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Supporting Information

Magnetic Actuation of Drops and Liquid Marbles Using a Deformable Paramagnetic Liquid Substrate

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1 Materials and Methods

Materials. Ultrapure water (resistivity: 18.2 MΩ·cm) was used for all the experiments. Holmium chloride, mineral oil (BioReagent, for molecular biology, light oil) and Sudan II dye, were purchased from Sigma-Aldrich and were used without any further purification.

Preparation of liquid marbles. Hydrophobized fumed silica nanoparticles were prepared as previously described in reference [1]. A spatula full of silica particles was placed in a mortar and was spread in order to cover the surface; afterwards a 2 μL drop of ultrapure water (except in the case of Figure 2C, where a 2 μL drop of 17 mM $HoCl_3$ was used) was carefully deposited on top of the particle layer and was rolled in all directions in order to completely cover the drop surface with the hydrophobic particles. The obtained liquid marble was transferred onto a watch glass to remove the excess of powder, and was then placed onto the liquid surface used for the experiment.

Magnetic manipulation of liquid entities. For all experiments, 30 mL of $HoCl_3$ solution of a given concentration were added to a plastic Petri dish (8.6 cm diameter) placed on an anti-vibration table. Subsequently a liquid marble, or a mineral oil drop of the desired volume, was carefully placed on top of the surface, in the center of the Petri dish to avoid interaction with the meniscus formed at the walls. All experiments were carried out at room temperature.

The magnet (NdFeB, 12 mm x 60 mm, Supermagnete) at the beginning of the experiment was placed along the axis perpendicular to the center of the Petri dish, at a distance from the liquid surface greater than or equal to 150 mm (position 1), where no actuation effects were detected. Then the magnet underwent free fall to approach the liquid surface in position 2. Our custom-built set-up for magnet release and positioning was idependent from the anti-vibration table so that almost no vibration occurred at the liquid surface upon switching the magnet position. In most experiments position 2 corresponded to 12.7 mm distance unless otherwise specified. Videos of the actuation of the drop or liquid marble were recorded with an EOS 5D Mark II camera (Canon), placed below the Petri dish perpendicular to the magnet axis. During the experiments, an opaque cover was placed on the Petri dish, and at the end of the video recording it was removed to obtain the magnet position.

In the case of drop manipulation, the magnet was placed at a distance of about 12 mm from the surface, and was moved manually following the desired trajectory. For the drop fusion experiment, two magnets were used to manually direct to the center of the Petri dish both oil drops; one of the drops was marked with the Sudan II dye.

Image analysis. All videos were analysed using the *ImageJ* software. A threshold was applied, and the "Analyze Particles" function was used to determine the position of the moving liquid entity in each frame. Further analysis to obtain the speed at different distances from the center of the magnet was done using the *MATLAB* software.

Measurements of the surface deformation. 30 mL of $HoCl_3$ solution (100 mM) were placed in a plastic Petri dish (8.6 cm diameter). A He-Ne laser beam (wavelength 543.5 nm, power 0.5 mW, diameter 0.8 mm) impinged on the surface of the solution at an angle of incidence of about 57°. For the calculation of each experimental point Δh in Figure 1C, two videos of the position of the reflected beam on a white screen were recorded (for 5 s at 30 fps) and the average position of the reflected spot was obtained. The first video was acquired with the magnet at 150 mm distance from the liquid surface (position 1), the second one with the magnet at 12.7 mm distance (position 2). The local slope of the interface at distance r from the center of the magnet axis was calculated as in reference [1]. The 2 mm steps between each point Δh were realized with a linear translation stage (0.01 mm resolution, Edmund Optics).

Measurements of the magnetic field. The magnetic field on a surface at a distance of 12.7 mm from the magnet, with 2 mm steps, was measured with a GM08 Gaussmeter (Hirst Magnetic Instruments Ltd.), equipped with a Standard Transverse Hall Probe.

Measurements of the magnetic susceptibility. The volume magnetic susceptibility of aqueous $HoCl_3$ solutions as a function of $HoCl_3$ concentration was measured using a magnetic susceptibility balance Mark1. For each concentration, the average of three independent measurements was obtained.

