# Mechanism of carbon nanotube formation in the arc discharge

Eugene G. Gamaly
*Laser Physics Centre, Research School of Physical Sciences and Engineering, Institute of Advanced Studies, Australian National University, Canberra, Australian Capital Territory 0200, Australia*

Thomas W. Ebbesen
*NEC Research Institute, Inc., 4 Independence Way, Princeton, New Jersey 08540*
(Received 22 February 1995)

A model for carbon nanotube formation in the arc discharge has been developed. The model is based on the physical properties of the arc discharge plasma where the interplay of the two major components of the bimodal carbon velocity distribution (Maxwellian and directed) dominates the nanotube creation process in a zone near the cathode surface. The processes of seed structures and nanoparticles formation, termination, and restart of nanotube growth, and multishell tube formation are considered self-consistently. The proposed model can explain qualitatively most of the known experimental facts related to the nanotube formation. Comparison to experiments has been provided and some consequences of the model discussed.

## I. INTRODUCTION

It is well established now that an arc discharge can produce in abundance either fullerenes[1] or nanotubes[2,3] by changing the conditions of the discharge. The changes in conditions on going from fullerene to nanotube production result in the introduction of an *axis of symmetry* in the medium where the formation process occurs, and consequently to a change in the velocity distribution of the carbon species from Maxwellian to anisotropic (unidirectional).

There are several distinctive features accompanying the process of nanotube creation. First, the nanotubes are formed in abundance (about $\frac{2}{3}$ of a total amount) in a central part of a rodlike deposit ("slug") on a flat cathode surface.[2–4] Second, the distribution of particles created in the slug is bimodal:[2] one mode represents the nanoparticles of a relatively small size with different shapes, while the other one relates to the nanotubes of typical length $\geq 1$ $\mu$m and outer diameters between 20 and 200 Å (the inner diameter is 10–30 Å). Most of the nanotubes are closed (capped) at both ends by the introduction of five-membered rings in the hexagonal network. Another important feature is the effect of proper cooling on the growth structure, and on the quality of the resulting nanotubes.[2–4] The deposit has a fractal-like structure comprising microbundles and macrobundles.[2–4] Each microbundle is composed of nanotubes having approximately the same length. This means that in a given microbundle all of the nanotubes appear to start and finish the growth process at roughly the same position and time. At the same time, next to the microbundle which stopped growing, the neighboring bundles keep on growing only a few nanometers away.

Such features raise many questions that need to be answered in order to clarity the process of nanotube formation. The most fundamental from our point of view are the following.

(i) What is the reason for the carbon cluster growth in one direction resulting in nanotube formation? Which of the arc plasma parameters are responsible for that process?

(ii) Why does nanotube growth terminate after a period much shorter than the discharge duration?

(iii) What is the mechanism of the capping of the tube ends and how does it relate to the tube growth mechanism?

(iv) What are the reasons and mechanisms for the simultaneous growth of the nanotube in length and width, leading to the multishell structure?

There are several qualitative models of nanotube formation in the absence of a catalyst[5–9] which can answer some of these questions reasonably well. Nevertheless, we are still far from a full and self-consistent quantitative description of the processes of nanotube formation in hot dense vapors of carbons (or plasma of carbon ions). In particular, earlier attempts to not analyze in detail the physical state of the arc plasma from which some of the key features for the growth process of nanotubes can be understood.

The time- and space-dependent set of parameters of a plasma (the mixture of carbon ions and atoms of a buffer gas) in the interelectrode space of an arc discharge is a necessary basis for any model of carbon cluster formation. The large carbon cluster formation process on a microscopic level can be described as a succession of binary random sticky (leading to attachment) collisions of carbon atoms, ions, and clusters of a different size and form, in time and three dimensions of space. For such a calculation it is necessary to know three-dimensional, temperature-dependent attachment probabilities for different clusters. Calculations of this kind are very complicated, and three-dimensional (3D) (as well as 1D) attachment probabilities for large carbon cluster formation are still unavailable either from calculations or experiments. On the other hand, by use of some reasonable ap-

 

proximations in the frames of such an approach[10] it is possible step by step to come closer to a quantitative description, allowing us to give reasonable answers to the above questions.

