Unified Description of Static and Dynamic Scaling for Kinetic Cluster Formation

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A scaling theory is developed for aggregation by means of kinetic clustering of clusters. A global picture of static and dynamic critical properties emerges, whereby the dynamic critical exponent can be related to the fractal dimension. Furthermore, the growth process is described in terms of a purely kinetic model. The scaling predictions agree well with numerical results.

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Aggregation phenomena occur in many different experimental situations.[1-9] The best studied model describing such growth processes is diffusive particle aggregation[10] which has been investigated numerically[10,11] and with mean-field arguments.[12-14] Furthermore, time-dependent properties were studied in a continuum formulation.[15,16] Here, I wish to study aggregation by kinetic clustering of clusters.[17,18] This is a simple model for irreversible cluster growth which applies to two physical situations: flocculation and kinetically induced gelation. In both cases, the random growth process leads to large ramified structures. Flocculation corresponds to the limit of low cluster concentration and gelation to the limit of high cluster concentration (to be defined precisely below). The flocculation limit has been investigated numerically to determine the fractal dimension D of individual clusters[17,18] and gelation will be considered elsewhere.[19] In the present calculation, I explore the assumption that the whole system of diffusing clusters is scale invariant in the flocculation region. As a consequence, time-dependent properties and the mass distribution of the clusters can be described in terms of scaling. The static and dynamic exponents then are related to each other. The arguments used to obtain this result also suggest that a purely kinetic approach in terms of the Smoluchowski equation with appropriately chosen kernel should describe this process correctly. Direct simulations analyzed in terms of scaling variables are in good agreement with these theoretical predictions.

The precise definition of clustering of clusters is as follows: N_0 particles (considered to be clusters of mass $m=1$) are randomly distributed on a periodic d-dimensional hypercubic lattice of volume $V_0=L^d$. No two clusters can occupy the same site. They move independently of each other in a random-walk fashion. The velocity v of a diffusing cluster of mass m is

$$v(m)=m^{\alpha}, \tag{1}$$

where the exponent α can be adjusted to suit the experimental situation of interest. This motion is simulated on the lattice by randomly picking a cluster and moving it with a probability proportional to $v(m)$ by one lattice spacing in one of the $2d$ possible directions (also chosen at random). Whenever two (or more) clusters touch each other, i.e., when they are nearest neighbors on the lattice, they stick together permanently and thus form a new, larger cluster with a mass equal to the sum of the masses of the constituent clusters. This new cluster also diffuses according to Eq. (1), along with the other clusters in the system. The sticking rule makes this growth process completely irreversible: The number of clusters N steadily decreases and, correspondingly, the average mass $\bar{m}=N_0/N$ increases.

Simulations of this growth model show that at any given moment the clusters all have about the same size; thus small clusters are formed from single particles first, then larger clusters are generated from smaller ones, etc. Hence the name kinetic clustering of clusters. The different stages of the growth are shown in Fig. 1 of Ref. 18. Large clusters of mass m are very ramified and can be characterized by a radius $R\sim m^{1/D}$, where D is their fractal dimension. A useful quantity for this growth process is the cluster density (quantities with a bar denote averages over all the clusters in the system)

$$\rho=N/V=\rho_0\bar{m}^{(d-D)/D}, \tag{2}$$

where $V=V_0/\bar{R}^d$ is the volume measured in units of the cluster radius $\bar{R}$ and $\rho_0=N_0/V_0$ is the initial density. ρ defines two interesting regimes for a scaling analysis: For $\rho\ll 1$ the distance $\bar{l}$ between clusters is much larger than $\bar{R}$ (flocculation) while for $\rho\simeq 1$ the two lengths are comparable (gelation). It is easy to understand why the two situations have different properties. For $\rho\ll 1$ the clusters travel a distance much larger than $\bar{l}$ before they meet each other ($d\gg 2$), and hence the correlation between them can be neglected. For $\rho\simeq 1$, however, neigh-

boring clusters are strongly correlated. From Eq. (2) it is clear that there is always a crossover to the compact regime, no matter how small ρ_0 ($D < d$, $L \to \infty$). This picture is supported by the numerical results, which give different exponents for flocculation[17,18] (D_f) and gelation[19] (D_g), $D_f < D_g$.

