Generation and manipulation of “smart” droplets

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We report the generation and manipulation of electrorheological (ER) droplets that exhibit the giant ER effect. The experiments were carried out on specially designed microfluidic chips, in which the ER droplets were generated by using the microfluidic flow-focusing approach. Both the size and formation rate of these droplets can be controlled through digitally applied electrical signals. The principle of droplet manipulation is based on the electrical responsiveness of ER droplets and hence the denotation of “smart” when the electrical signals can be triggered by sensing/control devices. Due to the unique characteristics of the ER effect, the smart droplets can deform and even stop the microfluidic channel flow under an applied electric field. The pressure difference induced by the smart droplets inside the micro-channel is controllable by varying the field strengths, droplet sizes and particle concentrations in the GER suspension. By trapping and timed release of smart droplets in different micro-branch channels, we demonstrate that the smart droplets generated upstream cannot only be stored or displayed in the desired downstream channel(s) and thereby offer the potential of micro-droplet display, but also be useful in counting, flow directing and sorting the desired number of passive droplets sandwiched between two smart droplets. Such capabilities of smart droplets will enable the programmable control of discrete processes in bio-analysis, chemical reactions, digital microfluidics, and digital droplet display.

1. Introduction

Droplets in miniaturized microfluidic systems have established a new dimension in micro chemical reactions and biological processing. In the form of tiny droplets, ranging from nano to femto litres in volume, reagents may be conveyed precisely in discrete packets, with rapid mixing easily achieved inside the droplets. High throughput chemical reactions as well as single cell/molecule manipulation can be performed.1-5 The most commonly encountered droplet manipulations include droplet generation, fission, fusion and sorting. Recent papers also demonstrate simple Boolean logic operations in droplet fluidic systems, a critical step towards the realization of a microfluidic computer chip.6,7 The ability to address a single droplet is crucial in these logic microfluidic circuits, as well as in other high throughput assays.

Various approaches were employed to achieve the aforementioned manipulations. Hydrodynamic viscous force and surface/interfacial tension, as the intrinsic forces present in microfluidics, play important roles in properly designed channel geometries. Droplets can be generated in a T-junction or in a flow-focusing channel.1,2,8,9 Fission of generated droplets was achieved using either T-junctions or obstacles installed in the channels.10 Droplet traffic can be passively regulated with channel branches of different lengths or connections between outlets placed within a short distance of the junctions.11,12 By expanding the channel width, droplets can be slowed down so as to enable droplet fusion within a merging chamber.13-15 Various fabrication technologies have also enabled electrodes to be integrated into microdevices, to provide electrical control and to enable electrohydrodynamics methods such as dielectrophoresis and electrowetting in droplet generation, fusion and sorting.16,17 Mechanical forces were also utilized in droplet generation either in a multi-layer chip18 or in a moving-wall approach.19 Optical approaches were studied in droplet manipulation. Localized heating caused by laser beams can affect the motion and merging of droplets, and a “total optic toolbox” was a goal.20 In another related investigation, Jeffries et al. have shown that an optical vortex trap can expand or shrink single droplets.21

Rheological characteristics of the droplets were utilized to manipulate the droplets, e.g., ferrofluid droplets can be actuated in a magnetic field, by changing its magnetic rheological properties.22,23 By incorporating nano particles,24 or other materials such as wax,25 into droplets, the surface tension or viscosity of the fluid droplets can be made to be temperature dependent. By taking advantage of the vastly different freezing points of aqueous solutions and immiscible oils, Sgro has demonstrated an “ice valve” to stop fluid flow in a microchannel.26 While individual droplet manipulations can be achieved, their large-scale integration or fast-response actuation still remains a challenge, owing to the comparably large magnetic coils and/or fast heat transfers required inside the chips.

Electrorheological fluid has been widely studied on the macroscale as a type of “smart” material.27,28 More recently, a new kind of ER fluid was developed with the giant electrorheological (GER) effect that can reach a yield strength of 130 kPa under an applied electric field of 5kV/mm. Such GER fluids have found successful applications in microfluidics.29,30 It was shown that through the flow control of GER fluids in microfluidic channels, a variety of microfluidic devices such as valve,
pump and mixer can be realized. In these applications, the chip was designed to have a multi-layer structure, with the GER fluid in separated channels in one layer, exerting forces on the flow streams in other layers via thin elastic membranes.