2 Supplementary text

Text S1. Theoretical description of liquid marble motion

Equation of motion for the liquid marble. We consider a liquid marble (LM) of volume $V = 2\ \mu$L deposited on the surface of a paramagnetic fluid having a surface tension γ. We describe the position of the liquid marble at time t by the radial coordinate $r(t)$. Under the effect of a magnetic field $\mathbf{B}(r)$, the liquid surface is deformed. The local elevation of the surface is denoted $h(r)$. Under the combined effect of gravity and diamagnetic repulsion, the LM is expected to move down along the deformed interface with a speed $v(r, t)$, t being time. Here we derive the equation of motion of the liquid marble.

The forces acting on the LM are:

- The effective weight $\mathbf{P}_{eff} = \mathbf{P} + \mathbf{\Pi}$, where $\mathbf{P}$ is the weight and $\mathbf{\Pi}$ is the buoyancy.
- The tension force $\mathbf{f}_\gamma$, which is normal to the interface. In the hypothesis of a perfectly non-wetting LM, we have

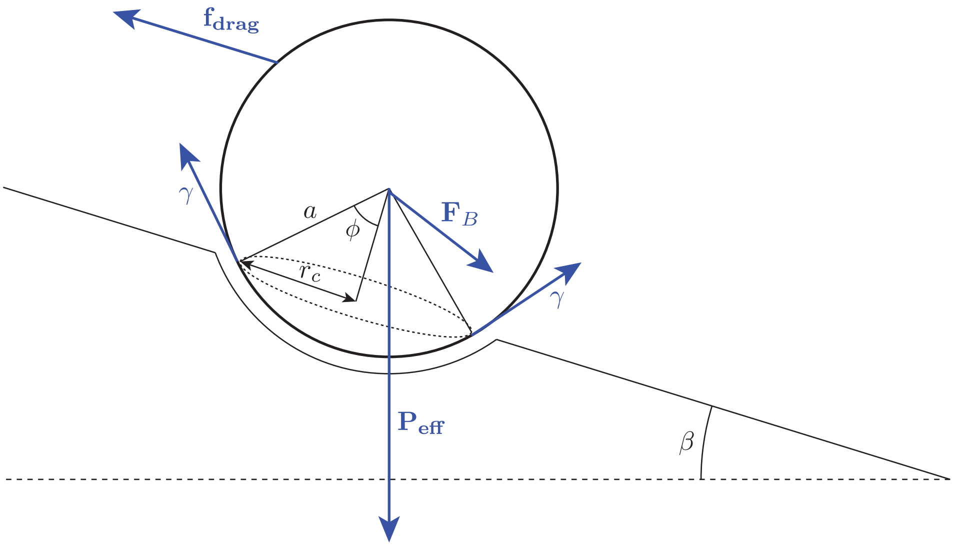
  $$f_\gamma = 2\pi r_c \gamma \sin\phi \tag{1}$$

  where we define r_c the radius of the contact line, γ the surface tension and ϕ the wrapping angle.
- The diamagnetic repulsion force $\mathbf{F}_B = \nabla(\mathbf{M} \cdot \mathbf{B})$, where $\mathbf{M} = V\frac{\chi}{\mu_0(1+\chi)}\mathbf{B}$, is the magnetisation of the liquid marble. Here V and χ are respectively the volume and the dimensionless magnetic susceptibility of the liquid marble (identified to that of the liquid inside the marble); μ_0 is the vacuum permeability. This can be re-written as

  $$\mathbf{F}_B = V\frac{\chi}{1+\chi}\frac{\nabla(\mathbf{B}^2)}{2\mu_0} \tag{2}$$
- The drag force $\mathbf{f}_{drag}$, which is parallel to the interface and which is expected to be of the form

  $$f_{drag} = 2\pi C \eta r_c v(r, t) \tag{3}$$

  where C is a numerical coefficient that is expected to be of the order of 1, and η the viscosity.



Scheme S1. Forces acting on a liquid marble floating at the air-solution interface, and geometrical parameters characterising its position.

The directions of the forces and the relevant geometrical parameters are specified in Scheme S1.

