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2 AUTHORS:

Denis Wirtz
Johns Hopkins University

Marc Fermigier
MINES ParisTech

Periodic Structures and Substructures in Magnetic Suspensions

Denis Wirtz*

Chemical Engineering Department, The Johns Hopkins University, 3400 North Charles Street, Baltimore, Maryland 21218

Marc Fermigier

Laboratoire PMMH, ESPCI, 10 Rue Vauquelin, F-75231, Paris Cedex, France

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We investigate the phase transitions induced by external fields in magnetic colloidal suspensions. We report video microscopy experiments showing the onset of unidimensional phase-segregated patterns composed of self-similar periodic structures induced by a pulsed magnetic field. Similar periodic patterns are shown to occur in the presence of combined shear flow and dc magnetic fields. The wavevector of these patterns can be tuned by the shear viscosity or the frequency of the pulsed field.

A suspension of fine dielectric particles in a dielectric medium can undergo large, rapid, and reversible shear-thickening upon the inception of an electric field, leading to the well-known electrorheological effect.[1-7] Since the original report of the electrorheological effect in 1949 by Winslow,[1] dielectric and similar magnetic suspensions[8-13] have been the focus of tremendous interest in research and industry. For instance, electromechanical devices such as shock absorbers, valves, clutches, brakes, and robotic actuators have been designed using these fluids.[1,2,5,6] However, surprisingly few detailed structural studies have been reported, especially in the case of magnetic suspensions in flow and time-dependent magnetic fields.[2-12]

This Letter presents the unexpected experimental evidence of unidimensional patterns composed of a principal periodic structure and identical periodic substructures induces in magnetic suspensions. These self-similar structures are generated by an external pulsed magnetic field, which not only controls the wavevector of the periodic structures but also induces a dramatic enhancement of the domain-growth kinetics compared to the (usual) dc case. The resulting rapid onset of a coarsened structure is expected to improve the rheological properties of currently available fluids. Moreover, we present the first observation of macroscopic phase separation in the presence of combined shear flow and dc magnetic fields. In this case, the organized fibrous structure is periodic and spans the width of the fow cell but does not possess a periodic substructure. The present system is a monodisperse suspension of superparamagnetic particles suspended in water. Our use of magnetic particles instead of dielectric particles alleviates several experimental complications such as the transport of mobile charge carries in the electric field due to residual suspension conductivity, electrode polarization, absorbed water, and field inhomogeneities.[2,6,11]

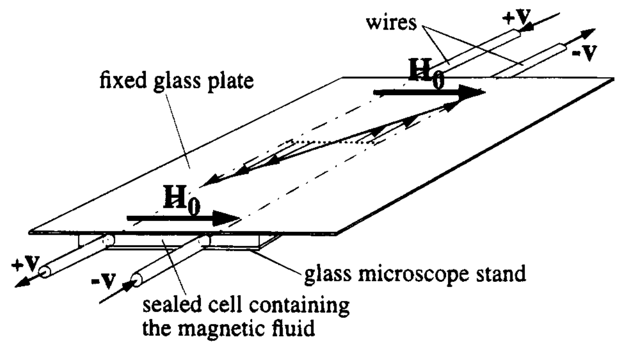

Figure 1. Flow cell geometry for the observation of magnetic suspensions in combined flow and magnetic fields. Two Helmoltz coils (not shown) placed on each side of the capillary create a uniform magnetic field $\mathbf{H}_0$ which may then be pulsed; two wires moving in opposite directions create a shear flow with a zero average velocity.

To study the different states induced by the application of flow and magnetic fields in well-defined model systems, suspensions of spherical monodisperse superparamagnetic particles (diameter, 0.25 μm; polydispersity, 5%) are prepared by fractionated crystallization[13] and suspended in water. A single magnetic particle (or droplet) consists of a large collection of Fe_2O_3 monodomain grains ($\sim 10^4$ grains per particle) dispersed in oil and stabilized with surfactant (sodium dodecyl sulfate) to avoid aggregation between particles in the absence of an external field. The magnetic suspensions are introduced into a sealed glass cell with rectangular cross section, held horizontally on a microscope stage, and maintained at room temperature. Two coaxial Helmoltz coils are placed on each side of the cell to produce an homogeneous magnetic field of constant magnitude H_0 = 1450 A/m, which may then be pulsed. Two copper wires (circular cross section, diameter equal to the thickness of the capillary) separated by a constant distance d = 0.26 cm, placed normal to the magnetic field and moving in the plane of the stage with equal and opposite controlled velocities generate a shear flow with an average zero velocity across the cell. A schematic of the cell geometry is depicted in Figure 1. Using time-

* Author to whom all correspondence should be addressed.

