Effect of aggregates on the magnetization property of ferrofluids: A model of gaslike compression

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Abstract

The effect of field-induced aggregation of particles on the magnetization property of ferrofluids is investigated. From the viewpoint of energy, magnetizability of ferrofluids is more complicated than predicted by Langevin theory because the aggregation, i.e., the transition of ferrofluid microstructure, would consume the energy of the applied magnetic field. For calculating the effect of aggregates on the magnetization of ferrofluids, a model of gaslike compression (MGC) is proposed to simulate the evolution of the aggregate structure. In this model, the field-induced colloidal particles aggregating in ferrofluids is equivalent to the “gas of the particles” being compressed by the applied magnetic field. The entropy change of the ferrofluid microstructure is proportional to the particle volume fraction in field-induced aggregates \( f_H \). On the basis of the known behavior of ferrofluid magnetization and the aggregate structure determined from the present experiments, \( f_H \) is obtained and found to depend on the aggregating characteristic parameter of ferrofluid particles \( g \) in addition to the particle volume fraction in ferrofluids \( f \) and the strength of applied magnetic field \( H \). The effect of the nonmagnetic surface layer of ferrofluid particles is also studied. The theory of MGC conforms to our experimental results better than Langevin theory.

Keywords: Ferrofluids; Magnetization; Aggregate; Model; Gas

1. Introduction

Ferrofluids, or magnetic fluids, are magnetic colloids composed of nanosize one-domain magnetic particles of about 10 nm diameter dispersed in a carrier liquid. The volume fraction of the magnetic material is typically a few percent [1]. The particles are stabilized against aggregation by coating with surfactant or by the electrostatic repulsion of charge on their surfaces [2]. On a macroscopic scale, ferrofluids are liquid and have an intrinsic superparamagnetic property. If the magnetic interaction between the magnetic colloidal particles is neglected and only the interaction between the particle and an external magnetic field is taken into account, the ferrofluid magnetization \( M \) as a function of \( H \) is expressed, by applying the Langevin function \( L(x) = \coth(x) - 1/x \), as

\[
M = M_L = n m L(x), \quad x = \mu_0 m H / kT,
\]

where \( n \) is the particle number density, \( m \) is the moment of one particle, \( H \) is the strength of the applied magnetic field, \( \mu_0 \) is the permeability of free space, \( k \) is the Boltzmann constant and \( T \) is the absolute temperature \([3,4]\). \( M_L \) is called Langevin magnetization. Formula (1) can be rewritten as

\[
M = M_L = \phi M_s L(x), \quad x = \mu_0 \pi M_s d^3 H / 6kT,
\]

where \( M_s \) is the saturation magnetization of the particles, \( \phi \) is the particle volume fraction in the ferrofluid and \( d \) is the average diameter of the particles. \( \phi M_s \) is the saturation magnetization of the ferrofluid.

The experiments revealed an essential deviation from the Langevin formula for both ferrofluids and very dilute ferrofluids \([5,6]\). It is clear that field-induced interaction between the particles plays an important role in the deviation. Several theoretical models have been advanced for the evaluation of ferrofluid magnetization. There are mainly two types of models. One is the model of dipole–dipole interaction in which the particle is considered a magnetic dipole. The interaction is assumed to be...
equivalent to the amount of change in the intensity of an external magnetic field, with the amount of its contribution being proportional to the magnetization \( M \) of the ferrofluid [5,7]. The assumption is similar to Weiss’s molecular field theory, which is used to explain a magnetic solid. The other is the chain model. In this model, the magnetization property of ferrofluids is calculated by including chain formation [8–12]. However, the construction of a complete statistical theory for ferrofluid systems with the magnetic dipole interaction of particles or field-induced particle aggregation is still far from conclusion.

It is known, from experimental results, that an interaction between particles that act as magnetic dipoles is induced when an external magnetic field is applied to a ferrofluid [13]. If the particle–particle interaction energy exceeds the thermal energy, a transition of the ferrofluid microstructure will take place. Then the particles attract each other and form aggregates and are no longer well dispersed in the carrier liquid. With increasing field, the interaction between particles increases [14] and the dispersed in the carrier liquid. With increasing field, the microstructure will take place. Then the particles attract each other and form aggregates and are no longer well dispersed in the carrier liquid. With increasing field, the interaction between particles increases [14] and the dispersed in the carrier liquid. With increasing field, the microstructure will take place. Then the particles attract each other and form aggregates and are no longer well dispersed in the carrier liquid. With increasing field, the interaction between particles increases [14] and the dispersed in the carrier liquid. With increasing field, the microstructure will take place. Then the particles attract each other and form aggregates and are no longer well dispersed in the carrier liquid.

