Clustering of clusters is introduced as a model to describe irreversible diffusion-limited aggregation of clusters. The scaling properties are determined using numerical simulations and mean field arguments. The results are compared with the Smoluchowski equation approach. The scaling behavior is different for low cluster concentration (floculation) and for high cluster concentration ("gelation"). Reversible cluster aggregation can be modeled by randomly breaking bonds. This leads to a different cluster structure, with scaling behavior like lattice animals. The clusters of irreversible cluster and particle (DLA) aggregation are investigated for their internal anisotropy: particle aggregates appear to scale differently parallel and perpendicular to the direction of growth.

Clustering of clusters has been introduced to describe irreversible diffusion-limited cluster aggregation as observed in colloidal growth processes. Here, we define the basic model and discuss its scaling properties. Then, it is shown that the classical approach due to Smoluchowski gives an adequate description of this growth process, provided the fractal aspect of the clusters is taken into account. At high cluster concentration, the growth mechanism is different because of the entanglement of the clusters. This leads to (infinite time) gelation.

Both irreversibility and diffusion are relevant factors in determining the fractal properties of cluster aggregation. This is shown clearly for reversible
cluster aggregation, where the bonds between the particles have a finite lifetime: the fractal dimension of the clusters becomes the same as the one for lattice animals. Finally, the question of the cluster anisotropy is addressed by calculating angular correlations for cluster aggregation (CA) and particle aggregation (PA or DLA). The PA growth process leads to different scaling along and orthogonal to the growth direction, whereas CA is isotropic.

THE CLUSTERING OF CLUSTERS MODEL

The model for irreversible, diffusion-limited cluster aggregation is defined as follows: two particles are randomly placed on a hypercubic d-dimensional lattice of length $L$. Each particle moves independently and randomly (hopping to nearest neighbors). If two particles sit on neighboring sites, a bond is placed between them—they form a dimer. The dimer diffuses like the particles and larger clusters form in the same way. As the bonds are never broken, this leads to ever larger, rigid clusters. The growth ends when all particles belong to one big cluster. No rotation and no restructuring is allowed. Aggregates of many particles can be analyzed as fractals, i.e., $m = R^D$. $R$ is the radius of gyration of the aggregate and $m$ its mass (number of particles). The fractal dimension $D$ is $D = 1.42 \pm 0.04 \ (d = 2)$ and $D = 1.78 \pm 0.05 \ (d = 3)$. Physically, the diffusivity of the clusters depends on the cluster size. This can be taken into account by fixing the diffusive velocity to be

$$V(m) = m^\alpha$$

for a cluster of mass $m$. The parameters of the model are then $N_0$, $L$, and $\alpha$. The quoted fractal dimensions describe aggregation at low cluster concentration and for $\alpha < 0$, when large clusters diffuse slower than small clusters. This result agrees with experimental observations in aerosols and colloids.

The following scaling arguments can be used to describe the static and dynamic properties of this model. Let $N(t)$ be the number of clusters at time $t$ ($N(t = 0) = N_0$). The average mass then is $\bar{m}(t) = N_0/N(t)$ and the average radius $\bar{R}(t) = \bar{m}(t)^{1/D}$. Scaling implies that a system of $N$ clusters of size $\bar{R}$ in a box of length $L$ can be described by $N$ particles of unit size in a box of length $L/\bar{R}$. The initial cluster concentration $\rho_0$ becomes at time $t$ effectively

$$\rho = \frac{N}{(L/\bar{R})^d} = \rho_0 \bar{m}^{(d - D)/D}.$$

For fractal clusters ($D < d$), the concentration $\rho$ increases steadily. The intercluster distance eventually becomes comparable to the cluster radius $\bar{R}$ (if $L \to \infty$), no matter how small $\rho_0$. The scaling regime relevant for colloids is $\rho \ll 1$, and will be considered first. The situation where $\rho > 1$ will be discussed further below. Supposing that mean field theory is valid, similar arguments can be used to describe the time dependent scaling of clustering of clusters. Here, of course, the diffusivity $v(m)$ will enter the formulas through the exponent $\alpha$. The average mass scales in time like $\bar{m} \sim t^\theta$ with

$$\theta = 1/(1 - \alpha - \frac{d - 2}{D}).$$
Direct numerical simulations confirm this behavior qualitatively for monodisperse systems, and $\theta < 1$.

