## A BÉNARD-MARANGONI INSTABILITY AND NUCLEATION OF NANOTUBES

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## Abstract

We present a novel model describing the nucleation and the initial growth of bundles of carbon single-walled nanotubes (C-SWNTs). The formation of the catalyst nanoparticle, on which bundles of C-SWNTs grow, is first investigated. A qualitative analysis of the carbon-catalyst phase diagram shows that the gas-phase synthesis process leads to the formation of a nanometric liquid layer, supersaturated in carbon, surrounding the catalyst nanoparticle. It is then claimed that a solutal Bénard-Marangoni instability governs the flow of carbon in the liquid layer. Using results from linear stability analyses, it is shown, for a planar and a spherical geometry, that the onset of the solutal Bénard-Marangoni instability in the liquid layer is possible and favoured with respect to other fluid instabilities. Subsequently, results from a weakly nonlinear stability analysis (in a planar geometry) and from a bifurcation analysis (in a spherical geometry), are leveraged in order to show that the instability leads to the formation of hexagonal convection cells. It is argued that, once initiated, the solutal Bénard-Marangoni instability provides the kinetic mechanism necessary for the nucleation and the initial growth of bundles of C-SWNTs. This model provides an explanation for aspects of the growth still unclear, such as the nucleation mechanism, the nanometric diameter of C-SWNTs and their collective organization into bundles, at the onset of the growth.

## Résumé

Un nouveau modèle décrivant la nucléation et la croissance initiale de fagots de nanotubes de carbone mono-paroi (C-SWNTs) est ici présenté. La formation de la nanoparticule catalysant la croissance des fagots de C-SWNTs est tout d'abord investiguée. Une analyse qualitative du diagramme de phase carbone-catalyseur démontre que le procédé de synthèse en phase gazeuse mène à la formation d'une couche liquide nanométrique, supersaturée en carbone, entourant la nanoparticle. Il est ensuite affirmé qu'une instabilité de Bénard-Marangoni de type solutal gouverne la circulation du carbone à l'intérieur de la couche liquide. Utilisant les résultats d'analyses linéaires, il est démontré, pour une géométrie plane et sphérique, que la génération de l'instabilité de Bénard-Marangoni à l'intérieur de la couche liquide est possible et même favorisée par rapport aux autres instabilités hydrodynamiques. Par la suite, les résultats d'une analyse non-linéaire faible (géométrie plane) et d'une analyse de bifurcation (géométrie sphérique), sont utilisés pour démontrer que l'instabilité mène à la formation de cellules de convection hexagonales. L'hypothèse est ensuite faite qu'une fois générée, l'instabilité de Bénard-Marangoni est le mécanisme cinétique permettant d'expliquer la nucléation et la croissance initiale des fagots de C-SWNTs. Ce modèle explique des aspects de la croissance encore inexpliqués, tels que le mécanisme de nucléation, le diamètre nanométrique des C-SWNTs et leur croissance organisée, lors des premiers instants de la croissance, sous forme de fagots.

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To my Mother.

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## Chapter 1

## Introduction

### **1.1** Carbon nanotubes

Since their discovery in 1991 by S. Iijima [1], there has been a significant interest in the carbon nanotubes and in their synthesis. In addition to their nanometric dimension, their exceptional mechanical properties make of them a unique material in the world: highly stiff, flexible and light, stable at high temperature. Moreover, the covalent bonds between the carbon atoms composing the structure are strong, which leads to specific electronic properties. For instance, carbon nanotubes can behave either like a metal or a semi-conductor, depending on the spatial organization of the carbon atoms [2, 3].

The mechanical and electronical properties of carbon nanotubes could be used in many different applications, which differ by the type of properties exploited. On the one hand, the mechanical properties of carbon nanotubes are used to reinforce composite materials [4, 5, 6] and to build nanometric electromechanical devices [7, 8, 9]. On the other hand, the electronical properties are used to build junctions of nanotubes [10, 11] and supraconductors [12], in field emission [13, 14] and also in the stockage of energy [14]. A deeper understanding of the properties of carbon nanotubes would certainly lead to other interesting applications. However, the present low level of production (few grams per day) slows down the commercial development of carbon nanotubes.

There exist two main families of carbon nanotubes: the carbon single-walled nanotubes (C-SWNTs), constituted of a single sheet of graphite rolled into a cylinder, and the carbon multi-walled nanotubes (C-MWNTs), formed by many concentrical sheets. In this thesis, we only consider the case of C-SWNTs since they are easier to characterize than C-MWNTs. In the latter, the interactions between the sheets have also to be considered. The morphology of the C-SWNTs do not depend on the synthesis technique used. They are usually found in the form of crystalline bundles of five to few tens of individual nanotubes, arranged in a triangular lattice structure, each C-SWNT having a nanometric diameter (0.7nm-3nm) and a micrometric length (many microns) [15]. Experimental observations have shown that these C-SWNTs grow collectively, even at the onset of the growth [16]. This suggests that a common mechanism, independent of the synthesis technique, is responsible for the nucleation and growth of bundles of C-SWNTs [15, 16, 17].

Several techniques for the synthesis of C-SWNTs have been developed and optimized over the last few years. Typically, C-SWNTs are produced at high temperatures  $(750^{\circ}C - 1200^{\circ}C)$  using gas-phase techniques such as the laser ablation [18, 19], the solar furnace [20], the electric arc [21, 22, 23, 24] and the plasma torch [25]. Basically, these techniques consist in the covaporisation, at a high temperature (> 3000^{\circ}C), of carbon and of a metal catalyzing the growth, referred as the metallic catalyst. The mixture, highly concentrated in carbon (97%-98%at. of carbon with respect to 2%-3%at. of metal) is then rapidly cooled ( $\approx 10^6 {}^{\circ}C/s$ ) [26, 27] down to the solidification temperature of the carbon-catalyst mixture (usually near 1100°C), leading subsequently to the formation of C-SWNTs. Although there is some exceptions, the C-SWNTs resulting from this particular process are generally arranged in crystalline bundles, as described above. Whatever the method, the use of a metallic catalyst is always necessary for the synthesis to occur. Transition metals such as the cobalt [28, 29], the nickel [21, 30] and the iron [31, 32] are the most successful catalysts.

### **1.2** The problem and the approach

Since the discovery of carbon nanotubes, numerous studies on the subject have been undertaken in order to improve the different synthesis techniques. However, we are still far from a profitable marketting of products based on carbon nanotubes. Presently, the best way of optimizing the production of carbon nanotubes is via a better understanding of their growth mechanism. Since they are synthetized in extreme conditions and difficult to observe, the mechanism of formation of carbon nanotubes is still not fully understood. Actually, it is impossible to observe these nanometric objects *in-situ* in order to analyze the growth in real time. Only measures at discrete moments of the growth can be performed using different characterization techniques such as: transmission electron microscopy (TEM), diffraction of X-rays and Raman spectroscopy. Apart from this kind of experimental characterization, which gives good but insufficient informations on the growth mechanism of nanotubes, the theoretical approach is the modelization. In literature, there exist three possible types of models:

1. Semi-empirical models, where hypotheses are made on the interatomic interactions;

2. Ab initio models, based on the resolution of quantum systems. These models are limited to simple cases since the calculations are quite demanding. The use of computers is always necessary;

3. Phenomenological models, mainly based on experimental results and on conclusions from models 1 and 2.

#### CHAPTER 1. INTRODUCTION

In the last few years, models of the three types have been proposed to clarify the growth mechanism of these bundles of C-SWNTs. On the one hand, semi-empirical and *ab initio* calculations have shown the necessity of a metallic catalyst in the growth of C-SWNTs [33, 34, 35, 36, 37]. Indeed, the growth cannot result from direct condensation of carbon vapors into C-SWNTs. It needs the support of a catalyst on which C-SWNTs can grow. On the other hand, phenomenological models have been formulated to understand the precise role of the catalyst in the growth of C-SWNTs. The latter models have succeeded in describing the general scenario leading to the growth. However, important aspects such as the nucleation, the individual structure of C-SWNTs and their collective organization into bundles are still unexplained or unclear. Elucidating these aspects is fundamental in the formulation of a consistent model.

Recently, a review of the nucleation and growth of C-SWNTs [17] has suggested that a surface instability could be responsible for the nucleation of C-SWNTs. Stimulated by this idea, Frédéric Larouche, a Ph.D. student at INRS-Varennes, has proposed that a specific fluid instability, the solutal Bénard-Marangoni instability, could play a role in the mechanism of formation of bundles of C-SWNTs [38, 39]. The main objective of this thesis is to leverage this idea in order to develop a new phenomenological model explaining the nucleation and growth of bundles of C-SWNTs: the Bénard-Marangoni instability (BMI) model. Basically, this model postulates that the generation of a solutal Bénard-Marangoni instability and the formation of patterns of hexagonal convection cells within a thin liquid layer located at the surface of the catalyst nanoparticle, are responsible for the nucleation and growth of bundles of C-SWNTs.

### **1.3** Outline of the thesis

In Chapter 2, we provide an overview of the most important phenomenological models which have been proposed since 1995. Since the most recent models [15, 16, 17, 40] have pointed out that the catalyst nanoparticles are the key to the formation of C-SWNTs, a re-examination of the nature of the catalyst nanoparticle is performed in Chapter 3, in order to clarify its role in the growth process. This will lead us to conclude that the formation of a thin liquid layer surrounding the catalyst nanoparticle had not been considered in the previous models. In addition, an overview of the Bénard-Marangoni instability and a compilation of experimental data will be presented. Chapters 4 and 5 are respectively dedicated to the formulation of the BMI model in Cartesian and spherical coordinates. Linear stability analyses and nonlinear analyses (weakly nonlinear stability analysis and bifurcation analysis) are performed for both geometries, in order to show that 1. the onset of the solutal Bénard-Marangoni instability is possible within the liquid layer under the conditions of synthesis of C-SWNTs and 2. the resulting pattern of convection is hexagonal in these conditions. The last part of the thesis (Chapter 6) will be devoted to describe the mechanism by which a bundle of C-SWNTs nucleates and initially grows at the center of a hexagonal convection cell, and to substantiate how our model accounts for some aspects still unexplained by the existing models.

## Chapter 2

## C-SWNTs growth mechanisms

Carbon nanotubes are synthetized via gas-phase methods or chemical vapor deposition (CVD) methods. The former is at high-temperatures and typically leads to the synthesis of single-walled carbon nanotubes (C-SWNTs) which are arranged in crystalline bundles. Chemical methods, in contrast, occur at medium-temperatures and the tendency is to obtain multi-walled carbon nanotubes (C-MWNTs). Since our study concerns the mechanism of formation of bundles of C-SWNTs, we will only consider models based on gas-phase methods throughout this thesis.

In this chapter, we present an overview of the most important phenomenological models which have been formulated in the last few years to explain the nucleation and growth of bundles of C-SWNTs. We mention that this overview is mainly based on the PhD thesis of Julie Gavillet [15], which is an excellent work on the subject. We want to determine which aspects of the growth still need an explanation and on which aspects the differents models agree, in order to formulate a coherent basis for a new model. Section 2.1 discusses some early C-SWNT growth mechanisms (1995-2002), from the one first proposed by Saito in 1995 to the model of Gorbunov *et al.*, proposed in 2002. Section 2.2 presents the root-growth mechanism of Loiseau *et al.* [16, 15],

an important synthetic model which has been proposed in 2002. We will emphasize this model since it provides insights into specific aspects of the growth such as the nucleation process and the organization of C-SWNTs into bundles, which are at the center of the model proposed in this thesis.

### 2.1 The first models (1995-2002)

In this section, we present five important phenomenological models which have been proposed since the beginning of the investigation of the growth mechanism. Although many aspects of the growth are not yet completely clear, a lot of progress has been made, particularly concerning the nature and the role of the catalyst. The main questions these five models tried to answer are the following: is the catalyst active at the atomic level or is it active at a larger scale? Also, is the catalyst active in a liquid or in a solid state? Different conceptions have prevailed during the years, evolving slightly and even recurring, which we now present and discuss. In order to make natural transitions from one model to the other, we present the following models in a conceptual rather than the chronological order.

#### 2.1.1 Smalley et al. (1996): The "Scooter" model

Before the formulation of the first growth mechanism, calculations based on semiempirical and *ab initio* models had shown that the presence of a metallic catalyst was necessary for the growth of C-SWNTs to occur [35]. Trying to explain the exact role played by the catalyst is then the first major challenge models had to face. The "Scooter" model [41] is one of the first phenomenological models which was formulated to answer this question. It was proposed specifically to explain the narrow distribution of the C-SWNTs diameters that were observed in experiments



Figure 2.1: The growth mechanism proposed by Smalley *et al.* [41]. We see on this picture that the catalyst atom, scooting around the open edge of the tube, prevents the formation of five-membered rings that would curve the open edge of the tube and lead to a closed cap.

(1.3nm-1.4nm with Ni and Co catalysts) [41, 42].

In this model, the production of C-SWNTs is considered to result from an off-shoot of the process that otherwise would produce fullerenes<sup>1</sup> in high yield, a sensible assertion since carbon nanotubes were originally discovered as a by-product of fullerene research [1, 29, 31]. It is assumed that the C-SWNT embryos are partly constituted of a fullerene structure, i.e a tube opened at one end and closed by a hemi-fullerene cap (with a hemispherical shape) at the other end. Total energy calculations then show that in a system containing a few hundred atoms, the most stable configuration is obtained when the diameter of these embryos is fixed to 1.4nm, which explains the narrow distribution of the C-SWNTs diameters observed in experiments and also the nanometric dimension of the diameter [41, 42].

<sup>&</sup>lt;sup>1</sup>The fullerene structure is a form of carbon having a large spheroidal molecule consisting of an empty cage of 60 or more carbon atoms. R. F. Curl, Sir H. W. Kroto and R. E. Smalley have won the Nobel Prize in 1996 for their discovery of fullerenes.

#### CHAPTER 2. C-SWNTS GROWTH MECHANISMS

In the high temperature conditions present in the synthesis, the authors claim that such a structure would tend to close itself except if a metallic atom or a metallic aggregate was present at the open edge of the tube to prevent its closure. The main idea of the model is therefore that a single catalyst atom, "scooting" from one carbon atom to the other around the open edge of the tube, could prevent the closure of the tube and continuously allow the growth to continue by  $adsorption^2$  of carbon aggregates  $(C_2, C_3, ...)$  from the surrounding gas (Fig. 2.1). Calculations were made to support this hypothesis, showing that a single Ni atom located at the open edge of the tube could move freely from one side to the other even if the bonds with the carbon atoms were strong. The growth of the C-SWNT would result from the adsorption of surrounding aggregates of carbon at the dangling bonds present at the open edge of the tube. The addition of a new aggregate of carbon on the tube would always be accompanied by the corresponding displacement of the catalyst atom, in order to annihilate immediately the defect caused by this further incorporation of carbon in the structure. During the growth process, other metallic atoms would bind to the first metallic atom, resulting in the formation of a bigger catalyst aggregate less bound to the open edge of the tube; the capacity of the catalyst to move freely and to annihilate the defects would then continuously decrease until the aggregate is detached and the structure finally closes itself to form the C-SWNT.

Although it was successful in explaining the formation of C-SWNTs, this onemetal catalyst atom growth model presents a major weakness. It is known from experiments [20, 43, 44] that the average diameter of C-SWNTs depends on the nature of the metallic catalyst used in the experiment. A relation of this kind between the catalyst and the C-SWNT is not possible in this model since the diameter of the C-SWNT is simply determined from total energy calculations on a few hundred

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<sup>&</sup>lt;sup>2</sup>There is an important distinction to make between the term "absorption" and the term "adsorption". The first one indicates a process by which one or more soluble components of a gas mixture are dissolved in a liquid while the second indicates a process by which a free flowing fluid (gas or liquid) contacts a phase which selectively stores one or more of the specie contained in the fluid.

atoms, without considering the influence of the catalyst. Moreover, recent calculations [33, 34] have ended the speculations on this model, showing that an open embryo with a metallic catalyst at the open edge would close itself instantaneously in the conditions of synthesis.

### 2.1.2 Yudasaka et al. (1999)

This model [45] is based on laser ablation, a specific gas-phase method; however, it is valid whatever the synthesis technique used. Initially, a solid target composed of carbon and metal (Ni or Co) is placed in an inert gas environment. The laser ablation of this target heats the carbon-metal mixture up to 3000K-4000K, which leads to the formation of carbon-metal droplets on the target. The droplets suddenly evaporate due to the laser-beam irradiation and are ejected into the surrounding gas where the temperature is around 1200K. The rapid cooling of the droplets induces the metal present in the droplets to condense into nanometric aggregates of 1nm-2nm [46, 47]. These aggregates then catalyze the formation of C-SWNTs, using the surrounding carbon to supply the growth.

The diameter of the C-SWNTs is expected to be 1nm or 2nm since the model considers that a single C-SWNT grows on each metallic aggregate, which agrees with the dimension of the C-SWNT observed in experiments. Contrary to the "Scooter" model, the diameter of the C-SWNT is here fixed by the size of the catalyst aggregate, which itself depends on the nature of the catalyst via parameters such as the solubility and the solidification temperature of the metal. Hence, this model is a major improvement compared to the previous one since the experimental dependence of the C-SWNT diameter with the nature of the catalyst is now taken into account.

However, there are still major weaknesses in this model. On the one hand, the spontaneous expulsion of carbon-metal droplets from the target surface has never been



Figure 2.2: The growth mechanism proposed by Yudasaka et al. [15, 45]

observed. Even in the case where the evaporation of such droplets would be possible, it has been shown that the cooling would lead to the segregation of the carbon *before* the segregation of the metal [48, 49]. On the other hand, the organization of C-SWNTs into a bundle structure cannot be explained using this model. We could think that the formation of the bundle results from the agglomeration of the C-SWNTs by van der Waals interactions and by the coalescence of the different aggregates on which C-SWNTs grow. However, such a configuration is usually not observed in experiments. The coalescence of the aggregates has only been observed in particular experimental conditions where the C-SWNTs were isolated and not organized into bundles.



Figure 2.3: The radial growth of a *sea-urchin* structure [43].

#### 2.1.3 Saito (1995): A pioneer model

At the beginning, this model [30, 50] was proposed to explain the growth of a particular structure, the *sea-urchin* structure (Fig. 2.3), which consists in many bundles of C-SWNTs growing radially on a single catalyst nanoparticle. Today, the model of Saito is recognized as the first model describing the growth of bundles of C-SWNTs. Among other things, this pioneering work introduced the concept of segregation, which is still used today to describe the growth of C-SWNTs.

Typically, segregation is defined as the partial separation of one or more elements from a solution during a solidification process. In the model of Yudasaka *et al.*, the metal is the main segregating element: due to rapid cooling of the droplet, the metal condenses into an aggregate where the carbon is subsequently organized in a C-SWNT. In the model of Saito, it is the carbon which segregates from the metal towards the surface of the droplet, leading to the subsequent growth of C-SWNTs. This hypothesis agrees with the fact that, under the conditions of synthesis, the segregation of carbon preceeds the segregation of metal.

We now describe the steps of the model. As in the previous model, the rapid cooling of the gaseous carbon-metal mixture induces the formation of carbon-metal droplets. Since the cooling rate is high, the limit of solubility of carbon into the droplet is rapidly reached and the carbon is expulsed radially towards the surface (Fig. 2.4a) in the form of small graphene sheets<sup>3</sup>. If the segregation is strong enough, these sheets have a random orientation and some of them, perpendicular to the surface, are then curved in order to saturate the dangling bonds on the surface; this is how the formation of the C-SWNTs embryos is said to occur (Fig. 2.4b). The subsequent radial growth of the embryos continues until the segregation/diffusion process and the solidification of the droplet are completed (Fig. 2.4c). We notice how this model can explain the radial growth of the C-SWNTs in a *sea-urchin* structure.

The formation of the C-SWNTs embryos always corresponds to the beginning of the growth and is referred to as the *nucleation* step of the growth. Generally, nucleation occurs when a liquid is cooled very rapidly and spontaneously solidifies. Under these conditions, the transformation from the liquid state to the solid state is done via the formation of very small solid particles or *nuclei*. The *heterogeneous* nucleation is defined as the formation of nuclei on the surface of a preexisting condensed phase (such as impurities) while the *homogeneous* nucleation occurs when nuclei form directly from the liquid phase. In the present case, the C-SWNTs embryos (or nuclei) need the catalyst nanoparticle to develop and thus, we refer to the beginning of the growth as a heterogeneous nucleation process.

Contrary to the model of Yudasaka *et al.* where the growth takes place on a metallic aggregate of 1nm-2nm, the growth here occurs on a solid metallic nanoparticle of 10nm-30nm [30]. Such a diameter for the catalyst allows many C-SWNTs

<sup>&</sup>lt;sup>3</sup>For a more detailed description of the segregation process, see the analysis made by Loiseau et al., pp. 28-29.