The structure of the present paper is as follows. At first we reconstruct, from numerous experimental and theoretical studies of arc discharges,[11–14] the main physical parameters of the space region of an arc next to the cathode surface where the nanotubes are created: the space and time distribution of density, velocity, and temperature of carbon vapors, electric charge, potential, and electric field. On the basis of these data, we present a scenario for the cycle of nanotube formation—seed creation, tube growth and termination—in time and space along with some numerical estimates of the main features of the process. We conclude with a discussion of the results, a comparison to experiments, and proposals of experiments in order to further justify the model.

## II. ANALYSIS OF THE PHYSICAL CONDITIONS OF THE ARC DISCHARGE

### A. Typical characteristics of discharge for efficient nanotube production

Nanotubes are produced efficiently when the following typical experimental conditions are maintained in the arc discharges.[2–4]

(i) The potential drop between electrodes is $V=20$ V.

(ii) The current density is $j=150$ A/cm$^2$.

(iii) The interelectrode distance during the stationary period of discharge $d \leq 1$ mm.

(iv) The average temperature of an interelectrode plasma is $T \sim 4\times10^3$ K.

(v) The deposit rate on the cathode surface is 1 mm/min$=16$ $\mu$m/s. Assuming the average material density of the deposit to be 1.5 g/cm$^3$, and a deposit area of 0.5 cm$^2$, this corresponds to $6.25\times10^{19}$ carbons/s (the flux density of carbons is $1.3\times10^{20}$ cm$^{-2}$ s$^{-1}$).

(vi) The pressure of the helium fill in the discharge chamber is $P=500$ Torr. Thus the number density of helium is $n_{\rm He}=6.4\times10^{18}$ cm$^{-3}$ ($T_{\rm pl}/300$ K), where $T_{\rm pl}$ is the plasma temperature in K.

(vii) The electrodes are carbon rods with flat surfaces approximately parallel to each other (the cathode surface is larger than that of the anode).

### B. Space charge, potential, and electric-field distribution

As is well known,[11–14] the space distribution of a potential has a steep drop near the cathode in a region of a positive space charge. Practically all of the potential drop occurs in this region. The scale of a space-charge sheath can be calculated from the familiar Child's formula for the ion current density $j$ (A/cm$^2$):[12]

$$j=\frac{5.46\times10^{-8}\ \mathrm{V}^{3/2}}{\Delta^2 M_c^{1/2}} ,$$

where $V$ is the potential in V, $\Delta$ is the space-charge sheath size in cm, and $M_c$ is the carbon mass number. The ion current density $j$ can be easily determined from the electron current density $j_e$:

$$j=j_e\left[\frac{m_e}{M_c}\right]^{1/2}=j_e\times8.2\times10^{-3} .$$

Combining the above equations, one finds a space-charge scale equal to $\Delta=12$ $\mu$m for typical conditions of the arc discharge ($V=20$ V, $j_e=150$ A/cm$^2$). This is also the distance of the main potential drop in the interelectrode region, and thus the distance for the positive ion acceleration moving toward the cathode. The average electric field in this region is $E\sim2\times10^4$ V/cm. The electric field in the outer region is several orders of magnitude lower.

### C. Ionization state and density of plasma in interelectrode space

The interelectrode gas is a mixture of neutral helium atoms, singly ionized carbon ions, and neutral carbon species. The first ionization potential of He is 24.87 eV, while the highest electron energy is 20 eV in these arcs. If the potential drop $V$ is larger than the first ionization potential $I_{\rm ion}$ of the buffer gas, the appearance of the ions of the buffer gas (for instance, He ions) would lead to a destabilization of the ion current and finally to the destruction of the discharge. This relation $V<I_{\rm ion}$ between the potential drop $V$ and the first ionization potential of a buffer gas, $I_{\rm ion}$, is a necessary condition for the existence of a stable discharge. Several experiments have been done with $V>I_{\rm ion}$ in order to try to improve the quality of the nanotubes produced. They failed for the above-mentioned reason.

