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A Mathematical model of SWNT growth

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Abstract

This study focuses on a mechanism to stabilize the growth modes of single-walled carbon nanotube (SWNT) in the catalytic chemical vapor deposition (CVD) method. On the basis of experimental and theoretical knowledge about SWNT growth, we constructed a phenomenological model of SWNT growth as a reaction-diffusion system. The reaction field was approximated as a one-dimensional ring, which enables to deal with the mode of tube growth by numerical calculations. Computer simulations showed that a reaction spot emerges with various dynamics, depending on the value of parameters. These dynamics are interpreted in terms of growth modes. For instance, the dynamics where a reaction spot rotates along the ring is regarded as a helical growth mode, which may be relevant to chiral structure of SWNT. Stability of these growth modes were discussed in connection with the heat supply and the growth rate, and the diameter of catalyst.

Keywords: SWNT, Growth, Model, One-dimensional ring,

1 Introduction

Since the discovery of nanotubes by Iijima (1991), it has been revealed that a nanotube has various interesting properties. For instance, Single-Walled Carbon Nanotubes (SWNTs) exhibit either metallic or semiconducting behavior depending on their structural characteristics such as helicity and diameter (Lieber 1998, Hu and Odum 1999). It is very important to clarify the SWNT growth mechanism for its industrial production with controlling its structural characteristics such as helicity or diameter, etc. Among many factors to be considered, the most fundamental is that the SWNT seems to grow stably with a high aspect ratio of more than a thousand. This study focuses on such a mechanism to stabilize the growth modes of SWNT in the catalytic chemical vapor deposition (CVD) method.

In line with experimental methods of NT production such as the arc discharge, the laser oven, and the CVD method, researchers have hypothesized the SWNT production process (Thess et al. 1996, Dai et al. 1996, Kiang and Goddard III 1996, Yudasaka et al. 1999, Kataura et al. 2000, Scott et al. 2001). These hypotheses commonly claim that a SWNT grows after the nucleation, i.e., the formation of the SWNT precursor, and metal catalysts are required for the growth. And the growth is considered mainly in its two processes that are an inflow of material carbons to a reaction field and the transformation of carbons to the wall, although each hypothesis supposes its own two processes. We believe that these two processes are connected to a certain extent, refering to following arguments. The hypothesis of SWNT growth in the CVD method (Dai et al. 1996) suggests that these two processes, which occur on a metal particle, may connect to stabilize the surface energy of the particle. Little (2003) claims that the NT growth is resulted from

the comlexly thermal cycle that connects the material carbon production with the carbon transformation on a metal particle. From these knowledges, we consider the steady growth process of SWNT in the CVD method to be " the auto-catalyze heat generation that induces both the material carbon inflow to the reaction field on a metal particle and the carbon transformation into the SWNT". Moreover, experiments in the CVD method (Murakami et al. 2003) recently revealed that a SWNT grows from a metal particle with the diameter similar to the particle. This strongly suggests that a reaction field for the steady growth is a ring-like line around the about middle of the metal particle, as shown in figure 1.

