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Carbon Nanotubes Interactions: Theory and Applications

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Carbon Nanotubes Interactions:
Theory and Applications

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy
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Dedication

To my wife, Elena.
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Abstract

A theoretical framework describing the carbon nanotubes interaction, involving two distinct approaches, is presented. Based on the results obtained practical applications using carbon nanotubes are further proposed.

First a classical approach is employed for different geometrical configurations, such as parallel or concentric carbon nanotubes. For all the cases analytical expressions for the systems potential energies are derived.

The results obtained using the classical approach are used to propose a few practical applications. These applications include a non-contact device for profiling surfaces and a custom telescopie double wall carbon nanotube for nanolithography applications. It is expected that such devices can be effectively used with major advantages.

Next the interaction between nanotubes is considered using a quantum electrodynamics approach suitable for dispersing and absorbing media. Each carbon nanotube is characterized by its individual full dielectric response. The method also allows taking into account the full carbon nanotube cylindrical geometry by imposing the appropriate boundary conditions at the nanotubes surfaces.
It is found that at small nanotube separations, similar to their equilibrium distances, the interaction is dominated by the collective excitations in the electron energy loss spectra originating from interband transitions. Furthermore, it is shown that the collective surface excitations and their chirality dependent characteristics play a profound role in the interaction strength in double wall carbon nanotube systems. The obtained results are in good agreement with experimental measurements on determining the chirality of individual double wall carbon nanotubes.
Chapter I

Introduction

The interactions between carbon nanotubes have been of increasing interest because of their important impact on many areas of science. These interactions are described as forces originating from the electromagnetic interaction between the nanotubes. In particular, the use of carbon nanotubes as miniaturized components in nanotechnology can be strongly affected by these forces. Therefore, the detailed knowledge of the inter-tube interaction is essential for the realization of future nanoscale devices. Recent progress in experimental techniques has led to the possibility of measuring these forces, thus confirming some of the theoretical predictions while posing new questions at the same time.

In this chapter the fundamental parameters and relations used to describe the geometrical structure of carbon nanotubes are given. Next a summary of the theoretical approaches used to describe the interaction between carbon nanotubes is presented.
I.1. Parameters and relations for carbon nanotubes

Carbon nanotubes (CNTs) are quasi-one dimensional structures which are obtained by rolling up graphene sheets into cylinders. There are single-wall carbon nanotubes, consisting of one sheet, and multi-wall carbon nanotubes, consisting of two and more concentric cylindrical sheets. Considerable experimental and theoretical research has shown that CNTs have remarkable properties suitable for many potential applications, such as sensors, gas storage, functionalized elements, parts of electrical and mechanical devices, and more [1-4]. The long ranged van der Waals (vdW) forces between CNTs is of fundamental importance for many of these applications. vdW forces are also important for understanding the growth of CNT bundles, ropes, and networks [5-7], and their stability [8], as well as their properties [9,10].

The graphene honeycomb lattice is described by the basis vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, shown in Fig. I.1.1(a). The distance between carbon atoms in the graphene layer is $a_{c\text{-}c} = 1.41\text{Å}$ and the length of the unit vector $a = \sqrt{3}a_{c\text{-}c}$. The vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are further expressed, in respect with the reference shown in Fig. I.1.1(a), as

\begin{equation}
\mathbf{a}_1 = \left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right)\mathbf{a}
\end{equation}

\begin{equation}
\mathbf{a}_2 = \left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right)\mathbf{a}
\end{equation}

The reciprocal lattice vectors are given by
\[ b_1 = \left( \frac{1}{\sqrt{3}}, 1 \right) \frac{2\pi}{a} \] (I.1.3)

\[ b_2 = \left( \frac{1}{\sqrt{3}}, -1 \right) \frac{2\pi}{a} \] (I.1.4)

With these definitions set, it is convenient to specify a general CNT by a pair of two integers \((n, m)\). This definition, with the convention \(0 \leq |m| \leq n\), will be used throughout this manuscript. The two integers \((n, m)\), usually referred to as chirality, uniquely determine the CNT geometrical features, such as its chiral vector \(C_n\), the chiral angle \(\theta\), and diameter \(d_t\).

The chiral vector \(C_n\) (see Fig. I.1.1 (b)) is defined in terms of the chirality \((n, m)\) and the basis vectors \(a_1\) and \(a_2\) as

![Figure I.1.1](image_url)

Figure I.1.1. (a) Basis vectors of the honeycomb lattice and (b) the unit cell of the nanotube and the chiral angle \(\theta\).
The chiral angle $\theta$, with $0 \leq |\theta| \leq 30$ deg, is given by

$$\sin \theta = \frac{\sqrt{3}m}{2\sqrt{n^2 + m^2 + nm}}$$ (I.1.6)

$$\cos \theta = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}}$$ (I.1.7)

$$\tan \theta = \frac{\sqrt{3}m}{2n + m}$$ (I.1.8)

It is customary to call CNTs with $(n,0)$ “zigzag nanotubes” and CNTs with $(n,n)$ “armchair nanotubes”. The example depicted in Fig. I.1.1(b) corresponds to a (4,2) nanotube.

The length of the chiral vector $|C_h|$ gives the circumference of the CNT

$$|C_h| = a\sqrt{n^2 + m^2 + nm}$$ (I.1.9)

while its diameter is expressed as

$$d_t = \frac{\sqrt{n^2 + m^2 + nm}}{\pi} a$$ (I.1.10)

The unit cell of the CNT is shown in Fig. I.1.1(b) as the rectangle bounded by the vectors $C_h$ and $T$, where $T$ is the translation vector of the nanotube. $T$ is expressed in terms of the integers $(t_1, t_2)$ as follows

$$T = t_1a_1 + t_2a_2$$ (I.1.11)

$${t_1} = \frac{2m + n}{d_R}$$ (I.1.12)
If one denotes the highest common denominator of \((n,m)\) by \(d\), the quantity \(d_R\) in the denominator is either equal to \(3d\) or to \(d\), depending on whether \(n-m\) is a multiple of \(3d\) or not, respectively. The length of the translation vector \(T\) is given by

\[
T = \frac{\sqrt{3}}{d_R} |C_h| \\
(I.1.14)
\]

The number of carbon atoms per unit cell of the CNT is \(2N\), with

\[
N = \frac{2(n^2 + m^2 + nm)}{d_R} \\
(I.1.15)
\]

and each unit cell of the honeycomb lattice containing two carbon atoms.
I.2. Theoretical approaches

Next some considerations regarding the interaction forces between general material objects are presented. These forces, called dispersion forces, originate from the electromagnetic interaction between electrically neutral objects which do not carry permanent electric and magnetic moments. The interaction is considered within two major frameworks: a classical and a quantum electrodynamics approach.

According to classical electrodynamics, electrically neutral, unpolarized material objects will not interact with each other, even if they are polarizable. An interaction can only occur on one of these two scenarios: (i) at least one of the objects is polarized or (ii) an electromagnetic field is applied to at least one of the objects. In case (i) the object polarization will give rise to an electromagnetic field which can induce a polarization of the other polarizable object(s). In case (ii) the applied field induces a polarization of the object which in turn gives rise to an electromagnetic field acting on the other object. Both cases result in polarized objects interacting with each other via an electromagnetic field, the interaction and the resulting attractive forces between them being a consequence of the change from the classical ground state.

According to quantum electrodynamics, the state that most closely corresponds to the classical ground state is given by the material objects being in their (unpolarized) quantum ground states and the electromagnetic field being in its vacuum state, such that both the electromagnetic field and the polarization of all objects vanish on the quantum average. At first glance, one could hence
expect the absence of any interaction between the objects. However, the Heisenberg uncertainty principle necessarily implies the existence of ground state fluctuations, i.e., both (i) fluctuating polarizations of the objects and (ii) a fluctuating electromagnetic field will always be present. These fluctuations give rise to an interaction between the objects which is a purely quantum effect manifested in the dispersion forces acting on them.

Therefore, one can say that dispersion forces arise from quantum zero-point fluctuations, namely the fluctuating charge and current distributions of the interacting objects and the vacuum fluctuations of the (transverse) electromagnetic field.

If the separation of the objects is smaller than the wavelengths of the relevant field fluctuations, then the vacuum fluctuations of the electromagnetic field can be disregarded, allowing for a simplified treatment of dispersion forces. In this nonretarded regime, dispersion forces are dominated by the Coulomb interaction of fluctuating charge distributions. In particular, the Coulomb interaction between two atoms separated by a distance \( z \) may within a leading-order multipole expansion be regarded as the interaction of two electric dipoles \( \hat{d} \) and \( \hat{d}' \)

\[
V = \frac{\hat{d} \cdot \hat{d}' - 3\hat{d}_z \hat{d}'_z}{4\pi\varepsilon_0 z^3}
\]  

(1.2.1)

This approach was first used in conjunction with leading-order perturbation theory to derive the potential energy of two isotropic ground-state atoms to be [164]
\[ V(z) = -\frac{C}{z^6} \]  

\[ C = \frac{1}{24\pi^2\varepsilon_0^2} \sum_{k,k'} \left| \langle 0 | \hat{d} | k \rangle \right|^2 \left| \langle 0 | \hat{d} | k' \rangle \right|^2 \]  

\[ = \sum\sum_{r \in A,r' \in A'} \frac{C}{|r - r'|^6} \]  

with \( |k'\rangle \) and \( E_{k'} \) denoting the eigenstates and eigenenergies of the unperturbed atoms [11]. The interaction of two macroscopic bodies A and A' is then treated by pairwise summation over the microscopic potentials between the atoms constituting the bodies [12,13]

This approach will be employed in Chapter II to describe the interaction between two parallel and concentric CNTs. The pairwise summation will become an integration over the nanotube surface within the continuum model approximation.

When the separation of the objects becomes comparable or larger than the wavelengths of the relevant field fluctuations, the vacuum fluctuations of the electromagnetic field cannot be disregarded. The CNTs interaction will be dominated by the long ranged Casimir force, which is induced by quantum electromagnetic fluctuations. The Casimir force is purely quantum mechanical and relativistic in its nature, and it has been studied extensively since the prediction of the existence of an attraction between neutral mirrors in vacuum [14]. After the first report of experimental observation of this effect [15], new measurements with improved accuracy have been done involving different
geometries [16-19]. The Casimir force has also been considered theoretically with methods primarily based on the zero-point summation approach and Lifshitz theory [20,21]. In recent years, the Casimir effect has acquired a much broader impact due to its importance for nanostructured materials and devices. For instance, the efficient development and operation of micro- and nanoelectromechanical systems are limited due to unwanted effects, such as stiction, friction, and adhesion, originating from the Casimir force [22]. This interaction is also an important component for the stability of many materials, including graphitic systems.

Since the Lifshitz theory cannot be easily applied to geometries other than parallel plates, in the case of CNTs interactions the proximity force approximation was used to calculate the Casimir forces between CNTs [23-25]. The method is based on approximating the curved surfaces at very close distances by a series of parallel plates and summing their energies using the Lifshitz result. Thus, the proximity force approximation is inherently an additive approach, applicable to objects at very close separations (still to be greater than the objects inter-atomic distances) under the assumption that the CNT dielectric response is the same as the one for the plates.

This last assumption is open to discussion as the quasi-one dimensional character of the electronic motion in CNTs is known to be of principal importance for the correct description of their electronic and optical properties [1,26]. In this sense, the collective surface excitations in terms of each CNT dielectric response must have a profound effect on their mutual interaction; however their specific
functionalities have not been qualitatively and quantitatively understood yet. Since CNTs of virtually the same radial size can possess different electronic properties, investigating their interactions presents a unique opportunity to obtain insight into specific dielectric response features affecting the force between metallic and semiconducting cylindrical surfaces. This can also bring some insight into the role of collective surface excitations in the energetic stability of multi wall CNTs of various chiral combinations.

Therefore here a quantum electrodynamic approach suitable for dispersing and absorbing media [27] is employed to describe the CNTs interaction. The method allows taking into account the full CNT cylindrical geometry by solving the Fourier-domain operator Maxwell equations with appropriate boundary conditions and including their particular dielectric functions. The dielectric functions are calculated beforehand based on the quasi-one dimensional energy band structure of each CNT. Such a technique was applied previously with success for distances larger than the carbon-carbon atomic separations to study near-field electromagnetic effects in pristine [28] and hybrid CNTs with near-surface atomic states present [29-32]. Here this approach is adapted for the case of concentric CNTs in Chapter IV and employed to determine the influence of the nanotubes chiralities on their mutual interaction in Chapter V.
Chapter II
Classical approach

In this chapter a classical approach to the interaction between carbon nanotubes is presented. The systems total potential energy is calculated within the continuum model approximation by using a Lennard-Jones type of interatomic potential. Because of its relative simplicity, this model has been widely used. It has been shown to be quite successful in describing those cohesive properties of graphitic systems that are not sensitive to the details of the orientational structure or the covalent binding. This approach will be applied for different geometrical configurations, such as parallel or concentric carbon nanotubes. For all the cases analytical expressions for the systems potential energies are derived.
II.1. Lennard-Jones potential and the continuum model

Calculations of the vdW energies of graphitic structures such as CNTs are usually performed by either *ab initio* methods or by using model potentials. Standard density functional theory based methods [33] have given good results for the total energies and band structures of nanotubes. However, density functional theory is known to be reliable in describing particularly the short-ranged electron correlation effects only, whereas the vdW energy has contributions from both short-ranged and long-ranged interactions. The short-ranged contribution consists of a repulsive part and an attractive part coming, respectively, from the overlap of the core electrons on adjacent molecules and from the decrease in the electron kinetic energy due to the electron delocalization. The long-range contribution (known as the London dispersion energy) originates from the vacuum fluctuations of an electromagnetic field through the virtual photon exchange between the polarization states of the spatially separated interacting quantum objects. Such an interaction, to the first non-vanishing order in the perturbation expansion, results in the attractive long-ranged electrodynamical coupling between the objects’ fluctuating electric dipole moments. While adequate in describing the first two contributions, density functional theory fails in reproducing the long-ranged dispersion forces correctly, especially in graphitic structures [31,34]. Attempts to improve density functional theory for calculating vdW interactions between carbon nanotubes have also been made by using a plasmon-pole model which uses an approximation for the local electron response [35,36].
The model potentials methods are based on the pairwise summation of the individual interatomic potentials. The continuum model assumes that the atomic distribution is uniform over the surfaces or volumes of the interacting bodies. For extended systems, the summation becomes integration over the volumes of the two interacting bodies. For CNTs the integration is over their surfaces, since they are hollow cylindrical structures.

The model potentials are based on empirical functions whose parameters are obtained from experiment and are restricted to computations that involve only physical forces. Given their simplicity, it is remarkable that they have been so successful in providing a unified, consistent description of the properties that depend on the weak interactions between graphene sheets. Among these potentials, models based on the pairwise summation of interatomic Lennard-Jones (LJ) potentials proved to be particularly suitable in determining the CNTs equilibrium structures [37,38]. For example, interacting parallel circular SWNTs [39,40], parallel circular MWNTs [41], spheroidal and ellipsoidal fullerenes interacting with circular SWNTs [42], polygonized SWNTs [43], and interacting MWNTs under hydrostatic pressure with different radial shapes [44] have been considered using the this approach. Experimental studies of different properties of nanotubes under hydrostatic pressures, such as Raman spectra [45,46] and X-ray diffraction spectra [47], have also been reported and explained using the LJ type of vdW potentials. In addition, it was found that the LJ-vdW interaction potentials between parallel identical SWNTs [39], arbitrary parallel SWNTs [40] and arbitrary parallel MWNTs [41], can be represented in terms of a universal
curve when reduced parameters with respect to the well depth and the equilibrium distance are used. Thus further simplification in the estimation of nanotube vdW interactions can be achieved.

The LJ potential for two atoms located at a distance $\rho$ apart is

$$v(\rho) = -\frac{A}{\rho^6} + \frac{B}{\rho^{12}} \quad \text{(II.1.1)}$$

or, equivalently

$$v(\rho) = 4\varepsilon \left[ \left( \frac{-\sigma_0}{\rho} \right)^6 + \left( \frac{\sigma_0}{\rho} \right)^{12} \right] \quad \text{(II.1.2)}$$

where $A$ and $B$ are the so-called Hamaker coefficients and $\sigma_0$ is the distance at which the interatomic potential is zero. The equilibrium distance $\rho_0$ is given by

$$\rho_0 = 2^{\frac{1}{12}} \sigma_0 = \left( \frac{2B}{A} \right)^{\frac{1}{6}} \quad \text{(II.1.3)}$$

and the well depth $\varepsilon$ is

$$\varepsilon = \frac{A^2}{4B} \quad \text{(II.1.4)}$$

The general expression for the vdW interaction between two nanotubes is then given by

$$V = \sigma^2 \iiint \left( -\frac{A}{\rho^6} + \frac{B}{\rho^{12}} \right) dS_1 dS_2 \quad \text{(II.1.5)}$$
Here $dS_1$ and $dS_2$ are the surface elements for each tube. The distance between the surface elements is $\rho$. The Hamaker coefficients $A$ and $B$ are taken to have the same values as for the graphene-graphene systems [39] $A = 15.2 \text{ eV} \cdot \text{Å}$ and $B = 24 \times 10^{-3} \text{ eV} \cdot \text{Å}$. The surface density $\sigma$ of carbon atoms is assumed to be uniform, according to the continuum model

$$\sigma = \frac{4}{\sqrt{3}a^2}$$

(II.1.6)

where $a = 2.49 \text{ Å}$ is the graphene lattice constant.

In the next sections this formalism will be applied to describe the interaction between parallel and concentric CNTs.
II.2. Case of parallel carbon nanotubes.

The vdW interaction between parallel CNTs has already been considered in earlier studies [39,40,48-51]. It was shown that the potential follows a universal curve in terms of certain reduced parameters defined in Refs. [39] and [40]. Also it was pointed out that in particular for cylindrical geometry, the evaluation of the vdW potential is rather a challenging problem. Although the LJ interaction of a point with a continuous cylinder can be expressed in terms of the hypergeometric function [52], when averaging over another surface this relative simplification is lost. The potential will contain integrals which must be evaluated numerically. Here, using an approach based on the ultraspherical polynomials properties, it is shown that it is possible to express the interaction defined in Eq. II.1.5 in an explicit analytical form.

The studied system is shown in Fig. II.2.1. It is composed of two infinitely long parallel CNTs with radii $R_1$ and $R_2$. The distance between their surfaces is $g$ and the distance between their centers is $d = g + R_1 + R_2$. Using cylindrical coordinates, the interaction potential from Eq. II.1.5 is expressed as

$$V = \sigma^2 \int_0^{2\pi} \int_0^\infty \int_{-\infty}^{\infty} \left( -\frac{A}{\rho^6} + \frac{B}{\rho^{12}} \right) R_1 R_2 \rho d\varphi_1 d\varphi_2 dz_1 dz_2$$

(II.2.1)

where $\rho$ is the distance between two surface elements located on the two nanotubes. In order to perform the integration along the $z$-direction, the distance $\rho$ is further expressed as $\rho = \left(r^2 + z^2\right)^{1/2}$ with $r$ being the radial variable in $xy$-plane. After the $z$-integration, the interaction potential per unit length becomes
where the in-plane distance between the two surface elements is

\[
\left[ (d - R_1 \cos \varphi_1 + R_2 \cos \varphi_2)^2 + (R_1 \sin \varphi_1 - R_2 \sin \varphi_2)^2 \right]^{1/2}
\]  

(II.2.3)

One notices that this expression of the interaction potential in Eq. II.2.2 is similar with the one obtained in other studies of vdW interactions between CNTs [48,49]. Further, to estimate \( V \), one usually performs a numerical integration over the angular variables [48,49]. Here the denominators in Eq. II.2.2 are written as a series expansion, and the expression is further manipulated using the expression of the generating function and the properties of the ultraspherical polynomials.
The interaction potential is then expressed for \( d > R_1 + R_2 \) in terms of an infinite series

\[
V = \frac{-8\pi^2 A\sigma^{3/2}}{3} \sum_{n,m} R_1^{n+1} R_2^{m+1} \left[ \frac{\Gamma\left(\frac{n+5}{2}\right)}{(n/2)! (m/2)!} \right]^2 \frac{1}{d^{n+m+5}} + \frac{16\pi^2 B\sigma^{3/2}}{14175} \sum_{n,m} R_1^{n+1} R_2^{m+1} \left[ \frac{\Gamma\left(\frac{n+m+11}{2}\right)}{(n/2)! (m/2)!} \right]^2 \frac{1}{d^{n+m+11}}
\]

\text{(II.2.4)}

where \( \Gamma(x) \) represents the Gamma function.

In Fig. II.2.2 the calculated interaction potential is shown for several pairs of parallel CNTs. The radii of the nanotubes are taken to correspond to (10,10)&(15,15), (11,11)&(15,15), (12,12)&(15,15), (13,13)&(15,15), (14,14)&(15,15) and (15,15)&(15,15). The equilibrium distance between their surfaces is found to be around 0.32 nm, which is similar to the equilibrium distance between the graphene layers in graphite. In addition to the ones shown on Fig. II.2.2, many other pairs of CNTs were examined and it was found that \( V \) follows similar curves with equilibrium distance \( g_0 \approx 0.32 \text{ nm} \) between the surfaces of the nanotubes.

