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# Relaxation in interacting nanoparticle systems

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**Abstract**

The effect of interparticle dipolar interaction on the magnetic relaxation of nanoparticle systems is discussed. While weak dipolar interaction can be described by a modified superparamagnetic behavior, experimental studies on strongly interacting nanoparticle systems give evidence for spin-glass-like dynamics in those systems.


*Keywords:* Interparticle dipolar interaction; Magnetic relaxation; Nanoparticle systems

## 1. Introduction

Magnetic relaxation in fine magnetic particle systems has been an active field of research since Neel predicted that the magnetization can overcome the energy-barrier as a result of thermal agitation [1]. The relaxation time of non-interacting particles can be obtained by solving the Fokker–Planck equation for the probability distribution of spin orientations [2]. In the case of particles with uniaxial anisotropy under the influence of a transverse magnetic field, a strong dependence of the relaxation time upon the damping parameter has recently been revealed [3]. The effective dipolar field in interacting nanoparticle systems will always have a transverse component [4], and a strong damping dependence of some physical properties of interacting nanoparticle systems has indeed been observed in Langevin dynamic simulations [5]. Energy based numerical simulations [6] and analytical models [7–9] for weakly interacting nanoparticle systems omit this damping dependence, and can therefore only be valid in the overdamped limit.

There are many applications of densely packed nanoparticle systems, e.g. magnetic storage devices, and it is therefore of interest to know how interparticle interactions affect the magnetic relaxation. While it is possible to treat very weak interparticle interactions by analytical models, the complexity of the problem makes it impossible in the general case. Slightly stronger interactions can be treated by numerical simulations [6,5], while strongly interacting nanoparticle systems so far only have been investigated experimentally. Frozen ferrofluids are ideal systems for studying the effects of interparticle dipolar interaction on the magnetic relaxation, since the strength of the dipolar interaction can be tuned by the particle concentration. It has been shown that strongly interacting nanoparticle systems exhibit non-equilibrium dynamics similar to spin glasses [10–12]. The relaxation is hence fundamentally different from the superparamagnetic relaxation in non-interacting systems.

## 2. A model for weak dipolar interaction

In this section, we discuss how weak dipolar interaction in nanoparticle systems can be modeled by assuming that the effect of the dipolar interaction can be described by the local thermodynamic averages of the dipolar field. The system studied consists of identical nanoparticles with uniaxial anisotropy. The Hamiltonian of the system is given by the sum of the anisotropy energy, the Zeeman energy, and the dipolar energy as,

$$-\frac{H}{k_B T} = \sigma \sum_i (\mathbf{s}_i \cdot \mathbf{n}_i)^2 + \xi \sum_i (\mathbf{s}_i \cdot \mathbf{h}) + \xi d \sum_{i>j} (\mathbf{s}_i \cdot \mathbf{G}_{ij} \cdot \mathbf{s}_j), \quad (1)$$

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where $\mathbf{G}_{ij}$ is the dipolar energy tensor and $\mathbf{s}_i$, $\mathbf{n}_i$ and $\mathbf{h}$ are unit vectors along the direction of the magnetic moment, the anisotropy axis, and the applied field, respectively.

$$\sigma = \frac{KV}{k_B T}, \quad \xi = \frac{\mu_0 m H}{k_B T}, \quad \xi d = \frac{\mu_0 m^2}{4\pi a^3}\frac{1}{k_B T}, \tag{2}$$

where $KV$ is the uniaxial anisotropy energy, $m$ is the magnetic moment of a nanoparticle, and $a$ is the characteristic distance between the particles defined from $c = V/a^3$.

