that the system evolves in a way that conserves the density of states and probability function  $f_d$  within a multi-dimensional space ( $\prod dp_i dq_i$ ), called the extension of phase<sup>26</sup>. For our system, this condition is fulfilled defining the probability  $f_d$  as a function of energy and including only conservative forces. Classical mechanics theory assigns energy states for an atom, or group of atoms, in terms of potential (U) and kinetic energy (K), these can be used to describe the configuration of the atoms for a microstate. Additional constraints to the degrees of freedom on the atoms are due to the C-C bonds in the nuclei layer that restrict the motion of the tubular nanoribbon. For this reason, we assumed that the carbon atoms on the tubular nanoribbon have a negligible velocity and the only relevant potential energy describing the intermolecular interactions is the energy stored as strain energy within the system (Equation 2), thanks to the flexible nature of the material.

$$E_{strain} = \frac{YLa^3\pi}{6d_T} \qquad Eq.2$$

The strain energy ( $E_{strain}$ ) is defined in terms of Young modulus (Y), tubular nanoribbon length (L), nanoribbon wall thickness (a), and tube diameter ( $d_T$ ). A schematic illustration of these variables can be found in Figure S1 (Supporting Information). The curvature energy ( $E_c$ ) is a function of Y, a,  $d_T$  and the carbon surface density  $\rho_s$  and is defined as the strain energy normalized by N, the total number of C atoms, and reduced to the expression in Equation 3.

$$E_c = \frac{E_{strain}}{N} = \frac{Ya^3}{6\rho_s d_T^2} = \frac{\alpha}{d_T^2} \qquad Eq.3$$

The parameter  $\alpha$  is defined in Equation 3. It is usually assumed constant for a defect and impurity-free material like the nanoribbon. Kudin et al. have shown the relation of  $\alpha$  to the flexural rigidity using the continuum shell approach<sup>27</sup>. Equations 2-3 are based on previous works<sup>18,28–31</sup> addressing diameter stability and their derivation can be found in the first section of the Supplemental Information.

The tubular nanoribbon system in its nascent form may exist in many different configurations (i.e. radial position and orientation on top the particle). Each configuration has a unique corresponding energy state (i.e. microstate) associated with it. Thus, to evaluate these microstates we define them mathematically using a continuous function for the curvature energy according to the work-energy principle for elastic materials. The probability  $f_d(d_T)$  of a tube having a certain diameter  $d_T$  will be proportional to the curvature energy  $E_c$  associated to a corresponding microstate as described by Equation 4.

$$f_d(d_T) \propto e^{-\frac{E_c(d_T)}{k_B T}} \quad Eq.4$$

According to equation 1, the system is at statistical equilibrium, this means that the probability distribution function  $(f_d)$  is independent of time. Strictly speaking, a finite number of systems cannot be distributed continuously in the phase space. But in the limit of an infinite number of states, we may approximate the discrete distribution to a continuous function<sup>26</sup>. The extension of phase's radial limits in Equation 5 accounts for all possible tube diameter  $(d_T)$  configurations and it is related to the nanocatalyst diameter  $(d_p)$  in the upper limit  $(d_{up} = d_p + \delta_0)$ .

$$d_0 < d_T < d_p + \delta_0 \qquad Eq. 5$$

Here,  $d_0$  is the minimum equilibrium distance between two graphene layers in a graphite structure at the absolute zero temperature ( $\approx 0.34$  nm), and  $\delta_0$  is approximated by the equilibrium average distance between the surface of the metal catalyst and the carbon nanoribbon as shown in Figure 2.



Figure 2. Cylindrical carbon nanoribbon interacting with a catalyst. The nanoribbon interacts with the catalytic surface and positions itself at an equilibrium average distance  $\delta_0$  at the most stable diameter  $d_T$ . For a stable particle with diameter  $d_p$ , the tube diameter  $d_T$  is constrained within a diameter range described in Eq. 5 as the extension of phase's radial limits.

For a nascent carbon cap supported by a metal particle, the interfacial stress will bend the carbon structure to find a stable curvature. This quasi-static process follows an intrinsic energetic path under the principle of least action. Therefore, we propose a probability function in the pseudo-canonical ensemble (Equation 6) with a phase function distributed according to the Boltzmann probability function. In principle, this can be better understood as an *a priori* probability.

$$f_d(d_T,T) = \frac{Boltzmann \, Energy \, Distribution}{Sum \, over \, all \, possible \, states} = \frac{e^{-E_c(d_T)/k_B T}}{\int_{d_0}^{d_p + \delta_0} e^{-E_c(x)/k_B T} \, dx} \qquad Eq.6$$

At fixed temperature,  $d_T$  is the only variable describing every possible microstate of the tubular nanoribbon. Therefore, we can use the expression for curvature energy found in Equation 3 to integrate the

denominator in Equation 6. The limits in the integral shown in the denominator of Equation 6 will match the boundaries in Equation 5 to account for all possible configurations. The resultant expression given in Equation 7 is a function only of the particle diameter  $(d_p)$ , temperature (T), and the additional parameters  $(\alpha, d_0, \delta_0)$ . As such, it depends strongly on the carbon and nanocatalyst intrinsic properties, as well as on the tube/nanocatalyst interactions.

$$f_d(d_T, T) = \frac{e^{-\left(\frac{\alpha}{d_T^2 k_B T}\right)}}{\left[\sqrt{\frac{\pi \alpha}{k_B T}} \operatorname{erf}\left(\frac{\sqrt{\alpha/k_B T}}{x}\right) + x e^{-\left(\frac{\alpha}{x^2 k_B T}\right)}\right]_{x_1 = d_0}^{x_2 = d_{up}}} \quad Eq. 7$$

From Equation 6, we have obtained a probability density distribution given by Equation 7. We note that this is an approximation because we have neglected the translational kinetic energy  $(K \rightarrow 0)$  and considered only the potential energy associated with the curvature of the nascent carbon structure  $(U = E_c)$ . This doesn't mean that the total energy of the tubular nanoribbon is not affected by other contributing factors, like chirality, and the velocity of the catalytic particle (if it is in motion). But the current approximation helps us to concentrate on the effect of the stability of the carbon nanostructure interacting with the catalytic particle that is assumed to be a dominant factor to determine the tube diameter.

$$< d_T > = \int_{x_1=d_0}^{x_2=d_p+\delta_0} x f_d(x, d_p, T) dx \quad Eq.8$$

The experimentally observed diameter is predicted by calculating the most probable value ( $\langle d_T \rangle$ ) according to the probability density distribution ( $f_d$ ) given by Equation 7, once the properties of the catalyst and catalyst/carbon interactions (mainly reflected in the  $\delta_0$  parameter) are determined from first principles as shown below. The result can be obtained by solving the expression in Equation 8. Moreover, the standard deviation ( $\sigma$ ) can be found using the definition in Equation 9 and the probability distribution obtained previously ( $f_d$ ). The standard deviation provides a measure of the most probable region where SWCNTs can grow, and it depends on temperature T and the particle diameter ( $d_p$ ) through the upper integration limit  $d_{up}$ .

$$\sigma^{2} = Var(d_{T}) = \int_{d_{0}}^{d_{up}} x^{2} f_{d}(x,T) \, dx - \langle d_{T} \rangle^{2} \quad Eq.9$$

We note that some other conditions may affect the proposed representation of SWCNT curvature stability and the model parameters. For example, intrinsic properties of the growing tube, such as chirality and defects may cause small changes of quantum origin on the physical properties of the tube<sup>32</sup> (e.g. elasticity Young modulus). Additionally, the distribution of accessible diameters should be discrete based on the existence of known distances between covalently bonded carbon atoms<sup>28–30</sup>. However, the use of a classical expression for the elastic energy and the subsequent statistical analysis are valid under the equipartition theorem and the ergodic hypothesis<sup>26,33</sup>.