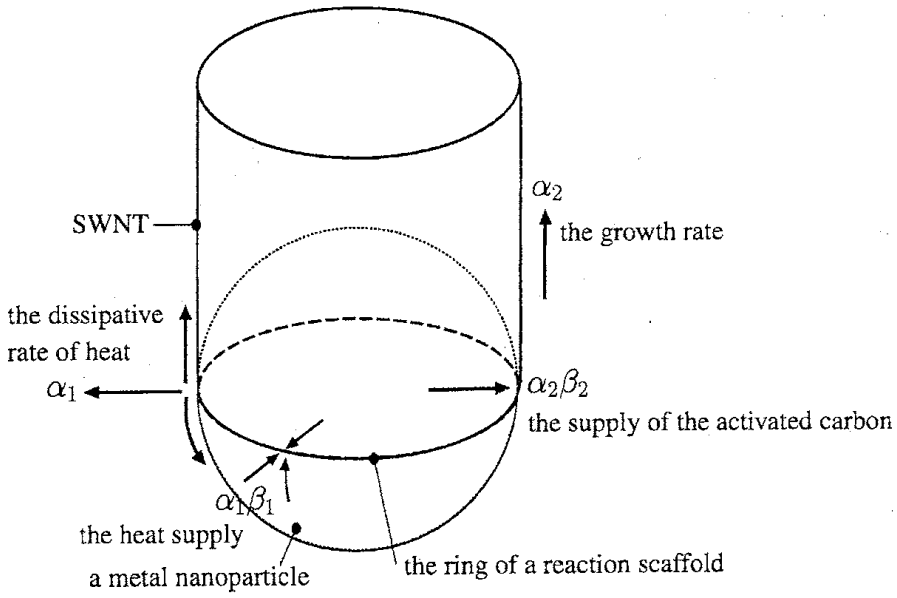

Figure 1: The model of a SWNT steady growth in the CVD method. The reaction field for the steady growth is a line around the about middle of the metal particle. α_1, β_1, α_2, and β_2 are parameters used in (4).

In this paper, we describe this growth system as a reaction-diffusion system, and in this modeling we approximate the reaction field as a one-dimensional ring

of a continuum. Although numerical models of NT growth have been proposed (Louchev 2002, Louchev et al. 2001, 2003), the growth has been modeled as the elongation of a one-dimensional stick. That is, the mode of the tube growth has not been theoretically dealed with. This study attains it by modeling a reaction field as a one-dimensional ring. We believe that such a modeling may also lead to the first step towards a theoretical solution of the formation process of SWNT lattice structures.

The reaction field model as a ring will be relevant to SWNT growth process hypothesized by some researchers, as mentioned as follows. In the scooter hypothesis (Thess et al. 1996) it is supposed that a piece composed of an metal atom or some ones rotates along the edge of SWNT tip to elongate its tube. In the polyyne ring nucleus growth hypothesis (Kiang and Goddard III 1996, Kiang 2000), it is supposed that the precursor of a SWNT is a carbon ring, and adding carbons along the carbon ring, the growth is initiated.

Our model could generate a reaction spot where material carbons are transformed into a SWNT, in a self-organized manner. Moreover, depending on the parameter, the reaction spot could appear with various dynamics, such as a traveling mode where a reaction spot rotates along the ring or a steady mode where a reaction spot is formed uniformly along the ring. These dynamics could be interpreted in terms of growth modes. For instance, it seems reasonable to suppose that a traveling mode is the helical growth mode. The growth mode supposed in the scooter hypothesis (Thess et al. 1996) may correspond to such a helical growth mode. How a helical growth mode is stabilized is especially interesting in terms of steady growth mode of SWNT, because it seems to be difficult that the growth continues helically without changing with a high aspect ratio of more than a thousand.

In this paper, by use of our model we try to investigate the conditions that stabilize a helical growth mode of SWNT.

This model can be pointed out to be advantageous in a point of calculation cost. Even in use of usual personal computers, a calculation time does not take one minute for checking that a dynamics of the reaction spot converges. This is in contrast with molecular dynamics simulations (Maiti et al. 1997, Maruyama and Shibuta 2002, Shibuta and Maruyama 2003).

2 The SWNT growth model

The self-propagating high-temperature synthesis (SHS)(e.g., Munir and Anselmi-Tamburini 1989, Ohyanagi et al., 1992) is well known as the auto-catalyze heat generation system that self-organizes a reaction spot with various dynamics. In conformity to the numerical model of the SHS (Nagayama et al. 2001), we construct the phenomenological model of SWNT growth. Because the SWNT growth structurally differ from the SHS in respect of a material inflow, we should reconsider the materials. Here, we define the carbon which flows in the reaction scaffold as the material carbon. It will be adequate that the material carbons are not necessarily in a similar state when they flow in the reaction scaffold. We assume that the states of the material carbon can be roughly divided into two states. For being transformed into SWNT, the one needs the heat generation and the another does not need it. Where, we call the former carbon the carbon atom, the latter carbon the active carbon. This mean that for being transformed into SWNT, the carbon atom has to be activated through the heat generation and the active carbon is the already activated carbon. From a chemical point of view, the reaction field can be

illustrated as Fig. 2, and, if anything, it should be called the reaction scaffold.

