Aggregation of Magnetic Microspheres: Experiments and Simulations

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(Received 6 June 1988)

Uniformly sized microspheres interacting via long-range magnetic dipolar forces are used to study diffusion-limited cluster aggregation in a plane. The results show that it is possible to scale the temporal evolution of the cluster size distribution and that there is a crossover in fractal dimension from $D=1.52\pm0.05$ to $D=1.16\pm0.05$ in the limit of weak and strong dipolar coupling. External magnetic fields are shown to produce pronounced chaining with D approaching 1. The results compare favorably with computer simulations of aggregation of the same type of particles.

PACS numbers: 64.60.Cn, 05.40.+j, 68.70.+w, 82.70.Dd

Colloidal microspheres confined to a monolayer have proved to be very useful model systems to study pattern formation in diffusion-controlled aggregation.[1] It has been possible to obtain a variety of structures ranging from ramified clusters with fractal scaling to faceted crystals by varying the attractive potential energy between the diffusion particles relative to the thermal energy. This has been achieved by balancing the short-range attractive van der Waals force against the net repulsive electrostatic forces between the charged particles controlled by the counter-ion concentration in the dispersions. The growth patterns have also been obtained in computer simulations[2] with various modifications of the original diffusion-limited aggregation model.[3]

It is expected that the global growth patterns for irreversible aggregation are relatively insensitive to the details of the short-range particle forces.[4] However, particles interacting via long-range dipolar forces produce aggregation with quite different scaling properties. This has already been observed qualitatively in earlier studies of ferrofluids,[5] magnetic aerosols,[6] and so-called magnetic holes.[7,8] However, there is at present relatively little quantitative information about the effects of long-range interactions on the scaling properties based on fractal geometries. This is especially the case for experimental realization in two dimensions (2D), which is particularly important as this offers clear observations of local structures and movements of individual particles. The purpose of this paper is to report such measurements and also to provide comparison with computer simulations.

The magnetic particles[9] used in these experiments consisted of very uniformly sized $d=3.6$-μm sulfonated polystyrene spheres containing 30% (weight) iron oxide in the form of evenly distributed grains in a thin shell (~0.2 μm) near the surface. The spheres were dispersed in water and confined to a monolayer between two plane-parallel glass plates separated by about 5 μm. The spheres could be magnetized to various levels of remanent magnetization $M=0$–2.1 ± 0.2 emu/cm^3, as found in independent measurements.[10]

The dispersion was stabilized so that the electrostatic and van der Waals interactions between the spheres were negligible compared to the magnetic forces. The distribution of the iron oxide in the spheres is not known precisely, but the production process should ensure that the spheres possess fairly uniform remanent magnetization after having experienced external magnetizing fields. An independent check of this could be made by the use of an external field normal to the layer. It was thus possible to produce regular triangular lattices, signifying a many-body system of repulsive dipoles of the same magnitude.

For estimating the long-range interactions, the magnetized spheres may be considered as point dipoles of magnetic moment $\mu=M(\pi d^3/6)$. The magnetic interaction between two spheres i and j separated by the distance $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$ is

$$D_{ij}=\mu^2[\mathbf{u}_i\cdot\mathbf{u}_j-3(\mathbf{u}_i\cdot\mathbf{r}_{ij})(\mathbf{u}_j\cdot\mathbf{r}_{ij})/r_{ij}^2]/r_{ij}^3. \quad (1)$$

Here, $\mathbf{u}_i$ and $\mathbf{u}_j$ are unit vectors along the moments on spheres i and j. The dipole-field interaction energy is given by $\boldsymbol{\mu}\cdot\mathbf{H}$. The dimensionless parameter which determines the effective strength of the dipole-dipole interaction relative to the disruptive thermal energy is

$$K_{\rm dd}=\mu^2/d^3k_{\rm B}T, \quad (2)$$

and that which determines the strength of the dipole-field interaction is

$$K_{\rm df}=\mu H/k_{\rm B}T. \quad (3)$$

For spheres of maximum magnetization $M=2.1\pm0.2$ emu/cm^3, $K_{\rm dd}\simeq1360$ and $K_{\rm df}\simeq1250H$ (Oe) at room temperature. This would indicate aggregating behavior at zero field and alignment even for the earth's magnetic field with $H\simeq0.5$ Oe.