Figure 2.4: The growth mechanism proposed by Saito. (a) Segregation of carbon towards the surface of the carbon-metal droplet, (b) Nucleation of the C-SWNTs on the surface, (c) Radial growth of the C-SWNTs [30, 50].

to grow on a single catalyst nanoparticle. This conception has many advantages; while correctly maintaining the correlation between the C-SWNT diameter and the nature of the catalyst, it opens the door to the investigation of the bundle structure. Indeed, we will see later that the growth of multiple C-SWNTs from a single catalyst nanoparticle is the precursor of a collective growth of the C-SWNTs into a bundle structure. But as it is, the model does not explain well the nucleation process and the beginning of the growth still needs clarification to understand how the organization of the C-SWNTs into a bundle structure is done.

#### 2.1.4 Kataura et al. (2000)

In this model, it is claimed that during the cooling process leading to the formation of the carbon-metal droplets, fullerene structures are also able to be formed in the surrounding gas; some of these structures are then absorbed by the droplets to form the C-SWNTs embryos. This hypothesis is partly supported by experiments [51] showing that the conditions for the synthesis of C-SWNTs are nearly the same as for the synthesis of fullerene structures, an argument used previously in the model of Smalley *et al.* 



Figure 2.5: The growth mechanism proposed by Kataura *et al.* Step 1: Formation of fullerenes and hemi-fullerene caps which are eaten by the carbon-metal droplets, Step 2: The carbon-metal droplets stop to eat the fullerene structures and the surface is covered with cap-like structures, the C-SWNTs embryos, Step 3: Growth of the C-SWNTs by incorporation of amorphous carbon at the root of the embryos [51].

The model consists of three steps. The first step of the growth (high temperature state) consists in the absorption of fullerenes and hemi-fullerene caps in the carbon-metal droplets. The second step (medium temperature state) occurs when the droplets solidify and stop incorporating these structures, in such a way that the surface is covered with cap-like structures (the C-SWNTs embryos). The final step of the growth (near the melting temperature) consists in the growth of the C-SWNTs by the further incorporation of surrounding amorphous carbon at the root of the embryos.

The proportional relation, observed in experiments [51, 52, 53, 54], between the C-SWNT synthesis temperature and the C-SWNTs diameter is explained as follows. On the one hand, it is known that the formation of smaller fullerenes is always faster than the formation of bigger fullerenes. On the other hand, when the synthesis temperature increases, the cooling velocity of the carbon-metal droplets decreases (since the gradient of temperature is lower) and the second step, described above, starts later. Globally, it thus gives time for bigger fullerenes to be formed and consequently thicker C-SWNTs should grow at the third step when the synthesis temperature is higher.

However, the model does not explain correctly the proportional relation between the melting temperature of the carbon-metal mixture and the C-SWNT diameter observed in experiments. This is a direct consequence of the fact that the initial formation of the cap-like structures does not depend at all on the presence of the catalyst. It implies that if the melting temperature of the carbon-metal mixture is higher, the solidification of the catalyst nanoparticle will be faster and bigger cap-like structures will not have time to form. Consequently, this model predicts that the C-SWNT diameter decreases when the melting temperature increases, which is in contradiction with the experimental observations [20].

### 2.1.5 Gorbunov et al. (2002)

This model [40] proposes that the growth of C-SWNTs results from the graphitization of amorphous carbon via molten catalyst nanoparticles supersaturated<sup>4</sup> in carbon. Indeed, Gorbunov *et al.* have deduced from a previous experimental study [55] that the initial carbon concentration in the molten catalyst nanoparticle can be as high as 50%at., an important result which will be discussed in detail in the model of Loiseau *et al.* The main experimental result obtained by Gorbunov *et al.* is that the catalyst nanoparticle is active in a liquid state, a conclusion which corroborates most of the previous models and will have a major importance in the formulation of our model. This result has been obtained from a study of the temperature dependence of the C-SWNT yield in the production of C-SWNTs. Using an Arrhenius plot presentation of the data (Fig. 2.6), Gorbunov *et al.* have determined that the activation energy of the C-SWNT formation is  $E_a=37$  kJ/mol near the yield maximum. Similarly, previous experimental studies on carbon nanofibers [56] had shown that their growth was directly related to the diffusion of carbon through *solid* catalyst nanoparticles. They had arrived at this conclusion in observing that the activation energy associated

<sup>&</sup>lt;sup>4</sup>The supersaturation is an unstable condition where more solutes are dissolved in a solvent that can normally be held in solution.



Figure 2.6: The temperature dependence of the C-SWNT yield Y in the Arrhenius coordinates. The activation energy  $E_a$  near the maximum yield is 37 kJ/mol [40].

to the growth was correlated with the diffusion rate of carbon through solid metals. In the present case, the activation energy calculated is 3-4 times smaller: it corresponds to the diffusion of carbon through *liquid* metals, suggesting that the catalyst nanoparticle is active in a liquid state. To account for these observations, they have proposed the following growth mechanism.

The growth process begins with the formation of the molten catalyst nanoparticles<sup>5</sup>. The first step occurs when the molten catalyst nanoparticle penetrates a solid amorphous carbon aggregate, dissolving it and precipitating carbon atoms on the surface (Fig. 2.7a). The precipitating atoms then arrange in a graphene sheet at the surface of the catalyst (Fig. 2.7b). The parallel orientation of the graphene sheet to the surface is not energetically favorable since near the synthesis temperature, the carbon-metal melt does not wet graphite at all [56]. Thus, any local defect of the graphene sheet, which certainly arises due to the curvature of the nanoparticle, will result in the buckling (Fig. 2.7c) and in the subsequent formation of the C-SWNT nucleus (Fig. 2.7d). Finally, the precipitating carbon atoms are incorporated at the basis of the C-SWNTs nuclei by overlapping the metal orbitals of the catalyst

<sup>&</sup>lt;sup>5</sup>The term "molten catalyst nanoparticle", used by Gorbunov *et al.*, is equivalent to the term "carbon-metal droplet".



Figure 2.7: The growth mechanism proposed by Gorbunov et al. [40]

nanoparticle (Fig. 2.7e). Hence, growth results from the transformation of one solid form (amorphous carbon) into another solid form (the C-SWNT) via the dissolution and the precipitation of carbon in a molten catalyst nanoparticle.

The main difference between this model and the model of Saito resides in the mechanism leading to the nucleation of the C-SWNTs. In one case, the carbon is initially in a solid form and nucleates at the surface of the nanoparticle via a dissolution/precipitation process; in the other case, the carbon is initially in a liquid form and nucleates at the surface of the nanoparticle via a segregation/diffusion process. However, the difference is only in the initial form of carbon and basically, both models agree that it is the same physical phenomena which takes place in the catalyst.

Moreover, the nucleation processes described in both models are quite similar. On the one hand, Saito has proposed that the graphene sheets are first perpendicular to the surface and are then curved in order to saturate the dangling bonds on the surface, thus forming the C-SWNTs embryos. On the other hand, Gorbunov *et al.* have postulated that the graphene sheets are first parallel to the surface and are then curved in response to a local defect in the graphene sheet. Although boths models agree on the effect of curvature of the sheet to form the C-SWNT nucleus, the nucleation step of the growth is still not clear and obviously needs a deeper investigation.

#### 2.1.6 Discussion

We have seen that the first major issue investigated by the early models published concerned the nature and the role of the catalyst in the formation of C-SWNTs. In which state (liquid or solid) and at which scale (atomic or not) does the catalyst act, are the main questions these models have tried to answer.

The "Scooter" model is rather different from the other models on these points since the catalyst is in an atomic form. A first consequence of this assumption is that there is no consideration of a particular state for the catalyst during the formation of the C-SWNTs; however, we have seen with Gorbunov *et al.* that the catalyst seems to be active in a liquid state. The model of Yudasaka *et al.* is also in contradiction with Gorbunov's observation since the catalyst aggregate is active in a solid form. These two models cannot thus be accepted as coherent phenomenological models.

An important experimental result concerns the narrow distribution of the C-SWNTs diameters when using the same catalyst. At first sight, the most plausible explanation is given by the growth of multiple C-SWNTs from the same catalyst nanoparticle. Indeed, since the same phenomena is at the origin of the nucleation of each embryo on the catalyst, it is easier to explain why they would all have the same diameter. Moreover, we have concluded from the model of Yudasaka *et al.* that the organization of the C-SWNTs into a bundle structure cannot be explained by assuming that only a single C-SWNT grows from the catalyst; the organization of many C-SWNTs on the same catalyst nanoparticle seems already to provide a better

explanation. Definitively, the catalyst seems to be active at a larger scale (such as the nanoparticle scale) than the atomic or aggregate scale, in order to allow the growth of multiple C-SWNTs from the same catalyst.

On the other hand, the idea that C-SWNTs embryos come from pre-existent fullerene structures, used in models of Smalley *et al.* and Kataura *et al.*, presents a major weakness: the dependence between the catalyst and the formation of the embryos does not explain the relation between the diameter of the C-SWNTs and the nature of the catalyst, observed in experiments. This problem is solved in the other models where a more intimate relation between the C-SWNT and the catalyst is assumed. These are beautiful examples of how experiments helped to refine the modeling.

From the five models presented, only two now remain to explain correctly the growth of bundles of C-SWNTs: the model of Saito and the model of Gorbunov *et al.* Both models agree that the catalyst is active in a liquid state and in the form of a nanoparticle. Even today, the segregation/diffusion process of carbon in the nanoparticle, proposed by Saito, is still the most coherent way of explaining the nucleation of the C-SWNTs from the catalyst nanoparticle. However, the simple explanation of the nucleation process given in these models is not sufficient to explain how the C-SWNTs are grouped together into a bundle structure. The next model, the root-growth mechanism of Loiseau *et al.*, investigates this aspect of the growth and also emphasizes the mechanism by which carbon is incorporated in the C-SWNT structure.

## 2.2 Loiseau *et al.* (2002): The root-growth mechanism

The group of Loiseau obtained impressive pictures of bundles of C-SWNTs using high-resolution transmission electron microscopy (HRTEM), allowing them to reach important conclusions on the nature and the role of the catalyst. Based on these conclusions, they have proposed a new phenomenological model, the "root-growth mechanism" [57], to explain the nucleation and growth of bundles of C-SWNTs. In this section, we will first present some important experimental results, especially HRTEM images showing the interaction between the catalyst nanoparticle and the C-SWNT. Subsequently, we will present the mechanism of formation they have proposed.

#### 2.2.1 Experimental observations

We present here HRTEM images of bundles of C-SWNTs obtained using the electric arc method, a specific gas-phase method. This technique, which was used in the beginning for the synthesis of fullerenes, is relatively simple and inexpensive. It consists of two carbon-metal electrodes, located in a neutral gas environment, between which an electric arc is created. The discharge creates a plasma where the temperature can reach 5700°C around the electrodes. The subsequent cooling of the gaseous carbon-metal mixture due to the surrounding temperature leads to the synthesis of C-SWNTs on the electrodes. Fig. 2.8 shows a typical deposit of C-SWNTs synthetized with this technique. In this picture, we see long (length > 400nm) bundles of C-SWNTs and nearly spherical metallic catalyst nanoparticles (black dots). The average diameter of the C-SWNTs on the picture is 1.2nm. Typically, the size of the catalyst nanoparticles varies between 5nm and 20nm. Hence, it confirms that the catalyst is neither an atom nor a nanometric aggregate but rather a nanoparticle, as claimed by Saito and Gorbunov *et al.*.



Figure 2.8: A typical deposit of bundles of C-SWNTs produced in an electric arc experiment [15].

The simultaneous identification of the two ends of the bundles is fundamental to characterize the interaction between the catalyst nanoparticle and the C-SWNTs. In Fig. 2.9, we clearly see that one of the ends of a short bundle (length < 400nm) is in the catalyst nanoparticle while at the other end, the C-SWNTs are closed by a hemi-fullerene cap. Clearly, this configuration suggests that the growth of short bundles is catalyzed by a *single* nanoparticle. Moreover, we notice that the C-SWNTs in the bundle embryo have nearly the same length, suggesting that the growth has a collective and cooperative character, even at the onset of the growth.

Bundles of C-SWNTs growing from a single catalyst nanoparticle are called *primary* bundles. Often, primary bundles coming from different nanoparticles join together to form a composite bundle. This is why it is usually difficult to observe the free end of long bundles since they are mixed together. However, after proper manipulations, the group of Loiseau *et al.* has succeeded in observing long bundles attached to catalyst nanoparticles and having a free end closed by a hemi-fullerene cap (Fig. 2.10). Moreover, the observation of short C-SWNTs (length < few nm)



Figure 2.9: An embryo bundle emerging from a catalyst nanoparticle [15].

in Fig. 2.11, identified as embryos of C-SWNTs having nucleated at the surface of the nanoparticle, shows that short bundles result from an early interruption of the growth. Thus, we conclude that the growth of all bundles, either short or long, is catalyzed by single nanoparticles in the same way.

On the other hand, in Fig. 2.12, we observe that the bundle of C-SWNTs has no direct interface with the catalyst nanoparticle but is separated by one or many graphene sheets surrounding the nanoparticle. It directly suggests a growth of the bundles by the root, at the interface between the catalyst nanoparticle and the C-SWNT. Indeed, if we consider that the growth proceeds by the incorporation of carbon at the root of the C-SWNT, the interface between the catalyst nanoparticle and the bundle should give information on the last steps of the growth. Since the interruption of the growth always result from a perturbation in the local conditions (low temperature, a lack of metal or carbon,...), it is reasonable to expect that the region of the bundle where the carbon joins the structure will be perturbed and consequently structurally disorganized. Hence, the disorganization of the carbon structure in graphene sheets, always observed at the interface between the C-SWNT and the catalyst nanoparticle, clearly suggests that the growth is generated by the incorporation of carbon at the root of the C-SWNTs [15, 57].



Figure 2.10: HRTEM picture of a long bundle emerging from a catalyst nanoparticle. The \* indicates the free end of a long bundle composed of closed C-SWNTs [15].

#### 2.2.2 The root-growth mechanism

Experiments by Loiseau *et al.* [16, 17, 15] have determined the relation between the catalyst nanoparticle and the C-SWNTs. They have shown that, independent of the synthesis technique, both long and short bundles of C-SWNTs grow the same way from a single catalyst nanoparticle. Experiments have also indicated that the nucleation and growth of the C-SWNTs in a bundle is collective and cooperative. Finally, they have concluded that the nucleation of the bundles is done at the surface of the catalyst nanoparticle and that the growth results from the incorporation of carbon at the root of the C-SWNTs. Based on these conclusions, they have developed a new phenomenological model, the root-growth mechanism. Basically, this model synthesizes conclusions from Saito and Gorbunov *et al.* and provides insights into specific aspects of the growth such as the nucleation, the collective organization of the C-SWNTs into a bundle structure and the incorporation of carbon in the C-SWNT structure. This model [57] consists in three steps: **1**) the formation of the catalyst nanoparticles supersaturated in carbon; **2**) the nucleation of the C-SWNTs and **3**) the root-growth of the C-SWNTs.


Figure 2.11: HRTEM pictures of C-SWNTs embryos. (a) Embryo of a bundle of C-SWNTs. The \* indicates an aggregate of fullerenes, (b) Embryo of an individual C-SWNT, (c) Embryo of a bundle composed of three C-SWNTs, (d) Embryo of a bundle composed of two C-SWNTs [15].

#### 1) Formation of the catalyst nanoparticles

Recent spectroscopic measurements made by Puretsky *et al.* [27] have shown the temporal evolution of C-SWNTs formation (Fig. 2.13). First, there is the formation of carbon nanoparticles (or clusters of carbon), then the formation of carbon-metal catalyst nanoparticles and finally the formation of the C-SWNTs. This means that the catalyst nanoparticles contribute to the assembly of the carbon nanoparticles into C-SWNTs, which reaffirms the important role played by the catalyst.

We know from experiments that the formation of the catalyst nanoparticles depends critically on the synthesis parameters. In particular, the cooling rate and the



Figure 2.12: HRTEM pictures of the interface between bundles of C-SWNTs and the catalyst nanoparticle. They clearly show the presence of graphene sheets surrounding the catalyst nanoparticle [15].



Figure 2.13: Spectroscopic measurements and *in situ* imaging of the growth of C-SWNTs inside a hot furnace, made by Puretzky *et al.* [27]. During the solidification process, there is first the formation of carbon nanoparticles (or clusters of carbon) followed by the formation of the carbon-metal catalyst nanoparticles and finally by the formation of the C-SWNTs.

initial concentration of carbon and metal in the mixture are the main factors determining the size and the composition of the catalyst nanoparticle. The analysis of the carbon-metal phase diagram (temperature vs. concentration) is thus a useful way of studying qualitatively the formation of the catalyst nanoparticles in the synthesis process. The group of Loiseau *et al.* has made such an analysis to obtain crucial information.

Their study first indicates that the maximum solubility of carbon in the carbonmetal droplets (where the metal is either Fe, Co or Ni) is 25% at. at equilibrium (Fig. 2.14) [17, 58]. However, this solubility limit can increase when the system is under non-equilibrium conditions and the size of the droplet is small. Indeed, it has been shown that the maximum solubility of carbon can even reach 40%-50% at. for droplets of Ni-C with a diameter less than 50nm [59, 60]. This phenomenon, characterized by a non-equilibrium carbon concentration (> 25% at. for Fe-C, Ni-C and Co-C), is called supersaturation. A direct consequence of this phenomenon is that the liquid phase will still exist a few hundred degrees below the melting temperature since a solution having a non-equilibrium carbon concentration has a lower melting temperature than the equilibrium melting temperature. We can thus define a non-equilibrium melting temperature for a supersaturated solution.



Figure 2.14: Carbon-nickel phase diagram. On this phase diagram is indicated the limit of solubility of carbon in the liquid nickel (25%at.). This limit is the same whether the metal is nickel, iron or cobalt [15].

Looking at the carbon-nickel phase diagram (Fig. 2.14), we see that the lowering of temperature leads to the lowering of the solubility of carbon in the carbon-nickel droplet; the same behavior occurs whether the metal is nickel, iron or cobalt. Since the cooling rate present in the synthesis of C-SWNTs is very rapid ( $\approx 10^6 \text{ °}C/s$ ), it is expected that each droplet undergoes a non-equilibrium solidification process and that the solubility limit of carbon in the droplet is reached and exceeded. It shows, in agreement with Gorbunov *et al.*, that the molten catalyst nanoparticle involved in the growth of C-SWNTs is supersaturated in carbon. Morever, in order to recover its equilibrium carbon concentration, each droplet undergoes a rapid segregation process and expulses its carbon radially towards the surface in the form of graphite. The expulsion of carbon is due to the much lower surface energy of the carbon than the surface energy of the metal (Fe, Co, Ni); indeed, instead of precipitating in the form of graphene sheets in the liquid, carbon will tend to be expelled towards the surface to minimize the total energy. We notice that the segregation becomes stronger as the temperature decreases and attains its maximum near the melting temperature of the carbon-metal mixture.

The hypothesis of such a segregation process taking place in carbon-metal droplets was introduced in the model of Saito to explain the nucleation of the C-SWNTs at the surface of the catalyst nanoparticle. Loiseau *et al.* have adopted the same idea in their model and have supported it with an analysis of the carbon-metal phase diagram. In addition, they have also investigated the segregation process at the atomic level via quantum molecular dynamics (**QMD**) *ab initio* simulations. Precisely, they have studied the behavior of a group of carbon and cobalt atoms upon cooling from high temperature. A mixture of 153 atoms (with a proportion of 66%at. of carbon) is initially heated to 2000K and progressively cooled down to 1500K at a cooling rate of 100K/ps. After a simulated time of 5ps at 1500K, nearly 80% of the carbon atoms had segregated to the surface of the group of atoms, which is in agreement with the expected segregation process near the surface of the catalyst nanoparticle.

Finally, experiments have shown [16] that the carbon concentration in the catalyst nanoparticle after the growth of the C-SWNTs was consistent with such a rapid



Figure 2.15: Line scan analysis along the section of a metallic catalyst nanoparticle, showing the segregation process of carbon. (a) Low magnification image of the nanoparticle where a line scan has been recorded between A and B, (b) Elemental profiles of carbon and nickel of the line scan. We can see that there is an expulsion of carbon towards the surface of the nanoparticle [16].

segregation process (Fig. 2.15).

#### 2) Nucleation of the C-SWNTs

Throughout this section, we will focus our attention on a single catalyst nanoparticle and see which types of structures are able to nucleate on it and under which conditions.

We have already mentioned that segregation is directly related to a non-equilibrium solidification process occuring in the catalyst nanoparticle. Furthermore, since the intensity of segregation increases near the solidification temperature, most of the carbon is expelled when the center of the droplet is solid. Hence, the nucleation of the C-SWNTs occurs when the segregating carbon crystallizes in the form of graphite on the surface of the solid metallic  $core^{6}$ .

Depending on the intensity of segregation, different graphitic morphologies can be formed on the surface of the metallic core. Loiseau *et al.* have given a good

<sup>&</sup>lt;sup>6</sup>During the growth process, the carbon-metal droplet transforms into a solid metallic core on which the nucleation of the C-SWNTs occurs. The term "catalyst nanoparticle" corresponds generally to this transformed object.

description of the possible scenarios leading to different morphologies. Here, we only consider the precise morphology of one or many bundles of C-SWNTs growing on a single catalyst nanoparticle. We will see that, once expelled, carbon nucleates at the surface of the metallic core according to two competing graphitization paths, which lead either to graphene sheets surrounding the metallic core or to the formation of bundles of C-SWNTs.