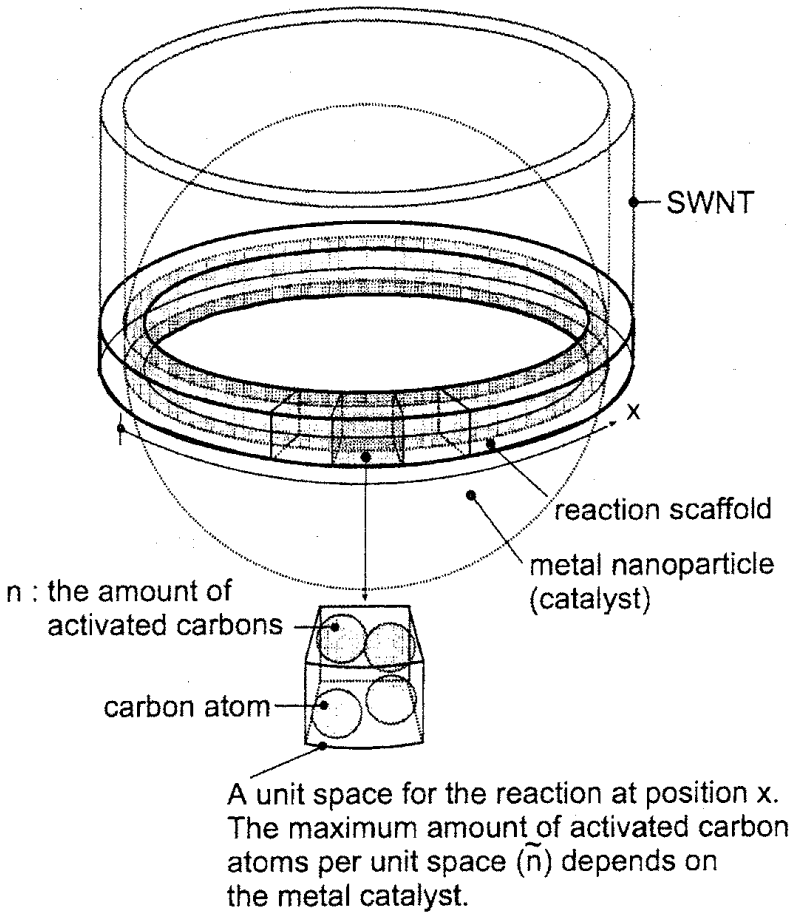

Figure 2: A reaction scaffold for the growth of SWNT.

Used the amount of activated carbons as the variable n, the numerial model of the SWNT growth is presented ;

$$\begin{cases} \frac{\partial T}{\partial t} = D\frac{\partial^2 T}{\partial x^2} + \gamma_t(\tilde{n}-n)^m f(T) - \alpha_1(T-T_e) \\ \frac{\partial n}{\partial t} = \gamma_n(\tilde{n}-n)^m f(T) - \alpha_2(n-n_e) \\ x=[0,\pi\phi],\ \ T(0,t)=T(\pi\phi,t),\ \ n(0,t)=n(\pi\phi,t), \end{cases} \tag{1}$$

where, the variables T is the temparature, the activated carbon amount n is approximated as a continuum; t and x are time and position, respectively, in the reaction scaffold which is a one-dimensional ring ; $\tilde{n}$ is a constant and denotes the maximum occupation amount of carbons in position x, and the value of this will be determined by a sort of a metal catalysis ; ϕ is the diameter, π is the ratio of the circumference of a circle to its diameter; D is a diffusion constant, and γ_t, γ_n are coefficients of the reaction rate. The parameter α_1 is the dissipation rate of the temparature, T_e the environmental temparature, α_2 the growth rate, n_e the supply amount of the active carbons (strictly, $\alpha_2 n_e$). The value of these parameters will be determined by a sort of a metal catalysis and material (e.g., hydrocarbon) gas and the pressure of the gas etc. The reaction rate $f(T)$ is a function of temparature T, governed by the Arrhenius law, and is expressed as

$$f(T) = \begin{cases} exp(-E/RT) & T \geq T_{ig} \\ 0 & T < T_{ig} \end{cases} \tag{2}$$

by an activation energy E, the universal gas constant R, and an reaction temparature T_{ig}.