2. Aggregate effect on ferrofluid magnetization

When a ferrofluid is stable, it may be compared to a “gas of particles” using the now common description of colloidal solutions [28]. The magnetization law for a paramagnetic gas is described by the Langevin theory [29]. There are two conditions in this theory.

1. There is no interaction between minimum magnetic units \( m \).
2. When the external magnetic field \( H = 0 \), the magnetic moment in the system \( M = \Sigma m = 0 \) because the magnetic unit is influenced by thermodynamic turbulence and the dipole of the magnetic unit \( m \) is random in this case of equilibrium.

In ferrofluids, the minimum magnetic unit is the one-domain particle \( (m = \pi M_d d^3/6) \) dispersed in carrier liquid. Under zero magnetic field, the particles exhibit Brownian motion and their moments are in random directions, similar to paramagnetic gas, and they lack spontaneous magnetization. However, dipole interparticle interaction results in an effective attraction between the particles that increases as the strength of the externally applied magnetic field rises [30]. The field-induced interaction between the particles will lead to the aggregation of particles when an external magnetic field is applied. However, once the applied magnetic field is removed, the aggregates may break up or disappear via thermal motion [31–33]. These indicate that the aggregates are dissipative structures and the external magnetic field affects the aggregates. Therefore, the effect of the interaction between particles can be equivalent to the effect of the field-induced aggregate structure in the investigation of the magnetic property of ferrofluids.

While the ferrofluids are magnetized by an external magnetic field, thermal rotation of the particle moments is suppressed and the moments all follow the field direction. An interaction between the particles is induced at the same time and Brownian particles form the aggregate structure [34]. Therefore, the total energy of the ferrofluids obtained from an applied magnetic field \( W_T \) can be described as

\[ W_T = W_M + W_S, \]

where \( W_M = \mu_0 MHV \) and \( W_S = -T \Delta S \) are the magnetized energy and the structurized energy of the ferrofluids, respectively, \( V \) is the volume of the ferrofluid sample and \( \Delta S \) is the entropic change due to the microstructure transition of the ferrofluid. The total energy should equal the Langevin magnetized energy \( W_L \) when the interaction between the particles is neglected and the particles do not aggregate. That is,

\[ W_T = W_L = \mu_0 M_L HV. \]

Thus, we obtain

\[ M = M_L - \left( \frac{-T \Delta S}{\mu_0 HV} \right). \]
Ferrofluids consist of magnetic nanoparticles (magnetic phase) and carrier liquid (nonmagnetic phase). In the absence of an external magnetic field, Brownian motion keeps the particles randomly dispersed throughout the carrier liquid, similar to gas molecules spreading throughout a container. When an external magnetic field is applied, the particles form aggregates, because of the magnetic particle–particle interaction, so that a separation of the particles from the liquid matrix will occur, leading to a phase transition in which a phase that is concentrated with particles separates from a dilute phase, following the orientation of the particle moments in the direction of the field. Phase separation or particle aggregation corresponds to the decrease of the freely moving space between them, and particle aggregation can be viewed as the particles being located in an “aggregate space”. The higher the field intensity is, the more compact the aggregates will be. Consequently, the “aggregate space” would decrease with enhanced magnetic field, similar to a compressed gas. Therefore, the process of particle aggregation and the change of the aggregate structure can be treated in a similar way to the process of gas compression.

The system of ferrofluids is believed to satisfy the following three points:

1. The minimum magnetic units (the particles) are all the same and are all rigid.
2. The “aggregate space” decreases continuously as if the space is compressed with increasing applied magnetic field.
3. The processes of particle aggregation and aggregate structure transformation in the ferrofluids are isothermal when the ferrofluid is magnetized.

Aggregation of the particles and change of the aggregate structure, which are treated equally as effects of compression, result from the field-induced interaction between the particles, so that the interaction is not considered again in the model. Thus, the entropy change in the isothermal compression process of an ideal gas can be used to describe the entropic change in the field-induced microstructure transition in ferrofluid, and ΔS in formula (5) can be written as

\[ \Delta S = Nk \ln(V_H/V), \]  

where \( N \) is the number of particles in the ferrofluid sample, \( V \) is the volume of the ferrofluid sample or the space in which the particles act freely in the absence of an external magnetic field and \( V_H \) is the volume of aggregates or the “aggregate space” under a magnetic field. A similar description of entropy difference ΔS has been proposed by Scholten for the transition between dispersed and aggregated states [34].

