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Annealing two-dimensional diffusion-limited aggregates

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Abstract. We have studied the structure of annealed two-dimensional diffusion-limited aggregates (DLA). The annealing process consists of introducing internal flexibility to the original DLA rigid structure as well as excluded volume interactions between particles. From extensive Monte Carlo simulations we obtained aggregates with fractal dimension slightly higher than that obtained for two-dimensional DLA structures. This is somehow surprising since the fractal dimension of the annealed structure is determined not only by connectivity but also by the competing effects of excluded volume interactions and configurational entropy, whilst in the rigid DLA only diffusion counts for the fractal-dimension value.

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

Aggregation of particles in colloidal suspensions is an important example of a nonequilibrium process. Patterns formed by this process have much practical importance, since they appear in a wide range of phenomena in different areas of science and technology [1]. Diffusion-limited aggregation (DLA) [2] and other related models [3,4] have become paradigms for growth phenomena in far from equilibrium conditions [5]. DLA model was introduced to describe growth where the limiting step is diffusion to the surface of the growing object. Such processes are quite common in nature [6]. In colloidal suspensions and other systems well described by these models [7], the elementary units that successively stick to form the aggregate remain thereafter at relative fixed positions, thus conferring an intrinsic rigidity to the structure. That is, the statistical properties characterizing the disorder of the particle positions are quenched by the growth process itself. This is an important limitation that impedes the application of the conventional diffusion-limited aggregation model to diverse aggregating systems. Examples of systems in which the DLA model cannot be applied are: aggregates involving rearrangement within the clusters [8–10], and polymer chains in solution that are formed by fluctuating elements [11]. To obtain a better description of these fluctuating structures other models have been developed [1,12,13,15]. A realistic model for describing growth in systems with fluctuating constituents must include information not only about the colliding events that lead to the irreversible build up of the structure, but also about the equilibrium configurations that result from the Brownian motion of the internally articulated elements [14]. Therefore, the statistical properties characterizing the positional disorder are in this case a combination of quenched and annealed rearrangements.

Clusters formed by aggregation processes generally have a fractal structure [16]. Fractal dimension is a crucial parameter that defines many properties of aggregates [10,17–21]. By definition, if the density ρ and the size R of an object are related through, $\rho \sim R^{d_f - d}$, with d_f a non-integer number less than d, – d the dimension of the space –, then one is dealing with a fractal structure. The exponent d_f represents the fractal dimension of the aggregate. The smaller the fractal dimension, the less compact the aggregate.

Since the first aggregation models were introduced, many modifications of them have been introduced to describe systems under a wide range of circumstances [16]. It has been found that fractal dimensionality depends on the nature of the aggregation process [2–4,22]. The least dense structure occurs for a diffusion-limited aggregation in which particles stick together irreversibly and permanently at contact. Computer simulations have shown [3,4] that for diffusion-limited cluster aggregates (DLCA) $d_f \approx 1.75$ while experiments with colloidal gold particles have yielded $d_f = 1.75 \pm 0.05$ [7]. For reaction-limited (RLCA) processes the clusters are more compact than those formed by DLCA. The formation of more compact structures than expected for RLCA processes has been encountered and explained in terms of

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cluster restructuring [23–25]. Recently, a general class of diffusion-mediated reversible aggregate-reorganization processes have been shown to exhibit globally attracting equilibrium distributions that are universal [26,27]. Additionally, aggregate restructuring is found to be an important mechanism in explaining aggregation kinetics [10].

A rather interesting question with regard to the structure of a DLA aggregate is the following: What happens to the structure of a DLA aggregate when the rigidity constriction at the bonds of each constituent is relaxed and monomers originally distant in the structure come close to each other in space due to Brownian motion? Since each monomer has a finite volume other monomers cannot come into its own region, so the natural interaction that comes into play is the excluded volume interaction or steric effect. In such a situation the net result is a repulsive force between the different branches of the aggregate because two or more interacting branches always have reduced configurational freedom as compared to the case when each branch is isolated in space.