The convergence of the series in Eq. II.2.4 is found to be rather slow and to depend on the nanotubes size. For example, for CNTs with diameters less than 2 nm a number of at least 50 terms of the series are needed to achieve a satisfactory agreement with the corresponding numerical integration. For larger diameters CNTs more terms have to be included. For example, for nanotubes with diameters in the 2-5 nm range at least 150 terms are needed.
Furthermore some limiting cases can be obtained from the exact expression for \( V \) in Eq. II.2.4. Using the large inter-tube distance limit in the exact formula one obtains that \( V \propto d^{-5} \) corresponding to the vdW interaction between two parallel lines separated at large distances. At small distances, the vdW potential is repulsive. Its behavior is determined by the behavior of the ultraspherical polynomials and \( V \propto (d - R_1 - R_2)^{-3/2} \).
II.3. Case of concentric carbon nanotubes.

Next the interaction between two concentric CNTs is considered. The inner and outer nanotube have radii $R_1$ and $R_2$, and lengths $2L_1$ and $2L_2$, respectively. The system is shown in Fig. II.3.1. For generality purpose, the inner nanotube is allowed to move along the CNTs common $z$-axis. The relative displacement between the nanotubes centers is denoted by $z_0$. The vdW potential is calculated using the LJ type of interatomic potential within the continuum model. It is shown that the interaction between the CNTs can be expressed in a closed form in terms of the so-called hypergeometric function.

The vdW potential is expressed, using cylindrical coordinates, as

$$V = \sigma^2 \int\int\int \rho^6 \left( \frac{A}{\rho^6} + \frac{B}{\rho^{12}} \right) \rho^0 d\rho_1 d\phi_1 \int dz_1 dz_2 R_1 R_2$$

where $\rho$ is the distance between two points located on the two tubes as shown on Fig. II.3.1. The corresponding coordinates of two typical points located on the inner (denoted as $in$) and outer (denoted as $out$) tubes are:

$$x_{in} = R_1 \cos \varphi_1$$

$$y_{in} = R_1 \sin \varphi_1$$

$$z_{in} = z_1 + z_0$$

$$x_{out} = R_2 \cos \varphi_2$$

$$y_{out} = R_2 \sin \varphi_2$$

$$z_{out} = z_2$$
where $\varphi_1$ and $\varphi_2$ are the azimuthal angles for each nanotube (shown in Fig. II.3.1). The relative distance $\rho$ is then calculated as

$$\rho = \left[ (x_{out} - x_{in})^2 + (y_{out} - y_{in})^2 + (z_{out} - z_{in})^2 \right]^{1/2} \quad \text{(II.3.8)}$$

After performing the angular integration in Eq. II.3.1, the expression for the vdW interaction between the two CNTs becomes

$$V = 4\pi^2 \sigma^2 R_1 R_2 \int_{-L_1}^{L_1} \int_{-L_2}^{L_2} \left( -\frac{A}{\eta_1^3} F\left(3, \frac{1}{2}, \frac{1}{\eta_1} - \frac{\eta_2}{\eta_1}\right) + \frac{B}{\eta_1^6} F\left(6, \frac{1}{2}, \frac{1}{\eta_1} - \frac{\eta_2}{\eta_1}\right) \right) \quad \text{(II.3.9)}$$

Here $F(a,b,c;d)$ represents the hypergeometric function. Also the parameters $\eta_1$ and $\eta_2$ are defined as
\[ \eta_1 = (R_1 - R_2)^2 + (z_0 + z_1 - z_2)^2 \]  \hspace{1cm} (II.3.10)

\[ \eta_2 = R_1 R_2 \]  \hspace{1cm} (II.3.11)

Details of the formal derivation of Eq. II.3.9 are given in Appendix A.

Next the interaction potential is numerically estimated as a function of the CNTs relative displacement \( z_0 \) and the results are shown in Fig. II.3.2. The inner nanotube is chosen to be a (5,0) CNT with radius \( R_1 = 0.195 \text{ nm} \) and the outer nanotube a (9,7) CNT with radius \( R_2 = 0.544 \text{ nm} \), respectively. The CNTs are

![Figure II.3.2. The vdW potential as a function of the inner nanotube displacement along the z-axis. The inset shows the force acting on the moving CNT.](image)

Figure II.3.2. The vdW potential as a function of the inner nanotube displacement along the z-axis. The inset shows the force acting on the moving CNT.
chosen to have the same lengths $2L_1 = 2L_2 = 7 \text{ nm}$.

The force acting on the CNTs can be estimated from the gradient of the interacting potential

$$F = -\frac{dV}{dz_0}$$

(II.3.12)

and it is shown as an inset in Fig. II.3.2. One notices that for larger extrusions of the inner CNT the force is basically constant, while for smaller displacements the dependence presents a linear region. A change in sign occurs when the CNTs centers coincide denoting a change in the force direction. The system will naturally evolve to its equilibrium position $z_0 = 0$ characterized by the minimum potential energy.
Chapter III

Applications to the classical approach

The results derived in the previous sections are used in this chapter to propose a few practical applications. First a method for profiling surfaces based on the concept of a double wall carbon nanotube oscillator is suggested. By studying the details of the carbon nanotubes motion, a non-contact device for profiling surfaces is proposed as an alternative to a conventional atomic force microscope probe. Next carbon nanotubes with different types of radial deformations are considered. By describing these deformations with analytical models, interesting results in terms of the carbon nanotubes preferred mutual orientations are found. Furthermore, the concept of an universal graphitic potential curve, valid for undeformed carbon nanotubes, is extended for the case of radially deformed carbon nanotubes. Last, a custom telescopic double wall carbon nanotube for nanolithography applications is proposed. Such a device can be effectively used for thermally producing patterns on surfaces with major advantages. These advantages include high spatial resolution and the elimination of the active feedback mechanism.
III.1. Surface profiling

The increasing need for novel nanostructures and the decreasing length scale of devices have brought much attention to CNTs as potential integrated nanoscale components. Among these elements, low-friction, low-wear nanobearings and nanosprings are essential ingredients for the efficient functionality of the various devices. It was demonstrated [53], through the controlled and reversible telescopic extension of multiwall CNTs, the possibility of realization of nanoscale linear bearings and constant force nanosprings. The schematics of the experiments performed are shown in Fig. III.1.1.(a). First a nanomanipulator is attached to the end of the inner tube of a multiwall CNT. Then the manipulator is moved right and left, thus telescoping the core out from or reinserting it into the housing of the outer CNTs. Repeated extension and retraction of telescoping inner nanotube revealed no wear or fatigue on the atomic scale. Hence, these nanotubes may constitute near perfect, wear free surfaces. Finally, when the manipulator is disengaged, the inner nanotube is drawn back into the outer CNTs by the intertube vdW force, consequently lowering the total system energy. Such devices were reported to have very low friction, at least two orders of magnitude smaller, than the vdW force [54-57].

These results led to the proposal of the nano-oscillator concept [58]. From the experimental setting presented in Fig. III.1.1.(a), the inner nanotube is expected to have a certain amount of kinetic energy at the fully retracted position where the van der Waals energy is minimized, and therefore it would pass over this position in its retracting motion. The inner CNT should be subjected to a
repulsive force as soon as it passes the position of minimum potential energy and thus the motion will be reversed, causing it to extrude again. This leads the inner nanotube to oscillate with respect to the position of minimum van der Waals energy, when both ends of the outer nanotube are opened. This situation is illustrated in Fig. III.1.1.(b). The inner CNT will extrude from the opposite end after it passes over the position of minimum potential energy where the restoring force reverses its direction to decelerate the motion and then to reverse the motion after it reaches the maximum extrusion from the opposite end. Thus, inner nanotube oscillates with respect to the fully retracted position where the vdW potential energy is minimized and the kinetic energy has its maximum. The estimated frequency was found to be in the GHz range. This concept was later extended to systems with a C60 fullerene [59] or a spheroidal fullerene [60] oscillating inside a single wall CNT, a nanotorus [61] oscillating outside a stationary single wall CNT, or two inner tubes from a triple wall CNT oscillating inside the stationary outer one [62].
Molecular dynamics simulations have confirmed the GHz regime of the CNT oscillator [63]. These studies also have revealed that the structure of the double CNT oscillator has a profound effect on the energy dissipation processes of nanotube based oscillating systems. It was shown that although dissipation is much less than the vdW interaction, it can further be reduced by varying the size and chiralities of the nanotubes. For example, for shorter oscillating CNTs (length less than 3 nm) an off-axial rocking motion occurs when the inner nanotube is pulled out at a distance larger than a certain extrusion length (about 1/3 out of the outer nanotube) [54]. This effect is schematically illustrated in Fig. III.1.2.(a). Also, for stationary longer outer nanotubes with lengths greater than 3 nm, energy is transferred from the translational oscillation of the moving tube to vibrational modes through wavy radial deformations of the outer nanotubes, when the length of the inner nanotube is longer than or comparable to the characteristic length scale of the outer nanotube wavy motion [54] (see Fig. III.1.2.(b)). The dissipation is stronger for commensurate systems (e.g. armchair/armchair or zigzag/zigzag) and weaker for incommensurate systems (e.g. zigzag/armchair) [64]. Nevertheless, it was found that a smooth and low-frictional oscillatory motion can be achieved when the following conditions are fulfilled: the difference in radii between the two nanotubes is about 0.34 nm, the two nanotubes are incommensurate, and the initial extrusion of the oscillating nanotube is less than 1/3 out of the outer nanotube.
An additional challenging problem is sustaining the oscillatory motion over long periods of time. It was proposed to stimulate the oscillatory motion (i.e., supply an external energy to the system) by applying an external electric field \[53,58,65\], in which case the nanotubes must be electrically charged. A possible way to achieve this is through chemical doping. Another proposal is magnetically driving the inner CNT \[63\], in which case one needs a combination with an outer semiconducting CNT and an inner metallic CNT. In this case, the magnetic field can selectively and controllably be applied to the metallic nanotube.

In this section, a different possibility of using a double wall CNT oscillator is explored. We present calculations investigating the oscillatory motion of an inner nanotube from a double wall CNT when the outer tube is kept stationary near a sample surface. The CNT is oriented with its axis perpendicular to the sample surface. Possible losses in the motion process due to the proximity of the

![Diagram](image-url)
surface are also included in the calculation through a phenomenological friction parameter. We find that the distance between the surface and the double wall nanotube can influence the motion significantly. The role of the length and the initial extrusion of the moving tube are also investigated. Our results allow us to propose that such features can be utilized to evaluate the smoothness of surfaces. By calculating the oscillatory characteristic times as a function of the relative distance to the studied surface, the CNT oscillator is proposed to be used as a surface profiling device in a similar manner as an atomic force microscope (AFM) tip operating in non-contact mode.

**III.1.1. Concept**

The proposed system consists in an open ended double wall CNT, with the outer nanotube fixed and attached to an atomic force microscope cantilever, and the inner nanotube free to move along the CNTs common z-axis, as shown in Fig. III.1.3. The inner and outer CNTs have equal lengths $2L$ and radii $R_1$ and $R_2$, respectively. Let the carbon bonds at the nanotubes ends be saturated to prevent chemical reaction with the environment [66]. Let the outer tube be stationary and the inner one be extruded from the outer one along their common axis at some initial distance. This can be done, for example, by electrostatically telescoping the inner nanotube using the procedure outlined in Ref. [67], where CNT-based nonvolatile memory devices were considered. The inner nanotube is then released and, due to the mutual vdW forces, it can oscillate in time [58]. We refer to this case as “free oscillation”.

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The double wall CNT system is next brought to a close proximity of a sample modeled as an infinite slab with thickness $L_s$. The configuration is such that the common axis of the nanotubes is perpendicular to the sample surface, as shown on Fig. III.1.3. The inner nanotube is extruded from the outer one at some initial position $z_0$ and then released from rest. The forces governing the motion in this case are the intertube vdW forces in the double wall CNT and the vdW force between the inner CNT and the sample. In addition, there is a friction force between the surface and the moving nanotube due to tube-surface dissipation processes [68]. The motion of the inner nanotube is oscillatory again, but it has different characteristics as compared to the free oscillation case. For
the free oscillation, the inner tube will oscillate between \( -z_{0,j} \) and \( +z_{0,j} \). When the sample is present, the oscillation will be between \( -z_{0,j} \) and \( z_{0,f} \neq z_{0,j} \), where \( -z_{0,f} \) is determined by the repulsive part of the vdW interaction between the moving nanotube and the sample and the dissipation force. This in turn will cause changes in the oscillatory motion as compared to the free oscillation case.

The motion of the inner nanotube is described using the pairwise additive LJ type of vdW potential for extended systems and the continuum model, as presented in Section II.3. for the case of concentric CNTs. The total LJ-vdW potential, and consequently, the vdW force in the system are calculated by adding the contributions from the interaction between the inner and outer nanotubes \( V_{1-2} \), between the inner nanotube and the sample \( V_{1-s} \), and between the outer nanotube and the sample \( V_{2-s} \). Since the motion of the inner nanotube is affected only by the first two contributions, the interaction between the outer nanotube and the sample is not considered here.

The intertube interaction potential \( V_{1-2} \) was estimated in Section II.3. and its expression is given in Eq. II.3.9 with \( L_1 = L_2 = L \). The interaction between the inner nanotube and the sample is estimated in a similar manner and the obtained expression is

\[
V_{1-s} = 4\pi^2\sigma_s^2 \int_{0}^{L} \int_{-L}^{L} dz_1 \int_{0}^{\infty} dr_1 r_1 R_1 \left( -\frac{A}{\xi_1^3} F(3, \frac{1}{2}; t; -\frac{\xi_2}{\xi_1}) + \frac{B}{\xi_1^6} F(6, \frac{1}{2}; t; -\frac{\xi_2}{\xi_1}) \right) \tag{III.1.1}
\]

where \( \sigma_s \) represents the atomic density of the sample. The parameters \( \xi_1 \) and \( \xi_2 \) are defined as
Details of the formal derivation of Eqs. II.3.9 and III.1.1 are given in Appendix A. Having these contributions calculated, the total vdW potential of the moving inner nanotube is

\[ V = V_{1-2} + V_{1-s} \]  

The vdW force acting on the inner tube is then expressed as

\[ F_{\text{vdW}} = -\frac{dV}{dz_0} \]  

Regarding the intertube energy dissipation processes, it is assumed that the responsible friction forces are negligible compared to the vdW forces. This assumption is supported by the fact that the friction between the nanotubes is at least two orders of magnitude less than the vdW interaction [54-57]. In addition, the structure parameters, such as the chiral combination of the tubes, their radii and lengths, and the initial extrusion of the mobile tube, can be chosen in such a way as to further minimize the inter-tube energy dissipation and to make the oscillatory motion dynamically stable [54,64]. Also, experimental measurements have shown that even defective oscillating tubes maintain their ultralow friction [57].

Another source of energy loss in the oscillatory motion is the presence of the sample. The oscillating nanotube near an infinite surface is in fact an example of a system with non-contact friction [69]. The origin of such friction has been related to vdW interactions, to the creation of collective excitations, such as
phonons, or to the spatial variation of the surface potential when an external voltage bias is applied. As a result, there is damping associated with a friction force

\[ F_r = m \gamma v \]  

(III.1.6)

where \( m \) is the mass of the object, \( v \) is the velocity, and \( \gamma \) is the friction coefficient. Much effort has been devoted in calculating \( \gamma \) due to the various forces. It was found [69] that the dominant contribution to the friction (main energy loss) is obtained when the oscillating nanotube is in the close vicinity of its equilibrium position with respect to the surface. In this case, the nanotube creates stresses which excite acoustic waves on the sample. Calculations of the friction parameter due to this phenomenon were done in studies related to non-contact atomic force microscopy, molecule adsorbates on surfaces, and Brownian motion of molecules on surfaces [69-71]. The vdW interaction itself between the nanotube and the surface can also give rise to friction. However, following the results from Ref. [69], for a cylindrical object the friction coefficient \( \gamma \sim d^{-7} \), and here it is estimated that in this case the friction force \( F_r \) is even smaller than the intertube friction.

Therefore, it is assumed that the main energy loss in the system is due to the excitations of acoustic waves in the sample, when the oscillating nanotube comes close to the surface. Subsequently, the friction force is described by the following proposed expression

\[ F_r = -m \gamma z_0 \Theta(z_0 - z_c) \]  

(III.1.7)
where \( m \) is the mass of the moving nanotube and \( \gamma \) is the appropriate friction coefficient. \( \Theta(z) \) represents the Heaviside step function with \( z_0(t) \) being the displacement of the inner tube along the \( z \)-axis. The friction will be effective only within a region described by a cut-off distance \( z_c \) from the vdW repulsive barrier of the sample.

To conclude, the motion of the inner nanotube in time is described by

\[
 m\ddot{z}_0 + m\gamma \dot{z}_0 \Theta(z_0 - z_c) = F_{vdW}
\]

where \( \dot{z}_0 \) and \( \ddot{z}_0 \) denote the moving tubes’ instantaneous velocity and acceleration

\[
 \dot{z}_0 = \frac{dz_0(t)}{dt}
\]

\[
 \ddot{z}_0 = \frac{d^2z_0(t)}{dt^2}
\]

In the next sections the oscillator system will be numerically characterized, which involves obtaining the the potential from Eq. III.1.4 governing the motion of the inner tube, the vdW force corresponding to this potential, and solving the equation of motion from Eq. III.1.8. In all subsequent calculations, the sample is taken to be semi-infinite \( L_s \rightarrow \infty \). The coefficients \( A=15.2 \text{ eV} \cdot \text{Å} \) and \( B=24 \times 10^3 \text{ eV} \cdot \text{Å} \) are taken to be the same as the ones for graphene-graphene systems [39], and the sample volume atomic density \( \sigma_s \) is taken to correspond to the CNTs values. All the assumptions above do not change qualitatively the oscillatory behavior of the system described below.

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### III.1.2. System energetics

The double wall CNT consists of an inner (5,0) CNT with radius $R_1 = 0.195 \text{nm}$ and an outer (9,7) CNT with radius $R_2 = 0.544 \text{nm}$, respectively. The CNTs are chosen to have the same lengths $2L = 7 \text{nm}$. This particular choice of the CNTs is consistent with the conditions for a smooth and low-frictional motion: the difference in radii between the two nanotubes is about $0.34 \text{ nm}$, and the two nanotubes are incommensurate. In order to avoid the off-axial rocking motion and thus further reduce the energy dissipation in the system, the extrusion length must not exceed $30\%$ of the total nanotube length, as shown in Ref. [62]. Here, the initial extrusion length is taken to be $|z_{0,i}| = 0.75 \text{nm}$, which is approximately $11\%$ of the total nanotube length. The excess energy, defined in Refs. [54,62], of the moving nanotube corresponding to the extrusion $z_{0,i}$ is $|E_0| = 10.5 \text{meV/atom}$.

Fig. III.1.4 shows the vdW potential of the inner nanotube for several locations of the semi-infinite sample with respect to the edge of the fixed outer tube. The potential for the free oscillation is also shown indicating that the motion of the inner nanotube is between $-z_{0,i}$ and $z_{0,i}$ in this case. One notices that when the sample is at $d > 11.5 \text{Å}$, the potential of the oscillating nanotube in the region $z_0 \in [-z_{0,i}, z_{0,i}]$ is the same as the one for the free oscillation. For $d < 11.5 \text{Å}$, the influence of the sample becomes apparent and the characteristic shape of the vdW potential with an attractive and a repulsive regions is obtained within $z_0 \in [-z_{0,i}, z_{0,i}]$. It is found that the minimum of $V_{1-s}$ always occurs when
the distance between the edge of moving nanotube and the sample surface is about 2.5 Å. Thus bringing the sample closer causes the position of the $V_{1-a}$ minimum to appear closer to the edge of the stationary outer nanotube and its repulsive tail has stronger effect on the motion of the inner nanotube. The curve for $d = 0$ corresponds to the limiting case of the outer nanotube being in contact with the sample surface.

Next the corresponding vdW force acting on the moving nanotube is calculated according to Eq. III.1.4 and the results are shown in Fig. III.1.5. One sees that for the free oscillation, the force has a constant value region...
followed by a linear region in the vicinity of the equilibrium position (potential minimum) and again by a constant value region \((F = -0.62 \text{ nN})\). When the sample is at \(d < 11.5 \text{ Å}\), \(F_{vdW}\) has an additional non-linear contribution corresponding to the attractive and repulsive parts of the vdW potential \(V_{1-s}\) from the sample.

An interesting question will be what region of the sample is responsible for the main contribution to the integrated numerical value of the vdW potential \(V_{1-s}\)? By examining the values of \(V_{1-s}\) for various nanotubes with different chiralities,
lengths and extrusions it was found that for all cases the potential is primarily
determined by a rather localized circular region from the sample with a radius
\( r_s \leq 5R_1 \). The result is not affected by the relative position of the outer nanotube
to the sample. The rest of the surface sample contributes less than 1% to the
numerical integration of \( V_{t-s} \). Thus the vdW interaction and consequently, the
oscillatory behavior of the nanotube oscillator are determined mainly by a
relatively limited circular region of the sample. Also, the vdW potential and force
have similar shapes as the ones shown in Figs. III.1.4. and III.1.5. However, the
absolute value of the minimum of \( V \) (maximum of \( F \)) decreases for longer
nanotubes, and the linear regions for \( V \) and \( F \) extend over larger distances for
larger extrusions.