Because the particles are rigid, the total volume of particles in the ferrofluid is conserved. Then,

\[ V\phi = V_H\phi_H, \]  

where \( \phi_H \) is the particle volume fraction of aggregates and depends on the field. Thus, formula (6) can be rewritten as

\[ \Delta S = Nk \ln(\phi/\phi_H) = -Nk \ln(\phi_H/\phi). \]  

Substituting formulas (8) and (1) or (2) into formula (5), we obtain

\[ M = n m \left( \frac{1 + \ln(\phi_H/\phi)}{x} \right) \]  

or

\[ M = \phi M_s \left( \frac{1 + \ln(\phi_H/\phi)}{x} \right). \]  

3. Particle volume fraction of field-induced aggregates

Formula (9) or (10) shows that the particle volume fraction of field-induced aggregates \( \phi_H \) must be known if we intend to calculate the effect of aggregates on \( M \). The aggregate structure may transform continuously with enhancing external magnetic field, so that \( \phi_H \) is difficult to obtain from thermodynamics relationships. However, \( \Delta S (\phi_H) \) is only a function depending on the thermodynamic state of a system. Hence, \( \phi_H \) can be constructed as an approximate treatment for satisfying some characteristic state of the ferrofluid.

First, we note that the transition of aggregates should be in relation to both the interaction between the particles and the volume fraction of particles in ferrofluids \( \phi \) [24,25]. The particle–particle interaction is an effect induced by an external magnetic field. Thus, we can assume that the interaction between particles is proportional to the interaction between a particle and an applied magnetic field \( x \). The parameters of \( \phi \) and \( x \) are related to \( \phi_H \) independently, so a cooperative effect with \( \phi_H \) can be assumed for the product of \( \phi \) and \( x \). Therefore, the relation of \( \phi_H \) with \( \phi \) as well as with external magnetic field \( H \) can be described with a function \( h \) that is dependent on \( x\phi \); \( \phi_H \) has a linear relationship with \( h(x\phi) \). Here, \( \gamma \) is a proportionality coefficient and means the degrees of interaction between particles while an external magnetic field is being applied. Thus, \( \phi_H \) is written as

\[ \phi_H = Ah(\gamma\phi x) + B, \]  

where \( A \) and \( B \) are undetermined factors.

Second, \( \phi_H \) should have the following characteristics:

1. \( \phi_H/\phi = 1 \) while \( x \to 0 \) because there is no interaction between the particles under zero magnetic field.
2. \( \phi_H \to \phi \) with \( \phi \to 0 \) because the interaction between the particles can be neglected if ferrofluids are very dilute.
3. \( \phi_H \to \text{maximal/saturated value } \phi_{H_{m}} \) while \( x \to \infty \), because the magnetization should become saturated under a sufficiently strong magnetic field.
Therefore, formula (11) can be rewritten further as
\[ \phi_H = Ah(\gamma \phi x) + \phi. \]  
(12)

Here, \( h(\gamma \phi x) \) should be in the range between 0 (while \( \gamma \phi x \rightarrow 0 \)) and 1 (while \( \gamma \phi x \rightarrow \infty \)) according to the characteristic conditions, so it can be described with a tangent hyperbola function. In addition, \( \phi_H \) should also satisfy
\[ \lim_{x \to 0} \frac{\ln(\phi_H/\phi)}{x} = 0 \]
because \( M \to 0 \) while \( x \to 0 \).

Therefore, \( \phi_H \) can be rewritten as
\[ \phi_H = A \tanh(\gamma(\phi x)^2) + \phi. \]  
(13)

The packing fraction of randomly placed sphere is 0.638 [23], so \( \phi_H = \phi_{Ho} \) is approximately 0.638 while \( \gamma(\phi x)^2 \to \infty \). Thus, \( A \) can be obtained from formula (13) as
\[ A = 0.638 - \phi. \]  
(14)

Indeed, substituting formula (14) into formula (13), we eventually obtain
\[ \phi_H = (0.638 - \phi) \tanh(\gamma(\phi x)^2) + \phi. \]  
(15)

The relationship between \( \phi_H \) and \( x \) with different \( \phi \) while \( \gamma = 10 \) and with different \( \gamma \) while \( \phi = 1\% \) is shown in Fig. 1. Fig. 1 shows that the bigger \( \phi \) or \( \gamma \) is, the faster the change of \( \phi_H \) is. Then \( \gamma \) can be defined as a compression parameter and reflects the aggregate behavior of ferrofluid particles that may be related to both the treatment method of the particles against aggregation and the magnetism of the particles. The treatment method of the particles can be, for example, treatment using ferric nitrate, coating with surfactant or the induction of charge.

