Scaling of Kinetically Growing Clusters

M. Kolb, R. Botet, and R. Jullien
Laboratoire de Physique des Solides, Université Paris-Sud, Centre d'Orsay, F-91405 Orsay, France
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A model describing the process of cluster growth by aggregation of clusters is introduced and investigated with the Monte Carlo method. It is found that the clusters are scale invariant. The fractal dimension of this new class of kinetic critical behavior is $D = \nu^{-1} = 1.38 \pm 0.06$ in $d = 2$ dimensions as determined by the radii of gyration and the density correlations of the aggregates. The process is compared with other types of kinetic and equilibrium critical phenomena.

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The aggregation process, i.e., the mechanism of cluster formation from isolated single particles, is of interest in many areas of science such as physics (dendritic growth[1]), chemistry (flocculation of colloids,[2] formation of gels[3]), polymer physics (kinetics of polymerization[4]), medicine (growth of tumors[5]), and metereology and ecology (cloud formation, coagulation of smoke particles[6-8]).

The enormous progress made in the theory of critical phenomena has influenced the way one looks at the geometrical objects encountered in the above examples. This was recognized when a connection could be established between polymer statistics,[9] respectively percolation,[10] and critical phenomena that leads to a characterization of such systems in terms of scaling and universality.[11] Alternatively, the theory of fractals[12] describes the same phenomena on purely geometrical grounds, showing that it is not necessary to make reference to a statistical mechanical system governed by a Hamiltonian.

The field of critical behavior of clusters has been very active recently, particularly in the domain of growth models, whose irreversibility leads to scaling properties that are possibly different from those of equilibrium systems.[13]

In the present calculation, we establish scaling for a process encountered in a wide range of kinetic clustering phenomena, notably flocculation and coagulation. The model is a growth model that describes the clustering of clusters. One starts with an assembly of Brownian particles which stick together upon contact to form rigid clusters. The newly formed clusters diffuse along with the particles and continue to grow by aggregation when they meet other clusters or particles. The connection of this model with previously studied models is as follows: Single-particle diffusion-limited aggregation[8] has critical properties which are different from percolation and probably different from lattice animals.[14] The growth process under investigation resembles diffusion-limited aggregation in its kinetic mechanism. However, as we deal with many clusters, there are similarities to ordinary or kinetic percolation as used to describe gelation. As a consequence, one expects that the scaling properties are qualitatively different from both of the above situations. Our simulation indicates that, in two dimensions, the clusters are much more stringy than in all of these models. In the low-density regime, the model scales, suggesting that it may be self-similar, with a fractal dimension $D = 1.38 \pm 0.06$ as determined from the radii of gyration and the density correlations. As the clusters grow, the effective cluster density increases and eventually they cover the whole space.

The actual calculation is performed on a periodic square lattice with $V = L^2$ sites with initially N_0 randomly distributed particles. Clusters (particles connected by nearest-neighbor bonds) are rigid and move randomly one lattice spacing at a time. Clusters that touch (occupy nearest-neighbor sites) become part of a new, larger cluster. The clusters do not rotate. This idealized motion presumably does not affect the critical properties; thus a continuous movement of spherical particles forming rotating clusters would yield the same results.[14] According to our calculation, the type of kinetic motion does not affect the results. Most of the calculations were performed supposing that a cluster of N particles moves like a Brownian particle of mass N (probability to move $\propto 1/\sqrt{N}$), but the same exponents were obtained when we let all clusters move alike independent of their size or when heavy clusters hardly moved at all. Though the size distribution varies somewhat with the kinetic prescription, the qualitative aspects remain unchanged.

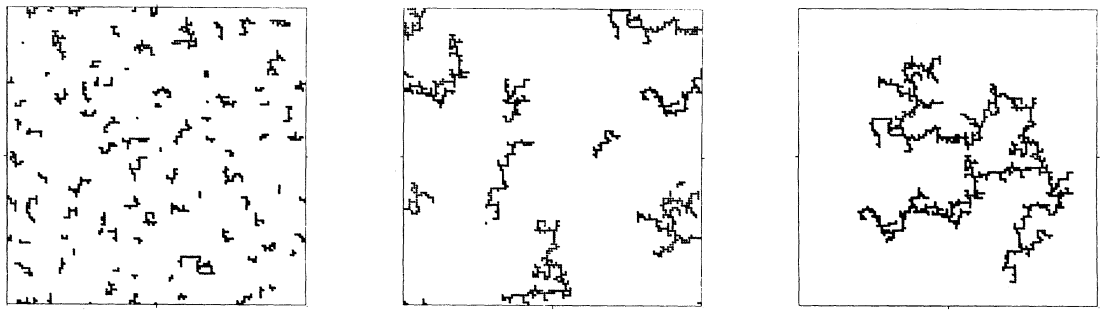

FIG. 1. Simulation of the growth of clusters. The three situations correspond to $N_c = 86$, 8, and 1 cluster, respectively. The system has a size $L = 128$ and initially $N_0 = 1024$ particles; the effective density grows from $\rho_0 = 0.06$ to $\rho_f \cong 1$. Note the chainlike appearance and the few branchings of the clusters.

