Diffusion-limited aggregation in which cluster sites have a distribution of reaction times

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Studies of the growth of aggregates have been limited so far to those cases where the aggregate particles can react with incoming Brownian particles for infinite time. Recently, Miyazima *et al.* have investigated the effect of a fixed reaction time τ and have found that the long-time aggregates in two dimensions have a fractal dimension $d_f \simeq 1.04 \pm 0.03$ for all finite τ values. Here we study square lattices, in which, in the more general case, each aggregate site is randomly assigned an infinite reaction time (with probability q) or a finite reaction time (with probability $1-q$). We find a dynamical phase transition at $q=q_c=0.5$ and three different values for d_f: $d_f \simeq 1.04$ ($q<q_c$), $d_f \simeq 1.5$ ($q=q_c$), and $d_f \simeq 1.7$ ($q>q_c$), irrespective of the magnitude of τ.

In recent years considerable attention has been addressed to models for aggregation processes (for reviews see Refs. 1–4). In nature there exists a large variety of aggregates, including snow flakes, polymer aggregates, and colloids. One of the major scientific goals is to develop an understanding of the relationship between the pattern of an aggregate and the aggregation mechanism.

A classical model for diffusion-limited aggregation is the Witten-Sander (WS) model, where Brownian particles are added, one at a time, to a growing cluster or aggregate. The particles perform random walks originating far away from the aggregate, and stick when they come in contact with the aggregate.[5] The WS model has been successfully used to describe electrical deposition,[6] dielectric breakdown,[7] viscous fingering,[8] and, with slight modifications, some types of snow flakes.[9]

Very recently, Miyazima *et al.*[10] have studied the effect of a finite reaction time τ on diffusion-limited aggregation. In their model, time t is identical to the number of sites in the aggregate and it is assumed that a site generated at time t_1 can be active and can react with incoming Brownian particles only up to time $t_1+\tau$. This means that a particle can stick at that site only up to time $t_1+\tau$; for larger times the site is inactive. Clearly, WS aggregation corresponds to the limit of $\tau=\infty$, the diffusion-limited self-avoiding walk (DLSAW) introduced by Bradley and Kung[11] corresponds to $\tau=1$.

Similar types of time correlations have been studied in the Eden model and in models for epidemics.[12–14] In all cases it was found that finite lifetimes (as is the finite reaction time here) have a strong effect on the structure and the kinetics of aggregates.

In WS aggregation, finite reaction times change the pattern drastically. When all sites in the aggregate have the same reaction time τ, the growth process can be characterized by a crossover time t_x; for times well below t_x, WS aggregates ($d_f \simeq 1.7$) are formed, while for times well above t_x, chainlike patterns are generated, with a fractal dimension $d_f \simeq 1.04$. The crossover time increases with increasing τ value.

Motivated by the desire to describe more general types of aggregation, where not all aggregate particles are identical, we introduce here a model for diffusion-limited aggregation, in which a fraction q of the particles have an infinite reaction time (as in the WS model), with the remaining fraction $1-q$ having a finite reaction time τ_0, i.e.,

$$\tau = \begin{cases} \infty & \text{with probability } q \\ \tau_0 & \text{with probability } 1-q \end{cases} . \tag{1}$$

This new model reduces to the WS model for $q=1$ and to the model discussed by Miyazima *et al.*[10] for $q=0$. We find that at a critical value of the parameter q, q_c, the fractal dimension changes from $d_f \simeq 1.04$ ($q<q_c$) to $d_f \simeq 1.5$ ($q=q_c$) and to $d_f \simeq 1.7$ ($q>q_c$). On the square lattice we find $q_c=\frac{1}{2}$ which is identical to the critical bond concentration. The change in the pattern of the aggregate, for $\tau_0=10$, can be seen in Fig. 1. Below q_c, the aggregates look more like chains, with side branches getting larger when q_c is approached. At q_c the structure changes; the pictures for $q=0.5$, 0.6, and 0.8 look more like WS aggregates ($q=1$), but with larger holes inside. The size of the holes increases when q_c is approached.