Here we report the design and implementation of microfluidic chips capable of generating GER fluid droplets. These droplets flow in the same channels with the other fluidic droplets to be manipulated. The GER droplets can respond to applied electric fields by deforming their shapes and thereby generating pressure differentials across the droplets. These electrically induced rheological variations can occur within 10 milliseconds and are reversible when the field is removed. Since the electric field can be generated through sensors, the rheological change may be made in response to external environmental variations, hence the designation of “smart” droplets. It is noted that in this work, in order to achieve the maximum ER effect and to better control the smart droplets, integrated electrodes patterned directly on the inside walls of the microfluidic channels are a necessity. In contrast to the usual practice of evaporating metallic electrodes on the surface of the microfluidic chips, the present electrodes were fabricated by embedding the conductive PDMS with a lithographic process that is compatible with three dimensional structures.

2. Materials, methods, and experimental setup

2A. Giant electrorheological fluid for smart droplets

ER fluids/suspensions constitute a type of colloid whose rheological characteristics are tunable under the application of an electric field. Under a sufficiently strong electric field, ER fluid can transform into an anisotropic solid, with a yield stress characterizing its strength.

The GER particles were fabricated by first dissolving barium chloride and rubidium chloride in distilled water at 50–70 °C. Oxalic acid was dissolved in water at 65 °C in an ultrasonic tank; titanium tetrachloride and urea solution were slowly added thereafter. The two solutions were mixed in an ultrasonic bath at 65 °C, and a nanometre-sized precipitate was formed. The precipitate was washed with DI water, filtered, and then dried to remove all trace water. The nanoparticles obtained have a 50 nm core of barium titanyl oxalate.

Sunflower seed oil (Soon Hup Edible Oil Sdn Bhd) and GER particles were mixed in a mixer/mill (SPEX 8000) for 30 minutes in a weight ratio of 20% to 40% GER particles. The mixture was further filtered with sieves (with pore size around 10 µm) to remove the large aggregates. Fig. 1 shows the calibration results on the dynamic shear stress of the GER fluid with a rheometer (Haake RS1) under 0.1 sec shear rate. Under an applied field larger than 1 kV/mm, the GER fluid exhibits solid-like behavior, e.g., ability to transmit shear stress. The measured dynamic shear stress of the sunflower oil based GER fluid is comparable to that of the silicone oil based GER fluid under similar electric fields. In particular, the variation with the applied electric field displays a behavior that is in-between $E$ and $E^2$ (GER fluid displays a linear $E$ variation of the yield stress, in contrast to the traditional $E^2$ dependence). The transformation from liquid-like to solid-like behavior is relatively fast, of the order of 1–10 milliseconds, and reversible. Compared to conventional ER fluids, the GER fluid has a much larger ER response under the same applied field. This is a crucial aspect of the GER droplets, so that a sufficient pressure differential can be generated under an applied electric field for stopping the microfluidic channel flow.

2B. Microfluidic chip

The microfluidic chip shown in Fig. 2 has one channel circuit and five pairs of embedded electrodes. The cross section of the main channel is 200µm wide and 100µm in depth. Its downstream is divided into four branch channels with one used as a by-pass channel while the others are for droplet storage or patterning. The functions of each electrode are as follows. Electrode 1 is used to generate and control the smart droplets while electrodes 2–5, located at the outlet of each branch, are used to control the flow behavior of the smart droplets.

A soft lithographic technique was employed for the microchannel fabrication. Parallel electrodes were fabricated from...
three dimensional patterning of conductive PDMS. Specifically, a negative photoresist SU8 was used to fabricate the channel mold. PDMS electrodes were first patterned with a carbon-black/PDMS mixture. The mixture was placed on the substrate with the channel mold. After curing and bonding to another bottom layer of PDMS, a microfluidic chip was achieved with embedded parallel electrodes on the channel walls.

In the experiment, the chip was mounted on a platform and its electrodes were connected to a DC high voltage controller, with the voltage adjustable in the range of 0 to 1500 V, and the frequency from 0 to 250 Hz. A syringe pump (KDS 200 syringes infusion pump) was used to inject the GER fluid into the chip through a flexible tube.

3. Experimental results and discussion

3A. GER droplets generation

Smart droplets were generated by the flow-focusing approach shown schematically in Fig. 2, where a continuous-phase GER fluid and two streams of silicone oil (Sigma-Drich, 50 cSt (25 °C)) were injected into the main channel through a center inlet and two side inlets, respectively. Since sunflower oil is immiscible with silicone oil, the latter was chosen to be the carrier fluid for the GER droplet generation. The interfacial tension between the silicone oil and sunflower oil based GER fluid was measured to be 12.9 mN/m.

When the voltage on electrode 1 was set to zero, GER droplets can be generated in a passive scheme. Inset (a) of Fig. 3 shows monodispersed droplet generation when the ER flow rate \( R_{ER} = 0.2 \text{ ml/h} \) and the ratio of silicone oil to GER flow is 3:1. The situation deteriorated when the flow rate was high \( (R_{ER} = 4 \text{ ml/h}) \) and the oil ratio was increased to 10:1 (see inset (b)). The generated GER droplets had a higher polydispersity.