Moreover, as we demonstrate in this paper, the model can reproduce observed nanotube's diameter distributions using exclusively the measured catalyst diameter distribution profile. Additional simplifications to the model and approximations for the probability distribution  $f_d$  and the most probable diameter  $\langle d_T \rangle$  are discussed in the supplementary information. We observed that a numerical evaluation of Equation 8 is the most accurate method for solving the expression, especially for small particles (Figures S3 and S4). In the following section we use this probability function to determine the most probable tube diameter as a function of particle size where the model parameters are evaluated for sets of experimental synthesis data of SWCNTs grown on cobalt nanoparticles.

# **RESULTS AND DISCUSSION**

A critical part of the model and the basis to understand nanotube formation and its relationship to the nanocatalyst properties relies on studying the stability of the nascent tube and the associated catalyst-nanoribbon interaction. A deeper analysis of the interfacial interaction between the metal surface and the graphene layer is crucial to comprehend the forces involved during the tube's nucleation. We use DFT to quantify the interaction between some common metal catalysts and carbon structures. These calculations are necessary to find an adequate model parameter value for the distance between the nascent nanotube wall and the catalyst surface. Additionally, we use our experimental data to assess the model and analyze its capabilities and limitations.

# The Strength of Graphene-Metal Interaction and Evaluation of Model Parameters

Interlayer adhesion energies obtained using spin polarized DFT calculations reveal the information about the strength of interaction between metal (and metal carbide) catalysts and graphene. Table 1 displays values obtained by DFT under periodic boundary conditions. The calculations were set minimizing any graphene curvature contribution that could arise due to the finite size of the model. The values for energy in previous works shown in Table 1 correspond to multiple metal facets or in the case for cobalt carbide is the closer approximation found to the infinite layer approximation for this system. Previous work has reported the existence of a relation between the exposed metal (or metal-carbide) catalyst facet and the graphene/catalyst adhesion energy<sup>34</sup>.

$$\Delta E_{int} = E_{slab\&grap} - E_{slab} - E_{grap} \qquad Eq.\,10$$

The values for the interfacial interaction energy ( $\Delta E_{int}$ ) were calculated using Equation 10, where  $E_{slab\&grap}$  is the energy of each of the systems shown in the DFT section of the supplemental information,  $E_{slab}$ , and  $E_{grap}$  are the energies of the isolated slab and graphene respectively. The (100) facet was chosen for the metal and metal carbide structures because it facilitates (in general) the match with the graphene lattice structure and therefore helps to minimize the catalyst/graphene lattice mismatch when modeling graphene in the infinite layer approximation. Details of the calculations are given in the Methodology section and in the supplemental information.

**Table 1.** Adhesion energy  $(E_{adh})$ , metal-carbon interaction energy  $(E_{MC})$  and equilibrium distance  $(\delta_0)$  between (100) slabs and graphene layer. The calculated values are compared to previous published energies and distances.

System	E <sub>adh</sub> [eV/nm <sup>2</sup> ]		E <sub>MC</sub> [meV/atom]		$\delta_0^{\infty}$ [nm]		
	Calc	Prev.	Calc	Prev.	Calc	Prev.	
Iron (Fe)	-2.81	-5.55 <sup>35</sup>	-74.20	-149 <sup>35</sup>	0.204	[0.211 - 0.232] 35,36	
Nickel (Ni)	-0.94	-9.13 <sup>37</sup>	-24.77	[-19; -135] <sup>38-41</sup>	0.205	[0.204 - 0.280] 38,40,42*43-45	
Cobalt (Co)	-2.22	<b>-7.6</b> 1 <sup>46</sup>	-55.49	$[-24.7; -160]^{46-48}$	0.338	$[0.205 - 0.340]^{47,48}$	
Cobalt Carbide (Co <sub>2</sub> C)	-2.96	[-14.4; -26.5] <sup>34</sup>	-77.59	-	0.220	[0.180 - 0.309] <sup>34</sup>	

\*Experimental Techniques (43-45)

The metal-carbon interaction energy  $(E_{MC})$  and the adhesion energy  $(E_{adh})$  were obtained dividing the interfacial interaction energy  $(\Delta E_{int})$  by the number of carbon atoms and by the transverse area of the simulation box respectively. This value is crucial because it defines the region where multiple stable carbon allotropes start to form<sup>49,50</sup> (e.g. fullerene vs. nanotube). In other words, the metal-carbon strength of interaction is an indicator of the encapsulation-growth transition. As such, it can help us to determine the minimum tube diameter value  $(d_T)$  where deactivation of the particle due to encapsulation becomes possible and may be used to characterize the stability regions as discussed further in the stability analysis.

The equilibrium distance  $(\delta_0)$  is a parameter of the model that defines the extension of phase upper boundary  $(d_{up} = d_p + \delta_0)$  and therefore the number of accessible microstates. The values  $\delta_0^{\infty}$  shown in Table 1 correspond to the infinite layer approximation, two periodic metal – graphene layers interacting in the interface, this method is especially good to obtain a measure of the non-bonding, van der Waals interaction. Usually, bulk carbon atoms in a graphene sheet have a coordination number of three; however, edge carbon atoms may have a reduced coordination number. For example, the  $\delta_0^{\infty}$  equilibrium distance in the cobalt slab (0.338 nm) decreases to 0.190 nm, 0.179 nm and 0.161 nm by reducing the number of neighbor carbon atoms coordinating with a central bulk graphene atom to two, one and zero respectively. This decrease in the equilibrium distance is related to a stronger interaction due to free electrons available to form bonds at the edge of the tube ( $\delta_o^{edge} \approx [0.5 - 0.6] \delta_0^{\infty}$ ). The tubular nanoribbon region, on which the model is based, is composed of a bulk – edge combination of carbon atoms. For this reason, we assumed that  $\delta_0$  in the upper limit of the radial extension of phase ( $d_{up}$ ) is approximately equal to the infinite layer value ( $\delta_0 \approx \delta_0^{\infty} \approx 2\delta_0^{edge}$ ) for the entire diameter.



**Figure 3.** Surface carbon density ( $\rho_s$ ) dependence on chiral angle. Estimated values (•) using periodic units of different chiral tubes.

An interesting observation based on the work-energy principle equations (Equations 2 and 3) is that the carbon surface density ( $\rho_s$ ) has a role defining the curvature energy function, or more explicitly the  $\alpha$  parameter. We evaluated the surface carbon density dependency on chirality for SWCNTs with similar diameter. A quick analysis of the smallest repetitive section of different chiral tubes shown in Figure 3 indicates that the surface carbon density is almost independent of the chiral angle and has a constant average value of 38.2 atoms nm<sup>-2</sup>.

# **Experimental Results**

The diameters of approximately 22 particles and the tubes associated with them were measured from the high resolution ETEM images recorded during SWCNT growth (see methods for details). It was not always possible to take images with both the particle and associated nanotube to be clearly visible in the 2D projection as often the particles are embedded in the support. Therefore, only the images with clear connection between the two were used for the data analysis. A broad distribution of three types of relationship can be established from the *in situ* data: (a) tube diameter is smaller than the particle diameter (Figure 4a and Figure 4b); (b) tube diameter is almost the same as particle diameter (Figure 4c and Figure 4d); and (c) tube diameter is larger than the particle diameter (Figure 4e). This last observation is intriguing as it results in a different metal to carbon interaction than the first two.



