Phase transitions in ferrofluid films

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Abstract

An overview of phase transitions and ordering in thin ferrofluid films. The application of a magnetic field to a ferrofluid can cause both magnetic chains of particles and non-magnetic "holes" in the fluid to undergo phase transitions to ordered hexagonal states and disordered labyrinthine states. Theoretical phase diagrams based on lattice gas and hard sphere models are compared to experimental results, using magnetic field strength and magnetic particle volume packing fraction as order parameters.

1. Introduction

Ferrofluids consist of magnetic particles, such as magnetite, coated with a surfactant and immersed in a liquid solution. When placed in a magnetic field, the force on the magnetic particles cause the fluid as a whole to exhibit enormously rich and complex behavior. Ferrofluids already see industrial applications, including use as sealants in the spinning drive shafts of hard disks and as heat dissipaters in speaker coils.[4] As these are relatively simple applications of a complex substance, ferrofluids remain an active area of research, with potential applications in medicine, optics and elsewhere.

Because the response of a ferrofluid to a magnetic field is heavily dependent not only on the properties of the field itself, e.g. its uniformity, but also on the physical constraints and boundary conditions on the fluid, it has proven difficult to make anything but highly general statements about the expected reaction, even when the discussion is restricted to a specific ferrofluid. Instead, much research focuses on restricting the system to a set of constraints, such as a ferrofluid compressed in a cylinder or a thin ferrofluid film. This paper is concerned with very thin films (on the order of 1-100μm), which is confined enough to let us focus on the behavior of the magnetic particles in the fluid while still exhibiting interesting if poorly understood phase transitions. Although we are not explicitly concerned with the practical applications of such a system, some research has been done in this area, such a setup where a ferrofluid film can be used an optical modulator by tuning its refractive index with an applied magnetic field.[7]

1.1 Theoretical predictions

One of the more successful models predicting phase transitions for a ferrofluid film is the LL (Lacoste and Lubensky) model,[8] whose results we draw from in this section. Lacoste and Lubensky treat the system as being essentially 2D, and focus on a hard sphere potential couple with a magnetic dipole interaction. As such they considered the impact of two order parameters: ϕ, the volume packing fraction of the hard ferrofluid spheres, and h, the external magnetic field, assumed perpendicular to the 2D sample. Much of the behavior is also dependent on a physical parameter λ, which is a measure of the dipole-dipole interaction:

$$\lambda = \frac{m_0^2}{4\pi\mu_0 d^3 k_B T} \tag{1}$$

Where m_0 is the magnetic moment of a single magnetic particle and d is the diameter. The parameter λ primarily influences the shape of the phase diagram, and determines whether any phase transitions are possible.

The LL model actually consists of two different models, based on the use of two different equations for entropy:

(2) $$S_1 = \phi \log \phi + (1-\phi)\log(1-\phi) \qquad S_2 = \phi\left(\log\phi + \phi\frac{4-3\phi}{(\phi-1)^2}\right)$$

The 1st model is a lattice gas model, and the 2nd treats the fluid as a Carnahan-Starling (hard sphere) fluid.

The LL model treats the system as spatially uniform using mean field theory, so that $m = \bar{m}$ and $\phi = \bar{\phi}$ everywhere. To generate a phase diagram, Lacoste and Lubensky calculate the Helmholtz free energies for three expected phases: an isotropic disordered phase, a hexagonal packing phase, and a striped phase where the magnetic particles align themselves in rows or columns alternating with empty liquid.[5] The free energies are then minimized at difference values of h and ϕ to predict the phase diagram. These derivations are somewhat complex and can be viewed in full at Lacoste and Lubensky's paper.[8] Instead, we focus on the interesting results.

