One-Dimensional Patterns and Wavelength Selection in Magnetic Fluids

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We present the first experimental evidence of macroscopic one-dimensional patterns and forced wavelength selection in magnetic colloidal suspensions in an oscillating magnetic field. The resulting dramatic enhancement of the domain growth kinetics gives rise to concentration patterns composed of a main periodic structure and similar periodic substructures, which have a wave vector increasing with the excitation frequency, and decreasing with the suspension concentration.

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Pattern forming systems driven away from equilibrium by an external time-dependent forcing have recently received much attention [1]. In particular, the Faraday instability of a thin liquid layer in a modulated effective gravity [2], the forced time-dependent convection in fluids [3], and the parametric excitation of magnetization waves in ferromagnetic bodies [4] are examples of model systems where the nonlinear wave excitation of the system gives rise to an instability towards new and unexpected structural features [1]. Enhanced alignment, transport, and pattern formation kinetics in an oscillating field also occur in a wide variety of physicochemical systems including microphase-separated block copolymers under dynamic shear [5] and proteins in an oscillating electric field [6]. Structural and rheological properties of ferro and magnetorheological fluids [7–11] have long been a subject of intense theoretical and experimental work. However, the study of the rich structural dynamics induced in a magnetic fluid subjected to a time-dependent driving force has yet remained undisclosed and is the subject of the present work.

In this Letter, we investigate the effects of a square wave magnetic field acting on a colloidal suspension of magnetizable particles in a nonmagnetic fluid. We observe three new phenomena. First, we observe the formation of macroscopic one-dimensional periodic patterns composed of high-concentration regions of magnetic particles, aligned in the field direction, and sharply separated from low-concentration regions. Inside these depleted regions also appear similar but thinner periodic columnar structures spanning the width of the containing capillary. Self-similarly, periodic phase-separated regions appear over several length scales down to the particle size. Second, we study the dramatic enhancement of the domain growth kinetics within the suspension in an oscillating field compared to the dc case. Third, we find that the final macroscopic patterns have a spatial wavelength which can be monitored: The wavelength decreases with the excitation frequency of the external field within a narrow frequency window, and decreases with the colloidal concentration.

In order to study the structural evolution of the various patterns induced in magnetic fields, we use time-resolved optical microscopy of suspensions of superparamagnetic polystyrene particles (mean sphere radius of $a=0.75$ μm) loaded with iron oxide grains (62% FeO by weight) and suspended in water, with added sodium dodecyl sulfate to prevent irreversible aggregation. As revealed by transmission electron microscopy, particles are spherical but rather polydisperse in size (magnetic M 70/60 Estapor Rhône-Poulenc lattices). We recently synthesized monodisperse colloidal suspensions, which gave rise to identical patterns. The suspensions are held on the microscope stand in sealed glass microslides with a rectangular cross section (cross section, 0.1×1 mm; length, 50 mm) and kept at room temperature. The particles, having a high density, sediment rapidly onto a layer at the bottom of the capillary with a typical velocity of 5 μm/s, before the magnetic field is applied. Therefore, it is expected that the volume fractions quoted in this paper are smaller than the actual volume fractions of this layer. A spatially uniform magnetic field is generated by two coils placed on each side of the capillary, and directed along the longer side of the cross section. The governing parameter λ [8], which compares the magnetic interaction energy between particles to the thermal Brownian motion energy, is held constant throughout all the experiments, $\lambda=\pi\mu_0 a^3\chi^2 H_0^2/9k_BT\cong375\gg1$, corresponding to an external field strength of $H_0=2150$ A/m. Here, μ_0 is the magnetic permeability of the vacuum, $\chi\cong1$ is the magnetic susceptibility of the particles, k_B is the Boltzmann constant, and T is the absolute temperature of the system. Images of 512×430 pixels with 256 grey levels are recorded via a CCD video camera. Further experimental details can be found in Ref. [8].