The experiments were performed with samples with concentrations less than 10% with a random initial distribution of spheres and studied by digital image analysis

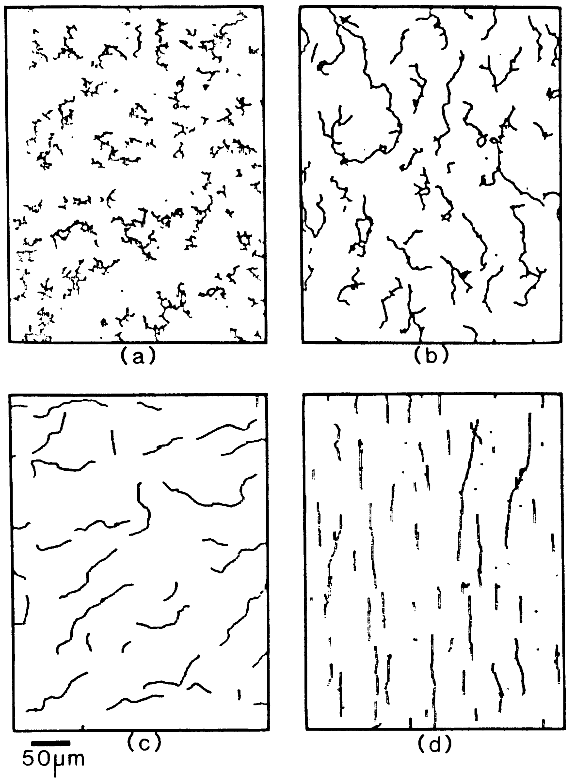

FIG. 1. Aggregates of 3.6-μm spheres for increasing magnetization for zero field: (a) $M=0.23$ emu/cm^3, $K_{dd}=16$; (b) $M=0.57$ emu/cm^3, $K_{dd}=100$; (c) $M=2.1$ emu/cm^3, $K_{dd}=1360$. For nonzero field: (d) $H=1$ Oe for the maximum magnetized spheres $M=2.1$ emu/cm^3.

(512×512 pixels). To avoid the influence of the earth's magnetic field and stray fields, the samples were enclosed in permalloy.

Figure 1 shows a series of aggregated structures formed after a few hours for various experimental conditions. In Figs. 1(a)-1(c) it is seen that there is an increasing tendency to form chains and open loops as M increases, reflecting the preference of alignment of the dipoles. For higher concentrations of the beads close to gelation, it was observed that the average loop size became larger as M increased. Figure 1(d) shows that there is a strong tendency for alignment even at a relatively low external field of $H=1$ Oe corresponding to $K_{df}=1250$.

The fractal dimensions of these aggregates were determined from the usual log-log plot of the radius of gyration versus the number of particles in each cluster. Figure 2 shows the variation of D versus the reduced magnetization K_{dd} [Eq. (2)] for no external fields. These results are based on approximately 70 measurements. As may be seen, D becomes significantly lower as K_{dd} increases, and agrees within experimental error with the simulated value $D=1.23\pm0.12$ for large K_{dd} as discussed below. Also included in Fig. 2 is the earlier value

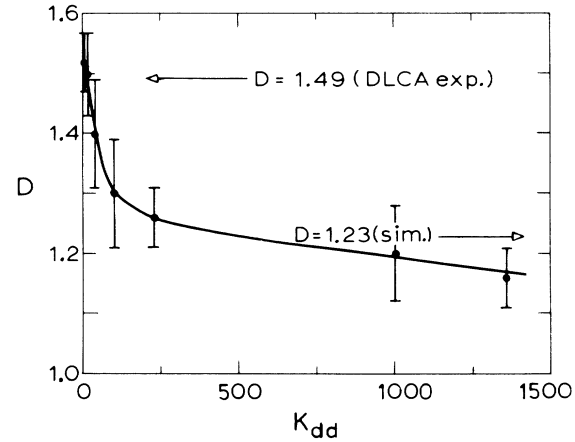

FIG. 2. Fractal dimension D vs dipolar coupling constant K_{dd}. The value $D=1.49\pm0.06$ for $K_{dd}\rightarrow0$ was found in earlier aggregation experiments (Ref. 1) for nonmagnetic spheres. It is also seen that for large K_{dd}, D approaches the simulated value $D=1.23\pm0.12$ as discussed in the text. The solid line is only a guide to the eye.

