

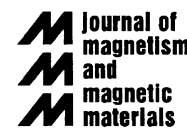


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Peculiar magnetic aftereffect of highly diluted frozen magnetic fluids

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Abstract

A very stably dispersed magnetic fluid (mother MF) and its 1000-times diluted solution were independently zero-field-cooled from room temperature to 5 K followed by application of a magnetic field of 2.86 MA/m for 300 s. After the field was removed ($t = 0$), its residual magnetization M was measured as a function of time t for 80 000 s. After measurement, the MF sample was heated to room temperature, and the experiment was repeated after cooling to 5 K and again applying and removing the 2.86 MA/m field. We performed the same experiment several times, and obtained a different M vs t curve each time. With each cycle, the average M increased and the M vs t curve converged to a universal curve. In the initial few cycles, the value of M is very small, fluctuates and surprisingly increases with t in some time region. These characteristics are common in both the mother MF and diluted MF. We consequently propose the following physical model. When the MF is cooled, the isolated surfactant molecules in the solvent trigger the generation of magnetic colloid micelles. In other words, there occurs a phase transition from the magnetic colloids' monodispersed phase to a micelle phase. The magnetic dipoles of the micelle's colloids make a closed magnetic flux loop. That is the origin of the anomalously small value of the residual magnetization in the early cycles. After a certain time elapses the micelles spontaneously break due to their residual stress, and a finite magnetic moment of the individual micelle develops. Consequently, M increases with t during this period.

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1. Introduction

Conventionally, it is believed there is no interaction between the magnetic colloidal particles in a magnetic fluid (MF) [1,2]. In fact, the magnetic field which is induced at a colloidal particle by the nearest neighbor colloids' magnetic dipoles is so weak that the dipole–dipole interaction is negligible [3]. However, in real experiments, especially in experiments of the MF under an external field, there were found many phenomena which could only be explained by the mutual interaction or agglomeration of the colloidal particles [4]. In order to overcome this contradiction, we assumed that the particles move so freely in the MF solvent that the particle–particle distance can become very short

instantaneously, and in that short period of time a strong interaction between the particles exists. Accordingly when averaged over time, an inter-particle interaction is found in the MF [3]. In a previous paper, we ascribed the MF's strong magneto-optical effect to the presence of a second order phase transition from the colloid's monodispersed phase to an instantaneous agglomerate phase under application of an external magnetic field [5]. In the present paper, in order to make clear whether or not there is a mutual interaction between the magnetic colloidal particles in the frozen MF, we measured the magnetic aftereffect of the mother MF and its 1000-fold diluted MF at a low temperature, 5 K. The average distance between the particles in the diluted MF is so large that their magnetic interaction is negligible and the individual particle's magnetic dipole should obey the Néel rotational relaxation model. On the other hand, if there is a magnetic interaction between the particles in the mother MF, the magnetic dipole's rotational relaxation should no longer follow

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the Néel relaxation behavior. Then by comparing the magnetic aftereffect of these two MFs, we can detect any difference in the inter-particle interaction. The experimental result was far from our expectation. The residual magnetization was far less than we expected for both the fluids and it sometimes increased with time. From these experimental results, we concluded that the phase transition was not between agglomeration of the colloids and their being monodispersed. Instead, the transition appeared to be between a micelle phase and a monodispersed phase. This micelle model is supported by other different experiments in our recently published paper [6].

2. Experimental procedure

We used “Marpomagna FV-42” made by Matsumoto Yushi-Seiyaku Co. as the mother MF [7]. (This MF used a magnetite colloid (5 nm diameter) of 0.104 solution volume fraction and alkylnaphthalene as the solvent.) Anion type surfactants were used for this MF and their molar weight was much less than that of the solvent, and accordingly, they were much easier to evaporate than the solvent. The colloidal dispersivity of this MF was excellent [8,9]. We also used its 1000-fold diluted MF, (colloid volume fraction = 8.0×10^{-5}). These MFs were the same MFs used in Refs. [9] and [10]. The MF was filled in a glass tube (inner diameter = 3.3 mm, axial length = 9 mm) followed by hermetically sealing with a glass lid attached using an epoxy adhesive (Hardman red) [7].

