Percolation of two-dimensional attractive coagulated particles

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The aggregation of two-dimensional polystyrene particles, induced by an external alternating electric field, is experimentally studied by means of *in-situ* microscopy; specifically, the percolation behavior is addressed. The experimental results show that a percolation transition occurs approximately at the particle concentration $p_c=0.42$, which is less than the value predicted by the lattice percolation theory. The fractal dimensions of clusters are calculated and are in agreement with those predicted by the percolation theory.

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I. INTRODUCTION

Percolation as a paradigm for all forms of connectivity has been of both theoretical and experimental interest due to the application of the concept of a percolation transition to diverse physical systems, e.g., the connectivity of disordered systems, Ising systems, statistical topography, turbulent diffusion, heterogeneous media, etc. [1,2].

In its original form, percolation is a static model [1]. The simplest percolation model can be defined on a lattice. Randomly occupying each lattice site with a probability p, one can then identify clusters connected by nearest neighbors. For the occupation probability p below a critical value, all clusters are finite. Once the occupation probability exceeds the critical value, an infinite cluster spanning the system suddenly appears, which signifies a percolation transition.

In nature, however, particles usually have mutual interaction and get where they are by some natural processes such as diffusion. In such systems where particles are mutually interacting and coagulating, the percolation behavior is affected not only by the particle concentration but also by the interactions between the particles.

Several researchers [3,4] have investigated the percolation of interacting particles. Experimental measurements of the conductivity of microemulsions (spherical dispersions of water in oil with surfactant at the globule surface) [5] and theoretical studies [6] have revealed that the percolation threshold is a function of both volume fraction and temperature and that the attractive interaction between globules is essential in understanding the phase diagram and scattering data. The theoretical work of Selinger and Stanley [7] demonstrates that attractive interactions between particles would lower the percolation threshold and repulsive interaction would raise the percolation threshold.

For systems where particles undergo coagulation (i.e., there exist short-range attractions between particles and a bond would form when two clusters collide), it is now understood that there exist two regimes [8]: (i) a low density regime, i.e., when the distance between particles is much larger than their linear size, the clusters formed being fractals with fractal dimension $D_f=1.44$ for a diffusion condition in two dimensions; and (ii) a high density regime, i.e., when the distance between the clusters is less than their radius, the clusters formed being fractals with fractal dimension $D_f=1.8$ in two-dimensions, which is close to that of percolation clusters.

This paper is devoted to the percolation behavior of a two-dimensional polystyrene particle system, confined between two conducting glasses, subject to a homogeneous external alternating electrical field. We restrict our interest to the effect of initial particle concentration on the morphology of aggregates, i.e., the percolation behavior and the structure (external and internal) of clusters. The percolation threshold determined is about 0.42, which is less than the value predicted by the static percolation model in two dimensions. The geometries of clusters at

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different particle concentrations are studied and the results of the fractal dimension are close to that in the theoretical model.

II. EXPERIMENTAL DESCRIPTION

The monodisperse suspension of spherical polystyrene colloidal particles used in our experiments is synthesized by emulsion polymerization and the two step swelling method according to Ref. [9]. The diameter of the particle is about 1.4 μm, and the polydispersity is better than 4%.

A cell is composed of two parallel glass slides coated with conducting materials by which an external electrical field can be applied. The polystyrene latex is sealed into the cell by capillarity, forming a two-dimensional colloidal film. The thickness of the cell is controlled by the Mylar spacer placed between two glasses. The thickness throughout our experiments is kept at 50 μm.

The external alternating electrical field that is applied is perpendicular to the surface of the cell. It has been observed that the electrical field can initiate the aggregation of particles when its frequency is in the range of from several hundred Hz to several kHz and its strength exceeds some value (about 0.5 V/50 μm). The aggregation process is observed through an optical microscope equipped with a video system, recorded on the tape, and analyzed later by using an image processor.