In this paper we address this issue and study the structure of aggregates, that are created from a two-dimensional DLA structure by introducing flexibility to the rigid DLA bonds and taking into account excluded volume interactions. Nonetheless, it is important to point out that the present model is not aimed at explaining aggregation processes with internal mobility *during* aggregation or processes in which any two particles bind to each other upon touching, even if the particles are already bound to some other ones. Models of aggregation which treat these cases have been introduced and studied previously [14,15]. Rather than studying models in which reorganization leads to a change in topology, here we investigate the equilibrium properties of the already grown DLA structure without further changing its connectivity. This model could be relevant to experimental systems in which presumeably flexible fractal structures in solution are formed. For example, in the experimental system of reference [11], the polymers could be thought of as a flexible globules that could be modeled as soft spheres. These spheres have a small number of reactive sites where other spheres can be attached building up large flexible aggregates. Once the reactive sites of a given particle are filled no other particle can be bind to it even if they get close.

The annealing process induced by flexibility, yields structures with a fractal dimension that is only slightly higher than that of the original DLA. This is an unexpected result since the fractal dimension of the annealed structure is determined not only by connectivity but also by the competing effects of excluded volume interactions and configurational entropy. Excluded volume interactions introduce a repulsion between particles that in principle should lead to a stretching of the branches of the aggregate which is opposed by the effect of configurational entropy. In other words, flexibility tends to increase configurational entropy while excluded volume interactions reduce the number of possible configurations of the aggregate. In contrast, in the rigid DLA only diffusion counts for the fractal-dimension value. This entropy dominated process should be distinguished from other mechanisms that lead to the restructuring and compaction of colloidal aggregates. For instance, in the colloidal silica aggregates experimentally studied in reference [9] the breaking of bonds and formation of new ones are responsible for compactation.

2 Simulation

In what follows we briefly describe how to arrive to the two dimensional aggregates under study. We start by forming a two-dimensional DLA in the usual way, i.e., we begin with a seed particle of diameter r_0 located at the origin of coordinates. Then we release another identical particle at a random position some distance away. The new particle is allowed to diffuse, i.e. take steps of length r_0 in random directions, until it reaches a position within a distance r_0 from the first. Then it is stopped and added to the aggregate at the point of contact. Successive particles are released, one at a time, and the process is repeated until an aggregate of N particles is completed. Once the 2D DLA is grown we introduce internal degrees of freedom to anneal the aggregate. These internal degrees of freedom substitute the rigid bonds between monomers at the contact points and provide the aggregate with some flexibility which is determined by the type of interaction potentials between the constituent particles that form the aggregate. To make contact with some other interesting soft condensed matter systems, for instance, polymer systems, we model this internal flexibility applying the finitely extensible nonlinear elastic (FENE) potential [28]. The FENE potential is applied only to the monomers that are nearest neighbors and has the property that it is harmonic at its minimum and the “bonds” between nearest monomers cannot be stretched beyond a maximum length. This potential is defined by,

$$V_b(r_{ij}) = -\frac{k}{2}\left(r_{sup}-r_0\right)^2 \ln\left[1-\left(\frac{r_{ij}-r_0}{r_{sup}-r_0}\right)^2\right], \quad (1)$$

where k is the spring constant, and r_{ij}, r_0, and r_{sup} are the instantaneous length of bond ij, the equilibrium bond length (or equivalently, the particle size), and the maximum bond length, respectively. The self-avoiding properties of the aggregate are modeled by considering the excluded volume interaction potential between monomers not directly connected. This interaction is modeled with the hard sphere potential,

$$V_{nb}(r_{ij}) = \begin{cases} \infty, & \text{if } r_{ij} \le r_0 \\ 0, & \text{if } r_{ij} > r_0 \end{cases} \quad (2)$$

where r_{ij} is the instantaneous distance between particles i and j. The internal mobility of the aggregate means that if it is embedded in a thermal bath, then due to the Brownian motion of the monomers it changes its conformation. The statistical nature of this flexible aggregate is now determined not only by the initial quenched disorder contained in the original DLA but also by the annealing process that arises when the conformations of the