In this experiment we used a SQUID magnetometer made by Quantum Design Co. [7] calibrated using the pure Ni sphere NIST SRM #772a [11]. We kept the temperature of the sample chamber (located in the middle of the cryostat) at 5 K during the experiment. Before inserting the sample into the cryostat, we quenched the superconducting magnet, thereby assuring the field in the sample chamber was zero. We inserted the sample slowly, lowering it from the top of the cryostat (at room temperature) to the sample chamber at 5 K. We refer to this state as the “zero-field-cooled” condition. It took about 2 min to insert the sample from the inlet at room temperature to the cryostat’s center position where the temperature was 5 K. Inside the cryostat the chamber was kept under vacuum by an oil diffusion vacuum pump. During the magnetic after effect measurement, the sample was considered to be under an adiabatic state for the time scale of a second while it was considered to be under an isothermal state for the time scale of a few tens of minutes. After the sample temperature was stabilized, a magnetic field of 2.86 MA/m (36 kOe) was applied to the sample in the axial direction for $t_H = 300$ s. Again the superconducting magnet was quenched to completely remove the field. It took approximately 2 min to stabilize the cryostat temperature after quenching. After the temperature was stabilized we began to measure the sample’s residual magnetization, $M(t = 0)$, as a function of time t for 80 000 s. Therefore, the experimental M at $t = 0$ s

was not the initial residual magnetization in its strictest sense.

After the measurement, the MF sample was taken out of the cryostat and warmed to room temperature. Then the same experiment was repeated. We performed the same experiment several times, and obtained a different M vs t curve each time.

3. Results

3.1. Mother MF

For the mother MF (sample A), Fig. 1(a) shows the M vs t curves from the first cycle through the sixth cycle. Fig. 1(b) shows the enlarged M vs t data for the first and second cycles. Also shown are the enlarged M vs t curves for the third through the sixth cycles in Fig. 1(c). With each cycle, the average M increased and the M vs t curve converged to one universal curve. However, during the first and second cycles, in addition to M being much less, it fluctuates greatly and surprisingly increases with t for $t > 100$ s. In fact, when we were performing the first cycle experiment, seeing this anomalous increase in M , we thought something was wrong in the experimental setup and stopped the experiment at the halfway point. In this paper, we call the M vs t curve such as those for the first and second cycles of this sample as an extraordinary M vs t curve. On the other hand, we call the sixth cycle’s M vs t curve as a universal curve for convenience [6]. We made more than 10 similar samples filled with the mother MF. They all showed similar experimental results. However, a sample whose hermetical sealing was improved, showed only M vs t curves similar to those shown in Fig. 1(b), even after many cycles [6].

3.2. 1000-fold diluted MF

Figs. 2(a) and (b) show the M vs t curves of sample B filled with the diluted MF. For convenience, we multiplied the true residual magnetization by the dilution factor, 819.7. This dilution factor is the ratio of the colloidal particles weight fraction in the mother MF divided by that in the diluted MF [9]. Fig. 2(a) shows the M vs t curves of the first through the third cycles. Though the first cycle measurement was made at $T = 5$ K, the second and third cycles were performed at 6 and 4.2 K, respectively. In addition, for all cycles the duration time, t_H , during which the field of 2.86 MA/m was applied prior to quenching the magnet was 0 s. The experimental condition, $t_H = 0$ s, means the following. It took a few minutes to increase the applied field from 0 to 2.86 MA/m. As soon as the field reached 2.86 MA/m, we quenched the superconducting magnet and defined this as the $t_H = 0$ state. Though the temperature, T , and the duration time t_H differed slightly between the three cycles, the characteristics of their M vs t curves (i.e., small M values and the existence of a region with M increasing with t) are similar to those of the mother MF.

