Discrete magnetic microfluidics

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We present a method to move and control drops of water on superhydrophobic surfaces using magnetic fields. Small water drops (volume of 5–35 μl) that contain fractions of paramagnetic particles as low as 0.1% in weight can be moved at relatively high speed (7 cm/s) by displacing a permanent magnet placed below the surface. Coalescence of two drops has been demonstrated by moving a drop that contains paramagnetic particles towards an aqueous drop that was previously pinned to a surface defect. This approach to microfluidics has the advantages of faster and more flexible control over drop movement. © *2006 American Institute of Physics*.
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There is a continued and growing interest in achieving controlled droplet motion on surfaces using an external stimulus. Over the past years, many researchers have succeeded in controlling drop contact angles by chemical modification of the surface[1,2] or by using external stimuli, such as light[3] or electric fields.[4] Recently, a major goal in this area has been to control wetting phenomena, such as capillary rise and fall and liquid drop movement on surfaces using gradients.[5–7] For example, wettability gradients were induced by a chemical reaction at the substrate.[8–10] Recently, two alternative strategies were used to move droplets: thermal gradients controlled by a laser beam[11] and asymmetric lateral vibration.[12] Also, studies have focused on the dynamics of drops rolling down an inclined superhydrophobic surface (SHS) under the action of gravity.[13,14] However, little is known about aqueous drop movement on a horizontal, flat, nonpatterned SHS by mechanisms other than gravity. Much interest is focused on water because of its ubiquity and importance in biomedicine and environmental studies. Several technologies can benefit from key advances in this field, namely, SHSs capable of self-cleaning by the action of a rolling drop[15,16] and microfluidic devices that take advantage of new effects and better performance derived from manipulating fluids at small scales.[17] "Digital microfluidics is an alternative paradigm to channel-based techniques where fluid is processed in unit-sized packets, which are transported, stored, mixed, reacted, or analyzed in a discrete manner."[18] This concept has already been demonstrated using electrowetting arrays for droplet transportation without the use of pumps or valves.[19] In this letter, we present a method to displace, coalesce, and split paramagnetic particle-containing aqueous drops on flat, nonpatterned, Si nanowire SHSs using magnetic fields as the only driving force.

SHSs were prepared using vapor-liquid-solid (VLS) growth systems to create high aspect ratio Si nanowires covalently coated with a perfluorinated hydrocarbon. The resulting superhydrophobic nanowire surfaces do not follow a simple geometric pattern but rather exhibit fractal, multidimensional, random roughness, with high contact angles.[20] In these experiments, the SHSs contained nanowires with diameters ranging from 20 to 50 nm and with a height of approximately 2 μm. The separation distance between nanowires was between 60 and 100 nm. The contact angle θ_c ranged from 145° to 160° for particle-containing water drops on these Si nanowire surfaces [Fig. 1(a)]. Drop volume was varied from 5 to 35 μl and prepared from aqueous suspensions with different particle concentrations (0.1%–5% in weight). Spherical, paramagnetic, carbonyl iron particles were supplied by Lord Corporation. These particles are moderately polydisperse in size (diameter d ranging from 0.2 to 4.0 μm) and have a high saturation magnetization (211 emu/g) (see particle characterization in Ref. 21). The magnetic field was generated by a cylindrical NdFeB bar magnet located below the SHS. The drop motion was recorded with a digital charge-coupled device (CCD) camera using a Navitar 12× zoom system positioned at the side or above the SHS.

We studied the effect of the magnet motion on drops with different sizes and particle concentrations. We observed drop movement following the magnet motion for drops with particle concentrations down to 0.1 wt % and speeds up to 7 cm/s, both in straight and circular paths (see EPAPS,[22] videos 1 and 2). The main characteristics of drop dynamics can be summarized as follows: (a) Hydrophobic powders placed on top of 2 mm diameter drops were not observed to move during drop displacement. This observation strongly supports the notion that the drop slides rather than rolls on the SHS. (b) Side views during drop motion show that particle clusters appear on the lateral drop surface [see Fig.

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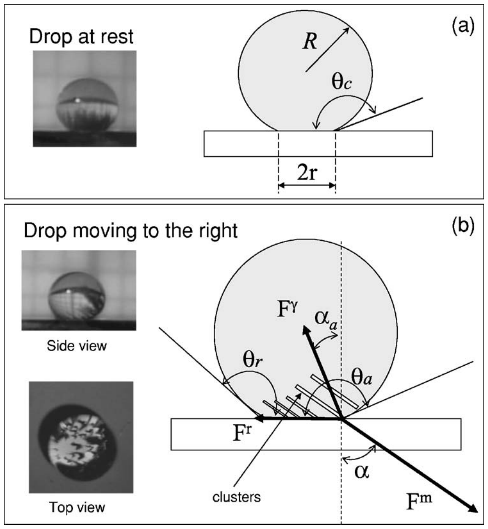

FIG. 1. (a) A water drop of 6 μl resting on a nanowire surface under a magnetic field. Paramagnetic particle chains are vertically aligned along the magnet axis. (b) The same water drop sliding to the right and under the influence of a magnet, which is positioned beneath the surface. Paramagnetic particle chains push against the lateral surface of the drop. A force diagram accompanies the drop images.

