Aging in a Magnetic Particle System

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The influence of dipolar interaction in a frozen ferrofluid has been experimentally studied. The ferrofluid consisted of particles of γ- Fe_2O_3 with mean diameter 70 Å. Four samples with volume concentration of magnetic particles ranging from 0.03% to 17% have been investigated. The magnetic relaxation of the most concentrated particle system shows typical spin glass dynamics at low temperature, e.g., the relaxation depends on the time spent at constant temperature before applying the magnetic field—the system ages. The most diluted sample shows isolated particle dynamics and no aging.

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By simple dilution, a concentrated ferrofluid offers a continuously tunable strength of interparticle dipole-dipole interaction and is thus ideally suited for studies of the influence of this unavoidable interaction on the magnetic properties of small magnetic particle systems. A frozen, strongly diluted, ferrofluid is an experimental model system for superparamagnetism. The static and dynamic magnetic properties of such a system are governed by the size distribution and physical characteristics of the individual magnetic particles contained in the fluid, and the dynamics is described by the Néel theory for noninteracting magnetic particles [1]. The equilibrium low field susceptibility follows a simple Curie law, and the relaxation time τ of a magnetic particle increases with decreasing temperature according to

$$\tau = \tau_0 \exp(E/kT), \quad (1)$$

where τ_0 is a microscopic relaxation time and E the energy barrier for flipping the magnetic moment of the particle. Reducing the temperature of an ensemble of noninteracting particles results, on the finite time scale of an experimental probe, in a progressive blocking of the particle magnetic moments along their anisotropy axes and hence at low temperatures in a frozen disordered arrangement of the particle moments.

Interaction between magnetic entities causes collective phenomena at low enough temperature, and, if the dimensionality of the interacting system is above the lower critical dimension, it results in an ordered low temperature phase. Random and competing interaction—e.g., RKKY interaction in diluted metal alloys, short range interaction in insulating systems or random dipolar interaction between atomic spins—introduces spin glass behavior. One might thus expect that the interparticle dipole-dipole interaction in a concentrated frozen ferrofluid enforces a spin-glass-like phase to the system at low enough temperatures. Two signifying characteristics of spin glass dynamics are as follows [2]: (i) a continuous closely logarithmic relaxation evolves at low temperatures, beginning at the microscopic spin flip time [3] and ending at a strongly temperature dependent maximum relaxation time (in 3D spin glasses the maximum relaxation time diverges at a finite temperature, whereas in 2D systems it diverges at $T = 0$ K) and (ii) an aging phenomenon appears at low temperatures.

In this Letter, by comparing the dynamics of differently diluted samples of a ferrofluid, we show that the interparticle dipole-dipole interaction causes spin glass dynamics. The measurements were performed on an ferrofluid [4] consisting of closely spherical particles of maghemite, γ-Fe_2O_3, with a mean diameter of 70 Å. The particles are suspended in a hydrocarbon oil that freezes at a temperature around 180 K. Hence, at lower temperatures, the easy axis of each particle moment is fixed in a random direction. The saturation magnetization of bulk maghemite is $M_s = 4.2 \times 10^5$ A/m and the critical temperature 860 K [5]. Employing these values also for small particles, the magnetic moment of an average-sized single domain particle at low temperatures is $\overline{\mu} \approx 10^4 \mu_B$, and it remains essentially constant below 100 K. The concentrated ferrofluid contains 17% particles by volume. By successive dilution of this ferrofluid, also samples of volume concentration $\varepsilon = 3\%$, 0.3%, and 0.03% were prepared. Using the average moment and mean distance r between the particles, the magnitude of the dipole interaction between two neighboring particles in the different samples can be estimated from the relation $E_d = (\mu_0/4\pi k_B)\overline{\mu}^2/r^3$. This gives $E_d \approx 0.05$, 0.5, 5, and 28 K, respectively, starting from the most diluted sample.

