Dynamic Scaling for Aggregation of Clusters

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The model of cluster growth by diffusion-limited aggregation of clusters is studied in two dimensions and the cluster size distribution $n_s(t)$ is determined as a function of the cluster size s and the time t. A dynamic scaling function of the form $n_s(t) \sim t^{-w} s^{-\tau} f(s/t^z)$ is proposed and is shown to lead to the scaling relation $w = (2-\tau)z$ among the critical exponents. The simulation results support this scaling law.

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The formation of large, random clusters by nonequilibrium growth processes such as aggregation, coagulation, flocculation, and polymerization is one of the main features of a wide range of phenomena in science and technology.[1] At the present time, however, our understanding of the basic physics of such nonequilibrium processes is relatively limited in comparison to equilibrium phenomena.

Very recently, Meakin[2] and independently Kolb, Botet, and Jullien[3] have introduced a dynamic growth model to describe cluster formation by aggregation of clusters. This model is a combination of the diffusion-limited aggregation process of Witten and Sander[4] and Sutherland's model[5,6] of aggregation of clusters moving along straight trajectories, and embodies many of the features present in experimental situations. Initially the system consists of a fixed concentration of Brownian particles which irreversibly join together upon contact to form a cluster. The clusters and the single particles continue to diffuse and form new, larger clusters by binding together. Previous studies of this model[2,3] have shown that on a finite lattice the final stage of the process is a highly ramified, scale-invariant structure possessing the relatively low fractal dimension[7] $D \sim 1.4$–1.5 in two dimensions. Although it appears that the Sutherland's aggregates have nearly the same value of D in two dimensions, the dynamics of the two aggregation processes is different, because the time dependence of the distances traveled by the diffusing clusters differs from that of the clusters moving via straight-line trajectories. The fractal nature of these aggregates is a feature shared by other diffusion-limited aggregation models.[4,8]

In this Letter we investigate the cluster size distribution $n_s(t)$ as a function of the cluster size s and the time t in order to describe the temporal evolution of the aggregation process. In contrast, earlier studies have been mainly concerned with the morphology of the large aggregates. The results show that $n_s(t)$ has a *power-law decay*—characteristic of a critical type behavior—in *both s and t*. A new dynamic scaling form for $n_s(t)$ is proposed and is shown to be in agreement with the simulation results. Our approach is analogous to the dynamic scaling theory[9] developed for the time-dependent behavior in thermal critical phenomena. Cluster size distribution has been extensively studied in equilibrium models[10] and its importance in nonequilibrium processes has already been recognized.[11–14] However, the dynamic scaling function introduced here has not been proposed before. We expect this scaling form of $n_s(t)$ to have a wide range of applications in other dynamic aggregation processes.

The two-dimensional simulations of the aggregation of clusters were carried out on a square lattice with periodic boundary conditions. Initially $N_0 = \rho L^2$ particles are randomly placed at N_0 sites of an $L \times L$ lattice. The particles are then allowed to diffuse by use of standard methods.[2,3] Particles at nearest-neighbor positions are permanently joined together to form a cluster. Clusters and particles are picked at random and moved with a mobility independent of their size. Clusters that touch stick together and form a new, larger cluster.

The cluster size distribution is defined by $n_s(t) = N_s(t)/L^2$, where $N_s(t)$ is the number of clusters containing s particles at time t. It is important to point out that in numerical experiments the time unit can be defined in a number of ways. For example, the time interval Δt by which t is increased after a cluster has been moved by one lattice unit can be chosen to be equal to unity ($\Delta t = 1$) or to s/N_0 ($\Delta t = s/N_0$), where s is the number of sites in the shifted cluster. Choosing $\Delta t = 1$ leads to an unphysical acceleration of the clusters with increasing time. The reason is that the number of clusters decreases with time and on the average more steps are made by a given cluster in the same time interval as time increases. In order to have a physical time (i.e., a time-independent cluster diffusivity) we

choose $\Delta t = s/N_0$, because the number of clusters decreases as the inverse of the average cluster size. The definition $\Delta t = s/N_0$ is analogous to the time increment used in the equilibrium calculations[15] (where t is measured in Monte Carlo steps per site and Δt is equal to unity if on the average all of the spins in the cell have been checked once). Therefore, in the following, $\Delta t = s/N_0$ will be used for controlling the time.

The dependence of the cluster size distribution on s at fixed values of t is shown in Fig. 1. These results were obtained with use of an initial particle density $\rho = 0.05$ on a square lattice with $L = 400$. The corresponding results for fixed s and varying t are displayed in Fig. 2. Several important conclusions can be drawn from these figures. The straight lines in Fig. 1 correspond to an algebraic decay of $n_s(t)$ as a function of s. However, in contrast to equilibrium models, the exponent τ characterizing this decay is less than 2. The cluster size at which this decay cuts off scales with t. The plots in Fig. 2 indicate a novel dynamic behavior: For fixed s, $n_s(t)$ decreases with time according to a power law.