The LL predicts that no phase transition is possible when the dipole-dipole parameter λ is below a certain value (~0.57 for the lattice gas model, and ~2.68 in the Carnahan-Starling model). Lacoste and Lubensky provided examples of the phase diagrams for both models with λ just large enough to allow phase transitions, which are reproduced below:

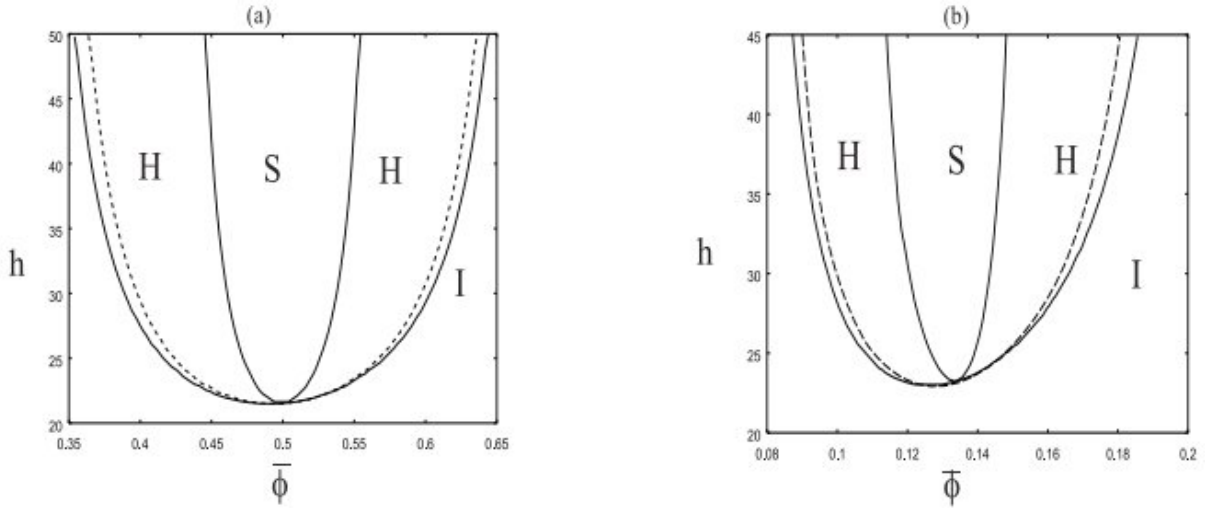

Fig 1. Left: lattice gas model for λ=0.578; right: Carnahan-Starling model for λ=3. Here, “I” is the disordered phase, “H” is the hexagonal phase, and “S” is the stripe phase.

Note that while the graphs appear qualitatively similar, the range of packing fractions is very different. In both models the phase diagram stays

essentially the same as h becomes large; in the case of infinite field, the model can be treated as only having the packing fraction ϕ as an order parameter.

2. Experimental results

2.1 Setup and experimental complications

Most research on thin ferrofluid films has involved one of two basic systems. The simplest is a ferrofluid alone, consisting of an aqueous solution filled with magnetic “monomers” - small magnetic particles (often magnetite, FE_3O_4) of size approximately 5-20 nm, representing single magnetic domains. The second is much like the first, with the addition of nonmagnetic (e.g. latex, polystyrene) spheres the same size as (or larger than) the magnetic monomers. As discussed in Skjeltorp, the nonmagnetic spheres function as magnetic “holes” in the ferrofluid, causing them to express an apparent magnetic dipole moment and function essentially the same way as the monomers do alone, albeit expressing some different behavior.[1] A broad range of film thicknesses is used in these experiments, anywhere from 2 μm to 125 μm. The thicker films exhibit superficially similar but qualitatively different behavior, such as glassy states.[9]

While most research has focused on magnetic fields applied perpendicular to the sample, some research has been done on magnetic fields applied at other angles (at field strength high enough to induce hexagonal ordering in the perpendicular case).