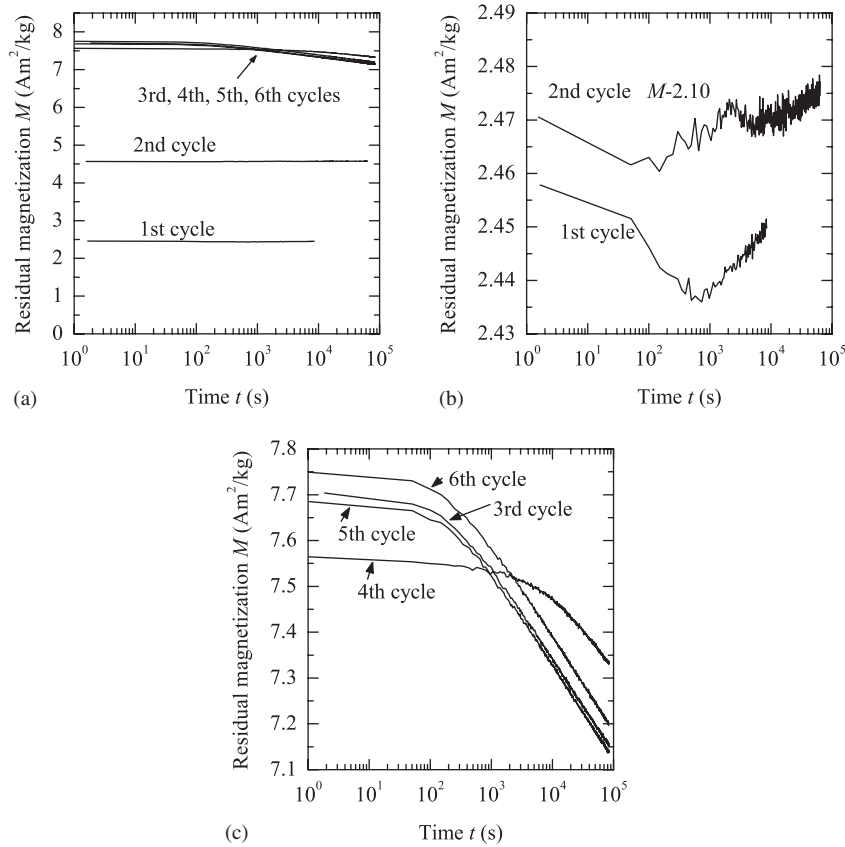


Fig. 1. Residual magnetization M as a function of time t for the mother MF, sample A, (a) for cycles 1–6, (b) magnified for cycles 1 and 2 (reduced by $2.1 \text{ Am}^2/\text{kg}$), and (c) magnified for cycles 3–6.

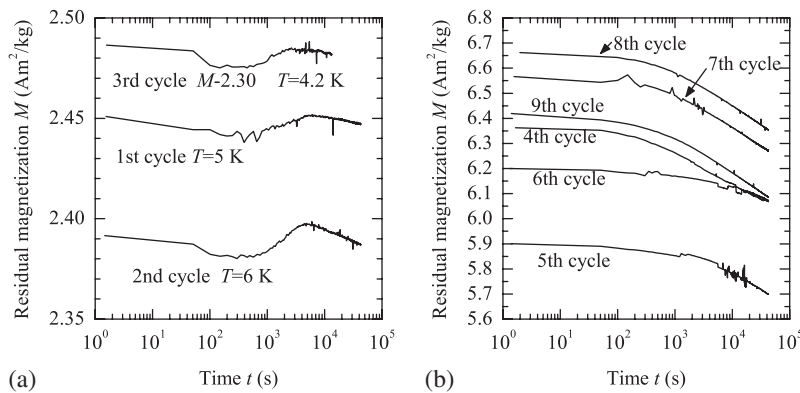


Fig. 2. Residual magnetization M as a function of time t for the diluted MF, sample B, (a) for cycles 1, 2 and 3 (reduced by $2.3 \text{ Am}^2/\text{kg}$), and (b) for cycles 4–9. The M is the measured residual magnetization multiplied with the dilution factor, 819.7. The temperatures, T (K), and field application times, t_H (s), (T, t_H), for the individual cycles are as follows: first cycle—(5, 0), second cycle—(6, 0), third cycle—(4.2, 0), fourth cycle—(4.2, 0), fifth cycle—(6, 0), sixth cycle—(5, 0), seventh cycle—(4.2, 300), eighth cycle—(5, 300), ninth cycle—(5, 300).

Fig. 2(b) shows the M vs t curves of the fourth cycle through the ninth cycle. Here the experimental parameters (temperature T and duration time t_H) differed only slightly from $T = 5 \text{ K}$ and $t_H = 300 \text{ s}$ except for the eighth and ninth cycles. It can still be concluded that the M vs t curves converge to a universal curve at high cycle numbers, even for the highly diluted MF.

3.3. Difference from cooling manner

We also performed similar experiments on a mother MF sample (sample C) cooled differently. In this experiment the cryostat temperature was stabilized at 320 K when sample C was inserted. Then the cryostat was cooled to 5 K at a rate of $10 \text{ K}/\text{min}$. Immediately following this cooling

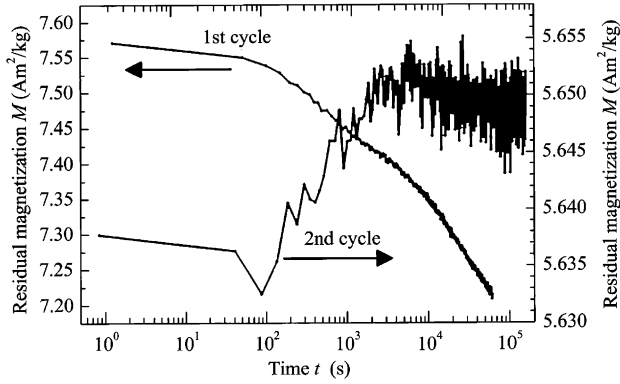


Fig. 3. Residual magnetization M as a function of time t for the mother MF, sample C. The first cycle was performed with the sample under quasi-equilibrium conditions, slowly cooled down to 5 K; the second cycle was performed with the same sample cooled the ordinary fast way as described in the text.