$D=1.49\pm0.06$ found for diffusion-limited cluster aggregation (DLCA) of nonmagnetic spheres.[1] As may be seen, this result appears to be close to the limiting value also for magnetized spheres as $K_{dd}\rightarrow0$. The clusters of magnetized spheres in the presence of an external field of 1 Oe, as shown in Fig. 1(d), have fractal dimension $D=1.05\pm0.03$. This will be compared with simulated results discussed below.

The temporal evolution of the cluster size distribution was analyzed with the following proposed scaling relation[11] for cluster-cluster aggregation:

$$n_s(t)\simeq S^{-2}(t)f(s/S(t)). \tag{4}$$

Here, $n_s(t)=N_s(t)/N_0$ with $N_s(t)$ the number of clusters with s particles and N_0 the total number of particles. The mean cluster size is given by

$$S(t)=\sum n_s(t)s^2/\sum n_s(t)s, \tag{5}$$

where the sums are taken over all clusters. It is expected that

$$S(t)\sim t^z \tag{6}$$

for $t\rightarrow\infty$ with z a critical exponent.[11]

Figure 3 shows the experimental results for the clustering of the $M=2.1$ emu/cm^3 particles according to Eqs. (4) and (5) for a time span of $t=8$–165 min. As may be seen, there is fair data collapse. The inset of Fig. 3 shows that $S(t)$ appears to approach a power-law dependence for large t according to Eq. (6) with an exponent $z=1.7\pm0.2$. For the less magnetized spheres, similar results were obtained. The fitted exponent z was thus found to decrease slightly with reduced M, reaching a limiting value $z=1.4\pm0.2$ for low values of M. A possible exponential time dependence[12] was also con-

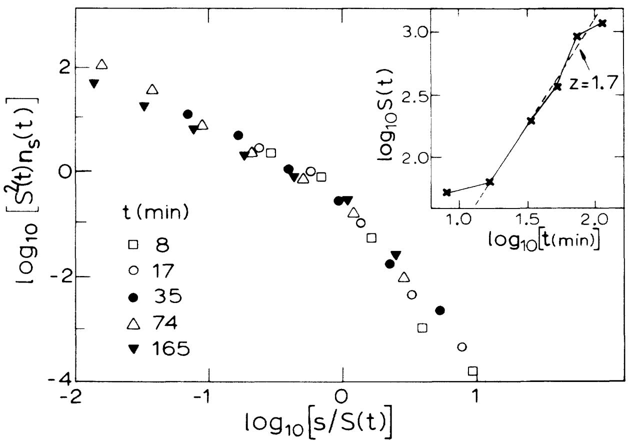

FIG. 3. Scaling of the temporal evolution of the cluster size distribution of the aggregation of 3.6-μm magnetized spheres ($M=2.1$ emu/cm^3) as discussed in the text. Inset: Fit of $z=1.7\pm0.2$ to the log-log plot of average cluster size vs time [Eq. (5)].

sidered, but it turned out that the only reasonable fit was obtained for the power-law dependence.

Simulations of the 2D aggregation process were done, having as a basis the cluster-cluster diffusion-limited aggregation model,[13,14] and were carried out off-lattice with 100 equal-sized spherical particles. The dipolar interactions among the moments attached to each particle were included through a Monte Carlo approach, as was previously done in three dimensions.[15] However, in Ref. 15 calculations were performed within the hierarchical version[16] of cluster-cluster aggregation, which neglects a spread in cluster sizes during the process. Here, the growth occurs in a box with periodic conditions imposed on its sides. Brownian diffusion is either translational or rotational, alternately, with a cluster diffusion coefficient proportional to $m^{-1/D}$ (m = mass of the cluster; D = fractal dimension of a Brownian cluster-cluster model aggregate in 2D, taken as[14] $D=1.4$). Rotation of a cluster (about its center of mass) occurs in the same interval of time, and with the same mean kinetic energy as its translation (of a distance equal to a particle's diameter). The particle separation, r_{ij}, is taken as the shortest distance in the extended zone under the periodic boundary conditions. The dipole moments have three spatial components, and in Fig. 4 they are projected onto the plane. Also, as was done in Ref. 15, after each Brownian step all particles are visited (at random, to avoid any bias), each one having its dipole moment relaxed, i.e., oriented in the direction of the total field, at its position.