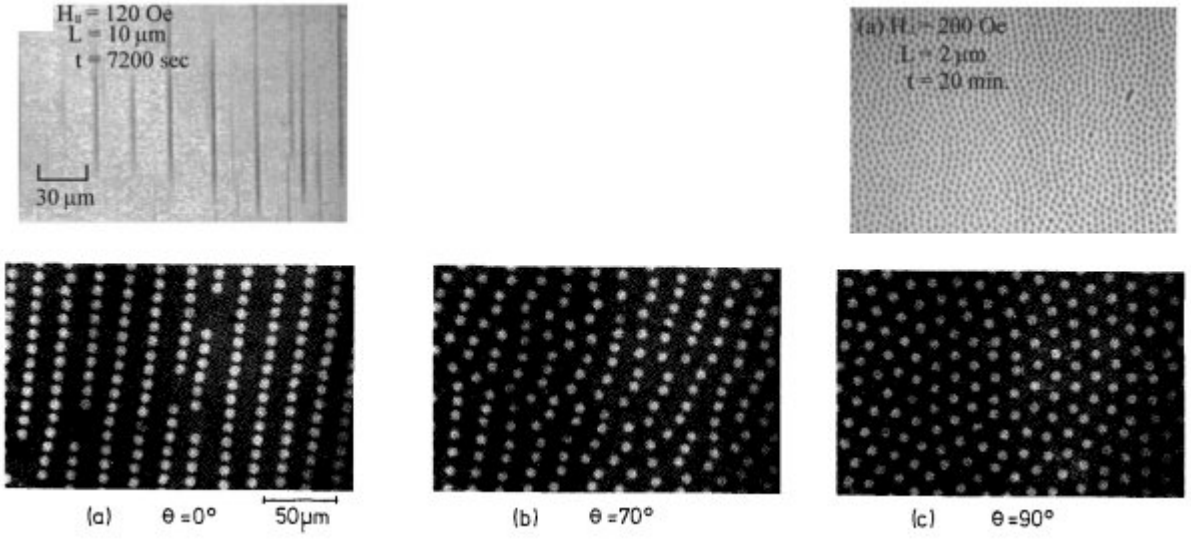

Fig 2. Pictures of samples of magnetic particles alone (top)[6] and magnetic particles with added nonmagnetic polystyrene beads (bottom)[1] in magnetic fields at different angles

As the parallel field case simply results in columns of particles oriented along the field lines and tuning the field angle (at least at low to moderate field strengths) simply results in a smooth transition between the parallel and perpendicular states, from here on out we focus only on the more interesting perpendicular case.

There are two major complications to drawing results from data on the perpendicular case. First of all, ferrofluids are notoriously temperamental, and their behavior in the perpendicular field case has been shown to depend on many factors, including film thickness, particle size and type, sweep rate, temperature, and packing fraction of nonmagnetic particles. In spite of this, the qualitative results are usually consistent across different experimental setups. The second major complication is the long time it takes ferrofluids to reach an equilibrium state. As shown in the top row of Fig. 2, Chin-Yih Hong et al. in some cases waited 2 hours for the system to stabilize.[6] Islam et al. attempted to get around this difficulty by repeatedly varying the magnetic field in their "hexagonal" (glassy – see section 2.3) state until the separation between columns became relatively consistent, finding that 11 cycles resulted in a stable state they took to be equilibrium:

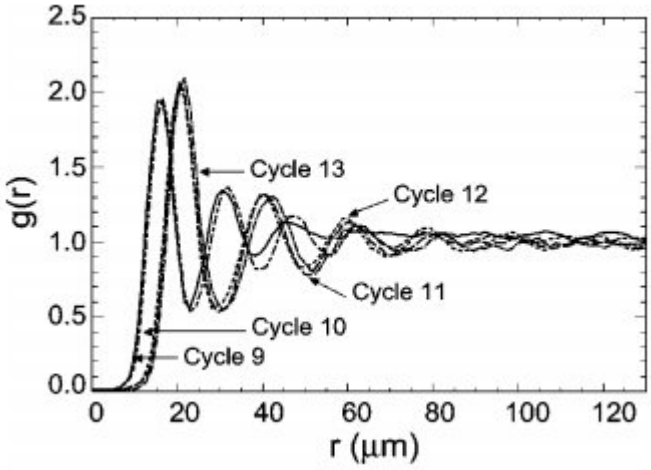

Fig 3. Pair correlation function vs. distance between columns over repeated field cycling[4]