procedure, the above-mentioned quenching and M vs t experiment was performed. Fig. 3 shows the first cycle of this M vs t experiment. Though this was only the first cycle, the M vs t curve resembles the universal curve except for the existence of a prominent shoulder in the region, $1000\text{ s} < t < 10000\text{ s}$. After taking the sample out of the cryostat, we performed the same sequence of experiments as that for samples A and B. In this latter sequence, accordingly the cryostat was pre-cooled to 5 K in advance before inserting sample C into the cryostat. These latter results are shown as the second cycle in Fig. 3. In this latter case, the M vs t curve is similar to the early cycle M vs t curves for samples A and B.

4. Discussion

4.1. Particle distribution and the dipole blocking condition

The colloidal magnetic particles in the MF possess a distribution in size with an average diameter of 5 nm. A reasonable approximation is that the colloidal particle is a sphere of radius r , and that the particles are distributed in a log-normal distribution with respect to r . Let the particle's distribution function, $f(r)$, be defined such that $N_0 f(r) dr$ is the number of particles whose radii fall in the range $(r, r + dr)$. Here N_0 is the total number of the particles per unit volume of the MF. Then $f(r)$ is expressed by [12]

$$f(r) = \frac{1}{\sqrt{2\pi}\sigma r} \exp\left\{-\frac{[\ln(r/r_0)]^2}{2\sigma^2}\right\}. \quad (1)$$

Here r_0 and σ are positive constants denoting the mean radius and standard deviation, respectively. Assuming that the magnetic dipole–dipole interaction between the colloidal magnetic particles in the MF is negligible, the MF's magnetization per unit mass, $\bar{M}(H)$ as a function of the external magnetic field, H , is expressed by

$$\bar{M}(H) = \frac{M_s N_0}{\rho} \int_0^\infty \frac{4\pi r^3}{3} L\left(\frac{M_s(4\pi r^3/3)H}{k_B T}\right) f(r) dr. \quad (2)$$

Here ρ , M_s and k_B are the specific gravity of the MF, the saturation magnetization per unit volume of the colloidal particles and the Boltzmann constant, respectively. The function, $L(x)$, is the Langevin function:

$$L(x) = \coth x - \frac{1}{x}. \quad (3)$$

The MF's saturation magnetization, \bar{M}_{sat} , is obtained as

$$\bar{M}_{\text{sat}} = \frac{M_s}{\rho} N_0 \frac{4\pi r_0^3}{3} e^{9\sigma^2/2}, \quad (4)$$

by inserting $H = \infty$ into Eq. (2). Therefore, $\bar{M}(H)$ can be determined by the three parameters, r_0 , σ and \bar{M}_{sat} . On the other hand, the MF's $\bar{M}(H)$ at room temperature can be easily obtained by measuring the MF magnetization. Accordingly, by curve fitting of the \bar{M} vs H curve calculated by Eq. (2) to the experimental \bar{M} vs H curve, we can obtain the true r_0 , σ and \bar{M}_{sat} . Fig. 4 shows the present mother MF's \bar{M} vs H curve fitting result and the particle distribution function obtained by this curve fitting. From this analysis, we obtained $r_0 = 2.40\text{ nm}$, $\sigma = 0.360$ and $\bar{M}_{\text{sat}} = 21.4\text{ Am}^2/\text{kg}$.

For temperatures below the “blocking temperature” of a single magnetic domain particle, the magnetic dipole of that particle is fixed along its easy magnetization axis. The present MF's colloidal particles are magnetite and the magnetite has cubic magnetic crystallographic anisotropy. We, however, assume the present colloidal particles possess a uniaxial magnetic anisotropy based on the following reasons. First, it is well known that a considerable amount of the magnetite colloidal particles in the MFs changes to $\gamma\text{-Fe}_2\text{O}_3$ which has a large uniaxial magnetic anisotropy. In fact our MF was prepared several years ago and its magnetization slightly decreased compared with that

