Phase Transitions of Iron-Nitride Magnetic Fluids

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Phase transitions of magnetic fluids in the zero field were studied from the viewpoint of static susceptibility and typical relaxation time in order to distinguish between the transitions and the blocking phenomena. We used iron-nitride magnetic fluids containing nearly uniform particles so as to remove the effects of particle-size distribution. In the densest sample, we observed the growth of ferromagnetic fluctuations and, in the diluted samples, a temperature-induced first-order phase transition.

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In the last decade, considerable research has been conducted on questions about the phase diagram of magnetic fluids as a typical dipolar fluid [1–8]. One question is whether or not magnetic fluids with low particle densities show first-order phase transitions similar to the liquid-gas phase transition [2–8]. For a long time, it was believed there coexisted two phases: a "liquid phase" with higher particle density and a "gas phase" with lower particle density [9,10]. However, in the 1990s, some numerical and analytical studies predicted no "liquid-gas" coexistence for the dipolar hard- or soft-sphere fluid in the zero field [2,5,6]. Instead, particles were expected to associate into chainlike clusters [2,5,6]. Recently, a simulation suggested once again a kind of phase coexistence for the dipolar hard-sphere fluid [8]. Another question is whether magnetic fluids with high particle densities have a ferromagnetic liquid phase in the zero field [1,3–6]. In this phase, the theories have predicted a long-ranged orientational order of magnetic moments without long-ranged spatial order of particles.

In contrast with this large body of numerical and analytical studies, the amount of experimental knowledge is limited [11]. With respect to whether or not any liquid-gas coexistence appears in the zero field, clusters of particles or droplets have been observed [12]. However, further progress has been hindered by the polydispersity of particles in conventional magnetic fluids. A detailed study was first carried out for monodisperse ionic magnetic fluids [13]. Although this work showed a clear temperature-induced phase separation, the roles of the electrostatic forces, which may cause a phase separation by themselves [14], could not be overlooked. For this reason, surfactant-coated magnetic fluids containing uniform particles are required in order to answer the first question. On the other hand, the second question, namely whether the ferromagnetic liquid exists in the zero field, is still open, although the Curie–Weiss-like behavior has been discussed for magnetic fluids [15,16]. The key seems to be also monodispersity [16]. Therefore, we will discuss the behavior of surfactant-coated iron-nitride magnetic fluids that have very narrow distributions of particle size [17].

In addition to the quality of samples, each analysis of experimental results presents various difficulties. An example is the analysis of magnetic properties. Such analyses have provided clear knowledge on phase transitions of ordinary magnetic materials. However, the knowledge obtained for magnetic fluids has been ambiguous because of the difficulty in distinguishing between the phase transitions and the blocking phenomena [18]. As the magnetic relaxation slows down at lower temperatures, the magnetic moment on each particle cannot follow the variation of applied field (the blocking). This delay of the response causes hysteresis of the magnetization curve and decrease of the susceptibility observed within finite time. Because the static susceptibility for the superparamagnetic state increases monotonously with decreasing temperature, the competition between the decrease and the increase makes a peak on the temperature dependence of the observable susceptibility. We must not mistake these phenomena for the evidence of the phase transitions.

In this study, in order to facilitate the distinction between the phase transitions and the blocking phenomena, we separately discuss static and dynamic behavior. Concerning the former, we focus on the static susceptibility estimated by means of the Cole-Cole plot for ac susceptibility $\chi' + i\chi''$ [19]. In addition, the field-cooled magnetization is discussed as needed. Regarding the latter, we focus on the typical magnetic relaxation time estimated from the frequency dependence of χ''.