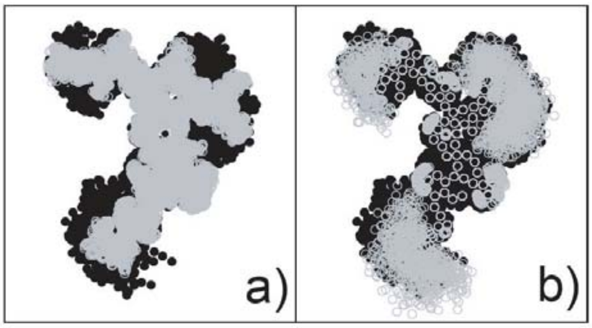

Fig. 1. Superposition of 100 snapshots of a partially relaxed aggregate with $N = 100$ particles. In black we show the output of an hybrid method which combines classical MC and CBMC, and in light grey we show the output of classical MC [panel (a)] and CBMC [panel (b)]. One can see that CBMC relax well the tips of the branches but can not relax the central part of the structure whilst classical MC relax all the structure albeit less efficiently. The hybrid procedure applies CBMC to the tips while it uses MC for the rest of the structure.

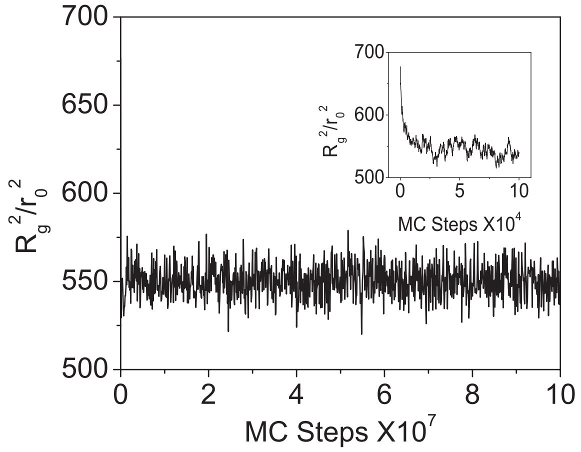

Fig. 2. Evolution of the square of the radius of gyration as a function of number of Monte Carlo steps. In the inset we show the evolution of the square of the radius of gyration as a function of number of Monte Carlo steps right after the initial quenching. This result clearly indicates that the initial DLA shrinks rapidly. Averages over 10 different aggregates of $N = 1000$ monomers have been taken in both cases.

aggregate sweep the allowed configurational space. In this paper, this annealing process is simulated using a Monte Carlo (MC) algorithm that is a combination of three different types of moves, since we found that it was extremely difficult to obtain a complete relaxation of the aggregate using just one kind of move. This is due to the fact that DLA are aggregates with a rich branched structure, so that, most of the time a movement is intended, it will be rejected due to attrition problems. The simplest type of MC moves are local updates according to the standard Metropolis criteria [29] using the interaction potentials defined in equations (1), (2). That is, we choose a particle of the aggregate at random and carry out a random displacement $\delta \boldsymbol{r}$. The move is accepted or rejected according to the standard Metropolis criteria. The second type of move consists of choosing at random a monomer of the aggregate, and freely rotate, by an arbitrary angle, all the branches emanating from it. This kind of move is called a "pivot move" [30]. This latter MC move has been applied to annealing random branched polymers in three dimensions with number of monomers up to 2000 [31]. Although this type of moves do not mimic the real dynamics of the macromolecules at all, it is acceptable as long as we are interested in the equilibrium properties of the aggregate. The third type of MC move introduced in the simulations is the conventional Configurational Bias Monte Carlo algorithm (CBMC) [29]. In this method the aggregate is partially regrown starting from a random particle. As one would expect the Metropolis moves work well for all the monomers located at the core of the aggregate, while the CBMC moves are more efficient for the monomers located near the free ends of the branches of the aggregate. This is shown in Figure 1 where we can see the effect of these two kinds of movements on a small DLA. For monomers located deep inside the aggregate, the probability of acceptance of a CBMC move is very small due to steric effects. On the other hand, the "pivot moves", that are essentially rotations around a given monomer, contribute to rearrange more efficiently the branches of the aggregates. These type of moves proved to be crucial to successfully achieve the relaxation of the aggregates. As a matter of fact, we found that the more efficient way of annealing the aggregate was using a random combination of the three types of MC moves. The Metropolis and the pivot moves were applied to any monomer in the aggregate while the CBMC moves were applied only to monomers near the tips of the branches. We now describe some parameters and details of the numerical simulations.