In the equilibrium case, when the cooling rate and the segregation process are slow, we expect a specific structure to nucleate on the surface of the metal. Indeed, a slow segregation of the carbon towards the surface of the catalyst nanoparticle implies a slow crystallization of the carbon atoms on the entire surface of the metallic core. During the crystallization, the carbon atoms will be organized by surface and bulk diffusion in their most stable configuration, which is the graphene sheet. Hence, the particular morphology which will nucleate under these precise conditions consists in one or more graphene sheets surrounding a metallic solid core (Fig. 2.16b).

In the non-equilibrium case, when the cooling rate and the segregation process are rapid, the diffusion of the carbon atoms at the surface is too rapid to allow the progressive incorporation of the atoms at the edges of a graphene sheet. Since surface energy arguments play in favour of the equilibrium configuration of the graphene sheet, Loiseau *et al.* have suggested that the formation of the C-SWNTs graphitic nuclei (Fig. 2.16c) would result from particular surface processes such as surface instabilities. They have made different hypothesis such as particular dynamic instabilities occuring in the formation of dendrites in solidification processes (Mullins-Sekerka instability [61]) or quasi-static instabilities similar to those involved in crystal growth [62]. However, the precise nature of these instabilities has not been investigated in detail; this is precisely the aspect that our model will be addressing.



Figure 2.16: The root-growth mechanism of bundles of C-SWNTs proposed by Loiseau et al. [16].

#### 3) Root-growth of the C-SWNTs

Loiseau *et al.* have done calculations showing that the carbon incorporated into the C-SWNT structure does not come only from the nanoparticle itself but mostly from the surrounding gas. Postulating that the carbon dissolved in the nanoparticle is the only supply for the growth, they have calculated that a nanoparticle of 15nm in diameter which initially contains 50% at. of carbon would give rise to either a single C-SWNT of  $1\mu$ m or to a bundle containing ten C-SWNTs of 100nm each (Fig. 2.17). It clearly does not explain the existence of bundles several micrometers long, observed in experiments. Hence, after the carbon contained in the nanoparticle is spent, carbon has necessarily to be supplied continuously from the vapor phase surrounding the catalyst nanoparticle.

The external supply in carbon can be made either at the root or at the free end of the C-SWNT. *Ab initio* simulations [33] have shown that a growth by the free end of the C-SWNT would need the presence of metallic atoms in the nucleating graphitic structure; this hypothesis has been excluded since no metallic atoms have yet been detected experimentally at the free end of the C-SWNTs. On the other hand, we have already mentioned that the root-growth mechanism explains the existence of



Figure 2.17: Diagram showing the length of a C-SWNT growing on a catalyst nanoparticle (here composed of Ni) as a function of the initial concentration of carbon in the nanoparticle and of the diameter of the nanoparticle after solidification [16].

the graphene sheets at the interface between the C-SWNTs and the catalyst nanoparticle. Moreover, they have modeled the migration of carbon atoms at the surface of a carbon-cobalt catalyst nanoparticle and observed their incorporation into the bases of the C-SWNT [16, 57]. This incorporation as well as the absence of formation of a closed fullerene-like structure, suggest that the root-growth mechanism explains correctly the growth of C-SWNTs from the catalyst nanoparticle. This mechanism also agrees with the experimental observation of an increase of the yield of C-SWNTs with the synthesis temperature [52, 53]. Indeed, an increase of the synthesis temperature induces an increase of the surface/volume diffusion coefficients which thus accelerates the incorporation of carbon at the root. All these arguments are in favor of a growth of the C-SWNTs by the root.

Observations by microscopy have shown that in order to produce bundles of C-

SWNTs several micrometers long (Fig. 2.16d), the root-growth mechanism should continue for a sufficiently long time, the carbon being adsorbed at the root by surface and/or volume diffusion in the nanoparticle. The growth of the C-SWNTs would then continue until the temperature is sufficiently high to prevent the complete solidification of the nanoparticle. The last steps of the growth occur when the nanoparticle achieves its solidification and the segregation of carbon decreases abruptly. At this moment, the carbon on the surface of the solid metallic core tends to encapsulate the nanoparticle in the form of graphene sheets, in order to recover a stable configuration. The closure of the C-SWNTs occurs simultaneously either by the incorporation of pentagons at the root of each C-SWNT or in continuity with the first graphene sheet.

If the stationary regime is perturbed during the growth (for instance, if the cooling rate is too fast), the growth of the embryos is aborted, leading to the condensation of the carbon into amorphous carbon (Fig. 2.16e) or into a few graphene sheets (Fig. 2.16f). This situation corresponds to the embryos of bundles observed in experiments (Fig. 2.9).

## 2.2.3 Discussion

According to the root-growth mechanism, the formation of C-SWNTs is mediated by a segregation/diffusion process of carbon inside a catalyst nanoparticle. Depending on the intensity of segregation, the segregating carbon crystallizes on the surface of a solid metallic core either in the form of graphene sheets surrounding the nanoparticle (in the equilibrium case) or as C-SWNTs nuclei (in the non-equilibrium case). In the latter case, the growth of the C-SWNT continues via the progressive incorporation of carbon at the root of the C-SWNTs, until the catalyst nanoparticle is completely solid.

#### CHAPTER 2. C-SWNTS GROWTH MECHANISMS

The first step of the model, the formation of the catalyst nanoparticles, is not very different from the pioneering model of Saito. The presence of a molten catalyst nanoparticle during the growth and the description of the segregation process are supported by the analysis of the carbon-metal phase diagram. In agreement with Gorbunov *et al.*, it is shown that the molten catalyst nanoparticle is supersaturated in carbon during the growth. As a consequence, the carbon is expelled towards the surface of the nanoparticle in order to recover the equilibrium conditions dictated by the phase diagram. The idea of the incorporation of carbon at the root of the C-SWNTs constitutes another important contribution from Loiseau *et al.* Even if the concept had already been proposed before, the arguments brought by Loiseau *et al.* have been essential to remove any doubt, reinforcing the root-growth mechanism idea.

The major contribution of the Loiseau et al. model has been to show that different graphitic morphologies can nucleate, depending on the intensity of the segregation process. The nucleation becomes a competition between different graphitization paths, among which the formation of the C-SWNTs embryos is one possibility. In the model of Saito, the nucleation process consists in the emergence of the segregating carbon from the nanoparticle in the form of graphene sheets where some are curved to form the embryos. In the model of Loiseau et al., it is proposed that the formation of the C-SWNTs embryos results from particular surface processes such as surface instabilities. Loiseau et al. have proposed different instabilities such as those involved in crystal growth, particularly in the formation of dendrites. One problem with this analogy is the scale difference between, for instance, the wavelength of the instability related to the formation of the dendrites (generally in the micrometer range) and the nanometric dimensions of the C-SWNTs. This is a weak aspect of the model of Loiseau et al. since a coherent model should take into account the particular scale of the dynamical process leading to the nucleation of C-SWNTs. Moreover, we would expect these instabilities to present a character of cooperation because most of the

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experiments have shown that this is a dominant aspect in the formation of bundles of C-SWNTs; this is not the case with the proposed surface instabilities. Furthermore, it is the nucleation step which fixes the diameter and the shape of the C-SWNT; it is also through the nucleation process that we can understand how the organization of the C-SWNTs into the bundle structure is achieved. Hence, the type of instability involved at the moment of nucleation is fundamental in the formulation of a coherent phenomenological model and it is the main concern of the model presented in this thesis.

We know that the maximum yield of C-SWNTs occurs near the solidification temperature, where the catalyst nanoparticle is in a liquid supersaturated state, i.e in a state where the solid and liquid phases coexist. Loiseau *et al.* have proposed surface instabilities similar to those involved in the growth of solid crystalline structures, but it led to inconsistencies. What about fluid instabilities involving flow patterns or, in other words, convective instabilities? We shall investigate such an hypothesis since convective instabilities are known to lead, under precise conditions, to organized patterns of convection; this could possibly lead us to explain the organization of the C-SWNTs in the bundle structure.

# Chapter 3

# Toward a new model

The model of Loiseau *et al.* [16, 17, 57] synthetizes the existing models [41, 45, 50, 51, 40] while offering insights into specific aspects of the growth of C-SWNTs such as the collective organization of C-SWNTs into a bundle structure and the incorporation of carbon at the root of the C-SWNTs. In addition to these important contributions, the model elucidates the nucleation process by showing that the nucleating morphology depends on the intensity of the segregation process, via the experimental cooling rate. In particular, Loiseau *et al.* have proposed that in order to understand the nucleation of bundles of C-SWNTs, which occurs when the cooling rate is high, one must invoke particular surface processes such as surface instabilities. However, the instabilities proposed in the root-growth mechanism do not seem to satisfy all the criteria observed in experiments. In order to develop a better model, we now look more carefully at these criteria and investigate the dynamics surrounding the catalyst nanoparticle during the nucleation of the C-SWNTs.

In Section 3.1, we proceed to a re-examination of the catalyst nanoparticle in order to determine what kind of instability is really involved in the nucleation of bundles of C-SWNTs. In Section 3.2, we describe this instability in detail and in Section 3.3, we proceed to a compilation of important experimental data.

# **3.1** Re-examination of the catalyst nanoparticle

Essentially, experiments have shown that three specific aspects characterize the nucleation of C-SWNTs: the small diameter of the individual C-SWNTs, their collective organization into a bundle structure and the triangular lattice symmetry exhibited by the bundle. In this section, we look at these aspects to confirm that the model of Loiseau *et al.* [16, 17, 57] does not give a sufficient explanation of the nucleation process. Since the catalyst nanoparticle is at the center of the nucleation process, we then proceed to a re-examination of the nature of the catalyst nanoparticle via a detailed analysis of the carbon-metal phase diagram; this will lead us to conclude that an important intermediate step in the formation of the catalyst nanoparticle had not been considered in previous models. In conjunction with this new result, we will then be able to propose a fluid instability to explain the nucleation of bundles of C-SWNTs.

## 3.1.1 A missing kinetic mechanism

Recently, Fan *et al.* [63] have studied the nucleation pathway of C-SWNTs on a metal surface using a series of total energy calculations. In particular, they have shown that the nucleation of a closed hemispherical graphitic cap is overwhelmingly favoured compared to any other structure with dangling bonds. Even more important are their calculations showing that starting from such a structure, it is favorable for the C-SWNT to increase its diameter up to 10nm before increasing the length of the tube. However, such diameters have never been observed in practice, the diameter observed in experiments being comprised between 0.7nm and 3nm [16]. To explain this

#### CHAPTER 3. TOWARD A NEW MODEL

result, Fan *et al.* have conjectured that the C-SWNT diameter may be constrained by additional kinetic factors during the nucleation process. Up to now, no model has proposed a sensible kinetic mechanism to explain the nanometric diameter of C-SWNTs.

The fact that a kinetic mechanism may intervene in the nucleation process is also obvious from pictures of bundle embryos. We see in Fig. 3.1(a) that, right from their birth, all the C-SWNTs present in the bundle have nearly the same height, suggesting that they grow simultaneously and collectively [16]. Another evidence for a cooperative nucleation process is in the recent observations showing that for small bundles, all the C-SWNTs have the same helicity [64]. These observations suggest that the nucleation process is governed by a kinetic mechanism acting through the entire bundle in a cooperative manner.



Figure 3.1: HRTEM images of a bundle embryo emerging from a catalyst nanoparticle. (a) Inclined view showing that all the C-SWNTs have nearly the same height at the beginning of the growth, (b) Top view showing that the triangular arrangement is imposed right at the beginning of the growth [16].

Another interesting feature of the growth of bundles of C-SWNTs is the triangular lattice symmetry exhibited by the bundle. Indeed, bundles of C-SWNTs are always found to exhibit this particular symmetry, independently of the synthesis technique and the nature of the catalyst [16]. Moreover, it has been observed that the triangular arrangement is imposed on the bundle right from its birth (Fig. 3.1(b)), indicating that this arrangement is already present at the moment of nucleation of C-SWNTs. The common explanation is that van der Waals forces<sup>3</sup> between the C-SWNTs tend to induce the minimum energy configuration in the bundle: the hexagonal "close-packed" configuration [65]. However, this explanation in terms of van der Waals forces does not consider how the C-SWNTs move toward each other or are organized together into the bundle structure; it only claims that the principle of minimization of energy *implies* the "close-packed" configuration of the bundle. Although these forces are certainly present during the nucleation process, it seems that a complementary explanation, taking in account the dynamical aspect of the nucleation process, is needed to understand how the C-SWNTs are *organized* together into a bundle structure with a triangular lattice symmetry.

It is clear from this short analysis that the role of the catalyst nanoparticle is not only to provide a substrate on which bundles can grow, but also to favor a substantial kinetic mechanism which would explain in a coherent manner the three aspects mentioned above. Precisely, this mechanism should be able to explain the nanometric diameter of an individual C-SWNT; also, it should be able to act at a sufficiently large scale in order to explain how the carbon atoms are organized collectively, during the nucleation process, under the specific symmetry exhibited by the bundle.

The most plausible kinetic mechanism which has been proposed up to now (Loiseau *et al.* [16, 17], discussed in Section 2.2.2), consists in surface instabilities such as those involved in the formation of dendrites in solidification processes (the Mullins-Sekerka instability [61]) or as those involved in the crystal growth produced by molecular beam epitaxy deposition [62]. For instance, in the former case, the nucleation of a bundle of C-SWNTs in the presence of a carbon gas, is seen as analog to the nucleation of dendrites in a snowflake in the presence of a water vapor. However, there is a problem with this analogy: the difference of scale between the size of the dendrites and the

<sup>&</sup>lt;sup>3</sup>Weak forces contributing to intermolecular bonding between the tubes.

diameter of the C-SWNTs. Indeed, the wavelength of the Mullins-Sekerka instability is usually in the micrometer range [16, 17] while the diameter of C-SWNTs is nanometric. Obviously, in order to explain the nanometric diameter of the C-SWNT, the surface instabilities should also act at the nanometric scale; this is not the case with the instabilities proposed by Loiseau *et al.* [16, 17]. Moreover, even if the structures resulting from these instabilities present a certain degree of organization, it does not particularly account for the triangular symmetry exhibited by the bundle. Although the mechanism proposed by Loiseau *et al.* [16, 17, 57] deals with the dynamical aspect of the nucleation process, it does not satisfy all the criteria encountered in experiments. A different kinetic mechanism is still needed to explain correctly the nucleation of bundles of C-SWNTs and it is the main aim of the present model to provide this mechanism.

In order to obtain further information, we now re-examine the formation of the catalyst nanoparticle.

# 3.1.2 The nature of the catalyst nanoparticle

Throughout this thesis, we will only consider the case of the iron catalyst, which is known to result in synthesis of C-SWNTs [25]. Although the treament remains valid for any catalyst, this choice is useful because there is much more literature concerning the synthesis of C-SWNTs with iron. We now look at the formation of the catalyst nanoparticle via the analysis of the carbon-iron phase diagram. We will show that the non-equilibrium synthesis conditions lead to the formation of a catalyst nanoparticle composed of a metallic solid core surrounded by a layer of liquid supersaturated in carbon. This will lead us to propose hydrodynamic instabilities as good candidates to describe the nucleation of bundles of C-SWNTs.

In gas-phase methods, the synthesis process begins by the creation of a mixture of



Figure 3.2: A detailed analysis of the carbon-iron phase diagram. The rapid solidification of the droplet leads to the formation of two phases: a metallic solid core (from **P2** to **P3**) surrounded by a liquid layer supersaturated in carbon (from **P2** to **P4**). The liquid layer still exists below the eutectic temperature (from **P4** to **P5**).

carbon and iron vapors in an inert gas. The carbon-iron mixture is initially at a high temperature (5000°C) (point **P0** in Fig. 3.2) and contains a fraction of about 2%-3% of iron atoms with respect to carbon atoms. The vapor mixture is then cooled very rapidly ( $\approx 10^6$  °C/s) down to few hundreds of degrees below the eutectic temperature of the carbon-iron mixture (750°C-1200°C) [17]. As the temperature decreases to around 2300°C (**P0** to **P1**), the vapor mixture condenses to form nanometric droplets of a carbon-iron solution having a carbon concentration of about 25%at.-30%at. of carbon in iron [17]. We now focus our attention on the cooling of a single droplet from the point **P1** to the eutectic temperature, near which the synthesis of C-SWNTs is known to occur [16, 17].

We first analyze the case where the cooling rate is low from P1 to P3. In this situation, the carbon-iron droplet transforms, once the liquidus line is reached, into a mixture composed of a carbon-iron solution (L) and of graphitic flakes  $(C_{(graphite)})$  floating on the surface of the solution because of their lower density. Thus, at point P2, the droplet is composed of graphite floating on a carbon-iron solution having a carbon concentration indicated by the liquidus line at the height of P2. Then, toward P3, the liquid part of the droplet is progressively transformed into a metallic solid core saturated in carbon (P3) while the graphitic flakes agglomerate at the surface of the core to form graphene sheets. In the model of Loiseau *et al.* [16, 17], this corresponds to the equilibrium case, represented in Fig. 2.16(b).

If the cooling rate is high from P1 to P3, the scenario is quite different. In this situation, the carbon-iron droplet undergoes a non-equilibrium solidification process from P1 to P2, maintaining the droplet in a supersaturated state. Hence, at point P2, the carbon concentration of the carbon-iron solution is higher than the equilibrium concentration. To recover the equilibrium state, a rapid segregation of the carbon is therefore necessary from P2 to P3: the carbon is expelled radially from the center toward the surface of the droplet until the composition of the carbon-iron solution reaches the equilibrium concentration and solidifies at the eutectic temperature. Thus, at point P3, the droplet is constituted of an inner solid core saturated in carbon surrounded by a phase highly concentrated in carbon. The model of Loiseau et al. [16, 17] postulates that the non-equilibrium conditions at the surface of the solid core (due to the high carbon concentration) are such that graphene sheets are not able to form during the process. Instead, the expelled carbon is seen to undergo a nucleation process, via a hypothetic instability at the surface of the solid core, afterwhat it is subsequently arranged in bundles of C-SWNTs (Fig. 2.16(c)). Let's now analyze the latter solidification process in detail.

First, the droplet center solidifies to a metallic solid core (P2 to P3) at the eutectic temperature,  $T_{eut}$ , by a eutectic transformation that results in the formation of an

iron  $\gamma - Fe$  phase and of a carbide ( $Fe_3C$ ) phase:

$$L_{(17.1\% at.)} \rightarrow \gamma - Fe_{(9\% at.)} + Fe_3 C_{(25\% at.)}, \qquad T_{eut} = 1153^{\circ}C.$$
 (3.1)

Since the carbon is expelled from the center toward the surface of the droplet during the segregation process, the solid phase with the higher carbon concentration is located at the surface of the metallic solid core. Consequently, the carbide phase surrounds the iron phase. In agreement with this analysis, the presence of a carbide layer has already been observed at the surface of different catalysts in C-SWNTs synthesis experiments [43, 66]. For a further investigation of the role of the carbide phase in the synthesis of C-SWNTs, we refer to the paper of Gavillet *et al.* [17].

As mentioned by Loiseau et al. [16, 17], the carbon present in the outer layer of the droplet does not have enough time to nucleate into small graphitic flakes since the segregation process is too rapid; this is why, when the cooling rate is high, we do not observe the formation of graphene sheets. In fact, under these conditions, the expelled carbon remains dissolved in atomic form in the outer layer of the droplet during the entire cooling process from P2 to P3. But the high concentration of carbon in solution in this layer weakens all the atomic bonds and, consequently, decreases the melting temperature of the solution below the eutectic temperature. This implies the existence of a state, below the eutectic temperature, where the outer part of the droplet is liquid while the inner part is solid. In other words, the non-equilibrium conditions resulting from the high cooling rate, involve the progressive formation of a thin liquid layer supersaturated in carbon, from P2 to P4, which surrounds the metallic solid core below the eutectic temperature. The existence of such a thin liquid surface film at temperatures below the melting point is a well-known phenomenon in surface physics, called *surface melting* [67]. This effect is known to be more pronounced when the solid particle is small, which is obviously the case here. Recent *in-situ* observations have shown that small droplets of Ni-C (< 50nm) supersaturated in carbon can still be liquid few hundreds of degrees below the eutectic temperature, confirming our hypothesis [59, 60].

a)

Hence, the rapid segregation process taking place in the carbon-iron droplet leads to the simultaneous existence of two phases (Fig. 3.3). The most stable phase is the core of the droplet, composed of a carbide phase and of an iron phase, both saturated in carbon; the second phase, resulting from the expulsion of carbon, consists in a liquid layer supersaturated in carbon surrounding the metallic solid core. As we mentioned in Section 2.2.2, the carbon concentration in such a supersaturated carbon-iron solution can reach values of 40% at.-50% at. [59]. Thus, since the liquid layer surrounds the carbide phase (25% at.), we estimate the carbon concentration in the liquid layer to vary between 25% at. and 45% at. We estimate the melting temperature of the supersaturated carbon-iron solution to vary from 800°C to 1000°C depending on the carbon concentration, a higher concentration leading to a lower melting temperature [59]. Therefore, we claim that a liquid layer supersaturated in carbon surrounds the metallic solid core below the eutectic temperature of the system, from P4 to P5. We can now incorporate this intermediate step of the formation of the catalyst nanoparticle into the general scenario for the nucleation and growth of bundles of C-SWNTs (Fig. 3.4).



