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# Slow relaxation in ferromagnetic nanoparticles: Indication of spin-glass behavior

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We use Monte Carlo simulations to study the influence of dipolar interactions and polydispersion on the magnetic relaxation of single-domain ferromagnetic particles below the blocking temperature. We find the surprising result that for all particle densities the relaxation rate decays by a power law, with a density-dependent exponent *n* and a temperature-dependent prefactor. Depending on the value of *n*, the relaxation function shows a simple exponential decay, a stretched exponential decay, or a power-law decay, and seems to approach a finite remanent magnetization at high densities. We interpret the results for intermediate and large densities as indications of spin-glass behavior.

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In the last decade, magnetic nanoparticles have received considerable interest, due both to their important technological applications (mainly in magnetic storage and recordings) and their rich and often unusual experimental behavior, which is related to their role as a complex mesoscopic system.[1] An important scientific question concerns the relaxation behavior of an assembly of magnetic particles; the problem is also of practical relevance, since it is related to the way recorded patterns decay.[2] Experimentally, after switching off the magnetic field, the remanent magnetization decays very slowly with time. There is no clear answer to the functional form of the decay, and usually the remanent magnetization has been fitted by a logarithmic time dependence or by exponentials with specific relaxation time distributions, e.g., gamma distribution functions.[3–7] In general, the problem is difficult and not always well defined, since the magnetic nanoparticles are polydisperse and sometimes the shape and size of the particles are not well known. In addition, the particles may form long chains or other types of aggregates, and apart from the dipolar interaction between the magnetic nanoparticles other types of interactions, for example exchange or superexchange interactions, may also become relevant.[8,9] Moreover, it is not clear if, in some relaxation phenomena at low temperature, quantum tunneling is involved or not.[8,10]

Related to the relaxational behavior is the question of the magnetic structure of the system. It is a matter of controversy if, at large concentrations of nanoparticles at temperatures well below the blocking temperature $T_B$, a spin-glass phase exists or not. While some experiments present indications of a spin-glass phase,[7,11] others favor the existence of a random anisotropy system.[12] On the theoretical side, the problem is also open. While Monte Carlo simulations on aging[13] seem to favorize the spin-glass hypothesis, simulations of the zero-field cooling and field-cooling susceptibility showed no indication of a spin-glass phase.[14]

To gain insight into the slow magnetic relaxation and the underlying magnetic structure, we focus on perhaps the most basic model of magnetic nanoparticles, which (i) assumes a coherent magnetization rotation within the anisotropic particles, and (ii) takes into account the magnetic dipolar interaction between them. We consider both monodisperse and polydisperse systems where the particles are arranged as in a frozen liquid and are randomly oriented. To study the slow magnetic relaxation we have employed Monte Carlo simulations. As been shown in Ref. 15, the Monte Carlo method is well suited to treat the relaxation of magnetic particles when the Monte Carlo time steps are large compared with the precession time of the magnetic moments. Alternative molecular-dynamic simulations are not useful for treating slow relaxational processes, since the accessible time scales are too short. We find that, below $T_B$, the relaxation function depends crucially on the concentration of the magnetic particles and thus on the strength of the dipolar interaction. In the dilute limit, the remanent magnetization decays exponentially for monodisperse particles and in a stretched exponential fashion for polydisperse particles. With increasing density, we observe the following scenario: (i) stretched exponential decay at low densities, (ii) a power-law decay at intermediate densities, and (iii) relaxation toward a nonvanishing remanent magnetization at very high densities. We consider this scenario, in particular steps (ii) and (iii), as clear indications of a spin-glass phase.[3,16–18]