**Figure 4.** ETEM images of SWCNTs growing on Co particles. a and b) Tube diameter smaller than particle diameter, apparent perpendicular growth; c and d) Tube diameter very close to the particle diameter, apparent tangential growth; e) Tube diameter larger than particle diameter, apparent tangential growth; f) Observed correlation between tube diameter and particle diameter in this study.

SWCNT production using a catalyst-support combination results in a clear dependence on particle diameter as indicated in Figure 4f. For particles above  $\approx$  3 nm, no SWCNT growth was observed. The proposed model does not predict a maximum diameter for the SWCNT growth on active particles. However, previous studies have shown the importance of the nanotube elastic behavior to keep its cylindrical structure and the existence of a transition between the cylindrical vs. the collapsed structure as a function of tube diameter<sup>51,52</sup>. The elastic collapse has not been explored in this study, but it has been reported to impede the growth of SWCNTs above particle size of 3 nm<sup>53</sup>.

Figure 4f shows the experimental correlation between the tube and particle diameter. There is a clear change in behavior of this function with respect to the straight line in Figure 4f ( where  $d_T = d_p$ ). The tube diameter is larger than that of the particle below  $\approx 2$  nm and above this value is smaller than particle diameters. This change agrees with the reported transition from tangential (Figures 4c, d, and e) to perpendicular growth mode<sup>20</sup> (Figures 4a and b). Note that in the tangential growth mode the small nanoparticle has more flexibility to let the tube diameter accommodate on its surface. Such flexibility (which depends on intrinsic properties of the catalyst such as its cohesive energy reflected in its melting point) disappears in the perpendicular mode, where the fate of the nascent tube is more related to the strength of the catalyst-carbon interaction. Moreover, in the tangential growth mode, the contact area between particle facets and nascent tube wall is much larger (Figures 4 c, d, e); thus we expect that the interfacial energies between carbon and catalyst be dominant. In contrast, in the perpendicular growth mode, the tube sits over the larger particle (Figures 4 a and b) and the interfacial interactions are predominantly between the tube rim and the catalyst surface. In addition, we know that the curvature energy of SWCNTs increases as the tube diameter decreases<sup>18</sup>. Therefore, the tube diameters from the smaller particles may be relatively larger. Molecular dynamics simulations have shown that the tube diameter is also dependent on the metal-support interactions and tubes with diameters within a stable region will nucleate from larger particles as the metal-support adhesive energy increases<sup>54</sup>. The tube diameter has also been reported to depend on the carbon availability. However, as the C<sub>2</sub>H<sub>2</sub> pressure in our ETEM experiments was kept constant, the availability of carbon can only vary with particle size. In other words, for the data in our study, the tube diameter will increase with increasing particle size, which is generally true, except for the fact that there appears to be at a minimum ( $\approx 1.1$  nm) and a maximum ( $\approx 2.8$  nm) limit for tube diameters from particles of diameters varying from  $\approx 0.85$  nm to  $\approx 3.14$  nm.

# Model Predictive Capability

# *Test of the model for the small particle range* $(d_p < 5nm)$

We first attempt to replicate the trend observed in our experimental data relating the diameter of the particle to the tube (Figure 4f). The interfacial distance  $\delta_0$  found previously for cobalt is used to define the upper integration limit  $d_{up}$ . The parameter  $\alpha$  as discussed previously can be estimated using Equation 3 from the work-energy theory for elastic materials presented in the first part of the supplemental information. This relation makes  $\alpha$  exclusively dependent of tube properties like Young modulus (Y), the atomic surface density ( $\rho_s$ ) and the wall thickness (*a*). Values of Young moduli obtained from prior atomistic studies are largely scattered varying from (0.95 TPa to 5.5 TPa) for *Y* and [0.06 nm to 0.69 nm] for wall thickness (*a*) <sup>53,55–58</sup>. The uncertainty on the definition and estimated values for these properties can impact  $\alpha$  greatly. For this reason, a convenient procedure for including the variations in the carbon nanoribbon properties is to numerically optimize the  $\alpha$  value from the experimental data and compare with previous estimations.



**Figure 5.** Adjusting the parameter  $\alpha$  to our SWCNT experimental data. (+) High-resolution TEM experimental Data (this work). (-) Most probable or average diameter and (--) standard deviation limits ( $\pm \sigma$ ) obtained after  $\alpha_{opt}$  has been found.

Figure 5 shows the results of fitting the model to our experimental data. The optimized  $\alpha_{opt}$  value for our SWCNT data using a cobalt catalyst is 1.15 eV nm<sup>2</sup> atom<sup>-1</sup>. The inflection point (i.e. the point where the ratio  $d_T/d_P$  is approximately one) in the diameter's behavior can be observed and explained within the model. For very small particles (< 2 nm) the most probable diameter (solid line) is close to the upper limit  $(d_T \rightarrow d_p + \delta_0)$  in the extension of phase. This is due to the small range of possible states that results from a very sharp narrow probability distribution (Figure S1). On the other hand, the probability distribution for large particles is broader and the average is expected to be in an intermediate value between both limits of the range  $[d_0, d_{up}]$ . Hence, the most probable tube diameter in small particles is larger than  $d_p$  and the growth should be tangential to the particle  $(d_T > d_p)$ , whereas the growth for large particles is expected to be perpendicular  $(d_T < d_p)$ .

It is important to further analyze the meaning of the  $\alpha$  parameter. For this reason, it is also necessary to consider previous evaluations of this parameter. For example, Gülseren et al reported a value of  $\alpha = 0.0214$  eV nm<sup>2</sup> atom<sup>-1</sup> obtained from ab-initio calculations<sup>31</sup> ( $E_c = \alpha/R^2 = E_{CNT} - E_{grap}$ ). This value is equivalent to  $\alpha = 0.0856$  eV nm<sup>2</sup> atom<sup>-1</sup> in our curvature energy representation ( $E_c = \alpha/d_T^2$ ). However,

 $\alpha_{opt}$  (1.15 eV nm<sup>2</sup>atom<sup>-1</sup>) is one order of magnitude higher than the one predicted by Gülseren et al. This difference in  $\alpha$  values can be related to the uncertainty in the evaluation of the SWCNT wall thickness where approximations also vary in orders of magnitude<sup>53,55,58</sup>. In an atomic thin shell model, the wall thickness is considered to be the graphite inter-layer spacing (0.34 nm), Cai et al. demonstrated that this value also corresponds closely to the thickness of the SWCNT electron cloud<sup>57</sup>. To test the accuracy of our  $\alpha$ , we estimated the Young modulus (*Y*) using the optimized  $\alpha_{opt}$  value. Thus, using the 2D approximation (bending tubular carbon nanoribbon) in Equation 3, the previously calculated surface carbon density  $\rho_s$ ,  $\alpha_{opt}$ , and the value of 0.34 nm for the tubular nanoribbon thickness, we estimate a value of 1.07 TPa for the Young's modulus of SWCNTs, that is within the range of many model approximations<sup>56,59,60</sup> (0.97 TPa to 5.5 TPa) and very close to the few experimental values reported for SWCNTs<sup>61-63</sup> (1.20 TPa to 1.25 TPa).