Figure 3.3: Intermediate step in the formation of the catalyst nanoparticle. (a) Rapid segregation of carbon toward the surface of the droplet, (b) Formation of a liquid layer supersaturated in carbon surrounding a metallic solid core  $(\gamma - Fe + Fe_3C)$ . The concentrations in parentheses are carbon concentrations in % at.



Figure 3.4: General scenario for the nucleation and growth of bundles of C-SWNTs. We notice the liquid layer at the surface of the catalyst nanoparticles.

## 3.1.3 Discussion

Our analysis has shown that a supplementary kinetic mechanism is needed to explain correctly the nucleation of bundles of C-SWNTs. In order to uncover this mechanism, we have investigated the formation of the catalyst nanoparticle and concluded that the previous models had not considered the existence of a thin liquid layer supersaturated in carbon surrounding the metallic solid core. This implies that the C-SWNTs nucleation mechanism would not only be influenced by the processes occuring at the surface of the solid core but also by the dynamics at work in the liquid layer surrounding this core.

A recent study made by Jost *et al.* [68] has suggested that *convection* could play a role in the formation of C-SWNTs. They have found that the activation energy associated with the formation of C-SWNTs is not correlated with the diffusion in a liquid, as Gorbunov *et al.* [40] had suggested before, but with a faster process. One of their hypotheses to explain this result was that convection could dominate over diffusion in the process of formation of C-SWNTs. However, they did not investigate this further, expecting that such a phenomena would not be pronounced for nanoparticles. But there exists a convective instability, called the Bénard-Marangoni instability, which is especially dominant at small scales.

We now postulate that a Bénard-Marangoni convective instability, taking place in the liquid layer surrounding the metallic solid core, could be the kinetic mechanism we are searching for. Indeed, the onset of such convective instabilities is known to lead to organized patterns of convection, which could possibly explain the collective organization of the C-SWNTs into bundles and also the particular symmetry exhibited by the bundle. Furthermore, such a convective activity at the surface of the catalyst nanoparticle could explain why the diameter of the C-SWNTs is smaller than expected by energy calculations. We now analyze the Bénard-Marangoni instability in detail and state the conditions under which it would appear.

# 3.2 The Bénard-Marangoni instability

Experiments on instabilities caused by heating a layer of fluid from below were first conducted by Henri Bénard in 1900 [69]. His classical experiment on the formation of hexagonal convection cells is at the origin of the modern study of convection and instabilities. Bénard experimented on very thin liquid layers (a millimeter or less) having a free surface open to a gas, and observed the formation of hexagonal convection cells when the instability developed (Fig. 3.5). In 1916, Lord Rayleigh [70] analyzed this phenomenon mathematically and demonstrated that a critical temperature gradient exists above which convection appears and leads to the formation of patterns. He attributed this effect to the competition between the destabilizing effect of buoyancy (or gravitational) forces and the stabilizing effect of viscous forces. Indeed, when gravity is present, temperature differences cause density differences which could generate a buoyancy-driven flow. The resulting buoyancy-driven convection is known as thermal Rayleigh-Bénard convection. However, there were several discrepancies between the results of Rayleigh and the experiments of Bénard; for instance, the values of the critical temperature gradient and the wavelength of the expected pattern did not agree.



Figure 3.5: Photograph of hexagonal convection cells in a viscous fluid layer heated from below, taken by Bénard in 1901 [69].

#### 3.2.1 The thermocapillary Bénard-Marangoni instability

Although Bénard himself was aware of the important role played by surface tension, it took several decades to demonstrate both experimentally and theoretically the dominance of surface forces in sufficiently shallow fluid layers. Pearson [71] was the first to perform a linear stability analysis showing that the temperature dependence of the surface tension is able to produce an instability in a heated fluid layer, a phenomenon that had hitherto been attributed to buoyancy forces alone. Indeed, any surface tension gradient induces a shear stress on the interface directed from points of low to locations of high surface tension. Afterwards, due to the viscosity present in the liquid, the shear stress induces bulk motion. The generation of interfacial shear stresses by surface tension gradients is called the *Bénard-Marangoni* effect, after Marangoni [72], who first observed this phenomenon.

In the specific case where the gradients of surface tension depend on temperature

gradients, the effect is referred to as the *thermocapillary Bénard-Marangoni* effect. These temperature gradients can be the result of heat transfer processes as well as mass transfer processes involving enthalpy changes. Usually, the relation between the surface tension  $\sigma$  and the temperature T is given by the following linear relation:

$$\sigma = \sigma_0 + \gamma_T (T - T_0), \tag{3.2}$$

where  $\sigma_0$  and  $T_0$  are respectively arbitrary reference surface tension and temperature and  $\gamma_T = d\sigma/dT$  is the thermal surface tension coefficient. In most experiments, this coefficient is negative, i.e the surface tension decreases when the temperature increases.

We now explain how the thermocapillary Bénard-Marangoni effect leads to convection in a liquid layer heated from below, in the common case where  $\gamma_T < 0^4$ . Since, in this case, a positive temperature fluctuation on the free surface leads to a local decrease in the surface tension, any gradients of surface tension induced by such a positive temperature fluctuation necessarily cause surface traction forces *away* from the warmer spot. Due to these forces, a flow then develops in the bulk of the liquid layer. Since the flow has to be compensated by fluid from below, warm fluid is pumped up from the lower part of the layer, which amplifies the initial temperature fluctuation and subsequently leads to a convection flow driven by surface tension forces.

The reaction of the fluid to the initial fluctuation is determined by the different properties of the liquid such as the density, the viscosity, the thermal diffusivity and mostly by the temperature gradient across the layer. Typically, the strength of the thermocapillary driving is characterized by the dimensionless *thermocapillary Marangoni number*:

$$Ma_T = \frac{\gamma_T d\Delta T}{\mu\kappa},\tag{3.3}$$

<sup>4</sup>This description is still exact when  $\gamma_T > 0$ ; the only difference lies in the sense of convection.

where d is the liquid layer thickness,  $\Delta T = T_{LG} - T_{SL}$  the temperature difference across the liquid layer,  $T_{LG}$  the temperature at the liquid-gas interface,  $T_{SL}$  the temperature at the solid-liquid interface,  $\mu$  the dynamic viscosity and  $\kappa$ , the thermal diffusivity. Similarly, there is a dimensionless number characterizing the buoyancydriven instability mentioned above, called the *thermal Rayleigh number*:

$$Ra_T = \frac{\alpha_T \rho g d^3 \Delta T}{\mu \kappa},\tag{3.4}$$

where  $\alpha_T$  is the liquid's thermal expansion coefficient,  $\rho$  the liquid's density and g, the gravitational acceleration.

In both cases, the onset of the instability occurs when the critical number (namely the critical thermocapillary Marangoni number or the critical thermal Rayleigh number) is reached (see Table 3.1). This critical number, which is determined from a linear stability analysis of the fluid flow, usually depends on three parameters: the geometry of the problem, the type of boundary at the bottom wall and the rate of heat exchanged at the upper surface (quantified by the thermal Biot number  $Bi_T^{5}$ ). The geometry of the problem plays an important role in the determination of the critical number. For instance, in a spherical geometry, the value of the critical thermocapillary Marangoni number varies with the thickness of the liquid layer while it is not the case in a planar geometry [73]. However, when the thermal Biot number is small, the critical Marangoni number is nearly the same in both geometries, whatever the thickness considered. The second important parameter, the boundary at the bottom wall, can be of two types. The most common is referred as the *conducting* type, where the bottom wall is visualized as a semipermeable membrane through which heat diffuses infinitely rapidly from a supply solution located beneath the membrane; the second is the *insulating* type, where no flux of heat is allowed through the wall. Depending on the boundary of the physical context, the critical number is seen to be quite different. The third parameter, representing the rate of heat exchanged at

<sup>&</sup>lt;sup>5</sup>The thermal Biot number  $Bi_T$  represents the ratio of the liquid-phase heat-transfer resistance to the gas-phase one.

the upper interface, is also quite fundamental. Indeed, the neutral curves determined by the linear stability analysis always depend on the Biot number; it has a major influence on the critical number (see Chapter 4).

In most experiments, the value of the critical temperature gradient depends on both the buoyancy-driven and surface tension-driven mechanisms [74]. This is true also of the resulting convection, which is generally called *Rayleigh-Bénard-Marangoni* convection. Since  $Ma_T$  is proportional to d and  $Ra_T$  to  $d^3$  for a constant temperature difference  $\Delta T$ , the surface tension-driven mechanism will dominate in thin layers; it will also be dominant in micro-gravity conditions ( $g \approx 0$ ). On the other hand, the Rayleigh-Bénard convection will dominate in liquid layers where the upper surface is a rigid lid since no surface tension gradients are able to develop in such situations. Since experiments of Bénard were done with thin layers, it was normal to find discrepancies with the results of Rayleigh, who had only considered the effects of gravity.

## 3.2.2 The solutal Bénard-Marangoni instability

The Bénard-Marangoni instability can also result from concentration gradients since the surface tension of a liquid also depends on the concentration of a component which may be dissolved in the liquid (namely the surfactant, or surface-active solute). The mechanisms which control this instability, known as the *solutal Bénard-Marangoni* instability, are similar to the mechanisms which control the thermocapillary instability. The difference is that a mass gradient drives the instability rather than a temperature gradient. Mass gradients (or concentration gradients) can be the result of a mass transfer between phases as well as heat transfer processes involving chemical potential changes. The relation between the surface tension  $\sigma$  and the concentration c is given by:

$$\sigma = \sigma_0 + \gamma_c (c - c_0), \tag{3.5}$$

where  $\sigma_0$  and  $c_0$  are respectively arbitratry reference surface tension and concentration and  $\gamma_c = d\sigma/dc$  is the solutal surface tension coefficient. Similarly to the thermocapillary case, there exists a dimensionless number which characterizes the solutal Bénard-Marangoni instability, called the *solutal Marangoni number*:

$$Ma_s = \frac{\gamma_c d\Delta c}{\mu D_L},\tag{3.6}$$

where  $\Delta c = c_{LG} - c_{SL}$  is the concentration difference across the liquid layer,  $c_{LG}$  the concentration at the liquid-gas interface,  $c_{SL}$  the concentration at the solid-liquid interface and  $D_L$ , the molecular diffusivity in the liquid. This instability also has its counterpart in the buoyancy-driven type of convection, which is the *solutal Rayleigh-Bénard* instability, where the buoyancy forces are driven by concentration gradients. The associated dimensionless number is called the *solutal Rayleigh number*:

$$Ra_s = \frac{\alpha_c g d^3 \Delta c}{\mu D_L},\tag{3.7}$$

where  $\alpha_c$  is the liquid's solutal expansion coefficient.

In fact, much of the theory that has been developed for the thermocapillary Bénard-Marangoni instability and the thermal Rayleigh-Bénard instability may be transferred to the solutal case, by interchanging temperature with concentration dependencies (see Appendix A). However, there is a fundamental difference between heat and mass transfer: contrary to heat, material species, such as the surfactant, can accumulate at the liquid-gas interface. This phenomenon is known to result in the formation of an elastic surface film at the interface where the surfactant can accumulate, diffuse and convect. In literature, the mechanism governing this phenomenon is known as the *Gibbs adsorption mechanism* [75, 76].

The first important works on the solutal Bénard-Marangoni instability have been done by Brian *et al.* [77, 78, 79]. In order to determine the conditions under which the liquid-gas system is stable to transfer of mass, they extend Pearson's linear stability analysis of the thermocapillary problem in a planar geometry [71] to the solutal case. In particular, they have found that the critical value of the solutal Marangoni number depends on the quantity of surfactant which is adsorbed at the interface, expressed by the dimensionless *adsorption number*  $N_A$ . Since the only difference between the solutal and thermal problems consists in the adsorption of matter at the interface, we recover the thermal critical values when  $N_A = 0$  (see Table 3.1). We notice that the thermal Biot number also has its counterpart in the solutal problem, namely the solutal or mass Biot number  $Bi_s^{6}$ .

The stability conditions obtained by Brian *et al.*, presented in Table 3.2, mainly depend on the solutal surface tension coefficient  $\gamma_c$  and the concentration difference  $\Delta c$ . The results showed in the two first rows come directly from the expression of the solutal Marangoni number (Eq. 3.6). Since under these conditions the solutal Marangoni number is necessarily negative, the critical Marangoni number cannot be reached and the instability cannot be generated. The results presented in the two last rows show that the system is necessarily stable when the adsorption number  $N_A$ exceeds a specific saturation value, which depends on the boundaries of the problem. For smaller values than the critical adsorption number, the system will be stable only if the solutal Marangoni number is below the critical value of the solutal Marangoni number, also specified by the boundaries of the problem.

We can also apply the same reasoning to the thermocapillary case to determine the conditions under which the instability is generated. For instance, in the experiments of Bénard, the liquid layer was heated from below ( $\Delta T = T_{LG} - T_{SL} < 0$ ) and the liquid had the property of decreasing its surface tension when the temperature was increasing ( $\gamma_T < 0$ ). Under such conditions, it was thus normal to observe convection once a certain temperature gradient was reached.

<sup>&</sup>lt;sup>6</sup>The solutal or mass Biot number  $Bi_s$  represents the ratio of the liquid-phase mass-transfer resistance to the gas-phase one.

Type of instability	Critical value		
Thermal Rayleigh-Bénard	$Ra_T^c = 1101 \text{ (conducting case)}$		
Solutal Rayleigh-Bénard	$Ra_s^c = 1101 \text{ (conducting case)}$		
Thermocapillary Bénard-Marangoni	$Ma_T^c = 80$ (conducting case)		
	$Ma_T^c = 48$ (insulating case)		
Solutal Bénard-Marangoni	$Ma_s^c = 80$ (conducting case)		
	$Ma_s^c = 48$ (insulating case)		

Table 3.1: Critical values corresponding to each fluid instability in the situation of a free surface at the top and a rigid wall at the bottom, in a planar geometry [75, 80, 81]. The critical values correspond to the case where the solutal Biot number  $Bi_s$  and the adsorption number  $N_A$  are equal to zero.

# 3.2.3 Patterns of convection in surface tension-driven flows

We have just seen that the solutal Bénard-Marangoni (or the thermocapillary Bénard-Marangoni) instability is generated when the concentration (or the temperature) gradient exceeds a critical value. Indeed, once the Marangoni number characterizing the system becomes larger than the critical Marangoni number, certain perturbations have a tendency to grow and set the whole liquid in a particular motion called convection. It is known that at the onset of convection, the flow organizes itself in particular patterns composed of convection cells, called *patterns of convection* [82].

Different patterns can arise depending on the geometry of the problem and on the value of the Marangoni number. If the experimental conditions are horizontally isotropic, with no preferred directions, regular polygons in the form of equilateral triangles, squares, and regular hexagons are all patterns that can possibly appear at the onset of convection. However, it has been shown that small asymmetries in physical properties between the upper and lower parts of a liquid layer favor the onset of convection in the form of hexagonal convection cells [83, 84]. Thus, in the case of Marangoni convection where there is a temperature/concentration gradient across the layer, hexagons are usually present at the onset of convection.

$\gamma_c$	$\Delta c$	Behavior
< 0	> 0	Stable
> 0	< 0	Stable
< 0	< 0	Stable if $N_A > 0.05$ or if $Ma_s < 80$ (conducting case)
		Stable if $N_A > 0.083$ or if $Ma_s < 48$ (insulating case)
> 0	> 0	Stable if $N_A > 0.05$ or if $Ma_s < 80$ (conducting case)
		Stable if $N_A > 0.083$ or if $Ma_s < 48$ (insulating case)

Table 3.2: Conditions for the stability of the solutal Bénard-Marangoni instability in a planar geometry [75, 77] when the solutal Biot number  $Bi_s$  is equal to zero. The symbols  $\gamma_c$ ,  $\Delta c$  and  $N_A$  represent the solutal surface tension coefficient, the concentration difference across the layer and the adsorption number, respectively.

There are two types of hexagonal convection cells, namely the *l*-hexagons and the g-hexagons (Fig. 3.6). The former often occurs in liquids and corresponds to the case where the liquid rises at the center of the hexagons and goes down along the edges of the hexagons. The latter type mostly occurs in gases and corresponds to the case where the gas goes down in the center and rises along the edges. We notice that the l-hexagons tend to be preferred when the layer is contained between a rigid lower boundary and a stress-free upper surface [85].

The most recent studies [87, 88] indicate that either patterns in the form of rolls or in the form of square convection cells, can succeed to the hexagonal regime; the selection of the right pattern mostly depends on the boundary conditions of the problem. At very high Marangoni numbers, the convection cells are seen to acquire large irregular polygonal shapes and also to become time-dependent [88]. Although it is a rather complicated theoritical problem, a lot of progress has been made in the last few years to explain the transitions between the different patterns observed in experiments. For a further investigation of this topic, we refer to the excellent book of P. Colinet, J.C Legros and M.G Velarde [88].



Figure 3.6: The two types of hexagonal convection cells: the l-hexagons and the g-hexagons [86].



Figure 3.7: Two-dimensional convection in the form of rolls [86].

# 3.3 Compilation of the experimental data

Before studying the role of the Bénard-Marangoni instability in the nucleation of bundles of C-SWNTs, we first need to collect the experimental data related to the properties of the carbon-iron liquid layer surrounding the metallic solid core. In particular, this will be useful to calculate the dimensionless numbers characterizing the hydrodynamic instabilities which could take place in the liquid layer. Since there are no data in the literature for the supersaturated case (usually, experiments are done under equilibrium conditions), we have performed some extrapolations to determine the most important quantities; other quantities have been compiled in a table at the end of this section.

The first important quantity to evaluate is the dynamic viscosity of the liquid layer near the eutectic temperature, where the growth of C-SWNTs occurs. To do that, we use a value of viscosity which has been measured in a liquid cast iron<sup>7</sup>, at the eutectic temperature (Table 3.3). In order to calculate the viscosity over the entire range of carbon concentration in the liquid layer, we extrapolate linearly the curves presented in Fig. 3.8 to carbon concentrations of 25%at. (6.7%wt.) and 45%at. (15.0%wt.). Since the slope is independent of the temperature, we can use any of the curves to perform the extrapolation. We determine the dynamic viscosity  $\mu$  at 25%at. using the following calculation:

$$slope = -0.5 \frac{mN \cdot s}{m^2 \cdot \% wt.} = \frac{11.38 \frac{mN \cdot s}{m^2} - \mu}{4.23\% wt. - 6.7\% wt.} \to \mu = 10.1 \frac{mN \cdot s}{m^2},$$
(3.9)

and similarly at 45% at.:

$$slope = -0.5 \frac{mN \cdot s}{m^2 \cdot \% wt.} = \frac{11.38 \frac{mN \cdot s}{m^2} - \mu}{4.23\% wt. - 15.0\% wt.} \to \mu = 6.0 \frac{mN \cdot s}{m^2}.$$
 (3.10)

We therefore conclude that the dynamic viscosity of the carbon-iron solution, near the eutectic temperature, is comprised between 6  $mN \cdot s/m^2$  and 10  $mN \cdot s/m^2$ .

Two other important quantities to determine are the solutal and thermal surface tension coefficients. In order to obtain the solutal surface tension coefficient  $\gamma_c$ , we use Fig. 3.9, valid for cast irons in general. We assume a linear behavior of the surface

<sup>7</sup>A carbon-iron alloy with a carbon content between 2%wt. and 4.5%wt. We notice that the concentration is always expressed either in weight (%wt.) fraction or in atomic (%at.) fraction. The conversion, in the case of a carbon-iron mixture, is done this way:

$$\%at. = \frac{1}{1 + (\frac{m_{carbon}}{m_{iron}})(\frac{1}{\%wt.} - 1)},$$
(3.8)

where  $m_{carbon} = 12$ g/mol and  $m_{iron} = 55.85$ g/mol.

Carbon concentration	Carbon concentration	Temperature	Viscosity
(%wt.)	(%at.)	$(^{\circ}C)$	$(mN\cdot s/m^2)$
4.23	17.05	1147	11.38

Table 3.3: Viscosity of a cast iron near the eutectic temperature [89].



