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PhD. Thesis
Summary

Mathematical aspects of macroscopic models for carbon nanotubes

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Content

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Summary

The discovery of carbon nanotubes in 1991 by Iijima [12] generated new directions for the development of high-resolution nanodevices. Carbon nanotubes have unique physical and chemical properties, which have been intensively studied in recent decades for biological applications. Ultra-sensitive detection of biological species with carbon nanotubes can be performed after their functionalization. Carbon nanotube-based nanosensors open a new approach in the microscopic analysis of biological samples. The nanodimensions of carbon nanotubes offer the possibility of their integration in sensors with wide applications in non-invasive and minimally invasive techniques for detecting biological compounds and measuring medical parameters.

This doctoral thesis is structured in five chapters, namely: an introductory chapter, three chapters containing original results, results of personal research conducted during doctoral studies on the mechanical, electrical and thermal behaviour of carbon nanotubes and a final chapter that summarizes the final conclusions, the dissemination of the results obtained through the published articles, through the participations in international specialized conferences, the original contributions of the author, as well as future research directions.

The aim and objectives of this doctoral thesis is to investigate the mechanical, electrical and thermal behavior of carbon nanotubes. The research materializes in the realization of a theoretical basis and mathematical models to describe the behaviour of nanotubes, through solutions to problems with initial and limit data. The applications capitalize on the developed theoretical models.

The main original results of this paper are two practical applications - two non-invasive sensors - based on two macroscopic models of the elastic behaviour of carbon nanotubes, namely the Timoshenko şi Gere [23] of the classical elastic bar for the study of transverse oscillations and the Aydogdu model [1] of the non-local elastic bar for the study of the longitudinal oscillations of carbon nanotubes, the determination of the weak solution for the longitudinal oscillations of the carbon nanotube in an elastic external environment based on the Aydogdu non-local bar model [1] and two macroscopic models for the electrical and thermal behaviour of the carbon nanotube, namely a macroscopic model for the electrical properties of the two-walled carbon nanotube virtually divided into annular domains, expressing the electric potential in the nanotube-occupied domain as a solution to the above problem 3.1.1., respectively another macroscopic model for the description of the thermal and electrical behaviour of the nanotube, respectively, provided that the ends of the nanotube are maintained at different constant electrical potentials, respectively, with the ends maintained at constant temperatures different as a solution to the above problem 4.1.1.

The original results obtained during the doctoral studies presented in Chapters 2, 3 and 4 are based on four articles published during the doctoral studies: three of them indexed to ISI, namely [2], [16], [17] and an article published in the BDI indexed journal, [15].

Subchapter 2.2 proposes, based on the Timoshenko and Gere model [23] aof the classical elastic bar for the study of transverse oscillations, a mathematical model for a sensor based on changes in the frequency of transverse oscillations of the carbon nanotube modelled as a linear elastic body. The idea of operation of such a sensor is to change the pulsation of the own oscillations of the nanotube after connecting to its free end of a molecule that functions, or to attach one or more molecules to the functionalized end.

The analysis model proposed in this paper incorporates the detection of acetone from the patient's breathing using a carbon nanotube sensor. In this sensor, each of the carbon nanotubes is attached at one end to one substrate and the other end is free. Carbon nanotubes are placed in the vicinity of the surface of a selective membrane. A second variant of the sensor involves the functionalization of the free end of the nanotube with a molecule with high affinity for acetone.

The oscillation frequencies of the nanotubes are measured and the spectrum of the nanotube frequencies before and after the attachment of the acetone molecules is compared. By measuring the

relative variation of frequency following the coupling of acetone molecules, detection can be made up to the level of a single acetone molecule and, implicitly, the concentration of acetone molecules and the partial pressure of acetone in the investigated sample can be measured indirectly.

To study the transverse oscillations of the carbon nanotube, we used the classic elastic bar model fixed at one end on the substrate and the other free end. By activating the piezoelectric (as in Yasuda et al. [29]), the carbon nanotube will oscillate freely in the y direction. In the approximation of small oscillations, the oscillation of the nanotube can be expressed by equation [23]:

$$EI\frac{\partial^2 u_y}{\partial x^2} - \rho A\frac{\partial^2 u_y}{\partial t^2} = 0, \tag{2.100}$$

where E is the Young modulus of elasticity of the carbon nanotube, I is the moment of inertia of the nanotube, ρ is the average density of the carbon nanotube, A is the area the cross section of the carbon nanotube at a distance x from O, and u_y is the displacement of the nanotube at the x-coordinate point.

Equation (2.100) shows that any point on the bar oscillates harmonically in the case of unamortized, which allows us to make an analogy between the oscillation of the free end of the nanotube and the oscillation of an elastic pendulum. The nanotube subjected to free oscillations can be modelled as a discrete system - the elastic pendulum - that oscillates with the same frequency as the free end ($x = L$) of the nanotube. The equation of motion for this pendulum model elastic is:

$$-k_{ech}\mathbf{x} = m_{ech}\frac{\partial^2 \mathbf{x}}{\partial t^2} = -4\pi^2\nu^2 m_{ech}\mathbf{x}, \tag{2.101}$$

where k_{ech} is the elastic constant of the equivalent pendulum and m_{ech} is its mass equivalent. The own frequency of the oscillator equivalent to the carbon nanotube, in the case of small ones oscillations can be expressed through equation

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k_{ech}}{m_{ech}}}. \tag{2.102}$$

The analogy criteria derive from the condition that the elastic pendulum has the same frequency of oscillation as the free end ($x = L$) of the nanotube, so:

- the elastic constant of the pendulum must be the factor of proportionality between the maximum force exerted on the free end of the bar and its amplitude of oscillation;
- the mass of the pendulum must correspond to the equality between the maximum kinetic energy of the bar and the maximum kinetic energy of the equivalent pendulum.