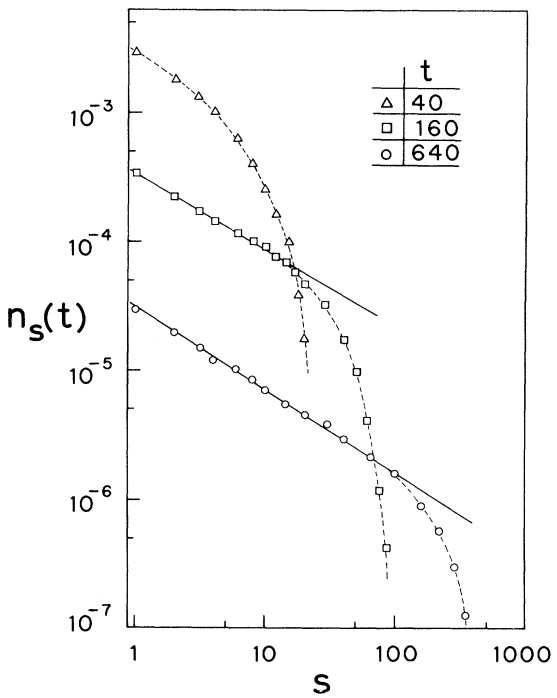

FIG. 1. The cluster size distribution function $n_s(t)$ vs s at times $t = 40$, 160, and 640. These results were obtained by averaging fifty runs on a 400×400 cell for a density $\rho = 0.05$. The straight lines have a slope $\tau \simeq 0.75$ and indicate a power-law dependence of $n_s(t)$ on s. Dashed lines are guides to the eye.

The cluster size distribution found above can be well represented by the following scaling form

$$n_s(t) \sim t^{-w} s^{-\tau} f(s/t^z), \tag{1}$$

where the cutoff function $f(x) \simeq 1$ for $x << 1$ and $f(x) << 1$ for $x >> 1$. A novel feature of (1) is the presence of two new dynamic exponents w and z in addition to the usual static exponent τ. The term t^{-w} describes the power-law decay of $n_s(t)$ with time for every s. This is a specific feature of the cluster-cluster aggregation process, because for $t >> s$, small clusters die out by forming larger clusters. On the other hand, the characteristic cluster size is determined by the denominator t^z. Note that the assumed s dependence of $n_s(t)$ resembles the scaling *Ansatz* used in the theory of thermal and geometrical critical points.[10,16] However, unlike other kinetic growth models,[4,8,17] the time in the cluster-cluster aggregation model is not related to the number of occupied sites in the system since ρ remains constant during the aggregation process.

The scaling function (1) is expected to be valid in the limit $\rho \to 0$ at large s and t. However, the region of t values for which (1) holds depends on L. In a finite system the distribution $n_s(t)$ loses its meaning when the number of clusters is very small or—as it happens at the final stage of the simu-

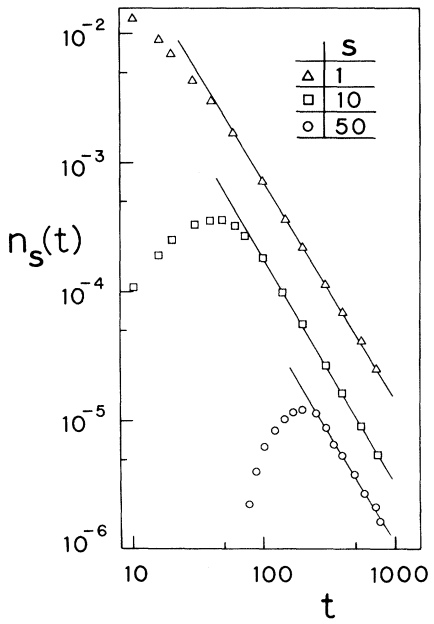

FIG. 2. Dependence of $n_s(t)$ on the time t for three selected clusters sizes $s = 1$, 10, and 50 calculated from the same simulations as Fig. 1. The slopes of the straight lines give the exponent $w \simeq 1.7$ determining the algebraic decay of $n_s(t)$ in time.

lations[2,3]—it becomes equal to 1. Of course, in the thermodynamic limit ($L \to \infty$) this problem does not arise.

