Pattern transitions induced by the surface properties of suspended microspheres in electrorheological fluid

Weijia Wen
Department of Physics, Hong Kong University of Science and Technology, Hong Kong and Institute of Physics, Chinese Academy of Science, Beijing, 100080, People's Republic of China

Kunquan Lu
Institute of Physics, Chinese Academy of Science, Beijing, 100080, People's Republic of China

(Received 4 December 1996; accepted 29 January 1997)

In our previous Letter [Phys. Fluids **8**, 2789 (1996)] we reported a new kind of netlike structure formed by metal microspheres suspended in silicon oil. In this paper we present further experimental results showing that different patterns are formed depending on whether metal, semiconducting, or dielectric microspheres are presented in the electric field. In addition, several experiments are performed on the surface properties of suspended microspheres and it is found that a pattern transition occurs when the surface conductivity of the solid phase is changed. This phenomenon can also be observed in a glass/oil ER fluid if the glass particles absorb enough water. © *1997 American Institute of Physics.* [S1070-6631(97)00406-6]

I. INTRODUCTION

Electrorheological (ER) fluids are a class of materials whose rheological properties are controllable by the application of an electric field. In the past decade, research in ER fluids has attracted much renewed interest due to its possible application in the fields of industry and engineering, and much theoretical and experimental work has been done in this area. The theoretical model used to explain the physical mechanism of the ER effect is based on the interaction of dipoles induced on the particles under an external electric field.[1–4] The evidence for the model has been obtained experimentally.[5,6] However, it is difficult for the polarization model to explain certain experimental results, and there exists a clear gap between theoretical prediction and experimental observation when the particles contain a certain amount of water. In particular, the effects of conductivity of the suspended solid or liquid phase on ER response were proposed in the last few years.[7–10] Recently, the theoretical model of the effect of conductivity in electric-field-induced aggregation in ER fluids was presented by Khusid and Acrivos.[11] It is found experimentally that, under an ac electric field, the frequency response of an ER fluid containing the conducting particles is totally different from that of an ER fluid containing insulating particles. A possible explanation is that both the dielectric constant and the conductivity of the ER fluid contribute to the ER effect.

In this paper, we present further experimental observations showing that different patterns are formed depending on whether metal, semiconducting, or dielectric microspheres are presented in the field. In addition, several experiments are performed on the surface properties of suspended microspheres, and it is found that a pattern transition occurs when the surface conductivity of the solid phase is changed. Finally, the effect of the dielectric properties of the glass surface on pattern formation is also investigated in this paper.

II. EXPERIMENT

Two-dimensional patterns were obtained using a traditional ER fluid cell (see Ref. 1), where two electrodes were mounted on a glass slide and the gap of two electrodes was 4 mm. A dc electric field was applied in the process of pattern formation. The ER fluids used in our experiment consist of silicone oil (the conductivity of oil is about 1.7×10^{-11} S/m) containing different kinds of microspheres including metal (Cu), semiconductor (Si), $SrTiO_3$ (high dielectric constant and low conductivity), PMMA (very low dielectric constant and conductivity), and glass (low dielectric constant and conductivity). The volume fraction of all samples used in the experiment are about 0.05–0.07. The sample fabrication procedure is described below.

A. Fabricating of microspheres

The metal microspheres used in our experiments were made with purified copper grade (Fisher Scientific). Copper was chosen as a solid phase because its melting point is higher than that of indium, which were used in our earlier experiments. Copper particles of about 40 μm in size were selected and were fabricated into the microspheres using a high-temperature spouting device.[12] The prepared microspheres were put into the dilute HCl for surface treatment and then the cleaned microspheres were baked in an oven at a temperature of 60 °C for 5 h. The processes for making $SrTiO_3$ and Si microspheres are the same as those detailed above for copper. We found it very difficult to fabricate semiconducting microspheres such as Si particles because a considerable proportion (about 30%) could not be made in the spherical form. However, this did not affect the observation of the pattern formation in our system.