*Test of the model for large particle range*  $(d_p > 5 nm)$ 



**Figure 6.** Adjusting the parameter  $\alpha$  to inner diameters in the MWCNTs data set from Tibbetts. (x) Data collected for iron particles from Tibbets<sup>18</sup>. (-) Most probable or average diameter and (--) standard deviation limits ( $\pm \sigma$ ) obtained after  $\alpha_{opt}$  has been found.

Next we used the experimental set by Tibbetts<sup>18</sup>, that reports inner diameters of multi-walled carbon nanotubes (MWCNTs) for very large particles. Although the growth mechanism of MWCNTs is not yet clear, we assume that the inner tube structure nucleation occurs under similar conditions to the ones mentioned previously for SWCNTs. Figure 6 shows that the *inner* diameters in MWCNTs can also be adjusted to our model yielding an  $\alpha_{opt}$  value of 2.063 eV nm<sup>2</sup> atom<sup>-1</sup> using  $\delta_0$  for iron (Table 1). To explain the difference between the  $\alpha_{opt}$  for SWCNTs in small particles and MWCNTs in larger particles it should be noted that the inner diameter in a MWCNT may be affected by the presence of compressive/attractive forces due to the additional walls. This can cause an increase in the ability of storing potential elastic energy within the curvature of the tube. An increase in the bending momentum stored by the carbon atoms at the edge of the tube is expected to affect the flexural rigidity (bending stiffness) of the tube and therefore the  $\alpha$  value in the inner tube structure of MWCNTs. The difference could also be attributed to the van der Waals forces between the inner nuclei and the concentric layers of a MWCNT. These additional forces can modify the mechanical properties of the inner tube. Using the same approximation utilized for the SWCNT thickness (0.34 nm) and the  $\alpha_{opt}$  obtained for MWCNTs, a Young's modulus of 1.93 TPa is estimated, that is in reasonable agreement with reported Young moduli for MWCNTs<sup>64</sup>.

We remark that the range of particle diameters in the two sets of data shown in Figure 5 and 6 is very large. To compare and test the applicability of the  $\alpha$  values, we evaluated both data sets with the  $\alpha_{opt}$  obtained for the smallest tubes and the value reported from Gülseren<sup>31</sup> (Supplementary Information, Figure S6). The model shows that even using a rough approximation of  $\alpha$  from the literature or that previously obtained in the fitting of our data, the model predicts a good estimate of the inner diameter value in large particles. It is found that the predicted tube diameters are much more sensitive to the  $\alpha$  value in the small tube range. For larger tubes, where the probability function is distributed over many possible configurations, the  $\alpha$  dependence becomes weaker. We note that although  $\alpha_{opt}$  was obtained for the previous described experimental sets of data, it could be applied to other metal catalysts because its calculation only involves tube properties. For this reason, the prediction of a SWCNT diameter distribution in a bed of iron nanoparticles is proposed as a final test for  $\alpha_{opt}$ .

Prediction of a nanotube diameter distribution corresponding to a given catalyst size distribution (experimental data from supported CVD)



**Figure 7.** SWCNT's diameter distribution prediction using Iron catalyst particle profiles measured by Zou et al<sup>11</sup>. Figure 7a-c correspond to the experimental tube diameter distribution profile (orange) vs the prediction of the model (blue). Predictions were based on experimental catalyst particle diameters for particles (a) without etching, and (b and

c) after 10 s to 15 s of etching, respectively. The darkest colored regions show the overlap between the experimental and the theoretical descriptions.

Another validation and possible application of this model is shown in Figure 7. The model was used to *predict* the SWCNT diameter distributions corresponding to catalyst diameter profiles measured on a support of Si-SiO<sub>2</sub> wafer by Zou et al<sup>11</sup>. The predictions were obtained using the diameter profiles for the catalyst particles at different etching times to define the upper limit ( $d_{up}$ ). This is because the range of the particle diameter distribution is reduced after exposed to a longer etching time. The experimental data was normalized using Equation 11 and the parameters used for the prediction (Equations 7 and 8) were the equilibrium distance  $\delta_0$  for Iron (Table 1) and the parameter  $\alpha_{opt}$  (1.15 eV nm<sup>2</sup>/atom).

# Normalization = $\frac{Frequency}{\# Measurements} Eq 11$

We observe that all the predicted profiles in Figure 7a-c are in good agreement with the reported experimental sets. The slight right shift in the distributions of the three examples could be attributed to the assumptions on the estimation of  $\delta_0$  and  $\alpha_{opt}$ . The equilibrium distance approximation for the nanoribbon  $(\delta_0 \approx \delta^{\infty} \approx 2\delta^{edge})$ , as discussed before, will affect the probability distribution for small particles. An overestimation of  $\delta_0$  may cause this type of shift due to an increase in the upper limit  $(d_{up})$  and the number of possible accessible microstates. However, for the  $\delta_0$  range found in this and previous studies (0.2 to 0.35 nm) the shift due exclusively to  $\delta_0$  will not account for the total difference. A lack of information in the inactive particles and non-growth events may be contributing to overestimate the amount of tubes from the particle distribution as well.

# Stability Analysis

An important question relates to the probability of a nascent SWCNT cap to develop a stable tube growth or stop the growth and encapsulate the catalytic particle (stable fullerene). Early studies in carbon allotropes have established the relation between curvature energy and tube diameter<sup>18,28–31,65</sup> as described in the theoretical background (i.e. Equations 2, 3 and Equations S1 to S6). Burgos et al, for example, showed the existence of an explicit relation between adhesion energy, curvature and nucleation<sup>49</sup>, as expressed in Equation 12. Furthermore, the analysis of an approximated support-particle interaction showed that the support nature has a strong influence on the catalyst structure, therefore on the catalyst shape (i.e. curvature) and tube's diameter<sup>54,66</sup>. Note that this discussion relates only to systems where the reaction conditions favor a slow carbon supply rate on the catalyst surface (e.g. low pressure of precursor gas). Lowering the carbon

supply flow will likely allow the carbon structures to form more slowly, this annealing process may favor evolution to low energetic configurations<sup>65</sup>. In this section we analyze the stability conditions and locate the estimated tube diameter prediction within the growth stability limits.

$$E_{cT} \leq E_{cF} - E_{MC} Eq. 12$$
Tube Curvature Energy Metal-Graphene interaction energy
$$Eq. 12$$
Metal supported Fullerene Energy

Comparing the curvature energy per atom of the tube  $(E_{cT})$  with the one for a fullerene with similar diameter  $(E_{cF})$  shows that the tube is always more stable. However, the attractive metal-graphene interaction  $(E_{MC})$  may reduce the energy necessary to bend the carbon bonds and therefore the curvature energy per atom of the fullerene capsule  $(E_{sF} = E_{cF} - E_{MC})$ . Hafner et al. introduced the stability criteria graphically using empirically fitted functions to represent the curvature energy of tubes and fullerenes<sup>65</sup>. Following Hafner's work, Figure 8 shows that the energy difference between both states is in the order of meV.



**Figure 8.** Stability analysis for the nucleation of carbon allotropes on metal catalysts. Empirically fitted functions for the curvature energy in SWCNTs ( $E_{cT}$ ) and fullerenes ( $E_{sF}$ ) and the critical diameter of transition ( $d_c$ ) for a cobalt catalyst.

Figure 8 offers a better understanding of Equation 12. Here, we used the interfacial cobalt-carbon interaction energy (Table 1) to estimate the fullerene capsule energy  $(E_{sF})$ . For this reason, even if a tube is less stable for diameters approximately above  $d_c$  in a cobalt particle, the energy difference is extremely small, and in many cases, nanotubes are observed to grow with a nucleation probability proportional to  $e^{(-E_{MC})/k_bT}$ . An interesting observation is that  $d_c$  corresponds to the point where the ratio between  $d_T/d_P$  is approximately one for our experimental data, and the growth behavior changes from tangential to

perpendicular. Therefore, we could use this value as a point of reference and merge the stability analysis with our model.