We assume in the following that $\beta = \partial_r h$ is small (∂_r is the derivative with respect to r). Given the geometry of our system, the gradient of the magnetic field along the vertical direction is expected to be of the same order of magnitude as along the horizontal direction. Moreover, a simple calculation [2] shows that, when neglecting surface tension effects, the surface deformation due to the magnetic field is approximately

$$h(r) \approx \frac{\chi}{1+\chi} \frac{\mathbf{B}(\mathbf{r})^2}{2\mu_0 \rho g} \tag{4}$$

where ρ is the density of the fluid and g is gravity. Hence the gradient of $\mathbf{B}^2$ along the horizontal direction is of order $\beta = \partial_r h$, and so is the gradient of $\mathbf{B}^2$ along the vertical direction. Thus it can be neglected in the force balance along the direction normal to the surface, which we write at order 0 in β as

$$P_{eff} = -2\pi r_c \gamma \sin\phi \tag{5}$$

Newton's second law projected on the tangential direction reads

$$m\frac{\mathrm{d}v}{\mathrm{d}t} = P_{eff}\partial_r h - f_{drag} + F_B \tag{6}$$

that is

$$\boxed{\frac{\mathrm{d}v}{\mathrm{d}t} = -\frac{v_0}{\tau}(\sin\phi)^2 \partial_r h - \frac{C\sin\phi}{\tau} v(r,t) + V\frac{\chi}{1+\chi}\frac{\partial_r \mathbf{B}^2}{2\mu_0 m}} \tag{7}$$

with $\tau = m/(2\pi\eta a)$ and $v_0 = \gamma/\eta$.

Equation (7) is our main result: it can be integrated numerically in order to predict the motion of the liquid marbles in various conditions. It still contains however an undetermined geometrical parameter: the wrapping angle ϕ of the LM. The shape of the liquid-air interface around a floating LM has been specifically studied by Ooi *et. al.* [3]. Briefly, the height of the meniscus ξ can be expressed using the balance between weight, buoyancy and surface tension as

$$\xi = \frac{a}{3\sin^2\phi}\left(1 + 3\cos\phi - \cos^3\phi - \frac{6\ell_c^2}{a^2}\sin^2\phi\right) \tag{8}$$

Another expression of ξ can be obtained from the Young-Laplace equation for the shape of the liquid-air interface. This equation usually has no closed analytical solution, however, Ooi *et. al.* find that for $a\sin\phi/\ell_c \leq 0.2$ an approximate solution is

$$\xi = a\sin\phi\sin\beta\left(\ln\left[\frac{4\ell_c}{a\sin\phi(1+\cos\beta)}\right] - C_{EM}\right) \tag{9}$$

where $C_{EM} \approx 0.5772$ is the Euler-Mascheroni constant and $\tan\beta = \sin\phi$. Eliminating ξ between eqs. (8) and (9) yields an equation for ϕ, which can be solved numerically to obtain, with our system's parameters, $\phi \approx 14°$. This corresponds to $a\sin\phi/\ell_c = 0.07$, which justifies the use of the approximate solution (9).

Comparison to experimental data. Equation (7) was numerically integrated with a time step $\mathrm{d}t = 1$ ms and space discretisation $\mathrm{d}r = 0.1$ mm, using the experimentally obtained values of the magnetic field and the surface deformation. The experimental data were linearly interpolated up to the desired space discretisation. The value of the constant C was adjusted so as to fit the data from liquid marbles made of water moving on a 100 mM $HoCl_3$ substrate, leading to $C = 3.84$. This value of C was used for all the displayed curves. The curves in Figures 1 and 2 were obtained by integrating eq. (7) having set B to 0 or $\partial_r h$ to 0.

