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Dynamical scaling of fractal aggregates in dense colloidal solutions

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We present results from a detailed Monte Carlo study of a two-dimensional off-lattice system of a dense colloidal solution undergoing a diffusion-limited-cluster-aggregation (DLCA) process. We find that the dynamical structure factor, $S(k,t)$, scales with the characteristic linear size of the aggregates, $R_g(t)$, according to $S(k,t)=R_g^{D_f}\mathcal{F}(kR_g(t))$, where D_f is the fractal dimension of the clusters and $\mathcal{F}$ is a universal scaling function. We have verified that the shape of this scaling function compares well with the experimentally obtained scaling function. Although this behavior is similar to the dynamical scaling law found in systems undergoing spinodal decomposition, we find that some details of the evolution process of the DLCA model are quite different from the dynamics of phase-separating systems.

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Dilute colloidal systems in a thermodynamically unstable state have attracted considerable research interest during recent years. Much theoretical and experimental effort have been directed towards understanding the kinetic aspect of the aggregation process, which leads to the formation of fractal structures [1–4]. The evolution of these systems has been successfully understood by the well known diffusion-limited-cluster-aggregation (DLCA) model [5], where the initial colloidal monomers execute a Brownian motion until small clusters are formed, and then the clusters themselves diffuse and aggregate to form even larger clusters.

Recently, low-angle light scattering experiments [6,7] and numerical simulations [8,9] in colloidal solutions of high monomer concentration have shown a dynamical scaling behavior surprisingly similar to that observed in systems undergoing spinodal decomposition (SD). This result was quite unexpected since, in dilute systems, scattering data showed a maximum in the structure factor only at zero wave number, indicating that, during the growth process, clusters are randomly positioned in space and no correlation is established between them. However, in concentrated solutions the scattered intensity distribution shows a pronounced peak at a finite value of the the wave, k_m. Furthermore, the position of the peak moves to smaller values as the aggregation proceeds, while the peak intensity increases. In the later stages of the aggregation process, the dynamical structure factor, $S(k,t)$, is found to scale according to the following form:

$$S(k,t)=k_m^{-D_f}F(k/k_m), \tag{1}$$

where $F(\xi)$ is a time-independent scaling function, and D_f is the fractal dimension of the colloidal clusters. This scaling form is characteristic of the physical systems undergoing SD [10], except that the exponent in the scaling function is d, the spatial dimension of the system, instead of D_f.

The purpose of this paper is to understand how the irreversible aggregation of colloidal particles in dense systems may lead to the same type of dynamical scaling behavior observed in SD processes. Also, one would like to find out the similarity and the differences between the detailed dynamical evolution of the two types of systems. For this purpose, we have carried out a detailed Monte Carlo simulation of a DLCA model in a two-dimensional off-lattice system with periodic boundary conditions. We find that the SD-type dynamical scaling is satisfied in the DLCA model, while the structure of the interface and the growth law for the characteristic size of the clusters show nonuniversal features.

In the simulation, we have considered a cell of dimensions $L\times L$, where L is equal to 256 times the monomer diameter, the unit of length considered here. We start by randomly placing single particles in the cell, in such a way that the area fraction occupied by the monomers covers 10% of the total area available. Such area fractions compare well with experimental values [7]. The excluded volume criterion is assumed, so that the particles are not allowed to overlap with each other. We have implemented a *link cell* (LC) method [11] to efficiently compute the subset of clusters with which a particular cluster interacts. The simulation process continues, first by choosing at random one of the clusters (initially the clusters are equivalent to single monomers), and then this cluster is moved, by executing a translation motion in a randomly chosen direction. If, during this motion, any monomer in this cluster comes into contact with a monomer in another cluster, these two clusters aggregate and form a larger cluster. The geometry of the clusters is explicitly taken into account during movements or aggregation. Time is measured in units of Monte Carlo steps per cluster (MCS).

