Scaling Behavior of Field-Induced Aggregates in Ferrofluids

F. Marty Ytreberg
Department of Physics, Whitman College, Walla Walla, WA 99362

Susan R. McKay
Department of Physics and Astronomy, The U. of Maine, Orono, ME 04469-5709

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An ordered hexagonal array of aggregates can form in thin ferrofluid layers when an external magnetic field is applied. Using the Helmholtz free energy for this system, we calculate the optimum spacing for these aggregates. Results show excellent agreement with experimental findings as a function of field strength and layer thickness. Our analysis yields a crossover in the exponent for the scaling behavior of the aggregate spacing as a function of plate separation, in agreement with experiment. For the first time, we report a similar crossover in the scaling behavior of the aggregate spacing as a function of the magnetic field. The mechanisms responsible for both crossovers are introduced and discussed.

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I. INTRODUCTION

Ferrofluids are composed of small single-domain magnetic particles dissolved in a liquid carrier. With no external magnetic field, Brownian motion keeps the particles homogeneously distributed throughout the liquid. When a sample of ferrofluid is confined between two glass plates with a separation \( L \), and an external magnetic field \( H_0 \) is applied normal to the plates, the particles aggregate. These aggregates are of approximately uniform size, and the separation of the aggregates is periodic with an average spacing \( d \). A view normal to the plates displays a hexagonal pattern of aggregates [1, 2, 3].

In this paper we present a new model for predicting the aggregate spacing, and compare the results of this model to experiment. We demonstrate that this model shows good agreement with experimental data for the aggregate spacing as a function of field \( H_0 \) and plate separation \( L \). We compare our results to experimental data from Refs. [1, 4]. The model also yields the scaling behavior of the aggregate spacing \( d \) as a function of \( H_0 \) and \( L \). In 1994, Wang et al. [4] showed that there was a crossover in the exponent for \( d \) as a function of \( L \). They attributed this crossover to an experimentally observed structural change in the aggregates. In 1995, Liu et al. [5] also showed a crossover in this exponent for ferrofluid emulsions, but no explanation for the crossover was provided. In our model, this crossover takes place, and is not attributed to the mechanism in Ref. [4]. We also report, for the first time, a crossover in the scaling behavior for \( d \) as a function of \( H_0 \). The mechanisms responsible for both crossovers in our model are identified and discussed.

II. HELMHOLTZ FREE ENERGY

Experiments show that, when the field is first turned on, the particles form single-particle-diameter chains; the system then evolves by the chains sticking together to form aggregates. The time scale associated with the chain formation is much smaller than the time scale observed for the formation of aggregates from chains [1]. Due to this observation, we treat the formation of the aggregates as a quasiequilibrium process. Other examples of this treatment can be seen in Refs. [4, 5, 6]. With this assumption, the separation of the aggregates can be determined by minimizing the Helmholtz free energy for the ferrofluid system.

There are three contributions to the Helmholtz free energy that must be considered: the magnetic energy, the entropy and the surface energy. For the purpose of notational simplicity, we introduce the constants \( \alpha \) and \( \beta \), such that

\[
d = \beta b, \quad \beta \equiv \sqrt{\frac{2\pi\gamma}{\phi\sqrt{3}}},
\]

\[
N_0 = \frac{\alpha}{b^2} = \frac{\alpha\beta^2}{d^2}, \quad \alpha \equiv \frac{\phi b^2}{\gamma\pi},
\]
where \( N_0 \) is the total number of aggregates in the system. Here, \( b \) is the aggregate radius, \( \phi \) is the volume fraction of the ferrofluid, \( \gamma \) is the packing fraction of the particles in an aggregate and \( \ell^2 \) is the area of one glass plate. These relationships are purely geometric, using the assumption that the aggregates are of uniform size and spacing.

### A. Magnetic Energy

The magnetic energy contains three parts corresponding to the self-energy of the aggregates, the aggregate-aggregate interactions, and the aggregate-external field interactions. The model approximates the aggregates as cylinders that are uniformly magnetized.