**Figure 9.** Diameter stable regions during the growth process of SWCNTs and high probability zones within one standard deviation from the most probable diameter ( $\langle d_T \rangle \pm \sigma$ ). (+) High-resolution TEM experimental Data for Co catalysts. (--) Upper limit for the radial extension of phase  $(d_{up})$ . (...) Transition critical diameter  $(d_c)$  between stable fullerene and tube allotropes. (-) Most probable or average diameter and standard deviation limits  $(\pm \sigma)$ . In the purple region, the probability of finding a diameter  $d_T$  is  $\approx 0$ .

Curvature stability plays a role delineating the stable tube growth regions. These are tube diameter stable zones for a specific particle diameter with boundaries defined by the critical diameter  $(d_c)$  horizontal line and the upper boundary in the extension of phase  $(d_{up} = d_p + \delta_0)$  shown as a dashed red line in Figure 9. The small particle zone  $(d_p/d_c \ll 1)$  has an upper limit in stability and it is the  $d_c$  line. This means that the tube is always trying to reduce its curvature energy making the transversal area as big as possible until  $< d_T >$  or a value energetically accessible is reached. We can also observe that most of the experimental data is close to  $d_{up}$  for this zone, this is due to the existence of a very low standard deviation, leading to a small region with a high probability of nucleating the tube  $(< d_T > \pm \sigma)$ . Above  $d_{up}$  the probability distribution  $f_d$  rapidly collapses to zero  $(f_d \rightarrow 0)$  so wider tubes beyond this limit will not grow. In our model the accuracy of the  $d_{up}$  limit will depend on the  $\delta_0$  estimation that has an associated error as discussed in the model parameters section.

For SWCNTs growing from large particles  $(d_p/d_c \gg 1)$ , the upper limit in stability (Figure 9) will be the line corresponding to  $d_{up}$ . Figure 9 shows that the tube diameter (for  $d_p > d_c$  and  $d_p$  approximately smaller than 2.5 nm) is also slightly smaller than the particle diameter in the transition zone. This is because the tube will try to minimize its internal strain energy by reducing the transversal area until reaching the stable

diameter region with a value close to  $d_c$ . That is why we see an inversion in the data trend between the two zones (i.e. the tube diameter is no longer bigger than the particle). This zone also is characterized by a coexistence between fullerenes and tube allotropes. For carbon allotropes with a weak metal-carbon interaction (< 1 eV) and large transversal area, the curvature energy will favor nucleation, but a strong metal-carbon binding energy (1 eV to 2 eV) favors encapsulation in every event for particles with a diameter above the transition diameter ( $d_c$ ). The nature of the metal catalyst will change the value for  $d_c$ . For example, iron, with a strong attractive interaction with carbon is expected to slightly decrease the value of  $d_c$ , therefore the probability of encapsulation will increase, and the transition between tangential and perpendicular growth may be below 2 nm. However, a better estimation should include the distribution of stable facets and the average metal-carbon interaction energy ( $E_{MC}$ ) according to the percentage of covered area for the case of metal particles below the melting point.

# CONCLUSIONS

Using a combination of experimental data, quantum mechanical calculations, and statistical mechanics we developed a model to describe the relationship between catalyst size and SWCNT diameter. Good agreement of the predicted and the measured tube diameters demonstrates that the curvature energy of the nascent carbon nanostructure is a major contributor to the process of carbon nanotube nucleation. The proposed model offers a simple description of the correlation between tube diameter and catalyst particle diameter for a tube growing on an approximately spherical solid active nanocatalyst. Real conditions may show that a particle, especially less crystalline particles, are not completely spherical and multiple curvatures can be present in the catalyst (i.e. a nonhomogeneous particle diameter ). For this scenario, our model could include those multiple curvatures ( $k = 1/d_p$ ) as individual events represented in the probability distribution function  $f_d$ .

The DFT calculations of the interlayer adhesion energies provide important information about the strength of interaction between common metal catalyst particles and graphene. These data are valuable for the evaluation of model parameters like the tube-particle equilibrium distance and to develop a discussion about the stability of SWCNT's diameters. CVD data collected using ETEM provided an insight into the tube-particle diameter relationship and allowed determination of an "optimized" model parameter  $\alpha$ . We show that the value obtained ( $\alpha_{opt}$ ) is only dependent of intrinsic properties of a graphene-like structure such as surface carbon density, wall thickness, and Young modulus, and could be used in many systems independently of the catalyst selection. The predicted Young moduli obtained from the optimized parameter for SWCNTs and MWCNTs are in good agreement with experimental values.

We recognize that particle composition and surface stability may play an important role during the SWCNT nucleation vs. catalyst encapsulation dynamics. Magnin et al<sup>67</sup> recently highlighted a correlation between the carbon concentration in the particle and graphene/catalyst wetting properties, thus leading to tangential vs. perpendicular growth. This analysis is based in partially molten (liquid) particles where surface tension can deform the particle and wet the tube. However, the direct effect between the formation of solid carbide phases, the mode of growth (perpendicular vs tangential) and deactivation is not yet completely explained. Our own unpublished work suggests that metal particles for which many possible carbide structures may exist, multimodal surface composition distributions may be responsible of the change of growth mode. But the effects of these observations on the tube diameter-particle diameter are not yet well understood and possibly could be incorporated into future models.

Moreover, Bets et al<sup>68</sup> demonstrated the important and interesting nature of the tube edge interacting with the metal surface. The analysis of the rim-metal interaction shows the stability of specific edge configurations and the effect on the chirality selectivity. Nevertheless, the study suggests that the influence of the catalyst particle size on the nucleation probability has to be added separately. This is because the edge-catalyst interaction does not account for the stability of the tube's wall internal elastic energy. It could be concluded that for the perpendicular mode of growth (usually larger catalyst particles with  $d_p > d_c$ ), the tube edge/metal interaction may be especially important to define chirality/diameter. This interaction could help to reduce the number of possible states of similar curvature energy, this aspect is not accounted in our current model.

Finally, the central focus of our paper was on whether single-walled carbon nanotube diameters are defined by catalyst particle diameters. With respect to the specific correlation between tube diameters and particle diameters, various new insights are obtained. It is found that for small catalyst particle diameters, the tube diameter is larger than or equal to the particle diameter, thus favoring tangential tube growth, and the range of possible tube diameters for a given particle is rather narrow corresponding to a sharp tube diameter distribution function. We identified a critical diameter that separates regions of stable nanotube and stable fullerene. Such critical diameter depends on the intrinsic catalyst properties and on its interactions with carbon. For  $d_T$  larger than such critical diameter, he growth behavior changes and the tube diameter tend to become smaller than the particle diameter, leading to a perpendicular growth. This transition to the perpendicular mode of growth, coincides with much broader probability distribution functions allowing a wider range of possible tube diameters for a given particle size. Interestingly, the model has also proved useful for the prediction of inner diameters of MWCNTs as well as to reproduce nanotube's diameter distributions using exclusively the catalyst diameter distribution profile for supported CVD particles. A more complete characterization of inactive and encapsulated particles may improve the agreement of the model with the experimental results.