The fractal dimensions reported below were estimated from the log-log plot of the radius of gyration versus the number of particles, averaging over several runs, each run itself being an average over a given number of individual samples. Altogether, four different cases were simulated. As a check, Fig. 4(a) shows a typical aggregate without dipolar interactions and without Brownian rotation. The fractal dimension was determined to be $D=1.41\pm0.02$ (10 runs, 10 samples per run, box size 50×50), which agrees within the stated error with the earlier value found for 2D translational Brownian diffusion: $D=1.38\pm0.06$.[14] Figure 4(b) shows a typical cluster including rotational diffusion, but still without dipolar interactions. The averaged fractal dimension is found to be $D=1.39\pm0.04$ (10 runs, 10 samples per run, box size 50×50), which is close to the value found above without rotational diffusion. Figure 4(c) shows a typical cluster with dipolar interactions and with rotational diffusion in the limit of very large moments ($K_{dd}^{-1}=0$). The averaged fractal dimension is found to be $D=1.23\pm0.12$ (10 runs, 1 sample per run, box size 40×40). Although the error is rather large, this value is significantly smaller than the preceding values. As may be seen from Fig. 4(c), the dipoles are rather well aligned. This result corresponds to the present experimental realization in Fig. 1, in the limit of large M as indicated in Fig. 2. Finally, Fig. 4(d) shows the effect of an added external field corresponding to $K_{df}=0.2K_{dd}$. As may be seen, the net result is an almost straight chain

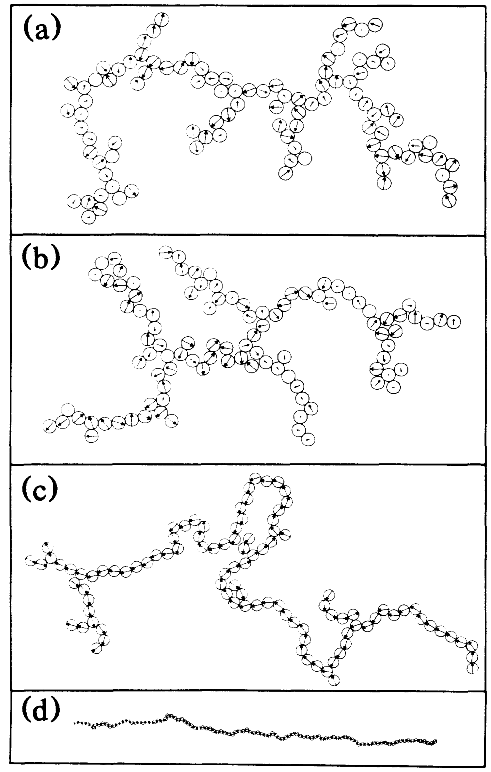

FIG. 4. Typical simulated clusters of 100 particles for various conditions: (a) without dipolar interactions and rotational diffusion; (b) without dipolar interactions but including rotational diffusion; (c) with dipolar interactions ($K_{dd}^{-1}=0$) and rotational diffusion; and (d) added external field corresponding to $K_{df}=0.2K_{dd}$.

with well-aligned moments as seen in the experiments. The corresponding fractal dimension was determined to be $D = 1.009 \pm 0.016$ (7 runs, 1 sample per run, box size 99×99).

In summary, it has been shown that diffusing magnetized spheres in a plane produces aggregates with fractal dimensions which decrease with increasing magnetic moments. This effect of long-range interactions has also been seen in the present computer simulations. The effect of external fields is to reduce the fractal dimension towards 1.

The research was supported in part by Dyno Industries Ltd. and the Norwegian Council of Science and Humanities. The advice of Paul Meakin, assistance from Helmer Fjellvåg and samples supplied by John Ugelstad and collaborators at the Foundation of Scientific and Industrial Research at the Norwegian Institute of Technology are also gratefully acknowledged. Numerical simulations have been done at Centre Inter-Régional de Calcul Electronique (Orsay) with a support from Action de Recherche Concertée, Centre National de la Recherche Scientifique and Direction des Recherches, Etudes et Techniques, Contract No. 87/1354. P.M.M. acknowledges financial support from Conselho Nacional de Desenvolvimento Científico e Tecnológico, Brazil.

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