

Number of arm selection in two-dimensional diffusion processes

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Abstract. We introduce an algorithm to generate two-dimensional diffusion-limited star-branched aggregates (DLSA) attaching bi-functional monomers successively to a central colloidal particle with any desired number of reactive sites. The proposed algorithm produces star-shaped aggregates that grow forever and show a power law polydispersity in the chemical length of the arms near the central colloid. More interestingly, it gives rise to a number of arm selection consisting in that only a small number of arms (around five) define the final structure at relatively large distances from the central colloid, independently of the initial number of reactive sites and the size of the central colloid. We characterize the structure of the aggregates by means of the particle-particle correlation function, analyze its scaling properties and obtain the fractal dimension.

PACS. 61.43.Hv Fractals; macroscopic aggregates (including diffusion-limited aggregates) – 05.40.-a Fluctuation phenomena, random processes, noise, and Brownian motion – 82.70.Dd Colloids

1 Introduction

Considerable attention has been focused on the question of how to describe the configuration of both linear and branched polymers [1]. Although most models are based on the concepts of equilibrium statistical mechanics [2], in the case of linear polymers, models based on the nonequilibrium diffusion-limited aggregation (DLA) have been devised [3–6]. The primary interest in this kind of models is that they lead to self-avoiding walks (SAWs) which grow forever. The construction of such a walk is of great physical importance in connection with the kinetics of irreversible growth processes such as polymerization and kinetic gelation. Two-dimensional versions of these models have also been used to describe submonolayer vapor-deposition polymerization [7] and diffusion-limited polymerization mechanisms have been applied to the problem of surface growth [6] and *in situ* polymerization [8]. In these models, many chains grow from a line or plane of active sites to represent growth from a surface. Similarly, more sophisticated models have been introduced to describe growth of polymers having higher-order connectivity [9]. However, no such models have been applied to the specific case of star-branched polymers or aggregates. That is, no related models have been proposed to describe the growth of many chains from a central colloidal particle.

The subject of this letter is to propose a kinetic mechanism to grow star-branched aggregates that are fully determined by diffusion. We consider specifically the case of two-dimensional growth and found that these diffusion-limited star-branched aggregates (DLSA) grow indefinitely, are self-avoiding and contain arms with a distribution of lengths. More interestingly, the large-scale structure of the aggregate is determined by only a small amount of arms (around five) independently of the size and the number of active sites of the central colloidal particle. The model is an interesting cross between SAWs, DLAs, and star polymers.

2 Model

We start the construction of a DLSA in two dimensions with a central colloidal particle of radius R_c with f equidistant reactive sites as shown in Figure 1. Then, an incoming bifunctional monomer is released from a random point far away from the central colloid. This monomer moves in random directions in steps of size equal to its diameter a . When the distance of this monomer to any reactive site is less than its diameter, then it is attached to the reactive site at the contact point. Successive monomers are incorporated to the aggregate in a similar way, *i.e.*, the incoming monomer is attached to a reactive site of the central colloid or to the monomer located at the end

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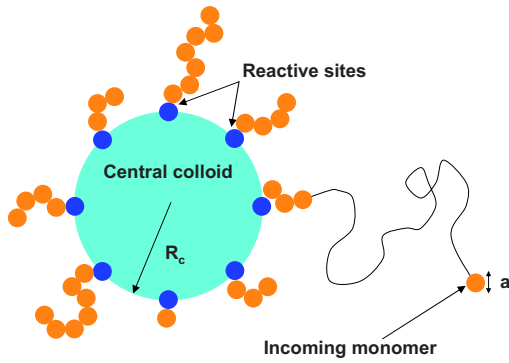


Fig. 1. Schematic drawing of the aggregation process to build diffusion-limited star aggregates (DLSA). In the figure the number of reactive sites is $f = 8$.

of any branch of the aggregate. Since the monomers are bifunctional, no additional branching points are generated. We adopt absorbing boundary conditions at the inactive (nongrowing chain) sites. This means that when an incoming monomer touches either the central colloid or the aggregate at a point that is not reactive, including all the monomers that are not located at the end of any branch, then the incoming monomer is discarded and a new one is released. By iterating this procedure, consecutive monomers are released and eventually attached to the original aggregate. In this way, the algorithm produces star-branched structures of N monomers and with f polydisperse arms. Since the incoming monomers diffuse to the growing tips from faraway, there must always be a path from the tips to infinity that does not touch the aggregate. Therefore, this growing mechanism produces structures that grow endlessly. This growing procedure is summarized in Figure 1.