In Figs. 1 and 2 we show snapshots during a typical evolution process obtained from a DLCA model at late stages of the aggregation process. These resemble the experimentally observed structures in two dimensions [7] quite well. In these figures one observes that the clusters grow by draining material from their immediate neighborhood, thus creating depletion zones around them. One expects, then, that this general structure comprised of alternating clusters and depletion regions may lead to a density modulation with a wavelength of the order of the mean size of the clusters. This particular observation can easily explain the peak of the

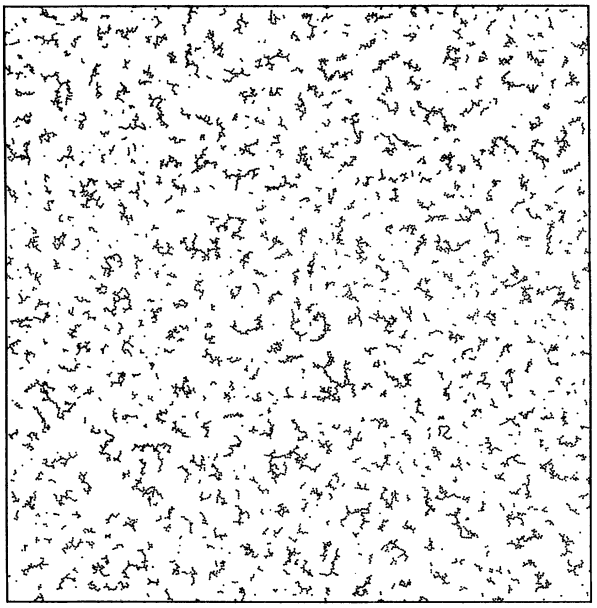

FIG. 1. Snapshot at $t=25$ MCS of a typical configuration during the DLCA process. The monomers cover an area fraction of 10%. Observe the depletion zones formed around the colloidal clusters.

structure factor at a finite k value. Figures 1 and 2 also suggest that the aggregation process is self-similar in time, if one does a time-dependent length rescaling. One can then expect a dynamical scaling form for the structure factor similar to the one found in phase-separating systems.

In order to test the scaling hypothesis we have computed the time-dependent structure factor defined as

$$S(\mathbf{k},t)=\left\langle \frac{1}{N}\sum_{\mathbf{r}} e^{i\mathbf{k}\cdot\mathbf{r}}\sum_{\mathbf{r}'} [n(\mathbf{r}+\mathbf{r}')n(\mathbf{r}')-\langle n\rangle^2]\right\rangle. \quad (2)$$

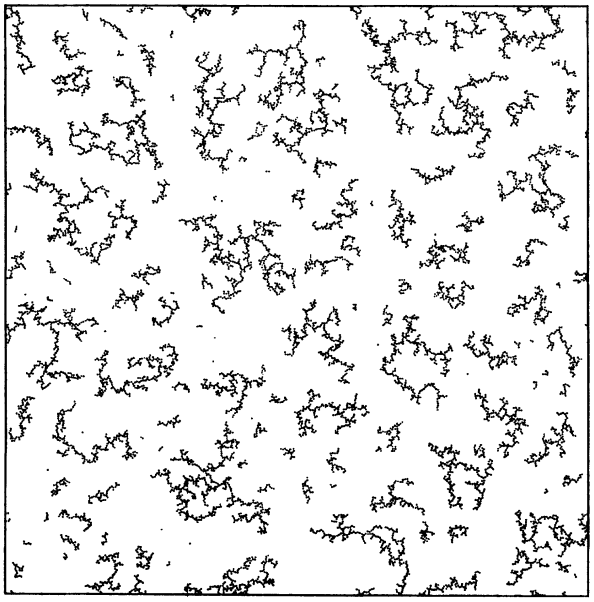

FIG. 2. Same as Fig. 1 except that $t=100$ MCS here.