To obtain the phase diagram, we carried out an extensive series of Monte Carlo simulations for $q=0.2$, 0.4, 0.5, 0.6, and 0.8 and several τ_0 values. We used square lattices of size 800×800 and t up to 5000 time steps. To determine d_f, we calculated $\langle r^2 \rangle$, the mean-square distance of the last added site from the seed of the aggre-

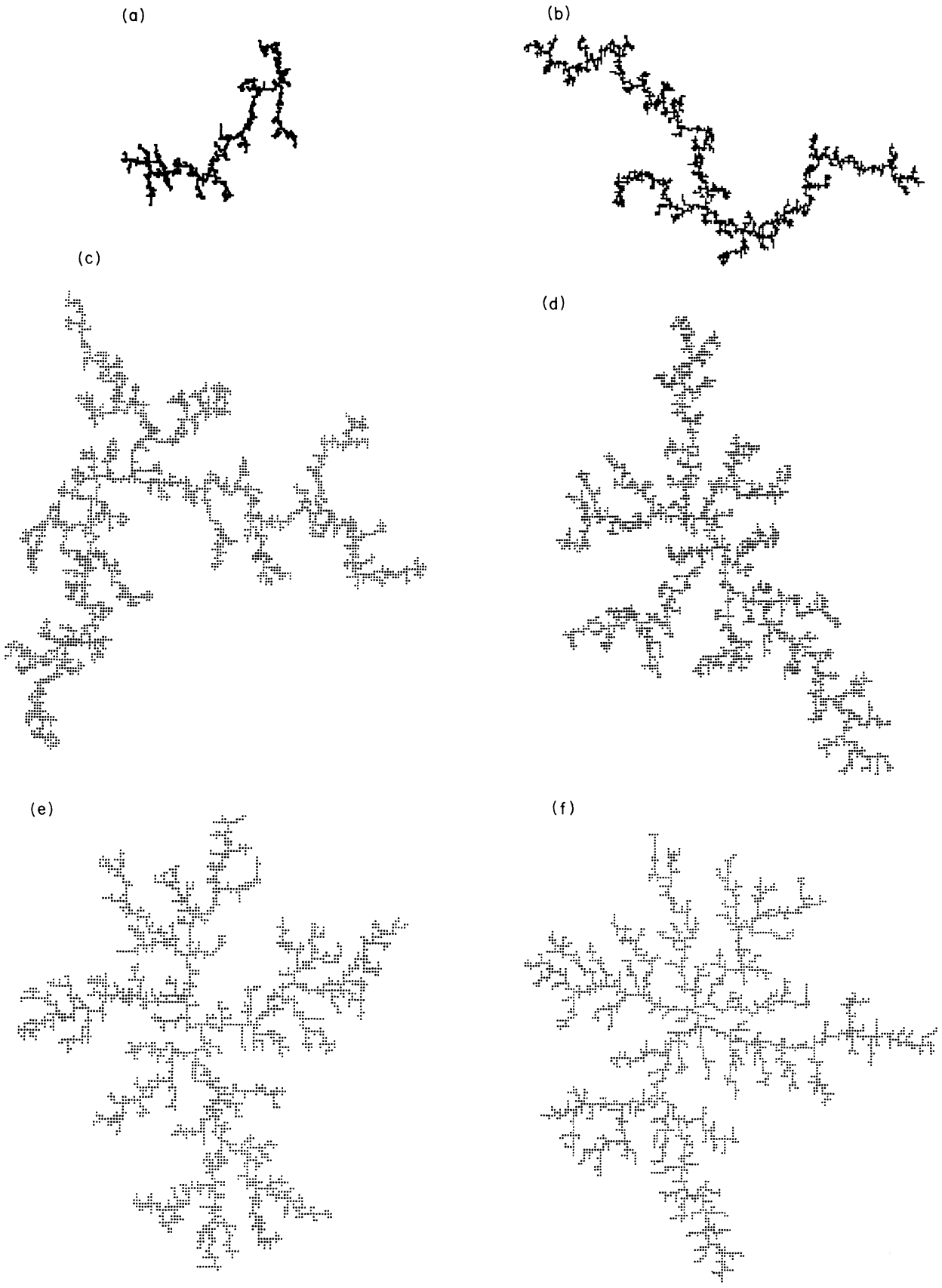

FIG. 1. Typical clusters for $\tau_0=10$ and (a) $q=0.2$, (b) $q=0.4$, (c) $q=0.5$, and (d) $q=0.6$, and (e) $q=0.8$ compared with the Witten-Sander aggregate, (f) $q=1$. The number of cluster sites is (a) $s=600$, (b) $s=1000$, and (c)–(f) $s=2500$.

gate. Since a new site is added at each unit of time, the cluster mass is given by t and, asymptotically,

$$\langle r^2 \rangle \sim t^{2/d_f} . \tag{2}$$

For $q=0.2$ and 0.4 we obtained $d_f=1.04$, for $q=0.5$ we found $d_f=1.5$, and for $q=0.6$ and 0.8 we obtained $d_f=1.7$, independent of τ_0.