The partial density of helium is $n_{\rm He}=6.4\times10^{18}$ $(T_{\rm pl}/300\ \mathrm{K})^{-1}=4.8\times10^{17}$ cm$^{-3}$ ($T_{\rm pl}=4\times10^3$ K). The density of carbon ions, $n_{\rm ion}$, may be deduced from the quasineutrality condition which is fulfilled for the major part of the interelectrode plasma (apart from the space-charge regions). The diffusion velocity $v_{\rm ion}$ of carbon ions responsible for the current in the major part of the interelectrode plasma is approximately equal to the thermal velocity $v_{\rm th}$, due to the high collisional frequency of carbons in the dense gas. Thus one obtains

$$j_e=j_{\rm ion}=en_{\rm ion}v_{\rm th} ,$$

where $v_{\rm ion}=v_{\rm th}=(T_{\rm pl}/M_c)^{1/2}=2\times10^5$ cm/s. It immediately follows that $n_{\rm ion}=5\times10^{15}$ cm$^{-3}$. Consequently, the density of the mixture is dominated by helium.

Now one can calculate the density of carbons near the cathode surface based on the experimentally measured carbon deposition rate on the cathode $n_c v_c=1.3\times10^{20}$ cm$^{-2}$ s$^{-1}$. The carbon ions moving in the gap between the positive space charge and cathode are accelerated by the sharp potential drop. Thus the velocity of the ions can be estimated from a simple equality

$$M_c v_c^2/2=\mathrm{eV} .$$

The velocity of these ions is $v_c=1.8\times10^6$ cm/s. Note that this is the velocity *directed* along the axis of the discharge, or along the direction of the electric field, because the ion motion during acceleration is collisionless;

i.e., the ion's direction is unchanged because the mean free path for collision is much larger than the acceleration length. Now simple arithmetic gives the density of carbon ions near the cathode surface, $n_c = 6.9 \times 10^{13}$ cm$^{-3}$. Once again one can see that the density of the mixture is dominated by helium.

### D. Carbon vapor sheath on the cathode surface-formation zone for nanotubes

The temperature of the interelectrode gas, $T_{pl} = 4 \times 10^3$ K, is close to the melting ($T_m = 4.1 \times 10^3$ K) and boiling temperatures ($T_b = 4.47 \times 10^3$ K) of graphite. For this reason the carbon surface must begin to evaporate, producing a thin layer of saturated carbon vapors near the surface. One can calculate the vapor density near the cathode surface by making use of the conventional formula from the kinetic theory of evaporation. It is also possible to use the Kirchhoff-like formula with experimentally corrected coefficients[15]

$$n_{vap} = n_0 \left[ \frac{c_s}{v_{th}} \right]^3 (2\pi)^{3/2} \exp\left\{ -\frac{\varepsilon_b}{T} - 1 \right\} .$$

Here $n_0$, $c_s$, $v_{th}$, and $\varepsilon_b$, respectively, are the density of solid carbon, sound velocity in cold carbon, thermal velocity of carbons at temperature $T$, and binding energy (or heat of evaporation per one carbon atom). Taking $n_0 = 10^{23}$ cm$^{-3}$, $c_s \approx 10^5$ cm/s, $v_{th} = 2 \times 10^5$ cm/s, $\varepsilon_b = 3.7$ eV (355 kJ/mole C), and $T = 4 \times 10^3$ K, one obtains $n_{vap} \approx 1.35 \times 10^{18}$ cm$^{-3}$, which is close to the density of the surrounding gas, taking into account the approximate character of the estimates. Thus after the initial expansion, the carbon vapor forms a thin shield over the cathode surface. Note that the velocity distribution of carbon atoms in the vapor layer is Maxwellian (isotropic). The collision frequency of carbons with either isotropic or directed velocity in this layer is much higher (due to the higher density of carbons) than in the plasma of the interelectrode space. For this reason the vapor layer is the most appropriate place for all reactions attaching carbon to carbon, or carbon to carbon clusters, to occur.

### E. Energy balance and the heat losses from the plasma

The energy deposited in the plasma due to Joule losses is $Q = jE = 3 \times 10^4$ W/cm$^3$ (for $j = 150$ A/cm$^2$, and $V = 20$ V, $d \approx 1$ mm). The time for the temperature rise to $T = 4 \times 10^3$ K can be estimated from the equality $C_c n_0 dT/dt = Q$, thus $t_h \sim C_c n_0 T/Q \sim 1$ s. The number density of carbon in electrodes is $n_0 = 10^{23}$ cm$^{-3}$, and the specific heat of a solid carbon (graphite) $C_c$ at $T \sim 10^3$ K is approximately twice as large as the specific heat calculated in accordance with the Dulong-Petit law,[16] $C_c = 8.28 \times 10^{-23}$ J/K and $T = 10^3$ K.