The approximation of cylindrical aggregates is consistent with the experiments in Refs. [4, 5], where it was found that a few particles away from the end of the aggregate the shape was cylindrical. Since we are dealing with \( L \sim 10 \mu m \) and \( b \sim 5 \text{ nm} \), the length of an aggregate is on the order of a thousand particles. Given these experimental features, the approximation of cylindrical aggregates is a good one.

The approximation that the magnetization is uniform throughout the aggregates is reasonable. Near the ends of the aggregates one would expect the average magnetic moment of the particles to be different than that of the bulk. However, the magnetization of the aggregates is determined mainly by the particles in the bulk. A correction for surface effects is included in the surface energy, discussed below. The uniform magnetization approximation has also been used in Refs. [4, 5].

From magnetostatics we know that the effective surface and volume charge densities are \( \sigma_m = \vec{M} \cdot \hat{n} \) and \( \rho_m = \nabla \cdot M \) respectively, where \( \hat{n} \) is the unit outward normal, and \( M \) represents the magnetization of an aggregate. For the case of uniform magnetization parallel to the external magnetic field, \( \sigma_m = M \) on the top and bottom of the aggregates, \( \sigma_m = 0 \) on the sides and \( \rho_m = 0 \) everywhere. Thus, the total magnetic energy of the system can be calculated as interactions between disks of uniform equivalent charge density \( \sigma_m = M \). [8]

The approximation that the magnetization is uniform throughout the aggregates is a good one. Near the ends of the aggregates, where a few particles away from the end of the aggregate, the shape was cylindrical. Since we are dealing with experimental features, the approximation of cylindrical aggregates is consistent with the experiments in Refs. [5, 7], where it was found that a few particles away from the end of the aggregate, the shape was cylindrical. Since we are dealing with a few particles away from the end of the aggregate, the shape was cylindrical. Since we are dealing with a few particles away from the end of the aggregate, the shape was cylindrical.
where $\vec{m}$ is the magnetic moment of an aggregate. This term does not depend on $d$, and therefore will be considered a constant in the minimization process.

The last contribution to the magnetic energy is due to the interactions between the disks. We must account for interactions between disks in the same plane ($E_{\text{same}}$) and disks in opposite planes. For the interaction of the disks on opposite planes, two terms must be included. One is the interaction of disks due to the same aggregate ($E_{\text{opp}}$, i.e. one disk directly over the other disk), and the other is the interaction of disks positioned diagonally to each other ($E_{\text{diag}}$). Using the point charge approximation, as previously mentioned, the total disk interaction energy will be

$$E_{\text{inter}} = E_{\text{opp}} + E_{\text{diag}} + E_{\text{same}} = \alpha \sigma_m^2 \pi^2 \left( -\frac{d^2}{\beta^2 L} - \frac{d^2}{\beta^2 \sqrt{d^2 + L^2}} + \frac{6d}{\beta^2} \right).$$

It should be noted that $E_{\text{opp}}$ arises from particle-particle interactions in a single aggregate, while $E_{\text{same}}$ and $E_{\text{diag}}$ arise from the interaction between two separate aggregates.

In Ref. [1], Hong and collaborators found that the magnetization of their ferrofluid sample was well approximated by to the Langevin function. Since this functional form for the magnetization is also in agreement with Refs. [2, 3], and for small $\phi$ in Ref. [3], we have used it for our model. Combining these contributions yields a total magnetic energy of

$$E_{\text{mag}} = \left[ \left( \frac{16}{3\pi} + \frac{6}{\beta} \right) \frac{d}{\beta} - \frac{d^2}{\beta^2 L} - \frac{6d^2}{\beta^2 \sqrt{d^2 + L^2}} \right] \alpha \pi^2 M^2 + \text{const}, \quad (2)$$

where

$$M = \frac{\phi}{\gamma} M_S \left( \coth \eta - \frac{1}{\eta} \right), \quad \eta = \frac{\mu}{k_B T} H_0. \quad (3)$$

Here, $\mu$ is the magnetic moment of the particles in the ferrofluid and $M_S$ is the saturation magnetization of the fluid.