Figure 2 shows $\langle r^2 \rangle$ as a function of time for $\tau_0=10$ and four representative q values. For $q=0.2$ and 0.4, the asymptotic slope is $2/d_f \simeq 1.92$, which gives $d_f \simeq 1.04$. As in Ref. 10, we cannot exclude the case $d_f=1$. For $q=0.5$, we find $d_f=1.5\pm0.1$, while for $q=0.8$, we find $d_f=1.7\pm0.1$, which agrees with the fractal dimension for WS aggregates ($q=1$).

To reveal the asymptotic behavior of $\langle r^2 \rangle$ we have plotted, in Fig. 3, $\langle r^2 \rangle / t^{2/d_f}$ for $q=0.2$, 0.5, and 0.8 with $d_f=1.04$, 1.5, and 1.7, respectively. The results for $q=0.2$ and 0.5 are for two reaction times, $\tau_0=5$ and 10, and the result for $q=0.8$ is for $\tau_0=10$. For large times, all curves reach a plateau, which supports the anticipated values of the fractal dimensions.

Clearly, the asymptotic slopes are not affected by the magnitude of τ_0, but for $q<q_c$ the crossover time above, for which asymptotic behavior is observed, increases strongly with an increasing value of τ_0 (Fig. 4). Below the crossover time (which is about 200 for $\tau_0=20$ in Fig. 4), small diffusion-limited aggregation (DLA) clusters are formed and $\langle r^2 \rangle \sim s^{2/1.7}$, accordingly. The asymptotic result for d_f agrees with the $q=0$ result of Miyazima *et al.*,[10] but it differs from the result of Bradley and Kung[11] ($d_f \simeq 1.29$) for the DLSAW which corresponds to $q=0$, $\tau_0=1$. The discrepancy may be due to the fact that

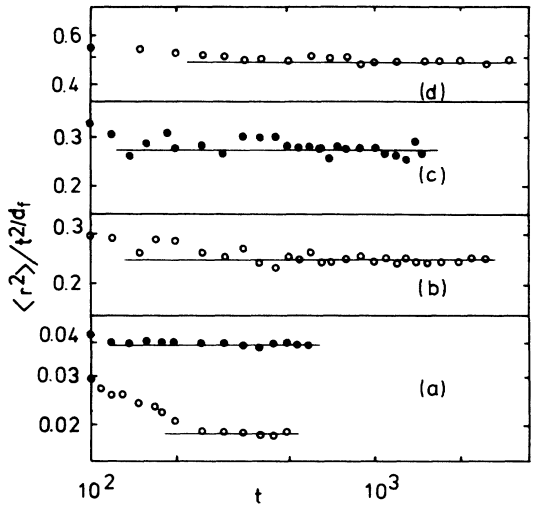

FIG. 3. Double logarithmic plot of $\langle r^2(t) \rangle / t^{2/d_f}$ vs $t=s$ for aggregates with (a) $q=0.2$, $\tau_0=5$ (●) and 10 (○); (b) $q=0.5$, $\tau_0=10$; (c) $q=0.5$, $\tau_0=5$; (d) $q=0.8$, $\tau_0=10$. The anticipated values for the fractal dimensions are $d_f=1.04$ ($q=0.2$), $d_f=1.5$ ($q=0.5$), and $d_f=1.7$ ($q=0.8$). The data in (a) and (b) are based on averages over 200 configurations each. For obtaining (c) and (d) we averaged over 100 and 225 configurations, respectively.

Bradley and Kung considered only small chains (32 sites) where transient behavior may be dominant. Such a situation occurs, e.g., in kinetic growth walks (KGW), where d_f is considerably overestimated ($\frac{3}{2}$ instead of $\frac{4}{3}$) when small systems ($\sim 10^2$ sites) are studied.[15] As can be seen from Figs. 2–4, the crossover times increase with increas-