The results showed that the careful estimation of model parameters like  $\alpha_{opt}$  and the tube wall-catalyst surface distance  $\delta_0$  is a requirement for a good accuracy of the model. We have noticed, for example, the ability of  $\delta_0$  and  $\alpha$  for shifting the predicted tube diameter profile based on experimental catalyst size distributions. Thus, changes in  $\delta_0$  increase or reduce the amount of possible states in the proposed continuous function approximation for the tube diameter probability distribution ( $f_d$ ). A different approach for the estimation of these parameters can be further explored for each metal or alloy after a detailed study of the stable facets present in the nanoparticle at growth conditions and their interaction with graphene.

# METHODOLOGY

## In-situ CVD growth

A high-resolution environmental transmission electron microscope (ETEM), with differentially pumped column capable of tolerating up to 2000 Pa gas pressure, monochromated high intensity field-emission gun, image corrected, operated at 80 KV, was used for in-situ observation of SWCNT nucleation and growth process. Co-Mo/MgO catalyst/support was dispersed on micro-electro-mechanical system (MEMS) based heating chip that were then loaded on the heating holder and introduced in the ETEM column. It is important to note that although the nominal composition of catalyst was Co-Mo, the catalyst particles active for SWCNT growth did not contain any Mo, as explained in previous publications<sup>34</sup>. The sample was first heated to 900 °C in flowing O<sub>2</sub>, maintaining  $\approx$  3000 Pa gas pressure in the sample area. This pre-treatment was needed to clean the catalyst/support from any contaminants that may be present. The ETEM column was then evacuated to initial high vacuum condition while keeping the sample at 900 °C. It is important to note the temperature is as measured by the heating holder and may not be the exact temperature at the investigated zone in the sample. We did not try to measure the actual temperature as it was not critical for the current experiments. Approximately, 0.055 Pa of C2H2 was then introduced to the sample chamber and videos were recorded at a rate of 6 frames<sup>-1</sup>. Atomic-resolution images were also recorded from the area under observation as well as from the regions that were not exposed to electron beam under reaction condition. Both the images extracted from the videos and recorded post-synthesis were used to measure the diameters of the carbon nanostructures and associated catalyst particle.

# Density Functional Theory (DFT) Calculations

We perform DFT calculations for geometry relaxations and adhesion energy for graphene on metallic slabs (e.g Nickel, Cobalt, Iron) with [100] and [111] orientation. All metal-graphene systems were modeled using

periodic boundary conditions (PBC) to recreate two infinite long flat surfaces at absolute zero temperature. The Monkhorst-Pack scheme<sup>69</sup> was used for Brillouin zone's k-point sampling with a characteristic length  $(l_c)$  optimized for each metal. Table 2 shows the optimization results for  $l_c$ , K-points, and the energy cut off used in every system.

Metal Slab System	Length $(l_c)$	K-points-Mesh	Energy Cutoff (eV)
Nickel	40	9 x 16 x 2	700
Cobalt	60	25 x 15 x 4	600
Cobalt Carbide (Co <sub>2</sub> C)	50	10 x 12 x 3	700
Iron	40	16 x 5 x 2	700

 Table 2. Metal slabs parameters for the modeled system.

The exchange-correlation functional given by the Perdew-Burke-Ernzerhof (PBE) approximation<sup>70</sup>, and the Projector Augmented Wave Method<sup>71,72</sup> (PAW) was employed for calculating core-electron energies. The dispersion correction to the Kohn-Sham energy was implemented using the DFT-D2<sup>73</sup> based method of Steinmann and Corminboeuf<sup>74</sup> (DFT-dDsC). This Van-der Waals energy correction method has the special characteristic that the dispersion coefficients and damping function are charge-density dependent<sup>75</sup>.



**Figure 10.** Metal – graphene interfacial systems for Cobalt carbide ( $Co_2C$ ), Nickel, and Iron. Periodic boundaries were defined in all systems after relaxing a primitive cell with similar graphene's lattice constant.

The interfacial interaction energies and equilibrium distances ( $\delta_0^{\infty}$ ) were calculated using a [100] metal slab with lattice vectors optimized for the graphene-metal system. The approach for the [111] structures was different, the metal slab lattice was kept fixed and the graphene layer was rotated until reducing the mismatch with the periodic image. We constructed a vacuum space of 10 Å for every slab and it was reduced to 7 Å after the graphene was coupled to the metal system.



**Figure 11.** Test for optimizing the initial lattice vectors  $a_0$ ,  $b_0$  in the [100] system. The 0.7 – 1.2 range was tested for the ratio  $a_0/a_c$ , where  $a_c$  corresponds to the graphene lattice vector (0.246 nm). The iron system was optimized against  $2a_c$  for a better fit.

Figure 11 shows the test for the [100] structures in the graphene-metal slab system, we changed the lattice parameters and observed the variation in the system energy. We searched within the 0.7 - 1.2 range for the ratio  $(a_0/a_c)$  to ensure an energy minimum of the initial system and reduce the graphene's curvature (lateral stress). The maximum change of the graphene lattice constant  $(a_c = 0.246 \text{ nm})$  after the relaxation of the system (Table S2) was a measure of the mismatch of graphene with respect the relaxed graphene periodic unit. The length of the lattice vectors and a measure of the mismatch caused by them can be found in the DFT calculation section of the supporting information.

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# NOMENCLATURE

- T Temperature
- P Pressure
- $\dot{\rho}$  Material flow at the open reactor system
- $k_B$  Boltzmann constant
- $f_D$  Probability distribution function

- p generalized momentum coordinate
- q generalized position coordinate
- $d_p$  Particle diameter
- $d_T$  Tube diameter
- $d_c$  Transition critical diameter
- U Potential energy
- K Kinetic energy
- $E_c$  Curvature energy
- *M* Flat 2D sheet momentum
- *Y* Young modulus
- *I* Moment of Inertia
- *R* Curvature radius
- *L* Flat 2D sheet length
- *a* Flat 2D sheet thickness
- *N* Number of atoms in the sheet
- $\rho_s$  Surface atomic density
- $\sigma_a$  Nanoribbon cylindrical length
- $d_0$  Equilibrium distance between two graphene layers at absolute zero temperature (T = 0K).
- $\delta_0$  Equilibrium distance between metal catalyst and graphene walls
- $\delta_o^{edge}$  Equilibrium distance between metal catalyst and carbon atoms at the tube edges
- $\delta_0^{\infty}$  Equilibrium distance between an infinite metal catalyst slab and an infinite graphene layer
- $\alpha$  Material parameter
- $\alpha_{opt}$  Optimized material parameter
- $x_1, x_2$  Integration limits corresponding to the extension of phase boundaries

*l<sub>c</sub>* Characteristic length for Brillouin zone's k-point sampling using Monkhorst-Pack scheme

- $E_{adh}$  Adhesion metal-graphene energy
- $\Delta E_{int}$  Interfacial metal-graphene energy
- $E_{slab\&grap}$  Energy for the interacting slab-graphene system.
- $E_{slab}$  Energy for the metal catalyst slab using PBC
- $E_{grap}$  Energy for the graphene layer using PBC
- $E_{MC}$  Interfacial metal carbon interaction energy
- $E_{cF}$  Curvature energy for a fullerene
- $E_{sF}$  Supported curvature energy for a fullerene
- $E_{cT}$  Curvature energy for a tube

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## **Supplementary Information for**

#### Can single-walled carbon nanotube diameter be defined by catalyst particle diameter?

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# 1. Elastic Energy stored in tubular nanoribbon

