MECHANISM AND THE EFFECT OF MICROWAVE-CARBON NANOTUBE INTERACTION

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A series of experimental results about unusual heating of carbon nanotubes by microwaves is analyzed in this dissertation. Two of vibration types, cantilever type (one end is fixed and the other one end is free), the second type is both ends are fixed, have been studied by other people. A third type of forced vibration of carbon nanotubes under an alternating electromagnetic field is examined in this paper. Heating of carbon nanotubes (CNTs) by microwaves is described in terms of nonlinear dynamics of a vibrating nanotube. Results from the model provide a way to understand several observations that have been made. It is shown that transverse vibrations of CNTs during microwave irradiation can be attributed to transverse parametric resonance, as occurs in the analysis of Melde’s experiment on forced longitudinal vibrations of a stretched elastic string. For many kinds of carbon nanotubes (SWNT, DWNT, MWNT, ropes and strands) the resonant parameters are found to be located in an unstable region of the parameter space of Mathieu’s equation. Third order wave equations are used to qualitatively describe the effects of phonon-phonon interactions and energy transfer from microwaves to CNTs. This result provides another way to input energy from microwaves to carbon nanotubes besides the usual Joule heating via electron-phonon interaction. This model appears to be the first to point out the role of nonlinear dynamics in the heating of CNTs by microwaves.
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CHAPTER 1
BACKGROUND OF THE TOPIC

1.1 General Comments

The topic of this dissertation comes from several experimental results from work done in the Department of Physics, the University of North Texas. The results showed that carbon nanotubes (CNTs) were very sensitive to microwave (wave length is from millimeters to meters) irradiation [1-4]. These results prompted intense discussion about the physics mechanism of the response of CNTs to microwaves. In reference [4], the authors proposed that the mechanism was due to the magnetic resonant absorption of residual metals (especially Fe) which was introduced into CNTs from the production process. In reference [3], a PIXE experiment showed that when irradiated by the same microwave source, different CNT samples exhibited definitely different results, although all the CNT samples contained almost the same amount of residual metals. Detailed results of reference [3] will be discussed later in this chapter. The main purpose of this dissertation is to offer a clear physics picture to explain the main physical processes involved in the above reports. Meanwhile, the model offered here might predict some extreme results, which will remain to be studied by both further experimental and theoretical works.

Carbon nanotubes are newly man-made carbon allotropes. Before the model is discussed, it is necessary to explore some pure carbon based materials and review the geometric, electronic and mechanical properties of CNTs. One thing needs to be
emphasized that, up to now, there are many aspects not well recognized and even unknown about the properties of CNTs. For example, theoretical studies and some experiments show that electronic properties of some single-walled carbon nanotube (SWNT) exhibited metallic properties. The mean-free-path (MFP) of electrons in a metallic SWNT is on the order of magnitude of 10nm ($10^{-8}$m) [15, 16], but other experiments show that electrons are ballistically transported in SWNT and the MFP of electrons is high, up to 14µm ($1.4\times10^{-6}$m) at room temperature [19, 20, 21]. For another example, SWNT samples were reported to undergo a diameter doubling process when heated to about 1500°C in a hydrogen environment [61], but undergo a diameter enlargement process at the same temperature in an argon environment [62]. It is not clear what the mechanism is to explain this behavior. Thus, in this dissertation, the analysis is made based on experimental results and some well accepted theoretical models.

1.2 A Question Arising from a Cavity Experiment

In this experiment, the Single-Walled Carbon Nanotubes (SWNT) were randomly blended in a selected material which was placed in a wave guide and a cavity to measure the behavior of the microwave absorption under a power of about 30m watts operating at frequencies of 35GHz, 11GHz, 9GHz and 6.7GHz (See figure 1.1 for a picture of the cavity.). Lorentzian shape resonant absorption curves (Fig. 1.2) [1] of both electric and magnetic components were obtained and analyzed (Fig. 1.3) [1]. For a
given medium, bell shape absorption peaks vs. weight percentage of SWNT mixed in the medium were observed (Fig. 1.3) [1].

In Fig. 1.3, at first, as the weight percentage of SWNTs increases, the efficiency of microwave absorption increases also. But, beyond some value of weight percentage, the efficiency of microwave absorption decreases as the weight percentage of SWNT increases. If we think SWNTs are the origin of microwave absorption, how can we understand this bell shape absorption curve? Actually, we tested two kinds of samples: polycarbonate and Nile. Pure polycarbonate is a rigid solid at room temperature, but Nile is very soft. For a given weight percentage of SWNT, Nile sample was more effective in absorbing the microwaves. It seems here that the efficiency of microwave absorption is correlated to the Young’s modulus of the media. Thus, it furthermore prompted us to propose that there is a mechanical process involved in the microwave
absorption of SWNTs. The principle and detailed description of the experiment in the cavity is described in reference [1].

![Figure 1.2 Spectra scan of the resonant cavity for two different volumes of load. The upper part of the figure shows the scan for no load in the cavity with the uppermost scan the cavity profile and the lower scan the Lorentzian profile. The lower set of traces is for a load of ten units of volume for the sample of SWNTs of 11% blend in polycarbonate. Ref. [1] Reproduced with permission from American Institute of Physics Publishing.]

![Figure 1.3 Efficiency of microwave absorption vs. weight percentage of SWNTs. In the figure, diamond represents the data of the electric vector, circle represents the data of the magnetic vector. Ref. [1] Reproduced with permission from American Institute of Physics Publishing.]

1.3 Experiments Executed In High Vacuum Environments

This experiment was to study CNTs (both raw and purified) which were put into a high vacuum system and irradiated with a high power microwave field (several
hundreds Watts at 2.4GHz). Out-gassing, plasma excitation and nanotube reconstruction with a wide range of light emission were found in the experiment (See Fig. 1.4-1.7) [2]. The system to be studied in the high vacuum experiment consists of three components:

1. Something inside the tubes, e.g., residual metals (As was mentioned above, it was introduced from the CNT synthesis process.).
2. Something adsorbed onto the tubes, e.g., gases.
3. The carbon nanotube (or nanotube rope, strand) itself.

To answer the question “What’s going on here?”, we have to identify the roles of each component in the phenomenon. First, we have to determine the real effect of the microwave-CNT interaction. The reason to emphasize it is, as pointed out by authors in reference [3], once plasma was excited, an independent window is opened to transfer energy from the microwave to the CNT system [3]. Thus, with plasma appearance the true effect of microwave-CNT interaction emerges by the interaction between highly ionized particle in plasma and the CNT samples. But, how was plasma excited in the experiment? Is there any relation between the effect of microwave-CNT interaction and plasma excitation? The following discussions and reviews of papers will be focused on the exact description of the experimental results of the effect of microwave-CNT interaction.
Fig. 1.4 SWNTs in an UHV tube suspended above (~ 8mm) an active microwave source show the white light emission. Room lights were off.

Fig. 1.5 Spectrum of light from raw (green) and purified (burgundy) SWNTs when subjected to the microwave irradiation. The background spectrum showed no peaks.
Fig. 1.6 TEM image of the fused nanotubes after microwave irradiation. There were numerous such regions observed in the irradiated samples. A portion of the lacey carbon grid is evident in the top right portion of the photo.

Fig. 1.7 TEM image showing looped nanotubes after microwave irradiation. There were numerous such regions observed in the irradiated samples.

1.3.1 A Proposal about the Role of the Residual Metal

Residual metal (nanosized) was introduced into the CNT samples from the production process of CNTs. Some authors attributed the microwave absorption of SWNTs to the magnetic resonance of residual metal with certain size and distribution, especially the Fe particles [4].
In another article, reference [3], the authors proved experimentally that there is no correlation between the temperature of CNTs and the amount of residual metal during microwave irradiation. If the reason is the residual metal that causes the microwave absorption, it does not explain the Young’s modulus dependent absorption efficiency in the first part of the experiments, where the same weight percentage of SWNTs produced the same amount and distribution of SWNTs and residual metals. In reference [4], the authors showed that after microwave irradiation, the size and distribution of the residual metals were significantly changed, as shown in Fig. 1.8 [4].

Fig. 1.8 TEM images showing (a) unpurified HiPco nanotubes before microwave irradiation, and (b) unpurified HiPco nanotubes after microwave irradiation. The Fe nanoparticles in (a) have coalesced into large crystallites, indicated by the arrow, having a diameter about four times greater than that of the original nanoparticles. [4] Reproduced with permission from American Institute of Physics Publishing.

But, the key to the problem is that all experiments showed that the glowing process is repeatable, which means the efficiency of microwave absorption of the SWNT samples has nothing to do with the distribution of the residual metals. From the point of view of the philosophy of physics, a reversible process should not be attributed
to the result of a process, which results in an irreversible result. A recent published experimental result, furthermore, showed that for the SWNT case, where the size of the residual metal is on the order of nanometer, the magnetic resonance of the nano-sized metallic particles to the electromagnetic wave should be on the order of magnitude of several hundred gigahertz, not on the order of magnitude of several gigahertz [5] used in the above experiments. Thus, the mechanism of magnetic resonance of residual metal with the microwave (2.45GHz) appears to be incorrect. But, although the authors of reference [3] demonstrated that there is no correlation between the amount of residual metal and heating of CNTs by microwave, the role of the residual metal in the phenomenon is still unclear.

1.3.2 A Proposal about the Maximum Temperature Reached by the Glowing Part of the Samples

In reference [4], the authors claimed that during microwave irradiation the raw samples reached a temperature about 2150K (1850°C as claimed in reference [4]), while the purified ones reached to only 1000K (650°C as claimed in reference [4]) and there is no density effect [4]. In reference [2], the authors claimed that both raw and purified samples reached a temperature about 2300K [2]. As it was pointed out in reference [3], the temperature estimated in both reference [2] and reference [4] were not accurate because of the existence of the excited plasma (once the plasma was excited, it opened another window to input energy from the microwave to the nanotube system). Otherwise, here it is pointed out that the method used to estimate the temperature of the
microwave irradiated samples in reference [4] is inaccurate. The authors in reference [4] estimated the temperature of the samples by measuring the temperature increase of a water bath after the heated samples were dropped into it. This method assumes that the sample must be heated uniformly. But, as we observed in our experiments and even as it was mentioned in reference [4] by the authors, the purified samples were not heated uniformly.

The authors in reference [3] measured the temperature of many CNT samples by degassing the sample first to eliminate the plasma and then comparing the emission spectrum from the glowing part of the samples with the blackbody emission curves. By executing a PIXE (Particle Induced X-ray Emission) experiment, they showed that there were totally different amount of residual metals in the CNT samples. Thus, a conclusion that there is no correlation between the microwave heating of CNTs and the residual metals was made by the authors. Their result showed that all unpurified CNTs were heated to a temperature about 1900K which followed the conventional Joule heating curve of the microwave, but all the purified ones (both SWNT and MWNT) were heated to a temperature about 1000K higher than the unpurified ones.