Figure 3.8: Dependence of the viscosity  $(0.1N \cdot s \cdot m^{-2})$  of a carbon-iron alloy with the concentration of carbon (%wt.) for 6 different temperatures  $(1400^{\circ}C, 1450^{\circ}C, 1500^{\circ}C, 1550^{\circ}C, 1600^{\circ}C)$ . The lower curve represents the higher temperature [90].

tension with respect to carbon concentration in the hypereutectic region (> 16.2% at.), in order to evaluate the solutal surface tension coefficient between 25% at and 45% at. Since the slope is independent of temperature, the coefficient is obtained by taking the slope of any of the curves in the hypereutectic region:

$$\gamma_c = \frac{d\sigma}{dc} = 0.03 \frac{N}{m \cdot \% at.}.$$
(3.11)

We notice that most studies are only concerned with low concentrations and consequently the solutal surface tension coefficient is usually negative.

Similarly, we use Fig. 3.10 to determine the thermal surface tension coefficient  $\gamma_T$ . Assuming a linear behavior of surface tension with respect to temperature around the eutectic temperature, we obtain the following value for the thermal surface tension coefficient:

$$\gamma_T = \frac{d\sigma}{dT} = -0.5 \frac{N}{m \cdot K}.$$
(3.12)



Figure 3.9: Dependence of the surface tension (dynes/cm = mN/m) of a cast iron with the concentration of carbon (%at.) for three different temperatures [91].



Figure 3.10: Dependence of the surface tension (N/m) of a carbon-iron alloy with the temperature (K) [91].

The thickness of the liquid layer is also an important parameter to determine. We have estimated its value by making the following assumptions:

1. The carbon atoms initially contained in the droplet remain in the metallic solid core and in the liquid layer during the formation of the catalyst nanoparticle;

2. We do not consider the carbide layer in the calculations;

**3.** The volume of the initial droplet is equal to the volume of the final catalyst nanoparticle;

4. Since the maximum yield of C-SWNTs is always obtained for synthesis parameters giving rise to a narrow nanoparticle distribution centered on 15nm [16], we assume that the diameter of the catalyst nanoparticle is 15nm.

Based on these hypotheses, the calculations have shown that the thickness of the liquid layer is comprised between 1nm and 4nm (see Appendix B). We now present a summary of all the important quantities related to the carbon-iron liquid layer surrounding the metallic solid core.

Symbol	Appellation	Value	Dimension	Details
$c_{SL}$	Carbon concentration at the bottom	25	%at.	
$c_{LG}$	Carbon concentration at the top	45	%at.	-
d	Liquid layer thickness	1-4	nm	_
ν	Kinematic viscosity	10-6	$m^2/s$	$\nu = \mu / \rho$
$\mu$	Dynamic viscosity	6 - 10	$mN \cdot s/m^2$	-
κ	Thermal diffusivity	10-6	$m^2/s$	$\kappa = \lambda_T / C_P \cdot \rho$
$\lambda_T$	Thermal conductivity	29	$W/m \cdot K$	-
$C_P$	Specific heat	946	$J/kg \cdot K$	-
ρ	Liquid density	7000	$kg/m^3$	-
$D_L$	Carbon diffusivity	$10^{-9}$	$m^2/s$	-
$\alpha_T$	Coefficient of thermal expansion	10 <sup>-5</sup>	/K	-
$\alpha_c$	Coefficient of solutal expansion	60	$kg/m^3 \cdot \% at.$	
$\gamma_T$	Thermal surface tension coefficient	-0.5	$N/m \cdot K$	_
$\gamma_c$	Solutal surface tension coefficient	0.03	$N/m\cdot\% at.$	-

Table 3.4: Compilation of important data related to the physical properties of the liquid layer surrounding the catalyst nanoparticle [89, 90, 91, 92, 93].
## Chapter 4

# The BMI model in a planar geometry

In the last chapter, we have suggested that a Bénard-Marangoni instability could be the missing kinetic mechanism explaining the nucleation of bundles of C-SWNTs. The model we propose in this thesis, the Bénard-Marangoni instability (BMI) model, describes how the generation of this instability and the subsequent formation of a pattern of hexagonal convection cells in the fluid layer surrounding the catalyst nanoparticle, could explain the collective nucleation of C-SWNTs into a bundle structure<sup>8</sup>. In order to simplify the problem, we first develop a model in a planar geometry, a useful approximation since most of the theory related to the Bénard-Marangoni instability has been developed for this geometry. The aim of the next chapter will be to extend the results of this chapter to a spherical geometry, which is nearly the real shape of the catalyst nanoparticle observed in some experiments.

In Chapter 3, we showed that the liquid layer surrounding the metallic solid core is *supersaturated* in carbon. Consequently, if C-SWNTs synthesis conditions would

<sup>&</sup>lt;sup>8</sup>The description of the growth mechanism will be done in Chapter 6.

lead to the generation of a Bénard-Marangoni instability in the liquid layer, we would expect the solutal effect to dominate over the thermal effect; indeed, in conditions of supersaturation, the flow in the liquid layer should mostly be governed by the transport of carbon atoms rather than by the transfer of heat. Thus, the first objective of this planar model is to determine that a *solutal* Bénard-Marangoni instability can appear in the conditions of synthesis of C-SWNTs and to verify that it dominates on the other fluid instabilities that could develop in the liquid layer. This can be achieved by a linear stability analysis of the fluid flow. The second objective is to determine, exploiting a weakly nonlinear stability analysis, if the configuration in the form of hexagonal convection cells is favoured in the conditions of synthesis of C-SWNTs.

In Section 4.1, we focus on a single catalyst nanoparticle and formulate the equations describing the transport of carbon in a planar liquid layer. Section 4.2 and Section 4.3 are respectively dedicated to the linear and weakly nonlinear stability analyses of the fluid flow.

#### 4.1 Formulation of the equations

In this section, we study the simplest configuration observed in some experiments: a bundle of C-SWNTs growing on one side of the catalyst nanoparticle (see Fig. 2.9). Our approach consists in approximating the region where the bundle grows with a planar layer (Fig. 4.1). We consider a horizontal liquid layer, composed of a carbon-iron solution supersaturated in carbon, of thickness d and of infinite horizontal extent. We model the carbon-iron solution as a Newtonian and incompressible fluid. Above the liquid-gas interface, there is an ambient gas phase and below the solid-liquid interface, there is a solid phase (the metallic solid core) where no flux of carbon is allowed. The liquid-gas interface is free, but, in our model, is considered to be undeformable. We neglect gravity effects because Rayleigh-Bénard convection is negligible compared to



the Bénard-Marangoni convection, as will be shown by our calculations.

Figure 4.1: Geometry of the planar model

The initial conditions of the problem are those right after the formation of the liquid layer. We assume that due to the rapid segregation process, the concentration of carbon in the liquid layer varies from 25% at. at the solid-liquid interface to 45% at. at the liquid-gas interface; this is derived from the analysis made in Section 3.1.2. For simplicity, we also assume that the layer is initially at rest in an unperturbed state. We consider the initial carbon concentration profile  $\overline{c}$  to be linear with respect to the vertical distance z, which is directed toward the free surface:

$$\bar{c} = c_{SL} + \beta z, \tag{4.1}$$

where  $c_{SL}$  is the carbon concentration at the solid-liquid interface and  $\beta = \Delta c/d$  is a positive and constant concentration gradient. We notice that when  $\beta$  is positive, which is the case here, the gas surfactant is absorbing [75].

As remarked by Loiseau *et al.* [16, 17], the length of the nanotubes observed in experiments indicates that there is necessarily a contribution of carbon from the surrounding gas during the growth process. We therefore consider a potential absorption of carbon at the liquid-gas interface. The absorption is quantified by the solutal Biot number  $Bi_s$ , characterizing the rate of carbon exchanged at the liquid-gas interface. However, we assume that only the carbon *absorbed* in the liquid layer is used to grow the nanotubes and neglect the effects due to the *adsorption* or the accumulation of carbon at the interface. This implies that the adsorption number  $N_A$ , characterizing the Gibbs adsorption of carbon at the liquid-gas interface (see section 3.2.2), is equal to zero in our model:

$$N_A = 0. \tag{4.2}$$

This assumption will allow us, in Chapter 5, to use the results already obtained for the thermocapillary problem.

Since the solutal Bénard-Marangoni instability is driven by gradients of surface tension  $\sigma$ , which in turn are caused by gradients of carbon concentration  $\tilde{c}$ , a mathematical relationship between these two quantities is needed. This relation has already been derived in Section 3.2.2:

$$\sigma = \sigma_0 + \gamma_c (\tilde{c} - c_0), \tag{4.3}$$

where  $\sigma_0$  and  $c_0$  are respectively the eutectic composition surface tension and concentration. The solutal surface tension coefficient  $\gamma_c$  is assumed constant. We recall from Section 3.3 that since the carbon-iron solution is supersaturated in carbon, the carbon will act as a surface-tension increasing solute (i.e.,  $\gamma_c > 0$ ).

The fluid motion within the liquid layer is described by the continuity and Navier-Stokes equations:

$$\nabla \cdot \vec{\tilde{u}} = 0, \tag{4.4}$$

$$\rho(\frac{\partial \tilde{u}}{\partial t} + \vec{\tilde{u}} \cdot \nabla \vec{\tilde{u}}) = -\nabla \tilde{p} + \mu \nabla^2 \vec{\tilde{u}}, \qquad (4.5)$$

where (x, y, z) are the three Cartesian coordinates of a point in the liquid layer,  $\vec{u} = (u, v, w)$  is the velocity vector,  $\rho$  the carbon-iron solution density,  $\tilde{p}$  the pressure and  $\mu$  the dynamic viscosity. We couple these equations to a solutal diffusion equation for the carbon in the liquid layer:

$$\frac{\partial \tilde{c}}{\partial t} + \vec{\tilde{u}} \cdot \nabla \tilde{c} = D_L \nabla^2 \tilde{c}, \qquad (4.6)$$

where  $D_L$  is the diffusivity of carbon in the liquid layer.

At the solid-liquid interface (z = 0), the carbon concentration is  $c_{SL} = 25\% at$ . and the no-slip and Neumann<sup>9</sup> conditions apply:

$$\vec{\tilde{u}} = 0, \tag{4.7}$$

$$\frac{\partial c}{\partial z} = 0. \tag{4.8}$$

At the liquid-gas interface (z = d), the carbon concentration is  $c_{LG} = 45\% at$ . and the surface is considered undeformable:

$$w = 0. \tag{4.9}$$

The boundary condition expressing the diffusion of carbon across the surface is given by [75]:

$$D_L \frac{\partial \tilde{c}}{\partial z} + H k_g \tilde{c} = 0, \qquad (4.10)$$

where H is the Henry's law constant and  $k_g$  is the gas-phase mass transfer coefficient.

Finally, the tangential stress balance at the liquid-gas interface is given by [81]:

$$\vec{t_x} \cdot \vec{T} \cdot \vec{n} = \vec{t_x} \cdot \nabla \sigma, \qquad \vec{t_y} \cdot \vec{T} \cdot \vec{n} = \vec{t_y} \cdot \nabla \sigma, \quad \text{at } z = d$$
(4.11)

where  $\vec{t_x}$  and  $\vec{t_y}$  are orthonormal tangent vectors to the liquid-gas interface in the x and y directions respectively,  $\vec{T}$  the stress tensor and  $\vec{n}$ , the unit normal vector. These vectors are expressed like:

$$\vec{t_x} = (1,0,0), \qquad \vec{t_y} = (0,1,0), \qquad \vec{n} = (0,0,1), \qquad (4.12)$$

and

$$T_{ij} = -p\delta_{ij} + \mu \left(\frac{\partial \tilde{u}_i}{\partial x_j} + \frac{\partial \tilde{u}_j}{\partial x_i}\right).$$
(4.13)

<sup>9</sup>We use the term "Neumann" instead of the term "insulating" since the latter term is mostly associated with the heat transfer problems.

The tangential stress condition then becomes:

$$\mu \frac{\partial \tilde{u}}{\partial z} = \frac{\partial \sigma}{\partial x}, \qquad \mu \frac{\partial \tilde{v}}{\partial z} = \frac{\partial \sigma}{\partial y}, \quad \text{at } z = d.$$
(4.14)

The set of equations can be summarized as follows:

$$\nabla \cdot \vec{u} = 0,$$
  

$$\rho \left( \frac{\partial \vec{u}}{\partial t} + \vec{u} \cdot \nabla \vec{u} \right) = -\nabla \tilde{p} + \mu \nabla^2 \vec{u},$$
  

$$\frac{\partial \tilde{c}}{\partial t} + \vec{u} \cdot \nabla \tilde{c} = D_L \nabla^2 \tilde{c}.$$
(4.15)

The boundary conditions at z = 0 are the following:

$$c_{SL} = 25\% at.,$$
  

$$\frac{\partial \tilde{c}}{\partial z} = 0,$$
  

$$\tilde{u} = 0,$$
  
(4.16)

while the boundary conditions at z = d are given by:

$$c_{LG} = 45\% at.,$$
  

$$D_L \frac{\partial \tilde{c}}{\partial z} + H k_g \tilde{c} = 0,$$
  

$$w = 0,$$
  

$$\mu \frac{\partial \tilde{u}}{\partial z} = \frac{\partial \sigma}{\partial x}; \\ \mu \frac{\partial \tilde{v}}{\partial z} = \frac{\partial \sigma}{\partial y}.$$
  
(4.17)

Since in our model, the solutal surface tension coefficient  $\gamma_c > 0$ , the concentration difference  $\Delta c > 0$  and the adsorption number  $N_A = 0$ , we can readily conclude that the instability will be generated if the Marangoni number characterizing the system is above the critical Marangoni number (see Table 3.2). We now determine the value of this critical number using a linear stability analysis of the fluid flow.

#### 4.2 Linear stability analysis

In a linear stability analysis, sufficient conditions for stability of a flow are investigated. Usually, a method of analysis involving the examination of Fourier components is used, called the *normal mode method*. It first consists in the introduction of harmonic perturbations on the initial state (also called the background or basic state), which is the flow whose stability is being investigated. Since these perturbations are small with respect to the initial state, the nonlinear terms are neglected in the equations for the perturbations. Then, the perturbations are decomposed into normal modes and since the linearity of the problem implies that the various modes do not interact, each mode can be examined separately. It leads to an eigenvalue problem from which we can subsequently determine the regions of stability and instability of the system.

Let us recall (4.15):

$$\nabla \cdot \vec{\tilde{u}} = 0, \tag{4.18}$$

$$\rho\left(\frac{\partial \tilde{u}}{\partial t} + \vec{u} \cdot \nabla \vec{u}\right) = -\nabla \tilde{p} + \mu \nabla^2 \vec{u}, \qquad (4.19)$$

$$\frac{\partial \tilde{c}}{\partial t} + \vec{\tilde{u}} \cdot \nabla \tilde{c} = D_L \nabla^2 \tilde{c}. \tag{4.20}$$

We decompose the motion into a initial state of no motion plus perturbation as follows:

$$\vec{\tilde{u}} = 0 + \vec{u}(\vec{x}, t), \tag{4.21}$$

$$\tilde{c} = \bar{c}(z) + c(\vec{x}, t), \tag{4.22}$$

$$\tilde{p} = \overline{p}(z) + p(\vec{x}, t). \tag{4.23}$$

The basic state equations are:

$$0 = -\nabla \overline{p},\tag{4.24}$$

$$0 = \nabla^2 \overline{c}. \tag{4.25}$$

Substituting equations (4.21), (4.22) and (4.23) into (4.18), (4.19) and (4.20) and subtracting the basic state equations, we obtain the equations for the perturbations:

$$\nabla \cdot \vec{u} = 0, \tag{4.26}$$

$$\rho\left(\frac{\partial \vec{u}}{\partial t} + \vec{u} \cdot \nabla \vec{u}\right) = -\nabla p + \mu \nabla^2 \vec{u}, \qquad (4.27)$$

$$\frac{\partial c}{\partial t} + \vec{u} \cdot \nabla \vec{c} + \vec{u} \cdot \nabla c = D_L \nabla^2 c.$$
(4.28)

We then linearize these equations by neglecting terms of order higher than one:

$$\nabla \cdot \vec{u} = 0, \tag{4.29}$$

$$\rho \frac{\partial \vec{u}}{\partial t} = -\nabla p + \mu \nabla^2 \vec{u}, \qquad (4.30)$$

$$\frac{\partial c}{\partial t} + w\beta = D_L \nabla^2 c, \qquad (4.31)$$

where we have used (4.1) in the diffusion equation. We now write the perturbation equations in terms of w and c only. Taking the Laplacian of the z-component in (4.30), we obtain:

$$\rho \frac{\partial \nabla^2 w}{\partial t} = -\nabla^2 \frac{\partial p}{\partial z} + \mu \nabla^4 w.$$
(4.32)

We now take the divergence of (4.30):

$$\rho \frac{\partial}{\partial t} (\nabla \cdot \vec{u}) = -\nabla^2 p + \mu \nabla^2 (\nabla \cdot \vec{u})$$
(4.33)

and use the continuity equation to obtain:

$$0 = -\nabla^2 p. \tag{4.34}$$

Differentiating the last equation with respect to z, we can eliminate the pressure term in (4.32). Finally, we obtain a new set of equations governing the evolution of the perturbations, in terms of w and c only:

$$\rho \frac{\partial \nabla^2 w}{\partial t} = \mu \nabla^4 w, \tag{4.35}$$

$$\frac{\partial c}{\partial t} + w\beta = D_L \nabla^2 c. \tag{4.36}$$

We now proceed to the nondimensionalization of the equations and the boundary conditions. In order to use dimensionless independent variables in the rest of the analysis, we make the following transformation:

$$t = \frac{d^2}{D_L} t^*, \tag{4.37}$$

$$(x, y, z) = (x^*d, y^*d, z^*d),$$
(4.38)

$$(u, v, w) = \left(\frac{D_L}{d}u^*, \frac{D_L}{d}v^*, \frac{D_L}{d}w^*\right), \qquad (4.39)$$

$$c = (c_{LG} - c_{SL})c^*, (4.40)$$

where the superscript \* indicates the dimensionless variables. For convenience, we will drop the superscript \*. We remind that d,  $D_L$ ,  $c_{LG}$  and  $c_{SL}$  are respectively the thickness of the liquid layer, the carbon diffusivity, the carbon concentration at the liquid-gas interface and the carbon concentration at the solid-liquid interface.

Under this transformation, the system of equations becomes:

$$Sc^{-1}\frac{\partial}{\partial t}\nabla^2 w = \nabla^4 w,$$
  

$$\frac{\partial c}{\partial t} = \nabla^2 c - w,$$
(4.41)

while the boundary conditions at z = 0 and z = 1 are respectively given by:

$$c_{SL} = 1.25,$$
  

$$\frac{\partial c}{\partial z} = 0,$$
  

$$\vec{u} = 0.$$
  
(4.42)

and

$$c_{LG} = 2.25,$$

$$\frac{\partial c}{\partial z} + Bi_s c = 0,$$

$$w = 0,$$

$$\frac{\partial^2 w}{\partial z} = -Ma_s \nabla_H^2 c,$$
(4.43)

where  $\nabla_H^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$  is the horizontal Laplace operator. In these equations appear the dimensionless numbers Sc (Schmidt number),  $Bi_s$  (solutal Biot number) and  $Ma_s$  (solutal Marangoni number) appear, which are defined as:

$$Sc = \frac{\mu}{\rho D_L}, \qquad Bi_s = \frac{Hk_g d}{D_L}, \qquad Ma_s = \frac{\gamma_c d^2 \beta}{\mu D_L}.$$
 (4.44)

The last equation of (4.43) comes from the nondimensionalization of the tangential stress equation (4.14) (see Appendix D).

The method of normal modes is now introduced. Since the problem (4.41 - 4.43) is separable in space and in time, we assume normal modes of the form:

$$w(x, y, z, t) = W(z)\phi(x, y)e^{\lambda t}, \qquad (4.45)$$

$$c(x, y, z, t) = \Theta(z)\phi(x, y)e^{\lambda t}, \qquad (4.46)$$

where  $\lambda = \lambda_R + i\lambda_I$  is a complex eigenvalue. The function  $\phi$  satisfies the Helmholtz equation:

$$\nabla_H^2 \phi + l^2 \phi = 0, \qquad (4.47)$$

where  $\phi(x, y) = e^{i(l_x x + l_y y)}$  and  $l = \sqrt{l_x^2 + l_y^2}$  is the wavenumber of the particular disturbance. With this new dependence, the operators present in (4.41 - 4.43) transform as follows:

$$\frac{\partial}{\partial t} \to \lambda,$$
 (4.48)

$$\nabla_H^2 \to -l^2, \tag{4.49}$$

$$\nabla^2 \to D^2 - l^2, \tag{4.50}$$

where  $D = \frac{d}{dz}$ .