Iron-nitride ε-Fe_3N magnetic fluid was prepared by a method of vapor-liquid chemical reaction between iron carbonyl and ammonia [17]. In this method, the iron-nitride particles were dispersed in kerosene by using surfactant of polybutenylsuccinpolyamine. The solidification temperature of kerosene is below 200 K. Transmission electron microscopy showed that the iron-nitride particles are nearly spherical and their diameters are almost uniform in 11.5 ± 1 nm. The thickness of the surfactant layer was shown to be about 1.5–2.0 nm [17]. Because the diameters are adequately small, each particle has a single domain. For this reason, the magnetization of each particle can be treated as a dipole moment whose magnitude μ is about $(1 \times 10^5)\mu_B$, if we assume that spontaneous magnetization in particles is equal to that in bulk. By using the magnitude μ, the dipolar interaction energy $(\mu^2/r_{\min}^3)/k_B$ is estimated at about 1000–2000 K on condition that the

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particles are at their closest position ($r_{\min} \approx 15$ nm), k_B being the Boltzmann constant. In other words, the reduced temperature $T^* = k_B T/(\mu^2/r_{\min}^3)$ is about 0.1–0.3 in the vicinity of room temperature. On the other hand, the van der Waals forces seem to be relatively weak, although it is difficult to clarify their exact magnitudes. Their energy $4\varepsilon/k_B$ at $r_{\min}$ is about 300 K, if the Hamaker constant is assumed to be 2×10^{-12} erg [20]. In order to prepare samples with various particle-number densities n, the as-prepared magnetic fluid was diluted using kerosene with the surfactant. The saturation magnetization M_s at room temperature thus decreased from 8×10 to 0.9 emu/cm^3 with the dilution. In other words, the reduced density $\rho^* = nr_{\min}^3 = M_s/\mu r_{\min}^3$ varies from about 0.3 to about 0.004.

ac susceptibility $\chi' + i\chi''$ was measured by using a conventional mutual-induction method. The magnitude of the ac field was 1 Oe, and the frequency f was in the range from 10 Hz to 10 kHz. The environmental static field was reduced to almost zero. The samples were heated to 321 K and then cooled to 210 K. After the cooling, they were reheated to 321 K. At 321 K, we continued the measurement for 6×10^5 s. The effective cooling (heating) rate is about 10^{-3} K/s. The shape of the sample cells was that of a long cylinder with a demagnetizing factor $N_d \approx 0.7$. The exception was the measurement for the densest sample with $\rho^* \approx 0.3$. This measurement was also conducted by using a toroidal cell because the demagnetizing field becomes comparable to the applied field when the susceptibility becomes quite large in the cylindrical cell. To conduct the measurement using the toroidal cell, the thermal cycle was limited in the temperature range between 278 and 327 K.

We will begin the discussion by the estimation of relaxation time τ and static susceptibility χ_s, because it is ineffectual to analyze the temperature dependence of the ac susceptibility $\chi' + i\chi''$ immediately, as stated above. Figure 1 shows a typical frequency dependence of ac susceptibility, which was observed for a diluted sample with $\rho^* \approx 0.09$ at 300 K on cooling and reheating. We can find that the dependence is similar to that expected for the Debye's relaxation. For the Debye's relaxation, the relationship $\tau = (1/2\pi) f_{\max}^{-1}$ holds, where $f_{\max}$ is the frequency at which out-of-phase component χ'' shows a maximum. Because χ'' for all the samples has a narrow peak at each temperature as shown in Fig. 1, it is easy to estimate $f_{\max}$ except at the lower temperatures where $f_{\max}$ is out of the observed range. Since a narrow peak of χ'' indicates a narrow distribution of τ, we can consider $(1/2\pi) f_{\max}^{-1}$ as typical relaxation time $\langle\tau\rangle$ without discussing the distribution. As an example, $\langle\tau\rangle$ is shown in the inset for the sample with $\rho^* \approx 0.09$. On the other hand, we can extract χ_s from the frequency dependence of ac susceptibility in the following relationship. For the Debye's relaxation, χ_s is given by the intercept of the χ' axis at the low-frequency side in the Cole-Cole plot [19]. Figure 2 shows the Cole-Cole plots of ac susceptibility for the same sample as shown in Fig. 1. It is found that the results obtained at low frequencies are