2.2 Chain formation and the disordered state

As the perpendicular magnetic field strength is slowly increased from zero, the magnetic monomers in the ferrofluid form chains (which Islam et al. refer to as "needles") aligned along the magnetic field.[4] While exact numbers are lacking, this typically happens by 50 gauss and is a result of the dipolar energy of the particles exceeding the thermal energy,[9] and has been shown in at least systems to be irreversible by magnetic field tuning alone.[6] Viewed from above, the chains (or nonmagnetic particles) are

initially distributed randomly through the sample. This represents the disordered phase, where the field strength is not yet high enough for the chains to order themselves. The exact field strength at which this ordering occurs depends on, among other things, the film thickness.[6]

2.3 The hexagonal state and glassy state

For thin films (e.g. 2-15 μm), when the field strength is high enough (often 50-100 gauss), the magnetic chains (or nonmagnetic particles) once in equilibrium will align themselves into the hexagonal pattern predicted by theory.[6][1] Due to the timescale required for the system to reach equilibrium, the hexagonal ordering is typically short-range, and there are likely to be a significant minority of chains with 5 or 7 nearest neighbors.

For thick films, such as the 125 μm film used by Islam et al., the chains eventually evolved to what they referred to as “columns” which spanned the entire thickness of the sample.[4] While repulsion between columns at higher magnetic fields did bias them towards a hexagonal configuration, Islam et al. rejected this as evidence of a “true” hexagonal phase consisting of free chains aligning themselves hexagonally, but rather as the start of a glassy phase of columns pinned in place by the sample boundaries.

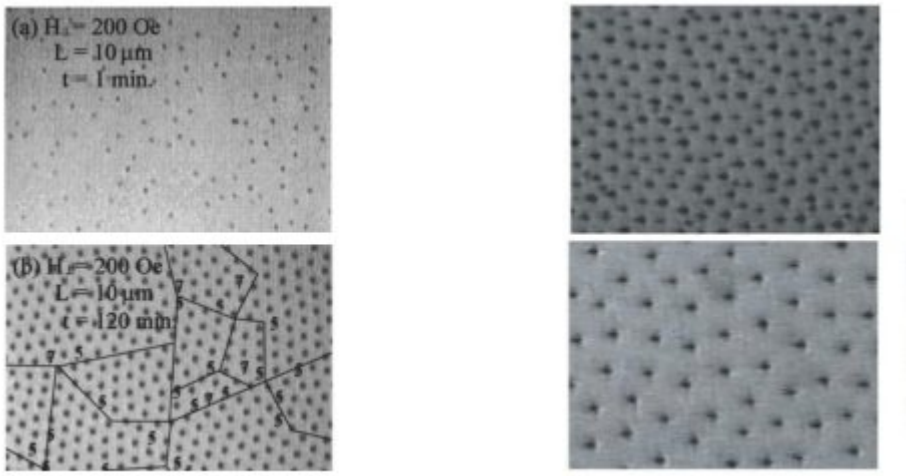

Fig 4. Left: 10 μm film at 200G[6], right: 125 μm film at 100 and 600G[4]. The top images are the disordered phases, and the bottom images are (respectively) the hexagonal and glassy phases. Note that the magnetic field is the same in both images on the left, due to how long the system takes to reach equilibrium.

