Laplacian growth of amorphous carbon filaments in a non-diffusion-limited experiment

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(Received 9 May 1995; revised manuscript received 25 July 1995)

Ramified amorphous filaments grow by the aggregation of hydrocarbon molecules on charged specimens in a transmission electron microscope. The molecules move on deterministic trajectories and are attracted by the aggregate. Fractal, dense branching, and compact morphologies appear. Under suitable conditions, dense branching aggregates show an oscillating growth behavior. The aggregation is of the Laplacian type but not diffusion limited. The morphology of the deposit is determined by surface migration of the molecules on the aggregate. Due to the transformation of the material into amorphous carbon under electron irradiation, the morphology depends on the aggregation rate. The experiment shows that particles following simple Newtonian trajectories can form ramified objects of various morphologies by aggregation.

PACS number(s): 68.70.+w, 61.43.Hv, 61.16.Bg

I. INTRODUCTION

In recent years there has been considerable interest in the formation of ramified structures during nonequilibrium disordered growth [1–4]. These phenomena are of importance not only in some basic physics experiments but also in many biological systems. A variety of morphologies is observed, the most outstanding ones being fractal, dense branching, and compact [5–7]. Despite their widespread occurrence in nature, it is not completely understood to date under which general conditions a specific morphology appears. In particular, it is unclear whether the selection of morphologies is determined by special properties of the aggregates or of the medium surrounding them. A large number of simulations have been carried out in the past few years in order to establish specific models and to explain the occurrence of different morphologies. Most of the simulations are based on the model of diffusion-limited aggregation (DLA) [5], which has been most successful in the theory of fractal growth. Another direction has been followed in a recent simulation study [8], which suggests that particles following deterministic trajectories can also form an aggregate with tunable fractal dimension if an attractive interaction between particles and aggregate is assumed. However, only a few simple experiments of ramified growth are known. Electrodeposition [9], viscous fingering [10], dielectric breakdown [11], crystallization of amorphous materials [6], and some other phenomena have been studied in detail. In all these experiments the propagation of particles or growth fronts occurs in a medium that surrounds the seed of growth, i.e., the growth is more or less diffusion limited. Since no experiment was known where this was not the case, the role of diffusion has never been testified experimentally.

Very recently, a different phenomenon of ramified growth has been found [12] where the aggregation is clearly not influenced by diffusion and is surprisingly rich in morphologies. The growth of amorphous carbon filaments during an *in situ* experiment in a transmission electron microscope enables us to study Laplacian growth in a system that, from a general point of view, is rather simple. The growth dynamics of the aggregates can be easily observed *in situ* so that this experiment seems to be well suited for studies of non-diffusion-limited disordered growth. Fractal, dense branching, and compact objects are obtained and show remarkable similarities to the shapes of many biological systems. Some interesting features can be observed, such as an oscillating growth behavior of dense branching objects. Meanwhile, sufficient experimental evidence exists to involve the phenomenon into the field of disordered growth. In this paper the experimental findings are collected and related to a qualitative growth model. It is found that the morphology is determined by the properties of the aggregates, not by their environment.

II. EXPERIMENTAL PROCEDURE AND RESULTS

The transmission electron microscope serves as a "microlaboratory" in these *in situ* studies. Micrometer-sized fragments of electrically insulating solids of any composition are irradiated with an electron beam of energy 100–1000 keV and a current density of 10^4–10^5 A/m^2. The insulating fragments collect positive electric charge due to the emission of secondary electrons. The charge of the specimens is limited by surface conduction, breakdown, and recapture of emitted electrons to approximately 10^{-14}–10^{-12} C. The specimen is located in the vacuum of the microscope column (total pressure 10^{-4} Pa), where, as in most vacuum systems, a small amount of hydrocarbon contamination exists. At that low pressure the mean-free-path length of the hydrocarbon molecules (centimeters) is much larger than the irradiated object (micrometers). The molecules move with thermal energy ($\approx$40 meV) and suffer collisions only with the wall of the vacuum chamber. The propagation of the molecules is therefore ballistic and not diffusive.