The main heat losses occur due to heat conduction losses into the carbon electrodes and into the surrounding helium, and due to radiation losses. Thus the energy balance can be written in the form:

$$Q\pi r_0^2 d = Q_{rad} 2\pi r_0 d + 2(a_c dT/dz)\pi r_0^2 + (a_{He} dT/dr) 2\pi r_0 d .$$

One can neglect heat losses into the helium because the heat conductivity in the helium $a_{He} = 1.06 \times 10^{-2}$ W/cm K at $T = 4 \times 10^3$ K (Ref. 17) is much lower than that of the carbon $a_c = 4.18$ W/cm K [at $T = 10^3$ K (Ref. 16)]. It is necessary to take into account that variations in the heat conductivity coefficients are rather large for different modifications of carbon at high temperatures.[18] On the other hand, radiation losses are very important and equal to $Q_{rad} = \sigma T^4 = 5.67 \times 10^{-12}\ T^4$ J/cm$^2$ s K$^4$, thus appearing to be almost half of the total losses at $T = 4 \times 10^3$ K. The fact that the heat losses are divided between thermal losses to electrodes and radiation just confirms the importance of the electrode cooling, as has already been established experimentally by Ebbesen and co-workers.[2,4] The scale length of a temperature gradient in carbon electrodes is (for $T = T_{pl} = 4 \times 10^3$ K) $dT/dz = 0.26 \times 10^2$ K/cm.

## III. SCENARIO FOR DEPOSIT FORMATION ON THE CATHODE SURFACE

Comparing reaction rates (which are proportional to the collision frequency) in different regions of the interelectrode plasma, one finds that the layer of carbon vapors next to the solid cathode surface is the most appropriate area for the large carbon clusters (e.g., nanotubes) formation. It is a thin (approximately 2–3 $\mu$m in thickness) layer of saturated carbon vapors at $T \sim 4 \times 10^3$ K with an average density close to the density of the mixture (helium plus carbon) in the main part of the discharge ($n_{vap} \sim n_{mix} = 4.8 \times 10^{17}$ cm$^{-3}$ at equilibrium).

*The growth of a deposit occurs in this layer of carbon vapor due to the competitive input of two groups of carbon particles having different velocity distributions.* The first group—the carbons evaporated from the cathode surface—has a Maxwellian velocity distribution corresponding to the temperature $T \sim 4 \times 10^3$ K. The second group is composed of ions arriving with the ion current (the ions being accelerated in the gap between the positive space charge and the cathode). This group has a monoenergetic (with the energy $M_c v^2/2 = $ eV) monodirected ( along the current direction) velocity distribution. The velocity of a singly charged carbon ion accelerated to $V = 20$ V equals $2 \times 10^6$ cm/s, which is ten times higher than the thermal velocity of a carbon atom at $T = 4 \times 10^3$ K.

It is worth noting that in the case of an exact Maxwellian distribution of carbons there is no axis of symmetry in the reaction region. Thus the isotropic velocity distribution of the reacting particles [in the temperature range for large carbon clusters, e.g., fullerene, formation, 780 K $< T <$ 5.6$\times 10^3$ K (Ref. 19)] is appropriate for formation of 3D carbon clusters. On the other hand, conditions when reacting particles arrive in the reaction region in the form of a directed flux are appropriate for creation of the elongated structures (e.g., nanotubes) *along the symmetry axis.* The importance of having asymmetry in the reaction region for nanotube formation has been discussed by many authors.[2,7–9]

However, it is the notion that there are two competing sources of carbon, one with asymmetric and the other

with symmetric velocity distributions, which is the key to understanding many of the experimental observations as will be discussed below.

The process of deposit consists of many cycles of formation of nanotubes and nanotube microbundles. One cycle comprises (i) seed structure (and nanoparticle) formation at the stage of increase and stabilization of the current (or after the reappearance of a current at a particular place of cathode surface); (ii) a multishell tube growth process; (iii) a termination of tube growth due to current instabilities; and (iv) tube end capping by rearrangement of carbons having Maxwellian (isotropic) distribution in the absence of a current. The next cycle follows after the current reappears at the same location of the cathode surface. Let us now consider each stage of the cycle in more detail.