We have fixed the frequency and the voltage of the field throughout our experiments ($f=1.5$ kHz, $V=0.5$ V) in order to achieve the same mutual particle interactions and thus the same sticking probabilities, and we have performed aggregations at different particle concentrations. The pictures of coagulated particles obtained were digitized with a resolution of 256×256 and then analyzed with a personal computer. One pixel corresponds to 1 $\mu m\times1$ μm. The results are presented in the next section.

III. RESULTS AND DISCUSSION

It is worth pointing out that the colloidal system here is two dimensional and that this does not depend on the thickness of the cell. A colloidal particle, possessing an induced electrical dipole moment under the electrical field, interacts with the conductive cell surface by an electrical image interaction which is attractive. Preliminary quantitative analysis by Richetti, Prost, and Clark [10] has shown that the interaction energy will be larger than the thermal energy kT when the strength of the field exceeds some threshold, depending on the surface charge of the particles. As a result, when the particles are close to the cell surface and the electrical field strength exceeds some critical value, the particle mobility perpendicular to the cell surface decreases dramatically, while the mobility parallel to the cell surface does not change much.

Direct observations in our experiments have shown that the particles would sediment close to the bottom surface of the cell under gravity because the density of polystyrene is slightly higher than that of water. When the electrical field is turned on, the particles are attracted swiftly to the surface where they aggregate and can diffuse freely in the plane parallel to the cell surface, but the motion of the particles in the direction of the field is restricted. This indicates that the colloidal particle suspension confined between two conductive glass slides under the electrical field perpendicular to the slides is a two-dimensional system, and that the thickness of the cell only controls the strength of the electrical field.

The colloidal suspension is generally stable and no clusters exist without an external field, due to the screened Coulomb repulsion between particles. The application of an external alternative electrical field would introduce attraction between particles and induce the aggregation of particles. The interaction between particles has been preliminarily analyzed in Ref. [11]. We will study it in a following paper.

The aggregation kinetics at low particle concentration p has been studied by us in a previous paper [11]. The aggregation process at high particle concentration ($p>p_c$), similar to that at low p, has two stages. In the first stage, some large clusters are formed, which are immobile and do not span the system. In the late stage, i.e., diffusion-limited aggregation, the large clusters formed grow larger by consuming particles between them, for sometimes the clusters are linked together through the aggregation of particles between them.

Photos of aggregates at four typical particle concentrations are shown in Fig. 1. The cluster assumed by the spheres is a triangular lattice in a small scale but irregularly shaped in a large scale. It can be seen that the average size of the clusters increases with the increase of the particle concentration, a spanning cluster occurs when the concentration exceeds the percolation threshold, and the morphologies of clusters at different concentrations are different. In Fig. 1(a), the concentration is far below the percolation threshold and the clusters formed are small and droplike; in Fig. 1(b), the concentration is just below the percolation threshold and the clusters are large and ramified, but still finite; in Fig. 1(c), the concentration is just above the threshold and a spanning cluster with holes of different sizes on it is formed, indicating a percolation transition; in Fig. 1(d), the concentration is far above the percolation threshold and practically all that exists is an infinite cluster.

For each digitized picture, the probability $P_N(p)$ of a site belonging to the largest cluster and the particle concentration, equal to the ratio of the number of occupied sites to the lattice size 256×256 are calculated. The subscript N of $P_N(p)$ corresponds to the size of view 256. The result of various samples is shown in Fig. 2. For low p, P_N is negligible. As p is increased the probability belonging to the largest cluster increases drastically near $p_c\approx0.42$, and then P_N increases almost linearly with p, as p is much larger than p_c.

Both Figs. 1 and 2 demonstrate that a percolation transition takes place approximately at concentration $p_c=0.42$. Both renormalization group theory and computer simulation [1] on the triangular lattice give the precise percolation threshold in two dimensions, $p_c=0.5$. this indicates that the aggregation process (or, equivalently, the attraction between particles) has lowered the percolation threshold.