We found that a set of ten different DLA's configurations with a total of $N = 1000$ monomers yielded statistically meaningful results. Note that it is relatively easy to grow a DLA with thousands of particles, however, the annealing of such aggregate becomes extremely difficult. In fact, we tried larger systems but it proved to be computationally quite expensive, since it took too long to achieve a relaxed state. The parameters used in the FENE potential were, in reduced units: $k = 50$, $r_0 = 1$, and the largest bond length was set $r_{sup} = 1.2r_0$ to avoid bond crossing. To carry out the annealing of each DLA aggregate we performed a total of 10^8 combined MC moves considering a monomer displacement $|\delta \mathbf{r}|$ ($\delta r_\alpha \leq 0.2r_0$, with $\alpha = x, y, z$), when it was required. The simulations were done at constant temperature $T = 1/k_B$, with k_B the Boltzmann constant.

3 Results

In Figure 2 we show the evolution of R_g^2, as a function of MC time. There one sees that right after initial quenching it decreases significantly, as shown in the inset. However, after 10^6 MC steps have elapsed this quantity oscillates with relatively small amplitude around an average value.

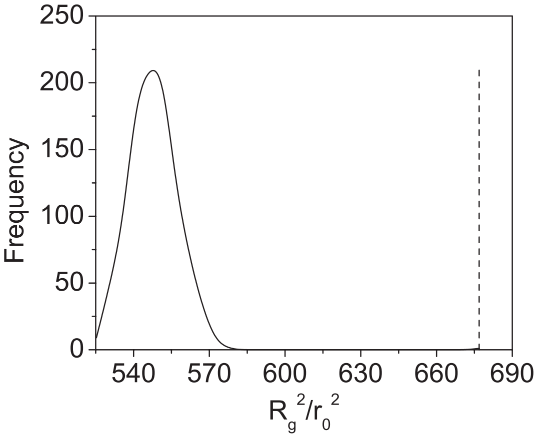

Fig. 3. Average of the distribution of the square of the radius of gyration. The average was taken over 10 different annealed DLA aggregates and over 100 snapshots taken each 10^6 simulation steps. The position of the dashed vertical line represents the average value of the square of the radius of gyration of the initial 10 DLA configurations. From this figure it is obvious that there is a net shrinking of the annealed DLA aggregates.

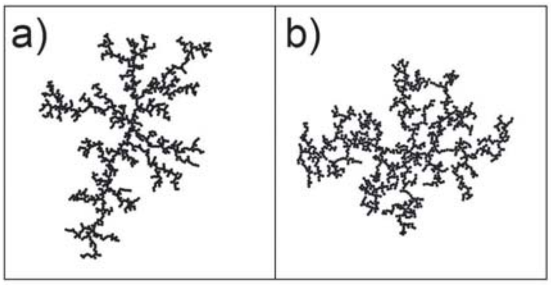

Fig. 4. Snapshots of a DLA before and after the annealing process. Note that the annealed aggregate looks more compact than the original DLA.