### A. Seed formation

In the beginning of a discharge the processes of ionization and heating of the electrodes and interelectrode gas are very important for the establishment of a steady ion current. The longest of these processes, heating, needs time of the order of one second. During the time of the increase of the ion current to a stable value, the velocity distribution of carbons in the vapor layer is predominantly Maxwellian. From the point of view of the model presented, the formation of 3D structures without any axis of symmetry, such as nanoparticles, is only possible if the Maxwellian distribution dominates the velocity distribution of the interacting particles in the reaction region. Along with an increase in the directed current the open structures—concave and convex (coranulene-like)—appear to prevail. These formations may be considered seed structures for the tube growth process. That such seed structures do exist has been convincingly demonstrated by Harris *et al.*[20]

The process of carbon cluster growth starts from $C_2$ formation. The characteristic time of the process ($C^*+C^*$ collision time) is of the order of $10^{-7}$–$10^{-8}$ s. Therefore, about $10^7$ seed structures can be formed in the $\mu$m-thick layer of the carbon vapor on the cathode surface ($\sim$cm$^2$) before the ion current reaches the steady-state value.

### B. Carbon tube growth at the stage of a quasisteady ion current

In the stable stage of the discharge the current of carbon ions flows to the vapor layer in a direction perpendicular to the cathode surface. Note that the mean free path for a carbon-carbon collision in this layer ($l=1/n\sigma-15$ $\mu$m) is larger than the thickness of the layer (2–3 $\mu$m). For this reason randomization (or isotropization) of the directed ion motion by collisions in the vapor layer is negligibly small. The main deceleration of the carbon ions occurs due to collisions with carbons on the cathode surface. Thus, before these collisions *the ions of the current keep their direction unchanged.*

Therefore the carbons arriving with the ion current are involved in the formation process of elongated structures (single-shell and multishell nanotubes); in other words, they are mainly responsible for the building of the tubes in the direction of the motion. One can see that the interaction process of directed carbons with solid surfaces is almost three orders of magnitude more intense than carbon-carbon collisions in a vapor layer due to differences in the densities of the solid and vapor (and, of course, more intense than directed carbon-vapor carbon collisions). This means that the formation process proceeds with a higher rate of building along the axis of symmetry, thus favoring the creation of tubelike structures. On the other hand, the presence in the layer of carbons having a Maxwellian distribution leads to the attachment of these carbons to the elongated structure formed before from directions which are parallel to the cathode surface (along the vapor layer). This process favors the thickening of the tube, i.e., formation of multishell nanotubes.

On the other hand, it might be that the reaction rate for the formation of a multishell tube due to attachment of the carbons to the smooth side of a tube is less than for a single-shell tube. In this case the experimental ratio of the number of single-shell tubes to the number of multishell ones must be large. To our knowledge, experiments show that this ratio is rather in favor of the multishell tubes.[2–4]

There is a similar explanation for the process of nanotube thickening based on experience with carbon fibers.[18] The nucleation on the sides of the tube can be due simply to the condensation (attachment) and annealing of carbon on the inner tube. This is well known to occur in carbon fiber science.[18] Thus the nucleation of a layer on the outside of a tube will not be the rate-determining step. However, in general the thickening will be affected by both unidirectional and isotropic carbons.

When, from the beginning, no current is locally present, the seeds form nanoparticles from the Maxwellian isotropic carbon which is always present due to the high temperature. One can assume that processes of deceleration, recombination of carbon ions, and attachment occur almost simultaneously.

### C. Termination, capping, and restart of nanotube growth

It can be seen by scanning tunneling microscopy (STM) and atomic force microscopy (AFM) that nanotubes are often combined in microbundles, and that all of the tubes in the bundle have about the same length ($\gtrsim 1$ $\mu$m).[2–4,9] The other striking feature relates to the fractal-like structure of the deposit, containing bundles of nanotubes of a successively increasing size.[4] In a given microbundle, all nanotubes appear to start and finish the growth process at roughly the same position and time. A very important and revealing fact is that, near the bundle which stopped growing, neighboring bundles, only a few nanometers away, keep on growing.[2,4] It follows from the measured deposit growth rate that the nanotube growth terminates approximately every 0.07 s and restarts again. It is difficult to account for these observations by invoking any reasonable chemical processes for the nanotube termination in the presence of a strong stable ion current.