We introduce dimensionless valiables defined by

$$u = T/T_{ig}, \quad n/\tilde{n} = v, \tag{3}$$

where, u is called the nondimensional temparature, v is the nondimensional activated carbon amount approximated as a continuum, respectively. And $(1 - v)$ expresses the vacant space occupied by the carbon atoms and catalyst. Assumed $\gamma_t \tilde{n}^m / T_{ig} = \gamma_n \tilde{n}^{m-1} / T_{ig} = k$ and usd $m = 3$ (see, discussion section), we derive

the following normalized system from (1),

$$\begin{cases} \frac{\partial u}{\partial t} = D\frac{\partial^2 u}{\partial x^2} + k(1-v)^3 f(u) - \alpha_1(u-\beta_1), \\ \frac{\partial v}{\partial t} = k(1-v)^3 f(u) - \alpha_2(v-\beta_2), \\ x = [0, \pi\phi], \;\; u(0,t) = u(\pi\phi, t), \;\; v(0,t) = v(\pi\phi, t), \end{cases} \tag{4}$$

where, $\beta_1 = T_e/T_{ig}$, $\beta_2 = n_e/\tilde{n}$,, and $f(u)$ is expressed as

$$f(u) = \begin{cases} exp(-e/u), & u \geq 1 \\ 0, & u < 1 \end{cases} \tag{5}$$

by using the constants $e = E/(RT_{ig})$.

From a viewpoint of the thermodynamics, the four parameters α_1, β_1, α_2, and β_2 can be regarded as follows (see, figure 1); α_1 the dissipation rate of heat, $\alpha_1\beta_1$ the heat supply from the environment, α_2 a rate of growth, $\alpha_2\beta_2$ a supply rate of the active carbons.

Since the activated (and active) carbons are immediately transformed into the SWNT, the activated carbon amount v could be considered to be eqiuvalent to the carbon amount transformed into a SWNT. Just then, it is found that this model expresses the growth process supposed by us in section 1, as mentioned below. The temparature u is auto-catalytically produced through the NT synthesis (the second term in the right side of the 1st equation in (4), i.e., $k(1-v)^3 f(u)$). As described in the 2nd equation in (4), an increases of v (the carbon amount transformed into the SWNT) is induced by the synthesis, depending on the produced temparature u. Here, because $(1-v)$ expresses the vacant space occupied by the carbon atoms and catalyst in a position x, a decrease of v will mainly correspond to an inflow of the

carbon atoms to a position x. Actually, with NT growth, a series of transformed carbons will be eliminated in succession from a position x. This elimination effect is described in the last term in the 2nd equation in (4), i.e., $-\alpha_2 v$, that causes v to decrease according to the growth amount v in the position x. Consequently also again, an inflow of the carbon atoms is induced depending on the produced heat u. Thus, this model expresses the thermal cycle that induces both the carbon inflow to the reation scaffold and the carbon transformation.

This model will be able to generate various dynamics of a reaction spot, such as a traveling mode or a steady mode. As mentioned in introduction section, we should investigate the stability of a traveling mode.

3 Simulation result

The initial condition was set up so that the the dynamics of traveling mode, where a reaction spot travels along the ring, is always generated at the initial stage regardless of parameters (Appendix B). By using the parameters $\alpha_1, \beta_1, \alpha_2, \beta_2, and\ \phi$, the conditions to stabilize the dynamics were investigated. Given the value of parameters and the initial condition, the simulation was continued until a dynamics was stabilized.