3 Results

In what follows, we utilize this model to construct aggregates made of up to $N = 50000$ monomers and $f = 3, 6, 12, 18, 24, 30, 100,$ and 200 reactive sites in the central colloid. The radii of the central colloid were $R_c = 25, 50, 100,$ and 200 monomer diameters. Averages over 200 different realizations of the aggregates for the values of f and R_c indicated above were performed. A typical configuration is shown in Figure 2 for an aggregate with $f = 100$ reactive sites and $R_c = 100a$. The large-scale structure of this aggregate seems to show only few surviving arms. In the inset we show an early stage of formation of the aggregate showing the large initial number of arms. It can be seen that the structures generated by the algorithm are stars whose arms have a distribution of lengths. An analysis of this polydispersity is shown in Figure 3 where the histograms showing the number of monomers per arm are plotted against the arm number. The arms were numbered according to its chemical length, that is, the first arm is the one that has the largest number of monomers, the second arm is the one with the second largest number of monomers and so on. In other words, the

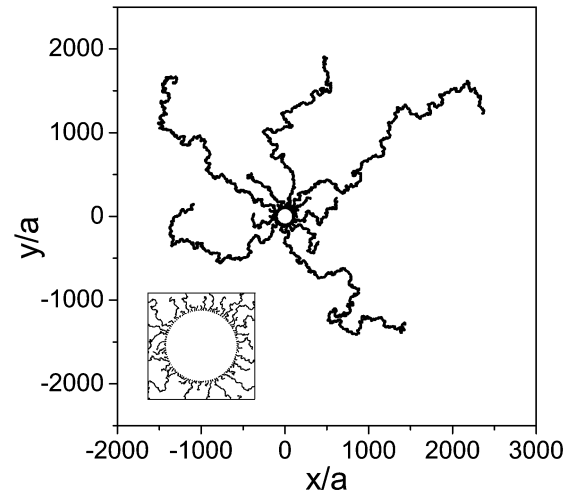


Fig. 2. Large-scale realization of a DLSA with $N = 50000$, $f = 100$ and $R_c/a = 100$. This figure shows that for large-scale aggregates only a few arms remain. The inset shows the corona region near the central aggregate with a large number of arms.

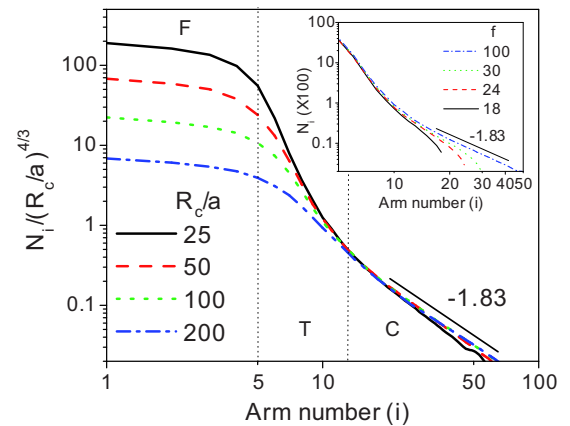


Fig. 3. Histograms showing the number of monomers per arm versus arm number for $N = 50000$, $f = 100$ and different sizes of the central colloid. Three regions are apparent, the far region (labeled F), the transition region (labeled T), and the corona (labeled C). In the corona region, near the central colloid, the chemical length of the arms shows a power law scaling of the form $N_i \sim (R_c/a)^{4/3} i^{-\alpha}$. For $f = 100$ the value of the exponent α is $\alpha \simeq 1.83$. The hump indicates that around five arms grow more than the others. The vertical dotted lines indicate the border between the different regions. The inset shows the same but for $R_c/a = 25$ and different values of f . The corona is not yet fully developed for a small number of reactive sites f . To guide the eye, we have also plotted a straight line with a slope -1.83 .

arm number represents the rank of an arm with respect to its mass. In all the cases the histograms show clearly three different regions. The first region (labeled C) represents a corona of short arms around the central colloid. In this corona region, the arm size polydispersity follows a power law behavior $N_i \sim i^{-\alpha}$. It is found that the data in region C collapses onto a single line, independently of the size of

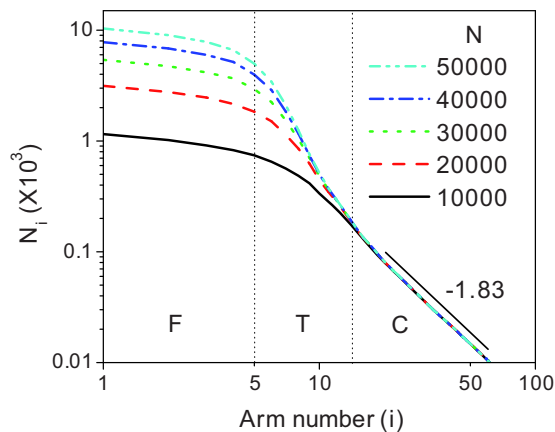


Fig. 4. Same as in Figure 3 but for $R_c/a = 100$, $f = 100$, and different values of N . The height of the hump increases with the mass of the aggregate whilst the corona region remains fixed.