By applying an electric field signal on electrode 1 (square wave DC electric field was applied), very uniform droplets—stable over a wider range of flow rates—were obtained. This is seen from insets (c) and (d) in Fig. 3, where \( R_{ER} = 0.6 \text{ ml/h} \), and the period \( T \) was changed from 200 ms to 100 ms. By design, electrode 1 was to impose manipulation capability on a continuous GER fluid flow. Once a voltage was applied, the viscosity of the GER fluid was increased owing to the formation of nanoparticle chains across the electrodes and thus less ER fluid was injected into the flow-focusing part. When the E-field was higher than 2 kV/mm, the 40 wt% GER fluid stream was observed to be temporarily stopped, and only silicone oil was injected into the main channel through the two side inlets. When the electric field was removed, the GER fluid flow would resume. Thus the smart droplets’ generation can be electrically controlled.

Moreover, the droplet size and separation between two successive droplets may be tuned by adjusting the frequency and duty cycle of the control signal on electrode 1. Such control is illustrated in the right lower inset of Fig. 2, in which the correspondence is shown between the electrical control signals applied to electrode 1 and the generated smart droplets.

A series of experiments was carried out to investigate the relationship between the droplet length and the frequency (and duty cycle) of the electric pulse at different GER fluid flow rates. The results are shown in Fig. 3. The period \( T \) of the electric pulse is noted to be a very critical parameter for stable GER droplet production. For example, smart droplet generation becomes unstable when \( T \) is beyond a certain working range, from 100 ms to 1000 ms at a flow rate of \( R_{ER} = 0.4 \text{ ml/h} \). However, by controlling two or more GER inlets independently in the stable region, GER droplet synchronization and relative phase variation were easily achieved using the same approach.

3B. Behavior of the smart droplets under an external field

Morphology change under an applied electric field. To understand the behavior of smart droplets, we have investigated their flow characteristics in a channel under the influence of a pulsed electric field. Fig. 4 shows two types of smart droplets generated from GER fluids with two different nanoparticle concentrations. The top three panels, Fig. 4 (a), (b) and (c) pertain to droplets with 40 wt% nanoparticles, whereas Fig. 4 (d) is for a particle with a lower percentage, 5 wt%, of nanoparticles.

Fig. 4 (a) shows a smart droplet with no electric field applied. It has a spherical shape. In Fig. 4 (b), when an electric field (1500 V/mm) was applied, the droplet was elongated with the two ends touching the electrodes. The droplet has stopped moving. When the field was removed, the droplet resumed its original spherical shape and moved on again, as shown in Fig. 4 (c). Fig. 4 (d) shows the deformation of several smart droplets with a lower nanoparticle concentration. For the one droplet to the left that is outside the influence of the electric field, it has a spherical shape. But for those droplets under an applied electric field, every droplet was stretched, accompanied by the clearly visible separation of the nanoparticles from the sunflower oil. In particular, the chains/columns formed by the nanoparticles are plainly identifiable, and the sunflower oil is seen to be pushed forward to form a curved front with the silicone oil, owing to the pressure differential generated by the slowed channel flow.
This journal is a smart droplet with no electric field and under an electric field fluid. The length of the electrodes is 1 mm. The insets show the status of electric fields, for two different nanoparticle concentrations of the GER Pressure differential generated by smart droplets under different Fig. 5 process when the smart droplet train is under an electric field. From GER fluid with 5 wt% nanoparticles. It shows the deformation was applied, the droplet has stopped. (d) pertains to droplets generated shape when the electric field was turned off. When the electrical signal was applied, the droplet has stopped. (d) pertains to droplets generated from GER fluid with 5 wt% nanoparticles. It shows the deformation process when the smart droplet train is under an electric field.

**Pressure differentials induced by smart droplets.** In order to determine the pressure difference across a smart droplet stopped under the application of an electric field, an experiment was carried out as shown in Fig. 5. A smart droplet was squeezed into a channel to form a plug between two electrodes as shown in the upper panel of the inset. When an electric field was applied, the droplet/plug displayed columns formed by nanoparticles stretching across the two electrodes, shown in the lower panel of the inset. As a result, the flow was stopped and a pressure differential \( \Delta p = P_1 - P_2 \), was established. This \( \Delta p \) was measured with a pressure sensor (Sensym ASCX15DN, Honeywell Inc., USA) connected to the channel at the upstream and downstream electrodes (1 mm in length) via two branch channels. GER droplets were generated in the flow-focusing part and pushed through the channel between the electrodes. A ramping-up electrical field was applied between the parallel electrodes. The critical field strength that can stop the droplets was determined, along with the corresponding pressure differential.