One of the biggest differences between the thin and thick film results was the near opposite dependence of the hexagonal lattice spacing on magnetic field strength:

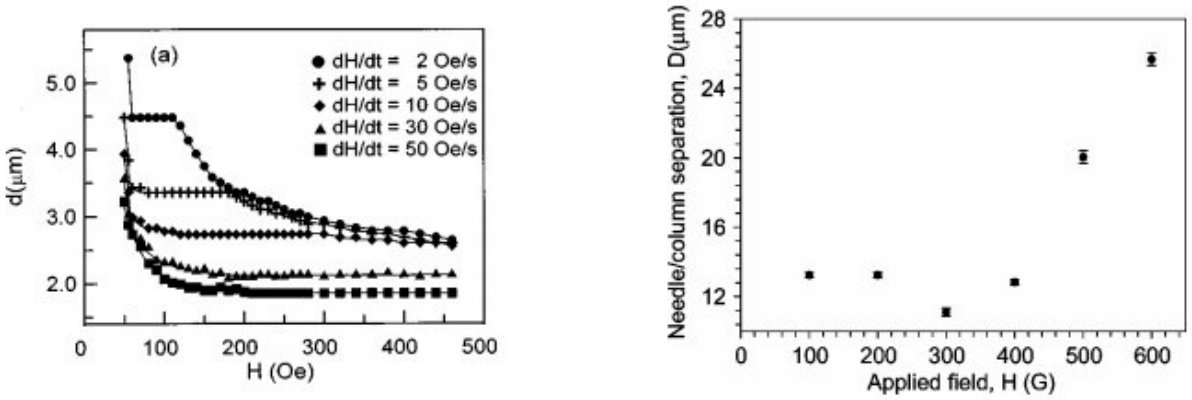

Fig 5. Lattice spacing vs. applied field. Left: thin 6.2μm film at different sweep rates[3], right: thick 125μm film[4]

The reason for the different behavior is not immediately clear. The thick film result is somewhat more intuitive: as the field strength increases, the magnetization of a given column increases, and so the repulsion force between adjacent columns increases. One possible explanation for the discrepancy involves the difference in system parameters. The volume packing fraction in the thick film experiment was very small, 0.5%, whereas in the thin film experiment it was 10.9%. There were simply more magnetic particles in the thin film sample, and the increasing magnetic field resulted in at least some additional chains forming.[3]

Another possible explanation involves the chain dimensions themselves. It has been noted by S. Y. Yang et al. that in the thin film case the chain radius decreases, resulting in a smaller dipole moment per chain and therefore a smaller repulsive force.[2] Furthermore, while the column length is effectively constant in the thick film case (since the columns reach across the entire sample), Chin-Yih Hong et al. note the breakup of columns at a critical point during low sweep rates, which they consider a transition to a “second” hexagonal phase.

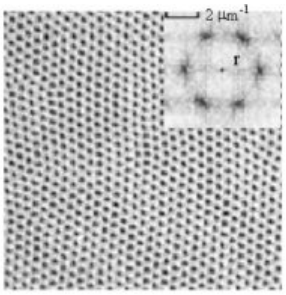

Fig 6. “Second” hexagonal phase in 6.2μm film, with inset of its FFT image showing good hexagonal ordering[3]

They speculate the breakup may be due to wrongly-aligned dipole

segments in a chain, which break free when the field strength is great enough. Either way, this second hexagonal phase – which is not predicted by theory and seems to be an artifact of the experimental technique – is characterized by much tighter hexagonal structure than the "first" phase. As shown in Fig. 5, higher sweep rates result in a tight hexagonal structure from the start; it is primarily the 2 G/s and 5 G/s sweep rates that result in an early plateau later transitioning to a tighter lattice.