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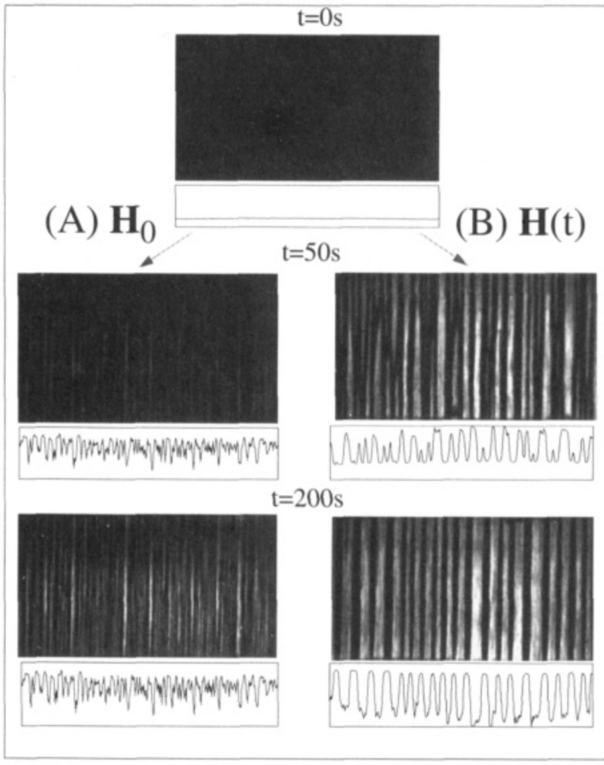

Figure 2. Structural evolution and corresponding optical density profiles of a 1% magnetic suspension in a dc and a 0.5 Hz pulsed magnetic field of amplitude $H_0 = 1450$A/m. Dark and bright zones correspond to regions rich and poor in particles, respectively. (A) dc field: quiescent state ($t = 0$ s); local phase separation ($t = 50$ s); microphase-separated steady state ($t = 200$ s). (B) Pulsed field: quiescent state ($t = 0$ s); two-dimensional domain growth ($t = 50$ s); steady state, nonequilibrium, unidimensional, periodic concentration patterns with a spatial wavelength $\lambda_s \cong 0.1$ mm ($t = 200$ s).

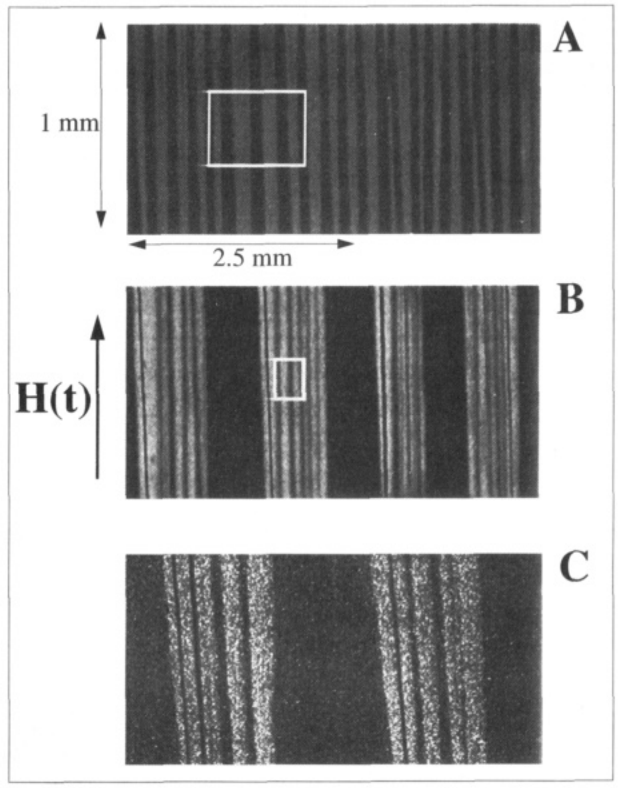

Figure 3. Main periodic structure and substructures obtained with a magnetic suspension subjected to a 5-Hz square-wave magnetic field for 10 min. The magnified zones (white frames) in each depleted region reveal the self-similarity of the concentration patterns. Same magnetic suspension as in Figure 2 with $\varphi = 3\%$; microscope magnification in Figure 4a is 2.5.

resolved video microscopy, we investigate the growth dynamics of field-induced concentration patterns in several configurations of external fields. Images of 512 $\times$ 430 pixels with 256 gray levels are acquired using the NIH Image software via a CCD video camera mounted on a high-resolution microscope.

