Fractal-chain transition of field-induced colloid structure

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Electric-field-induced fractal and chain patterns formed by microspheres in liquid have been investigated. While conducting microspheres form fractal patterns, insulating microspheres form chains. The reversible fractal-chain transition is mainly controlled by the surface conductivity of microspheres. We have demonstrated the transition with glass microspheres coated with conducting and insulating films. Moreover, we observed that the suspended chains would aggregate to form columns under high field conditions. This aggregation, nevertheless, cannot be observed in the fractal case. [S1063-651X(98)12912-4]

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I. INTRODUCTION

Both fractal and chain patterns have been observed and studied in many branches of modern science. In complex fluids, polymolecular materials, biological fluids, and liquid crystals, chain and fractal structures are generally formed by the solid particles phase separating from the liquid [1–8]. In the case of fractal patterns, the well-known diffusion-limited aggregation (DLA) model [9] has often been applied to explain a certain class of patterns induced by aggregation of particles [10–13]. Yet another kind of fractal pattern formation was reported recently, resulting from long-range forces, under the influence of external magnetic or electric fields [14,15]. However, the difference between chain and fractal formation is unclear.

In this paper we report field-induced fractal and chain patterns formed, respectively, by conducting and insulating particles suspended in liquid. We further report that these two patterns can be transformed into each other if we start with glass microspheres and coat them sequentially with conducting and nonconducting materials. We conclude that it is the surface properties that effect their pattern formation.

II. EXPERIMENT AND RESULTS

The dielectric particles of $SrTiO_3$ with size of $10\pm5\ \mu m$ are chosen as the insulating solid phase due to its high dielectric constant and low conductivity. For the conducting particles, irregular copper powder (Fisher Science) was fabricated into spheres ($65\pm5\ \mu m$ in diameter) by using a high-temperature flaming device. Each of them was mixed with the silicone oil (Dow Corning No. 705) with a total volume fraction less than 10%.

To investigate the effect of surface properties on the fractal and chain patterns, the glass microspheres (SiO_2, 47 μm in diameter) were chosen as the core material onto which a conducting (Ni metal) and an insulating [lead zirconic titanate (PZT) ceramic] layer were sequentially coated. As for the Ni coating, five solutions were prepared using proprietary nickel coating chemicals purchased from Enthone OMI Co. Ltd. They are Enplate Promoter 846, Activator 850, Accelerator 860, Ni-426A and 426B. The coating process takes the following sequence: 10 g of glass spheres were first dispersed in solution 846 for about 7 min, then the particles were filtered and washed with distilled water. The washed particles were put into the 850 solution for 12 min. After being filtered and washed again the particles were suspended in 860 for 15 min. The rinsed and filtered particles were finally placed in the mixed solution of 426A and 426B at 60 °C for Ni coating (~1.5 μm thickness). After that, the conducting microspheres were heated in a vacuum oven for stress relaxation. A fraction of the Ni-coated microspheres was then coated with a PZT insulating film, and a minimum thickness of 1 μm was found necessary to prevent electric breakdown under high field. This is because when a high electric field is applied across the colloid, at least one continuous path of contacted particles can be found between the two electrodes. If the PZT layer is too thin, its dielectric strength may not be able to prevent local electrical breakdown and a short circuit between the two electrodes occurs. (For the details of nickel and PZT coating methods, see Ref. [16].)

Different patterns formed by the insulating and conducting particles suspended in the silicone oil under various modes of external electric field are shown in Fig. 1. Figures 1(a)–1(c) demonstrate chains formed by $SrTiO_3$ particles aligning themselves in the direction of the external electric-field lines, while Figs. 1(d)–1(f) illustrate fractal patterns formed instead by conducting Cu microspheres. These modes of electric fields were realized by mounting the brass electrodes on a glass slide under various geometric configurations.