**III.1.3. Oscillatory motion**

The inner CNT motion in time is governed by Eq. III.1.8, which involves
the phenomenological coefficient \( \gamma \) describing the friction due to the acoustic
wave excitations in the sample [69-74]. An analytical model for an oscillating
molecule near a surface [70] is employed for the moving nanotube. The friction
coefficient is expressed as

\[
\gamma = \frac{m\omega_0^2 \xi}{8\pi \rho} \left( \frac{\omega_0}{c_T} \right)^3 \tag{III.1.11}
\]

where \( m \) is the mass of the molecule oscillating perpendicular to the sample
surface, \( \omega_0 \) is the oscillation frequency, \( \rho \) is the mass density of the sample, \( c_T \)
is the transverse sound velocity in the sample, and the parameter \( \xi = 3.29 \).

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This expression takes into account the vibrational energy relaxation of the molecule motion due to acoustic wave excitations in the sample. For the CNT oscillator case case, $m$ is the mass of the oscillating nanotube which is estimated as the sum of the masses of the carbon atoms comprising the tube, and $\omega_0$ is taken to be the frequency of the “free” oscillations of that nanotube. It is found that the friction coefficient for metallic systems (eg. Al, Cu, Au, Fe) is in the range $\gamma \in (10^9, 10^{10}) \text{s}^{-1}$, and for semiconducting systems (eg. Si, GaAs, or GaN) is in the range $\gamma \in (10^8, 10^9) \text{s}^{-1}$. Such values have also been reported experimentally for various metallic and semiconducting materials [72-75]. The
most relevant probably for this case is the one reported in Ref. [74], where synchrotron infrared radiation experiments of fullerenes approaching metallic surfaces have determined $\gamma \approx 10^9$ s$^{-1}$.

Numerical calculations are performed next for a $(5,0)@(9,7)$ double wall CNT with lengths $2L = 15$ nm. The initial extrusion is $|z_{0,i}| = 3$ nm, which corresponds to 20% of the initial nanotube length. In this case, the vdW force due to the infinite surface sample affects the motion of the inner nanotube if the edge of the outer nanotube is at a distance $d \leq 3.5$ nm. Fig. III.1.6. shows the evolution in time of the displacement $z_0$ of the oscillating inner CNT for three values of the friction parameter when the outer nanotube is stationary at $d = 15$ Å from the sample surface.

One notices that the CNT motion has two characteristic regions: damped oscillatory region and “friction-free” oscillatory region. The damping occurs over a certain time interval $\Delta t_\gamma$ with a length inverse proportional with the friction coefficient. Specifically for the considered example $\Delta t_\gamma \approx 0.3 \mu s$ for $\gamma = 10^{10}$ s$^{-1}$, $\Delta t_\gamma \approx 1 \mu s$ for $\gamma = 10^9$ s$^{-1}$, and $\Delta t_\gamma \approx 20 \mu s$ for $\gamma = 10^8$ s$^{-1}$. This behavior is explained by realizing that every time the inner nanotube comes close to the surface, it looses some energy and it consequently does not reach the same distance from the surface the next time. However, since the friction is effective only when the tube is in the vicinity of the surface (determined by the cut-off distance $z_c$), the energy loss process continues until the nanotube is far enough from the sample surface. After that the friction process will not be effective.
anymore and the nanotube will oscillate freely but with less energy than the initial one. For larger $\gamma$ more energy is lost at each step, therefore the interval $\Delta t_{\gamma}$ is shorter.

Other important features are the time dependence of the inner CNT displacement $z_0$ and its corresponding velocity $v$ for the first few periods. These quantities bring further insight on how the sample surface affects the motion of the nanotube at smaller time scale. These dependences are shown in Figs. III.1.7 and III.1.8 for a friction coefficient $\gamma = 10^9 \text{s}^{-1}$ and different distances $d$ between the edge of the outer nanotube and the sample surface. One sees that

Figure III.1.7. Displacement of the oscillating inner tube as a function of time for different locations of the semi-infinite sample with respect to the edge of the outer tube.
for $ d > 35 \text{Å} $ the surface is too far from the nanotube and the motion is determined mainly by the intertube contribution $ F_{1-2} $. The velocity has linearly increasing and decreasing portions corresponding to the appropriate segments of the vdW force between the nanotubes. As the surface is brought closer, the duration of each period of the displacement $ z_0 $ is shortened with the shortest time for one cycle corresponding to $ d = 0 $. The attractive part of the inner CNT/sample contribution $ F_{1-s} $ causes the nanotube to accelerate and non-linear features of $ v $ are found when the nanotube is near the minimum of $ F_{1-s} $. There

Figure III.1.8. Velocity of the oscillating inner tube as a function of time for different locations of the semi-infinite sample with respect to the edge of the outer tube.
the nanotube is accelerated for a short time, and then it is quickly repelled by the repulsive part at a distance about 2 Å from the sample surface. The velocity of the nanotube reverses its direction and the oscillating nanotube starts accelerating in the opposite direction. The motion process is then repeated in reversed order.

**III.1.4. Characteristic times**

Next some characteristic parameters (called characteristic times) associated with the inner CNT oscillatory motion are defined in order to describe the sensitivity of the system to the presence of the sample surface. The focus will be on the first period of the oscillations (denoted $T_1$) and the duration of each period after the inner nanotube has reached the regime of friction-free oscillations (denoted $T_f$). The inverses of these characteristic times, $1/T_1$ and $1/T_f$, are shown in Figs. III.1.9 and III.1.10 as a function of the distance $d$ between the edge of the outer nanotube and the sample surface. The calculations are performed for two double wall CNT systems, one with shorter nanotubes $2L = 7$ nm and one with longer nanotubes $2L = 15$ nm. The initial extrusion for the first system is $z_{0,i} = 7$ Å, while for the second one is $z_{0,i} = 30$ Å.

Fig. III.1.9 shows that the proximity of the surface has a rather profound effect on $1/T_1$ for both short and long CNT systems. In both cases there is a free oscillation regime, determined by the restrictions imposed by the initial extrusion. For shorter systems this regime occurs when $d > 12$ Å, while for longer systems this regime occurs when $d > 35$ Å. As the double wall CNT oscillator is brought
closer to the sample surface, $1/T_1$ shows an increasing trend. The changes are more dramatic for the shorter nanotubes, but they are over a shorter range of distances $d$ since the inner nanotube can be extruded at smaller $z_{0,i}$ as compared to the longer one.

One notices in Fig. III.1.9 that in the vicinity of $d \approx 11\text{Å}$ for shorter CNTs and $d \approx 34\text{Å}$ for longer CNTs there is a decrease in $1/T_1$. Since the inner nanotube-surface vdW potential minimum is very very close to the stopping position of the moving tube at these locations, the inner nanotube will be further

Figure III.1.9. Inverse of the time $T_1$ for the inner nanotube to undergo the first complete cycle starting from rest for different friction coefficients $\gamma$, as a function of the distance $d$. 

![Graph showing inverse time $T_1$ vs. distance $d$ with different colors representing different friction coefficients $\gamma$.]
attracted by the sample and slowed down as a result. Thus the inner nanotube
spends extra time around that location before it is suddenly repelled by the
repulsive part of the vdW interaction, resulting in a reversal of the motion. As the
sample is brought closer to the edge of the stationary tube, the influence of the
repulsive part of the vdW potential becomes more significant and a rather large
increase in $1/T_1$ is found. In fact, the period for the first cycle of oscillations for
both shorter and longer nanotubes can be changed by more than 2 times by
bringing the surface at the very edge of the stationary tube ($d \approx 0$).

Figure III.1.10. Inverse of the period $T_1$ of oscillations after the inner nanotube
has reached the friction-free regime, as a function of the distance $d$. 

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$1/T_1 (10^9 \text{s}^{-1})$

d (Å)
Another feature apparent from Fig. III.1.9 is that the role of the friction on the characteristic time $1/T_1$ is relatively small. It is known that friction does not affect too much the time for the first several periods of a mechanical underdamped oscillator, while it can change significantly its amplitude [76], and this is what it is obtained here.

Similar behavior is found in Fig. III.1.10, showing the characteristic time $1/T_f$ after the inner nanotube has reached the regime of friction-free oscillations. When the oscillator is in the close proximity of the surface ($d < 12\,\text{Å}$ for the shorter nanotubes and $d < 35\,\text{Å}$ for the longer ones), the oscillating nanotube loses some of its initial energy due to the friction. The loss continues until the nanotube amplitude decreases below the cut-off distance $z_c$, when it becomes a friction-free double wall CNT oscillator. In this case $1/T_f$ may be referred as the regular frequency of oscillations. Again, for both shorter and longer nanotubes, the oscillations frequency can be changed by more than 2 times by bringing the surface at the edge of the outer nanotube.

**III.1.5. Surface profiling device**

The features of the oscillatory motion described in the previous sections led to the proposal of a practical device for profiling of surfaces. The operation of such a device is determined mainly by two factors: i) some CNT characteristic times show dramatic changes as a function of the outer nanotube-surface separation distance and are not affected by friction, and ii) the main contribution from the sample to the oscillatory motion comes from a rather localized circular
region of radial size about $5R_1$. The goal is to be able to measure the characteristic times and relate them to the outer nanotube-surface distance. Fig. III.1.11 shows a schematic drawing of a laser-detector system, where the change in the beam intensity during the tube motion can be used for such measurements.

The principles of operating the proposed device will be the following: the double wall CNT is brought in the vicinity of the sample and the oscillatory motion is initiated by extruding the inner nanotube by some initial distance $z_{0,i}$. Then one can measure either $1/T_1$ or $1/T_f$ and relate it to a specific distance $d$ using the model described above. Since the oscillatory motion is determined mainly by a localized region of the sample described by a radial size $r_s$, the sample (or the oscillator) is moved along the $xy$-plane parallel to another position $\Delta r_s$. One
measures $1/T_i$ and/or $1/T_f$ again and relates them to $d$. Thus repeating this process many times, allows one to map the shape of the studied surfaces.

Different double wall CNTs with various lengths and chiralities can be used for such a device. Shorter nanotubes result in more dramatic changes in the characteristic times, but they have lesser extrusion capabilities, thus surfaces with lesser roughness can be studied. Longer nanotubes result in less dramatic changes in the characteristic times, but they can be extruded more, and surfaces with larger roughness can be studied. In addition, for nanotubes with larger radial dimensions, larger regions from the sample will determine the vdW interaction and the oscillatory motion. Thus for nanotubes with smaller radial dimensions the step of surface mapping is smaller resulting in a better in-plane resolution.

The double wall CNT oscillator can be viewed as an alternative to a conventional atomic force microscope tip for investigating surfaces. The main difficulties come from accurately measuring the first period of the oscillations and reinitiating the oscillatory motion. However, there can be some advantageous features. Since it operates in a non-contact mode, it can be a virtually a non-fatigue, non-wear system. Also, the interaction between the oscillating nanotube and a rather localized region from the surface (about 1 nm for the (5,0)@(9,7) CNT) makes it equivalent to a very sharp atomic force microscope tip (a typical tip has a 10-20 nm size [77]), therefore it is possible to obtain a higher in-plane resolution as compared to the best atomic force microscope ones. Furthermore, the steep characteristic times vs. distance dependence slope leads to the possibility of achieving a high perpendicular to the surface resolution as well, and
consequently, to profile surfaces with relatively small roughness (less than 9 Å in the presented example with the 2L=70 Å system). Finally, the double CNT oscillator can be used even if the nanotubes do not have a perfect structure. This is suggested by experimental studies showing that sliding nanotubes have the ability to absorb induced damages and defects by self-healing mechanisms and maintain low dissipation processes [57].
III.2. Deformed carbon nanotubes interactions

A recent topic of considerable interest is the study of compressed CNTs under external hydrostatic pressure or by using different mechanical methods. Experimental and theoretical studies have shown that radially deformed CNTs can experience not only geometrical modifications, but also changes in their electronic properties [78-81]. The mechanical methods include pressing the CNTs between two hard surfaces, such as AFM tips [82] or an AFM tip and a substrate [83]. Also, CNTs under high pressures have shown transitions in geometrical shapes and electronic properties [84-87]. These transitions have been also studied using molecular dynamics methods [88-90] and density functional theory calculations [91-93].

It was shown that with increasing pressure the CNTs cross section undergo a series of modifications. First the circular cross section is transformed to an elliptical one [90]. Upon further compression, the elliptical shape is deformed into a flattened one, where two flat parallel graphene sections connected by two high curvature regions are created. If the pressure is increased even further, the tube is deformed into a peanut-like shape. Figure III.2.1 illustrates the progression of these shapes. These transitions are characteristic for single wall nanotubes [91], multi wall nanotubes [94], and CNT bundles [92].

Here the focus is not on the geometrical transformations or on the changes in the electronic properties, but rather in the interactions between the CNTs themselves. These interactions determine the stability and the mutual orientation of the compressed CNTs and, consequently, the performance of
CNTs devices that might operate under extreme conditions. The goal is to present a working model for CNTs interaction with different shapes as a result of radial squashing or hydrostatic pressure in order to understand how the vdW interaction will change. Two nanotubes, arranged in parallel, with circular, elliptical, flattened and peanut-like radial shapes are considered. The approach is based on calculating the vdW potential by using the LJ type of interatomic potential within the continuum model, as discussed in Sections II.1 and II.2. Different mutual orientations between the deformed CNTs are considered and the equilibrium configurations, potentials and characteristic distances are found. The results are also presented in terms of a universal curve (see Section II.2), thus extending this concept to deformed nanotubes.

Figure III.2.1. Evolution of the CNTs cross section shape with increasing pressure.
III.2.1. Perfect carbon nanotubes

The case of parallel interacting CNTs is discussed in detail in Section II.2. It is shown that the vdW interaction potential can be expressed in a closed form in terms of an infinite (convergent) series. The interaction is evaluated numerically for several pairs of CNTs and the results are found to be consistent with those obtained in different studies of nanotubes interactions. Furthermore, some limiting cases for small and large separation distances between the CNTs are obtained from the exact expression of the potential.

III.2.2. Elliptically deformed carbon nanotubes

The elliptical shape is the first geometrical transformation that a CNT experiences after radial squashing [82,83] or after external hydrostatic pressure [89-92,95] is applied. Fig. III.2.2 shows the geometrical details of the possible orientations of two parallel elliptically deformed nanotubes. The CNTs major semiaxis are $a_1$ and $a_2$, and minor semiaxis $b_1$ and $b_2$, respectively. The distance between two surface elements is $\rho$. The nanotubes are separated by an intercenter distance $d$ and the angles $\theta$ and $\phi$ describe their relative orientation. Each tube’s axis is along the z-axis, perpendicular to the $xy$-plane.

The transformation to the elliptical shape is done in such a way to keep the perimeter of the perfect circular nanotubes constant. The perimeter is calculated using

$$p = \pi[3(a + b) - \sqrt{(3a + b)(a + 3b)}]$$  \hspace{1cm} (III.2.1)
where \( a \) and \( b \) are the major and minor semiaxis of the ellipse \([96]\), respectively.

The degree of radial deformation is described by introducing a parameter

\[
x = 1 - \frac{S}{S_0}
\]

(III.2.2)

where \( S \) and \( S_0 \) represent the cross section areas for the elliptically deformed and perfect (not deformed) nanotubes, respectively. A similar parameter describing the fractional decrease in the volume

\[
x = 1 - \frac{V}{V_0}
\]

(III.2.3)

of the deformed nanotubes was also defined in other references \([91,92,95]\). For the cases described here the parameters in Eqs. III.2.2 and III.2.3 are equivalent.

Figure III.2.2. Schematic drawing of the geometry of the possible orientations of two parallel elliptically deformed nanotubes.
Due to the lower symmetry of the elliptical shapes as compared to the perfect circular case, two angles are needed to describe the CNTs relative orientation (see Fig. III.2.2). The angle $\theta$ between the major semiaxis $a_2$ and the x-axis describes the “rotational” orientation of elliptical CNT (2) relative to elliptical CNT (1), and angle $\phi$ between the intercenter direction $d$ and the x-axis describes the CNTs “overall” relative orientation.

The vdW interaction between the elliptically deformed CNTs is calculated using Eq. II.1.5 in Section II.1. The coordinates of two typical points on the surface of each nanotube (with respect to their centers) are

$$x_1 = a_1 \cos \varphi_1$$  (III.2.4)
$$y_1 = b_1 \sin \varphi_1$$  (III.2.5)
$$x_2 = a_2 \cos \varphi_2$$  (III.2.6)
$$y_2 = b_2 \sin \varphi_2$$  (III.2.7)

The distance between the two surface elements is expressed as

$$\rho = \left[ (d \cos \phi + x_2 \cos \theta - y_2 \sin \theta - x_1)^2 
+ (d \sin \phi + x_2 \sin \theta + y_2 \cos \theta - y_1)^2 \right]^{1/2}$$  (III.2.8)

The surface elements in Eq. II.1.5 are expressed as

$$dS_1 = R_1^e d\varphi_1 dz_1$$  (III.2.9)
$$dS_2 = R_2^e d\varphi_2 dz_2$$  (III.2.10)

where

$$R_1^e = \left[ \rho_1^2 + \left( \frac{d\rho_1}{d\varphi_1} \right)^2 \right]^{1/2}$$  (III.2.11)
\[ R_2^e = \left( \rho_2^2 + \left( \frac{d \rho_2}{d \phi_2} \right)^2 \right)^{\frac{1}{2}} \]  

(III.2.12)

The polar distances \( \rho_1 \) and \( \rho_2 \) are

\[ \rho_1 = \frac{a_1 b_1}{\sqrt{a_1^2 + b_1^2 - x_1^2 - y_1^2}} \]  

(III.2.13)

\[ \rho_2 = \frac{a_2 b_2}{\sqrt{a_2^2 + b_2^2 - x_2^2 - y_2^2}} \]  

(III.2.14)

Next the interaction is numerically exemplified for the case of two parallel identical CNTs with elliptically deformed cross sections. Note that according to Refs. [91] and [95] this type of deformation occurs for pressures corresponding to deformation parameters \( x < 0.2 \). Here a deformation characterized by \( x = 0.12 \) is applied to two (15,15) CNTs. From the constraints of keeping the perimeter of the original (not deformed) CNTs one obtains elliptical cross sections with major semiaxis \( a_i = a_2 = 12.9 \text{ Å} \) and minor semiaxis \( b_i = b_2 = 7 \text{ Å} \).

As mentioned above, the nanotubes mutual orientation is characterized by two angles. First the angle \( \theta \) is kept constant (\( \theta = 0 \)) and the vdW potential is calculated for different values of the angle \( \phi \). The results per unit length for the vdW interaction of the elliptically deformed CNTs as a function of the intertube separation are shown in Fig. III.2.3.

One sees that the absolute values of the equilibrium potential depths \(|V_0|\) are in the limits of \( 113 \div 326 \text{ meV} \) and the equilibrium separation \( d_0 \) changes in the \( 17 \div 29 \text{ Å} \) range. The most stable configuration is found when \( \theta = 0 \) and \( \phi = 0 \)
with characteristics $|V_0| \approx 325.78$ meV and $d_0 = 29$ Å. This orientation corresponds to the regions with highest curvature from the ellipses being closest to each other. The interaction potential was also examined for different values of the angle $\theta$ and it was found, as a general trend, that the intercenter equilibrium distance $d_0$ in all cases changes in such a way as to keep the distance between the nanotubes surfaces $g_0 \approx 3.1 \pm 3.2$ Å.

The evolution of the equilibrium vdW potential depths for different mutual orientations of the two CNTs is shown next in Fig. III.2.4. The absolute values of $|V_0|$ are plotted as a function of the angle $\phi$ for several values of the angle $\theta$. 

Figure III.2.3. vdW potential as a function of the separation distance between the centers of the ellipses.
One sees that the curves representing the equilibrium interaction potential intersect each other at several points, indicating the existence of several equally preferred mutual orientations. For example, at $(\theta, \phi) = (0, 23) \text{deg}$ and $(\theta, \phi) = (75, 23) \text{deg}$ the absolute values of the minimum potential are the same $|V_0| = 258.4 \text{meV}$, thus these two configurations are energetically equivalent. Moreover, some of the curves are very close to each other in certain regions, such as when $\theta \in (0, 15) \text{deg}$ and $\phi \in (0, 5) \text{deg}$, indicating that these mutual orientations are very similar.
The interaction between the elliptically deformed CNTs is further examined for different degrees of deformation characterized by the parameter $x$ defined in Eq. III.2.2. It is found that for elliptical deformations with $x < 0.7$ the most preferred configuration is $(\theta, \phi) = (0,0) \text{deg}$, corresponding to the higher curvature regions being closer to each other. The numerical integration of Eq. II.1.5 shows that the dominant contribution to the numerical value of the potential (close to 90%) comes from the relatively small high curvature sections (about 15% of the total circumference of each ellipse). For elliptical deformations with $x > 0.7$ the most preferred configuration is $(\theta, \phi) = (0,90) \text{deg}$, corresponding to the lower curvature regions being closer to each other. Again, from the numerical integration of Eq. II.1.5, the potential value is determined mainly by the relatively large overlapping low curvature sections (about 40% of the total circumference of each ellipse). These most preferred mutual orientations are schematically illustrated in Fig. III.2.5.