However, there are several processes well known from numerous studies of arc discharges[11–14] which may well be responsible for a quasiperiodical interruption of the tube formation process (e.g., interruption of the ion current) at different places on a cathode surface, namely current instabilities.

First, the cathode spot instability results in a random, erratic motion of the cathode spot (and the current) along the cathode surface. Another instability results in a spontaneous interruption and restriking of a discharge without any significant changes in the external conditions of a discharge (voltage, current, etc.). There is also instability resulting in splitting of the current into many thinner threads (filaments) accompanied by a random, erratic motion of the filaments along the cathode surface.

The motion of a cathode spot (or current filament) from one particular place to another leads to termination of an ion current in this place, and to the dominance in the interaction zone of carbons having a Maxwellian distribution. This circumstance immediately leads to the closure of the tube ends (capping) and, consequently, to the termination of the tube growth. At the same time new seed structures and nanoparticles may start to form. Conversely, the return of the current spot to the same place helps to restart the ion current and formation of tubes during the next cycle.

### D. Estimate of reaction rates for nanotube formation

In what follows we will estimate some characteristics of nanotube formation based on the model which suggests that, in a hot dense vapor of carbon atoms, random binary collisions dominate the process of large carbon cluster (e.g., nanotubes) creation.[10] The nanotube formation occurs in a thin layer of hot carbon atoms at the cathode surface. There the carbon density is approximately constant due to the fact that consumed carbons are continuously replaced by the ion current from the anode. In this model the main characteristic of the process is the frequency of a random sticky (leading to attachment) collision of two carbon clusters, comprising $m$ and $k$ carbon atoms. One can write it as follows:

$$\nu_{m,k}^{(\mathrm{st})} = n_k P_{m,k} \sigma_{m,k} v_{m,k} \equiv n_k K_{m,k} ,$$

where $n_k$, $\sigma_{m,k}$, and $v_{m,k}$ are the number density of carbon clusters with $k$ carbon atoms, the cross section (geometric) for elastic scattering, and the relative velocity of the $m$ and $k$ clusters, respectively. $P_{m,k}$ is the attachment probability for formation of a larger cluster $(m+k)$, and $K_{m,k}$ is a reaction constant.

We apply this model to the case of collisions between hot carbon atoms, which are the starting point for the construction of larger clusters (e.g., nanotubes). We will assume in what follows that the collision of the newly arrived carbon atom plays the main role in the formation of a cluster, and that the main saturation process for the cluster with $k$ carbons is the creation of a cluster with $k+1$ carbons. The resulting set of rate equations can be solved numerically and for some cases even analytically (we will present these solutions elsewhere). The main conclusion one can make from this solution is that the efficiency of carbon transformation into large clusters (with the use of reaction time close to the time of elastic collision) may be very high.

Let us now make several estimates based on an assumption that the characteristic reaction time for carbon-carbon attachment is proportional to the carbon-carbon collision time. The number of C+C collisions due to ion current impact on a solid cathode surface which lead to the nanotube formation in length equals

$$\begin{aligned} R_{\mathrm{length}} &\sim n_{\mathrm{solid}} (nv)_{\mathrm{current}} (\sigma P) \\ &\sim 10^{23} \times 10^{20} \times 10^{-16} \\ &\sim 10^{27} \text{ events/cm}^3 \text{ s} . \end{aligned}$$

A nanotube of 1-$\mu$m length and an outer radius of 5 nm has a volume of $V_{\mu\mathrm{m\,tube}} = 2.5 \times 10^{-17}$ cm$^3$ and $N \sim 10^5 - 10^6$ atoms. Thus the time required for nanotube formation in length is $t_{\mathrm{form}} \sim (V_{\mu\mathrm{m\,tube}} R_{\mathrm{length}})^{-1} N \sim 10^{-3} - 10^{-4}$ s. Now let us estimate the time for the growth of the nanotube in the transverse direction (thickening) due to carbon-carbon collisions in a vapor layer. By the same procedure one obtains

$$\begin{aligned} R_{\mathrm{width}} &\sim (n_{\mathrm{vapor}})(n_{\mathrm{vapor}}) v_{\mathrm{th}} (\sigma P) \\ &\sim 5 \times 10^{17} \times 5 \times 10^{17} \times 2 \times 10^5 \times 10^{-16} \\ &\sim 5 \times 10^{24} \text{ events/cm}^3 \text{ s} . \end{aligned}$$

Comparing with the previous calculation, one can see that the nanotube growth in length is almost 200 times more efficient than in the width ($R_{\mathrm{length}}/R_{\mathrm{width}} = 200$), thus quantitatively explaining the nanotube aspect ratio observed experimentally (100–1000).