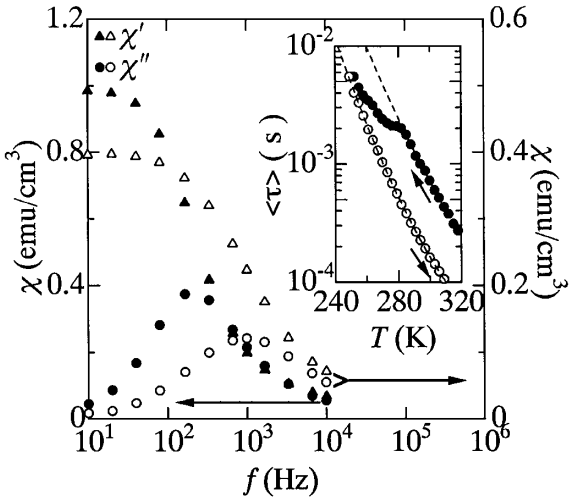

FIG. 1. ac susceptibility $\chi' + i\chi''$ for the sample with $\rho^* \approx 0.09$ at 300 K in the zero field. The solid symbols show the results on cooling, while the results on reheating are shown by using open symbols. The inset shows the typical relaxation time $\langle\tau\rangle$ estimated by the frequency at which χ'' has a maximum.

on circular arcs and that the intercepts can be estimated by their extrapolations. Here, we note that the estimation becomes difficult at lower temperatures, because the observable range between 10 Hz and 10 kHz is not suited to the extrapolation when the relaxation slows down too much. Figures 3 and 4 show χ_s that can be estimated at higher temperatures. Having identified $\langle\tau\rangle$ and χ_s, we can now answer the questions posed at the beginning of this Letter.

The first question is whether the particles in magnetic fluids with low densities condense into droplets or associate into chainlike clusters. Figure 3 shows χ_s for the diluted samples with $\rho^* \approx 0.004$ and $\rho^* \approx 0.09$ in the thermal cycles. It can be found that χ_s shows a thermal hysteresis. Obvious variations of its temperature dependence occur suddenly. For easy understanding, the sketches show schematized results including extrapolated ones. Regarding the dynamic behavior, we also find a thermal hysteresis of $\langle\tau\rangle$, as shown in the inset of Fig. 1. The results stated here clearly indicate that there is a

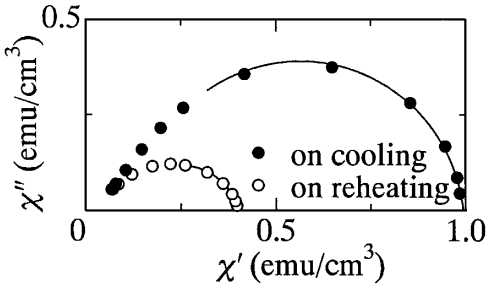

FIG. 2. Cole-Cole plots of the same $\chi' + i\chi''$ as shown in Fig. 1. The solid lines show the extrapolations by using circular arcs.

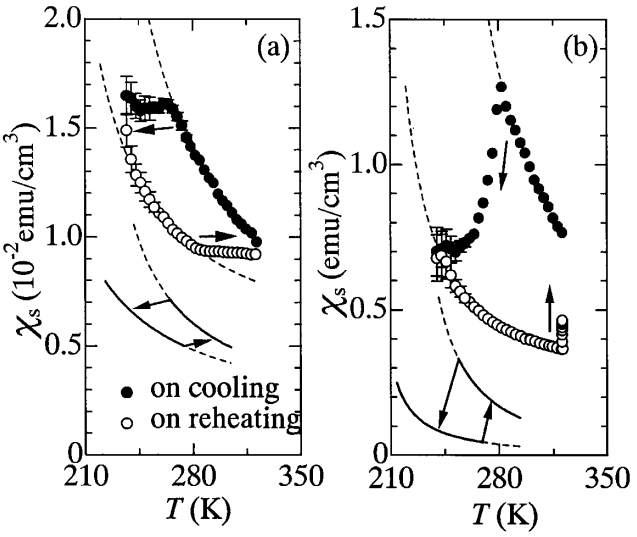

FIG. 3. Static susceptibility χ_s for the diluted samples (a) with $\rho^* \approx 0.004$ and (b) with $\rho^* \approx 0.09$ in the thermal cycle between 321 and 210 K. In addition, (b) shows the results when the measurement was continued at 321 K after the cycle. The broken lines are guidelines. The sketches show schematized results.