3 Supplementary figures

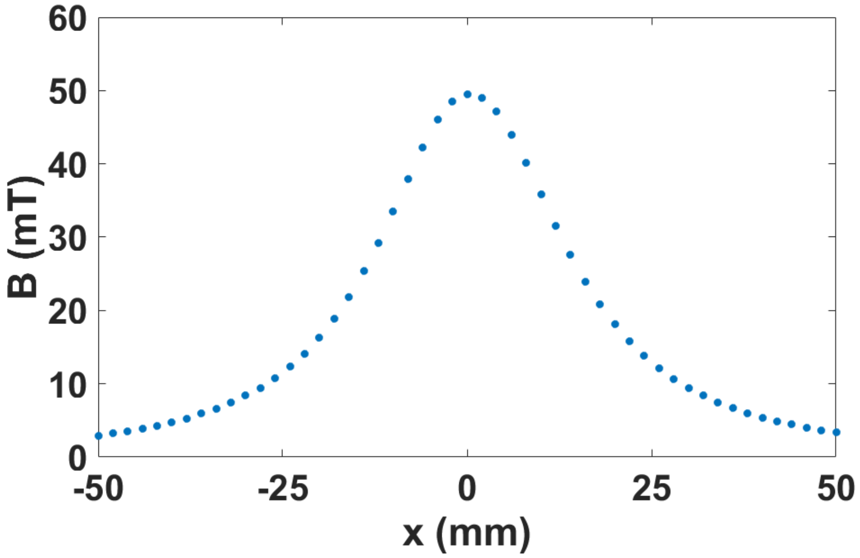


Figure S1. Norm of the magnetic field profile on the liquid surface. The distance between the magnet and the probe was 12.7 mm. Symbols are mean data on triplicates with error bars (sd) smaller than the symbol size.

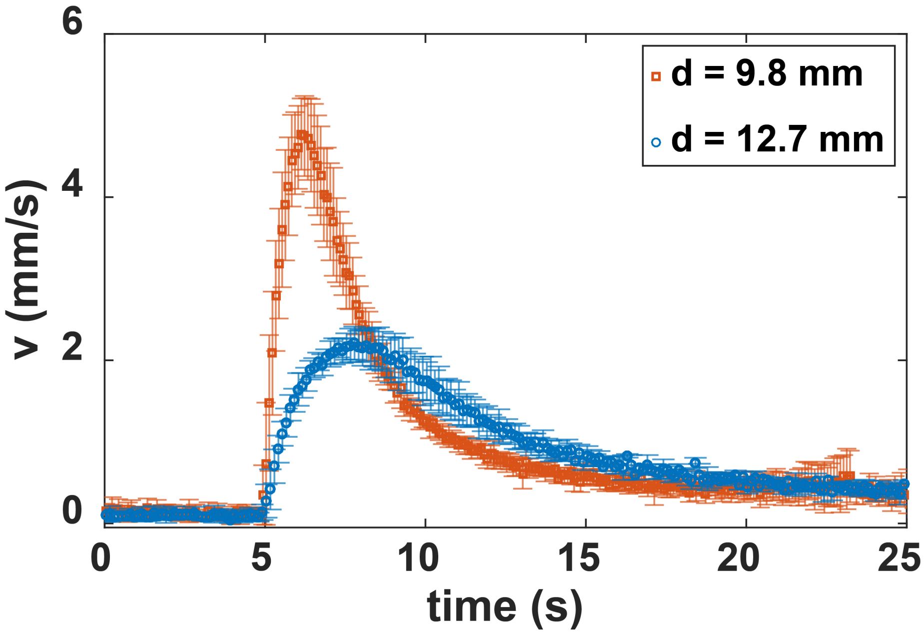


Figure S2. Temporal profiles of the speed of a 2 μL water liquid marble for two different approaching distances. The magnet was released at t = 5 s from position 1 to reach position 2 at 9.8 mm (orange squares) or 12.7 mm (blue circles). Symbols and error bars show mean ± sd from 6 individual experiments.

