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Ferrofluidic aqueous two-phase system with ultralow interfacial tension and micro-pattern formation

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Ferrofluids are magnetic liquids known for the patterns they form in external magnetic fields. Typically, the patterns form at the interface between a ferrofluid and another immiscible non-magnetic fluid with a large interfacial tension $\gamma \sim 10^{-2}$ N m⁻¹, leading to large pattern periodicities. Here we show that it is possible to reduce the interfacial tension several orders of magnitude down to ca. $\gamma \sim 10^{-6}$ N m⁻¹ by using two immiscible aqueous phases based on spontaneous phase separation of dextran and polyethylene glycol and the asymmetric partitioning of superparamagnetic maghemite nanoparticles into the dextran-rich phase. The system exhibits classic Rosensweig instability in a uniform magnetic field with a periodicity of ~200 µm, significantly lower than in traditional systems (~10 mm). This system paves the way towards the science of pattern formation at the limit of vanishing interfacial tension and ferrofluid applications driven by small external magnetic fields.

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errofluids are strongly magnetic colloids that consist of magnetic nanoparticles dispersed in a carrier fluid. They exhibit a great variety of properties and magnetic functionalities with a flexibility that makes them particularly relevant in a wide range of technological applications¹⁻⁵. In addition, ferrofluids are well-known for their instabilities in magnetic fields that lead to the formation of various patterns. The most famous ones, known since the 1960s, include the normal-field instability (Rosensweig instability), which occurs when a magnetic field is applied perpendicularly to the interface between a ferrofluid and a non-magnetic fluid, and the labyrinthine instability where the magnetic field is parallel to the interface and the ferrofluid is confined in a Hele-Shaw cell geometry⁶⁻⁸. More recently, elongation of sessile ferrofluid droplets in perpendicular magnetic field^{9,10} and their instability leading to the splitting of the droplets¹¹, formation of self-assembled droplet patterns^{11,12} and soliton features at the interface have been reported¹³. The normal-field instability, in particular, has proven to be an emerging phenomenon also in exotic systems like the magnetic Bose-Einstein condensates¹⁴ and in dissipative electrically driven gradients of magnetic nanoparticles¹⁵.

Classically, the normal-field instability has been studied almost exclusively in systems consisting of one magnetic fluid (ferrofluid) with an interface towards a non-magnetic fluid (Fig. $1a)^{6,16,17}$. In these systems the periodicity of the pattern generated by the normal-field instability is given by⁵

$$\lambda_0 = 2\pi \sqrt{\frac{\gamma}{g\Delta\rho}},\tag{1}$$

where λ_0 is the pattern periodicity, γ is the interfacial tension, g is the gravitational acceleration, and $\Delta \rho$ is the density difference between the two phases. The interfacial tension also influences the critical value of magnetization that needs to be reached for the onset of the instability⁵

$$M_{\rm c}^2 = \frac{2}{\mu_0} \left(1 + \frac{\mu_0}{\mu'} \right) \sqrt{g \Delta \rho \gamma},\tag{2}$$

where M_c is the magnetization of the ferrofluid at the threshold at which the pattern appears and μ_0 and μ' are the magnetic permeabilities of the non-magnetic phase and the ferrofluid, respectively. The aforementioned classic systems have large periodicities because of the high interfacial tension. For the same reason, the critical magnetization M_c is high. Therefore, observing the instabilities has been previously limited to strongly magnetic systems with high concentrations of magnetic nanoparticles.

To explore new phenomena and to probe the interaction between the magnetic instability patterns and other microscale behaviors like the thermal capillary waves¹⁸ we need to miniaturize the pattern well below the typical millimetric size. Achieving this is unfortunately not feasible in most cases since the interfacial tension of the air-liquid boundary is around 70 mN m⁻¹ for water and, typically, 15–30 mN m⁻¹ for different oils near room temperature. Two liquid phases seem more promising as e.g., 0.1 mN m⁻¹ has been reached by using surfactants¹⁹ but even smaller interfacial tensions would be desired to miniaturize the pattern size of more than one order of magnitude.

In this article, we demonstrate a ferrofluidic system where we can achieve several orders of magnitude smaller interfacial tensions than in previously studied systems. The presented system is based on the utilization of the so-called aqueous two-phase systems (ATPS)^{20,21}. These systems are obtained by creating an aqueous solution of different solutes like polymers or salts at so high concentrations that the mixture phase separates into two phases with different compositions. ATPS have been exploited in a diverse set of applications, in particular in the fields of biotechnology and bioengineering22-24. We chose a particular ATPS known for its biocompatibility and simplicity, consisting of polyethylene glycol (PEG) and dextran dissolved in water^{25,26}. In these systems interfacial tensions as low as $\sim 1 \,\mu N \,m^{-1}$ can be achieved²⁷. These values are orders of magnitude lower than the usual value measured between two immiscible liquids. The interfacial tension can also be regulated by controlling the polymers concentrations: increasing the concentrations will increase the interfacial tension while diluting the solution will decrease it. In this way, the interfacial tension can be, in principle, controlled to be arbitrarily close to zero. However, ATPS are essentially non-magnetic and can not reach the critical magnetization for pattern formation (eq. (2)). To make the ATPS responsive to magnetic fields we take advantage of the asymmetric partitioning of magnetic nanoparticles in the two phases



Fig. 1 Scheme and experimental realization of a ferrofluidic aqueous two-phase system (FF-ATPS). a A scheme of a regular water-based ferrofluidic system. **b** A scheme of the FF-ATPS. **c** Components of the FF-ATPS and structural formulas of PEG and dextran. **d** Photographs of a standard PEG-dextran ATPS (left), a maghemite-PEG-dextran FF-ATPS (center), and the same maghemite-PEG-dextran FF-ATPS in a vertical magnetic field of 20.0 mT exhibiting a quasi-1D magnetic instability at the interface (right). All the three images correspond to samples in a glass capillary of thickness of 200 μm.

that have been observed previously for several nanoparticles and macromolecules^{24,28–30}.