The hydrocarbon molecules are polarized or ionized and attracted by the charged specimen where an aggregation takes place. Filamentlike ramified objects develop (Figs. 1 and 2), their overall sizes range from 100 nm to

more than 10 μm. The aggregation occurs preferably where the local electric field E is high, i.e., on exposed positions on the substrate or on tips of the growing filaments (estimated local electric field $E \approx 10^6 - 10^7$ V/m). Making use of the action of the charged specimen as an electrostatic lens, the distribution of local electric fields can easily be imaged by overfocusing the objective lens of the electron microscope. The growth velocity of the filament tips depends on the beam intensity and on the hydrocarbon pressure in the microscope column and ranges from 1 to 5 nm/s. The capture radius around the charged specimen is estimated to be several centimeters and therefore orders of magnitude larger than the size of the object. Thus an escape of particles from close to the object should be impossible. On a typical ramified object of 1 μm in size some $10^4 - 10^7$ molecules aggregate per second. An arriving molecule traverses an object of this size within a time that is 4–6 orders of magnitude shorter than the period of time between two aggregation events. Hence mutual shielding or other interactions between the approaching molecules before the aggregation should be negligible.

The filaments show a distinct tendency to split during growth, however, only on the tips. As long as the growth front of the aggregate still consists of hydrocarbons, a high surface mobility of the molecules [13] leads to a rounding of the tips under the influence of surface tension. Under electron irradiation, however, the polymerized hydrocarbons decompose within a short time and amorphous carbon is left. We may thus assume that only the tips of the growing filaments consist of hydrocarbons. Since amorphous carbon is electrically conductive, the electric potential is the same over the whole transformed object. On growing tips that still consist of nonconductive hydrocarbons, however, the local potential may deviate slightly from that of the remaining aggregate.

The transformed carbon filaments are very stable against any changes in shape under electron irradiation at moderate beam intensities. The influence of thermal effects on the action of surface tension and thus on the splitting behavior is investigated by heating the carbon filaments up to 900 °C in a TEM high-temperature stage. No changes in shape occur, the surface tension of amorphous carbon is thus not influenced visibly at temperatures much higher than those that can be expected to prevail during growth. It is furthermore of interest whether the action of surface tension is influenced by the intense electron bombardment of the filaments during growth. Atoms in the specimen are displaced by knock-on collisions with electrons from the beam and by subsequent displacement cascades [14]. A total rate of 0.1 displacements of each carbon atom per second during typical growth conditions is calculated. It is much too low to account for considerable effects on the shape of the filaments. This is also verified experimentally: without a supply of hydrocarbon molecules (suppressed by the use of cryopumps) only very small changes of the filament shape are observed during the irradiation at moderate beam intensities.

Examples of fractal, dense branching, oscillating, and compact objects are shown in Fig. 1. These objects have grown on boron nitride crystals within 10–20 min of irradiation. Electron diffraction reveals that the filaments are fully amorphous, therefore no growth anisotropy such as in dendrites can occur. The growth is observed *in situ* with a reasonably high resolution of about 0.5 nm. It is found that the tips have a diameter of less than 1 nm during growth. The tip surface may be regarded as "rough" since it consists of single molecules that have sizes of several tenths of a nanometer. Observing the aggregation and splitting process at higher resolution on an atomic scale could be an interesting challenge for future work. After each splitting event a "competition" between the two growing tips can be observed: in most cases one of the tips grows faster and, due to shielding, leads to a retarding of the other. Only the most exposed tips of the object proceed. Retarded filaments round off by the migration of hydrocarbon molecules on the surface under the influence of surface tension. Filaments with rounded tips increase in thickness only by uniform