Figure 1 displays the quasi steady state macroscopic periodic structures induced in the presence of a square wave magnetic field over 2 decades in frequency, and the corresponding optical density profiles (related to the concentration profiles) taken along the median line of the

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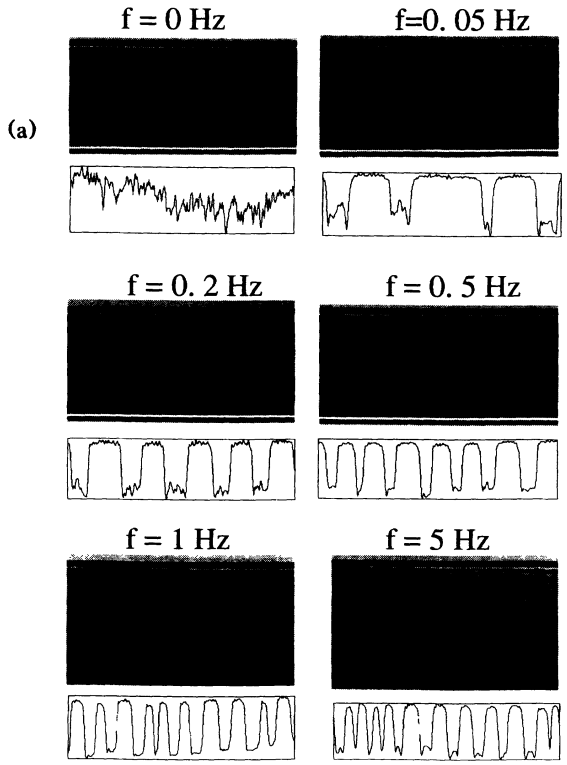

FIG. 1. Concentration patterns and corresponding optical density profiles (in arbitrary units) for a magnetic fluid subjected to a square wave magnetic field of increasing frequency (H_0=2150 A/m). Field applied for 5 min, microscope magnification of 2.5, and suspension volume fraction of φ=3.3%. At frequencies larger than 10 Hz, featureless structures are induced resembling those of (a).

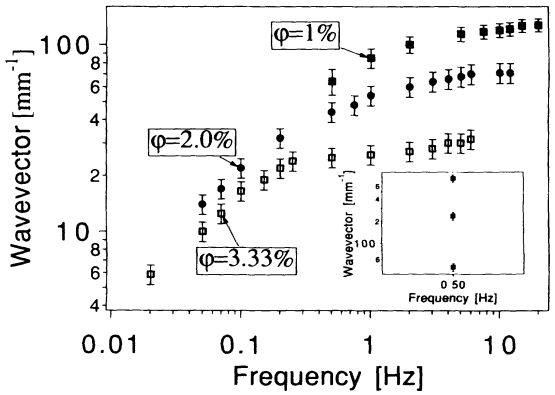

FIG. 2. Wave vectors of the main one-dimensional patterns as a function of the excitation frequency for three different suspension concentrations. One-dimensional patterns are only induced within a frequency window which is shifted to high frequencies for low suspension concentrations. For this value of the field strength, no patterns arise for $\varphi \geq 4.5\%$. The inset displays the increasing wave vectors of the main structure and substructures in a φ=3.3% suspension subjected to a 0.5 Hz magnetic field.

capillary. The dark and light zones correspond to the regions rich and poor in colloids, respectively. A higher excitation frequency induces a higher spatial frequency. Even though the spatial organization and the formation of concentration patterns are intrinsically two dimensional, the final structure is one dimensional as witnessed in Fig. 1. To our knowledge, this is the first experimental evidence of such wavelength selection in magnetic fluids by an external field. Note the absence of any structural feature in the presence of a dc field for such highly concentrated suspensions [Fig. 1(a)], and the presence of domain branching near the capillary walls at high frequencies [loss of the one-dimensionality property, Fig. 1(f)] [12]. For this system, magnetic fields with a frequency larger than $f \sim 10$ Hz produce featureless structures similar to those of Fig. 1(a).