the central colloid, if we make the following ansatz:

$$N_i \sim \left(\frac{R_c}{a}\right)^{4/3} i^{-\alpha}, \quad (1)$$

where i labels the arm number and N_i is the number of monomers of the i -th arm. The exponent α is practically independent of the colloidal radius R_c , as shown in Figure 3. Note that for a small number of reactive sites, the corona region is not yet fully developed (see inset). For the case $f = 100$ and $R_c/a = 100$, it is found that $\alpha \approx 1.83$. The second region or far region (labeled F) represents the few surviving arms (around five) that determine the large-scale structure of these star aggregates and the third region (labeled T) is a transition region formed by a few arms of intermediate lengths between those of the far region and the corona. This region consist of arms $i \simeq 6$ to $i \simeq 14$, approximately. The far region appears as a hump in the histograms. The hump is more evident as the number of monomers in the aggregate increases, as can be seen in Figure 4. Thus, as the aggregation proceeds, the inner arms do not grow anymore and all the incoming monomers attach to one of the few largest arms belonging to regions F or T. A confirmation of this behavior is observed in Figure 5, where the mass of each arm N_i weighted by the mass of the largest arm N_1 , denoted by N_i/N_1 is plotted for the fourteen largest arms (F and T regions) as a function of the mass of the aggregate, N . This plot appears to indicate that these few arms are the only ones that will survive in the far and transition regions as the mass of the aggregate increases. The reason of it is that the curves seem to approach asymptotically values different from zero, meaning that these arms will grow indefinitely as the mass of the aggregate increases. It also gives an indication of the polydispersion of the arms in the F and T regions. For the remaining arms, located in the corona region, one has that the quantity ($i \gtrsim 14$), N_i/N_1 goes to zero as N grows indefinitely. The existence of these regions has to do with screening processes in which the largest arms precludes the incoming monomers to explore

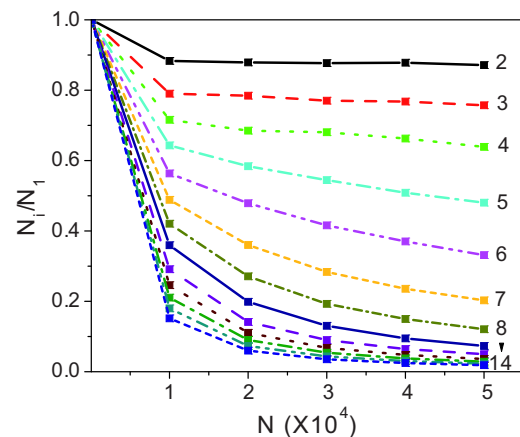


Fig. 5. Length N_i/N_1 of the fourteen largest arms as a function of the mass of the aggregate N . This plot seems to confirm that only few arms survive. The parameters used in this figure are $R_c/a = 100$, $f = 100$.

the regions of the space deep inside the cluster, preventing in this way further growing of the shorter arms. Nonetheless, in the far zone the screening regions are not large enough to further prevent the growing of the largest arms (about five). Although from the results of Figures 4 and 5 is evident that only a few arms survive, it is difficult to define with precision the position of the borders between the three different regions (F, T, and C). However, based on the generalized opinion that usual DLA aggregates have 5 dominant branches [10], we have chosen the border between the F and T regions to be about 5. Due to the very slow approach of the curves plotted in Figure 5 to their asymptotic limits, extremely large simulations would be needed to provide a better estimate of these borders.

To further characterize the structure of the aggregates, we calculated the density-density correlation function $C^r(\theta) = \langle \rho(r, \theta) \rho(r', 0) \rangle$, where $\rho(r, \theta) = n/(r\delta\theta\delta r)$, is the particle density on a cell of area ($r\delta\theta\delta r$) located at a distance r from the center of the central colloid and with angular position θ , and n is the number of particles in the cell. This quantity measures the probability of finding a monomer at an angular distance θ from another monomer both located at positions separated a distance r from the center of the central colloid. The behavior of these correlations is shown in Figure 6 where we observe that the density-density correlation function oscillates in the neighborhood of the perimeter of the central colloid. The oscillations reflect the uniform angular distribution of the reactive sites at its border. The uniformity is lost progressively as one moves away from the center of the aggregate due to the sinuosities of the arms. This suggest that at relatively large distances the uniform angular distribution of the reactive sites becomes irrelevant. In other words, if the original reactive sites were not uniformly distributed on the perimeter of the central colloid the angular separation between the maxima would not be uniform. However, at larger distances the angular correlations should also decrease and become similar in both cases. Even more,