This is a clear indication that the aggregate has converged statistically to a relaxed configuration. We also studied the distribution of R_g^2 by counting the number of times a given value of this quantity falls within a given interval. The result is shown in Figure 3 where we plotted the distribution averaged over 10 different configurations. The dashed vertical line shows the value of R_g^2 averaged over the 10 initial DLA configurations. From this figure it becomes evident that the annealed aggregates show an average value of R_g^2 smaller than that corresponding to the average of the original DLA configurations. An example of this is shown in Figure 4 where we present snapshots of an aggregate before and after the annealing process. It can be seen that the annealed aggregate is effectively more compact than the original DLA.

Further evidence of this behavior is given in Figure 5. There we plotted the distance from a given monomer to a monomer of reference – the DLA seed monomer – as a function of its chemical distance, defined as the number of particles that connect the monomer of interest with the monomer of reference. We note that for the annealed aggregate each of its monomers is closer to the reference monomer than the corresponding distance in the original DLA configuration. This results are an indication that the annealing process has produced a more compact aggregate. The slope of this curve – see Figure 5 – is related to chain stretching along that chemical path [32]. As seen in the figure, a leveling of the curve close to the ends indicates that such particular branch has underwent thermal relaxation whereas the internal monomers have retained their original stretching. This is a well known steric effect that is also present in polymer brushes [33] and star polymers [34]. Close to the center of the structure, where the monomer density is higher, excluded volume interactions stretch branches outwards from their central attachment point. On the contrary, there is no force acting on the free ends of the branches. Therefore, chain stretching decreases from its maximum at the center to a minimum vanishing value at the free-ends.

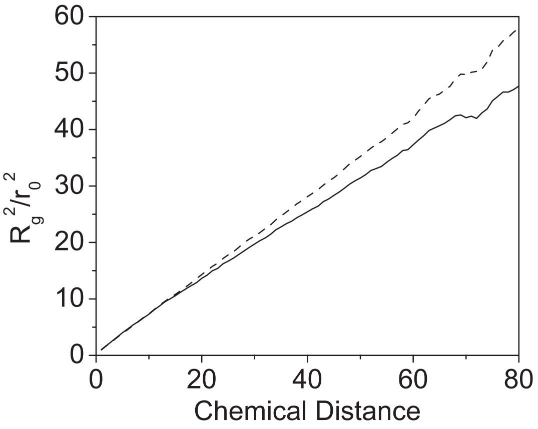

Fig. 5. Distance from any given monomer to the DLA seed monomer, as a function of the chemical distance between them. DLA aggregates (dashed line) and annealed aggregates (solid line). The slope of the curve measures the stretching of the branches. This figure shows clearly that the branches of the annealed aggregates are less stretched than those of the regular DLA. Results are the average over 10 different configurations with $N = 1000$ monomers each one.

At this point it is important to recall that the final aggregate is the result of a quenching process (DLA formation) plus the annealing one that in some sense mimic the statistical and thermodynamic fluctuations produced by the conformations due to the Brownian motion of each monomer. To make a quantitative estimate of the compactness of the aggregates we calculated the fractal dimension of each aggregate after the annealing process has taken place . This quantity was calculated using two different procedures: (i) the well known box counting method [35] and (ii) the particle density correlation function. Using the first method the fractal dimension of an annealed aggregate was the result of averaging the fractal dimensions of 100 different configurations taken every 10^6 MC moves. In doing so for each one of the ten aggregates we obtained the average fractal dimension $d_f = 1.69 \pm 0.01$. Using the same procedure we obtained, for the regular two-dimensional DLA, $d_f = 1.66 \pm 0.04$. We applied the second procedure to calculate the fractal