The problem can be rewritten as follows:

$$Sc^{-1}\lambda(D^{2} - l^{2})W = (D^{2} - l^{2})^{2}W,$$
  

$$\lambda\Theta = (D^{2} - l^{2})\Theta - W,$$
  

$$\Theta(0) = 1.25; D\Theta(0) = 0; W(0) = 0,$$
  

$$\Theta(1) = 2.25; D\Theta(1) + Bi_{s}\Theta(1) = 0,$$
  

$$W(1) = 0; D^{2}W(1) - Ma_{s}l^{2}\Theta(1) = 0.$$
  
(4.51)

This set of equations defines an eigenvalue problem where  $\lambda$  is the eigenvalue and  $(W, \Theta)$  is the eigensolution. If for some choice of the parameters, all eigenvalues  $\lambda$  are in the left complex halfplane, the basic state (or motionless) solution is linearly stable and the perturbation amplitude decays to zero. On the contrary, if at least one eigenvalue  $\lambda$  has a positive real part, the perturbation will grow and the basic state solution will be unstable. Consequently, the transition from stable to unstable state occurs when  $\lambda$  crosses the imaginary axis, i.e  $\lambda_R = 0$ . This transition state is called the *neutral state*. In most cases, the parameter values defining this state, called the critical values, are found by assuming that the imaginary part  $\lambda_I$  is also equal to zero, which means that  $\lambda = 0$  [81]; this assumption is called the principle of exchange of stability. In particular, it implies that the neutral state will be stationary rather than oscillatory. This principle has been shown to be valid in the case of Bénard-Marangoni convection [94].

The neutral-stability curves for the problem (4.51) have already been obtained [75, 77]. The formula relating the solutal Marangoni number  $Ma_s$  to the wavenumber l of the instability, when  $N_A = 0$ , is given by:

$$Ma_{s} = \frac{8k(\sinh l \cosh l - l)(l \sinh l + Bi_{s} \cosh l)}{\cosh l(l^{2} + \sinh^{2} l) - l(2 + l^{2}) \sinh l}.$$
(4.52)

The level sets  $Ma_s = Ma_s(l, Bi_s)$  are called the neutral-stability curves of the system. They separate the regions of stability and instability of the system (see Fig. 4.2). For each value of the Biot number  $Bi_s$ , there exists a neutral curve with a minimum characterized by two important values: the critical Marangoni number  $Ma_s^c$  and the critical wavenumber  $l_c$  of the instability. Depending on the value of the Marangoni number  $Ma_s$  characterizing the system, three possible regimes exist:

• A subcritical regime  $(Ma_s < Ma_s^c)$ , where the motionless state of the fluid in the layer is stable with respect to infinitesimal perturbations;



Figure 4.2: Neutral-stability curves when  $N_A = 0$ . The different curves correspond to different Biot numbers  $(Bi_s=0,1,3,5,7)$ ; the lower curve represents the lower Biot number. The region of stable states is below the curve and the region of unstable states is above the curve. The symbols  $Ma_s^c$  and  $l_c$  respectively represent the critical Marangoni number and the critical wavenumber of the instability (in this case, when  $Bi_s = 1$ ).

• A critical regime  $(Ma_s = Ma_s^c)$ , where a steady-state motion with an infinitesimal amplitude and with a unique wavenumber  $l = l_c$  is onset;

• A supercritical regime  $(Ma_s > Ma_s^c)$ , where the layer becomes convectively unstable, and the perturbations with wavenumbers corresponding to  $Ma_s > Ma_s^c$  grow exponentially.

The main purpose of the linear stability analysis is to provide the value of  $Ma_s^c$ and  $l_c$ . Within certain limits, the knowledge of these values can be useful to determine which mode will dominate after the onset of the Marangoni instability. The mode which dominates on the others is usually referred to as the "most unstable mode". The linear stability analysis tells us that there always exists a particular wavenumber  $l_{max}$  for which the amplification rate is maximal. When the Marangoni number characterizing the system is near the critical Marangoni number  $(Ma_s \simeq Ma_s^c)$ , this wavenumber is close to the critical wavenumber  $(l_{max} \simeq l_c)$  and does indeed predict the size of convection cells observed experimentally [95]. However, when the Marangoni number increases, the number of modes having a wavenumber comprised within the unstable region also increases, making more and more difficult the prediction of the most unstable mode in a nonlinear case. A nonlinear stability analysis becomes consequently necessary. In order to relax the latter difficulty, most of the nonlinear stability analyses (for instance, the weakly nonlinear stability analysis) assume that the wavenumber of the most unstable mode is located in a narrow region centered on the critical wavenumber. In cases where it is impossible to make such an assumption (when  $Ma_s$  is very high), the use of numerics is essential.

As shown in Fig. 4.2, an increase of the Biot number has a direct effect on both the value of the critical Marangoni number and the value of the critical wavenumber. First, it has a stabilizing effect: for a given system, at the increase of the Biot number, the critical Marangoni number will become larger than the Marangoni number characterizing the system and the convection will be inhibited. Second, the Biot number has an effect on the size of the convection cells because the wavelength of the most unstable mode increases at the increase of the Biot number. Consequently, the knowledge of the Biot number is essential to determine the critical values of the problem.

Referring to data coming from C-SWNTs synthesis experiments, we have estimated the value of the solutal Biot number to be between 1 and 7 in our case (see Appendix C). However, since the liquid layer is initially supersaturated in carbon, it is reasonable to expect that the onset of the instability is possible without an external supply of carbon ( $Bi_s = 0$ ). Thus, in our problem, we have computed the critical values for the following range of Biot numbers (see Table 4.1):

$$0 < Bi_s < 7.$$
 (4.53)

Now that the critical values of the problem are known, we verify if a solutal Bénard-Marangoni instability can be generated in the conditions of synthesis of C-SWNTs. We only need to estimate the solutal Marangoni number characterizing our system,

Bis	$(l_c, Ma^c_s)$
0	(1.0, 48.0)
1	(1.7, 96.3)
3	(2.1, 163.9)
5	(2.3, 227.7)
7	(2.4,290.2)

Table 4.1: The critical Marangoni number  $Ma_s^c$  and the critical wavenumber  $l_c$  in function of the solutal Biot number  $Bi_s$ , in a planar geometry. These values have been found by determining the minimum of each of the neutral curves.

using the compilation of experimental data done in Section 3.3:

$$60 < Ma_s = \frac{\gamma_c d\Delta c}{\mu D_L} < 400. \tag{4.54}$$

From Table 4.1, we conclude that whatever the value of the Biot number, the Marangoni number characterizing the system can be higher than the critical Marangoni number:

$$48.0 < Ma_s^c < 290.2 \Rightarrow Ma_s > Ma_s^c. \tag{4.55}$$

This means that the onset of a solutal Bénard-Marangoni instability is possible in the conditions of synthesis of C-SWNTs. Moreover, the fact that the Marangoni number is higher than the minimal critical Marangoni number (calculated when  $Bi_s = 0$ ) indicates that the quantity of carbon initially contained in the liquid layer is sufficient to generate the instability, if a correct carbon concentration gradient is established.

Now, in order to justify our hypothesis of the dominancy of the solutal effect on the other possible hydrodynamic effects, we calculate the thermal and solutal Rayleigh numbers and the thermocapillary Marangoni number, using the calculation done in Section 3.3:

$$Ra_T = \frac{\alpha_T \rho g d^3 \Delta T}{\mu \kappa} \approx 10^{-21} <<\sim 10^3$$
(4.56)

$$Ra_s = \frac{\alpha_c g d^3 \Delta c}{\mu D_L} \approx 10^{-11} << \sim 10^3$$
(4.57)

$$Ma_T = \frac{\gamma_T d\Delta T}{\mu\kappa} \approx 10^{-3} \ll 10^{2}.$$
(4.58)

Since these numbers are much lower than their respective critical values<sup>10</sup>, the solutal effect dominates on the other hydrodynamic effects in the conditions of synthesis of C-SWNTs. We note that the temperature difference  $\Delta T$  appearing in both thermal numbers has been estimated to  $\Delta T = 0.1K$ , as appears in the literature on carbon fibers [96]. This comparison between the growth of carbon fibers and of carbon nanotubes is often made in literature. On the other hand, the temperature difference should have been of a thousand degrees in order to generate the thermocapillary Bénard-Marangoni instability, which is clearly impossible at the surface of a nanoparticle.

Hence, two important results have been obtained using the linear stability analysis. On the one hand, it has been shown that a solutal Bénard-Marangoni instability can be generated in the conditions of synthesis of C-SWNTs. On the other hand, our initial hypothesis of the dominancy of the solutal effect on the other hydrodynamic effects has been justified. We now look at a weakly nonlinear stability analysis of the fluid flow in order to determine if the formation of hexagonal convection cells is favoured under these conditions.

#### 4.3 Nonlinear stability analysis

We have just seen that above the critical value of the Marangoni number, not all perturbations are damped out but some of them are characterized by an exponential growth rate. Although some selection criteria exists, in the frame of the linear theory it is rather impossible to determine which mode possesses the maximal growth rate in practical flows without considering the interactions between the unstable modes. For instance, normal modes having different orientations in the horizontal plane can

 $<sup>^{10}</sup>$ We have not been able to find the exact critical values for the all the Biot numbers in the insulating case. Instead, we have used the order of magnitude of the values calculated in Table 3.1.

be associated with the same wavenumber (because all horizontal directions are indistinguishable); from the strict point of view of linear theory, these modes are all equivalent and possess the same growth rate. This "orientational degeneracy" is also obvious from the fact that every superposition of plane-wave solutions of the linear problem is itself a solution; it shows the absence of competition between the different modes. There is also a second degeneracy corresponding to the infinite variety of patterns of convection associated with each direction. Hence, linear stability theory cannot predict the shape of the pattern of convection arising from the instability [88]. Although the orientational degeneracy cannot be removed since it is an intrinsic property of the system, the pattern degeneracy can be resolved by considering the nonlinear problem [86].

The nonlinear thermal Bénard-Marangoni problem in a planar geometry has received wide attention in the past [97, 98, 99, 100]. To the contrary, the nonlinear solutal problem, to our knowledge, has been studied only by Bragard *et al.* [75]. In this section, we use the results of the latter work to determine which types of convection cells can form in a planar liquid layer. In particular, we want to determine if hexagonal convection cells can be stable under the conditions of synthesis of C-SWNTs.

A nonlinear stability analysis is a perturbation technique based on the expansion of the dependent variables of the problem. In the solutal problem, this expansion takes the following form [81]:

$$w = \epsilon (w^{(1)} + \epsilon w^{(2)} + \epsilon^2 w^{(3)} + \dots)$$
(4.59)

$$c = \epsilon (c^{(1)} + \epsilon c^{(2)} + \epsilon^2 c^{(3)} + \dots)$$
(4.60)

$$Ma_s = Ma_s^{(0)} + \epsilon (Ma_s^{(1)} + \epsilon w^{(2)} + \epsilon^2 w^{(3)} + \dots),$$
(4.61)

where the parameter  $\epsilon$ , characterizing the flow amplitude and the degree of supercriticality, is given by:

$$\epsilon = \frac{Ma_s - Ma_s^c}{Ma_s^c}.\tag{4.62}$$

We first notice that the substitution of these expansions in the governing equations of the problem recovers the linear problem at  $\mathcal{O}(\epsilon)$ . The linear problem allows us to determine the critical Marangoni number  $Ma_s^{(0)} = Ma_s^c$ . In a weakly nonlinear stability analysis, all the terms up to the second-order are considered. Without entering in the technical details, the substitution of the expansions in the governing equations leads to a specific condition on  $Ma_s^{(1)}$  at order  $\mathcal{O}(\epsilon^2)$ . This condition is different for each pattern of convection, which consequently allows one to resolve the pattern degeneracy at a certain extent. It has been shown that in the weakly nonlinear domain, the patterns in the form of rolls and hexagons exist [81]. The final step of the analysis is to evaluate the stability of each of these patterns of convection to arbitrary perturbations. The results of the stability analysis of the modes are presented in Table 4.2.

ε	Stable configurations	
$\epsilon < \epsilon_c$	Conductive state	
$\epsilon_c < \epsilon < 0$	Conductive state, hexagons	
$0 < \epsilon < \epsilon_1$	Hexagons	
$\epsilon_1 < \epsilon < \epsilon_2$	Hexagons, rolls	
$\epsilon > \epsilon_2$	Rolls, hybrid cells	

Table 4.2: Stable configurations according to the  $\epsilon$  values. We note that the hexagons are *l*-hexagons, i.e hexagons where the fluid rises at the center of the cell and descends along the edges [75].

Since the Marangoni number characterizing our system is relatively close to the critical Marangoni number, we can use the latter technique to determine which stable configurations are favoured in the conditions of synthesis of C-SWNTs. Precisely, we need to evaluate the value of  $\epsilon_c$ ,  $\epsilon_1$ ,  $\epsilon_2$  and  $\epsilon$  in order to find out in which range is located the value of  $\epsilon$ . The value of the coefficient  $\epsilon_c$  can be estimated from Fig. 4.3, obtained by Bragard *et al.* [75]: its value tends to 0 when  $N_A$  tends to zero, whatever the value of the Biot number. The value of  $\epsilon_1$  and  $\epsilon_2$ , in the cases when  $Bi_s = 0, 3, 5, 7$ , can be estimated by linearly extrapolating the curves presented in

Fig. 4.4. The results are summarized in Table 4.3. Finally, using the value of the Marangoni number calculated in the last section, we calculate the value of the parameter  $\epsilon$  to be in the following range:



 $0.3 < \epsilon < 7.3. \tag{4.63}$ 

Figure 4.3: Coefficient  $\epsilon_c$  versus the adsorption number  $N_A$  in the insulating case. The Biot values are  $Bi_s = 1$  (higher curve) and  $Bi_s = 2$  (lower curve) [75].



Figure 4.4: Coefficients  $\epsilon_1$  and  $\epsilon_2$  versus the adsorption number  $N_A$  in the insulating case. The Biot values are  $Bi_s = 1$  (continued line) and  $Bi_s = 2$  (dashed line) [75].

From Table 4.2 and Table 4.3, we can exclude hybrid cells as a stable configuration in a planar layer at the conditions of synthesis of C-SWNTs because the value of  $\epsilon_2$ 

Bis	$\epsilon_1$	$\epsilon_2$
0	2	6
1	4	14
3	2382	7379
5	$\sim 10^{17}$	$\sim 10^{18}$
7	$\rightarrow \infty$	$\rightarrow \infty$

Table 4.3: Values of the coefficients  $\epsilon_1$  and  $\epsilon_2$  when  $N_A = 0$ .

is larger than the value of  $\epsilon$  for most of the Biot numbers. It is also clear that the hexagonal configuration dominates over the rolls configuration because the value of  $\epsilon$  is lower than the value of  $\epsilon_1$  for most of the Biot numbers. The latter result is fundamental since, in the frame of the BMI model, it is the formation of patterns of hexagonal convection cells which explains the nucleation of C-SWNTs into a bundle structure as we shall present in Chapter 6.

We can finally evaluate the size of these hexagonal convection cells by determining the wavenumber of the pattern. Indeed, there exists a relation between the nondimensional wavenumber l of the pattern (which is the wavenumber of the most unstable mode) and the side length of the hexagons  $L_H$  [81] (Fig. 4.5):

$$L_H = \frac{4\pi d}{3l}.\tag{4.64}$$

In weakly nonlinear stability analyses, the wavenumber of the most unstable mode is the critical wanenumber  $l_c$ , determined by the linear stability analysis [101]. Thus, using the values of the critical wavenumbers calculated in the last section, we estimate the side length of the hexagons to be comprised in the following range:

$$5.2nm < L_H < 12.6nm,$$
 (4.65)

depending on the value of the Biot number (Table 4.4).

The main results presented in this chapter can be summarized as follows:



Figure 4.5: The side length  $L_H$  of an hexagon in a pattern of hexagonal convection cells.

$Bi_s$	$l_c$	$L_H$
0	1.0	12.6nm
1	1.7	7.4nm
3	2.1	6.0nm
5	2.3	$5.5 \mathrm{nm}$
7	2.4	$5.2 \mathrm{nm}$

Table 4.4: The dependence of the side length of the hexagons on the Biot number. These values have been calculated for an average thickness of the liquid layer equal to d=3nm.

1. The solutal Bénard-Marangoni instability can be generated in a planar liquid layer, in the conditions of synthesis of C-SWNTs;

2. The solutal Bénard-Marangoni effect dominates over the other possible hydrodynamic effects in these conditions;

**3.** The l-hexagonal configuration is favoured in a planar liquid layer, in the conditions of synthesis of C-SWNTs;

4. The side length of the hexagonal convection cells is comprised between 5.2nm and 12.6nm.

The positive results obtained with the simple planar model clearly justify the extension of the analyses to a spherical geometry.

### Chapter 5

# The BMI model in a spherical geometry

The aim of this chapter is to extend the results obtained in the last chapter to a spherical geometry. Precisely, we want to determine if the solutal Bénard-Marangoni instability is still generated in a spherical geometry, under the usual synthesis conditions for C-SWNTs, and if configurations in the form of hexagonal convection cells are still favoured under these conditions. As mentioned earlier, these hexagonal convection cells are crucial to our explanation of the nucleation process.

In contrast with the planar case, much less work has been published on the onset of the Bénard-Marangoni convection in a spherical geometry. To the best of our knowledge, there is no linear stability analysis of the solutal instability in the literature; only linear stability analyses of the thermocapillary instability have been reported up to now [73, 102, 103, 104, 105]. Furthermore, no nonlinear stability analyses have been published yet for this geometry, either for the thermal case or the solutal case. However, other approaches like bifurcation analyses [106, 107, 108, 109] have been used. In order to solve the linear part of our problem, we invoke a rescaling argument and use a linear stability analysis of the thermocapillary instability to compute the neutral-stability curves corresponding to our problem. Regarding the nonlinear part of the problem, we use a bifurcation analysis to determine which patterns of convection appear in a spherical shell of fluid, at the conditions of synthesis of C-SWNTs.

In Section 5.1, we formulate the equations describing the flow of carbon in the liquid layer surrounding the metallic solid core, similar to those presented in Section 4.1 for the planar case. In Section 5.2, we proceed to a linear stability analysis of the fluid flow and use the results published by Wilson [73] to compute the neutral-stability curves; this provides us with critical Marangoni numbers. In Section 5.3, we leverage the results of a recent bifurcation analysis developed by Matthews [109, 110].

#### 5.1 Formulation of the equations

We consider a spherical layer of fluid, composed of a carbon-iron solution supersaturated in carbon, with an outer free surface of radius  $r_2$  and concentration  $c_{LG}$  and an inner solid sphere of radius  $r_1 < r_2$ . The concentration of carbon at the solid surface is  $c_{SL}$  (Fig. 5.1). For convenience, we define  $d = r_2 - r_1$  to be the thickness of the layer of fluid. As in the planar case, the free surface is considered to be undeformable and gravity effects are neglected. We assume the layer of fluid to be initially in an unperturbed state. The fluid is at rest and the initial concentration profile  $\bar{c}$  is given by [105]:

$$\overline{c}(r) = c_{SL} + \frac{r_1 r_2}{r_1 - r_2} (\frac{1}{r} - \frac{1}{r_1})(c_{LG} - c_{SL}), \qquad (5.1)$$

where r is the radial distance and where  $c_{SL}$  and  $c_{LG}$  are the carbon concentration at the solid-liquid interface and at the liquid-gas interface, respectively. The relation between the surface tension and the concentration is still given by:

$$\sigma = \sigma_0 + \gamma_c (\tilde{c} - c_0). \tag{5.2}$$



Figure 5.1: Geometry of the spherical model.