An additional mass attached to the end of the carbon nanotube will cause the frequency of its small oscillations to change. To express the dependence of the oscillation frequency of the nanotube on the mass of the molecule or the group of gas molecules attached to the free end of the nanotube, we solved two problems:

Problem 2.2.1 *Let be a nanotube with a recessed end, subjected to bending under the action of a force distributed along the length of the nanotube and directed along the Oy axis. Determine the elastic constant of the nanotube (the proportionality factor between the maximum force exerted on the free end of the nanotube and its amplitude of oscillation).*

To solve this problem, we used equations of material strength and followed the description given by Timoshenko and Gere [23], Timoshenko şi Young [24]. We obtained the elastic constant of the spring equivalent to the nanotube with one end embedded in the shape of:

$$k_{ech} = \frac{3EI}{L^3}. \tag{2.136}$$

Problem 2.2.3 *Let be a nanotube with a embedded end, which oscillates after* (2.100)*. Determine the mass* m_{ech} *of an oscillator caught by the described equivalent spring* (2.136) *which oscillates with* *the same frequency as the nanotube. Static deformation of the nanotube described in Problem 2.2.1. is assimilated to the dynamic problem*

$$m_{ech}\frac{d^2\mathbf{x}}{dt^2} = -k_{ech}\mathbf{x}. \tag{2.137}$$

To solve this problem, we used an approach equivalent to that used by Zacarias, Wang and Reimbold in [27]. The method that was used to determine the equivalent mass, m_{ech}, is to make an energetic analogy between the nanotube and the equivalent oscillator. The principle of equivalence is that the nanotube and the equivalent oscillator have the same dynamic effect, i.e. the same maximum kinetic energy. We consider that the system formed by the nanotube modelled as a nanobar of equivalent mass m_0 and a molecule or a group of attached gas molecules, of mass m, is set in motion by oscillation. We obtained the equivalent mass of the oscillator:

$$m_{ech} = m_0 + m, \quad m_0 = \frac{33L}{140}\rho A \tag{2.147}$$

Based on equations (2.102), (2.136) and (2.147) we expressed the dependence of the oscillation frequency on the mass of the molecule or the group of molecules attached to the free end of the nanotube by the formula

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k_{ech}}{m_{ech}}} = \frac{1}{2\pi}\sqrt{\frac{3EI}{(m_0+m)\,L^3}}. \tag{2.148}$$

If no gas molecule is attached, then $m = 0$, then, according to equation (2.148), the oscillation frequency of the nanotube is:

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{3EI}{m_0 L^3}}. \tag{2.149}$$

Denoting with $\dfrac{\nu-\nu_0}{\nu_0}$ the relative variation of the nanotube frequency following the attachment of the gas molecule or group of molecules, we obtain the mass attached to the free end of the nanotube:

$$m = m_0\left[\frac{1}{\left(1+\frac{\Delta\nu}{\nu_0}\right)^2} - 1\right]. \tag{2.152}$$

In the case of the analysis of a gaseous sample with several components, in order to ensure the selectivity of the sensor with carbon nanotubes, their functionalization is made. Depending on the gas sought in the atmosphere sample, a molecule with high affinity is chemically attached to each nanotube to the target gas component. Using the result, we reached previously, we obtained the formula of the dependence of the gas mass attached to the free end of the nanotube on the oscillation frequency of the functionalized nanotube. By denoting with m_f the mass of the molecule that functions the nanotube, we obtain

$$m_{eq} = m_0 + m_f + m. \tag{2.154}$$

and we obtain the mass attached to the free functionalized end of the nanotube:

$$m = (m_0 + m_f)\left[\frac{1}{\left(1+\frac{\Delta\nu}{\nu_0}\right)^2} - 1\right]. \tag{2.159}$$

Between blood glucose (BG) and acetone concentration in expired air (C_a) there is the empirical formula [28]

$$BG = \alpha C_a + \beta, \tag{2.160}$$

where α and β are experimentally determined constants.

The result of this subchapter is Application 2.2.2.6 which allows the evaluation of a patient's blood glucose. The results of this subchapter were published in the paper A.E. Nicolescu, L. Rusali, M. Vasile [15].

Subchapter 2.3 proposes, based on the Aydogdu model [1] of the non-local elastic bar, a mathematical model for the longitudinal oscillations of the nanotube. Problems 2.3.1 and 2.3.2 are solved in the introductory paragraph, and the solutions obtained are used in paragraph 2.3. Based on the solution of Problem 2.3.3 it is formulated Practical application 2.3.3 on which the carbon nanotube can be used to identify a macromolecule. The principle used is the modification of the frequency of the longitudinal oscillations of the nanotube following the attachment of a macromolecule to its free end. We solved the following problem:

Problem 2.3.3 Find the specific frequencies of $u(x,t)$, $u:[0;L]\times[0;\infty)\to\mathbb{R}$, to satisfy the equation

$$EA\frac{\partial^2 u(x,t)}{\partial x^2}+(e_0a)^2\, m\frac{\partial^4 u(x,t)}{\partial x^2\partial t^2}=m\frac{\partial^2 u(x,t)}{\partial t^2}. \tag{2.192}$$