Due to the inversion symmetry of the uniaxial anisotropy, the relaxation time of an isolated particle can only contain even powers of the longitudinal and transverse field components. In the presence of a longitudinal field, the low temperature relaxation time $\tau$ is given by [2,13].

$$1/\tau(\xi_{\|}, \xi_{\perp} = 0) = \tau_0^{-1} \times \left[(1+h)\mathrm{e}^{-\sigma(1+h)^2} + (1-h)\mathrm{e}^{-\sigma(1-h)^2}\right] \tag{3}$$

where $h = \xi/2\sigma$, $\tau_0 = \tau_D\sqrt{\pi}/\sigma^{3/2}$ and $\tau_D$ is the relaxation time of an isotropic spin. At low temperatures and weak transversal fields, $\tau$ is given by [3]

$$1/\tau(\xi_{\|} = 0, \xi_{\perp}) \simeq 1/\tau_0 \mathrm{e}^{-\sigma}\left[1 + \frac{1}{4}F(\lambda\sigma^{1/2})\xi_{\perp}^2\right], \tag{4}$$

$$F(\alpha) = 1 + 2(2\alpha^2 e)^{1/(2\alpha^2)}\gamma\left(1 + \frac{1}{2\alpha^2}, \frac{1}{2\alpha^2}\right), \tag{5}$$

where $\gamma(a,z) = \int_0^z \mathrm{d}t \cdot t^{a-1}\mathrm{e}^{-t}$ is the incomplete gamma function and $\lambda$ is the damping parameter. It can be noted that due to the transversal field, the relaxation time will strongly depend on the value of the damping parameter through $F(\lambda\sigma^{1/2})$.

By combining Eqs. (3) and (4), an expression for the relaxation rate in a weak arbitrary field can be derived [4],

$$1/\tau \simeq \tau_0^{-1}\mathrm{e}^{-\sigma}\left[1 + \frac{1}{2}\xi_{\|}^2 + \frac{1}{4}F(\lambda\sigma^{1/2})\xi_{\perp}^2\right] \tag{6}$$

For weakly interacting nanoparticle systems, the dipolar interaction energy can be treated as a perturbation to the anisotropy energy. Thermodynamic perturbation theory can then be used in order to study the effect of dipolar interaction in various thermodynamic quantities [14]. The components of the dipolar field were calculated in [4] to second order in $\xi_d$. In the case of random anisotropy they read

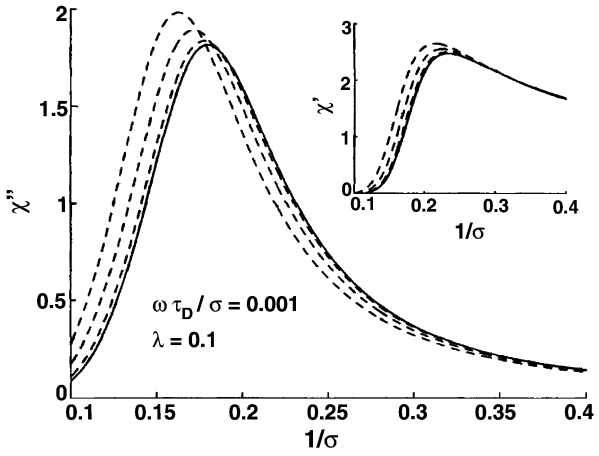


Fig. 1. Imaginary component of the dynamical susceptibility vs. temperature (the real component is shown in the inset) obtained by a Debye-type formula $\chi = \chi_{\mathrm{eq}}/(1 + i\omega\tau)$ The sample shape is spherical with the spins placed on a simple cubic lattice and the anisotropy axes are randomly distributed. The dipolar interaction strength $h_d = \xi_d/2\sigma = 0$ (solid lines), 0.002, 0.004 and 0.006 (dashed lines).