The moment *M* of a tubular nanoribbon is related to its radius of curvature *R* through Equations (S1 to S3), where *Y* is the Young's modulus, *I* is the moment of inertia, L is the length of the cylindrical wall, *a* is the thickness of the nanoribbon surface layer ( $\approx 0.34$  nm), *N* is the number of atoms in the tubular nanoribbon, and  $\rho_s$  is the surface carbon density.

$$M = \frac{YI}{R} \qquad \qquad Eq.S1$$

$$I = \frac{La^3}{12} \qquad \qquad Eq. S2$$

 $N = 2\pi RL * \rho_s \qquad Eq.S3$ 



Figure S 1. Laminar sheet of graphene bended to form a tubular ribbon

The energy  $(dW_{bend})$  needed to bend a flat 2D graphene nanoribbon with moment *M* through an angle  $d\theta$  to form a tubular nanoribbon, as shown in Figure S1, corresponds to the total strain energy stored in the nanoribbon's bonds with a curvature  $1/d_T$ . Therefore, the strain energy  $(E_{strain})$  can be defined in terms of Young modulus (*Y*), tubular nanoribbon length (*L*), nanoribbon wall thickness (*a*), and tube diameter ( $d_T$ ).

$$dW_{bend} = \int_{0}^{2\pi} M/2 \ d\theta \qquad Eq.S4$$
$$W_{bend} \approx E_{strain} = \frac{YLa^{3}\pi}{12R} = \frac{YLa^{3}\pi}{6d_{T}} \qquad Eq.S5$$

The curvature energy ( $E_c$ ) is a function of *Y*, *a*, *d<sub>T</sub>* and the carbon surface density  $\rho_s$  and is defined as the strain energy (Equation S4) normalized by N, the total number of C atoms and reduced to the expression in Equation S6.

$$E_c = \frac{E_{strain}}{N} = \frac{Ya^3}{6\rho_s d_T^2} = \frac{\alpha}{d_T^2} \quad Eq.S6$$

#### 2. Model Approximations

The dimensional analysis is useful to reduce some of the expressions obtained in the *Theoretical Background and Model Development* section. We can start by defining the characteristic diameter  $\beta$  as a temperature dependent function, this allows us to separate the temperature effect in a simple expression (Equation S7) and group the particle effect using the variable  $d_{up}$  (i.e. the upper limit in the extension of phase).

$$\beta(T) \equiv \sqrt{\frac{\alpha}{k_B T}} \quad Eq.S7$$
$$d_{up} = d_p + \delta_0 \quad Eq.S8$$

We obtain a friendlier form of the probability distribution  $f_d$  (Equation S9) reducing the expression in Equation 7 with the new variables  $\beta$ , and  $d_{up}$ . In this expression, the denominator is a function of the dynamic particle curvature  $(d_p)$ , and the strength of interaction  $(\delta_0)$ , both contained in  $d_{up}$ . For simplicity, we will call  $\phi(x)$  the function evaluated at the denominator for both limits of the extension of phase.  $\phi(x)$ is almost constant for an independent SWCNT growth event due to the small variation of particle diameter during the dynamic process.

$$f_d(d_T,\beta) = \frac{e^{-(\beta/d_T)^2}}{\left[\sqrt{\pi\beta}\operatorname{erf}\left(\frac{\beta}{x}\right) + xe^{-(\beta/x)^2}\right]_{x_1=d_0}^{x_2=d_{up}}} = \frac{e^{-(\beta/d_T)^2}}{\phi(d_{up}) - \phi(d_0)} \quad Eq \ S9$$

The probability distribution is only valid for diameters within the extension of phase. Then, It is logical to assume that the probability of reaching a diameter with a value bigger than  $d_{up}$  or lower than  $d_0$  is null

 $(d_T > d_{up} \text{ or } d_T < d_0 \rightarrow f_d(d_T) = 0)$ . For this reason, we can constraint the Equation S9 multiplying the probability distribution by the Heaviside function<sup>1</sup>  $H(d_T)$  and fulfill the previous condition.

$$f_d(d_T,\beta) = \frac{e^{-(\beta/d_T)^2}}{\phi(d_{up}) - \phi(d_0)} [H(d_T) - H(d_T - d_{up})] \quad Eq \ S10$$

Equation S10 can be easily used to calculate the probability of obtaining a specific diameter range for different independent particle conditions. Taking the limit when  $d_0 \rightarrow 0$ , we can observe that  $\phi(d_0) \rightarrow \sqrt{\pi\beta}$ , this value will be used in the simplifications that follow instead of the evaluated value for  $d_0 (= 0.34 \text{ nm})$ .

#### **2.1 Probability Distribution Function**

The probability distribution for five different particle sizes between 1 nm to 5 nm are shown in Figure S2 (left). We can see that the distribution collapses to zero above  $d_{up}$ , this is due to the Heaviside function  $H(d_T - d_{up})$  constraint. However, it naturally converges to zero in the lower limit due to the rapid increase in curvature energy  $(E_c \rightarrow \infty)$ , reducing the probability of reaching this microstate according to the Boltzmann energy distribution  $(e^{-\infty} \rightarrow 0)$ . The  $f_d$  distribution evolves from a very pronounced Dirac like-form for a small catalyst to almost a uniform distribution when the particle gets bigger.



Figure S 2. Probability distribution  $f_d$  using optimized parameters for a cobalt particle. [Left] Probability distribution function ( $f_d$ ) for different particle curvatures (e.g. 1 nm to 5 nm). [Right] Cumulative distribution function. The probability of obtaining a 4 nm diameter tube using different particle sizes (4 nm and 5 nm) is calculated for this scenario.

A quick example for the probability calculation is proposed with the parameters fitted from our experimental data set (e.g.  $\alpha_{opt}$ ). Figure S2 (right) shows the cumulative distribution function (CDF) in Equation S11 for our model.

$$CDF(d_T) = \int_{-\infty}^{d_T} f_d(x,T) dx \ Eq \ S11$$

Using the CDF properties, we can calculate the probability of obtaining a tube within a certain diameter range. The probability of obtaining a tube diameter of at least 4 nm is 84% with a particle diameter of 4 nm and only 47% with a particle diameter of 5 nm.

#### 2.2 Dimensional analysis

We define two extreme limits for the analysis as shown in Figure S3. The first case is for  $\beta/d_{up} \gg 1$ : most of the small particle zone  $(d_p/d_c \ll 1)$  considered in the stability analysis is under this approximation due to the linear dependency of the denominator with the particle curvature. Figure S3 shows the simplifications for the probability distribution function  $(f_d)$  and the average diameter ( $\langle d_T \rangle$ ) using both approximations for the first case. It is remarkable to observe that the model foresees an approximate linear behavior corresponding to the upper limit in the extension of phase  $d_{up}$  for the lower stable region. This result agrees with our experimental data (Figure 5).



Figure S 3. Approximations for the model using dimensional analysis. Expressions for  $f_d$  and  $\langle d_T \rangle$  were obtained using both extreme scenarios.

Figure S4 shows that the deviation between the final approximated expressions and the numerical estimate is still large for the region of interest ( $\beta / d_{up} \gg 1$ ). Nevertheless, the error decreases with the particle size and we can observe that for large particles there is even a reasonable agreement with the experimental data (Figure S4 - right).



Figure S 4. Reduced functions obtained for the first case ( $\beta / d_{up} \gg 1$ ) scenario in the dimensional analysis. Both approximations were compared against Tibbets's experimental set (Right) and our experimental wdata (Left).