In the case of a ferrofluid emulsion, each drop has a magnetization described by the Langevin function. In this case, the magnetization of an aggregate is still given by Eq. (3), with an important reminder that $\mu$ is the magnetic moment of the particles in the drop, not the magnetic moment of the drop itself.

Performing an expansion of Eq. (2) in powers of $d/L$ (with $d = \beta b$), and keeping up to quadratic terms, this magnetic energy reduces to the one used in Refs. [3, 10]. However, one should note that the assumption $d \ll L$ is a much stronger assumption than $b \ll L$. For very small volume fractions, one can have the situation where $d \sim L$ with the condition $b \ll L$ easily satisfied, since $\beta$ increases as the volume fraction decreases.

This magnetic energy offers a significant advantage over the model presented in Ref. [10], due to the elimination of all free parameters in the magnetic energy. With no free parameters in the magnetic energy, we can compare the orders of magnitude of the magnetic energy and entropy, as discussed in the next section.

### B. Entropy and Surface Energy

To calculate the entropy we treat the aggregates as distinguishable. The number of states accessible to the system is $N_0!$, and the configurational entropy of the system is $S = k_B \ln (N_0!)$. For the experimental systems that we are modelling, $E_{\text{mag}}/TS \sim 10^4$, where $T$ is taken to be room temperature. Thus, the entropy is negligible for this particular set of experimental conditions.

The last contribution to the energy to be considered is the surface energy. We have already accounted for particle-particle interactions in the bulk in calculating the magnetic energy. The surface energy allows us to include interactions on the surface of the aggregates, such as those between the surfactant and the solvent.

Assuming a surface tension that is constant over the surface of the aggregate (as in Ref. [3]), the surface energy of the system can be calculated as

$$E_{\text{surf}} = 2\pi \alpha \beta \sigma \left( \frac{L}{d} \right) + \text{const},$$

where $\sigma$ is the surface tension of the sides of the aggregate, and the surface energy due to the ends of the aggregate is independent of $d$. There are several ways of dealing with the surface tension (see for example Refs. [11, 12, 13]). We tried each surface tension and found that our results were closest to experiment using the surface energy found experimentally in Ref. [13]. Here it was determined that the surface tension goes as $\eta^{1/3}$. Since the surface tension
includes interactions between the particles on the surface of the aggregate, we would expect the surface tension to saturate at large field values. To build this saturation into our model we assume that the surface energy goes as $M^{4/5}$. The final form of the surface energy is then

$$E_{\text{surf}} = 2\pi \alpha \beta \Sigma \frac{L}{d} M^{4/5}, \quad (4)$$

where $\Sigma$ is a constant determining the magnitude of the surface tension.

### C. Total Helmholtz Free Energy

Combining these contributions, the Helmholtz free energy of the ferrofluid system is given by

$$F = E_{\text{mag}} + E_{\text{surf}} - TS \approx E_{\text{mag}} + E_{\text{surf}}, \quad (5)$$

with $E_{\text{mag}}$ and $E_{\text{surf}}$ given by Eqs. (2) and (4) respectively. Factoring out common terms and writing the magnetization in terms of $\beta$ we obtain

$$F \approx \left[ \left( \frac{16}{3\pi} + \frac{6}{\beta^2} \right) - \frac{d^2}{\beta^2 L} - \frac{6d^2}{\beta^2 \sqrt{d^2 + L^2}} \right] m^2 + \frac{2\beta \Delta L}{\pi d} m^{4/5} \right] \alpha \pi^2 M_S^2 + \text{const}, \quad (6)$$

where

$$m = \frac{M}{M_S} = \frac{\sqrt{3} \beta^2}{2\pi} \left( \coth \eta - \frac{1}{\eta} \right), \quad \Delta = \frac{\Sigma}{M_S^{6/5}}.$$

We minimize this free energy with respect to $d$ numerically using Mathematica 4.0. The values of $\beta$, $L$, and $\alpha$ are fixed by the experimental conditions, so $\Delta$ is the only free parameter in the model. The value of $M_S$ is used only to calculate other quantities such as $\mu$ and $\phi$. $\beta$ can also be varied slightly, but only within reasonable limits established by the value of $\phi$ which is given for each experiment.

