Labyrinthine Instability in Magnetic Fluids Revisited

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The field-induced formation of labyrinthine patterns is studied theoretically. A theory proposed by Rosensweig, Zahn and Shumovich (*J. Magn. Magn. Mater.* **1983**, *39*, 127) for the spacing of the labyrinthine strips is corrected. At low magnetic fields, the corrected theory predicts the strip widths in good agreement with experiment. At high fields, there is a discrepancy between theory and experiment that is attributed to the approximations inherent in the theoretical approach. A more accurate theory is proposed that correctly describes the experimental decrease in strip widths on increasing the field.

When a ferrofluid is confined with an immiscible nonmagnetic fluid between closely spaced parallel plates, and a uniform magnetic field is applied normal to the plates, the so-called labyrinthine instability occurs.[1] Static patterns appear that exhibit labyrinthine structures having walls of opaque ferrofluids separated by analogous bands of clear immiscible fluids.

The phenomenon was observed for the first time in the late 1970s.[2,3] In 1983, Rosensweig et al.[4] proposed a simple theory for spacing between the walls of the labyrinthine pattern, which is discussed in detail in Rosensweig's classical textbook.[1] They assumed that the demagnetization field within the ferrofluid is uniform and equal to that in the center of the labyrinthine strips. From the comparison with measurements, Rosensweig et al. concluded that this approach correctly predicts the variations in the width of the walls as a function of the separation of the plates and of the applied field. In a recent paper,[5] a very similar theory based upon the same approximation was used to interpret the change in the strip width in a cell with variable height. Again, the authors found rough agreement between experiment and theory despite the approximation used.

In the past few years, the experimental and theoretical studies of the pattern formation in ferrofluids have attracted much interest.[6] The field-induced formation of mazes between two immiscible fluids studied by Rosensweig et al.[4] is closely related to labyrinthine or hexagonal patterns observed in magnetic fluid emulsions[7] and in demixed ferrofluids.[8,9] The approach proposed in ref 4 could be used to interpret these experiments. Similar theories have been proposed in the literature,[7,10] but they are based upon a different approximation for the magnetic energy.

In our laboratory, solid micrometric hexagonal and labyrinthine patterns of cobalt nanocrystals were recently observed, when a solution of these magnetic nanoparticles was evaporated under an applied magnetic field.[11] To understand the formation of these patterns, the theories in refs 4 and 5 were used. However, the calculated results differ from those published by Rosensweig et al.[4] and by Elias et al.[5,12] using the same approximation. The approximation of a uniform demagnetization field leads to a discrepancy between experiment and theory that was not previously observed because of a cancellation of errors.

The aim of this Letter is to show the influence of the approximation proposed in ref 4 upon the calculated width of the strips. First, it is pointed out where the results given in ref 4 are not correct. Then, our theoretical results are compared to the experimental data published in ref 4 and the deviations show the validity of the approximation. Finally, a new theory is proposed that takes the nonuniformity of the demagnetization field into account. We focus on the theory in ref 4 because it has been often referred to in the literature and Rosensweig reported it in his book[1] without corrections.

In ref 4, the labyrinth is idealized, for analysis, as a repeating pattern of infinitely long parallel strips. t and w_f denote the height and the width of the magnetic fluid "walls" separated by the nonmagnetic "lanes". r is the ratio of lane to wall width. The width w_f is obtained by an energy minimization. The total energy per surface area perpendicular to the field direction can be written as (see ref 4)

$$U = -\frac{\mu_0}{2(1+r)}\frac{\chi {H_0}^2 t}{1+\chi D} + \frac{2t\gamma}{(1+r)w_f} \qquad (1)$$