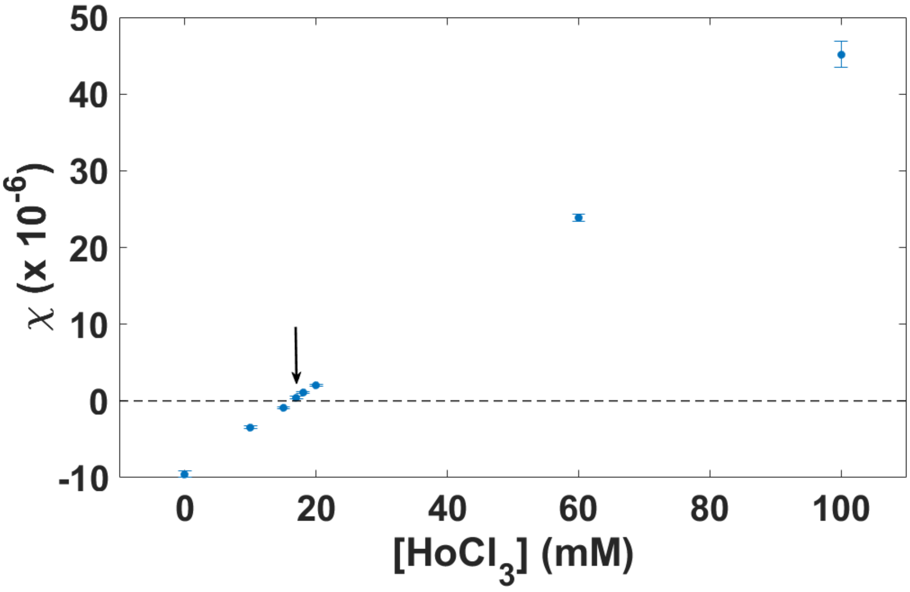


Figure S3. Volume magnetic susceptibility (χ) of $HoCl_3$ aqueous solutions as a function of $HoCl_3$ concentration. Symbols and error bars show mean ± sd from 3 independent measurements. The arrow indicates the concentration ([$HoCl_3$] = 17 mM) used for experiments with $\chi \approx 0$.

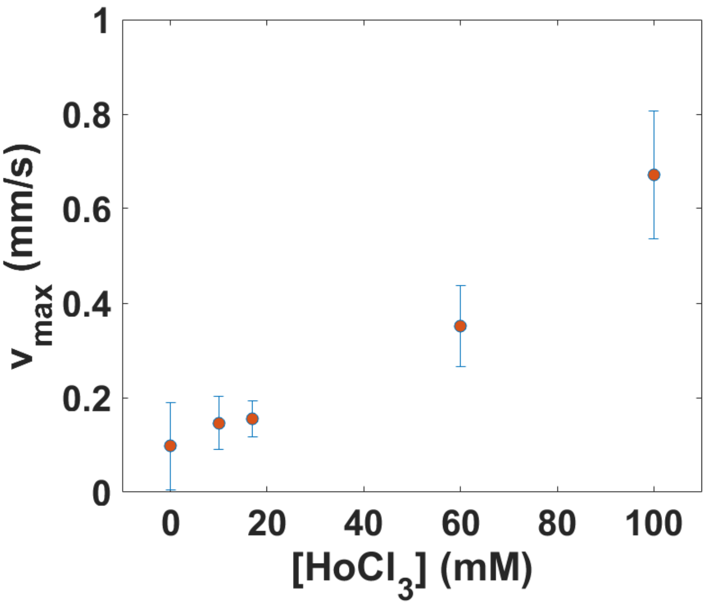


Figure S4. Maximum speed of a 2 μL oil drop at the air-solution interface, as a function of $HoCl_3$ concentration. Symbols and error bars show mean ± sd from at least 6 independent measurements.