It is clear that the results of reference [3] demonstrate that during the microwave irradiation, besides the conventional electron-phonon interaction, there must exist another mechanism to obtain the result that extra energy is transferred from the microwave source to part of the purified samples (because the glowing of the samples is not uniform.). The analysis in Chapter 3 will be based on results of reference [3].
1.3.3 Mechanism of Plasma Excitation

There are three sets of experiment. In reference [3], after pre-degassing at temperature about 500°C for about 30 minutes, in a vacuum environment of 10^{-7} torr, during microwave irradiation, the authors found that there is no plasma excited. This phenomenon demonstrated that degassing played a key role in plasma appearance. By immersing the glass tube, which contained the CNT sample, into a water bath, we found that degassing of CNTs started at about 100°C, the temperature of boiling water. The range of temperature that produced degassing was from 100°C to about 700°C. RGA analysis showed that about 1000K degassing temperature range of gasses absorbed by CNTs means that both physical and chemical adsorption is predicted. In reference [4], the authors observed that in a 10^{-10} torr environment the SWNT sample was heated first, then plasma was excited (Fig. 1.9 [4]). The authors there did not mention if pre-degassing was conducted. Whatever, the phenomenon showed that the extent of degassing depended on not only the temperature, but also the pumping ability of the vacuum system.

In order to clarify the reason of the plasma excitation, a series of experiments were designed and conducted and reported in this dissertation. The detailed description of the experiments is attached as Appendix I. The main idea of the experiment is to add a layer of porous medium (insulator: Salt grains were selected.) on top of the original
Fig. 1.9 Unpurified HiPco carbon nanotubes in a test tube evacuated to $< 10^{-10}$ torr under microwave irradiation at time durations, t. (a) before microwave irradiation, (b) after $t = 0.04$s, and (c) after $t = 4$s. Ref. [4] Reproduced with permission from American Institute of Physics Publishing.

CNT samples to suppress the degassing process during the microwave irradiation. The experiments showed that the thicker the cover layer was, the slower the rate of degassing. For a 5cm thickness of the cover layer, no plasma was excited. Decreasing the thickness of the salt layer to 3.5cm, plasma was excited above the salt layer. It seemed that the plasma excitation had nothing to do with the SWNT. To confirm this conclusion, another experiment was conducted: By pumping a spare glass tube from atmospheric pressure to vacuum ($10^{-7}$ torr), and vice versa, during the same microwave irradiation, plasma excitation was observed. Because at atmosphere pressure and high vacuum ($10^{-7}$ torr) the same microwave field excited nothing in the spare glass tube, we propose that the experiment proved that there is a pressure window for residual gas arching to excite the plasma for the given microwave field (Fig. 1.10). The salt layer is a porous medium. The result of microwave degassing is a sudden pressure increase.
from $10^{-7}$ to some value $P_0$ below the salt layer. Gases flow through the salt layer follows Darcy’s law. Thus, the pressure right on top of the salt layer is $P = P_0 e^{-\kappa h}$, where $\kappa$ is the permeability of the salt layer and $h$ the height of the salt layer. Because $\kappa$ is a fixed value for a given porous medium, by tuning the $h$, we can change the value of $P$. While the value of $P$ drops into the window of residual gas arching, plasma will be excited. If the value of $h$ is too high to cause the value of $P$ to be too small and beyond the pressure window, there will be no gas arching to result in the plasma. Thus, we experimentally proved that for CNT samples without pre-degassing treatment, at least at the beginning of the microwave degassing, the plasma excitation has nothing to do with CNTs themselves.

Fig. 1.10 Schematic graph of the results of CNTs with a cover of NaCl layer irradiated by microwave, where the orange lines represent sparking at the CNT-NaCl interface.
As shown in Fig. 1.10, when covered by a layer of porous medium, the CNT sample were not heated during the microwave irradiation: This phenomenon is obviously contrary to both the explanation by magnetic resonance and the conclusion that there is no density effect given by the authors in reference [4], because the magnetic resonance of residual metal would not be affected by the existence of adsorbed gases, and the density of the sample will be obviously changed by degassing.

1.4 Summary of the Questions to Be Answered

Obviously, to qualitatively interpret all the above phenomena, we have to establish a model to answer all the following questions:

1. How is the microwave absorbed by the CNTs?

2. Why and how do the nanotubes reach the glowing stage so rapidly?
3. Why is there about 1000K temperature difference between purified and unpurified CNT samples during the microwave irradiation?

4. Why is there a broad bell shape absorption peak for a given medium that was blended with CNTs?

The list above is the motivation of the topic of this dissertation. The mechanism of magnetic resonance of the residual metals has been excluded. Our analysis will be concentrated on the effect of the electric response of CNTs to the microwave field. Thus, first, we have to evaluate the intensity of the electric field produced by the magnetron, and to review the up-to-date knowledge about the behaviors of the electric response of CNTs to an external electric field (including both static and dynamic). Otherwise, the fact that all the authors acknowledged, heating of CNTs by microwaves is repeatable, promotes us to exclude all the mechanisms which will result in irreversible processes, such as chemical reaction, etc.. The required mechanism must be a reversible dynamics process.
CHAPTER 2
A BRIEF REVIEW OF BEHAVIORS OF CARBON NANOTUBES UNDER AN EXTERNAL ELECTRIC FIELD

2.1 Estimation of the Intensity of the Electric Field in High Vacuum Cases

The intensity of the electric field produced by the magnetron is very difficult to measure directly. But, considering that our aim is to establish a model to make a qualitative explanation to the phenomena mentioned above, here, we just need to make an estimate of the order of magnitude of the intensity of the electric field. We noticed that in the above experiments, the magnetron was exposed to the air, and during the operation of the magnetron there was no observation about the phenomenon of air penetration reported, formerly. The threshold value of the intensity of the electric field to result in air penetration is 20,000V/cm. Thus, the intensity of the electric field produced by the magnetron must be less than 20,000V/cm. But, indeed, occasionally we observed a “flame” excited outside the quartz tube. (The explanation for this is not clear, at this time.) So, as an evaluation, the value of the intensity of the electric field near the magnetron is taken to be 10,000V/cm in the following analysis.

2.2 Behaviors of CNTs under an External Static Electric Field

2.2.1 Electronic Structure of SWNT
Theoretically speaking, a SWNT can be realized by seamlessly mapping a graphene sheet on to a cylindrical surface.

From the website of Dr. R. E. Smalley’s group, many types of CNT materials can be found [7]. The electronic property of graphene mainly depends on the π electron in the valence band and the π* electrons in the conduction band near the Fermi level. So, to study the electronic structure of graphene we can consider only the π electrons in graphene. The unit cell of graphene consists of two non-identical carbon atoms. The electronic structure can be acquired by solving a 2×2 secular equation [6],

$$E_{g2D}^\pm(k) = \frac{\varepsilon_{2p} \pm \gamma_0 \omega(k)}{1 \pm s \omega(k)}, \quad (2.1)$$

where $\varepsilon_{2p}$ is the site energy of a 2p orbit, $\gamma_0$ is the interaction energy among the closest atoms, $s$ is the tight binding overlap integral related to the non-symmetry between the conduction and valance bands.

When $\gamma_0 > 0$, $E^+$ and $E^-$ are the energies corresponding to the π and π* electrons, respectively. $\omega(k)$ in (2.1) is

$$\omega(k) = \sqrt{f(k)} = \sqrt{1 \pm 4 \cos \frac{\sqrt{3}k_xa}{2} \cos \frac{\sqrt{3}k_ya}{2} + 4 \cos^2 \frac{k_ya}{2}}, \quad (2.2)$$

where $a = 0.246$ nm is the length of the unit vector in graphene.
From equation (2.1) we can show that when \( s = 0 \) the \( \pi \) and \( \pi^* \) electrons are symmetric about \( E = \varepsilon_{2p} \). So, the energy dispersion relation can be approximated by the case with \( s = 0 \) as:

\[
E_{g2D}(k_x, k_y) = \pm \gamma_0 \sqrt{1 + 4 \cos \frac{\sqrt{3} k_x a}{2} \cos \frac{\sqrt{3} k_y a}{2} + 4 \cos^2 \frac{k_y a}{2}}. 
\]  

(2.3)

In a SWNT, the wave function of an electron is confined in the radial direction \([6, 8]\); in circumference, because of the spiral symmetry, the periodic boundary condition can be applied in real space to form a unit cell of the SWNT. The electronic state in the longitudinal direction is infinite in extent, but finite in the radial direction. So, we can calculate the electronic structure of a SWNT by folding one in a graphene sheet as R. Satio etc. did \([6, 8]\). The relation between the wave vector and the chiral vector is:

\[
\mathbf{C} \cdot \mathbf{k} = \sqrt{3} N_x k_x a + N_y k_y a = 2 \pi q. 
\]  

(2.4)

The wave vector of the wave function of an electron in a SWNT along \( K_1 \) in the Brillouin zone is discrete, which demonstrates that the Brillouin zone of a SWNT is 1-D. The magnitude of the Brillouin zone is a segment along \( K_2 \) of 2-D Brillouin zone of graphene.

The extended Brillouin zone is a set of \( N \) segments of wave vectors with length of \(|K_2|\), each one is separated by the wave vector \( K_1 \). Thus, by folding the \( N \) segments of the wave vectors in the 2-D dispersion relation of graphene into the first Brillouin zone of a 1-D SWNT we can get the 1-D electron dispersion relation of an \( N \) electron energy...
band of a SWNT. When \((n-m)\) is multiple of 3, there are wave vectors of electron states on the corner of the first Brillouin zone; when \((n-m)\) is not a multiple of 3, there is no wave vector through the corner of the first Brillouin zone. Zigzag and armchair types of SWNT are special cases. There are 4 carbon atoms and 2 hexagons in the unit cell of real space and two wave vectors in the unit cell of reciprocal space. The dispersion relation of a zigzag and armchair SWNT is to fold \(N/2\) times the dispersion relation of 2-D graphite, and then project it in its 1-D Brillouin zone. There are two assumptions in the Brillouin zone folding method: 1. neglect the warping effect of the carbon nanotube; 2. suppose the neighbor-neighbor interaction of carbon-carbon atoms is the same as it is in graphite. In equation (2.2), taking \(\varepsilon_{2p} = 0\) and \(s = 0\) yields:

\[
E_{g2D}(k_x, k_y) = \pm \gamma_0 \sqrt{1 \pm 4 \cos \frac{\sqrt{3} k_x a}{2} \cos \frac{\sqrt{3} k_y a}{2} + 4 \cos^2 \frac{k_y a}{2}}. \tag{2.5}
\]

Once the finite number of the wave vectors is determined in the circumference, from (2.5) we can get a series of 1-D dispersion relations [8].