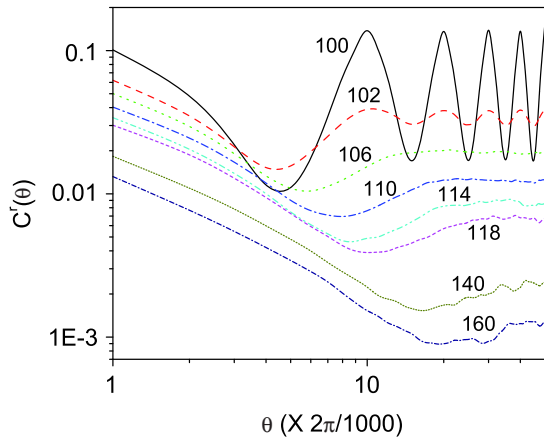


Fig. 6. Two-point density-density correlation function measured on a circumference of constant radius r for a DLSA with $N = 50000$, $f = 100$ and $R_c/a = 100$. Density-density correlation functions were calculated at $r = 100, 102, 106, 110, 114, 118, 140,$ and 160 .

if the number of reactive sites f were very large, one could think of a situation in which all the perimeter of the central colloid was covered by the reactive sites. This situation would be equivalent to saying that all the perimeter of the central colloid was reactive. Therefore, although the results obtained from our model seem to be specific, they are not, as argued in this paragraph.

We also performed an analysis of the scaling properties of the aggregates by means of the two particle correlation function $g_2(r)$ from which the fractal dimension can be calculated. To check the consistency of the d_f values, we also calculated the fractal dimension by the box counting algorithm. A representative value for the aggregates fractal dimension is, $d_f \simeq 1.23$. This value depends slightly on the values of f and R_c . Since the large-scale of all the aggregates is the same, then, for larger aggregates these small differences in d_f should disappear. In the case of a single-arm aggregate we also obtained, $d_f \simeq 1.23$. This value is in good agreement with that obtained from on-lattice simulations of polymer growth on two-dimensional strips with periodic boundary conditions [6]. The fact that only a very small number of arms of similar size grows indefinitely allows a comparison with a monodisperse two-dimensional star polymer whose fractal dimension was found to be [11] $d_f \simeq 1.33$. This value is larger than the ones we have found for the DLSA, since the diffusive procedure used here to build the aggregate yields clusters slightly stretched as compared to the equilibrated structures [12, 13].

One of the most interesting aspects of these DLSA is the distribution of sizes of the arms in the corona region, which is given by equation (1). Following reference [14], one can write down a relationship between the exponent α , in equation (1), the dimensionality of the embedding space and the fractal dimension of a single chain,

$$\alpha = 1 + (d - 1)/d_f, \quad (2)$$

where d is the dimensionality of space (in our case $d = 2$). Using the value $d_f \simeq 1.23$, we get $\alpha \simeq 1.81$, which is

in excellent agreement with the result found numerically (see Figs. 3 and 4). It is quite interesting to note that the same relationship between these quantities, given by equation (2), has also been found for diffusion-limited deposition by Racz and Vicsek [14]. However, in that case, the exponent α appears in the scaling form, $N_s(N) \sim s^{-\alpha} f(s^\sigma/N)$, where $N_s(N)$ is the number of clusters of size s after N particles per growth site have been deposited with the scaling function satisfying $f(x) \simeq 1$ for $x \ll 1$ and $f(x) \simeq 0$ for $x \gg 1$.

Previous multiple-chain-growth models and diffusion-limited growth from a surface were done on a square lattice [6, 15]. This study raised the question of whether the two exponents corresponding to diverging length scales arise from the anisotropy of the square lattice. Since our simulations are done off-lattice, it is clear that the square lattice is not responsible of the diverging length scales.

In reference [6] the results for the polydispersion of cluster sizes show a strong analogy between diffusion-limited aggregation and diffusion-limited polymerization on a stripe. This suggests that the same analogy should be present for our DLSA and the usual DLA. This is in agreement with the fact that off-lattice DLA shows five dominant arms.

4 Conclusions

In summary, we have proposed an algorithm to grow two-dimensional star-branched aggregates whose structure is completely determined by diffusion. Surprisingly, we have found that the final structure seems to be general in the sense that all the DLSA end up with the same number of large arms independently of the initial number of reactive sites and the size of the central colloid. This result is a clear indication that a selection of the number of arms occurs and a final structure with 5 arms emerges spontaneously. Although the boundary conditions (circular colloidal particle of fixed radius with regularly spaced reactive sites) are particular, we believe that similar simulations performed using different boundary conditions will lead to the same large-scale structure. In other words, if the initial reactive sites were not distributed on a colloidal particle but rather in a different geometry, like a straight line segment or even randomly distributed in a finite region of the plane, then the same final structure with approximately 5 arms would emerge. Work along these lines is currently under progress. Finally, extensions of this work should be done to build aggregates embedded in a space with a higher number of dimensions to see how this symmetry breaking is modified or even canceled for a large enough number of dimensions of the embedding space.

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