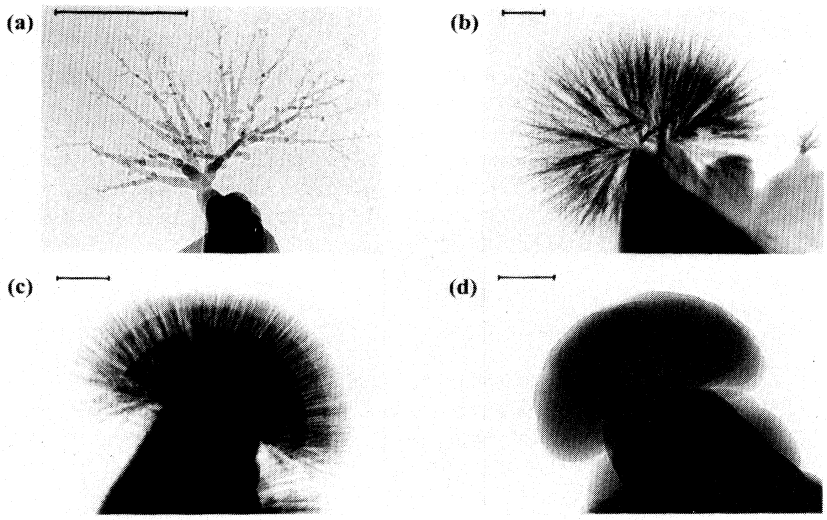

FIG. 1. Examples of four typical morphologies of amorphous carbon aggregates: (a) fractal, (b) dense branching, (c) oscillating, and (d) compact. The aggregates have grown on electrically charged boron nitride crystals during irradiation in an electron microscope. Each scale bar is 0.25 μm.

aggregation and by migration of particles along the branches; no preferred growth in the filament direction and no further splittings occur.

A most important observation is that the morphology of the objects depends sensitively on the aggregation rate, which is controlled by the hydrocarbon pressure in the microscope and the electron-beam intensity. The tendency of the filament tips to round off increases with increasing aggregation rate. Table I shows the obtained morphologies as a function of the aggregation rate. At low aggregation rate fractal growth is observed, with increasing aggregation rate the objects become densely branched and eventually compact. The fractal dimension therefore increases with increasing aggregation rate. However, the fractal dimension is difficult to measure precisely, since we obtain projections of three-dimensional objects onto the two-dimensional image plane. Different morphologies may coexist within single aggregates, as shown in Fig. 2. At the "trunk" of the treelike aggregate, where growth has started, the material is almost compact. The whole object could rather be characterized as dense branching, particularly since the envelope of the tips is perfectly spherical. On the other hand, the periphery close to the tips shows a fractal structure. During the course of growth the boundaries between the morphologies move outward.

If the deposition rate is slightly below the limit of compact growth, dense branching objects with an interesting growth behavior are observed [Fig. 1(c)]. After some time of growth all tips of filaments, which were initially very sharp, suddenly round off and do not proceed further. Aggregation is then uniform over the rounded tips and surface migration leads to a thickening of the branches. After a further period of time, new filaments with sharp tips start to grow simultaneously on the meanwhile spherically rounded tips. This sequence may repeat itself several times and leaves an object with a concentric-shell structure. The distance between the shells decreases with increasing aggregation rate. More than ten shell develop under suitable conditions. With respect to the temporal dependence of the growth velocity, we may characterize this phenomenon as "oscillating growth." Another remarkable feature of the dense branching morphology is that the envelope of the tips, especially in larger objects, almost conforms to the shape of the substrate surface.

TABLE I. Morphologies of aggregates that develop at different deposition rates. The deposition rate was calculated by analyzing a typical series of micrographs taken during the electron irradiation experiments. Single aggregates of comparable size (approximately 0.5 μm in diameter) were considered.