This behavior can be related to the definitions of the terms $R_{12}^e$ entering the CNTs surface elements $dS_{12}$ in Eqs. III.2.9-12. The absolute values of the derivatives $|d\rho_{12}/d\phi_{12}|$ are large when the corresponding arguments $\phi_{12}$ pass through the highly curved segments of the ellipses, yielding $dS_{12} \approx |d\rho_{12}/d\phi_{12}|d\phi_{12}dz_{12}$. On the other hand, for the lower curvature segments of the ellipses the derivatives $|d\rho_{12}/d\phi_{12}|$ are small, so that $dS_{12} \approx \rho_{12}d\phi_{12}dz_{12}$. The relative contributions of the higher and lower curvature segments depend on the degree of the deformation $x$, i.e. on the ellipse eccentricity, respectively.
Therefore, two competing effects are present in the vdW interaction between elliptically shaped objects: one coming from the curvature when the ellipses are not very much elongated and the other one from the overlap between the low curvature regions when the ellipses are more elongated.

When the pressure is further increased and $x \approx 0.2$, the CNTs cross section will no longer be elliptical but it will experience a transition to a flattened shape\textsuperscript{47}.

### III.2.3. Flattened carbon nanotubes

According to previous works [92,95], further compression of the elliptically deformed CNTs leads to a geometrical transition to a shape characterized by the occurrence of two flat regions, similar to the graphene planes in graphite (see Fig. III.2.6(a)). It was reported [91,92,95] that such a transition always happens at a deformation $x \approx 0.2$ regardless of the nanotube diameter. Here an analytical parameterization is given for this shape, consisting of two linear regions and two
elliptical regions. All parts are smoothly connected. The characteristics of the straight lines and elliptical parts are determined from the conditions of constant perimeter and particular fractional deformation $x$.

Such mathematical description of the flattened nanotube shape has already been used in analytical models studying the deformation energies and stability of CNTs as a function of their degree of deformation. Here the definition of the flattened shape follows the procedure outlined in Ref. [91], where the cross sections of CNTs under different degrees of external hydrostatic pressure were described with such a parameterization. The geometrical model from Fig. III.2.6.(a) is also in agreement with results from variational analysis calculations [95] which argue that the flattened shape transformation is universal for cylindrical hollow tubes.

The relative position of two parallel flattened CNTs is described by two angular variables $\theta$ and $\phi$ and the distance $d$ between their centers in a similar
manner as for the case of elliptically deformed CNTs. A schematic illustration of this configuration is shown in Fig. III.2.6(b). To allow comparison with the previous cases, a flattened deformed CNT originating from a (15,15) perfect CNT is considered. By keeping the perimeter constant and imposing a deformation characterized by \( x = 0.2 \), one obtains a flattened shape with a distance between the flat regions \( 2b = 13.34 \) Å and a ratio \( b/a = 0.528 \).

The vdW potential per unit length as a function of the separation distance \( d \) between the centers of the flattened CNTs is shown in Fig. III.2.7. The results are plotted for different values of the angle \( \phi \) when the angle \( \theta \) is kept constant.
Figure III.2.8. Evolution of the absolute values of the equilibrium vdW potential depths for different mutual orientations of the two CNTs.

$(\theta = 0)$. It is found that the most stable configuration is for $(\theta, \phi) = (0,0)\,\text{deg}$. This corresponds to the two flattened CNTs being in a position where the flat regions are stacking on top of each other. In fact, the dominating contribution to the integration from Eq. II.1.5 in this case is determined to come mainly from the two flat regions from the different nanotubes closest to each other. The absolute interaction is also stronger for flattened CNTs as compared to the previous considered cases. The minimum interaction potential for this $b/a$ ratio is found to be $|V_0| = 355.751\,\text{meV}$ which is about 2 times larger as compared to the perfect circular CNTs and about 10% larger as compared to the most preferred mutual
orientation of the elliptically deformed CNTs. The intercenter distance for the equilibrium orientation is $d_0 = 16.7 \, \text{Å}$ corresponding to a distance $g_0 = 3.36 \, \text{Å}$ between the two flat surfaces which is comparable to the graphene layers equilibrium distance.

The evolution of the equilibrium vdW potential depths for different mutual orientations of the two CNTs is shown next in Fig. III.2.8. Again the curves representing the equilibrium interaction potential intersect each other at several points, indicating the existence of several equally preferred mutual orientations. One sees that the vdW interaction is stronger when more overlap is present between the flat sections from the nanotubes. This overlap is characterized by lower values of the angle $\theta$ and larger values of the angle $\phi$ indicating a tendency towards stacking in a similar manner as the graphene planes in graphite.

### III.2.4. Peanut-like carbon nanotubes

When the external pressure is increased even further with deformations $x > 0.2$ the CNTs cross section will undergo a final transition [91,95] to a peanut-like shape, as shown in Fig. III.2.9(a). This shape can also be achieved if the CNT is squashed between two surfaces with dimensions smaller than its diameter [84]. At a certain critical value of the applied pressure the CNT will eventually collapse [90].

The peanut-like shape is described in a similar manner as the flattened shape from Section III.2.3. Four regions, which are parts of ellipses, are joined
together as shown on Fig. III.2.9(a). All parts are connected smoothly. The characteristic parameters of the elliptical regions are obtained in such a way as to keep the perimeter of the original not deformed CNT constant and to specify a certain degree of deformation. There is a smooth transition between the flattened shape considered in Section III.2.3 and the peanut-like shape. The flattened shape can be obtained as the limiting case when the two elliptical regions on top and bottom have their eccentricities approaching unity.

The mutual orientations of two parallel peanut-like CNTs are described similarly as in the previous cases. The interaction is numerically exemplified for the case of two peanut shaped CNTs with the same perimeter as the one corresponding to (15,15) not deformed nanotubes. The fraction volume parameter is chosen to be $x = 0.36$. The vdW interaction is plotted for different values of the angle $\phi$ when the angle $\theta$ is kept constant ($\theta = 0$).
After examining all possible orientations of the two nanotubes, it is found that the most stable configuration is with $(\theta, \phi) = (0, 0)\, \text{deg}$. The corresponding equilibrium potential is $|V_0| = 208.014 \, \text{meV}$, the separation distance between the CNTs centers is $d_0 = 33.8 \, \text{Å}$, and the distance between their surfaces is $g_0 = 3.16 \, \text{Å}$. One notices that the $(\theta, \phi) = (90, 0)\, \text{deg}$ configuration, with nanotubes on top of each other, is not energetically favorable in this case. This is traced to the large repulsion between the inflated ends of the peanut shape. Thus in this case the equilibrium configuration of the peanut-like nanotubes resembles more

![Figure III.2.10. vdW potential per unit length as a function of the separation distance between the centers of the peanut-like deformed.](image-url)
with the one between the elliptically deformed nanotubes, where the regions with highest curvature are closest to each other.

For a smaller degree of deformation, such as $x = 0.23$, when the peanut-like shape does not differ much from the flattened one, it is found that the preferred orientation is with the lowest curvature sites closest to each other. Thus the preferred configurations change as the deformation degree of the peanut-like nanotube shape changes. The competing effects from the interacting higher curvature regions and the overlap between the lower curvature regions are found here as well. In fact, for $0.2 < x < 0.32$ the numerical integration of Eq. II.1.5 is
determined mainly by the relatively flat regions from the peanut-like nanotubes closest to each other. For $x > 0.32$, the numerical integration is determined mostly by the higher curvature regions from the two nanotubes when they are closest to each other.

Finally, tracking the change of the equilibrium distances for the different mutual orientations can bring some more insight into understanding the vdW interaction between the deformed nanotubes. Fig. III.2.11 shows the equilibrium intercenter distance $d_0$ for all the considered deformed shapes when $\theta = 0$ and $\phi$ undergoes a full rotation from 0 to 360deg, corresponding to one of the nanotubes sweeping around the other one a full turn. It is interesting to see that for the elliptical and flattened CNTs, the path of $d_0$ is in the form of an ellipse, while for the peanut-like shape a more complicated pattern is shown. Similar curves are found for other values of the angle $\theta$. In all cases, the intercenter distance changes in such a way as to keep the distance between the surfaces $g_0$ to be almost the same. For example, for all mutual orientations of the elliptical shapes $g_0 \approx 3.15 \text{ Å}$, for the flattened shapes $g_0 \approx 3.36 \text{ Å}$, and for the peanut-like shapes $g_0 \approx 3.16 \text{ Å}$.

**III.2.5. Universal graphitic potential concept**

It was found [39] that all the vdW potentials between two arbitrary CNTs fall on the same curve when plotted in terms of certain reduced parameters, the well depth $|V_0|$ and the equilibrium vdW gap $g_0$. These findings were later
verified for different single wall and multiwall carbon nanotubes [40,41]. The applicability of the universal graphitic potential concept is tested next for the case of radially deformed CNTs. It is found that with a proper choice of reduced parameters one obtains a universal potential curve for all perfect and radially deformed nanotubes. The results are shown in Fig. III.2.12, where the reduced potential depth $V/V(d_0)$ is plotted as a function of the reduced distance $(d - \rho)/(d_0 - \rho)$. $V(d_0)$ represents the potential minimum for each configuration and $d_0$ is the equilibrium spacing corresponding to $V(d_0)$. The parameter $\rho$ is defined as the distance between the centers of the interacting nanotubes when

Figure III.2.12. The universal potential curves per unit length for perfect and radially deformed nanotubes.
\[ g = 0. \] The figure shows that the reduced potential curves for each type of deformation coincide, thus extending the concept of the universal graphitic potential to deformed nanotubes. It is known that even using numeral integrations and simplified expressions the calculations involving vdW interactions in graphitic structures may be quite complex. Therefore the above extension of the universal graphitic potential for radially deformed CNTs represents an effective, universal, and simple approach of obtaining the vdW interaction between deformed nanotubes without time consuming integrations.
III.3. Hot nanolithography

In today’s continuous race for miniaturization, one particular field of interest is the modification of hard or soft materials surfaces with high spatial resolution. There is a need for writing different circuits for nanoelectronics, creating nanowires, or producing arrays of various nanostructures in a simple, low cost and high output manner.

III.3.1. Methods and challenges

Nanolithography can be accomplished by mechanically scratching the surface with a sharp atomic force microscope (AFM) tip [97], by exploiting the electromagnetic enhancement of a laser field in the vicinity of a sharp tip for surface ablation [98], by using hot tips for thermal imprinting on the surface [99,100], or by writing with foreign molecules on the surface [101]. Regardless of the implementation of the particular method for surface modification, two main challenges in improving the use of an AFM tip for nanolithography have been identified. One challenge is achieving high spatial resolutions, which is directly related to the sharpness of the tip. The other one is the accurate control of the tip-surface distance, which affects the quality of the nanolithography surface modification.

Among these methods, hot nanolithography has received particular attention due to its promise, in conjunction with the use of AFM capabilities, to meet the demands of high spatial resolution. The AFM usually operates in contact, tapping or non-contact mode. The contact mode is done with the tip in contact with the surface, and the force between the tip and the surface is kept
constant during scanning by maintaining a constant deflection of the cantilever. In tapping mode, the AFM cantilever is driven to oscillate near its resonance frequency with the tip tapping the sample surface. The information about the surface is given by the changes in the oscillation amplitude. In non-contact mode, the cantilever is oscillated at or close to its resonance frequency, and the tip does not touch the surface. The image is produced by monitoring the frequency or amplitude modulations of the tip oscillations. A comprehensive review of the AFM characteristics is given in Ref. [77]. Hot nanolithography is usually done in contact or tapping modes.

Recently, imprinting on polymer and metal films with spatial resolution of about 20 nm width and a few nm depth using hot conventional Si tips was reported [102,103]. Since the imprinting resolution is directly related to the tip sharpness, carbon nanotubes, with their high aspect ratio, appeared naturally as promising candidates for hot tips [104]. CNTs also have the advantage of a more robust chemical and mechanical structure, as compared to the conventional Si tips, which are brittle and can change their sizes and shapes during operation [105,106]. Progress in producing patterns with resolution as high as 10 nm by using CNT tips, was reported [107]. However, the performance of the nanotube tips when operating in AFM both tapping or contact mode is affected by forces which laterally bend the CNT, thus limiting the possibility of producing sharp turns on the surface. At the same time, the AFM conventional non-contact operating mode is rather not suitable for hot nanolithography applications, regardless of the type of tips used, since it involves a mean distance too large for proximity tip-surface heat interactions necessary for thermal imprinting. This is
due to the feedback loop that involves large amplitude oscillations of the cantilever at its mechanical resonance frequency. One proposed way to overcome this is based on small amplitude (<1 nm) forced oscillations of the cantilever at a frequency different from its resonant frequency, together with a custom feedback circuit [102,103]. However, the main disadvantage is that such feedback circuit has to be designed differently for each situation since it is specific to the experimental conditions, such as humidity, sample material, position of the laser spot on the cantilever, etc.

A different problem to be addressed is approaching a surface with a sharp tip and maintaining a constant tip-surface distance. The conventional scheme involves approaching the tip until contact is made with the surface, and then raising it to the desired distance. If one uses stiff cantilevers, sharp tips are likely to break during the contact with the surface. If one uses soft cantilevers, the tip may stick to the surface and upon lifting it may jump to a distance larger than the desired one [102].

Regarding the time efficiency of AFM nanolithography, it was proposed to use parallel arrays of probes [108] in order to decrease the scanning time for a given imaging area. Again, the difficulties come from controlling the distance between the sample and the individual tips, since there is only one feedback control for the entire array of cantilevers. The lack of feedback control for the individual tips produces large variation in the nanolithography quality from tip to tip. Therefore, new methods are needed to address these challenges for improved nanolithography applications.
III.3.2. Carbon nanotubes for lithography

As discussed in the previous section, carbon nanotubes, due to their high aspect ratio, appear naturally as promising candidates for hot tips. Here a custom double wall carbon nanotube (DWNT) is proposed as a surface thermal imprinting tool that improves the spatial resolution and successfully solves the accurate tip-surface distance control. The system is shown in Fig. III.3.1 and consists of a finite length outer tube attached to an AFM cantilever, while the inner tube with length larger than the outer one is not constraint. The DWNT is initially heated up to a sufficiently high temperature by a collimated pulse laser and brought in the vicinity of the surface. By studying the heat transfer in the DWNT/surface, it is found that enough heat is transmitted to the surface to allow thermal imprinting. Also, the size of the thermal spot on the surface is mainly determined by the inner tube radius indicating that high spatial resolution can be achieved if small diameter nanotubes are used. The interaction forces in the DWNT/surface system are of van der Waals (vdW) type and it is shown that the inner tube is located always at the same energetically favorable distance from the surface. Since the inner tube can move telescopically along the DWNT axis, the tip/surface distance is maintained constant due to the vdW interaction, which in turn eliminates the need of an active feedback loop.

To quantitatively describe the system, a (5,0)@(7,9) DWNT is chosen with corresponding radii $R_1 = 1.95\,\text{Å}$ and $R_2 = 5.44\,\text{Å}$ and lengths $L_1 = 20\,\text{nm}$ and $L_2 = 10\,\text{nm}$, respectively. The DWNT is open ended with chemically saturated end bonds to avoid chemical interactions. The interaction in the system is described by using a pairwise additive Lennard-Jones vdW potential for
extended systems [39]. Since the outer tube is subject to constraints (see Fig. III.3.1), its interaction with the surface has no effect in this discussion and it is not considered here. The vdW potential energy in the system is calculated following the procedure outlined in Section III.1.2 and the details of the calculations are shown in Appendix A. The numerical results for the example considered here are shown in Fig. III.3.2 for different separation distances between the edge of the outer tube and the surface.

When the DWNT is far from the surface, its equilibrium position occurs when the centers of mass of the inner and outer nanotubes coincide ($z_{rel} = 0$). When approaching the surface, the inner tube will start to sense its influence. As
a result, the potential energy in the system will exhibit a displaced minimum. One sees from Fig. III.3.2 that the potential minimum is always located at the same inner nanotube-surface distance \( d_0 \approx 2.5 \text{ Å} \), independent of the position of the outer nanotube relative to the surface. The equilibrium position relative to the surface \( d_0 \) slightly differs for different sample materials because of the material dependent Hamaker constants, but it is always on the order \( d_0 = 2 \div 3 \text{ Å} \), which is characteristic for systems that are stable due to vdW forces.

The force acting on the inner nanotube is calculated as
and it is shown in Fig. III.3.3 for the same distances. between the edge of the outer tube and the surface. The inner nanotube equilibrium positions correspond to the zero values of the vdW force.

Therefore, by laterally scanning the surface, it is possible for the inner nanotube to follow the surface at a constant distance $d_0$ without the need of an active feedback mechanism. This can also be advantageous for an array of DWNT tips operating in parallel, since each inner nanotube will independently follow the surface at that constant distance with no active feedback required.
### III.3.3. Heat transfer

The DWNT tip is initially heated by a pulse laser to the desired temperature $T_{\text{tip}}$. This can be achieved easily since nanotubes were reported [109] to sustain temperatures exceeding 2000 K. The surface is assumed to be at room temperature $T_0 = 300$ K, and the entire system is in the environment of air also at $T_0 = 300$ K. Heat can be exchanged from the tip to the surface through convection [110] or radiation [111]. The convection heat transfer is due to the air molecules which can be modeled as nitrogen molecules to a first approximation. At room temperature and atmospheric pressure, their mean free path is $\lambda = 55$ nm [112]. Since the tip equilibrium distance to the surface $d_0 = 2 \div 3$ Å is much smaller than the mean free path $\lambda$, it is assumed in this model that the heat transport is mainly ballistic. Furthermore, it is assumed that an incident molecule at $T_0 = 300$ K is heated instantaneously when impacting the hot nanotube by adopting a Maxwellian velocity distribution at $T_{\text{tip}}$. Then the molecule will travel from the nanotube to the surface ballistically, where it will transfer all of its kinetic energy.

The heat flux per unit area emitted from the surface of one tube is

$$\Phi_{\text{tip}} = n_{\text{tip}} \frac{m v_{\text{rms}}^2}{2} \quad \text{(III.3.2)}$$

where $n_{\text{tip}}$ is the number of air molecules per unit area emerging from the tube surface and $m$ is the diatomic molecular mass. $v_{\text{rms}}$ represents the root mean square of the velocity $v$ and it is calculated as
\[ v_{\text{rms}} = \left( \int_0^\infty v^2 f(v) dv \right)^{1/2} \]  

(III.3.3)

with \( f(v) \) being the Maxwell distribution. \( n_{\text{tip}} \) is calculated by imposing an equilibrium condition which requires that the molecular flux emitted from the tube surface equals the molecular flux incident at the surface [113]

\[
n_{\text{tip}} = n_0 \left( \frac{T_{\text{tip}}}{T_0} \right)^{3/2} \int_0^\infty v^3 \exp \left( \frac{-mv^2}{2k_B T_0} \right) dv \int_0^\infty v^3 \exp \left( \frac{-mv^2}{2k_B T_{\text{tip}}} \right) dv
\]

(III.3.4)

where \( n_0 \) is the number of incident air molecules per unit area at room temperature and \( k_B \) is the Boltzmann constant.

The other transport mechanism, heat radiation, is described in detail in Ref. [111], where it was shown that the heated object behaves like an antenna radiating electromagnetic field. It was demonstrated that the radiation heat flux is much smaller than the convection heat transport ranging from one order of magnitude smaller for a silicon surface to four orders of magnitude smaller for a silver surface. Therefore this kind of heat transport is neglected here.

The surface heat distribution is determined by the total incident heat flux \( \Phi = \Phi_1 + \Phi_2 \), where \( \Phi_1 \) and \( \Phi_2 \) are the heat fluxes from the inner and outer nanotube, respectively. In order to understand the distance characteristics of the heat transfer due to one tube only, \( \Phi_1 \) is considered first. In steady state conditions, \( \Phi_1 \) is expressed in terms of the emitted heat flux per unit area \( \Phi_{\text{tip}} \) as

\[
\Phi_1 = \frac{R_1 \Phi_{\text{tip}}}{4\pi} \sum_{i=1}^{\theta} \int_{\theta_i}^{\theta} d\theta \left[ \frac{1}{\sqrt{d^2 + r^2 + R_1^2 - 2rR_1 \cos \theta}} - \frac{1}{\lambda} \right]
\]

(III.3.5)
where $r$ is the radial cylindrical coordinate, shown in Fig. III.3.4. The integration limits $\theta_1$, $\theta_2$, and $\theta_3$ are

\[
\theta_1 = \pi \quad \text{(III.3.6)}
\]

\[
\theta_2 = \cos^{-1}\left(\frac{R_1}{r}\right) \quad \text{(III.3.7)}
\]

\[
\theta_3 = -\cos^{-1}\left(\frac{R_1}{r}\right) \quad \text{(III.3.8)}
\]

and they correspond to the heat coming from the interior of the nanotube to the surface delimited by $r < R_1$, by $r > R_1$, and from the exterior of the nanotube to the surface, respectively.
The ratio of the incident heat flux on the surface and the emitted heat flux of one tube is shown in Fig. III.3.4 for several values of the separation distance \(d\). For separations smaller than a certain threshold value \(d_t\), the thermal spot reproduces the tube cylindrical geometry. For separations larger than \(d_t\), this signature is lost and the deposited heat flux becomes axisymmetric with one maximum at \(r = 0\). Similar findings were reported in Ref. [113] for a pyramidal tip. By considering nanotubes with various radii it is found that the threshold separation distance \(d_t\) is approximately half of the nanotube radius \(d_t \approx R_t/2\).
Next the total heat flux $\Phi$ emitted from both nanotubes is considered. Due to the vdW forces, the inner nanotube will be in its equilibrium position $d_0 \approx 2.5 \text{Å}$, while the outer nanotube will be located at a separation $d$. Fig. III.3.5 shows the total heat flux $\Phi$ emitted from both nanotubes for different values of $d$ in terms of the emitted heat flux per unit area $\Phi_{\text{tip}}$. The heat flux $\Phi_1$ coming from the inner nanotube only is also shown for reference. The inset in Fig. III.3.5 shows the relative contribution of the heat flux from the outer nanotube with respect to the one from the inner nanotube as a function of the radial distance $r$.