$$\langle\xi_{\|}^2\rangle = \frac{\xi_d^2}{3}R, \quad \langle\xi_{\perp}^2\rangle = \frac{\xi_d^2}{3}2R, \tag{7}$$

with $R = 16.8$ for a simple cubic lattice structure. It was argued that these formulae are valid not only in the superparamagnetic state but also below the blocking temperature if the system is demagnetized. The relaxation time for weakly interacting nanoparticles can be obtained by inserting the dipolar field components in Eq. (6). Combining the relaxation time of weakly interacting nanoparticles with the equilibrium linear susceptibility calculated for a system with random anisotropy and a spherical sample shape [14],

$$\chi_{\mathrm{eq}} = \frac{\mu_0 m^2}{3k_B T}\left(1 - \frac{1}{18}\xi_d^2 R\right), \tag{8}$$

in a Debye-type formula, we can obtain the dynamic susceptibility around the paramagnetic blocking as shown in Fig. 1. It can be seen that the blocking temperature decreases with increasing interaction strength. It should be noted that the thermodynamic perturbation theory is valid only if $\xi_d \ll 1$. The model described here can therefore only be used to investigate the paramagnetic blocking at very weak interaction strengths.

## 3. Experimental results on strongly interacting systems

In this section, we discuss some results on a ferrofluid of single-domain particles of the amorphous alloy $\mathrm{Fe}_{1-x}\mathrm{C}_x$ ($x \approx 0.2$–$0.3$). The particles are coated with a

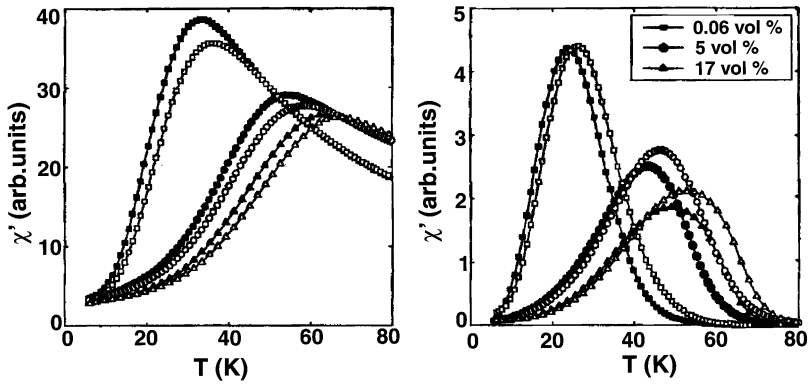


Fig. 2. AC susceptibility vs. temperature at frequencies $\omega/2\pi=125$ Hz (filled symbols) and $\omega/2\pi=1000$ Hz (open symbols) for the 0.06 vol.% sample (squares), the 5 vol.% sample (circles), and the 17 vol.% sample (triangles).

surfactant in order to prevent direct contact between the particles. The particle shape is nearly spherical and the average particle diameter $d=5.3\pm0.3$ nm. The saturation magnetization was estimated to $M_s=1\times10^6$ A $m^{-1}$, and the uniaxial anisotropy constant to $K=0.9\times10^5$ J $m^{-3}$ [15]. These parameters yield the dipolar interaction strength $h_d\approx0.56c$, where $c$ is the volume concentration of nanoparticles. The interparticle interaction strength can hence be varied by changing the particle concentration of the ferrofluid.

The AC-susceptibility vs. temperature is shown in Fig. 2 for three different particle concentrations of the Fe–C sample: $c=0.06$, 5, and 17 vol.%. With increasing concentration, the peak in the AC-susceptibility is shifted to higher temperatures and the curve is at the same time suppressed. This behavior is opposite to that shown in Fig. 1. The dipolar interaction strength ($\xi_d=0.56$ for the 5 vol.% sample and $\xi_d=1.9$ for the 17 vol.% sample at $T=50$ K) is, however, too strong for the model described in the previous section to be valid.

