Diffusion-Limited Aggregation in Two Dimensions

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We have studied the aggregation of silica microspheres confined to two dimensions at an air-water interface. Under microscopic observation, both monomers and clusters are seen to aggregate by a diffusion-limited process. The clusters' fractal dimension is 1.20 ± 0.15, smaller than values obtained from current models of aggregation. We propose that anisotropic repulsive interactions account for the low dimensionality by more effectively repelling particles from the side of an existing dendrite than from the end.

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Colloid aggregation is the prototypical example of a random process which generates highly ramified dendritic structures. Although the qualitative features of aggregates have been well known, it was the recent discovery by Witten and Sander1 of a computer simulation technique for diffusion-limited aggregation that spawned renewed interest in the structure of these curious objects. The Witten-Sander (WS) model and most subsequent modifications suggest that clusters possess universality in the sense that long-range structure is independent of the details of the interparticle potential. By now the number of theoretical results (including simulations) far exceeds the number of experimental results, and, since for practical reasons many simulations are carried out in two dimensions, measurements from real two-dimensional systems are particularly important.

Here we report the results of a two-dimensional aggregation experiment that we believe is the first reported physical realization of diffusion-limited aggregation in a plane, although the aggregation of nondiffusive floating wax particles2 and the case of two-dimensional electrodeposition3 have been reported. In our experiment, charged colloidal particles trapped by surface tension at the interface between air and water are allowed to aggregate by raising the salt concentration of the water substrate, thereby screening the repulsive electrostatic interactions. The aggregation process is studied by direct observation in an optical microscope.

In addition to the unusual two dimensionality, interfacial colloids provide a unique opportunity to characterize aggregation in detail. By direct observation one can gain insight into the controlling factors. Image-processing techniques can be applied to extract new information, such as the topological exponent4 and the persistence length. Cluster-mass distributions and coagulation kinetics are also readily available. Internal dynamics as well as annealing processes can be observed directly or by light scattering. Finally, our experiment is not subject to the ambiguities inherent in many others experiments such as the projection of a three-dimensional object onto a two-dimensional surface and the effects of gravity. In the present work we measure the fractal dimension and cluster-mass distribution; other properties are under study.

In situ scattering measurements of three-dimensional clusters, though scarce, currently offer the most reliable information for comparisons between competing models. Schaefer et al.5 found that the fractal dimension D of colloidal silica aggregates, defined by \( M \sim R_s^D \) where \( M \) is the mass and \( R_s \) the radius of gyration, is 2.1. The WS model, in which single diffusing particles aggregate onto a growing cluster, predicts \( D = 2.56 \) for three dimensions; the more realistic cluster-cluster (CLCL) model,6,7 which allows many clusters to form and to aggregate among themselves, yields \( D = 1.8 \). Structures produced by the CLCL model are more "stringy" than those of the WS model because the colliding clusters cannot inter-penetrate deeply. In both models, the particles are dilute and, until they stick together irreversibly on contact, noninteracting. The scattering experiments suggest that not all physical systems satisfy the assumptions of either model, perhaps most importantly with respect to the assumed absence of finite-range interactions.

In the presence of repulsive forces the Brownian motion of each particle cannot be considered independent; one would expect the motion to be biased away from existing clusters. The end of a charged dendrite therefore presents less of an electrostatic potential barrier than the side.9 Although no simulations of diffusion-limited aggregation have yet appeared that include repulsive forces, anisotropic diffusion10 and repulsive forces in an Eden model11 have been simulated with the result that the fractal dimension decreases, consistent with structures having less branching. In our system of charged colloidal particles, finite-range forces would be expected to be important because the charge is largely responsible for the stability of the initial suspension.

The samples were prepared by spreading techniques outlined by Goodwin, Ottewill, and Parentich,12 which were adapted for making small, controlled samples for microscopic examination [Fig. 1(a)]. A fresh suspension of silica microspheres (3000 Å diameter) with a
methanol spreading agent was dispensed onto a flat surface of "salty" water (1.0N CaCl) with a micrometer-driven syringe. Care was taken to avoid turbulence in the sample during spreading since the colloid is unstable to aggregation in the presence of high electrolyte concentrations.

Optical observations and photomicrographs were made as the sample proceeded to aggregate. Single particles could be seen sticking to each other and to developing clusters, but by the time reasonable cluster sizes were achieved (1 h) there were very few monomers left and the clustering of clusters was evident. The structures were digitized from photographs [Fig. 1(b)] by assigning a set of coordinates to each segment of equal mass as judged by eye, approximately ten microspheres per segment. The individual particles within a cluster could not be resolved in the photos because of their small size; larger, more resolvable spheres were found to take too long to aggregate. Thus a compromise was made in using small microspheres since the definition of the equal-mass segments during the digitization procedure was somewhat arbitrary. The scaling relation between the radius of gyration and the mass of a cluster is not greatly affected by this compromise, however, other than by the potential introduction of systematic errors and the loss of information about small length scales. To test for errors, the experiment was repeated with higher resolution and the results did not change significantly. In addition, several negatives were analyzed with image-processing equipment by digitizing the full area of a cluster image and then calculating the total area (mass) and second moment of the area (radius of gyration). Again, after accounting for the spreading of the optical image, the results did not change.