The relationship between 1-D energy dispersion relation of a general chiral type SWNT and the energy dispersion relation of 2-D graphite is

\[
E_{\mu}(k) = E_{g2D}(k \frac{\vec{K}_2}{K_2} + \mu \vec{K}_1), \quad \mu = 1, \cdots, N, \quad -\frac{\pi}{T} < k < \frac{\pi}{T} \tag{2.6}
\]

where \(N\) is the number of hexagons in unit cell of the SWNT and \(k\) is the wave vector in axis direction. Calculations of the electronic structure for all the chiral type SWNT shows that its electric property is different because of the difference of the geometry structure (mainly the diameter and chiral angle), although there is no change for the
local chemical bond and no doping [8-10]. When the \((n, m)\) index satisfies the condition 
\((2n+m) = 3q\) (q is an integer), the tube has a metal property; otherwise it has a semiconductor property. This means that \(1/3\) SWNTs are metallic and \(2/3\) are semiconductor. Those results are obtained from the electronic structure of 2-D graphite [6, 10, 11]. 2-D graphene is a semiconductor with an energy gap of zero. Its binding and anti-binding \(\pi\) electron bands overlap and are degenerate at the K point in the 2-D hexagon Brillouin zone of graphene. The periodic boundary condition of the 1-D SWNT allows only a few wave vectors existing in the circumference. If the wave vectors pass through the K point in the Brillouin zone, the SWNT is metallic, if not, the SWNT is a semiconductor with a fixed energy gap. The allowed k values of metallic and semiconductor SWNT in the 2-D Brilouin zone of graphite can be derived theoretically. For metallic SWNT, the solid line crosses the K point; for semiconductor SWNT, the K point is always at one third the distance between two solid lines. For each K wave vector, there is a minimum energy value for both the conduction and valence bands. These are the Van Hove singularities of the density of states of electrons. There is an energy gap between each pair of Van Hove singularities.

The electromagnetic properties of SWNTs are mainly dominated by the conjugated \(\pi\) bond of the graphene sheet. There are two crossed energy bands at the Fermi level in a metallic SWNT. Thus, there are two channels and 4 electrons contributing to electron transportation. Under conditions of no electron scattering and ideal contact, there are two units of quantum electric conductance \((G = 2G_0 = 4e^2/h)\), where \(G_0\) is unit quantum electric conductance), its electric resistance is \(R = h/4e^2 = \)
6.45K Ω, which means each channel contributes one unit of quantum electric conductance [12]. Calculation based on Boltzmann’s transportation equation shows that the electric resistance of a metallic SWNT is 4.2K Ω, the resistance of a semiconductor SWNT is 190K Ω [13]. Usually the measured electric resistance is larger than the calculated one. This may be the result of the defects in SWNT. From the point of view of the density of states, a SWNT is a typical quantum wire. Its electric conductance is discontinuous. Because of its nano-scale, difficulty to be dispersed, and closely relating structure, it is very difficult to measure the electronic properties of SWNTs accurately. Measurement by using an atomic force microscope proves that it is a quantum wire. Single electron transportation and resonant tunneling effects, because of the discrete energy levels produced by the quantum confinement, are observed. Realization of single electron transport requires that the system consisting of the electrode and the SWNT is small enough, the contact resistance between electrode and SWNT is larger than the quantum resistance (1/G₀) and the SWNT between the electrodes is small enough so that the capacity is small enough to cause the energy e²/C (the energy to add an electron to the system) to be greater than k_BT. Generally, liquid helium temperature is required to observe this phenomenon for a metallic SWNT of several micrometers in length [17], however, it can be observed at room temperature for a semiconductor SWNT [18]. In studies of the electric properties of a SWNT at low temperature, large contact electric resistance between a SWNT and the electrode, Coulomb blockage at different temperatures and the Luttinger Liquid effect (Electron gas with strong interaction among electrons because the Coulomb interaction cannot be screened. It has long-range
density wave function with low energy excitation, called a Luttinger Liquid.) is found [14]. There are two characters in the electron transportation in a SWNT: finite electron states and ballistic transportation [15, 16]. Ballistic transportation means that there is no scattering with impurities or phonons during electron motion in a conductor; therefore, there is no energy dissipation in the movement of the electrons. Based on experimental results [19, 20, 21], SWNTs exhibit intrinsic weak electron-phonon, e-ph, interaction. In references [20, 21], carbon nanotubes had been found to sustain very large current densities of $10^7$-$10^8$A/cm$^2$ at room temperature without suffering current induced damage. In reference [19], by using femtosecond time-resolved photoemission as a tool, the e-ph interaction in the metallic nanotube was determined directly at room temperature through analyzing the dynamics of the electron distribution in the vicinity of the Fermi level. The observed electron dynamics was then used to calculate the e-ph scattering matrix elements for two likely scattering scenarios: forward scattering from twisting and backward scattering by longitudinal acoustic phonons. The corresponding results revealed an intrinsic weak e-ph interaction approximately 50% smaller than the one predicted by tight-binding calculations [60], and the directly measured scattering time was long, up to 18ps at Fermi level, which proved a room temperature mean-free path of 14 microns for a metallic SWNT (The Fermi velocity of metallic type SWNTs at room temperature is about 8Å/fs.).

In summary, both theoretical and experimental studies showed that electronic properties of CNTs, especially SWNTs, exhibit characteristics of single electron transportation, ballistic transportation of electrons (very long MFP, or very weak
electron-phonon interaction), etc.; one third of SWNTs are metallic, two thirds are semiconductor.

2.2.2. Behaviors of CNTs under a Static Electric Field

Mainly, there are two types of response of CNTs to an external electric field: cases with and without a closed loop and an electron source. In the case with a closed loop, a d.c. current will be driven by the field to pass through the CNT. As mentioned above, in references [20] and [21], experiments showed that CNT can sustain very large current densities of $10^7$-$10^8$ A/cm$^2$ at room temperature without suffering current induced damage. Thus, CNTs are very good candidates for filament usage. In the case without a closed loop, the response of CNTs to an external electric field can be divided into two categories, weak and very strong fields. In the case of a very strong field, field emission of electrons is the main effect.

The electrons cannot escape from a metal surface because of two reasons:

1. Double electric layers consisting of an electron cloud. Near the vacuum side, the lattice of the metal does not satisfy a periodic condition. Because of the thermal movement, some of the electrons are trying to escape from the surface, which results in asymmetric distribution around the surface. The center of the electron cloud moves a little toward to the vacuum side and meanwhile some of the metal atoms are polarized to be ions because of the non-equilibrium electric field. Thus, a dipolar layer is formed near the metal surface...
with negative charges outside and positive charges inside the surface. An electron passing through this dipole layer must do work against the field of the layer. So, the dipole layer is a barrier to prevent electrons from escaping the surface.

(2) Image force. From the point of view of static electricity, the periodic distribution of the atoms in the metal can be replaced by a uniform surface of a good conductor, if an electron is far away from the surface. A force from a positive image charge located inside the surface will be exerted on the electron. The direction of the force points to the interior of the metal.

Within $x_0$, a distance of several intervals between the atoms, the force exerted on the electron mainly comes from the dipole layer; for a greater distance, the force mainly comes from the image force. Based on Sommerfield’s free electron model, at zero Kelvin electrons at the Fermi level of the metal have the highest energy. So, the smallest energy that allows an electron to escape from the surface of the metal is $\chi_m = W_s - E_F$, where, $W_s$ is the barrier of the surface, $E_F$ is the Fermi energy. Usually, $E_F$ is a function of the temperature, but, for metal the change of $E_F$ as the temperature change is very small. In the case of the change of temperature from 0K to 2500K, the change of $E_F$ is only 0.1% of that at 0K. So, the $E_F$ and, thus, $\chi_m$ of metal is not a strong function of temperature.

Actually, there are several ways to make electrons overcome the surface barrier to escape from the surface of a metal:
(1) thermal electron emission;
(2) field emission;
(3) secondary electron emission;
(4) photo-electron emission.

Within the above emissions, field emission is a special case. In other emissions, the free electrons in the metal acquire enough energy to overcome the surface energy barrier by capturing external energy. During the process, the height of the barrier does not change. In the case of field emission, the barrier is depressed by the external field to make the barrier lowered or narrowed. When the width of the barrier is narrowed down to the order of the quantity of the wave length of electrons, the tunneling effect will cause the electrons to pass through the barrier to get into the vacuum.

Experiments show that the initial threshold and the critical threshold of the field emission of MWNT and SWNT is, respectively about 1.5-4.5V/μm and 3.7-7.8V/μm [22-25], smaller than diamond [24] and amorphous carbon [26] films and much smaller than silicon [25]. The sensitivity of field emission of SWNT relative to the environment is much less than general metal materials [27]. The reason is that SWNTs have very strong C-C bonds and a perfect structure, which makes it stable during the field emission process.

Although field emission of CNTs is a very valuable topic, considering the fact that the threshold voltage is larger than the maximum value of voltage in our case (1×10⁴V/cm, or 1V/μm, as mentioned in Chapter 1), we neglect this effect in the following discussions.

25
In the case where the intensity of the external electric field is lower than the threshold voltage for field emission, the main effect of the external electric field on the CNT is the polarization of the CNT. Quantum theory of polarization of SWNTs was studied by Marvin L. Cohen et al. in 1995, based on tight-binding theory [28]. Based on their study, when exposed to an external static electric field, a SWNT is strongly polarized in the axial direction and weakly polarized in the radial direction. The polarization in the axial direction is strongly dependent on the electronic structure of the SWNT. The one in the radial direction has no correlation to the electronic structure, but is in proportion to the square of the radius of the SWNT. Considering the fact that a CNT, especially a SWNT, is quantum confined in the radial direction, thus, the polarization of a CNT in the radial direction is very weak. We will neglect the effect of the polarization in the radial direction of a CNT and concentrate on the effect of polarization in the axial direction of the CNT.

An accompanying effect of the polarization of a CNT in the axial direction under an external static electric field is an extension of the CNT. By using a quantum molecular dynamics method (QMDM), Y. F. Guo and W. L. Guo calculated this effect in 2003 [29].

The red line in Fig. 2.1 is the result of quantum-molecular dynamics simulation of the extension of a (5, 5) SWNT with a length of 1nm, diameter of 0.7nm under an external static electric field. The black line is the result of a (9, 0) SWNT with the same length and diameter. (Note, both of the SWNTs are metallic.) Both lines show an approximately linear relation between the electric field and the strain. Based on the two
lines, the order of the magnitude of the strain of a metallic SWNT under an external electric field of $E = 1 \times 10^4 \text{V/cm}$ is $0.5 \times 10^{-6}$ (Calculations are based on 1 a.u. = $5.142 \times 10^9 \text{V/cm}$, the slopes of the both curves are about 16.25 and 28.0, respectively, and show that the strain is proportional to the electric field intensity.)

Fig. 2.1 Deformation of two types of SWNTs (an armchair type and a zigzag type) Versus Electric Field Intensity. Ref. [29] Reproduced with permission from IOP Publishing Limited.