Here, only flocculation will be considered. For the simulations this means that one has to choose ρ_0 sufficiently small and L large enough to satisfy simultaneously $1 \ll N \ll N_0$ and $\rho \ll 1$. The results in two dimensions show that D_f does not—to within numerical accuracy—depend on $\alpha \lesssim 0$. I have extended the simulations to higher dimensions obtaining $D_f = 1.72 \pm 0.10$, 2.02 ± 0.10, 2.30 ± 0.15, and 2.60 ± 0.15 for $d = 3$, 4, 5, and 6. Again, D_f appears insensitive to the values of $\alpha \lesssim 0$. The exponent has been extracted from the radius of gyration $R(m)$. The same answer was obtained when analyzing $\bar{R}(t)$ vs $\bar{m}(t)$ (average over all clusters at fixed times) or $R(m)$ vs m (average over all clusters of mass m, no matter at what time they are grown). The results also agree with those of a simplified hierarchical version of the model.[20] Typically, an average over twenty independent trials was taken with $N_0 = 512$, 1024, and 2048 at a concentration $\rho_0 < 0.01$.

Now I will explore a scaling hypothesis for the entire system. It postulates that the whole growth process is invariant, if length, mass, and time are rescaled simultaneously. Suppose that the cluster radius is changed by a factor b. Then mass must be changed by b^D and time by b^z, where z is the dynamic critical exponent. z will now be calculated. The (physical) time is defined such that during the interval Δt *each* cluster moves by a distance $v\Delta t$ (the Monte Carlo time t_M, which appears naturally in the simulations, is measured in units where *one* randomly chosen cluster moves by $v\Delta t_M$ during Δt_M; thus $\Delta t_M = N\Delta t$). Let us calculate the time until each cluster has paired up ($\bar{m} \to 2\bar{m}$, $b = 2^{1/D}$). The motion of the clusters shall be described on a lattice with lattice spacing $\bar{R}$. The time it takes to move the clusters by one such lattice spacing is $\bar{R}^2/v$. As the density of clusters on this lattice is ρ, it takes $1/\rho$ steps to pair up. Hence the average time between collisions is

$$\bar{R}^2/\rho v \sim \bar{m}^{1-\alpha-(d-2)/D} \sim \bar{R}^{D(1-\alpha)-(d-2)}.$$

Scale invariance ($t \sim R^z$, $t_M \sim R^{z-D}$) determines $z = D(1-\alpha)-(d-2)$, dependent on the fractal dimension. Note that this derivation neglects cluster correlations and assumes that all the clusters have the same size. The mass then depends on time as[21]

$$\bar{m} \sim t^{D/z} \sim t^{D/[D(1-\alpha)-(d-2)]}, \quad D(1-\alpha) > d-2, \tag{3}$$

and higher moments scale accordingly (in terms of t_M, $\bar{m} \sim t^{-D/(D\alpha+d-2)}$, $D\alpha + d - 2 < 0$).

The mass $\bar{m}(t)$ has been calculated from the simulations for different values of α and d. In Fig. 1, $\bar{m}$ vs t_M is plotted logarithmically along with the slope expected from Eq. (3) for $d = 2, 3$ and $\alpha = -1, -2$. The agreement is good. For $d = 2$, $\alpha = 0$ (inset), $\bar{m}(t_M)$ can be fitted better by an exponential than by a power law.[22]

Another consequence of the scaling postulate is a scaling form for the cluster size distribution. The number of clusters $N(m,t)$ of mass m at time t can be expressed in terms of a scaling function $p(x)$,

$$N(m,t) = \frac{N(t)}{\bar{m}(t)} p\left[\frac{m}{\bar{m}(t)}\right], \tag{4}$$

whereby the time dependence enters solely through $\bar{m}(t)$. From the definition of N and $\bar{m}$, it follows that $\int dx\, p(x) = \int dx\, xp(x) = 1$. The moments of $N(m,t)$ then can be expressed in terms of $\bar{m}$.[23]