The formation mechanism of the patterns shown in Fig. 1 may be interpreted as follows. As the electric field is applied, field-induced dipole moment $p=a^3\varepsilon_f\beta E_l$ is induced on each microsphere, where $\beta=(\varepsilon_p-\varepsilon_f)/(\varepsilon_p+2\varepsilon_f)$. E_l defines the local effective field acting on each microsphere, and ε_p and ε_f represent the dielectric constant of the solid and liquid phase, respectively. The local field can be written as $E_l=E+E_d$, where E and E_d are the external and induced dipole fields, respectively. The force $f_{d\text{-}d}$ between dipoles has been calculated rigorously for the case of two spherical particles separated by a distance r_{ij} much greater than their radius a,

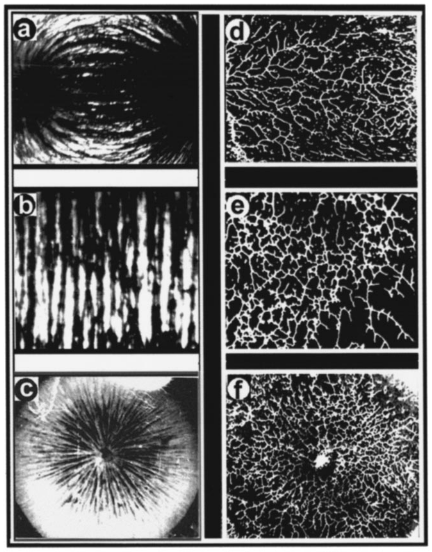

FIG. 1. Electric-field-induced two-dimensional patterns formed by insulating (a)–(c) and conducting (d)–(f) particles, where the field strength is 500 V/mm. The volume fraction is about 8.0 $\pm 0.5\%$. (a) and (d) correspond to needle-shaped electrodes pointing towards each other, (b) and (e) correspond to parallel plate electrodes, and (c) and (f) correspond to cylindrically symmetric electrode configurations.

$$f_{d\text{-}d}=\left(\frac{6}{4\pi\varepsilon_f}\right)\frac{p^2}{r_{ij}^4}.$$

The attractive force between the particles leads to chains aligned in the direction of the external electric-field line as can be identified in Figs. 1(a)–1(c). On the other hand, the fractal pattern forms if conducting particles replace the insulating ones, as demonstrated in Figs. 1(d)–1(f). For the formation of the fractal pattern, the conducting particles aggregate and adhere to the electrodes to form a seed, then the nearest one to the seed is attracted to form a short cluster. It is envisioned that the cluster and the electrode are at equipotential, suggesting that conducting particles modify the global electric-field line from a regular to a random distribution. We note that at a protrusion (single particle) of the aggregate, its electric-field strength is the highest and the forces acting on the surrounding particles are the largest, thus resulting in branching, which is the essential growth step of fractal patterns. Recently, Kun and Pál reported a computer simulation of this kind of fractal pattern [17].

We also observed three-dimensional (3D) chain and fractal patterns as shown in Fig. 2. As depicted in the center-right inset of Fig. 2, the cell containing the particle/liquid mixture was sandwiched between two [indium tin oxide (ITO)] glasses during testing, where the two transparent electrodes were connected to a high voltage power supply. The 3D images in Fig. 2 were taken by tilting the cell 45° to the observation direction. For the insulating particles, at high electric-field strength and large volume fraction, they form columns spanning the electrodes, as shown in the lower left-hand side inset of Fig. 2(a). This spanning phenomenon is not observed for the conducting particles, rather they form netlike structures as shown in Fig. 2(b).