Figure 2 displays the wave vector of the one-dimensional patterns as a function of the excitation frequency, for suspension volume fractions ranging from 1% to 3.3%, and for a constant value of the field strength applied for 5 min. This wave vector corresponds to the largest periodic structure and has been averaged over the total length of the capillary. At low and high excitation frequencies, no one-dimensional structures are formed. As a result, one-dimensional concentration patterns can only be induced in a narrow frequency window, which is itself shifted towards low frequencies for high suspension concentrations. In addition, within this frequency window, one-dimensional patterns only occur in a narrow suspension concentration region: At small concentrations, linear aggregate structures are formed [7,8], while no macroscopic phase separation is induced at all at higher concentrations, as demonstrated in Fig. 1(a). In Fig. 1, we arbitrarily decided to record the resulting patterns after 5 min; however, it is worth mentioning that the formation kinetics of these patterns was also particularly enhanced for frequencies around $f \cong 0.5$ Hz, between the two cutoff frequencies for one-dimensional concentration pattern formation. The existence of a narrow frequency region of excitable periodic patterns can be explained as follows. In a dc field, for low enough concentration systems, a rapid quench produces local phase separation, but the motion of the resulting columns is greatly restricted due to hindrance of the Brownian motion of the columns by the surrounding fixed network of columns, especially at high concentrations. As a result, the system does not macroscopically phase separate completely and rather forms an interconnected network, due to severe transport limitations [8]. In a square wave magnetic field, instead, the periodic annealing allows for particle Brownian motion, which relaxes the columnar network facilitating the diffusion when the field is turned off. As a consequence, the excitation frequency of the external field should be neither too small nor too large, since the magnetic field ought to be reapplied before total thermal destruction of the patterns occurs, but not too soon to facili-

tate enhanced diffusion of the large columns. As a support for this simple physical picture, we found that applied sinusoidal magnetic fields of the same amplitude did not give similar periodic patterns, since the time over which $\lambda \leq 1$ is always too short to allow for diffusion of the columns.

Enclosed in Fig. 2 is a graph which displays the wavelengths of the principal periodic pattern and periodic substructures inside the depleted zones in a magnetic colloidal suspension ($\varphi = 3.3\%$) subjected to a square wave magnetic field ($f = 0.5$ Hz). This graph shows the different spatial wave vectors of the substructures. Here, the cutoff wave vector is determined by the size of the particles. However, when these wave vectors are rescaled by the microscope magnification used in each wave vector measurement, they all collapse on a single value within 15% error. Figure 3 shows a typical set of concentration patterns at three different length scales obtained after applying the field for 10 min with $f = 2$ Hz, and $\varphi = 1\%$. The creation of these "self-similar" patterns can be explained as follows. Concentration fluctuations generated by thermal noise are subjected to two competing forces: the magnetic interaction between fluctuations which tends to facilitate tip to tip alignment and lateral magnetic aggregation, and the osmotic pressure which tends to reduce the anisotropic domain aggregation. On one hand, each concentration fluctuation has a corresponding magnetic permeability fluctuation, and therefore a fluctuating dipolar force, which effectively couples with the motion of the concentration fluctuations giving rise to enhanced anisotropic diffusion. On the other hand, the formation of a higher concentration region is naturally accompanied by the formation of depleted regions in its close neighborhood. Magnetic particles trapped in the middle of these depleted regions cannot always favorably diffuse toward the large surrounding domains and prefer to generate new columns creating themselves depleted regions, etc. For such a particle in a depleted region, the time to diffuse a distance $\lambda_s \cong 2\pi/k_s \cong 0.1$ mm corresponding to a typical pattern spacing is approximately given by $t_D \cong \lambda_s^2/(k_B T/6\pi\eta\varphi a) \cong 10^9$ s, where η is the viscosity of water. In conclusion, such particles will more preferentially reorganize themselves inside the depleted zones, and create elongated fibers in the direction of the magnetic field. The same reasoning holds at any smaller length scale, where both φ and λ_s diminish. In view of Fig. 2, it can be added that a condition for "self-similar" patterns to appear is that the suspension is of high enough concentration.