The customary definition of the spatial resolution for nanolithography tips is defined as the full width half maximum (FWHM) of the heat profile [113]. One sees from Fig. III.3.5 that the FWHM is mainly determined by the heat flux from the inner nanotube (half of the FWHM is shown). The heat contribution coming from the outer tube, for this range of distances $d$ and lengths of the DWNT accounts for less than 10% of the total FWHM. Thus one concludes that it is possible to achieve high spatial resolutions by using CNTs with small diameters. In the example shown with a (5,0)@(7,9) DWNT, for separations $d = 5 \text{nm}$ and $d = 3 \text{nm}$, the FWHM (resolution) is about 1.2 nm and 1.4 nm, respectively.

**III.3.4. Thermal vibration**

Next the limitations coming from the thermal vibration of the DWNT tip as a whole are considered. It is assumed that most of the outer nanotube is attached to the AFM cantilever, therefore the outer nanotube does not thermally vibrate. Since the part of the inner nanotube contained inside the outer nanotube is constrained to stay radially symmetric by the vdW forces between the
nanotubes, only the vibrations of the telescoped portion of the inner nanotube closest to the surface are important here. This phenomenon is illustrated in Fig. III.3.6. The extruded part of the inner nanotube closest to the surface, with length $L$, has an amplitude of the thermal vibrations $w$ at its end. The vibrating system is described as a cylinder clamped at one end using a mechanical model from Refs. [114,115], and the vibration amplitude is estimated as

$$w = \left( \frac{4k_BT L^3}{3 \pi R_1^4 Y} \right)^{1/2}$$

(III.3.9)

where $Y$ is the CNT Young modulus and $T$ its absolute temperature. Since $w \propto T^{1/2}$ and $w \propto L^{3/2}$, it is expected that the amplitude of the thermal vibrations will be larger for longer nanotubes heated at higher temperatures.
Some of these features are seen in Fig. III.3.7, where the heat flux distribution incident on the surface is shown in the presence of the thermal vibrations. The Young modulus is taken to have its experimental [115] value $Y = 1\text{TPa}$ for nanotubes with this radial size. One sees from Fig. III.3.7 that, for example, the FWHM for the inner nanotube with $L = 3\text{nm}$ is $1.5\text{nm}$, while it is $1.7\text{nm}$ for the nanotube with $L = 5\text{nm}$. However, even though the increase in FWHM in this case is relatively large, the resolution of the tip is still high due to the small diameter CNT.

Figure III.3.7. Reduced incident heat flux with thermal vibration taken into account; HWHM is also shown.
**III.3.5. Nanolithography device**

The features described in the previous sections led to the proposal of a practical device for thermal imprinting on surfaces. The operation of the device is the following: the heated finite length DWNT tip is being brought in a close proximity of a sample surface with the aid of the AFM cantilever. The axis of the tube is perpendicular to the surface. The inner nanotube will move to its equilibrium position determined by the minimum potential energy due to the vDW forces in the system regardless of the location of the outer nanotube with respect to the surface. Heat is transferred to the surface of the material mainly due to convection and an imprinted spot on the surface appears. By moving the cantilever parallel to the surface, the inner nanotube will always be at the equilibrium position due to the vDW forces, and the DWNT will thermally imprint on the surface. Thus the sample surface can be laterally scanned with the inner nanotube at a constant separation without the need of an active feedback mechanism.

High quality DWNT with minimal defects and deformations can be prepared by high-temperature discharge methods and attached to conventional AFM tips by nanomanipulation [106]. Also, alternative methods to attach the CNT to scanning probes were developed using a liquid deposition technique together with magnetic field alignment [116]. The radial dimension of the carbon nanotubes allows achieving high spatial resolutions for hot nanolithography surface modifications. Even though the thermal vibrations of the nanotube limit the performance of the device, however, spatial resolution less than 5nm can
still be achieved. Finally such a DWNT tip can further benefit from the chemical and structural robustness of CNTs, being a virtually non-wear system.
Chapter IV

Quantum electrodynamics approach

In this chapter the interaction between carbon nanotubes is studied using a quantum electrodynamics approach suitable for dispersing and absorbing media. Each carbon nanotube is characterized by its individual dielectric response, which is a complex function of frequency. The quantization scheme considers the Fourier images of the electric and magnetic fields as quantum mechanical observables of the corresponding electric and magnetic field operators. They satisfy the Fourier-domain operator Maxwell equations with the additional exterior operator sources, which account for the medium-induced absorption. The electromagnetic field is further represented using the dyadic Green function technique. The method allows taking into account the full carbon nanotube cylindrical geometry by imposing the appropriate boundary conditions at the nanotubes surfaces. The quantum electrodynamics approach is applied to the case of two concentric carbon nanotubes and the forces acting on the nanotubes surfaces are determined from the electromagnetic stress tensor.
IV.1. General theory

A quantization scheme for the phenomenological Maxwell theory of the electromagnetic field in dispersive and absorbing dielectric medium is presented. The classical Maxwell equations are regarded as operator-valued field equations, introducing additional current density and charge density operator fields in order to take into account the noise associated with the dissipation in the medium. The permittivity of the medium is a space dependent, complex function of frequency, consistent with the Kramers-Kronig relations [Landau, Lifshitz-Electrodynamics of continuous media]. The quantization of the radiation field is based on the classical Green function representation of the electromagnetic field, identifying the external sources with the noise sources associated with the losses in the medium. The Green function is essentially determined by the permittivity of the medium, while the configuration of the dielectric bodies is described by the dependence on space of the permittivity. Further the effects of dispersion and absorption are described by the real and imaginary part of the dielectric response.

IV.1.1. Classical Maxwell equations

The phenomenological Maxwell equations in the frequency domain are

\[ \nabla \cdot \mathbf{B}(r, \omega) = 0 \]  \hspace{1cm} (IV.1.1)

\[ \nabla \cdot \mathbf{D}(r, \omega) = 0 \]  \hspace{1cm} (IV.1.2)

\[ \nabla \times \mathbf{E}(r, \omega) = i\omega \mathbf{B}(r, \omega) \]  \hspace{1cm} (IV.1.3)

\[ \nabla \times \mathbf{H}(r, \omega) = -i\omega \mathbf{D}(r, \omega) \]  \hspace{1cm} (IV.1.4)
It is assumed that the background medium contains no charges or currents. The constitutive relations for linear dielectric media are given by

\[ D(r, \omega) = \varepsilon(r, \omega)E(r, \omega) \]  
\[ B(r, \omega) = \mu_0 H(r, \omega) \]

where the relative permittivity is a complex function of frequency

\[ \varepsilon(r, \omega) = \text{Re} \varepsilon(r, \omega) + i \text{Im} \varepsilon(r, \omega) \]

For causality reasons, the real and imaginary parts of the permittivity are uniquely related through the Kramers-Kronig relations.

The next step will be to promote the Maxwell equations to quantum theory, by regarding the electromagnetic field vectors as operator-valued quantities. However, transferring these equations to the quantum theory will yield equations for the expectation values of the fields, which may be damped to zero. Therefore a noise associated with absorption must be introduced as an additional source in the Maxwell equations. This term can be thought of as arising from noise polarization in the constitutive relation

\[ D(r, \omega) = \varepsilon(r, \omega)E(r, \omega) + P(r, \omega) \]

and will be described in the following section.

**IV.1.2. Quantum Maxwell equations**

The classical Maxwell equations in the previous section are now transferred to quantum theory by regarding the electromagnetic field vectors and the noise polarization field as operators
\[ \nabla \cdot \mathbf{B}(r, \omega) = 0 \]  \hspace{1cm} (IV.1.9)

\[ \nabla \cdot [\varepsilon(r, \omega)\mathbf{E}(r, \omega)] = \dot{\rho}(r, \omega) \]  \hspace{1cm} (IV.1.10)

\[ \nabla \times \mathbf{E}(r, \omega) = i \omega \mathbf{B}(r, \omega) \]  \hspace{1cm} (IV.1.11)

\[ \nabla \times \mathbf{B}(r, \omega) = -i \omega \mu_0 \varepsilon(r, \omega)\mathbf{E}(r, \omega) + \mu_0 \mathbf{j}(r, \omega) \]  \hspace{1cm} (IV.1.12)

Here the charge density operator \( \dot{\rho} \) and the current density operator \( \mathbf{j} \) are related to the noise polarization operator as follows

\[ \dot{\rho}(r, \omega) = -\nabla \cdot \mathbf{P}(r, \omega) \]  \hspace{1cm} (IV.1.13)

\[ \mathbf{j}(r, \omega) = -i \omega \mathbf{P}(r, \omega) \]  \hspace{1cm} (IV.1.14)

and they fulfill the equation of continuity

\[ \nabla \cdot \mathbf{j}(r, \omega) = i \omega \dot{\rho}(r, \omega) \]  \hspace{1cm} (IV.1.15)

As already mentioned, these sources account for the medium-induced absorption and are described by the imaginary part of the permittivity. They are chosen in such a way to ensure the correct quantum electrodynamics equal-time commutation relations for the electric and magnetic field operators [27]. Following Ref. [27] the current density operator \( \mathbf{j} \) is related to a bosonic field \( \mathbf{f} \) as

\[ \mathbf{j}(r, \omega) = \frac{\omega}{\mu_0 c^2} \sqrt{\frac{\hbar}{\pi \varepsilon_0}} \text{Im} \varepsilon(r, \omega) \mathbf{f}(r, \omega) \]  \hspace{1cm} (IV.1.16)

The bosonic operators satisfy the standard commutation relations

\[ \left[ \hat{f}_i(r, \omega), \hat{f}_j^+(r', \omega') \right] = \delta_{ij} \delta(r - r') \delta(\omega - \omega') \]  \hspace{1cm} (IV.1.17)

\[ \left[ \hat{f}_i(r, \omega), \hat{f}_j(r', \omega') \right] = 0 = \left[ \hat{f}_i^+(r, \omega), \hat{f}_j^+(r', \omega') \right] \]  \hspace{1cm} (IV.1.18)
The above equations do not refer to a specific picture. In particular, in the
Heisenberg picture the bosonic field \( \hat{f} \) carries an exponential time dependence

\[
\hat{f}(r, \omega, t) = \hat{f}(r, \omega, t') e^{-i \omega (t-t')}
\]

which is governed by the Hamiltonian

\[
\hat{H} = \int d^3r \int d\omega \hat{f}^+ (r, \omega) \cdot \hat{f}(r, \omega)
\]

These equations represent a complete system. In particular, all the
electromagnetic field commutation relations are determined from the above
equations.

**IV.1.3. Integral representation of the electromagnetic field**

From the Maxwell equations it follows that the electric field obeys the
partial differential equation

\[
\nabla \times \nabla \times \hat{E}(r, r', \omega) - \frac{\omega^2}{c^2} \epsilon(r, \omega) \hat{E}(r, r', \omega) = i \omega \mu_0 \hat{j}(r, \omega)
\]

The solution of this equation can be represented as

\[
\hat{E}(r, \omega) = i \omega \mu_0 \int d^3r' \hat{G}(r, r', \omega) \cdot \hat{j}(r', \omega)
\]

where \( \hat{G}(r, r', \omega) \) represents the dyadic Green function (Green tensor) and
satisfies the equation

\[
\nabla \times \nabla \times \hat{G}(r, r', \omega) - \frac{\omega^2}{c^2} \hat{G}(r, r', \omega) = \delta(r - r') \mathbf{l}
\]
This equation, together with the appropriate boundary conditions, completely determines the Green function. The advantage of this method is that the calculation of the Green function becomes purely a classical problem.

**IV.1.4. Electromagnetic stress tensor**

The interaction between bodies is next described by constructing the electromagnetic stress tensor

\[
T(r, r') = T_1(r, r') + T_2(r, r') - \frac{1}{2} ITr[T_1(r, r') + T_2(r, r')] \tag{IV.1.24}
\]

Its components are calculated using the vacuum expectation values of the electromagnetic fields [27,117,118]

\[
T_1(r, r') = \varepsilon_0 \int \int \langle \hat{E}(r, \omega) \otimes \hat{E}(r', \omega') \rangle d\omega d\omega' \tag{IV.1.25}
\]

\[
T_2(r, r') = \frac{1}{\mu_0} \int \int \langle \hat{B}(r, \omega) \otimes \hat{B}(r', \omega') \rangle d\omega d\omega' \tag{IV.1.26}
\]

Using the expressions for the electric and magnetic fields and the following property of the dyadic GF [27]

\[
\frac{\omega^2}{c^2} \int ds \varepsilon(s, \omega) G_{ik}(r, s, \omega) G^*_{jk}(r', s, \omega) = \text{Im} G_{ij}(r, r', \omega) \tag{IV.1.27}
\]

the Maxwell stress tensor components are further expressed in terms of the dyadic GF as

\[
T_1(r, r') = \frac{\hbar}{\pi} \int_0^\infty d\omega \frac{\omega^2}{c^2} \text{Im} [G(r, r', \omega)] \tag{IV.1.28}
\]

\[
T_2(r, r') = -\frac{\hbar}{\pi} \int_0^\infty d\omega \text{Im} [\nabla \times G(r, r', \omega) \times \nabla^*] \tag{IV.1.29}
\]
where $\nabla$ introduces differentiation to the left.

In the next section the formalism shown above will be applied to determine the interaction between two concentric CNTs.
IV.2. Case of concentric carbon nanotubes

In this section the formalism developed in Section IV.1 is used to describe the interaction between two concentric CNTs. More specific, the goal is to determine the force per unit area (pressure) acting on each CNT surface and to relate it to the nanotubes individual dielectric response.

The system is modeled by two infinitely long, infinitely thin, continuous concentric cylinders with radii $R_1$ and $R_2$, immersed in vacuum, as shown in Fig. IV.2.1. Regarding the infinitely thin shells model, it proved to be a suitable description for interactions between CNTs since the electromagnetic interaction wavelength is much greater than the transverse size of the system. This model was successfully employed to explain experimental data involving long range interactions between CNTs and graphene layers [39]. Each cylinder is further characterized by the complex dynamic axial dielectric function $\varepsilon_{zz}(R_{1,2},\omega)$ with

![Figure IV.2.1. Schematics of the concentric nanotubes immersed in vacuum.](image-url)
the z-direction along the CNTs common axis. The transverse components of the
dielectric function are strongly suppressed [26,119-122], as compared to the
longitudinal component, due to the strong transverse depolarization effect in
CNTs. *Ab initio* calculations [119] show that the transverse dielectric function is
about 5 times smaller than the longitudinal dielectric function. When local field
effects are also included, the suppression is even stronger (10 to 100 times)
[120,121]. Experimental works also report that CNTs are almost completely
transparent for the electromagnetic radiation polarized perpendicular to the
nanotube axis [122]. Therefore, the transverse components of the dielectric
function are neglected here.

**IV.2.1. Quantization scheme**

The quantum theory applied to the interaction between CNTs involves an
electromagnetic field quantization scheme in the presence of dispersing and
absorbing bodies. The unified macroscopic quantum electrodynamics approach
developed in Section IV.1 is adapted to the particular cylindrical geometry of the
nanotubes. This procedure yields the second-quantized Hamiltonian

$$
\hat{H} = \sum_{i=1}^{2} \int d\omega \int d\mathbf{R}_j \hat{f}^+(\mathbf{R}_j,\omega) \cdot \hat{f}(\mathbf{R}_j,\omega)
$$

(IV.2.1)

of the vacuum-type medium assisted electromagnetic field field, with the bosonic
operators $\hat{f}^+$ ($\hat{f}$) creating (annihilating) surface electromagnetic excitations of
frequency $\omega$ at points $\mathbf{R}_{i,2} = (R_{i,2},\varphi_{i,2},z_{i,2})$. They satisfy the standard bosonic
commutation relations in Eqs. IV.1.17 and IV.1.18.
The Fourier images of the electric and magnetic fields are considered as quantum mechanical observables of the corresponding electric and magnetic field operators. They satisfy the Fourier-domain operator Maxwell equations with the additional exterior operator sources $\hat{\rho}$ and $\hat{j}$, as shown in Section IV.1, Eqs. IV.1.9-12. The sources, called the charge and noise current densities, account for the medium-induced absorption and are described by the imaginary part of the dielectric function. They are chosen in such a way to ensure the correct quantum electrodynamics equal-time commutation relations for the electric and magnetic field operators [27]. Following Ref. [27,31,32] the current density $\hat{j}$ is expressed as

$$\hat{j}(\mathbf{R}, \omega) = \frac{i}{\mu_0 c^2} \sqrt{\frac{\hbar}{\pi \epsilon_0}} \text{Im} \epsilon_{zz}(\mathbf{R}, \omega) \hat{f}(\mathbf{R}, \omega) \mathbf{e}_z$$

(IV.2.2)

where $\mathbf{e}_z$ is the unit vector along the CNTs common axis, and $\epsilon_0$, $\mu_0$ and $c$ are the vacuum dielectric constant, magnetic permeability and speed of light, respectively.

**IV.2.2. Dyadic Green function technique**

The Fourier-domain electric field operator at an arbitrary point $\mathbf{r} = (r, \varphi, z)$ is given by

$$\hat{E}(\mathbf{r}, \omega) = i \omega \mu_0 \sum_{i=1}^{2} d\mathbf{R}_i \mathbf{G}(\mathbf{r}, \mathbf{R}_i, \omega) \cdot \hat{j}(\mathbf{R}_i, \omega)$$

(IV.2.3)

where $\mathbf{G}(\mathbf{r}, \mathbf{R}_i, \omega)$ is the dyadic electromagnetic field Green function, satisfying the wave equation.
\[ \nabla \times \nabla \times G(r, r', \omega) - \frac{\omega^2}{c^2} G(r, r', \omega) = \delta(r - r') I \]  

(IV.2.4)

with \( I \) the unit tensor. Boundary conditions for the electromagnetic field components at the CNTs surfaces are further imposed

\[
\begin{align*}
&\mathbf{e}_r \times \left[ \hat{E}(r, \omega) \bigg|_{R_{l2}} - \hat{E}(r, \omega) \bigg|_{R_{l1}} \right] = 0 \\
&\mathbf{e}_r \times \left[ \hat{B}(r, \omega) \bigg|_{R_{l2}} - \hat{B}(r, \omega) \bigg|_{R_{l1}} \right] = \mu_0 \hat{J}(r, \omega) \bigg|_{R_{l1}}
\end{align*}
\]

(IV.2.5)  

(IV.2.6)

where \( \mathbf{e}_r \) is the unit vector along the radial direction. Eqs. IV.2.5 and IV.2.6 translate into the respective boundary conditions for the dyadic Green function

\[
\begin{align*}
&\mathbf{e}_r \times \left[ G(r, r', \omega) \bigg|_{R_{l2}} - G(r, r', \omega) \bigg|_{R_{l1}} \right] = 0 \\
&\mathbf{e}_r \times \nabla \times \left[ G(r, r', \omega) \bigg|_{R_{l2}} - G(r, r', \omega) \bigg|_{R_{l1}} \right] = i \omega \mu_0 \sigma^{(12)}(r, \omega) \cdot G(r, r', \omega) \bigg|_{R_{l1}}
\end{align*}
\]

(IV.2.7)  

(IV.2.8)

The discontinuity in Eq. IV.2.8 results from the full account of the finite absorption and dispersion for both CNTs by means of their conductivity tensors \( \sigma^{(12)} \), approximated, as earlier discussed, by their largest components \( \sigma^{(12)}_{zz} \) only

\[
\sigma^{(12)}_{zz}(R_{l1}, \omega) = -i \omega \varepsilon_0 \frac{\varepsilon_{zz}(R_{l2}, \omega) - 1}{S \rho_T}
\]

(IV.2.9)

with \( S \) being the CNT surface area and \( \rho_T \) the cubic density of the nanotubes.