Two different kinds of data points in Fig. 2 correspond

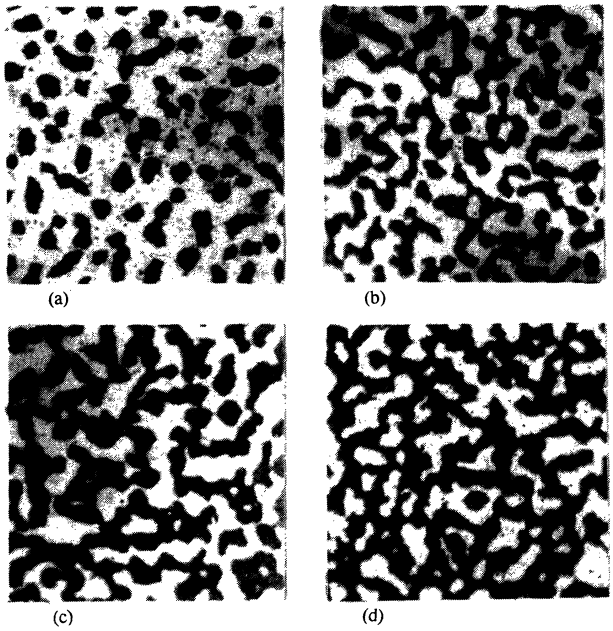

FIG. 1. Microscopic view of aggregates formed at different particle concentrations p. (a) $p=0.24$; (b) $p=0.39$; (c) $p=0.44$; (d) $p=0.48$.

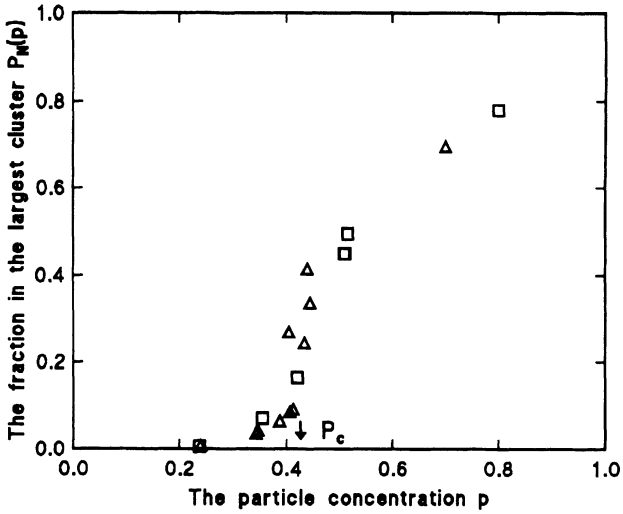

FIG. 2. The plot of the probability of belonging to the largest cluster $P_N(p)$ vs the particle concentration p. The arrow shows the percolation threshold. Δ, $V=0.55$ V; □, $V=0.80v$.

to two different field strengths (or to, say, different mutual interaction magnitudes). It can be seen from Fig. 2 that the effect on the electrical field strength on the percolation threshold can hardly have been distinguished in our experimental condition.

To illustrate the external structure of the aggregates formed, we have calculated their fractal dimensions. For the particle concentration below the percolation threshold, the radius of gyration method is used, in which the scaling law between the mass of clusters and their size is considered, that is, $N\sim R_g^D$, where R_g is the radius of gyration of the cluster and D is the fractal dimension. For the particle concentration larger than the percolation threshold, the sand-box method is used, in which the scaling law of the mass within a box with the length scale of the box is considered. The mass within a box, of side L and centered on the point near the cluster mass center should scale as $N\sim L^D$, where D is the fractal dimension. In our calculation we averaged $N(L)$ over boxes that center on the pixel closest on the cluster to the mass center and its four adjacent pixels.

The data for the pictures in Fig. 1 are shown in Fig. 3. The scaling is evident. The lines shown represent the best fits of linear variation, and the slopes of the line give the fractal dimensions. Data for different particle concentrations are summarized in Fig. 4.

From Fig. 4 it can be seen that the fractal dimensions obtained increase from 1.5 to 1.9 as p increases, and two limit regimes exist: (i) the particle concentration far below the percolation threshold p_c, where the fractal dimensions are around 1.6; and (ii) the particle concentration p far above P_c, where the fractal dimensions approach 1.9. In the intermediate case, the fractal dimensions are around 1.7.