Fig. 5 provides the results for smart droplets at two different nanoparticle concentrations. It is shown that the increase in the pressure differential displays a nonlinear behavior, with saturation at a higher electric field strength that is different from the near-linear dependence of the dynamic shear stress shown in Fig. 1. Detailed inspection of the second inset in Fig. 5 reveals that the particles are less dense close to the channel wall than in the middle. Moreover, there are tiny droplets of silicone oil trapped close to the channel wall. It is postulated that these tiny droplets decrease the full contact of the ER particles to the electrodes and give rise to the saturation behavior. However, the maximum differential pressure is more than 90 kPa/mm for the GER fluid with 40 wt% nanoparticles. Such a pressure differential is fairly adequate for most of the microfluidic applications. From our experiments we can thus conclude that the pressure differential induced by the smart droplets can be adjusted readily by varying the strength of the electric field, droplet size and nanoparticle concentration in the GER fluid.

**Droplet manipulations.** We demonstrate two types of droplet manipulations by using the smart droplets formed by the GER fluid: one involves only the smart droplets and the other involves using the smart droplets to deliver a “package” containing a certain number of passive droplets (formed from other types of fluid, like water) to the targeted destination. Shown in Fig. 6 (a) is a schematic illustration of the chip designed to achieve the functions of smart droplet encoding, sorting and storage. In this experiment, three downstream channels were used to store the smart droplets so as to form a display panel with the desired characteristics. An example for displaying the word “H” is illustrated in Fig. 6 (a). Here the basic principle of directing the smart droplets to the desired channel is simply to apply voltages to other (non-targeted) channels so as to stop the flow in all these channels, leaving only the desired channel open for flow.

By using a Labview controlled high voltage switching device, encoded signals were applied to electrode 1 to generate the smart droplets on demand, while the signals applied to electrodes 2–5 are for the purposes of sorting and storing the smart droplets into different channels. During sorting and storage, the character “H” can be pre-programmed by the control box and transferred onto control signals on electrodes 3, 4 and 5, in which 4 smart droplets are to be in channels a and c, with one in channel b. Simultaneously, the corresponding coding signals to form the desired smart droplet sequence were sent to electrode 1, shown as signals a, b and c marked in the middle of Fig. 6 (a). In accordance to the above operations, the encoded droplet sequence can be sorted and stored in the channels a, b and c as desired. The subsequent characters “K-U-S-T” can be similarly formed. When the word was finished, the unused droplets were moved out from the side.

![Fig. 4](image_url) Optical images of smart droplet deformation under an applied electric field. (a)–(c) pertain to droplets generated from GER fluid with 40 wt% nanoparticles. They show the deformation process when the electric field was turned off. (d) pertains to droplets generated from GER fluid with 5 wt% nanoparticles. It shows the deformation of the droplet when an electric field was applied and its subsequent reversion back to a spherical shape when the electric field was turned off.

![Fig. 5](image_url) Pressure differential generated by smart droplets under different electric fields, for two different nanoparticle concentrations of the GER fluid. The length of the electrodes is 1 mm. The insets show the status of a smart droplet with no electric field (top) and under an electric field (bottom).
channel by switching off electrode 2. Fig. 6 (b) shows the resulting display with the characters “HKUST” clearly visible.

In the second type of droplet manipulation, it is well known that many chemical reactions and bio-processing usually require an accompanying liquid, such as water or another liquid. Therefore, control and sorting of water droplets are very critical and challenging. From the experiments described above, it is seen that the smart droplets can provide an approach to control water droplets. That is, by injecting smart droplets among the water droplet trains, one can form “packages” of any desired number of water droplets sandwiched between two smart droplets. Fig. 6 (c) shows the schematic illustration for one part of such a chip (left) and some snapshots of the experimental results (right). The injection frequency and phase (relative to the water droplets) of the smart droplets are adjusted so that one smart droplet leads the train of desired water droplets. By controlling the smart droplets, the train of water droplets can be directed, sorted and delivered to a targeted destination inside the chip, where mixing, heating and/or other processing may be carried out. All such controls can be digitally programmed. It should be noted that while our current setup allows only one letter output each time from the Labview® program, with extended channel geometries coupled with more complex coding, there is no intrinsic difficulty in displaying a continuous array of letters/words following instructions from a computer.

4. Concluding remarks

We have realized the generation and manipulation of smart droplets through the design of PDMS microfluidic chips with embedded electrodes for digital control. Droplets of GER fluid were generated on demand with adjustable size, frequency and phase. The smart droplets can undergo morphological/rheological changes under an applied electric field to form solid-like plugs for stopping the channel flow. By utilizing such capability, individual droplet manipulations were demonstrated. The novel functions may find applications in a wide variety of lab-chips for chemical reaction, bio-assays or even microfluidic logic computation.

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References