A plot of the logarithm of the radius of gyration \( R_g \) against the logarithm of the number of segments \( N \) (which is proportional to, but not equal to, the number of particles) is shown in Fig. 2 for 81 clusters ranging in size from 3 to about 150 segments (circa 30 to 1500 particles). Linear behavior holds over the decade and a half in mass that was measured. From the inverse slope, the fractal dimension is 1.20 \( \pm 0.15 \), fitted with the data points weighted in favor of the larger clusters; this value is to be compared with 1.7 and 1.4, obtained for the two-dimensional WS and CLCL models, respectively.

Figure 3 illustrates the cluster-mass distribution \( P(N) \). The most noteworthy feature is the existence of a well-defined peak, also seen in CLCL simulations. Evidently the mobility is an important factor in the aggregation rate since the smaller clusters are nearly depleted. We note that a scaling prediction for CLCL aggregation based on Smoluchowski's coagulation equation has the same qualitative form as \( P(N) \).

The low dimensionality of the clusters is consistent
with their stringy appearance, which is quite different from WS clusters but similar to CLCL aggregates.\(^8\)

Guided by the work of Thomas and McCorkle on the formation of strings in the flocculation of thoria particles,\(^9\) we analyzed the local details of the potential barriers surrounding the end of a dendrite. In the presence of repulsive electrostatic forces, the barrier encountered by a particle approaching a dendrite from the end is lower than the barrier for approaching the side: In the latter case, there are two or more particles in close proximity to a given growth site whereas at the end there is only one. Typically, the attractive van der Waals forces are not large enough to reverse this trend.

The particles are assumed to be trapped by surface-tension forces at the interface by the “flotation” mechanism commonly employed in many fields of chemical engineering, such as the removal of ore particles from suspension. Pieranski argues that the depth of the surface-energy potential well is several orders of magnitude greater than \(kT\); therefore we can consider the particles to be confined strictly to two dimensions.\(^14\) Moreover, since the potential well is very steep, gravitational forces can be neglected,\(^14\) and the interface can be considered to be perfectly flat up to the particles’ surfaces (no dimples). It is possible that significant deformations in the water surface around the spheres could be caused by electrical mechanisms, making surface-tension forces between spheres important. However, for simplicity we confine our attention to the electrostatic interactions.

On a dilute electrolyte substrate, the short-range interactions between two interfacial particles are dominated by a screened-Coulomb law according to Debye-Huckel theory.\(^15\) For high concentration of electrolyte used in the present experiment, the use of a simple Debye-Huckel theory is not well justified. However, since the screening ions are repelled from the interface by their own image charges, the electrolyte is depleted near the interface in a zone roughly of thickness equal to the Debye screening length\(^16\); consequently the effective screening length is extended, and Debye-Huckel theory is more applicable. In any case, lack of a better theory forces us to use the simplest available expressions. Our estimates for a particle approaching a dimer show that the barrier for end-on approach is orders of magnitude lower than for side-on approach, an anisotropy whose magnitude can be attributed to the very high surface-charge density of colloidal silica. Thus, a growing aggregate has a strong tendency not to branch when there are large repulsive forces present.

Excluded-volume effects may also account for the low observed fractal dimension. Repulsive barriers expand the excluded volume (or, in the two-dimensional case, the excluded area) of each segment in a cluster. In flexible, equilibrium structures such as linear and branched polymers, excluded-volume effects lead to substantial swelling as the segments test various configurations by thermal motion.\(^17\) We consider this effect to be secondary in importance because our structures are not very flexible, and they display distinct linearity on both long and short length scales, suggesting a bias in the growth process itself.

A similar possibility relates to the electrical contributions to the persistence length: a cluster with mutually repelling segments tends to straighten out. In the present experiment, however, the Debye screening length is smaller than the monomer diameter; therefore, we have rejected the electrical mechanism for stretching the clusters to a lower fractal dimension.

Finally, it should be realized that the clusters studied here may not be asymptotically large. The fact that the clusters seem to have a persistence length comparable to the size of the clusters themselves means that very large aggregates are required to see asymptotic exponents: The normal CLCL process requires at least \(10^4\) particles and, with biased growth\(^18\) or a finite concentration\(^19\) of particles in the bath, it probably requires more. Since many simulations are not carried out to the asymptotic limit, however, comparisons to them remain valid tests of our understanding. Moreover, our data show no sign of curvature, suggesting that, if there is a separate asymptotic regime, our results reflect the behavior for distances small compared to some unknown crossover length. Clearly the regime we have studied is an experimentally important one because it is readily accessible.

In summary, the differences between our results and extant models of aggregation indicate the importance of interparticle repulsive forces. Even though these are relatively short range, the local tendency to form strings is reflected in the global properties of the

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FIG. 3. Cluster-mass distribution. The well developed peak is a characteristic of both simulations and scaling predictions for the clustering of clusters (Ref. 13).
cluster.
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4D. C. Hong, S. Havlin, H. J. Herrmann, and H. E. Stanley, to be published; J. E. Martin, to be published.
18H. E. Stanley, private communication.
FIG. 1. (a) Schematic of aggregating interfacial colloids. A suspension of silica particles with a spreading agent is dispensed onto the surface of a salty-water substrate where the particles are trapped by surface tension. (b) Photomicrograph of actual two-dimensional clusters.