Results and discussion

Material preparation and phase behavior. In the present work, we prepare a ferrofluidic aqueous two-phase system (FF-ATPS, Fig. 1b) based on polyethylene glycol (PEG, Mw = 35 kDa), dextran (Mw = 500 kDa) and sodium citrate stabilized maghemite nanoparticles (Fig. 1c). In water at room temperature, the polymers have approximate radii of gyration of 8³¹ and 16 nm³², respectively, and the diameter of the maghemite nanoparticles follows a log-normal distribution with a mean (μ) of 6.9 nm and standard deviation (σ) of 3.3 nm (Supplementary Note 1). When the concentrations of the two polymers are high enough for the system to form two phases, the maghemite nanoparticles partition preferentially in the phase with higher dextran concentration which can be observed from the sample color (Fig. 1d). However, the details of the mechanisms behind the partitioning of nanoparticles in ATPS are complex^{21,33-35}. It is likely that the partitioning is driven by favorable interactions between the dissolved dextran and the surface of the iron oxide nanoparticles with citrate groups³⁶⁻³⁸. As expected, the maghemite nanoparticles that are stabilized by electrostatic double-layer forces form stable colloidal dispersions in both aqueous phases with the noncharged PEG and dextran (Fig. 1d). The concentration of the maghemite nanoparticles can be increased to a high enough level to allow the formation of magnetic instabilities at the interface, for example in a quasi-1D geometry (Fig. 1d). Notably, the periodicity of the pattern is ca. two orders of magnitude smaller than in classic systems.

In the rest of the manuscript, the partitioning of nanoparticles in PEG-dextran solutions with different concentrations will be quantified (Fig. 2) and the instability and pattern formation in quasi-1D (Figs. 3, 4) and quasi-2D (Figs. 5, 6) geometries will be described with appropriate modifications to the theoretical predictions (eq. (1), (2)) taking into account the dimensionality and the fact that both phases are ferrofluidic with non-vanishing magnetic susceptibility.

We investigated the phase behavior of the maghemite-PEGdextran system by preparing a concentrated two-phase sample (Sample 0) showing magnetic instabilities, and by diluting it gradually by adding deionized water (Sample 1, 2, 3) until the system transitioned into the one-phase state (Sample 8) (Fig. 2a). Sample 0 was prepared by mixing known amounts of the two polymers, water, and a well-characterized aqueous dispersion of the maghemite nanoparticles (stock ferrofluid) with a density of 1.28 g ml⁻¹ (Supplementary Note 2), nanoparticle mass fraction of 28.5% (Supplementary Note 3), the saturation magnetization of 20.82 kA m⁻¹ and magnetic susceptibility of 0.535 (Supplementary Note 4), to create a dispersion with 1.80 w/w % of PEG, 3.93 w/w % of dextran, and 3.54 w/w % of nanoparticles (Supplementary Note 5). A two-phase state was maintained up to 3 v/v % dilution (corresponding to Sample 3), above which the system transitioned first to a gradient state and then to a single-phase state (Fig. 2a, b).

To give an exhaustive description of the phase equilibria, behavior the PEG-dextran phase composition of all the samples was investigated using Fourier-Transform Infrared Spectroscopy (FTIR) and the asymmetric partitioning of the polymers was confirmed (Supplementary Note 5). Furthermore, the higher relative hydrophobicity of the light, PEG-rich phase over the denser, dextran-rich phase was confirmed (Supplementary Note 6). The partitioning of the nanoparticles was quantified by measuring the densities (Supplementary Note 7), saturation magnetizations (Supplementary Note 8), and optical absorptions (Supplementary Note 9) of the nanoparticle-rich (dense) and nanoparticle-poor (light) phases. All three methods confirmed that the progressive dilution leads to a decrease in the density (Fig. 2c), saturation magnetization (Fig. 2d), and nanoparticle concentration (Fig. 2e)



Fig. 2 Phase behavior and nanoparticle partitioning in the maghemite-PEG-dextran FF-ATPS. a Scheme of the behavior of a FF-ATPS during progressive dilution with water. **b** Transmitted light images of FF-ATPS samples in a vertical rectangular glass capillary (size $0.10 \times 2.00 \text{ mm}$) with different dilutions. Note: the differences in the color of the interface between samples are due optical effects caused by slight differences in the focusing. **c** density, **d** saturation magnetization (M_{sat}) and susceptibility (χ), and **e** $- \ln(I/I_0)$ of the light (yellow squares) and dense (dark red circles) phases as a function of dilution. Dashed lines indicate the one-phase state values corresponding to 8% dilution. Unless shown, the standard deviation error bars are of comparable size to the size of the data points in all graphs.