2.4 The striped or lamellar phase

Although it is predicted by theory, the "striped" phase predicted to occur at higher field strengths has so far not been observed in a standard ferrofluid film.[4][6] However, in their thick film sample, Islam et al. noted that the addition of nonmagnetic particles resulted in the existence of a pseudo-striped phase at higher field strengths, which they refer to as a lamellar phase. The effect was more pronounced at apparent at lower field strengths for higher volume fractions of nonmagnetic particles, as shown below:

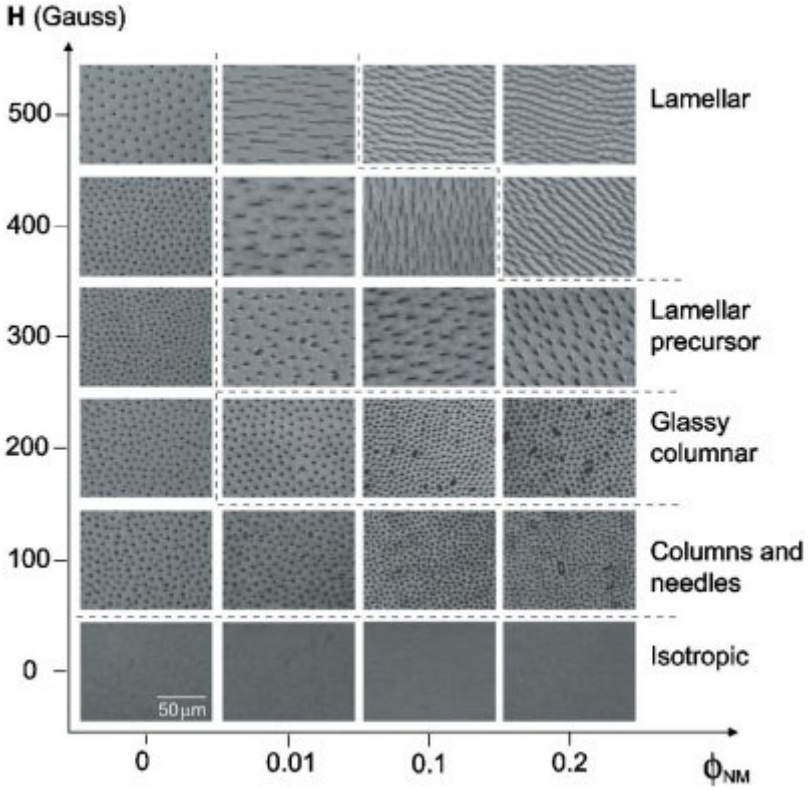

Fig 7. The "lamellar" phase: images of ferrofluid at different field strengths and nonmagnetic sphere packing fraction[4]

Islam et al. explain that while this behavior is novel and potentially useful, it is not very well explained theoretically as they are unaware of any

predicted phase diagrams for mixtures of ferrofluids and nonmagnetic particles. They point out some necessary modifications to Lacoste and Lubensky's theory to describe the new system, including entropic energy terms and energy terms related to the nonmagnetic spheres functioning as magnetic holes in the ferrofluid, but note that these terms are unlikely on their own to account for the drastic difference in behavior.[4]

2.5 The “labyrinthine” phase

While not predicted by standard theory, the so-called “labyrinthine” phase comes up in several places in the literature on ferrofluid films. In general the term refers to a second disordered phase that a ferrofluid film proceeds to at very high field strengths, rather than the the ordered striped phase predicted by theory.

Visually, the hexagonal structure breaks down completely, and the phase appears to have either clumps of chains arranged in a seemingly random order throughout the sample. Since the phase is not predicted by most theories and the source of the disorder is unknown,[4] there is relatively little that can be said about it. Islam et al. suggested that it may be related in some way to the slow dynamics of a ferrofluid film once chains or columns form, and that the disorder may be the result of the film being unable to or having difficulty in reaching any equilibrium state.[4]