The method of scattering superposition is further used [123,124] and the dyadic Green function is decomposed as \( G^{(fs)} = G^{(0)} \delta_{fs} + G^{(scatt)} \), where \( G^{(0)} \) and \( G^{(scatt)} \) represent the contributions of the direct and scattered waves, respectively, with a point-like field source located in region (s) and the field registered in region (f) (see Fig. IV.2.1). Following the procedure described in Refs. [123,124], the
dyadic Green function unbounded and scattering components $G^{(0)}$ and $G^{(fs)}_{scatt}$ are expanded into series of even and odd vector cylindrical functions with unknown coefficients. The specific representation of these components for cylindrical structures is given in Appendix B. This splits the electromagnetic modes in the system into transverse electric and magnetic polarizations, with Eqs. IV.2.7 and IV.2.8 yielding a set of 32 equations (16 for each polarization) with 32 unknown coefficients. Details about determining the unknown coefficients are given in Appendix C.

**IV.2.3. Forces (pressures) on the carbon nanotubes surfaces**

The electromagnetic stress tensor was constructed in Section IV.1.4. Here the interest is in the radial component $T_{rr}$ which describes the radiation pressure (force per unit area) of the virtual electromagnetic field on each CNT surface in the system. The net force per unit area exerted on one CNT is then calculated by subtracting the radiation pressures from both sides of the CNT surface [27,117], in the coincidence limit $r' \rightarrow r$

$$F_{i,2}/S = \lim_{r \rightarrow R, r' \rightarrow r} \left| \lim_{i \rightarrow R} \left( T^{(i)}_{rr}(r, r') - T^{(i+1)}_{rr}(r, r') \right) \right| i = 1, 2 \quad (IV.2.10)$$

It is found that the forces $F_{i,2}$ from Eq. IV.2.10 are of equal magnitude and opposite direction indicating attraction between the cylindrical surfaces. Their absolute values are given by
\[
|F_{12}/S| = \frac{\hbar c}{8\pi^3} \int_0^\infty \int_0^\infty \sum_n (2 - \delta_n^0) \eta^2 K_n^*(\eta R_{12}) K_n(\eta R_{12}) \\
+ \left( \frac{n^2}{R_{12}^2} + \eta^2 \right) K_n(\eta R_{12}) K_n(\eta R_{12}) \text{Re}(C^{(11)}_{\text{IV}} - C^{(22)}_{\text{IV}}) \\
- \left[ \eta^2 I_n(\eta R_{12}) K_n^*(\eta R_{12}) + \left( \frac{n^2}{r^2} + \eta^2 \right) I_n(\eta R_{12}) K_n(\eta R_{12}) \right] \text{Re}C^{(22)}_{\text{IV}} \\
- \left[ -\eta^2 I_n'(\eta R_{12}) I_n'(\eta R_{12}) + \left( \frac{n^2}{R_{12}^2} + \eta^2 \right) I_n'(\eta R_{12}) I_n'(\eta R_{12}) \right] \text{Re}C^{(22)}_{\text{IV}}
\]

where \( I_n(x) \) and \( K_n(x) \) are the modified Bessel functions of the first and second kind, respectively. The expressions of the coefficients in the above formula are given in Appendix C, and \( \eta^2 = \hbar^2 - k^2 \). Details about the derivation of the forces per unit area in Eq. IV.2.11 are given in Appendix D.

One notices that the Casimir force obtained by using the above approach accounts \textit{simultaneously} for the geometrical curvature effects (through the Green tensor) and the finite absorption and dissipation of each CNT (through their dielectric response).

As a final remark, it is interesting to compare the results with the well-established formula for the Casimir force between two perfectly conducting parallel plates [14], separated by a distance \( d \)

\[
\frac{F_{pp}}{S} = -\frac{\hbar c \pi^2}{240d^4}
\]

Taking the limit \( \sigma^{(1,2)} \to \infty, R_{12} \to \infty \) while keeping \( R_1 - R_2 = d \) it is found that
\[
\frac{|F|}{|S|} = \frac{\hbar c}{16\pi^2 R_1^4} \int x_i dx_i \sum_{n=0}^{\infty} I_n(x_1)K_n(x_2) - I_n(x_2)K_n(x_1)
\]
\[
\times \left[ x_i^2 K_n^2(x_1) + (n^2 + x_i^2)K_n^2(x_1) \right] \times \left[ \frac{l_n^2(x_1)K_n(x_2)}{K_n(x_1)} - 2l_n(x_1)i_n(x_2) \right] - \left[ x_i^2 l_n^2(x_1) + (n^2 + x_i^2)l_n^2(x_1) \right] \times K_n(x_1)K_n(x_2)
\]
\[
- 2\left[ x_i^2 l_n^2(x_1)K_n^2(x_1) + (n^2 + x_i^2)l_n(x_1)K_n(x_1) \right] \times l_n(x_2)K_n(x_1) \right] \right] (IV.2.13)
\]

where \( x_{1,2} = \eta R_{1,2} \). The above expression is obtained by making the transition to imaginary frequencies \( \omega \rightarrow i\omega \) and using the Euclidean rotation technique as described in Ref. [117,118]. This can be further evaluated by summing the series over \( n \) using the large-order Bessel function expansions [125]. The contributions from \( n = 0 \) and \( n \neq 0 \) are evaluated separately, as follows

\[
\frac{|F|}{|S|}_{n=0} = \frac{\hbar c}{8\pi^2} \int_0^\infty d\eta \eta^3 \frac{e^{-\eta d}}{e^{\eta d} - e^{-\eta d}} = \frac{\hbar c}{8\pi^2} \Gamma(4) \zeta(4) \frac{1}{(2d)^4} (IV.2.14)
\]

\[
\frac{|F|}{|S|}_{n \neq 0} = \frac{\hbar c}{4\pi^2} \sum_{n=1}^{\infty} \int_0^\infty \eta^3 d\eta \frac{e^{-n\eta d}}{e^{n\eta d} - e^{-n\eta d}} = \sum_{n=1}^{\infty} n^4 \int_0^{\infty} \eta^3 d\eta \sum_{m=1}^{\infty} e^{-2n\eta dm} \approx \frac{6\zeta(4)}{(2d)^4} (IV.2.15)
\]

This results in

\[
\frac{|F|}{|S|} = \frac{9\zeta(4) \hbar c}{64 \pi^2 d^4} (IV.2.16)
\]

which is about \( \frac{1}{3} \) of the Casimir formula for parallel plates. The difference is attributed to the uniaxial model used for the CNTs dielectric response. Furthermore, the result correctly reproduces the power law dependence of the pressure to the plates separation distance \( d \).
Chapter V

Applications to the quantum electrodynamics approach

The interaction between two concentric carbon nanotubes is considered using the previously developed quantum electrodynamical approach. The method includes the absorptive and dispersive properties via the chirality dependent dielectric response functions for each carbon nanotube. It is found that at small nanotube separations, similar to their equilibrium distances, the interaction is dominated by the collective excitations in the electron energy loss spectra originating from interband transitions. The existence of strong low frequency transitions peaks from both tubes and their overlap are responsible for their stronger interaction. Nanotube chiralities possessing such collective excitation features are found to have the strongest interaction. Furthermore, this study determines unambiguously the role of the collective surface excitations in the energetic stability of double wall carbon nanotubes of various chiral combinations.
V.1. Chirality dependent interactions

The quantum electrodynamics approach is applied next to the case of two interacting concentric cylindrical graphene sheets comprising a double wall carbon nanotube. As previously shown, the method allows taking into account the full CNTs cylindrical geometry by solving the Fourier-domain operator Maxwell equations with appropriate boundary conditions and including their particular dielectric functions. The individual nanotubes are characterized by their chirality dependent dielectric response. Since CNTs of virtually same radial size can possess different electronic properties, investigating their interactions presents a unique opportunity to obtain insight into the specific dielectric response features affecting the force between different cylindrical surfaces. This approach allows to investigate these features together, or separately, and to uncover the underlying mechanisms of the energetic stability of different double wall carbon nanotubes combinations. An additional advantage here is that the dielectric function can be calculated explicitly for each chirality. Therefore, one can determine clearly how the semiconducting or metallic nature of each CNT contributes to their mutual interaction.

V.1.1. Axial dielectric response

The calculation of the forces on CNT surfaces requires full knowledge of the frequency dependence of their dielectric response. Following the procedure outlined in Ref. [26] the nearest neighbor tight binding model and the random phase approximation are used to determine the chirality dependent dielectric
response, with the electronic dissipation processes taken into account in the relaxation time approximation. It was shown [1,26,29] that the $\pi$-bands of an $(a,b)$ CNT are well described within the tight-binding approximation

$$E_{\pm}(N,k) = \pm t_0 \sqrt{1 + 4 \cos \left( \frac{2\pi N}{a} - \frac{a + 2b}{2a} kl \right) \cos \frac{kl}{2} + 4 \cos^2 \frac{kl}{2}} \quad (V.1.1)$$

where $t_0$ is the hopping energy, $l$ is $3/2$ times the interatomic distance, $N = 0,1,\ldots,a-1$, and $-\pi/l \leq k \leq \pi/l$. The minus and plus subscripts stand for the valence and conduction band, respectively. The main contribution to the conductivity is given by the parallel dielectric function [26], which is decomposed into a Drude part and a part originating from (transversely quantized) interband electronic transitions

$$\varepsilon_{zz} = \varepsilon_{zz}^D + \varepsilon_{zz}^{\text{inter}} \quad (V.1.2)$$

The interband transition term is given by [26]

$$\varepsilon_{\text{inter}}^{\omega}(\omega) = 1 + \left( \frac{\hbar^2}{m} \right)^2 \frac{4 \rho_c}{al} \sum_{N} \int_{-\pi/l}^{\pi/l} \frac{dp}{E_+(N,p) - E_-(N,p)} \frac{f(E_+(N,p)) - f(E_-(N,p))}{E_+(N,p) - E_-(N,p)}$$

$$\times \frac{[\text{Re} \tilde{K}_0(N,p)]^2}{(\hbar \omega)^2 + i\hbar \omega / \tau_r - [E_+(N,p) - E_-(N,p)]^2} \quad (V.1.3)$$

where $\tau_r$ is a phenomenological relaxation time, $f(E)$ is the Fermi distribution function, and $\rho_c = 2a \rho_T$ is the density of carbon atoms per volume. The quantity $K_0(N,p)$ corresponds to the matrix element of the momentum operator and is described in detail in Ref. [26].

The Drude term is given by
where $\omega_{pl}$ is the plasma frequency

$$\omega_{pl}^2 = -\left(\frac{e^2}{m}\right)^2 \frac{2\rho_e}{a l} \sum_{N} \int_{-\pi/l}^{\pi/l} dp [\text{Im} K_0(N, p)]^2$$

$$\times \left[f^* (E_+(N, p)) + f^* (E_-(N, p))\right]$$

The numerical values for all parameters are taken from Ref. [26].

**V.1.2. Chirality dependent interactions**

Next the pressure on the CNTs surfaces is numerically evaluated as a function of the inter-tube surface-to-surface distance for various pairs of CNTs. The inner CNT is chosen to be the achiral (12,12) metallic nanotube, and the outer tubes are of various chiralities. The results are shown in Fig. V.1.1. As a general trend, the pressure decreases in strength as the surface-to-surface distance increases. For zigzag $(m,0)$ and armchair $(n,n)$ outer nanotubes this dependence is monotonic, whereas for chiral nanotubes the pressure decreases as a function of the separation distance $d$ in a rather irregular fashion. As the outer CNT is changed, one can imagine double wall CNTs consisting of metal/metal or metal/semiconductor combinations of different chiralities but of similar radial dimensions. One notices that the attraction is stronger if the outer CNT is an armchair $(n,n)$ type as compared to the attraction for the outer $(m,0)$ zigzag CNTs. At small separation distances the difference can be quite significant. For example, the attraction between $(27,4)@(12,12)$ and
(21,13)@(12,12) differ by about 20% in favor of the second pair, even though the radial difference is only 0.2 Å. These differences become smaller as the inter-tube surface to surface separation becomes larger, and they eventually become negligible as the force diminishes at large distances.

The pressure on CNTs surfaces is also calculated using the Drude contribution only in each CNT dielectric response and it is shown in the inset of Fig. V.1.1. The attraction is stronger when the interband transitions are neglected, and the decrease of the pressure as a function of the separation $d$ is monotonic. As the full dielectric response is considered, the pressure is
differently affected due to the chirality dependent interband electronic transitions of each individual CNT. These differences become less significant at large surface to surface separations, and it is found that for $d \approx 15\text{Å}$, this difference is less than 10%.

To further investigate the role of the CNTs geometry and dielectric response on their mutual interaction, different pairs of nanotubes with the same chiralities and different radial sizes, or nanotubes with similar radial dimensions and different chiralities are considered. For CNTs with the same chiralities and different radial sizes, the increase in the surface to surface separation results in a
monotonic decrease in their mutual interaction strength, as shown in Fig. V.1.2. Regarding the case of CNT pairs with similar radial dimensions and different chiralities, additional semi-metallic (21,0) and semiconducting (20,0) inner nanotubes are considered in combination with various achiral outer nanotubes. These CNTs are of comparable radii, 8.22Å and 7.83Å, respectively, and similar to the 8.14Å radius of the (12,12) CNT. The calculated pressure versus the inter-tube separation distance is shown in Fig. V.1.2. Depending on the outer CNTs type, it is found that the interaction is weaker when there are two zigzag concentric CNTs. The fact that some of these are semi-metallic and others are semiconducting does not seem to influence the magnitude and monotonic decrease of their mutual interaction with the separation distance. By comparing Figs. V.1.1 and V.1.2 one notices that the curves for \((m,0)@(12,12)\), \((n,n)@(21,0)\), and \((n,n)@(20,0)\) are practically overlapping, meaning that the specific location of the zigzag and armchair tubes (inner or outer) is of no significance to the interaction. The small deviations can be attributed to the small differences in the inner CNT radii. However, it is found that the strongest interaction occurs between two armchair CNTs. The same calculations were performed for many different achiral nanotubes, and it was found that these features are not unique just for the considered CNTs. The strongest interaction always occurs between two armchair CNTs, provided that their radial dimensions are similar.

These results are strongly indicative that the CNTs detailed electronic properties have a strong effect on their mutual interaction, particularly for
relatively small separation distances of interest here. The dominant contribution of collective excitations (plasmonic modes in particular) to the Casimir interactions has already been realized for planar [126,127] and linear [128] metallic systems. To further investigate the features originating from the CNTs collective excitation properties, the electron energy loss spectroscopy (EELS) spectra, given by \(-\text{Im}[1/\varepsilon(\omega)]\), are calculated using the formalism described in Section V.1.1. The results for the representative CNT types are given in Fig. V.1.3. The peaks in EELS spectra are interpreted as collective plasmon excitations originating from interband transitions between the Brillouin zone van...
Hove singularities [1,129] of each CNT. Comparison of these spectra for various inner and outer CNTs combinations shows that the low frequency plasmon peaks are key to the strength of their mutual interaction. It is found that, in general, armchair tubes always have strong, well pronounced interband plasmon excitations in the low frequency range (see Fig. V.1.3(a) and (c)). Zigzag and most chiral CNTs have low frequency interband plasmons, too, but they are not as near as well pronounced as those in armchair tubes (Fig. V.1.3(b) and (d)); their stronger plasmon modes are found at higher frequencies. For example, for
the cases shown in Fig. V.1.3, one finds well pronounced plasmon transitions for the (12,12) CNT at $\omega_1 = 2.18$ eV and $\omega_2 = 3.27$ eV, and at $\omega_1 = 1.63$ eV and $\omega_2 = 2.45$ eV for the (17,17) CNT. At the same time, no such well-defined strong low frequency excitations in the (21,0) and (30,0) CNTs cases are found. Fig. V.1.4 shows that the attraction in (17,17)@(12,12) system is much stronger than the attraction in (30,0)@(21,0), even though the radial sizes of the involved CNTs are approximately the same. One also notes that for the case of (17,17)@(21,0) there is only one such low frequency excitation coming from the armchair tube, and consequently the interaction force has an intermediate value as compared to the above discussed two cases.

These results suggest that the strongest interaction occurs between CNTs with well pronounced overlapping low frequency plasmon excitations. This is also consistent with the conclusion of Ref. [128] for generic one-dimensional plasmonic structures. However, in this case involving CNTs the interband plasmons originate from the space quantization of the transverse electronic motion, and therefore have a different frequency-momentum dispersion law (constant) as compared to that normally assumed (linear) for plasmons [130]. Further, the interaction is weaker when only one of the CNTs supports strong low frequency interband plasmon modes, and the weakest interaction occurs when neither CNT has strong low frequency plasmons.

To bring more insight into the role of the collective response properties of the involved CNTs, a generic case of two concentric CNTs where each nanotube supports only one plasmon excitation peak is considered next. This configuration
allows individually changing the relative position and strength of the CNT plasmon peaks and uncovering more characteristic features originating from the EELS spectra. The considered CNT system has radii \( R_1 = 11.63 \text{Å} \) and \( R_2 = 8.22 \text{Å} \). The dielectric function of each nanotube is taken to be of the generic Lorentzian form

\[
\varepsilon(R_{12}, \omega) = 1 - \frac{\Omega^2}{\omega^2 - \omega_{12}^2 + i\omega\Gamma}
\]  

\( \text{(V.1.6)} \)
with typical values for nanotubes $\Omega = 2.7 \text{ eV}$ and $\Gamma = 0.03 \text{ eV}$ [29]. Then, the EELS spectrum has only one plasmon resonance at $\omega_{2}$ for each nanotube. The plasmon peak location for the inner nanotube is kept constant (four values are chosen for $\omega_{2}$ ) while the plasmon transition location for the outer nanotube is varied (see inset of Fig. V.1.5). The calculated pressure on the tubes surfaces as a function of the outer nanotube plasmon frequency resonances is shown in Fig. V.1.5. One notices the occurrence of local minima when the plasmonic excitations of both CNTs overlap. In fact, the strongest attraction occurs when both CNTs have the lowest plasmon excitations at the same frequency $\omega_{1} = \omega_{2}$. This indicates that the existence of relatively strong low frequency EELS spectrum and an overlap between the relevant plasmon peaks of the two structures are necessary to achieve a strong interaction.

This study clearly demonstrates the crucial importance of the collective low energy surface plasmon excitations along with the cylindrical geometry for the long-ranged interaction in a double wall CNT system. The presented approach provides the unique opportunity to investigate these features together and to uncover underlying mechanisms of the energetic stability of different double wall CNT combinations. The results are in good agreement with experimental measurements on determining the chirality of individual double wall CNTs. Electron diffraction methods [131,132] have shown that the chiral spectrum of nanotubes with average size distributions has displayed a tendency for both the inner and outer nanotubes to be of armchair type. Thus these results
may be viewed as describing one of the possible reasons for the preference of having a double wall CNT formed by two armchair ones.
Chapter VI

Concluding remarks

In the continuous race for miniaturization, nanotubes are of great interest because of their prospective as components in various nanoscale devices. Therefore, the detailed knowledge of CNTs interaction is essential for their proper use in nanotechnological applications.

A theoretical framework describing the nanotubes interaction, involving two distinct approaches, was presented. Based on the results obtained practical applications using CNTs were further proposed.

First a classical approach to the interaction between CNTs is considered. The systems total potential energy is estimated within the continuum model approximation by using a Lennard-Jones type of interatomic potential. This approach was then applied for different geometrical configurations, such as parallel or concentric carbon nanotubes. For all the cases analytical expressions for the systems potential energies were derived.

The results obtained using the classical approach were used to propose a few practical applications. First a method for profiling surfaces based on the concept of a double wall carbon nanotube oscillator is suggested. By studying the details of the carbon nanotubes motion, a non-contact device for profiling
surfaces is proposed as an alternative to a conventional atomic force microscope probe. Next carbon nanotubes with different types of radial deformations were considered. By describing these deformations with analytical models, interesting results in terms of the carbon nanotubes preferred mutual orientations were found. The concept of an universal graphitic potential curve, valid for undeformed carbon nanotubes, was extended for the case of radially deformed carbon nanotubes. Last, a custom telescopic double wall carbon nanotube for nanolithography applications was proposed. Such a device can be effectively used for thermally producing patterns on surfaces with major advantages. These advantages include high spatial resolution and the elimination of the active feedback mechanism.

Next the interaction between nanotubes was considered using a quantum electrodynamics approach suitable for dispersing and absorbing media. Each carbon nanotube is characterized by its individual dielectric response, which is a complex function of frequency. The quantization scheme considers the Fourier images of the electric and magnetic fields as quantum mechanical observables of the corresponding electric and magnetic field operators. They satisfy the Fourier-domain operator Maxwell equations with the additional exterior operator sources, which account for the medium-induced absorption. The electromagnetic field is further represented using the dyadic Green function technique. The method allows taking into account the full carbon nanotube cylindrical geometry by imposing the appropriate boundary conditions at the nanotubes surfaces.
forces acting on the nanotubes surfaces are determined from the electromagnetic stress tensor.