The experiments were performed using two different magnetometer systems. All ac susceptibility measurements were performed in a LakeShore 7225 ac susceptometer system. Magnetic relaxation and magnetization (M) vs temperature measurements were recorded in a noncommercial, low field SQUID magnetometer. This magnetometer is equipped with a small superconducting magnet with a switch time $<10^{-3}$ s allowing for reliable time dependent magnetization measurements on time scales starting from 3×10^{-1} s after the field change has been made. In the M vs T measurements, the sample was cooled in zero field to a low temperature where the

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magnetic field was applied. The magnetization was then recorded on heating the sample to a high temperature [zero field cooled (ZFC)] and on cooling in the field [field cooled (FC)]. All measurements were made using quite low magnetic fields ($\leq$3 Oe) to avoid nonlinear effects.

The properties governing the relaxation time of a small particle are its anisotropy and volume, $E = KV$ in Eq. (1), where K is the anisotropy constant and V the volume of the particle. The effective magnetic anisotropy energy of our ferrofluid was estimated from experimental results on the most dilute sample ($\varepsilon = 0.03\%$), which models a system of noninteracting particles. Using the fact that the particle volumes are approximately log-normally distributed, the temperature and frequency dependences of the ac susceptibility can be calculated and fitted to the experimental curves [6]. A good fit was obtained using the value $K = 1.9 \times 10^4$ J/m^3 for the anisotropy constant that corresponds to $E_a = KV_m \approx 250$ K for a particle of size equal to the average particle volume.

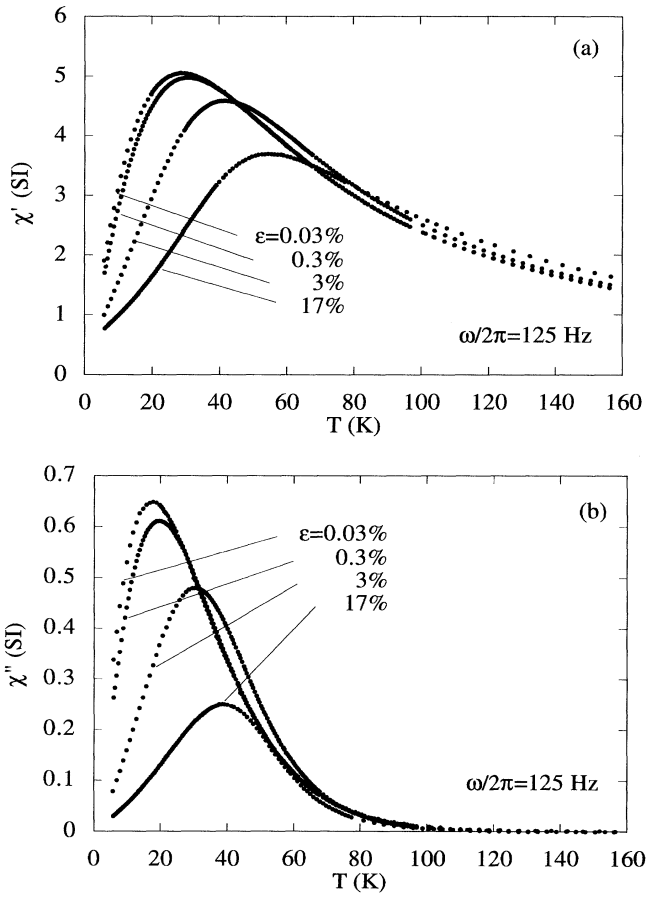

FIG. 1. The temperature dependence of the in- (a) and out-of-phase (b) components of the ac susceptibility at frequency $\omega/2\pi = 125$ Hz for samples with different volume concentration ε of particles. The measured values of the volumes susceptibility for the different samples have been normalized by the factor $17\%/\varepsilon$. $h_{ac} = 1$ Oe.

In Figs. 1(a) and 1(b) the in-phase, $\chi'(\omega)$, and out-of-phase, $\chi''(\omega)$, components of the ac susceptibility are plotted vs temperature for the four samples. There is a striking difference between the susceptibility curves of the three most concentrated samples, whereas the susceptibility of the $\varepsilon = 0.03\%$ and 0.3% samples are closely similar. This shows that the dipole interaction in the most diluted sample has become too weak to influence the measured susceptibility and hence only the dynamics of isolated particles is probed [Eq. (1)]. With increasing volume concentration of particles, i.e., increasing dipole-dipole interaction, the peak in both the in-phase and out-of-phase components of the ac susceptibility shifts to higher temperatures.