Fig. 3 Low-field response of the phase interface in a vertical glass capillary. a Front and side view schemes of a FF-ATPS sample in a capillary, showing the direction of the magnetic field and gravity. The contact angle between the dense phase and the capillary wall is ~180°. **b** Front view images of the interface at different magnetic-field strengths (Sample 0). **c** Mathematical reconstruction of the cross-section (side view) profiles as a function of the applied magnetic field corresponding to the images in **b** (note that *t* corresponds to the thickness of the meniscus as a function of the vertical space coordinate and *h* is the height of the meniscus). **d** Plot of the meniscus height as a function of the applied magnetic field and corresponding quadratic fit of the low-field data.

in the dense phase and a parallel increase of the same properties in the light phase. Furthermore, transmission electron microscopy imaging of the nanoparticles in the two phases shows no strong evidence of size sorting mechanisms (Supplementary Note 10). Given that the average size of the nanoparticles does not change considerably between the two phases, the most reliable indicator for the nanoparticle partitioning is the saturation magnetization, suggesting that the fraction of the nanoparticles in the dense phase can be approximated as $\Phi = M_{\text{sat,dense}}/(M_{\text{sat,dense}} + M_{\text{sat,light}})$. This vield $\Phi = 94\%$ for Sample 0 and $\Phi = 91\%$ for Sample 3. A measurement of the interfacial tension with the standard techniques (pendant or sessile drop) is particularly difficult because of the low interfacial tension and the ferrofluid opacity to visible light at the thicknesses needed for those measurements. Finally, approximate measurements of the interfacial tension using the puddle area method were performed. The values measured are in the range between $\sim 4 \,\mu N \,m^{-1}$ for Sample 0 and $\sim 0.1 \,\mu N \,m^{-1}$ for Sample 3 (Supplementary Note 11). The fact that interfacial tension changes considerably with dilution while nanoparticle partitioning remains nearly unchanged suggests that nanoparticles strongly prefer the dextran-rich phase, irrespective of the number of dextran molecules present in this phase compared to PEG.

Magnetic instabilities and patterns in quasi-1D geometry. Pattern formation in the FF-ATPS is a non-linear phenomenon and depends on the sample geometry and confinement. In the quasi-1D case of strong lateral confinement (Fig. 3a) the pattern formation is preceded by symmetric deformation of the interface (Fig. 3b, c). When no magnetic field is applied, the shape of the interface is determined by gravity, interfacial tension, and contact angle ($\theta_c \sim 180^\circ$) between dense phase and glass capillary walls. Increasing the strength of the magnetic field induces a progressive larger elongation of the meniscus and deviation from the ground state (Fig. 3b). The cross-section meniscus shape can be reconstructed from the front view images by using a grayscale analysis and the Beer-Lambert law for light attenuation (Fig. 3c, Supplementary Note 12)

$$t(z) = -\frac{1}{\alpha} \ln\left(\frac{I(z)}{I_{\text{ref}}}\right),\tag{3}$$

where t(z) is the thickness of the dense phase as a function of the z coordinate, α is a parameter that includes the attenuation factor in both the dense and light phases, I(z) is the intensity of light in the function of the z coordinate and I_{ref} is the intensity in the region where the dense phase occupies the whole thickness of the

capillary. The Beer-Lambert law is not valid where the curvature at the top of the meniscus and the three-phase contact line at its base introduce deviations in the optical path of the collimated light source. The top region of the meniscus has been reconstructed by polynomial fitting. As can be noticed, the meniscus is originally almost flat and then curves first to a hemispherical and then to a conical section with increasing height (Fig. 3d). The deformation is driven by the increase of the electromagnetic surface force at the interface. The increase in height is quadratic at low fields. The same dependence on the magnetic field has been observed also in the case of the elongation of a ferrofluid droplet in a viscous medium⁹. The deviation from the quadratic dependence can be associated with the transition from the hemispherical to the conical section of the meniscus.

Further increasing the magnetic field in the quasi-1D configuration (Fig. 4a) induces a magnetic normal-field instability. At first, the instability appears as a sinusoidal pattern on top of the deformed meniscus along the longer side of the capillary. If the magnetic field is further increased, the amplitude of the pattern increases and the pattern slowly transitions from a sinusoidal profile to a triangular wave with sharp spikes and valleys (Fig. 4b). Diluting the system induces an average decrease in the pattern periodicity from the ~160 µm of Sample 0 to the ~80 µm of Sample 3 (Fig. 4c, d). Furthermore, pattern periodicity is affected slightly by hysteresis behavior which causes it to be larger at the end of a measurement cycle than the initial one observed while increasing the field. Sample dilution does not affect the pattern amplitude (Fig. 4e). A similar non-linear dependency has been observed for Rosensweig instability in classic systems with large interfacial tensions¹⁷. The critical magnetic-field strength B_c for the onset of the instability can be extracted by a linear fit of the data for small deformation of the interface (Supplementary Note 12). The value of the critical threshold field decreases from 7.6 ± 0.9 mT for Sample 0 with the highest interfacial tension to 5.3 ± 0.9 for Sample 2 with the lowest interfacial tension.

The behavior of a single FF-ATPS sample in glass capillaries of different thicknesses was studied following the same protocol for the magnetic field as in the previous measurements (Fig. 4f). The pattern periodicity seems to be linked to the thickness of the capillary as it decreases with the smaller capillary thickness (Fig. 4g). As in the measurements performed changing the samples changing the thickness does not affect much the dependency as a function of the magnetic field (Fig. 4h). Furthermore, the critical magnetic field (B_c) values in the three