**KINETIC EQUATION APPROACH TO CLUSTER AGGREGATION**

The Smoluchowski equation has been used very successfully as a mean field description of irreversible cluster aggregation. The cluster size distribution, the number $N(m)$ of clusters of mass $m$, evolves in time according to

$$\frac{dN(m)}{dt} = \frac{1}{2} \sum_{m' + m'' = m} K(m', m'')N(m')N(m'') - \sum_{m'} K(m, m')N(m)N(m'),$$

where the kernel $K(m, m')$ contains all the physics. In order to describe clustering of clusters in terms of the Smoluchowski equation, the fractal geometrical aspects have to determine the kernel. For a scaling analysis, one attempts to express the size distribution $N(m)$ in terms of a scaling function $p(x)$

$$N(m, t) \sim m^{-2} p(m/m),$$

which, for large times, is time-independent and universal.\textsuperscript{4-6} The time dependence then enters only through $\bar{m}$. Using this scaling Ansatz for $N(m)$ and a homogenous kernel of degree $2\omega$,

$$K(\lambda m, \lambda m') = \lambda^{2\omega} K(m, m'),$$

i.e., $K(m, m') = (mm')^\omega$, the total number of clusters $N = \sum_m N(m) \sim t^{-\theta}$ or $m \sim t^\theta$, with $\theta = 1 - 2\omega$. Comparing $\theta$ with the expression obtained above yields $2\omega = (d - 2)/D$. For monodisperse cluster size distribution ($p(x \to 0) \to 0$) there is agreement between $p(x)$ obtained from direct numerical simulations and $p(x)$ calculated from the Smoluchowski equation with the corresponding $\omega$. For the polydisperse case, $\omega > 0$, care must be taken to distinguish between average and typical cluster size. The Smoluchowski equation distinguishes qualitatively between monodisperse ($\omega < 0$), polydisperse non-gelling ($0 < \omega < 1/2$) and gelling ($\omega > 1/2$). Varying $\alpha$ in the simulations lets one cover all three regions. In particular for $\omega > 1/2$ one finds that the fractal dimension is the same as DLA. The case where larger clusters move faster than small ones corresponds to this situation. While the cluster-size distribution has the characteristics of gelation, this process does not actually describe gel formation, as we restrict ourselves to low concentration, $\rho \ll 1$. This condition fails before a gelling network appears.

**KINETIC GEL FORMATION**

As pointed out above, the density $\rho$ increases monotonically, as long as $D < d$. This leads necessarily to the interpenetration of the clusters when $\rho > 1$. The growth then is not determined by the diffusive screening which causes two clusters to form bonds at the outermost tips at low concentration. Nevertheless, one may still attempt to use a scaling analysis.\textsuperscript{7} The fractal dimension measured for $\rho > 1$ is $D = 1.75 \pm 0.07$ ($d = 2$), and the cluster size distribution is monodisperse when $\alpha < 0.40$. Consistent with the Smoluchowski picture,
the time to form an infinite cluster is infinite. Experimentally, structures with a fractal dimension close to the one reported here have been observed in the aggregation of wax and latex spheres. The model of cluster aggregation at high concentration effectively induces long range interactions across large, rigid clusters. This is probably valid experimentally only up to a certain cluster size, then the condition of total irreversibility must be relaxed.