This free energy can be compared to the theoretical models in Refs. [4, 5, 10]. Our new model differs from these previous models in three significant ways. First, this model has only one free parameter. All other parameters are specified by experimental conditions; even this parameter could be determined by experiment. The second difference is our treatment of the surface energy using the results of Ref. [11]. Thirdly, this model permits direct comparison between the magnitudes of the magnetic energy and entropy.

### III. RESULTS OF THEORETICAL MODEL AND CROSSOVER MECHANISMS

For the figures below, all parameter values except $\Delta$ are assigned according to the experimental conditions. Then $\Delta$ is chosen so that the theoretical results give the best fit to the experimental data. For all of the sets of data, $T = 300.0$ K and $\mu = 3.0 \times 10^{-16}$ erg/Oe (\approx 10 nm magnetite particles). For Hong et al. [1] the parameter values are: $\beta = 8.0$ (calculated from $\phi = 0.04$ and $\gamma = 0.71$), and $\Delta = 3.09 \times 10^{-4} \text{ cm}^2 \text{ erg}/\text{ cm}^2$. For Wang et al. [3] the parameter values are: $\beta = 4.5$ (calculated from $\phi = 0.12$ and $\gamma = 0.67$), and $\Delta = 2.69 \times 10^{-4} \text{ cm}^2 \text{ erg}/\text{ cm}^2$. As a point of interest, due to the fact that the surface tension includes the interaction of the particles at the surface of an aggregate, one might expect the surface tension of an aggregate in a ferrofluid emulsion to be much smaller than that of an aggregate in a ferrofluid. Using our parameters, we obtain $\sigma \approx 10^{-3} \text{ erg} \text{ cm}^2$ for the ferrofluid emulsion in Ref. [3] and $\sigma \approx 10 \text{ erg} \text{ cm}^2$ for the ferrofluid in Refs. [1][4], confirming this expectation.

We first compare our model to the experiments in Ref. [4], where experimental data was recorded for $d$ as a function of $L$ for fixed $H_0 = 300$ Oe. They report an exponent of 0.47, changing to an exponent of 0.67 at $L \approx 20 \mu\text{m}$. In Fig. [4] the results of our model are shown as diamonds, squares and triangles for three different values of $H_0$. The solid lines are power law fits of our numerical results. Although, we predict lower exponents than the data suggests, the crossover in the exponent is present. We have included results for three values of $H_0$ to show the effect of changing $H_0$ in our model. It is clear that increasing the field produces three significant effects: decreasing the critical value of $L$ where the crossover takes place, increasing the value of both exponents, and decreasing the difference between the exponents. It is our hope that these effects will be probed experimentally.

A closer look at our model reveals the mechanism responsible for the crossover. In Ref. [4], the crossover in the exponent was thought to be the result of a structural change in the aggregates for increasing $L$. In their experiment,
as $L$ is increased, the aggregates begin to lose their circular cross sections, forming branching structures between aggregates. A theoretical model was developed to account for these branched structures, predicting a larger exponent as the branching occurs. We have obtained a crossover in the exponent assuming cylindrically shaped aggregates with no structural changes, and thus the crossover in our model cannot be attributed to the mechanism in Ref. [1].