Deposition rate (C atoms/sec)	Morphology
2×10^4	fractal
3×10^5	dense branching
5×10^7	compact

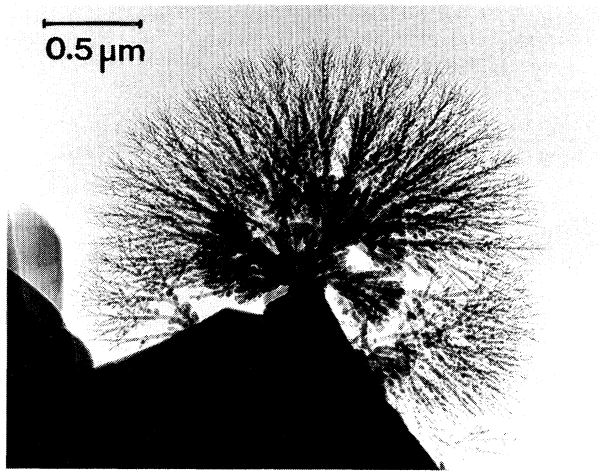

FIG. 2. Coexistence of different morphologies in an amorphous carbon aggregate. From inside to outside the morphology changes from compact to fractal.

III. DISCUSSION

The formation of ramified aggregates in a nondiffusion process has already been investigated in a simulation study by Block, Bloh, and Schellnhuber [8,15]. These authors find that aggregates generated by an attractive interaction between particles and clusters according to an $r^{-\alpha}$ law exhibit a fractal dimension that is determined by the interaction exponent α. In spite of the differences, it is interesting to compare their system with the present experiment. The common thing is that the trajectories of the particles are determined by the attractive interaction between the aggregate and the approaching particles and not by a random walk. Hence it is now also experimentally established that particles moving on deterministic trajectories can form aggregates within a wide range of fractal dimensions. The boundary conditions, however, are different in the two systems. The system of Block, Bloh, and Schellnhuber resembles a dielectric with tunable interaction exponent, whereas our aggregate is conductive, with the possible exception of the growing tips. The Coulomb interaction exponent is constant ($\alpha=2$). The present system may somehow resemble a lightning rod with a small insulating tip.

In contrast to diffusion-limited aggregation where the particles describe a random walk, we are now dealing with free particles following the simple Newtonian equations of motion. For charged particles or dipoles these well-known equations are, respectively,

$$m\ddot{\mathbf{r}}=-q\mathbf{E}(\mathbf{r}) , \tag{1}$$

$$m\ddot{\mathbf{r}}=-qd\nabla\mathbf{E}(\mathbf{r}) , \tag{2}$$

where m denotes the mass, q the charge, d the spacing of the charges in the dipole, and $\mathbf{r}$ the location of the particle. Since the particles initially move with thermal velocity $\mathbf{v}_{\text{th}}$, we may use the starting condition $\dot{\mathbf{r}}(t=0)=\mathbf{v}_{\text{th}}$. There is practically no charge outside the object, therefore the Laplace equation for the electric potential Φ

$$\Delta\Phi=0 \tag{3}$$

is strictly valid. The boundary condition

$$\phi_s=0 \tag{4}$$

holds for the whole conductive aggregate. As mentioned above, the surface potential ϕ_s on the insulating tips of a rapidly growing aggregate may be slightly different. If we consider a positively charged sphere with a surface field E_i, which is exposed to a uniform flux of negatively charged particles, we obtain an aggregation rate

$$dn/dt \propto E_i \ . \tag{5}$$

The aggregation therefore occurs preferably but not exclusively on the tips. Although the dielectric breakdown model [11] may not be appropriate for a complete treatment of the present phenomenon, we should consider the role of the growth exponent η. Since the aggregation rate depends on the first order of the electric field [Eq. (5)], we have a growth exponent $\eta=1$ and, with this, the same functional dependence as in DLA. It has been found by simulations of the dielectric breakdown model [5,16] that the growth exponent determines the morphology of the simulated object. For $\eta=0$ a compact object has been obtained according to the Eden model [7], $\eta=1$ corresponds to the diffusion-limited aggregation model of fractal growth [5], whereas for the dense branching morphology η is expected to be between 0 and 1. With the growth exponent $\eta=1$ we should only obtain one distinct morphology. However, we observe a variety of morphologies in the present experiment and therefore have to include surface motion of particles [17] into the growth model.