Actually, there is an easier way, shown below, to make the estimation. The Fermi surface in a metallic SWNT crosses the K point of the first Brillouin zone. For this consideration, there are only two conduction channels, as mentioned earlier. Thus, there are only 4 free electrons involved in the transportation process, if there is no external electron source. Considering a straight metallic type SWNT with an external
electric field parallel to the axis of the tube, because of its finite length (typically 1-100 micron), free electrons in the SWNT will move to and concentrate on its end caps. Thus, for a given $Y = 1 \text{TPa} = 10^{12} \text{N/m}^2$ (The Young’s modulus of SWNT), a SWNT of diameter 1nm, $S \approx 1 \text{nm}^2 = 10^{-18} \text{m}^2$, and strain $\varepsilon$, we get $F_{\text{elastic}} = YS\varepsilon = 10^{-6} \varepsilon \text{ N}$ (N represents Neuton). Let $F_{\text{elastic}} = F_{\text{electric}} = neE$, Thus, we get $\varepsilon = \frac{F_{\text{electric}}}{YS} = \frac{neE}{YS} = \frac{n \times 1.6 \times 10^{-19} C \times E}{10^{12} N/m^2 \times 10^{-18} m^2}$, or, $\varepsilon = 1.6 \times 10^{13} \text{nE}$, where $n$ is the number of electrons. As mentioned above, there are only 4 free electrons in a pure metallic SWNT. Take $n = 4$, under an electric field of $E = 10^4 \text{V/cm} = 10^6 \text{V/m}$ to get $\varepsilon = 0.64 \times 10^{-6}$, the same order of magnitude as the result of the above QMDM calculation. This result reveals a typical electromechanical response of a SWNT under an external static electric field.

2.2.3. Behaviors of CNTs under an Alternating Electric Field

In the case of an alternating electric field, the behavior of CNTs are more fascinating. As it was mentioned above, a mechanical process always comes with the electric response of a CNT to the external electric field. Thus, it is necessary to make a comment on the mechanical properties of CNTs.

2.2.3.1 Mechanical Properties of CNTs

There are two categories about the mechanical properties of CNTs related to our topic. The first one is the mechanical property of CNTs in the radial direction. The
second one is the value of Young’s modulus of CNTs, the mechanical property of CNTs in the axial direction.

G. G. Tibbetts discussed the relation between the bending of a graphene sheet and the related structures using a continuous theory [30]. The result is

\[
\sigma = \pi E L a^3 / (12r),
\]

where \(\sigma\) is the stress, \(E\) is the elastic modulus, \(r\), \(L\), \(a\), are the curvature, length of the cylinder, and the distance between two neighboring graphite planes, respectively. The result shows that the stress is inversely proportion to the curvature.

When considering the increased stress energy of each atom, from the above formula we can get a very important relation between the stress energy and the radius of a SWNT: The stress energy per atom is proportion to \(r^{-2}\) (as shown in Fig. 2.2).

![Fig. 2.2 Energy per atom as a function of the radius of a carbon nanotube. Ref. [31] Reproduced with permission from IOP Publishing Limited.](image)
As the diameter of a SWNT increases, the SWNT becomes more and more unstable [31] (as shown in Fig. 2.3).

There are two critical diameters $d_1$ and $d_2$. When the diameter of a SWNT is less than $d_1$, the circular structure is stable; when the diameter of a SWNT is greater than $d_2$, the collapsed structure is more stable. For examples, for (n, n) type SWNT, $d_1$ is between 1.077nm (16, 16) and 1.144nm (17, 17), and $d_2$ is between 2.962nm (45, 45) and 3.030nm (46, 46); for (n, 0) type SWNT, $d_1$ is between 1.049nm (27, 0) and 1.088nm (28, 0), and $d_2$ is between 2.993nm (77, 0) and 3.032nm (78, 0). Fig. 2.8 shows a schematic diagram of the stable and unstable structures of SWNTs.

![Fig. 2.3 Cross sections of the optimum (n, n) tubes (started from the collapsed forms shown). Ref. [31] Reproduced with permission from IOP Publishing Limited.](image)

Although CNTs, especially SWNTs, are found to be “stiff” in the axial direction, they are very “soft” in the radial direction. They are easily deformed when put in contact with an object [32]. Fig. 2.4 [32] shows the cases of deformations, when a SWNT contacts another object, by using MD simulation. Both theoretical and
experimental results showed that the radial modulus of carbon nanotube is on the order of magnitude of several GPa [33, 34].

Young's modulus is one of the fundamental parameters of the mechanical property of a material. From the microscopic point of view, Young’s modulus is related to the binding of atoms in the material. Young’s modulus of a material is inversely proportion to the forth power of the lattice constant. A very small change of the lattice constant will result in a dramatic change of the Young’s modulus [35]. Graphite is a typical example, its $C_{33}$ (Young’s modulus along the $c$ direction, which is perpendicular to the graphene sheet.) depends strongly on temperature. Variation of temperature
results in the change of the distance between two graphene layers, thus, results in the change of $C_{33}$. Because the basic covalence bond in a carbon nanotube is $sp^2$ hybridization bonds, its Young’s modulus must be closely related to the $sp^2$ covalence bond [6, 36].

M. S. Dresselhaus et al. [36], were the first who analyzed the Young’s modulus of a carbon nanotube using continuum elasticity theory based on $C_{11} = 1$TPa in graphite. They estimated the value of the Young’s modulus of a carbon nanotube was about 800GPa.

At present, most investigators use the Tersoff potential function [37, 38] which is based on the concept of the bond order. The merit of the Tersoff potential function is that it can accurately describe the interaction between atoms in an alkyl-like system. It can be used to calculate the bonding energy, angle of bond, etc., as well as to analyze the binding process and to mimic the crack process [38]. Many calculation results show that the Tersoff potential function is well suited to a carbon nanotube. The stress energy of each carbon atom in a nanotube is inversely proportion to the square of the diameter of the tube, and has no correlation to the chiral angle of the nanotube [39-41]. The empirical relation between the Young’s modulus and diameter of a carbon nanotube is

$$Y = \frac{4296}{d} + 8.24 \text{ (GPa)}$$ [40, 41]. Especially, for a carbon nanotube of diameter larger than 1nm, the result of a theoretical calculation is the same as the one based on the continuum theory. Based on the formula, the Young’s modulus of a carbon nanotube of diameter 1nm is about 4TPa. But, in the above calculation the thickness of a carbon nanotube was taken as a value of 0.07nm, the same value as the thickness of a graphene
sheet. If the thickness is taken as 0.34nm (the same as the distance between two graphite layers), the results would be reduced to about 1TPa. Others use the Constant of Force model and the Total Energy of Electrons of All the Occupied Bands method to make the calculation [42-44]. Considering that carbon nanotubes are usually self-organized to produce bundles [45], all the methods mentioned above were also used to calculate the Young’s modulus of a bundle of carbon nanotubes. At present, the well accepted value of the Young’s modulus of a carbon nanotube is 1TPa, the shear modulus is about 1 order of magnitude less than the Young’s modulus, and the values of the modulus are independent of the diameter, the chiral angle and the number of layers of a carbon nanotube. Meanwhile, all calculations showed that whatever the type is, the Poisson’s ratio of a carbon nanotube is between 0.15-0.28 (for graphite the value is 0.16), which is independent on the chiral angle.

As a summary, a CNT, especially a SWNT, is rigid in the axial direction, but soft in the transverse direction. The Young’s modulus of a carbon nanotube is 1TPa, and its transverse elastic modulus is several GPa.

2.2.3.2 Cantilever Vibration of CNTs

P. Poncharal, et al, using an in situ electromechanical resonance method measured the modulus of carbon nanotubes [46, 47]. They found that by introducing a transverse electric field into an isolated nanotube, a mechanical bending resulted. By tuning the frequency of the field, a cantilever resonance was observed (see Fig. 2.5). Based on their results, the Young’s modulus of MWNT is a function of the diameter of
the tube. For MWNT of diameter less than 8nm, the value of the Young’s modulus is about 1.2TPa. As the diameter increases from 8nm to 40nm, the value of Young’s modulus drops from 1TPa to 0.1TPa. This may be the result of an increase of defects in MWNTs of larger diameters.

Fig. 2.5 Nanotube response to resonant alternating applied potentials. (A) In the absence of a potential, the nanotube tip (L=6.25μm, D=14.5nm) vibrated slightly because of thermal effects. Although the thermal amplitude is difficult to evaluate, it was, nevertheless, used to measure the Young’s modulus in a previous study. (B) Resonant excitation of the fundamental mode of vibration (ν₁ = 530KHz); the shape corresponds closely to that expected for a cantilevered uniform beam. The high contrast at the extremes of the oscillations is caused by the relatively long times spent at the tuning points [compare with (A)]. (C) Resonant excitation of the second harmonic (ν₂ = 3.01MHz). Both the frequency and the shape correspond reasonably well to that expected for this harmonic. For this tube, the bending modulus Eₘ = 0.21TPa. Ref. [46] Reproduced with permission from AAAS.
In the above experiment, the mechanical vibration of the carbon nanotube was driven by the force of the interaction between the polarized nanotube and the alternating external electric field. From the point of view of applied mathematics, the above cantilever type vibration of a carbon nanotube can be categorized into the case of forced vibration of a rigid rod or wire with boundaries where one end is fixed and another end is free.

2.2.3.3 Effect of Transversal Vibration Excited by an Alternating Electric Field

B. Reulet, et al [48], studied the electromechanical effect of the case where two ends of a CNT were fixed. A d.c. current was passed through the CNT and transverse vibrations of the CNT were excited by a low power microwave source. Fig. 2.6 is the schematic graph of their experimental setup. Fig. 2.7 is the focused TEM image of the suspension of a rope of SWNTs on two metallic pads, where a SWNT rope of length of 1.7μm consisting of about 200 SWNTs with each with diameter of 1nm mounted on superconducting (Tc = 1.2K) Au/Re contacts.

Fig 2.6 Schematic setup of an experiment for studying the acoustoelectric effects of CNTs. Ref. [48] Reproduced with permission from American Physical Society.
By measuring the voltage drop across the SWNT rope (sample # RO1) under an environment where the temperature was almost 0K (The condition of 0K temperature guaranteed two things: 1. diminished contact resistance; 2. all vibration modes are frozen.). They found that the d. c. transport property of the rope was strongly affected by the presence of an r. f. electromagnetic field (The intensity of the electric field was estimated to be the order of magnitude of 1V/cm.) produced by an antenna located in the vicinity of the rope. The main results of the experiment are shown in Fig. 2.8. The results of this experiment proves that in the absence of transverse resonance, the resistance of the SWNT rope is very small (This result coincides with the result of reference [19], where an experiment showed that the mean-free-path of an electron in a metallic SWNT is long, up to 14μm.), which expresses an intrinsic weak electron-phonon interaction; near transverse resonance, the resistance of the same rope rises to a value which is at least 3 orders of magnitude larger than without a transverse resonance. Thus, during transverse resonance, electron-phonon interaction is strongly enhanced. One thing worth mentioning is that in the explanation of the experimental results, the
reason that transverse vibrations were excited was attributed by the authors to the Coulomb force exerted on the uncompensated charges on the SWNT rope arising from the noble metal contact because of the difference of work functions between the SWNT and the metal electrode [49]. The amount of the charge depleted from the metal to SWNT was estimated to be 100e [48, 49] with e the amount of charge of an electron.