With boundary conditions in the absence of the macromolecule

$$u(0,t)=0, \qquad N(L,t)=0. \tag{2.193}$$

With boundary conditions in the absence of the macromolecule

$$\nu=\frac{1}{2\pi}\sqrt{\frac{EA}{L\left[M+M_{CNT}\left(\frac{e_0a}{L}\right)^2\right]}}. \tag{2.207}$$

respectively in the absence of the macromolecule ($M=0$):

$$\nu_0=\frac{1}{2\pi}\sqrt{\frac{EA}{LM_{CNT}\left(\frac{e_0a}{L}\right)^2}}. \tag{2.208}$$

The dependence between the mass of the biological macromolecule or of a viral structure attached to the nanotube and the variation of the oscillation frequencies before and after the attachment to the longitudinally oscillating nanotube is expressed by

$$M=M_{CNT}\left(\frac{e_0a}{L}\right)^2\left[\left(\frac{\nu_0}{\nu}\right)^2-1\right]. \tag{2.209}$$

The original contribution of the author in paragraph 2.4, based on the Aydogdu nonlocal bar model [1],], is the determination of the weak solution for the longitudinal oscillations of the carbon nanotube in an elastic external medium. We used the theoretical foundations of weak solutions for the wave equation from the books by H. Brezis [5], V. Barbu [3], Singh et al. [22], O. A. Ladyzhenskaia [13], G. Shilov [21] to which the work of C. Mortici [14] is added.

We considered that the external elastic medium acts on the nanotube with an axial force per unit length $f=-ku$, k is a strictly positive real constant. In this hypothesis, based on equation (2.104), we formulated the following problem:

Problem 2.4.1 Let $\Omega=(0,L)\subset\mathbb{R}$ (the spatial domain occupied by the carbon nanotube) with boundary $\Gamma=\{0,L\}$. We define $Q=\Omega\times(0,\infty)$ şi $\Sigma=\Gamma\times(0,\infty)$. We studied the existence and uniqueness of the weak solution u of the problem at the limit:

(i) $\left[EA-k(e_0a)^2\right]\frac{\partial^2 u}{\partial x^2}-m\frac{\partial^2 u}{\partial t^2}+(e_0a)^2\, m\frac{\partial^4 u}{\partial x^2\partial t^2}-ku=0$ in Q;

(ii) $u=0$ on Σ;

(iii) $u(x,0)=g(x)$ in Ω;

(iv) $\frac{\partial u}{\partial t}(x,0)=h(x)$ in Ω.

We denoted

$$p_0 = EA - k\left(e_0 a\right)^2, \ p_1 = m\left(e_0 a\right)^2, \tag{2.210}$$

We wrote the equation (i) as it follows

$$m\frac{\partial^2 u}{\partial t^2} - \frac{\partial}{\partial x}\left[p_0\frac{\partial u}{\partial x} + p_1\frac{\partial^3 u}{\partial x\partial t^2}\right] + ku = 0 \qquad t > 0, \qquad x \in (0, L). \tag{2.211}$$

The boundary conditions associated with equation (2.211) are

$$u|_{x=0} = u|_{x=L} = 0, \tag{2.212}$$

to which the initial conditions are added

$$u|_{t=0} = g(x), \ \left.\frac{\partial u}{\partial t}\right|_{t=0} = h(x), \quad x \in (0, L). \tag{2.213}$$

We determined the solution of the problem (2.211)-(2.213) in the form of a Fourier series using the method of separation of variables and proved the existence, uniqueness and regularity of the weak solution of the problem (2.211)-(2.213).

To define the weak solution of problem (2.211)-(2.213), considering boundary conditions, we will consider the Sobolev space $H_0^1(0, L)$ (H. Brézis [5], V. Barbu [3]) with the scalar product and its associated norm:

$$\begin{aligned} \langle u, v\rangle_1 &:= p_1\int_0^L u'v'dx + m\int_0^L uvdx, \\ \|u\|_1^2 &:= p_1\int_0^L \left(u'\right)^2 dx + m\int_0^L u^2 dx \forall u, v \in H_0^1(0, L). \end{aligned} \tag{2.214}$$

To obtain the definition of a weak solution, we will multiply in a scalar way (2.211) with a function $v \in H^1\left(0, T; H_0^1(0, L)\right)$ and then we will integrate related to t, for $t \in (0, T)$. Following the integration by parts and the boundary conditions (2.212)-(2.213) we obtain the following definition

Definition 2.4.2 Let $g, h \in H_0^1(0, L)$ be given functions. The function $u : (0, L) \times (0, \infty) \to \mathbb{R}$ is called a weak solution to the boundary problem (2.211)–(2.213) if:

1. $u \in C^1\left([0, T]; H_0^1(0, L)\right)$ and

$$\begin{aligned} &\tilde{k}\int_0^t\int_0^L u(x,\tau)\, v(x,\tau)\, dxd\tau \ + \ \tilde{p}_1\int_0^L \frac{\partial^2 u(x,t)}{\partial x\partial t}\frac{\partial v(x,t)}{\partial x}dx \\ &- \tilde{p}_1\int_0^t\int_0^L \frac{\partial^2 u(x,\tau)}{\partial x\partial t}\frac{\partial^2 v(x,\tau)}{\partial x\partial t}dxd\tau + \\ &+ \int_0^t\int_0^L \left[\tilde{p}_0\frac{\partial u(x,\tau)}{\partial x}\frac{\partial v(x,\tau)}{\partial x} - \frac{\partial u(x,\tau)}{\partial t}\frac{\partial v(x,\tau)}{\partial t}\right] dxd\tau \\ &+ \int_0^L \frac{\partial u(x,t)}{\partial t}v(x,t)\, dx \\ &= \int_0^L h(x)\, v(x,0)\, dx + \tilde{p}_1\int_0^L h'(x)\,\frac{\partial v}{\partial x}(x,0)\, dx \\ &\quad \forall v \in H^1\left(0, T; H_0^1(0, L)\right) \ , \forall T > 0, \ \ \forall t \in (0, T); \end{aligned} \tag{2.216}$$