B. Surface coating

In order to change the surface properties of the materials being investigated, three different coating methods were used on the different microspheres (Fig. 1): (a) an insulating layer was coated on the copper sphere; (b) a monolayer of

 1070-6631/97/9(6)/1826/4/$10.00

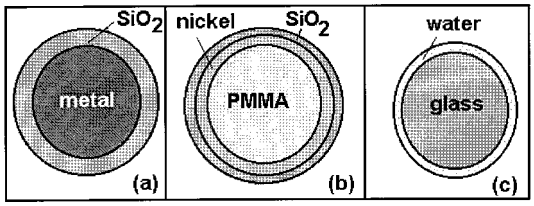

FIG. 1. Microspheres with different coating materials.

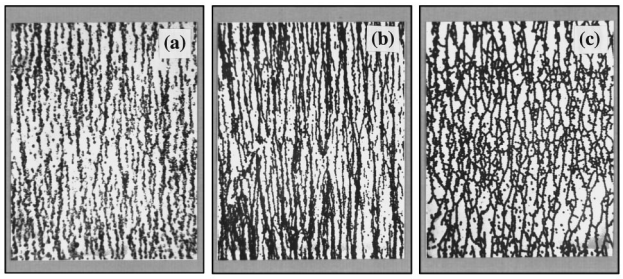

FIG. 2. Pattern formations performed with different kinds of microspheres, where (a), (b), and (c) show the patterns formed by $SrTiO_3$, Si, and Cu microspheres, respectively.

metal or double layer of metal SiO_2 was coated on the PMMA microsphere; and (c) water was coated on the glass sphere.

The insulating layer on the copper microsphere was plated by the sol-gel process. The surface-cleaned copper microspheres were put into the SiO_2 sol gel solution, which was prepared with tetramethoxysilane (STREM CHEMICALS) and methoxyethanol. The solution used in the experiment was diluted to 0.1 mol by adding distilled water. Next, the mixed particles were stirred at about 60 °C for 2 h. To prevent the oxidation of the copper surface by air, the filtered spheres were heated at 500 °C in a vacuum chamber at 10^{-5} Torr for 5 h. In order to obtain a good insulating layer, at least a triple coating of the microsphere was needed.

The bulk of one sample was chosen for the PMMA microspheres (very good light transparency), and nickel was first plated on the surface to form a conducting sphere. Five solutions were prepared using the following nickel-coating chemicals obtained from Enthone OMI Co., Ltd: Enplate Promoter 846, Activator 850, Accelerator 860, Ni-426A and 426B. The coating process is detailed as follows: 5 g PMMA spheres with 70 μm in diameter were dispersed in solution 846 for about 5 min, then the filtered particles were washed with distilled water. The washed particles were then put into solution 850 for 8–10 min. After filtering and washing again, the particles were dispersed in solution 860 for 6 min. Finally, the rinsed and filtered particles were placed in the mixed solution (426A and 426B), which was maintained at 50 °C. The thickness of the nickel layer depended on the reaction time. After being rinsed and filtered, the coated particles were heated in the oven at 80 °C until all trace water was removed. An anneal temperature of less than 150 °C was used because PMMA has a low melting point. Finally, the well-coated spheres were no longer transparent to light.

The water-coating process was carried out as follows. First, glass spheres of a selected size (45 μm) were heated in the oven at 120 °C to remove any surface water. The dried particles were immediately placed in the glass tubes into which different amounts of water were injected with a volume pipette, and the respective weights of the water and glass particles were measured with a electronic balance (OHAUS CORP AP250D). The mouths of the tubes were sealed with a torch and the tubes were then placed in an oven at a temperature of 120 °C for 5 h. The tubes were rotated continuously to ensure uniform vaporization.