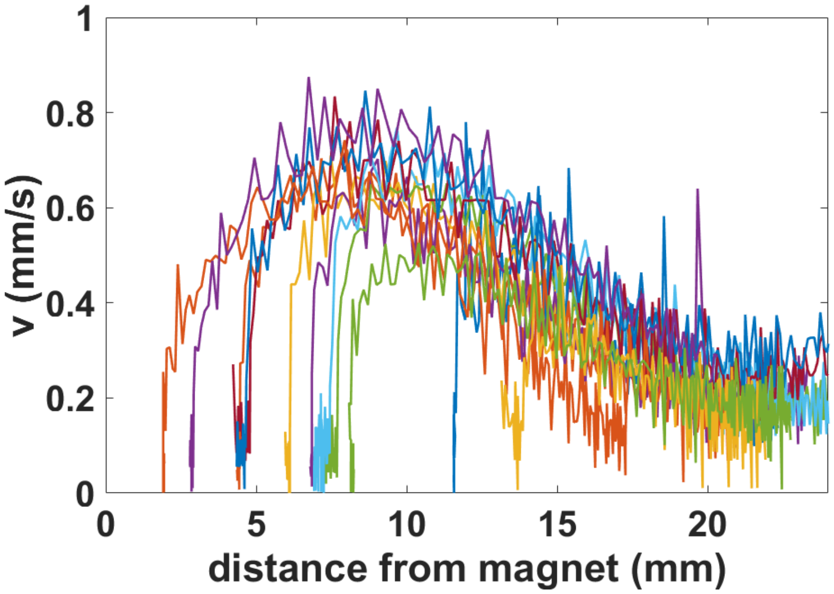


Figure S5. Speed profile of a 2 μL oil drop on 100 mM $HoCl_3$ liquid substrate as a function of the initial distance from the magnet axis.

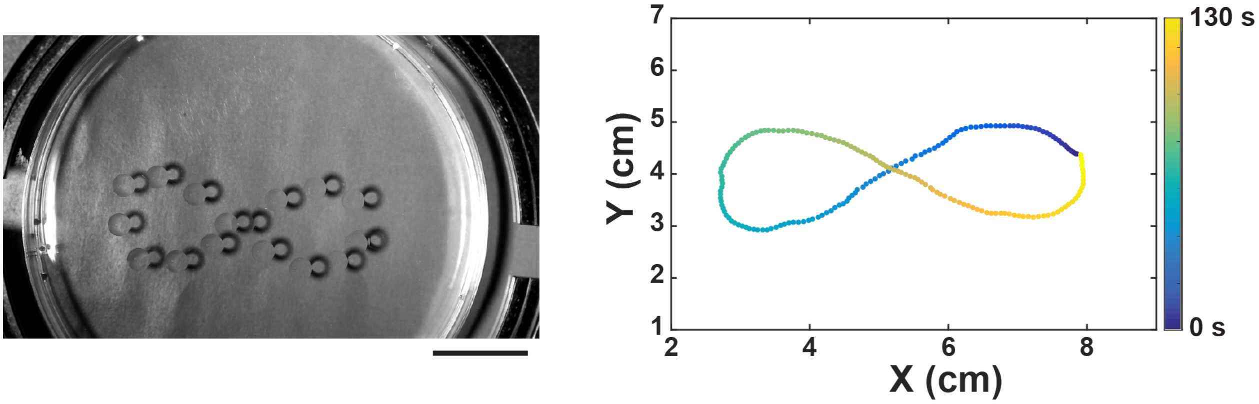


Figure S6. Magnetic transport of a drop along an ∞-shaped trajectory. The magnet is moved along an ∞-shaped pathway to transport a 5 μL oil drop on a 100 mM $HoCl_3$ liquid substrate. Left panel: superposition of images showing the drop motion (one image per 8 s). The scale bar is 2 cm. Right panel: plot of the position of the drop as a function of time.