1(b)]. The magnet drives the clusters which pull the drop surface due to capillary forces and strongly distort the drop shape. There is clear evidence of dynamically induced contact angle hysteresis, with the advancing contact angle θ_a being larger than the receding contact angle θ_r [Fig. 1(b)]. (c) Top views during drop motion show that the particle clusters which are visible from above are regularly distributed in a pattern that is reminiscent of the Rosensweig instability[23] [Fig. 1(b)]. More importantly, they appear to slide with the drop. (d) In terms of the magnet-to-drop distance there is a magnetic field threshold, B_{th}, below which no motion of the drop occurs. It is not clear if the magnet velocity affects this threshold. (e) Within the range measured here (Fig. 2), the drop size does not affect the threshold field required to move drops on these SHSs, which suggests that frictional resistance is extremely low. These results are in accordance with molecular studies that predict that roughness from the nano- to the microscale at the solid-liquid interface can greatly enhance slippage, probably due to the existence of nanoscale bubbles at the liquid-solid interface.[24] (f) B_{th} increases upon decreasing the particle concentration; if there are fewer magnetic particles in the drop, higher magnetic field intensities are needed to start the drop motion (Fig. 2). This increase is not surprising because the total force exerted by the magnetic field is roughly proportional to the magnetic dipole moment of the clusters, which in turn is proportional to the number of magnetic particles present in the cluster.

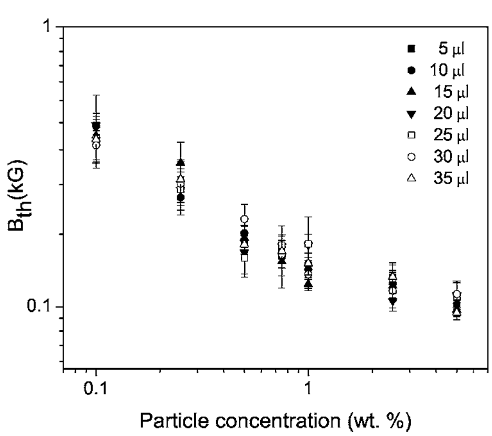

FIG. 2. The minimum magnetic field needed to displace the drop, B_{th}, as a function of particle concentration for drops of different sizes. Each point is an average of at least ten measurements and indicates that drop size does not affect B_{th}.

Coalescence and/or drop splitting are essential processes in microfluidic applications. Coalescence of two drops was achieved on SHSs using an approach where a moving, particle-laden drop is moved into a second, standing drop lacking particles and deliberately held at a surface defect. Movement of the resultant drop away from the defect was then demonstrated using a magnet (EPAPS,[22] video 3). A drop was split into two smaller drops by progressively separating two magnets held below the surface (EPAPS,[22] video 4).

A more detailed physical characterization of this system is beyond the scope of this letter. Here, the physics involved in drop motion is only briefly sketched. When there is no external magnetic field, the particles do not have a permanent magnetic dipole moment and simply sediment to the bottom of the drop. The permanent magnet generates a spatially nonuniform magnetic field and magnetizes the paramagnetic particles that, due to the induced magnetic dipolar interaction, aggregate into cylindrical clusters that follow the magnetic field lines.[25,26] We note that the particles are always kept inside the drop by capillary forces.[27] When the magnet is displaced, the clusters move and drive the motion of the drop. At first, the clusters slide inside the drop following the motion of the magnet until they reach the contact line. When the first clusters reach the contact line, the competition between the capillary (F^{γ}) and magnetic forces (F^m) makes the clusters start to climb along the drop surface. Now F^m acts along the cluster axis (forming an angle α with the vertical direction) while $F^{\gamma}=(\pi\gamma D)/[\cos(\alpha-\alpha_a)]$ acts along the local normal to the drop surface (forming an angle α_a with the vertical direction). Here D is the diameter of the cluster. The horizontal component of F^m is responsible for drop motion. The vertical component of F^m will twist the drop surface at the contact line and distort the drop surface, increasing the advancing contact angle (decreasing $\alpha_a=\pi-\theta_a$). This creates a difference between the contact angles at the advancing and receding segments of the contact line, leading to a retention force $F^r=2\gamma rJ$ that opposes drop motion.[28] Here $r=R\cos(\theta_c-\pi/2)$ is the radius of the circle of contact between the drop and the SHS, and $J=\cos\theta_a-\cos\theta_r$. Thus the drop will move when the horizontal component of the magnetic force compensates the capillary and retention forces. In Fig. 1(b), the contact angle difference and the inclination of the clusters can be appreciated. Calculations based on the actual measured values of the angles ($\theta_c\approx 147°$, $\theta_a\approx 160°$, $\theta_r\approx 136°$, and $\alpha\approx 44°$) show that the magnetic force modulus needed to balance the capillary and retention forces is within an order of magnitude of the range achievable in our experimental setup.

In conclusion, we have demonstrated the feasibility of using magnetic fields to move, combine, and split aqueous drops containing paramagnetic particles on SHSs. These drops can be moved at relatively high velocities—on the order of a few centimeters per second. Thus, this technology is a promising method for manipulating small, discrete amounts of water. Future studies will explore the maximum attainable speed, the quantitative relationship between drop velocity and the advancing and receding contact angles, and the system response in other magnetic field configurations.

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