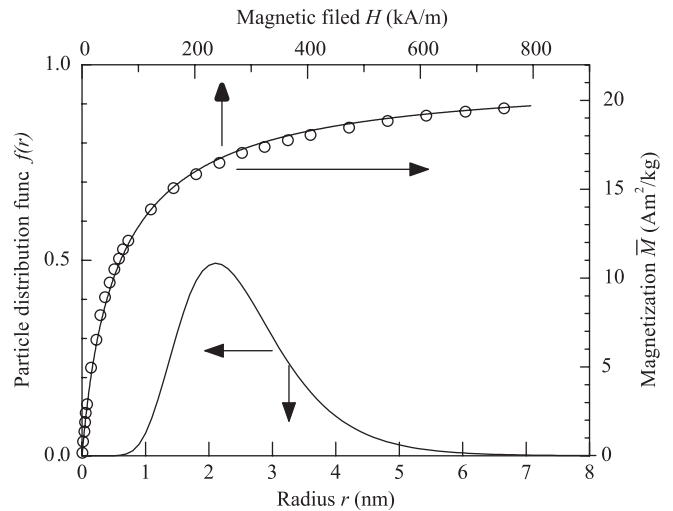


Fig. 4. Magnetization curve, \bar{M} vs. field, H , at 300 K for the mother MF and its colloidal particle distribution function $f(r)$, calculated from Eq. (1) using $r_0 = 2.40\text{ nm}$ and $\sigma = 0.360$. The open symbols are the measured $\bar{M}(H)$ data and the solid line is obtained from Eq. (2) using $\bar{M}_{\text{sat}} = 21.4\text{ Am}^2/\text{kg}$.

measured when it was initially prepared. Second, the colloidal particles' shape deviates slightly from spherical and we have to consider the presence of a magnetic shape anisotropy. Accordingly we considered the present particles' magnetic anisotropy as uniaxial. The condition for this blocking is given by

$$1 = \frac{1}{k_B T} \left(K \frac{4\pi r^3}{3} \right), \quad (5)$$

where K is the anisotropy constant for the particle. The radius, $r = 1.06$ nm, satisfies Eq. (5) for magnetite's $K = 1.4 \times 10^4$ J/m³ and $T = 5$ K. Therefore, from Fig. 4 and the fact that γ -Fe₂O₃'s K is much greater than that of the magnetite, it is apparent that almost all the particles would be in a blocked dipole state at 5 K. The particle anisotropy is assumed to be uniaxial, and the individual magnetic moment of the particle is randomly oriented due to the zero-field-cooling from room temperature. When a strong magnetic field is applied to the particles in the z -axis direction followed by the removal of the field, the z -component of all the particles' magnetic moments becomes positive. If the angle between the magnetic dipole and the z -axis is θ , then the average of $\cos \theta$, $\langle \cos \theta \rangle$, would be $\frac{1}{2}$ due to a random orientation of easy magnetization axes. As the MF's saturation magnetization, \bar{M}_{sat} is 21.4 Am²/kg at room temperature, \bar{M}_{sat} at $T = 0$ K should be 22.8 Am²/kg due to the increase in the magnetite saturation magnetization. Accordingly the residual magnetization M should be $\bar{M}_{\text{sat}} \langle \cos \theta \rangle = 11.4$ Am²/kg at $T = 0$ K. This value is close to the initial value of the universal function, 7.75 Am²/kg in Fig. 1 in order of magnitude. The still-existing discrepancy of these two values is perhaps due to the magnetic colloidal particles' micelles formation, which is to be described in the next subsection.

Let us compare the M vs t curves of later cycles between the mother MF and the highly diluted MF. Fig. 5 shows the sixth cycle's M vs t curve of the sample A and that of sample B's eighth and ninth cycles. As they are normalized, the initial value of M should be unity. Apparently the eighth and ninth cycles' M vs t curves of the diluted MF have a different $\log t$ dependence from the sixth cycle's M vs t curve of the mother MF. However, at this stage, it does not lead to the conclusion that there is a mutual interaction between the particles in the mother MF. This conclusion cannot be reached because there is a more significant mechanism, micelle formation, existing; that will be described in the next subsection.