First, β_1, β_2 and ϕ were fixed to moderate values, and α_1, α_2 were modulated. Regardless of parameter values, the traveling mode always appeared in the initial stage except when the heat generation did not occur. And depending on the combination of values of α_1 and α_2, the traveling mode was stabilized, or was replaced with other various dynamics, as shown in Fig. 3 and 4. In each dynamics appeared here, u and v were always synchronized. Another traveling mode where the re-

action spot is larger and travels faster was also confirmed. We call this the fast traveling mode. The future of other dynamics appeared here is as follows. In the node mode, from or after the initial stage, the heat generation (a reaction spot) is not generated and v become uniformly static state (β_2). In the focus mode, after the initial stage, the traveling mode or the fast traveling mode is attenuated and v converges to uniformly static state. In the oscillatory mode, after the initial stage, v oscillates uniformly on the ring. This phase diagram shows that the stabilization of the traveling modes requires the value beyoud a certain value of both α_1 and α_2, and is strongly affected by the ratio of α_1 to α_2.

Second, fixed α_1 to the about middle value ($\alpha_1 = 4.0$) in the horizontal axis of Fig. 3, the influence by β_1 to the dynamics was investigated (β_2 and ϕ were fixed to the values similar to that in Fig. 3). As shown in Fig. 5a, the traveling modes are stabilized within the narrow range of β_1 (the heat supply). This result suggests that large areas of the traveling modes in Fig. 3 is supported by the moderate value of β_1.

Third, fixed again α_1 to the same value ($\alpha_1 = 4.0$), the influence by β_2 was investigated (β_1 and ϕ were fixed to the values similar to that in Fig. 3). The phase diagram of Fig. 5b shows that the traveling modes require β_2 less than a certain value.

The parameter ϕ also influenced strongly to the stabilization of these modes, as shown in Fig. 5c. The domain of traveling modes becomes narrow with decrease of the diameter ϕ, and it completely disappears below a certain value of the diameter. This phase diagram shows that ϕ more than a certain value is required for traveling modes.

Since the parameters $\alpha_1, \beta_1, \alpha_2, \beta_2, and\ \phi$ correspond to the dissipative rate

of heat, the heat supply, the growth rate, the supply of the active carbons, and the ring diameter of the reaction scaffold, respectively, the conditions which stabilize the traveling modes can be concluded as follows. The dissipative rate of heat and the growth rate are more than a certain value and are about proportional. And the heat supply within the moderate range, the active carbon supply less than a certain value, and the diameter more than a certain length are needed.

Since carbon atoms are activated in a reaction spot, the movement of the reaction spot may be interpreted in terms of the growth modes. Then, we regard the dynamics appeared here as the growth mode. It seems reasonable to interpret as follows. The traveling modes are the helical growth mode and the other modes are the symmetrical growth mode. Therefore, the conditions which stabilize the helical growth mode will attribute to conditions for the traveling modes.