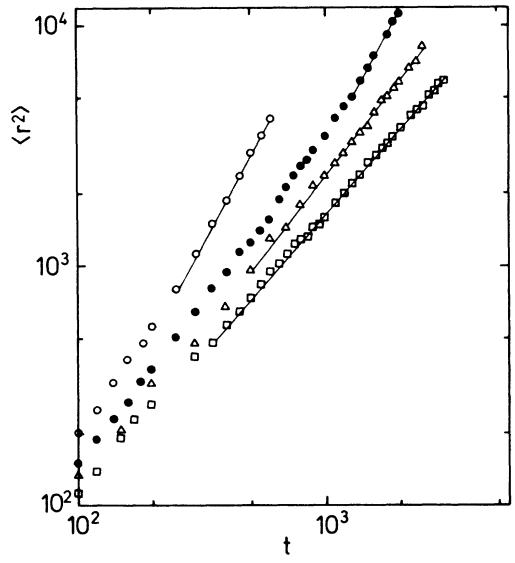

FIG. 2. Plot of the mean square of the end-to-end distance $\langle r^2(t) \rangle$ vs $t=s$ for aggregates with $\tau_0=10$. ○, $q=0.2$; ●, $q=0.4$; △, $q=0.5$; □, $q=0.8$. For $q=0.2$, 0.4, and 0.5, the data are based on averages over 200 configurations each; for $q=0.8$ averages over 225 configurations have been made. The reaction time τ_0 is $\tau_0=10$.

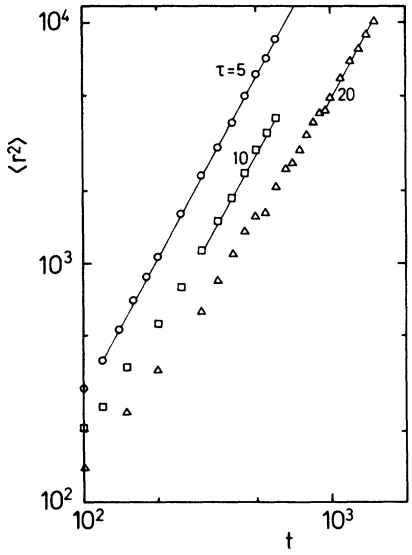

FIG. 4. Plot of the mean square of the end-to-end distance $\langle r^2(t) \rangle$ vs $t=s$ for aggregates with $q=0.2$ and several values of reaction times τ_0. The lines denote the asymptotic slopes of the curves. $\tau_0=5$ and 10, averages over 200 configurations have been made. The results for $\tau_0=20$ are based on averages over 100 configurations. The reaction time τ_0 is $\tau_0=10$.

ing τ_0 and when approaching q_c.

For the square lattice, the critical concentration is $\frac{1}{2}$, which is identical to the critical bond concentration. To see why the parameter q plays the same role as the concentration of bonds in percolation, consider first the case $\tau_0=0$. A fraction q of the aggregate sites has an infinite reaction time and a remaining fraction $1-q$ has zero reaction time, becoming inactive immediately. That is, of the z bonds where incoming Brownian particles can stick to the aggregate, a fraction q are open and a fraction $1-q$ are blocked. Below the critical bond concentration q_c, only finite aggregates can be formed, while for q close to 1 we expect Witten-Sander-type clusters. Since q_c is the only critical concentration here, we anticipate finding WS exponents for all q above q_c.

Next consider $\tau_0>0$. Below q_c, the short reaction times dominate the process and we find chainlike structures, as for $q=0$. At the critical concentration, an infinite cluster consisting only of particles with infinite reaction time (which is fractal on all length scales) can be generated and d_f is intermediate. But note that our value for d_f differs from the value for WS aggregation on the infinite percolation cluster, where either $d_f \simeq 1.40$ (if also the mobile particles are confined to the infinite cluster) or $d_f \simeq 1.89$ (Ref. 16) (if the mobile particles are unrestricted). Above q_c, the particles with infinite reaction time dominate the aggregation process and $d_f \simeq 1.7$, as in the WS model.

So far we have considered aggregation processes where the elapsed time was identical to the number of sites s in the aggregate: If an aggregate site was assigned to a finite reaction time τ_0, then the next τ_0 incoming Brownian particles could stick to this site. A more natural way of counting time would involve the diffusion constant of the embedding medium: Time is enhanced by 1 when the Brownian particle moves to a nearest-neighbor site. However, we can argue that such a more complicated system can be mapped onto the system considered here, but with τ_0 distributed around some mean value $\bar{\tau}_0$ (Ref. 17). Since our basic results for the critical concentration and the fractal dimensions do not depend on the magnitude of τ_0, they should also apply in this case.

In summary, then, we have introduced a new model for diffusion-limited aggregation where a fraction $1-q$ of aggregate particles can react with incoming Brownian particles only for a certain time range after getting stuck in the aggregate. We have found a dynamical phase transition at a critical concentration q_c which is identical to the critical bond concentration of the lattice. Below q_c the aggregate is described by the fractal dimension $d_f \simeq 1.04$, at q_c we have $d_f \simeq 1.5$, and above q_c we found $d_f \simeq 1.7$. We believe that the type of heterogeneous time correlations discussed here for the Witten-Sander aggregate will also have drastic effects on other aggregation processes, e.g., on cluster-cluster aggregation.