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Fig. 4 Meniscus magnetic normal-field instability of a FF-ATPS in a quasi-1D configuration. a Scheme of glass capillary geometry, and front view scheme of a FF-ATPS sample in a capillary, showing the direction of the magnetic field and gravity in relation to the interface between light and dense phases. **b** Pattern instability in FF-ATPS Sample 0 at different magnetic-field strengths observed from the front view. **c** Front view images of the capillary for three different samples at 24.0 mT. All images are relative to samples in a vertical glass capillary with a rectangular cross-section (size $0.10 \times 2.00 \text{ mm}$). **d** Plot of the pattern periodicity as a function of the magnetic field applied for three different samples (red squares for Sample 0, blue circles for Sample 1, and black triangles for Sample 2; the arrows mark the order in which the measurements are collected). **e** Plot of the pattern amplitude as a function of the magnetic field applied for three different samples (same colors and shape coding of panel **d**). **f** Front view images of Sample 0 at 24.0 mT with three capillaries with different thicknesses (w). **g** Plot of the pattern periodicity as a function of the magnetic field applied for three as a function of the magnetic field applied for three sizes of the capillary (yellow circles for w = 200 µm, red squares for w = 100 µm, and purple triangles for w = 50 µm). **h** Plot of the pattern amplitude as a function of the magnetic field applied for three sizes of the capillary (same colors and shape coding of panel **d**), the dashed line marks the amplitude equal to zero value).

capillaries are closer than the standard deviation of their measure (Supplementary Note 13). This kind of pattern observed in FF-ATPS samples resembles previous studies of the normal-field instability in 2D systems³⁹ with the main difference being that in our case the system has the additional thickness of the capillary in which it can deform. Despite this, the model for the 2D systems can be used in our case and calculate an approximate value of the interfacial tension. For the case of one magnetic phase, a relationship that links the values of the critical magnetization M_c and the critical wave number k_c has been derived as³⁹

$$\frac{\mu_0 M_c^2 w}{2\gamma} = \frac{\pi}{2} \frac{(k_c w)^2 + (k_0 w)^2}{\int_0^{+\infty} dt \frac{1 - \cos(t)}{t^2} \left(\sqrt{(k_c w)^2 + t^2} - t\right)} = \frac{\pi}{2} \frac{(k_c w)^2 + (k_0 w)^2}{f(k_c w)},$$
(4)



Fig. 5 Interfacial normal-field instability of a FF-ATPS in a horizontal glass capillary. a Scheme of glass capillary geometry, and front view scheme of a FF-ATPS sample in a capillary, showing the direction of the magnetic field and gravity in relation to the interface between light and dense phases. **b** Images of the view along the *z*-axis in function of the magnetic field applied (first row), zoom of the central area of the images (second row), and scheme of the proposed shape of the interface between the two phases for a section along the x-z plane. **c** processed $-\ln(I/I_0)$ image detail of the pattern. The two red arrows represent the two main directions in the unit cell of the pattern lattice. **d** 3-dimensional reconstruction of the pattern shape. **e** Plot of the $-\ln(I/I_0)$ values calculated along the **a**₁ + **a**₂ direction for three different magnetic fields (yellow squares for B = 0.0 mT, red circles for B = 5.2 mT and purple triangles for B = 6.4 mT). **f** Plot of the pattern periodicity as a function of the magnetic field applied for three different samples (red squares for Sample 0, blue circles for Sample 1, and black triangles for Sample 2). The full lines represent linear interpolation of the data. **g** Plot of the pattern amplitude as a function of the magnetic field applied for three different samples (for three different samples (for B = 6.4 mT).

where μ_0 is the vacuum magnetic permeability, *w* is the capillary thickness and k_0 is the critical wave number of the normal-field instability in a pool of ferrofluid: $k_0 = 2\pi/\lambda_0$ where λ_0 is the critical pattern periodicity calculated as in eq. (1). Introducing the presence of two magnetic phases substituting M_c with ΔM_c eq. (4) can be rewritten to calculate the interfacial tension as

$$\gamma = \frac{1}{\left(k_{\rm c}w\right)^2} \cdot \left[\frac{\mu_0 \Delta M_{\rm c}^2 w}{\pi} \cdot f(k_{\rm c}w) - w^2 \Delta \rho g\right].$$
 (5)

At this point, the values of the critical magnetic field (B_c) measured with the fit from the amplitude graph and the values of the periodicity near the critical point can be used to calculate the interfacial tension. The pattern periodicity near the critical point increasing the field is measured to be: $135.7 \pm 0.5 \,\mu\text{m}$ for Sample 0, $118.2 \pm 0.5 \,\mu\text{m}$ for Sample 1, and $86.5 \pm 0.5 \,\mu\text{m}$ for Sample 2. This leads to the following approximate values for γ : ~ $1.2 \,\mu\text{N} \,\text{m}^{-1}$ for Sample 0, ~ $0.7 \,\mu\text{N} \,\text{m}^{-1}$ for Sample 1, and ~ $0.33 \,\mu\text{N} \,\text{m}^{-1}$ for Sample 2 (Supplementary Note 13). These values are clearly approximations since there are several possible discrepancies in the model, for example, the slightly different geometry between our case and a pure 2D case or the effect of the demagnetizing field³⁹. However, the model is precise enough to evaluate the order

of magnitude of the interfacial tension and how interfacial tension decreases as a function of the concentration of the polymer.