2. $u(x, 0) = g(x), \ \frac{\partial u}{\partial t}(x, 0) = h(x), \ \ 0 < x < L.$

We denote $\tilde{p}_0 = \dfrac{p_0}{m}; \ \tilde{p}_1 = \dfrac{p_1}{m}; \ \tilde{k} = \dfrac{k}{m}.$

In order to obtain the existence and uniqueness of the weak, propagation-type solution from the above definition, we applied the method of variable separation. The longitudinal wave equation is determined by looking for solutions of the form

$$u(x,t)=\varphi(x)\,e^{i\omega t},\quad t>0,\quad x\in(0,L).$$

Substituting u of this form in equation (2.211), and taking into account the boundary conditions (2.212), i.e. the Sturm-Liouville problem (G. Şilov [21][Chapter V, Section 5])

$$\begin{cases}\left(p_0-p_1\omega^2\right)\varphi''+\left(-k+m\omega^2\right)\varphi=0, & x\in(0,L)\\ \varphi(0)=\varphi(L)=0.\end{cases}\tag{2.217}$$

We found eingenvalues of the problem (2.217), λ_n:

$$\omega_n=\sqrt{\frac{n^2\pi^2p_0+kL^2}{n^2\pi^2p_1+mL^2}}.\tag{2.222}$$

And the eingenfunctions of the problem (2.217)(2.217)

$$\varphi_n(x)=a_n\sin\frac{n\pi x}{L},\quad x\in[0,L],\ \ n\in\mathbb{N}^*,$$

Where a_n has been determined so as to form an orthonormal system which will be a complete system according to G. Şilov [21][Chapter V, Section 5] and C. Mortici [14] in the space $H_0^1(0,L)$ related with the norm and the scalar product found in (2.214).

We found

$$u(x,t)=\sum_{n=1}^{\infty}a_n\sin\frac{n\pi x}{L}\left(c_n\cos\omega_n t+d_n\sin\omega_n t\right),\tag{2.234}$$

Where the constants a_n,ω_n,c_n,d_n are given by the formulas:

$$a_n=\sqrt{\frac{2L}{n^2\pi^2p_1+mL^2}},\quad n\in\mathbb{N}^*.\tag{2.226}$$

$$c_n=\langle g,\varphi_n\rangle=p_1\int_0^L g'\varphi_n'dx+m\int_0^L g\varphi_n dx\ \ \forall n\in\mathbb{N}^*.\tag{2.232}$$

$$d_n\omega_n=\langle h,\varphi_n\rangle_1\text{, de unde } d_n=\frac{1}{\omega_n}\left(p_1\int_0^L h'\varphi_n'dx+m\int_0^L h\varphi_n dx\right)\forall n\in\mathbb{N}^*,\tag{2.233}$$

To prove the existence and uniqueness of the weak solution of problem 2.4.1 we used results previously obtained and standard arguments (Ladyzhenskaya [[13], Chapter IV, Sections 2-4] and Barbu [[3], pp. 168-189]). In conclusion, we have:

Theorem 2.4.3 If $g,\ h\in H_0^1(0,L)$ and there are verified the hypotheses on the material constants (2.215), then the problem (2.211) – (2.213) accepts o unique weak solution $u\in C^1\left([0,T];H_0^1(0,L)\right)$ given by the equality (2.234).

The results of subchapter 2.4 were published in the paper A.E. Nicolescu, A. Bobe [16].

In chapter 3 we studied a general overdetermined problem whose general solution we customized to describe the electric potential distribution inside a double-walled nanotube. Since both Dirichlet and Neumann boundary conditions are imposed, Problem 3.1.1 is overdetermined and then, in general, there is a solution only if the studied domain Ω satisfies an additional symmetry property.

Nanotubes can be used in the components of electromechanical, electrochemical, electrothermal sensors, high capacity electric batteries, electronic nanocircuits and ultracapacitors. For the design of these sensors, it is necessary to know some electrical sizes/quantities/features characteristic of nanotubes, for example the electric potential, the intensity of the electric field, the electric capacity.

The electrical and electronic models for single-walled or double-walled carbon nanotube with semiconductor behaviour proposed by Collins et al. [8], Devoret et al. [9], Neto et al. [18], Postma et al. [19] include in their component an equivalent capacitor.

The electrical macroscopic model proposed in this chapter to determine the electric potential distribution inside a double-walled nanotube divides the cylindrical nanotube into ring domains. Based on the physical significance of the boundary conditions imposed in the general problem (the two walls of the nanotube maintained at different constant electric potentials), the model proposes the decomposition of the nanotube into ring domains, all these domains, connected to the same electric potential difference, are equivalent to elementary capacitors connected in parallel.