Figure 2 compares pattern formations in magnetic suspensions when the applied magnetic field is constant and time-dependent. Concentration patterns are monitored for a $\varphi = 1\%$ suspension subjected to a dc field and to a 2-Hz pulsed magnetic field.[14] Dark and bright zones in the figures correspond to regions rich and poor in particles, respectively. When the applied magnetic field is constant (Figure 2A) and the dipolar magnetic energy is larger than the disordering thermal energy, the interaction between the induced dipoles of the particles allows for rapid "head-to-tail" aggregation of the particles into chains, and subsequent (slower) lateral aggregation of the chains into columns oriented in the field direction. Only local phase separation without lateral ordering occurs, producing two-dimensional interconnected domains. The columnar structure becomes rapidly frozen because the Brownian diffusion of the columns is hindered by the surrounding branched network constituted by the other columns. When the applied magnetic field (of same amplitude) is pulsed (Figure 2B),[14] the pattern formation is dramatically different. In this case, macroscopic phase-separation is induced, rapidly yielding unidimensional periodic structures aligned in the magnetic field direction. This new structure seems to result from a forced "periodic annealing" between a state of aggregation when the field is turned on and a state of relaxation when the field is turned off. These alternating states enable the system to efficiently explore its space of configurations. When the pulsed field is applied, the Brownian diffusion of the columns can proceed each time the field is turned off.

The observed dramatic domain coarsening, shown in Figure 2, may be due to the large chain (or column) fluctuations generated by the pulsed field. For perfectly directed chains, the transverse magnetic field decays approximately as $H \sim e^{-r/a}$ with a the particle radius.[3] Thus, "stiff" chains do not interact strongly if they are separated by a distance greater than their interparticle spacing. In our case, the large chain fluctuations induced by the pulsed field create a transverse fluctuating field $\langle H^2\rangle^{1/2} \sim (k_B Ta)^{1/2}/r^2$, which gives rise to long-range dipolar attraction and repulsion between neighboring chains, as modeled by Halsey and Toor.[3] k_B, T, and r are the Boltzmann constant, the temperature of the system, and the transversal distance between the chain and the observation point, respectively.

Figure 3 displays successive magnifications of the depleted zones within a periodic structure induced by a pulsed magnetic field. This figure reveals the unexpected result that unidimensional periodic substructures are present on several discrete decreasing length scales all the way down to the particle size. Further, the hierarchy of patterns is shown to be self-similar; i.e. the wavelengths of the substructures rescaled by the microscope magnification used in each picture have the same value as that of the main structure within 15% error. The wavevector of the main periodic structure, equal to the rescaled wavevectors of the substructures, can be tuned by the excitation frequency of the external field. These periodic patterns are excited within a large frequency window. In a recent paper,[12] we showed that a 1% magnetic suspension

(14) A pulsed field consists in a square-wave field when the field is alternatively turned on and turned off for equal periods of time.

displays unidimensional patterns with increasing wavevectors for increasing frequencies between 0.05 and 7 Hz.[15] Moreover, a periodic structure initially created by a low (high)-frequency pulsed field can rapidly be transformed into a new periodic structure with an increased (decreased) wavevector by increasing (decreasing) the frequency of the external magnetic field.

The onset of a main structure and fine substructures can be explained as follows. When the system is quenched in a magnetic field, local phase separation is induced (see Figure 2). As a result, some particles are trapped in local depleted zones because they would take a time too long to diffuse a typical domain spacing toward concentrated regions ($\sim 10^9$ s); such particles rearrange themselves more favorably into columns via dipolar interaction. These create new depleted zones in their close neighborhood, where again enmeshed particles form chains and columns, etc. The mechanism of self-similar wavelength selection remains unexplained.[16] Compared to the dc case, these pulsed-field-induced macroscopic structures are more tenuous and should therefore improve the rheological properties of the fluid. Moreover, since the columnar aggregation kinetics is speedier, the system's response is faster (see Figure 2).

We now show that periodic patterns in magnetic suspensions are also induced by shear flows. Figure 4 displays the macroscopic phase separation induced by a steady shear flow (Figure 4b,c) in a system initially prepared by application of a dc magnetic field for 10 min (Figure 4a). The suspension volume fraction is 0.3%. At early times, as both the shear flow and the dc magnetic fields are applied, we observe that local lateral aggregation occurs by simple tilting of the columns in the flow direction and subsequent merging by dipolar attraction, resulting in local coarsening and phase separation. Subsequent *macroscopic* phase separation is observed to occur, which creates *periodic* patterns of regions alternately concentrated and depleted in particles. This macroscopic phase segregation is caused by concurrent mechanisms of advection of the free particles and flow-induced random breaking and flow-enhanced fluctuations of the chains. Periodic structures are induced with a spatial wavevector observed to decrease with increasing shear velocity and increasing suspension concentration. However, structural self-similarity is absent over a wide range of shear velocities, 0.004 mm/s $\leq v \leq$ 4 mm/s,[17] unlike the case of a pulsed magnetic field presented above. When the dc magnetic field is turned off, the organized patterns disappear via advection of the free magnetic particles within a time decreasing with increasing shearing velocity. A more detailed discussion regarding the influence of both suspension concentration and shear velocity on the structural dynamics, the link between structure and fluid rheology,[4] and the kinetics of phase segregation will be presented in a future publication.[18]