It was found that at small nanotube separations, similar to their equilibrium distances, the interaction is dominated by the collective excitations in the electron energy loss spectra originating from interband transitions. The existence of strong low frequency transitions peaks from both tubes and their overlap are responsible for their stronger interaction. Nanotube chiralities possessing such collective excitation features were found to have the strongest interaction. Furthermore, this study determines unambiguously the role of the collective surface excitations in the energetic stability of double wall carbon nanotubes of various chiral combinations.
References


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Appendix A

Intertube van der Waals potential for concentric nanotubes

The intertube vdW potential is calculated by the integrating the LJ type of potential over the surfaces of the nanotubes

$$V = \sigma^2 \int_0^{2\pi} d\varphi_1 \int_0^{2\pi} d\varphi_2 \int_{-L_1}^{L_1} d\zeta_1 \int_{-L_2}^{L_2} d\zeta_2 R_1 R_2 \left( -\frac{A}{\rho^6} + \frac{B}{\rho^{12}} \right)$$  \hspace{1cm} (A1)

where the distance between two points located on the two nanotubes $\rho$ is expressed as

$$\rho = \left[ (x_{\text{out}} - x_{\text{in}})^2 + (y_{\text{out}} - y_{\text{in}})^2 + (z_{\text{out}} - z_{\text{in}})^2 \right]^{1/2}$$  \hspace{1cm} (A2)

The corresponding coordinates for the inner (denoted as $\text{in}$) and outer (denoted as $\text{out}$) nanotubes are:

$$x_{\text{in}} = R_1 \cos \varphi_1$$ \hspace{1cm} (A3)

$$y_{\text{in}} = R_1 \sin \varphi_1$$ \hspace{1cm} (A4)

$$z_{\text{in}} = z_1 + z_0$$ \hspace{1cm} (A5)

$$x_{\text{out}} = R_2 \cos \varphi_2$$ \hspace{1cm} (A6)

$$y_{\text{out}} = R_2 \sin \varphi_2$$ \hspace{1cm} (A7)

$$z_{\text{out}} = z_2$$ \hspace{1cm} (A8)

where $\varphi_1$ and $\varphi_2$ are the azimuthal angles for each nanotube.
Further, the distance between two typical points located on the two tubes is rewritten as

\[ \rho = (\eta_1 + \eta_2 \sin^2 x)^{1/2} \]  

(A9)

where

\[ x = \frac{\varphi_1 - \varphi_2}{2} \]  

(A10)

\[ \eta_1 = (R_1 - R_2)^2 + (z_0 + z_1 - z_2)^2 \]  

(A11)

\[ \eta_2 = R_1 R_2 \]  

(A12)

Next, the integration over the first angular variable in Eq. (A1) is performed, and one obtains integrals of the following form:

\[ I_m = 2 \int_{-\frac{\pi}{2}}^{\frac{\varphi_2}{2}} \frac{1}{(\eta_1 + \eta_2 \sin^2 x)^m} dx \]  

(A13)

with \( m = 6 \) and \( m = 12 \). Without loss of generality the integration limits can be shifted, for example making \( \varphi_2 = 0 \), and the integrals become:

\[ I_m = 4 \int_{0}^{\frac{\pi}{2}} \frac{1}{(\eta_1 + \eta_2 \sin^2 x)^m} dx \]  

(A14)

Using the substitutions

\[ t = \cot x \]  

(A15)

\[ \eta_3 = \frac{\eta_1}{\eta_1 + \eta_2} \]  

(A16)

\[ n = \frac{m}{2} \]  

(A17)

in (A14), one obtains
\[ I_{2n} = \frac{4}{(\eta_1 + \eta_2)^n} \int_0^\infty \frac{(t^2 + 1)^{n-1}}{(\eta_3 t^2 + 1)^n} dt \]  \hspace{1cm} (A18)

By substituting further

\[ t = \frac{z}{\sqrt{1 - z^2}} \]  \hspace{1cm} (A19)

in (A18) the integrals become

\[ I_{2n} = \frac{2}{(\eta_1 + \eta_2)^n} \int_0^1 \frac{(1 - z^2)^{-1/2}}{(1 - z^2(1 - \eta_3))^{n}} dz \]  \hspace{1cm} (A20)

Using the definition of the hypergeometric function [133]:

\[ F(\alpha, \beta, \gamma; z) = \frac{1}{B(\beta, \gamma - \beta)} \int_0^1 t^{\beta-1}(1-t)^{\gamma-\beta-1}(1-tz)^{-\alpha} dt \]  \hspace{1cm} (A21)

where \( B(x, y) \) is the beta function [133]:

\[ B(x, y) = 2 \int_0^{\pi/2} \sin^{2x-1} \varphi \cos^{2y-1} \varphi d\varphi \]  \hspace{1cm} (A22)

and making the substitutions

\[ \alpha = n \]  \hspace{1cm} (A23)
\[ \beta = \frac{1}{2} \]  \hspace{1cm} (A24)
\[ \gamma = 1 \]  \hspace{1cm} (A25)
\[ z = \frac{\eta_2}{\eta_1 + \eta_2} \]  \hspace{1cm} (A26)

one obtains:

\[ I_{2n} = \frac{2\pi}{(\eta_1 + \eta_2)^n} F(n, \frac{1}{2}, \frac{\eta_2}{\eta_1 + \eta_2}) \]  \hspace{1cm} (A27)

Using the transformation formula [133]:
\[
F(\alpha, \beta, \gamma; z) = (1 - z)^{\alpha} F(\alpha, \gamma - \beta, \gamma; \frac{z}{z - 1})
\]  

(A28)

one finally gets Eq. II.3.9.
Appendix B

Dyadic Green function representation for cylindrical structures

Using the method of scattering superposition [123,124], the dyadic Green function is decomposed as $G^{(fs)} = G^{(0)} \delta_{fs} + G^{(fs)}_{\text{scatt}}$. The unbounded part $G^{(0)}$ represents the contribution of the direct waves from sources in an unbounded medium, and the scattering part $G^{(fs)}_{\text{scatt}}$ describes additional contribution of the multiple reflection and transmission waves from the CNT surfaces. The indices $(f)$ and $(s)$ stand for point-like field sources located in region $(s)$ and fields located in region $(f)$, according to Fig. IV.2.1.

In order to satisfy the homogeneous Helmholtz equation (Eq. IV.2.4) and the radiation condition at infinity, the two contributions are taken to be in the following forms:

$$G^{(0)}(r, r', \omega) = -\frac{e_r e_r \delta(r - r')}{k^2} + \frac{i}{8\pi} \int dh \sum_{n=0}^\infty (2 - \delta_n^2) \frac{(2 - \delta_n)}{\eta^2} \left\{ M_n^{(1)}(h) M_n^{(1)*}(-h) + N_n^{(1)}(h) N_n^{(1)*}(-h), r > r' \right\}$$

$$\times \left\{ M_n^{(1)}(h) M_n^{(1)*}(-h) + N_n^{(1)}(h) N_n^{(1)*}(-h), r < r' \right\} \quad (B1)$$
\[ \mathbf{G}^{(fs)}_{\text{scat}}(\mathbf{r}, \mathbf{r}', \omega) = \frac{i}{8\pi} \int_{-\infty}^{\infty} dh \sum_{n=0}^{\infty} \frac{(2-\delta_n^3)}{\eta^2} \]

\[
\left\{ (1-\delta_n^3) \mathbf{M}_{n\eta}^{(1)}(h) + (1-\delta_n^3) \mathbf{N}_{n\eta}^{(1)}(h) \right\} \mathbf{M}_{n\eta}^{(1)}(-h) + (1-\delta_n^3) \mathbf{N}_{n\eta}^{(1)}(-h)
\]

\[ + (1-\delta_n^3) \mathbf{M}_{n\eta}^{(1)}(h) \mathbf{M}_{n\eta}^{(1)}(-h) + (1-\delta_n^3) \mathbf{N}_{n\eta}^{(1)}(h) \mathbf{N}_{n\eta}^{(1)}(-h) \]

\[ + (1-\delta_n^3) \mathbf{M}_{n\eta}^{(1)}(h) + (1-\delta_n^3) \mathbf{N}_{n\eta}^{(1)}(h) \]

\[ + (1-\delta_n^3) \mathbf{M}_{n\eta}^{(1)}(h) (1-\delta_n^3) \mathbf{M}_{n\eta}^{(1)}(h) + (1-\delta_n^3) \mathbf{N}_{n\eta}^{(1)}(h) \mathbf{N}_{n\eta}^{(1)}(h) \]

\[ + (1-\delta_n^3) \mathbf{M}_{n\eta}^{(1)}(h) (1-\delta_n^3) \mathbf{M}_{n\eta}^{(1)}(h) + (1-\delta_n^3) \mathbf{N}_{n\eta}^{(1)}(h) \mathbf{N}_{n\eta}^{(1)}(h) \]

\[ + (1-\delta_n^3) \mathbf{M}_{n\eta}^{(1)}(h) (1-\delta_n^3) \mathbf{M}_{n\eta}^{(1)}(h) + (1-\delta_n^3) \mathbf{N}_{n\eta}^{(1)}(h) \mathbf{N}_{n\eta}^{(1)}(h) \]

\[ + (1-\delta_n^3) \mathbf{M}_{n\eta}^{(1)}(h) (1-\delta_n^3) \mathbf{M}_{n\eta}^{(1)}(h) + (1-\delta_n^3) \mathbf{N}_{n\eta}^{(1)}(h) \mathbf{N}_{n\eta}^{(1)}(h) \]

where \( h^2 = k^2 - \eta^2 \) and \( k = \omega/c \). The even (e) and odd (o) cylindrical vector wave functions are defined as

\[ \mathbf{M}_{n\eta}(h) = \nabla \times \left[ Z_n(\eta r) \cos(n\varphi) e^{i\eta z} \right] \]

\[ \mathbf{N}_{n\eta}(h) = \frac{1}{\sqrt{h^2 + \eta^2}} \nabla \times \nabla \times \left[ Z_n(\eta r) \cos(n\varphi) e^{i\eta z} \right] \]

The symbol \( Z_n(x) \) has to be replaced either by the Bessel function \( J_n(x) \)
or, if the superscript (1) is present, by the Hankel function of the first kind \( H^{(1)}_n(x) \).
The prime denotes the cylindrical coordinates \((r', \varphi', z')\) of the source. The coefficients \( c_{m\eta}^{(fs)} \), with \( m = 1,2,3,4 \) and \( P = H \) for transverse electric waves or \( P = V \) for transverse magnetic waves, are to be determined from the boundary conditions.

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Appendix C

Green tensor for concentric carbon nanotube systems

The boundary conditions for the electromagnetic field components at the CNTs surfaces, in terms of the dyadic Green function components, are given in Section IV.2.2 (Eqs. IV.2.7 and IV.2.8). Using dyadic analysis definitions for the anterior vector product

\[ \hat{r} \times \mathbf{G} = \sum_{j=1}^{3} (\hat{r} \times \mathbf{G}_j) \hat{e}_j \]  

(C1)

and the curl of a dyadic function

\[ \nabla \times \mathbf{G} = \sum_j (\nabla \times \mathbf{G}_j) \hat{e}_j = \sum_i \sum_j (\nabla \mathbf{G}_{ij} \times \hat{e}_j) \hat{e}_j \]  

(C2)

one gets the boundary conditions in matrix form

\[
\begin{pmatrix}
0 & 0 & 0 \\
\mathbf{G}^{(1)}_{zr} & -\mathbf{G}^{(1)}_{zp} & -\mathbf{G}^{(1)}_{zz} \\
\mathbf{G}^{(1)}_{\varphi r} & \mathbf{G}^{(1)}_{\varphi p} & \mathbf{G}^{(1)}_{\varphi z}
\end{pmatrix}_{R_1^{-}} \left[ \begin{array}{c}
0 \\
0 \\
0
\end{array} \right]_{R_1^{+}} = 0
\]  

(C3)
The decomposition scheme for the Green tensor components is given in Appendix B. Here the explicit form of the dyadic Green's functions components are shown next for zone 1 (outside the CNTs system), for illustration purposes. The source is chosen to be always in zone 2 in these examples, so it was omitted further from the coefficients superscripts for simplicity.

\[
\begin{pmatrix}
-\frac{1}{r} G^{(1)}_{\varphi r} - \frac{\partial G^{(1)}_{\varphi r}}{\partial r} + \frac{1}{r} \frac{\partial G^{(1)}_{\varphi \varphi}}{\partial \varphi} \\
-\frac{1}{r} G^{(2)}_{\varphi r} - \frac{\partial G^{(2)}_{\varphi r}}{\partial r} + \frac{1}{r} \frac{\partial G^{(2)}_{\varphi \varphi}}{\partial \varphi} \\
-\frac{1}{r} G^{(1)}_{\varphi \varphi} - \frac{\partial G^{(1)}_{\varphi \varphi}}{\partial \varphi} + \frac{1}{r} \frac{\partial G^{(1)}_{\varphi \varphi}}{\partial r}
\end{pmatrix}_{R_1} = \pm i \omega \mu_0 \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
\sigma_{zz} G_{zz}^{(1)} & \sigma_{zz} G_{zz}^{(1)} & \sigma_{zz} G_{zz}^{(1)}
\end{pmatrix}_{R_1} \tag{C4}
\]

\[
(G^{(1)}_{a r}) = \frac{i}{8\pi} \sum_{n=0}^{\infty} \frac{2 - \delta_{n0}}{\eta^2} \times \left(\begin{pmatrix}
c^{(1)}_{1m} \frac{n^2}{r^2} H_{n} (\eta r) J_{n} (\eta r') \\
c^{(1)}_{1m} \frac{n^2}{r^2} H_{n} (\eta r) J_{n} (\eta r')
\end{pmatrix} \right) \sin(n\varphi) \sin(n\varphi') + c^{(1)}_{1m} \frac{n^2}{r^2} H_{n} (\eta r) H_{n} (\eta r') \cos(n\varphi) \cos(n\varphi')
+ \left(\begin{pmatrix}
\eta^2 h^2 H'_{n} (\eta r) J_{n} (\eta r') + c^{(1)}_{1m} \eta^2 h^2 H'_{n} (\eta r) H_{n} (\eta r')
\end{pmatrix} \right) \cos(n\varphi) \sin(n\varphi') \sin(n\varphi) \sin(n\varphi')
+ \left(\begin{pmatrix}
\frac{in\eta h}{kr} H_{n} (\eta r) J_{n} (\eta r') + c^{(1)}_{1m} \frac{in\eta h}{kr} H_{n} (\eta r) H_{n} (\eta r')
\end{pmatrix} \right) \sin(n\varphi) \cos(n\varphi') \cos(n\varphi) \cos(n\varphi')
+ \left(\begin{pmatrix}
\frac{in\eta h}{kr} H_{n} (\eta r) J_{n} (\eta r') + c^{(1)}_{1m} \frac{in\eta h}{kr} H_{n} (\eta r) H_{n} (\eta r')
\end{pmatrix} \right) \cos(n\varphi) \sin(n\varphi') \sin(n\varphi) \sin(n\varphi') \tag{C5}
\]

\[
\int \sum e^{i(2 - \delta_{n0})} \frac{2 - \delta_{n0}}{\eta^2} \times \left(\begin{pmatrix}
c^{(1)}_{1m} \frac{n^2}{r^2} H_{n} (\eta r) J_{n} (\eta r') \\
c^{(1)}_{1m} \frac{n^2}{r^2} H_{n} (\eta r) J_{n} (\eta r')
\end{pmatrix} \right) \sin(n\varphi) \sin(n\varphi') + c^{(1)}_{1m} \frac{n^2}{r^2} H_{n} (\eta r) H_{n} (\eta r') \cos(n\varphi) \cos(n\varphi')
+ \left(\begin{pmatrix}
\eta^2 h^2 H'_{n} (\eta r) J_{n} (\eta r') + c^{(1)}_{1m} \eta^2 h^2 H'_{n} (\eta r) H_{n} (\eta r')
\end{pmatrix} \right) \cos(n\varphi) \sin(n\varphi') \sin(n\varphi) \sin(n\varphi')
+ \left(\begin{pmatrix}
\frac{in\eta h}{kr} H_{n} (\eta r) J_{n} (\eta r') + c^{(1)}_{1m} \frac{in\eta h}{kr} H_{n} (\eta r) H_{n} (\eta r')
\end{pmatrix} \right) \sin(n\varphi) \cos(n\varphi') \cos(n\varphi) \cos(n\varphi')
+ \left(\begin{pmatrix}
\frac{in\eta h}{kr} H_{n} (\eta r) J_{n} (\eta r') + c^{(1)}_{1m} \frac{in\eta h}{kr} H_{n} (\eta r) H_{n} (\eta r')
\end{pmatrix} \right) \cos(n\varphi) \sin(n\varphi') \sin(n\varphi) \sin(n\varphi') \tag{C5}
\]
\[
\left( G_\phi \right)_{\nu \phi} = \frac{i}{8\pi} \int dh \sum_{n=0}^\infty \frac{2 - \delta_n^0}{\eta^2} \times \left\{ \pm c_{\nu \phi}^{(t)} \frac{n \eta}{r} H_n(\eta r) J_n(\eta r') \right. \\
\left. \pm c_{\nu \phi}^{(t)} \frac{n \eta}{r} H_n(\eta r) H_n(\eta r') \sin(n\phi) \cos(n\phi') \cos(n\phi) \sin(n\phi') \right\} e^{i(n\phi - n\phi')}
\]
\[
\left( G_\phi \right)_{\nu z} = \frac{i}{8\pi} \int dh \sum_{n=0}^\infty \frac{2 - \delta_n^0}{\eta^2} \times \left\{ c_{\nu \phi}^{(t)} \frac{n \eta^3}{k^2} H_n(\eta r) J_n(\eta r') \right. \\
\left. + c_{\nu \phi}^{(t)} \frac{n \eta^2}{k^2} \cos(n\phi) \cos(n\phi') \sin(n\phi) \sin(n\phi') \right\} e^{i(n\phi - n\phi')}
\]
\[
\left( G_\phi \right)_{\nu r} = \frac{i}{8\pi} \int dh \sum_{n=0}^\infty \frac{2 - \delta_n^0}{\eta^2} \times \left\{ \pm c_{\nu \phi}^{(t)} \frac{n \eta}{r'} H_n(\eta r) J_n(\eta r') \right. \\
\left. \pm c_{\nu \phi}^{(t)} \frac{n \eta}{r'} H_n(\eta r) H_n(\eta r') \sin(n\phi) \cos(n\phi') \cos(n\phi) \sin(n\phi') \right\} e^{i(n\phi - n\phi')}
\]
\[
\left( G_\phi \right)_z = \frac{i}{8\pi} \int dh \sum_{n=0}^\infty \frac{2 - \delta_n^0}{\eta^2} \times \left\{ \pm c_{\nu \phi}^{(t)} \frac{n \eta}{r'} H_n(\eta r) J_n(\eta r') \right. \\
\left. \pm c_{\nu \phi}^{(t)} \frac{n \eta}{r'} H_n(\eta r) H_n(\eta r') \sin(n\phi) \cos(n\phi') \cos(n\phi) \sin(n\phi') \right\} e^{i(n\phi - n\phi')}
\]
\(G_{\varphi}^{(1)}\) = \(i \frac{\gamma}{8\pi} \int dh \sum_{n=0}^{\infty} \frac{2 - \delta_{n}^0}{\eta^2} \times \left\{ c_{2H}^{(1)} \eta^2 H_n^* (\eta \gamma) J_n^* (\eta \gamma') \cos(n \varphi) \cos(n \varphi') + \frac{c_{2H}^{(1)} n^2 \eta^2}{k^2 r^2} H_n (\eta \gamma) H_n (\eta \gamma') \sin(n \varphi) \sin(n \varphi') \right\} + \left( c_{2H}^{(1)} \eta^2 H_n (\eta \gamma) J_n (\eta \gamma') + \frac{c_{2H}^{(1)} n \eta^2}{k^2 r} H_n (\eta \gamma) H_n (\eta \gamma') \right) \cos(n \varphi) \sin(n \varphi') \right\} e^{\theta(z - z')} \) (C9)

\(G_{\varphi}^{(1)}\) = \(i \frac{\gamma}{8\pi} \int dh \sum_{n=0}^{\infty} \frac{2 - \delta_{n}^0}{\eta^2} \times \left\{ c_{2H}^{(1)} \eta^2 H_n (\eta \gamma) J_n (\eta \gamma') \sin(n \varphi) \cos(n \varphi') + \frac{c_{2H}^{(1)} n^2 \eta^2}{k^2 r^2} H_n (\eta \gamma) H_n (\eta \gamma') \cos(n \varphi) \cos(n \varphi') \right\} + \left( c_{2H}^{(1)} \eta^2 H_n (\eta \gamma) J_n (\eta \gamma') + \frac{c_{2H}^{(1)} n \eta^2}{k^2 r} H_n (\eta \gamma) H_n (\eta \gamma') \right) \sin(n \varphi) \sin(n \varphi') \right\} e^{\theta(z - z')} \) (C10)

\(G_{z}^{(1)}\) = \(i \frac{\gamma}{8\pi} \int dh \sum_{n=0}^{\infty} \frac{2 - \delta_{n}^0}{\eta^2} \times \left\{ c_{2H}^{(1)} \eta^3 \frac{3}{k^2 r} H_n (\eta \gamma) J_n^* (\eta \gamma') \cos(n \varphi) \cos(n \varphi') + \frac{c_{2H}^{(1)} n \eta^3}{k^2 r^2} H_n (\eta \gamma) H_n^* (\eta \gamma') \sin(n \varphi) \sin(n \varphi') \right\} + \left( c_{2H}^{(1)} \eta^3 \frac{3}{k} H_n (\eta \gamma) J_n (\eta \gamma') + \frac{c_{2H}^{(1)} n \eta^3}{k} H_n (\eta \gamma) H_n^* (\eta \gamma') \right) \sin(n \varphi) \cos(n \varphi') \right\} e^{\theta(z - z')} \) (C11)