The Euclidean norm, which reflects the isotropy of space and the Laplace operator, which in turn is determined by the isotropy of the dielectric and dictates the use of the Euclidean norm in expressing the electric field in the isotropic case, is replaced in this chapter by an arbitrary norm and an anisotropic operator, respectively N-laplacian, which reflects the anisotropy of the medium. By replacing the usual Euclidean norm of the gradient with an arbitrary norm F, then the resulting symmetry of the solution is that of the so-called Wulff form (a ball in the dual norm F^*). In the case of the particularization of the results of Problem 3.1.1, for the carbon nanotube virtually divided into ring domains, the function u represents the electrostatic potential V. Like the general solution of Problem 3.1.1, the potential is a bounded function and Holder continuous in the domain Ω. The proposed mathematical model for the distribution of the electric potential V in the carbon nanotube can be seen as a particular case of the general problem 3.1.1 for the anisotropic N-laplacianul in ring domain in $\mathbb{R}^N$.

$$\begin{aligned} &F \in C^{3,\alpha}_{loc}\left(\mathbb{R}^N \setminus \{\mathbf{0}\}\right), \ \text{with}\alpha \in (0,1)\,, \\ &\text{Hess}\left(F^N\right) \ \text{is positive definite in } \mathbb{R}^N \setminus \{\mathbf{0}\}\,. \end{aligned} \tag{3.1}$$

$C^{3,\alpha}_{loc}\left(\mathbb{R}^N \setminus \{\mathbf{0}\}\right)$ represents the space of C^3 class functions for whom the 3^rd order partial derivate are local Hölder continuous on $\mathbb{R}^N \setminus \{\mathbf{0}\}$ with α exponent (conform Fiorenza [11, Chapter 1] and L. Evans [10, Chapter 5]).

We denoted F cu $F(\xi) = F(\xi_1, ..., \xi_N)$, and$F_{\xi_i} = \dfrac{\partial F}{\partial \xi_i}$, $i \in 1, 2, ..., N$ and $\text{Hess}\left(F^N\right) := (F^N_{\xi_i\xi_j})_{1\le i,j\le N}$, where $F_{\xi_i\xi_j} = \dfrac{\partial^2 F}{\partial \xi_i \partial \xi_j}$

We are dealing with the following free boundary problem:

Problem 3.1.1

$$\begin{cases} Qu := \sum_{i=1}^N \dfrac{\partial}{\partial x_i}\Big(F^{N-1}(\nabla u) F_{\xi_i}(\nabla u)\Big) = 0 \text{ in } \Omega := \Omega_0 \setminus \overline{\Omega}_1 \subset \mathbb{R}^N, \\ u = 0,\ F(\nabla u) = c_0 \text{on} \ \ \partial\Omega_0, \\ u = 1,\ F(\nabla u) = c_1 \ \text{ on } \ \partial\Omega_1. \end{cases} \tag{3.2}$$

Here Ω_0 and Ω_1 are bounded domains of $\mathbb{R}^N$ having boundaries of class C^2, such that $\Omega_0 \supset \overline{\Omega}_1$, while $c_1 > c_0 > 0$ are some real constants. Furthermore, we also assume that Ω_0 and Ω_1 are star shaped with respect to the origin, which is supposed to lie inside Ω_1. By $\nu = (\nu^1, \cdots, \nu^N)$ we denote the outer normal to $\partial\Omega$. We used the following definitions in the demonstrations in this chapter:

Definition 3.1.2 We will say that $u \in W^{1,N}(\Omega)$ is a weak solution of the Problem 3.1.1 if

$$\int_\Omega F^{N-1}(\nabla u) F_{\xi_i}(\nabla u) v_i \, dx = 0 \quad \forall v \in C_0^\infty(\Omega) \tag{3.3}$$

and u satisfies the boundary conditions $(3.2)_{2,3}$.

Definition 3.1.4 Let F^* be the dual norm of F that is

$$F^*(\mathbf{x}) = \sup_{\xi \neq \mathbf{0}} \frac{\langle \mathbf{x}, \xi\rangle}{F(\xi)} \ \ \forall \ \ \mathbf{x} \in \mathbb{R}^N.$$

F^* also called the polar of F.

For $r>0$, we define

$$W_F(r) := \{\mathbf{x}\in\mathbb{R}^N:\ F^*(\mathbf{x})<r\},\ W_{F^*}(r) := \{\mathbf{x}\in\mathbb{R}^N:\ F(\mathbf{x})<r\}.$$

Definition 3.1.5 In general, for $r>0$, we say that $W_F(r)$ eis the *Wulff* shape of F, of radius r and center $\mathbf{0}$. A set $D\subset\mathbb{R}^N$ is a *Wulff* shape of F if there exist $r>0$ such that $D=\{\mathbf{x}\in\mathbb{R}^N:\ F^*(\mathbf{x})<r\}$.

The main genuine result of this chapter is the theorem 3.1.6.

Theorem 3.1.6 If problem (3.2) has a weak solution u, then Ω_1 and Ω_0 are concentric Wulff shapes, up to translations, whose radii are given by:

$$r_i = \Big(c_i(\ln c_1 - \ln c_0)\Big)^{-1},\ i=0,1. \tag{3.9}$$

Moreover, if $F^*\in C^1(\mathbb{R}^N\setminus\{\mathbf{0}\})$, then the solution $u(\mathbf{x})$ is given explicitly by the following formula

$$u(\mathbf{x}) = \Big((\ln r_0 - \ln r_1)^{-1}(\ln r_0 - \ln F^*(\mathbf{x}))\Big)\quad \forall\mathbf{x}\in\Omega. \tag{3.10}$$

The demonstration of Theorem 3.1.6. is presented through a sequence of lemmas:

Lemma 3.2.1 Assume that u is a weak solution to problem $(3.2)_1$. Then the auxiliary function P, defined by (3.16)-(3.17), is either identically constant on $\overline{\Omega}$, or it has no maximum point in în Ω and it satisfies $P_\nu>0$ on $\partial\Omega=\partial\Omega_0\cup\partial\Omega_1$.