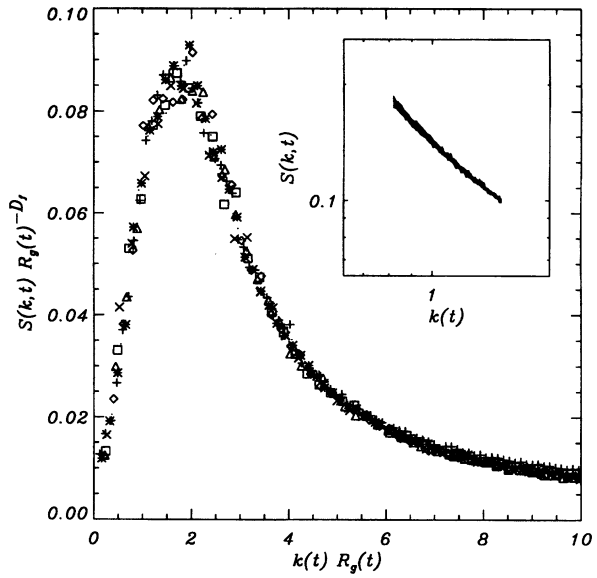

FIG. 3. Plot of the universal function $\mathcal{F}(kR_g(t))$ against $kR_g(t)$ at late stage of the aggregation process. The symbols refer to the following: $t=30$ (+); $t=50$ (*); $t=60$ ($\cdot$); $t=70$ ($\diamond$); $t=80$ ($\triangle$); $t=90$ ($\square$); $t=100$ ($\times$). Note that all data collapse reasonably well into a single master curve, supporting the scaling hypothesis (see text) for the structure factor. Inset: log-log plot of $S(k,t)$ for large k values, demonstrating the fractal scaling at short length scales, and yielding $D_f=1.4\pm0.05$.

In order to compute this quantity we have used a grid of $N=256\times256$ lattice points, and considered $n(\mathbf{r})$ to be the number of monomers having the integer part of their coordinates equal to the lattice vertex $\mathbf{r}$. We have then calculated the circularly averaged structure factor $S(k,t)$ from $t=1$ MCS to $t=100$ MCS. Data has been finally averaged over 20 different initial configurations. One now needs to determine the position of the maximum of the structure factor, $k_m(t)$, and the fractal dimension, D_f of the clusters, in order to test the scaling hypothesis for $S(k,t)$.

The fractal dimension D_f can be computed from the asymptotic behavior of the structure factor for large k. Since the colloidal structures are fractal aggregates, the large-k behavior of $S(k,t)$ has the following form [14]:

$$S(k,t)\sim k^{-D_f}. \quad (3)$$

The inset plot of Fig. 3 shows, in a logarithmic scale, a plot of $S(k,t)$ for large k at latest time. The best least-square fit to the data yields an exponent of $D_f=1.40\pm0.05$ which is consistent with the values found in the experiments [7] and two-dimensional DLCA simulations [15,16].

The discrete nature of the lattice used to compute the structure factor makes it difficult to precisely determine the location of the peak of the structure factor, $k_m(t)$. Since the inverse of this quantity should be proportional to the characteristic linear size of the fractal aggregates, $R_g(t)$, we tried to compute this latter quantity from the real space pair-correlation function, $G(\mathbf{r},t)$, which is the Fourier transform of the structure factor $S(\mathbf{k},t)$. As before, we consider a circularly averaged pair-correlation function $G(r,t)$ and then define a normalized correlation function: $g(r,t)=G(r,t)/$

$G(0,t)$. The characteristic length, $R_g(t)$, is then taken to be the location of the first zero of $g(r,t)$. The scaled form for the pair-correlation function and the structure factor in terms of $R_g(t)$ can be written as

$$g(r,t)=\mathcal{G}[r/R_g(t)], S(k,t)=R_g^{D_f}\mathcal{F}(kR_g(t)). \quad (4)$$

If the scaling hypothesis is satisfied, $\mathcal{G}(\rho)$ and $\mathcal{F}(\xi)$ should be time-independent functions.