The critical properties were extracted with use of two related measures characterizing the clusters. First, we determined the average size $R(N)$ of a cluster as a function of the number of particles in it. The radius of gyration behaves like

$$R \sim N^{\nu}, \quad N \sim R^{D}, \quad D = 1/\nu,$$

as $N \to \infty$. Secondly, we determined the density correlation function $C(\vec{r}) = \langle \rho(\vec{r}_0 + \vec{r}) \rangle$ at a point $\vec{r}_0$ of the cluster. It scales like

$$C \sim r^{-A}, \quad A + D = d, \quad 1 \ll r \ll R,$$

where d is the space dimension ($d = 2$). The averages are over all cluster configurations. In the simulation the average is taken over all the clusters with N particles for R and over all r_0 and all directions for $C(r)$.

In Fig. 1, the evolution of the clusters is shown for a system of size $L = 128$ with initially 1024 particles. As the number of clusters N_c decreases and the average number of particles per cluster $n = N_0/N_c$ increases, the size of a cluster is $V_c = R^d \sim n^{\nu d}$ and the effective density $\rho_{\text{eff}} = N_c(V_c/V) \sim \rho_0 n(d-D)/D$ grows for ramified ($D < d$) structures. No matter how low the initial concentration, the clusters eventually cover the whole space ($\rho_{\text{eff}} \sim 1$). The anticipated self-similarity under a change of scale then breaks down. In order to stay in the scaling region of interest, one has to lower the initial concentration with increasing system size L. In Fig. 2, the regions of different effective concentrations are indicated. The correlation function $C(r)$ distinguishes between an initial nonuniversal region and the following scaling region which terminates for low final concentration (all particles in one cluster) $\rho_f \ll 1$ at $r \sim R$ and for $\rho_f \lesssim 1$ crosses over to a more compact region. Our calculation determines the exponents A and ν and we find that this kinetic growth model is scale invariant, as shown in Figs. 3 and 4. The values $A = 0.61 \pm 0.05$ and $\nu = 0.73 \pm 0.04$ satisfy $d - A = D = 1/\nu$. As in other simulations of this kind we find that each simulation is quite smooth but that there are quite large statistical errors between different trials.[14]

There are other quantities which can be measured in the simulation. One, which explains why this model has very different critical properties than previously studied systems, is the size distribution of the clusters. It shows a broad and flat peak which allows clustering of clusters over

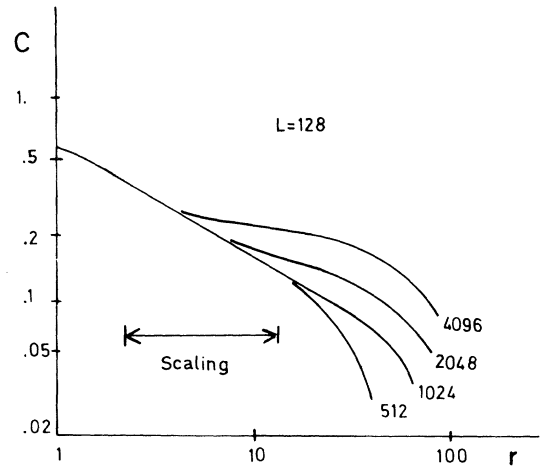

FIG. 2. Correlation function $C(r)$ (log-log plot) at different densities ρ_{eff}: crossover from dilute to compact region. The number of particles are $N_0 = 512$, 1024, 2048, and 4096, and the radii of gyration $R = 27$, 44, 51, and 55, respectively. While the radius of gyration limits the scaling region for low densities $\rho_f \ll 1$, the mutual hindrance of the clusters terminates it for $\rho_f \sim 1$.

