

Simulation of Fractal-Like Crystal Growth

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Z. Naturforsch. **46a**, 203–205 (1991); received January 9, 1991

Dedicated to Dr. Heinzinger for his 60th birthday

Non-equilibrium crystallization was simulated on a two dimensional square lattice. Several clusters were grown simultaneously by using the model of diffusion limited aggregation. The growing process was reversible, i.e. dissolution of particles from the boundary of any cluster was made possible. The rate of growth and dissolution was determined by a stochastic method. The simulation resulted in an aggregate pattern having a few large and several small clusters. The fractal dimensions of the large clusters were found in the range of $D = 1.62 - 1.72$.

Introduction

Under non-equilibrium conditions, the aggregation of particles frequently leads to complex objects which can be described by their fractional geometry. One of the most frequently studied pattern-forming processes is crystallization. Crystallization from a supersaturated solution is often a diffusion limited process. Random fluctuations, however, can modify the crystallization process, resulting in a disordered structure.

Theory

The diffusion limited aggregation (DLA) proposed by Witten and Sander [1] consists of two steps: (i) diffusion of particles and (ii) their sticking to a cluster. The model starts with a seed particle at the center of an empty lattice. One particle after the other moves randomly from far away until it arrives at a vacant site adjacent to an occupied site. This irreversible growing process leads to a dendritic pattern with the fractal dimensionality $D \simeq 1.67$ for $d = 2$ and $D \simeq 2.5$ for $d = 3$, where d is the euclidean dimension. The Witten-Sander model provides a basis for understanding dielectric breakdown [2], electrochemical deposition [3], fluid-fluid displacement in Hele-Shaw cells [4] or porous media [5], dissolution of porous materials [6] and random dendritic growth [7].

The diffusion limited cluster-cluster aggregation developed by Meakin [8] and Kolb [9] is more suitable

for modeling the aggregation of colloid-like structures. At the start of the simulation, lattice sites are selected at random and occupied until a given particle density (the ratio of the number of occupied and total sites) is reached. The aggregation process is simulated by selecting clusters at random and moving them by one lattice unit in a random direction. If a particle or a cluster arrives at a site adjacent to another particle or cluster they stick together forming a larger cluster. Single particles as well as clusters of particles are allowed to diffuse. The growing is irreversible, that is once a cluster is formed it is not allowed to break up, and only translational diffusion is regarded. The fractal dimensionality of such clusters ($D \simeq 1.45 - 1.5$ for $d = 2$ and $D \simeq 1.8$ for $d = 3$) is smaller than those generated by the Witten-Sander model.

Meakin [10] investigated also the effect of rotational diffusion. The rotation of clusters slightly decreases the fractal dimensionality to a limiting value $D = 1.0$ for $d = 2$, as the rotational diffusion increases. However in most real cases this effect will be small. The effects of sticking probabilities smaller than 1.0 have also been investigated [11]. In the limit of very small sticking probabilities the fractal dimensionality increased to about $D \simeq 1.55$ for $d = 2$ and $D \simeq 2.0$ for $d = 3$.

A kind of reorganization was also regarded by Meakin [12]. Each bond in all of the clusters is cut with a given probability, and if the bond is the only one between two parts of a cluster, the two pairs are allowed to move independently. This reorganization somewhat increased the fractal dimensionality. The fractal dimensionality of cluster-cluster aggregation was found to be independent of model details such as lattice or non-lattice simulation. In addition, the de-

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pendence of cluster diffusivity on cluster mass has no influence on the fractal dimension, provided smaller clusters diffuse at least as fast as larger clusters [13].

Up to now only a few experiments have been published on fractal-like crystal growth. Honjo et al. reported an experiment in which DLA-like crystal growth was observed by using a supersaturated NH_4Cl solution [7] in a cell of two parallel glass plates. The fractal dimension of the crystal pattern was found to be $D = 1.671 \pm 0.002$, which is in very good agreement with two dimensional DLA ($D = 1.67$).

Model

In the present work, the rate of nucleation is determined by the Gibbs free energy [14], i.e. crystallization may take place only when the Gibbs free energy decreases. The total change in the Gibbs free energy on transition of n particles from the liquid phase to a solid cluster is

$$\Delta G = n(\mu_s - \mu_l) + A\gamma, \quad (1)$$

where A is the surface of the cluster, μ_s and μ_l are the chemical potentials per particle in the solid and the liquid, respectively, and γ is the interfacial tension.

Equation (1) can be written as

$$\Delta G = n(\mu_s - \mu_l) + n^{2/3} v^{2/3} \beta \gamma, \quad (2)$$

where v is the volume obtained by division of the molar volume in the solid phase by Avogadro's number, and β is the geometric shape factor (see e.g. [14]).

Since $\mu_s - \mu_l$ is negative and γ is positive, ΔG passes through a maximum at a critical cluster size, n_{crit} . In the formation of a cluster with size $n < n_{\text{crit}}$, $d\Delta G/dn$ is positive and consequently this process is thermodynamically unfavourable. A cluster with size n_{crit} has the same probability of growth and dissolution. Addition of further particles to a critical cluster is accompanied by a decrease in ΔG and thus further growth of a critical nucleus is favoured.