For the numerical calculation, we use the same model as in Ref. 14, where every particle *i* was considered to be a single magnetic domain with all its atomic magnetic moments rotating coherently. This results in a constant absolute value $|\mu_i| = M_s V_i$ of the total magnetic moment of each particle, where $M_s$ is the saturation magnetization, which is supposed to be independent of the particle volume $V_i$. The energy of each particle *i* consists of three contributions: anisotropy energy, field energy, and dipolar interaction energy. We assume a temperature independent uniaxial anisotropy energy $E_A^{(i)} = -KV_i((\boldsymbol{\mu}_i \mathbf{n}_i)/|\boldsymbol{\mu}_i|)^2$, where $K$ is the anisotropy constant and the unit vector $\mathbf{n}_i$ denotes the easy directions. As usual, the coupling to an applied external field $\mathbf{H}$ is described by the field energy $E_H^{(i)} = -\boldsymbol{\mu}_i \mathbf{H}$, and the energy of the magnetic dipolar interaction between two particles *i* and *j* separated by $\mathbf{r}_{ij}$ is given by $E_D^{(i,j)} = (\boldsymbol{\mu}_i \boldsymbol{\mu}_j)/r_{ij}^3 - 3(\boldsymbol{\mu}_i \mathbf{r}_{ij})(\boldsymbol{\mu}_j \mathbf{r}_{ij})/r_{ij}^5$. Adding up the three energy contributions and summing over all particles we obtain the total energy

$$E=\sum_{i} E_A^{(i)}+\sum_{i} E_H^{(i)}+\frac{1}{2}\sum_{i} \sum_{j\neq i} E_D^{(i,j)}. \tag{1}$$

In the Monte Carlo simulation we concentrate on samples of $N=64$ particles placed in a liquidlike arrangement with periodic boundary conditions (a doubling of the system size showed no significant difference in the results). The volumes $V_i$ are considered as (i) monodisperse or (ii) polydisperse with a distribution of volumes $V_i$ drawn from a normal distribution $P(V)\propto\exp\{-(V-\overline{V})^2/(2\sigma_V^2)\}$, with fixed width $\sigma_V=0.4$ and a normalized mean volume $\overline{V}$. The anisotropy axis is chosen randomly, and the easy axis vector $\mathbf{n}_i$ is defined to be parallel to the easy axis with a positive $z$ component. The unitless concentration $c$ is defined as the ratio between the total volume $\Sigma_i V_i$ occupied by the particles and the volume $V$ of the sample. We varied the concentration from the dilute limit ($c\rightarrow 0$) to very dense systems with $c=0.384c_0$, where $c_0\equiv 2K/M_s^2$ is a dimensionless constant specific for each material, $c_0\cong 1.4$ for iron nitride and $c_0\cong 2.1$ for maghemite nanoparticles.[19] The relaxation of the individual magnetic moments per time step (Monte Carlo step) $t$ is simulated by the standard Metropolis algorithm, and the interaction energies are calculated using the Ewald sum method.[14,20]

To study the magnetic relaxation we first align all moments $\boldsymbol{\mu}_i$ along the $z$ direction by applying a strong external field. At a time $t=0$ we switch off the field and determine the normalized remanent magnetization

$$m(t)=\frac{1}{N}\sum_{i=1}^{N}\frac{V_i}{\overline{V}}\cos\theta_i(t)$$

as a function of time, where $\theta_i$ is the angle between the magnetic moment of particle $i$ and the $z$ axis. By definition, $m(0)=1$. In our analysis, we follow early works,[3,21] and focus on the relaxation rate $W(t)$, which is related to $m(t)$ by $W(t)=-(d/dt)\ln m(t)$, or

$$m(t)=\exp\left[-\int_0^t W(t')dt'\right]. \tag{2}$$

For the relevant case of a power-law decay of $W(t)$ above some crossover time $t_0$,

$$W(t)=At^{-n}, \quad t\geqslant t_0, \tag{3}$$

we obtain, well above $t_0$,

$$\frac{m(t)}{m(t_0)}\simeq\begin{cases} \exp\left[-c_n\left(\dfrac{t}{t_0}\right)^{1-n}\right], & 0\leqslant n<1 \quad \text{(a)}\\ \left(\dfrac{t}{t_0}\right)^{-A}, & n=1 \quad \text{(b)}\\ e^{-c_n}\left[1+c_n\left(\dfrac{t}{t_0}\right)^{1-n}\right], & n>1, \quad \text{(c)} \end{cases} \tag{4}$$

with $c_n=At_0^{1-n}/|1-n|$. For $n>1$, according to Eq. (4c), $m(t)$ approaches the finite value