In Fig. 2 the FC and the ZFC magnetization are plotted vs temperature for the most diluted and the most concentrated samples. The cooling/warming rate was $\sim$0.3 K/min and the applied magnetic field 3 Oe. The in-phase component of the ac susceptibility at $\omega/2\pi = 125$ Hz has also been included in the figure. For the diluted sample the irreversibility between the FC and ZFC curves occurs at approximately 40 K, while the corresponding temperature for the concentrated sample is around 55 K. There is also a striking difference between the two FC curves where the increase of the magnetization for the concentrated sample levels off at low temperatures in contrast to the diluted sample that shows a continuous, rather steep, increase of the magnetization with decreasing temperature.

We now turn to the prime dynamic spin glass characteristic, aging [2,7]. The very existence of an aging phenomenon unequivocally distinguishes correlated dynamics from only individual particle relaxation. To investigate if magnetic dipole-dipole interaction imposes aging effects upon frozen ferrofluids, time dependent magnetization measure-

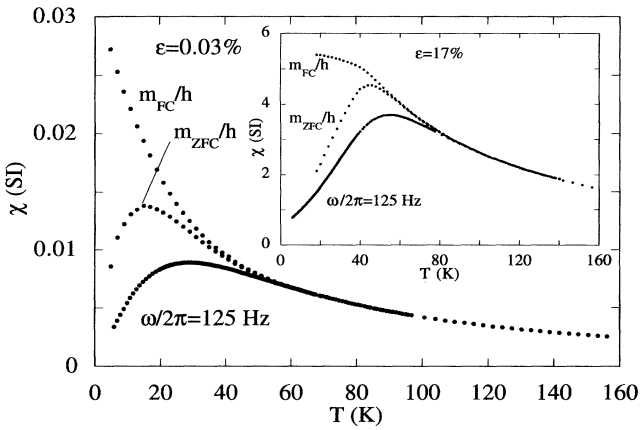

FIG. 2. Temperature dependence of the field cooled (FC) and zero field cooled (ZFC) susceptibility (m/h) for the $\varepsilon = 0.03$ and the $\varepsilon = 17\%$ (inset) samples. $h = 3$ Oe. The in-phase components of the corresponding ac susceptibility at $\omega/2\pi = 125$ Hz and $h_{ac} = 1$ Oe are also included.

ments for the most concentrated sample and the most diluted sample were performed. The sample was cooled in zero field from a temperature where it shows a reversible superparamagnetic behavior, in this case 70 K, to a measurement temperature, T_m. After a wait time t_w, at T_m, a small probe field h was applied and the magnetization m was recorded vs time t. To illustrate a wait time dependence of the relaxation it is convenient to use the relaxation rate S defined according to $S = (1/h)\partial m/\partial \ln(t)$. In Figs. 3(a)–3(c) the relaxation rate at different wait times is plotted vs the logarithm of observation time at three temperatures: $T_m = 15$, 25, and 35 K. The wait times used at each temperature were $t_w = 10^2$, 10^3, and 10^4 s, and the magnetic field was $h = 2$ Oe. It is clearly seen from the different curves that the magnetic relaxation depends on the wait time. For the diluted sample, the corresponding experiment has been performed at $T_m = 20$ K. The relaxation rates for this sample are shown in Fig. 3(d). In contrast to what is observed for the concentrated sample the relaxation is independent of the wait time; i.e., aging exists. The relaxation is only governed by thermally activated dynamics of individual particles.