4.2. Micelles formation

The dominant contradictions in the present experimental results from that expected according to conventional wisdom in magnetism are the early cycles' M vs t curves for both the mother and highly diluted MFs. The first contradiction is the anomalously small residual magnetization, M , which increases with thermal cycling. The second contradiction of the increasing M residual with time is

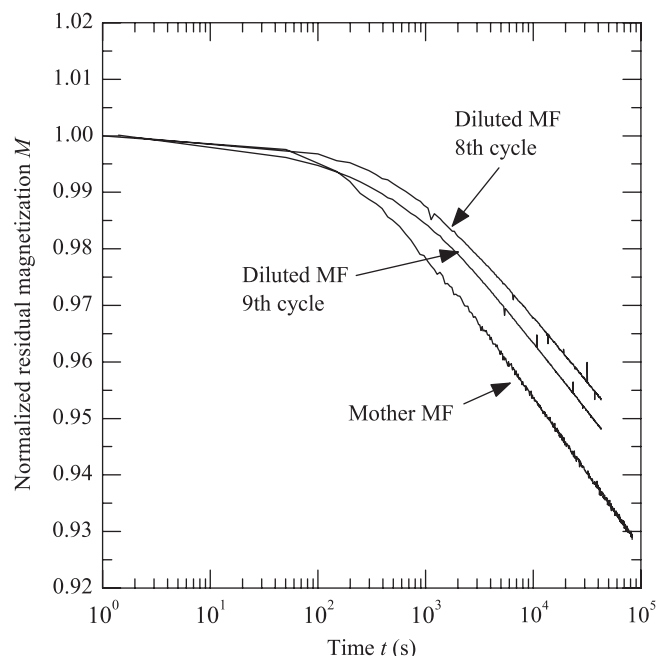


Fig. 5. Normalized residual magnetization M (as described in the text) as a function of time t for the mother MF and its diluted form. The diluted MF's results are the eighth and ninth cycle results for sample B. The mother MF's result is the universal curve (or the sixth cycle result) for sample A.

especially surprising. The magnetization is often considered an order parameter of the magnetic spin system. The residual magnetization's spontaneous increase with time means the spin entropy is spontaneously decreasing with time, and that would appear to violate the second law of thermodynamics. One can explain this contradiction if in addition to the spin entropy one also takes into consideration the configurational entropy of the surfactant molecules.

In practice, when a MF is prepared, a very little excess amount of surfactant over that theoretically needed is usually added to the MF so that there is minimal chance for coagulation of the colloidal magnetic particles. Theoretically, the required amount of surfactant is that amount which is needed to exactly cover the surface of all the colloidal particles with one molecular layer. Accordingly, even though the excess amount is small, there is considerable number of excess surfactant molecules (isolated and monodispersed in the solvent) in a conventional MF¹ (Fig. 6(a)). We feel these isolated and monodispersed extra surfactant molecules play an important role. In order to interpret these anomalous experimental results, we

¹There was experimental evidence that supported the existence of the free excess surfactant in the MF. After filling a glass test tube with a fresh MF, FV-42, we evacuated the inside of the tube by a vacuum pump [13,14]. When the evacuation started, the MF boiled fiercely and many large gas bubbles were generated from the MF. The boiling, however, continued only for a few seconds and ceased. Perhaps the bubbles were excess surfactant or dissolved water. We will discuss the dissolved water later.

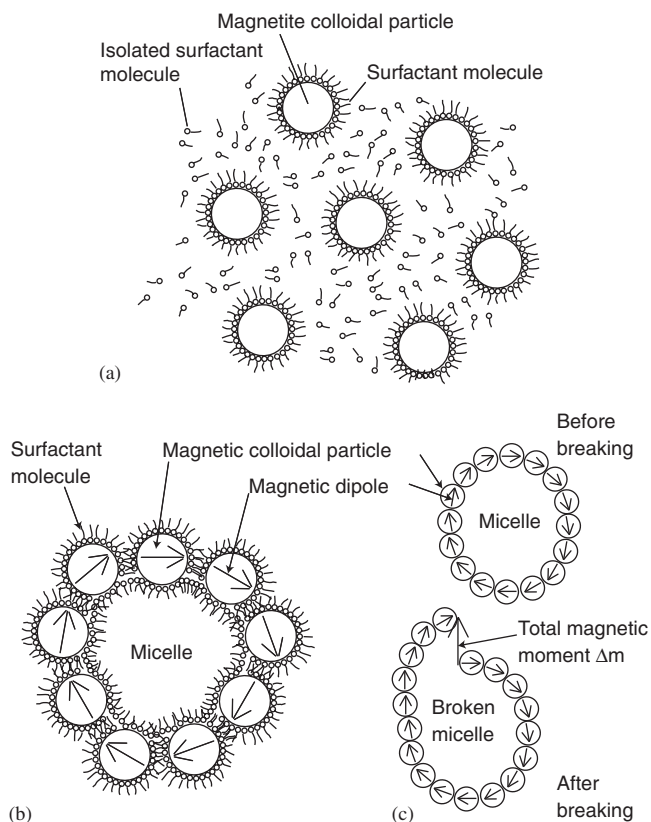


Fig. 6. Schematic figure of the magnetic fluid structure showing (a) the magnetic colloid's monodispersed phase, (b) the micelle formation of magnetic colloids, and (c) the magnetic colloid dipoles before and after breaking the micelle. For (a) there are not only attached surfactant molecules on the colloid surface but also isolated surfactant molecules in the solvent.