The relationship between \( M/\phi M_s \) and \( x \) is shown in Fig. 2. It can be seen that the curves comply with Langevin theory while \( \phi \) or \( \gamma \) is very small. On the other hand, Langevin theory is a specific example of MGC. Fig. 2(a) shows that the smaller \( \phi \) is, the faster the curve increases under low field, but the curve tends more slowly toward saturation under high field (see the inset in Fig. 2(a)). Fig. 2(b) shows that the smaller \( \gamma \) is, the faster the curve increases under low field, and all curves tend to coincide under high field (see the inset in Fig. 2(b)).

### 4. Effect of nonmagnetic surface layer of the particles

Generally, ferrofluid particles comprise a nonmagnetic surface layer on a magnetic core while the particles are dispersed in carrier liquid [35–37]. The diameter of a particle with such a surface layer can be called the geometric diameter \( d \), and the diameter without the layer as the magnetic diameter \( d_m \). Corresponding to this, \( \phi \) is the geometric volume fraction and \( \phi_m \) is the magnetic volume fraction of the particles in the ferrofluid. If the thickness of the nonmagnetic surface is \( \delta \), \( d_m \) and \( \phi_m \), respectively, are
\[ d_m = d - 2\delta, \]
where the number of the particles in the ferrofluid is assumed to be constant.

Thus, the magnetization relation should be described as
\[ M = M_s \phi_m \left( \coth(x) - \frac{1 + \ln(\phi_H/\phi)}{x} \right), \]  
(17)

\[ x = \mu_0 \pi M_s d_m^3 H / 6kT, \]
\[ \phi_H = (0.638 - \phi) \tanh(\gamma(\phi x)^2) + \phi. \]

When the distribution of the particle size is considered, formula (16) should be
\[ d_m = \langle x_m \rangle = \int_0^\infty (x - 2\delta) f(x) \, dx, \]
different magnetic nanoparticles and ferrofluids as the magnetization is measured because the magnetization $M$ is difficult to measure directly [39]. By transmission electron microscopy (TEM) analysis, it is known that the particle diameter distribution function is $f(x)$ is the distribution function of the particle diameter [38].

Usually, the specific saturation magnetization of magnetic nanoparticles and ferrofluids $\sigma$ is measured because the magnetization $M$ is difficult to measure directly [39]. Because of $M = \sigma \rho$ ($\rho$ is the specific gravity of the magnetic system) and formula (17), $\sigma$ can be described as

$$\sigma = \frac{\mu_0 \pi \phi \rho_f}{\rho_s} \sigma_s \phi_m \left[ \coth(\alpha) - \frac{1 + \ln(\phi_H/\phi)}{\alpha} \right],$$

(19)

$$\alpha = \mu_0 \pi \phi \rho_s d_m^3 H / 6kT,$$

$$\phi_H = (0.638 - \phi) \tanh[\gamma(\phi x)^2] + \phi,$$

where $\rho_f$ is the specific gravity of the ferrofluid, and $\rho_s$ and $\sigma_s$ are the specific gravity and the specific saturation magnetization of the particles. Correspondingly, Langevin magnetization is written as

$$\sigma_L = \frac{\rho_f}{\rho_s} \sigma_s \phi_m \left[ \coth(\alpha) - \frac{1}{\alpha} \right].$$

(20)

5. Comparison of experiment with theories

The parameters in formula (19) are all measurable values other than $\gamma$. Fig. 3 shows the experimental and theoretical results. The magnetization data of the sample were measured with vibration sample magnetization at room temperature. The sample was CoFe$_2$O$_4$ ionic ferrofluid prepared by coprecipitation and acid treatment. The ferrofluid $\phi$ was 1.4%, $\rho_f = 1.05$ g/ml and $\sigma_s$ of the nanoparticles was 34.07 emu/g. The specific gravity of CoFe$_2$O$_4$ solid $\rho_s = 5.29$ g/cm$^3$. The average distance between the particles in the ferrofluids sample is so large that their magnetic interaction is negligible under zero field [37]. By transmission electron microscopy (TEM) analysis, it is known that the particle diameter distribution function is

$$f(x) = 1.035x^{-1} \exp[-3.37(\ln x - 2.52)^2]$$

and the particles in the ferrofluid have a nonmagnetic surface layer about 2 nm thick. Inserting the data into formulas (18)–(20), the theoretical relations of the magnetization versus $H$ at room temperature are obtained and plotted in Fig. 3. Fig. 3 shows that the experimental result deviates from Langevin theory, but the theory based on the MGC is highly coincident with the experimental result if the coefficient $\gamma$ is taken to be 10.