It is worth noting that there obviously exists a small scale of triangular structures due to the local rearrangements of particles during the aggregation process and that these local rearrangements do not affect the long-range scaling properties of clusters, as also pointed out by Richetti, Prost, and Clark [10].

In previous papers [10,12], Richetti, Prost, and Clark have studied the morphology of clusters formed at high particle concentrations. The fractal dimensions calculated are in agreement with our results at high particle concentrations. However, the clusters at very low particle concentrations are not obtained and studied by them.

The aggregates formed at p far below p_c are not fractals individually, which can be seen from Fig. 1(a), whereas the N-R_g data for large clusters still exhibit scaling. Hence the fractal dimension (evaluated from the relation between N and R_g), or so-called effective dimension as in Ref. [1], is still used in order to be compared with percolation theory.

In the scaling theory of percolation clusters, Stauffer proposed a "hyper" scaling assumption between R and N, which gives $N\sim R^{d'}$ (N is infinite, at fixed p), with the exponent

$$d'(p>p_c)=d,\quad d'(p=p_c)=d/(1+1/\delta),$$
$$d'(p<p_c)=1/\nu_0,$$

where R is the radius of cluster N, N is the mass of cluster N, and the scaling exponent $\delta=18$ in two dimensions. Computer simulations [1,13] have confirmed this scaling ansatz and give $\nu_0=\frac{2}{3}$. So, in two dimensions, $d'(p>p_c)=2$; $d'(p=p_c)=1.89$, $d'(p<p_c)=1.5$. However, the results of the computer simulation do not give exponent values which are constant in certain intervals and jump discontinuously at p_c; instead, the numerically determined exponents vary continuously with p. Stauffer

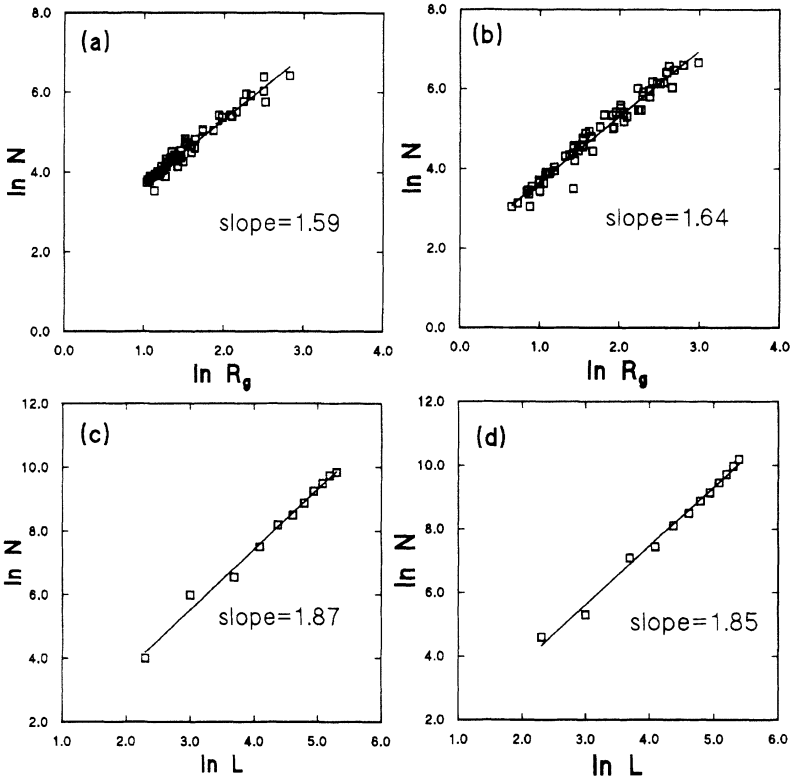

FIG. 3. The double-logarithmic plot of N vs R_g and $N(L)$ vs L. Here the data plotted in (a), (b), (c), and (d) correspond to (a), (b), (c), and (d) in Fig. 1, respectively The slopes of linear fits give the fractal dimensions.

argued that only the date for p close to zero or unity and for $p=p_c$ are reasonably reliable and that the exponents at other concentrations are effective exponents and not yet close to the true asymptotic exponents.