The last term corresponds to the interfacial energy, where γ denotes the interfacial tension between the immiscible fluids. The first term gives an approximation of the magnetostatic energy, where H_0 is the strength of the applied field. The demagnetization coefficient D is evaluated from (see ref 4)

$$D = \frac{2}{\pi}\left\{\tan^{-1}\frac{w_f}{t} + \sum_{n=0}^{N_c}\left[\tan^{-1}\frac{(n+1)rw_f + \left(n+\frac{3}{2}\right)w_f}{t/2} - \tan^{-1}\frac{(n+1)rw_f + \left(n+\frac{1}{2}\right)w_f}{t/2}\right]\right\} \qquad (2)$$

where the sum is over the neighbor strips of a given strip. To arrive at eq 1, a linear relationship between the magnetization and the field ($M = \chi H$) is used, which was already employed by Rosensweig et al. in their study.[4] The major approximation in eq 1 is the assumption that the demagnetization field is uniform at all points within the magnetic strip. To find the energetically preferable width w_f for a constant height t, the

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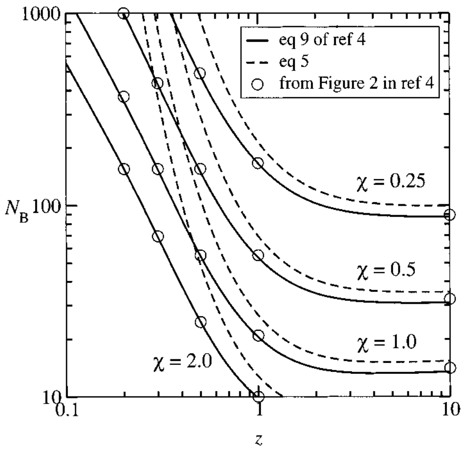

Figure 1. Dependence of the magnetic bond number N_B on $z = w_f/t$ calculated from eq 9 of ref 4 (full line) and from eq 5 (dashed line). The dots are points taken from Figure 2 in ref 4. The results are shown for various values of magnetic susceptibility χ, which are indicated on the curves. The phase ratio is fixed at $r = 0.5$.

expression of U is differentiated with respect to $z = w_f/t$:

$$\frac{\mathrm{d}U}{\mathrm{d}z} = \frac{\gamma}{(1+r)}\left\{\frac{\chi^2 N_B}{(1+\chi D)^2}\frac{\mathrm{d}D}{\mathrm{d}z} - \frac{2}{z^2}\right\} = 0 \tag{3}$$

where the magnetic bond number is

$$N_B = \frac{\mu_0 H_0^{\,2} t}{2\gamma} \tag{4}$$

Using eqs 2 and 3 we arrive at the relationship

$$N_B = \frac{\pi}{\chi^2 z^2}\left\{1 + \frac{2\chi}{\pi}\left[\tan^{-1} z + \sum_{n=0}^{N_c} \tan^{-1} 2z\left[(n+1)r + n + \frac{3}{2}\right] - \tan^{-1} 2z\left[(n+1)r + n + \frac{1}{2}\right]\right]\right\}^2 \Bigg/ \left\{\frac{1}{1+z^2} + \sum_{n=0}^{N_c}\left[\frac{\underline{2}\left[(n+1)r + n + \frac{3}{2}\right]}{1 + 4z^2\left[(n+1)r + n + \frac{3}{2}\right]^2} - \frac{\underline{2}\left[(n+1)r + n + \frac{1}{2}\right]}{1 + 4z^2\left[(n+1)r + n + \frac{1}{2}\right]^2}\right]\right\} \tag{5}$$

This expression differs from eq 9 of ref 4, where both the numbers "2" underlined in eq 5 are missing. In Figure 1, we compare the dependence of N_B on z given by eq 9 of ref 4 (full lines) and by eq 5 (dashed lines) for various values of χ. The circles in Figure 1 are taken from Figure 2 in ref 4. They lie on the curves calculated using eq 9 of ref 4. This shows that eq 9 of ref 4 was not corrected before calculating the curves published in ref 4. For small values of z in particular, the bond numbers calculated from both equations deviate markedly.