propose the following physical model taking the extra surfactant molecules into account. In general, when the temperature of the MF is decreased, or when the external magnetic field is applied to the MF, the isolated surfactant molecules trigger the generation of surfactant micelles. In addition, because of their mutual interaction, a considerable amount of the colloidal magnetic particles sticks to the surface of the micelles. These particle-coated micelles resemble somewhat aggregates of particles (Fig. 6(b)). In other words, with a temperature decrease or the application of an external magnetic field, there occurs a phase transition from a phase of monodispersed magnetic colloids to a magnetic colloid micelle phase. In addition, the micelles generated by the temperature decrease are spherical in shape and contain magnetic dipoles of the colloidal particles which make a closed magnetic flux circuit. However, the micelles produced by the application of an external field are elongated in shape due to the magnetic interaction between the magnetic particle dipoles, and the dipoles do not make a closed circuit. This is the origin of the MF's magneto-optical effect [5,8,13,14].

Many years ago, it was found that needle-like clusters of magnetic colloidal particles were formed under an external field in some kinds of MFs of which surfactant's dispersing

ability was slightly weak [15]. It was widely believed that these clusters were the precipitants of the magnetic colloidal particles. However, the precipitants disappeared when the external field was removed. It was contradictory, because the agglomeration was induced by the mutual molecular force between the colloidal particles and agglomeration should have been irreversible. The present micelle model offers a simple solution to this age-old contradiction. The precipitants were the agglomerates of the micelles. Accordingly, when the external field was removed, the micelles disappeared and naturally, the precipitants themselves disappeared. Other different experiments also support this micelle model [6].

According to this new surfactant micelle model, we can now interpret the present experimental results. At some temperature below 300 K, the MF's spherical micelles which were generated by the temperature decrease became fixed in position in the frozen solvent. When a strong external magnetic field was applied to these frozen micelles for a short time, the magnetic dipoles of the colloidal particles which were stuck to the surfactant micelles rotated their orientations toward the field direction, and at the same time, a magnetic force between the magnetic colloidal particles was generated resulting in a slight distortion of the micelle shape. After removal of the field, the magnetic moments of the particles once again made a closed flux circuit, but an internal stress was left in the shape-distorted micelle. After a certain time had passed following removal of the field, a spontaneous break in the micelle developed due to the internal stress and a finite magnetization was generated (see Fig. 6(c)). At the same time the configurational entropy of the surfactant molecules was increased due to the micelle breaking, and this entropy increase compensated for the decrease in magnetic spin entropy resulting from the magnetization generation. In fact, Figs. 1(b) and 2(a) show the residual magnetization not only increased with time but also fluctuated greatly. Perhaps this fluctuation was due to a tremendous number of micelles spontaneously breaking.

The change in the M vs t curve from that observed in the early experimental cycles of Fig. 1(b) to that observed in the later experimental cycles of Fig. 1(c) for the mother MF is interpreted as follows. For this sample, the sample holder was incompletely sealed by fixing the glass tube and lid with an epoxy adhesive after filling the holder with the MF. When the sample was left in the cryostat under vacuum, the isolated surfactant molecules in the MF evaporated through the improperly glued space. Accordingly after many experimental cycles, the isolated surfactant molecules sooner or later all evaporated away and the micelle formation did not occur. Consequently, the M vs t curve changed from Figs. 1(b) to (c). In fact, when we improved the hermetic sealing of the sample, only the M vs t curves of Fig. 1(b) were observed, even after many experimental cycles [6]. This hermetic experiment was reported in Ref. [6]. Other experiments in Ref. [6] also confirmed this interpretation.