III. RESULTS

Two-dimensional patterns of the dielectric, semiconducting, and metal spheres in the silicone oil are presented in Fig. 2. Figure 2(a) shows clearly the chains formed by the dielectric spheres $SrTiO_3$ under an external electric field. This situation is also observed in Fig. 2(b) when the semiconducting spheres are substituted as the solid phase. However, it is found that the chains formed by Si spheres are better than those formed with dielectric spheres in the same strength of the electric field. Even in a weak electric field, the semiconductor can easily form perfect chains. This phenomenon is highly abnormal. According to the polarization theory, the interaction force is determined by the dielectric constant of the solid phase if other parameters are the same. The dielectric constant of $SrTiO_3$ is much larger than that of the semiconductor Si, which means that the dipole–dipole force of the $SrTiO_3$ should be stronger than that of the Si semiconductor. However, the experimental result shows the opposite phenomenon. A realistic explanation for this result is unclear at present. However, we can infer that the conductivity of the particles may be another factor that influences the chain's formation if the conductivity is below a certain value. As can be seen from Fig. 2(c), a net-like formation occurred when copper spheres were presented in the field. When the copper surface was coated with an insulating layer of SiO_2, however, the situation was very different, as shown in Fig. 3. Figure 3(b) demonstrates that the pattern formation of coated copper microspheres is the same as that formed with dielectric particles. The change from Fig. 3(a) to 3(b) demonstrates

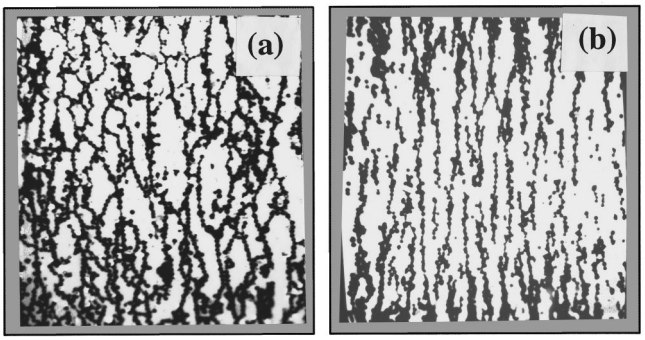

FIG. 3. Pattern transition when an insulating layer is coated on the copper microsphere, where (a) is a pure copper microsphere and (b) is the microsphere after coating.

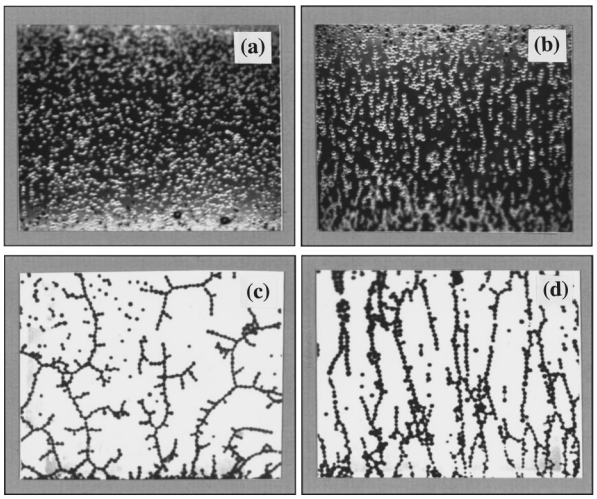

FIG. 4. Development of the pattern transition performed with PMMA-based microspheres, where (a) is pure PMMA, (b) is PMMA with a thin layer of nickel coating, (c) is PMMA coated with a good conducting nickel layer, and (d) is PMMA double coated with an inner conducting and outer insulating layer. The field strength is fixed at 600 V/mm.

that the pattern transition occurs when the surface conductivity of the particles changes, even though their buck conductivities are the same.