Now let us estimate the deposit growth rate under the assumption that the solidification time roughly equals the time of collisional cooling of carbons from the energy of 20 eV to the temperature of carbon deposit of approximately several hundred K. This time is larger than the formation time of the single $\mu$m-long nanotube in vapor by the ratio of initial to final temperature. Now the time for the formation of a 1-$\mu$m-long nanotube (or deposit growth time) one can be estimated as $t_{\mathrm{deposit}} \sim (20 \text{ eV}/T_{\mathrm{deposit}}) t_{\mathrm{form}} \sim 2 \times 10^2 \times 10^{-4}$ s $\sim 0.02$ s, which is in qualitative agreement with the experimental time of the deposit growth (1 $\mu$m per 0.07 s).

## IV. DISCUSSION AND CONCLUSION

The probability of cluster to cluster (or carbon to cluster) attachment in general depends on the symmetry of the atomic-orbital structure, the symmetry features of the reacting particles (e.g., the velocity distribution of the particles), and the properties of the cluster to which the attachment occurs. Thus, for the formation of any asymmetric structures, at least one of the above-mentioned features must be asymmetrical. In the arc discharge this main feature is the bimodal carbon velocity distribution, because the orbital structure of the excited carbon (at $T \approx 4 \times 10^3$ K) is almost symmetrical: all four orbitals are close to $sp^3$.

The model for nanotube formation in the arc discharge

presented here is based mainly on the carbon velocity distribution in the reaction zone near the cathode surface. That is, the velocity distribution contains two groups of carbons which have different angular dependences of velocities—isotropic and directed. These groups compete in the large carbon cluster formation process. The first group, having a directed velocity ten times larger than the thermal one, arrives at the cathode with the ion current. This group is mainly responsible for building a nanotube in length. The existence of this group in a discharge is a clear manifestation of *the axial symmetry* of the apparatus. The other group of carbons from the vapor layer has a Maxwellian (isotropic) velocity distribution. This group is primarily responsible for building a nanotube in width forming multishell structures. The hot soup of carbons with an isotropic, thermal, velocity distribution is also suitable for formation of seed structures and nanoparticles, and it also favors tube capping after termination of the current. The cessation of the current at any particular place on the cathode surface occurs due to current instabilities, and the asymmetry source disappears. Afterwards isotropic carbons dominate the formation process, leading to capping of the ends of the tubes and to formation of nanoparticles without any axis of symmetry.

It is well known that any small deviations in the material density, temperature, or charge density immediately lead to instabilities, the physical nature of which is well understood: they are the pinchlike instabilities. This means that the current has the tendency of splitting into smaller self-pinching current filaments moving quasiperiodically along the cathode surface. Only this phenomenon can explain the experimental observation that near the microbundle of nanotubes which stopped growing the neighboring microbundle only several nanometers apart continues growing. Such observations cannot be explained by local variations in temperature and composition of the plasma, since there are no statistical grounds why such variations would surround just a given microbundle in its entirety and not the next one.

Using simple kinetic arguments, based on the bimodal nature of the velocity distribution for carbons, it is possible to estimate the aspect ratio and deposit rate for nanotubes formed in agreement with experimental data. The bimodal nature of the carbon velocity distribution also explains the presence of the bimodal distribution of particles in the deposit.[2]

One can understand the important role of cooling observed experimentally[2–4] from the microscopic point of view. The cooling of electrodes leads to a reduced velocity of carbons having a Maxwellian distribution, thus reducing the thickness of the reaction layer and the rate for lateral attachment of carbon. The lower velocity of thermal carbons also reduces the perturbation amplitude and consequently decreases the erratic motion of the current along the cathode surface. Improved cooling should therefore improve the yield and quality of the nanotubes, as observed experimentally. Thus the model allows us to explain self-consistently and qualitatively most of the experimental observations of nanotube formation in the arc discharge. It seems plausible that the similar mechanism of nanotube formation takes place in a condensation of the directed flow of carbon atoms on a cold surface in vacuum.[21,22] The temperature of the cathode and the deposit is also important for the proper graphitization of the nanotubes. As we have shown elsewhere, the amount of defects in the nanotubes, and therefore their properties, are affected by such an annealing process.[23,24] However, excessive heating due either to a slow growth rate or improper cooling will result in sintering of the nanotubes into solid useless masses.[2,9] Obviously, it will not be easy to find the optimal cooling rate which allows for maximum yield of nanotubes, and maximum annealing of their structure all the while keeps sintering to minimum.