The surface migration of particles lowers the surface energy and determines decisively the morphology of the object. The transformation of hydrocarbons into amorphous carbon under electron irradiation is a transition that drastically decreases the mobility of the particles on the surface. At high aggregation rate the tips consist entirely of hydrocarbons and are therefore able to round off immediately. At low aggregation rates, splitting instabilities are "frozen in" by the transformation before the surface of the filaments can be smoothed. The growth velocity v_n depends therefore in a nontrivial way on the aggregation rate dn/dt. Surface tension properties such as the product $d_0\kappa$ of a characteristic length d_0 and the curvature κ of the tips have to be taken into consideration. However, the microscopic processes determining the surface motion of molecules and the transition from hydrocarbon polymers to amorphous carbon under electron irradiation have not yet been very well investigated. Charging effects should also be considered since thin filaments tremble slightly during growth; this is a phenomenon that has also been observed during electron microscopy observations of carbon nanotubes and is typical for local charging effects [18].

We may also understand the selection of morphologies from a macroscopic point of view. During fractal growth the object is of low density (low fractal dimension) and the growth velocity of the tips v_n is large. If the aggregation rate increases, v_n of the sharp tips also has to increase. As observed in this experiment, this is no longer possible above a critical value. The tips round off, instabilities can no longer survive, and the approaching particles find a larger area where the aggregation can take place. The object becomes more dense, the fractal dimension increases until, at very high aggregation rate, equilibrium conditions are approached, and the compact morphology prevents the object from growing too large within a short time. The dense branching morphology may be considered as a natural phenomenon between fractal (deposition only on tips, high surface energy) and compact (deposition everywhere, low surface energy). Thus the optimum morphology is selected under given growth conditions [3,19]. It is interesting to note that also in other kinds of growth experiments the dense branching morphology preferably develops if the aggregation rate is high. For example, in electrodeposition the transition from fractal to dense branching is observed with increasing voltage applied to the cell [20]. In the growth of bacterial colonies [21] a similar phenomenon is observed at increasing nutrient concentration.

A characteristic feature of the dense branching morphology is the uniform length of all filaments. This leads to a spherical envelope of the object if growth starts on an exposed seed or, more generally, to an envelope conform to the surface of the substrate. The envelope of the tips reflects the shape of the equipotentials far from the object. Due to "competition" effects, only the most protruding tips advance and these are the filaments that are aligned radially along the electric field of the whole object. Surface motion of hydrocarbon molecules and the critical growth velocity ensure that all filaments have the same length. This also serves as an explanation for the oscillating growth: it is an interplay between aggregation on tips and surface migration. However, these two coun-

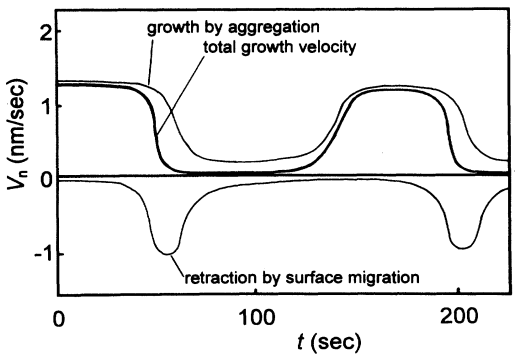

FIG. 3. Oscillating growth: growth velocity v_n of the filament tips of a dense branching object as a function of time at constant deposition rate dn/dt. The temporal dependence of the total growth velocity is based on the experimental observations and is plotted schematically rather than as a precise result of measurements within the given scale. The total growth velocity is assumed to consist of the sum of the contributions of aggregation and surface migration. Since these two contributions cannot be measured separately, the corresponding curves result from a qualitative consideration. The interplay between these contributions determines the growth of the filaments.

teracting effects influence each other so that a self-adjusting structure (Fig. 3) results.