The equations describing the motion of the liquid layer can be summarized as follows:

$$\nabla \cdot \vec{\hat{u}} = 0,$$
  

$$\rho \left( \frac{\partial \vec{\hat{u}}}{\partial t} + \vec{\hat{u}} \cdot \nabla \vec{\hat{u}} \right) = -\nabla \tilde{p} + \mu \nabla^2 \vec{\hat{u}},$$
  

$$\frac{\partial \tilde{c}}{\partial t} + \vec{\hat{u}} \cdot \nabla \tilde{c} = D_L \nabla^2 \tilde{c}.$$
(5.3)

The boundary conditions at  $r = r_1$  are the following:

$$c_{SL} = 25\% at.,$$
  

$$\frac{\partial \tilde{c}}{\partial r} = 0,$$
  

$$\tilde{\vec{u}} = 0,$$
  
(5.4)

while the boundary conditions at  $r = r_2$  are given by:

$$c_{LG} = 45\% at.,$$
  

$$\frac{\partial \tilde{c}}{\partial r} + Hk_g \tilde{c} = 0,$$
  

$$u_r = 0,$$
  
(5.5)

where  $(r, \theta, \phi)$  are the three spherical coordinates and  $\vec{\tilde{u}} = (u_r, u_\theta, u_\phi)$  is the velocity of the fluid flow. We obtain the condition for the tangential stress at the liquid-gas interface by transforming the condition (4.14) into spherical coordinates:

$$\mu r \frac{\partial}{\partial r} \left( \frac{u_{\theta}}{r} \right) = \frac{1}{r} \frac{\partial \sigma}{\partial \theta}, \qquad \mu r \frac{\partial}{\partial r} \left( \frac{u_{\phi}}{r} \right) = \frac{1}{r \sin \theta} \frac{\partial \sigma}{\partial \phi}, \quad \text{at } r = r_2.$$
(5.6)

We notice that the Laplace operator now takes the following form:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{1}{r^2} L^2, \qquad (5.7)$$

where the operator  $L^2$  is the angular momentum operator defined by:

$$L^{2} = -\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^{2}\theta}\frac{\partial^{2}}{\partial\phi^{2}}\right].$$
(5.8)

#### 5.2 Linear stability analysis

As in the planar case, in order to obtain the equations for the perturbations, we decompose the motion into an initial state of no motion plus perturbation. Once linearized, the equations take the following form:

$$\nabla \cdot \vec{u} = 0, \tag{5.9}$$

$$\rho \frac{\partial \vec{u}}{\partial t} = -\nabla p + \mu \nabla^2 \vec{u}, \qquad (5.10)$$

$$\frac{\partial c}{\partial t} + \vec{u} \cdot \nabla \vec{c} = D_L \nabla^2 c. \tag{5.11}$$

We then proceed to the nondimensionalization of the equations via the following scaling:

$$t = \frac{d^2}{D_L} t^*, \tag{5.12}$$

$$r = r^* d, \tag{5.13}$$

$$(u_r, u_\theta, u_\phi) = \left(\frac{D_L}{d} u_r^*, \frac{D_L}{d} u_\theta^*, \frac{D_L}{d} u_\theta^*\right), \qquad (5.14)$$

$$c = (c_{LG} - c_{SL})c^*,$$
 (5.15)

$$p = \frac{\mu D_L}{d^2} p^*, \tag{5.16}$$

where the superscript \* indicates the dimensionless variables. For simplicity, we drop the superscript \*. The system of dimensionless equations becomes:

$$\nabla \cdot \vec{u} = 0, \tag{5.17}$$

$$\left(\nabla^2 - Sc^{-1}\frac{\partial}{\partial t}\right)\vec{u} = Sc^{-1}\nabla p, \qquad (5.18)$$

$$\left(\nabla^2 - \frac{\partial}{\partial t}\right)c = \frac{r_1 r_2 u_r}{r^2}.$$
(5.19)

Note that the last equation has been derived by using the nondimensionalized form of (5.1) in the diffusion equation (5.11):

$$\overline{c}(r) = -\frac{r_1 r_2}{r} + r_2 c_{LG} - r_1 c_{SL}.$$
(5.20)

As in the planar case, we use the continuity equation in the divergence of (5.18) to eliminate the pressure term in (5.18). This leads to the following form:

$$\nabla^2 \left[ \nabla^2 - Sc^{-1} \frac{\partial}{\partial t} \right] (ru_r) = 0.$$
(5.21)

In order to determine the nondimensionalized form of the tangential stress condition (5.6), we rescale the result obtained in the linear stability analysis of the thermocapillary instability, presented by Wilson [73]:

$$\left[\frac{\partial^2}{\partial r^2} - \frac{(2-L^2)}{r^2}\right](ru_r) - \frac{Ma_s}{r}L^2c = 0.$$
 (5.22)

This is possible since we neglect the contribution of adsorption in our problem,  $N_A = 0$ (see Appendix A).

We now introduce the normal modes in order to formulate the eigenvalue problem, from which we will derive the neutral-stability curves of the system:

$$ru_r = W(r)Y_l^m(\theta,\phi)e^{\lambda t},\tag{5.23}$$

$$c = \Theta(r) Y_l^m(\theta, \phi) e^{\lambda t}, \tag{5.24}$$

where  $Y_l^m(\theta, \phi)$  are the spherical harmonics, which satisfy the equation:

$$L^{2}Y_{l}^{m}(\theta,\phi) = l(l+1)Y_{l}^{m}(\theta,\phi), \qquad (5.25)$$

where l, m = 1, 2, 3, ... and  $\lambda$  is a complex eigenvalue. Note that in the spherical problem, only integer values of l correspond to physically realisable situations.

With this new dependence, the operators present in (5.17 - 5.19) transform as follows:

$$\frac{\partial}{\partial t}(ru_r) = \lambda W Y_l^m e^{\lambda t} = \lambda (ru_r)$$

$$\vdots \frac{\partial}{\partial t} \to \lambda$$
(5.26)

and,

$$\begin{aligned} \nabla^{2}(ru_{r}) &= \frac{1}{r^{2}} \frac{\partial}{\partial r} (r^{2} \frac{\partial}{\partial r} (ru_{r})) - \frac{1}{r^{2}} L^{2}(ru_{r}) \\ &= \frac{1}{r^{2}} \frac{\partial}{\partial r} (r^{2} \frac{dW}{dr} Y_{l}^{m} e^{\lambda t}) - \frac{1}{r^{2}} W Y_{l}^{m} e^{\lambda t} l(l+1) \\ &= \frac{1}{r^{2}} Y_{l}^{m} e^{\lambda t} (2r \frac{dW}{dr} + r^{2} \frac{d^{2}W}{dr^{2}}) - \frac{1}{r^{2}} W Y_{l}^{m} e^{\lambda t} l(l+1) \\ &= (\frac{2}{r} \frac{d}{dr} + \frac{d^{2}}{dr^{2}}) W Y_{l}^{m} e^{\lambda t} - \frac{1}{r^{2}} l(l+1) W Y_{l}^{m} e^{\lambda t} \\ &= (\frac{d^{2}}{dr^{2}} + \frac{2}{r} \frac{d}{dr} - \frac{1}{r^{2}} l(l+1)) (ru_{r}) \\ &: \nabla^{2} \to D^{2} + \frac{2}{r} D - \frac{1}{r^{2}} l(l+1), \end{aligned}$$
(5.27)

where  $D = \frac{d}{dr}$ .

The problem can now be rewritten as follows:

$$\begin{pmatrix} D^2 + \frac{2}{r}D - \frac{l(l+1)}{r^2} \end{pmatrix} \begin{pmatrix} D^2 + \frac{2}{r}D - \frac{l(l+1)}{r^2} - Sc^{-1}\lambda \end{pmatrix} W = 0, \\ \begin{pmatrix} D^2 + \frac{2}{r}D - \frac{l(l+1)}{r^2} - \lambda \end{pmatrix} \Theta - \frac{r_1 r_2}{r^3} W = 0, \\ \Theta(r_1) = 1.25; D\Theta(r_1) = 0; W(r_1) = 0, \\ \Theta(r_2) = 2.25; W(r_2) = 0, \\ \Theta(r_2) + Bi_s\Theta(r_2) = 0, \\ \begin{pmatrix} D^2 - \frac{(2-l(l+1))}{r^2} \end{pmatrix} W(r_2) - \frac{Ma_s l(l+1)}{r}\Theta(r_2) = 0. \end{cases}$$
(5.28)

In a spherical problem, in addition to the solutal Biot number  $Bi_s$ , the neutralstability curves are seen to depend on another important parameter, in the spherical problem: the nondimensional radius  $R_1(=r_1/d)$  of the metallic solid core. In the conditions of synthesis, we estimate that the value of this parameter is in the following range (see Appendix B):

$$2 < R_1 < 7.$$
 (5.29)

We now invoke the rescaling argument and use the general solutions obtained by Wilson [73] to compute the neutral-stability curves for the problem (5.28), as functions of  $R_1$  and  $Bi_s$  (Fig. 5.2). The critical values of the problem have been calculated by finding the minimum of these neutral curves (Table 5.1).





$R_1$	Bis	$(l_c, Ma_s^c)$	$R_1$	Bis	$(l_c, Ma_s^c)$
2	0	(1, 36.5)	5	- 0	(1,41.9)
2	1	(4,85.7)	5	1	(9,90.9)
2	3	(5,157.4)	5	3	(11, 160.1)
2	5	(5,225.4)	5	5	(12, 225.6)
2	7	(6, 296.1)	5	7	(13,290.6)
3	0	(1, 39.1)	6	0	(1, 42.7)
3	1	(6,88.4)	6	1	(11,91.6)
3	3	(7,158.5)	6	3	(13,160.6)
3	5	(7,225.8)	6	5	(14, 225.9)
3	7	(8,291.3)	6	7	(15,290.1)
4	0	(1, 40.7)	7	0	(1, 43.3)
4	1	(7, 90.0)	7	1	(13, 92.3)
4	3	(9,159.4)	7	3	(16,161.2)
4	5	(10, 225.6)	7	5	(17,226.2)
4	7	(11, 292.4)	7	7	(18,290.6)

Table 5.1: The critical Marangoni number  $Ma_s^c$  and the critical wavenumber  $l_c$  as function of the radius  $R_1$  of the metallic solid core and of the solutal Biot number  $Bi_s$ , in a spherical geometry.

To verify that a solutal Bénard-Marangoni instability can be generated under the conditions of synthesis of C-SWNTs, we compare the Marangoni number  $Ma_s$ characterizing our system ( $60 < Ma_s < 400$ ) with the range of critical values shown in Table 5.1. Since the solutal Marangoni number can be higher than the critical Marangoni number, the onset of the solutal Bénard-Marangoni instability is still possible in a spherical geometry.

The order of magnitude of the critical Marangoni numbers (the solutal and thermocapillary critical numbers are equal since  $N_A = 0$  [75, 111]) is the same as that in the planar case. Moreover, recent numerical simulations [112] have shown that the critical Rayleigh numbers (solutal and thermal) are nearly the same in planar and spherical geometries. We thus conclude that the solutal effect is still dominant in a spherical geometry, in conditions where we observe the synthesis of C-SWNTs.

Now that we have derived these two important results, we use a bifurcation analysis to determine if the formation of hexagonal convection cells is still possible in a spherical geometry, and if it is favoured in conditions where we obtain synthesis of C-SWNTs.

#### 5.3 Bifurcation analysis

To the best of our knowledge, no nonlinear stability analysis of the Bénard-Marangoni instability (either thermocapillary or solutal) has been developed in a spherical geometry. However, there exists another approach to determine the formation of convection patterns in a spherical liquid layer: the *bifurcation analysis*. In 1952, Turing [113] proposed the use of this technique in order to explain how specific early spherical embryos developed into a non-spherical structure (a problem often referred as *morphogenesis*<sup>11</sup>). Later, this technique has been used to study the development of certain solid tumours evolving into a highly asymmetric form [114, 115, 116]. Its use in studying the formation of convection patterns only became popular in the mid 1960s, when the hypothesis of continental drift started to be investigated [106, 117, 118]. We now explain how this particular analysis can be used to solve the problem of the formation of convection patterns.

In the problem of convection in a spherical layer, the fundamental assumption made by the bifurcation analysis is the following: the transition from the diffusive state to the convective state of motion is equivalent to the bifurcation from a spher-

<sup>&</sup>lt;sup>11</sup>The term *morphogenesis* refers to the process by which living things develop organized structures. A morphogenic system is capable of maintaining its continuity and integrity by changing essential aspects of its structure or organization.

ically symmetric state. Indeed, at the onset of convection, the initial spherical symmetry is lost due to the formation of specific patterns of convection.

From a linear stability point of view, the symmetric state becomes unstable and a linear stability analysis selects a particular value of the wavenumber l, for which there exists 2l + 1 spherical harmonics. However, all these harmonics are equally unstable, which implies a competition between the several different patterns of convection.

The purpose of the bifurcation analysis is to resolve this degeneracy by including nonlinear interaction terms in the equations governing the bifurcation from the spherically symmetric state. Depending on whether l is odd or even, the methods for solving the bifurcation equations are quite different, since they involve different types of bifurcation. For odd values of l, there are no quadratic terms in the bifurcation equations, and the system undergoes a *pitchfork* bifurcation. For even values of l, quadratic interaction terms are present in the equations, and the system undergoes a *transcritical* bifurcation<sup>12</sup> [109, 110].

In this section, we focus on an approach to the problem of transcritical bifurcation from spherical symmetry which uses group theory, known to describe the phenomenon of convection in a spherical liquid layer [109, 106]. It was first proposed by Sattinger [119] in 1978, and subsequently elaborated in the recent works of Matthews and Chossat [109, 108]. This approach, referred as the *bifurcation with* O(3) symmetry, is based on the fact that the quadratic terms present in the transcritical bifurcation equations are uniquely determined by the symmetry of the problem and are not dependent on the physical context. This is a powerful result which allows one to determine, without any particular physical consideration, which patterns can be formed on a sphere. It

 $^{12}$ A bifurcation is a change in the character and stability of possible steady states of a nonlinear system, which occurs when a particular parameter passes through a critical point. A *pitchfork* bifurcation consists in the division, at the critical point, of a stable branch into two stable branches and one unstable branch. A *transcritical* bifurcation occurs when the division is done between two regions, one stable and one unstable [101].

explains, for instance, why similar patterns appear in completely different physical contexts (as an example, hexagonal cells appear in stars and also on certain kind of embryos).

For every integer and even value of the wavenumber l selected by the linear stability analysis, there exist many different solutions or patterns. The bifurcation analysis shows that the different symmetries exhibited by these patterns are directly related to the subgroups of the group O(3) (Table 5.2). The existence and stability of these symmetries on a sphere have been investigated by Matthews [109, 110] for wavenumbers below l = 18. In most cases, he has used a variational method to determine which symmetry is preferred among the possible symmetries. In cases where it was impossible to resolve the degeneracy theoretically, he has done numerical simulations using a Swift-Hohenberg model [120].

Subgroups of $O(3)$	Symmetry
O(2)	Circle
Ι	Icosahedron
0	Cube
T	Tetrahedron
$D_n, n > 2$	Regular <i>n</i> -gon
$D_2$	Rectangle

Table 5.2: Subgroups of the group O(3) [109].

We now determine if the hexagonal configuration, which has a  $D_6$  symmetry, can be favoured in the conditions of synthesis of C-SWNTs. As we did in the planar model, we assume that the wavenumber of the most unstable mode developing on the catalyst nanoparticle (i.e the wavenumber of the pattern of convection) is equal to the critical wavenumber  $l_c$  of the instability. We recall that this is a reasonable assumption since the Marangoni number characterizing our system is near the critical Marangoni number. This implies that the wavenumber l of the patterns that might appear on the catalyst nanoparticle, should be within the following range (see Table 5.1):

$$1 < l < 18.$$
 (5.30)

l	Preferred solution
2	O(2)
4	0
6	Ι
8	$D_6^*$
10	Ι
12	Ι
14	$D_6$
16	Т
18	$D_6$

Table 5.3: Preferred solutions for even wavenumbers from l = 2 to l = 18. The \* indicates that it has been determined using a numerical simulation [109].

In Table 5.3, we show the preferred solutions obtained by Matthews [109]. It appears from these results that the hexagonal configuration is favoured when the wavenumber of the most unstable mode is either equal to l = 8, 14 or 18. It follows that the configuration in the form of hexagonal convection cells can indeed be favoured under the conditions of synthesis of C-SWNTs.

The morphology corresponding to the case l = 8 consists in patches of 7 hexagons located at both poles and in a single strip of 6 hexagons located 40° above the equator (which gives a total of 20 hexagons on the sphere). In the case l = 14, the morphology of the sphere consists in patches of 7 hexagons located at both poles and in a pattern of 44 hexagons surrounding the equator (which gives a total of 58 hexagons on the sphere). Finally, in the case l = 18, the morphology consists in a pattern of 94



Figure 5.3: Possible hexagonal configurations on a sphere, where each blob represents an hexagon. The hexagons on the sphere are either all l-hexagons or all g-hexagons. Left: l = 8; Middle: l = 14; Right: l = 18. [109].

hexagons located around the equator [109]. All the hexagons present on a sphere (see Fig. 5.3) have the same sense of convection, i.e, that they are either all l-hexagons or g-hexagons [109, 110], depending on the physical context. We notice that when the wavenumber increases, the number of hexagons on the sphere increases<sup>13</sup> while the size of the hexagons decreases.

Using (4.64), we evaluate the side length  $L_H$  of these hexagons, in a liquid layer with a thickness d equal to 3nm, to be the following:

$$l = 8 \rightarrow L_H = 1.6 \text{nm}$$

$$l = 14 \rightarrow L_H = 0.9 \text{nm}$$

$$l = 18 \rightarrow L_H = 0.7 \text{nm}.$$
(5.32)

Based on our previous analysis, we are able to formulate the following important conclusions:

1. The solutal Bénard-Marangoni instability can be generated in a spherical geometry, under the conditions of synthesis of C-SWNTs;

<sup>13</sup>The number of hexagons  $N_H$  is related to the wavenumber l in the following way:

$$N_H = \frac{\sqrt{3l(l+1)}}{2\pi}.$$
(5.31)

Thanks to Pr. Matthews for this information.

2. The solutal Bénard-Marangoni effect dominates over the other possible hydrodynamic effects, under these conditions;

**3.** The hexagonal configuration is favoured in a spherical geometry when the wavenumber of the most unstable mode is either equal to 8, 14 or 18;

4. The side length of the hexagons, in cases l = 8, l = 14 and l = 18, is respectively equal to 1.6nm, 0.9nm and 0.7nm.

Although these results are similar to those obtained in the planar model, they differ on three important points:

• The formation of hexagonal convection cells is not necessarily a dominant process in the spherical model. Indeed, in contrast with the planar model, the most unstable mode developing on the sphere must have a particular wavenumber to permit the formation of hexagons. Although our analysis has shown that the conditions of synthesis of C-SWNTs allow these particular modes to exist, the use of numerical simulations would be necessary to determine in which proportion they are favoured;

• The arrangement of the hexagonal convection cells in the liquid layer differ in both models. In the spherical model, the formation of hexagons is only allowed in specific regions of the sphere while in the planar model, a pattern of hexagons occupies the entire layer;

• The size of the hexagons is all different in both models. Indeed, the curvature of the sphere constraints the hexagons to have a smaller size.

### Chapter 6

# Nucleation and growth of C-SWNTs

Up to now, we have been able to show that the conditions under which C-SWNTs are synthetized can lead to the onset of a solutal Bénard-Marangoni instability and to the subsequent formation of patterns of hexagonal convection cells within the liquid layer, supersaturated in carbon, surrounding a catalyst nanoparticle. We now postulate that the nucleation and the initial growth of a bundle of C-SWNTs are intimately related to the flow of carbon within a pattern of hexagonal convection cells. Precisely, we propose that one C-SWNT can nucleate and grow at the center of a hexagonal cell of the pattern, giving rise to a cooperative growth of the C-SWNTs into a bundle structure.

In Section 6.1, we describe the kinetic mechanism by which a single C-SWNT nucleates and initially grows at the center of a hexagonal convection cell and calculate the diameter of a single C-SWNT using results obtained in Chapter 5. We also briefly discuss the bundle structure. In Section 6.2, we show that this mechanism provides a correct explanation of the experimental observations mentioned in Chapter

3, namely the small diameter of individual C-SWNTs and the cooperative character of the growth of C-SWNTs into a bundle with a triangular lattice symmetry.

#### 6.1 Nucleation and growth of C-SWNTs

We recall from Chapter 5 that a hexagonal configuration of convection cells is favoured, in a spherical geometry, when the wavenumber of the most unstable mode is either equal to 8, 14 or 18. We now assume that the conditions of synthesis of C-SWNTs are such that these particular modes are selected. The hexagonal cells which form on the catalyst nanoparticle are cells where the liquid rises in the center of the hexagon and descends along the edges of the hexagon (see Fig. 6.1). For a specific wavenumber, all the convection cells within the patterns have the same size and convect at the same velocity.

We now focus on a single hexagonal convection cell and explain how a C-SWNT nucleates and initially grows at its center. We neglect the influence of the other cells in the pattern since there is no mass transport between the cells. The center of the top and bottom faces of the cell are stagnation points where the fluid velocity is zero. The stagnation point at the bottom of the cell, lying on the solid-liquid interface, is of crucial importance since we expect the C-SWNT to nucleate near this point. We envision the steps leading to the growth of a single C-SWNT in a hexagonal convection cell as follows:

Step 1. A fraction of the carbon atoms present in the cell are transported close to the stagnation point on the metallic solid core by the convective fluid flow (Fig. 6.1). The velocity of the carbon atoms decreases close to the stagnation point and consequently, their kinetic energy falls below the adhesion energy associated to the metallic solid core. In other words, there is an *influence zone* around the stagnation point, where the carbon atoms move slowly enough to be adsorbed on the solid surface. Because


Figure 6.1: First step of the growth: flow of carbon toward the stagnation point.

of the axial-symmetry of the flow near the center of the cell, this zone has a semispherical shape.

**Step 2.** Once the carbon enters the influence zone, it is adsorbed at the solid-liquid interface and, subsequently, crystallizes (or nucleates) under its minimum energy configuration: the closed hemispherical graphitic cap (Fig. 6.2). Indeed, total energy calculations have shown that, in presence of a metal surface, the nucleation of a closed hemispherical cap is strongly favoured compared to any other structure with dangling bonds [63]. Hence, the influence zone surrounding the stagnation point at the bottom of the cell, acts as a heterogeneous nucleation site (see Section 2.1.3).