Some authors have argued (most convincingly, Smalley[7]) that the presence of an extremely high local electric field ($\sim 10^8$ V/cm) on the cathode surface may be responsible for the formation of nanotubes preventing the tubes from closing. The scale of such an electric field would be sufficient to influence the formation process.[7] However, the average electric field in the gap between the space charge and the cathode is only 20 V/10 $\mu$m$\sim 2\times 10^4$ V/cm. It seems to be very difficult to point out a reasonable mechanism for the creation and existence of such a field for a sufficiently long time. Even if it exists, such a field may have a manyfold influence on different processes. The capping rate might be slowed to some extent by the electric field.[2,7,8,9] Perhaps more effective for reducing the capping reaction rate is the repulsion between charged dipoles existing at the tips of the nanotubes during their growth.[2,4] On the other hand, such a field can increase the attraction of the positive ions from the current to the negative charges on the tips, thus increasing the attachment probability for nanotube formation in length.

The simple model presented here seemingly does not need any additional processes to be included. The rate of capping is obviously smaller than the anisotropic growth rate considering the aspect ratios of the tubes formed. The reason nanotubes form instead of balls, which are thermodynamically more stable,[7] is primarily due to a kinetic advantage. The anisotropic rate of formation is far greater than the isotropic rate, and therefore elongated structures win out under appropriate conditions.

It follows directly from previous arguments that three-dimensional clusters without any axis of symmetry (e.g., fullerenes) can be formed in the cloud of carbons having an isotropic velocity distribution. Let us now discuss briefly the role of the electrode shape in the structure of the carbon clusters created. Because the formation process occurs near the cathode surface, it seems that the cathode shape is very crucial. As one can see from the previous discussion, when both electrodes have flat parallel surfaces a clear axial symmetry exists which strongly affects the structure of carbon clusters, leading to a predominant formation of the nanotubes. Let us consider the other limiting case of the cathode shape, when the area of the flat surface goes to zero: the needlelike cathode. In this case the velocity of ions arriving at the cathode has a large tangential component along the cathode surface (its magnitude inversely depends on the

magnitude of the solid angle forming the needle). The presence of this tangential component leads to the turbulization of the plasma flow near the cathode surface, thus creating a roughly homogeneous mixture *without any axis of symmetry*. Consequently, with this form of cathode the creation of 3D carbon clusters (e.g., fullerenes) is favored over elongated structures (e.g., nanotubes) with a scale length exceeding several interatomic distances (which is a characteristic scale length for this case).

The proposal of a series of simple experiments quite naturally follows from the previous discussion: to make experiments with a gradually changing cathode from a rod with a flat surface to a rod with a sharpened, needlelike end. The intermediate forms of the cathode end must have the shape of a truncated cone with a gradually decreasing (from one experiment to another) flat surface area which must be parallel to the surface of the anode. In accordance with the scenario presented, the number of nanotubes formed will decrease as the cathode shape changes from rod to needle. At the same time the number of nanoparticles should increase.

To increase the nanotube aspect ratio it is necessary to reduce the lateral growth rate and the amplitude of the instabilities of the ion current. The most trivial and obvious way to do this is to reduce the amplitude of all initial perturbations: to increase the surface finish of the cathode and anode, to look carefully at the form of the rising part of the current pulse (and make it as smooth as possible), to eliminate the electrode motion during the discharge time, etc. All these improvements will probably increase the period of stability of the current. One could also employ other known ways for the stabilization of a discharge such as an external magnetic field.

We believe that efforts on all of these factors to stabilize the current and optimize the cooling will result in improving the quality and efficiency of the nanotube production.

## ACKNOWLEDGMENTS

One of the authors (E.G.G.) wishes to acknowledge many useful discussions with Dr. K. A. Gamaly, Professor L. T. Chadderton, and Dr. Salvador Cruz Jimenez.

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