Here, ν is the exterior unit normal to $\partial\Omega$, while P_ν is the normal derivative of P.

Lemma 3.2.2 Assume that u is a weak solution to equation $(3.2)_1$. Let a_{ij} be the coefficients defined by

$$a_{ij}(\nabla u) := \frac{\partial^2}{\partial\xi_i\partial\xi_j}\left(\frac{1}{N}F^N(\nabla u)\right) = F^{N-1}F_{ij} + (N-1)F^{N-2}F_iF_j,$$

where $i,j\in\{1,...,N\}$. Then the following inequality holds:

$$a_{ij}a_{kl}u_{ik}u_{jl} \geq \frac{(a_{ij}u_{ij})^2}{N} + \frac{N}{N-1}\left[\frac{a_{ij}u_{ij}}{N} - (N-1)F^{N-2}F_iF_ju_{ij}\right]^2 \quad \text{on}\ \ \Omega\setminus\mathcal{C}, \tag{3.18}$$

where set

$$\mathcal{C} = \{x\in\Omega;\ \nabla\ u(\mathbf{x})=\mathbf{0}\}.$$

First we will define the anisotropic mean curvature, H_F (G. Wang and C. Xia [26, p. 313]). For this purpose we will consider a bounded domain $D\subset\mathbb{R}^N$ with the boundary, ∂D - $N-1$ dimensional sub-variety oriented and compact, with no boundary in $\mathbb{R}^N$. We denoted with $\{e_\alpha\}_{\alpha=1}^{N-1}$ a base in the tangent space ∂D, with $\left(g_{\alpha\beta}\right)_{\alpha\beta}$, $\left(h_{\alpha\beta}\right)_{\alpha\beta}$ the matrices of the first fundamental form, respectively, of the second fundamental form.

Definition 3.3.1 The second F - fundamental form $\left(h^F_{\alpha\beta}\right)_{\alpha\beta}$, and the anisotropic mean curvature H_F of boundary ∂D as folow:

$$h^F_{\alpha\beta} = \langle F_{\xi\xi}\circ\overline{\nabla}_{e_\alpha}, e_\beta\rangle,\quad H_F = \sum_{\alpha,\beta=1}^{N-1} g^{\alpha\beta}h^F_{\alpha\beta}, \tag{3.34}$$

where $\left(g^{\alpha\beta}\right)_{\alpha\beta}$ it is the inverse matrix $\left(g_{\alpha\beta}\right)_{\alpha\beta}$, and $\overline{\nabla}$ is covariant derivative în $\mathbb{R}^N$.

We olso say that ∂D is weakly convex if matrix $\left(h_{\alpha\beta}\right)_{\alpha\beta}$ is semi positive defined ă (G. Wang and C. Xia [26, p. 313]).

Lema 3.3.2 If problem (3.2) admits a weak solution $u(\mathbf{x})$, then the F- mean curvature, H_F, of $\partial\Omega$ satisfies either:

$$H_{1F} > \alpha\frac{(N-1)c_1}{N}\ \text{on}\ \partial\Omega_1 \qquad \text{and} \qquad H_{0F} < \alpha\frac{(N-1)c_0}{N}\ \text{on}\ \partial\Omega_0, \tag{3.35}$$

sau

$$H_{1F} = \alpha\frac{(N-1)c_1}{N} \text{ on } \partial\Omega_1 \quad \text{and} \quad H_{0F} = \alpha\frac{(N-1)c_0}{N} \text{ on } \partial\Omega_0, \tag{3.36}$$

where $H_{iF} := H_{F|\partial\Omega_i}$, $i = 0, 1$.

Lemma 3.3.3 A necessary condition for the existence of a solution $u(\mathbf{x})$ of problem (3.2) is

$$c_0^N \mid \Omega_0 \mid = c_1^N \mid \Omega_1 \mid, \tag{3.41}$$

where c_0, c_1 are real constants defined from conditions $(3.2)_{2,3}$.

In the end we obtained:

$$u(\mathbf{x}) = k_0 \int_{F^*(\mathbf{x})}^{r_0} s^{-1}\, ds = k_0\Big(\ln r_0 - \ln F^*(\mathbf{x})\Big) \text{ on } \Omega. \tag{3.57}$$

$$\nabla u(\mathbf{x}) = -\frac{\nabla F^*(\mathbf{x})}{(\ln r_0 - \ln r_1)F^*(\mathbf{x})}. \tag{3.58}$$

Finally, to obtain (3.9) we use the boundary conditions $(3.2)_{2,3}$, (3.58) and equality $F(\nabla F^*(\mathbf{x})) = 1$. Thus, the Theorem 3.1.6. is proved. The original results from chapter 3 were published in the paper by A. E. Nicolescu and S. Vlase [17].

Knowing the electric potential distribution and the temperature distribution on the spatial domain occupied by a nanotube allows its use in a vast field of measuring devices based on the Seebeck thermoelectric effect (Chakraborty et al. [6]), on the Peltier effect (Shafraniuk [20]), on the Hall effect (Baumgartner et al. [4]), or on the Nernst effect (Checkelsky and Ong [7]).