The structural dynamics of identical suspensions in a dc magnetic field has been previously reported by Fermigier and Gast using a similar video microscopy technique [8]. For high suspension concentrations, local phase separation and fully interconnected fibrous structures were observed [8], but neither wavelength selection between domains [13] nor self-similarity occurred in dc magnetic fields. In order to study the difference of domain growth kinetics in various magnetic fields, we subjected the suspension to a dc magnetic field followed by a square wave magnetic field. Figure 4 is a spatiotemporal graph of the resulting pattern evolution, accompanied by the relevant optical density profiles of the different states. Starting from a quiescent magnetic suspension ($t = 0$ s), a dc field

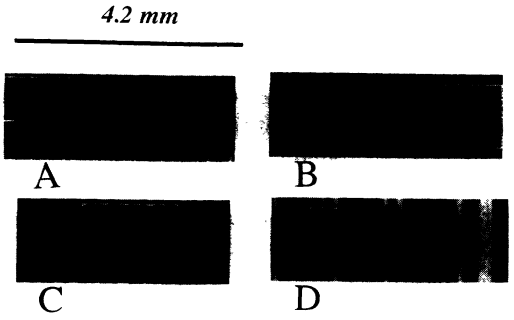

FIG. 3. Main periodic structure and substructures obtained with a magnetic suspension subjected to a 2 Hz square wave magnetic field for 10 min. The magnified zones (white frames) in each depleted region reveal the self-similarity of the concentration patterns. Same magnetic suspension as in Fig. 1 with $\varphi = 1\%$; magnification in (a) is 2.5.

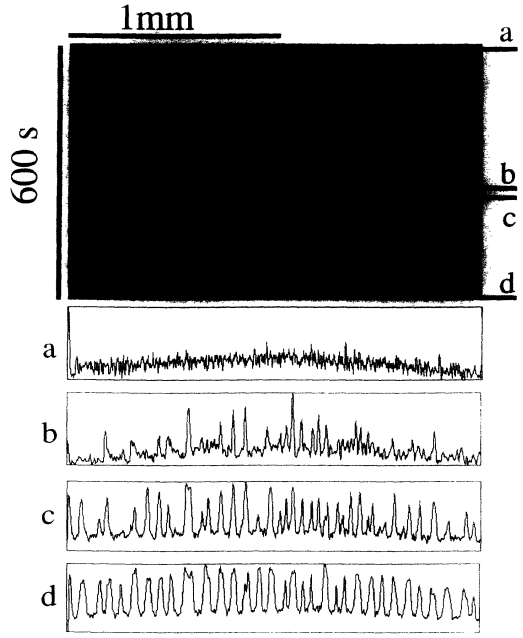

FIG. 4. Spatiotemporal evolution of the suspension structure after successive application of a dc and a 2 Hz square wave magnetic field. The acquisition line is the median line of the capillary. (a) Quiescent state. (b) Final structure after a dc field has been applied for 330 s. (c) Onset of a more regularly spaced concentration pattern after a square wave magnetic field has been applied at $t = 330$ s, $t = 340$ s. (d) Periodic concentration pattern with a selected wave vector of $k_s \cong 85$ mm^{-1}, $t = 600$ s. Same magnetic suspension as in Fig. 1 with $\varphi = 1\%$.

creates an interconnected structure without wavelength selection. The optical density profile at $t = 330$ s confirms the presence of a local phase separation of the suspension, but no true lateral ordering. The pattern is composed of highly connected interpenetrating domains. At $t = 330$ s, a 1 Hz square wave magnetic field is applied, and already after 10 s a concentration wave has grown with a preferential wavelength. Figure 4 shows that, from $t = 330$ s, domain coarsening is observed, creating widely spaced domains of one phase: Some high and low concentration domains grow while some others disappear in a manner similar to spinodal decomposition in binary liquids subjected to a temperature quench. The optical density profile at $t = 600$ s displays the emergence of a single principal wavelength. Higher magnification would reveal the existence of similar concentration patterns in the depleted zones as seen above. Conversely, if a square wave magnetic field is first applied until a self-similar structure arises, followed by a dc field of equal magnitude, then the structure does not vary any further, and the resulting structure is frozen due to hindered Brownian motion, over time scales of hours. Figures 1, 2, and 4 show that since each steady state pattern depends on the external excitation frequency, the final structure is not an equilibrium structure corresponding to a minimum of the system energy, but instead strongly depends on the formation kinetics and the properties of the external field. As a result, Fig. 2 can be considered as a nonequilibrium phase diagram defining the concentration/frequency region where one-dimensional concentration patterns are induced.