Fig. 2.8 (A) Effect of a r.f. electromagnetic radiation on the dc voltage drop across a CNT rope RO₁ when it carried a d.c. current below the critical current. (B) Evolution of the resonance line shapes of the sixth harmonic on RO₁ with the temperature of the contacts. (C) Resistance of RO₁ versus frequency near the sixth harmonic, at 110mK and for different applied r.f. powers. Ref. [48] Reproduced with permission from APS.
A carefully look at Fig. 2.8, shows that there are two resonant peaks of voltage (which corresponds to the peaks of resistance because the d. c. current is constant.) between 2000MHz (2.0GHz) and 2500MHz (2.5GHz), which is in the region of the frequency of microwaves used in our case (2.45GHz). As the temperature and power of the rf field increase the resonant peaks become broader. It is reasonable to imagine that at room temperature, one of the peaks would be broad enough to cover the 2.45GHz, the frequency of the microwave used by Imholt et al.[2].

Finally, a summary of all the important results in this chapter that are related to our findings is shown below:

1. CNTs, especially metallic type SWNTs, exhibit intrinsic weak electron-phonon interaction, even at room temperature;

2. Under an external electric field, polarization along the axial direction and the accompanied electromechanical response are the main effects if the intensity of the electric field is less than the critical threshold value for field emission of electrons;

3. Electron-phonon interaction in a SWNT is dramatically enhanced at transverse resonance. As the temperature and the power of the r. f. field increase, the peaks of the resonances become wider and wider.

4. By close contact with noble metals, an amount of about $10^2 e$ charges will be depleted from the metal to the CNT. This is the foundation of the physics of the Coulomb force in Reulet’s experiment.
CHAPTER 3
A NEW MODEL AND THE THEORETICAL RESULTS

Before the proposed model is discussed, it is necessary to point out the differences between the models mentioned in chapter 2 and the case mentioned in chapter 1.

In chapter 2, there are two kinds of electromechanical responses of CNTs to an alternating electric field proposed by P. Poncharal et al. [46], the cantilever vibration of a rigid rod, and B. Reulet, et al. [48], the forced transversal vibration of a rigid rod, respectively. In Poncharal’s case, one end of a CNT is fixed on the substrate with another end free. The vibration is the result of the coupling between the Coulomb force and the bending moment of the CNT or torque. The observed resonant frequencies cover a wide range from several hundreds of KHz to several hundreds of MHz for CNTs with lengths of several microns. In Reulet’s case, the CNT (length of a couple of microns) is suspended with two ends fixed. The r. f. field exerts a Coulomb force perpendicular to the axial direction of the CNT. Meanwhile, a d. c. current passes through the CNT along the axial direction. Although in Reulet’s case one of the resonant peak may cover the frequency (2.45GHz) of the microwave mentioned in chapter 1, the boundary conditions that two ends are fixed and the condition of d. c. current obviously do not match the situation mentioned in chapter 1 where CNTs in the
quartz tube are flexible and there is no d.c. current, instead, an a.c. current driven by the microwave exists. Another important difference between Reulet’s case and the experiments discussed in chapter 1 is the peak value of the electric field. In Reulet’s experiment, the value is estimated as 1V/cm; in the cases we are considering, the value is estimated as high as 10^4V/cm. These differences prompted us to develop a new model which has not been reported by others to describe the phenomena mentioned in chapter 1.

3.1 The Model and Assumptions

The Fermi velocity of electrons in a CNT has been measured to be as much as \( V_F = 8.2 \times 10^5 \text{m/s} \) [50] at room temperature. The time that an electron moves from one end to another end of a SWNT (~10^{-12}s for a CNT with a length of 1\( \mu \text{m} \)) is much less than a period of the microwave (~10^{-10}s), even if we do not consider the acceleration of the electron by the microwave field. Thus, it is reasonable to assume that the polarization of a CNT under the microwave field instantaneously follows the electric field.

In references related to CNTs, it is seen that the geometric models to describe a CNT, especially a SWNT, include cylindrical thin shell, rigid rod, and wire, depending on the dimension of the CNT to be studied. A criteria suitable to the three models, respectively, is given in reference [51], where the authors experimentally proved that when the aspect ratio of the studied SWNT is less than 10, between 10 and 100, and greater than 500, a cylindrical thin shell, a rigid rod, and a wire is suitable, respectively.
Fig. 3.1 shows different behaviors of SWNT with different aspect ratios under a compression load.

Fig. 3.1 Overview of deformations of SWNTs in compression: Shell-rod-wire transition as a function of the length-to-diameter aspect ratio of the CNT. The plot shows different modes of deformation: (a) buckling of the cylindrical shell structure; (b) rod-like behavior with localized buckling along the length of the tube; and (c) a flexible macromolecule. Ref. [51] Reproduced with permission from ASME.

Considering the fact that the CNT samples used in the experiments mentioned in chapter 1 fall into a region of diameter of 1-2nm and length of 1-10μm, the aspect ratio is larger than 500. Thus, we adopt the wire model. Furthermore, for the reason of simplification, we treat a SWNT of diameter of 1nm and length of 1μm as an elastic string.

As seen in chapter 1, there are many nanosize metal particles in the sample. These residual metals are introduced into the samples from the production process and mainly located at, inside and in close contact to an end of a nanotube. Based on W. Ekardt’s work [52], when the number of atoms in a metal cluster is about 100, the work
function of electrons in the cluster approaches the value of the work function of the bulk material. When there are less than 100 atoms, the value of the work function oscillates as the number of atoms changes. Considering the fact that the diameter of a SWNT is 1nm, the number of atoms in the metal nanoparticle is on the order of magnitude of 100 atoms. Thus, we can reasonably assume that the value of the work function of the residual metal is the same value as the bulk. Thus, the hypothesis that charge of an amount of $10^2 e$ is depleted into the nanotube is validated, based on Reulet’s work.

Under a high electric field, these depleted charges will overcome the confinement of the local Coulomb potential to become free charges. Thus, furthermore, based on Y. F. Guo and W. L. Guo’s work [29] and the simplified calculation mentioned in chapter 2, as the number of free charges is increased from $10^0$ to $10^2$, the strain, $\varepsilon_o$, of a SWNT under a static electric field of intensity of $10^4 V/cm$ would be increased from $10^{-6}$ to $10^{-4}$.

The microwave field used in chapter 1 (2.45GHz) can be treated as a quasi-static field compared to a typical microscopic mechanical process in a solid (10THz). Thus, the above analysis is applicable. When exposed to the microwave field, because of the polarization, a mechanical extension process can be applied to such a case as described in chapter 2 [29] and schematically described in Fig.3.2.

In Fig.3.2, assume the electric field is started from 0, during the first half period (part A of the blue curve), as the intensity of the electric field increase and decrease (blue curve) the SWNT completes a period of mechanical vibration along its axial direction because of the Coulomb force arising by polarization. During the second half period of the electric field (part B of the blue curve), the same mechanical process is
repeated, although the direction of the polarization is inverted. By setting the new equilibrium position (Actually, this position is equivalent to the equilibrium length of the SWNT with respect to its natural length.) represented by the green line, we find that the frequency of the mechanical vibration is twice the value of the microwave frequency.

Fig.3.2 A schematic description of the mechanical behavior of a straight SWNT during microwave irradiation (assume the direction of the field is parallel to the axis of the SWNT), where the mechanical response of the SWNT (red curve) to the electric field (blue curve) in one period of the electric field is shown. The first and the second half period of the microwave field are labeled A and B, respectively. The x-axis is the normalized time, and y-axis is arbitrary unit.
In summary, in order to perform a detailed analysis, we have simplified the problem to a solvable model: A longitudinally forced vibrating elastic string (Young’s modulus 1TPa) with an equilibrium strain of $10^{-4}$.

3.2 Mathematical Expressions of the Model

To completely express the model, the longitudinal-transverse coupled wave equations presented by Morse and Ingard [53] are applied.

\[
\frac{\partial^2 u}{\partial t^2} - c_T^2 \frac{\partial^2 u}{\partial x^2} = \frac{1}{2} (c_L^2 - c_T^2) \frac{\partial}{\partial x} \left[ (v_x^2 + w_x^2)(1 - 2u_x) \right], \quad (3.1)
\]

\[
\frac{\partial^2 v}{\partial t^2} - c_T^2 \frac{\partial^2 v}{\partial x^2} = \frac{1}{2} (c_L^2 - c_T^2) \frac{\partial}{\partial x} \left[ v_x (v_x^2 + w_x^2) + 2u_x v_x (1 - u_x) \right], \quad (3.2)
\]

\[
\frac{\partial^2 w}{\partial t^2} - c_T^2 \frac{\partial^2 w}{\partial x^2} = \frac{1}{2} (c_L^2 - c_T^2) \frac{\partial}{\partial x} \left[ w_x (v_x^2 + w_x^2) + 2u_x w_x (1 - u_x) \right], \quad (3.3)
\]

where, $u$, $v$, and $w$ represent the displacements of an infinitesimal piece of the string at position $r(x,y,z)$ in $x$, $y$, $z$ direction, respectively; $c_T$ and $c_L$ represents the transverse and longitudinal speed of sound in the string, respectively; the footnote x represents the first order partial derivative with respect to x. Consider that the left side of the string is set at $(0,0,0)$, the right side of the string is set at $(L_0,0,0)$ with $L_0$ the equilibrium length of the string. The boundary conditions suitable to the model are expressed as:

\[
u (0,t) = u_0 \cos(2\omega_E t), \quad (3.4)\]

\[
u (L_0,t) = u_0 \cos(2\omega_E t), \quad (3.5)\]

\[
u_x (0,t) = v_x (L_0,t) = w_x (0,t) = w_x (L_0,t) = 0, \quad (3.6)\]
where $u_0 = \varepsilon_0 L_0$ is the maximum displacement with $\varepsilon_0$, the equilibrium strain. Equations (3.4) and (3.5) represent equivalent driving forces which are exerted on both sides of the string along opposite directions in the x-axis, and the forces are alternated with a frequency twice the value of the frequency of the microwave, $\omega_E$. The boundary condition (3.6) is set to match the requirement of continuous stress at the two sides of the string [54].

The solutions of Equations (3.1-3.3) can be taken as the summation of two symmetric parts, $u_1(x,t), v_1(x,t), w_1(x,t)$, and $u_2(x,t), v_2(x,t), w_2(x,t)$, such that each one satisfies:

$$u_1(0,t) = u_0 \cos(2\omega_E t),$$  \hspace{1cm} (3.7)

$$u_1(L_0, t) = 0,$$  \hspace{1cm} (3.8)

$$v_{1x}(0, t) = v_{1x}(L_0, t) = w_{1x}(0, t) = w_{1x}(L_0, t) = 0.$$  \hspace{1cm} (3.9)

and

$$u_2(L_0, t) = 0,$$  \hspace{1cm} (3.10)

$$u_2(L_0, t) = -u_0 \cos(2\omega_E t),$$  \hspace{1cm} (3.11)

$$v_{2x}(0, t) = v_{2x}(L_0, t) = w_{2x}(0, t) = w_{2x}(L_0, t) = 0.$$  \hspace{1cm} (3.12)

respectively. And,

$$u(x, t) = u_1(x, t) + u_2(x, t),$$  \hspace{1cm} (3.13)

$$v(x, t) = v_1(x, t) + v_2(x, t),$$  \hspace{1cm} (3.14)

$$w(x, t) = w_1(x, t) + w_2(x, t).$$  \hspace{1cm} (3.15)
A similar model, known as Melde’s experiment, has been thoroughly studied by many researchers [55].