$$m(\infty)=m(t_0)\exp[-At_0^{1-n}/|1-n|]. \tag{5}$$

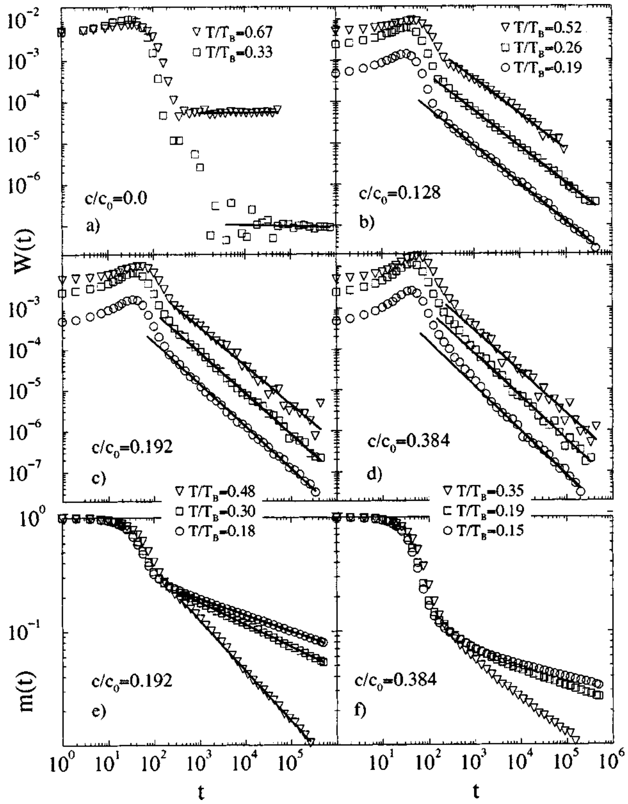

FIG. 1. Monodisperse systems. Relaxation rate $W(t)$ in (a) the dilute limit, and for (b)–(d) increasing density with volume fraction $c/c_0$ for different reduced temperatures $T/T_B$. Corresponding remanent magnetization $m(t)$ for the two most dense systems [(e) and (f) correspond to the relaxation rates in (c) and (d)]. The solid lines correspond to the power-law regression in (b)–(d). The $W(t)$ curves of the two lowest temperatures are shifted by factors of 0.5 and 0.1, respectively.

In the following we will show explicitly that the decay of the remanent magnetization well below $T_B$ indeed follow the scenario described by Eq. (3), with $n=0$ for dilute systems of monodisperse particles, $n\approx 2/3$ for dilute systems of polydisperse particles, and $n\geqslant 1$ for dense systems independently of size distribution.

First we consider monodisperse systems. Figure 1 shows, in a double logarithmic presentation, the relaxation rate $W(t)$ and the remanent magnetization $m(t)$. The relaxation rate $W(t)$ is shown for (a) very diluted systems where the dipolar interaction is negligible and (b)–(d) systems with increasing density where dipolar interactions become increasingly important. We also show the corresponding remanent magnetization $m(t)$ for the two most dense systems [(e) and (f) correspond to (c) and (d)]. The different curves in each figure correspond to different temperatures well below $T_B$ (see Ref. 14). In all curves we can distinguish between two time regimes. In the short-time regime, *intrawell* relaxation occurs, where the magnetic moments $\boldsymbol{\mu}_i$ relax toward the easy axis $\mathbf{n}_i$ of the particles. This motion does not require thermal activation, and thus is independent of temperature. Since it is a local relaxation, it depends only weakly on the concentration of particles. In the second time regime, which occurs after about $10^2$ time steps, *interwell* relaxation takes place where the magnetic moments try to overcome the local potential barrier.