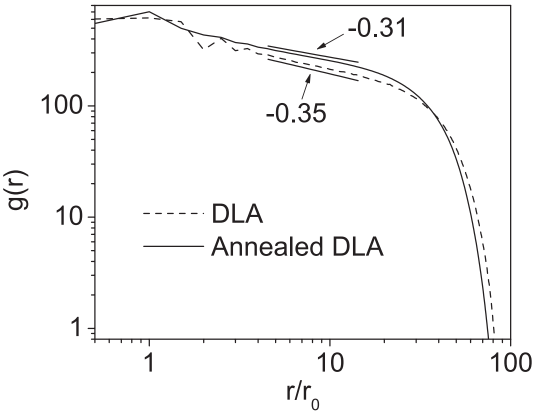

Fig. 6. Particle density correlation function for the DLA and the annealed aggregate. The fractal dimensions are extracted from the slopes of the plotted straight lines.

dimension of the aggregates after performing 10^6 MC moves, by averaging the fractal dimensions of all the consecutive configurations, and further averaging over the ten different aggregates obtaining, $d_f = 1.69 \pm 0.05$, while for the regular two-dimensional DLA we obtained, $d_f = 1.65 \pm 0.08$, in agreement with the results obtained using the box counting method. In Figure 6, we show the two-particle density correlation function, $g(r)$, from which the fractal dimension was obtained. The fractal dimension is obtained from the slopes of the straight lines shown in the figure by, $d_f = 2 + \text{slope}$.

As one can see, in both cases, annealed and regular DLA, the fractal dimensions are very similar within the error bars. However, we obtained consistently that the average fractal dimension of the annealed aggregate is slightly larger than that of the regular DLA. This finding is similar to those found in reference [14] where a fluctuating three-dimensional DLA was considered, and in reference [31] where a randomly branched polymer was annealed. We should mention that the fractal dimension we get for the regular DLA (1.66) is consistent with the value obtained in reference [36] for small aggregates. Nevertheless, we should recall that the fractal dimension of a large off-lattice two-dimensional DLA is $d_f = 1.71$, (see Refs. [36,37]). Therefore one should expect that for a large annealed aggregate the fractal dimension should be slightly larger than 1.71, to be consistent with the result we get in the present study. As a point of statistical comparison of the present results we may bring to our attention the study of reference [14]. There, a total of $N = 3000$ monomeres were used to build up successfully three-dimensional fluctuating DLA structures. Nonetheless, in our present study, due to the reduced dimensionality of the space – two dimensions – the spatial extension of the aggregates is larger than that of reference [14]. Because of this, one would expect results with better statistics. Thus, the conformational properties of the aggregates with $N = 1000$ monomers studied here should be statistically meaningful. The slightly increased compactness of the annealed aggregates is due to its internal flexibility and steric effects produced by the excluded volume interactions. This may be readily understood by considering a directed one dimensional growth process without internal mobility – rigid bonds. This process would yield a rod-like object with fractal dimension $d_f = 1$. However, by introducing flexibility at the "bonds" this one-dimensional object would eventually undergo a self-avoiding walk process due to excluded volume effects. The resulting object would have fractal dimension $d_f \approx 1.33$ in two dimensions [38], a fractal dimension much larger than the original rod-like object. The results obtained here mean that the conventional DLA growth process does prepare quenched but statistically stretched and rigid structures.

4 Conclusions

In conclusion, we have shown by means of extensive MC simulations that when the rigid bonds in a regular DLA are substituted by flexible ones with excluded volume interactions, the system relaxes to a structure with a fractal dimension only slightly higher than that of the original diffusion-limited aggregate in spite of the important compaction of the aggregate that the annealing process causes. That is to say, two different processes, diffusion and excluded volume interactions with flexible bonds, yield structures with fractal dimensions that differ by a small amount in spite of the large difference in the value of their respective radius of gyration. This is somehow surprising since excluded volume interactions always introduce a repulsion between particles that is opposed by the effect of configurational entropy. These two competing effects together with connectivity determine the fractal dimension of the annealed structure, whilst in the rigid DLA only diffusion counts for the fractal dimension value.

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