As an important consequence of the scaling form (1) and the normalization condition

$$N_0/L^2 = \rho = \sum_s n_s(t)s \sim \int^{\infty} n_s(t)s\, ds, \tag{2}$$

one can obtain a scaling relation among the exponents τ, w, and z. In fact, using (1) and (2) we find

$$\rho \sim t^{-w}\int^{\infty} s^{-\tau+1} f(s/t^z)\, ds \sim t^{-w+(2-\tau)z}. \tag{3}$$

Since ρ remains constant ($\rho < 1$) as t goes to infinity, (3) implies that

$$w = (2-\tau)z. \tag{4}$$

Clearly, τ must be less than 2, because $w,z > 0$ are the only physically meaningful values of w and z. This result is a direct consequence of the dynamics of the model, because in equilibrium models $\tau > 2$. The significance of the inequality $\tau < 2$ for cluster statistics has been pointed out in Ref. 13, where $\tau < 2$ was obtained for diffusion-limited deposition.

The mean cluster size $S(t)$ diverges as $t \to \infty$. Expressing $S(t)$ in terms of $n_s(t)$ and using (1) and (4) we find

$$S(t) = \frac{\sum n_s(t)s^2}{\sum n_s(t)s} \sim t^{-w}\int^{\infty} s^{-\tau+2} f(s/t^z)\, ds \sim t^z. \tag{5}$$

The time dependence of $S(t)$ is shown in Fig. 3. From Figs. 1–3 the following values are obtained for the critical exponents w, z, and τ:

$$w = 1.70 \pm 0.2, \quad z = 1.4 \pm 0.2, \quad \tau = 0.75 \pm 0.15. \tag{6}$$

All three exponents are nonclassical and different from the exponents for related models. The uncertainties given in (6) are only statistical and errors due to finite system size may be significantly larger. The fact that $\tau < 1$ implies that $n_s(t)t^{+w}$ decays very slowly with s. Perhaps the most significant feature of the values in (6) is that they satisfy the scaling relation (4) and support the scaling assumption (1).

The scaling expression (1) can be written in an alternative form

$$n_s(t) \sim s^{-\theta} g(s/t^z) \tag{7}$$

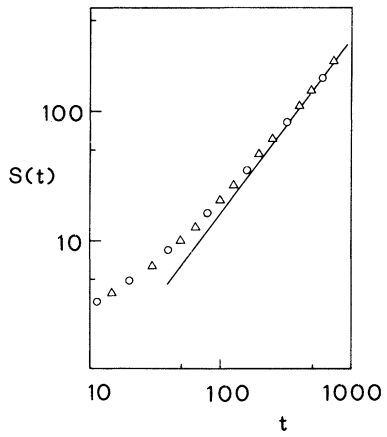

FIG. 3. The mean cluster size $S(t)$ as a function of time. The straight line corresponds to an asymptotic slope $z \simeq 1.4$. Circles and triangles refer to the data obtained from 200 runs with cell size $L = 200$ and 50 runs with $L = 400$, respectively.

with a scaling function $g(x) << 1$ for $x >> 1$ and $g(x) \sim x^{\Delta}$ for $x << 1$, where Δ is usually called the crossover exponent. Although (7) does not contain the power-law decay of $n_s(t)$ in t and s as explicitly as (1), it enables us to discuss the crossover in cluster statistics as a function of time. For $x << 1$, $n_s(t) \sim t^{-z\Delta} s^{-\theta+\Delta}$ and the scaling expression (1) is recovered with $f(x) \simeq 1$ and $z\Delta = w$, $\theta - \Delta = \tau$. Using these expressions in the scaling relation (1) we obtain $\theta = 2$. For $x >> 1$, $n_s(t)$ decays as $1/s^2$, *independent of the dimension,* modified by a function which decreases faster than any power of s.

Our work is the first dynamical scaling and Monte Carlo study of the time-dependent cluster size distribution in the diffusion-limited cluster-cluster aggregation model. The present results can be compared with those obtained from the Smoluchowski coagulation equation approach in which the cluster size distribution has been determined by assuming certain restricted forms for the rate constant. In an early study Sutherland and Goddarz-Nia[6] used a form for $n_s(t)$ which was independent of s at long times. This result disagrees with our Monte Carlo and scaling expression. The main reason for the different simulation result is that the Smoluchowski equation is a mean-field approximation in which the spatial fluctuations are not taken into account, although they play an essential role in the aggregation process.

Although in this Letter we studied the dynamics of the cluster-cluster aggregation model in two dimensions, we would like to point out that a similar type of dynamics is expected in one dimension.

This is in contrast to the static properties, such as the fractal dimension, which are trivial in $d = 1$. Finally, the dynamical scaling approach presented here is perhaps useful in the study of a number of other dynamic processes such as antigen-antibody aggregation,[12] coagulation of Ising droplets in the metastable state,[11] and kinetics of gelation and aggregation as described by the Smoluchowski equation.[14]

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