In order to verify the dynamical scaling *ansatz* for the structure factor, Eq. (4), we have plotted in Fig. 3 the universal function $\mathcal{F}(kR_g(t))$ against $kR_g(t)$ (with $D_f=1.40$). Note that the data fall remarkably well onto the same time-independent scaling function [17]. We have verified that the shape of this scaling function compares well with the experimentally obtained scaling function [7]. As dynamical scaling is verified, the peak of the structure factor, $S(k_m,t)$, should scale as a power law with the characteristic cluster size, $R_g(t)$, where the exponent of this power law is equal to the fractal dimension, D_f. The best least-square fit to the above data in a logarithmic representation gives $D_f=1.38\pm0.04$ which, within the error, is in good agreement with the one obtained from the analysis of the structure factor for large k. We can conclude then, that at late time, the scattering intensity and the pair-correlation function are well described by dynamical scaling forms [Eq. (4)].

The previous results, supporting dynamical scaling, have suggested an underlying common mechanism in the dynamics of this irreversible process, with that of phase-separating systems. However, we point out that for binary mixtures undergoing SD, the structure factor behaves as $S(k,t)\sim k^{-(d+1)}$ for large k. This is the so-called Porod's law [12,13], which arises due to the presence of a sharp interface between the domains [18]. As we have shown before, the situation is completely different here, and $S(k,t)\sim k^{-D_f}$ for large k, due to the fractal nature of the clusters. Thus the details of the interface structure are quite different in the DLCA and the SD models.

We now show that the irreversible aggregation process in dense colloidal systems leads to a completely different growth law for the characteristic size of the clusters, when compared to the growth law obtained for SD. In the latter case, it is well established now that the growth law is given by the Lifshift-Slyozov (LS) law [19], $R(t)\sim t^{1/3}$. For the present model, we have computed the asymptotic growth law exponent (α) for the characteristic linear cluster size, $R_g(t)\sim t^{\alpha}$, by plotting in a logarithmic scale (see Fig. 4), $R_g(t)$ vs t. A least-squares fit gives an effective exponent of $\alpha=0.7\pm0.1$ at late times, which is quite different from the LS type growth law observed in SD. As we show in the following, the growth law exponent for the DLCA model is not a universal quantity and depends strongly on the details of the aggregation process.

The mean radius of gyration, R_g, of a fractal aggregate satisfies $R_g\sim s(t)^{1/D_f}$, where $s(t)$ is the mean cluster size. If we assume that the asymptotic behavior of $s(t)$ can be written as $s(t)\sim t^{\beta}$, we can derive the following algebraic relation among the exponents: $\beta=\alpha D_f$. In order to get the value of the exponent β, we have computed $s(t)$ in our numerical model and found that $\beta=1.2\pm0.1$, (see Fig. 5) at late times. Another way to independently check this value of β is to compute it from $S(k_m,t)$. Since $S(k_m,t)\sim R_g(t)^{D_f}$ and $R_g(t)\sim t^{\beta/D_f}$, we get $S(k_m,t)\sim t^{\beta}$. A log-log plot of $S(k_m,t)$ versus t yields $\beta=1.0\pm0.1$ which, despite the numerical difficulty in precisely determining $S(k_m,t)$, is in agreement with our previous results. Note that, within the errors, the relation between α, β, and D_f is also well satisfied.

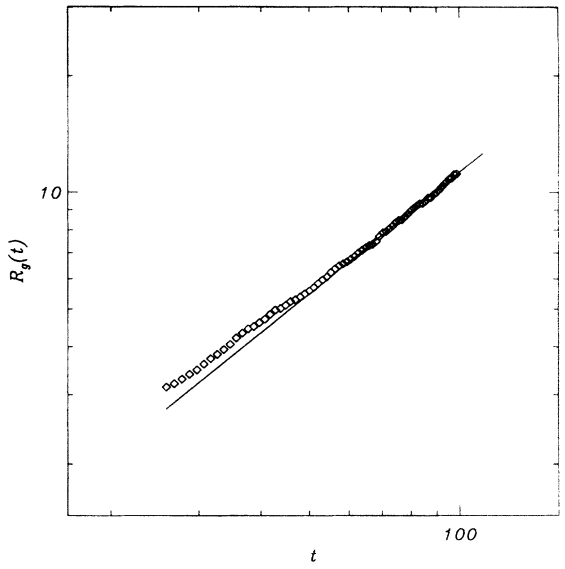

FIG. 4. Log-log plot of the growth of the characteristic linear size of the colloidal clusters, $R_g(t)$. The straight line is the least-squares fit at late times which gives an effective growth exponent of $\alpha=0.7\pm0.1$ (see text).