The second limit case is for  $\beta/d_{up} \ll 1$ . This scenario corresponds to the tube diameter behavior for most large particles. The reduced expression for  $\langle d_T \rangle$  in Figure S3 can be difficult to visualize only with the function obtained. However, we can observe that both, the denominator and numerator increase to similar rates creating a counterweight for the final diameter expression. The effect is a linear trend for large particles, and an especially accurate agreement using any approximation (i.e. either for the distribution or the final diameter expressions) as shown in Figure S5.



Figure S 5. Reduced functions obtained for the second case ( $\beta/d_{up} \ll 1$ ) scenario in the dimensional analysis. Both approximations were compared against Tibbets's experimental set (Right) and our experimental data (Left).

#### 3. Optimization of Parameter $\alpha$

In this work, we decided to estimate a useful reference value for  $\alpha$  from our experimental data. Gulseren et al, as mentioned before, obtained a value of 0.086 *eV nm*<sup>2</sup> using ab-initio calculations in their work about the energetics and curvature effects in CNTs<sup>2</sup>, therefore we used this value as an initial guess. The  $\alpha$  parameter is the only unknown variable in the model and for this reason, we proposed the following optimization model to fit the data:

Minimize:  $\sum (\langle d_T \rangle - d_{T_{measure}})^2$  Eq S12

with, 
$$< d_T > = \int_{d_0}^{d_{up}} x \frac{e^{-(\beta/x)^2}}{\phi(d_{up}, d_0)} dx$$
 Eq S13

Constraints,  $\alpha \ge 0$  Eq S14

Figure S5 shows the results and comparison between the optimization and DFT method. The fitted value for the  $\alpha$  parameter ( $\alpha_{opt} = 1.15 \ eV \ nm^2$ ) reduces the error for the small particle region and gives good results even against Tibbett's data set that wasn't adjusted with the optimization model.



Figure S 1. Optimization of the parameter  $\alpha$ . (+) High-resolution TEM experimental Data. (x) Data collected from Tibbets<sup>3</sup>. A comparison between the optimized value  $\alpha_{opt}$  and the value from Gulseren et al<sup>2</sup> is shown.

In the left image, the particle diameters yielding SWCNTs range between  $\approx 0.8$  nm and slightly above 3 nm, whereas the range is much wider for the MWCNTs (between  $\approx 10$  nm and  $\approx 80$  nm). It is evident that the prediction for inner tube diameters using either Gülseren reported value for  $\alpha$ , or the value optimized for SWCNT is very similar. We can observe that the model is more sensitive for small particle sizes and

produces small deviations for the large particles. For this reason, an accurate  $\alpha$  parameter will allow the design of a narrower diameter profile in the growth of supported SWCNTs.

## 4. DFT Calculations

The graphene – metal system has been studied extensively for transition metals like cobalt<sup>4–7</sup> (Co) and nickel<sup>7–15</sup> (Ni), and on a lesser extent for the iron<sup>16,17</sup> (Fe) and cobalt carbide<sup>18</sup> (Co<sub>2</sub>C) surfaces. A general trend observed in these DFT studies is that the interfacial interaction energy between graphene and the metal is strongly dependent on the correlation used to calculate the dispersion energy. Other factors like the rotation of the graphene layer above the metal slab, crystal structure and lattice mismatch may also affect this interaction as well. GGA-type density functionals with a long-range dispersion correction are exceptionally good for noncovalently bound systems including many pure van der Waals (vdW) complexes<sup>19</sup>. Additionally, the use of exchange-hole dipole moment dispersion correction has been recently improved the prediction of the DFT studies in comparison with experimental results<sup>11,20</sup>. For this reason, Steinmann's dispersion correction<sup>21</sup> was chosen, this method can account variations in the vdW contribut ion of atoms due to their local chemical environment. Note that our model requires the equilibrium distance only.

	Crystal Structure	$E_{adh} [eV/nm^2]$		<i>E<sub>MC</sub></i> [ <i>meV</i> /atom]		$\delta_0^\infty [nm]$	
System		[100]	[111]	[100]	[111]	[100]	[111]
Iron (Fe)	Bcc	-2.81	-2.66	-74.20	-63.11	0.204	0.306
Nickel (Ni)	Fcc	-0.94	-2.04	-24.77	-54.85	0.205	0.309
Cobalt (Co)	Нср	-2.22	-6.68	-55.49	-205.86	0.338	0.219
Cobalt Carbide (Co <sub>2</sub> C)	Orthorhombic	-2.96	-2.63	-77.59	-68.66	0.220	0.348

Table S1. Metal structure effect in the interaction energy between catalyst and graphene. Adhesion Energy, Metal-Carbon interaction and equilibrium distance are calculated for [100] and [111] metal surfaces.

Table S1 shows the variations for the adhesion energy, metal-carbon interaction and equilibrium distance for the different metal-graphene structures showed in Figures S7 and S8. Graphene-like ribbons allow a stronger interaction thanks to carbon dangling bonds at the edges<sup>16</sup>, the infinite layer approximation used here focus in the metal-carbon regions where the bulk sp<sup>2</sup> structure is interacting weakly with the metal. It

is observed the preference of certain facets to attract strongly the carbon structure, this could give an indication in the type of adsorption (chemisorption vs physisorption) as proposed by some previous works.



Figure S 7. Top and side views for the metal – graphene systems using [100] metal slabs. The black rectangle at the top view corresponds to the periodic unit area,  $a_0$  and  $a_1$  are vectors conforming the shape of the simulation box.



Figure 1. Top and side views for the metal – graphene systems using [111] metal slabs. The black parallelogram at the top view corresponds to the periodic unit area,  $a_0$  and  $a_1$  are vectors conforming the shape of the transversal area.

The (1x1) unit cell corresponding to the metal slab lattice vectors ( $a_0 \ x \ a_1$ ) was used in most [100] and [111] systems. However, the Fe (100) and Co<sub>2</sub>C (111) systems were optimized with a (3x1) and (2x1)

supercell respectively to reduce the lattice mismatch with the graphene periodic unit. All the systems were started with an initial separation of approximately 0.3 nm between the graphene layer and the metal slab and they were relaxed until reach the energy tolerance of  $1 \times 10^{-6} eV$ . Table S2 shows the maximum stretch or compression after the relaxation for the graphene lattice constant<sup>22</sup> (0.246 nm). We decided to use the [100] surface for the analysis because this facet minimized the lattice mismatch with the graphene layer.

System	[100]	[111]
Carbon Carbide (Co <sub>2</sub> C)	1.32%	6.61%
Cobalt (Co)	-3.02%	15.79%
Nickel (Ni)	0.69%	1.31%
Iron (Fe)	1.75%	-4.87%

Table S 2. Percentage of change from the graphene lattice constant due to mismatch with the metal slab.

The difference in the equilibrium distance  $\delta_0$  between surfaces [100] and [111] is expected due to different surface interactions and graphene alignment. Previous works in Nickel<sup>11</sup> and many other metals<sup>8,12,20</sup> have shown that even for the same facet the chemisorption/physisorption behavior is observed due to a double minimum in the interaction energy. It is then reasonable to assume most works report one of the two minimum equilibrium distances in the energy profile. Table S1 shows that one of the metal facet converges to either the chemisorption distances (~0.2 nm) or the physisorption distances (~ 0.3 nm) for the interaction with the graphene layer. The model doesn't distinguish between facets due to the approximately spherical shape assumption, but neither  $\alpha_{opt}$  nor the tube profiles predicted for the Iron particles show significative changes for the range 0.2 – 0.3 nm. The results obtained of the interaction energies and the equilibrium distance compared to other DFT works are within the reported ranges as shown in Table 1.

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