For very dilute systems [Fig. 1(a)], the potential barriers are determined solely by the anisotropy energy of each particle $i$, $KV_i$. In this case $W(t)$ becomes a constant at large times, i.e., $n=0$, giving rise to the (expected) simple exponential relaxation of $m(t)$. With increasing concentration $c$, cooperative effects set in and $W(t)$ shows a power-law behavior, $W(t)\propto t^{-n}$, with an increasing exponent $n$. For $c/c_0=0.128$ [Fig. 1(b)], we see a power-law behavior over more than three decades, with $n$ around 0.9 for all temperatures considered. The slowing down of the relaxation with decreasing temperature is due to the prefactor $A$ in $W(t)$, which decreases with decreasing temperature. For $c/c_0=0.192$, $W(t)$ decays simply as $1/t$ for all temperatures [Fig. 1(c)]. According to Eq. (4b), this leads to a power law decay of the remanent magnetization $m(t)\propto t^{-A}$, which also can be observed directly when plotting $\log[m(t)]$ vs $\log(t)$ [Fig. 1(e)]. The exponent $A$ decreases with decreasing temperature, $A\cong 0.45$, 0.19 and 0.14 for $T/T_B=0.48$, 0.30, and 0.18 respectively. For very dense systems [Figs. 1(d) and 1(f)] the relaxation rate seems to decay faster than $1/t$, with exponents $n$ around 1.1 for all temperatures considered. According to Eq. (4c) we may expect a nonvanishing remanent magnetization in this case. The value of $m(\infty)$ is not directly accessible, but can be estimated from Eq. (5). We obtain $m(\infty)\cong 10^{-8}$, $5\times 10^{-3}$, and $10^{-2}$ for $T/T_B=0.35$, 0.19, and 0.15.

Next we consider the more realistic case of a polydisperse system of particles. The broad distribution of particle sizes leads to a broad distribution of individual particle barriers $KV_i$. Accordingly, in the dilute limit the relaxation rate $W(t)$ is also no longer a constant. We find that asymptotically $W(t)$ decays by a power law, which becomes more pronounced at lower temperatures, with an exponent $n$ close to 2/3. With increasing concentration we obtain qualitatively the same picture as for monodisperse systems. For $c/c_0=0.128$ [Fig. 2(b)], $W(t)$ shows a clear power-law decay over nearly four orders of magnitude where the exponent $n$ has already reached 1. Accordingly, the remanent magnetization decays with a power law $m(t)\propto t^{-A}$. As for the monodisperse case, the exponent $A$ decreases with decreasing temperature, $A\cong 0.33$, 0.16, and 0.11 for $T/T_B=0.49$, 0.24, and 0.18, respectively. With higher concentrations, $W(t)$ seems to decay faster than $1/t$. For $c/c_0=0.192$ [Figs. 2(c) and 2(e)] we find $n\cong 1.05$, while for $c/c_0=0.384$ [Figs. 2(d) and 2(f)] we find $n\cong 1.11$ for all temperatures considered. From the values for $A$, $n$ and $t_0$ we can again estimate $m(\infty)$. For example, for the highest concentration $c/c_0=0.384$ we obtain $m(\infty)\cong 10^{-3}$, $2\times 10^{-2}$ and $3\times 10^{-2}$ at $T/T_B=0.39$, 0.19, and 0.14, respectively.

According to Fig. 2, polydisperse systems follow the same scenario as monodisperse systems when the particle concentration is increased, but the transition from a stretched exponential decay toward a power-law decay occurs at a considerably lower concentration, which should be around 0.15 for iron nitride and 0.25 for maghemite particles. These concentrations are easily experimentally accessible and low enough to guarantee that the dipolar interaction is still the dominant one.