temperature-induced first-order phase transition at $T^* = 0.1-0.3$. The following features are obvious in the figures: (a) χ_s of the low-temperature phase are relatively smaller than that of the high-temperature phase (see Fig. 3); (b) χ_s increases with decreasing temperature even in the low-temperature phase (see Fig. 3); (c) $\langle\tau\rangle$ of the low-temperature phase is relatively shorter than that of the high-temperature phase (see Fig. 1, inset). Such transitions were also found for the samples with $\rho^* \approx 0.03$, 0.06, and 0.11. The transition temperatures for $\rho^* \approx 0.03$ and 0.06 are comparable to that for $\rho^* \approx 0.09$, while the transition for $\rho^* \approx 0.11$ seems to occur at the lower temperatures as seen for $\rho^* \approx 0.004$. For the samples with higher densities $\rho^* \approx 0.13$ and 0.2, we cannot find apparent hystereses for χ_s and $\langle\tau\rangle$ in the observable range.

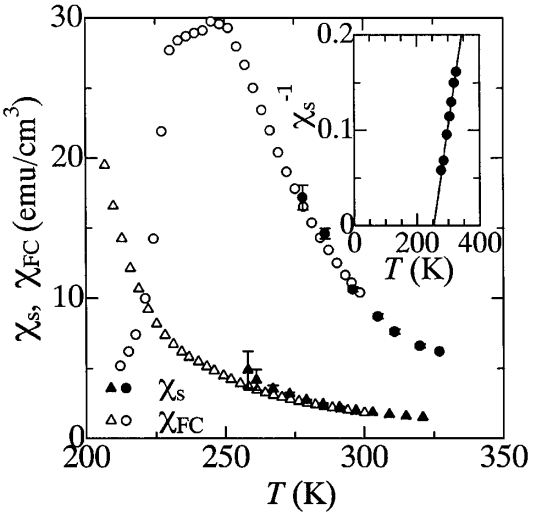

FIG. 4. Static susceptibility χ_s and field-cooled susceptibility χ_{FC} for the dense samples on cooling. Because there is no hysteresis, χ_s on reheating is omitted. The triangles show the results for the slightly diluted sample with $\rho^* \approx 0.2$, while the circles show the results for the densest sample with $\rho^* \approx 0.3$. The inset shows the reciprocal static susceptibility $1/\chi_s$ for the sample with $\rho^* \approx 0.3$.

Following is a comparison of the observed features and the predictions for association into chainlike clusters. Some theoretical studies have pointed out the possibility that free particles associate into chainlike clusters as a phase transition [5,6]. The microscopic structure of chainlike clusters resembles that of a polydisperse mixture of living linear polymers and ring polymers [2]. A transition has been predicted to occur within the ranges $T^* = 0.11-0.16$ and $\rho^* = 0.005-0.2$ [5]. In our study, the transitions were observed within a similar range, which would support the prediction. Furthermore, feature (a) supports the prediction as well, since closed chains such as rings have little total magnetization in the zero field. Feature (b) indicates that dipole moments on some particles do not lose the rotational degrees of freedom completely even in the low-temperature phase. In the phase containing chainlike clusters, this must be attributed to the rotations or deformations of open chains with total magnetization. In this description, feature (c) can be accounted for by assuming that the rotations or deformations of chains are faster than the rotations of free particles. However, this assumption cannot be readily accepted. Therefore, we will examine the condensation of particles instead.