Magnetic instabilities and patterns in quasi-2D geometry. The normal-field instability can also be observed in horizontal capillaries (Fig. 5a). Therein, the interface is flat and horizontal similarly to classic experiments done using ferrofluid pools⁶. In contrast to vertical capillaries with a curved interface that gradually deforms with increasing field (Fig. 3), the horizontal flat interface is stable up to a critical field at which it develops instability (Fig. 5b). The shape of the deformed interface can not be directly observed as in vertical capillaries (Figs. 3, 4), but it can be indirectly extracted from intensity variations in the transmitted light images analogously to the x-ray intensity analysis used previously in classic ferrofluid systems¹⁶. At low fields, the perturbation of the interface is small and does not touch either the upper or the lower glass wall. The Beer-Lambert law can be used to reconstruct the 3D shape of the pattern remembering that the thickness of the dense phase layer is proportional to the value of $-\ln(I/I_0)$ (Fig. 5c, d). Furthermore, it is possible to confirm that the profile of the perturbation is sinusoidal with the amplitude increasing while increasing the B-field strength (Fig. 5e). It is important to notice that the pattern is sinusoidal (without offset)



Fig. 6 Transitioning from the normal-field instability pattern to the labyrinthine pattern. a Images of the view along the *z*-axis in function of the magnetic field applied (first row), zoom of the central area of the images (second row), and scheme of the proposed shape of the interface between the two phases for a section along the x-z plane. **b** Behavior of the pattern at 36.0 mT in three different samples.

around the unperturbed interface only in the direction $\mathbf{a}_1 + \mathbf{a}_2$ (see Fig. 5c for reference). The overall periodicity of the pattern was instead determined by looking at the intensity in the fast Fourier transformed (FFT) images (Supplementary Note 14). The periodicity increases with *B*-field and sample concentration (Fig. 5f). Similar to the vertical capillary configuration the amplitude of the pattern increases non-linearly with the magnetic field (Fig. 5g).

The periodicity values can be then used to calculate approximate values of the interfacial tension in the system from eq. (1) and then compare the theoretical and experimental values for the critical field using eq. (2). Because nanoparticles do not fully partition to the dextran-rich phase, both phases are magnetic, and so we expect the equation for the critical magnetization (eq. (2)) to be modified as

$$\Delta M_{\rm c}^2 = \frac{2}{\mu} \left(1 + \frac{\mu}{\mu'} \right) \sqrt{g \Delta \rho \gamma},\tag{6}$$

where ΔM_c is the difference of the magnetization between the two phases when the instability appears and μ and μ' are the permeabilities of the weakly magnetic and strongly magnetic phases, respectively.

It is important to notice that, even if eq. (1) and (2) were calculated for an infinite layer of ferrofluid, for a ferrofluid with a magnetic susceptibility $\chi \sim 0.05$ and depth of the layer less than the pattern periodicity, the critical magnetic field and the critical wave number are altered less than 2%. Moreover, if the depth is larger than the pattern periodicity, this effect can be completely ignored¹⁷. This observation applies very well to our case since for all our samples $\chi \sim 0.06$ but the thickness of the dense phase is larger than the periodicity of the pattern implying that it is not needed to take into account the effects of the layer thickness when calculating the critical wavelength and magnetization. The values of the average periodicity for the three different samples right after the onset of the instability are 244.3 ± 0.8 µm for Sample 0, 225.7 ± 0.8 µm for Sample 1, and 189.4 ± 0.7 µm for Sample 2 (Supplementary

 Table 1 Interfacial tension measured with three different techniques.

_	Sample O	Sample 1	Sample 2
	(µN m ⁻¹)	(µN m ⁻¹)	(μN m ⁻¹)
Puddle area method	~4.0	~0.2	~0.1
Quasi-1D normal-field instability	~1.2	~0.7	~0.33
Quasi-2D normal-field instability	0.9 ± 0.1	0.6 ± 0.1	0.45 ± 0.09

Note 14). The values of the interfacial tension obtained from eq. (1) and the periodicity data are presented in Table 1 alongside the values obtained from the puddle area method and the normal-field instability in a vertical capillary. The values of the interfacial tension can be finally used to calculate the critical value of the *B*-field at which the instability is expected to take place. Since the magnetization of both phases is linear with the magnetic field in the range of interest for all the samples, we can write $B_c = \mu_0 \chi \Delta M_c^2$, where ΔM_c^2 can be calculated from eq. (6). The critical *B*-field is calculated as 5.0 ± 0.6 mT for Sample 0, 4.3 ± 0.6 mT for Sample 1, and 4.4 ± 0.6 mT for Sample 2. All the calculated values are very close to the experimental value of 4.8 mT confirming the good agreement with the model (Supplementary Note 14).

The main difference between this pattern and the typical normal-field instability pattern is that in this case, it does not have a long-range order: the consistency in the alignment of the peaks is confined in small domains. Inside the domains, the square pattern seems to be favored instead of the hexagonal one typical of the classical normal-field instability near the onset (Fig. 5c). The square geometry appears also for the normal-field instability but only as a second stage feature at higher fields far from the critical value⁴⁰. The other known square geometry pattern for an interface is the Faraday instability, which is induced by vertical vibrations of the sample⁴¹.

If the magnetic field is further increased, at a certain point, the dense phase peaks make contact with the upper glass wall (Fig. 6a, first column). This fact can be confirmed by looking at the histogram of the pixel intensity in the image: suddenly a peak in the range of the darker pixels appears, corresponding to the value of the whole thickness of the capillary occupied by the dense phase (Supplementary Note 14). Increasing the field from this point leads to topological changes where the light phase forms small wells organized in a hexagonal pattern (Fig. 6a, second column). Further increasing the field makes the light phase elongate enough to touch the glass wall on the other side, leading to the formation of holes in the dense phase. Since the contact angle for the dense phase is ~180° when the light phase makes contact with the lower glass wall the shape became symmetric with respect to the central plane of the capillary (Supplementary Note 11). This geometry reminds of the one used in the labyrinthine instabilities experiments, with B-field along with the interface. Further increase in the B-field indeed leads to a minilabyrinthine instability and pattern (Fig. 6a, third column). Pattern formation is reversible so that by reducing the field we observe the exact same topological transitions in reverse order. The same behavior is observed for Samples 0, 1, and 2 (Fig. 6b). All the behavior observed can, in principle, be combined with the extreme flexibility of FF-ATPS even more: we can approach the classical systems by increasing the polymer concentration (Supplementary Note 15) and, simultaneously, theoretical estimates show that the instabilities and pattern formation are possible with nanoparticle concentrations as low as $\phi \approx 10^{-4}$ in ferrofluidic ATPS, whereas in the classical system the required concentrations are ca. two orders of magnitude larger $\phi \approx 10^{-2}$ (see Supplementary Note 16).