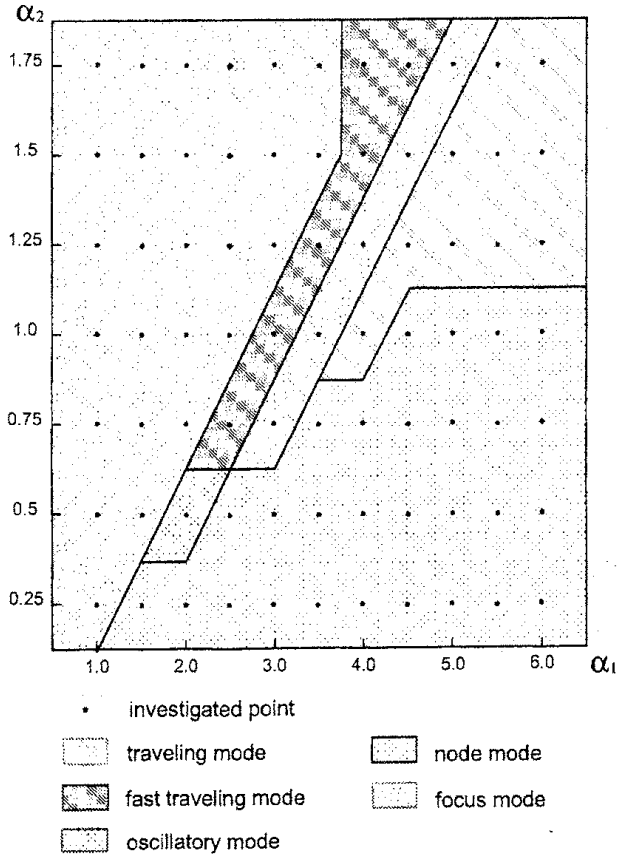

Figure 3: the phase diagram of dynamics stabilized by parameters α_1, α_2. Within the range of the used values of the parameters, five dynamics, i.e., the tranveling mode, the fast traveling mode, the one time travering mode, attenuation mode, and no ignition mode, were confirmed. The values of other parameters, β_1, β_2, and ϕ, were fixed to $0.45, 0.13$, and 0.3, respectively.