Several kinds of liquid-gas phase coexistence have been discussed [3,4,7–10]. Here we will compare the observed features with the simplest predictions of usual coexistence [9]. Because the phase separation is expected for a system with $\rho^* \sim 0.1$ at about $T^* \sim 0.2$, the observed range is consistent. Since some particles condense into microdroplets in the low-temperature phase, the magnetic flux should be closed in each droplet with high susceptibility. In other words, the droplets do not have total magnetization in the zero field. This can explain feature (a). On the other hand, the other particles remain free in the surrounding gas phase. Feature (b) can be attributed to their rotations. The particle density in the gas phase is lower than the density in the uniform phase. It is reasonable that their rotations become slightly faster when the particle density decreases, which could explain feature (c). Therefore, we now find a prediction that can account for all the features. However, it is difficult to give a full description by using the complicated predictions of phase coexistence in recent studies [7,8], because the detailed comparison requires exact knowledge of T^*, ρ^*, 4ε, and the shape of particles. Needless to say, no samples contain completely spherical particles with strictly uniform size. Furthermore, we must consider the effects of the fluctuation of dipole moments

by the Néel mechanism [21], because most of the models do not take it into account. Therefore, we leave room for further studies on the first question.

The second question to discuss is whether or not magnetic fluids with high particle densities have a ferromagnetic liquid phase in the zero field. Figure 4 shows the temperature dependence of static susceptibility χ_s for the dense samples. It can be observed that χ_s for the sample with $\rho^* \approx 0.3$ dramatically increases without anomaly as the temperature decreases from 327 to 278 K. This result indicates dominance of the ferromagnetic fluctuation in the temperature range $T^* \sim 0.2$. The trend of χ_s is more clearly shown by using the variation of $1/\chi_s$ in the inset. If the trend is extrapolated to the slightly lower temperatures, divergence of χ_s is expected at temperature $\theta \approx 250$ K. What has to be noticed here is not the linear variation of $1/\chi_s$. We should notice that the extrapolation in the narrow range gives considerable validity to the divergence of χ_s at θ, in contrast with the uncertainties of positive or negative ordering temperatures T_0 estimated by the Curie–Weiss-like behavior at much higher temperatures compared to T_0 [15,16]. Therefore, a ferromagnetic transition suggested by the divergence is worth discussing for the sample with $\rho^* \approx 0.3$.

Now, we will focus on whether or not any ferromagnetic phase exists at lower temperatures. However, we cannot prove its existence by discussing the magnetization curves as stated at the beginning. Furthermore, the temperatures discussed here are too low to estimate χ_s. For this reason, we shall discuss magnetization M_{FC} after cooling in a constant field $H = 10$ Oe, although the behavior of M_{FC} is not static in a strict sense. Since M_{FC} cannot be measured by using the toroidal cell, the cylindrical cell was used even for the densest sample. For this reason, we must accept some uncertainty of the field-cooled susceptibility $\chi_{\mathrm{FC}} = M_{\mathrm{FC}}/(H - N_d M_{\mathrm{FC}})$ originating from the lack of exact N_d for the cylindrical cell, when χ_{FC} is large enough. Figure 4 shows χ_{FC} for dense samples. The plateau of χ_{FC} in the vicinity of 240 K may come from the uncertainty. However, there is no doubt about the fall of χ_{FC} with decreasing the temperature below 230 K. This behavior indicates that the phase at lower temperatures is different from the high-temperature phase, although the observed behavior of χ_{FC} seems different from that of usual ferromagnets.

For the system with $\rho^* = 0.3$, Klapp and Forstmann [6] have predicted the dominance of the ferromagnetic fluctuation in the vicinity of $T^* \sim 0.26$. On the other hand, they have shown that the low-temperature phase of this system is different from the usual ferromagnetic liquid phase. These predictions are consistent with the experimental results observed here. However, what happens in the low-temperature phase is still debatable. Zhang and Widom have predicted that a ferromagnetic liquid coexists with an isotropic fluid in the systems with slightly lower densities $\rho^* \sim 0.2$ [4]. Although this prediction is suggestive, the experimental information is too little to discuss the nature of the low-temperature phase. Because studies on ferromagnetic liquid have just been started, much remains to be done. At this point, we can only report the dominance of the ferromagnetic fluctuations for the densest sample, which is considered as a symptom of the usual ferromagnetic liquid phase.

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