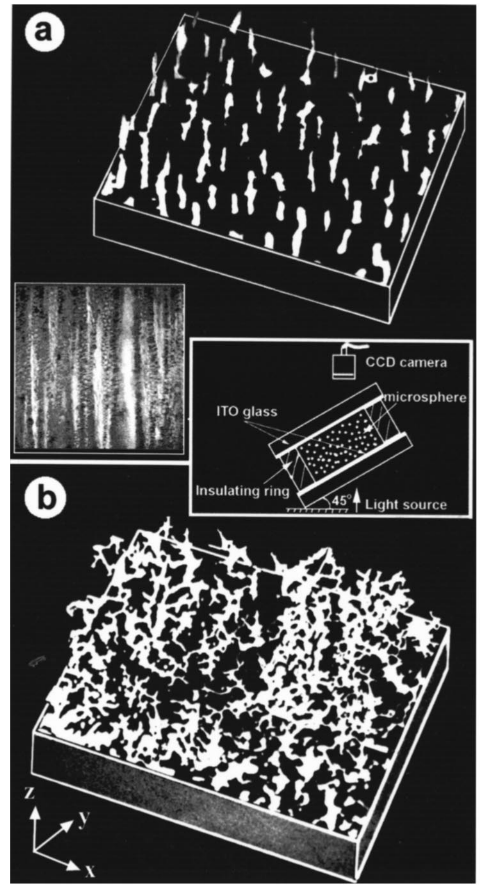

FIG. 2. Three-dimensional configurations built by glass microspheres without (a) and with (b) conducting layer coating. Inset depicts the cell for photo taking, where the microspheres are suspended in the silicone oil. The volume fractions for (a) and (b) are 7.5%. The field strength for (a) and (b) is 700 V/mm. The lower left-hand side inset in (a) shows side view of glass column formed at field strength of 1200 V/mm.

To further investigate the growth mechanisms, a series of experiments were carried out starting with a glass core material coated sequentially with thin layers of conducting (Ni) and isolating (PZT) materials. Figure 3(a) is the pattern formed by the dry (not moistened) glass microspheres in silicone oil, where the chains align perfectly along the external electric lines. However, the treelike fractal pattern, see Fig. 3(b), appeared when the glass microspheres were only coated with a nickel layer. Moreover, the pattern transformed back to chains when another PZT insulating layer was coated over the Ni layer (here the structure of microsphere is glass/Ni/PZT, i.e., a double coating), see Fig. 3(c). From Fig. 3, we conclude that the mutual transition between fractal and chain patterns is mainly controlled by the surface properties and not the bulk material used. It should be pointed out that the chains formed in Figs. 3(a) and 3(c) are not perfect; this is because, at fixed electric-field strength and volume fraction, the interaction among the dielectric particles is much weaker than that of metal particles. Our conclusion can be understood by realizing that the polarization charges must be distributed on the surface of the microspheres.

Our work confirms earlier studies of the influence of the particle surface conductivity on the patterns formed by hu-

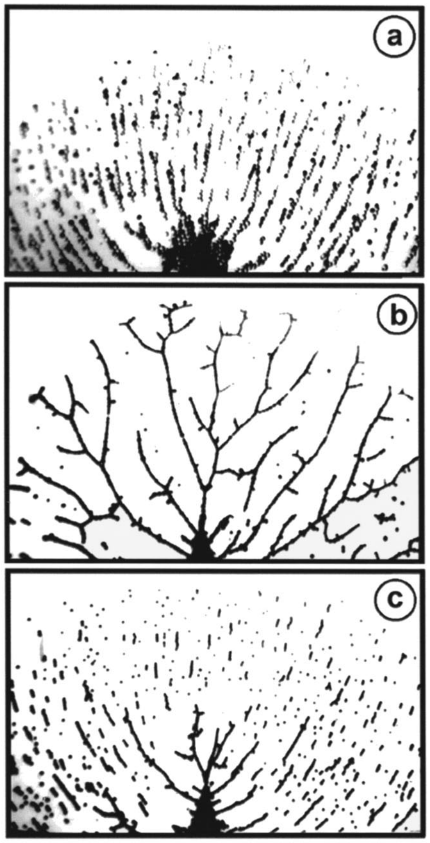

FIG. 3. Chain-fractal pattern transition as surface property of the microsphere is changed, where (a) is the case of a glass particle, while (b) and (c) are the situations when thin films of conducting and insulating layers are coated sequentially onto glass microspheres. Here the field strength is fixed at 500 V/mm.

man tooth enamel under electric fields [18]. Two different patterns were seen depending on whether or not the enamel is coated with carbon during the transmission electron microscopy (TEM) observation. The uncoated enamel grew straight chains but the coated enamel formed a tree fractal. We believe, as detailed above, that the carbon coating has changed the surface conduction of the enamel, resulting in the transformation from chains to fractal growth.