Conclusions

In conclusion, we have presented and thoroughly characterized the miniaturized magnetic instabilities and patterns exhibited by a ferrofluidic aqueous two-phase system with ultralow interfacial tension close to ~1 μ N m⁻¹. Possibly due to the ultralow interfacial tension, the long-range hexagonal order typically seen in the classic Rosensweig instability is lost and domain-like local square patterns with 1–2 orders of magnitude smaller periodicities than typical appear. We also observed less common patterns by introducing confinement, leading to e.g., quasi-1D Rosensweig pattern and a transition from a Rosensweig pattern to a labyr-inthine pattern. The pattern wavelengths can be also used to evaluate the ultralow interfacial tensions as small as ~0.2 μ N m⁻¹, which is challenging with most other experimental techniques⁴¹.

The presented results point toward new avenues in several fields of research. In the field of physics of pattern formation, the verified ultralow interfacial tension and the ability to generate magnetic instabilities and patterns suggest a realistic possibility for direct observation of thermal capillary waves on the interface¹⁸ and their coupling to the Rosensweig pattern. In the field of biosciences, the ferrofluidic ATPS may enable magnetic-field-enhanced purification of biomolecules such as proteins based on their partitioning in the ATPS^{29,42,43}. In the field of materials science, the ultralow interfacial tensions combined with the strong magnetic response allow the generation of strong deformations and motion at the interface even with small magnetic fields, which can lead to practical magnetically controllable non-compartments as microreactors^{44,45}, for in situ synthesis or biological reactions mimicking the environment of living cells⁴⁶.

Methods

Materials. Iron (III) chloride hexahydrate (FeCl₃ · $6H_{2O}$, \geq 99%, 31232, Sigma–Aldrich), iron (II) chloride tetrahydrate (FeCl₂ · $4H_{2O}$, \geq 99%, 44939,

Sigma–Aldrich), iron (III) nitrate nonahydrate (Fe(NO₃)₃ · 9H₂₀, ≥98%, 216828, Sigma–Aldrich), hydrochloric acid (HCl, 37%, 258148, Sigma–Aldrich), ammonium hydroxide (NH_{4OH}, 28–30% NH₃ basis, 221228, Sigma–Aldrich), nitric acid (HNO₃, 70%, 438073, Sigma–Aldrich), acetone (≥99.8%, A/0606/17, Fisher Scientific), diethyl ether (C₂H₃)₂₀, ≥99.8%, A/0606/17, Sigma–Aldrich), polyethylene glycol (PEG 35000, ≥99.9%, 81310, Sigma–Aldrich), dextran (Dextran T500, ~95%, 40030, Pharmacosmos), Rose Bengal (≥95%, 330000, Sigma–Aldrich), Sulforhodamine B (acid form, ≥95%, 341738, Sigma–Aldrich), glass capillaries (Vitrocom Inc. hollow rectangular capillaries, borosilicated glass, open ends, flame polished: 0.05 × 1.00 × 50 mm, wall thickness 0.10 mm, tolerances ± 10%, product ID 5012-050; 0.20 × 4.00 × 50 mm, wall thickness 0.20 mm, tolerances ± 10%, product ID 3524-050; 0.40 × 8.00 × 50 mm, wall thickness 0.40 mm, tolerances ± 10%, product ID 2548-050), and UV curable adhesive (Norland Optical Adhesive 61) were used as obtained.

Synthesis of citrated maghemite nanoparticles dispersed in water

Formation of maghemite nanoparticles. Maghemite (γ -Fe₂O₃) nanoparticles were synthesized by coprecipitation of Fe²⁺ and Fe³⁺ salts in an alkaline medium^{47,48}. In detail, 210 g of FeCl₃ · 6H₂O (0.78 mol) were added to distilled water and dissolved by magnetic stirring (total volume of 1500 ml). A second solution was prepared by dissolving 90 g of FeCl₂ · 4H₂O (0.45 mol) in an acidic solution (50 ml of HCl 37% w/w added to 250 ml of distilled water). The two solutions were mixed under mechanical stirring (400 rpm) and 360 ml of NH₄OH (28–30% w/w of NH₃) was poured quickly into the iron salt solution. The solution was stirred for 30 min and then washed twice with distilled water by magnetic sedimentation using a cube-shaped NdFeB magnet (5 × 5 × 5 cm) (the supernatant was discarded).

Acidification of the nanoparticles. A solution of HNO_3 (2 mol l^{-1}) was poured over the decanted sediment until 1 l was reached. Afterward, the solution was stirred at 400 rpm for 30 min and decanted on a strong magnet (the supernatant was discarded).