**Step 3.** As the cap is formed, the topography of the bottom of the cell changes. The initial stagnation point is lost while a circular stagnation line at the base of the cap (precisely on the circumference) is created (Fig. 6.2). The shape of the influence zone changes, becoming a sector of a torus surrounding the stagnation line. The angle of contact between the cap and the solid surface is nearly vertical; this is guaranteed by the hemispherical shape of the cap observed in experiments [16]. Consequently, the carbon atoms can decelerate sufficiently in the influence zone in order to be incorporated between the cap and the solid surface. The strong binding between the cap and the metal surface prevents its closure at the bottom and then allows the progressive growth of the C-SWNT by the root, as described in the model





of Loiseau *et al.* (Fig. 6.3). Since at a certain point the growth can be influenced by factors other than the flow of carbon within the cell (such as the flow of carbon or metallic aggregates in the gas), our model can only describe the initial growth of the C-SWNT. We notice that, outside the influence zone, it is more favorable for carbon atoms to follow the convection flow than to bind laterally on the tube since the binding of carbon atoms to other carbon atoms only occurs at much higher temperatures than the synthesis temperatures [59].



Figure 6.3: Third step of the growth: initial growth of the C-SWNT.

We now estimate the diameter of an individual C-SWNT, using the results obtained in Chapter 5. According to our model, the diameter of a C-SWNT is roughly equal to the diameter of the influence zone; this is true whether we use the planar model or the spherical model. Assuming the latter quantity to be equal to one third of the distance between a vertex of the hexagon and its opposite vertex (Fig. 6.4), the diameter D of an individual C-SWNT, as a function of the side length  $L_H$  of the hexagon, is given by:

$$D = \frac{2L_H}{3}.\tag{6.1}$$

Using the side lengths calculated in Chapter 5, we thus estimate the diameter of an individual C-SWNT growing on a spherical catalyst nanoparticle to be between 0.5nm and 1.1nm. This is in excellent agreement with experimentally observed diameters ranging between 0.7nm and 3nm, with a peak located around 1nm [16]. We notice that the results obtained in the planar case give a diameter between 3.5nm and 8.4nm, which is greater than the diameters observed in experiments. This difference certainly comes from the neglecting of the curvature of the catalyst nanoparticle in the calculations.



Figure 6.4: The diameter D of the nanotube is assumed to be equal to one third of the distance between a vertex of the hexagon and its opposite vertex.

Since the same process potentially occurs in each cell of the pattern of convection, we now claim that the collection of hexagonal convection cells is responsible for the nucleation and the initial growth of a bundle of C-SWNTs (Fig. 6.5). In the case where the nucleation process occurs at one of the poles of the catalyst nanoparticle (l = 8, 14), the symmetry imposed on the bundle by the hexagonal pattern agrees with the triangular lattice symmetry exhibited by bundles in experiments. In the case



Figure 6.5: Final step of the growth: collective growth of the C-SWNTs into a bundle structure.

where the nucleation process occurs around the equator (l = 8, 14, 18), the symmetry imposed by the pattern of hexagons surrounding the equator is the one of a sea-urchin structure, where several C-SWNTs grow radially around the equator (see Fig. 2.3, Chapter 2). We also notice that the number of hexagons constituting the different patterns in the cases l = 8, 14, 18 (see the description of these configurations in Section 5.3) is in the same range than the number of C-SWNTs per bundle observed in experiments<sup>14</sup>. Our model cannot explain why a specific region is chosen to grow a bundle since a variety of factors may influence this process. Consequently, it cannot predict the exact localization of the bundles on the catalyst nanoparticle. This is an important limit to the present model.

#### 6.2 The kinetic mechanism

The purpose of the BMI model is to provide a kinetic growth mechanism which accounts for the experimental observations still unexplained by the existing models.

<sup>&</sup>lt;sup>14</sup>For a catalyst nanoparticle with a diameter between 10nm-20nm, the number of C-SWNTs per bundle varies between 5 and 50 C-SWNTs per bundle [15].

As discussed in Chapter 3, these experimental facts are the nanometric diameter of the individual C-SWNTs and the collective and structural character of the nucleation and growth of C-SWNTs into a bundle structure. Explaining these aspects of the growth is a necessary and complementary step in the understanding of the growth mechanism of C-SWNTs, which lies in the line of the models that have been proposed up to now.

We recall from our discussion of Chapter 3 that an additional kinetic mechanism had been invoked to explain why the diameter of the C-SWNT is nearly 1nm in practice, when the theoretical energy calculations predict that it should be around 10nm. The present model provides this kinetic mechanism: it is the size of the convection cell which constrains the diameter of the C-SWNT to a nanometric size. The calculations of the diameter done in Section 6.1 confirm this assertion, the predicted diameter being nearly equal to the diameter observed in experiments.

The hypothesis that a bundle of C-SWNTs results from the organization of carbon atoms within a pattern of hexagonal convection cells explains in a coherent manner the cooperative aspect of the growth and also the symmetry exhibited by the bundles at the onset of the growth. On the one hand, the fact that the convection flow in the cells is nearly the same explains why C-SWNTs grow simultaneously and collectively [16] into a bundle structure. On the other hand, the symmetry of the hexagonal pattern explains naturally why the triangular arrangement is imposed on the bundle right from its birth (see Fig. 3.1(b), Chapter 3). Although we have not verified the importance of the van der Waals forces in the formation of this particular arrangement, we can readily claim that our model has the advantage of explaining the *dynamical* process by which the triangular lattice symmetry is favoured in bundles of C-SWNTs at the initial stages of the growth.

In our model, the growth of a bundle of C-SWNTs is thus not only the result of the aggregation, via van der Waals forces, of many C-SWNTs growing independently but mostly the result of the "self-organization"<sup>15</sup> of several carbon atoms within a network of hexagonal convection cells generated by the non-equilibrium conditions present during the synthesis of C-SWNTs.

<sup>&</sup>lt;sup>15</sup>The concept of self-organization is progressively emerging in physics and biology. It is used to describe systems where the development of new and complex structures takes place in and through the system itself and where the effect of environment is minimal.

#### Chapter 7

#### Conclusions

#### 7.1 Overview and Discussion

The growth mechanism proposed in this thesis complements and extends the models that have been proposed up to now to explain the nucleation and growth of bundles of C-SWNTs under gas-phase synthesis conditions [16, 40, 41, 45, 50, 51]. For instance, our model agrees with the model of Saito [50] on the fact that the origin of the nucleation process lies in a segregation process and with the model of Gorbunov *et al.* [40] on the fact that the catalyst is in the form of a nanoparticle. It also supports the fundamental ideas of the model of Loiseau *et al.* [15, 16, 17], such as the root-growth mechanism and the importance of surface instabilities in explaining the nucleation mechanism. In that sense, our model complements these previous models. On the other hand, our model provides insights into initial aspects of the growth which were unexplained by these models, such as the nucleation process, the diameter of the C-SWNTs and the collective organization of C-SWNTs into a bundle structure at the onset of the growth.

#### CHAPTER 7. CONCLUSIONS

In order to formulate our model, we first proceeded to a re-examination of the nature of the catalyst nanoparticle via a detailed analysis of the carbon-catalyst phase diagram. By investigating the steps leading to the formation of the catalyst, we described the formation of a thin liquid layer supersaturated in carbon, surrounding the metallic solid core on which grow C-SWNTs, a phenomenon which had not been considered by the previous models. We then postulated that the generation of a solutal Bénard-Marangoni instability within this liquid layer, and particularly the subsequent formation of patterns of hexagonal convection cells, was responsible for the nucleation and the initial growth of bundles of C-SWNTs.

The main contribution of this thesis has been to verify that the onset of a solutal Bénard-Marangoni instability was possible under the conditions of synthesis of C-SWNTs. The formulation of the model in a planar geometry has been motivated by the fact that most of the theoretical work on the Bénard-Marangoni convection has been done for this geometry. The extension of the model to a spherical geometry has been motivated to account for the shape of the catalyst nanoparticles seen in experiments. The first step of the verification has been to demonstrate, using linear stability analyses of the fluid flow [73, 75], that the generation of a solutal Bénard-Marangoni instability is possible under the conditions of synthesis of C-SWNTs, and that it dominates over the other fluid instabilities. The second step of the verification has been to determine, using specific nonlinear analyses, if the configuration in the form of hexagonal convection cells can appear in the conditions of synthesis. Regarding this point, our approach has been different depending on the geometry: in the planar case, we have used a weakly nonlinear stability analysis [75], while we have applied a recent bifurcation analysis [109, 110] to the spherical case. This led us to conclude that the generation of the solutal Bénard-Marangoni instability and the subsequent formation of hexagonal convection cells are indeed possible under the conditions of synthesis of C-SWNTs.

The second contribution of this thesis has been to describe the kinetic mechanism

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by which a bundle of C-SWNTs nucleates and initially grows on a catalyst nanoparticle and also to show that our model accounts for some important experimental observations. We have presented a kinetic mechanism which explains the nanometric diameter of C-SWNTs [63] and the collective character of the growth of C-SWNTs into a bundle with a triangular lattice symmetry [16, 17]. Precisely, we have seen that the size of the convection cells constrains the diameter of the C-SWNTs to a nanometric size while the convection process explains naturally the nucleation and the initial growth of the C-SWNTs into a bundle with a triangular lattice symmetry. This represents an important step in understanding the growth mechanism of bundles of C-SWNTs.

#### 7.2 Future work

A first obvious extension of this work is to take into account some of the effects neglected by our model, such as the rotation of the catalyst nanoparticle and the deformability of the liquid-gas interface. This is potentially feasable because these effects have already been studied in theoretical works on the Bénard-Marangoni convection [73, 104, 121]. A more challenging extension would be to perform a nonlinear stability analysis of the problem in a spherical geometry in order to elucidate how the localization of the bundles on the catalyst nanoparticle occurs. Finally, solving the problem for non-spherical catalyst nanoparticles could also be insightful to determine the influence of the shape of the catalyst nanoparticle on the onset of the solutal Bénard-Marangoni instability.

## Appendix A

## Rescaling

The rescaling of the thermocapillary problem into the solutal problem can be achieved by a simple change of variable:

$$T = \eta c, \tag{A.1}$$

where  $\eta$  is an arbitrary transformation constant. We replace this new expression for the temperature in the heat diffusion equation and take away the  $\eta$ :

$$\partial_t T + \vec{u} \cdot \nabla T = \kappa \nabla^2 T \tag{A.2}$$

$$\partial_t(\eta c) + \vec{u} \cdot \nabla(\eta c) = \kappa \nabla^2(\eta c) \tag{A.3}$$

$$\eta \partial_t c + \eta \vec{u} \cdot \nabla c = \eta \kappa \nabla^2 c, \tag{A.4}$$

where  $\kappa$  is thermal diffusivity. The last equation becomes the molecular diffusion equation (4.6):

$$\partial_t c + \vec{u} \cdot \nabla c = D_L \nabla^2 T, \tag{A.5}$$

if we make the following transformation:

$$\kappa = D_L. \tag{A.6}$$

Proceeding the same way with the expression relating the surface tension to the

temperature:

$$\sigma = \sigma_0 + \gamma_T (T - T_0) \tag{A.7}$$

$$\sigma = \sigma_0 + \gamma_T (\eta c - \eta c_0) \tag{A.8}$$

$$\sigma = \sigma_0 + \eta \gamma_T (c - c_0), \tag{A.9}$$

and comparing with the expression relating the surface tension to the concentration:

$$\sigma = \sigma_0 + \gamma_c (c - c_0), \tag{A.10}$$

we obtain:

$$\eta = \frac{\gamma_c}{\gamma_T}.\tag{A.11}$$

Hence, the following transformations:

$$T \to \eta c$$
 (A.12)

$$\gamma_T \to \frac{\gamma_c}{\eta}$$
 (A.13)

$$\kappa \to D_L,$$
 (A.14)

allow us to rescale the thermocapillary problem into the solutal problem. Using this transformation, we can thus derive a correct expression for the solutal Marangoni number from the expression of the thermocapillary Marangoni number:

$$Ma_T = \frac{\gamma_T d\Delta T}{\mu\kappa} \to Ma_s = \frac{(\frac{\gamma_c}{\eta})d\eta\Delta c}{\mu D_L} = \frac{\gamma_c d\Delta c}{\mu D_L}.$$
 (A.15)

In this work, we will take  $\eta = 1$  and consequently use the following transformations to perform the rescaling between the thermocapillary problem and the solutal problem:

$$T \to c$$
 (A.16)

$$\gamma_T \to \gamma_c \tag{A.17}$$

$$\kappa \to D_L$$
 (A.18)

$$Ma_T \to Ma_s.$$
 (A.19)

We notice that this rescaling is correct only for the specific case of no accumulation of matter at the interface  $(N_A = 0)$ .

## Appendix B

# An estimate of the thickness of the liquid layer



1) The initial diameter of the droplet is  $D_I = 15nm$ .

2) The initial density of atoms in the droplet,  $n_I$ , is calculated for an initial carbon concentration of  $\chi_I \in [25\% at., 30\% at.]$ .

3) The initial number of carbon atoms in the droplet is equal to:

$$\phi_I = n_I \chi_I \frac{4\pi}{3} (\frac{D_I}{2})^3. \tag{B.1}$$

4) The density of atoms in the solid core,  $n_{core}$ , is calculated for a carbon concentration of  $\chi_{core} = 9\% at$ . Since the iron core occupies the major part of the solid core, the carbide layer is not considered here.

5) The density of atoms in the liquid layer,  $n_{layer}$ , is calculated for a carbon concentration comprised between  $\chi_{layer} = 32\% at$ . and  $\chi_{layer} = 42\% at$ . Outside this range, the computation does not give realistic results.

6) The final number of carbon atoms in the catalyst nanoparticle is equal to:

$$\phi_F = n_{core} \chi_{core} \frac{4\pi r_1^3}{3} + n_{layer} \chi_{layer} \frac{4\pi}{3} (r_2^3 - r_1^3). \tag{B.2}$$

7) There is conservation of the number of carbon atoms during the formation of the liquid layer:

$$\phi_I = \phi_F. \tag{B.3}$$

8) The equation (B.3) is finally solved in Maple in order to find the value of the thickness of the liquid layer  $(d = r_2 - r_1)$  and of the nondimensional radius  $R_1$   $(R_1 = r_1/d)$ .

We obtain the following results:

$\chi_I$ (%at.)	$\chi_{layer}$ (%at.)	$d \;(\mathrm{nm})$	$R_1$
25	32	2.1	$\sim 4$
25	34	1.8	$\sim 3$
25	38	1.4	$\sim 4$
25	42	1.1	$\sim 7$
30	32	3.6	$\sim 2$
30	34	3.1	$\sim 2$
30	38	2.2	$\sim 3$
30	42	1.7	$\sim 4$

### Appendix C

#### An estimate of the Biot number

The solutal Biot number describes the ratio of the liquid-phase mass-transfer resistance to the gas-phase one. There are several different expressions of the Biot number in the literature. The most general one is given by [75, 111]:

$$Bi_s = \frac{Hk_g d}{D_L},\tag{C.1}$$

where H is the Henry's law constant,  $k_g$  the gas-phase mass transfer coefficient, d the thickness of the liquid layer and  $D_L$ , the carbon diffusivity. In order to approximate the value of the Biot number, we first estimate the value of  $Hk_g$  (units of m/s) by assuming that the number of carbon atoms absorbed in the liquid layer is equal to the number of carbon atoms which are released from the liquid layer during the growth process. To determine the latter quantity, we use the average growth velocity of a bundle of C-SWNTs, known from experiments to be around 1  $\mu m/s$  [27].

1) We assume the catalyst nanoparticle has a diameter of 15nm and is mainly composed of iron atoms. We calculate the density of iron atoms, n, in a single catalyst nanoparticle (NP):

$$n = 8.5 * 10^{22} \frac{atoms}{cm^3} \cdot \frac{4\pi (7.5nm)^3}{3} \approx 150000 \frac{atoms}{NP}.$$
 (C.2)



2) From [38], we know that the typical density of nanoparticles in experiments is equal to  $10^9 \frac{NPs}{cm^3}$ . Using the ratio of carbon/iron atoms in the mixture, known from experiments (98%at./2%at.)[38], we calculate the density of clusters of carbon ( $C_4$ ) for an arbitrary volume:

$$n_c = 10^9 \frac{NPs}{cm^3} \cdot n \cdot \frac{98}{2} \cdot \frac{1}{4} = 1.8 * 10^{15} \frac{clusters}{cm^3}.$$
 (C.3)

3) We calculate the mean free path of clusters  $\lambda$ , before they enter in collision with a catalyst nanoparticle:

$$\lambda = \frac{1}{n_c \sigma},\tag{C.4}$$

where  $\sigma$  is the cross-sectional area of a catalyst nanoparticle. It gives:

$$\lambda = 1 \cdot \frac{1}{1.8 * 10^{15} \frac{clusters}{cm^3}} \cdot \frac{1}{4\pi (7.5nm)^2} = 0.79\mu m.$$
(C.5)

4) In order to evaluate the term  $Hk_g$  ([m/s]), we use the following calculation:

 $Hk_g$  = growth velocity of a bundle \* number of C-SWNTs per bundle \* number of atoms per C-SWNT \* mean free path of a cluster,

which gives:

$$Hk_g = \frac{1\mu m}{s} \cdot (5 - 10) \cdot 10^6 \frac{atoms}{\mu m} \cdot \frac{1}{4} \cdot \lambda \in [1.0\frac{m}{s}, 2.0\frac{m}{s}].$$
(C.6)

5) Finally, we calculate the Biot number  $Bi_s$ :

$$Bi_s = Hk_g \cdot \frac{d}{10^{-9}\frac{m^2}{s}} \in [1.1, 7.2], \tag{C.7}$$

where we have used a thickness of the liquid layer d comprised between 1.1nm and 3.6nm. We approximate the range for the Biot number to the following one:

$$1 < Bi_s < 7.$$
 (C.8)

## Appendix D

# The tangential stress equation

We proceed to the nondimensionalization of the balance of the tangential stress at the liquid-gas interface:

$$\mu \partial_z u = \partial_x \sigma, \qquad \mu \partial_z v = \partial_y \sigma, \quad \text{at } z = d.$$
 (D.1)

Using the following scaling:

$$(x, y, z) \to (xd, yd, zd)$$
 (D.2)

$$(u, v, w) \rightarrow (\frac{D_L}{d}u, \frac{D_L}{d}v, \frac{D_L}{d}w)$$
 (D.3)

$$c \to \beta dc,$$
 (D.4)

and the equation governing the surface tension behavior with concentration:

$$\sigma = \sigma_0 + \gamma_c (\tilde{c} - c_0), \tag{D.5}$$

we first nondimensionalize the first equation:

$$\mu \frac{\partial u}{\partial z} = \frac{\partial \sigma}{\partial x} = \frac{\partial \sigma}{\partial c} \frac{\partial c}{\partial x}$$
(D.6)

$$\rightarrow \mu(\frac{D_L}{d})(\frac{1}{d})\frac{\partial u}{\partial z} = \gamma_c(\beta d)(\frac{1}{d})\frac{\partial c}{\partial x}$$
(D.7)

$$\rightarrow \frac{\partial c}{\partial x} = \frac{\mu D_L}{d^2 \beta \gamma_c} \frac{\partial u}{\partial z} = \frac{1}{M a_s} \frac{\partial u}{\partial z},$$
(D.8)

where  $Ma_s = \frac{\gamma_c d^2 \beta}{\mu D_L}$  is the nondimensional solutal Marangoni number. We obtain a similar result for the second equation:

$$\frac{\partial c}{\partial y} = \frac{1}{Ma_s} \frac{\partial v}{\partial z}.$$
 (D.9)

Derivating (D.8) and (D.9) with respect to x and y respectively, we obtain that

$$\nabla_{H}^{2}c = \frac{\partial^{2}c}{\partial x^{2}} + \frac{\partial^{2}c}{\partial y^{2}} = \frac{1}{Ma_{s}}\left(\frac{\partial^{2}u}{\partial z\partial x} + \frac{\partial^{2}v}{\partial z\partial y}\right).$$
 (D.10)

We now use the continuity equation  $\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0$  to obtain:

$$\frac{\partial^2 u}{\partial z \partial x} = \frac{\partial}{\partial z} \left( -\frac{\partial v}{\partial y} - \frac{\partial w}{\partial z} \right) = -\left( \frac{\partial^2 v}{\partial z \partial y} + \frac{\partial^2 w}{\partial z^2} \right)$$
(D.11)

$$\rightarrow \frac{\partial^2 w}{\partial z^2} = -\left(\frac{\partial^2 u}{\partial z \partial x} + \frac{\partial^2 v}{\partial z \partial y}\right),\tag{D.12}$$

$$\frac{\partial^2 v}{\partial z \partial y} = -\frac{\partial}{\partial z} \left( \frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} \right) = -\left( \frac{\partial^2 u}{\partial z \partial x} + \frac{\partial^2 w}{\partial z^2} \right) \tag{D.13}$$

$$\rightarrow \frac{\partial^2 w}{\partial z^2} = -(\frac{\partial^2 u}{\partial z \partial x} + \frac{\partial^2 v}{\partial z \partial y}). \tag{D.14}$$

Therefore, using this result in (D.10), we obtain that:

$$\nabla_{H}^{2}c = -\frac{1}{Ma_{s}} \left(\frac{\partial^{2}w}{\partial z^{2}}\right) \tag{D.15}$$

$$\rightarrow \frac{\partial^2 w}{\partial z^2} + M a_s \nabla_H^2 c = 0. \tag{D.16}$$

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