The value of β can be found, in a mean field (MF) approximation, from the Smoluchowski coagulation equation [20]. The estimated coagulation kernel for fractal aggregates i and j, that coalesce upon contact, is given by [21]

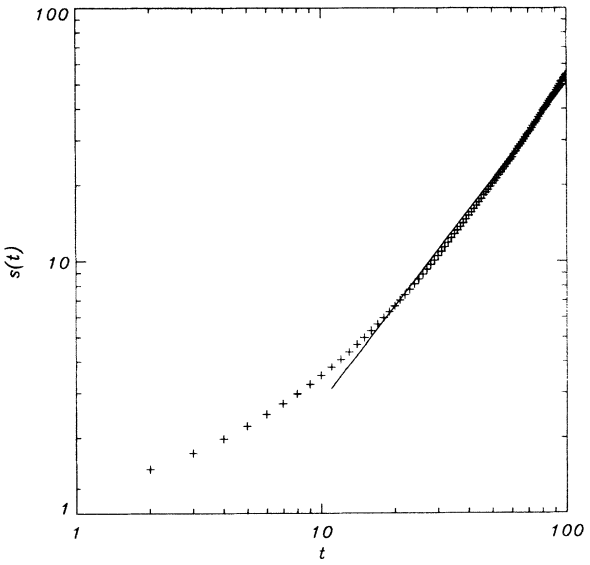

FIG. 5. Log-log plot of the mean cluster size evolution, $s(t)$, vs t. The data at late times are consistent with a power law with an exponent $\beta=1.2\pm0.1$ (see text).

$$K(i,j)=\Lambda(i^{1/D_f}+j^{1/D_f})^{d-1}\left(\frac{1}{i}+\frac{1}{j}\right)^{1/2}. \quad (5)$$

The first factor corresponds to the size dependence of the collision cross section and the second one to the average relative velocity on the reduced mass of the cluster. Here Λ is a constant which depends on physical parameters of the system such as temperature and density of particles. The evolution equation for the mean size, $s(t)$, can then be written easily from the Smoluchowski equation [22,23], and we obtain an asymptotic growth exponent $\beta=2D_f/[3D_f-2(d-1)]$. For $d=2$ and $D_f=1.40\pm0.05$, MF calculations yield $\beta=1.27\pm0.05$ (and as a result $\alpha=0.92\pm0.06$). We should note that the MF approximation should be valid for $d>d_c=2$ [22]. Since our model calculations are carried out *at* the critical dimension, logarithmic corrections to the MF results are expected to be present [22], which might reduce the effective exponent β and α computed in the numerical simulation. However, the MF results are in agreement with the values obtained in our Monte Carlo simulations within the error bars.

In conclusion, we found that the scattering intensity for the DLCA model for dense colloidal solutions satisfies a dynamical scaling behavior characteristic of a SD system. However, there are important differences between the dynamics of the DLCA model and SD models. For example, the interface structure of the two models is quite different, as reflected in the behavior of the tail of the structure factor for large k. Moreover, in SD the growth law exponent is 1/3 independent of the spatial dimension, while for DLCA the growth law exponent is not a universal quantity and it does depend on spatial dimensionality and the fractal dimension of the clusters.

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[16] Computing cluster by cluster the radius of gyration, r_g, and plotting in a logarithmic scale r_g vs the number of particles for each cluster, one could also obtain a slope of $1/D_f$. The best fit to the above data yields $D_f=1.4\pm0.1$ in agreement with our previous result.

[17] We have verified the scaling behavior for the normalized pair-correlation function by plotting $g(r,t)$ against $r/R_g(t)$. Data for various times collapse into a single master curve supporting the scaling hypothesis. We have also verified that there is no multiscaling [for a discussion of multiscaling see, for example, M. Siegert and M. Rao, Phys. Rev. Lett. **70**, 1956 (1993)] in our system.

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