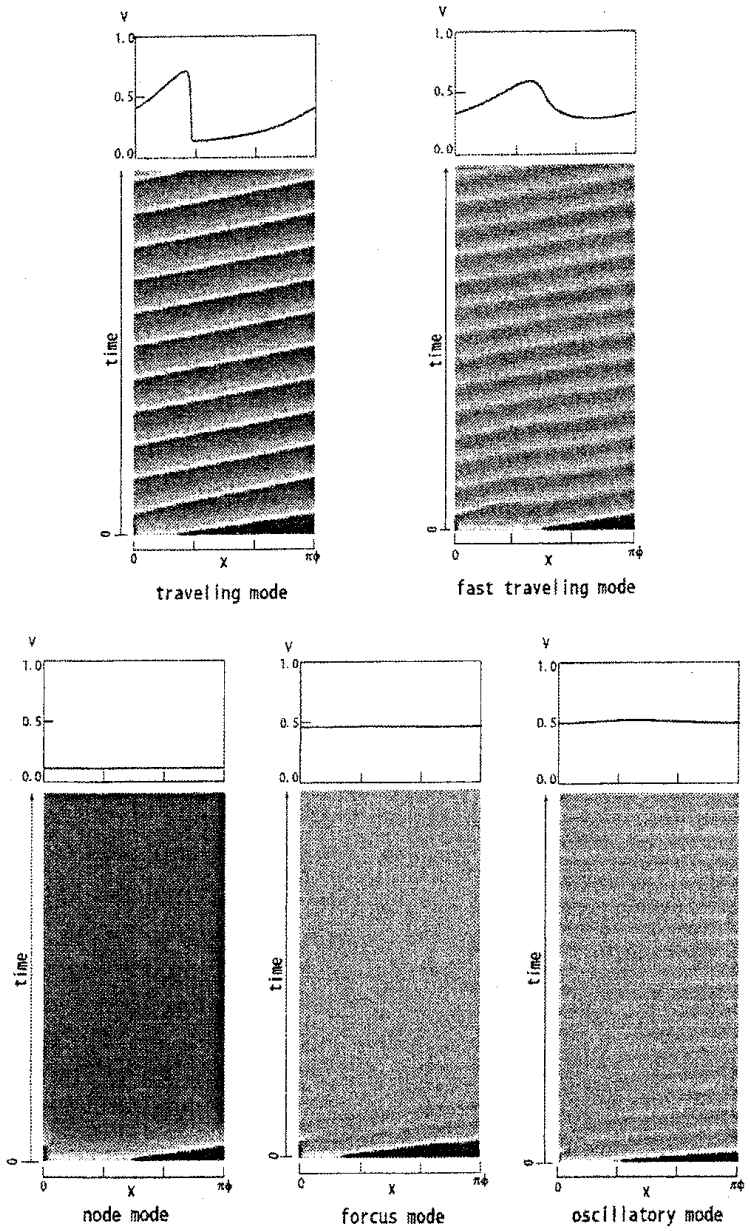

Figure 4: dynamics appeared in firgure 3. The state of v (the wallizing carbon

amount) in each dynamics is represented by two figures, i.e., two graphs where the vertical axis is v (the upper) and is time t (the bottom). For the sake of convenience, the one-dimensional ring of the reaction field is straightened, and represented as the horizontal axis (x) in these graphs. Therefore, both ends of the $x-$ axis are actually linked together, and the $x-$ axis represents the position in the reaction scaffold. The upper graph shows the converged spatial pattern on a certain time. The bottom graph shows the spatiotemporal pattern of v. Shading applid in the bottom graph indicates the value of v. The brighter the color becomes, the larger the value of v becomes.

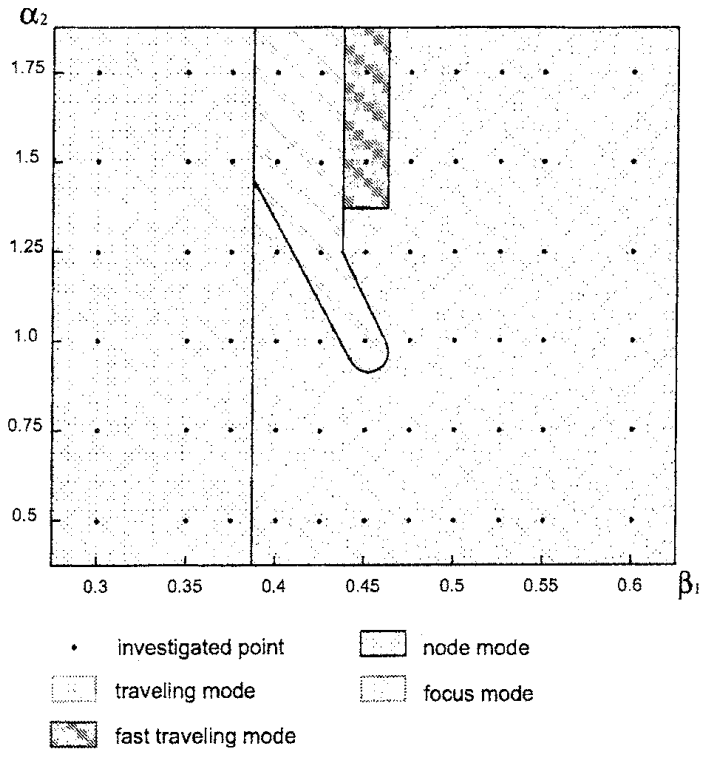

Figure 5a: the phase diagram of dynamics stabilized by parameters α_2, β_1. The values of other parameters, α_1, β_2, and ϕ, were fixed to $4.0, 0.13$, and 0.3, respectively.