Another problem in ref 4 is the restriction to a small number N_c of neighbor strips in the sum of the demagnetization coefficient. In computing the curves of Figure 1, a value $N_c =$ 100 was used for the number of neighbor strips. In ref 4 Rosensweig et al. state that neglecting neighbors by a reduced value of N_c in their eq 9 only slightly changes the bond number. In the case of eq 9 of ref 4, this is true for values of z larger than 0.1. Below $z = 0.1$ the bond number calculated from eq 9 of ref 4 markedly changes with the values of N_c, even for large values of N_c. In the case of eq 5 this strong dependence on N_c is already observed at values of z smaller than 0.25. These problems encountered in computing the bond numbers for small z are due to the long-range interactions between the magnetic strips. They were solved in the following way. At a large separation, s, from a given strip ($s >> w_f$), the contribution of a strip to the demagnetization coefficient can be approximated by $D_s(s) = w_f t/(2\pi s^2)$. Then, a long-range correction for D in eq 2 can be found by integrating $D_s(s)$ due to all the neighbor strips beyond the cutoff s_c:

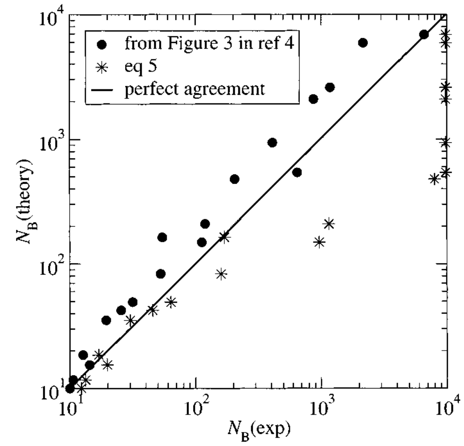

Figure 2. Comparison of N_B(theory) and N_B(exp) calculated from eqs 4 and 5 (stars). The filled circles are taken from Figure 3 in ref 4. The closeness to the parity line indicates the agreement between theory and experiment. The stars plotted on the left side of the frame denote N_B(theory) values for which the corresponding values of z are smaller than 0.2. Under these conditions the N_B(exp) in eq 5 becomes undefined (see text).

$$D_{lr} = \frac{2t}{(1+r)w_f}\int_{s_c}^{\infty} \mathrm{d}s\, D_s(s) = \frac{t}{\pi(1+r)s_c} \tag{6}$$

where s_c is calculated from $s_c = (N_c + {}^3/_2)(r + 1)w_f$.

The values of the bond numbers N_B(theory) and N_B(exp) marked by filled circles in Figure 2 were taken from Figure 3 of ref 4. In this paper, N_B(theory) values were computed from the applied field and the cell height using eq 4, while N_B(exp) values were calculated from the measured z and r values using eq 9 of ref 4. The rough agreement between N_B(theory) and N_B(exp) observed in Figure 2 has led to the conclusion that the theory proposed in ref 4 is able to reproduce the experimental data.

To study the influence of the corrections proposed here on the agreement between experiment and theory, we calculated again corrected N_B(exp) from the z and r values using eq 5 and taking the long-range correction in eq 6 into account. The measured z values are obtained from the N_B(exp) using eq 9 of ref 4 with $N_c = 100$. From an analysis of the figures showing labyrinthine patterns in ref 4 we deduced a phase ratio of $r =$ 1.0. The comparisons of the new N_B(exp) to the N_B(theory) are shown in Figure 2 (stars). For bond numbers up to 100, the corrected values of N_B(exp) are in better agreement with N_B(theory) than the published results. As the bond number increases, eq 5 greatly overestimates the values of N_B(theory).