IV. CONCLUSIONS

The growth of ramified carbon filaments in an electron microscope is determined by the Laplace field around the filaments and their intrinsic properties. The particles move on deterministic trajectories and are attracted by the aggregate via Coulomb interaction. A diffusive random walk of particles outside the object such as in DLA does not occur. The important properties of the object are the surface tension and the migration behavior of particles on the surface, which together are influenced by the aggregation rate. After the aggregation a transformation of the material takes place. The transformation of the insulating tip that rounds off under the influence of surface tension into rigid conductive material under electron irradiation determines the splitting behavior and thus the morphology of the object. The similarity of shapes of the ramified carbon filaments with other phenomena, especially in the living world (see also the figures in [12]), may lead us to the assumption that some similar principles are valid and form a basis of many disordered growth phenomena.

ACKNOWLEDGMENTS

The author would like to thank A. Seeger for his continuous interest in this work and critically reading the manuscript and U. Bahr and her collaborators (University and MPG-Arbeitsgruppe in Dresden) for stimulating discussions.

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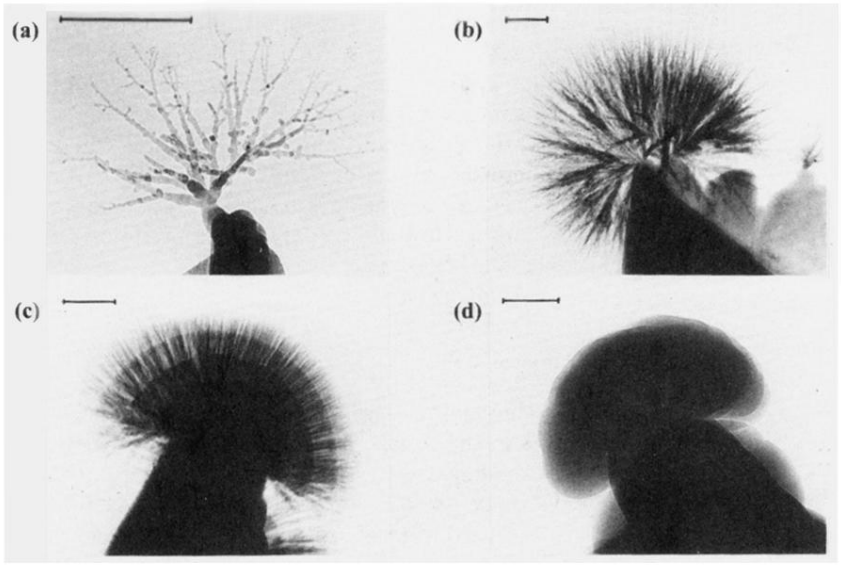

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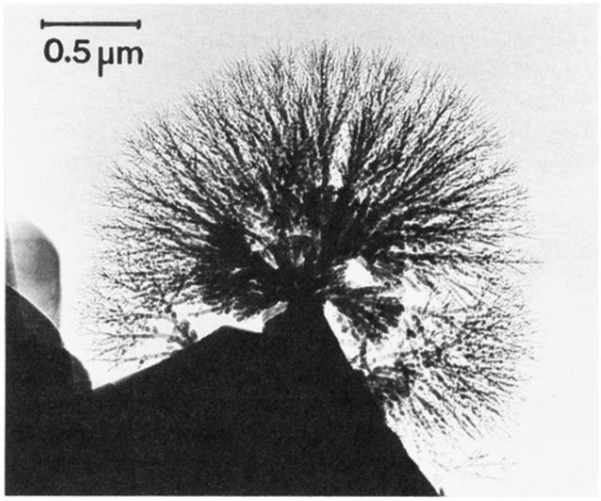

FIG. 2. Coexistence of different morphologies in an amorphous carbon aggregate. From inside to outside the morphology changes from compact to fractal.