In chapter 4 we formulated a general overdetermined limit problem 4.1.1, on a cylindrical domain $\Omega \subset \mathbb{R}^N$, $N \geq 2$, for a function $u : \mathbb{R}^N \to \mathbb{R}$ with conditions on the free boundaries$\partial\Omega_0$ and $\partial\Omega_1$.

Based on the general problem 4.1.1, we further formulated two particular overdetermined boundary value problems, problem 4.1.5. and problem 4.1.6, whose solutions allow a possible description of the electrical and thermal behaviour of carbon nanotubes for which conditions are set on the free boundaries $\partial\Omega_0$ and $\partial\Omega_1$. Through the interpretations of the electric potential V and, respectively, the temperature T as the solutions of particular problems 4.1.5 and 4.1.6 respectively, mathematical models of the distribution of isothermal surfaces in the carbon nanotube with the ends maintained at constant electric potentials were proposed in the thesis, respectively for equipotential surfaces in the nanotube with thermostated ends.

The macroscopic model proposed in this chapter to describe the thermal, respectively, electrical behaviour of the nanotube, is a cylindrical domain $\Omega \subset \mathbb{R}^3$, with its ends maintained at different electrical potentials, respectively with its boundaries maintained at different temperature on which problems 4.1.5. and 4.1.6. are formulated.

Problems 4.1.5. and 4.1.6. are particular cases of overdetermined problem 4.1.1, the limit problem, more general on a cylindrical domain $\Omega \subset \mathbb{R}^N$, $N \geq 2$, for a function $u : \mathbb{R}^N \to \mathbb{R}$ which conditions are set on the free boundaries $\partial\Omega_0$ and $\partial\Omega_1$.

For the macroscopic model, u represents the electric potential V for the electrical behaviour, respectively , temperature T for the thermal behaviour. The macroscopic model of the carbon nanotube proposed in this chapter leads to the conclusion that the isothermal surfaces of the thermostated nanotube at its ends, respectively, the equipotential surfaces of the nanotube with the ends maintained by constant electric potentials are hyperplanes parallel to the free boundaries $\partial\Omega_0$ and $\partial\Omega_1$ in the case of dimensional N.

This model is a particular case of a overdetermined problem for a general class of anisotropic equations on a cylindrical $\Omega \subset \mathbb{R}^N$, $N \geq 2$.

Our goal is to show if problem 4.1.1 accepts a solution in a weak way, then the domain Ω şi soluţia u and the corresponding solution u meet specific symmetry properties. We approached the following boundary problem in this chapter:

Problem 4.1.1

$$\begin{cases} Qu := \sum_{i=1}^{N} \dfrac{\partial}{\partial x_i}\Big(G'\big(F(\nabla u)\big)F_{\xi_i}(\nabla u)\Big) = 0 \ \text{ in } \ \ \Omega, \\ u = 0,\ F(\nabla u) = a_0 = \text{const.} > 0 \ \text{ on } \ \partial\Omega_0, \\ u = 1,\ F(\nabla u) = a_1 = \text{const.} > 0 \ \text{ on } \ \partial\Omega_1, \\ G'\big(F(\nabla u)\big)\nabla F(\nabla u)\cdot\nu = 0 \ \text{ on } \ \partial\Omega_c. \end{cases} \tag{4.7}$$

The main result of this chapter states the following:

Theorem 4.1.4 Assume that the boundary portion $\partial\Omega_c$ is weakly convex and, in addition, the function F also verifies the assumption

$$\sum_{i=1}^{N-1} x_i \frac{\partial F}{\partial x_i}(x) \geq 0, \quad \forall \ \ x \in \mathbb{R}^N. \tag{4.10}$$

If problem 4.1.1. has a weak solution $u \in C^1(\overline{\Omega})$, then $a_0 = a_1 = a > 0$ and the free boundary portions $\partial\Omega_i$ are contained in two horizontal hyperplanes, $h_i = c_i = \text{const.},\ \ i = 0, 1$. Moreover, the solution u to problem 4.1.1. depends only x_N.

The demonstration of Theorem 4.1.4 is given by a sequence of lemmas:

Lemma 4.2.1 The function $P(u;\cdot)$ defined

$$P(u;x) = G'\Big(F\big(\nabla u(x)\big)\Big)F\big(\nabla u(x)\big) - G\Big(F\big(\nabla u(x)\big)\Big) \overset{\text{not.}}{=} H\Big(F\big(\nabla u(x)\big)\Big)\forall x \in \overline{\Omega},$$

attains its maximum over $\overline{\Omega}$ only on $\partial\Omega$, unless $P(u;\cdot) \equiv$ const. în $\overline{\Omega}$.

Lemma 4.2.2 Assume that u is a weak solution to Equation $(4.7)_1$. Let a_{ij} be the coefficients defined by

$$a_{ij}(\nabla u) := \frac{\partial^2}{\partial\xi_i\partial\xi_j}\left(G\circ F\right)(\nabla u) = G'F_{ij} + G''F_iF_j,$$
$$a_{ijk}(\nabla u) := \frac{\partial^3}{\partial\xi_i\partial\xi_j\partial\xi_k}\left(G\circ F\right)(\nabla u).$$

.

then the following inequality holds

$$a_{ij}a_{kl}u_{ik}u_{jl} \geq \frac{(a_{ij}u_{ij})^2}{N} + \frac{N}{N-1}\left[\frac{a_{ij}u_{ij}}{N} - G''F_iF_ju_{ij}\right]^2 \text{ pe } \ \Omega\setminus\mathcal{C}. \tag{4.30}$$

Lemma 4.2.3 A necessary condition for the existence of a weak solution u to problem (4.7) (4.7) is $a_0 = a_1 = a > 0$.