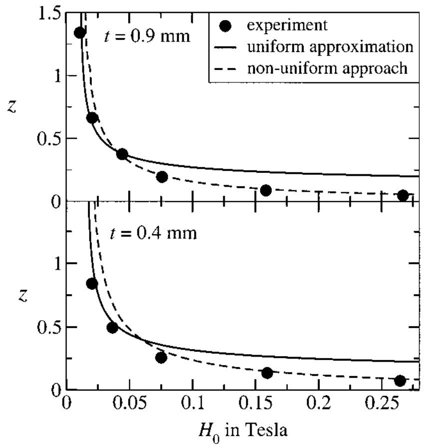

Figure 3. Dependence of the normalized labyrinthine width $z = w_f/t$ on the external field H_0. The cell height is fixed at $t = 0.9$ mm for the upper plot and at $t = 0.4$ mm for the lower plot. The experimental points were calculated from N_B(theory) and N_B(exp) of Figure 3 of ref 4 using eq 4 and eq 9 of ref 4. The full line denotes the theoretical results, when the approximation by Rosensweig et al.[4] is used. The dashed line corresponds to the new approach using a nonuniform demagnetization field.

When N_B(theory) is larger than 500, then, for the values of z smaller than 0.2 measured under these conditions the N_B(exp) in eq 5 becomes undefined. [The N_B(theory) values where this happens are marked by stars on the left side of the frame.] This is explained as follows. For the limit $z \rightarrow 0$, the demagnetization coefficient D in eq 2 should be equal to that of a hypothetical homogeneous mixture of the magnetic and the nonmagnetic fluids, which can be computed from $D_{hl} = 1/(1 + r)$. A plot of D as a function of z obtained from eq 2 shows that the homogeneous limit D_{hl} is already reached for $z = 0.2$ if $r = 1.0$. For smaller values of z, the demagnetization coefficient is constant and $dD/dz = 0$. As dD/dz corresponds to the denominator in eq 5, N_B is not well-defined at these values of z.

Up to now we compared experiment and theory using the bond numbers. An additional insight can be obtained, when the evolution of z with increasing field strength is studied at constant plate separation. The theoretical results for z as a function of H_0 obtained using eqs 4 and 5 are plotted in Figure 3. The plate separation is fixed at $t = 0.9$ mm and $t = 0.4$ mm and the experimental susceptibility and interfacial tension are used ($\chi = 1.6$, $\gamma = 0.0042$).[4] The experimental fields shown in Figure 3 are calculated from the N_B(theory) in ref 4 using eq 4, while the measured z values are obtained from the N_B(exp) via eq 9 of ref 4, as explained above. According to eq 4, high field strengths correspond to large bond numbers. The corrected approach proposed by Rosensweig et al. predicts constant values of z at large fields, in contrast to the decay observed by the experiment. Due to the theory artifact, the small measured z values for large N_B(theory) in Figure 1 cannot be attributed to a bond number N_B(exp) when eq 5 is employed.

A new question arises: Does the assumption of a uniform demagnetization field within the ferrofluid cause the discrepancy between theory and experiments?

Therefore, a new theory is proposed that takes the nonuniformity of the demagnetization field into account. This markedly complicates the calculations. The demagnetization field H_d is calculated over a grid of points in the strip. At each point the magnetization M is evaluated from H_d using the equation $M = \chi(H_0 + H_d)$. The magnetic energy is obtained from equation $E_m = -{}^1/_2\, \mu_0 \int M H_0 \, dv$. The only approximation is that the variation of the magnetization in the direction of the external field is neglected in computing the demagnetization field. A detailed description of the new approach is published elsewhere.[13] The new theoretical results for z as a function of the external field are shown in Figure 3. At low fields the agreement with the experiment is not as accurate as the predictions of the former theory. On increasing the field, the new approach correctly reproduces the experimental decrease of z.

We conclude that the theory proposed in ref 4 and corrected here gives excellent estimates of the wall width in magnetic fluid labyrinths at low fields. In contrast, the approach predicts a wrong trend of the width at larger fields. This can be corrected when the nonuniformity of the demagnetization field within the ferrofluid strips is taken into account.

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