To visualize the evolution of the dynamic response of a slowly relaxing system with temperature or interaction strength, it is also quite illustrative to plot the relaxation rate vs $\log(t)$. The available time window can be enlarged by employing the "$\pi/2$ law" relating the relaxation rate to the out-of-phase component of the ac susceptibility [8], $\chi''(\omega) \approx \pi/2\, S(t)$, $t \approx 1/\omega$. Using this method for our ferrofluid we can plot the relaxation rate of the "noninteracting" and the strongly interacting system at the same temperatures and immediately observe the effect on the dynamic response of imposing dipolar interaction upon the system. In Fig. 4 the relaxation rate is plotted vs t for the most concentrated and most diluted samples at two temperatures, 20 K (filled symbols) and 35 K (open symbols). The squares represent experimental χ'' data obtained for the most dilute sample and circles the corresponding data for the most concentrated sample. The triangles represent relaxation rates for the most concentrated sample extracted from the magnetic relaxation measurements (at $t_w = 10^4$ s). The solid and dashed lines are calculated relaxation rates for noninteracting particles at 20 and 35 K, respectively. These curves have been extracted

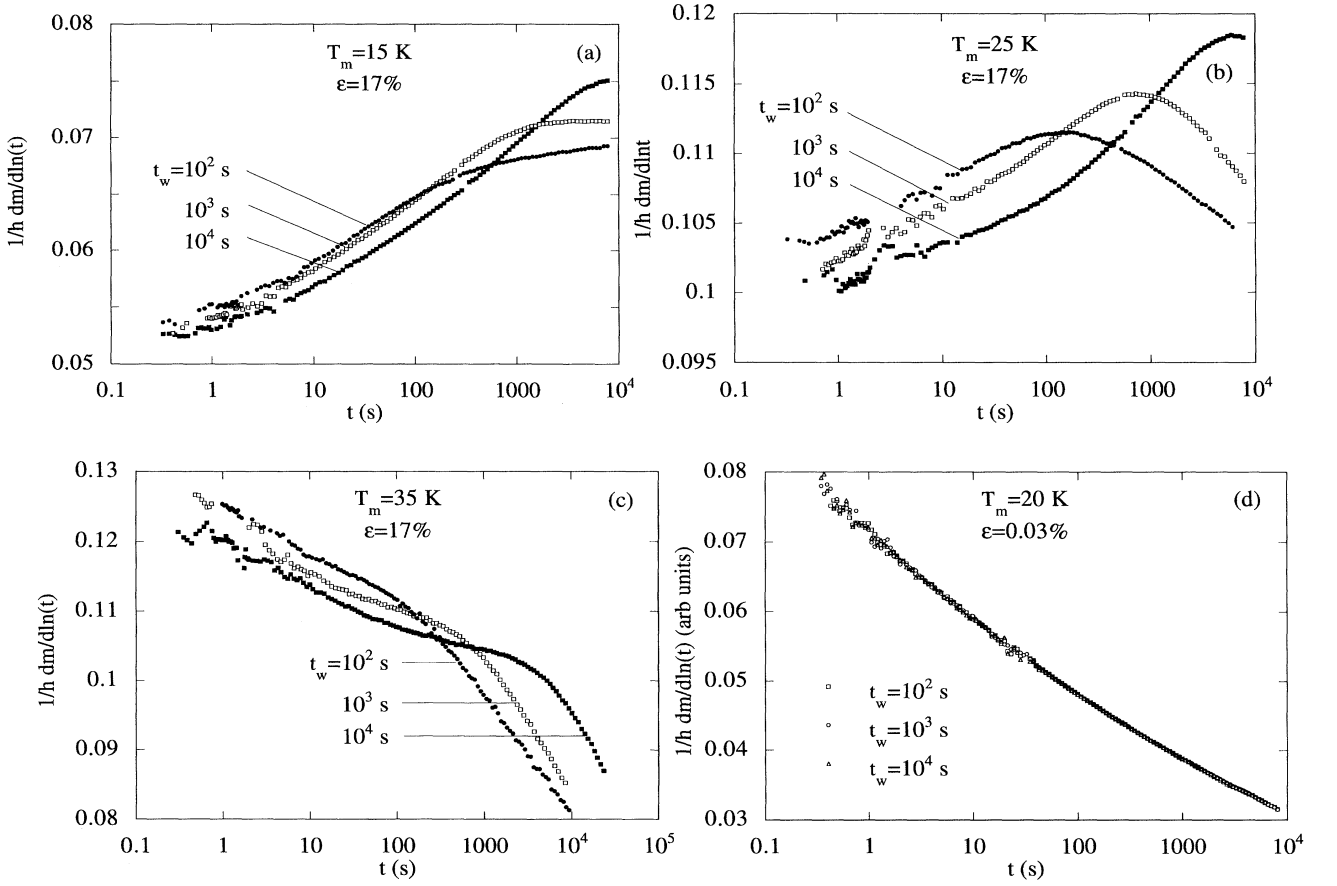

FIG. 3. The relaxation rate S vs $\log(t)$ at different wait times t_w and different temperatures, for the concentrated sample 15 K (a), 25 K (b), and 35 K (c), for the most diluted sample 20 K (d). $h = 2$ Oe.