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[17] In a recent work, Havlin and Trus (unpublished) studied the distribution of arrival times of Brownian particles at DLA, which are released from a circle with fixed radius. They found that the arrival times were distributed around some mean value $\bar{t}$, with fluctuations of the order of $\bar{t}$.

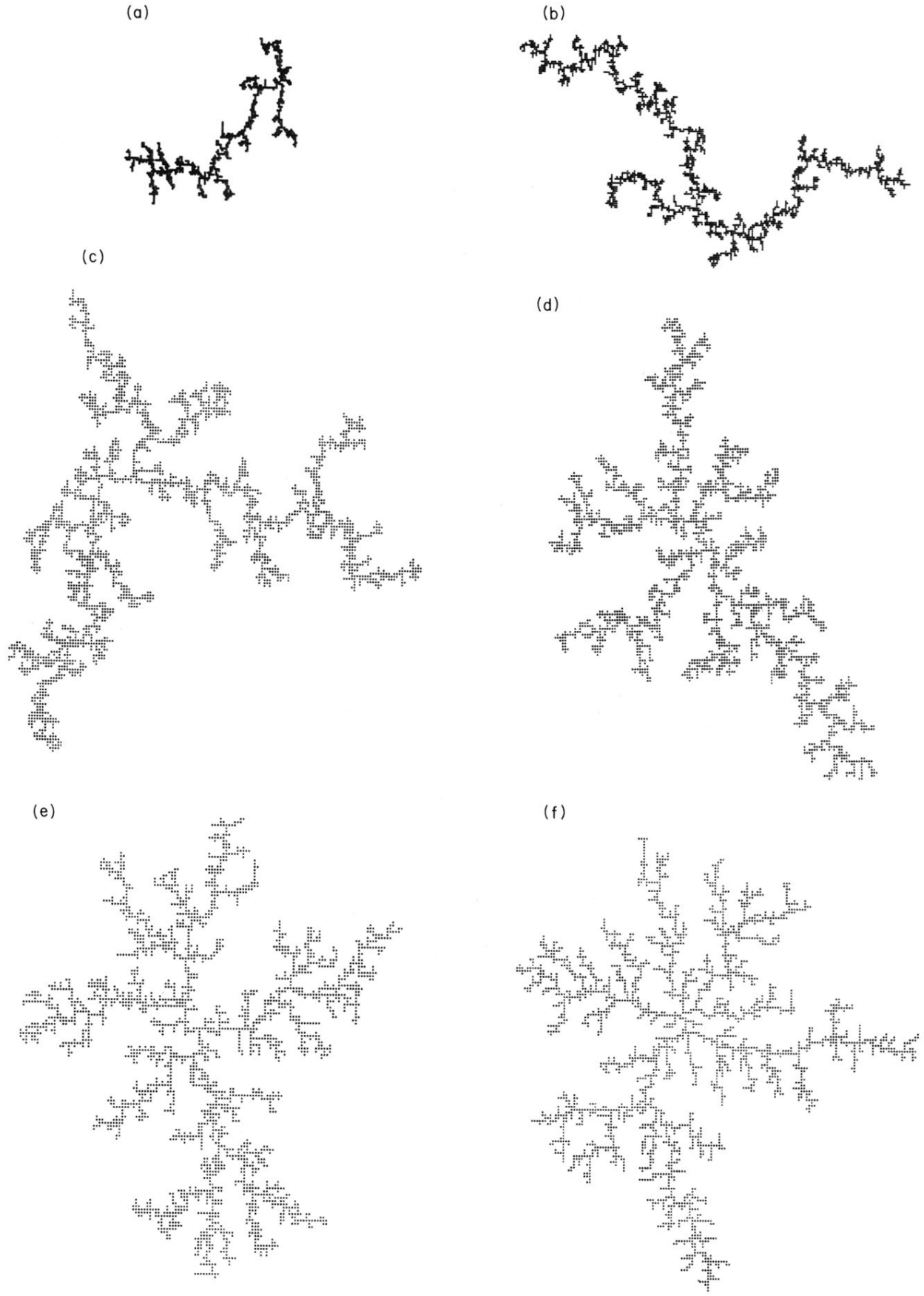

FIG. 1. Typical clusters for $\tau_0 = 10$ and (a) $q = 0.2$, (b) $q = 0.4$, (c) $q = 0.5$, and (d) $q = 0.6$, and (e) $q = 0.8$ compared with the Witten-Sander aggregate, (f) $q = 1$. The number of cluster sites is (a) $s = 600$, (b) $s = 1000$, and (c)–(f) $s = 2500$.