Computational Procedure

The aggregation was simulated on a square lattice, containing 160,000 sites. About 20 sites were filled at random. Then a new particle was generated far from the occupied sites and moved randomly until it reached a site adjacent to a occupied site. The asym-

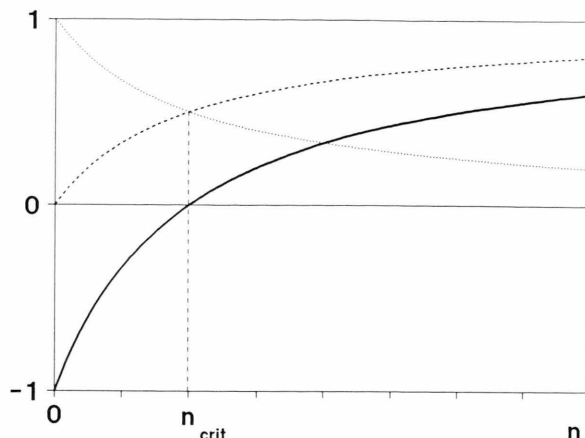


Fig. 1. The rate of growth (dashed line), dissolution (dotted line) and their difference, i.e. the rate of crystallization (solid line) as function of n .

metry of the clusters was reduced by filling such a site only after it had been reached 15 times by a random walker whose random walk is terminated at the first unoccupied site which it reaches. At the beginning of the simulation bonds were not allowed to break up. After each of the growing clusters had absorbed about n_{crit} particles, the process was turned reversible, i.e. particles were allowed to dissolve. In the present calculation $n_{\text{crit}} = 100$ was chosen.

In order to decide if a particle was to stick to a cluster of n particles, a uniformly distributed random number was generated in the range of 0 and 1. If the random number was greater than $n_{\text{crit}}/(n + n_{\text{crit}})$, the particle was allowed to stick to the cluster, otherwise it was allowed to dissolve. The growth and dissolution rates are shown in Figure 1.

The resulting rate of crystal growth (solid line) is negative for $n < n_{\text{crit}}$ (dissolution) and positive for $n > n_{\text{crit}}$ (growth). This is in conformance with the shape of the ΔG vs. n relationship which is a monotonously increasing and decreasing function for $n < n_{\text{crit}}$ and $n > n_{\text{crit}}$, respectively.

The above procedure leads to a stochastic process in which small clusters can hardly grow. The simulation results in the formation of a few large clusters. Most of the clusters slowly dissolve.

Results and Conclusion

In Fig. 2 the moment is shown when the simulation is turned to reversible. At this point each of the clus-

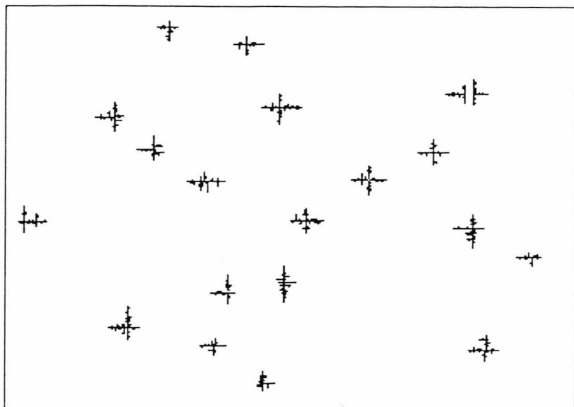


Fig. 2. Simulated clusters at the moment when the average particle number in a cluster is n_{crit} . The simulation is turned to reversible at this point.

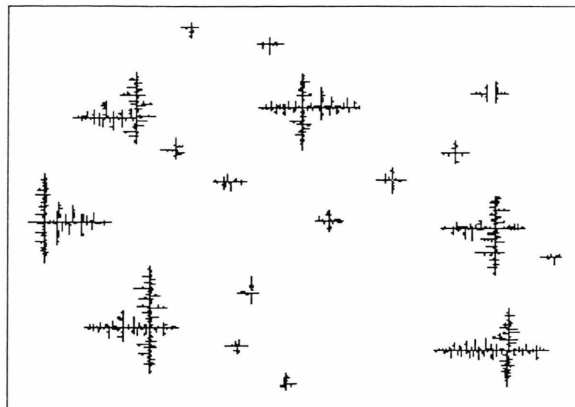


Fig. 3. The simulated clusters at the end of the reversible growth.

ters contains about 100 particles. In Fig. 3 the end of the simulation is shown. Only six clusters were able to grow. One was dissolved completely. Each of the six large clusters contains about 1000 particles. The fractal dimension of a cluster was determined in the following way: first, the center of the cluster was determined, then the number of particles (m) within the range between the center and the distance r were counted as a function of r . The initial slope of the $\log(m)$ vs. $\log(r)$ curve gives the fractal dimension. The fractal dimensions of the six clusters were found to be 1.673 ± 0.016 , 1.663 ± 0.019 , 1.621 ± 0.014 , 1.721 ± 0.018 , 1.622 ± 0.015 and 1.671 ± 0.015 .

The simulation described here, in which small particles dissolve and only clusters larger than a critical value are able to grow with a significant rate, leads to an aggregate of fractal structure whose fractal dimensionality ($D = 1.62 - 1.72$ for different clusters) differs from those reported on cluster-cluster aggregation but is in good agreement with the fractal dimensionality ($D = 1.67$) of structures generated by the DLA model, where only one cluster is grown.

Acknowledgement

The authors gratefully acknowledge Alfred Klemm's helpful comments in the preparation of this manuscript.

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