REVERSIBLE CLUSTER AGGREGATION

In addition to the fact that, experimentally, growth can only be considered irreversible over some range of cluster sizes, it is also useful from a theoretical point of view to study the effect of relaxation of the clusters. The following model of reversible cluster aggregation has been investigated. Clusters aggregate in the same fashion as described above; they diffuse and form bonds whenever they touch each other. In addition, a fragmentation mechanism is introduced. Every bond now has a finite lifetime \( \tau \). If a bond breaks and a cluster breaks into two pieces, the two clusters diffuse independently of each other. In practice, every bond is cut with probability \( 1/\tau \) per unit time. Thus, aggregation is diffusion limited, fragmentation is random. Two situations have been considered, though the results do not depend on it. The clusters are either loopless (when in a collision, several bonds would form; one is picked at random) or with loops (when a bond is broken, a cluster only falls apart if no other bond connects the pieces).

Starting initially with single particles and \( \tau \) large, the clusters grow until they reach a size where aggregation and fragmentation balance each other. The scaling analysis of the clusters has been performed in this regime of dynamic equilibrium. The fractal dimension of the clusters in \( d = 2 \) (\( d = 3 \)) is \( D = 1.57 \pm 0.06 \) (\( 2.03 \pm 0.05 \)), both for clusters with and without loops. (Varying the lifetime \( \tau \) varies \( m \) and hence \( R \)). The mobility parameter \( \alpha \) does not change this value appreciably, even for \( \alpha > 0 \). This indicates that there is no crossover analogous to the irreversible model. If one lets the clusters stick together with a sticking probability \( p < 1 \) (the actual value used is \( p = 0.05 \)), the results do not change either. This independence of the exponent \( D \) with respect to the kinetics suggests that the fractal properties are those of static lattice-animals (which have the same \( D \) to within numerical errors). As the aggregation and fragmentation mechanisms are very different, there is no detailed balance in this process. A reduced cluster size distribution can be determined for this model as well. For every value of \( \tau \), a characteristic \( m(x) \) (and \( R(x) \)) exist, from which \( p(x) \) with \( x = m/m \) can be calculated. The shape of the size distribution is different from irreversible aggregation; notably the distribution is much broader for the monodisperse kinetics (i.e., \( \alpha = -2 \)). It suggests that the Smoluchowski equation produces a different solution when a fragmentation term is added.

INTERNAL STRUCTURE OF AGGREGATION CLUSTERS

The many simulations on growth processes indicate that the irreversible growth influences the structure in an important way. In order to quantify this statement in a specific example, both cluster (CA) and particle aggregation (PA) have been investigated for cluster anisotropy. This is motivated by the
observation that PA grows out of a center, while CA does not. To measure the anisotropy, the correlation function \( c(r) \) inside the cluster has been calculated as a function of the angle with respect to the center of the cluster.\(^{11}\) In order to eliminate the effects of the underlying lattice, both parallel and diagonal correlations (with respect to the square lattice) were determined. In both CA and PA an amplitude anisotropy with respect to the lattice is observed. More importantly, (for PA only), the scaling powers parallel and perpendicular to the direction of growth appear to differ:

\[
\eta_{\|} - \eta_{\perp} = 0.16 \pm 0.05.
\]

If this anisotropy persists asymptotically, the scaling region around a particle inside the cluster, where the correlation function \( c(r) \) has scaling form, is narrower in the lateral direction. This suggests that DLA in different geometries could give a better idea of how the growth direction influences the resulting cluster.

\(^1\) An introduction to random aggregation processes can be found in *Kinetics of Aggregation and Gelation*, eds. F. Family and D. P. Landau (North Holland, 1984).


\(^9\) M. Kolb, preprint; R. Botet and R. Jullien (preprint) have considered restructuring of DLA clusters.


\(^{11}\) M. Kolb, J. de Physique LETT. 46, L 631 (1985); similar anisotropy studies for DLA have been performed independently by P. Meakin, by T. Vicsek and by R. Voss (preprints).