Figure 5b

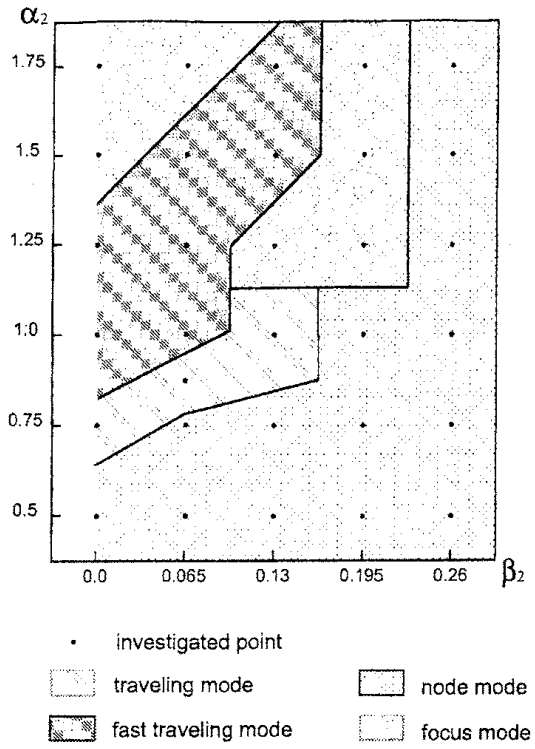

Figure 5c

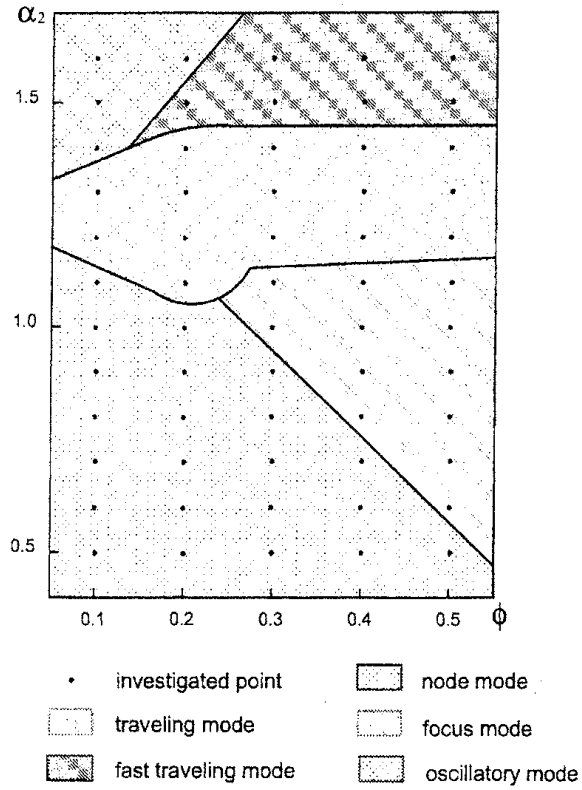

Figure 5b: the phase diagram of dynamics stabilized by parameters α_2, β_2. The values of other parameters, α_1, β_1, and ϕ, were fixed to $4.0, 0.45$, and 0.3, respectively.

Figure 5c: the phase diagram of dynamics stabilized by parameters α_2, ϕ. The values of other parameters, α_1, β_1, and β_2, were fixed to $4.0, 0.45$, and 0.13, respectively.

4 Discussion

In this paper, we discussesd the conditions which stabilize the helical growth mode of a SWNT, according to the following procedure. 1) The phenomenological model of SWNT growth was constructed as a reaction-diffusion system where the reaction field was approximated as a one-dimenssional ring of continuum. 2) Through computer simulations of this model, the conditions which stabilize the dynamics of traveling reaction spot were elucidated by modulation of the parameters. 3) Through interpretation of the dynamics, the suitable conditions were applied to that of the growth mode.

It is a great fruits on this study that the mode of the tube growth could be dealed with by numerical caluculation by modeling a reaction field as a ring,

In connection with the simulation results that the helical growth modes are destabilized with decrease of the diameter and completely disappear below a certain diameter, experiments () show following results. Although NT production experiments usually synthesize SWNTs with various diameters and with different lattice structures at a time, a distribution of helically latticed SWNTs decreases according to the grade of the shortness of their diameters. And helically latticed

SWNTs can not be found below a certain diameter. This agreement between the simulation results and the experimental results suggests that SWNT lattice structures may be relevant to SWNT growth modes. In the future, it will be important to investigate the connection between the growth mode and the lattice structure.

5 Acknowledgments

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Appendix

A. Parameters

$D = 10^{-4}$, $k = 5.0 \times 10^{5}$.

Nondimensional parameters

$e = 7.9$.

B. Initial condition

$$u(x,0) = \begin{cases} a & \text{for } 0 \leq x \leq c \\ b & \text{otherwise,} \end{cases}$$

$v(x,0) = 0.0$, $a = 0.6$, $b = 0.1$, $c = \pi\phi/2$, ($\pi\phi$ is the ring length).

Moreover, in order to induce always a herical growth mode in the initial stage, the

following asymmetry was introduced about the boundary. The Dirichlet boundary condition is set during time $t \ll 1s$, but otherwise the periodic boundary condition is set up.