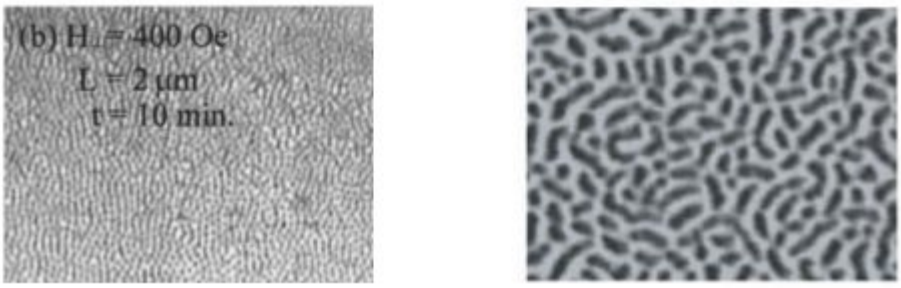

Fig 8. The “labyrinthine” phase. Left: thin, 2μm film at 400G[6]; right: thick 150μm film at 1100G[4]

3. Comparison with theory

Experimental results currently line up very poorly with theory. Most experimental papers on the topic do not even have comparisons to theory, but instead compare their results exclusively to results from other experiments. The phase diagrams in Fig. 1 in particular are almost entirely incorrect. For instance, $\lambda=2.2$ in the experiment of Islam et al., which is too small for phase transitions to occur in the Carnahan-Starling version of the Lacoste and Lubensky model.[8] Furthermore, the packing fraction of 0.5% in the same experiment is too small for phase transitions to occur apparently in either version of the model, at least not until significantly higher magnetic

field strengths. Islam et al. note that their experimental results do not correlate at all with the LL model numerically.[4]

While the LL model has some success in predicting the existence of the hexagonal phase, Islam et al. argue that no true hexagonal phase occurs for their system, and in either event the striped phase proposed by the LL model has not yet been observed. Similar lamellar phases were observed only with the addition of substantial quantities of nonmagnetic spheres, which has an unknown impact on the system that is itself not currently explained theoretically. There is broad evidence that a labyrinthine phase not predicted by theory does exist, and unlike in the phase diagrams in Fig. 1 has not been shown to proceed directly or quickly from the isotropic disordered phase at any packing fraction, if we were to take the labyrinthine phase as merely a “striped” phase unable to reach equilibrium.

While the LL model of a hard sphere plus magnetic dipole ineraction potential makes sense, and while the model makes intelligent choices for order parameters, it is either invalid or else needs a significant amount of work to be physically reasonable based on current experimental data. Islam et al. suggest that a 2D model alone may be insufficient to describe the behavior of the 3D chains in ferrofluid films, and believe a mean field theory approach does not offer a complete interpretation. They suggest the development of a model that includes fluctuations and inhomogeneities in the direction of the field.[4]

4. Future work and observations

Whether or not it is possible to already come up with useful applications of ferrofluid films, such as the optical modulator idea mentioned earlier,[7] it is clear that the phases of ferrofluid films are poorly understood despite being simpler than those of other ferrofluid systems. Research is ongoing, but slow; in a 2009 paper, Ciftja presents another lattice gas model that predicts a striped phase and argues that the labyrinthine phase has some qualitative similarities to the striped phase,[5] but even in the best case scenario the reason for the differences in the phases remains unclear. Furthermore, the theoretical models are of limited value to the extent that they are unable to demonstrate even approximate numerical agreement with experiment.

Better theoretical models, however, will require much better experimental data. Islam et al.'s paper[4] represents one of the most complete studies of a ferrofluid film system available. In one paper, for example, a group repeatedly mentions a magnetic field “critical value” above which they see a transition, without providing any data on what that critical value might be.[6] It is also unclear if the difference between results in different papers is solely due to a parameter like film thickness, or if it has

to do with, for example, the different ways groups chose to reach an equilibrium state. With so much ambiguity, coming up with a working theory of ferrofluid films alone (let alone films mixed with nonmagnetic particles) will likely prove very difficult. Additional comprehensive studies of films are needed to help to resolve this problem.

References

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