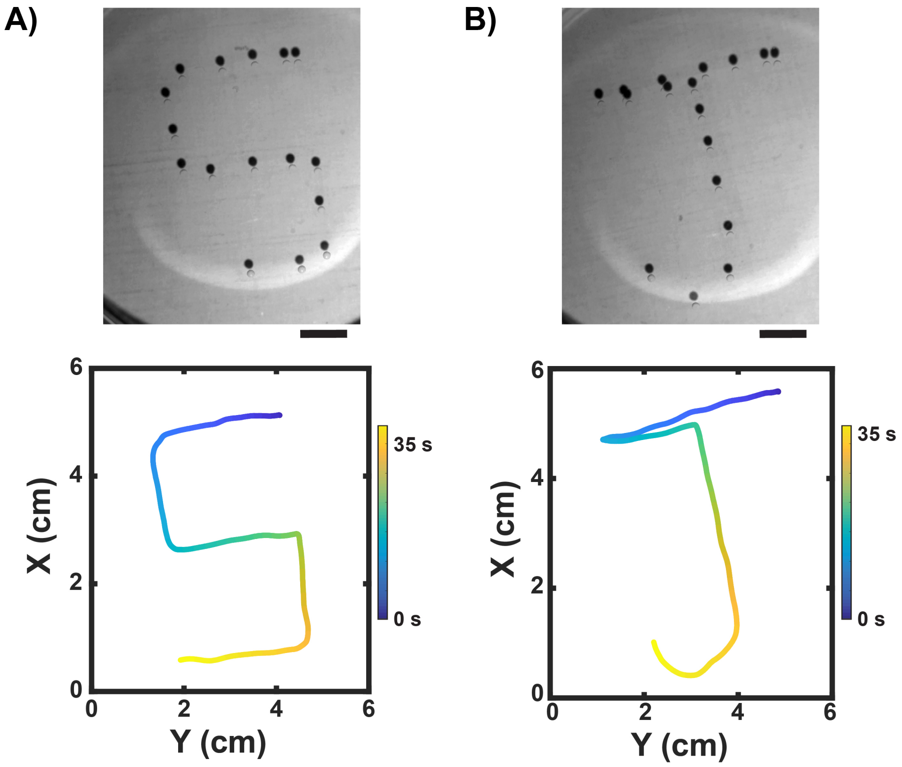


Figure S7. Magnetic transport of a liquid marble along various trajectories. The magnet is moved along a pathway having shapes of letters *S* (A) and *J* (B) to transport a 2 μL water liquid marble on a 100 mM $HoCl_3$ liquid substrate. Top: superposition of images showing the liquid marble motion (one image per 2.3 s). The marble and its shadow (black disk) are both visible. The scale bar is 1 cm. Bottom: plot of the position of the liquid marble as a function of time.

4 Legends of the movies

Movie S1. Actuation of a liquid marble. A 2 μL liquid marble is placed on a 100 mM $HoCl_3$ liquid substrate. After 10 s, the magnet underwent free fall to reach a distance of 12.7 mm from the liquid surface. In the video a grey circle is displayed when the magnet is at 12.7 mm from the surface. The movie is displayed three times the actual speed.

Movie S2. Actuation of a liquid marble at higher magnetic field. A 2 μL liquid marble is placed on a 100 mM $HoCl_3$ liquid substrate. After 5 s, the magnet underwent free fall to reach a distance of 9.8 mm from the liquid surface. In the video a black circle is displayed when the magnet is at 9.8 mm from the surface. The movie is displayed two times the actual speed.

Movie S3. Actuation of an oil drop. A 2 μL mineral oil drop is placed on a 100 mM $HoCl_3$ liquid substrate. After 2.5 s, the magnet underwent free fall to reach a distance of 12.7 mm from the liquid surface. In the video a black circle is displayed when the magnet is at 12.7 mm from the surface. The movie is displayed four times the actual speed.

Movie S4. Controlled drop motion along an S-shaped trajectory. A 5 μL mineral oil drop is placed on a 100 mM $HoCl_3$ liquid substrate and a magnet is used to manually direct its motion along the desired trajectory. The movie is displayed three times the actual speed.

Movie S5. Controlled drop motion along an ∞-shaped trajectory. A 5 μL mineral oil drop is placed on a 100 mM $HoCl_3$ liquid substrate and a magnet is used to manually direct its motion along the desired trajectory. The movie is displayed three times the actual speed.

Movie S6. Fusion of two oil drops. Two magnets were used to direct to the center of the Petri dish two mineral oil drops (5 μL) placed on a $HoCl_3$ liquid substrate (100 mM), to induce their fusion. One of the drops was marked with the Sudan II dye. The movie is displayed at the actual speed.

References

[1] N. Kavokine, M. Anyfantakis, M. Morel, S. Rudiuk, T. Bickel & D. Baigl. Light-Driven Transport of a Liquid Marble with and against Surface Flows. *Angew. Chem. Int. Ed.*, **55**, 11183-11187, (2016).

[2] C. R. Reisin and S. G. Lipson. Optical imaging of inhomogeneous magnetic fields through the deformation of paramagnetic liquid films. *Applied Optics*, **35**, 1120-1125, (1996)

[3] Chin Hong Ooi, Raja K. Vadivelu, James St John, Dzung Viet Daoa and Nam-Trung Nguyen. Deformation of a floating liquid marble. *Soft Matter*, **11**, 4576-4583, (2015)