We have obtained the temperature dependence of the relaxation time from AC-susceptibility data measured for a large set of frequencies; the relaxation time $\tau=1/\omega$ and a possible criterion for the freezing is the temperature where $\chi''(T,\omega)$ attains 15% of its maximum value. The relaxation time as a function of temperature is shown in Fig. 3 (the AC data used to extract $T_f$ can be found in Ref. [15]). In the two concentrated samples, we expect the slow relaxation to arise from spin-glass correlations and not from thermal blocking as in the weakly interacting case. If the system, in addition, exhibits a spin-glass phase transition, the relaxation time is expected to diverge at the transition temperature $T_g$ according to conventional critical slowing down

$$\tau_c\sim\tau_m|1-T/T_g|^{-z\nu} \tag{9}$$

with $\tau_m$ being a microscopic time scale. For nanoparticles, $\tau_m$ can be assigned to the superparamagnetic relaxation time of a single particle of average size. A

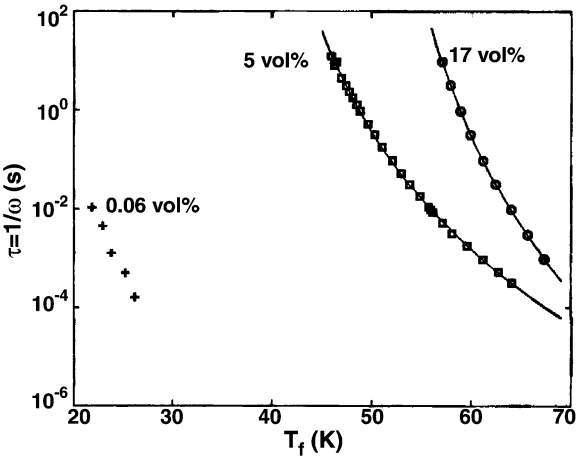


Fig. 3. Relaxation time $\tau_c=1/\omega$ vs. $T_f$ obtained from AC-susceptibility data. For the 5 and 17 vol.% samples the lines are fits to the critical slowing down relation [Eq. (9)].

Table 1
Parameters obtained from a critical slowing down analysis according to Eq. (9) of $\tau(T_f)$ data obtained from AC-susceptibility measurements

| Sample (vol.%) | $KV/k_B$ (K) | $z\nu$ | $T_g$ (K) | $\tau_0$ (s) |
|---|---|---|---|---|
| 17 | 0 | 11.4 | 48.8 | $2\times10^{-8}$ |
| 17 | 500 | 8.8 | 49.9 | $5\times10^{-11}$ |
| 5 | 0 | 10.3 | 36.0 | $2\times10^{-5}$ |
| 5 | 500 | 6.4 | 37.9 | $1\times10^{-8}$ |

dynamic scaling analysis according to critical slowing down was performed for $\tau(T_f)$ extracted from AC data for the two concentrated samples. Two different assumptions concerning the anisotropy energy were compared: (i) $KV=0$, which corresponds to a temperature-independent microscopic flip time; and (ii) $KV/k_B=500$ K, which is an estimate of the anisotropy barrier energy for a particle of average size. The values obtained for $z\nu$, $T_g$, and $\tau_0$ in each case are given in Table 1 (the

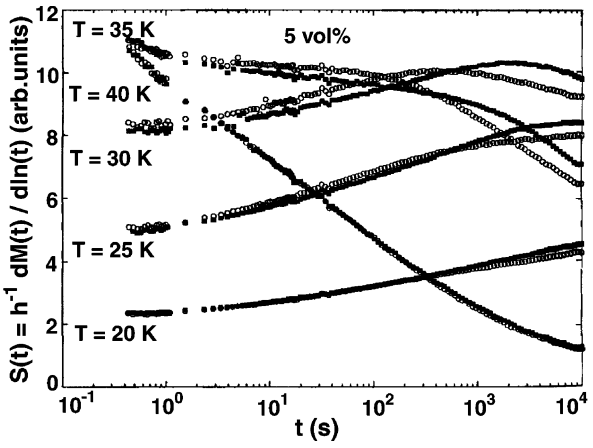


Fig. 4. $h^{-1}dM(t)/d\log(t)$ vs. time on a logarithmic scale for the 5 vol.% sample obtained from zero-field-cooled relaxation experiments waiting a time $t_w$ at $T_m$ before applying the probing field and recording the magnetization as a function of time. $t_w = 300$ s (open symbols) and 3000 s (filled symbols).

temperature dependence of $\tau_0$ was neglected). The quality of the fit of Eq. (9) to the experimental data is equally good for assumptions (i) and (ii). In fact, the lines in Fig. 3 correspond to any of the assumptions. In addition, the values of $T_g$ and the critical exponents depend strongly on the criterion used when determining $T_f$. Also by introducing $\tau(T_f)$ extracted from zero-field-cooled relaxation data in the critical slowing down analysis and performing a full dynamic scaling analysis, it was shown in Ref. [15] that the 5 vol.% sample does, in fact, not exhibit a spin-glass-like phase transition.