Lemma 4.2.4 The auxiliary function P verifies the following identity

$$\int_\Omega \Big(P(u;x) - G'\Big(F\big(\nabla u(x)\big)\Big)\sum_{i=1}^{N-1} F_i(\nabla u(x))u_i(x)\Big)\ dx = H(a) \mid \Omega \mid, \tag{4.30}$$

where $\mid \Omega \mid$ is the volume of Ω.

Remark 4.2.5

We modify the free boundary value problem (4.7) by taking $h_0 = 0$, i.e.

$$\partial\Omega_0 = \{(x', 0) \in \mathbb{R}^N; x' \in \Omega'\},$$

but $F(\nabla u)$ is not prescribed any more on $\partial\Omega_0$.

If this modified version of problem (4.7) has a weak solution $u \in C^1(\overline{\Omega})$ and the assumptions of Theorem 4.1.4 hold, then the free boundary portion $\partial\Omega_1$ is contained in a horizontal hyperplane $h_1 =$ const. > 0 and u depends only on x_N.

Indeed, the conclusion of Lemma 4.2.1 remains valid if $(4.7)_2$ remains true.

$$u = 0 \ \text{ pe } \ \partial\Omega_0 = \{(x', 0) \in \mathbb{R}^N ; x' \in \Omega'\}. \tag{4.46}$$

The macroscopic model proposed presumes the description of thermal behaviour, respectively, electrical behaviour of the nanotube, that the domain occupied by the nanotube is cylindrical and that the ends of the nanotube are maintained at different constant electrical potentials, respectively, equipotential surfaces of the nanotube with its ends maintained by constant electrical potentials are parallel hyperplanes to the free boundaries $\partial\Omega_0$ and $\partial\Omega_1$. The values of temperatures, respectively of the electrical potential in a point of the nanotube depend only on the x_N variable along the axis of the cylinder. This chapter proposes two directions, namely:

- An abstract problem at the overdetermined limit (Problem 4.1.) which generalizes the proposed model, namely the problem of the anisotropic equation on a cylindrical domain $\Omega \subset \mathbb{R}^N$, $N \geq 2$, for a function $u : \mathbb{R}^N \to \mathbb{R}$ that satisfies conditions on the free boundaries $\partial\Omega_0$ and $\partial\Omega_1$.

- Two applications (Problem 4.1.5. and Problem 4.1.6.) of Problem 4.1.1. through particularization of function u in the tridimensional case, represented the electric potential in Problem 4.1.5., respectively, the temperature in Problem 4.1.6.

The most important result of this chapter is Theorem 4.1.4. To demonstrate theorem 4.1.4. through a series of lemmas, we established a principle of maximum for $P-$function, a Rellich type identity and some geometrical arguments concerning the anisotropic curves of the free boundaries $\partial\Omega_0$ and $\partial\Omega_1$.

If in chapter 3 the solution to the general problem is applicable to determine the electrical potential in the spatial domain occupied by a two-walled nanotube, at different constant electrical potentials maintained with the aim to evaluate its equivalent electrical capacity, in chapter 4, the solution to the problem 4.1.1. is applicable to determine the distribution of the electrical potential and, respectively, to determine the distribution of temperature for one-walled nanotube when its ends are maintained at different constant electrical potentials, respectively, its ends are maintained at different constant temperatures. The problems related to nanotubes in chapters 3 and 4 are disconnected. Deformability or propagation in the presence of the electric or thermal field is not studied in chapters 3 and 4.

Based on the obtained results in this chapter (Problem 4.1.5.) the equipotential surfaces of the carbon nanotubes are parallel planes to $\partial\Omega_0$ and $\partial\Omega_1$, and as for problem 4.1.6. the isothermal surfaces of the carbon nanotubes are planes parallel to $\partial\Omega_0$ and $\partial\Omega_1$), we can propose two practical applications, namely, the implementation of the carbon nanotube either as an element of a thermoelectrical sensor or to use it as a voltage nanogenerator based on the electric Seebeck effect.

The original results from this chapter were published in the paper L. Barbu and A.E. Nicolescu [2].

Some directions of study that I will consider in connection with the problems studied in this doctoral thesis are the following:

(i) (i) Study of electromagnetic sensors with carbon nanotubes. The nanostructure of carbon nanotubes allows their use as detectors of electromagnetic radiation and gamma radiation based on changes in electrical properties (electrical capacity, electrical resistance and magnetic inductance) following interactions with these radiations;

(ii) Although most carbon nanotubes can be elastically assimilated to chiral one-dimensional systems, two families of nanotubes, zigzag and armchair, were considered in this work. The nonlocal models presented in the paper were applied to these two families, and their extension to chiral nanotubes represents one of the ways to further generalize the results of this paper;

(iii) The study of the piezoelectric behavior of axially deformed nanotubes and the use of the obtained results in the design of electromechanical nanosensors.

(iv) Another research direction is the study of the vibrations of laterally functionalized composite nanotubes. Lateral functionalization of carbon nanotubes allows both the increase of the active attachment surface of the molecules that are the object of detection, and the significant increase of the probability of attachment of these molecules to the nanotube.

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