Another interesting phenomenon can be seen in Fig. 4, where a PMMA is used as the bulk material. Figure 4(a) shows that no chains can be observed if pure PMMA spheres are presented in a field strength of about 600 V/mm. This is because the PMMA sphere is not easily polarized under the external electric field, which can be seen also from the common ER effect measurement where the viscosity is largely unchanged when the PMMA is used as the solid phase. However, some short chains can be observed in Fig. 4(b), where the PMMA is coated with a very thin layer of nickel. The thin layer nickel leads to the increment of the polarization on the surface of PMMA spheres, thus increasing the interaction force between the particles. Figure 3(c) shows the pattern when the thickness of nickel is increased to form a uniform conductive layer; the pattern is the same as that formed by the copper spheres [Fig. 2(c)]. Figure 4(d) shows the pattern transition from Fig. 4(c) when the outer nickel layer is coated with an insulating layer of SiO_2. In this case, the net-like pattern cannot be observed and the chains begin to appear again. Figures 3 and 4 demonstrate that the surface property of the solid phase is the main factor affecting pattern formation, even though different core materials are used.

Most materials show a strong ER effect if a small amount of water is added to them.[13,14] It has been suggested that surface moisture serves to enhance polarization through ionic migration or through the formation of an electric double layer. Another reason for the enhancement of the induced dipole is the large dielectric constant of water. It is found that the ER strength of glass particles depends strongly on the water content. The frequency and field dependencies are in agreement with the polarization theory, and the recently proposed DER model if water-free or slightly hydrous particles are presented in the electric field.[7,15] However, the model is not applicable if the water content exceeds a certain

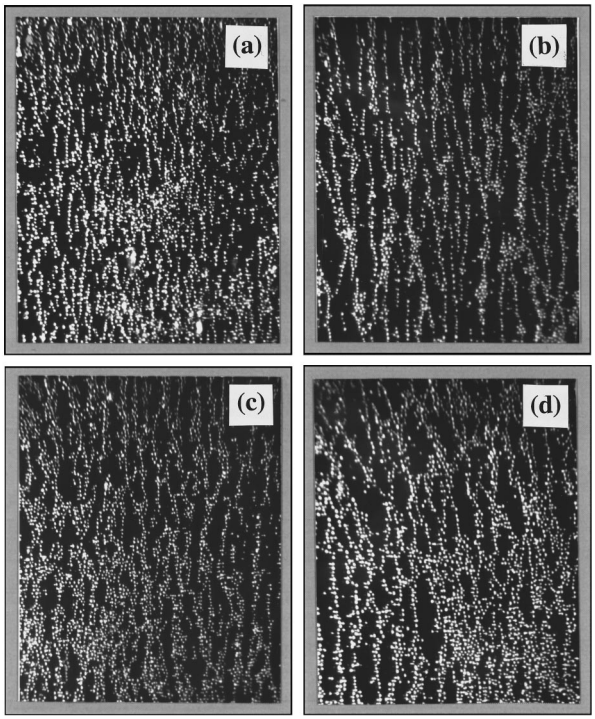

FIG. 5. The patterns formed by glass microspheres with different water contents. The water contents in (a), (b), (c), and (d) are 0, 0.254, 1.673, and 5.348 wt. %, respectively. The applied field strength is 700 V/mm.

value. In this case, the Debye form with a lognormal distribution of relaxation time should be introduced.[16] In fact, the pattern formation changes if the glass particles absorb a different amount of water, as can be seen in Fig. 5. Figures 5(a) and 5(b) show the patterns formed by water-free and slightly hydrous glass spheres, respectively, where, under the same electric field strength, the chains formed by the water-free spheres are much shorter than those formed by moist particles. The reason for this is that both the dielectric constant and the interaction force of watered particles are much larger than those of water-free particles. Figure 5(c) is the pattern formed by spheres with a higher water content, and indicates that the chains begin to break up when the water content is increased. If the water content continues to increase, the pattern formation becomes similar to that shown in Fig. 2(c) and Fig. 4(c); where a net-like pattern can be seen clearly. We believe that the pattern transition observed for the watered glass sphere is due to the thickness of the water layer on the surface, which results in a change of dielectric constant as well as a change in conductivity. When glass particles absorb a very small amount of water their dielectric constant increases to become the main factor dominating the ER properties, but, if the particles contain enough water, their surface conductivity is the main influence on the ER effect. In this case, both the pattern formation and the frequency response of watered particles are similar to those of conducting particles. This is why the gap appeared between the theoretical model and the experimental observations when the water content of the solid phase exceeded a certain value.