The fractal dimensions obtained in our experiments for p far away from p_c and $p=p_c$ are in agreement with the exponents predicted by the scaling assumption and by the computer simulation. The fractal dimensions for other intermediate particle concentrations p, changing continuously with p, are also in agreement with the computer simulation.

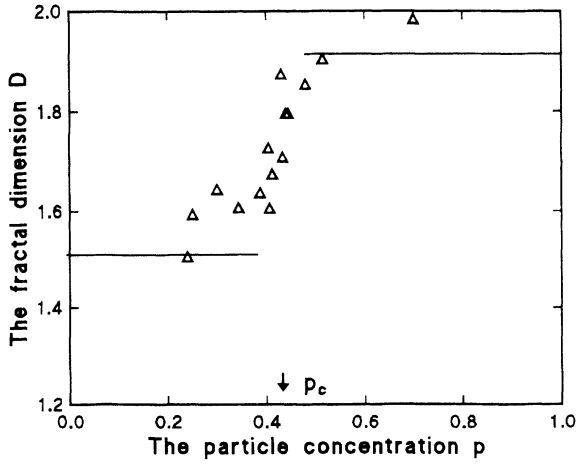

FIG. 4. The variation of the fractal dimension with the particle concentration p.

It can be seen that although the aggregation process lowers the percolation threshold, the scaling exponents seem to agree with the static percolation theory. However, the reasonable model for the aggregation process is the "clustering of clusters" (known as the CCA model) and the differences between our experiments and the CCA model are that there are local rearrangements and some upper critical mass for the mobility of the clusters; i.e., when the mass of a cluster is larger than the critical value, the mobility of the cluster becomes zero and thus cannot move. What the physics behind this is an interesting problem. We consider computer simulations; further experiments are needed to understand this and research is underway in this direction.

IV. CONCLUSIONS

In conclusion, the percolation behavior of two-dimensional aggregated clusters, induced by an external alternating electrical field, has been studied experimentally. The aggregation kinetics, i.e., the sol-gel transition, has not been involved. The internal structures of the clusters are triangular lattices. The external morphologies are different for different particle concentrations. The percolation threshold obtained is 0.42, which is less than the value 0.5 predicted by the static percolation model on the triangular lattice. The effect of a different electrical field strength on the percolation threshold is not obvious in our experimental condition. The fractal dimension of the clusters at different concentrations changes with the particle concentration p. For the limiting cases ($p \ll p_c$, $p=p_c$, and $p \gg p_c$) it is in agreement with the percolation theory.

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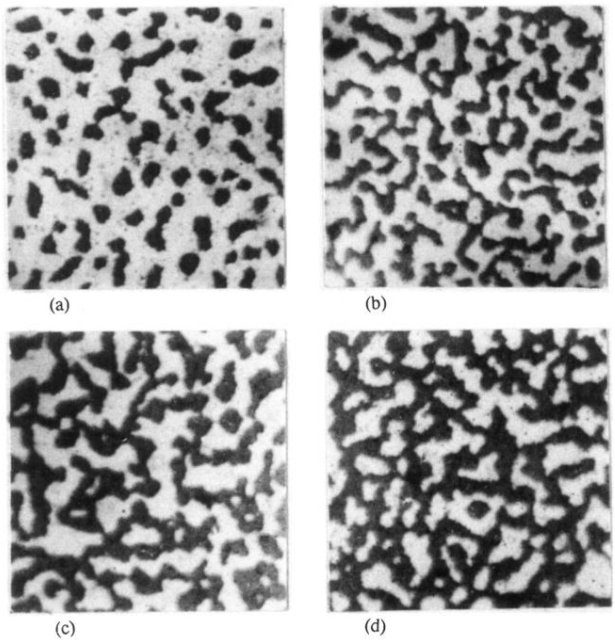

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