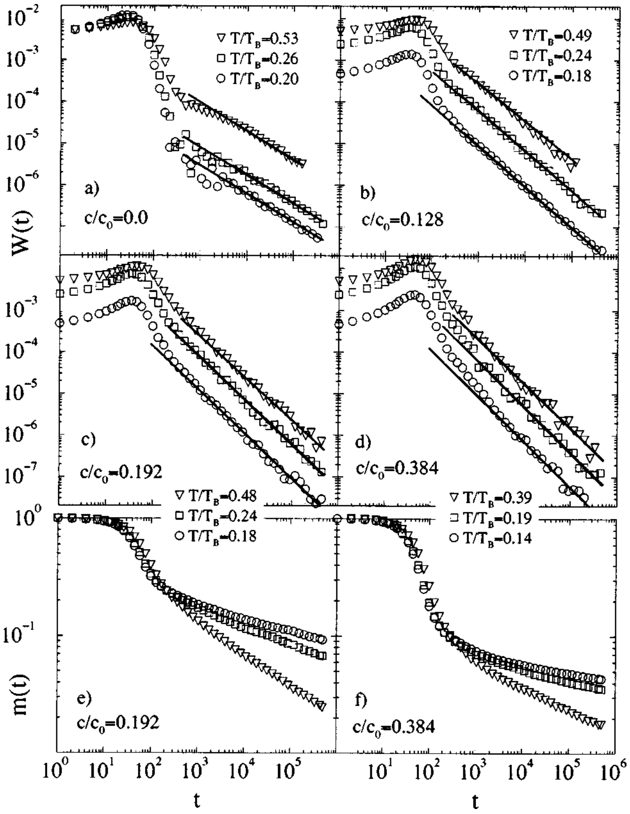

FIG. 2. Polydisperse systems. Relaxation rate $W(t)$ in (a) the dilute limit, and for (b)–(d) increasing density with volume fraction $c/c_0$ for different reduced temperatures $T/T_B$. Corresponding remanent magnetization $m(t)$ for the two most dense systems [(e) and (f) correspond to the relaxation rates in (c) and (d)]. The solid lines correspond to the power-law regression in (b)–(d). The $W(t)$ curves of the two lowest temperatures are shifted by factors of 0.5 and 0.1, respectively.

The ultraslow power-law relaxation observed in Figs. 1(c)–1(f) and 2(b)–2(f) must have its origin in the occurrence of a collective state well below the blocking temperature, which may even hinder all particles to relax fully at high concentrations. In this case, the system attains a very small but finite remanent magnetization, but without long range-order, and seems to approach some glassy ferromagnetic state. Power-law approaches toward a finite magnetization were discussed earlier in the context of the flipping of clusters (see Ref. 16, and references therein), but in contrast to the situation there the exponent $(1-n)$ in Eq. (4c) is practically independent of temperature. The power-law decay at intermediate particle concentration that we find [cf. Eq. (4b)] is reminiscent to the relaxation behavior of canonical spin glasses, where the exponent decreases approximately linear with temperature.[17,18] Having this in mind, we consider the relaxation behavior at intermediate and large concentrations as clear indications of a collective spin-glass-like phase below $T_B$. The stretched exponential behavior that we see at small concentrations has not been assigned to a spin-glass behavior from a theoretical point of view. It has, however, been observed in relaxation experiments on real spin glasses.[16] We hesitate to interpret the stretched exponential decay we observe here as an indication of a spin-glass behavior, since it also occurs in dilute polydisperse systems where cooperative effects are absent.

The interpretation of our results is not in conflict with previous results on field-cooling processes below $T_B$, where monodisperse systems with different initial conditions (demagnetized or saturated sample) were shown to relax toward the same equilibrium point when a weak magnetic field was maintained. This result was interpreted as an indication of the absence of a spin-glass phase. However, as pointed out already by Binder and Young[16] and further elaborated experimentally by Garcia del Muro *et al.*[23] in systems of magnetic fine particles, the collective states of glassy systems can be erased by a magnetic field of moderate strength, and we think that this was the case in the simulations of Ref. 14.

In summary, we have investigated the relaxation behavior of the most basic model for magnetic nanoparticles, that takes into account the polydispersivity and anisotropy of the particles as well as the dipolar interaction between them. We found the surprising result that the relaxation rate, from the dilute limit toward very dense systems, is always characterized by a power-law decay. The exponent $n$ depends strongly on the concentration, the prefactor $A$ depends strongly on temperature, and the crossover time $t_0$, above which the power-law decay can be seen, is nearly independent of the concentration and temperature. Depending on the value of $n$, we observed a simple exponential decay, a stretched exponential decay, or a power-law decay of the relaxation function. For high densities, the power-law decay seems to lead to a finite remanent magnetization. We believe that our results for intermediate and large concentrations of polydisperse particles are clear indications of some type of glassy phase at low temperatures.

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[19] To give an estimate for the concentrations in real units, in iron-nitride nanoparticles we have (Ref. 22) $M_s = 1182$ emu/cm$^3$ and $K = 10^6$ erg/cm$^3$, which yields $c_0 = 1.43$. Maghemite particles with a mean diameter around 7.5 nm reported in Ref. 7 show $M_s = 420$ emu/cm$^3$ and $K = 1.9\times 10^5$ erg/cm$^3$, which give $c_0 = 2.15$. Accordingly the largest concentration in this letter corresponds to $c = 0.55$ for iron-nitride nanoparticles and $c = 0.83$ for maghemite particles.

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