Oxidation of the nanoparticles. A solution was prepared by dissolving 270 g of $Fe(NO_3)_3 \cdot 9H_2O$ (0.67 mol) in 400 ml of distilled water. The solution was heated until boiling on a hot plate and then poured over the moist nanoparticles obtained after the last sedimentation. Boiling was then maintained for 30 min, followed by magnetic sedimentation and discarding of the supernatant. A solution of HNO₃ (2 mol l^{-1}) was poured over the nanoparticles until 1 l was reached and the solution was stirred at 400 rpm for 10 min, followed by magnetic sedimentation and discarding of the supernatant. The precipitate was then washed three times with acetone and two times with diethyl ether using magnetic sedimentation. Distilled water was added until 600 ml was reached and the remaining ether was evaporated at 40 °C for a few hours.

Stabilization of nanoparticles at neutral pH with sodium citrate. Fourteen grams of sodium citrate ($Na_3C_6H_5O_7$, 47.6 mmol) were added to the solution, followed by stirring for 30 min at 80 °C. The solution was then washed twice with acetone and twice with ether using magnetic sedimentation. Afterward, particles were dispersed by adding distilled water until 100 ml was reached, and the remaining ether was evaporated at 40 °C. Finally, the ferrofluid was filtered through 0.2 µm pores (Fisherbrand Sterile PES Syringe Filter), and distilled water was added to reach a final volume of 135 ml. The volume fraction of nanoparticles in this stock dispersion was determined to be ~8.3% (Supplementary Note 3). This value includes both the iron oxide and the adsorbed citrated surfactant contributions.

Characterization of the citrated maghemite nanoparticles and the citrated ferrofluid

Transmission electron microscopy (TEM). Nanoparticle morphology and size distribution were determined using a transmission electron microscope (JEOL JEM-2800, 200 kV). The calculated average value for the size of the nanoparticles is $\mu = 6.9 \pm 0.2$ nm and the standard deviation is $\sigma = 3.3 \pm 0.1$ nm. See Supplementary Note 1 for further details.

Densitometry. The density was measured with a precision pipette (Eppendorf Multipette E3× equipped with Combitips advanced 0.1 ml) and an analytical balance (Ohaus Pioneer PX224). The final averaged value of the density of the citrated ferrofluid was calculated to be 1.28 ± 0.01 g ml⁻¹. Our homemade density setup was validated against a commercial densimeter (Mettler Toledo DensitoPro) by measuring a 6% PEG solution, 6% dextran solution, deionized water, and the citrated ferrofluid. The relative difference in the density between the two techniques was at most 0.2%. See Supplementary Note 2 for further details.

Mass and volume fraction determination. Mass and the volume fraction of the citrated maghemite nanoparticles in the ferrofluid were determined by evaporation measurements. The values obtained are $w = 28.5 \pm 0.2$ w/w % for the mass fraction

Table 2 Water added to prepare each FF-ATPS dilution.					
Sample	1	2	3	8	
Water dilution (w/w %)	0.927 ± 0.003	1.833 ± 0.003	2.756 ± 0.003	7.035 ± 0.009	

and $\phi=8.3\pm0.3$ v/v % for the volume fraction. See Supplementary Note 3 for further details.

Magnetometry. Magnetic properties of the citrated ferrofluid were measured with a vibrating sample magnetometer (QuantumDesign PPMS VSM) and analyzed with the Langevin model. Final results for the saturation magnetization and the magnetic susceptibility are $M_{\rm s,FF} = 20.82 \pm 0.03$ kA m⁻¹ and $\chi_{\rm FF} = 0.535 \pm 0.007$, respectively. See Supplementary Note 4 for further details.

Preparation of the FF-ATPS samples. The main FF-ATPS sample (Sample 0) was obtained by mixing 4 ml of the synthesized citrated ferrofluid with 36 ml of concentrated PEG-dextran solution. The concentrated PEG-dextran solution was obtained by weighing 740.0 mg of PEG, 1615.0 mg of dextran, and 33560.0 mg of deionized water in a centrifuge tube and mixing it mechanically at 300 rpm overnight. 5112.2 mg of citrated ferrofluid, equivalent to the 10% in volume of the whole mixture, were then mixed and the whole dispersion was put in a vortex mixer at 300 rpm for 10 min and centrifuged (Beckman Coulter / Allegra X-22R) for 2 h at $5000 \times g$. The other samples (Samples 1, 2, 3, and 8) were obtained as follows: 2 ml of the main batch were extracted after vigorous mixing for 2 min to be sure that each batch would have the same light/dense phase ratio, then different amounts of water were added to each sample. The water mass dilution for each sample is reported in Table 2. All mass measurements during the preparation were carried out after discharging the object to be weighted by passing it through an electrostatic gate for better precision.

Capillary filling and sealing. Before filling the capillaries, the samples were vigorously mixed for 2 min. After that, a certain amount of the samples was pipetted depending on the thickness of the capillary to fill (2 µl for the 0.05×1.00 mm, 8 µl for the 0.10×2.00 mm, 20 µl for the 0.20×4.00 mm, and 80 µl for the 0.40×8.00 mm). After filling, the capillary was sealed with UV curable adhesive (Norland Optical Adhesive 61) and cured under a UV lamp (Thorlabs Solis 365C). Particular care was taken to avoid that only the UV glue was under direct illumination by protecting the sample region with black tape. Each filled and sealed capillary was left to rest vertically overnight to allow phase separation before using them for the measurements.

Characterization of the FF-ATPS samples

Fourier-Transform Infrared Spectroscopy (FTIR). The PEG and dextran content of each phase of all the phase-separated samples prepared has been measured using Attenuated Total Reflection FTIR (Nicolet 380 FTIR Spectrometer). To calibrate the system six different dilutions of PEG and dextran with concentrations 1–6% w/ w were prepared and their FTIR signal was measured. See Supplementary Note 5 for further details.