No available dynamical model [10,11] can predict the existence of the periodic structures and substructures described above. As a consequence, our experimental findings require a new nonequilibrium dynamical theory that would take account of the effective magnetic coupling between the large local permittivity variations and the transport of the concentration fluctuations in a square wave magnetic field.

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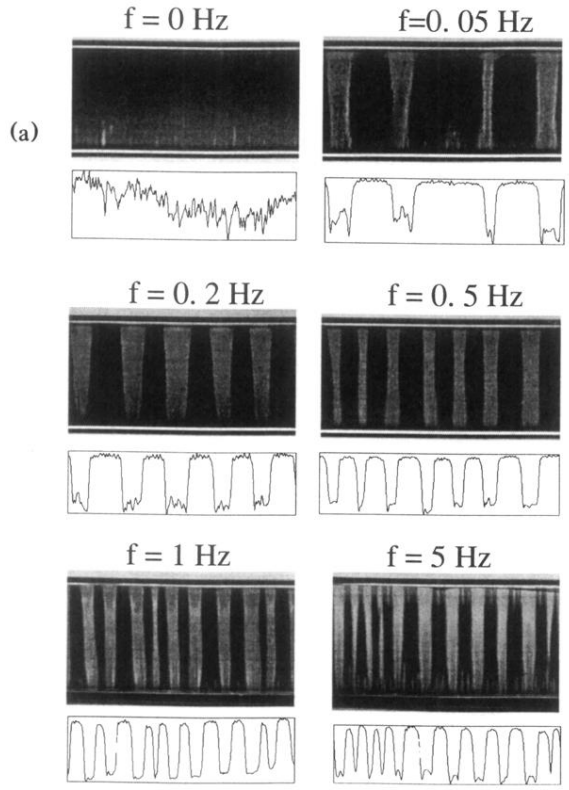

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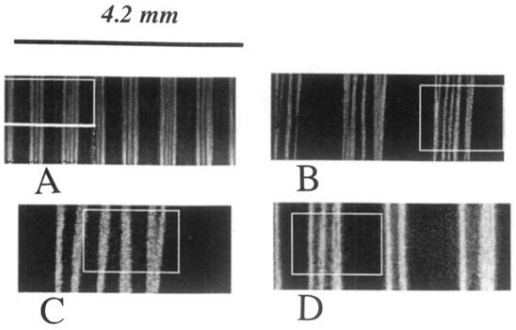

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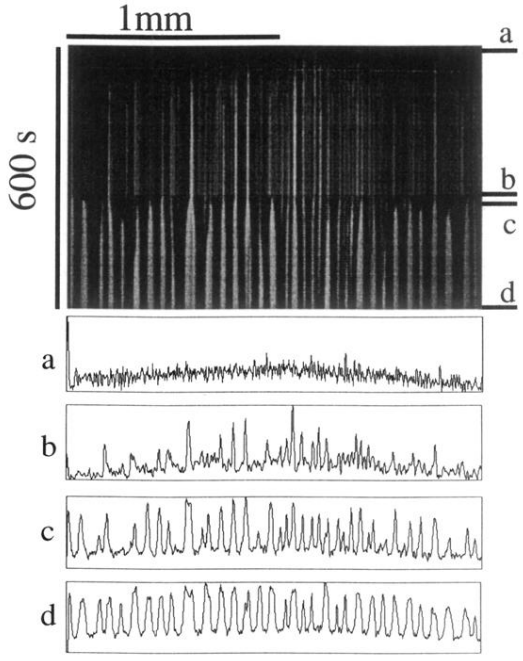

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