There is an objection against this micelle model. Generally speaking, micelle formation usually requires at least a binary solution. The present MF, however, consists of a single solvent and accordingly micelle formation should not occur. We present the following possible explanations for this unusual behavior. (1) The MF may contain some water contamination. The water contaminant could then easily act as the nucleation seed for forming the micelle. (2) A second explanation is based on the fact that two different surfactants were used in the present MF. One of the surfactants could then play the role of seeding the micelle formation. (3) Since the present MF is a complex fluid containing magnetic colloidal particles, the micelle prepared here might indeed be much different from the ordinary micelle found in multi-component solutions. This point, however, is still an open question at the present time. The difference in free energy between the monodisperse phase and the micelle phase appears to be very small. When we cooled down sample C filled with the mother MF to 5 K at the slow rate of 10 K/min, the M vs t curve resembled the curve measured when no micelles had formed. This is analogous to the supercooling of water. No phase transition occurred during the slow cooling. If the phase transition is easily suppressed by the quasi-equilibrium cooling, the difference in free energy between the two phases must be small.

The present experimental results have not been observed prior to this study despite the many previous investigations of the magnetic aftereffect and the magnetic anisotropy of frozen MFs for the following reasons [16–25]. First, the present MF possesses excellent dispersivity [26]. MFs with poor magnetic colloidal particle dispersivity will easily allow the formation of agglomerated particles under application of a very weak external magnetic field. A considerable fraction of conventional MFs have such agglomeration characteristics in greater or less degree. If such MFs are frozen, real colloidal particle aggregates are formed instead of the micelles and the present experimental result would not be observed. The present results can only be measured in a MF with high dispersivity of the colloidal particles. The second reason such results have not been recognized earlier is that the origin of the present result is due to the present MF's isolated surfactant molecules in the solvent. Therefore, if the sample holder is not hermetically sealed, the present result could hardly be obtained because the present experiment is performed at low temperature and inevitably under vacuum. Consequently the isolated surfactant molecules evaporated before the micelle formation. The last reason for not recognizing this effect earlier is that the present effect is very subtle. It took more than 10 months to confirm these experimental results by sequentially identifying and removing many sources of noise and possible experimental error.

5. Conclusion

A very stably dispersed magnetic fluid (MF) and its 1000-times diluted solution were independently zero-field-

cooled rapidly from room temperature to 5 K followed by application of a magnetic field of 2.86 MA/m for 300 s. After the field was removed ($t = 0$), its residual magnetization M was measured as a function of time t for 80 000 s. After measurement, the MF sample was heated to room temperature, and the experiment was repeated after cooling to 5 K and again applying and removing the 2.86 MA/m field. We performed the same experiment several times, and obtained a different M vs t curve each time. With each cycle, the average M increased and the M vs t curve converged to a universal curve in which M decreased in proportion to $\ln t$. In the initial few cycles, the value of M was very small, displayed fluctuations, and surprisingly increased with t in some time regime. We call this early cycle M vs t curve as an extraordinary curve. The above characteristics are common for both the mother MF and the diluted MF.

In an experiment where the mother MF was slowly cooled down to 5 K, we obtained an M vs t curve on the first cycle which was similar to the universal curve. However, in the second cycle after rapid cooling, we obtained the extraordinary M vs t curve.

From the particle-size distribution determined for the mother MF from its room temperature M vs H curve, it was concluded that almost all the particles' magnetic dipoles would be thermally blocked at 5 K. In fact, if the individual particles obeyed the Néel relaxation model, the initial value of the residual magnetization agreed within an order of magnitude with that of the universal function.

Noticing the occurrence of isolated monodispersed surfactant molecules in the MF solvent of our samples, we propose the following physical model. When the MF is cooled, the isolated surfactant molecules trigger the generation of micelles on which the magnetic colloids are absorbed and resulting in the particles' magnetic dipoles making a closed magnetic flux loop. In other words, there occurs a phase transition from magnetic colloids' monodispersed phase to a micelle phase with the temperature decrease. Further cooling results in the micelles being fixed in the frozen solvent. When a strong magnetic field is applied to the frozen MF, a stress is generated in the micelle, and it remains after the field is removed. After removal of the field, the magnetic dipoles of the micelle's colloids once again make a closed magnetic flux loop. That is the origin of the anomalously small initial value measured for M . After a certain time elapses, the micelle spontaneously breaks due to its residual stress and the surfactant molecules' configurational entropy increases. In order to compensate for this entropy increase, the magnetic spin entropy decreases by generating a finite magnetic moment of the micelle. Further breakage of micelles leads to an increase in the residual magnetization, M , with time, t .

During the many experimental cycles of the present investigation, the MF sample was under vacuum for many hours. During this time we feel the isolated surfactant in the solvent gradually evaporated through the incompletely

glued space of the sample holder. Accordingly, after many experimental cycles, all the isolated surfactant molecules originally in the solvent and required to form the micelles had evaporated. Consequently, the M vs t curve converged to a universal curve after many experimental cycles.

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