6. Conclusions

When an external magnetic field is applied to a ferrofluid that is dilute enough to avoid the interaction between particles in the absence of the field, a transition of the
ferrofluid microstructure can be induced. Brownian particles form aggregates, but the structure of the aggregates changes with increasing strength of the applied magnetic field. From the viewpoint of energy, the transition would consume some energy of the magnetic field. Thus, the magnetization of ferrofluids is more difficult than predicted by Langevin theory until the magnetization reaches saturation. The process of aggregate structure transition is very complex and a model of gaslike compression (MGC) can be used to describe the process. In the model, the evolution of the aggregate structure is viewed as a change in the particle volume fraction of the aggregates \( \phi_H \) with increasing magnetic field intensity, i.e., \( \dot{\phi}_H \) or \( V_H \) is an equivalent description of the interparticle interaction that increases with external magnetic field [14]. According to the well-known characteristic state of ferrofluids, \( \phi_H \), which is a parameter that continuously varies depending on the external magnetic field, is constructed to calculate the effect of aggregates on the magnetization of ferrofluids. Besides the particle volume fraction of the ferrofluids and the intensity of applied magnetic field, \( \phi_H \) depends on the aggregation characteristics of ferrofluid particles, which are described with \( \gamma \). If \( \gamma = 0 \) for a ferrofluid, the ferrofluid cannot be compressed or form aggregates, and formula (19) from MGC becomes the same description as the Langevin magnetization formula (20). Chantrell and co-workers previously investigated the effects of the particle interaction on the magnetization of ferrofluids using Monte-Carlo techniques. For more strongly interacting systems, the reduced initial susceptibility \( \chi (=d(M/\phi M_s)/dH) \) decreases, and if the interactions are relatively weak, the susceptibility is enhanced [40,41]. Clearly, the results are in agreement with the MGC (see Fig. 2(b)). Taketomi et al. investigated the macrocluster formation of magnetic colloidal particles in some ferrofluid thin films under an external magnetic field. Under an optical microscope, no macrocluster formation was observed in an alkynaphthalene-based ferrofluid, but it was observed in a water-based and a paraffin-based ferrofluid, and the macroclusters remained after the removal of the external field in the water-based ferrofluid [31]. Popescu et al. found that magnetic particles in technical-grade oleic acid surfactant ferrofluids exhibit a greater tendency to agglomerate than those in pure oleic acid surfactant ferrofluids [42]. These results indicate that \( \gamma \) is an important characteristic parameter for describing the interaction behavior between particles in ferrofluids independent of \( \phi \) and \( z \), and that it may be related to not only the dipolar coupling constant \( \lambda (=\mu_0m^2/4\pi\varepsilon_0kT) \) [1], but also the treatment method for preventing particle aggregation, e.g., \( \gamma \) may be different for particles coated with surfactant (surfactated ferrofluids) and for charged particles (ionic ferrofluids). Huang et al. found that in bi-dispersed ferrofluids that consist of two fractions of magnetic particles with significant size differences, most of the chains are formed by large particles, but the aggregation behavior of large particles is hindered by the presence of small particles [43]. Obviously, the behavior of bi-dispersed ferrofluids can be described using the \( \gamma \) parameter. The \( \gamma \) parameter can be determined from the initial susceptibility and will be further investigated. Here, the interaction parameter \( \gamma \) is an intrinsic parameter of ferrofluids and is different from the magneto-dipole interaction parameter that describes the thermodynamic stability region for ferrofluids and depends upon the field strength [44]. If the ferrofluids are very dilute, i.e., particle volume fraction \( \phi \) is low, the magnetization calculated using the MGC is identical to that obtained from Langevin theory. If there is a nonmagnetic surface layer on ferrofluid particles, the layer will influence the magnetization of the ferrofluid. The effect can be considered in the MGC. The magnetization curve simulated with the MGC shows better coincidence with our experimental results than does the Langevin theory.

It must be pointed out that the effects of temperature or a shift in concentration on aggregates are disregarded [45,46] because they are weaker than the effect of field-induced aggregation on the magnetization property of ferrofluids. In summary, the merit of the MGC theory is that both field-induced aggregate structure evolution with varying external magnetic field and the difference in anti-aggregation treatment for different ferrofluids can be considered. Also, the MGC has extensive universality. For example, Langevin theory is contained in the MGC, and the MGC is applicable whether a system is strongly or weakly interacting.

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