The significant effect of surface conductivity can be further demonstrated that there exists a threshold value of surface conductivity on the pattern transition. It is illustrated in Fig. 4. Figure 4(a) shows the case when water-poor (the surface of the particles contains a small amount of water, which is done by evaporating vapor on the particles) glass microspheres were put in between two parallel electrodes, they form short chains. However, netlike fractals are observed when water-rich (the surface of the particles contain a larger amount of water, which is done by wetting the particles with water) glass microspheres were used, see Fig. 4(b). For the effect of water coating on the dielectric properties of particles, see Ref. [19]. Figure 4(c) gives the relationship between the fractal dimension D_f and the water content of the microspheres. The threshold value can be identified easily. When the water content surpasses the threshold of 0.1 wt %,

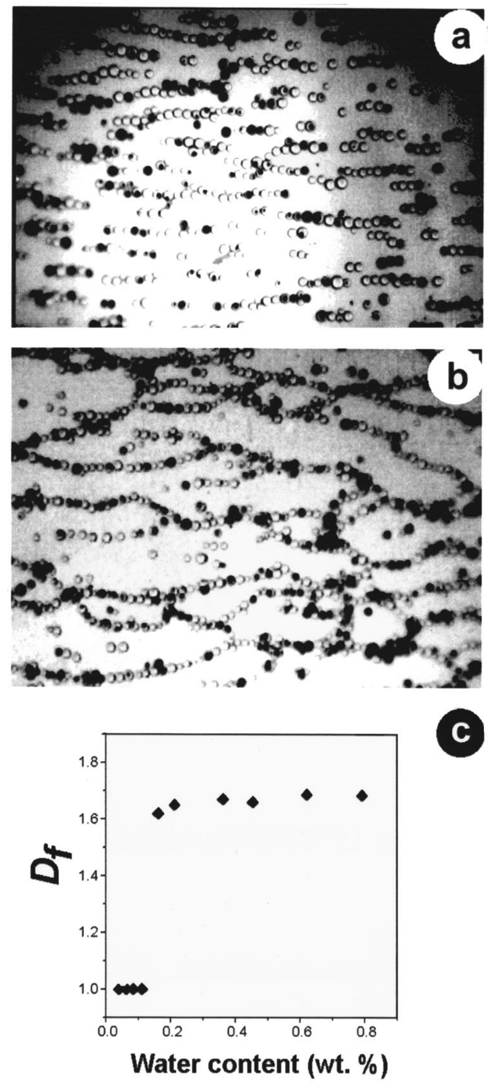

FIG. 4. Straight chain – netlike fractal transition resulting from water content of glass particles, where patterns (a) and (b) are formed by glass microspheres with water content of 0.12 and 0.2 wt. %, respectively. (c) shows a critical change of the fractal dimension as water content is increased.

chains become disordered and they transformed to the netlike fractal pattern. We suggest that, given a similar threshold behavior, our system may be an appropriate model for field-induced growth phenomena. Structural transitions of this kind of system provide a means to alter and control colloid structures by varying only the surface properties of suspensions.

III. SUMMARY

Field-induced fractal and chain patterns formed with respective conducting and insulating particles suspended in the liquid have been investigated in the paper. We found that the two patterns can be interchangeable depending only on the surface conductivity of particle used. Furthermore, this transition can also occur if the glass particles were moistened.

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