![Fig. 3.3 A schematic expression of Melde’s experiment. Ref. [55] COPYRIGHT Reproduced with permission from American Association of Physcs Teachers Publications.](image)

Fig. 3.3 describes a forced vibrating string with left side fixed; the right side is horizontally driven by a sound fork. The result of the Melde’s experiment is a transverse resonance. The solution of Melde’s experiment is acquired by solving equations (3.1), (3.2), and (3.3) with boundary conditions [55] given by:

\[
\begin{align*}
  u(0, t) &= 0, \\
  u(L_0, t) &= -u_0 \cos(\omega t), \\
  v(0, t) &= v(L_0, t) = w(0, t) = w(L_0, t) = 0.
\end{align*}
\]

Comparing Melde’s experiment and our model, we see that the only difference is the boundary conditions at the two sides of the string where, in Melde’s case, displacements in both y and z directions are confined; in ours, they are free. In the following discussion, we will adapt the treatment by David R. Rowland [55] in analyzing the Melde’s case.
The effect of boundary conditions (3.4) and (3.5) results in a change of tension of a carbon nanotube given by

$$\tau = SY \left[ \frac{(L_0 - u_0 \cos(2\omega_E t)) - L_r}{L_r} \right] = \tau_0 [1 - b \cos(2\omega_E t)],$$  \hspace{1cm} (3.19)

with

$$\tau_0 = SY \frac{L_0 - L_r}{L_r} = SY\epsilon_0,$$ \hspace{1cm} (3.20)

and

$$b = \frac{u_0}{L_0 - L_r},$$ \hspace{1cm} (3.21)

where, \( S \) is the cross section of the string; \( Y \) is the Young’s modulus of the string; \( \tau_0 \) is the equilibrium stress; \( \epsilon_0 \) is the equilibrium strain; \( L_0 \) is the equilibrium length of the string; \( L_r \) is the relaxed length or natural length of the string and \( 2\omega_E \) is the frequency of the mechanical driving force. Based on the above analysis, it can be seen that the frequency of the mechanical driving force is twice the value of the frequency of the microwave with \( \omega_E \) the frequency of the microwave.

By assuming a (17, 17) type SWNT with length of 1\( \mu \)m and strain \( \epsilon_0 = 10^{-4} \), (which corresponds to \( L_0 - L_r = 1 \) angstrom.), and taking Young’s modulus of the tube as 1TPa, with \( \omega_1 = c_\tau k_1 \) (fundamental frequency) of the transverse mode is approximately 2.1GHz which, approaches the microwave frequency applied in our experiments (2.45GHz). Here \( k_1 = \frac{2\pi}{\lambda} \) is the wave vector.
Note that $c_r^2 = \frac{\tau_0}{\rho}$ (Where, $\rho$ is the mass density of the string. In our case, the mass density of the carbon nanotube.) is proportion to the cross section and inversely proportion to the density of mass. As the number of walls increases, the cross-section of the carbon nanotube increases. But, meanwhile, the mass density of the CNT increases also. The changes of these two factors approximately cancel each other under the assumption that $\rho$ is proportion to the number of the walls of a carbon nanotube. Thus, the analysis can be applied to all carbon nanotubes, such as SWNT, DWNT, MWNT and even carbon nanotube ropes and strands. Even though coalescence and diameter change processes are involved, as long as the structure of the system is still a carbon nanotube, the basic mechanical process under microwave irradiation still applies. Thus, the physical process described by the model is repeatable for all types of carbon nanotube during microwave irradiation. In the following, for simplification, we neglect the transverse-transverse coupling and concentrate on the two dimensional case, that is $w \equiv 0$.

In the initial stage of excitation, while the amplitude is small, the linear wave equation:

$$\rho_0 \frac{\partial^2 v}{\partial t^2} - \tau \frac{\partial^2 v}{\partial x^2} = 0,$$

(3.22)

describes the transverse wave. Substitute the time-dependent tension from (3.19) into (3.22) to get:

$$\frac{\partial^2 v}{\partial t^2} - c_r^2 [1 - b \cos(2\omega_t t)] \frac{\partial^2 v}{\partial x^2} = 0,$$

(3.23)
where \( c_T = \sqrt{\frac{E}{\rho_0}} \) is the speed of transverse sound waves. Writing the solution as

\[
v(x, t) = \sum_{n=1,3,5,...} v_n(t) \cos(k_n x), \tag{3.24}
\]

with \( k_n = \frac{n \pi}{L_r} \), \( v_n(t) \) satisfies the Mathieu equation,

\[
\frac{d^2 v_n}{dT^2} + [\alpha - \beta \cos(T)]v_n = 0, \tag{3.25}
\]

where \( \alpha = \frac{\beta}{2} = \frac{\omega_v^2}{4 \omega_E^2}, \omega_v = c_T k_n, T = 2 \omega_E t \); the spatial part of the solution is taken as a cosine function to satisfy the boundary condition \( \frac{\partial v}{\partial x} = 0 \) at \( x = 0 \), and \( x = L_0 \) (In Melde’s case, it is a sine function [55],) and the integer \( n \) is odd to match the fact that the total applied force is zero. Thus, the center of mass of the carbon nanotube does not move.

In Melde’s experiment, a resonant response occurs at \( \omega_n \approx \frac{\Omega}{2} \), where \( \Omega \) is the frequency of the driving force. This is a standard result for parametric resonance [54]. In our case \( \Omega = 2 \omega_E \). Thus, resonance occurs at \( \omega_n \approx \omega_E \) so that \( \alpha = \frac{\beta}{2} = \frac{1}{4} \). The solutions of equation (3.23) are stable or unstable depending on the values of \( \alpha \) and \( \beta \).

In (\( \alpha - \beta \)) parameter space, boundaries between stable and unstable regions near the value \( \alpha = \frac{1}{4} \) are given by: [56-58]

\[
\alpha \approx \frac{1}{4} \pm \frac{\beta}{2} - \frac{\beta^2}{8} \tag{3.26}
\]
Fig. 3.4 shows the region of stable and unstable solutions for different values of $\alpha$ and $\beta$ [55]. It is seen that the point $(\alpha = \frac{1}{4}, \beta = \frac{1}{2})$ lies in an unstable region.

![Diagram showing stable and unstable regions for Mathieu's equation parameters $\alpha$ and $\beta$.](image)

In region I and III of Fig. 3.4, the general solution of (3.25) is a steady state solution:

$$v_n(T) = c_1 e^{i\eta T} p_1(T) + c_2 e^{-i\eta T} p_2(T), \quad (3.27)$$

where $c_1$, $c_2$ are arbitrary constants, $\eta$ is a real number that depends on $\alpha$ and $\beta$, and $p_1(T)$ and $p_2(T)$ are periodic functions depending on $\alpha$ and $\beta$ with period $2\pi$ [59].

In region II of Fig. 3.4, the general solution of equation (3.25) is:

$$v_n(T) = c_1 e^{\mu T} q_1(T) + c_2 e^{-\mu T} q_2(T), \quad (3.28)$$

where $\mu$ is a real number dependent on $\alpha$ and $\beta$, and $q_1(T)$ and $q_2(T)$ are periodic functions. As $T \to \infty$, $v_n(T) \to c_1 e^{\mu T} q_1(T) \to \infty$. 

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A limited growth of $v_n(T)$ can be realized by introducing a damping term into equation (3.25), as in the case for ordinary resonance, giving the new, more comprehensive equation:

$$\frac{d^2 v_n}{dT^2} + \kappa \frac{dv_n}{dT} + [\alpha - \beta \cos(T)]v_n = 0. \quad (3.29)$$

By making a transformation

$$v_n(T) = e^{-\frac{\kappa T}{2}} \psi(T), \quad (3.30)$$

the first derivative term in equation (3.29) is eliminated, and $\psi(T)$ satisfies another Mathieu equation,

$$\frac{d^2 \psi}{dT^2} + [\alpha - \kappa^2/4 - \beta \cos(T)]\psi = 0, \quad (3.31)$$

with $\alpha^* = \alpha - \frac{\kappa^2}{4} = \frac{1}{4}(1 - \kappa^2)$. As the value of $\kappa$ changes, the value of $\alpha^*$ changes. In the $(\alpha^* - \beta)$ space, which represents the state of carbon nanotubes, as the value of $\kappa$ changes, the state of the system in our model is represented by a vertical straight line as shown in figure 3.5.

In figure 3.5, as $\kappa$ increases from 0 to 1, the value of $\alpha^*$ falls from 1 to 0 along the vertical line. Along the vertical straight line, in the region represented by the blue color, the system is unstable; after that, the green color shows that the system runs into a stable region. In stable region, the steady state general solution of equation (3.27) holds. This is important in the physical explanation to part of the questions that arose in
chapter 1, but not mathematically significant. In the following, we will discuss the behaviors of the system in the unstable region.

Fig. 3.5 A schematic of stable and unstable regions for the damped Mathieu’s equation. The vertical straight line (blue and green) corresponds to \( \alpha' = \frac{1}{4}(1 - \kappa^2) \), in \( \alpha' - \beta \) space at \( \beta = \frac{1}{2} \).

In unstable region, equations (3.28) and (3.30) imply that the general solutions of equation (3.29) have the form

\[
v_n(T) = c_1 e^{(\mu - \kappa/2)T} q_1(T) + c_2 e^{-(\mu + \kappa/2)T} q_2(T).
\]

(3.32)

The case \( \kappa > 2\mu \) yields no lasting transverse motion. For \( \kappa < 2\mu \), transverse motion persists and is unbounded. Thus, any motion of interest remains unstable in the presence
of damping. To give meaning to the physical parameter $\beta$, the boundaries in parameter space near $\alpha^* = \alpha - \frac{\kappa^2}{2} = \frac{1}{4}$ and $\beta << 1$ are given by $\alpha = \frac{1}{4} \pm \frac{1}{2} \sqrt{\beta^2 - \kappa^2}$, or, [55]

$$\frac{\omega_n}{\omega_\varepsilon} = \sqrt{1 \pm 2 \sqrt{\beta^2 - \kappa^2}}. \tag{3.33}$$

Equation (3.33) shows that if the damping coefficient is larger than the driving coefficient ($\kappa > \beta$) transverse vibration of the carbon nanotube doesn’t occur.

As time increases, the amplitude of the transverse wave grows exponentially and the linear wave equation must be modified to include non-linear terms. In a two dimensional case, let $w(x,t) \equiv 0$ in equations (3.1), (3.2), (3.3), then equations (3.34) and (3.35) become:

$$\frac{\partial^2 u}{\partial t^2} - c_L^2 \frac{\partial^2 u}{\partial x^2} = \frac{1}{2} \left( c_L^2 - c_T^2 \right) \frac{\partial}{\partial x} \left[ v_x^2 (1 - 2u_x) \right], \tag{3.34}$$

$$\frac{\partial^2 v}{\partial t^2} - c_T^2 \frac{\partial^2 v}{\partial x^2} = \frac{1}{2} \left( c_L^2 - c_T^2 \right) \frac{\partial}{\partial x} \left[ v_x^2 + 2u_x v_x (1 - u_x) \right]. \tag{3.35}$$

Considering $c_L >> c_T$, and assuming $u_x << 1$, after dividing equations (3.34) and (3.35) by $c_L^2$, then taking $c_L \to \infty$, and assuming that $(1 - 2u_x)$ and $(1 - u_x)$ can be approximated by unity, we find that

$$u_{xx} = -\frac{1}{2} \frac{\partial}{\partial x} (v_x^2). \tag{3.36}$$

Using the boundary conditions, equations (3.4), (3.5), and (3.6), can be integrated to give:
\[ u(x,t) = -\frac{u_0}{L_0} x \cos(2\omega_c t) + \frac{x}{2L_0} \int_0^L v_s^2 dx - \frac{1}{2} \int_0^L v_s^2 dx. \] (3.37)

Equation (3.37) shows that longitudinal motion of the carbon nanotube results, not only from the longitudinal driving force, but also from the stretching result from transverse motion.