The function $p(x)$ has been calculated in the nu-

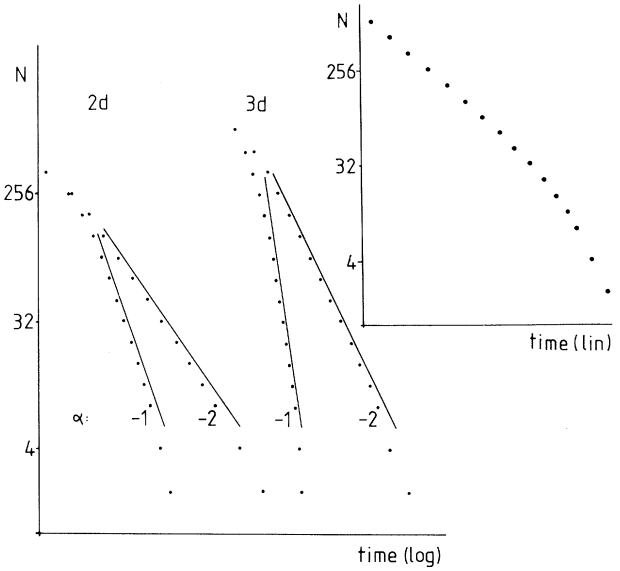

FIG. 1. Number of clusters $N = N_0/\bar{m}$ as a function of (Monte Carlo) time t_M (log-log plot). In the intermediate region $N \gtrsim 8$, $\bar{m} \gtrsim 5$ there is scaling. To the left $d = 2$, $\alpha = -1, -2$, $N_0 = 512$, and $L = 128$; to the right $d = 3$, $\alpha = -1, -2$, $N_0 = 1000$, and $L = 50$. For comparison, the straight lines indicate the exponent derived from the scaling argument [Eq. (3), with D values given in the text for $d \geq 3$]. The inset shows semilogarithmic plot for $d = 2$, $\alpha = 0$, $N_0 = 1024$, $L = 128$.

merical experiments. For $1 \ll N \ll N_0$ it is invariant, confirming the scaling *Ansatz*. In Fig. 2 results are shown for $d = 2, 4$ and $\alpha \leq 0$. For $d = 2$, $\alpha = -1, -2$ and for $d = 4$, $\alpha = -3$, $p(x)$ peaks at a finite value of x whereas for $d = 2$, $\alpha = 0$ it peaks at $x = 0$. Note that the points for $d = 2$, $\alpha = -2$ and $d = 4$, $\alpha = -3$ give approximately the same $p(x)$.

The principal assumption made to calculate the dynamic exponent is that the clusters are not correlated in space. This is also the starting point for the Smoluchowski-equation approach to cluster formation. Suppose that we try to describe flocculation by the following equation for $N(m,t)$ [24]:

$$N_0 \, dN/dt = \tfrac{1}{2} \sum_{m'+m''=m} m'^{\omega} m''^{\omega} N(m') N(m'') - m^{\omega} N(m) \sum_{m'} m'^{\omega} N(m'), \tag{5}$$

where the exponent ω shall contain all the geometrical and kinetic information. Using the scaling form, Eq. (4), for $N(m,t)$ one finds that $\bar{m} \sim 1/N \sim t^{1/(1-2\omega)}$. Comparison with Eq. (3) gives

$$2\omega = \alpha + (d-2)/D. \tag{6}$$

From Eq. (5) an equation for $p(x)$ can be obtained[25]:

$$\bar{m}^{1-2\omega} \, dp(x)/dt = [p(x) + \tfrac{1}{2} x \, dp(x)/dx] I_\omega^2 + \tfrac{1}{2} \int^x dy \, y^{\omega} p(y) (x-y)^{\omega} p(x-y) - x^{\omega} p(x) I_\omega,$$
$$I_\omega = \int dx \, x^{\omega} p(x). \tag{7}$$