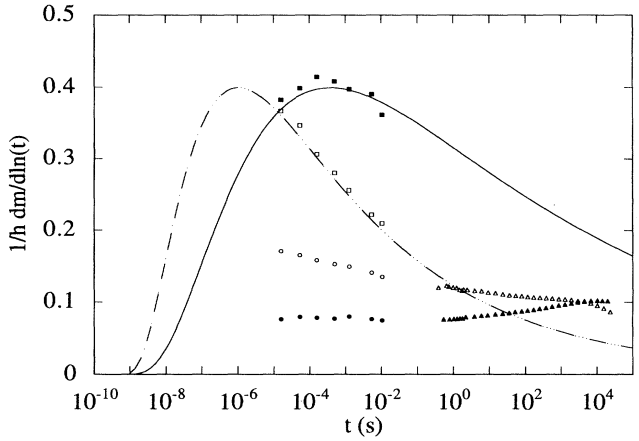

FIG. 4. Relaxation rates vs $\log(t)$ at 20 K (filled symbols) and 35 K (open symbols), for the $\varepsilon = 17\%$ sample from ac susceptibility at different frequencies (circles) and form ZFC-relaxation measurements (triangles); and for the $\varepsilon = 0.03\%$ sample from ac data (squares). The solid (20 K) and dashed (35 K) lines are calculated curves for noninteracting particles using a log-normal distribution of the particle volume. The data for the $\varepsilon = 0.03\%$ sample are normalized by the factor 17/0.03.

from the $\chi''(\omega)$ results using a log-normal distribution of particle volumes [6]. It is clearly seen from this figure that the collective behavior introduced by dipole-dipole interaction in the most concentrated sample extends the magnetic relaxation towards longer times and at the same time suppresses the relaxation at short observation times—a behavior that conforms to characteristic spin glass dynamics.

So far we have focused on the similarities of the low temperature dynamics in an interacting small particle system and spin glass dynamics. These imply that the correlation between the particle moments develops in a similar way as the correlation between the spins in spin glasses. It also means that when interpreting the dynamic behavior of interacting magnetic particle systems the effects of spin-glass-like correlations should be accounted for, as well as possible modifications of the energy barriers of individual particles [9]. However, the existence of characteristic spin glass dynamics in a magnetic system does not by itself imply that there is a thermodynamic spin glass phase at low temperatures.

The most evident difference between the magnetic particle system and an ordinary spin glass is that the particle volume is broadly distributed and that the magnetic moments of these are some orders of magnitude larger than an atomic spin [10]. In spin glasses the atomic spin flip time remains essentially constant ($\sim 10^{-13}$ s) down to low temperatures, also through the spin glass transition temperature where $\tau_{\max}$ diverges in zero field for 3D systems. In analyzing ac susceptibility or magnetic relaxation experiments, there is thus no possibility to confuse the slow dynamics due to correlations with the single spin flip time. In small particle systems the particle "flip" time develops essentially according to Eq. (1) and for larger particles it exceeds our experimental time window already at rather high temperatures (see Figs. 2 and 4). As can be seen from Fig. 4, there is an overlap between the increasing relaxation time of individual particles and the broadening towards longer times due to spin-glass-like correlations. At lower temperatures a large part of the particles are blocked in the time window where our experiments are made (at $T = 15$ K, particles with diameters $d > 8.5$ nm have relaxation times $>10^3$ s). In fact, on all experimental time scales, large enough particles are blocked and act as "temporary" random fields in the system. Whether such temporary fields eventually even impede a thermodynamic spin glass phase at low temperatures is difficult to judge from experiments [11], but might have a theoretical answer.

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