The mechanism of phase separation in sheared magnetic suspensions is different from that of sheared suspensions of dielectric particles. As in the case of dielectric suspensions, the columnar domains of particles span the cell

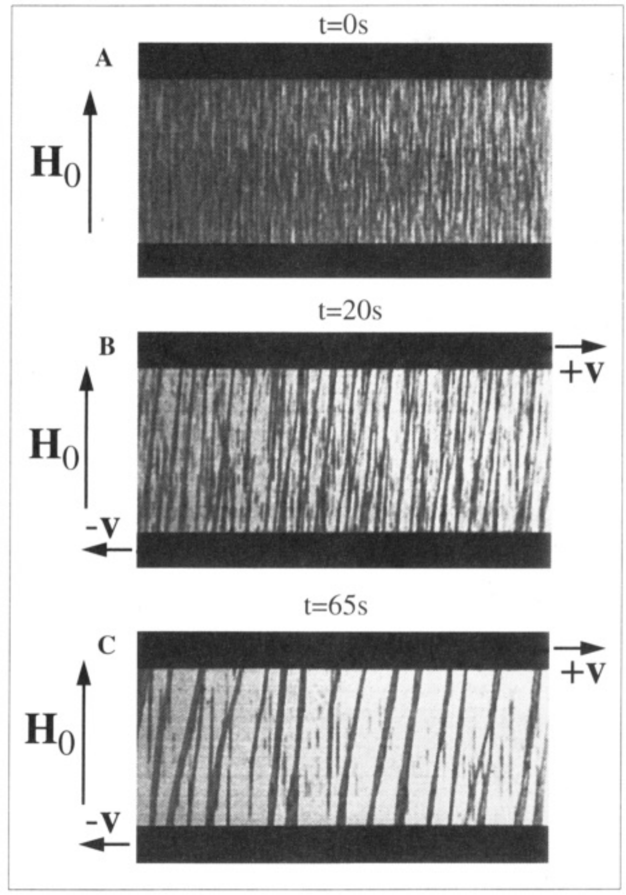

Figure 4. Macroscopic phase separation of an ordered fluid induced by a shear flow: (a) quiescent ordered state in the direction of the magnetic field applied for 10 min; (b) dynamics of phase separation by chain breaking and advection (shear velocity v = 0.1 mm/s, magnetic field still applied); (c) steady state macroscopically phase-separated structure. Same magnetic suspension as in Figure 2 with φ = 0.3%.

gap, but here columns are not attached to the surface of the shearing wires. As a result, the fluid yield stress is reduced compared to the case of a dielectric suspension subjected to a similar shear flow.[6,7,8,19] As shown in Figure 4, columns do not rupture in the center; i.e. shear-induced melting and recrystallizing of the columns do not occur, unlike previously modeled (and observed) for electrorheological fluids.[6] In addition, due to the absence of both electrophoretic effects and particle attachment to the electrodes,[6] the onset of a separate depleted fluid zone supporting most of the deformation near one of the two electrodes and of a solid mass supporting most of the shear stress (see Figures 2−7 in ref 6) is absent in sheared magnetic fluids.

In conclusion, magnetic suspensions display structures that are far richer than previously observed and can be considered as a model system to study pattern formation and field-induced scale-invariant periodic structures. These periodic structures have a wavevector that can be monitored by external fields such as a shear flow or a pulsed magnetic field.

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(15) The wavevector k_s corresponds to the interspacing $\lambda_s = 2\pi/k_s$ between domains in the *unidimensional* periodic patterns generated by pulsed fields. No unidimensional patterns are generated outside the frequency range [0.05 Hz, 7 Hz] for a 1% magnetic suspension. In particular, no unidimensional patterns are generated in dc fields.

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(17) If one assumes Stokesian diffusion, the corresponding Peclet number $Pe \equiv va/D = 6\pi\eta va^2/k_BT$ ranges between 1.12×10^{-6} and 1.12×10^{-3}. Here D and $\eta \approx 10^{-3}$ N·s·m^{-1} are the diffusion constant of the particles and the viscosity of the suspending water, respectively ($k_BT \approx 4.045 \times 10^{-21}$ J).

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(19) The value of the fluid yield stress depends strongly on the physicochemical nature of the surface of the shearing plates and the interaction between the plates and the suspension.