\(G_{z}^{(1)}\) = \(i \frac{\gamma}{8\pi} \int dh \sum_{n=0}^{\infty} \frac{2 - \delta_{n}^0}{\eta^2} \times \left\{ c_{2H}^{(1)} \eta^3 \frac{3}{k^2 r} H_n (\eta \gamma) J_n^* (\eta \gamma') \cos(n \varphi) \cos(n \varphi') + \frac{c_{2H}^{(1)} n \eta^3}{k^2 r^2} H_n (\eta \gamma) H_n^* (\eta \gamma') \sin(n \varphi) \sin(n \varphi') \right\} + \left( c_{2H}^{(1)} \eta^3 \frac{3}{k} H_n (\eta \gamma) J_n (\eta \gamma') + \frac{c_{2H}^{(1)} n \eta^3}{k} H_n (\eta \gamma) H_n^* (\eta \gamma') \right) \sin(n \varphi) \cos(n \varphi') \right\} e^{\theta(z - z')} \) (C12)

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\[
\left( G_{zz}^{(1)} \right)_{2z} = \frac{i}{8\pi} \int_{\infty}^{\infty} dh \sum_{n=0}^{\infty} \frac{(2 - \delta_{n0})}{\eta^2} \left\{ \left( c_{n}^{(1)} \frac{\eta^4}{k^2} H_n(\eta r)J_n(\eta r') \right) + c_{n}^{(1)} \frac{\eta^4}{k^2} H_n(\eta r')H_n(\eta r) \right\} \cos(n\varphi) \cos(n\varphi') \sin(n\varphi) \sin(n\varphi') \end{eqnarray}
\]

\begin{equation}
\left( G_{zz}^{(1)} \right)_{2z} = \frac{i}{8\pi} \int_{\infty}^{\infty} dh \sum_{n=0}^{\infty} \frac{(2 - \delta_{n0})}{\eta^2} \left\{ \left( c_{n}^{(1)} \frac{\eta^4}{k^2} H_n(\eta r)J_n(\eta r') \right) + c_{n}^{(1)} \frac{\eta^4}{k^2} H_n(\eta r')H_n(\eta r) \right\} \cos(n\varphi) \cos(n\varphi') \sin(n\varphi) \sin(n\varphi') \end{equation}

\begin{equation}
\left( G_{zz}^{(1)} \right)_{2z} = \frac{i}{8\pi} \int_{\infty}^{\infty} dh \sum_{n=0}^{\infty} \frac{(2 - \delta_{n0})}{\eta^2} \left\{ \left( c_{n}^{(1)} \frac{\eta^4}{k^2} H_n(\eta r)J_n(\eta r') \right) + c_{n}^{(1)} \frac{\eta^4}{k^2} H_n(\eta r')H_n(\eta r) \right\} \cos(n\varphi) \cos(n\varphi') \sin(n\varphi) \sin(n\varphi') \end{equation}

\begin{equation}
\left( G_{zz}^{(1)} \right)_{2z} = \frac{i}{8\pi} \int_{\infty}^{\infty} dh \sum_{n=0}^{\infty} \frac{(2 - \delta_{n0})}{\eta^2} \left\{ \left( c_{n}^{(1)} \frac{\eta^4}{k^2} H_n(\eta r)J_n(\eta r') \right) + c_{n}^{(1)} \frac{\eta^4}{k^2} H_n(\eta r')H_n(\eta r) \right\} \cos(n\varphi) \cos(n\varphi') \sin(n\varphi) \sin(n\varphi') \end{equation}

\begin{equation}
\left( G_{zz}^{(1)} \right)_{2z} = \frac{i}{8\pi} \int_{\infty}^{\infty} dh \sum_{n=0}^{\infty} \frac{(2 - \delta_{n0})}{\eta^2} \left\{ \left( c_{n}^{(1)} \frac{\eta^4}{k^2} H_n(\eta r)J_n(\eta r') \right) + c_{n}^{(1)} \frac{\eta^4}{k^2} H_n(\eta r')H_n(\eta r) \right\} \cos(n\varphi) \cos(n\varphi') \sin(n\varphi) \sin(n\varphi') \end{equation}

\begin{equation}
\left( G_{zz}^{(1)} \right)_{2z} = \frac{i}{8\pi} \int_{\infty}^{\infty} dh \sum_{n=0}^{\infty} \frac{(2 - \delta_{n0})}{\eta^2} \left\{ \left( c_{n}^{(1)} \frac{\eta^4}{k^2} H_n(\eta r)J_n(\eta r') \right) + c_{n}^{(1)} \frac{\eta^4}{k^2} H_n(\eta r')H_n(\eta r) \right\} \cos(n\varphi) \cos(n\varphi') \sin(n\varphi) \sin(n\varphi') \end{equation}

\begin{equation}
\left( G_{zz}^{(1)} \right)_{2z} = \frac{i}{8\pi} \int_{\infty}^{\infty} dh \sum_{n=0}^{\infty} \frac{(2 - \delta_{n0})}{\eta^2} \left\{ \left( c_{n}^{(1)} \frac{\eta^4}{k^2} H_n(\eta r)J_n(\eta r') \right) + c_{n}^{(1)} \frac{\eta^4}{k^2} H_n(\eta r')H_n(\eta r) \right\} \cos(n\varphi) \cos(n\varphi') \sin(n\varphi) \sin(n\varphi') \end{equation}

where \( J_n \) and \( H_n \) denote the derivatives

\begin{equation}
J'_n(\eta r) = \frac{dJ_n(\eta r)}{d(\eta r)} \quad \text{(C14)}
\end{equation}

\begin{equation}
H'_n(\eta r) = \frac{dH_n(\eta r)}{d(\eta r)} \quad \text{(C15)}
\end{equation}

\( H_n \) always represents the Hankel function of the first kind, so the superscript \( 1 \) was omitted for simplicity.

From the boundary conditions (Eqs. IV.2.7 and IV.2.8) one obtains two sets of 16 equations for the Green tensor coefficients, one for each polarization \( H \) and \( V \), respectively.

A useful relation, which can be proven using the Bessel's functions recursion relations, is

\begin{equation}
H''_n(x) J'_n(x) - H'_n(x) J''_n(x) = \left( 1 - \frac{n^2}{x^2} \right) \frac{2}{\pi x} \quad \text{(C16)}
\end{equation}

Also the next relation will be used to further manipulate these equations

\begin{equation}
J'_n(x) H''_n(x) - J''_n(x) H'_n(x) = \frac{2}{\pi x} \quad \text{(C17)}
\end{equation}

Next a subset of 8 equations containing the coefficients for zone 2 (field and source between the CNTs surfaces) and for polarization \( V \) is shown. The other subsets of equations will have similar forms.
\[ -\omega_0 \sigma_{zz} \eta^2 H_n(\eta R_1) J'_n(\eta r') c_{4V}^{(2)} - \omega_0 \sigma_{zz} \eta^2 H_n(\eta R_1) H'_n(\eta r') c_{3V}^{(2)} \]
\[ + \left[ \frac{2ik^2}{\pi R_1} J'_n(\eta r') - \omega_0 \sigma_{zz} \eta^2 J_n(\eta R_1) J'_n(\eta r') \right] c_{3V}^{(2)} \]
\[ + \left[ \frac{2ik^2}{\pi R_1} H'_n(\eta r') - \omega_0 \sigma_{zz} \eta^2 J_n(\eta R_1) H'_n(\eta r') \right] c_{3V}^{(2)} \]
\[ - \frac{2\hbar k}{\pi \eta R_1^2} J'_n(\eta r') c_{4V}^{(2)} - \frac{2\hbar k}{\pi \eta R_1^2} H'_n(\eta r') c_{4V}^{(2)} = \omega_0 \sigma_{zz} \eta^2 H_n(\eta R_1) J'_n(\eta r') \]

\[ = - \frac{2\hbar k}{\pi \eta R_1^2} H'_n(\eta r') c_{4V}^{(2)} - \omega_0 \sigma_{zz} \eta^2 H_n(\eta R_1) H'_n(\eta r') c_{4V}^{(2)} \]

\[ J'_n(\eta r') c_{4V}^{(2)} + H'_n(\eta r') c_{4V}^{(2)} = 0 \]

\[ J_n(\eta r') c_{4V}^{(2)} + H_n(\eta r') c_{4V}^{(2)} = 0 \]
\[
\begin{align*}
- \left[ \frac{2ik^2}{\pi R_2^2} J_n(\eta r') - \omega \mu_0 \sigma_{zz} \eta^2 H_n(\eta R_2) J_n(\eta r') \right] c_2^{(2)} \\
- \left[ \frac{2ik^2}{\pi R_2} H_n(\eta r') - \omega \mu_0 \sigma_{zz} \eta^2 H_n(\eta R_2) H_n(\eta r') \right] c_3^{(2)} \\
+ \frac{2nhk}{\pi \eta R_2^2} J_n(\eta r') c_2^{(2)} + \frac{2nhk}{\pi \eta R_2^2} H_n(\eta r') c_3^{(2)} \\
+ \omega \mu_0 \sigma_{zz} \eta^2 J_n(\eta R_2) J_n(\eta r') c_2^{(2)} + \omega \mu_0 \sigma_{zz} \eta^2 J_n(\eta R_2) H_n(\eta r') c_3^{(2)} \\
= -\omega \mu_0 \sigma_{zz} \eta^2 J_n(\eta R_2) H_n(\eta r') \\
\end{align*}
\]  

(C23)

\[
J_n'(\eta r') c_2^{(2)} + H_n'(\eta r') c_3^{(2)} = 0 \quad (C24)
\]

\[
J_n(\eta r') c_2^{(2)} + H_n(\eta r') c_3^{(2)} = 0 \quad (C25)
\]

where \( J_n'(\eta R_{1,2}) \) and \( H_n'(\eta R_{1,2}) \) denote

\[
J_n'(\eta R_{1,2}) = \frac{dJ_n(\eta r)}{d(\eta r)} \bigg|_{R_{1,2}} \quad (C26)
\]

\[
H_n'(\eta R_{1,2}) = \frac{dH_n(\eta r)}{d(\eta r)} \bigg|_{R_{1,2}} \quad (C27)
\]

Using the notations

\[
f(R_1) = \frac{2ik^2}{\pi R_1^2} \frac{1}{H_n^{(1)}(\eta R_1)} - \gamma_1 J_n(\eta R_1) \quad (C28)
\]

\[
g(R_2) = \frac{2ik^2}{\pi R_2^2} \frac{1}{J_n(\eta R_2)} - \gamma_2 H_n^{(1)}(\eta R_2) \quad (C29)
\]

\[
\gamma_{1,2} = \omega \mu_0 c_{zz}^{(1,2)} \eta^2
\]

one obtains for the coefficients in zone 2
\[ c_{2v}^{(22)} = c_{2v}^{(22)} = 0 \]  
\[ c_{3v}^{(22)} = \frac{\gamma_1 J_n(\eta R_1) H_n^{(1)}(\eta R_2)}{f(R_1)g(R_2) - \gamma_1 \gamma_2 J_n(\eta R_2) H_n^{(1)}(\eta R_1)} \]  
\[ c_{4v}^{(22)} = c_{4v}^{(22)} = 0 \]

Similarly for the coefficients in zone 1 (exterior)

\[ c_{1v}^{(12)} = \frac{g(R_2) \left[ f(R_1) + \gamma_2 J_n(\eta R_1) \right]}{f(R_1)g(R_2) - \gamma_1 \gamma_2 J_n(\eta R_2) H_n^{(1)}(\eta R_1)} \]  
\[ c_{1v}^{(12)} = \frac{\gamma_2 J_n(\eta R_2) \left[ f(R_1) + \gamma_1 J_n(\eta R_1) \right]}{f(R_1)g(R_2) - \gamma_1 \gamma_2 J_n(\eta R_2) H_n^{(1)}(\eta R_1)} \]  
\[ c_{2v}^{(12)} = c_{2v}^{(12)} = 0 \]

and coefficients in zone 3 (interior)

\[ c_{3v}^{(32)} = \frac{f(R_1) \left[ g(R_2) + \gamma_2 H_n^{(1)}(\eta R_2) \right]}{f(R_1)g(R_2) - \gamma_1 \gamma_2 J_n(\eta R_2) H_n^{(1)}(\eta R_1)} \]  
\[ c_{3v}^{(32)} = \frac{\gamma_1 H_n^{(1)}(\eta R_1) \left[ g(R_2) + \gamma_2 H_n^{(1)}(\eta R_2) \right]}{f(R_1)g(R_2) - \gamma_1 \gamma_2 J_n(\eta R_2) H_n^{(1)}(\eta R_1)} \]

For polarization H (transverse electric mode) it is found that all the coefficients in zone 2 are zero. The only non-zero coefficients for this case are

All the coefficients in zone 2 are zero.
\( c_{IH}^{(12)} = 1 \) \hspace{1cm} (C41)

\( c_{3H}^{(12)} = 1 \) \hspace{1cm} (C42)
Appendix D

Forces on carbon nanotubes surfaces

The electromagnetic tensor was constructed in Section IV.1.4 using the vacuum expectation values of the electromagnetic fields. Here the expressions are given for completeness

\[
T(r, r') = T_1(r, r') + T_2(r, r') - \frac{1}{2} ITr[T_1(r, r') + T_2(r, r')]
\]  
(D1)

\[
T_1(r, r') = \varepsilon_o \int \left\{ \hat{E}(r, \omega) \otimes \hat{E}(r', \omega') \right\} d\omega d\omega'
\]  
(D2)

\[
T_2(r, r') = \frac{1}{\mu_o} \int \left\{ \hat{B}(r, \omega) \otimes \hat{B}(r', \omega') \right\} d\omega d\omega'
\]  
(D3)

The electric and magnetic fields have the integral representation

\[
\hat{E}(r, \omega) = i \omega \mu_o \int d^3 r' G(r, r', \omega) \cdot \hat{j}(r', \omega)
\]  
(D4)

\[
\hat{B}(r, \omega) = \mu_o \int d^3 r' \nabla \times \left[ \nabla \left[ G(r, r', \omega) \right] \right] \cdot \hat{j}(r', \omega)
\]  
(D5)

with the current density operator

\[
\hat{j}(r, \omega) = \frac{\omega}{\mu_0 c^2} \sqrt{\frac{\hbar}{\pi \varepsilon_0}} \text{Im} \varepsilon(r, \omega) \hat{f}(r, \omega)
\]  
(D6)

Using the definition of the dyadic posterior scalar product

\[
\hat{T} \cdot \hat{v} = \sum_i \sum_j v_j T_{ij} \hat{e}_i
\]  
(D7)
one obtains for the electric and magnetic fields

\[
E(r, \omega) = i \sqrt{\frac{\hbar}{\pi \varepsilon_0 c^2}} \int dr' \sqrt{\text{Im} \varepsilon_{zz}(r', \omega)} \left( G_{rz} \hat{e}_r + G_{rz} \hat{e}_\phi + G_{zz} \hat{e}_z \right) \tilde{f}(r', \omega)
\]  \hspace{1cm} (D8)

\[
B(r, \omega) = \sqrt{\frac{\hbar}{\pi \varepsilon_0 c^2}} \int dr' \sqrt{\text{Im} \varepsilon_{zz}(r', \omega)} \left[ \left( \frac{1}{r} \frac{\partial G_{zz}}{\partial \varphi} - \frac{\partial G_{oz}}{\partial z} \right) \hat{e}_r 
+ \left( \frac{\partial G_{oz}}{\partial z} - \frac{\partial G_{zz}}{\partial r} \right) \hat{e}_\varphi 
+ \left( \frac{1}{r} \frac{\partial G_{oz}}{\partial r} + \frac{1}{r} \frac{\partial G_{zz}}{\partial \varphi} \right) \hat{e}_z \right] \tilde{f}(r', \omega)
\]  \hspace{1cm} (D9)

Using the relation

\[
\frac{\omega^2}{c^2} \int ds \text{Im} \varepsilon(s, \omega) G_{jk}(r, s, \omega) G_{jk}^*(r', s, \omega) = \text{Im} G_{ij}(r, r', \omega)
\]  \hspace{1cm} (D10)

the following forms are obtained for the electromagnetic stress tensor components

\[
\tilde{T}_1(r, r') = \frac{\hbar}{\pi} \int d\omega \frac{\omega^2}{c^2} \text{Im} \begin{pmatrix}
G_{rr}(r, r', \omega) & 0 & 0 \\
0 & G_{\varphi\varphi}(r, r', \omega) & 0 \\
0 & 0 & G_{zz}(r, r', \omega)
\end{pmatrix}
\]  \hspace{1cm} (D11)

\[
\tilde{T}_2(r, r') = \frac{\hbar}{\pi \rho f r'} \int d\omega \text{Im} X
\]  \hspace{1cm} (D12)
The radial component $T_r$, which describes the radiation pressure (force per unit area) of the virtual electromagnetic field on each CNT surface in the system, is found to be

$$T_r(r, r') = \frac{\hbar}{2\pi} \int d\omega \text{Im} \left[ \left( \frac{\omega^2}{c^2} - \frac{\partial^2}{\partial z \partial z'} - \frac{1}{rr'} \frac{\partial}{\partial \phi \partial \phi'} \right) G_{\phi \phi}(r, r', \omega) + \left( \frac{1}{rr'} \frac{\partial}{\partial \phi} + \frac{1}{r} \frac{\partial^2}{\partial \phi \partial \phi'} \right) G_{\phi \phi}(r, r', \omega) ight]$$

$$+ \left( \frac{\partial^2}{\partial z \partial r'} + \frac{1}{rr'} + \frac{1}{r} \frac{\partial}{\partial \phi'} \frac{\partial^2}{\partial \phi \partial r} \right) \frac{\partial^2}{\partial z \partial r'} G_{\phi \phi}(r, r', \omega)$$

$$- \left( \frac{1}{rr'} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r'} \frac{\partial}{\partial r'} \frac{\partial^2}{\partial \phi \partial \phi'} \right) \frac{\partial^2}{\partial z \partial r'} G_{\phi \phi}(r, r', \omega)$$

$$- \frac{1}{r} \frac{\partial^2}{\partial \phi \partial \phi'} G_{\phi \phi}(r, r', \omega) + \frac{\partial^2}{\partial r \partial r'} G_{\phi \phi}(r, r', \omega) - \frac{1}{r} \frac{\partial}{\partial \phi \partial \phi'} G_{\phi \phi}(r, r', \omega)$$

$$+ \left( - \frac{\partial^2}{\partial r \partial r'} + \frac{1}{rr'} \frac{\partial}{\partial \phi \partial \phi'} \frac{\partial^2}{\partial \phi \partial r} \right) G_{\phi \phi}(r, r', \omega) \right]$$

(D14)
The forces per unit area acting on each CNT are found in the coincidence limit

\[ F_1/S = \lim_{r \to R_1} \lim_{r' \to R_1} \left[ T^{(1)}_{rr}(r, r') - T^{(2)}_{rr}(r, r') \right] \quad (D15) \]

\[ F_2/S = \lim_{r \to R_2} \lim_{r' \to R_2} \left[ T^{(2)}_{rr}(r, r') - T^{(3)}_{rr}(r, r') \right] \quad (D16) \]

and are expressed as

\[ F_1/S = -\frac{\hbar}{(2\pi)^3} \int d\omega \Im \left[ i \int dh \sum_n (2 - \delta_n^0) \frac{\eta}{R_1 H^{(1)}_n(\eta R_1)} \right. \]

\[ \times \left( J'_n(\eta R_1) c_3^{(2)} + H'^{(1)}_n(\eta R_1) c_3^{(2)} \right) \quad (D17) \]

\[ F_2/S = -\frac{\hbar}{(2\pi)^3} \int d\omega \Im \left[ i \int dh \sum_n (2 - \delta_n^0) \frac{\eta}{R_2 J_n(\eta R_2)} \right. \]

\[ \times \left( J'_n(\eta R_2) c_3^{(2)} + H'^{(1)}_n(\eta R_2) c_3^{(2)} \right) \quad (D18) \]

Using the expressions for coefficients given in Appendix C and making the transition to the modified Bessel function

\[ I_n(x) = i^{-n} J_n(ix) \quad (D19) \]

\[ K_n(x) = \frac{\pi}{2} i^{-n-1} H_n^{(1)}(ix) \quad (D20) \]

one obtains the forces on carbon nanotubes surfaces given in Eq. IV.2.11.
About the Author

Adrian Popescu received his B.S. and M.S. degrees from University of Bucharest, Romania. He joined the Department of Applied Physics at University of South Florida in 2006 as a USF Presidential Fellow. He was also the recipient of the Bright House Networks Endowed Fellowship in 2011. His publication record during the Ph.D. program includes several peer reviewed journal publications, conference proceedings, and book chapters. Also he presented his research at several international scientific conferences. His work has generated two utility patents and it was recognized as a runner up for the 2010 American Physical Society Best Student Paper Award.