Then, substituting equation (3.37) into equation (3.35), and using the boundary conditions, equations (3.4), (3.5), and (3.6), equation (3.35) can be integrated to give:

\[
\frac{\partial^2 v}{\partial t^2} - c_T^2 \frac{\partial^2 v}{\partial x^2} = \frac{1}{2} \left( c_f^2 - c_T^2 \right) \left[ -4u_0 \cos(2\omega_c t) \frac{L_0}{L_0} + \frac{1}{L_0} \int_0^L v_s^2 dx \right] \frac{\partial^2 v}{\partial x^2}. \] (3.38)

Equation (3.38) is the usual linear wave equation with the value of \( c_T^2 \) revised to allow for the change in tension of the nanotube due to its change in length as it vibrates.

Physically speaking, the above processes to derive equation (3.37) and equation (3.38) correspond to the process that energy is transferred back and forth between the longitudinal and transverse motions of the system.

Substituting equation (3.24) into equation (3.38), gives the coupled nonlinear Mathieu equations for \( v_n \). The transverse motion of the nanotube in mode \( n \) is given by:

\[
\frac{d^2 v_n}{dT^2} + \left[ \alpha_n - \beta_n \cos(T) \right] v_n + \gamma_{nn} v_n^3 + \sum_{j \neq n} \gamma_{nj} v_j^2 v_n = 0, \] (3.39)

where \( \alpha_n = n^2 \alpha_1, \beta_n = 2n^2 \alpha_1, \gamma_{nn} = (n\pi)^2 \frac{\alpha_n}{4\varepsilon_0}, \gamma_{nj} = (j\pi)^2 \frac{\alpha_n}{4\varepsilon_0}. \)

Deering [63] has studied the process of energy transfer from one mode to another according to equation (3.39). In the following, use another approach offered by
Rowland [55] to study the same energy transfer process by analyzing the power spectrum of equation (3.41) for the consideration that damping is involved.

Making the assumption that a single mode, for example, \( \nu = \nu_1 \) is excited (As in our case, energy is input from the microwave into the carbon nanotube by resonantly exciting a specific mode.), and rescaling \( \nu \) according to \( \nu = \frac{V}{L_0} \), we obtain

\[
\frac{d^2V}{dT^2} + (\alpha - \beta \cos T)V + \gamma V^3 = 0,
\]

where all coefficients have been defined earlier. Including a linear damping term, as was done above in equation (3.29), equation (3.40) can be revised to give:

\[
\frac{d^2V}{dT^2} + (\alpha^* - \beta \cos T)V + \gamma V^3 = 0,
\]

where \( \alpha^* \) is defined as \( \alpha^* = \alpha - \frac{\kappa^2}{4} \), and \( \kappa \) is the damping coefficient.

3.3 Numeric Solutions of Equation (3.41) Using the Fourth-Order Runge-Kutta Method

The Runge-Kutta method was used to produce the set of graphs given in figures 3.6, 3.7, 3.8, 3.9, 3.10 and 3.11.

Choose \( \alpha = \frac{1}{4}, \beta = \frac{1}{2}, n = 1, \) and \( \omega = \omega_E \), to get \( \gamma = \frac{\pi^2}{16 \varepsilon_0} \), and \( \varepsilon_0 = 10^{-4} \), the following graphs show the time evolution of the function \( y(t) = V(T) \) with different \( \kappa \) values for \( \alpha = 0.25, \beta = 0.5 \) and \( n=1 \):
Case (1): $\alpha=0.25$, $\beta=0.5$, $\gamma=\pi^2/0.0016$, $\kappa=0.45$, $y(0)=0.0001$, $y'(0)=0$

Fig. 3.6 Numerical solution of the time evolution of the amplitude of the transverse vibration. The horizontal axis represents the time and the vertical axis represents the amplitude of the transverse vibration that is normalized by the length of the nanotube. In the following, all the upper graphs have the same meaning as this one. This is the case that the damping approaches the driving force. Exponential decay to zero of the amplitude of the transverse vibration is reached. The result shows that in this case, the transverse resonance cannot be realized.

Case (2): $\alpha=0.25$, $\beta=0.5$, $\gamma=\pi^2/0.0016$, $\kappa=0.05$, $y(0)=0.0001$, $y'(0)=0$
Fig. 3.7 This set of graphs shows the case that as the damping decreases, the system falls into the stable region of the parametric space. The lower graph is the power spectrum of upper one, its horizontal axis represents the frequency normalized by the frequency of the microwave, the vertical axis is in arbitrary unit. It shows that within the stable region the system undergoes single mode vibration.

Case (3): $\alpha=0.25, \beta=0.5, \gamma=\pi^2/0.0016, \kappa=0.001, y(0)=0.0001, y'(0)=0$
Fig. 3.8 This set of graphs shows that as the damping becomes very small, the system falls into the unstable region. Thus, nonlinear effect appears. The lower graph proves that energy is transferred from one mode to others and the third mode and other higher modes store most of the energy.

Case (4): $\alpha=0.25$, $\beta=0.5$, $\gamma=\pi^2/0.0016$, $\kappa=0.0005$, $y(0)=0.0001$, $y'(0)=0$
Fig. 3.9 This set of graph shows that as the damping decrease, nonlinear effect becomes more and more significant.
Case (5): $\alpha=0.25, \beta=0.5, \gamma=\pi^2/0.0016, \kappa=0.0001, \ y(0)=0.0001, \ y'(0)=0$

Fig. 3.10 This set of graphs shows that as the damping tends to zero, more and more energy is transferred from lower modes to higher ones.

Case (6): $\alpha=0.25, \beta=0.5, \gamma=\pi^2/0.0016, \kappa=0.0, \ y(0)=0.0001, \ y'(0)=0$
Fig. 3.11 This set of graphs is the extreme case of no damping. It is seen from the upper graph that the maximum transverse amplitude is about 1.7% of the length of the tube.
Case (1), Fig. 3.6 shows the time evolution of the vibrating system with damping approaching to the driving force ($\kappa$~$\beta$). In this case, the transverse vibration is frozen by the damping, which correspond to the system being at a state near the crossing point of the $\beta$ axis and the vertical straight line of the ($\alpha^* - \beta$) parameter space, where $\alpha^* \approx 0$.

In case (2), Fig. 3.7, the upper graph is the time evolution profile at the given values of the parameters. The lower graph is the power spectrum of the Fourier analysis of the upper profile. In this case, damping is a median value ($0 < \kappa < \beta$). It is shown that only a single frequency vibration holds because the system is within the stable region represented by the green line in the above ($\alpha^* - \beta$) parameter space in Fig. 3.5. In this region, the amplitude of the system is bounded by the damping, and the energy is input from the external source into the system in a steady rate, because there is no phonon-phonon interaction in this region.

In case (3) to case (6), Fig. 3.8-Fig. 3.11, the damping is small. The vibration profile becomes more complex. The power spectrum shows that many other frequency components are involved. The energy is transferred from a single frequency mode to others. The system now is at the unstable region of the parametric space represented by the blue line. In this region, the amplitude of the system is bounded, not by the damping, but by the non-linear term, and the energy is more and more efficiently input from the external energy source into the system, because multi-phonon processes, or, phonon-phonon interactions, are involved more and more strongly as the damping coefficient becomes less and less. From the time evolution profile of case (6), Fig. 3.11, without
damping, the maximum vibration amplitude of the system could be as high as $1.7 \times 10^{-2}$. That is, for a CNT with a length of $1 \mu m$, the maximum amplitude of the transverse vibration could reach to $0.017 \mu m$. 
The physical picture depicted in Chapter 3 indicates that damping plays a significant role in controlling the nonlinear transverse parametric resonance. It predicts three kinds of processes: When damping is large enough to suppress the driving force, transverse vibration is actually prevented, the system is over damped. When the damping is medium, the system is located in a stable region of the parameter space, where the effects of the driving and dissipation forces produce a steady state transverse motion of small amplitude oscillating at a single frequency without phonon-phonon interaction. When the damping is small, the system moves into an unstable region of the parameter space, where the transverse amplitude of the system is, nevertheless, bounded by damping, and reaches to large enough values that the behavior of the system is dominated by non-linear effects which involve multi-phonon processes or phonon-phonon interactions and more energy is allowed to be input into the system from the external energy source. Applying this picture to the experimental results provided in chapter 1, makes the system studied in this work simply a carbon nanotube with the external energy source or the driving force microwaves. Besides a carbon nanotube, there are impurities, such as residual metals and particles of other carbon formations, e.g. amorphous carbon, inside the system. Additionally, there are gases adsorbed on the
carbon nanotubes. Although impurities and gases absorb microwaves also. When the studied target is concentrated on the carbon nanotubes, those impurities and gases are assumed to primarily play the role of damping of the carbon nanotube vibration. When a carbon nanotube system contains a sufficient number of impurities and gases, the system is over damped. Thus, under the microwave field, the transverse vibration of the carbon nanotube is suppressed.

From chapter 2, we understand that a carbon nanotube is an ideal quantum wire, under an electric field an electron is transported ballistic in the carbon nanotube without electron-phonon interaction. Thus, there is no heating effect as in the usual Joule heating case.

A test was made to determine what the role of the gas is. The result of the experiment, where a salt layer covered the top of the carbon nanotube sample to reduce degassing of the carbon nanotubes, is shown in Fig. 1.13. In that case, the longitudinal vibration resulted by polarization of the carbon nanotube, produces a sudden increase of pressure by degassing, which corresponds with a high value of damping of the transverse vibration of carbon nanotubes. Thus, the system exhibits no heating effect. At the sample-salt boundary, the damping is relatively small because of the flow of gas over there: Transverse vibration can be excited, resulting in heating of carbon nanotubes.

If the samples are pre-degassed, damping of the transverse vibration is dramatically decreased. Under this condition, transverse parametric resonance of carbon nanotubes is excited, and heating, or energy transfer from the microwave source to carbon nanotubes becomes efficient. Only absorbed gasses are removed in the pre-
degassing process. Damping resulting from impurities still exists. The greater the amount of impurities, the larger the damping. For unpurified carbon nanotube samples (Usually the weight percentage of impurities is higher than 10% in unpurified carbon nanotubes.), damping results in the system falling into the stable region of the parametric space. There, a single transverse mode is excited resonantly to result in the carbon nanotubes being the Reulet’s case, where Joule heating is dominated by electron-phonon interaction. Thus, the temperature of the unpurified carbon nanotube sample must be located at the Joule heating curve of the microwave source. Because most of the impurities in the system are good thermal conductors, it is not strange that the heating in such samples is uniform.