Although the 5 vol.% sample does not exhibit a spin glass phase transition it does exhibit glassy dynamics [16]. Glassy dynamics can be evidenced by measuring the zero-field-cooled relaxation at a low temperature after a fast cooling from a temperature in the paramagnetic phase using different waiting times before applying the magnetic probing field and recording the magnetization as a function of time. In spin glasses, the magnetic relaxation depends on the waiting time in zero field, a phenomenon known as magnetic ageing [17]. In a non-interacting nanoparticle system, the zero-field-cooled relaxation is a function of the temperature due to the distribution of relaxation times. It does not depend on the waiting time at $T_m$ before applying the probing field, as was shown experimentally in Ref. [10]. The relaxation rate $S(t) = h^{-1}dM(t)/d\log t$ at different temperatures between 20 and 40 K are shown in Fig. 4 for the 5 vol.% sample. The zero-field-cooled relaxation measurements are repeated for two different waiting times, 300 and 3000 s. A clear difference between the $S(t,t_w)$ curves for $t_w = 300$ and 3000 s can be seen for all temperatures $< 40$ K, presenting evidence for glassy dynamics at those temperatures.

## 4. Discussion

The model for how the relaxation time is affected by weak dipolar interaction presented in Section 2 is most useful when comparing to high frequency measurements. There are two reasons: (i) the thermodynamic perturbation theory is valid only at high enough temperatures satisfying $\xi_d \ll 1$, and since the blocking temperature increases with increasing frequency, the model will have a larger range of validity when studying the blocking behavior at high frequencies. (ii) The factor $F(\lambda\sigma^{1/2})$ is larger at high temperatures. The dependence of the transverse dipolar field component on the relaxation time is therefore stronger at high temperatures. A blocking temperature that decreases with increasing interaction strength has indeed been observed in Mössbauer spectroscopy [8], a method that probes the high frequency behavior.

In Section 3, the slow relaxation in strongly interacting nanoparticle systems is discussed in terms of spin-glass-like dynamics arising due to the interparticle interactions. We expect that the relaxation time will always increase with the interaction strength if energy barriers are created due to strong interparticle interactions. However, whether the dipolar interaction will give rise to glassy dynamics or not will be determined by two parameters: the randomness (in particle positions and direction of the anisotropy axes) and the width of the anisotropy energy-barrier distribution. Randomness is crucial in order to observe glassy dynamics, while it has been shown experimentally that glassy dynamics is more easily observed in a sample with a comparatively narrow anisotropy energy-barrier distribution than in a sample with a wide distribution. An explanation was given in Ref. [11]; if the energy-barrier distribution is wide, a fraction of particles will be blocked on the experimental time scales and hence act as random magnets instead of taking active part in the dynamics.

To conclude, by treating the dipolar interaction as a perturbation, the relaxation time decreases with increasing interaction strength. Such a picture can by definition only be valid for very weak interaction strengths. In the case of strong interparticle interactions, energy-barriers will be created by the interparticle interaction and the relaxation time will hence increase with increasing interaction strength. It has been shown experimentally that strongly interacting particle systems with randomness and a comparatively narrow anistropy energy-barrier distribution exhibit spin-glass-like dynamics. The slow relaxation of such systems originates from spin-glass correlations and the relaxation is hence fundamentally different from the simple superparamagnetic blocking in non-interacting and weakly interacting nanoparticle systems.

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