In conclusion, different pattern formations were observed depending on whether metal, semiconducting, or di-

electric microspheres were presented in the field, where the conducting and semiconducting particles formed chain-like patterns while the conducting ones formed a net-like pattern in which some fractals appear clearly. Several experiments focusing on the surface properties of the solid phase were performed and the results show that a pattern transition can be obtained by adjusting the surface conductivity of suspended particles. It is confirmed that the pattern formed by changes in the suspended particles related only to the surface conductivity and not to the core properties of the materials. Finally, it is found that the pattern transition can also be observed in hydrous ER fluids such as glass/oil fluids, whereby the chains begin to disorder and the structure is lost when the water content of the suspended glass spheres exceeds a certain value.

ACKNOWLEDGMENTS

The author thanks Dr. Guanghua Yi for helpful discussions in sol-gel techniques and much thanks Camilla Erskine for her editorial suggestions.

[1]W. Wen and K. Lu, ''A new net-like structure formed by a metal/oil electrorheological fluid,'' Phys. Fluids **8**, 2789 (1996).
[2]R. Tao and J. M. Sun, ''Three dimensional structure of induced electrorheological fluid,'' Phys. Rev. Lett. **67**, 398 (1991).
[3]T. C. Halsey, ''Electrorheological fluids,'' Science **258**, 273 (1992).
[4]D. J. Klingenberg, C. F. Zukoski, and J. C. Hill, ''Kinetics of structure formation in electrorheological suspensions,'' J. Appl. Phys. **73**, 4644 (1993).
[5]R. A. Anderson, ''Electrostatic forces in an ideal spherical-particle electrorheological fluid,'' Langmuir **10**, 2917 (1994).
[6]H. Conrad, in *Particulate Two-Phase Flow*, edited by M. C. Roco (Butterworths, Boston, MA, 1992), p. 355.
[7]W. Wen and K. Lu, ''Experimental investigation of dipole–dipole interaction in a water-free glass particle/oil electrorheological fluid,'' Appl. Phys. Lett. **68**, 3659 (1996).
[8]F. E. Filisko and L. H. Radzilowski, ''An intrinsic mechanism for the activity of alumino-silicate based electrorheological materials,'' J. Rheol. **34**, 539 (1990).
[9]M. Whittle, W. A. Bllough, D. J. Peel, and R. Firoozian, ''Dependence of electrorheological response on conductivity and polarization time,'' Phys. Rev. E. **49**, 5249 (1994).
[10]L. C. Davis, ''Polarization force and conductivity effects in electrorheological fluids,'' J. Appl. Phys. **72**, 1334 (1992).
[11]A. Khusid and A. Acrivos, ''Effect of conductivity in electric-field-induced aggregation in electrorheological fluids,'' Phys. Rev. E **52**, 1669 (1995).
[12]W. Wen and K. Lu, ''A simple and low cost method for fabricating single crystal microspheres,'' J. Cryst. Growth **165**, 191 (1996).
[13]Y. Z. Xu and R. F. Liang, ''Electrorheological properties of semiconducting polymer-based suspensions,'' J. Rheol. **35**, 1335 (1991).
[14]H. See, H. Tamura, and M. Doi, ''The role of water capilliary forces in electrorheological fluids,'' J. Phys. D **26**, 746 (1993).
[15]H. Ma, W. Wen, W. Y. Tam, and P. Sheng, ''Frequency dependent electrorheological properties: Origin and bounds,'' Phys. Rev. Lett. **77**, 2499 (1996).
[16]W. Wen, H. Ma, W. Y. Tam, and P. Sheng, ''Frequency and water content dependencies of electrorheological fluids,'' Phys. Rev. E **55**, R1294 (1997).