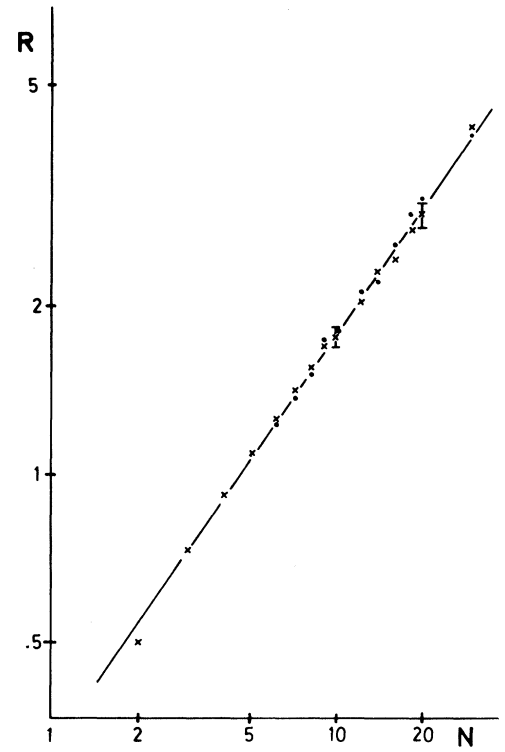

FIG. 3. Radius of gyration (log-log plot) in the scaling region. Average of ten samples with $L = 128$ and $N_0 = 1024$ with typical error bars (crosses) and two samples with $L = 450$ and $N_0 = 5000$ (dots). The straight line has slope 0.73.

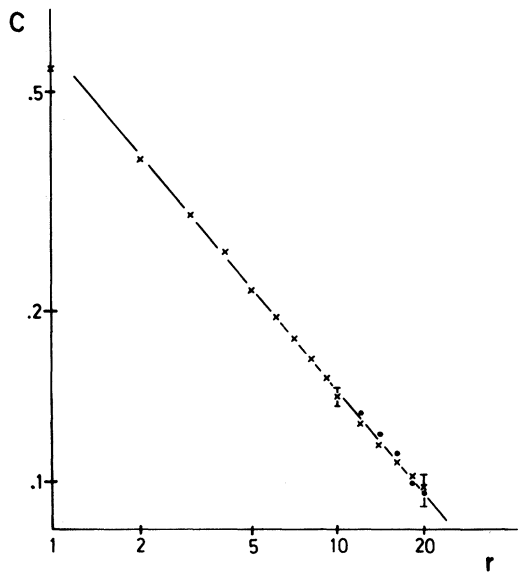

FIG. 4. Correlation function $C(r)$ for the same samples as in Fig. 3. The slope of the straight line is 0.61.

a wide range of sizes (provided $1 \ll N_c \ll N_0$), totally different from single-cluster aggregation.

Recently, Allain and Jouhier[15] observed clustering of clusters in a macroscopic experiment. At the percolation threshold[16] they find $\nu = 0.61$, intermediate between percolation and irreversible clustering. The experiment shows a slight tendency to restructure the clusters which may explain that the effective exponent $D_{\text{eff}} > D$. Another aspect of their experiment is important: The motion of the clusters has both a random and a hydrodynamic element. Experimentally the influence of both parts cannot be separated. In our simulation we study the irreversible part alone.[17]

In Table I, the exponent $D = 1/\nu$ for kinetic and equilibrium critical phenomena are compared. The present model is far more ramified than lattice animals and single-particle aggregation. The linear appearance and the few branchings suggest a behavior not unlike linear polymers. In the light of the present calculation and the experiment of Allain and Jouhier,[15] the smoke-particle aggregation (Ref. 7) could be described by clustering of clusters with restructuring.[22]

The present study suggests various extensions. The simulation could be complemented with other approaches on the same model.[23] Also, it would be interesting to consider higher dimensions (preliminary results for $d = 3$ are analogous to $d = 2$: the clusters are much more ramified than other growth models, and D is close to the fractal dimension of linear polymers), time dependence,

TABLE I. Comparison of the fractal dimension $D = 1/\nu$ of the present model and of other kinetic and equilibrium critical phenomena. The estimate of D for the present model is based on the data of Figs. 3 and 4.

Phenomena	Exponent D ($d = 2$)
Present work	1.38 ± 0.06
Eden model[a]	2.0
Percolation[b]	1.80
Single-particle aggregation[c]	1.67
Lattice animals[d]	1.56
Linear polymers[e]	1.33
Smoke particles ($d = 3$)[f]	1.55–1.69
Experimental simulation[g]	1.64 ± 0.13

[a]Ref. 18.
[b]Ref. 19.
[c]Ref. 8.
[d]Ref. 20.
[e]Ref. 21.
[f]Ref. 7.
[g]Ref. 15.

the influence of hydrodynamic motion, and the crossover when partial restructuring is possible.

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[16]Allain and Jouhier originally tried to explain their experiment in terms of percolation (at a concentration when the largest cluster spans the system) and then found that the irreversible, kinetic clustering plays an important role (private communication).

[17]If no restructuring takes place the system is not related to percolation (the irreversibility guarantees a memory of the regime $\rho_{\text{eff}} \ll 1$ even when later on the clusters percolate, Fig. 2) and simply becomes compact when $\rho_{\text{eff}} \sim 1$. This is no longer true when it is allowed to restructure.

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[22]The clusters shown in Ref. 7 have an appearance that suggest a rather stringy structure, despite the projection from $d = 3$ to $d = 2$.

[23]A renormalization-group calculation is under way with encouraging results. It supports the notion that the relative size of the coalescing clusters determines the type of kinetic phenomena observed.