Examination of Eq. (6) for $L \gg d$ provides a mechanism for the crossover. In this limit, the free energy reduces to the form

$$F_{L \gg d} \approx C_0d + C_1\frac{L}{d},$$

where $C_0$ and $C_1$ are constants with respect to $d$ and $L$. This form of the free energy predicts that $d \propto \sqrt{L}$. When $d \sim L$, the exponent will be less than 0.5, with the exponent depending upon the value of $\beta$. Thus, the mechanism for the crossover in our model is a competition between terms in the magnetic energy. For $L \gg d$, the magnetic energy is dominated by the self-energy of the disks and the energy due to disks in the same plane. As $L$ is reduced, the contributions due to the disks in opposite planes become more important, until at some critical value of $L$, they can no longer be ignored, lowering the value of the exponent.

Fig. 2 shows the aggregate spacing as a function of $H_0$. The crosses represent the experimental data for $L = 10.0 \mu$m obtained from Ref. [1], and the diamonds, squares and triangles represent the numerical results for three different values of $L$. The solid lines are power law fits to our results. More experimental data points would prove beneficial in testing the theory in this case; however the theory agrees very well with this experimental data. Fig. 2 shows that our model predicts a crossover in the exponent for $d$ as a function of $H_0$. This is the first time such a prediction has been reported in the literature. Three values of $L$ are shown to demonstrate another prediction; the critical value of $H_0$ where the crossover occurs, and the value of the exponents, have essentially no dependence on $L$.

From Fig. 2, it is clear that, for large $L$, the crossover in the exponent for $d$ as a function of $H_0$ occurs with approximately the same exponents as for small $L$. Therefore, to understand the mechanism responsible for this crossover, it is beneficial to look again at Eq. (6) in the limit of $L \gg d$. In this limit,

$$F_{L \gg d} \approx C_2dM^2 + C_3\frac{1}{d}M^{4/5},$$

where $C_2$ and $C_3$ are constants with respect to $M$ and $d$. This predicts that $d \propto M^{-3/5}$. Thus, for small $\eta$, the aggregate spacing goes as $H_0^{-3/5}$, and for large $\eta$ the magnetization saturates and the aggregate spacing does not depend upon $H_0$. For the results presented in Fig. 2, this saturation occurs $\sim 2000$ Oe. Since the magnetization of an aggregate is proportional to the Langevin function, it is clear that a change in the magnetic moment of the particles in the ferrofluid changes the value of the field where the crossover takes place. Thus, the mechanism for the crossover in the exponent for $d$ as a function of $H_0$ in our model is the field dependence of the magnetization of the aggregates. This is a direct result of the form chosen for the field dependence of the surface and magnetic energies in our model, so experimental studies of this crossover could be used to determine the appropriateness of these field dependencies.

IV. CONCLUSION

We have shown that aggregate spacing can be determined by minimization of the Helmholtz free energy. We have developed a simple model and compared its predictions to experiments in Refs. [1, 4]. Our model predicts trends as a function of external field strength and plate separation. The results of our model are in good agreement with experiment.

The scaling behavior of the aggregate spacing as a function of plate separation and external field is discussed. For aggregate spacing as a function of plate separation, there is a predicted crossover in the value of the exponent at some critical plate separation. This feature of our model is in agreement with Refs. [4], where similar results were reported. The mechanism responsible for this crossover in our model is a competition between terms in the magnetic energy.

Our model also predicts a crossover in the exponent as a function of external field. This has not been reported in the literature to date. The mechanism responsible for this crossover in our model is the field dependence of the magnetization of the aggregates. Different forms of the magnetization, surface energy or magnetic energy would change this behavior. This result suggests that experiments measuring this crossover could be used to probe the forms of these quantities.

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FIG. 1: Aggregate spacing as a function of plate separation for $H_0 = 100.0$ Oe (upper), $H_0 = 300.0$ Oe (middle) and $H_0 = 600.0$ Oe (lower), with other parameters chosen to model the system in Ref. [4]. The exponents obtained by a power law fit of our numerical results are shown in the figure.
FIG. 2: Aggregate separation as a function of external field for $L = 100$ µm (upper), $L = 50$ µm (middle) and $L = 10$ µm (lower), with other parameters chosen to model the system in Ref. [1]. The exponents obtained by a power law fit of our numerical results are shown in the figure.