Relative hydrophobicity. The relative hydrophobicity of the light and dense phase of Sample 0 was estimated by using the selective partitioning of fluorescent dyes (Rose Bengal, Sulforhodamine B, acid form) and their light absorption properties with visible spectrophotometry (Thermo Scientific[™] GENESYS[™] 30 Visible Spectrophotometer). See Supplementary Note 6 for further details.

Densitometry. The density of both the light and the dense phases was measured for Samples 0, 1, 2, 3, and of the single phase of Sample 8. The measurements were carried out following the same procedure described for the citrated ferrofluid. See Supplementary Note 7 for further details.

Magnetometry. The magnetic properties of both the light and the dense phase were measured for Samples 0, 1, 2, 3, and of the single phase of Sample 8. The measurements were carried out following the same procedure described for the citrated ferrofluid. The saturation magnetization was obtained by fitting the measured magnetization curves with the Fröhlich–Kennelly model for superparamagnetism and the magnetic field. See Supplementary Note 8 for further details.

Light absorption. Light absorption was measured for both the light and the dense phase of Samples 0, 1, 2, 3, and the single phase of Sample 8. The gray pixel values of the images were measured using ImageJ/Fiji^{49,50}. See Supplementary Note 9 for further details.

Transmission electron microscopy (TEM). Nanoparticle morphology and size distribution were determined in both phases of Sample 0 using a transmission electron microscope as done for the citrated ferrofluid. See Supplementary Note 10 for further details.

Interfacial tension and contact angle. The interfacial tension between the PEG and dextran-rich phase of the FF-ATPS samples is approximated using the sessile drop method. See Supplementary Note 11 for further details.

Experimental setup for microscopic observation of the FF-ATPS in the glass capillaries under magnetic field

Magnetic field. The magnetic field was generated and controlled as before¹⁵. Briefly, a pair of small electromagnetic coils (GMW 11801523 and 11801524) connected to DC power supply (BK Precision 9205 Multi-Range DC Power Supply) was used to generate a nearly uniform magnetic field. The magnetic field between the coils was calibrated using a 3-axis teslameter (Senis 3MTS).

Microscopy. The capillaries were illuminated in the transmitted light configuration using an LED light source (Thorlabs MCWHLP1), a collimator (Thorlabs COP4-A Zeiss), and a light diffuser (Thorlabs DG10-1500). All images were captured using a $4 \times finite-conjugate$ objective lens (Nikon $4 \times /0.25$ 160/- WD25) or a $1 \times Tele$ $centric Gauging Lens (Melles Griot Macro Invaritar <math>1 \times 59LGM601$) connected to a 5 MP grayscale camera (Basler acA2440-75um). The image length scale was calibrated using a calibration target (Thorlabs R1L3S2P).

Methods for the meniscus elongation study. All the meniscus elongation measurements were performed by looking at the FF-ATPS Sample 0 in a rectangular glass capillary of 0.20×4.00 mm. The capillary was positioned vertically, parallel to the gravitational acceleration. The magnetic field was applied parallel to the gravitational acceleration, with progressive steps of 0.8 mT from 0.0 to 8.0 mT. At each step, 2 min were waited from the increase of the magnetic field to the image acquisition to reach a relative equilibrium shape of the meniscus. The light intensity profiles were measured and then studied using the Beer-Lambert equation. See Supplementary Note 12 for further details.

Methods for quasi-1D instability study. Instability patterns in quasi-1D were measured using different sample dilutions and capillaries. Samples 0, 1, 2, and 0.05×1.00 mm, 0.10×2.00 mm, and 0.20×4.00 mm capillaries were used. The capillaries were positioned vertically, parallel to the gravitational acceleration. The magnetic field was applied parallel to the gravitational acceleration with progressive steps of different intensities. At each step, 2 min were waited from the increase of the magnetic field to the image acquisition to reach a relative equilibrium shape of the instability pattern. The magnetic field is applied in a cycle starting from 0 mT to a maximum value of 36.0 mT and then decreasing the field to 0 mT again. The pattern was analyzed by image analysis of the interface profiles. See Supplementary Note 13 for further details.

Methods for quasi-2D instability study. The measurements were performed with Samples 0, 1, and 2 in 0.40×8.00 mm capillaries. The capillaries were positioned horizontally, perpendicular to the gravitational acceleration. The magnetic field was applied parallel to the gravitational acceleration with progressive steps of different intensities. At each step, 2 min were waited from the increase of the magnetic field to the image acquisition to reach a relative equilibrium shape of the instability pattern. The pattern was analyzed by image analysis of the interface profiles. See Supplementary Note 14 for further details.

Data availability

The microscopy images and other experimental data that support the findings of this study are available in Zenodo with the identifier: https://doi.org/10.5281/zenodo. 5336835.

Code availability

The custom codes used for the analysis are available in Zenodo with the identifier: https://doi.org/10.5281/zenodo.5336835.

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Author contributions

G.B. and C.R. synthesized and characterized the citrated ferrofluid. G.B. carried out the FTIR, density, and interfacial tension measurements. F.S. performed transmission electron microscopy and magnetometry measurements. C.R. prepared the FF-ATPS samples, designed, and constructed the magnetic-field setups, carried out all measurements of the FF-ATPS samples in magnetic fields, analyzed the data, wrote the manuscript, and compiled the figures. J.V.I.T. conceived the concept, performed preliminary experiments with G.B. and B.H., and guided and supervised the experimental work, data analysis, and writing of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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