After the CNTs have been pre-degassed, damping of the purified carbon nanotube is small enough to bring the system into the unstable region of the parameter space. There, not only electron-phonon interactions participate in the energy transfer from the microwave to carbon nanotubes, but also phonon-phonon interaction is involved. The temperature of matter is determined by the energy flux input and dissipation in the CNT. Involving of a phonon-phonon interaction significantly increases the amount of energy transferred from the microwave source into the carbon nanotubes in a unit time. As a result, the temperature of the purified samples must be much higher than the unpurified ones. The non-uniform distribution of the carbon nanotubes in this case can be attributed to the non-uniform distribution of the density of the samples resulting from the degassing process. As shown by equation (3.32), within the unstable region, the solution is either unbounded or over damped. Of the carbon
nanotubes, only those that are highly dispersed by degassing can undergo the “ultra-heating”; the ones that are more entangled by degassing exhibits no heating because of the increased damping. This means that the model predicts a significant density effect. To increase the density is equivalent to an increase of the damping of carbon nanotubes. This can be explained by the fact that transverse vibration of a carbon nanotube requires the space around the tube to be large enough to make a free vibration. If there is not enough space, transverse vibration would be impossible. To test this effect, an experiment was arranged, where the pre-degassed purified carbon nanotubes were compressed by about 20% in volume. It was found that heating of the samples was stopped during the microwave irradiation, with no visible heating except the ones at the very top, free boundary at the upper boundary.

This model can also help to understand the bell shape absorption efficiency curve presented in chapter 1 for the polycarbonate blends. Based on the model, each carbon nanotube can be seen as a microwave acceptor. Increasing the number of carbon nanotubes in a given medium is equivalent to increasing the number of microwave acceptors. Thus, as the number of the carbon nanotubes is increased (increasing the weight percentage of carbon nanotubes in the material), the samples exhibit more and more efficiency in absorbing the microwave. But, because the volume of the sample is fixed, as the number of carbon nanotubes is increased, the density of carbon nanotubes is increased also. Transverse vibration of a carbon nanotube in a medium produces a dynamic stress-strain field, or, elastic wave, propagating in the medium. As the density of the number of carbon nanotube is increased to some extent, the stress-strain fields
produced by each carbon nanotube will be overlapped and suppressed by each other. To continuously increase the number of carbon nanotubes in the medium, the efficiency of each microwave acceptor is deceased. It is these two factors that result in the bell shape absorption efficiency curve.

Finally, in summary, the main points of the explanations of the experimental results mentioned in chapter 1 are outlined below:

Residual metal plays a dual role in the phenomena. It acts as a charge donor to the carbon nanotubes. Because of the existence of residual metal, extension of a carbon nanotube due to longitudinal polarization under the microwave field is strongly enhanced. It also damps the transverse vibration of the carbon nanotube.

Gases absorbed by a carbon nanotube play the role of damping. It is also responsible for the appearance of plasma excitation because of residual gas excitation.

The carbon nanotube itself undergoes a transverse parametric resonance excited by a longitudinal forced vibration that arises due to the polarization of the carbon nanotubes under the microwave field. It is the transverse parametric resonance that results in the carbon nanotube samples being heated so quickly. The heating behavior of a carbon nanotube by the microwave source is controlled by damping. When over damped, the system will not be heated because of the intrinsic weak electron-phonon interaction of CNTs; when damped to the stable region of the parameter space, the system is dominated by Joule heating because of the enhanced electron-phonon interaction by the transverse single frequency resonance. When the system is damped to
the unstable region, both electron-phonon interaction and phonon-phonon interaction will be involved because of the significant transverse non-linear effect.
APPENDIX A

SOURCE CODE OF THE C PROGRAM USED TO SOLVE THE NON-LINEAR DAMPED MATHIEU EQUATION
#include <stdio.h>
#include <math.h>
#include <stdlib.h>
#define NR_END 1
#define FREE_ARG char*
#define K 0.0000
#define NSTEP 1000000
#define pi 3.14159265359
#define my_r (pi*pi/0.0016)

double **y,*xx;
void myfunc(double x, double y[], double dydx[]);
void rkdumb(double vstart[], int nvar, double x1, double x2, int nstep,
void (*derivs)(double, double [], double []));
void rk4(double y[], double dydx[], int n, double x, double h, double
yout[], void (*derivs)(double, double [], double []));
double *dvector(long nl, long nh);
void free_dvector(double *v, long nl, long nh);
double **dmatrix(long nrl, long nrh, long ncl, long nch);
void free_dmatrix(double **m, long nrl, long nrh, long ncl, long nch);
void nrerror(char error_text[]);

void main()
{
    double x1=0,x2=3000;
    double *vstart;
    int i,nstep=NSTEP;
    FILE *fp;
    if( (fp = fopen( "s_k.dat", "w" )) == NULL )
    { printf( "The file 's_k.dat' was not opened\n" );
      exit(-1);
    }
    vstart=dvector(1,2);
    xx=dvector(1,NSTEP+1);
    y=dmatrix(1,2,1,NSTEP+1);
    vstart[1]=0.00001;
    vstart[2]=0;
    rkdumb(vstart,2,x1,x2,nstep,&myfunc);
    for(i=1;i<=nstep+1;i++)
      fprintf(fp,"%f	%e\n",xx[i],y[1][i]);
    free_dmatrix(y,1,2,1,NSTEP+1);
    fclose(fp);
}

void myfunc(double x, double y[], double dydx[])
{
    dydx[1]=y[2];
    //dydx[2]=cos(x)*y[1]/8.0-(1-K*K)*y[1]/4.0-my_r*y[1]*y[1]*y[1];
    dydx[2]=0.0125*cos(x)*y[1]-y[1]/4.0-my_r*y[1]*y[1]*y[1]-K*y[2];
}
void rkdumb(double vstart[], int nvar, double x1, double x2, int nstep, void (*derivs)(double, double [], double []))
/*
Starting from initial values vstart[1..nvar] known at x1 use fourth-order Runge-Kutta
to advance nstep equal increments to x2. The user-supplied routine
derivs(x,v,dvdx)
evaluates derivatives. Results are stored in the global variables
y[1..nvar][1..nstep+1]
and xx[1..nstep+1].
*/
{
    void rk4(double y[], double dydx[], int n, double x, double h, double yout[], void (*derivs)(double, double [], double []));
    int i,k;
    double x,h;
    double *v,*vout,*dv;
    v=dvector(1,nvar);
    vout=dvector(1,nvar);
    dv=dvector(1,nvar);
    for (i=1;i<=nvar;i++)
    { //Load starting values.
        v[i]=vstart[i];
        y[i][1]=v[i];
    }
    xx[1]=x1;
    x=x1;
    h=(x2-x1)/nstep;
    for (k=1;k<=nstep;k++)
    { //Take nstep steps.
        (*derivs)(x,v,dv);
        rk4(v,dv,nvar,x,h,vout,derivs);
        if ((double)(x+h) == x) nrerror("Step size too small in
routine rkdumb");
        x += h;
        xx[k+1]=x; //Store intermediate steps.
        for (i=1;i<=nvar;i++)
        { v[i]=vout[i];
            y[i][k+1]=v[i];
        }
    }
    free_dvector(dv,1,nvar);
    free_dvector(vout,1,nvar);
    free_dvector(v,1,nvar);
}

void rk4(double y[], double dydx[], int n, double x, double h, double yout[], void (*derivs)(double, double [], double []))
/*
Given values for the variables y[1..n] and their derivatives dydx[1..n]
known at x, use the
fourth-order Runge-Kutta method to advance the solution over an
interval h and return the
incremented variables as yout[1..n], which need not be a distinct
array from y. The user
supplies the routine derivs(x,y,dydx), which returns derivatives dydx
at x.
*/
{
    int i;
    double xh, hh, h6, *dym, *dyt, *yt;
    dym = dvector(1,n);
    dyt = dvector(1,n);
    yt = dvector(1,n);
    hh = h*0.5;
    h6 = h/6.0;
    xh = x + hh;
    for (i=1; i<=n; i++)
        yt[i] = y[i] + hh*dydx[i];  //First step.
        (*derivs)(xh, yt, dym);  //Second step.
    for (i=1; i<=n; i++)
        yt[i] = y[i] + hh*dyt[i];
        (*derivs)(xh, yt, dym);  //Third step.
    for (i=1; i<=n; i++)
        {
            yt[i] = y[i] + h*dym[i];
            dym[i] += dyt[i];
        }
        (*derivs)(x+h, yt, dym);  //Fourth step.
    for (i=1; i<=n; i++)  //Accumulate increments with proper weights.
        yout[i] = y[i] + h6*(dydx[i] + dyt[i] + 2.0*dym[i]);
    free_dvector(yt, 1, n);
    free_dvector(dyt, 1, n);
    free_dvector(dym, 1, n);
}

double *dvector(long nl, long nh)
/* allocate a double vector with subscript range v[nl..nh] */
{
    double *v;
    v = (double *)malloc((size_t)((nh-nl+1+NR_END)*sizeof(double)));
    if (!v) nrerror("allocation failure in dVector()");
    return v-nl+NR_END;
}
void free_dvector(double *v, long nl, long nh)
/* free a double vector allocated with dvector() */
{
    free((FREE_ARG) (v+nl-NR_END));
}
void nrerror(char error_text[])
/* Numerical Recipes standard error handler */
{
    fprintf(stderr,"Numerical Recipes run-time error...\n");
    fprintf(stderr,"%s\n", error_text);
    fprintf(stderr,"...now exiting to system...\n");
    exit(1);
}
double **dmatrix(long nrl, long nrh, long ncl, long nch)
/* allocate a double matrix with subscript range m[nrl..nrh][ncl..nch]
*/
{  
    long i, nrow=nrh-nrl+1, ncol=nch-ncl+1;
    double **m;
    /* allocate pointers to rows */
    m=(double **) malloc((size_t)((nrow+NR_END)*sizeof(double*)));
    if (!m)
       nrerror("allocation failure 1 in matrix()");
    m += NR_END;
    m -= nrl;
    /* allocate rows and set pointers to them */
    m[nrl]=(double *) malloc((size_t)((nrow*ncol+NR_END)*sizeof(double)));
    if (!m[nrl])
       nrerror("allocation failure 2 in matrix()");
    m[nrl] += NR_END;
    m[nrl] -= ncl;
    for(i=nrl+1;i<=nrh;i++)
       m[i]=m[i-1]+ncol;
    /* return pointer to array of pointers to rows */
    return m;
}

void free_dmatrix(double **m, long nrl, long nrh, long ncl, long nch)
/* free a double matrix allocated by dmatrix() */
{
    free((FREE_ARG) (m[nrl]+ncl-NR_END));
    free((FREE_ARG) (m+nrl-NR_END));
}
BIBLIOGRAPHY


[63] W. D. Deering, private communication.