The desired scaling function $p(x)$ is the stationary solution ($t \to \infty$) of this equation for the initial condition $p(x, t=0) = \delta(x-1)$. Expansion of Eq. (7) for small and for large x indicates that p vanishes faster than any power for $x \to 0$ and decays exponentially as $x \to \infty$, for $\omega < 0$. For $\omega = 0$, $p(x) = e^{-x}$. I have solved for $p(x, t \to \infty)$ numerically for the values of ω corresponding to the values of d and α used in Fig. 2 and find agreement between the kinetic approach and the flocculation experiments, except for $\omega \cong 0$ and $x \cong 0$.[26] Note that $p(x)$ should agree for $d = 2$, $\alpha = -2$ and $d = 4$, $\alpha = -3$ as ω calculated from Eq. (6) is the same. Another test for the kinetic description to flocculation is the behavior of $p(x)$ for small x. Direct simulations and the kinetic approach agree that $p(x \to 0)$ vanishes rapidly for $\omega \lesssim 0$ and becomes large when $\omega \gtrsim 0$.

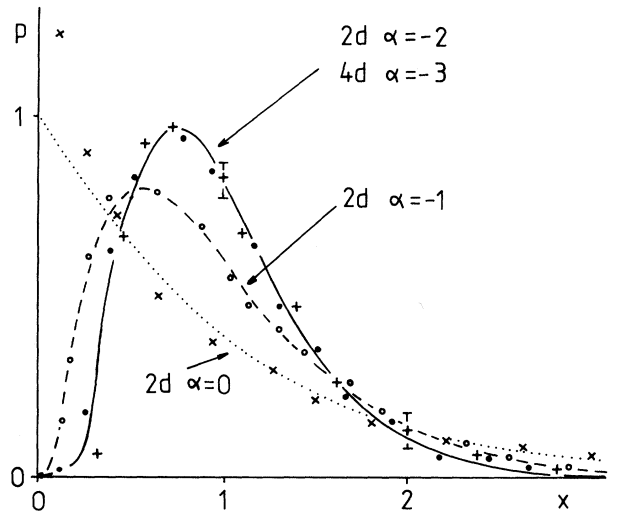

FIG. 2. Scaling function $p(x)$ of the cluster size distribution [Eq. (4)]. The points are results from the simulations in the scaling region. The curves are the numerical solutions of the kinetic equations with ω corresponding to the values of α and d simulated [Eq. (6)]. The symbols are as follows: crosses, $d = 2$, $\alpha = 0$, $N_0 = 1024$, $L = 128$ ($\omega = 0$, dotted curve); open circles, $d = 2$, $\alpha = -1$, $N_0 = 1024$, $L = 128$ ($\omega = -0.5$ dashed curve); dots, $d = 2$, $\alpha = -2$, $N_0 = 1024$, $L = 128$, and plusses, $d = 4$, $\alpha = -3$, $N_0 = 1000$, $L = 30$ (both $\omega = -1$, solid curve). The kinetic theory fits the data quite well.

Finally let me sketch how the proposed scaling provides a starting point for a qualitative description of this model.[27] In contrast to particle-to-cluster aggregation, where the particle and the cluster play different roles in the growth process, cluster-to-cluster aggregation is democratically organized, that is, all the clusters participate in the growth process in the same way. Thus it is reasonable to study how two clusters of the same size (both with $m \cong \bar{m}$ and $R \cong \bar{R}$) aggregate. When they coalesce, they penetrate each other (on average) a distance ξ. As scaling postulates that there is a single characteristic length, ξ has to be proportional to $\bar{R}$. Qualitatively ξ results from balancing the repulsive forces due to volume exclusion of the clusters and the attractive diffusive forces. The density ($\propto \bar{m}^{1-d/D}$) within the clusters decreases with increasing dimension d, and for sufficiently high dimension the clusters interpenetrate freely. This is exactly like the self-avoiding walk, which reduces to the random walk in high dimensions. The model for flocculation in high dimensions can be defined as follows: Two clusters of mass m_1 and m_2 coalesce into a cluster of mass $m_1 + m_2$ by forming, with the same proba-

bility, a rigid bond between any particle of the first cluster with any particle of the second cluster. As the excluded-volume effects can be neglected for large d, the properties of this model do not depend on d. Different versions of this model can be conceived: While in the hierarchical variant always two clusters of the same mass stick together,[28] in a more realistic version growth can be governed by a kernel as in Eq. (5). The same model can also be studied[27] below the upper critical dimension (analogous to the random walk) by letting the particles occupy the same sites.

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